Identification of a covalent importin-5 inhibitor, goyazensolide from a collective synthesis of furanoheliangolides

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a) General information (Chemistry)

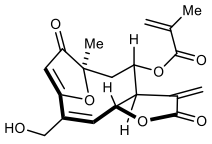
NMR spectra were recorded on AMX-300, AMX-400 and AMX-500 Bruker Avance spectrometers at 298 K with $CDCl_3$ as the solvent unless otherwise stated. Chemical shifts are reported in parts per million, relative to chloroform (^1H, δ 7.26; ^{13}C, δ 77.16) unless otherwise stated. Data for ^1H NMR are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuple， sept. = septuple, m = multiplet) and coupling constants. Infrared spectra (IR) were recorded on a Perkin-Elmer 1650 FT-IR spectrometer using neat samples on a diamond ATR Golden Gate sampler. High-resolution mass spectra (HRMS) were obtained on a Xevo G2 Tof spectrometer (Ionization mode: ESI positive polarity; Mobile phase: MeOH 100 µl/min). Optical rotations were recorded on OMNI Lab JASCO P-1030 polarimeter at 589 nm and are recorded as $[\alpha]_D^T$ (concentration in grams/100 mL solvent). Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel 60-F_{254} plates from *Merck*, using 250nm UV light as the visualizing agent and a solution of phosphomolybdic acid or $KMnO_4$ and heat as developing agents. Flash chromatography was performed using 200-400 mesh silica gel. Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated. Reverse phase column chromatography was performed using Isolera Biotage using SNAP Cartridge KP-C18-HS of 60 g or 12 g. The X-ray diffraction data was collected on an Agilent Supernova diffractometer equipped with an ATLAS CCD detector using Cu radiation. The enantiomeric excess (*ee*) was determined by HPLC analysis. Chiral HPLC analysis was performed on Waters Acquity UPC2 with column OJ-H. All reagents were used as supplied by Aldrich, Fluka, Acros or Strem and used without purification unless otherwise noted. All reactions were carried out in oven-dried glassware under nitrogen atmosphere unless otherwise noted.

Safety Statement

No unexpected or unusually high safety hazards were encountered.

b) Summary of synthesized natural products (Figure S1) and other structurally similar natural products (Figure S2)

Figure S1. Isolation, structure and activity of compounds **1-17**.



Goyazensolide (**1**)

Isolation

Eremanthus goyazensis

^{1}H, ^{13}C, misassignment as C_8 lactone

Phytochemistry, **1976**, *15*, 191-193

Vanillosmopsis brasiliensis/Vanillosmopsis pohlii

Phytochemistry, **1981**, *20*, 731-734

Lychnophora passerina

Phytochemistry, **1981**, *20*, 1149-1151

Eremanthus mollis

Phytochemistry, **1981**, *20*, 1609-1612

Vanillosmopsis erythropappa

Phytochemistry, **1989**, *28*, 1441-1451

Lychnophora diamantinana

Phytochemistry, **1993**, *34*, 261-263

Eremanthus mattogrossensis

J. Braz. Chem. Soc. **1995**, *6*, 307-311

Centratherum punctatum ssp. punctatum

Biochem. Syst. Ecol. **1998**, *26*, 805-808

Lychnophora granmongolense

Phytother. Res. **2000**, *14*, 203-206

Lychnophora pohlii

Fitoterapia, **2005**, *73*, 73-82

Lychnophora ericoides

Chem. Pharm. Bull. **2004**, *52*, 1433-1435

Minasia alpestris

J. Braz. Chem. Soc. **2005**, *16*, 677-680

Piptocoma rufescens

Tetrahedron, **2012**, *68*, 2671-2678

X-Ray and structure revision

J. Org. Chem. **1982**, *47*, 2798-2800

Detail assignment

Magn. Reson. Chem. **2001**, *39*, 219-221

Activity

Trypanocidal/schistosomicidal/antiplasmodial/

Antiparasitic/antileishmanial

IC_{50} 3-70 μM, related MoA: DHODH

Phytochemistry, **1976**, *15*, 191-193

Phytother. Res. **1996**, *10*, 292-295

Phytother. Res. **2000**, *14*, 203-206

Fitoterapia, **2005**, *76*, 73-82

Planta Med. **2006**, *72*, 1427-1430

Eur. J. Med. Chem. **2018**, *157*, 852-866

Parasitology, **2020**, *147*, 108-119

NF-κB inhibition

IC_{50} 3.8μM, docking, QSAR

Bioorg. Med. Chem. **1999**, *7*, 2343-2352

J. Med. Chem. **2004**, *47*, 6042–6054

J. Med. Chem. **2006**, *49*, 2241-2252

Tetrahedron, **2012**, *68*, 2671-2678

Anti-cancer/cytotoxicity/antiproliferative activity

IC_{50} 0.1-2.3 μM, related MoA,

inhibitors of Myb-dependent gene expression

Chem. Pharm. Bull. **2004**, *52*, 1433-1435

Planta Med. **2006**, *72*, 1427-1430

Tetrahedron, **2012**, *68*, 2671-2678

Eur. J. Med. Chem. **2013**, *63*, 313-320

J. Nat. Prod. **2019**, 82, 657–679

Anti-inflammatory

10 mg/Kg, carrageenan-induced paw edema

Planta Med. **2015**, *81*, 1296-1307

J. Ethnopharmacol. **2017**, *198*, 444-450

Induces Apoptosis

related MoA

selectively target the transcription factor NF-κB

Int. J. Cancer, **2013**, 9, 36-53

J. Nat. Prod. **2018**, 81, 554-561

Anti-hyperuricemic effects

in vivo liver xanthine oxidase (XOD)

activity in mice.10 mg/Kg

J. Ethnopharmacol. **2017**, *198*, 444-450

Goyazensolide (**1**)**-continued**

Antibacterial/antimicrobial

MIC 10.5 μM

related MoA: inhibition quorum sensing

Planta Med. **2006**, *72*, 1427-1430

Phytomedicine, **2012**, *19*, 1173-1177

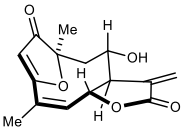
Molluscicidal

LD_{50} 135μM

Chem. Biodivers. **2009**, *6*, 513-519

Immuno-modulatory/ROS generation

J. Pharm. Pharmacol. **2006**, *58*, 853-858



Atripliciolide (**2**)

Isolation

Eremanthus glomerulatus

Phytochemistry, **1982**, *21*, 1669-1673

Minasia alpestris

J. Braz. Chem. Soc. **2005**, *16*, 677-680

Structure

^{1}H, misassignment as 8β-OH

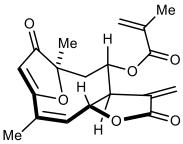
Phytochemistry, **1982**, *21*, 1669-1673

Revised by us as 8α-OH

Whole assignment

(^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY)

and X-Ray by us



15-Deoxygoyazensolide (**3**)

Isolation

Vanillosmopsis erythropappa

^{1}H, misassignment as C_8 lactone

Phytochemistry, **1976**, *15*, 1775-1776

^{13}C NMR

Phytochemistry, **1989**, *28*, 1441-1451

Lychnophora villosissiima

Trans. R. Soc. Trop. Med. Hyg. **1991**, *85*, 372-374

Lychnophora pseudovillosissima

Phytochemistry, **1992**, *31*, 692-695

Minasia alpestris

J. Braz. Chem. Soc. **2005**, *16*, 677-680

Piptocoma rufescens

X-Ray

J. Nat. Prod. **2018**, 81, 554-561

Structure revision

J. Org. Chem. **1982**, *47*, 2798-2800

Detail assignment

Magn. Reson. Chem. **2004**, *42*, 364-367

Activity

Trypanosomicidal/schistosomicidal/Trypanocidal

IC_{50} 514 μM

Phytochemistry, **1976**, *15*, 1775-1776

Trans. R. Soc. Trop. Med. Hyg. **1991**, *85*, 372-374

Fitoterapia, **2005**, *76*, 73-82

Anti-inflammatory

IC_{50} 4.6 μM fMLP 7.4 μM PAF

Biologicals, **2005**, *33*, 175-184

Genotoxicity in bacteria and yeast

Mutat. Res. **2007**, *631*, 16-25

Antibacterial

MIC 116 μM

Nat. Prod. Res. **2009**, *25*, 326-331

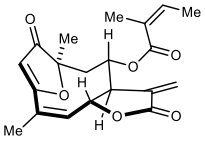
Cytotoxicity and NF-kB p65 inhibition

IC_{50} 0.26 μM IC_{50} 0.26 μM

Tetrahedron, **2012**, *68*, 2671-2678

Induces Apoptosis

same as goyazensolide



Lychnopholide (**4**)

Isolation

Lychnophora hakeaefolia

^{1}H NMR, misassignment as C_8 lactone

Phytochemistry, **1980**, *19*, 2381-2385

Lychnophora blanchetii

Phytochemistry, **1980**, *19*, 2669-2673

Proteopsis argentae

Phytochemistry, **1981**, *20*, 739-741

Lychnophora uniflora Sch. Bip.

Phytochemistry, **1981**, *20*, 1149-1151

Alcantara Ekmaniana

Phytochemistry, **1982**, *21*, 456-457

Lychnophora sellowii/Lychnophora

bahiensis/Lychnophora crispa

Phytochemistry, **1982**, *21*, 1087-1091

Piptolepis leptospermoides

Phytochemistry, **1982**, *21*, 1439-1441

Eremanthus crotonoides

Phytochemistry, **1982**, *21*, 1669-1673

Vanillosmopsis erythropappa

^{13}C NMR

Phytochemistry, **1989**, *28*, 1441-1451

Lychnophora rupestris

Phytochemistry, **1995**, *39*, 387-389

Lychnophora trichocarpha

Phytother. Res. **1996**, *10*, 292-295

Lychnophora pseudovillosissima

Biochem. Syst. Ecol. **1998**, *26*, 671-676

Lychnophora pohlii

Fitoterapia, **2005**, *73*, 73-82

Structure revision

J. Org. Chem. **1982**, *47*, 2798-2800

Activity

Trypanocidal

IC_{50} 585 μM

Phytother. Res. **1996**, *10*, 292-295

Fitoterapia, **2005**, *76*, 73-82

WO 2013059898 A1 20130502

Antimicrob. Agents Chemother. **2014**, *58*, 2067-2075

Antimicrob. Agents Chemother. **2016**, *60*, 5215-5222

Sci. Rep. **2017**, *7*, 44998

Antimicrob. Agents Chemother. **2020**, *64*, e01937-19

Immuno-modulatory/ROS generation

J. Pharm. Pharmacol. **2006**, *58*, 853-858

Anti-hyperuricemic

Rev. Bras. Farmacogn. **2019**, *29*, 241-245

J. Ethnopharmacol. **2012**, *142*, 845-850

Anti-inflammatory

dose 25mg/Kg

J. Ethnopharmacol. **2012**, *142*, 845-850

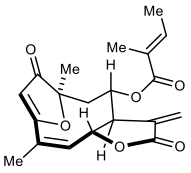
Phytother. Res. **2013**, *27*, 384-389

Cytotoxicity and NF-kB p65 inhibition

IC_{50} 1.4 μM IC_{50} 2.9 μM

Tetrahedron, **2012**, *68*, 2671-2678

WO 2013059898 A1 20130502



Atripliciolide-tiglate (**5**)

Isolation

Eremanfhus bicolor

^{1}H NMR, misassignment as C_8 lactone

Phytochemistry, **1980**, *19*, 2663-2668

Eremanthus crotonoides

Phytochemistry, **1982**, *21*, 1669-1673

Lychnophora crispa

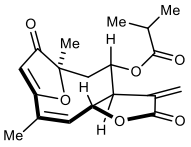
Phytochemistry, **1982**, *21*, 1087-1091

Minasia alpestris

J. Braz. Chem. Soc. **2005**, *16*, 677-680

Whole assignment by us

(^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY)



Atripliciolide-isobutyrate (**6**)

Isolation

Eremanthus crotonoides

^{1}H NMR, misassignment as C_8 lactone

Phytochemistry, **1982**, *21*, 1669-1673

Minasia alpestris

J. Braz. Chem. Soc. **2005**, *16*, 677-680

Piptocoma rufescens

Tetrahedron, **2012**, *68*, 2671-2678

Whole assignment by us

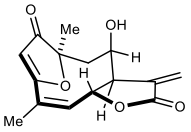
(^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY)

Activity

Cytotoxicity

IC_{50} 0.58 μM

Tetrahedron, **2012**, *68*, 2671-2678



8-*epi*-Atripliciolide (**7**)

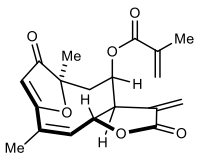
Original name: Atripliciolide

Revised in this manuscript as structure 2

Isolation has not been reported

Whole assignment by us

(^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY)



Calaxin (**8**)

Calaxin is also the name of a protein

Isolation

Helianthus ciliaris ^{1}H NMR

Rev. Latinoam. Quim. **1970,** *1*, 81-85

Isocarpha atriplicifolia, ^{1}H NMR

Phytochemistry, **1978**, *17*, 471-474

Calaxin (**8**) **-** continued

Calea pilosa

Phytochemistry, **1981**, *20*, 743-749

Calea species

Phytochemistry, **1981**, *20*, 1643-1647

Sclerocarpus sessilifolius

Biochem. Syst. Ecol. **1991**, *19*, 523

Heliomeris obscura

Phytochemistry, **1997**, *46*, 969-972

Viguiera eriophora

Phytochemistry, **2000**, *55*, 255-261

C_8-stereochemistry

J. Org. Chem. **1980**, *45*, 4993-4997

Whole assignment by us

(^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY)

Activity

Anti-fungal

Pesticides, **1979**, *13*, 31-32

Pesticides, **1982**, *16*, 19-20

Pesticides, **1985**, *19*, 58-60

Toxicity/cytotoxicity

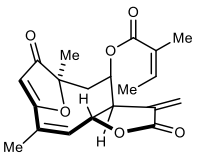
Arch. Invest. Med. **1980**, *11*, 435-443

Acta Hydrochim. Hydrobiol. **1984**, *12*, 563-565

Acta Hydrochim. Hydrobiol. **1985**, *13*, 391-394

Anti cancer

WO 2017079429 A1 20170511



8-*epi*-Lychnopholide
(15-deoxybudlein A, **9**)

Isolation

Calea pilosa ^{1}H NMR

Phytochemistry, **1981**, *20*, 743-749

Disynaphia halimifolia

Phytochemistry, **1981**, *20*, 1077-1080

Calea teucrifolia

Phytochemistry, **1981**, *20*, 1643-1647

Calea villosa

Phytochemistry, **1982**, *21*, 2593-2595

Calea angusta

Phytochemistry, **1982**, *21*, 2117-2118

Trichogoniopsis morii

Phytochemistry, **1982**, *21*, 2035-2040

Calea hymenolepis

Phytochemistry, **1982**, *21*, 2045-2048

Calea lantanoides ^{13}C NMR

Phytochemistry, **1982**, *21*, 464-465

Helianthus nuttallii

J. Nat. Prod. **1984**, *47*, 1021–1023

Calea divaricata

J. Nat. Prod. **1985**, *48*, 302-306

Helianthopsis bishopii

Phytochemistry, **1985**, *24*, 1108-1110

Viguiera sylvatica

Phytochemistry, **1989**, *28*, 2737-2740

Helianthus species (Asteraceae)

Biochem. Syst. Ecol. **1989**, *17*, 519-528

Helianthus stuebelii/sagasteguii

Phytochemistry, **1991**, *30*, 1861-1867

Sclerocarpus sessilifolius ^{13}C

Biochem. Syst. Ecol. **1991**, *19*, 523

Heliomeris obscura

Phytochemistry, **1997**, *46*, 969-972

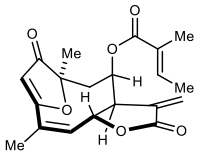
Activity

NF-kB p65 inhibition

QSAR, IC_{100} 2.5-5 μM

J. Med. Chem. **2004**, *47*, 6042–6054

J. Med. Chem. **2006**, *49*, 2241-2252



8-*epi*-Atripliciolide-tiglate (**10**)

Isolation

Isocarpha artiplicifolia ^{1}H NMR

Phytochemistry, **1978**, *17*, 471-474

Calea pilosa/ Calea morii

Phytochemistry, **1981**, *20*, 743-749

Bejaranoa semistriata

Phytochemistry, **1981**, *20*, 1639-1642

Chresta sphaerocephala

Phytochemistry, **1982**, *21*, 1669-1673

Calea angusta

Phytochemistry, **1982**, *21*, 2117-2118

Helianthus species

Biochem. Syst. Ecol. **1989**, *17*, 519-528

Helianthus sagasteguii

Phytochemistry, **1991**, *30*, 1861-1867

Viguiera species

Fitoterapia, **1998**, *69*, 86-87

Whole assignment by us

(^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY)

Activity

Antibacterial activity

Fitoterapia, **1998**, *69*, 86-87

NF-kB p65 inhibition

QSAR, IC_{100} 5 μM

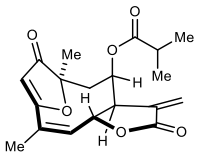
J. Med. Chem. **2004**, *47*, 6042–6054

J. Med. Chem. **2006**, *49*, 2241-2252

Antileishmanial

IC_{50} 872 μM, related MoA: DHODH

Eur. J. Med. Chem. **2018**, *157*, 852-866



Ciliarin (**11**)

Isolation

Helianthus ciliaris ^{1}H NMR

Rev. Latinoam. Quim. **1970,** *1*, 81-85

Isocarpha artiplicifolia ^{1}H NMR

Phytochemistry, **1978**, *17*, 471-474

Calea rupicola

Phytochemistry, **1986**, *25*, 1753-1754

Viguiera acutifolia/ Helianthus sagasteguii

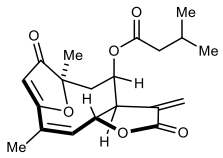
Phytochemistry, **1991**, *30*, 1861-1867

C_8-stereochemistry

J. Org. Chem. **1980**, *45*, 4993-4997

Whole assignment by us

(^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY)



8-*epi*-Atripliciolide-isovalerate (**12**)

Isolation

Isocarpha artiplicifolia ^{1}H NMR

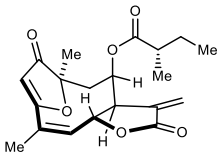
Phytochemistry, **1978**, *17*, 471-474

Calea rupicola

Phytochemistry, **1986**, *25*, 1753-1754

Whole assignment by us

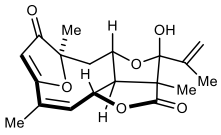
(^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY)



8-*epi*-Atripliciolide-2'-(*S*)-MeBu (**13**)

Isolation

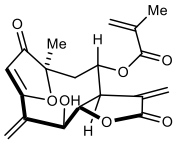
Helianthus lehmannii ^{1}H NMR
Phytochemistry, **1979**, *18*, 676
Calea angusta
Phytochemistry, **1982**, *21*, 2117-2118
Calea rupicola
Phytochemistry, **1986**, *25*, 1753-1754
Helianthus species
Biochem. Syst. Ecol. **1989**, *17*, 519-528
Helianthus stuebelii/sagasteguii
Phytochemistry, **1991**, *30*, 1861-1867
Structure elucidation-(*S*)-MeBu
Whole assignment by us
(^{1}H, ^{13}C, ^{1}H-^{1}H COSY, HSQC, HMBC, NOESY)



Eremantholide C (**14**)

Isolation

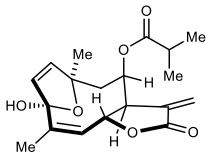
Eremanthus elaeagnus Schultz-Bip ^{1}H NMR
J. Chem. Soc., Perkin Trans. 1, **1978**, 1572-1580
Eremanthus bicolor
Phytochemistry, **1980**, *19*, 2663-2668
Lychnophora uniflora
Phytochemistry, **1981**, *20*, 1149-1151
Lychnophora affinis Gardn.
J. Org. Chem. **1982**, *47*, 1519-1521
Piptolepis leptospermoides
Phytochemistry, **1982**, *21*, 1439-1441
Eremanthus crotonoides
Phytochemistry, **1982**, *21*, 1669-1673
Eremanthus glomerulatus
Planta Med **1985**, *51*, 38-39
Eremanthus goyazensis
Phytochemistry, **1989**, *28*, 1441-1451
Lychnophora rupestris
Phytochemistry, **1995**, *39*, 387-389
Lychnophora trichocarpha
Phytother. Res. **1996**, *10*, 292-295
Cunninghamella echinulata
Fitoterapia, **2000**, *71*, 60-64
Minasia alpestris
J. Braz. Chem. Soc. **2005**, *16*, 677-680
^{1}H and ^{13}C NMR
J. Org. Chem. **2012**, *77*, 9374-9378
NMR assignment
Magn. Reson. Chem. **2008**, *46*, 576-581
Activity
Anti-Inflammatory
J. Ethnopharmacol. **2012**, *142*, 845-850
Phytother. Res. **2013**, *27*, 384-389
Planta Med. **2015**, *81*, 1296-1307
J. Pharm. Pharmacol. **2019**, *71*, 910-919
Trypanocidal
Phytother. Res. **1996**, *10*, 292-295
Molecules, **2013**, *18*, 7761-7847
Antifungal
Fitoterapia, **2000**, *71*, 60-64
Anti-hyperuricemic
J. Ethnopharmacol. **2012**, *142*, 845-850
Rev. Bras. Farmacogn. **2019**, *29*, 241-245
Cytotoxicity
J. Chem. Soc., Perkin Trans. 1, **1978**, 1572-1580
Molluscidal
Planta Med. **1985**, *51*, 38-39



5-*epi*-Isogoyazensolide (**15**)

Isolation

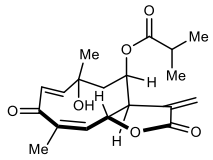
Vanillosmopsis brasiliensis/pohlii
^{1}H NMR misassignment as C_8 lactone
Phytochemistry, **1981**, *20*, 731-734
Eremanthus mattogrossensis
^{1}H ^{13}C NMR, structure revision
J. Braz. Chem. Soc. **1995**, *6*, 307-311
Camchaya calcarea
Planta Med. **2006**, *72*, 1427-1430
Piptocoma rufescens
Tetrahedron, **2012**, *68*, 2671-2678
Piptocoma antillana
Nat. Prod. Commun. **2014**, *9*, 1403-1406
Activity
Antiplasmodial, Antimycobacterial, and Cytotoxic
Planta Med. **2006**, *72*, 1427-1430
Cytotoxic and NF-kB inhibitory
Tetrahedron, **2012**, *68*, 2671-2678
Antiproliferative and antimalarial
Nat. Prod. Commun. **2014**, *9*, 1403-1406



Tagitinin F (**16**)

Isolation

tithonia tagitiflora (no NMR)
J. Pharm. Sci. **1976**, *65*, 918-920
C_8 revised
Indian. J. Chem. B, **1977**, *15B*, 208-211
Tithonia diversifolia
J. Org. Chem. **1979**, *44*, 1831-1835
Greenmaniella resinosa
Phytochemistry, **1987**, *26*, 1999-2006
^{1}H and ^{13}C
Photochem. Photobiol. **2020**, *96*, 14-20
Activity
Anti-tumor
WO 2005051955 A1 20050609
Chem. Pharm. Bull. **2007**, *55*, 1240-1244
FR 2941697 A1 20100806
Cytotoxicity
IC_{50} 3μM
J. Pharm. Sci. **1976**, *65*, 918-920
Leishmanicidal
Molecules, **2014**, *19*, 6070-6079
Anti-inflammatory
Planta Med. **2015**, *81*, 450-458
Rev. Bras. Farmacogn. **2015**, *25*, 111-116
Metabolites, **2015**, *5*, 404-430

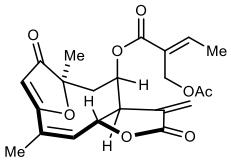


Tagitinin C (**17**)

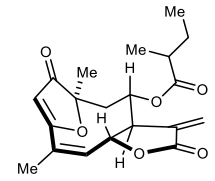
Isolation

Tithonia tagitiflora (no NMR)
J. Pharm. Sci. **1976**, *65*, 918-920
Tithonia diversifolia
C_8 revision ^{1}H, ^{13}C
J. Org. Chem. **1979**, *44*, 1831-1835
Greenmaniella resinosa
Phytochemistry, **1987**, *26*, 1999-2006
^{1}H and ^{13}C
Photochem. Photobiol. **2020**, *96*, 14-20
Activity
Feeding deterrents/antifeedant
Phytoparasitica, **1986**, *14*, 77-80
Phytochemistry, **2008**, *69*, 2052-2060
Chemistry & Industry, **1985**, *5*, 167-168
Arab. J. Chem. **2020**, *13*, 5292-5298
Germination and growth inhibitory
Phytochemistry, **1994**, *36*, 29-36
Phytotoxicity
Acta. Biol. Hung. **2017**, *68*, 187-195
Antiplasmodial activity
Planta Med. **2002**, *68*, 543-545
anti-tumor/anticancer/cytotoxicity
WO 2005051955 A1 20050609
Chem. Pharm. Bull. **2007**, *55*, 1240-1244
FR 2941697 A1 20100806
Fitoterapia, **2011**, *82*, 331-341
J. Nat. Med. **2013**, *67*, 98-106
Eur. J. Med. Chem. **2013**, *63*, 313-320
J. Nat. Prod. **2002**, *65*, 532–536
J. Agric. Food Chem. **2011**, *59*, 2347-2355
Curr. Top. Med. Chem. **2017**, *17*, 3256-3268
Anti-inflammatory
Metabolites, **2015**, *5*, 404-430
Rev. Bras. Farmacogn. **2015**, *25*, 111-116
Planta Med. **2015**, *81*, 1296-1307
Anti-Tobacco mosaic virus
Pestic. Biochem. Phys. **2017**, *140*, 24-29
Anti-ulcer
Molecules, **2011**, *16*, 665-674
Antitrypanosomal/leishmanicidal/trypanocidal
Molecules, **2014**, *19*, 6070-6079
Fitoterapia, **2018**, *124*, 145-151
Eur. J. Med. Chem. **2018**, *157*, 852-866
Int. Immunopharmaco. **2019**, *77*, 105961
Antimalarials
Bioorg. Med. Chem. **2009**, *17*, 3229-3256
Hsp90 Inhibitors
Biology, **2014**, *3*, 101-138

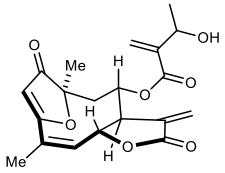
Figure S2. Other structurally similar natural products.



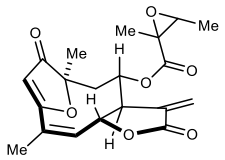
Phytochemistry, **1981**, *20*, 1639-1642
Phytochemistry, **1996**, *41*, 1543-1546



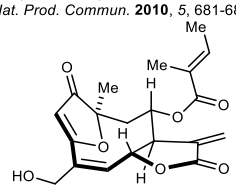
Phytochemistry, **1982**, *21*, 1439-1441



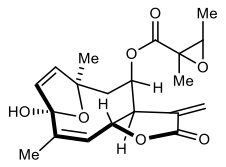
Phytochemistry, **1982**, *21*, 1669-1673



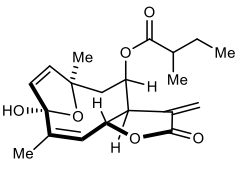
Phytochemistry, **1981**, *20*, 739-741
Phytochemistry, **1982**, *21*, 1669-1673
Phytochemistry, **1982**, *21*, 456-457
Nat. Prod. Commun. **2010**, *5*, 681-684



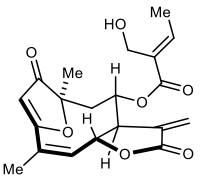
Lychnophorolide B (Centratherin)
Isolation
Phytochemistry, **1980**, *19*, 593-597
Phytochemistry, **1982**, *21*, 1669-1673
Biochem. Syst. Ecol. **1996**, *24*, 585-587
Phytochemistry, **1991**, *30*, 519-522
Phytochemistry, **1991**, *30*, 1861-1867
Activity
Eur. J. Med. Chem. **2018**, *157*, 852-866
Phytochem. Lett. **2013**, *6*, 21-25
Antimicrob. Agents Chemother. **2014**, *58*, 325-332



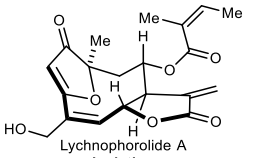
Phytochemistry, **1984**, *23*, 1281-1287



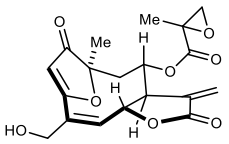
Isolation
Phytochemistry, **1987**, *26*, 1999-2006
Activity
Phytochemistry, **2008**, *69*, 2052-2060



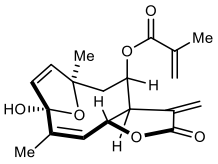
Phytochemistry, **1982**, *21*, 1669-1673



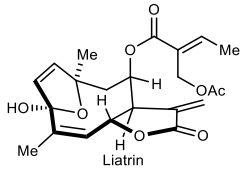
Lychnophorolide A
Isolation
Biochem. Syst. Ecol. **1998**, *26*, 671-676
J. Braz. Chem. Soc. **1995**, *6*, 307-311
Phytochemistry, **1993**, *34*, 261-263
Biochem. Syst. Ecol. **1991**, *19*, 440
Phytochemistry, **1982**, *21*, 1087-1091
Phytochemistry, **1982**, *21*, 685-689
J. Org. Chem. **1982**, *47*, 1519-1521
Phytochemistry, **1981**, *20*, 1609-1612
Phytochemistry, **1979**, *18*, 681-682
Activity
S. Afr. J. Bot. **2018**, *117*, 79-82
Molecules, **2016**, *21*, 782
Nat. Prod. Res. **2016**, *30*, 2611-2615
Molecules, **2013**, *18*, 7761-7847
Rev. Bras. Farmacogn. **2012**, *22*, 1295-1300
Phytomedicine, **2012**, *19*, 1173-1177
Planta Med. **2006**, *72*, 1427-1430
J. Pharm. Pharmacol. **2006**, *58*, 853-858
J. Med. Chem. **2006**, *49*, 2241-2252
Fitoterapia, **2005**, *76*, 73-82
J. Med. Chem. **2004**, *47*, 6042–6054
Teratog. Carcinog. Mutagen. **2001**, *21*, 383-393
Phytother. Res. **2000**, *14*, 203-206
Bioorg. Med. Chem. **1999**, *7*, 2343-2352



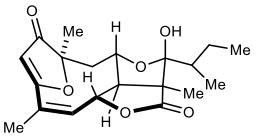
ChemdInform, **1987**
(10.1002/chin.198723280)



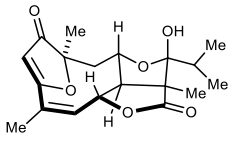
1,2-dehzdroyexbrevin B
Isolation
J. Nat. Prod. **1986**, *49*, 1165–1166
Phytochemistry, **1984**, *23*, 1967-1970
Activity
Phytochemistry, **1999**, *52*, 613-621



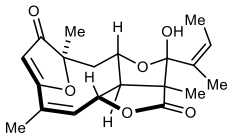
Liatrin
Isolation
J. Am. Chem. Soc. **1971**, *93*, 4916–4918
J. Org. Chem. **1973**, *38*, 1853–1858
Activity
Med. Chem. **2018**, *14*, 626-640
Eur. J. Med. Chem. **2008**, *43*, 2197-2205
Bioorg. Med. Chem. **2007**, *15*, 2927-2934
QSAR. Comb. Sci. **2002**, *21*, 276-287
J. Med. Chem. **1971**, *14*, 1147–1152



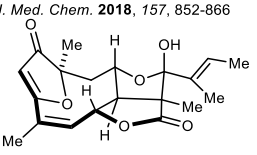
Eremantholide B
Isolation
J. Chem. Soc., Perkin Trans. 1, **1978**, 1572-1580
J. Org. Chem. **1980**, *45*, 2503-2506
Activity
J. Pharm. Pharmacol. **2019**, *71*, 910-919
J. Org. Chem. **1980**, *45*, 2503-2506



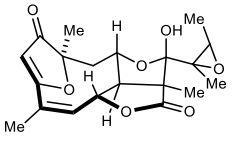
Eremantholide A
Isolation
Biochem. Syst. Ecol. **1998**, *26*, 671-676
Phytochemistry, **1982**, *21*, 1669-1673
Phytochemistry, **1980**, *19*, 2663-2668
Phytochemistry, **1980**, *19*, 2669-2673
J. Org. Chem. **1980**, *45*, 2503–2506
J. Am. Chem. Soc. **1975**, *97*, 6884-6886
Activity
J. Pharm. Pharmacol. **2019**, *71*, 910-919
Bioorg. Med. Chem. **1999**, *7*, 2343-2352
Total synthesis
Org. Lett. **2007**, *9*, 1267–1270
J. Org. Chem. **1995**, *60*, 8179–8193
Tetrahedron Lett. **1995**, *36*, 1487-1490



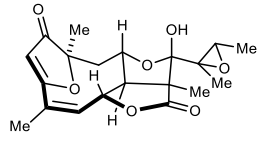
Isolation
Phytochemistry, **1982**, *21*, 1087-1091
Phytochemistry, **1982**, *21*, 1669-1673
J. Org. Chem. **1982**, *47*, 1519-1521
Phytochemistry, **1981**, *20*, 739-741
Phytochemistry, **1981**, *20*, 1149-1151
Phytochemistry, **1995**, *39*, 387-389
Activity
Eur. J. Med. Chem. **2018**, *157*, 852-866



Phytochemistry, **1980**, *19*, 2663-2668
Phytochemistry, **1982**, *21*, 1669-1673



Phytochemistry, **1981**, *20*, 739-741
Phytochemistry, **1982**, *21*, 1669-1673



Phytochemistry, **1982**, *21*, 1669-1673

c) Structure revision of atripliciolide (2)

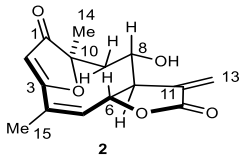
The name atripliciolide was initially used for the proposed structure of a parent compound of an 8*β*-OH derivative by King and Robison in 1978 (*Phytochemistry*, **1978**, *17*, 471-474). Its isolation was reported by the same group in 1982 (*Phytochemistry*, **1982**, *21*, 1669-1673).

The structure was confirmed by ^{1}H NMR comparison with other known 8*β*-OH furanoheliangolides (*structure of 19 followed from its molecular formula and the ^{1}H NMR spectrum (Table 2). The presence of a 6, 12-lactone was deduced from the characteristic signals of H-5 through H-8, which were similar to those of 20. The 8*β-hydroxyl group was assigned from the couplings observed and from the chemical shifts of H-13, which were at lower fields due to the free hydroxyl at C-8.* --**original sentences** from *Phytochemistry*, **1982**, *21*, 1669-1673).

However, the proposed 8*β*-OH compound was isolated along with other 8*α*-esters instead of 8*β*-esters. For example, *Phytochemistry*, **1982**, *21*, 1669-1673 and *J. Braz. Chem. Soc.*, **2005**, *16*, 677-680, indicating that atripliciolide might be 8*α*-OH.

Both 8*α*-OH and 8*β*-OH compounds were synthesized and the spectral data was compared with the data optained from the natural product (based on 2D NMR spectroscopic analyses as well). The structure of atripliciolide was finally revised to have an 8*α*-OH (**2**). The absolute configuration of **2** was also determined by X-ray diffraction.

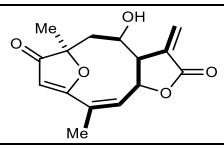
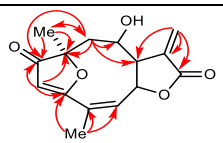
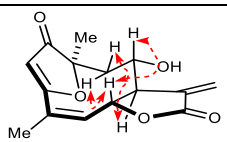
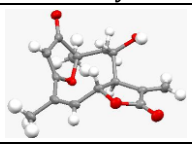
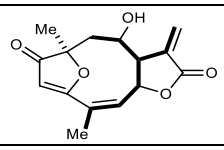
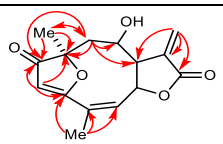
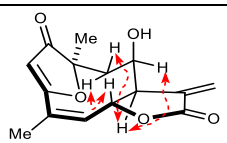
Table S1. Comparison of natural and synthetic proposed/revised atripliciolide (**2**) ($CDCl_3$)[1]



2

	^{1}H NMR			**^{13}C NMR**		
	Natural (400 MHz)	8α-OH **2** (Revised) (500 MHz)	8β-OH **7** (Proposed) (500 MHz)	Natural	**2** (125 MHz)	**7** (125 MHz)
1	-	-	-	-	206.0	206.0
2	5.60, s	5.60, s	5.59, s	-	103.2	103.2
3	-	-	-	-	186.4	186.4
4	-	-	-	-	131.4	131.4
5	5.90, dq (3.5, 1.5)	5.91, dq (3.6, 1.7)	5.95, dq (4.4, 1.8)	-	134.6	134.6
6	4.86, ddq (4, 3.5, 1.5)	4.86, tq (4.0, 1.9)	5.63, tq (4.5, 2.0)	-	81.0	81.0
7	3.68, dddd (4, 3, 2.5, 2)	3.66, tt (5.2, 2.7)	3.44, dtd (4.5, 2.9, 1.5)	-	52.3	52.3
8	3.82, m	3.82, m	4.21, qd (3.3, 1.6)	-	71.8	71.8
9α	2.31, dd (14.5, 2.5)	2.31, dd (14.7, 2.5)	2.44, dd (14.7, 2.5)	-	44.9	44.9
9β	2.17, dd (14.5, 8.3)	2.18, dd (14.6, 8.6)	2.30, dd (14.6, 8.6)	-	-	-
10	-	-	-	-	89.9	87.7
11	-	-	-	-	134.1	140.6
12	-	-	-	-	169.7	169.7
13a	6.45, dd (3, 0.7)	6.43, dd (3.0, 0.7)	6.35, d (3.1)	-	127.4	123.6
13b	5.86, dd (2.5, 0.7)	5.84, dd (2.6, 0.7)	5.61, d (2. 7)	-	-	-
14	1.44, s	1.56, s	1.45, s	-	20.7	21.8
15	2.07, dd (1.5, 1.5)	2.07, t (1.9)	2.06, t (1.9)	-	19.9	19.6
OH	-	2.32	2.32	-	-	-

2D NMR correlations

	^{1}H-^{1}H COSY	HMBC	NOESY	X-Ray
2				
7				

[1] Only the ^{1}H NMR data was available in the literature (*Phytochemistry*, **1982**, *21*, 1669-1673). The solvent peak was set to be 7.27 ppm instead of 7.26 ppm. The chemical shift of 14-Me was erroneous, and has been correct by our full assignment. To the best of our knowledge no carbon NMR had been previously reported.

d) Structure elucidation of 13

8-*epi*-Atripliciolide-2'-methyl butylate was first reported by Bohlmann and Dutta in 1979 (*Phytochemistry*, **1979**, *18*, 676). The configuration of the side chain was not assigned.

In this work 2'-(*S*)-MeBu-**13** was prepared from commercially available (*S*)-(+)-2-methyl butyric anhydride and 2'-(*R*+*S*)-MeBu-**13** from (±)-2-methyl butyric anhydride. The diastereomers are inseparable. The structures were fully elucidated based on 2D NMR spectroscopic analyses.

Based on ^{1}H NMR comparison (**Figure S3**), the structure of natural product was finally elucidated as 8-*epi*-atripliciolide-2'-(*S*)-MeBu (**13**).

Figure S3. ^{1}H NMR comparison of 8-*epi*-atripliciolide-2'-(*S*)-MeBu (**13**) and 8-*epi*-atripliciolide-2'-(*R*+*S*)-MeBu.

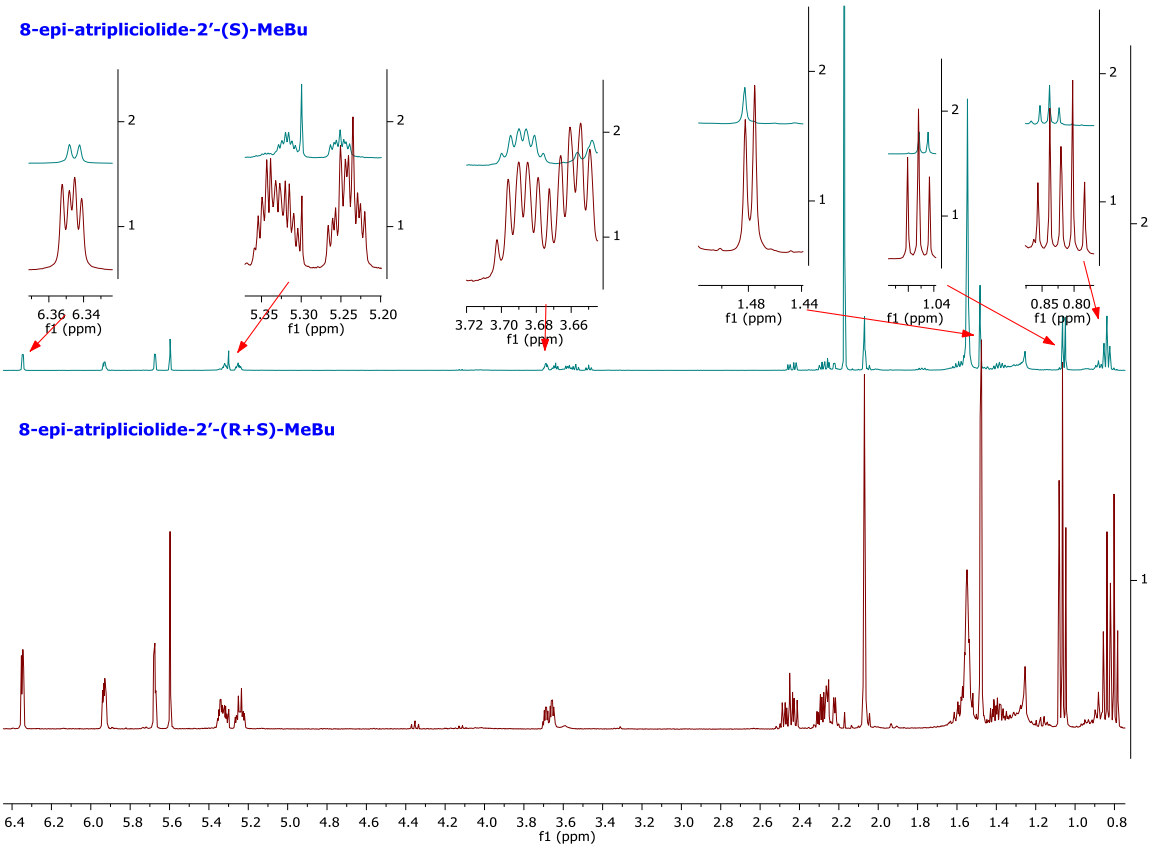
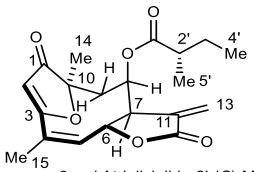


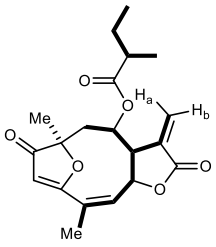
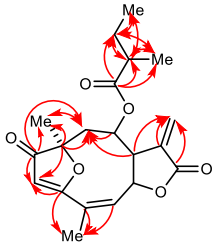
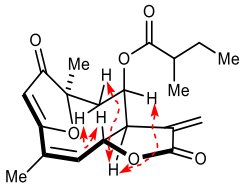
Table S2. Comparison of 2'-(*S*)-MeBu-**13**, 2'-(*R*)-MeBu-**13** and natural **13** (^{1}H NMR)[2]



8-*epi*-Atripliciolide-2'-(*S*)-MeBu (**13**)

	^{1}H NMR			^{13}C NMR		
	Natural (270 MHz)	2'-(*S*)-MeBu-**13** (400 MHz)	2'-(*R*)-MeBu-**13** (400 MHz)	Natural	2'-(*S*)-MeBu-**13** (100 MHz)	2'-(*R*)-MeBu-**13** (100 MHz)
1	-	-	-	-	205.44	205.50
2	5.60, s	5.60, s	5.60, s	-	102.99	103.09
3	-	-	-	-	185.10	185.10
4	-	-	-	-	131.92	131.97
5	5.93, dq (2.5, 1.5)	5.93, dq (3.6, 1.7)	5.93, m	-	134.29	134.23
6	5.32, br dq (2.5, ~2)	5.32, dq (4.4, 2.1)	5.34, m	-	87.48	87.51
7	3.69, m	3.69, dq (4.9, 2.6)	3.66, dq (4.9, 2.6)	-	138.29	138.46
8	5.25, ddd (5.5, 3.5, 2)	5.25, ddd (6.1, 3.7, 2.2)	5.23, m	-	168.92	168.87
9α	2.45, dd (15.5, 5.5)	2.45, dd (15.1, 6.1)	2.46, dd (15.1, 6.1)	-	124.01	124.07
9β	2.24, dd (15.5, 3.5)	2.24, dd (15.1, 3.7)	2.24, dd (15.1, 3.7)	-	-	-
10	-	-	-	-	89.9	87.7
11	-	-	-	-	134.1	140.6
12	-	-	-	-	169.7	169.7
13a	6.35, d (3)	6.35, d (2.9)	6.35, d (2.9)	-	127.4	123.6
13b	5.67, d (2.5)	5.67, d (2.5)	5.68, d (2.5)	-	-	-
14	1.49, s	1.48, s	1.47, s	-	20.7	21.8
15	2.07, dd (1.5, 1.5)	2.07, t (1.8)	2.07, t (1.8)	-	19.9	19.6
1'	-	-	-	-	175.16	175.21
2'	2.30, tq (7, 7)	2.28, m	2.28, m	-	41.16	41.06
3'a	1.4, m	1.38, m	1.38, m	-	26.37	26.62
3'b	1.6, m	1.60, m	1.60, m	-	-	-
4'	0.83, t (7)	0.83, t (7)	0.80, t (7)	-	11.62	11.53
5'	1.05, d (7)	1.05, d (7.1)	1.07, d (7.1)	-	16.50	16.16

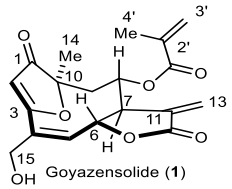
2D NMR correlations

	^{1}H-^{1}H COSY	HMBC	NOESY	
13				

[2] Previous report (*Phytochemistry*, **1979**, *18*, 676-676) provided ^{1}H NMR data without showing the spectra and did not assigned the side chain configuration. To the best of our knowledge no carbon NMR had been previously reported.

e) Data comparison and full analyses of 1, 3-6, 8-12, 14-17

Table S3. Comparison of natural and synthetic goyazensolide (**1**) ($CDCl_3$)[3]

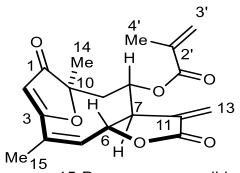


Goyazensolide (**1**)

	^{1}H NMR		**^{13}C NMR**	
	Natural (270 MHz)	Synthetic (500MHz)	Natural (68 MHz)	Synthetic (126 MHz)
1	-	-	204.6	204.6
2	5.83, s	5.82, s	106.4	106.6
3	-	-	184.6	184.2
4	-	-	135.6	135.5
5	6.27, dt (1.5, 1.5)	6.30, dt (1.5)	134.6	134.2
6	5.33, dt (1.3, 2.5)	5.36, dd (4.9, 2.6)	81.7	81.5
7	3.80, m (2.5, 2.5, 3.3, 3.0)	3.82, t (5.3)	51.0	50.9
8	4.53, dt (2.5, 13)	4.57, dt (2.2, 11.7)	73.5	73.2
9α	2.50, dd (13, 15)	2.56-2.48, m	43.3	43.9
9β	-	-	-	-
10	-	-	89.7	89.8
11	-	-	135.6	135.3
12	-	-	166.8	166.8
13a	6.22, d (3.3)	6.25, d (3.1)	126.2	126.6
13b	5.49, d (3.0)	5.49, d (2.7)	-	-
14	1.52, s	1.56, s	20.6	20.7
15	4.38, s (1.5, 1.3)	4.42, dt (3.1, 1.7)	62.9	63.2
1’	-	-	168.7	168.7
2’	-	-	133.6	133.1
3’a	6.02, s (1)	6.03, s	124.5	124.6
3’b	5.56, m (1.5)	5.59-5.54, m	-	-
4’	1.83, m	1.85, s	17.8	18.0

[3] For NMR, see: *Phytochemishy*, **1976**, *15*, 191-193, structure misassignment as C-8 lactone. For structure revision, see: *J. Org. Chem.* **1982**, *47*, 2798-2800. For detailed full spectral assignments, see: *Magn. Reson. Chem.* **2001**, *39*, 3219-221.

Table S4. Comparison of natural and synthetic 15-deoxygoyazensolide (**3**) ($CDCl_3$)[4]

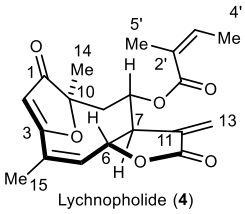


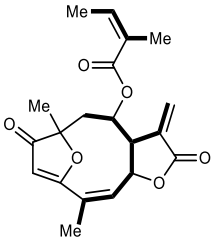
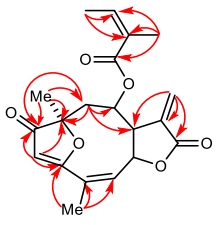
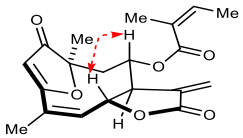
15-Deoxygoyazensolide (**3**)

	^{1}H NMR		**^{13}C NMR**	
	Natural (500 MHz)	Synthetic (400 MHz)	Natural (125 MHz)	Synthetic (100 MHz)
1	-	-	204.8	204.8
2	5.71, s	5.71, s	104.7	104.7
3	-	-	186.8	186.9
4	-	-	130.4	130.3
5	6.00, m	6.00, m	135.0	135.0
6	5.26, m	5.26, m	81.5	81.5
7	3.72, m	3.73, dq (5.7, 2.9)	51.1	51.1
8	4.55, dt (11.5, 2.9)	4.54, dt, (11.6, 2.5)	73.4	73.3
9α	2.48, dd (13.8, 11.5)	2.48, dd (13.9, 11.6)	43.8	43.8
9β	2.31, dd (13.8, 2.0)	2.31, dd (13.9, 2.1)	-	-
10	-	-	89.6	89.6
11	-	-	133.5	133.4
12	-	-	168.8	168.8
13a	6.22, d (3.1)	6.21, d (3.1)	124.4	124.5
13b	5.46, d (2.8)	5.45, d (2.7)	-	-
14	1.53, s	1.53, s	20.6	20.6
15	2.08, t (2.2)	2.07, t (2.0)	20.3	20.4
1’	-	-	166.7	166.7
2’	-	-	135.5	135.4
3’a	6.01, dq (1.6, 1.0)	6.01, m	126.4	126.5
3’b	5.54, quint (1.6)	5.54, m	-	-
4’	1.83, dd (1.6, 1.0)	1.83, dd (1.6, 1.0)	18.0	18.0

[4] Previous report (*Magn. Reson. Chem.* **2004**, *42*, 364–367) provides detailed full spectral assignments; for first isolation, see: *Phytochemishy*, **1976**, *15*, 1775-1776; for structure revision, see: *J. Org. Chem.* **1982**, *47*, 2798-2800. ^{13}C chemical shifts are reported relative to chloroform δ 77.00 ppm instead of 77.16 ppm.

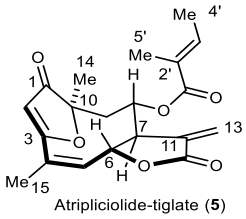
Table S5. Comparison of natural and synthetic lychnopholide (**4**) ($CDCl_3$)[5]



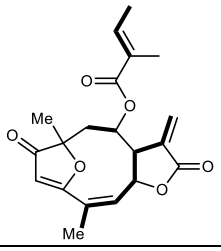
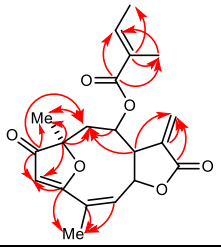
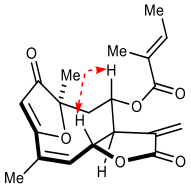
	^{1}H NMR		^{13}C NMR	
	Natural (270 MHz)	Synthetic (400 MHz)	Natural (68 MHz)	Synthetic (100 MHz)
1	-	-	204.71	204.85
2	5.72, s	5.72, s	104.69	104.75
3	-	-	186.83	186.91
4	-	-	130.44	130.31
5	6.02, dq (3, 1.7)	6.02, dt (3.2, 1.7)	135.12	135.06
6	5.30, ddq, (5, 3, 2.7)	5.31, dt (5.1, 2.6)	81.61	81.69
7	3.72, dddd (5, 3.5, 2.8, 2.5)	3.72, dq (5.5, 2.8)	51.23	51.17
8	4.54, ddd, (12, 2.5, 2)	4.54, dt (11.8, 2.4)	73.00	72.97
9α	2.49, dd (14, 12)	2.48, dd (13.8, 11.7)	44.04	44.04
9β	2.32, dd (14, 2)	2.31, dd (13.9, 2.1)	-	-
10	-	-	89.64	89.70
11	-	-	133.84	133.72
12	-	-	168.02	168.91
13a	6.23, d (3.2)	6.23, d (3.1)	124.10	124.27
13b	5.44, d (2.8)	5.44, d (2.7)	-	-
14	1.54, s	1.54, s	20.65	20.70
15	2.09, dd (2.7, 1.7)	2.09, t (2.0)	20.22	20.35
1’	-	-	167.00	167.06
2’	-	-	126.51	126.38
3’	6.09, qq (7, 1.5)	6.09, qq (7.3, 1.4)	140.54	140.80
4’	1.90, dq (7, 1.5)	1.89, dq (7.3, 1.5)	15.64	15.71
5’	1.80, dq (1.5, 1.5)	1.79, p (1.6)	19.93	20.03
2D NMR correlations				
	^{1}H-^{1}H COSY	HMBC	NOESY	
4				

[5] Previous report (*phytochemistry*, **1980**, *19*, 2381-2385) provides the ^{1}H NMR. Solvent peak was set up at 7.27 ppm instead of 7.26 ppm. And the ^{13}C NMR was provided in a later publication (*phytochemistry*, **1989**, *28*, 1441-1451) with the solvent peak set up at 77 ppm instead of 77.16 ppm.

Table S6. Comparison of natural and synthetic atripliciolide-tiglate (**5**) ($CDCl_3$)[6]

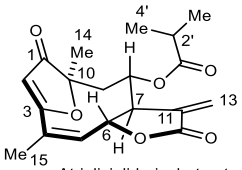


Atripliciolide-tiglate (**5**)

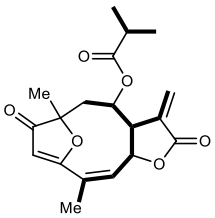
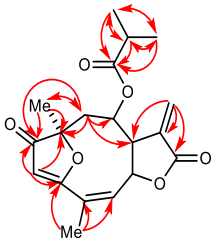
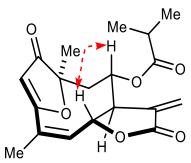
	^{1}H NMR		**^{13}C NMR**	
	Natural (270 MHz)	Synthetic (400 MHz)	Natural	Synthetic (100 MHz)
1	-	-	-	205.0
2	5.71, s	5.70, s	-	104.8
3	-	-	-	187.0
4	-	-	-	130.4
5	6.00, dq (3, 1.7)	6.01, dq (3.4, 1.7)	-	135.2
6	5.28, ddq, (5, 3, 2.5)	5.28, dt (5.2, 2.7)	-	81.7
7	3.73, dddd (5, 3.2, 2.8, 2.5)	3.72, dq (5.6, 2.9)	-	51.3
8	4.54, ddd, (12, 2.5, 2)	4.54, dt (11.6, 2.5)	-	73.3
9α	2.47, dd (14, 12)	2.47, dd (13.9, 11.6)	-	44.1
9β	2.30, dd (14, 2)	2.31, dd (14.0, 2.1)	-	-
10	-	-	-	89.8
11	-	-	-	133.7
12	-	-	-	169.1
13a	6.20, d (3.2)	6.20, d (3.1)	-	124.4
13b	5.44, d (2.8)	5.44, d (2.6)	-	-
14	1.53, s	1.53, s	-	20.8
15	2.08, dd (2.5, 1.7)	2.08, t (2.0)	-	20.5
1’	-	-	-	167.5
2’	-	-	-	127.9
3’	6.77, qq (7, 1.5)	6.77, qq (7.1, 1.4)	-	138.8
4’	1.77, dq (7, 1.5)	1.76, dd (7.1, 1.2)	-	14.6
5’	1.73, dq (1.5, 1.5)	1.73, t (1.3)	-	11.9
2D NMR correlations				
	^{1}H-^{1}H COSY	HMBC	NOESY	
5				

[6] Solvent peak was set up at 7.27ppm instead of 7.26 ppm. ^{1}H NMR had been previously reported (*Phytochemistry*, **1980**, *19*, 2663-2668). To the best of our knowledge no carbon NMR had been previously reported.

Table S7. Comparison of natural and synthetic atripliciolide-isobutyrate (**6**) ($CDCl_3$)[7]

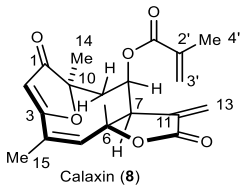


Atripliciolide-isobutyrate (**6**)

	^{1}H NMR		**^{13}C NMR**	
	Natural (270 MHz)	Synthetic (500 MHz)	Natural	Synthetic (125 MHz)
1	-	-	-	205.0
2	5.70, s	5.70, s	-	104.7
3	-	-	-	187.1
4	-	-	-	130.4
5	**5.90, dq, (3, 1.5)**	5.99, dt (3.1, 1.8)	-	135.2
6	5.23, ddq (5, 3, 1.5)	5.23, dp, (4.9, 2.3)	-	81.8
7	3.72, dddd (5, 3, 2.5, 2.5)	3.71, dq (5.6, 2.8)	-	51.3
8	4.42, ddd (11.5, 2.5, 2)	4.42, dt, (11.8, 2.4)	-	72.8
9α	**2.40, dd (14, 2)**	2.42, dd (13.9, 11.6)	-	44.1
9β	**2.25, dd (14, 11.5)**	2.25, dd (13.9, 2.0)	-	-
10	-	-	-	105.0
11	-	-	-	133.3
12	-	-	-	168.9
13a	6.26, d (3)	6.26, d (3.1)	-	124.4
13b	5.47, d (2.5)	5.46, d (2.6)	-	-
14	1.52, s	1.52, s	-	20.8
15	2.08, dd (1.5, 1.5)	2.07, t (2.0)	-	20.5
1’	-	-	-	176.7
2’	2.39, qq (7, 7)	2.39, sept, (7)	-	33.8
3’/4’	**1.40, d (7)**	1.04, d (7)	-	18.9
3’/4’	1.08, d (7)	1.08, d (7)	-	18.7
2D NMR correlations				
	^{1}H-^{1}H COSY	HMBC	NOESY	
7				

[7] ^{1}H NMR had been previously reported (*phytochemistry*, **1982**, *21*, 1669-1673) with different chemical shifts for H_5 and $H_{3'}$, and J coupling constants of 9α and 9β swapped. To the best of our knowledge no carbon NMR had been previously reported.

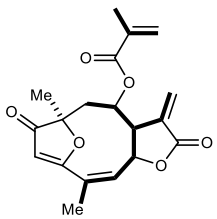
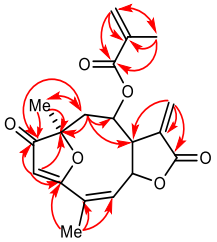
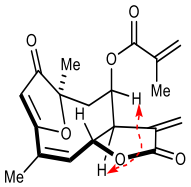
Table S8. Comparison of natural and synthetic calaxin (**8**) ($CDCl_3$)[8]



Calaxin (**8**)

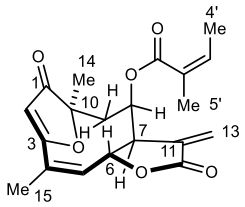
	^{1}H NMR		**^{13}C NMR**	
	Natural (270 MHz)	Synthetic (500 MHz)	Natural	Synthetic (125 MHz)
1	-	-	-	205.4
2	5.59, s	5.60, s	-	103.3
3	-	-	-	185.2
4	-	-	-	131.9
5	5.94, dq (2.5, 1.5)	5.95, dq (3.6, 1.8)	-	134.2
6	5.28, dq (2, 1.5)	5.28, tq (4.0, 1.9)	-	75.3
7	3.70, m	3.69, dtd (4.6, 2.7, 1.9)	-	48.5
8	5.18, ddd (5, 3, 3)	5.19, ddd, (5.4, 3.4, 1.9)	-	75.1
9α	2.55, dd (15, 5)	2.55, dd (15.2, 5.4)	-	42.6
9β	2.31, dd (15, 3)	2.31, dd (15.1, 3.4)	-	-
10	-	-	-	87.8
11	-	-	-	139.0
12	-	-	-	168.9
13a	6.35, d (3)	6.35, d (2.9)	-	123.6
13b	5.67, d (2.5)	5.67, d (2.6)	-	-
14	1.48, s	1.49, s	-	21.5
15	2.07, dd (1.5, 1.5)	2.07, t (1.9)	-	19.7
1’	-	-	-	165.9
2’	-	-	-	135.2
3’a	6.02, br s	6.02, p (1.0)	-	127.6
3’b	5.60, dq (7, 1)	5.61, dq (7.1, 1.1)		18.3
4’	1.86, br s	1.86, dd (1.6, 0.9)	-	21.5

2D NMR correlations

	^{1}H-^{1}H COSY	HMBC	NOESY
8			

[8] For ^{1}H NMR, see: *Phytochemistry*, **1978**, *17*, 471-474. To the best of our knowledge no carbon NMR had been previously reported.

Table S9. Comparison of natural and synthetic 8-*epi*-lychnopholide (**9**) ($CDCl_3$)[9]

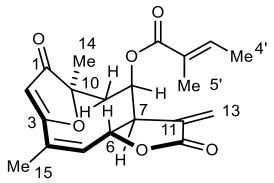


8-*epi*-Lychnopholide (**9**)

	^{1}H NMR		
	Natural (270 MHz)	Synthetic (300 MHz)	
1	-	-	Z/E isomerization from anglate to tiglate happened during the esterification and we obtained the tiglate **10** as major product. We couldn't obtain enough 8-*epi*-lychnopholide (**9**) for full analysis. For detailed information, see Supplementary Section f.
2	5.59, s	5.60, s	
3	-	-	
4	-	-	
5	5.95, dq (4, 1.5)	5.95, m	
6	5.35, ddq (4, 4, 1.5)	5.35, m	
7	3.71, ddd (4, 2)	3.70, m	
8	**5.14, d (6, 3, 2)**	5.28, m	
9α	2.53, dd (15, 6)	2.54, dd (15.3, 5.6)	
9β	2.30, dd (15, 3)	2.30, dd (15.1, 3.7)	
10	-	-	
11	-	-	
12	-	-	
13a	6.36, d (4.5)	6.34, d (2.9)	
13 b	5.70, d (4.5)	5.70, d (2.6)	
14	1.49, s	1.49, s	
15	2.08, dd (1.5, 1.5)	2.08, t (1.8)	
1'	-	-	
2'	-	-	
3'	6.13, qq (7, 1.5)	6.12, m	
4'	1.94, dq (7, 1.5)	1.94, m	
5'	1.80, dq (7, 1.5)	1.80, m	

[9] A previous report (*Phytochemistry*, **1981**, *20*, 743-749) gave the chemical shift for H-8 to be at 5.14 ppm. A later report (*Phytochemistry*, **1982**, *21*, 464-465) assigned a chemical shift for H-8 to be at 5.25 ppm very similar to ours.

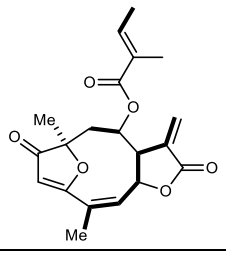
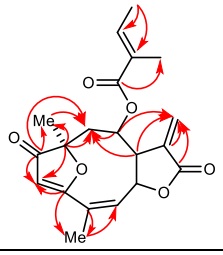
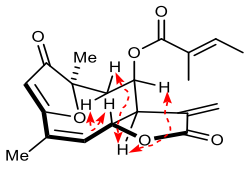
Table S10. Comparison of natural and synthetic 8-*epi*-atripliciolide-tiglate (**10**) ($CDCl_3$)[10]



8-*epi*-Atripliciolide-tiglate (**10**)

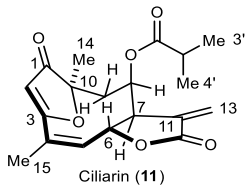
	^{1}H NMR		**^{13}C NMR**	
	Natural (270 MHz)	Synthetic (400 MHz)	Natural	Synthetic (100 MHz)
1	-	-	-	205.4
2	5.59, s	5.59, s	-	103.3
3	-	-	-	185.1
4	-	-	-	131.8
5	5.94, dq (2.5, 1.5)	5.94, dq (3.6, 1.8)	-	134.3
6	5.28, dq (2, 1.5)	5.28, m	-	75.4
7	3.70, m	3.69, m	-	48.6
8	5.18, ddd (5, 3, 3)	5.19, ddd, (5.4, 3.4, 1.9)	-	74.8
9α	2.52, dd (15, 5)	2.52, dd (15.1, 5.4)	-	42.7
9β	2.30, dd (15, 3)	2.30, dd (15.1, 3.4)	-	-
10	-	-	-	87.8
11	-	-	-	139.1
12	-	-	-	169.0
13a	6.33, d (3)	6.33, d (2.9)	-	123.5
13b	5.65, d (2.5)	5.66, d (2.5)	-	-
14	1.48, s	1.48, s	-	21.5
15	2.07, dd (1.5, 1.5)	2.07, t (1.9)	-	14.8
1'	-	-	-	166.6
2'	-	-	-	127.6
3'	6.76, qq (7, 1)	6.76, qq (7, 1.4)	-	139.7
4'	1.78, dq (7, 1)	1.78, dq (7.1, 1.1)	-	19.7
5'	1.74, br s	1.74, p (1.1)	-	12.0

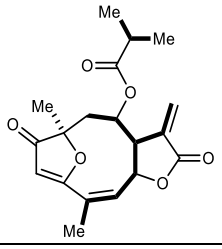
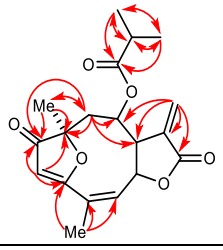
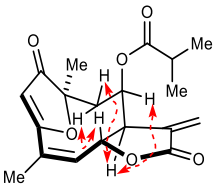
2D NMR correlations

	^{1}H-^{1}H COSY	HMBC	NOESY
10			

[10] For ^{1}H NMR, see: *Phytochemistry*, **1978**, *17*, 471-474. To the best of our knowledge no carbon NMR had been previously reported.

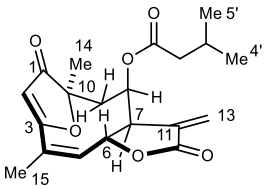
Table S11. Comparison of natural and synthetic ciliarin (**11**) ($CDCl_3$)[11]



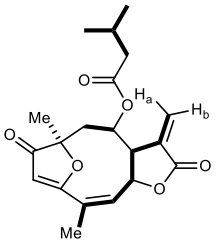
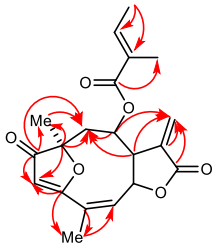
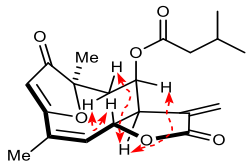
	^{1}H NMR		^{13}C NMR	
	Natural (270 MHz)	Synthetic (400 MHz)	Natural	Synthetic (100 MHz)
1	-	-	-	205.5
2	5.59, s	5.60, s	-	103.1
3	-	-	-	185.1
4	-	-	-	132.0
5	5.94, dq (2.5, 1.5)	5.93, dq (3.6, 1.8)	-	134.2
6	5.34, dq (2, 1.5)	5.34, tq (3.9, 1.9)	-	75.4
7	3.67, m	3.67, dq (4.8, 2.6)	-	48.6
8	5.21, ddd (5, 3, 3)	5.21, ddd, (5.7, 3.6, 2.1)	-	74.0
9α	2.48, dd (15, 5)	2.48, dd (15.1, 5.4)	-	42.0
9β	2.24, dd (15, 3)	2.24, dd (15.1, 3.6)	-	-
10	-	-	-	87.5
11	-	-	-	138.5
12	-	-	-	168.9
13a	6.35, d (3)	6.35, d (2.9)	-	124.1
13b	5.67, d (2.5)	5.67, d (2.5)	-	-
14	1.48, s	1.47, s	-	21.3
15	2.07, dd (1.5, 1.5)	2.07, t (1.8)	-	19.7
1’	-	-	-	175.6
2’	2.46, qq	2.46, m	-	34.1
3’/4’	1.08, d	1.10, d (2.5)	-	19.0
3’/4’	1.07, d	1.08, d (2.6)	-	18.6
2D NMR correlations				
	^{1}H-^{1}H COSY	HMBC	NOESY	
11				

[11] For ^{1}H NMR, see: *Phytochemistry*, **1978**, *17*, 471-474. To the best of our knowledge no carbon NMR had been previously reported.

Table S12. Comparison of natural and synthetic 8-*epi*-atripliciolide-isovalerate (**12**) ($CDCl_3$)[12]

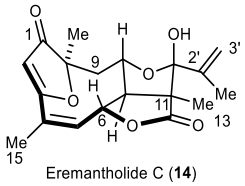


8-*epi*-Atripliciolide-isovalerate (**12**)

	^{1}H NMR		**^{13}C NMR**	
	Natural (270 MHz)	Synthetic (400 MHz)	Natural	Synthetic (100 MHz)
1	-	-	-	205.6
2	5.59, s	5.60, s	-	103.2
3	-	-	-	185.1
4	-	-	-	132.0
5	5.93, dq (2.5, 1.5)	5.93, dq (4.4, 1.7)	-	134.2
6	5.34, dq (2, 1.5)	5.34, td (4.4, 2.1)	-	75.5
7	3.65, m	3.64, dq (4.9, 2.5)	-	48.5
8	5.23, ddd (5, 3, 3)	5.24, ddd, (5.8, 3.6, 2.1)	-	74.0
9α	2.48, dd (15, 5)	2.48, dd (15.2, 6)	-	42.0
9β	2.22, dd (15, 3)	2.23, dd (15.1, 3.6)	-	-
10	-	-	-	87.5
11	-	-	-	138.5
12	-	-	-	168.9
13a	6.36, d (3)	6.36, d (2.9)	-	124.1
13b	5.68, d (2.5)	5.68, d (2.6)	-	-
14	1.48, s	1.47, s	-	21.2
15	2.07, dd (1.5, 1.5)	2.07, t (1.8)	-	19.7
1’	-	-	-	171.6
2’	2.09, dd	2.10, m	-	42.9
3’	1.98, m	1.97, ddd (12.9, 7.5, 6.4)	-	25.5
4’/5’	0.90	0.89, d (4.8)	-	22.5
4’/5’	0.87	0.88, d (4.8)	-	22.4
2D NMR correlations				
	^{1}H-^{1}H COSY	HMBC	NOESY	
12				

[12] For ^{1}H NMR, see: *Phytochemistry*, **1978**, *17*, 471-474. In this report the chemical shift of 0.87 ppm was wrongly moved to another column on the results table. To the best of our knowledge no carbon NMR had been previously reported.

Table S13. Comparison of natural and synthetic eremantholide C (**14**) ($CDCl_3$)



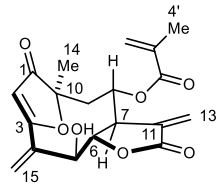
Eremantholide C (**14**)

	^{1}H NMR			**^{13}C NMR**		
	Natural [13] (500 MHz)	Natural[14] (500 MHz)	Synthetic (500 MHz)	Natural[13] (125MHz)	Natural[14] (125 MHz)	Synthetic (125 MHz)
1	-	-	-	205.2	205.8	205.3
2	5.62, s	5.63, s	5.61, s	104.5	104.5	104.7
3	-	-	-	186.8	187.2	186.9
4	-	-	-	130.2	130.0	130.3
5	6.03, dq (2.7, 1.6)	6.03, dq (2.7, 1.6)	6.03, dq (3.6, 1.8)	134.6	134.7	134.7
6	4.98, dddq (7, 2.7, 2.4, 0.6)	5.00, dddq (7.1, 2.7, 2.2, 0.6)	4.98, dp (7.2, 2.4)	81.5	81.4	81.6
7	2.85, dd (7, 4.2)	2.82, dd (7.1, 4.2)	2.86, dd (7.2, 4.3)	62.5	62.5	62.5
8	4.14, dddd (11.9, 4.2, 2.6, 0.6)	4.10, dddd (11.9, 4.2, 2.6, 0.6)	4.15, ddd (11.8, 4.3, 2.8)	78.5	78.3	78.6
9α	2.06, dd (13.6, 11.9)	2.01, dd (13.6, 11.9)	2.05, m	43.7	43.5	43.9
9β	2.41, dd (13.6, 2.6)	2.47, dd (13.6, 2.6)	2.39, dd, (13.6, 2.6)	-	-	-
10	-	-	-	89.9	90.2	90.1
11	-	-	-	59.8	59.8	59.9
12	-	-	-	175.4	175.7	175.6
13	1.19, s	1.18, s	1.20, s	21.9	21.9	22.0
14	1.49, s	1.46, s	1.50, s	20.6	20.5	20.7
15	2.06, dd (2.4, 1.6)	2.05, dd (2.2, 1.6)	2.06, m	20.3	20.3	20.5
1’	-	-	-	106.2	106.1	106.3
2’	-	-	-	142.0	142.1	142.1
3’a	5.08, dd (2.0, 1.5)	5.07, dq (2.0, 1.8)	5.08, p (1.6).	116.1	115.8	116.4
3’b	5.33, dd (2.0, 0.9)	5.30, dq (2.0, 1.1)	5.33, dq (1.8, 0.8).	-	-	-
4’	1.90, dd (1.5, 0.9)	1.90, dd (1.8, 1.1)	1.89, dd (1.6, 0.9)	18.9	18.9	19.1
-OH	-	3.62, br s	-	-	-	-

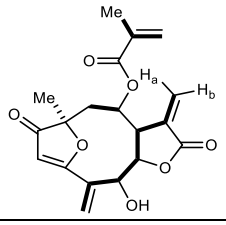
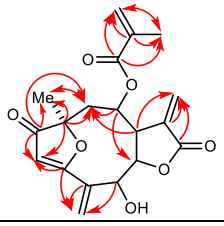
[13] Sass, D. C., Heleno, V. C. G., Cavalcante, S., da Silva Barbosa, J., Soares, A. C. F., Constantino, M. G. *J. Org. Chem.* **2012**, *77*, 9374–9378.

[14] Heleno, V. C. G., de Oliveira, K. T., Lopes, J. L. C., Lopes, N. P., Ferreira, A. G. *Magn. Reson. Chem.* **2008***, 46,* 576-581.

Table S14. Comparison of natural and synthetic 5-*epi*-isogoyazensolide (**15**) ($CDCl_3$)



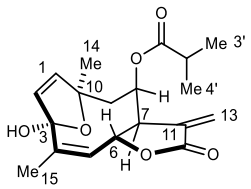
5-*epi*-Isogoyazensolide (**15**)

	^{1}H NMR		**^{13}C NMR**	
	Natural[15] (270 MHz)	Synthetic (400 MHz)	Natural[16] (100 MHz)	Synthetic (100 MHz)
1	-	-	203.7	203.8
2	5.97, s	5.96, s	106.5	106.5
3	-	-	185.2	185.2
4	-	-	137.3	137.1
5	4.69, ddd (9.5, 2, 2)	4.67, dt (9.6, 2.2)	74.0	73.9
6	4.60, dd (9.5, 5)	4.60, dd (9.6, 6)	85.0	85.0
7	3.66, dddd (5, 2, 3.5, 3)	3.66, m	51.2	51.1
8	4.39, ddd (2, 11.5, 2)	4.37, dt (12, 1.8)	70.6	70.5
9α	2.50, dd (13, 11.5)	2.50, dd (13.7, 11.9)	45.2	45.2
9β	2.37, dd (13, 2)	2.37, dd (13.9, 1.7)	-	-
10	-	-	90.2	90.2
11	-	-	**133.0**	**132.8**
12	-	-	167.6	167.6
13a	6.28, d (3.5)	6.28, d (3.5)	124.7	124.9
13b	5.57, d (3)	5.56, d (3.1)	-	-
14	1.53 s	1.54, s	21.2	21.2
15a	6.26, dd (2, 1)	6.25, dd (2.3, 0.9)	123.1	123.3
15b	6.01, m	6.01, m	-	-
1’	-	-	166.8	166.8
2’	-	-	**135.4**	**135.3**
3’a	6.01, m	6.01, m	126.6	126.7
3’b	5.56, br s	5.55, m	-	-
4’	1.83, br s	1.83, dd (1.6, 1)	17.9	18.0
2D NMR correlations				
	^{1}H-^{1}H COSY	HMBC		
15				

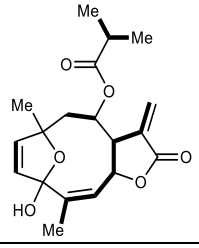
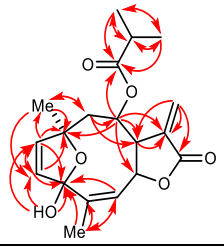
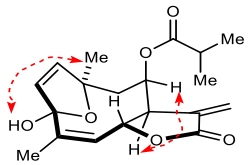
[15] Bohlmann, F., Zdero, C., Robinson, H., King, R. M. *Phytochemistry*, **1981**, *20*, 731-734.

[16] Lopes, J. L. C. *J. Braz. Chem. Soc.* **1995**, *6*, 307-311. In this manuscript the chemical shift for protons 11 and 2’ were wrongly assigned and they should have been swapped.

Table S15. Comparison of natural and synthetic tagitinin F (**16**) ($CDCl_3$)[17]

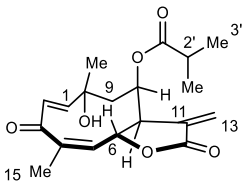


Tagitinin F (**16**)

	^{1}H NMR		**^{13}C NMR**	
	Natural (300 MHz)	Synthetic (400 MHz)	Authentic sample (100 MHz)	Synthetic (100 MHz)
1	5.81, d (6)	5.81, (d, 5.5)	127.9	127.9
2	6.31, d (6)	6.33, (d, 5.7)	139.6	139.6
3	-	-	108.5	108.5
4	-	-	139.5	139.5
5	5.69, m	5.68, m	131.3	131.3
6	5.90, dd (5, 3)	5.91, dh (6.1, 1.3)	74.7	74.7
7	3.42, ddd (2.5, 2, 1)	3.42, m	48.0	48.0
8	5.08, t (5, 4)	5.08, td, (3.6, 0.9)	76.6	76.6
9α	2.36, dd (15, 4)	2.36, dd (16.2, 3.9)	43.9	43.9
9β	2.28, dd (15, 5)	2.28, dd (16.2, 3.3)	-	-
10	-	-	87.2	87.2
11	-	-	139.0	139.0
12	-	-	169.7	169.7
13a	6.30, d (2.5)	6.35, d (2.9)	124.3	124.3
13b	5.69, d (2)	5.67, d (2.5)	-	-
14	1.41, s	1.40, s	31.8	31.8
15	1.93, t (1.5)	1.93, t (1.5)	20.8	20.8
1’	-	-	175.9	175.9
2’	2.49, hept (7.2)	2.50, hept (7)	34.4	34.4
3’	1.11, d (7.2)	1.11, d (7)	19.1	19.1
4’	1.13, d (7.2)	1.13, d (7)	18.9	18.9
2D NMR correlations				
	^{1}H-^{1}H COSY	HMBC	NOESY	
16				

[17] Fernandes, V. H. C. Viera, N. B. Zanini, L. B. L. Silva, A. F. Salem, P. P. O. Soares, M. G. Nicacio, K. J. de Paula, A. C. C. Virtuoso, L. S. Oliveira, T. B. Silva, E. O. Dias, D. F. Chagas-Paula, D. A. *Photochem. Photobiol.* **2020**, *96*, 14-20.

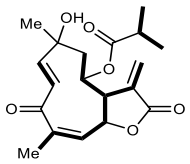
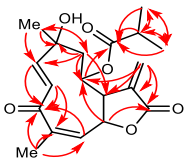
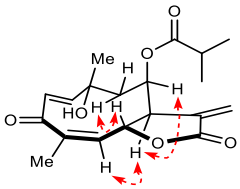
Table S16. Comparison of natural and synthetic tagitinin C (**17**) ($CDCl_3$)



Tagitinin C (**17**)

	^{1}H NMR			**^{13}C NMR**	
	Natural[17] (500 MHz)	Natural[18] (270 MHz)	Synthetic (500 MHz)	Natural[18] (68 MHz)	Synthetic (125 MHz)
1	6.94, (d, 17.1)	6.94, (d, 17)	6.91, (d, 17.1)	160.49	159.88
2	6.26, (d, 17.1)	6.26, (d, 17)	6.24, (d, 17.1)	129.57	129.72
3	-	-	-	196.85	196.57
4	-	-	-	138.84	138.96
5	5.87, like d (9)	5.88, br d (10)	5.87, br d (9.5)	137.14	137.15
6	5.41, like d (9)	5.42, br d (10)	5.39, br d (9.1)	76.05	75.93
7	3.54, m	3.55, m	3.53, m	47.05	47.06
8	5.37, m	5.33, m	5.36, m	74.11	73.73
9α	2.49	~2.4	2.46	48.37	48.47
9β	2.02	~2	2.01, dd (14.4, 4.5)	-	-
10	-	-	-	71.91	72.18
11	-	-	-	136.11	136.00
12	-	-	-	169.75	169.58
13a	6.34, d (1.5)	6.36, d (2)	6.36, d (1.8)	124.43	124.49
13b	5.81, d (1.5)	5.81, d (2)	5.80, d (1.7)	-	-
14	1.53, s	1.56	1.54, s	28.88	29.16
15	1.95, like s	1.97, br	1.96, br s	19.65	19.69
1’	-	-	-	176.18	176.06
2’	2.42, m	2.44, m	2.43, m	34.06	34.03
3’	1.07, d (4.5)	1.10, d (7.1)	1.08, d (7)	18.80	18.81
4’	1.05, d (4.5)	1.08, d (7.1)	1.06, d (7)	18.64	18.62

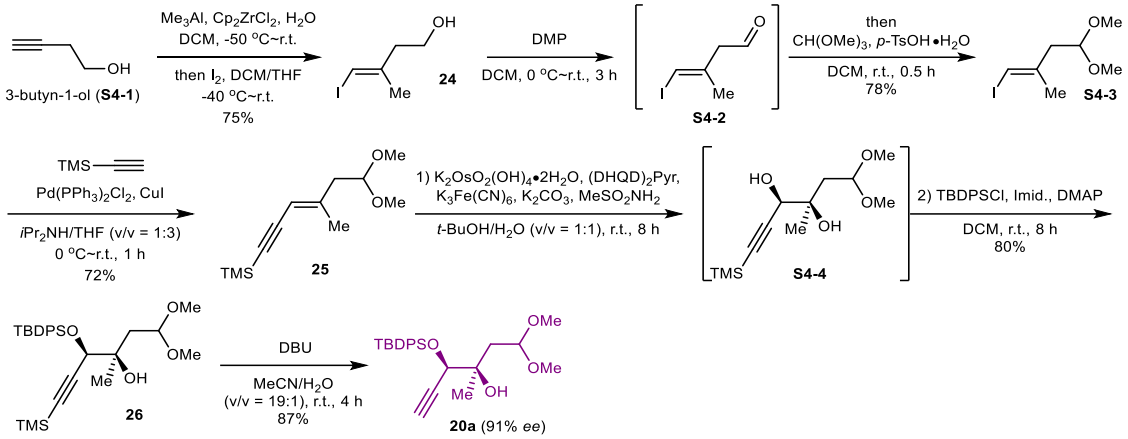
2D NMR correlations

	^{1}H-^{1}H COSY	HMBC	NOESY		
17					

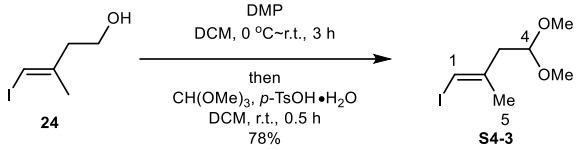
[18] Baruah, N. C., Sharma, R. P., Madhusudanan, K. P., Thyagarajan, G., Herz, W., Murari, R. *J. Org. Chem*, **1979**, *44*, 1831-1835.

f) Experimental procedures for Scheme 1

Figure S4. Synthesis of **20a** from commercially available 3-butyn-1-ol (**S4-1**).



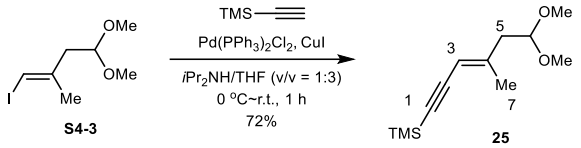
Vinyl iodide **24** was prepared from commercially available 3-butyn-1-ol using a carboalumination /iodination process.[19] The reaction can be ran in a decagram scale and the product can be used in the next step without further purification.



To a 0 °C solution of alcohol **24** (~132 mmol) in CH_2Cl_2 (250 mL) Dess–Martin periodinane (DMP, 56 g, 132 mmol) was slowly added in portions. The mixture was stirred at room temperature for 3 hours, till TLC analysis showed disappearance of starting material (aldehyde, Rf = 0.60, Pentane/Ethyl acetate = 5/1). Then, the mixture was cooled down again to 0 °C and a catalytic amount of *p*-TsOH•H_2O (1.0 g) was added, followed by addition of $CH(OMe)_3$ (21.6 mL, 198 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 30 minutes. the mixture was then quenched with saturated aqueous NH_4Cl and Na_2SO_3(v/v = 1:1, 500 mL) and extracted with CH_2Cl_2 (3 × 500 mL). The combined organic layers were washed with brine (500 mL), dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 30/1) to provide the **S4-3** as yellow oil (26.4 g, 78%).

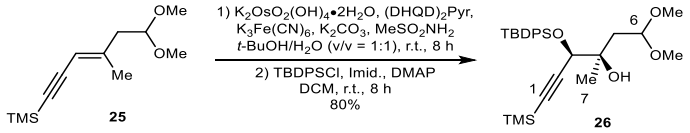
Data of vinyl iodide **S4-3**: yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (m, 1H, *H*$_1$), 4.47 (t, *J* = 5.7 Hz, 1H, *H*$_4$), 3.32 (s, 6H, -*OMe*), 2.50 (dd, *J* = 5.7, 1.0 Hz, 2H, *H*$_3$), 1.88 (d, *J* = 1.1 Hz, 3H, *H*$_5$) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δδ 143.4 (*C*$_2$), 102.9 (*C*$_4$H), 77.8 (*C*$_1$H), 53.1 (-*OMe*), 42.5 (*C*$_3$H$_2$), 24.6 (*C*$_5$H$_3$) ppm;
IR (film, cm^{-1}) 2931, 1729, 1118, 1072;
TLC: Rf = 0.40, Pentane/Ethyl acetate = 25/1).

[19] Prasad, K. R., Pawar, A. B. *Org Lett.*, **2011**, *13*, 4252-4255.



To a stirred solution of vinyl iodide **S4-3** (20.8 g, 81 mmol) in THF/*i*-Pr_2NH (150 mL/50 mL) was added trimethylsilyl acetylene (13.5 mL, 97.5 mmol) at 0 °C. Then $Pd(PPh_3)_2Cl_2$ (2.8 g, 4.05 mmol) and CuI (1.54 g, 8.1 mmol) were added at the same temperature. The reaction mixture was allowed to reach room temperature and stirred for 1 hour till TLC analysis showed disappearance of starting material. Then, pentane (800 mL) was added to the reaction mixture, stirred for 30 minutes, the mixture was filterred and the solution washed with saturated aqueous NH_4Cl (200 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 50/1 ~ 25/1) to provide the **25** as light-yellow oil (13.3 g, 72%).

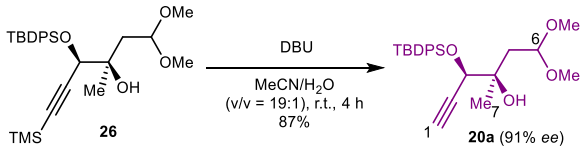
Data of vinyl iodide **25**: light-yellow oil;
^1H NMR (400 MHz, $CDCl_3$) δ 5.38 (m, 1H, *H3*), 4.47 (t, *J* = 5.7 Hz, 1H, *H6*), 3.30 (s, 6H, -*OMe*), 2.37 (d, *J* = 5.8 Hz, 2H, *H5*), 1.94 (d, *J* = 0.8 Hz, 3H, *H7*), 0.18 (s, 9H, -*TMS*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9 (*C4*), 107.9 (*C6*H), 103.2 (*C2*), 103.1 (*C3*H), 97.6 (*C1*), 52.9 (-OMe), 41.8 (*C5*H_2), 20.2 (*C7*H_3), 0.2 (-*TMS*) ppm;
IR (film, cm^{-1}) 2957, 2135, 1249, 1120, 1064, 838, 509;
HRMS(ESI) $[M + H]^+$ calculated for $C_{12}H_{23}O_2Si$: 227.1467, found: 227.1250;
TLC: Rf = 0.30 (Pentane/Ethyl acetate = 25/1).



A 500 mL round bottom flask equipped with a magnetic stir bar was charged with $K_2OsO_2(OH)_2$•$2H_2O$ (320 mg, 0.9 mmol), $(DHQD)_2Pyr$ (1.2 g, 1.36 mmol), $K_3Fe(CN)_6$ (44.6 g, 136 mmol), K_2CO_3 (18.8 g, 136 mmol) and *t*-BuOH/H_2O (100 mL/100 mL). The bi-phasic mixture was stirred at room temperature for 30 minutes, then $MeSO_2NH_2$ (4.8 g, 50.5 mmol) was added and the mixture was stirred for another 30 minutes. Enyne **25** (10.2 g, 45 mmol) was added to the AD-mix-β mixture and stirred at room temperature for 8 hours. The reaction was followed by NMR analysis till disappearance of the starting material. The reaction slurry was filterred and the filtrate was extrated with CH_2Cl_2 (4 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo* and then used directly for silyl protection without further purification. The crude product was dissolved in CH_2Cl_2 (300 mL) and imidazole (7.7 g, 113 mmol) was added. Then TBDPSCl (21 mL, 81 mmol) was added dropwise together with a catalytic amount of DMAP (100 mg). The reaction mixture was then stirred at room temperature for 8 hours or till the TLC analysis showed disappearance of starting material. Then, the mixture was quenched with water (100 mL) and extracted with CH_2Cl_2 (2 × 200 mL). The combined organic layers were washed with brine (500 mL), dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 15/1 ~ 5/1) to provide the **26** as a colorless oil (18 g, 80%).

The enantiomers were found not to be separated by chiral HPLC using various columns under different conditions. The *ee* value was confirmed after TMS deprotection.

Data of alcohol **26**: Colorless oil;
$[\alpha]_D^{20}$ -53.0 (c 1.0, $CHCl_3$);
^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.68 (m, 4H, -*TBDPS*), 7.45-7.32 (m, 6H, -*TBDPS*), 4.69 (t, *J* = 5.6 Hz, 1H, *H6*), 4.18 (s, 1H, *H3*), 3.29 (s, 3H, -*OMe*), 3.28 (s, 3H, -*OMe*), 2.05 (dd, *J* = 14.4, 5.2 Hz, 1H, *H5*), 1.88 (dd, *J* = 14.8, 6 Hz, 1H, *H5*), 1.31 (s, 3H, *H7*), 1.07 (s, 9H, -*TBDPS*), -0.01 (s, 9H, -*TMS*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4 (*TBDPS*), 136.3 (*TBDPS*), 133.7 (*TBDPS*), 133.0 (*TBDPS*), 130.0 (*TBDPS*), 129.7 (*TBDPS*), 127.7 (*TBDPS*), 127.4 (*TBDPS*), 104.4 (*C2*), 102.4 (*C6*H), 92.1 (*C1*), 73.8 (*C4*), 71.7 (*C3*H), 53.1 (-*OMe*), 53.0 (-*OMe*), 39.5 (*C5*H_2), 27.2 (*TBDPS*), 23.6 (*C7*H_3), 19.6 (*TBDPS*), -0.3 (*TMS*) ppm;
IR (film, cm^{-1}) 2957, 1719, 1428, 1250, 1111, 843, 701;
HRMS(ESI) $[M + Na]^+$ calculated for $[C_{28}H_{42}NaO_4Si_2]^+$: 521.2514, found: 521.2520;
TLC: Rf = 0.50 (Pentane/Ethyl acetate = 10/1).

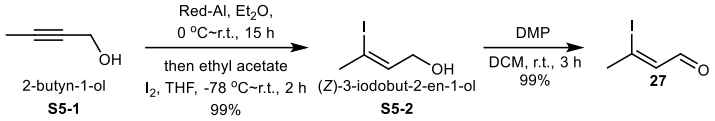


To a stirred solution of TMS alkyne **26** (18 g, 36 mmol) in $MeCN/H_2O$ (90 mL/5 mL) was added DBU (8.1 mL, 54 mmol) at room temperature. The reaction mixture was stirred at for 4 hours or till the TLC analysis showed disappearance of starting material. The reaction mixture was concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 20/1 ~ 3/1) to provide the alkyne **20a** as colorless oil (13.3 g, 87%).

Chiral HPLC analysis of **20a**: chiral stationary column: AD-H, mobile phase: *n*-hexane/*i*-PrOH = 99:1, 1.0 mL/min, 210 nm, 30 °C, t_R (major) = 12.80 min, t_R (minor) = 11.05 minutes. The result indicated 91% *ee*. See **Supplementary Section k** for details.

Data of alkyne **20a**: colorless oil;
$[\alpha]_D^{20}$ -39.8 (c 0.19, $CHCl_3$);
^1H NMR (400 MHz, $CDCl_3$) δ 7.79-7.67 (m, 4H, -*TBDPS*), 7.46-7.33 (m, 6H, -*TBDPS*), 4.66 (t, *J* = 5.7 Hz, 1H, *H6*), 4.22 (d, *J* = 2.2 Hz, 1H, *H3*), 3.28 (s, 3H, -*OMe*), 3.27 (s, 3H, -*OMe*), 3.07 (s, 1H, -*OH*), 2.26 (d, *J* = 2.2 Hz, 1H, *H1*), 2.06 (dd, *J* = 14.4, 6 Hz, 1H, *H5*), 1.89 (dd, *J* = 14.5, 5.5 Hz, 1H, *H5*), 1.31 (s, 3H, *H7*), 1.10 (d, *J* = 2.9 Hz, 9H, -*TBDPS*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4 (*TBDPS*), 136.3 (*TBDPS*), 133.3 (*TBDPS*), 132.9 (*TBDPS*), 130.1 (*TBDPS*), 129.9 (*TBDPS*), 127.8 (*TBDPS*), 127.4 (*TBDPS*), 102.3 (*C6*H), 82.6 (*C2*), 75.1 (*C1*), 73.8 (*C10*), 71.0 (*C3*H), 53.2 (-*OMe*), 52.9 (-*OMe*), 39.3 (*C5*H_2), 27.2 (*TBDPS*), 23.6 (*C7*H_3) ppm;
IR (film, cm^{-1}) 3501, 2933, 1427, 1107, 1092, 700;
HRMS(ESI) $[M + Na]^+$ calculated for $[C_{25}H_{34}NaO_4Si]^+$: 449.2119, found: 449.2124;
TLC: Rf = 0.50 (Pentane/Ethyl acetate = 7/1).

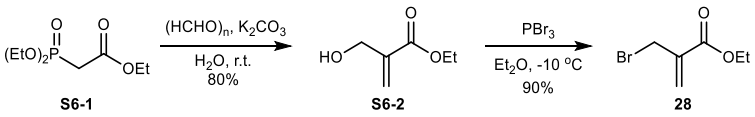
Figure S5. Synthesis of **27** from 2-butyn-1-ol (**S5-1**)



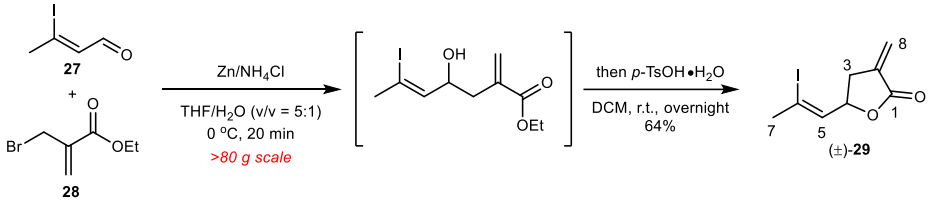
Aldehyde **27** was prepared from commercially available 2-butyn-1-ol (**S5-1**) in 2 steps using a carboalumination / iodination then modified DMP oxidation process. All spectroscopic and spectrometric analyses were in agreements with the literature accordingly for allylic alcohol (Z)-3-iodobut-2-en-1-ol (**S5-2**)[20] and aldehyde **27**.[21]

Modified DMP oxidation: To a stirred solution of crude allylic alcohol **S5-2** (~ 42 g, 212 mmol) in CH_2Cl_2 (400 mL) was added DMP (90 g, 212 mmol) in portions at 0 °C. The reaction was monitored by TLC until no starting material remained (2 hours). Then pentane (1.2 L) was added to the reaction and stirred at rom temperature for 30 minutes. The white precipitate was filtered off and the resulting colorless solution was concentrated *in vacuo* to give a yellow to brown oil **27** (~ 42 g) which was used directly for Barbier reaction without any further purification.

Figure S6. Synthesis of **28**



Allylic bromide **28** is known compound and was prepared in 2 steps including Baylis–Hillman reaction [22] and bromination [23] from triethyl phosphonoacetate (**S6-1**). All spectroscopic and spectrometric analyses were in agreements with the literature accordingly.

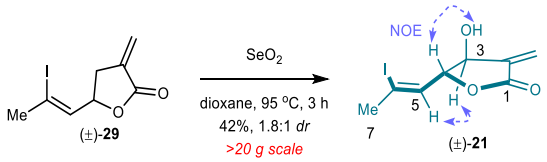


A 2.5 L round bottom flask equipped with a magnetic stir bar was charged with aldehyde **27** (82 g, 418 mmol), allylic bromide **28** (121 g, 627 mmol), THF (800 mL) and NH_4Cl saturated solution (160 mL). The yellow bi-phasic mixture turned colorless and was cooled down to 0 °C. Then Zn (54 g, 836 mmol) was added in small portions within 30 minutes (caution the reaction is very exothermic). The reaction mixture was stirred at 0 °C for 20 minutes or till the TLC analysis showed disappearance of the starting material. The reaction mixture was filterred, the filtrate was concentrated *in vacuo* and redissolved

[20] Dakoji, S.; Li, D.; Agnihotri, G.; Zhou, H.; Liu, H. *J. Am. Chem. Soc.* **2001**, *123*, 9749-9759.
[21] Meyer, C., Marek, I., Normant, J. F. *Synlett*. **1993**, *6*, 386-388.
[22] Patil, S., Chen, L., Tanko, J. M. *Eur. J. Org. Chem.* **2014**, *3*, 502-505.
[23] Li, Y., Zhang, J., Li, D., Chen, Y. *Org. Lett.* **2018**, *20*, 3296-3299.

in CH_2Cl_2 (800 mL). The organic layer was washed with water (200 mL) and brine (200 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo* and used directly for cyclization without further purification. The crude product was dissolved in CH_2Cl_2 (500 mL) and a catalytic amount *p*-TsOH•H_2O (1.0 g) was added. The reaction mixture was stirred at room temperature for 12 hours or till the TLC analysis showed disappearance of starting material. Then the mixture was washed with *sat. aq.* $NaHCO_3$ (100 mL), brine (100 mL), dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 20/1 ~ 5/1) to provide the **29** as light-yellow oil (70.6 g, 64%).

Data of lactone **29**: light-yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25-6.20 (m, 1H, *H*$_8$), 5.71 (dt, *J* = 7.6, 1.8 Hz, 1H, *H*$_5$), 5.65 (q, *J* = 2.2 Hz, 1H, *H*$_8$), 5.04 (dt, *J* = 9.8, 6.8 Hz, 1H, *H*$_4$), 3.25 (ddt, *J* = 17.1, 7.7, 2.3 Hz, 1H, *H*$_3$), 2.64 (ddtd, *J* = 17.2, 6.2, 3.0, 1.3 Hz, 1H, *H*$_3$), 2.54 (d, *J* = 1.7 Hz, 3H, *H*$_7$) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ170.0 (*C*$_1$), 133.8 (*C*$_5$H), 133.8 (*C*$_2$), 122.6 (*C*$_8$H$_2$), 104.3 (*C*$_6$), 81.3 (*C*$_4$H), 33.8 (*C*$_7$H$_3$), 33.6(*C*$_3$H$_2$) ppm; ^{13}C NMR of C_2 overlaps with C_5;
IR (film, cm^{-1}) 1765, 1242, 1116, 1016;
HRMS(ESI) $[M + H]^+$ calculated for $C_8H_{10}IO_2$: 264.9725, found: 264.9709;
TLC: Rf = 0.60 (Pentane/Ethyl acetate = 5/1).

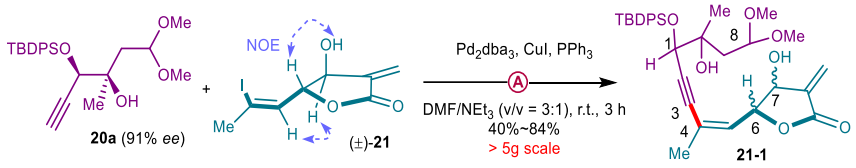


To a stirred solution of lactone **29** (22 g, 83 mmol) in dioxane (500 mL) was added SeO_2 (50 g, 450 mmol) in 3 portions at 95 °C within 2 hours. The reaction mixture was stirred at the same temperature for another hour and cooled down to room temperature. Then dioxane was evaporated and Et_2O (800 mL) was added, stirred for 30 min, filtered and the solution was washed with saturated aqueous $NaHCO_3$ (100 mL), diluted Na_2S (50 mL) and brine (100 mL). The organic phase was dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 1/1) to provide the **21** as light-yellow oil (9.8 g, 42%).

Lactone **21** was obtained as a mixture of inseparable 1.8/1 diastereomers (determined by ^{1}H NMR). The structures were fully elucidated based on 2D NMR spectroscopic analyses, which indicated *trans* as the major product.

Data of lactone **21**: Light yellow oil;
IR (film, cm^{-1}) 3420, 1753, 1250, 1129, 973;
HRMS(ESI) $[M + H]^+$ calculated for $[C_8H_{10}IO_3]^+$: 280.9669, found: 280.9675;
TLC: Rf = 0.50 (Pentane/Ethyl acetate = 1/1);
Major-*trans*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (d, *J* = 2.3 Hz, 1H, *H*$_8$), 6.00 (d, *J* = 2.1 Hz, 1H, *H*$_8$), 5.65 (dq, *J* = 8.0, 1.5 Hz, 1H, *H*$_5$), 4.89 (ddd, *J* = 8.1, 4.5, 0.7 Hz, 1H, *H*$_4$), 4.67 (ddt, *J* = 6.5, 4.4, 2.2 Hz, 1H), 2.89 (d, *J* = 6.1 Hz, 1H, -*OH*), 2.59 (dd, *J* = 1.6, 0.6 Hz, 3H, *H*$_7$) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ168.5 (*C*$_1$), 137.7 (*C*$_2$), 131.3 (*C*$_5$H), 126.6 (*C*$_8$H$_2$), 106.9 (*C*$_6$), 88.7 (*C*$_4$H), 73.7 (*C*$_3$H), 34.2 (*C*$_7$H$_3$) ppm; ^{13}C NMR of C_2 of cis and trans are overlaped;

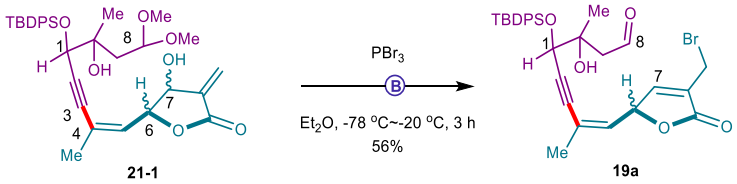
Minor-*cis*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (d, *J* = 1.7 Hz, 1H, H_8), 6.04 (d, *J* = 1.5 Hz, 1H, H_8), 5.81 (dq, *J* = 7.5, 1.5 Hz, 1H, H_5), 5.06 (ddd, *J* = 7.5, 5.7, 0.8 Hz, 1H, H_4), 5.03-4.97 (m, 1H, H_3), 2.63 (dd, *J* = 1.6, 0.6 Hz, 3H, H_7), 2.50 (d, *J* = 4.8 Hz, 1H, -OH). ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ168.9 (C_1), 137.7 (C_2), 128.8 (C_5H), 127.5 (C_8H_2), 107.2 (C_6), 86.4 (C_4H), 69.1 (C_3H), 34.3 (C_7H_3) ppm; ^{13}C NMR of C_2 of cis and trans are overlaped.



To a stirred solution at room temperature and under inert atmosphere of N_2 of alkyne **20a** (8.0 g, 18.8 mmol) and vinyl iodide **21** (8.0 g, 28.6 mmol) in DMF/NEt_3 (60 mL/10 mL) was added PPh_3(1.1 g, 4.2 mmol) followed by Pd_2dba_3 (3.6 g, mmol) and CuI (0.6 g, mmol). The resulted mixture was stirred for 3 hours or till the TLC analysis showed disappearance of starting material. The reaction was then quenched by addition of *sat. aq.* NH_4Cl (100 mL) and extracted with ethyl acetate (3 × 200 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 1/2) to provide enyne **21-1** as yellow oil (4.3 g, 40%). The reaction can be run from milligrams to a eight grams scale with yields variying from 40% ~ 84% depending on the scale.

Enyne **21-1** was obtained as a complicated mixture of diastereomers and that could not be seperated by convencional chromatographic techniques.

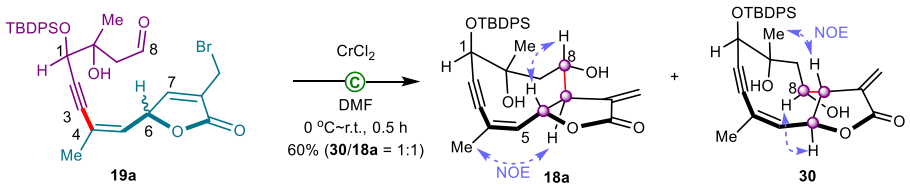
Data of enyne **21-1**: yellow oil;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.69 (m, 4H), 7.50-7.31 (m, 6H), 6.39-6.37 (m, 1H), 6.02-5.80 (m, 1H), 5.59-5.54 (m, 0.88H), 5.26 (t, *J* = 9.3 Hz, 0.13H), 5.08-4.77 (m, 1H), 4.75 – 4.61 (m, 1.27H), 4.56 (dd, *J* = 6.2, 4.5 Hz, 0.23H), 4.48-4.46 (m, 0.56H), 4.37 (dd, *J* = 16.1, 4.2 Hz, 1H), 4.00 (dd, *J* = 20.7, 6.8 Hz, 0.44H), 3.32-3.26 (m, 6H), 2.45 (d, *J* = 4.9 Hz, 0.24H), 2.31 (d, *J* = 4.8 Hz, 0.27H), 2.22-1.85 (m, 2.5H), 1.73-1.62 (m, 2.5H), 1.39-1.29 (m, 3H), 1.14-1.05 (m, 9H) ppm;
^{13}C NMR (75 MHz, $CDCl_3$) δ 175.2, 168.7, 136.2, 136.2, 136.1, 133.4, 132.6, 130.3, 129.9, 129.7, 129.6, 127.9, 127.6, 126.1, 102.8, 102.3, 94.6, 80.9, 80.5, 74.4, 74.2, 71.6, 53.7, 53.5, 53.1, 52.8, 39.4, 27.1, 27.0, 24.1, 22.9, 22.3, 19.6 ppm;
IR (film, cm^{-1}) 3414, 2929, 2213, 1969, 1769, 1428, 1113, 824, 704;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{33}H_{42}NaO_7Si$: 601.2596, found: 601.2598;
TLC: Rf = 0.30 (Pentane/Ethyl acetate = 1/1).



A 100 mL round bottom flask equipped with a magnetic stir bar was charged with enyne **21-1** (1.7 g, 2.9 mmol) and Et_2O (30 mL). The reaction mixture was cooled down to -78 °C and PBr_3 (0.7 mL, 7.35 mmol) was added. The temperature was allowed to rise to -20

°C and stirred for 3 hours or till the TLC analysis showed disappearance of starting material. Then, the reaction was quenched with water (5.0 mL) and extracted with Et_2O (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 5/1 ~ 3/1) to provide bromolactone **19a** as colorless oil (0.98 g, 56%) as a 1:1 mixture of inseperable diastereomers.

Data of bromolactone **19a**: colorless oil;
IR (film, cm^{-1}) 3482, 2933, 1764, 1428, 1110, 1077, 1040, 703;
HRMS(ESI) $[M + H]^+$ calculated for $C_{31}H_{36}BrO_5Si$: 595.1510, found: 595.1516;
TLC: Rf = 0.60 (Petroleum ether/Ethyl acetate = 2/1);
Diastereomer I:
^1H NMR (400 MHz, $CDCl_3$) δ 9.90 (m, 1H, *H8*), 7.75-7.67 (m, 4H, *TBDPS*), 7.49-7.35 (m, 6H, *TBDPS*), 7.00 (q, *J* = 1.4 Hz, 1H, *H7*), 5.24-5.16 (m, 2H, *H5*+*H6*), 4.47 (s, 1H, *H1*), 4.02-4.05 (m, 2H, *H13*), 2.77 (dd, *J* = 15.8, 2 Hz, 1H, *H9*), 2.69 (dd, *J* = 15.7, 2.8 Hz, 1H, *H9*), 1.67 (d, *J* = 0.8 Hz, 3H, *H15*), 1.47 (s, 3H, *H14*), 1.06 (s, 9H, *TBDPS*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.81 (*C8*), 170.97 (*C12*), 151.03 (*C7*H), 136.13 (*TBDPS*), 135.98 (*TBDPS*), 133.12 (*TBDPS*), 131.65 (*TBDPS*), 130.75 (*C11*), 130.62 (*TBDPS*), 130.11 (*TBDPS*), 129.48 (*C5*H), 128.19 (*TBDPS*), 127.73 (*TBDPS*), 124.56 (*C4*), 94.20 (*C2*), 85.16 (*C3*), 79.64 (*C6*H), 74.71 (*C10*), 71.43 (*C1*H), 50.80 (*C9*H_2), 26.94 (*TBDPS*), 23.66 (*C14*H_3), 22.77 (*C15*H_3), 20.83 (*C13*H_2), 19.66 (*TBDPS*) ppm;
Diastereomer II:
^1H NMR (400 MHz, $CDCl_3$) δ 9.88 (m, 1H, *H8*), 7.75-7.67 (m, 4H, *TBDPS*), 7.49-7.35 (m, 6H, *TBDPS*), 6.65 (d, *J* = 1.3 Hz, 1H, *H7*), 5.24-5.16 (m, 2H, *H5*+*H6*), 4.47 (s, 1H, *H1*), 4.02-4.05 (m, 2H, *H13*), 2.76 (dd, *J* = 15.7, 2 Hz, 1H, *H9*), 2.66 (dd, *J* = 15.7, 2.8 Hz, 1H, *H9*), 1.65 (d, *J* = 1.4 Hz, 3H, *H15*), 1.46 (s, 3H, *H14*), 1.07 (s, 9H, *TBDPS*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8 (*C8*), 170.95 (*C12*), 150.84 (*C7*H), 136.03 (*TBDPS*), 135.91 (*TBDPS*), 132.91 (*TBDPS*), 132.05 (*TBDPS*), 130.87 (*C11*), 130.50 (*TBDPS*), 130.22 (*TBDPS*), 129.54 (*C5*H), 128.11 (*TBDPS*), 127.74 (*TBDPS*), 124.31 (*C4*), 94.36 (*C2*), 85.07 (*C3*), 79.64 (*C6*H), 74.80 (*C10*), 71.44 (*C1*H), 50.78 (*C9*H_2), 27.00 (*TBDPS*), 23.71 (*C14*H_3), 22.81 (*C15*H_3), 20.97 (*C13*H_2),19.61 (*TBDPS*) ppm;

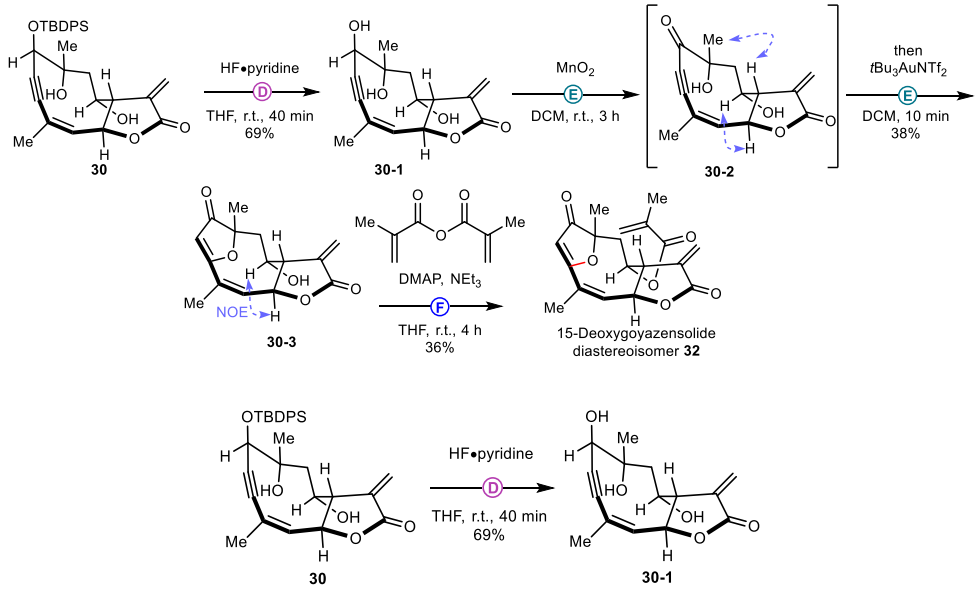


A 50 mL round bottom flask equipped with a magnetic stir bar was charged with bromolactone **19a** (1.03 g, 1.73 mmol) and DMF (10 mL). The reaction mixture was cooled down to 0 °C and $CrCl_2$ (532 mg, 4.3 mmol) was added. The temperature was allowed to rise to room temperature and stirred for 1 hour or till the TLC analysis showed disappearance of starting material. Then, the reaction was quenched with *sat. aq.* NH_4Cl (20 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 3/1 ~ 1/3) to provide **18a** as a waxy solid (272 mg, 30%) and **30** as a light yellow solid (270 mg, 30%).

The structures of **18a** and **30** were fully elucidated based on 2D NMR spectroscopic analyses. The absolute configuration of **30** was determined by X-ray diffraction. Single crystals of **30** suitable for X-ray crystallographic analysis were obtained by a single recrystallization at room temperature by slow evaporation using *n*-hexanes/CH_2Cl_2 as solvent mixture. See **Supplementary Section m** for detail.

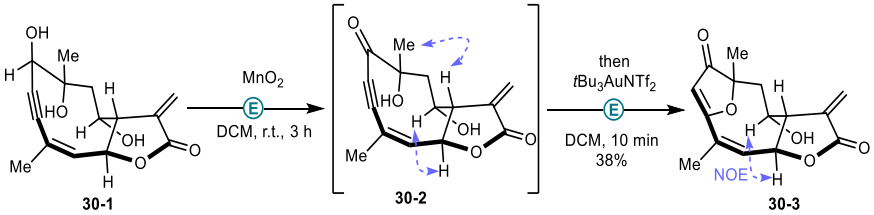
Data of **18a**: waxy solid;
$[\alpha]_D^{20}$ -130.2 (c 0.2, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ7.69 (ddd, *J* = 10.3, 8.1, 1.5 Hz, 4H, -*OTBDPS*), 7.47-7.31 (m, 6H, -*OTBDPS*), 6.36 (br s, 1H, *H13*), 5.86 (m, 1H, *H5*), 5.73 (br s, 1H, *H13*), 5.02 (dt, *J* = 3.7, 1.9 Hz, 1H, *H6*), 4.15 (s, 1H, *H1*), 3.92 (br s, 1H, *H7*), 3.88 (m, 1H, *H8*), 2.72 (br d, *J* = 15.3 Hz, 1H, *H9*), 2.07 (dd, *J* = 15.2, 6.1 Hz, 1H, *H9*), 1.61 (t, *J* = 1.8 Hz, 3H, *H15*), 1.41 (s, 3H, *H14*), 1.11 (s, 9H, -*OTBDPS*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$)δ 170.3 (*C12*), 139.6 (*C5*H), 136.4 (*TBDPS*), 136.1 (*TBDPS*), 135.8 (*C11*), 133.2 (*TBDPS*), 133.0 (*TBDPS*), 130.13 (*TBDPS*), 130.05 (*TBDPS*), 127.8 (*TBDPS*), 127.5 (*TBDPS*), 125.7 (*C13*H_2), 120.3 (*C4*), 99.4 (*C2*), 84.7 (*C3*), 79.5 (*C6*H), 77.5 (*C10*), 71.9 (*C1*H), 71.1 (*C8*H), 50.7 (*C7*H), 31.7 (*C14*H_3), 27.2 (*TBDPS*), 20.9 (*C15*H_3), 19.5 (*TBDPS*) ppm;
Signal of C_2/C_3/C_9 could not be detected on ^{13}C NMR because of the conformational changes, the chemical shift of C_2 and C_3 were confirmed by HMBC, but the chemical shift of C_8 could not be confirmed by any 2D NMR. ^{13}C NMR of C_{10} overlaps with the solvent peak, the chemical shift was confirmed by HMBC;
IR (film, cm^{-1}) 3475, 2963, 1765, 1429, 1269, 1112, 823, 743, 703, 547;
HRMS(ESI) $[M + H]^+$ calculated for $C_{31}H_{37}O_5Si$: 517.2417, found: 517.2410;
TLC: Rf = 0.40 (Pentane/Ethyl acetate = 2/1).

Data of **30**: light yellow solid, m.p. = 124.4 - 125.8 °C;
$[\alpha]_D^{20}$ -86.6 (c 1.0, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.65 (m, 4H, -*OTBDPS*), 7.34-7.45 (m, 6H, -*OTBDPS*), 6.44 (d, *J* = 3.3 Hz, 1H, *H13*) 5.94 (dt, *J* = 2.6, 1.6 Hz, 1H, *H5*), 5.76 (d, *J* = 2.8 Hz, 1H, *H13*), 4.91 (dt, *J* = 6.8, 2.3 Hz, 1H, *H6*), 4.61-4.42 (m, 1H, *H8*), 4.23 (s, 1H, *H1*), 3.96-3.76 (m, 1H, *H7*), 2.54 (dd, *J* = 15.0, 7.6 Hz, 1H, *H9*), 1.91 (dd, *J* = 15.0, 3.0 Hz, 1H, *H9*), 1.58 (t, *J* = 1.8 Hz, 3H, *H15*), 1.44 (s, 3H, *H14*), 1.09 (s, 9H, -*OTBDPS*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$)δ 169.5 (*C12*), 136.5 (*C5*H), 136.2 (*TBDPS*), 136.1 (*TBDPS*), 134.9 (*C11*), 133.2 (*TBDPS*), 132.6 (*TBDPS*), 130.3 (*TBDPS*), 130.1 (*TBDPS*), 128.0 (*TBDPS*), 127.6 (*TBDPS*), 123.3 (*C13*H_2), 118.7 (*C4*), 95.9 (*C2*), 87.1 (*C3*), 80.3 (*C6*H), 75.8 (*C10*), 70.3 (*C1*H), 67.9 (*C8*H), 49.0 (*C7*H), 46.0 (*C9*H_2), 27.2 (*C14*H_3), 27.2 (*TBDPS*), 22.2 (*C15*H_3), 19.6 (*TBDPS*) ppm; ^{13}C NMR of C_{14} is overlap with TBDPS, the chemical shift is confirmed by HMBC.
IR (film, cm^{-1}) 3475, 2963, 1765, 1429, 1269, 1112, 823, 743, 703, 547;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{31}H_{36}NaO_5Si$: 539.2236, found: 539.2230;
TLC: Rf = 0.05 (Pentane/Ethyl acetate = 2/1).



To a solution of TBDPS-protected alcohol **30** (50 mg, 0.097 mmol) in an Eppendorf safe-lock tube 1 drop of THF followed by hydrogen fluoride pyridine (hydrogen fluoride ~70%, 0.2 mL) were added. The reaction mixture was left on a shaker at room temperature for 40 minutes. Then, CH_2CL_2 (2.0 mL) was added and the reaction was quenched carefully with *sat. aq.* $NaHCO_3$ (caution the mixture bubbles out while quenching) until the evolution of gas stopped. The mixture was extracted with ethyl acetate (5 × 10 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 1/1 ~ 1/3) to provide **30-1** as a white powder (18.7 mg, 69%).

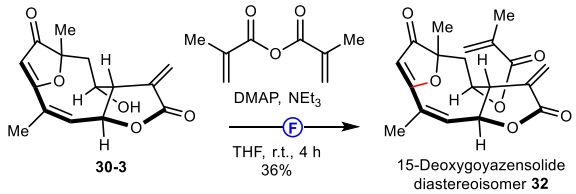
Data of **30-1**: white powder, m.p. = 64 - 66 °C;
$[\alpha]_D^{20}$ +58.9 (c 1.0, $CHCl_3$);
^{1}H NMR (400 MHz, methanol-d^4) δ ^{1}H NMR (400 MHz, methanol-d^4) δ 6.30 (d, *J* = 3.3 Hz, 1H, *H*$_{13}$), 6.08 (dq, *J* = 3.1, 1.6 Hz, 1H, *H*$_5$), 5.79 (d, *J* = 2.8 Hz, 1H, *H*$_{13}$), 5.04 (dp, *J* = 6.9, 2.2 Hz, 1H, *H*$_6$), 4.73 (ddd, *J* = 7.0, 2.5, 1.2 Hz, 1H, *H*$_8$), 4.11 (ddd, *J* = 7.1, 3.6, 1.2 Hz, 1H, *H*$_7$), 4.07 (s, 1H, , *H*$_1$), 2.55 (dd, *J* = 15.2, 6.9 Hz, 1H, *H*$_9$), 1.89 (t, *J* = 1.8 Hz, 3H, *H*$_{15}$), 1.82 (ddd, *J* = 15.2, 2.6, 1.0 Hz, 1H, *H*$_9$), 1.34 (s, 3H, *H*$_{14}$) ppm;
^{13}C NMR (100 MHz, methanol-d^4) δ ^{13}C NMR (101 MHz, methanol-d^4) 172.1 (*C*$_{12}$), 137.1 (*C*$_5$H), 136.1 (*C*$_{11}$), 124.1 (*C*$_{13}$H$_2$), 120.1 (*C*$_4$), 98.5 (*C*$_2$), 85.8 (*C*$_3$), 82.2 (*C*$_6$H), 75.7 (*C*$_{10}$), 69.5 (*C*$_1$H), 68.3 (*C*$_8$H), 50.6 (*C*$_7$H), 46.7 (*C*$_9$H$_2$), 27.7 (*C*$_{14}$H$_3$), 23.0 (*C*$_{15}$H$_3$) ppm;
IR (film, cm^{-1}) 3391, 2928, 1743, 1277, 140, 1022;
HRMS(ESI) [M + Na]$^+$ calculated for $C_{15}H_{18}NaO_5$: 301.1068, found: 301.1052;
TLC: Rf = 0.20 (Petroleum ether/Ethyl acetate = 1/2).



To a stirred solution of triol **30-1** (15 mg, 0.054 mmol) in CH_2Cl_2 (5.0 mL) was added MnO_2 (47 mg, 0.79 mmol). The reaction mixture was stirred at room temperature for 3 hours or till TLC analysis showed disappearance of starting material. Then, MnO_2 was filtered off and washed with CH_2Cl_2 (1.0 mL). *t*Bu_3AuNTf_2 (2.2 mg, 0.003 mmol) was added to the CH_2Cl_2 solution and the mixture was stirred for 10 minutes or till the TLC analysis showed disappearance of starting material. The resulted solution was concentrated *in vacuo* and the residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 2/1~1/1) to provide the **30-3** as waxy solid (5.6 mg, 38%).

Data of **30-2**: waxy solid;
$[\alpha]_D^{20}$ +345.3 (c 0.2, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, *J* = 3.0 Hz, 1H, *H*$_{13}$), 6.38 (dq, *J* = 4.6, 1.6 Hz, 1H, *H*$_5$), 5.94 (dd, *J* = 2.6, 0.5 Hz, 1H, *H*$_{13}$), 5.05 (ddt, *J* = 6.0, 3.6, 1.8 Hz, 1H, *H*$_6$), 4.24 (p, *J* = 4.9 Hz, 1H, *H*$_8$), 3.54 (d, *J* = 1.4 Hz, 1H, -*OH*), 3.49 (ddt, *J* = 5.8, 4.9, 2.9 Hz, 1H, *H*$_7$), 2.51 (ddd, *J* = 15.6, 4.8, 1.4 Hz, 1H, *H*$_9$), 2.29 (dd, *J* = 15.5, 5.1 Hz, 1H, *H*$_9$), 2.23 (d, *J* = 4.9 Hz, 1H, -*OH*), 1.99 (t, *J* = 1.7 Hz, 3H, *H*$_{15}$), 1.50 (s, 3H, *H*$_{14}$) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5 (*C*$_1$H), 169.2 (*C*$_{12}$), 144.9 (*C*$_5$H), 133.2 (*C*$_{11}$), 127.1 (*C*$_{13}$H$_2$), 118.1 (*C*$_4$), 102.2 (br, *C*$_3$), 93.8 (*C*$_2$), 81.2 (*C*$_{10}$), 80.5 (*C*$_6$H), 70.5 (*C*$_8$H), 50.0 (*C*$_7$H), 48.1 (br, *C*$_9$H$_2$), 26.7 (*C*$_{14}$H$_3$), 20.8 (*C*$_{15}$H$_3$)nppm;
IR (film, cm^{-1}) 3450, 2925, 2184, 1763, 1671, 1326, 1278, 1135, 1077, 1010, 817;
HRMS(ESI) [M + Na]$^+$ calculated for $C_{15}H_{16}NaO_5$: 299.0905, found: 299.0895;
TLC: Rf = 0.40 (Petroleum ether/Ethyl acetate = 1/2).

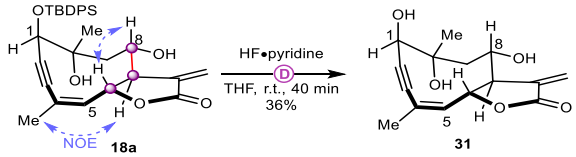
Data of **30-3**: waxy solid;
$[\alpha]_D^{20}$ +249.9 (c 0.2, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, *J* = 2.7 Hz, 1H, *H*$_{13}$), 6.09-5.98 (m, 1H, *H*$_5$), 5.80 (d, *J* = 2.4 Hz, 1H, *H*$_{13}$), 5.63 (m, 2H, *H*$_6$ + *H*$_2$), 4.06 (td, *J* = 7.1, 3.5 Hz, 1H, *H*$_8$), 2.85 (dq, *J* = 6.1, 2.8 Hz, 1H, *H*$_7$), 2.29 (dd, *J* = 14.5, 2.4 Hz, 1H, *H*$_9$), 2.17 (dd, *J* = 14.5, 9.7 Hz, 1H, *H*$_9$), 2.04 (possible d, 1H, -*OH*), 2.03 (d, *J* = 2.0 Hz, 3H, *H*$_{15}$), 1.56 (s, 3H, *H*$_{14}$) ppm;
^{13}C NMR (100 MHz, $CDCl_3$)δ 206.7 (*C*$_1$), 183.5 (*C*$_3$), 169.8 (*C*$_{12}$), 140.0 (*C*$_5$H), 133.4 (*C*$_{11}$), 129.5 (*C*$_{13}$H$_2$), 127.6 (*C*$_4$), 102.0 (*C*$_2$), 86.3 (*C*$_{10}$), 82.4 (*C*$_6$H$_1$), 71.1 (*C*$_8$H$_1$), 55.4 (*C*$_7$H$_1$), 45.0 (*C*$_9$H$_2$), 21.0 (*C*$_{14}$H$_3$), 18.2 (*C*$_{15}$H$_3$) ppm;
IR (film, cm^{-1}) 3522, 1760, 1692, 1567, 1276, 1120, 995, 546;
HRMS(ESI) [M + Na]$^+$ calculated for $C_{15}H_{16}NaO_5$: 299.0905, found: 299.0895;
TLC: Rf = 0.35 (Petroleum ether/Ethyl acetate = 1/2).



To a stirred solution of alcohol **30-3** (5.6 mg, 0.02 mmol) in THF (1.0 mL) was added NEt_3 (50 µL, 0.36 mmol) and methylacrlic anhydride (25 µL, 0.17 mmol) followed by a trace of DMAP. The reaction mixture was stirred at room temperature for approximately 3 hours or till the TLC analysis showed disappearance of the starting material. Then, the reaction was quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, filterred and

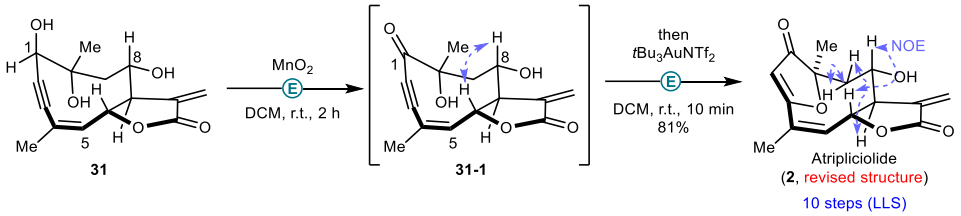
concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 4/1 ~ 5/2) to provide the **32** as a waxy solid (2.5 mg, 36%).

Data of **32**: waxy solid;
$[\alpha]_D^{20}$ +327.9 (c 0.2, $CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$) δ 6.25 (d, *J* = 2.6 Hz, 1H, *H*$_{13}$), 6.05 (dt, *J* = 2.6, 1.4 Hz, 2H, *H*$_5$ + *H*$_{3'}$), 5.73 (dp, *J* = 4.6, 2.2 Hz, 1H, *H*$_6$), 5.64 (s, 1H, *H*$_2$), 5.57 (m, 1H, *H*$_{3'}$), 5.47 (d, *J* = 2.3 Hz, 1H, *H*$_{13}$), 5.03 (ddd, *J* = 11.3, 4.8, 2.3 Hz, 1H, *H*$_8$), 2.89 (dq, *J* = 6.5, 2.5 Hz, 1H, *H*$_7$), 2.38 (dd, *J* = 14.0, 11.3 Hz, 1H, *H*$_9$), 2.25 (dd, *J* = 14.1, 2.3 Hz, 1H, *H*$_9$), 2.04 (t, *J* = 1.9 Hz, 3H, *H*$_{15}$), 1.87 (dd, *J* = 1.6, 1.0 Hz, 3H, *H*$_{4'}$), 1.58 (s, 3H *H*$_{14}$) ppm;
^{13}C NMR (126 MHz, $CDCl_3$)δ 206.3 (*C*$_1$), 183.6 (*C*$_3$), 169.1 (*C*$_{12}$), 166.9 (*C*$_{1'}$), 140.0 (*C*$_5$H), 135.9 (*C*$_{2'}$), 133.9 (*C*$_{11}$), 127.3 (*C*$_4$), 126.6 (*C*$_{3'}$H$_2$), 126.3 (*C*$_{13}$H$_2$), 102.1 (*C*$_2$), 85.6 (*C*$_{10}$), 82.8 (*C*$_6$H$_1$), 73.8 (*C*$_8$H$_1$), 54.0 (*C*$_7$H$_1$), 41.6 (*C*$_9$H$_2$), 21.3 (*C*$_{14}$H$_3$), 18.6 (*C*$_{15}$H$_3$), 18.2 (*C*$_{4'}$H$_3$) ppm;
IR (film, cm^{-1}) 1768, 1706, 1635, 1570, 1303, 1158, 1125, 1020, 996;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{19}H_{20}NaO_6$: 367.1151, found: 367.1158;
TLC: Rf = 0.60 (Petroleum ether/Ethyl acetate = 1/2).



To a solution of TBDPS-protected alcohol **18a** (130 mg, 0.25 mmol) in an Eppendorf safe-lock tube was added 1 drop of THF followed by hydrogen fluoride pyridine (hydrogen fluoride ~70%, 0.3 mL). The reaction mixture was left on a shaker at room temperature for 40 minutes. Then CH_2Cl_2 (2.0 mL) was added and the reaction was quenched carefully with *sat. aq.* $NaHCO_3$ (caution the mixture bubbles out while quenching) until the evolution of gas stopped. The mixture was extracted with ethyl acetate (5 × 10 mL), the combined organic layers were dried over Na_2SO_4, filterred and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 2/1 ~ 1/2) to provide the **31** as a waxy solid (25 mg, 36%).

Data of **31**: waxy solid;
$[\alpha]_D^{20}$ -183.3 (c 1.0, $CHCl_3$);
^1H NMR (400 MHz, $CDCl_3$) δ 6.40 (d, *J* = 1.8 Hz, 1H, *H*$_{13}$), 5.97 (dt, *J* = 3.6, 1.8 Hz, 1H, *H*$_5$), 5.78 (dd, *J* = 1.6, 0.7 Hz, 1H, *H*$_{13}$), 5.12 (dt, *J* = 3.8, 2.0 Hz, 1H, *H*$_6$), 4.21 (d, *J* = 4.1 Hz, 1H, *H*$_1$), 4.02 (br, d, *J* = 9.1 Hz, 1H, *H*$_7$), 3.86 (br s, 1H, *H*$_8$), 3.23 (br s, 1H, -*OH*), 2.60 (br d, *J* = 15.7 Hz, 1H, *H*$_9$), 2.12 (d, *J* = 4.4 Hz, 1H, *C*$_1$-*OH*), 2.06 (dd, *J* = 15.5, 6.5 Hz, 1H, *H*$_9$), 1.83 (t, *J* = 1.8 Hz, 3H, *H*$_{15}$), 1.49 (s, 3H, *H*$_{14}$) ppm;
^{13}C NMR (100 MHz, $CDCl_3$)δ 170.2 (*C*$_{12}$), 140.5 (*C*$_5$H), 135.8 (*C*$_{11}$), 126.0 (*C*$_{13}$H$_2$), 120.2 (*C*$_4$), 99.3 (*C*$_2$), 84.4 (*C*$_3$), 79.3 (*C*$_6$H), 76.9 (*C*$_{10}$), 71.0 (*C*$_8$H), 70.5 (*C*$_1$H), 50.7 (br, *C*$_7$H), 31.3 (br, *C*$_{14}$H$_3$), 21.0 (*C*$_{15}$H$_3$) ppm; Signal of C_2/C_3 could not be detected on ^{13}C NMR because of the conformational changes, the chemical shift of C_2 and C_3 were confirmed by HMBC;
IR (film, cm^{-1}) 3403, 2958, 2350, 1746, 1277, 1153, 1019, 818, 533;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{15}H_{18}NaO_5$: 301.1068, found: 301.1052;
TLC: Rf = 0.30 (Petroleum ether/Ethyl acetate = 1/2).

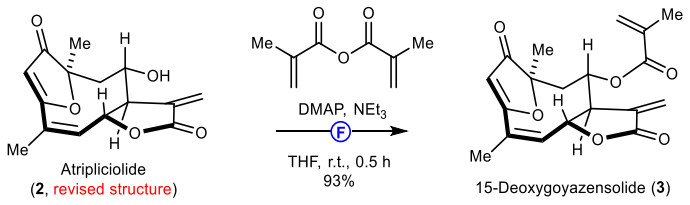


To a stirred solution of triol **31** (22 mg, 0.079 mmol) in CH_2Cl_2 (1.0 mL) was added MnO_2 (69 mg, 0.79 mmol). The reaction mixture was stirred at room temperature for 2 hours or till TLC analysis showed disappearance of starting material. Then, MnO_2 was filtered off and washed with CH_2Cl_2 (1.0 mL). tBu$_3$AuNTf$_2$ (3.3 mg, 0.004 mmol) was added to the CH_2Cl_2 solution and stirred for 10 minutes or till the TLC analysis showed disappearance of starting material. The resulted solution was concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 2/1) to provide the **2** as white solid (17.6 mg, 81%).

The absolute configuration of **2** was determined by X-ray diffraction measurements. Single crystals of **2** suitable for X-ray crystallographic analysis were obtained by a single recrystallization by slow evaporation at room temperature using *n*-hexanes/ CH_2Cl_2 as a solvent mixture. See **Supplementary Section m** for detail.

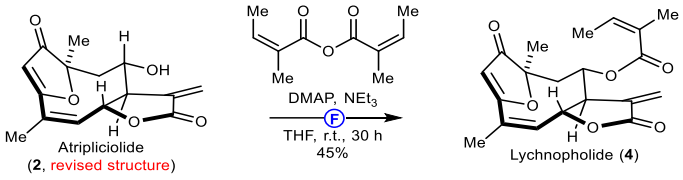
Data of **31-1**: waxy solid;
$[\alpha]_D^{20}$ -376.9 (c 0.1, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (d, J = 2.5 Hz, 1H, H_{13}), 6.37 (dt, J = 3.0, 1.5 Hz, 1H, H_5), 5.85 (d, J = 2.2 Hz, 1H, H_{13}), 5.15 (dp, J = 4.6, 2.3 Hz, 1H, H_6), 4.22 (br s, 1H, H_8), 4.00 (br s, 1H, H_7), 3.61 (br s, 1H, -*OH*), 2.45-2.43 (m, 2H, H_9), 1.97 (like t, J = 1.9 Hz, 3H, H_{15}), 1.51 (s, 3H, H_{14}) ppm;
^{13}C NMR (100 MHz, $CDCl_3$)δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.1 (C_1), 169.1 (C_{12}), 145.8 (br, C_5H), 134.3 (C_{11}), 125.7 (br, $C_{13}H_2$), 117.6 (C_4), 98.5 (C_3), 93.7 (br, C_2), 80.6 (C_{10}), 78.9 (br, C_6H), 70.5 (C_8H), 50.2 (C_7H), 42.1 (C_9H_2), 27.4 (br, $C_{14}H_3$), 21.10 (br, $C_{15}H_3$) ppm; Signal of C_9 could not be detected on ^{13}C NMR because of the conformational changes, the chemical shift was confirmed by HMBC;
IR (film, cm^{-1}) 3443, 2927, 2183, 1751, 1675, 1278, 1136, 1014;
HRMS(ESI) $[M + H]^+$ calculated for $C_{15}H_{17}O_5$: 277.1068, found: 277.1076;
TLC: Rf = 0.20 (Petroleum ether/Ethyl acetate = 3/1).

Data of **2**: white solid; m.p. = 210 - 211 °C;
$[\alpha]_D^{20}$ -50.4 (c 0.25, $CHCl_3$);
^{1}H NMR and ^{13}C NMR data, see **Table S1**;
IR (film, cm^{-1}) 3454, 1765, 1701, 1577, 1289, 1135, 1001, 815;
HRMS(ESI) $[M + H]^+$ calculated for $C_{15}H_{17}O_5$: 277.1068, found: 277.1076;
TLC: Rf = 0.60 (Petroleum ether/Ethyl acetate = 1/1).



To a stirred solution of alcohol **2** (4.0 mg, 0.014 mmol) in THF (1.0 mL) was added NEt_3 (50 μL, 0.36 mmol) and methylacrlic anhydride (25 μL, 0.17 mmol) followed by a trace of DMAP. The reaction mixture was then stirred at room temperature for 30 minutes or till the TLC analysis showed disappearance of starting material. Then, the reaction was quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 5/1) to provide the **5** as a waxy solid (3.9 mg, 93%).

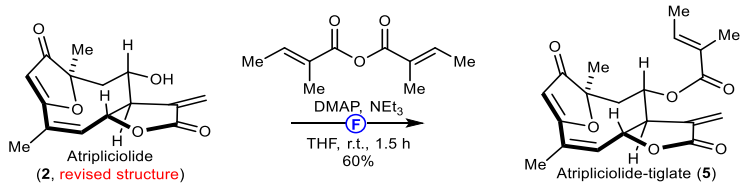
Data of **3**: waxy solid;
$[\alpha]_D^{20}$ -38.5 (c 0.20, $CHCl_3$); lit. $[\alpha]_D^{24}$ -38 (c 0.76, $CHCl_3$) *(Phytochemishy*, **1976**, *15*, 1775-1776.);
^1H NMR and ^{13}C NMR data, see **Table S4**;
IR (film, cm^{-1}) 2925, 2854, 1769, 1707, 1588, 1292, 1138, 1027, 520;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{19}H_{20}NaO_6$: 367.1151, found: 367.1158;
TLC: Rf = 0.50 (Petroleum ether/Ethyl acetate = 3/1).



To a stirred solution of alcohol **2** (2.0 mg, 0.007 mmol) in THF (1.0 mL) was added NEt_3 (50 μL, 0.36 mmol) and angelic anhydride (25 μL, 0.14 mmol) followed by a trace of DMAP. The reaction mixture was then stirred at room temperature for 30 hours or till the TLC analysis showed disappearance of starting material. Then, the reaction was quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 5/1) to provide the **4** as a waxy solid (1.1 mg, 45%).

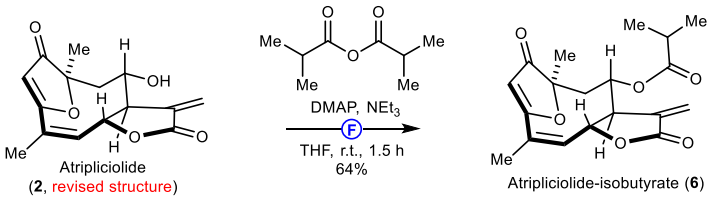
We observed partial isomerization from angelate to tiglate (angelate/tiglate = 11/1 as determined by crude ^1H NMR) and a little amount of **5** was isolated from this reaction.

Data of **4**: waxy solid;
$[\alpha]_D^{20}$ -50.0 (c 0.035, $CHCl_3$); lit. $[\alpha]_D^{24}$ -56.9 (c 0.26, $CHCl_3$) *(Phytochemishy*, **1980**, *19*, 2381-2385.);
^1H NMR and ^{13}C NMR data see **Table S5**;
IR (film, cm^{-1}) 1769, 1709, 1589, 1291, 1234, 1138, 1030, 527;
HRMS(ESI) $[M + H]^+$ calculated for $C_{20}H_{23}O_6$: 359.1495, found: 359.1517;
TLC: Rf = 0.55 (Petroleum ether/Ethyl acetate = 3/1).



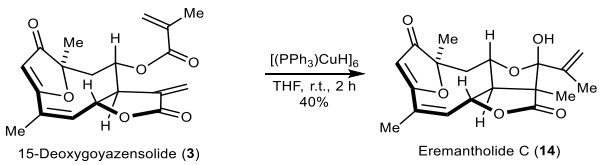
To a stirred solution of alcohol **2** (2 mg, 0.007 mmol) in THF (1 mL) was added NEt_3 (50 μL, 0.36 mmol) and tiglic anhydride (25 μL, 0.14 mmol). Then trace DMAP was added. The reaction mixture was stirred at room temperature for 90 min or till the TLC analysis showed disappearance of starting material. Then, the reaction was quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 5/1) to provide the **5** as a waxy solid (1.5 mg, 60%).

Data of **5**: waxy solid;
$[\alpha]_D^{20}$ -49.5 (c 0.020, $CHCl_3$); lit. $[\alpha]_D^{24}$ -54.3 (c 2.0, $CHCl_3$) *(Phytochemishy*, **1980**, *19*, 2663-2668.);
^1H NMR and ^{13}C NMR data see **Table S6**;
IR (film, cm^{-1}) 1769, 1706, 1589, 1291, 1274, 1137, 1029;
HRMS(ESI) $[M + H]^+$ calculated for $C_{20}H_{23}O_6$: 359.1495, found: 359.1478;
TLC: Rf = 0.50 (Petroleum ether/Ethyl acetate = 3/1).



To a stirred solution of alcohol **2** (2.0 mg, 0.007 mmol) in THF (1.0 mL) was added NEt_3 (50 μL, 0.36 mmol) and isobutyric anhydride (25 μL, 0.15 mmol) followed by a trace of DMAP. The reaction mixture was stirred at room temperature for 90 minutes or till the TLC analysis showed disappearance of starting material. Then, the reaction was quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 5/1) to provide the **6** as a waxy solid (1.6 mg, 64%).

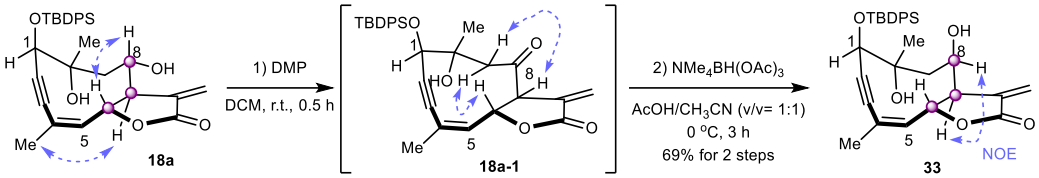
Data of **6**: waxy solid;
$[\alpha]_D^{20}$ -88.0 (c 0.025, $CHCl_3$); lit. $[\alpha]_D^{24}$ -158 (c 0.54, $CHCl_3$) *(Phytochemishy*, **1982**, *21*, 1669-1673.);
^1H NMR and ^{13}C NMR data see **Table S7**;
IR (film, cm^{-1}) 1770, 1709, 1588, 1291, 1139, 1029;
HRMS(ESI) $[M + H]^+$ calculated for $C_{19}H_{23}O_6$: 347.1495, found: 347.1512;
TLC: Rf = 0.60 (Petroleum ether/Ethyl acetate = 3/1).



The reaction was conducted following a previously reported procedure.[24]

A solution of 15-deoxygoyazensolide (**3**) (1.0 mg, 0.0029 mmol) in THF (0.2 mL) and commercially available Stryker's reagent (3.0 mg, 0.0015 mmol), were mixed together forming a homogeneous solution that was stirred at room temperature for 2 hours in a glove box under an inert N_2 atmosphere. The reaction was then quenched with *sat. aq.* NH_4Cl (1.0 mL), extracted with ethyl acetate (3 × 5.0 mL), dried over Na_2SO_4, filterred and concentrated *in vacuo*. The residue was purified by preparative TLC (Pentane/Ethyl acetate = 3/1) to provide **14** as a waxy solid (0.4 mg, 40%).

Data of **14**: waxy solid;
^1H NMR and ^{13}C NMR data see **Table S13**;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{19}H_{22}NaO_6$: 369.1314, found: 369.1323;
TLC: Rf = 0.60 (Petroleum ether/Ethyl acetate = 1/1).



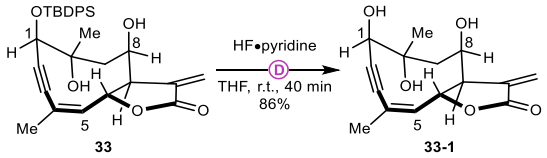
A 10 mL round bottom flask equipped with a magnetic stir bar was charged with alcohol **18a** (40 mg, 0.078 mmol) and CH_2Cl_2 (2.0 mL), followed by addition of DMP (50 mg, 0.12 mmol). The reaction was stirred for 30 minutes or till the TLC analysis showed disappearance of starting material. The reaction was then quenched with diluted $Na_2S_2O_3$ solution (2.0 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo* to provide **18a-1** as a waxy solid. The crude product was used directly as starting material for the Evans–Saksena reduction without further purification. A 10 mL round bottom flask equipped with a magnetic stir bar was charged with **18a-1**, MeCN (2.0 mL) and AcOH (2.0 mL). Then, the mixture was cooled down to 0 °C, $Me_4NBH(OAc)_3$ (102 mg, 0.39 mmol) was added in portions and the reaction was stirred for 3 hours or till the TLC analysis showed disappearance of starting material. Then, the reaction was quenched with *sat. aq.* $NaHCO_3$ (15 mL, caution the mixture bubbles out while quenching) until the evolution of gas stopped and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 2/1) to give alcohol **33** as a waxy solid (27 mg, 30%).

Data of **18a-1**: yellow oil;
$[\alpha]_D^{20}$ -120.9 (c 1.0, $CHCl_3$);
^1H NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 4H, *-OTBDPS*), 7.45-7.36 (m, 6H, *-OTBDPS*), 6.28 (d, *J* = 3.5 Hz, 1H, *H13*), 5.97 (dq, *J* = 3.3, 1.6 Hz, 1H, *H5*), 5.57 (d, *J* = 3.1 Hz, 1H, *H13*), 5.55-5.50 (m, 1H, *H6*), 4.42-4.39 (m, 1H, *H7*), 4.40 (s, 1H, *H1*), 2.93 (d, *J* = 13.7 Hz, 1H, *H9*), 2.68 (d, *J* = 13.7 Hz, 1H, *H9*), 1.58 (t, *J* = 1.8 Hz, 3H, *H15*), 1.51 (s, 3H, *H14*), 1.10 (s, 9H, *-OTBDPS*) ppm;

[24] Sass, D. C., Heleno, V. C. G., Cavalcante, S., da Silva Barbosa, J., Soares, A. C. F., Constantino, M. G. *J. Org. Chem.* **2012**, *77*, 9374-9378.

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1 (*C*$_8$), 167.37 (*C*$_{12}$), 136.3 (*TBDPS*), 136.1 (*TBDPS*), 134.9 (*C*$_{11}$), 134.7 (*C*$_5$H), 132.8 (*TBDPS*), 132.5 (*TBDPS*), 130.3 (*TBDPS*), 130.1 (*TBDPS*), 128.0 (*TBDPS*), 127.6 (*TBDPS*), 122.8 (*C*$_{13}$H$_2$), 119.5 (*C*$_4$), 97.0 (*C*$_2$), 86.9 (*C*$_3$), 79.6 (*C*$_{10}$), 77.8 (*C*$_6$H), 71.8 (*C*$_1$H), 59.0 (*C*$_7$H), 48.2 (*C*$_9$H$_2$), 27.1 (*TBDPS*), 24.3 (*C*$_{14}$H$_3$), 21.6 (*C*$_{15}$H$_3$), 19.5 (*TBDPS*) ppm;
IR (film, cm^{-1}) 1767, 1703, 1288, 1110, 1041, 703;
HRMS(ESI) [M + Na]$^+$ calculated for $C_{31}H_{34}NaO_5Si$: 537.2067, found: 537.2073;
TLC: Rf = 0.20 (Petroleum ether/Ethyl acetate = 5/1).

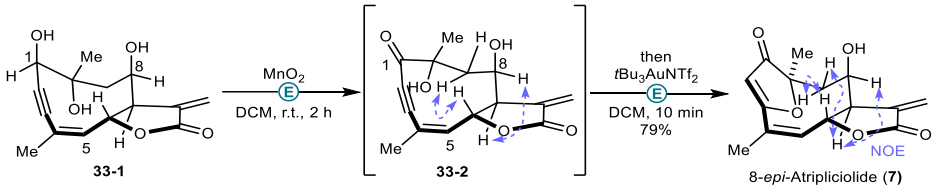
Data of **33**: waxy solid;
$[\alpha]_D^{20}$ -198 (c 0.53, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.68 (m, 4H, -*OTBDPS*), 7.33-7.45 (m, 6H, -*OTBDPS*), 6.31 (d, *J* = 2.9 Hz, 1H, *H*$_{13}$) 5.96 (m, 1H, *H*$_{13}$), 5.95 (m, 1H, *H*$_5$), 5.14 (br t, *J* = 7 Hz, 1H, *H*$_6$), 4.63 (br s, 1H, *H*$_8$), 4.01 (s, 1H, *H*$_1$), 3.32 (br s, 1H, *H*$_7$), 2.61 (br d, *J* = 15.6 Hz, 1H, *H*$_9$), 2.13 (br s, 1H, -*OH*), 1.75 (br s, 1H, -*OH*), 1.73 (dd, *J* = 15.6, 6.3 Hz, *H*$_9$), 1.64 (t, *J* = 1.5 Hz, 3H, *H*$_{15}$), 1.39 (s, 3H, *H*$_{14}$), 1.08 (s, 9H, -*OTBDPS*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6 (*C*$_{12}$), 138.8 (*C*$_5$H), 136.3 (*C*$_{11}$), 136.3 (*TBDPS*), 136.1 (*TBDPS*), 133.2 (*TBDPS*), 132.9 (*TBDPS*), 130.2 (*TBDPS*), 130.1 (*TBDPS*), 127.9 (*TBDPS*), 127.5 (*TBDPS*), 123.4 (*C*$_{13}$H$_2$), 121.4 (*C*$_4$), 98.4 (*C*$_2$), 86.1 (*C*$_3$), 78.1 (*C*$_6$H), 76.3 (*C*$_{10}$), 72.0 (*C*$_1$H), 70.1 (*C*$_8$H), 52.0 (*C*$_7$H), 39.3 (*C*$_9$H$_2$), 30.4 (*C*$_{14}$H$_3$), 27.2 (*TBDPS*), 20.8 (*C*$_{15}$H$_3$), 19.5 (*TBDPS*) ppm; The signal of C_8 could not be detected on ^{13}C NMR because of the conformational changes, the chemical shift was confirmed by HSQC. ^{13}C NMR of C_{11} overlaps with TBDPS, the chemical shift was confirmed by HMBC;
IR (film, cm^{-1}) 3475, 2933, 1753, 1428, 1111, 703;
HRMS(ESI) [M + Na]$^+$ calculated for $C_{31}H_{36}NaO_5Si$: 539.2236, found: 539.2230;
TLC: Rf = 0.30 (Petroleum ether/Ethyl acetate = 2/1).



To a solution of TBDPS-protected alcohol **33** (27.6 mg, 0.1 mmol) in an Eppendorf safe-lock tube was added 1 drop of THF followed by hydrogen fluoride pyridine (hydrogen fluoride ~70%, 0.1 mL). The mixture was left on shaker at room temperature for 40 minutes. Then CH_2Cl_2 (2.0 mL) was added to the reaction followed by addition of *sat. aq.* $NaHCO_3$ for quenching (caution the mixture bubbles out while quenching) until the evolution of gas stopped. The mixture was extracted with ethyl acetate (5 × 10 mL), the combined organic layers were dried over Na_2SO_4, filterred and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 2/1 ~ 1/2) to provide the **33-1** as waxy solid (12.8 mg, 86%).

Data of **33-1**: waxy solid;
$[\alpha]_D^{20}$ -205 (c 1.0, $CHCl_3$);
^{1}H NMR (400 MHz, acetone-d^6) δ 6.07 (dd, *J* = 2.5, 1.1 Hz, 1H, *H*$_{13}$), 5.99 (br s, 1H, *H*$_5$), 5.74 (br s, 1H, *H*$_{13}$), 5.35 (br s, 1H, *H*$_6$), 4.71 (d, *J* = 6.2 Hz, 1H, *H*$_8$), 4.49 (br s, 1H, -*OH*), 4.02 (t, *J* = 3.1 Hz, 2H, *H*$_1$+-*OH*), 3.74 (br d, *J* = 4.5 Hz, 1H, *H*$_7$), 3.70 (br s, -*OH*), 2.69 (br s, *H*$_9$), 1.80 (t, *J* = 1.6 Hz, 3H, *H*$_{15}$), 1.63 (dd, *J* = 15.1, 4.7 Hz, 1H, *H*$_9$), 1.41 (s, 3H, *H*$_{14}$) ppm;

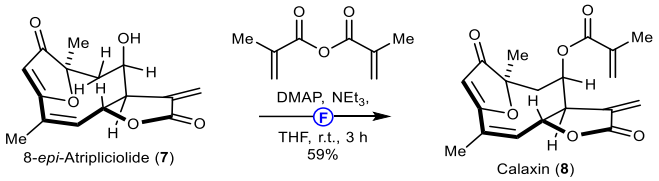
^{13}C NMR (100 MHz, acetone-d^{6}) δ 170.8 (*C*$_{12}$), 141.0 (br, *C*$_{5}$H), 121.0 (*C*$_{13}$H$_2$), 121.0 (*C*$_{4}$), 101.6 (*C*$_{2}$), 84.0 (br, *C*$_{3}$), 77.7 (br, *C*$_{6}$H), 75.3 (*C*$_{10}$), 71.3 (*C*$_{1}$H), 71.3 (*C*$_{8}$H), 52.0 (br, *C*$_{7}$H), 40.4 (*C*$_{9}$H$_2$), 30.4 (*C*$_{14}$H$_3$), 21.0 (*C*$_{15}$H$_3$) ppm; signal of C$_3$/C$_5$/C$_{11}$ could not be detected on ^{13}C NMR because of the conformational changes, the chemical shift of C$_3$ was confirmed by HMQC. The chemical shift of C$_5$ was confirmed by HSQC. ^{13}C NMR of C$_{11}$ could not be assigned;
IR (film, cm^{-1}) 3427, 2930, 1747, 1272, 1143, 1021, 977;
HRMS(ESI) [M + Na]$^+$ calculated for C$_{15}$H$_{18}$NaO$_5$: 301.1068, found: 301.1052;
TLC: Rf = 0.20 (Petroleum ether/Ethyl acetate = 1/2).



To a stirred solution of triol **33-1** (11.2 mg, 0.04 mmol) in CH_2Cl_2 (1.0 mL) was added MnO_2 (35 mg, 0.4 mmol). The reaction mixture was stirred at room temperature for 2 hours or till the TLC analysis showed disappearance of starting material. Then MnO_2 was filtered off and washed with CH_2Cl_2 (1.0 mL). *t*Bu$_3$AuNTf$_2$ (1.7 mg, 0.002 mmol) was added to the CH_2Cl_2 solution and stirred for 10 minutes till the TLC analysis showed disappearance of starting material. The resulted solution was concentrated *in vacuo* and the residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 1/1) to provide the **7** as waxy solid (9.8 mg, 79%).

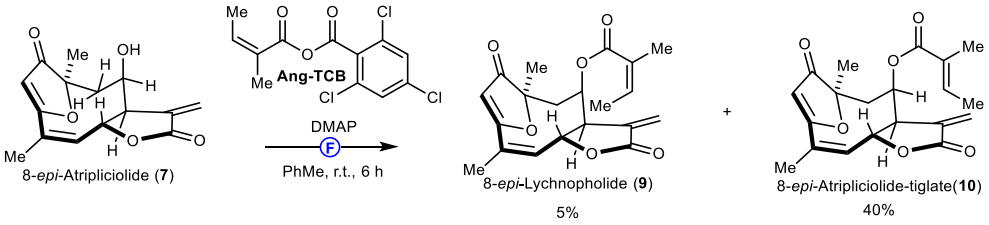
Data of **33-2**: waxy solid;
$[\alpha]_D^{20}$ -215.6 (c 0.2, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (dq, *J* = 6.1, 1.6 Hz, 1H, *H*$_5$), 6.37 (dd, *J* = 3.3, 1.0 Hz, 1H, *H*$_{13}$), 6.23 (dd, *J* = 2.9, 1.0 Hz, 1H, *H*$_{13}$), 5.27 (ddq, *J* = 8.8, 6.0, 1.3 Hz, 1H, *H*$_6$), 4.71 (ddd, *J* = 7.0, 4.4, 2.3 Hz, 1H, *H*$_8$), 3.47 (ddt, *J* = 9.1, 4.4, 3.1 Hz, 1H, *H*$_7$), 3.12 (br s, 1H, -*OH*), 2.78 (br s, 1H, -*OH*), 2.58 (dd, *J* = 15.9, 2.2 Hz, 1H, *H*$_9$), 2.10 (dd, *J* = 15.8, 7.3 Hz, 1H, *H*$_9$), 1.98 (t, *J* = 1.5 Hz, 3H, *H*$_{15}$), 1.40 (s, 3H, *H*$_{14}$) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5 (*C*$_1$), 169.5 (*C*$_{12}$), 146.5 (*C*$_5$H), 134.6 (*C*$_{11}$), 125.4 (*C*$_{13}$H$_2$), 120.4 (*C*$_4$), 102.0 (*C*$_3$), 95.4 (*C*$_2$), 79.7 (*C*$_{10}$), 78.1 (*C*$_6$H), 69.1 (*C*$_8$H), 50.6 (*C*$_7$H), 40.6 (*C*$_9$H$_2$), 28.2 (*C*$_{14}$H$_3$), 20.5 (*C*$_{15}$H$_3$) ppm;
IR (film, cm^{-1}) 3480, 2179, 1765, 1671, 1323, 1274, 1239, 1127, 1026, 986, 555;
HRMS(ESI) [M + Na]$^+$ calculated for C$_{15}$H$_{17}$NaO$_5$: 299.0905, found: 299.0895;
TLC: Rf = 0.40 (Petroleum ether/Ethyl acetate = 3/1).

Data of **7**: waxy solid;
$[\alpha]_D^{20}$ -142.7 (c 0.15, $CHCl_3$);
^{1}H NMR and ^{13}C NMR data see **Table S1**;
IR (film, cm^{-1}) 3430, 2924, 1761, 1704, 1589, 1280, 1143, 611;
HRMS(ESI) [M + Na]$^+$ calculated for C$_{15}$H$_{16}$NaO$_5$: 299.0905, found: 299.0895;
TLC: Rf = 0.50 (Petroleum ether/Ethyl acetate = 1/1).



To a stirred solution of alcohol **7** (1.5 mg, 0.005 mmol) in THF (1.0 mL) was added NEt_3 (25 μL, 0.18 mmol) and methacrylic anhydride (13 μL, 0.09 mmol) followed by a trace of DMAP. The reaction mixture was then stirred at room temperature for 3 hours or till the TLC analysis showed disappearance of starting material. Then, the reaction was quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 3/1) to provide the calaxin **8** as a waxy solid (1.1 mg, 59%).

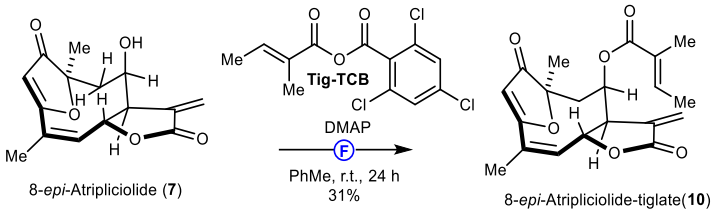
Data of calaxin **8**: waxy solid;
$[\alpha]_D^{20}$ -63.2 (c 0.05, $CHCl_3$);
^1H NMR and ^{13}C NMR data see **Table S8**;
IR (film, cm^{-1}) 2362, 2343, 1771, 1707, 1593, 1291, 1151, 617;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{19}H_{20}NaO_6$: 367.1151, found: 367.1158;
TLC: Rf = 0.50 (Petroleum ether/Ethyl acetate = 2/1).



To a stirred solution of alcohol **7** (1.5 mg, 0.005 mmol) in PhMe (1.0 mL) was added angelic 2,4,6-trichlorobenzoic anhydride (**Ang-TCB**, 4.6 mg, 0.015 mmol) and DMAP (1.8 mg, 0.016 mmol). The reaction mixture was stirred at room temperature for 6 hours or till the TLC analysis showed disappearance of starting material. Then, the reaction was filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 3/1) to provide compound **9** as a waxy solid (<0.1 mg, ~5%) together with 8-*epi*-atripliciolide-tiglate **10** (0.8 mg, 40%).

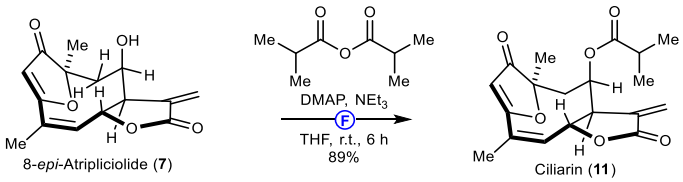
We observed major isomerization from angelate to tiglate (angelate/tiglate = 1/8 as determined by crude ^1H NMR). Unfortunately, the material obtained was not enough for full characterization, but ^1H NMR data comparison showed unequivocally the compound to be natural product **9**. See **Table S9** for detail.

Data of **9**: waxy solid;
HRMS(ESI) $[M + H]^+$ calculated for $C_{20}H_{23}O_6$: 359.1495, found: 359.1517;
TLC: Rf = 0.50 (Petroleum ether/Ethyl acetate = 2/1).



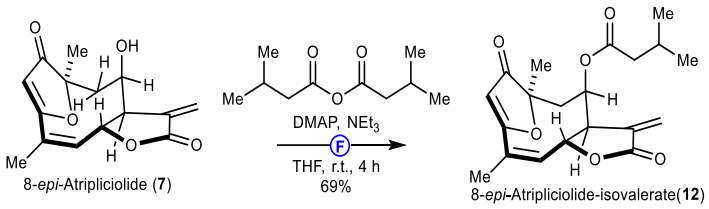
To a stirred solution of alcohol **7** (1.5 mg, 0.005 mmol) in PhMe (1.0 mL) was added tiglic 2,4,6-trichlorobenzoic anhydride (**Tig-TCB**, 4.6 mg, 0.015 mmol) and DMAP (1.8 mg, 0.016 mmol). The reaction mixture was stirred at room temperature for 24 hours till the TLC analysis showed disappearance of the starting material. Then the reaction was filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 3/1) to provide 8-*epi*-atripliciolide-tiglate **10** (0.5 mg, 31%) as a waxy solid.

Data of 8-*epi*-atripliciolide-tiglate **10**: waxy solid;
$[\alpha]_D^{20}$ -204.4 (c 0.025, $CHCl_3$);
^1H NMR and ^{13}C NMR data, see **Table S10**;
IR (film, cm^{-1}) 1767, 1710, 1594, 1291, 1127, 1080, 593;
HRMS(ESI) $[M + H]^+$ calculated for $C_{20}H_{23}O_6$: 359.1495, found: 359.1478;
TLC: Rf = 0.55 (Petroleum ether/Ethyl acetate = 2/1).



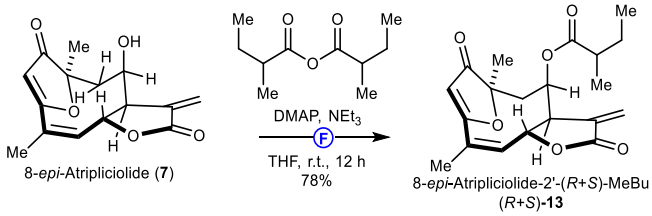
To a stirred solution of alcohol **7** (1.5 mg, 0.005 mmol) in THF (1.0 mL) was added NEt_3 (25 μL, 0.18 mmol) and isobutyric anhydride (13 μL, 0.08 mmol) followed by a trace of DMAP. The reaction mixture was stirred at room temperature for 6 hours till the TLC analysis showed disappearance of the starting material. The reaction was then quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 3/1) to provide the **11** as awaxy solid (1.6 mg, 89%).

Data of **11**: waxy solid;
$[\alpha]_D^{20}$ -132.1 (c 0.10, $CHCl_3$);
^1H NMR and ^{13}C NMR data see **Table S11**;
IR (film, cm^{-1}) 1770, 1706, 1592, 1290, 1144;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{19}H_{22}NaO_6$: 369.1323, found: 369.1314;
TLC: Rf = 0.50 (Petroleum ether/Ethyl acetate = 2/1).



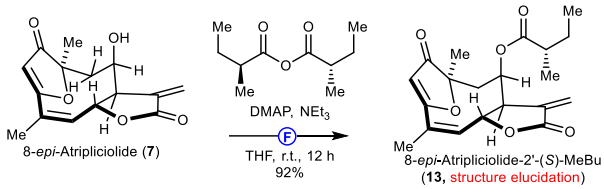
To a stirred solution of alcohol **7** (1.0 mg, 0.0036 mmol) in THF (0.5 mL) was added NEt_3 (15 μL, 0.11 mmol) and isovaleric anhydride (10 μL, 0.05 mmol) followed by a trace of DMAP. The reaction mixture was stirred at room temperature for 4 hours till the TLC analysis showed disappearance of the starting material. The reaction was then quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 2/1) to provide the **12** as awaxy solid (0.9 mg, 69%).

Data of **12**: waxy solid;
$[\alpha]_D^{20}$ -51.8 (c 0.045, $CHCl_3$); lit. $[\alpha]_D^{24}$ -41 (c 0.8, $CHCl_3$) *(Phytochemishy*, **1978**, *17*, 471-474.);
^1H NMR and ^{13}C NMR data, see **Table S12**;
IR (film, cm^{-1}) 2960, 1770, 1739, 1709, 1595, 1291, 1162, 1130, 1005, 815;
HRMS(ESI) $[M + H]^+$ calculated for $C_{20}H_{25}O_6$: 361.1651, found: 361.1625;
TLC: Rf = 0.60 (Petroleum ether/Ethyl acetate = 2/1).



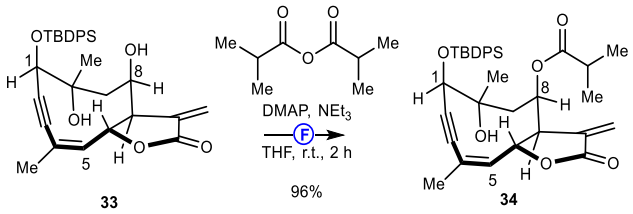
To a stirred solution of alcohol **7** (1.4 mg, 0.0051 mmol) in THF (0.5 mL) was added NEt_3 (15 μL, 0.11 mmol) and (±)-2-methylbutyric anhydride (10 μL, 0.05 mmol)followed by a trace of DMAP. The reaction mixture was stirred at room temperature for 12 hours till the TLC analysis showed disappearance of the starting material. The reaction was then quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 2/1) to provide the (*R+S*)-**13** as a waxy solid and a mixture 1:1 of inseparable diastereomers (1.4 mg, 78%).

Data of (*R+S*)-**13**: waxy solid;
^1H NMR and ^{13}C NMR data, see **Supplementary Section d**;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{20}H_{24}NaO_6$: 383.1471, found: 383.1475;
TLC: Rf = 0.70 (Petroleum ether/Ethyl acetate = 2/1).



The same procedure for synthesis of (*R+S*)-**13** was used and 1.2 mg of 8-e*pi*-atripliciolide-2'-(*S*)-MeBu (**13**) were obtained from 1.0 mg of **7**, representing a yield of 92%.

Data of 8-e*pi*-atripliciolide-2'-(*S*)-MeBu **13**: waxy solid;
$[\alpha]_D^{20}$ -47.3 (c 0.06, $CHCl_3$);
^1H NMR and ^{13}C NMR data, see **Supplementary Section d**;
IR (film, cm^{-1}) 2912, 2193, 1982, 1595, 1263, 1132, 1023, 800;
TLC: Rf = 0.70 (Petroleum ether/Ethyl acetate = 2/1).

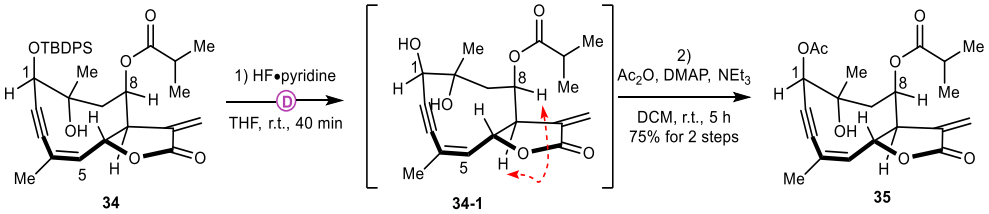


To a stirred solution of alcohol **33** (11 mg, 0.021 mmol) in THF (2.0 mL) was added NEt_3 (18 μL, 0.13 mmol) and isobutyric anhydride (11 μL, 0.06 mmol) followed by a trace of DMAP. The reaction mixture was stirred at room temperature for 2 hours till the TLC analysis showed disappearance of the starting material. The reaction was then quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (3 × 10 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 5/1 ~ 2/1) to provide **34** as a white solid (12 mg, 96%).

The absolute configuration of **34** was determined by X-ray diffraction measurements. Single crystals of **34** suitable for X-ray crystallographic analysis were obtained by a single recrystallization by slow evaporation at room temperature using *n*-hexanes/CH_2Cl_2 as a solvent mixture. See **Supplementary Section m** for detail.

Data of **53**: white solid, m.p. 154-156 °C;
$[\alpha]_D^{20}$ -669.7 (c 0.2, $CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$) δ 7.73-7.57 (m, 4H, -*OTBDPS*), 7.53-7.32 (m, 6H, -*OTBDPS*), 6.25 (d, *J* = 2.2 Hz, 1H, H_{13}) 5.88 (dq, *J* = 3.3, 1.6 Hz, 1H, H_5), 5.72 (br s, 1H, H_{13}), 5.39 (br s, 2H, H_6 + H_8), 4.01 (s, 1H, H_1), 3.68 (br s, 1H, H_7), 2.81 (dd, *J* = 15.0, 9.7 Hz, 1H, H_9), 2.49 (hept, *J* = 7.0 Hz, 1H, $H_{2'}$), 1.72 (dd, *J* = 15.1, 3.9 Hz, 1H, H_9), 1.63 (t, *J* = 1.7 Hz, 3H, H_{15}), 1.42 (s, 3H, H_{14}), 1.13 (d, *J* = 7.0 Hz, 3H, $H_{3'/4'}$), 1.11 (d, *J* = 7.0 Hz, 3H, $H_{3'/4'}$), 1.09 (s, 9H, -*OTBDPS*) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5 ($C_{1'}$), 170.5 (C_{12}), 140.4 (br, C_5H), 137.2 (br C_{11}), 136.4 (*TBDPS*), 136.1 (*TBDPS*), 133.2 (*TBDPS*), 132.9 (*TBDPS*), 130.2 (*TBDPS*), 130.1 (*TBDPS*), 127.9 (*TBDPS*), 127.5 (*TBDPS*), 123.4 ($C_{13}H_2$), 120.4 (br, C_4), 98.8 (C_2), 85.2 (br, C_3), 77.0 (C_6H), 75.4 (C_{10}), 75.4 (C_8H), 72.6 (C_1H), 49.3 (br, C_7H), 36.0 (C_9H_2), 34.3 ($C_{2'}H$), 30.2 ($C_{14}H_3$), 27.2 (*TBDPS*), 20.9 ($C_{15}H_3$), 19.5 (*TBDPS*), 18.9 ($C_{3'}H_3$), 18.8 ($C_{4'}H_3$) ppm; ^{13}C NMR

signal of C_3 C_4 C_5 C_7 C_{11} are broad because of the conformational changes. ^{13}C NMR of C_8 and C_{10} overlap, and C_8 most likely has very weak signal. ^1H NMR of H-6 and H-8 overlap and makes the NOESY hard to detect. There is a correlation between H-5 and H-7;
IR (film, cm^{-1}) 3475, 2933, 1753, 1428, 1111, 703;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{35}H_{42}NaO_6Si$: 609.2661, found: 609.2648;
TLC: Rf = 0.85 (Petroleum ether/Ethyl acetate = 1/1).

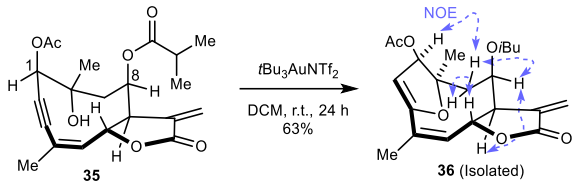


To a solution of TBDPS-protected alcohol **34** (13.6 mg, 0.023 mmol) in an Eppendorf safe-lock tube was added hydrogen fluoride pyridine (hydrogen fluoride ~70%, 0.1 mL). The reaction mixture was left on a shaker at room temperature for 40 minutes. Then CH_2Cl_2 (2.0 mL) was added to the reaction mixture and followed by addition of *sat. aq.* $NaHCO_3$ for quenching (caution the mixture bubbles out while quenching) until the evolution of gas stopped. The mixture was extracted with ethyl acetate (3 × 10 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was used for acetylation without further purification. To a solution of crude propargyl alcohol **34-1** in CH_2Cl_2 (1.0 mL) was added NEt_3 (16 µL, 0.12 mmol) and acetic anhydride (4.3 µL, 0.046 mmol) followed by a trace of DMAP. The reaction mixture was stirred at room temperature for 5 hours or till the TLC analysis showed disappearance of starting material. The reaction was then quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 4/1) to provide **35** as waxy solid (7.7 mg, 75%).

Data of propargyl alcohol **34-1**: waxy solid;
$[\alpha]_D^{20}$ -301.2 (c 0.06, $CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$) δ 6.28 (d, *J* = 2.3 Hz, 1H, *H13*), 6.02 (dq, *J* = 4.7, 1.6 Hz, 1H, *H5*), 5.77 (d, *J* = 2.1 Hz, 1H, *H13*), 5.48 (br s, 2H, *H6* + *H8*), 4.09 (d, *J* = 4.1 Hz, 1H, *H1*), 3.73 (br s, 1H, *H7*), 2.65 (dd, *J* = 15.2, 8.9 Hz, 1H, *H9*), 2.49 (hept, *J* = 7.0 Hz, 1H, *H2'*), 2.00 (d, *J* = 4.2 Hz, 1H, *-OH*), 1.85 (t, *J* = 1.7 Hz, 3H, *H15*), 1.73 (dd, *J* = 15.1, 4.2 Hz, 1H, *H9*), 1.49 (s, 3H, *H14*), 1.12 (d, *J* = 6.1 Hz, 3H, *H3'/4'*), 1.11 (d, *J* = 6.2 Hz, 3H, *H3'/4'*) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5 (*C1'*), 170.3 (*C12*), 141.0 (br, *C5*H), 136.9 (br, *C11*), 123.5 (*C13*H_2), 120.4 (br, *C4*), 98.4 (*C2*), 85.1 (br, *C3*), 77.1 (*C6*H), 74.8 (*C10*), 74.8 (*C8*H), 71.0 (*C1*H), 49.4 (*C7*H), 35.8 (*C9*H_2), 34.3 (*C2'*H), 29.6 (*C14*H_3), 21.0 (*C15*H_3), 18.9 (*C3'*H_3), 18.8 (*C4'*H_3) ppm; ^{13}C NMR signal of C_3 C_4 C_5 C_{11} are broad because of the conformational changes. ^{13}C NMR of C_8 and C_{10} overlap, and C_8 most likely has very weak signal. ^1H NMR of H-6 and H-8 overlap and makes the NOESY hard to be detected;
IR (film, cm^{-1}) 3441, 2977, 1752, 1270, 1200, 1147, 1008;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{19}H_{24}NaO_6$: 371.1472, found: 371.1471;
TLC: Rf = 0.20 (Petroleum ether/Ethyl acetate = 3/1).

Data of **35**: waxy solid;

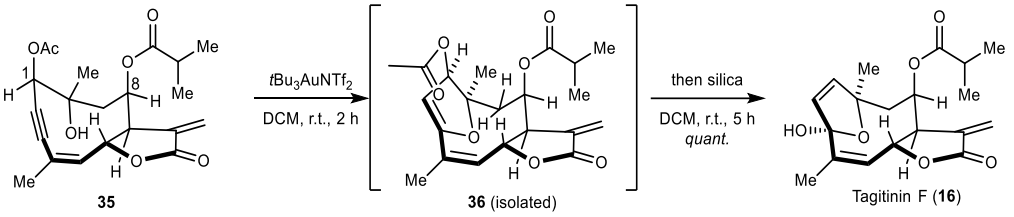
$[\alpha]_D^{20}$ -219.7 (c 0.2, $CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$) δ 6.28 (d, *J* = 2.3 Hz, 1H, *H13*), 6.04 (dq, *J* = 4.7, 1.6 Hz, 1H, *H5*), 5.78 (d, *J* = 2.1 Hz, 1H, *H13*), 5.48 (br s, 2H, *H6* + *H8*), 5.08 (s, 1H, *H1*), 3.74 (br s, 1H, *H7*), 2.67 (dd, *J* = 15.1, 8.9 Hz, 1H, *H9*), 2.49 (hept, *J* = 7.0 Hz, 1H, *H2'*), 2.12 (s, 3H, *-OAc*), 1.84 (t, *J* = 1.7 Hz, 3H, *H15*), 1.79 (dd, *J* = 15.1, 4.2 Hz, 1H, *H9*), 1.42 (s, 3H, *H14*), 1.12 (like t, *J* = 7.0, 6H, *H3'* + *H4'*) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.5 (*C1'*), 170.3 (*C12*), 169.6 (*OAc*), 141.5 (br, *C5*H), 136.9 (br, *C11*), 123.6 (*C13*H_2), 120.4 (br, *C4*), 95.3 (*C2*), 85.0 (br, *C3*), 77.0 (*C6*H), 74.5 (*C8*H), 74.0 (*C10*), 71.2 (*C1*H), 49.4 (*C7*H), 36.8 (*C9*H_2), 34.3 (*C2'*H), 29.6 (*C14*H_3), 21.0 (*OAc*), 20.9 (*C15*H_3), 18.9 (*C3'*H_3), 18.8 (*C4'*H_3) ppm; ^{13}C NMR signal of C_3 C_4 C_5 C_8 C_{11} are broad and C8 disappears because of the conformational changes. ^{13}C NMR of C_8 can be detected by weak HSQC. ^1H NMR of H-6 and H-8 overlap and what makes the NOESY correlation hard to be detected;
IR (film, cm^{-1}) 2926, 2230, 1743, 1223, 1006;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{21}H_{26}NaO_7$: 413.1579, found: 413.1576;
TLC: Rf = 0.50 (Petroleum ether/Ethyl acetate = 3/1).



To a solution of **35** (3.0 mg, 0.0077 mmol) in CH_2Cl_2 (1.0 mL) was added *t*Bu_3AuNTf_2 (0.3 mg, 0.0004 mmol) and stirred for 24 hours or till the TLC analysis showed disappearance of the starting material. The resulted solution was concentrated *in vacuo*. The residue was purified on NEt_3 pre-treated silica gel chromatography (Pentane/Ethyl acetate = 5/1~3/1) to provide the **36** as a waxy solid (1.9 mg, 63%).

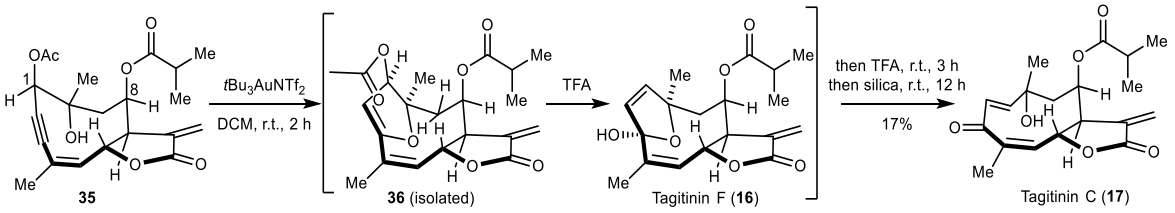
The low isolated yield of **36** may result from the instability under acidic conditions.

Data of **36**: waxy solid;
$[\alpha]_D^{20}$ -333.8 (c 0.1, $CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$) δ 6.28 (d, *J* = 2.6 Hz, 1H, *H13*), 5.85 (d, *J* = 1.4 Hz, 1H, *H1*), 5.73 (dq, *J* = 3.6, 1.7 Hz, 1H, *H5*), 5.62 (d, *J* = 2.3 Hz, 1H, *H13*), 5.56 (dt, *J* = 11.5, 4.5 Hz, 1H, *H8*), 5.37 (dq, *J* = 4.0, 2.0 Hz, 1H, *H6*), 4.99 (d, *J* = 1.4 Hz, 1H, *H2*), 3.94 (tt, *J* = 4.1, 2.4 Hz, 1H, *H7*), 2.84 (dd, *J* = 14.6, 11.5 Hz, 1H, *H9*), 2.44 (hept, *J* = 7.0 Hz, 1H, *H2'*), 2.08 (s, 3H, *-OAc*), 1.88 (t, *J* = 1.8 Hz, 3H, *H15*), 1.65 (s, 3H, *H14*), 1.62 (dd, *J* = 14.6, 4.7 Hz, 1H, *H9*), 1.07 (d, *J* = 6.9 Hz, 3H, *H3'*), 1.05 (d, *J* = 7.0 Hz, 3H, *H4'*) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3 (*C1'*), 170.7 (*OAc*), 169.9 (*C12*), 157.7 (*C3*), 136.0 (*C11*), 133.1 (*C5*H), 130.6 (*C4*), 123.3 (*C13*H_2), 100.8 (*C2*), 87.9 (*C10*), 84.9 (*C1*H), 75.6 (*C6*H), 71.6 (*C8*H), 50.0 (*C7*H), 34.2 (*C2'*H), 32.1 (*C9*H_2), 22.8 (*C14*H_3), 21.5 (*C15*H_3), 21.1 (*OAc*), 19.2 (*C3'*H_3), 18.8 (*C4'*H_3) ppm;
IR (film, cm^{-1}) 2924, 1768, 1738, 1462, 1375, 1281, 1230, 1135, 1034, 1004;
HRMS(ESI) $[M + H]^+$ calculated for $C_{21}H_{27}O_7$: 391.1729, found: 391.1757;
TLC: Rf = 0.60 (Petroleum ether/Ethyl acetate = 3/1).



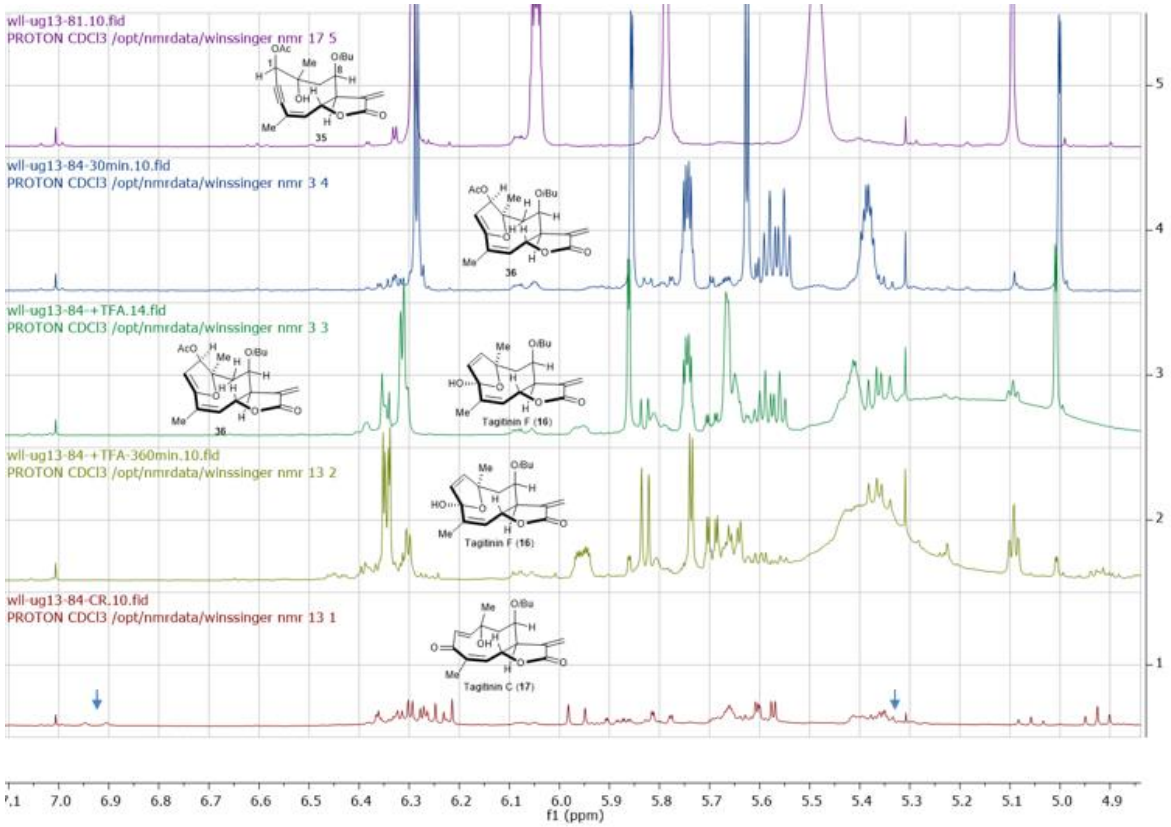
To a solution of **35** (1.9 mg, 0.0049 mmol) in CH_2Cl_2 (0.5 mL) was added *t*Bu_3AuNTf_2 (0.2 mg, 0.00024 mmol) and stirred for 2 hours till the TLC analysis showed disappearance of the starting material. Then silica gel (cat. 2.0 mg) was added to the solution and stirred at same temperature for 5 hours. The residue was directly purified on silica gel chromatography (Pentane/Ethyl acetate = 2/1) to provide the tagitinine F (**16**) as a waxy solid (1.7 mg, *quant.*).

Data of tagitinine F **16**: waxy solid;
$[\alpha]_D^{20}$ -117.8 (c 0.075, MeOH); lit. $[\alpha]_D^{24}$ -12.5 (c 0.1, MeOH) (*Photochem. Photobiol.*, **2020**, *96*, 14-20.);
^1H NMR and ^{13}C NMR data, see **Table S15**;
IR (film, cm^{-1}) 3453, 2972, 2927, 1759, 1736, 1280, 1148, 1099, 1063, 1021, 982;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{19}H_{24}NaO_6$: 371.1472, found: 371.1471;
TLC: Rf = 0.55 (Petroleum ether/Ethyl acetate = 1/1).



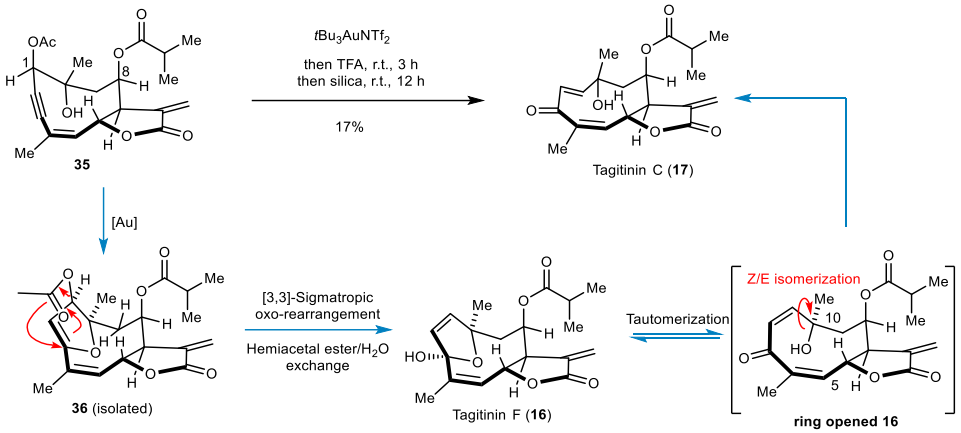
To a solution of **35** (2.0 mg, 0.0051 mmol) in $CDCl_3$ (0.5 mL) in NMR tube was added *t*Bu_3AuNTf_2 (0.2 mg, 0.00024 mmol) and left on a shaker for 2 hours till the crude ^1H NMR analysis showed disappearance of the starting material and formation of **36**. Then TFA (1 μL, 0.013 mmol) was added to the solution and the tube was left on shaker at same temperature for 3 hours. Crude ^1H NMR showed formation tagitinine F **16**. The residue was treated with silica (cat. 2.0 mg) and left of shaker for another 12 hours. The crude ^1H NMR showed disappearance of tagitinine F. The resulted mixture was directly purified on silica gel chromatography (Pentane/Ethyl acetate = 5/1~2/1) to provide the tagitinine C **17** as awaxy solid (0.3 mg, 17%) together with other compounds. Similar reaction with CH_2Cl_2 as solvent was repeated and same result was obtained.

Figure S7. Reaction pathway-crude ^{1}H NMR monitoring.



When **35** (wll-ug13-81) is treated with *t*Bu$_3$AuNTf$_2$, cyclization happens fast to give **36** (wll-ug13-84-30min). This reaction is accomplished within 2 hours depending on the amount of the catalyst. When the cyclized product **36** is treated with TFA and the transformation to tagitinine F **16** happens gradually (wll-ug13-84-+TFA/wll-ug13-84-+TFA-360min), which indicating that TFA plays a similar function as silica gel. Addition of silica gel induces yet a different reaction. Directing monitoring by ^{1}H NMR gives no signals because all the compounds are adsorbed by the silica gel. A Simple filtration followed by a wash with ethyl acetate followed by concentration shows the unequivocal formation of tagitinine C **17** together with two other compounds (wll-ug13-84-CR), in a ratio of **20**: compound 1 : compound 2 = 1:2:1.

Figure S8. Proposed mechanism.

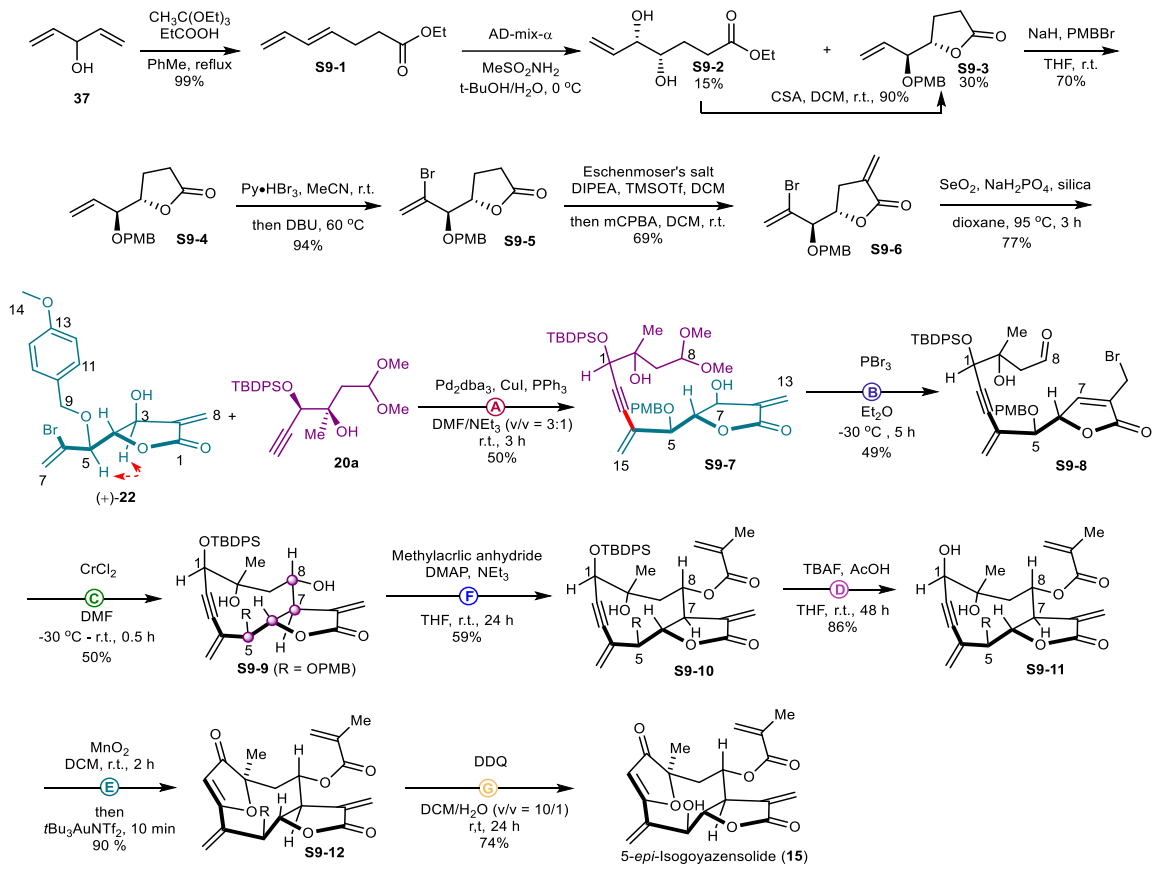


When **35** is treated with the gold catalyst, the alkyne could be activated inducing the cyclization between C10-OH and alkyne-C3 giving **36**. Then reaction would be slower than when C1 is a ketone. Compound **36** is not stable and a [3,3]-Sigmatropic oxo-rearrangement/ Hemiacetal ester/H_2O exchange could give rise to tagitinine F **16**. Tautomerizaation then could generate the enone **ring opened 16**. Tagitinine C **17** could derive from a Z/E isomerization of the 1,2-double bond. The cocktail of TFA and silica would be necessary for this reaction. A control experiment was also conducted where TFA itself lead to no transformation without silica gel under various conditions (heat, light, etc).

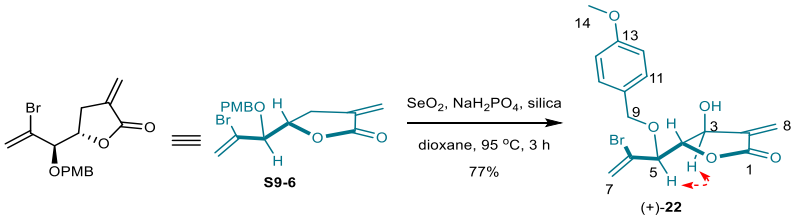
Data of tagitinine C **17**: waxy solid;
$[\alpha]_D^{20}$ -268.8 (c 0.07, MeOH); lit. $[\alpha]_D^{24}$ -23.5 (c 0.1, MeOH) (*Photochem. Photobiol.*, **2020**, *96*, 14-20.);
^{1}H NMR and ^{13}C NMR data see **Table S16**;
IR (film, cm^{-1}) 3480, 2974, 2927, 1768, 1736, 1656, 1121, 993;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{19}H_{24}NaO_6$: 371.1472, found: 371.1471;
TLC: Rf = 0.50 (Petroleum ether/Ethyl acetate = 1/1).

g) Experimental procedures for Scheme 2

Figure S9. Synthesis of 5-*epi*-isogoyazensolide (**15**) from **37** and **20a**.



Lactone **S9-6** is a known compound and was prepared in 5 steps from **37** as previously reported.[25]



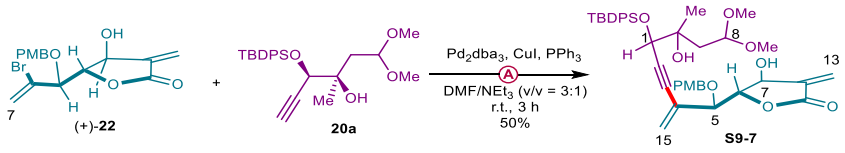
To a stirred solution of lactone **S9-6** (1.7 g, 4.8 mmol), NaH_2PO_4 (2.5 g, 20.8 mmol) and silica (5.0 g) in dioxane (50 mL) was added SeO_2 (2.5 g, 22.5 mmol) in 3 portions at 95 °C within 2 hours. The reaction mixture was stirred for 1 more hour and then cooled down to room temperature. Then dioxane was evaporated and Et_2O (200 mL) was added, the mixture was stirred for 30 minutes, filtered and the solution was washed with saturated aqueous $NaHCO_3$ (100 mL), diluted Na_2S (10 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified

[25] Kutsumura, N., Kiriseko, A., Saito, T. *Heterocycles*, **2012**, *86*, 1367-1378.

on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 1/1) to provide **22** as light-yellow oil (1.36 g, 77 %), which gradually became solid in the fridge.

The structure of lactone **22** was fully elucidated based on 2D NMR spectroscopic analyses, indicating a *trans* product. See **Supplementary Section l** for detail information.

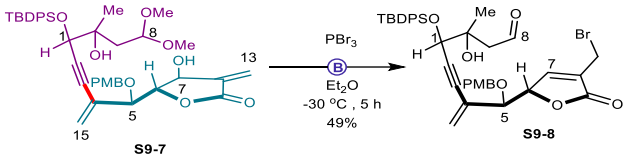
Data of lactone **22**: yellow oil to waxy solid;
$[\alpha]_D^{20}$ +43.3 (c 0.2, $CHCl_3$);
^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (m, 2H, H_{11}), 6.89 (m, 2H, H_{12}), 6.41 (d, J = 2.3 Hz, 1H , H_8), 6.12 (dd, J = 2.1, 1.0 Hz, 1H, H_7), 5.93 (d, J = 1.9 Hz, 1H, H_8), 5.90 (dd, J = 2.0, 0.6 Hz, 1H, H_7), 4.68 (d, J = 11.7 Hz, 1H, H_9), 4.60 (ddt, J = 5.8, 4.1, 2.1 Hz, 1H, H_3), 4.53 (t, J = 3.7 Hz, 1H, H_4), 4.30 (d, J = 11.7 Hz, 1H, H_9), 4.04 (ddd, J = 3.7, 1.1, 0.5 Hz, 1H, H_5), 3.82 (s, 3H, H_{14}), 2.09 (d, J = 6.1 Hz, 1H, -*OH*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2 (C_1), 159.8 (C_{13}), 138.4 (C_2), 130.1 ($C_{11}H$), 128.6 (C_{10}), 127.3 (C_6), 125.9 (C_8H_2), 121.4 (C_7H_2), 114.2 ($C_{12}H$), 83.5 (C_4H), 80.8 (C_5H), 71.0 (C_9H_2), 70.1 (C_3H), 55.5 ($C_{14}H_3$) ppm;
IR (film, cm^{-1}) 3453, 1770, 1613, 1514, 1251, 1033, 818;
TLC: Rf = 0.40 (Petroleum ether/Ethyl acetate = 2/1).



To a stirred solution of alkyne **20a** (51 mg, 0.12 mmol) and vinyl bromide **22** (40 mg, 0.11 mmol) in DMF/NEt_3 (3.0 mL/1 mL) was added Pd_2dba_3 (20 mg, 0.022 mmol) and CuI (2 mg, 0.011 mmol). The mixture was then stirred for 2 hours or till TLC analysis showed disappearance of the starting material. The reaction was quenched by addition of *sat. aq.* NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 5/1 ~ 1/1) to provide enyne **S9-7** as a yellow oil (39 mg, 50%).

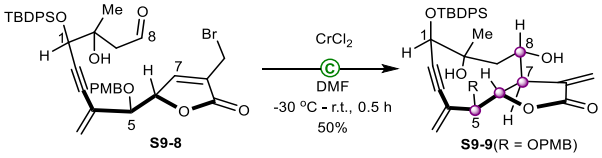
Data of enyne **S9-7**: yellow oil;
$[\alpha]_D^{20}$ -40.2 (c 0.5, $CHCl_3$);
^1H NMR (400 MHz, $CDCl_3$) δ 7.75-7.73 (m, 4H, TBDPS), 7.44-7.33 (m, 6H, TBDPS), 7.19 (like d, J = 8.6 Hz, 2H, PMB), 6.87 (like d, J = 8.7 Hz, 2H, PMB), 6.32 (d, J = 2.6 Hz, 1H, H_7), 5.81 (d, J = 2.1 Hz, 1H, H_7), 5.53 (br t, J = 1.3 Hz, 1H, H_{15}), 5.40 (br s, 1H, H_{15}), 4.65 (dd, J = 6.5, 4.6 Hz, 1H, H_8), 4.53 (d, J = 11.6 Hz, 1H, PMB), 4.49 (br s, 1H, H_7), 4.35 (s, 1H, H_1), 4.25-4.14 (m, 2H, *PMB* + H_6), 3.81 (s, 3H, PMB), 3.71 (br d, J = 5.4 Hz, 1H, H_5), 3.26 (s, 3H, C_8-OMe), 3.25 (s, 3H, C_8-OMe), 2.11 (dd, J = 14.6, 6.6 Hz, 1H, H_9), 1.91 (dd, J = 14.6, 4.6 Hz, 1H, H_7), 1.34 (s, 3H, H_{14}), 1.09 (s, 9H, TBDPS) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2 (C_{12}), 159.6 (PMB-*C*), 138.6 (C_{11}), 136.3 (*TBDPS*), 136.2 (*TBDPS*), 133.5 (*TBDPS*), 132.6 (*TBDPS*), 130.2 (*TBDPS*), 129.9 (*TBDPS*), 129.7 (PMB-*C*H), 129.3 (PMB-*C*), 127.9 (*TBDPS*), 127.6 (*TBDPS*), 126.0 ($C_{15}H_2$), 125.8 (C_4), 125.0 ($C_{13}H_2$), 114.0 (PMB-*C*H), 102.4 (C_8H), 90.9 (C_2), 85.0 (C_6H), 84.7(C_3), 79.5 (C_5H), 74.3 (C_{10}), 71.4 (C_1H), 70.6 (PMB-*C*H_2), 69.5 (C_7H), 55.5 (PMB-*C*H_3), 53.6 (C_8-OMe), 52.8 (C_8-OMe), 39.4 (C_9H_2), 27.1 (*TBDPS*), 24.0 ($C_{14}H_3$), 19.6 (*TBDPS*) ppm;
IR (film, cm^{-1}) 3434, 2935, 2860, 1768, 1613, 1514, 1450, 1112, 821, 705;

HRMS(ESI) $[M + Na]^+$ calculated for $C_{41}H_{50}NaO_9Si$: 737.3122, found: 737.3108;
TLC: Rf = 0.10 (Pentane/Ethyl acetate = 2/1).



A 10 mL round bottom flask equipped with a magnetic stir bar was charged with enyne **S9-7** (30 mg, 0.042 mmol) and Et_2O (3.0 mL). The reaction was cooled down to -30 °C and PBr_3 (7 μL, 0.084 mmol) was added. The mixture was stirred for 5 hours or till the LC-MS analysis showed disappearance of the starting material. Then the reaction was quenched with water (5.0 mL) and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 3/1 ~ 1/1) to provide bromolactone **S9-8** as a colorless oil (15 mg, 49%).

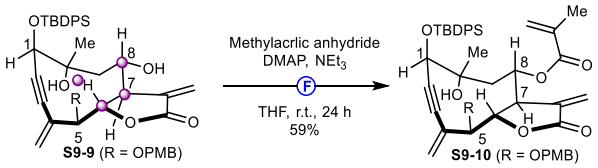
Data of bromolactone **S9-8**: colorless oil;
$[\alpha]_D^{20}$ -59.2 (c 0.1, $CHCl_3$);
^1H NMR (300 MHz, $CDCl_3$) δ 9.85 (t, *J* = 2.5 Hz, 1H, *H9*), 7.78 – 7.66 (m, 4H, *TBDPS*), 7.45 – 7.35 (m, 6H, *TBDPS*), 7.18 (like d, *J* = 8.6 Hz, 2H, *PMB*), 6.98 (m, 1H, *H7*), 6.87 (like d, *J* = 8.5 Hz, 2H, *PMB*), 5.42 (br s, 1H, *H15*), 5.30 (br s, 1H, *H15*), 4.72 (dd, *J* = 5.8, 1.6 Hz, 1H, *H6*), 4.50 (d, *J* = 11.5 Hz, 1H, *PMB*), 4.38 (s, 1H, *H1*), 4.21 (d, *J* = 11.5 Hz, 1H, *PMB*), 3.93 (dt, *J* = 6.8, 1.4 Hz, 2H, *H13*), 3.81 (s, 3H, *PMB*), 3.73 (d, *J* = 5.7 Hz, 1H, *H5*), 2.78 – 2.70 (m, 1H, *H9*), 2.66 (dd, *J* = 15.6, 2.9 Hz, 1H, *H9*), 1.44 (s, 3H, *H14*), 1.07 (s, 9H, *TBDPS*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1 (*C8*H), 170.6 (*C12*), 159.7 (PMB-*C*), 149.7 (*C7*H), 136.2 (*TBDPS*), 136.0 (*TBDPS*), 133.3 (*TBDPS*), 132.0 (*TBDPS* + *C11*), 130.5 (*TBDPS*), 130.0 (*TBDPS*), 129.8 (PMB-*C*H), 128.9 (PMB-*C*), 128.1 (*TBDPS*), 127.6 (*TBDPS*), 127.0 (*C15*H_2), 125.8 (*C4*), 114.1 (PMB-*C*H), 90.4 (*C2*), 85.2 (*C3*), 81.5 (*C6*H), 80.0 (*C5*H), 74.8 (*C10*), 71.6 (*C1*H), 70.8 (PMB-*C*H_2), 55.5 (PMB-*C*H_3), 50.7 (*C9*H_2), 27.0 (*TBDPS*), 23.7 (*C14*H_3), 20.9 (*C13*H_2), 19.6 (*TBDPS*) ppm;
IR (film, cm^{-1}) 3457, 2942, 2314, 1977, 1768, 1513, 1248, 1108, 823, 705;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{39}H_{43}BrNaO_7Si$: 753.1859, found: 753.1861;
TLC: Rf = 0.50 (Pentane/Ethyl acetate = 2/1).



A 10 mL round bottom flask equipped with a magnetic stir bar was charged with bromolactone **S9-8** (15 mg, 0.02 mmol) and DMF (1.0 mL). The reaction mixture was cooled down to -30 °C and $CrCl_2$ (6.2 mg, 0.5 mmol) was added. The temperature was allowed to rise to room temperature and stirred for 30 minutes or till the TLC analysis showed disappearance of starting material. Then, the reaction was quenched with *sat. aq.* NH_4Cl (5.0 mL) and extracted with ethyl acetate (3 × 5.0 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was

purified on silica gel chromatography (Pentane/Ethyl acetate = 2/1) to provide **S9-9** as a waxy solid (6.7 mg, 50%).

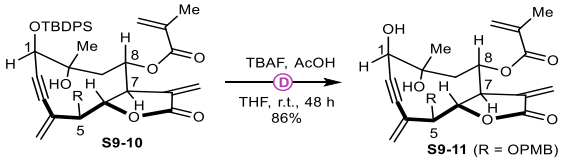
Data of **S9-9**: waxy solid;
$[\alpha]_D^{20}$ -93.2 (c 0.04, $CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 4H, *TBDPS*), 7.43 – 7.34 (m, 6H, *TBDPS*), 7.29 (likd d, *J* = 8.6 Hz, 2H, *PMB*), 6.87 (d, *J* = 8.7 Hz, 2H, *PMB*), 6.40 (d, *J* = 2.6 Hz, 1H, H_{13}), 5.78 (d, *J* = 2.3 Hz, 1H, H_{13}), 5.75 (d, *J* = 1.8 Hz, 1H, H_{15}), 5.32 (t, *J* = 1.8 Hz, 1H, H_{15}), 4.58 (d, *J* = 11.2 Hz, 1H, *PMB*), 4.52 (d, *J* = 11.1 Hz, 1H, *PMB*), 4.40 – 4.36 (m, 2H, H_6 + H_8), 4.11 (s, 1H, H_1), 4.05 (br s, 1H, H_7), 3.82 – 3.81 (m, 1H, H_5), 3.80 (s, 3H, *PMB*), 2.38 (dd, *J* = 14.8, 3.4 Hz, 1H, H_9), 1.97 (dd, *J* = 14.9, 9.2 Hz, 1H, H_9), 1.38 (s, 3H, H_{14}), 1.10 (s, 9H, TBDPS) ppm;
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9 (C_{12}), 159.5 (PMB-*C*), 136.4 (*TBDPS*), 136.2 (*TBDPS*), 135.0 (C_{11}), 133.0 (*TBDPS*), 132.6 (*TBDPS*), 130.3 (*TBDPS*), 130.1 (*TBDPS*), 129.8 (PMB-*C*H), 129.7(PMB-*C*), 128.0 (*TBDPS*), 127.7 (*TBDPS*), 125.9 (C_4), 125.2 ($C_{15}H_2$), 124.5 ($C_{13}H_2$), 114.0 (PMB-*C*H), 94.1 (C_2), 85.9 (C_3), 84.1 (C_6H), 81.7 (C_5H), 76.6 (C_{10}), 73.0 (PMB-*C*H_2), 71.2 (C_1H), 70.3 (C_8H), 55.4 (PMB-*C*H_3), 47.8 (C_7H), 42.5 (C_9H_2, br), 29.2 ($C_{14}H_3$, br), 27.2 (*TBDPS*), 19.5 (*TBDPS*) ppm; the signal of C_9/C_{14} are broad on ^{13}C NMR because of the conformational changes, the chemical shift were confirmed by HMBC;
IR (film, cm^{-1}) 3429, 2944, 1984, 1900, 1758, 1516, 1250, 1108, 826, 706;
HRMS(ESI) $[M + H]^+$ calculated for $C_{39}H_{45}O_7Si$: 653.2935, found: 653.2936;
TLC: Rf = 0.25 (Pentane/Ethyl acetate = 2/1).



To a stirred solution of alcohol **S9-9** (2.5 mg, 0.004 mmol) in THF (1.0 mL) was added NEt_3 (50 μL, 0.36 mmol) and methacrylic anhydride (25 μL, 0.17 mmol) followed by a trace of DMAP. The reaction mixture was stirred at room temperature for 24 minutes or till the TLC analysis showed disappearance of starting material. The reaction was then quenched with *sat. aq.* $NaHCO_3$ (2.0 mL), the mixture was extracted with ethyl acetate (2 × 5.0 mL), the combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 5/1) to provide the **S9-10** as a waxy solid (1.7 mg, 59%).

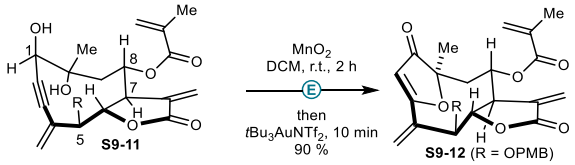
Data of **S9-10**: waxy solid;
$[\alpha]_D^{20}$ -95.8 (c 0.10, $CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 4H, *TBDPS*), 7.48 – 7.34 (m, 6H, *TBDPS*), 7.28 (like d, *J* = 8.7 Hz, 2H, *PMB*), 6.85 (d, *J* = 8.7 Hz, 2H, *PMB*), 6.40 (d, *J* = 3.0 Hz, 1H, H_{13}), 5.99 (m, 1H, $H_{3'}$), 5.93 (dd, *J* = 10.3, 3.9 Hz, 1H, H_8), 5.86 (d, *J* = 2.5 Hz, 1H, H_{13}), 5.83 (t, *J* = 1.9 Hz, 1H, H_{15}), 5.52 (t, *J* = 1.6 Hz, 1H, $H_{3'}$), 5.23 (t, *J* = 1.9 Hz, 1H, H_{15}), 4.62 (d, *J* = 11.0 Hz, 1H, *PMB*), 4.50 (d, *J* = 11.1 Hz, 1H, *PMB*), 4.41 – 4.35 (m, 1H, H_7), 4.21 (dd, *J* = 9.3, 5.5 Hz, 1H, H_6), 4.09 (s, 1H, H_1), 3.85 – 3.80 (m, 1H, H_5), 3.79 (s, 3H, *PMB*), 2.36 (dd, *J* = 14.6, 4.0 Hz, 1H, H_9), 2.02 – 1.98 (m, 1H, H_9), 1.87 (t, *J* = 0.9 Hz, 3H, $H_{4'}$), 1.36 (s, 3H, H_{14}), 1.12 (s, 9H, *TBDPS*) ppm;
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9 (C_{12}), 166.2 ($C_{1'}$), 159.5 (PMB-*C*), 136.5 (*TBDPS*), 136.3 (*TBDPS*), 136.2 ($C_{2'}$), 134.6 (C_{11}), 132.9 (*TBDPS*), 132.5 (*TBDPS*), 130.3 (*TBDPS*), 130.0

(*TBDPS*), 129.74 (PMB-*C*H), 129.70 (PMB-*C*), 128.0 (*TBDPS*), 127.6 (*TBDPS*), 126.3 (*C3'*), 125.5 (*C4*), 124.7 (*C15*H2), 123.9 (*C13*H2), 114.0 (PMB-*C*H), 94.1 (*C2*), 86.8 (*C3*), 84.2 (*C6*H), 81.6 (*C5*H), 76.2 (*C10*), 73.6 (PMB-*C*H2), 72.3 (*C8*H), 70.8 (*C1*H), 55.4 (PMB-*C*H3), 46.2 (*C7*H), 40.6 (*C9*H2), 28.3 (*C14*H3, br), 27.1 (*TBDPS*), 19.5 (*TBDPS*), 18.4 (*C4'*) ppm;
IR (film, cm^{-1}) 3444, 2923, 2178, 1936, 1108;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{43}H_{48}NaSiO_8$: 743.3016, found: 743.2993;
TLC: Rf = 0.70 (Petroleum ether/Ethyl acetate = 2/1).



AcOH (1.4 µL, 0.024 mmol) and TBAF (1M solution in THF, 24 µL, 0.024 mmol) were mixed and stirred in THF (0.1 mL) at room temperature for 30 minutes and the resulting mixture was added to a stirred solution of **S9-10** (1.7 mg, 0.0024 mmol) in THF (0.5 mL). The reaction was then stirred at room temperature for further 48 hours, until the TLC analysis showed disappearance of the starting material. The reaction was diluted with ethyl acetate (25 mL) and washed with brine (5.0 mL), dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on preparative TLC (Pentane/Ethyl acetate = 1/1) to provide the **S9-11** as a waxy solid (1.0 mg, 86%).

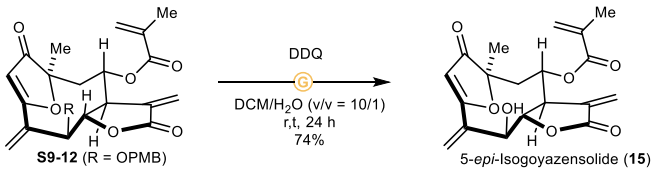
Data of lactone **S9-11**: waxy solid;
$[\alpha]_D^{20}$ -35.4 (c 0.1, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (like d, *J* = 8.7 Hz, 2H, *PMB*), 6.87 (d, *J* = 8.7 Hz, 2H, *PMB*), 6.44 (d, *J* = 2.9 Hz, 1H, *H13*), 6.00 - 5.98 (m, 2H, *H3'* + *H15*), 5.91 (d, *J* = 2.5 Hz, 1H, *H13*), 5.78 (dd, *J* = 10.7, 3.5 Hz, 1H, *H8*), 5.70 (t, *J* = 1.8 Hz, 1H, *H15*), 5.55 (p, *J* = 1.6 Hz, 1H, *H3'*), 4.68 (d, *J* = 11.1 Hz, 1H, *PMB*), 4.57 (d, *J* = 11.1 Hz, 1H, *PMB*), 4.40 (dt, *J* = 5.8, 2.8 Hz, 1H, *H7*), 4.24 (br s, 1H, *H1*), 4.19 (dd, *J* = 9.1, 5.4 Hz, 1H, *H6*), 3.97 (dt, *J* = 9.3, 1.9 Hz, 1H, *H5*), 3.80 (s, 3H, *PMB*), 2.26 – 2.20 (m, 1H, *H9*), 2.12 – 2.06 (m, 1H, *H9*), 1.85 (t, *J* = 1.6, 1.0 Hz, 3H, *H4'*), 1.46 (s, 3H, *H14*) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7 (*C12*), 166.9 (*C1'*), 159.6 (PMB-*C*), 135.8 (*C2'*), 134.4 (*C11*), 129.8 (PMB-*C*H), 129.6 (PMB-*C*), 126.9 (*C3'*), 125.7 (*C4*), 125.6 (*C15*H2), 124.1 (*C13*H2), 114.0 (PMB-*C*H), 93.7 (*C2*), 86.7 (*C3*), 84.1 (*C6*H), 81.6 (*C5*H), 75.6 (*C10*), 73.8 (PMB-*C*H2), 72.6 (*C8*H), 69.6 (*C1*H), 55.4 (PMB-*C*H3), 45.9 (*C7*H), 40.3 (*C9*H2), 28.1 (*C14*H3, br), 18.2 (*C4'*) ppm;
IR (film, cm^{-1}) 3497, 2934, 2455, 1744, 1513, 1254, 1113, 1045, 826;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{27}H_{30}O_8Na$: 505.1838, found: 505.1802;
TLC: Rf = 0.25 (Pentane/Ethyl acetate = 2/1).



To a stirred solution of **S9-11** (1.0 mg, 0.0021 mmol) in CH_2Cl_2 (1.0 mL) was added MnO_2 (2.7 mg, 0.031 mmol) and the solution was stirred at room temperature for 2 hours, or till the TLC analysis showed disappearance of the starting material. The reaction was

filterred and a trace of *t*Bu$_3$PAuNTf$_2$ was added to the solution and stirred for 10 minutes till the the TLC analysis showed disappearance of the starting material. The resulted solution was concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 5/1) to provide **S9-12** as a white solid (0.9 mg, 90%).

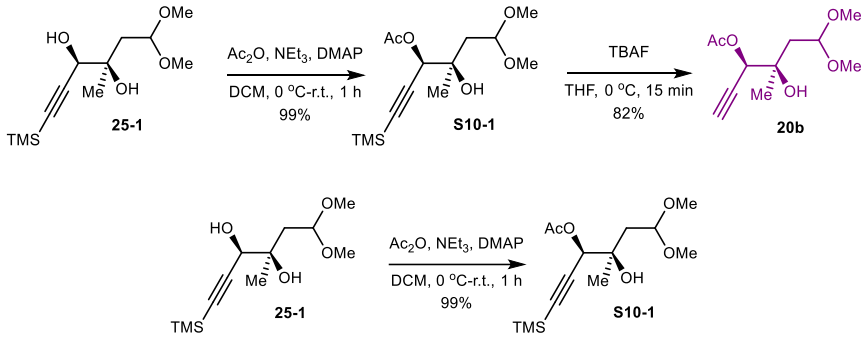
Data of lactone **S9-12**: waxy solid;
$[\alpha]_D^{20}$ +5.05 (c 0.04, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (like d, *J* = 8.6 Hz, 2H, PMB), 6.89 (like d, *J* = 8.6 Hz, 2H, PMB), 6.27 (d, *J* = 3.4 Hz, 1H, *H*$_{13}$), 6.20 (dd, *J* = 2.1, 1.0 Hz, 1H, *H*$_{15}$), 5.99 (p, *J* = 1.2 Hz, 1H, *H*$_{3'}$), 5.97 (dd, *J* = 2.1, 1.0 Hz, 1H, *H*$_{15}$), 5.95 (s, 1H, *H*$_2$), 5.53 (p, *J* = 1.5 Hz, 1H, *H*$_{3'}$), 5.52 (d, *J* = 3.0 Hz, 1H, *H*$_{13}$), 4.85 (d, *J* = 11.1 Hz, 1H, PMB), 4.67 (dd, *J* = 9.4, 5.8 Hz, 1H, *H*$_6$), 4.59 (d, *J* = 11.1 Hz, 1H, PMB), 4.40 – 4.35 (m, 2H, *H*$_8$ + *H*$_5$), 3.81 (s, 3H, PMB), 3.62 (dt, *J* = 6.3, 3.0 Hz, 1H, *H*$_7$), 2.52 – 2.47 (m, 1H, *H*$_9$), 2.35 (dd, *J* = 13.8, 1.8 Hz, 1H, *H*$_9$), 1.82 (dd, *J* = 1.6, 1.0 Hz, 3H, *H*$_{4'}$), 1.52 (s, 3H, *H*$_{14}$) ppm;
^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1 (*C*$_1$), 185.1 (*C*$_3$), 168.7 (*C*$_{12}$), 166.7 (*C*$_{1'}$), 159.6 (PMB-*C*), 137.4 (*C*$_4$), 135.5 (*C*$_{2'}$), 133.1 (*C*$_{11}$), 129.9 (PMB-*C*H), 129.6 (PMB-*C*), 126.7 (*C*$_{3'}$), 124.3 (*C*$_{13}$H$_2$), 123.9 (*C*$_{15}$H$_2$), 114.1 (PMB-*C*H), 106.9 (*C*$_2$H), 90.5 (*C*$_{10}$), 85.6 (*C*$_6$H), 80.8 (*C*$_5$H), 74.8 (PMB-*C*H$_2$), 70.8 (*C*$_8$H), 55.5 (PMB-*C*H$_3$), 51.9 (*C*$_7$H), 45.5 (*C*$_9$H$_2$), 21.2 (*C*$_{14}$H$_3$), 18.1 (*C*$_{4'}$H$_3$) ppm;
IR (film, cm^{-1}) 3498, 2170, 1769, 1713, 1250, 1159, 1040, 813;
HRMS(ESI) [M + Na]$^+$ calculated for $C_{27}H_{28}O_8Na$: 503.1682, found: 503.1685;
TLC: Rf = 0.5 (Pentane/Ethyl acetate = 2.5/1).



To a stirred solution of **S9-12** (0.9 mg, 0.0019 mmol) in CH_2Cl_2/H_2O (1.0 mL/ 4 drops) was added DDQ (1.3 mg, 0.0057 mmol) and the mixture was stirred at room temperature for 24 hours till the TLC analysis showed disappearance of the starting material. The reaction mixture was then quenched by saturated aqueous $NaHCO_3$ (1.0 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo* and purified on silica gel chromatography (Pentane/Ethyl acetate = 5/1 ~ 2/1) to provide **15** as a waxy solid(0.5 mg, 74%).

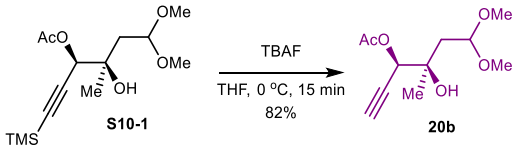
Data of **15**: waxy solid;
$[\alpha]_D^{20}$ -18 (c 0.04, $CHCl_3$);
^{1}H NMR and ^{13}C NMR data, see **Table S14**;
IR (film, cm^{-1}) 3678, 2921, 1988, 1711, 1261, 1144, 819;
HRMS(ESI) [M + Na]$^+$ calculated for $C_{19}H_{20}NaO_7$: 383.1107, found: 383.1115;
TLC: Rf = 0.20 (Petroleum ether/Ethyl acetate = 3/1).

Figure S10. Synthesis of **20b** from **25-1**.



Compound **25-1** can also be obtained after SAD from **25**. To a mixture of compound **25-1** (13.4 g, 51.5 mmol), acetic anhydride (5.84 mL, 61.85 mmol) and DMAP (628 mg, 5.15 mmol) in CH_2Cl_2 (200 mL) was added dropwise Et_3N (17.8 mL, 129 mmol) at 0 °C. then the mixture was allowed to warm to room temperature and stirred 1 hour. After the reaction was diluted with CH_2Cl_2 (200 mL) and washed with HCl 0.1 M (100 mL), followed by H_20 (100 mL) and Brine (100 mL). The organic layer was then dried over sodium sulfate, the solvent was removed and a pale-yellow oil was obtained **S10-1** (15.5 g, yield 99%).

Data of **S10-1**: pale-yellow oil;
$[\alpha]_D^{20}$ -34 (c 0.3, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (s, 1H), 4.73 (dd, *J* = 6.4, 5.3 Hz,1H), 3.40 (d, *J* = 9.9 Hz, 6H), 2.15 (s, 3H), 2.09 (dd, *J* = 14.6, 5.3 Hz, 1H), 1.91 (dd, *J* = 14.6, 6.5 Hz, 1H), 0.19 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 102.3, 100.4, 92.0, 72.7, 69.7, 53.5, 53.2, 39.8, 23.0, 21.0, -0.2 ppm;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{14}H_{26}O_5Si$: 325.1550, found: 325.1437;
TLC: Rf = 0.35 (Pentane/Ethyl acetate = 2/1).

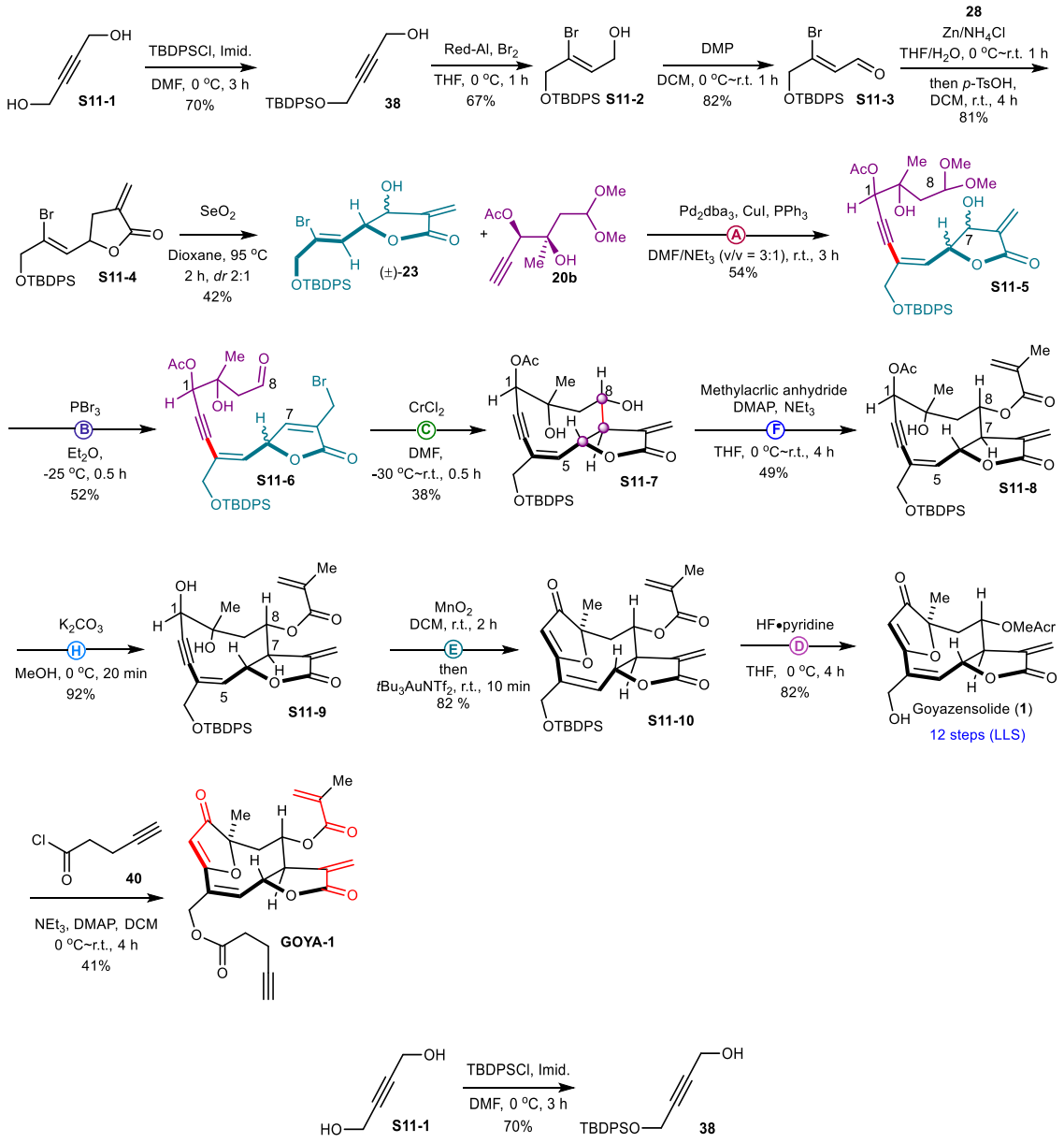


To a solution of **S10-1** (15.5 g, 51.5 mmol) in THF (170 mL) was added dropwise TBAF (51.5 mL, 1M in THF, 51.5 mmol) at 0 °C. The reaction mixture was then stirred for 15 minutes and quenched with saturated NH_4Cl (50 mL), then diluted with Et_2O (200 mL) and washed with HCl 0.1M (100 mL) H_20 (100 mL) and Brine (100 mL). The Organic layer was extracted and dried over Na_2SO_4. The solvent was removed and the residue was purifiyed by chromatography on silica gel (pentane/ethyl acetate 7/3) to give a pale-yellow oil **20b** (9.75 g, yield 82%).

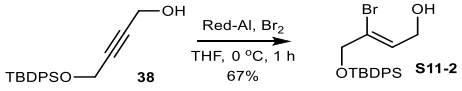
Data of **20b**: pale-yellow oil;
$[\alpha]_D^{20}$ -19.4 (c 0.1, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (d, *J* = 2.2 Hz, 1H), 4.74 (t, *J* = 5.8 Hz, 1H), 3.40 (d, *J* = 4.4 Hz, 6H), 2.50 (d, *J* = 2.2 Hz, 1H), 2.15 (s, 3H), 2.11 (dd, *J* = 14.6, 5.6 Hz, 1H), 1.93 (dd, *J* = 14.6, 6.0 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 102.2, 79.0, 74.8, 72.5, 69.3, 53.4, 53.2, 39.5, 23.2, 20.9 ppm;
TLC: Rf = 0.25 (Pentane/Ethyl acetate = 2/1).

Figure S11. Synthesis of Goyazensolide (**1**) and **GOYA-1** from **38** and **20b**.



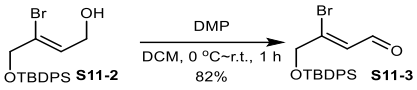
38 was prepared from **S11-1** according to the reported procedure.[26]



[26] Koura, M., Yamaguchi, Y., Kurobuchi, S., Sumida, H., Watanabe, Y., Enomoto, T., Matsuda, T., Koshizawa, T., Matsumoto, Y., Shibuya, K. *Bioorg. Med. Chem.* **2016**, *24*, 3436-3446.

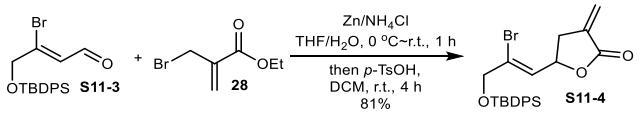
To a solution of **38** (38 g, 104 mmol) in THF (400 mL), was added vitride (53 mL, 3.5 M in toluene, 185 mmol) at 0 °C. The mixture was stirred at 0 °C for 15 minutes, and then Br_2 (6.96 mL, 135 mmol) was added over 5 minutes. After 15 minutes, saturated aqueous $Na_2S_2O_3$ (100 mL) and saturated aqueous Rochelle's salt (100 mL) were added at room temperature, and the mixture was stirred for 30 minutes. The mixture was then extracted with ethyl acetate (100 mL × 3), and the combined organic layers were washed with brine (200 mL), dried over $MgSO_4$, and concentrated to give the crude alcohol as a colorless oil (28 g, 67%).

Data of **S11-2**: colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.9, 1.5 Hz, 4H), 7.44 (ddd, *J* = 18.9, 7.6, 6.1 Hz, 6H), 6.39 (tt, *J* = 6.1, 1.6 Hz, 1H), 4.34 (d, *J* = 6.1 Hz, 2H), 4.30 (d, *J* = 1.5 Hz, 2H), 1.11 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 132.9, 129.9, 127.8, 126.8, 126.6, 68.0, 61.8, 26.7, 19.2 ppm;
TLC: Rf = 0.4 (Pentane/Ethyl acetate = 3/1).



To a solution of **S11-2** (25 g, 61.7 mmol) in CH_2Cl_2 (300 mL) was added DMP (31.3 g, 74 mmol) in portions at 0 °C. The mixture was stirred at 0 °C for 15 minutes, and mixture allowed to warm to room temperature. After 30 minutes, saturated aqueous Na_2S_2O3 (50 mL) and saturated aqueous $NaHCO_3$ (50 mL) were added at room temperature, and the mixture was stirred for 10 more minutes. The whole was extracted with Et_2O (150 mL × 3), and the combined organic layers were washed with brine (200 mL) dried over $MgSO_4$, and concentrated to give crude aldehyde as a paled yellow oil (20.3 g, yield 82%).

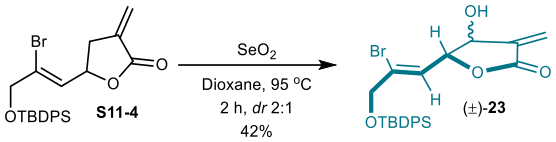
Data of **S11-3**: paled yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (d, *J* = 6.9 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 4H), 7.47 (dd, *J* = 15.8, 6.0 Hz, 6H), 6.93 (d, *J* = 6.9 Hz, 1H), 4.43 (s, 2H), 1.11 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 147.3, 135.1, 131.8, 129.9, 127.7, 125.2, 68.1, 26.4, 18.9 ppm;
TLC: Rf = 0.6 (Pentane/Ethyl acetate = 4/1).



To a mixture of **S11-3** (8.5 g, 21.2 mmol), allylic bromide **28** (6.13 g, 31.8 mmol) in THF/water (6/1, 140 ml) at 0 °C under a vigorous stirring was added Zn (2.48 g, 38.2 mmol) in portions. The mixture was allowed to warm to room temperature for 1 hour. The reaction mixture was then diluted with Et_2O (200 mL) and water (150 mL). The organic phase was washed with Brine (100 mL), dried over Na_2SO_4 and volatiles were evaporated *in vacuo*. The crude was diluted in CH_2Cl_2 (150 mL) and to the solution was added PTSA (0.86 g, 5.0 mmol). Then the mixture was stirred for 4 hours at room temperature. The reaction was then diluted with HCl (0.1M, 100 mL), the organic phase was then washed with H_20 (100 mL) and Brine (100 mL), dried over Na_2SO_4 and the

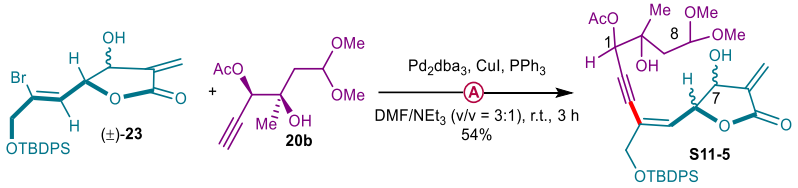
solvent was removed *in vacuo*. Chromatography on silica gel (pentane/ethyl acetate 8/2) gave a pale-yellow oil (8.1 g, yield 81%).

Data of **S11-4**: pale-yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.7, 3.8 Hz,4H), 7.50–7.39 (m, 6H), 6.36 (dt, *J* = 7.6, 1.7 Hz, 1H), 6.30 (t, *J* = 2.8 Hz, 1H), 5.70 (t, *J* = 2.5 Hz, 1H), 5.37 (dd, *J* = 14.6, 7.6 Hz, 1H), 4.36–4.24 (m, 2H), 3.30 (dd, *J* = 17.1, 7.9 Hz, 1H), 2.66 (dd, *J* = 17.1, 6.7 Hz, 1H), 1.10 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 135.4, 135.4, 133.7, 132.7, 132.5, 130.0, 130.0, 128.9, 127.9, 127.8, 126.1, 122.5, 76.0, 67.8, 33.8, 26.7, 19.2;
HRMS(ESI) $[M + H]^+$ calculated for $C_{24}H_{27}BrO_3Si$: 471.0913, found 471.1007;
TLC: Rf = 0.5 (Pentane/Ethyl acetate = 4/1) ppm.



To a stirred solution of lactone **S11-4** (2,0 g, 4.2 mmol) in dioxane (20 mL) was added SeO_2 (2.8 g, 25.2 mmol) in 3 portions at 95 °C within 1.5 hours. After the addition, the reaction mixture was stirred at the same temperature for another 30 minutes and then cooled down to room temperature. Then dioxane was evaporated and Et_2O (80 mL) was added, stirred for 30 minutes, filtered and the solution was washed with saturated aqueous $NaHCO_3$ (20 mL), diluted Na_2S (10 mL) and brine (20 mL). The organic phase was dried over Na_2SO_4, then filterred and concentrated *in vacuo*. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 10/1 ~ 1/1) to provide **23** as a light yellow oil (860 mg, 42%).

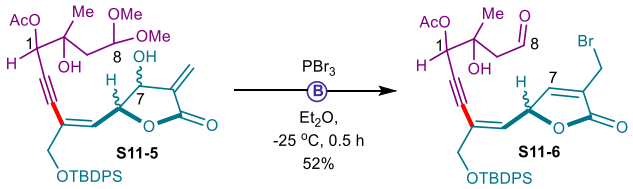
Data of **23**: light yellow oil;
Obtained as a mixture of diastereomers (*dr* = 2:1 as determined by ^{1}H NMR);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (td, *J* = 7.2, 1.5 Hz, 4H), 7.48–7.39 (m, 6H), 6.51 (d, *J* = 1.7 Hz, 0.33H), 6.49 (d, *J* = 2.4 Hz, 0.66H), 6.40 (dt, *J* = 7.6, 1.7 Hz, 0.33H), 6.26 (dt, *J* = 8.0, 1.7 Hz, 0.66H), 6.06 (d, *J* = 1.5 Hz, 0.33H), 6.02 (d, *J* = 2.1 Hz, 0.66H), 5.35 (dd, *J* = 7.5, 5.6 Hz, 0.33H), 5.14 (dd, *J* = 8.0, 4.7 Hz, 0.66H), 5.01 (dt, *J* = 5.6, 1.6 Hz, 0.33H), 4.63 (dt, *J* = 4.6, 2.3 Hz, 0.66H), 4.36 (d, *J* = 5.0 Hz, 0.66H), 4.34 (s, 1.32H), 1.10 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 137.4, 135.5, 132.7, 132.4, 131.0, 130.1, 130.0, 127.9, 126.1, 123.5, 121.1, 83.4, 81.0, 73.8, 69.1, 67.9, 26.7, 26.7, 19.2 ppm;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{24}H_{27}BrO_4Si$: 509.0862, found 509.0772;
TLC: Rf = 0.25 (Pentane/Ethyl acetate = 4/1).



To a stirred solution of alkyne **20b** (269 mg, 1.17 mmol) and vinyl bromide **23** (860 mg, 1.76 mmol) in DMF/Et_3N (6.0 mL/2.0 mL) was added PPh_3 (60 mg, 0.23 mmol) at room temperature. under N_2. Then Pd_2dba_3 (109 mg, 0.12 mmol) and CuI (11 mg, 0.06 mmol)

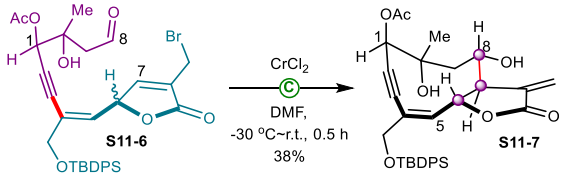
were added to the reaction. The resulted mixture was stirred at the same temperature for 3 hours or till the TLC analysis showed disappearance of starting material. The reaction was quenched by *sat. aq.* NH_4Cl (5.0 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filterred and concentrated *in vacuo*. The residue was purified on silica gel chromatography (CH_2Cl_2/ethyl acetate = 1/1) to provide enyne **S11-5** as mixture of diastereomers as a yellow oil (402 mg, 54%).

Data of **S11-5**: yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (m, 4H), 7.42 (m, 6H), 6.47 (m, 1H), 6.22 (m, 1H), 6.01 (m, 1H), 5.51–5.33 (m, 1H), 5.30–4.97 (m, 1H), 4.77–4.55 (m, 2H), 4.23 (m, 2H), 3.45–3.24 (m, 6H), 2.18–1.98 (m, 4H), 1.96–1.79 (m, 1H), 1.33 (t, 3H), 1.08 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 168.4, 137.9, 137.6, 135.5, 133.4, 133.0, 132.8, 132.8, 132.7, 132.7, 129.9, 129.8, 128.0, 127.8, 126.3, 126.1, 126.0, 126.0, 102.3, 102.1, 102.0, 92.4, 92.4, 84.0, 83.9, 81.6, 80.1, 74.1, 74.1, 72.8, 72.7, 72.7, 70.5, 70.4, 70.2, 69.8, 65.0, 64.7, 64.7, 53.6, 53.5, 53.4, 53.3, 53.2, 53.2, 39.4, 39.4, 39.3, 26.7, 26.7, 23.9, 23.8, 23.7, 20.9, 20.9, 19.2 ppm;
HRMS(ESI) [M + Na]$^+$ calculated for $C_{35}H_{44}O_9Si$: 659.2755, found 659.2652;
TLC: Rf = 0.3 (DCM/Ethyl acetate = 1/1).



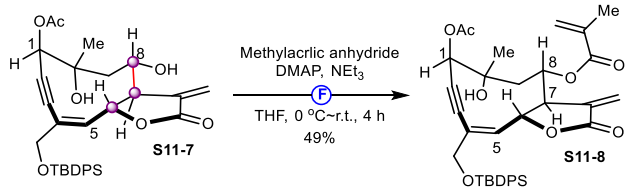
To a solution of **S11-5** (402 mg, 0.63 mmol) in Et_2O (20 mL) at -25 °C, was added dropwise a solution of PBr_3 (1.2 mL, 1M in Et_2O). After 30 minutes, the mixture was quenched with cold H_20 (1 mL) and allowed to warm to room temperature. Then the reaction was extracted with CH_2Cl_2 (50 mL), and the organic layer was dried over Na_2SO_4 and concentrated. The residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 7/3 ~ 3/7) to give a yellow solid corresponding to **S11-6** as a mixture of inseparable 1:1 diasteroisomers (213 mg, yield 52%).

Data of **S11-6**: yellow solid;
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (t, *J* = 3.8 Hz, 1H), 7.71–7.60 (m, 4H), 7.52–7.37 (m, 7H), 7.35 (d, *J* = 1.2 Hz, 1H), 5.96 – 5.81 (m, 2H), 5.48 (d, *J* = 2.6 Hz, 1H), 4.21 (d, *J* = 0.7 Hz, 2H), 4.14 (d, *J* = 0.8 Hz, 2H), 2.70 (ddd, *J* = 29.0, 15.2, 9.3 Hz, 2H), 2.13 (s, 3H), 1.41 (s, 3H), 1.07 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.30, 201.28, 170.98, 170.95, 169.66, 169.64, 150.55, 135.68, 135.66, 135.63, 135.61, 132.85, 132.74, 131.53, 131.51, 130.18, 129.33, 129.32, 128.04, 127.88, 92.58, 92.52, 81.81, 81.79, 79.31, 79.28, 77.41, 77.16, 76.91, 73.45, 70.19, 70.17, 65.17, 50.65, 50.60, 26.91, 24.18, 24.16, 20.98, 20.96, 19.38 ppm;
HRMS(ESI) [M + Na]$^+$ calculated for $C_{33}H_{37}BrO_7Si$: 675.1492, found 675.1390;
TLC: Rf = 0.25 (Pentane/Ethyl acetate = 2/1).



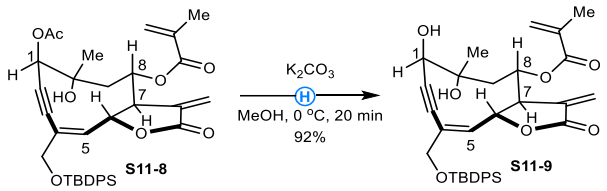
A 10 mL round bottom flask equipped with a magnetic stir bar was charged with bromolactone **S11-6** (213 mg, 0.33 mmol) and DMF (10 mL). The reaction mixture was cooled down to -30 °C and $CrCl_2$ (405 mg, 3.3 mmol) was added. The temperature was allowed to rise to room temperature and stirred for 30 minutes till the TLC analysis showed disappearance of the starting material. Then the reaction was quenched with *sat. aq.* NH_4Cl (50 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried over Na_2SO_4, then filtered and concentrated *in vacuo*. The residue was purified on silica gel chromatography (CH_2Cl_2/Ethyl acetate = 1/1) to provide **S11-7** as a yellow solid (72 mg, 38%).

Data of **S11-7**: yellow solid;
$[\alpha]_D^{20}$ -108 (c 0.25, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 6.5, 5.0 Hz, 4H), 7.48–7.36 (m, 6H), 6.46 (s, 1H), 6.41 (s, 1H), 5.81 (s, 1H), 5.20 (s, 1H), 5.16 (s, 1H), 4.15 (s, 2H), 4.10 (s, 1H), 3.98 (s, 1H), 2.63 (d, *J* = 14.0 Hz, 1H), 2.16–2.09 (m, 4H), 1.42 (s, 3H), 1.07 (s, 9H) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 169.3, 139.2, 135.5, 135.5, 132.8, 132.8, 129.9, 129.9, 127.8, 125.7, 70.8, 70.4, 63.9, 29.7, 26.8, 20.8, 19.2 ppm;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{33}H_{38}O_7Si$: 597.2387, found 597.2284;
TLC: Rf = 0.35 (DCM/Ethyl acetate = 1/1).



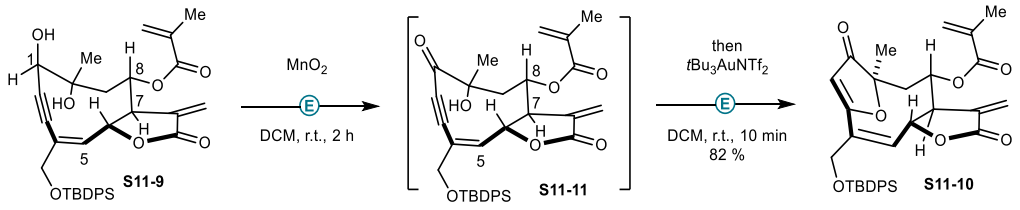
To a solution of **S11-7** (50 mg, 0.087 mmol), methlacrylic anhydride (20 µL, 0.13 mmol) and DMAP (1.0 mg, 9.0 µmol) in CH_2Cl_2 (1.0 mL) at 0 °C, was added dropwise a solution of Et_3N (30 µL, 0.22 mmol) in CH_2Cl_2 (0.5 mL). Mixture allowed to warm at room temperature and after 4 hours, HCl 0.1M (1.0 mL) was added. The whole was extracted with CH_2Cl_2 (2.0 mL × 2), and the combined organic layers were washed with brine (1.0 mL), dried over $MgSO_4$, and purified by silica gel chromatography (pentane/ethyl acetate = 6/4) to give a yellow oil (27.5 mg, yield 49%).
Data of **S11-8**: yellow oil;
$[\alpha]_D^{20}$ -61 (c 0.15, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.64 (m, 4H), 7.45–7.38 (m, 6H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.43 (d, *J* = 2.8 Hz, 1H), 6.04 (s, 1H), 5.86 (s, 1H), 5.84 (d, *J* = 2.3 Hz, 1H), 5.59 (s, 1H), 5.02 (dd, *J* = 5.1, 2.6 Hz, 1H), 4.53 (dd, *J* = 5.1, 2.5 Hz, 1H), 4.20–4.12 (m, 2H), 2.39 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.20 (t, *J* = 8.3 Hz, 4H), 1.91 (s, 3H), 1.39 (s, 3H), 1.09 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 166.2, 138.5, 135.8, 135.5, 134.8, 132.8, 129.9, 127.8, 126.4, 124.0, 122.7, 95.9, 80.4, 74.7, 72.6, 69.4, 64.2, 46.2, 29.6, 26.8, 20.8, 19.2, 18.2 ppm;
Traces of DCM (integration = 0.9), water (integration = 9.51) and grease (integration = 4.28), purity of the compound is 80.7%.

HRMS(ESI) $[M + H]^+$ calculated for $C_{37}H_{42}O_8Si$: 643.2649, found 643.2888;
TLC: Rf = 0.25 (Pentane/Ethyl acetate = 2/1).



To a solution of **S11-8** (27.5 mg, 0.043 mmol) in MeOH (2.0 mL) at 0 °C, was added dropwise a solution of K_2CO_3 (27 µL, 1M in H_20). The mixture was stirred 20 minutes at 0 °C and quenched with a cold mixture of CH_2Cl_2/H_20 (10mL). The reaction was then extracted with CH_2Cl_2 (5.0 mL), and the combined organic layers were washed with brine (5.0 mL), dried over $MgSO_4$, concentrated and purified by PTLC (pentane/ethyl acetate = 1/1) to give propargyl alcohol **S11-9** as a yellow oil (24 mg, yield 92%).

Data of **S11-9**: yellow oil;
$[\alpha]_D^{20}$ -48 (c 0.12, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.9, 1.5 Hz, 4H), 7.47–7.37 (m, 6H), 6.46 (dd, *J* = 6.5, 2.6 Hz, 2H), 6.06 (s, 1H), 5.92 (d, *J* = 9.4 Hz, 1H), 5.86 (d, *J* = 2.5 Hz, 1H), 5.63–5.58 (m, 1H), 4.95 (dd, *J* = 5.6, 2.6 Hz, 1H), 4.43 (td, *J* = 4.6, 2.5 Hz, 1H), 4.26 (s, 1H), 4.23–4.16 (m, 2H), 4.14 (d, *J* = 7.1 Hz, 1H), 2.29 (dd, *J* = 15.0, 3.3 Hz, 1H), 2.19–2.10 (m, 1H), 1.90 (s, 3H), 1.45 (s, 3H), 1.09 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 166.9, 137.7, 135.6, 135.5, 134.6, 132.8, 129.9, 127.8, 126.9, 123.8, 122.6, 98.7, 84.5, 80.3, 75.7, 72.5, 69.6, 64.4, 60.4, 53.4, 46.0, 39.8, 29.0, 26.8, 21.0, 19.2, 18.0, 14.2 ppm;
HRMS(ESI) $[M + H]^+$ calculated for $C_{35}H_{40}O_7Si$: 601.2543, found 601.2622;
TLC: Rf = 0.25 (Pentane/Ethyl acetate = 2/1).

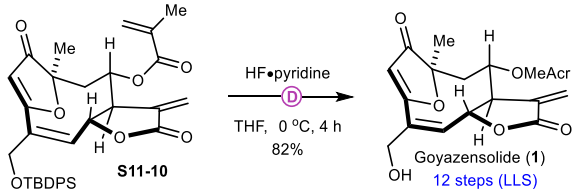


To a stirred solution of **S11-9** (24 mg, 40 µmol) in CH_2Cl_2 (5.0 mL) was added MnO_2 (35 mg, 0.4 mmol) and the solution was stirred at room temperature for 2 hours, till the TLC analysis showed disappearance of the starting material. The reaction was filterred and a trace of *t*Bu_3PAuNTf_2 was added and the solution was stirred for 10 more minutes till the TLC analysis showed disappearance of the starting material. The resulted solution was concentrated *in vacuo* and the residue was purified on silica gel chromatography (Pentane/Ethyl acetate = 3/1) to provide the **S11-10** as a white solid (19 mg, 82%).

Data of **S11-11**: white solid;
$[\alpha]_D^{20}$ -36 (c 0.12, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.62 (m, 4H), 7.51–7.39 (m, 6H), 6.80 (q, *J* = 2.0 Hz, 1H), 6.49 (d, *J* = 3.3 Hz, 1H), 6.09 (s, 1H), 5.84 (t, *J* = 4.5 Hz, 1H), 5.81 (d, *J* = 2.9 Hz, 1H), 5.66–5.59 (m, 1H), 5.28 (dq, *J* = 7.3, 2.5 Hz, 1H), 4.32–4.25 (m, 2H), 4.01 (dt, *J* = 6.0, 2.8 Hz, 1H),

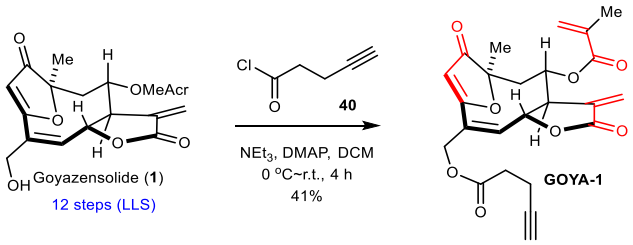
2.51 (dd, *J* = 15.5, 5.7 Hz, 1H), 2.36 (dt, *J* = 6.4, 2.9 Hz, 1H), 1.92 (s, 3H), 1.47 (s, 3H), 1.10 (d, *J* = 6.4 Hz, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 169.0, 167.0, 143.8, 136.1, 135.9, 133.5, 133.0, 130.7, 128.5, 127.7, 125.1, 121.4, 96.0, 94.4, 80.3, 80.2, 71.2, 64.8, 50.9, 44.4, 27.3, 25.6, 19.8, 18.7 ppm;
HRMS(ESI) $[M + H]^+$ calculated for $C_{35}H_{38}O_7Si$: 599.2387, found 599.2465;
TLC: Rf = 0.3 (Pentane/Ethyl acetate = 2/1).

Data of **S11-10**: white solid;
$[\alpha]_D^{20}$ -2 (c 0.1, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.65 (m, 4H), 7.50–7.38 (m, 6H), 6.26 (d, *J* = 3.2 Hz, 1H), 6.14 (d, *J* = 2.9 Hz, 1H), 6.03 (s, 1H), 5.68 (s, 1H), 5.58–5.54 (m, 1H), 5.48 (d, *J* = 2.7 Hz, 1H), 5.30 (td, *J* = 5.0, 2.3 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.40 (dd, *J* = 34.3, 13.9 Hz, 2H), 3.77–3.72 (m, 1H), 2.49 (dd, *J* = 13.8, 11.8 Hz, 1H), 2.32 (d, *J* = 11.9 Hz, 1H), 1.85 (s, 3H), 1.51 (s, 3H), 1.09 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 184.7, 168.7, 166.7, 135.6, 135.5, 135.4, 134.3, 133.9, 133.3, 132.6, 130.1, 127.8, 127.8, 126.4, 124.3, 106.4, 89.6, 81.5, 73.1, 64.1, 50.8, 43.9, 29.6, 26.7, 20.6, 19.2, 17.9 ppm;
HRMS(ESI) $[M + H]^+$ calculated for $C_{35}H_{38}O7Si$: 599.2387, found 599.2450;
TLC: Rf = 0.25 (Pentane/Ethyl acetate = 2/1).



To a solution of **S11-10** (17 mg, 0.029 mmol) in THF (2.0 mL) at 0 °C, was added dropwise a solution of HF·pyridine 70% (85 μL) in THF (1.0 mL). The mixture was stirred 4 hours at 0 °C and quenched with saturated $NaHCO_3$ (2.0 mL). The quenched mixture was then extracted with Et_2O (5.0 mL × 2), and the combined organic layers were washed with brine (5.0 mL), dried over $MgSO_4$, and purified by PTLC (Pentane/Ethyl acetate = 2/8) to give (-)-Goyazensolide (8.5 mg, yield 82%).

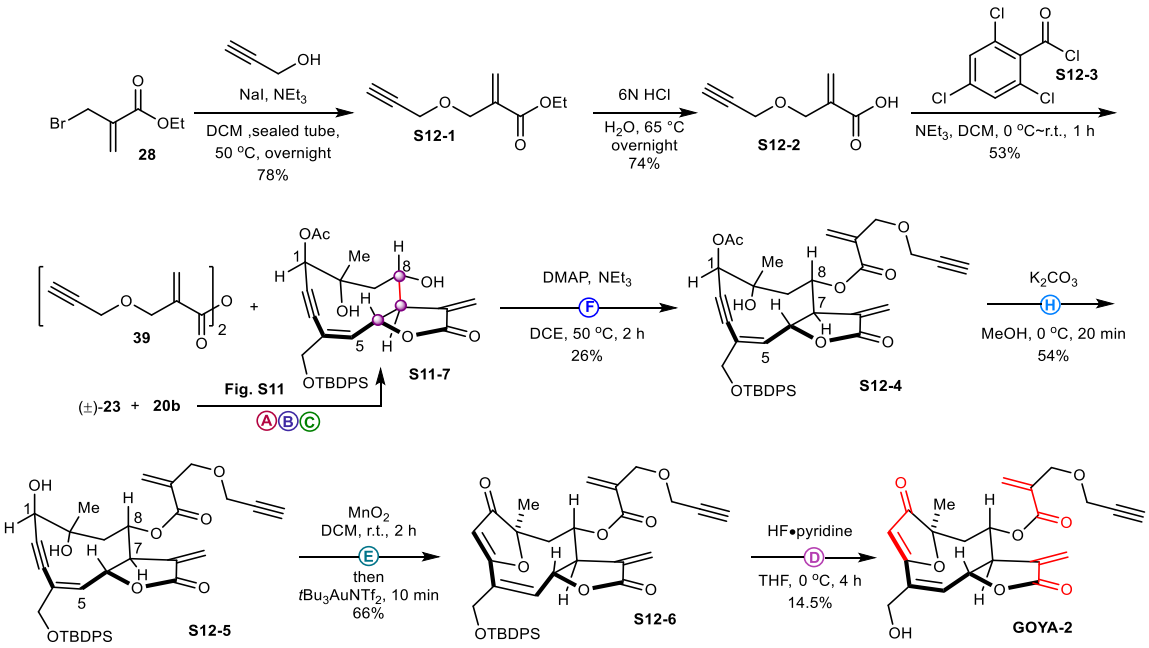
Data of **1**: waxy solid;
$[\alpha]_D^{20}$ -19 (c 0.1, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.30 (dt, *J* = 3.0, 1.5 Hz, 1H), 6.25 (d, *J* = 3.1 Hz, 1H), 6.03 (s, 1H), 5.82 (s, 1H), 5.59–5.54 (m, 1H), 5.49 (d, *J* = 2.7 Hz, 1H), 5.36 (dd, *J* = 4.9, 2.7 Hz, 1H), 4.57 (dt, *J* = 11.7, 2.2 Hz, 1H), 4.42 (dt, *J* = 3.1, 1.7 Hz, 2H), 3.82 (t, *J* = 5.3 Hz, 1H), 2.56–2.48 (m, 1H), 1.85 (s, 3H), 1.56 (s, 3H) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.6, 184.2, 166.8, 135.5, 135.3, 134.2, 133.1, 126.6, 124.6, 106.6, 89.8, 81.5, 73.2, 63.2, 50.9, 43.9, 20.7, 18.0 ppm;
HRMS (ESI) $[M + H]^+$ calculated for $C_{19}H_{20}O_7$: 361.1209, found 361.1392;
TLC: Rf = 0.2 (DCM/Ethyl acetate = 1/2).

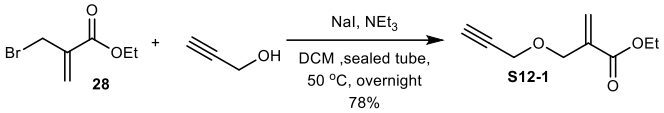


To a solution of **1** (5.0 mg, 14 μmol), pent-4-ynoyl chloride (2.4 mg, 21 μmol) and DMAP (0.17 mg, 0.0014 mmol) in CH_2Cl_2 (0.3 mL) at 0 °C, was added dropwise a solution of Et_3N (6.0 μL, 42 μmol) in CH_2Cl_2 (0.1 mL). The mixture was allowed to warm to room temperature and after 4 hours, HCl (0.1M, 0.2 mL) was added. The solution was then extracted with CH_2Cl_2 (1.0 mL × 2), and the combined organic layers were washed with brine (1.0 mL), dried over $MgSO_4$, and purified by PTLC (Pentane/Ethyl acetate = 1/1) to give a white solid (2.5 mg, yield 41%).

Data of **GOYA-1**: white solid;
$[\alpha]_D^{20}$ -13 (c 0.1, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39–6.34 (m, 1H), 6.26 (d, *J* = 3.1 Hz, 1H), 6.03 (s, 1H), 5.83 (s, 1H), 5.57 (s, 1H), 5.49 (d, *J* = 2.7 Hz, 1H), 5.35 (d, *J* = 1.9 Hz, 1H), 4.86 (s, 2H), 4.60 – 4.51 (m, 1H), 3.80 (d, *J* = 2.5 Hz, 1H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.59–2.49 (m, 3H), 2.34 (dd, *J* = 13.9, 1.9 Hz, 1H), 2.02 (t, *J* = 2.6 Hz, 1H), 1.85 (s, 3H), 1.57 (d, *J* = 7.8 Hz, 3H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 183.0, 170.9, 168.4, 166.8, 138.7, 135.3, 132.9, 129.5, 126.6, 124.7, 106.8, 89.8, 82.0, 81.2, 73.2, 69.5, 63.6, 50.8, 43.9, 33.1, 20.6, 17.9, 14.3 ppm;
HRMS(ESI) $[M + H]^+$ calculated for $C_{24}H_{24}O_8$: 441.1471, found 441.1394;
TLC: Rf = 0.2 (Pentane/Ethyl acetate = 1/1).

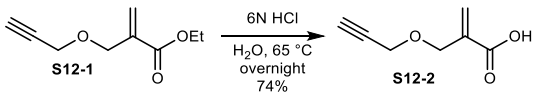
Figure S12. Synthesis of **GOYA-2**.





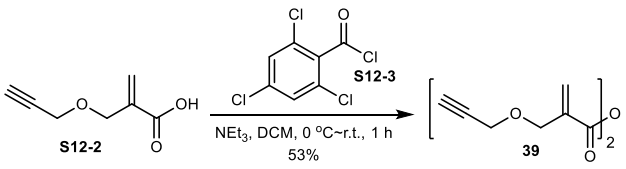
A sealed solution of propargyl alcohol (1.2 g, 21.4 mmol), ethyl 2-(bromomethyl) acrylate **28** (5.8 g, 30 mmol), NaI (320 mg, 2.1 mmol) and Et_3N (12 mL, 85.6 mmol) in CH_2Cl_2 (80 mL) was heated overnight at 50 °C. The mixture was then diluted with CH_2Cl_2 (50 mL) and HCl (0.1M, 100 mL). The aqueous phase was extracted with CH_2Cl_2 (100 mL), and the combined organic layers were washed with brine (200 mL), dried over $MgSO_4$, concentrated and purified by silica gel chromatography (Pentane/Ethyl acetate = 8/2) to give a pale yellow oil (2.8 g, yield 78%).

Data of **S12-1**: pale yellow oil;
^1H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 1H), 5.89 (s, 1H), 4.30 (s, 2H), 4.27 – 4.20 (m, 4H), 2.46 (t, *J* = 2.4 Hz, 1H), 1.31 (d, *J* = 7.1 Hz, 3H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 136.7, 126.2, 79.3, 74.7, 67.9, 60.7, 57.8, 14.1 ppm;
TLC: Rf = 0.4 (Pentane/Ethyl acetate = 4/1).



A solution of **S12-1** (500 mg, 2.98 mmol) in 6N HCl (5.0 mL) was heated at 65 °C overnight. The mixture was then diluted with H_20 (20 mL) and CH_2Cl_2 (20 mL). The solution was then extracted with CH_2Cl_2 (10 mL × 2), and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated to give crude acid **S12-2** as a brownish solid (308 mg, yield 74%).

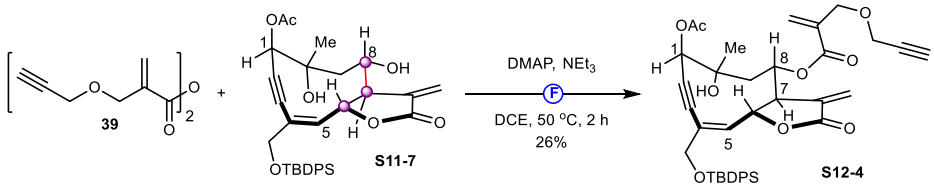
Data of **S12-2**: brownish solid;
^1H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 1H), 6.04 (s, 1H), 4.31 (s, 2H), 4.24 (s, 2H), 2.48 (s, 1H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 135.9, 129.0, 79.2, 74.9, 67.4, 57.9 ppm;
TLC: Rf = 0.3 (Pentane/Ethyl acetate/AcOH = 1/1/0.01).



To a solution of **S12-2** (308 mg, 2.2 mmol) and Et_3N (608 μL, 4.4 mmol) in CH_2Cl_2 (6.0 mL) at 0 °C, was added dropwise a solution of acyl chloride **S12-3** (644 mg, 2.64 mmol) in CH_2Cl_2 (2.0 mL). The mixture was then allowed to warm to room temperature and after 30 minutes, HCl (0.1M, 5.0 mL) was added. The solution was then extracted with CH_2Cl_2 (5.0 mL × 2) and the combined organic layers were washed with brine (5.0 mL), dried

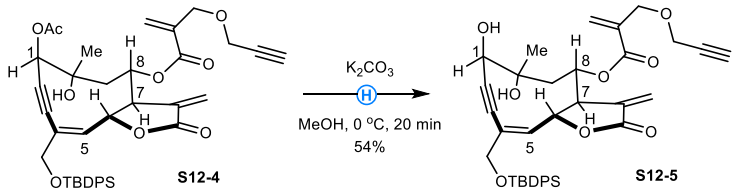
over $MgSO_4$, and purified by Isolera Biotage using SNAP Cartridge KP-C18-HS 12 g column (Water/acetonitrile 9/1 to 1/1) to give a yellow oil (153 mg, yield 53%).

Data of **39**: yellow oil, compound unstable on silica gel;
^1H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 1H), 6.19 (s, 1H), 4.35 (s, 2H), 4.26 (s, 2H), 2.48 (s, 1H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 136.0, 130.3, 75.1, 67.2, 65.8, 58.0 ppm;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{14}H_{14}O_5$: 285.0841, found 285.0836.



To a solution of **S11-7** (50 mg, 0.087 mmol), **39** (103 mg, 0.39 mmol) in DCE (1.0 mL) at 50 °C, was added dropwise a solution of DMAP (46 mg, 0.38 mmol) in CH_2Cl_2 (0.3 mL). The mixture was stirred 2 hours and then allowed to cool at room temperature. HCl (0.1M, 1.0 mL) was added and the mixture was extracted with CH_2Cl_2 (5.0 mL × 2), the combined organic layers were washed with brine (5.0 mL), dried over $MgSO_4$, the solvent was evaporated *in vacuo* and the serulting residue was purified by silica gel chromatography (Pentane/Ethyl acetate = 7/3) to give **S12-4** as a yellow oil (16 mg, yield 26%).

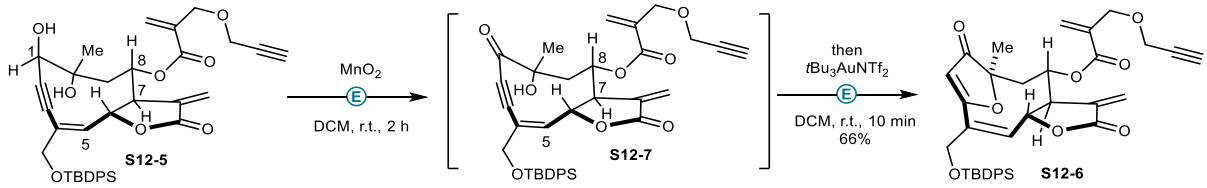
Data of **S12-4**: yellow oil;
$[\alpha]_D^{20}$ -57 (c 0.1, $CHCl_3$);
^1H NMR (400 MHz, $CDCl_3$) δ 7.66–7.62 (m, 4H), 7.46–7.38 (m, 6H), 6.47 (dd, *J* = 3.3, 2.0 Hz, 2H), 6.42 (d, *J* = 2.3 Hz, 1H), 6.04 (d, *J* = 1.4 Hz, 1H), 5.90 (d, *J* = 1.2 Hz, 1H), 5.64 (s, 1H), 5.19 (s, 1H), 5.09 (s, 1H), 4.49 (d, *J* = 2.1 Hz, 1H), 4.36–4.30 (m, 2H), 4.25 (d, *J* = 2.4 Hz, 2H), 4.21 (dd, *J* = 5.0, 2.4 Hz, 2H), 2.49 (m, *J* = 3.5 Hz, 2H), 2.17 (m, 4H), 1.36 (s, 3H), 1.08 (s, 9H) ppm;
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 168.4, 164.3, 138.7, 135.9, 135.5, 134.8, 132.8, 129.9, 128.8, 127.8, 127.7, 79.1, 78.9, 75.2, 74.9, 74.7, 72.8, 69.8, 68.2, 67.6, 64.0, 57.9, 57.7, 30.0, 29.7, 20.8, 19.2 ppm;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{40}H_{44}O_9Si$: 719.2755, found 719.2653;
TLC: Rf = 0.3 (Pentane/Ethyl acetate = 2/1).



To a solution of **S12-4** (8.0 mg, 11 μmol) in MeOH (1.0 mL) at 0 °C, was added dropwise a solution of K_2CO_3 (0.6 μL, 1M in H_20). The reaction was stirred for 20 minutes at 0 °C

and quenched with a cold mixture of CH_2Cl_2/H_20 (1 mL/1mL). The solution was then extracted with CH_2Cl_2 (2.0 mL) and the combined organic layers were washed with brine (1.0 mL) dried over $MgSO_4$, concentrated and purified by PTLC (Pentane/Ethyl acetate = 1/1) to give propargyl alcohol **S12-5** as a pale-yellow oil (4.1 mg, yield 54%).

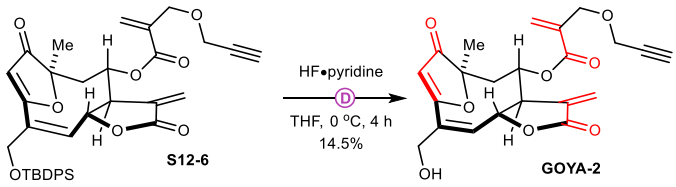
Data of **S12-5**: pale-yellow oil;
$[\alpha]_D^{20}$ -51 (c 0.2, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 6.6, 1.3 Hz, 4H), 7.48–7.39 (m, 6H), 6.43 (d, *J* = 2.5 Hz, 2H), 6.33 (s, 1H), 5.92 (d, *J* = 1.1 Hz, 1H), 5.84 (d, *J* = 2.1 Hz, 1H), 5.77 (s, 1H), 5.02 (d, *J* = 2.1 Hz, 1H), 4.42 (s, 1H), 4.28 (s, 1H), 4.24 (s, 1H), 4.22–4.20 (m, 2H), 4.19 (d, *J* = 1.8 Hz, 1H), 4.17 (d, *J* = 2.3 Hz, 1H), 4.14 (d, *J* = 7.1 Hz, 1H), 2.49 (t, *J* = 2.3 Hz, 1H), 2.40 (d, *J* = 13.1 Hz, 1H), 2.15 (dd, *J* = 14.5, 10.5 Hz, 1H), 1.43 (s, 3H), 1.08 (s, 9H) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 170.9, 169.4, 165.0, 137.9, 135.8, 135.5, 134.7, 132.8, 129.9, 129.3, 127.8, 124.4, 123.1, 79.8, 78.9, 75.7, 75.2, 72.7, 69.8, 68.0, 64.3, 60.4, 57.77, 53.4, 46.4, 31.9, 29.7, 29.3, 26.8, 22.7, 21.0, 19.2, 14.2, 14.2, 14.1 ppm;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{38}H_{42}O_8Si$: 677.2649, found 677.2546;
TLC: Rf = 0.3 (Pentane/Ethyl acetate = 1/1).



To a stirred solution of **S12-5** (4.1 mg, 6.26 μmol) in CH_2Cl_2 (1.0 mL) was added MnO_2 (5.0 mg, 63 μmol) and the solution was stirred at room temperature for 2 hours, till the TLC analysis showed disappearance of the starting material. The reaction was filterred and a trace of *t*Bu_3PAuNTf_2 was added to the CH_2Cl_2 solution and the mixture stirred for 10 more minutes till the TLC analysis showed disappearance of the starting material. The resulted reaction was then concentrated *in vacuo*, and the residue optained was purified on a PTLC (Pentane/Ethyl acetate = 3/1) to provide **S12-6** as a white solid (2.7 mg, 66%).

Data of **S12-7**: white solid;
$[\alpha]_D^{20}$ -56 (c 0.1, $CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (ddd, *J* = 8.0, 2.5, 1.4 Hz, 4H), 7.50–7.39 (m, 6H), 6.78 (d, *J* = 2.3 Hz, 1H), 6.49 (d, *J* = 3.2 Hz, 1H), 6.32 (d, *J* = 0.9 Hz, 1H), 5.96 (d, *J* = 1.3 Hz, 1H), 5.82 (d, *J* = 2.8 Hz, 2H), 5.27 (dd, *J* = 6.6, 2.6 Hz, 1H), 4.28 (dd, *J* = 4.0, 2.1 Hz, 2H), 4.24 (d, *J* = 1.0 Hz, 2H), 4.23–4.19 (m, 2H), 4.03 (d, *J* = 5.1 Hz, 1H), 2.50 (dt, *J* = 4.7, 4.1 Hz, 2H), 2.42 – 2.37 (m, 1H), 1.47 (s, 3H), 1.10 (s, 9H) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 189.2, 168.3, 164.8, 143.2, 135.8, 135.5, 132.9, 132.4, 130.1, 128.7, 127.9, 124.7, 120.9, 95.3, 94.0, 79.0, 75.1, 70.9, 67.7, 64.1, 60.4, 57.8, 53.4, 50.1, 31.9, 29.7, 26.8, 25.2, 22.7, 21.0, 19.2, 14.1 ppm;
HRMS(ESI) $[M + Na]^+$ calculated for $C_{38}H_{44}O_8Si$: 675.2492, found 675.2390;
TLC: Rf = 0.35 (Pentane/Ethyl acetate = 2/1).

Data of **S12-6**: white solid;
$[\alpha]_D^{20}$ -11 (c 0.1, $CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$) δ 7.68–7.65 (m, 4H), 7.44–7.39 (m, 6H), 6.26 (dd, *J* = 3.7, 2.2 Hz, 2H), 6.15–6.12 (m, 1H), 5.91 (d, *J* = 1.3 Hz, 1H), 5.68 (s, 1H), 5.50 (d, *J* = 2.7 Hz, 1H), 5.28 (d, *J* = 2.3 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 4.46–4.33 (m, 2H), 4.18 (d, *J* = 2.6 Hz, 2H), 4.14 (d, *J* = 7.2 Hz, 2H), 3.75 (d, *J* = 2.6 Hz, 1H), 2.54–2.46 (m, 2H), 2.36–2.31 (m, 1H), 1.52 (s, 3H), 1.09 (s, 9H) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 204.5, 168.6, 135.7, 135.6, 135.5, 134.3, 133.9, 132.6, 130.1, 127.9, 127.8, 124.7, 106.4, 89.5, 81.5, 74.9, 73.5, 67.4, 64.1, 60.4, 57.8, 50.8, 43.9, 31.9, 29.7, 29.3, 26.8, 22.7, 20.6, 19.2, 14.1 ppm;
HRMS(ESI) $[M + H]^+$ calculated for $C_{38}H_{40}O_8Si$: 653.2492, found 653.2570;
TLC: Rf = 0.3 (Pentane/Ethyl acetate = 2/1).



To a solution of **S12-6** (2.3 mg, 3.5 μmol) in THF (1.0 mL) at 0 °C, was added dropwise a solution of hydrogen fluoride pyridine (hydrogen fluoride ~70%, 10 μL) in THF (0.2 mL). The mixture was stirred 4 hours at 0 °C and quenched with saturated $NaHCO_3$ (0.5 mL). The mixture was then extracted with Et_2O (2.0 mL × 2), and the combined organic layers were washed with brine (1.0 mL), dried over $MgSO_4$, and purified by PTLC (Pentane/Ethyl acetate = 2/8) to give **GOYA-2** (0.21 mg, yield 14.5%) as a waxy solid.

Data of **GOYA-2**: waxy solid;
$[\alpha]_D^{20}$ -14 (c 0.1, $CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$) δ 6.30 (s, 1H), 6.23 (s, 2H), 5.91 (s, 1H), 5.82 (s, 1H), 5.51 (s, 1H), 5.35 (s, 1H), 4.63–4.40 (m, 3H), 4.24–4.12 (m, 4H), 3.83 (d, *J* = 2.4 Hz, 1H), 2.58–2.48 (m, 1H), 2.47 (t, *J* = 2.3 Hz, 1H), 2.37 (dd, *J* = 15.7, 8.7 Hz, 1H), 1.32 (s, 9H) ppm;
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 184.1, 135.6, 132.8, 127.9, 124.9, 106.6, 89.6, 81.0, 75.0, 73.4, 63.1, 57.6, 50.8, 43.2, 31.8, 29.3, 22.7, 20.6, 13.9 ppm; Traces of water (integration = 135.65) and grease (integration = 75.65). Purity 19%. DMSO stock solutions have been prepared by weighting residues after high vacuum evaporation.
HRMS(ESI) $[M + H]^+$ calculated for $C_{22}H_{22}O_8$: 414.1315, found 415.1394;
TLC: Rf = 0.25 (CH_2Cl_2/Ethyl acetate = 1/1).

h) Experimental procedures for Figure 2

General information

Biological materials. All materials were purchased from Sigma Aldrich unless otherwise stated. DMEM/High glucose medium, F12-K media, phosphate buffered saline (PBS), MEM Non-Essential Amino Acids, Penicillin-Streptomycin (Pen/Strep) and Trypsin-EDTA were obtained from Life Technologies. Protein concentration was determined using a Q-Bit assay. HeLa cell line (Adenocarcinoma), PC3 cell line (Prostate; derived from metastatic site: bone), HT29 cell line (Colorectal adenocarcinoma), U2OS cell line (Metastatic: lung, other bones), SW620 cell line (Colorectal adenocarcinoma) obtained from ATCC. IPO5 (Sigma-Aldrich, HPA056548) antibody was purchased from Sigma Aldrich. Phospho-AKT (Ser 473) antibody was purchased from Cell signaling. Karyopherin β1, Karyopherin β2, IPO7, IPO8 and IPO12 antibodies were purchased from Santa Cruz biotechnology. UBA1, ACLY, RASAL2, β-actin, anti-rabbit and anti-rabbit Alexa Fluor 488 antibodies were purchased from ABCAM. Images were obtained by image stacking (Confocal microscope Zeiss LSM800). Fluorescence measured with ImageJ software.

Cell culture and preparation of lysates. HeLa, PC3, HT29, U2OS and SW620 cells were maintained in their corresponding media supplemented with 10% (v/v) fetal calf serum (FCS) and Penicillin-Streptomycin 1% (v/v). Cells were grown at 37 °C under 5% CO_2 atmosphere in a humidified incubator. Cells were allowed to grow to confluence and harvested by scraping, centrifuged at 4 °C and resuspended in PBS. Cells were then lysed by sonication in lysis buffer and protein concentration was determined using a Q-Bit assay.

Pull-down experiments. PC3 cells were seeded (350,000 cells/mL) on 10 cm dishes and grown to confluence for 2 days. The cells were harvested and lysates (3 mg/mL, 100 µL each) were prepared as described above. Lysates were treated with DMSO (1 µL) or goyazensolide 10 µM (1 mM, 1 µL) for 30 minutes and then incubated with **GOYA-2** 10 µM (1 mM, 1 µL) for 30 minutes. Click reaction was achieved by addition of **desthiobiotinylated Cy3-N_3** (20 µM, 50X stock in DMSO, **Figure S13** for synthesis), TCEP (1 mM, 50X fresh stock in H_20), TBTA (100 µM, 16X stock in DMSO: *t*Butanol = 1:4), copper (II) sulfate (1 mM, 50X stock in H_20) and incubated for 1 hour at room temperature in the dark. Proteins were precipitated by adding 450 µL of cold MeOH, 117 µL of cold $CHCl_3$ and 350 µL of cold H_20, vortexed and centrifuged for 5 minutes at 14000 g (4 °C). The protein layer was isolated, dried and solubilized in 100 µL of 0.2% SDS in PBS via sonication. Tubes were centrifuged at 4,700 g for 5 minutes, and soluble fractions were transferred to new tubes. Streptavidin agarose beads (25 µL) were added and incubated for 2 hours. Supernatant was discarded and the beads were washed three times with PBS (100 µL). Then 10 µL of 2% SDS and 5 µL of Laemmli buffer were added to the beads and heated 5 minutes at 95°C. Proteins were separated using a 10% SDS-PAGE gel. Gels were visualized at 625 nm using a fluorescence scanner.

In-Gel tryptic digestion. The bands cutted from the SDS-PAGE were cut in smaller pieces and washed twice with a mixture of 50% NH_4HCO_3 50 mM in CH_3CN, twice with 200 µL CH_3CN, then twice again with 200 µL NH_4HCO_3 100 mM and finally twice with 200 µL

CH_3CN. The gel fragments were incubated then for 30 minutes at 37 °C with 30 µL of DTT 10mM in H_20, followed by 30 minutes with 30 µL iodoacetamide 30 mM in H_20. Gel pieces were washed again twice with CH_3CN, followed by NH_4HCO_3 100 mM and finally twice with CH_3CN. Then, the in-gel digestion started with 30 µL of a mixture of Trypsin + Glu-C + Chymotrypsin (1.0 µg each in 500 µL of NH_4HCO_3 50 mM) at 37 °C for 18 hours. 50 µL of NH_4HCO_3 50 mM were added to the digested mixture and incubate for 10 minutes at room temperature. The supernatant was removed and place into a microtube and the remaining gel fragments were incubated for 10minutes with 50 µL of extraction *buffer 1* (20% CH_3CN, 80% H_20, 1% formic acid). The supernatant was then collected and the fragments incubate for another 10 minutes with 50 µL of extraction *buffer 2* (95% CH_3CN, 5% H_20, 1% formic acid). The combined supernatants were lyophilized and summited to MS/MS analysis.

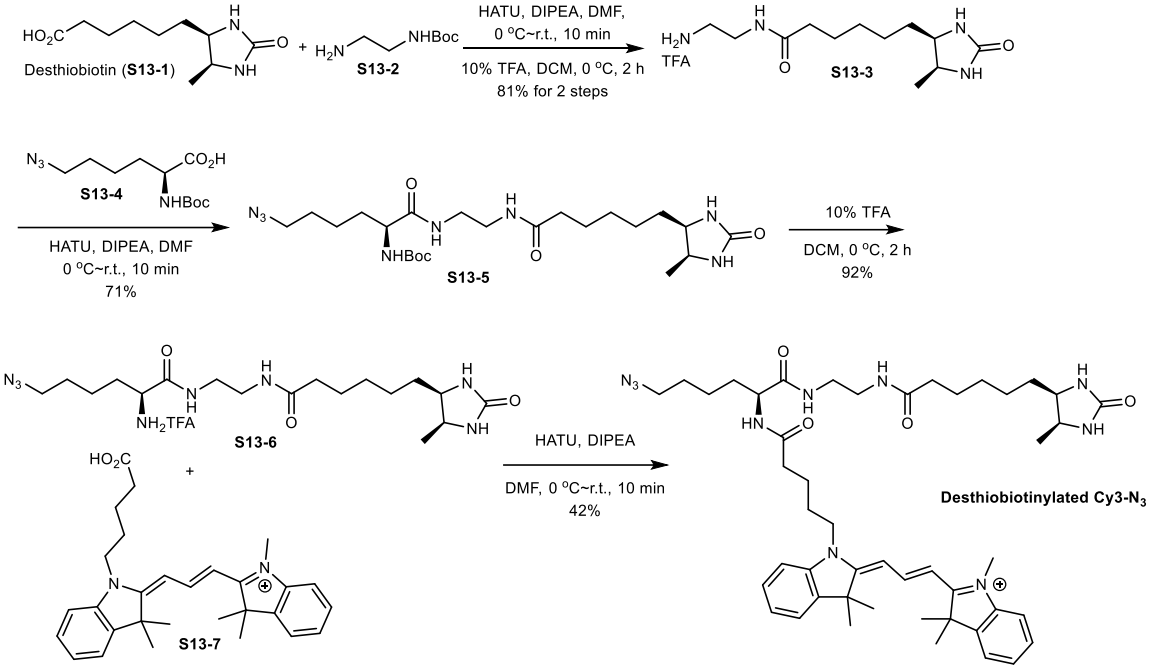
LC-MS/MS analysis. Peptides were resuspended in water with 2% MeCN, 0.1% formic acid (FA) and analyzed using an EASY-nLC 1000 nano-UHPLC coupled to an Orbitrap Fusion mass spectrometer (Thermo Scientific). Chromatography was performed on a 50 cm EASY-spray column (75µm i.d.), LC solvents were 0.1% formic acid in H_2O (Buffer A) and 0.1% FA in MeCN (Buffer B), peptides were eluted into the mass spectrometer at a flow rate of 300 nL/min over a 30 minutes linear gradient (5-35% Buffer B) at 45 °C, data was acquired in a data-dependent mode, MS scans were acquired at 120000 resolution with an AGC-target of 20000 and 118 ms fill-time, and MS/MS-scans using HCD, CID and EThcD fragmentation were acquired in the Orbitrap on each selected precursor using an AGC-target of 20000 and a fill time of 200 ms.

Mass spectrometry analysis. MS data were analyzed using ProteomeDiscoverer 2.0 software (Thermo Scientific) and MSMS-spectra were grouped according by fragmentation technique and searched against the homo sapiens Uniprot database using the Sequest and MS-Amanda algorithms. Search against b- and y-ions was specified for HCD and CID spectra and against c- and z-ions for EThcD spectra. A search tolerance of 10 ppm was applied for the precursor and 0.05 Da for fragmen-ions. Oxidation of methionine and modification of cysteines by carbamidomethylation or by Goyazensolide or thiolated Goyazensolide were allowed as variable modifications.

Safety Statement

No unexpected or unusually high safety hazards were encountered.

Figure S13. Synthesis of Desthiobiotinylated Cy3-N_3.



To a solution of desthiobiotin **S13-1** (100 mg, 0.46 mmol), N-Boc-ethylenediamine **S13-2** (90 mg, 0.56 mmol), HATU (213 mg, 0.56 mmol) in DMF (4.0 mL) was added Et_3N (190 µL, 1.38 mmol) at 0 °C. The mixture was allowed to warm to room temperature stirred 10 more minutes, and then diluted with ethyl acetate (20 mL) and HCl 0.1N (10 mL). The solutions was extracted with ethyl acetate (10 mL × 3) and the combined organic layers were washed with brine (20 mL) dried over $MgSO_4$, concentrated and purified by silica-gel chromatography (CH_2Cl_2/ ethyl acetate = 8/2) to give the amide as a pale-yellow oil. The crude product was dissolved in dichloromethane (3.0 mL) and cooled down to 0 °C. Trifluoro acetic acid (0.3 mL) was added to the solution and the reaction was carried out for 2 hours at 0 °C. The solvents were evaporated to give **S13-3** as a yellow oil (137 mg, yield 81%).

To a solution of deprotected amine **S13-3** (137 mg, 0.37 mmol), (S)-6-azido-2-(tert-butoxycarbonylamino) hexanoic acid **S13-4** (121 mg, 0.44 mmol), HATU (167 mg, 0.44 mmol) in DMF (4.0 mL) was added Et_3N (153 µL, 1.11 mmol) at 0 °C. The mixture was allowed to warm to room temperature, stirred for 10 more minutes, and then was diluted with ethyl acetate (20 mL) and HCl 0.1N (10 mL). The solution was extracted with ethyl acetate (10 mL × 3), and the combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, concentrated and purified by silica-gel chromatography (CH_2Cl_2/ethyl acetate = 7/3) to give the amide **S13-5** as a pale-yellow oil (188 mg, yield 71%).

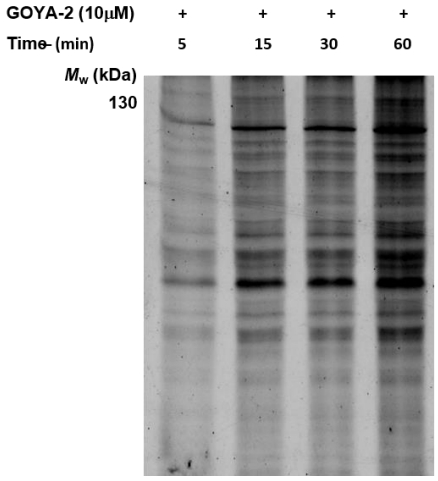
HRMS(ESI) $[M + Na]^+$ calculated for $C_{23}H_{42}O_8N_5$: 511.3278, found 511.3366.

S13-5 (188 mg, 0.37 mmol) was dissolved in dichloromethane (3.0 mL) and cooled down to 0 °C. Trifluoro acetic acid (0.3 mL) was added to the solution and the reaction was carried out for 2 hours at 0 °C. The solvents were evaporated to give a yellow oil **S13-6** (178 mg, yield 92%).

To a solution of **S13-6** (178 mg, 0.34 mmol), Cy3 **S13-7** (194 mg, 0.34 mmol), HATU (155 mg, 0.41 mmol) in DMF (5.0 mL) was added Et_3N (141 µL, 1.02 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred 10 minutes. The mixture directly purified by reverse chromatography (H_20/acetonitrile 8/2) followed by lyophilization to give **Desthiobiotinylated Cy3-N_3** as a pink powder (135 mg, yield 42%).

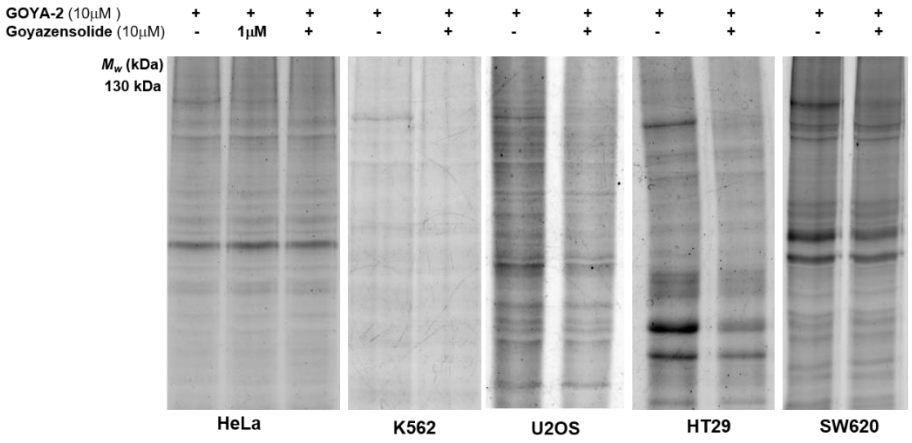
HRMS(ESI) $[M + H]^+$ calculated for $C_{47}H_{67}N_{10}O_4$: 835.5341, found 835.5364.

Figure S14. Competition experiment with **GOYA-2** with different incubation time.



SW620 cell lysate was labeled with 10 µM of **GOYA-2** in different incubation time followed by CuAAC reaction with **Cy3-N_3**. The labeling experiment shows optimal conditions with 30 min of incubation.

Figure S15. Competition experiments with **GOYA-2** with different cell lines.



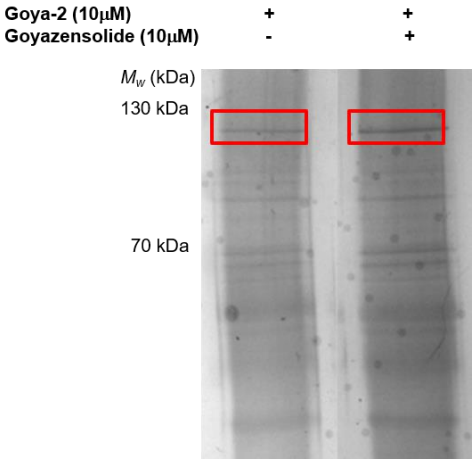
The cell lysates were preincubate for 30 min with the indicated concentration of goyazensolide and then labelled with 10 µM of **GOYA-2** followed by CuAAC reaction with **Cy3-N_3**. The labelling/competition experiment showed the target is not cell-line specific. **Cy3-N_3** = Cyanine3-azide.

Table S17. Full protein list.

	Description	Coverage	Unique Peptides	MW [kDa]
1	**Importin-5 OS=Homo sapiens GN=IPO5 PE=1 SV=4**	**40.65634**	**63**	**123.55**
2	**Pyruvate carboxylase, mitochondrial OS=Homo sapiens GN=PC PE=1 SV=2**	**32.85229**	**52**	**129.55**
3	Heterogeneous nuclear ribonucleoprotein U OS=Homo sapiens GN=HNRNPU PE=1 SV=6	28.84848	33	90.528
4	Acetyl-CoA carboxylase 1 OS=Homo sapiens GN=ACACA PE=1 SV=2	10.99744	27	265.39
5	Keratin, type II cytoskeletal 1 OS=Homo sapiens GN=KRT1 PE=1 SV=6	36.3354	26	65.999
6	**Ubiquitin-like modifier-activating enzyme 1 OS=Homo sapiens GN=UBA1 PE=1 SV=3**	**17.76938**	**19**	**117.77**
7	Alanine--tRNA ligase, cytoplasmic OS=Homo sapiens GN=AARS PE=1 SV=2	17.56198	19	106.74
8	**ATP-citrate synthase OS=Homo sapiens GN=ACLY PE=1 SV=3**	**13.44233**	**18**	**120.76**
9	Keratin, type I cytoskeletal 10 OS=Homo sapiens GN=KRT10 PE=1 SV=6	28.42466	16	58.792
10	Keratin, type I cytoskeletal 9 OS=Homo sapiens GN=KRT9 PE=1 SV=3	28.73194	15	62.027
11	Importin-7 OS=Homo sapiens GN=IPO7 PE=1 SV=1	11.75337	11	119.44
12	iRT Kit Fusion	89.55224	10	14.157
13	Ran-binding protein 6 OS=Homo sapiens GN=RANBP6 PE=1 SV=2	6.244344	10	124.63
14	Matrin-3 OS=Homo sapiens GN=MATR3 PE=1 SV=2	10.27155	9	94.565
15	Heterogeneous nuclear ribonucleoprotein U-like protein 2 OS=Homo sapiens GN=HNRNPUL2 PE=1 SV=1	9.638554	9	85.052
16	Keratin, type II cytoskeletal 2 epidermal OS=Homo sapiens GN=KRT2 PE=1 SV=2	19.40532	8	65.393
17	Heat shock protein 105 kDa OS=Homo sapiens GN=HSPH1 PE=1 SV=1	9.440559	8	96.804
18	Keratin, type II cytoskeletal 5 OS=Homo sapiens GN=KRT5 PE=1 SV=3	18.30508	8	62.34
19	Transcription intermediary factor 1-beta OS=Homo sapiens GN=TRIM28 PE=1 SV=5	8.263473	8	88.493
20	Fatty acid synthase OS=Homo sapiens GN=FASN PE=1 SV=3	3.345281	8	273.25
21	Heat shock 70 kDa protein 4 OS=Homo sapiens GN=HSPA4 PE=1 SV=4	8.452381	8	94.271
22	Trifunctional purine biosynthetic protein adenosine-3 OS=Homo sapiens GN=GART PE=1 SV=1	7.425743	8	107.7
23	Putative elongation factor 1-alpha-like 3 OS=Homo sapiens GN=EEF1A1P5 PE=5 SV=1	17.74892	8	50.153
24	Elongation factor 1-alpha 1 OS=Homo sapiens GN=EEF1A1 PE=1 SV=1	17.74892	8	50.109
25	Acetyl-CoA carboxylase 2 OS=Homo sapiens GN=ACACB PE=1 SV=3	3.091945	7	276.37
26	Protein transport protein Sec24C OS=Homo sapiens GN=SEC24C PE=1 SV=3	5.758684	6	118.25
27	Eukaryotic translation initiation factor 3 subunit C-like protein OS=Homo sapiens GN=EIF3CL PE=3 SV=1	5.36105	6	105.41
28	Eukaryotic translation initiation factor 3 subunit C OS=Homo sapiens GN=EIF3C PE=1 SV=1	5.366922	6	105.28

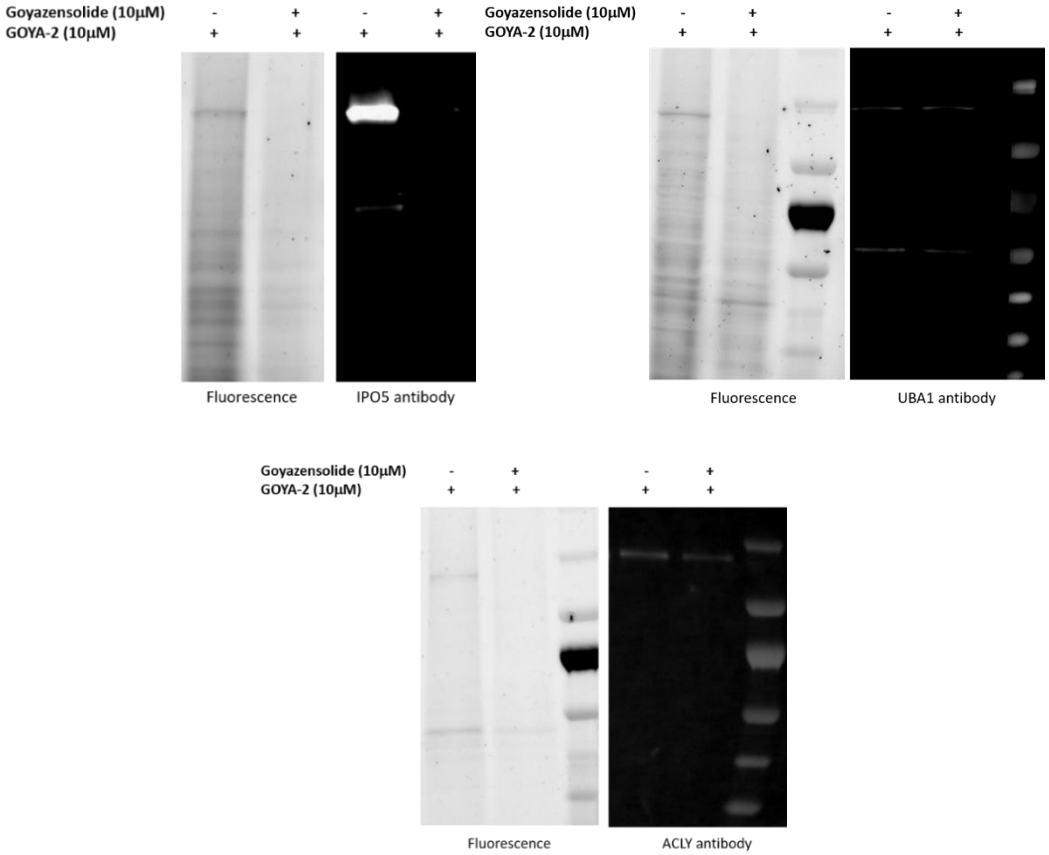
29	Keratin, type II cytoskeletal 6B OS=Homo sapiens GN=KRT6B PE=1 SV=5	13.65248	5	60.03
30	Keratin, type II cytoskeletal 6C OS=Homo sapiens GN=KRT6C PE=1 SV=3	13.47518	5	59.988
31	Keratin, type II cytoskeletal 6A OS=Homo sapiens GN=KRT6A PE=1 SV=3	13.47518	5	60.008
32	Unconventional myosin-Ib OS=Homo sapiens GN=MYO1B PE=1 SV=3	3.961268	5	131.9
33	Elongation factor 1-alpha 2 OS=Homo sapiens GN=EEF1A2 PE=1 SV=1	9.50324	5	50.438
34	Chymotrypsinogen B2 OS=Homo sapiens GN=CTRB2 PE=2 SV=2	10.64639	4	27.905
35	Chymotrypsinogen B OS=Homo sapiens GN=CTRB1 PE=2 SV=1	10.64639	4	27.852
36	116 kDa U5 small nuclear ribonucleoprotein component OS=Homo sapiens GN=EFTUD2 PE=1 SV=1	4.835391	4	109.37
37	Heat shock protein HSP 90-beta OS=Homo sapiens GN=HSP90AB1 PE=1 SV=4	5.662983	4	83.212
38	Staphylococcal nuclease domain-containing protein 1 OS=Homo sapiens GN=SND1 PE=1 SV=1	4.395604	4	101.93
39	Phosphorylase b kinase regulatory subunit beta OS=Homo sapiens GN=PHKB PE=1 SV=3	3.385178	4	124.81
40	Tubulin alpha-1C chain OS=Homo sapiens GN=TUBA1C PE=1 SV=1	9.35412	4	49.863
41	Tubulin alpha-1B chain OS=Homo sapiens GN=TUBA1B PE=1 SV=1	9.312639	4	50.12
42	Tubulin alpha-1A chain OS=Homo sapiens GN=TUBA1A PE=1 SV=1	9.312639	4	50.104
43	Keratin, type I cytoskeletal 14 OS=Homo sapiens GN=KRT14 PE=1 SV=4	13.55932	3	51.529
44	Keratin, type II cytoskeletal 2 oral OS=Homo sapiens GN=KRT76 PE=1 SV=2	6.269592	3	65.8
45	Heat shock protein HSP 90-alpha A2 OS=Homo sapiens GN=HSP90AA2P PE=1 SV=2	8.746356	3	39.34
46	Heat shock protein HSP 90-alpha OS=Homo sapiens GN=HSP90AA1 PE=1 SV=5	4.098361	3	84.607
47	Ubiquitin-like modifier-activating enzyme 6 OS=Homo sapiens GN=UBA6 PE=1 SV=1	2.471483	3	117.9
48	Trypsin-3 OS=Homo sapiens GN=PRSS3 PE=1 SV=2	8.552632	3	32.508
49	Tubulin alpha-3E chain OS=Homo sapiens GN=TUBA3E PE=1 SV=2	5.777778	3	49.827
50	Tubulin alpha-3C/D chain OS=Homo sapiens GN=TUBA3C PE=1 SV=3	5.777778	3	49.928
51	Actin, cytoplasmic 2 OS=Homo sapiens GN=ACTG1 PE=1 SV=1	8.266667	3	41.766
52	Actin, cytoplasmic 1 OS=Homo sapiens GN=ACTB PE=1 SV=1	8.266667	3	41.71
53	Asparagine synthetase [glutamine-hydrolyzing] OS=Homo sapiens GN=ASNS PE=1 SV=4	5.525847	3	64.329
54	Drebrin OS=Homo sapiens GN=DBN1 PE=1 SV=4	5.701079	3	71.385
55	Filamin-A OS=Homo sapiens GN=FLNA PE=1 SV=4	1.511145	3	280.56

Figure S16. Pyruvate carboxylase as non-competed target.



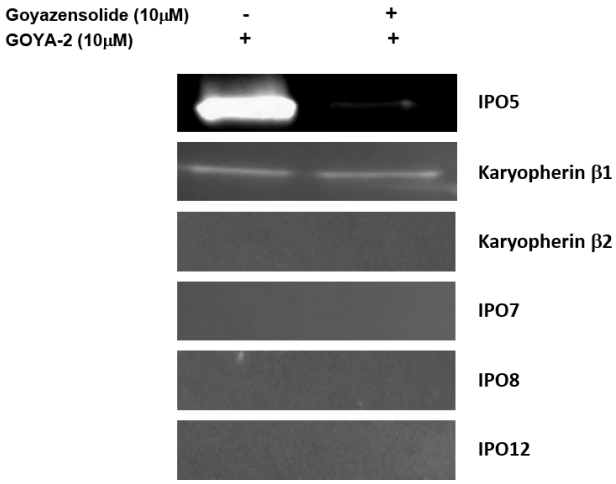
Treatment of PC3 cell lysate with DMSO or 10 μM goyazensolide for 30 min followed by treatment with **GOYA-2** (10 μM, 30 min). CuAAC reaction with the biotinylated fluorophore and streptavidin enrichment, SDS-PAGE followed by silver staining. gave a band that was not eliminated upon competition with 10 μM goyazensolide. MS analysis from tryptic in-gel digests of these bands yielded Pyruvate Carboxylase (red rectangle).

Full gel of Figure 2d. Immunoblot of IPO5, ACLY and UBA1 (Full gels and western blots).



Western blots of α-IPO5, α-UBA1 and α-ACLY. SDS-PAGE/Immunoblot of goyazensolide upon treatment of SW620 lysate with DMSO or 10 μM goyazensolide for 30 min followed by treatment with **GOYA-2** (10 μM, 30 min). CuAAC reaction with the desthiobiotinylated fluorophore, streptavidin enrichment and SDS-PAGE.

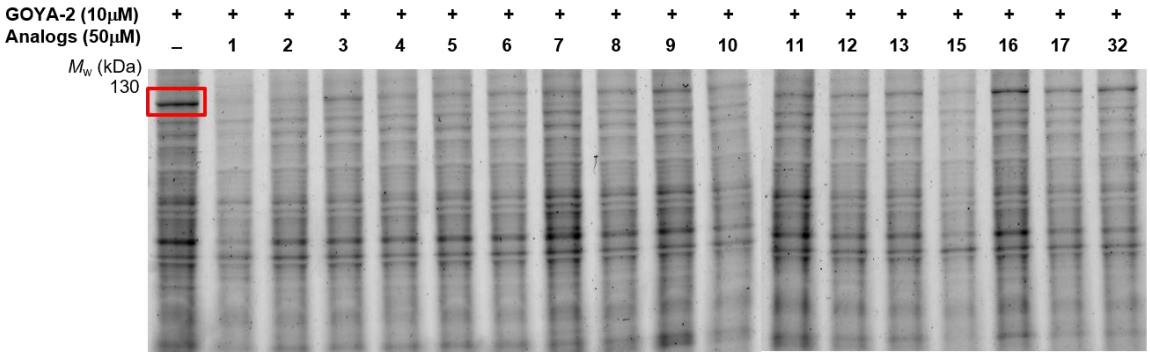
Figure S17. Goyazensolide is a selective binder for IPO5 compared to other importins.



Western blots of α-IPO5, α-KPNB1, α-Karyopherin β2, α-IPO7, α-IPO8, α-IPL12. SDS-PAGE/Immunoblot of goyazensolide upon treatment of SW620 lysate with DMSO or 10 μM goyazensolide for 30 min followed by treatment with **GOYA-2** (10 μM, 30 min). CuAAC reaction with the desthiobiotinylated fluorophore, streptavidin enrichment and SDS-PAGE.

i) Experimental procedures for Figure 3

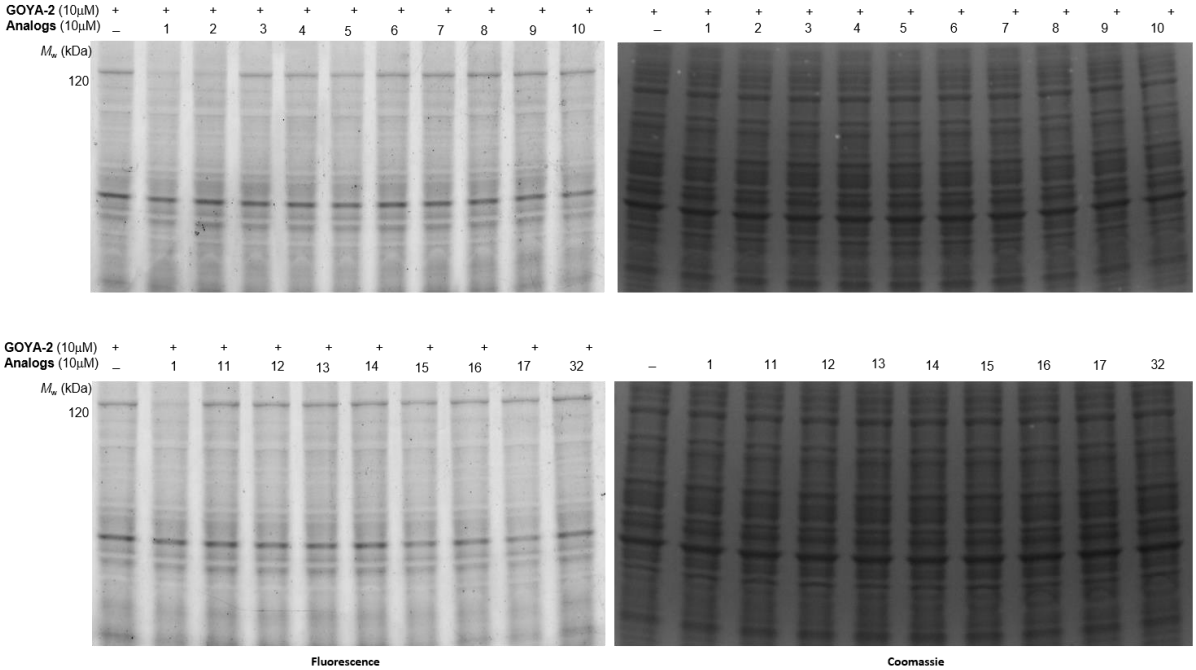
Figure S18. Competition experiment with 50 µM of **1**-**17** and **32**.



Goyazensolide and atripliciolide selectively bind IPO5 versus other members of the same family of heliangolides. Competition experiment. A SW620 Lysate was incubated for 30 minutes with DMSO or one of the natural products (50 µM) for 30 min, and then labeled with 10 µM of **GOYA-2** followed by CuAAC reaction with **Cy3-N$_3$.** The labelling/competition experiment shows selective binding of goyazensolide (**1**) and atripliciolide (2) to IPO5 protein.

Quantification (ImageJ software)

Figure S19. Competition experiment with 10 µM of analogs **1**-**17** and **32**.

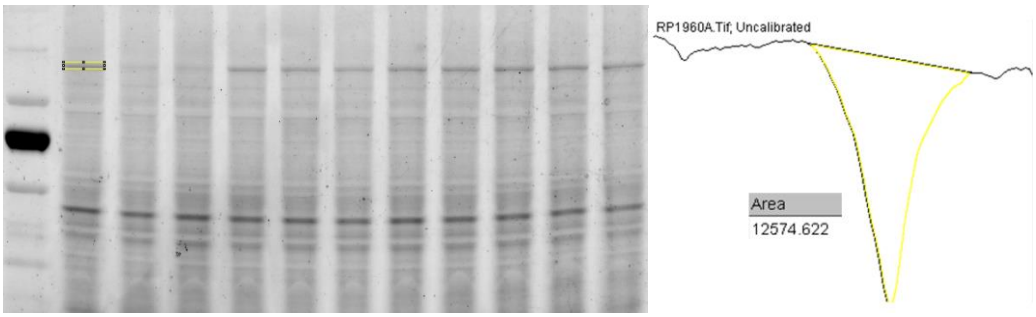


PC3 cell lysate were preincubate for 30 min with 10 µM of DMSO or analogs and then labeled with 10 µM of **GOYA-2** followed by CuAAC reaction with **Cy3-N$_3$**. Proteins were separated using a 10% SDS-PAGE gel. Gels were visualized at 625 nm using a fluorescence scanner and then stained with Coomassie brilliant blue.

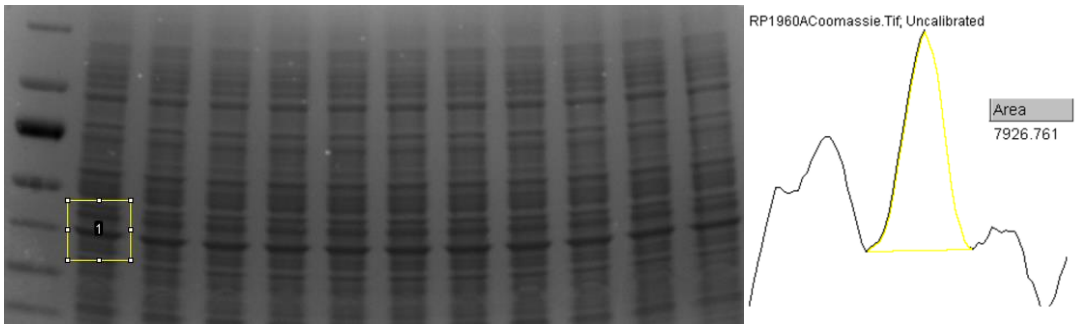
Quantification

The binding efficiency was calculated by density of the fluorescent band. We used Coomassie as reference.

1) Grey intensity determination for fluorescence



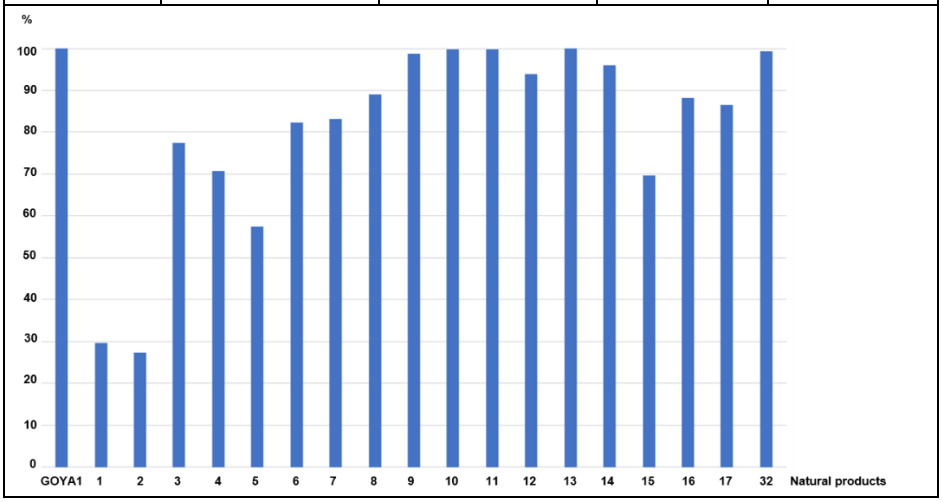
2) Grey intensity determination for Coomassie



3) Calculation

Table S18. Quantification for competition.

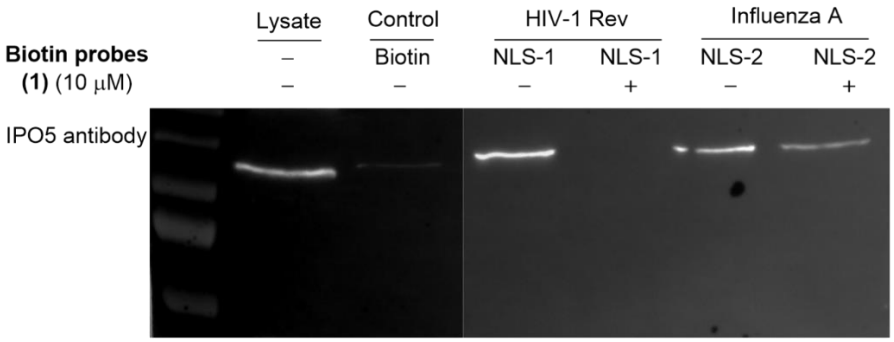
Gel1				
Analogs	Fluorescence density	Coomassie density (dye)	F/C	Fraction
-	9938.844	5119.347	1.941428	1
1	3166.782	5275.811	0.600246	0.309177
2	2863.225	5417.861	0.528479	0.272211
3	8507.43	5651.154	1.505432	0.775425
4	7714.823	5615.276	1.373899	0.707675
5	6462.045	5792.276	1.115631	0.574645
6	9374.38	5868.276	1.597467	0.822831
7	9108.43	5645.276	1.613461	0.831069
8	10058.309	5812.811	1.730369	0.891287
9	9769.966	5093.296	1.918201	0.988036
10	11011.693	5687.468	1.936133	0.997272
Gel2				
-	11349.67	4811.569	2.35883	1
1	3077.953	4637.569	0.6637	0.281368
11	11662.79	4956.861	2.352859	0.997469
12	10525.38	4756.154	2.213002	0.938178
13	10426.62	4422.326	2.357724	0.999531
14	10538.92	4654.569	2.264209	0.959886
15	8101.48	4933.326	1.642194	0.69619
16	10379.97	4987.983	2.080995	0.882215
17	9482.602	4648.619	2.039875	0.864783
32	11447.21	4881.447	2.345044	0.994156



Binding efficiency representation. We observed a difference of binding efficiency by comparison of compounds **1-6** versus **7-13**. The C8 stereochemistry plays an important role in the binding efficiency.

Pulldown experiment with viruses NLS. 10µL of 100µM solutions of the corresponding NLS (0.2% SDS in PBS) were added to 30 µL of magnetic streptavidin beads and the suspension was shaken for 1 hour. The supernatant was discarded and the beads were washed 5× with a solution of 0.2% SDS in PBS. The pre-treated lysates (30 µL of treated lysate (3 mg/mL) with DMSO or goyazensolide 10 µM fro 30 min) were added to the beads and shaken 3 hours. The supernatants were discarded and the beads were washed 2× times (20 µL) with 0.2% SDS in PBS. 15 µL of SDS 5%. For elutions 5 µL of Laemli buffer were added to the beads and the mixtures were shaken and heated at 95°C for 3 minutes followed by SDS-PAGE and western blot. Incubation with IPO5 antibody (1 : 1000) followed by rabbit secondary antibody (1 : 10000). Chemoluminescence was used for detection.

Full gel of Figure 3b. Immunoblot of competitive interaction between NLS and IPO5. Magnetic streptavidin beads were saturated with corresponding NLS and then incubated for 2 hours with HT29 lysate treated with DMSO or goyazensolide (10 µM, 30 min).

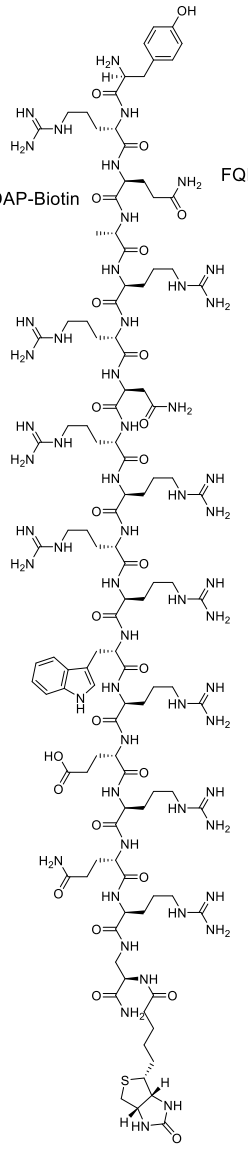


Preparation of NLS-1 and NLS-2

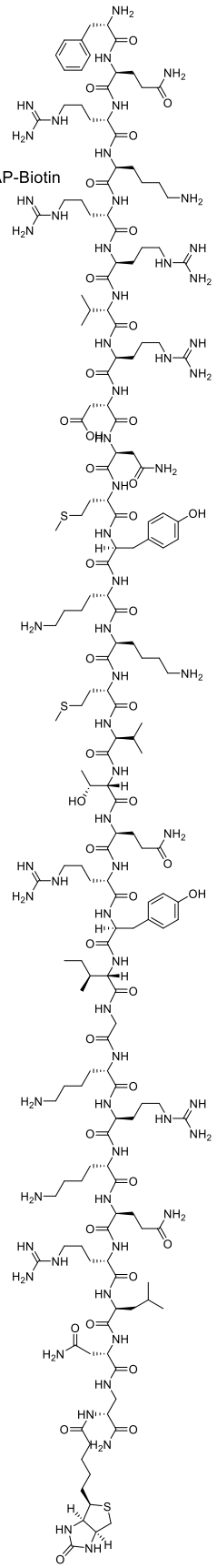
NLS-1 and **NLS-2** were synthesized using solid-phase synthesis. General procedure described in PLoS One **2020,** *15*, e0238089.

Figure S20. Chemical structures of **NLS-1** and **NLS-2**.

NLS-1 =
TRQARRNRRRRWRERQR-DAP-Biotin

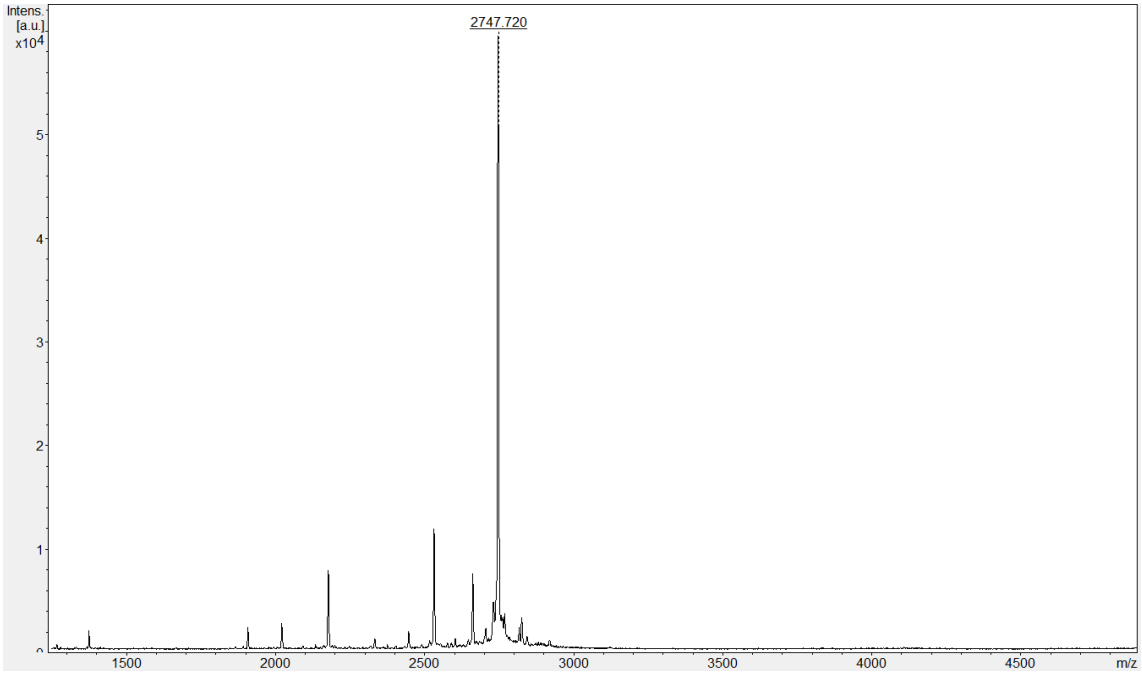


NLS-2 =
FQRKRRVRDNMTKKMVTQRTIGKRKQRLN-DAP-Biotin



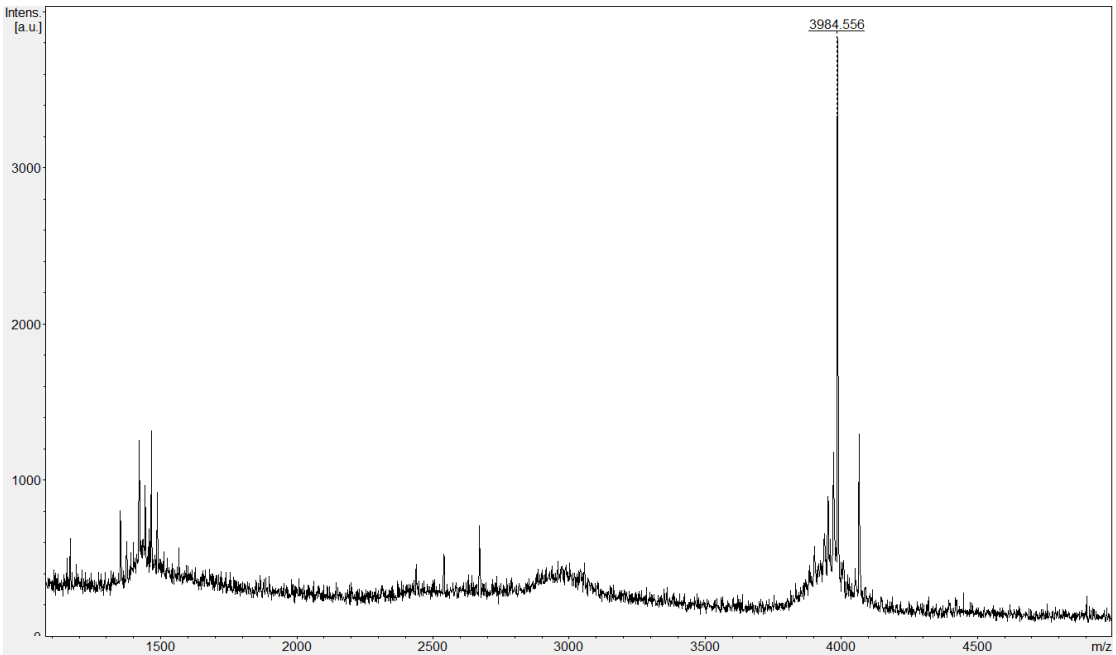
Data of **NLS-1**:

($C_{110}H_{194}N_{56}O_{26}S$), $[M+H]^+$ isotopic peaks with relative distribution : 2748.53 (100.0%), 2747.53 (84.1%), 2749.54 (35.9%)



Data of **NLS-2**:

($C_{167}H_{299}N_{65}O_{42}S_3$), $[M+H]^+$ isotopic peaks with relative distribution : 3984.24 (100.0%), 3985.25 (66.1%), 3983.24 (55.4%), 3986.25 (46.9%), 3985.24 (24.0%)



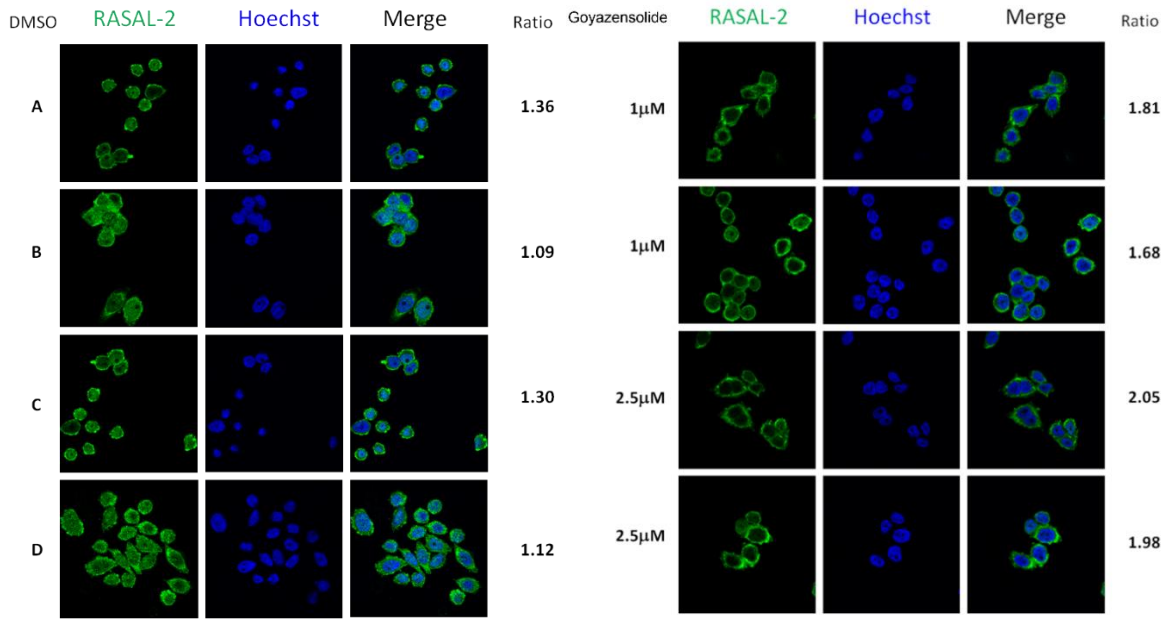
j) Experimental procedures for Figure 4

Microscopy. Cells (50000/well) were seeded on coverslips in a 12 well plate. After 24 hours, cells were treated with goyazensolide (**1**) or DMSO for 3 hours. Cells were fixed with PFA 4% for 25 minutes at room temperature. After a wash 3× with PBS, cells were blocked using 5% BSA + 0.1% saponin in PBS for 2 hours. Then they were incubate with anti IPO5 antibody (1 : 100) in 1% BSA in PBS (30 µL/well) for 3 hours at room temperature.

For the incubation, the coverslips were taken out of the plate, and place on a drop of antibody solution on parafilm in a humidity chamber, then they were washed 3× with PBS, incubated with anti-rabbit AlexaFluor488 (1 : 400), washed 3× with PBS, incubate with Hoescht diluted 2000× in PBS for 10min, washed 3× with PBS, then water and finally the edges were dried. The coverslips were then mounted on a clean slide treated with 5 µL ProlongDiamond per coverslip for 24 hours at room temperatue and finally sealed with nail polish.

Ratio (cytosol/nucleus) caculation of RASAL2.

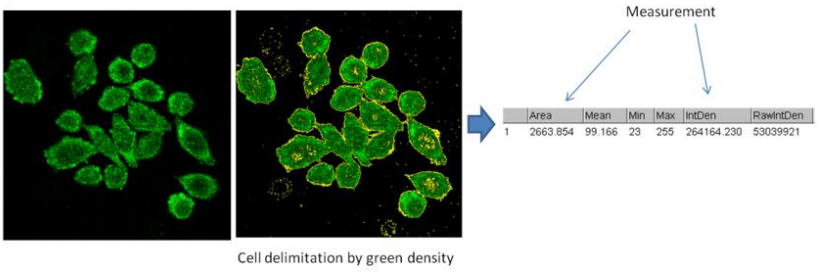
Figure S21. Confocal microscopy images of SW620 cells after treatment with DMSO or goyazensolide. Ratio of RASAL2 levels in the cytosol and nucleus was calculated applying a threshold mask to quantify fluorescence intensity in the cytosol and in the nucleus.



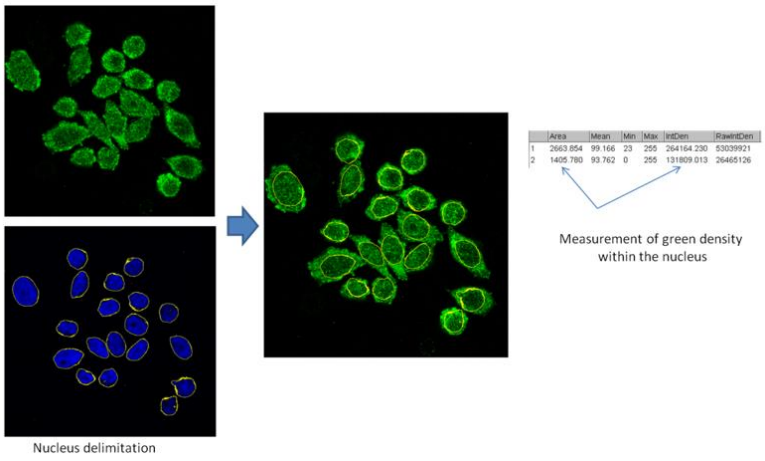
Calculation of fluorescence intensity in the cytosol/nucleus.

Threshold masks were generated in ImageJ softwqre to calculate the integrated dendity of the signal in the green channel (Alexa488, RASAL2) and blue channel (Hoecht, nuclei).

Step 1 : Cell surface and green density determination.

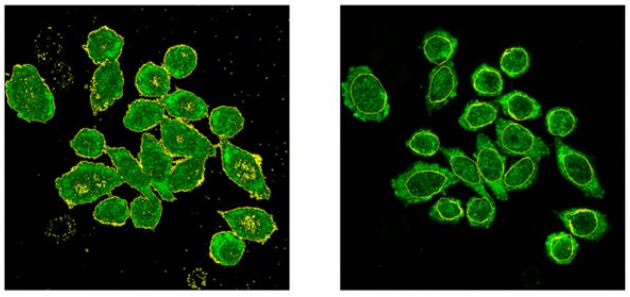


Step 2 : Determination of the surface and green density within the nucleus



Step 3 : Determination of the surface and green density within the cytosol by difference

		Area	Mean	Min	Max	IntDen	RawIntDen
Whole cells →	1	2663.854	99.166	23	255	264164.230	53039921
Nucleus →	2	1405.780	93.762	0	255	131809.013	26465126



By difference, we obtain the cytosol area and RASAL-2 density

Cytosol area 2663.854-1405.78 = 1258.074
Cytosol RASAL-2 density 264164.23-131809.13 = 132355.1

FRACTION RASAL-2 Nucleus = 131809.013/ 1405.78 = 93.762
FRACTION RASAL-2 Cytosol = 132355.1/1258.074 = 105.204

Ratio = 105.204/93.762 = 1.12

Step 4 : Ratio calculation to all pictures

Table S19. Ratio calculation.

DMSO				
	Area	Integrated density	Int/Area	Ratio
No Treatment	**A**			
Whole cells	999.836	79215.392	79.22839	
Nucleus	524.499	35443.651	67.5762	
Cytosol	475.337	43771.741	92.0857	1.362694
	B			
Whole cells	1326.899	122651.425	92.43464	
Nucleus	726.149	64428.407	88.72615	
Cytosol	600.75	58223.018	96.91722	1.092318
	C			
Whole cells	1143.299	47116.191	41.21073	
Nucleus	559.298	20005.295	35.76858	
Cytosol	584.001	27110.896	46.42269	1.297862
	D			
Whole cells	2663.854	264164.23	99.16618	
Nucleus	1405.78	131809.013	93.76219	
Cytosol	1258.074	132355.217	105.2046	1.122037
		Average Ratio DMSO	1.218728	
Goyazensolide				
	Area	Integrated density	Int/Area	Ratio
Goyazensolide	**1A**			
Whole cells	1036.597	70567.839	68.07645	
Nucleus	383.935	17332.133	45.1434	
Cytosol	652.662	53235.706	81.56704	1.806843
	1B			
Whole cells	2079.43	142805.488	68.6753	
Nucleus	1030.202	52726.816	51.18105	
Cytosol	1049.228	90078.672	85.85233	1.677424
	25A			
Whole cells	1452.821	70476.786	48.5103	
Nucleus	618.297	18677.594	30.20813	
Cytosol	834.524	51799.192	62.07034	2.054756
	25B			
Whole cells	890.415	42677.438	47.92983	
Nucleus	405.471	12686.904	31.2893	
Cytosol	484.944	29990.534	61.84329	1.9765
		Average Ratio 1 µM	1.742134	
		Average Ratio 2.5 µM	2.015628	
		Ratio increasing (%)	65.38786	

Table S20. Raw data

RAW DATA	**ImageJ Software**		**1 : Whole cells**			
			2 : Nucleus			
PICTURE A	Area	Mean	Min	Max	IntDen	RawIntDen
1	999.836	79.228	11	255	79215.392	15905174
2	524.499	67.576	0	255	35443.651	7116514
PICTURE B	Area	Mean	Min	Max	IntDen	RawIntDen
1	1326.899	92.435	19	255	122651.425	24626430
2	726.149	88.726	0	255	64428.407	12936186
PICTURE C	Area	Mean	Min	Max	IntDen	RawIntDen
1	1143.299	41.211	5	255	47116.191	9460172
2	559.298	35.769	0	225	20005.295	4016741
PICTURE D	Area	Mean	Min	Max	IntDen	RawIntDen
1	2663.854	99.166	23	255	264164.23	53039921
2	1405.78	93.762	0	255	131809.013	26465126
PICTURE 1A	Area	Mean	Min	Max	IntDen	RawIntDen
1	1036.597	68.076	12	255	70567.839	14168885
2	383.935	45.143	0	255	17332.133	3480013
PICTURE 1B	Area	Mean	Min	Max	IntDen	RawIntDen
1	2079.43	68.675	6	255	142805.488	28673041
2	1030.202	51.181	0	255	52726.816	10586695
PICTURE 25A	Area	Mean	Min	Max	IntDen	RawIntDen
1	1452.821	48.51	5	255	70476.786	14150603
2	618.297	30.208	0	227	18677.594	3750160
PICTURE 25B	Area	Mean	Min	Max	IntDen	RawIntDen
1	890.415	47.93	6	255	42677.438	8568942
2	405.471	31.289	1	255	12686.904	2547326

Figure S22. Plot profile determination (Image J software).

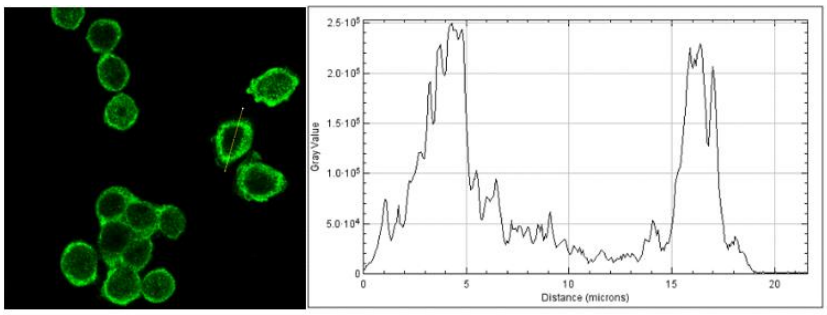


Figure S23. DMSO treatment.

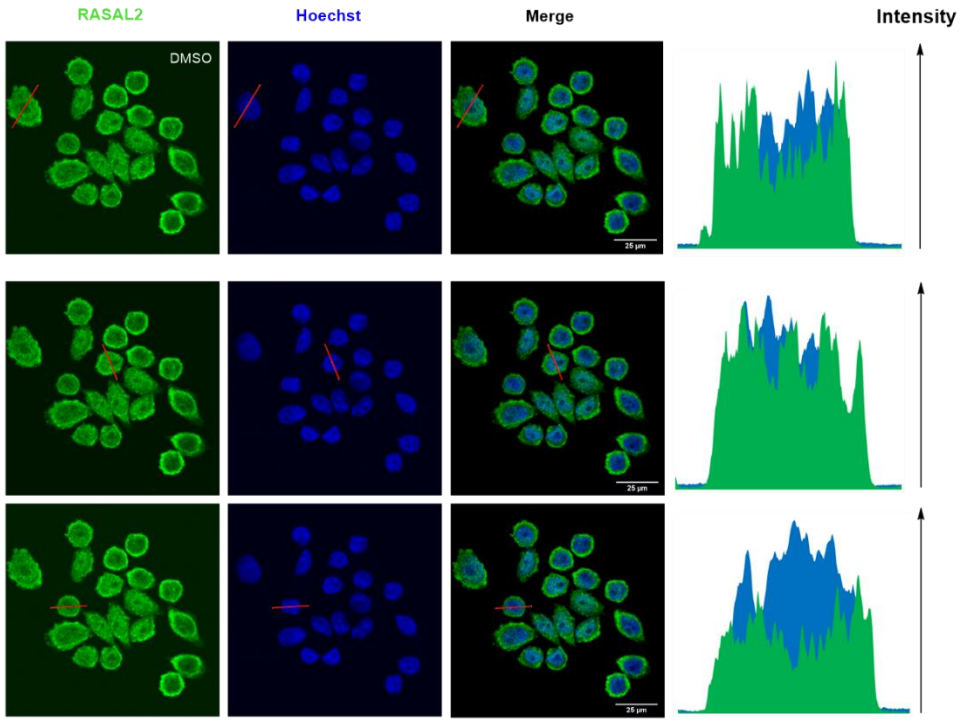


Figure S24. Goyazensolide 1 μM treatment.

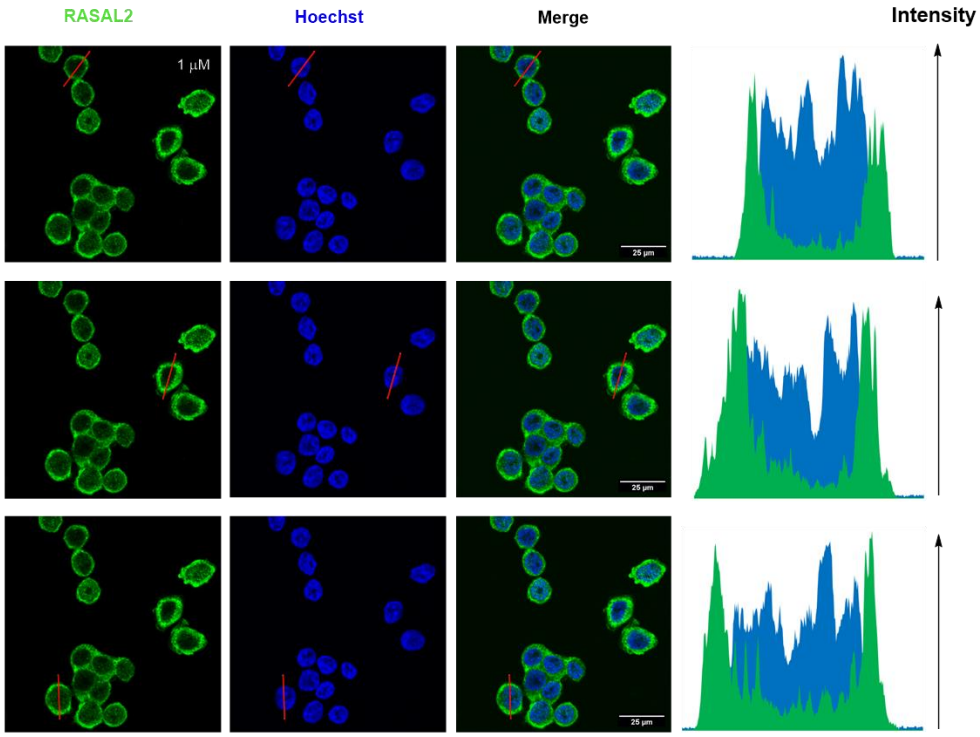


Figure S25. Goyazensolide 2.5 µM treatment.

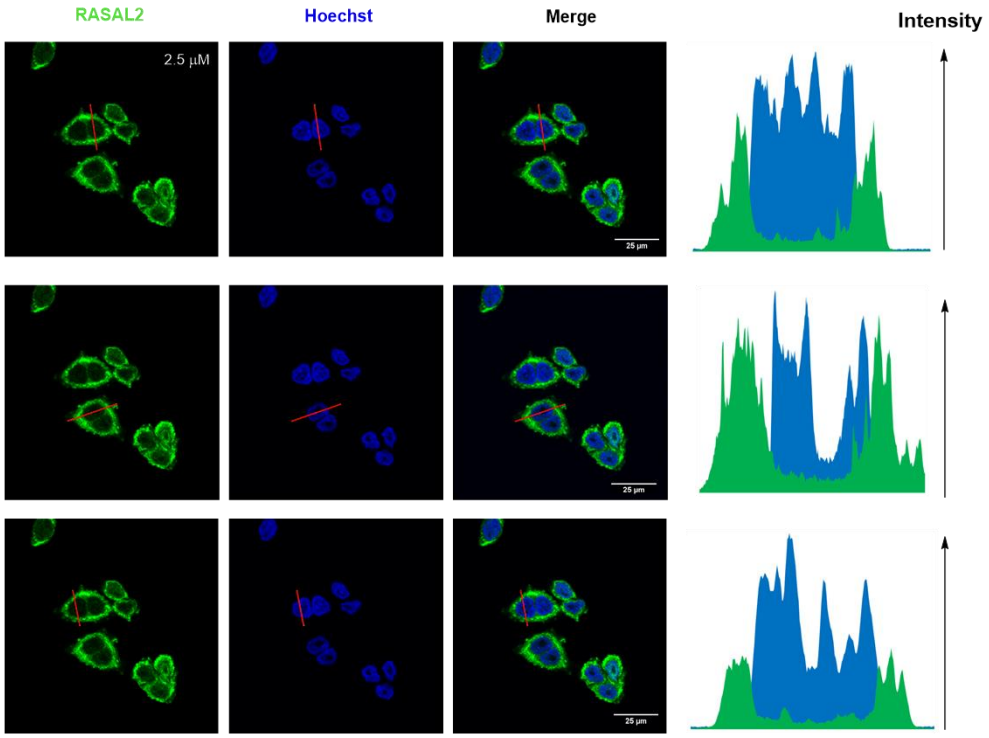


Table S21. Standard deviation (STDEV) and Standard error of mean (SEM)

Ratio	Ratio	Ratio			
DMSO	**Goyazensolide 1 µM**	**Goyazensolide 2.5 µM**	**Standard deviation**		**Standard error of mean**
1.362694	1.806843	2.054756	0.132056852	4	0.066028426
1.092318	1.677424	1.9765	0.091513053	2	0.0647095
1.297862			0.055335348	2	0.039128
1.122037					
DMSO	**Goyazensolide 1 µM**	**Goyazensolide 2.5 µM**			
1.218728	1.7421335	2.015628			

pAKT assay.

SW620 Cells were seeded (350.000 cells/mL) in a 6 well plate and left two days to attach and grow. Cells were incubated with DMSO or goyazensolide (5 µM) in a time dependant manner. Cells were lysed and scrapped in the presence of phosphatase inhibitors at 4 °C. Lysates were centrifuge at 14000g for 15 minutes at 4 °C. SDS-PAGE followed by western blot treated with respective antibodies (pAKT and actin).

Full gel of Figure 4d. Immunoblot of p-AKT (p-AKT Ser473 antibody) expression upon treatment of SW620 cells with DMSO or goyazensolide (5 μM, 4 h).

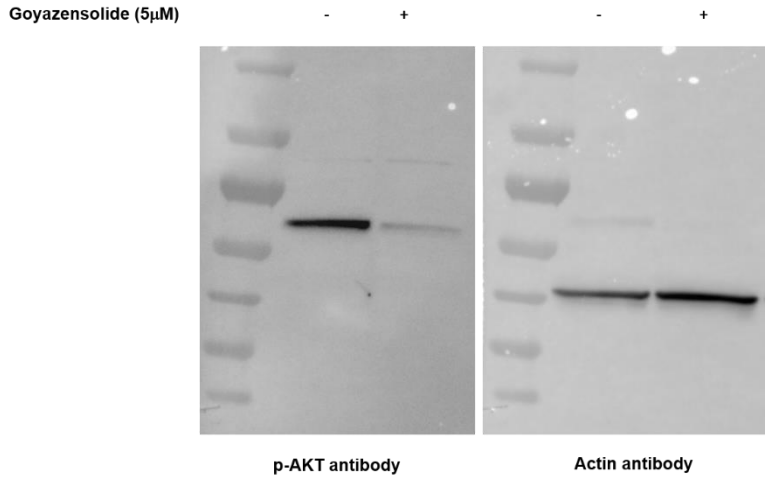
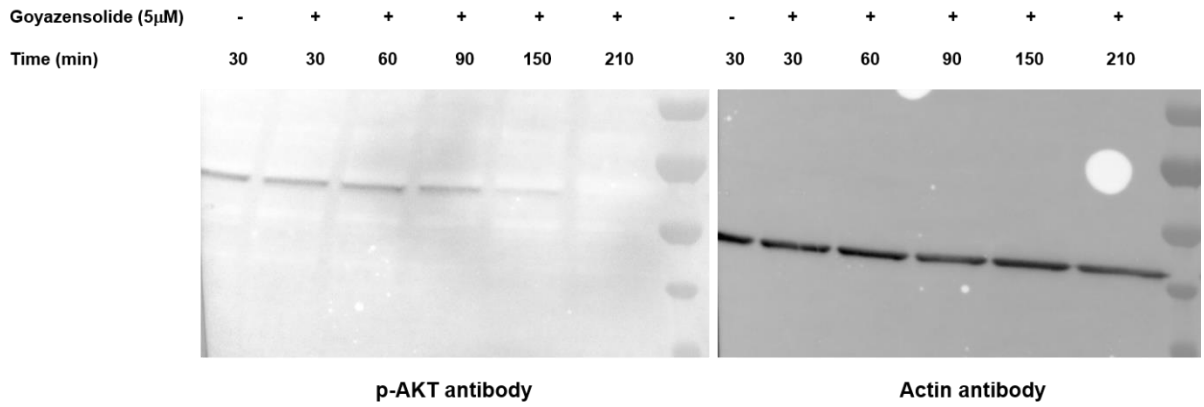
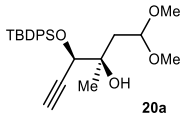
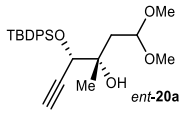


Figure S26. Time-/Dose-dependent manner of pAKT assay.



Immunoblot of p-AKT (p-AKT Ser473 antibody) expression upon treatment of SW620 cells with DMSO or goyazensolide (5 μM, 4 h).

k) Chiral-HPLC spectra of 20a

Major	 **20a**	12.797 min
Minor	 *ent*-**20a**	11.048 min

14/02/2020 18:46:56 Pag

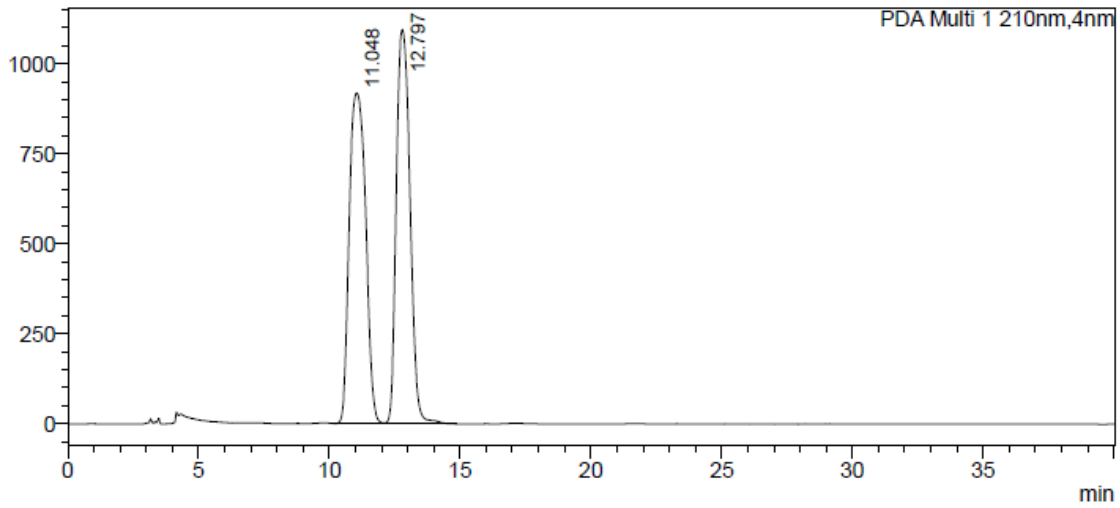
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: wll-ug-13-54-rac		
Sample ID	:		
Data Filename	: wll-ug-13-54-rac-AD-9901.lcd		
Method Filename	: Aqu Col1 99-1 1mL 40 MIN.lcm		
Batch Filename	: new template.lcb		
Vial #	: 1-91	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 14/02/2020 15:43:44	Acquired by	: System Administrator
Date Processed	: 14/02/2020 16:23:46	Processed by	: System Administrator

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area%
1	11.048	50.182
2	12.797	49.818
Total		100.000

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

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Sample ID	:		
Data Filename	: wll-ug-13-54-chiral-AD-9901.lcd		
Method Filename	: Aqu Col1 99-1 1mL 40 MIN.lcm		
Batch Filename	: new template.lcb		
Vial #	: 1-92	Sample Type	: Unknown
Injection Volume	: 10 uL		
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Date Processed	: 14/02/2020 17:04:17	Processed by	: System Administrator

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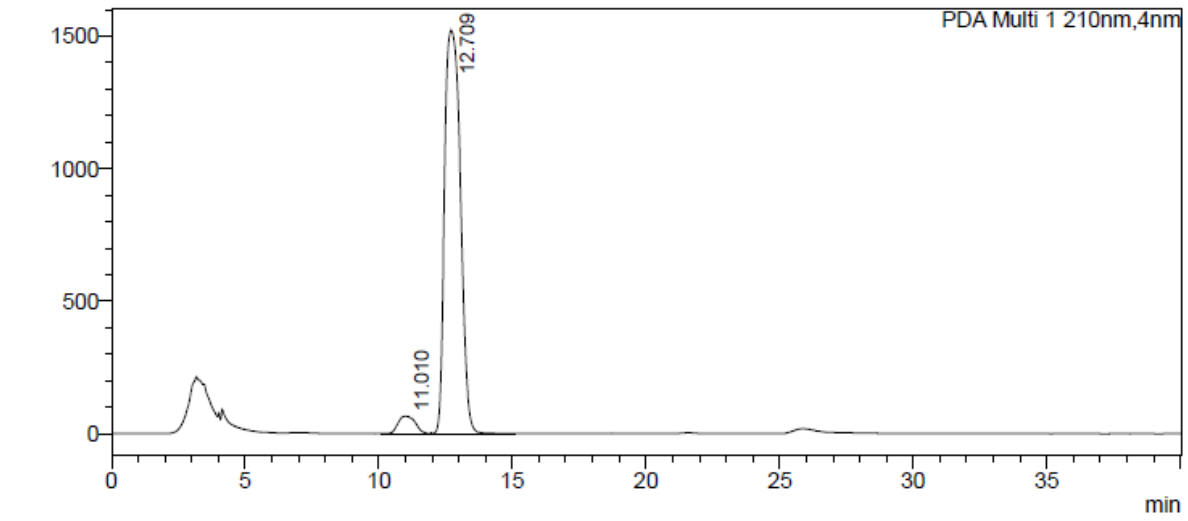

<Peak Table>

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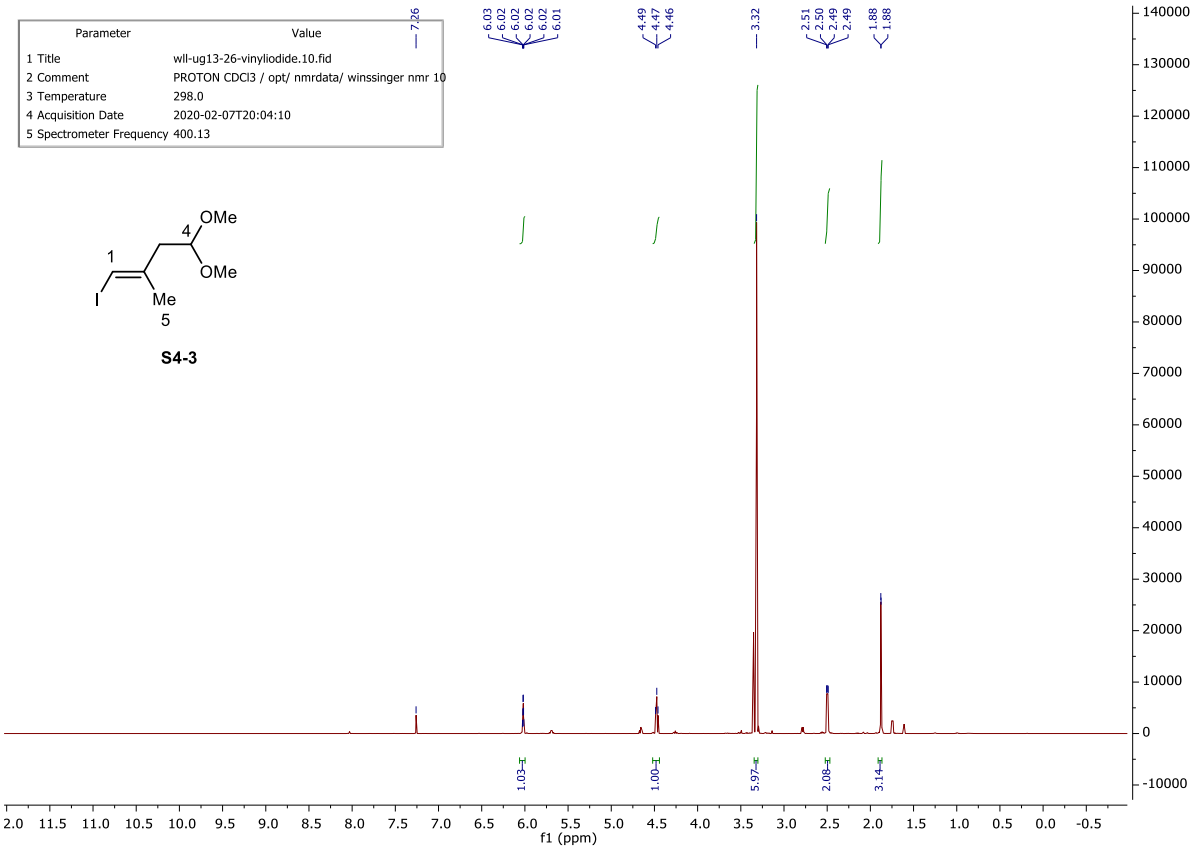
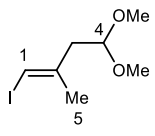
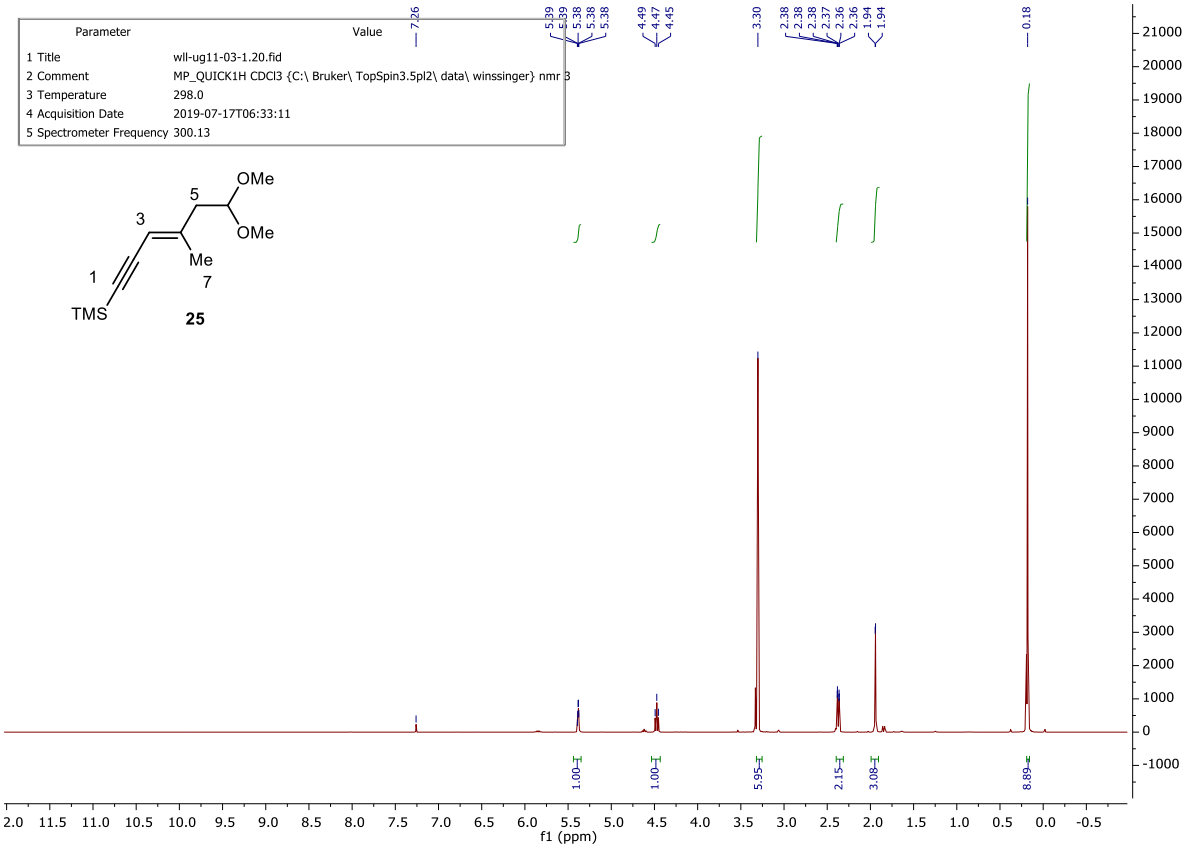
l) ^{1}H and ^{13}C NMR spectra





S4-3

S4-3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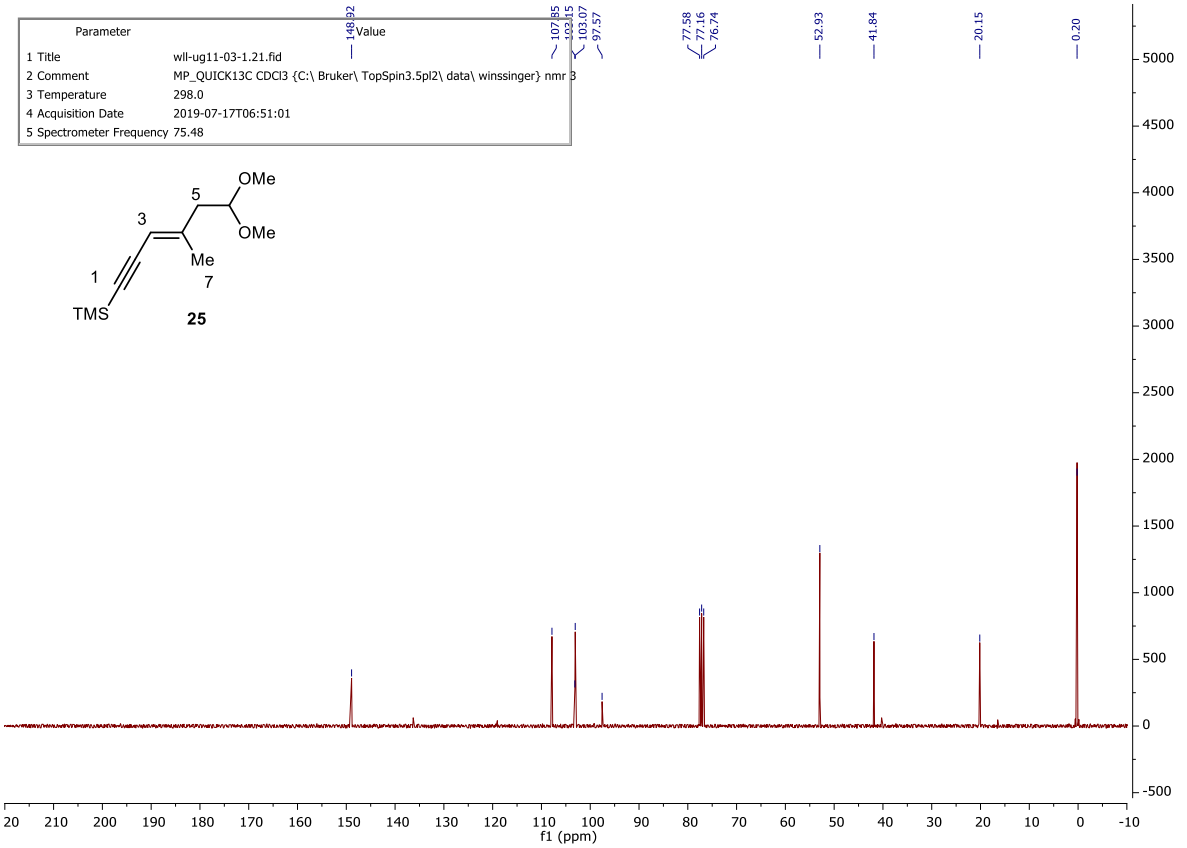
7.26
5.39
5.38
4.49
4.47
4.45
3.30
2.38
2.37
2.36
1.94
0.18
OMe
OMe
Me
TMS
1
3
5
7
25
1.00
1.00
5.95
2.15
3.08
8.89
f1 (ppm)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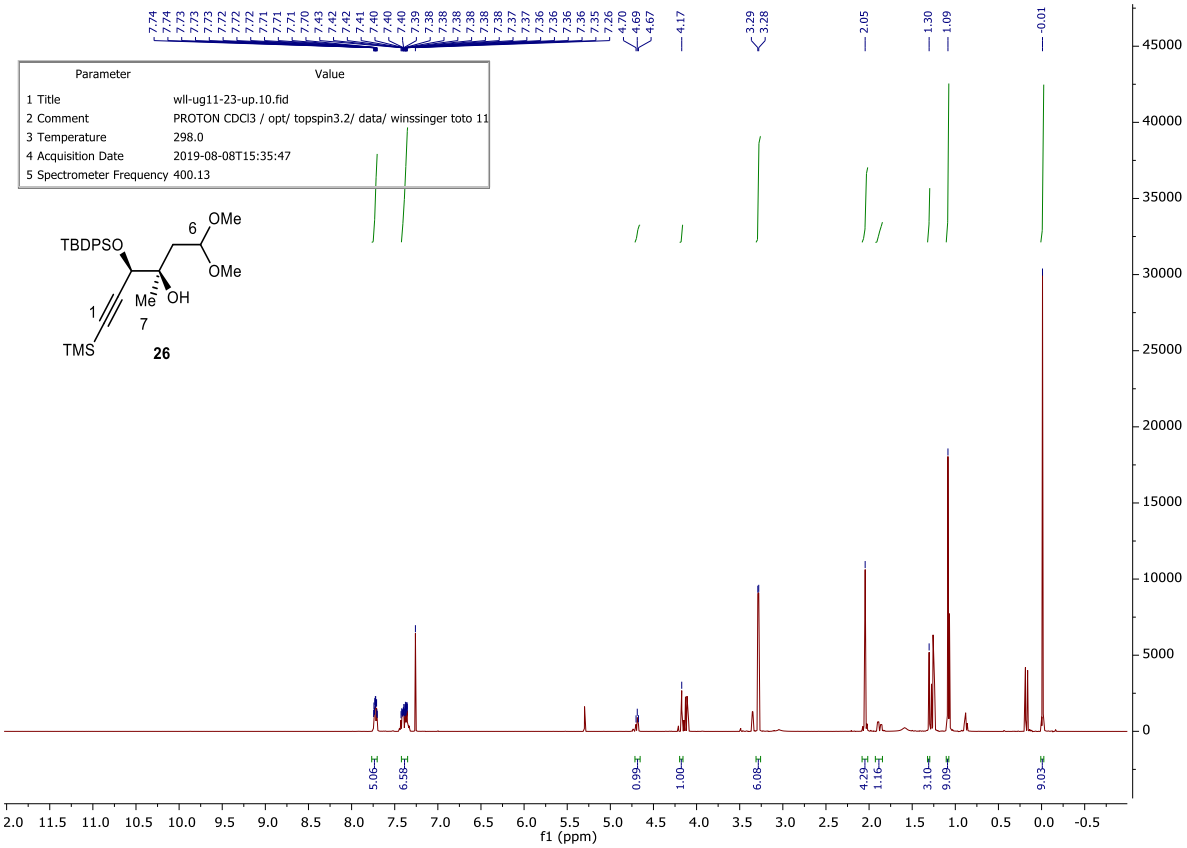
3 Temperature 298.0
4 Acquisition Date 2019-07-17T06:51:01
5 Spectrometer Frequency 75.48
148.92
107.85
103.15
103.07
97.57
77.58
77.16
76.74
52.93
41.84
20.15
0.20
OMe
OMe
Me
TMS
1
3
5
7
25
f1 (ppm)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3 Temperature 298.0
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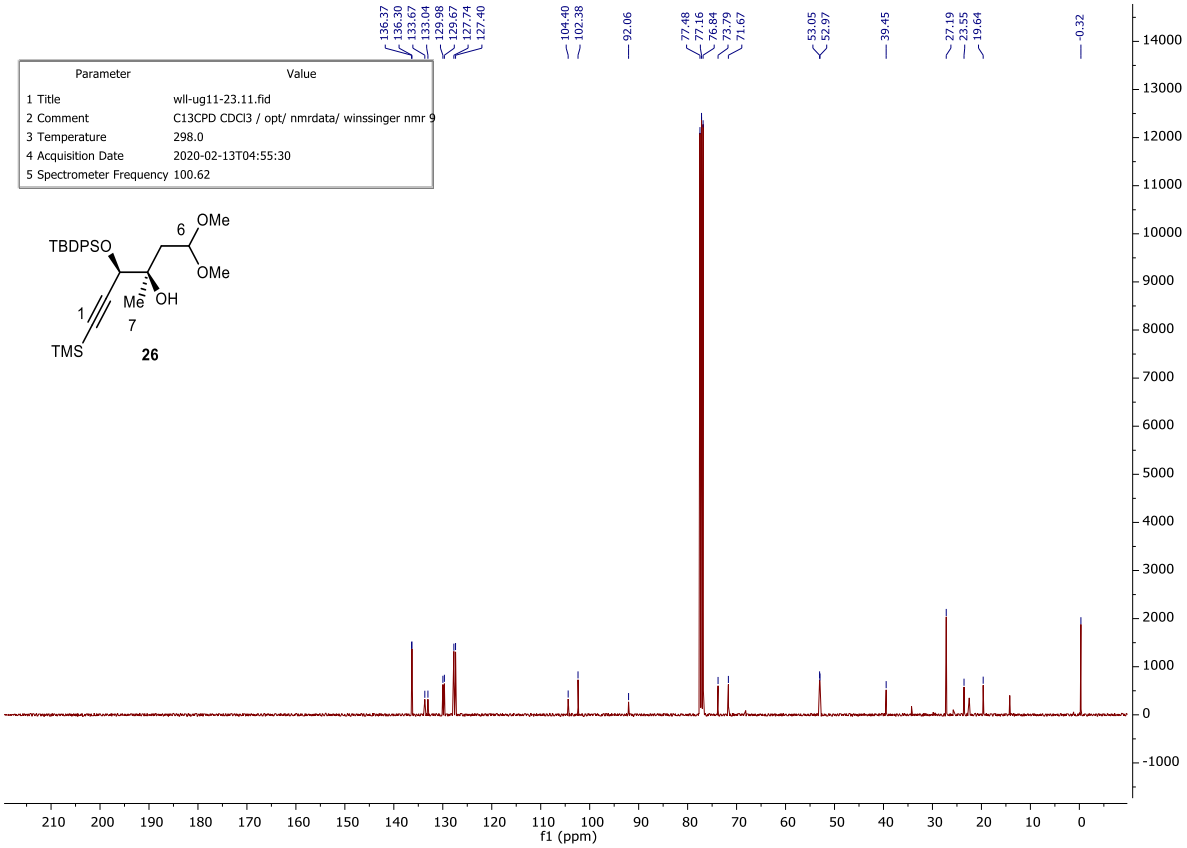
5 Spectrometer Frequency 400.13
TBDPSO
OMe
OMe
Me
OH
TMS
26
f1 (ppm)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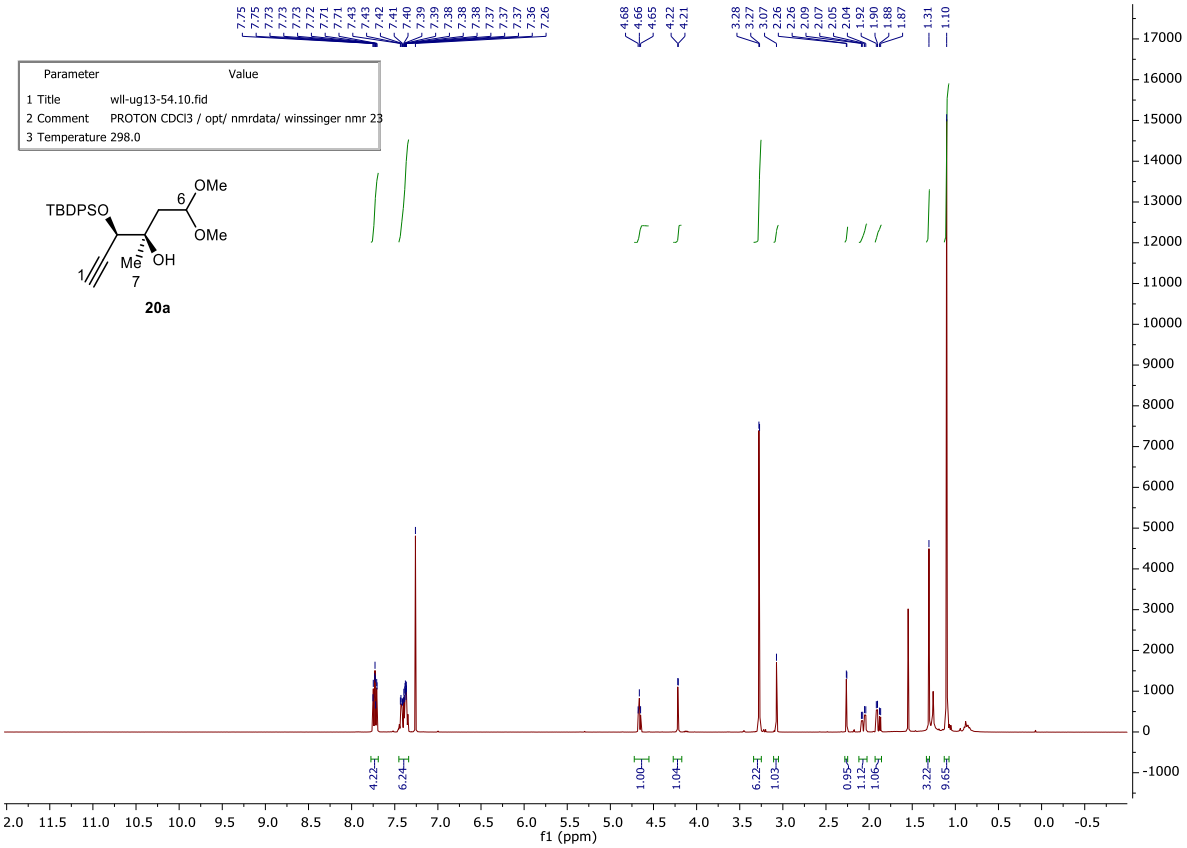
TBDPSO
OMe
OMe
Me
OH
TMS
26
f1 (ppm)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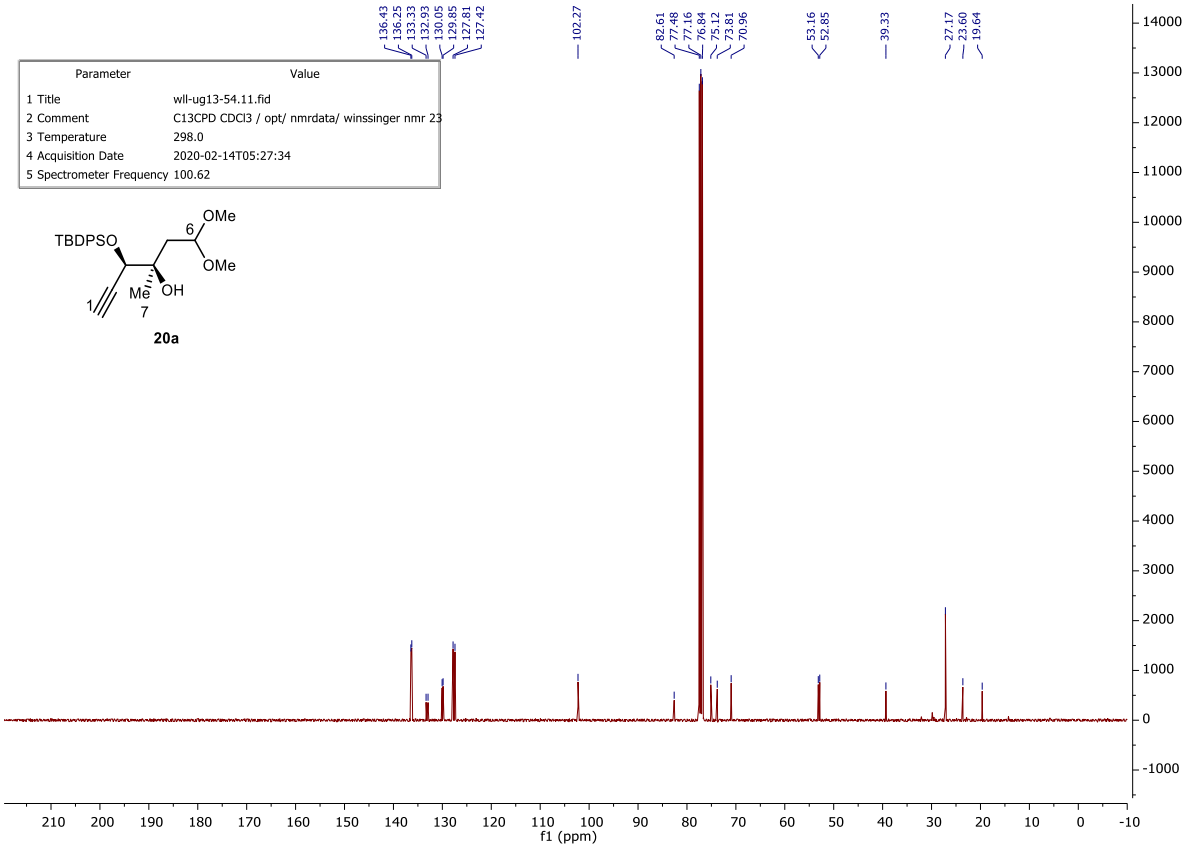
3 Temperature 298.0
TBDPSO
OMe
OMe
Me
OH
20a
f1 (ppm)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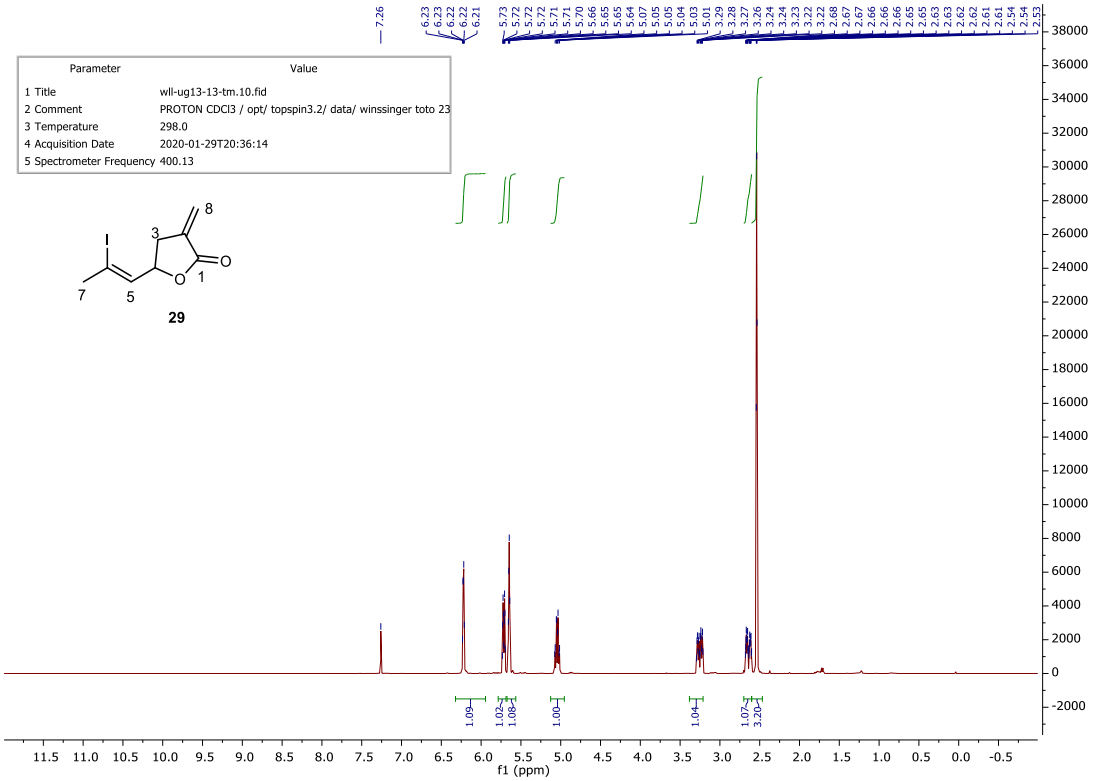
TBDPSO
OMe
OMe
Me
OH
20a
f1 (ppm)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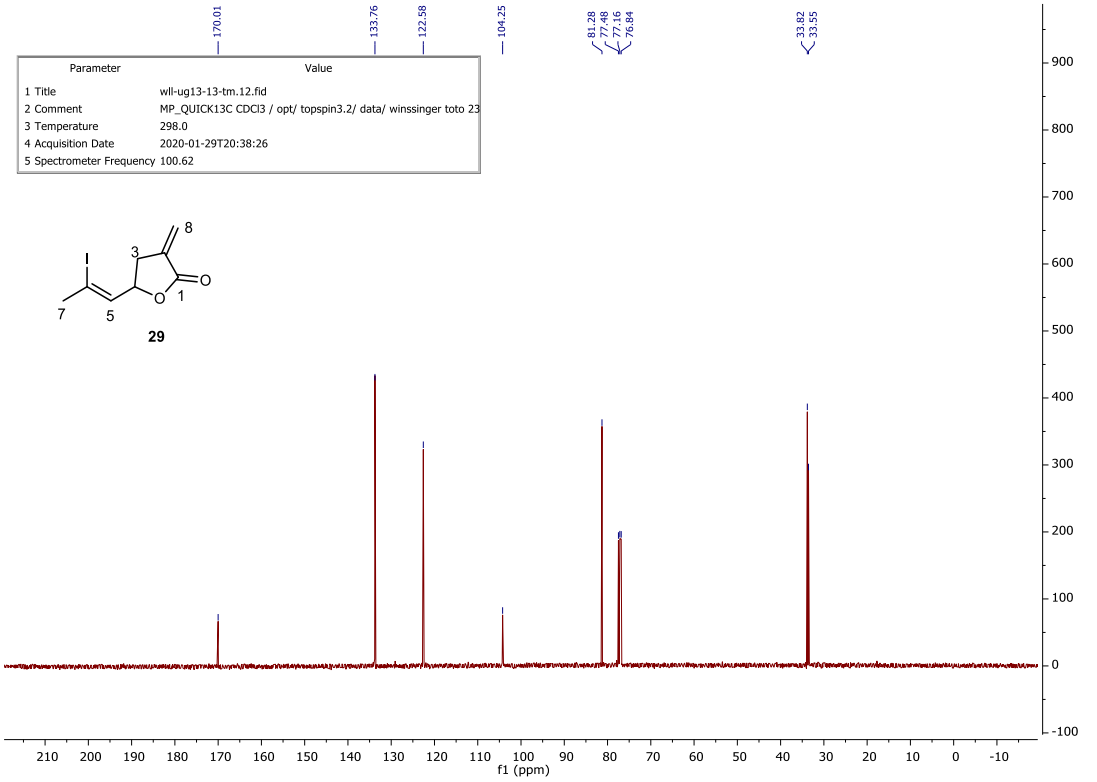
5 Spectrometer Frequency 400.13
29
f1 (ppm)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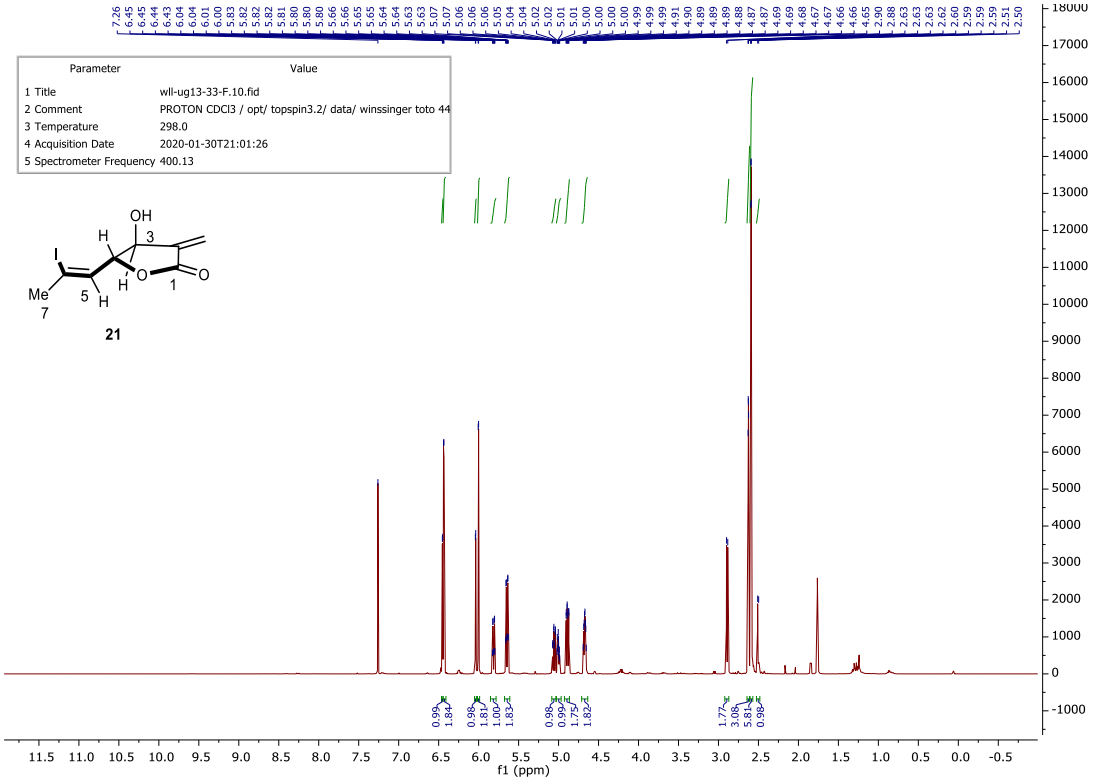
29
f1 (ppm)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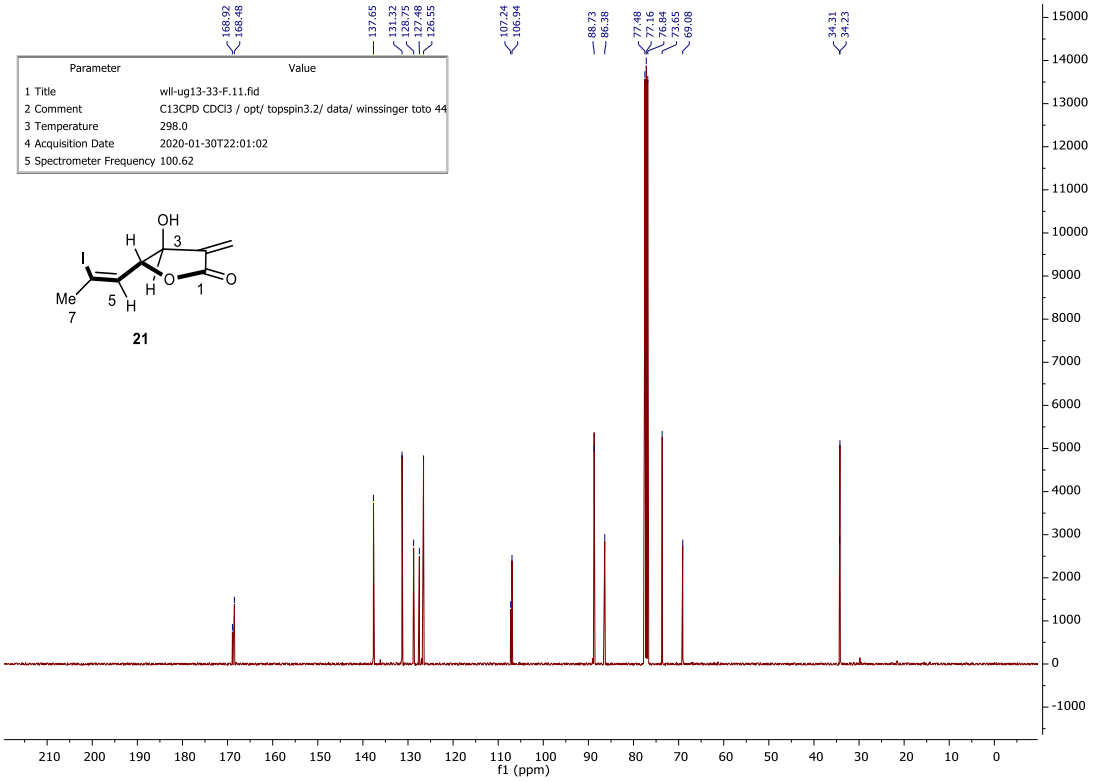
OH
H
3
I
O
O
Me
5
H
H
7
1
21
f1 (ppm)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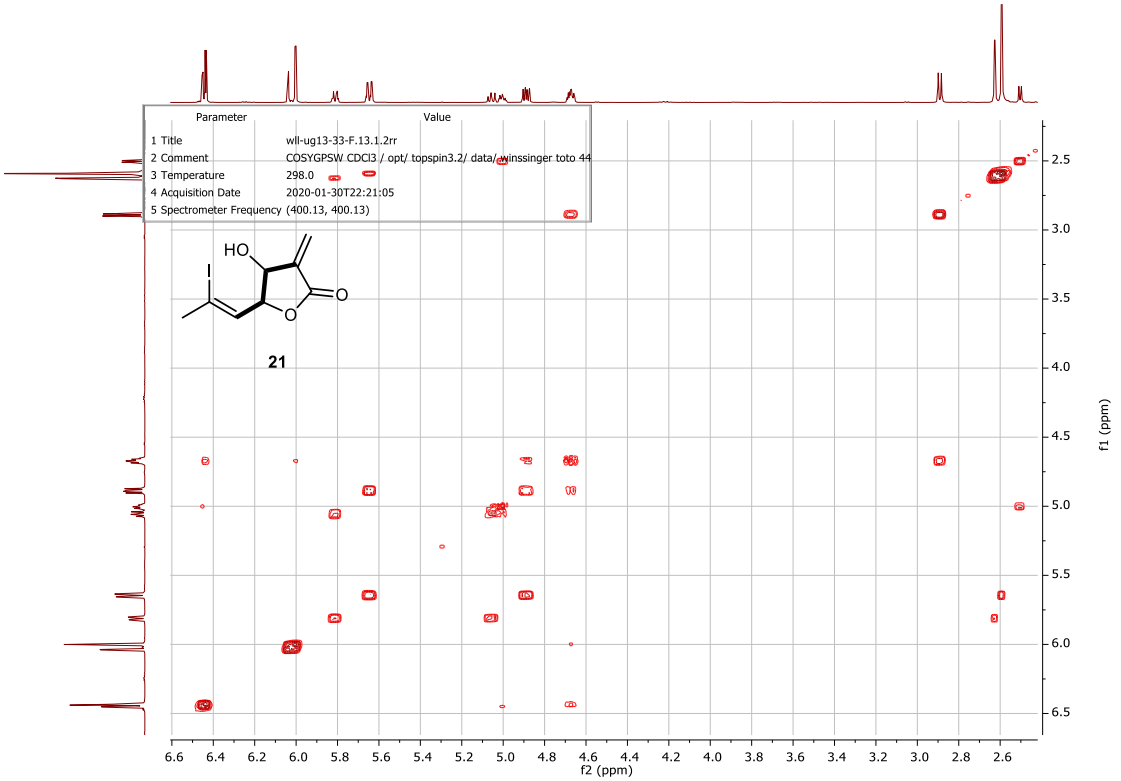
OH
H
3
I
O
O
Me
5
H
H
7
1
21
f1 (ppm)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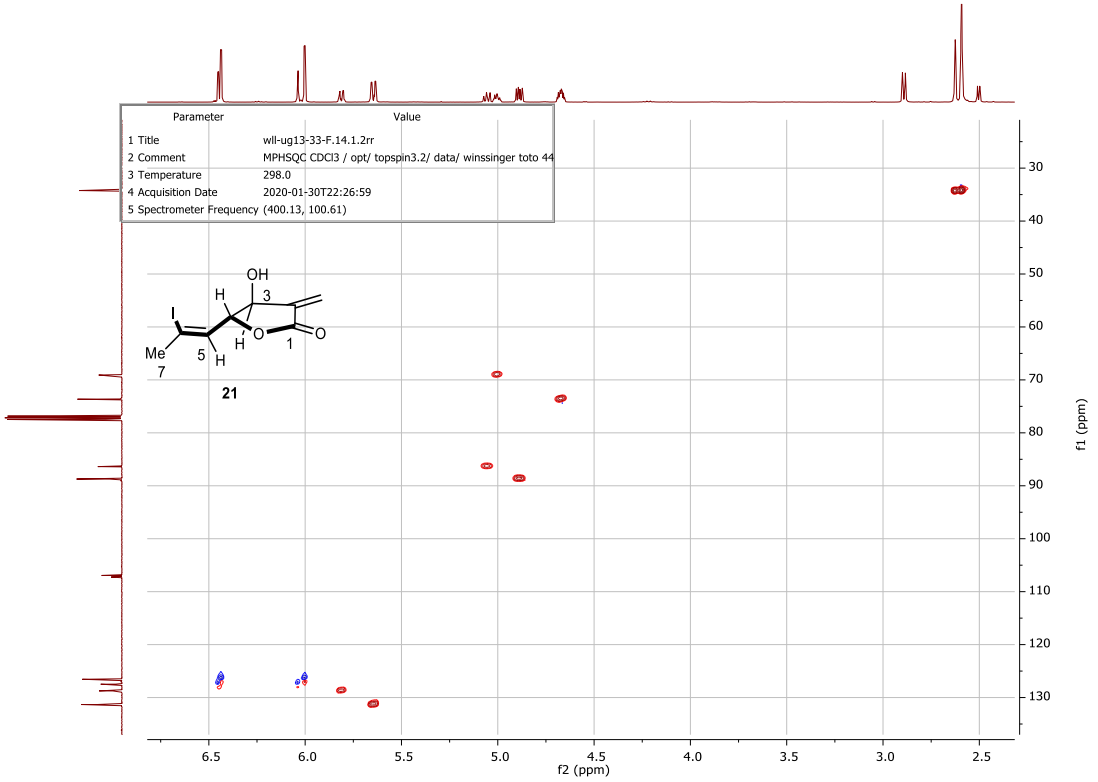
HO
I
O
O
21
f2 (ppm)
f1 (ppm)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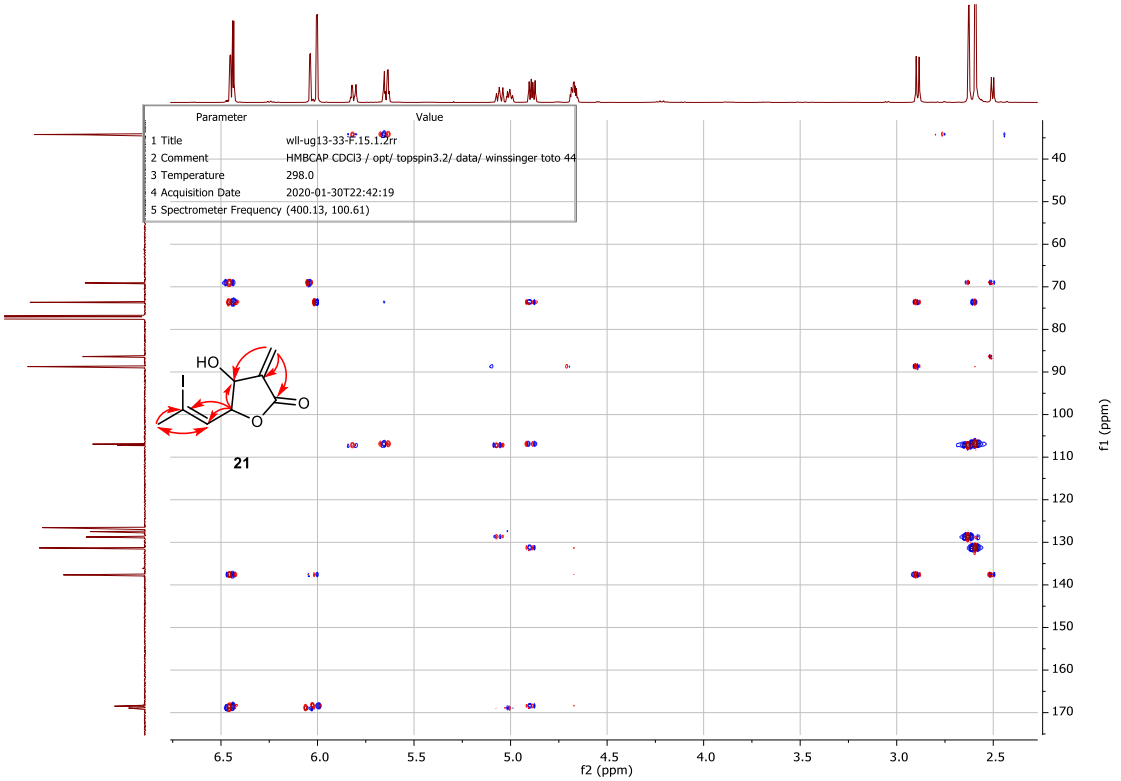
H
3
I
O
O
Me
7
5
H
H
1
21
f2 (ppm)
f1 (ppm)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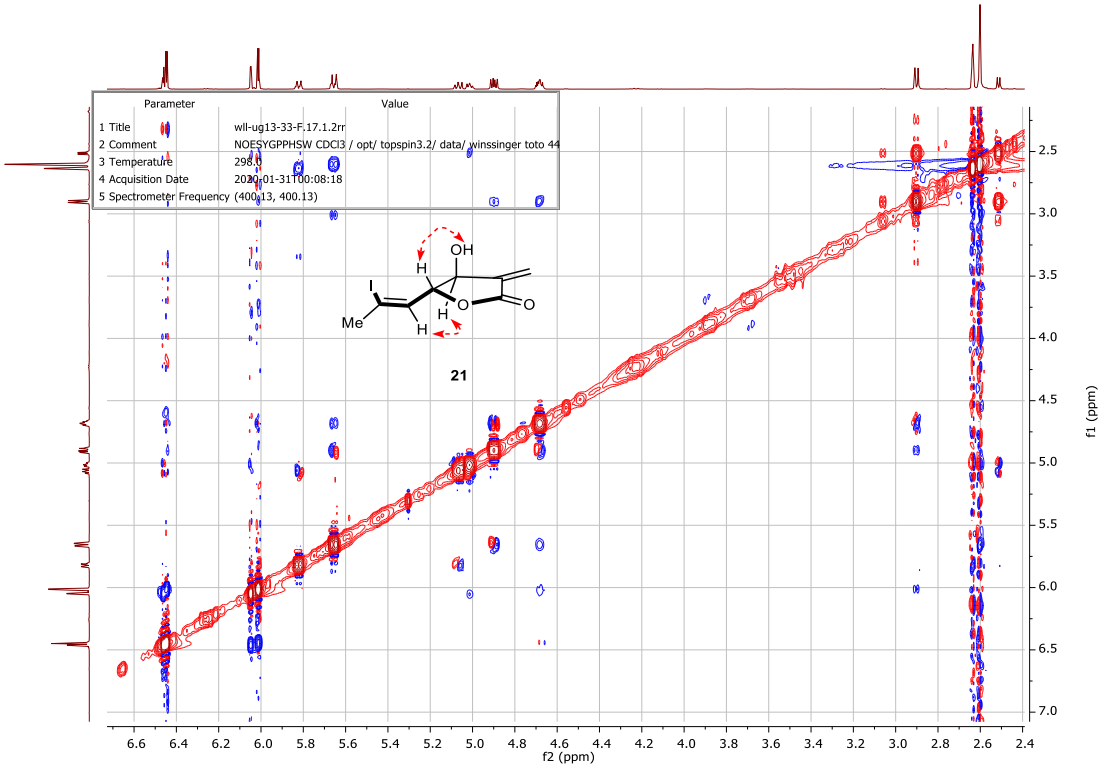
HO
O
O
21
f2 (ppm)
f1 (ppm)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2020-01-31T00:08:18
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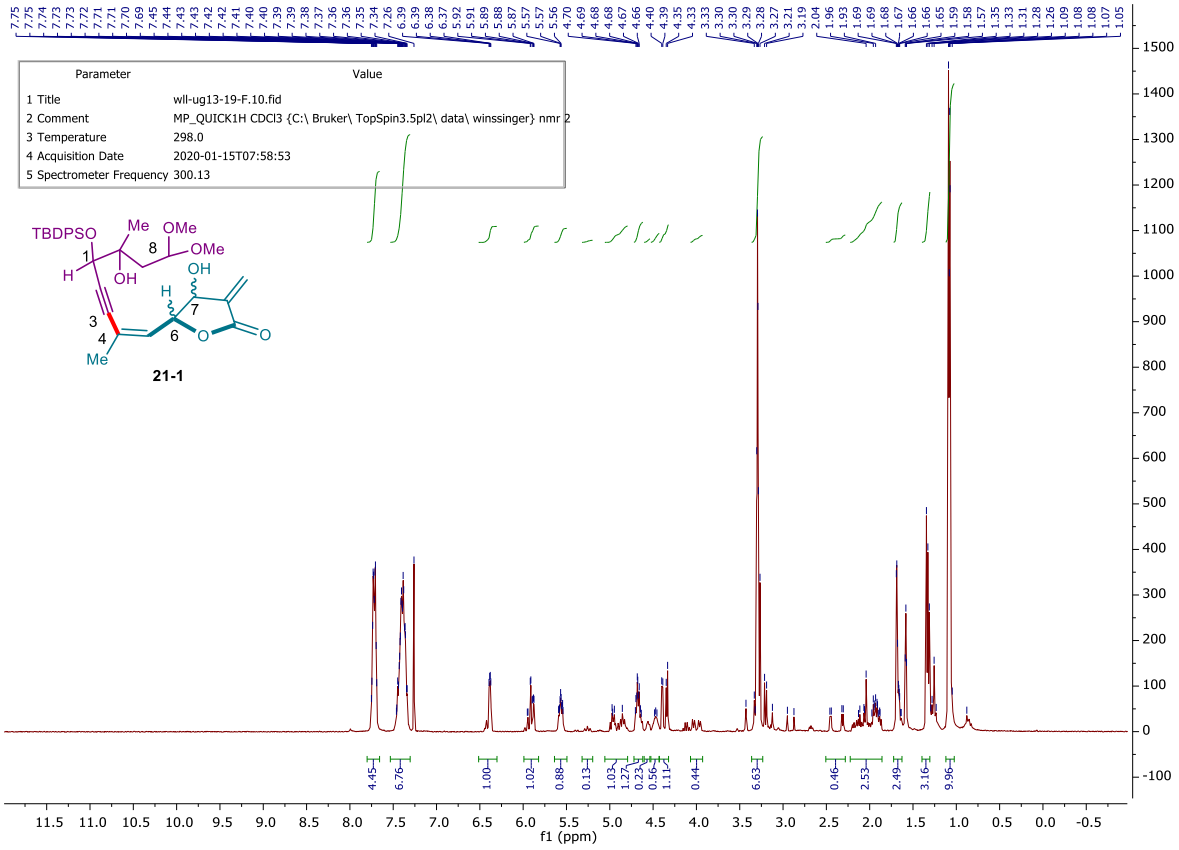
H
I
Me
H
O
H
O
21
f2 (ppm)
f1 (ppm)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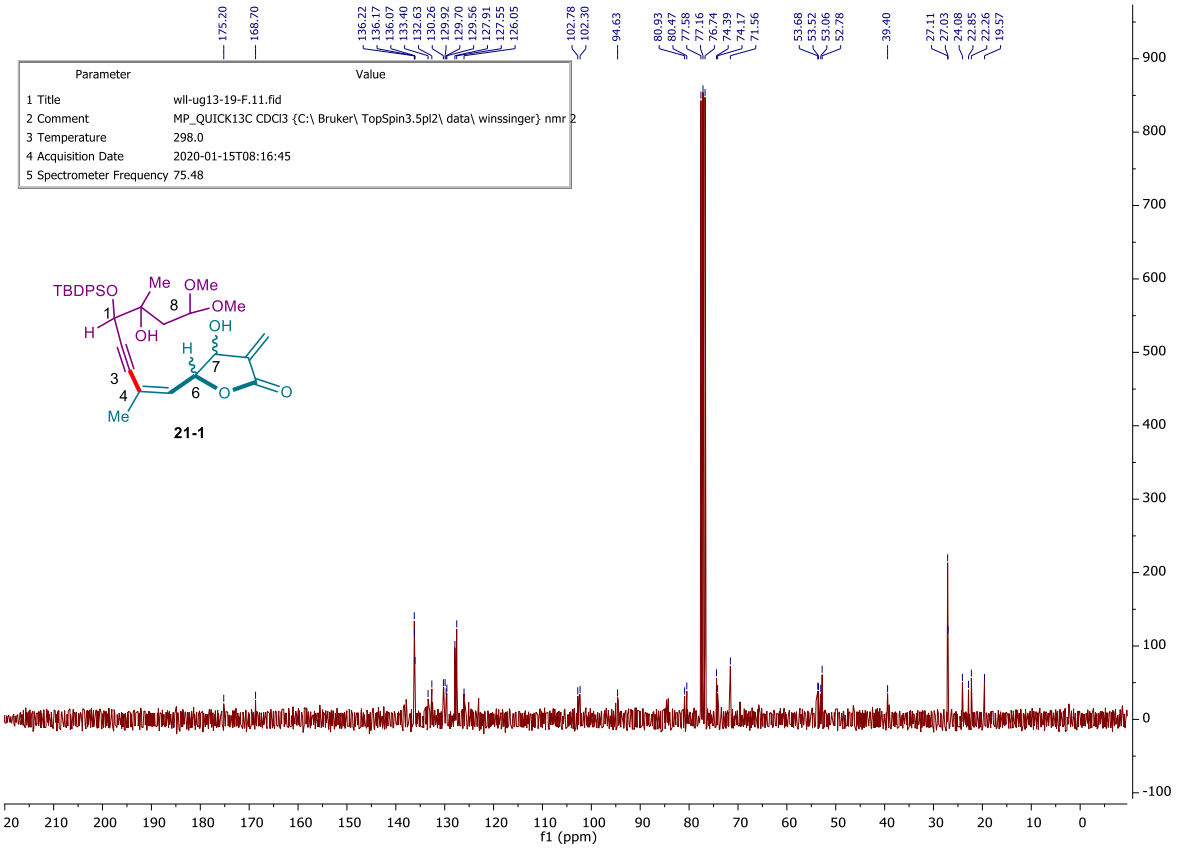
Me
OMe
OMe
OH
OH
H
Me
21-1
f1 (ppm)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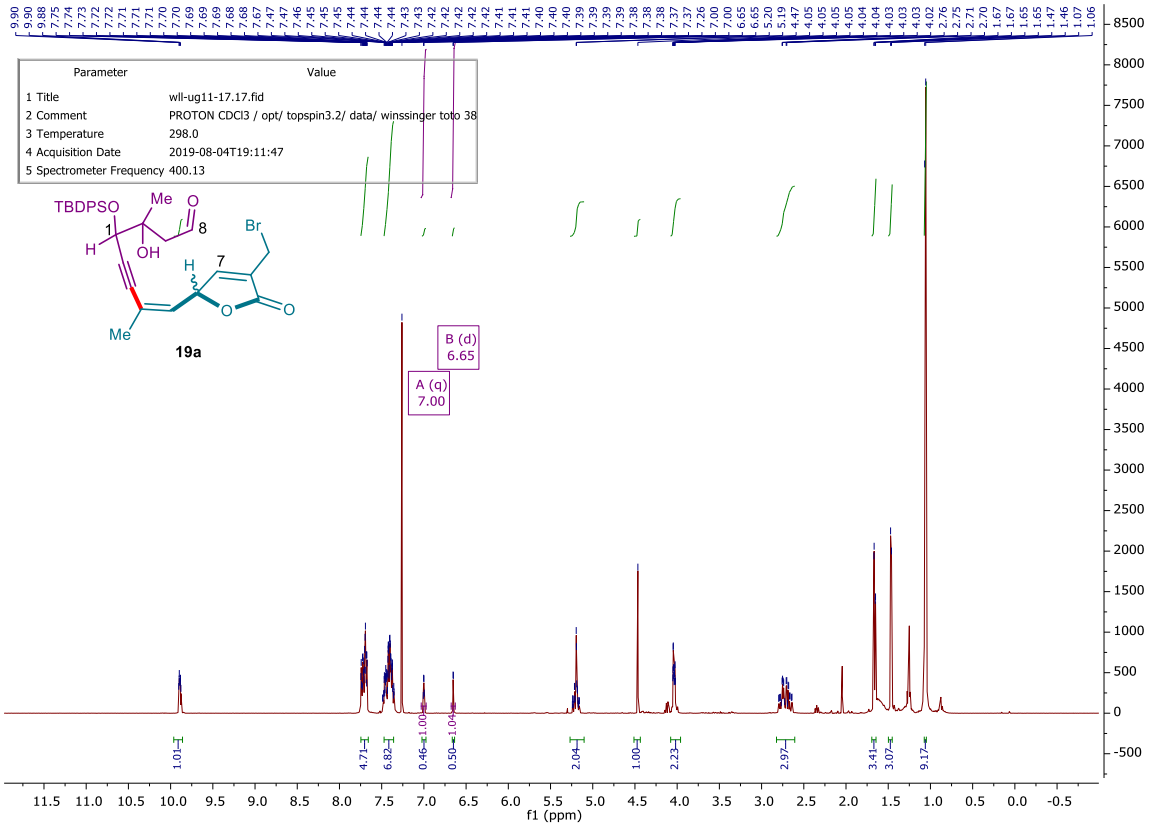
Me
OMe
OMe
OH
OH
H
Me
21-1
f1 (ppm)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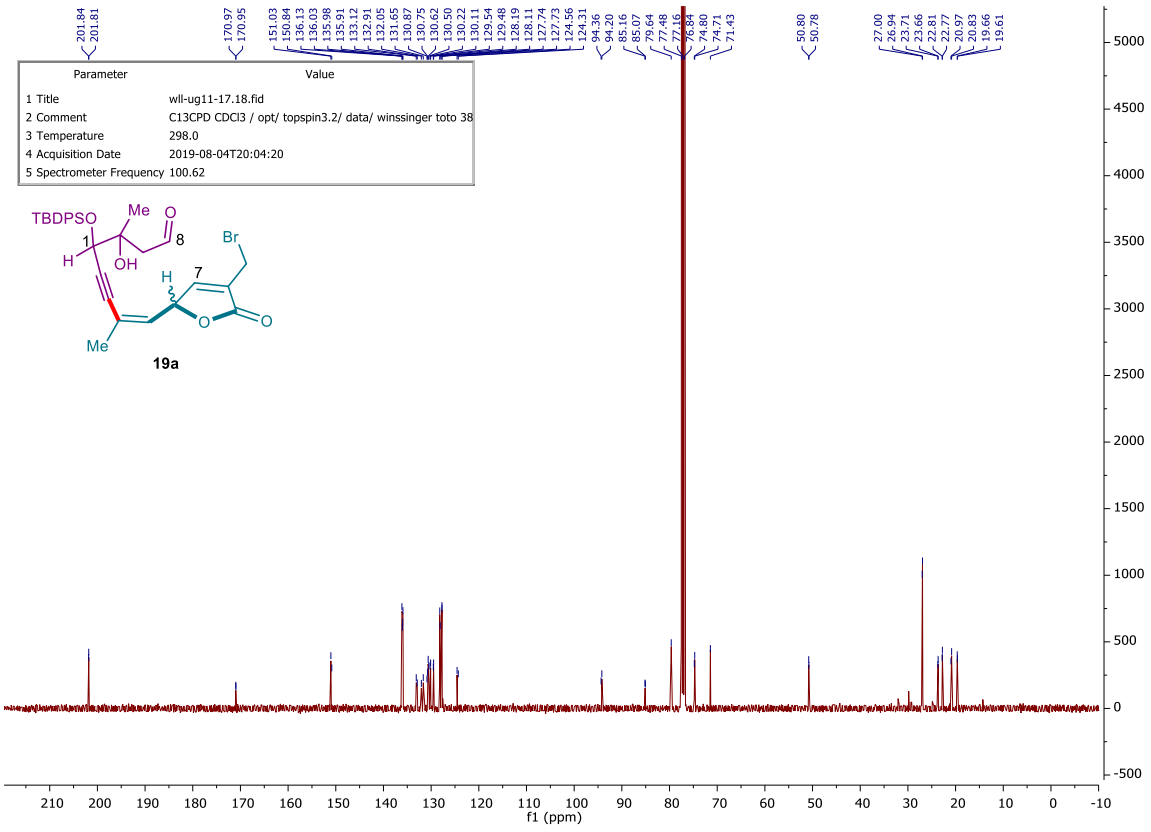
5 Spectrometer Frequency 400.13
TBDPSO
Me
O
1
8
Br
H
OH
H
7
O
O
Me
19a
B (d) 6.65
A (q) 7.00
f1 (ppm)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TBDPSO
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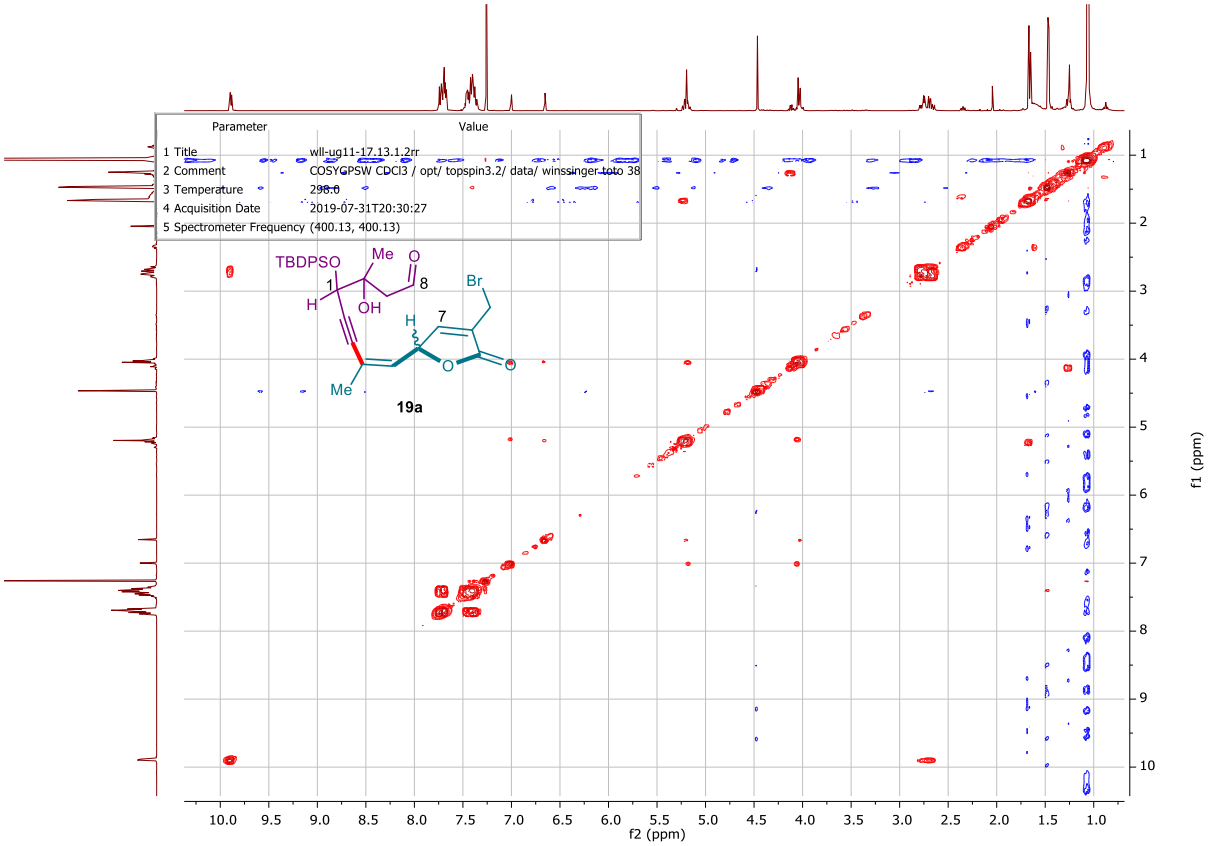
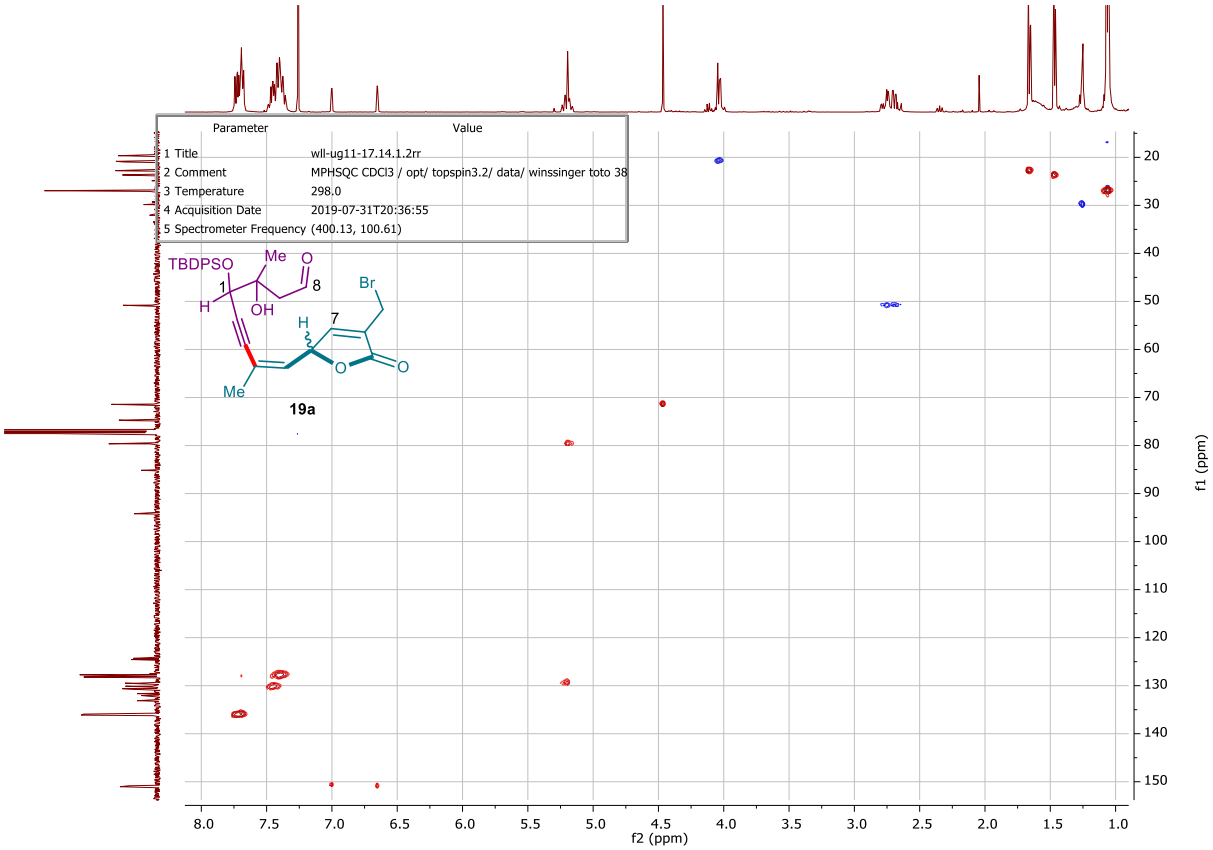
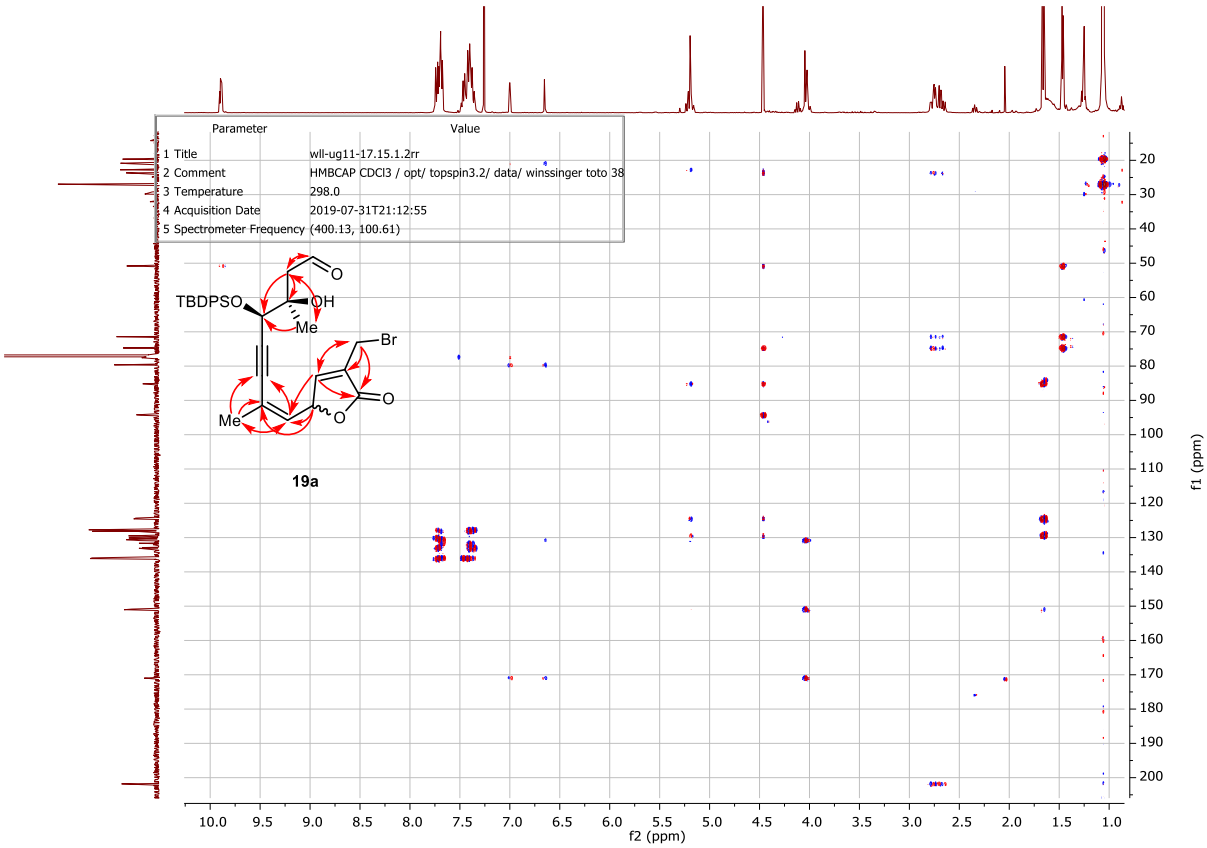
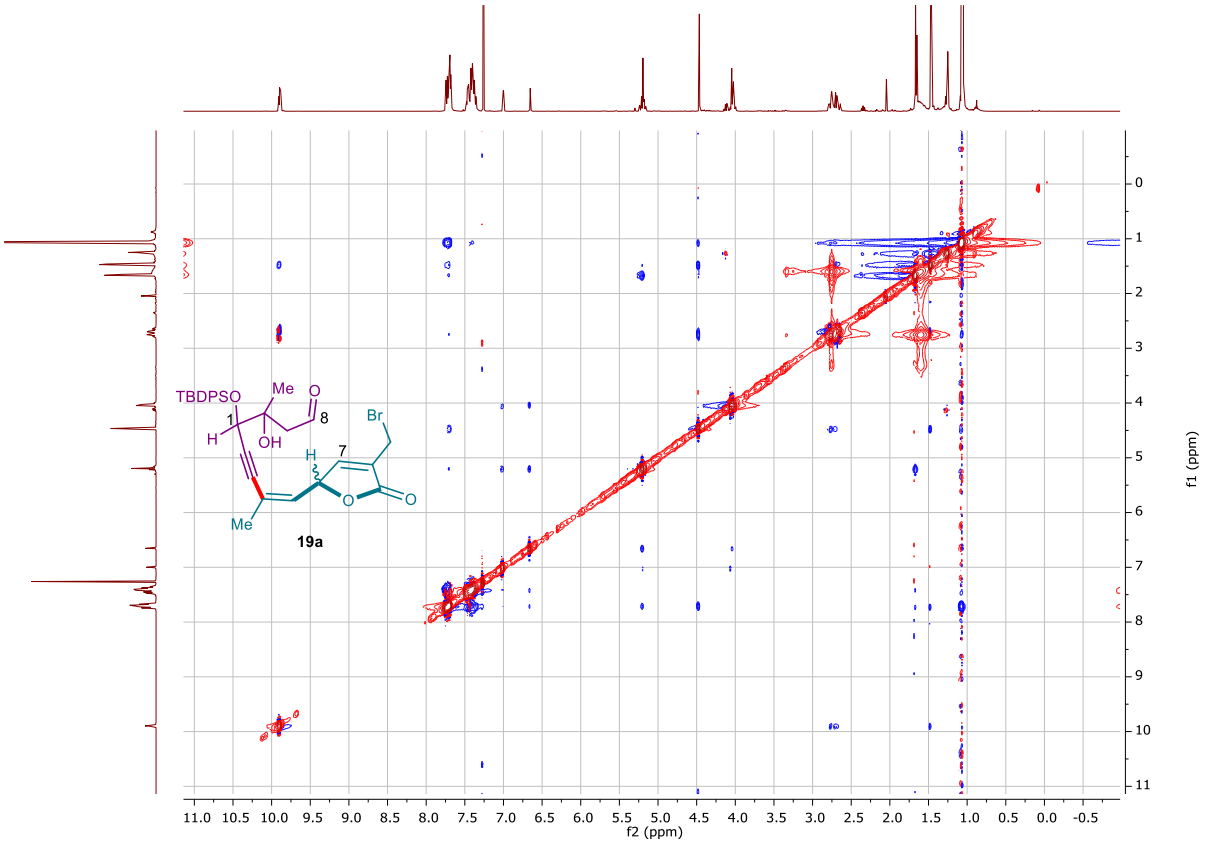
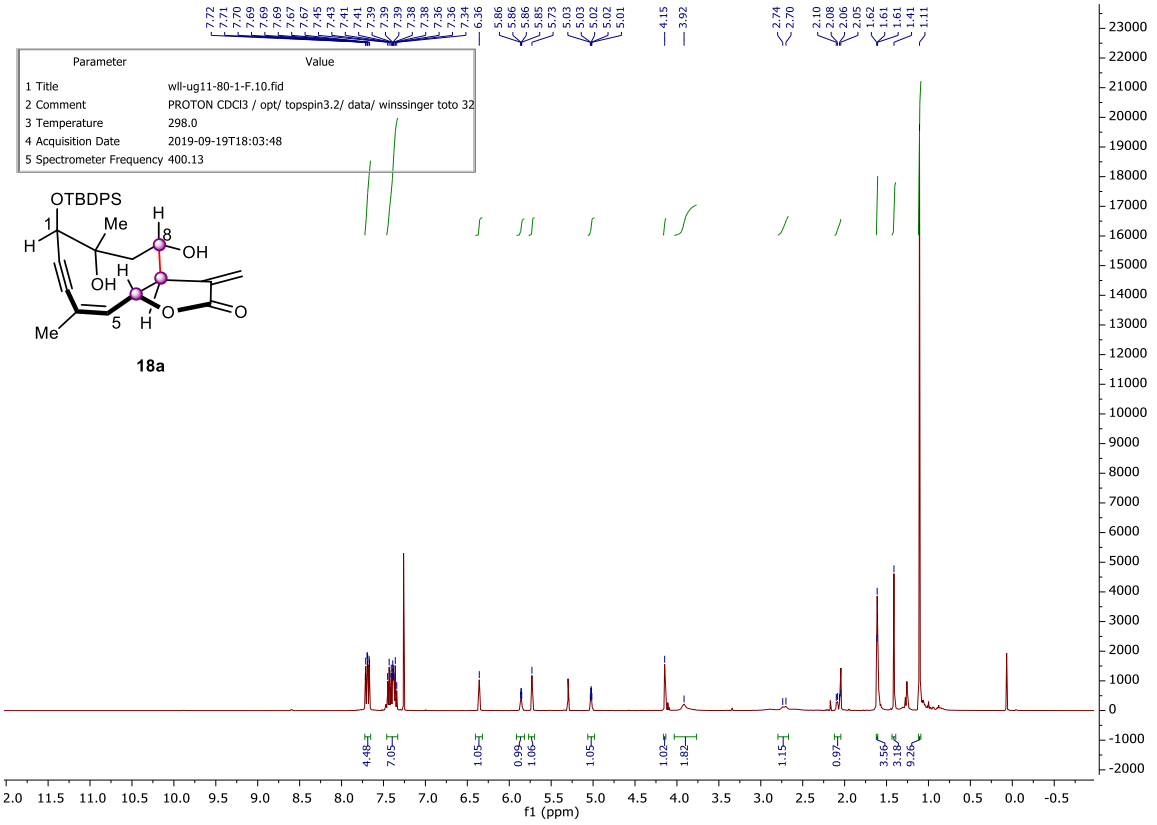
O
1
8
Br
H
OH
H
7
O
O
Me
19a
f1 (ppm)


Parameter Value
1 Title wll-ug11-17.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ topspin3.2/ data/ winssinger-toto 38
3 Temperature 298.0
4 Acquisition Date 2019-07-31T20:30:27
5 Spectrometer Frequency (400.13, 400.13)
TBDPSO
Me
O
1
8
Br
H
OH
H
7
O
Me
19a
f2 (ppm)
f1 (ppm)

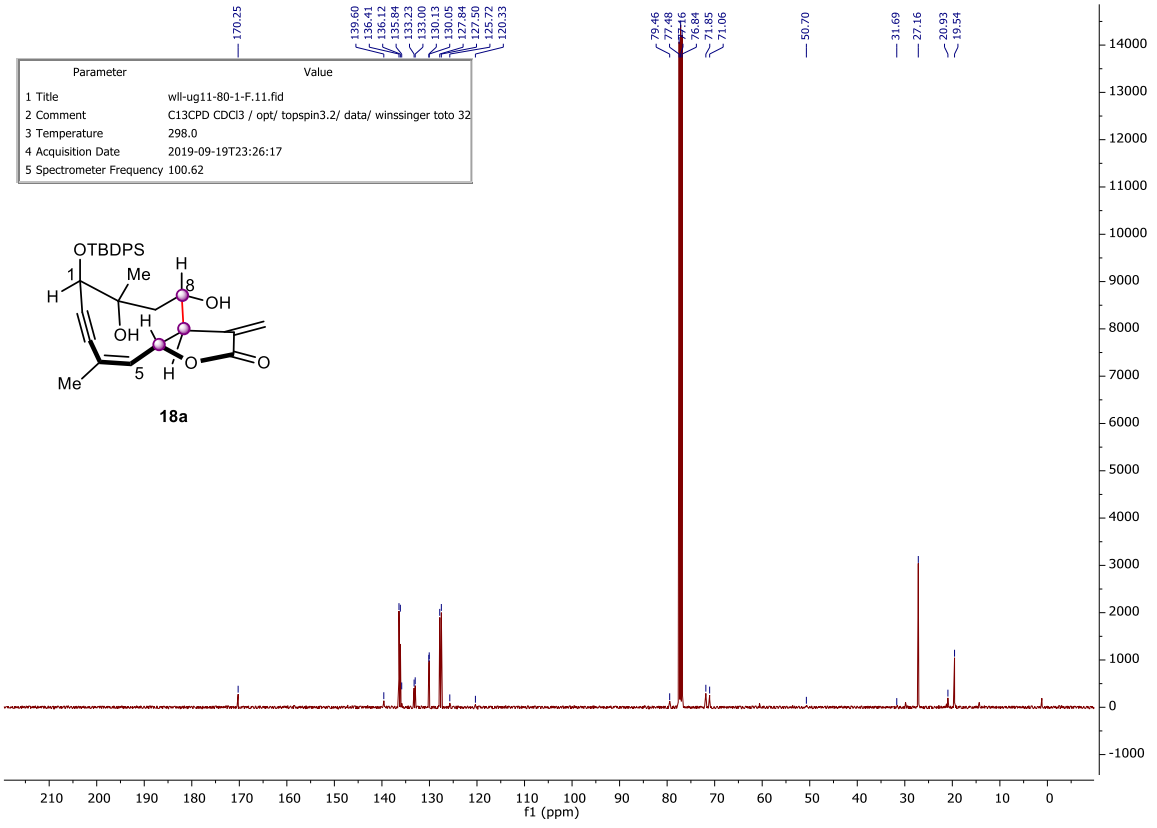

Parameter Value
1 Title wll-ug11-17.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ topspin3.2/ data/ winssinger toto 38
3 Temperature 298.0
4 Acquisition Date 2019-07-31T20:36:55
5 Spectrometer Frequency (400.13, 100.61)
TBDPSO
Me
O
1
8
Br
H
OH
H
7
O
Me
19a
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug11-17.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ topspin3.2/ data/ winssinger toto 38
3 Temperature 298.0
4 Acquisition Date 2019-07-31T21:12:55
5 Spectrometer Frequency (400.13, 100.61)
TBDPSO
OH
Me
Br
O
Me
19a
f2 (ppm)
f1 (ppm)

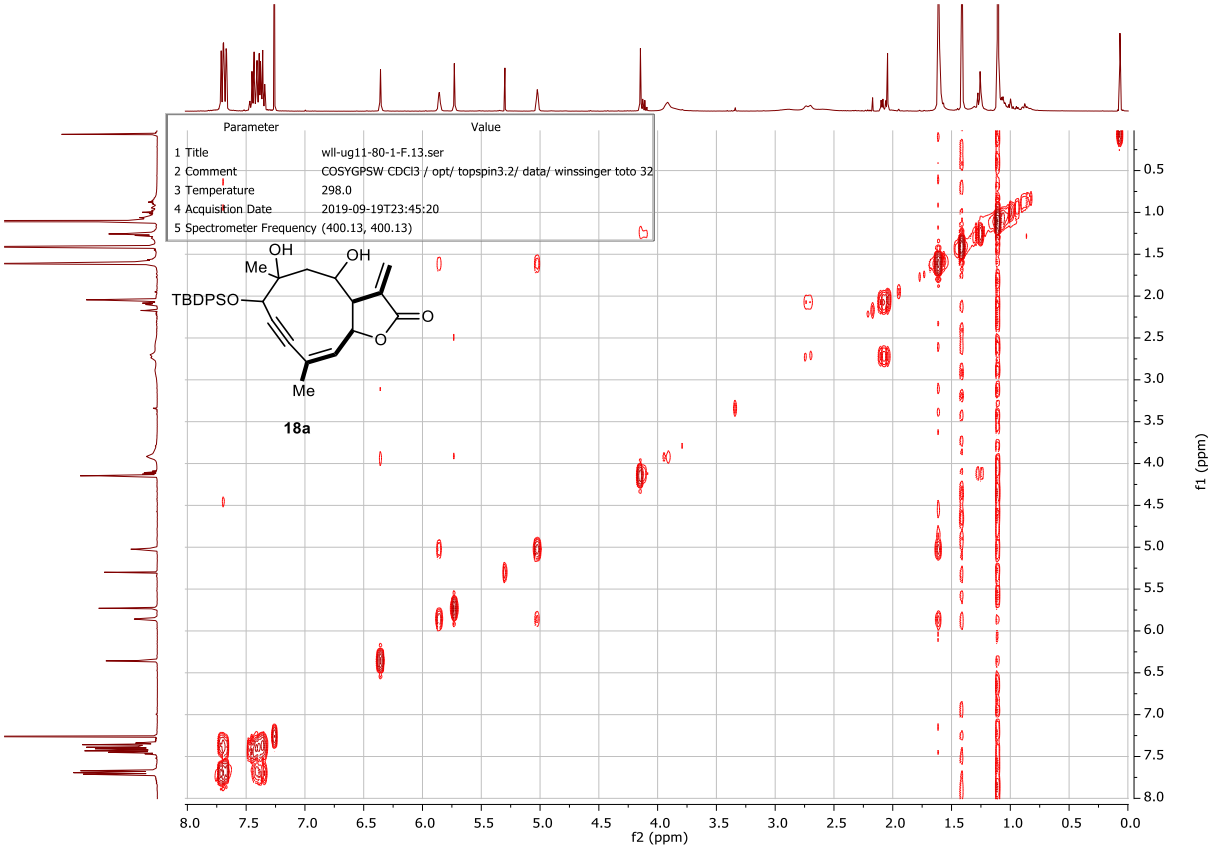

TBDPSO
Me
O
1
8
H
OH
Br
H
7
O
O
Me
19a
f2 (ppm)
f1 (ppm)

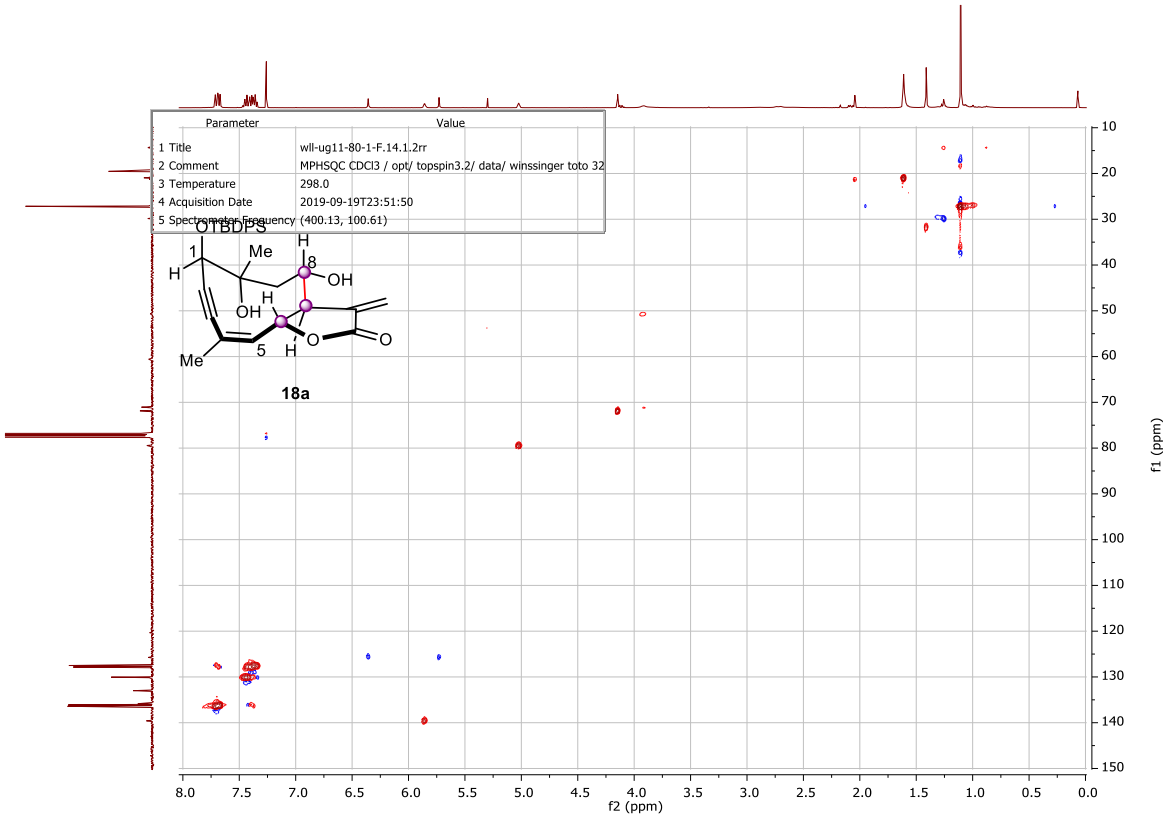

Parameter Value
1 Title wll-ug11-80-1-F.10.fid
2 Comment PROTON CDCl3 / opt/ topspin3.2/ data/ winssinger toto 32
3 Temperature 298.0
4 Acquisition Date 2019-09-19T18:03:48
5 Spectrometer Frequency 400.13
OTBDPS
Me
OH
OH
Me
O
O
f1 (ppm)

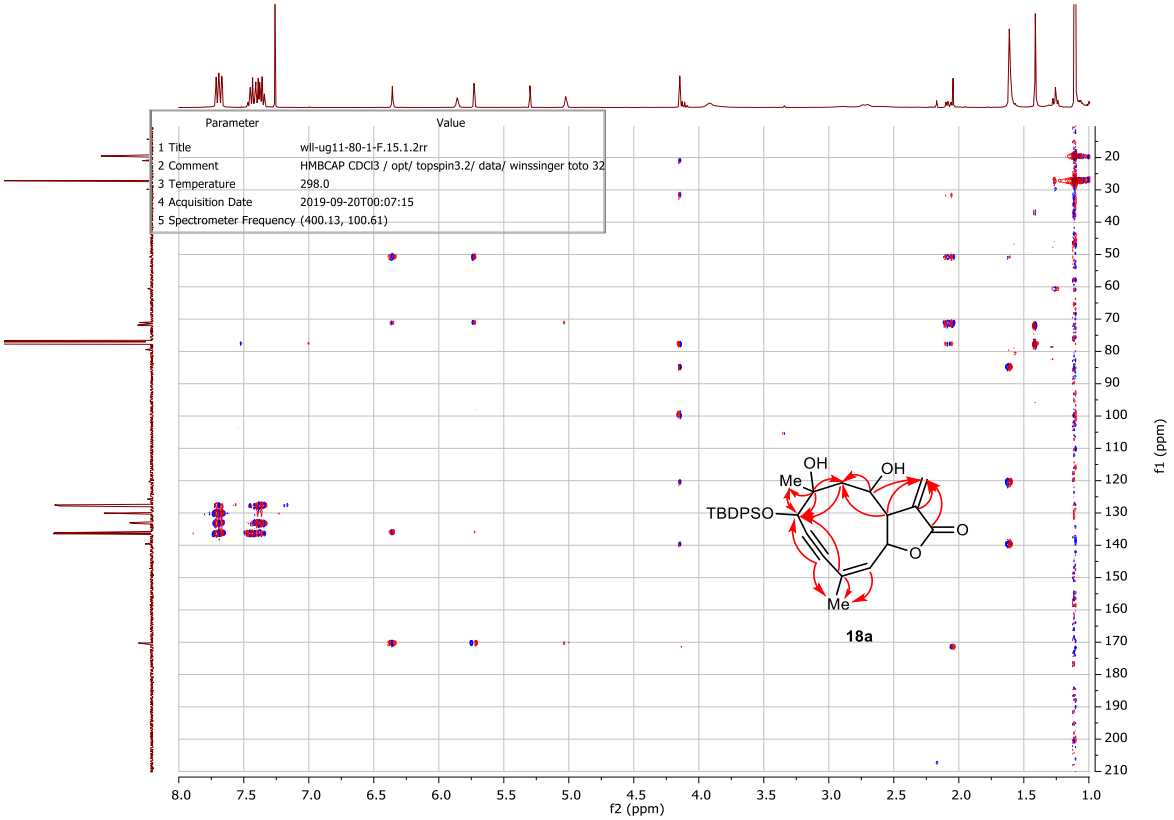
18a

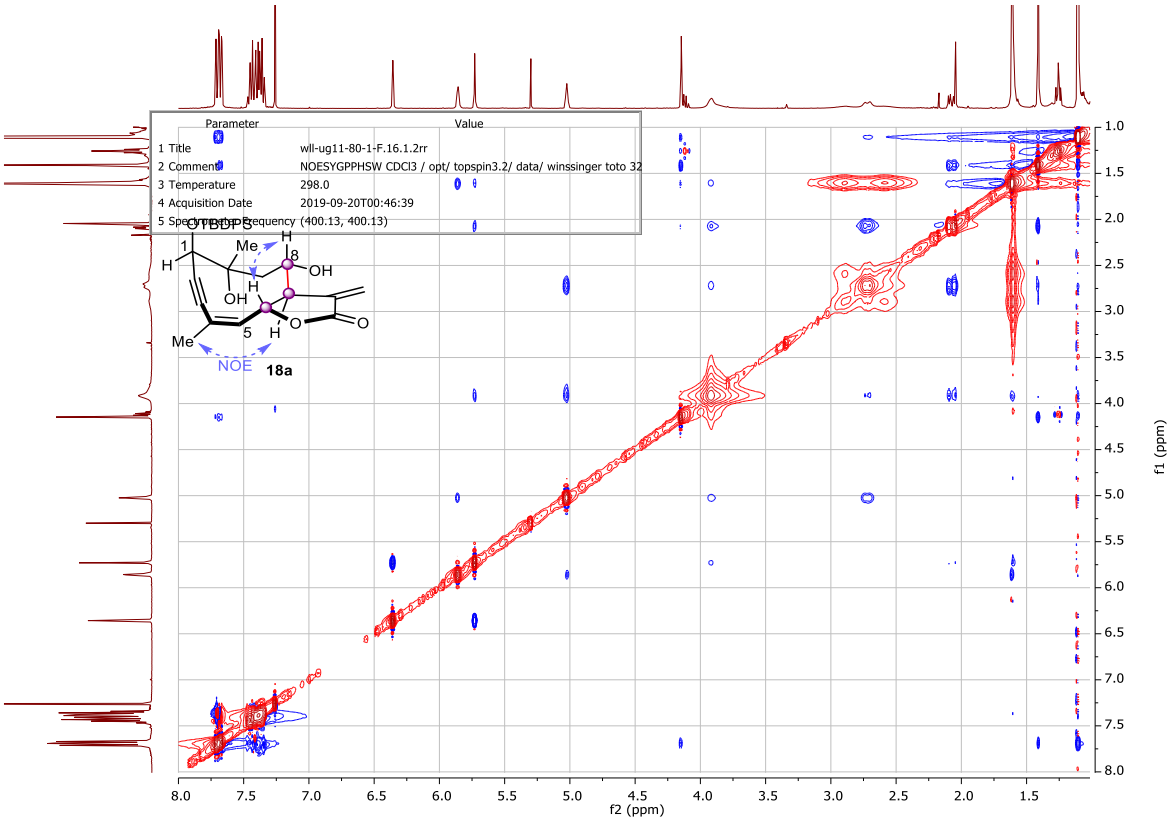

Parameter Value
1 Title wll-ug11-80-1-F.11.fid
2 Comment C13CPD CDCl3 / opt/ topspin3.2/ data/ winssinger toto 32
3 Temperature 298.0
4 Acquisition Date 2019-09-19T23:26:17
5 Spectrometer Frequency 100.62
OTBDPS
Me
OH
OH
Me
O
O
f1 (ppm)

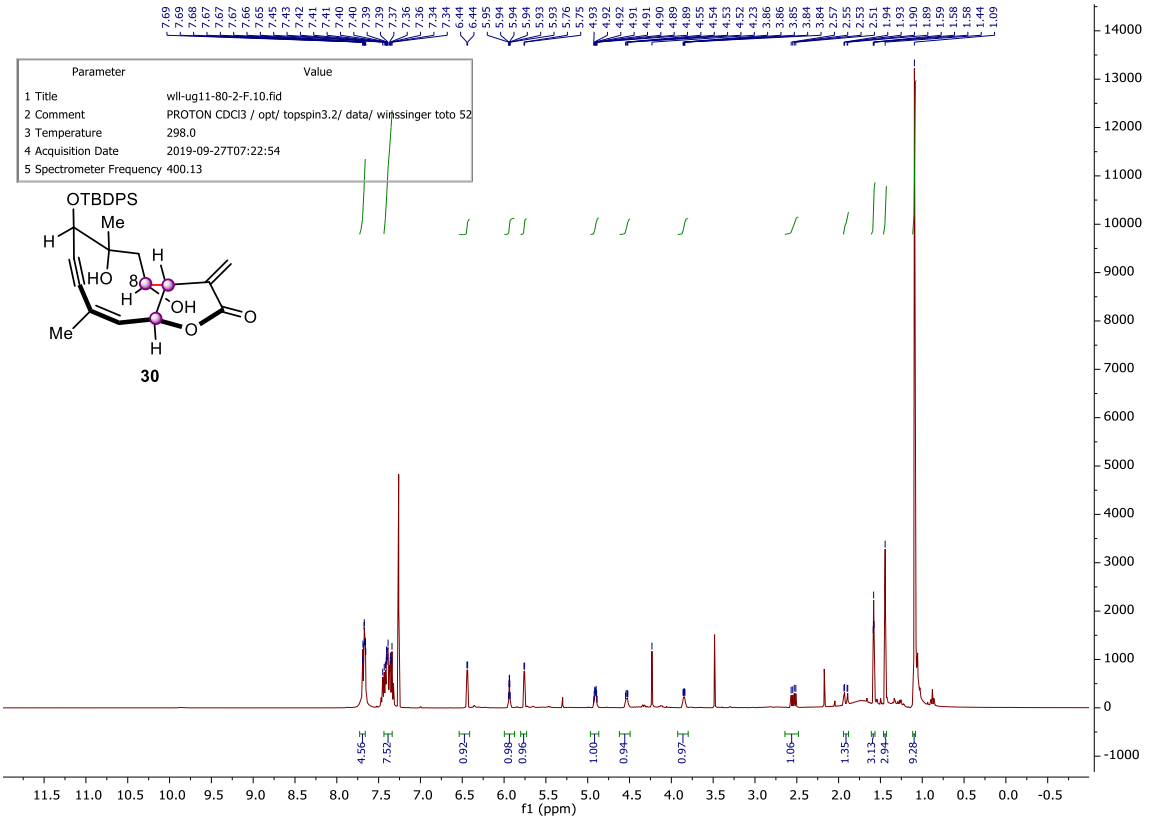
18a

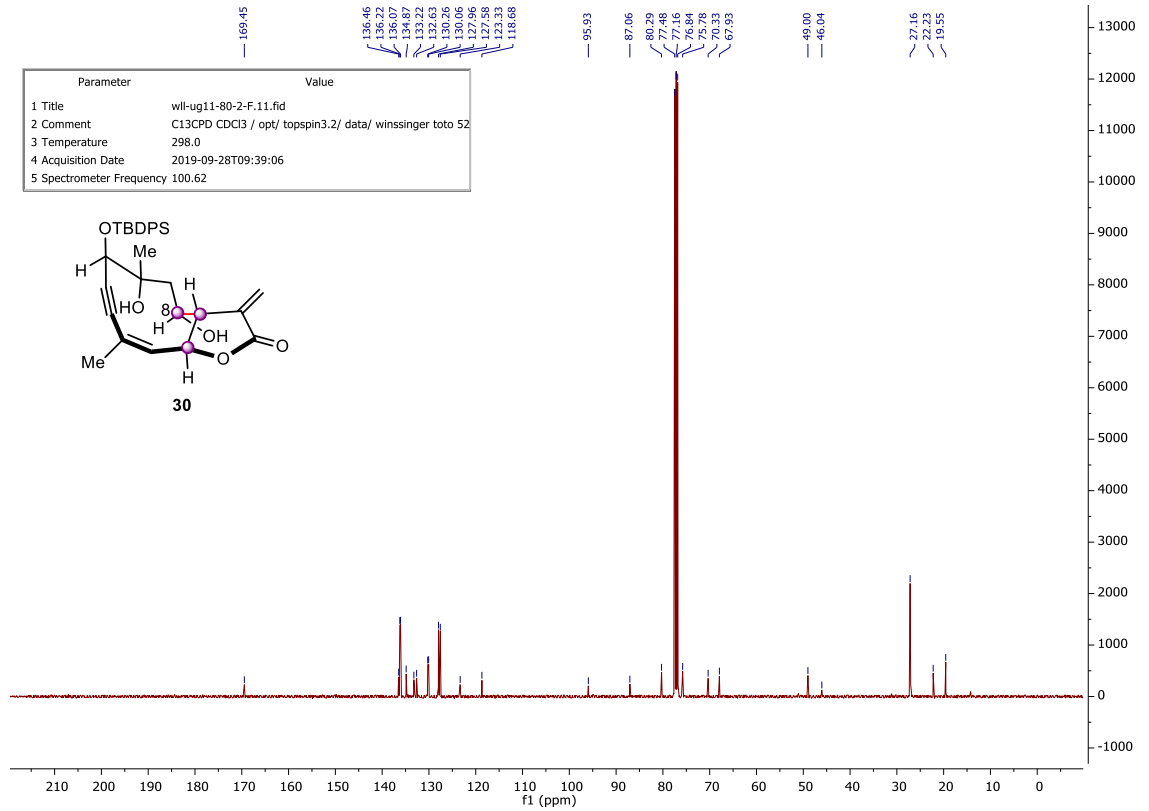

Parameter Value
1 Title wll-ug11-80-1-F.13.ser
2 Comment COSYGPSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 32
3 Temperature 298.0
4 Acquisition Date 2019-09-19T23:45:20
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
OH
TBDPSO
O
O
Me
18a
f2 (ppm)
f1 (ppm)

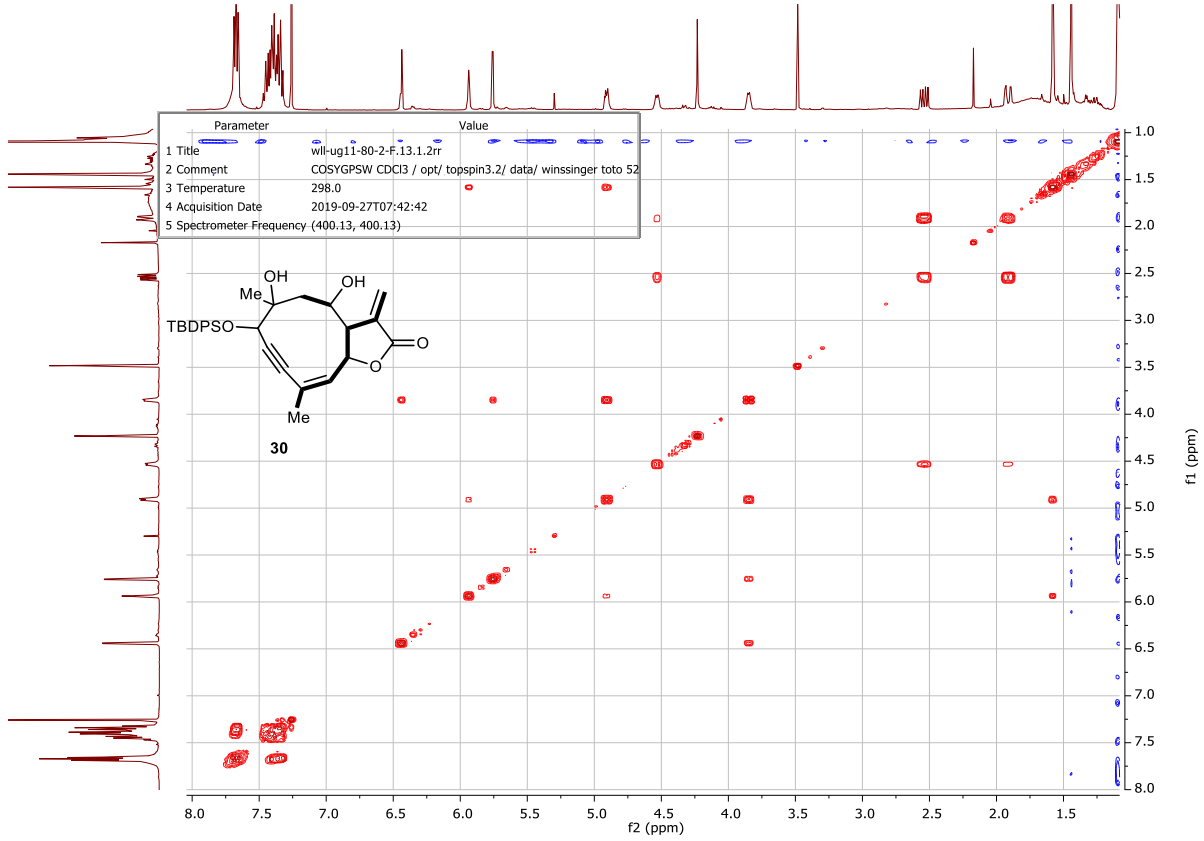

Parameter Value
1 Title wll-ug11-80-1-F.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ topspin3.2/ data/ winssinger toto 32
3 Temperature 298.0
4 Acquisition Date 2019-09-19T23:51:50
5 Spectrometer Frequency (400.13, 100.61)
OTBDPS
1
Me
H
8
OH
H
H
OH
O
O
5
H
Me
18a
f2 (ppm)
f1 (ppm)

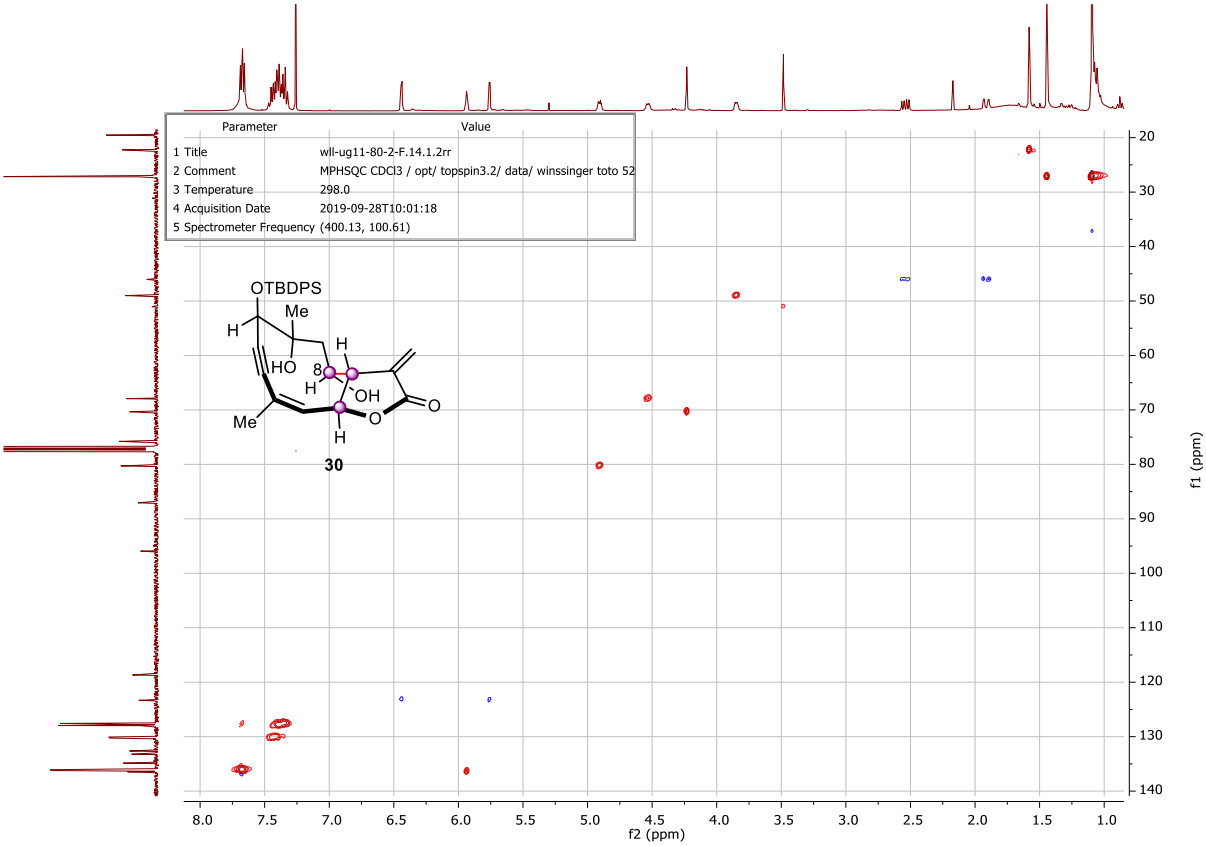

Parameter
Value
1 Title
wll-ug11-80-1-F.15.1.2rr
2 Comment
HMBCAP CDCl3 / opt/ topspin3.2/ data/ winssinger toto 32
3 Temperature
298.0
4 Acquisition Date
2019-09-20T00:07:15
5 Spectrometer Frequency (400.13, 100.61)
OH
OH
Me
TBDPSO
O
O
Me
18a
f2 (ppm)
f1 (ppm)

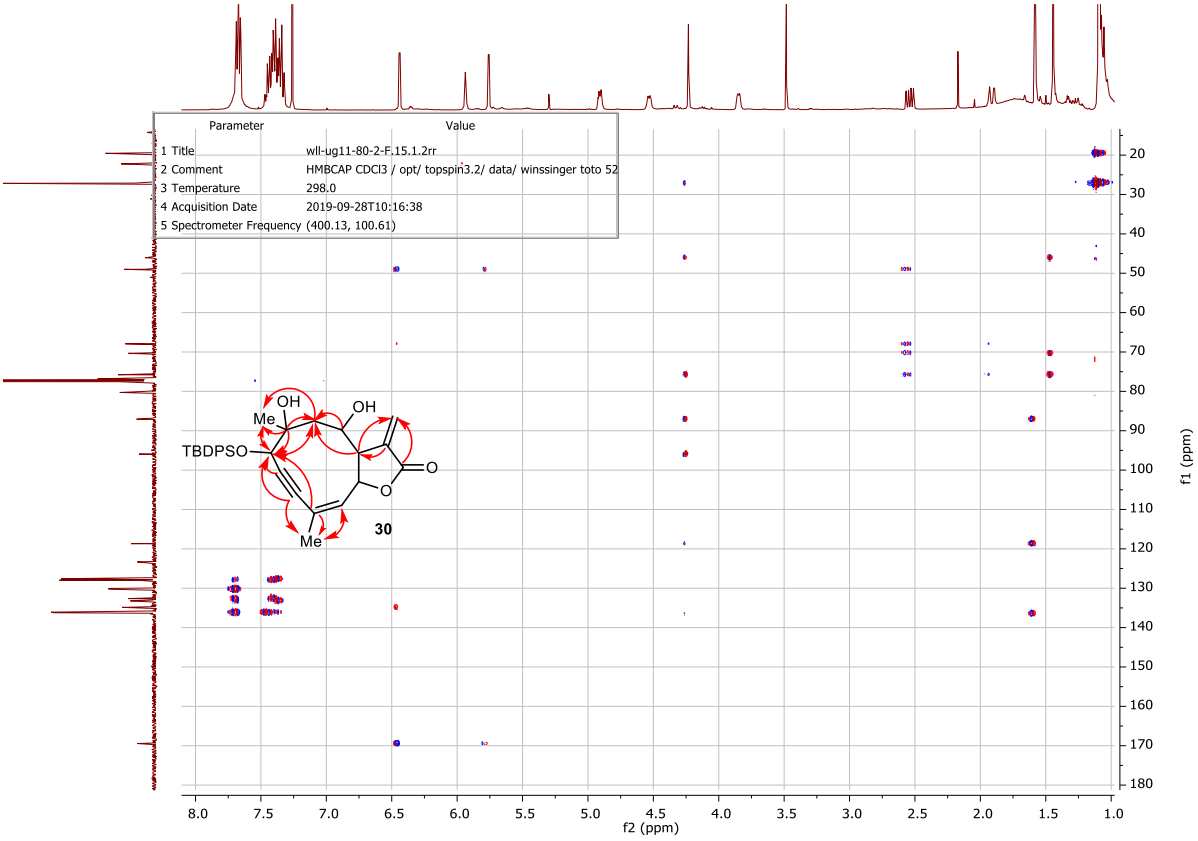

Parameter
Value
1 Title
wll-ug11-80-1-F.16.1.2rr
2 Comment
NOESYGPPHSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 32
3 Temperature
298.0
4 Acquisition Date
2019-09-20T00:46:39
5 Spectrometer Frequency (400.13, 400.13)
OTBDPS
H
1
Me
8
H
OH
H
OH
O
O
Me
5
H
NOE
18a
f2 (ppm)
f1 (ppm)

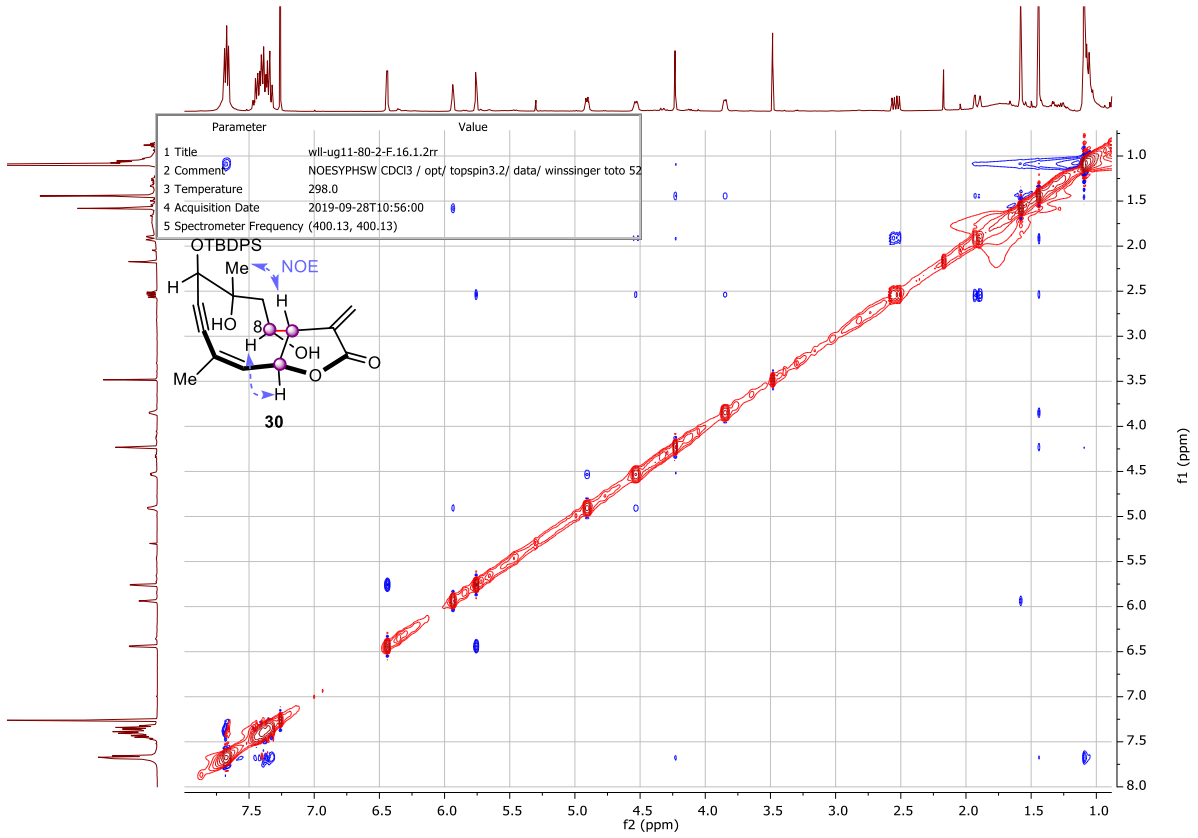

Parameter Value
1 Title wll-ug11-80-2-F.10.fid
2 Comment PROTON CDCl3 / opt/ topspin3.2/ data/ winssinger toto 52
3 Temperature 298.0
4 Acquisition Date 2019-09-27T07:22:54
5 Spectrometer Frequency 400.13
OTBDPS
Me
H
HO
8
H
OH
O
Me
H
30
f1 (ppm)

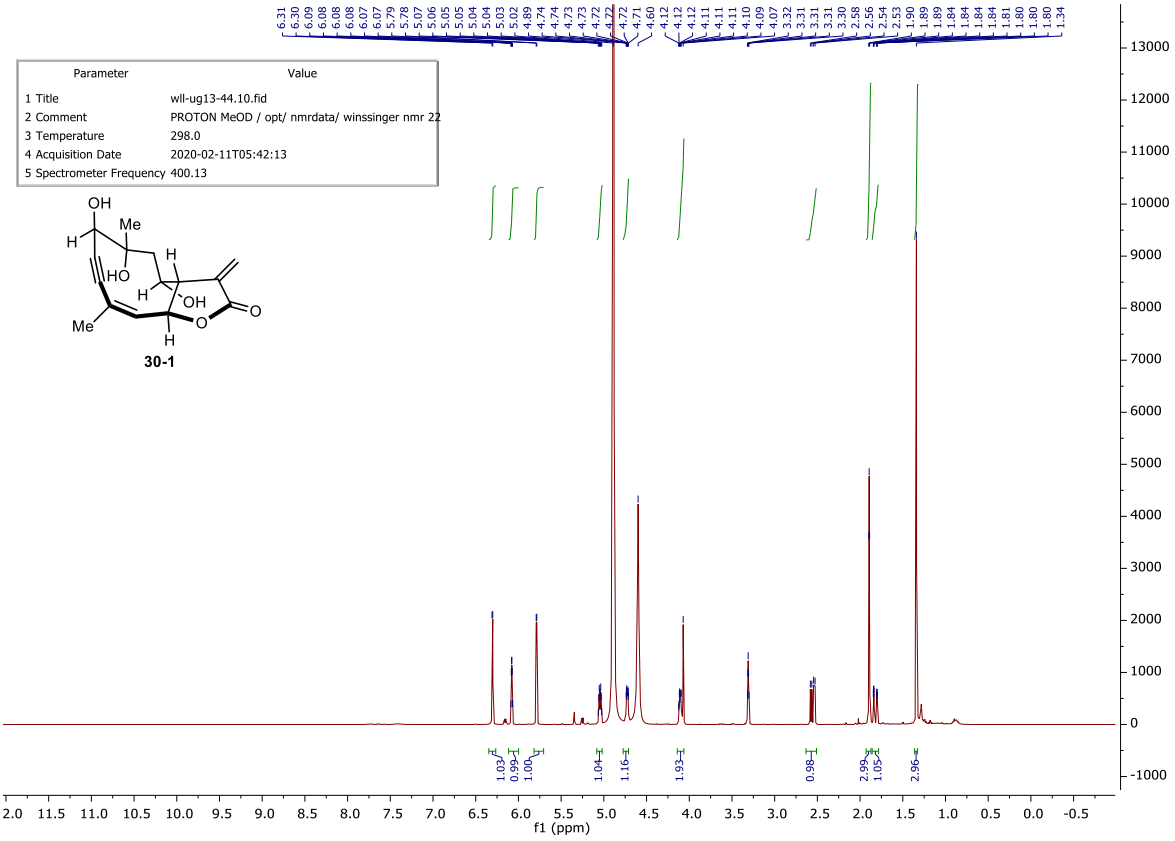

Parameter Value
1 Title wll-ug11-80-2-F.11.fid
2 Comment C13CPD CDCl3 / opt/ topspin3.2/ data/ winssinger toto 52
3 Temperature 298.0
4 Acquisition Date 2019-09-28T09:39:06
5 Spectrometer Frequency 100.62
OTBDPS
Me
H
HO
8
H
OH
O
Me
H
30
f1 (ppm)

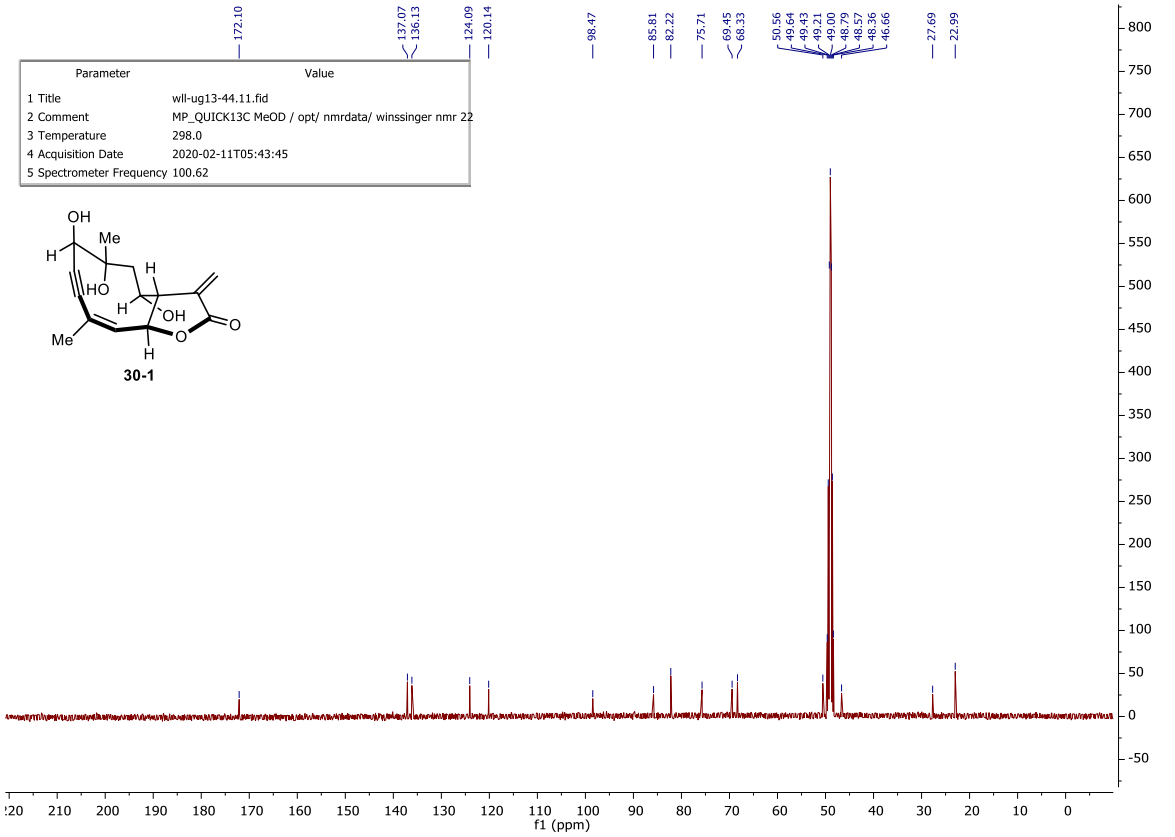

Parameter Value
1 Title wll-ug11-80-2-F.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 52
3 Temperature 298.0
4 Acquisition Date 2019-09-27T07:42:42
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
OH
TBDPSO
O
O
Me
30
f2 (ppm)
f1 (ppm)

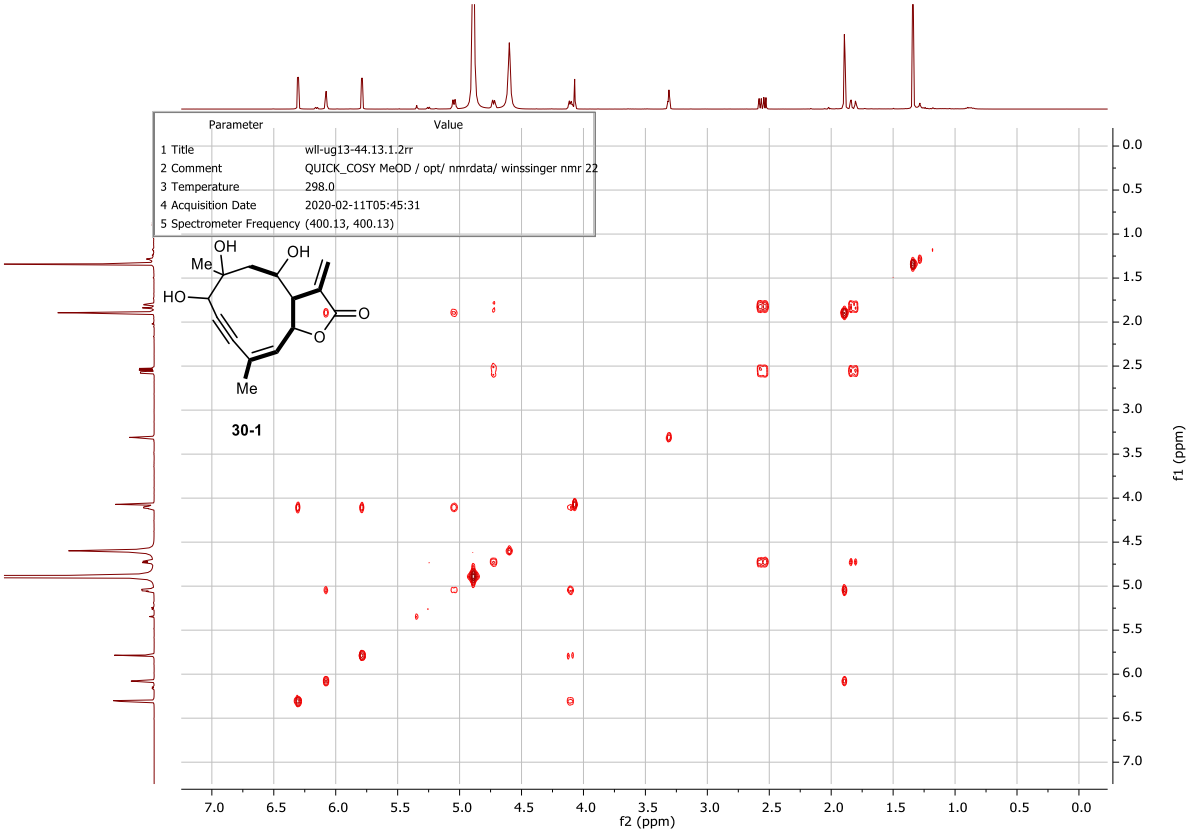

Parameter Value
1 Title wll-ug11-80-2-F.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ topspin3.2/ data/ winssinger toto 52
3 Temperature 298.0
4 Acquisition Date 2019-09-28T10:01:18
5 Spectrometer Frequency (400.13, 100.61)
OTBDPS
Me
H
H
HO
8
H
OH
O
O
Me
H
30
f2 (ppm)
f1 (ppm)

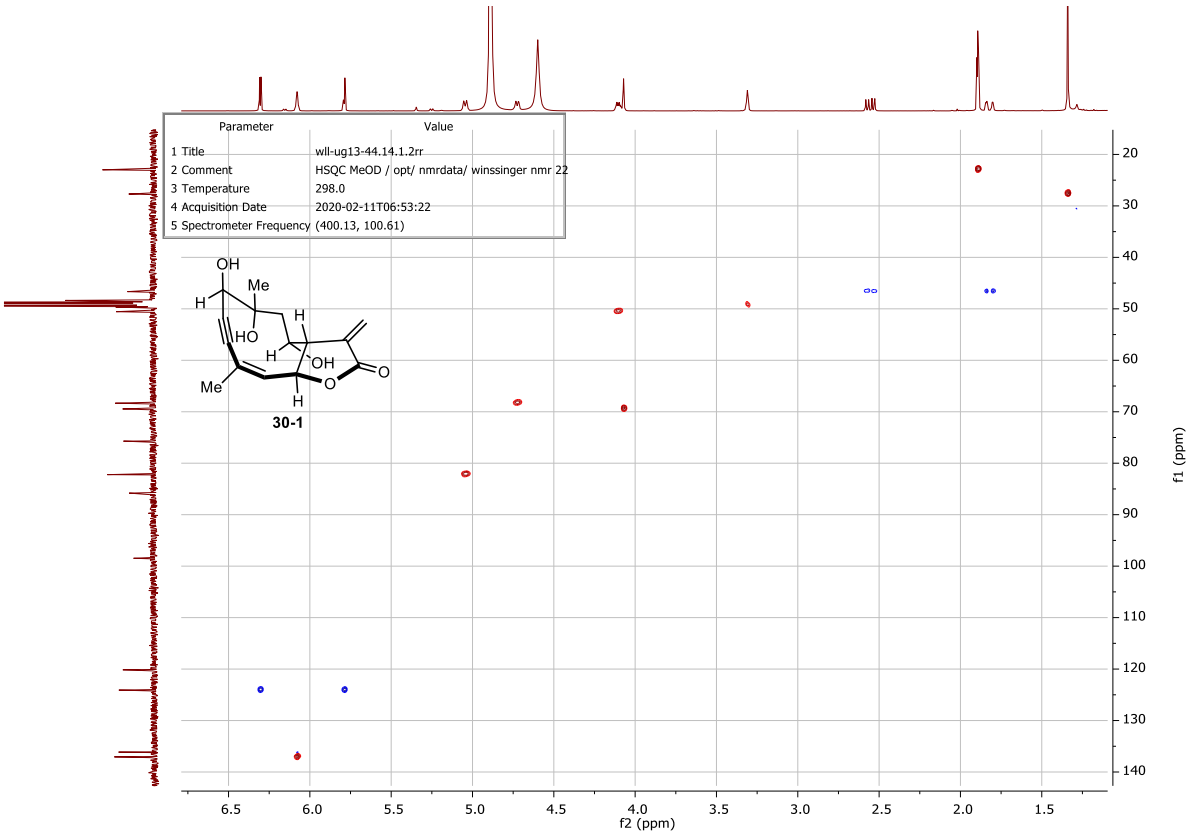

Parameter Value
1 Title wll-ug11-80-2-F.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ topspin3.2/ data/ winssinger toto 52
3 Temperature 298.0
4 Acquisition Date 2019-09-28T10:16:38
5 Spectrometer Frequency (400.13, 100.61)
OH
Me
OH
TBDPSO
O
O
Me
30
f2 (ppm)
f1 (ppm)

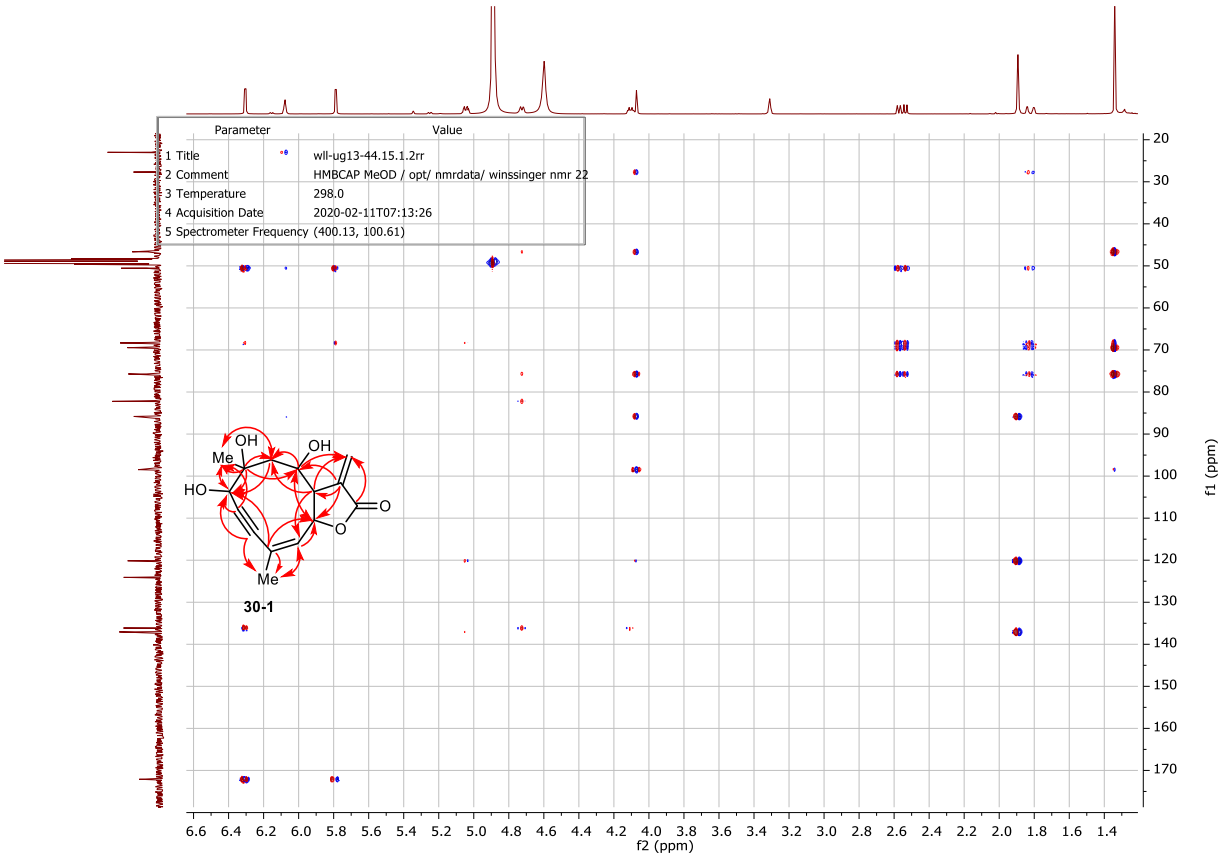

Parameter Value
1 Title wll-ug11-80-2-F.16.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 52
3 Temperature 298.0
4 Acquisition Date 2019-09-28T10:56:00
5 Spectrometer Frequency (400.13, 400.13)
OTBDPS
Me
NOE
H
H
HO
8
H
OH
O
Me
H
30
f2 (ppm)
f1 (ppm)

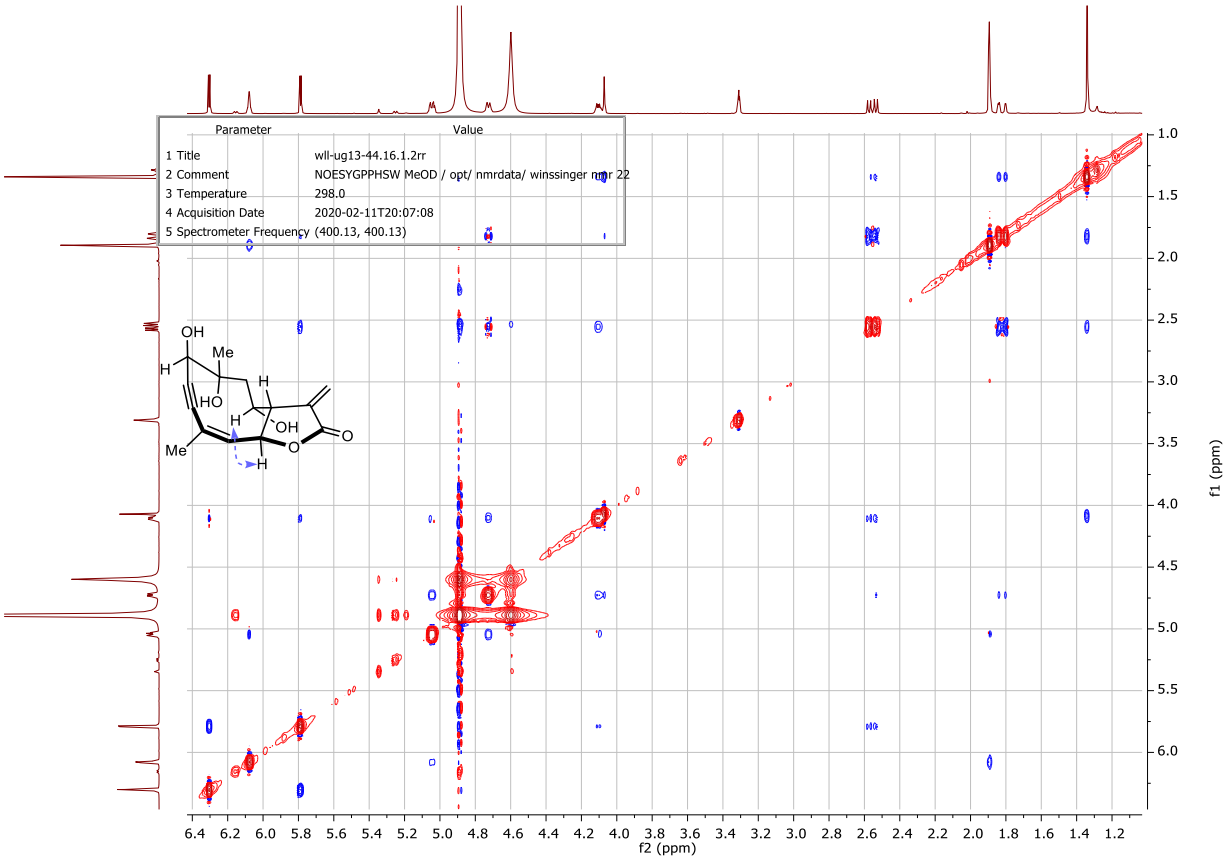

Parameter Value
1 Title wll-ug13-44.10.fid
2 Comment PROTON MeOD / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-11T05:42:13
5 Spectrometer Frequency 400.13
30-1
f1 (ppm)

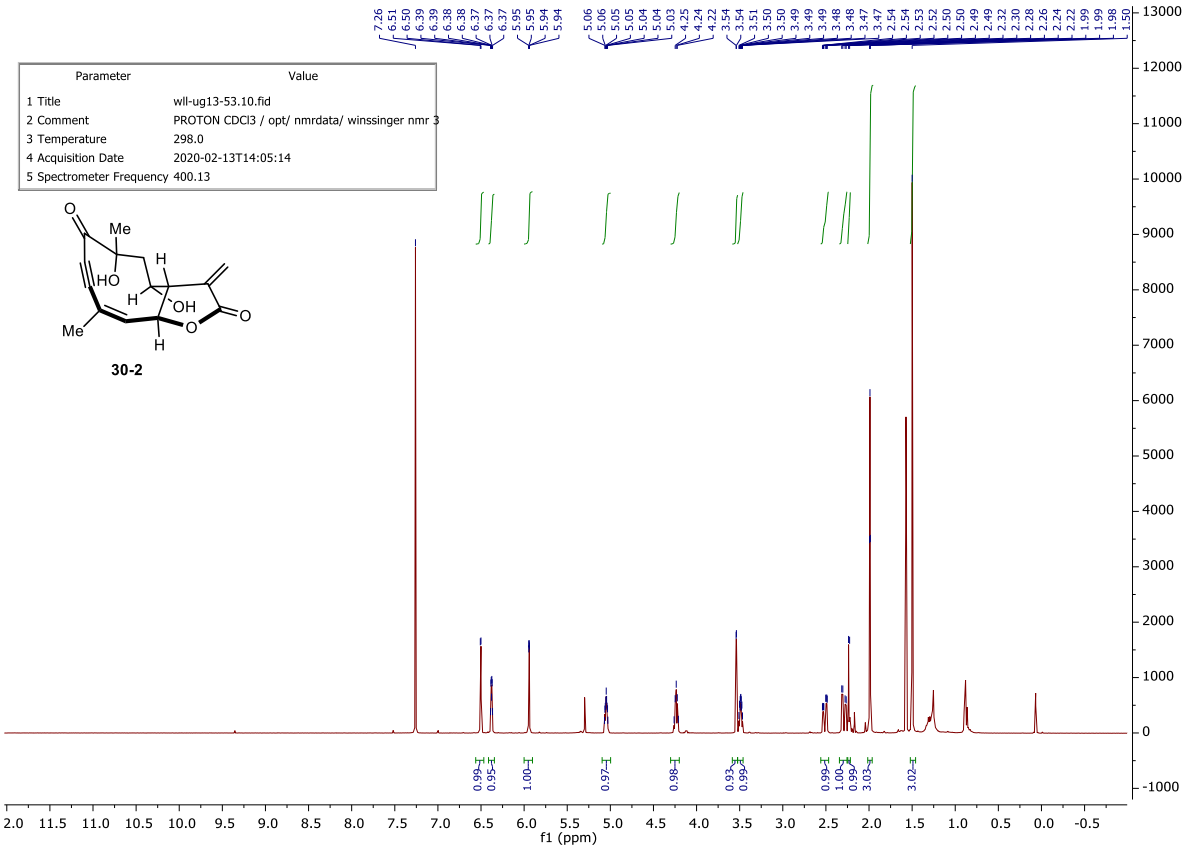

Parameter Value
1 Title wll-ug13-44.11.fid
2 Comment MP_QUICK13C MeOD / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-11T05:43:45
5 Spectrometer Frequency 100.62
30-1
f1 (ppm)

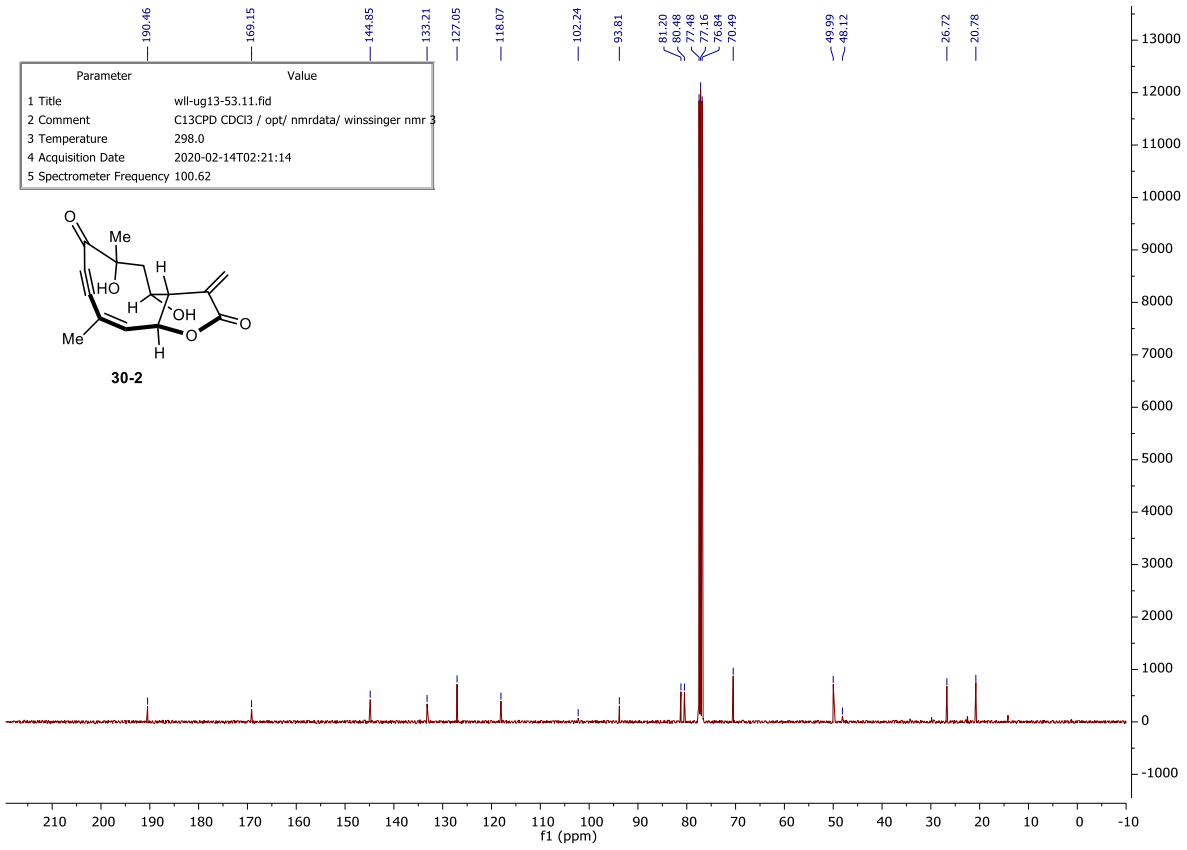

Parameter Value
1 Title wll-ug13-44.13.1.2rr
2 Comment QUICK_COSY MeOD / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-11T05:45:31
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
OH
HO
O
O
Me
30-1
f2 (ppm)
f1 (ppm)

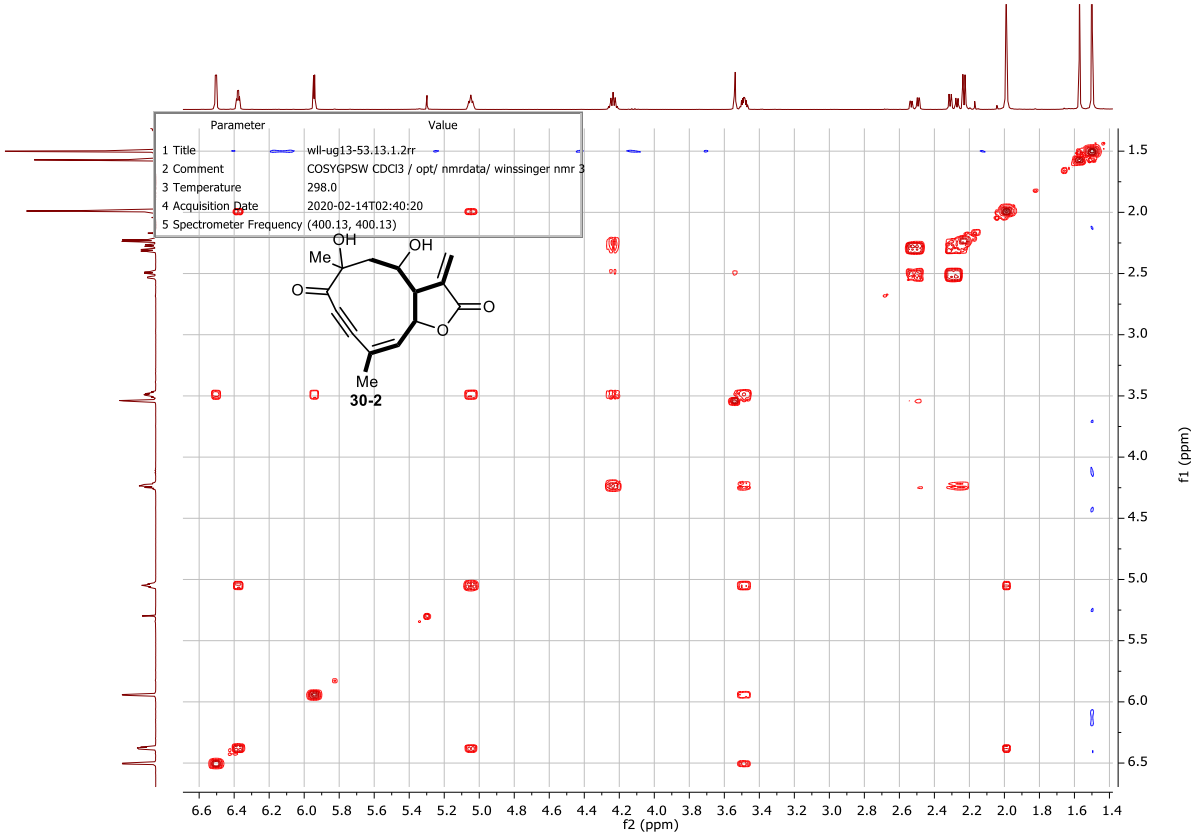

Parameter Value
1 Title wll-ug13-44.14.1.2rr
2 Comment HSQC MeOD / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-11T06:53:22
5 Spectrometer Frequency (400.13, 100.61)
OH
H
Me
HO
H
H
OH
O
O
Me
H
30-1
f2 (ppm)
f1 (ppm)

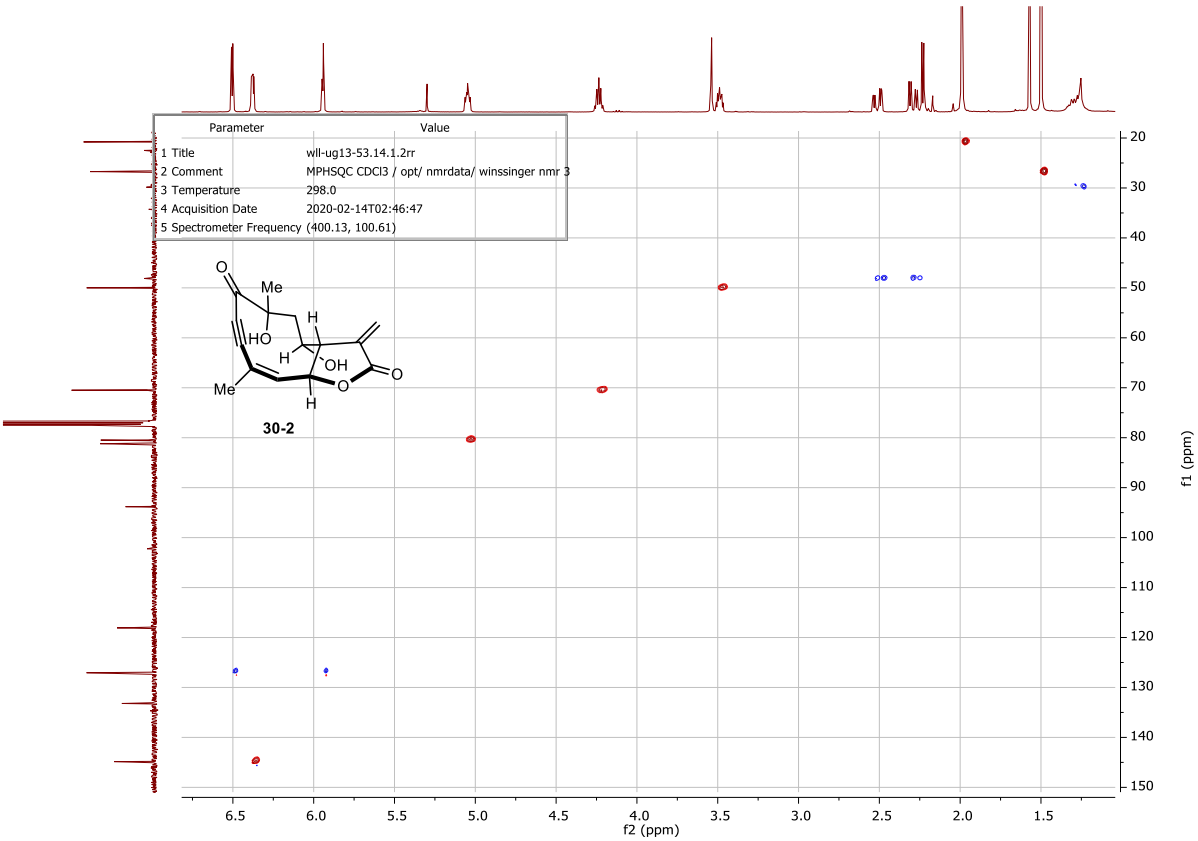

Parameter Value
1 Title wll-ug13-44.15.1.2rr
2 Comment HMBCAP MeOD / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-11T07:13:26
5 Spectrometer Frequency (400.13, 100.61)
OH
Me
HO
OH
O
O
Me
30-1
f2 (ppm)
f1 (ppm)

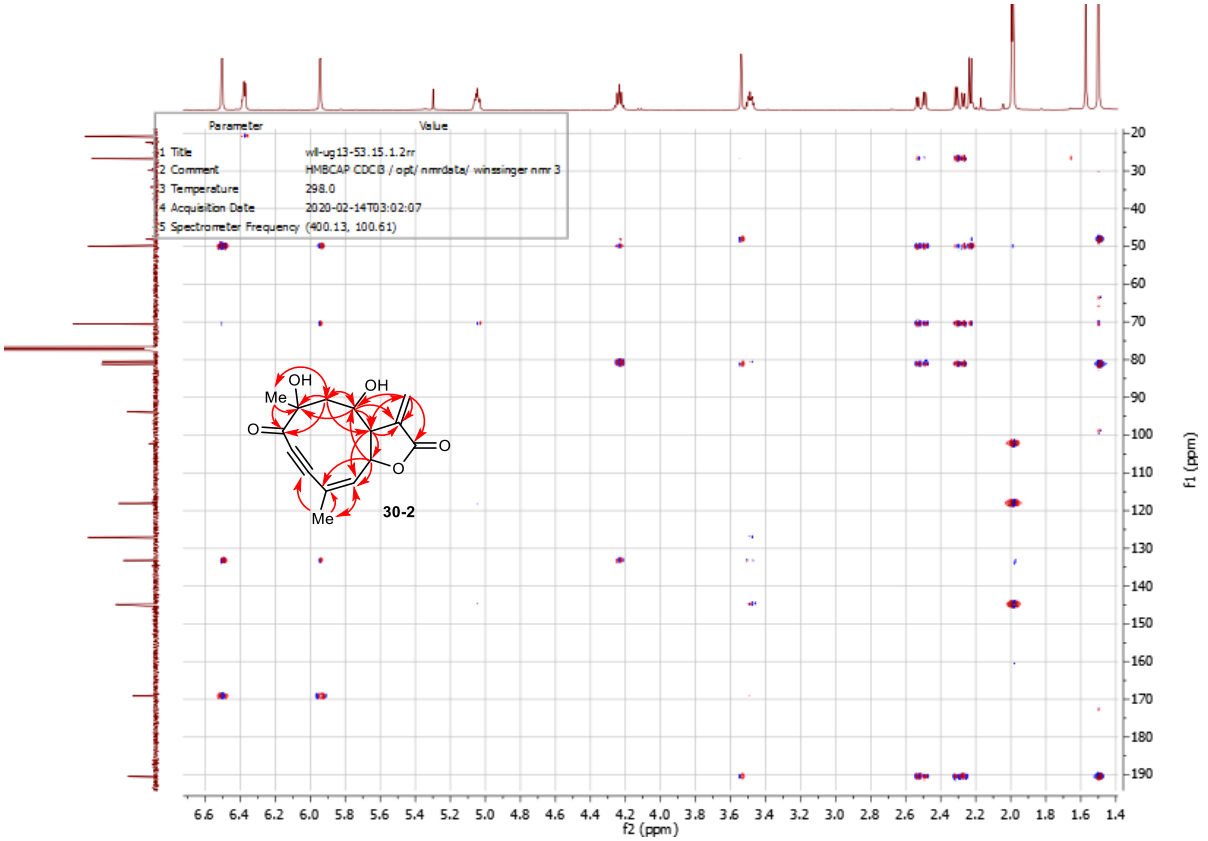

Parameter Value
1 Title wll-ug13-44.16.1.2rr
2 Comment NOESYGPPHSW MeOD / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-11T20:07:08
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
H
HO
H
H
OH
O
O
Me
H
f2 (ppm)
f1 (ppm)

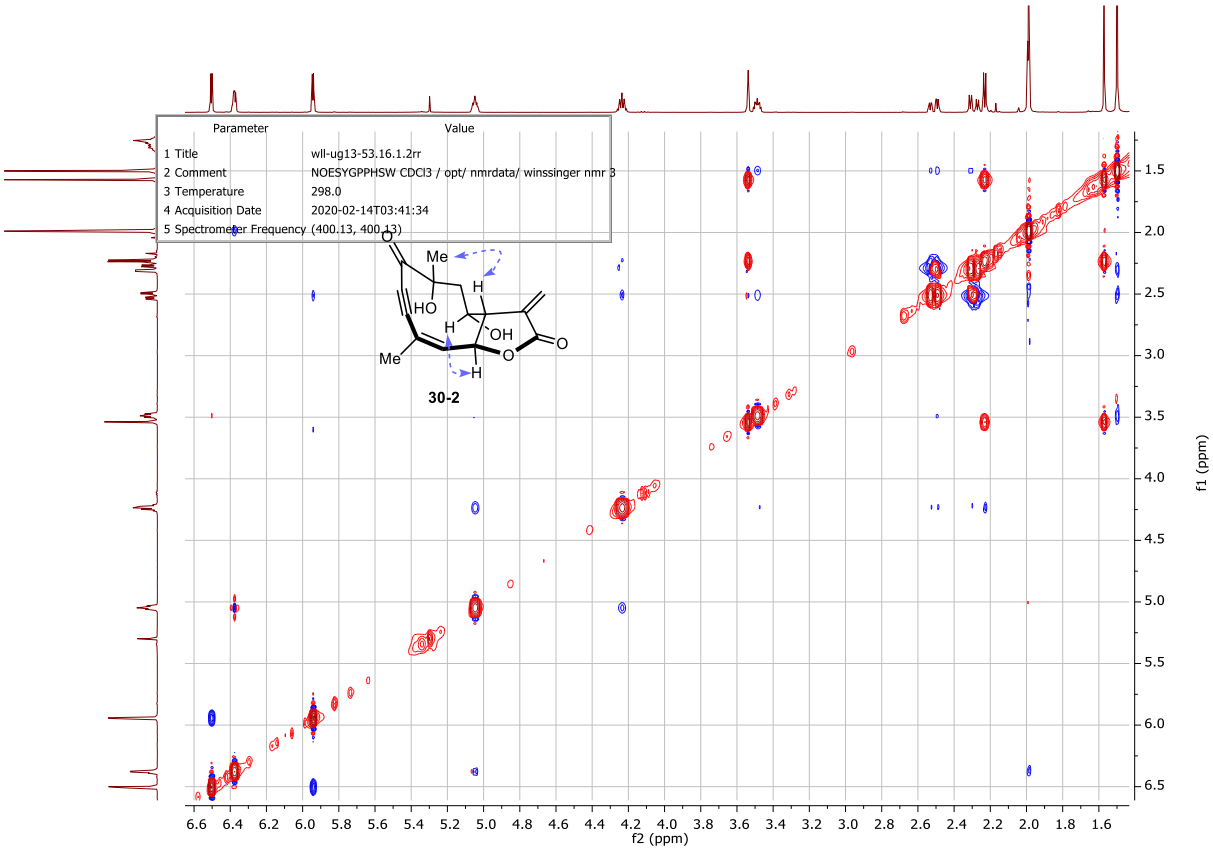

Parameter Value
1 Title wll-ug13-53.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-02-13T14:05:14
5 Spectrometer Frequency 400.13
Me
HO
H
H
OH
O
Me
O
H
O
30-2
f1 (ppm)

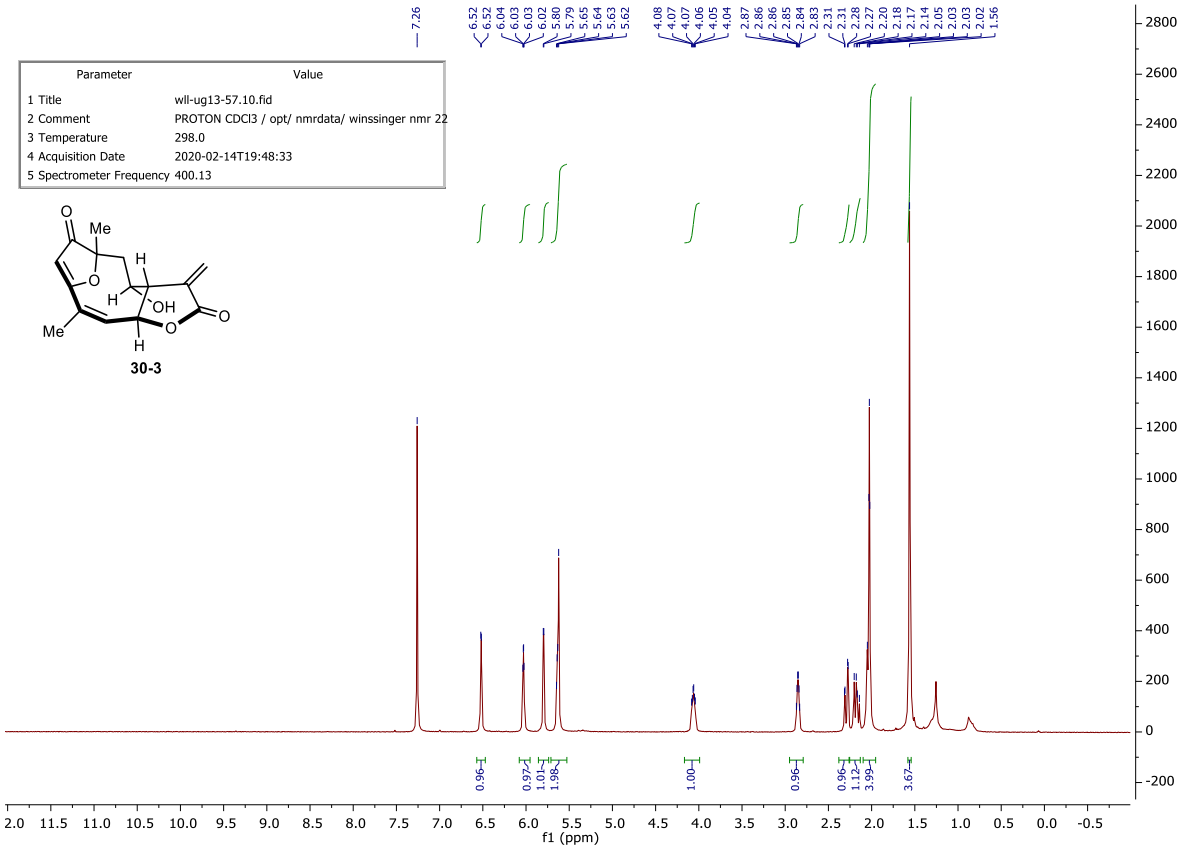

Parameter Value
1 Title wll-ug13-53.11.fid
2 Comment C13CPD CDCl3 / opt/ nmrdata/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-02-14T02:21:14
5 Spectrometer Frequency 100.62
Me
HO
H
H
OH
O
Me
O
H
O
30-2
f1 (ppm)

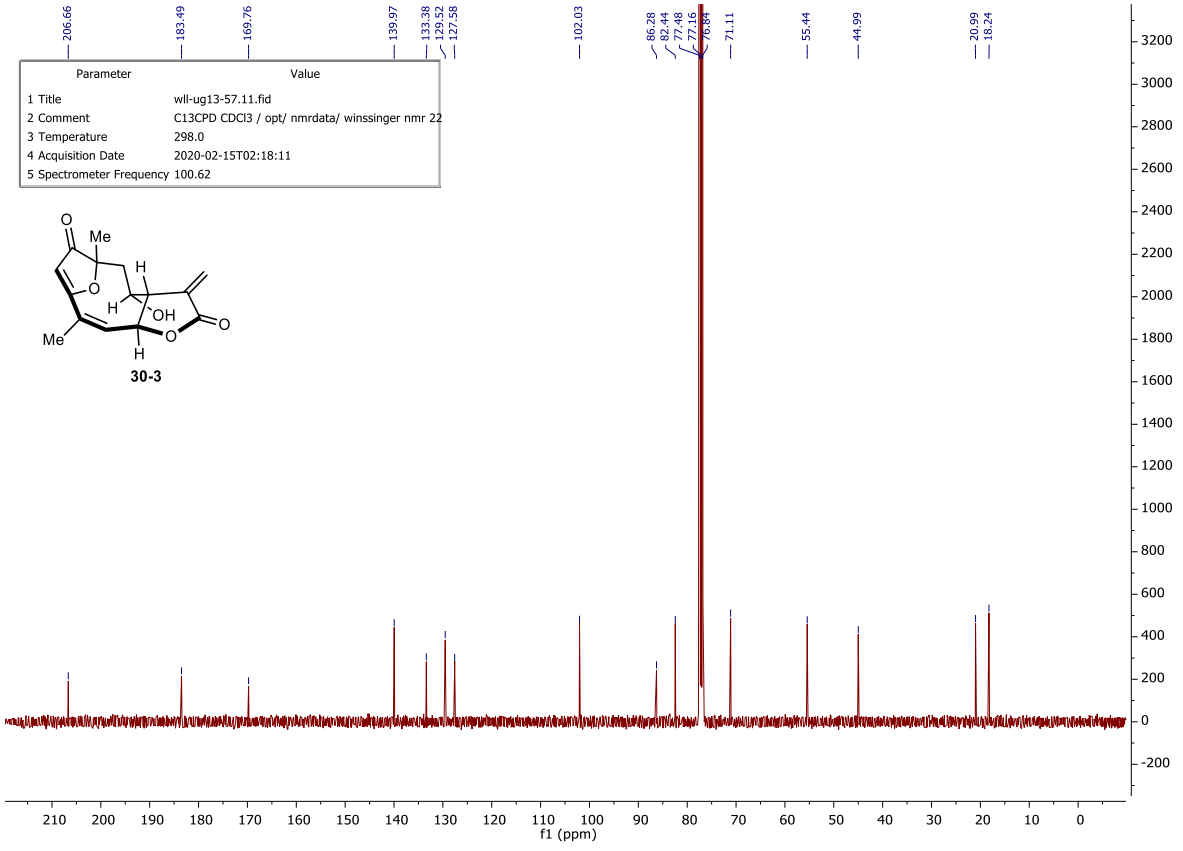

Parameter Value
1 Title wll-ug13-53.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-02-14T02:40:20
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
OH
O
O
O
Me
30-2
f2 (ppm)
f1 (ppm)

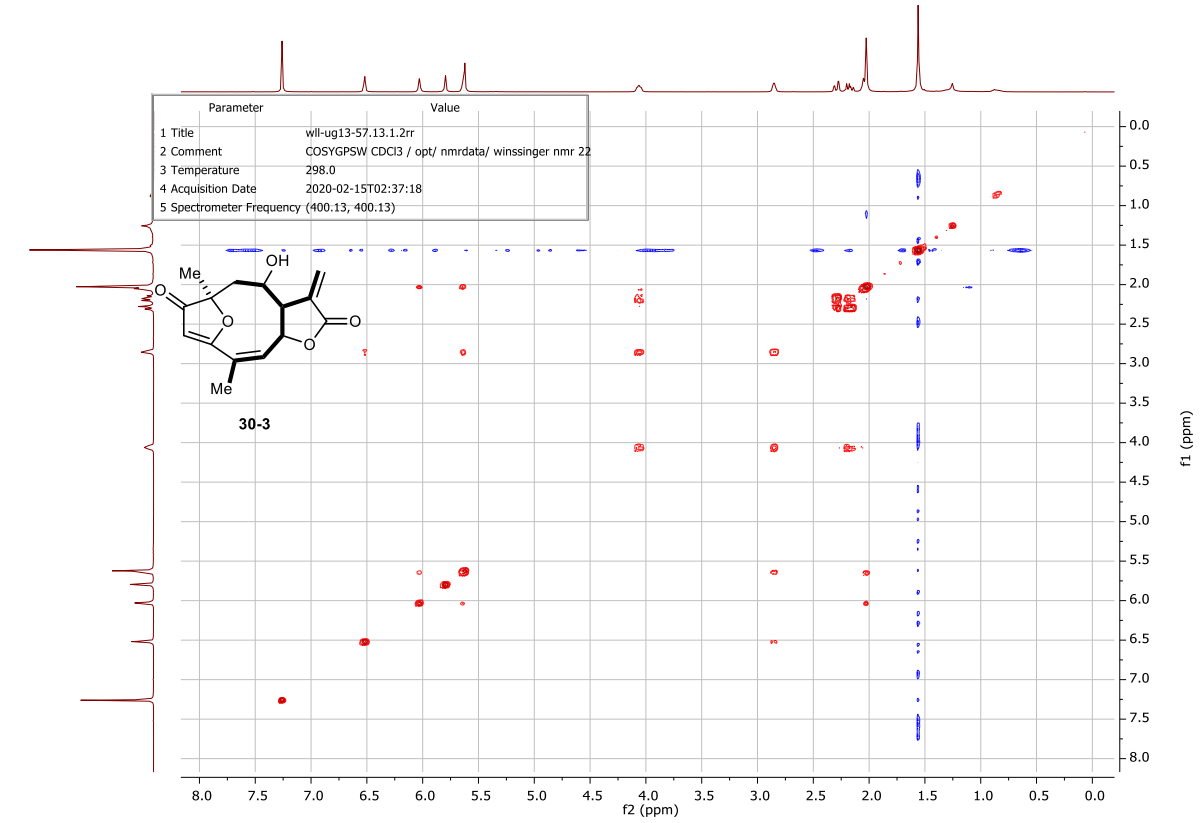

Parameter Value
1 Title wll-ug13-53.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-02-14T02:46:47
5 Spectrometer Frequency (400.13, 100.61)
O
Me
HO
H
H
OH
O
Me
O
H
30-2
f2 (ppm)
f1 (ppm)

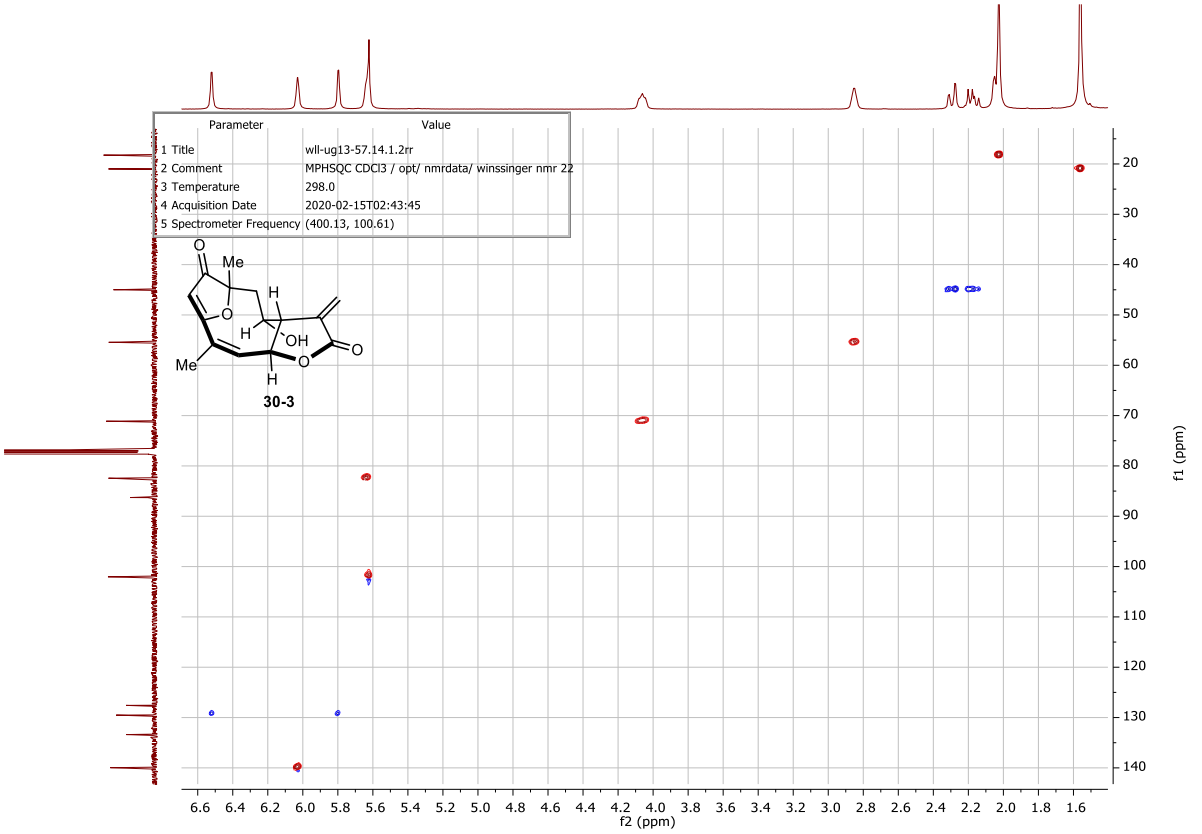

Parameter Value
1 Title wll-ug13-53.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-02-14T03:02:07
5 Spectrometer Frequency (400.13, 100.61)
OH
Me
OH
O
O
O
Me
30-2
f2 (ppm)
f1 (ppm)

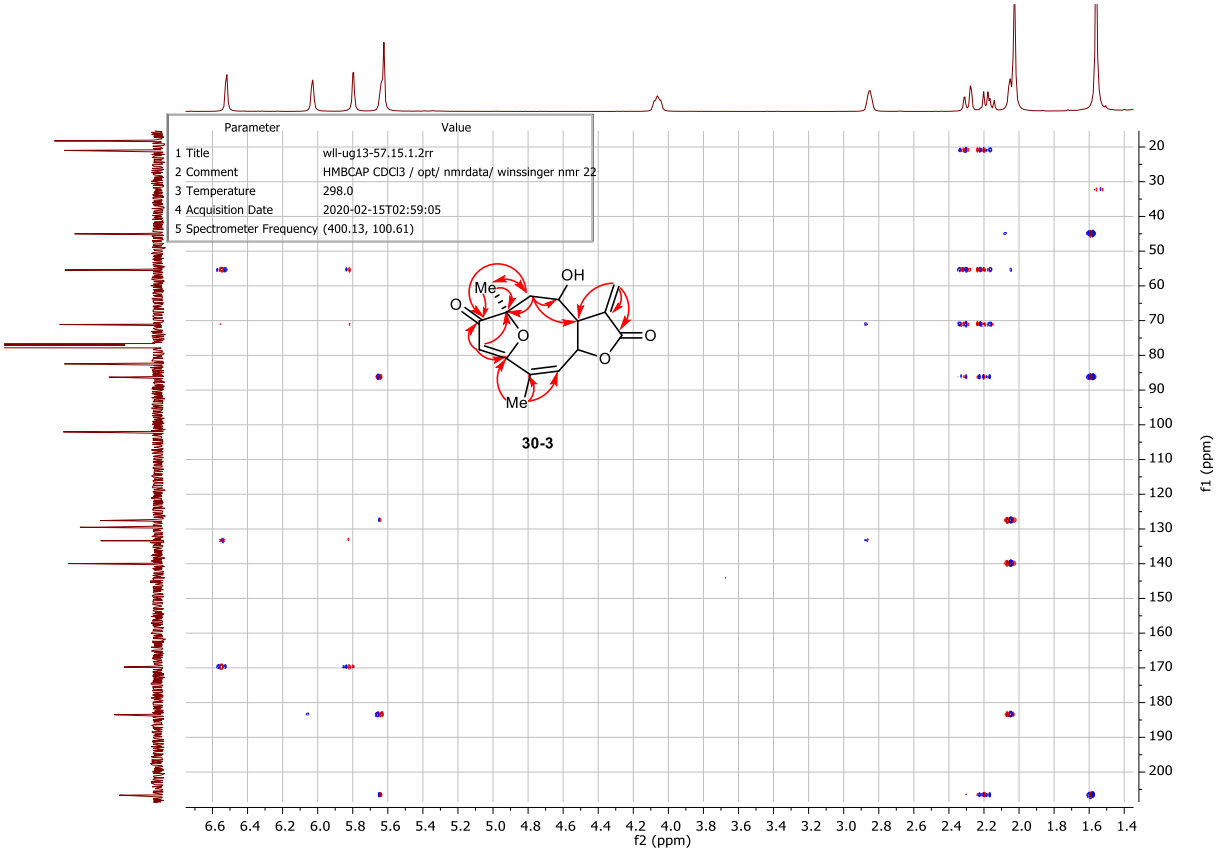

Parameter Value
1 Title wll-ug13-53.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-02-14T03:41:34
5 Spectrometer Frequency (400.13, 400.13)
O
Me
H
HO
H
OH
O
O
Me
H
30-2
f2 (ppm)
f1 (ppm)

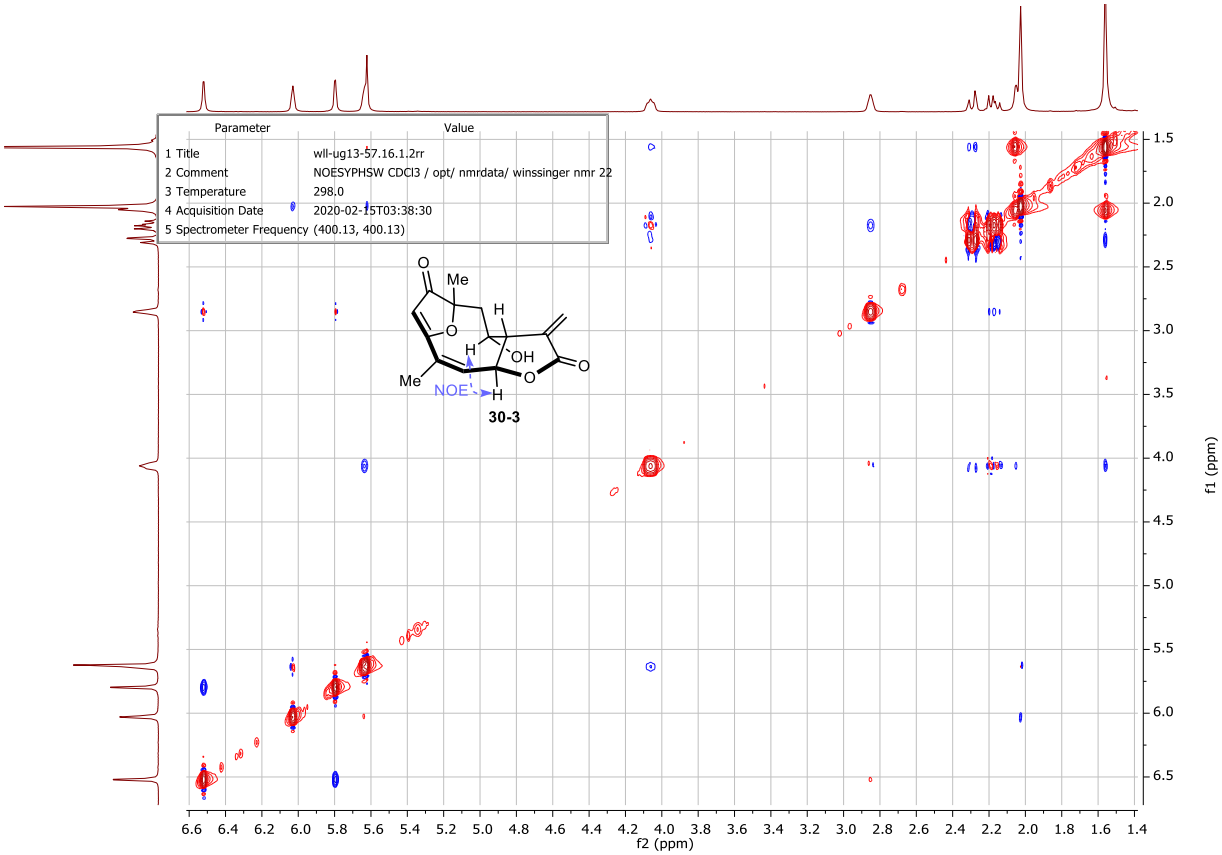

Parameter Value
1 Title wll-ug13-57.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-14T19:48:33
5 Spectrometer Frequency 400.13
30-3
f1 (ppm)

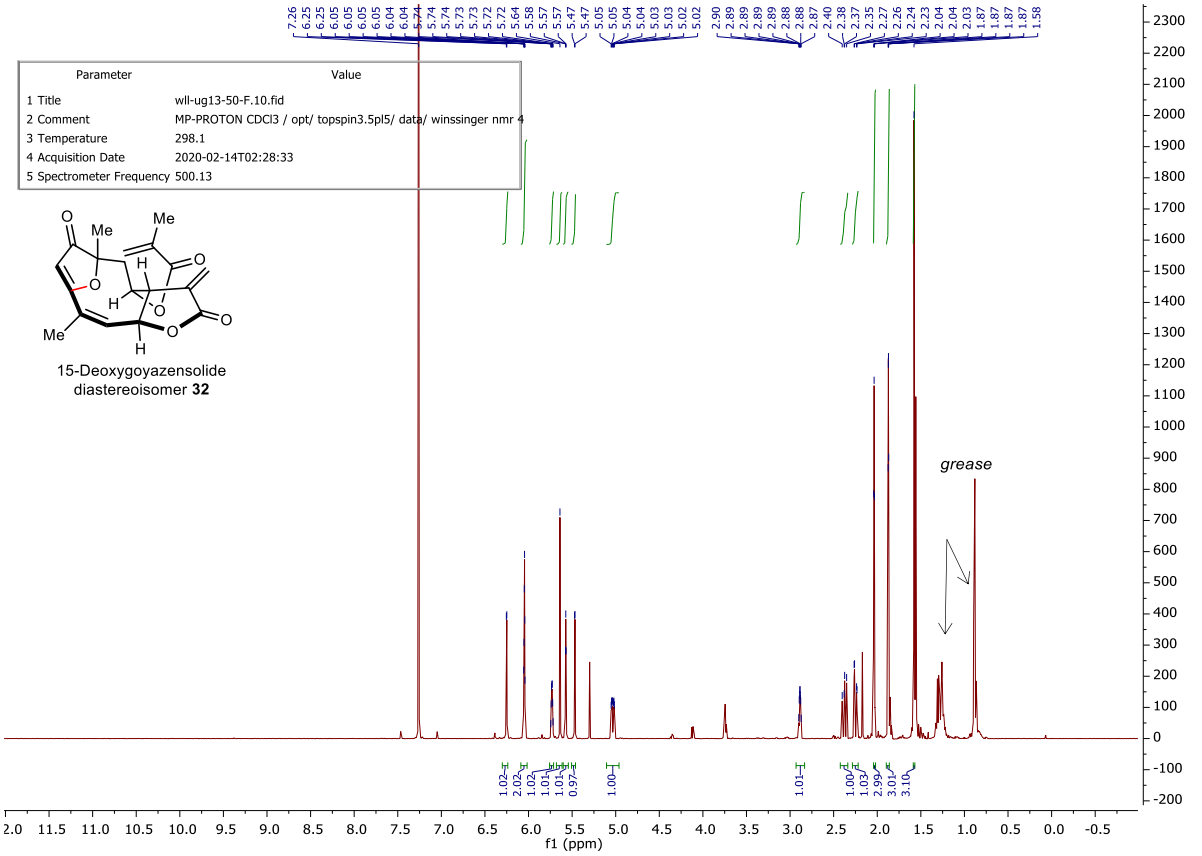

Parameter Value
1 Title wll-ug13-57.11.fid
2 Comment C13CPD CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-15T02:18:11
5 Spectrometer Frequency 100.62
30-3
f1 (ppm)

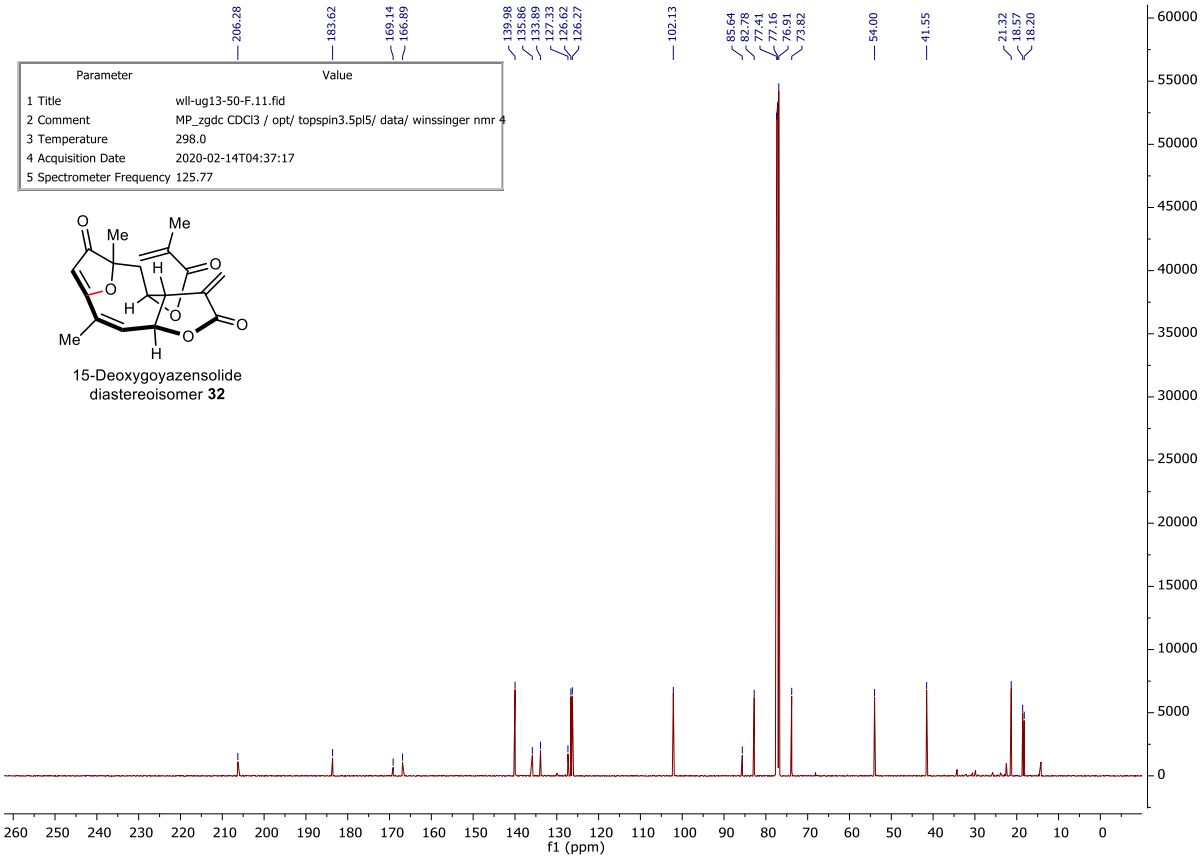

Parameter Value
1 Title wll-ug13-57.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-15T02:37:18
5 Spectrometer Frequency (400.13, 400.13)
Me
OH
O
O
O
O
Me
30-3
f2 (ppm)
f1 (ppm)

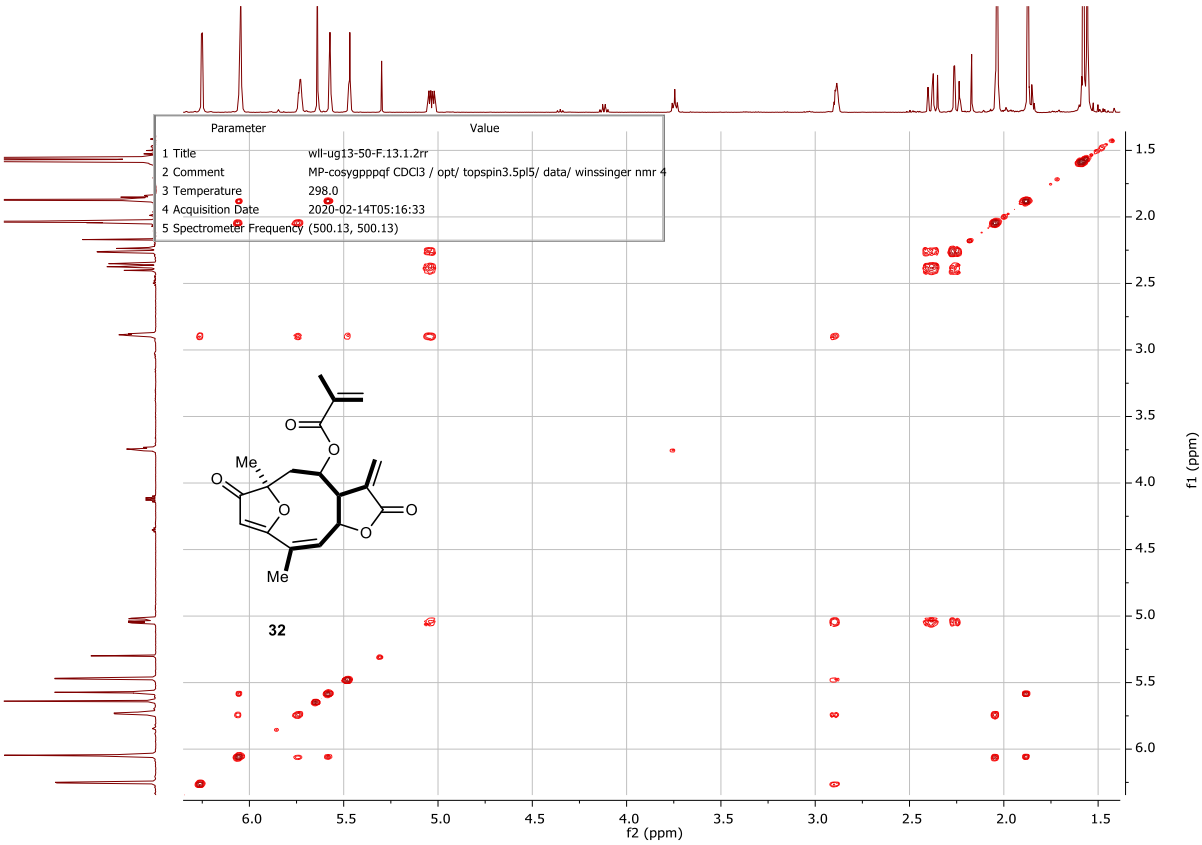

Parameter Value
1 Title wll-ug13-57.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-15T02:43:45
5 Spectrometer Frequency (400.13, 100.61)
O
Me
H
O
H
OH
O
Me
O
H
30-3
f2 (ppm)
f1 (ppm)

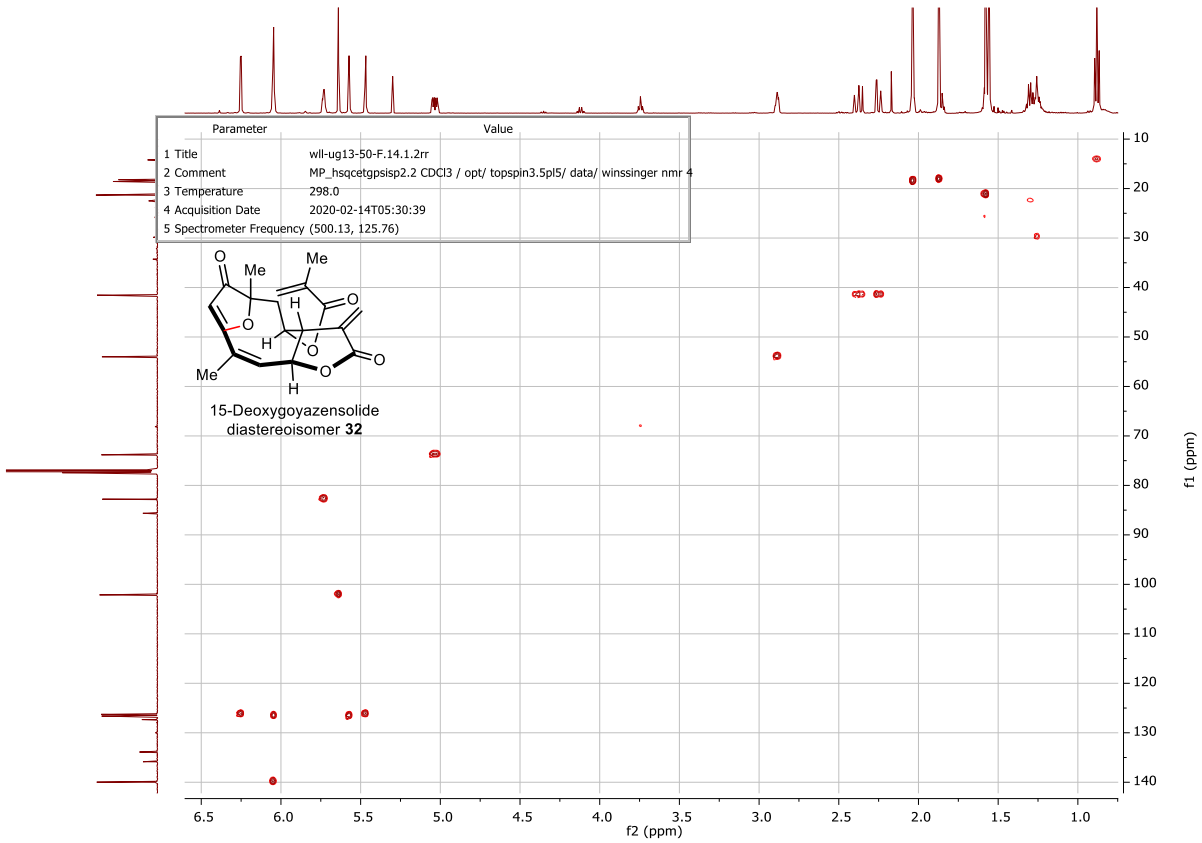

Parameter Value
1 Title wll-ug13-57.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-15T02:59:05
5 Spectrometer Frequency (400.13, 100.61)
Me
OH
O
O
O
O
Me
30-3
f2 (ppm)
f1 (ppm)

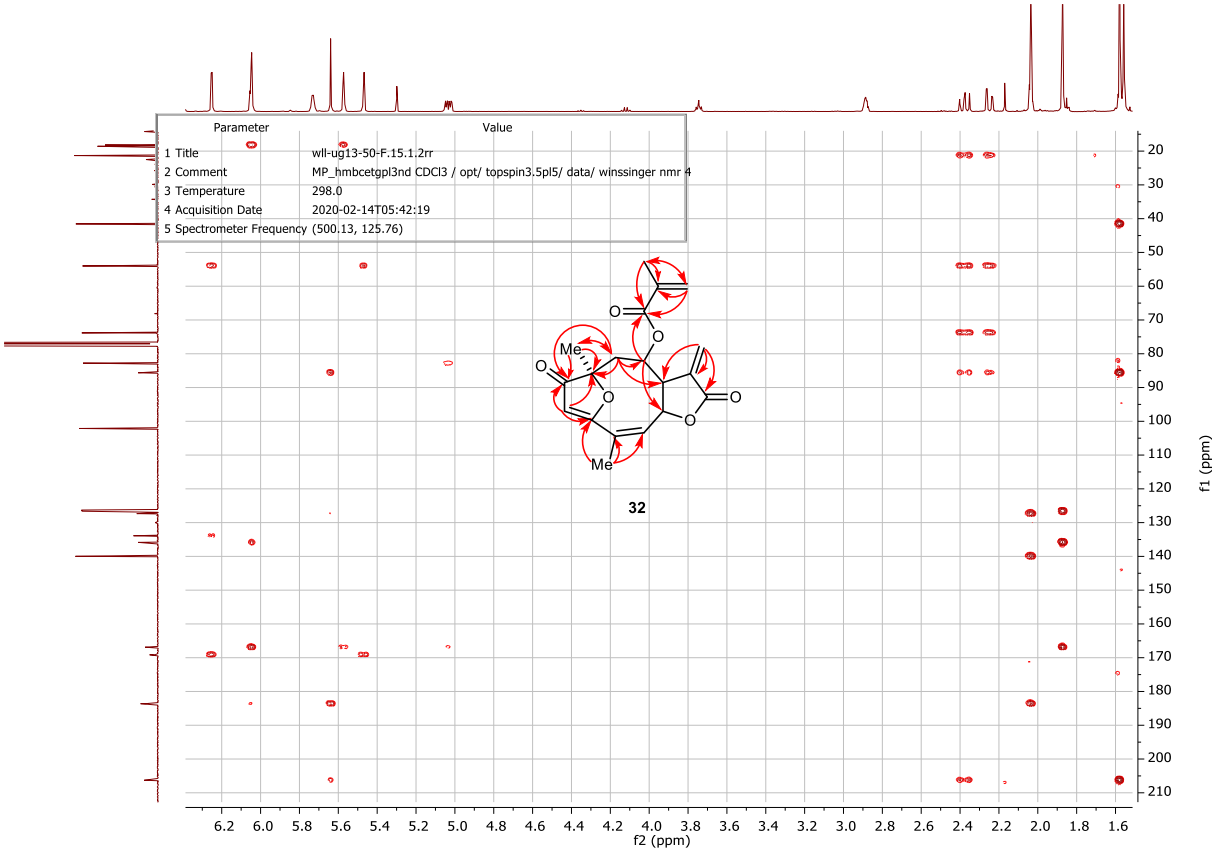

Parameter Value
1 Title wll-ug13-57.16.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-15T03:38:30
5 Spectrometer Frequency (400.13, 400.13)
O
Me
H
O
H
OH
Me
NOE
H
O
O
30-3
f2 (ppm)
f1 (ppm)

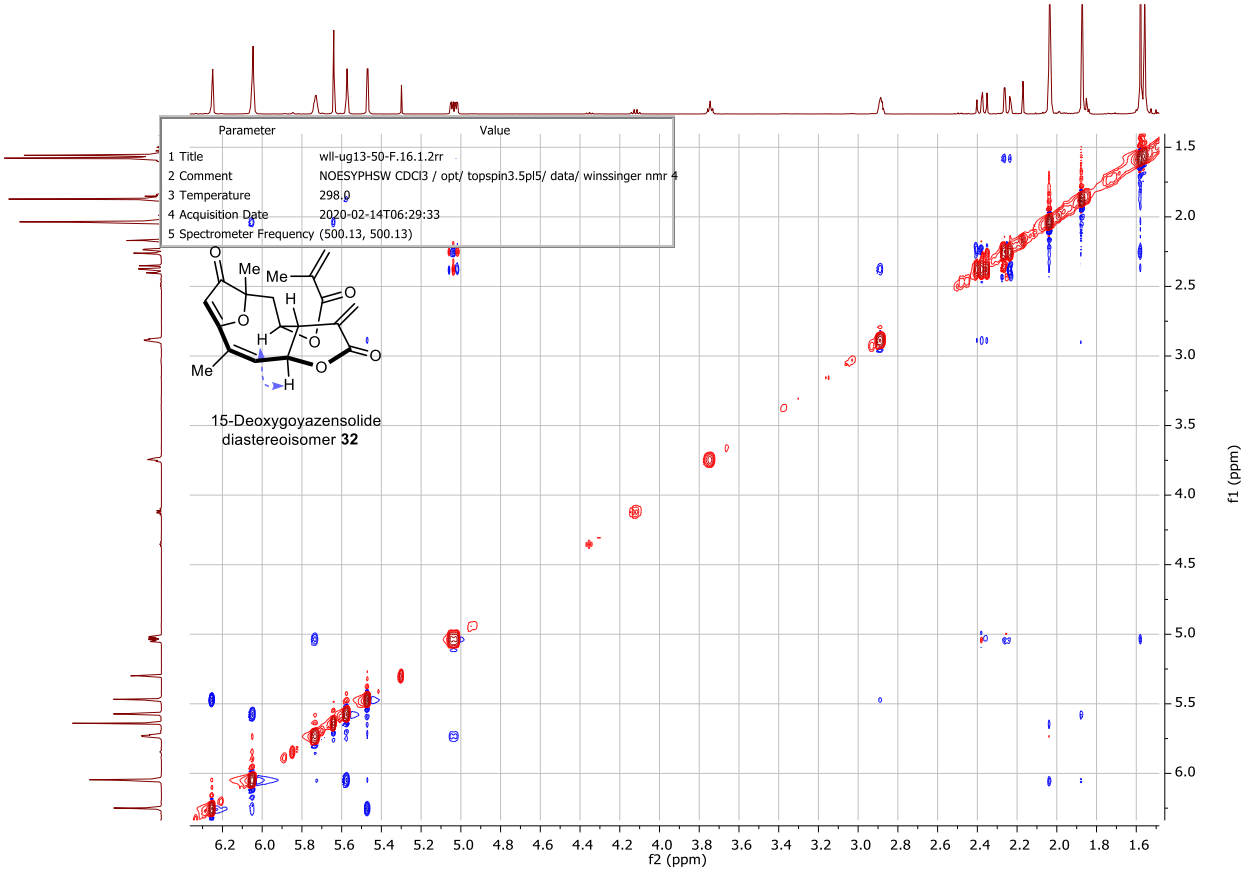

Parameter Value
1 Title wll-ug13-50-F.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 4
3 Temperature 298.1
4 Acquisition Date 2020-02-14T02:28:33
5 Spectrometer Frequency 500.13
15-Deoxygoyazensolide diastereoisomer 32
grease
f1 (ppm)

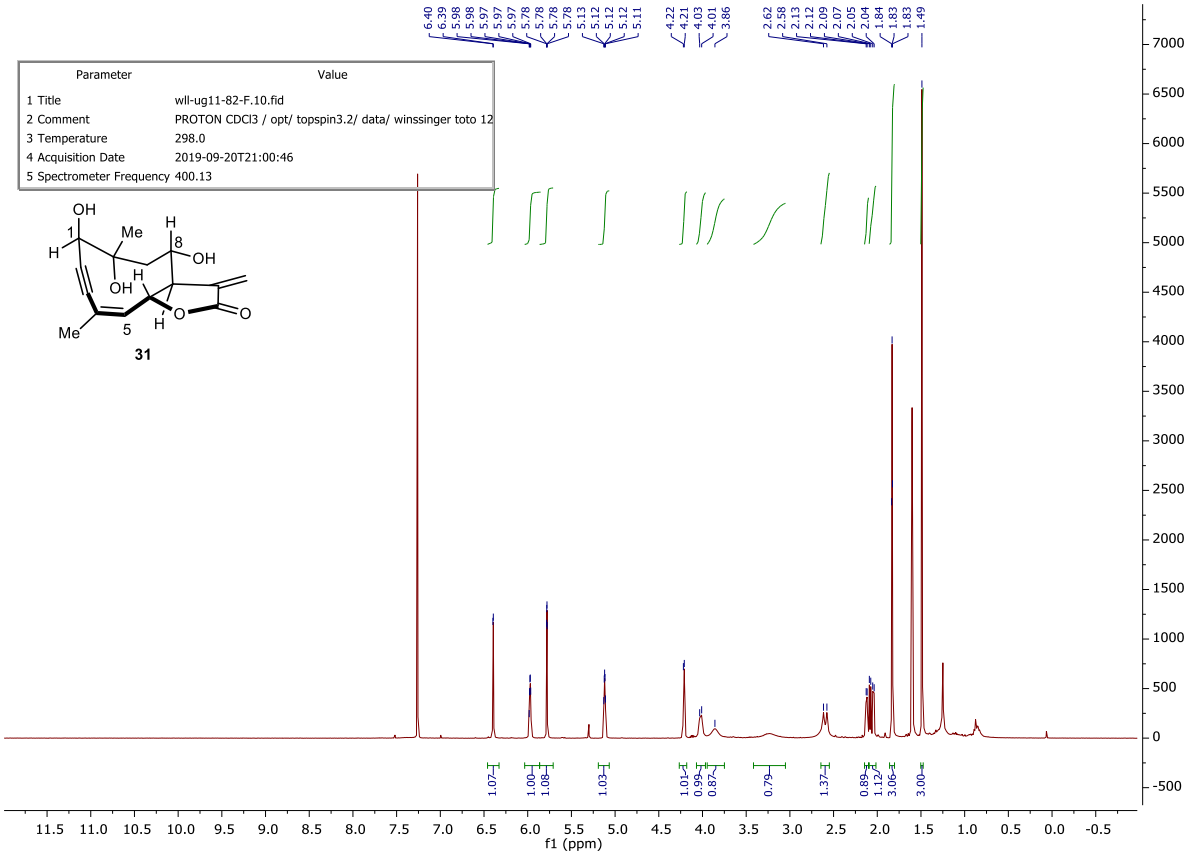

Parameter Value
1 Title wll-ug13-50-F.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 4
3 Temperature 298.0
4 Acquisition Date 2020-02-14T04:37:17
5 Spectrometer Frequency 125.77
15-Deoxygoyazensolide diastereoisomer 32
f1 (ppm)

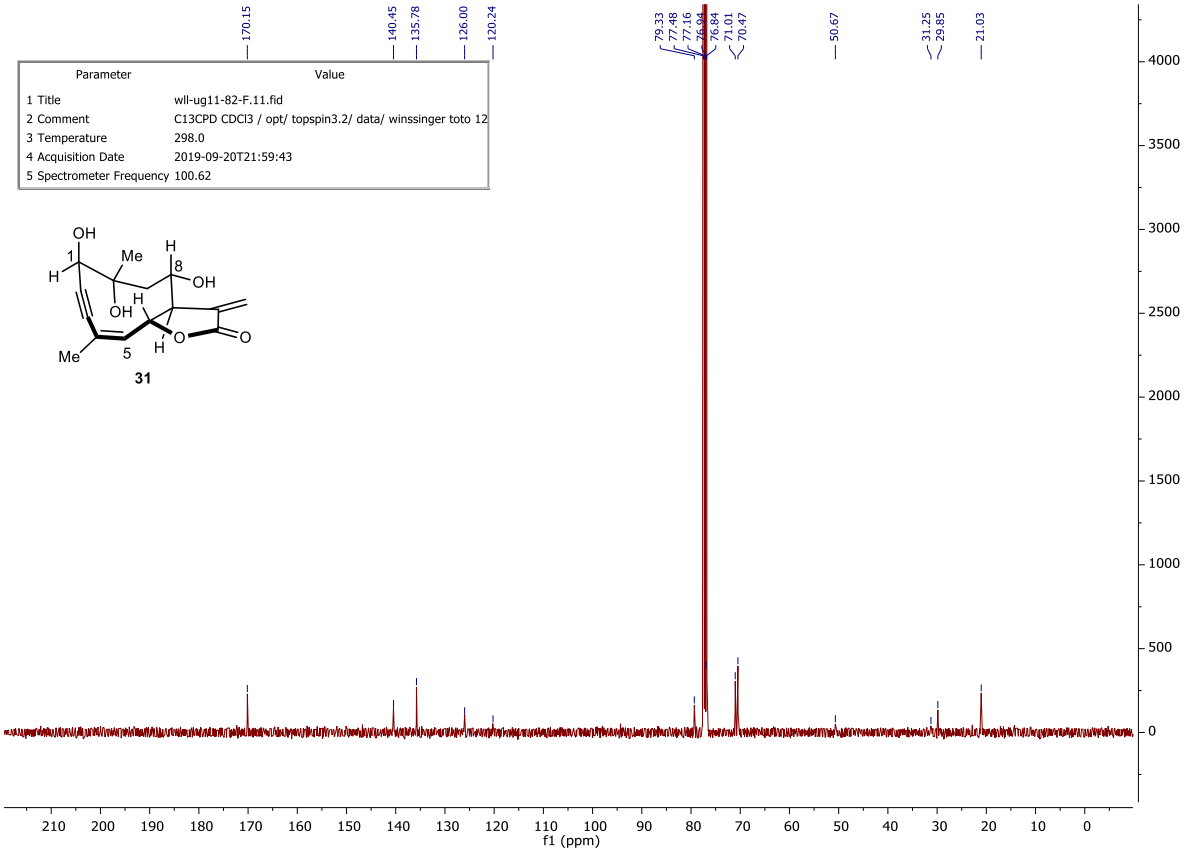

Parameter Value
1 Title wll-ug13-50-F.13.1.2rr
2 Comment MP-cosygpppqf CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 4
3 Temperature 298.0
4 Acquisition Date 2020-02-14T05:16:33
5 Spectrometer Frequency (500.13, 500.13)
Me
Me
32
f2 (ppm)
f1 (ppm)

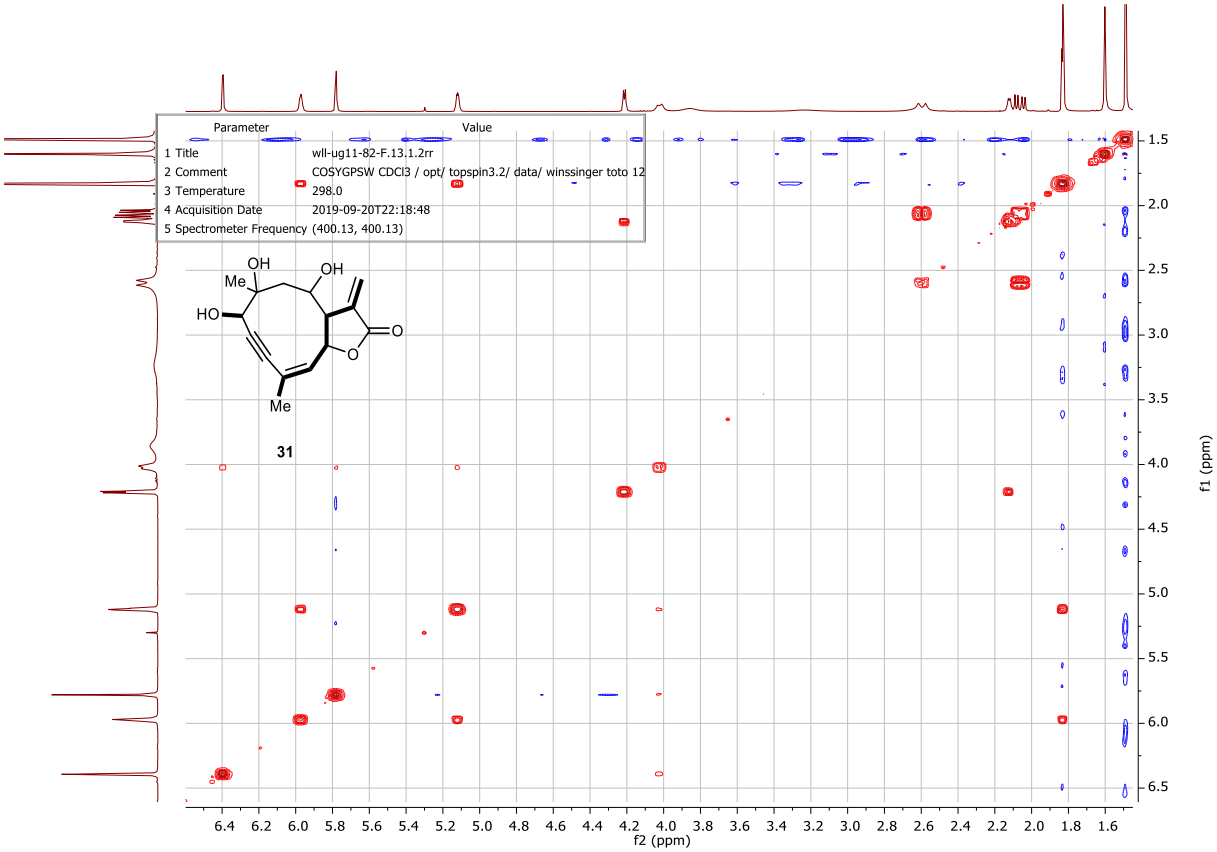

Parameter Value
1 Title wll-ug13-50-F.14.1.2rr
2 Comment MP_hsqcetgpsisp2.2 CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 4
3 Temperature 298.0
4 Acquisition Date 2020-02-14T05:30:39
5 Spectrometer Frequency (500.13, 125.76)
Me
Me
Me
H
H
H
15-Deoxygoyazensolide
diastereoisomer 32
f2 (ppm)
f1 (ppm)

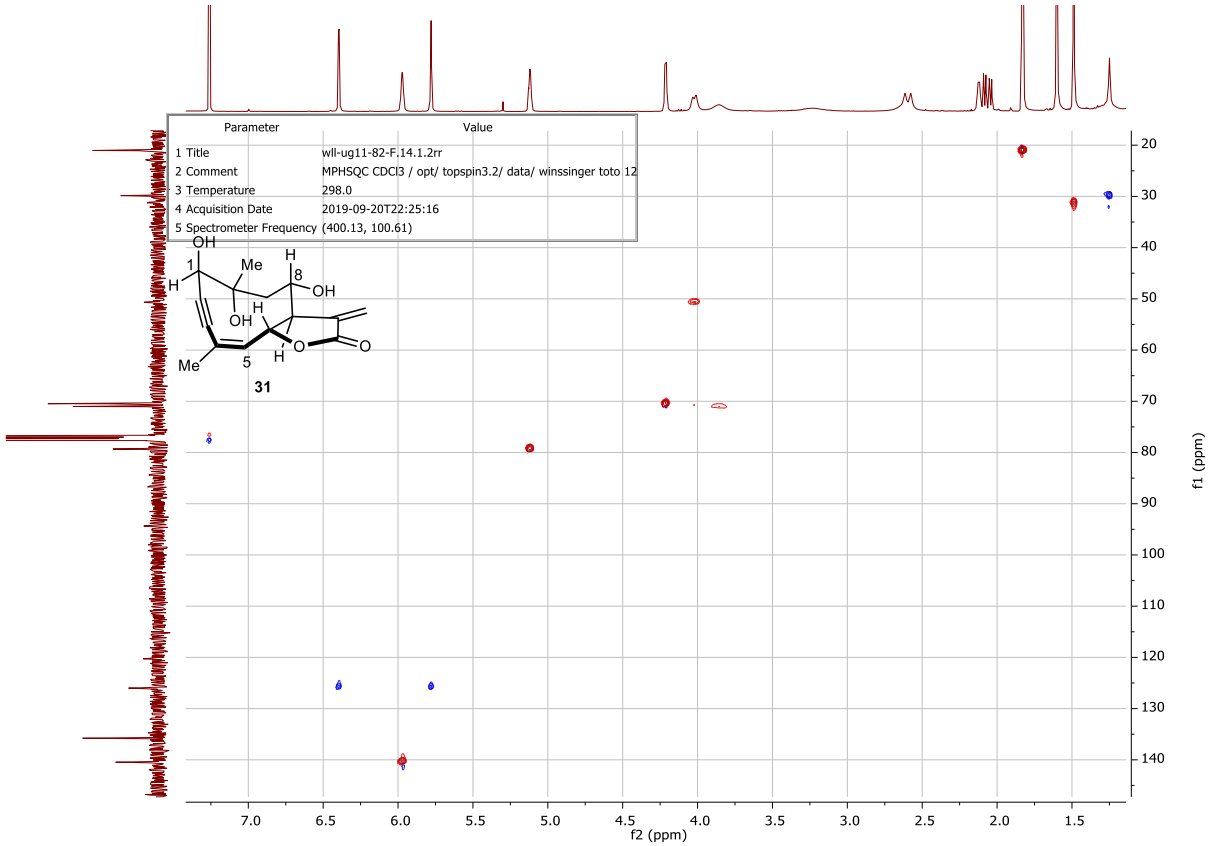

Parameter Value
1 Title wll-ug13-50-F.15.1.2rr
2 Comment MP_hmbcetgpl3nd CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 4
3 Temperature 298.0
4 Acquisition Date 2020-02-14T05:42:19
5 Spectrometer Frequency (500.13, 125.76)
Me
Me
32
f2 (ppm)
f1 (ppm)

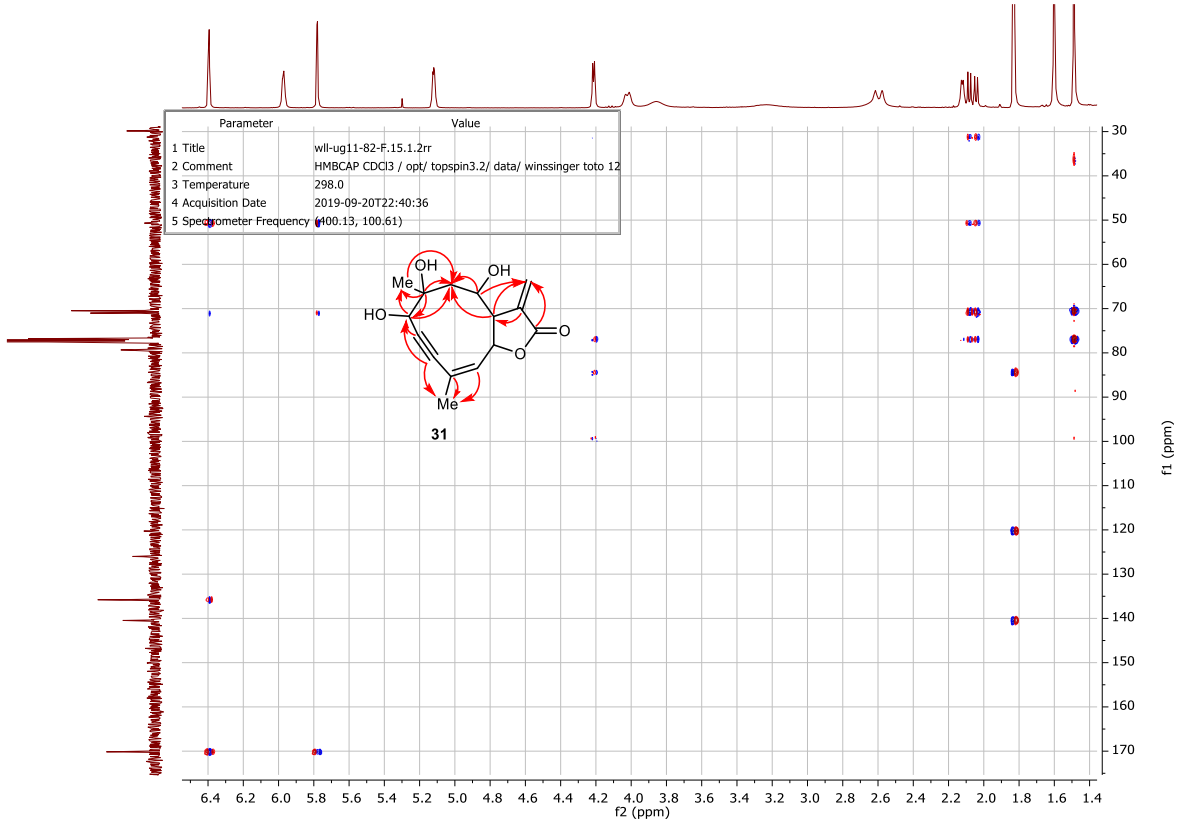

Parameter Value
1 Title wll-ug13-50-F.16.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 4
3 Temperature 298.0
4 Acquisition Date 2020-02-14T06:29:33
5 Spectrometer Frequency (500.13, 500.13)
Me
Me
H
H
Me
H
15-Deoxygoyazensolide
diastereoisomer 32
f2 (ppm)
f1 (ppm)

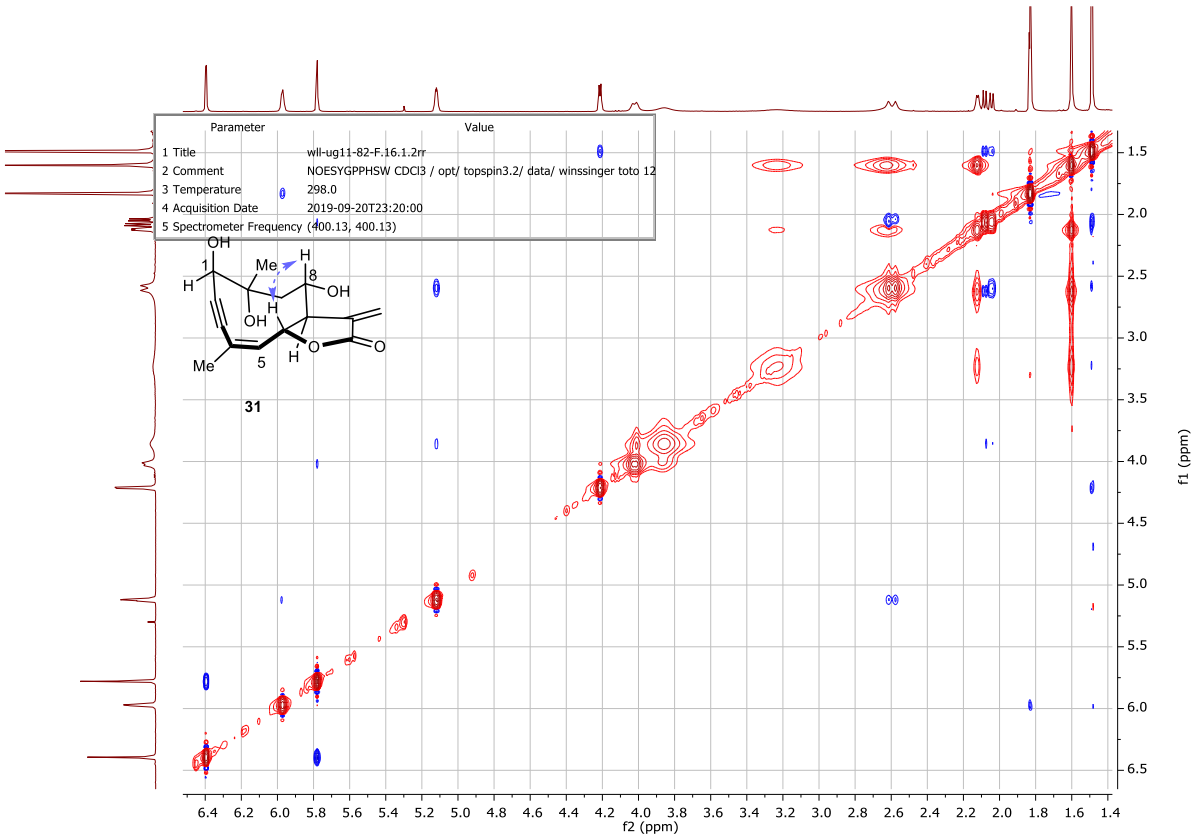

Parameter Value
1 Title wll-ug11-82-F.10.fid
2 Comment PROTON CDCl3 / opt/ topspin3.2/ data/ winssinger toto 12
3 Temperature 298.0
4 Acquisition Date 2019-09-20T21:00:46
5 Spectrometer Frequency 400.13
31
f1 (ppm)

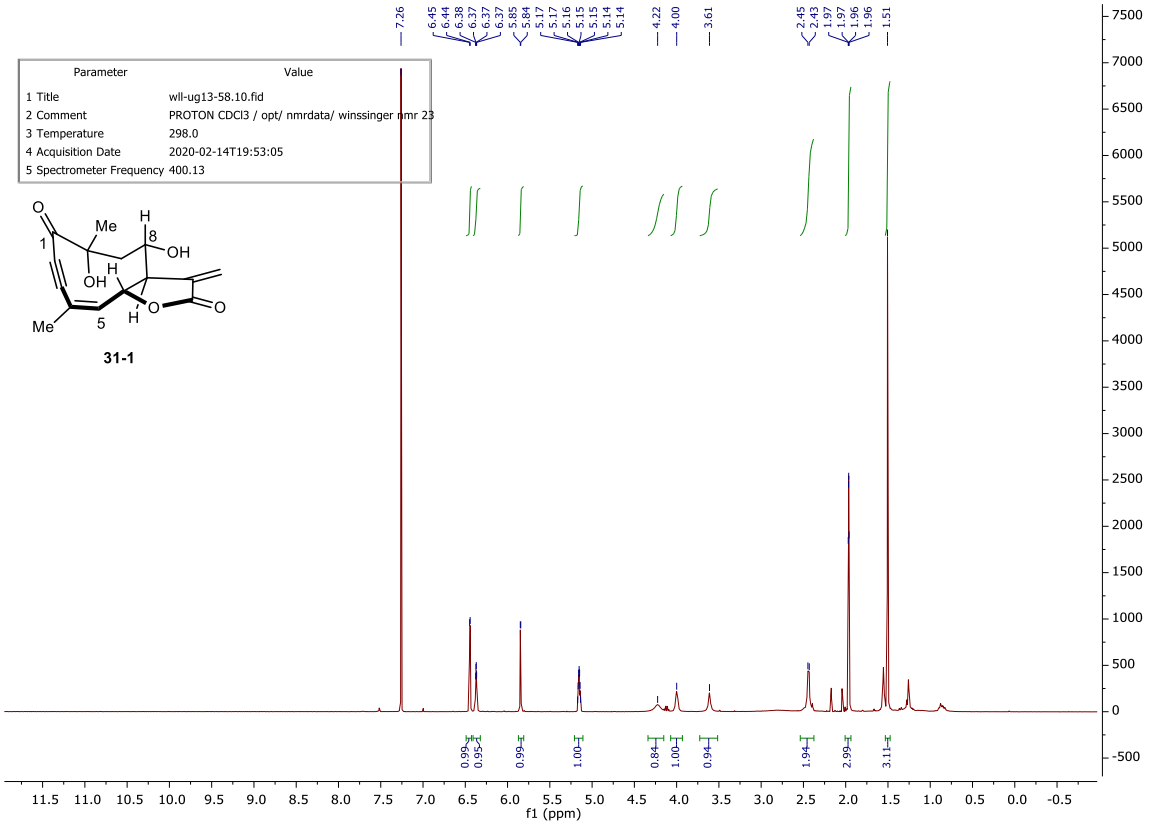

Parameter Value
1 Title wll-ug11-82-F.11.fid
2 Comment C13CPD CDCl3 / opt/ topspin3.2/ data/ winssinger toto 12
3 Temperature 298.0
4 Acquisition Date 2019-09-20T21:59:43
5 Spectrometer Frequency 100.62
31
f1 (ppm)

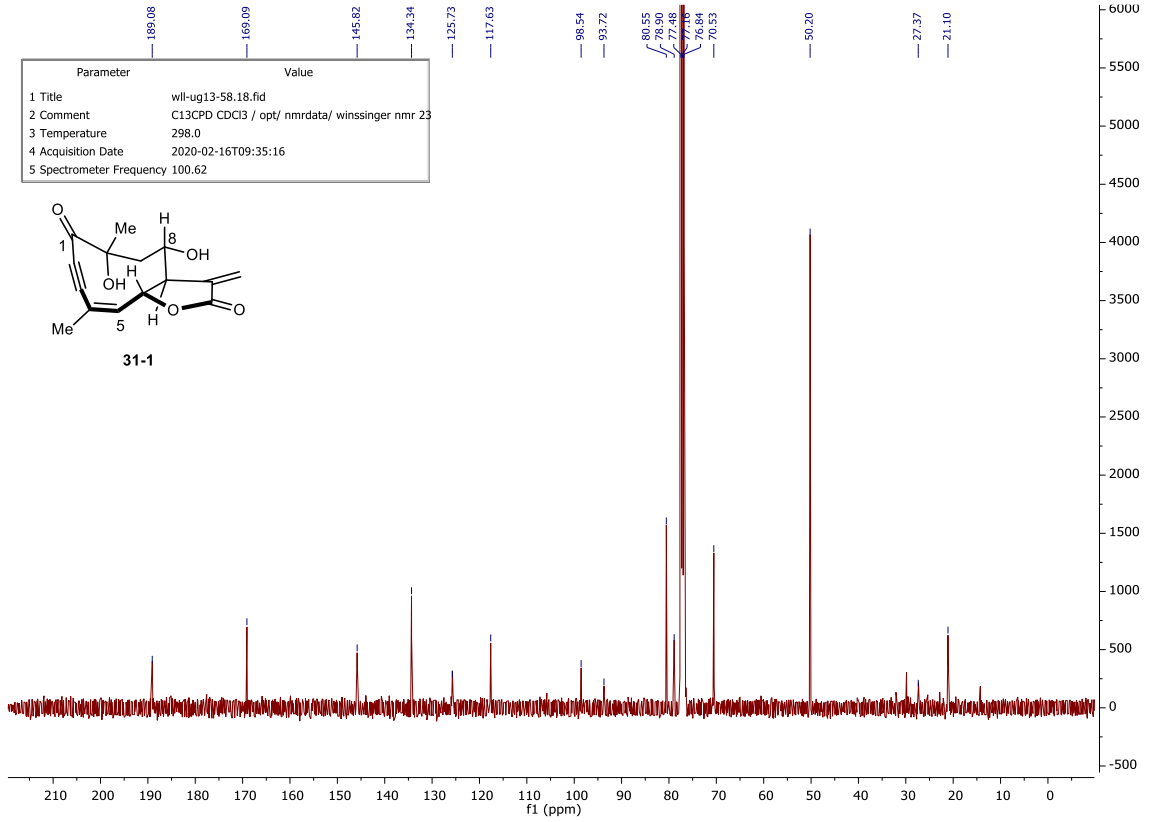

Parameter Value
1 Title wll-ug11-82-F.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 12
3 Temperature 298.0
4 Acquisition Date 2019-09-20T22:18:48
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
OH
HO
O
O
Me
31
f2 (ppm)
f1 (ppm)

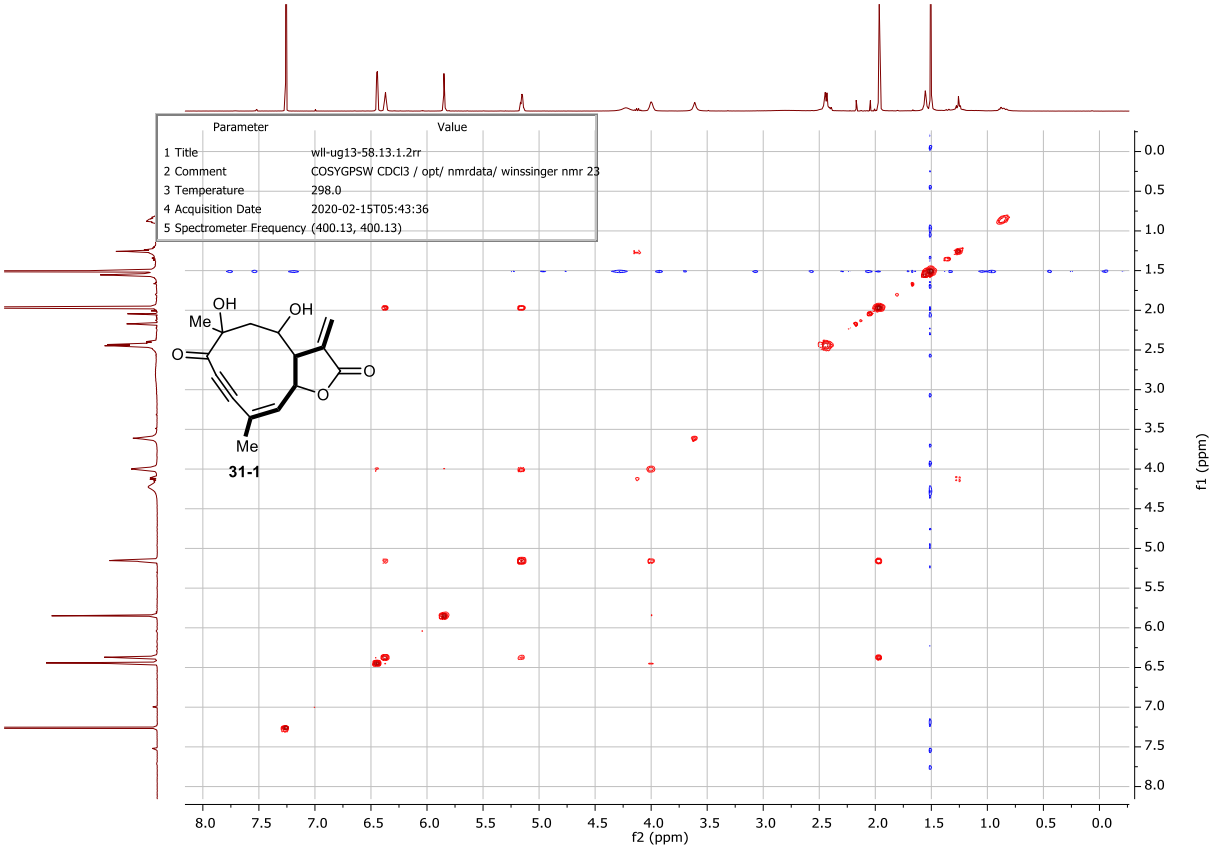

Parameter Value
1 Title wll-ug11-82-F.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ topspin3.2/ data/ winssinger toto 12
3 Temperature 298.0
4 Acquisition Date 2019-09-20T22:25:16
5 Spectrometer Frequency (400.13, 100.61)
OH
1
H
Me
H
8
OH
H
OH
O
O
Me
5
H
31
f2 (ppm)
f1 (ppm)

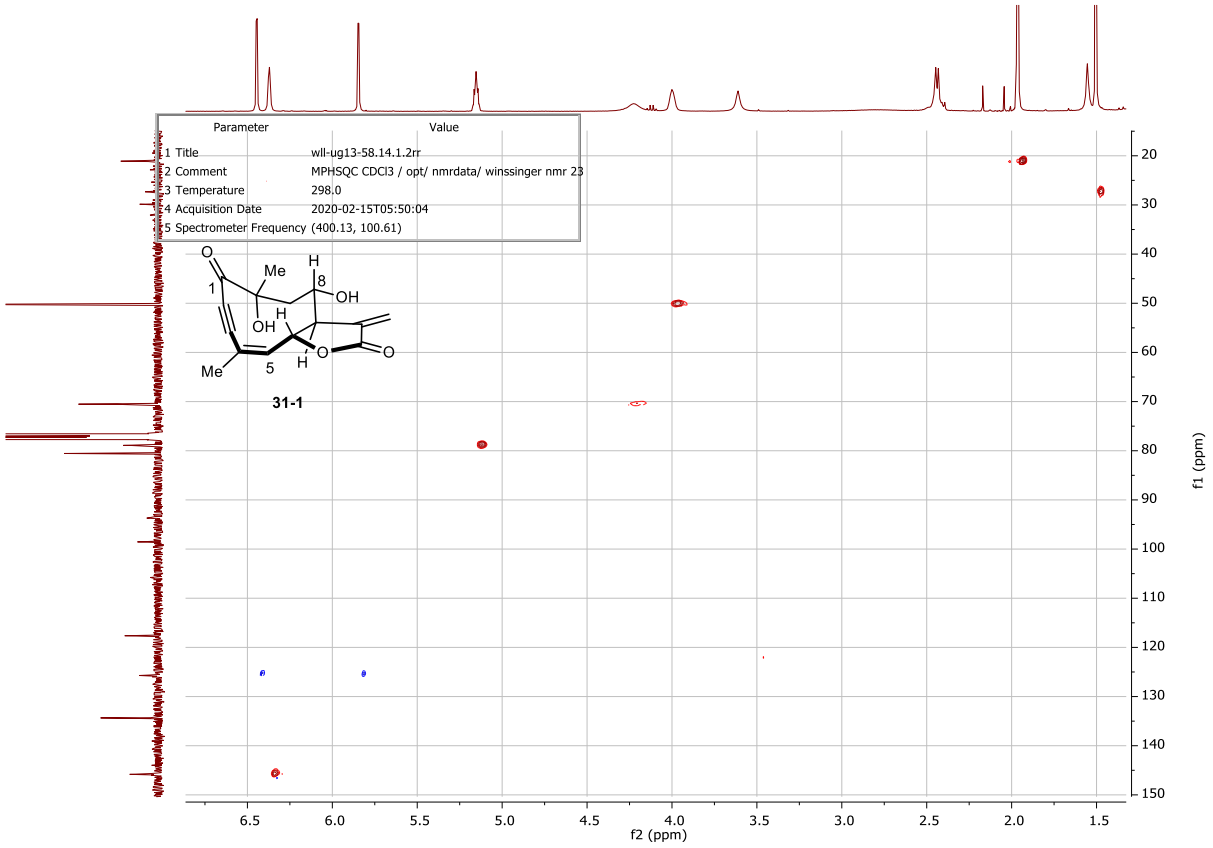

Parameter Value
1 Title wll-ug11-82-F.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ topspin3.2/ data/ winssinger toto 12
3 Temperature 298.0
4 Acquisition Date 2019-09-20T22:40:36
5 Spectrometer Frequency (400.13, 100.61)
OH
Me
OH
HO
O
O
Me
31
f2 (ppm)
f1 (ppm)

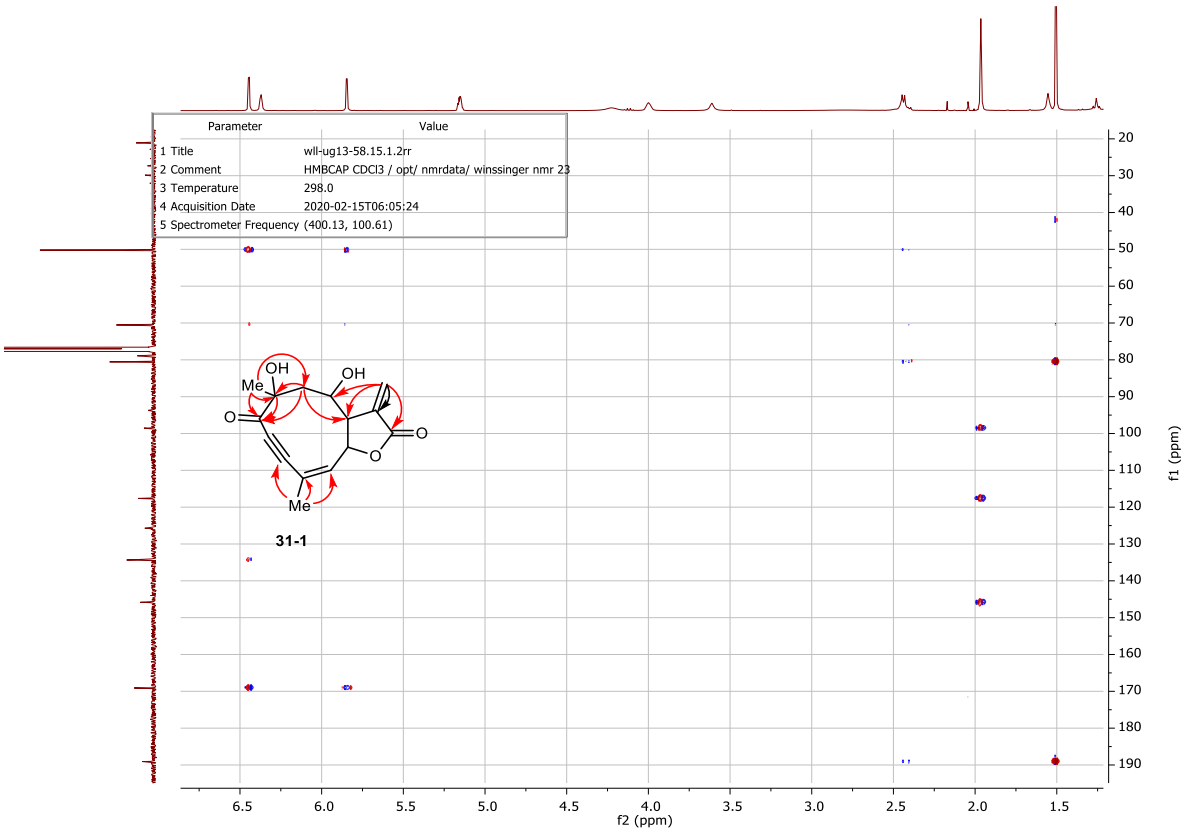

Parameter Value
1 Title wll-ug11-82-F.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 12
3 Temperature 298.0
4 Acquisition Date 2019-09-20T23:20:00
5 Spectrometer Frequency (400.13, 400.13)
OH
1
H
Me
H
8
OH
H
OH
O
O
Me
5
H
31
f2 (ppm)
f1 (ppm)

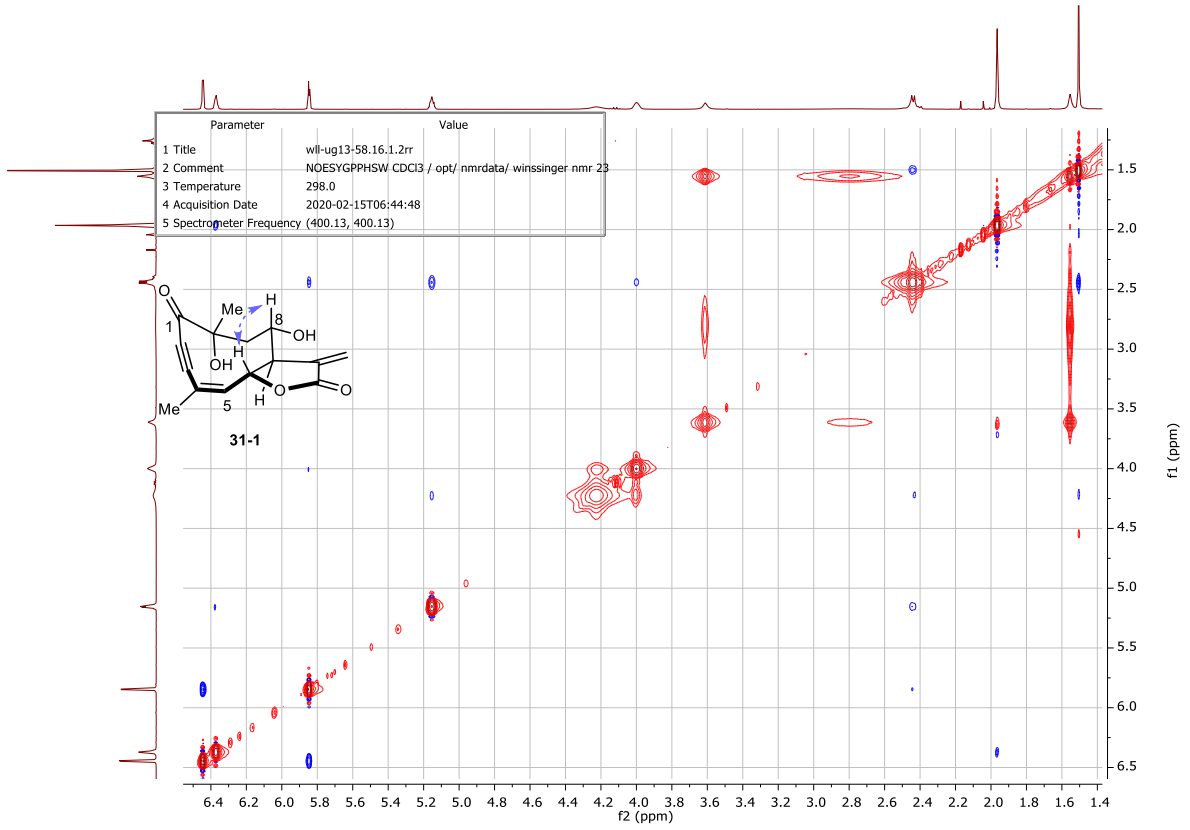

Parameter Value
1 Title wll-ug13-58.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-14T19:53:05
5 Spectrometer Frequency 400.13
31-1
f1 (ppm)

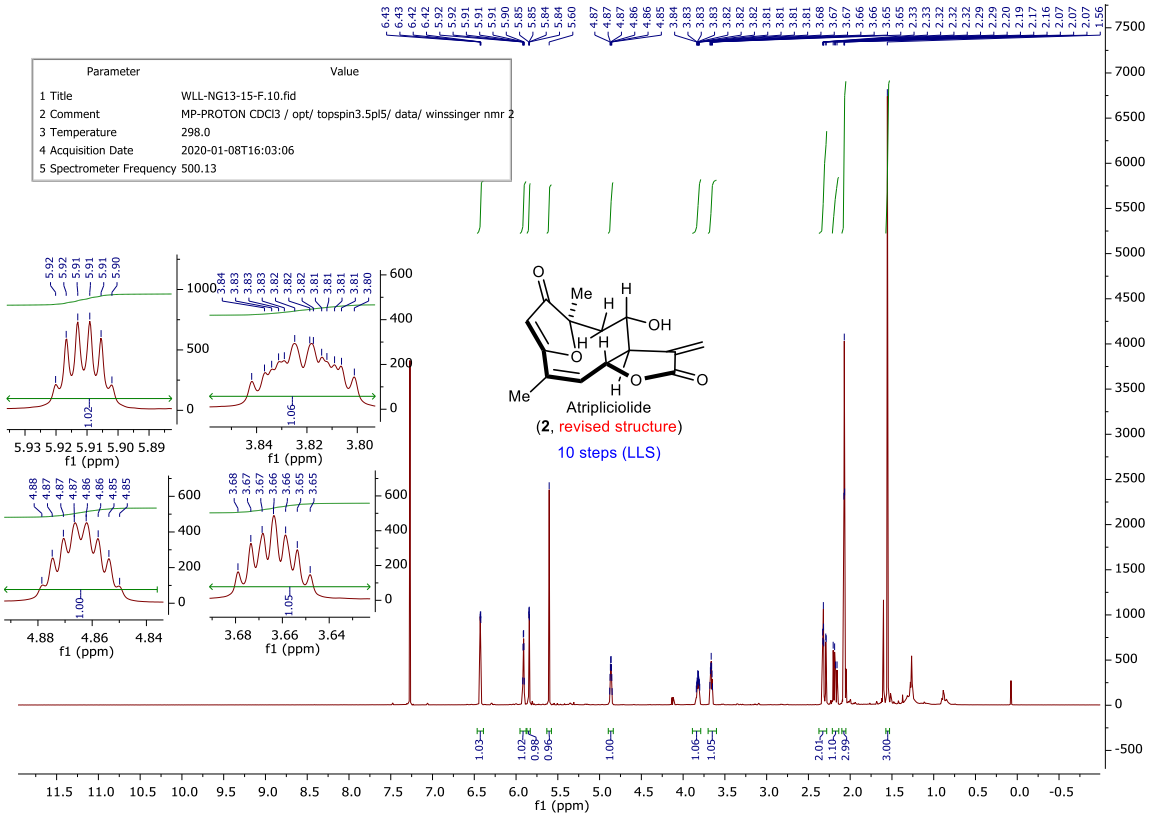

Parameter Value
1 Title wll-ug13-58.18.fid
2 Comment C13CPD CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-16T09:35:16
5 Spectrometer Frequency 100.62
31-1
f1 (ppm)

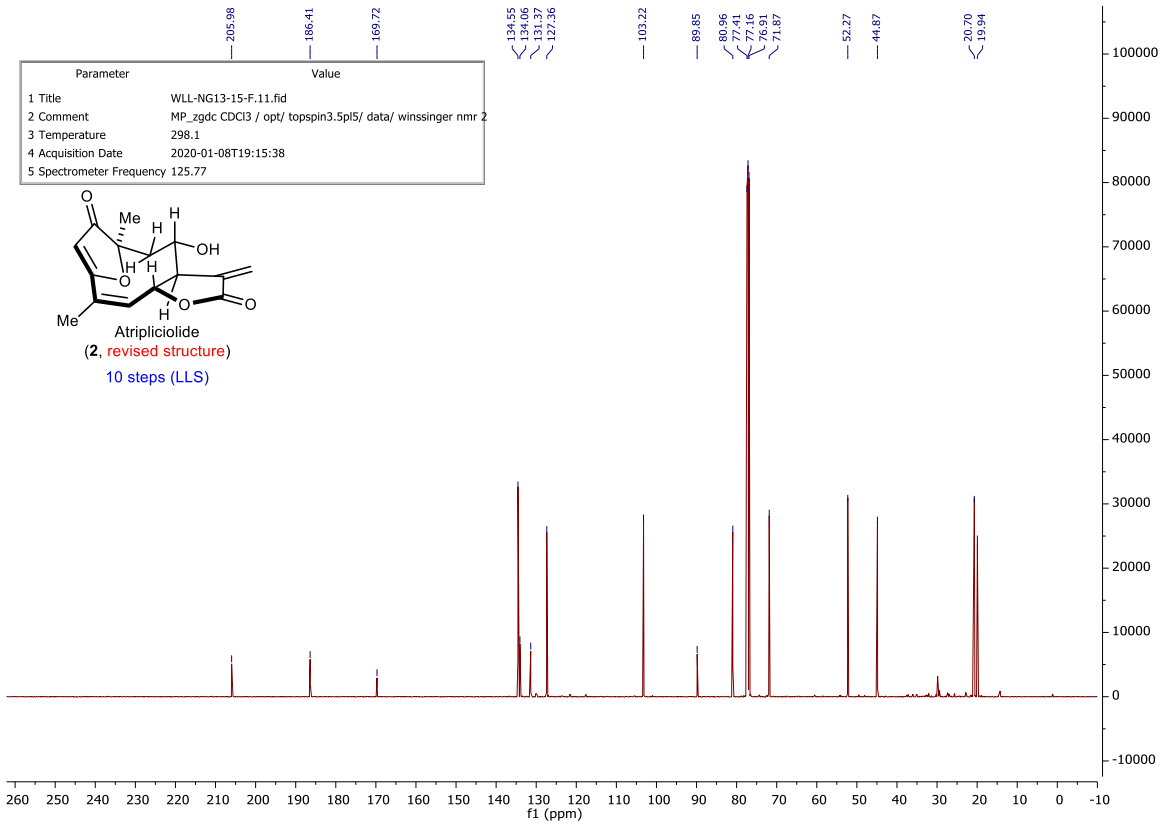

Parameter Value
1 Title wll-ug13-58.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-15T05:43:36
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
OH
O
O
O
Me
31-1
f2 (ppm)
f1 (ppm)

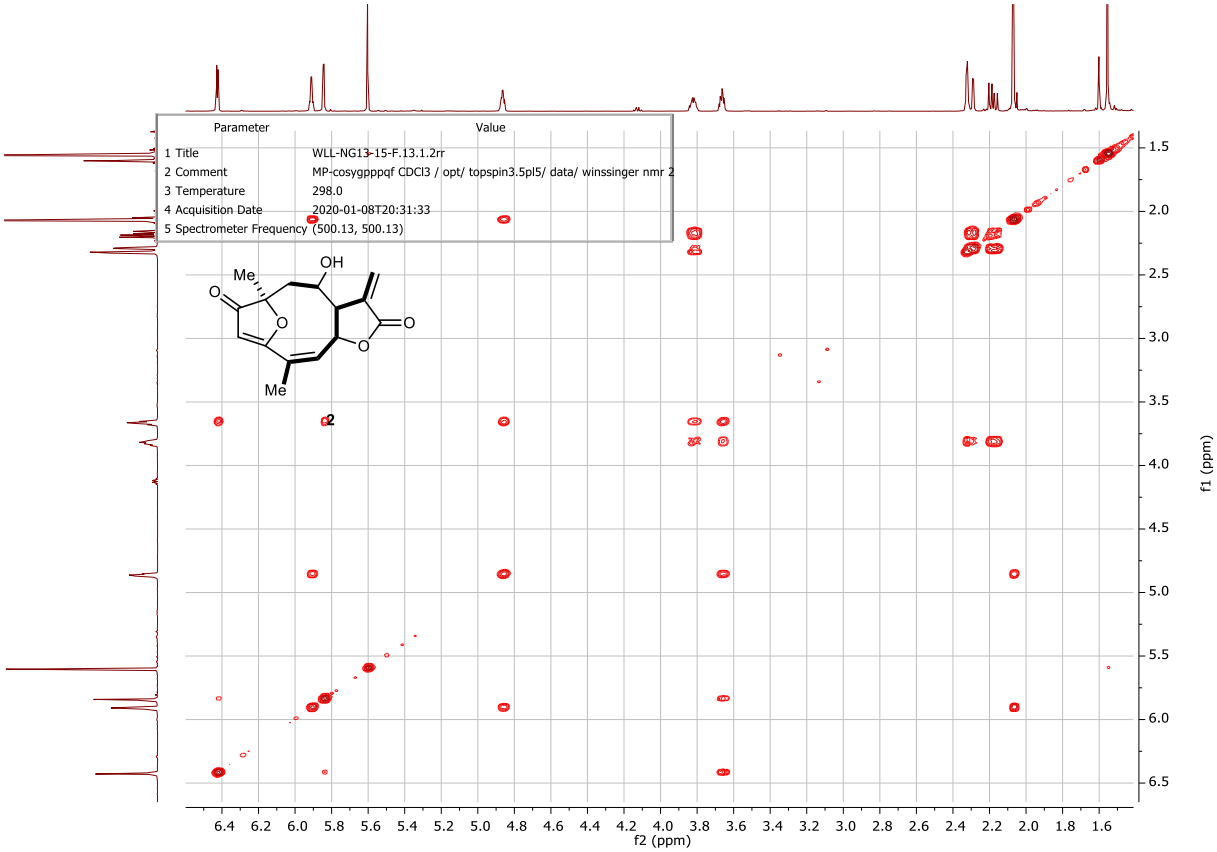

Parameter Value
1 Title wll-ug13-58.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-15T05:50:04
5 Spectrometer Frequency (400.13, 100.61)
O
1
Me
H
8
OH
H
OH
O
O
Me
5
H
31-1
f2 (ppm)
f1 (ppm)

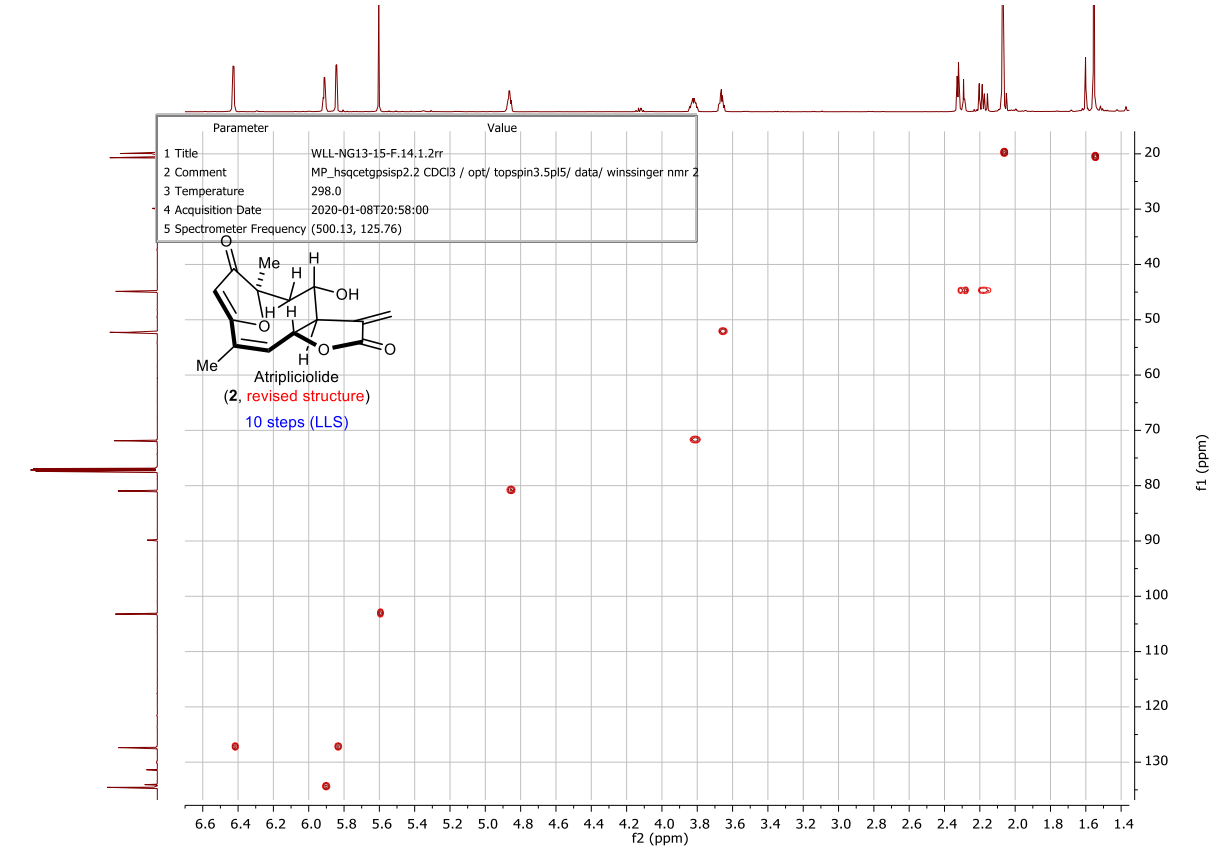

Parameter Value
1 Title wll-ug13-58.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-15T06:05:24
5 Spectrometer Frequency (400.13, 100.61)
OH
Me
OH
O
O
O
Me
31-1
f2 (ppm)
f1 (ppm)

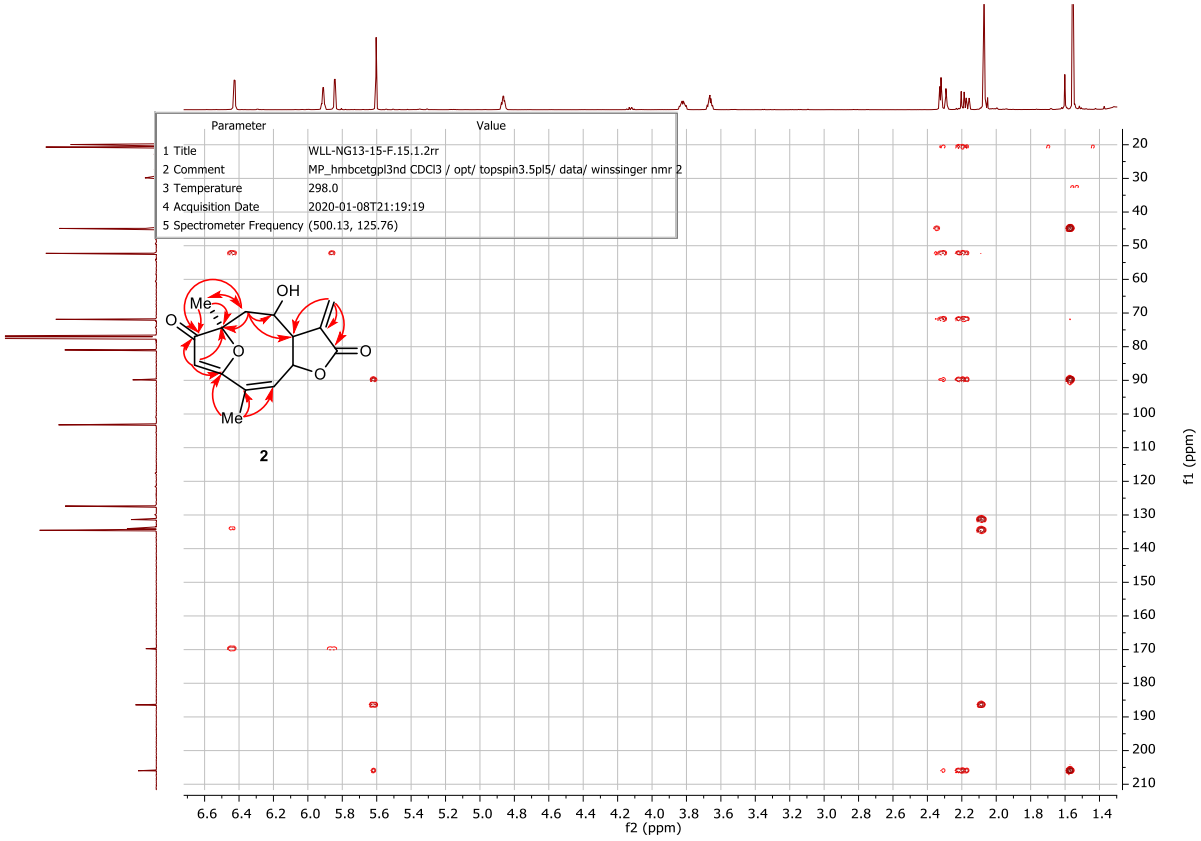

Parameter Value
1 Title wll-ug13-58.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-15T06:44:48
5 Spectrometer Frequency (400.13, 400.13)
O
1
Me
H
8
OH
H
OH
O
O
Me
5
H
31-1
f2 (ppm)
f1 (ppm)

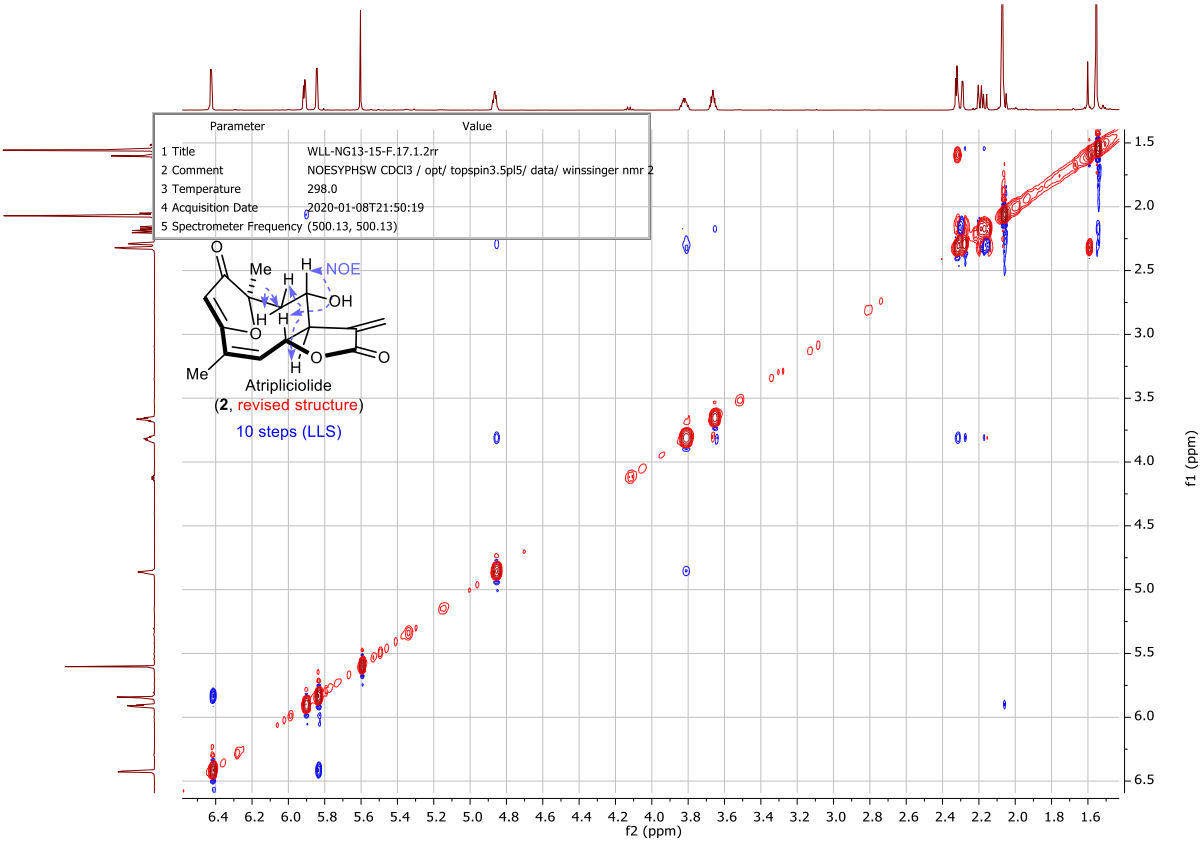

Parameter Value
1 Title WLL-NG13-15-F.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.0
4 Acquisition Date 2020-01-08T16:03:06
5 Spectrometer Frequency 500.13
Me
H
OH
O
Atripliciolide
(2, revised structure)
10 steps (LLS)
f1 (ppm)

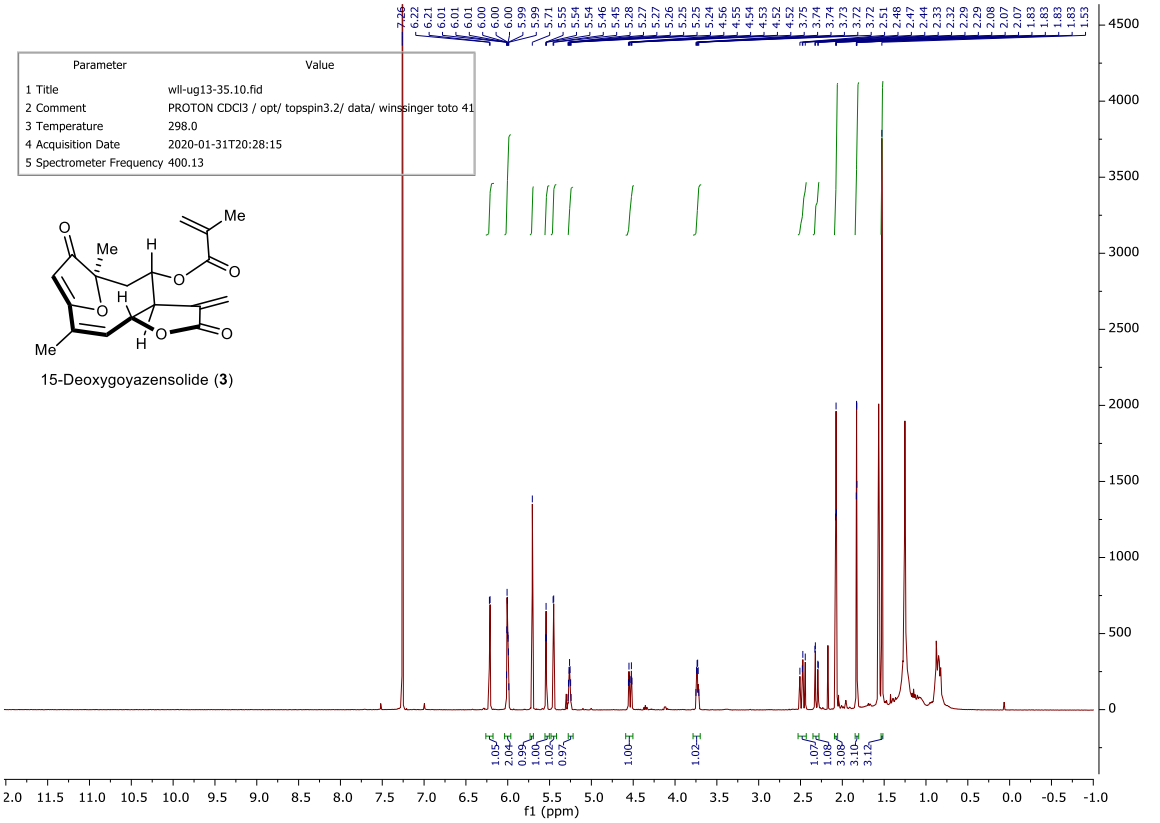

Parameter Value
1 Title WLL-NG13-15-F.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.1
4 Acquisition Date 2020-01-08T19:15:38
5 Spectrometer Frequency 125.77
Me
H
OH
O
Atripliciolide
(2, revised structure)
10 steps (LLS)
f1 (ppm)

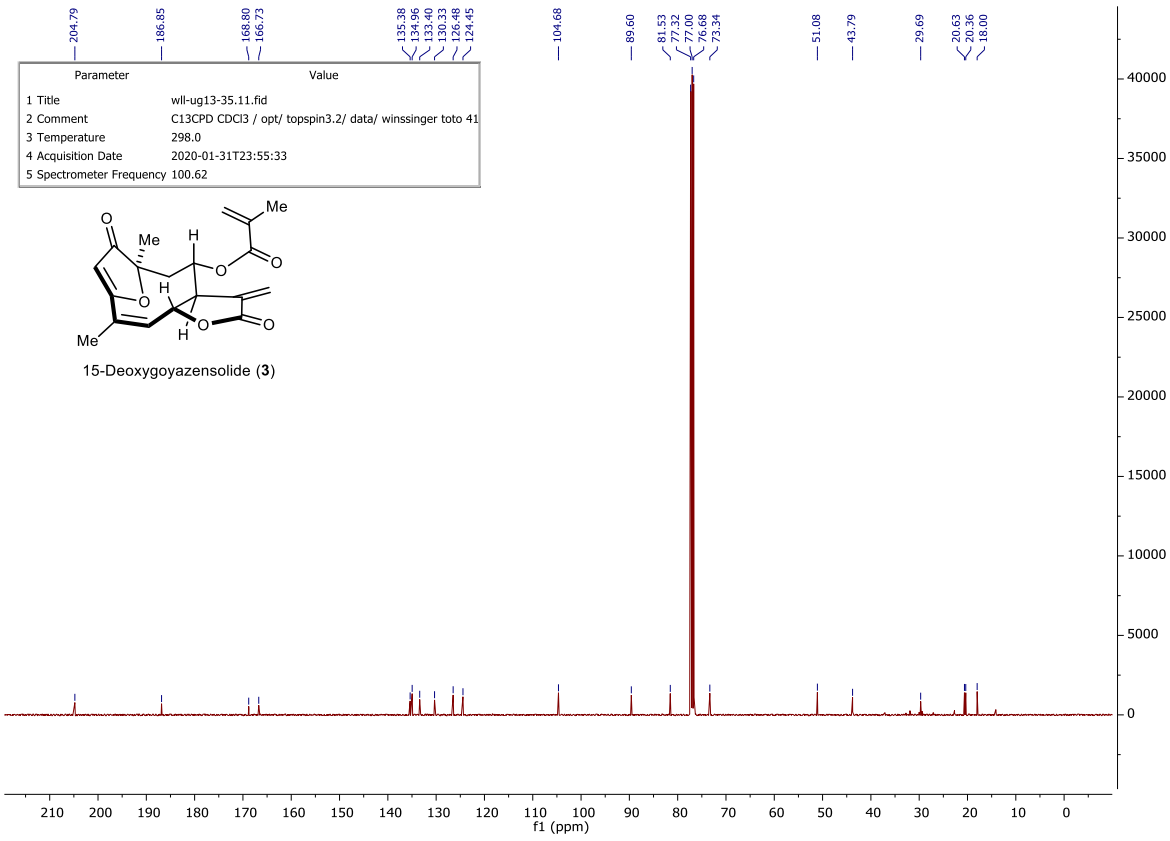

Parameter Value
1 Title WLL-NG13-15-F.13.1.2rr
2 Comment MP-cosygpppqf CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.0
4 Acquisition Date 2020-01-08T20:31:33
5 Spectrometer Frequency (500.13, 500.13)
Me
OH
O
O
O
O
Me
2
f2 (ppm)
f1 (ppm)

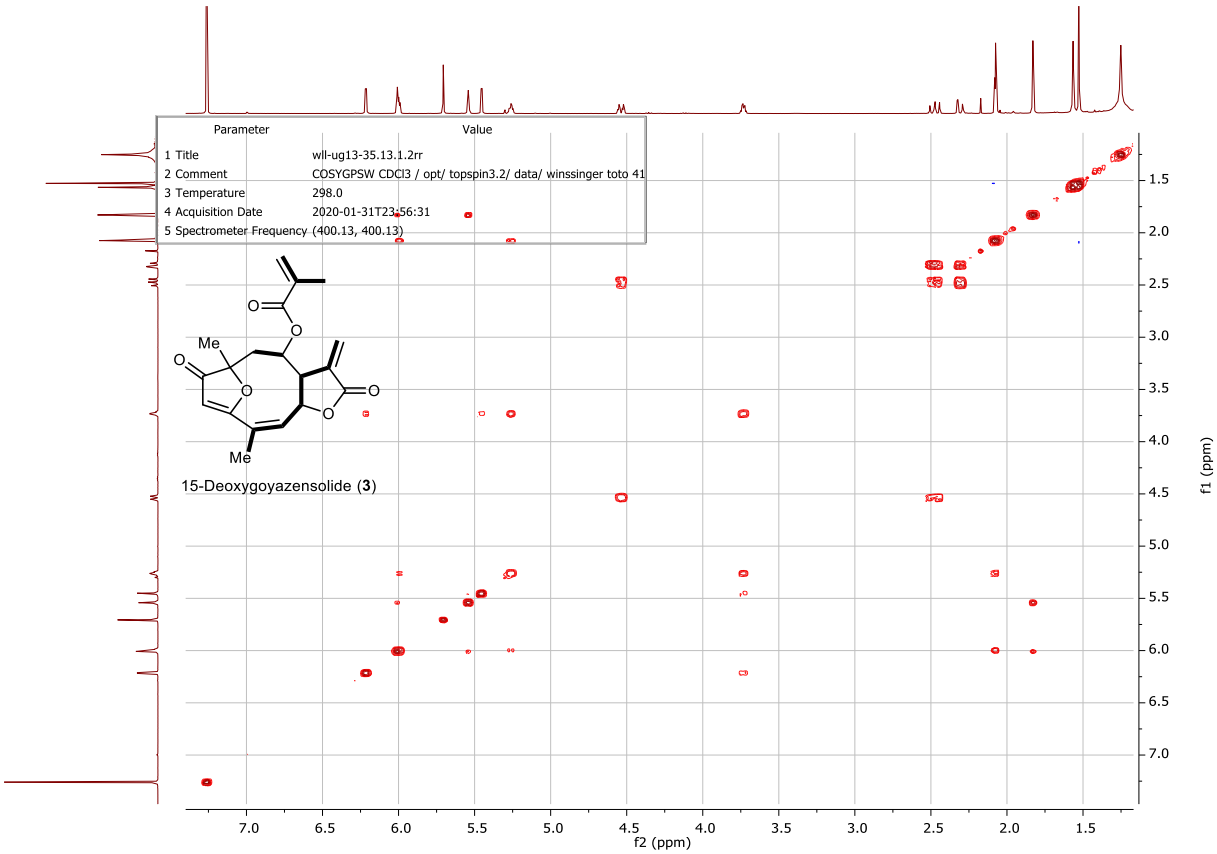

Parameter Value
1 Title WLL-NG13-15-F.14.1.2rr
2 Comment MP_hsqcetgpsisp2.2 CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.0
4 Acquisition Date 2020-01-08T20:58:00
5 Spectrometer Frequency (500.13, 125.76)
Me
H
OH
H
H
O
O
H
O
Me
Atripliciolide
(2, revised structure)
10 steps (LLS)
f2 (ppm)
f1 (ppm)

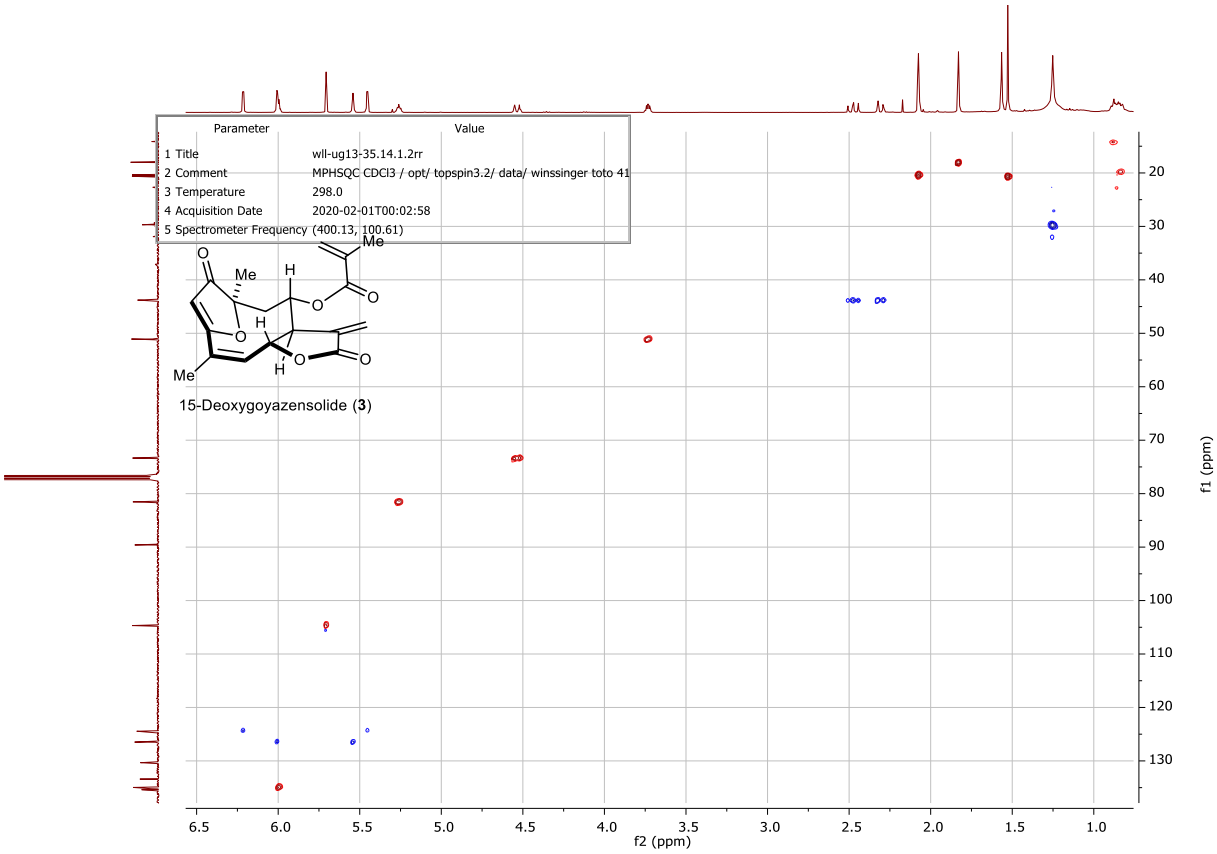

Parameter Value
1 Title WLL-NG13-15-F.15.1.2rr
2 Comment MP_hmbcetgpl3nd CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.0
4 Acquisition Date 2020-01-08T21:19:19
5 Spectrometer Frequency (500.13, 125.76)
Me
OH
O
O
O
O
Me
2
f2 (ppm)
f1 (ppm)

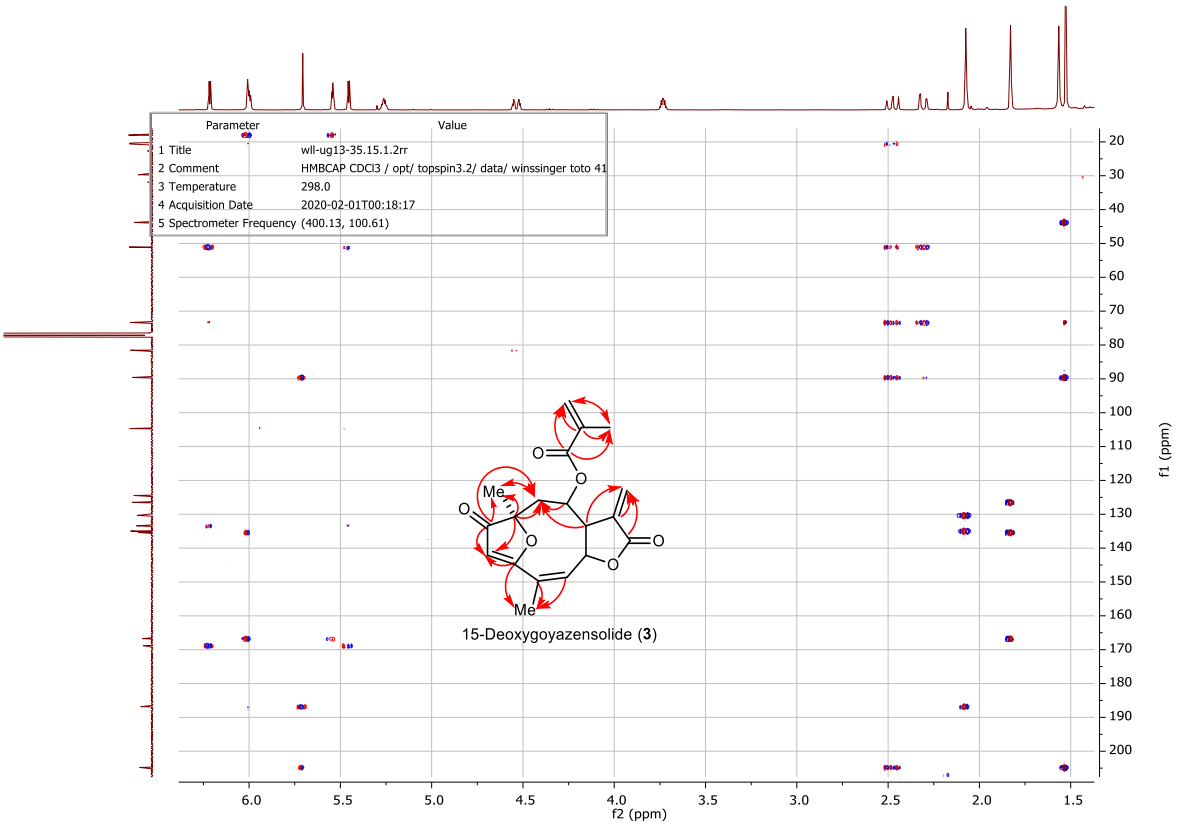

Parameter Value
1 Title WLL-NG13-15-F.17.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.0
4 Acquisition Date 2020-01-08T21:50:19
5 Spectrometer Frequency (500.13, 500.13)
NOE
Me
OH
Me
Atripliciolide
(2, revised structure)
10 steps (LLS)
f2 (ppm)
f1 (ppm)

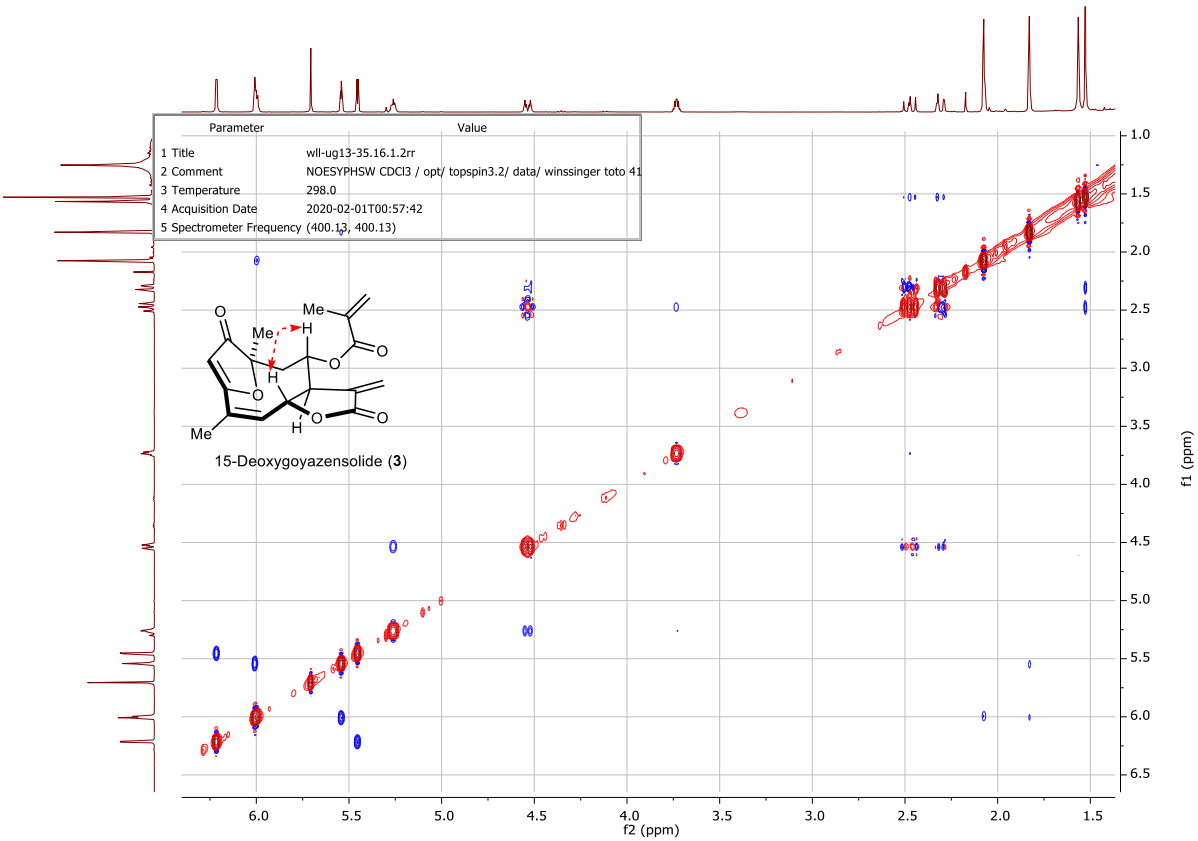

Parameter Value
1 Title wll-ug13-35.10.fid
2 Comment PROTON CDCl3 / opt/ topspin3.2/ data/ winssinger toto 41
3 Temperature 298.0
4 Acquisition Date 2020-01-31T20:28:15
5 Spectrometer Frequency 400.13
15-Deoxygoyazensolide (3)
f1 (ppm)

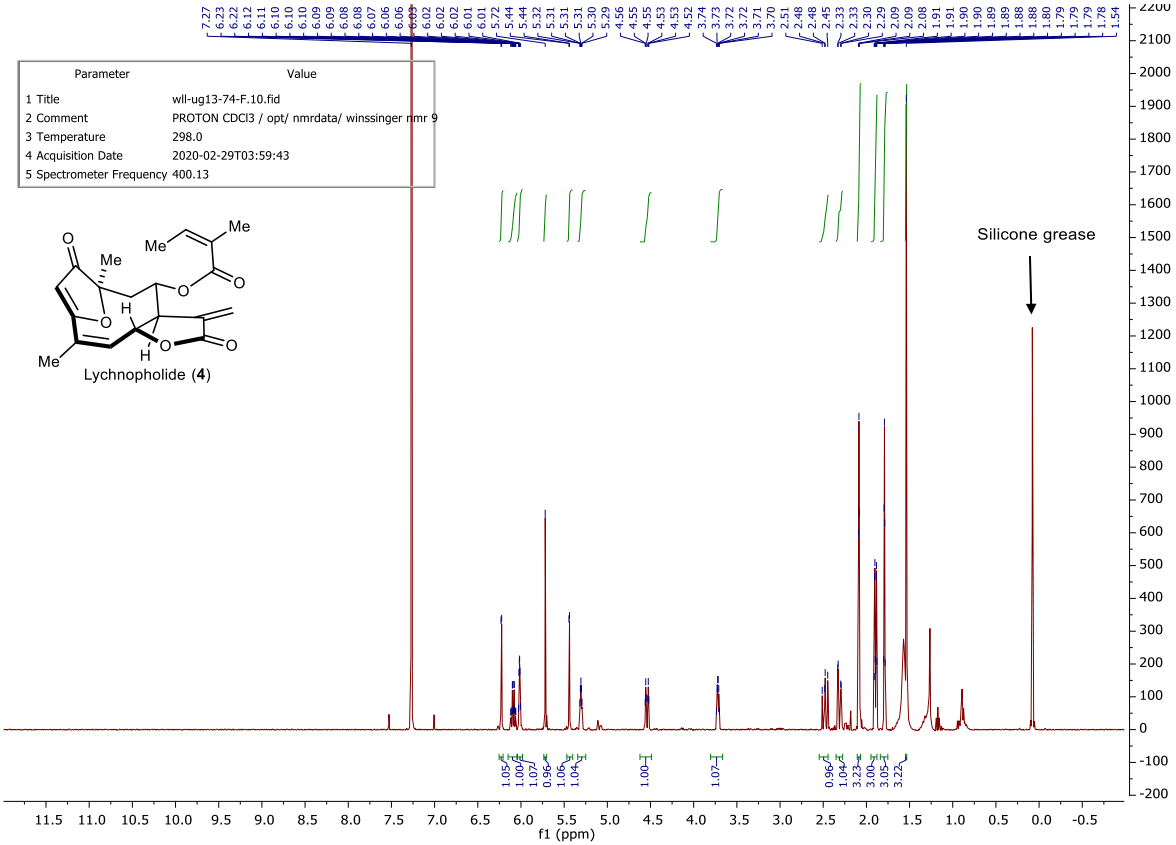

Parameter Value
1 Title wll-ug13-35.11.fid
2 Comment C13CPD CDCl3 / opt/ topspin3.2/ data/ winssinger toto 41
3 Temperature 298.0
4 Acquisition Date 2020-01-31T23:55:33
5 Spectrometer Frequency 100.62
15-Deoxygoyazensolide (3)
f1 (ppm)

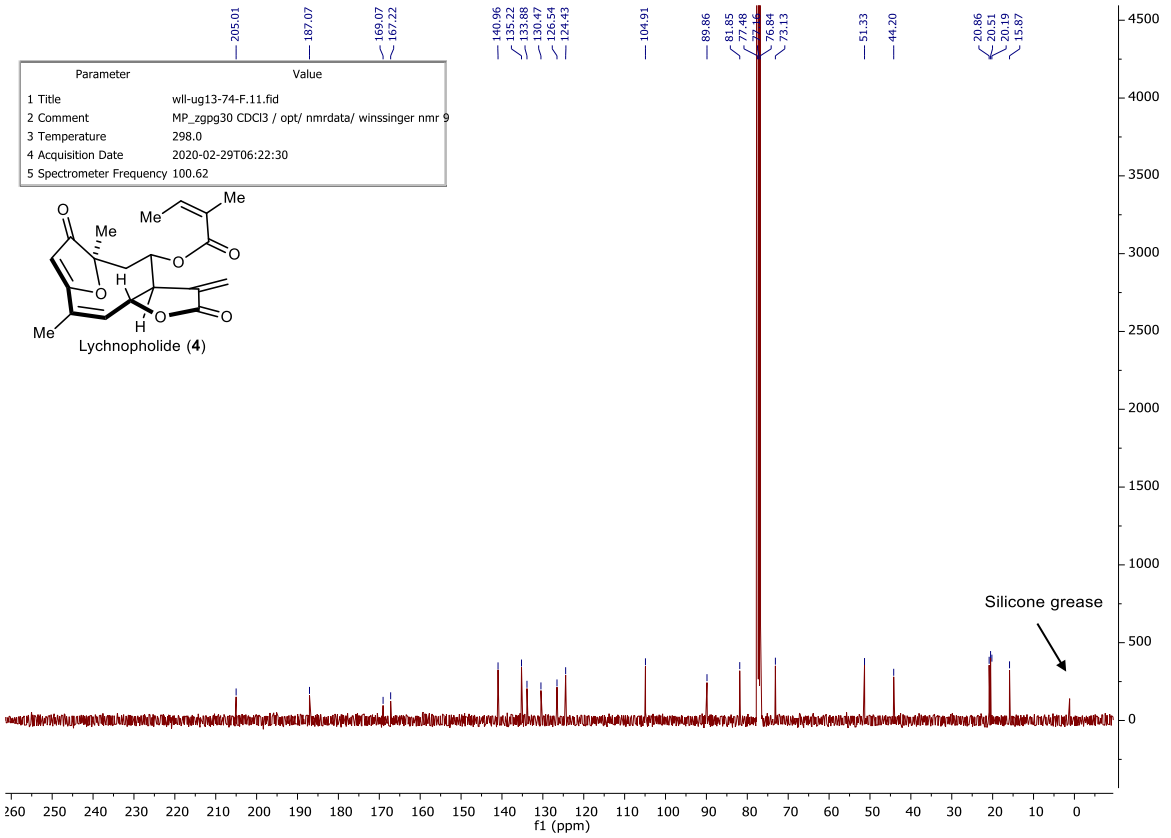

Parameter Value
1 Title wll-ug13-35.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 41
3 Temperature 298.0
4 Acquisition Date 2020-01-31T23:56:31
5 Spectrometer Frequency (400.13, 400.13)
15-Deoxygoyazensolide (3)
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug13-35.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ topspin3.2/ data/ winssinger toto 41
3 Temperature 298.0
4 Acquisition Date 2020-02-01T00:02:58
5 Spectrometer Frequency (400.13, 100.61)
15-Deoxygoyazensolide (3)
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug13-35.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ topspin3.2/ data/ winssinger toto 41
3 Temperature 298.0
4 Acquisition Date 2020-02-01T00:18:17
5 Spectrometer Frequency (400.13, 100.61)
Me
Me
15-Deoxygoyazensolide (3)
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug13-35.16.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 41
3 Temperature 298.0
4 Acquisition Date 2020-02-01T00:57:42
5 Spectrometer Frequency (400.13, 400.13)
Me
Me
H
H
H
Me
15-Deoxygoyazensolide (3)
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug13-74-F.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 9
3 Temperature 298.0
4 Acquisition Date 2020-02-29T03:59:43
5 Spectrometer Frequency 400.13
Lychnopholide (4)
Silicone grease
f1 (ppm)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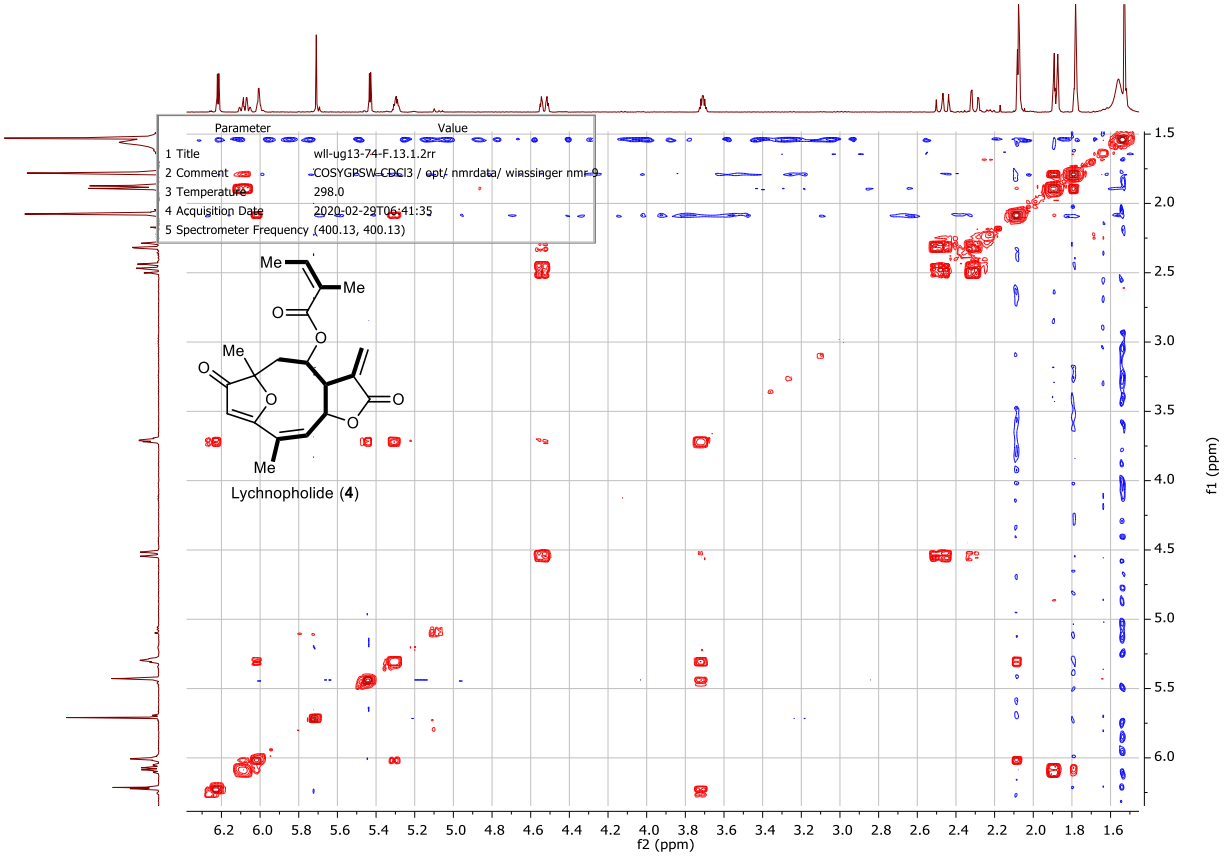
1 Title wll-ug13-74-F.11.fid
2 Comment MP_zgpg30 CDCl3 / opt/ nmrdata/ winssinger nmr 9
3 Temperature 298.0
4 Acquisition Date 2020-02-29T06:22:30
5 Spectrometer Frequency 100.62
Lychnopholide (4)
Silicone grease
f1 (ppm)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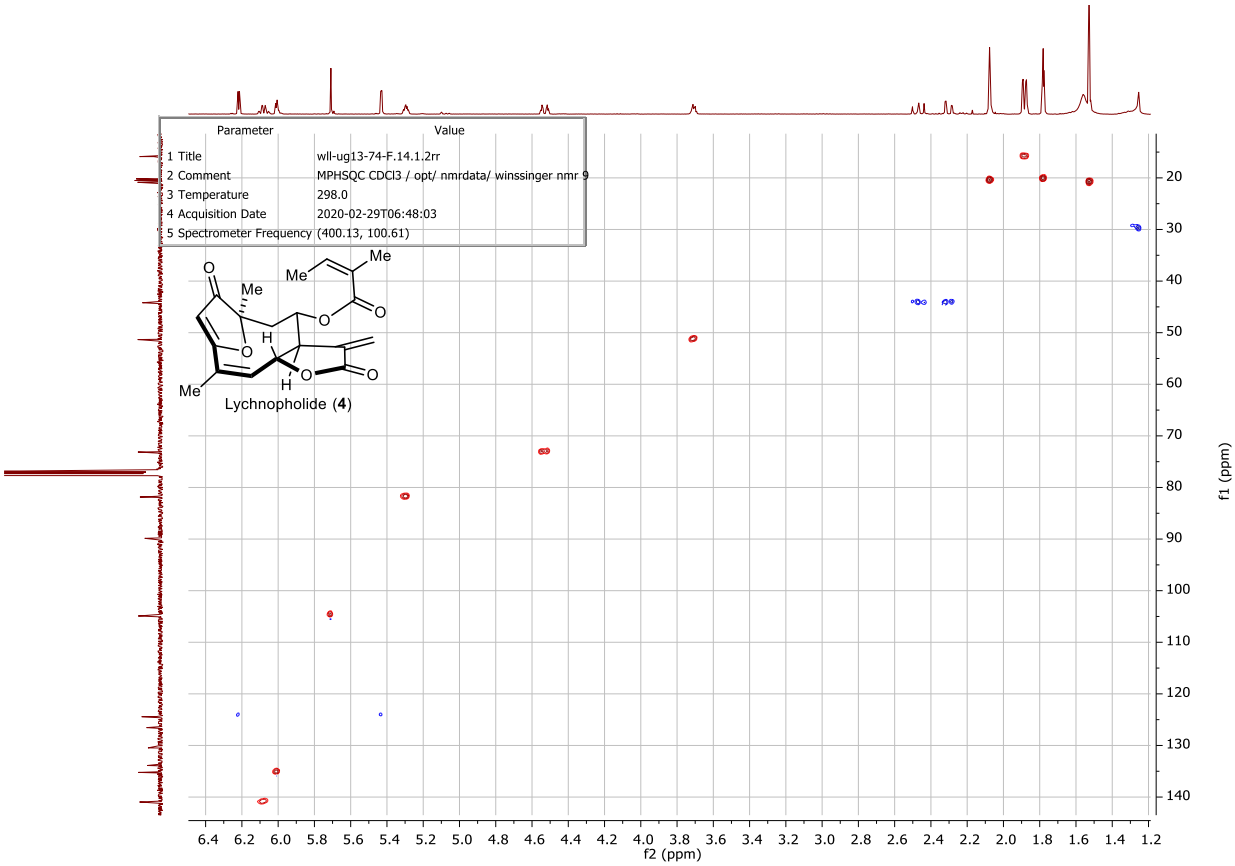
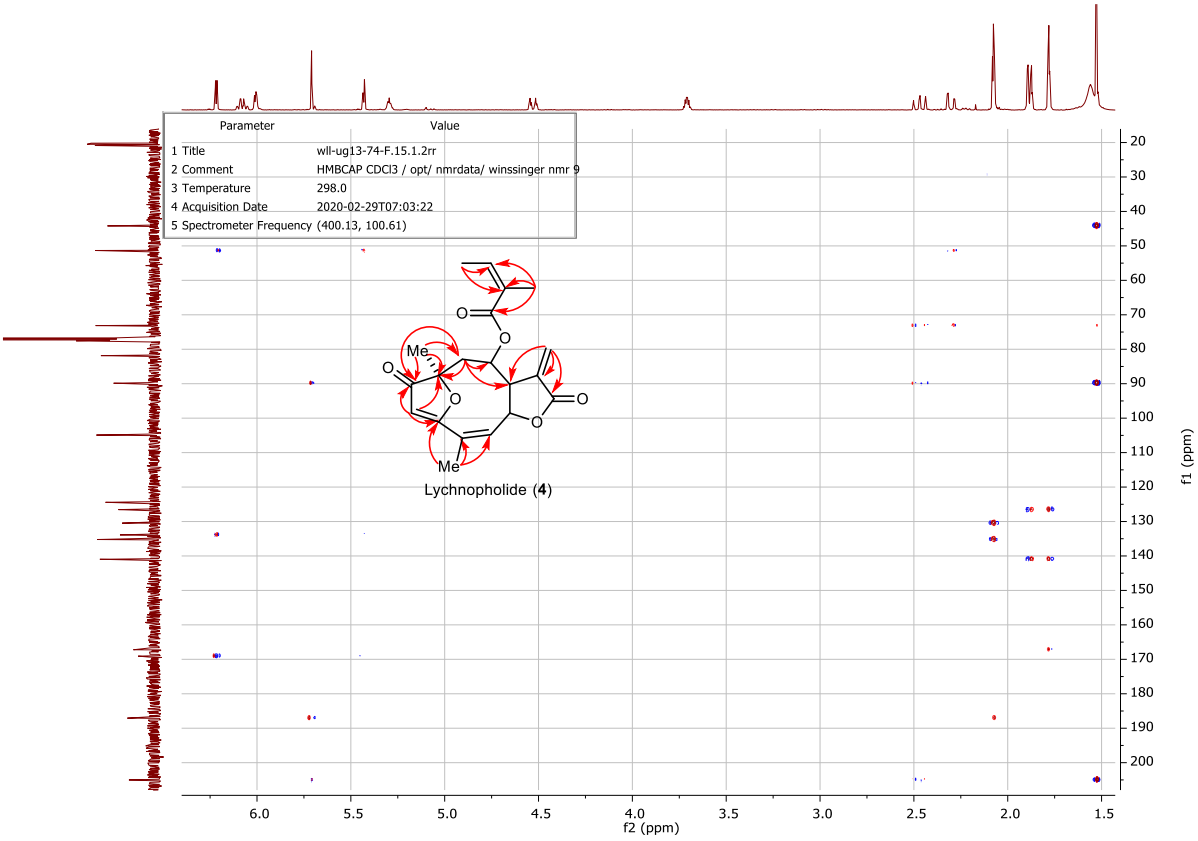
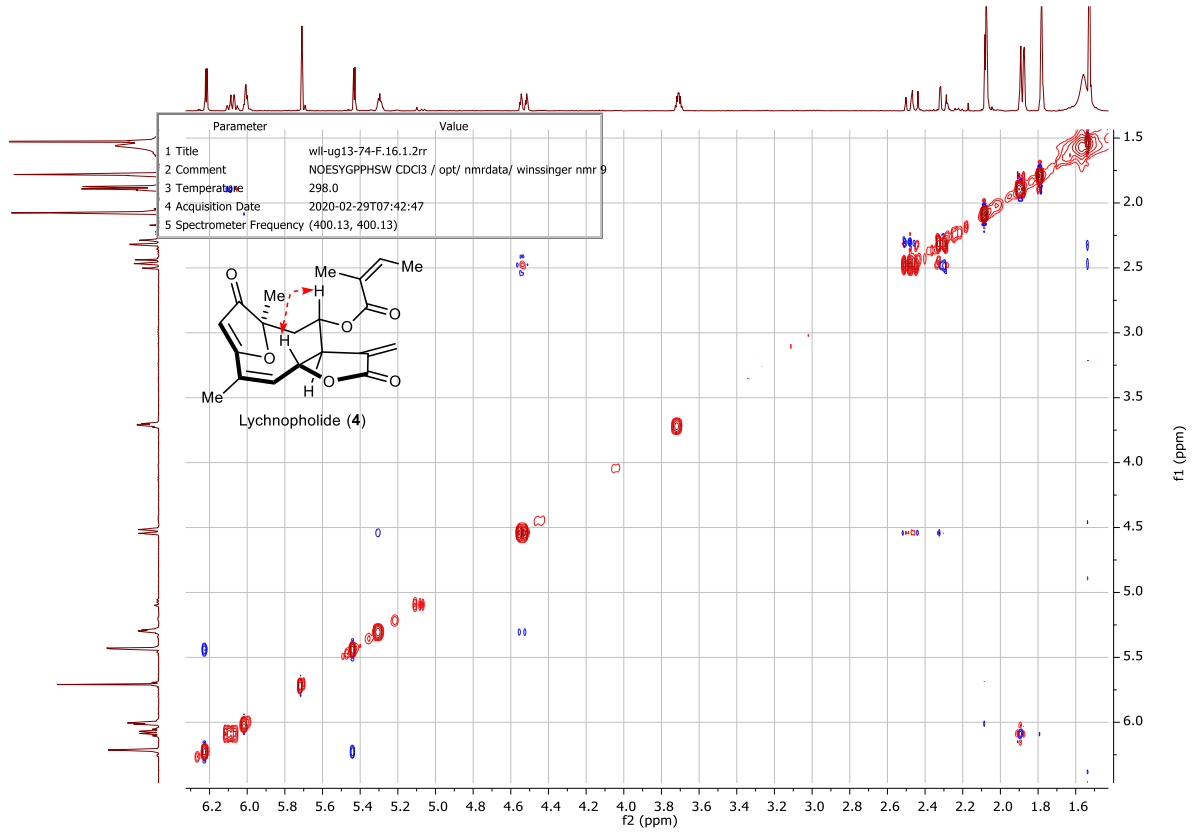
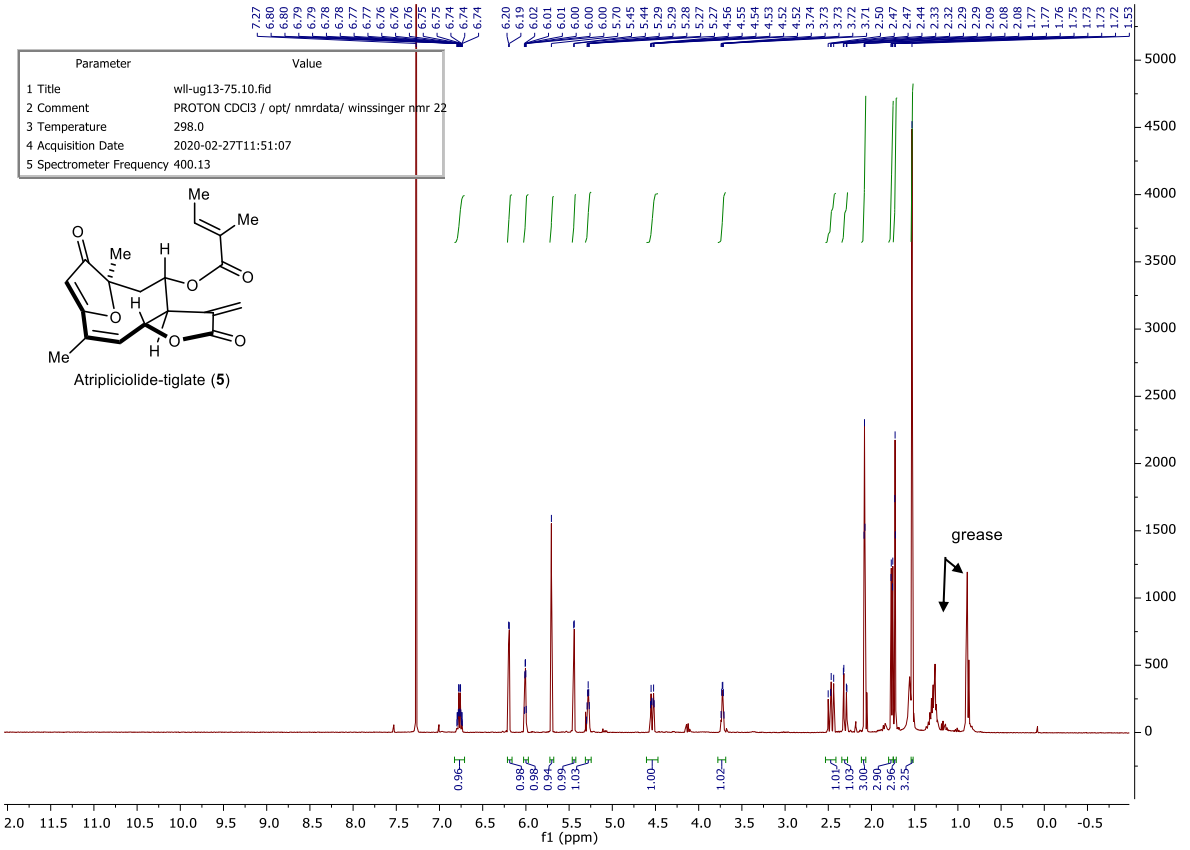
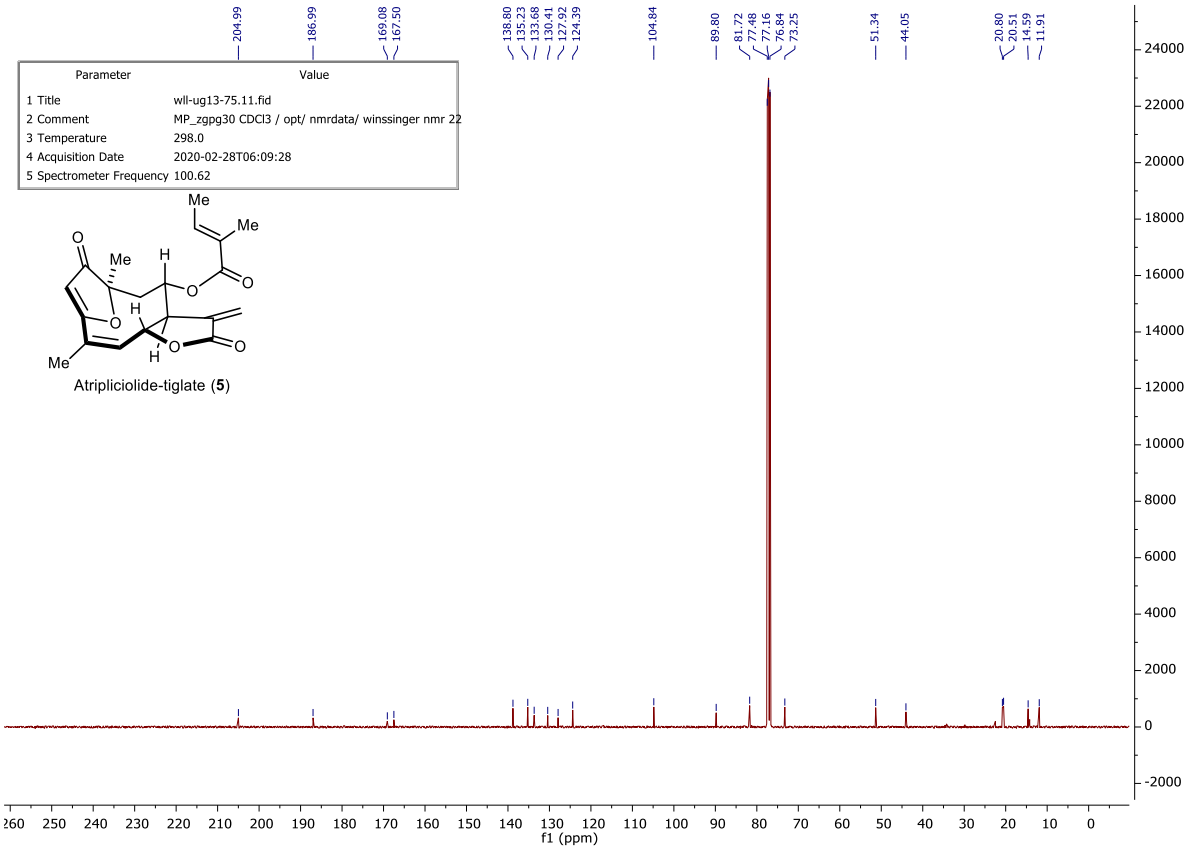
1 Title wll-ug13-74-F.13.1.2rr
2 Comment COSYGPSW-CDCl3 / opt/ nmrdata/ winssinger nmr 9
3 Temperature 298.0
4 Acquisition Date 2020-02-29T06:41:35
5 Spectrometer Frequency (400.13, 400.13)
Lychnopholide (4)
f2 (ppm)
f1 (ppm)

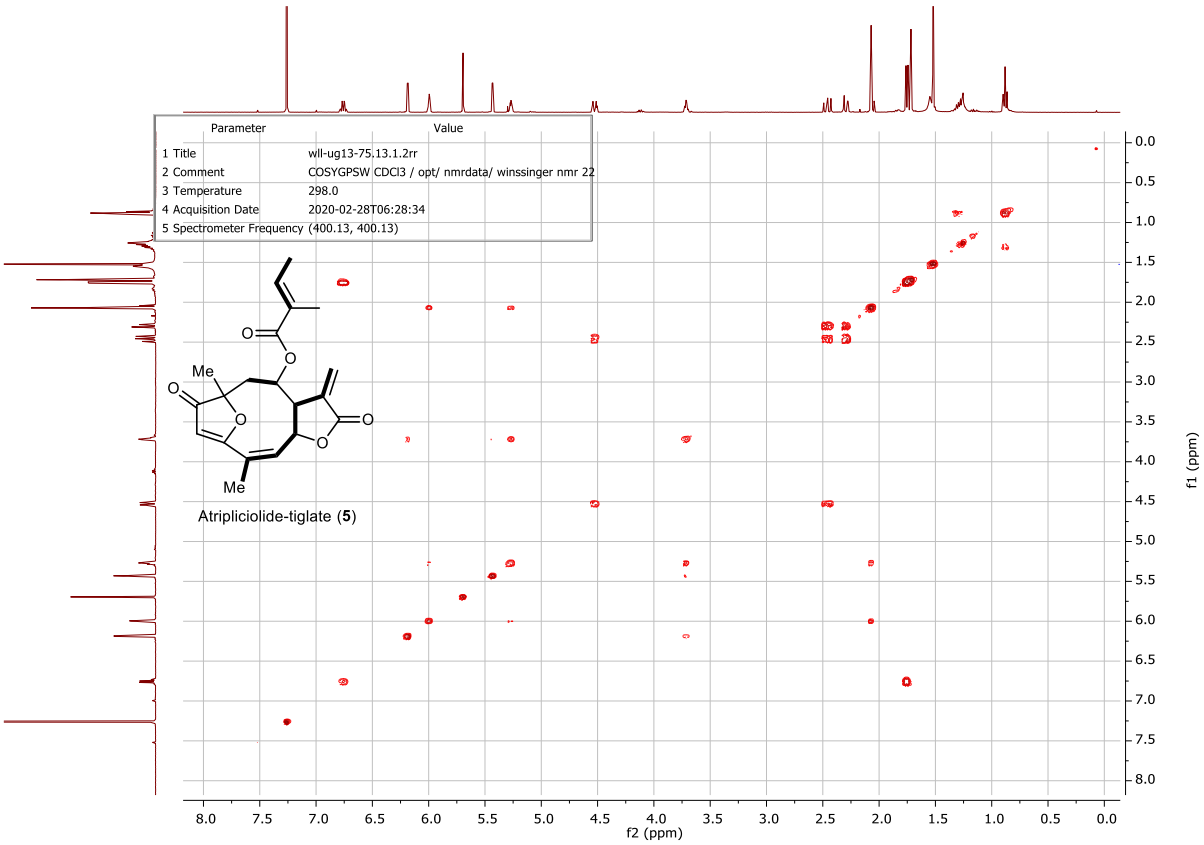

Parameter Value
1 Title wll-ug13-74-F.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 9
3 Temperature 298.0
4 Acquisition Date 2020-02-29T06:48:03
5 Spectrometer Frequency (400.13, 100.61)
Lychnopholide (4)
f2 (ppm)
f1 (ppm)

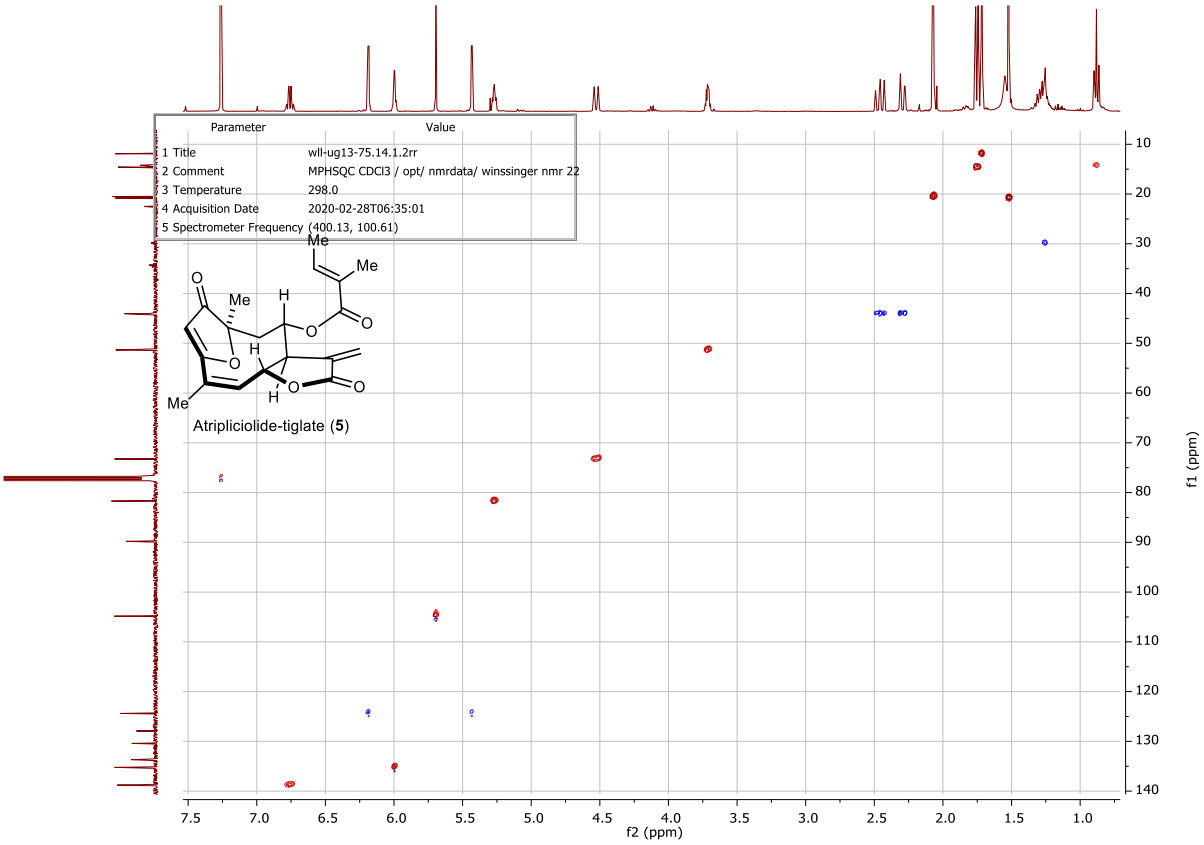

Parameter Value
1 Title wll-ug13-74-F.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 9
3 Temperature 298.0
4 Acquisition Date 2020-02-29T07:03:22
5 Spectrometer Frequency (400.13, 100.61)
Me
Me
Lychnopholide (4)
f2 (ppm)
f1 (ppm)

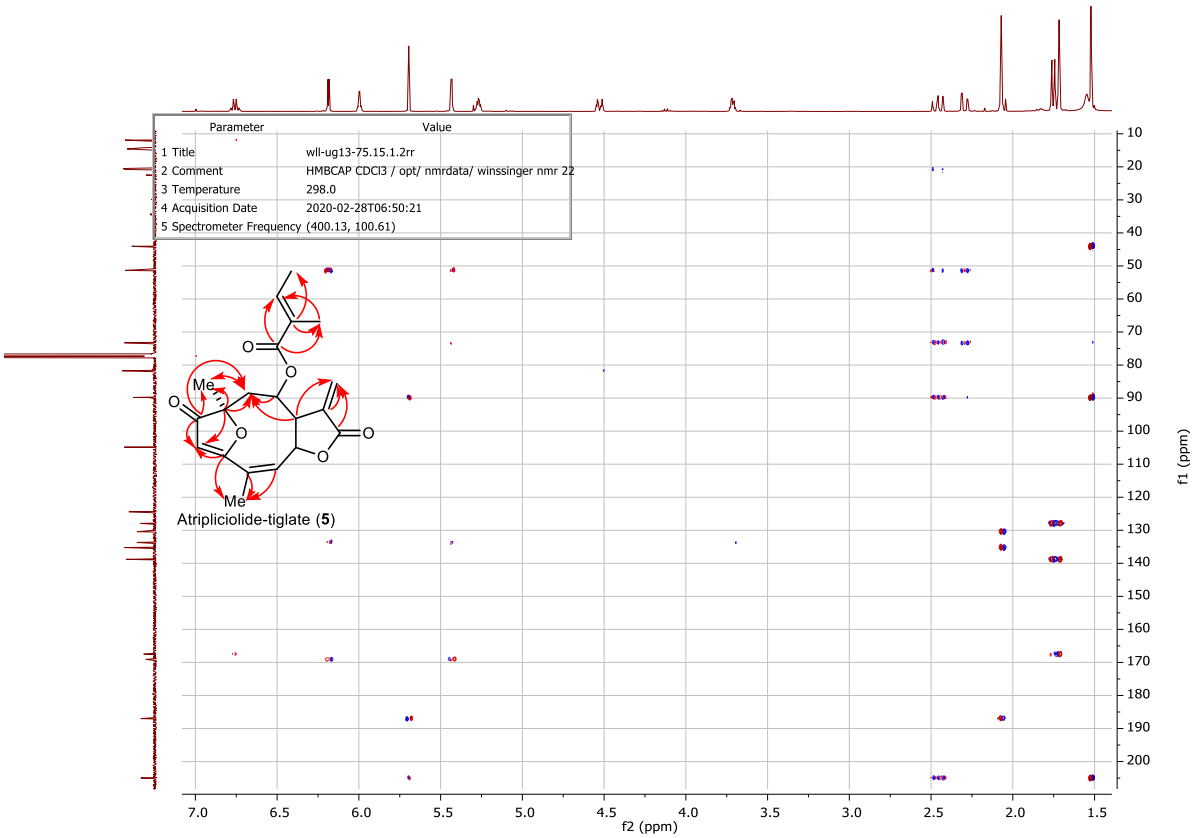

Parameter Value
1 Title wll-ug13-74-F.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 9
3 Temperature 298.0
4 Acquisition Date 2020-02-29T07:42:47
5 Spectrometer Frequency (400.13, 400.13)
Me
Me
Me
Lychnopholide (4)
f2 (ppm)
f1 (ppm)

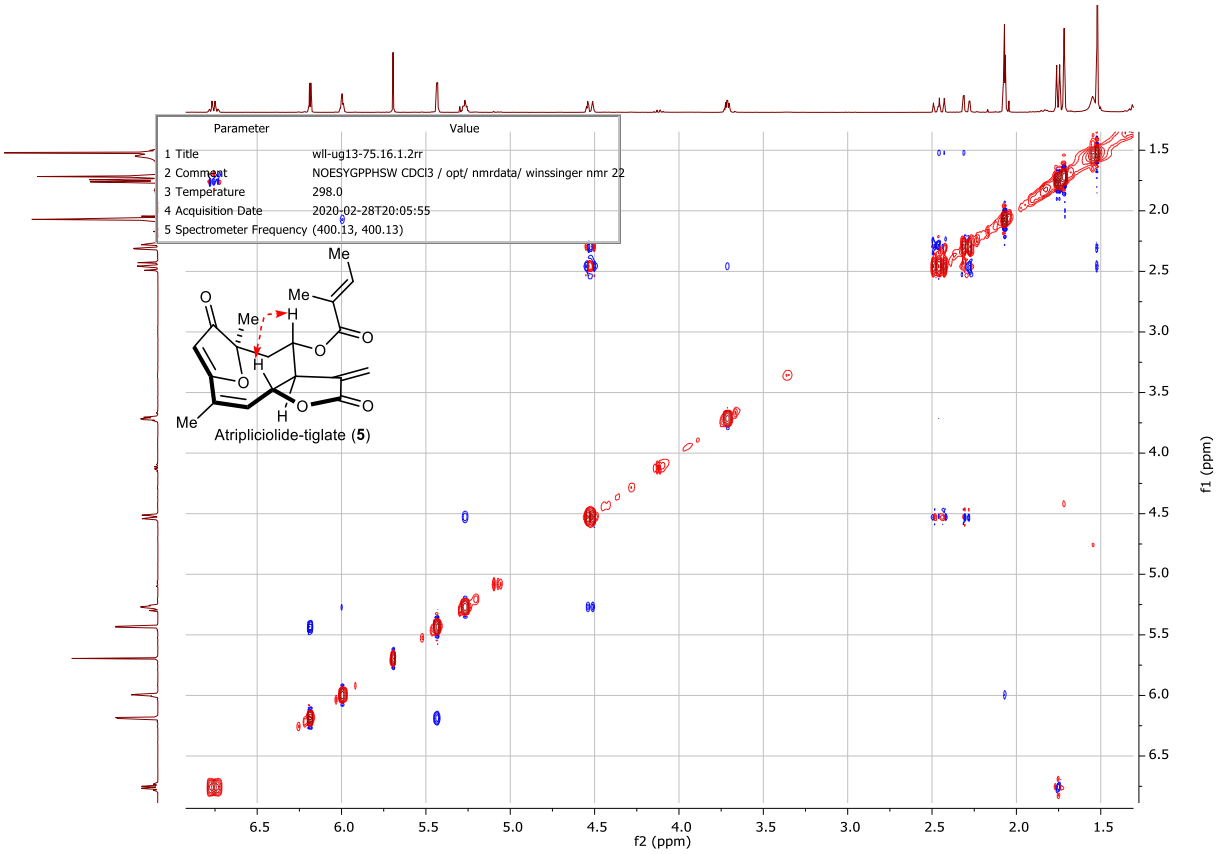

Parameter Value
1 Title wll-ug13-75.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-27T11:51:07
5 Spectrometer Frequency 400.13
Atripliciolide-tiglate (5)
grease
f1 (ppm)

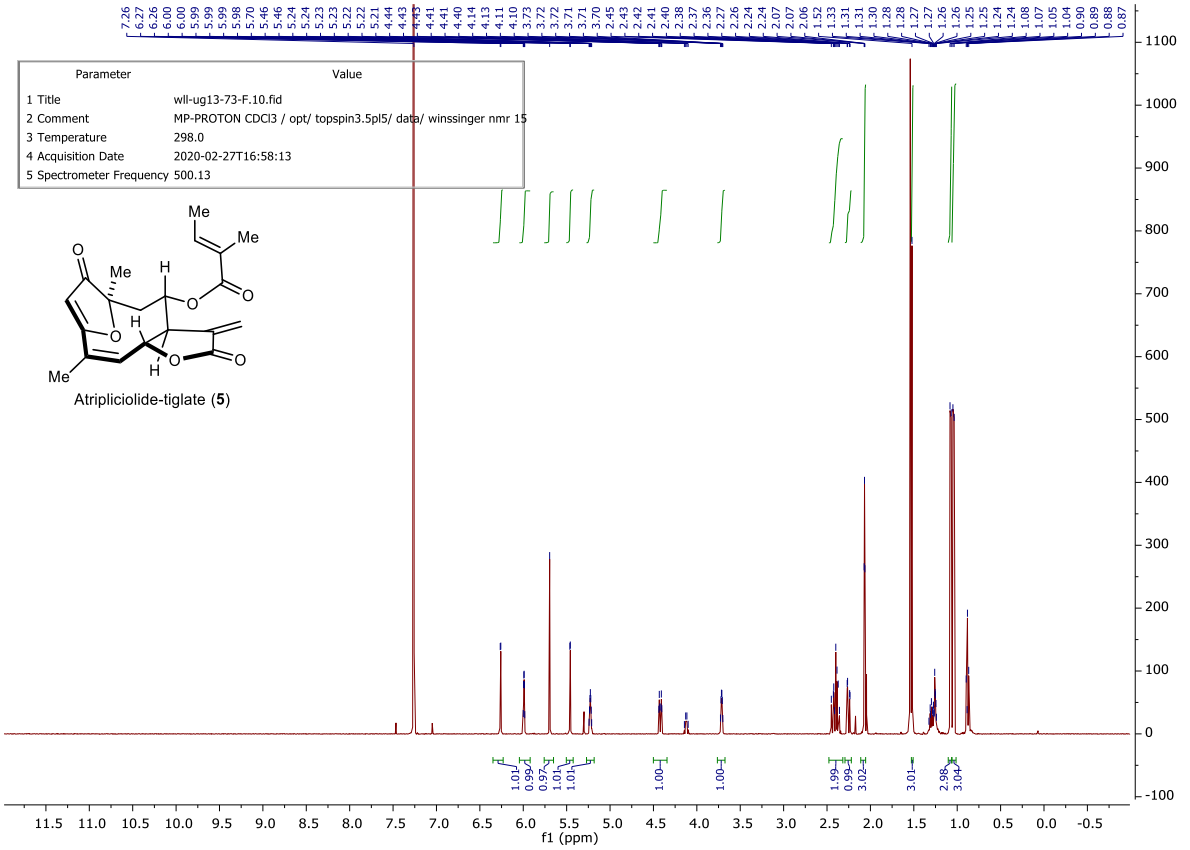

Parameter Value
1 Title wll-ug13-75.11.fid
2 Comment MP_zgpg30 CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-28T06:09:28
5 Spectrometer Frequency 100.62
Atripliciolide-tiglate (5)
f1 (ppm)

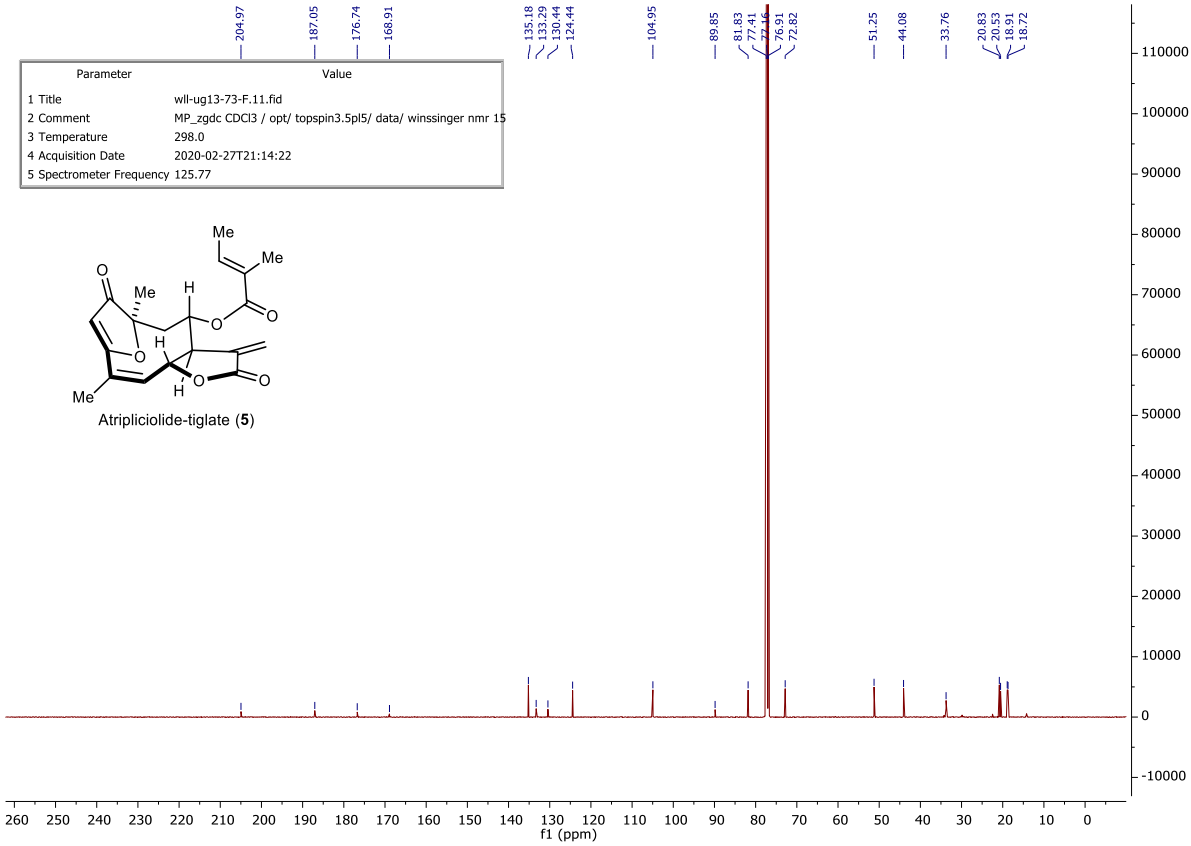

Parameter Value
1 Title wll-ug13-75.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-28T06:28:34
5 Spectrometer Frequency (400.13, 400.13)
Me
Me
Atripliciolide-tiglate (5)
f2 (ppm)
f1 (ppm)

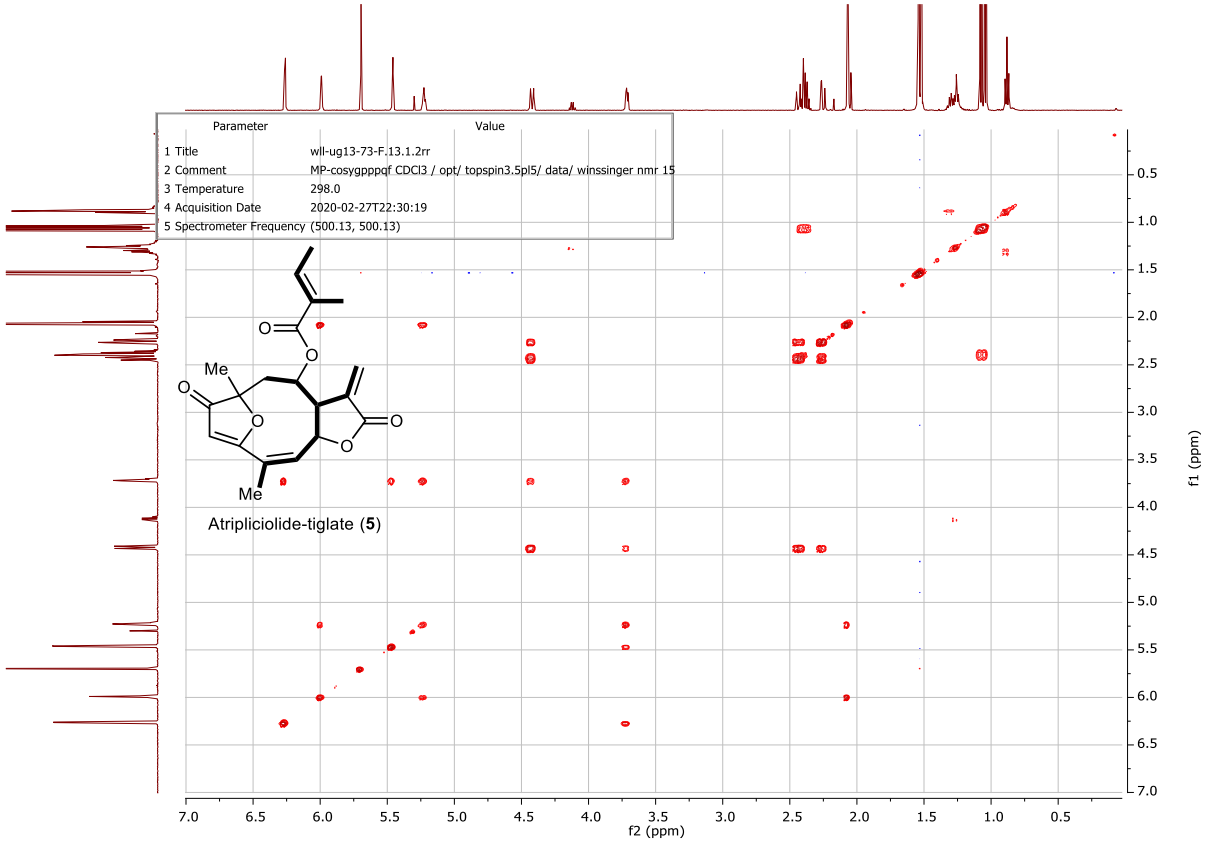

Parameter Value
1 Title wll-ug13-75.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-28T06:35:01
5 Spectrometer Frequency (400.13, 100.61)
Me
Me
Me
Atripliciolide-tiglate (5)
f2 (ppm)
f1 (ppm)

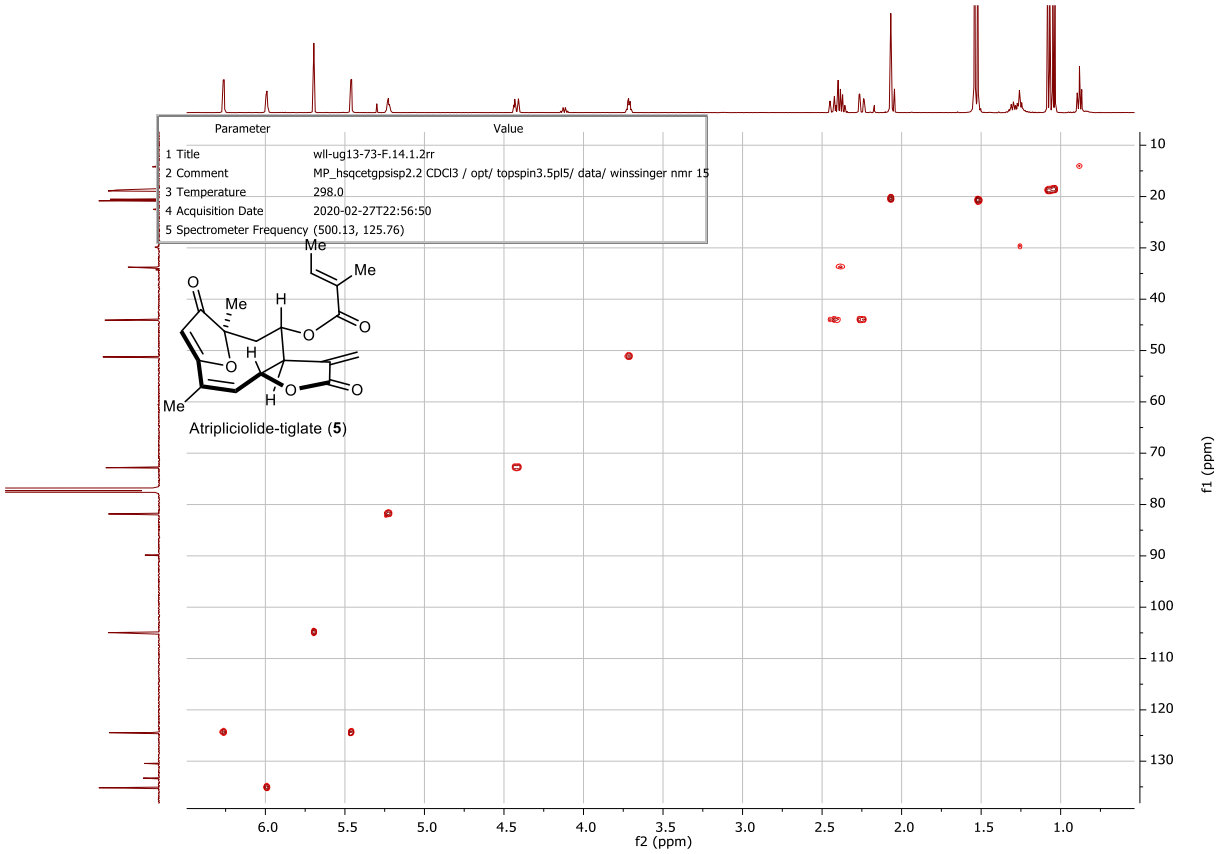

Parameter Value
1 Title wll-ug13-75.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-28T06:50:21
5 Spectrometer Frequency (400.13, 100.61)
Me
Me
Atripliciolide-tiglate (5)
f2 (ppm)
f1 (ppm)

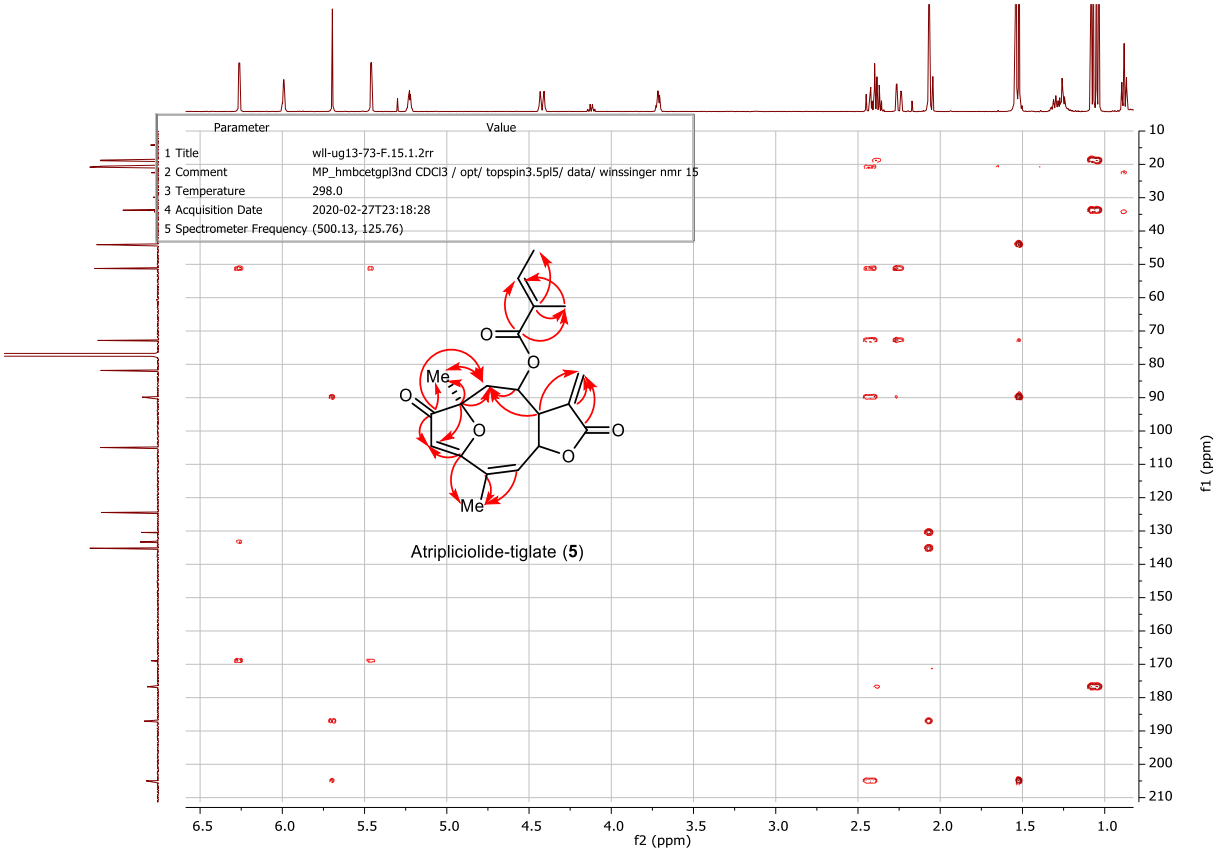

Parameter Value
1 Title wll-ug13-75.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 22
3 Temperature 298.0
4 Acquisition Date 2020-02-28T20:05:55
5 Spectrometer Frequency (400.13, 400.13)
Me
Me
Me
Me
Atripliciolide-tiglate (5)
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug13-73-F.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Temperature 298.0
4 Acquisition Date 2020-02-27T16:58:13
5 Spectrometer Frequency 500.13
Atripliciolide-tiglate (5)
f1 (ppm)


Parameter Value
1 Title wll-ug13-73-F.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Temperature 298.0
4 Acquisition Date 2020-02-27T21:14:22
5 Spectrometer Frequency 125.77
Atripliciolide-tiglate (5)
f1 (ppm)


Parameter Value
1 Title wll-ug13-73-F.13.1.2rr
2 Comment MP-cosygpppqf CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Temperature 298.0
4 Acquisition Date 2020-02-27T22:30:19
5 Spectrometer Frequency (500.13, 500.13)
Me
Me
Atripliciolide-tiglate (5)
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug13-73-F.14.1.2rr
2 Comment MP_hsqcetgpsisp2.2 CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Temperature 298.0
4 Acquisition Date 2020-02-27T22:56:50
5 Spectrometer Frequency (500.13, 125.76)
Me
Me
Me
Atripliciolide-tiglate (5)
f2 (ppm)
f1 (ppm)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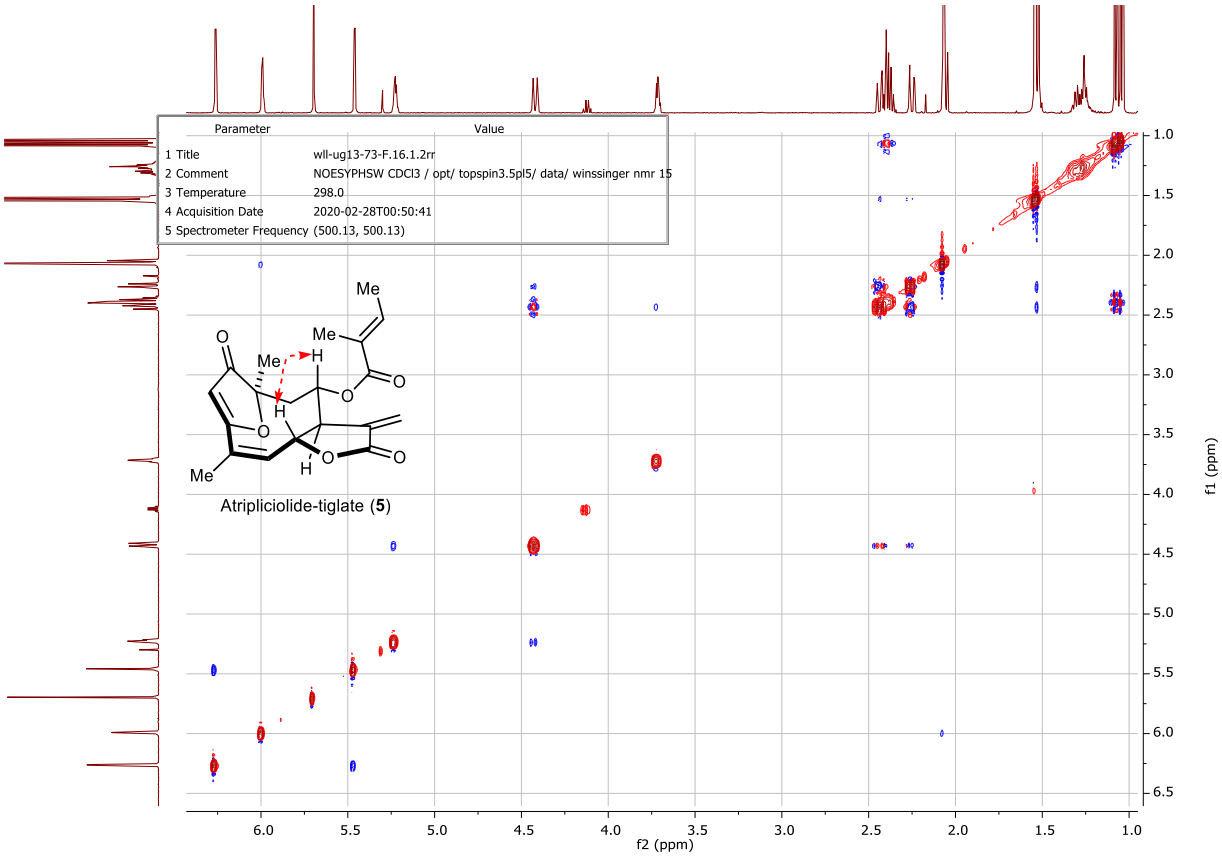
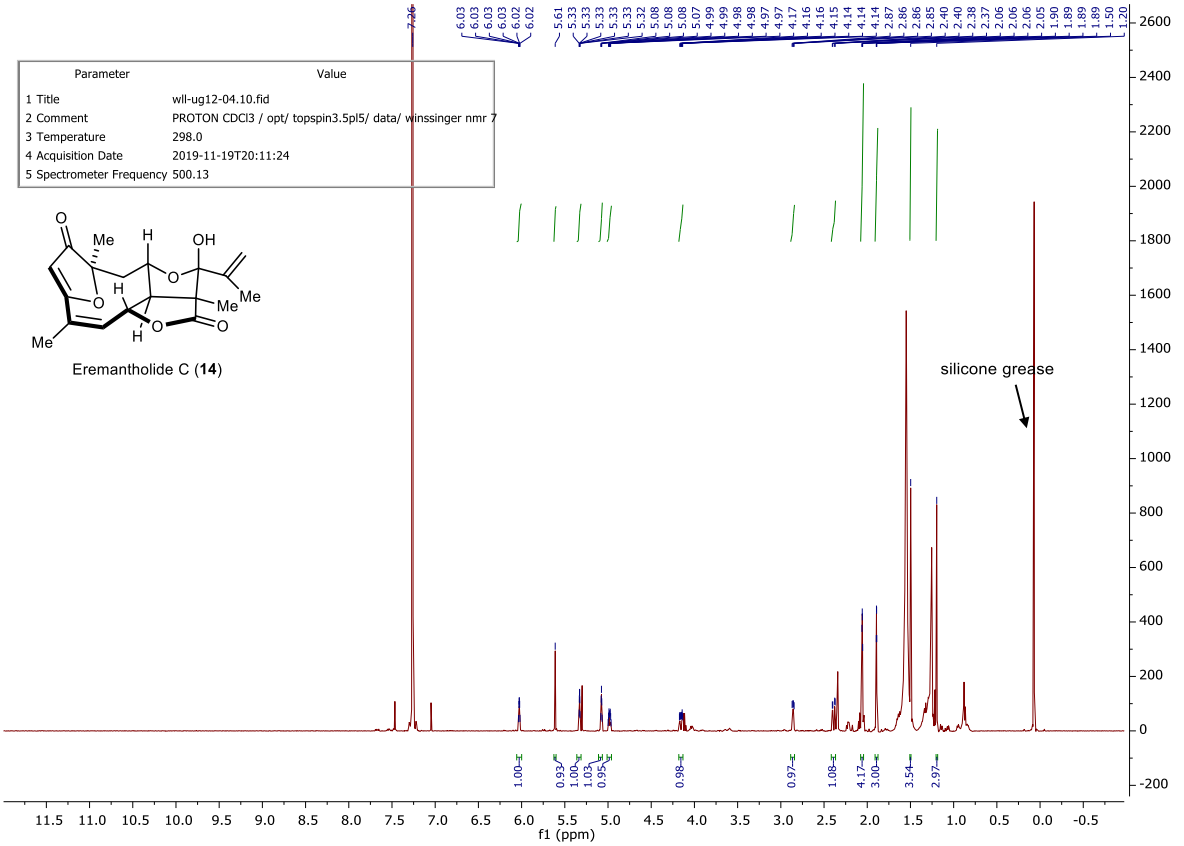
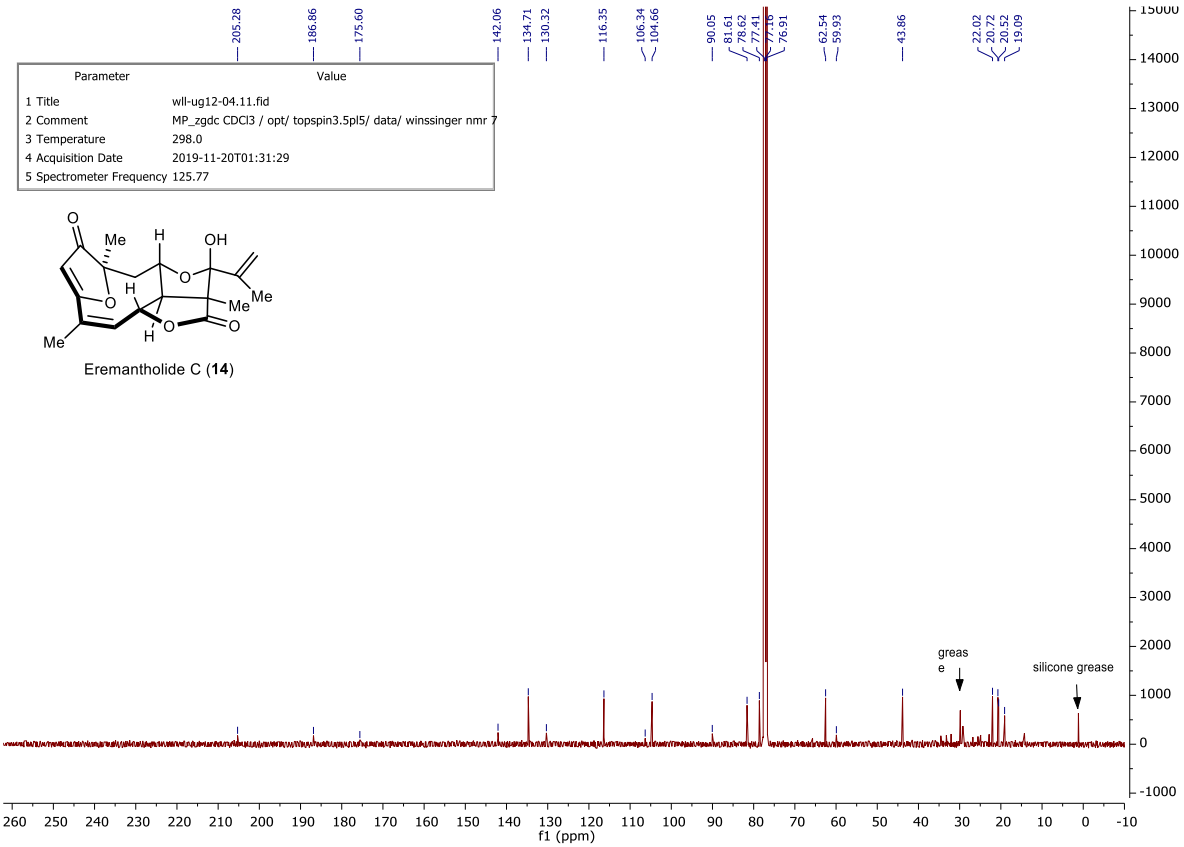
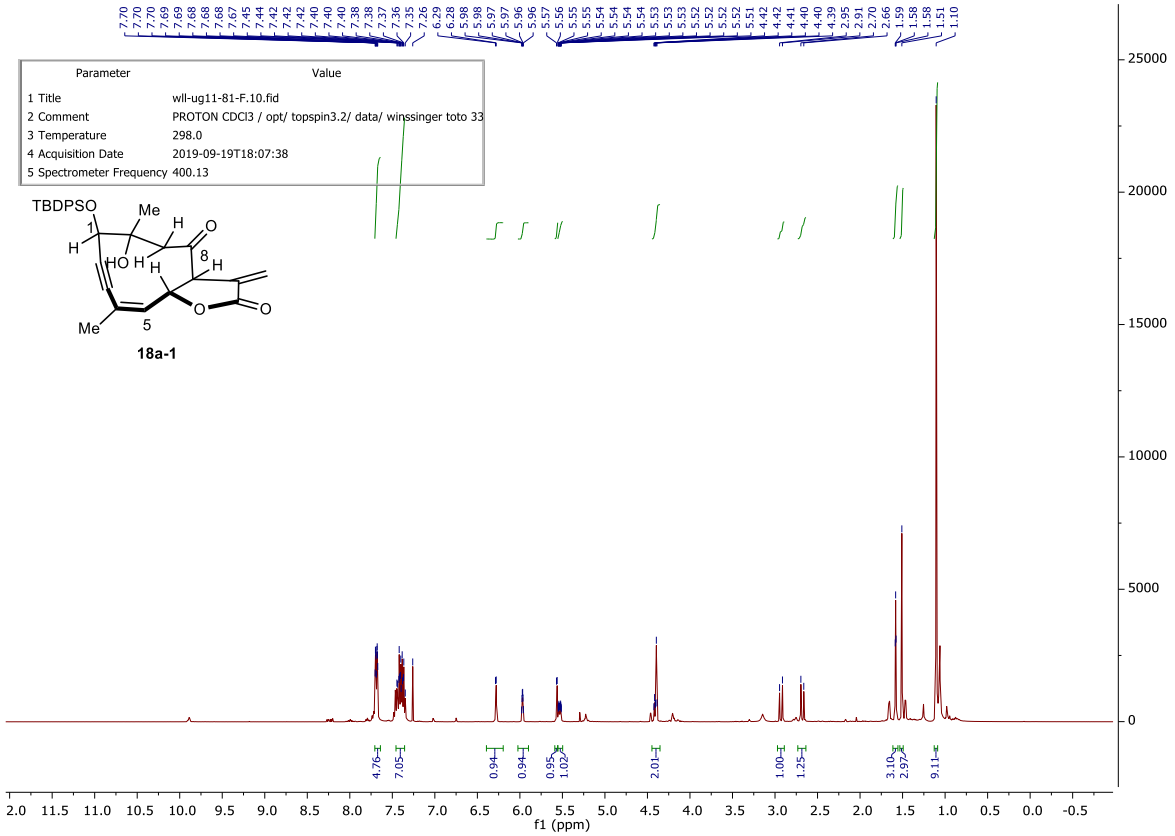
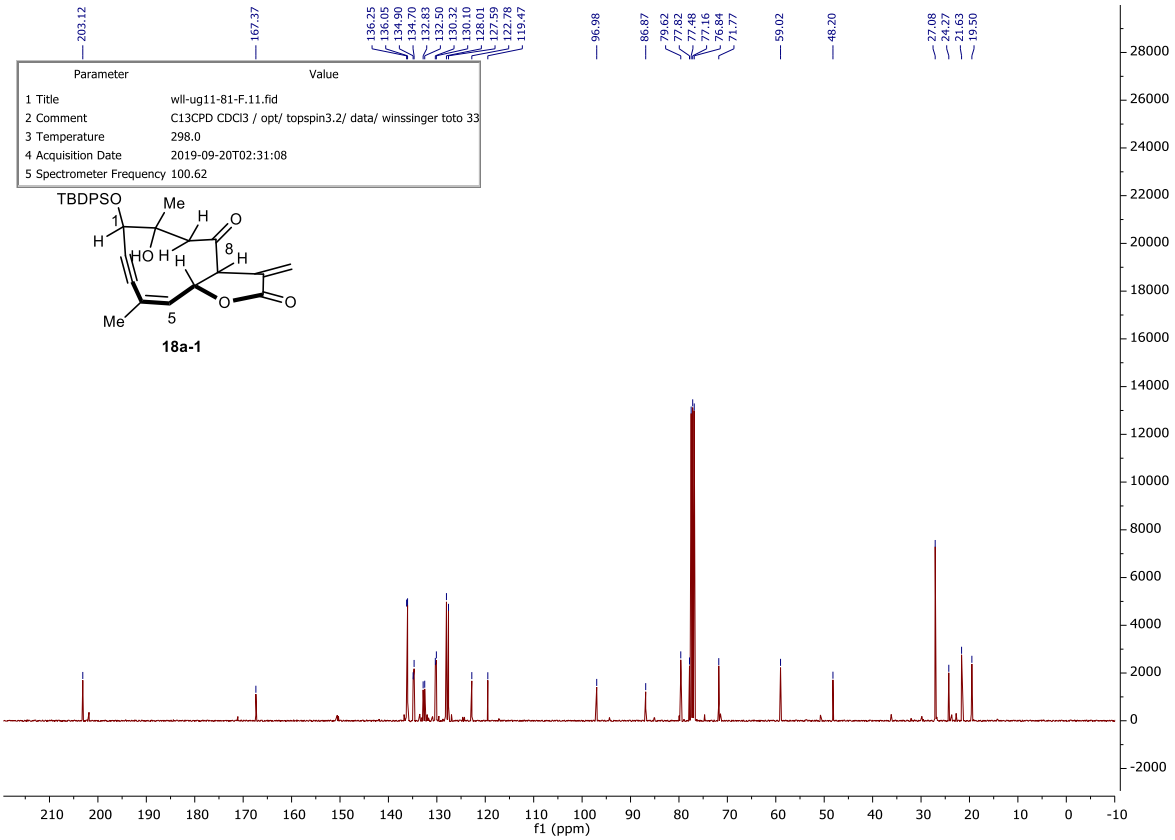
1 Title wll-ug13-73-F.15.1.2rr
2 Comment MP_hmbcetgpl3nd CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Temperature 298.0
4 Acquisition Date 2020-02-27T23:18:28
5 Spectrometer Frequency (500.13, 125.76)
Me
Me
Atripliciolide-tiglate (5)
f2 (ppm)
f1 (ppm)

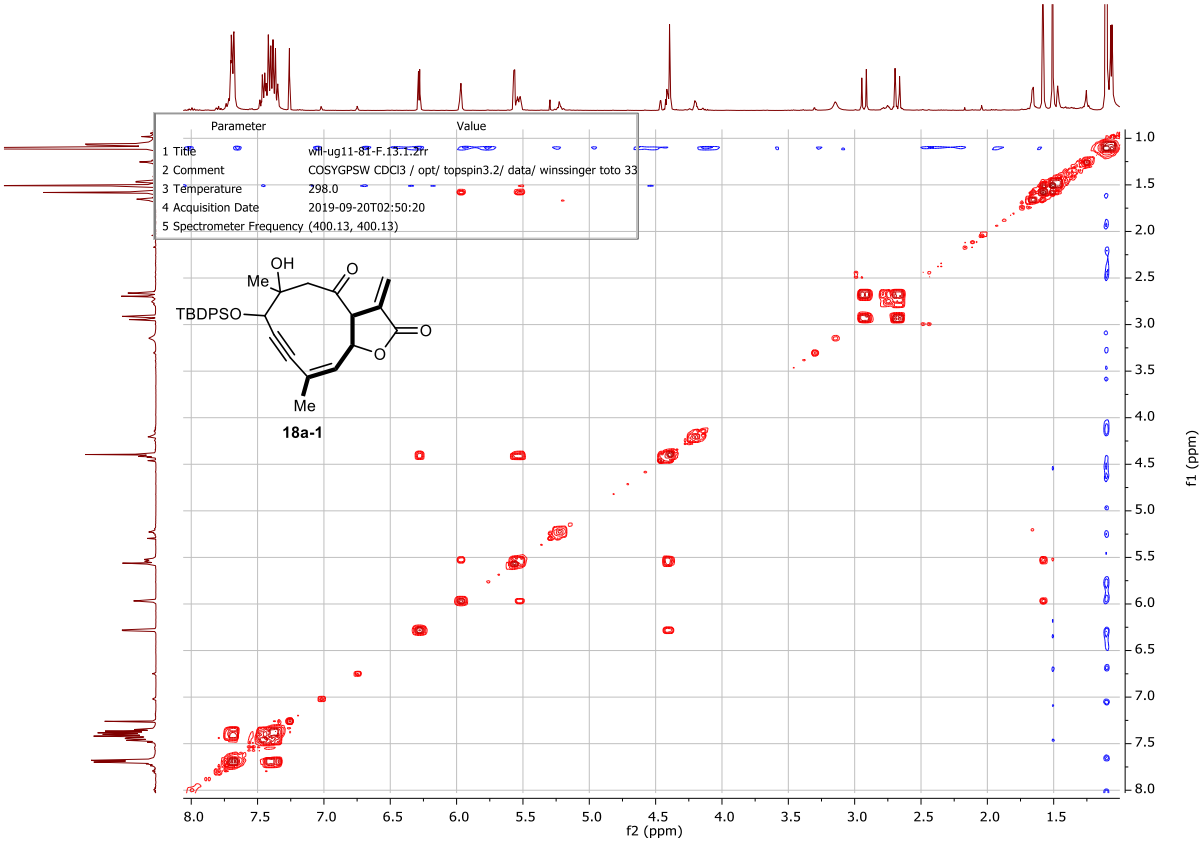

Parameter Value
1 Title wll-ug13-73-F.16.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Temperature 298.0
4 Acquisition Date 2020-02-28T00:50:41
5 Spectrometer Frequency (500.13, 500.13)
Me
Me
Me
Atripliciolide-tiglate (5)
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug12-04.10.fid
2 Comment PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 7
3 Temperature 298.0
4 Acquisition Date 2019-11-19T20:11:24
5 Spectrometer Frequency 500.13
Eremantholide C (14)
silicone grease
f1 (ppm)


Parameter Value
1 Title wll-ug12-04.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 7
3 Temperature 298.0
4 Acquisition Date 2019-11-20T01:31:29
5 Spectrometer Frequency 125.77
Eremantholide C (14)
greas e
silicone grease
f1 (ppm)


Parameter Value
1 Title wll-ug11-81-F.10.fid
2 Comment PROTON CDCl3 / opt/ topspin3.2/ data/ winssinger toto 33
3 Temperature 298.0
4 Acquisition Date 2019-09-19T18:07:38
5 Spectrometer Frequency 400.13
TBDPSO
Me
H
O
1
H
HO H
H
8
H
O
O
Me
5
18a-1
f1 (ppm)


Parameter Value
1 Title wll-ug11-81-F.11.fid
2 Comment C13CPD CDCl3 / opt/ topspin3.2/ data/ winssinger toto 33
3 Temperature 298.0
4 Acquisition Date 2019-09-20T02:31:08
5 Spectrometer Frequency 100.62
TBDPSO
Me
H
O
1
H
HO H
H
8
H
O
O
Me
5
18a-1
f1 (ppm)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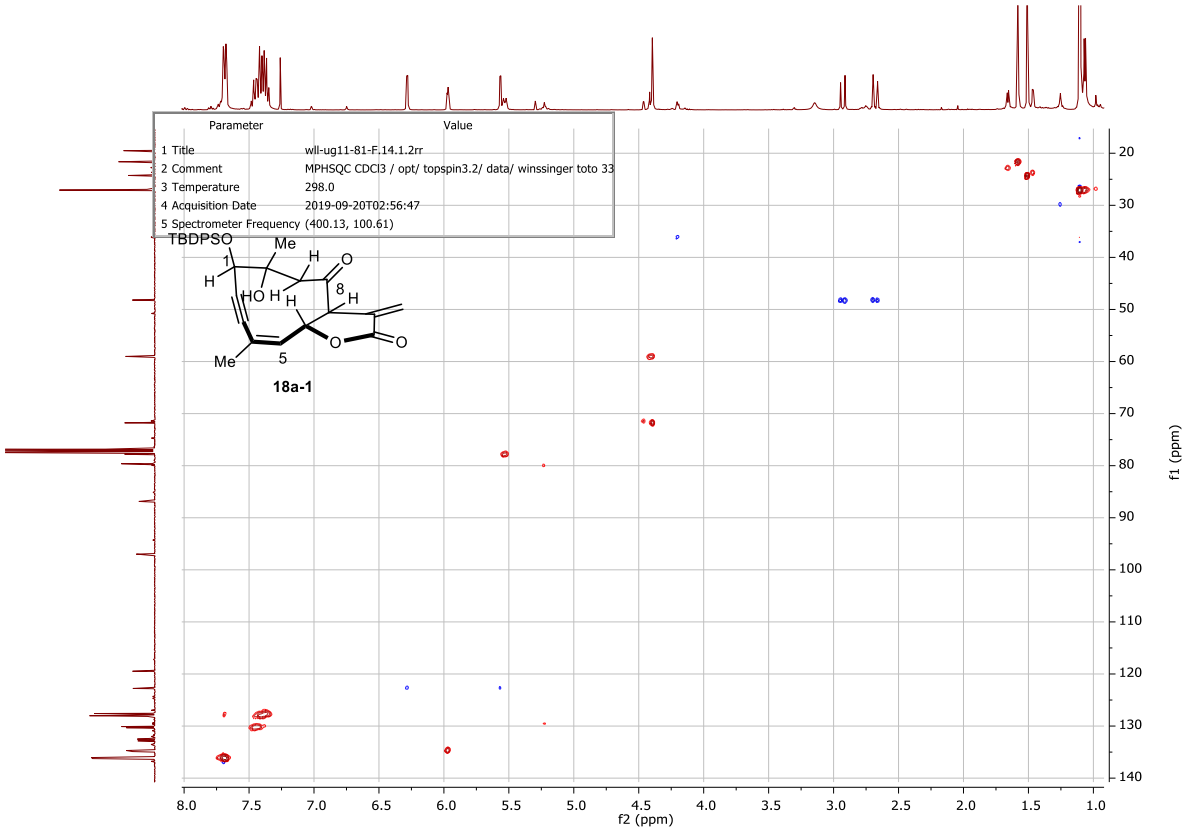
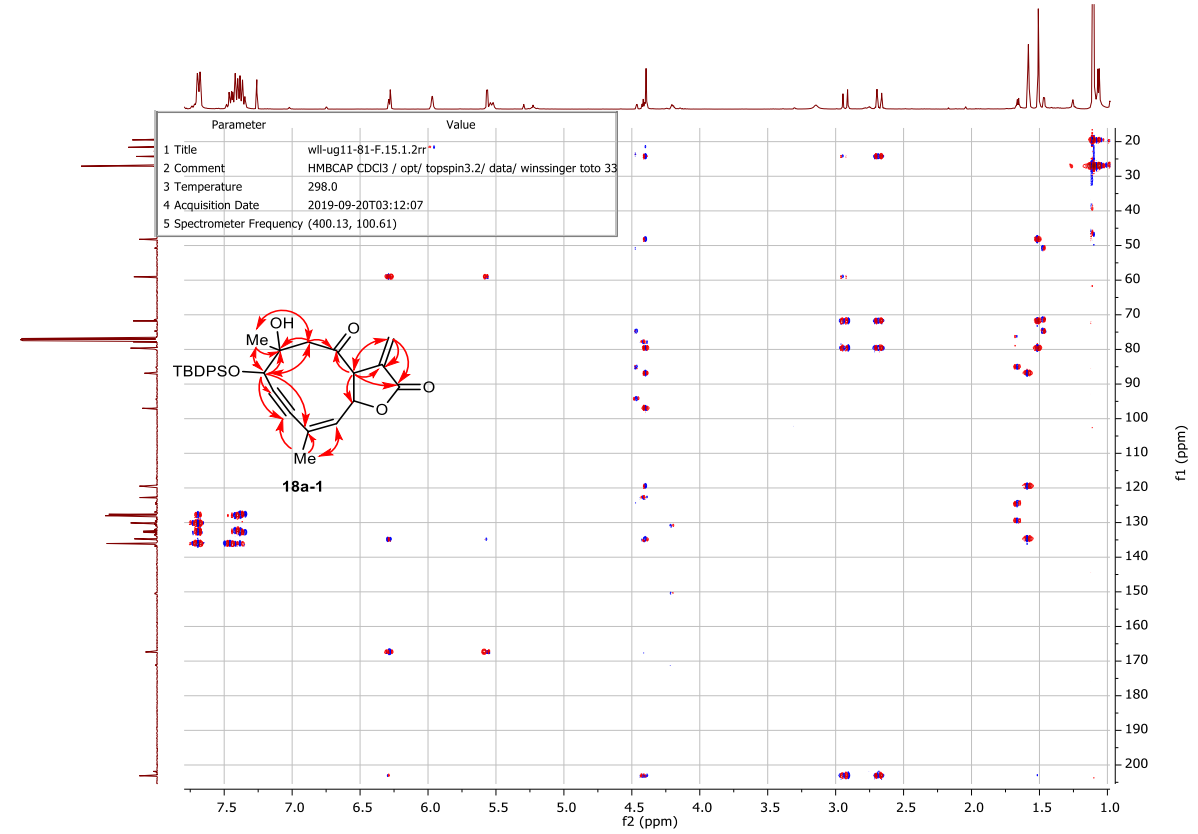
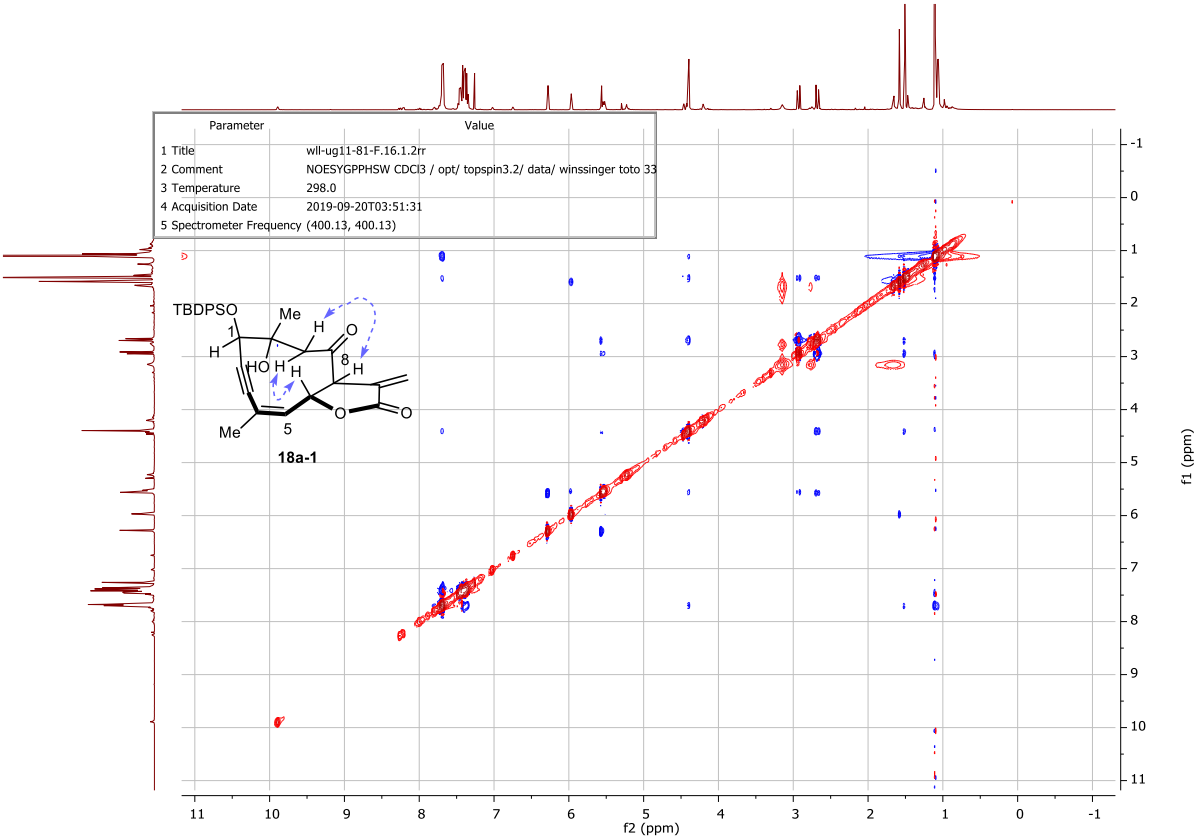
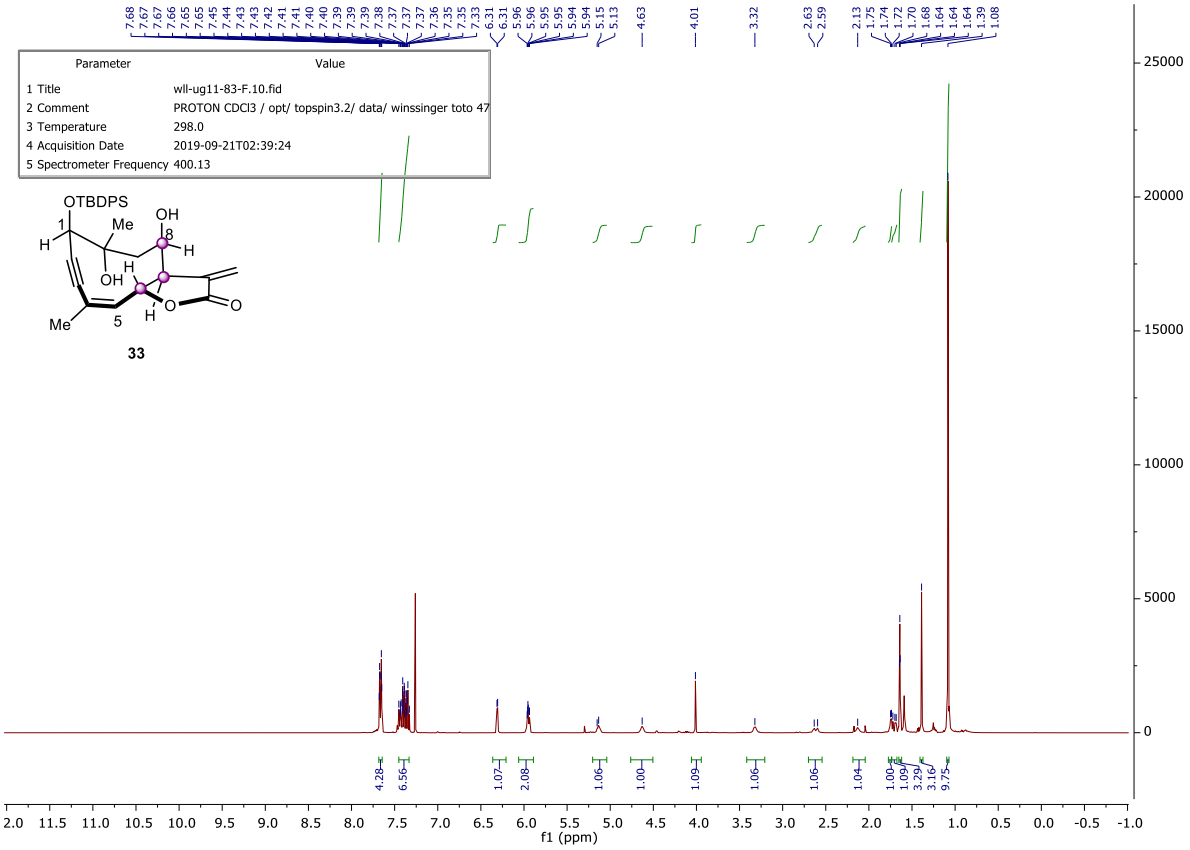
1 Title wll-ug11-81-F.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 33
3 Temperature 298.0
4 Acquisition Date 2019-09-20T02:50:20
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
TBDPSO
O
O
O
Me
18a-1
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug11-81-F.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ topspin3.2/ data/ winssinger toto 33
3 Temperature 298.0
4 Acquisition Date 2019-09-20T02:56:47
5 Spectrometer Frequency (400.13, 100.61)
TBDPSO
Me
H
O
1
H
HO H
H
8
H
O
O
Me
5
18a-1
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug11-81-F.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ topspin3.2/ data/ winssinger toto 33
3 Temperature 298.0
4 Acquisition Date 2019-09-20T03:12:07
5 Spectrometer Frequency (400.13, 100.61)
OH
Me
TBDPSO
O
O
O
Me
18a-1
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug11-81-F.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 33
3 Temperature 298.0
4 Acquisition Date 2019-09-20T03:51:31
5 Spectrometer Frequency (400.13, 400.13)
TBDPSO
Me
H
O
1
H
HO H
H
8
H
O
O
Me
5
18a-1
f2 (ppm)
f1 (ppm)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1 Title wll-ug11-83-F.10.fid
2 Comment PROTON CDCl3 / opt/ topspin3.2/ data/ winssinger toto 47
3 Temperature 298.0
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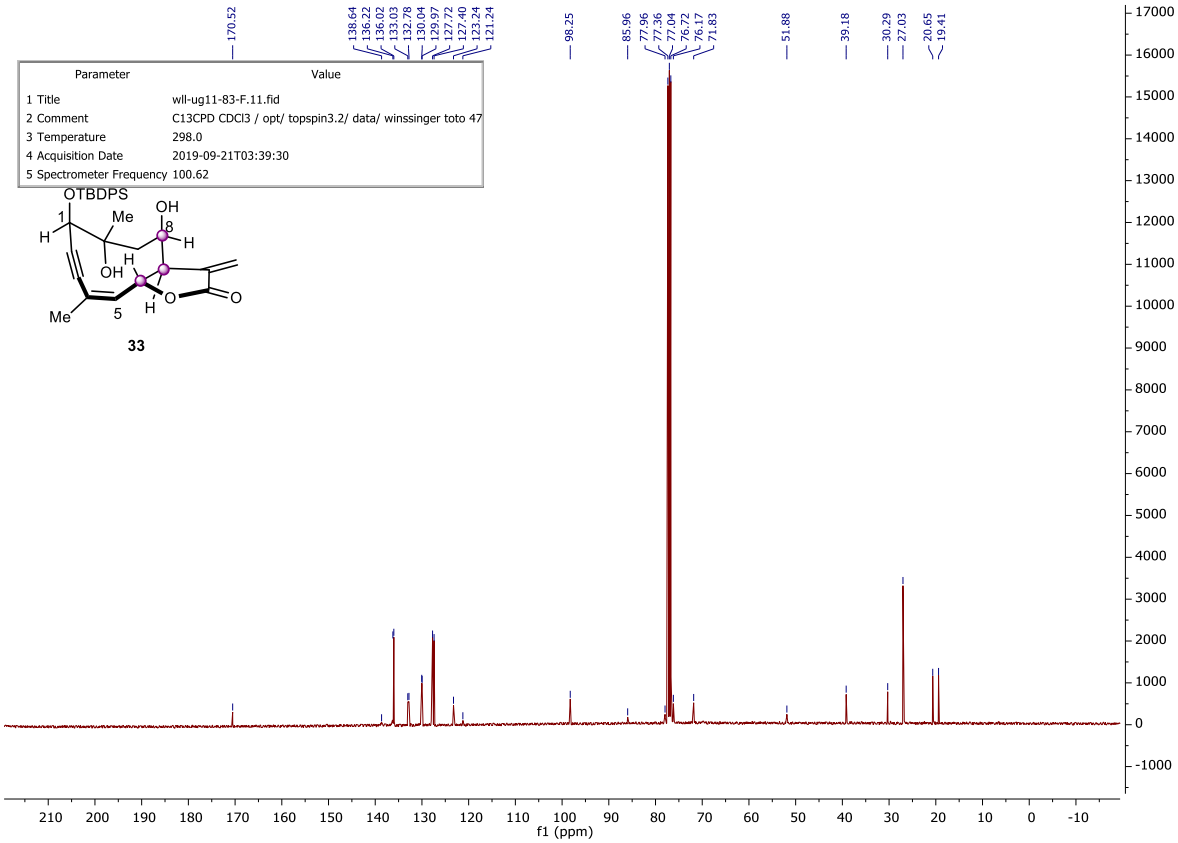
5 Spectrometer Frequency 400.13
OTBDPS
OH
Me
H
OH
Me
33
f1 (ppm)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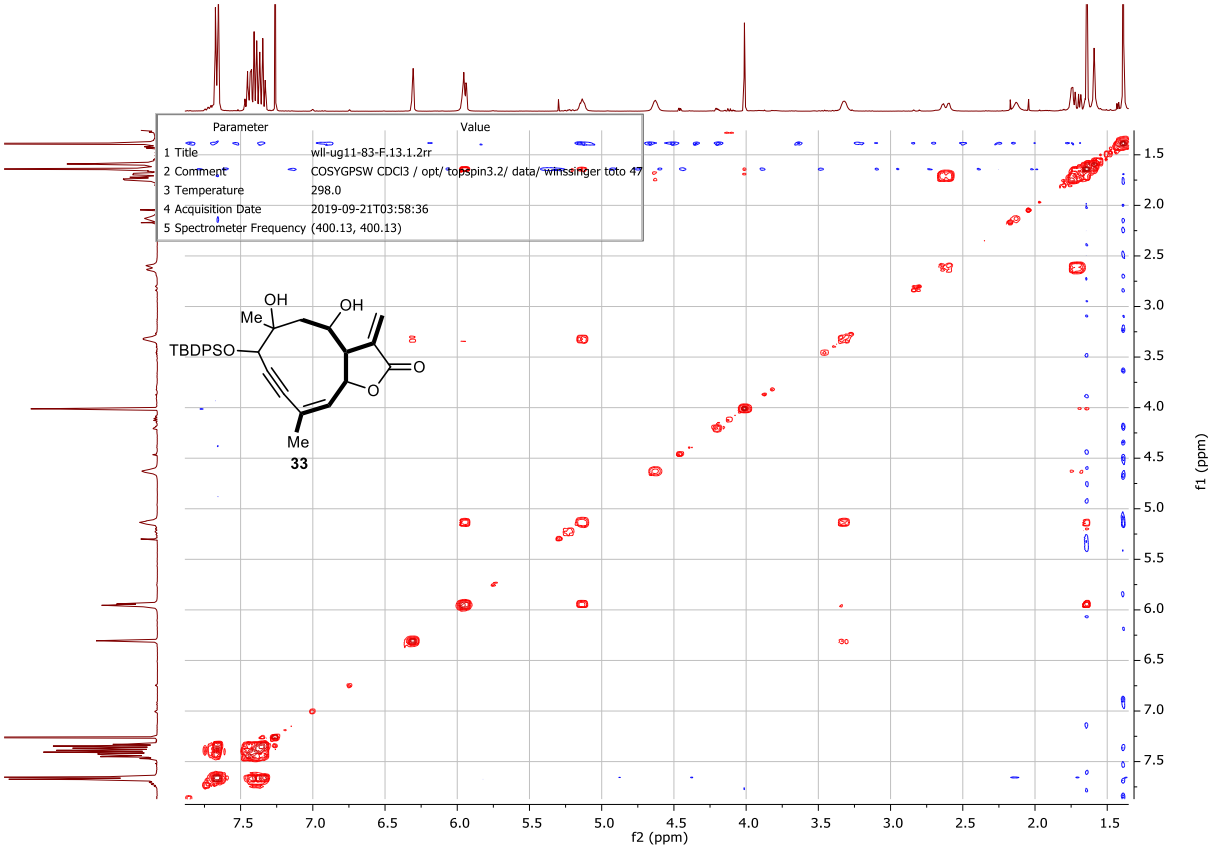
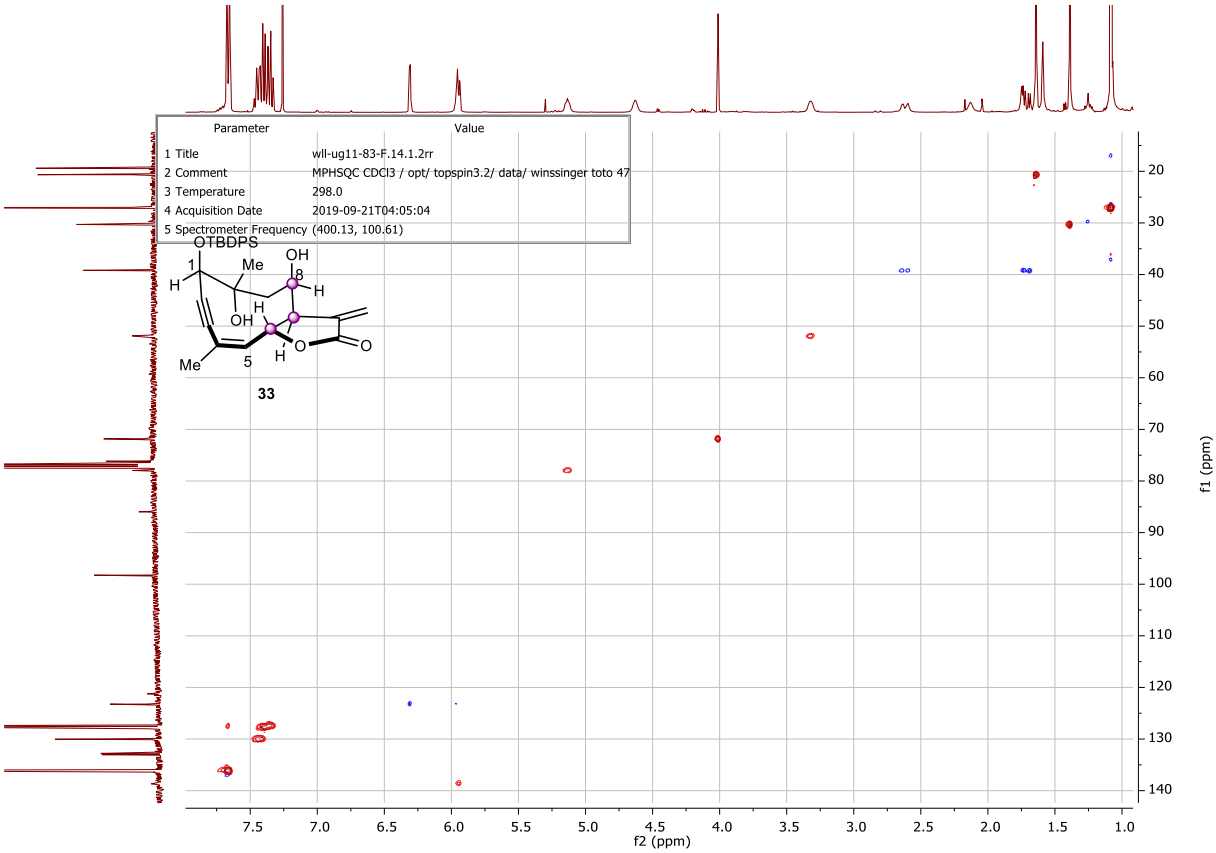
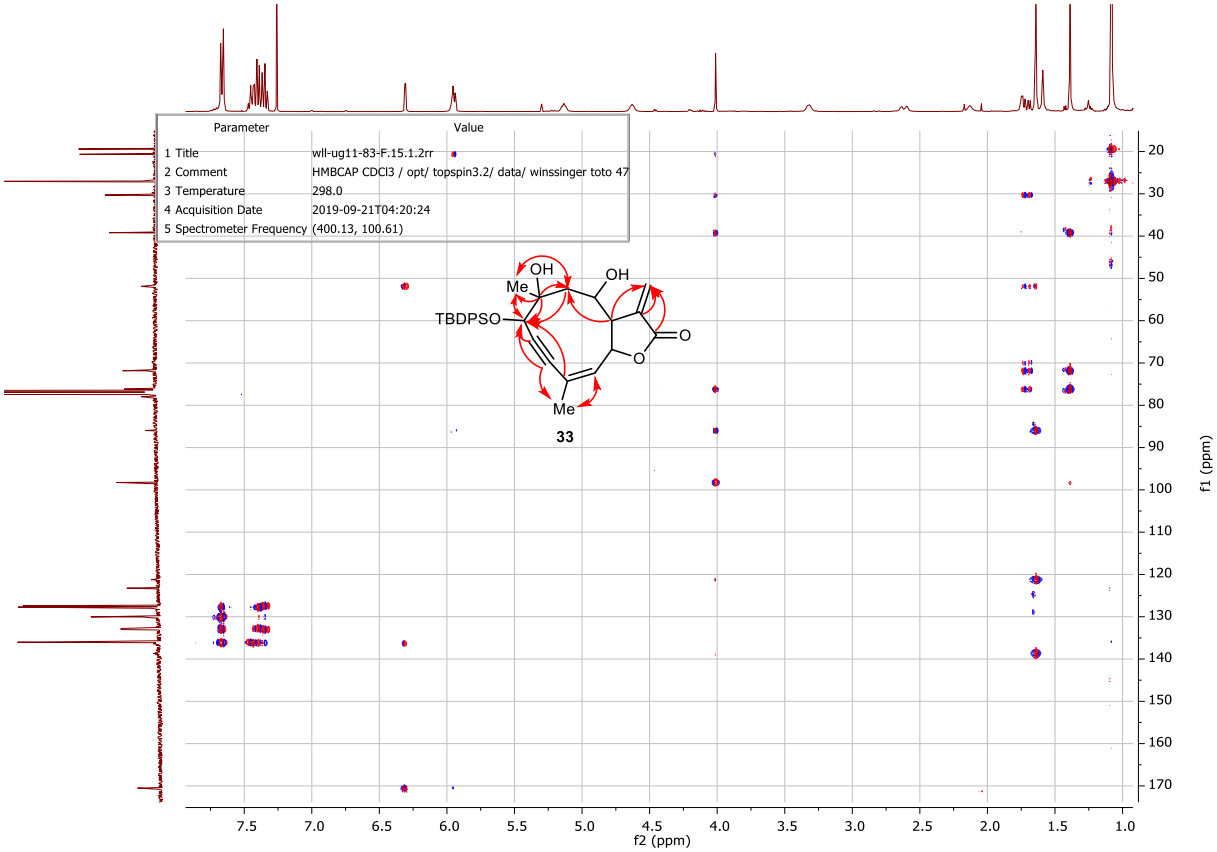
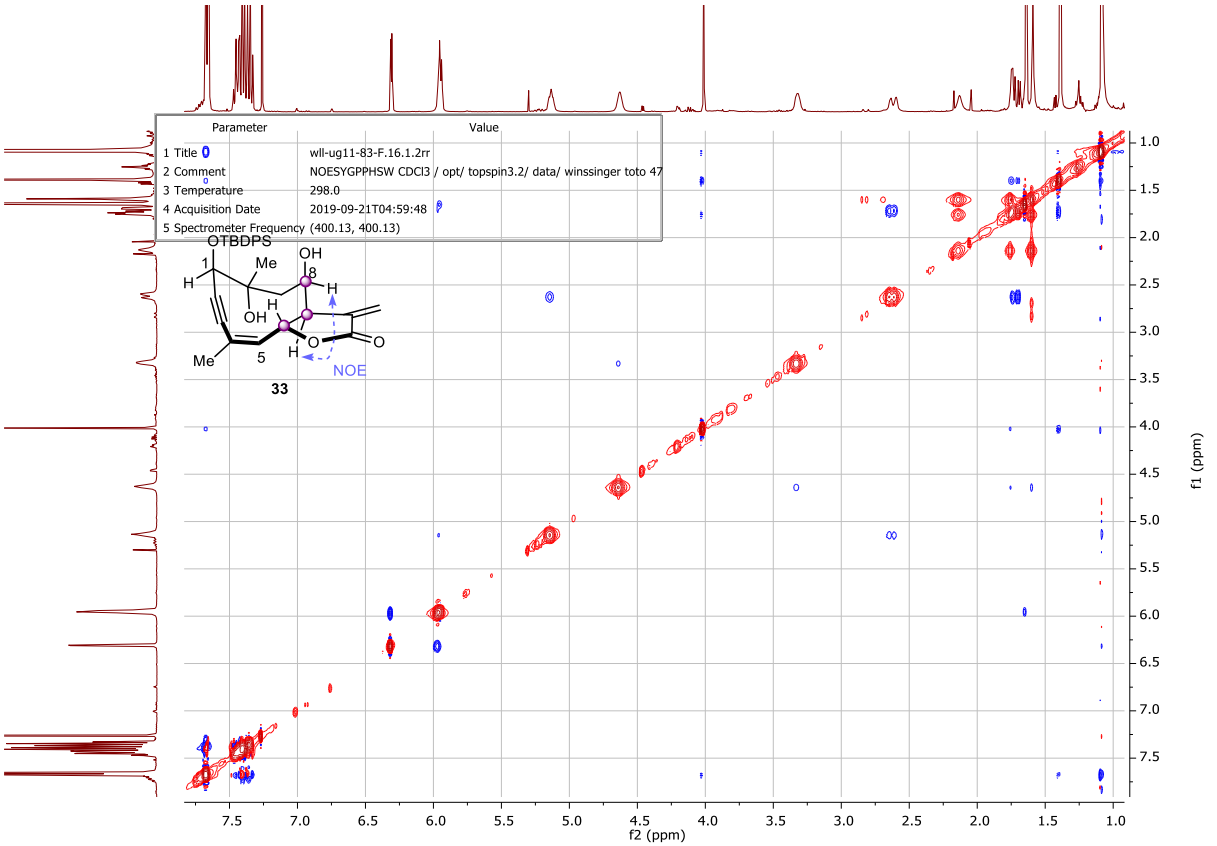
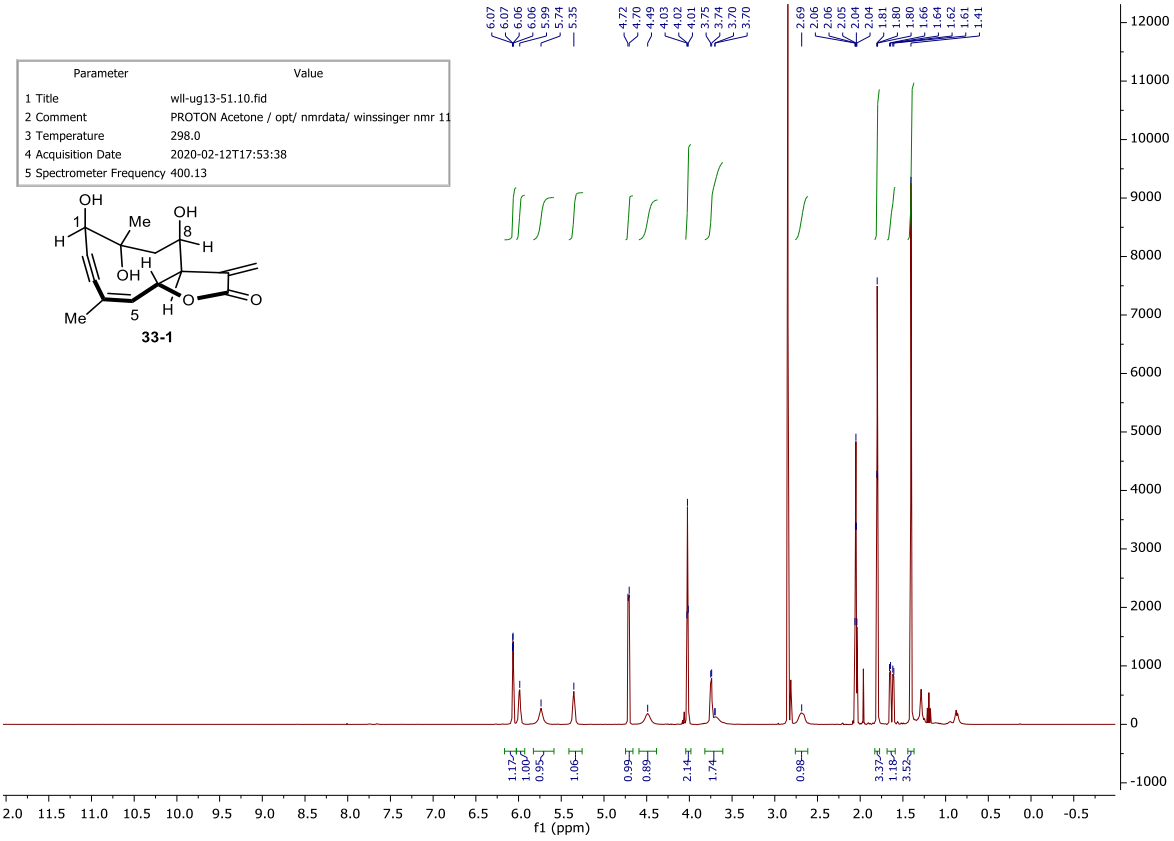
1 Title wll-ug11-83-F.11.fid
2 Comment C13CPD CDCl3 / opt/ topspin3.2/ data/ winssinger toto 47
3 Temperature 298.0
4 Acquisition Date 2019-09-21T03:39:30
5 Spectrometer Frequency 100.62
OTBDPS
OH
Me
H
OH
Me
33
f1 (ppm)

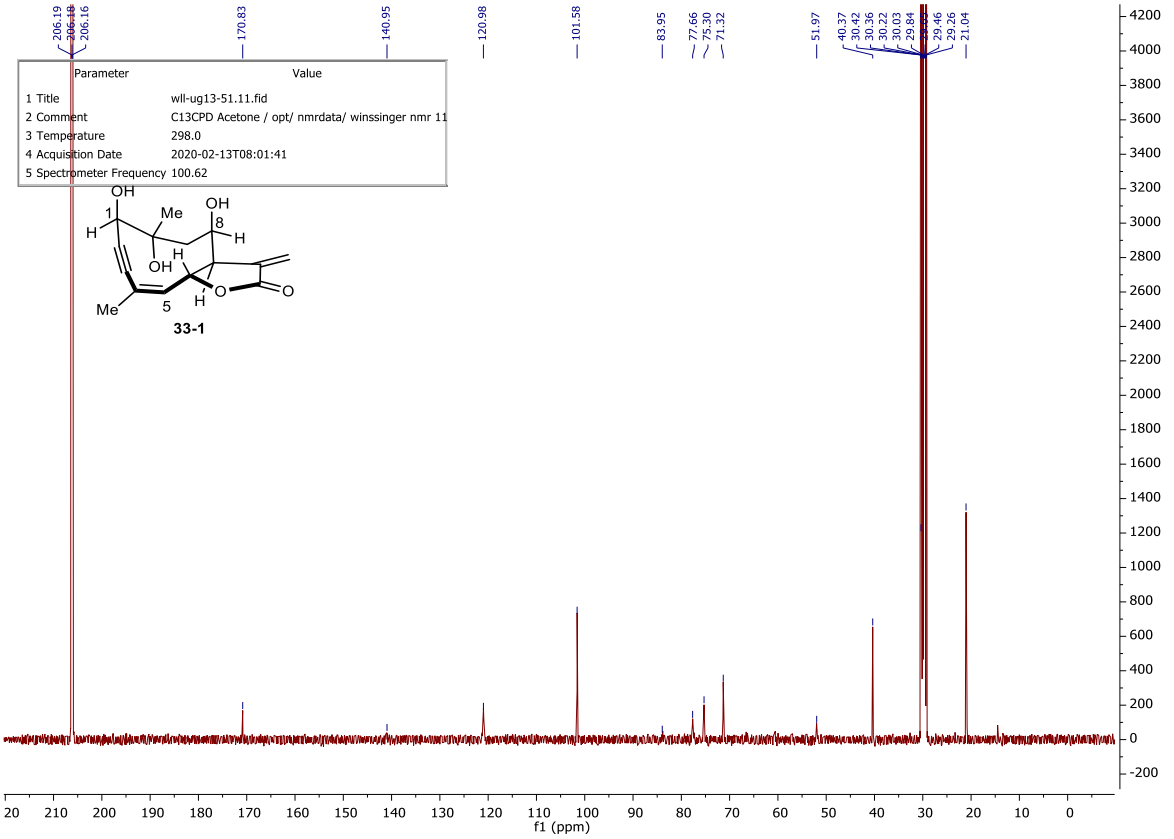

Parameter Value
1 Title wll-ug11-83-F.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 47
3 Temperature 298.0
4 Acquisition Date 2019-09-21T03:58:36
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
OH
TBDPSO
O
O
Me
33
f2 (ppm)
f1 (ppm)

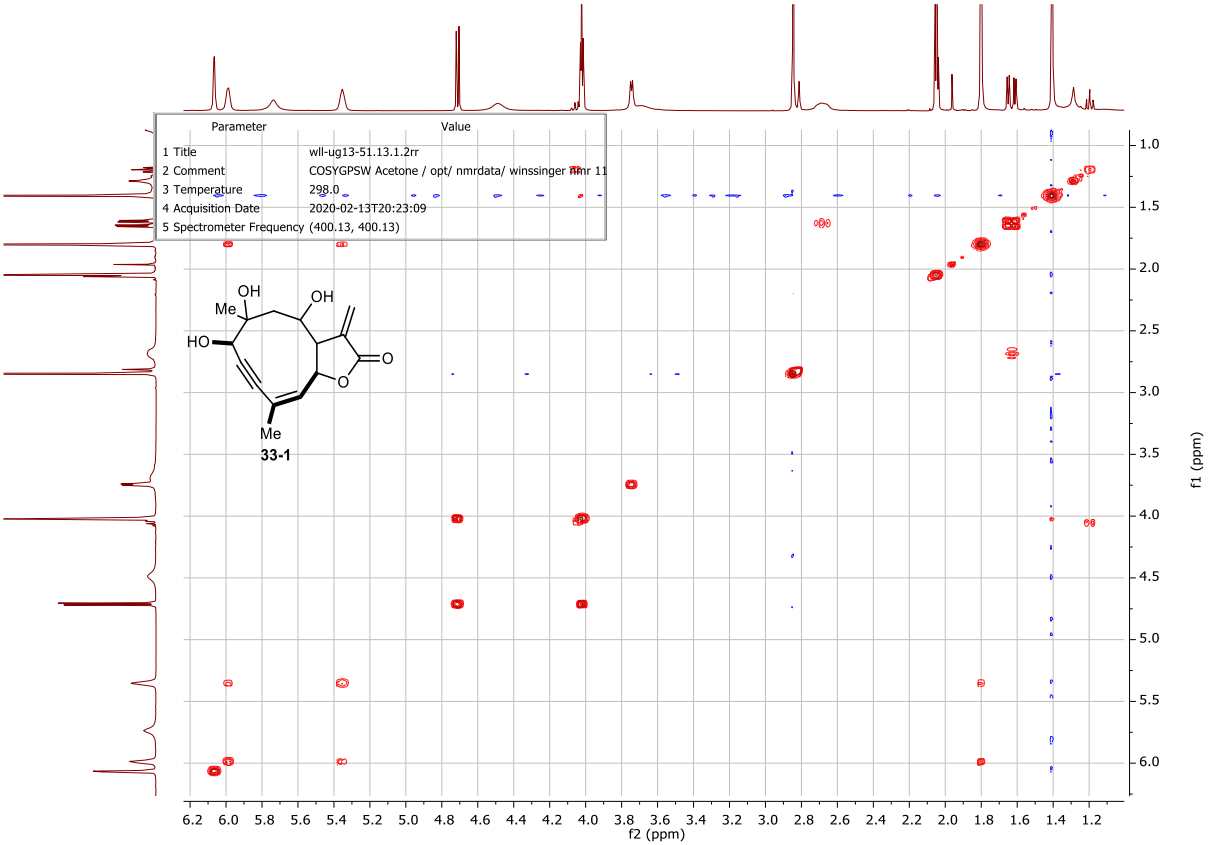

Parameter Value
1 Title wll-ug11-83-F.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ topspin3.2/ data/ winssinger toto 47
3 Temperature 298.0
4 Acquisition Date 2019-09-21T04:05:04
5 Spectrometer Frequency (400.13, 100.61)
OTBDPS
1
H
Me
OH
8
H
H
OH
O
O
H
Me
5
33
f2 (ppm)
f1 (ppm)

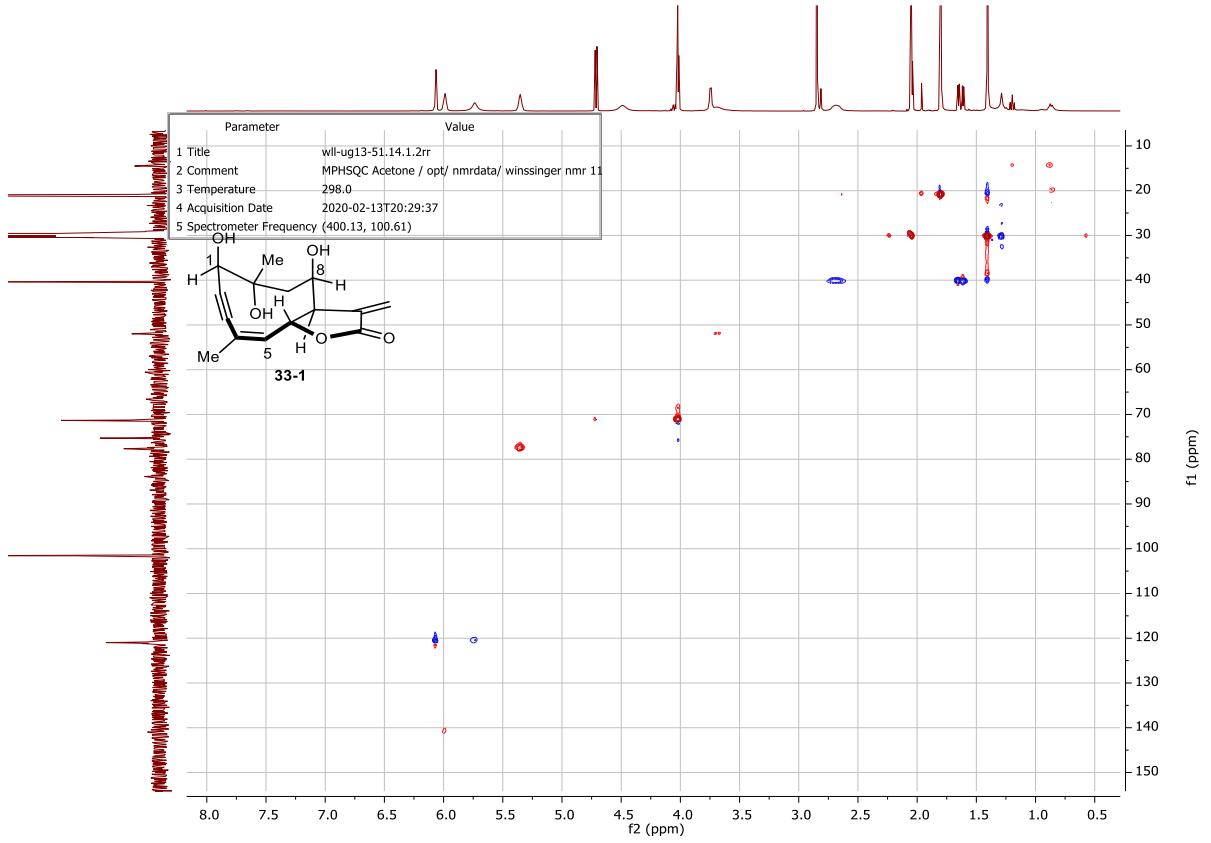

Parameter Value
1 Title wll-ug11-83-F.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ topspin3.2/ data/ winssinger toto 47
3 Temperature 298.0
4 Acquisition Date 2019-09-21T04:20:24
5 Spectrometer Frequency (400.13, 100.61)
OH
Me
OH
TBDPSO
O
O
Me
33
f2 (ppm)
f1 (ppm)

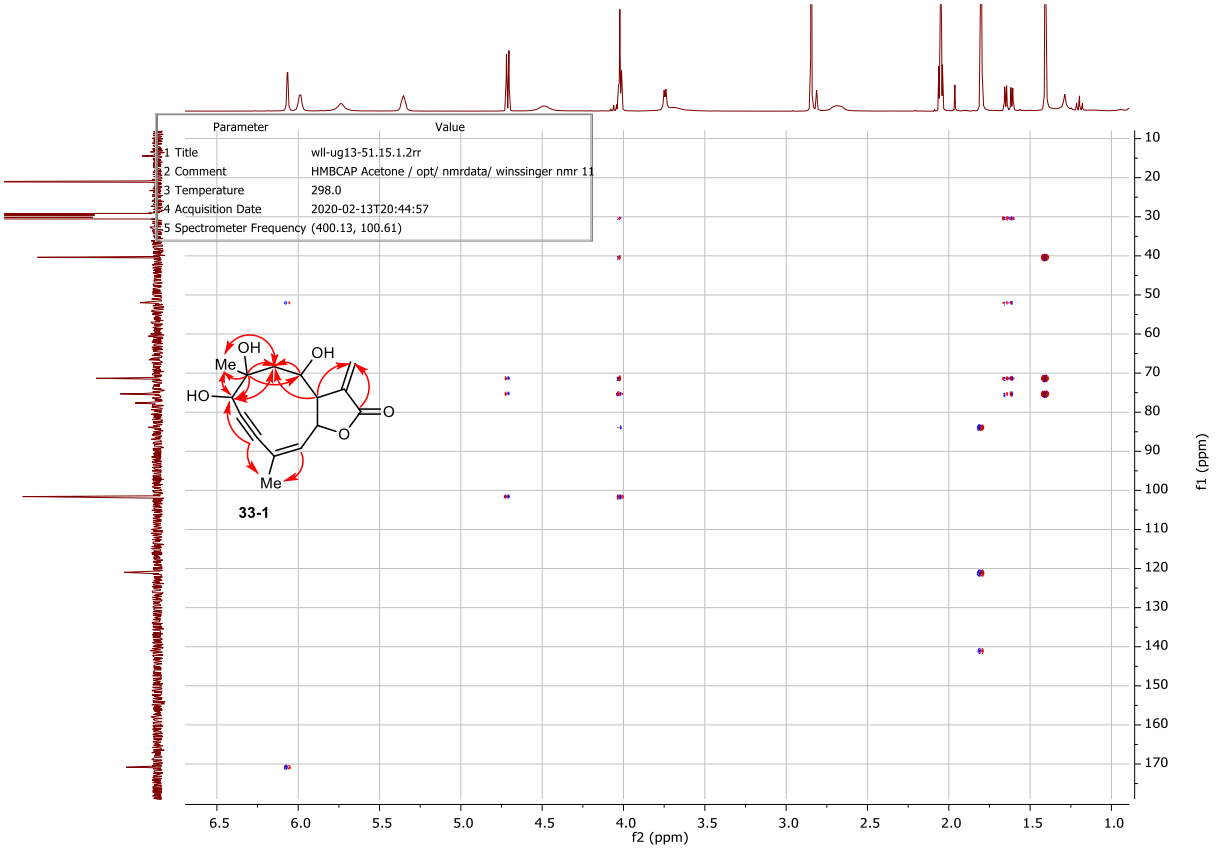

Parameter Value
1 Title 0 wll-ug11-83-F.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ topspin3.2/ data/ winssinger toto 47
3 Temperature 298.0
4 Acquisition Date 2019-09-21T04:59:48
5 Spectrometer Frequency (400.13, 400.13)
OTBDPS
1
Me
OH
8
H
H
OH
H
Me
5
H
O
O
NOE
33
f2 (ppm)
f1 (ppm)

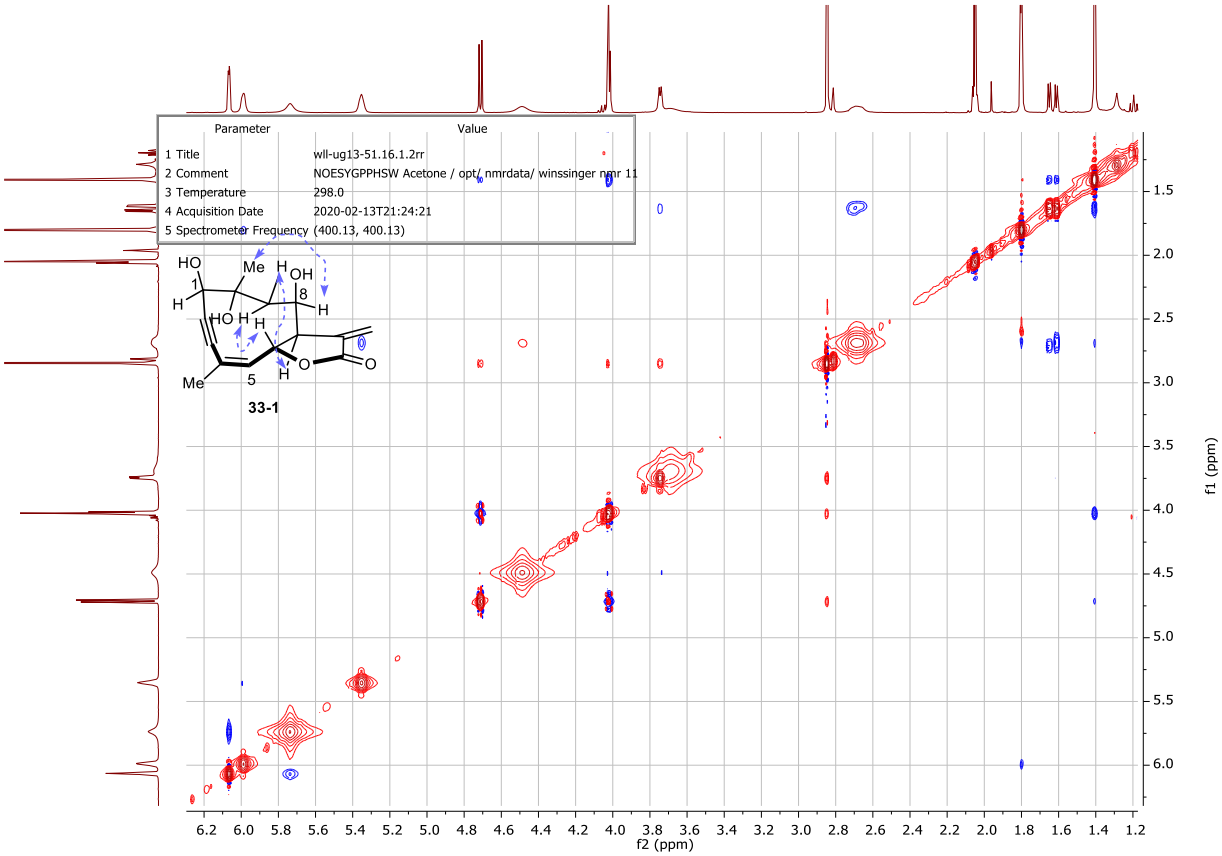

Parameter Value
1 Title wll-ug13-51.10.fid
2 Comment PROTON Acetone / opt/ nmrdata/ winssinger nmr 11
3 Temperature 298.0
4 Acquisition Date 2020-02-12T17:53:38
5 Spectrometer Frequency 400.13
33-1
f1 (ppm)

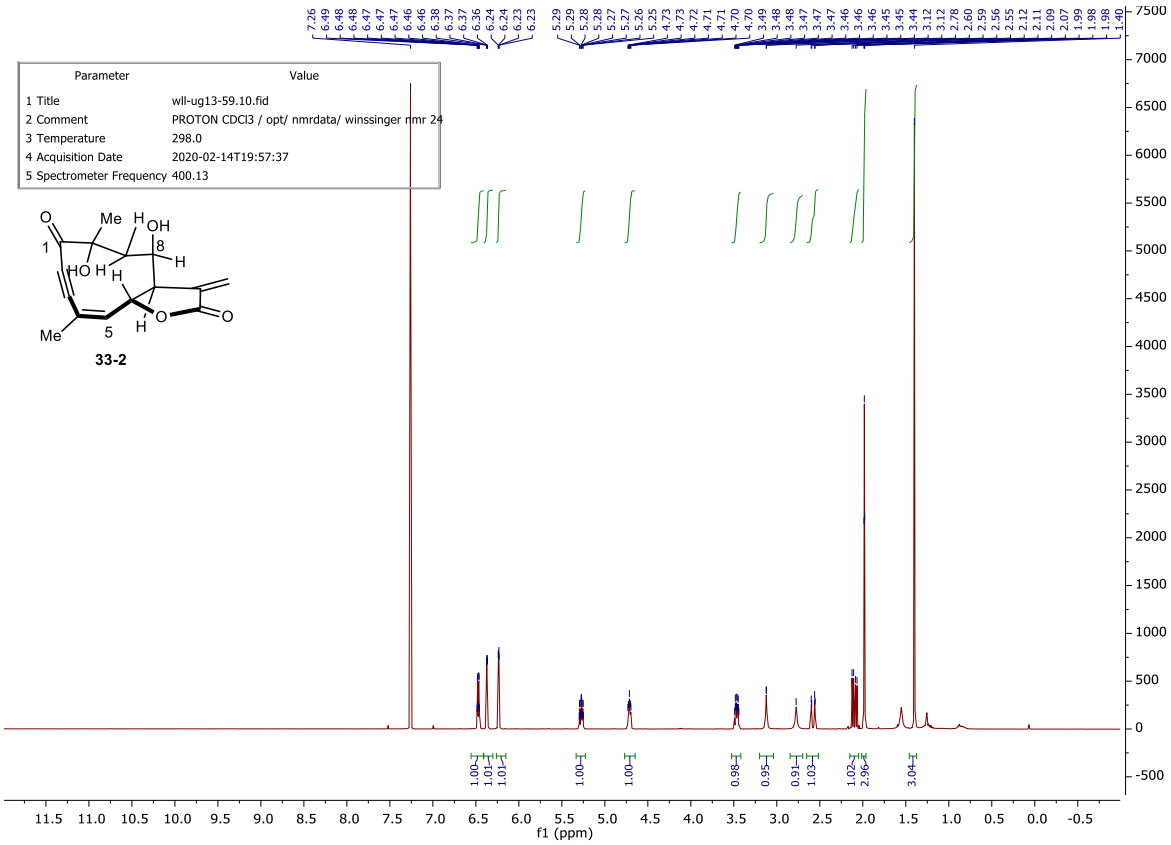

Parameter Value
1 Title wll-ug13-51.11.fid
2 Comment C13CPD Acetone / opt/ nmrdata/ winssinger nmr 11
3 Temperature 298.0
4 Acquisition Date 2020-02-13T08:01:41
5 Spectrometer Frequency 100.62
33-1
f1 (ppm)

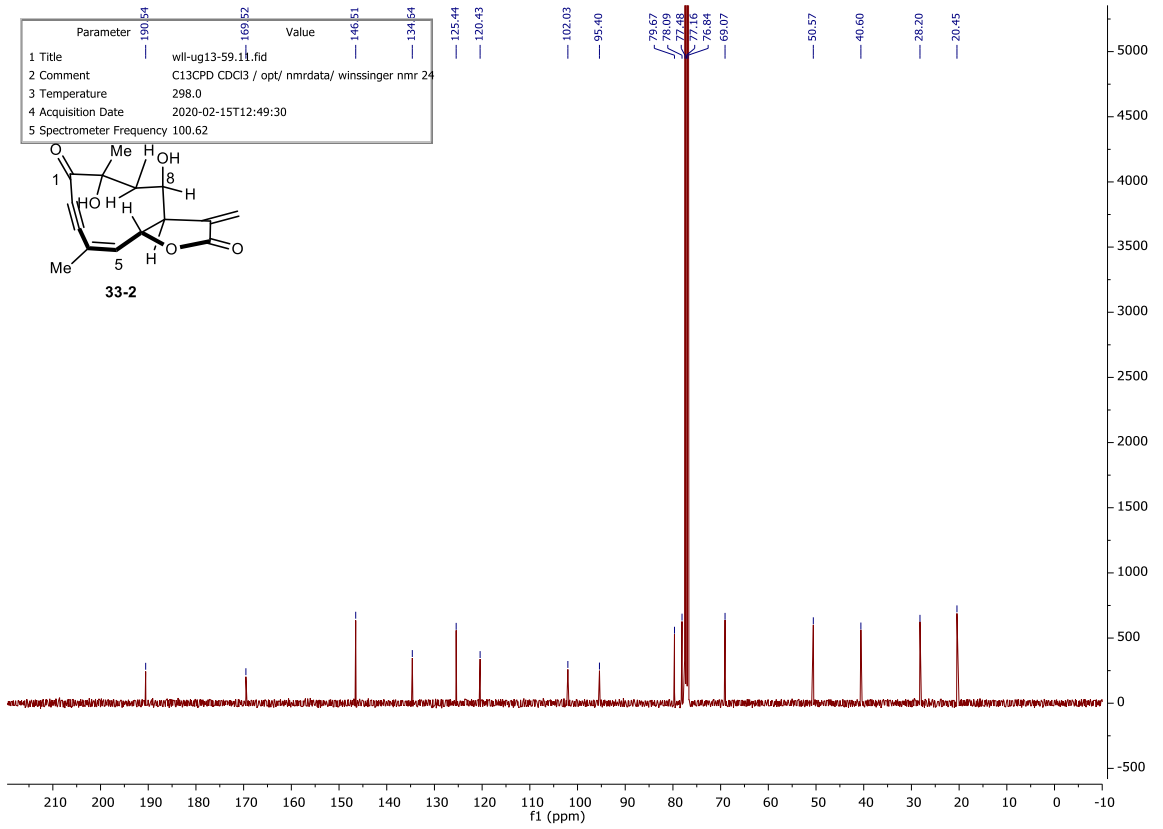

Parameter Value
1 Title wll-ug13-51.13.1.2rr
2 Comment COSYGPSW Acetone / opt/ nmrdata/ winssinger nmr 11
3 Temperature 298.0
4 Acquisition Date 2020-02-13T20:23:09
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
OH
HO
O
O
Me
33-1
f2 (ppm)
f1 (ppm)

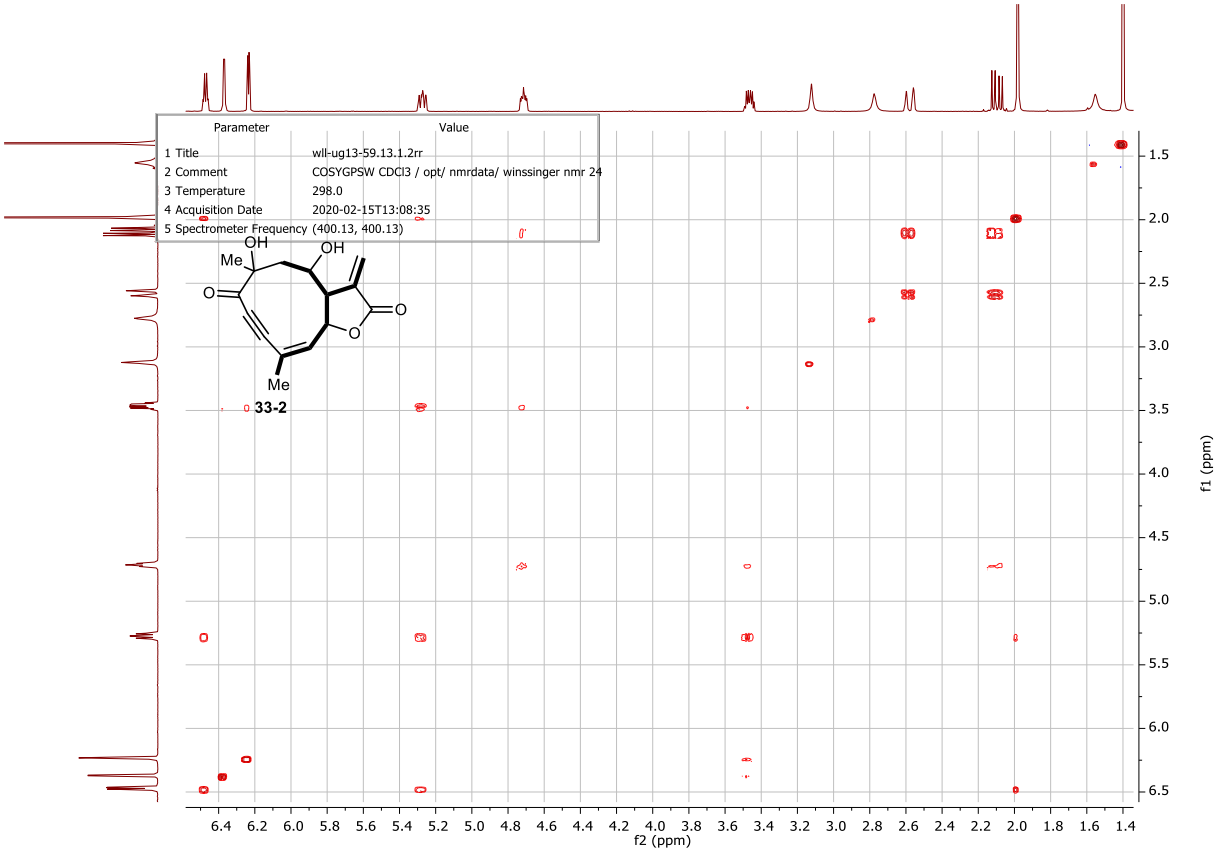

Parameter Value
1 Title wll-ug13-51.14.1.2rr
2 Comment MPHSQC Acetone / opt/ nmrdata/ winssinger nmr 11
3 Temperature 298.0
4 Acquisition Date 2020-02-13T20:29:37
5 Spectrometer Frequency (400.13, 100.61)
OH
1
H
Me
OH
8
H
H
OH
Me
5
H
O
O
33-1
f2 (ppm)
f1 (ppm)

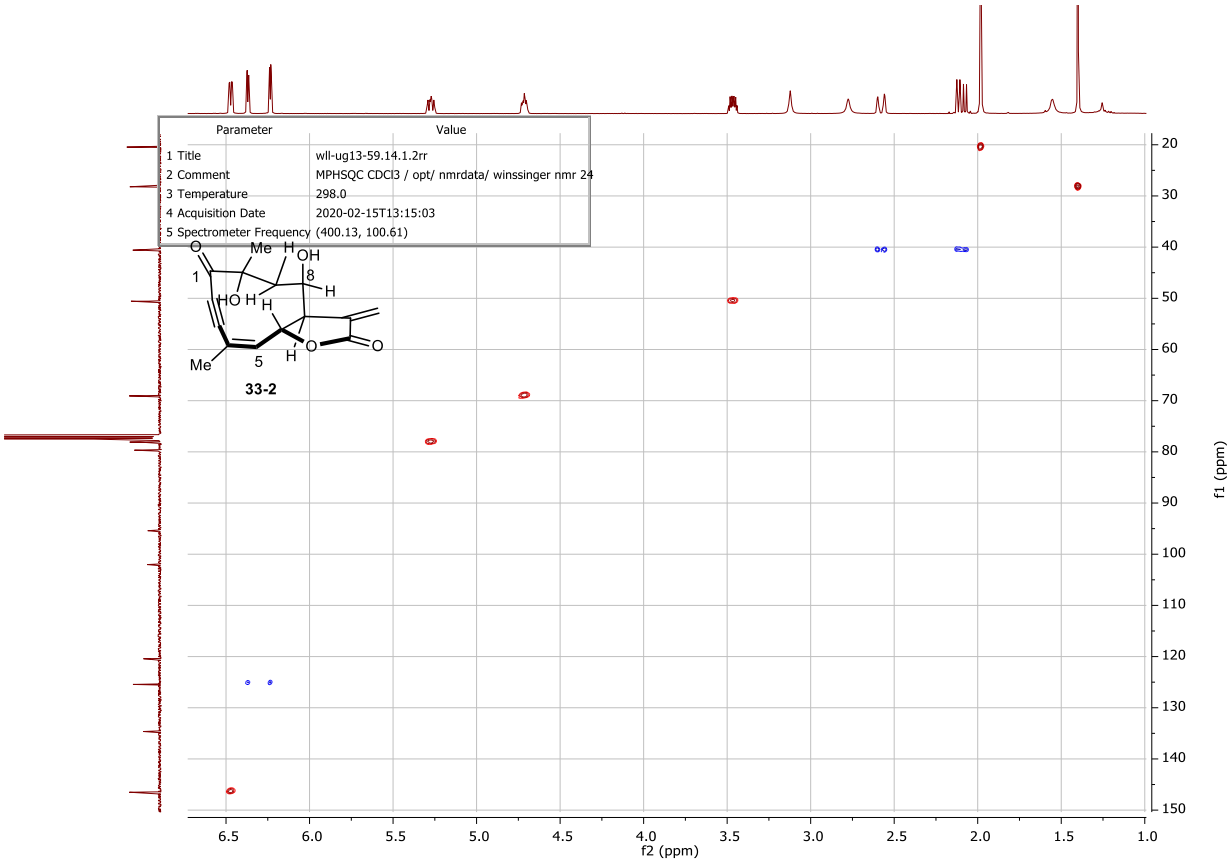

Parameter Value
1 Title wll-ug13-51.15.1.2rr
2 Comment HMBCAP Acetone / opt/ nmrdata/ winssinger nmr 11
3 Temperature 298.0
4 Acquisition Date 2020-02-13T20:44:57
5 Spectrometer Frequency (400.13, 100.61)
OH
Me
OH
HO
O
O
Me
33-1
f2 (ppm)
f1 (ppm)

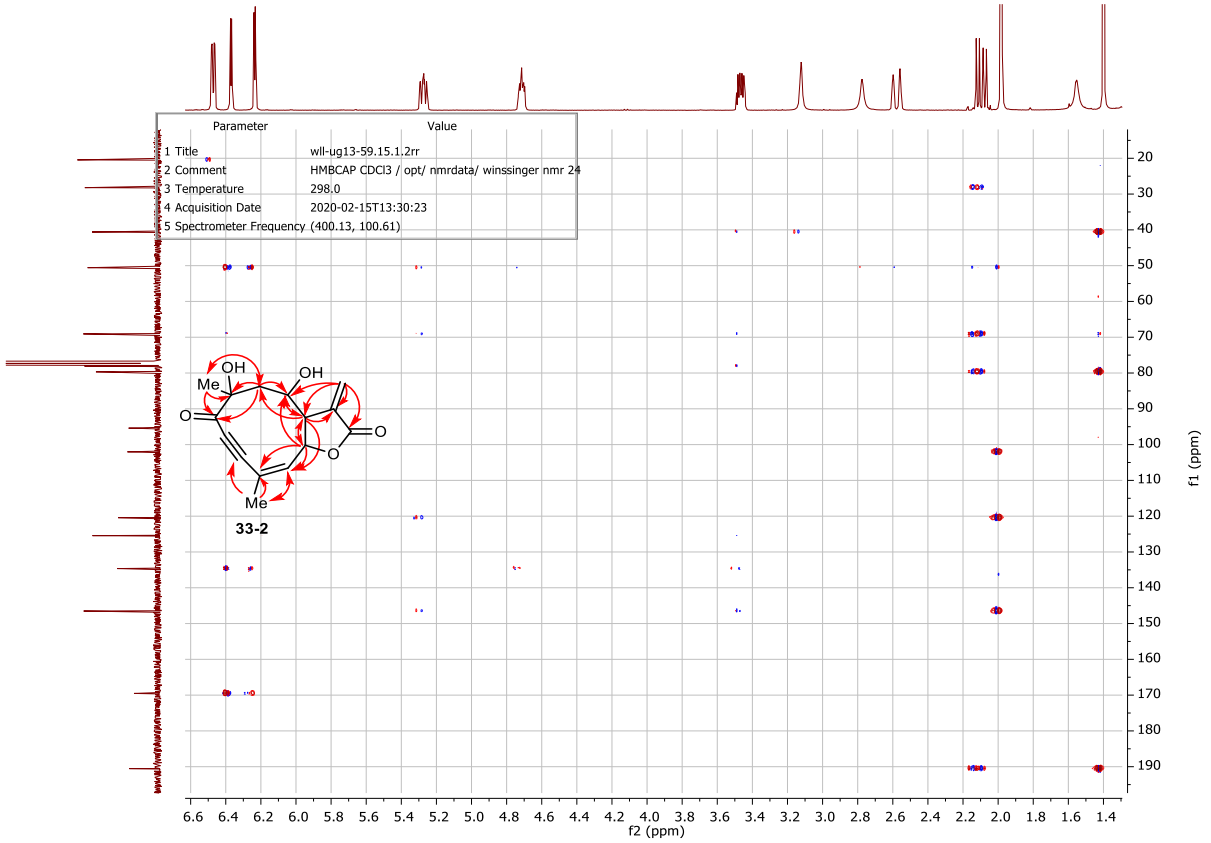

Parameter Value
1 Title wll-ug13-51.16.1.2rr
2 Comment NOESYGPPHSW Acetone / opt/ nmrdata/ winssinger nmr 11
3 Temperature 298.0
4 Acquisition Date 2020-02-13T21:24:21
5 Spectrometer Frequency (400.13, 400.13)
HO
Me
H
OH
1
8
H
H
HO
H
H
O
O
Me
5
33-1
f2 (ppm)
f1 (ppm)

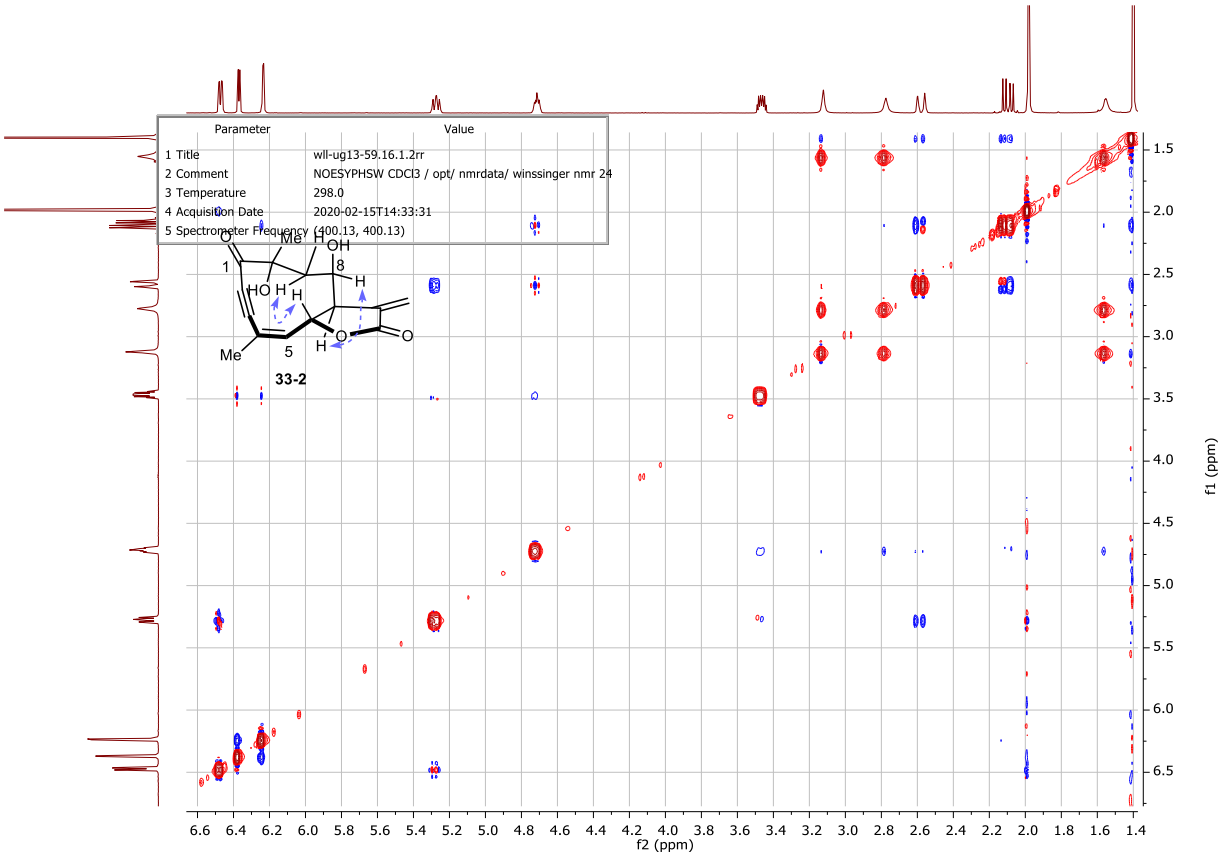

Parameter Value
1 Title wll-ug13-59.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 24
3 Temperature 298.0
4 Acquisition Date 2020-02-14T19:57:37
5 Spectrometer Frequency 400.13
33-2
f1 (ppm)

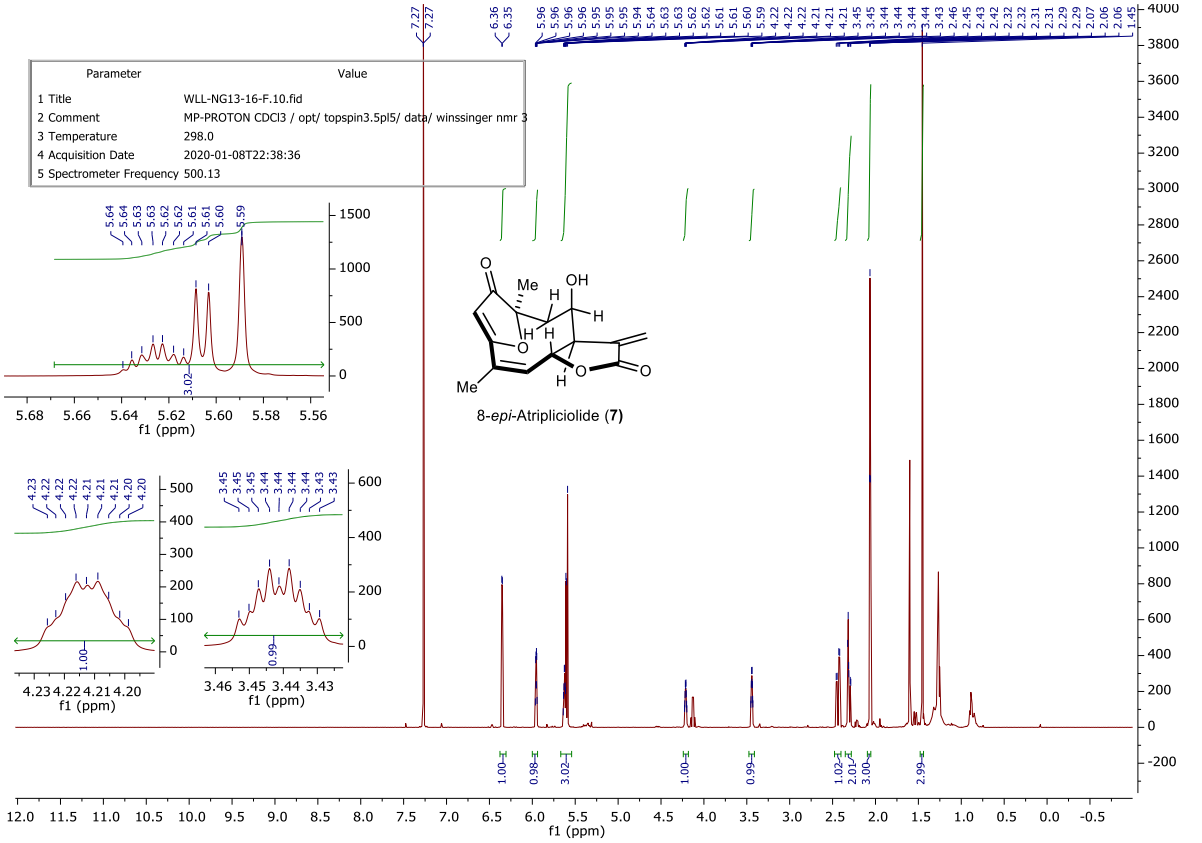

Parameter Value
1 Title wll-ug13-59.11.fid
2 Comment C13CPD CDCl3 / opt/ nmrdata/ winssinger nmr 24
3 Temperature 298.0
4 Acquisition Date 2020-02-15T12:49:30
5 Spectrometer Frequency 100.62
33-2
f1 (ppm)

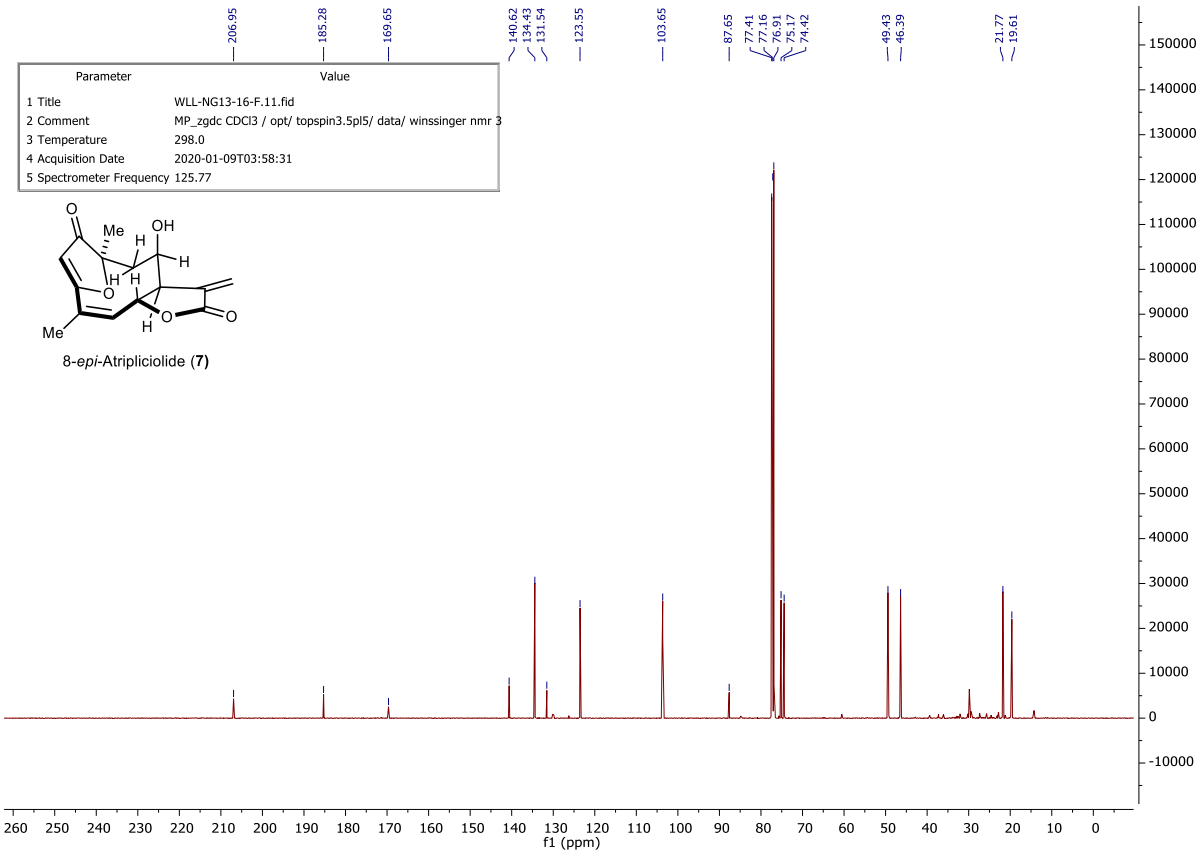

Parameter Value
1 Title wll-ug13-59.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 24
3 Temperature 298.0
4 Acquisition Date 2020-02-15T13:08:35
5 Spectrometer Frequency (400.13, 400.13)
OH
Me
OH
O
O
O
Me
33-2
f2 (ppm)
f1 (ppm)

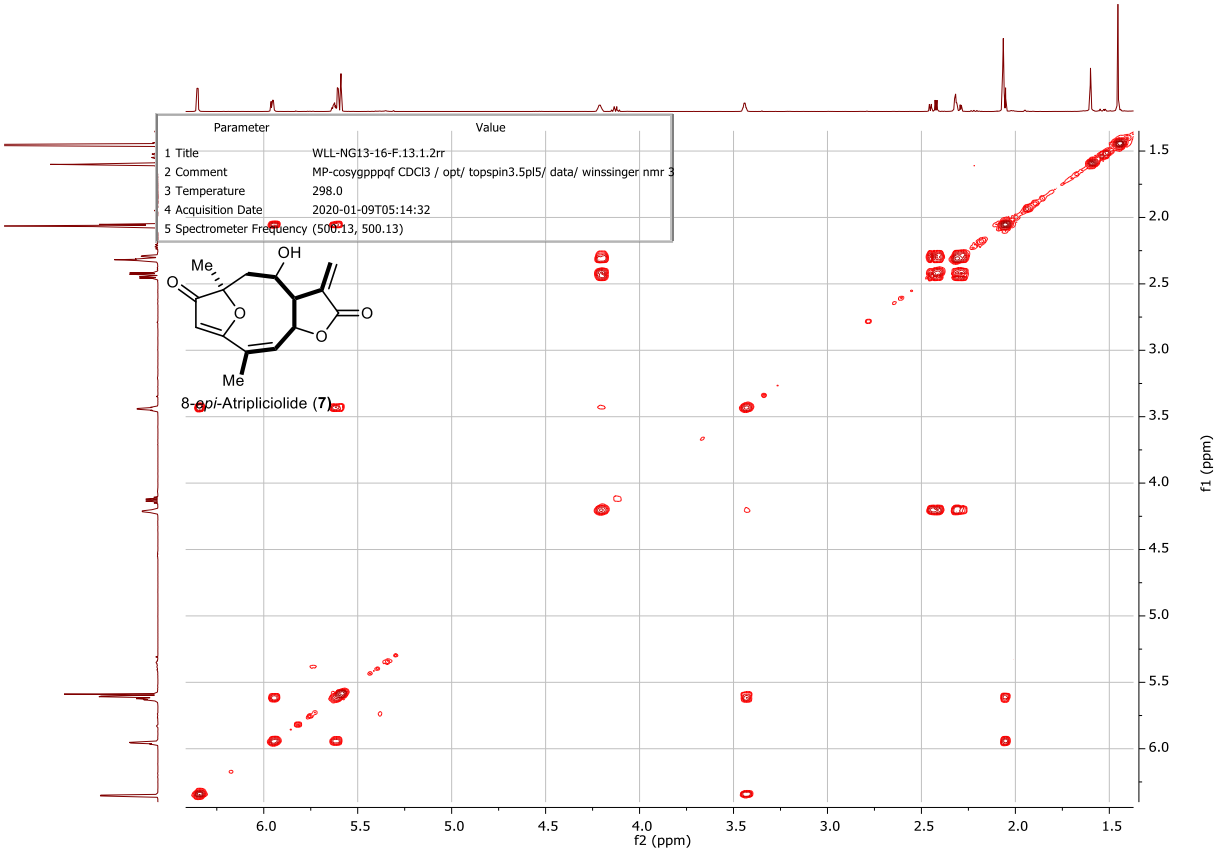

Parameter Value
1 Title wll-ug13-59.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 24
3 Temperature 298.0
4 Acquisition Date 2020-02-15T13:15:03
5 Spectrometer Frequency (400.13, 100.61)
O
Me
H
OH
1
8
HO
H
H
O
Me
5
H
33-2
f2 (ppm)
f1 (ppm)

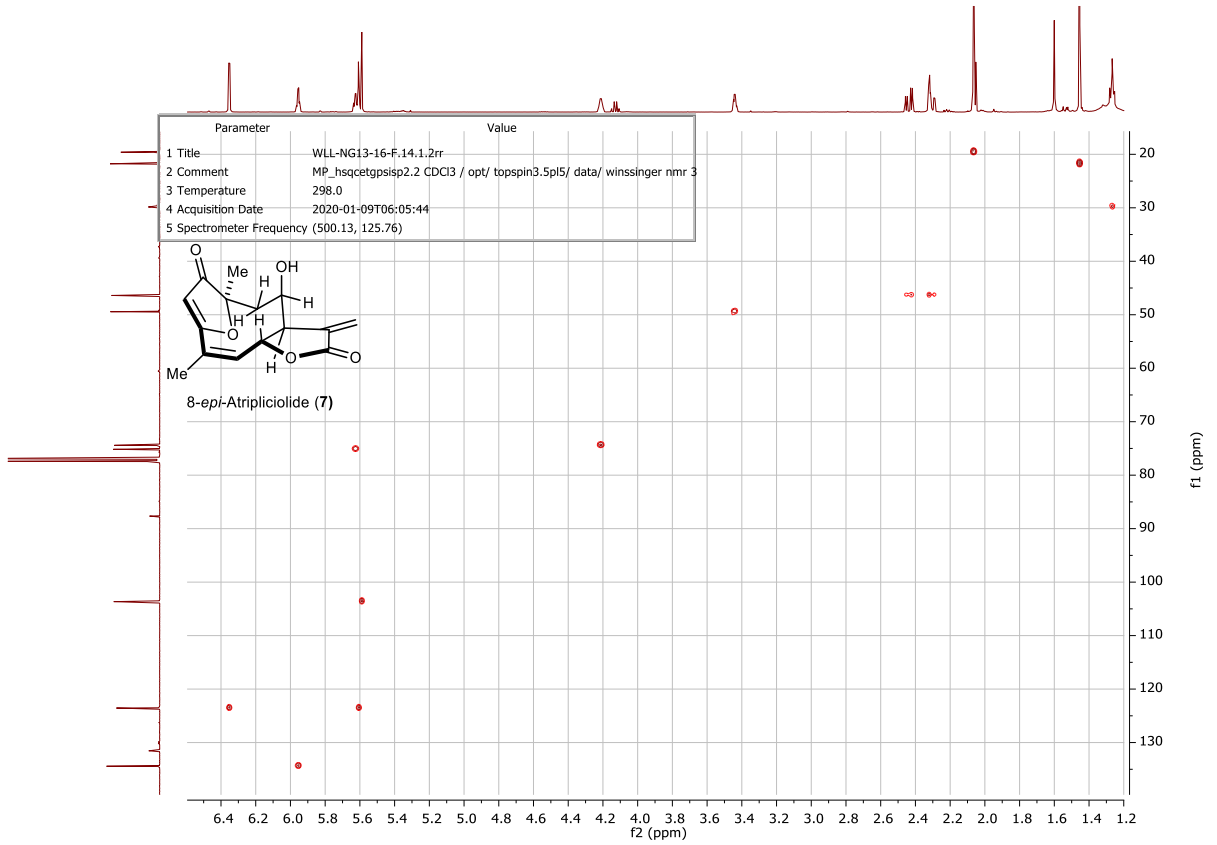

Parameter Value
1 Title wll-ug13-59.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 24
3 Temperature 298.0
4 Acquisition Date 2020-02-15T13:30:23
5 Spectrometer Frequency (400.13, 100.61)
OH
Me
OH
O
O
O
Me
33-2
f2 (ppm)
f1 (ppm)

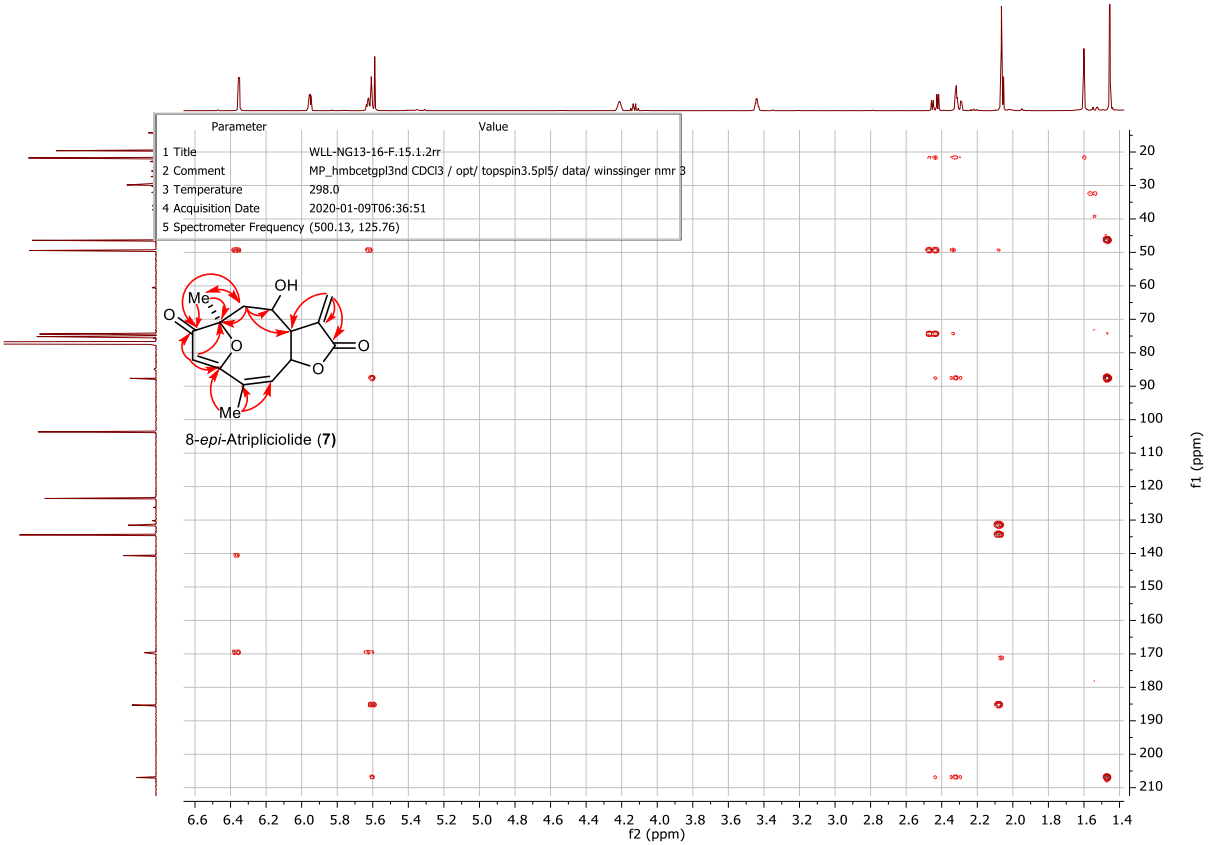

Parameter Value
1 Title wll-ug13-59.16.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 24
3 Temperature 298.0
4 Acquisition Date 2020-02-15T14:33:31
5 Spectrometer Frequency (400.13, 400.13)
O
Me
H
OH
1
8
HO
H
H
H
O
H
Me
5
33-2
f2 (ppm)
f1 (ppm)

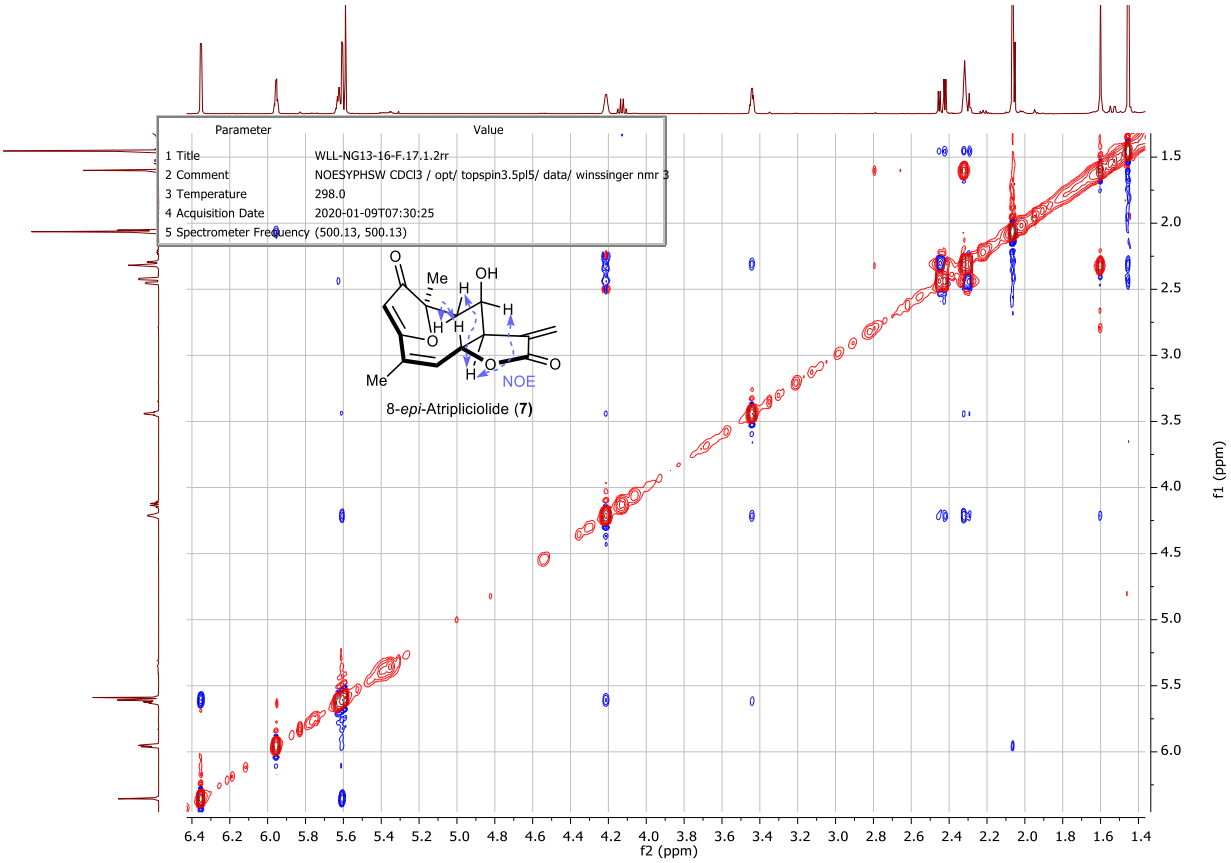

Parameter Value
1 Title WLL-NG13-16-F.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-01-08T22:38:36
5 Spectrometer Frequency 500.13
8-epi-Atripliciolide (7)
f1 (ppm)

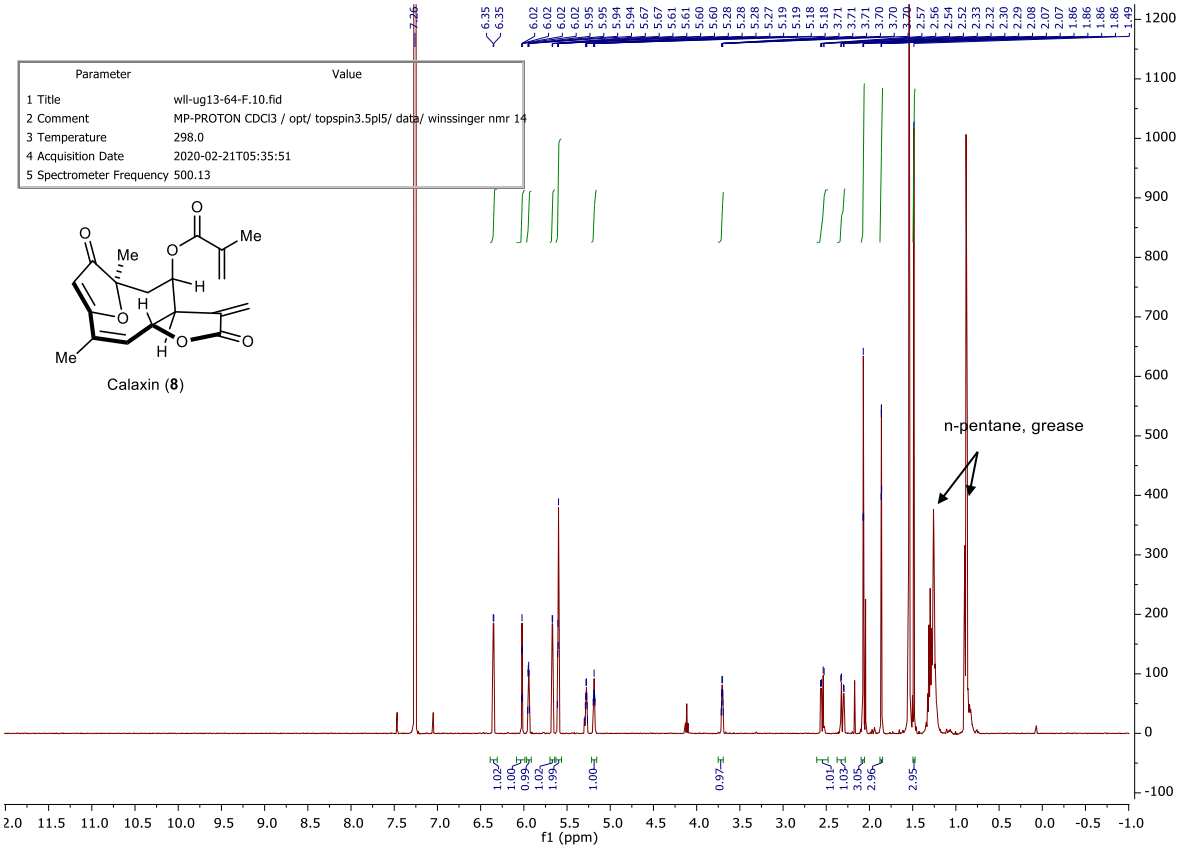

Parameter Value
1 Title WLL-NG13-16-F.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-01-09T03:58:31
5 Spectrometer Frequency 125.77
8-epi-Atripliciolide (7)
f1 (ppm)

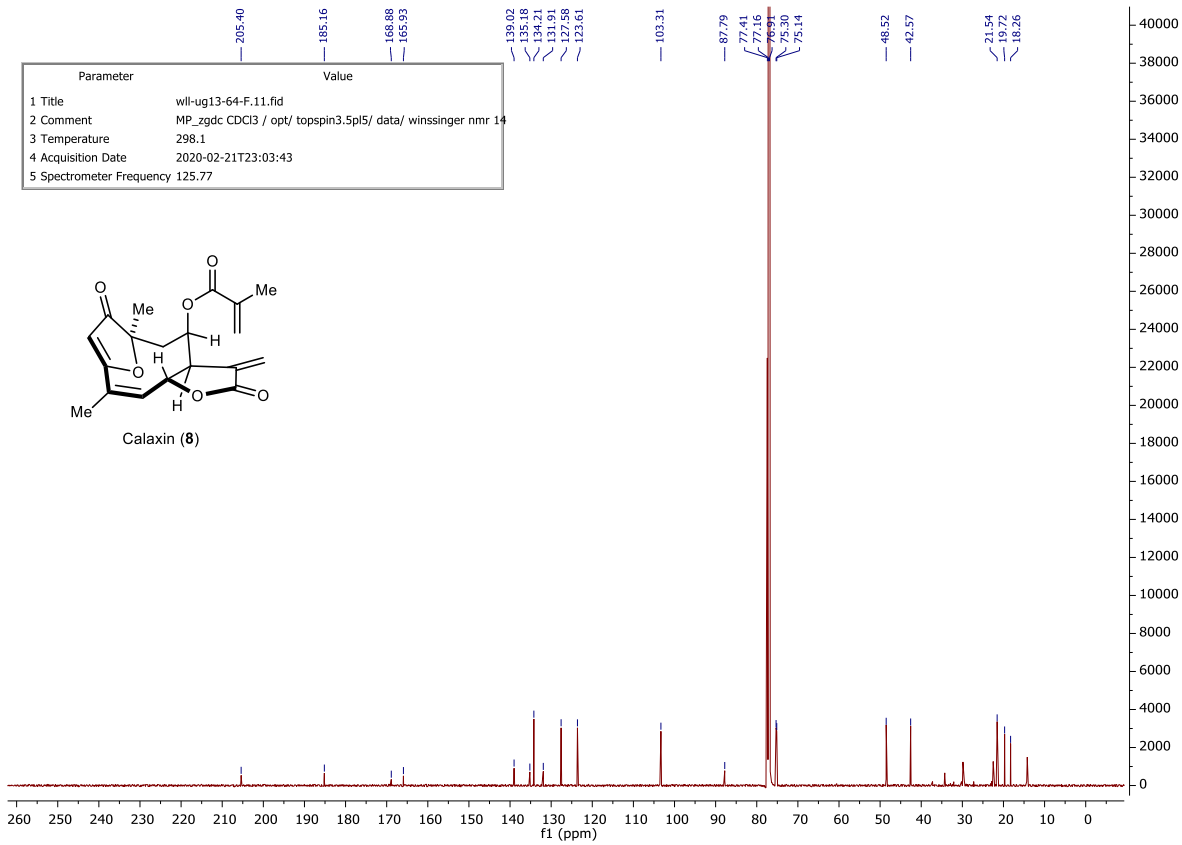

Parameter Value
1 Title WLL-NG13-16-F.13.1.2rr
2 Comment MP-cosygpppqf CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-01-09T05:14:32
5 Spectrometer Frequency (500.13, 500.13)
Me
OH
O
O
O
O
Me
8-epi-Atripliciolide (7)
f2 (ppm)
f1 (ppm)

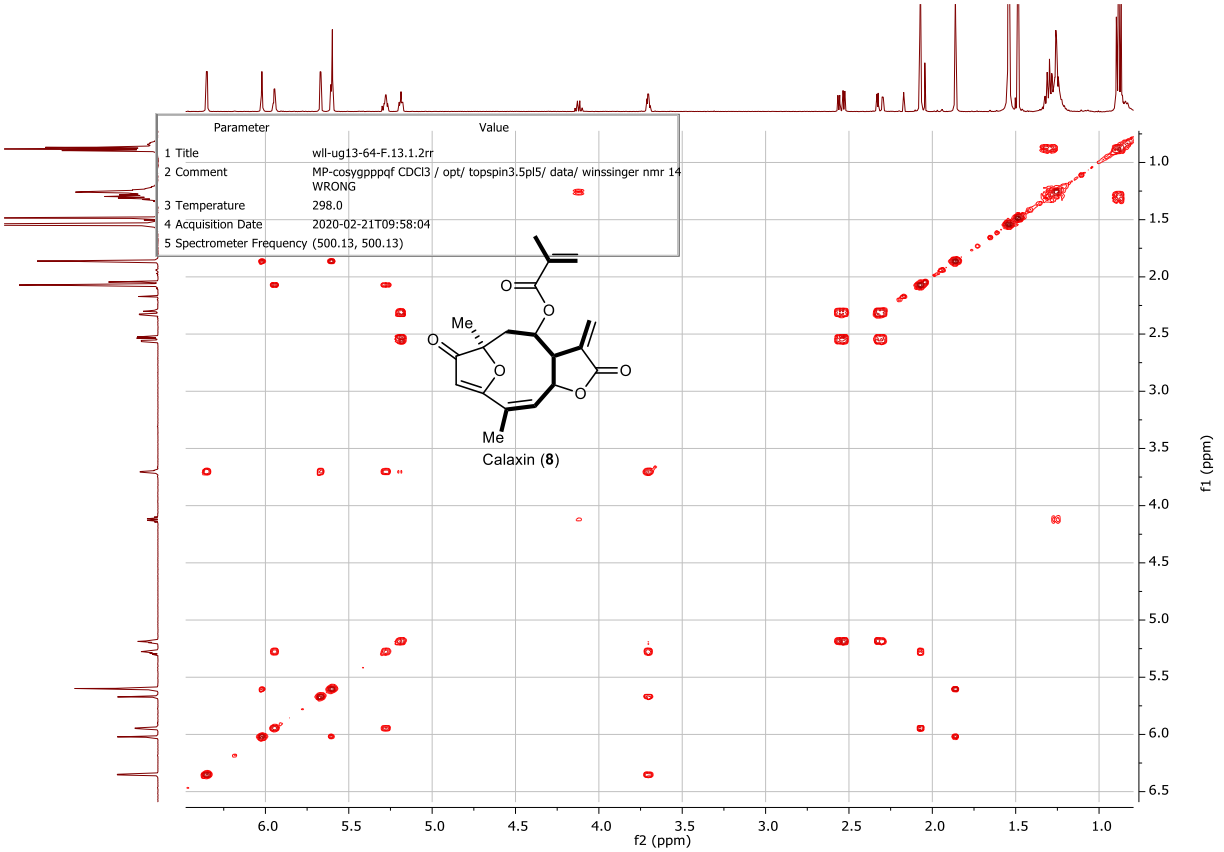

Parameter Value
1 Title WLL-NG13-16-F.14.1.2rr
2 Comment MP_hsqcetgpsisp2.2 CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-01-09T06:05:44
5 Spectrometer Frequency (500.13, 125.76)
O
Me
H
OH
H
H
H
O
O
H
Me
8-epi-Atripliciolide (7)
f2 (ppm)
f1 (ppm)

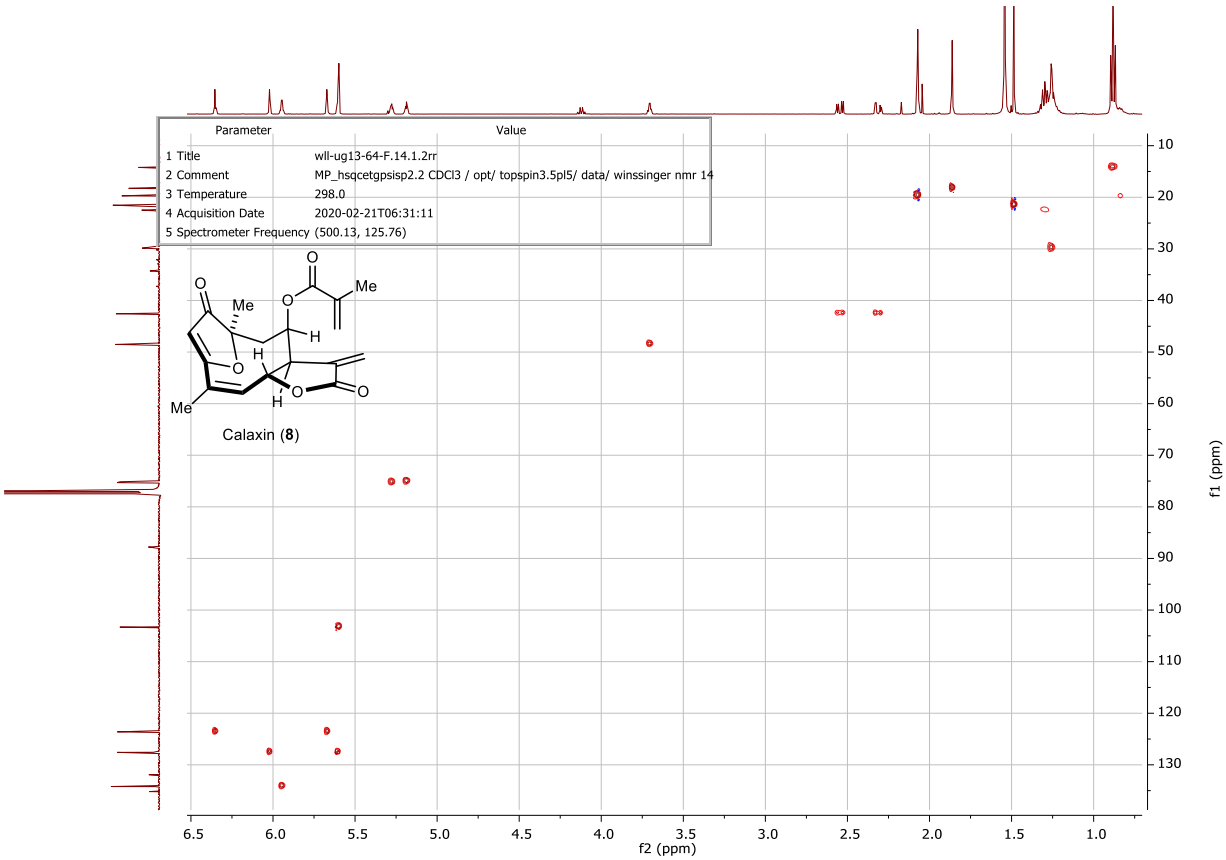

Parameter Value
1 Title WLL-NG13-16-F.15.1.2rr
2 Comment MP_hmbcetgpl3nd CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-01-09T06:36:51
5 Spectrometer Frequency (500.13, 125.76)
Me
OH
O
O
O
O
Me
8-epi-Atripliciolide (7)
f2 (ppm)
f1 (ppm)

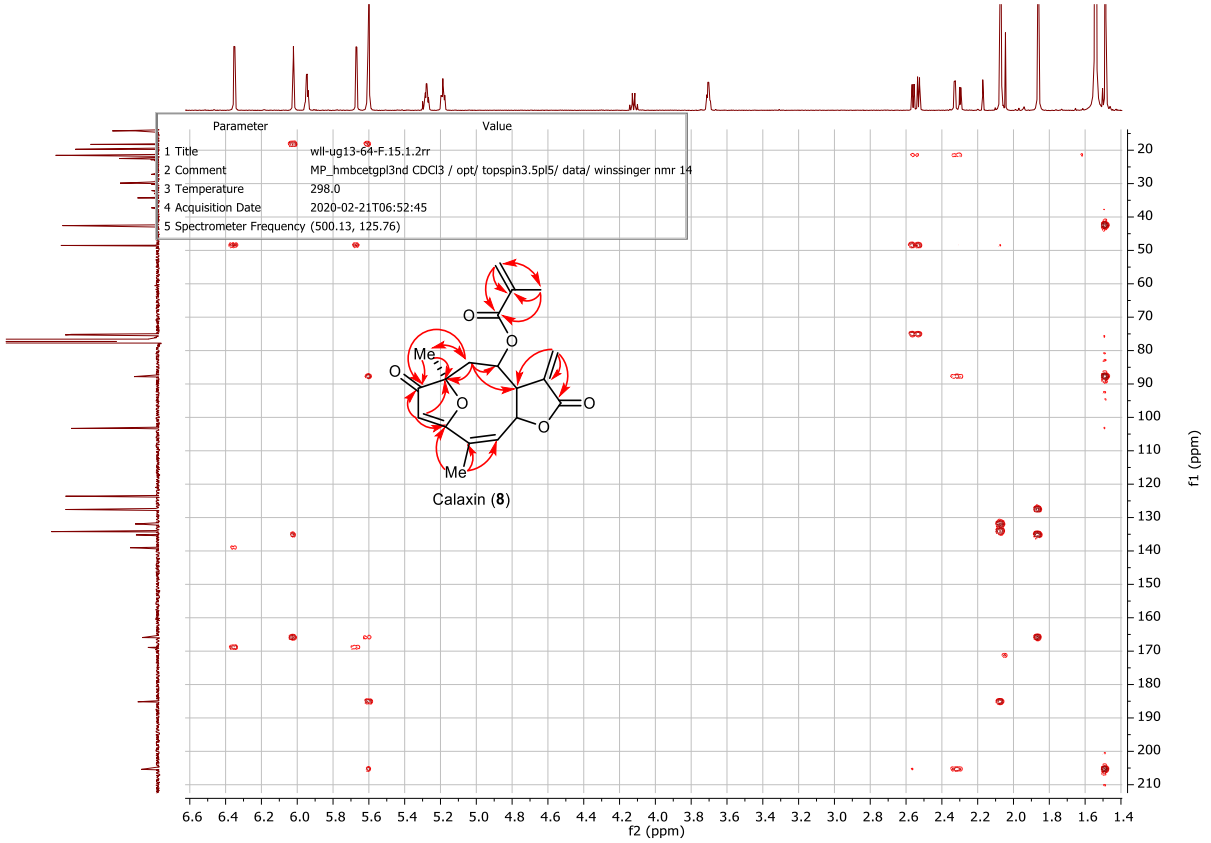

Parameter Value
1 Title WLL-NG13-16-F.17.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 3
3 Temperature 298.0
4 Acquisition Date 2020-01-09T07:30:25
5 Spectrometer Frequency (500.13, 500.13)
Me
OH
H
H
H
H
O
O
O
O
Me
NOE
8-epi-Atripliciolide (7)
f2 (ppm)
f1 (ppm)

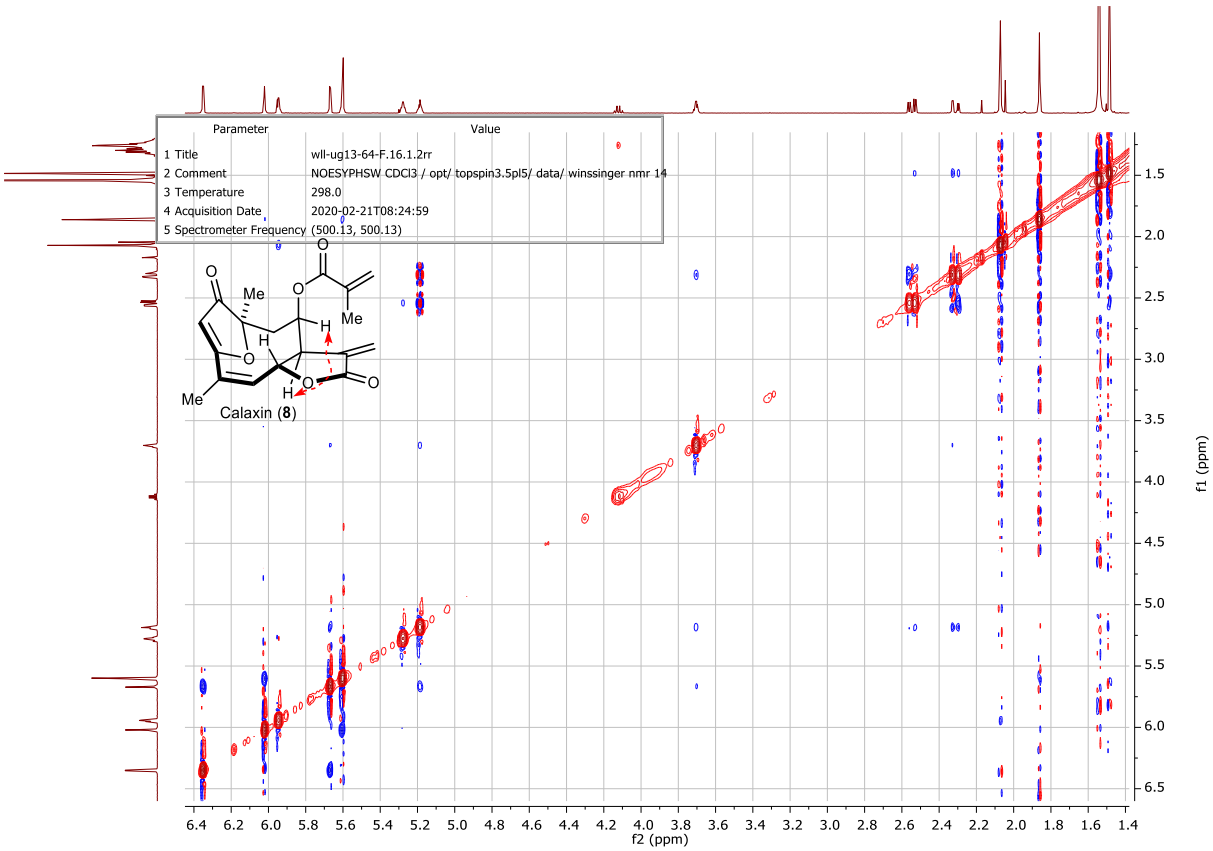

Parameter Value
1 Title wll-ug13-64-F.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 14
3 Temperature 298.0
4 Acquisition Date 2020-02-21T05:35:51
5 Spectrometer Frequency 500.13
Calaxin (8)
n-pentane, grease
f1 (ppm)

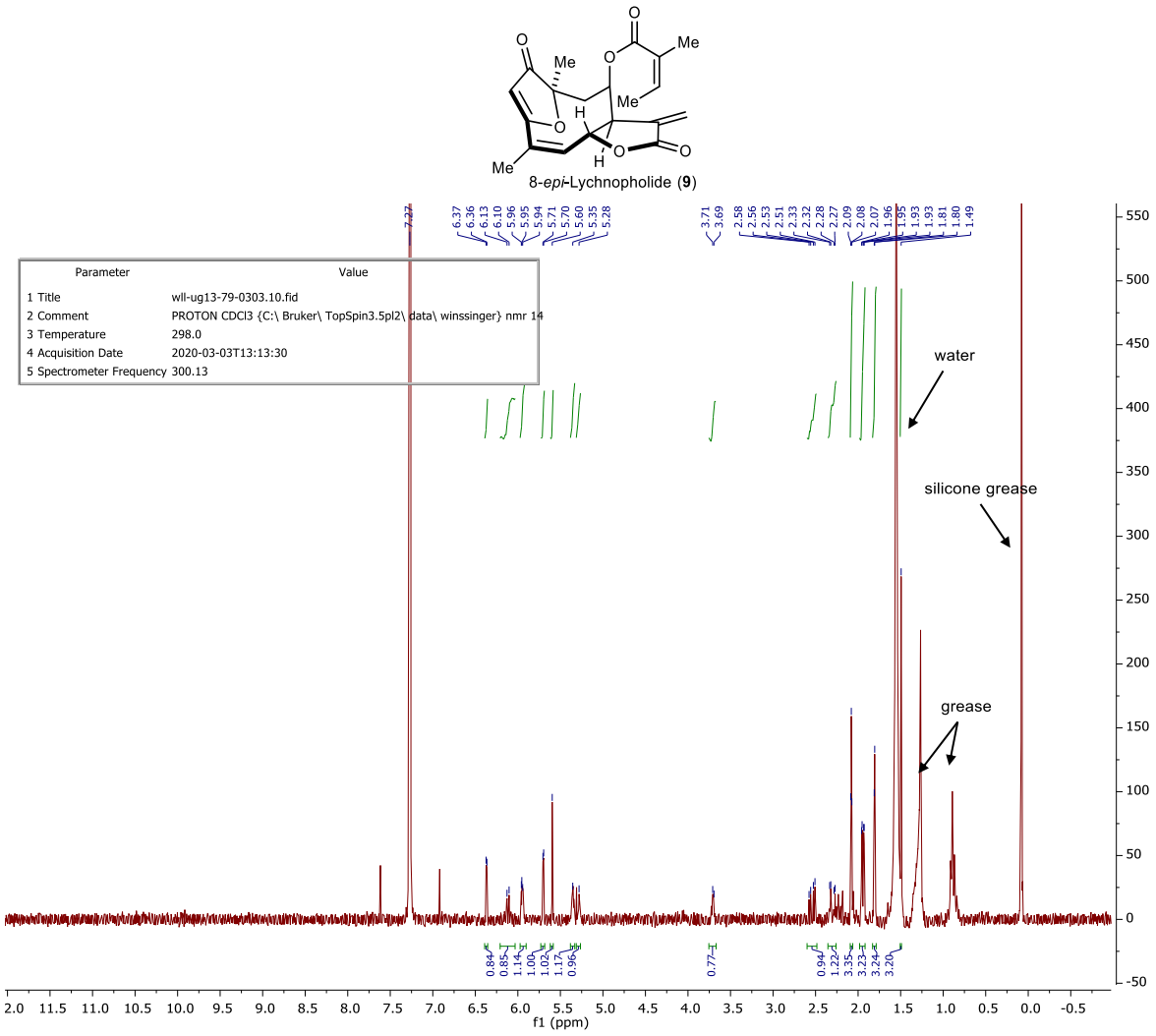

Parameter Value
1 Title wll-ug13-64-F.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 14
3 Temperature 298.1
4 Acquisition Date 2020-02-21T23:03:43
5 Spectrometer Frequency 125.77
Calaxin (8)
f1 (ppm)

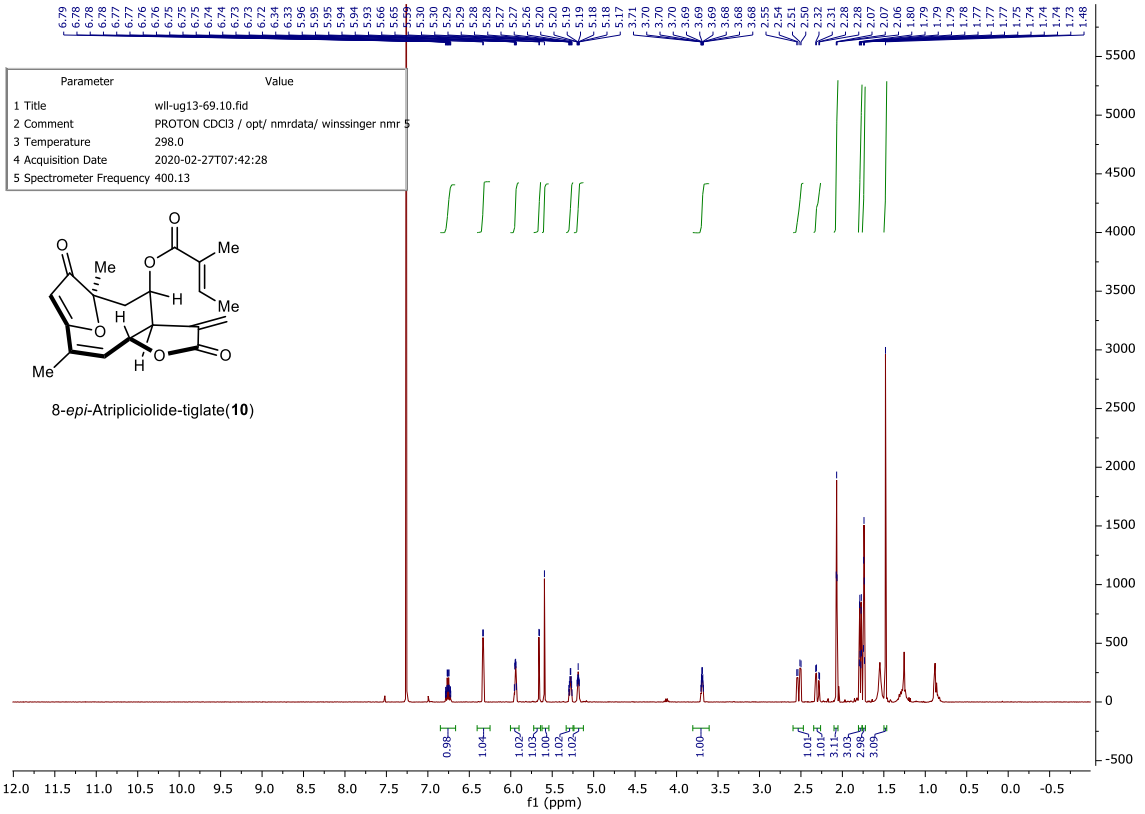

Parameter Value
1 Title wll-ug13-64-F.13.1.2rr
2 Comment MP-cosygpppqf CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 14 WRONG
3 Temperature 298.0
4 Acquisition Date 2020-02-21T09:58:04
5 Spectrometer Frequency (500.13, 500.13)
Me
Me
Calaxin (8)
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug13-64-F.14.1.2rr
2 Comment MP_hsqcetgpsisp2.2 CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 14
3 Temperature 298.0
4 Acquisition Date 2020-02-21T06:31:11
5 Spectrometer Frequency (500.13, 125.76)
Me
Me
Me
Calaxin (8)
f2 (ppm)
f1 (ppm)

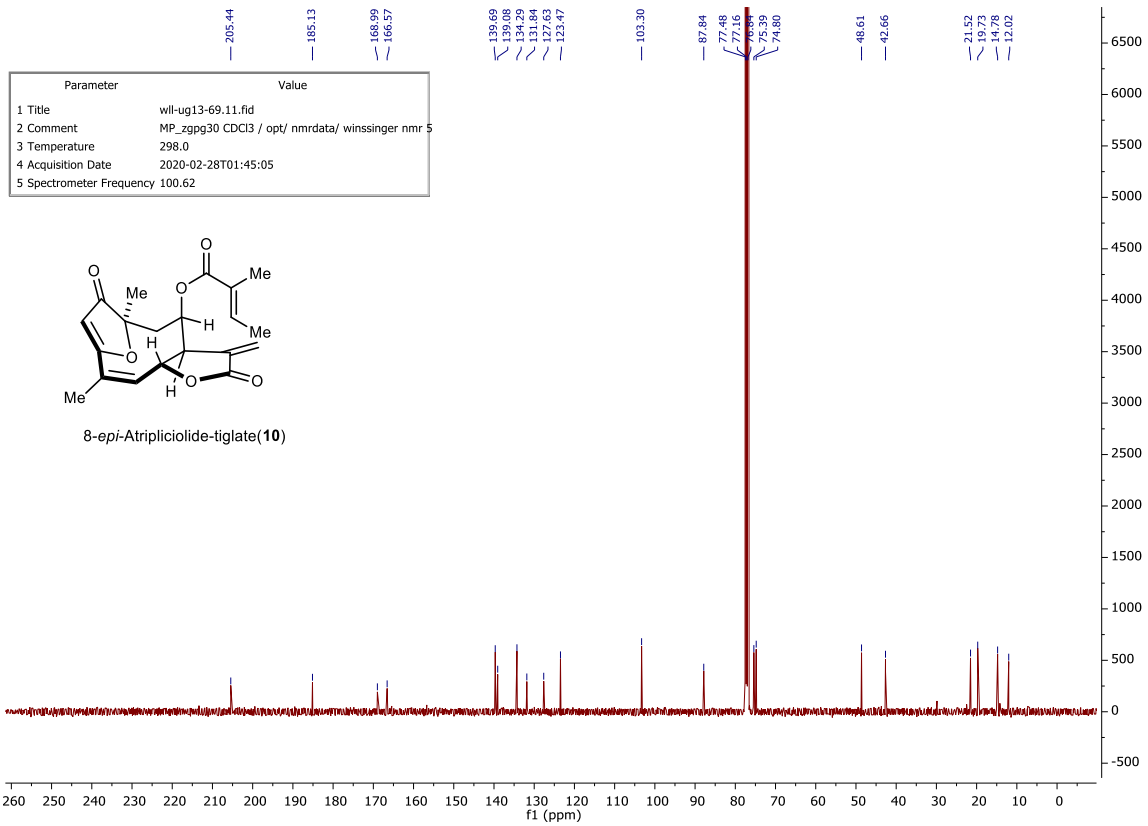

Parameter
Value
1 Title
wll-ug13-64-F.15.1.2rr
2 Comment
MP_hmbcetgpl3nd CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 14
3 Temperature
298.0
4 Acquisition Date
2020-02-21T06:52:45
5 Spectrometer Frequency
(500.13, 125.76)
Me
Me
Calaxin (8)
f2 (ppm)
f1 (ppm)


Parameter
Value
1 Title
wll-ug13-64-F.16.1.2rr
2 Comment
NOESYPHSW CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 14
3 Temperature
298.0
4 Acquisition Date
2020-02-21T08:24:59
5 Spectrometer Frequency
(500.13, 500.13)
Me
Me
Me
Calaxin (8)
f2 (ppm)
f1 (ppm)

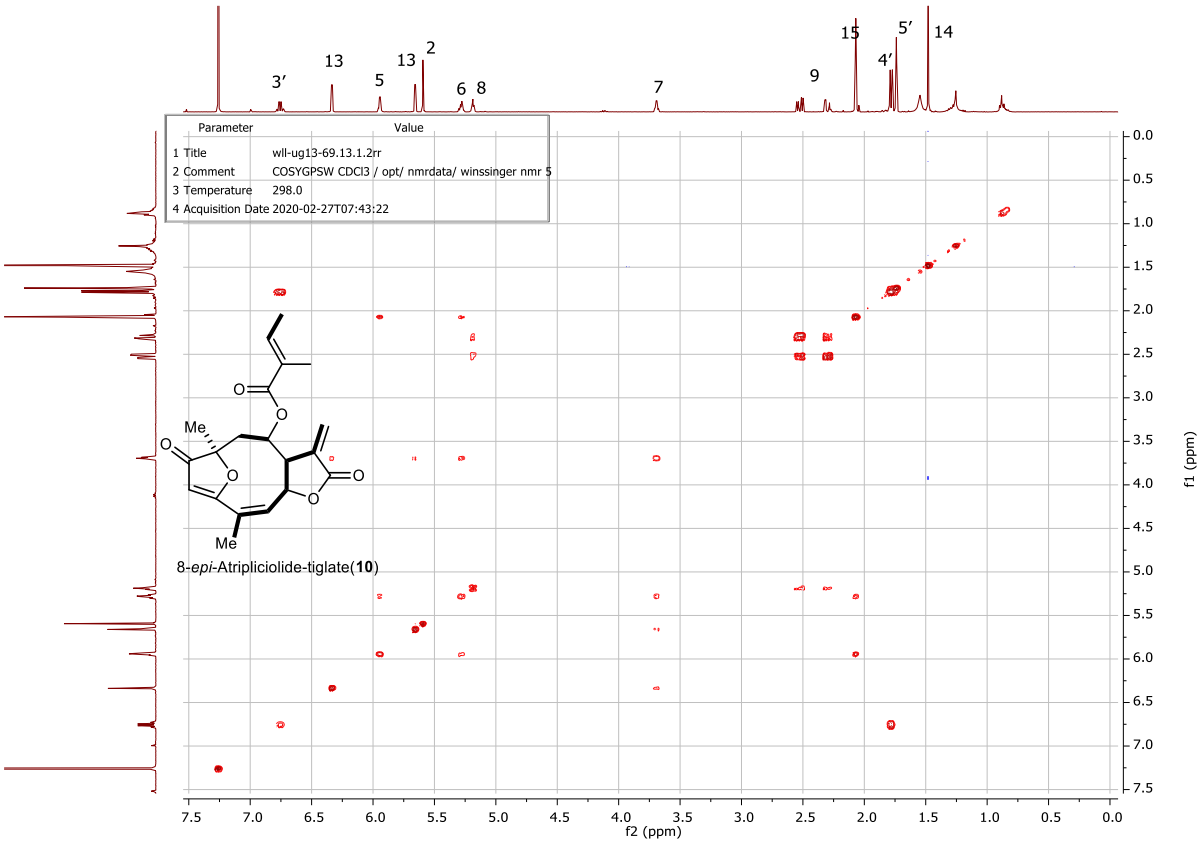

8-epi-Lychnopholide (9)
Parameter Value
1 Title wll-ug13-79-0303.10.fid
2 Comment PROTON CDCl3 {C:\ Bruker\ TopSpin3.5pl2\ data\ winssinger} nmr 14
3 Temperature 298.0
4 Acquisition Date 2020-03-03T13:13:30
5 Spectrometer Frequency 300.13
water
silicone grease
grease
f1 (ppm)

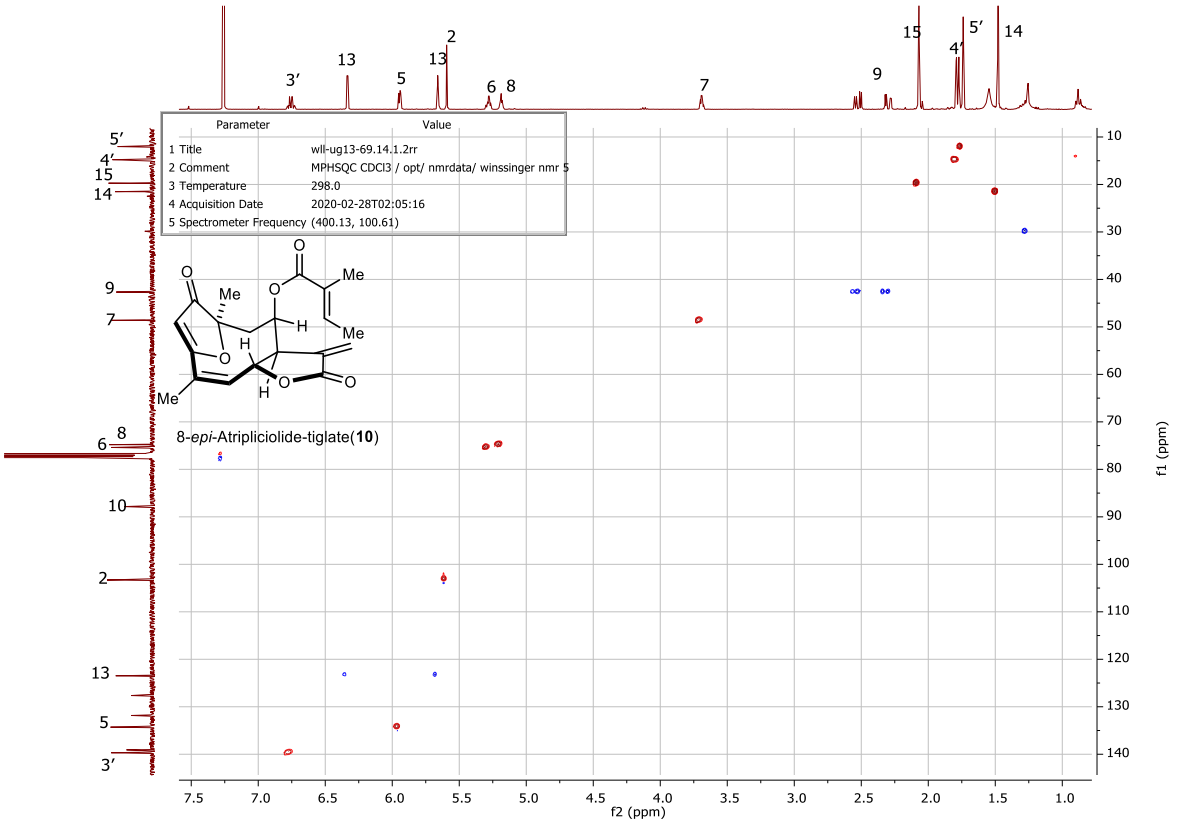


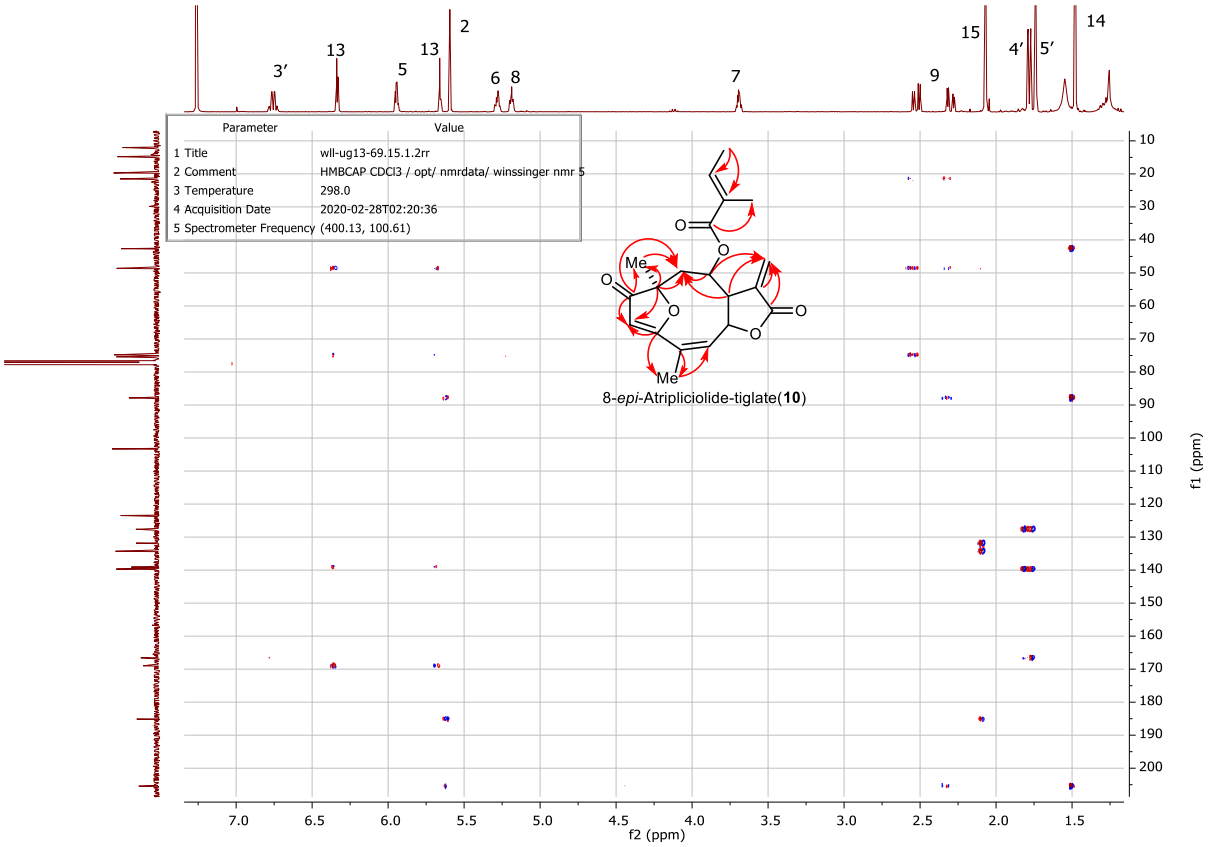
8-*epi*-Atripliciolide-tiglate(**10**)

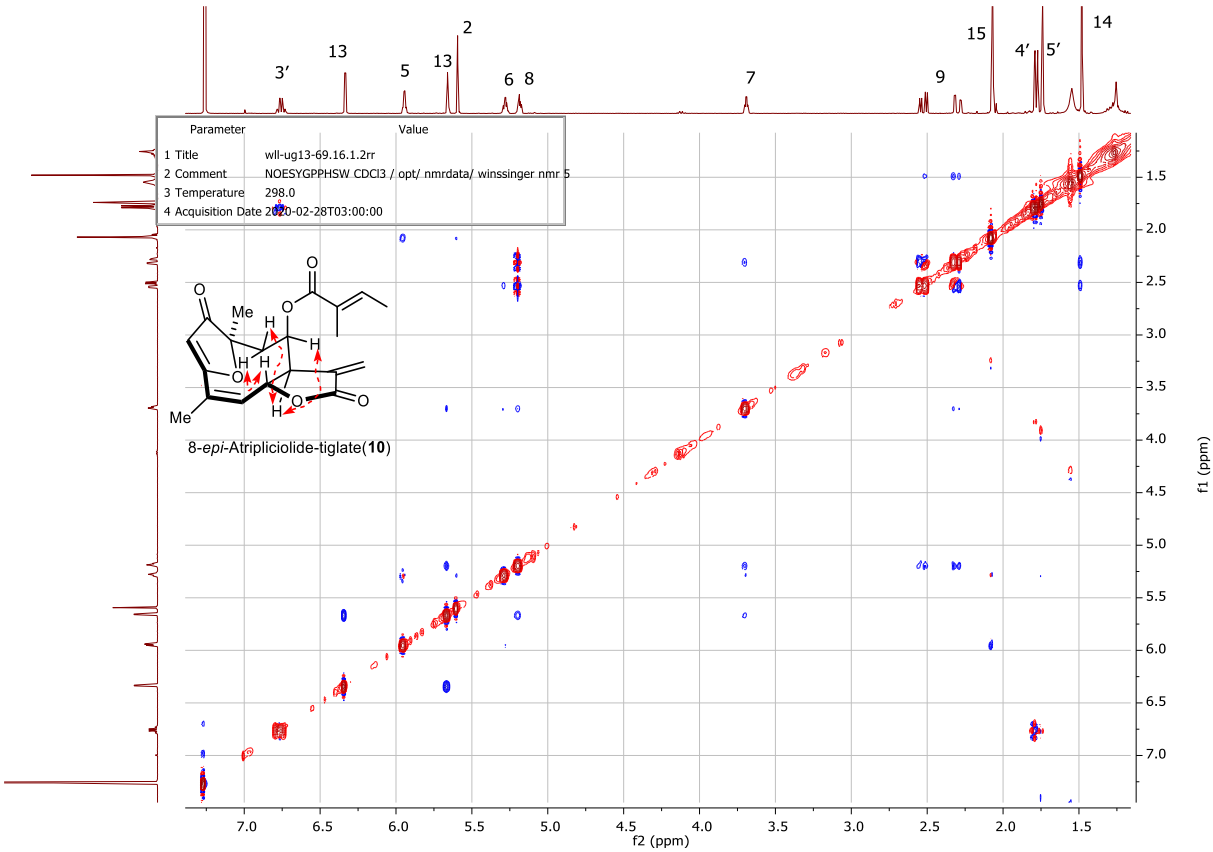


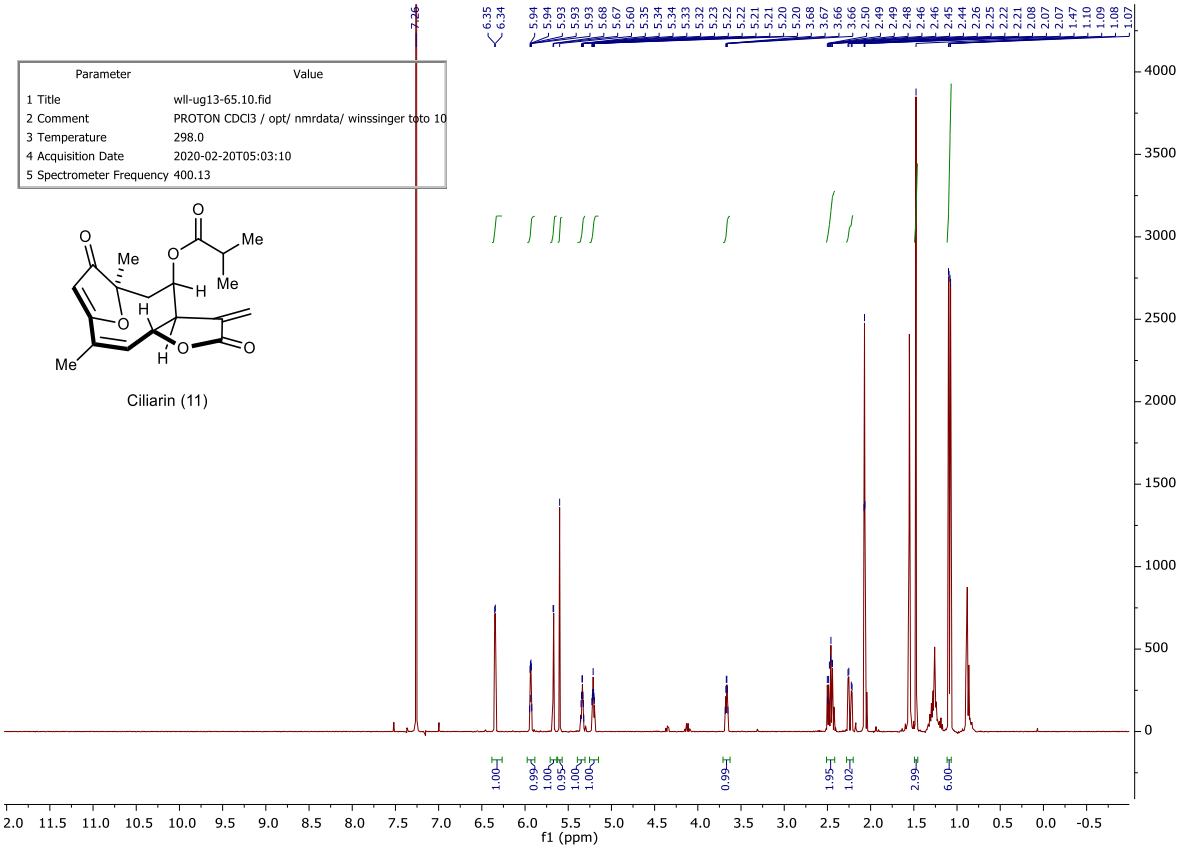
8-*epi*-Atripliciolide-tiglate(**10**)

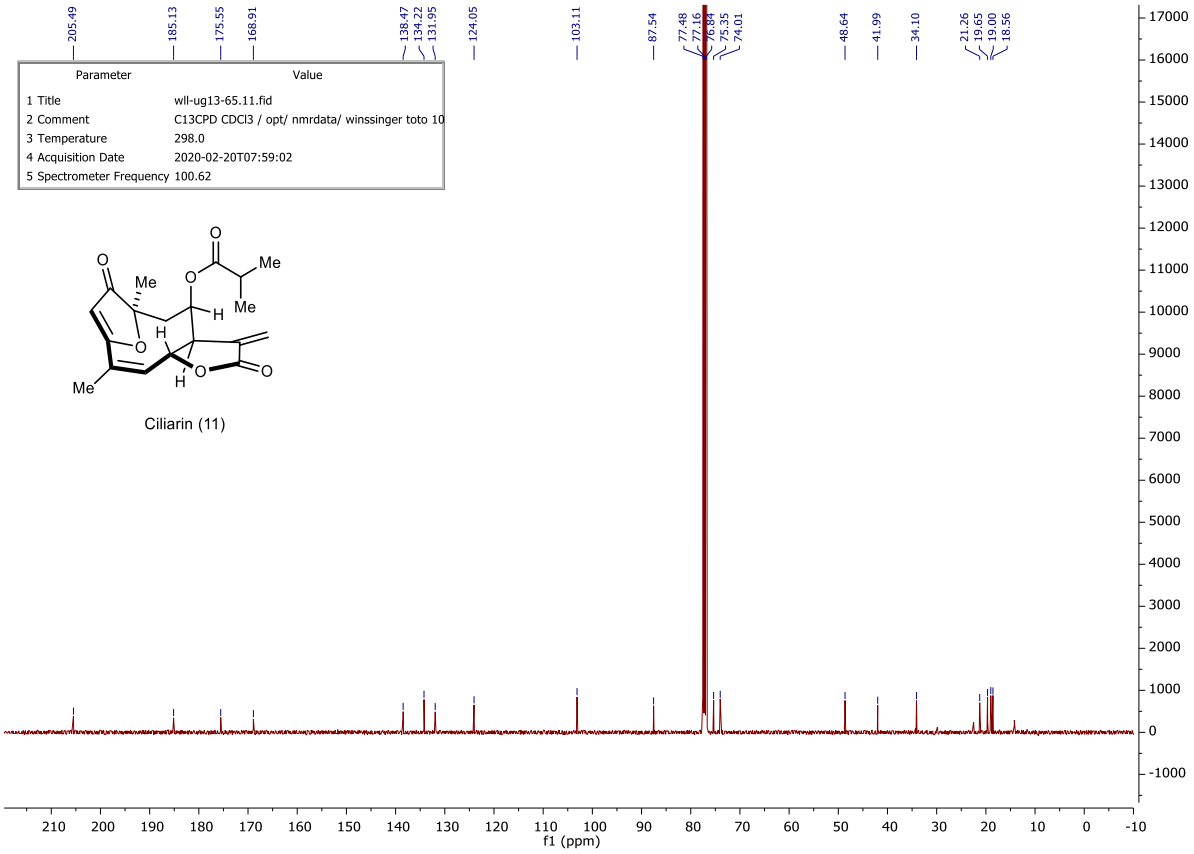

Parameter Value
1 Title wll-ug13-69.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 5
3 Temperature 298.0
4 Acquisition Date 2020-02-27T07:43:22
8-epi-Atripliciolide-tiglate(10)
f2 (ppm)
f1 (ppm)

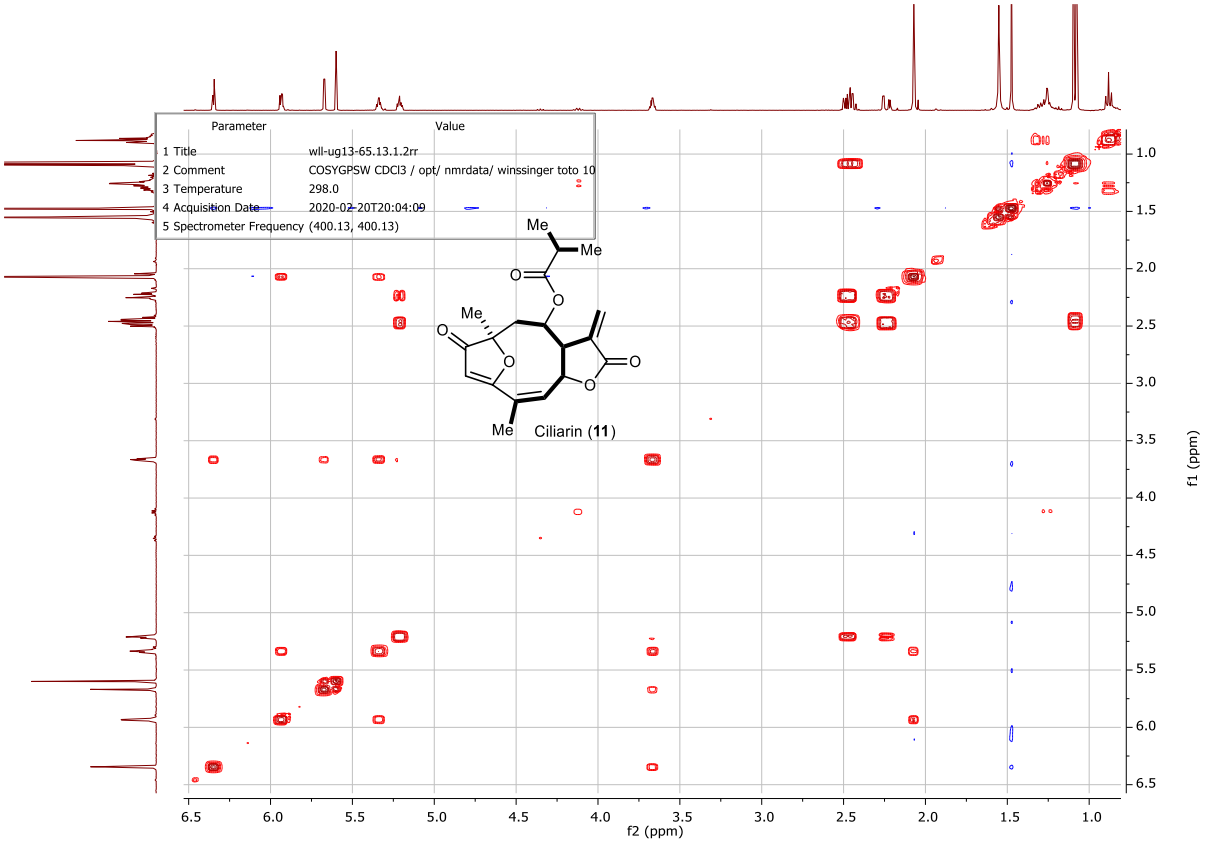

Parameter Value
1 Title wll-ug13-69.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 5
3 Temperature 298.0
4 Acquisition Date 2020-02-28T02:05:16
5 Spectrometer Frequency (400.13, 100.61)
8-epi-Atripliciolide-tiglate(10)
f2 (ppm)
f1 (ppm)

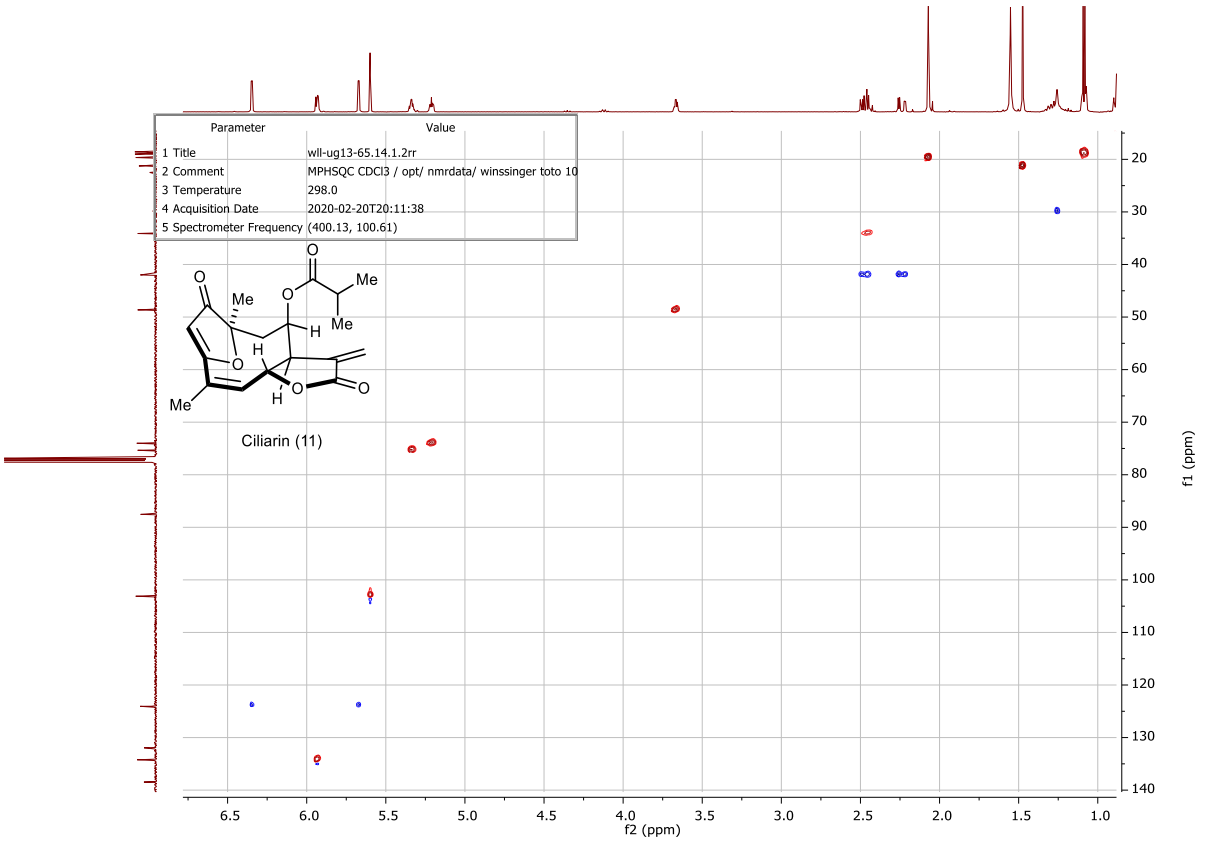

3′
13
5
13
2
6 8
7
9
15
4′
5′
14
Parameter Value
1 Title wll-ug13-69.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 5
3 Temperature 298.0
4 Acquisition Date 2020-02-28T02:20:36
5 Spectrometer Frequency (400.13, 100.61)
Me
Me
8-epi-Atripliciolide-tiglate(10)
f2 (ppm)
f1 (ppm)

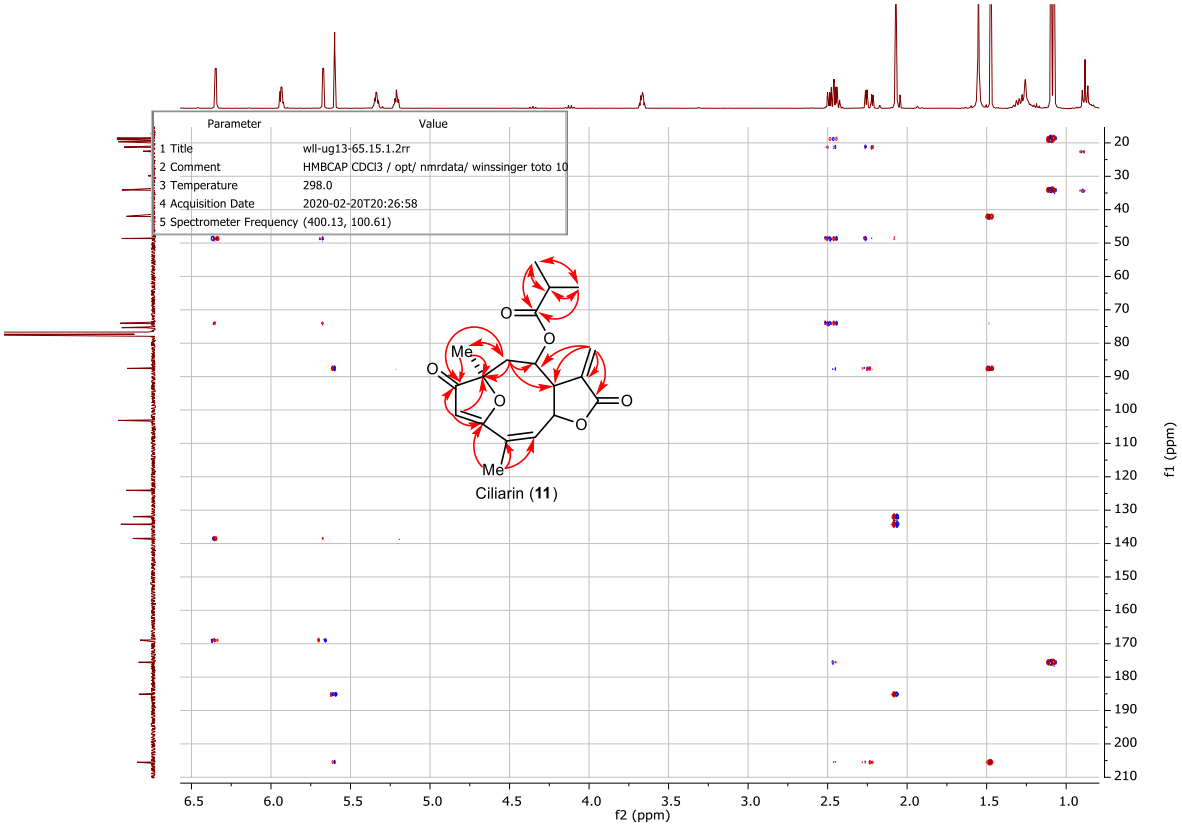

3′
13
5
13
2
6 8
7
9
15
4′
5′
14
Parameter Value
1 Title wll-ug13-69.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 5
3 Temperature 298.0
4 Acquisition Date 2020-02-28T03:00:00
Me
Me
8-epi-Atripliciolide-tiglate(10)
f2 (ppm)
f1 (ppm)

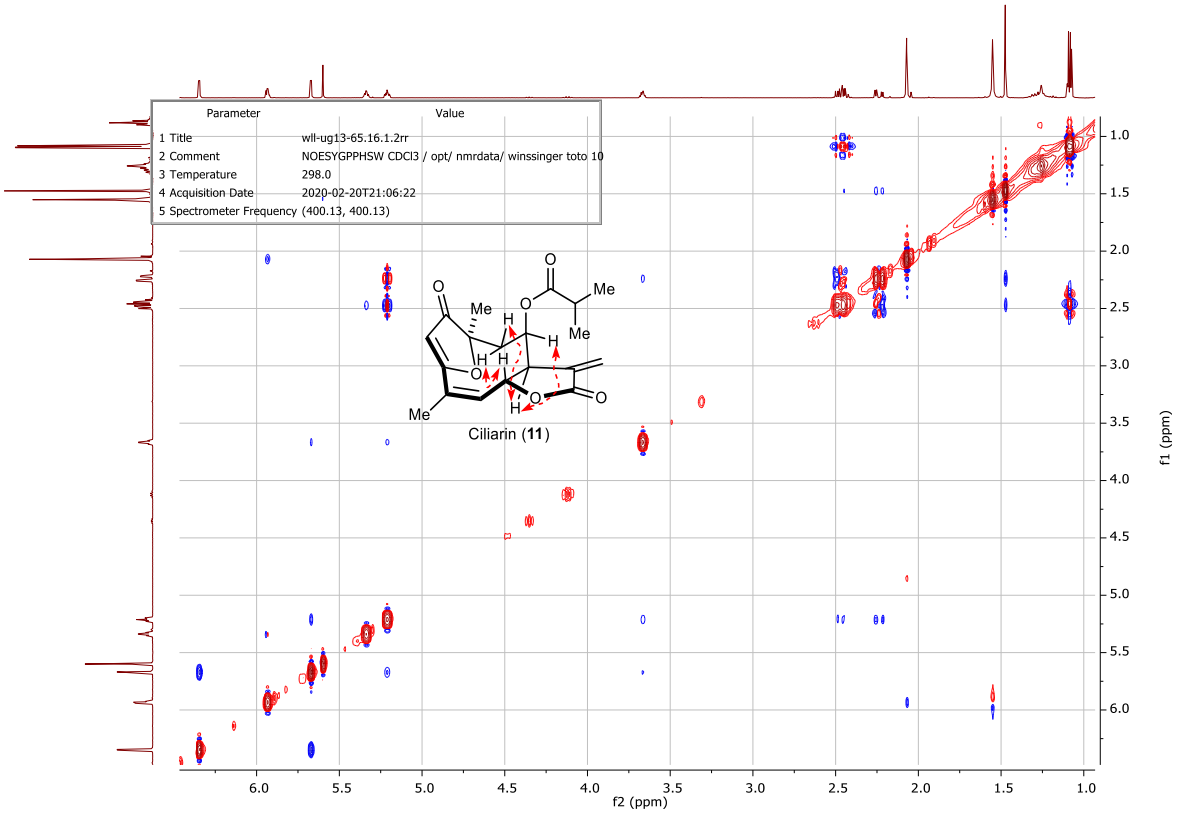

Parameter Value
1 Title wll-ug13-65.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger toto 10
3 Temperature 298.0
4 Acquisition Date 2020-02-20T05:03:10
5 Spectrometer Frequency 400.13
Ciliarin (11)
f1 (ppm)

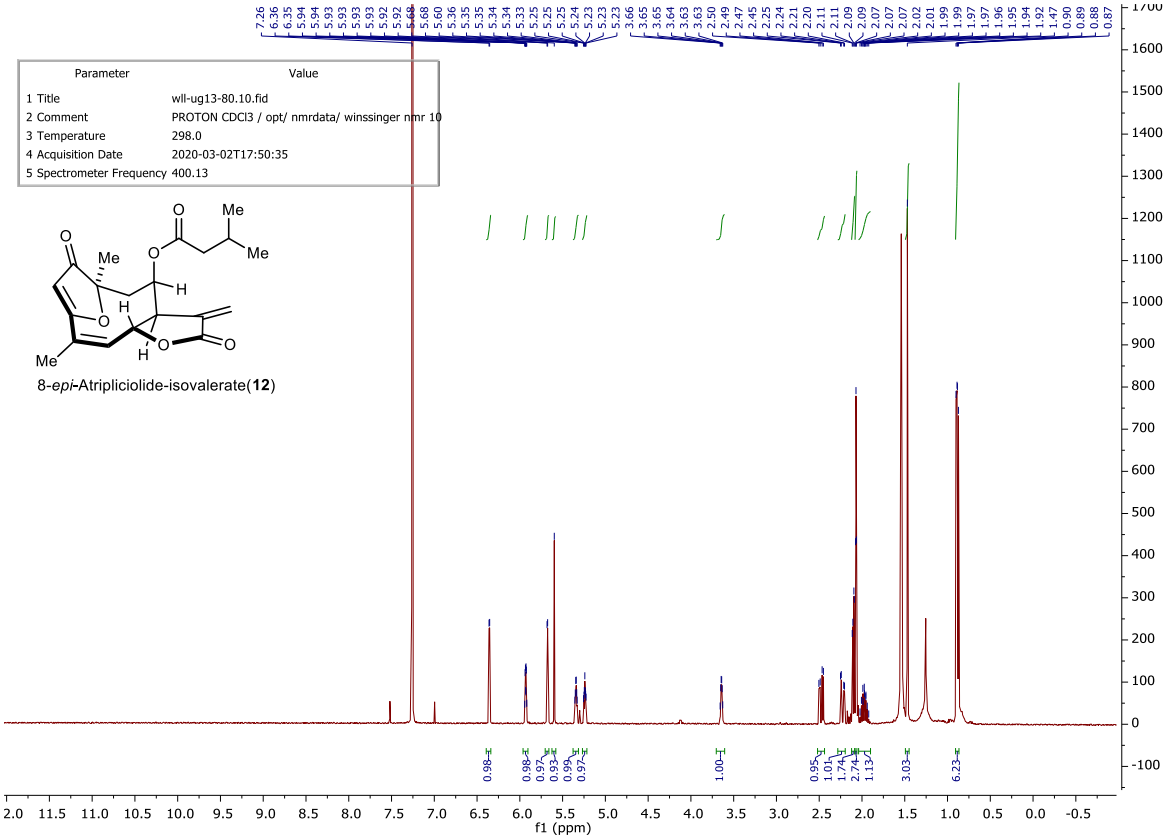

Parameter Value
1 Title wll-ug13-65.11.fid
2 Comment C13CPD CDCl3 / opt/ nmrdata/ winssinger toto 10
3 Temperature 298.0
4 Acquisition Date 2020-02-20T07:59:02
5 Spectrometer Frequency 100.62
Ciliarin (11)
f1 (ppm)

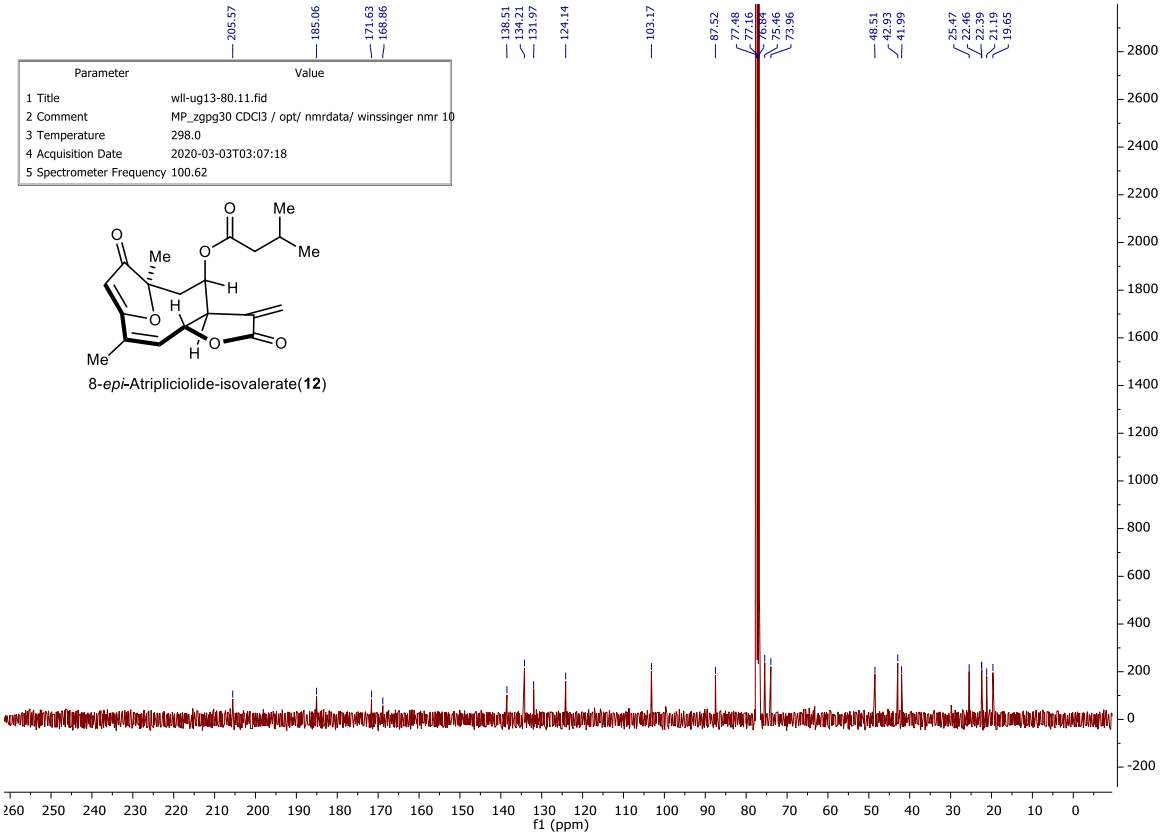

Parameter Value
1 Title wll-ug13-65.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger toto 10
3 Temperature 298.0
4 Acquisition Date 2020-02-20T20:04:09
5 Spectrometer Frequency (400.13, 400.13)
Ciliarin (11)
f2 (ppm)
f1 (ppm)

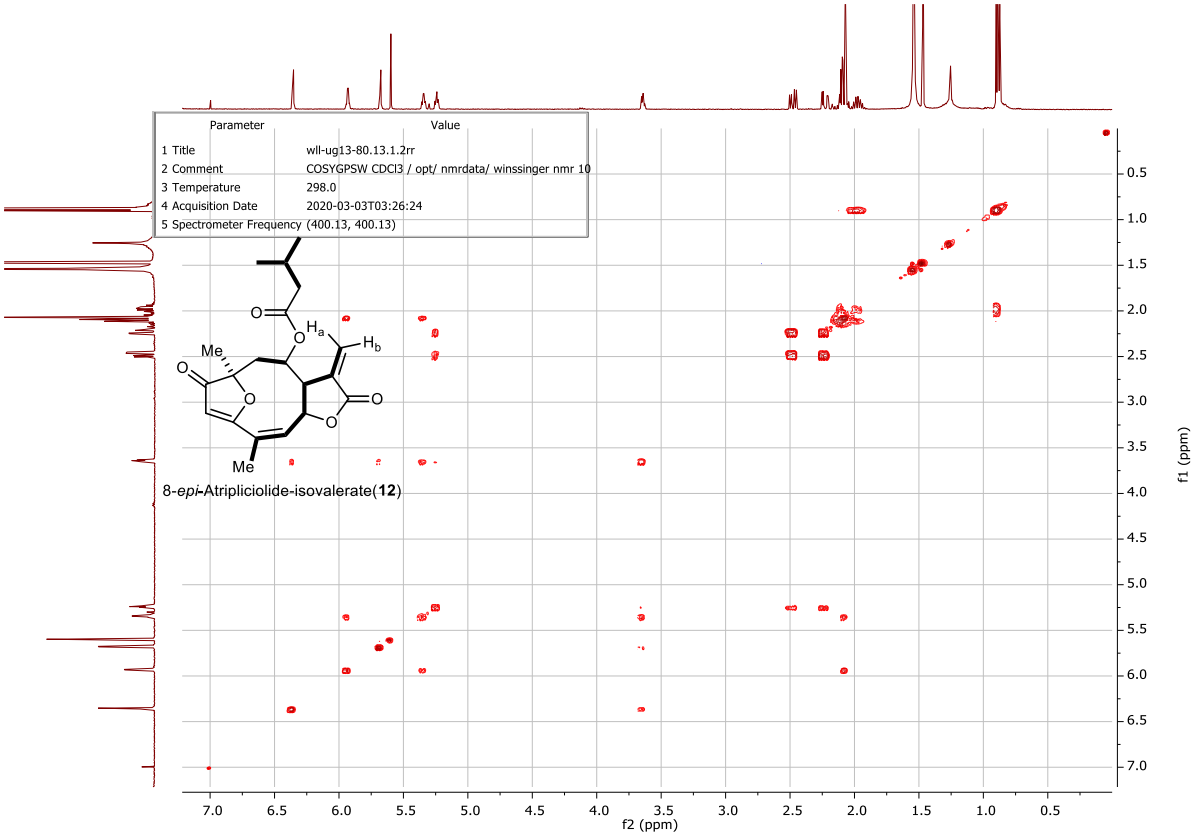

Parameter Value
1 Title wll-ug13-65.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger toto 10
3 Temperature 298.0
4 Acquisition Date 2020-02-20T20:11:38
5 Spectrometer Frequency (400.13, 100.61)
Ciliarin (11)
f2 (ppm)
f1 (ppm)

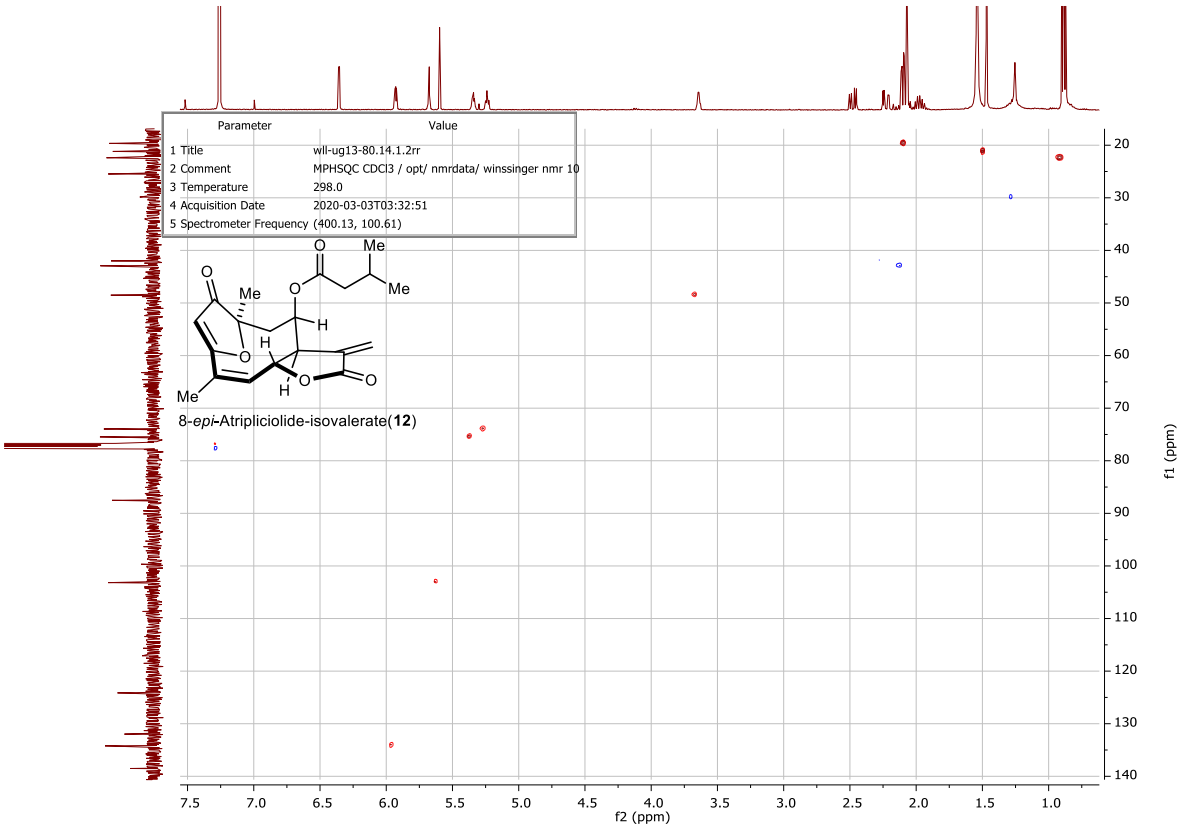

Parameter Value
1 Title wll-ug13-65.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger toto 10
3 Temperature 298.0
4 Acquisition Date 2020-02-20T20:26:58
5 Spectrometer Frequency (400.13, 100.61)
Me
Me
Ciliarin (11)
f2 (ppm)
f1 (ppm)

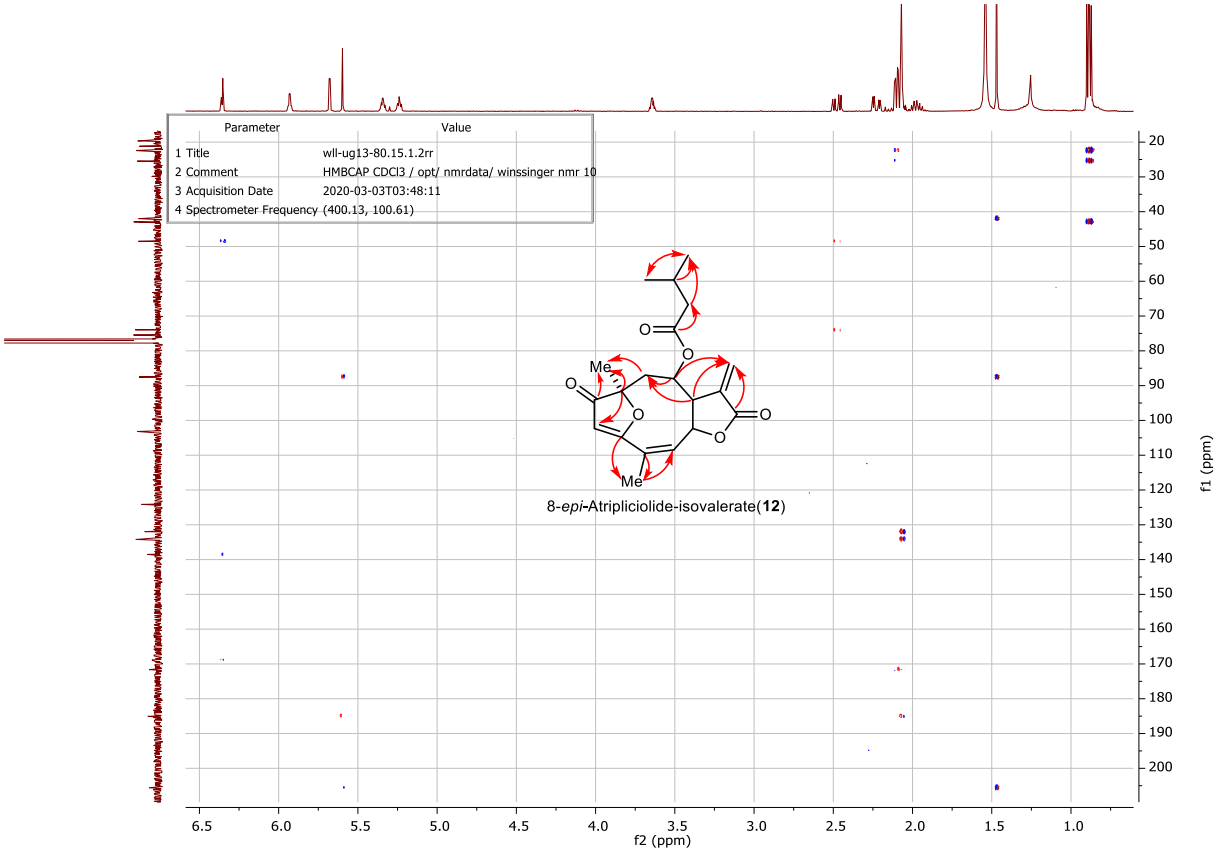

Parameter Value
1 Title wll-ug13-65.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ nmrdata/ winssinger toto 10
3 Temperature 298.0
4 Acquisition Date 2020-02-20T21:06:22
5 Spectrometer Frequency (400.13, 400.13)
Me
Me
Me
Ciliarin (11)
f2 (ppm)
f1 (ppm)

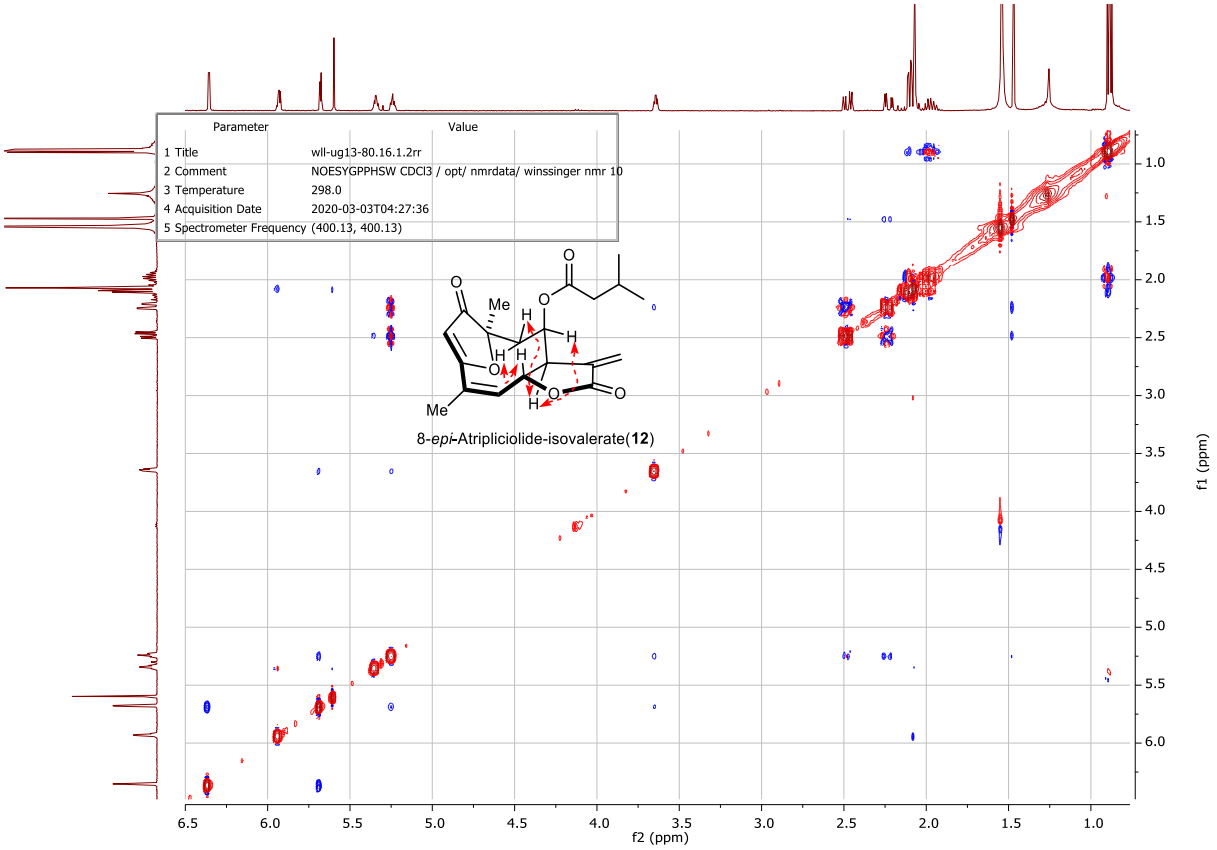

Parameter Value
1 Title wll-ug13-80.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 10
3 Temperature 298.0
4 Acquisition Date 2020-03-02T17:50:35
5 Spectrometer Frequency 400.13
8-epi-Atripliciolide-isovalerate(12)
f1 (ppm)

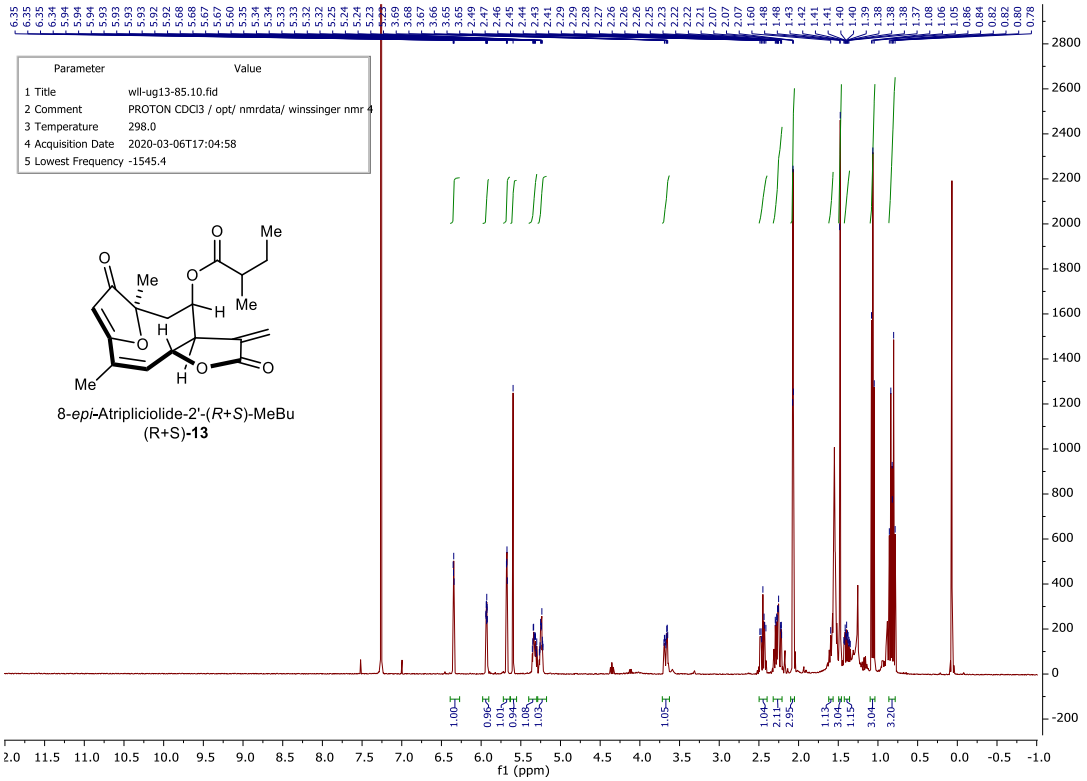

Parameter Value
1 Title wll-ug13-80.11.fid
2 Comment MP_zgpg30 CDCl3 / opt/ nmrdata/ winssinger nmr 10
3 Temperature 298.0
4 Acquisition Date 2020-03-03T03:07:18
5 Spectrometer Frequency 100.62
8-epi-Atripliciolide-isovalerate(12)
f1 (ppm)


Parameter Value
1 Title wll-ug13-80.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 10
3 Temperature 298.0
4 Acquisition Date 2020-03-03T03:26:24
5 Spectrometer Frequency (400.13, 400.13)
8-epi-Atripliciolide-isovalerate(12)
f2 (ppm)
f1 (ppm)

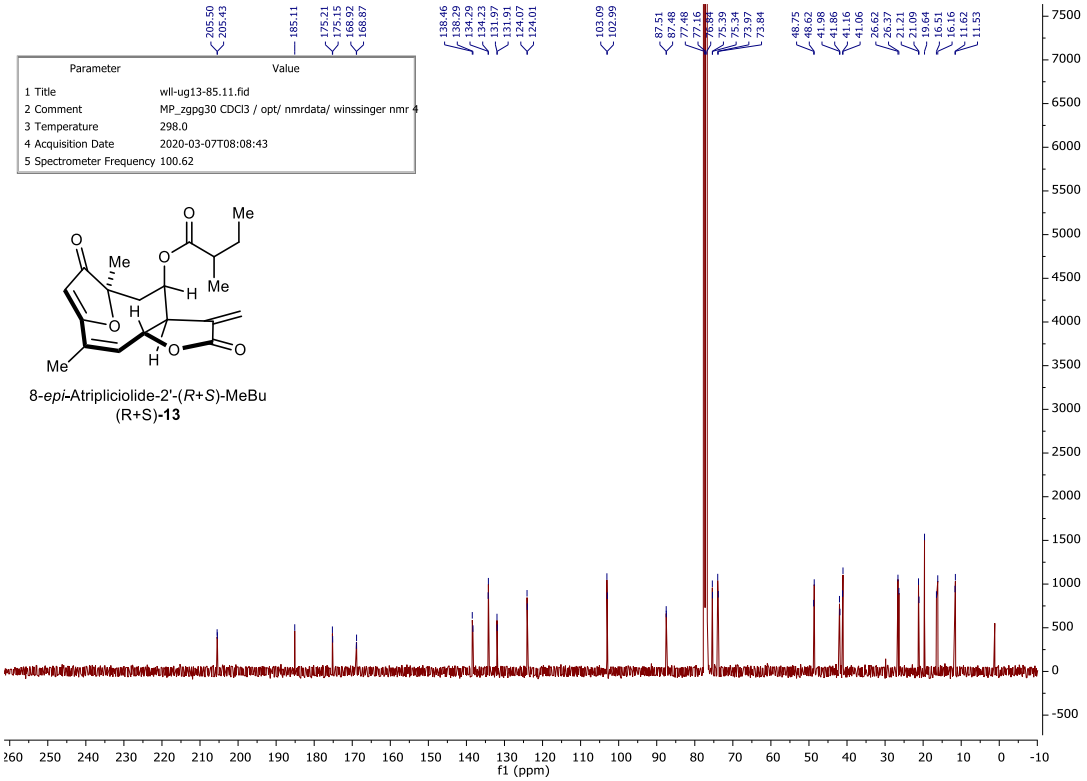

Parameter Value
1 Title wll-ug13-80.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 10
3 Temperature 298.0
4 Acquisition Date 2020-03-03T03:32:51
5 Spectrometer Frequency (400.13, 100.61)
8-epi-Atripliciolide-isovalerate(12)
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug13-80.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 10
3 Acquisition Date 2020-03-03T03:48:11
4 Spectrometer Frequency (400.13, 100.61)
Me
Me
8-epi-Atripliciolide-isovalerate(12)
f2 (ppm)
f1 (ppm)

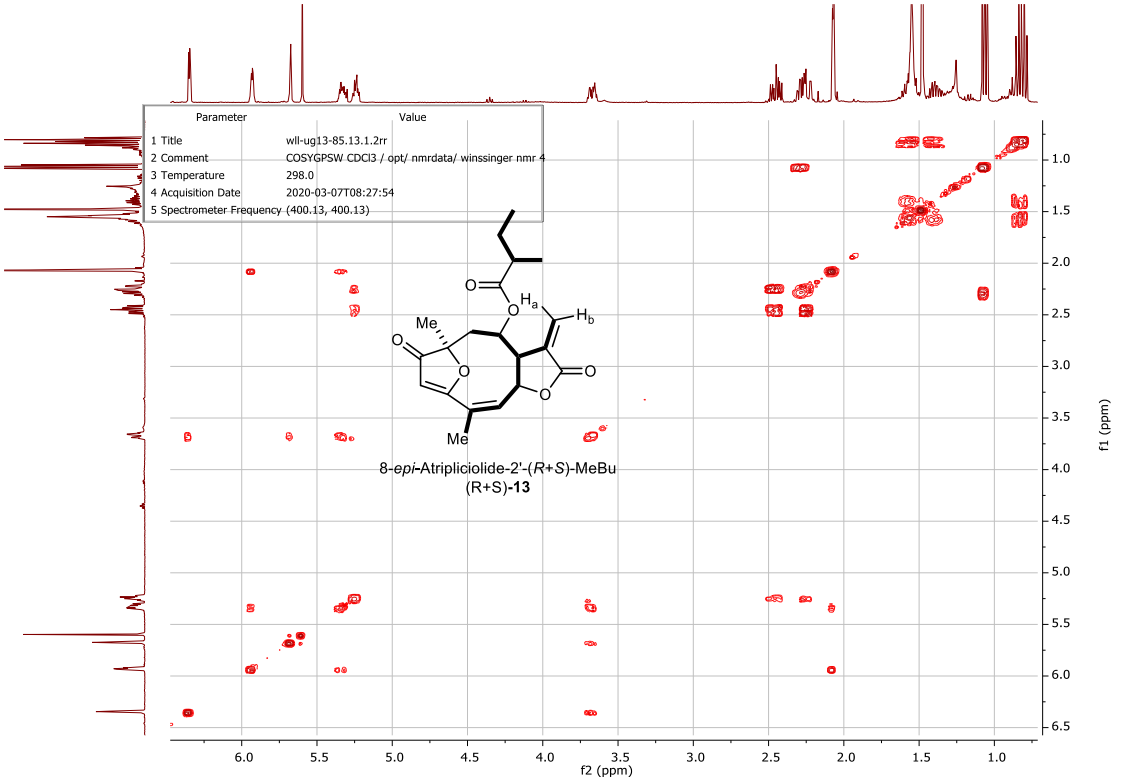

Parameter Value
1 Title wll-ug13-80.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 10
3 Temperature 298.0
4 Acquisition Date 2020-03-03T04:27:36
5 Spectrometer Frequency (400.13, 400.13)
Me
Me
8-epi-Atripliciolide-isovalerate(12)
f2 (ppm)
f1 (ppm)

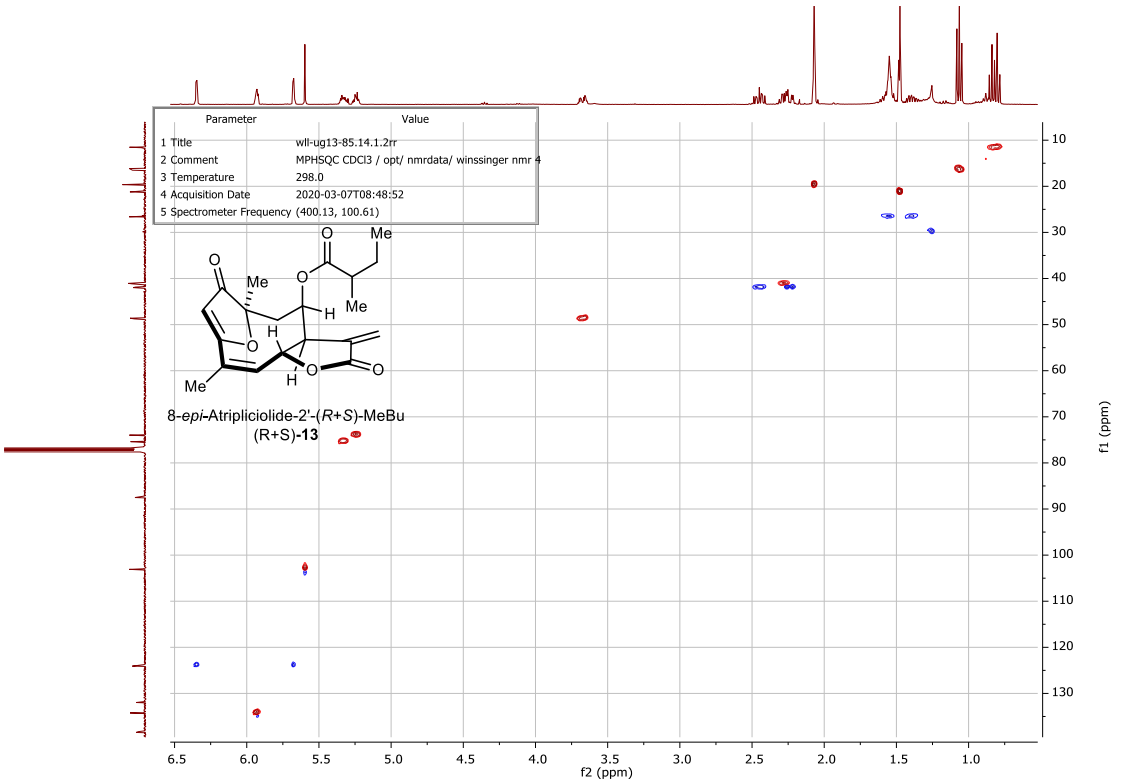


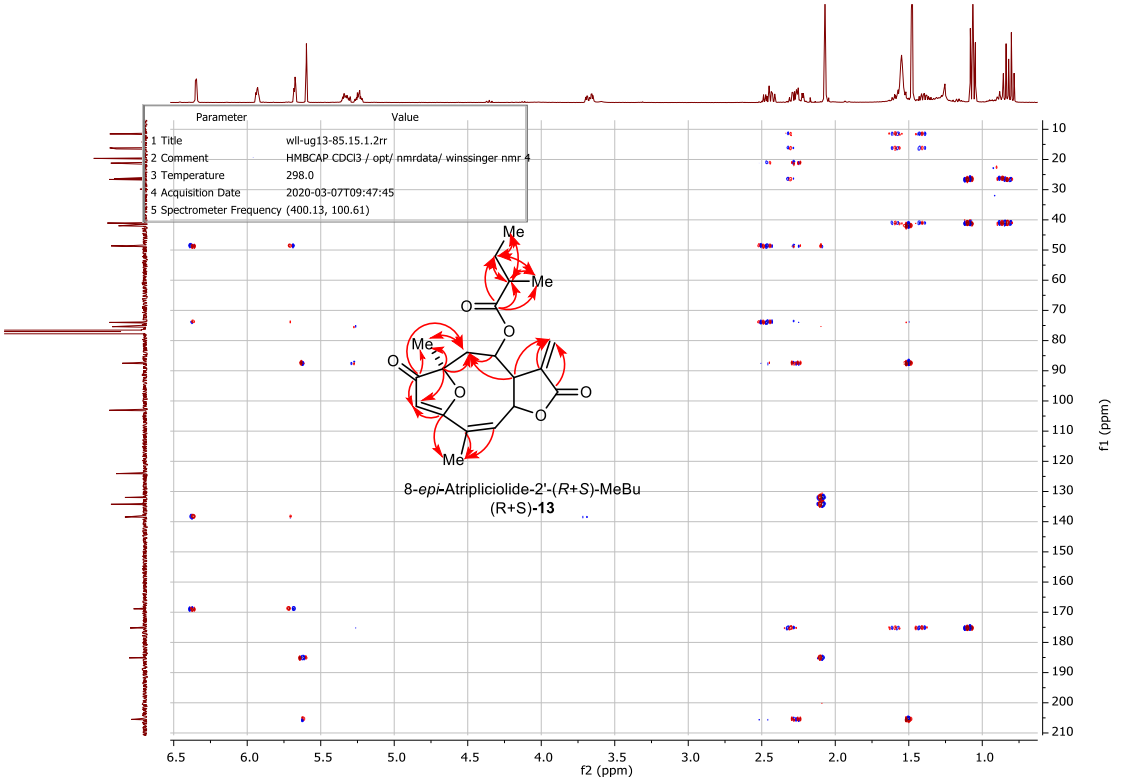
8-*epi*-Atripliciolide-2'-(*R*+*S*)-MeBu
(R+S)-**13**

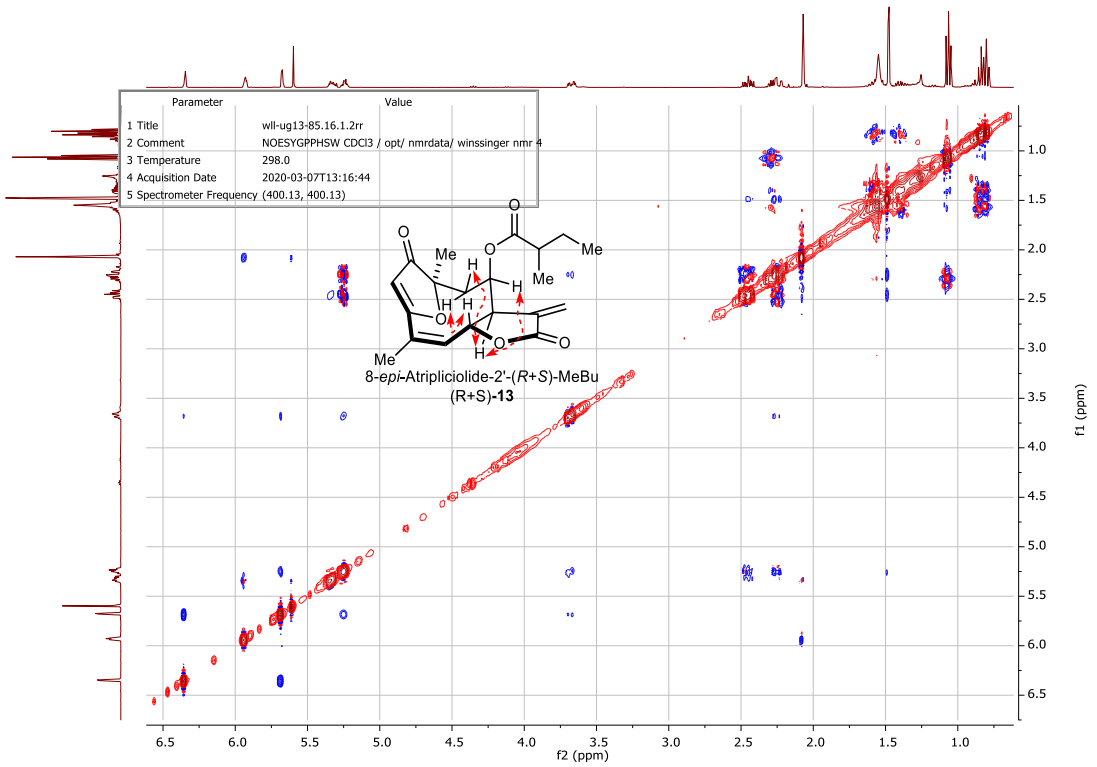


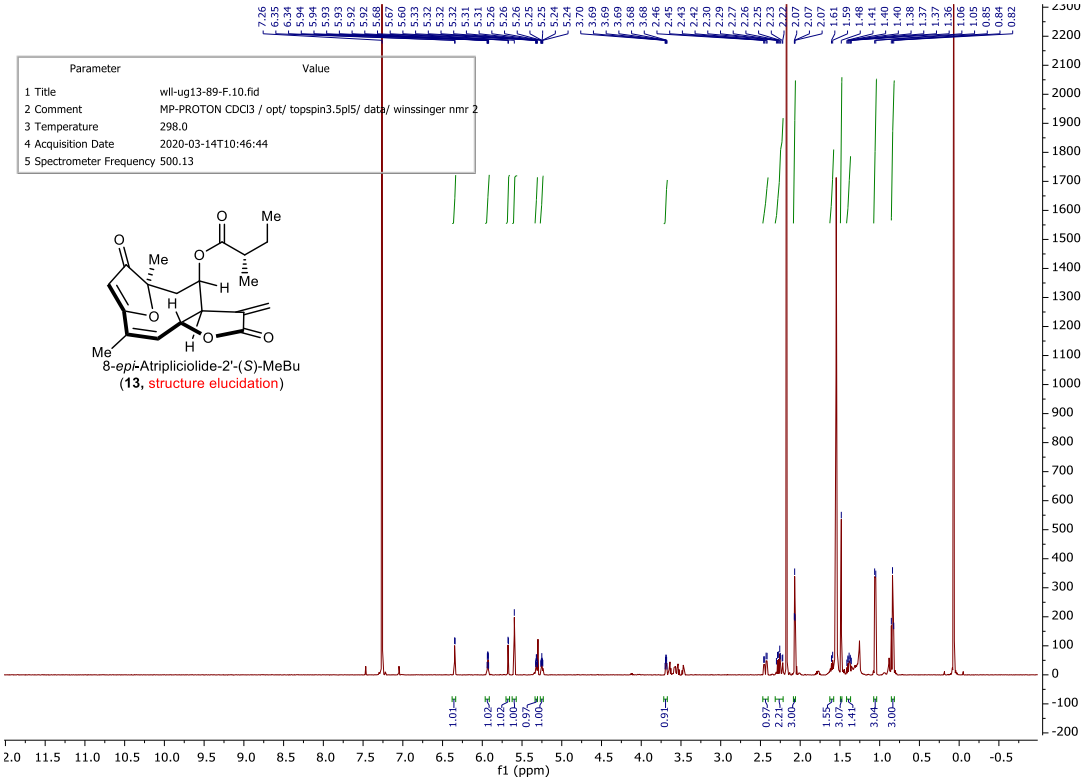
8-*epi*-Atripliciolide-2'-(*R*+*S*)-MeBu
(R+S)-**13**


Parameter Value
1 Title wll-ug13-85.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 4
3 Temperature 298.0
4 Acquisition Date 2020-03-07T08:27:54
5 Spectrometer Frequency (400.13, 400.13)
8-epi-Atripliciolide-2'-(R+S)-MeBu
(R+S)-13
f2 (ppm)
f1 (ppm)

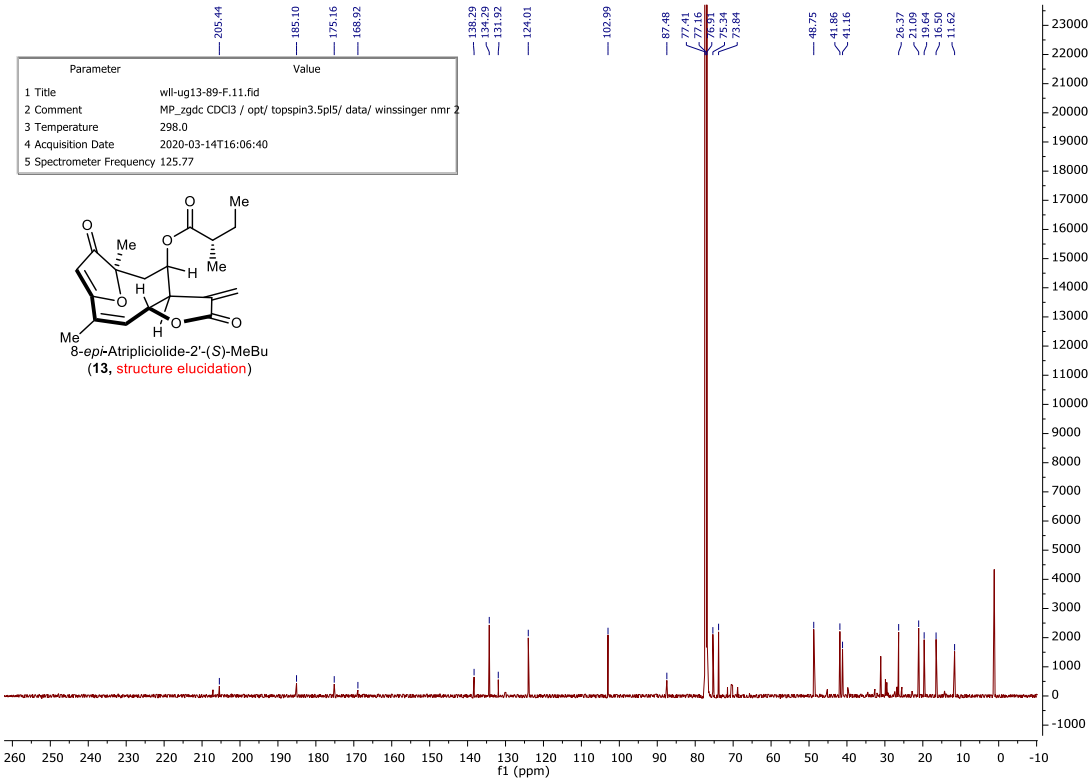

Parameter Value
1 Title wll-ug13-85.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 4
3 Temperature 298.0
4 Acquisition Date 2020-03-07T08:48:52
5 Spectrometer Frequency (400.13, 100.61)
8-epi-Atripliciolide-2'-(R+S)-MeBu
(R+S)-13
f2 (ppm)
f1 (ppm)


Parameter Value
1 Title wll-ug13-85.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 4
3 Temperature 298.0
4 Acquisition Date 2020-03-07T09:47:45
5 Spectrometer Frequency (400.13, 100.61)
Me
Me
O
O
Me
O
O
O
O
Me
8-epi-Atripliciolide-2'-(R+S)-MeBu
(R+S)-13
f2 (ppm)
f1 (ppm)

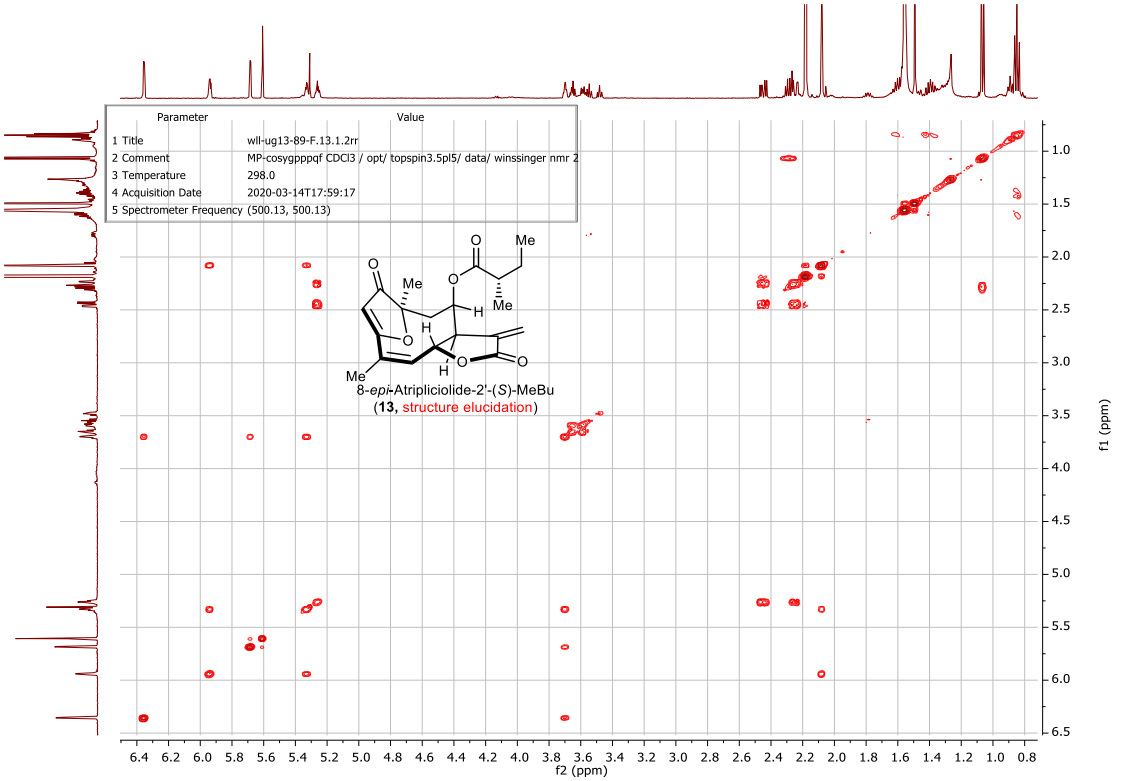

Parameter Value
1 Title wll-ug13-85.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 4
3 Temperature 298.0
4 Acquisition Date 2020-03-07T13:16:44
5 Spectrometer Frequency (400.13, 400.13)
O
O
Me
O
Me
Me
H
H
H
H
O
O
H
Me
8-epi-Atripliciolide-2'-(R+S)-MeBu
(R+S)-13
f2 (ppm)
f1 (ppm)

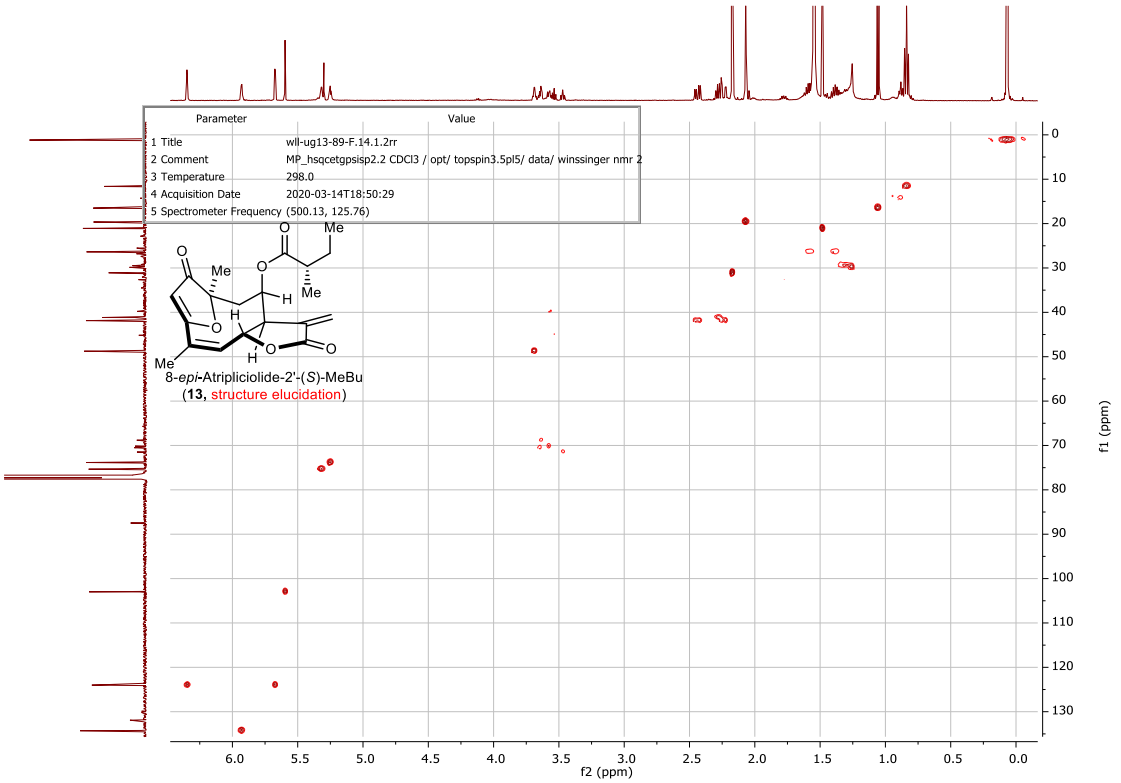


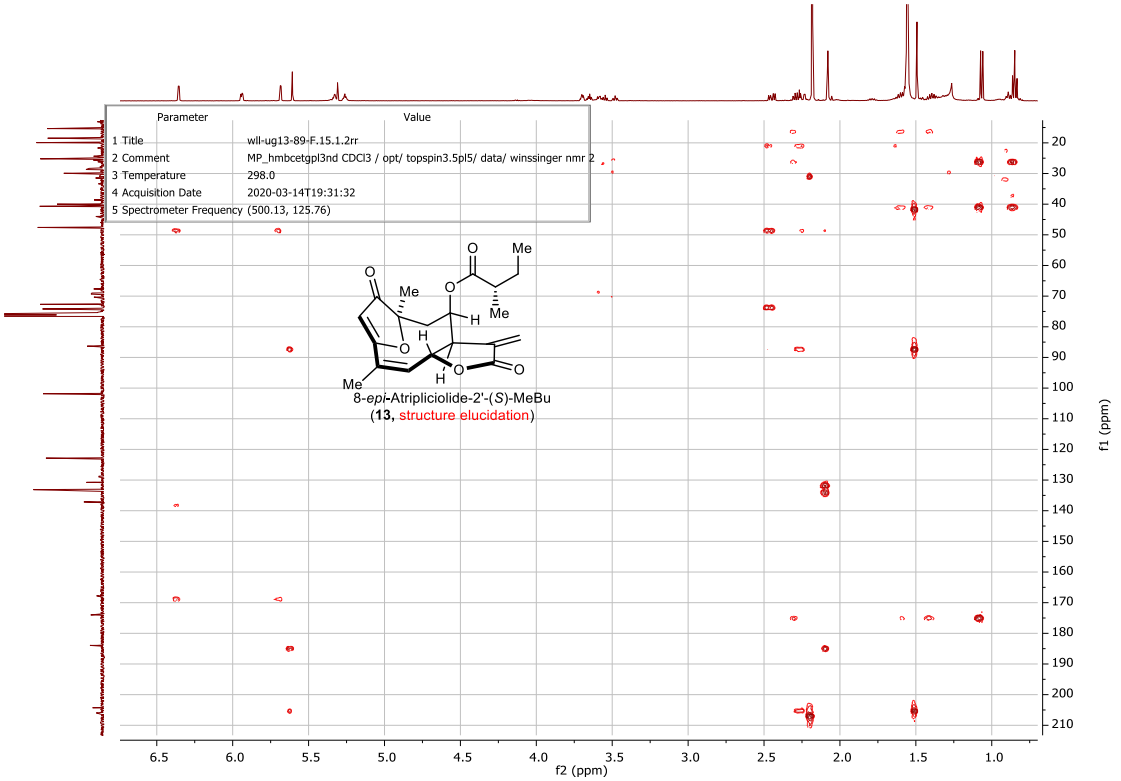
8-*epi*-Atripliciolide-2'-(*S*)-MeBu
(**13**, structure elucidation)

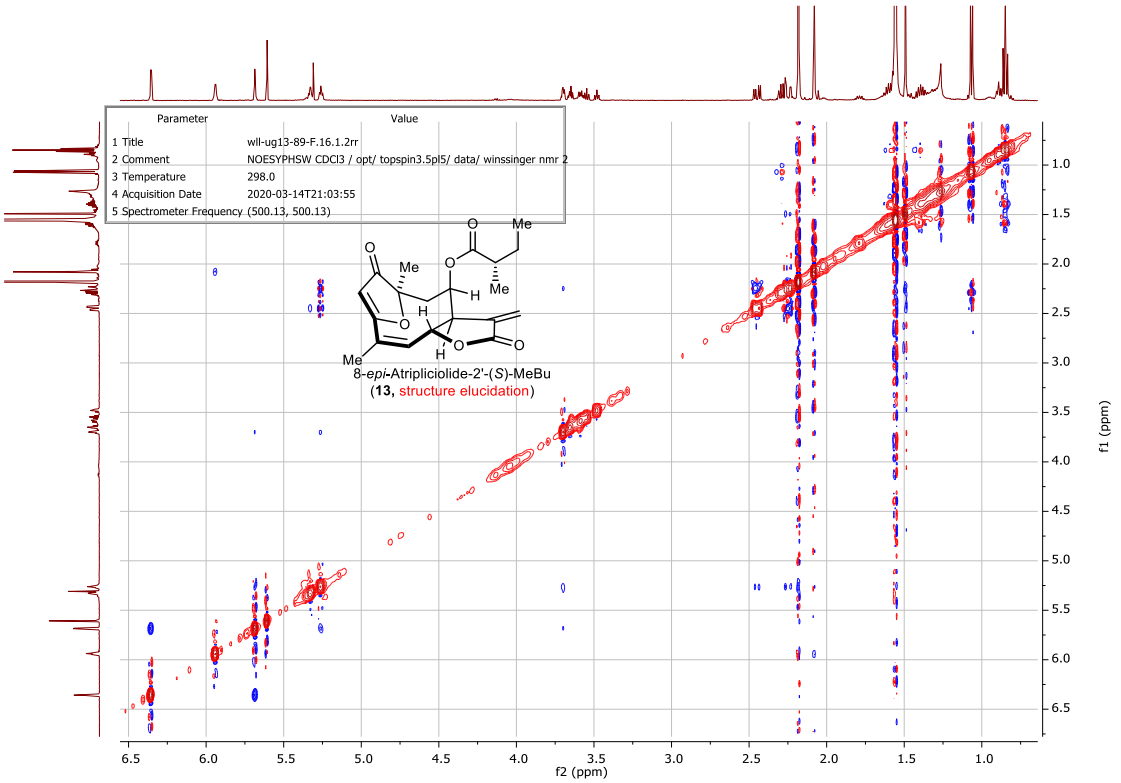


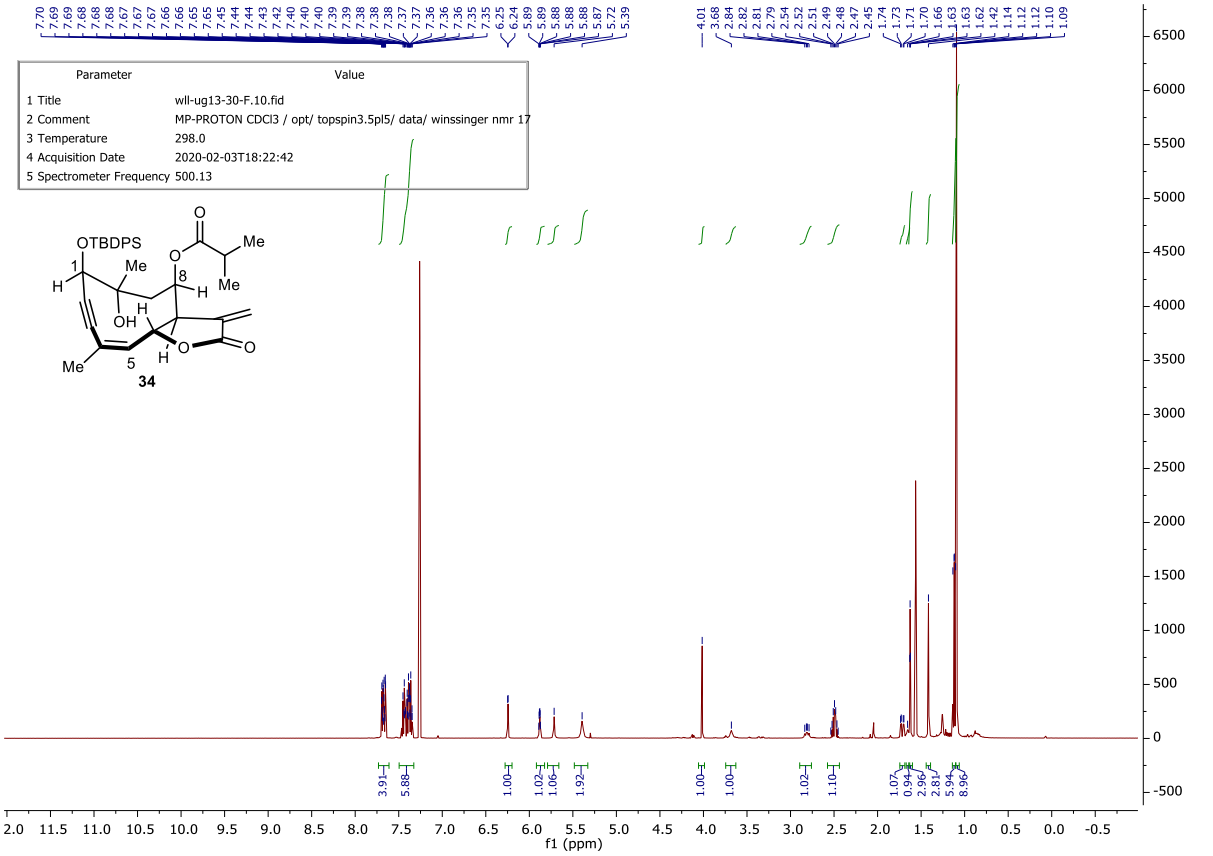
8-*epi*-Atripliciolide-2'-(*S*)-MeBu
(**13**, structure elucidation)

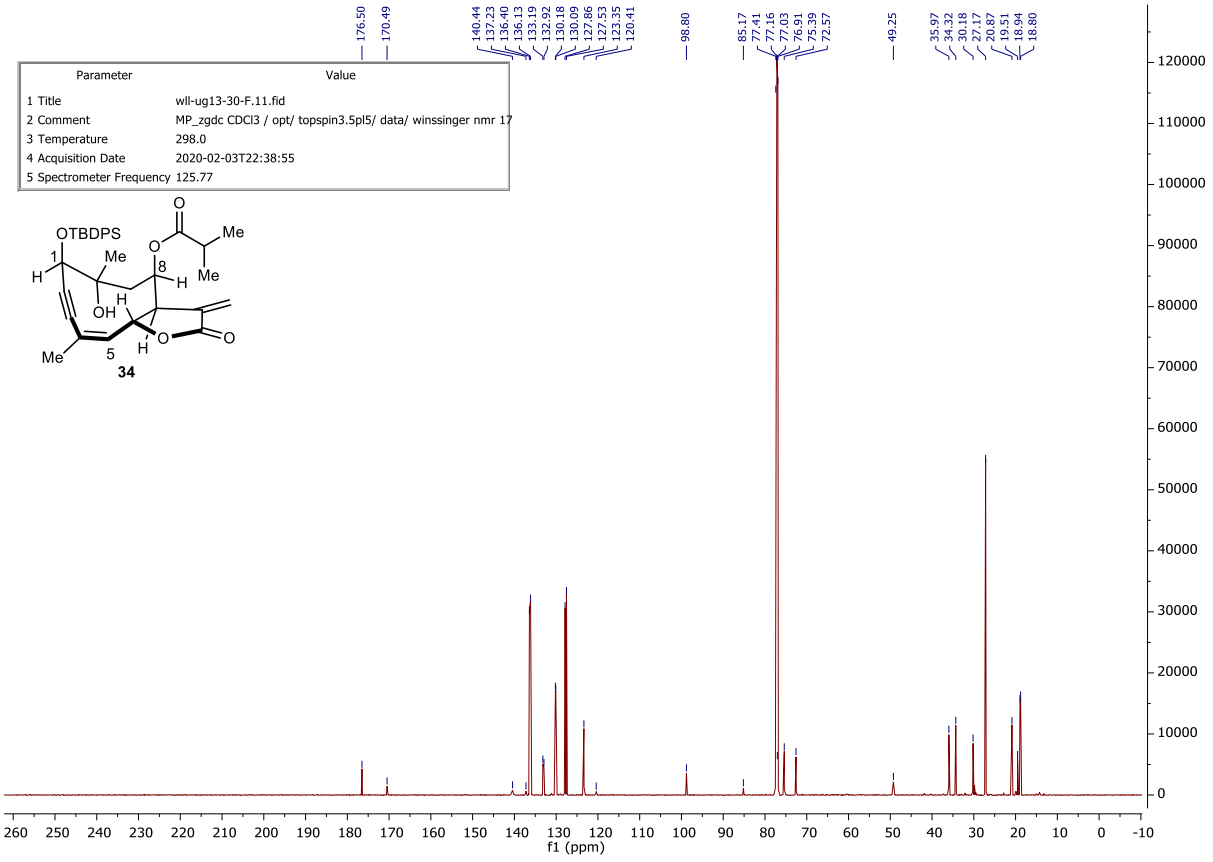

Parameter Value
1 Title wll-ug13-89-F.13.1.2rr
2 Comment MP-cosygpppqf CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.0
4 Acquisition Date 2020-03-14T17:59:17
5 Spectrometer Frequency (500.13, 500.13)
8-epi-Atripliciolide-2'-(S)-MeBu
(13, structure elucidation)
f2 (ppm)
f1 (ppm)

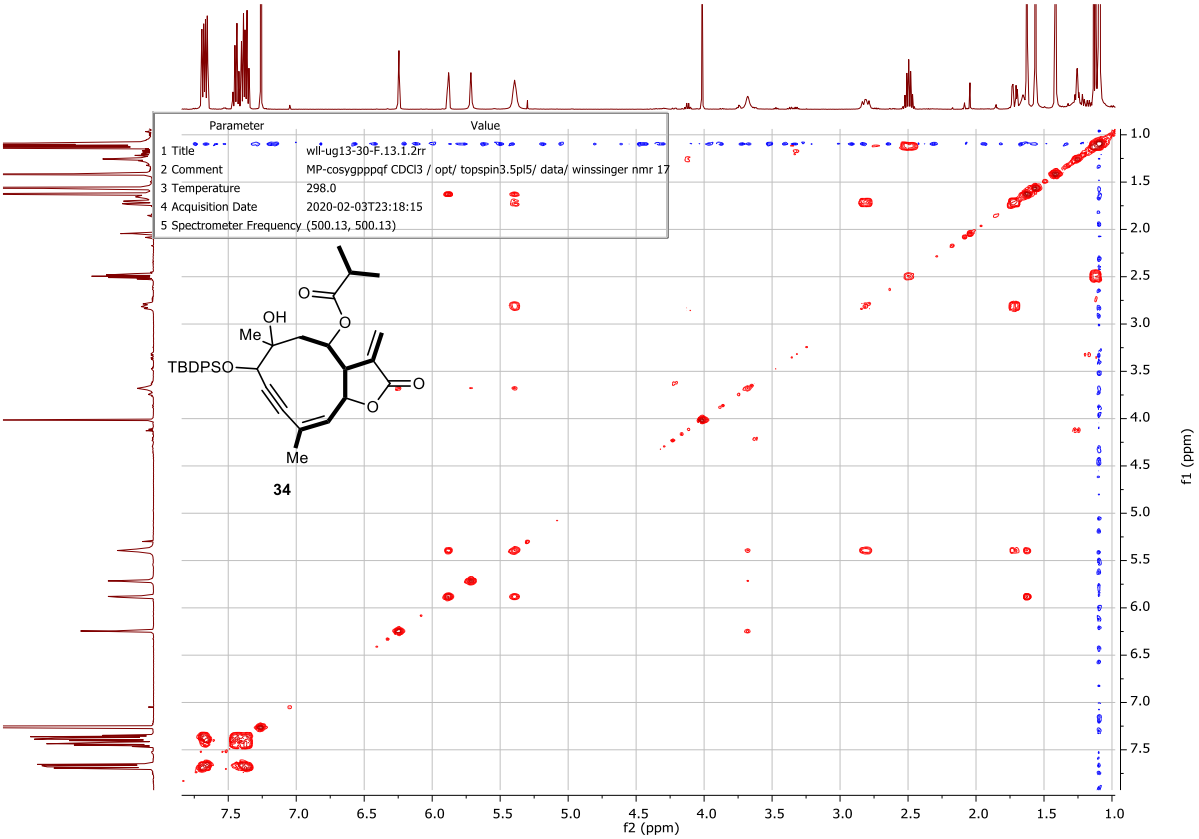

Parameter Value
1 Title wll-ug13-89-F.14.1.2rr
2 Comment MP_hsqcetgpsisp2.2 CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.0
4 Acquisition Date 2020-03-14T18:50:29
5 Spectrometer Frequency (500.13, 125.76)
8-epi-Atripliciolide-2'-(S)-MeBu
(13, structure elucidation)
f2 (ppm)
f1 (ppm)

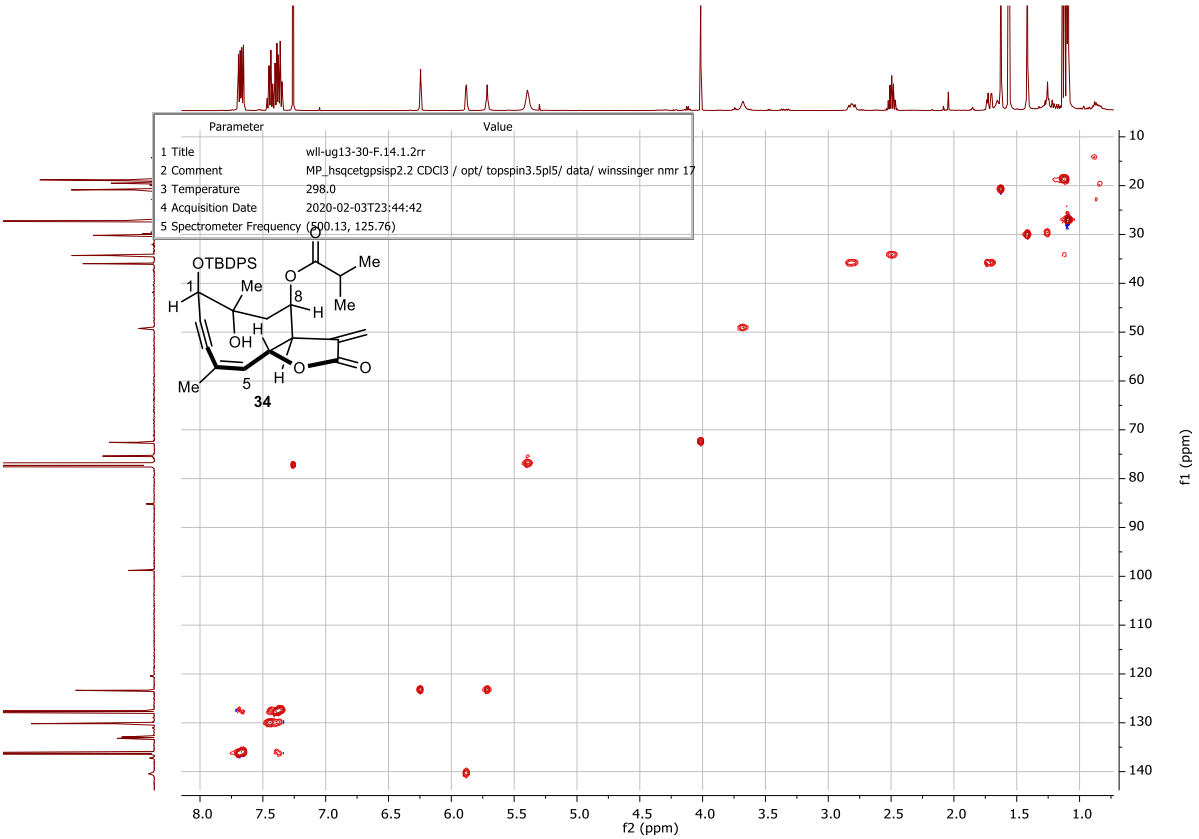

Parameter Value
1 Title wll-ug13-89-F.15.1.2rr
2 Comment MP_hmbcetgpl3nd CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.0
4 Acquisition Date 2020-03-14T19:31:32
5 Spectrometer Frequency (500.13, 125.76)
8-epi-Atripliciolide-2'-(S)-MeBu
(13, structure elucidation)
f2 (ppm)
f1 (ppm)

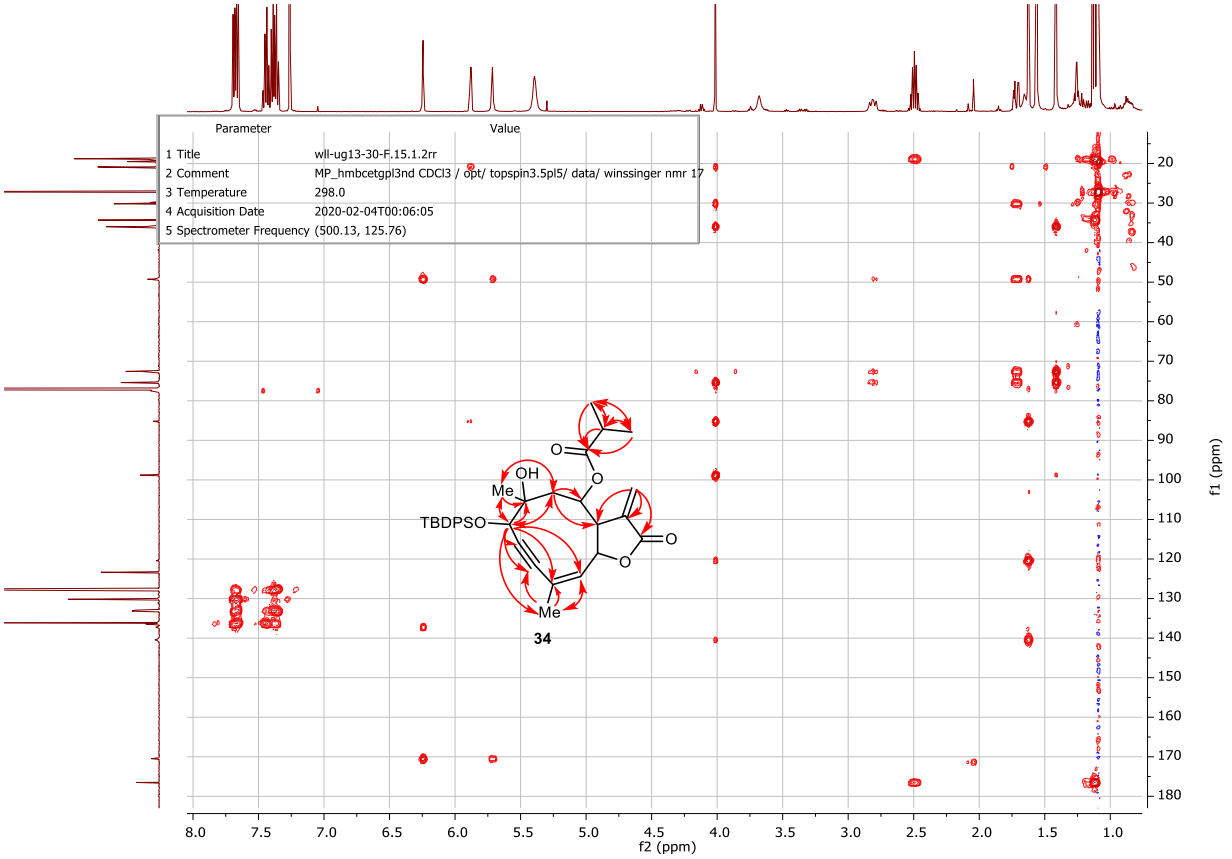

Parameter Value
1 Title wll-ug13-89-F.16.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 2
3 Temperature 298.0
4 Acquisition Date 2020-03-14T21:03:55
5 Spectrometer Frequency (500.13, 500.13)
8-epi-Atripliciolide-2'-(S)-MeBu
(13, structure elucidation)
f2 (ppm)
f1 (ppm)

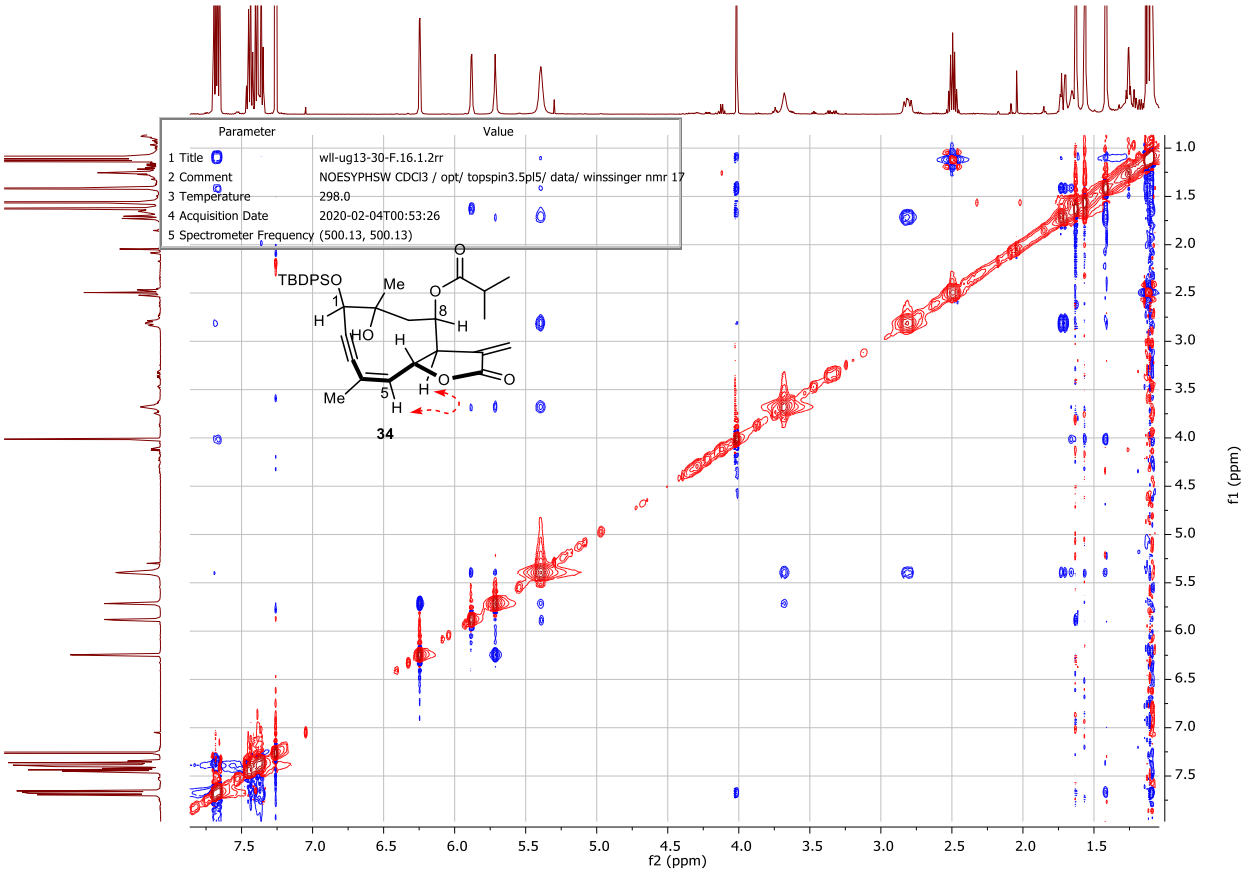

Parameter Value
1 Title wll-ug13-30-F.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 17
3 Temperature 298.0
4 Acquisition Date 2020-02-03T18:22:42
5 Spectrometer Frequency 500.13
OTBDPS
Me
Me
Me
OH
Me
34
f1 (ppm)

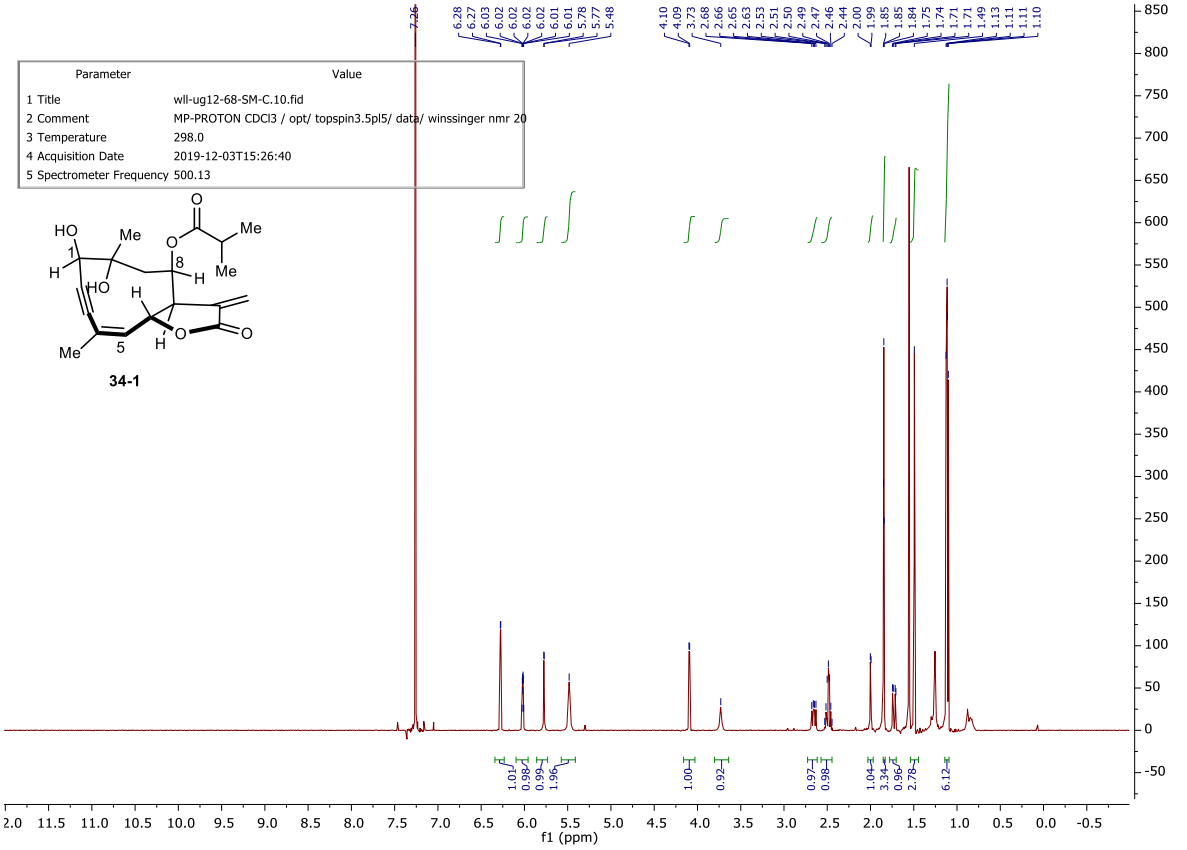

Parameter Value
1 Title wll-ug13-30-F.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 17
3 Temperature 298.0
4 Acquisition Date 2020-02-03T22:38:55
5 Spectrometer Frequency 125.77
OTBDPS
Me
Me
Me
OH
Me
34
f1 (ppm)

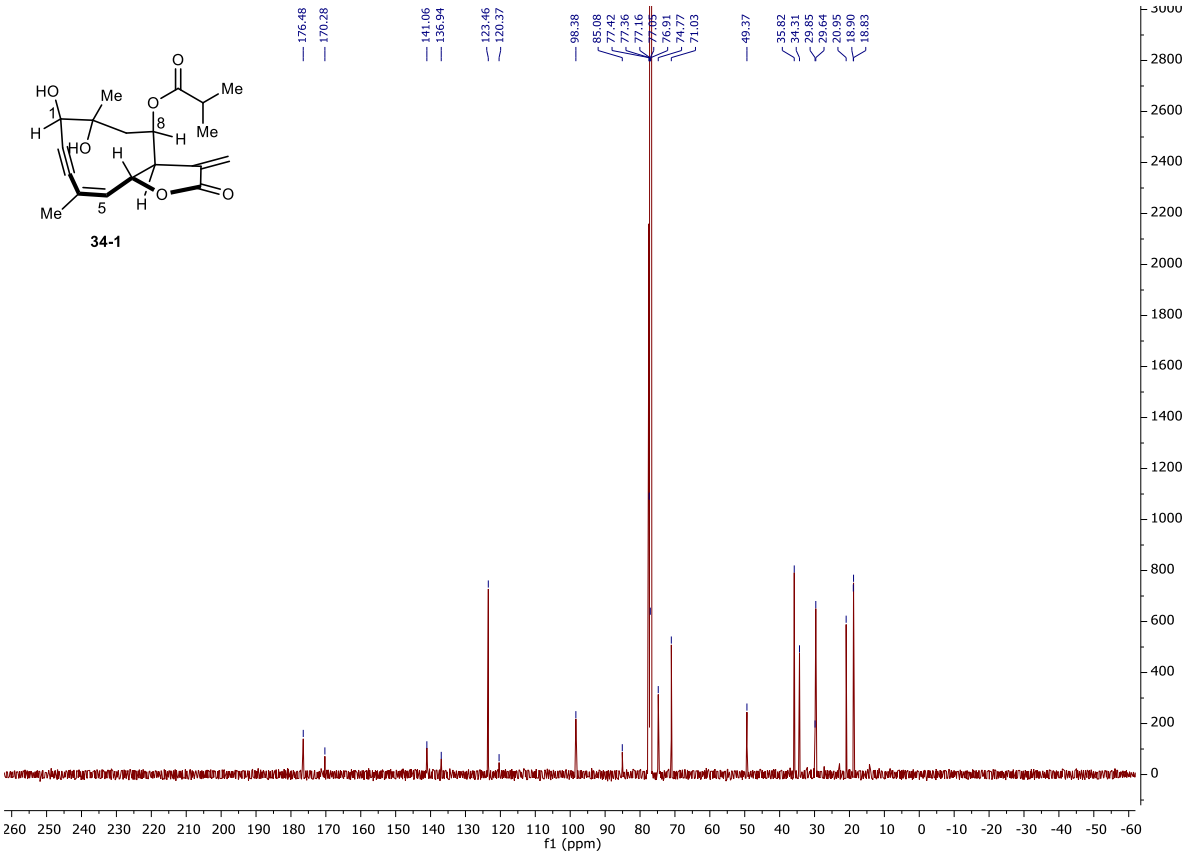

Parameter Value
1 Title wll-ug13-30-F.13.1.2rr
2 Comment MP-cosygpppqf CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 17
3 Temperature 298.0
4 Acquisition Date 2020-02-03T23:18:15
5 Spectrometer Frequency (500.13, 500.13)
OH
Me
TBDPSO
O
O
O
O
Me
34
f2 (ppm)
f1 (ppm)

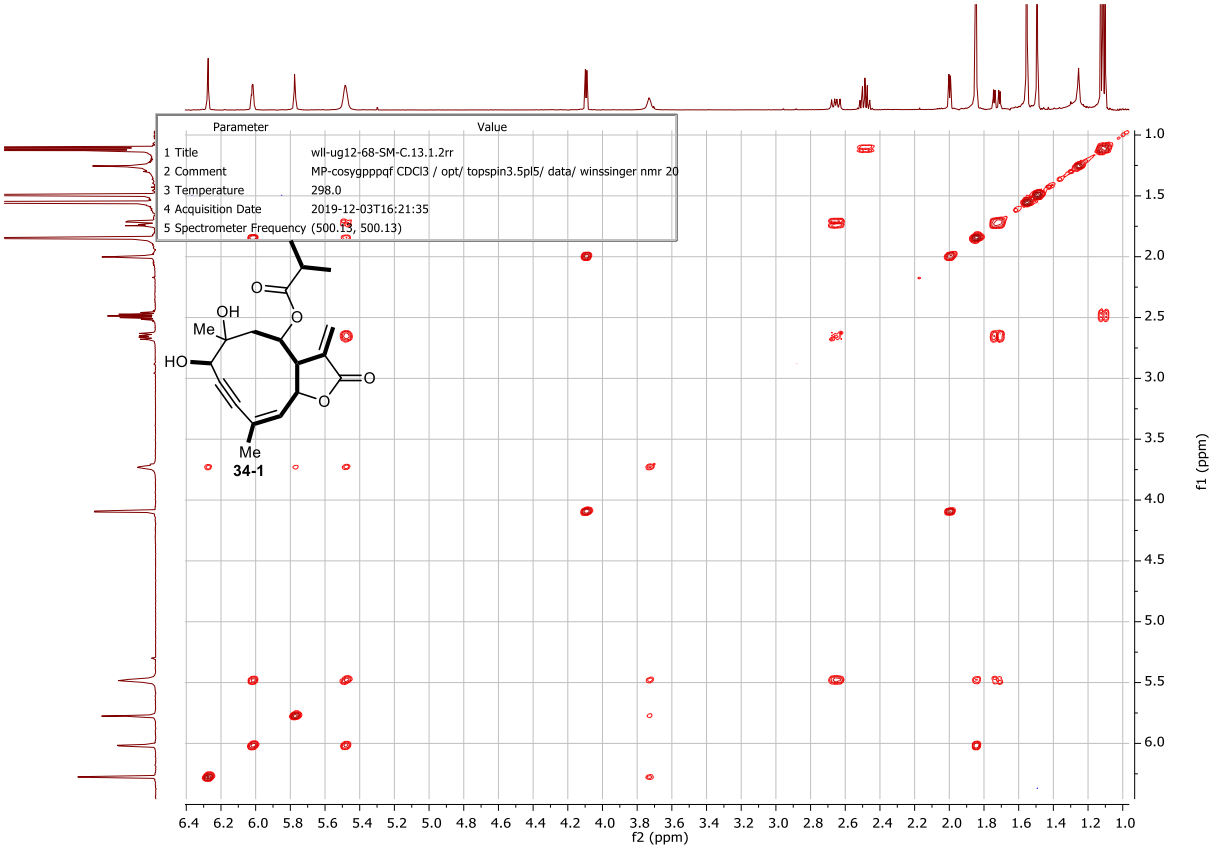

Parameter Value
1 Title wll-ug13-30-F.14.1.2rr
2 Comment MP_hsqcetgpsisp2.2 CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 17
3 Temperature 298.0
4 Acquisition Date 2020-02-03T23:44:42
5 Spectrometer Frequency (500.13, 125.76)
OTBDPS
Me
Me
Me
H
H
H
OH
Me
O
O
O
H
1
5
8
34
f2 (ppm)
f1 (ppm)

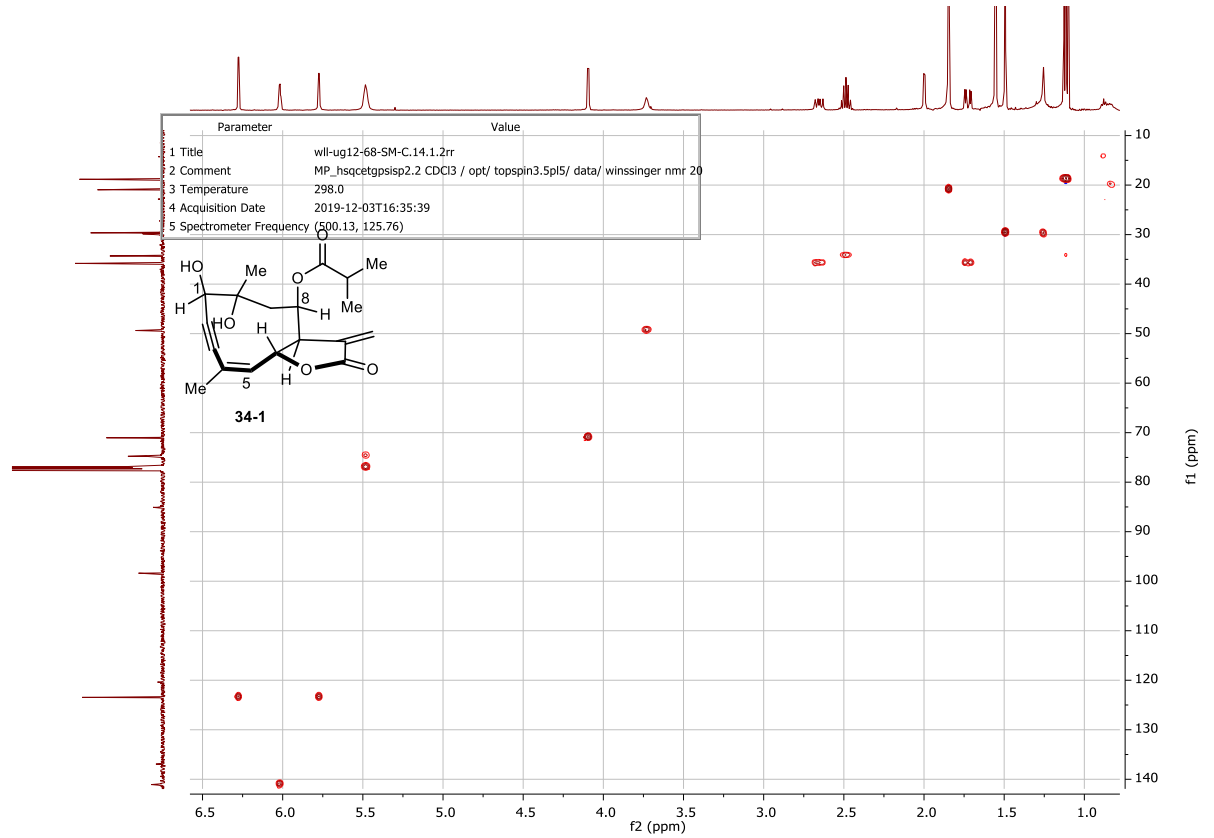

Parameter Value
1 Title wll-ug13-30-F.15.1.2rr
2 Comment MP_hmbcetgpl3nd CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 17
3 Temperature 298.0
4 Acquisition Date 2020-02-04T00:06:05
5 Spectrometer Frequency (500.13, 125.76)
OH
Me
TBDPSO
O
Me
34
f2 (ppm)
f1 (ppm)

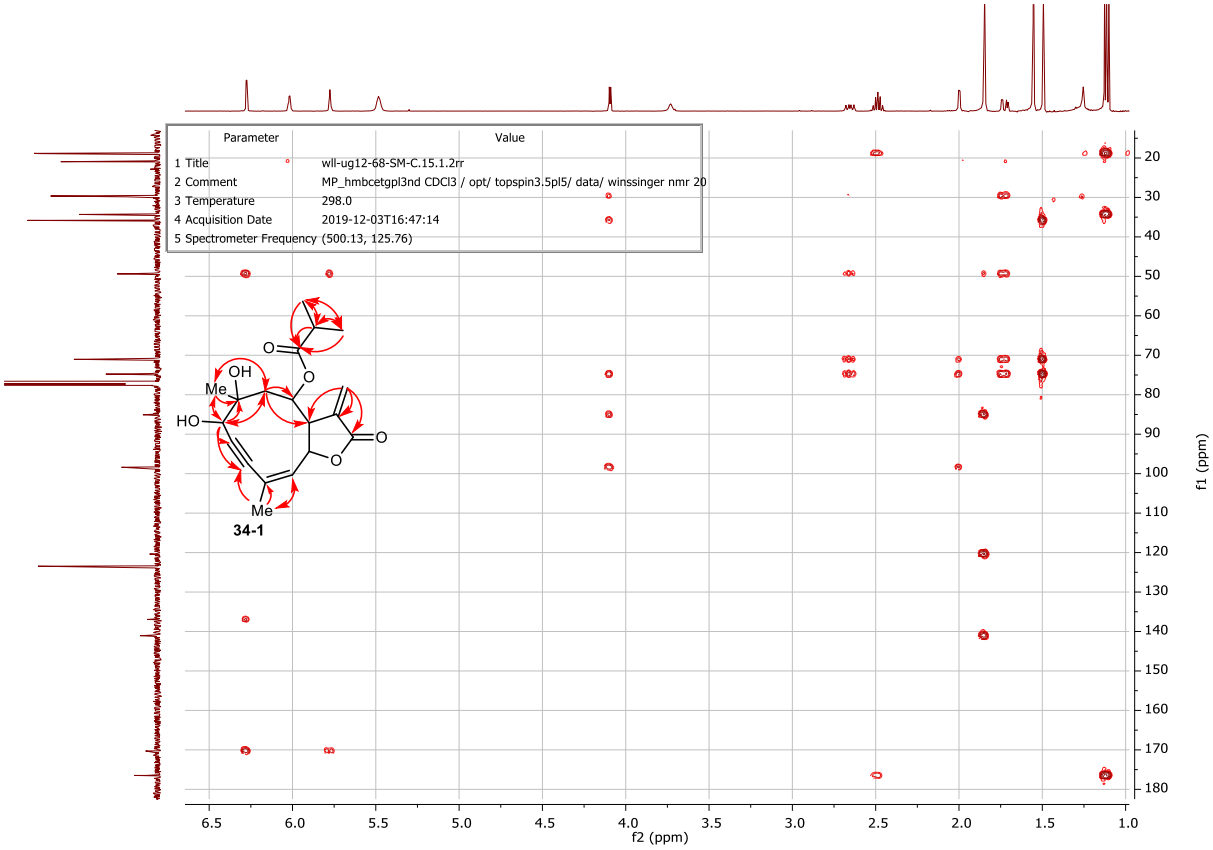

Parameter Value
1 Title wll-ug13-30-F.16.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 17
3 Temperature 298.0
4 Acquisition Date 2020-02-04T00:53:26
5 Spectrometer Frequency (500.13, 500.13)
TBDPSO
Me
HO
Me
34
f2 (ppm)
f1 (ppm)

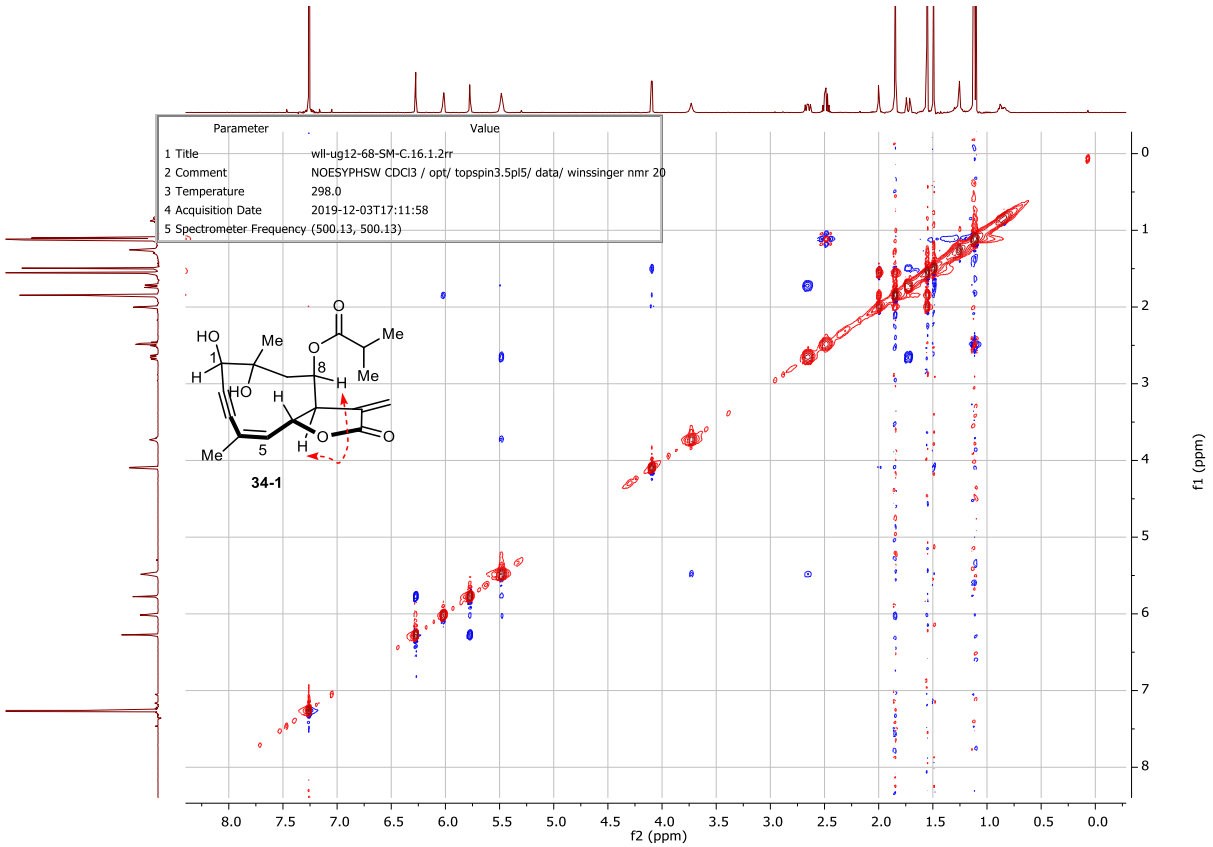

Parameter Value
1 Title wll-ug12-68-SM-C.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 20
3 Temperature 298.0
4 Acquisition Date 2019-12-03T15:26:40
5 Spectrometer Frequency 500.13
34-1
f1 (ppm)

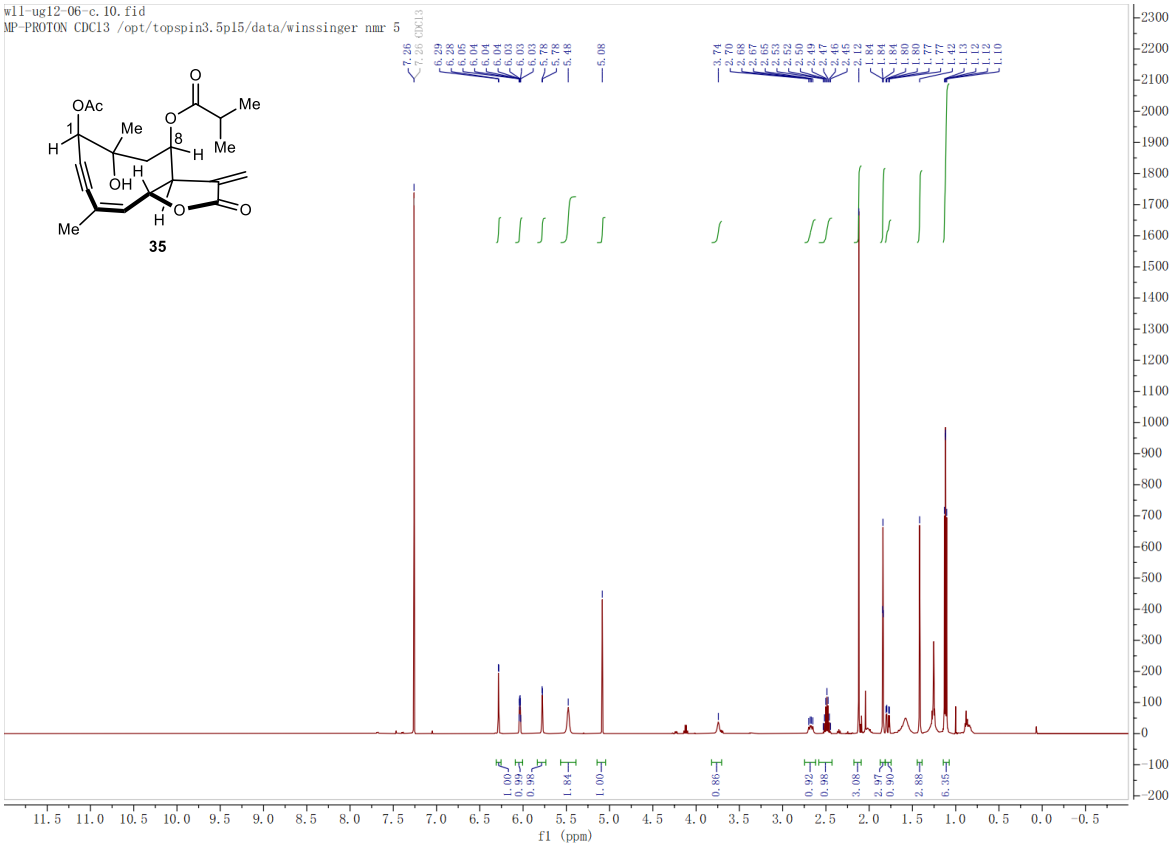

34-1
f1 (ppm)

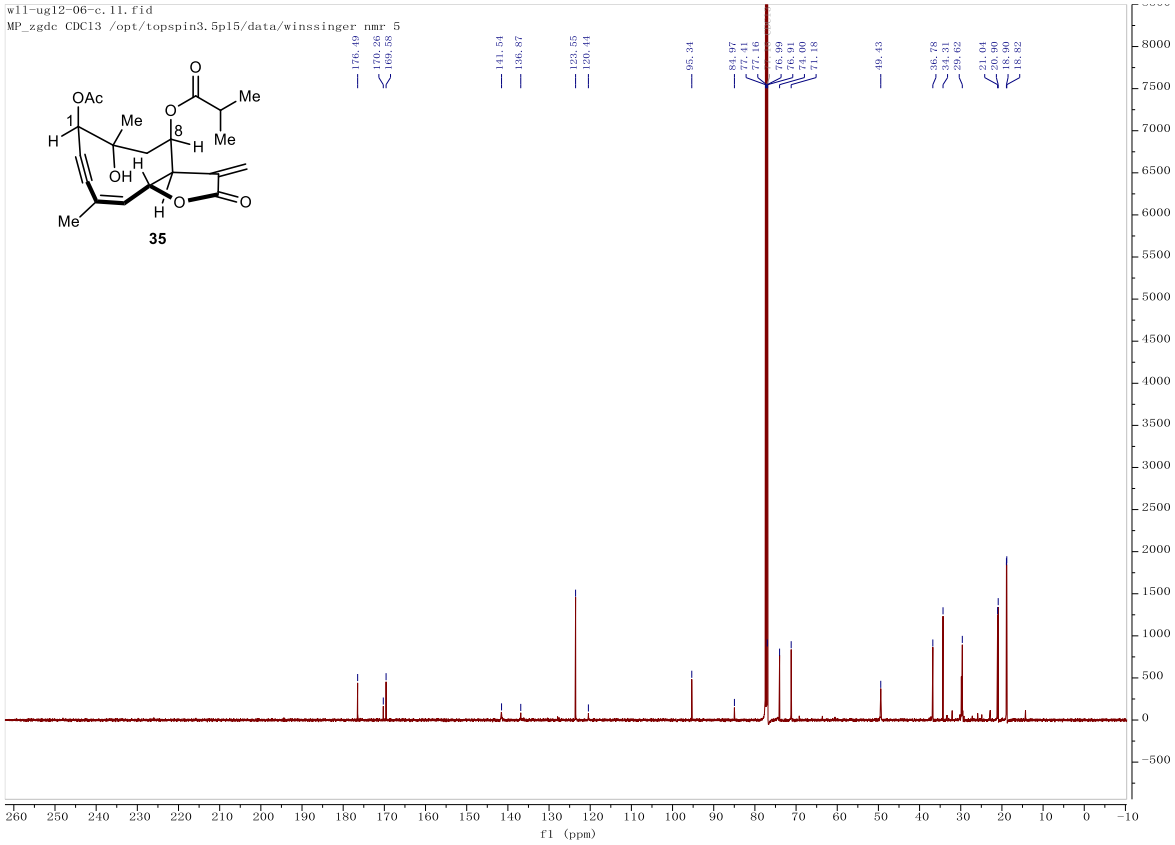

Parameter Value
1 Title wll-ug12-68-SM-C.13.1.2rr
2 Comment MP-cosygpppqf CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 20
3 Temperature 298.0
4 Acquisition Date 2019-12-03T16:21:35
5 Spectrometer Frequency (500.13, 500.13)
OH
Me
HO
O
O
O
O
Me
34-1
f2 (ppm)
f1 (ppm)

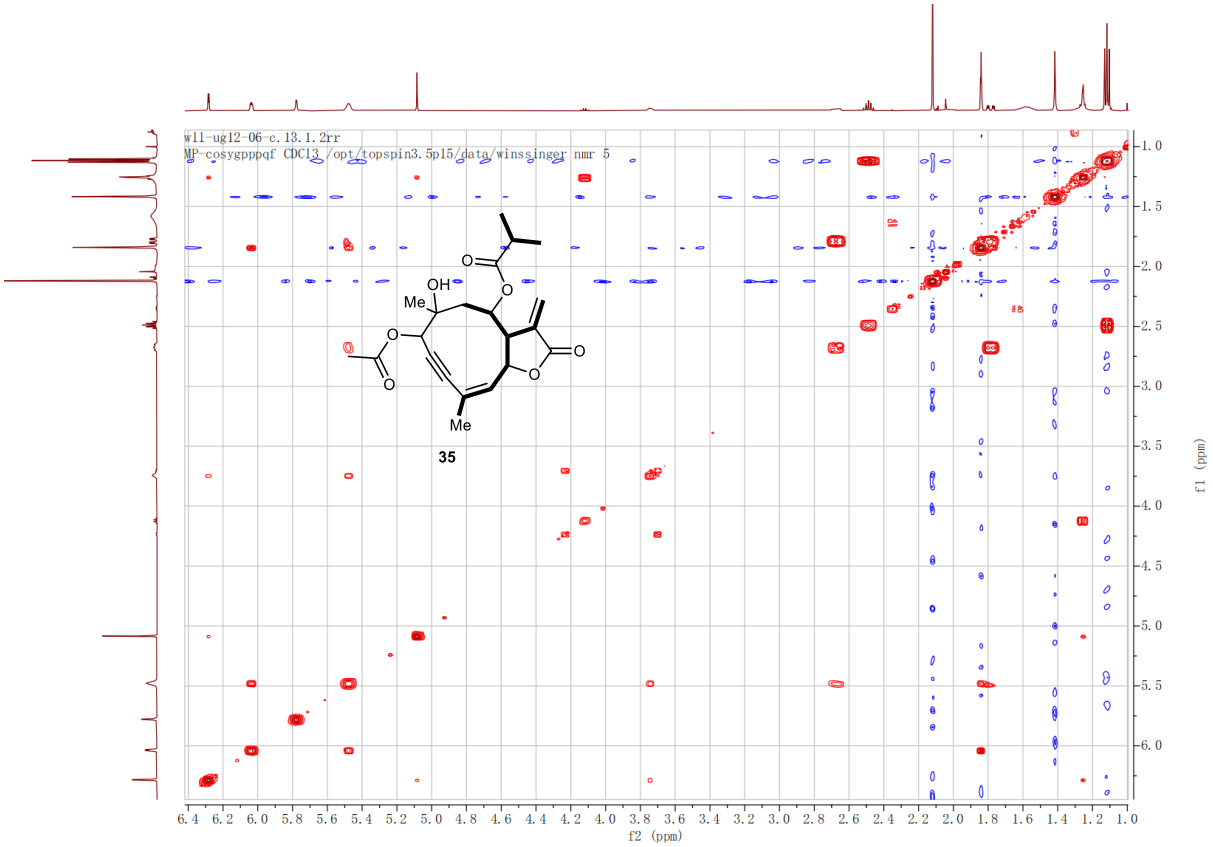

Parameter Value
1 Title wll-ug12-68-SM-C.14.1.2rr
2 Comment MP_hsqcetgpsisp2.2 CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 20
3 Temperature 298.0
4 Acquisition Date 2019-12-03T16:35:39
5 Spectrometer Frequency (500.13, 125.76)
HO
Me
O
Me
1
8
H
H
HO
H
Me
5
H
O
O
34-1
f2 (ppm)
f1 (ppm)

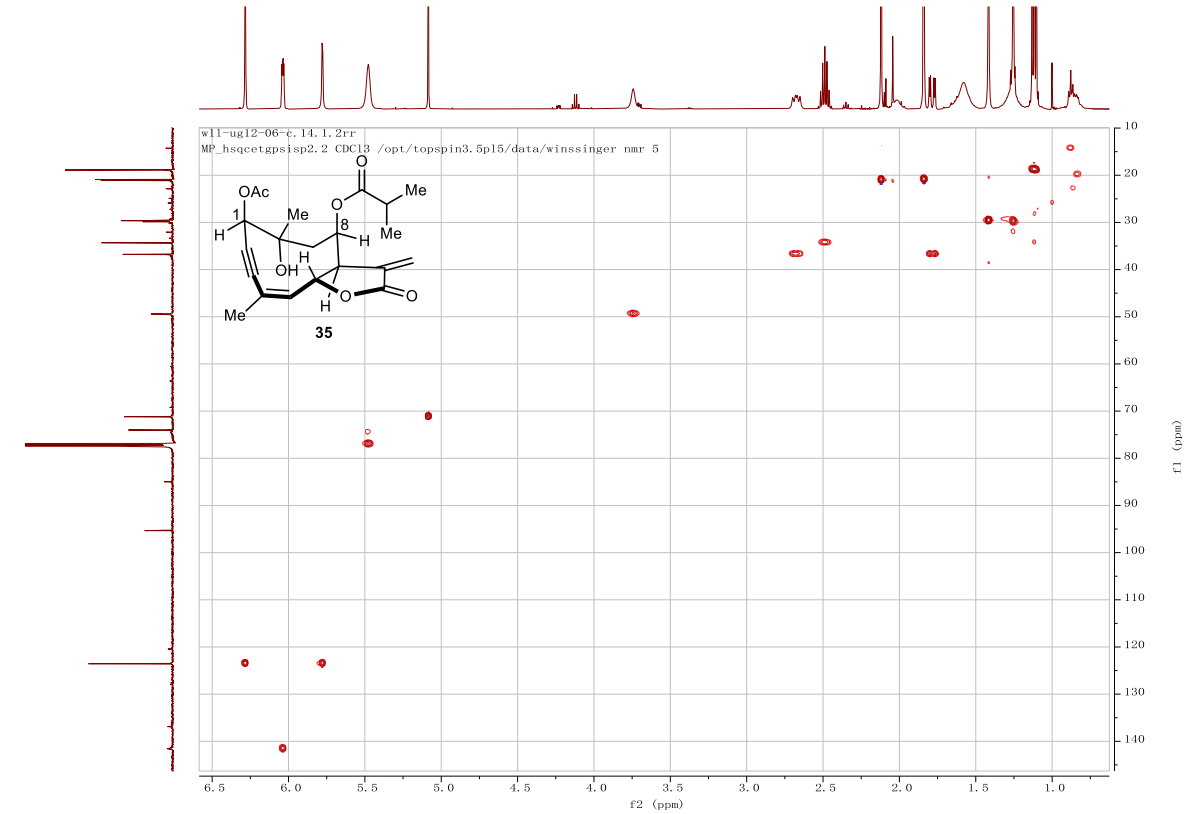

Parameter Value
1 Title wll-ug12-68-SM-C.15.1.2rr
2 Comment MP_hmbcetgpl3nd CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 20
3 Temperature 298.0
4 Acquisition Date 2019-12-03T16:47:14
5 Spectrometer Frequency (500.13, 125.76)
OH
Me
HO
O
O
O
O
Me
34-1
f2 (ppm)
f1 (ppm)

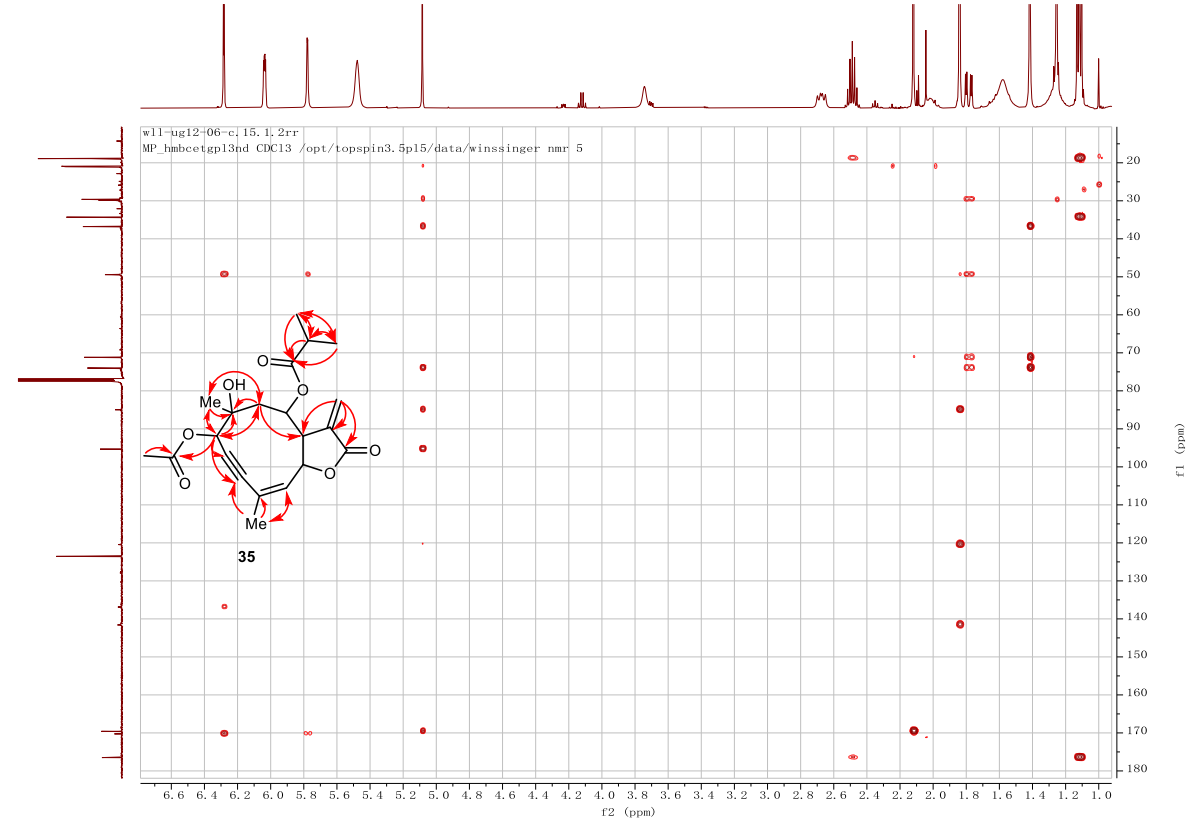

Parameter Value
1 Title wll-ug12-68-SM-C.16.1.2rr
2 Comment NOESYPHSW CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 20
3 Temperature 298.0
4 Acquisition Date 2019-12-03T17:11:58
5 Spectrometer Frequency (500.13, 500.13)
HO
Me
1
H
HO
O
8
H
Me
H
Me
5
H
O
O
34-1
f2 (ppm)
f1 (ppm)

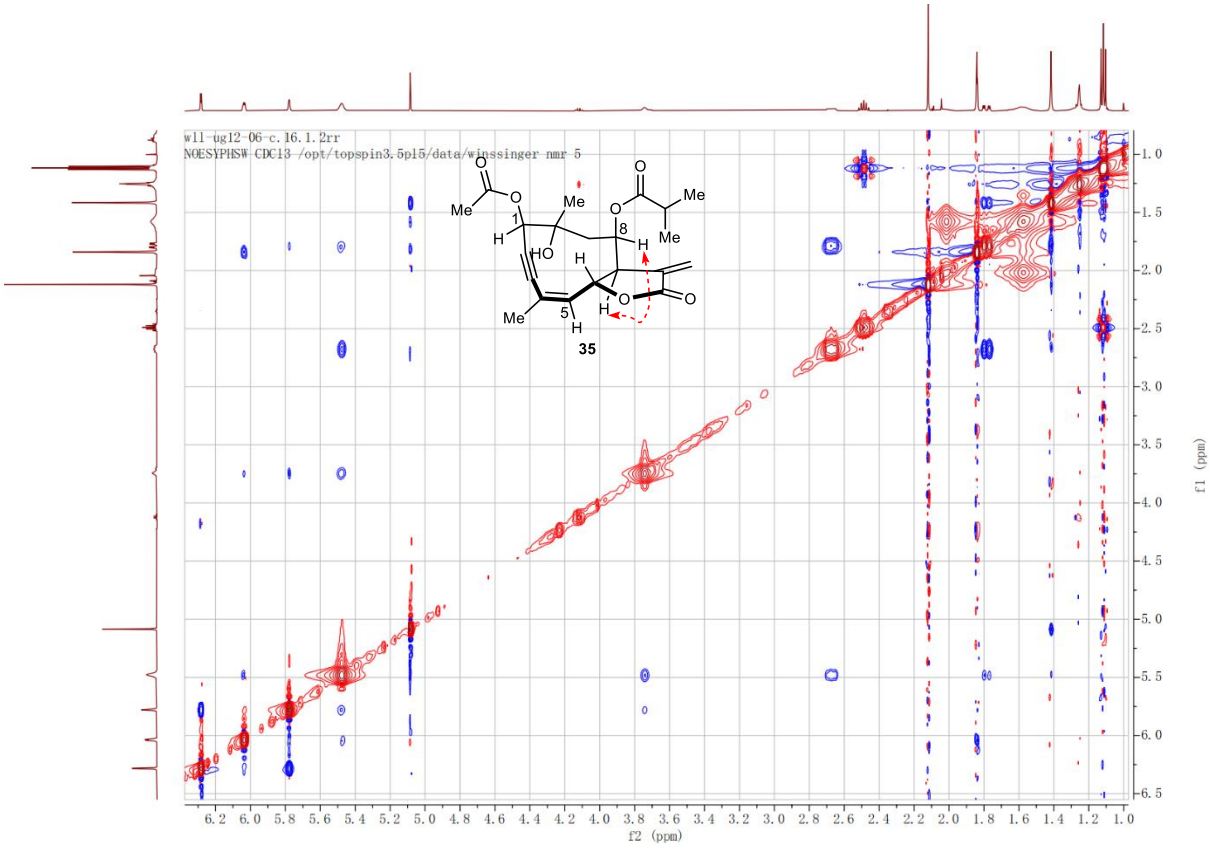

wll-ug12-06-c.10.fid
MP-PROTON CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 5
OAc
Me
Me
Me
OH
Me
35
f1 (ppm)

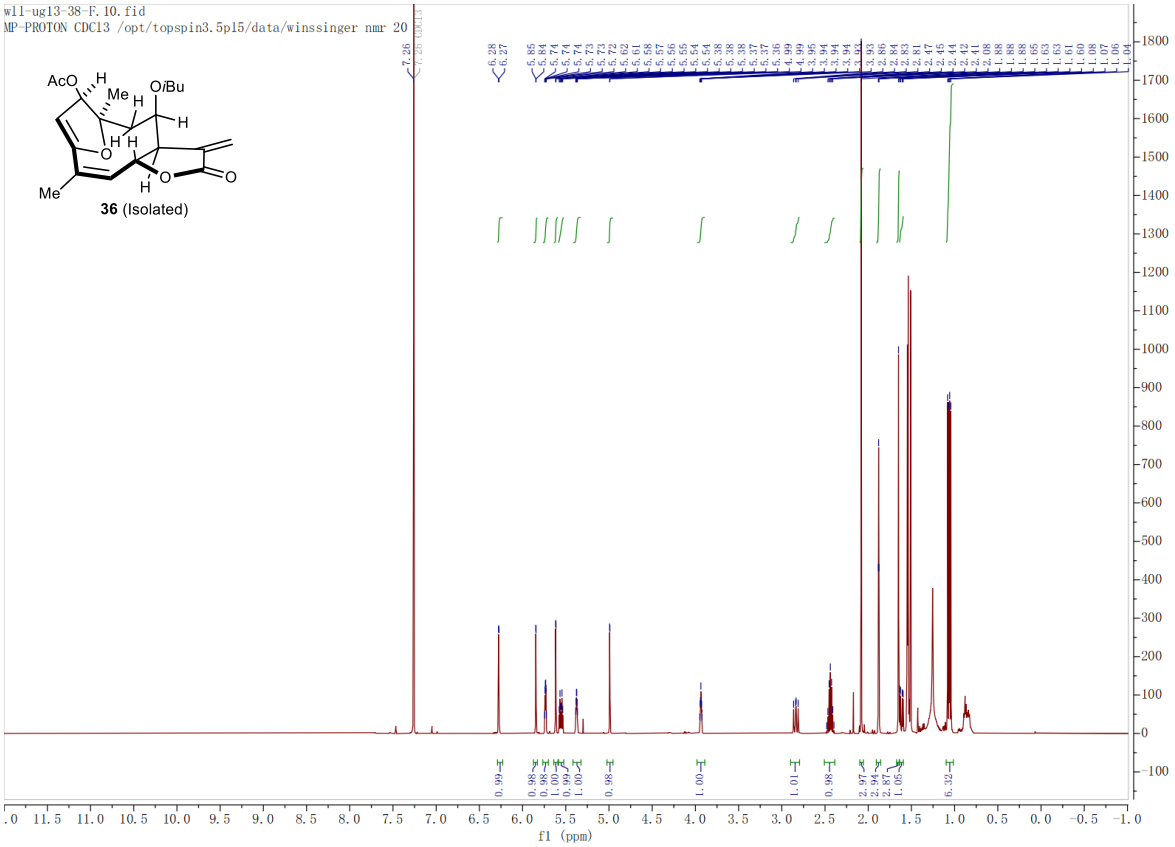

wll-ug12-06-c.11.fid
MP_zgdc CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 5
OAc
Me
Me
Me
OH
Me
35
f1 (ppm)

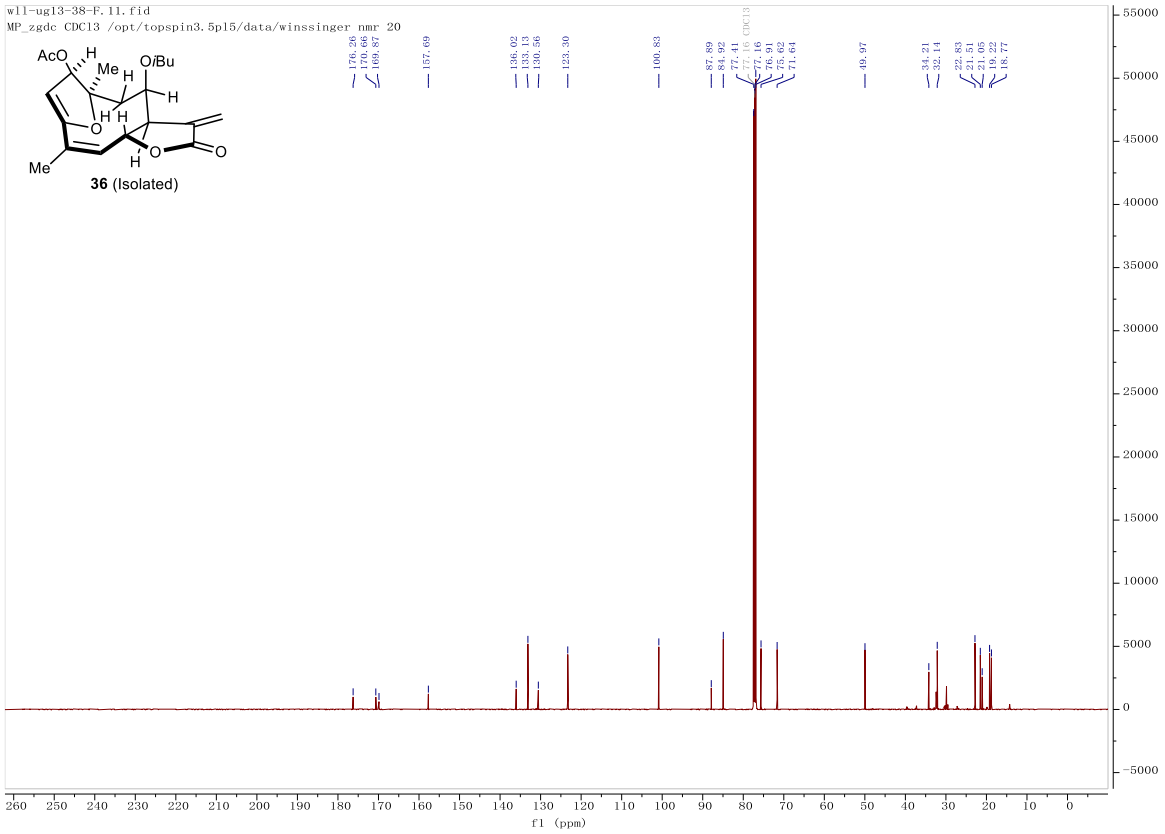

wll-ugl2-06-c.13.1.2rr
MP-cosygpppqf CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 5
OH
Me
O
O
O
O
O
O
Me
35
f2 (ppm)
f1 (ppm)

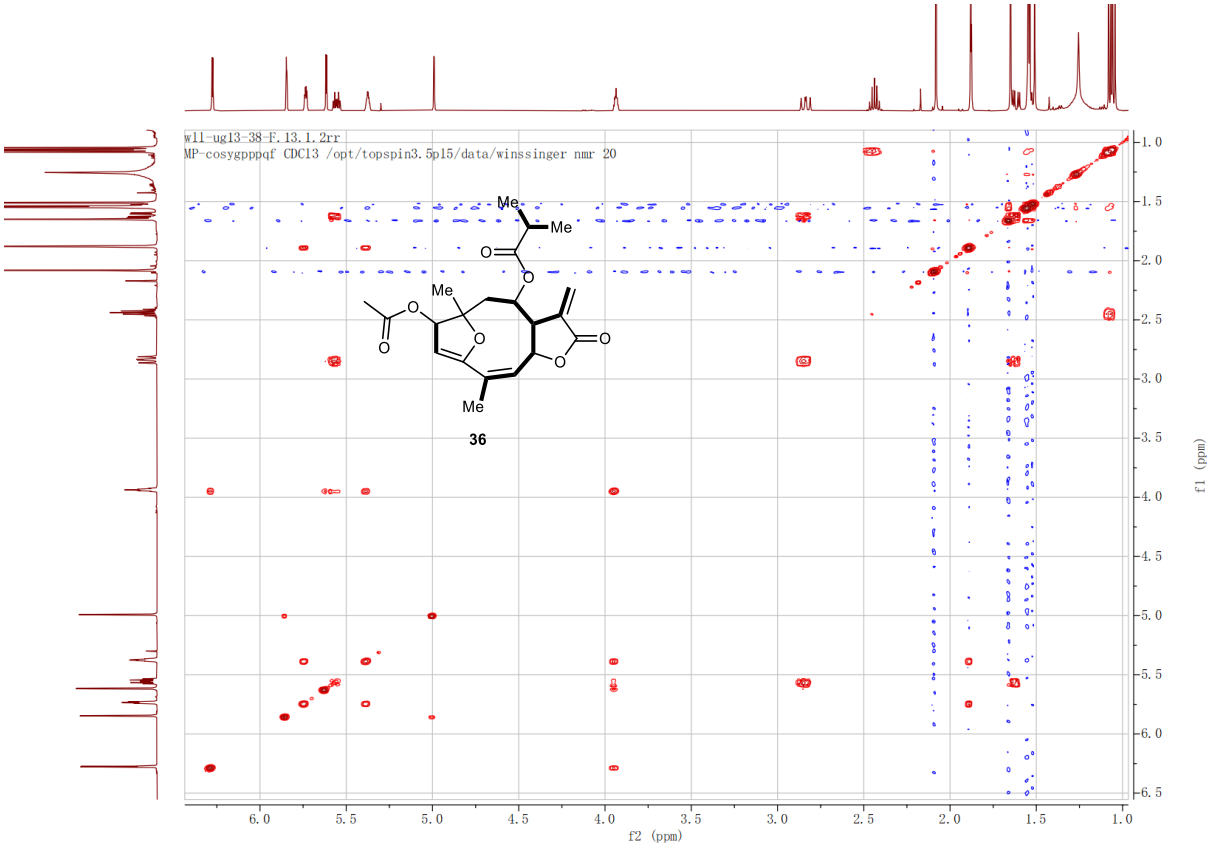

wll-ugl2-06-c.14.1.2rr
MP_hsqcetgpsisp2.2 CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 5
OAc
Me
O
Me
1
H
Me
8
H
Me
H
OH
H
O
O
Me
35
f2 (ppm)
f1 (ppm)

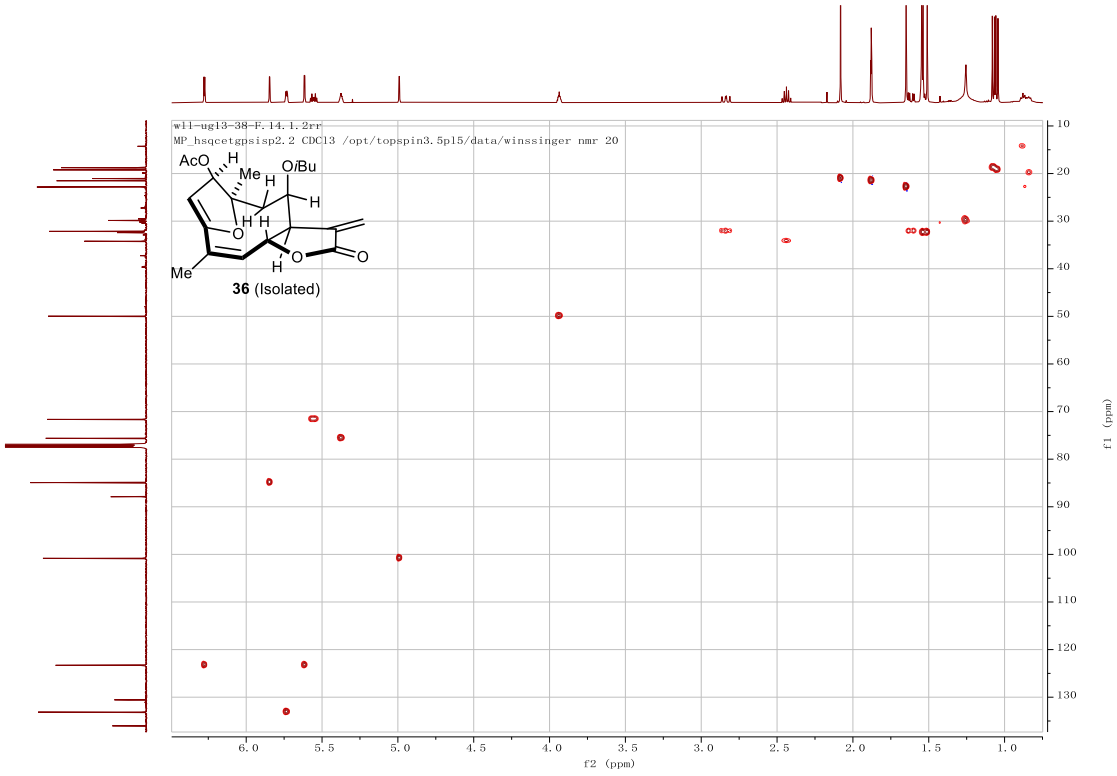

wll-ug12-06-c.15.1.2rr
MP_hmbcetgp13nd CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 5
OH
Me
Me
35
f2 (ppm)
f1 (ppm)


wll-ug12-06-c.16.1.2rr
NOESYPHSW CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 5
Me
Me
Me
Me
HO
35
f2 (ppm)
f1 (ppm)


wll-ug13-38-F.10.fid
MP-PROTON CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 20
AcO
Me
O/Bu
Me
36 (Isolated)
f1 (ppm)


wll-ug13-38-F.11.fid
MP_zgdc CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 20
AcO
Me
O/Bu
Me
36 (Isolated)
f1 (ppm)


wll-ug13-38-F.13.1.2rr
MP-cosygpppqf CDCl3 /opt/topspin3.5p15/data/winssinger nmr 20
Me
Me
O
O
Me
O
O
O
O
Me
36
f2 (ppm)
f1 (ppm)


wll-ug13-38-F.14.1.2rr
MP_hsqcetgpsisp2.2 CDCl3 /opt/topspin3.5p15/data/winssinger nmr 20
AcO
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Me
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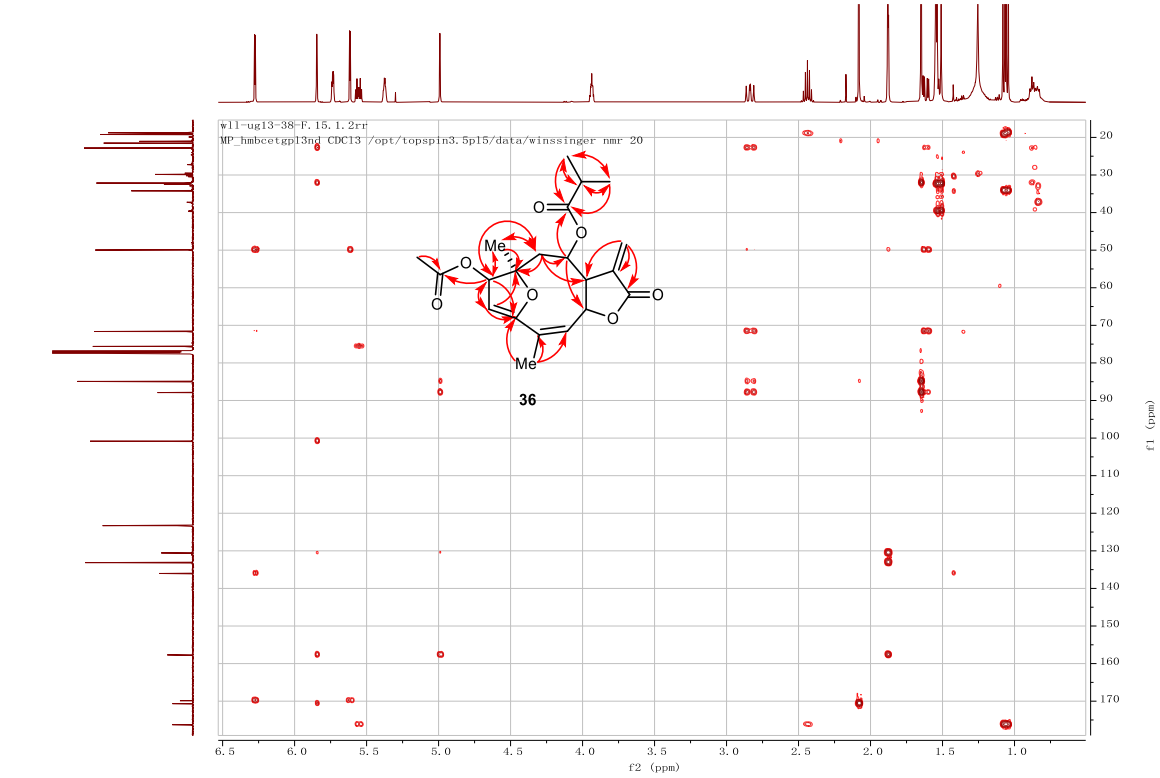
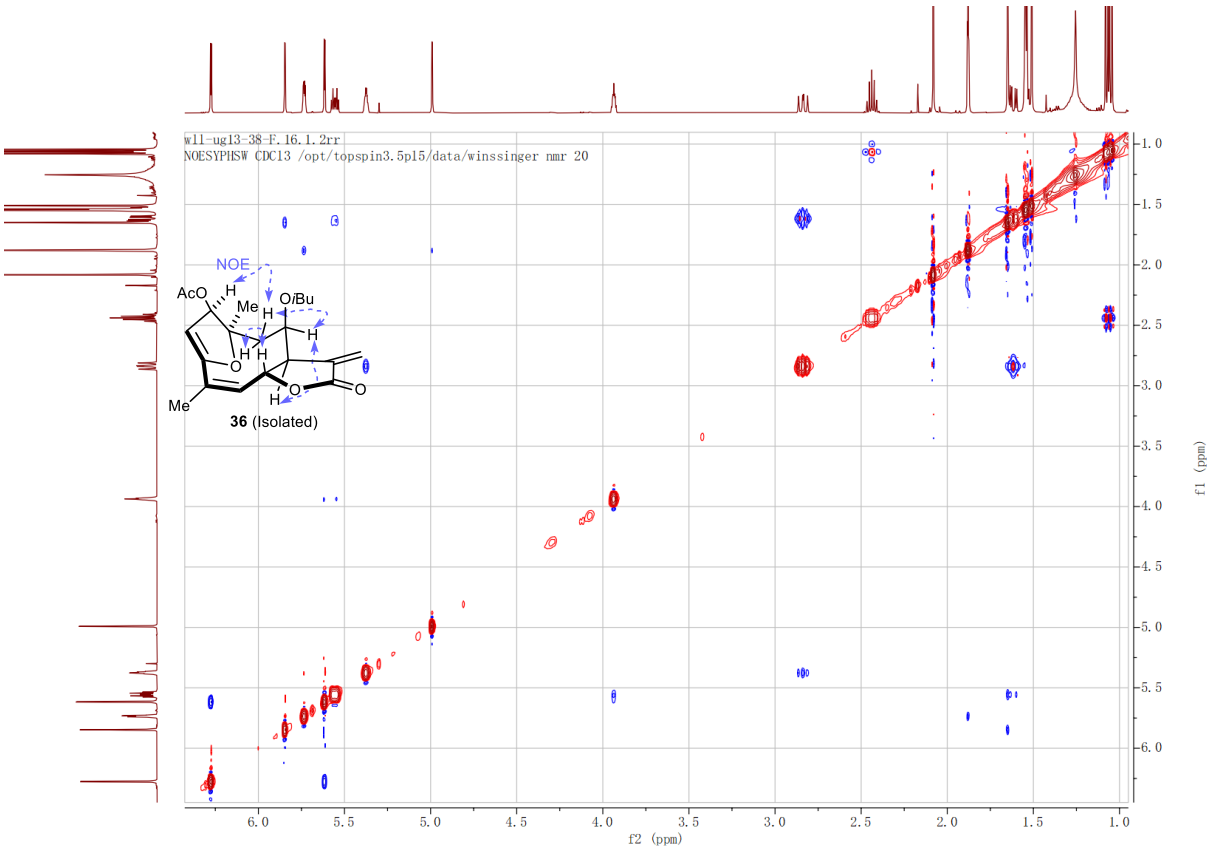
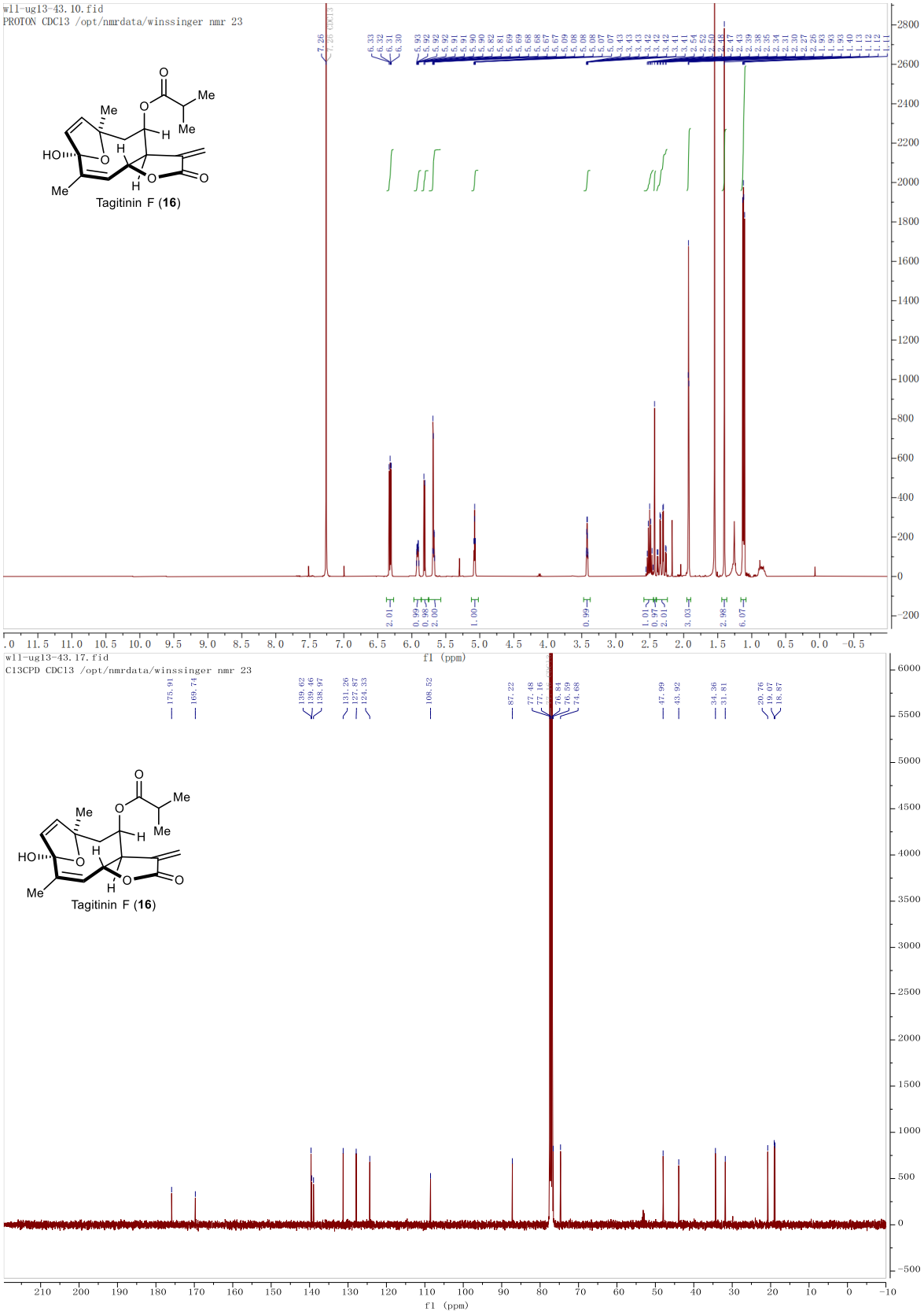
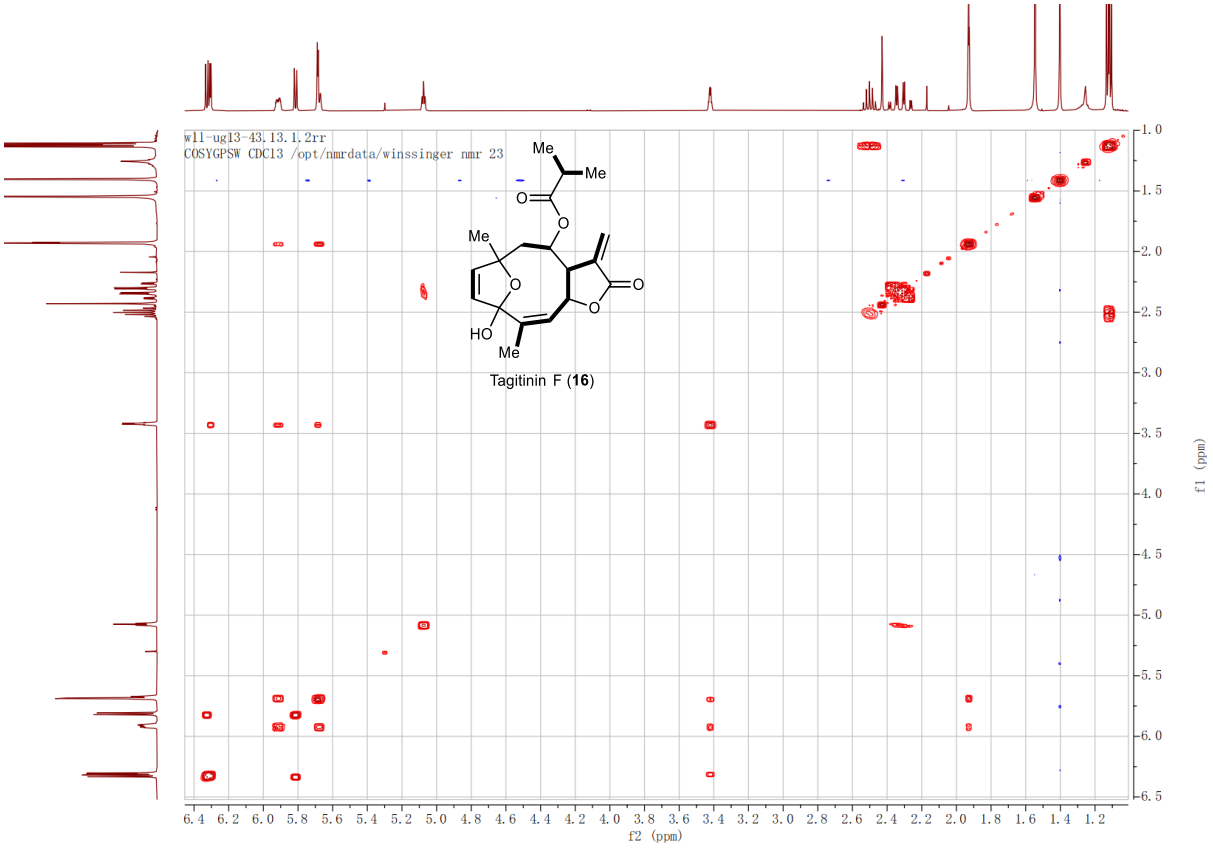
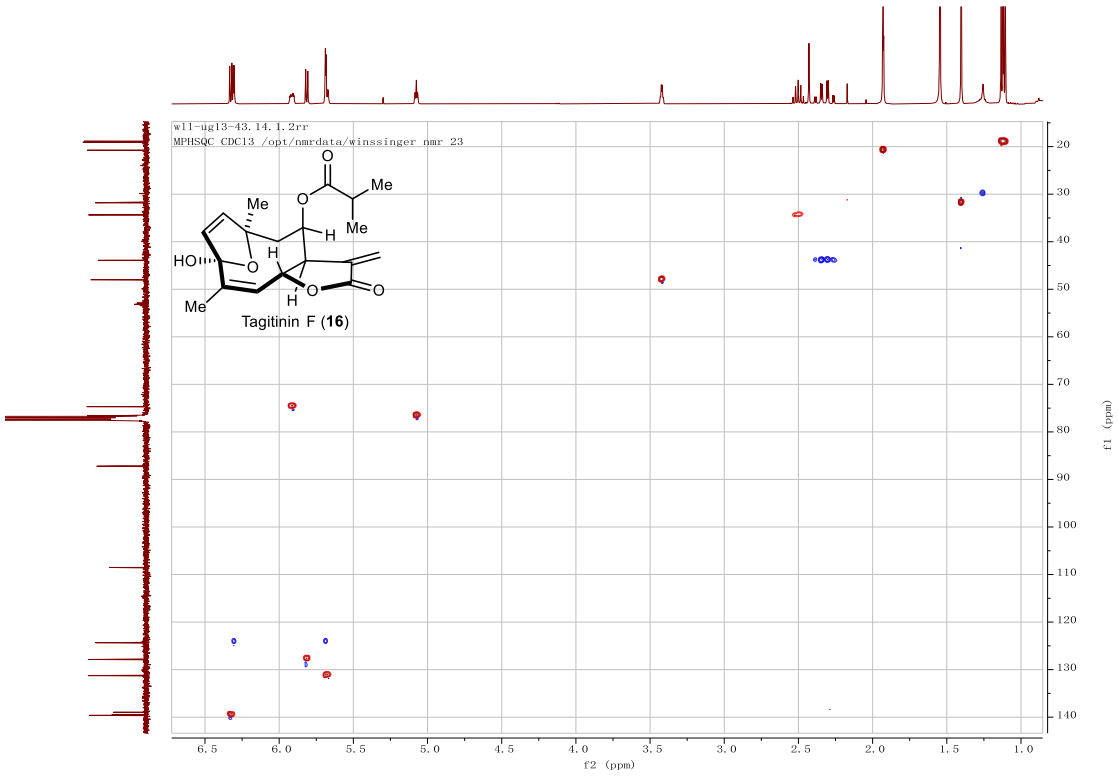
O/Bu
H
H
H
O
O
O
H
Me
36 (Isolated)
f2 (ppm)
f1 (ppm)

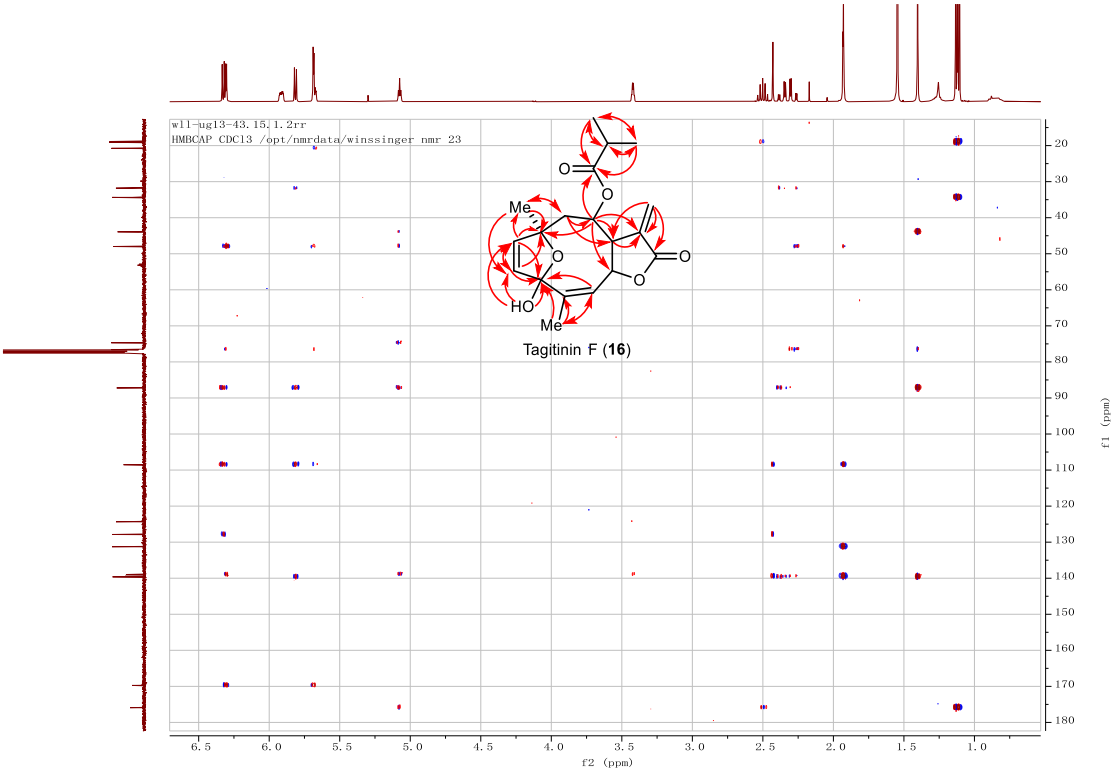

wll-ug13-38-F.15.1.2rr
MP_hmbcetgpl3nd CDC13 /opt/topspin3.5pl5/data/winssinger nmr 20
Me
Me
36
f2 (ppm)
f1 (ppm)

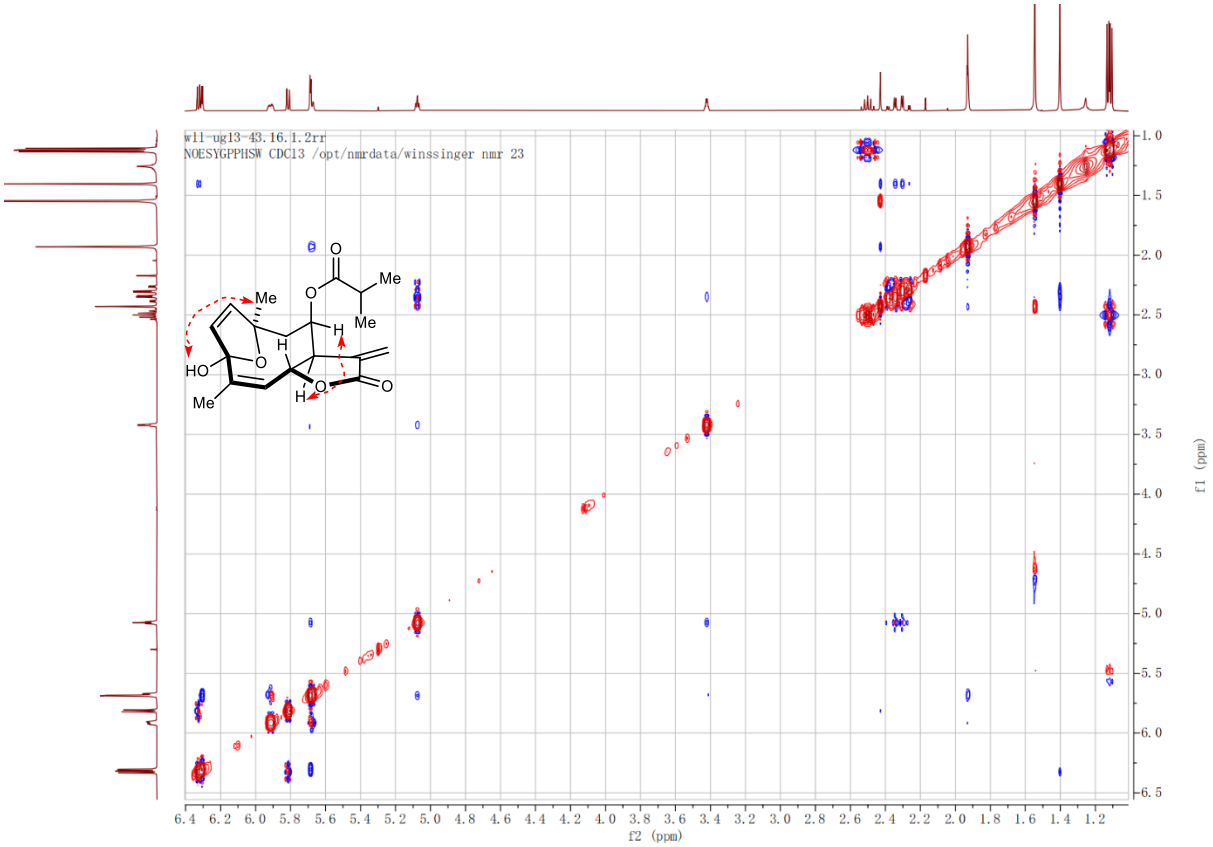

wll-ug13-38-F.16.1.2rr
NOESYPHSW CDC13 /opt/topspin3.5pl5/data/winssinger nmr 20
NOE
AcO
Me
OiBu
Me
36 (Isolated)
f2 (ppm)
f1 (ppm)

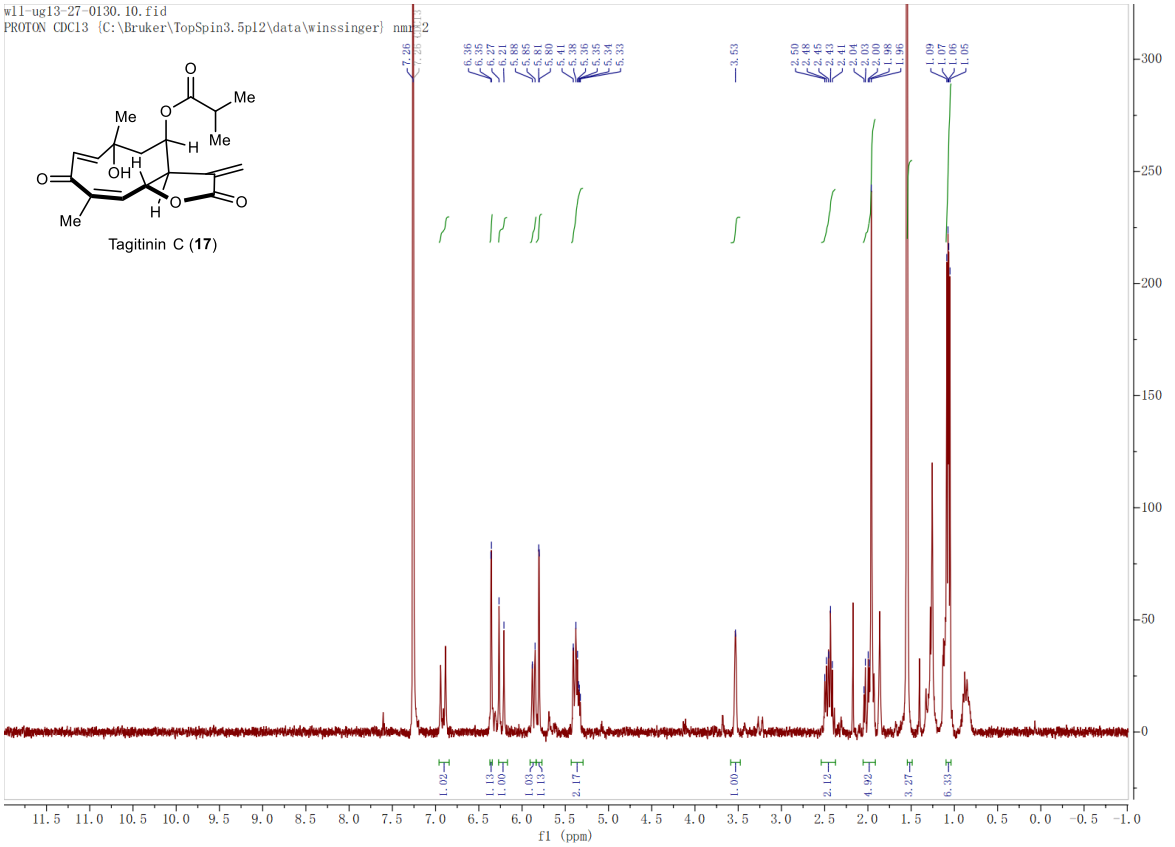

w11-ug13-43.10.fid
PROTON CDC13 /opt/nmrdata/winssinger nmr 23
Tagitinin F (16)
f1 (ppm)
w11-ug13-43.17.fid
C13CPD CDC13 /opt/nmrdata/winssinger nmr 23
Tagitinin F (16)
f1 (ppm)

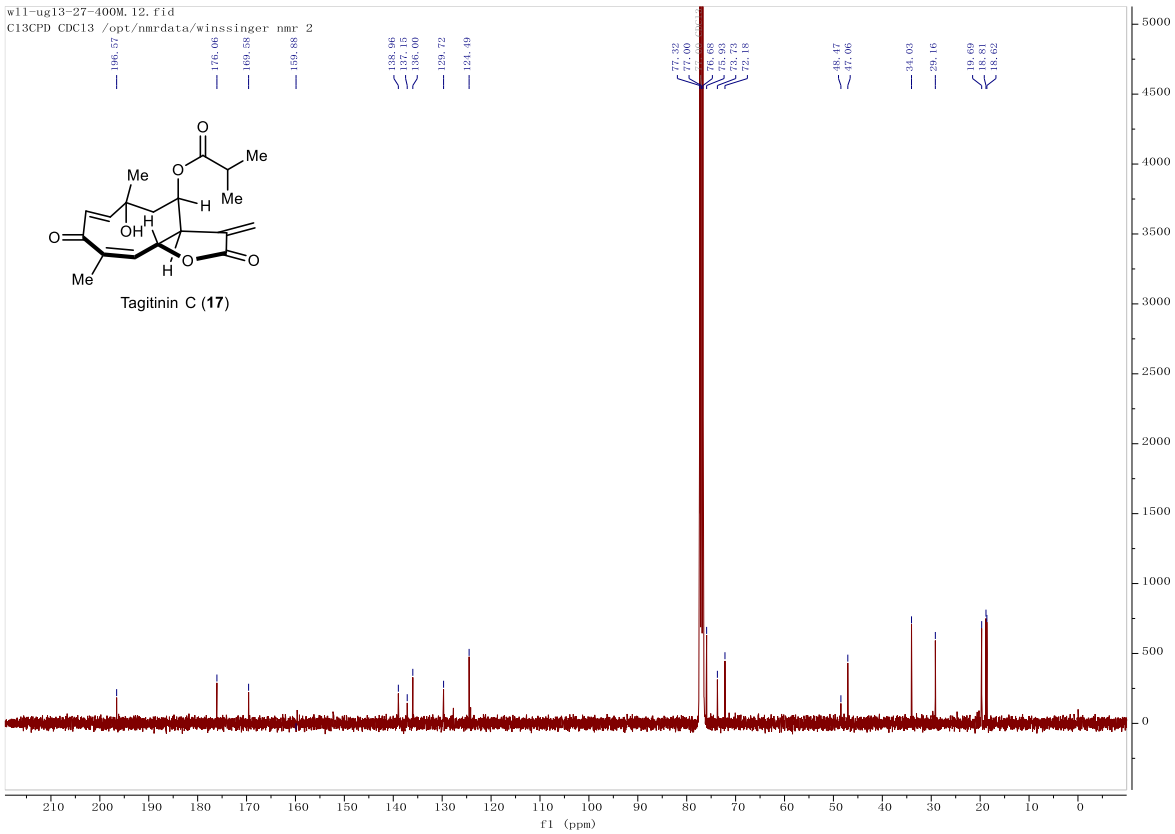

wll-ug13-43.13.1.2rr
COSYGPSW CDC13 /opt/nmrdata/winssinger nmr 23
Tagitinin F (16)
f2 (ppm)
f1 (ppm)

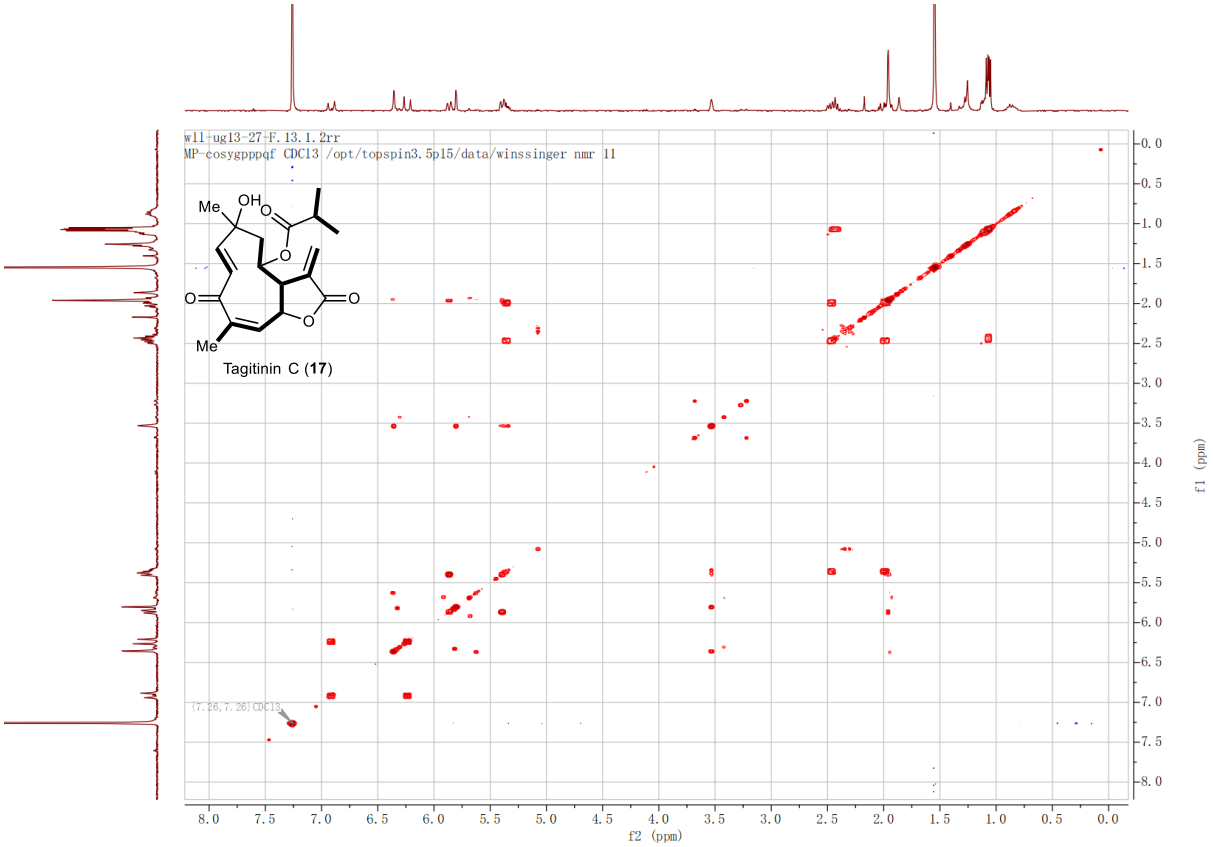

wll-ug13-43.14.1.2rr
MPHSQC CDC13 /opt/nmrdata/winssinger nmr 23
Tagitinin F (16)
f2 (ppm)
f1 (ppm)

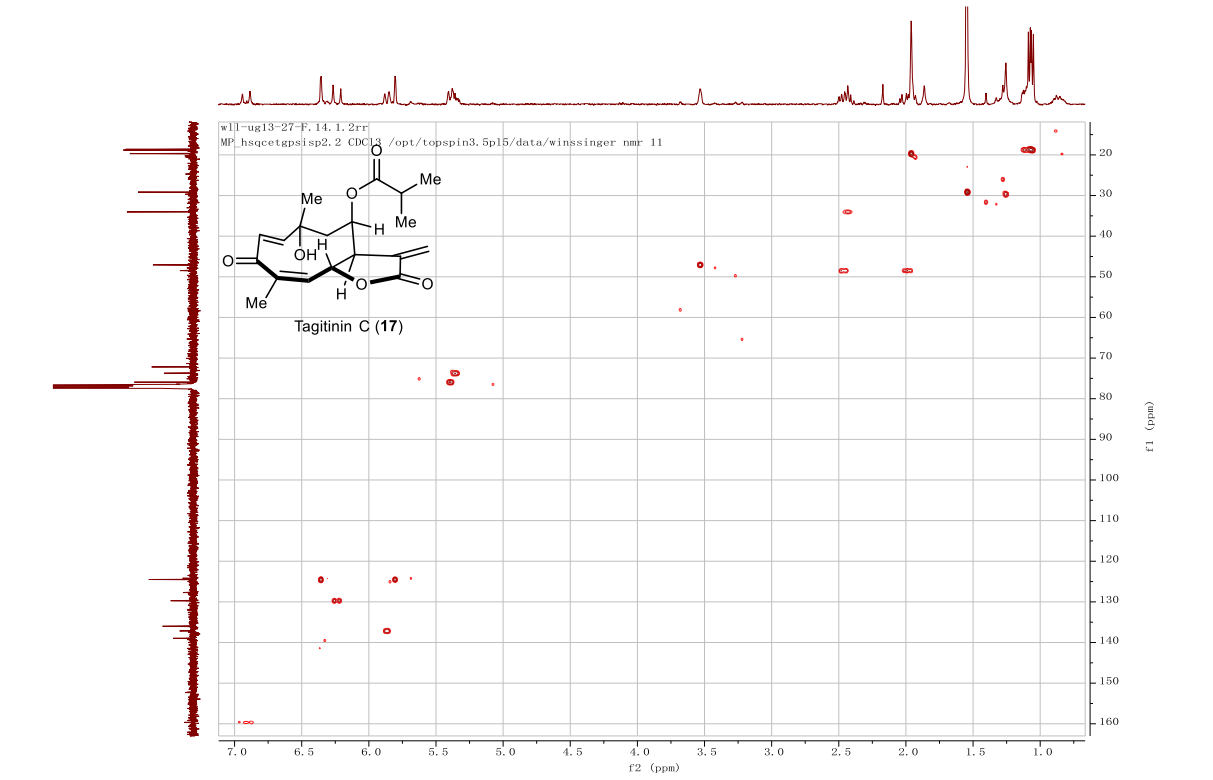

wll-ug13-43.15.1.2rr
HMBCAP CDCl3 /opt/nmrdata/winssinger nmr 23
Me
HO
Me
Tagitinin F (16)
f2 (ppm)
f1 (ppm)


wll-ug13-43.16.1.2rr
NOESYGPPHSW CDCl3 /opt/nmrdata/winssinger nmr 23
Me
Me
Me
HO
Me
f2 (ppm)
f1 (ppm)


w11-ug13-27-0130.10.fid
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl2\data\winssinger} nmr 2
Tagitinin C (17)
f1 (ppm)


w11-ug13-27-400M.12.fid
C13CPD CDCl3 /opt/nmrdata/winssinger nmr 2
Tagitinin C (17)
f1 (ppm)


wll-ug13-27-F.13.1.2rr
MP-cosygpppqf CDCl3 /opt/topspin3.5p15/data/winssinger nmr 11
Me
OH
O
O
O
O
Me
Tagitinin C (17)
f2 (ppm)
f1 (ppm)


wll-ug13-27-F.14.1.2rr
MP_hsqcetgpsisp2.2 CDCl3 /opt/topspin3.5p15/data/winssinger nmr 11
Me
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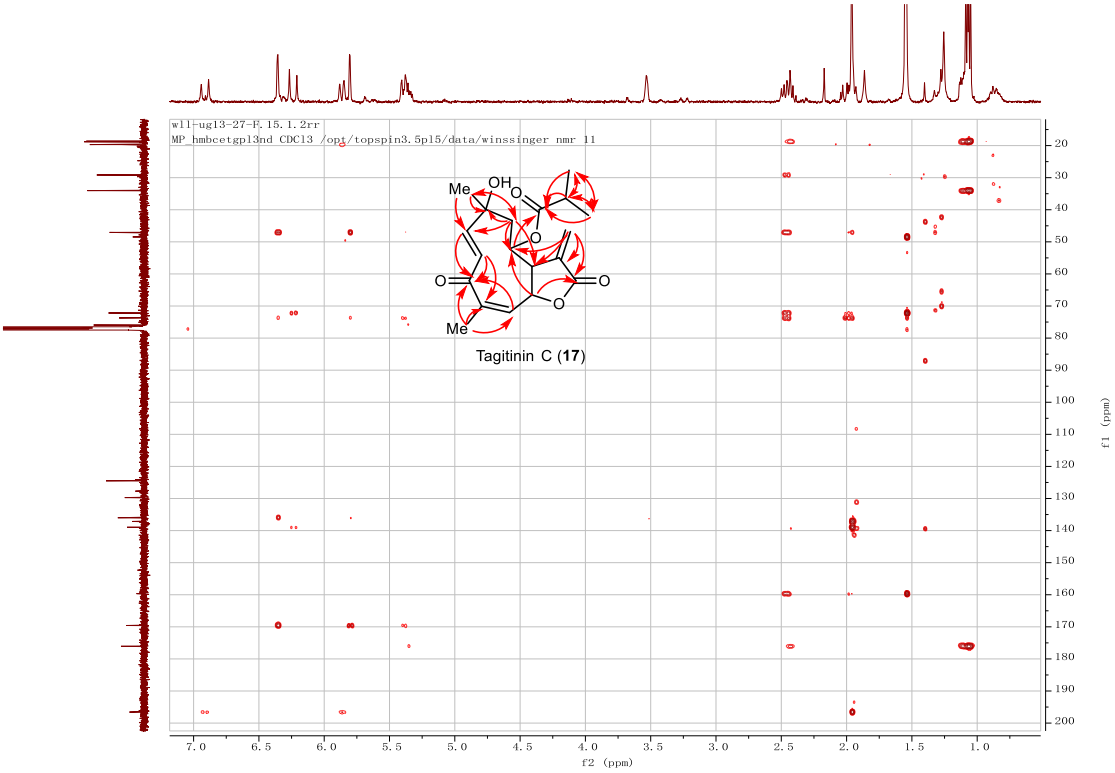
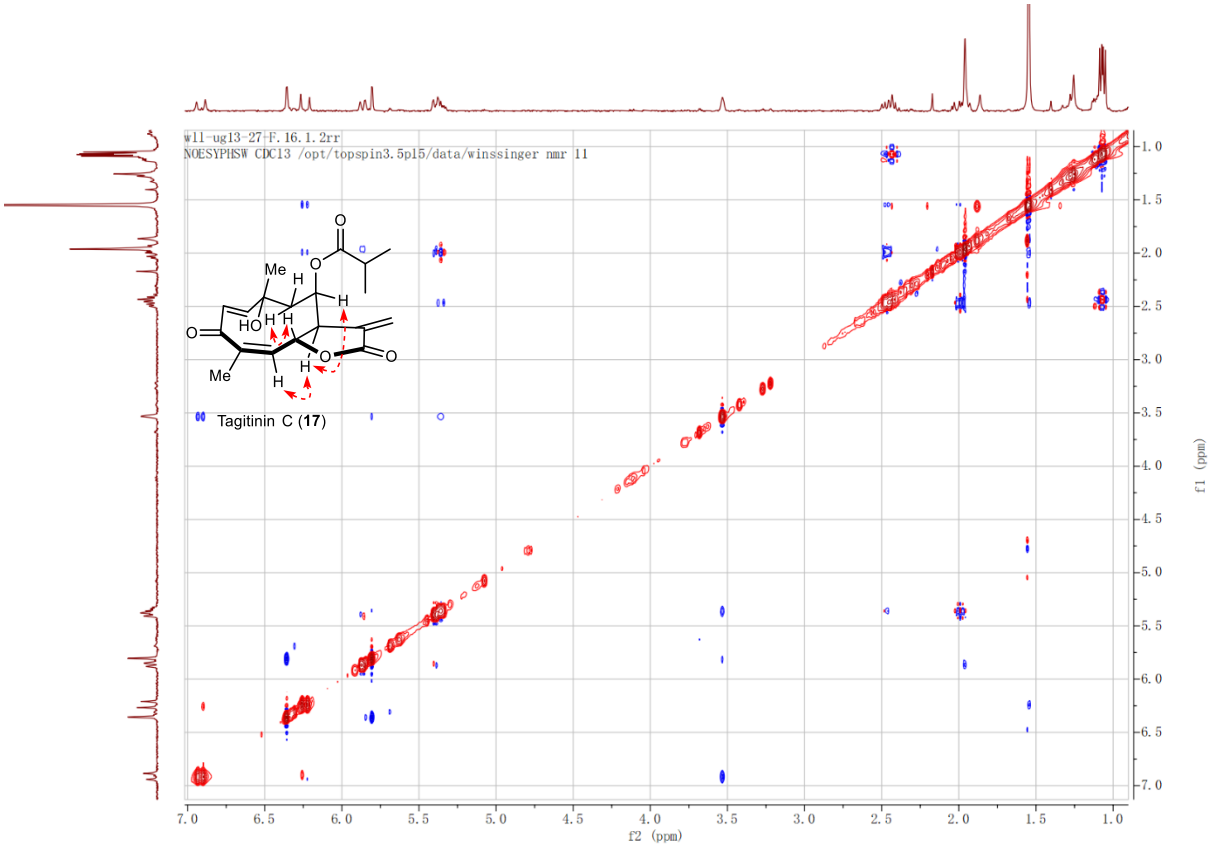
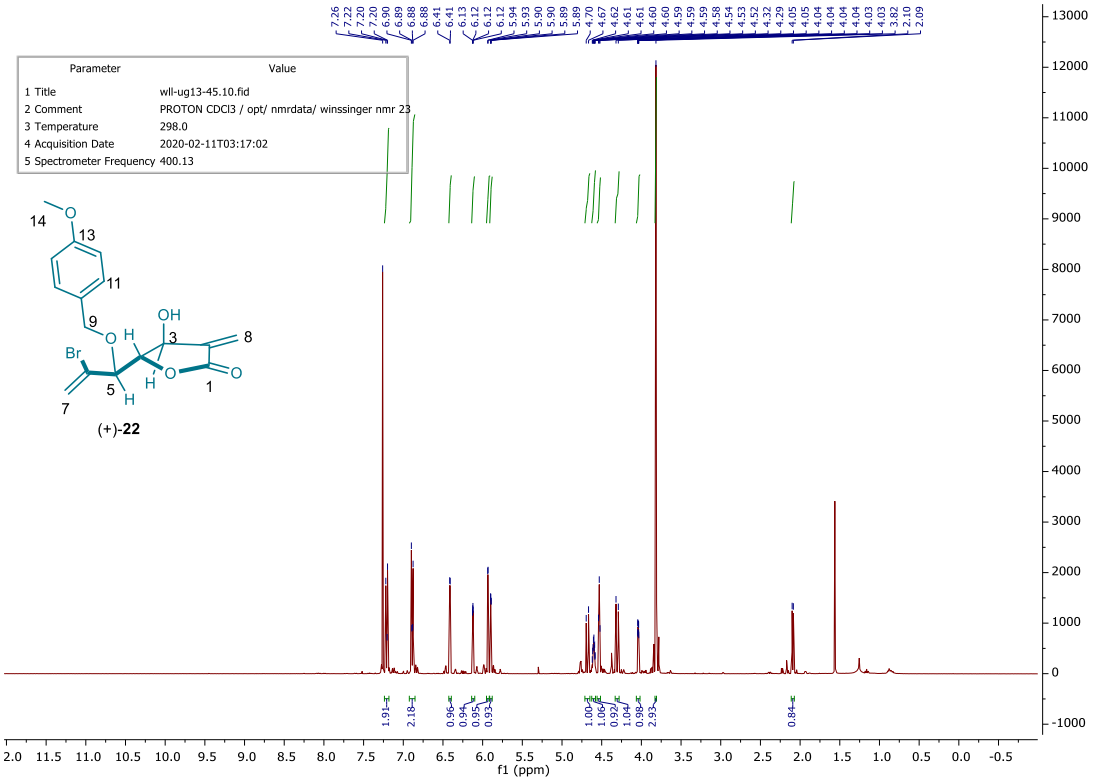
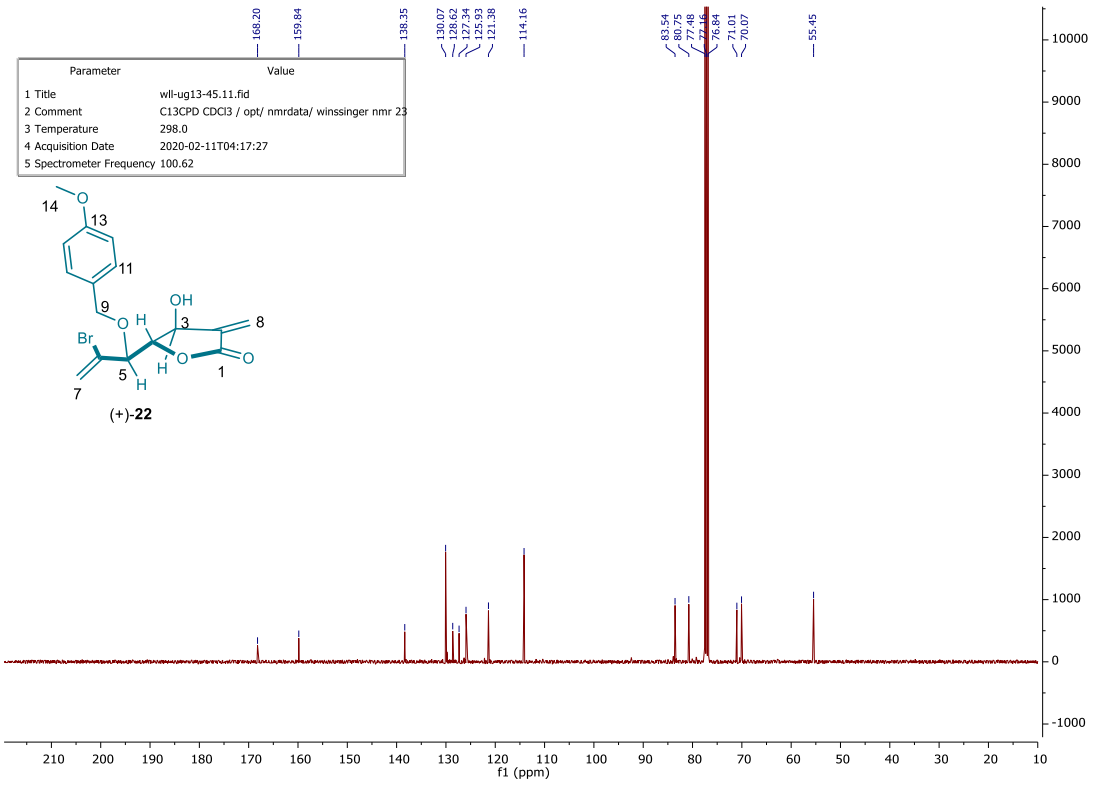
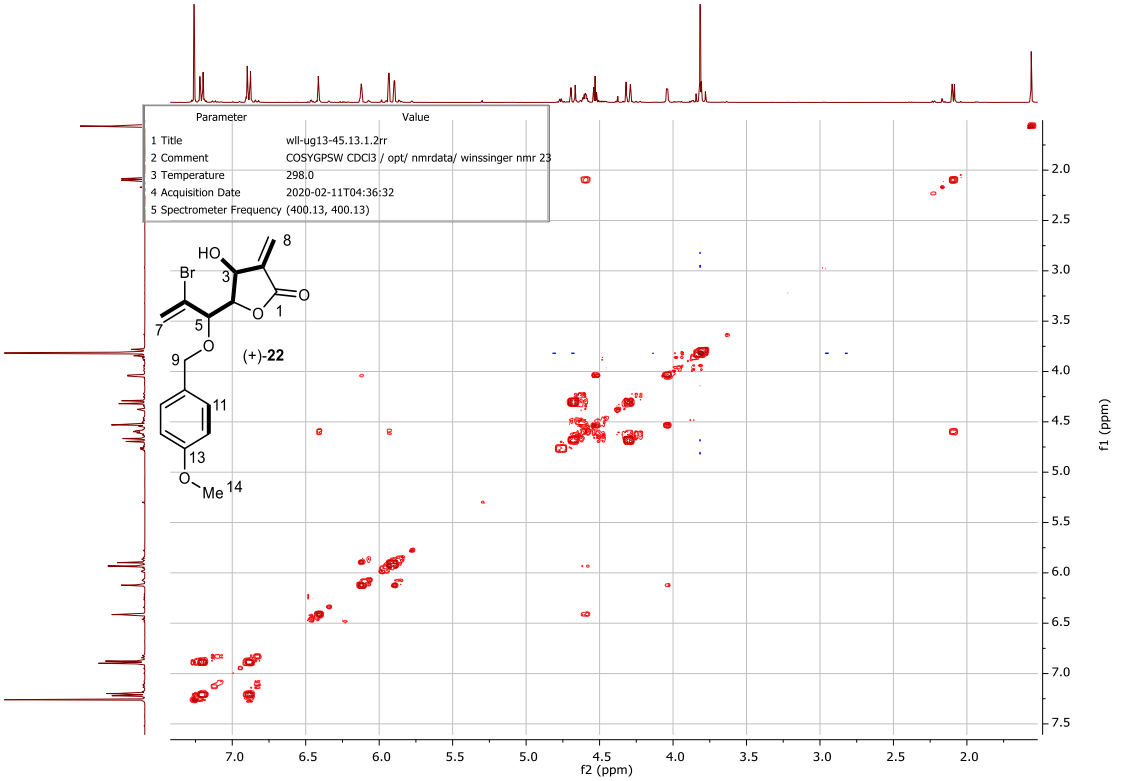
O
H
Me
OH
H
O
O
H
Me
Tagitinin C (17)
f2 (ppm)
f1 (ppm)

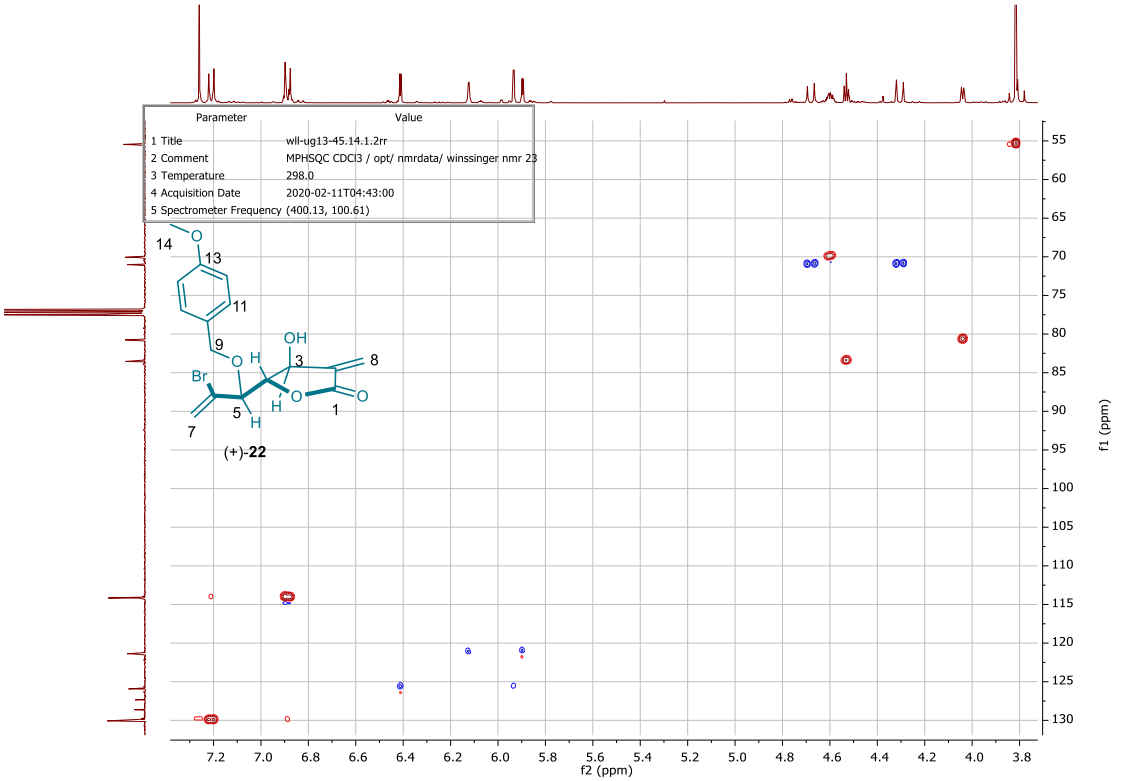

wll-ug13-27-F. 15. 1. 2rr
MP_hmbcetgpl3nd CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 11
Me
OH
O
O
O
O
O
Me
Tagitinin C (17)
f2 (ppm)
f1 (ppm)

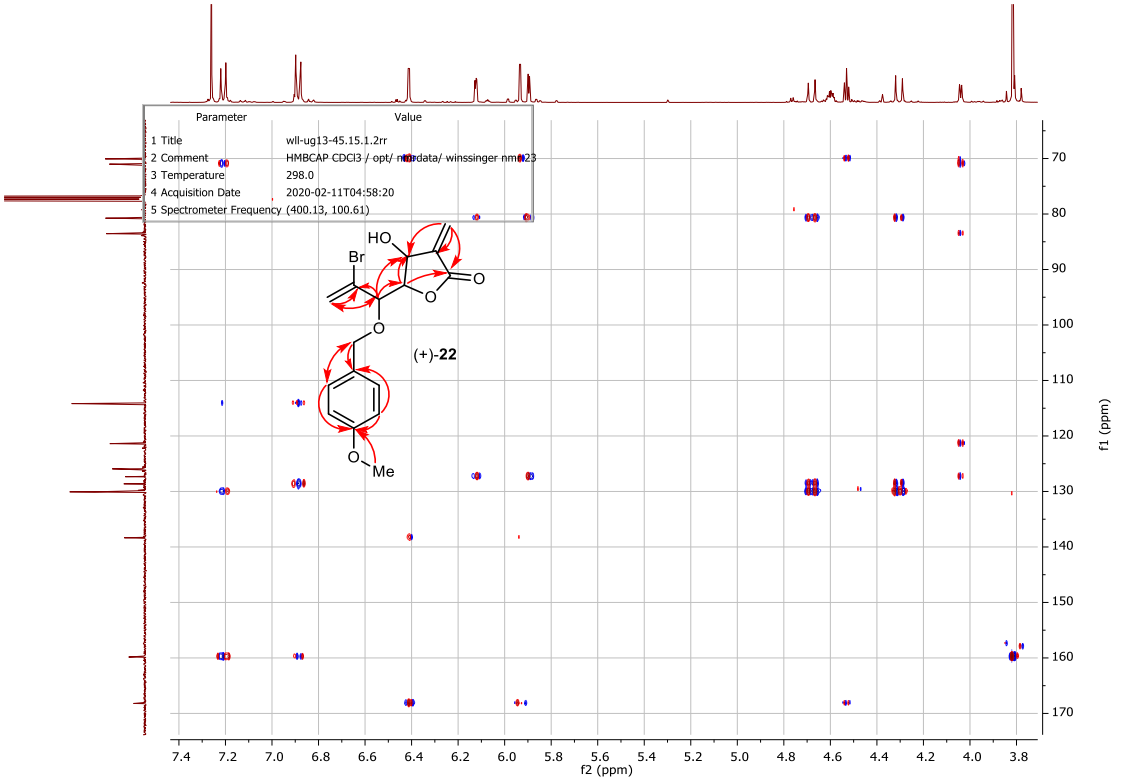

wll-ug13-27+F. 16. 1. 2rr
NOESYPHSW CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 11
Me
H
O
H
HO
H
H
O
O
Me
H
H
O
Tagitinin C (17)
f2 (ppm)
f1 (ppm)

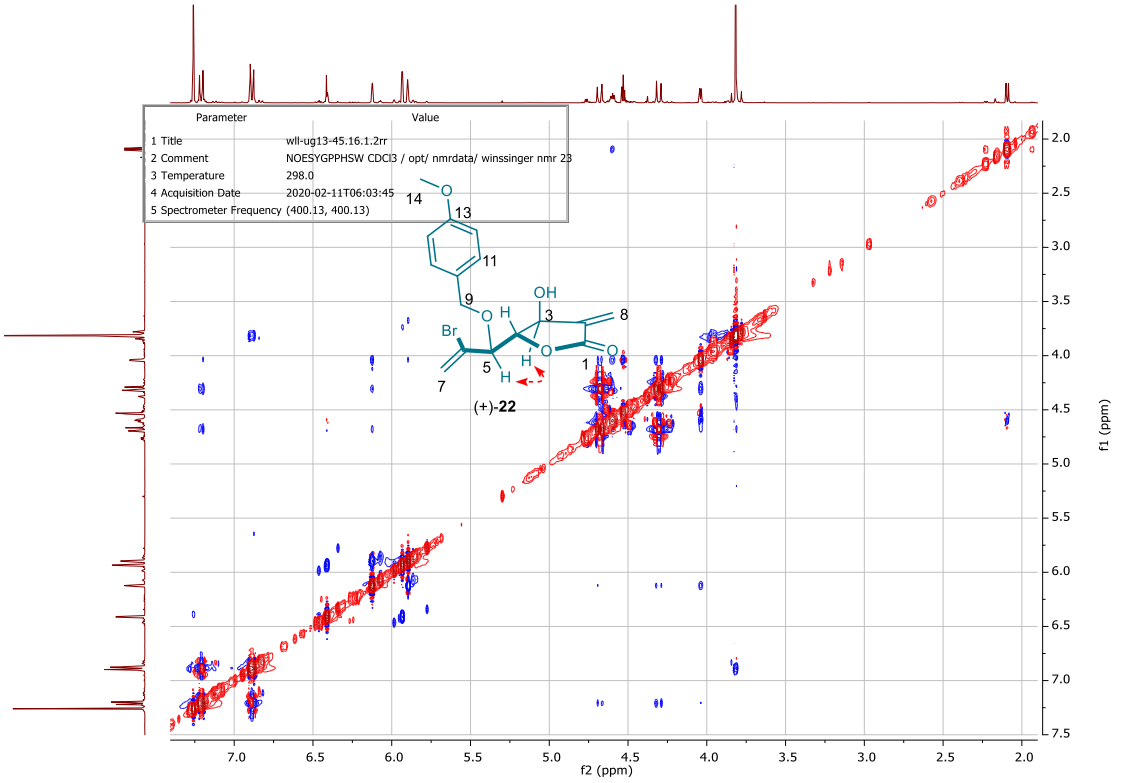

Parameter Value
1 Title wll-ug13-45.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-11T03:17:02
5 Spectrometer Frequency 400.13
(+)-22
f1 (ppm)

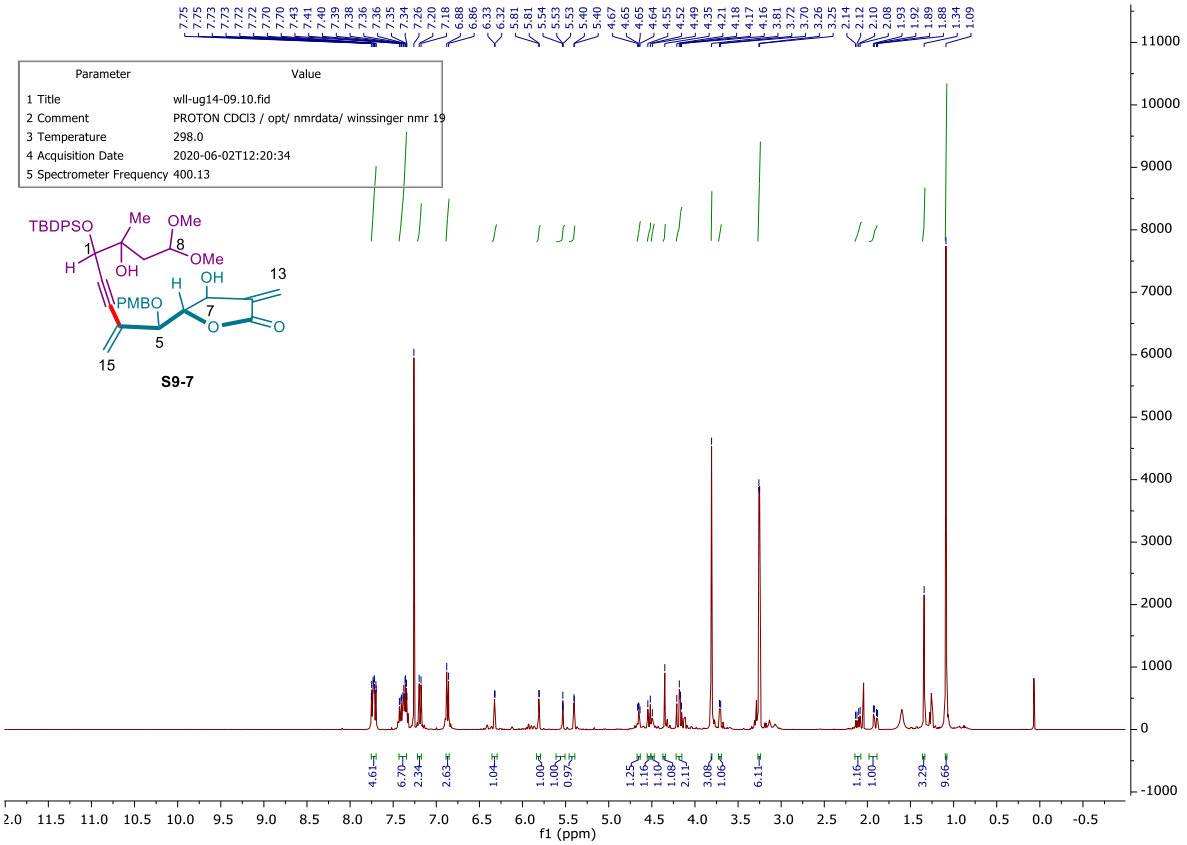

Parameter Value
1 Title wll-ug13-45.11.fid
2 Comment C13CPD CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-11T04:17:27
5 Spectrometer Frequency 100.62
(+)-22
f1 (ppm)

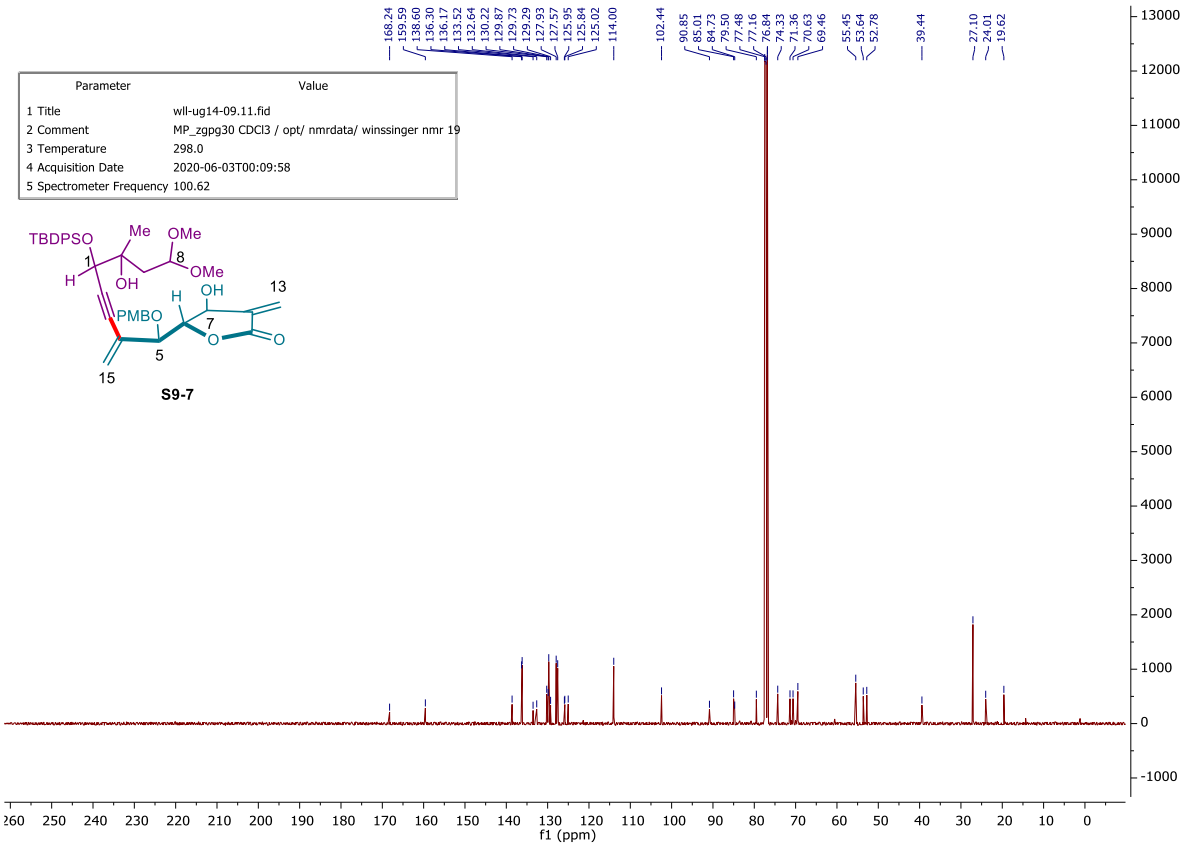

Parameter Value
1 Title wll-ug13-45.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-11T04:36:32
5 Spectrometer Frequency (400.13, 400.13)
HO
Br
O
Me
(+)-22
f2 (ppm)
f1 (ppm)

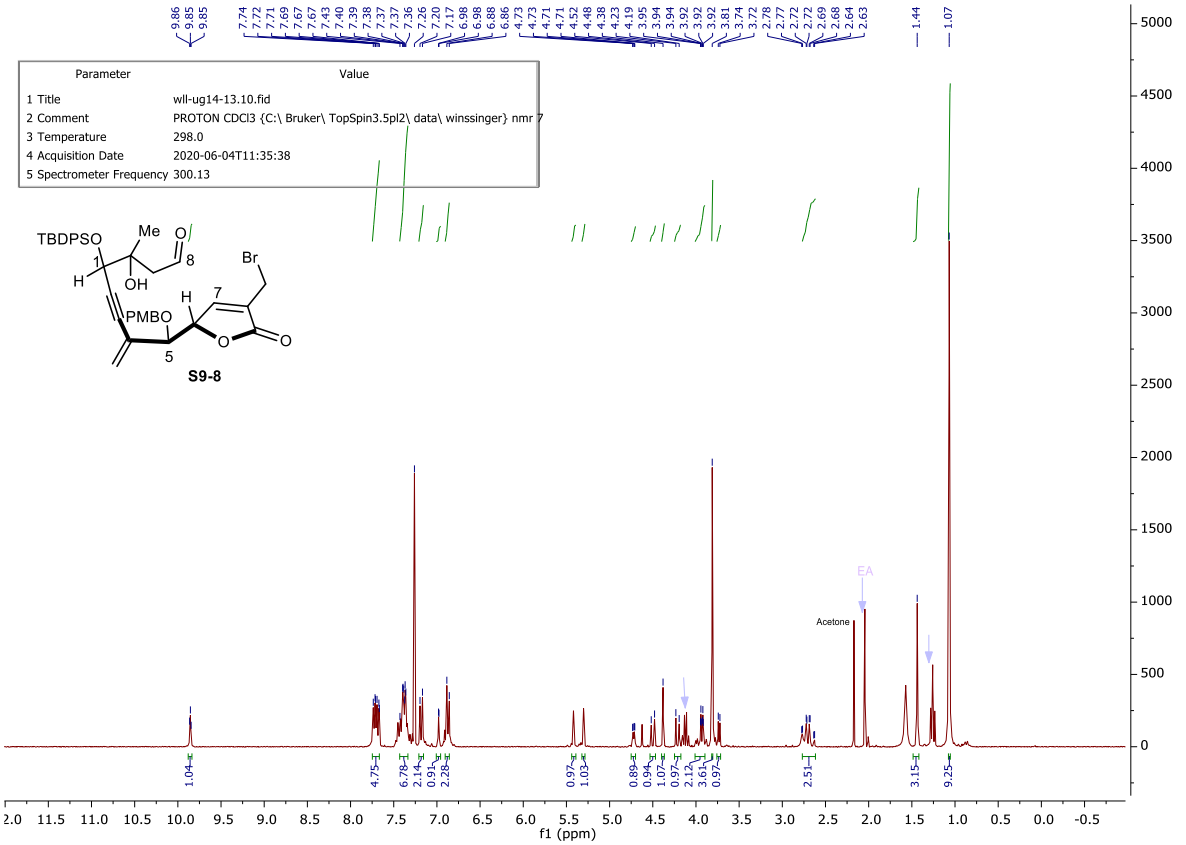

Parameter Value
1 Title wll-ug13-45.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-11T04:43:00
5 Spectrometer Frequency (400.13, 100.61)
OH
Br
(+)-22
f2 (ppm)
f1 (ppm)

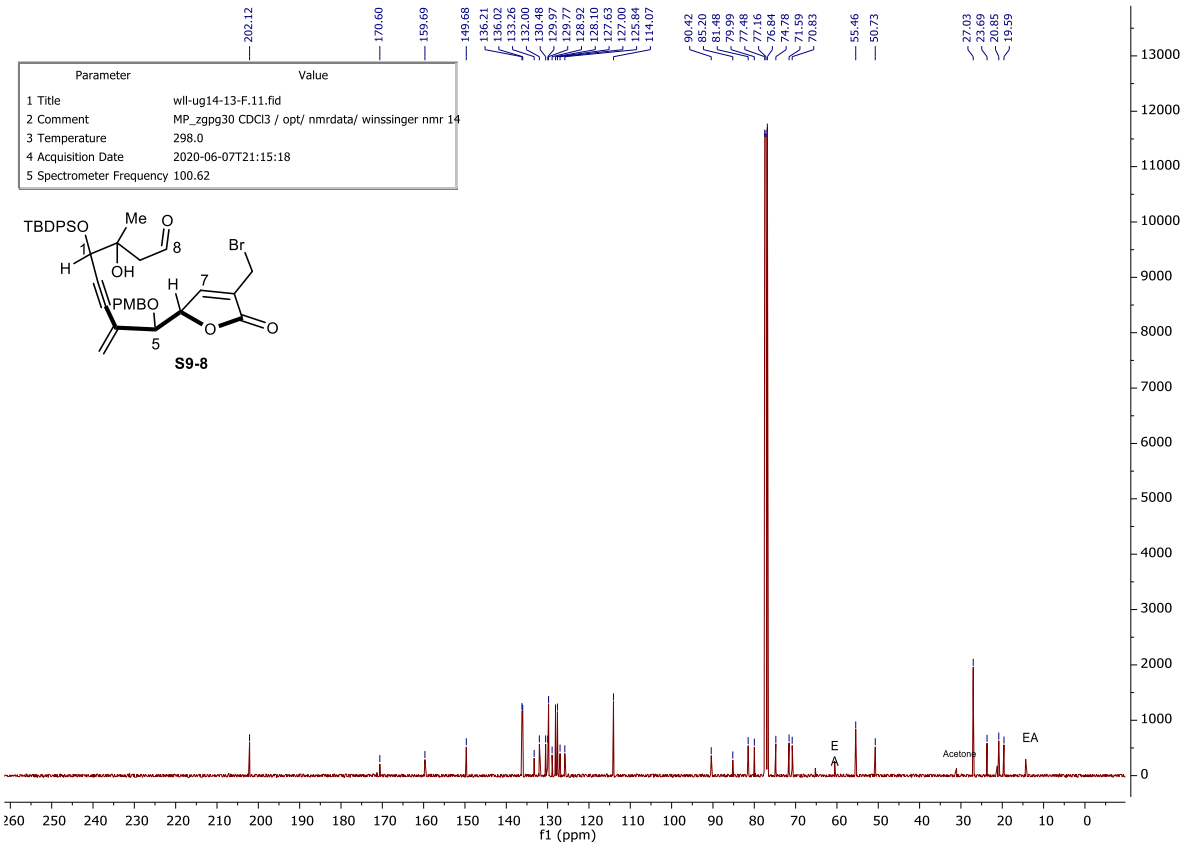

Parameter Value
1 Title wll-ug13-45.15.1.2rr
2 Comment HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr23
3 Temperature 298.0
4 Acquisition Date 2020-02-11T04:58:20
5 Spectrometer Frequency (400.13, 100.61)
HO
Br
O
O
O
(+)-22
O
Me
f2 (ppm)
f1 (ppm)

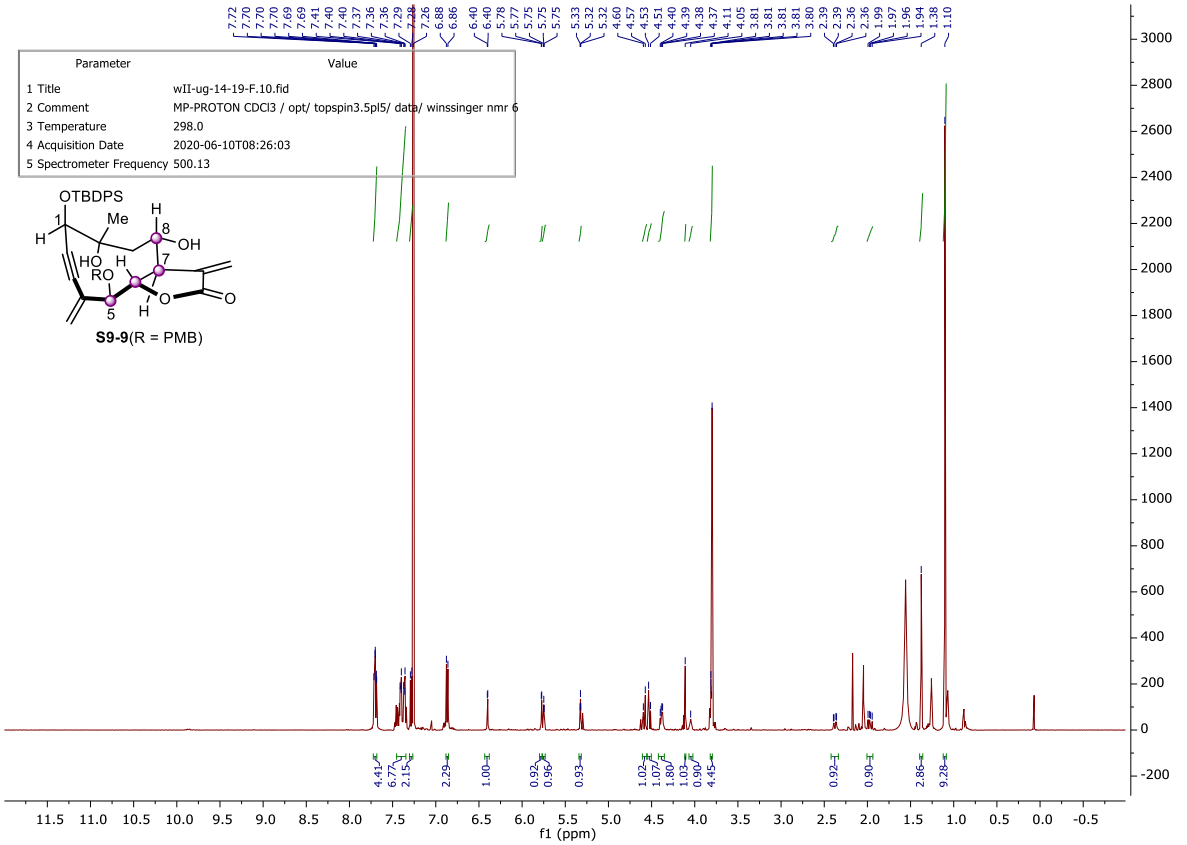

Parameter Value
1 Title wll-ug13-45.16.1.2rr
2 Comment NOESYGPPHSW CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.0
4 Acquisition Date 2020-02-11T06:03:45
5 Spectrometer Frequency (400.13, 400.13)
14
O
13
11
9
O
H
OH
3
8
Br
5
H
H
7
O
O
1
(+)-22
f2 (ppm)
f1 (ppm)

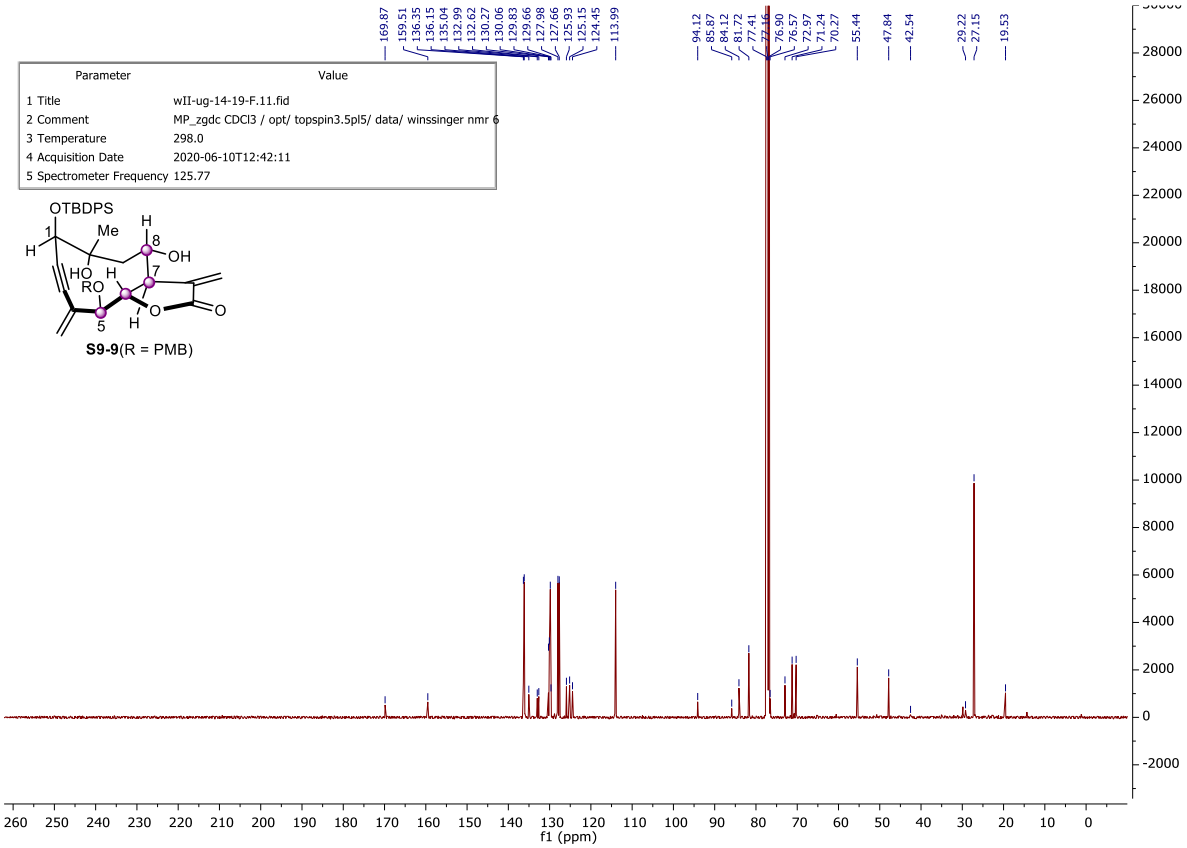

Parameter Value
1 Title wll-ug14-09.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 19
3 Temperature 298.0
4 Acquisition Date 2020-06-02T12:20:34
5 Spectrometer Frequency 400.13
TBDPSO
Me
OMe
OMe
OH
H
PMBO
OH
H
O
O
S9-7
f1 (ppm)

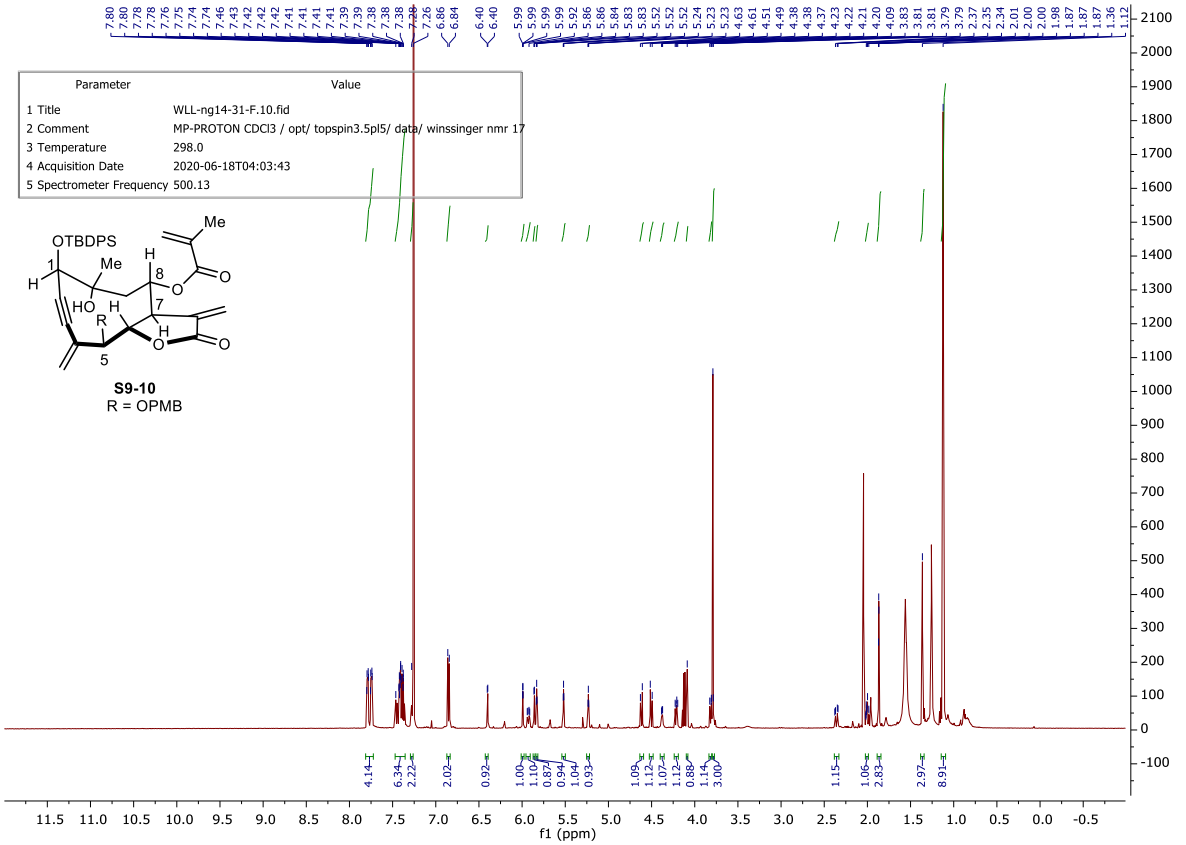

Parameter Value
1 Title wll-ug14-09.11.fid
2 Comment MP_zgpg30 CDCl3 / opt/ nmrdata/ winssinger nmr 19
3 Temperature 298.0
4 Acquisition Date 2020-06-03T00:09:58
5 Spectrometer Frequency 100.62
TBDPSO
Me
OMe
OMe
OH
H
PMBO
OH
H
O
O
S9-7
f1 (ppm)

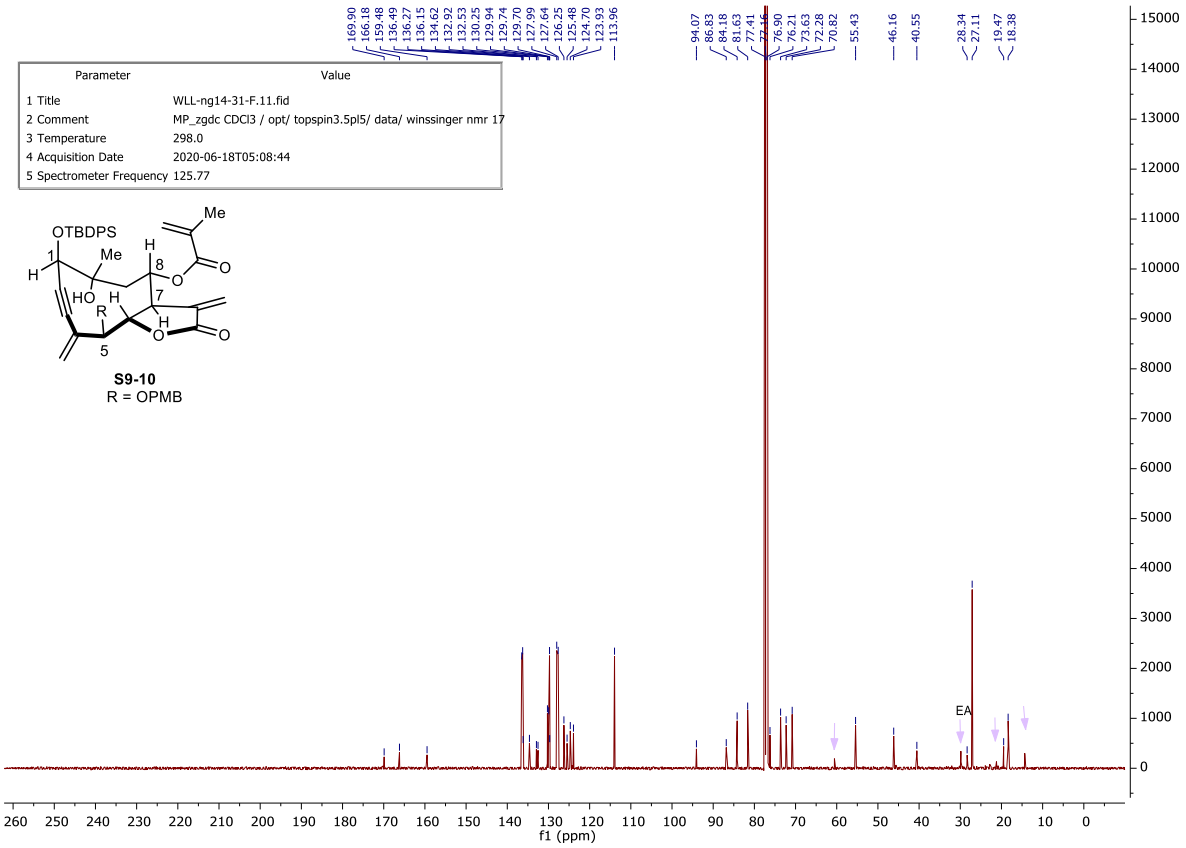

Parameter Value
1 Title wll-ug14-13.10.fid
2 Comment PROTON CDCl3 {C:\ Bruker\ TopSpin3.5pl2\ data\ winssinger} nmr 7
3 Temperature 298.0
4 Acquisition Date 2020-06-04T11:35:38
5 Spectrometer Frequency 300.13
TBDPSO
Me
O
8
Br
H
1
OH
H
7
PMBO
O
O
5
S9-8
EA
Acetone
f1 (ppm)

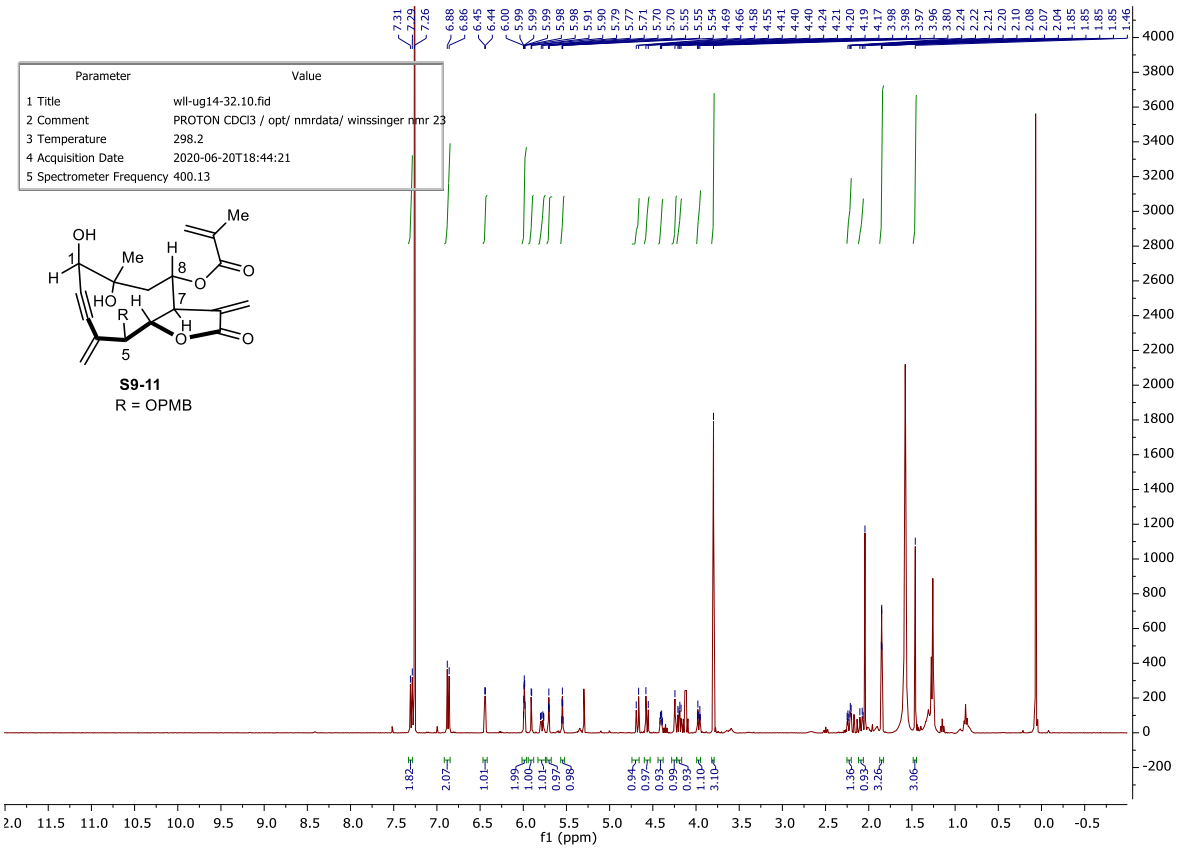

Parameter Value
1 Title wll-ug14-13-F.11.fid
2 Comment MP_zgpg30 CDCl3 / opt/ nmrdata/ winssinger nmr 14
3 Temperature 298.0
4 Acquisition Date 2020-06-07T21:15:18
5 Spectrometer Frequency 100.62
TBDPSO
Me
O
8
Br
H
1
OH
H
7
PMBO
O
O
5
S9-8
E
A
Acetone
EA
f1 (ppm)

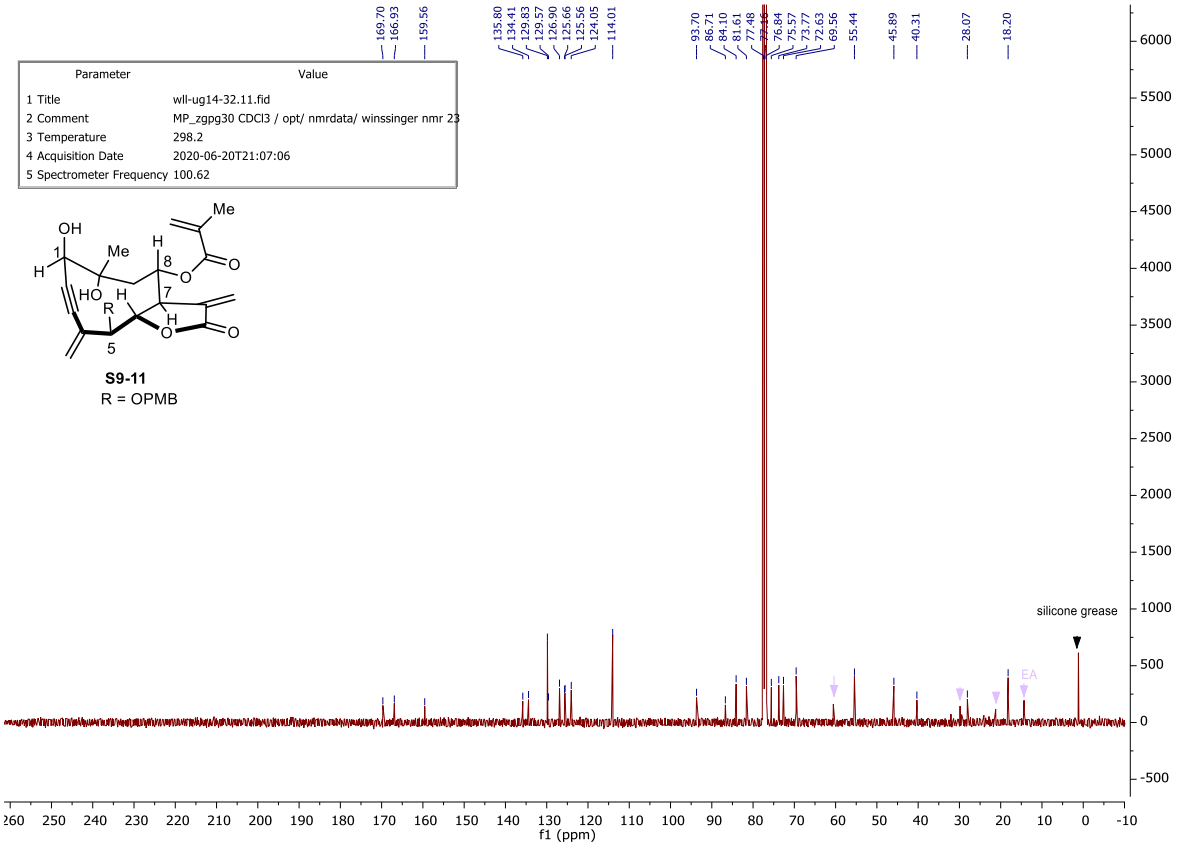

Parameter Value
1 Title wII-ug-14-19-F.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 6
3 Temperature 298.0
4 Acquisition Date 2020-06-10T08:26:03
5 Spectrometer Frequency 500.13
OTBDPS
Me
H
OH
HO
RO
S9-9(R = PMB)
f1 (ppm)

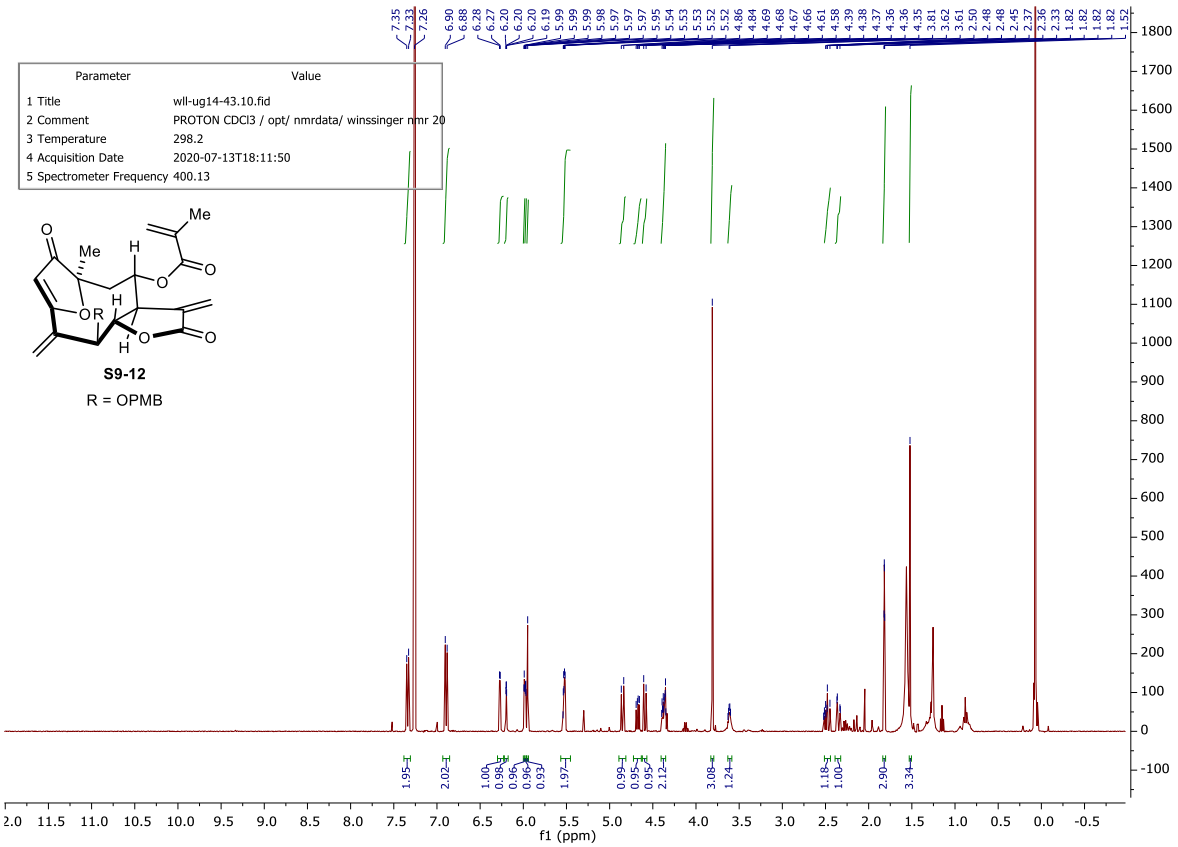

Parameter Value
1 Title wII-ug-14-19-F.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 6
3 Temperature 298.0
4 Acquisition Date 2020-06-10T12:42:11
5 Spectrometer Frequency 125.77
OTBDPS
Me
OH
HO
RO
S9-9(R = PMB)
f1 (ppm)

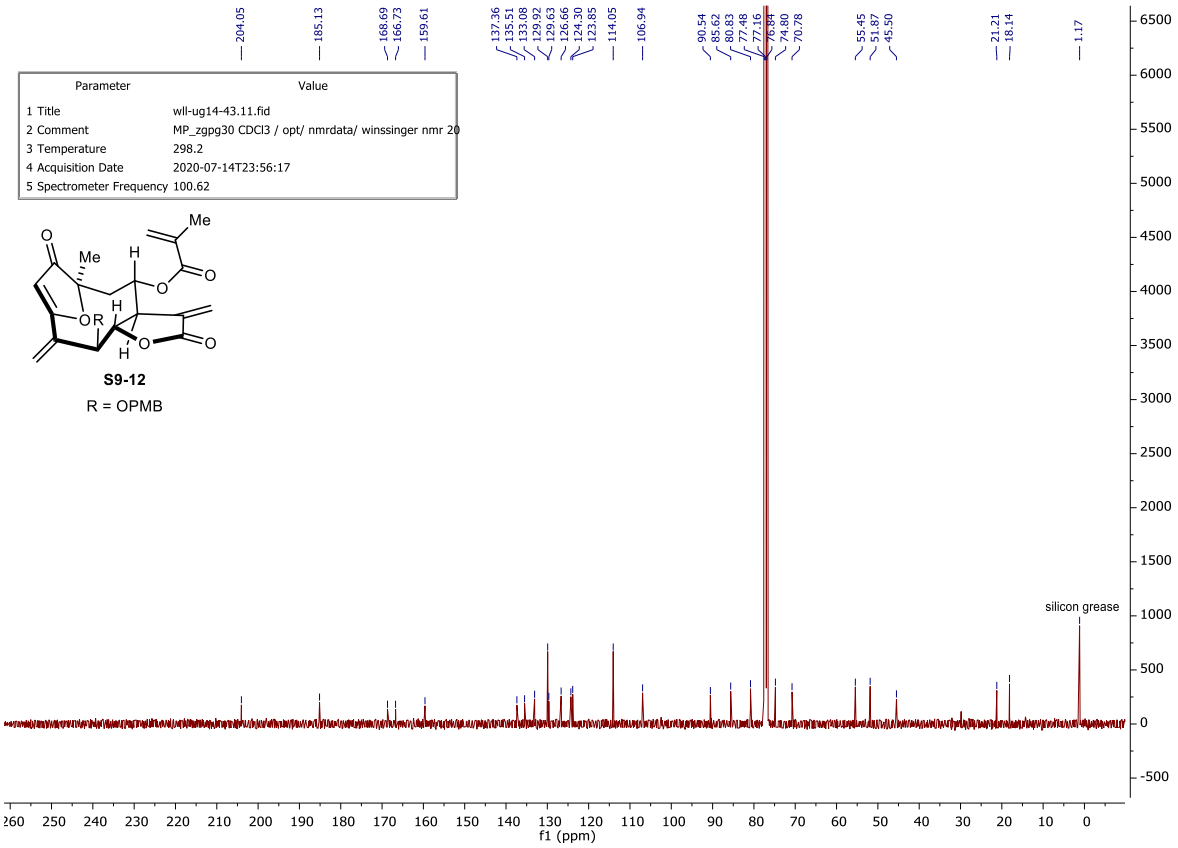

Parameter Value
1 Title WLL-ng14-31-F.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 17
3 Temperature 298.0
4 Acquisition Date 2020-06-18T04:03:43
5 Spectrometer Frequency 500.13
OTBDPS
Me
H
1
H
Me
HO
H
R
8
O
O
7
H
O
O
5
S9-10
R = OPMB
f1 (ppm)

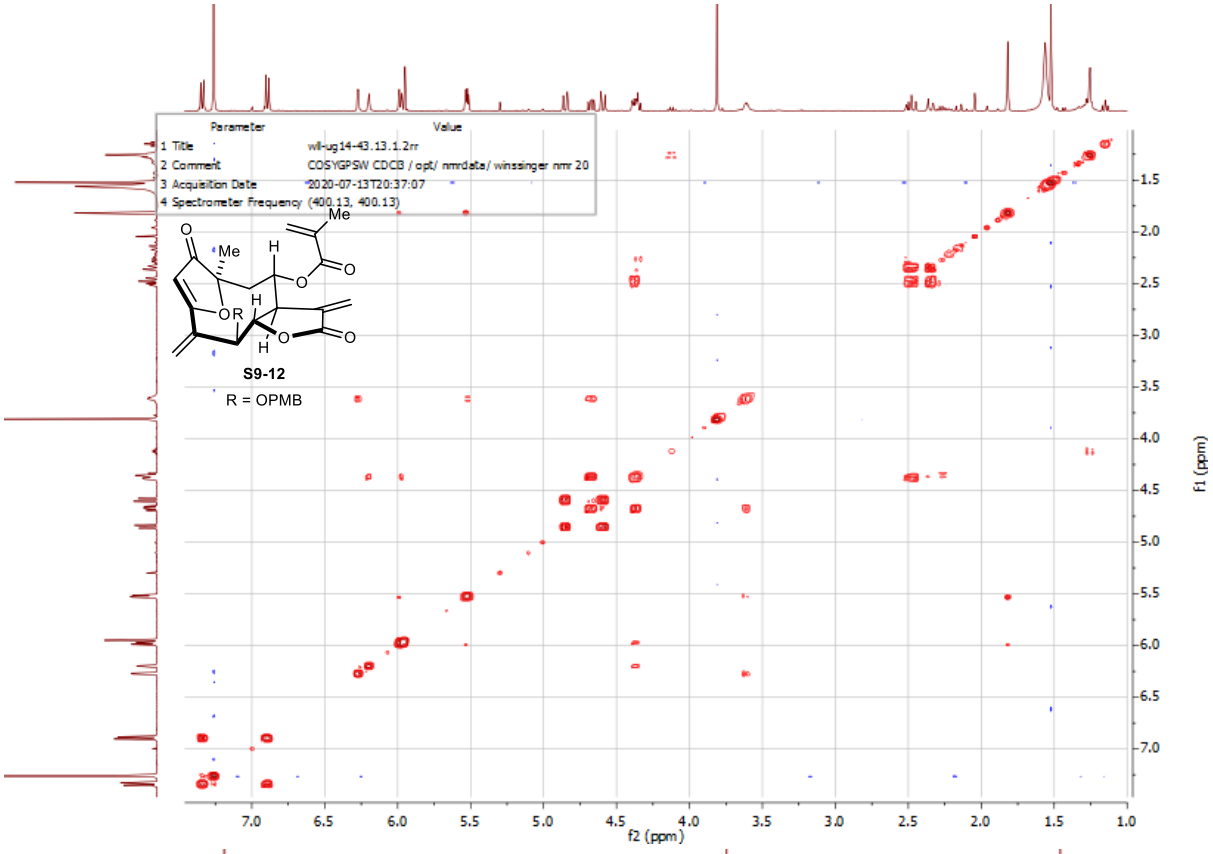

Parameter Value
1 Title WLL-ng14-31-F.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 17
3 Temperature 298.0
4 Acquisition Date 2020-06-18T05:08:44
5 Spectrometer Frequency 125.77
OTBDPS
Me
H
1
H
Me
HO
H
R
8
O
O
7
H
O
O
5
S9-10
R = OPMB
EA
f1 (ppm)

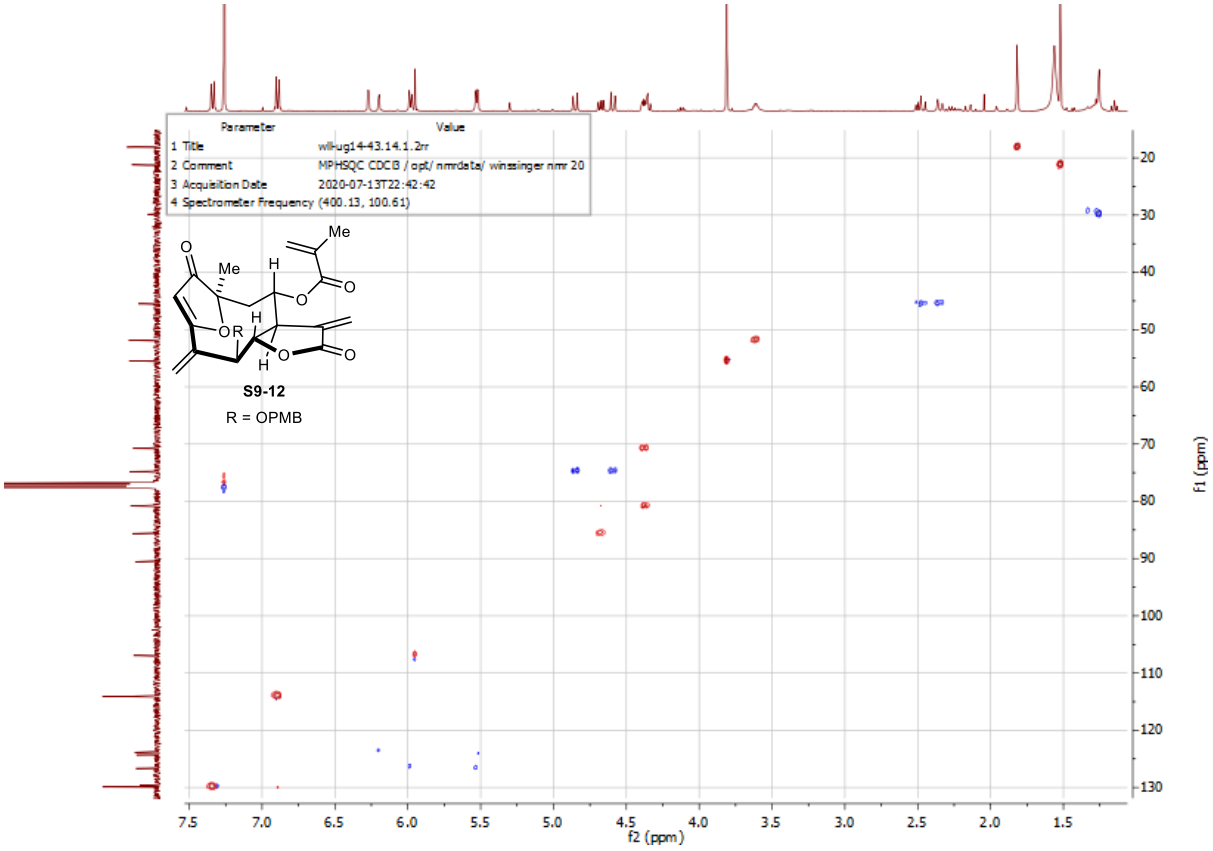

Parameter Value
1 Title wll-ug14-32.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.2
4 Acquisition Date 2020-06-20T18:44:21
5 Spectrometer Frequency 400.13
S9-11
R = OPMB
f1 (ppm)

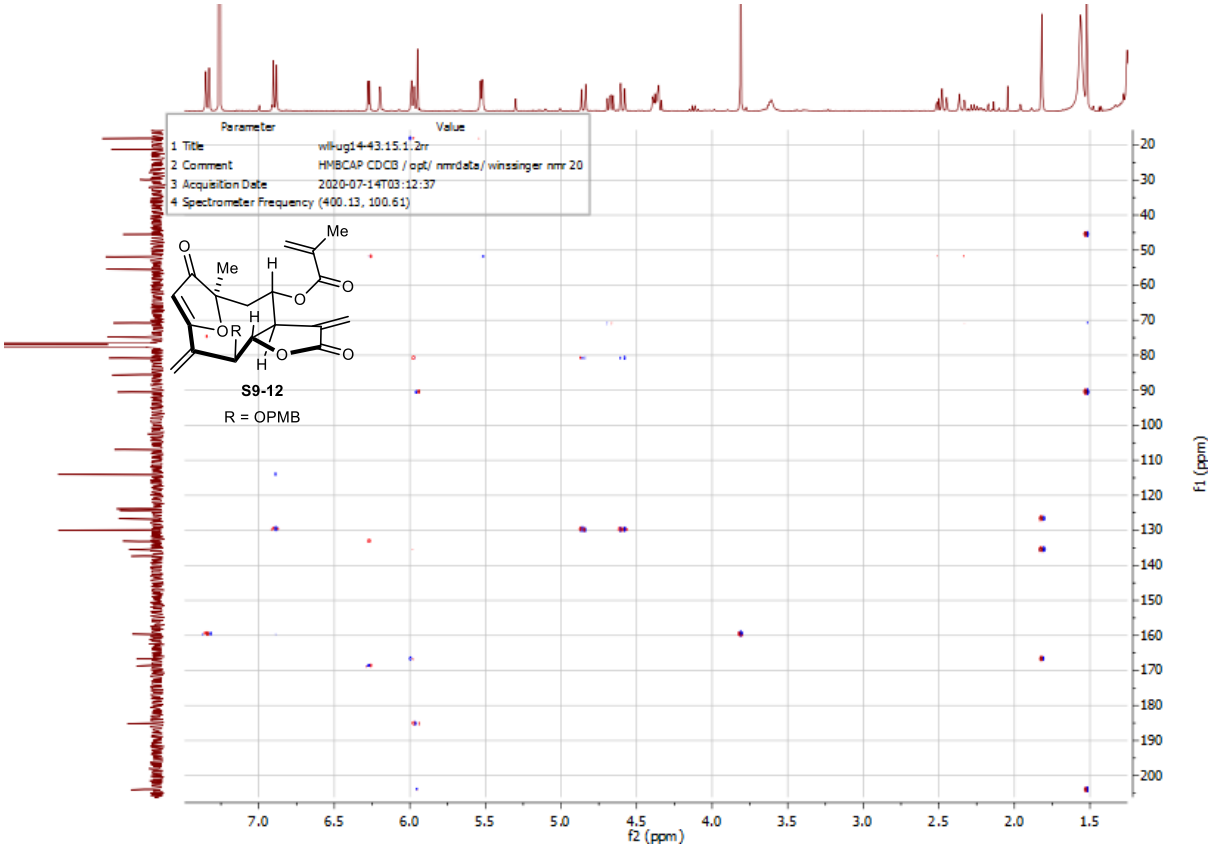

Parameter Value
1 Title wll-ug14-32.11.fid
2 Comment MP_zgpg30 CDCl3 / opt/ nmrdata/ winssinger nmr 23
3 Temperature 298.2
4 Acquisition Date 2020-06-20T21:07:06
5 Spectrometer Frequency 100.62
S9-11
R = OPMB
silicone grease
EA
f1 (ppm)

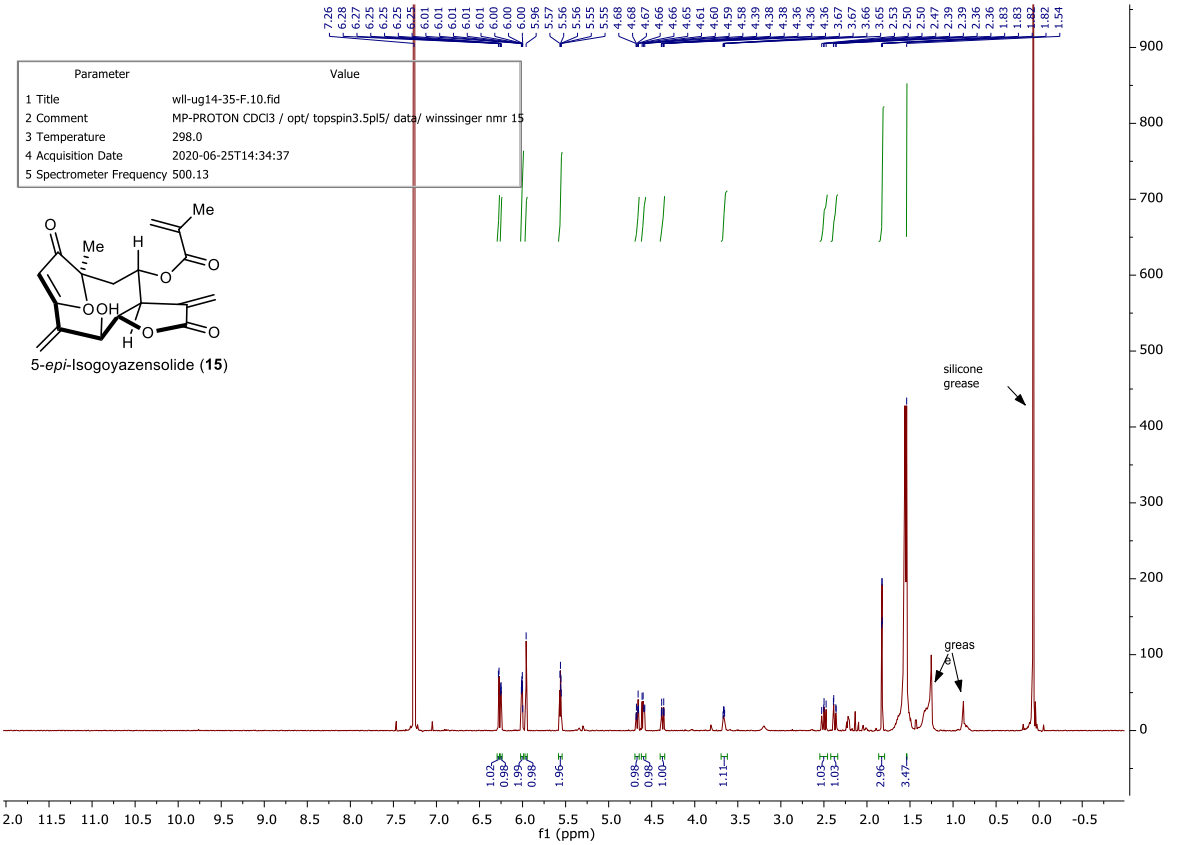

Parameter Value
1 Title wll-ug14-43.10.fid
2 Comment PROTON CDCl3 / opt/ nmrdata/ winssinger nmr 20
3 Temperature 298.2
4 Acquisition Date 2020-07-13T18:11:50
5 Spectrometer Frequency 400.13
Me
O
Me
H
O
O
OR
H
O
O
H
S9-12
R = OPMB
f1 (ppm)

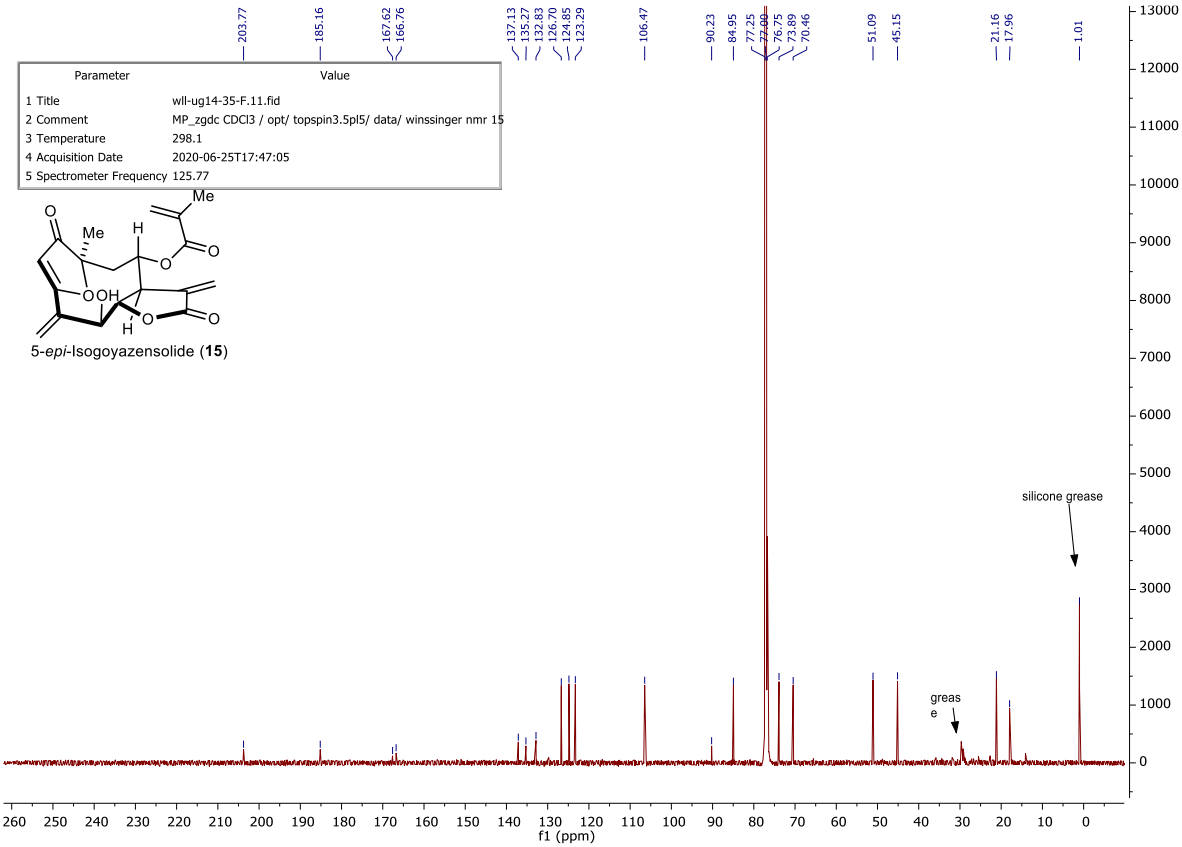

Parameter Value
1 Title wll-ug14-43.11.fid
2 Comment MP_zgpg30 CDCl3 / opt/ nmrdata/ winssinger nmr 20
3 Temperature 298.2
4 Acquisition Date 2020-07-14T23:56:17
5 Spectrometer Frequency 100.62
Me
O
Me
H
O
O
OR
H
O
O
H
S9-12
R = OPMB
silicon grease
f1 (ppm)

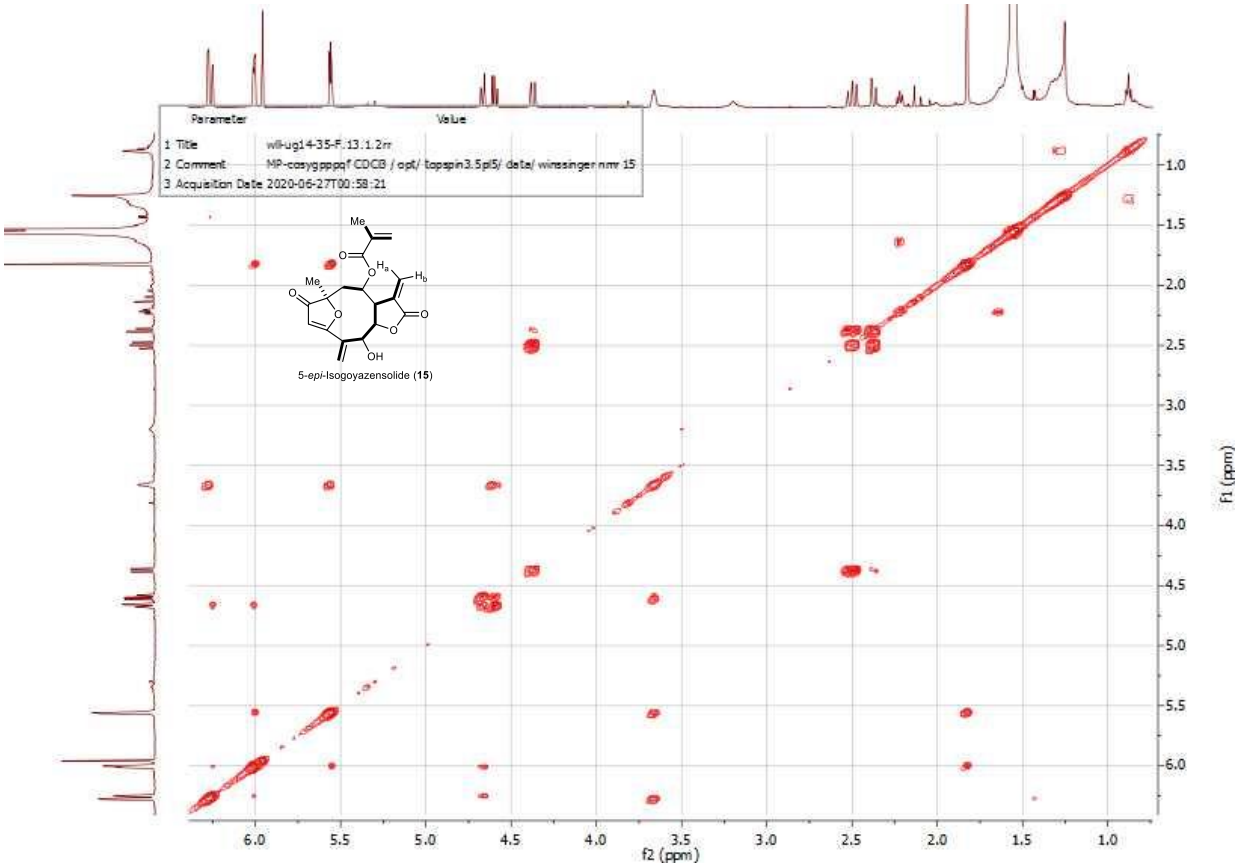

Parameter Value
1 Title wil-ug14-43.13.1.2rr
2 Comment COSYGPSW CDCl3 / opt/ nmrdata/ winssinger nmr 20
3 Acquisition Date 2020-07-13T20:37:07
4 Spectrometer Frequency (400.13, 400.13)
Me
Me
H
O
O
OR
H
O
O
H
S9-12
R = OPMB
f2 (ppm)
f1 (ppm)

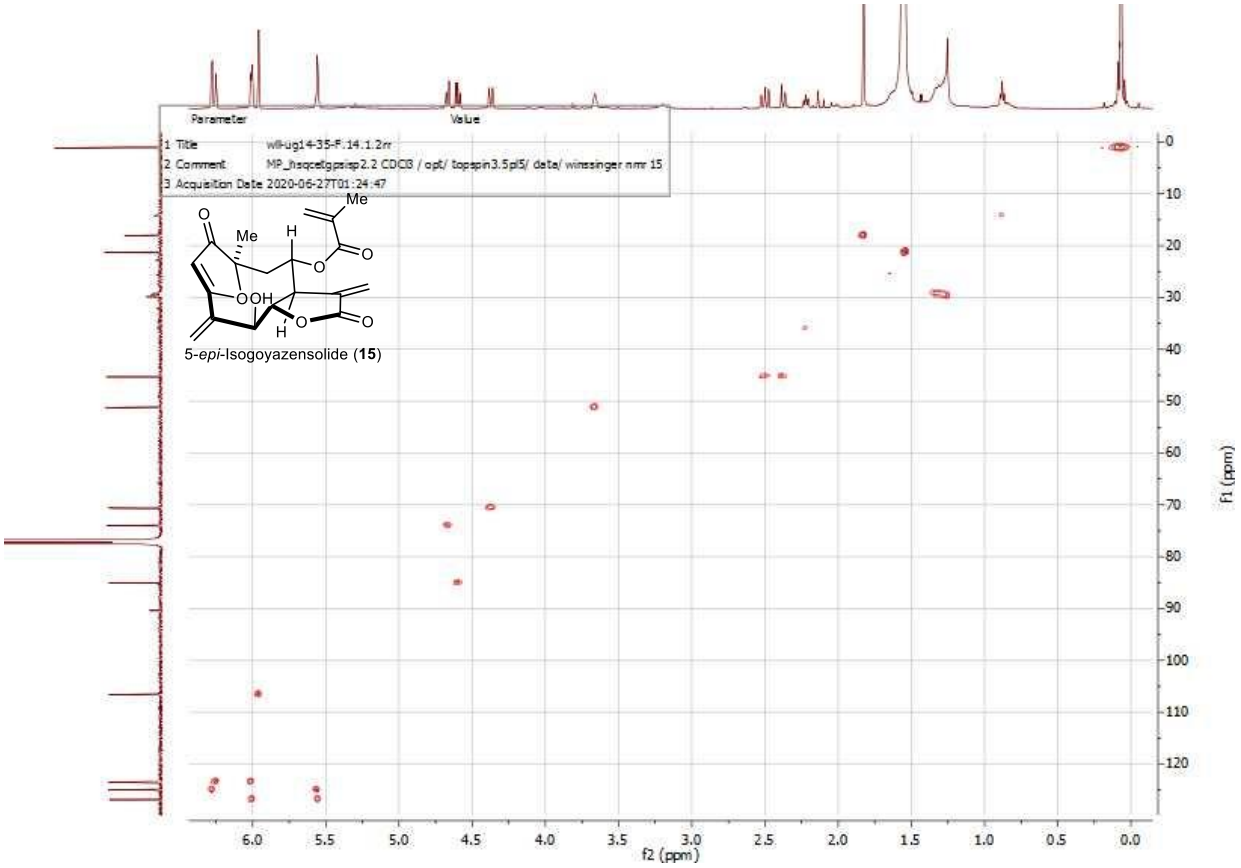

Parameter Value
1 Title wil-ug14-43.14.1.2rr
2 Comment MPHSQC CDCl3 / opt/ nmrdata/ winssinger nmr 20
3 Acquisition Date 2020-07-13T22:42:42
4 Spectrometer Frequency (400.13, 100.61)
Me
Me
H
O
O
OR
H
O
O
H
S9-12
R = OPMB
f2 (ppm)
f1 (ppm)

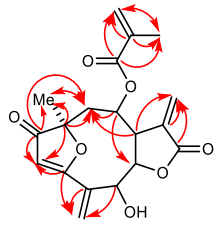

Parameter
Value
1 Title
wlk-ug14-43.15.1.2rr
2 Comment
HMBCAP CDCl3 / opt/ nmrdata/ winssinger nmr 20
3 Acquisition Date
2020-07-14T03:12:37
4 Spectrometer Frequency (400.13, 100.61)
Me
O
Me
H
O
OR
H
H
O
O
S9-12
R = OPMB
f1 (ppm)
f2 (ppm)


Parameter Value
1 Title wll-ug14-35-F.10.fid
2 Comment MP-PROTON CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Temperature 298.0
4 Acquisition Date 2020-06-25T14:34:37
5 Spectrometer Frequency 500.13
5-epi-Isogoyazensolide (15)
silicone grease
greas e
f1 (ppm)

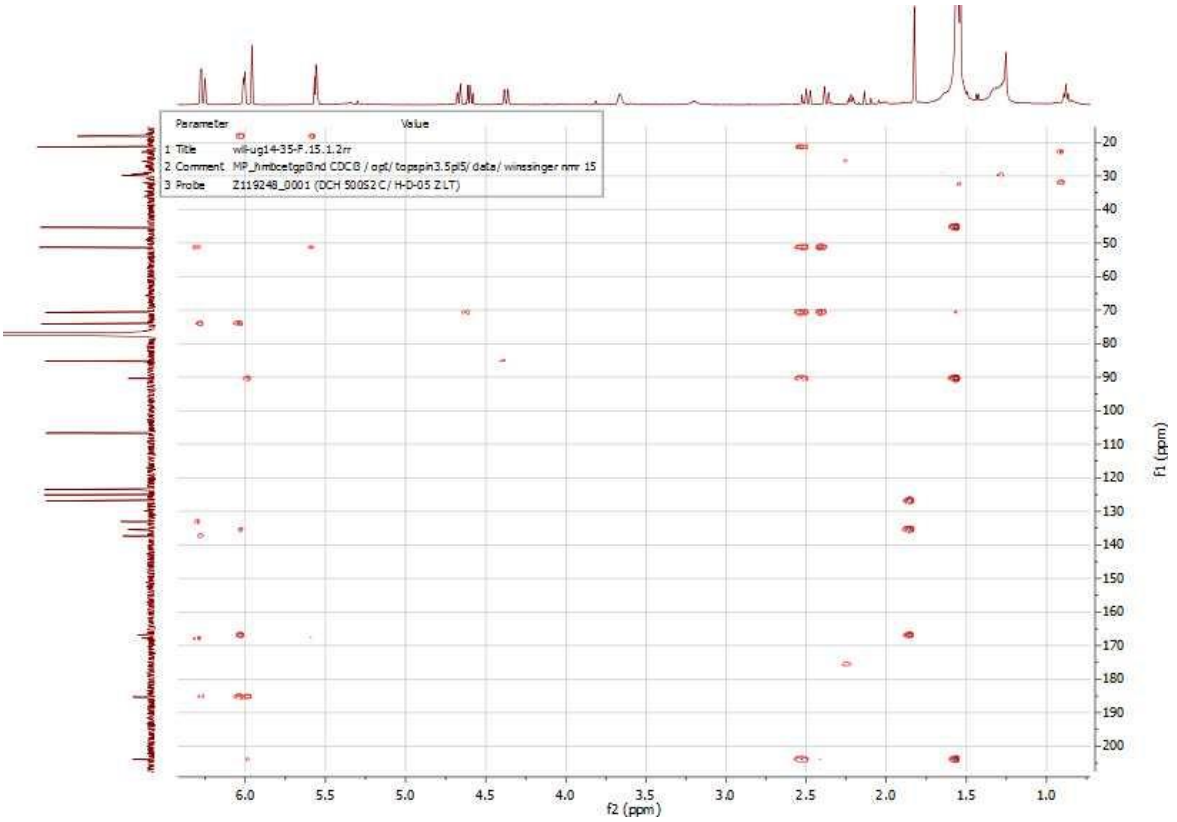

Parameter Value
1 Title wll-ug14-35-F.11.fid
2 Comment MP_zgdc CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Temperature 298.1
4 Acquisition Date 2020-06-25T17:47:05
5 Spectrometer Frequency 125.77
5-epi-Isogoyazensolide (15)
silicone grease
greas e
f1 (ppm)

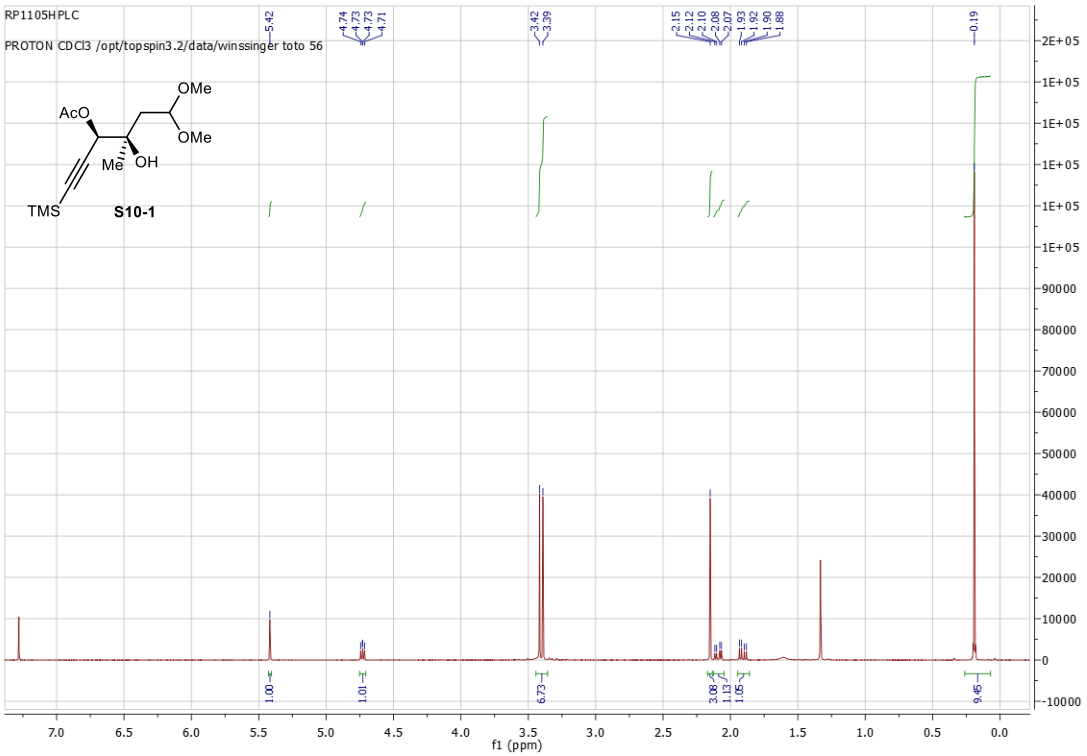

Parameter
Value
1 Title
wll-ug14-35-F:13:1.2rr
2 Comment
MP-cosygpppqf CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Acquisition Date 2020-06-27T00:58:21
5-epi-Isogoyazensolide (15)
f2 (ppm)
f1 (ppm)

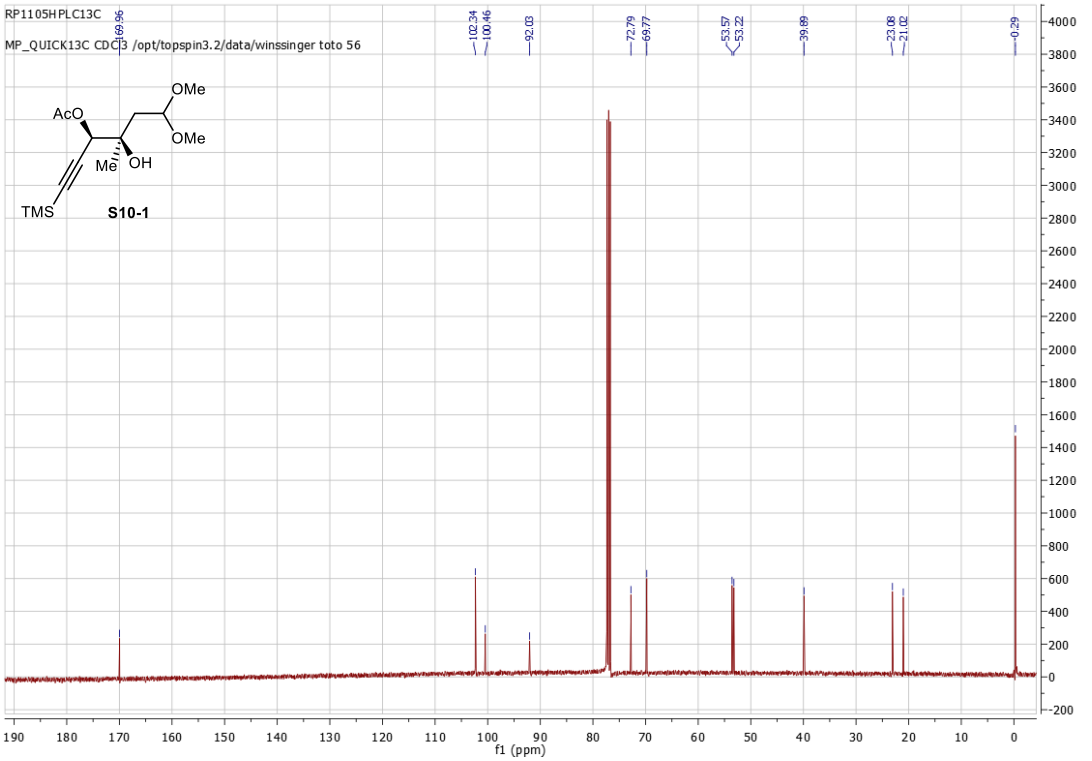

Parameter
Value
1 Title
wll-ug14-35-F:14:1.2rr
2 Comment
MP_hsqcetgpsisp2.2 CDCl3 / opt/ topspin3.5pl5/ data/ winssinger nmr 15
3 Acquisition Date 2020-06-27T01:24:47
5-epi-Isogoyazensolide (15)
f2 (ppm)
f1 (ppm)

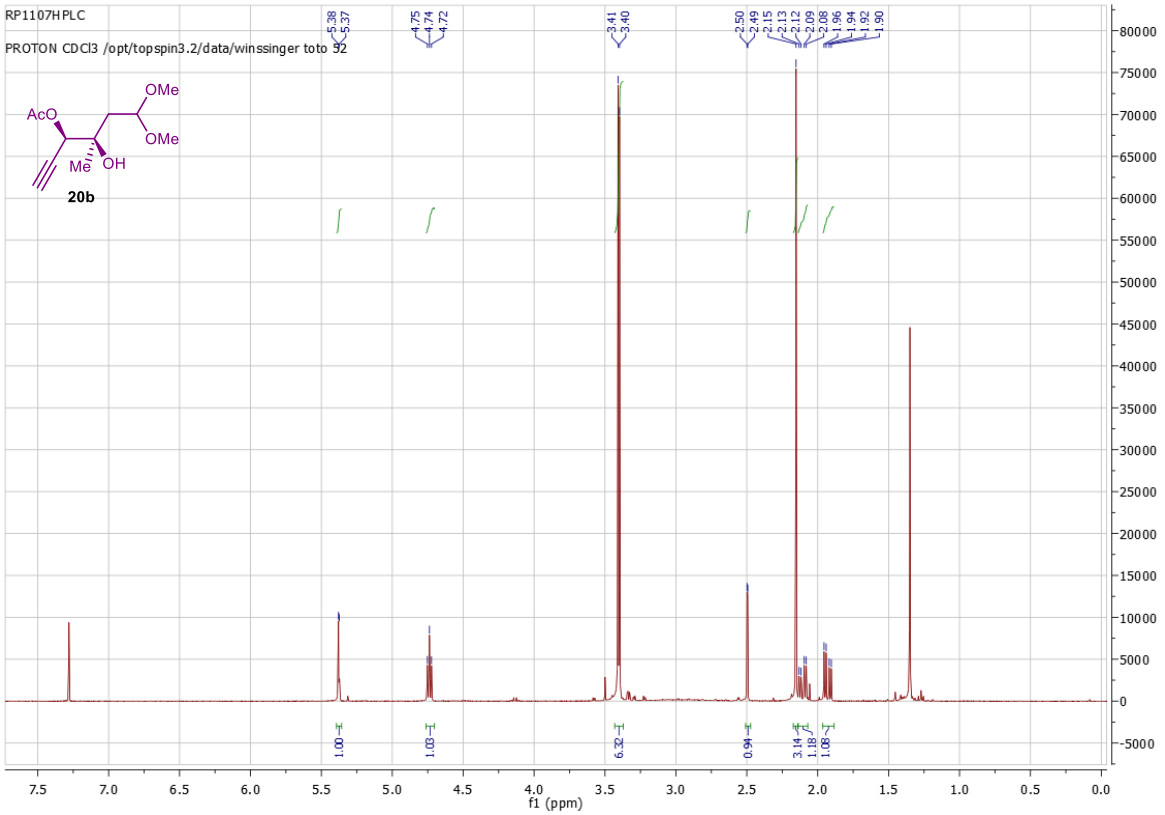


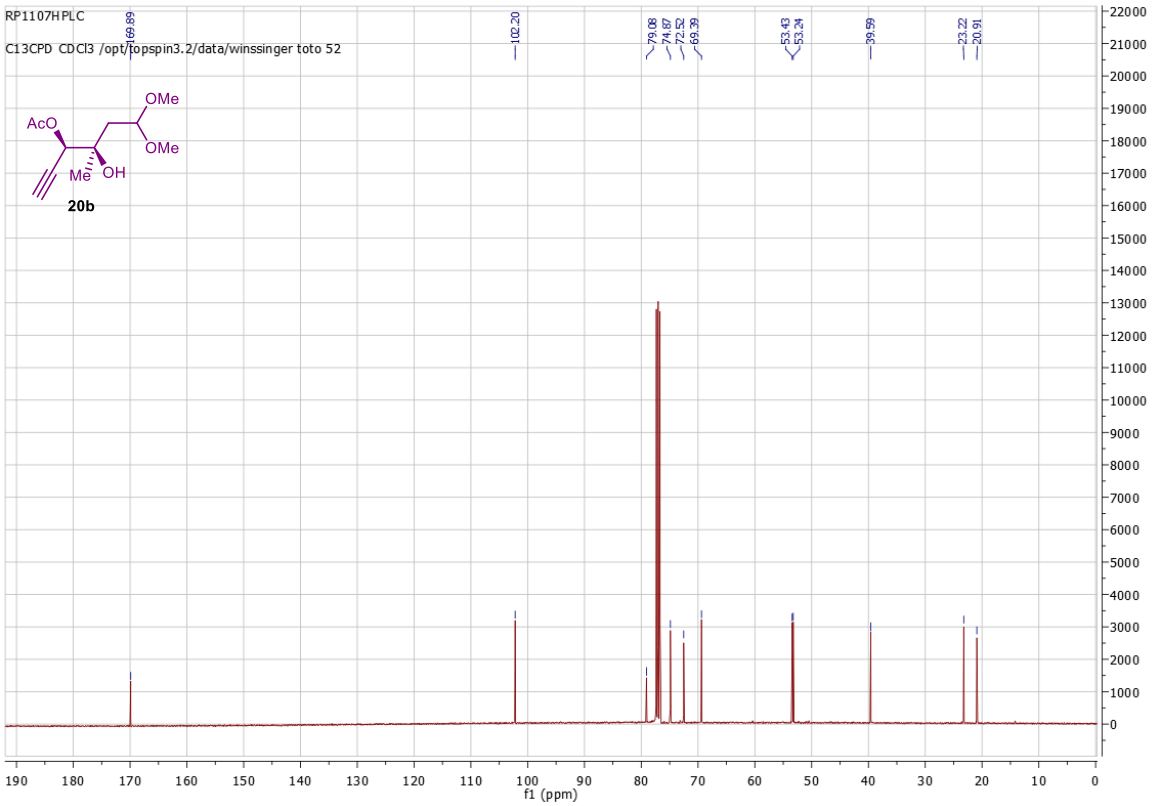
5-*epi*-Isogoyazensolide (**15**)

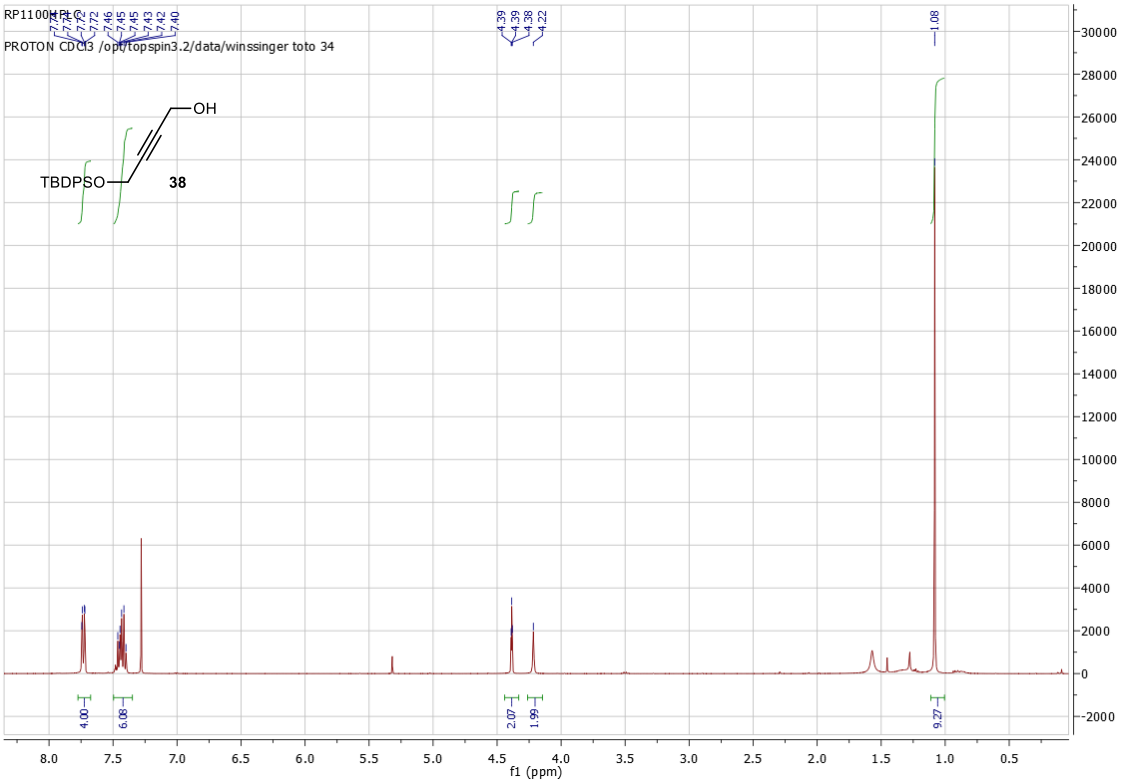


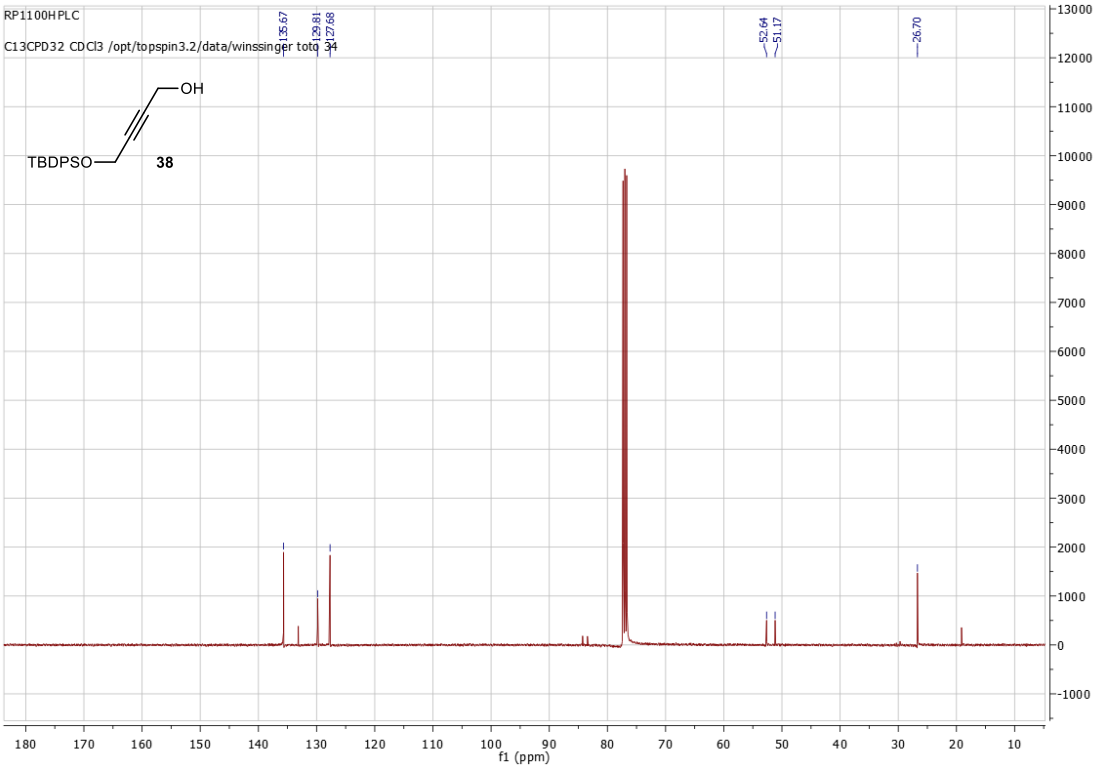

RP1105HPLC
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 56
AcO
OMe
OMe
Me
OH
TMS
S10-1
f1 (ppm)

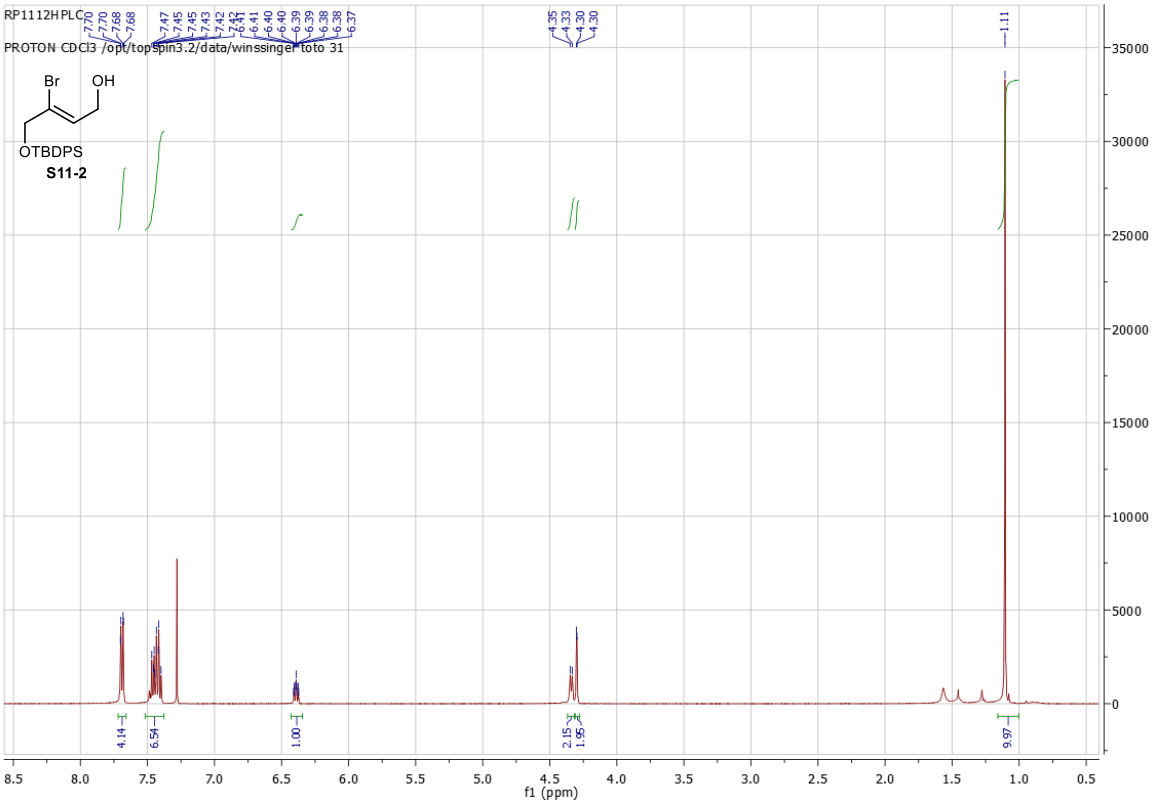

RP1105HPLC13C
MP_QUICK13C CDCl3 /opt/topspin3.2/data/winssinger toto 56
AcO
OMe
OMe
Me
OH
TMS
S10-1
f1 (ppm)

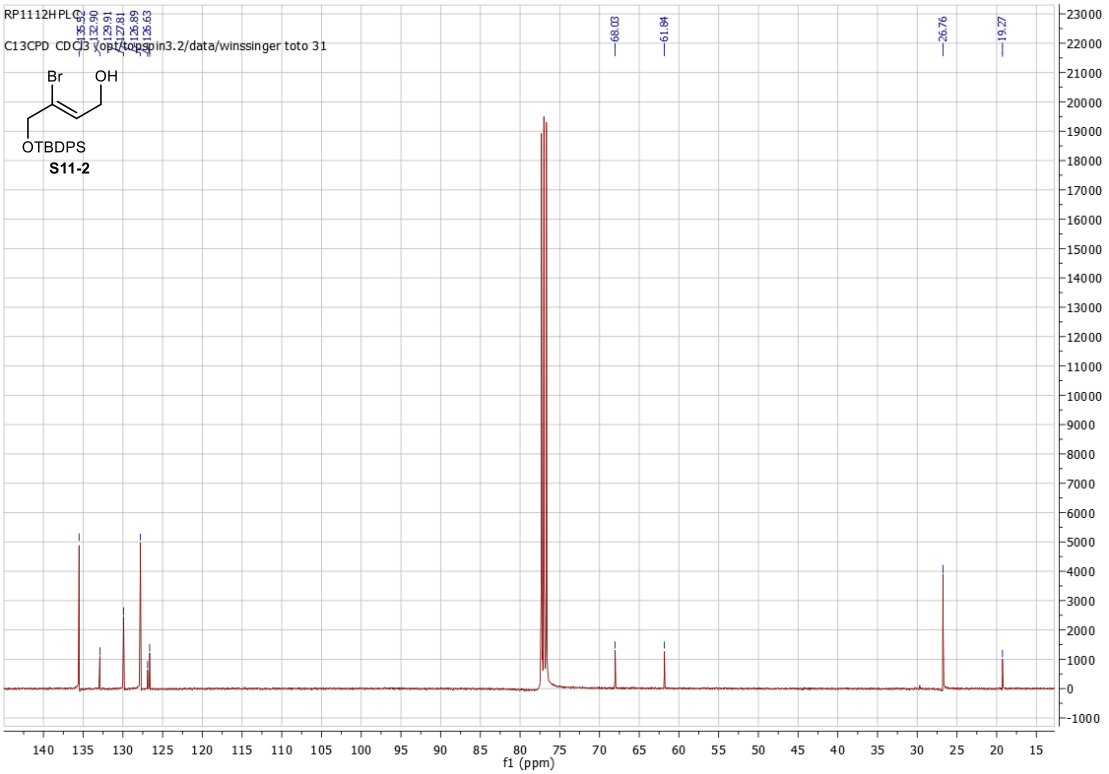

RP1107HPLC
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 52
AcO
OMe
OMe
Me
OH
20b
f1 (ppm)

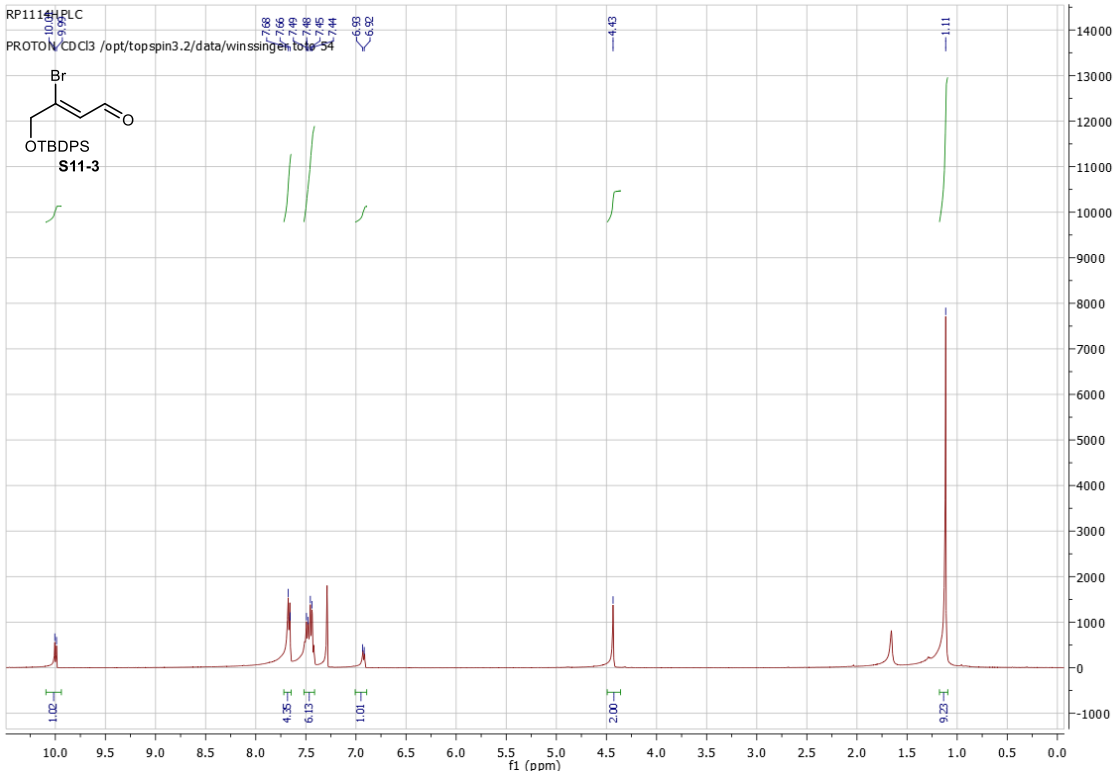

RP1107HPLC
C13CPD CDCl3 /opt/topspin3.2/data/winssinger toto 52
AcO
OMe
OMe
Me
OH
20b
f1 (ppm)

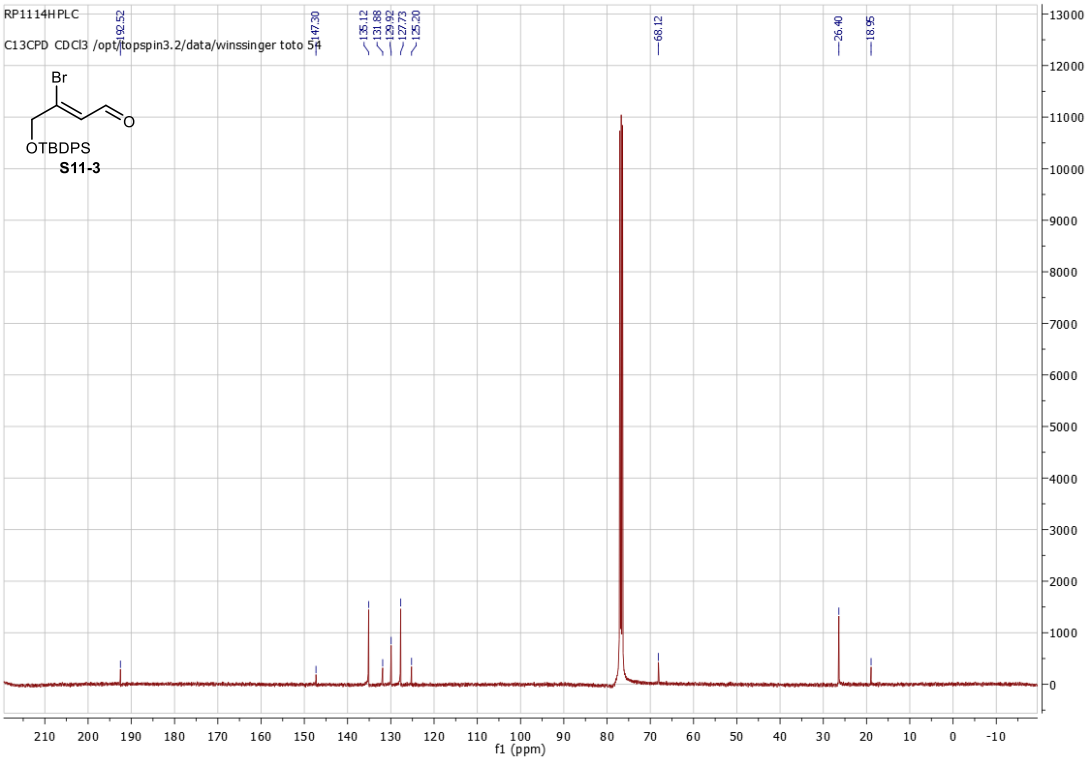

RP1100HPLC
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 34
OH
TBDPSO
38
f1 (ppm)

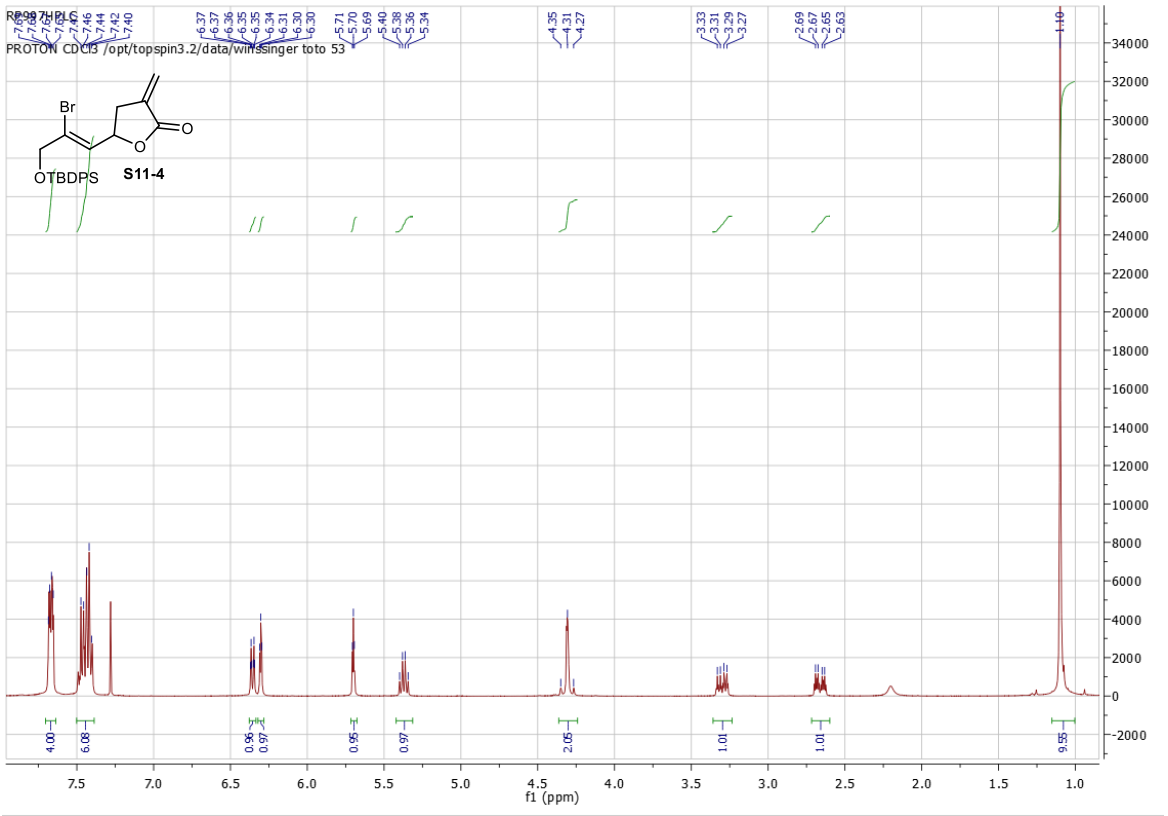

RP1100HPLC
C13CPD32 CDCl3 /opt/topspin3.2/data/winssinger toto 34
OH
TBDPSO
38
f1 (ppm)

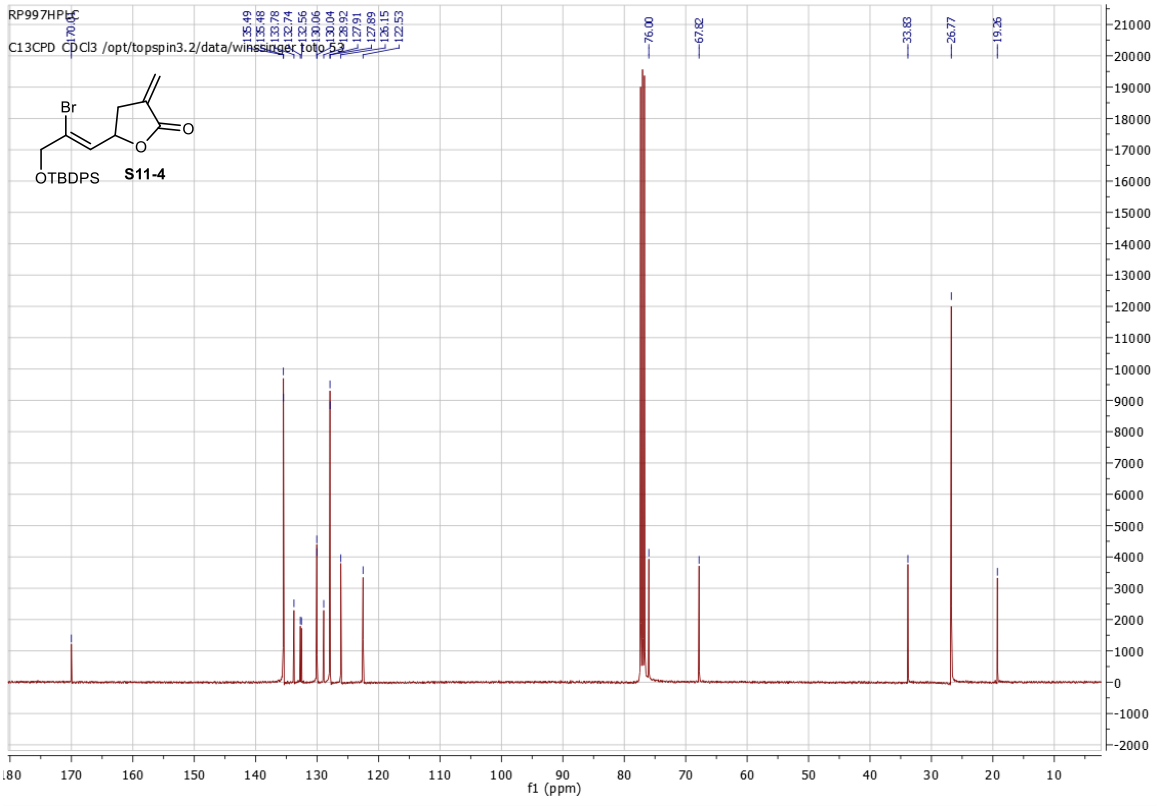

RP1112HPLC
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 31
Br
OH
OTBDPS
S11-2
f1 (ppm)

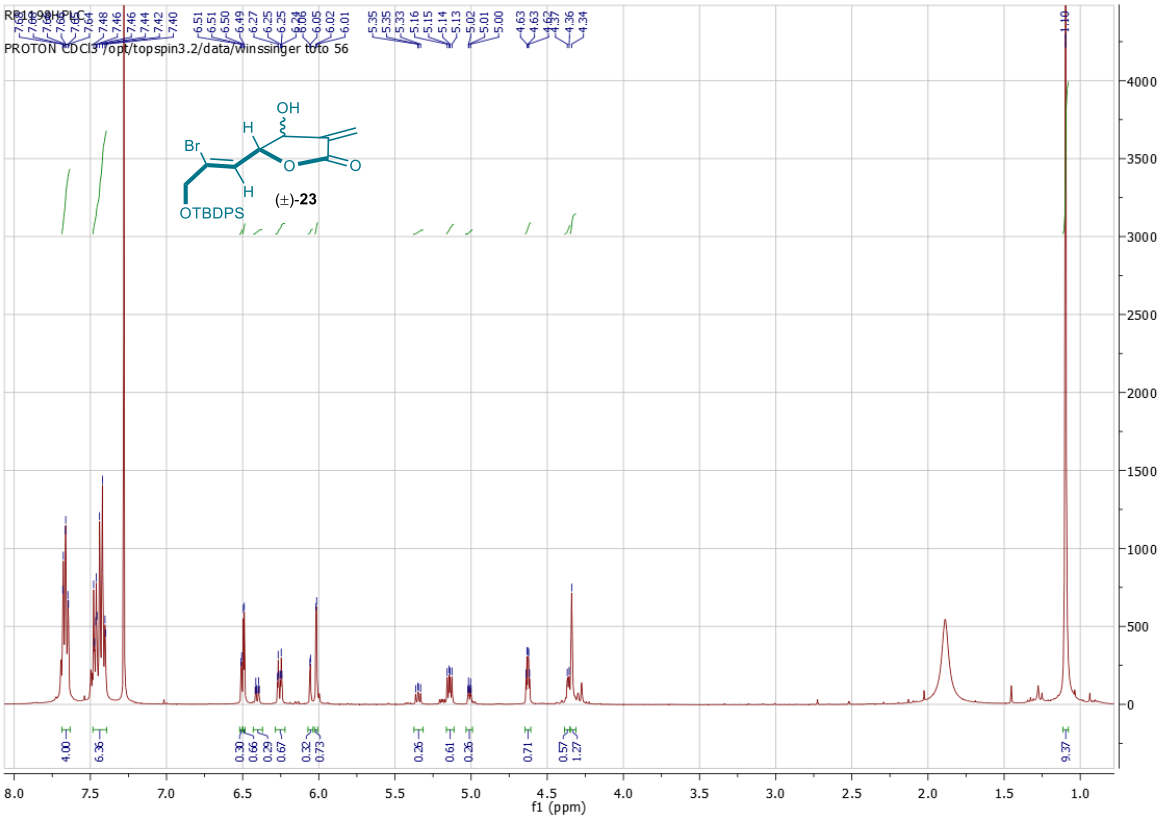

RP1112HPLC
C13CPD CDCl3 /opt/topspin3.2/data/winssinger toto 31
Br
OH
OTBDPS
S11-2
f1 (ppm)

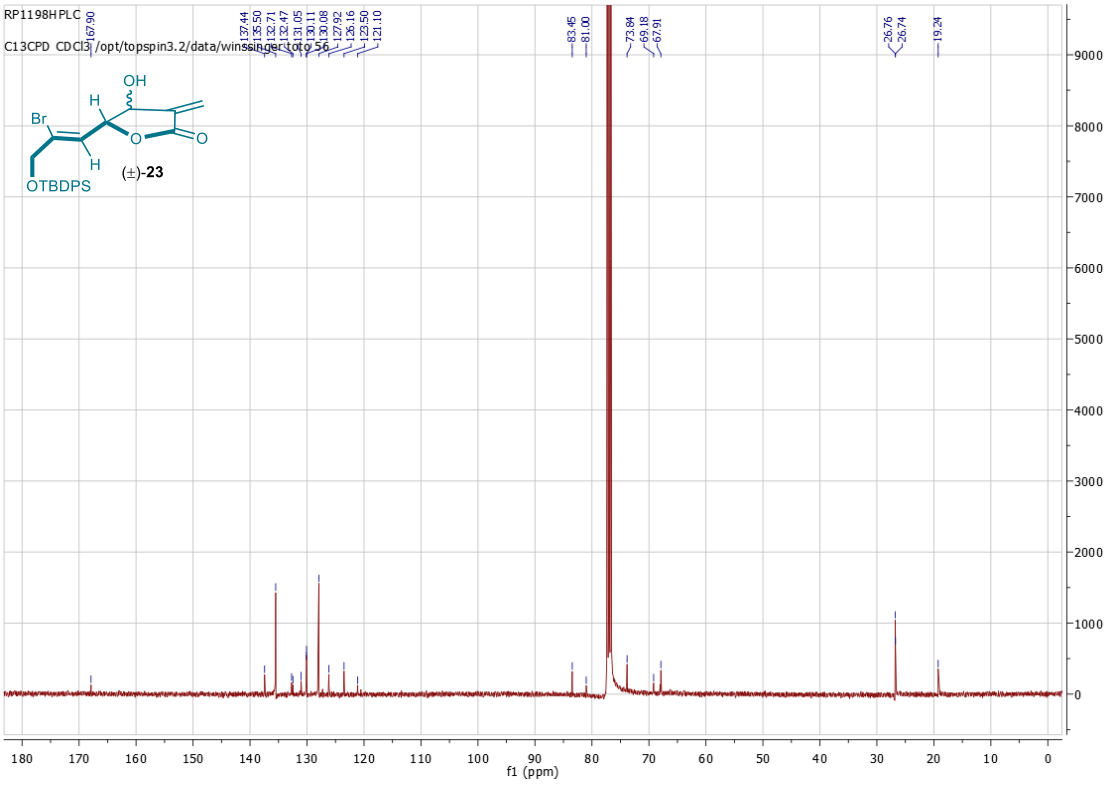

RP1114HPLC
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 54
Br
OTBDPS
S11-3
10.02
9.95
7.68
7.66
7.49
7.48
7.45
7.44
6.93
6.92
4.43
1.11
1.02
4.35
6.13
1.01
2.00
9.23
f1 (ppm)

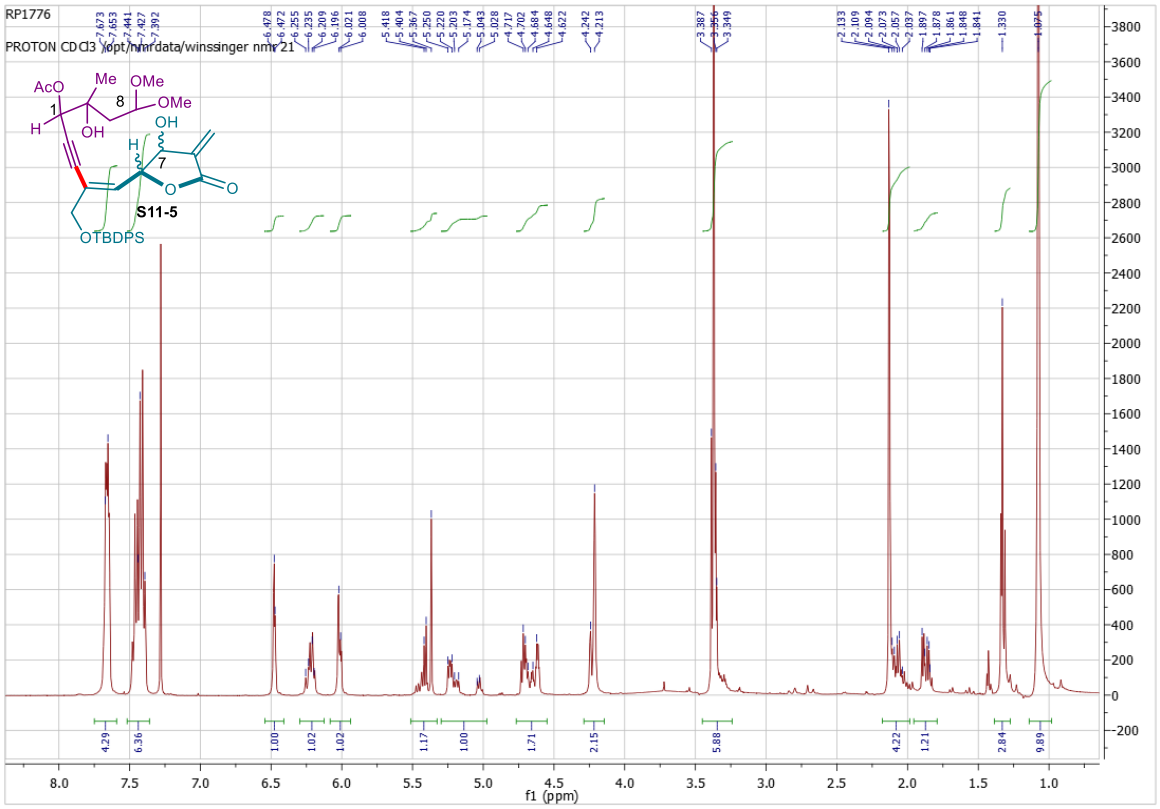

RP1114HPLC
C13CPD CDCl3 /opt/topspin3.2/data/winssinger toto 54
Br
OTBDPS
S11-3
192.52
147.30
135.12
131.88
129.92
127.73
125.20
68.12
26.40
18.95
f1 (ppm)

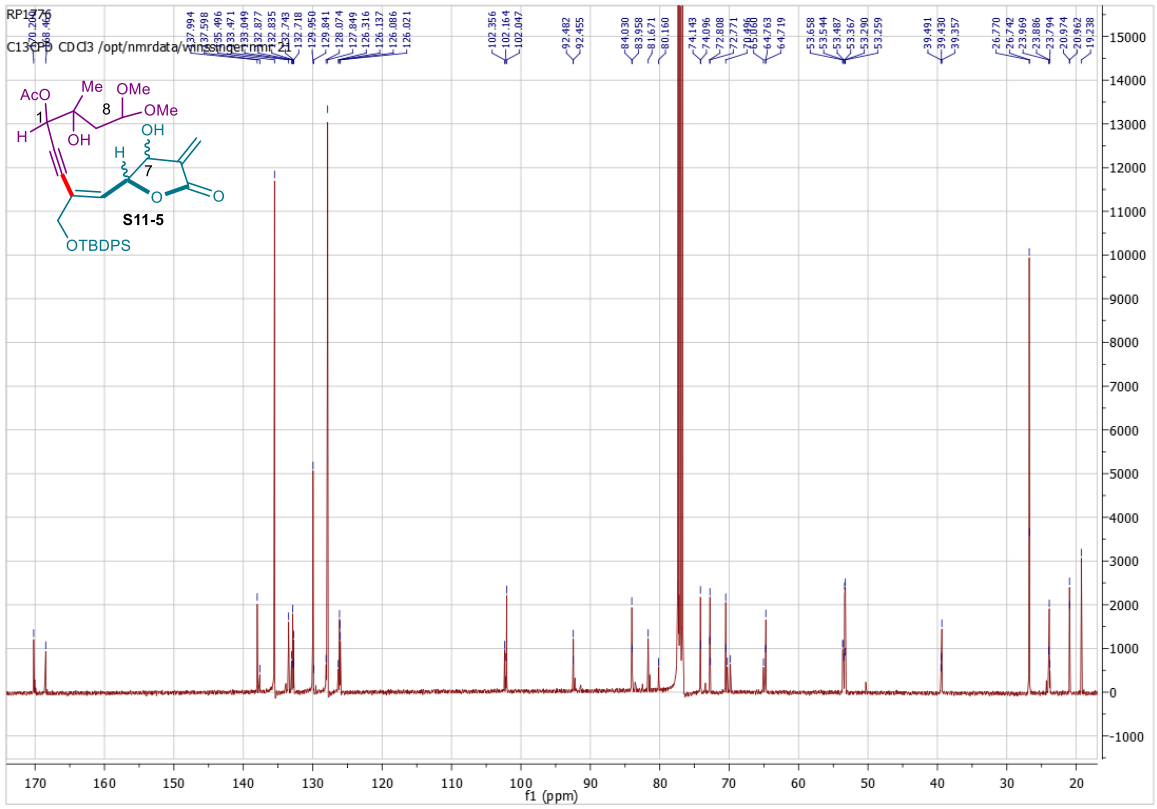

RP997HPLC
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 53
Br
O
O
OTBDPS
S11-4
f1 (ppm)

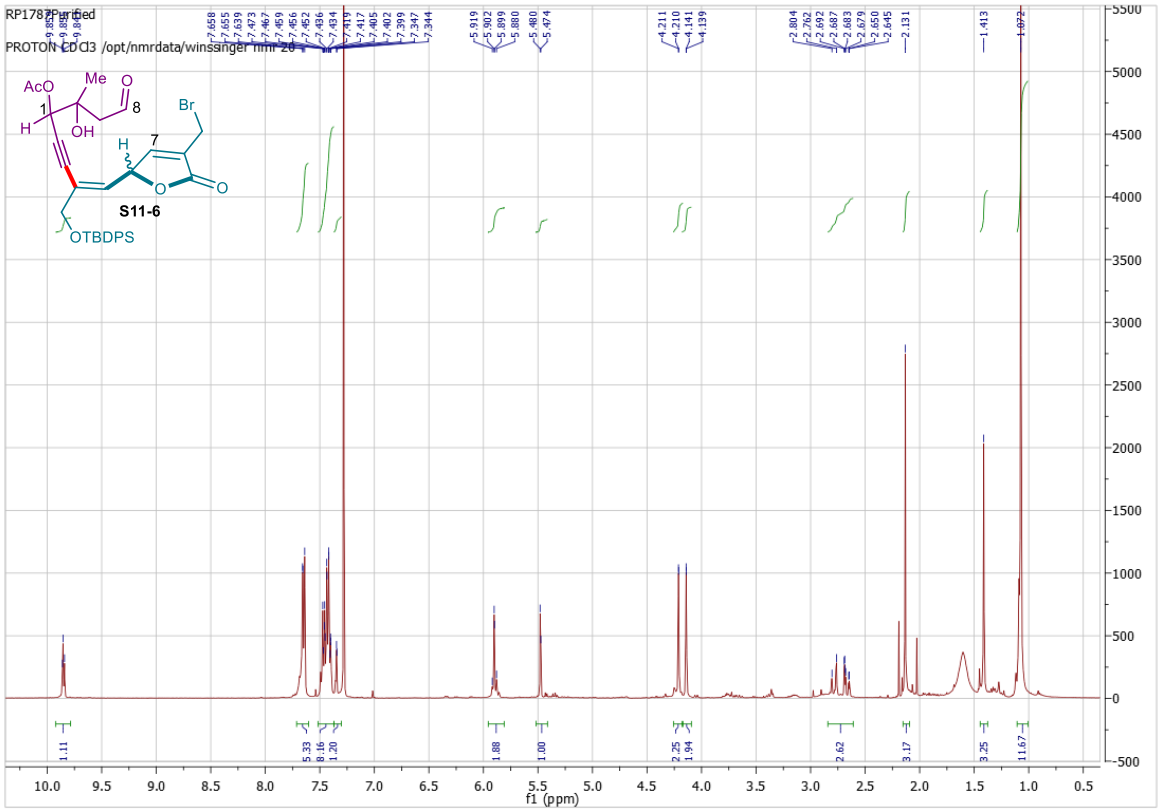

RP997HPLC
C13CPD CDCl3 /opt/topspin3.2/data/winssinger toto 53
Br
O
O
OTBDPS
S11-4
f1 (ppm)

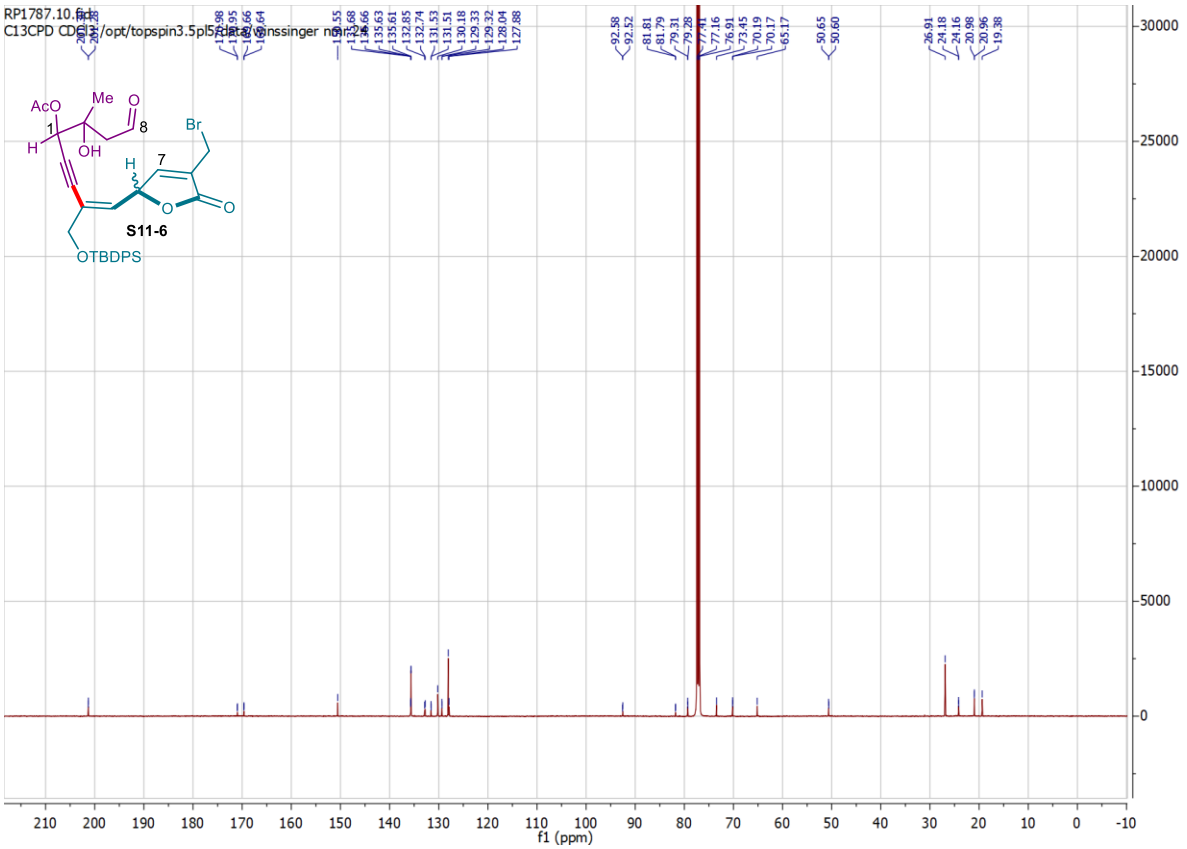

RP1198HPLC
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 56
OH
H
Br
O
O
H
OTBDPS
(±)-23
f1 (ppm)

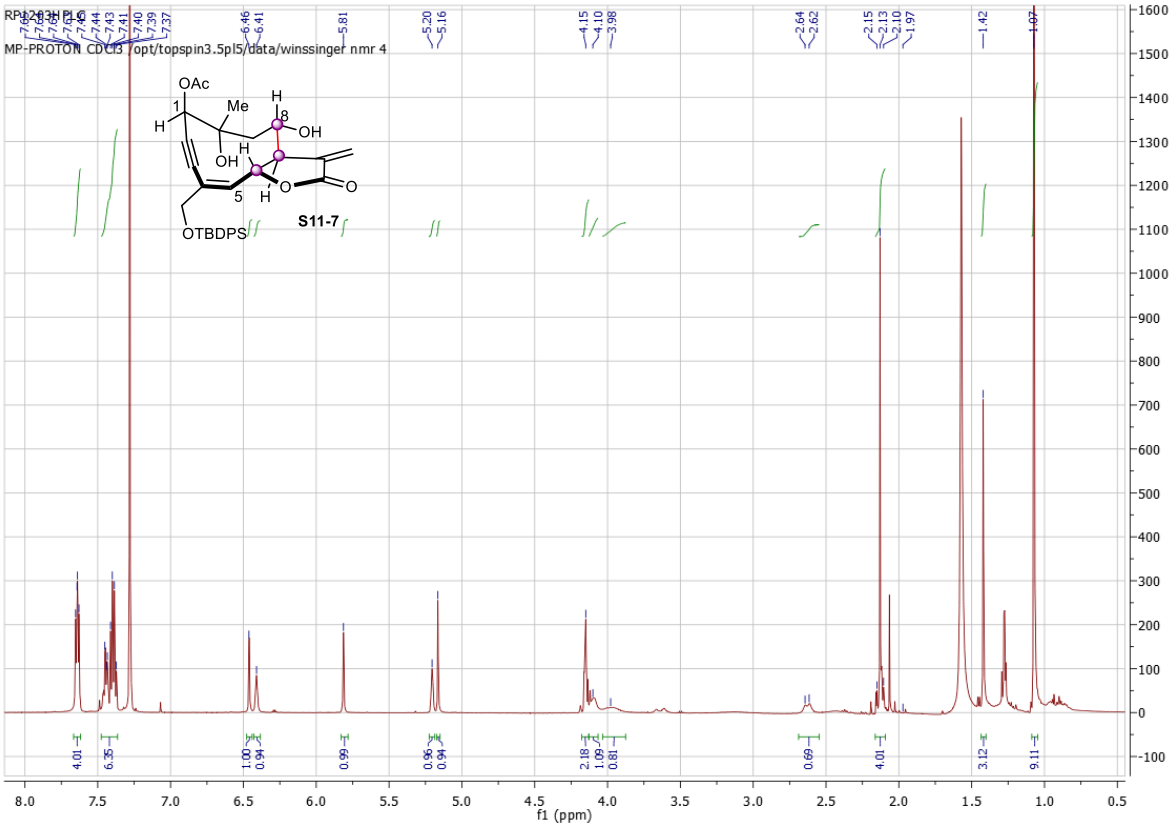

RP1198HPLC
C13CPD CDCl3 /opt/topspin3.2/data/winssinger toto 56
OH
H
Br
O
O
H
OTBDPS
(±)-23
f1 (ppm)

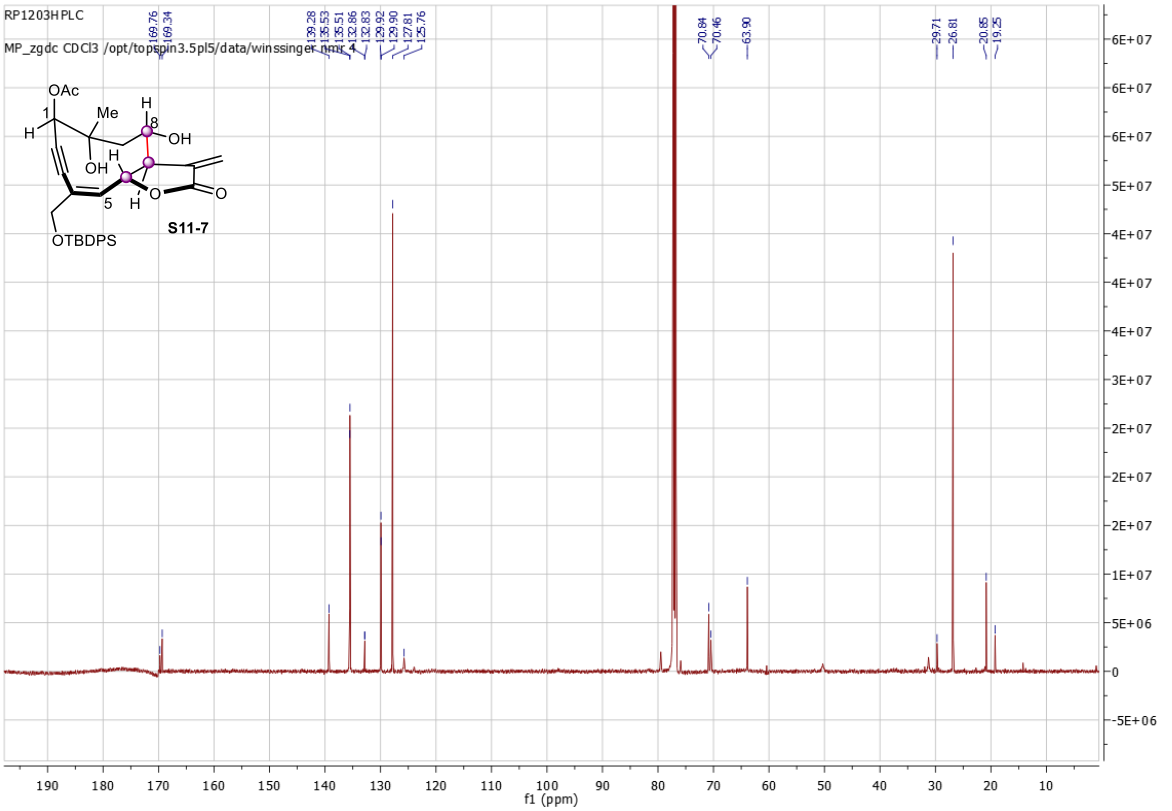

RP1776
PROTON CDCl3 /opt/nmrdata/winssinger nmr 21
AcO
Me
OMe
OMe
OH
H
OH
H
7
O
O
1
8
S11-5
OTBDPS
f1 (ppm)

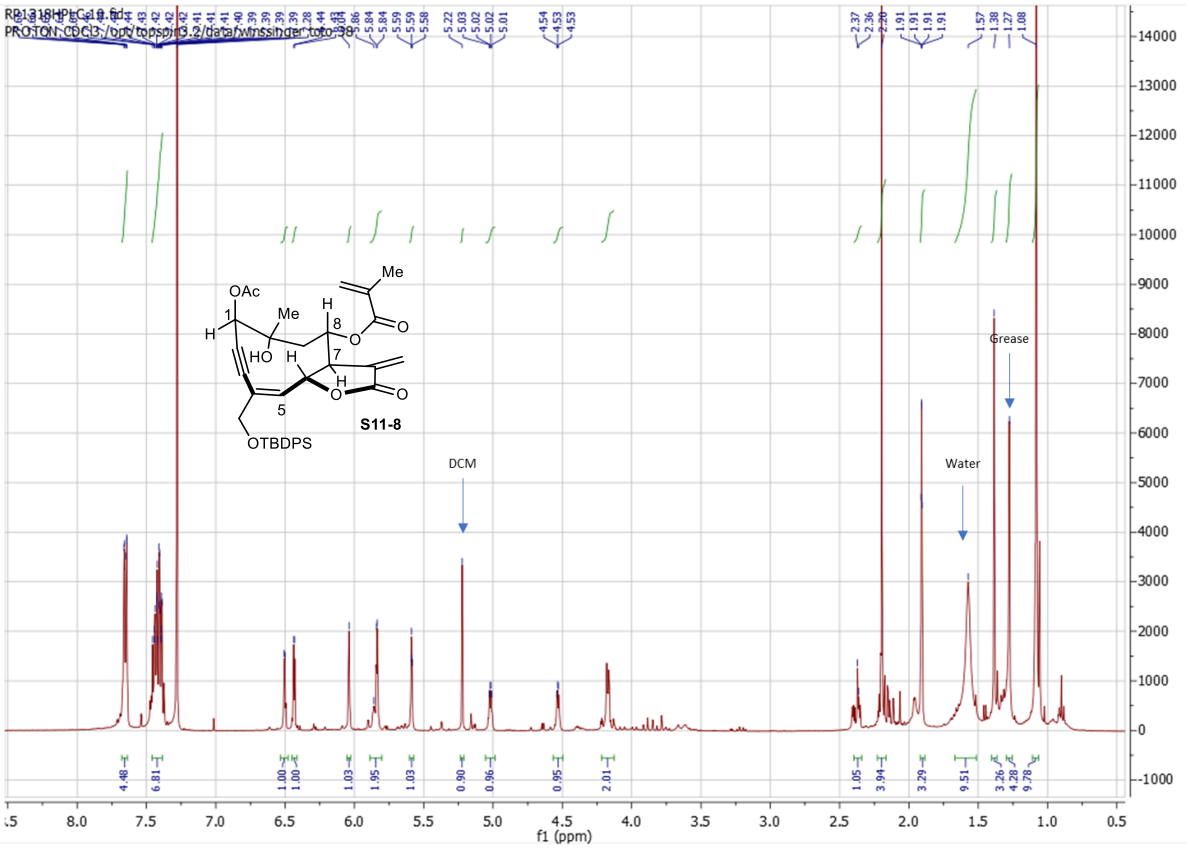

RP1776
C13CPD CDCl3 /opt/nmrdata/winssinger nmr 21
AcO
Me
OMe
OMe
OH
H
OH
H
7
O
O
1
8
S11-5
OTBDPS
f1 (ppm)

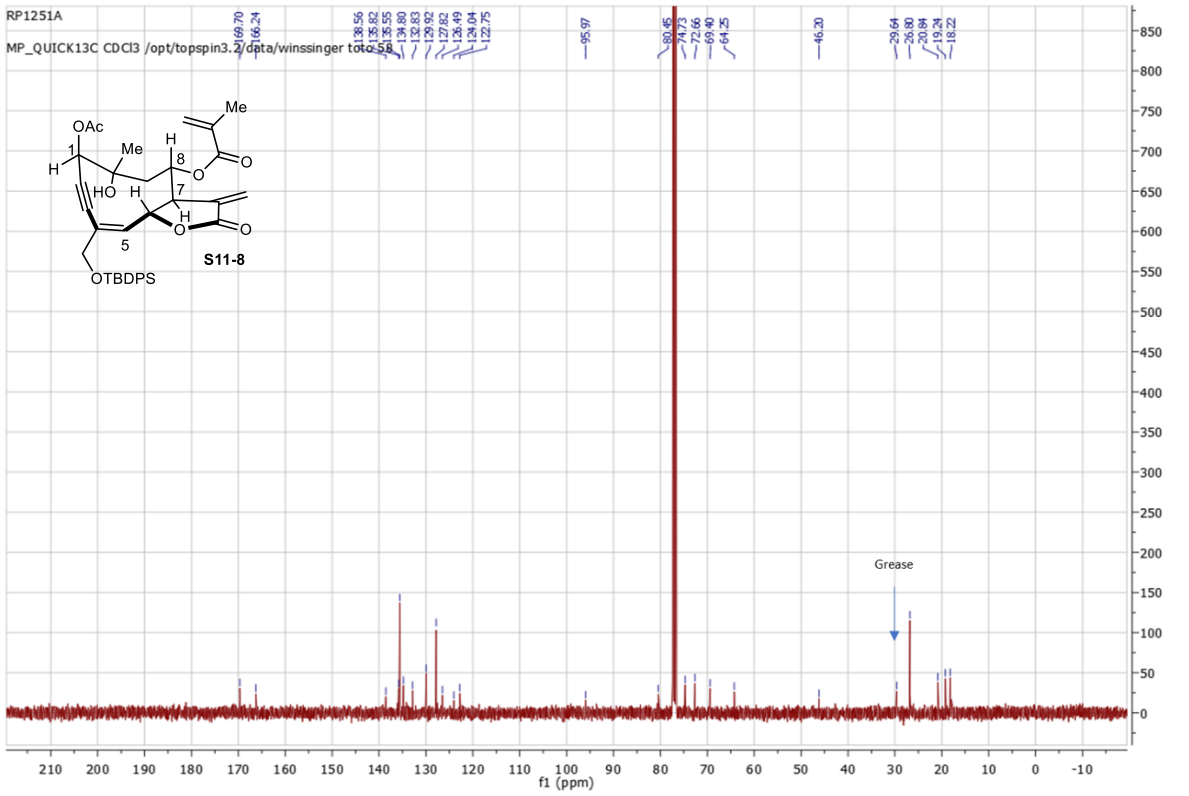

RP1787Purified
PROTON-CDCl3 /opt/nmrdata/winssinger nmr 26
AcO
Me
O
1
8
Br
H
OH
H
7
O
O
S11-6
OTBDPS
f1 (ppm)

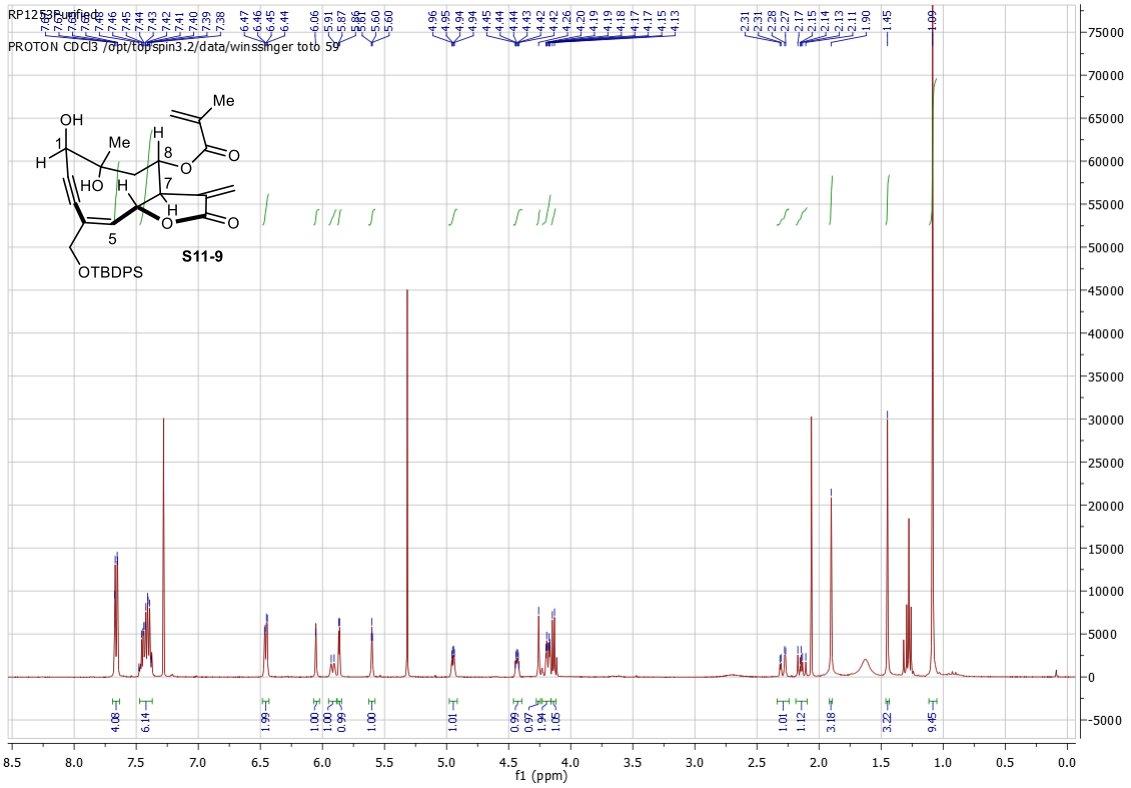

RP1787.10.fid
C13CPD CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 24
AcO
Me
O
1
8
Br
H
OH
H
7
O
O
S11-6
OTBDPS
f1 (ppm)

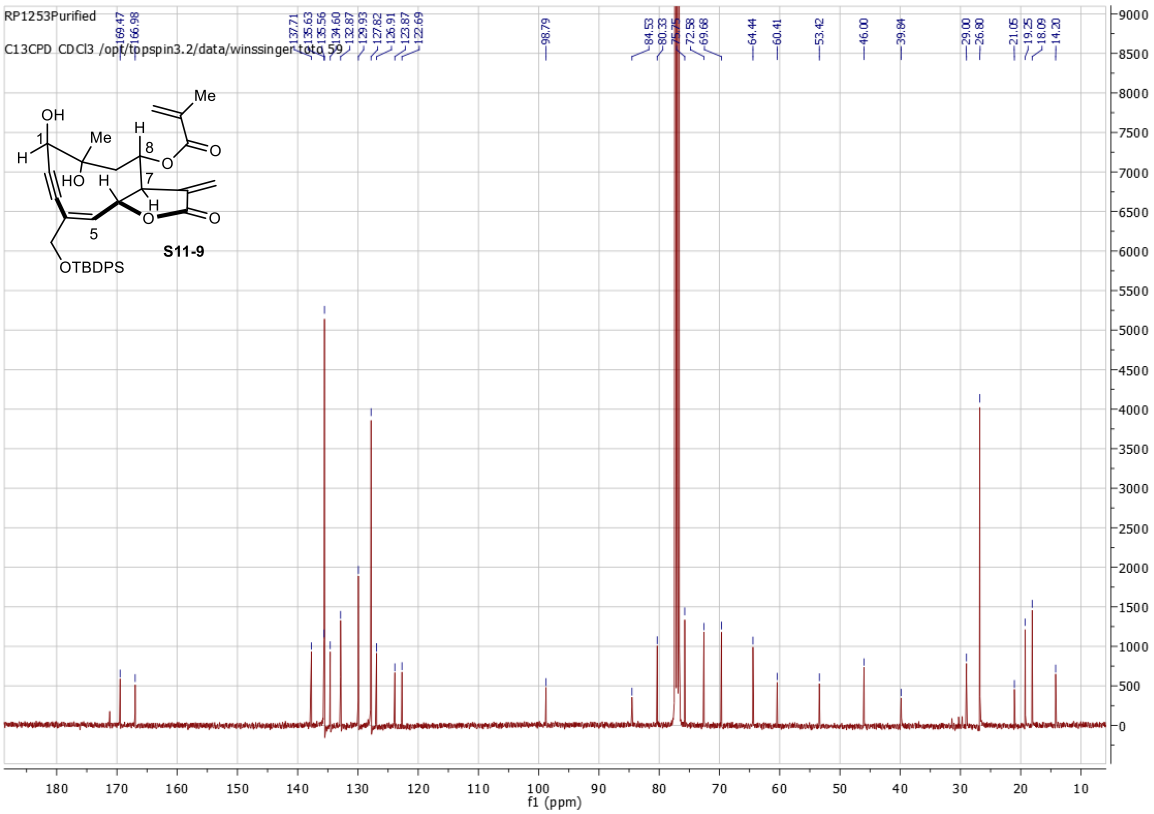

RP1203HPLC
MP-PROTON CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 4
OAc
Me
H
OH
OH
H
O
O
H
OTBDPS
S11-7
f1 (ppm)

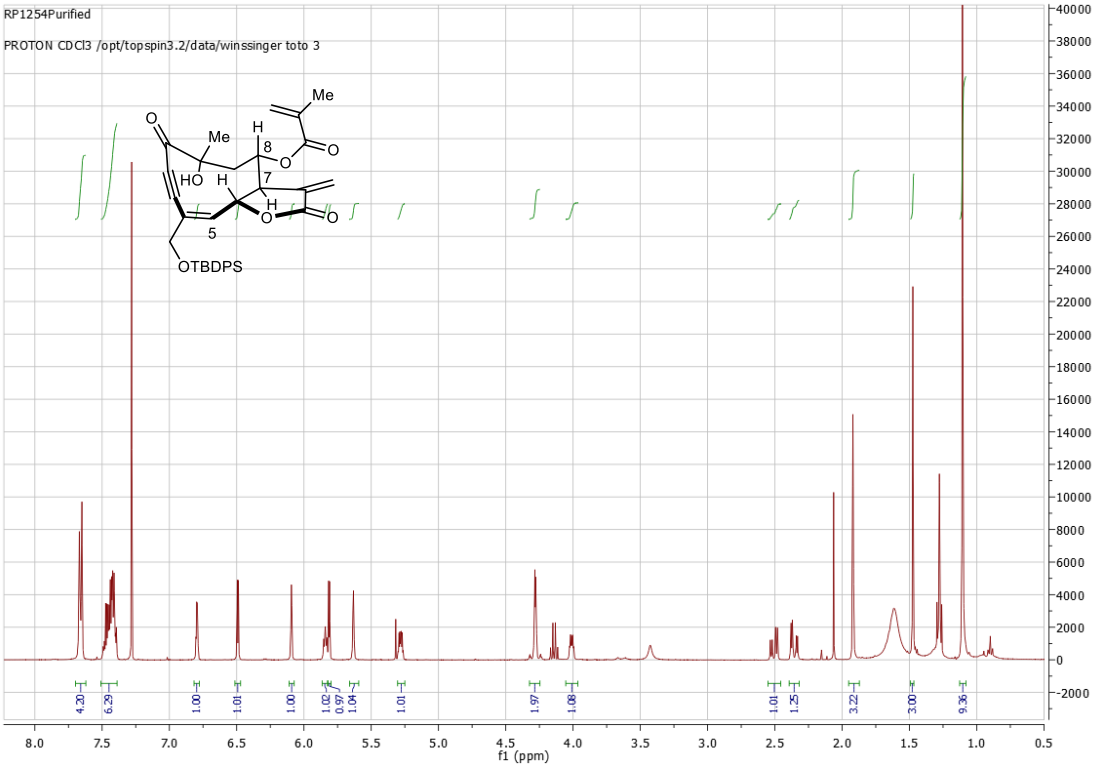

RP1203HPLC
MP_zgdc CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 4
OAc
Me
H
OH
OH
H
O
O
H
OTBDPS
S11-7
f1 (ppm)

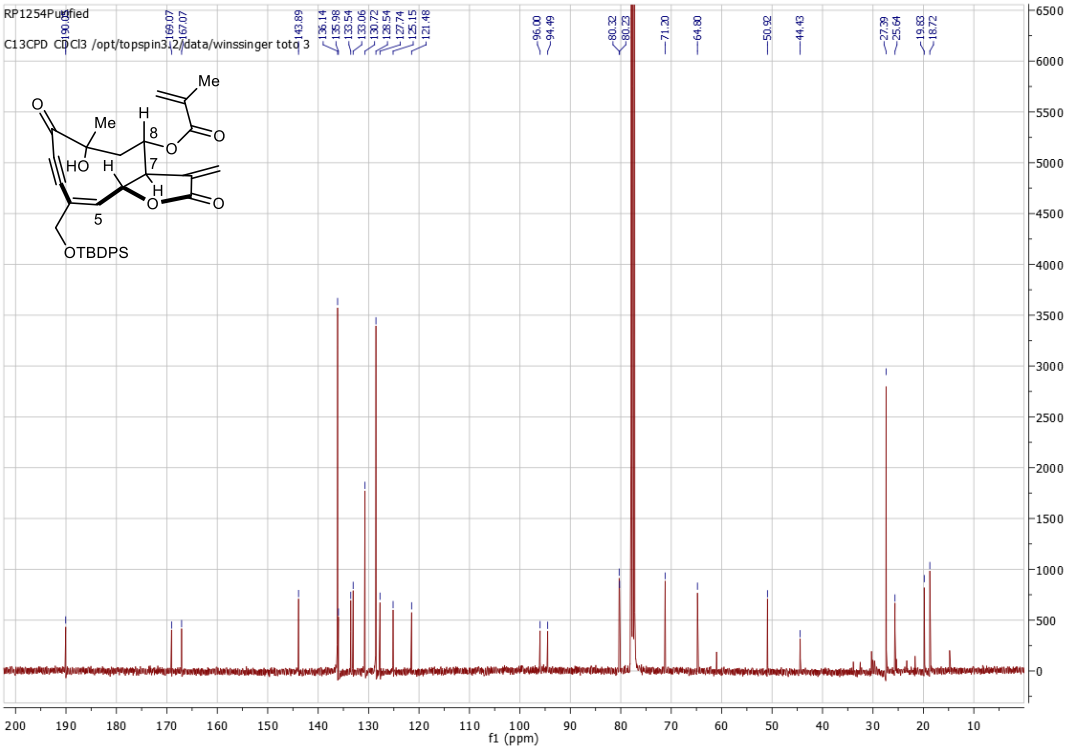

PROTON CDCl3 /opt/topspin3.2/data/winssinger toto-38
OAc
Me
H
1
Me
8
H
HO
H
7
O
O
H
O
5
OTBDPS
S11-8
DCM
Water
Grease
f1 (ppm)

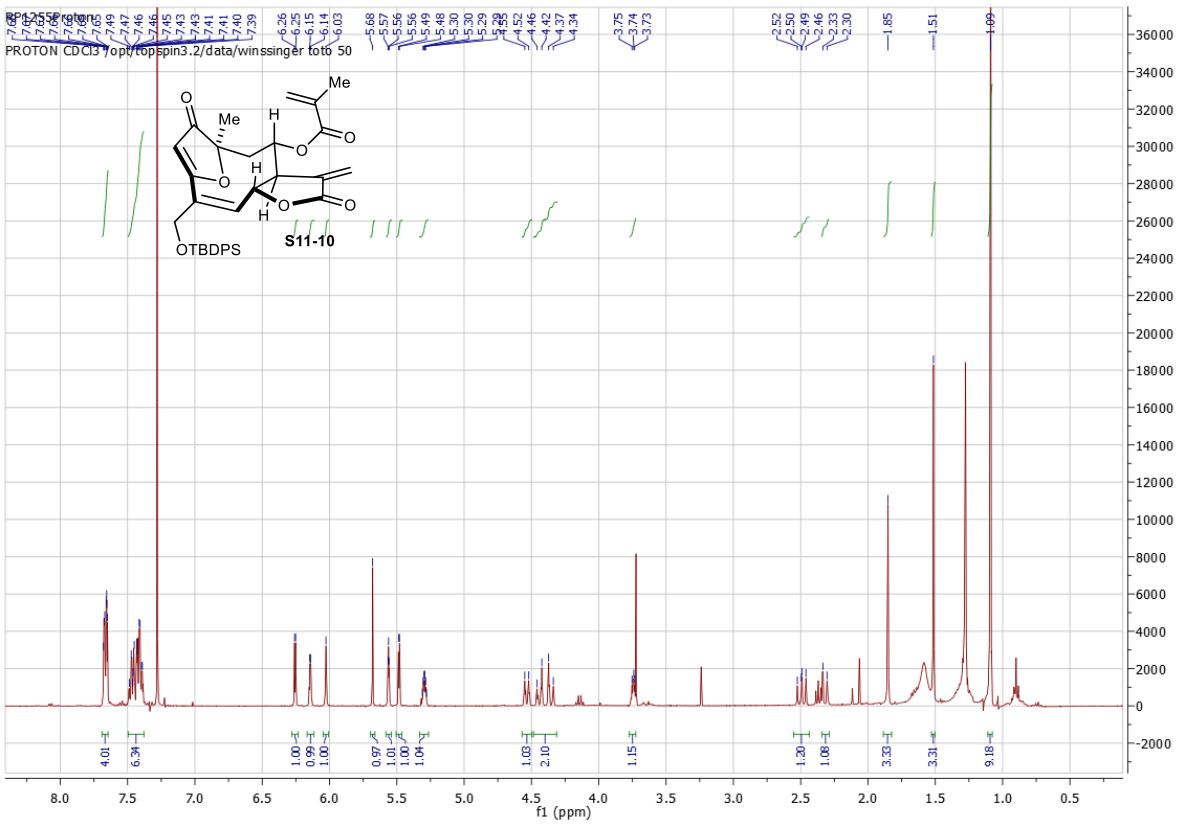

RP1251A
MP_QUICK13C CDCl3 /opt/topspin3.2/data/winssinger toto-58
OAc
Me
H
1
Me
8
H
HO
H
7
O
O
H
O
5
OTBDPS
S11-8
Grease
f1 (ppm)

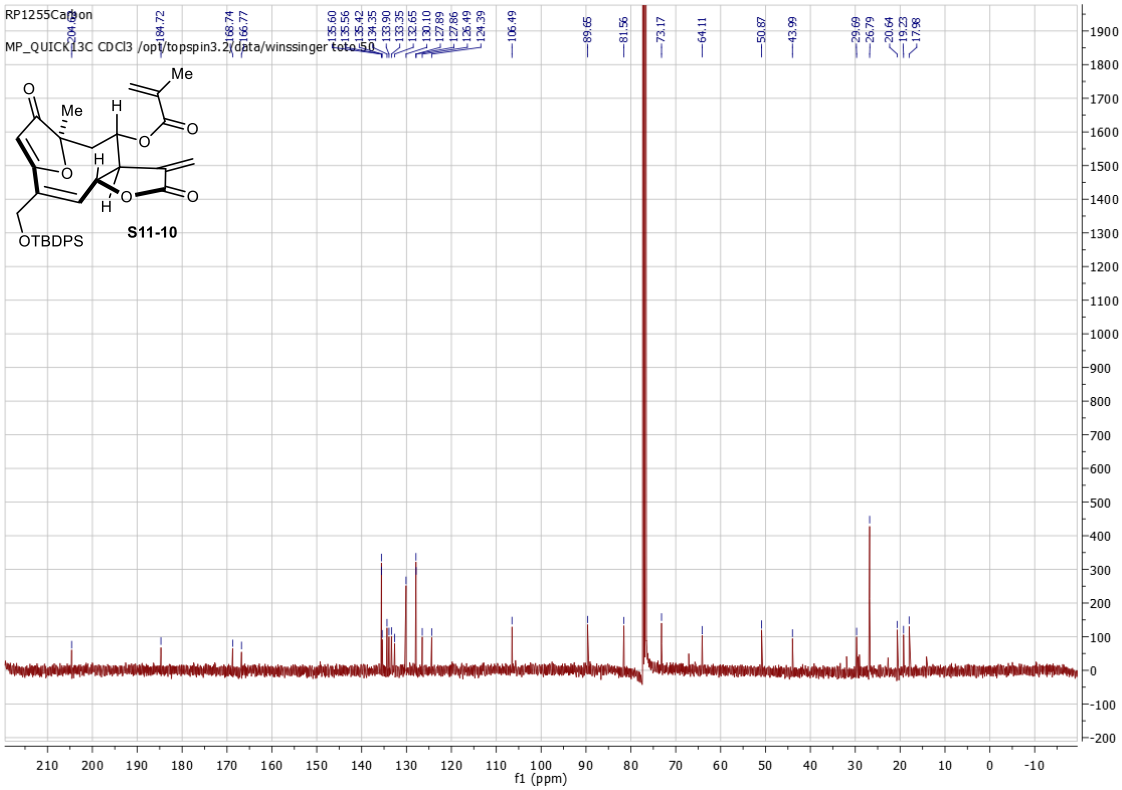

RP1253Purified
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 59
OH
Me
H
1
Me
H
8
O
HO
H
7
O
H
O
O
5
OTBDPS
S11-9
f1 (ppm)

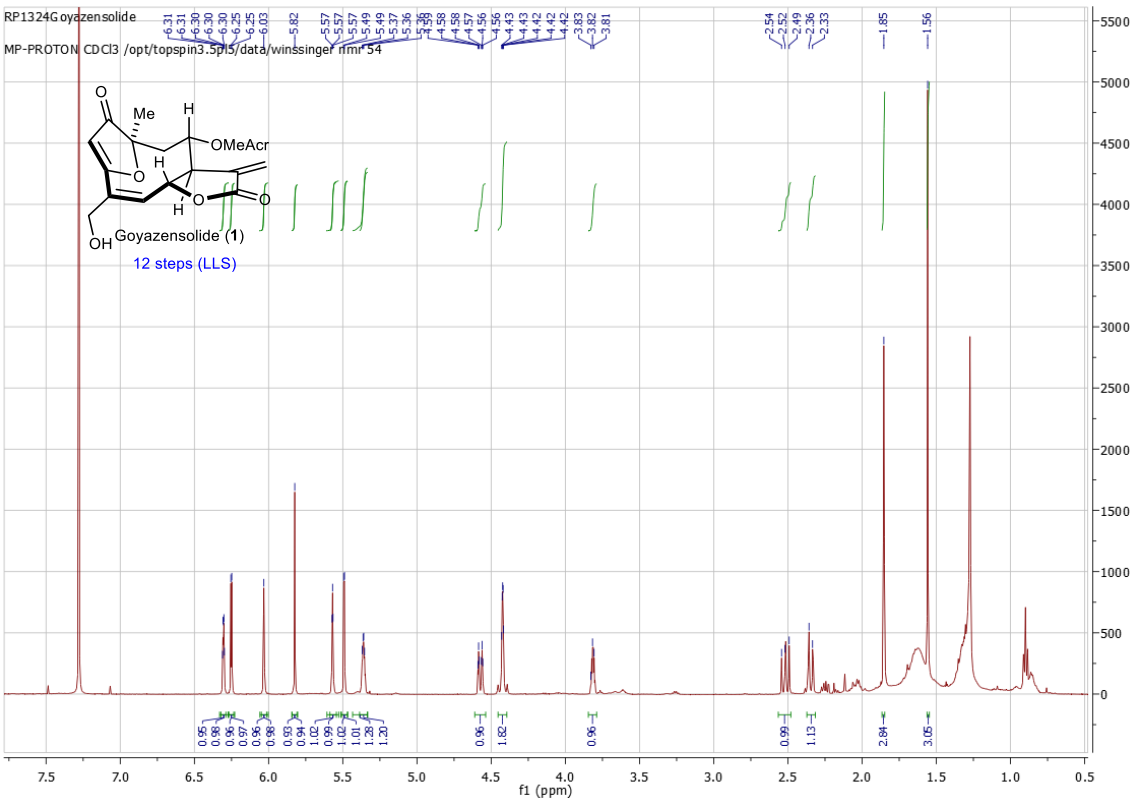

RP1253Purified
C13CPD CDCl3 /opt/topspin3.2/data/winssinger-toto 59
OH
Me
H
1
Me
H
8
O
HO
H
7
O
H
O
O
5
OTBDPS
S11-9
f1 (ppm)

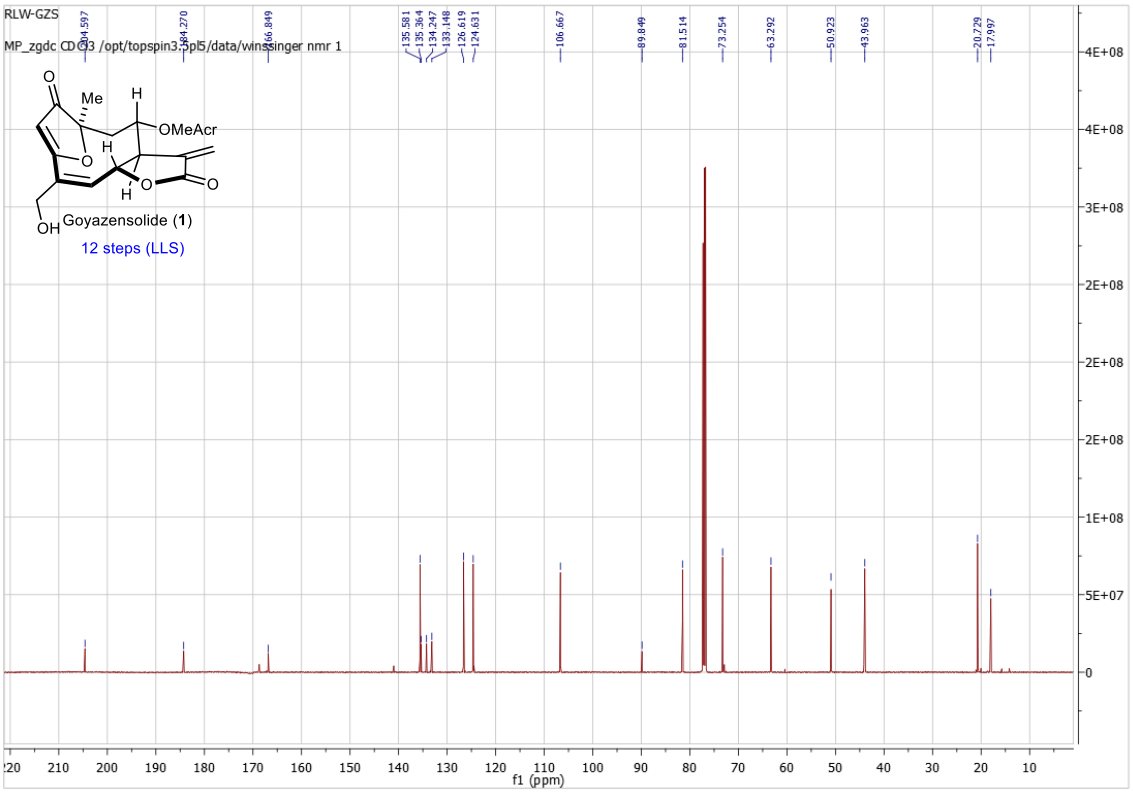

RP1254Purified
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 3
Me
O
Me
H
8
O
O
HO
H
7
H
O
O
5
OTBDPS
f1 (ppm)

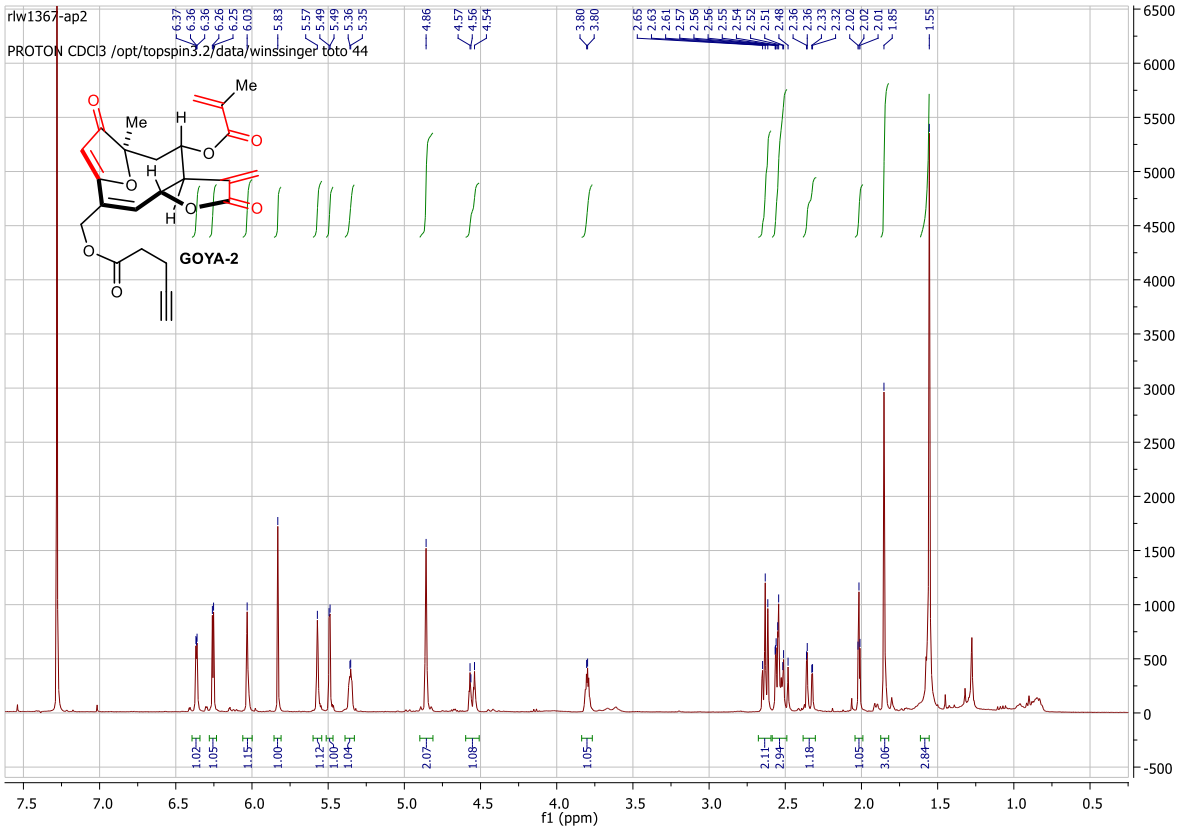

RP1254Purified
C13CPD CDCl3 /opt/topspin3.2/data/winssinger toto 3
Me
O
Me
H
8
O
O
HO
H
7
H
O
O
5
OTBDPS
f1 (ppm)

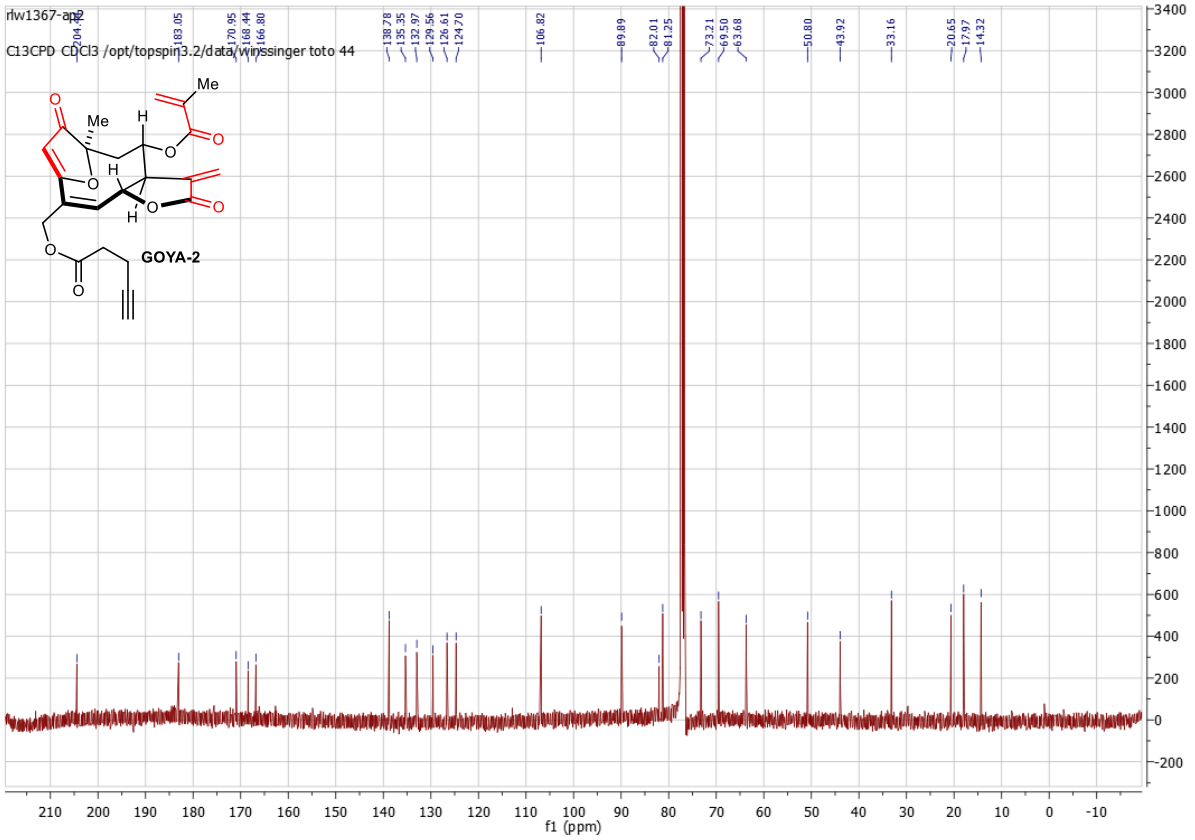

RP1255Proton
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 50
Me
H
O
OTBDPS
S11-10
f1 (ppm)

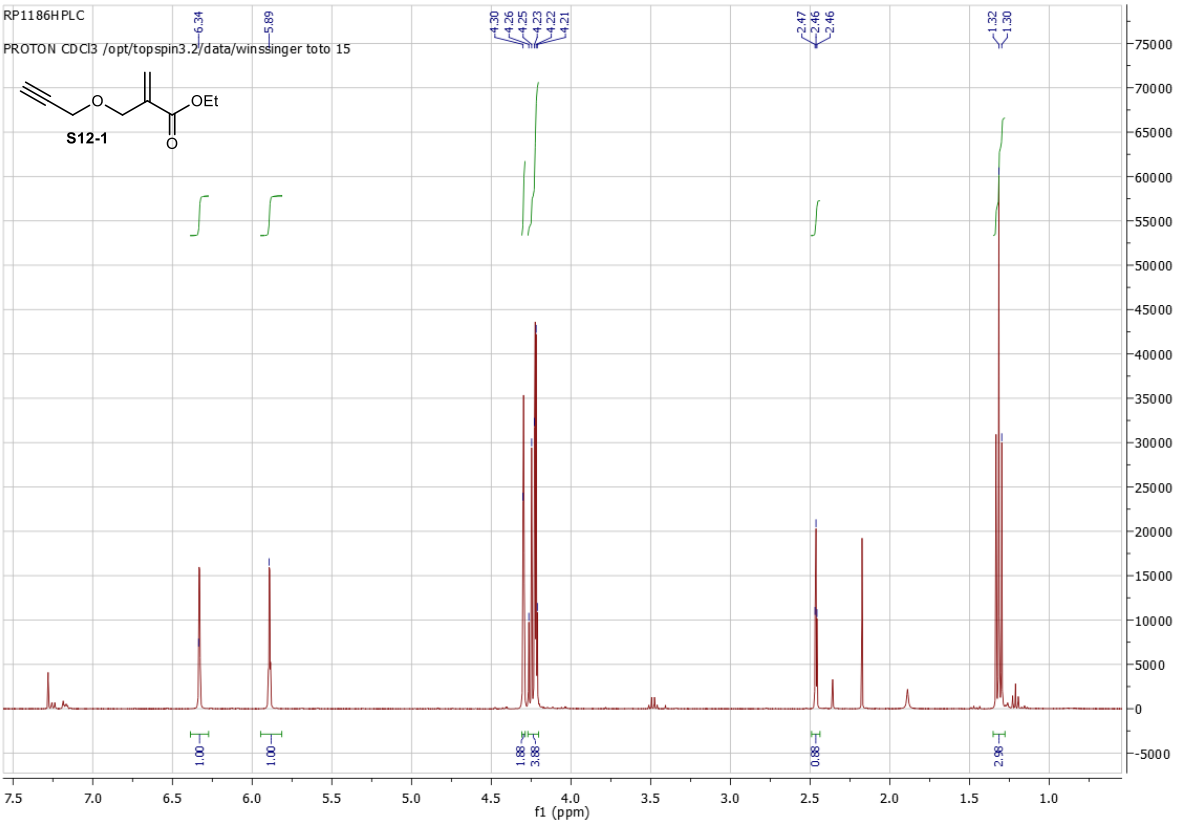

RP1255Carbon
MP_QUICK.13C CDCl3 /opt/topspin3.2/data/winssinger toto 50
Me
H
O
OTBDPS
S11-10
f1 (ppm)

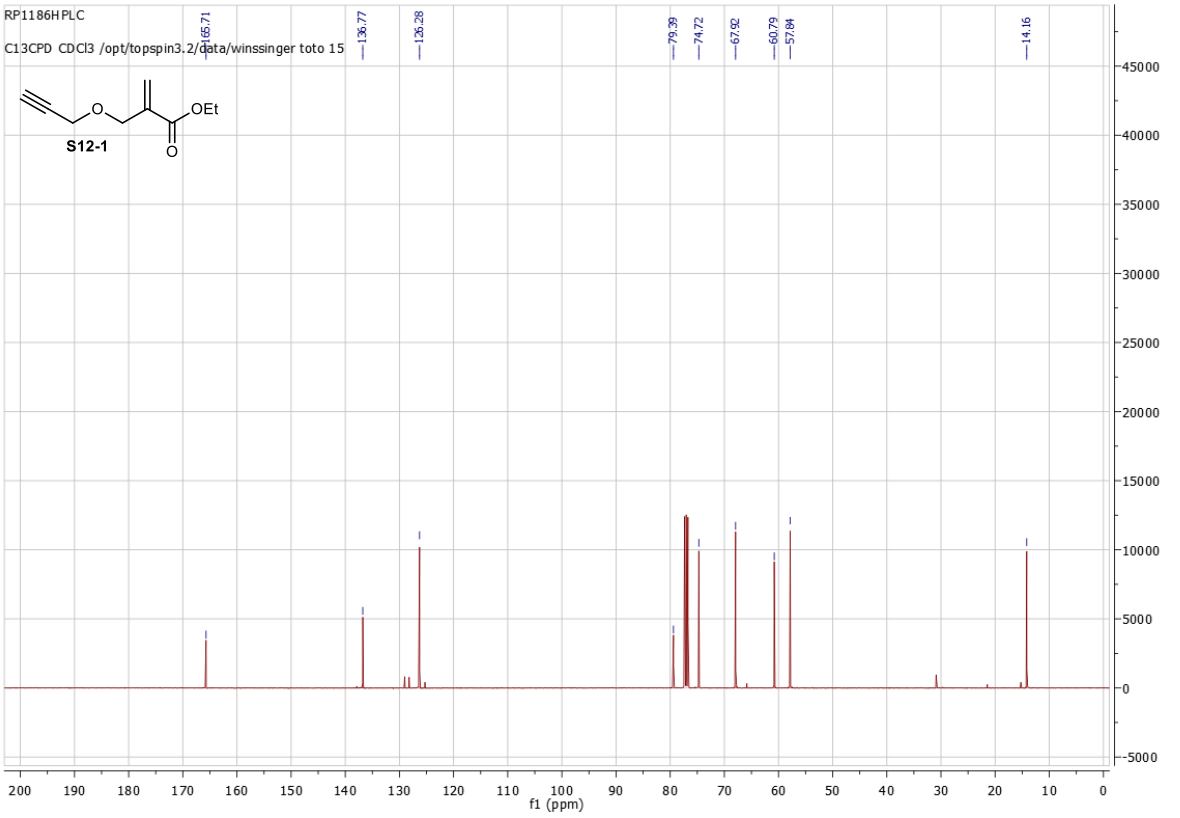

RP1324Goyazensolide
MP-PROTON CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 54
Goyazensolide (1)
12 steps (LLS)
f1 (ppm)

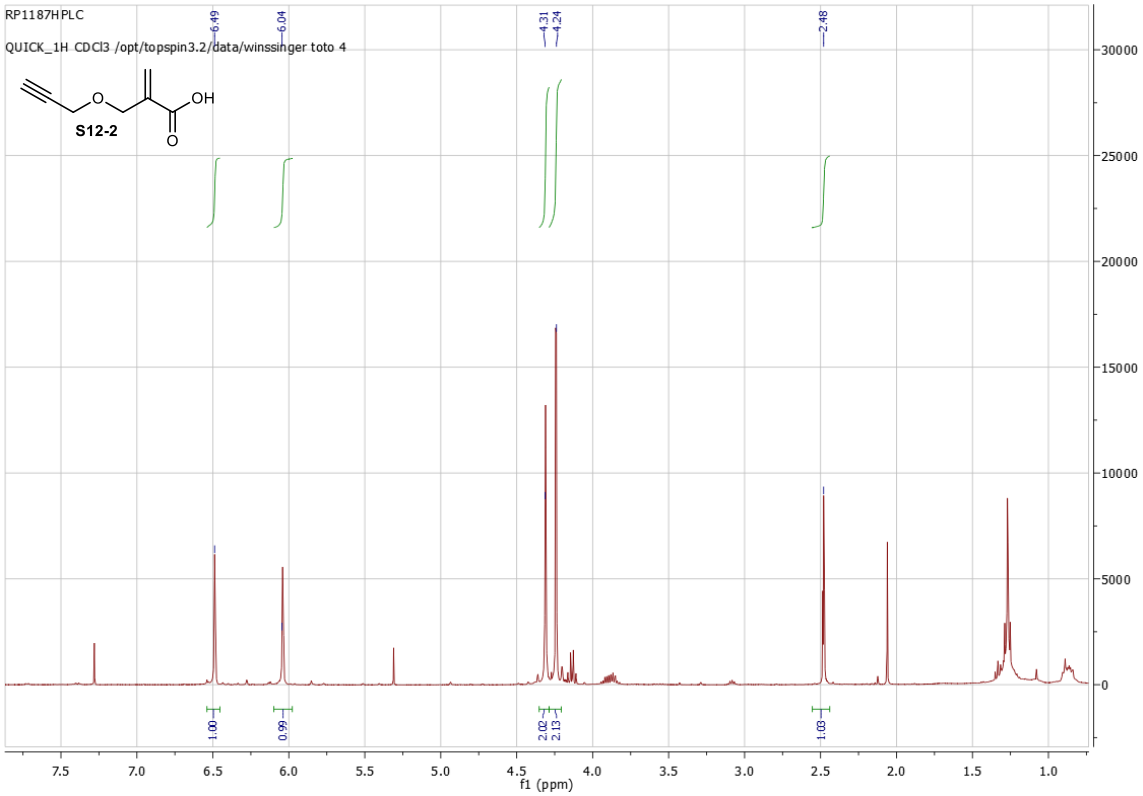

RLW-GZS
MP_zgdc CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 1
Goyazensolide (1)
12 steps (LLS)
f1 (ppm)

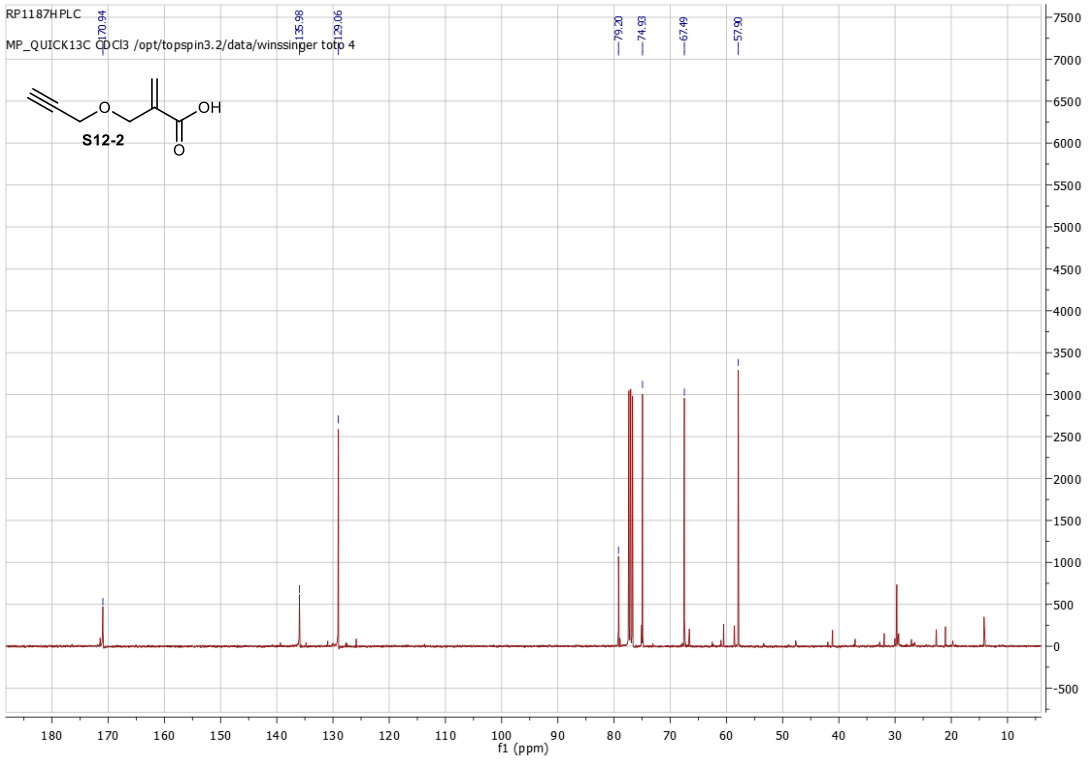

rlw1367-ap2
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 44
GOYA-2
f1 (ppm)

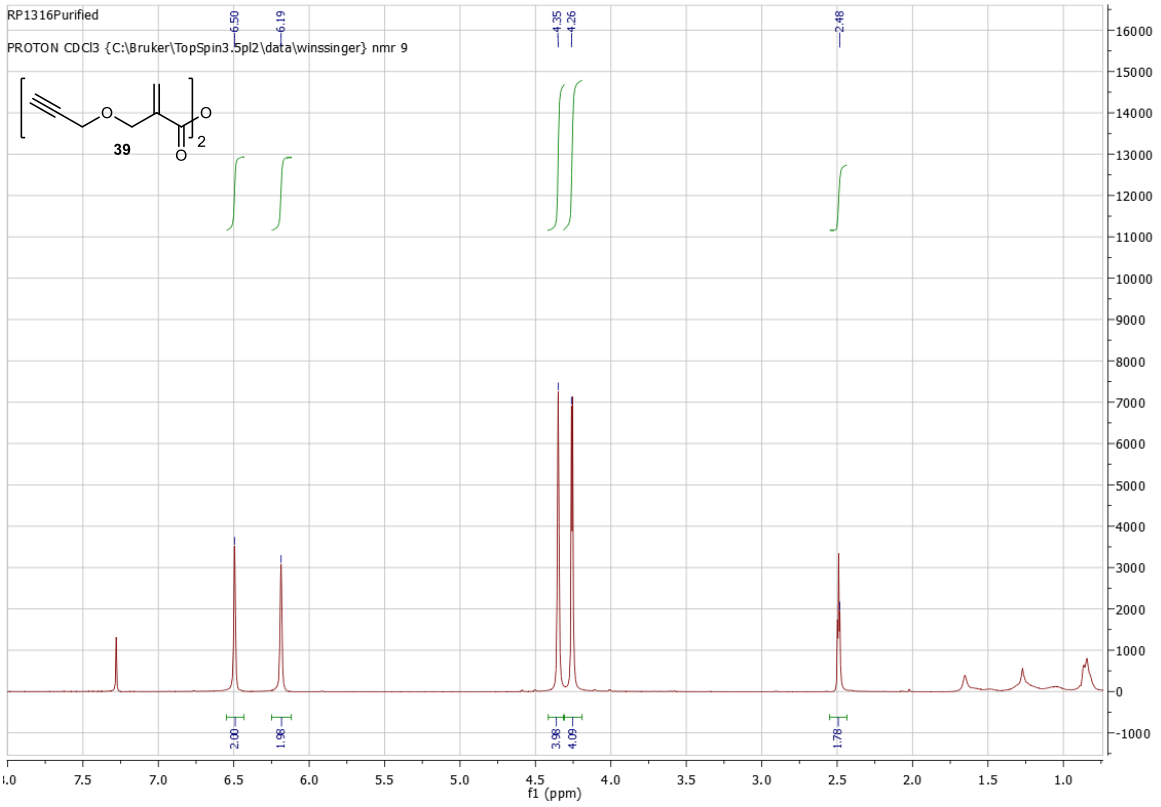

rlw1367-ap2
C13CPD CDCl3 /opt/topspin3.2/data/winssinger toto 44
GOYA-2
f1 (ppm)

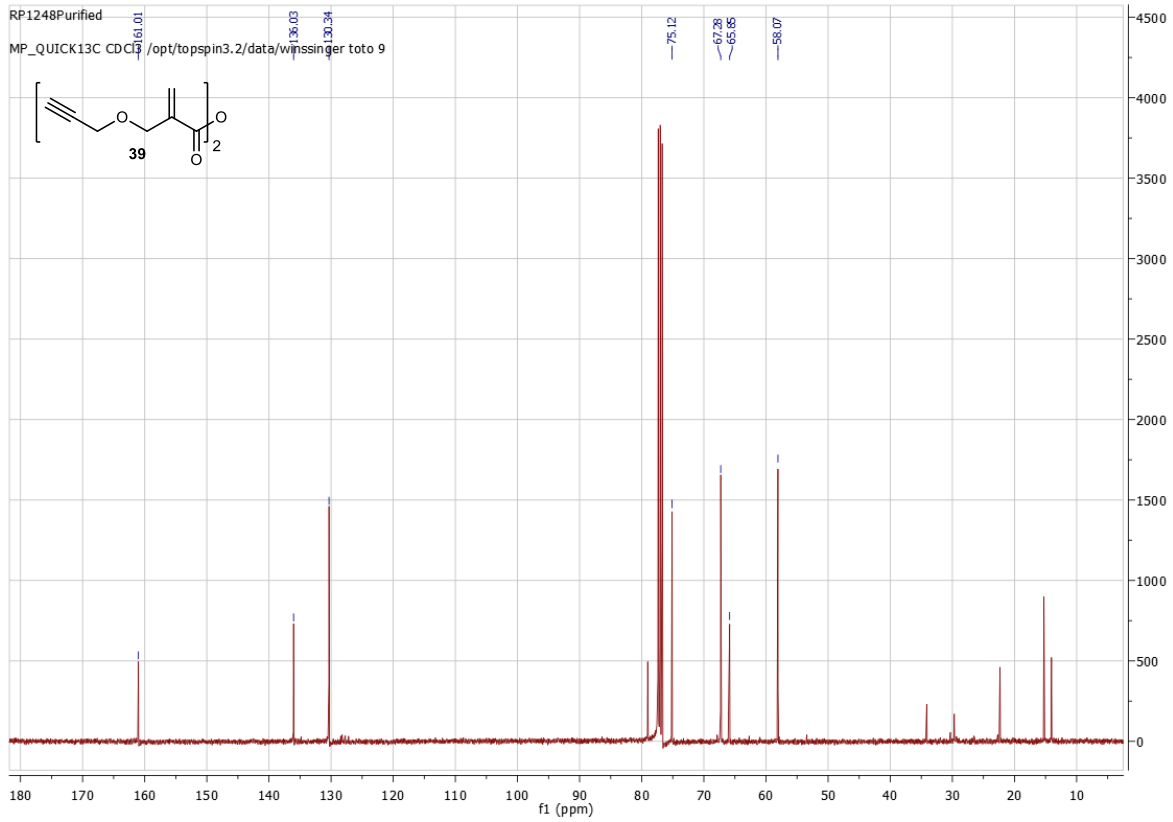

RP1186HPLC
PROTON CDCl3 /opt/topspin3.2/data/winssinger toto 15
S12-1
f1 (ppm)

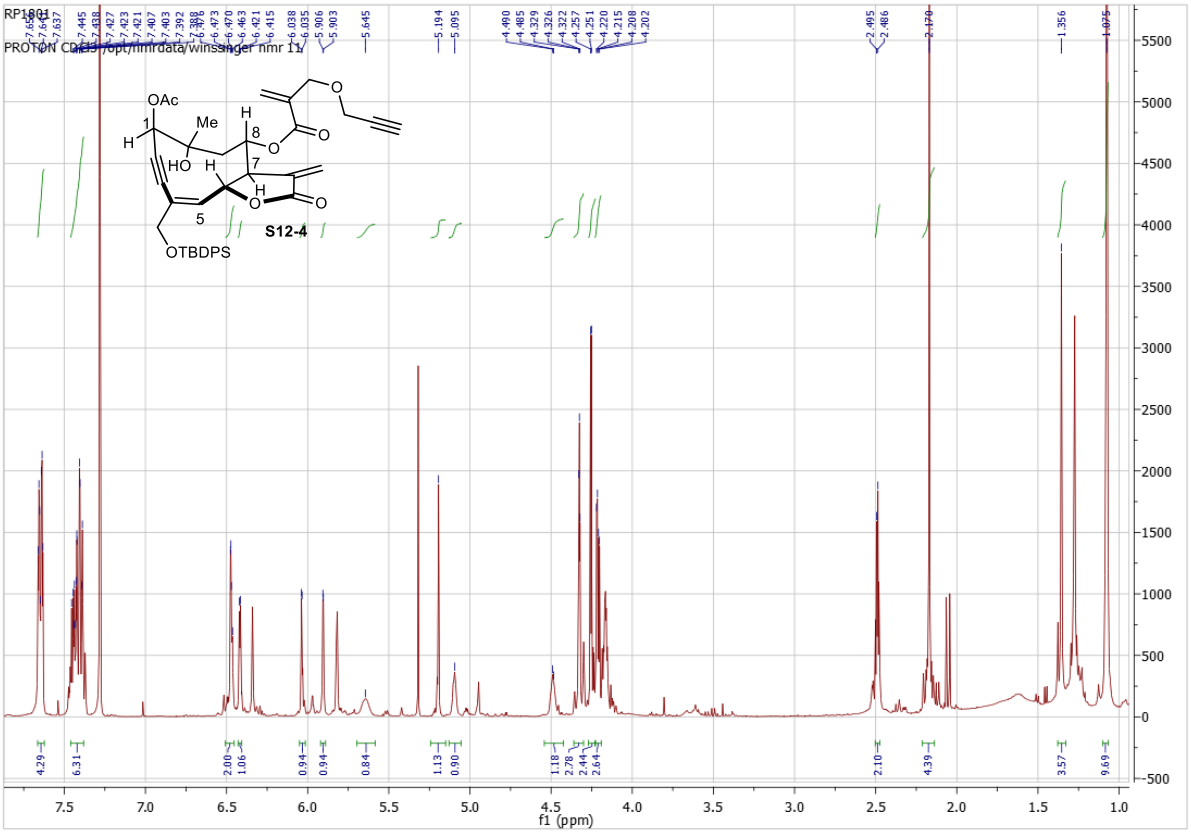

RP1186HPLC
C13CPD CDCl3 /opt/topspin3.2/data/winssinger toto 15
S12-1
f1 (ppm)

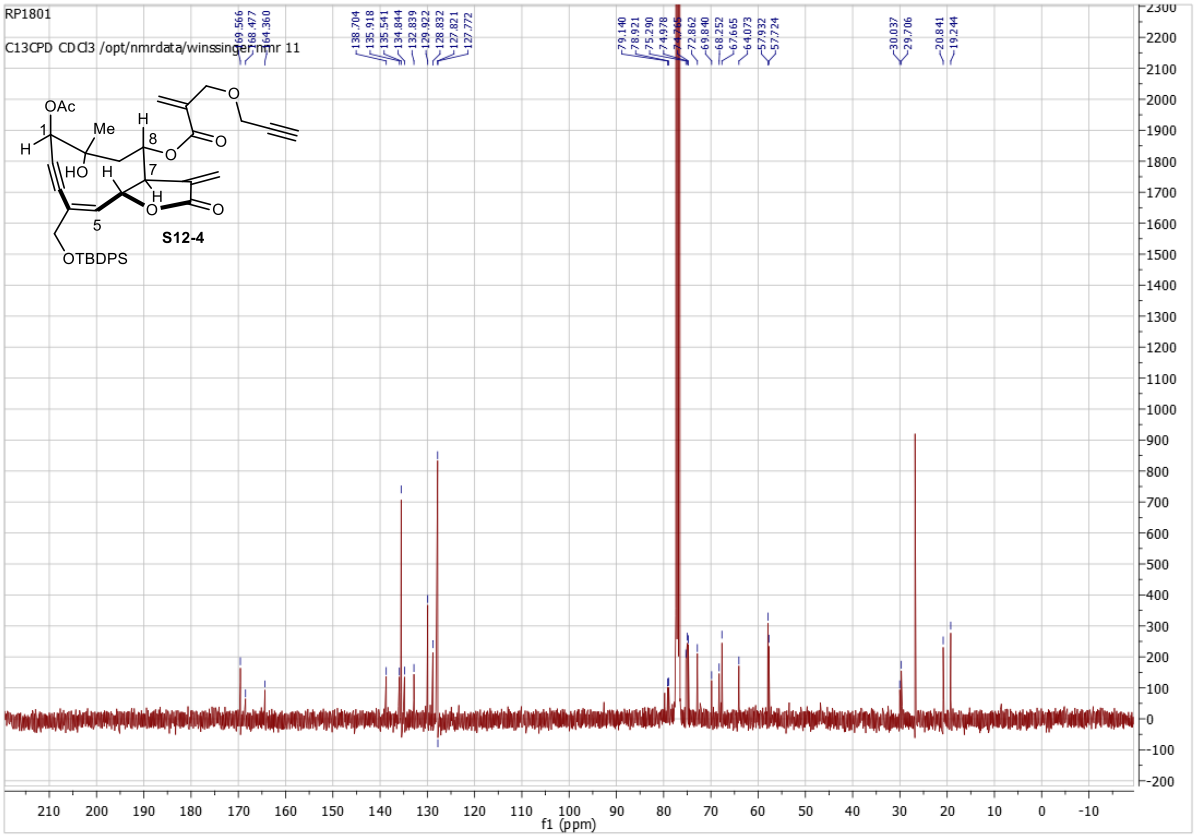

RP1187HPLC
QUICK_1H CDCl3 /opt/topspin3.2/data/winssinger toto 4
S12-2
6.49
6.04
4.31
4.24
2.48
1.00
0.99
2.02
2.13
1.03
f1 (ppm)

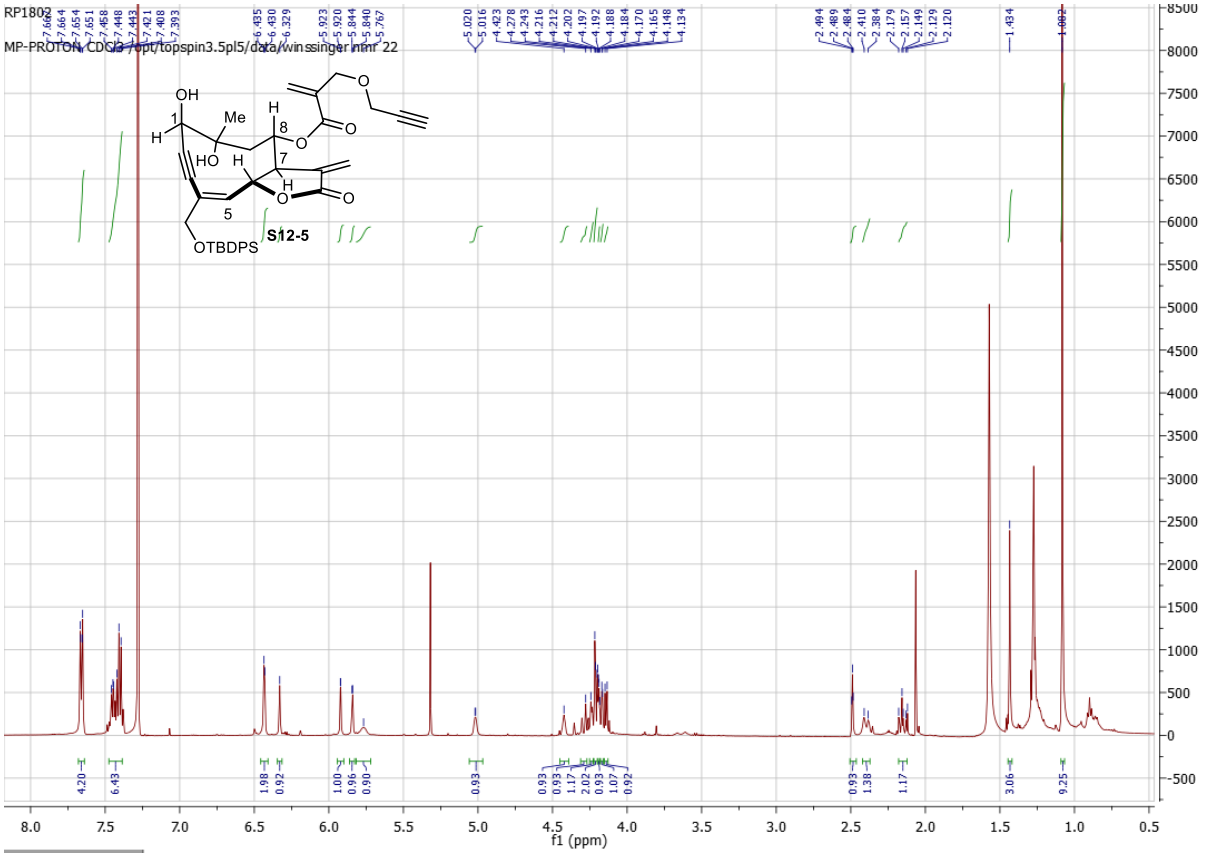

RP1187HPLC
MP_QUICK13C CDCl3 /opt/topspin3.2/data/winssinger toto 4
S12-2
170.94
135.98
129.06
79.20
74.93
67.49
57.90
f1 (ppm)

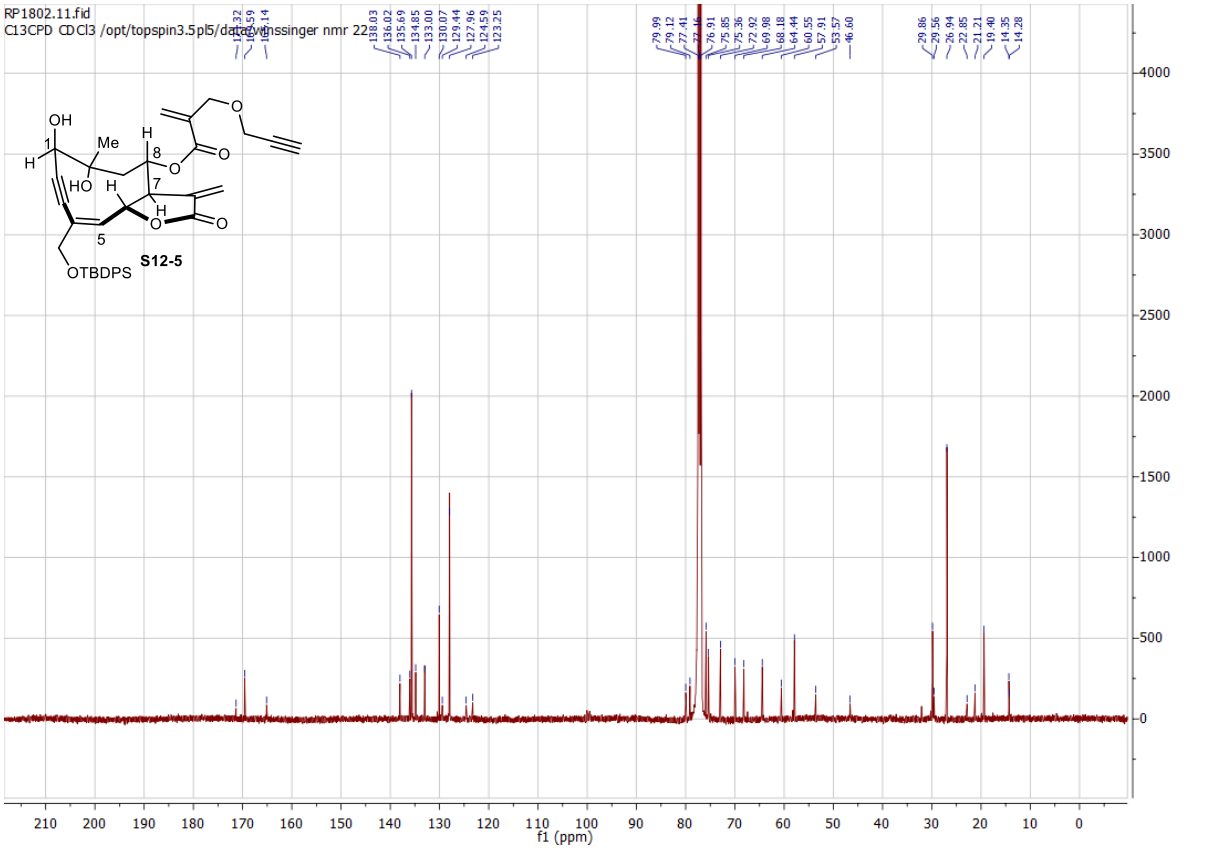

RP1316Purified
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl2\data\winssinger} nmr 9
39
6.50
6.19
4.35
4.26
2.48
2.00
1.98
3.98
4.09
1.78
f1 (ppm)

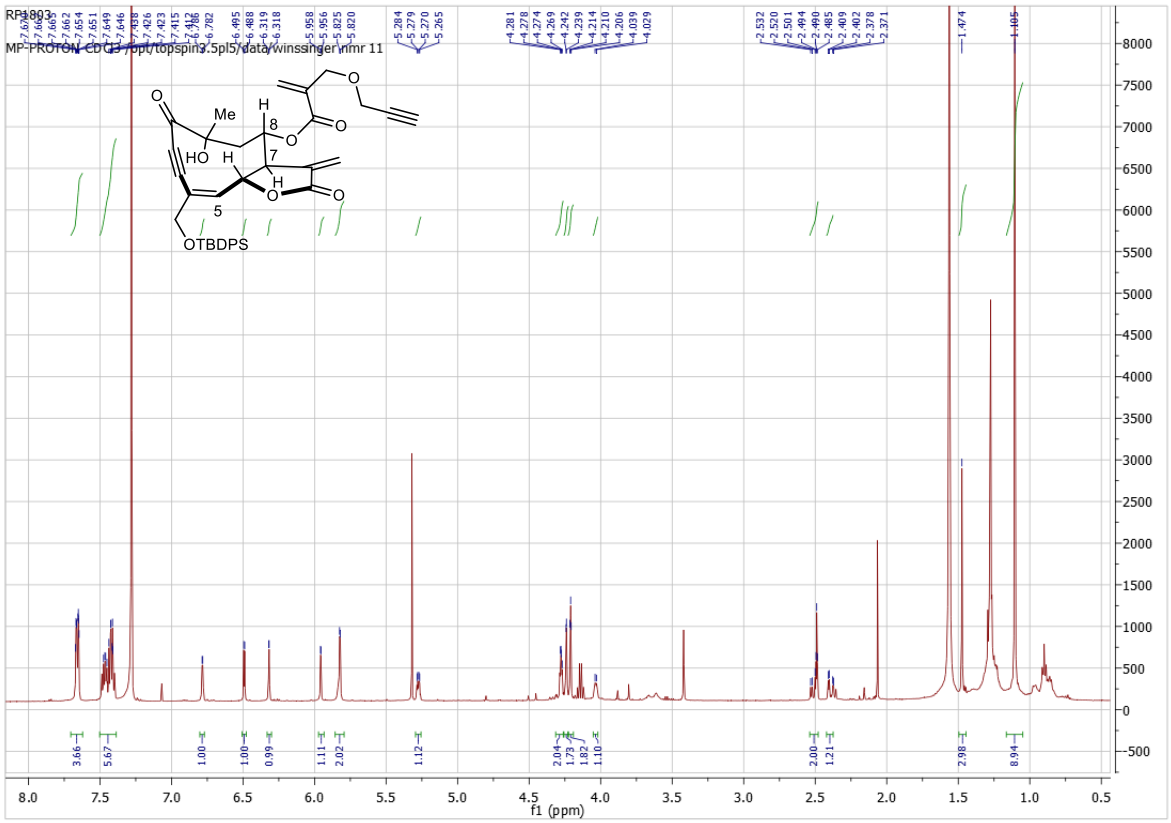

RP1248Purified
MP_QUICK13C CDCl3 /opt/topspin3.2/data/winssinger toto 9
39
161.01
136.03
130.34
75.12
67.28
65.85
58.07
f1 (ppm)

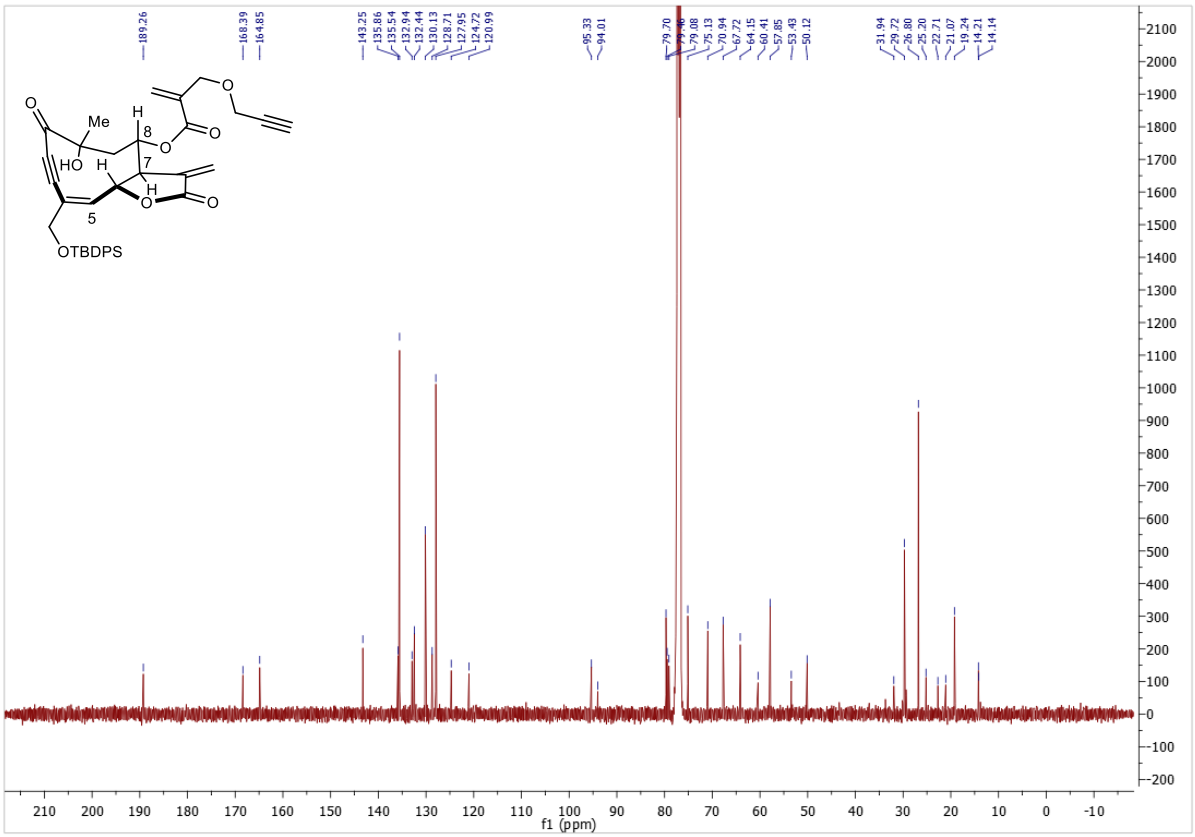

RP1801
PROTON CDCl3 /opt/nmrdata/winssinger nmr 11
OAc
Me
H
1
8
HO
7
5
O
OTBDPS
S12-4
f1 (ppm)

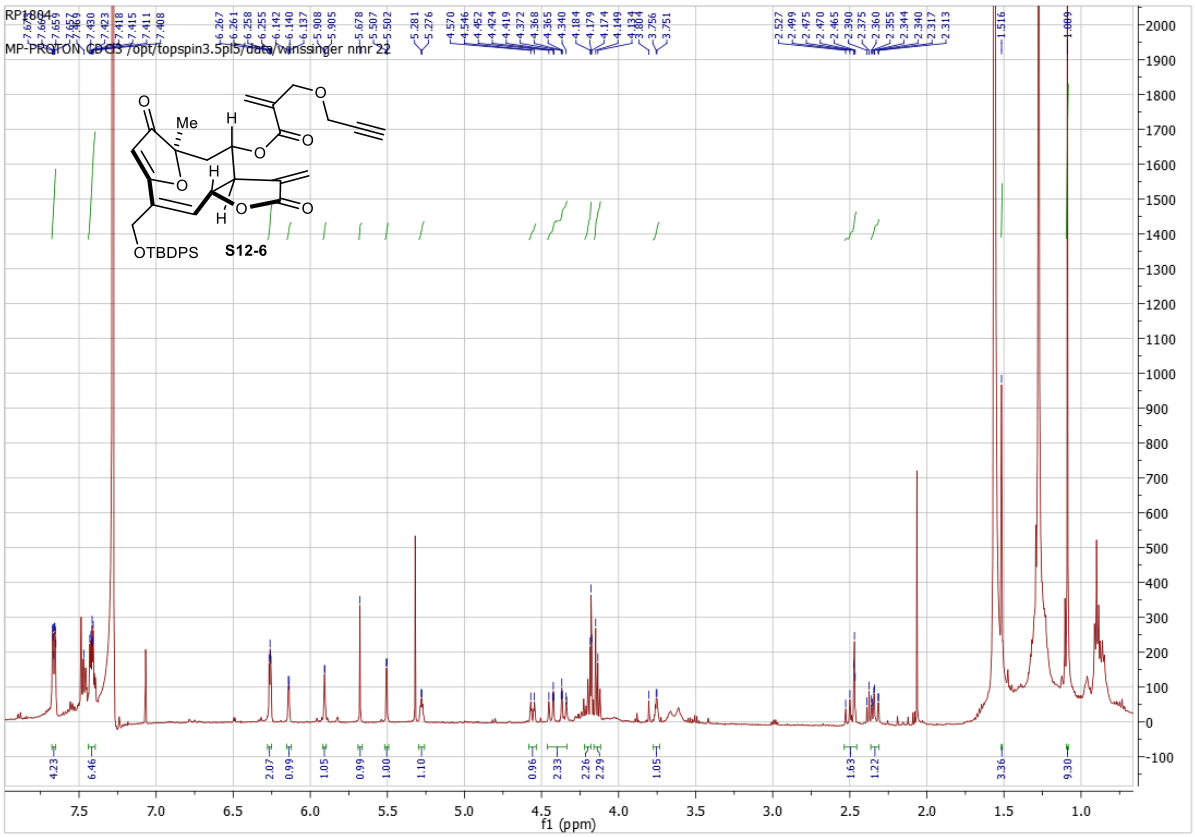

RP1801
C13CPD CDCl3 /opt/nmrdata/winssinger nmr 11
OAc
Me
H
1
8
HO
7
5
O
OTBDPS
S12-4
f1 (ppm)

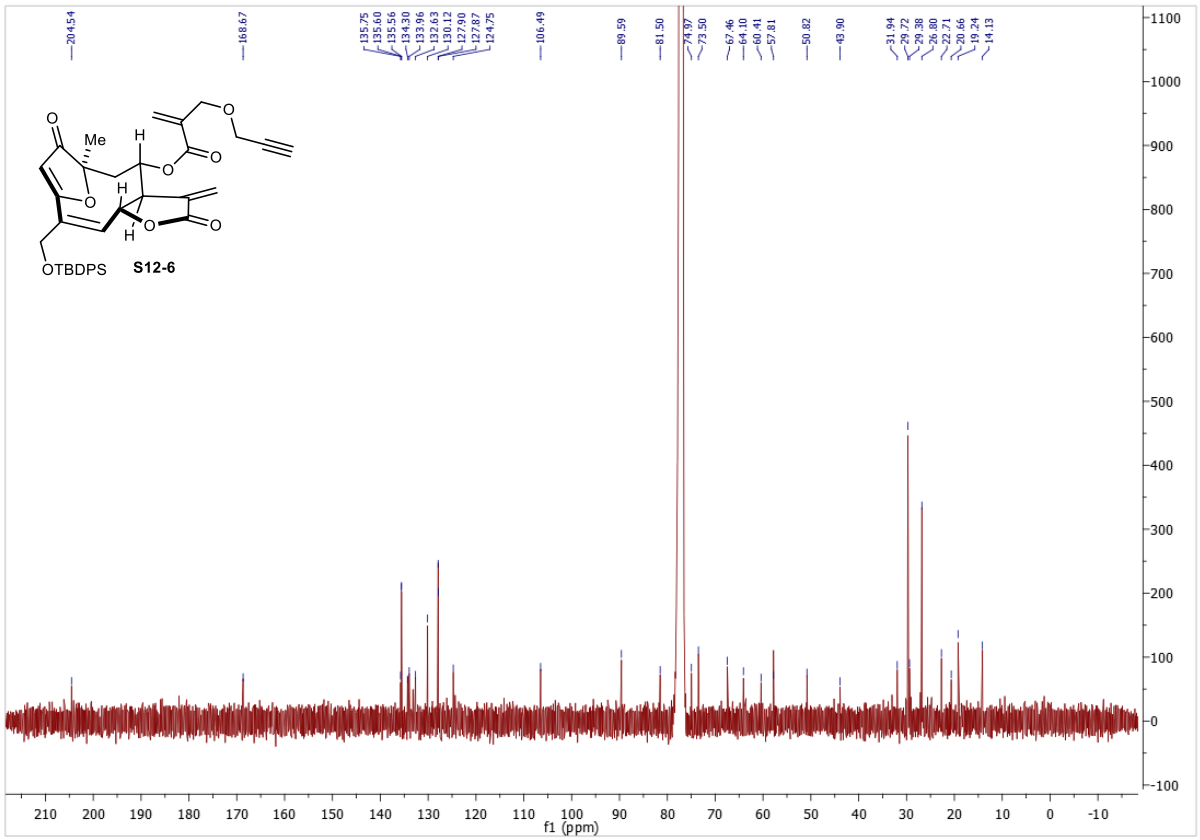

RP1802
MP-PROTON CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 22
OH
Me
H
HO
OTBDPS
S12-5
f1 (ppm)

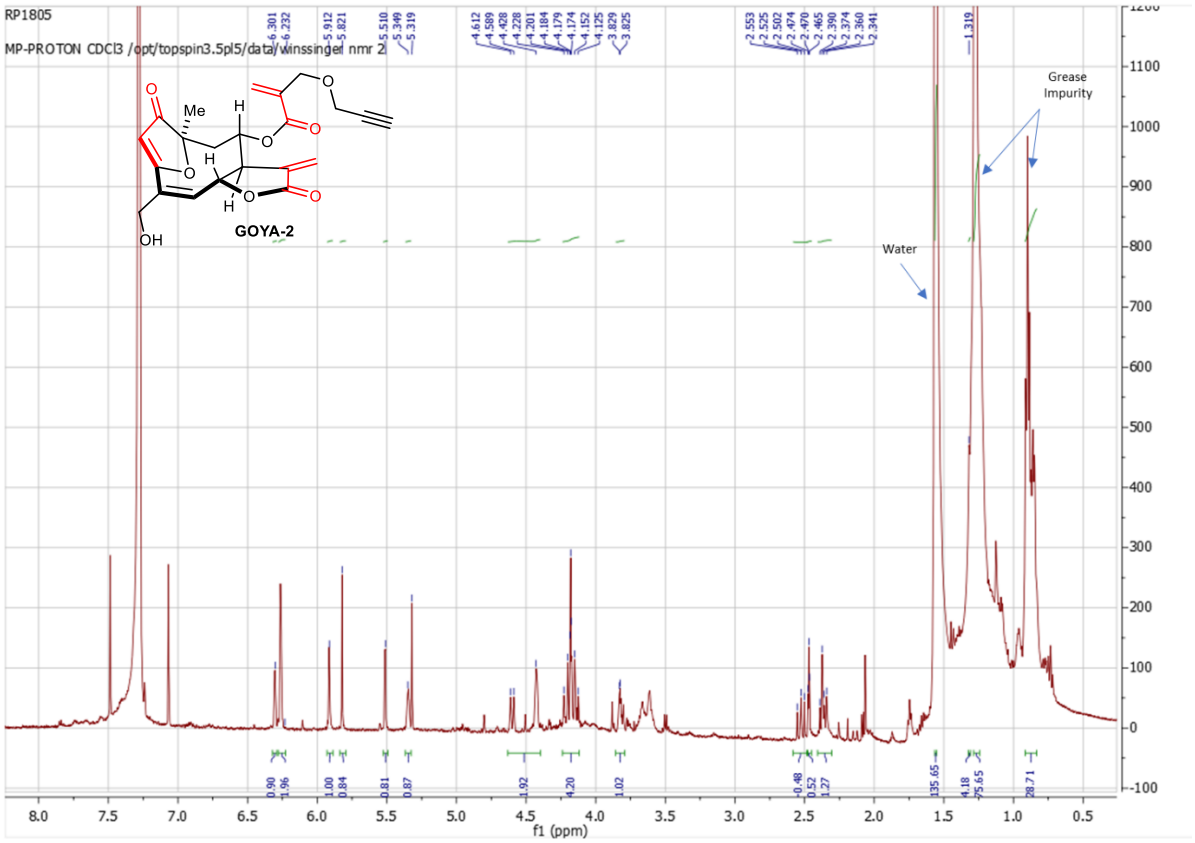

RP1802.11.fid
C13CPD CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 22
OH
Me
H
HO
OTBDPS
S12-5
f1 (ppm)

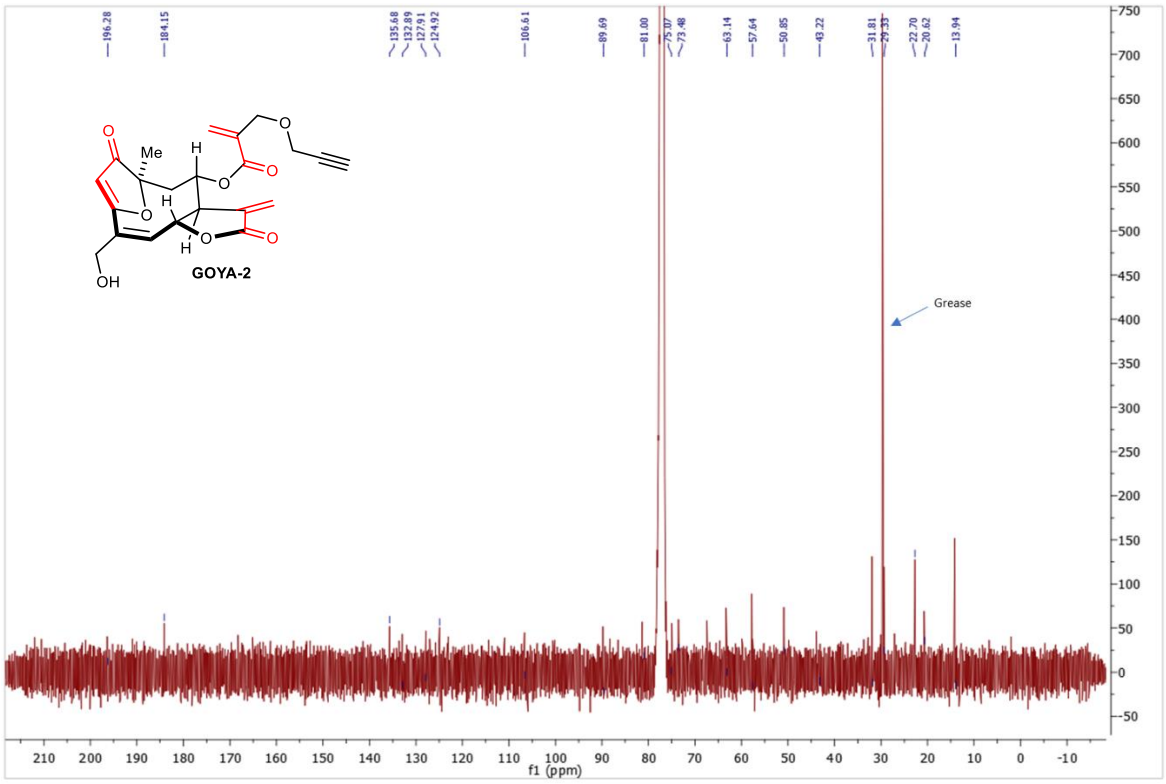

RP1803
MP-PROTON-CDCl3 /ppt/topspin3.5pl5/data/winssinger/nmr 11
Me
H
8
O
HO
H
7
5
OTBDPS
f1 (ppm)


Me
H
8
O
HO
H
7
5
OTBDPS
f1 (ppm)

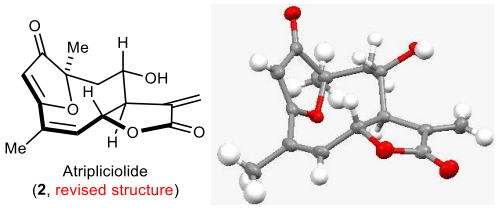

RP1804
MP-PROTON CDCl3 /opt/topspin3.5pl5/data/winssinger nmr 22
Me
H
O
OTBDPS
S12-6
f1 (ppm)


Me
H
O
OTBDPS
S12-6
f1 (ppm)


RP1805
MP-PROTON CDCl3 /opt/topspin3.5pl5/data/winssingel nmr 2
Me
H
O
OH
GOYA-2
Grease
Impurity
Water
f1 (ppm)


Me
H
O
OH
GOYA-2
Grease
f1 (ppm)

m) X-Ray data of 2, 30 and 34



Atripliciolide
(**2**, revised structure)

Table 1 Crystal data and structure refinement for WL2.

Identification code	WL2
Empirical formula	$C_{15}H_{16}O_5$
Formula weight	276.28
Temperature/K	149.99(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.11197(3)
b/Å	9.30326(4)
c/Å	17.61440(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1329.320(9)
Z	4
ρ_{calc}g/cm^3	1.380
μ/mm^{-1}	0.866
F(000)	584.0
Crystal size/mm^3	0.214 × 0.169 × 0.102
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.044 to 147.598
Index ranges	-10 ≤ h ≤ 9, -11 ≤ k ≤ 11, -21 ≤ l ≤ 21
Reflections collected	61110
Independent reflections	2690 [R_{int} = 0.0304, R_{sigma} = 0.0071]
Data/restraints/parameters	2690/0/189
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0233, wR_2 = 0.0605
Final R indexes [all data]	R_1 = 0.0235, wR_2 = 0.0606
Largest diff. peak/hole / e Å^{-3}	0.18/-0.12
Flack parameter	-0.01(17)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for WL2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	5570.9(15)	8694.9(15)	7454.2(7)	40.0(3)
O7	6273.6(13)	5594.8(12)	5471.0(7)	28.7(3)
O12	2119.0(17)	2290.0(12)	4442.5(7)	39.2(3)
O13	1707.8(15)	3217.2(12)	5595.5(6)	33.1(3)

O19	2185.6(12)	8008.4(11)	6258.8(6)	23.8(2)
C2	4301.7(19)	8275.6(18)	7156.7(9)	29.0(3)
C3	3849.5(18)	8589.2(16)	6328.7(8)	24.0(3)
C4	3839(2)	10179.8(17)	6142.1(10)	33.8(4)
C5	4943.2(18)	7730.0(15)	5784.2(8)	22.6(3)
C6	4828.0(17)	6088.2(15)	5841.6(8)	20.9(3)
C8	3182.2(17)	5477.9(14)	5492.6(8)	21.1(3)
C9	3368.3(17)	4549.8(15)	4799.1(8)	23.5(3)
C10	4209(2)	4768.4(19)	4166.9(9)	33.1(4)
C11	2368.5(19)	3238.0(16)	4899.9(9)	28.0(3)
C14	2193.1(19)	4481.9(16)	6043.1(9)	25.7(3)
C15	621.2(19)	5048.5(18)	6391.9(9)	30.5(3)
C16	447.3(19)	6240.3(19)	6801.7(9)	29.4(3)
C17	-1153(2)	6710(2)	7159.3(11)	40.6(4)
C18	1883.6(19)	7206.5(17)	6890.2(8)	26.1(3)
C20	3000(2)	7374(2)	7447.9(9)	33.7(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for WL2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	29.3(6)	54.5(8)	36.2(6)	-14.2(6)	-6.2(5)	-2.3(6)
O7	18.9(5)	25.9(5)	41.5(6)	-8.5(5)	0.7(5)	2.9(4)
O12	48.4(7)	27.2(6)	42.1(7)	-5.8(5)	-3.4(6)	-11.7(5)
O13	39.2(7)	25.2(5)	34.9(6)	2.1(4)	0.8(5)	-11.1(5)
O19	19.8(5)	24.6(5)	27.0(5)	2.1(4)	-0.4(4)	2.1(4)
C2	24.8(7)	35.5(8)	26.8(7)	-9.5(6)	-0.2(6)	4.3(6)
C3	19.9(7)	22.9(7)	29.1(7)	-2.5(6)	0.3(6)	0.4(5)
C4	32.4(8)	22.6(7)	46.5(9)	-4.0(7)	4.3(7)	1.3(6)
C5	20.1(7)	21.6(7)	26.2(7)	-1.7(6)	1.0(6)	-1.8(5)
C6	18.1(6)	20.7(7)	24.0(7)	-1.0(5)	-1.3(5)	1.2(5)
C8	18.0(7)	21.2(6)	24.0(6)	2.4(5)	-1.2(5)	-0.3(5)
C9	21.3(7)	21.9(7)	27.4(7)	-0.2(6)	-4.9(5)	-1.1(5)
C10	33.1(9)	36.1(9)	30.0(8)	-6.9(7)	1.7(7)	-9.0(7)
C11	28.4(8)	24.1(7)	31.4(7)	1.6(6)	-5.2(6)	-2.4(6)
C14	24.6(7)	25.8(7)	26.7(7)	2.4(6)	-2.3(6)	-5.5(6)
C15	22.2(7)	38.9(9)	30.4(7)	6.7(7)	0.5(6)	-7.7(7)
C16	20.1(7)	40.9(9)	27.2(7)	8.5(7)	2.8(6)	-0.6(6)
C17	23.7(8)	54.7(11)	43.4(9)	1.6(9)	8.2(7)	0.1(8)
C18	22.0(7)	31.6(7)	24.6(7)	0.7(6)	4.3(6)	4.5(6)
C20	28.7(8)	49.2(10)	23.1(7)	2.3(7)	1.3(6)	1.8(7)

Table 4 Bond Lengths for WL2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C2	1.219(2)	C5	C6	1.5336(18)
O7	C6	1.4185(17)	C6	C8	1.5756(18)
O12	C11	1.2115(19)	C8	C9	1.504(2)
O13	C11	1.337(2)	C8	C14	1.5628(19)
O13	C14	1.4701(18)	C9	C10	1.321(2)
O19	C3	1.4591(17)	C9	C11	1.476(2)
O19	C18	1.3615(18)	C14	C15	1.510(2)
C2	C3	1.532(2)	C15	C16	1.331(2)
C2	C20	1.443(2)	C16	C17	1.508(2)

C3	C4	1.516(2)	C16	C18	1.480(2)
C3	C5	1.532(2)	C18	C20	1.345(2)

Table 5 Bond Angles for WL2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O13	C14	111.86(11)	C10	C9	C8	130.40(14)
C18	O19	C3	107.48(11)	C10	C9	C11	120.80(14)
O1	C2	C3	123.40(15)	C11	C9	C8	108.78(12)
O1	C2	C20	130.63(16)	O12	C11	O13	122.12(14)
C20	C2	C3	105.89(12)	O12	C11	C9	127.86(15)
O19	C3	C2	103.38(11)	O13	C11	C9	110.02(13)
O19	C3	C4	109.76(12)	O13	C14	C8	106.22(11)
O19	C3	C5	106.84(11)	O13	C14	C15	105.75(12)
C4	C3	C2	113.19(13)	C15	C14	C8	118.61(13)
C4	C3	C5	112.13(13)	C16	C15	C14	126.94(14)
C5	C3	C2	110.98(12)	C15	C16	C17	124.01(15)
C3	C5	C6	116.30(12)	C15	C16	C18	118.68(14)
O7	C6	C5	103.98(12)	C18	C16	C17	117.26(15)
O7	C6	C8	113.85(11)	O19	C18	C16	112.86(13)
C5	C6	C8	112.63(11)	C20	C18	O19	114.33(14)
C9	C8	C6	116.03(11)	C20	C18	C16	132.65(15)
C9	C8	C14	102.42(11)	C18	C20	C2	107.49(14)
C14	C8	C6	113.99(11)				

Table 6 Torsion Angles for WL2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C2	C3	O19	-174.50(14)	C8	C14	C15	C16	-56.1(2)
O1	C2	C3	C4	-55.8(2)	C9	C8	C14	O13	-8.00(14)
O1	C2	C3	C5	71.28(19)	C9	C8	C14	C15	-126.73(13)
O1	C2	C20	C18	-178.89(17)	C10	C9	C11	O12	-4.1(3)
O7	C6	C8	C9	-3.60(17)	C10	C9	C11	O13	176.64(14)
O7	C6	C8	C14	115.04(14)	C11	O13	C14	C8	5.74(16)
O13	C14	C15	C16	-175.11(15)	C11	O13	C14	C15	132.62(13)
O19	C3	C5	C6	-50.30(16)	C14	O13	C11	O12	179.96(15)
O19	C18	C20	C2	-5.94(19)	C14	O13	C11	C9	-0.76(17)
C2	C3	C5	C6	61.72(17)	C14	C8	C9	C10	-173.89(16)
C3	O19	C18	C16	-164.15(12)	C14	C8	C9	C11	7.74(15)
C3	O19	C18	C20	11.69(17)	C14	C15	C16	C17	-177.47(15)
C3	C2	C20	C18	-2.05(18)	C14	C15	C16	C18	5.2(2)
C3	C5	C6	O7	-162.34(12)	C15	C16	C18	O19	76.26(18)
C3	C5	C6	C8	73.94(16)	C15	C16	C18	C20	-98.6(2)
C4	C3	C5	C6	-170.60(13)	C16	C18	C20	C2	168.85(16)
C5	C6	C8	C9	114.45(13)	C17	C16	C18	O19	-101.23(16)
C5	C6	C8	C14	-126.90(13)	C17	C16	C18	C20	83.9(2)
C6	C8	C9	C10	-49.1(2)	C18	O19	C3	C2	-11.74(14)
C6	C8	C9	C11	132.55(13)	C18	O19	C3	C4	-132.77(13)
C6	C8	C14	O13	-134.15(12)	C18	O19	C3	C5	105.43(13)
C6	C8	C14	C15	107.12(14)	C20	C2	C3	O19	8.37(15)
C8	C9	C11	O12	174.43(16)	C20	C2	C3	C4	127.05(15)
C8	C9	C11	O13	-4.80(17)	C20	C2	C3	C5	-105.85(14)

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for WL2.

Atom	*x*	*y*	*z*	U(eq)
H7	6290(30)	4680(20)	5494(12)	45(6)
H4A	3497.02	10315.37	5613.29	51
H4B	4948.34	10574.92	6213.23	51
H4C	3065.47	10677.44	6478.95	51
H5A	6103.62	8013.21	5873.34	27
H5B	4659.92	8013.13	5258.35	27
H6	4884.8	5807.29	6389	25
H8	2462.37	6311.53	5356.35	25
H10A	4173.87	4076.8	3770.46	40
H10B	4847.59	5617.07	4108.93	40
H14	2944.46	4162.26	6460.27	31
H15	-346.59	4494.77	6309.98	37
H17A	-1002.74	6813.04	7708.6	61
H17B	-2005.57	5987.95	7058.8	61
H17C	-1492.36	7634.32	6942.81	61
H20	2941.55	6972.47	7943	40

Experimental

Single crystals of $C_{15}H_{16}O_5$ **[WL2]** were **[2]**. A suitable crystal was selected and **[2]** on a **XtaLAB Synergy, Dualflex, HyPix-Arc** diffractometer. The crystal was kept at 149.99(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [WL2]

Crystal Data for $C_{15}H_{16}O_5$ (M =276.28 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 8.11197(3) Å, b = 9.30326(4) Å, c = 17.61440(7) Å, V = 1329.320(9) Å^3, Z = 4, T = 149.99(10) K, μ(Cu Kα) = 0.866 mm^{-1}, *Dcalc* = 1.380 g/cm^3, 61110 reflections measured (10.044° ≤ 2Θ ≤ 147.598°), 2690 unique (R_{int} = 0.0304, R_{sigma} = 0.0071) which were used in all calculations. The final R_1 was 0.0233 (I > 2σ(I)) and wR_2 was 0.0606 (all data).

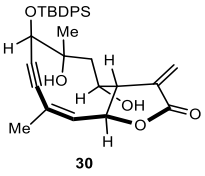
Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Twinned data refinement
Scales: 1.01(17)
-0.01(17)
2. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All C(H,H,H) groups
3.a Ternary CH refined with riding coordinates:
C6(H6), C8(H8), C14(H14)
3.b Secondary CH2 refined with riding coordinates:
C5(H5A,H5B)
3.c Aromatic/amide H refined with riding coordinates:
C15(H15), C20(H20)
3.d X=CH2 refined with riding coordinates:
C10(H10A,H10B)
3.e Idealised Me refined as rotating group:
C4(H4A,H4B,H4C), C17(H17A,H17B,H17C)

This report has been created with Olex2, compiled on Nov 21 2019 18:26:39 for OlexSys.



30

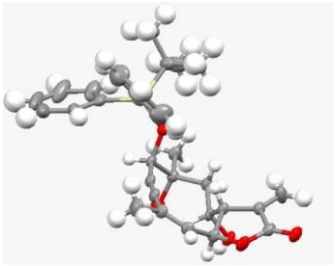


Table 1 Crystal data and structure refinement for exp_2516.

Identification code	exp_2516
Empirical formula	$C_{31}H_{36}O_5Si$
Formula weight	516.69
Temperature/K	180.01(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.52826(14)
b/Å	11.72660(18)
c/Å	25.7421(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2876.27(8)
Z	4
ρ_{calc}g/cm^3	1.193
μ/mm^{-1}	1.015
F(000)	1104.0
Crystal size/mm^3	0.312 × 0.144 × 0.039
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.868 to 141.618
Index ranges	-11 ≤ h ≤ 10, -10 ≤ k ≤ 14, -31 ≤ l ≤ 28
Reflections collected	22000
Independent reflections	5480 [R_{int} = 0.0418, R_{sigma} = 0.0306]
Data/restraints/parameters	5480/0/346
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1186
Final R indexes [all data]	R_1 = 0.0524, wR_2 = 0.1215
Largest diff. peak/hole / e Å^{-3}	0.69/-0.36
Flack parameter	0.02(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_2516. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Si1	4040.7(9)	4210.0(7)	4263.6(3)	28.0(2)
O5	850(3)	10947.3(18)	3223.4(9)	40.7(6)
O6	2309(2)	9819.9(18)	2780.1(9)	34.6(5)
O14	2806(2)	4793.0(18)	3898.9(8)	28.8(5)
O16	994(3)	4625.2(18)	2652.2(8)	30.5(5)
O19	-287(2)	7368.9(18)	2618.4(9)	29.8(5)
C1	1698(3)	7967(2)	3118.4(11)	25.9(6)
C2	778(4)	8894(2)	3335.9(11)	30.0(6)
C3	-349(5)	8840(3)	3638.2(16)	49.3(10)
C4	1260(3)	9997(3)	3122.9(13)	32.3(7)

C7	2557(3)	8601(2)	2698.8(12)	27.7(6)
C8	4122(3)	8431(3)	2699.7(12)	30.8(6)
C9	4833(3)	7478(3)	2800.8(12)	30.6(6)
C10	6416(3)	7417(3)	2758.6(17)	44.1(9)
C11	4151(3)	6432(3)	2951.6(12)	28.4(6)
C12	3541(3)	5594(3)	3100.7(11)	26.7(6)
C13	2670(3)	4712(2)	3346.1(11)	25.5(6)
C14	1092(3)	4827(2)	3198.0(11)	25.7(6)
C15	514(3)	6028(2)	3298.1(12)	27.5(6)
C17	237(4)	3959(3)	3503.6(13)	33.2(7)
C18	921(3)	6935(2)	2890.2(11)	23.6(5)
C20	5597(4)	5175(3)	4334.3(13)	36.5(7)
C21	5504(5)	6332(3)	4223.8(16)	49.5(9)
C22	6632(6)	7064(4)	4336(2)	71.3(14)
C23	7842(6)	6637(5)	4558(2)	72.2(15)
C24	7945(5)	5501(5)	4671(2)	65.1(13)
C25	6844(4)	4777(4)	4554.3(16)	49.3(9)
C26	4635(4)	2818(3)	3974.1(13)	40.0(8)
C27	3862(5)	1817(3)	4013(2)	59.6(12)
C28	4357(6)	798(4)	3808(2)	79.7(18)
C29	5635(7)	759(5)	3553(2)	80.0(19)
C30	6404(7)	1745(5)	3499.8(17)	72.9(16)
C31	5917(6)	2762(4)	3708.9(14)	54.9(11)
C32	3171(4)	4120(3)	4925.9(13)	38.0(7)
C33	2908(6)	5328(4)	5117.7(17)	61.6(12)
C34	1734(5)	3522(5)	4894.6(17)	62.1(12)
C35	4085(5)	3500(4)	5321.5(14)	55.0(10)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for exp_2516. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	29.9(4)	23.6(4)	30.6(4)	1.0(3)	-2.9(3)	0.0(3)
O5	52.0(14)	18.0(10)	52.2(13)	-4.4(9)	-12.1(12)	7.5(11)
O6	32.8(11)	18.6(10)	52.3(13)	7.0(9)	-3.7(10)	-2.6(9)
O14	32.2(11)	25.2(10)	28.8(10)	0.3(8)	-3.1(8)	2.8(9)
O16	38.4(11)	19.2(9)	33.8(10)	-1.1(8)	-6.3(9)	-1.1(9)
O19	23.3(10)	20.5(10)	45.7(13)	-0.8(9)	-9.2(9)	2.8(8)
C1	25.5(14)	19.0(13)	33.1(14)	0.0(11)	-1.3(11)	-1.3(11)
C2	35.6(16)	21.4(14)	32.9(14)	-3.3(10)	-0.5(13)	1.2(12)
C3	61(2)	32.2(18)	55(2)	-1.5(15)	22.5(19)	10.6(17)
C4	35.6(17)	23.4(15)	37.9(15)	-1.1(12)	-9.7(12)	1.2(13)
C7	26.6(14)	20.6(13)	35.8(14)	1.6(11)	-1.4(12)	-3.9(12)
C8	28.3(14)	25.5(14)	38.4(15)	1.0(11)	2.9(13)	-10.3(13)
C9	20.6(14)	33.0(16)	38.4(16)	0.7(13)	1.2(11)	-2.4(13)
C10	21.3(15)	43(2)	68(2)	3.7(17)	6.4(14)	-0.7(14)
C11	21.2(13)	26.2(14)	37.9(14)	1.4(12)	-1.7(12)	5.5(12)
C12	22.0(13)	24.8(15)	33.4(14)	0.5(11)	-1.6(11)	5.8(12)
C13	29.2(14)	18.2(13)	29.2(13)	0.6(10)	-4.1(11)	6.0(12)
C14	26.3(14)	19.7(13)	31.1(13)	0.4(10)	-4.0(11)	-2.4(12)
C15	24.8(13)	20.3(14)	37.4(15)	1.8(11)	1.8(11)	-0.5(11)
C17	36.3(17)	20.9(14)	42.4(17)	3.5(12)	-2.3(13)	-4.7(13)
C18	20.3(12)	15.8(12)	34.6(13)	1.0(10)	-1.5(11)	3.0(11)

C20	33.5(16)	38.2(17)	37.7(16)	0.4(13)	-1.8(13)	-8.5(14)
C21	60(2)	36.5(18)	52(2)	2.2(16)	-14.0(18)	-15.2(18)
C22	89(4)	51(3)	75(3)	10(2)	-18(3)	-30(3)
C23	64(3)	81(4)	71(3)	-1(3)	-13(2)	-37(3)
C24	32.9(19)	83(4)	79(3)	2(3)	-6.6(19)	-16(2)
C25	36.0(19)	57(2)	55(2)	5.0(18)	-3.4(16)	-4.7(18)
C26	52(2)	34.1(17)	33.6(16)	-1.8(13)	-14.5(15)	12.1(16)
C27	52(2)	39(2)	88(3)	-20(2)	-28(2)	4.2(19)
C28	83(4)	39(2)	117(4)	-26(3)	-55(3)	12(3)
C29	114(5)	59(3)	68(3)	-31(2)	-47(3)	52(3)
C30	108(4)	73(3)	37.7(19)	-4(2)	1(2)	49(3)
C31	81(3)	46(2)	37.4(17)	3.5(15)	8(2)	25(2)
C32	34.4(16)	45(2)	34.3(15)	4.4(14)	-2.0(13)	-2.0(16)
C33	77(3)	60(3)	48(2)	-5.2(19)	13(2)	16(2)
C34	48(2)	92(4)	47(2)	13(2)	2.2(18)	-18(2)
C35	53(2)	75(3)	37.4(17)	13.4(18)	0.7(18)	14(2)

Table 4 Bond Lengths for exp_2516.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	O14	1.653(2)	C12	C13	1.468(4)
Si1	C20	1.874(3)	C13	C14	1.557(4)
Si1	C26	1.882(4)	C14	C15	1.535(4)
Si1	C32	1.899(3)	C14	C17	1.522(4)
O5	C4	1.209(4)	C15	C18	1.544(4)
O6	C4	1.350(4)	C20	C21	1.389(5)
O6	C7	1.464(3)	C20	C25	1.396(5)
O14	C13	1.432(3)	C21	C22	1.406(6)
O16	C14	1.428(3)	C22	C23	1.380(8)
O19	C18	1.440(3)	C23	C24	1.367(8)
C1	C2	1.505(4)	C24	C25	1.383(6)
C1	C7	1.546(4)	C26	C27	1.390(6)
C1	C18	1.535(4)	C26	C31	1.401(6)
C2	C3	1.327(5)	C27	C28	1.388(6)
C2	C4	1.478(4)	C28	C29	1.385(10)
C7	C8	1.504(4)	C29	C30	1.375(9)
C8	C9	1.332(5)	C30	C31	1.389(6)
C9	C10	1.514(4)	C32	C33	1.522(6)
C9	C11	1.441(4)	C32	C34	1.540(6)
C11	C12	1.205(4)	C32	C35	1.524(5)

Table 5 Bond Angles for exp_2516.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O14	Si1	C20	111.62(14)	O16	C14	C17	111.3(2)
O14	Si1	C26	110.37(13)	C15	C14	C13	112.6(2)
O14	Si1	C32	102.85(13)	C17	C14	C13	109.4(2)
C20	Si1	C26	108.90(17)	C17	C14	C15	109.6(2)
C20	Si1	C32	106.98(16)	C14	C15	C18	115.4(2)
C26	Si1	C32	116.02(17)	O19	C18	C1	107.0(2)
C4	O6	C7	111.3(2)	O19	C18	C15	111.9(2)
C13	O14	Si1	126.99(19)	C1	C18	C15	113.8(2)
C2	C1	C7	102.7(2)	C21	C20	Si1	121.3(3)
C2	C1	C18	115.5(3)	C21	C20	C25	117.6(4)

C18	C1	C7	111.5(2)	C25	C20	Si1	120.7(3)
C3	C2	C1	130.9(3)	C20	C21	C22	120.4(4)
C3	C2	C4	120.7(3)	C23	C22	C21	120.1(5)
C4	C2	C1	108.3(3)	C24	C23	C22	120.1(4)
O5	C4	O6	121.4(3)	C23	C24	C25	119.8(5)
O5	C4	C2	128.8(3)	C24	C25	C20	121.9(4)
O6	C4	C2	109.8(3)	C27	C26	Si1	123.0(3)
O6	C7	C1	106.5(2)	C27	C26	C31	117.3(4)
O6	C7	C8	106.8(2)	C31	C26	Si1	119.7(3)
C8	C7	C1	117.4(3)	C28	C27	C26	121.3(5)
C9	C8	C7	128.0(3)	C29	C28	C27	120.5(5)
C8	C9	C10	122.1(3)	C30	C29	C28	119.2(4)
C8	C9	C11	122.5(3)	C29	C30	C31	120.4(6)
C11	C9	C10	115.4(3)	C30	C31	C26	121.3(5)
C12	C11	C9	176.1(3)	C33	C32	Si1	108.1(3)
C11	C12	C13	169.8(3)	C33	C32	C34	107.1(4)
O14	C13	C12	109.2(2)	C33	C32	C35	108.7(3)
O14	C13	C14	109.0(2)	C34	C32	Si1	111.5(3)
C12	C13	C14	112.3(2)	C35	C32	Si1	112.2(3)
O16	C14	C13	106.8(2)	C35	C32	C34	109.0(3)
O16	C14	C15	107.1(2)				

Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for exp_2516.

Atom	*x*	*y*	*z*	U(eq)
H16	820(50)	3960(40)	2618(17)	46
H19	-470(50)	6940(40)	2407(18)	45
H1	2349.84	7696.53	3396.82	31
H3A	-853.87	9515.38	3719.8	59
H3B	-649.54	8126.97	3773.05	59
H7	2184.75	8385	2349.17	33
H8	4670.46	9082.85	2618.02	37
H10A	6804.41	7105.76	3081.19	66
H10B	6792.75	8184.19	2700.24	66
H10C	6674.11	6922.84	2467.01	66
H13	3013.07	3946.21	3232.1	31
H15A	849.83	6287.31	3642.44	33
H15B	-522.46	5983.48	3314.59	33
H17A	-724.92	3939.66	3368.98	50
H17B	221.14	4176.68	3871.17	50
H17C	663.81	3203.18	3467.47	50
H18	1552.91	6565.36	2629.67	28
H21	4672.63	6629.79	4071.67	59
H22	6561.62	7854.18	4259.09	86
H23	8603.75	7133.74	4631.92	87
H24	8771.12	5210.54	4829.72	78
H25	6938.86	3985.89	4625.83	59
H27	2976.78	1829.49	4182.69	72
H28	3815.08	122.23	3843.38	96
H29	5977.06	60.34	3415.32	96
H30	7273.79	1729.2	3319.42	87
H31	6464.22	3434.6	3671.19	66

H33A	3804.23	5731.59	5150.01	92
H33B	2443.68	5300.99	5457.26	92
H33C	2305.46	5730.75	4869.43	92
H34A	1149.53	3902.62	4633.75	93
H34B	1269.94	3560.33	5233.91	93
H34C	1868.1	2721.82	4796.23	93
H35A	4234.73	2712.13	5207.84	83
H35B	3615.51	3501.37	5660.27	83
H35C	4991.63	3889.32	5350.75	83

Experimental

Single crystals of $C_{31}H_{36}O_5Si$ **[exp_2516]** were **[30]**. A suitable crystal was selected and **[30]** on a **SuperNova, Dual, Cu at home/near, Atlas** diffractometer. The crystal was kept at 180.01(10) K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [exp_2516]

Crystal Data for $C_{31}H_{36}O_5Si$ (M =516.69 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.52826(14) Å, b = 11.72660(18) Å, c = 25.7421(4) Å, V = 2876.27(8) Å^3, Z = 4, T = 180.01(10) K, μ(CuKα) = 1.015 mm^{-1}, *Dcalc* = 1.193 g/cm^3, 22000 reflections measured (6.868° ≤ 2Θ ≤ 141.618°), 5480 unique (R_{int} = 0.0418, R_{sigma} = 0.0306) which were used in all calculations. The final R_1 was 0.0473 (I > 2σ(I)) and wR_2 was 0.1215 (all data).

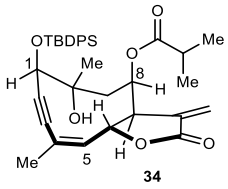
Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Twinned data refinement
Scales: 0.98(4)
0.02(4)
2. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All C(H,H,H) groups, All O(H) groups
3.a Ternary CH refined with riding coordinates:
C1(H1), C7(H7), C13(H13), C18(H18)
3.b Secondary CH2 refined with riding coordinates:
C15(H15A,H15B)
3.c Aromatic/amide H refined with riding coordinates:
C8(H8), C21(H21), C22(H22), C23(H23), C24(H24), C25(H25), C27(H27), C28(H28), C29(H29), C30(H30), C31(H31)
3.d X=CH2 refined with riding coordinates:
C3(H3A,H3B)
3.e Idealised Me refined as rotating group:
C10(H10A,H10B,H10C), C17(H17A,H17B,H17C), C33(H33A,H33B,H33C), C34(H34A,H34B, H34C), C35(H35A,H35B,H35C)

This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys.



34

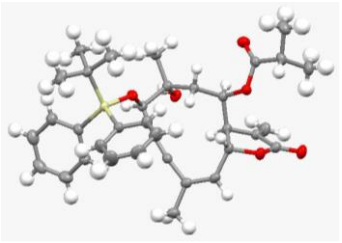


Table 1 Crystal data and structure refinement for WL3c.

Identification code	WL3c
Empirical formula	$C_{35}H_{42}O_6Si$
Formula weight	586.77
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.10599(3)
b/Å	15.40214(5)
c/Å	23.08098(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3237.148(18)
Z	4
ρ_{calc}g/cm^3	1.204
μ/mm^{-1}	0.985
F(000)	1256.0
Crystal size/mm^3	0.376 × 0.195 × 0.097
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.9 to 148.85
Index ranges	-11 ≤ h ≤ 10, -19 ≤ k ≤ 19, -28 ≤ l ≤ 28
Reflections collected	144009
Independent reflections	6598 [R_{int} = 0.0487, R_{sigma} = 0.0108]
Data/restraints/parameters	6598/0/390
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0250, wR_2 = 0.0665
Final R indexes [all data]	R_1 = 0.0252, wR_2 = 0.0666
Largest diff. peak/hole / e Å^{-3}	0.16/-0.23
Flack parameter	0.00(2)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for WL3c. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Si1	5657.2(4)	4971.8(3)	8198.2(2)	22.72(9)
O8	12510.2(12)	3724.5(8)	6543.6(5)	29.2(2)
O10	13658.7(13)	3370.7(9)	5723.0(5)	36.7(3)
O15	10518.9(11)	5071.3(7)	6018.1(4)	25.8(2)
O17	9170.8(13)	5934.8(8)	5436.8(5)	35.4(3)
O23	6620.0(12)	3719.5(7)	6160.3(5)	27.5(2)
O25	6173.2(12)	4904.2(7)	7512.8(4)	26.7(2)
C1	6264.9(17)	4155.7(9)	7152.0(6)	23.8(3)
C2	7420.3(17)	3558.4(10)	7350.6(6)	25.8(3)
C3	8492.8(17)	3132.7(10)	7452.5(6)	25.9(3)

C4	9849.3(18)	2668.8(10)	7515.5(7)	26.9(3)
C5	9922(2)	1913.1(11)	7927.0(8)	33.3(4)
C6	11010.6(17)	2927.9(11)	7203.5(7)	28.4(3)
C7	11027.2(16)	3680.3(10)	6789.3(7)	25.9(3)
C9	12520.7(18)	3445.0(10)	5990.7(7)	28.6(3)
C11	10993.1(17)	3273.4(10)	5798.1(7)	26.4(3)
C12	9971.3(16)	3607.9(10)	6261.9(6)	24.3(3)
C13	10691(2)	2882.4(12)	5302.8(8)	36.9(4)
C14	9277.5(16)	4474.7(9)	6082.8(6)	23.8(3)
C16	10320.7(18)	5767.2(10)	5669.2(6)	27.1(3)
C18	11738.5(19)	6271.1(12)	5599.7(7)	32.0(3)
C19	11439(2)	7202.7(13)	5413.2(9)	44.6(4)
C20	12701(2)	5789.6(14)	5162.2(9)	43.5(4)
C21	8197.3(15)	4876.1(9)	6513.3(6)	23.6(3)
C22	6636.3(16)	4468.0(9)	6529.7(6)	23.4(3)
C24	5497.9(17)	5128.2(10)	6333.9(7)	28.4(3)
C26	4535.8(17)	6003.9(10)	8225.4(7)	29.1(3)
C27	3274.0(19)	5988.0(12)	7780.5(8)	36.0(4)
C28	3936(2)	6171.1(13)	8836.5(8)	40.9(4)
C29	5546(2)	6763.9(11)	8060.4(10)	42.7(4)
C30	4645.1(18)	3976.7(10)	8443.0(7)	28.0(3)
C31	3116(2)	3934.2(12)	8492.2(8)	34.6(4)
C32	2425(2)	3194.6(13)	8696.7(8)	41.2(4)
C33	3231(2)	2471.8(13)	8849.4(8)	41.4(4)
C34	4743(2)	2493.1(12)	8799.7(9)	42.1(4)
C35	5439(2)	3236.5(11)	8600.9(8)	36.0(4)
C36	7334.9(17)	5122.7(11)	8651.7(7)	28.6(3)
C37	7325(2)	4964.3(16)	9247.6(8)	43.1(4)
C38	8506(2)	5201.3(18)	9593.2(9)	56.9(6)
C39	9723(2)	5600.2(16)	9353.3(9)	51.3(5)
C40	9770(2)	5748.8(14)	8762.0(9)	44.3(4)
C41	8594.2(19)	5509.6(12)	8416.6(8)	35.1(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for WL3c. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	19.62(18)	24.01(18)	24.53(18)	1.06(15)	1.26(14)	0.39(16)
O8	19.6(5)	39.2(6)	28.8(5)	-0.6(5)	-0.6(4)	-1.4(5)
O10	23.0(6)	47.7(7)	39.4(6)	-3.9(5)	5.1(5)	1.1(5)
O15	21.0(5)	29.3(5)	27.2(5)	4.3(4)	0.0(4)	-2.4(5)
O17	32.0(6)	38.4(6)	36.0(6)	7.9(5)	-5.6(5)	-0.2(5)
O23	21.4(5)	29.4(6)	31.8(5)	-8.4(4)	-2.0(4)	-0.4(4)
O25	31.3(5)	23.1(5)	25.8(5)	-0.4(4)	3.6(4)	0.6(4)
C1	21.4(7)	22.6(6)	27.5(7)	-0.6(6)	1.2(5)	0.1(6)
C2	25.2(7)	24.4(7)	27.7(7)	0.7(5)	2.2(6)	-2.0(6)
C3	26.8(8)	25.4(7)	25.5(7)	1.9(6)	1.3(6)	-2.2(6)
C4	26.6(8)	27.4(7)	26.7(7)	-0.9(6)	-4.1(6)	2.3(6)
C5	32.4(9)	32.6(8)	35.0(8)	7.1(7)	-6.0(7)	0.6(7)
C6	23.7(8)	32.2(8)	29.4(8)	0.7(6)	-3.9(6)	6.6(6)
C7	19.4(7)	31.9(7)	26.4(7)	-1.0(6)	0.1(6)	0.7(6)
C9	23.8(7)	30.3(8)	31.7(8)	-0.4(6)	-0.6(6)	1.5(6)
C11	23.1(7)	27.1(7)	29.0(7)	0.2(6)	0.3(6)	0.8(6)

C12	20.3(7)	27.4(7)	25.1(7)	-0.3(5)	-0.7(6)	0.1(6)
C13	31.5(8)	45.1(9)	34.1(8)	-9.4(7)	-0.1(7)	1.3(8)
C14	20.0(6)	26.5(7)	25.0(7)	0.7(5)	0.1(6)	-1.9(6)
C16	28.0(8)	29.5(7)	23.7(7)	0.8(6)	2.9(6)	-0.6(6)
C18	31.0(8)	36.3(9)	28.9(8)	3.3(6)	3.8(6)	-6.3(7)
C19	52.5(12)	37.1(9)	44.3(10)	7.1(8)	8.2(9)	-6.5(9)
C20	37.5(10)	50.3(11)	42.7(10)	3.6(8)	14.2(8)	0.2(8)
C21	21.2(7)	24.6(7)	25.0(6)	-0.5(6)	1.1(5)	-2.0(6)
C22	20.9(7)	23.3(7)	26.1(7)	-2.5(6)	-0.4(6)	-0.1(6)
C24	25.0(7)	31.4(8)	28.8(7)	2.3(6)	-1.0(6)	4.0(6)
C26	23.0(7)	25.7(7)	38.6(8)	-2.5(6)	1.2(7)	2.5(6)
C27	27.4(8)	35.0(9)	45.6(9)	3.6(7)	-3.7(7)	6.3(7)
C28	31.0(9)	45.2(10)	46.6(10)	-15.3(8)	3.3(8)	4.6(8)
C29	33.5(9)	25.9(8)	68.7(12)	1.8(8)	1.4(9)	0.4(7)
C30	28.8(8)	29.3(7)	25.9(7)	-0.1(6)	2.9(6)	-3.3(6)
C31	29.8(8)	36.9(9)	37.3(8)	0.8(7)	0.0(7)	-4.4(7)
C32	36.7(9)	45.8(10)	41.0(9)	-2.9(8)	1.4(8)	-15.6(8)
C33	54.3(12)	34.0(9)	35.9(9)	-0.4(7)	1.2(8)	-18.3(8)
C34	49.4(11)	29.0(8)	47.9(10)	4.5(8)	-2.4(9)	-2.4(8)
C35	35.6(9)	30.0(8)	42.5(9)	3.0(7)	4.1(7)	0.1(7)
C36	23.9(7)	32.6(8)	29.3(7)	3.7(6)	-0.4(6)	1.0(6)
C37	34.8(9)	62.2(12)	32.3(8)	11.3(8)	-2.4(7)	-3.7(10)
C38	46.8(11)	89.3(18)	34.5(10)	9.4(10)	-13.2(9)	0.1(12)
C39	34.4(10)	67.9(14)	51.5(11)	1.4(10)	-19.4(9)	-1.2(9)
C40	23.9(8)	55.0(12)	53.9(11)	5.7(9)	-4.6(8)	-5.3(8)
C41	25.6(8)	46.1(10)	33.6(8)	4.1(7)	-0.7(7)	-2.4(7)

Table 4 Bond Lengths for WL3c.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	O25	1.6537(11)	C12	C14	1.534(2)
Si1	C26	1.8904(16)	C14	C21	1.5289(19)
Si1	C30	1.8755(16)	C16	C18	1.515(2)
Si1	C36	1.8663(16)	C18	C19	1.523(3)
O8	C7	1.4662(18)	C18	C20	1.529(3)
O8	C9	1.3469(19)	C21	C22	1.5547(19)
O10	C9	1.212(2)	C22	C24	1.521(2)
O15	C14	1.4643(17)	C26	C27	1.541(2)
O15	C16	1.3528(19)	C26	C28	1.534(2)
O17	C16	1.204(2)	C26	C29	1.537(2)
O23	C22	1.4341(18)	C30	C31	1.399(2)
O25	C1	1.4246(17)	C30	C35	1.398(2)
C1	C2	1.471(2)	C31	C32	1.384(3)
C1	C22	1.552(2)	C32	C33	1.380(3)
C2	C3	1.200(2)	C33	C34	1.381(3)
C3	C4	1.434(2)	C34	C35	1.387(3)
C4	C5	1.504(2)	C36	C37	1.397(2)
C4	C6	1.340(2)	C36	C41	1.402(2)
C6	C7	1.502(2)	C37	C38	1.388(3)
C7	C12	1.555(2)	C38	C39	1.383(3)
C9	C11	1.484(2)	C39	C40	1.384(3)
C11	C12	1.509(2)	C40	C41	1.385(3)
C11	C13	1.321(2)			

Table 5 Bond Angles for WL3c.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O25	Si1	C26	103.78(7)	O17	C16	O15	123.42(14)
O25	Si1	C30	112.11(6)	O17	C16	C18	125.73(15)
O25	Si1	C36	108.16(7)	C16	C18	C19	111.10(15)
C30	Si1	C26	114.32(7)	C16	C18	C20	108.06(15)
C36	Si1	C26	108.60(7)	C19	C18	C20	111.90(15)
C36	Si1	C30	109.58(7)	C14	C21	C22	116.14(12)
C9	O8	C7	110.99(12)	O23	C22	C1	107.39(12)
C16	O15	C14	117.06(11)	O23	C22	C21	108.67(11)
C1	O25	Si1	128.82(9)	O23	C22	C24	110.72(12)
O25	C1	C2	111.46(12)	C1	C22	C21	110.31(12)
O25	C1	C22	107.64(11)	C24	C22	C1	109.49(12)
C2	C1	C22	109.05(12)	C24	C22	C21	110.22(12)
C3	C2	C1	170.17(16)	C27	C26	Si1	111.54(11)
C2	C3	C4	173.33(16)	C28	C26	Si1	111.34(12)
C3	C4	C5	119.18(14)	C28	C26	C27	110.49(14)
C6	C4	C3	118.47(14)	C28	C26	C29	108.24(15)
C6	C4	C5	122.35(14)	C29	C26	Si1	108.00(11)
C4	C6	C7	125.42(14)	C29	C26	C27	107.05(15)
O8	C7	C6	106.93(12)	C31	C30	Si1	123.50(13)
O8	C7	C12	105.67(11)	C35	C30	Si1	119.38(13)
C6	C7	C12	115.88(13)	C35	C30	C31	117.10(16)
O8	C9	C11	109.52(13)	C32	C31	C30	121.26(18)
O10	C9	O8	121.29(15)	C33	C32	C31	120.60(18)
O10	C9	C11	129.19(15)	C32	C33	C34	119.35(18)
C9	C11	C12	107.73(13)	C33	C34	C35	120.18(19)
C13	C11	C9	122.40(15)	C34	C35	C30	121.51(17)
C13	C11	C12	129.86(15)	C37	C36	Si1	121.68(13)
C11	C12	C7	101.45(12)	C37	C36	C41	117.42(15)
C11	C12	C14	111.10(12)	C41	C36	Si1	120.37(12)
C14	C12	C7	113.78(12)	C38	C37	C36	121.02(18)
O15	C14	C12	104.81(11)	C39	C38	C37	120.51(18)
O15	C14	C21	108.01(11)	C38	C39	C40	119.51(18)
C21	C14	C12	116.22(12)	C39	C40	C41	120.00(18)
O15	C16	C18	110.81(13)	C40	C41	C36	121.52(16)

Table 6 Torsion Angles for WL3c.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Si1	O25	C1	C2	-66.87(16)	C9	C11	C12	C14	103.15(14)
Si1	O25	C1	C22	173.60(10)	C11	C12	C14	O15	-61.81(14)
Si1	C30	C31	C32	-177.44(13)	C11	C12	C14	C21	179.07(12)
Si1	C30	C35	C34	178.22(14)	C12	C14	C21	C22	-77.34(16)
Si1	C36	C37	C38	-170.22(18)	C13	C11	C12	C7	161.06(18)
Si1	C36	C41	C40	170.09(15)	C13	C11	C12	C14	-77.7(2)
O8	C7	C12	C11	21.17(15)	C14	O15	C16	O17	3.6(2)
O8	C7	C12	C14	-98.21(14)	C14	O15	C16	C18	-174.44(12)
O8	C9	C11	C12	8.68(17)	C14	C21	C22	O23	5.93(17)
O8	C9	C11	C13	-170.58(16)	C14	C21	C22	C1	123.40(13)
O10	C9	C11	C12	-170.77(17)	C14	C21	C22	C24	-115.56(14)
O10	C9	C11	C13	10.0(3)	C16	O15	C14	C12	156.38(12)

O15	C14	C21	C22	165.29(11)	C16	O15	C14	C21	-79.12(14)
O15	C16	C18	C19	-158.42(14)	C26	Si1	O25	C1	-140.30(12)
O15	C16	C18	C20	78.46(16)	C26	Si1	C30	C31	16.56(17)
O17	C16	C18	C19	23.6(2)	C26	Si1	C30	C35	-161.77(13)
O17	C16	C18	C20	-99.5(2)	C26	Si1	C36	C37	85.96(17)
O25	Si1	C26	C27	55.31(13)	C26	Si1	C36	C41	-85.51(15)
O25	Si1	C26	C28	179.24(11)	C30	Si1	O25	C1	-16.43(14)
O25	Si1	C26	C29	-62.06(14)	C30	Si1	C26	C27	-67.10(14)
O25	Si1	C30	C31	-101.19(15)	C30	Si1	C26	C28	56.82(14)
O25	Si1	C30	C35	80.47(14)	C30	Si1	C26	C29	175.53(12)
O25	Si1	C36	C37	-162.02(16)	C30	Si1	C36	C37	-39.54(18)
O25	Si1	C36	C41	26.51(16)	C30	Si1	C36	C41	148.99(14)
O25	C1	C22	O23	-175.81(11)	C30	C31	C32	C33	-1.0(3)
O25	C1	C22	C21	65.93(15)	C31	C30	C35	C34	-0.2(3)
O25	C1	C22	C24	-55.54(15)	C31	C32	C33	C34	0.4(3)
C2	C1	C22	O23	63.13(15)	C32	C33	C34	C35	0.3(3)
C2	C1	C22	C21	-55.13(15)	C33	C34	C35	C30	-0.4(3)
C2	C1	C22	C24	-176.59(12)	C35	C30	C31	C32	0.9(3)
C3	C4	C6	C7	0.6(2)	C36	Si1	O25	C1	104.49(13)
C4	C6	C7	O8	-179.71(15)	C36	Si1	C26	C27	170.22(11)
C4	C6	C7	C12	-62.2(2)	C36	Si1	C26	C28	-65.86(13)
C5	C4	C6	C7	-179.33(15)	C36	Si1	C26	C29	52.85(14)
C6	C7	C12	C11	-97.01(15)	C36	Si1	C30	C31	138.71(14)
C6	C7	C12	C14	143.61(13)	C36	Si1	C30	C35	-39.63(15)
C7	O8	C9	O10	-174.59(15)	C36	C37	C38	C39	-0.1(4)
C7	O8	C9	C11	5.90(17)	C37	C36	C41	C40	-1.7(3)
C7	C12	C14	O15	51.93(15)	C37	C38	C39	C40	-1.1(4)
C7	C12	C14	C21	-67.20(17)	C38	C39	C40	C41	0.9(4)
C9	O8	C7	C6	106.40(14)	C39	C40	C41	C36	0.6(3)
C9	O8	C7	C12	-17.61(16)	C41	C36	C37	C38	1.5(3)
C9	C11	C12	C7	-18.13(16)					

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for WL3c.

Atom	*x*	*y*	*z*	U(eq)
H23	5680(30)	3606(14)	6043(9)	41
H1	5298	3847.9	7150.01	29
H5A	9299.83	1441.39	7782.5	50
H5B	9575.3	2095.79	8309.98	50
H5C	10939.24	1709.76	7956.67	50
H6	11896.82	2609.36	7247.9	34
H7	10815.03	4228.66	7005.58	31
H12	9186.88	3170.16	6343.12	29
H13A	11465.25	2699.95	5055.49	44
H13B	9698.38	2783.69	5194.05	44
H14	8780.38	4402.9	5699.41	29
H18	12258.13	6281.7	5981.34	38
H19A	10874.71	7201.83	5051.7	67
H19B	12373	7505.3	5352.24	67
H19C	10876.52	7500.55	5715.79	67
H20A	12890.31	5199.28	5301.95	65
H20B	13634.95	6098.4	5116.34	65

H20C	12195.24	5762.54	4787.88	65
H21A	8096.1	5501.01	6421.07	28
H21B	8628.31	4833.3	6906.08	28
H24A	5693.89	5295.58	5931.68	43
H24B	5550.63	5642.85	6582.71	43
H24C	4515.59	4871.49	6361.27	43
H27A	3673.56	5874.49	7393.55	54
H27B	2770.37	6550.26	7781.39	54
H27C	2575.91	5529.01	7883.51	54
H28A	3298.07	5688.67	8951.78	61
H28B	3371.53	6712.76	8838.26	61
H28C	4755.72	6218.57	9109.86	61
H29A	6342.53	6810.48	8344.14	64
H29B	4978.09	7304.42	8057.21	64
H29C	5960.8	6661.41	7674.69	64
H31	2540.57	4422.09	8383.24	42
H32	1385.5	3184.73	8732.21	49
H33	2752.32	1964.46	8987.43	50
H34	5306.36	1997.27	8901.92	51
H35	6479.82	3242.93	8571.32	43
H37	6497.54	4690.22	9418.85	52
H38	8477.6	5088.74	9997.74	68
H39	10521.69	5770.9	9592.45	62
H40	10608.05	6014.85	8593.29	53
H41	8642.39	5610.09	8010.97	42

Experimental

Single crystals of $C_{35}H_{42}O_6Si$ **[WL3c]** were **[34]**. A suitable crystal was selected and **[34]** on a **XtaLAB Synergy, Dualflex, HyPix-Arc** diffractometer. The crystal was kept at 150.00(10) K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [WL3c]

Crystal Data for $C_{35}H_{42}O_6Si$ (M =586.77 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.10599(3) Å, b = 15.40214(5) Å, c = 23.08098(7) Å, V = 3237.148(18) Å^3, Z = 4, T = 150.00(10) K, μ(Cu Kα) = 0.985 mm^{-1}, *Dcalc* = 1.204 g/cm^3, 144009 reflections measured (6.9° ≤ 2Θ ≤ 148.85°), 6598 unique (R_{int} = 0.0487, R_{sigma} = 0.0108) which were used in all calculations. The final R_1 was 0.0250 (I > 2σ(I)) and wR_2 was 0.0666 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Twinned data refinement
Scales: 1.00(2)
0.00(2)
2. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All C(H,H,H) groups, All O(H) groups
3.a Ternary CH refined with riding coordinates:
C1(H1), C7(H7), C12(H12), C14(H14), C18(H18)

3.b Secondary CH2 refined with riding coordinates:
C21(H21A,H21B)
3.c Aromatic/amide H refined with riding coordinates:
C6(H6), C31(H31), C32(H32), C33(H33), C34(H34), C35(H35), C37(H37), C38(H38), C39(H39), C40(H40), C41(H41)
3.d X=CH2 refined with riding coordinates:
C13(H13A,H13B)
3.e Idealised Me refined as rotating group:
C5(H5A,H5B,H5C), C19(H19A,H19B,H19C), C20(H20A,H20B,H20C), C24(H24A,H24B, H24C), C27(H27A,H27B,H27C), C28(H28A,H28B,H28C), C29(H29A,H29B,H29C)
This report has been created with Olex2, compiled on Nov 21 2019 18:26:39 for OlexSys.

n) Abbreviation

Ac	acetyl
ACLY	ATP-citrate synthase
AD-mix-α	a mixture of $(DHQ)_2PHAL$, potassium osmate dihydrate, potassium carbonate, and potassium ferricyanide
AKT	protein kinase B
Boc	*tert*-butyloxycarbonyl
*t*Bu	*tert*-butyl
CID	collision-induced dissociation
*m*CPBA	*meta*-chloroperoxybenzoic acid
CSA	camphorsulfonic acid
CuAAC	Cu^I-catalyzed azide/alkyne cycloaddition
Cy3	Cyanine 3
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DCM	CH_2Cl_2, dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
(DHQD)2Pyr	hydroquinidine-2,5-diphenyl-4,6-pyrimidinediyl diether
DIPEA	*N,N*-diisopropylethylamine
DMAP	4-dimethylaminopyridine
DMEM	Dulbecco's modified eagle medium
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
dr	diastereomeric ratio
DTT	dithiothreitol
DMP	Dess–Martin periodinane
EDTA	ethylenediaminetetraacetic acid
ee	enantiomeric excess
Et	ethyl
FCS	fetal calf serum
HATU	1-[bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-b]pyridinium 3-oxide hexafluorophosphate
HCD	higher-energy C-trap dissociation
HF	hydrofluoric acid
HPLC	high-performance liquid chromatography
HRMS	high resolution mass spectrometry
Imid.	imidazole
IPO5	importin-5
IR	infrared spectra

KPNB1	karyopherin subunit beta 1
LC-MS	liquid chromatography–mass spectrometry
Me	methyl
m.p.	melting point
NLS	nuclear localization sequence
NOE	nuclear overhauser effect
PBS	phosphate-buffered saline
PFA	paraformaldehyde
PhMe	toluene
PMB	*p*-methoxybenzyl
PPh_3	triphenylphosphine
PTLC	preparative thin-layer chromatography
PTSA	*p*-TsOH, p-toluenesulfonic acid
Py	pyridine
RASAL2	RAS protein activator like 2
Red-Al	vitride, sodium bis(2-methoxyethoxy)aluminium hydride
r.t.	room temperature
SAD	Sharpless asymmetric dihydroxylation
Sat. aq.	saturated aqueous solution
SDS	sodium dodecyl sulphate
SDS-PAGE	sodium dodecyl sulphate–polyacrylamide gel electrophoresis
SEM	standard error of mean
STDEV	standard deviation
TBAF	tetra-*n*-butylammonium fluoride
TBDPSCl	tert-Butyl(chloro)diphenylsilane
TBTA	tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine
TCEP	tris(2-carboxyethyl)phosphine hydrochloride
Tf	triflate
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin-layer chromatography
TMS	trimethylsilyl
TMSOTf	trimethylsilyl trifluoromethanesulfonate
UBA1	ubiquitin-like modifier-activating enzyme 1