Electronic Supplementary Material (ESI) for Chemical Communications.

Towards the stereochemical assignment and synthesis of hemicalide: DP4f GIAO-NMR analysis and synthesis of a revised C16-C28 subunit

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Contents

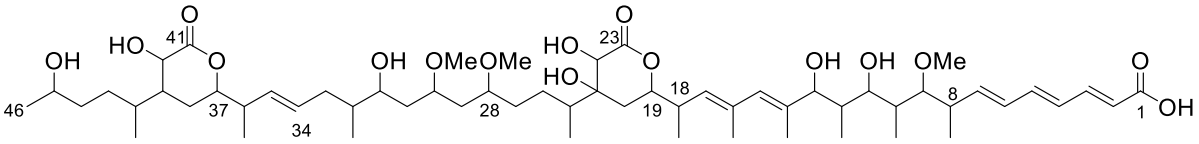
1. General experimental details

^{1}H nuclear magnetic resonance (NMR) spectra were recorded using an internal deuterium lock for the residual protons in $CDCl_3$ (δ_H 7.26) or d_4-MeOH (δ_H 3.31) at ambient probe temperatures on the following instruments: 500 MHz: Bruker AVANCE BB500 or TCI500 400 MHz: Bruker AM400 or DRX400 spectrometers. ^{1}H NMR data are presented as follows: chemical shift (in ppm relative to δ_{TMS} = 0 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, sext. = sextet, m= multiplet, b= broad, app = apparent), integration, coupling constants (*J* = Hz) and assignment. Coupling constants were taken directly from the spectra. Assignments were determined either on the basis of unambiguous chemical shift or coupling patterns, COSY experiments or by analogy to fully interpreted spectra for related compounds. ^{13}C NMR spectra were recorded by broadband proton spin decoupling at ambient probe temperatures on the following instruments: 500 MHz: Bruker AVANCE BB500 or TCI500 400 MHz: Bruker AM400 or DRX400 spectrometers, using an internal deuterium lock for $CDCl_3$ (δ_C 77.16) or d_4-MeOH (δ_C 49.00). All chemical shift values are recorded in ppm relative to δ_{TMS} = 0 ppm. Infra-red spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer fitted with a universal ATR sampling accessory. Wavelengths of maximum absorbance (vmax) are quoted in cm^{-1}. Optical rotations were measured on a Perkin Elmer 241 polarimeter at the sodium D-line (589 nm) and reported as follows: concentration (*c* in g/100 mL), and solvent. High resolution mass spectra (HRMS) were recorded by the EPSRC Mass Spectrometry service (Swansea, UK) using Electron Impact (EI) or Electrospray Ionization (ESI) techniques. The parent ion $[M]^+$ is quoted with the indicated cation.

All solvent mixtures are reported as vol/vol or % vol/vol unless otherwise stated. Analytical thin layer chromatography (TLC) was carried out on Merck Kieselgel 60 F254 plates with visualization by ultraviolet light (254 nm) and potassium permanganate or phosphomolybdic acid / $Ce_2(SO_4)_3$ dips. Flash chromatography was carried out on Merck Kieselgel 60 (240-400 mesh) silica gel under a positive pressure using distilled solvents. The procedure includes the subsequent evaporation of solvents *in vacuo*. Reagents and solvents were purified by standard means. Pet. Ether refers to Petroleum Ether 40/60 unless otherwise specified. Dichloromethane (CH_2Cl_2), toluene (PhMe), and ethyl acetate (EtOAc) were distilled from CaH_2 and stored under an argon atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium or potassium wire / benzophenone ketyl radical under an argon atmosphere. Triethylamine (NEt_3) and 2,6-lutidine were distilled from and stored over CaH_2. 4 Å molecular sieves were activated by heating under high vacuum or in a microwave. All other chemicals were used as received, except where otherwise stated in the experimental text. Solvents used for all extractions in work-up were distilled. All solutions of sodium bicarbonate ($NaHCO_3$), ammonium chloride (NH_4Cl), sodium thiosulfate ($Na_2S_2O_3$) and Rochelle's (Na / K tartrate) were saturated. The term "brine" describes a saturated aqueous solution of sodium chloride (NaCl).

All experiments were performed under anhydrous conditions in an atmosphere of argon, except where stated or when water or aqueous solutions were used, using oven-dried glassware and employing standard techniques for handling air-sensitive materials.

The atom numbering system for hemicalide (**1**) as proposed by Carletti *et al.* was adopted throughout.[1]



hemicalide (1)

[1] Carletti, I.; Massiot, G.; Debitus, C. Polyketide Molecules as Anticancer Agents. WO2011051380 (A1), May 5, 2011.

General computational procedure for DP4f probability analysis

The following procedure was performed for all DP4 calculations.[2] For the structure of interest, a conformational search was carried out in MacroModel [3] using a hybrid of Monte Carlo multiple−minimum (MCMM)[4] / low−mode sampling[5] with the Merck Molecular Force Field (MMFF),[6] interfaced with Maestro 9.3.[7] The searches were carried out with a sufficient number of steps to find all conformers within 10 kJ $mol^{-1}$of the global minima at least five times to ensure a thorough sampling of the conformational space for the molecule. Calculations were carried out using $CHCl_3$ as the solvent model. These calculations would typically generate between ten and 100 conformers and take around one week to complete. All conformers within 10 kJ mol^{-1} of the global minimum were then further subjected to quantum mechanical calculations. Single point energies and GIAO NMR shielding constants were evaluated at the B3LYP[8,9]/6−31G[10] (d,p) level, implemented in Jaguar 7.9.[11] The resulting shielding constants were then weighted according to the Boltzmann distribution using the single−point energies obtained, assuming T = 298K. Where appropriate, the shielding constants were also averaged over symmetry related positions (*e.g.* the three protons of a methyl group). The obtained shielding constants were then converted into NMR chemical shifts and then analysed using the DP4 web applet.[12]

A caveat: This procedure has the advantage that the computational cost of the analysis, whilst still demanding, is at least accessible. However, this computational tractability comes at the expense of introducing new uncertainties into the calculations. The available experimental NMR data for one small molecule would need to be compared with the calculated ^{1}H and ^{13}C chemical shifts for related but smaller molecules. Clearly, the NMR data for hemicalide will not precisely correspond to the calculated NMR shift data for these virtual fragments, even if the stereochemistry of the fragment matched. The DP4 method calculates probabilities for each assignment based on the assumption that one of the structures supplied is correct. In this case, we know that none of the fragments precisely correspond to the experiment, because we are not studying the whole molecule. We expect, therefore, that the DP4f probabilities will overstate the confidence that we can have in the assignments, but they will still provide guidance in the progressive assignment of the stereochemistry.

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[2] Smith, S. G.; Goodman, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 12946.

[3] MacroModel, Version 9.9, Schrodinger, LLC, New York, NY, 2012.

[4] Chang, G.; Guida, W. C.; Still, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4379.

[5] Kolossváry, I.; Guida, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 5011.

[6] Halgren, T. A. *J. Comput. Chem.* **1996**, *17*, 490.

[7] Maestro, version 9.3, Schrodinger, LLC, New York, NY, 2012.

[8] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[9] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

[10] Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

[11] Jaguar, version 7.9, Schrodinger, LLC, New York, NY, 2012.

[12] http://www-jmg.ch.cam.ac.uk/tools/nmr/DP4/

2. Computational modelling of the C13-C28 and C36-C46 subunits of hemicalide

2.1. DP4f GIAO-NMR analysis of the C13-C28 fragment 7

Figure S1 lists the structures of the 16 diastereoisomers **7A**-**P** of the virtual fragment **7** considered for assigning the stereochemistry within the C16-C25 region of hemicalide.

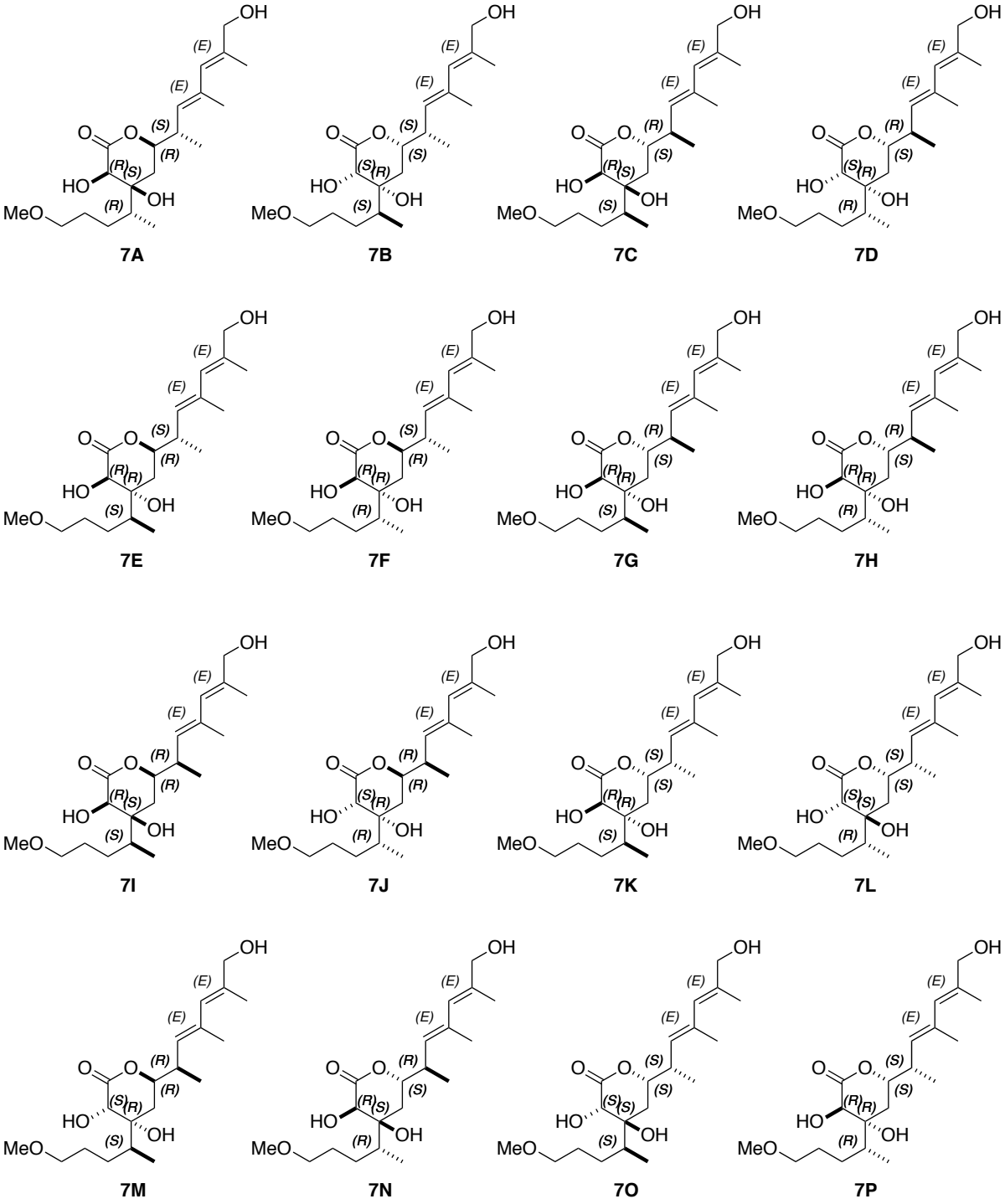


Figure S1. The 16 stereoisomers considered for the assignment of the C13-C28 region.

2.1.1. Molecular modelling of the C13-C28 region

Molecular modelling was carried out for all 16 diastereoisomers **7A**-**7P** using a 50,000 step hybrid Monte-Carlo multiple-minimum/ low-mode sampling using the MMFF force field and $CHCl_3$ as the solvent. No bond restraints were applied. Structures found within 21 $kJmol^{-1}$ of the lowest energy conformer were recorded.

Following redundant conformer elimination (RMS deviation cut-off 0.7Å, comparing all atoms), the number of conformers was reduced to a more computationally manageable number (See **Table S1**).

Isomer	Conformers ≤10 $kJmol^{-1}$ (Conformational search)	Conformers ≤10 $kJmol^{-1}$ Redundant conformer elimination
7A	268	101
7B	470	154
7C	171	59
7D	363	128
7E	222	56
7F	196	54
7G	200	64
7H	342	111
7I	226	89
7J	411	147
7K	441	139
7L	256	77
7M	340	108
7N	144	43
7O	327	97
7P	666	208

Table S1. Number of conformers generated from the conformational search and redundant conformation elimination for the C13-C28 region.

2.1.2 Atomic coordinates for the minimum energy conformers for 7A-P

Isomer 7A

atom	x	y	z
C1	-98.5805360000	3.4799460000	3.0018820000
C2	-98.8881530000	4.9235720000	2.6115880000
C3	-100.0781480000	4.9953950000	1.6211470000
C4	-100.0945510000	3.7980910000	0.6485510000
C5	-98.7473680000	3.0722890000	0.6404740000
O6	-98.4519120000	2.6061410000	1.9740460000
C7	-98.7092210000	1.8786110000	-0.3509880000
C8	-97.3234330000	1.2200770000	-0.3580540000
O9	-98.3782580000	3.1491220000	4.1680250000
O10	-99.2028200000	5.7273360000	3.7623050000
C11	-100.1306150000	6.3880940000	0.8923940000
C12	-101.4921420000	6.6372180000	0.2142310000
C13	-98.9776990000	6.5852170000	-0.1227940000

C14	-98.7834700000	8.0484300000	-0.5484560000
O15	-101.2831730000	4.8998310000	2.4177550000
C16	-97.5971070000	8.2187600000	-1.4967200000
C17	-99.7474980000	0.8213270000	-0.0356770000
C18	-100.7875370000	0.4187480000	-0.7925750000
C19	-101.1806560000	0.9797930000	-2.1320900000
C20	-101.6917340000	-0.6140970000	-0.3038080000
C21	-101.3788990000	-1.8890450000	0.0061310000
C22	-100.0137020000	-2.5066250000	-0.1546620000
C23	-102.4369810000	-2.8312690000	0.5188410000
O24	-102.1017150000	-3.2412020000	1.8371340000
O25	-96.3997190000	7.8112740000	-0.8350060000
C26	-95.2591400000	7.9812950000	-1.6687840000
H27	-97.9612730000	5.3251440000	2.1929730000
H28	-100.3570100000	4.1009740000	-0.3697730000
H29	-100.8798830000	3.1009680000	0.9689670000
H30	-97.9478840000	3.7647680000	0.3463710000
H31	-98.8686140000	2.2871630000	-1.3536540000
H32	-97.2738650000	0.4260060000	-1.1118690000
H33	-96.5478520000	1.9548860000	-0.5995200000
H34	-97.0756000000	0.7749140000	0.6119950000
H35	-98.6695020000	5.3604110000	4.4976500000
H36	-100.0394820000	7.1611050000	1.6682850000
H37	-101.5584030000	7.6568470000	-0.1769330000
H38	-102.3205950000	6.5247510000	0.9205220000
H39	-101.6618580000	5.9495100000	-0.6196930000
H40	-98.0376890000	6.2314740000	0.3086960000
H41	-99.1561810000	5.9763720000	-1.0173690000
H42	-99.6812290000	8.4273280000	-1.0463190000
H43	-98.6143800000	8.6563660000	0.3484640000
H44	-101.1281200000	5.4834900000	3.1913550000
H45	-97.7437290000	7.6138220000	-2.3989930000
H46	-97.5126880000	9.2723100000	-1.7868220000
H47	-99.6088410000	0.3434490000	0.9367130000
H48	-100.5398560000	1.7980110000	-2.4662300000
H49	-101.1360400000	0.1976000000	-2.8981020000
H50	-102.2040630000	1.3704680000	-2.0991480000
H51	-102.7256700000	-0.2808450000	-0.2035990000
H52	-100.0898210000	-3.4523830000	-0.7021480000
H53	-99.3192830000	-1.8758390000	-0.7161350000
H54	-99.5704190000	-2.7097700000	0.8253660000
H55	-103.4295960000	-2.3698730000	0.5495370000
H56	-102.5045390000	-3.7199100000	-0.1167930000
H57	-101.9117360000	-2.4280250000	2.3373220000
H58	-94.3762280000	7.6520260000	-1.1145120000
H59	-95.3522420000	7.3721040000	-2.5729620000
H60	-95.1328890000	9.0352650000	-1.9343120000

Isomer 7B

C1	-2.6105420000	1.3829100000	-1.9651110000
C2	-1.3146830000	1.2743660000	-2.7632190000
C3	-0.4639210000	2.5503610000	-2.5708280000
C4	-0.4450160000	3.0108150000	-1.0964290000
C5	-1.1406140000	2.0064480000	-0.1701920000
O6	-2.4720080000	1.7582020000	-0.6709960000
C7	-1.2530240000	2.5237690000	1.2878270000
C8	-2.0892280000	1.5674500000	2.1530870000
O9	-3.7009480000	1.0839690000	-2.4464000000
O10	-1.5757320000	1.0988900000	-4.1646000000

C11	0.9739200000	2.4084870000	-3.1915240000
C12	1.7427530000	3.7442390000	-3.1713560000
C13	1.7961040000	1.2660310000	-2.5473190000
C14	3.2196030000	1.1214610000	-3.1039720000
O15	-1.1214020000	3.5977990000	-3.3265570000
C16	3.9239760000	-0.1218700000	-2.5632250000
C17	0.1062310000	2.6935200000	1.9362260000
C18	0.7329650000	3.8433840000	2.2556140000
C19	0.1997450000	5.2297500000	2.0098110000
C20	2.0109010000	3.8255930000	2.9565220000
C21	3.1613530000	3.2369460000	2.5698270000
C22	3.3698770000	2.5068040000	1.2693680000
C23	4.3862830000	3.3133290000	3.4451120000
O24	4.7415990000	2.0053270000	3.8707770000
O25	4.0145010000	-0.0284380000	-1.1419610000
C26	4.6967170000	-1.1467250000	-0.5868780000
H27	-0.8138520000	0.3680950000	-2.4116720000
H28	0.5757160000	3.1775260000	-0.7452570000
H29	-0.9584260000	3.9784550000	-1.0155360000
H30	-0.5975080000	1.0514630000	-0.1628640000
H31	-1.8057470000	3.4694180000	1.2760020000
H32	-2.1347450000	1.9163230000	3.1911890000
H33	-3.1192900000	1.5012320000	1.7873830000
H34	-1.6667690000	0.5562080000	2.1548200000
H35	-2.4154990000	0.5973550000	-4.2202160000
H36	0.8476330000	2.1632070000	-4.2557440000
H37	2.6216540000	3.6963800000	-3.8228320000
H38	1.1298390000	4.5720260000	-3.5408810000
H39	2.0888610000	3.9998480000	-2.1652210000
H40	1.8497560000	1.4111500000	-1.4632350000
H41	1.2799940000	0.3142080000	-2.7110130000
H42	3.1899510000	1.0707720000	-4.1981330000
H43	3.8092330000	2.0006070000	-2.8203630000
H44	-1.3017390000	3.2104300000	-4.2090260000
H45	3.3668290000	-1.0247350000	-2.8386250000
H46	4.9312560000	-0.1839500000	-2.9907260000
H47	0.6040230000	1.7548740000	2.1867690000
H48	0.9566130000	5.8456380000	1.5103660000
H49	-0.6844650000	5.2443540000	1.3688010000
H50	-0.0654500000	5.7114710000	2.9571640000
H51	1.9931760000	4.3759060000	3.8989650000
H52	2.5552050000	2.6616740000	0.5589990000
H53	4.2829250000	2.8594670000	0.7776060000
H54	3.4671660000	1.4315700000	1.4487580000
H55	5.2293940000	3.7433530000	2.8950400000
H56	4.2261920000	3.9278450000	4.3372470000
H57	3.9307430000	1.6039050000	4.2290960000
H58	5.7214170000	-1.1972540000	-0.9672200000
H59	4.7323300000	-1.0228330000	0.4987640000
H60	4.1619540000	-2.0733530000	-0.8163100000

Isomer 7C

C1	-6.9747670000	-2.3679660000	3.9674360000
C2	-7.5703210000	-1.0012140000	3.6328160000
C3	-8.9037480000	-1.0867050000	2.8695590000
C4	-8.7526320000	-2.0845550000	1.7187630000
C5	-8.2822830000	-3.4371710000	2.2581250000
O6	-7.0572740000	-3.3174800000	3.0094830000
C7	-8.0971780000	-4.4923510000	1.1339830000

C8	-7.7261500000	-5.8606150000	1.7218230000
O9	-6.3232670000	-2.5446630000	4.9963510000
O10	-7.7728580000	-0.2396480000	4.8344790000
C11	-9.4322210000	0.3195330000	2.4043000000
C12	-8.4687050000	1.0545430000	1.4612130000
C13	-10.8473380000	0.2261170000	1.7697030000
C14	-11.5371700000	1.5843000000	1.6070580000
O15	-9.8889470000	-1.6072470000	3.7887320000
C16	-12.9740650000	1.4283820000	1.1165040000
C17	-7.0345340000	-4.0924380000	0.1289400000
C18	-7.1848300000	-3.8263120000	-1.1838110000
C19	-8.4844300000	-3.8137850000	-1.9424260000
C20	-6.0314960000	-3.4579010000	-1.9947510000
C21	-4.9336470000	-4.2042590000	-2.2342330000
C22	-4.7199860000	-5.6108340000	-1.7367160000
C23	-3.8180820000	-3.6677390000	-3.0936680000
O24	-2.6319960000	-3.5704820000	-2.3178430000
O25	-13.5433530000	2.7304070000	0.9767810000
C26	-14.8904500000	2.6651480000	0.5241400000
H27	-6.8025430000	-0.4903980000	3.0435320000
H28	-8.0276150000	-1.6941660000	0.9967560000
H29	-9.7059240000	-2.2350340000	1.2005840000
H30	-9.0362610000	-3.8351650000	2.9506030000
H31	-9.0662080000	-4.6163380000	0.6405840000
H32	-7.6687960000	-6.6198730000	0.9334500000
H33	-8.4821450000	-6.1888130000	2.4432770000
H34	-6.7580160000	-5.8389090000	2.2344730000
H35	-7.0045770000	-0.4395770000	5.4085200000
H36	-9.5414160000	0.9375420000	3.3065670000
H37	-8.8176480000	2.0707310000	1.2539620000
H38	-7.4726110000	1.1621630000	1.8972040000
H39	-8.3706710000	0.5370690000	0.5019870000
H40	-10.7852960000	-0.2582930000	0.7877390000
H41	-11.4903070000	-0.4055460000	2.3936000000
H42	-11.5390620000	2.1267890000	2.5604700000
H43	-10.9926080000	2.2173960000	0.8978100000
H44	-9.8251950000	-1.0423160000	4.5878600000
H45	-12.9901950000	0.9165840000	0.1473530000
H46	-13.5609000000	0.8485350000	1.8381610000
H47	-6.0293450000	-4.0308270000	0.5512620000
H48	-8.4743040000	-4.5820240000	-2.7235290000
H49	-9.3569980000	-3.9991500000	-1.3129820000
H50	-8.6408970000	-2.8399080000	-2.4202150000
H51	-6.1128800000	-2.4713280000	-2.4530090000
H52	-4.4201020000	-6.2622530000	-2.5647900000
H53	-3.9302960000	-5.6301650000	-0.9789390000
H54	-5.6189490000	-6.0545280000	-1.3004960000
H55	-3.6276440000	-4.3343980000	-3.9407790000
H56	-4.0411450000	-2.6746070000	-3.4974540000
H57	-2.8733250000	-3.0935130000	-1.5046880000
H58	-14.9412950000	2.1855370000	-0.4580750000
H59	-15.5098370000	2.1203290000	1.2430950000
H60	-15.2731960000	3.6853510000	0.4353470000

Isomer 7D

C1	0.9341880000	-0.0734730000	-2.4725060000
C2	0.3980740000	1.1316020000	-1.7033810000
C3	0.7606580000	1.0373670000	-0.2003440000
C4	2.1622130000	0.4291410000	0.0182070000

C5	2.9660560000	0.3994030000	-1.2841060000
O6	2.2431650000	-0.3621600000	-2.2737980000
C7	4.3889540000	-0.1946100000	-1.1037070000
C8	5.1693040000	-0.1512560000	-2.4239930000
O9	0.2452530000	-0.6888610000	-3.2828490000
O10	-1.0301540000	1.2434960000	-1.8236650000
C11	0.5621400000	2.4164400000	0.5295910000
C12	1.5676050000	3.4853660000	0.0739120000
C13	0.5714570000	2.2693730000	2.0769870000
C14	0.1968850000	3.5546440000	2.8213930000
O15	-0.1887230000	0.1197020000	0.3936990000
C16	0.0546130000	3.3130390000	4.3217330000
C17	4.3677790000	-1.6229740000	-0.5990870000
C18	4.8618340000	-2.1090820000	0.5568770000
C19	5.5216700000	-1.3091190000	1.6469850000
C20	4.7284840000	-3.5256450000	0.8713360000
C21	5.2356530000	-4.5646860000	0.1766370000
C22	6.1016580000	-4.4424380000	-1.0506000000
C23	4.9885990000	-5.9797690000	0.6313110000
O24	4.2485880000	-6.6706560000	-0.3653720000
O25	-0.2756790000	4.5543660000	4.9455460000
C26	-0.4311420000	4.4062710000	6.3518980000
H27	0.8255590000	2.0127130000	-2.1895590000
H28	2.7297410000	0.9691020000	0.7822140000
H29	2.0422190000	-0.5948170000	0.3951580000
H30	3.0859850000	1.4198370000	-1.6721070000
H31	4.9216930000	0.4536430000	-0.4011660000
H32	6.1982490000	-0.5000000000	-2.2794000000
H33	5.2177540000	0.8724370000	-2.8105820000
H34	4.7090080000	-0.7807350000	-3.1937200000
H35	-1.2527480000	0.8852870000	-2.7080900000
H36	-0.4418390000	2.7786760000	0.2669120000
H37	1.2881830000	4.4729910000	0.4541270000
H38	1.6067050000	3.5790790000	-1.0137190000
H39	2.5787870000	3.2664460000	0.4307730000
H40	-0.1417950000	1.4913310000	2.3732370000
H41	1.5579850000	1.9375760000	2.4204850000
H42	0.9542510000	4.3308060000	2.6633300000
H43	-0.7440580000	3.9610190000	2.4306030000
H44	-1.0613090000	0.3737950000	0.0235750000
H45	-0.7404490000	2.5837840000	4.5152920000
H46	0.9965390000	2.9352760000	4.7358810000
H47	3.8816400000	-2.3241710000	-1.2811250000
H48	4.9727210000	-1.4188600000	2.5891300000
H49	5.5732430000	-0.2400580000	1.4321110000
H50	6.5481590000	-1.6585320000	1.8047640000
H51	4.1594260000	-3.7215500000	1.7812160000
H52	6.4372170000	-3.4193650000	-1.2405110000
H53	7.0047920000	-5.0518890000	-0.9369890000
H54	5.5590680000	-4.7909220000	-1.9351200000
H55	5.9352580000	-6.5057070000	0.7910140000
H56	4.4220100000	-6.0262320000	1.5672300000
H57	3.4872020000	-6.1047210000	-0.5834660000
H58	-0.6810040000	5.3828840000	6.7749720000
H59	-1.2445980000	3.7094670000	6.5757590000
H60	0.5013370000	4.0566230000	6.8053090000

Isomer 7E

C1	-4.2856970000	3.7268740000	-2.7462330000

C2	-4.2520590000	2.2085750000	-2.6060250000
C3	-2.9458880000	1.7214080000	-1.9263370000
C4	-1.7342080000	2.5899140000	-2.3316660000
C5	-2.0491960000	3.4271400000	-3.5721120000
O6	-3.1735160000	4.2877720000	-3.2806040000
C7	-0.8471440000	4.2858000000	-4.0451030000
C8	-1.1912930000	5.0220200000	-5.3478590000
O9	-5.2808040000	4.3877130000	-2.4614490000
O10	-5.3977710000	1.6553350000	-1.9551370000
C11	-3.0462730000	1.5171580000	-0.3707450000
C12	-1.7405850000	0.9389390000	0.2078460000
C13	-3.4779810000	2.7964280000	0.3851650000
C14	-3.6897580000	2.5885150000	1.8919180000
O15	-2.6907940000	0.4083960000	-2.4924140000
C16	-4.2447820000	3.8419490000	2.5670320000
C17	-0.3988080000	5.3094330000	-3.0187920000
C18	0.7763010000	5.3676920000	-2.3608330000
C19	1.9090460000	4.3859300000	-2.4939750000
C20	1.0757010000	6.4874750000	-1.4770060000
C21	0.4064340000	6.8691230000	-0.3700710000
C22	-0.7797610000	6.1502040000	0.2151370000
C23	0.8546320000	8.0756110000	0.4140090000
O24	-0.1702340000	9.0594730000	0.3906090000
O25	-3.2942410000	4.8997590000	2.4434560000
C26	-3.7651680000	6.0996450000	3.0451630000
H27	-4.3076670000	1.8181680000	-3.6308670000
H28	-1.4866290000	3.2734340000	-1.5157870000
H29	-0.8506900000	1.9671810000	-2.5174910000
H30	-2.3324100000	2.7705370000	-4.4058780000
H31	-0.0288460000	3.5989950000	-4.2840220000
H32	-0.3233230000	5.5757280000	-5.7237090000
H33	-1.4918980000	4.3113010000	-6.1253010000
H34	-2.0103240000	5.7368890000	-5.2107470000
H35	-6.1391120000	2.2640550000	-2.1490330000
H36	-3.8102930000	0.7483320000	-0.1880250000
H37	-1.8904380000	0.5799320000	1.2310120000
H38	-1.3867690000	0.0818510000	-0.3737110000
H39	-0.9428870000	1.6883540000	0.2293170000
H40	-2.7369950000	3.5878390000	0.2368580000
H41	-4.4197810000	3.1665980000	-0.0319870000
H42	-4.3803640000	1.7541680000	2.0579660000
H43	-2.7335930000	2.3372760000	2.3638250000
H44	-3.4595730000	-0.1475670000	-2.2559270000
H45	-5.1925460000	4.1372360000	2.1021950000
H46	-4.4209530000	3.6359650000	3.6289260000
H47	-1.1281090000	6.1010930000	-2.8346640000
H48	1.6306180000	3.4762480000	-3.0303890000
H49	2.7519160000	4.8435600000	-3.0230660000
H50	2.2561460000	4.0680410000	-1.5039270000
H51	1.9604110000	7.0507140000	-1.7786110000
H52	-0.9458580000	5.1705370000	-0.2364750000
H53	-0.6279800000	5.9789690000	1.2863150000
H54	-1.6897850000	6.7442860000	0.0852110000
H55	1.0573280000	7.8070240000	1.4556800000
H56	1.7651900000	8.5260110000	0.0052230000
H57	-0.4356640000	9.1571020000	-0.5406830000
H58	-2.9982990000	6.8691800000	2.9226490000
H59	-4.6824720000	6.4388260000	2.5544900000
H60	-3.9418880000	5.9480400000	4.1142730000

Isomer 7F

C1	-1.9620900000	-4.0619360000	-2.8551450000
C2	-2.2262520000	-2.6134370000	-3.2543550000
C3	-2.6438910000	-2.4935130000	-4.7442570000
C4	-1.9306570000	-3.5468730000	-5.6196190000
C5	-0.7025060000	-4.1103870000	-4.9014570000
O6	-1.1392270000	-4.7533780000	-3.6818520000
C7	0.0933340000	-5.1222070000	-5.7675420000
C8	1.3387710000	-5.6166230000	-5.0196190000
O9	-2.4074990000	-4.5471510000	-1.8188510000
O10	-3.1565500000	-1.9328200000	-2.4106240000
C11	-4.1947870000	-2.4533590000	-4.9964360000
C12	-4.9276590000	-3.6882950000	-4.4527720000
C13	-4.5278170000	-2.2239360000	-6.4963110000
C14	-6.0034750000	-1.9077920000	-6.7566180000
O15	-2.1291050000	-1.2085940000	-5.1826650000
C16	-6.2501670000	-1.5463340000	-8.2187820000
C17	-0.7344160000	-6.3237160000	-6.1786090000
C18	-1.1111950000	-6.6928100000	-7.4189850000
C19	-0.8320520000	-5.9383240000	-8.6906550000
C20	-1.9136820000	-7.8932420000	-7.6149070000
C21	-1.5724920000	-9.1600090000	-7.3011760000
C22	-0.2434420000	-9.5796330000	-6.7277180000
C23	-2.5307790000	-10.2943920000	-7.5570790000
O24	-2.8783360000	-10.9038270000	-6.3217450000
O25	-7.6425170000	-1.2770480000	-8.3849790000
C26	-7.9499680000	-0.9287070000	-9.7295630000
H27	-1.2763930000	-2.0876370000	-3.0894690000
H28	-2.6164910000	-4.3759560000	-5.8205770000
H29	-1.6343410000	-3.1181690000	-6.5846070000
H30	-0.0152050000	-3.2979690000	-4.6296180000
H31	0.4520180000	-4.5832010000	-6.6499800000
H32	1.9397230000	-6.2752500000	-5.6570510000
H33	1.9721580000	-4.7731250000	-4.7244720000
H34	1.0785590000	-6.1755220000	-4.1138010000
H35	-3.0936300000	-2.3635760000	-1.5340990000
H36	-4.5903000000	-1.5775640000	-4.4630210000
H37	-6.0126860000	-3.5580690000	-4.5116520000
H38	-4.7006160000	-3.8645240000	-3.3985480000
H39	-4.6730520000	-4.5933350000	-5.0119950000
H40	-3.9292060000	-1.3884150000	-6.8783580000
H41	-4.2463030000	-3.1067780000	-7.0830200000
H42	-6.6374720000	-2.7627510000	-6.4962560000
H43	-6.3333490000	-1.0780880000	-6.1194220000
H44	-2.5554910000	-0.5335450000	-4.6180250000
H45	-5.6709290000	-0.6571540000	-8.4931050000
H46	-5.9586610000	-2.3789800000	-8.8693070000
H47	-1.0447610000	-6.9530740000	-5.3416470000
H48	-0.3215710000	-4.9869800000	-8.5283140000
H49	-0.2033640000	-6.5392310000	-9.3569980000
H50	-1.7669740000	-5.7088710000	-9.2146050000
H51	-2.8816440000	-7.7039860000	-8.0808940000
H52	0.1712290000	-10.4119130000	-7.3068160000
H53	0.5047360000	-8.7826640000	-6.7471000000
H54	-0.3633870000	-9.9070140000	-5.6900990000
H55	-3.4542830000	-9.9611180000	-8.0420320000
H56	-2.0720190000	-11.0501530000	-8.2025630000

H57	-3.1445770000	-10.1828460000	-5.7246170000
H58	-7.4113220000	-0.0225220000	-10.0229050000
H59	-7.6996350000	-1.7523510000	-10.4050620000
H60	-9.0237090000	-0.7346960000	-9.7976340000

Isomer 7G

C1	-1.9588820000	-1.8701890000	-6.0919020000
C2	-2.4542680000	-1.4563480000	-7.4701910000
C3	-3.9926430000	-1.3919910000	-7.5098660000
C4	-4.4334730000	-2.8291870000	-7.1939280000
C5	-3.9974420000	-3.2327600000	-5.7863860000
O6	-2.6296810000	-2.8627870000	-5.4666680000
C7	-4.1997060000	-4.7456480000	-5.5086860000
C8	-3.9642740000	-5.0634960000	-4.0250570000
O9	-0.9361640000	-1.3844670000	-5.6116840000
O10	-1.8771060000	-0.2454430000	-7.9588320000
C11	-4.6503290000	-0.3039780000	-6.5744160000
C12	-4.2214470000	1.1349720000	-6.9090630000
C13	-6.2017050000	-0.3950720000	-6.5994460000
C14	-6.9574450000	0.5151640000	-5.6172720000
O15	-4.3930070000	-1.1209830000	-8.8660080000
C16	-6.5258030000	0.3814990000	-4.1582660000
C17	-3.2809270000	-5.6188470000	-6.3416580000
C18	-3.6130330000	-6.4495720000	-7.3496800000
C19	-5.0028320000	-6.6765360000	-7.8809560000
C20	-2.5986980000	-7.2744540000	-7.9929360000
C21	-1.4914790000	-6.8605390000	-8.6424370000
C22	-1.1145670000	-5.4226430000	-8.8818110000
C23	-0.5363120000	-7.8641310000	-9.2356090000
O24	0.7278960000	-7.7382030000	-8.6000170000
O25	-6.5410590000	-0.9939270000	-3.7767420000
C26	-6.1873510000	-1.1585640000	-2.4081900000
H27	-2.0965730000	-2.2249280000	-8.1672730000
H28	-5.5099440000	-2.9753990000	-7.3322920000
H29	-3.9831410000	-3.4951930000	-7.9417820000
H30	-4.6208070000	-2.6925250000	-5.0639520000
H31	-5.2484840000	-4.9848880000	-5.7130020000
H32	-4.1661930000	-6.1203060000	-3.8163990000
H33	-4.6315300000	-4.4681200000	-3.3923220000
H34	-2.9336740000	-4.8531480000	-3.7181860000
H35	-0.9615850000	-0.2258650000	-7.6126840000
H36	-4.3166970000	-0.4955790000	-5.5487310000
H37	-4.7233530000	1.8651490000	-6.2676810000
H38	-3.1542500000	1.2862070000	-6.7320090000
H39	-4.4480030000	1.3953920000	-7.9473500000
H40	-6.5637720000	-0.1785070000	-7.6124660000
H41	-6.5169950000	-1.4188350000	-6.3766370000
H42	-6.8872370000	1.5631150000	-5.9272930000
H43	-8.0200590000	0.2477370000	-5.6863850000
H44	-3.8014030000	-0.4079240000	-9.1823110000
H45	-5.5197510000	0.7910510000	-4.0158370000
H46	-7.2189720000	0.9463450000	-3.5239890000
H47	-2.2304680000	-5.5648170000	-6.0485740000
H48	-5.3549440000	-7.6790990000	-7.6151040000
H49	-5.7312440000	-5.9550310000	-7.5043100000
H50	-5.0127320000	-6.5868080000	-8.9734160000
H51	-2.8042240000	-8.3442160000	-7.9273710000
H52	-0.2404720000	-5.1522350000	-8.2810140000
H53	-0.8700120000	-5.2662170000	-9.9380410000

H54	-1.9198250000	-4.7244400000	-8.6419990000
H55	-0.8790580000	-8.8963870000	-9.1087340000
H56	-0.4071390000	-7.6876540000	-10.3082190000
H57	0.5601150000	-7.7930130000	-7.6428420000
H58	-6.2109220000	-2.2261950000	-2.1740140000
H59	-5.1754030000	-0.7834910000	-2.2275920000
H60	-6.9037860000	-0.6420180000	-1.7623970000

Isomer 7H

C1	-2.0809050000	2.8668850000	-3.1881380000
C2	-2.9283860000	3.9820690000	-3.7800640000
C3	-2.6098110000	5.3299740000	-3.1072410000
C4	-2.9940710000	5.1127650000	-1.6361580000
C5	-2.1316950000	4.0225150000	-1.0004270000
O6	-1.9218280000	2.8604930000	-1.8463230000
C7	-2.6686140000	3.5639660000	0.3815410000
C8	-1.6593730000	2.6416960000	1.0805940000
O9	-1.6361090000	1.9627500000	-3.8928100000
O10	-2.8533340000	4.0878030000	-5.2021920000
C11	-1.1393030000	5.8710520000	-3.3000220000
C12	-0.9327170000	7.2013970000	-2.5497000000
C13	-0.7263460000	6.0292280000	-4.7878710000
C14	0.6765400000	6.6054590000	-5.0096900000
O15	-3.5192020000	6.3140540000	-3.6352250000
C16	1.0879880000	6.5313470000	-6.4781380000
C17	-3.9959710000	2.8369730000	0.2806920000
C18	-5.2020340000	3.2449700000	0.7231250000
C19	-5.4915310000	4.5520090000	1.4109840000
C20	-6.3639050000	2.3726230000	0.6125820000
C21	-6.9077310000	1.8646890000	-0.5122100000
C22	-6.4367920000	2.1611390000	-1.9109800000
C23	-8.1082980000	0.9569340000	-0.4356930000
O24	-7.7615790000	-0.3203880000	-0.9516990000
O25	2.3957780000	7.0904430000	-6.6049080000
C26	2.8479920000	7.0589980000	-7.9534110000
H27	-3.9733120000	3.7079000000	-3.5873590000
H28	-2.9489240000	6.0384380000	-1.0525190000
H29	-4.0555110000	4.8342420000	-1.5993440000
H30	-1.1308630000	4.4384490000	-0.8290200000
H31	-2.7635010000	4.4534460000	1.0129020000
H32	-2.0104940000	2.3684010000	2.0822200000
H33	-0.6925380000	3.1437190000	1.1948700000
H34	-1.4929890000	1.7147920000	0.5204780000
H35	-2.7603610000	3.1712590000	-5.5335630000
H36	-0.4407530000	5.1469000000	-2.8630260000
H37	0.1142380000	7.5180910000	-2.5792010000
H38	-1.1792160000	7.1151060000	-1.4886120000
H39	-1.5422950000	8.0018960000	-2.9811070000
H40	-0.7362910000	5.0426770000	-5.2607840000
H41	-1.4532980000	6.6558650000	-5.3175780000
H42	0.7221090000	7.6534760000	-4.6922960000
H43	1.4113060000	6.0651580000	-4.4002680000
H44	-3.5490470000	6.1608630000	-4.6017710000
H45	1.1028270000	5.4890000000	-6.8167810000
H46	0.3848200000	7.0998820000	-7.0976490000
H47	-3.9292020000	1.8521240000	-0.1861920000
H48	-5.7226450000	4.3847500000	2.4685240000
H49	-4.6617050000	5.2601710000	1.3573540000
H50	-6.3519610000	5.0458240000	0.9446610000

H51	-6.8226870000	2.1375280000	1.5744630000
H52	-5.9629210000	1.2773100000	-2.3495800000
H53	-7.2839300000	2.4489880000	-2.5429400000
H54	-5.7220320000	2.9861500000	-1.9538760000
H55	-8.4691580000	0.8228410000	0.5894540000
H56	-8.9359660000	1.3600170000	-1.0279890000
H57	-6.9617710000	-0.6013260000	-0.4734620000
H58	3.8490680000	7.4967710000	-7.9907050000
H59	2.9034030000	6.0275650000	-8.3145520000
H60	2.1842860000	7.6482490000	-8.5934400000

Isomer 7l

C1	-1.2312130000	-2.7022070000	1.2894580000
C2	-1.9421990000	-1.5791050000	0.5269300000
C3	-1.5195760000	-1.5349170000	-0.9620090000
C4	-0.0710810000	-2.0315980000	-1.1491360000
C5	0.7182960000	-1.9016360000	0.1553990000
O6	0.1118120000	-2.7895320000	1.1156190000
C7	2.2192920000	-2.2527140000	-0.0188100000
C8	2.9501610000	-2.2442060000	1.3278290000
O9	-1.8326610000	-3.4336590000	2.0732680000
O10	-3.3689700000	-1.7411940000	0.6024170000
C11	-1.7286490000	-0.1273200000	-1.6432140000
C12	-3.1893900000	0.3510420000	-1.5865040000
C13	-0.7752080000	0.9703460000	-1.1062340000
C14	-0.7685160000	2.2586750000	-1.9445630000
O15	-2.3491320000	-2.4663560000	-1.6952570000
C16	0.2683570000	3.2632780000	-1.4393160000
C17	2.8726430000	-1.2514100000	-0.9467500000
C18	3.6895950000	-1.4862560000	-1.9905950000
C19	4.2361180000	-2.8183890000	-2.4128020000
C20	4.0995390000	-0.3550420000	-2.8064710000
C21	3.3411280000	0.2296920000	-3.7564540000
C22	2.0076100000	-0.2942350000	-4.2236100000
C23	3.8030090000	1.4838010000	-4.4488330000
O24	2.8379200000	2.5137810000	-4.2744100000
O25	1.5850680000	2.7239720000	-1.5948750000
C26	2.5603340000	3.5812310000	-1.0032740000
H27	-1.6943380000	-0.6505020000	1.0511560000
H28	0.4087690000	-1.5028360000	-1.9766810000
H29	-0.0846310000	-3.0903140000	-1.4449020000
H30	0.6521970000	-0.8862150000	0.5665790000
H31	2.2854910000	-3.2696410000	-0.4216780000
H32	4.0157700000	-2.4638380000	1.1962020000
H33	2.5412620000	-3.0030150000	2.0030920000
H34	2.8659270000	-1.2706150000	1.8238950000
H35	-3.5476930000	-2.1484210000	1.4757510000
H36	-1.5054340000	-0.2658710000	-2.7115210000
H37	-3.3468510000	1.2105000000	-2.2456820000
H38	-3.8839390000	-0.4244400000	-1.9226390000
H39	-3.4728130000	0.6539640000	-0.5736570000
H40	-1.0348150000	1.2198210000	-0.0709070000
H41	0.2483430000	0.5894210000	-1.0928000000
H42	-0.5459600000	2.0046940000	-2.9874490000
H43	-1.7530800000	2.7358360000	-1.9151490000
H44	-3.2312420000	-2.4243670000	-1.2674610000
H45	0.1945780000	4.1888010000	-2.0213860000
H46	0.0805590000	3.4938980000	-0.3840090000
H47	2.6083890000	-0.2103170000	-0.7448350000

H48	4.0176810000	-3.6119720000	-1.6935150000
H49	3.8156150000	-3.1165120000	-3.3791120000
H50	5.3264550000	-2.7713130000	-2.5117610000
H51	5.0826290000	0.0469780000	-2.5637590000
H52	1.1960960000	0.3429370000	-3.8599960000
H53	1.9711310000	-0.3096060000	-5.3183160000
H54	1.8124320000	-1.3175140000	-3.8917810000
H55	4.7565130000	1.8480110000	-4.0528160000
H56	3.9307210000	1.3073400000	-5.5214490000
H57	2.4711010000	2.4199860000	-3.3712440000
H58	2.3832830000	3.6760660000	0.0722530000
H59	3.5462700000	3.1342810000	-1.1566060000
H60	2.5423310000	4.5656790000	-1.4803480000

Isomer 7J

C1	-0.2585260000	2.8770260000	4.9001840000
C2	1.1359880000	2.4517830000	5.3506090000
C3	1.4179600000	0.9579420000	5.1186060000
C4	1.0177090000	0.5927510000	3.6871160000
C5	-0.4425140000	0.9722440000	3.4285440000
O6	-0.7035500000	2.3606200000	3.7354760000
C7	-0.9256730000	0.7191030000	1.9738560000
C8	-0.9933390000	-0.7779660000	1.6498960000
O9	-0.8790220000	3.7572790000	5.4958610000
O10	1.3176470000	2.7463910000	6.7454190000
C11	2.8997920000	0.5584190000	5.4644180000
C12	3.9459750000	1.3005800000	4.6195190000
C13	3.1229890000	-0.9767480000	5.3786050000
C14	4.4369340000	-1.4416330000	6.0145420000
O15	0.5721860000	0.2164620000	6.0238820000
C16	4.5426160000	-2.9641640000	6.0342060000
C17	-0.0673350000	1.4218920000	0.9379650000
C18	-0.3314030000	2.5763080000	0.2943220000
C19	-1.5621440000	3.4239060000	0.4717580000
C20	0.6002310000	3.0933280000	-0.6983590000
C21	1.8763850000	3.4779970000	-0.4915150000
C22	2.5646600000	3.4978560000	0.8482550000
C23	2.7178970000	3.9783770000	-1.6366030000
O24	3.8238170000	3.1054270000	-1.8183390000
O25	5.7925850000	-3.3187570000	6.6263790000
C26	5.9613800000	-4.7301860000	6.6833570000
H27	1.8274690000	3.0850230000	4.7861630000
H28	1.6732410000	1.1216100000	2.9883210000
H29	1.1346150000	-0.4821520000	3.5185270000
H30	-1.0948320000	0.3885250000	4.0917080000
H31	-1.9531570000	1.0942180000	1.9014170000
H32	-1.4382780000	-0.9400520000	0.6614120000
H33	-1.6137350000	-1.3052000000	2.3824620000
H34	-0.0029640000	-1.2453160000	1.6459870000
H35	0.8637170000	3.6011740000	6.8976760000
H36	3.0715090000	0.8341490000	6.5143400000
H37	4.9597240000	1.0900570000	4.9736860000
H38	3.8258910000	2.3849650000	4.6791060000
H39	3.8966850000	1.0065010000	3.5665860000
H40	2.3014800000	-1.4975220000	5.8841200000
H41	3.1045880000	-1.2993460000	4.3306290000
H42	5.2986760000	-1.0384710000	5.4711310000
H43	4.5186480000	-1.0617150000	7.0403430000
H44	0.7353990000	0.6025110000	6.9104370000

H45	3.7242720000	-3.3940490000	6.6231970000
H46	4.4964060000	-3.3604610000	5.0132950000
H47	0.8643210000	0.9084490000	0.6953060000
H48	-1.2825020000	4.4638770000	0.6761320000
H49	-2.1733330000	3.4045520000	-0.4371010000
H50	-2.1926790000	3.1013510000	1.3032740000
H51	0.1735880000	3.1748700000	-1.6990100000
H52	1.8766820000	3.3553260000	1.6860820000
H53	3.0535820000	4.4650050000	1.0080290000
H54	3.3266610000	2.7135040000	0.8969650000
H55	2.1615890000	4.0235270000	-2.5787430000
H56	3.0970790000	4.9837280000	-1.4273170000
H57	3.4531530000	2.2103790000	-1.9113470000
H58	5.1768300000	-5.1850300000	7.2957020000
H59	5.9502190000	-5.1579020000	5.6762380000
H60	6.9305160000	-4.9423790000	7.1426500000

Isomer 7K

C1	-1.0795260000	-0.4836670000	-1.1945030000
C2	-1.1850230000	-1.9975570000	-1.2949250000
C3	-2.3194200000	-2.4088540000	-2.2515050000
C4	-3.5867670000	-1.8360650000	-1.5976980000
C5	-3.5278630000	-0.3099990000	-1.5400180000
O6	-2.2344900000	0.2122970000	-1.1232570000
C7	-4.6147200000	0.3519080000	-0.6516680000
C8	-6.0247470000	0.0951140000	-1.1965420000
O9	0.0136790000	0.0717950000	-1.0986390000
O10	0.0385740000	-2.6469600000	-1.6412110000
C11	-2.1295140000	-1.9754850000	-3.7573900000
C12	-0.8659950000	-2.5614460000	-4.4103380000
C13	-3.3703620000	-2.3459700000	-4.6169120000
C14	-3.3686180000	-1.8508520000	-6.0726110000
O15	-2.4400530000	-3.8431530000	-2.2074700000
C16	-3.1435190000	-0.3493390000	-6.2382650000
C17	-4.5451820000	-0.0883160000	0.7989740000
C18	-4.0094510000	0.5838960000	1.8374520000
C19	-3.3417650000	1.9309620000	1.7635740000
C20	-4.0853560000	0.0409690000	3.1869970000
C21	-3.5599900000	-1.1184230000	3.6326520000
C22	-2.7262360000	-2.0612970000	2.8063450000
C23	-3.7471800000	-1.5395640000	5.0672380000
O24	-4.4804710000	-2.7556290000	5.1053700000
O25	-4.0521010000	0.3675360000	-5.4028640000
C26	-3.9048580000	1.7741890000	-5.5602470000
H27	-1.4035670000	-2.3590070000	-0.2822640000
H28	-4.4966900000	-2.1857080000	-2.0953090000
H29	-3.6653110000	-2.2551220000	-0.5854250000
H30	-3.6735560000	0.0817760000	-2.5539180000
H31	-4.4599600000	1.4360410000	-0.7022650000
H32	-6.7700360000	0.6582020000	-0.6231970000
H33	-6.1000290000	0.4145860000	-2.2415680000
H34	-6.2999590000	-0.9637450000	-1.1456180000
H35	0.7497080000	-2.1137600000	-1.2307630000
H36	-2.0142010000	-0.8863730000	-3.7826290000
H37	-0.7839960000	-2.2726270000	-5.4621250000
H38	0.0420900000	-2.1795160000	-3.9383210000
H39	-0.8551570000	-3.6546240000	-4.3652750000
H40	-3.4943380000	-3.4362340000	-4.6282020000
H41	-4.2758340000	-1.9419270000	-4.1540900000

H42	-2.6328450000	-2.4012390000	-6.6684130000
H43	-4.3506470000	-2.0992340000	-6.4961400000
H44	-1.5254610000	-4.1897600000	-2.2529600000
H45	-2.1140130000	-0.0833210000	-5.9746250000
H46	-3.3116160000	-0.0729620000	-7.2857340000
H47	-5.0111200000	-1.0532180000	1.0053870000
H48	-3.1637510000	2.2688560000	0.7401770000
H49	-3.9537120000	2.6888040000	2.2646190000
H50	-2.3628810000	1.8985320000	2.2558320000
H51	-4.6243100000	0.6830930000	3.8853450000
H52	-2.4190230000	-1.6311610000	1.8498680000
H53	-1.8066110000	-2.3219020000	3.3413430000
H54	-3.2808300000	-2.9827100000	2.6026860000
H55	-2.7790950000	-1.7000870000	5.5523780000
H56	-4.2932340000	-0.7948360000	5.6557410000
H57	-5.2839980000	-2.6077790000	4.5764910000
H58	-2.8935830000	2.0858240000	-5.2817680000
H59	-4.1217460000	2.0691070000	-6.5913380000
H60	-4.6183250000	2.2699140000	-4.8965940000

Isomer 7L

C1	-0.2577840000	-3.8035750000	-1.2161450000
C2	-0.7937610000	-2.5805780000	-0.4781980000
C3	-0.9003890000	-1.3456860000	-1.4122290000
C4	-1.2835840000	-1.7527780000	-2.8528880000
C5	-1.8709560000	-3.1648230000	-2.8793900000
O6	-0.8551650000	-4.0776410000	-2.4020080000
C7	-2.3333230000	-3.5952950000	-4.2954680000
C8	-1.1816560000	-3.7556130000	-5.2956930000
O9	0.6110400000	-4.5274810000	-0.7375740000
O10	-0.0751820000	-2.2544170000	0.7130140000
C11	0.3345520000	-0.3743590000	-1.3708030000
C12	0.1014060000	0.8731760000	-2.2448360000
C13	1.6715350000	-1.0658560000	-1.7314160000
C14	2.9016110000	-0.1669300000	-1.5339670000
O15	-2.0310910000	-0.5854580000	-0.9097160000
C16	4.2086510000	-0.9305920000	-1.7408360000
C17	-3.0891510000	-4.9081430000	-4.2084380000
C18	-4.4085020000	-5.1211700000	-4.3823840000
C19	-5.4362510000	-4.0755970000	-4.7211500000
C20	-4.9538450000	-6.4688770000	-4.2898930000
C21	-4.9258180000	-7.2882420000	-3.2187490000
C22	-4.3579550000	-6.9288030000	-1.8701360000
C23	-5.5282420000	-8.6672220000	-3.2977010000
O24	-4.5096620000	-9.6365660000	-3.0951730000
O25	4.2752010000	-1.3914720000	-3.0901160000
C26	5.4762940000	-2.1130020000	-3.3367040000
H27	-1.7923700000	-2.8674040000	-0.1227710000
H28	-0.3900130000	-1.7452120000	-3.4837360000
H29	-1.9995750000	-1.0417950000	-3.2823690000
H30	-2.7369130000	-3.2259790000	-2.2057900000
H31	-2.9887130000	-2.8117100000	-4.6883920000
H32	-1.5582320000	-4.0877810000	-6.2702260000
H33	-0.6631780000	-2.8058390000	-5.4582480000
H34	-0.4433520000	-4.4910250000	-4.9578690000
H35	0.2752740000	-3.1005990000	1.0576580000
H36	0.4202910000	0.0031840000	-0.3420410000
H37	0.8508890000	1.6434200000	-2.0372520000
H38	-0.8745710000	1.3272960000	-2.0466170000

H39	0.1547190000	0.6331560000	-3.3115290000
H40	1.8063920000	-1.9525020000	-1.1042210000
H41	1.6475980000	-1.4152080000	-2.7694060000
H42	2.8670190000	0.6607740000	-2.2507860000
H43	2.8916510000	0.2584210000	-0.5241130000
H44	-1.8086420000	-0.3336810000	0.0084830000
H45	5.0548410000	-0.2622990000	-1.5444710000
H46	4.2649780000	-1.7828030000	-1.0537200000
H47	-2.4574630000	-5.7682190000	-3.9758810000
H48	-5.0550960000	-3.0549120000	-4.6463900000
H49	-5.8062610000	-4.2206060000	-5.7419390000
H50	-6.2880890000	-4.1412270000	-4.0343400000
H51	-5.4417080000	-6.8068110000	-5.2053340000
H52	-5.0830650000	-7.1589740000	-1.0819760000
H53	-3.4449010000	-7.5009130000	-1.6771080000
H54	-4.1182460000	-5.8664460000	-1.7732930000
H55	-6.2943000000	-8.7992530000	-2.5269830000
H56	-5.9966320000	-8.8651480000	-4.2675150000
H57	-3.7861400000	-9.4057200000	-3.7039690000
H58	6.3482000000	-1.4727400000	-3.1719090000
H59	5.5299170000	-2.9972800000	-2.6944280000
H60	5.4735940000	-2.4385970000	-4.3803290000

Isomer 7M

C1	1.0139580000	1.4470910000	3.6948900000
C2	2.3694940000	1.5067870000	4.3939440000
C3	3.3682950000	2.4424010000	3.6936130000
C4	2.6803610000	3.7826590000	3.4190920000
C5	1.4007920000	3.5668130000	2.6071120000
O6	0.5141240000	2.6157460000	3.2397450000
C7	0.5825280000	4.8595830000	2.3368540000
C8	1.3179420000	5.8076470000	1.3820380000
O9	0.3494490000	0.4112070000	3.6819990000
O10	2.9448180000	0.1928420000	4.4796170000
C11	4.7220540000	2.5933360000	4.4806190000
C12	5.7483460000	3.4302980000	3.6929230000
C13	4.5480110000	3.1432170000	5.9171340000
C14	5.8554730000	3.2034720000	6.7219230000
O15	3.7010400000	1.8408510000	2.4232540000
C16	5.6131160000	3.5608780000	8.1877510000
C17	0.2201830000	5.6081650000	3.6063850000
C18	-0.9633470000	5.6161180000	4.2514380000
C19	-2.1762750000	4.8086490000	3.8735150000
C20	-1.1325280000	6.3977610000	5.4692130000
C21	-1.0041220000	7.7336760000	5.6047380000
C22	-0.7103350000	8.6921030000	4.4794830000
C23	-1.1997500000	8.3864880000	6.9486780000
O24	0.0152210000	9.0022410000	7.3526010000
O25	5.0030090000	4.8488830000	8.2652170000
C26	4.7777000000	5.2394260000	9.6146770000
H27	2.1520880000	1.8394160000	5.4137020000
H28	2.4416950000	4.2630320000	4.3733140000
H29	3.3441240000	4.4471040000	2.8573960000
H30	1.6559370000	3.1369090000	1.6293080000
H31	-0.3381860000	4.5615780000	1.8218870000
H32	0.6825090000	6.6611550000	1.1189050000
H33	1.5823440000	5.2928460000	0.4522170000
H34	2.2382840000	6.2056300000	1.8223350000
H35	2.1946860000	-0.4146180000	4.6474210000

H36	5.1628680000	1.5895210000	4.5613530000
H37	6.7519630000	3.3164720000	4.1154170000
H38	5.8146720000	3.1141490000	2.6473710000
H39	5.4971300000	4.4955690000	3.7129900000
H40	4.1072620000	4.1457770000	5.8807410000
H41	3.8505440000	2.5066440000	6.4704720000
H42	6.3708470000	2.2378400000	6.6696400000
H43	6.5140970000	3.9629090000	6.2858600000
H44	3.9855160000	0.9262860000	2.6321570000
H45	4.9618080000	2.8149930000	8.6578610000
H46	6.5709200000	3.5785100000	8.7202810000
H47	1.0281370000	6.2117770000	4.0230240000
H48	-2.9981900000	5.4733000000	3.5856960000
H49	-1.9986730000	4.1240220000	3.0412530000
H50	-2.5097560000	4.1955690000	4.7186060000
H51	-1.4062650000	5.7999990000	6.3397200000
H52	0.2960160000	9.1088630000	4.5880680000
H53	-0.7808830000	8.2301480000	3.4910850000
H54	-1.4294090000	9.5184250000	4.4904480000
H55	-1.9796160000	9.1529210000	6.8969040000
H56	-1.4906270000	7.6700670000	7.7240870000
H57	0.7106870000	8.3285250000	7.2546830000
H58	4.3093950000	6.2272900000	9.6129080000
H59	4.1039020000	4.5335460000	10.1097060000
H60	5.7252500000	5.3021880000	10.1582910000

Isomer 7N

C1	-5.4180250000	2.8711490000	-2.0757840000
C2	-4.3346930000	2.6831650000	-3.1364620000
C3	-4.0928810000	3.9423420000	-3.9857660000
C4	-5.4440070000	4.4781020000	-4.4656160000
C5	-6.3621570000	4.7344160000	-3.2683340000
O6	-6.5203390000	3.5581550000	-2.4484050000
C7	-7.7608860000	5.2560340000	-3.6960830000
C8	-8.6161980000	5.6027710000	-2.4698310000
O9	-5.3521270000	2.2968250000	-0.9893530000
O10	-3.0962020000	2.2924230000	-2.5218880000
C11	-3.0686910000	3.7077370000	-5.1558400000
C12	-2.7605550000	5.0145720000	-5.9117140000
C13	-3.4904030000	2.5879240000	-6.1375290000
C14	-2.4515610000	2.2969100000	-7.2315760000
O15	-3.4990240000	4.9349940000	-3.1201580000
C16	-2.8107260000	1.0586720000	-8.0518140000
C17	-8.5178390000	4.2566700000	-4.5491930000
C18	-8.8835250000	4.3714650000	-5.8414230000
C19	-8.5592420000	5.5230460000	-6.7543590000
C20	-9.6118920000	3.2929860000	-6.4967600000
C21	-10.8252540000	2.8089390000	-6.1607010000
C22	-11.6922290000	3.3459160000	-5.0510190000
C23	-11.4374630000	1.6746480000	-6.9412800000
O24	-11.6111500000	0.5545000000	-6.0848920000
O25	-4.0646610000	1.2690300000	-8.7001550000
C26	-4.4358360000	0.1488600000	-9.4949210000
H27	-4.6782490000	1.8443130000	-3.7498290000
H28	-5.9013880000	3.7472940000	-5.1405710000
H29	-5.3227610000	5.4197840000	-5.0121100000
H30	-5.9148650000	5.5045890000	-2.6255920000
H31	-7.6082840000	6.1912140000	-4.2440020000
H32	-9.5747490000	6.0379800000	-2.7748910000

H33	-8.1051820000	6.3370510000	-1.8378260000
H34	-8.8310050000	4.7210930000	-1.8557900000
H35	-3.3419500000	1.6932190000	-1.7868020000
H36	-2.1173440000	3.4035070000	-4.6965410000
H37	-1.8716170000	4.9017910000	-6.5408220000
H38	-2.5521390000	5.8416640000	-5.2261150000
H39	-3.5924980000	5.3085710000	-6.5596360000
H40	-3.6528240000	1.6582510000	-5.5831740000
H41	-4.4429990000	2.8488220000	-6.6121880000
H42	-2.3908780000	3.1550470000	-7.9102910000
H43	-1.4639290000	2.1521720000	-6.7794200000
H44	-2.7270970000	4.4945200000	-2.7064170000
H45	-2.0349290000	0.8853860000	-8.8063940000
H46	-2.8738510000	0.1780120000	-7.4021870000
H47	-8.7922990000	3.3422150000	-4.0192610000
H48	-7.9201130000	6.2775830000	-6.2914590000
H49	-8.0319600000	5.1689530000	-7.6475880000
H50	-9.4799890000	6.0230880000	-7.0745280000
H51	-9.0908510000	2.8700870000	-7.3569250000
H52	-11.7553490000	2.6210190000	-4.2332400000
H53	-11.3278920000	4.2906450000	-4.6386610000
H54	-12.7049670000	3.5366540000	-5.4224850000
H55	-12.4146550000	1.9633750000	-7.3413180000
H56	-10.8133650000	1.3622690000	-7.7850980000
H57	-10.7587910000	0.4168150000	-5.6359830000
H58	-5.3994630000	0.3645090000	-9.9640780000
H59	-3.6948550000	-0.0250960000	-10.2810440000
H60	-4.5421510000	-0.7440490000	-8.8714220000

Isomer 7O

C1	-1.0222000000	-2.6903150000	-1.2105290000
C2	-0.6049330000	-2.4745980000	0.2410720000
C3	-0.2955020000	-3.8182360000	0.9545970000
C4	0.3382980000	-4.8421550000	-0.0138070000
C5	0.8926060000	-4.1420080000	-1.2558150000
O6	-0.2144580000	-3.5041760000	-1.9344610000
C7	1.6056430000	-5.1185210000	-2.2265210000
C8	0.6613910000	-6.1371180000	-2.8770690000
O9	-1.9885770000	-2.1175720000	-1.7062030000
O10	-1.5252810000	-1.6952590000	1.0064590000
C11	-1.4926890000	-4.4260030000	1.7719160000
C12	-2.7420340000	-4.6797460000	0.9161140000
C13	-1.0724680000	-5.7110180000	2.5372050000
C14	-2.1099000000	-6.1835920000	3.5599010000
O15	0.7387850000	-3.5069910000	1.9245320000
C16	-1.5892880000	-7.3567660000	4.3858260000
C17	2.3027450000	-4.3323350000	-3.3210730000
C18	3.6262970000	-4.1575520000	-3.5054960000
C19	4.7224410000	-4.7312740000	-2.6489930000
C20	4.1145370000	-3.3886390000	-4.6424730000
C21	3.8685480000	-2.0907560000	-4.9153550000
C22	3.0669620000	-1.1606730000	-4.0419340000
C23	4.4440660000	-1.4491130000	-6.1514170000
O24	3.3841160000	-1.0269950000	-6.9978690000
O25	-2.6109830000	-7.7467720000	5.3038450000
C26	-2.1952150000	-8.8397480000	6.1140100000
H27	0.3020090000	-1.8571620000	0.1967390000
H28	-0.4253550000	-5.5550230000	-0.3390710000
H29	1.1346140000	-5.4090770000	0.4831250000

H30	1.6139610000	-3.3667550000	-0.9626770000
H31	2.3402930000	-5.6893110000	-1.6499730000
H32	1.2086920000	-6.7833190000	-3.5733140000
H33	0.2036250000	-6.7883830000	-2.1263140000
H34	-0.1431550000	-5.6508450000	-3.4394770000
H35	-1.9731310000	-1.1016540000	0.3701820000
H36	-1.7680180000	-3.6926370000	2.5428500000
H37	-3.5943600000	-4.9647710000	1.5405740000
H38	-3.0512270000	-3.7835480000	0.3727310000
H39	-2.5829750000	-5.4812080000	0.1888470000
H40	-0.8788160000	-6.5246590000	1.8277940000
H41	-0.1314550000	-5.5266900000	3.0691120000
H42	-2.3827790000	-5.3616860000	4.2331490000
H43	-3.0367220000	-6.4904100000	3.0623920000
H44	0.3597210000	-2.8359120000	2.5264970000
H45	-1.3438040000	-8.2013230000	3.7316660000
H46	-0.6921010000	-7.0612290000	4.9418170000
H47	1.6199720000	-3.8630090000	-4.0327240000
H48	5.2755640000	-5.4992530000	-3.2005610000
H49	5.4273170000	-3.9451920000	-2.3542800000
H50	4.3568560000	-5.1832080000	-1.7244820000
H51	4.7571610000	-3.9605890000	-5.3134190000
H52	2.8367870000	-1.5835640000	-3.0602830000
H53	3.6269840000	-0.2367670000	-3.8610430000
H54	2.1215750000	-0.9016160000	-4.5291320000
H55	5.0493600000	-0.5759630000	-5.8877390000
H56	5.0809400000	-2.1337440000	-6.7213220000
H57	2.7928490000	-1.7933700000	-7.1003370000
H58	-3.0126830000	-9.0944900000	6.7937550000
H59	-1.9712170000	-9.7126810000	5.4933820000
H60	-1.3188830000	-8.5639310000	6.7084270000

Isomer 7P

C1	2.2353950000	-4.3437030000	-4.8905050000
C2	1.1264580000	-3.8370540000	-5.7975480000
C3	-0.1861140000	-4.5960080000	-5.5313120000
C4	0.1425920000	-6.0523720000	-5.8945230000
C5	1.2343680000	-6.6134960000	-4.9830060000
O6	2.3130450000	-5.6780660000	-4.6993430000
C7	1.8728360000	-7.9423740000	-5.4682240000
C8	0.8451000000	-9.0793290000	-5.5174430000
O9	3.0694740000	-3.5749920000	-4.4155050000
O10	0.9215160000	-2.4244640000	-5.7454990000
C11	-0.8025370000	-4.4327630000	-4.0871510000
C12	-2.0968950000	-5.2558270000	-3.9371980000
C13	-1.0609800000	-2.9557810000	-3.6865320000
C14	-1.7097750000	-2.7653990000	-2.3110130000
O15	-1.1620310000	-4.1383910000	-6.4867940000
C16	-1.7339090000	-1.2950430000	-1.9004760000
C17	2.5536250000	-7.8191000000	-6.8190140000
C18	3.8731240000	-7.6932590000	-7.0654490000
C19	4.9593400000	-7.6233380000	-6.0254300000
C20	4.3710510000	-7.6662800000	-8.4342610000
C21	4.0784340000	-6.7667210000	-9.3954150000
C22	3.2032640000	-5.5566670000	-9.2061820000
C23	4.6748560000	-6.9001140000	-10.7727490000
O24	3.6310790000	-7.0909410000	-11.7172570000
O25	-2.3562290000	-1.1986720000	-0.6189040000
C26	-2.4159730000	0.1493340000	-0.1681130000

H27	1.4601330000	-4.0207090000	-6.8262510000
H28	-0.7492870000	-6.6869750000	-5.8846450000
H29	0.4686800000	-6.0759200000	-6.9430780000
H30	0.7856600000	-6.8232130000	-4.0037230000
H31	2.6185270000	-8.2364690000	-4.7202880000
H32	1.3319230000	-10.0316920000	-5.7568390000
H33	0.3492420000	-9.1954250000	-4.5477780000
H34	0.0726350000	-8.9038860000	-6.2738690000
H35	1.8084750000	-2.0316190000	-5.6128930000
H36	-0.0872580000	-4.8283380000	-3.3555780000
H37	-2.4593400000	-5.2450550000	-2.9048020000
H38	-1.9413900000	-6.3101610000	-4.1787820000
H39	-2.8932240000	-4.8686500000	-4.5809620000
H40	-0.1024710000	-2.4289780000	-3.6548510000
H41	-1.6834220000	-2.4624100000	-4.4421370000
H42	-2.7398680000	-3.1396680000	-2.3108770000
H43	-1.1699990000	-3.3442370000	-1.5515350000
H44	-1.0723530000	-3.1637470000	-6.5156150000
H45	-0.7131700000	-0.9002040000	-1.8406530000
H46	-2.3037120000	-0.7074570000	-2.6295460000
H47	1.8804760000	-7.8723270000	-7.6761950000
H48	5.5680520000	-8.5337510000	-6.0465100000
H49	5.6153370000	-6.7662050000	-6.2167230000
H50	4.5767100000	-7.5005060000	-5.0096650000
H51	5.0666410000	-8.4761550000	-8.6599540000
H52	2.2592900000	-5.6797820000	-9.7463400000
H53	2.9714730000	-5.3604210000	-8.1566310000
H54	3.7063040000	-4.6615440000	-9.5876800000
H55	5.2294230000	-5.9958320000	-11.0430030000
H56	5.3639990000	-7.7474340000	-10.8518820000
H57	3.0990410000	-7.8375660000	-11.3906040000
H58	-2.8998500000	0.1629800000	0.8121220000
H59	-1.4084090000	0.5639390000	-0.0668280000
H60	-3.0073270000	0.7580650000	-0.8588440000

2.1.3. DP4f probability analysis of the C13-C28 region

DP4 NMR prediction analysis was performed following the protocol of Smith and Goodman. For the conformers found within <10 $kJmol^{-1}$ of the global minima generated from the previously described conformational search, Jaguar (version 7.9) was used to calculate both the carbon and proton GIAO shielding constants at the B3LYP/6-31G(d,p) level. Data for the hydroxyl protons was omitted, as was the data for the protons at C13 and C28 due to the significant differences in chemical environment compared to the natural product. The shielding constants for the methyl groups were averaged.

	Predicted ^{13}C NMR shifts (ppm)															
Atom #	7A	7B	7C	7D	7E	7F	7G	7H	7I	7J	7K	7L	7M	7N	7O	7P
C23	170.1	172.5	174.8	172.5	171.8	173.1	170.9	171.3	172.5	175.3	171.7	171.4	174.9	175.0	172.9	171.1
C22	72.9	72.4	73.4	71.4	77.6	80.6	78.9	81.3	70.3	73.6	80.8	78.9	72.0	72.3	80.3	81.2
C21	72.7	75.8	78.2	77.5	79.2	79.1	77.4	75.3	75.9	78.6	78.2	79.8	78.2	78.6	79.1	75.9
C20	34.4	41.0	34.5	36.6	36.2	39.2	37.0	38.7	41.4	32.6	37.9	36.1	30.8	33.4	39.1	37.7
C19	80.1	77.9	79.6	78.0	77.3	77.4	80.1	79.5	78.6	80.5	80.1	77.8	81.2	79.9	77.9	80.1
C18	40.5	41.3	41.1	40.2	40.9	40.5	40.9	41.0	41.6	40.9	41.0	40.4	40.4	40.9	41.0	41.0
C18-Me	18.0	19.6	20.6	18.8	20.4	19.3	20.2	19.7	19.7	19.4	19.7	19.1	19.3	20.3	19.5	19.4
C24	45.9	46.1	42.5	44.5	43.0	39.7	40.1	37.0	48.6	40.7	40.8	40.3	44.4	45.0	39.7	37.8
C24-Me	16.7	18.1	17.2	17.0	15.5	18.8	16.0	17.7	16.2	18.6	15.9	16.7	15.2	14.9	18.8	17.8
C25	31.3	31.1	32.9	32.2	29.2	36.4	30.0	30.3	31.0	34.6	29.7	28.3	31.0	31.7	36.4	30.9
C26	31.3	32.4	30.3	30.4	27.8	28.8	28.7	27.7	31.0	30.1	26.3	25.9	29.9	31.4	29.0	28.0
C17	126.5	127.5	127.8	127.1	126.4	127.9	127.3	127.3	127.8	127.6	127.6	126.8	127.3	127.5	127.8	126.9
C16	132.6	133.3	131.6	132.6	133.4	132.1	132.8	132.7	132.7	132.6	133.3	133.3	133.8	132.0	132.4	133.7
C16-Me	18.4	17.7	17.9	17.6	17.3	17.9	18.0	17.8	17.7	18.0	17.8	18.1	18.1	17.8	18.0	18.0
C15	126.6	124.6	126.4	126.5	125.2	127.1	126.7	127.0	126.9	127.1	126.5	126.7	126.3	125.7	127.1	127.3
C14	135.9	135.5	134.7	135.3	135.3	135.2	135.4	135.3	134.7	134.9	134.7	135.6	135.0	135.3	135.1	135.0
C14-Me	15.6	17.6	16.6	16.7	17.2	17.2	16.8	17.0	17.2	16.8	17.3	16.3	17.0	16.6	16.9	17.1

Table S2. Predicted ^{13}C NMR chemical shifts for isomers **7A-P**. Favoured isomer is highlighted in yellow.

		$\Delta\delta_C$(Predicted – Experimental) ppm														
Atom #	Experimental shift data for hemicalide[1]	7A	7B	7C	7D	7E	7F	7G	7H	7I	7J	7K	7L	7M	7N	7O	7P
C23	177.0	-6.9	-4.5	-2.2	-4.5	-5.2	-3.9	-6.1	-5.7	-4.5	-1.7	-5.3	-5.6	-2.1	-2.0	-4.1	-5.9
C22	72.5	0.4	-0.1	0.9	-1.1	5.1	8.1	6.4	8.8	-2.2	1.1	8.3	6.4	-0.5	-0.2	7.8	8.7
C21	76.4	-3.7	-0.6	1.8	1.1	2.8	2.7	1.0	-1.1	-0.5	2.2	1.8	3.4	1.8	2.2	2.7	-0.5
C20	32.2	2.2	8.8	2.3	4.4	4.0	7.0	4.8	6.5	9.2	0.4	5.7	3.9	-1.4	1.2	6.9	5.5
C19	82.8	-2.7	-4.9	-3.2	-4.8	-5.5	-5.4	-2.7	-3.3	-4.2	-2.3	-2.7	-5.0	-1.6	-2.9	-4.9	-2.7
C18	39.3	1.2	2.0	1.8	0.9	1.6	1.2	1.6	1.7	2.3	1.6	1.7	1.1	1.1	1.6	1.7	1.7
C18-Me	17.2	0.8	2.4	3.4	1.6	3.2	2.1	3.0	2.5	2.5	2.2	2.5	1.9	2.1	3.1	2.3	2.2
C24	39.3	6.6	6.8	3.2	5.2	3.7	0.4	0.8	-2.3	9.3	1.4	1.5	1.0	5.1	5.7	0.4	-1.5
C24-Me	13.1	3.6	5.0	4.1	3.9	2.4	5.7	2.9	4.6	3.1	5.5	2.8	3.6	2.1	1.8	5.7	4.7
C25	28.0	3.3	3.1	4.9	4.2	1.2	8.4	2.0	2.3	3.0	6.6	1.7	0.3	3.0	3.7	8.4	2.9
C26	40.8	-9.5	-8.4	-10.5	-10.4	-13.0	-12.0	-12.1	-13.1	-9.8	-10.7	-14.5	-14.9	-10.9	-9.4	-11.8	-12.8
C17	131.6	-5.1	-4.1	-3.8	-4.5	-5.2	-3.7	-4.3	-4.3	-3.8	-4.0	-4.0	-4.8	-4.3	-4.1	-3.8	-4.7
C16	135.4	-2.8	-2.1	-3.8	-2.8	-2.0	-3.3	-2.6	-2.7	-2.7	-2.8	-2.1	-2.1	-1.6	-3.4	-3.0	-1.7
C16-Me	17.9	0.5	-0.2	0.0	-0.3	-0.6	0.0	0.1	-0.1	-0.2	0.1	-0.1	0.2	0.2	-0.1	0.1	0.1
C15	131.7	-5.1	-7.1	-5.3	-5.2	-6.5	-4.6	-5.0	-4.7	-4.8	-4.6	-5.2	-5.0	-5.4	-6.0	-4.6	-4.4
C14	137.4	-1.5	-1.9	-2.7	-2.1	-2.1	-2.2	-2.0	-2.1	-2.7	-2.5	-2.7	-1.8	-2.4	-2.1	-2.3	-2.4
C14-Me	14.0	1.6	3.6	2.6	2.7	3.2	3.2	2.8	3.0	3.2	2.8	3.3	2.3	3.0	2.6	2.9	3.1

Table S3. The ^{13}C NMR $\Delta\delta_{(Predicted - Experimental)}$ values for isomers **7A-P**. Favoured isomer is highlighted in yellow.

	Predicted ^{1}H NMR shifts (ppm)															
Atom #	7A	7B	7C	7D	7E	7F	7G	7H	7I	7J	7K	7L	7M	7N	7O	7P
H22	5.00	3.98	4.10	4.16	4.34	4.57	4.18	3.97	4.14	4.03	4.35	4.27	4.07	4.12	4.53	4.01
H20A	1.85	2.50	2.11	1.99	2.17	1.90	2.01	1.96	2.37	1.69	2.35	1.69	1.67	1.81	1.71	2.23
H20B	1.18	1.62	1.54	2.15	1.66	1.65	1.92	1.94	1.95	1.97	1.75	1.98	1.98	1.59	2.03	1.69
H19	4.67	3.75	4.70	4.01	4.37	4.49	4.43	4.09	3.81	4.68	3.94	4.26	4.64	4.75	4.29	3.96
H18	2.59	2.72	2.43	2.75	2.53	2.62	2.56	2.55	2.74	2.81	2.77	2.80	2.92	2.42	2.74	2.79
H18-Me	1.33	1.21	1.26	1.14	1.24	1.21	1.25	1.23	1.20	1.16	1.18	1.15	1.11	1.24	1.20	1.13
H24	1.95	1.41	2.11	2.08	2.14	2.79	2.05	1.76	1.77	2.35	1.85	2.12	1.93	1.90	2.77	1.87
H24-Me	0.75	1.04	0.84	0.85	0.97	0.65	1.13	0.88	0.92	1.36	1.17	0.97	0.98	0.96	0.66	0.86
H25A	1.71	1.01	1.21	1.94	1.16	1.67	1.44	2.66	0.85	1.80	1.24	1.42	1.27	1.46	1.22	2.62
H25B	1.23	1.59	1.82	1.11	1.09	1.18	1.65	1.10	2.04	1.21	1.58	0.82	1.37	1.17	1.65	1.17
H26A	1.92	1.34	1.17	2.02	1.04	2.66	1.38	1.82	1.37	2.42	1.36	1.79	1.48	1.70	1.16	1.82
H26B	1.47	1.75	2.17	1.29	1.79	1.19	1.88	1.43	1.71	1.20	1.64	1.23	1.55	1.27	2.67	1.47
H17	5.18	5.12	5.53	5.40	5.65	5.48	5.37	5.39	5.22	5.28	5.18	5.28	5.25	5.43	5.26	5.21
H16-Me	1.52	1.61	1.58	1.57	1.58	1.58	1.54	1.53	1.62	1.60	1.60	1.61	1.59	1.56	1.61	1.58
H15	5.90	5.76	6.04	6.00	6.14	5.96	5.95	5.93	5.94	5.98	5.88	5.94	5.91	6.08	5.97	5.92
H14-Me	1.73	1.80	1.26	1.80	1.72	1.80	1.79	1.82	1.82	1.78	1.80	1.80	1.77	1.70	1.81	2.36

Table S4. Predicted ^{1}H NMR chemical shifts for isomers **7A-P**. Favoured isomer is highlighted in yellow

		$\Delta\delta_H$(Predicted – Experimental) ppm														
Atom #	Experimental shift data for hemicalide[1]	7A	7B	7C	7D	7E	7F	7G	7H	7I	7J	7K	7L	7M	7N	7O	7P
H22	4.27	0.73	-0.29	-0.17	-0.11	0.07	0.30	-0.09	-0.30	-0.13	-0.24	0.08	0.00	-0.20	-0.15	0.26	-0.26
H20A	1.62	0.23	0.88	0.49	0.37	0.55	0.28	0.39	0.34	0.75	0.07	0.73	0.07	0.05	0.19	0.09	0.61
H20B	1.62	-0.44	0.00	-0.08	0.53	0.04	0.03	0.30	0.32	0.33	0.35	0.13	0.36	0.36	-0.03	0.41	0.07
H19	4.42	0.25	-0.67	0.28	-0.41	-0.05	0.07	0.01	-0.33	-0.61	0.26	-0.48	-0.16	0.22	0.33	-0.13	-0.46
H18	2.81	-0.22	-0.09	-0.38	-0.06	-0.28	-0.19	-0.25	-0.26	-0.07	0.00	-0.04	-0.01	0.11	-0.39	-0.07	-0.02
H18-Me	1.10	0.23	0.11	0.16	0.04	0.14	0.11	0.15	0.13	0.10	0.06	0.08	0.05	0.01	0.14	0.10	0.03
H24	1.62	0.33	-0.21	0.49	0.46	0.52	1.17	0.43	0.14	0.15	0.73	0.23	0.50	0.31	0.28	1.15	0.25
H24-Me	0.96	-0.21	0.08	-0.12	-0.11	0.01	-0.31	0.17	-0.08	-0.04	0.40	0.21	0.01	0.02	0.00	-0.30	-0.10
H25A	1.62	0.09	-0.61	-0.41	0.32	-0.46	0.05	-0.18	1.04	-0.77	0.18	-0.38	-0.20	-0.35	-0.16	-0.40	1.00
H25B	1.62	-0.39	-0.03	0.20	-0.51	-0.53	-0.44	0.03	-0.52	0.42	-0.41	-0.04	-0.80	-0.25	-0.45	0.03	-0.45
H26A	1.62	0.30	-0.28	-0.45	0.40	-0.58	1.04	-0.24	0.20	-0.25	0.80	-0.26	0.17	-0.14	0.08	-0.46	0.20
H26B	1.62	-0.15	0.13	0.55	-0.33	0.17	-0.43	0.26	-0.19	0.09	-0.42	0.02	-0.39	-0.07	-0.35	1.05	-0.15
H17	5.16	0.02	-0.04	0.37	0.24	0.49	0.32	0.21	0.23	0.06	0.12	0.02	0.12	0.09	0.27	0.10	0.05
H16-Me	1.82	-0.30	-0.21	-0.24	-0.25	-0.24	-0.24	-0.28	-0.29	-0.20	-0.22	-0.22	-0.21	-0.23	-0.26	-0.21	-0.24
H15	5.95	-0.05	-0.19	0.09	0.05	0.19	0.01	0.00	-0.02	-0.01	0.03	-0.07	-0.01	-0.04	0.13	0.02	-0.03
H14-Me	1.69	0.04	0.11	-0.43	0.11	0.03	0.11	0.10	0.13	0.13	0.09	0.11	0.11	0.08	0.01	0.12	0.67

Table S5. The ^{1}H NMR $\Delta\delta_{(\text{Predicted – Experimental})}$ values for isomers **7A-P**. Favoured isomer is highlighted in yellow.

Isomer	Configuration	DP4 probability (%)		
		^{1}H and ^{13}C NMR	^{13}C NMR	^{1}H NMR
7A	18(*S*), 19(*R*), 21(*S*), 22(*R*), 24(*R*)	0.0	17.0	0.0
7B	18(*S*), 19(*S*), 21(*R*), 22(*S*), 24(*S*)	0.0	0.3	0.0
7C	18(*R*), 19(*S*), 21(*S*), 22(*R*), 24(*S*)	0.0	22.5	0.0
7D	18(*R*), 19(*S*), 21(*R*), 22(*S*), 24(*R*)	0.0	5.2	0.0
7E	18(*S*), 19(*R*), 21(*R*), 22(*R*), 24(*S*)	0.0	0.0	0.0
7F	18(*S*), 19(*R*), 21(*R*), 22(*R*), 24(*R*)	0.0	0.0	0.0
7G	18(*R*), 19(*S*), 21(*R*), 22(*R*), 24(*S*)	0.0	2.7	0.2
7H	18(*R*), 19(*S*), 21(*R*), 22(*R*), 24(*R*)	0.0	0.0	0.0
7I	18(*R*), 19(*R*), 21(*S*), 22(*R*), 24(*S*)	0.0	0.1	0.0
7J	18(*R*), 19(*R*), 21(*R*), 22(*S*), 24(*R*)	0.0	10.9	0.0
7K	18(*S*), 19(*S*), 21(*R*), 22(*R*), 24(*S*)	0.0	0.1	0.0
7L	18(*S*), 19(*S*), 21(*S*), 22(*S*), 24(*R*)	0.0	0.0	0.0
7M	18(*R*), 19(*R*), 21(*R*), 22(*S*), 24(*S*)	99.0	12.3	99.3
7N	18(*R*), 19(*S*), 21(*S*), 22(*R*), 24(*R*)	1.0	29.3	0.4
7O	18(*S*), 19(*S*), 21(*S*), 22(*S*), 24(*S*)	0.0	0.0	0.0
7P	18(*S*), 19(*S*), 21(*R*), 22(*R*), 24(*R*)	0.0	0.0	0.0

Table S6. DP4f NMR stereochemical prediction for the C13-C28 region. The highest probability stereoisomer **7M** is highlighted in yellow.

2.2. DP4f GIAO-NMR analysis of the C34-C42 fragment 8

Figure S2 lists the structures of the 16 diastereoisomers **8A**-**P** of the virtual fragment **8** initially considered for assigning the stereochemistry within the C34-C42 region of hemicalide.

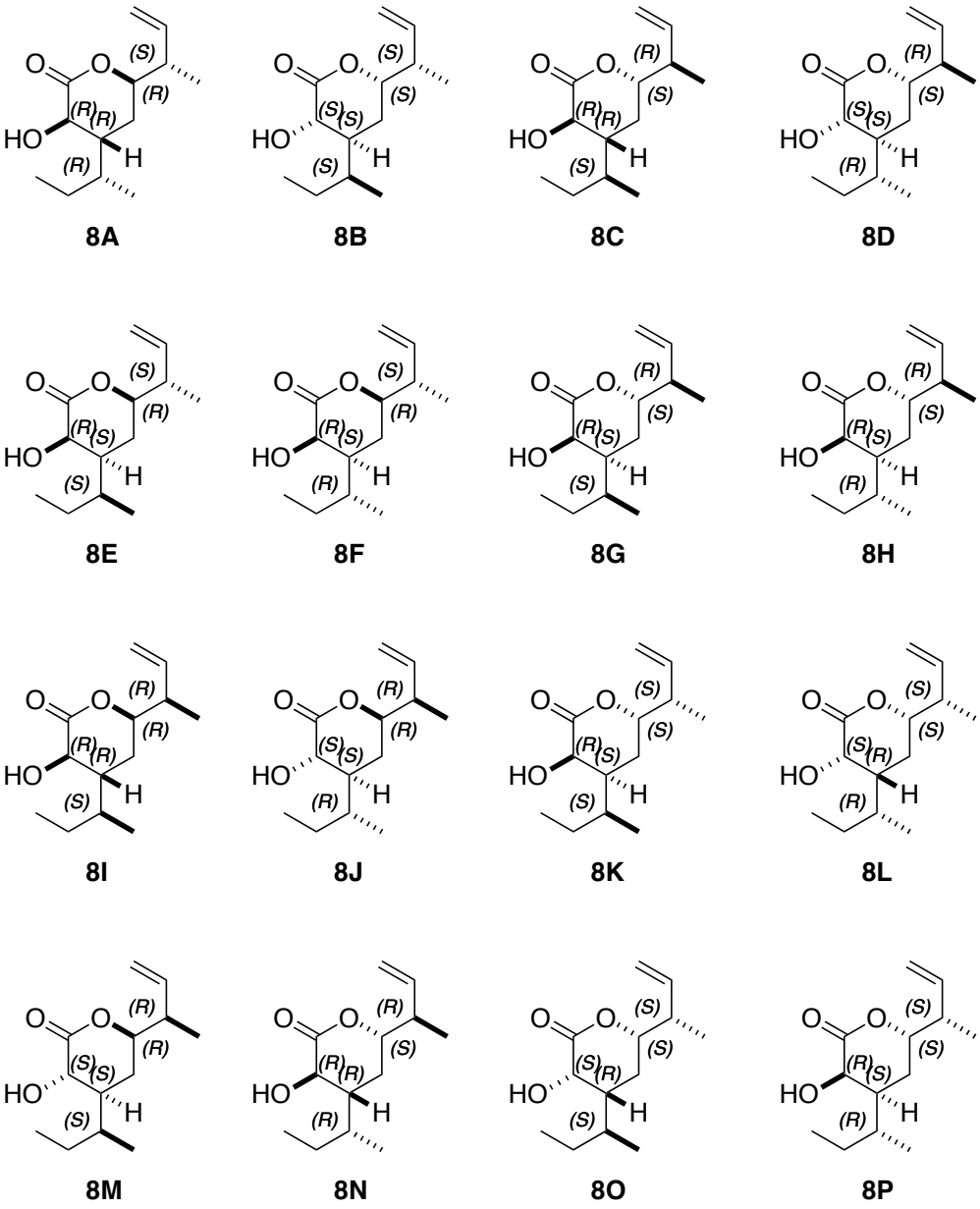


Figure S2. The 16 stereoisomers initially considered for the assignment of the C34-C42 region.

2.2.1. Molecular modelling of the C34-C42 fragment

Molecular modelling was carried out for all 16 diastereoisomers using a 50,000 step hybrid Monte-Carlo multiple-minimum/ low-mode sampling using the MMFF force field and $CHCl_3$ as the solvent. No bond restraints were applied. Structures found within 10 $kJmol^{-1}$ of the lowest energy conformer were recorded.

2.2.2. Atomic coordinates for the minimum energy conformers for 8A-P

Isomer 8A

atom	x	y	z
C1	-75.7423930000	-0.1972440000	-3.1370170000
C2	-75.4000700000	0.8405420000	-2.0639890000
C3	-74.0407490000	0.4814150000	-1.4449100000
C4	-74.0400160000	-0.9713960000	-0.9245450000
C5	-75.2664490000	-1.7685980000	-1.3917060000
O6	-75.5648800000	-1.4923460000	-2.7748770000
C7	-75.1190870000	-3.2985210000	-1.1760870000
C8	-76.4152220000	-4.0286130000	-1.5486090000
C9	-73.9752730000	-3.8998150000	-1.9651570000
C10	-72.9434510000	-4.5547970000	-1.4166410000
O11	-76.1706540000	0.1193580000	-4.2440040000
O12	-75.3374790000	2.1518410000	-2.6253690000
C13	-73.5139310000	1.5244960000	-0.4110710000
C14	-72.0859070000	1.1720300000	0.0321530000
C15	-74.4594270000	1.7146800000	0.7952080000
C16	-74.0138550000	2.8127820000	1.7539200000
H17	-73.3175890000	0.5106690000	-2.2759880000
H18	-76.2116470000	0.8393260000	-1.3296620000
H19	-73.9917680000	-1.0214900000	0.1680370000
H20	-73.1170040000	-1.4395470000	-1.2873620000
H21	-76.1376800000	-1.4450650000	-0.8047320000
H22	-74.9445950000	-3.4654200000	-0.1043810000
H23	-77.2605740000	-3.6317440000	-0.9762320000
H24	-76.6509780000	-3.9263060000	-2.6137700000
H25	-76.3382190000	-5.0988780000	-1.3254950000
H26	-74.0102690000	-3.7874270000	-3.0483940000
H27	-72.1541670000	-4.9663920000	-2.0390580000
H28	-72.8599470000	-4.7002220000	-0.3440260000
H29	-75.9724810000	2.1635270000	-3.3696300000
H30	-73.4465790000	2.4904990000	-0.9299600000
H31	-71.6216200000	2.0085840000	0.5639390000
H32	-71.4515230000	0.9526530000	-0.8333730000
H33	-72.0698850000	0.3021100000	0.6962120000
H34	-75.4606480000	1.9795880000	0.4391550000
H35	-74.5610200000	0.7809630000	1.3586880000
H36	-73.0887300000	2.5435540000	2.2717240000
H37	-73.8562320000	3.7574950000	1.2242680000
H38	-74.7814180000	2.9768440000	2.5173300000

Isomer 8B

C1	-2.1623610000	1.8617500000	-0.1605610000
C2	-1.9802280000	0.7715760000	0.8996790000
C3	-3.3666100000	0.2661990000	1.3290950000
C4	-4.1881020000	-0.1915840000	0.1051230000
C5	-3.5460220000	0.2225650000	-1.2265510000
O6	-3.0479910000	1.5732880000	-1.1469150000
C7	-4.5204410000	0.0870010000	-2.4259440000
C8	-5.6160700000	1.1588450000	-2.4454880000
C9	-3.7513150000	0.1542780000	-3.7307160000
C10	-3.6878510000	-0.8453580000	-4.6200750000
O11	-1.5387090000	2.9195900000	-0.1299130000
O12	-1.2842610000	1.2796950000	2.0379560000
C13	-3.3357710000	-0.7701140000	2.4951000000

C14	-4.7612280000	-1.0972050000	2.9650820000
C15	-2.5365910000	-2.0464320000	2.1522320000
C16	-2.4032230000	-3.0166460000	3.3202800000
H17	-3.8904710000	1.1445800000	1.7395920000
H18	-1.3597350000	-0.0173980000	0.4633940000
H19	-4.3414010000	-1.2755380000	0.0914530000
H20	-5.1862390000	0.2507290000	0.2030960000
H21	-2.6854520000	-0.4350610000	-1.4162660000
H22	-5.0088920000	-0.8943920000	-2.3566610000
H23	-5.1990050000	2.1696720000	-2.5138910000
H24	-6.2800700000	1.0177350000	-3.3063690000
H25	-6.2386060000	1.1110750000	-1.5474340000
H26	-3.2216990000	1.0824660000	-3.9442740000
H27	-3.1201490000	-0.7341220000	-5.5394670000
H28	-4.1984670000	-1.7901490000	-4.4608730000
H29	-0.6740350000	1.9672900000	1.7032480000
H30	-2.8336190000	-0.2877830000	3.3449010000
H31	-4.7474250000	-1.6290110000	3.9217340000
H32	-5.3417460000	-0.1810110000	3.1177170000
H33	-5.2939620000	-1.7222190000	2.2415200000
H34	-2.9954020000	-2.5762290000	1.3105250000
H35	-1.5235720000	-1.7724980000	1.8389330000
H36	-1.9886310000	-2.5171340000	4.2014460000
H37	-3.3676500000	-3.4570630000	3.5893090000
H38	-1.7315730000	-3.8378740000	3.0494650000

Isomer 8C

C1	-4.2523100000	1.5705510000	0.4117200000
C2	-3.5211000000	0.3300320000	-0.1066070000
C3	-4.1997860000	-0.9780280000	0.3153160000
C4	-4.3874040000	-0.9323910000	1.8342710000
C5	-5.2603960000	0.2723180000	2.1941290000
O6	-4.7333700000	1.5122310000	1.6738700000
C7	-5.4901290000	0.4089000000	3.7233410000
C8	-6.4587260000	1.5564000000	4.0337340000
C9	-4.2041160000	0.6285350000	4.4923820000
C10	-3.7417440000	-0.1986380000	5.4391660000
O11	-4.2888310000	2.6121750000	-0.2419920000
O12	-3.4206240000	0.3721710000	-1.5315460000
C13	-3.4589630000	-2.2531540000	-0.1943940000
C14	-2.0113990000	-2.3596590000	0.3069500000
C15	-4.1912560000	-3.5758200000	0.1328390000
C16	-5.6183650000	-3.6462090000	-0.3921650000
H17	-5.1925640000	-0.9832780000	-0.1554770000
H18	-2.5037350000	0.3963750000	0.2942910000
H19	-3.4071350000	-0.8494170000	2.3167950000
H20	-4.8655240000	-1.8448750000	2.2037790000
H21	-6.2458130000	0.1400480000	1.7262470000
H22	-5.9624970000	-0.5201600000	4.0707600000
H23	-6.6813900000	1.5990600000	5.1060120000
H24	-7.4071910000	1.4152580000	3.5043950000
H25	-6.0494000000	2.5293780000	3.7399640000
H26	-3.6327660000	1.5247840000	4.2532130000
H27	-2.8131030000	0.0175540000	5.9594810000
H28	-4.2730730000	-1.1021840000	5.7221530000
H29	-3.2648110000	1.3094430000	-1.7650540000
H30	-3.4092390000	-2.1873340000	-1.2899810000
H31	-1.5275730000	-3.2526020000	-0.1048260000
H32	-1.4105690000	-1.5018980000	-0.0073690000

H33	-1.9650320000	-2.4339840000	1.3977620000
H34	-3.6295980000	-4.4059410000	-0.3150910000
H35	-4.1932990000	-3.7600300000	1.2132240000
H36	-6.0203260000	-4.6545110000	-0.2488310000
H37	-6.2771530000	-2.9532660000	0.1390310000
H38	-5.6564380000	-3.4155980000	-1.4613290000

Isomer 8D

C1	-1.8294030000	-2.4806520000	-0.7702420000
C2	-0.6488420000	-1.5484830000	-1.0583710000
C3	-0.3882860000	-0.6829130000	0.1850620000
C4	-0.1808800000	-1.5680600000	1.4318910000
C5	-0.5703060000	-3.0340070000	1.1909310000
O6	-1.7861790000	-3.1260040000	0.4220610000
C7	-0.7075030000	-3.8540890000	2.5014640000
C8	-0.9778700000	-5.3318760000	2.1933790000
C9	-1.8011060000	-3.3370130000	3.4119830000
C10	-1.6013470000	-2.9241680000	4.6706320000
O11	-2.7438570000	-2.6499300000	-1.5728240000
O12	-0.9273290000	-0.7060050000	-2.1771040000
C13	0.7198890000	0.3945510000	-0.0158680000
C14	2.0722940000	-0.2099380000	-0.4207070000
C15	0.9228040000	1.3150370000	1.2098320000
C16	-0.3216250000	2.0968510000	1.6081490000
H17	-1.3215320000	-0.1239820000	0.3505260000
H18	0.2107660000	-2.1712450000	-1.3257360000
H19	0.8533230000	-1.5428560000	1.7905260000
H20	-0.7885750000	-1.1366800000	2.2361260000
H21	0.2214080000	-3.5117970000	0.5965740000
H22	0.2554160000	-3.7990370000	3.0273940000
H23	-0.9990760000	-5.9250470000	3.1147210000
H24	-0.1901390000	-5.7437000000	1.5533620000
H25	-1.9367950000	-5.4747610000	1.6828160000
H26	-2.8111190000	-3.3097570000	3.0041070000
H27	-2.4301330000	-2.5668440000	5.2749670000
H28	-0.6174410000	-2.9343780000	5.1293630000
H29	-1.5177350000	-1.2169770000	-2.7666640000
H30	0.4053690000	1.0417810000	-0.8461310000
H31	2.8160700000	0.5801430000	-0.5732590000
H32	1.9984250000	-0.7616710000	-1.3623060000
H33	2.4627140000	-0.8880760000	0.3437580000
H34	1.2794310000	0.7408600000	2.0724330000
H35	1.7127070000	2.0409660000	0.9777310000
H36	-0.7272820000	2.6513270000	0.7561950000
H37	-1.1028180000	1.4397220000	2.0003410000
H38	-0.0745850000	2.8178900000	2.3941800000

Isomer 8E

C1	-2.1430740000	-3.6185510000	0.4236050000
C2	-2.1727200000	-2.4451310000	-0.5591770000
C3	-1.9807230000	-1.0862450000	0.1473030000
C4	-2.6394680000	-1.0767080000	1.5443740000
C5	-3.6299210000	-2.2325980000	1.7073190000
O6	-2.9248430000	-3.4807300000	1.5232950000
C7	-4.3440250000	-2.2344900000	3.0853150000
C8	-5.3563610000	-3.3829480000	3.1722440000
C9	-3.3859110000	-2.3350870000	4.2532800000
C10	-3.2842070000	-1.4193960000	5.2257120000

O11	-1.5059370000	-4.6443120000	0.1982170000
O12	-1.2556260000	-2.5951840000	-1.6386680000
C13	-0.5182300000	-0.5324220000	0.1477490000
C14	-0.4793540000	0.8916700000	0.7241590000
C15	0.4922660000	-1.4602880000	0.8578660000
C16	1.9399350000	-1.0032510000	0.7187480000
H17	-2.5505920000	-0.3717370000	-0.4669950000
H18	-3.1691400000	-2.4753490000	-1.0184970000
H19	-1.8653060000	-1.1641950000	2.3128690000
H20	-3.1436410000	-0.1167480000	1.7080010000
H21	-4.4083390000	-2.1690450000	0.9349600000
H22	-4.9074130000	-1.2946140000	3.1638950000
H23	-4.8687570000	-4.3629290000	3.1225510000
H24	-5.9182210000	-3.3375440000	4.1121460000
H25	-6.0794590000	-3.3237240000	2.3516510000
H26	-2.7468780000	-3.2167760000	4.2926370000
H27	-2.5772460000	-1.5514650000	6.0396770000
H28	-3.8986830000	-0.5244810000	5.2388950000
H29	-1.1031860000	-3.5565550000	-1.7370310000
H30	-0.2057630000	-0.4449540000	-0.9019170000
H31	-1.2571410000	1.5168170000	0.2725440000
H32	-0.6263980000	0.8939210000	1.8088970000
H33	0.4800650000	1.3750690000	0.5146440000
H34	0.2576430000	-1.5462370000	1.9241930000
H35	0.4279850000	-2.4692950000	0.4386780000
H36	2.1194210000	-0.0662710000	1.2537020000
H37	2.6121590000	-1.7568330000	1.1419750000
H38	2.2088860000	-0.8627760000	-0.3328170000

Isomer 8F

C1	-5.2619810000	1.8404190000	1.7855680000
C2	-4.8626020000	0.4142830000	2.1728010000
C3	-4.2429760000	-0.3599420000	0.9886890000
C4	-4.9121350000	0.0274270000	-0.3485150000
C5	-6.2388670000	0.7581460000	-0.1253750000
O6	-5.9885200000	1.9545330000	0.6458570000
C7	-6.9601190000	1.1304360000	-1.4482570000
C8	-8.3019030000	1.8154960000	-1.1626290000
C9	-6.1331900000	2.0253740000	-2.3468090000
C10	-5.7616120000	1.7054120000	-3.5934160000
O11	-4.9996780000	2.8086280000	2.4944560000
O12	-4.0182040000	0.3584620000	3.3185520000
C13	-2.6819170000	-0.3389870000	0.9263730000
C14	-2.0974680000	1.0784310000	0.8306220000
C15	-2.0939010000	-1.2023650000	-0.2147430000
C16	-2.4680880000	-2.6759620000	-0.1307860000
H17	-4.5126500000	-1.4081070000	1.1823950000
H18	-5.7958170000	-0.0770860000	2.4768360000
H19	-4.2413790000	0.6810270000	-0.9148710000
H20	-5.0704040000	-0.8706070000	-0.9571430000
H21	-6.9229650000	0.1221320000	0.4525530000
H22	-7.1773460000	0.1929240000	-1.9782120000
H23	-8.1705560000	2.7752180000	-0.6505000000
H24	-8.8484790000	2.0063610000	-2.0932080000
H25	-8.9337280000	1.1803470000	-0.5324530000
H26	-5.8311640000	2.9898160000	-1.9394690000
H27	-5.1691390000	2.3938570000	-4.1890470000
H28	-6.0376850000	0.7602960000	-4.0507050000
H29	-4.1956190000	1.1737240000	3.8294440000

H30	-2.3090060000	-0.7703260000	1.8656090000
H31	-1.0022510000	1.0413120000	0.8383330000
H32	-2.3985190000	1.6987040000	1.6789440000
H33	-2.4015010000	1.5869490000	-0.0888830000
H34	-2.3934040000	-0.8088030000	-1.1928330000
H35	-0.9989530000	-1.1339740000	-0.1795680000
H36	-1.9193300000	-3.2447440000	-0.8885060000
H37	-2.2165690000	-3.0902070000	0.8505220000
H38	-3.5348880000	-2.8332450000	-0.3123130000

Isomer 8G

C1	-1.5620850000	-3.0910850000	-1.7614850000
C2	-0.4694490000	-2.1176390000	-1.3230360000
C3	-1.0178480000	-0.9916100000	-0.4347430000
C4	-2.0839510000	-0.2988330000	-1.2968910000
C5	-3.2123060000	-1.2698470000	-1.6597360000
O6	-2.7440760000	-2.5552510000	-2.1402760000
C7	-4.2090860000	-0.6683610000	-2.6879730000
C8	-5.4042120000	-1.6038340000	-2.9080140000
C9	-3.5637230000	-0.3741880000	-4.0261930000
C10	-3.4872520000	0.8459950000	-4.5736380000
O11	-1.3384790000	-4.2958740000	-1.8697880000
O12	0.6412650000	-2.7674660000	-0.7182030000
C13	-1.5379940000	-1.4419650000	0.9734560000
C14	-0.4341770000	-2.0461180000	1.8555510000
C15	-2.2553100000	-0.3149300000	1.7588680000
C16	-1.4016310000	0.9122010000	2.0519820000
H17	-0.1979740000	-0.2810210000	-0.2644270000
H18	-0.0768230000	-1.6847120000	-2.2525270000
H19	-2.4889650000	0.5926940000	-0.8078020000
H20	-1.5919140000	0.0639310000	-2.2083940000
H21	-3.7879890000	-1.4892810000	-0.7518800000
H22	-4.5998340000	0.2661550000	-2.2625680000
H23	-5.1018770000	-2.5571820000	-3.3555080000
H24	-6.1425090000	-1.1427760000	-3.5739980000
H25	-5.9053970000	-1.8204020000	-1.9584780000
H26	-3.1470080000	-1.2208080000	-4.5707020000
H27	-3.0166890000	0.9914480000	-5.5417800000
H28	-3.8923100000	1.7238520000	-4.0795090000
H29	0.7140220000	-3.6414240000	-1.1516070000
H30	-2.2830170000	-2.2357670000	0.8328540000
H31	0.4691920000	-1.4279950000	1.8522110000
H32	-0.7696770000	-2.1495060000	2.8934960000
H33	-0.1674940000	-3.0526070000	1.5212190000
H34	-3.1587010000	-0.0015680000	1.2241820000
H35	-2.6133440000	-0.7210040000	2.7139240000
H36	-1.0761360000	1.4074250000	1.1330340000
H37	-1.9822830000	1.6386800000	2.6300230000
H38	-0.5157750000	0.6543890000	2.6394970000

Isomer 8H

C1	0.7563490000	-0.1636240000	-1.6542900000
C2	0.1136360000	-1.4207880000	-2.2379110000
C3	-0.7464830000	-2.1642640000	-1.2068040000
C4	0.2222830000	-2.4990740000	-0.0607510000
C5	0.7974950000	-1.2244140000	0.5647880000
O6	1.2715650000	-0.2597310000	-0.4082080000
C7	1.9276110000	-1.5198150000	1.5887250000

C8	2.3685170000	-0.2383260000	2.3065660000
C9	3.1400750000	-2.1671980000	0.9524860000
C10	3.6063200000	-3.3792880000	1.2809020000
O11	0.8960350000	0.8547630000	-2.3301480000
O12	-0.6051610000	-1.1639690000	-3.4369500000
C13	-2.0391170000	-1.4101640000	-0.7407260000
C14	-2.7344310000	-2.1434390000	0.4204380000
C15	-3.0795960000	-1.1284970000	-1.8513620000
C16	-3.5860070000	-2.3544570000	-2.5994290000
H17	-1.0664530000	-3.1144730000	-1.6534040000
H18	0.9522330000	-2.0627540000	-2.5380400000
H19	-0.2526920000	-3.1223740000	0.7039580000
H20	1.0320230000	-3.1118790000	-0.4772680000
H21	-0.0030660000	-0.7149200000	1.1153930000
H22	1.5157010000	-2.1957020000	2.3506110000
H23	3.1106040000	-0.4614400000	3.0816270000
H24	1.5151230000	0.2440350000	2.7951900000
H25	2.8157520000	0.4853760000	1.6160710000
H26	3.6611750000	-1.5943620000	0.1861840000
H27	4.4864760000	-3.7866370000	0.7917220000
H28	3.1317180000	-3.9904990000	2.0425050000
H29	-0.1396480000	-0.4272330000	-3.8812850000
H30	-1.7465480000	-0.4247540000	-0.3556460000
H31	-3.6983880000	-1.6808440000	0.6589460000
H32	-2.1342540000	-2.0999470000	1.3343720000
H33	-2.9126490000	-3.1965380000	0.1804030000
H34	-3.9452870000	-0.6237680000	-1.4021420000
H35	-2.6787280000	-0.4055560000	-2.5685660000
H36	-2.7844110000	-2.8559360000	-3.1480870000
H37	-4.0469160000	-3.0776050000	-1.9205760000
H38	-4.3456900000	-2.0554740000	-3.3292970000

Isomer 8l

C1	-1.7548310000	-2.0057350000	1.7068060000
C2	-1.7416470000	-0.8390510000	0.7145480000
C3	-3.1875080000	-0.5504940000	0.2777710000
C4	-3.8473160000	-1.8236470000	-0.2920340000
C5	-3.0382180000	-3.0949320000	0.0035680000
O6	-2.5225060000	-3.0656400000	1.3494410000
C7	-3.8613590000	-4.3904930000	-0.2205280000
C8	-4.9203460000	-4.6338660000	0.8607530000
C9	-2.9371050000	-5.5910560000	-0.2743580000
C10	-2.7898220000	-6.3808720000	-1.3461600000
O11	-1.1055020000	-1.9897750000	2.7493740000
O12	-1.1809310000	0.3299290000	1.3124460000
C13	-3.3344890000	0.7013170000	-0.6389080000
C14	-2.4934260000	0.6038850000	-1.9200540000
C15	-4.7977870000	1.0277330000	-1.0170760000
C16	-5.6995070000	1.3000280000	0.1792610000
H17	-3.7281630000	-0.3067010000	1.2046470000
H18	-1.0960720000	-1.1190440000	-0.1239570000
H19	-3.9996060000	-1.7598890000	-1.3745340000
H20	-4.8485360000	-1.8951000000	0.1475580000
H21	-2.1756750000	-3.1223330000	-0.6779050000
H22	-4.3778340000	-4.3014460000	-1.1858430000
H23	-5.4785250000	-5.5547740000	0.6552000000
H24	-5.6478780000	-3.8180610000	0.8994240000
H25	-4.4736490000	-4.7351640000	1.8560440000
H26	-2.3628560000	-5.8126890000	0.6249550000

H27	-2.1114720000	-7.2288960000	-1.3207480000
H28	-3.3389530000	-6.2093520000	-2.2668910000
H29	-0.5118300000	0.0171500000	1.9540710000
H30	-2.9537740000	1.5670610000	-0.0796740000
H31	-1.4278960000	0.5059970000	-1.6929620000
H32	-2.7906830000	-0.2463320000	-2.5409440000
H33	-2.6072880000	1.5108590000	-2.5243070000
H34	-4.8057080000	1.9232560000	-1.6517070000
H35	-5.2321540000	0.2222480000	-1.6200030000
H36	-6.6800500000	1.6468220000	-0.1628620000
H37	-5.8611980000	0.3985210000	0.7767310000
H38	-5.2733840000	2.0744310000	0.8246730000

Isomer 8J

C1	-0.8255600000	-1.2280160000	0.0727290000
C2	-1.8978220000	-1.7968790000	1.0056570000
C3	-3.0407540000	-0.8093850000	1.2695080000
C4	-3.5492420000	-0.3095350000	-0.0865180000
C5	-2.3983850000	0.3734080000	-0.8290820000
O6	-1.2654570000	-0.5090080000	-0.9851050000
C7	-2.8328420000	0.9077070000	-2.2201700000
C8	-3.1005280000	-0.2055730000	-3.2390130000
C9	-1.7769590000	1.8404750000	-2.7793480000
C10	-1.9847050000	3.1347740000	-3.0549090000
O11	0.3613080000	-1.5235410000	0.2028040000
O12	-1.3180360000	-2.1919050000	2.2502540000
C13	-4.1586070000	-1.3887440000	2.1912180000
C14	-4.8359550000	-2.6410580000	1.6156820000
C15	-5.2560240000	-0.3642660000	2.5641990000
C16	-4.7314290000	0.8966440000	3.2366170000
H17	-2.6009900000	0.0416130000	1.8076730000
H18	-2.2644880000	-2.7047280000	0.5143750000
H19	-3.9251240000	-1.1583470000	-0.6675900000
H20	-4.3709410000	0.4025410000	0.0374170000
H21	-2.0526680000	1.2264060000	-0.2281300000
H22	-3.7652100000	1.4736380000	-2.0895890000
H23	-3.4006260000	0.2166940000	-4.2051610000
H24	-3.9118630000	-0.8604710000	-2.9076500000
H25	-2.2136810000	-0.8253610000	-3.4109630000
H26	-0.7899580000	1.4160930000	-2.9619230000
H27	-1.1849640000	3.7513810000	-3.4550110000
H28	-2.9477370000	3.6095460000	-2.8944810000
H29	-0.4401750000	-2.5662430000	2.0344770000
H30	-3.6822570000	-1.6923420000	3.1335480000
H31	-4.1178360000	-3.4480640000	1.4469070000
H32	-5.3459710000	-2.4280080000	0.6712190000
H33	-5.5863220000	-3.0267270000	2.3151260000
H34	-5.8423680000	-0.0863630000	1.6809510000
H35	-5.9600300000	-0.8435250000	3.2569280000
H36	-4.1562560000	1.5141710000	2.5408020000
H37	-5.5680560000	1.5036680000	3.5977040000
H38	-4.0968920000	0.6509880000	4.0937940000

Isomer 8K

C1	-5.8815900000	-2.4649330000	-1.0802870000
C2	-4.4708970000	-2.3179950000	-1.6434430000
C3	-3.5839540000	-1.4423310000	-0.7482310000
C4	-4.3002660000	-0.0845040000	-0.6981150000

C5	-5.6943890000	-0.2152240000	-0.0740110000
O6	-6.4532000000	-1.3572570000	-0.5587300000
C7	-6.5849560000	1.0504920000	-0.2341510000
C8	-6.0032730000	2.2374640000	0.5440430000
C9	-6.9021940000	1.3445660000	-1.6915480000
C10	-6.5925720000	2.4435260000	-2.3928630000
O11	-6.5060440000	-3.5192520000	-1.1892580000
O12	-3.8539050000	-3.5672400000	-1.9278550000
C13	-3.2626420000	-2.0374000000	0.6656530000
C14	-2.4797350000	-3.3576500000	0.5969500000
C15	-2.5154730000	-1.0509000000	1.5983750000
C16	-1.1654900000	-0.5699700000	1.0818860000
H17	-2.6262480000	-1.3077940000	-1.2685620000
H18	-4.5952520000	-1.8304900000	-2.6192550000
H19	-3.7037260000	0.6612960000	-0.1646950000
H20	-4.3838610000	0.2895460000	-1.7264600000
H21	-5.5807230000	-0.3908600000	1.0030590000
H22	-7.5559080000	0.8185880000	0.2272220000
H23	-5.0431070000	2.5697170000	0.1363600000
H24	-6.6906650000	3.0906180000	0.5252600000
H25	-5.8456190000	1.9687960000	1.5943120000
H26	-7.4639450000	0.5633230000	-2.2055250000
H27	-6.8908390000	2.5337410000	-3.4339540000
H28	-6.0456570000	3.2783270000	-1.9678330000
H29	-4.5753710000	-4.1725540000	-2.1923590000
H30	-4.2095090000	-2.2715380000	1.1692160000
H31	-3.1237490000	-4.1825910000	0.2794510000
H32	-1.6343640000	-3.2904100000	-0.0951380000
H33	-2.0894780000	-3.6375730000	1.5817820000
H34	-3.1478430000	-0.1811050000	1.8078410000
H35	-2.3591070000	-1.5333730000	2.5720170000
H36	-0.4785620000	-1.4045530000	0.9147390000
H37	-1.2660030000	-0.0108010000	0.1475860000
H38	-0.7032880000	0.0971560000	1.8169950000

Isomer 8L

C1	-3.9176370000	-1.0139290000	-3.1452280000
C2	-3.5989500000	-1.5460270000	-1.7461520000
C3	-4.8609160000	-1.6686000000	-0.8665580000
C4	-6.0959380000	-2.0809900000	-1.6990960000
C5	-5.6931770000	-2.6396060000	-3.0664310000
O6	-4.9490470000	-1.6228690000	-3.7804260000
C7	-6.8722370000	-3.0974720000	-3.9672900000
C8	-7.5480920000	-4.3544030000	-3.4104230000
C9	-7.9187180000	-2.0260190000	-4.1983540000
C10	-8.1468350000	-1.4432710000	-5.3829180000
O11	-3.2402910000	-0.1405260000	-3.6814500000
O12	-2.5820370000	-0.8020170000	-1.0817660000
C13	-5.1328850000	-0.4596450000	0.0876440000
C14	-6.3109130000	-0.7657130000	1.0260320000
C15	-5.3322990000	0.8798410000	-0.6555120000
C16	-5.4359740000	2.0826860000	0.2752990000
H17	-4.6476240000	-2.5136510000	-0.1933850000
H18	-3.1713320000	-2.5443740000	-1.9047800000
H19	-6.7375290000	-1.2079670000	-1.8509970000
H20	-6.6826220000	-2.8141260000	-1.1347650000
H21	-5.0263510000	-3.5029910000	-2.9389530000
H22	-6.4405920000	-3.3662460000	-4.9420460000
H23	-8.3001080000	-4.7338970000	-4.1117300000

H24	-6.8141780000	-5.1514620000	-3.2504910000
H25	-8.0529220000	-4.1620480000	-2.4578220000
H26	-8.5280880000	-1.7246640000	-3.3480970000
H27	-8.9150610000	-0.6833310000	-5.4903330000
H28	-7.5731290000	-1.7016570000	-6.2678310000
H29	-2.0482480000	-0.3802790000	-1.7849530000
H30	-4.2496320000	-0.3519450000	0.7321260000
H31	-6.3600010000	-0.0413610000	1.8451610000
H32	-6.1999270000	-1.7556210000	1.4815290000
H33	-7.2686050000	-0.7387120000	0.4965420000
H34	-4.4878180000	1.0607190000	-1.3279070000
H35	-6.2313570000	0.8472560000	-1.2801180000
H36	-5.4616780000	3.0074710000	-0.3103710000
H37	-6.3495170000	2.0494160000	0.8758470000
H38	-4.5755720000	2.1335490000	0.9498190000

Isomer 8M

C1	-0.6961700000	1.6033580000	-0.1958200000
C2	-0.8985420000	0.3810230000	0.7040300000
C3	-2.3759710000	0.0279330000	0.9072820000
C4	-3.0376270000	-0.0468140000	-0.4726040000
C5	-2.8923790000	1.3087370000	-1.1667370000
O6	-1.5069030000	1.7035760000	-1.2738050000
C7	-3.5433800000	1.3196550000	-2.5757740000
C8	-2.7783230000	0.4771670000	-3.6024140000
C9	-3.6556380000	2.7400160000	-3.0930920000
C10	-4.8141450000	3.3475420000	-3.3812900000
O11	0.2415010000	2.3801320000	-0.0207850000
O12	-0.2847410000	0.5955240000	1.9766840000
C13	-2.5934550000	-1.2470590000	1.7829230000
C14	-4.0685200000	-1.3674790000	2.1974750000
C15	-2.0955070000	-2.5475410000	1.1153230000
C16	-2.1349350000	-3.7594230000	2.0394020000
H17	-2.8321460000	0.8617900000	1.4618600000
H18	-0.3588450000	-0.4384150000	0.2176030000
H19	-2.5505730000	-0.8282050000	-1.0658330000
H20	-4.0987520000	-0.3015620000	-0.3872080000
H21	-3.3916860000	2.0720380000	-0.5533630000
H22	-4.5544440000	0.9000000000	-2.4848020000
H23	-1.7493820000	0.8288620000	-3.7357460000
H24	-3.2704570000	0.5172130000	-4.5811940000
H25	-2.7403770000	-0.5746590000	-3.3037590000
H26	-2.7249990000	3.2895700000	-3.2327650000
H27	-4.8273560000	4.3693690000	-3.7494780000
H28	-5.7705990000	2.8477370000	-3.2629760000
H29	0.5426790000	1.0868860000	1.7997780000
H30	-2.0229750000	-1.1080920000	2.7110120000
H31	-4.1924910000	-2.1050420000	2.9967780000
H32	-4.4471330000	-0.4144960000	2.5820810000
H33	-4.7017770000	-1.6741040000	1.3591810000
H34	-2.6920680000	-2.7718170000	0.2236500000
H35	-1.0599710000	-2.4232500000	0.7830100000
H36	-1.5857400000	-3.5654700000	2.9660240000
H37	-3.1613000000	-4.0388890000	2.2938690000
H38	-1.6727520000	-4.6208070000	1.5461940000

Isomer 8N

C1	-2.7370570000	-1.9531760000	0.6273930000

C2	-3.6138930000	-1.6728630000	-0.5956140000
C3	-5.0684290000	-1.3640900000	-0.2264440000
C4	-5.5673250000	-2.4893510000	0.6843880000
C5	-4.6910250000	-2.5415410000	1.9376310000
O6	-3.2887320000	-2.6839340000	1.6221140000
C7	-5.1173970000	-3.6660590000	2.9192980000
C8	-4.2886870000	-3.6144980000	4.2084450000
C9	-5.0001730000	-5.0492260000	2.3137810000
C10	-6.0297690000	-5.8908210000	2.1524440000
O11	-1.5486880000	-1.6348790000	0.6485320000
O12	-3.0758350000	-0.5835620000	-1.3487850000
C13	-5.9815170000	-1.1010260000	-1.4659550000
C14	-7.3340580000	-0.5213350000	-1.0225580000
C15	-6.1752890000	-2.3411730000	-2.3654690000
C16	-6.9123600000	-2.0408390000	-3.6657000000
H17	-5.0625540000	-0.4290290000	0.3536810000
H18	-3.5449580000	-2.5674970000	-1.2235760000
H19	-5.5122400000	-3.4416450000	0.1449420000
H20	-6.6102070000	-2.3298790000	0.9764800000
H21	-4.7883720000	-1.5864310000	2.4720770000
H22	-6.1644950000	-3.4827730000	3.1967560000
H23	-3.2276430000	-3.8144760000	4.0220590000
H24	-4.6454590000	-4.3573110000	4.9310240000
H25	-4.3688780000	-2.6292080000	4.6801040000
H26	-4.0068670000	-5.3681470000	1.9998820000
H27	-5.8796190000	-6.8737870000	1.7153490000
H28	-7.0393600000	-5.6277740000	2.4529560000
H29	-2.1031080000	-0.6825990000	-1.3119500000
H30	-5.4963840000	-0.3228250000	-2.0702660000
H31	-7.9679450000	-1.2816910000	-0.5558260000
H32	-7.8818930000	-0.1075650000	-1.8751850000
H33	-7.1951640000	0.2956060000	-0.3064860000
H34	-5.2013750000	-2.7639360000	-2.6319800000
H35	-6.7253910000	-3.1213730000	-1.8270140000
H36	-6.9232370000	-2.9308250000	-4.3034010000
H37	-7.9523070000	-1.7556880000	-3.4827570000
H38	-6.4211230000	-1.2343600000	-4.2190030000

Isomer 8O

C1	-1.7259930000	-2.4042430000	-1.1504580000
C2	-2.5645010000	-1.9767830000	0.0567900000
C3	-3.4802460000	-0.7753610000	-0.2675460000
C4	-4.0080090000	-0.8452440000	-1.7180720000
C5	-3.8210040000	-2.2406970000	-2.3183200000
O6	-2.4085110000	-2.5490060000	-2.3137290000
C7	-4.3742670000	-2.3489790000	-3.7633450000
C8	-3.5808260000	-1.5306540000	-4.7877470000
C9	-4.3945260000	-3.7990450000	-4.2047320000
C10	-5.5075650000	-4.4771710000	-4.5138030000
O11	-0.5274630000	-2.6567170000	-1.0588310000
O12	-1.7846860000	-1.7248830000	1.2217200000
C13	-2.8975280000	0.6244700000	0.1093830000
C14	-1.5650060000	0.9350770000	-0.5889720000
C15	-3.8792150000	1.7937240000	-0.1406840000
C16	-5.1823060000	1.6844120000	0.6394400000
H17	-4.3502200000	-0.9155870000	0.3899960000
H18	-3.1844870000	-2.8477070000	0.3052900000
H19	-3.4696980000	-0.1212030000	-2.3365790000

H20	-5.0660490000	-0.5592570000	-1.7403040000
H21	-4.3384870000	-2.9852180000	-1.6977220000
H22	-5.4052280000	-1.9698740000	-3.7584800000
H23	-3.6136780000	-0.4623570000	-4.5539670000
H24	-2.5297690000	-1.8364580000	-4.8310600000
H25	-4.0020520000	-1.6532630000	-5.7924440000
H26	-3.4332990000	-4.3082830000	-4.2704320000
H27	-5.4548650000	-5.5162550000	-4.8259640000
H28	-6.4909640000	-4.0192710000	-4.4696870000
H29	-0.9705360000	-2.2589190000	1.1268490000
H30	-2.6928130000	0.6163130000	1.1888680000
H31	-1.6722420000	0.9824720000	-1.6765120000
H32	-1.1755510000	1.9034930000	-0.2551490000
H33	-0.8011150000	0.1893370000	-0.3536590000
H34	-3.3918290000	2.7318670000	0.1545650000
H35	-4.1046010000	1.8895420000	-1.2089750000
H36	-5.7704960000	2.5994300000	0.5147120000
H37	-5.7956680000	0.8504010000	0.2873760000
H38	-4.9904330000	1.5492090000	1.7084290000

Isomer 8P

C1	-2.0856760000	-0.0769130000	2.0744210000
C2	-3.4563630000	-0.4187180000	1.4960700000
C3	-3.4396810000	-0.4567540000	-0.0373970000
C4	-2.9961480000	0.9542610000	-0.4573290000
C5	-1.5920280000	1.2747590000	0.0667030000
O6	-1.3818820000	0.8958070000	1.4545630000
C7	-1.1799420000	2.7671900000	-0.0876280000
C8	-1.0562040000	3.1553720000	-1.5665080000
C9	-2.0611450000	3.6917160000	0.7368750000
C10	-2.8409290000	4.6890020000	0.2976800000
O11	-1.6866160000	-0.5922400000	3.1178630000
O12	-4.0039360000	-1.6094490000	2.0463730000
C13	-2.5782670000	-1.6019650000	-0.6726040000
C14	-2.4797100000	-1.4546110000	-2.2016050000
C15	-3.0362930000	-3.0409320000	-0.3344090000
C16	-4.4719790000	-3.3766070000	-0.7155400000
H17	-4.4717770000	-0.5933480000	-0.3851450000
H18	-4.1235490000	0.3860840000	1.8314150000
H19	-3.0464520000	1.0786560000	-1.5433190000
H20	-3.7205630000	1.6697600000	-0.0476030000
H21	-0.8621290000	0.6829640000	-0.4996080000
H22	-0.1753640000	2.8679630000	0.3483290000
H23	-0.6530350000	4.1688970000	-1.6712050000
H24	-0.3712110000	2.4767760000	-2.0865040000
H25	-2.0192800000	3.1208850000	-2.0859180000
H26	-2.0277530000	3.5180410000	1.8133380000
H27	-3.4165370000	5.2868430000	0.9992650000
H28	-2.9326960000	4.9457550000	-0.7522250000
H29	-3.6769280000	-1.6594870000	2.9669560000
H30	-1.5539210000	-1.5210810000	-0.2864560000
H31	-3.4689300000	-1.3538050000	-2.6595020000
H32	-1.9834490000	-2.3218400000	-2.6507370000
H33	-1.8858450000	-0.5783320000	-2.4790220000
H34	-2.3742590000	-3.7504150000	-0.8485200000
H35	-2.8864120000	-3.2432790000	0.7306720000
H36	-4.6844330000	-4.4233100000	-0.4737150000
H37	-5.1922640000	-2.7616090000	-0.1696640000
H38	-4.6447400000	-3.2438840000	-1.7873470000

2.2.3. DP4f probability analysis of the C36-C42 region

For the conformers found <10 kJmol^{-1} of the global minima generated from the previously described conformational search, Jaguar (version 7.9) was used to calculate both the carbon and proton GIAO shielding constants at the B3LYP/6-31G(d,p) level. Data for the hydroxyl protons was omitted, as was the data for the protons at C34 and C43 due to the significant differences in chemical environments compared to the natural product. The shielding constants for the methyl groups were averaged.

Predicted ^{13}C NMR shifts (ppm)																
Atom #	8A	8B	8C	8D	8E	8F	8G	8H	8I	8J	8K	8L	8M	8N	8O	8P
C41	175.7	174.0	173.6	174.3	174.2	174.4	172.6	172.3	174.2	173.9	172.4	173.9	173.8	174.0	174.2	172.8
C40	66.5	68.0	70.5	68.1	69.1	68.7	70.8	72.9	68.5	70.2	70.7	69.6	70.2	70.3	68.7	70.6
C39	43.5	41.6	46.2	40.8	40.5	38.9	43.0	40.9	38.5	46.1	42.9	40.9	46.4	46.9	38.7	40.6
C38	30.9	31.5	30.2	26.4	30.4	28.4	32.4	32.7	28.6	28.8	30.2	32.9	31.2	31.0	28.8	30.5
C37	76.4	78.9	83.3	77.3	77.5	77.4	80.0	79.8	78.3	83.8	80.6	78.0	83.7	83.5	77.7	81.0
C36	47.7	47.8	48.6	46.7	47.0	46.9	48.2	47.6	48.0	47.3	47.1	47.0	47.3	47.7	47.3	47.5
C36-Me	22.0	18.8	20.5	18.8	18.9	18.5	20.1	19.1	18.9	18.1	17.8	18.0	18.1	18.9	18.1	18.1
C35	136.3	135.8	136.0	135.5	135.5	135.5	135.7	135.7	136.0	135.8	135.6	135.9	135.8	135.7	135.7	135.5
C42	40.4	40.4	37.3	37.0	39.0	37.7	39.1	37.4	37.7	37.1	37.9	42.5	39.5	39.1	37.6	37.3
C42-Me	16.9	17.1	14.2	13.2	17.1	14.2	18.3	20.4	16.5	14.3	18.6	14.7	17.4	17.8	14.1	18.5
C43	175.7	174.0	173.6	174.3	174.2	174.4	172.6	172.3	174.2	173.9	172.4	173.9	173.8	174.0	174.2	172.8

Table S7. Predicted ^{13}C NMR chemical shifts for isomers **8A-P**. Favoured isomer is highlighted in yellow.

		$\Delta\delta_C$(Predicted – Experimental) ppm														
Atom #	Experimental shift data for hemicalide[1]	8A	8B	8C	8D	8E	8F	8G	8H	8I	8J	8K	8L	8M	8N	8O	8P
C41	178.4	-2.7	-4.4	-4.8	-4.1	-4.2	-4.0	-5.8	-6.1	-4.2	-4.5	-6.0	-4.5	-4.6	-4.4	-4.2	-5.6
C40	68.2	-1.7	-0.2	2.3	-0.1	0.9	0.5	2.6	4.7	0.3	2.0	2.5	1.4	2.0	2.1	0.5	2.4
C39	41.4	2.1	0.2	4.8	-0.6	-0.9	-2.5	1.6	-0.5	-2.9	4.7	1.5	-0.5	5.0	5.5	-2.7	-0.8
C38	26.7	4.2	4.8	3.5	-0.3	3.7	1.7	5.7	6.0	1.9	2.1	3.5	6.2	4.5	4.3	2.1	3.8
C37	80.9	-4.5	-2.0	2.4	-3.6	-3.4	-3.5	-0.9	-1.1	-2.6	2.9	-0.3	-2.9	2.8	2.6	-3.2	0.1
C36	43.6	4.1	4.2	5.0	3.1	3.4	3.3	4.6	4.0	4.4	3.7	3.5	3.4	3.7	4.1	3.7	3.9
C36-Me	17.2	4.8	1.6	3.3	1.6	1.7	1.3	2.9	1.9	1.7	0.9	0.6	0.8	0.9	1.7	0.9	0.9
C35	132.5	3.8	3.3	3.5	3.0	3.0	3.0	3.2	3.2	3.5	3.3	3.1	3.4	3.3	3.2	3.2	3.0
C42	33.7	6.7	6.7	3.6	3.3	5.3	4.0	5.4	3.7	4.0	3.4	4.2	8.8	5.8	5.4	3.9	3.6
C42-Me	13.4	3.5	3.7	0.8	-0.2	3.7	0.8	4.9	7.0	3.1	0.9	5.2	1.3	4.0	4.4	0.7	5.1
C43	32.1	-8.3	-5.3	-2.2	-2.2	-6.6	-2.5	-1.7	-2.5	-3.2	-2.1	-3.5	-2.2	-4.8	-5.4	-2.5	-2.3

Table S8. The ^{13}C NMR $\Delta\delta_{(Predicted - Experimental)}$ values for isomers **8A-P**. Favoured isomer is highlighted in yellow.

Predicted ^{1}H NMR shifts (ppm)																
Atom #	8A	8B	8C	8D	8E	8F	8G	8H	8I	8J	8K	8L	8M	8N	8O	8P
H39	2.51	2.16	1.95	2.11	2.56	2.62	2.11	2.20	2.25	1.90	2.13	2.53	1.89	1.93	2.58	2.27
H40	4.16	4.22	4.02	4.24	4.36	4.36	4.23	4.29	4.21	4.00	4.26	4.39	4.03	4.01	4.33	4.26
H38A	1.44	1.65	1.86	1.33	1.72	1.75	1.55	1.65	1.62	1.50	1.89	1.46	1.57	1.78	1.51	1.91
H38B	2.65	1.83	1.31	1.95	1.57	1.50	2.04	1.97	1.74	1.66	1.74	1.98	1.63	1.33	1.78	1.69
H37	3.66	3.93	4.03	4.04	4.08	4.08	4.55	4.52	3.91	3.93	4.39	3.91	3.92	4.07	3.91	4.36
H36	2.46	2.42	2.15	2.33	2.28	2.33	2.16	2.21	2.40	2.47	2.46	2.36	2.47	2.25	2.46	2.44
H36-Me	0.94	1.20	1.23	1.18	1.18	1.18	1.23	1.22	1.21	1.17	1.13	1.18	1.16	1.21	1.18	1.16
H42	2.14	1.85	2.10	2.19	2.09	2.29	1.92	1.83	2.10	2.12	2.03	1.62	1.87	1.92	2.29	2.07
H42-Me	0.92	0.91	0.88	0.87	0.86	0.75	1.10	1.01	0.92	0.87	1.05	0.92	0.94	0.94	0.75	0.96
H43A	1.94	1.22	1.32	1.24	1.17	1.20	1.48	1.42	1.37	1.27	1.21	1.45	1.21	1.69	1.19	1.36
H43B	1.14	1.75	1.28	1.24	1.51	1.21	1.50	2.28	1.25	1.31	1.57	1.84	1.71	1.17	1.18	1.67

Table S9. Predicted ^{1}H NMR chemical shifts for isomers **8A-P**. Favoured isomer is highlighted in yellow.

$\Delta\delta_H$(Predicted – Experimental) ppm																
Atom #	Experimental shift data for hemicalide[1]	8A	8B	8C	8D	8E	8F	8G	8H	8I	8J	8K	8L	8M	8N	8O	8P
H39	1.62	0.89	0.54	0.33	0.49	0.94	1.00	0.49	0.58	0.63	0.28	0.51	0.91	0.27	0.31	0.96	0.65
H40	4.32	-0.16	-0.10	-0.30	-0.08	0.04	0.04	-0.09	-0.03	-0.11	-0.32	-0.06	0.07	-0.29	-0.31	0.01	-0.06
H38A	1.62	-0.18	0.03	0.24	-0.29	0.10	0.13	-0.07	0.03	0.00	-0.12	0.27	-0.16	-0.05	0.16	-0.11	0.29
H38B	1.62	1.03	0.21	-0.31	0.33	-0.05	-0.12	0.42	0.35	0.12	0.04	0.12	0.36	0.01	-0.29	0.16	0.07
H37	4.11	-0.45	-0.18	-0.08	-0.07	-0.03	-0.03	0.44	0.41	-0.20	-0.18	0.28	-0.20	-0.19	-0.04	-0.20	0.25
H36	2.34	0.12	0.08	-0.19	-0.01	-0.06	-0.01	-0.18	-0.13	0.06	0.13	0.12	0.02	0.13	-0.09	0.12	0.10
H36-Me	1.11	-0.17	0.09	0.12	0.07	0.07	0.07	0.12	0.11	0.10	0.06	0.02	0.07	0.05	0.10	0.07	0.05
H42	1.62	0.52	0.23	0.48	0.57	0.47	0.67	0.30	0.21	0.48	0.50	0.41	0.00	0.25	0.30	0.67	0.45
H42-Me	0.91	0.01	0.00	-0.03	-0.04	-0.05	-0.16	0.19	0.10	0.01	-0.04	0.14	0.01	0.03	0.03	-0.16	0.05
H43A	1.62	0.32	-0.40	-0.30	-0.38	-0.45	-0.42	-0.14	-0.20	-0.25	-0.35	-0.41	-0.17	-0.41	0.07	-0.43	-0.26
H43B	1.62	-0.48	0.13	-0.34	-0.38	-0.11	-0.41	-0.12	0.66	-0.37	-0.31	-0.05	0.22	0.09	-0.45	-0.44	0.05

Table S10. The ^{1}H NMR $\Delta\delta_{(\text{Predicted} - \text{Experimental})}$ values for isomers **8A-P**. Favoured isomer is highlighted in yellow.

Isomer	Configuration	DP4 probability (%)		
		^{1}H and ^{13}C NMR	^{13}C NMR	^{1}H NMR
8A	36(*S*), 37(*R*), 39 (*R*), 40 (*R*), 42 (*R*)	0.0	0.0	0.0
8B	36(*S*), 37(*S*), 39 (*S*), 40 (*S*), 42 (*S*)	0.4	0.1	5.8
8C	36(*R*), 37(*S*), 39 (*R*), 40 (*R*), 42 (*S*)	0.1	16.4	0.0
8D	36(*R*), 37(*S*), 39 (*S*), 40 (*S*), 42 (*R*)	0.1	34.6	0.0
8E	36(*S*), 37(*R*), 39 (*S*), 40 (*R*), 42 (*S*)	0.0	0.1	0.0
8F	36(*S*), 37(*R*), 39 (*S*), 40 (*R*), 42 (*R*)	0.0	8.1	0.0
8G	36(*R*), 37(*S*), 39 (*S*), 40 (*R*), 42 (*S*)	0.8	5.1	0.1
8H	36(*R*), 37(*S*), 39 (*S*), 40 (*R*), 42 (*R*)	0.0	0.1	0.0
8I	36(*R*), 37(*R*), 39 (*R*), 40 (*R*), 42 (*S*)	0.1	1.1	0.1
8J	36(*R*), 37(*R*), 39 (*S*), 40 (*S*), 42 (*R*)	6.0	22.0	0.2
8K	36(*S*), 37(*S*), 39 (*S*), 40 (*R*), 42 (*S*)	3.0	2.5	1.0
8L	36(*S*), 37(*S*), 39 (*R*), 40 (*S*), 42 (*R*)	0.0	0.0	0.0
8M	36(*R*), 37(*R*), 39 (*S*), 40 (*S*), 42 (*S*)	84.0	0.8	90.9
8N	36(*R*), 37(*S*), 39 (*R*), 40 (*R*), 42 (*R*)	0.9	0.9	0.9
8O	36(*S*), 37(*S*), 39 (*R*), 40 (*S*), 42 (*S*)	0.0	4.5	0.0
8P	36(*S*), 37(*S*), 39 (*S*), 40 (*R*), 42 (*R*)	4.7	3.9	1.0

Table S11. DP4f NMR stereochemical prediction for the C36-C42 region. The highest probability stereoisomer **8M** is highlighted in yellow.

2.3. Computational modelling of the C34-C46 region

As discussed in the main text, we next opted to extend our modelling to the C34-C46 region to include a more elaborate side chain containing the C45 hydroxyl group in virtual fragment **9**. Due to the increased complexity of the system, we decided to initially focus our efforts on the six stereoisomers shown in **Figure S3**. Isomers **9A**, **9B**, **9E** and **9F** correspond to the stereochemical permutations considered by Bultinck and Cossy which concur with the observed NOE constraints for the lactone substitution.[13,14] Isomers **9C** and **9D** are the two C45 epimers corresponding to the structure **8M** originally favoured by the DP4f NMR stereochemical prediction of the C36-C42 region (**Table S11**).

[13] De Gussem, E.; Herrebout, W.; Specklin, S.; Meyer, C.; Cossy, J.; Bultinck, P. *Chem. Eur. J.* **2014**, *20*, 17385.
[14] Specklin, S.; Boissonnat, G.; Lecourt, C.; Sorin, G.; Lannou, M.-I.; Ardisson, J.; Sautel, F.; Massiot, G.; Meyer, C.; Cossy J. *Org. Lett.* **2015**, *17*, 2446.

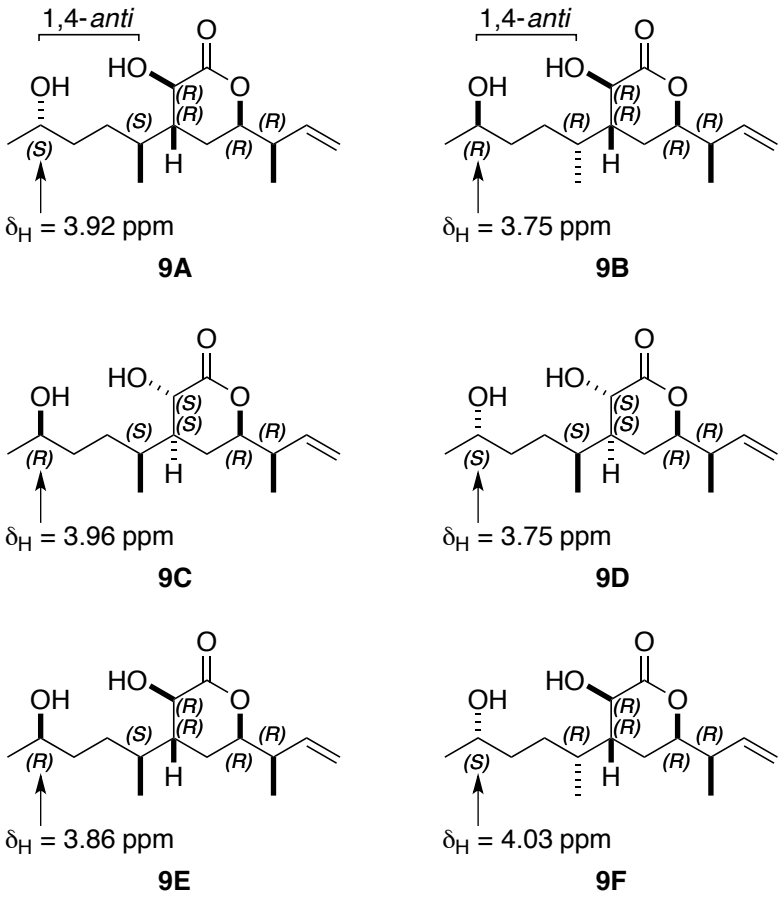


Figure S3. The six stereoisomers considered for the assignment of the C34-C46 region. See **Table S15** for more values of the predicted 1H signals.

2.3.1. Molecular Modelling of the C34-C46 region

Molecular modelling was carried out for these six diastereoisomers using a 50,000 step hybrid Monte-Carlo multiple-minimum/ low-mode sampling using the MMFF force field and $CHCl_3$ as the solvent. No bond restraints were applied. Structures found within 10 $kJmol^{-1}$ of the lowest energy conformer were recorded.

Isomer	Conformers ≤10 $kJmol^{-1}$ (Conformational search)
9A	204
9B	141
9C	115
9D	128
9E	203
9F	106

Table S12. Number of conformers generated from the conformational search for the C34-C46 region.

2.3.2. Atomic coordinates for the minimum energy conformers for 9A-F

Isomer 9A

atom	x	y	z
C1	-3.5475900000	0.5241460000	-1.3496030000
C2	-3.5877310000	-0.4220600000	-0.1386700000
C3	-4.0335090000	0.3372830000	1.1282540000
C4	-4.6288040000	1.7176330000	0.8153580000
O5	-5.4710090000	1.6550170000	-0.3530970000
C6	-4.9227290000	1.1816180000	-1.5000720000
O7	-5.4867200000	1.2848290000	-2.5864480000
C8	-5.4224760000	2.3086760000	2.0098890000
C9	-5.6670850000	3.7888030000	1.7901030000
C10	-5.1898530000	4.7570410000	2.5832100000
C11	-6.7702680000	1.6178360000	2.2467060000
O12	-3.2074500000	-0.2154200000	-2.5227080000
C13	-2.2898810000	-1.2632320000	0.0533910000
C14	-2.3577120000	-2.2529500000	1.2415980000
C15	-1.0329510000	-0.3923950000	0.1968480000
C16	-3.4861630000	-3.2871490000	1.1222300000
C17	-3.4268470000	-4.3319240000	2.2421840000
C18	-4.5087390000	-5.3898850000	2.0680200000
O19	-3.6176750000	-3.6793500000	3.4959900000
H20	-4.3834060000	-1.1475790000	-0.3645730000
H21	-2.8049110000	1.3205460000	-1.2379230000
H22	-3.2101360000	0.4748050000	1.8369990000
H23	-4.7693650000	-0.2910640000	1.6424460000
H24	-3.8025820000	2.4063370000	0.5867940000
H25	-4.8144870000	2.1839980000	2.9161510000
H26	-6.2721410000	4.0662800000	0.9272600000
H27	-5.4024050000	5.8012460000	2.3726300000
H28	-4.5849080000	4.5379500000	3.4577210000
H29	-7.2886640000	2.0645500000	3.1032230000
H30	-6.6418430000	0.5541560000	2.4667980000
H31	-7.4332750000	1.7051820000	1.3788230000
H32	-3.6209790000	0.2552940000	-3.2741280000
H33	-2.1499410000	-1.8680910000	-0.8530550000
H34	-1.4030910000	-2.7926850000	1.2982500000
H35	-2.4535490000	-1.7041720000	2.1856180000
H36	-1.0883490000	0.2647410000	1.0697070000
H37	-0.1415420000	-1.0194460000	0.3102930000
H38	-0.8727640000	0.2284100000	-0.6894310000
H39	-4.4531650000	-2.7740870000	1.1707520000
H40	-3.4205580000	-3.7869410000	0.1485510000
H41	-2.4416960000	-4.8116200000	2.2558280000
H42	-4.4610720000	-6.1236190000	2.8798890000
H43	-4.3992080000	-5.9179160000	1.1159590000
H44	-5.5069740000	-4.9403020000	2.1090940000
H45	-3.5581350000	-4.3615780000	4.1879420000

Isomer 9B

C1	-4.1938590000	1.6788070000	-1.8253080000
C2	-4.9355890000	0.9926740000	-0.6666380000
C3	-4.0727020000	0.9852010000	0.6130960000
C4	-2.8279770000	1.8754410000	0.4908590000
O5	-3.1652460000	3.1247080000	-0.1453690000
C6	-3.7505780000	3.0717590000	-1.3681750000

O7	-3.8996370000	4.0715740000	-2.0660350000
C8	-2.1501730000	2.1443030000	1.8600160000
C9	-0.7602350000	2.7119310000	1.6493520000
C10	0.3682400000	2.1063420000	2.0418290000
C11	-2.9424470000	3.1040580000	2.7548760000
O12	-5.0581900000	1.7649890000	-2.9586470000
C13	-5.5406050000	-0.3988090000	-1.0316490000
C14	-4.4722270000	-1.4336490000	-1.4535540000
C15	-6.4181150000	-0.9212740000	0.1158920000
C16	-5.0692590000	-2.7432110000	-1.9928390000
C17	-3.9845900000	-3.7090440000	-2.4869650000
C18	-4.5834300000	-5.0245120000	-2.9674160000
O19	-3.2529050000	-3.1204090000	-3.5602340000
H20	-5.8039540000	1.6351050000	-0.4482010000
H21	-3.2991570000	1.1322390000	-2.1387190000
H22	-3.7505020000	-0.0236320000	0.8901270000
H23	-4.7115160000	1.3314480000	1.4338190000
H24	-2.0966120000	1.3645370000	-0.1518570000
H25	-2.0613640000	1.1854110000	2.3883790000
H26	-0.6917360000	3.6754310000	1.1447640000
H27	1.3356150000	2.5667110000	1.8624860000
H28	0.3593240000	1.1476660000	2.5512950000
H29	-3.0726230000	4.0864540000	2.2876230000
H30	-2.4254260000	3.2592020000	3.7090940000
H31	-3.9347610000	2.7070550000	2.9873460000
H32	-4.7670110000	2.5484550000	-3.4671140000
H33	-6.2096670000	-0.2468320000	-1.8894410000
H34	-3.8395710000	-0.9993270000	-2.2340830000
H35	-3.8146040000	-1.6680580000	-0.6088450000
H36	-5.8165890000	-1.2540590000	0.9676170000
H37	-7.0335140000	-1.7651210000	-0.2110440000
H38	-7.1052850000	-0.1438440000	0.4668510000
H39	-5.6541960000	-3.2393200000	-1.2109970000
H40	-5.7504580000	-2.5028240000	-2.8186050000
H41	-3.2729300000	-3.9127670000	-1.6793970000
H42	-5.1236570000	-5.5327520000	-2.1629970000
H43	-5.2720000000	-4.8611330000	-3.8037610000
H44	-3.7951460000	-5.6905200000	-3.3345100000
H45	-3.8846020000	-2.9278620000	-4.2757660000

Isomer 9C

C1	-2.0007810000	-0.9952430000	-3.6029870000
C2	-2.6460190000	-0.3661220000	-2.3652530000
C3	-3.8198250000	0.5558650000	-2.7117650000
C4	-4.7724840000	-0.2209300000	-3.6265190000
C5	-4.0181640000	-0.6359670000	-4.8912930000
O6	-2.8400560000	-1.4117880000	-4.5783970000
C7	-4.9157230000	-1.4333200000	-5.8751390000
C8	-5.2637920000	-2.8389300000	-5.3729230000
C9	-4.2409890000	-1.5491830000	-7.2276110000
C10	-4.7406270000	-1.0468130000	-8.3644040000
O11	-0.7940610000	-1.2300170000	-3.6475180000
O12	-1.6746320000	0.3657450000	-1.6149600000
C13	-4.5120440000	1.1788530000	-1.4579200000
C14	-5.4829130000	2.2930970000	-1.8791910000
C15	-5.2122900000	0.1353550000	-0.5578760000
H16	-3.4076330000	1.4006700000	-3.2839920000
C17	-5.7508870000	0.7250270000	0.7554080000

C18	-6.2728690000	-0.3618360000	1.7023580000
C19	-6.7698610000	0.2386550000	3.0110790000
O20	-7.3485230000	-1.0537890000	1.0717090000
H21	-2.9715330000	-1.2058270000	-1.7420680000
H22	-5.1394550000	-1.1074120000	-3.0982010000
H23	-5.6389130000	0.3884690000	-3.9023360000
H24	-3.6702330000	0.2714750000	-5.4047790000
H25	-5.8562320000	-0.8797300000	-6.0001180000
H26	-5.8938900000	-3.3654270000	-6.0992780000
H27	-5.8215820000	-2.7978920000	-4.4326300000
H28	-4.3685180000	-3.4488070000	-5.2094190000
H29	-3.2879520000	-2.0766590000	-7.2602350000
H30	-4.2073450000	-1.1638160000	-9.3034210000
H31	-5.6861860000	-0.5140640000	-8.3909070000
H32	-0.8428370000	-0.1459630000	-1.6759310000
H33	-3.7286200000	1.6628200000	-0.8594560000
H34	-5.0152250000	2.9685580000	-2.6033920000
H35	-6.3951020000	1.8878880000	-2.3281120000
H36	-5.7763710000	2.9034840000	-1.0191780000
H37	-6.0391730000	-0.3323890000	-1.1048240000
H38	-4.5058670000	-0.6619650000	-0.3045110000
H39	-4.9580350000	1.2948760000	1.2542660000
H40	-6.5686340000	1.4183470000	0.5262870000
H41	-5.4794200000	-1.0886810000	1.9097420000
H42	-5.9721160000	0.7797990000	3.5287780000
H43	-7.6051880000	0.9253060000	2.8350380000
H44	-7.1442840000	-0.5476020000	3.6754470000
H45	-7.6612460000	-1.7322550000	1.6958970000

Isomer 9D

C1	-0.2427300000	-3.2747540000	-2.7785270000
C2	0.9870410000	-4.1400810000	-2.4881970000
C3	1.2080480000	-4.3907190000	-0.9919850000
C4	-0.1150330000	-4.8703250000	-0.3869160000
C5	-1.1807790000	-3.7970620000	-0.6115810000
O6	-1.3372590000	-3.4967230000	-2.0155780000
C7	-2.5550530000	-4.1994810000	-0.0127910000
C8	-3.2377660000	-5.3394940000	-0.7765730000
C9	-3.4861290000	-3.0037450000	0.0187230000
C10	-4.0004440000	-2.4784710000	1.1384890000
O11	-0.2753880000	-2.5095860000	-3.7413740000
O12	2.1568840000	-3.5299890000	-3.0395310000
C13	2.4137530000	-5.3405860000	-0.7004600000
C14	2.8108820000	-5.2573990000	0.7820620000
C15	2.1577390000	-6.8056850000	-1.1234230000
H16	1.4617850000	-3.4203560000	-0.5394730000
C17	3.4261240000	-7.6736960000	-1.1074680000
C18	3.1511580000	-9.1045120000	-1.5858100000
C19	4.4083730000	-9.9616550000	-1.5117470000
O20	2.6947330000	-9.0694480000	-2.9363010000
H21	0.8252500000	-5.0788610000	-3.0280590000
H22	-0.4164700000	-5.8060740000	-0.8699780000
H23	-0.0085980000	-5.0637880000	0.6853030000
H24	-0.8534240000	-2.8683000000	-0.1233080000
H25	-2.3884420000	-4.5398070000	1.0182620000
H26	-4.2046400000	-5.5862520000	-0.3226180000
H27	-2.6310680000	-6.2497350000	-0.7569220000
H28	-3.4222470000	-5.0777550000	-1.8242620000
H29	-3.7427810000	-2.5526600000	-0.9395470000

H30	-4.6632420000	-1.6190850000	1.0937090000
H31	-3.7804120000	-2.8879410000	2.1195540000
H32	1.8882180000	-3.1622030000	-3.9052610000
H33	3.2729710000	-4.9678580000	-1.2734450000
H34	3.7796050000	-5.7349870000	0.9582270000
H35	2.9075990000	-4.2149420000	1.1037510000
H36	2.0745880000	-5.7464760000	1.4273790000
H37	1.4099010000	-7.2608890000	-0.4626150000
H38	1.7397540000	-6.8261110000	-2.1345510000
H39	4.1748850000	-7.2076880000	-1.7602450000
H40	3.8430880000	-7.7119530000	-0.0955840000
H41	2.3615600000	-9.5558610000	-0.9744820000
H42	4.1999770000	-10.9785470000	-1.8614300000
H43	4.7917540000	-10.0183980000	-0.4884880000
H44	5.1944960000	-9.5609480000	-2.1611370000
H45	2.5388530000	-9.9895870000	-3.2132900000

Isomer 9E

C1	-19.6404440000	2.8844420000	-0.6331080000
C2	-20.5285950000	2.5441700000	-1.8402980000
C3	-21.0833720000	3.8287770000	-2.4912890000
C4	-20.3933770000	5.0996430000	-1.9756580000
O5	-18.9717040000	4.8903170000	-1.8584790000
C6	-18.5482430000	3.8571250000	-1.0880340000
O7	-17.3705670000	3.7203700000	-0.7665770000
C8	-20.6752410000	6.3355820000	-2.8696640000
C9	-20.2873310000	7.6057000000	-2.1381690000
C10	-21.1490690000	8.5747640000	-1.8026080000
C11	-19.9372310000	6.2971900000	-4.2126430000
O12	-19.0673370000	1.6862730000	-0.1089530000
C13	-21.6137660000	1.4616910000	-1.5484070000
C14	-22.3405670000	1.0521940000	-2.8523910000
C15	-22.6039680000	1.8864750000	-0.4564450000
C16	-23.2275810000	-0.1918810000	-2.6947420000
C17	-23.7933770000	-0.6674220000	-4.0378600000
C18	-24.6275460000	-1.9307650000	-3.8690860000
O19	-24.6157650000	0.3595710000	-4.5880970000
H20	-19.8574140000	2.0860890000	-2.5845600000
H21	-20.1967810000	3.3623500000	0.1792210000
H22	-22.1618020000	3.9377750000	-2.3369190000
H23	-20.9440840000	3.7282910000	-3.5738270000
H24	-20.7774260000	5.3182950000	-0.9687780000
H25	-21.7534790000	6.3652840000	-3.0771010000
H26	-19.2361070000	7.7228320000	-1.8758510000
H27	-20.8077280000	9.4634120000	-1.2794570000
H28	-22.2062490000	8.5123140000	-2.0417570000
H29	-20.1723820000	7.1866230000	-4.8089020000
H30	-20.2297230000	5.4256450000	-4.8052550000
H31	-18.8498760000	6.2669140000	-4.0817010000
H32	-18.2177910000	1.9445530000	0.3018500000
H33	-21.0919080000	0.5688610000	-1.1784260000
H34	-22.9507140000	1.8857370000	-3.2194630000
H35	-21.5886400000	0.8455880000	-3.6246990000
H36	-23.2623960000	1.0570620000	-0.1799840000
H37	-22.0875400000	2.1878240000	0.4591970000
H38	-23.2367650000	2.7179840000	-0.7802210000
H39	-22.6466480000	-1.0003200000	-2.2353210000
H40	-24.0606020000	0.0454360000	-2.0230190000
H41	-22.9751740000	-0.8586180000	-4.7413290000

H42	-25.0308440000	-2.2552440000	-4.8344110000
H43	-24.0323940000	-2.7473650000	-3.4493140000
H44	-25.4871480000	-1.7483970000	-3.2147980000
H45	-24.9541680000	0.0328520000	-5.4403780000

Isomer 9F

C1	-17.7726120000	-0.2871600000	-1.4804190000
C2	-18.2824360000	0.0653620000	-0.0728020000
C3	-17.3886810000	1.1530310000	0.5476320000
C4	-16.6116980000	1.9519170000	-0.5149700000
O5	-17.3872590000	2.1086990000	-1.7241760000
C6	-17.8593310000	0.9861310000	-2.3257000000
O7	-18.3256990000	0.9899950000	-3.4613560000
C8	-16.1512680000	3.3392210000	0.0034340000
C9	-15.0822990000	3.9081840000	-0.9084750000
C10	-13.8271080000	4.1735370000	-0.5234130000
C11	-17.2946220000	4.3545540000	0.1131830000
O12	-18.5427060000	-1.3593180000	-2.0274570000
C13	-18.5333750000	-1.1665620000	0.8401090000
C14	-17.2755180000	-2.0351450000	1.0476780000
C15	-19.1381650000	-0.7563430000	2.1892670000
C16	-17.5691070000	-3.5063790000	1.3775470000
C17	-18.3710630000	-4.2614710000	0.3056530000
C18	-18.3628670000	-5.7611760000	0.5741750000
O19	-17.8154260000	-4.0430580000	-0.9887310000
H20	-19.2744140000	0.5248040000	-0.2129350000
H21	-16.7278270000	-0.6134860000	-1.4839910000
H22	-16.6639600000	0.7270580000	1.2510610000
H23	-18.0302870000	1.8135150000	1.1414960000
H24	-15.7131200000	1.3774870000	-0.7831540000
H25	-15.7220540000	3.2017830000	1.0051340000
H26	-15.3690980000	4.1091160000	-1.9404810000
H27	-13.1067500000	4.5832840000	-1.2256770000
H28	-13.4874500000	3.9966150000	0.4924900000
H29	-16.9263230000	5.3107370000	0.5029440000
H30	-18.0755670000	4.0065400000	0.7953890000
H31	-17.7604920000	4.5530630000	-0.8584650000
H32	-18.6135200000	-1.1745620000	-2.9880130000
H33	-19.3024160000	-1.7611970000	0.3357790000
H34	-16.6350520000	-2.0192730000	0.1611210000
H35	-16.6646210000	-1.6144180000	1.8564060000
H36	-19.4466190000	-1.6370200000	2.7617980000
H37	-20.0260350000	-0.1321380000	2.0426240000
H38	-18.4252490000	-0.1937860000	2.8005150000
H39	-16.5964890000	-4.0001930000	1.5044530000
H40	-18.0839960000	-3.5828180000	2.3422140000
H41	-19.4130120000	-3.9248070000	0.2905090000
H42	-18.9389380000	-6.2884740000	-0.1940190000
H43	-18.7931920000	-5.9925340000	1.5532590000
H44	-17.3444860000	-6.1630810000	0.5322980000
H45	-18.1365700000	-3.1702160000	-1.3003440000

2.3.3. DP4f probablity analysis of the C34-C46 region

For the conformers found <10 kJmol^{-1} of the global minima generated from the previously described conformational search, Jaguar (version 7.9) was used to calculate both the carbon and proton GIAO shielding constants at the B3LYP/6-31G(d,p) level. Data for the hydroxyl protons was omitted, as was the data for the protons at C34 due to the significant differences in chemical environment compared to the natural product. The shielding constants for the methyl groups were averaged.

	Predicted ^{13}C NMR shifts (ppm)					
Atom #	9A	9B	9C	9D	9E	9F
C41	173.6	174.1	173	173.3	174	174.3
C40	69.5	69.1	70.6	70.8	66.8	68.6
C39	41.4	42.4	46.9	45.7	44	43.2
C38	29.4	29	28.5	29.5	35.5	28.2
C37	78.1	78.7	84.9	84.9	78.4	77.5
C36	47.4	47	47	47.3	48.7	46.7
C36-Me	18.4	18.1	18.2	18.1	19.5	17.5
C35	135.6	135.1	134.9	135.3	135.3	134.9
C42	37.3	34.6	30.4	34.5	38.4	30
C42-Me	16.4	20	19.2	20	20.1	19.7
C43	31.4	30.7	25.7	30.9	27.3	26.3
C44	36.2	36.9	35.5	37	37.6	35.7
C45	66.5	70.1	63.1	70.4	64	62.4
C46	23.9	24.8	23.5	24.7	27.6	23.7

Table S13. Predicted ^{13}C NMR chemical shifts for isomers **9A-F**. Favoured isomer is highlighted in yellow.

		$\Delta\delta_C$(Predicted – Experimental) ppm					
Atom #	Experimental shift data for hemicalide[1]	9A	9B	9C	9D	9E	9F
C41	178.4	−4.8	−4.3	−5.4	−5.1	−4.4	−4.1
C40	68.2	1.3	0.9	2.4	2.6	−1.4	0.4
C39	41.4	0	1	5.5	4.3	2.6	1.8
C38	26.7	2.7	2.3	1.8	2.8	8.8	1.5
C37	80.9	−2.8	−2.2	4	4	−2.5	−3.4
C36	43.6	3.8	3.4	3.4	3.7	5.1	3.1
C36-Me	17.2	1.2	0.9	1	0.9	2.3	0.3
C35	132.5	3.1	2.6	2.4	2.8	2.8	2.4
C42	40.6	−3.3	−6	−10.2	−6.1	−2.2	−10.6
C42-Me	13.4	3	6.6	5.8	6.6	6.7	6.3
C43	32.1	−0.7	−1.4	−6.4	−1.2	−4.8	−5.8
C44	38	−1.8	−1.1	−2.5	−1	−0.4	−2.3
C45	68.7	−2.2	1.4	−5.6	1.7	−4.7	−6.3
C46	23.1	0.8	1.7	0.4	1.6	4.5	0.6

Table S14. The ^{13}C NMR $\Delta\delta_{(\text{Predicted – Experimental})}$ values for isomer **9A-F**. Favoured isomer is highlighted in yellow.

	Predicted ^{1}H NMR shifts (ppm)					
Atom #	9A	9B	9C	9D	9E	9F
H39	2.06	2.02	1.82	1.93	2.21	1.8
H40	4.2	4.32	4.12	4.07	4.27	4.4
H38A	1.69	1.57	1.43	1.38	1.83	1.63
H38B	1.73	1.83	1.79	1.78	1.98	1.73
H37	3.94	3.98	3.97	4.05	3.74	4.07
H36	2.46	2.53	2.55	2.52	2.4	2.5
H36-Me	6.09	6.1	1.16	1.17	5.86	6.2
H35	1.32	1.18	6.09	6.15	1.15	1.04
H42	1.14	2.56	2.37	2.56	1.92	1.01
H42-Me	1.55	1.53	0.88	0.89	1.23	1.96
H43A	1.51	1.2	0.8	1.08	1.81	0.89
H43B	0.89	0.88	2.03	1.51	1.15	0.87
H44A	1.25	1.4	1.41	1.32	1.84	1.31
H44B	1.55	1.36	1.34	1.4	0.96	1.38
H45	3.92	3.75	3.96	3.75	3.86	4.03
H46	1.02	1.06	1.07	1.05	1.04	1.05

Table S15. Predicted ^{1}H NMR chemical shifts for isomers **9A-F**. Favoured isomer is highlighted in yellow.

		$\Delta\delta_H$(Predicted – Experimental) ppm					
Atom #	Experimental shift data for hemicalide[1]	9A	9B	9C	9D	9E	9F
H39	1.62	0.44	0.4	0.2	0.31	0.59	0.18
H40	4.32	−0.12	0	−0.2	−0.25	−0.05	0.08
H38A	1.62	0.07	−0.05	−0.19	−0.24	0.21	0.01
H38B	1.62	0.11	0.21	0.17	0.16	0.36	0.11
H37	4.11	−0.17	−0.13	−0.14	−0.06	−0.37	−0.04
H36	2.34	0.12	0.19	0.21	0.18	0.06	0.16
H36-Me	1.11	0.21	0.07	0.05	0.06	0.04	−0.07
H35	5.34	0.75	0.76	0.75	0.81	0.52	0.86
H42	1.62	−0.48	0.94	0.75	0.94	0.3	−0.61
H42-Me	0.91	−0.02	−0.03	−0.03	−0.02	0.24	−0.04
H43A	1.62	−0.11	−0.42	−0.82	−0.54	0.19	−0.73
H43B	1.62	−0.07	−0.09	0.41	−0.11	−0.39	0.34
H44A	1.62	−0.37	−0.22	−0.21	−0.3	0.22	−0.31
H44B	1.62	−0.07	−0.26	−0.28	−0.22	−0.66	−0.24
H45	3.7	0.22	0.05	0.26	0.05	0.16	0.33
H46	1.15	−0.13	−0.09	−0.08	−0.1	−0.11	−0.1

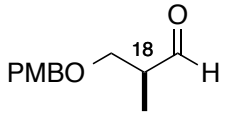
Table S16. The ^{1}H NMR $\Delta\delta_{(\text{Predicted – Experimental})}$ values for isomer **9A-F**. Favoured isomer is highlighted in yellow.

Isomer	Configuration	DP4 probability (%)		
		^{1}H and ^{13}C NMR	^{13}C NMR	^{1}H NMR
9A	36(*R*), 37(*R*), 39 (*R*), 40(*R*), 42(*S*), 45(*S*)	99.9	98.5	26.3
9B	36(*R*), 37(*R*), 39 (*R*), 40(*R*), 42(*R*), 45(*R*)	0.0	0.0	72.0
9C	36(*R*), 37(*R*), 39 (*S*), 40(*S*), 42(*S*), 45(*R*)	0.0	0.0	0.4
9D	36(*R*), 37(*R*), 39 (*S*), 40(*S*), 42(*S*), 45(*S*)	0.1	1.4	0.9
9E	36(*R*), 37(*R*), 39 (*R*), 40(*R*), 42(*S*), 45(*R*)	0.0	0.0	0.2
9F	36(*R*), 37(*R*), 39 (*R*), 40(*R*), 42(*R*), 45(*S*)	0.0	0.0	0.1

Table S17. DP4f NMR stereochemical prediction for the C34-C46 region. For the combined ^{1}H and ^{13}C NMR shift analysis, the highest probability isomer **9A** is highlighted in yellow; NB isomer **9B** (corresponding to its epimer at C43 and C45) appears to be equally probable to **9A** based on consideration of the ^{1}H NMR shift comparison alone. Therefore, it is not possible to make a confident assignment of the stereochemistry at C45.

3. Experimental Details

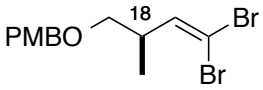
Aldehyde 16



Dry DMSO (6.10 mL, 91.5 mmol) was added to a stirred solution of $(COCl)_2$ (3.80 mL, 43.9 mmol) in CH_2Cl_2 (120 mL) at −78 °C. The solution was stirred at −78 °C for 20 min before adding a solution of (*R*)-3-((4-methoxybenzyl)oxy)-2-methylpropan-1-ol[15] (7.70 g, 36.6 mmol) in CH_2Cl_2 (30 mL) *via* cannula. The reaction mixture was stirred at −78 °C for 15 min, then NEt_3 (25.5 mL, 183.1 mmol) was added dropwise. The reaction was then monitored by TLC, quenched with NH_4Cl (50 mL) after 30 min and warmed to rt. The layers were separated and the organic phase washed with brine (3 x 50 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give aldehyde **16** as a yellow oil which was used immediately without further purification.

R_f: 0.66 (5% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ +25.5 (*c* 2.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 9.71 (1H, d, *J* = 1.6 Hz, C*H*O), 7.24 (2H, d, *J* = 8.9 Hz, Ar*H*), 6.88 (2H, d, *J* = 8.9 Hz, Ar*H*), 4.45 (2H, app s, OC*H*$_2$Ar), 3.80 (3H, s, ArO*Me*), 3.65 (1H, dd, *J* = 9.4 Hz, 6.7 Hz, H-19$_a$), 3.60 (1H, dd, *J* = 9.4 Hz, 5.1 Hz, H-19$_b$), 2.68-2.61 (1H, m, H-18), 1.12 (3H, d, *J* = 7.3 Hz, Me-18); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 204.1, 159.4, 130.1, 129.4, 113.9, 73.1, 69.9, 55.4, 46.9, 10.8. Data is in agreement with literature values reported by Kalesse.[16]

Vinyl dibromide 16a

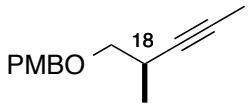


To a solution of CBr_4 (28.7 g, 86.4 mmol) in CH_2Cl_2 (200 mL) at 0 °C was added PPh_3 (45.0 g, 172.8 mmol) portionwise. The resulting orange solution was stirred for 5 min then cooled to −78 °C. A solution of aldehyde **16** (9.10 g, 43.2 mmol) in CH_2Cl_2 (80 mL) was added *via* cannula. The mixture was stirred at −78 °C for 30 min and then warmed to 0 °C. After 50 min, the reaction mixture was quenched with NH_4Cl solution (100 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 x 100 mL). The organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale brown solid. The residue was purified by flash column chromatography (5% → 10% EtOAc-Pet. Ether) to give vinyl dibromide **16a** as a pale yellow oil (10.0 g, 64.8 mmol, 75%).

[15] Mickel, S. J. *et al. Org. Proc. Res. Dev.*, **2004**, *8*, 92.
[16] Janssen, D.; Albert, D.; Jansen, R.; Müller, R.; Kalesse, M. *Angew. Chem. Int. Ed*. **2007**, *46*, 4898.

R_f: 0.52 (20% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ −24.0 (*c* 1.5, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.26 (2H, d, *J* = 8.8 Hz, Ar*H*), 6.89 (2H, d, *J* = 8.8 Hz, Ar*H*), 6.30 (1H, d, *J* = 8.8 Hz, H-17), 4.46 (1H, d, *J* = 11.5 Hz, OC$H_a$$H_b$Ar), 4.43 (1H, d, *J* = 11.5 Hz, PMBOCH$_a$$H_b$Ar), 3.81 (3H, s, ArO*Me*), 3.37 (1H, dd, *J* = 6.4 Hz, 4.9 Hz, H-19a), 3.33 (1H, dd, *J* = 6.1 Hz, 4.8 Hz, H-19b), 2.82-2.72 (1H, m, H-18), 1.05 (3H, d, *J* = 6.8 Hz, Me-18); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 159.3, 141.4, 130.4, 129.3, 113.9, 88.9, 72.9, 72.8, 55.4, 38.7, 16.0. Data is in agreement with literature values reported by Smith.[17]

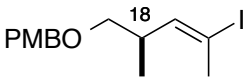
Alkyne 15



To a solution of **16a** (18.0 g, 27.5 mmol) in THF (300 mL) at −78 °C was added ^{n}BuLi (65.0 mL, 103.5 mmol, 1.6 M in hexanes) dropwise. The resulting brown solution was stirred at −78 °C for 1 h before adding MeI (12.0 mL, 197 mmol). The reaction mixture was stirred at −78 °C for 1h then warmed to 0 °C. After a further 30 min, the reaction was quenched with NH_4Cl solution (100 mL). The layers were separated and the aqueous layer extracted with Et_2O (2 x 300 mL). The combined organic phases were washed with brine (100 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% EtOAc-Pet. Ether) to give alkyne **15** as a yellow oil (9.78 g, 25.9 mmol, 94%).

R_f: 0.56 (20% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ **+**25.1 (*c* 2.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 7.28 (2H, d, *J* = 8.2 Hz, Ar*H*), 6.88 (2H, d, *J* = 8.2 Hz, Ar*H*), 4.51 (1H, d, *J* = 11.8 Hz, OC$H_a$$H_b$Ar), 4.47 (1H, d, *J* = 11.8 Hz, OCH$_a$$H_b$Ar), 3.81 (3H, s, ArO*Me*), 3.46 (1H, dd, *J* = 9.0, 6.1 Hz, H-19$_a$), 3.30 (1H, dd, *J* = 9.0, 7.5 Hz, H-19$_b$), 2.73-2.63 (1H, m, H-18), 1.80 (3H, d, *J* = 2.3 Hz, Me-16) and 1.16 (3H, d, *J* = 6.8 Hz, Me-18); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 159.1, 130.4, 129.1, 113.6, 81.1, 76.2, 74.0, 72.5, 55.0, 26.6, 18.0, 3.3. Data in agreement with literature values reported by Smith.[16]

Vinyl iodide 15a



Note: The following reaction was carried out in darkness due to the light sensitivity of Cp_2ZrHCl.

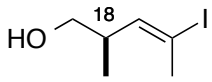
To a stirred suspension of Cp_2ZrCl_2 (19.7 g, 67.5 mmol) in THF (100 mL) at 0 °C was added DIBAL (67.5 mL, 67.5 mmol, 1 M solution in hexane) dropwise. The resulting white suspension was stirred for 30 min before adding a solution of **15** (7.40 g, 33.7 mmol) *via* cannula in THF (80 mL + 2 x 10 mL

[17] Smith III, A. B.; Lee, D. *J. Am. Chem. Soc*. **2007**, *129*, 10957.

wash). The reaction mixture was warmed to rt and stirred for 16 h before cooling to −78 °C. A solution of I_2 (25.7 g, 101 mmol) in THF (100 mL) was added *via* cannula. After 10 min, the reaction was quenched with 1 M HCl (30 mL) and warmed to rt. The mixture was diluted with Et_2O (200 mL) and the layers separated. The aqueous layer was extracted with Et_2O (3 x 200 mL) and the combined organic phases washed with $Na_2S_2O_3$ solution (150 mL), brine (150 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (5% EtOAc-Pet. Ether) to give vinyl iodide **15a** as a yellow oil (10.2 g, 59.4 mmol, 88%).

R_f: 0.37 (5% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ **+**34.0 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.25 (2H, d, *J* = 8.6 Hz, Ar*H*), 6.89 (2H, d, *J* = 8.6 Hz, Ar*H*), 5.99 (1H, dq, *J* = 9.7 Hz, 1.3 Hz, H-17), 4.32 (2H, app s, OC*H*$_2$Ar), 3.81 (3H, s, ArO*Me*), 3.29 (2H, dd, *J* = 6.7, 2.8 Hz, H-19), 2.74-2.65 (1H, m, H-18), 2.38 (3H, d, *J* = 1.3 Hz, Me-16), 0.97 (3H, d, *J* = 6.8 Hz, Me-18); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 159.3, 144.0, 136.6, 129.2, 113.9, 94.6, 74.0, 72.8, 55.4, 36.2, 28.0, 17.0. Data is in agreement with literature values reported by Smith.[16]

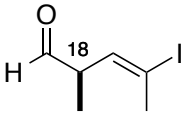
Alcohol 15b



To a stirred emulsion of **15a** (1.52 g, 4.40 mmol) in CH_2Cl_2 (150 mL) and pH 7 buffer solution (5 mL) at 0 °C was added DDQ (1.50 g, 6.59 mmol). After 45 min, the reaction was quenched with $NaHCO_3$ solution (50 mL) and the layers separated. The organic phase was washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% → 30% Et_2O-30/40 Pet. Ether) to give alcohol **15b** as a yellow oil (890 mg, 3.96 mmol, 90%).

R_f: 0.40 (40% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ **+**30.0 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 5.98 (1H, dq, *J* = 9.7, 1.5 Hz, H-17), 2.72-2.60 (1H, m, H-18), 2.43 (3H, d, *J* = 1.5 Hz, Me-16), 0.98 (3H, d, *J* = 6.8 Hz, Me-18); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 114.4, 95.4, 66.9, 38.5, 28.1, 16.4. Data is in agreement with literature values reported by Meiries.[18]

Aldehyde 14

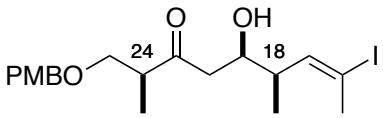


[18] Meiries, S.; Bartoli, A.; Decostanzi, M.; Parrain, J.-L.; Commeiras, L. *Org. Biomol. Chem*. **2013**, *11*, 4882.

To a stirred suspension of alcohol **15b** (730 mg, 3.23 mmol) and $NaHCO_3$ (1.63 g, 19.4 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added Dess-Martin periodinane (4.11 g, 9.69 mmol). After 1 h, the reaction mixture was cooled to 0 °C and quenched with $Na_2S_2O_3$ (15 mL) and $NaHCO_3$ solutions (10 mL). The layers were separated after settling for 1 h and the aqueous layer extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo* **CAREFULLY** (300 Torr, rt water bath). The residue was filtered through a plug of silica to give aldehyde **14** as a volatile yellow oil (575 mg, 2.57 mmol, 80%) which was immediately used in the subsequent aldol reaction.

R_f: 0.57 (20% EtOAc-Pet. Ether); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 9.51 (1H, d, *J* = 1.6 Hz, H-19), 6.06 (1H, dq, *J* = 9.5, 1.6 Hz, H-17), 3.30-3.23 (1H, m, H-18), 2.45 (3H, d, *J* = 1.5 Hz, Me-16), 1.21 (3H, d, *J* = 7.0 Hz, Me-18); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 199.4, 136.6, 98.1, 48.8, 25.4, 13.7. Data is in agreement with literature values reported by Meiries.[17]

Aldol adduct 17



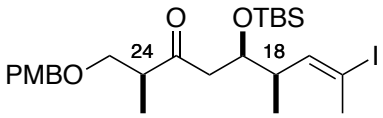
To a stirred solution of (+)-α-pinene (1.11 mL, 7.02 mmol) in Et_2O (1.88 mL) at –10 °C was added BH_3•SMe_2 (0.35 mL, 3.34 mmol). The mixture was stirred at 10 °C for 16 h to give a *ca.* 1.0 M solution of (–)-Ipc_2BCl.

A solution of ketone **13** (642 mg, 3.08 mmol) in Et_2O (5 mL + 5 mL wash) was added *via* cannula to a stirred solution of (–)-Ipc_2BCl (2.83 mL, 2.83 mmol, 1.0 M in Et_2O) and NEt_3 (0.57 mL, 4.11 mmol) at 0 °C. The resulting yellow suspension was stirred for 1 h at 0 °C then cooled to −78 °C. A solution of aldehyde **14** (575 mg, 2.57 mmol) in Et_2O (5 mL) was dried over activated 4 Å molecular sieves and added to the reaction mixture *via* cannula (3 mL wash). After 3 h, the reaction mixture was transferred to a freezer at −20 °C and left for a further 16 h. The reaction was then quenched with MeOH/pH 7 buffer solution (1:1, 10 mL) and H_2O_2 (30% aq., 5 mL). The mixture was warmed to rt, stirred for 1 h and the layers separated. The aqueous layer was extracted with EtOAc (5 x 10 mL) and the combined organic phases washed with water (5 mL), brine (5 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (20% → 50% EtOAc-Pet. Ether) to give aldol adduct **17** as a colourless oil (807 mg, 1.80 mmol, 70%) as a single diastereomer. The expected 1,4-*syn* relationship was confirmed by Mosher ester configurational analysis of the C19 alcohol stereocentre.

R_f: 0.13 (20% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ +46.6 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.21 (2H, d, *J* = 8.8 Hz, Ar*H*), 6.88 (2H, d, *J* = 8.7 Hz, Ar*H*), 5.96 (1H, dq, *J* = 10.2, 1.6 Hz, H-17), 4.43 (1H, d, *J*

= 11.8 Hz, OCH_aH$_b$Ar), 4.40 (1H, d, *J* = 11.6 Hz, OCH$_a$$H_b$Ar), 3.84-3.78 (1H, m, H-19), 3.83 (3H, s, ArO*Me*), 3.57 (1H, dd, *J* = 9.0, 8.4 Hz, H-25$_a$), 3.45 (1H, dd, *J* = 9.0, 5.0 Hz, H-25$_b$), 3.15 (1H, d, *J* = 4.1 Hz, O*H*), 2.92-2.85 (1H, m, H-24), 2.72 (1H, dd, *J* = 17.4, 2.5 Hz, H-20$_a$), 2.49 (1H, dd, *J* = 17.5, 9.5 Hz, H-20$_b$), 2.46 (1H, dd, *J* = 10.1, 7.2 Hz, H-18), 2.38 (3H, d, *J* = 1.6 Hz, Me-16), 1.05 (3H, d, *J* = 7.1 Hz, Me-24), 1.02 (3H, d, *J* = 6.8 Hz, Me-18); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 214.7, 159.4, 143.2, 129.9, 129.5, 114.0, 94.8, 73.2, 72.0, 70.9, 55.4, 46.9, 46.7, 41.1, 28.2, 16.2, 13.3; **IR** (thin film): 3485 (br), 2933, 1707, 1613, 1514, 1462, 1376, 1203, 1248, 1174, 1091, 1034, 821 cm^{-1}; **HRMS** (ES$^+$) Calc. for $C_{19}H_{27}IO_4$ $[M+NH_4]^+$ 464.1292, found 464.1282.

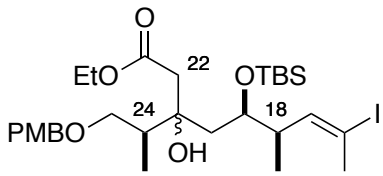
TBS ether 17a



To a stirred solution of **17** (980 mg, 2.20 mmol) in CH_2Cl_2 (20 mL) at −78 °C was added 2,6-lutidine (0.38 mL, 3.29 mmol) and TBSOTf (0.61 mL, 2.64 mmol). After 30 min the reaction was quenched with MeOH (5 mL) and $NaHCO_3$ solution (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL) and the organics dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (5-20% EtOAc-Pet. Ether) to give TBS ether **17a** as a colourless oil (1.18 g, 2.10 mmol, 95%).

R$_f$: 0.17 (5% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ +52.3 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.21 (2H, d, *J* = 8.6 Hz, Ar*H*), 6.87 (2H, d, *J* = 8.6 Hz, Ar*H*), 6.03 (1H, dq, *J* = 9.8, 1.4 Hz, H-17), 4.43 (1H, d, *J* = 11.6 Hz, OCH_aH$_b$Ar), 4.39 (1H, d, *J* = 11.7 Hz, OCH$_a$$H_b$Ar), 4.13 (1H, td, *J* = 6.0, 4.0 Hz, H-19), 3.80 (3H, s, ArO*Me*), 3.57 (1H, dd, *J* = 9.0, 7.7 Hz, H-25$_a$), 3.44 (1H, dd, *J* = 9.1, 5.4 Hz, H-25$_b$), 2.80 (1H, qnd, *J* = 7.2, 5.4 Hz, H-24), 2.67 (1H, dd, *J* = 17.7, 6.2 Hz, H-20$_a$), 2.60 (1H, dd, *J* = 17.7, 5.7 Hz, H-20$_b$), 2.53-2.46 (1H, m, H-18), 2.39 (3H, d, *J* = 1.4 Hz, Me-16), 1.05 (3H, d, *J* = 7.0 Hz, Me-24), 0.90 (3H, d, *J* = 6.8 Hz, Me-18), 0.86 (9H, s, OSi^t*Bu*Me$_2$), 0.07 (3H, s, OSi^{t}Bu*Me$_a$*Me$_b$), –0.02 (3H, s, OSi^{t}BuMe$_a$*Me$_b$*); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 211.2, 159.3, 144.7, 130.2, 129.4, 113.9, 94.3, 73.1, 72.0, 70.7, 55.4, 47.8, 47.2, 40.8, 28.1, 26.2, 18.2, 14.2, 13.3, –4.4, –4.7; **IR** (thin film): 2933, 2856, 1714, 1613, 1514, 1462, 1376, 1302, 1249, 1173, 1097, 1037, 836, 777 cm^{-1}; **HRMS** (ES$^+$) Calc. for $C_{25}H_{41}IO_4Si$ $[M+NH_4]^+$ 578.2157, found 578.2143.

Ester 19

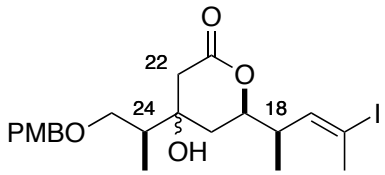


To a stirred solution of $^{i}Pr_2NH$ (3.00 mL, 21.4 mmol) in THF (4 mL) at 0 °C was added ^{n}BuLi (11.7 mL, 18.7 mmol, 1.6 M in hexane). The resulting pale yellow solution was stirred at 0 °C for 15 min then cooled to −78 °C. Ethyl acetate (1.74 mL, 17.8 mmol) was added dropwise. The reaction mixture was stirred at −78 °C for 1 h to give a *ca.* 0.90 M solution of the derived lithium enolate.

A solution of **17a** (1.00 g, 1.78 mmol) in THF (10 mL) was cooled to −78 °C before adding the above lithium enolate solution (9.89 mL, 8.90 mmol, 0.9 M in THF). The reaction was quenched after 1.5 h with $NaHCO_3$ solution (10 mL) and warmed to rt. The mixture was diluted with Et_2O (20 mL) and the aqueous layer extracted with Et_2O (3 x 20 mL). The organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% EtOAc-Pet. Ether) to give ester **19** as a colourless oil (1.12 g, 1.72 mmol, 97%) as a mixture of diastereomers (5:1 dr).

Major isomer: $\mathbf{R_f}$: 0.16 (5% EtOAc-Pet. Ether); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.24 (2H, d, *J* = 8.7 Hz, Ar*H*), 6.88 (2H, d, *J* = 8.8 Hz, Ar*H*), 6.18 (1H, dq, *J* = 9.5, 1.5 Hz, H-17), 4.44 (1H, d, *J* = 11.6 Hz, OCH_aH$_b$Ar), 4.40 (1H, d, *J* = 11.5 Hz, OCH$_a$$H_b$Ar), 4.12 (2H, q, *J* = 7.3 Hz, OCH_2CH$_3$), 3.99-3.95 (1H, m, H-19), 3.97 (1H, s, O*H*), 3.81 (3H, s, ArO*Me*), 3.60 (1H, dd, *J* = 9.2, 5.0 Hz, H-25$_a$), 3.39 (1H, dd, *J* = 9.3, 6.4 Hz, H-25$_b$), 2.74–2.66 (1H, m, H-24), 2.58 (1H, d, *J* = 15.3 Hz, H-22$_a$), 2.53 (1H, d, *J* = 15.3 Hz, H-22$_b$), 2.38 (3H, d, *J* = 1.4 Hz, Me-16), 2.12-2.03 (1H, m, H-18), 1.79 (1H, dd, *J* = 15.0, 5.8 Hz, H-20$_a$), 1.68 (1H, dd, *J* = 14.9, 5.9 Hz, H-20$_b$), 1.24 (3H, t, *J* = 7.1 Hz, OCH$_2$*CH$_3$*) 1.00 (3H, d, *J* = 7.0 Hz, Me-24), 0.93 (3H, d, *J* = 7.0 Hz, Me-18), 0.89 (9H, s, OSi^{t}*Bu*Me$_2$), 0.08 (3H, s, OSi^{t}Bu*Me$_a$*Me$_b$), 0.07 (3H, s, OSi^{t}BuMe$_a$*Me$_b$*); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 172.3, 159.2, 144.7, 130.4, 129.3, 113.8, 93.8, 74.3, 73.0, 72.1, 72.0, 60.6, 55.3, 42.1, 41.1, 40.8, 39.3, 28.1, 26.0, 18.1, 14.2, 14.1, 12.9, –4.1, –4.3; **HRMS** (ES^{+}) Calc. for $C_{29}H_{49}IO_6Si$ $[M+H]^{+}$ 649.2416, found 649.2407.

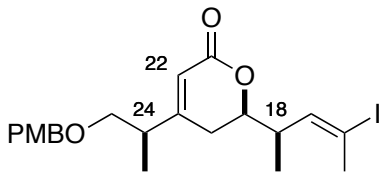
Lactone 19a



A solution of **19** (1.12 g, 1.72 mmol) in THF (5 mL) was cooled to 0 °C before slowly adding HF•pyr (1.5 mL). The reaction mixture was allowed to warm to rt and stirred for 3 h. The reaction mixture was transferred to ice-cold $NaHCO_3$ solution (20 mL) portionwise and stirred until effervescence ceased. The layers were separated and the aqueous layer extracted with EtOAc (3 x 30 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (30% → 50% EtOAc-Pet. Ether) to give lactone **19a** as a colourless oil (713 mg, 1.46 mmol, 85%) as a mixture of diastereomers (5:1 dr).

Major isomer: **R_f**: 0.32 (40% EtOAc-Pet. Ether); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.23 (2H, d, *J* = 8.7 Hz, Ar*H*), 6.90 (2H, d, *J* = 8.7 Hz, Ar*H*), 5.98 (1H, dq, *J* = 10.0, 1.5 Hz, H-17), 4.48 (1H, d, *J* = 11.5 Hz, OCH_aCH_bAr), 4.41 (1H, d, *J* = 11.5 Hz, OCH_aCH_bAr), 3.88 (1H, ddd, *J* = 11.4, 7.2, 4.5 Hz, H-19), 3.87 (1H, s, O*H*), 3.82 (3H, s, ArO*Me*), 3.70 (1H, dd, *J* = 9.6, 3.4 Hz, H-25$_a$), 3.44 (1H, dd, *J* = 9.8, 5.1 Hz, H-25$_b$), 2.75-2.65 (1H, m, H-18), 2.58 (2H, app s, H-22), 2.38 (3H, d, *J* = 1.6 Hz, Me-16), 2.00 (1H, dd, *J* = 14.6, 4.5 Hz, H-20$_a$), 1.85-1.77 (1H, m, H-24), 1.68 (1H, dd, *J* = 14.5, 11.1 Hz, H-20$_b$), 1.09 (3H, d, *J* = 6.7 Hz, Me-18), 1.04 (3H, d, *J* = 7.0 Hz, Me-24); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 171.4, 159.7, 141.2, 129.7, 129.1, 114.1, 96.0, 79.1, 73.6, 73.5, 72.1, 55.4, 42.6, 40.9, 40.4, 37.3, 28.3, 16.1, 12.7; **HRMS** (ES^+) Calc. for $C_{21}H_{29}IO_5$ $[M+NH_4]^+$ 506.1398, found 506.1386.

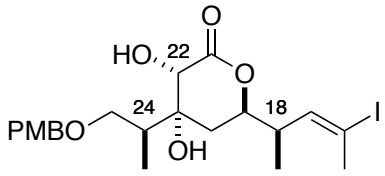
Lactone 18



To a stirred solution of **19** (480 mg, 0.983 mmol) in Ac_2O/pyr/PhH (1:5:5, 11 mL) was added DMAP (100 mg, 0.983 mmol). The reaction mixture was heated to reflux for 16 h then cooled to rt, diluted with CH_2Cl_2 (3 mL) and carefully quenched with $NaHCO_3$ solution (3 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (30% → 50% EtOAc-Pet. Ether) to give lactone **18** as a pale yellow oil (384 mg, 0.816 mmol, 83%).

R_f: 0.15 (20% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ +82.5 (*c* 0.67, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.22 (2H, d, *J* = 8.7 Hz, Ar*H*), 6.89 (2H, d, *J* = 8.7 Hz, Ar*H*), 5.97 (1H, dq, *J* = 10.1, 1.4 Hz, H-17), 5.82 (1H, br s, H-22), 4.44 (1H, d, *J* = 11.6 Hz, OCH_aH$_b$Ar), 4.39 (1H, d, *J* = 11.6 Hz, OCH_aCH_bAr), 4.06 (1H, ddd, *J* = 11.0, 6.8, 4.4 Hz, H-19), 3.81 (3H, s, ArO*Me*), 3.45 (1H, dd, *J* = 9.4, 5.6 Hz, H-25$_a$), 3.41 (1H, dd, *J* = 9.4, 7.6 Hz, H-25$_b$), 2.76-2.66 (1H, m, H-18), 2.66-2.54 (1H, m, H-24), 2.40 (3H, d, *J* = 1.6 Hz, Me-16), 2.26 (1H, dd, *J* = 17.6, 4.6 Hz, H-20$_a$), 2.19 (1H, dd, *J* = 17.6, 11.4, 1.4 Hz, H-20$_b$), 1.10 (3H, d, *J* = 7.0 Hz, Me-24), 1.09 (3H, d, *J* = 7.0 Hz, Me-18); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 165.2, 163.2, 159.5, 141.2, 130.0, 129.5, 115.7, 114.1, 96.0, 80.0, 73.1, 72.6, 55.5, 40.4, 39.9, 29.7, 28.3, 16.2, 15.7; **IR** (thin film): 2964, 2932, 2870, 1715, 1637, 1612, 1586, 1513, 1457, 1380, 1359, 1302, 1248, 1208, 1173, 1091, 1034, 868, 820, 733, 666 cm^{-1}; **HRMS** (ES^+) Calc. for $C_{21}H_{27}IO_4$ $[M+NH_4]^+$ 488.1292, found 488.1283.

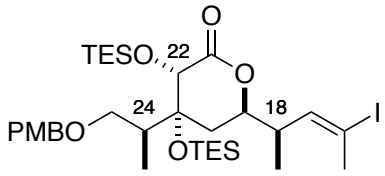
Dihydroxylactone 20



To a stirred solution of **18** (160 mg, 0.340 mmol) in THF/^{t}BuOH/H_2O (1:1:1, 0.6 mL) was added citric acid (130 mg, 0.680 mmol), K_2OsO_4•$2H_2O$ (2.5 mg, 6.8 μmol) and NMO (50 wt% in H_2O, 49 μL, 0.238 mmol). The reaction mixture was stirred for 5 h then quenched with Na_2SO_3 solution (0.5 mL) and $NaHCO_3$ solution (0.5 mL). The layers were separated and the aqueous layer extracted with EtOAc (3 x 3 mL). The organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% → 50% EtOAc-Pet. Ether) to give dihydroxylactone **20** as a colourless oil (94.3 mg, 0.187 mmol, 55%, 85% brsm) as a single diastereomer. The stereochemistry was confirmed by the diagonostic nOe interaction of H-20b and H-22.

R_f: 0.43 (50% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ –9.4 (*c* 0.67, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.23 (2H, d, *J* = 8.8 Hz, Ar*H*), 6.88 (2H, d, *J* = 8.7 Hz, Ar*H*), 6.02 (1H, dq, *J* = 10.0, 1.5 Hz, H-17), 4.50 (1H, ddd, *J* = 11.5, 6.6, 3.7 Hz, H-19), 4.44 (2H, app s, OC*H*$_2$Ar), 4.19 (1H, d, *J* = 1.2 Hz, H-22), 3.92 (1H, d, J = 1.9 Hz, OH-22), 3.81 (3H, s, ArO*Me*), 3.68 (1H, dd, *J* = 9.7, 8.4 Hz, H-25$_a$), 3.57 (1H, br s, OH-21), 3.50 (1H, dd, *J* = 9.7, 4.2 Hz, H-25$_b$), 2.71-2.61 (1H, m, H-18), 2.38 (3H, d, *J* = 1.5 Hz, Me-16), 2.22–2.12 (1H, m, H-24), 1.85 (1H, dd, *J* = 14.2, 3.7 Hz, H-20$_a$), 1.76 (1H, ddd, *J* = 14.5, 11.1, 1.9 Hz, H-20$_b$), 1.06 (3H, d, *J* = 6.7 Hz, Me-18), 0.98 (3H, d, *J* = 7.1 Hz, Me-24); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 174.8, 159.5, 141.0, 129.7, 129.6, 114.1, 96.1, 80.3, 74.4, 73.3, 73.0, 71.8, 55.4, 40.3, 40.1, 33.6, 28.3, 15.9, 12.2; **IR** (thin film): 3441 (br), 2963, 2933, 2862, 1731, 1637, 1613, 1586, 1514, 1461, 1302, 1218, 1174, 1100, 1033, 821, 760, 669 cm^{-1}; **HRMS** (ES$^+$) Calc. for $C_{21}H_{29}IO_6$ $[M+NH_4]^+$ 522.1347, found 522.1339.

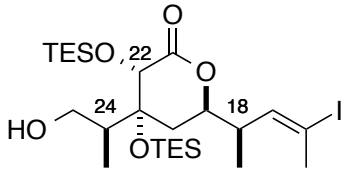
TES ether 20a



A solution of diol **20** (170 mg, 0.337 mmol) in CH_2Cl_2 (3 mL) was cooled to 0 °C and 2,6-lutidine (0.31 mL, 2.70 mmol) and TESOTf (0.38 mL, 1.69 mmol) were added sequentially. The reaction mixture was stirred at 0 °C for 24 h then quenched with $NaHCO_3$ solution (1 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (5% → 10% EtOAc-Pet. Ether) to give TES ether **20a** as a colourless oil (218 mg, 0.297 mmol, 88%).

R_f: 0.44 (10% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ +18.6 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 7.21 (2H, d, *J* = 8.6 Hz, Ar*H*), 6.89 (2H, d, *J* = 8.6 Hz, Ar*H*), 6.00 (1H, dq, *J* = 10.0, 1.3 Hz, H-17), 4.41 (1H, d, *J* = 11.6 Hz, OCH_aH$_b$Ar), 4.38 (1H, d, *J* = 11.6 Hz, OCH$_a$$H_b$Ar), 4.37-4.30 (1H, m, H-19), 4.22 (1H, s, H-22), 3.81 (3H, s, ArO*Me*), 3.32 (1H, dd, *J* = 9.5, 4.9 Hz, H-25$_a$), 3.23 (1H, dd, *J* = 9.5, 5.4 Hz, H-25$_b$), 2.69-2.59 (1H, m, H-18), 2.35 (3H, d, *J* = 1.5 Hz, Me-16), 2.36-2.28 (1H, m, H-24), 1.80 (1H, dd, *J* = 14.2, 3.5 Hz, H-20$_a$), 1.60 (1H, dd, *J* = 14.0, 11.8 Hz, H-20$_b$), 1.03 (3H, d, *J* = 6.8 Hz, Me-18), 0.99 (3H, d, *J* = 7.0 Hz, Me-24), 0.94 (9H, t, *J* = 8.0 Hz, OSiCH$_2$CH_3), 0.94 (9H, t, *J* = 8.0 Hz, OSiCH$_2$CH_3), 0.90 (12H, m, OSiCH_2CH$_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 172.7, 159.5, 141.4, 130.1, 129.7, 114.0, 96.0, 79.6, 78.8, 74.1, 73.5, 71.8, 55.4, 40.1, 37.7, 33.0, 28.3, 16.1, 11.9, 7.4, 7.2, 6.7, 5.3; **IR** (thin film): 2955, 2912, 2876, 1751, 1612, 1514, 1458, 1379, 1302, 1248, 1145, 1082, 1010, 978, 831, 731 cm^{-1}; **HRMS** (ES$^+$) Calc. for $C_{33}H_{57}IO_6Si_2$ $[M+H]^+$ 733.2811, found 733.2808.

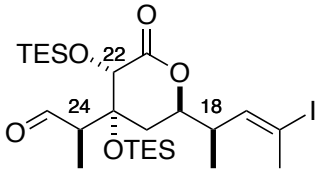
Alcohol 20b



To an emulsion of lactone **20a** (190 mg, 0.260 mmol) in CH_2Cl_2/pH 7 buffer solution (9:1, 2 mL) at 0 °C was added DDQ (118 mg, 0.520 mmol). The resulting green suspension was stirred for 2 h then quenched with $NaHCO_3$ solution (2 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were washed with brine (5 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% → 20% EtOAc-Pet. Ether) to give alcohol **20b** as a colourless oil (125 mg, 0.208 mmol, 80%).

R_f: 0.14 (10% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ +14.8 (*c* 1.0, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 6.00 (1H, dq, *J* = 9.7, 1.5 Hz, H-17), 4.36 (1H, ddd, *J* = 11.6, 6.6, 3.5 Hz, H-19), 4.29 (1H, s, H-22), 3.63-3.51 (2H, m, H-25), 2.71-2.61 (1H, m, H-18), 2.41 (3H, d, *J* = 1.5 Hz, Me-16), 2.31-2.22 (1H, m, H-24), 1.85 (1H, dd, *J* = 14.1, 3.6 Hz, H-20$_a$), 1.57 (1H, dd, *J* = 14.0, 11.8 Hz, H-20$_b$), 1.06 (3H, d, *J* = 6.8 Hz, Me-18), 1.02-0.97 (12H, m, Me-24, OSiCH$_2$CH_3), 0.92 (9H, t, *J* = 7.9 Hz, OSiCH$_2$CH_3), 0.84-0.72 (6H, m, OSiCH_2CH$_3$), 0.72-0.58 (6H, m, OSiCH_2CH$_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 172.5, 141.3, 95.9, 79.5, 79.7, 74.2, 64.6, 40.3, 39.6, 33.3, 28.4, 16.2, 11.4, 7.4, 7.3, 6.7, 5.4; **IR** (thin film): 3477 (br), 2955, 2876, 1731, 1638, 1458, 1416, 1380, 1239, 1161, 1044, 1008, 977, 832, 730 cm^{-1}; **HRMS** (ES$^+$) Calc. for $C_{25}H_{49}IO_5Si_2$ $[M+H]^+$ 613.2236, found 613.2228.

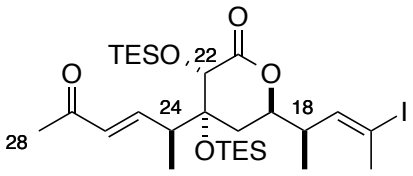
Aldehyde 21



Dess-Martin periodinane (125 mg, 294 µmol) and $NaHCO_3$ (49.4 mg, 588 µmol) were added to a stirred solution of alcohol **20b** (60.0 mg, 98.0 µmol) in CH_2Cl_2 (1 mL) at 0 °C then warmed to rt. After 1 h, the reaction was quenched with $Na_2S_2O_3$ solution (1 mL) and $NaHCO_3$ solution (1 mL) at 0 °C and stirred for 10 min at rt. The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give aldehyde **21** as a colourless oil which was used immediately without further purification.

R_f: 0.43 (10% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ +14.5 (*c* 0.4, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 9.69 (1H, d, *J* = 1.0 Hz, H-25), 5.98 (1H, dq, *J* = 9.9, 1.5 Hz, H-17), 4.44 (1H, s, H-22), 4.34 (1H, ddd, *J* = 11.3, 7.2, 4.0 Hz, H-19), 3.00 (1H, dq, *J* = 7.5, 0.9 Hz, H-24), 2.71-2.61 (1H, m, H-18), 2.40 (3H, d, *J* = 1.5 Hz, Me-16), 1.86 (1H, dd, *J* = 14.0, 4.0 Hz, H-20$_a$), 1.76 (1H, dd, *J* = 14.0, 11.5 Hz, H-20$_b$), 1.22 (3H, d, *J* = 7.6 Hz, Me-24), 1.07 (3H, d, *J* = 6.7 Hz, Me-18), 0.97 (9H, t, *J* = 7.9 Hz, $OSiCH_2C\mathit{H}_3$), 0.93 (9H, t, *J* = 7.9 Hz, $OSiCH_2C\mathit{H}_3$), 0.79-0.69 (6H, m, $OSiC\mathit{H}_2CH_3$), 0.69-0.59 (6H, m, $OSiC\mathit{H}_2CH_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 202.3, 171.6, 141.0, 96.2, 79.1, 77.7, 73.7, 50.7, 40.4, 33.9, 29.8, 28.3, 16.2, 7.3, 7.1, 6.7, 5.2; **IR** (thin film): 2953, 2877, 1755, 1722, 1457, 1379, 1240, 1147, 1010, 975, 830, 730 cm^{-1}; **HRMS** (ES^+) Calc. for $C_{25}H_{47}IO_5Si_2$ $[M+H]^+$ 611.2079, found 611.2070.

Enone 21a

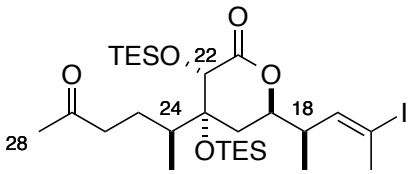


Dimethyl (2-oxopropyl)phosphonate (67.7 µL, 490 µmol) was added to a stirred suspension of oven-dried $Ba(OH)_2$ (50.3 mg, 294 µmol) in THF (0.5 mL) at rt. After 30 min, the reaction mixture was cooled to 0 °C and a solution of **21** (60.0 mg, 98.0 µmol) in THF/H_2O (40:1, 0.5 mL) added *via* cannula (0.5 mL wash). The reaction mixture was warmed to rt and after 16 h, the reaction was quenched with NH_4Cl solution (1 mL) and diluted with CH_2Cl_2 (5 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (10% → 20% EtOAc-Pet. Ether) to give the (*E*)-enone **21a** as a colourless oil (51.0 mg, 78.4 µmol, 80% over two steps).

R_f: 0.20 (10% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ –2.0 (*c* 0.20, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ_H 6.65 (1H, dd, *J* = 15.8, 8.3 Hz, H-25), 6.23 (1H, d, *J* = 15.8 Hz, H-26), 5.97 (1H, dq, *J* = 10.0, 1.4 Hz, H-17), 4.35 (1H, ddd, *J* = 11.3, 6.9, 3.4 Hz, H-19), 3.98 (1H, s, H-22), 3.02-2.93 (1H, m, H-18), 2.69-2.59

(1H, m, H-24), 2.41 (3H, d, *J* = 1.4 Hz, Me-16), 2.26 (3H, s, H-28), 1.89 (1H, dd, *J* = 13.9, 3.4 Hz, H-20_a), 1.76 (1H, dd, *J* = 13.9, 11.6 Hz, H-20_b), 1.10 (3H, d, *J* = 7.0 Hz, Me-24), 1.07 (3H, d, *J* = 6.7 Hz, Me-18), 1.00 (9H, t, *J* = 7.8 Hz, $OSiCH_2C\mathit{H_3}$), 0.93 (9H, t, *J* = 7.9 Hz, $OSiCH_2C\mathit{H_3}$), 0.83-0.74 (6H, m, $OSiC\mathit{H_2}CH_3$), 0.74-0.60 (6H, m, $OSiC\mathit{H_2}CH_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): δ_C 197.6, 171.8, 146.4, 141.0, 132.1, 96.2, 79.3, 78.8, 74.4, 41.5, 40.3, 32.6, 28.4, 28.2, 16.3, 13.4, 7.4, 7.3, 6.7, 5.6; **IR** (thin film): 2956, 2877, 1751, 1679, 1626, 1458, 1380, 1238, 1143, 1059, 1006, 978, 826, 730 cm^{-1}; **HRMS** (ES^+) Calc. for $C_{28}H_{52}IO_5Si_2$ $[M+H]^+$ 651.2392, found 651.2406.

Ketone 6

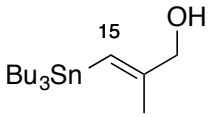


To a stirred suspension of $Cu(OAc)_2•H_2O$ (50 mg, 0.25 mmol) and PPh_3 (130 mg, 0.50 mmol) in degassed PhMe (9.3 mL) was added 1,1,3,3-tetramethyldisiloxane (0.70 mL, 3.78 mmol) at rt. The turquoise solution was stirred for 16 h at rt and the resulting blood red solution of Stryker's reagent was stored under an atmosphere of Ar at 4 °C. It was used as a *ca.* 0.025 M solution with respect to $Cu(OAc)_2•H_2O$.

To a solution of enone **21a** (45 mg, 69 μmol) in degassed PhMe (100 μL) at rt was added a solution of Stryker's reagent (2.73 mL, 1.0 eq wrt Cu, 69 μmol). The reaction mixture was stirred for 2 h and then diluted with 40-60 Pet. Ether (2 mL) and stirred vigorously with exposure to air. The resulting suspension was filtered through a plug of silica gel, eluting with 10% EtOAc-Pet. Ether. The solvent was removed *in vacuo* and the resulting residue purified by flash column chromatography (5% → 20% EtOAc-Pet. Ether) to give ketone **6** as a colourless oil (30 mg, 46 μmol, 67%).

R_f: 0.27 (10% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ +2.2 (*c* 0.50, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 5.98 (1H, dq, *J* = 10.1, 1.4 Hz, H-17), 4.34 (1H, ddd, *J* = 11.6, 7.0, 3.6 Hz, H-19), 4.22 (1H, s, H-22), 2.69-2.52 (2H, m, H-18 and H-26_a), 2.37-2.27 (1H, m, H-26_b), 2.41 (3H, d, *J* = 1.5 Hz, Me-16), 2.17 (3H, s, H-28), 2.02-1.92 (1H, m, H-24), 1.78 (1H, dd, *J* = 13.9, 3.5 Hz, H-20_a), 1.43 (1H, dd, *J* = 13.8, 11.7 Hz, H-20_b), 1.66-1.56 (1H, m, H-25_a), 1.27-1.17 (1H, m, H-25_b), 1.06 (3H, d, *J* = 6.7 Hz, Me-18), 0.98 (9H, t, *J* = 7.9 Hz, $OSiCH_2C\mathit{H_3}$), 0.91 (9H, t, *J* = 7.9 Hz, $OSiCH_2C\mathit{H_3}$), 0.90 (3H, d, *J* = 7.0 Hz, Me-24), 0.80-0.70 (6H, m, $OSiC\mathit{H_2}CH_3$), 0.68-0.58 (6H, m, $OSiC\mathit{H_2}CH_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): δ_C 208.2, 172.5, 141.2, 95.9, 79.8, 79.5, 73.2, 42.4, 40.4, 37.0, 32.1, 30.2, 28.4, 25.7, 16.3, 13.0, 7.4, 7.2, 6.8, 5.3; **IR** (thin film): 2957, 2877, 1751, 1718, 1459, 1380, 1259, 1157, 1091, 1014, 912, 829, 728 cm^{-1}; **HRMS** (ES^+) Calc. for $C_{28}H_{54}IO_5Si_2$ $[M+H]^+$ 653.2549, found 653.2542.

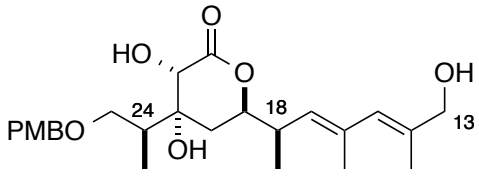
Vinyl stannane 22



Sodium hydride (60 wt% suspension in mineral oil, 101 mg, 2.53 mmol) was washed with hexane (2 × 3 mL), suspended in Et_2O (3 mL) and cooled to 0 °C. A solution of (*E*)-3-iodo-2-methylprop-2-en-1-ol (100 mg, 0.505 mmol) in Et_2O (2 mL) was added *via* cannula (2 x 1 mL wash) and the mixture was stirred at rt for 30 min before being cooled to −78 °C. Tributyltin chloride (205 µL, 0.758 mmol) was added followed by dropwise addition of ^{t}BuLi solution (1.7 M in pentane, 2.10 mL, 2.53 mmol). The reaction mixture was stirred for 15 minutes before quenching with NH_4Cl (5 mL) and immediately warmed to rt. The layers were separated and the aqueous phase extracted with Et_2O (4 × 5 mL), the combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by flash column chromatography (Et_3N washed silica gel, 5% → 20% EtOAc-Pet. Ether) gave vinyl stannane **22** as a colourless oil (109 mg, 0.303 mmol, 60%).

R_f: 0.18 (5% EtOAc-Pet. Ether); **^{1}H NMR** (400 MHz, $CDCl_3$): δ_H 5.80 (1H, br s, H-15), 4.08 (2H, br s, H-13), 1.78 (3H, s, Me-14), 1.49 (6H, m, Sn*Bu*$_3$), 1.31 (6H, m, Sn*Bu*$_3$), 0.94–0.87 (15H, m, Sn*Bu*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): δ_C 152.8, 120.3, 68.5, 28.8, 27.0, 13.3, 9.7; **IR** (Thin film): 3267 (br), 2956, 2922, 2872, 2856, 1620, 1464, 1376, 1292, 1133, 1072, 1009, 961, 863, 840, 796 cm^{-1}; **HRMS** (ES^+) calc. for $C_{16}H_{34}OSn$ [M-Bu]$^+$ 297.0948, found 297.0946.

Diene 23

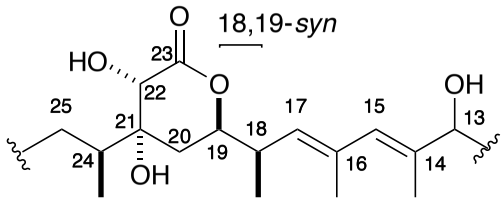


A solution of tetrakistriphenylphosphinepalladium(0) (5.5 mg, 4.8 µmol), copper thiophenecarboxylate (9.0 mg, 47.6 µmol) and [Ph_2PO_2][NBu_4] (21.9 mg, 47.6 µmol) was prepared in degassed DMF (0.2 mL) and cooled to 0 °C. A degassed solution of vinyl iodide **20** (12.0 mg, 23.8 µmol) and vinyl stannane **23** (9.0 mg, 25.0 µmol) in DMF (0.2 mL) was added via cannula (2 x 0.1 mL wash) and the reaction mixture was stirred at 0 °C in the dark for 2 h. H_2O (2 mL) and Et_2O (2 mL) were added and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 5 mL) and the combined organic extracts were washed with water (2 x 4 mL) dried (Na_2SO_4), concentrated *in vacuo* and purified by flash column chromatography (30% → 50% EtOAc-Pet. Ether) to give diene **23** as a colourless oil (7.9 mg, 17.7 µmol, 74%).

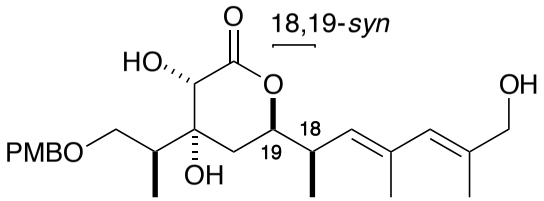
R_f: 0.20 (50% EtOAc-Pet. Ether); $[\alpha]_D^{20}$ +8.0 (*c* 0.20, $CHCl_3$); **^{1}H NMR** (500 MHz, CD_3OD): δ_H 7.25 (2H, d, *J* = 8.7 Hz, Ar*H*), 6.89 (2H, d, *J* = 8.7 Hz, Ar*H*), 5.87 (1H, br s, H-15), 5.10 (1H, d, *J* = 10.2 Hz, H-17), 4.42 (1H, d, J = 11.4 Hz, OC*H*$_2$Ar), 4.41 (1H, ddd, *J* = 11.6, 7.7, 3.7 Hz, H-19), 4.39 (1H, d, J =

11.4 Hz, OC*H*$_2$Ar), 4.23 (1H, s, H-22), 3.96 (2H, s, H-13) 3.78 (3H, s, ArO*Me*), 3.50 (1H, dd, *J* = 9.8, 5.6 Hz, H-25$_a$), 3.47 (1H, dd, *J* = 9.7, 5.1 Hz, H-25$_b$), 2.75–2.66 (1H, m, H-18), 2.31–2.23 (1H, m, H-24), 1.94 (1H, dd, *J* = 14.5, 3.8 Hz, H-20$_a$), 1.79 (1H, d, *J* = 14.5, 11.9 Hz, H-20$_b$), 1.75 (3H, s, Me-14), 1.71 (1H, s, Me-16), 1.07 (3H, d, *J* = 6.6 Hz, H-18), 1.00 (3H, d, *J* = 7.1 Hz, Me-24); **^{13}C NMR** (125 MHz, CD_3OD): δ_C 176.6, 160.8, 136.5, 135.2, 131.6, 131.1, 130.6, 129.6, 114.8, 82.6, 75.4, 74.0, 73.2, 73.0, 69.0, 55.7, 40.0, 39.2, 33.9, 17.6, 17.1, 15.5, 11.9; **IR** (Thin film): 3444 (br), 2933, 1730, 1613, 1514, 1455, 1380, 1247, 1174, 1103, 1033, 819 cm^{-1}; **HRMS** (ES$^+$) calc. for $C_{25}H_{36}O_7Na$ $[M+Na]^+$ 471.2353, found 471.2348.

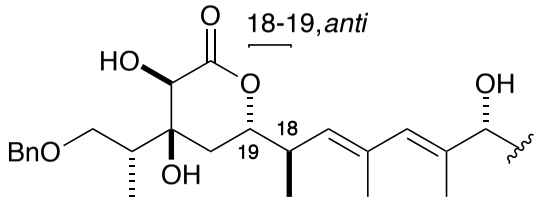
NMR comparison for the C13 – C25 region of hemicalide, subunit 23 and subunit 24 with 18,19-*anti* stereochemistry



Hemicalide **10**
C13 - C25 region



C13 - C25 subunit **23**

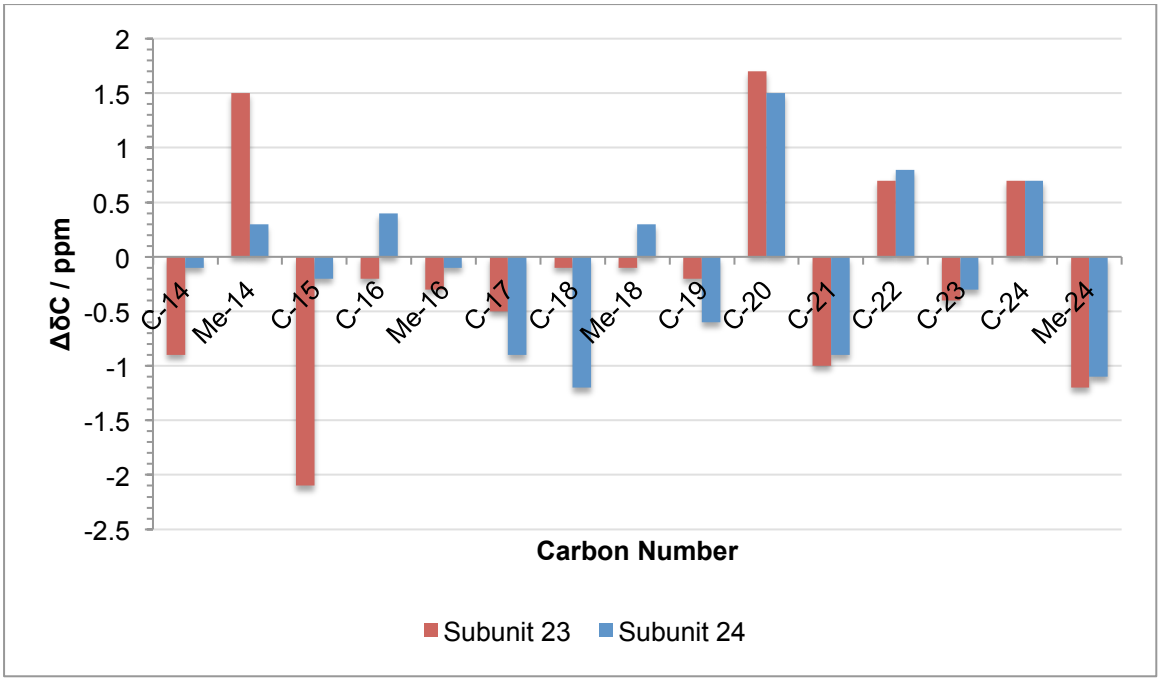


Ardisson and Cossy
C1 - C25 subunit **24**

atom	δ_C (125 MHz, CD_3OD)			δ_H (500 MHz, CD_3OD)								
	Hemicalide **10**	Subunit **23**	Subunit **24**[19]	Hemicalide **10**	Mult	*J* (Hz)	Subunit **23**	Mult	*J* (Hz)	Subunit **24**	Mult	*J* (Hz)
14	137.4	136.5	137.3									
Me-14	14.0	15.5	14.3	1.69	s		1.75	s		1.63	d	1.4
15	131.7	129.6	131.5	5.95	br s		5.87	br s		5.93	s	
16	135.4	135.2	135.8									
Me-16	17.9	17.6	17.8	1.82	s		1.71	s		1.74	d	1.5
17	131.6	131.1	130.7	5.16	d	9.8	5.10	d	10.2	5.15	dt	9.8, 1.4
18	39.3	39.2	38.1	2.81	m	n.d.	2.71	m	n.d.	2.73	m	n.d.
Me-18	17.2	17.1	17.5	1.10	d	6.7	1.07	d	6.6	1.09	d	6.9
19	82.8	82.6	82.2	4.42	ddd	11.3, 7.5, 3.5	4.41	ddd	11.6, 7.7, 3.7	4.54	ddd	13.2, 6.1, 3.9
20a	32.2	33.9	33.7	(part of a 22H multiplet)			1.94	dd	14.5, 3.8	1.89	m	n.d.
20b							1.79	dd	14.5, 11.9			
21	76.4	75.4	75.5									
22	72.5	73.2	73.3	4.27	s		4.23	s		4.17	s	
23	177	176.6	176.7									
24	39.3	40.0	40.0	(part of a 22H multiplet)			2.27	m	n.d.	2.29	m	n.d.
Me-24	13.1	11.9	12.0	0.96	d	6.7	1.00	d	7.1	1.02	d	7.1

Table S18. NMR comparison for hemicalide (**10**) versus subunit **23** and subunit **24**[19]

[19] Sorin, G.; Fleury, E.; Tran, C.; Prost, E.; Molinier, N.; Sautel, F.; Massiot, G.; Specklin, S.; Meyer, C.; Cossy, J.; Lannou, M.-I.; Ardisson, J. *Org. Lett*. **2013**, *15*, 4734.



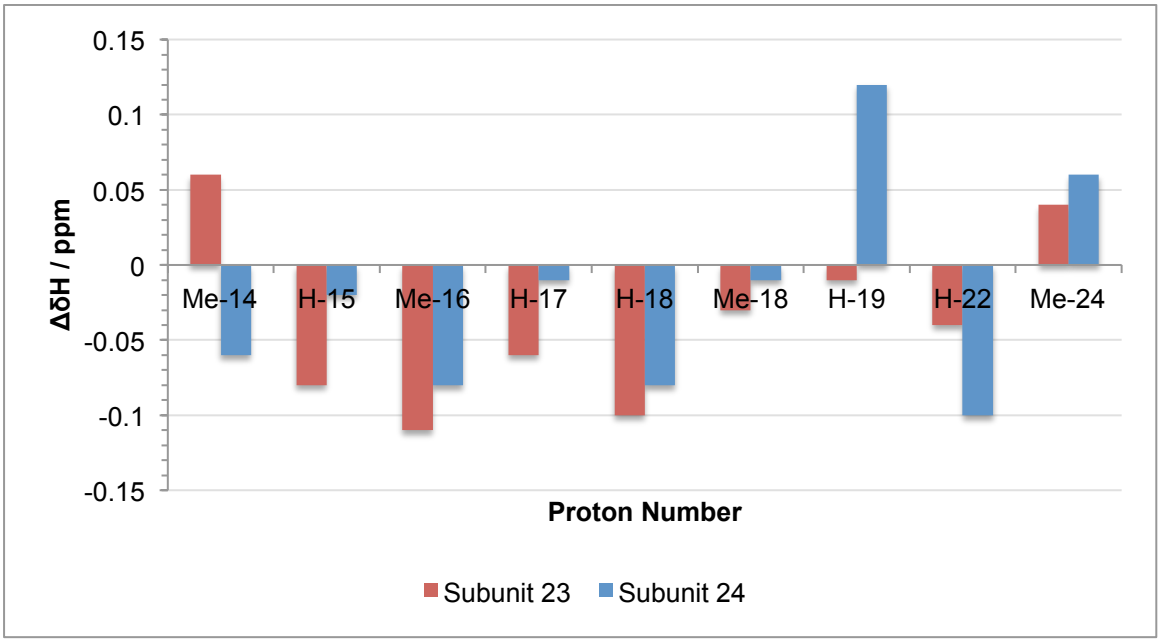
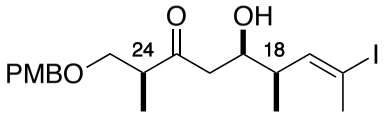


Figure S5. Δδ comparison for hemicalide (**10**) versus diene **23** and subunit **24**[19]. The correlations indicate that there is a significantly improved match for H-19 and H-22, which are considered diagnostic signals by Ardisson[20], to hemicalide in subunit **23** relative to the Cossy-Ardisson subunit **24**. However, some of the signals in the diene region are a better match for Cossy-Ardisson subunit **24**. This is to be expected as this includes the relevant substitution at C13 whereas subunit **23** is a truncate with a hydroxy methylene.

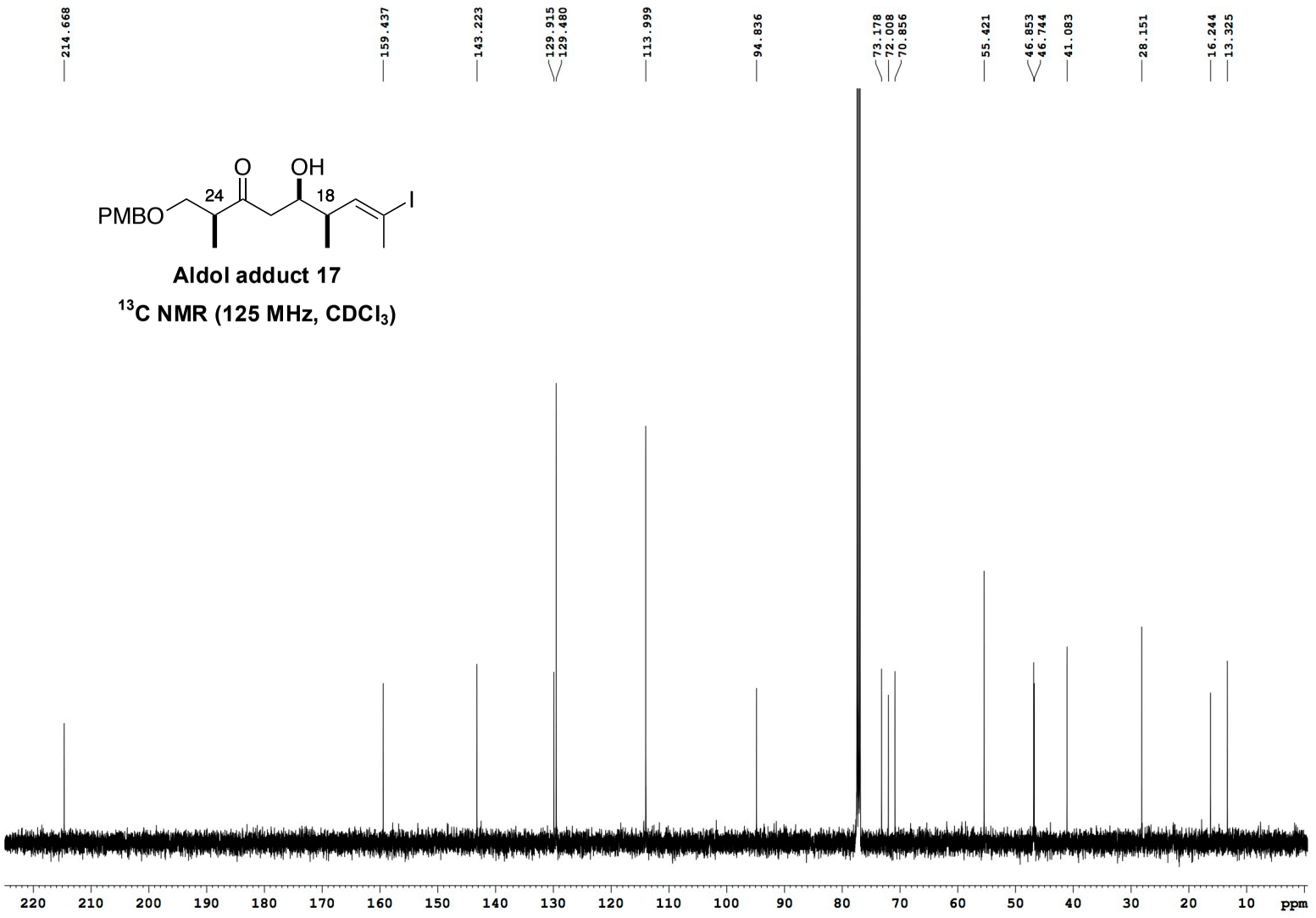
[20] Fleury, E.; Sorin, G.; Prost, E.; Pancrazi A.; Sautel, F.; Massiot, G.; Lannou, M.-I.; Ardisson, J. *J. Org. Chem.* **2013**, *78*, 855.

4. ^{1}H and ^{13}C NMR spectra for new compounds



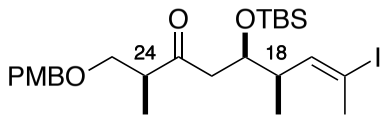
Aldol adduct 17

^{1}H NMR (500 MHz, $CDCl_3$)



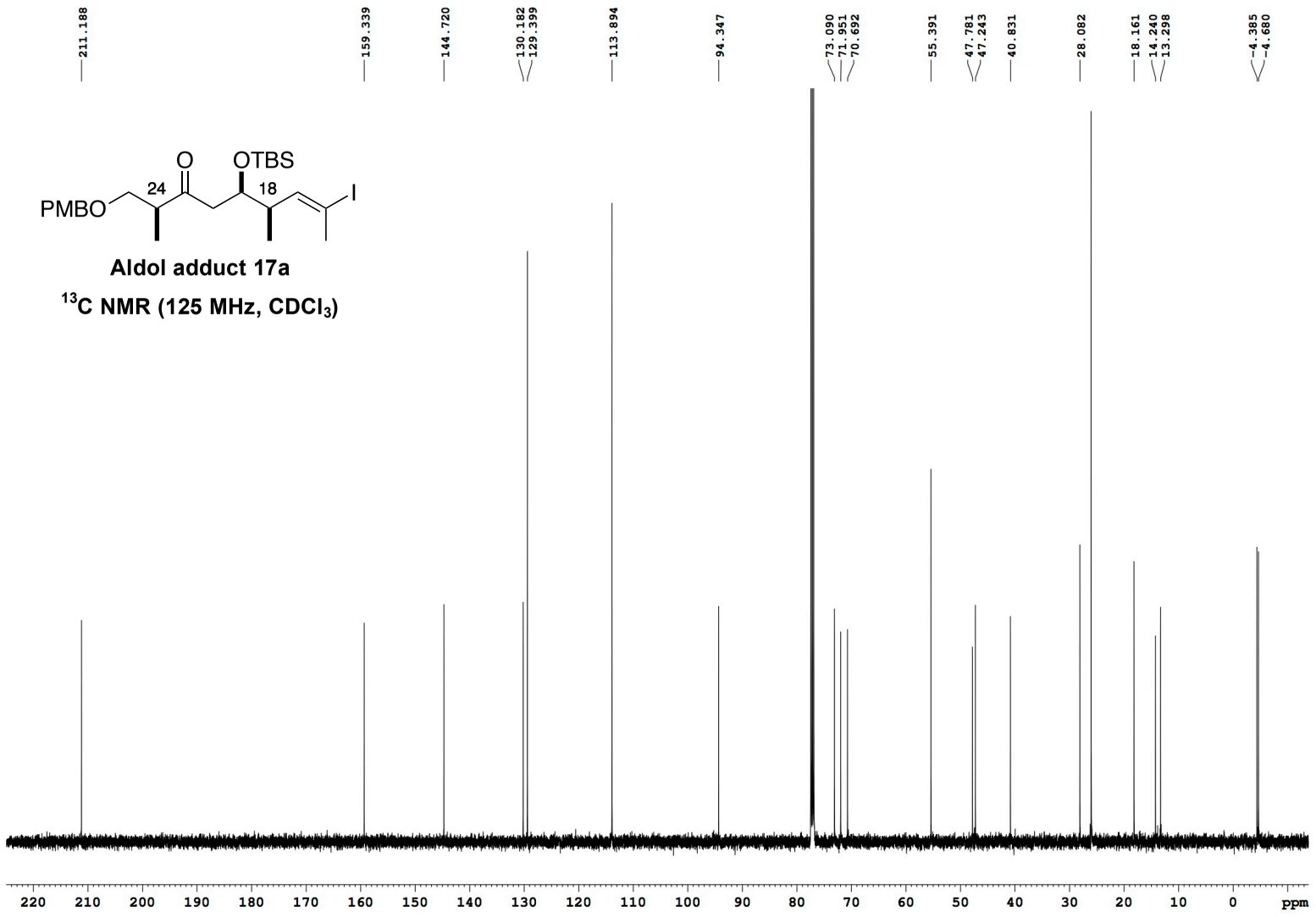
Aldol adduct 17

^{13}C NMR (125 MHz, $CDCl_3$)



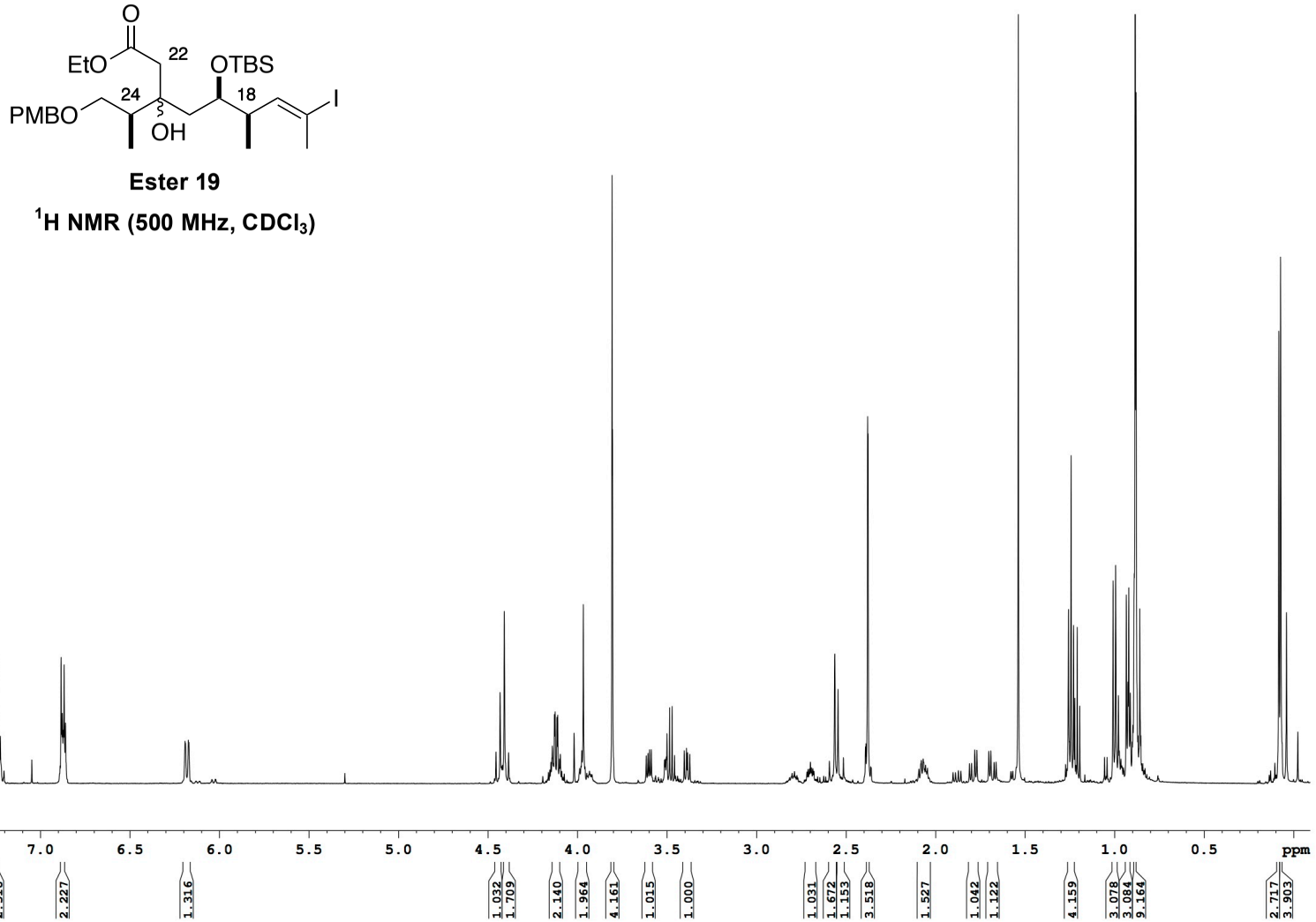
Aldol adduct 17a

^{1}H NMR (500 MHz, $CDCl_3$)



Aldol adduct 17a

^{13}C NMR (125 MHz, $CDCl_3$)


O
EtO
22
OTBS
24
18
I
PMBO
OH
Ester 19
^{1}H NMR (500 MHz, $CDCl_3$)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.318
2.227
1.316
1.032
1.709
2.140
1.964
4.161
1.015
1.000
1.031
1.672
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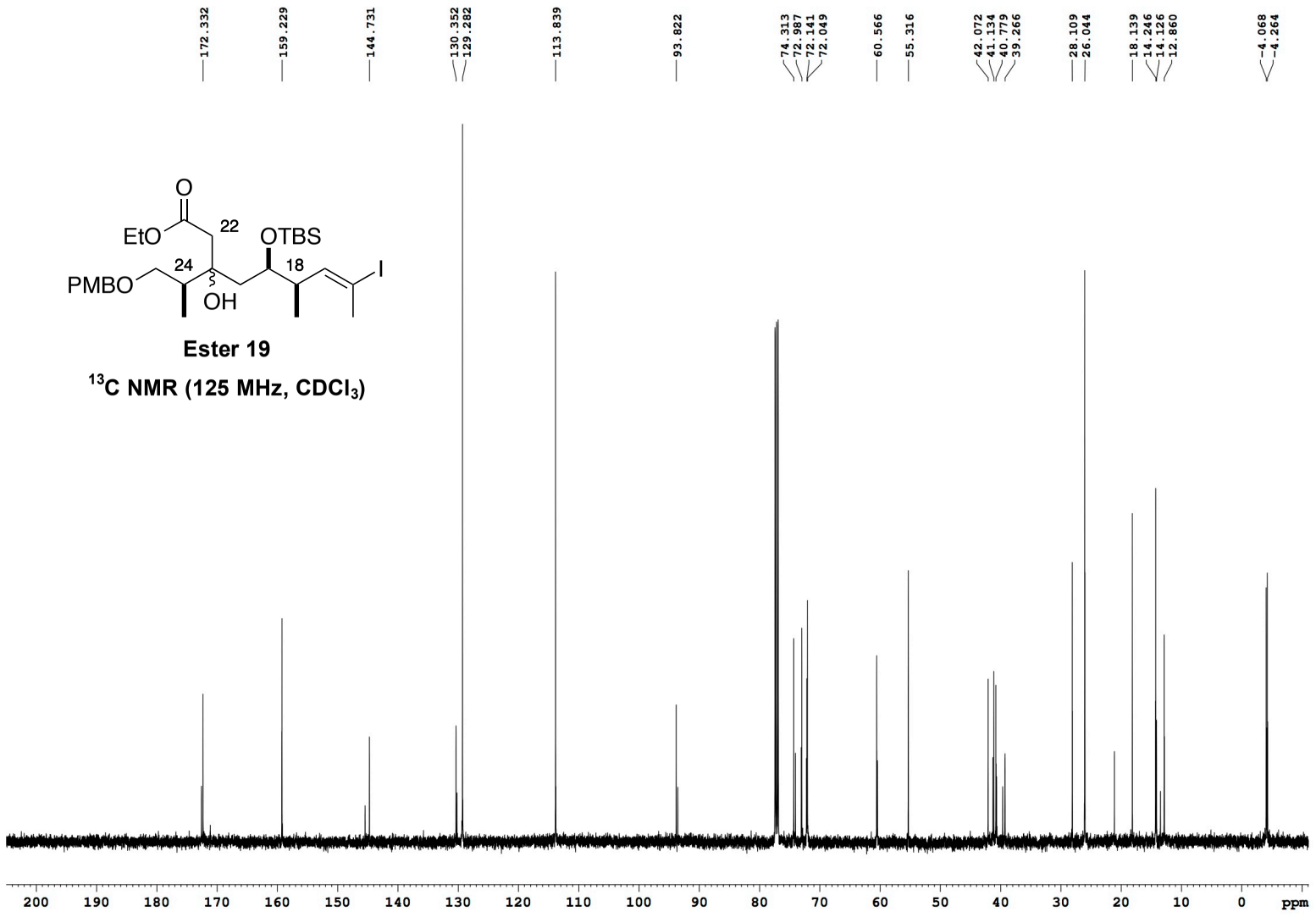
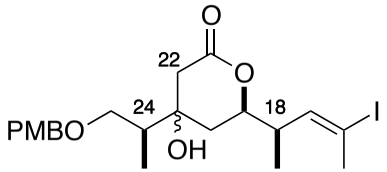
4.159
3.078
3.084
9.164
2.717
3.903



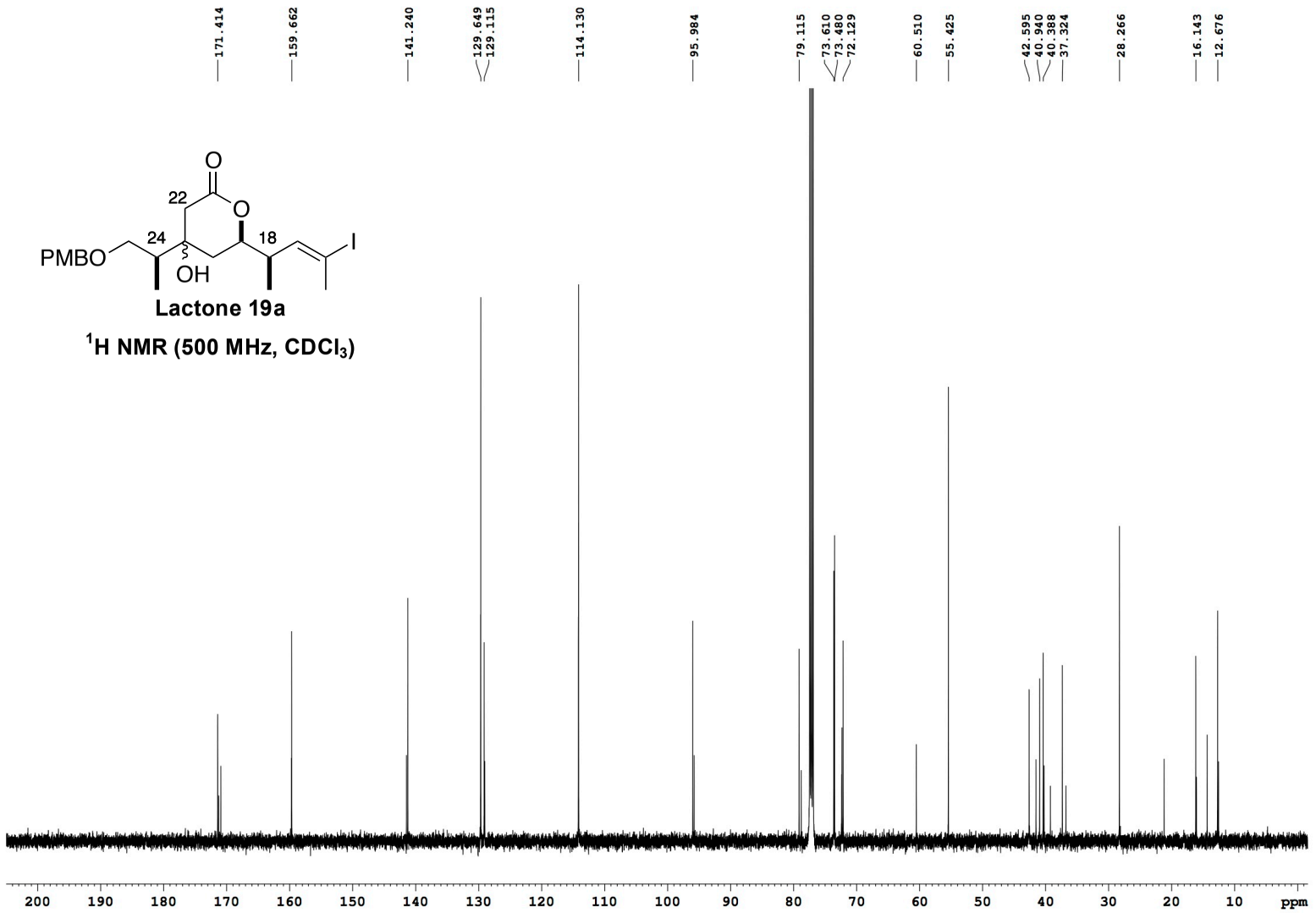
Ester 19

^{13}C NMR (125 MHz, $CDCl_3$)



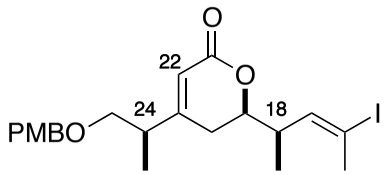
Lactone 19a

^{1}H NMR (500 MHz, $CDCl_3$)



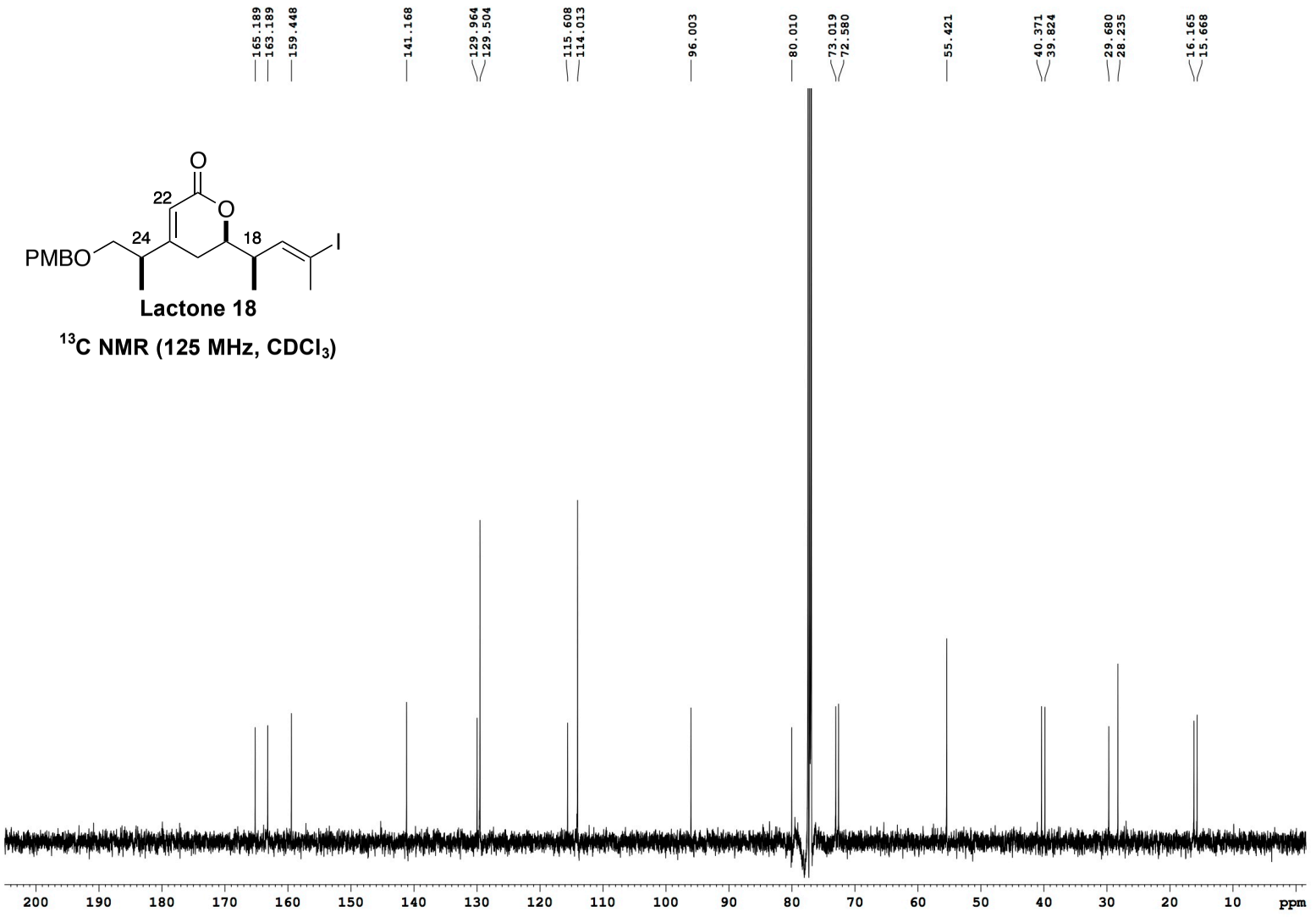
Lactone 19a

^{1}H NMR (500 MHz, $CDCl_3$)



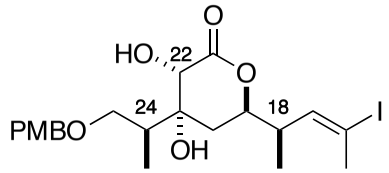
Lactone 18

^{1}H NMR (500 MHz, $CDCl_3$)



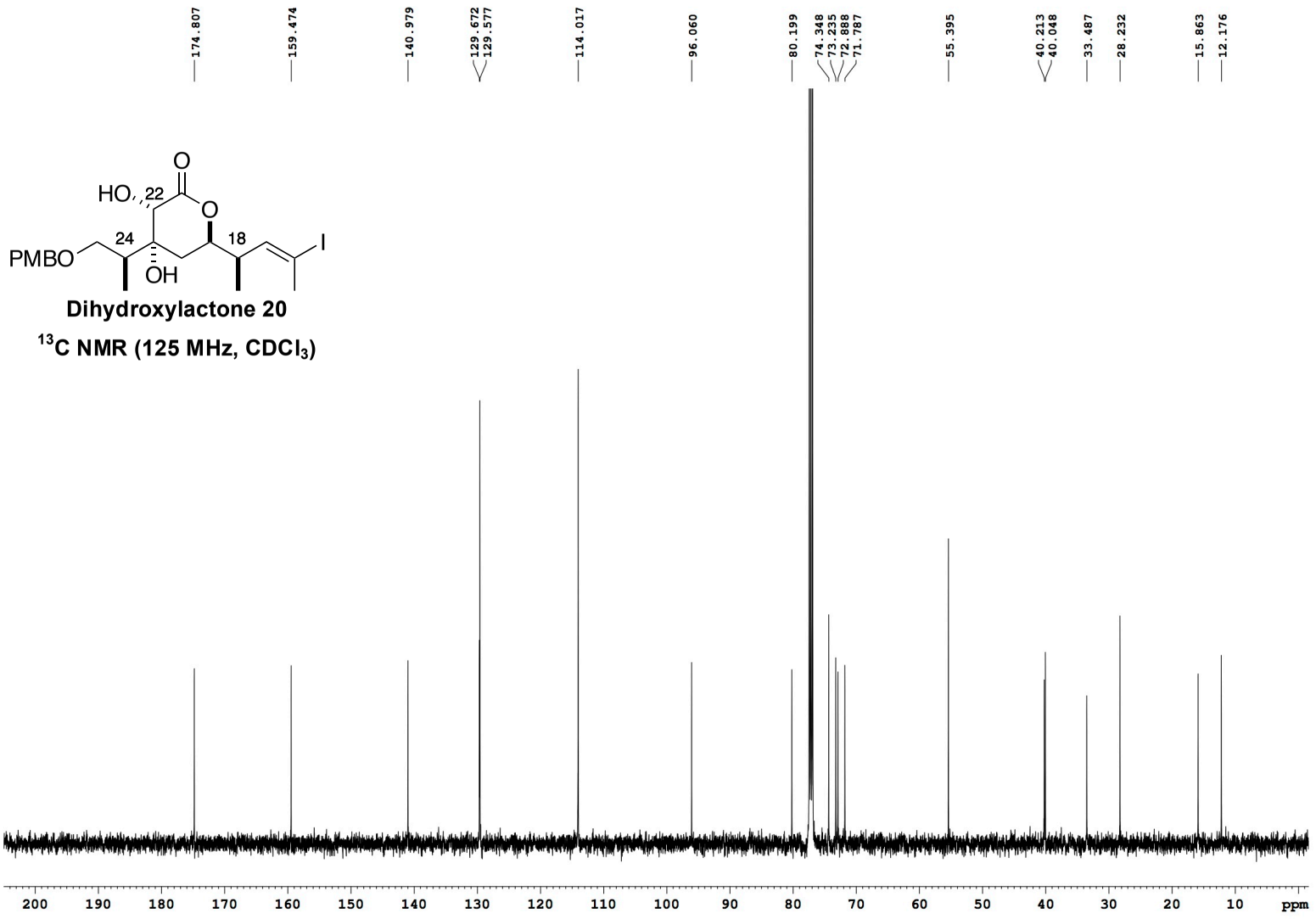
Lactone 18

^{13}C NMR (125 MHz, $CDCl_3$)



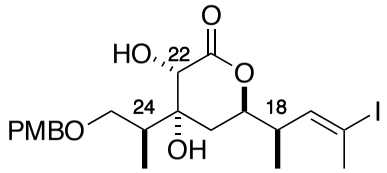
Dihydroxylactone 20

^{1}H NMR (500 MHz, $CDCl_3$)



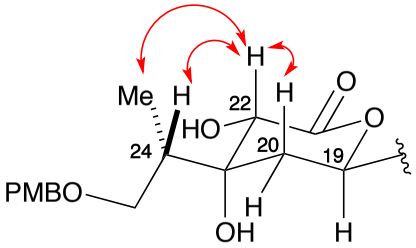
Dihydroxylactone 20

^{13}C NMR (125 MHz, $CDCl_3$)

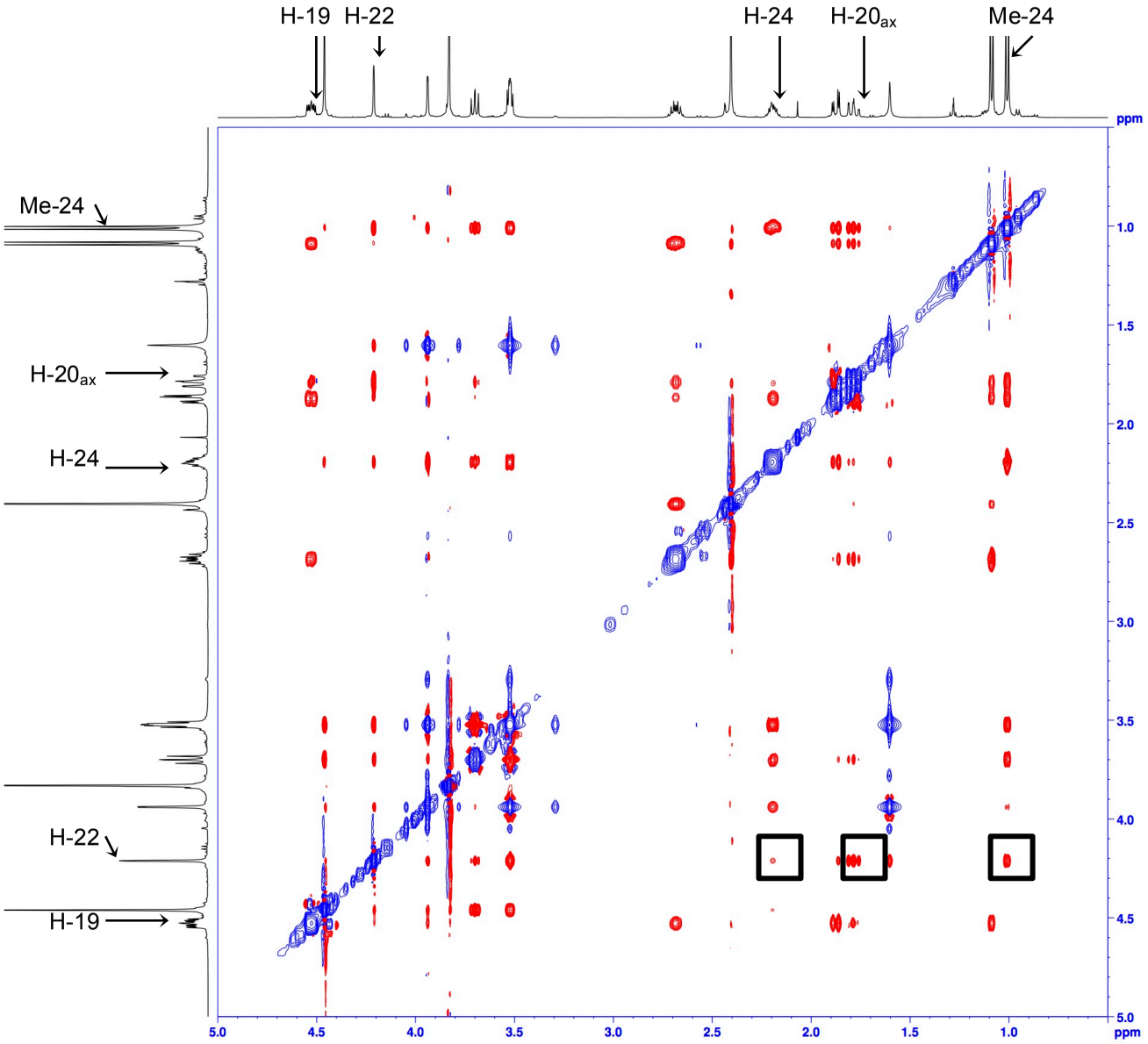


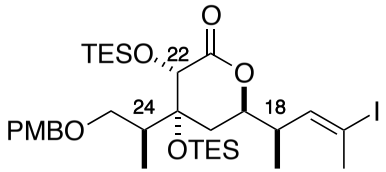
Dihydroxylactone 20

NOESY (500 MHz, $CDCl_3$)



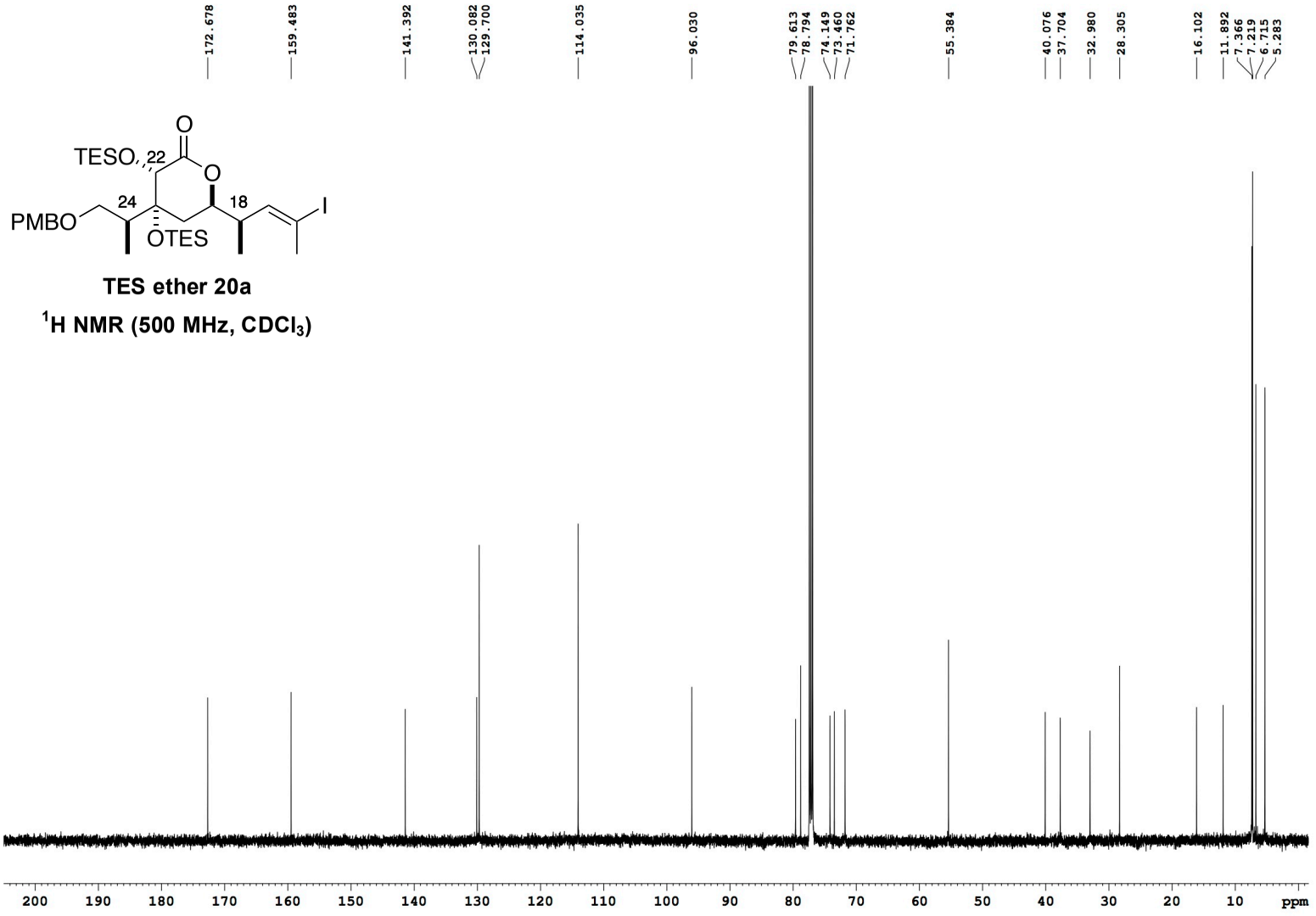
The NOE correlation between H-22 and H-20_{ax} together with the *trans* coupling of H-20_{ax} and H-19 (^3J = 11.1 Hz) suggest that H-22 is also *trans* to H-19, thus confirming the relative stereochemistry of the molecule as shown above.





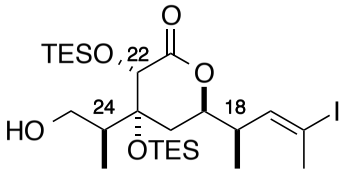
TES ether 20a

^{1}H NMR (500 MHz, $CDCl_3$)



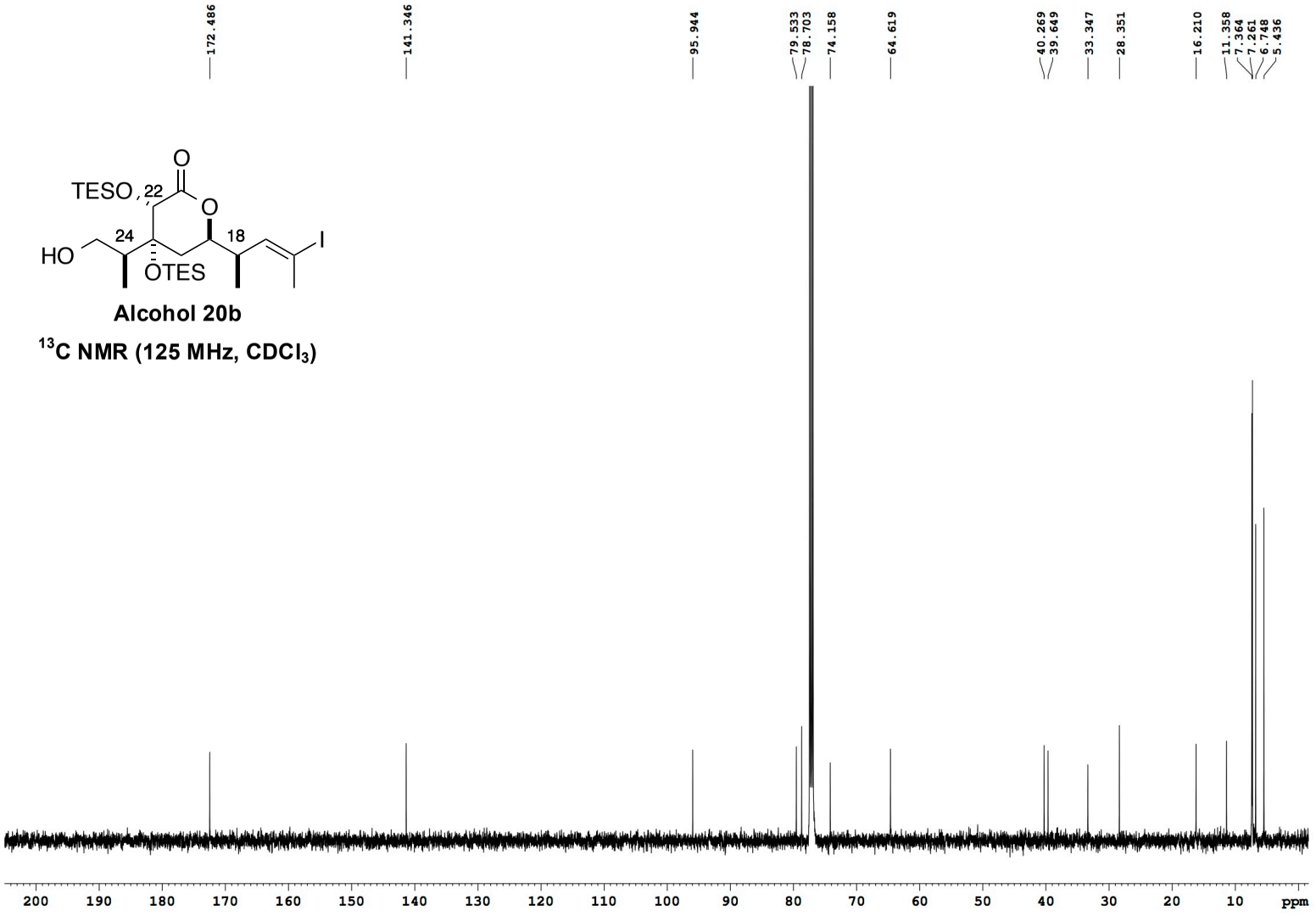
TES ether 20a

^{1}H NMR (500 MHz, $CDCl_3$)



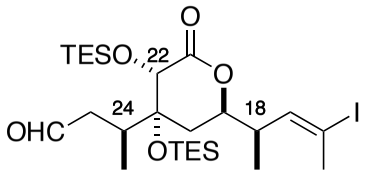
Alcohol 20b

^{1}H NMR (500 MHz, $CDCl_3$)



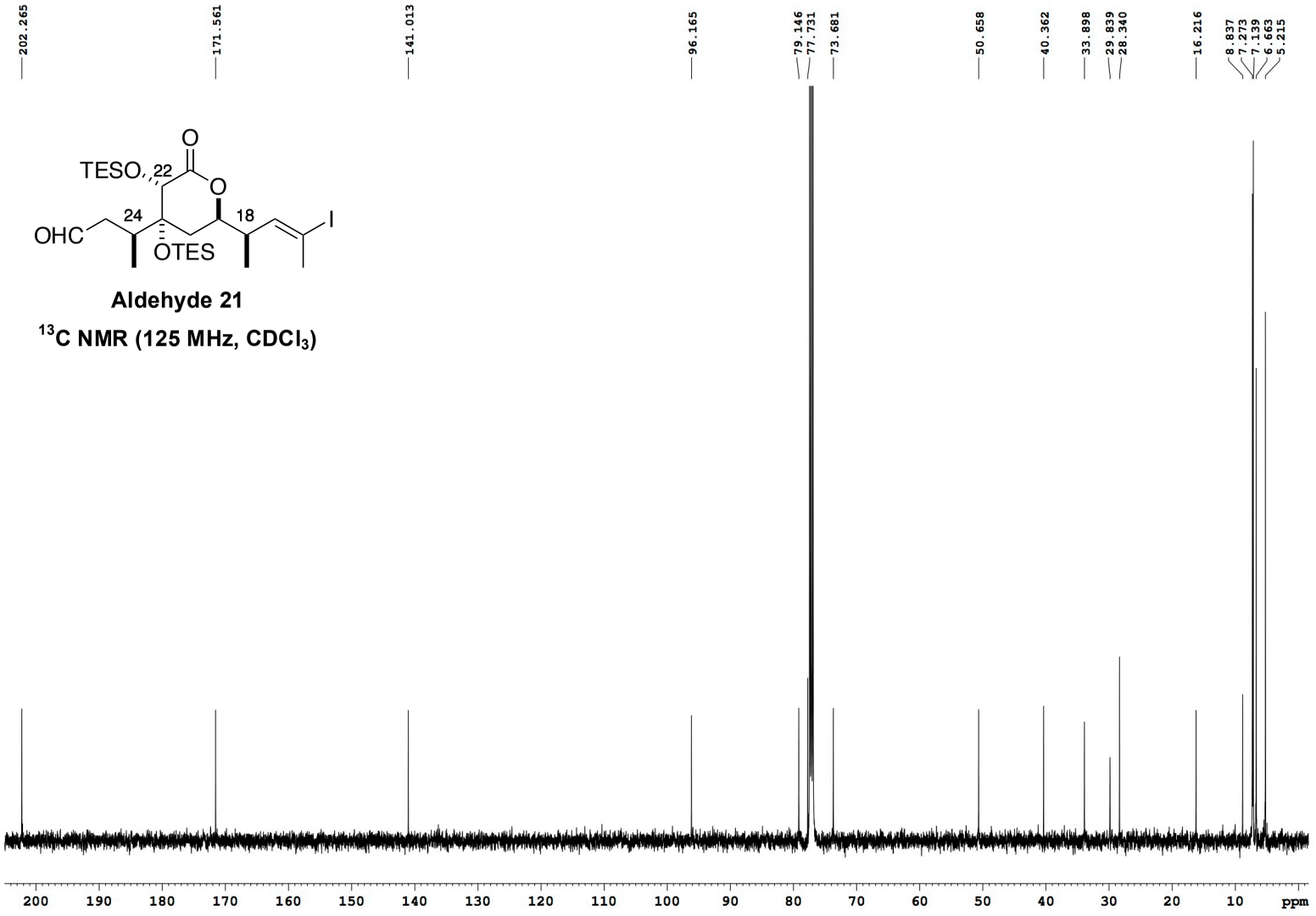
Alcohol 20b

^{13}C NMR (125 MHz, $CDCl_3$)



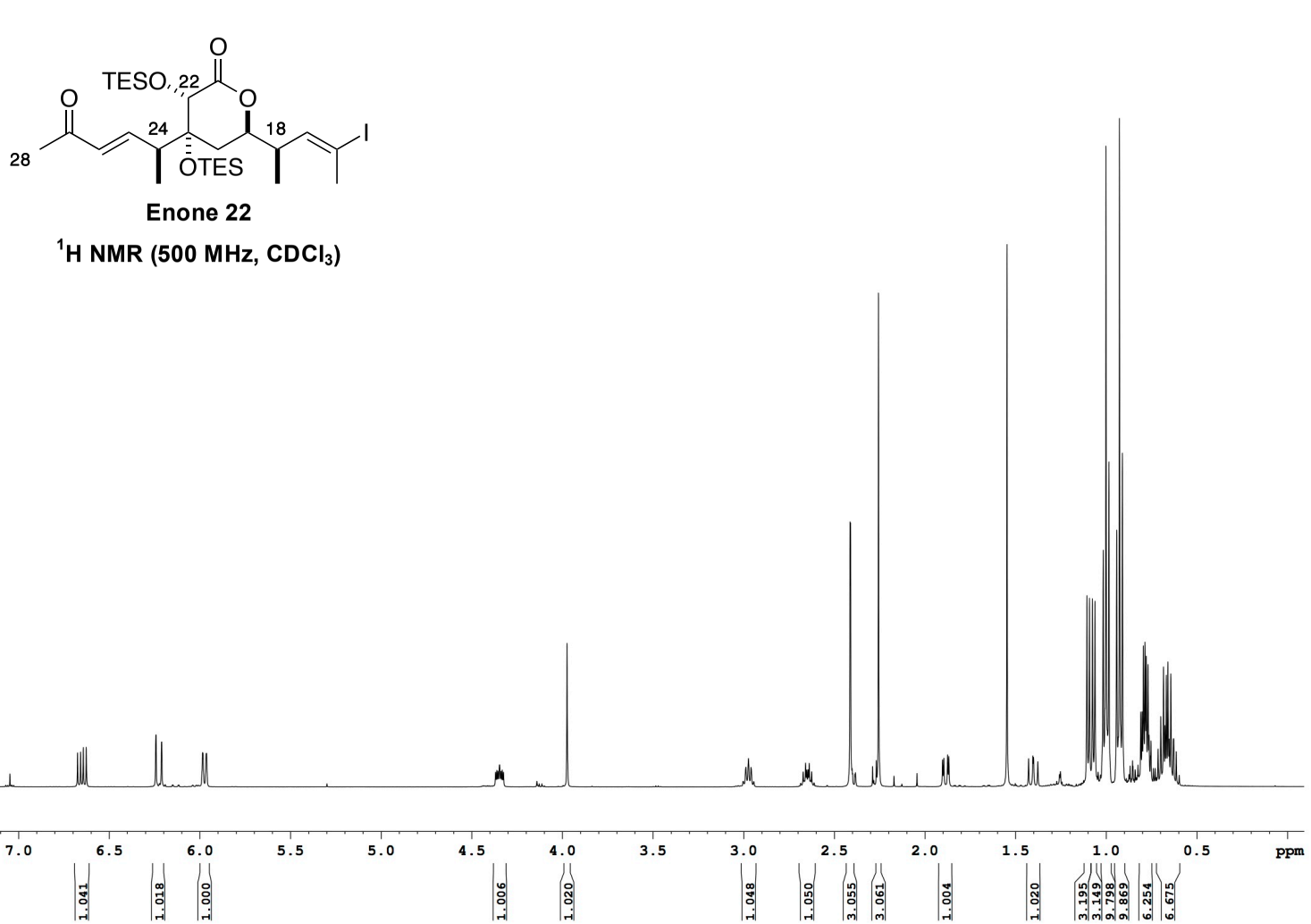
Aldehyde 21

^{1}H NMR (500 MHz, $CDCl_3$)



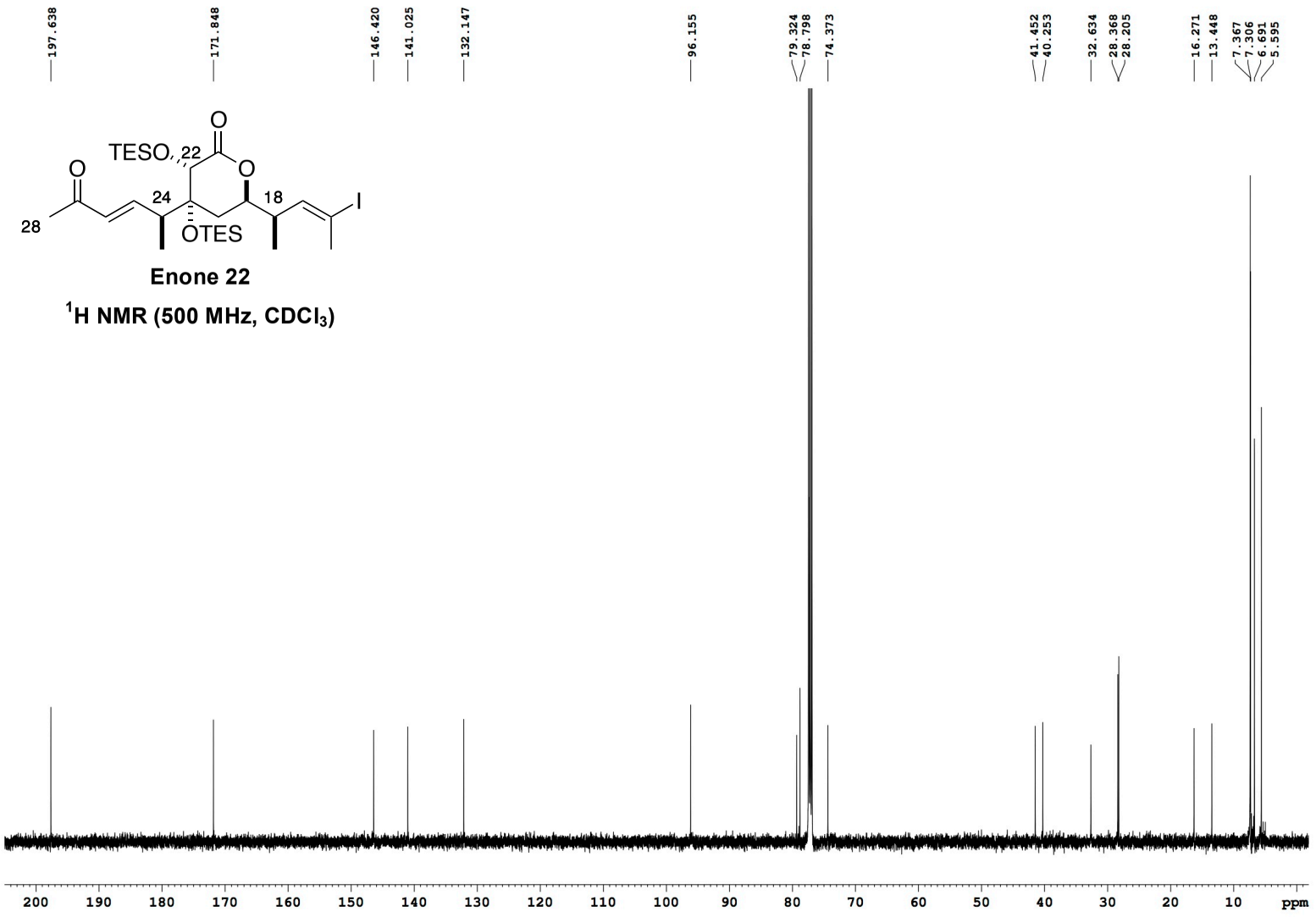
Aldehyde 21

^{13}C NMR (125 MHz, $CDCl_3$)



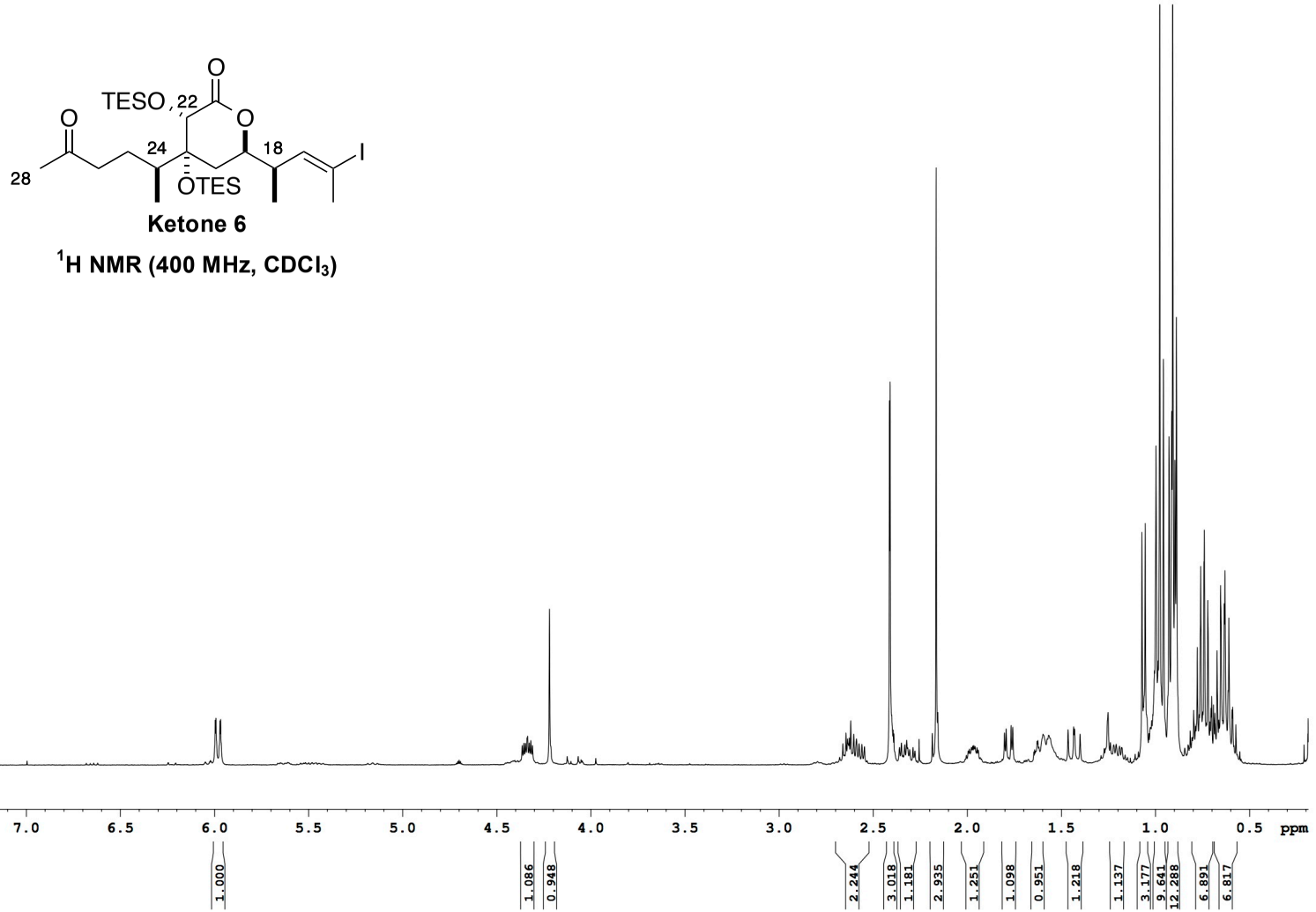
Enone 22

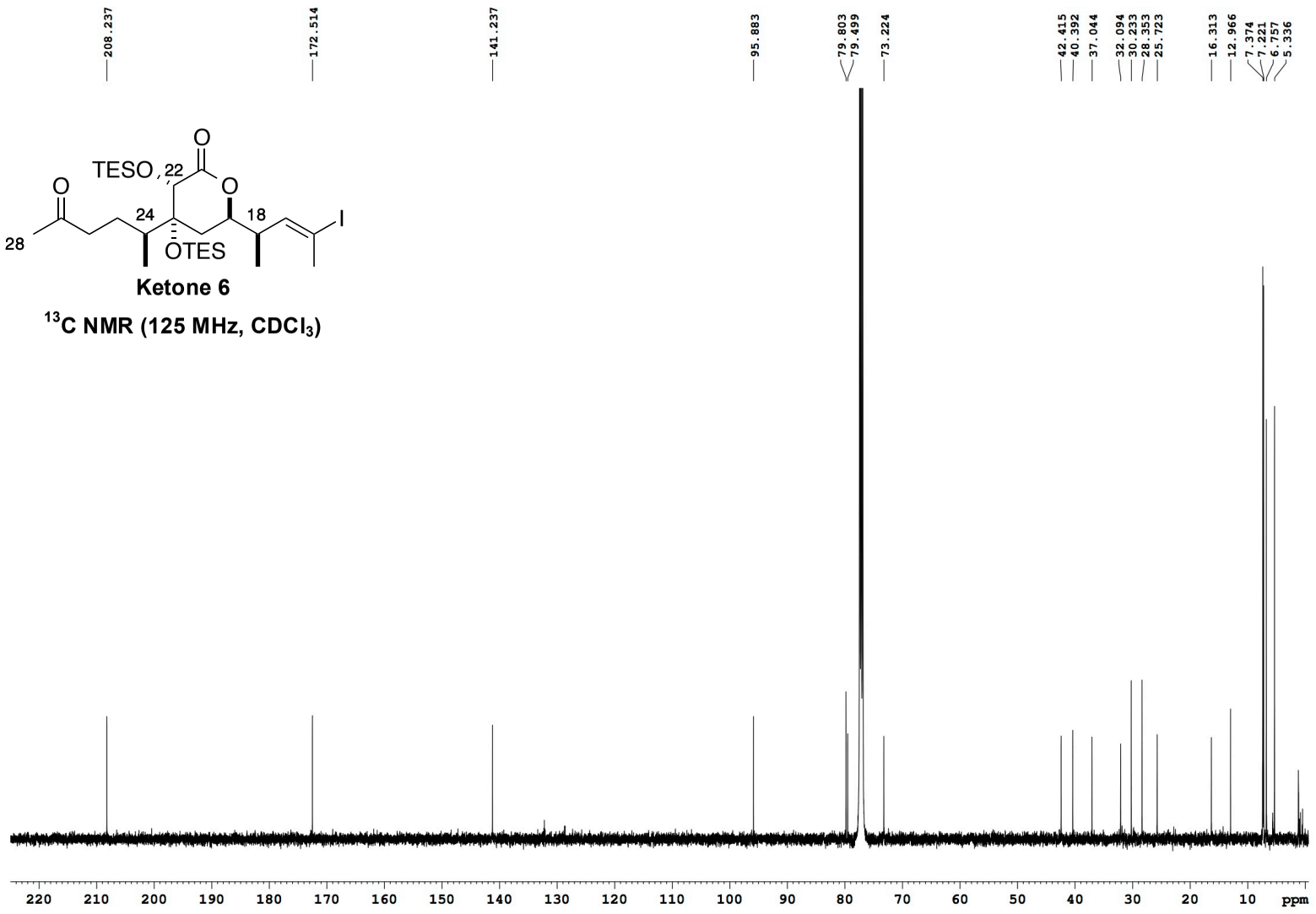
^{1}H NMR (500 MHz, $CDCl_3$)



Enone 22

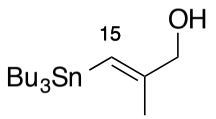
^{1}H NMR (500 MHz, $CDCl_3$)


TESO
22
24
18
28
OTES
I
O
Ketone 6
1H NMR (400 MHz, CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.086
0.948
2.244
3.018
1.181
2.935
1.251
1.098
0.951
1.218
1.137
3.177
9.641
12.288
6.891
6.817



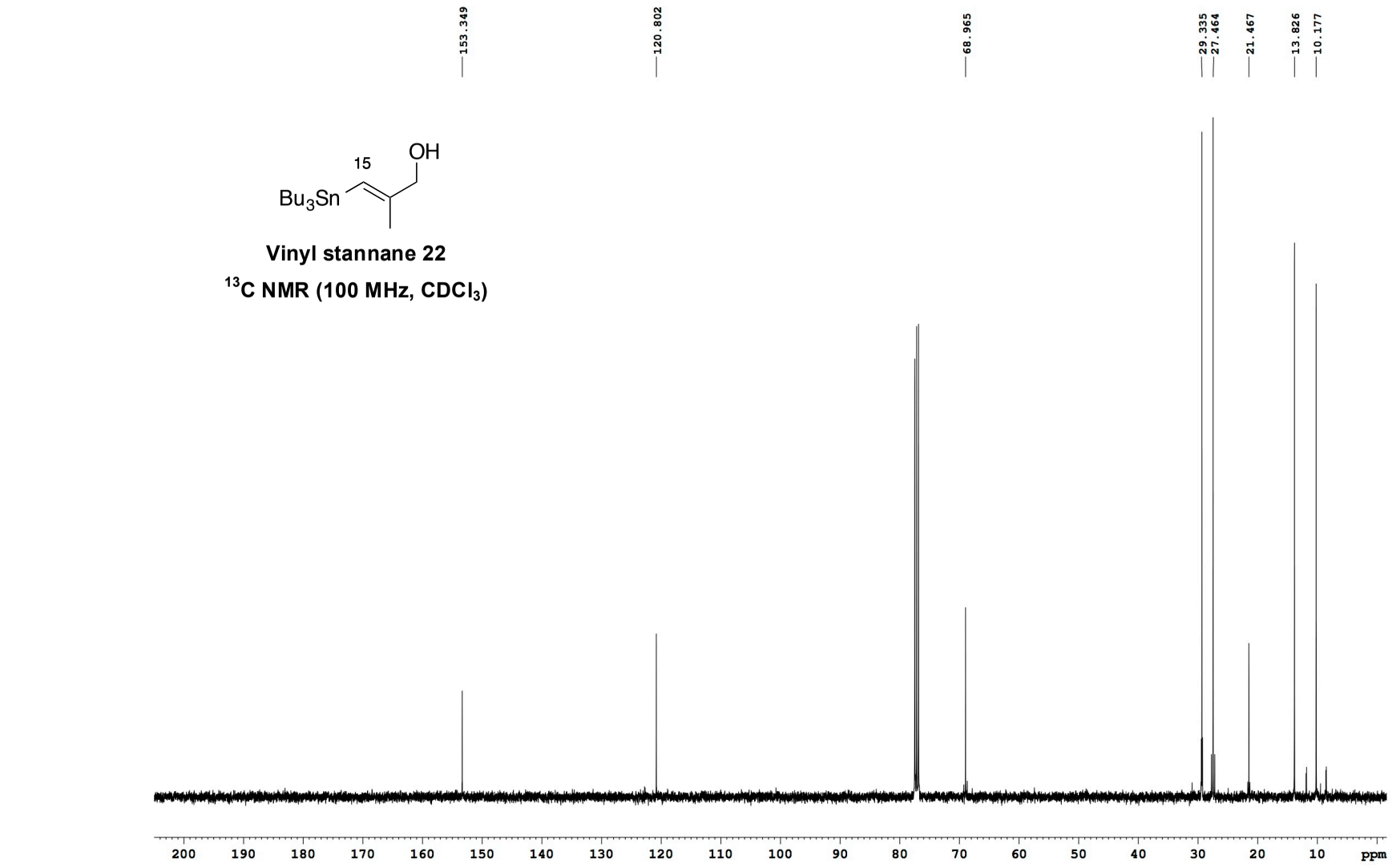
Ketone 6

^{13}C NMR (125 MHz, $CDCl_3$)



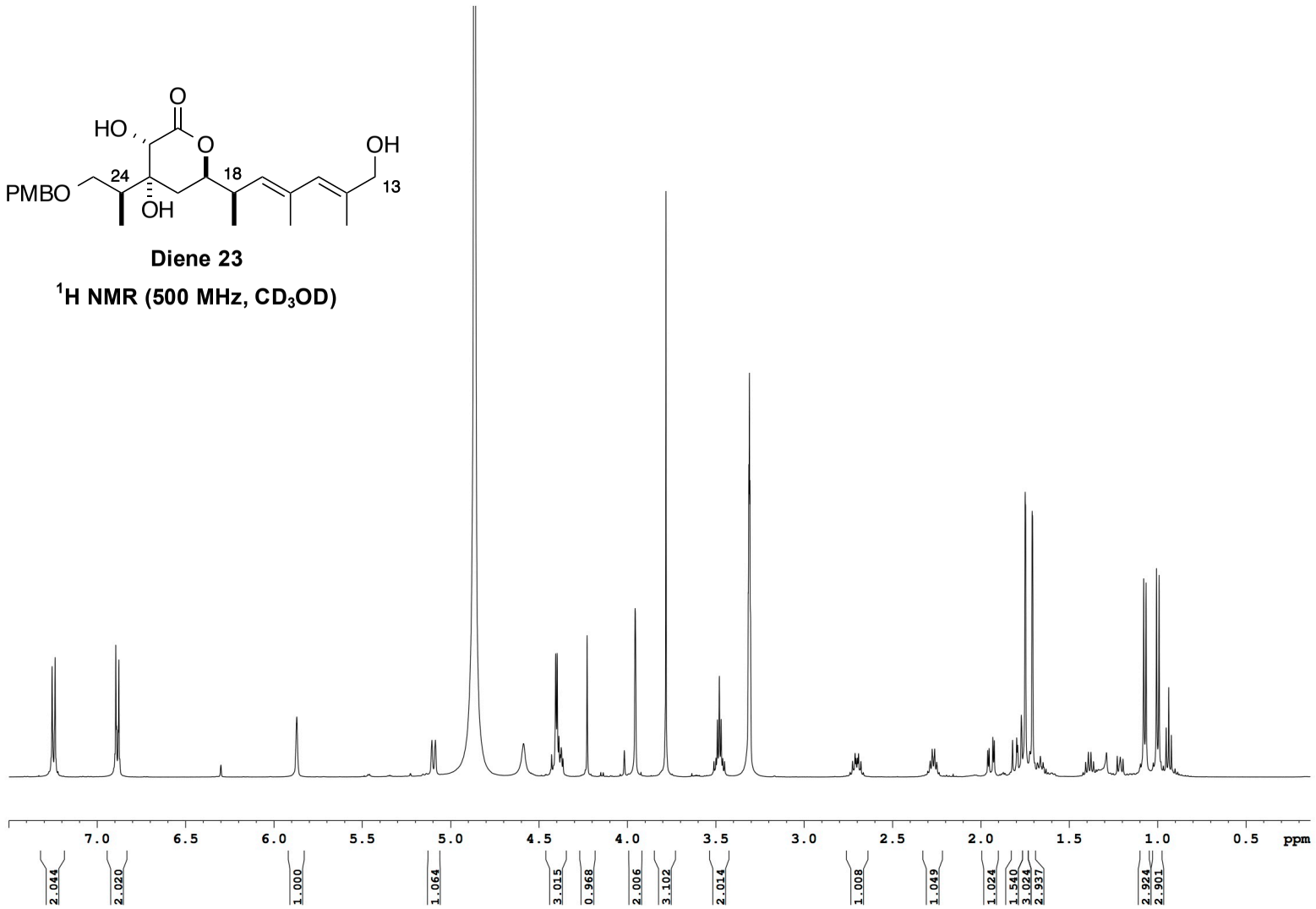
Vinyl stannane 22

^{1}H NMR (400 MHz, $CDCl_3$)



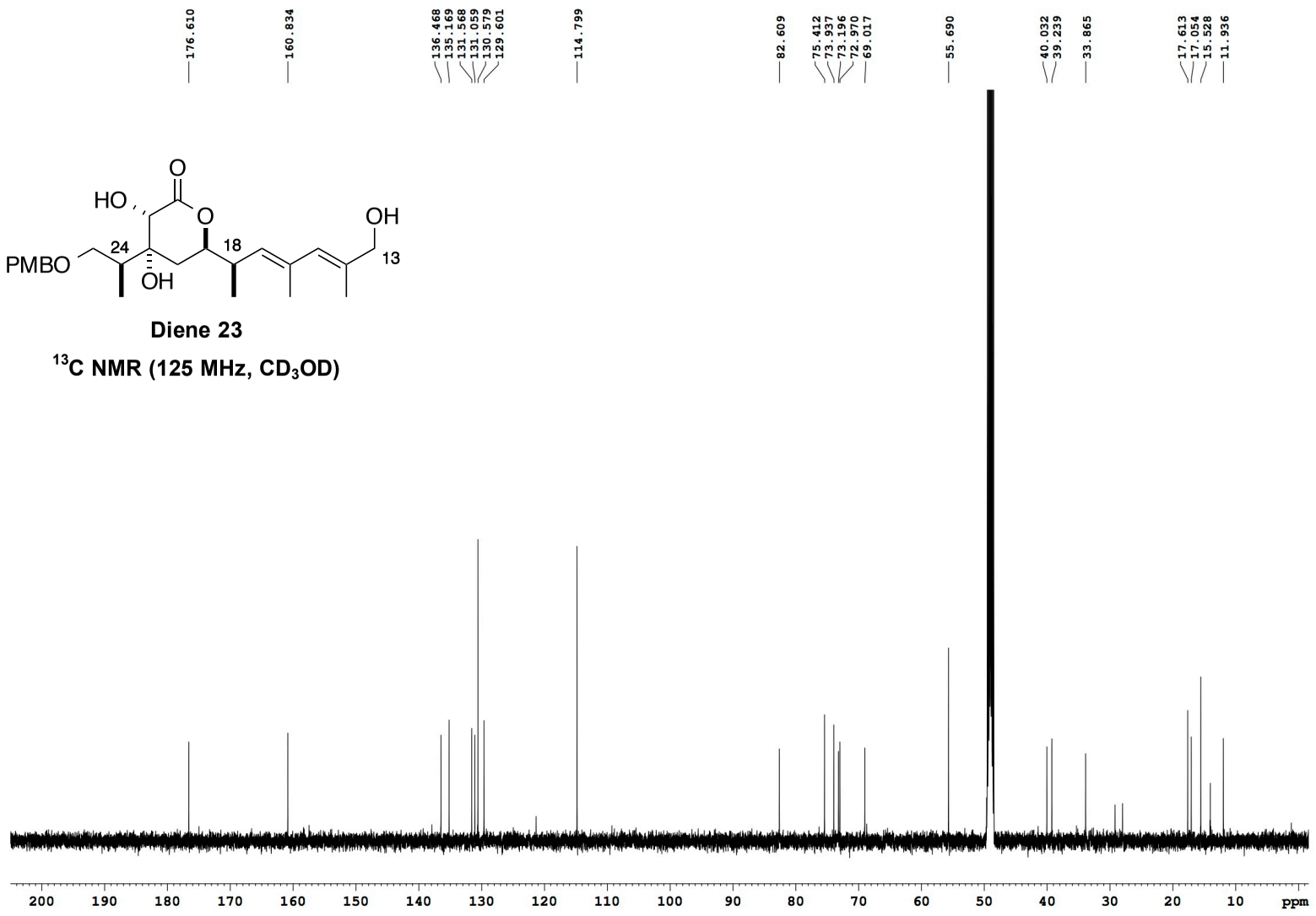
Vinyl stannane 22

^{13}C NMR (100 MHz, $CDCl_3$)



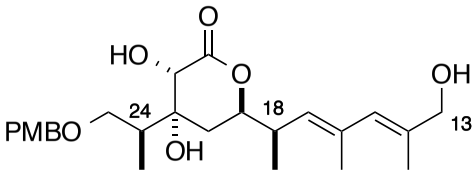
Diene 23

^{1}H NMR (500 MHz, CD_3OD)



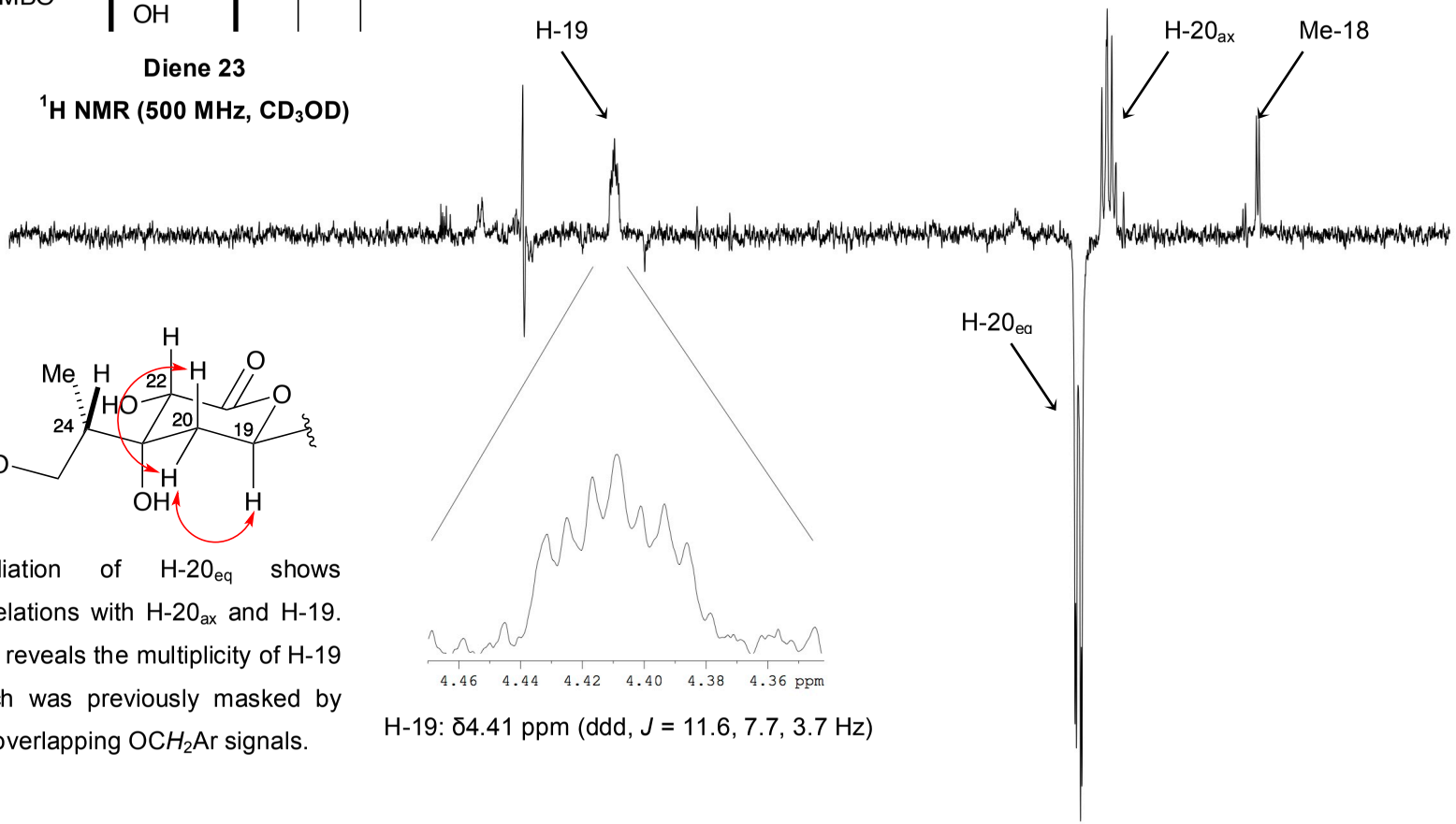
Diene 23

^{13}C NMR (125 MHz, CD_3OD)



Diene 23

^{1}H NMR (500 MHz, CD_3OD)



Irradiation of H-20$_{eq}$ shows correlations with H-20$_{ax}$ and H-19. This reveals the multiplicity of H-19 which was previously masked by the overlapping OCH_2Ar signals.

H-19: δ4.41 ppm (ddd, *J* = 11.6, 7.7, 3.7 Hz)