Asymmetric synthesis of (–)-dehydro-*exo*-brevicomin with photoisomerisation–intramolecular acetalisation sequence

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Supporting Information

Contents

Density Functional Theory Studies

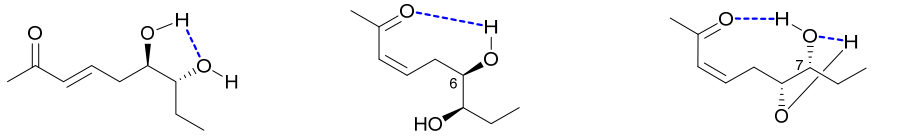
Conformational searches, structural optimisations, and solvation energy calculations of the ground state and the first excited state were conducted with Mac Spartan 18 (64 bit) version 1.4.5 (200203) (Wave function, Irvine, CA).

Ground state calculations for *trans*-6 and *cis*-5 of conformer A,B

Initial stable conformers for *trans*-**6** and *cis*-**5** of conformer **A**,**B** were calculated with Hartree-Fock (HF) theory with 3-21G basis set for each conformer generated by MMFF94 conformer searches. Conformers beyond 40 kJ/mol of the global minimum conformation were removed to generate sets of tentative stable conformers. Energies of these tentative conformers were calculated with density functional theory (DFT), employing the ωB97X-D functional and 6-31G* basis set and conformers within 15 kJ/mol from the global minimum conformation were selected and further optimised with DFT ωB97X-D/6-31G* calculation with solvent effect correction approximated by conductor-like polarisable continuum model (C-PCM) employing dichloromethane (DCM) as solvent (dielectric:8.82). Final energies were obtained by DFT calculation with ωB97X-V/6-311+G(2df,2p) with C-PCM solvation model (DCM) without geometry optimisation for selected conformers within 10 kJ/mol from global minimum conformation by the preceding calculations.

Energy calculations in gas state were also performed separately without solvent correlation.

DFT calculations predicted structure *cis*-**5** of conformer **B** to have the lowest energy in gas state and structure *trans*-**6** to be the lowest in energy in DCM solvent used for photoreactions in this work.



trans-6
E_{rel} (gas) = +9.33 kJ/mol
E_{rel} (DCM) = 0 kJ/mol

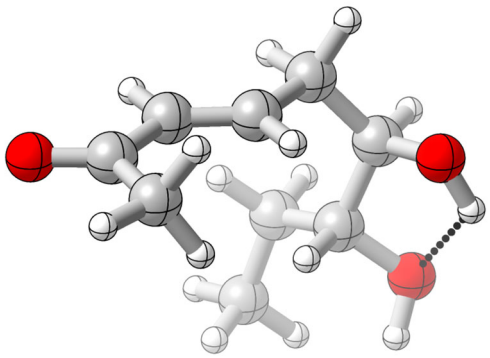
cis-5: conformer A
E_{rel} (gas) = +2.64 kJ/mol
E_{rel} (DCM) = +3.50 kJ/mol

cis-5: conformer B
E_{rel} (gas) = 0 kJ/mol
E_{rel} (DCM) = +0.83 kJ/mol

Figure S1. Relative energies of dehydrobrevicomin (DHB) precursors, *trans*-**6** and *cis*-**5** of conformer **A**,**B**.

Cartesian coordinates of the DFT-optimised structure of *trans*-6 and *cis*-5 of conformer A,B

Minimised structure, SCF energy and coordinate for *trans*-**6**



Optimised structure of *trans*-6 (Solvent: DCM)

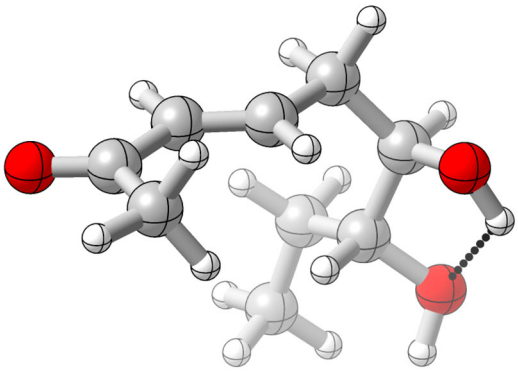
Minimised geometry using ωB97X-D/6-31G*/C-PCM (DCM)

SCF energy using ωB97X-V/6-311+G(2df,2p)/C-PCM (DCM) = -578.2952351 hartrees

Cartesian coordinates

Atom	X	Y	Z
H	-0.5749633269	1.6499120137	2.8970280178
C	-1.4452026185	1.1350092889	3.3167989370
H	-1.4102286959	1.1909270520	4.4054879499
H	-2.3394373373	1.6515993403	2.9530043589
C	-1.4599190602	-0.3176899681	2.8931011427
O	-1.4303764474	-1.2173671537	3.7219503173
C	-1.5054121868	-0.6520320474	1.4519160503
H	-1.5079433533	-1.7182978031	1.2312500008
C	-1.5367139345	0.2497015630	0.4640231952
H	-1.5271681386	1.3130458029	0.6974734773
C	-1.5694792775	-0.0908426574	-0.9937700168
H	-1.5421657911	-1.1750647098	-1.1399888490
H	-2.5115627748	0.2735852979	-1.4240549642
C	-0.4372032042	0.5729807549	-1.7820326122
H	-0.4743608929	0.1971889608	-2.8177185793
C	0.9605278914	0.2783073956	-1.2319986285
H	1.0102594301	0.6512760248	-0.1975005718
C	1.3254190590	-1.2040240722	-1.2512490248
H	1.1611901135	-1.5990501335	-2.2617552801
H	0.6420391509	-1.7371779998	-0.5801811402
C	2.7661499070	-1.4662290095	-0.8151933003
H	3.4784967953	-1.0093860461	-1.5097443719

H	2.9744671460	-2.5399869568	-0.7821363913
H	2.9533970082	-1.0558419194	0.1840968753
O	-0.6606412962	1.9727108771	-1.7679557780
H	0.1811433215	2.3613297653	-2.0534887979
O	1.8355831388	1.0552502230	-2.0527124422
H	2.6441053741	1.2301661165	-1.5546495740



Optimised structure of *trans*-6 (gas)

Minimised geometry using ωB97X-D/6-31G*

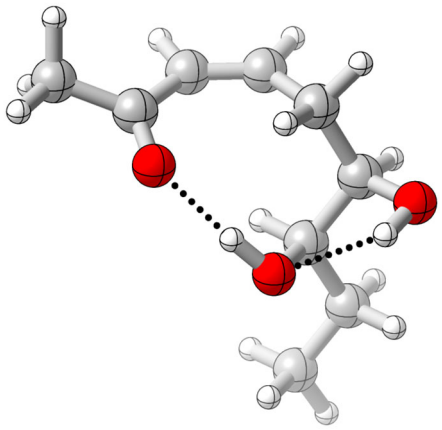
SCF energy using ωB97X-V/6-311+G(2df,2p) = -578.2778904 hartrees

Cartesian coordinates

Atom	X	Y	Z
H	-0.6461105003	1.7082148334	2.8901161147
C	-1.4858644534	1.1515209565	3.3204886285
H	-1.4367649887	1.2041235767	4.4087884357
H	-2.4088189362	1.6286490328	2.9733862425
C	-1.4415320008	-0.3059048728	2.8996804560
O	-1.3617982185	-1.1975578008	3.7241750366
C	-1.4895709839	-0.6399592491	1.4539900242
H	-1.4663315210	-1.7081360324	1.2437907994
C	-1.5498252349	0.2544302565	0.4625151817
H	-1.5661916667	1.3202011187	0.6840893780
C	-1.5695323521	-0.0890729351	-0.9952587764
H	-1.5391032592	-1.1737583302	-1.1405195647
H	-2.5042522636	0.2759849040	-1.4388650939
C	-0.4298045761	0.5807383796	-1.7679929028
H	-0.4574961365	0.2209632259	-2.8103159158
C	0.9637870727	0.2717097060	-1.2148563014
H	1.0034134745	0.6269384673	-0.1729868178

C	1.3279751288	-1.2104805122	-1.2554120605
H	1.1501938436	-1.5954124395	-2.2674932022
H	0.6555159500	-1.7490773686	-0.5774577980
C	2.7751833285	-1.4798221751	-0.8468516228
H	3.4770176114	-1.0205503945	-1.5510662542
H	2.9837428537	-2.5532059273	-0.8313541769
H	2.9827810732	-1.0873941853	0.1560217266
O	-0.6535662817	1.9742684429	-1.7265776584
H	0.1706331972	2.3704253056	-2.0456864764
O	1.8393318642	1.0624935409	-2.0197856212
H	2.6769879754	1.1596704762	-1.5545617807

Minimised structure, SCF energy and coordinate for *cis*-**5** of conformer **A**



Optimised structure of *cis*-5 of conformer A (Solvent: DCM)

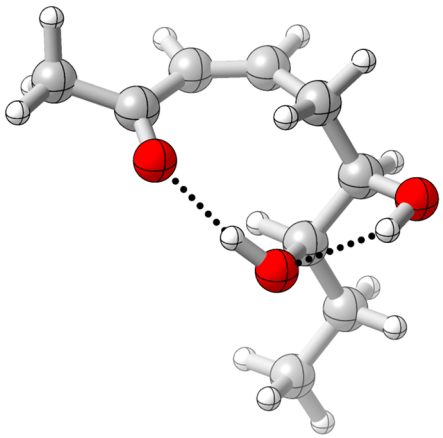
Minimised geometry using ωB97X-D/6-31G*/C-PCM (DCM)

SCF energy using ωB97X-V/6-311+G(2df,2p)/C-PCM (DCM) = -578.2949199 hartrees

Cartesian coordinates

Atom	X	Y	Z
H	4.0308749304	0.5759161626	1.6575983970
C	3.9123060203	-0.3240598732	1.0432754575
H	4.6739536247	-0.2784942857	0.2568652040
H	4.0624545228	-1.2127776800	1.6578897124
C	2.5356749166	-0.3379377307	0.4272734885
O	1.7525114360	-1.2508333462	0.6744269316
C	2.2199860217	0.8063075940	-0.4569793350
H	2.8551670212	1.6791806932	-0.3241329130
C	1.2967638170	0.8290568454	-1.4312239646
H	1.2142762744	1.7548014892	-2.0004183304

C	0.3682789552	-0.2619592697	-1.8611384192
H	0.3790871676	-0.3157954112	-2.9555309468
H	0.6849420261	-1.2329648799	-1.4724765475
C	-1.0985051298	-0.0096691414	-1.4447902864
H	-1.4300416134	0.9501234966	-1.8583111329
C	-1.2875412039	-0.0015688855	0.0815592141
H	-0.5627361803	0.6940787295	0.5289362764
C	-2.6936844916	0.4273460447	0.4847317714
H	-3.4139102294	-0.2567531744	0.0214014329
H	-2.8801522868	1.4211761217	0.0595526163
C	-2.8929542636	0.4617006500	1.9979334446
H	-2.7246469993	-0.5273750410	2.4327083509
H	-3.9089647753	0.7797778854	2.2527044238
H	-2.1917785850	1.1608577227	2.4699619149
O	-1.9225852010	-1.0108195036	-2.0135575006
H	-1.8259642148	-1.7691533657	-1.4132344997
O	-1.0600619225	-1.3199914597	0.5670814844
H	-0.0927496378	-1.4301703872	0.6178937559



Optimised structure of *cis*-5 of conformer A (gas)

Minimised geometry using ωB97X-D/6-31G*

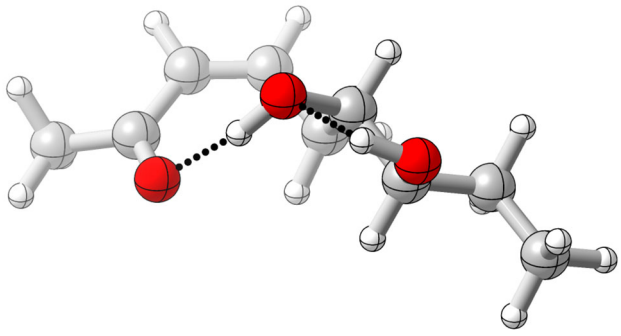
SCF energy using ωB97X-V/6-311+G(2df,2p) = -578.2814435 hartrees

Cartesian coordinates

Atom	X	Y	Z
H	3.9735906722	0.6754845422	1.6577884256
C	3.8514756574	-0.2634913723	1.1062687115
H	4.6491311776	-0.3015351271	0.3553564331
H	3.9480134007	-1.1080696500	1.7887869021

C	2.4998943207	-0.2990077102	0.4277927558
O	1.7096087731	-1.1994731296	0.6731667996
C	2.2294517412	0.8070893669	-0.5190192888
H	2.8829358338	1.6716567288	-0.4214620497
C	1.3189509166	0.8029901449	-1.5055486969
H	1.2705980769	1.7021668915	-2.1213233830
C	0.3624838123	-0.2790565271	-1.8892387368
H	0.3444202359	-0.3639204871	-2.9808837588
H	0.6685286094	-1.2437643265	-1.4798433603
C	-1.0959735185	0.0033578173	-1.4512193539
H	-1.4064580972	0.9807176530	-1.8411724154
C	-1.2658374883	-0.0230239211	0.0785897676
H	-0.5006237306	0.6161816383	0.5431031065
C	-2.6465933849	0.4612447681	0.5082417453
H	-3.3991576326	-0.1522726113	0.0009067607
H	-2.7797076213	1.4891118487	0.1458000340
C	-2.8439343398	0.4055751120	2.0201025799
H	-2.7067708400	-0.6161804098	2.3821053701
H	-3.8479385137	0.7422290641	2.2987232298
H	-2.1191755809	1.0460439488	2.5365857715
O	-1.9450607901	-0.9605426976	-2.0287160593
H	-1.8920811375	-1.7163441911	-1.4199988451
O	-1.1074327140	-1.3661739274	0.5117237317
H	-0.1523378390	-1.5109934365	0.6233838233

Minimised structure, SCF energy and coordinate for *cis*-**5** of conformer **B**



Optimised structure of *cis*-5 of conformer B (Solvent: DCM)

Minimised geometry using ωB97X-D/6-31G*/C-PCM (DCM)

SCF energy using ωB97X-V/6-311+G(2df,2p)/C-PCM (DCM) = -578.2939004 hartrees

Cartesian coordinates

Atom	X	Y	Z
H	1.9272281461	-2.1953816264	4.0753383385
C	1.8676282677	-2.7569142369	3.1421522700
H	2.8734241534	-2.9609415888	2.7585314675
H	1.3904625484	-3.7272783639	3.3248122969
C	1.0675446337	-1.9909007710	2.1208445655
O	0.5595759764	-0.9081466244	2.4060757665
C	0.9305302761	-2.6242579683	0.7906569425
H	1.0777780858	-3.7014941410	0.7664878542
C	0.7245797326	-1.9718993043	-0.3636466786
H	0.6657741653	-2.5764864615	-1.2676651833
C	0.5869337361	-0.4916360421	-0.5647217129
H	1.1317683736	0.0566796964	0.2109771633
H	1.0241846759	-0.2287776026	-1.5326516702
C	-0.8799274557	-0.0308843041	-0.5508627165
H	-1.4206239655	-0.4773668164	-1.3951398751
C	-1.0140590046	1.4994075980	-0.6451509402
H	-0.3708427450	1.9398163763	0.1387662419
C	-0.6119911025	2.0731946773	-1.9969041898
H	-1.2089100675	1.5832095225	-2.7764923464
H	0.4371605931	1.8242669484	-2.1901556699
C	-0.7930028070	3.5887266404	-2.0740147894
H	-1.8404548270	3.8651984865	-1.9278414009
H	-0.4711120820	3.9710577851	-3.0478010049
H	-0.2003112877	4.0910136383	-1.3011836448
O	-1.5546334503	-0.4665466020	0.6210902473
H	-0.9003432521	-0.4621841878	1.3478680673
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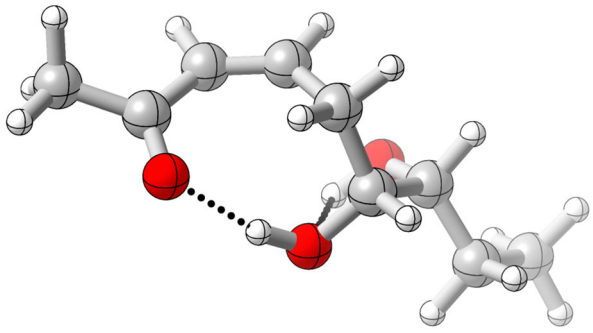


Optimised structure of *cis*-5 of conformer B (gas)

Minimised geometry using ωB97X-D/6-31G*

SCF energy using ωB97X-V/6-311+G(2df,2p) = -578.2804375 hartrees

Cartesian coordinates

Atom	X	Y	Z
H	2.1165188725	-3.8454708922	-2.1398241602
C	2.2529334898	-2.9156863029	-2.7048742248
H	3.3271311562	-2.6925414268	-2.7067075457
H	1.8987515703	-3.0566736302	-3.7269472751
C	1.4789066261	-1.7997366348	-2.0409068420
O	0.5564427223	-1.2509327359	-2.6347305522
C	1.9015557812	-1.4384867677	-0.6733506250
H	2.4836902178	-2.1902227526	-0.1448362194
C	1.6934505042	-0.2513878691	-0.0804124588
H	2.0824051965	-0.1292089166	0.9269239262
C	1.0036694796	0.9467033138	-0.6650613828
H	1.4819003147	1.8565577695	-0.2849774504
H	1.1067907526	0.9466872140	-1.7545505179
C	-0.5021200563	1.0307607967	-0.3321259016
H	-0.8867856126	1.9385167886	-0.8236214612
C	-0.7810710779	1.1304305225	1.1744435496
H	-0.1096654140	1.8786912258	1.6166119116
C	-2.2321161517	1.5311006754	1.4580376033
H	-2.8916637827	0.8034173498	0.9700528903
H	-2.4284765770	2.5021963357	0.9844508294
C	-2.5333435333	1.6038104379	2.9515545571
H	-2.3071989781	0.6476000456	3.4301050908
H	-3.5861321605	1.8430877543	3.1313417592
H	-1.9246254166	2.3737470206	3.4403769970
O	-1.2023891105	-0.1089379928	-0.7811655408
H	-0.7273930566	-0.4786308768	-1.5479493433
O	-0.4545193272	-0.1057482297	1.7841885335
H	-0.8166464285	-0.7696422221	1.1739538533

Excited state calculations for ES-A, ES-B and ES-C

Initial candidates for the first excited state conformers were generated by calculation of ground states with two unpaired electrons with Hartree-Fock (HF) theory with 3-21G basis set for each conformer of *trans*-**6** generated by the aforementioned method of DFT calculation. The conformers up to the

fifth lowest energy were tentatively designated as stable conformers. The structure optimisation of the first excited state was calculated using DFT employing ωB97X-D functional and 6-31G* basis function with CONVERGE as a keyword option. Solvent effect correction is approximated by C-PCM employing DCM as solvent (dielectric:8.82). Final energies were obtained by DFT calculation with ωB97X-V/6-311+G(2df,2p) with C-PCM solvation model (DCM) without geometry optimisation for all five conformers.

DFT calculations predicted structure ES-**A** to be the first excited states having the lowest energy, ES-**B** with the second lowest energy, and ES-**C** as the first excited states without hydrogen bond for carbonyl oxygen.

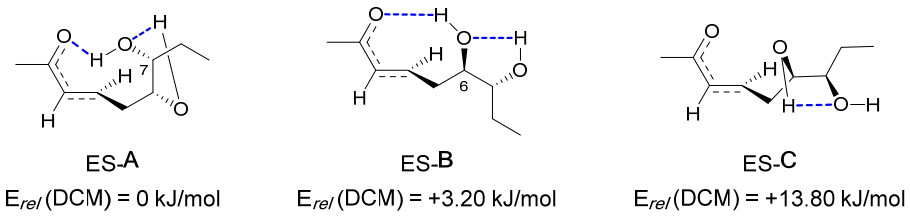
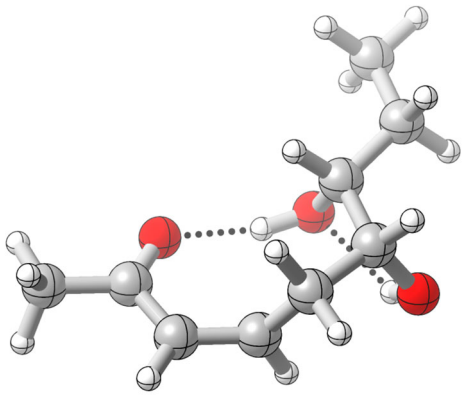


Figure S2. Relative energies of the first excited states, ES-**A,B** and **C**.

Minimised structure, SCF and CIS energies and coordinate for ES-**A**



Optimised structure of ES-A (Solvent: DCM)

Minimised geometry using ωB97X-D/6-31G*/C-PCM (DCM)

SCF energy using ωB97X-V/6-311+G(2df,2p)/C-PCM (DCM) = -578.1784593 hartrees

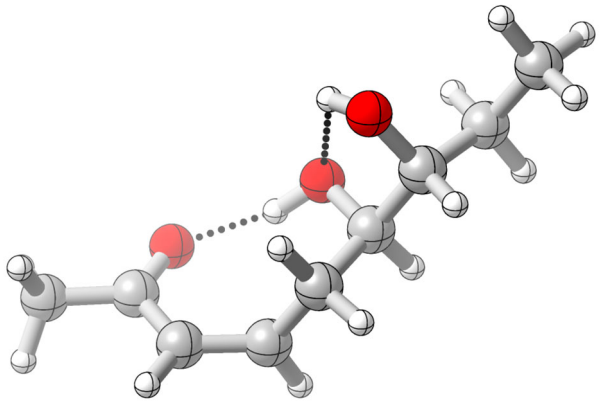
CIS energy using ωB97X-V/6-311+G(2df,2p)/C-PCM (DCM) = -578.1878670 hartrees: first excited state (singlet)

Cartesian coordinates

Atom	X	Y	Z
H	-0.3378122050	-1.7220500086	4.2426693345
C	-1.2318273002	-1.7552902879	3.6176633237
H	-1.4238807767	-2.7879319925	3.3076254595
H	-2.0979444092	-1.4255641852	4.2024297102
C	-1.0555665161	-0.8738209018	2.4058389649

O	0.0018384306	-0.2429923769	2.2272916273
C	-2.1281042528	-0.7753255844	1.4554518605
H	-3.0482835190	-1.3358331769	1.6382716081
C	-1.9733794680	0.0294553561	0.2681850034
H	-2.3444433506	1.0526017713	0.2596641073
C	-1.5346758188	-0.5503231239	-1.0401730508
H	-1.1365056058	-1.5619151942	-0.9032926601
H	-2.4132209670	-0.6365163299	-1.6982069884
C	-0.4884612318	0.3114753862	-1.7736468606
H	-0.3224446078	-0.1404146920	-2.7586366175
C	0.8581026413	0.3953431005	-1.0238735118
H	1.1014642668	-0.5940921043	-0.6100349586
C	1.9897679482	0.8455745522	-1.9418763342
H	1.7157000258	1.8155687154	-2.3752850065
H	2.0596526878	0.1338015942	-2.7738806137
C	3.3353415882	0.9470931489	-1.2285283574
H	3.2866660398	1.6728592517	-0.4121412678
H	4.1236046755	1.2608820949	-1.9205709640
H	3.6259573817	-0.0203489556	-0.8026901107
O	-0.9765473820	1.6237962813	-1.9897274907
H	-0.6782140973	2.1148200445	-1.2036132805
O	0.7347867463	1.3442451592	0.0299686353
H	0.3584290770	0.8749024573	0.8011184381

Minimised structure, SCF and CIS energies and coordinate for ES-**B**



Optimised structure of ES-B (Solvent: DCM)

Minimised geometry using ωB97X-D/6-31G*/C-PCM (DCM)

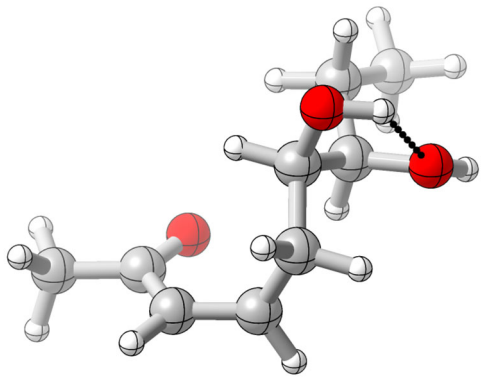
SCF energy using ωB97X-V/6-311+G(2df,2p)/C-PCM (DCM) = -578.1731052 hartrees

CIS energy using ωB97X-V/6-311+G(2df,2p)/C-PCM (DCM) = -578.1866478 hartrees: first excited state (singlet)

Cartesian coordinates

Atom	X	Y	Z
H	-4.4036309710	0.8062202817	2.0878752473
C	-4.5794059861	0.9045973592	1.0101766978
H	-5.3974887879	0.2263900529	0.7491718041
H	-4.8654474914	1.9347396913	0.7915014425
C	-3.3176285089	0.5464824944	0.2650739000
O	-2.6151490269	1.4294093529	-0.2582842685
C	-2.9178234090	-0.8321549207	0.1804259024
H	-3.5143368048	-1.5931695037	0.6882817224
C	-1.7344501764	-1.1880142672	-0.5669482350
H	-1.8312863336	-1.4513700274	-1.6197326130
C	-0.3702847998	-1.2650912121	0.0426885249
H	-0.4044181825	-1.0429323219	1.1133155295
H	0.0334639278	-2.2805996599	-0.0764967264
C	0.6081777421	-0.2873921606	-0.6328303618
H	0.6943238557	-0.5575836605	-1.6967413506
C	1.9983643366	-0.3504383307	0.0137073088
H	2.3046539297	-1.4008566239	0.0945868778
C	3.0466296384	0.4124911024	-0.8003512712
H	2.7255204872	1.4574537212	-0.8914679664
H	3.0671901791	-0.0038172237	-1.8158417991
C	4.4392549267	0.3409938472	-0.1792603202
H	4.4313405284	0.7572481157	0.8323944982
H	5.1666010973	0.9021250384	-0.7748062969
H	4.7859617328	-0.6973867541	-0.1135263141
O	0.1820921110	1.0571826886	-0.4968475391
H	-0.7926306891	1.0948427435	-0.5517591970
O	1.9081820157	0.1439221755	1.3431334797
H	1.3522246591	0.9367080020	1.2625613243

Minimised structure, SCF and CIS energies and coordinate for ES-**C**



Optimised structure of ES-C (Solvent: DCM)

Minimised geometry using ωB97X-D/6-31G*/C-PCM (DCM)

SCF energy using ωB97X-V/6-311+G(2df,2p)/C-PCM (DCM) = -578.1670260 hartrees

CIS energy using ωB97X-V/6-311+G(2df,2p)/C-PCM (DCM) = -578.1826094 hartrees: first excited state (singlet)

Cartesian coordinates

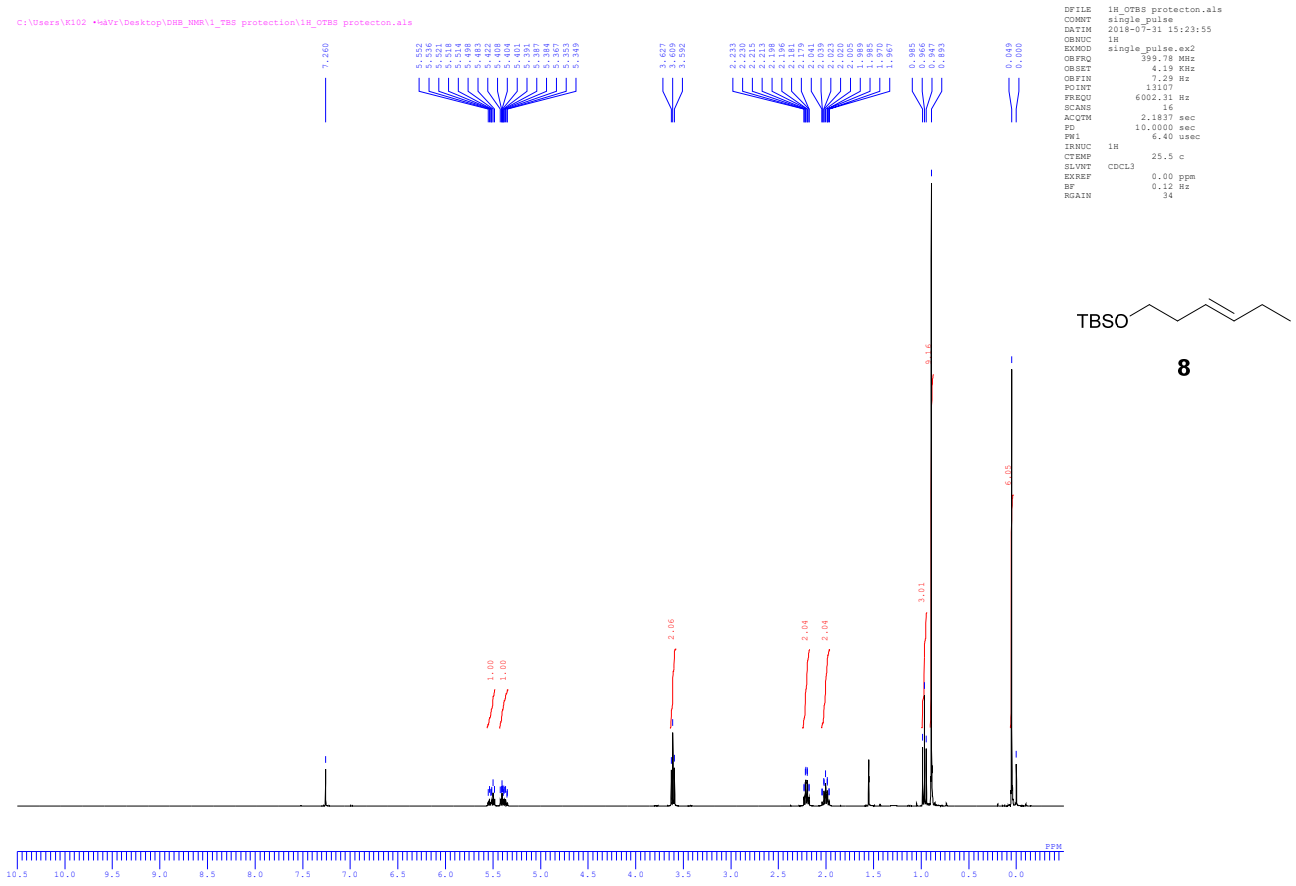
Atom	X	Y	Z
H	-2.1790408691	-4.1736142220	-0.7397611315
C	-1.8526863458	-3.3013134015	-1.3177621747
H	-1.1037975369	-3.6190994760	-2.0453198292
H	-2.7315486037	-2.9086006039	-1.8391685592
C	-1.2634336075	-2.2643003110	-0.3877329247
O	-0.0403581493	-2.0476948684	-0.3648316091
C	-2.1352796414	-1.5351622122	0.4879214985
H	-3.2089051683	-1.7422852283	0.4728248286
C	-1.5957712906	-0.5404232743	1.3933954007
H	-1.3800644777	-0.8254406752	2.4211796371
C	-1.5489781449	0.9067946398	1.0206263335
H	-2.5281519691	1.2259833489	0.6367299930
H	-1.3200260034	1.5164837480	1.9000492470
C	-0.5188451173	1.2294813947	-0.0850774512
H	-0.7080162696	0.5858804634	-0.9484536429
C	0.9212822514	1.0100342054	0.3873512590
H	0.9755473885	0.0308812366	0.8809374289
C	1.9147764033	1.0452821222	-0.7732456789
H	1.7677898960	1.9768873383	-1.3321852540
H	1.6627867624	0.2176111963	-1.4474503146
C	3.3717024903	0.9188654059	-0.3315614110
H	3.6839047719	1.7787332336	0.2715097872

H	4.0394455495	0.8708341525	-1.1974753228
H	3.5261279428	0.0106346227	0.2636291862
O	-0.6863476708	2.5642327088	-0.5342755093
H	-0.2358790265	3.1162999794	0.1228688470
O	1.1594867304	2.0536037820	1.3333492103
H	2.0142797048	1.8994106943	1.7519281560

NMR Spectra

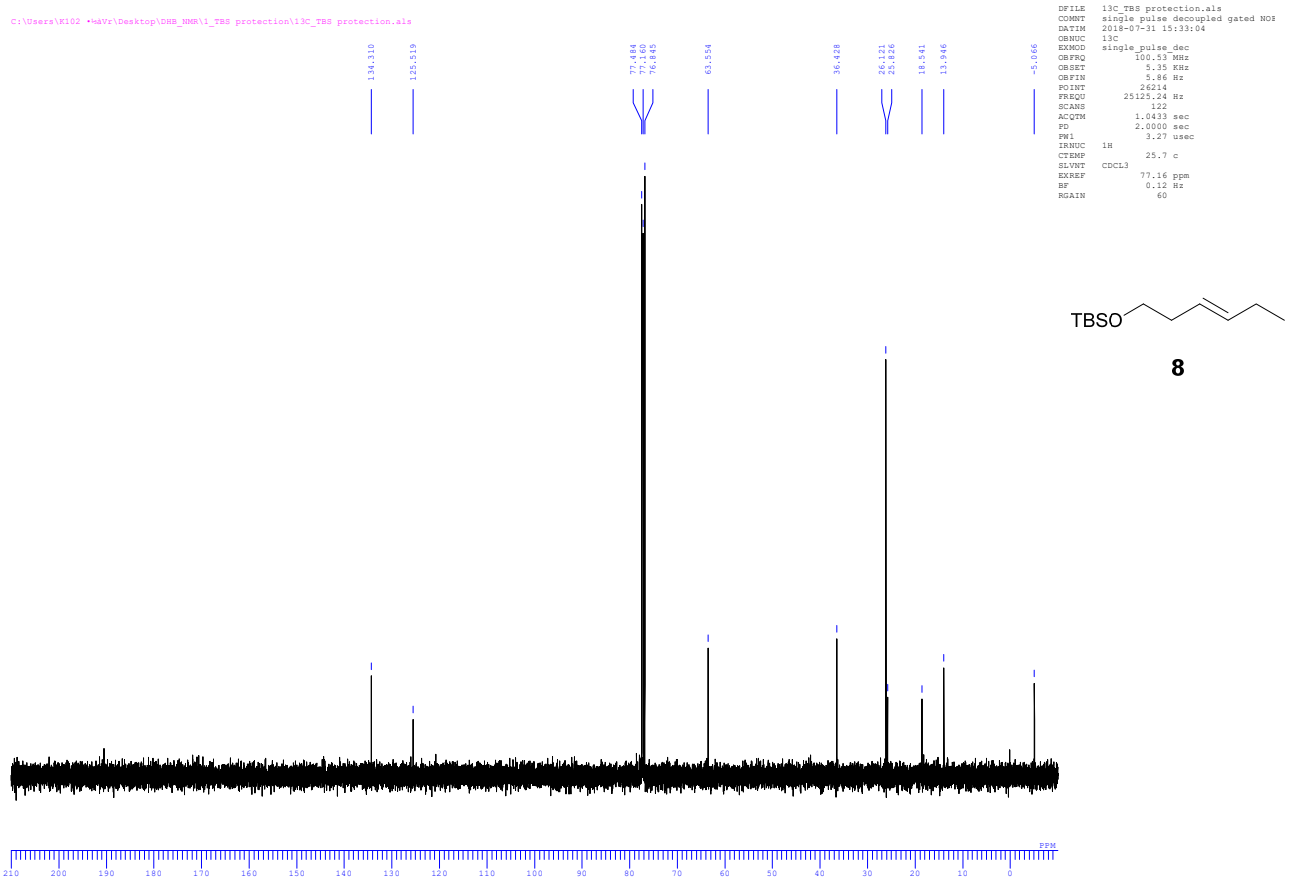
Compound **8**

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



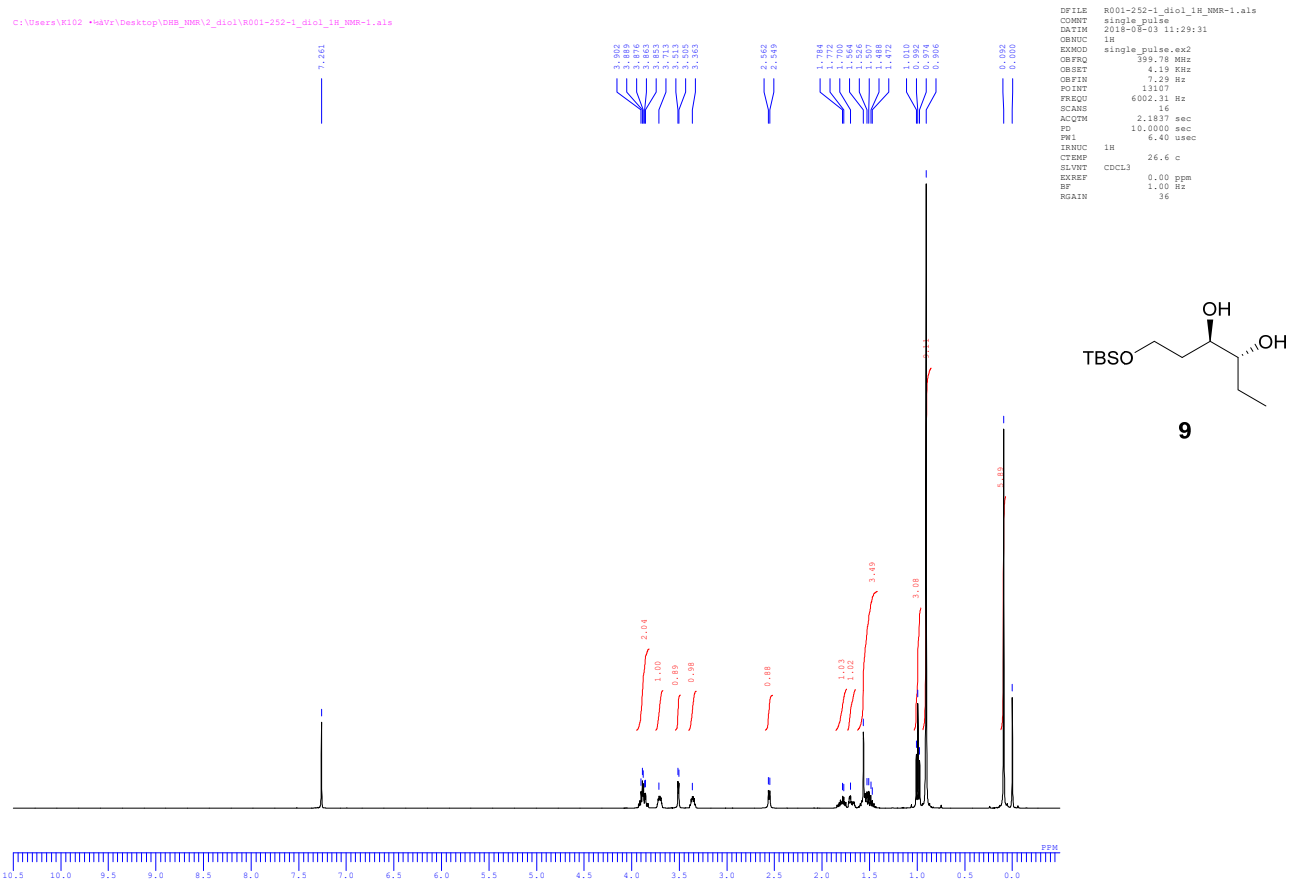
Compound **8**

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



Compound **9**

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

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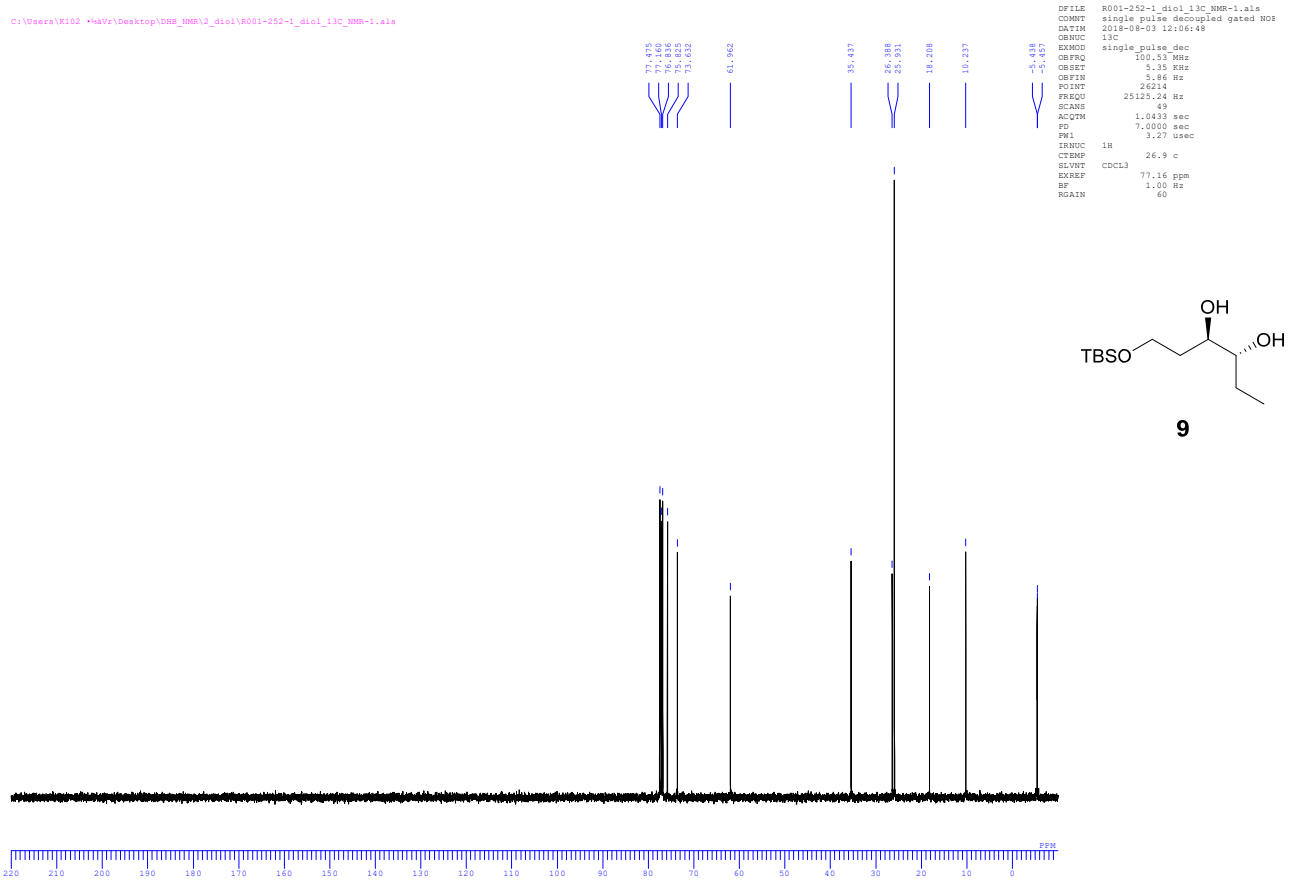
DATIM   2018-08-03 11:29:31
OBNUC   1H
EXMOD   single_pulse.ex2
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          13107
FREQU        6002.31 Hz
SCANS            16
ACQTM          2.1837 sec
PD            10.0000 sec
PW1            6.40 usec
IRNUC   1H
CTEMP          26.6 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             1.00 Hz
RGAIN            36
```


9

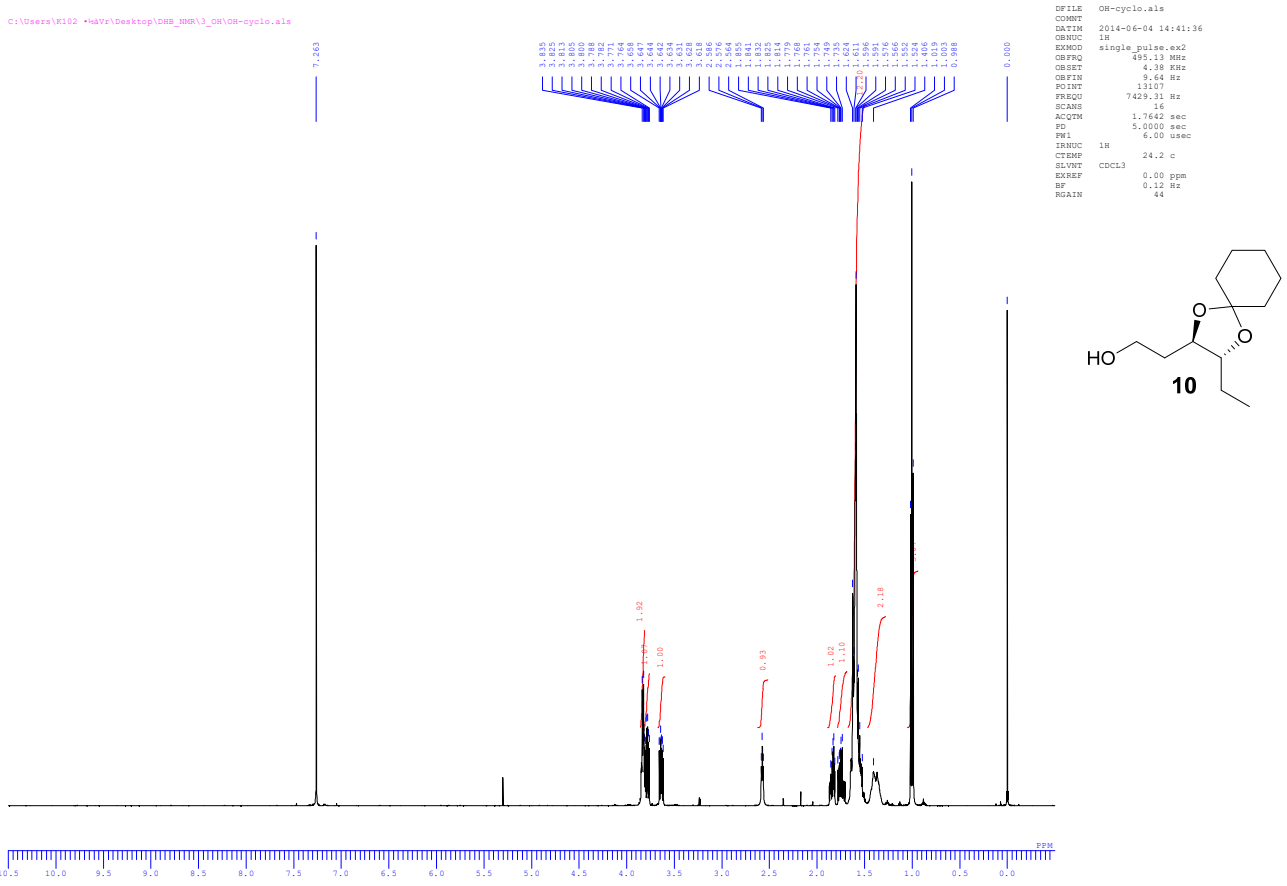
Compound **9**

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



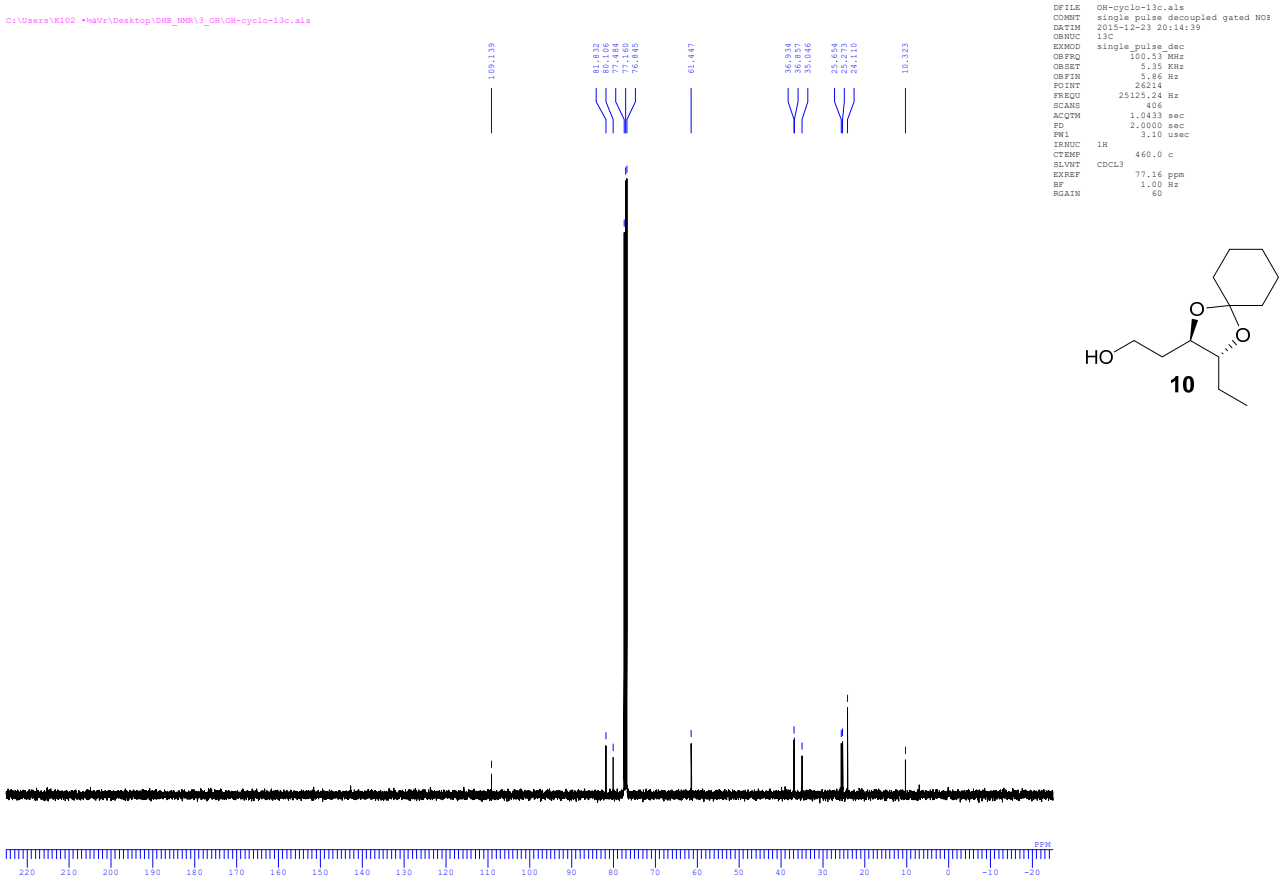
Compound **10**

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



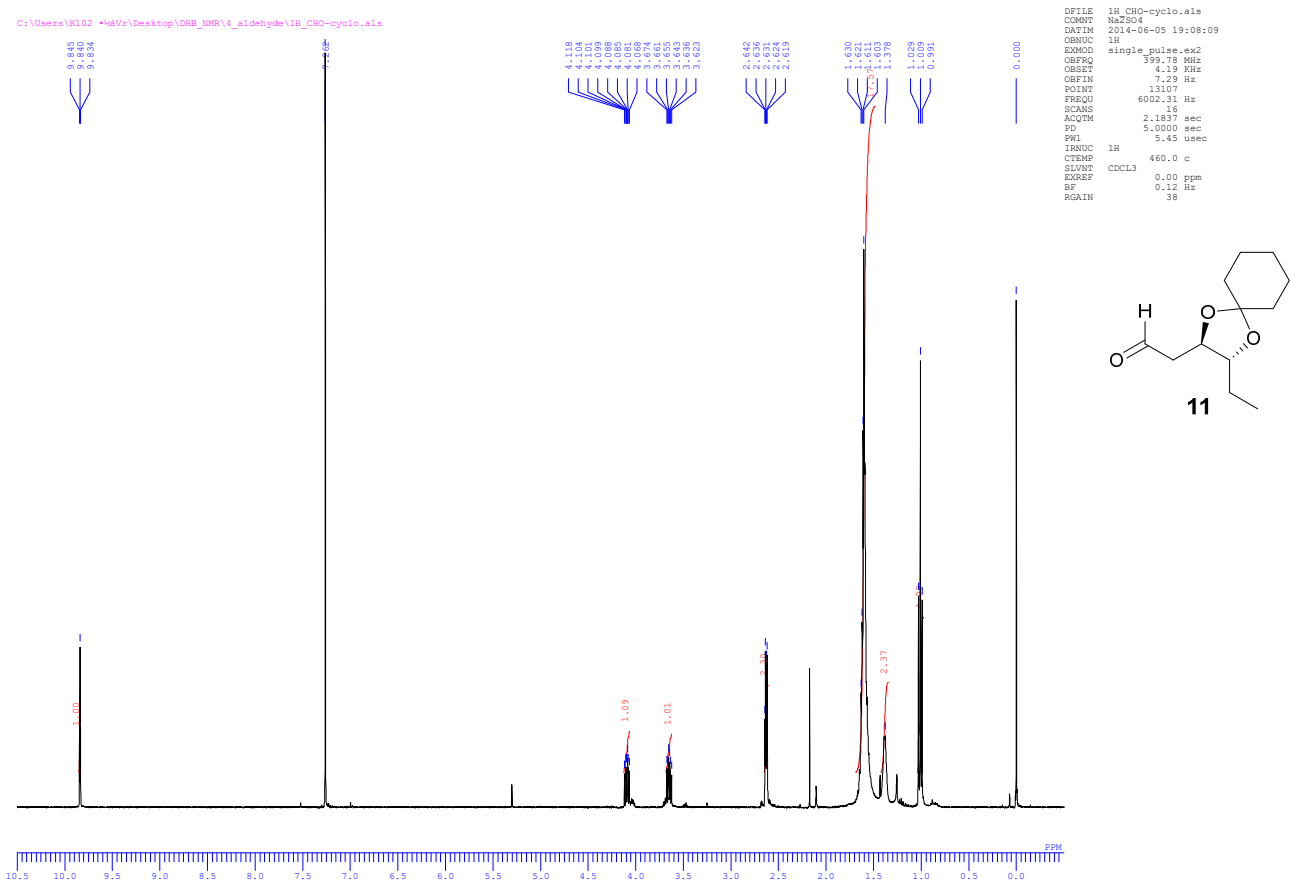
Compound **10**

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



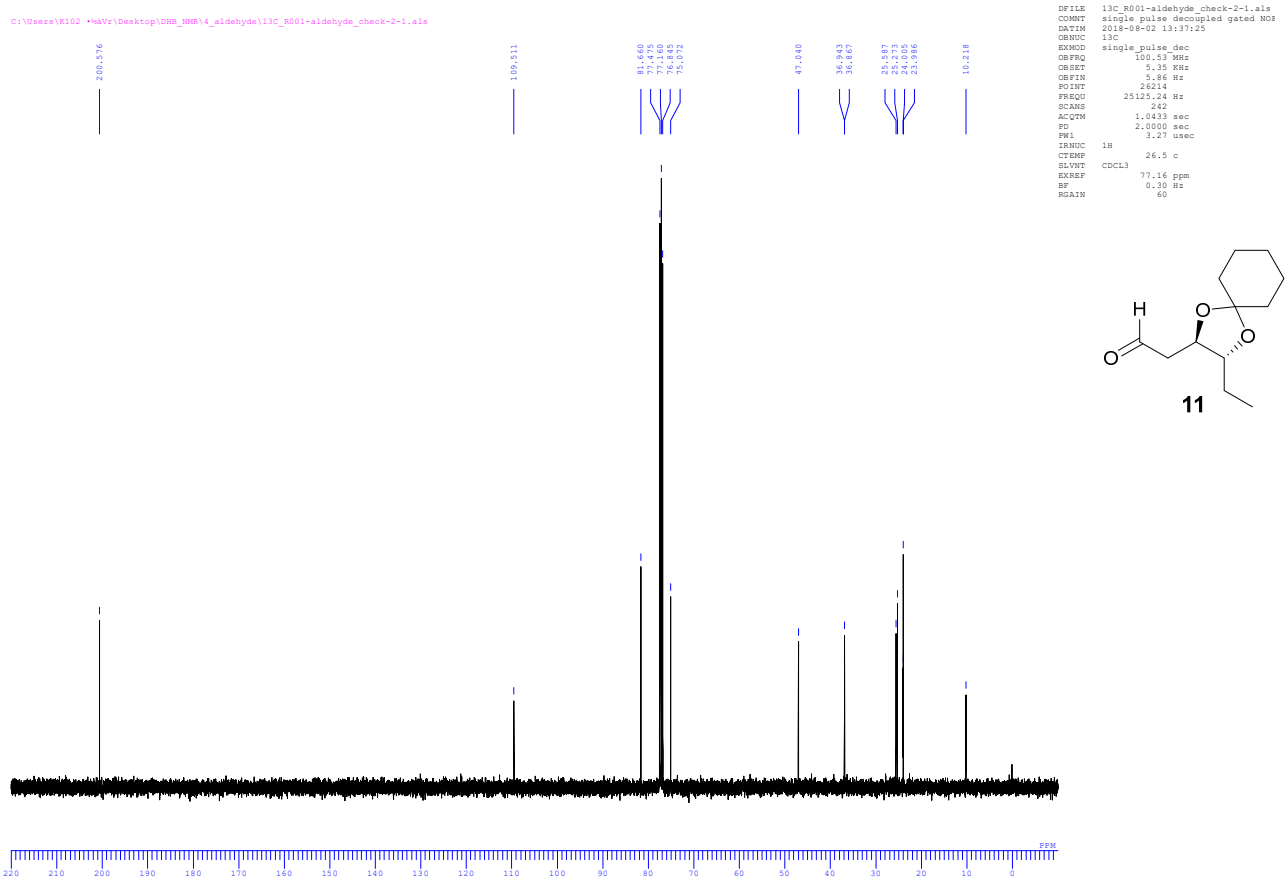
Compound **11**

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



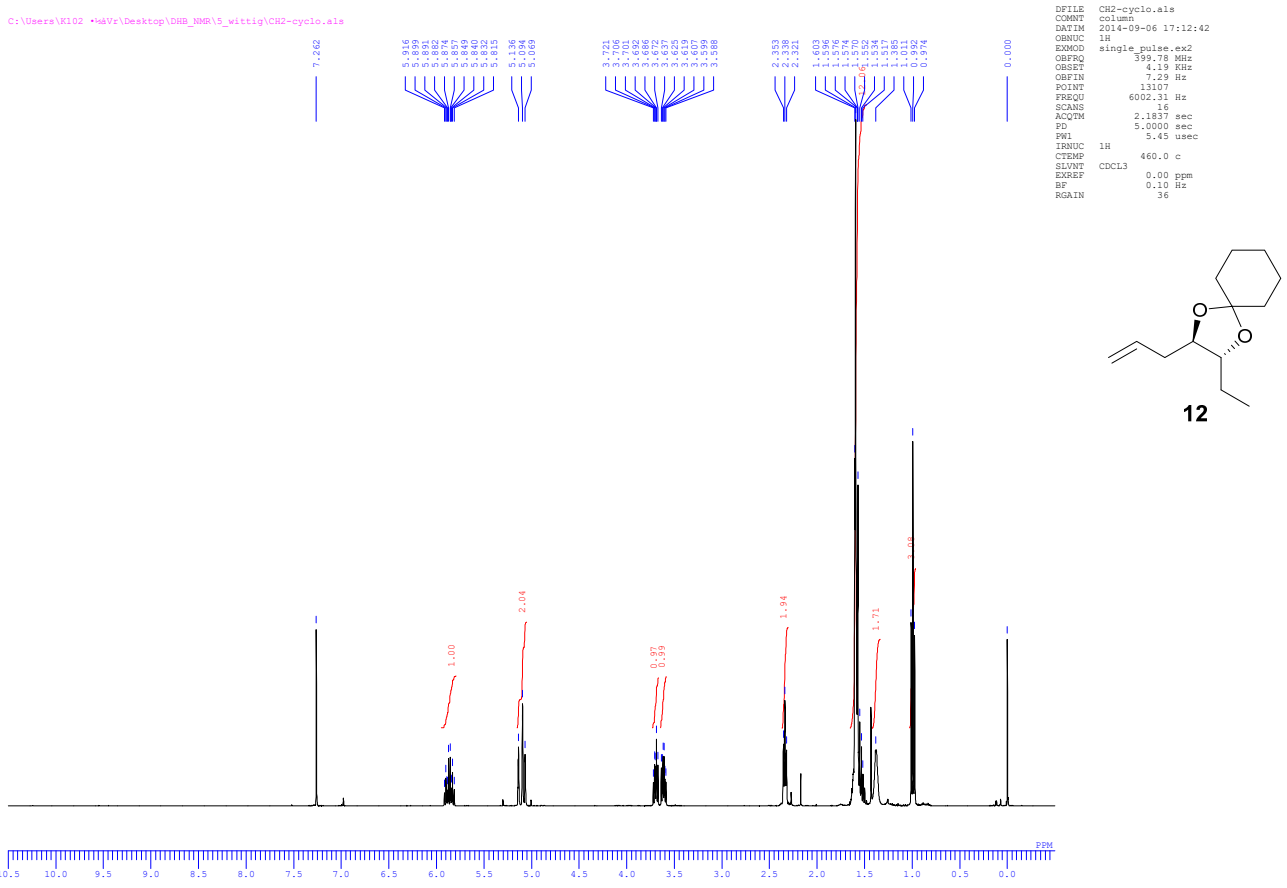
Compound **11**

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



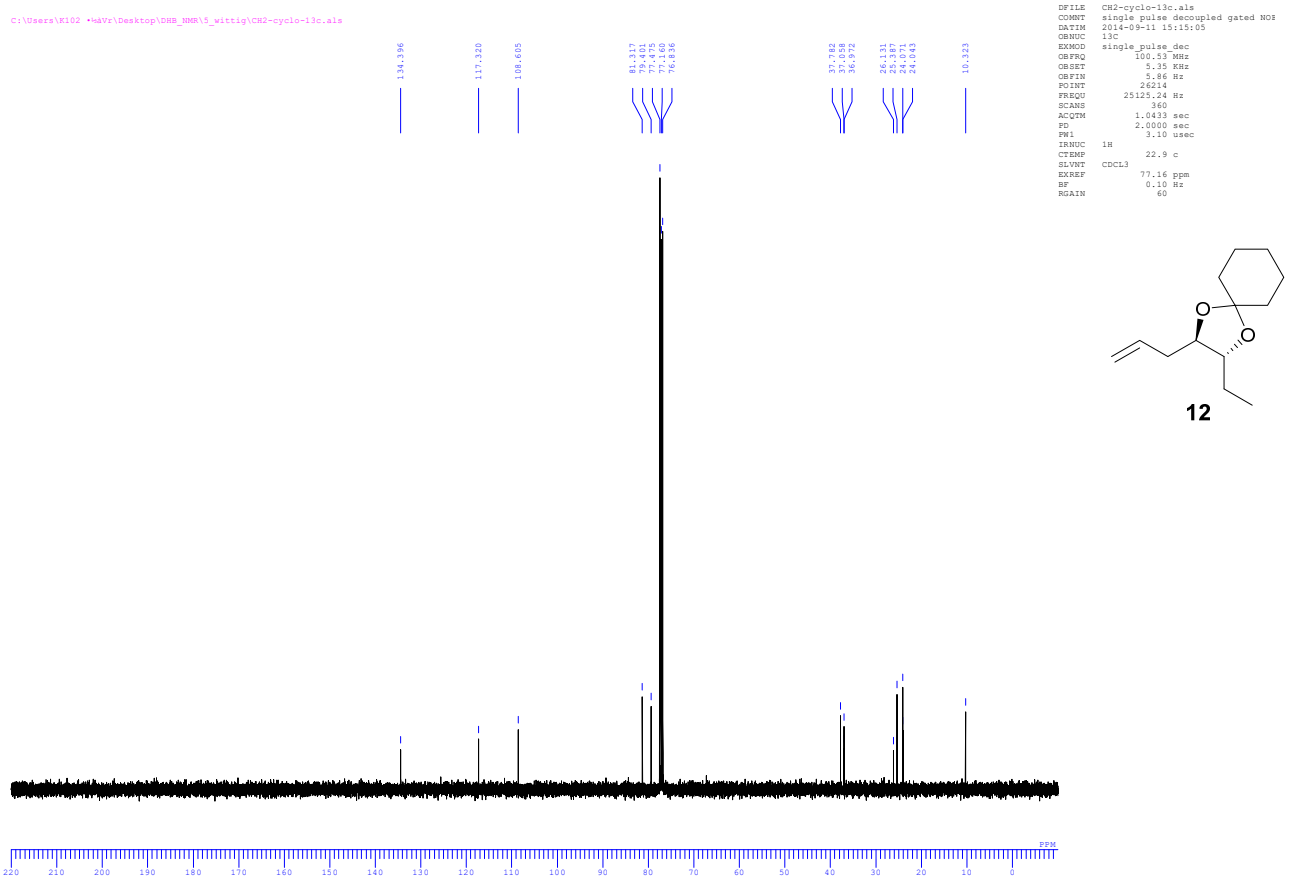
Compound **12**

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



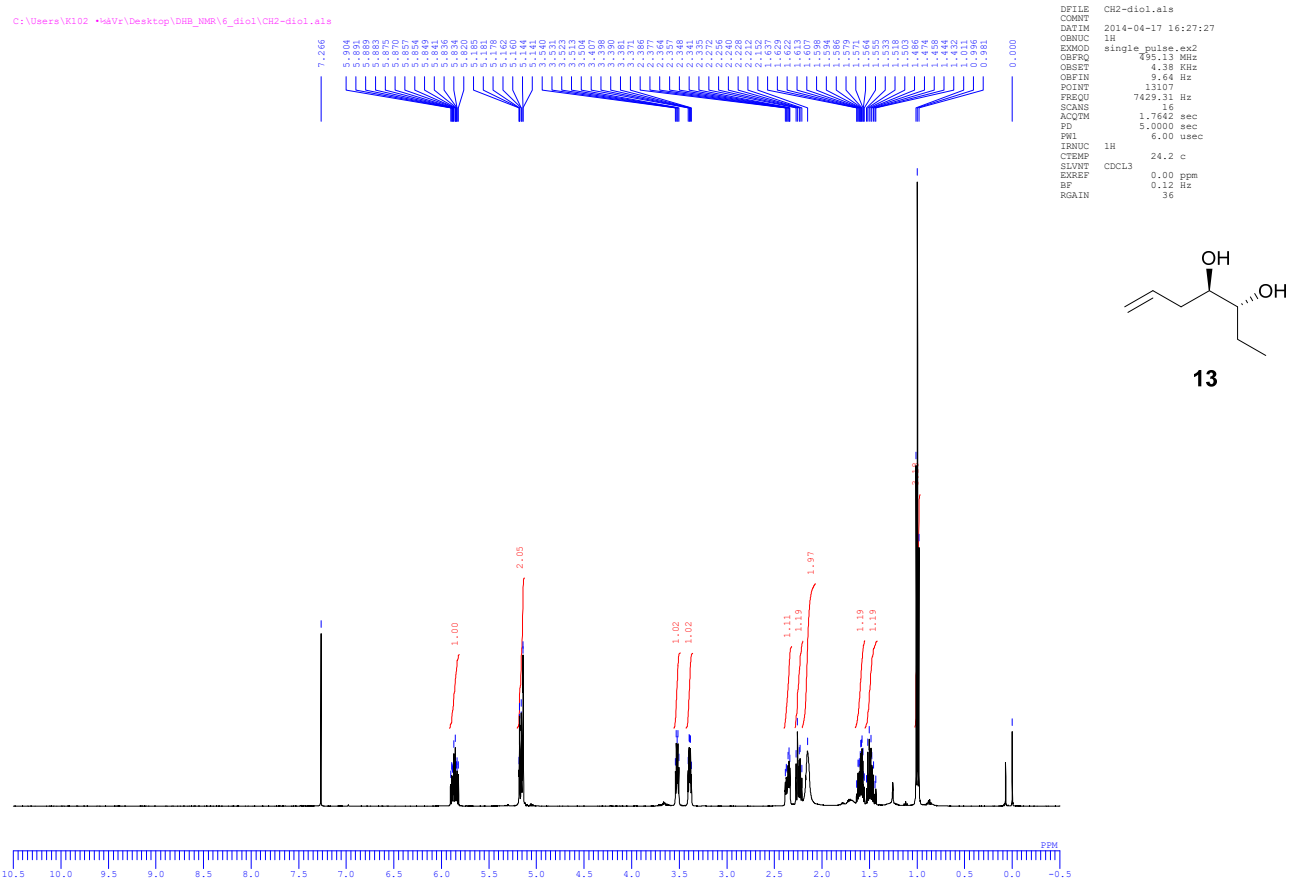
Compound **12**

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



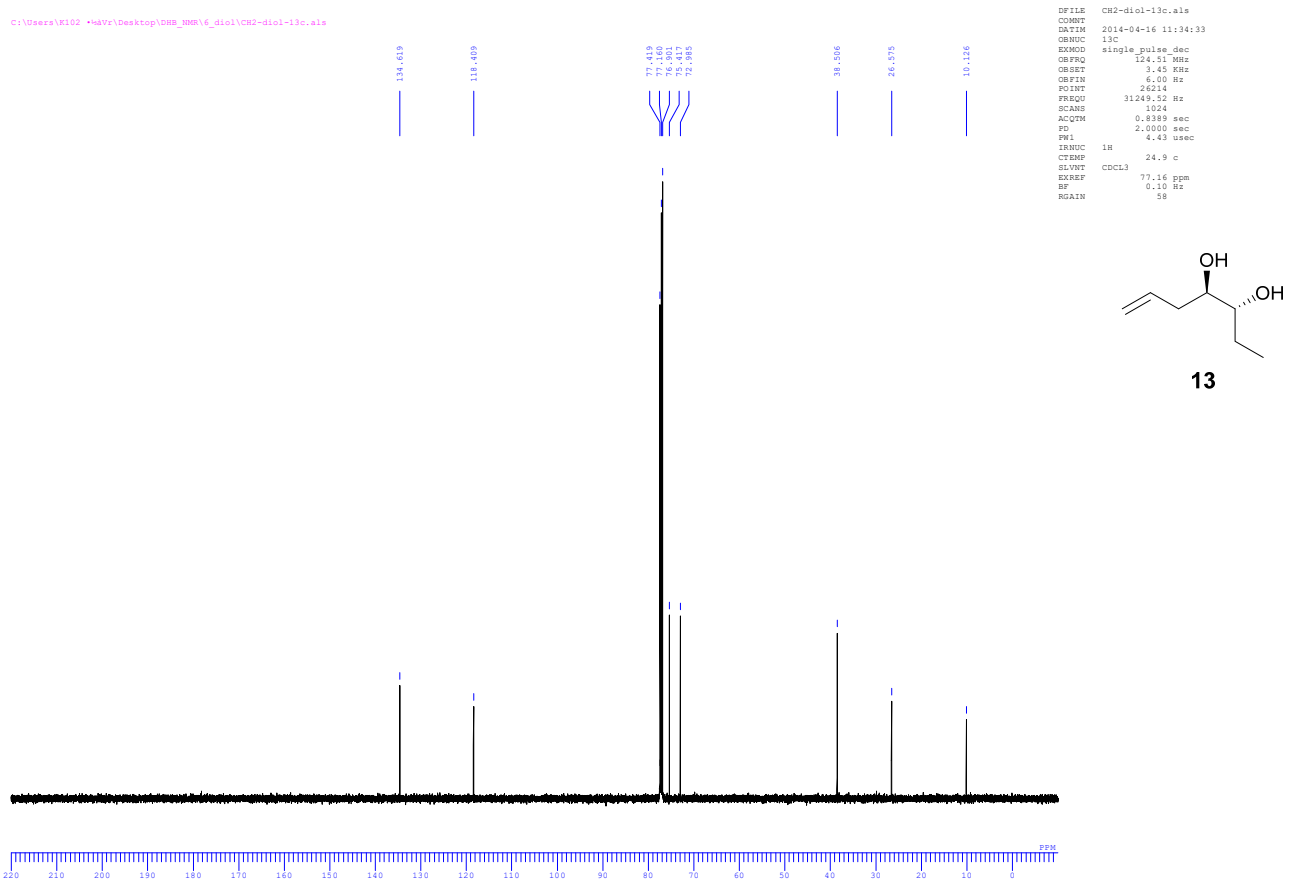
Compound **13**

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



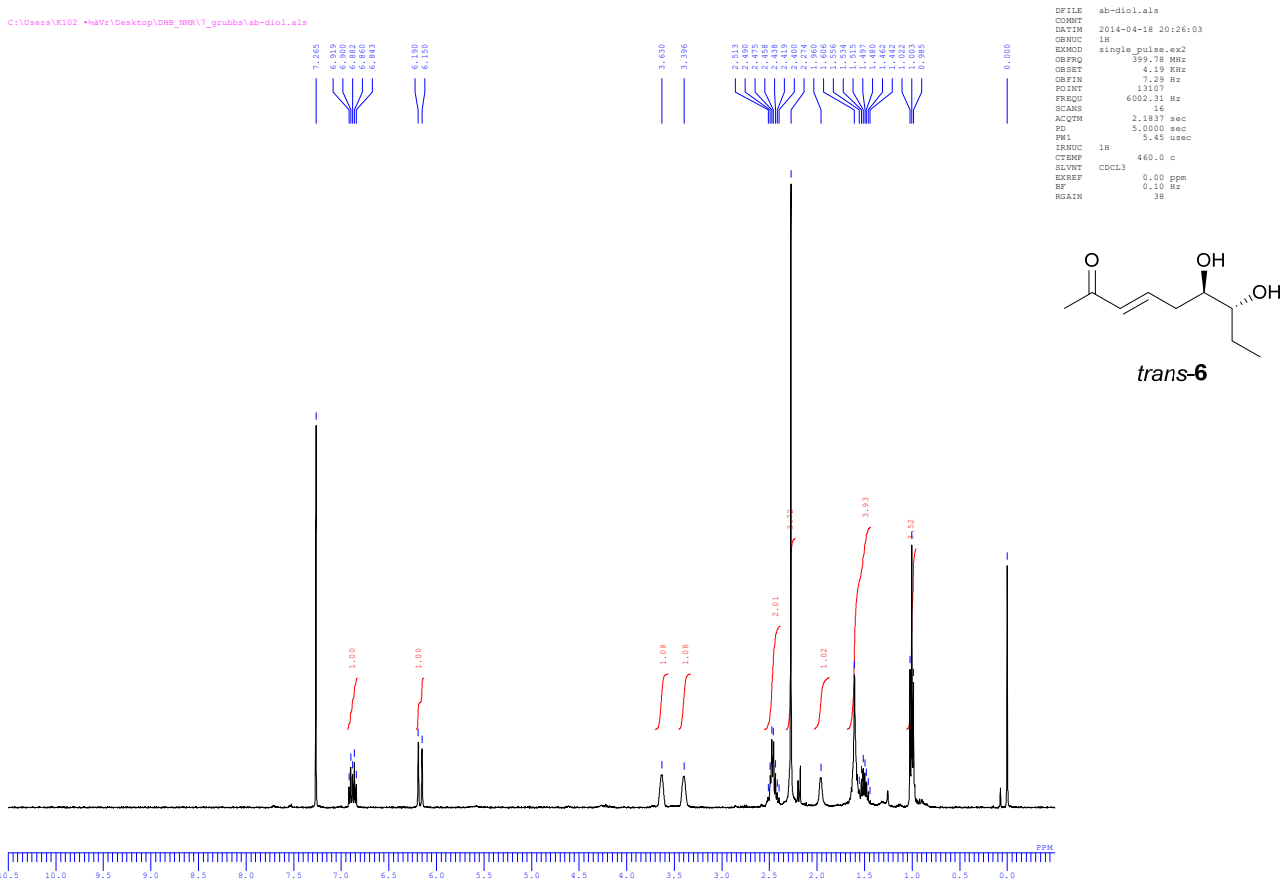
Compound **13**

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz)



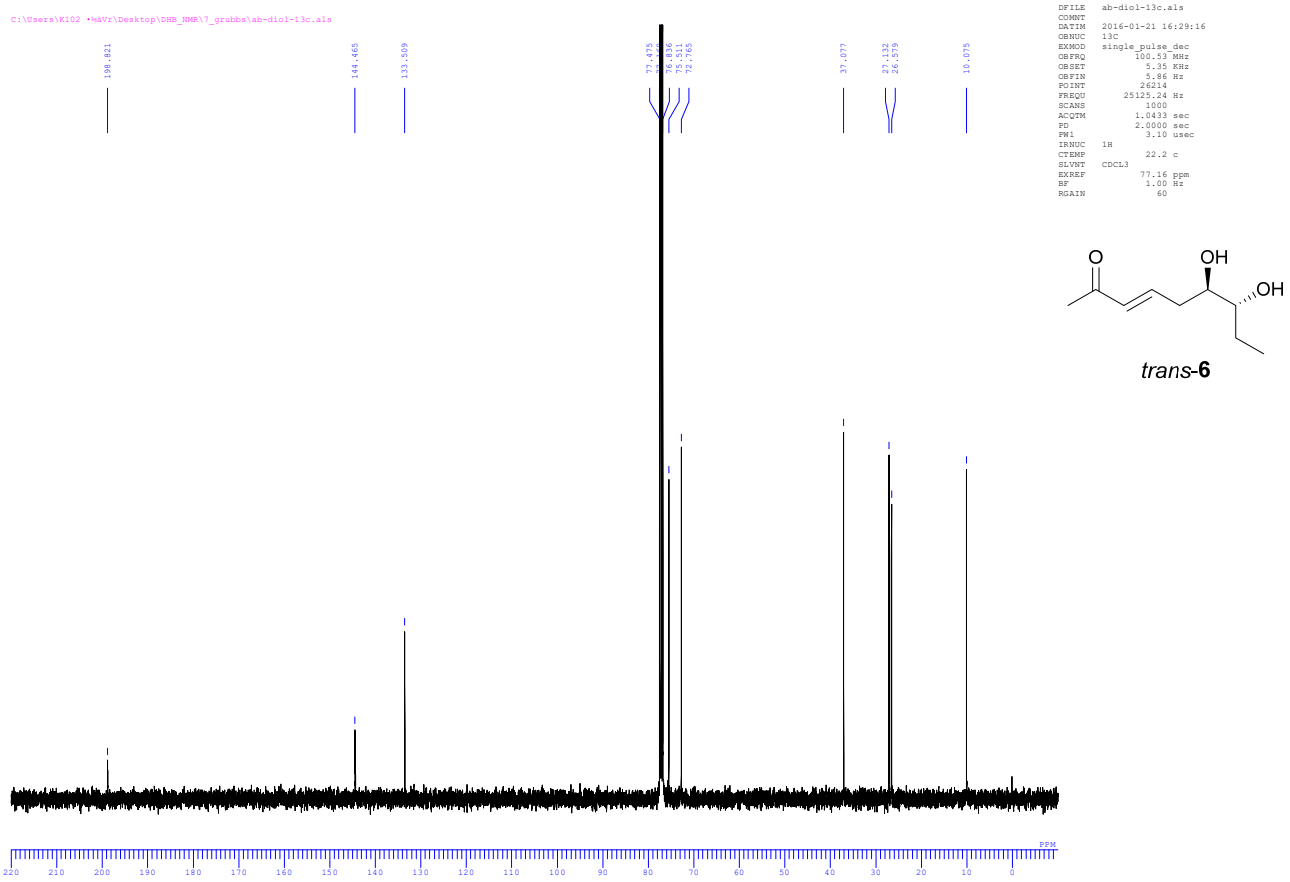
Compound *trans*-**6**

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



Compound *trans*-**6**

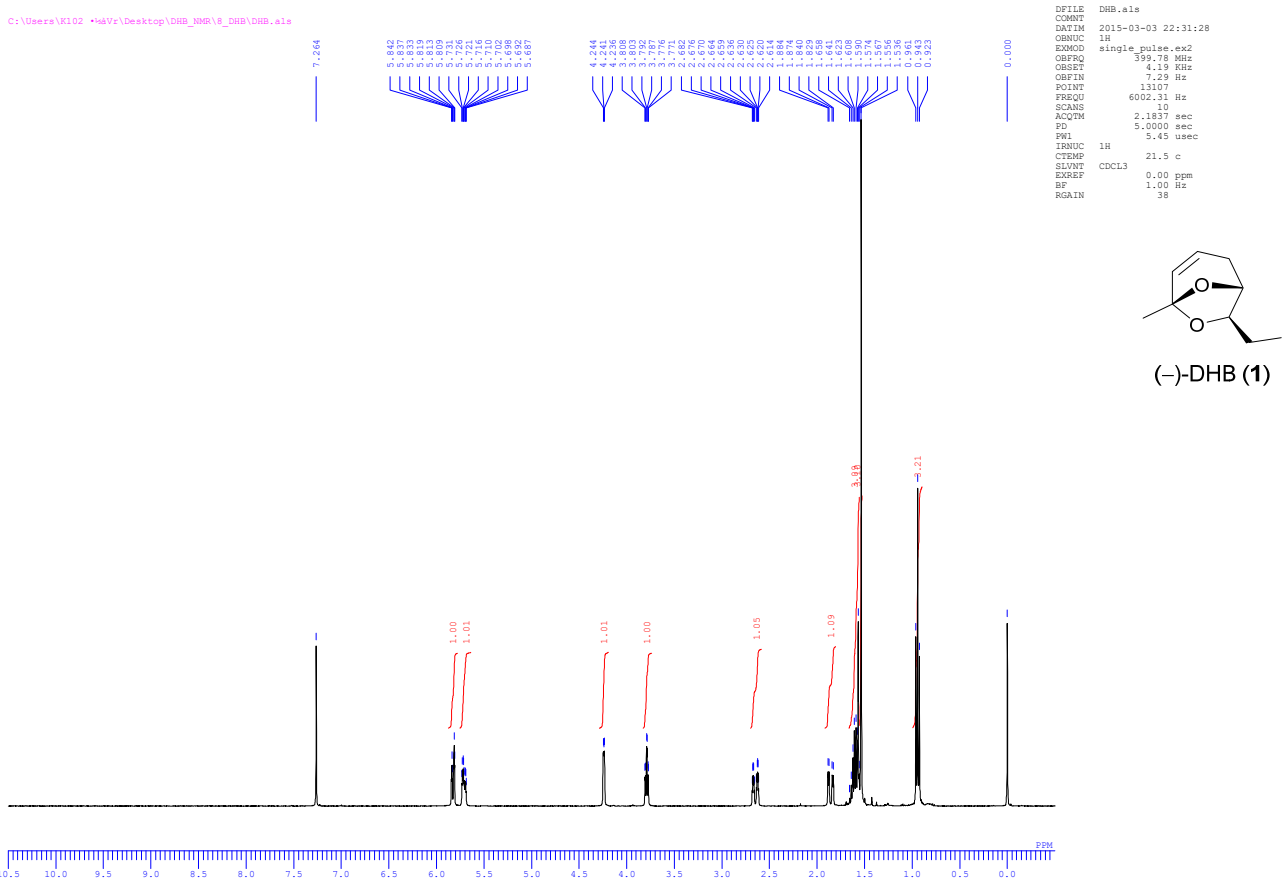
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



trans-**6**

Compound (−)-**1**

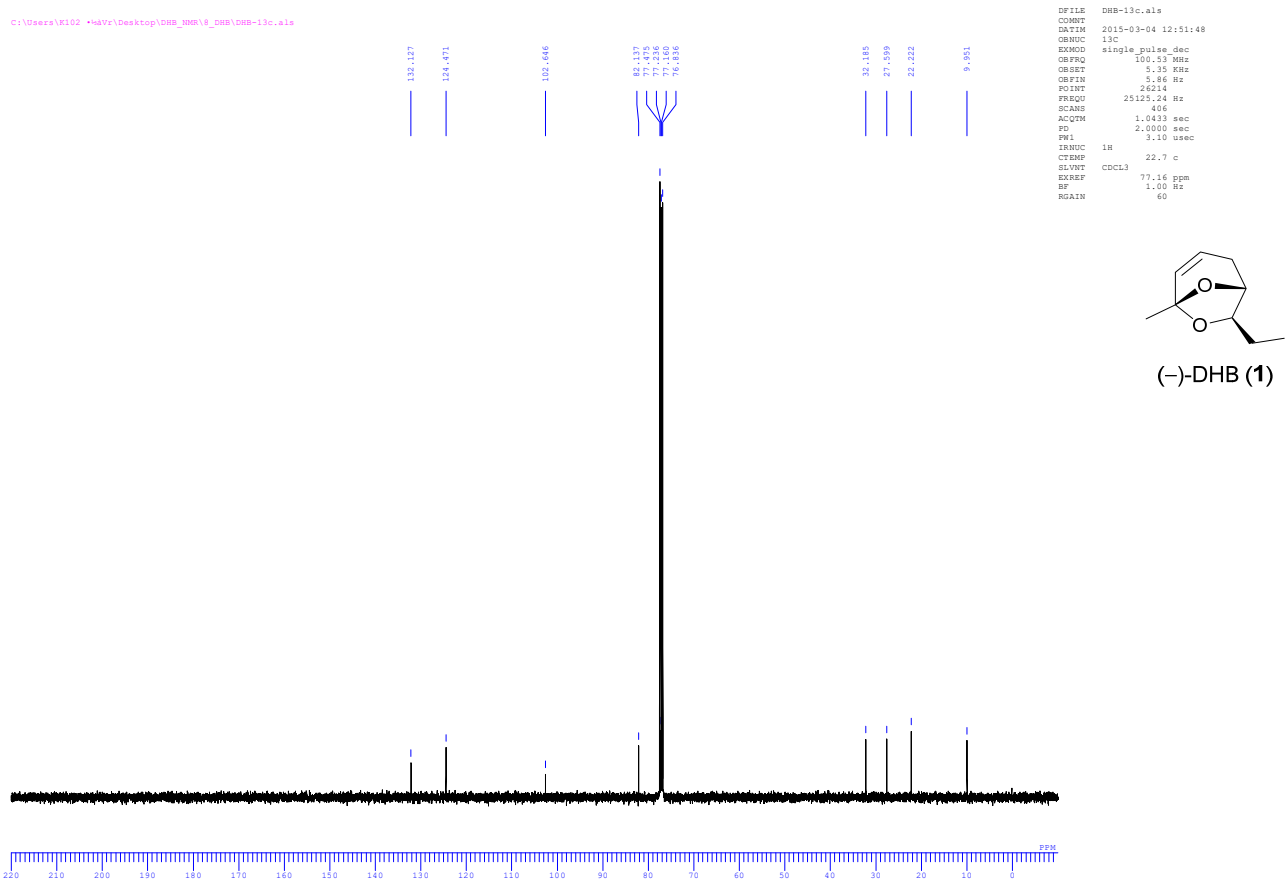
^{1}H NMR ($CDCl_3$, 400 MHz)



(−)-DHB (**1**)

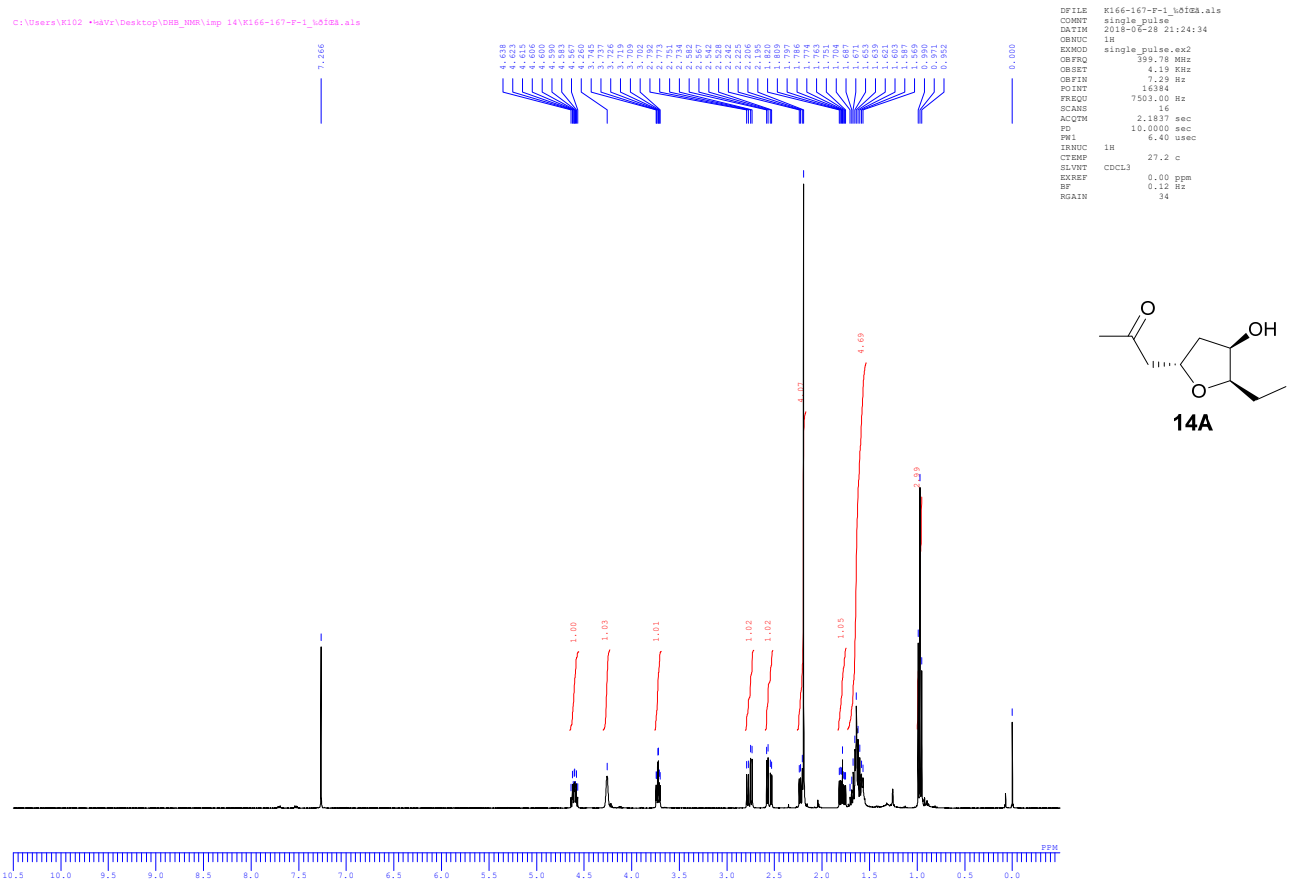
Compound (−)-**1**

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



Compound **14A**

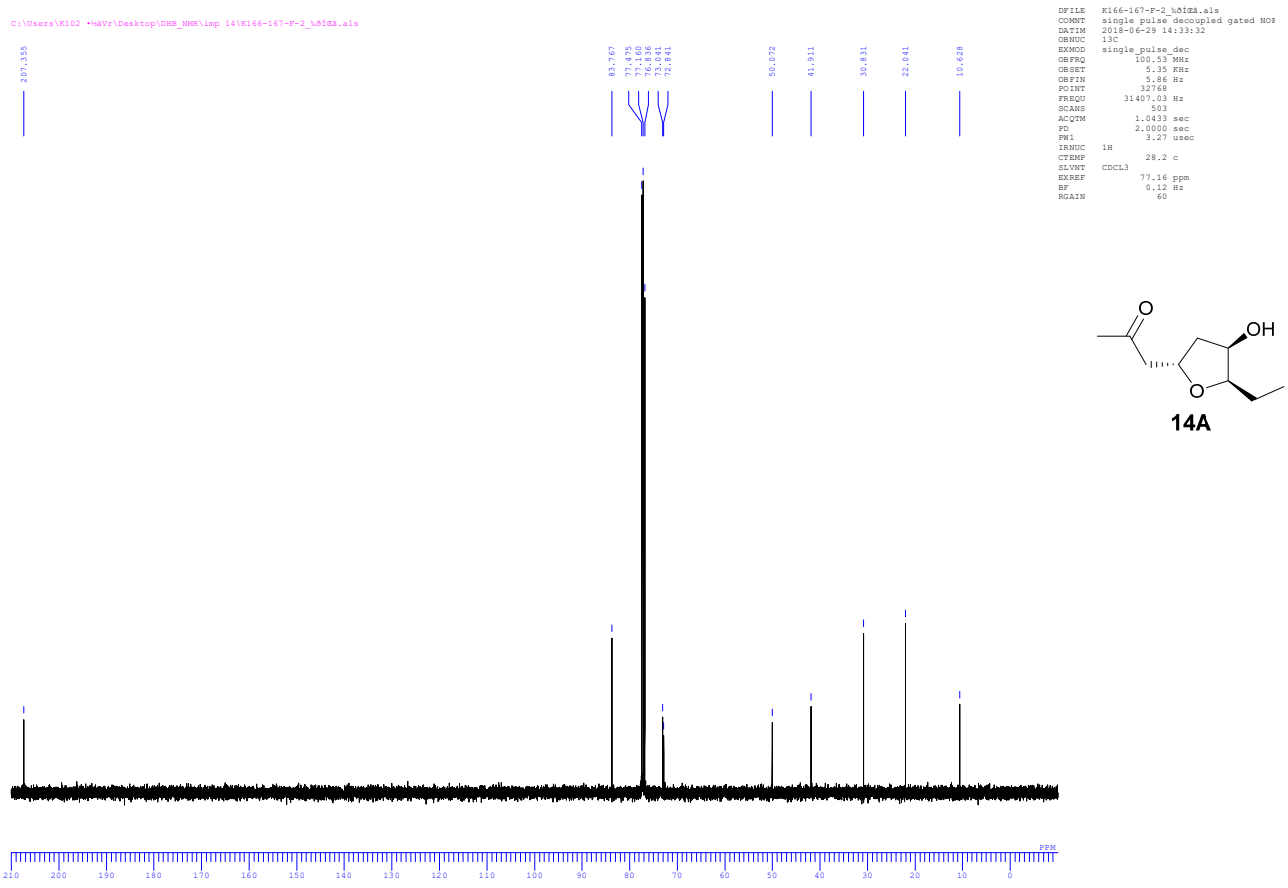
^{1}H NMR ($CDCl_3$, 400 MHz)



14A

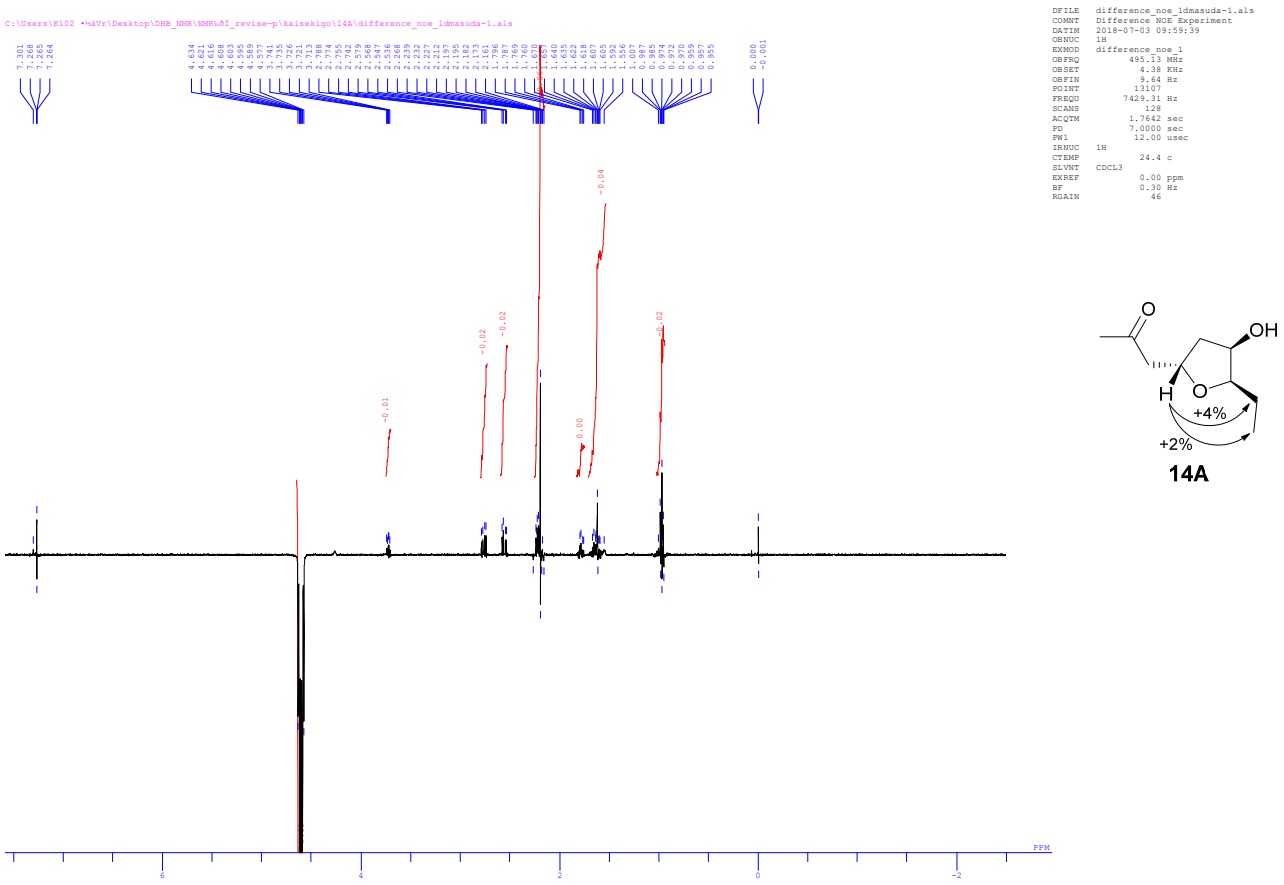
Compound **14A**

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



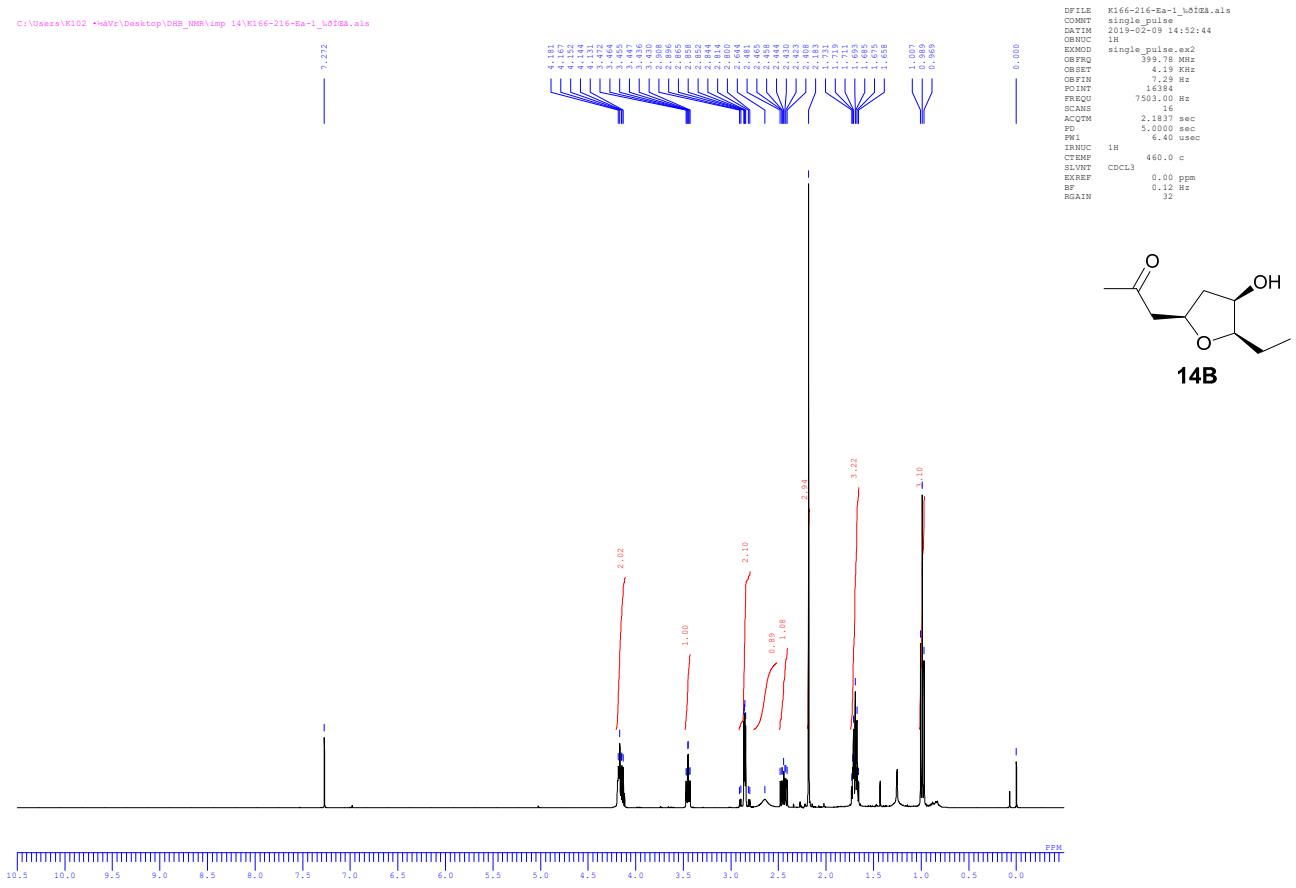
Compound **14A**

Difference NOE spectrum with irradiation of the proton at δ4.6 ($CDCl_3$, 500 MHz)



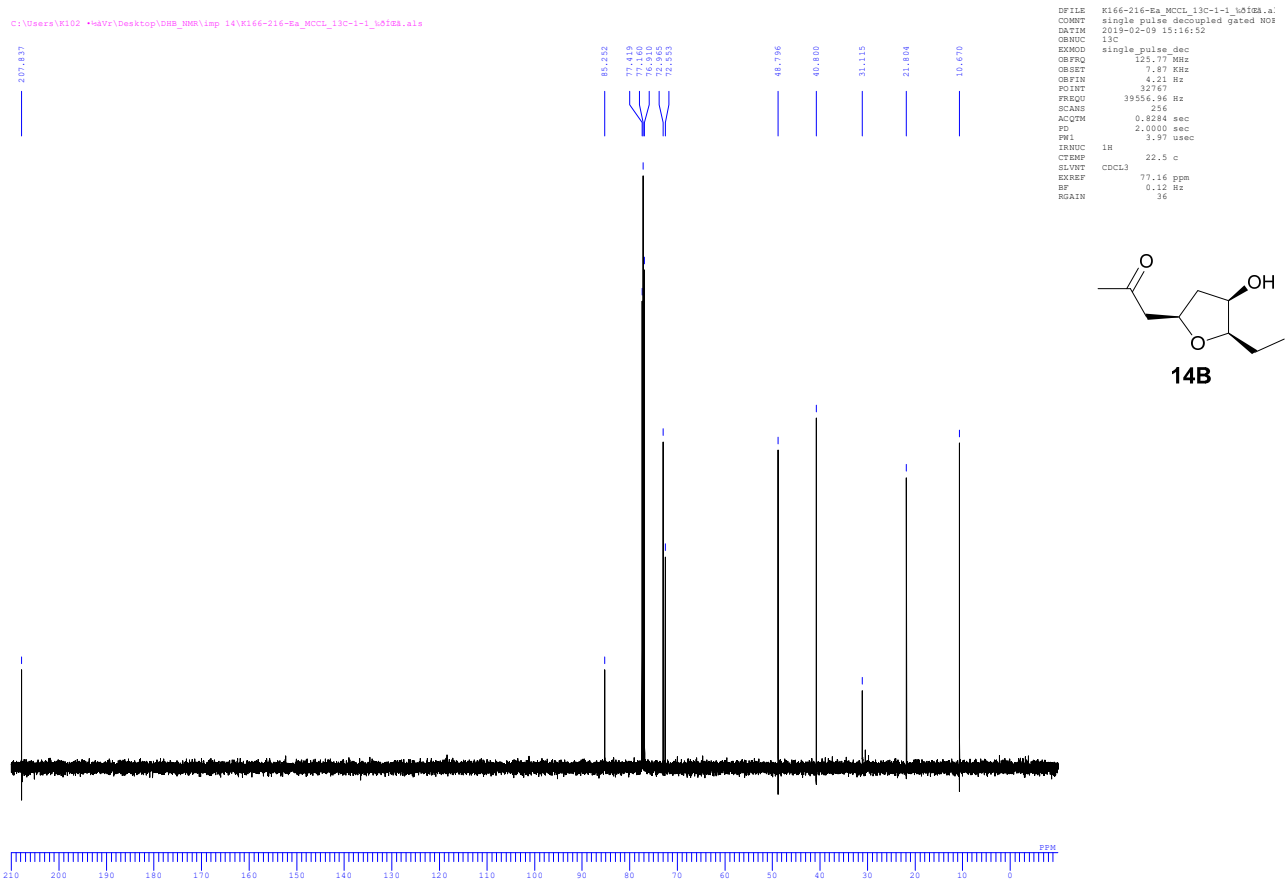
Compound **14B**

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



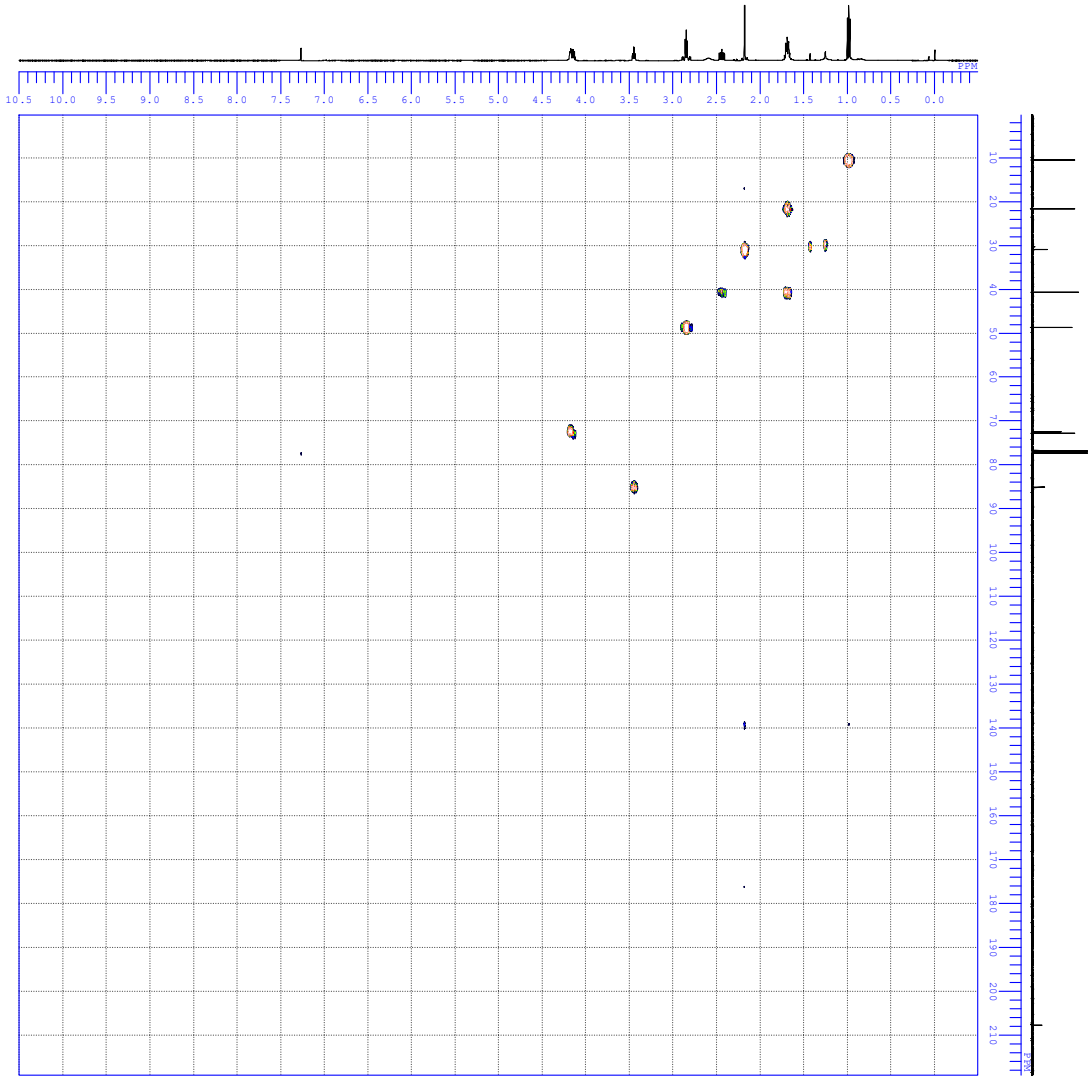
Compound **14B**

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



Compound **14B**

HMQC ($CDCl_3$, 500 MHz)



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DFILE    14B_K166-216-Ea_MCCL_HMQC-1-1.als
OBNUC    1H
EXMOD    hmqc_pfg.jxp
OFR            500.16 MHz
OBSET            2.41 KHz
OBFIN            6.01 Hz
POINT            2047
FREQU         9384.38 Hz
SCANS               4
ACQTM          0.2182 sec
PD             1.5000 sec
PW1              6.20 usec
IRN
CTEMP            22.6 c
SLVNT    CDCL3
EXREF            0.00 ppm
BF               1.00 Hz
RGAIN              50
```
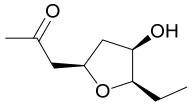
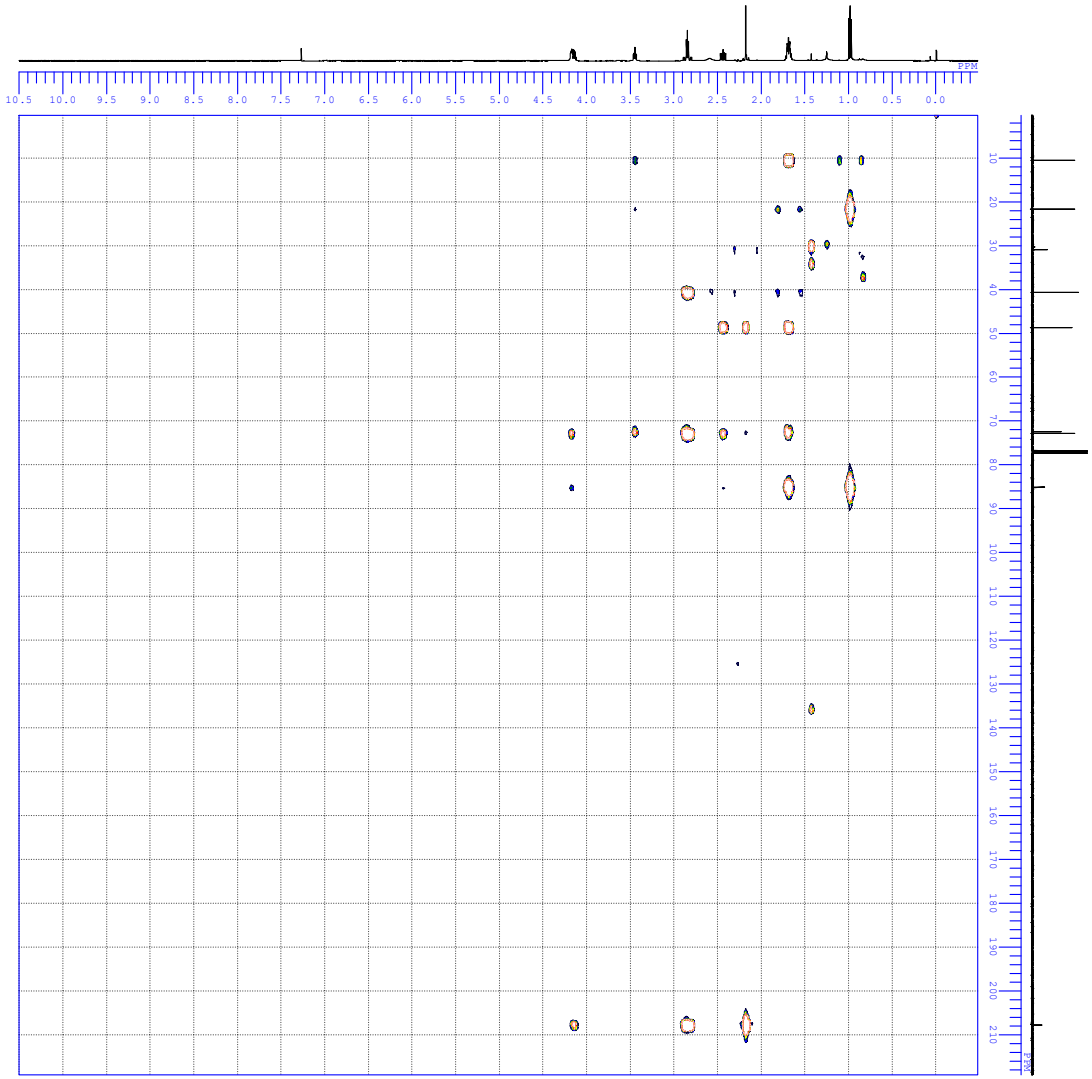



14B

Compound **14B**

HMBC ($CDCl_3$, 500 MHz)

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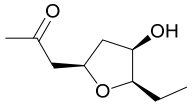
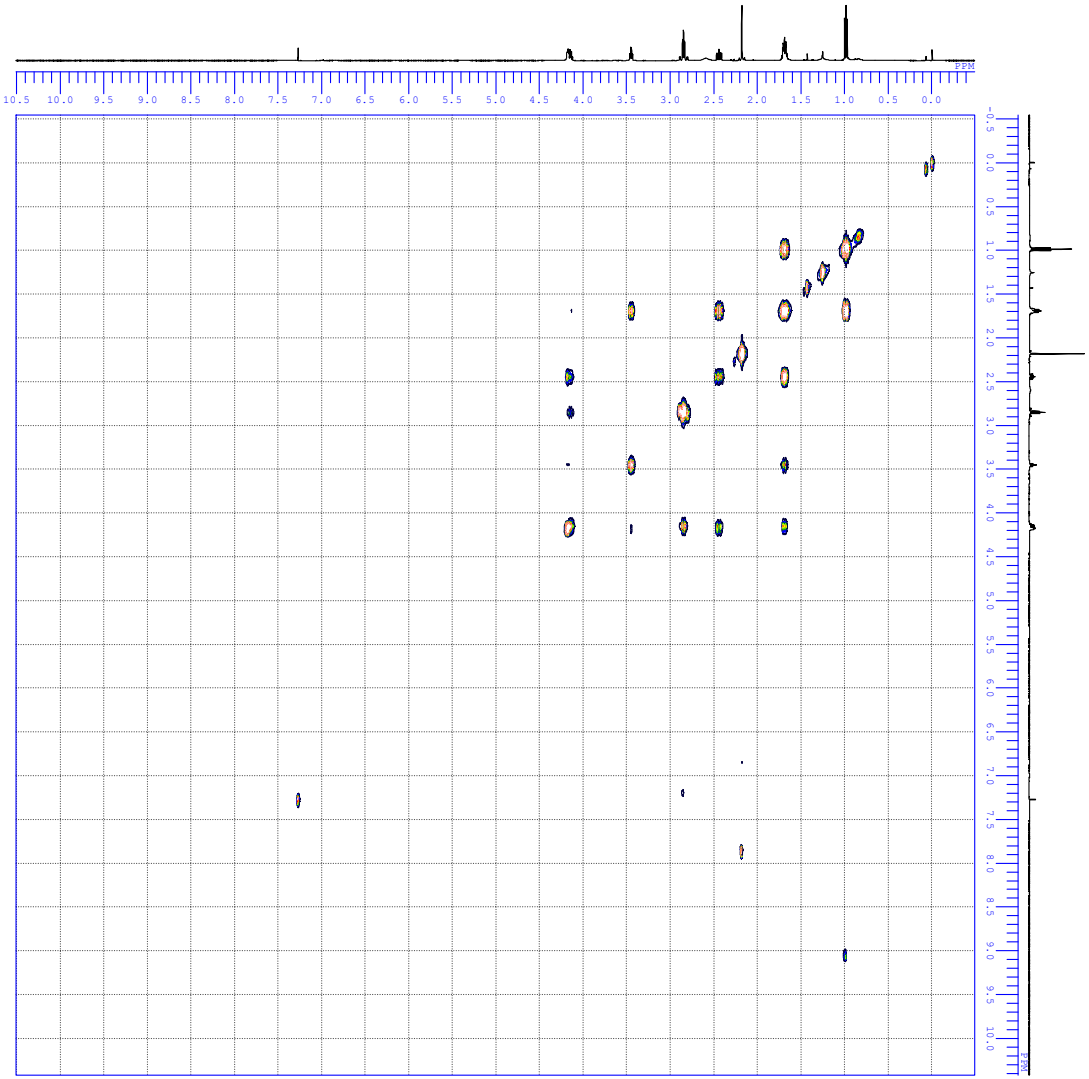
DATIM    09-02-2019 16:04:14
DFILE    K166-216-Ea_MCCL_HMBC-1-1.als
ORNUC    1H
EXMOD    hmbc_pfg.jxp
OFR           500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT           1024
FREQU        9384.38 Hz
SCANS              4
ACQTM         0.1091 sec
PD            1.5000 sec
PW1             6.20 usec
IRN
CTEMP           22.5 c
SLVNT    CDCL3
EXREF           0.00 ppm
BF              1.00 Hz
RGAIN             50
```



14B

Compound **14B**

COSY ($CDCl_3$, 500 MHz)



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EXMOD   cosy_pfg.jxp
OFR           500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT           2560
FREQU        9384.38 Hz
SCANS              1
ACQTM         0.2728 sec
PD            1.5000 sec
PW1             6.20 usec
IRN
CTEMP           22.5 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              1.00 Hz
RGAIN             50
```
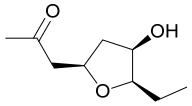
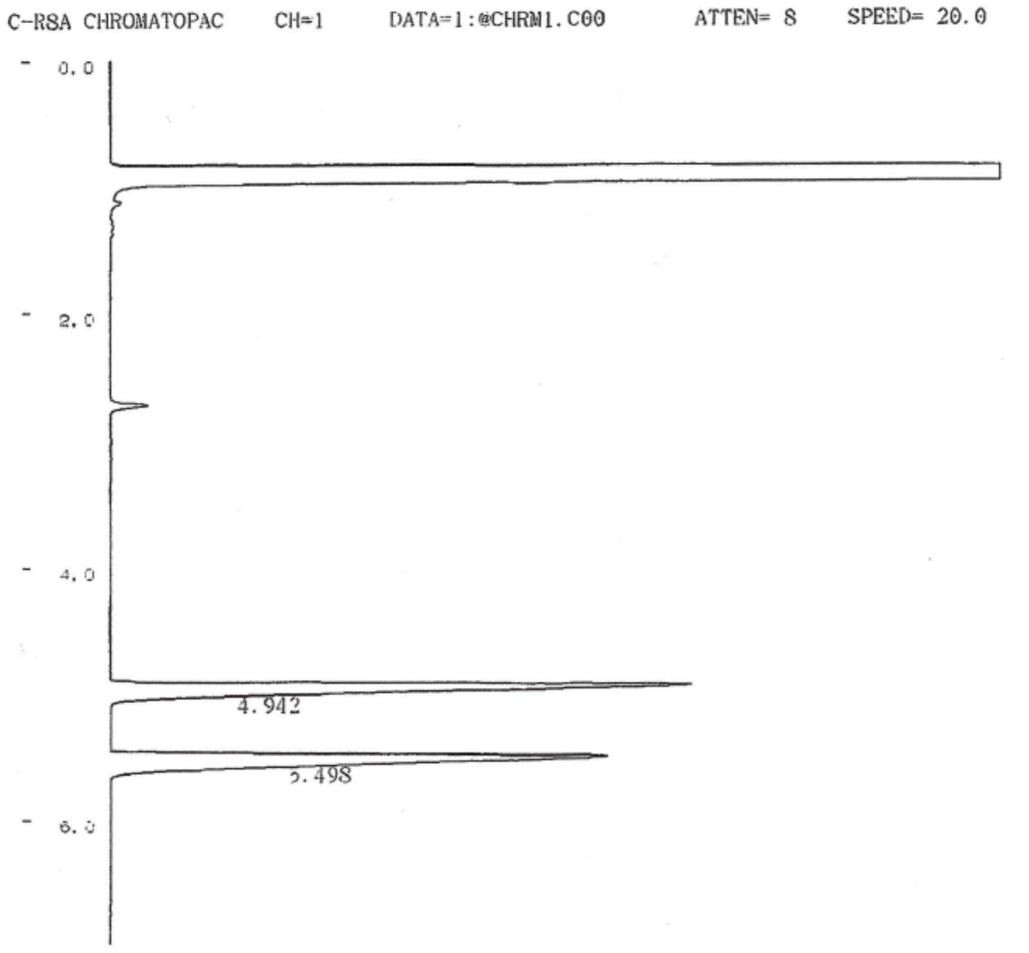



14B

GC Chromatograms of DHB (1)

GC conditions.
Column: Rt-βDEXsm, 30 m x 0.25 mm
Oven temp: 100 °C
Carrier gas: He
RT = 5.0 min for (−)-**1**, 5.6 min for (+)-**1**.

rac-**1**

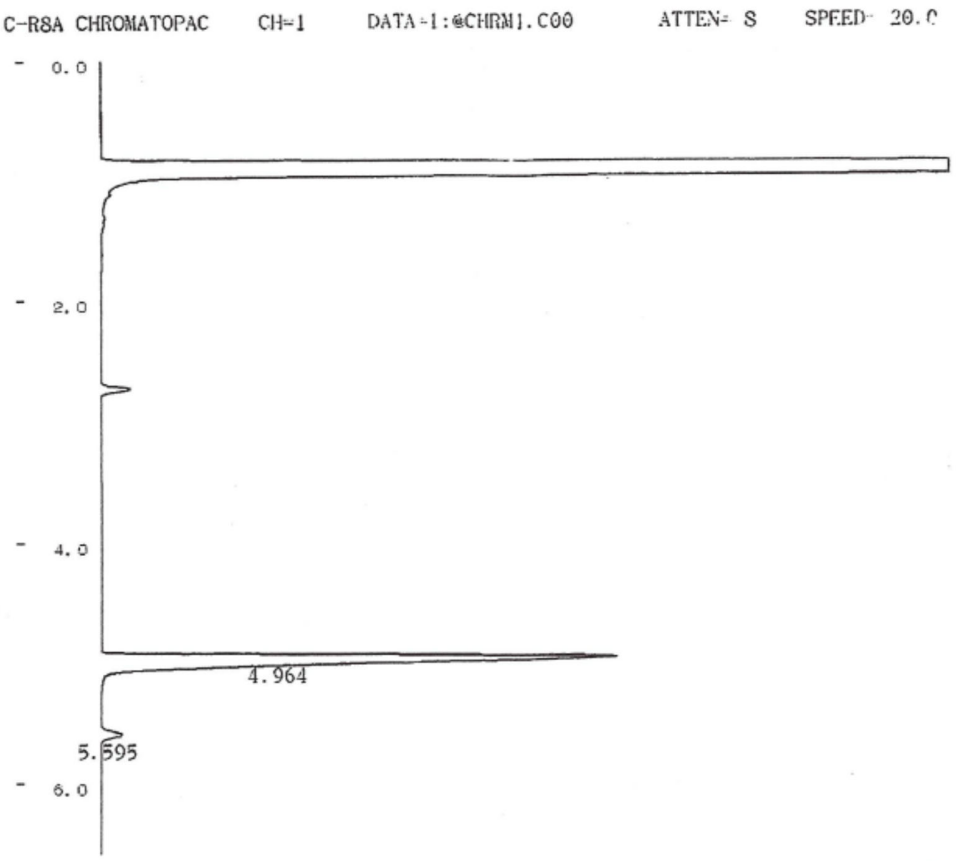


C-R8A CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 20/01/07 13:55:40

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	4.942	778148	164008			50.1307	
	2	5.498	774089	140538	V		49.8693	
	TOTAL		1552237	304547			100	

(−)-**1**



C-R8A CHROMATOPAC CH=1 Report No.=1 DATA=1:@CHRM1.C00 20/01/20 09:35:14

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	4.964	745150	153495			96.9789	
	2	5.595	23213	6132	V		3.0211	
		TOTAL	768363	159627			100	