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Intramolecular aldol condensation of Michael adducts of levoglucosenone and cyclododecanone

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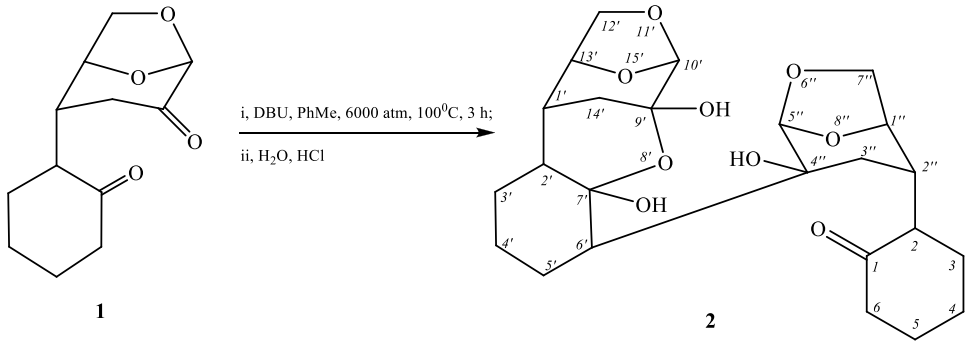
The spectral and analytical data were obtained using the equipment of the *Khimiya* Joint Center at the Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance III, (500.13 MHz for ^{1}H and 125.47 MHz for ^{13}C). IR spectra were recorded on spectrophotometers Shimadzu IRPrestige-21 or Bruker Tensor 27 (from films or mulls in mineral oil). Mass spectra were measured on a GC-MS instrument Hewlett Packard, chromatograph HP 6890 with a mass-selective detector HP 5973. Optical rotation was determined on a polarimeter Perkin Elmer-341. Analytic TLC was carried out on Sorbfil plates of the grade PTSKh-AF-A ("Sorbpolymer" Co., Krasnodar). The melting points were measured on a Boëtius 05 heating block.

2-[4-(7,9-Dihydroxy-8,11,15-trioxatetracyclo[7.4.1.1^{10,13}.0^{2,7}]pentadec-6-yl)-4-hydroxy-6,8-dioxabicyclo[3.2.1]oct-2-yl]cyclohexanone (2).



1 **2**

To a solution of diketone **1** (diastereomeric mixture, 0.31 g, 1.4 mmol) in toluene (2.0 ml), catalytic amount (10%) DBU was added. The mixture was kept at 100 °C and pressure 6,000 atm for 3 h. The mixture was then treated with 3% aqueous solution HCl, the reaction products were extracted with EtOAc (3x10.0 ml), the extract was dried with $MgSO_4$, the solvent was distilled off on a rotary evaporator, the residue was subjected to silica gel column chromatography. Yield 0.067 g (17%).

The structure of compound **2** is confirmed by on the basis of the ^{1}H NMR spectra and ^{13}C with using a standard two-dimensional correlation of methods HHCosy, HSQC, HMBC, NOESY. The ^{13}C spectra were recorded in modes of dept 90; dept 135 and in a complete suppression of proton and found chemical shifts of methine, methylene, and quaternary carbon atoms, from the spectra HSQC - corresponding chemical shifts of protons. Based on Cosy and HMBC spectra established the interaction between protons and protons of further cooperation with the carbon atoms.

So, the proton with δ_H 5.4 ppm belongs of anomeric C$^{5''}$ (according to HSQC δ_C 100.38 ppm), HMBC spectrum of which has cross-peaks of interaction with the carbon atoms with δ_C 73.57,

75.54, 68.37 ppm, which corresponds to $C^{4''}$, $C^{1''}$, $C^{7''}$. Doublet signal for proton with δ_H – 4.5 ppm according to the range HSQC belongs $C^{1''}$ and it gives a spectrum Cosy cross-peaks interaction with $H^{7''}$ with δ_H 3.75 ppm and $H^{3''}$ 2.45 ppm; in spectra HMBC interaction with the carbon atoms at 68.37 ppm ($C^{7''}$), 100.38 ppm ($C^{5''}$) and 43.35 ppm ($C^{3''}$). In spectra Cosy triplet-doublet signal of H^2 with δ_H 3.22 ppm (NMR ^{13}C – 52.26 m.d. C^2) interaction with $H^{2''}$ at 1.92 ppm (NMR ^{13}C 35.38 m.d. $C^{2''}$), and H^3 δ_H 1.18, 2.61 ppm. In spectra HMBC H^2 there is the interaction with C^1 – 214.84 ppm and with C^3 – 33.34 ppm fragment of cyclohexane. At that it has two large SSCC 12.1 Hz and one small 5.3 Hz, it is indicating its trans-orientation relative to the $H^{2''}$.

Anomeric $H^{10'}$ at δ_H 4.9 ppm gives cross-peaks C^9 with δ 97.86 ppm, $C^{13'}$ with 74.63 ppm, $C^{12'}$ with 65.65 ppm and $C^{14'}$ with 35.02 ppm. Triplet signal for proton with c δ_H 4.26 ppm (J 3.6 Hz) belongs $H^{13'}$, as in the spectrum HMBC registered interaction $C^{12'}$ with δ 65.65 ppm, $C^{10'}$ with 102.65 m.d. and $C^{14'}$ with 35.02 ppm, and in the spectrum Cosy $H^{13'}$ interaction with one of the $H^{12'}$ with δ_H 3.7 ppm and $H^{1'}$ with δ_H 1.95 ppm (NMR ^{13}C – 36.34 m.d. $C^{1'}$). Proton $H^{6'}$ is registered at 2.08 ppm (NMR ^{13}C – 42.16 m.d. $C^{6'}$), as in the spectrum HMBC it interacts with $C^{4''}$ at 73.57 ppm, $C^{7'}$ at 97.02 ppm and $C^{5'}$ at 29.29 ppm. Proton $H^{2'}$ with δ 2.05 ppm. (NMR^{13}C – 34.34 ppm $C^{2'}$) in spectrum HMBC it gives cross-peaks with signal of proton of carbons with δ 36.34 $C^{1'}$, 42.16 $C^{6'}$ and 29.02 $C^{3'}$. Proton H^6 with δ_H 1.88 ppm (^{13}C NMR – 25.79 m.d. C^6) in the spectrum HMBC it shows the interaction with the keto carbon atom C^1. Chemical shifts of other protons found from spectra of CH-correlation, since their signals overlap and occupy a region 1.18-2.1 ppm.

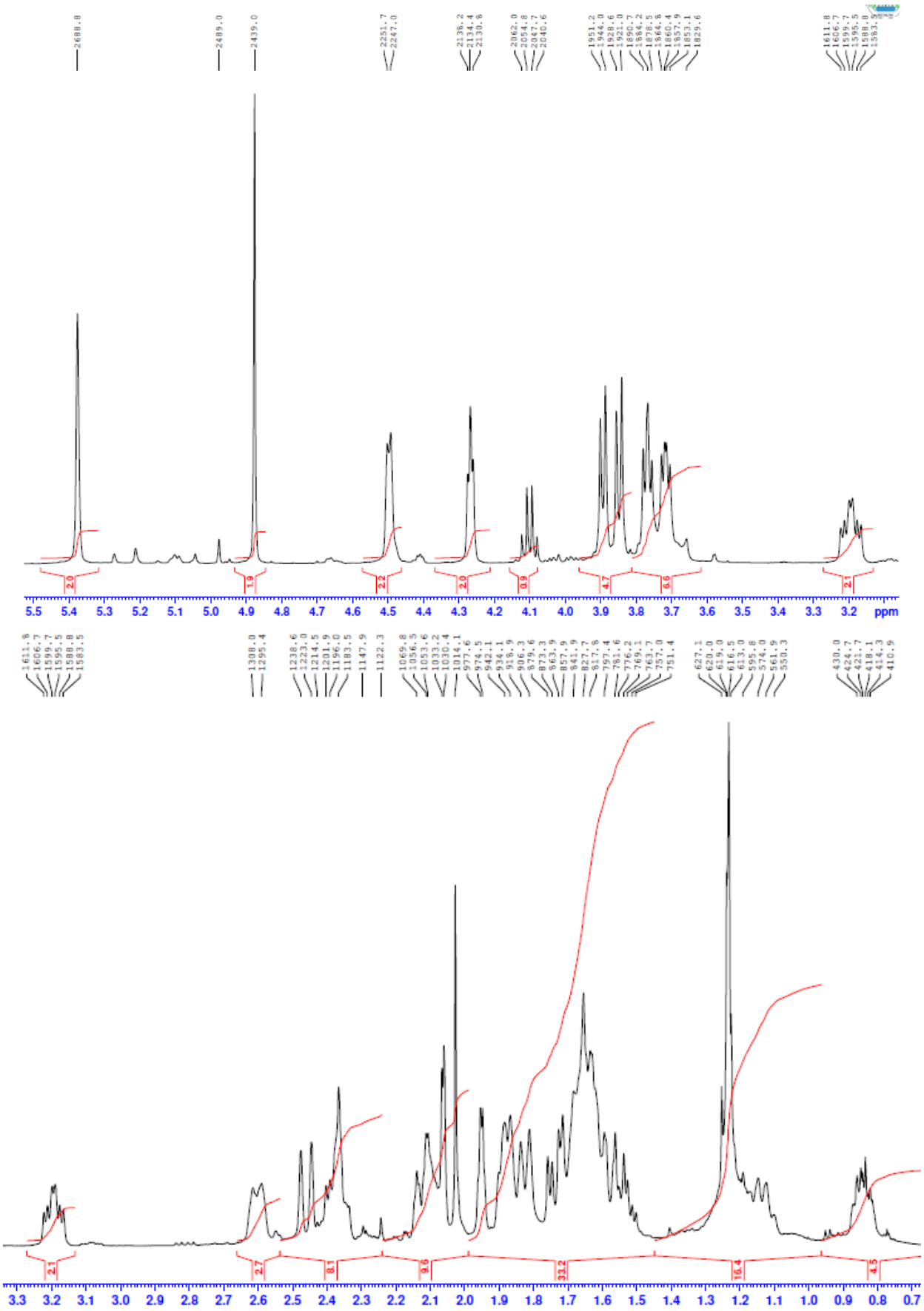


Figure S1.1. ^{1}H NMR (500 MHz) spectrum of compound **2** in $CDCl_3$.

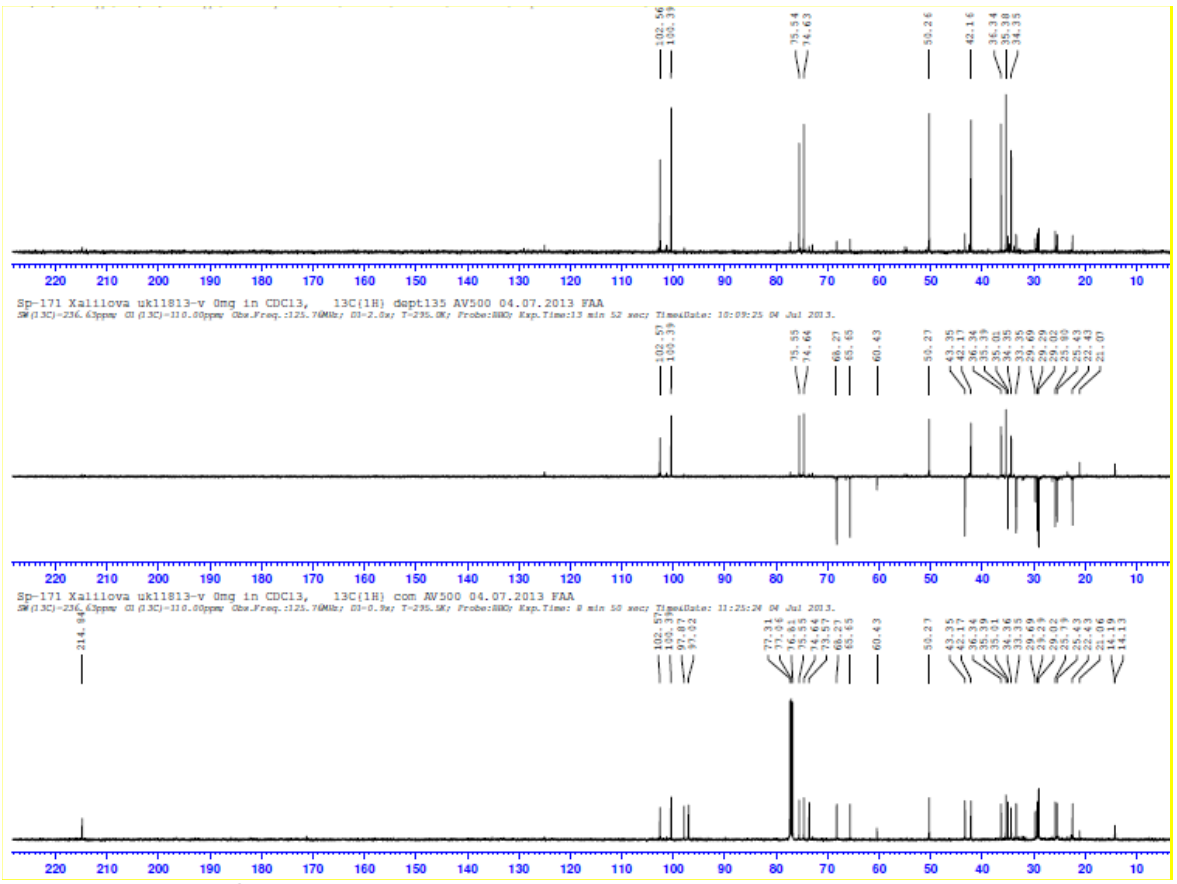


Figure S1.2. $^{13}C\{^{1}H\}$ NMR (500 MHz) spectrum of compound **2** in $CDCl_3$.

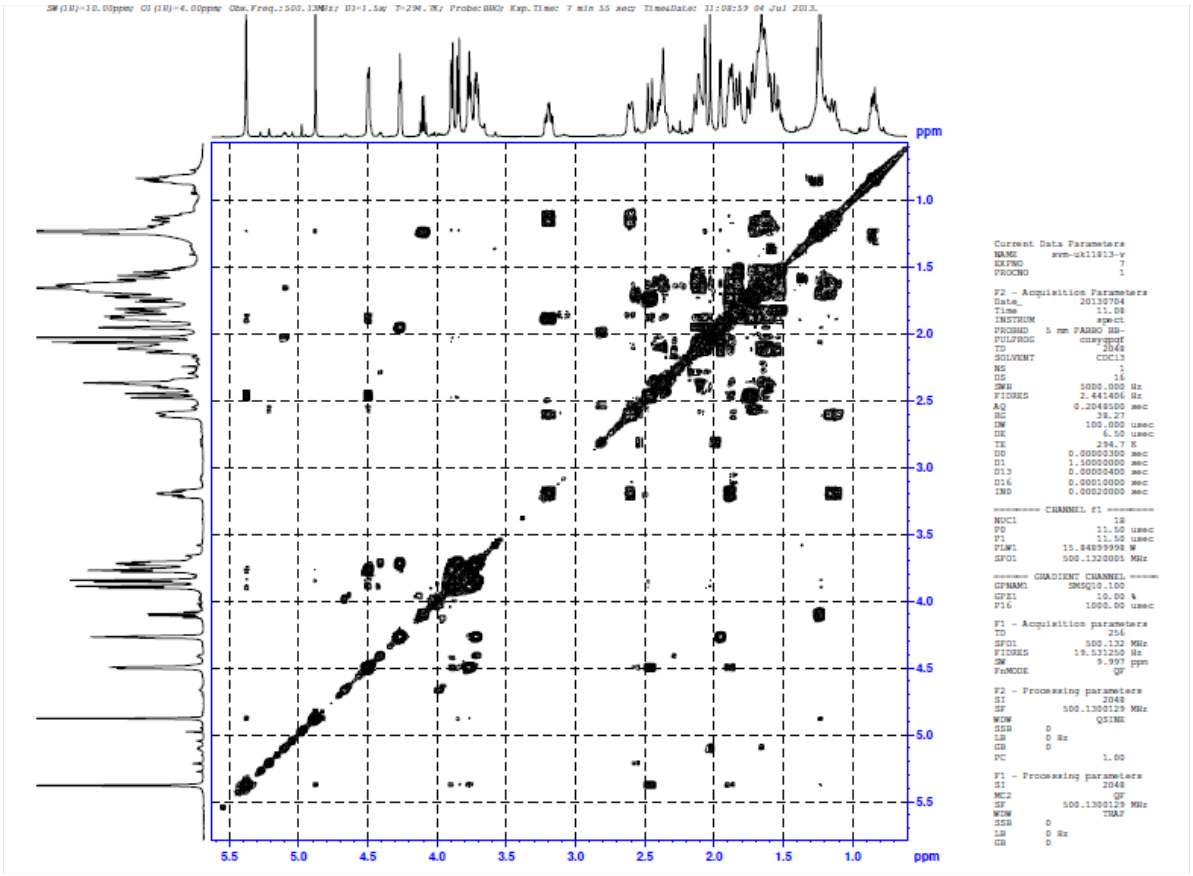


Figure S1.3. $\{^{1}H,^{1}H\}$ COSY NMR (500 MHz) spectrum of compound **2** in $CDCl_3$

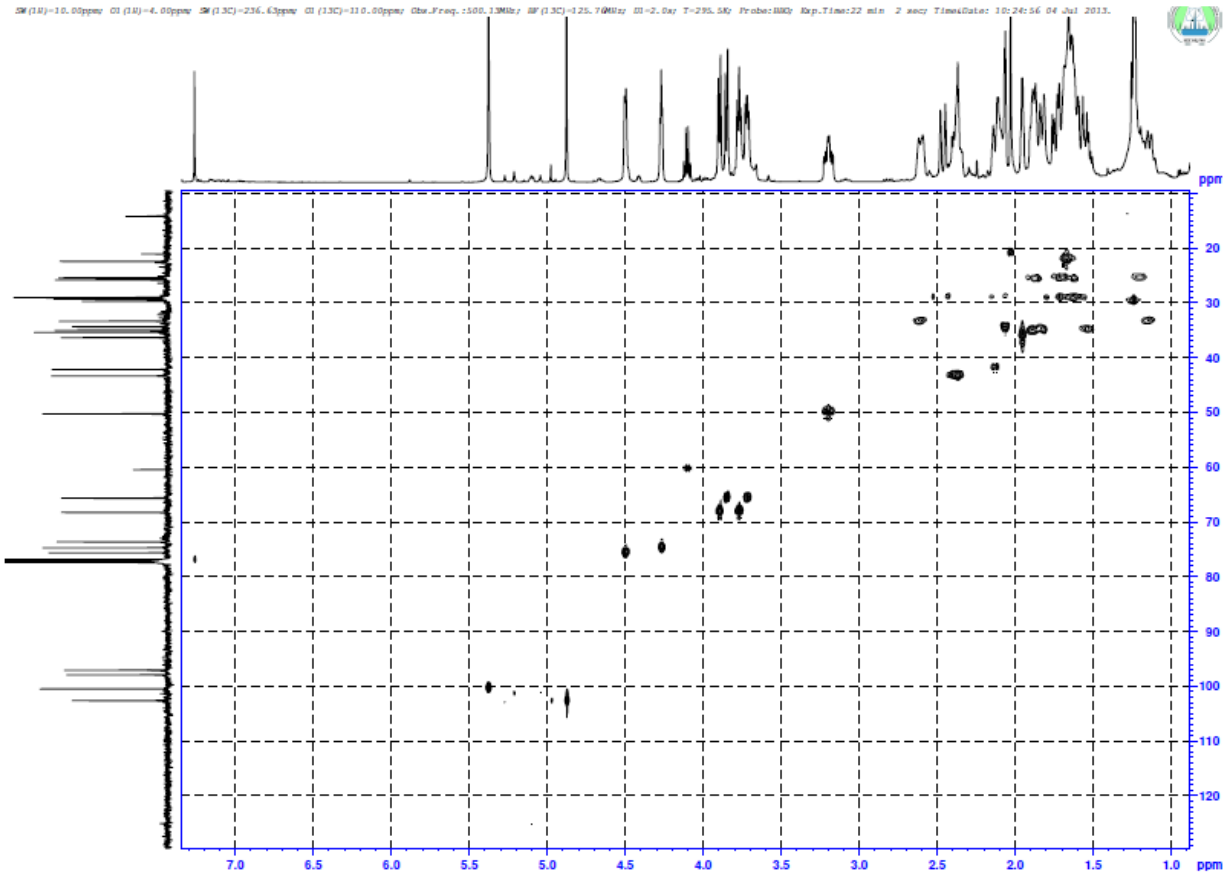


Figure S1.4. {^{1}H,^{13}C} HSQCED NMR (500 MHz) spectrum of compound **2** in $CDCl_3$.

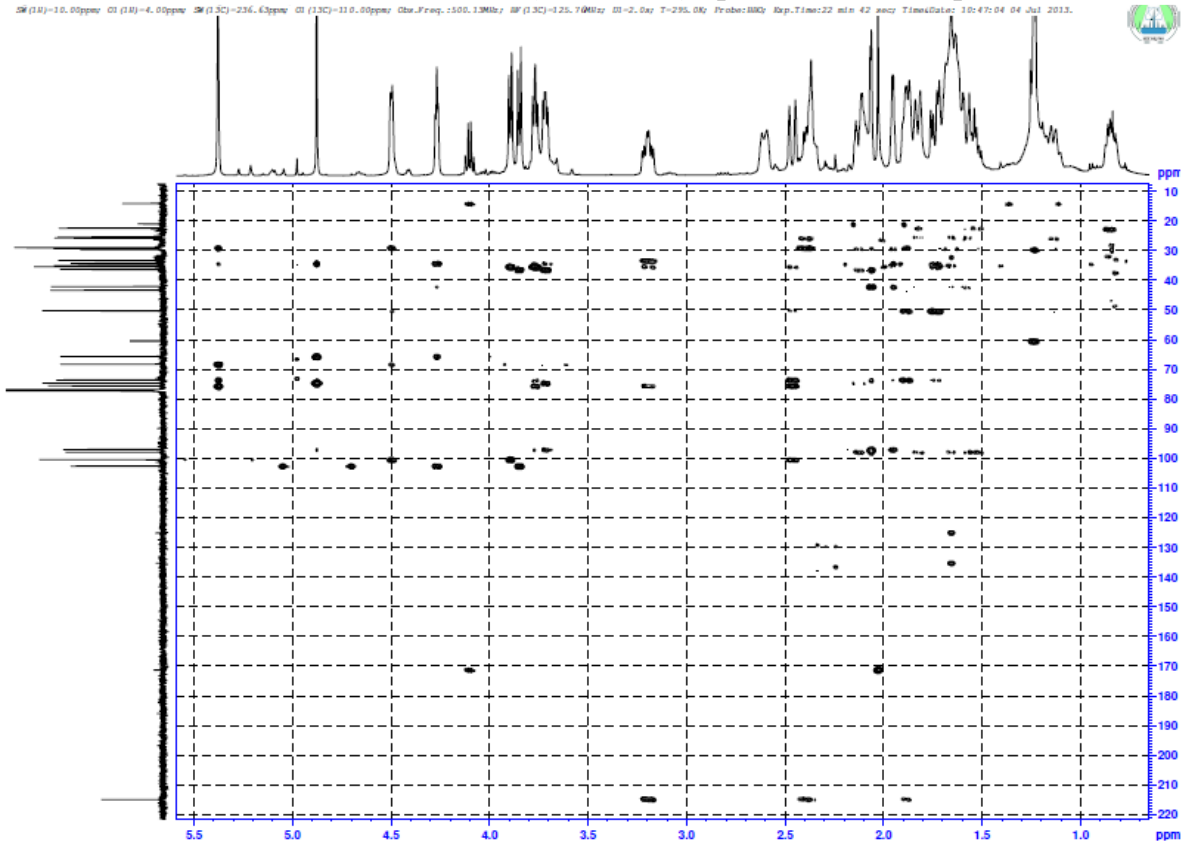


Figure S1.5. {^{1}H,^{13}C} HMBC NMR (500 MHz) spectrum of compound **2** in $CDCl_3$

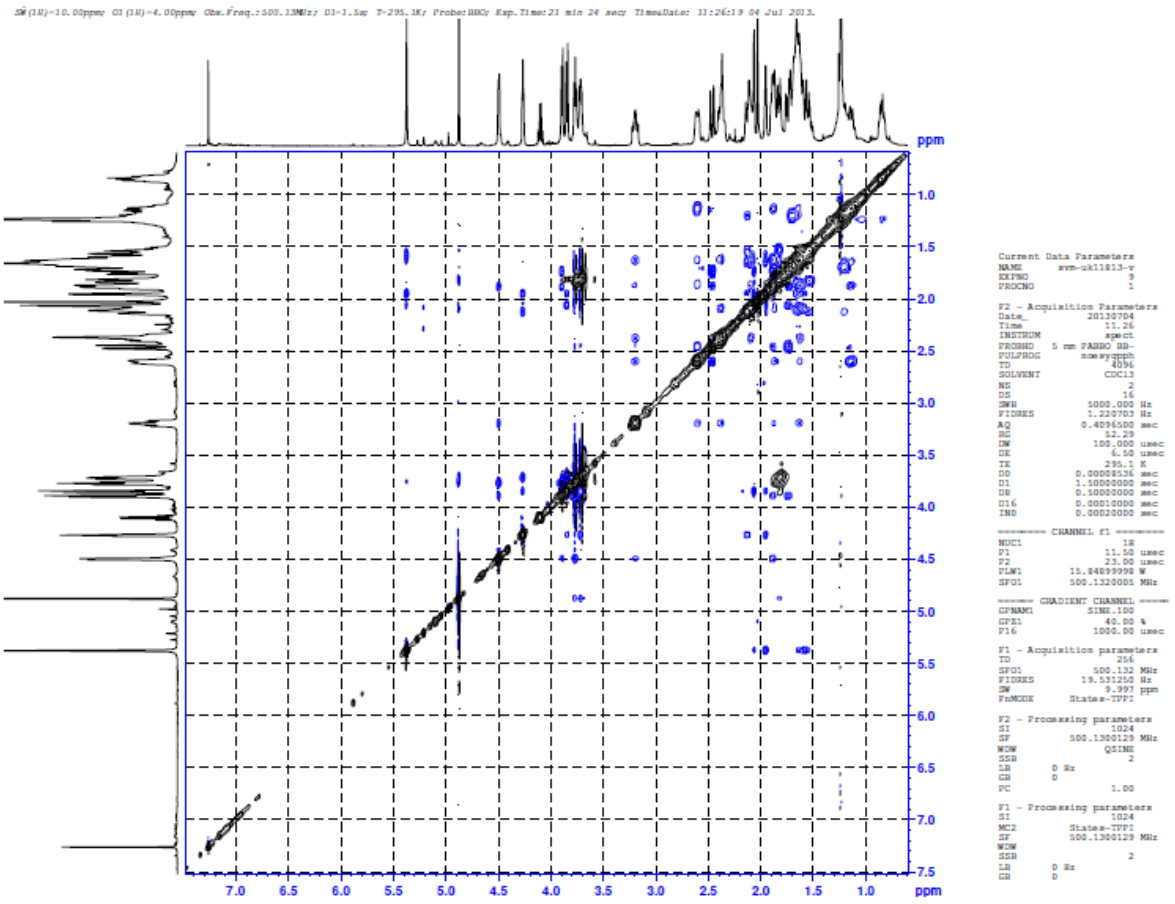


Figure S1.6. {^{1}H,^{1}H} NOESY NMR (500 MHz) spectrum of compound **2** in $CDCl_3$

Table S1 NMR data of compound **2**

Atom number	Type	Signals in 1D spectra, ppm		Correlations in 2D spectra		
		^{1}H	^{13}C	COSY H→H	HMBC H→C	NOESY H→H
1	C=O	-	214.8	-		-
2	CH	3.22 (td,1H, H^{2}, *J* 12.1, 5.3, 5.1 Hz),	52.3	2”,3	1,3	
3	CH_2	1.18 - 2.10 m	29.3			
4	CH_2	1.18 - 2.10 m	22.6			
5	CH_2	1.18 - 2.10 m	22.8			
6	CH_2	1.18 - 2.10 m	26.4		1	
1’	CH	1.18 - 2.10 m	36.3			
2’	CH	1.18 - 2.10 m	34.3		1’, 6’, 3’	
3’	CH_2	1.18 - 2.10 m	29.0			
4’	CH_2	1.18 - 2.10 m	25.4			
5’	CH_2	1.18 - 2.10 m	29.3			
6’	CH	1.18 - 2.10 m	42.2		4”, 7’,5’	
7’	C	-	97.0			
9’	C	-	97.9			
10’	CH	4.90 s	102.7		9’, 13’, 12’,14’	
12’	CH_2	3.69-3.70 m, 3.82-3.85 m,	65.7			
13’	CH	4.26 t	74.6	12’, 1’	12’, 10’, 14’	
14’	CH_2	1.18 - 2.10 m	35.0			
1’’	CH	4.50 d	75.5	7”, 3”	7”, 5”, 3”	
2’’	CH	1.18 - 2.10 m	35.4			
3’’	CH_2	1.18 - 2.10 m, 2.42-2.45 m	29.0			
4’’	C	-	73.6			
5’’	CH	5.40 s	100.4			
7’’	CH_2	3.74-3.75 m, 3.89-3.91 m	68.4			

^{1}H NMR ($CDCl_3$), *δ*: 1.18 - 2.10 (m, 24 H, H^{3}, H^{4}, H^{5}, H^{6}, H$^{1'}$, H$^{2'}$, H$^{3'}$, H$^{4'}$, H$^{5'}$, H$^{6'}$, H$^{14'}$, H$^{2''}$, H$^{3''B}$, OH), 2.42-2.45 (m, 1H, H$^{3''A}$), 3.22 (td,1H, H^{2}, *J* 12.1, 5.3, 5.1 Hz), 3.69-3.70 (m, 1H, H$^{12'\beta}$), 3.74-3.75 (m, 1H, H$^{7''\beta}$), 3.82-3.85 (m, 1H, H$^{12'\alpha}$), 3.89-3.91 (m, 1H, H$^{7''\alpha}$), 4.26 (t, 1H, H$^{13'}$, *J* 3.6, 3.8, 7.4 Hz), 4.50 (d, 1H, H$^{1''}$, *J* 4.7 Hz), 4.90 (s, 1H, H$^{10'}$), 5.40 (s, 1H, H$^{5''}$).

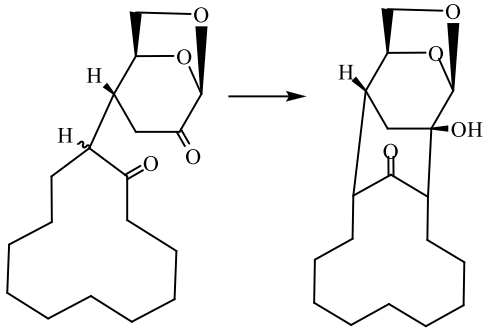
^{13}C NMR ($CDCl_3$) *δ*: 22.4 (C^{4}), 25.4 (C$^{4'}$), 25.8 (C^{6}), 29.0 (C$^{3'}$), 29.3 (C$^{5'}$), 29.7 (C^{5}), 33.3 (C^{3}), 34.3 (C$^{2'}$), 35.0 (C$^{14'}$), 35.4 (C$^{2''}$), 36.3 (C$^{1'}$), 42.2 (C$^{6'}$), 43.4 (C$^{3''}$), 52.3 (C^{2}), 65.7 (C$^{12'}$), 68.4 (C$^{7''}$), 73.6 (C$^{4''}$), 74.6 (C$^{13'}$), 75.5 (C$^{1''}$), 97.0 (C$^{7'}$), 97.9 (C$^{9'}$), 100.4 (C$^{5''}$), 102.7 (C$^{10'}$), 214.8 (C^{1}).

Mass spectrum, *m/z*: 467 [*M*H]$^{+}$. Found, %: C 61.79, H 7.35. $C_{24}H_{34}O_9$. Calculation, %: C 61.74, H 7.29.

IR: 3356, 2900, 1696, 1450, 1377, 1138, 1061, 980, 901..

Crystals, mp 221°C. $[\alpha]_D^{20}$ -92.8° (*c* 1.4, $CHCl_3$), R_f 0.18 (EtOAc–petroleum ether, 1:1).

(12*R*,13*R*,16*S*,17*S*)-12-Hydroxy-14,20-dioxatetracyclo[9.6.1.1^{12,17}.1^{13,16}]-icosan-18-one 4.



3 4

a) Adduct **3** (diastereomeric mixture, 0.050 g, 0.16 mmol) was dissolved in solution (2.0 ml), prepared from KOH (4.0 g), EtOH (40.0 ml), H_2O (20.0 ml), and stirred at room temperature for 2 h until the disappearance of the starting material (TLC control). The mixture was then treated with a 3% aqueous solution of HCl and the reaction was extracted with EtOAc (3×10.0 ml). The extract was dried with $MgSO_4$, the solvent was distilled off, the residue was chromatographed on a column of silica gel. Yield 0.015 g (30%).

b) To a solution of adduct **3** (diastereomeric mixture, 0.075 g, 0.24 mmol) in CH_2Cl_2 (4.0 ml), TMG (~7 mg, cat.) was added, and this was stirred at room temperature for 48 h until the disappearance of the starting material (TLC control). The mixture was treated with H_2O and extracted with CH_2Cl_2 (3×5.0 ml). The extract was dried with $CaCl_2$, the solvent was distilled off, the residue was chromatographed on a column of silica gel. Yield 0.036 g (48%) product of **4** and 0.031 g of unreacted compound **3** (diastereomeric mixture).

c) Adduct **3** (diastereomeric mixture, 0.100 g, 0.32 mmol) in DMSO (4.0 ml) was treated with $NaHCO_3$ (0.027 g, 0.32 mmol), and the resulting suspension was heated at 150-160°C for 15 minutes until the disappearance of the starting material (TLC control). The mixture was then treated with a saturated aqueous NaCl solution and extracted with Et_2O (3×7.0 ml). The extract was dried with $MgSO_4$, the solvent was distilled off, the residue was chromatographed on a column of silica gel. Yield 0.086 g (86%). Diastereomeric compound **4a,b,c**. IR: 3329, 2900, 1701, 1471, 1086, 976, 754, 552.

Mass spectrum, *m/z*: 309 $[MH]^+$. Found, %: C 70.08, H 9.11. $C_{18}H_{28}O_4$. Calculated, %: C 70.10, H 9.15.

Diastereomeric mixture **4a-c** was subjected to column chromatography on SiO_2. Diasteromer **4c** was the first eluted by EtOAc–petroleum ether, 1:1, R_f 0.18.

Mixture **4a,b** was eluted next, R_f 0.17 (EtOAc–petroleum ether, 1:1).

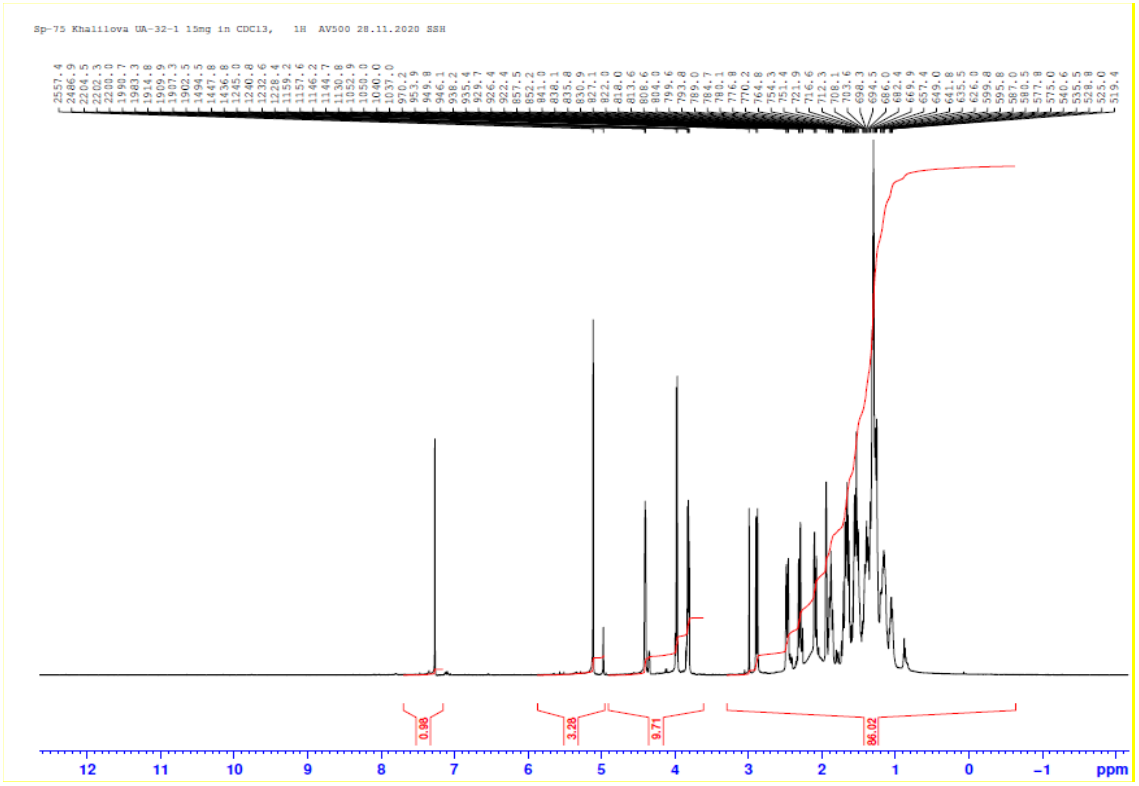


Figure S.2.1. ^{1}H NMR (500 MHz) spectrum of (1*S*,11*S*,12*R*,13*R*,16*S*,17*S*)-diastereomer **4c** in $CDCl_3$.

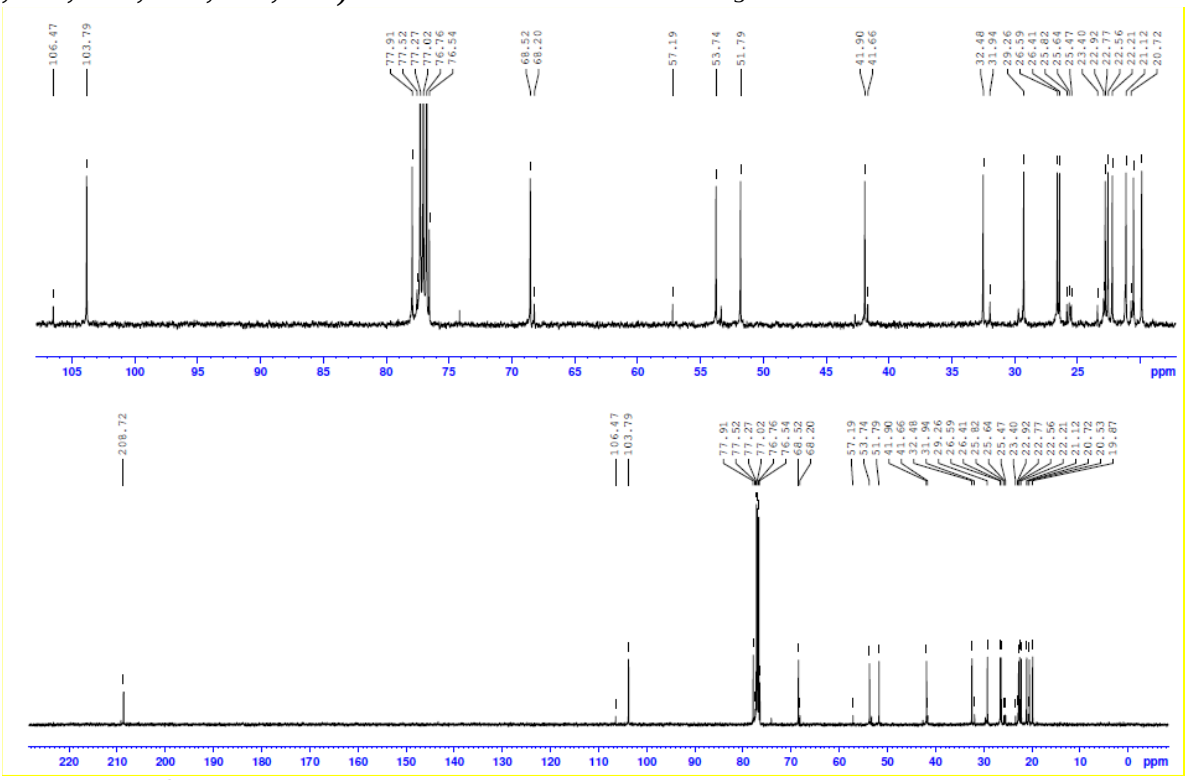


Figure S2.2. $^{13}C\{^{1}H\}$ NMR (500 MHz) spectrum of (1*S*,11*S*,12*R*,13*R*,16*S*,17*S*)-diastereomer **4c** in $CDCl_3$.

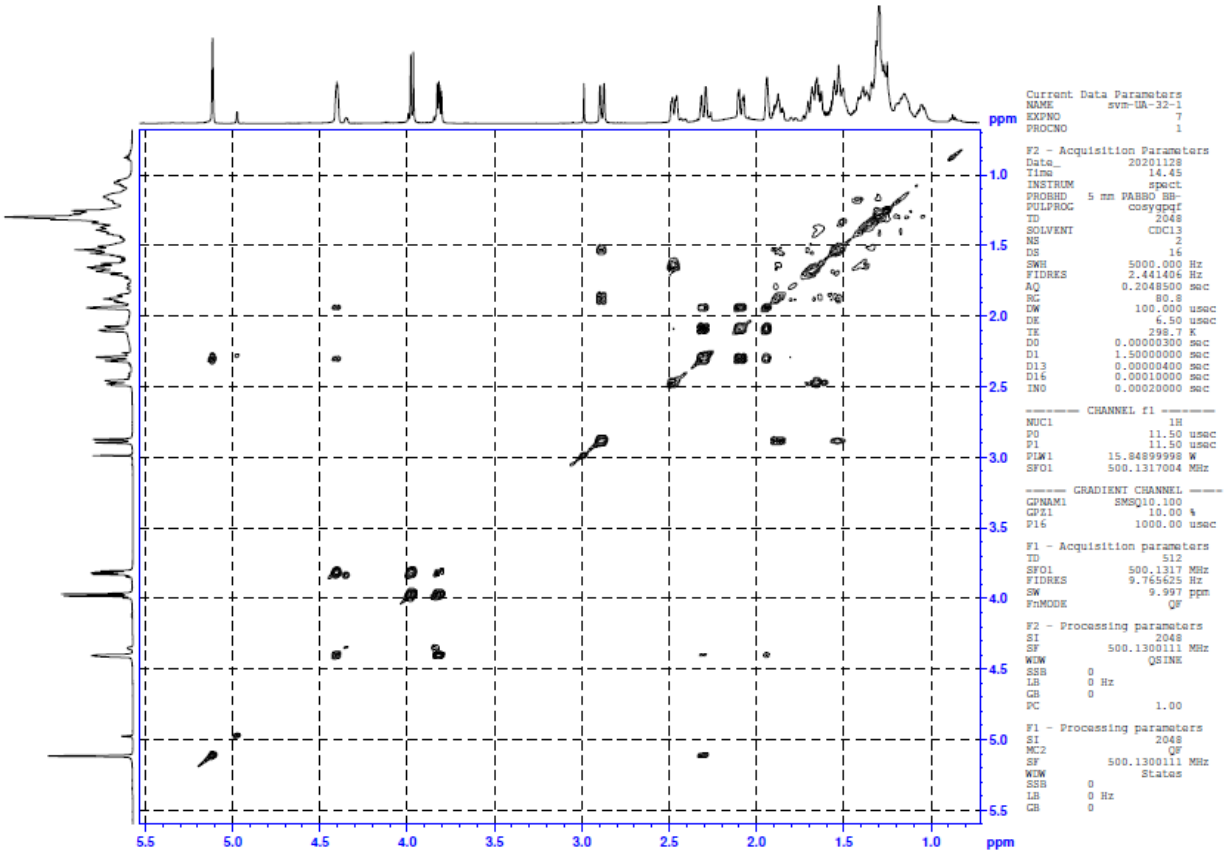


Figure S2.3. {^{1}H,^{1}H} COSY NMR (500 MHz) spectrum of (1*S*,11*S*,12*R*,13*R*,16*S*,17*S*)-diastereomer **4c** in $CDCl_3$

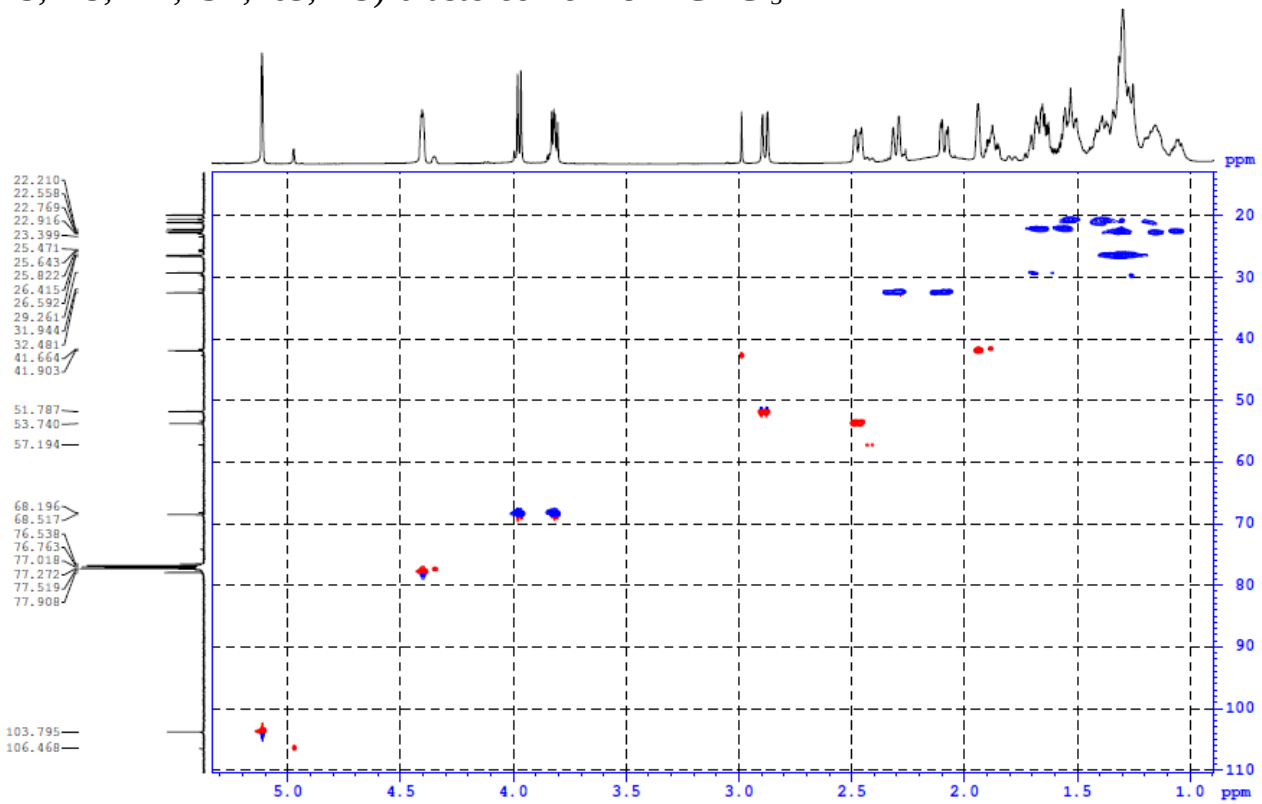


Figure S2.4. {^{1}H,^{13}C} HSQCED NMR (500 MHz) spectrum of (1*S*,11*S*,12*R*,13*R*,16*S*,17*S*)-diastereomer **4c** in $CDCl_3$.

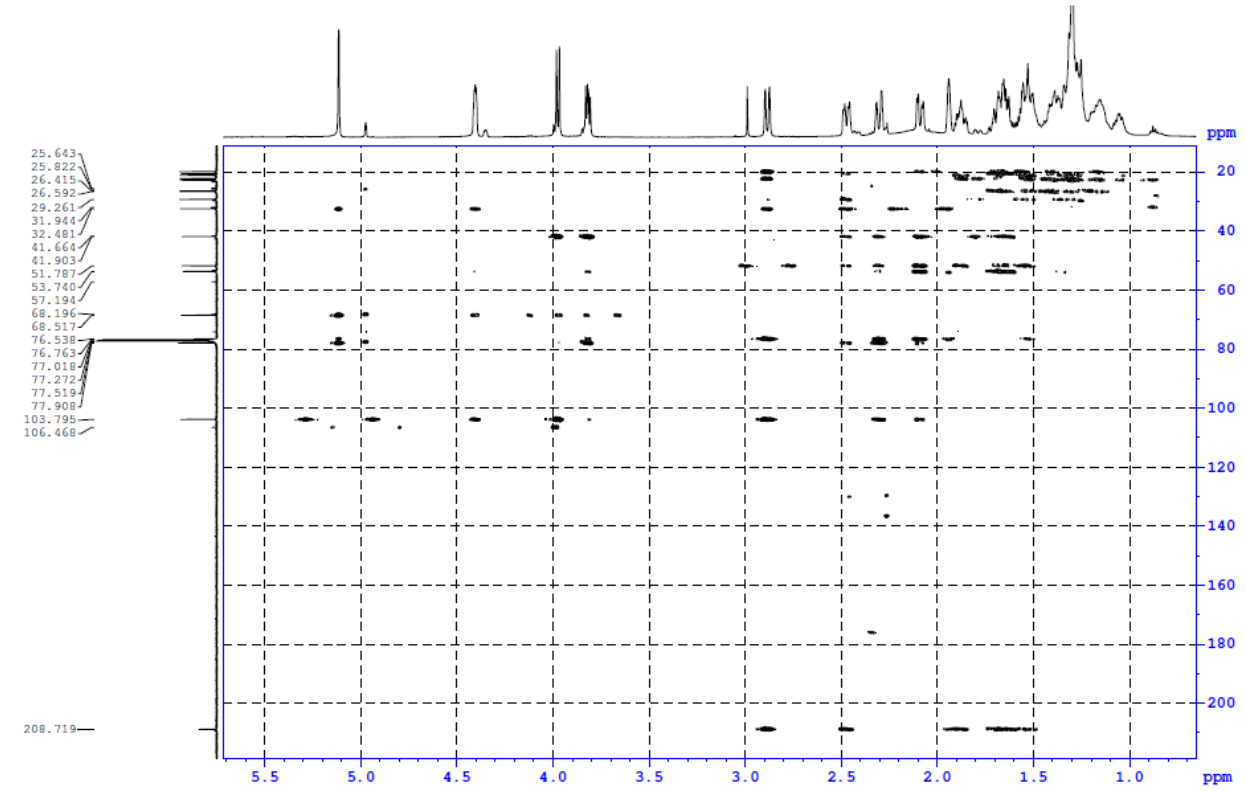


Figure S2.5. {^{1}H,^{13}C} HMBC NMR (500 MHz) spectrum of (1*S*,11*S*,12*R*,13*R*,16*S*,17*S*)-diastereomer **4c** in $CDCl_3$

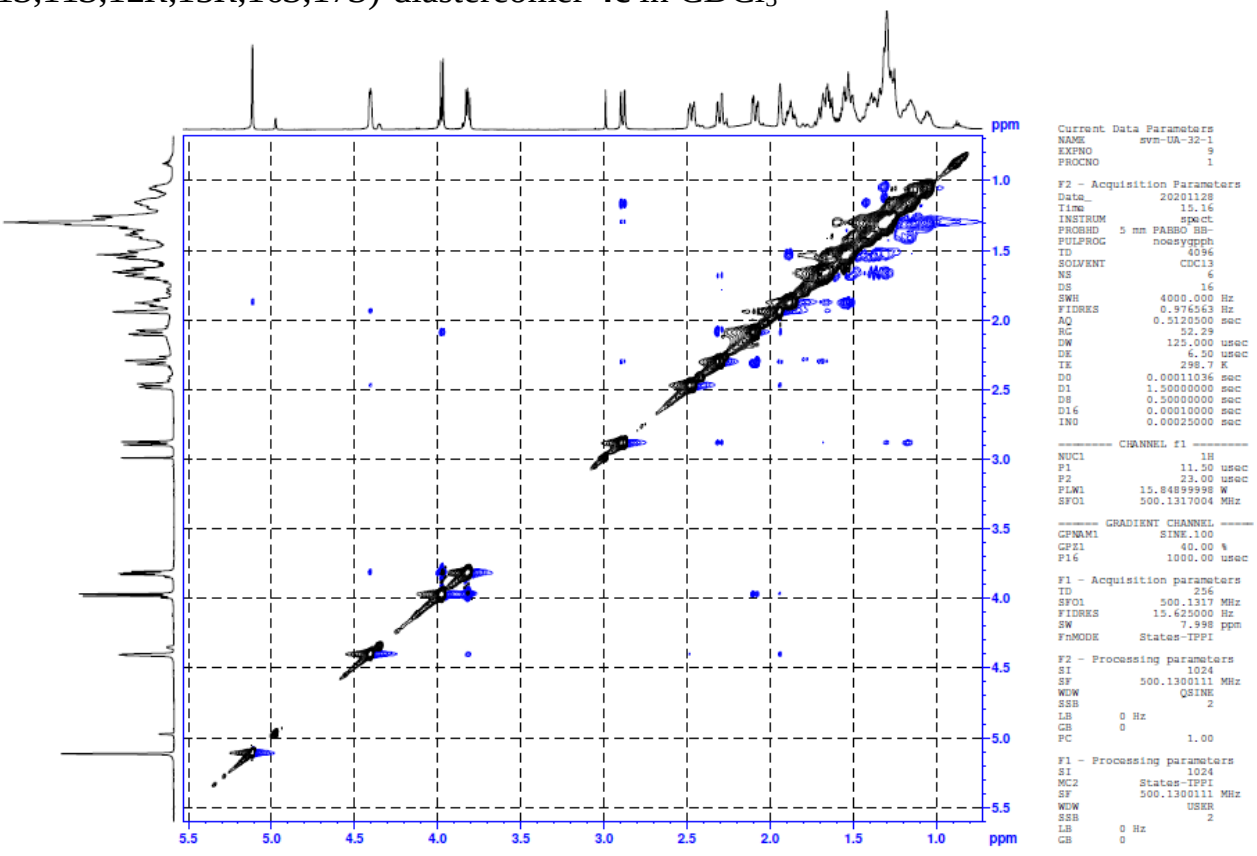


Figure S2.6. {^{1}H,^{1}H} NOESY NMR (500 MHz) spectrum of (1*S*,11*S*,12*R*,13*R*,16*S*,17*S*)-diastereomer **4c** in $CDCl_3$

Table S2 NMR data for compound **4c**

Atom number	Type	Signals in 1D spectra, ppm		Correlations in 2D spectra		
		^{1}H	^{13}C	COSY H→H	HMBC H→C	NOESY H→H
1	CH	2.47 dd (J 4.2, 12.4 Hz)	53.7	2	15B, 19$^{\beta}$, 17, 2, 3	17,16
2	CH_2	1.25-1.39 m	20.5		1	
3	CH_2	1.13-1.18 m, 1.25-1.39 m	29.3		1	
4	CH_2	1.02-1.08 m, 1.25-1.39 m	22.6			
5	CH_2	1.13-1.18 m, 1.25-1.39 m	22.8			
6	CH_2	1.25-1.39 m	26.4			
7	CH_2	1.25-1.39 m	26.6			
8	CH_2	1.61-1.70 m, 1.48-1.58 m	21.1			
9	CH_2	1.61-1.70 m, 1.48-1.58 m	19.9		11	
10	CH_2	1.25-1.39 m, 1.48-1.58 m	22.2		11, 9	
11	CH	2.90 d (J 11 Hz)	51.8	OH, 10	1, 19, OH,10	19$^{\alpha}$
12	C	-	76.5	-	13, 15$^{\alpha}$, 11, 19, 17, 9, 8	-
13	CH	5.12, s	103.8	19$^{\alpha}$, 15$^{\alpha}$, 17	12,16, 15, 19	OH
15	$^{\beta}$ CH_2	4.75, d	68.5	15$^{\alpha}$	13, 16	19$^{\beta}$, 17
15	$^{\alpha}$ CH_2	3.77-3.80 m		15$^{\beta}$, 16		16, 15
16	CH	3.28, t (J 2.2, 2.3, 4.2 Hz)	77.9	15$^{\alpha}$, 19$^{\alpha}$,17	13, 15$^{\alpha}$, 1, 19$^{\alpha}$, 19$^{\beta}$	17, 15$^{\alpha}$,1
17	CH	1.94, s	41.9	16, 19	15, 1, 19, OH, 2, 3	16, 2, 3
18	C=O	-	208.7	-	11, 1, 17, 2, 10	-
19	$^{\alpha}$ CH_2	2.30 dd (J 2.9, 12.9, 14.5 Hz)	32.5	17, 19	13, 16, 11, 17	15$^{\alpha}$, 17
	$^{\beta}$ CH_2	2.08 dd (J 1.6, 2.9, 12.9, 14.5 Hz)		13, 16, 19		11, 17
	OH	1.84-1.89 m	-	11, 10		13, 10
^{1}H NMR ($CDCl_3$), *δ*: 1.02-1.08 (m, 1H, H^{4A}), 1.13-1.18 (m, 2H, H^{3A}, H^{5A}), 1.25-1.39 (m, 10H, H^{2}, H^{3B}, H^{4B}, H^{6}, H^{5B}, H^{7}, H^{10A}), 1.48-1.58 (m, 3H, H^{8A}, H^{9A}, H^{10B}), 1.61-1.70 (m, 2H, H^{8B}, H^{9B}), 1.84-1.89 (br.s, 1H, OH), 2.08 (dd, 1H, H$^{19\beta}$, *J* 1.6, 2.9, 12.9, 14.5 Hz), 2.30 (dd, 1H, H$^{19\alpha}$, *J* 2.9, 12.9, 14.5 Hz), 2.47 (dd, 1H, H^{1}, *J* 4.2, 12.4 Hz), 2.90 (d, 1H, H^{11}, *J* 11.0 Hz), 3.28 (t, 1H, H^{16}, *J* 2.2, 2.3, 4.2 Hz), 3.77-3.80 (m, 1H, H$^{15\alpha}$), 4.75 (d, 1H, H$^{15\beta}$, *J* 7.4 Hz), 5.12 (s,1H, H^{13}).						
^{13}C NMR ($CDCl_3$) *δ*: 19.9 (C^{9}), 20.5 (C^{2}), 21.1 (C^{8}), 22.2 (C^{10}), 22.6 (C^{4}), 22.8 (C^{5}), 26.4 (C^{6}), 26.6 (C^{7}), 29.3 (C^{3}), 32.5 (C^{19}), 41.9 (C^{17}), 51.8 (C^{11}), 53.7 (C^{1}), 68.5 (C^{15}), 76.5 (C^{12}), 77.9 (C^{16}), 103.8 (C^{13}), 208.7 (C=O).						
Crystals, mp 101°C. $[\alpha]_D^{20}$ – 48,1° (*c* 1, $CHCl_3$), R_f 0.18 (EtOAc–petroleum ether, 1:1).						

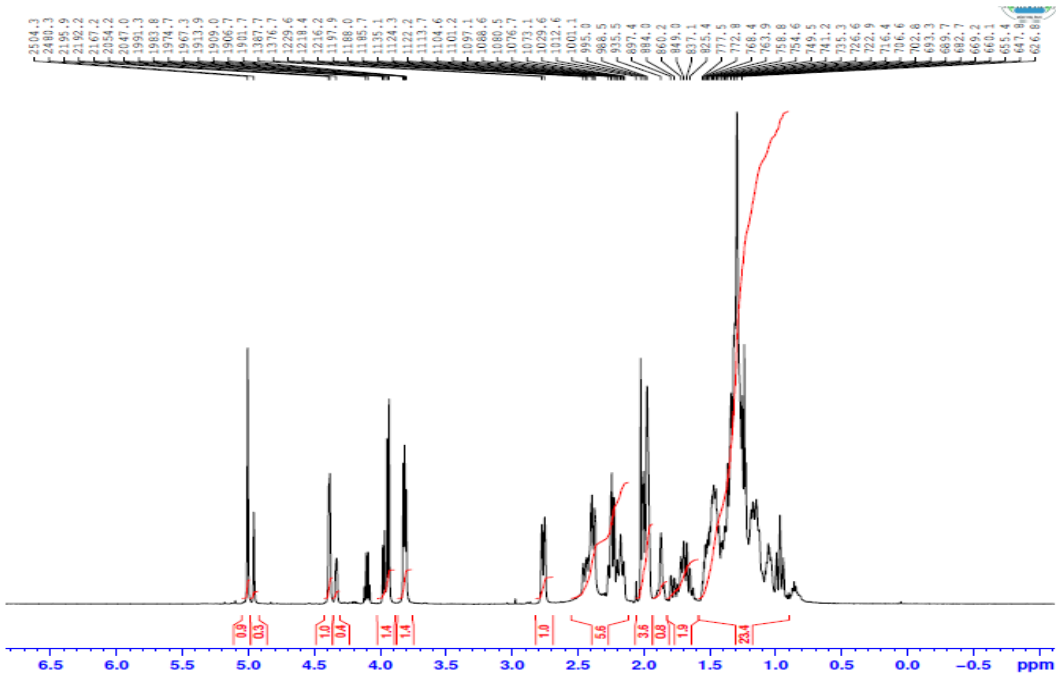


Figure S3.1. ^{1}H NMR (500 MHz) spectrum of (1*RS*,11*R*,12*R*,13*R*,16*S*,17*S*)-diastereomers **4a,b** in $CDCl_3$.

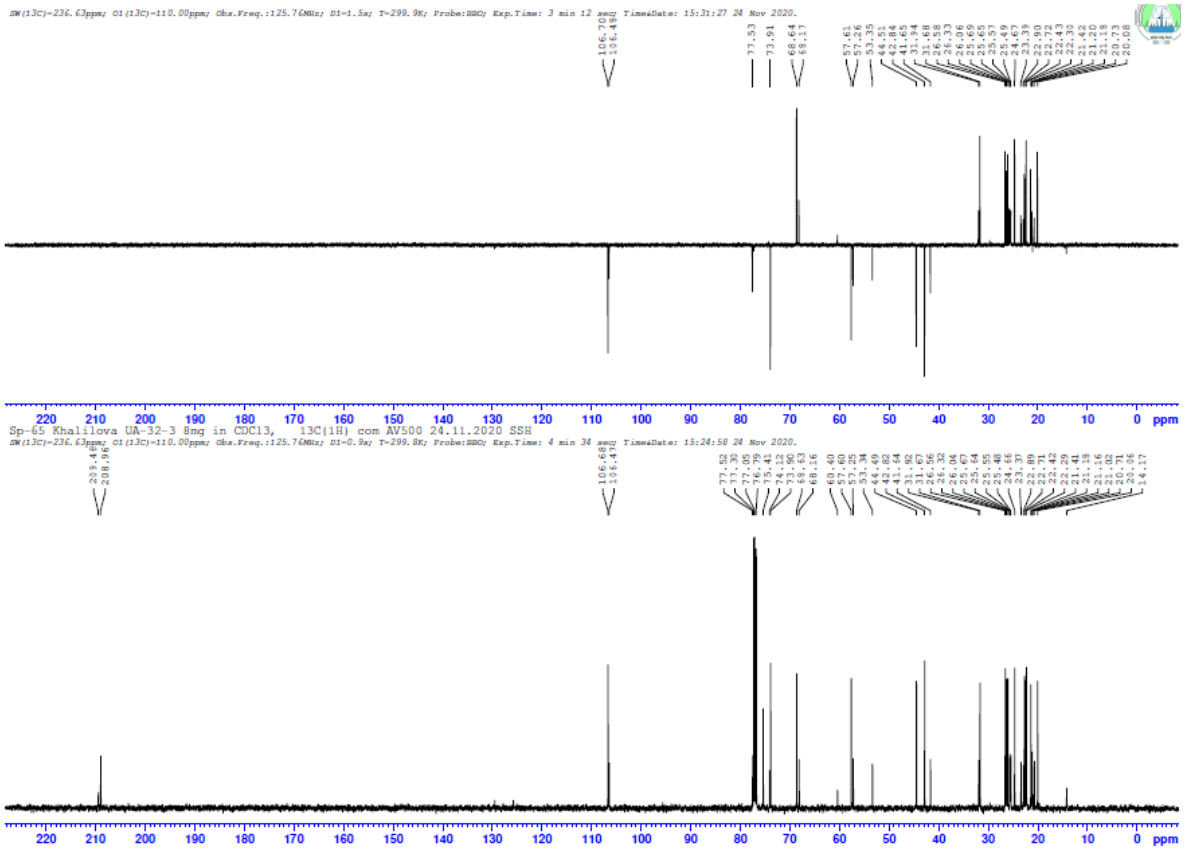


Figure S3.2. ^{13}C{^{1}H} NMR (500 MHz) spectrum of (1*RS*,11*R*,12*R*,13*R*,16*S*,17*S*)-diastereomers **4a,b** in $CDCl_3$.

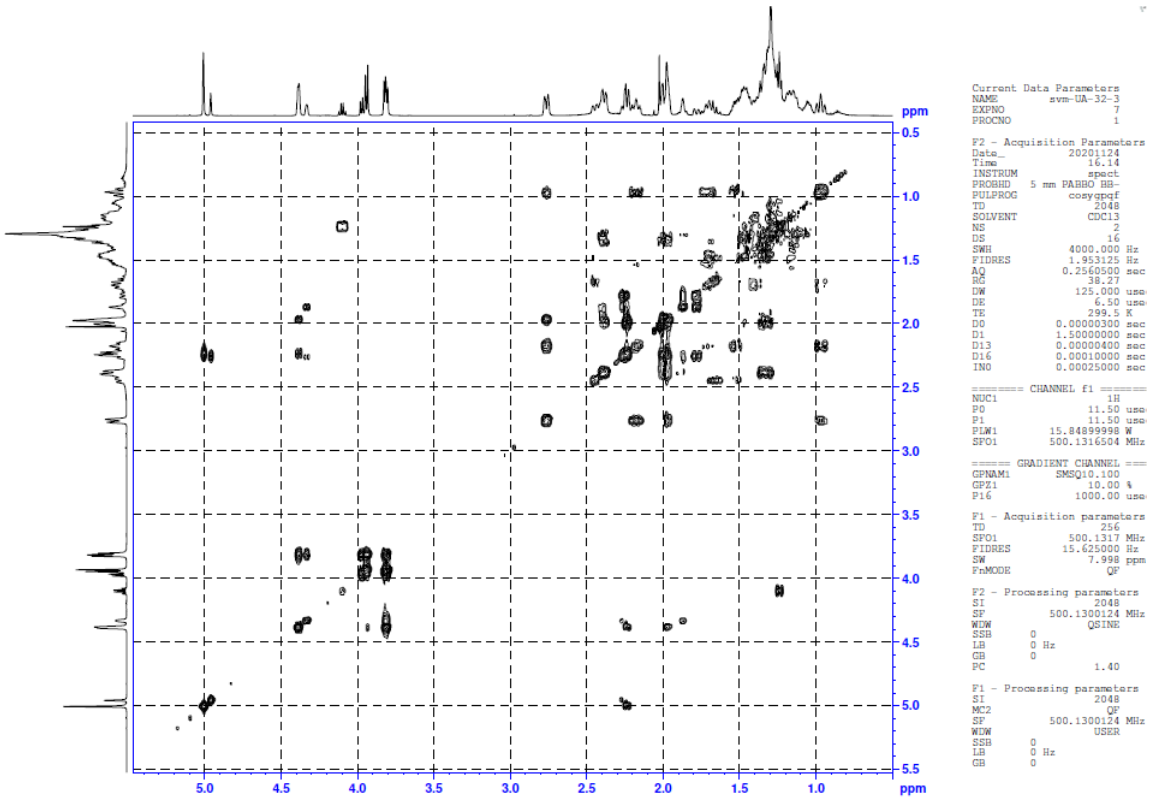


Figure S3.3. {^{1}H,^{1}H} COSY NMR (500 MHz) spectrum of (1*RS*,11*R*,12*R*,13*R*,16*S*,17*S*)-diastereomers **4a,b** in $CDCl_3$

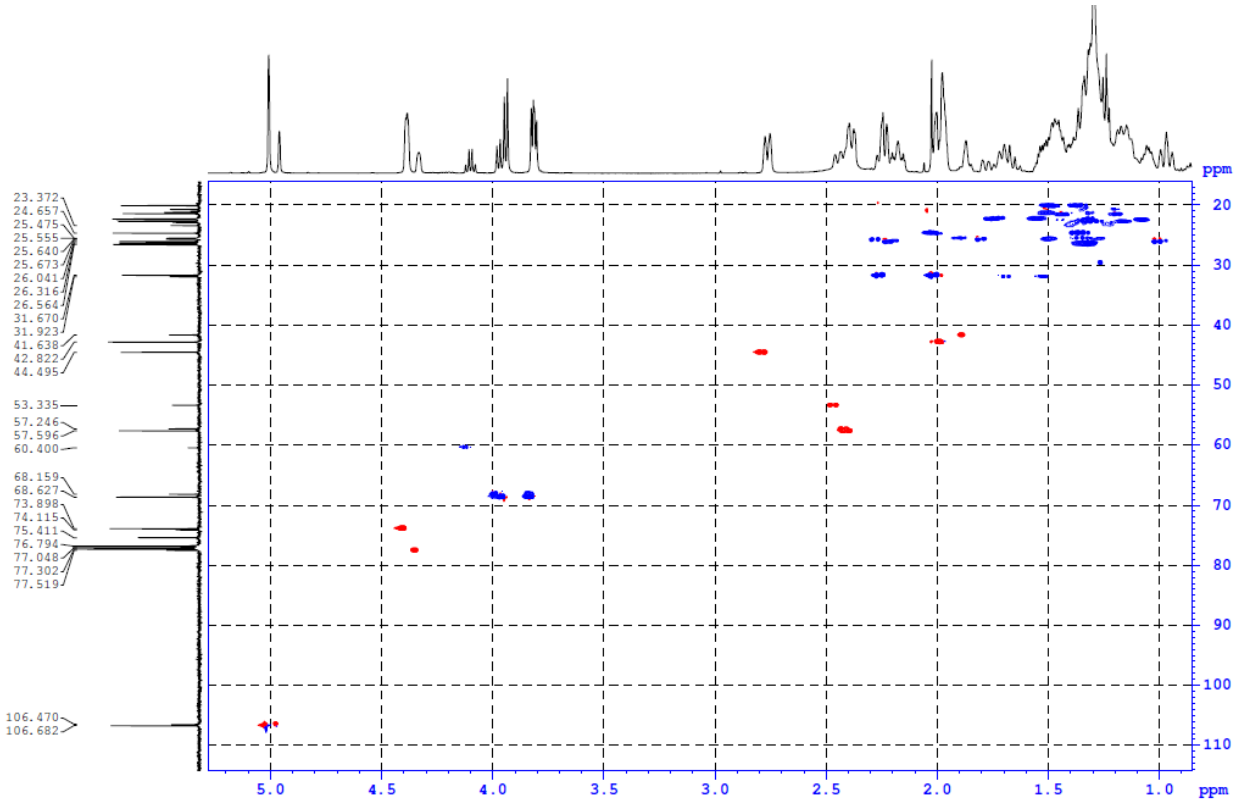


Figure S3.4. {^{1}H,^{13}C} HSQCED NMR (500 MHz) spectrum of (1*RS*,11*R*,12*R*,13*R*,16*S*,17*S*)-diastereomers **4a,b** in $CDCl_3$.

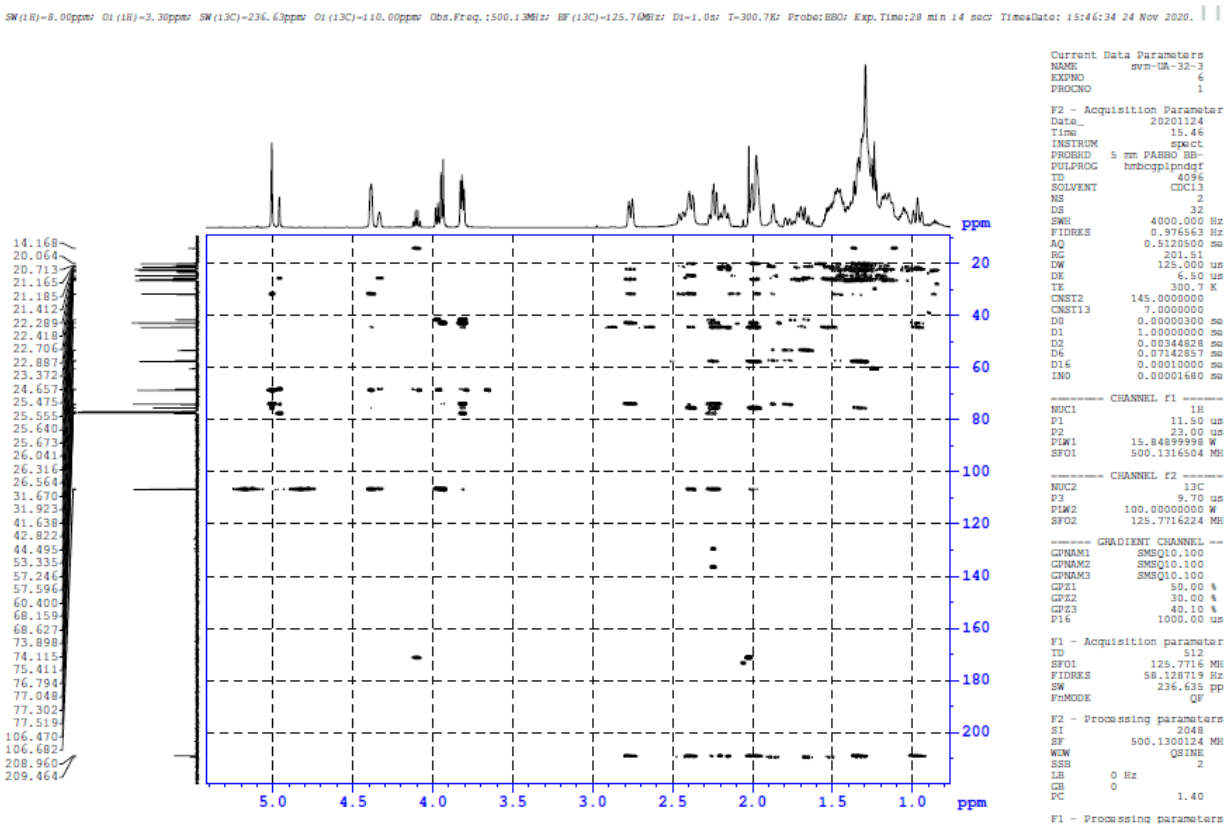


Figure S3.5. {^{1}H,^{13}C} HMBC NMR (500 MHz) spectrum of (1*RS*,11*R*,12*R*,13*R*,16*S*,17*S*)-diastereomers **4a,b** in $CDCl_3$

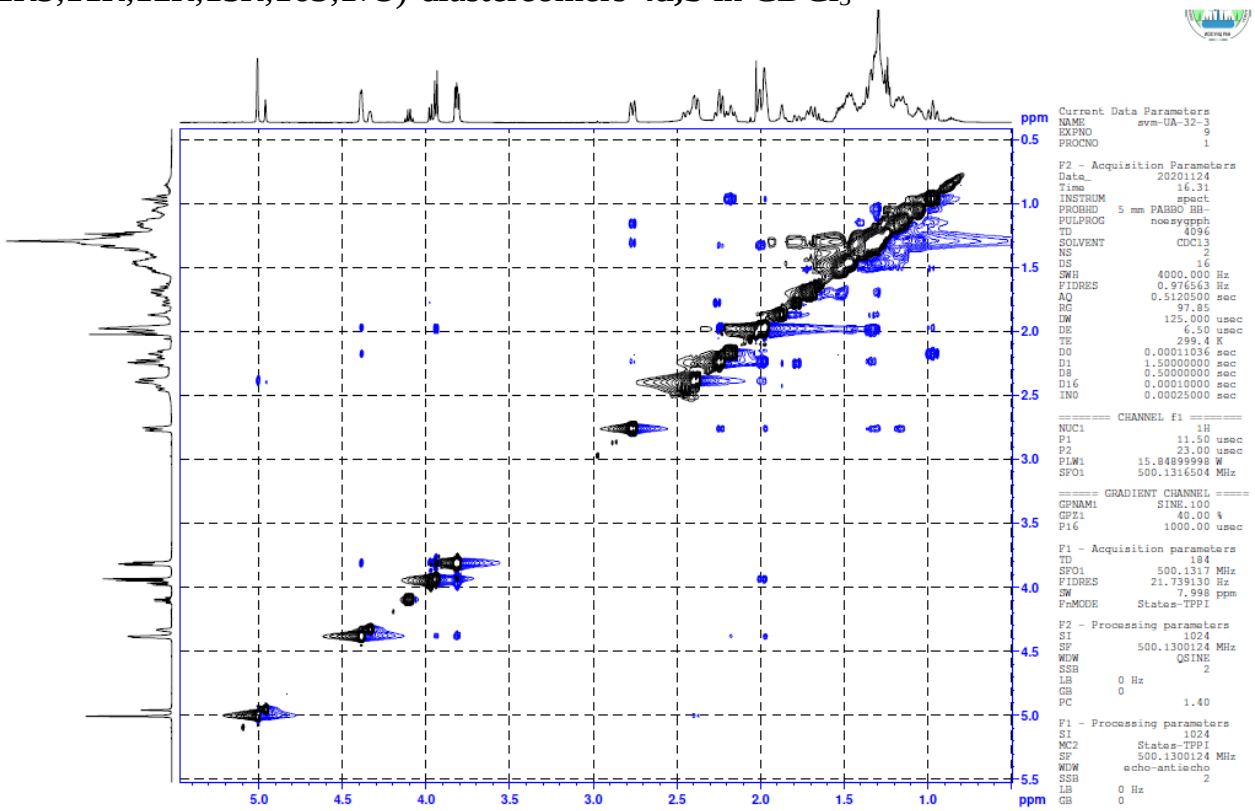
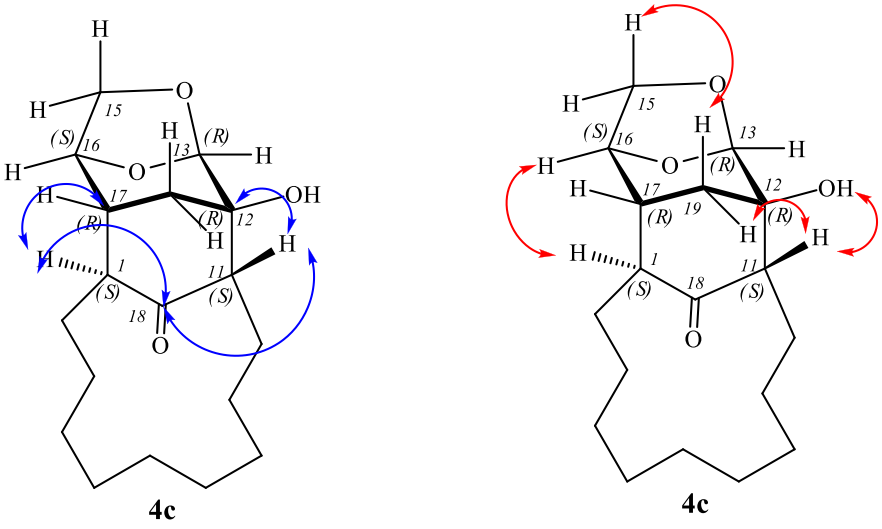


Figure S3.6. {^{1}H,^{1}H} NOESY NMR (500 MHz) spectrum of (1*RS*,11*R*,12*R*,13*R*,16*S*,17*S*)-diastereomers **4a,b** in $CDCl_3$

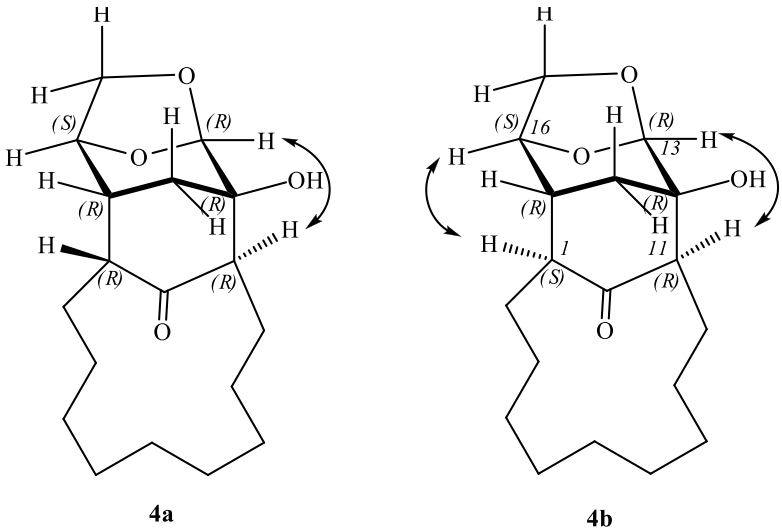
Table S3 NMR data for compound **4a,b**

Atom number	Type	Signals in 1D spectra, ppm		Correlations in 2D spectra		
		^{1}H	^{13}C	COSY H→H	HMBC H→C	NOESY H→H
1	**4a**: CH	2.76 d (J 11.0 Hz)	44.5	17	11,15$^{\beta}$,17, 18,19	17,19$^{\beta}$
	4b: CH	2.45 d (J 11.2 Hz)	53.3	17, 19	17, 19,18	17
2-10	**4a,b:** CH_2	0.93-1.54 m, 1.68-1.82 m, 1.85-1.92 m, 1.98-2.02 m, 2.12-2.26 m	20.1, 20.7, 21.2, 21.4,22.7, 22.9, 23.4, 24.6, 25.4, 25.5, 25.6,25.8, 26.0, 26.3, 26.6			
11	**4a**: CH	2.32-2.39 m	57.6	19	1, 12, 13, 17, 16, 18, 19	13, 19$^{\alpha}$
	4b: CH	2.32-2.39 m	57.2	19	19, 12	13
12	**4a**: C	-	75.4	-	13, 15$^{\alpha}$, 11, 19, 17	-
	4b: C	-	74.1	-	13, 15$^{\alpha}$, 11, 19, 17	-
13	**4a**: CH	5.02 s	106.7	19$^{\alpha}$	12, 15, 16, 19	11
	4b: CH	4.96 s	106.5	19$^{\alpha}$	12, 15, 16, 19	11
15	**4a**:$^{\beta}$ CH_2	3.82, d.d (J 2.3, 5.0, 7.2, 12.2 Hz)	68.6	16, 15$^{\alpha}$	12,13, 15, 16,17	19$^{\beta}$
	4b:$^{\beta}$ CH_2	4.10 d.d (J 7.2 Hz)		16, 15$^{\alpha}$		
	4a:$^{\alpha}$ CH_2	3.93 d (J 7.4 Hz)	68.2	15$^{\beta}$, 16	17	16
	4b:$^{\alpha}$ CH_2	3.97 d (7.5 Hz)		15$^{\beta}$, 16	17	
16	**4a**: CH	4.39 d (J 3.7 Hz)	73.9	15$^{\alpha}$, 19$^{\alpha}$,17	13, 15$^{\alpha}$, 1, 19$^{\alpha}$	15$^{\alpha}$,17
	4b: CH	4.31-4.34 m	77.5	15$^{\alpha}$,19$^{\alpha}$, 17	13, 15$^{\alpha}$	15 $^{\alpha}$
17	**4a**: CH	1.96-1.99 m	42.8	16, 19	15, 1, 19	16,15$^{\beta}$, 19
	4b: CH	1.85-1.92 m	41.6	16, 19	15,19	19
18	**4a**: C=O	-	208.9	-	1,11, 19,17	-
	4b: C=O	-	209.5	-	1,11, 19,17	-
19	**4a**:$^{\beta}$ CH_2	1.98-2.02 m	31.7	17, 19,1	1,13, 16, 11, 17	
	4b:$^{\beta}$ CH_2	1.48-1.55 m		17, 19,1		
	4a:$^{\alpha}$ CH_2	2.23-2.26 m	31.9	13, 16, 19	1,13, 16, 11, 17	
	4b:$^{\alpha}$ CH_2	1.68-1.82 m		1		
	OH	0.93-1.54 m				

^{1}H NMR ($CDCl_3$), δ: 0.93-1.54 m, 1.68-1.82 m, , 1.98-2.02 m, 2.12-2.26 m, 2.23-2.26 m (H^{2}-H^{10}, H^{19}), 1.96-1.99 m [1.85-1.92 m] (H^{17}), 2.32-2.39 m (H^{11}), 2.76 d (J 11.0 Hz) [2.45 d (J 11.2 Hz)] (H^{1}), 3.82, d.d (J 2.3, 5.0, 7.2, 12.2 Hz) [4.10 d.d (J 7.2 Hz)] ($H^{15\beta}$), 3.93 d (J 7.4 Hz) [3.97 d (7.5 Hz)] ($H^{15\alpha}$), 4.39, d (J 3.7 Hz) [4.31-4.34 m] (H^{16}), 5.02, s [4.96 s] (H^{13}).
^{13}C NMR ($CDCl_3$) δ: 20.1, 20.7, 21.2, 21.4,22.7, 22.9, 23.4, 24.6, 25.4, 25.5, 25.6,25.8, 26.0, 26.3, 26.6 (C^{2}-C^{10}), 31.7 [31.9] (C^{19}), 41.6 [42.8] (C^{17}), 44.5 [53.3] (C^{1}), 57.6 [57.2] (C^{11}), 68.6 [68.2] (C^{15}), 73.9 [77.5] (C^{16}), 75.4 [74.1] (C^{12}), 106.7 [106.5] (C^{13}), 208.9 [209.5] (C=O). The brackets contain signals for the second diastereomer.
Crystals, mp 151°C. $[\alpha]_D^{20}$ -52.8° (*c* 1, $CHCl_3$), R_f 0.17 (EtOAc–petroleum ether, 1:1).



HMBC and NOE coupling in diastereomer9c



NOE coupling in diastereomers **4a,b**