

The *Morita–Baylis–Hillman* Reaction of Chiral Highly Oxygenated Cyclopent-2-enones

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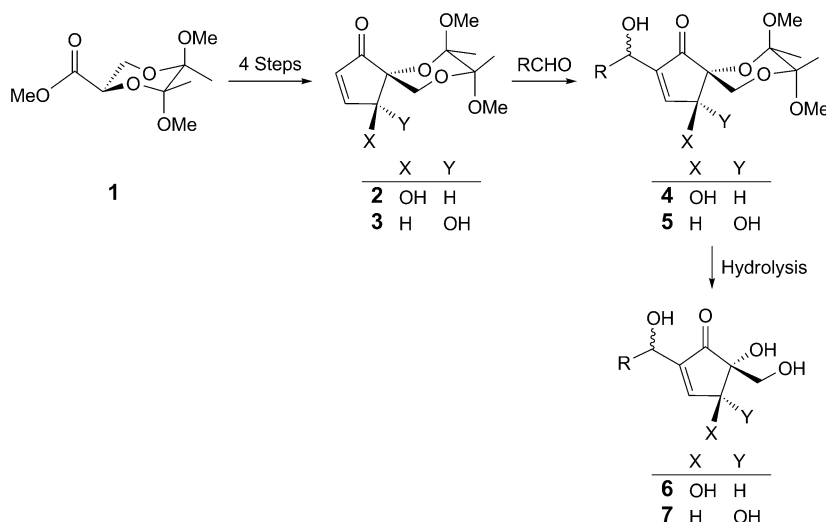
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Dedicated to Professor *Dieter Seebach* on the occasion of his 75th birthday

The *Morita–Baylis–Hillman* (*MBH*) reactions of (4*S*,5*R*,7*R*,8*R*)- and (4*R*,5*R*,7*R*,8*R*)-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-ones (**2** and **3**, resp.) with aldehydes using various catalysts were studied. A combination of Bu₃P/phenol in THF was found being optimum conditions giving the corresponding *MBH* adducts with high diastereoisomeric ratios. After separation, each stereomerically pure isomer of the *MBH* adducts was subjected to hydrolysis employing 1% aq. CF₃COOH (TFA) in a water bath of an ultrasonic cleaner to afford the corresponding polyhydroxylated cyclopentenones in good yields.

Introduction. – The *Morita–Baylis–Hillman* (*MBH*) reaction [1] is an efficient method used for creating C,C bond between the α -C-atom of electron-deficient alkenes with aldehydes and activated aldimines. The reaction is typically catalyzed by a wide range of organocatalysts such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), phosphines [2], and *Lewis* acids [3], providing α -functionalized activated alkenes. Synthetic applications of the *MBH* and *aza-MBH* adducts (functionalized allylic alcohols and amines, resp.) in organic synthesis have been extensively demonstrated [4]. Due to the versatilities of the *MBH* adducts as useful building blocks for the synthesis of complex natural products, studies towards asymmetric version of the *MBH* reactions have attracted considerable attention. By employing chiral amines, chiral *Lewis* acids, or chiral *Brønsted* acids as promoters, asymmetry can be achieved during the C,C bond formation, thus resulting in enantiomerically enriched *MBH* adducts [5]. Even though diastereoselective *MBH* reactions have been well-documented, few reports dealt with diastereoselective *MBH* reactions using chiral activated alkenes [4a][6]. We have recently reported an asymmetric synthesis of chiral oxygenated cyclopentenones **2** and **3** [7] from the chiral ester **1** [8], of which the synthetic sequence was based upon the intramolecular cyclization of α -sulfinyl carbanion as the key step. Compounds **2** and **3** were converted to the corresponding (–)-pentenomycin I and (–)-epipentenomycin I, and their analogs (*Scheme 1*) [7]. In a continuation of our research in this area [7][9], we report herein the study of the synthesis of chiral highly oxygenated cyclopent-2-enones

Scheme 1



involving *Lewis* base-mediated *MBH* reactions. It is anticipated that compounds **2** and **3** can be used as useful chiral starting oxygenated cyclopentenones for preparing compound of types **6** and **7**, which may be important synthons for further synthetic manipulations. Therefore, the present report involves diastereoselective *MBH* reactions between chiral oxygenated cyclopentenones **2** and **3** with various aldehydes.

Results and Discussion. – Initially, the reaction of **2** with benzaldehyde (PhCHO) employing several *Lewis* base catalysts such as DABCO, DMAP, Bu₃P, Cy₃P, and Ph₃P was investigated. The reaction performed using 20 mol-% of DABCO in the presence of PhOH in THF at room temperature for 10 d did not give the *MBH* adduct **4a**, and the starting compound **2** was recovered in 73% yield (*Table 1, Entry 1*). Gratifyingly, when 20 mol-% of Bu₃P was used in place of DABCO, the desired adduct **4a** was obtained in 73% as a mixture of two diastereoisomers (**4aA/4aB** 88:12) along with starting compound **2** (19%; *Table 1, Entry 2*). The two diastereoisomers of **4a** can be readily separated by preparative thin-layer chromatography (PLC; SiO₂) to afford **4aA** and **4aB** as the major and minor products, respectively. The reactions employing tricyclohexylphosphine (Cy₃P) and Ph₃P gave inferior results and lower yields of the expected *MBH* adduct **4a** (23 and 13% resp.; *Table 1, Entries 3–4*). It is worth noting that, even though the use of Ph₃P gave the adduct **4a** in low yield, the reaction was highly diastereoselective affording **4a** as a single diastereoisomer.

After identifying an appropriate promoters (Bu₃P/phenol; *Table 1, Entry 2*), we then further examined the effect of choice of solvent on the diastereoselectivity of the reaction (*Table 2*). The reaction performed in both AcOEt and CH₂Cl₂ gave moderate yields of **4a** (56 and 64%, resp.) with low diastereoselectivity (*Table 2, Entries 1 and 2*). Both yield and diastereoselectivity were deteriorated, when the reactions were carried out in toluene, acetone, MeOH, and MeCN (*Table 2, Entries 3–6*). Although THF afforded **4a** in low yield, good diastereoselectivity was obtained (*Table 2, Entry 7*).

Table 1. Optimization of the MBH Reaction between Compound **2** and Benzaldehyde by Employing Various Catalysts

2 + PhCHO $\longrightarrow$ **4aA** (major) + **4aB** (minor)

Entry	Reaction conditions ^{a)}	4a [%] ^{b)}	2 [%] ^{b)}	dr of 4a ^{c)}
1	DABCO, PhOH, THF ^{d)}	0	73	–
2	Bu ₃ P, PhOH, THF ^{d)}	73	19	88 : 12
3	Cy ₃ P, PhOH, toluene	23	64	73 : 27
4	Ph ₃ P, PhOH, THF	13	83	100 : 0

^{a)} Unless stated otherwise, the reactions were carried out by using 1 equiv. of **2** (0.2 mmol), 1 equiv. of PhCHO, 20 mol-% of catalyst and PhOH at room temperature for 10 d. ^{b)} Yields of isolated products. ^{c)} Determined after separation by PLC (SiO₂). ^{d)} 1.5 Equiv. of PhCHO was used.

Table 2. Solvent Effect on the Diastereoselectivity of the MBH Reaction of **2** with PhCHO

Entry ^{a)}	Solvent	4a [%] ^{b)}	2 [%] ^{b)}	dr of 4a ^{c)}
1	AcOEt	56	9	55 : 45
2	CH ₂ Cl ₂	64	13	58 : 42
3	Toluene	16	14	35 : 65
4	Acetone	21	12	51 : 49
5	MeOH	32	37	36 : 64
6	MeCN	29	23	39 : 61
7	THF	17	67	84 : 16

^{a)} The reaction on 0.1-mmol scale of **2** by using PhCHO (1.5 equiv.), Bu₃P (20 mol-%), PhOH (20 mol-%), and solvent (1 ml) was performed for 24 h. ^{b)} Yields of isolated products. ^{c)} Determined after separation by PLC (SiO₂).

To further optimize the reaction conditions, the reaction temperature and reaction time were varied. Comparable results were observed, when the reactions of **2** and PhCHO were carried out at room temperature for 15 and 24 h, respectively (Table 3, Entries 1 and 2). Adduct **4a** was obtained in good yield with good diastereoselectivity. High reaction temperature (refluxing THF for 16 h) was found harmful to the reaction, leading to lower yield and diastereoselectivity (Table 3, Entry 3). Neither yield nor diastereoselectivity was improved, when the reactions were carried out at prolonged reaction times (168 and 240 h, resp.; Table 3, Entries 4 and 5).

From the results compiled in Tables 1–3, the optimum conditions for the reaction of **2** with PhCHO are the presence of Bu₃P (20 mol-%), PhOH (20 mol-%), and THF, and room temperature for 24 h. These conditions were employed as optimized reaction conditions for the exploration of the applicability of compounds **2** and **3** as chiral activated alkenes in the MBH reaction with various aromatic and aliphatic aldehydes (Table 4, Entries 1–9 and 10–14, resp.). The results collected in Table 4 revealed that

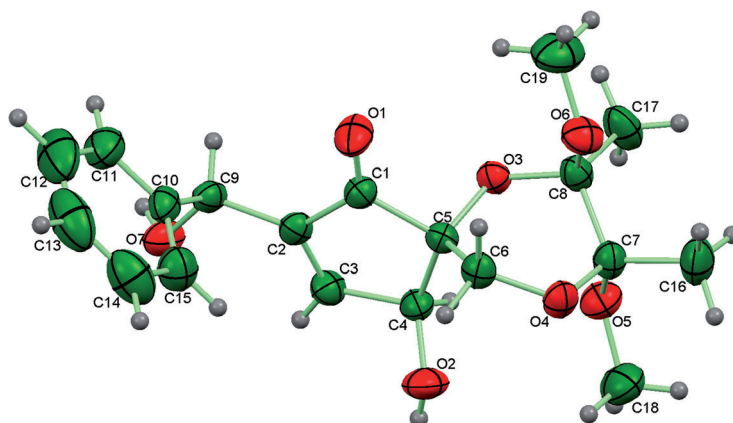
Table 3. Optimization for the Reaction Time of the MBH Reaction of **2** with PhCHO Using 20 mol-% of Bu₃P and PhOH at Room Temperature

Entry ^{a)}	Time [h]	4a [%] ^{b)}	2 [%] ^{b)}	dr of 4a ^{c)}
1	15	64	6	88:12
2	24	69	10	88:12
3 ^{d)}	16	44	15	66:34
4	168	70	7	73:27
5	240	77	13	79:21

^{a)} The reaction was performed on 0.2-mmol scale in degassed THF (2 ml). ^{b)} Yields of isolated products.

^{c)} Determined after separation on PLC (SiO₂). ^{d)} The reaction was performed under refluxing in THF.

the reactions of compounds **2** and **3** with benzaldehydes having both electron-withdrawing and electron-donating substituents readily proceeded with moderate-to-high diastereoselectivities and afforded the corresponding adducts **4** and **5** in moderate-to-good yields, together with the recovery of starting material in almost all cases (Table 4, Entries 2–8). With an heteroaromatic aldehyde, an α,β -unsaturated aldehyde, and aliphatic aldehydes, the reactions of compound **2** were not efficient, and the corresponding MBH adducts **4** were obtained in lower yields with low-to-moderate diastereoselectivities (Table 4, Entries 10–14). It should be mentioned that the two diastereoisomers of each adduct can be separated by PLC. The absolute configuration of the major isomer of **4a**, i.e., **4aA**, was determined by X-ray crystallography (Fig.), and the configuration of the newly created stereogenic center of **4aA** was assigned as (*S*)¹⁾. The observed stereochemical outcomes of compound **4aA** can be rationalized by closed transition state of Zimmerman–Traxler model as

Figure. X-Ray Structure of the Major Diastereoisomer of **4a** (**4aA**)

¹⁾ CCDC-893001 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

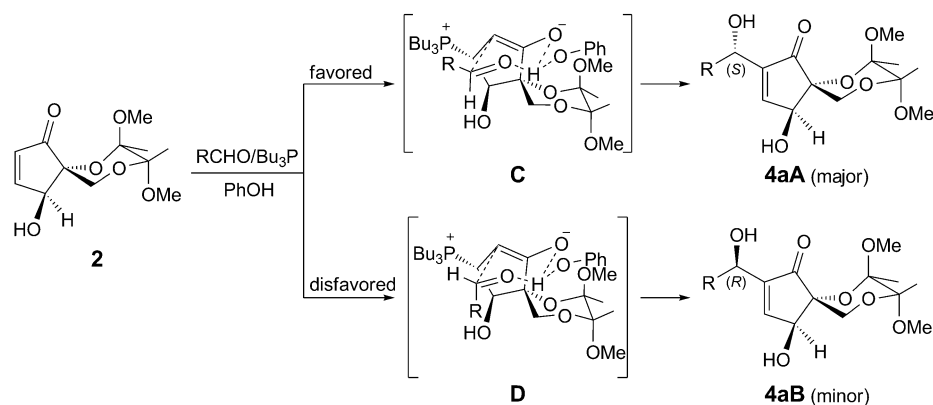
Table 4. The MBH Reaction of Chiral Oxygenated Cyclopentenones **2** and **3** with Aldehydes to Give the Corresponding Adducts **4** and **5**

$\mathbf{2 \text{ or } 3} + \text{RCHO} \xrightarrow[\text{THF (degassed), r.t., 24 h}]{20 \text{ mol-\% of Bu}_3\text{P, 20 mol-\% of PhOH}}$														
			<table> <tr> <td></td> <td>X</td> <td>Y</td> </tr> <tr> <td>4</td> <td>OH</td> <td>H</td> </tr> <tr> <td>5</td> <td>H</td> <td>OH</td> </tr> </table>			X	Y	4	OH	H	5	H	OH	
	X	Y												
4	OH	H												
5	H	OH												
Entry	RCHO	Enone 2 or 3 ^a)	Adducts	Yield [%] ^b)		2 or 3 [%] ^b)								
				A	B									
1	Benzaldehyde	2	4a (R = Ph)	61	8	10								
		3	5a (R = Ph)	37	24	9								
2	4-Nitrobenzaldehyde	2	4b (R = 4-NO ₂ -C ₆ H ₄)	55	32	6								
		3	5b (R = 4-NO ₂ -C ₆ H ₄)	67	22	–								
3	4-Chlorobenzaldehyde	2	4c (R = 4-Cl-C ₆ H ₄)	50	21	15								
		3	5c (R = 4-Cl-C ₆ H ₄)	41	27	13								
4	3-Methoxybenzaldehyde	2	4d (R = 3-MeO-C ₆ H ₄)	38	35	14								
		3	5d (R = 3-MeO-C ₆ H ₄)	52	9	23								
5	4-Methylaldehyde	2	4e (R = Me-C ₆ H ₄)	40	5	32								
		3	5e (R = Me-C ₆ H ₄)	46	12	22								
6	2-Chlorobenzaldehyde	2	4f (R = 2-Cl-C ₆ H ₄)	38	32	10								
7	<i>p</i> -Anisaldehyde	2	4g (R = 4-MeO-C ₆ H ₄)	23	9	32								
		3	5g (R = 4-MeO-C ₆ H ₄)	46	5	27								
8	Furan-2-carbaldehyde	2	4h (R = Furan-2-yl)	23	35	7								
9	2,3-Dimethoxybenzaldehyde	2	4i (R = 2,3-(MeO) ₂ -C ₆ H ₃)	57	8	21								
10	Cinnamaldehyde	2	4j (R = Ph-CH=CH)	22	21	13								
11	Propionaldehyde	2	4k (R = Et)	37	36	15								
12	Isobutyraldehyde	2	4l (R = ⁱ Pr)	34	10	14								
13	Butyraldehyde	2	4m (R = Pr)	31	38	–								
14	Hydrocinnamaldehyde (= 3-phenylpropanal)	2	4n (R = Ph-CH ₂ CH ₂)	22	28	15								

^a) The reaction on 0.2-mmol scale was carried out. ^b) Yields of isolated products.

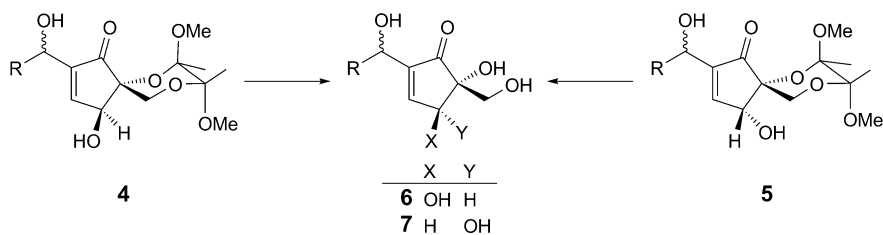
shown in *Scheme 2*. The reaction of **2** with PhCHO and other aldehydes was proposed to proceed through transition states **C** and **D** as depicted in *Scheme 2*. The transition state **C** is energetically more favorable than the transition state **D** due to minimized steric repulsion between the OH and R groups.

Having the MBH adducts **4** and **5** in hand, we have briefly studied the synthetic utilities of these adducts for the preparation of the corresponding polyhydroxylated cyclopentenones **6** and **7**, respectively. Thus, compound **4aA** as a single stereoisomer was subjected to hydrolysis mediated by 1% aq. CF₃COOH (TFA) to afford the expected polyhydroxylated cyclopentenone **6a** in good yield as a 3.8:1 mixture of two diastereoisomers (*Table 5, Entry 1*). This implies that epimerization at the stereogenic benzylic C-atom carrying the acidic H-atom took place under the reaction conditions. The reaction of **4aB** and **4mB** were also carried out under similar reaction conditions

Scheme 2. Proposed Transition State of the MBH Reaction of **2** with Aldehyde


leading to similar results (Table 5, Entry 2 and 3, resp.). Diastereoisomer ratio (dr) **6aA**/**6aB** was determined by integration of the signal of HO–C(4) of the major isomer (4.67 (*d*, *J* = 4.7 for **6aA**) and 4.72 (*dd*, *J* = 4.4, 1.5 for **6aB**)) and of the minor isomer (4.69 (*d*, *J* = 4.7 for **6aA**) and 4.64 (*dd*, *J* = 4.4, 1.5 for **6aB**)). Whereas, dr of **6mB**/**6mA** was determined by integration of the signal of H–C(3) of the major isomer (7.19 (*t*, *J* = 1.7)) and of the minor isomer (7.22 (*t*, *J* = 1.7)).

To our delight, the hydrolysis of **4eA**, **4fB**, **5dA**, **5dB**, and **5eA** with 1% aq. TFA using water bath of an ultrasonic cleaner at 40–60° for 3 h gave **6eA**, **6fB**, **7dA**, **7dB**,

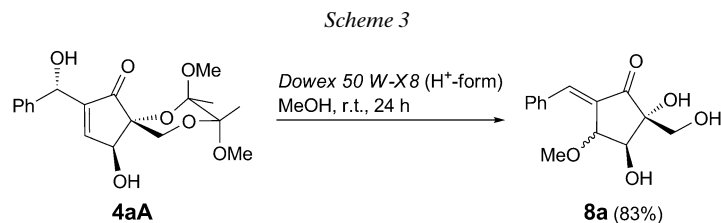
 Table 5. Hydrolysis of the MBH Adducts **4** or **5**


Entry	MBH Adducts	Reaction conditions	Hydrolysis adducts	Yield [%] ^{a)}
1	4aA	1% aq. TFA, r.t., 5 h	6aA	66 ^{b)}
2	4aB	1% aq. TFA, r.t., 5 h	6aB	76 ^{b)}
3	4mB	1% aq. TFA, r.t., 5 h	6mB	82 ^{c)}
4	4eA	1% aq. TFA, sonication ^{d)}	6eA	78
5	4fB	1% aq. TFA, sonication ^{d)}	6fB	72
6	5dA	1% aq. TFA, sonication ^{d)}	7dA	74
7	5dB	1% aq. TFA, sonication ^{d)}	7dB	63
8	5eA	1% aq. TFA, sonication ^{d)}	7eA	49

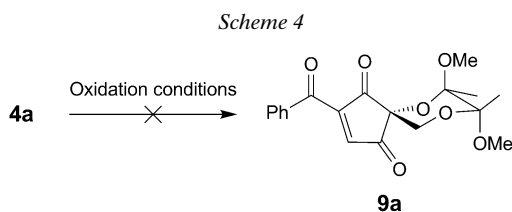
^{a)} Yields of isolated products. ^{b)} Diastereoisomer ratio 3.8:1, determined by ¹H-NMR. ^{c)} Diastereoisomer ratio 7.7:1, determined by ¹H-NMR. ^{d)} 35 kHz, 120/480 W, 40–60°, 3 h.

and **7eA** in 78, 72, 74, 63, and 49% yield; each as a single isomer, respectively (Table 5, Entries 4–8).

In addition, attempts to perform hydrolysis of **4aA** using *Dowex 50 W-X8* (H^+ -form) [10] in MeOH at room temperature for 24 h resulted in the formation of compound **8a** in 83% yield as a 1:1 mixture of diastereoisomers the ratio of which was determined by integration of the signals of benzylic H-atoms at 4.98 (s) and 4.96 (s) ppm. We assume that compound **8a** was derived from the formation of a benzylic carbonium ion under the reaction conditions, followed by an S_N2' addition of MeOH (Scheme 3).



Finally, our efforts to perform oxidation of **4a** to the expected triketo derivative **9a** by employing several oxidizing agents such as PCC, PDC, IBX, DIB, DMP, MnO_2 , $FeCl_3$, DDQ, TEMPO, and *Swern* oxidation were unsuccessful. In all cases, a complex mixture of products was obtained (Scheme 4).



Conclusion. – We have reported that *C*(2)-hydroxyalkylation of (4*S*,5*R*,7*R*,8*R*)- and (4*R*,5*R*,7*R*,8*R*)-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-ones (**2** and **3**, resp.) can be achieved through the *Morita–Baylis–Hillman* reaction with high diastereoselectivity. The diastereofacial selectivity of the reaction can be explained by the *Zimmerman–Traxler* model. We have also demonstrated that the resulting *MBH* adducts can be converted to highly chiral oxygenated cyclopent-2-enones. Due to particular flexibility and ease of the methodology, asymmetric *C*(2)-branched, highly oxygenated cyclopentenone adducts can be accessed, and they may be found useful as chiral synthons for organic synthesis.

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Experimental Part

General. Compounds **2** and **3** were synthesized according to the literature [7]. The org. solvents were dried over appropriate drying agents and distilled prior to use. TLC and prep. layer chromatography (PLC): silica gel (SiO₂); visualization with UV light. Column chromatography (CC): SiO₂ (60–120 mesh). M.p.: Büchi 501 melting-point apparatus, uncorrected. Bath of an ultrasonic cleaner: Bandelin SONOREX Digital 10P. Optical rotation: Jasco P-1020 polarimeter. IR Spectra: Jasco A-302 or Perkin-Elmer 683 spectrometer; in KBr, or CHCl₃, or neat. ¹H- and ¹³C-NMR: Bruker DPX-300 at 300 and 75 MHz, resp., or Bruker 500 at 500 and 125 MHz, resp., in CDCl₃ or (D₆)acetone with Me₄Si as an internal standard; chemical shifts (δ) downfield from Me₄Si; coupling constants (*J*) in Hz. MS: Thermo Finnigan Polaris Q mass spectrometer. HR-MS: HR-TOF-MS Micromass model VQ-TOF 2 or Finnigan MAT 95 mass spectrometer. X-ray crystallographic analysis: Kappa CCD.

The MBH Reaction of 2 and 3. General Procedure: A mixture of **2** or **3** (0.2 mmol), aldehyde (0.35 mmol), and 20 mol-% of PhOH in dry THF was degassed and then cooled to 15°. In a separated flask, a soln. of 20 mol-% of Bu₃P in dry THF was degassed and then added to the above mixture *via* cannula. The mixture was allowed to warm up to r.t. and stirred for 24 h. The solvent was removed *in vacuo*, and the crude product was purified by PLC (SiO₂, 20% AcOEt/CH₂Cl₂ (3 ×) and 30% AcOEt/hexanes (3 ×) for **2** and **3**, resp.).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(*S*)-hydroxy(phenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4aA**). Less polar. Yield: 44.5 mg (61%). White solid. M.p. 154–155°. [α]_D²⁵ = –30 (*c* = 1.02, CHCl₃). IR (KBr): 3385, 3271, 1720, 1455, 1215, 1038. ¹H-NMR (300 MHz, CDCl₃): 7.34–7.29 (*m*, 5 H); 7.18 (*t*, *J* = 1.6, 1 H); 5.53 (*s*, 1 H); 4.90 (*s*, 1 H); 4.08 (*d*, *J* = 11.0, 1 H); 3.81 (*d*, *J* = 11.0, 1 H); 3.47 (*s*, 3 H); 3.42 (*s*, 3 H); 3.46–3.35 (*br.*, OH); 3.17–3.00 (*br.*, OH); 1.43 (*s*, 3 H); 1.36 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 201.8; 154.2; 147.0; 140.2; 128.7 (2 ×); 128.3; 126.6 (2 ×); 100.6; 100.5; 82.5; 78.5; 69.6; 60.2; 49.4; 48.6; 18.9; 18.7. MS: 364 (1, *M*⁺), 333 (43, [*M* – MeO]⁺). HR-MS: 387.1412 ([*M* + Na]⁺, C₁₉H₂₄NaO₇; calc. 387.1420).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(*R*)-hydroxy(phenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4aB**). More polar. Yield: 6.1 mg (8%). White solid. M.p. 176–178°. [α]_D²⁵ = –75.5 (*c* = 0.99, CHCl₃). IR (KBr): 3434, 1703, 1456, 1226, 1145, 1109, 1033. ¹H-NMR (300 MHz, CDCl₃): 7.39–7.32 (*m*, 5 H); 7.18 (*t*, *J* = 1.7, 1 H); 5.54 (*s*, 1 H); 4.88 (*s*, 1 H); 4.17 (*d*, *J* = 11.0, 1 H); 3.90 (*d*, *J* = 11.0, 1 H); 3.43 (*s*, 3 H); 3.39 (*s*, 3 H); 3.29 (*d*, *J* = 2.6, OH); 3.12–2.62 (*br.*, OH); 1.43 (*s*, 3 H); 1.33 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 201.9; 154.4; 147.0; 140.3; 128.6 (2 ×); 128.2; 126.5 (2 ×); 100.6 (2 ×); 82.1; 78.6; 69.6; 60.3; 49.4; 48.5; 18.9; 18.7. MS: 364 (1, *M*⁺), 333 (20, [*M* – MeO]⁺). HR-MS: 387.1431 ([*M* + Na]⁺, C₁₉H₂₄NaO₇; calc. 387.1420).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(*S*)-hydroxy(4-nitrophenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4bA**). Less polar. Yield: 44.7 mg (55%). White solid. M.p. 182–183°. [α]_D²⁵ = –60.4 (*c* = 0.91, CHCl₃). IR (KBr): 3509, 3455, 1717, 1608, 1514, 1354, 1213, 1145, 1114, 1037. ¹H-NMR (300 MHz, CDCl₃): 8.23 (*d*, *J* = 8.8, 2 H); 7.58 (*d*, *J* = 8.8, 2 H); 7.17 (*dd*, *J* = 2.2, 1.3, 1 H); 5.66 (*s*, 1 H); 4.91 (*d*, *J* = 1.9, 1 H); 4.29 (*d*, *J* = 11.0, 1 H); 4.09 (*d*, *J* = 11.0, 1 H); 3.46 (*s*, 3 H); 3.42 (*s*, 3 H); 3.36 (*s*, 1 H); 3.35 (*s*, 1 H); 1.42 (*s*, 3 H); 1.35 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 201.7; 154.9; 147.8; 147.3; 146.0; 127.3 (2 ×); 123.9 (2 ×); 100.7, 100.6; 82.3; 78.5; 68.6; 60.1; 49.4; 48.6; 18.9; 18.7. MS: 409 (1, *M*⁺), 378 (28, [*M* – MeO]⁺). HR-MS: 432.1266 ([*M* + Na]⁺, C₁₉H₂₃NNaO₇; calc. 432.1271).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(*R*)-hydroxy(4-nitrophenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4bB**). More polar. Yield: 26.5 mg (32%). White solid. M.p. 220–221°. [α]_D²⁵ = –42.0 (*c* = 0.54, CHCl₃). IR (KBr): 3457, 1709, 1608, 1529, 1350, 1108. ¹H-NMR (300 MHz, CDCl₃): 8.23 (*d*, *J* = 8.8, 2 H); 7.60 (*d*, *J* = 8.8, 2 H); 7.25 (*s*, 1 H); 5.64 (*s*, 1 H); 4.89 (*s*, 1 H); 4.14 (*d*, *J* = 11.0, 1 H); 3.88 (*d*, *J* = 11.0, 1 H); 3.43 (*s*, 3 H); 3.38 (*s*, 3 H); 3.57–3.30 (*br.*, 2 H); 1.43 (*s*, 3 H); 1.32 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 201.7; 155.0; 147.7; 147.4; 146.1; 127.3 (2 ×); 123.8 (2 ×); 100.7; 100.6; 82.0; 78.6; 68.5; 60.1; 49.4; 48.5; 18.8; 18.7. MS: 405 (38, [*M* – 3]⁺). HR-MS: 432.1276 ([*M* + Na]⁺, C₁₉H₂₃NNaO₇; calc. 432.1271).

(4*S*,5*R*,7*R*,8*R*)-2-[(*S*)-(4-Chlorophenyl)hydroxymethyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4cA**). Less polar. Yield: 39.7 mg (50%). White solid. M.p. 141–142°. [α]_D²⁵ = –7.5 (*c* = 0.90, CHCl₃). IR (KBr): 3379, 1717, 1648, 1377, 1032. ¹H-NMR (300 MHz, CDCl₃):

7.35–7.28 (*m*, 4 H); 7.16 (*s*, 1 H); 5.50 (*s*, 1 H); 4.88 (*s*, 1 H); 4.06 (*d*, *J* = 11.0, 1 H); 3.79 (*d*, *J* = 11.0, 1 H); 3.45 (*s*, 3 H); 3.41 (*s*, 3 H); 3.45–3.41 (*br.*, OH); 3.33–3.10 (*br.*, OH); 1.42 (*s*, 3 H); 1.35 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 201.7; 154.3; 146.8; 138.8; 134.0; 128.8 (2 ×); 127.9 (2 ×); 100.6; 100.5; 82.3; 78.4; 68.9; 60.1; 49.3; 48.6; 18.9; 18.7. MS: 398 (0.5, *M*⁺), 367 (5, [*M* – MeO]⁺). HR-MS: 421.1025 ([*M* + Na]⁺, C₁₉H₂₃ClNaO₇⁺; calc. 421.1030).

(4*S*,5*R*,7*R*,8*R*)-2-[*(R)*-(4-Chlorophenyl)hydroxymethyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4cB**). More polar. Yield: 17.0 mg (21%). White solid. M.p. 177–178°. [*α*]_D²⁵ = –47.4 (*c* = 0.91, CHCl₃). IR (KBr): 3455, 1707, 1145, 1105, 1035. ¹H-NMR (300 MHz, CDCl₃): 7.34 (*s*, 4 H); 7.18 (*dd*, *J* = 2.3, 1.3, 1 H); 5.51 (*s*, 1 H); 4.88 (*t*, *J* = 1.9, 1 H); 4.16 (*d*, *J* = 11.0, 1 H); 3.88 (*d*, *J* = 11.0, 1 H); 3.43 (*s*, 3 H); 3.39 (*s*, 3 H); 3.18–2.83 (*br.*, OH); 1.43 (*s*, 3 H); 1.33 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 201.8; 154.5; 146.7; 138.8; 134.0; 128.8 (2 ×); 127.9 (2 ×); 100.6 (2 ×); 82.0; 78.6; 68.9; 60.2; 49.4; 48.5; 18.9; 18.7. MS: 398 (3, *M*⁺). HR-MS: 421.1057 ([*M* + Na]⁺, C₁₉H₂₃ClNaO₇⁺; calc. 421.1030).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[*(S)*-hydroxy(3-methoxyphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4dA**). Less polar. Yield: 29.8 mg (38%). White semi-solid. [*α*]_D²⁵ = –56.6 (*c* = 0.96, CHCl₃). IR (KBr): 3455, 1720, 1601, 1458, 1261, 1034. ¹H-NMR (300 MHz, CDCl₃): 7.27 (*t*, 1 H); 7.17 (*dd*, *J* = 2.2, 1.4, 1 H); 6.94–6.92 (*m*, 2 H); 6.85 (*ddd*, *J* = 8.2, 2.5, 1.0, 1 H); 5.51 (*s*, 1 H); 4.90 (*s*, 1 H); 4.11 (*d*, *J* = 11.0, 1 H); 3.82 (*d*, *J* = 11.0, 1 H); 3.81 (*s*, 3 H); 3.48 (*s*, 3 H); 3.43 (*s*, 3 H); 3.40–3.33 (*br.*, OH); 3.17–3.03 (*br.*, OH); 1.43 (*s*, 3 H); 1.36 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 201.8; 159.9; 154.4; 146.9; 141.8; 129.7; 118.8; 113.9; 112.0; 100.6; 100.5; 82.5; 78.5; 69.5; 60.3; 55.2; 49.4; 48.6; 18.9; 18.7. MS: 394 (2, *M*⁺), 363 (35, [*M* – MeO]⁺). HR-MS: 417.1527 ([*M* + Na]⁺, C₂₀H₂₆NaO₈⁺; calc. 417.1525).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[*(R)*-hydroxy(3-methoxyphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4dB**). More polar. Yield: 27.7 mg (35%). White solid. M.p. 150–151°. [*α*]_D²⁵ = –103.7 (*c* = 0.62, CHCl₃). IR (KBr): 3402, 1724, 1610, 1489, 1287, 1034. ¹H-NMR (300 MHz, CDCl₃): 7.28 (*t*, *J* = 8.2, 1 H); 7.18 (*dd*, *J* = 2.2, 1.3, 1 H); 6.97–6.95 (*m*, 2 H); 6.85 (*ddd*, *J* = 8.2, 2.5, 0.9, 1 H); 5.51 (*s*, 1 H); 4.87 (*s*, 1 H); 4.16 (*d*, *J* = 11.0, 1 H); 3.90 (*d*, *J* = 11.0, 1 H); 3.82 (*s*, 3 H); 3.43 (*s*, 3 H); 3.39 (*s*, 3 H); 3.35–3.27 (*br.*, OH); 3.13–2.97 (*br.*, OH); 1.43 (*s*, 3 H); 1.33 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 202.0; 160.0; 154.5; 147.0; 141.9; 129.7; 118.9; 113.9; 112.1; 100.6 (2 ×); 81.9; 78.4; 69.3; 60.3; 55.4; 49.4; 48.6; 18.9; 18.7. MS: 394 (2, *M*⁺), 363 (49, [*M* – MeO]⁺). HR-MS: 417.1523 ([*M* + Na]⁺, C₂₀H₂₆NaO₈⁺; calc. 417.1525).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[*(S)*-hydroxy(4-methylphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4eA**). Less polar. Yield: 30.2 mg (40%). White solid. M.p. 154–155°. [*α*]_D²⁵ = –0.6 (*c* = 1.12, CHCl₃). IR (KBr): 3274, 1721, 1150, 1109, 1039. ¹H-NMR (300 MHz, CDCl₃): 7.25 (*d*, *J* = 8.0, 2 H); 7.20 (*t*, *J* = 1.9, 1 H); 7.17 (*d*, *J* = 8.0, 2 H); 5.50 (*s*, 1 H); 4.91 (*d*, *J* = 1.9, 1 H); 4.10 (*d*, *J* = 10.9, 1 H); 3.81 (*d*, *J* = 10.9, 1 H); 3.49 (*s*, 3 H); 3.44 (*s*, 3 H); 3.34 (*d*, *J* = 2.7, 1 H); 2.88 (*d*, *J* = 3.0, 1 H); 2.35 (*s*, 3 H); 1.43 (*s*, 3 H); 1.36 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 201.7; 154.1; 147.2; 138.1; 137.3; 129.4 (2 ×); 126.5 (2 ×); 100.7; 100.6; 82.7; 78.6; 69.6; 60.4; 49.4; 48.6; 21.1; 18.9; 18.7. MS: 347 (19, [*M* – MeO]⁺). HR-MS: 401.1573 ([*M* + Na]⁺, C₂₀H₂₆NaO₇⁺; calc. 401.1576).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[*(R)*-hydroxy(4-methylphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4eB**). More polar. Yield: 3.7 mg (5%). White solid. M.p. 171–172°. [*α*]_D²⁵ = –19.7 (*c* = 0.69, CHCl₃). IR (KBr): 3448, 1706, 1145, 1108, 1035. ¹H-NMR (500 MHz, CDCl₃): 7.28 (*d*, *J* = 8.0, 2 H); 7.20 (*t*, *J* = 1.3, 1 H); 7.18 (*d*, *J* = 8.0, 2 H); 5.50 (*s*, 1 H); 4.88 (*s*, 1 H); 4.17 (*d*, *J* = 11.0, 1 H); 3.90 (*d*, *J* = 11.0, 1 H); 3.44 (*s*, 3 H); 3.40 (*s*, 3 H); 3.37–3.30 (*br.*, OH); 3.00–2.82 (*br.*, OH); 2.36 (*s*, 3 H); 1.44 (*s*, 3 H); 1.33 (*s*, 3 H). ¹³C-NMR (125 MHz, CDCl₃): 201.8; 154.3; 147.1; 138.0; 137.3; 129.3 (2 ×); 126.5 (2 ×); 100.6; 100.5; 82.2; 78.6; 69.5; 60.4; 49.4; 48.5; 21.1; 18.9; 18.7. MS: 347 (3, [*M* – MeO]⁺). HR-MS: 401.1576 ([*M* + Na]⁺, C₂₀H₂₆NaO₇⁺; calc. 401.1576).

(4*S*,5*R*,7*R*,8*R*)-2-[*(S)*-(2-Chlorophenyl)(hydroxy)methyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4fA**). Less polar. Yield: 30.0 mg (38%). White solid. M.p. 153–154°. [*α*]_D²⁵ = +17.4 (*c* = 1.27, CHCl₃). IR (KBr): 3279, 1718, 1444, 1214, 1160, 1100, 1038. ¹H-NMR (300 MHz, CDCl₃): 7.57 (*dd*, *J* = 7.5, 1.6, 1 H); 7.38–7.24 (*m*, 3 H); 7.02 (*s*, 1 H); 5.92 (*s*, 1 H); 4.88 (*s*, 1 H); 4.16 (*d*, *J* = 11.0, 1 H); 3.89 (*d*, *J* = 11.0, 1 H); 3.48 (*s*, 3 H); 3.42 (*s*, 3 H); 3.54–3.31 (*br.*, 2 OH); 1.44 (*s*, 3 H); 1.36 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 202.1; 155.4; 145.0; 137.5; 132.2; 129.6; 129.2; 127.8; 127.2; 100.6;

100.5; 82.6; 78.5; 65.9; 60.3; 49.3; 48.6; 18.8; 18.7. MS: 399 (0.2, $[M+1]^+$). HR-MS: 421.1036 ($[M+Na]^+$, $C_{19}H_{23}ClNaO_7^+$; calc. 421.1030).

(4S,5R,7R,8R)-2-[*(R)*-(2-Chlorophenyl)(hydroxy)methyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4fB**). More polar. Yield: 25.2 mg (32%). White solid. M.p. 160–161°. $[\alpha]_D^{25} = -96.6$ ($c = 1.08$, $CHCl_3$). IR (KBr): 3400, 1717, 1147, 1109, 1039. 1H -NMR (300 MHz, $CDCl_3$): 7.57 (*dd*, $J = 7.5$, 1.7, 1 H); 7.39–7.04 (*m*, 3 H); 6.97 (*dd*, $J = 2.0$; 1.4, 1 H); 5.93 (*s*, 1 H); 4.89 (*d*, $J = 1.8$, 1 H); 4.16 (*d*, $J = 11.1$, 1 H); 3.88 (*d*, $J = 11.1$, 1 H); 3.46 (*s*, 3 H); 3.52–3.38 (*br.*, OH); 3.42 (*s*, 3 H); 3.38–3.30 (*br.*, OH); 1.44 (*s*, 3 H); 1.36 (*s*, 3 H). ^{13}C -NMR (75 MHz, $CDCl_3$): 202.2; 155.3; 145.2; 137.7; 132.3; 129.5; 129.2; 128.2; 127.3; 100.7 (2 ×); 82.2; 78.4; 66.3; 60.3; 49.3; 48.6; 18.9; 18.7. MS: 398 (0.5, M^+), 367 (2, $[M-MeO]^+$). HR-MS: 421.1044 ($[M+Na]^+$, $C_{19}H_{23}ClNaO_7^+$; calc. 421.1030).

(4S,5R,7R,8R)-4-Hydroxy-2-[*(S)*-hydroxy(4-methoxyphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4gA**). Less polar. Yield: 17.9 mg (23%). White solid. M.p. 155–156°. $[\alpha]_D^{25} = +2.8$ ($c = 0.67$, $CHCl_3$). IR (KBr): 3491, 3386, 1692, 1461, 1217, 1146, 1055. 1H -NMR (300 MHz, $CDCl_3$): 7.28 (*d*, $J = 8.7$, 2 H); 7.20 (*dd*, $J = 1.8$, 1.6, 1 H); 6.89 (*d*, $J = 8.7$, 2 H); 5.48 (*s*, 1 H); 4.91 (*d*, $J = 2.2$, 1 H); 4.09 (*d*, $J = 10.9$, 1 H); 3.81 (*s*, 3 H); 3.80 (*d*, $J = 10.9$, 1 H); 3.48 (*s*, 3 H); 3.43 (*s*, 3 H); 3.37 (*d*, $J = 2.8$, 1 H); 2.88 (*d*, $J = 3.1$, 1 H); 1.43 (*s*, 3 H); 1.36 (*s*, 3 H). ^{13}C -NMR (75 MHz, $CDCl_3$): 201.7; 159.6; 154.0; 147.3; 132.5; 127.9 (2 ×); 114.1 (2 ×); 100.7; 100.6; 82.7; 78.5; 69.3; 60.3; 55.3; 49.4; 48.6; 18.9; 18.7. MS: 395 (0.7, $[M+1]^+$), 363 (8, $[M-MeO]^+$). HR-MS: 417.1508 ($[M+Na]^+$, $C_{20}H_{26}NaO_8^+$; calc. 417.1525).

(4S,5R,7R,8R)-4-Hydroxy-2-[*(R)*-hydroxy(4-methoxyphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4gB**). More polar. Yield: 6.7 mg (9%). White solid. M.p. 174–175°. $[\alpha]_D^{25} = -32.4$ ($c = 0.73$, $CHCl_3$). IR (KBr): 3392, 1720, 1611, 1510, 1248, 1036. 1H -NMR (500 MHz, $CDCl_3$): 7.31 (*dd*, $J = 8.7$, 2 H); 7.20 (*dd*, $J = 2.2$, 1.3, 1 H); 6.90 (*d*, $J = 8.7$, 2 H); 5.48 (*s*, 1 H); 4.89 (*d*, $J = 1.7$, 1 H); 4.18 (*d*, $J = 11.0$, 1 H); 3.90 (*d*, $J = 11.0$, 1 H); 3.82 (*s*, 3 H); 3.44 (*s*, 3 H); 3.40 (*s*, 3 H); 3.29 (*d*, $J = 2.9$, 1 H); 2.88–2.82 (*br.*, OH); 1.44 (*s*, 3 H); 1.34 (*s*, 3 H). ^{13}C -NMR (125 MHz, $CDCl_3$): 201.8; 159.5; 154.1; 147.2; 132.4; 127.9 (2 ×); 114.1 (2 ×); 100.6; 100.5; 82.2; 78.6; 69.3; 60.4; 55.3; 49.4; 48.5; 18.9; 18.7. MS: 394 (3, M^+). HR-MS: 417.1516 ($[M+Na]^+$, $C_{20}H_{26}NaO_8^+$; calc. 417.1525).

(4S,5R,7R,8R)-2-[*(R)*-(Furan-2-yl)(hydroxy)methyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4hA**). Less polar. Yield: 15.8 mg (23%). White solid. M.p. 133–134°. $[\alpha]_D^{25} = -23.8$ ($c = 0.57$, $CHCl_3$). IR (KBr): 3389, 3261, 1723, 1640, 1499, 1212, 1041. 1H -NMR (300 MHz, $CDCl_3$): 7.46–7.34 (*m*, 2 H); 6.35 (*dd*, $J = 3.2$, 1.9, 1 H); 6.28 (*d*, $J = 3.2$, 1 H); 5.58 (*s*, 1 H); 4.95 (*d*, $J = 1.9$, 1 H); 4.17 (*d*, $J = 10.9$, 1 H); 3.89 (*d*, $J = 10.9$, 1 H); 3.49 (*s*, 3 H); 3.45 (*s*, 3 H); 3.42 (*d*, $J = 2.6$, 1 H); 3.07–2.98 (*br.*, OH); 1.44 (*s*, 3 H); 1.37 (*s*, 3 H). ^{13}C -NMR (75 MHz, $CDCl_3$): 201.3; 155.2; 152.7; 144.3; 142.8; 110.5; 107.9; 100.7; 100.6; 82.6; 78.6; 63.3; 60.4; 49.4; 48.6; 18.9; 18.7. MS: 354 (23, M^+). HR-MS: 377.1212 ($[M+Na]^+$, $C_{17}H_{22}NaO_8^+$; calc. 377.1212).

(4S,5R,7R,8R)-2-[*(S)*-(Furan-2-yl)(hydroxy)methyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4hB**). More polar. Yield: 24.9 mg (35%). White solid. M.p. 142–143°. $[\alpha]_D^{25} = -33.4$ ($c = 0.54$, $CHCl_3$). IR (KBr): 3427, 1709, 1639, 1459, 1146, 1110, 1036. 1H -NMR (300 MHz, $CDCl_3$): 7.40–7.38 (*m*, 2 H); 6.38–6.33 (*m*, 1 H); 6.30 (*d*, $J = 3.2$, 1 H); 5.55 (*s*, 1 H); 4.94 (*s*, 1 H); 4.19 (*d*, $J = 11.0$, 1 H); 3.92 (*d*, $J = 11.0$, 1 H); 3.44 (*s*, 3 H); 3.48–3.31 (*br.*, OH); 3.42 (*s*, 3 H); 3.25–3.05 (*br.*, OH); 1.44 (*s*, 3 H); 1.35 (*s*, 3 H). ^{13}C -NMR (75 MHz, $CDCl_3$): 201.5; 155.3; 152.7; 144.1; 142.8; 110.5; 107.9; 100.6 (2 ×); 82.1; 78.6; 63.4; 60.3; 49.4; 48.5; 18.9; 18.7. MS: 354 (14, M^+). HR-MS: 377.1210 ($[M+Na]^+$, $C_{17}H_{22}NaO_8^+$; calc. 377.1212).

(4S,5R,7R,8R)-2-[*(S)*-(2,3-Dimethoxyphenyl)(hydroxy)methyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4iA**). Less polar. Yield: 48.6 mg (57%). White solid. M.p. 174–176°. $[\alpha]_D^{25} = +7.0$ ($c = 0.75$, $CHCl_3$). IR (KBr): 3380, 3275, 1715, 1485, 1294, 1040. 1H -NMR (300 MHz, $CDCl_3$): 7.24 (*s*, 1 H); 7.06 (*t*, $J = 7.9$, 1 H); 6.90 (*t*, $J = 7.9$, 2 H); 5.78 (*s*, 1 H); 4.91 (*s*, 1 H); 4.12 (*d*, $J = 10.8$, 1 H); 3.88 (*s*, 6 H); 3.85 (*d*, $J = 10.8$, 1 H); 3.48 (*s*, 3 H); 3.43 (*s*, 3 H); 3.42–3.30 (*br.*, 2 OH); 1.43 (*s*, 3 H); 1.35 (*s*, 3 H). ^{13}C -NMR (75 MHz, $CDCl_3$): 201.5; 154.5; 152.6; 146.8; 146.4; 133.9; 124.2; 119.4; 112.5; 100.6; 100.5; 82.6; 78.5; 65.3; 60.9; 60.4; 55.8; 49.3; 48.6; 18.9; 18.7. MS: 424 (0.7, M^+), 393 (5, $[M-MeO]^+$). HR-MS: 447.1613 ($[M+Na]^+$, $C_{21}H_{28}NaO_9^+$; calc. 447.1631).

(4S,5R,7R,8R)-2-[*(R)*-(2,3-Dimethoxyphenyl)(hydroxy)methyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4iB**). More polar. Yield: 6.5 mg (8%). White solid. M.p. 186–

187°. $[\alpha]_{\text{D}}^{25} = -55.0$ ($c = 0.66$, CHCl_3). IR (KBr): 3461, 2927, 1717, 1636, 1482, 1285, 1114. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.16 (dd , $J = 2.1, 1.5$, 1 H); 7.08 (t , $J = 7.9$, 1 H); 6.96 (dd , $J = 7.9, 1.5$, 1 H); 6.90 (dd , $J = 8.1, 1.5$, 1 H); 5.77 (d , $J = 5.2$, 1 H); 4.88 (m , 1 H); 4.17 (d , $J = 10.8$, 1 H); 3.90 (d , $J = 10.8$, 1 H); 3.89 (s , 3 H); 3.87 (s , 3 H); 3.45 (s , 1 H); 3.43 (s , 3 H); 3.40 (s , 3 H); 3.12 (d , $J = 3.1$, 1 H); 1.43 (s , 3 H); 1.34 (s , 3 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 201.8; 154.5; 152.5; 146.7; 146.4; 133.7; 124.3; 119.6; 112.4; 100.5 ($2 \times$); 82.0; 78.5; 65.4; 60.9; 60.3; 55.8; 49.3; 48.5; 18.9; 18.7. MS: 424 (0.5, M^+), 393 (1, $[M - \text{MeO}]^+$). HR-MS: 447.1634 ($[M + \text{Na}]^+$, $\text{C}_{21}\text{H}_{28}\text{NaO}_7^+$; calc. 447.1631).

(4S,5R,7R,8R)-4-Hydroxy-2-[(1S,2E)-1-hydroxy-3-phenylprop-2-en-1-yl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4jA**). Less polar. Yield: 17.2 mg (21%). White solid. M.p. 163–164°. $[\alpha]_{\text{D}}^{25} = -27.9$ ($c = 0.59$, CHCl_3). IR (KBr): 3447, 1719, 1655, 1450, 1376, 1216, 1144, 1115, 1035. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.41–7.29 (m , 6 H); 6.71 (d , $J = 15.9$, 1 H); 6.28 (dd , $J = 15.9, 6.6$, 1 H); 5.16 (d , $J = 6.6$, 1 H); 4.94 (s , 1 H); 4.20 (d , $J = 10.9$, 1 H); 3.89 (d , $J = 10.9$, 1 H); 3.51 (s , 3 H); 3.46 (s , 3 H); 3.40–3.27 ($br.$, OH); 2.96–2.60 ($br.$, OH); 1.45 (s , 3 H); 1.37 (s , 3 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 201.9; 154.2; 145.9; 136.1; 132.2; 128.6 ($2 \times$); 128.1; 127.5; 126.7 ($2 \times$); 100.7; 100.6; 82.4; 78.7; 68.2; 60.4; 49.4; 48.6; 18.9; 18.8. MS: (0.5, $[M + 1]^+$). HR-MS: 413.1578 ($[M + \text{Na}]^+$, $\text{C}_{21}\text{H}_{26}\text{NaO}_7^+$; calc. 413.1576).

(4S,5R,7R,8R)-4-Hydroxy-2-[(1R,2E)-1-hydroxy-3-phenylprop-2-en-1-yl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4jB**). More polar. Yield: 16.2 mg (21%). White solid. M.p. 182–183°. $[\alpha]_{\text{D}}^{25} = -33.6$ ($c = 0.71$, CHCl_3). IR (KBr): 3490, 1718, 1451, 1375, 1245, 1166, 1106, 1054. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.41–7.27 (m , 6 H); 6.71 (d , $J = 15.9$, 1 H); 6.29 (dd , $J = 15.9, 6.5$, 1 H); 5.14 (d , $J = 6.5$, 1 H); 4.93 (s , 1 H); 4.20 (d , $J = 11.0$, 1 H); 3.91 (d , $J = 11.0$, 1 H); 3.47 (s , 3 H); 3.45 (s , 3 H); 1.45 (s , 3 H); 1.36 (s , 3 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 201.8; 154.2; 146.1; 136.5; 132.1; 128.6 ($2 \times$); 128.0; 126.8 ($2 \times$); 100.8 ($2 \times$); 82.2; 78.8; 68.3; 60.4; 49.3; 48.6; 18.9; 18.7. MS: 390 (7, M^+). HR-MS: 413.1575 ($[M + \text{Na}]^+$, $\text{C}_{21}\text{H}_{26}\text{NaO}_7^+$; calc. 413.1576).

(4S,5R,7R,8R)-4-Hydroxy-2-[(1S)-1-hydroxypropyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4kA**). Less polar. Yield: 23.4 mg (37%). White solid. M.p. 121–122°. $[\alpha]_{\text{D}}^{25} = -46.4$ ($c = 0.89$, CHCl_3). IR (KBr): 3472, 3383, 1697, 1465, 1218, 1052. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.28 (dd , $J = 2.3, 1.4$, 1 H); 4.90 (d , $J = 1.8$, 1 H); 4.44–4.34 ($br.$, 1 H); 4.17 (d , $J = 10.9$, 1 H); 3.86 (d , $J = 10.9$, 1 H); 3.51 (s , 3 H); 3.45 (s , 3 H); 3.41 (d , $J = 2.4$, 1 H); 2.60–2.40 ($br.$, OH); 1.79–1.61 (m , 2 H); 1.44 (s , 3 H); 1.36 (s , 3 H); 0.95 (t , $J = 7.4$, 3 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 202.2; 153.7; 147.3; 100.7; 100.6; 82.5; 78.5; 68.5; 60.5; 49.4; 48.6; 28.4; 18.9; 18.8; 9.5. MS: 316 (0.2, M^+). HR-MS: 339.1405 ($[M + \text{Na}]^+$, $\text{C}_{15}\text{H}_{24}\text{NaO}_7^+$; calc. 339.1420).

(4S,5R,7R,8R)-4-Hydroxy-2-[(1R)-1-hydroxypropyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4kB**). More polar. Yield: 22.7 mg (36%). White solid. M.p. 133–134°. $[\alpha]_{\text{D}}^{25} = -13.5$ ($c = 0.85$, CHCl_3). IR (KBr): 3504, 1717, 1381, 1219, 1162, 1105, 1047. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.28 (d , $J = 2.0$, 1 H); 4.90 (dd , $J = 3.4, 2.0$, 1 H); 4.39–4.35 (m , 1 H); 4.17 (d , $J = 11.0$, 1 H); 3.87 (d , $J = 11.0$, 1 H); 3.48 (s , 3 H); 3.44 (s , 3 H); 2.92–2.20 ($br.$, 2 OH); 1.84–1.55 (m , 2 H); 1.44 (s , 3 H); 1.36 (s , 3 H); 0.97 (t , $J = 7.4$, 3 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 202.2; 153.9; 147.2; 100.6 ($2 \times$); 82.2; 78.6; 68.6; 60.4; 49.4; 48.5; 28.4; 18.9; 18.7; 9.5. MS: 317 (8, $[M + 1]^+$), 285 (19, $[M - \text{MeO}]^+$). HR-MS: 339.1415 ($[M + \text{Na}]^+$, $\text{C}_{15}\text{H}_{24}\text{NaO}_7^+$; calc. 339.1420).

(4S,5R,7R,8R)-4-Hydroxy-2-[(1S)-1-hydroxy-2-methylpropyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4lA**). Less polar. Yield: 22.3 mg (34%). White solid. M.p. 139–140°. $[\alpha]_{\text{D}}^{25} = -44.2$ ($c = 0.85$, CHCl_3). IR (KBr): 3491, 3386, 1692, 1640, 1461, 1299, 1217, 1145, 1104, 1055. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.28 (s , 1 H); 4.91 (s , 1 H); 4.25 (d , $J = 5.1$, 1 H); 4.18 (d , $J = 10.9$, 1 H); 3.87 (d , $J = 10.9$, 1 H); 3.52 (s , 3 H); 3.45 (s , 3 H); 2.46–2.23 ($br.$, OH); 2.06–1.87 (m , 1 H); 1.86–1.68 ($br.$, OH); 1.45 (s , 3 H); 1.37 (s , 3 H); 0.93 (d , $J = 6.8$, 3 H); 0.89 (d , $J = 6.8$, 3 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 201.9; 154.6; 146.5; 100.6; 100.5; 82.7; 78.4; 72.2; 60.5; 49.3; 48.5; 32.4; 18.9; 18.8; 18.7; 16.6. MS: 330 (0.5, M^+), 299 (3, $[M - \text{MeO}]^+$). HR-MS: 353.1567 ($[M + \text{Na}]^+$, $\text{C}_{16}\text{H}_{26}\text{NaO}_7^+$; calc. 353.1576).

(4S,5R,7R,8R)-4-Hydroxy-2-[(1R)-1-hydroxy-2-methylpropyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4lB**). More polar. Yield: 6.9 mg (10%). White solid. M.p. 149–151°. $[\alpha]_{\text{D}}^{25} = +5.8$ ($c = 0.51$, CHCl_3). IR (KBr): 3501, 3409, 1710, 1463, 1379, 1221, 1166, 1105, 1039. $^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.27 (dd , $J = 2.2, 1.0$, 1 H); 4.94 (dd , $J = 2.1, 0.9$, 1 H); 4.21 (d , $J = 10.8$, 1 H); 4.20 (d , $J = 5.6$, 1 H); 3.87 (d , $J = 10.8$, 1 H); 3.51 (s , 3 H); 3.46 (s , 3 H); 3.57–3.20 ($br.$, OH); 2.70–2.20 ($br.$, OH); 2.10–1.91 (m , 1 H); 1.45 (s , 3 H); 1.37 (s , 3 H); 0.93 (d , $J = 4.8$, 3 H); 0.91 (d , $J = 4.7$, 3 H).

^{13}C -NMR (75 MHz, CDCl_3): 202.4; 155.0; 146.2; 100.9; 100.8; 82.7; 78.8; 73.0; 60.6; 49.4; 48.6; 32.6; 19.0; 18.9; 18.8; 16.7. MS: 330 (6, M^+), 299 (24, $[M - \text{MeO}]^+$). HR-MS: 353.1555 ($[M + \text{Na}]^+$, $\text{C}_{16}\text{H}_{26}\text{NaO}_7$; calc. 353.1576).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*S*)-1-hydroxybutyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4mA**). Less polar. Yield: 25.3 mg (38%). White solid. M.p. 101–102°. $[\alpha]_D^{25} = -55.3$ ($c = 0.98$, CHCl_3). IR (KBr): 3481, 3406, 1690, 1376, 1319, 1217, 1158, 1107, 1057. ^1H -NMR (300 MHz, CDCl_3): 7.27 (*dd*, $J = 2.2, 1.3$, 1 H); 4.90 (*s*, 1 H); 4.46 (*t*, $J = 5.9$, 1 H); 4.17 (*d*, $J = 10.9$, 1 H); 3.86 (*d*, $J = 10.9$, 1 H); 3.50 (*s*, 3 H); 3.45 (*s*, 3 H); 3.41 (*s*, 1 H); 2.61–2.36 (*br.*, OH); 1.68–1.59 (*m*, 2 H); 1.50–1.33 (*m*, 2 H); 1.44 (*s*, 3 H); 1.36 (*s*, 3 H); 0.94 (*t*, $J = 7.3$, 3 H). ^{13}C -NMR (75 MHz, CDCl_3): 202.2; 153.5; 147.7; 100.7; 100.6; 82.5; 78.5; 67.1; 60.5; 49.4; 48.6; 37.6; 18.9; 18.7; 18.5; 13.8. MS: 327 (10, $[M - 3]^+$), 299 (20, $[M - \text{MeO}]^+$). HR-MS: 353.1589 ($[M + \text{Na}]^+$, $\text{C}_{16}\text{H}_{26}\text{NaO}_7$; calc. 353.1576).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*R*)-1-hydroxybutyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4mB**). More polar. Yield: 20.2 mg (31%). White solid. M.p. 127–128°. $[\alpha]_D^{25} = -7.3$ ($c = 0.79$, CHCl_3). IR (KBr): 3412, 3358, 1725, 1429, 1377, 1256, 1108, 1044. ^1H -NMR (300 MHz, CDCl_3): 7.27 (*dd*, $J = 2.5, 1.2$, 1 H); 4.91 (*s*, 1 H); 4.44 (*dd*, $J = 7.4, 4.3$, 1 H); 4.19 (*d*, $J = 10.9$, 1 H); 3.87 (*d*, $J = 10.9$, 1 H); 3.50 (*s*, 3 H); 3.45 (*s*, 3 H); 3.37 (*d*, $J = 3.4$, 1 H); 2.59–2.44 (*br.*, OH); 1.76–1.35 (*m*, 4 H); 1.45 (*s*, 3 H); 1.37 (*s*, 3 H); 0.95 (*t*, $J = 7.3$, 3 H). ^{13}C -NMR (75 MHz, CDCl_3): 202.2; 153.7; 147.5; 100.7; 100.6; 82.4; 78.6; 67.2; 60.5; 49.4; 48.6; 37.6; 18.9; 18.8; 18.5; 13.8. MS: 330 (0.5, M^+), 299 (5, $[M - \text{MeO}]^+$). HR-MS: 353.1566 ($[M + \text{Na}]^+$, $\text{C}_{16}\text{H}_{26}\text{NaO}_7$; calc. 353.1576).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*S*)-1-hydroxy-3-phenylpropyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4nA**). Less polar. Yield: 17.0 mg (22%). White solid. M.p. 135–137°. $[\alpha]_D^{25} = -41.8$ ($c = 0.72$, CHCl_3). IR (KBr): 3470, 1713, 1456, 1377, 1220, 1144, 1108, 1034. ^1H -NMR (300 MHz, CDCl_3): 7.32–7.18 (*m*, 6 H); 4.93–4.86 (*m*, 1 H); 4.45–4.42 (*m*, 1 H); 4.17 (*d*, $J = 10.9$, 1 H); 3.85 (*d*, $J = 10.9$, 1 H); 3.51 (*s*, 3 H); 3.45 (*s*, 3 H); 3.33 (*d*, $J = 2.6$, 1 H); 2.88–2.67 (*m*, 2 H); 2.61–2.48 (*br.*, OH); 2.09–1.90 (*m*, 2 H); 1.45 (*s*, 3 H); 1.37 (*s*, 3 H). ^{13}C -NMR (75 MHz, CDCl_3): 202.3; 153.7; 147.3; 141.3; 128.5 (4 $\times$); 126.0; 100.7; 100.6; 82.4; 78.5; 66.7; 60.4; 49.4; 48.6; 36.8; 31.5; 18.9; 18.8. MS: 392 (1, M^+), 361 (5, $[M - \text{MeO}]^+$). HR-MS: 415.1715 ($[M + \text{Na}]^+$, $\text{C}_{21}\text{H}_{28}\text{NaO}_7$; calc. 415.1733).

(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*R*)-1-hydroxy-3-phenylpropyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**4nB**). More polar. Yield: 22.1 mg (28%). White solid. M.p. 154–155°. $[\alpha]_D^{25} = -9.4$ ($c = 0.80$, CHCl_3). IR (KBr): 3502, 1718, 1455, 1382, 1223, 1164, 1105, 1057. ^1H -NMR (300 MHz, CDCl_3): 7.32–7.21 (*m*, 6 H); 4.93–4.86 (*br.*, 1 H); 4.52–4.39 (*m*, 1 H); 4.18 (*d*, $J = 10.9$, 1 H); 3.86 (*d*, $J = 10.9$, 1 H); 3.49 (*s*, 3 H); 3.45 (*s*, 3 H); 3.39–3.31 (*br.*, OH); 2.89–2.67 (*m*, 2 H); 2.69–2.54 (*br.*, OH); 2.13–1.88 (*m*, 2 H); 1.45 (*s*, 3 H); 1.36 (*s*, 3 H). ^{13}C -NMR (75 MHz, CDCl_3): 202.1; 153.7; 147.1; 141.2; 128.4 (4 $\times$); 125.9; 100.6 (2 $\times$); 82.2; 78.5; 66.7; 60.3; 49.3; 48.5; 36.7; 31.5; 18.8; 18.6. MS: 392 (0.5, M^+), 361 (6, $[M - \text{MeO}]^+$). HR-MS: 415.1722 ($[M + \text{Na}]^+$, $\text{C}_{21}\text{H}_{28}\text{NaO}_7$; calc. 415.1733).

(4*R*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(*R*)-hydroxy(phenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5aA**). Less polar. Yield: 26.8 mg (37%). Colorless oil. $[\alpha]_D^{25} = -24.5$ ($c = 0.99$, CHCl_3). IR (CHCl_3): 3492, 1723, 1455, 1376, 1240, 1111, 1035. ^1H -NMR (300 MHz, CDCl_3): 7.39–7.28 (*m*, 6 H); 5.53 (*s*, 1 H); 4.56 (*s*, 1 H); 4.22 (*d*, $J = 11.0$, 1 H); 4.00 (*s*, 1 H); 3.51 (*s*, 3 H); 3.38 (*s*, 3 H); 3.31 (*d*, $J = 11.0$, 1 H); 3.15–3.00 (*br.*, OH); 1.43 (*s*, 3 H); 1.40 (*s*, 3 H). ^{13}C -NMR (75 MHz, CDCl_3): 202.3; 154.6; 147.9; 140.2; 128.6 (2 $\times$); 128.2; 126.4 (2 $\times$); 100.9; 100.0; 78.4; 72.2; 69.5; 63.6; 48.6; 48.0; 18.8; 18.7. MS: 364 (0.5, M^+). HR-MS: 387.1411 ($[M + \text{Na}]^+$, $\text{C}_{19}\text{H}_{24}\text{NaO}_7$; calc. 387.1420).

(4*R*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(*S*)-hydroxy(phenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5aB**). More polar. Yield: 17.8 mg (24%). Colorless oil. $[\alpha]_D^{25} = -74.5$ ($c = 0.69$, CHCl_3). IR (CHCl_3): 3503, 1721, 1671, 1455, 1376, 1010. ^1H -NMR (300 MHz, CDCl_3): 7.39–7.25 (*m*, 6 H); 5.55 (*s*, 1 H); 4.53 (*s*, 1 H); 4.29 (*d*, $J = 11.0$, 1 H); 3.92 (*s*, 1 H); 3.45 (*d*, $J = 11.0$, 1 H); 3.41 (*s*, 3 H); 3.38 (*s*, 3 H); 3.08–2.90 (*br.*, OH); 1.40 (*s*, 6 H). ^{13}C -NMR (75 MHz, CDCl_3): 202.4; 154.9; 147.6; 140.1; 128.6 (2 $\times$); 128.3; 126.6 (2 $\times$); 100.8; 99.9; 78.3; 72.2; 69.6; 63.4; 48.5; 48.1; 18.7; 18.6. MS: 364 (0.5, M^+). HR-MS: 387.1423 ($[M + \text{Na}]^+$, $\text{C}_{19}\text{H}_{24}\text{NaO}_7$; calc. 387.1420).

(4*R*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(*R*)-hydroxy(4-nitrophenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5bA**). Less polar. Yield: 54.8 mg (67%). Pale yellow oil. $[\alpha]_D^{25} = -29.8$ ($c = 1.71$, CHCl_3). IR (CHCl_3): 3425, 1723, 1608, 1524, 1463, 1349, 1110, 1035. ^1H -NMR (500 MHz, CDCl_3): 8.18 (*d*, $J = 8.7$, 2 H); 7.57 (*d*, $J = 8.7$, 2 H); 7.46 (*dd*, $J = 3.0, 1.3$, 1 H); 5.63 (*d*, $J = 3.0$, 1 H); 4.56

(*t*, *J* = 1.9, 1 H); 4.19 (*d*, *J* = 11.0, 1 H); 4.13 (*d*, *J* = 1.9, 1 H); 3.99 (*d*, *J* = 4.3, 1 H); 3.51 (*s*, 3 H); 3.36 (*s*, 3 H); 3.25 (*d*, *J* = 11.0, 1 H); 1.39 (*s*, 3 H); 1.38 (*s*, 3 H). ¹³C-NMR (125 MHz, CDCl₃): 202.0; 155.1; 147.7; 147.6; 147.4; 127.1 (2 ×); 123.7 (2 ×); 101.0; 100.1; 78.4; 72.3; 68.2; 63.4; 48.5; 48.0; 18.7; 18.6. MS: 409 (0.5, *M*⁺), 378 (4, [*M* – MeO]⁺). HR-MS: 432.1263 ([*M* + Na]⁺, C₁₉H₂₃NNaO₅⁺; calc. 432.1271).

(4R,5R,7R,8R)-4-Hydroxy-2-[(*S*)-hydroxy(4-nitrophenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5bB**). More polar. Yield: 18.4 mg (22%). Pale yellow oil. [α]_D²⁵ = –60.1 (*c* = 0.75, CHCl₃). IR (CHCl₃): 3499, 1723, 1607, 1526, 1350, 1110, 1035. ¹H-NMR (500 MHz, CDCl₃): 8.23 (*d*, *J* = 8.6, 2 H); 7.61 (*d*, *J* = 8.6, 2 H); 7.29 (*dd*, *J* = 3.0, 1.4, 1 H); 5.66 (*s*, 1 H); 4.56 (*t*, *J* = 3.0, 1 H); 4.31 (*d*, *J* = 11.0, 1 H); 3.99 (*d*, *J* = 2.1, 1 H); 3.46 (*s*, 3 H); 3.42 (*d*, *J* = 11.0, 1 H); 3.38 (*s*, 3 H); 3.28–3.21 (*br.*, OH); 1.41 (*s*, 6 H). ¹³C-NMR (125 MHz, CDCl₃): 202.3; 155.6; 147.8; 147.1; 146.5; 127.4 (2 ×); 123.8 (2 ×); 101.0; 100.0; 78.3; 72.3; 68.6; 63.5; 48.5; 48.1; 18.7; 18.6. MS: 409 (0.3, *M*⁺), 378 (1, [*M* – MeO]⁺). HR-MS: 432.1246 ([*M* + Na]⁺, C₁₉H₂₃NNaO₅⁺; calc. 432.1271).

(4R,5R,7R,8R)-2-[(*R*)-(4-Chlorophenyl)(hydroxy)methyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5cA**). Less polar. Yield: 32.9 mg (41%). Colorless oil. [α]_D²⁵ = –23.8 (*c* = 1.12, CHCl₃). IR (CHCl₃): 3441, 1723, 1492, 1377, 1111, 1035. ¹H-NMR (300 MHz, CDCl₃): 7.38 (*s*, 1 H); 7.35–7.23 (*m*, 4 H); 5.50 (*s*, 1 H); 4.55 (*s*, 1 H); 4.22 (*d*, *J* = 11.0, 1 H); 4.03 (*s*, 1 H); 3.52 (*s*, 3 H); 3.37 (*s*, 3 H); 3.26 (*dd*, *J* = 11.0, 1 H); 3.33–3.15 (*br.*, OH); 1.42 (*s*, 3 H); 1.40 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 202.3; 154.7; 147.7; 138.8; 133.9; 128.8 (2 ×); 127.8 (2 ×); 100.9; 100.0; 78.4; 72.3; 68.8; 63.6; 48.6; 48.0; 18.7; 18.6. MS: 398 (0.4, *M*⁺). HR-MS: 421.1010 ([*M* + Na]⁺, C₁₉H₂₃ClNaO₅⁺; calc. 421.1030).

(4R,5R,7R,8R)-2-[(*S*)-(4-Chlorophenyl)(hydroxy)methyl]-4-hydroxy-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5cB**). More polar. Yield: 21.5 mg (27%). Colorless oil. [α]_D²⁵ = –69.0 (*c* = 0.95, CHCl₃). IR (CHCl₃): 3499, 1722, 1492, 1377, 1110, 1035. ¹H-NMR (300 MHz, CDCl₃): 7.34 (*s*, 4 H); 7.26 (*dd*, *J* = 2.8, 1.3, 1 H); 5.52 (*s*, 1 H); 4.53 (*s*, 1 H); 4.29 (*d*, *J* = 11.0, 1 H); 3.94 (*s*, 1 H); 3.44 (*s*, 3 H); 3.43 (*d*, *J* = 11.0, 1 H); 3.38 (*s*, 3 H); 3.04–2.92 (*br.*, OH); 1.41 (*s*, 6 H). ¹³C-NMR (75 MHz, CDCl₃): 202.4; 155.1; 147.2; 138.6; 134.0; 128.8 (2 ×); 128.0 (2 ×); 100.9; 99.9; 78.3; 72.2; 68.9; 63.5; 48.5; 48.1; 18.7; 18.6. MS: 398 (1, *M*⁺). HR-MS: 421.1012 ([*M* + Na]⁺, C₁₉H₂₃ClNaO₅⁺; calc. 421.1030).

(4R,5R,7R,8R)-4-Hydroxy-2-[(*R*)-hydroxy(3-methoxyphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5dA**). Less polar. Yield: 41.2 mg (52%). Colorless oil. [α]_D²⁵ = –28.1 (*c* = 1.74, CHCl₃). IR (CHCl₃): 3496, 1724, 1602, 1465, 1376, 1260, 1111, 1035. ¹H-NMR (300 MHz, CDCl₃): 7.38 (*s*, 1 H); 7.24 (*d*, *J* = 8.1, 1 H); 6.93 (*s*, 2 H); 6.83 (*d*, *J* = 8.1, 1 H); 5.50 (*s*, 1 H); 4.55 (*s*, 1 H); 4.22 (*d*, *J* = 11.0, 1 H); 3.80 (*s*, 3 H); 3.51 (*s*, 3 H); 3.37 (*s*, 3 H); 3.32 (*d*, *J* = 11.0, 1 H); 1.42 (*s*, 3 H); 1.40 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 202.3; 159.8; 154.7; 147.8; 141.9; 129.6; 118.7; 113.7; 111.8; 100.9; 100.0; 78.4; 72.2; 69.3; 63.5; 55.2; 48.6; 48.0; 18.7; 18.6. MS: 394 (3, *M*⁺). HR-MS: 417.1527 ([*M* + Na]⁺, C₂₀H₂₆NaO₈⁺; calc. 417.1525).

(4R,5R,7R,8R)-4-Hydroxy-2-[(*S*)-hydroxy(3-methoxyphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5dB**). More polar. Yield: 7.0 mg (9%). Colorless oil. [α]_D²⁵ = –75.5 (*c* = 1.70, CHCl₃). IR (CHCl₃): 3499, 1721, 1601, 1490, 1465, 1376, 1260, 1036. ¹H-NMR (300 MHz, CDCl₃): 7.33–7.19 (*m*, 2 H); 7.00–6.90 (*m*, 2 H); 6.89–6.80 (*m*, 1 H); 5.53 (*s*, 1 H); 4.52 (*s*, 1 H); 4.29 (*d*, *J* = 11.0, 1 H); 3.92 (*s*, 1 H); 3.82 (*s*, 3 H); 3.45 (*d*, *J* = 11.0, 1 H); 3.42 (*s*, 3 H); 3.38 (*s*, 3 H); 3.12–2.92 (*br.*, OH); 1.41 (*s*, 6 H). ¹³C-NMR (75 MHz, CDCl₃): 202.5; 159.8; 155.1; 147.4; 141.6; 129.7; 118.9; 113.9; 112.0; 100.9; 99.9; 78.3; 72.2; 69.4; 63.4; 55.2; 48.5; 48.1; 18.7; 18.6. MS: 395 (1, [*M* + 1]⁺), 363 (4, [*M* – MeO]⁺). HR-MS: 417.1513 ([*M* + Na]⁺, C₂₀H₂₆NaO₈⁺; calc. 417.1525).

(4R,5R,7R,8R)-4-Hydroxy-2-[(*R*)-hydroxy(4-methylphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5eA**). Less polar. Yield: 34.9 mg (46%). Colorless oil. [α]_D²⁵ = –23.1 (*c* = 1.56, CHCl₃). IR (CHCl₃): 3491, 1724, 1462, 1376, 1242, 1111, 1035. ¹H-NMR (300 MHz, CDCl₃): 7.41 (*s*, 1 H); 7.23 (*d*, *J* = 8.0, 2 H); 7.15 (*d*, *J* = 8.0, 2 H); 5.48 (*s*, 1 H); 4.56 (*s*, 1 H); 4.21 (*d*, *J* = 11.0, 1 H); 4.00 (*s*, 1 H); 3.52 (*s*, 3 H); 3.38 (*s*, 3 H); 3.30 (*d*, *J* = 11.0, 1 H); 3.11–2.89 (*br.*, OH); 2.34 (*s*, 3 H); 1.43 (*s*, 3 H); 1.39 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 202.3; 154.3; 148.1; 137.9; 137.3; 129.3 (2 ×); 126.4 (2 ×); 100.9; 100.0; 78.5; 72.2; 69.4; 63.6; 48.6; 48.0; 21.1; 18.8; 18.7. MS: 347 (5, [*M* – MeO]⁺). HR-MS: 401.1561 ([*M* + Na]⁺, C₂₀H₂₆NaO₇⁺; calc. 401.1576).

(4R,5R,7R,8R)-4-Hydroxy-2-[(*S*)-hydroxy(4-methylphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5eB**). More polar. Yield: 9.3 mg (12%). Colorless oil. [α]_D²⁵ = –64.1 (*c* = 0.84, CHCl₃). IR (CHCl₃): 3508, 1722, 1462, 1377, 1111, 1035. ¹H-NMR (300 MHz, CDCl₃): 7.31–

7.23 (*m*, 3 H); 7.18 (*d*, *J* = 7.8, 2 H); 5.52 (*s*, 1 H); 4.56–4.50 (*br.*, 1 H); 4.30 (*d*, *J* = 11.0, 1 H); 3.91 (*d*, *J* = 2.2, 1 H); 3.45 (*d*, *J* = 11.0, 1 H); 3.44 (*s*, 3 H); 3.38 (*s*, 3 H); 2.92–2.73 (*br.*, OH); 2.36 (*s*, 3 H); 1.41 (*s*, 6 H). ¹³C-NMR (75 MHz, CDCl₃): 202.5; 154.9; 147.7; 138.0; 137.1; 129.3 (2 ×); 126.6 (2 ×); 100.9; 99.9; 78.3; 72.2; 69.5; 63.6; 48.5; 48.1; 21.1; 18.7; 18.6. MS: 378 (0.5, *M*⁺), 347 (8, [*M* – MeO]⁺). HR-MS: 401.1575 ([*M* + Na]⁺, C₂₀H₂₆NaO₇; calc. 401.1576).

(4*R*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(*R*)-hydroxy(4-methoxyphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5gA**). Less polar. Yield: 35.9 mg (46%). Colorless oil. [*α*]_D²⁵ = –18.2 (*c* = 1.33, CHCl₃). IR (CHCl₃): 3493, 1724, 1612, 1513, 1464, 1376, 1250, 1111, 1035. ¹H-NMR (300 MHz, CDCl₃): 7.40 (*dd*, *J* = 2.7, 1.3, 1 H); 7.27 (*d*, *J* = 8.6, 2 H); 6.87 (*d*, *J* = 8.6, 2 H); 5.48 (*s*, 1 H); 4.57 (*s*, 1 H); 4.22 (*d*, *J* = 11.0, 1 H); 3.99 (*d*, *J* = 1.6, 1 H); 3.80 (*s*, 3 H); 3.52 (*s*, 3 H); 3.38 (*s*, 3 H); 3.30 (*d*, *J* = 11.0, 1 H); 2.93 (*s*, 1 H); 1.43 (*s*, 3 H); 1.40 (*s*, 3 H). ¹³C-NMR (75 MHz, CDCl₃): 202.3; 159.5; 154.3; 148.1; 132.4; 127.8 (2 ×); 114.0 (2 ×); 100.9; 100.0; 78.5; 72.3; 69.3; 63.7; 55.2; 48.6; 48.0; 18.8; 18.7. MS: 393 (0.2, [*M* – 1]⁺). HR-MS: 417.1522 ([*M* + Na]⁺, C₂₀H₂₆NaO₈; calc. 417.1525).

(4*R*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(*S*)-hydroxy(4-methoxyphenyl)methyl]-7,8-dimethoxy-7,8-dimethyl-6,9-dioxaspiro[4.5]dec-2-en-1-one (**5gB**). More polar. Yield: 4.0 mg (5%). Colorless oil. [*α*]_D²⁵ = –67.7 (*c* = 0.76, CHCl₃). IR (CHCl₃): 3503, 1721, 1613, 1514, 1464, 1251, 1111, 1035. ¹H-NMR (300 MHz, CDCl₃): 7.36–7.25 (*m*, 3 H); 6.90 (*d*, *J* = 8.7, 2 H); 5.50 (*s*, 1 H); 4.54 (*s*, 1 H); 4.30 (*d*, *J* = 11.0, 1 H); 3.92 (*s*, 1 H); 3.82 (*s*, 3 H); 3.45 (*d*, *J* = 11.0, 1 H); 3.43 (*s*, 3 H); 3.38 (*s*, 3 H); 2.91–2.76 (*br.*, OH); 1.40 (*s*, 6 H). ¹³C-NMR (75 MHz, CDCl₃): 202.4; 159.6; 154.7; 147.8; 132.3; 128.0 (2 ×); 114.1 (2 ×); 100.9; 99.9; 78.3; 72.2; 69.3; 63.5; 55.3; 48.5; 48.1; 18.7; 18.6. MS: 394 (0.3, *M*⁺). HR-MS: 417.1509 ([*M* + Na]⁺, C₂₀H₂₆NaO₈; calc. 417.1525).

Hydrolysis of 4aA with 1% aq. TFA. Compound **4aA** (31.5 mg, 86.4 μmol) was treated with 1% aq. TFA (0.5 ml) at r.t. After stirring for 5 h, the solvent was removed *in vacuo*, and the crude product was purified by PLC (SiO₂; 10% acetone/AcOEt (2 ×)).

(4*R*,5*R*)-4,5-Dihydroxy-5-(hydroxymethyl)-2-[(*S*)- and (*R*)-hydroxy(phenyl)methyl]cyclopent-2-en-1-ones (**6aA/6aB**). Yield: 14.2 mg (66%). *dr*: 3.8:1. Colorless oil. [*α*]_D²⁵ = +77.7 (*c* = 0.92, acetone). IR (neat): 3376, 1711, 1621, 1367, 1051. ¹H-NMR (500 MHz, (D₆)acetone, **6aA** marked*): 7.29–7.26 (*m*, 6 arom. H of **6aA** and **6aB**); 7.19–7.15 (*m*, 4 arom. H of **6aA** and **6aB**); 7.12–7.09 (*m*, 2 CH of **6aA** and **6aB**); 5.39–5.30 (*m*, 2 CH of **6aA** and **6aB**); 4.88 (*d*, *J* = 6.3, OH*); 4.86 (*d*, *J* = 6.3, OH of **6aB**); 4.69 (*d*, *J* = 4.6, OH of **6aB**); 4.67 (*d*, *J* = 4.6, OH*); 4.62–4.57 (*m*, 2 CH of **6aA** and **6aB**); 4.40 (*s*, OH*); 4.38 (*s*, OH of **6aB**); 3.53–3.47 (*m*, 2 CH₂ of **6aA** and **6aB**); 3.43 (*dd*, *J* = 6.8, 5.5, 2 OH of **6aA** and **6aB**). ¹³C-NMR (125 MHz, (D₆)acetone, **6aA** marked*): 205.2 (C=O of **6aA** and **6aB**); 155.8 (CH of **6aB**); 155.4 (CH*); 149.3 (C*); 149.2 (C of **6aB**); 143.4 (C of **6aB**); 128.9 (2 ×, CH of **6aA** and **6aB**); 128.2 (CH of **6aA** and **6aB**); 127.7 (2 ×, CH*); 127.5 (2 ×, CH of **6aB**); 82.7 (C*); 82.3 (C of **6aB**); 78.3 (CH of **6aB**); 77.9 (CH*); 69.0 (CH of **6aA** and **6aB**); 65.5 (CH₂ of **6aB**); 65.4 (CH₂*). MS: 251 (2, [*M* + 1]⁺). HR-MS: 273.0759 ([*M* + Na]⁺, C₁₃H₁₄NaO₅; calc. 273.0739).

Hydrolysis of 4 or 5 with 1% aq. TFA. Compound **4** or **5** was treated with 1% aq. TFA (0.5 ml) at r.t. After water bath sonication (35 kHz, 120/480 W, 40–60°) for 3 h, the solvent was removed *in vacuo*, and the crude product was purified by PLC (SiO₂; 10% acetone/AcOEt (2 ×)).

(4*S*,5*R*)-4,5-Dihydroxy-5-(hydroxymethyl)-2-[(*S*)-hydroxy(4-methylphenyl)methyl]cyclopent-2-en-1-one (**6eA**). Hydrolysis of **4eA** (27.3 mg, 72.1 μmol) gave **6eA** 14.8 mg (78%). Colorless, viscous oil. [*α*]_D²⁵ = +78.3 (*c* = 0.86, acetone). IR (neat): 3391, 1711, 1622, 1514, 1416, 1360, 1214, 1115, 1052. ¹H-NMR (300 MHz, (D₆)acetone): 7.39 (*dd*, *J* = 2.2, 1.4, 1 H); 7.26 (*d*, *J* = 8.0, 2 H); 7.09 (*d*, *J* = 8.0, 2 H); 5.42 (*s*, 1 H); 5.02 (*d*, *J* = 5.8, 1 H); 4.77–4.64 (*m*, 2 H); 4.51 (*s*, 1 H); 3.67–3.46 (*m*, 3 H); 2.67 (*s*, 3 H). ¹³C-NMR (75 MHz, (D₆)acetone): 205.2; 155.1; 149.4; 140.2; 137.6; 129.5 (2 ×); 127.7 (2 ×); 82.7; 77.9; 68.9; 65.4; 21.0. MS: 276 (5, [*M* – 4]⁺). HR-MS: 287.0897 ([*M* + Na]⁺, C₁₄H₁₆NaO₅; calc. 287.0895).

(4*S*,5*R*)-2-[(*S*)-(2-Chlorophenyl)(hydroxymethyl)methyl]-4,5-dihydroxy-5-(hydroxymethyl)cyclopent-2-en-1-one (**6fB**). Hydrolysis of **4fB** (26.5 mg, 66.4 μmol) gave **6fB** 13.6 mg (72%). Colorless, viscous oil. [*α*]_D²⁵ = +28.9 (*c* = 1.01, acetone). IR (KBr): 3378, 1697, 1629, 1397, 1281, 1269, 1129, 1057. ¹H-NMR (500 MHz, (D₆)acetone): 7.56 (*dd*, *J* = 7.6, 2.0, 1 H); 7.38 (*dd*, *J* = 7.6, 1.5, 1 H); 7.33 (*dt*, *J* = 7.6, 1.5, 1 H); 7.29 (*dt*, *J* = 7.6, 2.0, 1 H); 7.18 (*dd*, *J* = 2.0, 1.5, 1 H); 5.86 (*d*, *J* = 3.8, 1 H); 5.06–4.92 (*m*, 1 H); 4.78–4.69 (*br.*, 1 H); 4.55 (*s*, 1 H); 3.80–3.60 (*m*, 3 H). ¹³C-NMR (125 MHz, (D₆)acetone): 204.8; 156.8; 147.6;

140.4; 133.3; 130.0; 129.8; 129.4; 127.9; 82.7; 77.9; 65.4; 65.3. MS: 283 (3, $[M - 1]^+$), 249 (2, $[M - Cl]^+$). HR-MS: 307.0348 ($[M + Na]^+$, $C_{13}H_{13}ClNaO_3^+$; calc. 307.0349).

(4R,5R)-4,5-Dihydroxy-2-[(R)-hydroxy(3-methoxyphenyl)methyl]-5-(hydroxymethyl)cyclopent-2-enone (**7dA**). Hydrolysis of **5dA** (43.4 mg, 110.0 μ mol) gave **7dA** 22.9 mg (74%). Colorless, viscous oil. $[\alpha]_D^{25} = +82.4$ ($c = 1.03$, acetone). IR (neat): 3391, 1713, 1602, 1489, 1261, 1152, 1046. 1H -NMR (300 MHz, (D_6) acetone): 7.32 (*dd*, $J = 2.4, 1.3, 1$ H); 7.06 (*t*, $J = 8.2, 1$ H); 6.88–6.76 (*m*, 2 H); 6.65 (*ddd*, $J = 8.2, 2.4, 0.9, 1$ H); 5.33 (*d*, $J = 4.7, 1$ H); 4.75 (*d*, $J = 6.4, 1$ H); 4.70 (*ddd*, $J = 7.7, 2.4, 0.9, 1$ H); 4.66 (*d*, $J = 4.8, 1$ H); 4.12 (*s*, 1 H); 3.82 (*dd*, $J = 6.4, 4.8, 1$ H); 3.62 (*s*, 3 H); 3.48 (*dd*, $J = 10.5, 6.4, 1$ H); 3.39 (*dd*, $J = 10.5, 4.8, 1$ H). ^{13}C -NMR (75 MHz, (D_6) acetone): 205.2; 160.6; 156.3; 149.7; 144.9; 129.9; 119.8; 113.7; 113.1; 77.2; 70.8; 69.0; 64.3; 55.4. MS: 244 (20, $[M - 2 - OH (2 \times)]^+$). HR-MS: 303.0836 ($[M + Na]^+$, $C_{14}H_{16}NaO_6^+$; calc. 303.0845).

(4R,5R)-4,5-Dihydroxy-2-[(S)-hydroxy(3-methoxyphenyl)methyl]-5-(hydroxymethyl)cyclopent-2-enone (**7dB**). Hydrolysis of **5dB** (54.8 mg, 138.9 μ mol) gave **7dB** 24.8 mg (63%). White solid. M.p. 133–134°. $[\alpha]_D^{25} = +2.7$ ($c = 0.94$, acetone). IR (KBr): 3446, 3338, 3262, 1702, 1596, 1334, 1239, 1151, 1071, 1026. 1H -NMR (500 MHz, (D_6) acetone): 7.45 (*dd*, $J = 2.6, 1.3, 1$ H); 7.20 (*t*, $J = 8.0, 1$ H); 7.01–6.92 (*m*, 2 H); 6.79 (*ddd*, $J = 8.0, 2.6, 0.8, 1$ H); 5.43 (*d*, $J = 4.6, 1$ H); 4.92 (*d*, $J = 6.6, 1$ H); 4.87–4.78 (*m*, 2 H); 4.21 (*s*, 1 H); 4.05 (*t*, $J = 5.7, 1$ H); 3.75 (*s*, 3 H); 3.70 (*dd*, $J = 10.6, 5.7, 1$ H); 3.56 (*dd*, $J = 10.6, 4.6, 1$ H). ^{13}C -NMR (125 MHz, (D_6) acetone): 204.6; 160.5; 155.9; 149.8; 144.9; 129.9; 119.7; 113.5; 113.2; 76.9; 70.5; 68.8; 63.9; 55.4. MS: 229 (10, $[M - OH (3 \times)]^+$). HR-MS: 303.0838 ($[M + Na]^+$, $C_{14}H_{16}NaO_6^+$; calc. 303.0845).

(4R,5R)-4,5-Dihydroxy-5-(hydroxymethyl)-2-[(R)-hydroxy(4-methylphenyl)methyl]cyclopent-2-enone (**7eA**). Hydrolysis of **5eA** (24.7 mg, 65.3 μ mol) gave **7eA** 8.4 mg (49%). White solid. M.p. 131–132°. $[\alpha]_D^{25} = +40.4$ ($c = 0.96$, acetone). IR (KBr): 3471, 3350, 3291, 1719, 1638, 1359, 1226, 1152, 1051. 1H -NMR (300 MHz, (D_6) acetone): 7.44 (*dd*, $J = 2.4, 1.4, 1$ H); 7.23 (*d*, $J = 8.0, 2$ H); 7.07 (*d*, $J = 8.0, 2$ H); 5.42 (*d*, $J = 4.6, 1$ H); 4.87 (*d*, $J = 6.5, 1$ H); 4.84–4.77 (*m*, 1 H); 4.69 (*d*, $J = 4.6, 1$ H); 4.23 (*s*, 1 H); 3.72 (*dd*, $J = 6.3, 4.8, 1$ H); 3.57 (*dd*, $J = 10.6, 6.3, 1$ H); 3.49 (*dd*, $J = 10.6, 4.8, 1$ H); 2.26 (*s*, 3 H). ^{13}C -NMR (75 MHz, (D_6) acetone): 205.2; 155.9; 149.8; 140.3; 137.6; 129.5 (2 $\times$); 127.6 (2 $\times$); 77.1; 70.7; 69.0; 64.2; 21.0. MS: 276 (10, $[M - 4]^+$). HR-MS: 287.0899 ($[M + Na]^+$, $C_{14}H_{16}NaO_5^+$; calc. 287.0895).

Hydrolysis of **4aA** by Using Dowex 50 W-X8 (H^+ Form). A soln. of **4aA** (20 mg, 54.9 μ mol) in MeOH (0.5 ml) was treated with the Dowex 50 W-X8 (H^+ form; 20 mg) at r.t. After stirring for 24 h, Dowex resin was removed, and the crude product was purified by PLC (SiO_2 ; 10% acetone/AcOEt) to give a 1:1 mixture of diastereoisomers of **8a**.

(2R,3S,4R,5E)-5- and (2R,3S,4S,5E)-5-Benzylidene-2,3-dihydroxy-2-(hydroxymethyl)-4-methoxycyclopentanone (**8aA/8aB**). Yield: 12.1 mg (83%). White semi-solid. $[\alpha]_D^{25} = +54.7$ ($c = 0.83$, acetone). IR (KBr): 3422, 1711, 1629, 1455, 1384, 1100, 1075, 1067. 1H -NMR (500 MHz, (D_6) acetone): 7.38–7.25 (*m*, 12 H); 5.13–4.95 (*br.*, 2 H); 4.98 (*s*, 1 H); 4.96 (*s*, 1 H); 4.75 (*t*, $J = 1.9, 1$ H); 4.65–4.43 (*br.*, 2 H); 3.72 (*dd*, $J = 14.3, 11.0, 2$ H); 3.58 (*dd*, $J = 19.4, 11.0, 1$ H); 3.26 (*s*, 3 H); 3.25 (*s*, 3 H). ^{13}C -NMR (125 MHz, (D_6) acetone): 205.1; 204.9; 156.2; 155.7; 147.0; 146.9; 140.4; 140.1; 129.1 (2 $\times$); 129.0 (2 $\times$); 128.6 (2 $\times$); 128.3 (2 $\times$); 128.1 (2 $\times$); 82.6; 82.2; 78.4; 78.3; 78.2; 78.0; 65.5; 65.3; 56.9 (2 $\times$). MS: 213 (15, $[M - 3 OH]^+$). HR-MS: 287.0890 ($[M + Na]^+$, $C_{14}H_{16}NaO_5^+$; calc. 287.0895).

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