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

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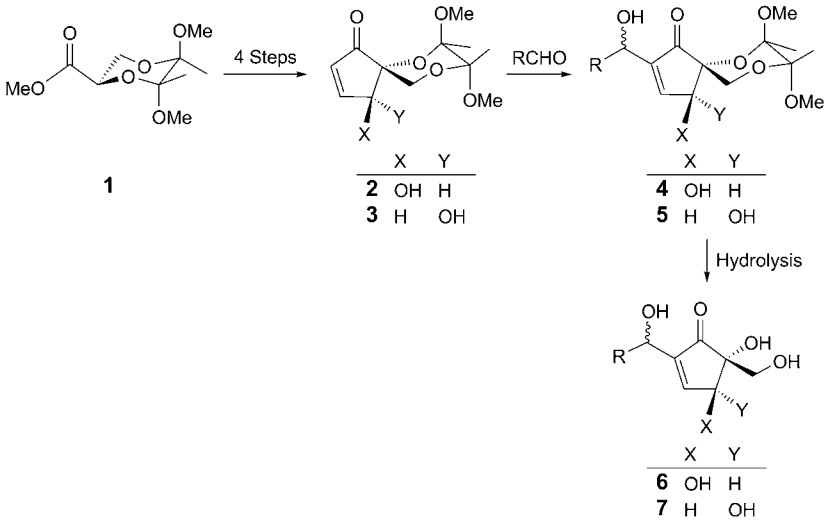
Dedicated to Professor *Dieter Seebach* on the occasion of his 75th birthday

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 Bu_3P/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. CF_3COOH (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

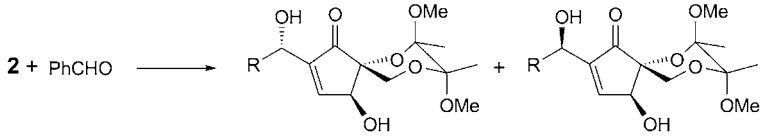


involving *Lewis* base-mediated *MBH* reactions. It is anticipated that compounds **2** and **3** can be used as useful chiral starting oxygenated cyclopentenones for preparing compound of types **6** and **7**, which may be important synthons for further synthetic manipulations. Therefore, the present 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, Bu_3P, Cy_3P, and Ph_3P 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 Bu_3P 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; SiO_2) to afford **4aA** and **4aB** as the major and minor products, respectively. The reactions employing tricyclohexylphosphine (Cy_3P) and Ph_3P 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 Ph_3P gave the adduct **4a** in low yield, the reaction was highly diastereoselective affording **4a** as a single diastereoisomer.

After identifying an appropriate promoters (Bu_3P/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 CH_2Cl_2 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*



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_3P, PhOH, THF[d])	73	19	88 : 12
3	Cy_3P, PhOH, toluene	23	64	73 : 27
4	Ph_3P, 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 (SiO_2). [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_2Cl_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.), Bu_3P (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 (SiO_2).

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 diastereoselecitvity 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 Bu_3P (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 Bu_3P 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 (SiO_2). [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 diastereoselectivites 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

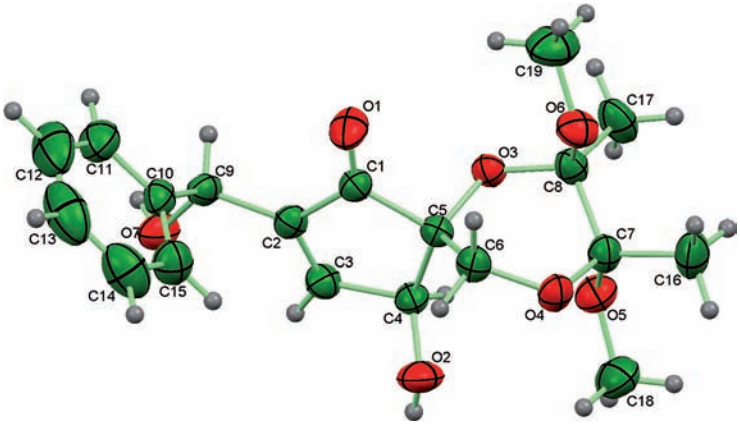
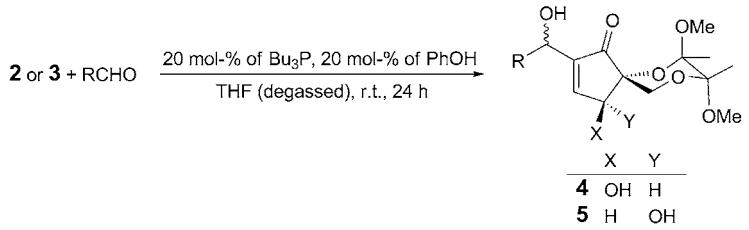


Figure. *X-Ray Structure of the Major Diastereoisomer of* **4a** (**4aA**)

[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**



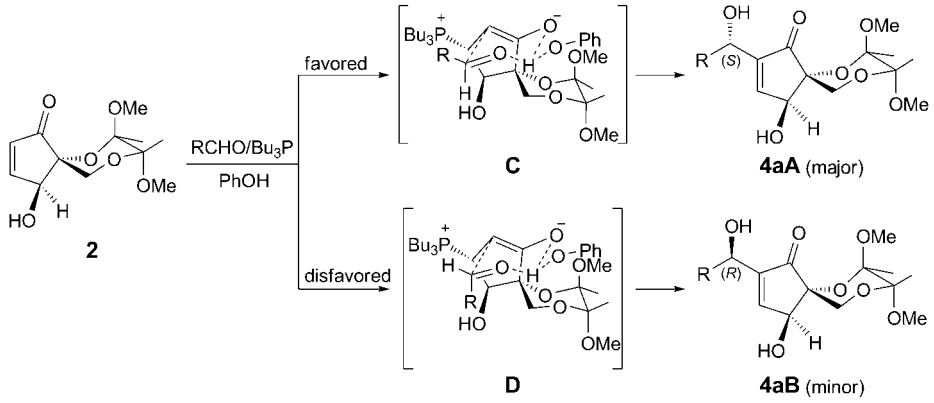
Entry	RCHO	Enone **2** or **3**[a])	Adducts	Yield [%][b])		**2** or **3** [%][b])
				A	**B**	
1	Benzaldehyde	**2**	**4a** (R = Ph)	61	8	10
		3	**5a** (R = Ph)	37	24	9
2	4-Nitrobenzaldehyde	**2**	**4b** (R = 4-NO_2–C_6H_4)	55	32	6
		3	**5b** (R = 4-NO_2–C_6H_4)	67	22	–
3	4-Chlorobenzaldehyde	**2**	**4c** (R = 4-Cl–C_6H_4)	50	21	15
		3	**5c** (R = 4-Cl–C_6H_4)	41	27	13
4	3-Methoxybenzaldehyde	**2**	**4d** (R = 3-MeO–C_6H_4)	38	35	14
		3	**5d** (R = 3-MeO–C_6H_4)	52	9	23
5	4-Methylaldehyde	**2**	**4e** (R = Me–C_6H_4)	40	5	32
		3	**5e** (R = Me–C_6H_4)	46	12	22
6	2-Chlorobenzaldehyde	**2**	**4f** (R = 2-Cl–C_6H_4)	38	32	10
7	*p*-Anisaldehyde	**2**	**4g** (R = 4-MeO–C_6H_4)	23	9	32
		3	**5g** (R = 4-MeO–C_6H_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_6H_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_2CH_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. CF_3COOH (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

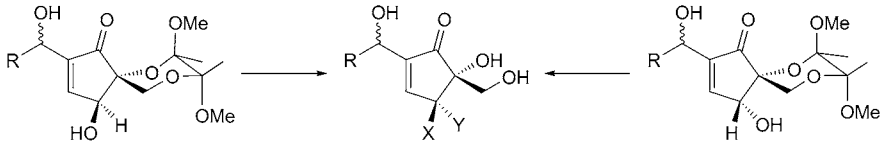
Scheme 2. *Proposed Transition State of the* MBH *Reaction of* **2** *with Aldehyde*



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**



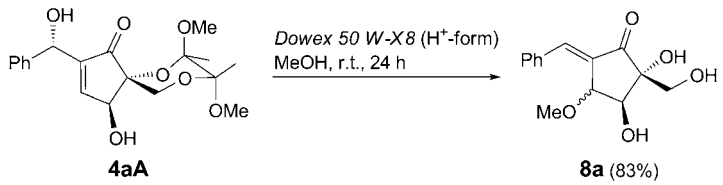
Entry	*MBH* Adducts	Reaction conditions	Hydrolysis adducts	Yield [%][a])
1	**4aA**	1% aq. TFA, r.t., 5 h	**6aA**	66[b])
2	**4aB**	1% aq. TFA, r.t., 5 h	**6aB**	76[b])
3	**4mB**	1% aq. TFA, r.t., 5 h	**6mB**	82[c])
4	**4eA**	1% aq. TFA, sonication[d])	**6eA**	78
5	**4fB**	1% aq. TFA, sonication[d])	**6fB**	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 ^{1}H-NMR. [c]) Diastereoisomer ratio 7.7 : 1, determined by ^{1}H-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*).

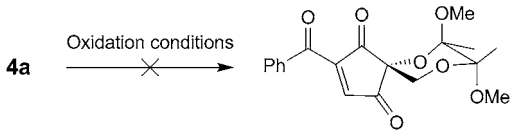
Scheme 3



4aA **8a** (83%)

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*).

Scheme 4



9a

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 (SiO_2); visualization with UV light. Column chromatography (CC): SiO_2 (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 $CHCl_3$, or neat. ^{1}H- and ^{13}C-NMR: *Bruker DPX-300* at 300 and 75 MHz, resp., or *Bruker 500* at 500 and 125 MHz, resp., in $CDCl_3$ or (D_6)acetone with Me_4Si as an internal standard; chemical shifts (δ) downfield from Me_4Si; 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 Bu_3P 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 (SiO_2, 20% AcOEt/CH_2Cl_2 (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°. $[\alpha]_D^{25} = -30$ ($c = 1.02$, $CHCl_3$). IR (KBr): 3385, 3271, 1720, 1455, 1215, 1038. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M + Na]^+$, $C_{19}H_{24}NaO_7^+$; 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°. $[\alpha]_D^{25} = -75.5$ ($c = 0.99$, $CHCl_3$). IR (KBr): 3434, 1703, 1456, 1226, 1145, 1109, 1033. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M + Na]^+$, $C_{19}H_{24}NaO_7^+$; 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°. $[\alpha]_D^{25} = -60.4$ ($c = 0.91$, $CHCl_3$). IR (KBr): 3509, 3455, 1717, 1608, 1514, 1354, 1213, 1145, 1114, 1037. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M + Na]^+$, $C_{19}H_{23}NNaO_9^+$; 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°. $[\alpha]_D^{25} = -42.0$ ($c = 0.54$, $CHCl_3$). IR (KBr): 3457, 1709, 1608, 1529, 1350, 1108. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M + Na]^+$, $C_{19}H_{23}NNaO_9^+$; 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°. $[\alpha]_D^{25} = -7.5$ ($c = 0.90$, $CHCl_3$). IR (KBr): 3379, 1717, 1648, 1377, 1032. ^{1}H-NMR (300 MHz, $CDCl_3$):

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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{19}H_{23}ClNaO_7^+$; 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°. $[\alpha]_D^{25} = -47.4$ (*c* = 0.91, $CHCl_3$). IR (KBr): 3455, 1707, 1145, 1105, 1035. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{19}H_{23}ClNaO_7^+$; 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. $[\alpha]_D^{25} = -56.6$ (*c* = 0.96, $CHCl_3$). IR (KBr): 3455, 1720, 1601, 1458, 1261, 1034. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.27 (*t*, *J* = 8.2, 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{20}H_{26}NaO_8^+$; 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°. $[\alpha]_D^{25} = -103.7$ (*c* = 0.62, $CHCl_3$). IR (KBr): 3402, 1724, 1610, 1489, 1287, 1034. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{20}H_{26}NaO_8^+$; 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°. $[\alpha]_D^{25} = -0.6$ (*c* = 1.12, $CHCl_3$). IR (KBr): 3274, 1721, 1150, 1109, 1039. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{20}H_{26}NaO_7^+$; 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°. $[\alpha]_D^{25} = -19.7$ (*c* = 0.69, $CHCl_3$). IR (KBr): 3448, 1706, 1145, 1108, 1035. ^{1}H-NMR (500 MHz, $CDCl_3$): 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). ^{13}C-NMR (125 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{20}H_{26}NaO_7^+$; 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°. $[\alpha]_D^{25} = +17.4$ (*c* = 1.27, $CHCl_3$). IR (KBr): 3279, 1718, 1444, 1214, 1160, 1100, 1038. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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).

*(4*S*,5*R*,7*R*,8*R*)-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. ^{1}H-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).

*(4*S*,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* (**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. ^{1}H-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).

*(4*S*,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* (**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. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.31 (*d*, *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).

*(4*S*,5*R*,7*R*,8*R*)-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. ^{1}H-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).

*(4*S*,5*R*,7*R*,8*R*)-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. ^{1}H-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).

*(4*S*,5*R*,7*R*,8*R*)-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. ^{1}H-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).

*(4*S*,5*R*,7*R*,8*R*)-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°. $[\alpha]_D^{25} = -55.0$ ($c = 0.66$, $CHCl_3$). IR (KBr): 3461, 2927, 1717, 1636, 1482, 1285, 1114. ^{1}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}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×); 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, $[M - MeO]^+$). HR-MS: 447.1634 ($[M + Na]^+$, $C_{21}H_{28}NaO_9^+$; calc. 447.1631).

*(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*S*,2*E*)-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°. $[\alpha]_D^{25} = -27.9$ ($c = 0.59$, $CHCl_3$). IR (KBr): 3447, 1719, 1655, 1450, 1376, 1216, 1144, 1115, 1035. ^{1}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}C-NMR (75 MHz, $CDCl_3$): 201.9; 154.2; 145.9; 136.1; 132.2; 128.6 (2×); 128.1; 127.5; 126.7 (2×); 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 ($[M + Na]^+$, $C_{21}H_{26}NaO_7^+$; calc. 413.1576).

*(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*R*,2*E*)-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°. $[\alpha]_D^{25} = -33.6$ ($c = 0.71$, $CHCl_3$). IR (KBr): 3490, 1718, 1451, 1375, 1245, 1166, 1106, 1054. ^{1}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}C-NMR (75 MHz, $CDCl_3$): 201.8; 154.2; 146.1; 136.5; 132.1; 128.6 (2×); 128.0; 126.8 (2×); 100.8 (2×); 82.2; 78.8; 68.3; 60.4; 49.3; 48.6; 18.9; 18.7. MS: 390 (7, M^+). HR-MS: 413.1575 ($[M + Na]^+$, $C_{21}H_{26}NaO_7^+$; calc. 413.1576).

*(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*S*)-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°. $[\alpha]_D^{25} = -46.4$ ($c = 0.89$, $CHCl_3$). IR (KBr): 3472, 3383, 1697, 1465, 1218, 1052. ^{1}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}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 ($[M + Na]^+$, $C_{15}H_{24}NaO_7^+$; calc. 339.1420).

*(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*R*)-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°. $[\alpha]_D^{25} = -13.5$ ($c = 0.85$, $CHCl_3$). IR (KBr): 3504, 1717, 1381, 1219, 1162, 1105, 1047. ^{1}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}C-NMR (75 MHz, $CDCl_3$): 202.2; 153.9; 147.2; 100.6 (2×); 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, $[M - MeO]^+$). HR-MS: 339.1415 ($[M + Na]^+$, $C_{15}H_{24}NaO_7^+$; calc. 339.1420).

*(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*S*)-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°. $[\alpha]_D^{25} = -44.2$ ($c = 0.85$, $CHCl_3$). IR (KBr): 3491, 3386, 1692, 1640, 1461, 1299, 1217, 1145, 1104, 1055. ^{1}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}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, $[M - MeO]^+$). HR-MS: 353.1567 ($[M + Na]^+$, $C_{16}H_{26}NaO_7^+$; calc. 353.1576).

*(4*S*,5*R*,7*R*,8*R*)-4-Hydroxy-2-[(1*R*)-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°. $[\alpha]_D^{25} = +5.8$ ($c = 0.51$, $CHCl_3$). IR (KBr): 3501, 3409, 1710, 1463, 1379, 1221, 1166, 1105, 1039. ^{1}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, $[M-MeO]^+$). HR-MS: 353.1555 ($[M+Na]^+$, $C_{16}H_{26}NaO_7^+$; 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. ^{1}H-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, $[M-MeO]^+$). HR-MS: 353.1589 ($[M+Na]^+$, $C_{16}H_{26}NaO_7^+$; 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. ^{1}H-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, $[M-MeO]^+$). HR-MS: 353.1566 ($[M+Na]^+$, $C_{16}H_{26}NaO_7^+$; 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. ^{1}H-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×); 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, $[M-MeO]^+$). HR-MS: 415.1715 ($[M+Na]^+$, $C_{21}H_{28}NaO_7^+$; 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. ^{1}H-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×); 125.9; 100.6 (2×); 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, $[M-MeO]^+$). HR-MS: 415.1722 ($[M+Na]^+$, $C_{21}H_{28}NaO_7^+$; 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. ^{1}H-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×); 128.2; 126.4 (2×); 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 ($[M+Na]^+$, $C_{19}H_{24}NaO_7^+$; 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. ^{1}H-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×); 128.3; 126.6 (2×); 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 ($[M+Na]^+$, $C_{19}H_{24}NaO_7^+$; 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. ^{1}H-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). ^{13}C-NMR (125 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{19}H_{23}NNaO_9^+$; calc. 432.1271).

*(4*R*,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* (**5bB**). More polar. Yield: 18.4 mg (22%). Pale yellow oil. $[\alpha]_D^{25} = -60.1$ ($c = 0.75$, $CHCl_3$). IR ($CHCl_3$): 3499, 1723, 1607, 1526, 1350, 1110, 1035. ^{1}H-NMR (500 MHz, $CDCl_3$): 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). ^{13}C-NMR (125 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{19}H_{23}NNaO_9^+$; calc. 432.1271).

*(4*R*,5*R*,7*R*,8*R*)-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. $[\alpha]_D^{25} = -23.8$ ($c = 1.12$, $CHCl_3$). IR ($CHCl_3$): 3441, 1723, 1492, 1377, 1111, 1035. ^{1}H-NMR (300 MHz, $CDCl_3$): 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 (*d*, *J* = 11.0, 1 H); 3.33–3.15 (br., OH); 1.42 (*s*, 3 H); 1.40 (*s*, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{19}H_{23}ClNaO_7^+$; calc. 421.1030).

*(4*R*,5*R*,7*R*,8*R*)-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. $[\alpha]_D^{25} = -69.0$ ($c = 0.95$, $CHCl_3$). IR ($CHCl_3$): 3499, 1722, 1492, 1377, 1110, 1035. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{19}H_{23}ClNaO_7^+$; calc. 421.1030).

*(4*R*,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* (**5dA**). Less polar. Yield: 41.2 mg (52%). Colorless oil. $[\alpha]_D^{25} = -28.1$ ($c = 1.74$, $CHCl_3$). IR ($CHCl_3$): 3496, 1724, 1602, 1465, 1376, 1260, 1111, 1035. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{20}H_{26}NaO_8^+$; calc. 417.1525).

*(4*R*,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* (**5dB**). More polar. Yield: 7.0 mg (9%). Colorless oil. $[\alpha]_D^{25} = -75.5$ ($c = 1.70$, $CHCl_3$). IR ($CHCl_3$): 3499, 1721, 1601, 1490, 1465, 1376, 1260, 1036. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{20}H_{26}NaO_8^+$; calc. 417.1525).

*(4*R*,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* (**5eA**). Less polar. Yield: 34.9 mg (46%). Colorless oil. $[\alpha]_D^{25} = -23.1$ ($c = 1.56$, $CHCl_3$). IR ($CHCl_3$): 3491, 1724, 1462, 1376, 1242, 1111, 1035. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M+Na]^+$, $C_{20}H_{26}NaO_7^+$; calc. 401.1576).

*(4*R*,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* (**5eB**). More polar. Yield: 9.3 mg (12%). Colorless oil. $[\alpha]_D^{25} = -64.1$ ($c = 0.84$, $CHCl_3$). IR ($CHCl_3$): 3508, 1722, 1462, 1377, 1111, 1035. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M + Na]^+$, $C_{20}H_{26}NaO_7^+$; 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. $[\alpha]_D^{25} = -18.2$ ($c = 1.33$, $CHCl_3$). IR ($CHCl_3$): 3493, 1724, 1612, 1513, 1464, 1376, 1250, 1111, 1035. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M + Na]^+$, $C_{20}H_{26}NaO_8^+$; 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. $[\alpha]_D^{25} = -67.7$ ($c = 0.76$, $CHCl_3$). IR ($CHCl_3$): 3503, 1721, 1613, 1514, 1464, 1251, 1111, 1035. ^{1}H-NMR (300 MHz, $CDCl_3$): 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). ^{13}C-NMR (75 MHz, $CDCl_3$): 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 ($[M + Na]^+$, $C_{20}H_{26}NaO_8^+$; 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 (SiO_2; 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. $[\alpha]_D^{25} = +77.7$ ($c = 0.92$, acetone). IR (neat): 3376, 1711, 1621, 1367, 1051. ^{1}H-NMR (500 MHz, (D_6)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 CH_2 of **6aA** and **6aB**); 3.43 (*dd*, *J* = 6.8, 5.5, 2 OH of **6aA** and **6aB**). ^{13}C-NMR (125 MHz, (D_6)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**); 143.2 (C*); 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 (CH_2 of **6aB**); 65.4 (CH_2*). MS: 251 (2, $[M + 1]^+$). HR-MS: 273.0759 ($[M + Na]^+$, $C_{13}H_{14}NaO_5^+$; 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 (SiO_2; 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. $[\alpha]_D^{25} = +78.3$ ($c = 0.86$, acetone). IR (neat): 3391, 1711, 1622, 1514, 1416, 1360, 1214, 1115, 1052. ^{1}H-NMR (300 MHz, (D_6)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). ^{13}C-NMR (75 MHz, (D_6)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 ($[M + Na]^+$, $C_{14}H_{16}NaO_5^+$; calc. 287.0895).

*(4*S*,5*R*)-2-[(*S*)-(2-Chlorophenyl)(hydroxy)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. $[\alpha]_D^{25} = +28.9$ ($c = 1.01$, acetone). IR (KBr): 3378, 1697, 1629, 1397, 1281, 1269, 1129, 1057. ^{1}H-NMR (500 MHz, (D_6)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). ^{13}C-NMR (125 MHz, (D_6)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 ($[M+Na]^+$, $C_{13}H_{13}ClNaO_5^+$; calc. 307.0349).

*(4*R*,5*R*)-4,5-Dihydroxy-2-[(*R*)-hydroxy(3-methoxyphenyl)methyl]-5-(hydroxymethyl)cyclopent-2-enone* (**7dA**). Hydrolysis of **5dA** (43.4 mg, 110.0 μmol) 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. ^{1}H-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).

*(4*R*,5*R*)-4,5-Dihydroxy-2-[(*S*)-hydroxy(3-methoxyphenyl)methyl]-5-(hydroxymethyl)cyclopent-2-enone* (**7dB**). Hydrolysis of **5dB** (54.8 mg, 138.9 μmol) 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. ^{1}H-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 ($[M+Na]^+$, $C1_4H_{16}NaO_6^+$; calc. 303.0845).

*(4*R*,5*R*)-4,5-Dihydroxy-5-(hydroxymethyl)-2-[(*R*)-hydroxy(4-methylphenyl)methyl]cyclopent-2-enone* (**7eA**). Hydrolysis of **5eA** (24.7 mg, 65.3 μmol) 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. ^{1}H-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); 3.91 (*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×); 127.6 (2×); 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 μmol) 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**.

*(2*R*,3*S*,4*R*,5*E*)-5- and (2*R*,3*S*,4*S*,5*E*)-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. ^{1}H-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×); 129.0 (2×); 128.6 (2×); 128.3 (2×); 128.1 (2×); 82.6; 82.2; 78.4; 78.3; 78.2; 78.0; 65.5; 65.3; 56.9 (2×). 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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