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Asymmetric cyclopropanation with diazoacetates induced by carbohydrate-derived chiral auxiliaries

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Abstract—α-Diazoacetates with carbohydrate-based chiral auxiliaries have been synthesized and screened in the asymmetric cyclopropanation of styrene in connection with the effect of the chiral Cu(I)-catalyzed reaction, showing the remarkable importance of the carbohydrate-based chiral auxiliaries on the enantioselectivities and an unexpected effect on the *trans*:*cis* ratios.

1. Introduction

Since both synthetic and naturally occurring chiral cyclopropane compounds show important biological activities,[1] many efforts have been devoted to the development of diastereo and enantioselective methods for the construction of cyclopropane rings.[2,3] Among them, the asymmetric cyclopropanation of olefins with diazoesters catalyzed by chiral complexes of transition metals, such as copper,[4] rhodium,[5] ruthenium,[6] and cobalt,[4] has been intensively studied over the last few decades.[2a,b,7]

The C_2-symmetric enantiopure bis(oxazolines) have emerged as one of the most efficient classes of ligands in asymmetric catalysis[8] and their Cu(I) and Cu(II) complexes are very attractive homogeneous catalysts for the asymmetric cyclopropanation with regards to their catalytic activity when compared with other metal complexes. Indeed, since Nozaki et al. reported the first copper-catalyzed asymmetric cyclopropanation of styrene with ethyl diazoacetate,[9] many successful copper-bis(oxazolines) catalysts have been reported in the cyclopropanation of olefins with diazoesters.[2,10] Usually diazoacetates derived from the bulky alcohols BHT and L-menthol have been chosen in order to produce cyclopropane esters in high *trans*:*cis* ratios. Furthermore, the enantioselectivity of the reaction has been attributed to the efficiency of the Cu-bis(oxazolines) complexes as chiral catalysts.[10a,11]

Carbohydrate derivatives have been employed as starting materials in asymmetric cyclopropanation[12] and the few examples of their use as chiral ligands in the Cu(I)-catalyzed reactions of olefins with diazoacetates show low *trans*:*cis* ratios and enantioselectivities.[13]

Recently, one of us described fluorous bis(oxazoline) **1** as an effective chiral ligand in the enantioselective palladium-catalyzed allylic alkylation[14] and in the asymmetric Cu(I)-catalyzed cyclopropanation of styrene with ethyl α-diazoacetate **2a** under homogeneous conditions to afford a mixture of the ethyl esters *trans*-**3a** and *cis*-**4a** in a *trans*-**3a**:*cis*-**4a** = 63:37 ratio and 65% ee (Scheme 1).[10a] Herein, we report the first study on the use of carbohydrate-based chiral auxiliaries in the asymmetric cyclopropanation by using the α-diazoacetates **2a**–**e** in connection with the effect of chiral ligand **1** in the Cu(I)-catalyzed reaction, showing the remarkable importance of the carbohydrate-based chiral auxiliaries on the enantioselectivities and the unexpected effect of **1** on the *trans*:*cis* ratios.

2. Results and discussion

The carbohydrate-based α-diazoacetates **2a**–**e** were prepared by reaction of ethyl acetoacetate with the respective

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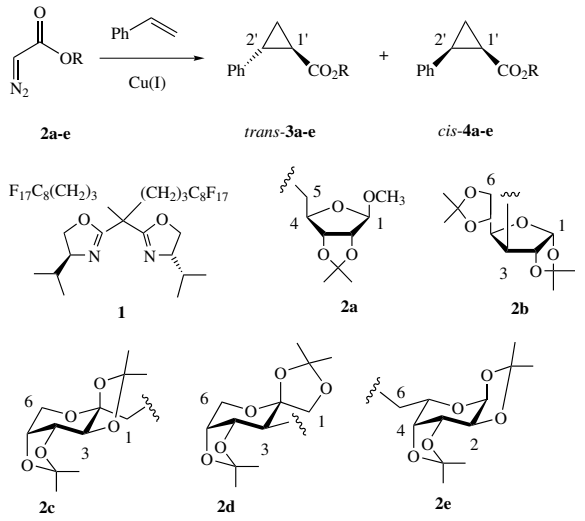
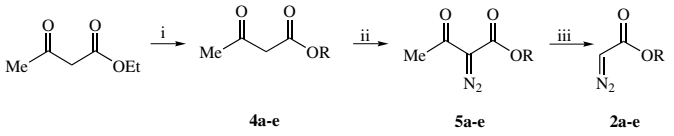


Scheme 1. Asymmetric Cu(I)-catalyzed cyclopropanation of styrene with ethyl α-diazoacetate **2a**.

isopropylidene-carbohydrate derivatives catalyzed by clays,[15] which led to the corresponding α-diazo-keto esters **5a**–**e** upon diazo-transfer reaction with mesyl azide as already described in the literature (Scheme 2).[16] These compounds, upon deacylation, produced the corresponding diazoacetates **2a**–**e**.[17]



Scheme 2. Preparation of the carbohydrate-based α-diazoacetates **2a**–**e**. Reagents and conditions: (i) R–OH, solid catalyst, reflux, 48 h, 50–98%; (ii) $CH_3SO_2N_3$, Et_3N, CH_2Cl_2, rt, 48 h, 73–85%; (iii) LiOH, CH_3CN, rt, 24 h, 50–85%.

The asymmetric cyclopropanation of the styrene with the carbohydrate-derived α-diazoacetates **2a**–**e**, leading to mixtures of the *trans*-**3a**–**e** and *cis*-**4a**–**e** adducts, was carried out either in the presence of the catalyst $Rh_2(OAc)_4$[17b] or the catalyst Cu(OTf)-fluorous bis(oxazoline) **1**[10a,18] following typical procedures described in the literature; this led to mixtures of the respective adducts **3a**–**e** and **4a**–**e** in low to acceptable stereoselectivities (Table 1). The best results were observed from the α-diazoacetate **2a** derived from monoacetonide of D-ribose where the *trans*:*cis* ratios are in agreement with the cyclopropanation of related α-diazoesters reported the literature (entries 1 and 2).[10a,11] An increase in the *trans*:*cis* ratios was observed when Rh(II) was replaced by the catalyst Cu(I)-**1**, although the diastereoselectivity obtained for the main isomer **3a** remained unchanged. This tendency was also observed in the cyclopropanations of **2b**–**e** (entries 3–10). The reactions catalyzed by Cu(I)-**1** led to mixtures of the adducts **3b**–**e** and **4b**–**e** in higher *trans*:*cis* ratios than those obtained using Rh(II) as the catalyst; however in these cases, the main isomers **3b**–**e** were obtained in low diastereoselectivities. It is noteworthy that the cyclopropanation of **2e** catalyzed by Cu(I)-**1** led to a improvement in the stereoselectivity of the *cis*-adduct **4e** (de up to 92%) and to a deleterious effect in the stereoselectivity of **3e** (de close to 0) when compared to the Rh(II)-catalyzed reaction (entries 9 and 10).

In all experiments, the cyclopropanations of **2a**–**e** catalyzed by Cu(I)-**1** led to a better *trans*:*cis* ratio than reactions performed in Rh(II), suggesting that the flourous bis(oxazoline) **1** had a prominent role in the control of this selectivity. Furthermore, in most of the cases (entries 1–8), the similar diastereoisomeric excesses obtained for each of the main adducts **3a**–**d** in reactions performed in the presence of Rh(II) or Cu(I)-**1** catalyst show that the chelating carbohydrate moieties in **2a**–**d** have an unexpected and effective role in control of the diastereoselectivity of **3b**–**d** irrespective of whichever system was employed, Rh(II) or Cu(I)-**1**. Indeed, this tendency was not explored in the asymmetric cyclopropanations of α-diazoacetates derived from the non-coordinating L-menthol.[11a–g]

3. Conclusions

The similar diastereoisomeric excesses obtained for each of the main adducts **3a**–**e** using Rh(II) or Cu(I)-**1** as catalysts suggest that the chelating carbohydrate moieties in **2a**–**e** are

Table 1. Stereoselectivities in the cyclopropanations of **2a**–**e**

Entry	**2**	Catalyst	Yield[a] (%)	**3**:**4**	**3** (% de)	**4** (% de)
1	**a**	$Rh_2(OAc)_4$	20	86:14[b]	60[c]	46[d]
2	**a**	**1**, CuOTf	30	95:05[b]	60[f]	53[d]
3	**b**	$Rh_2(OAc)_4$	21	72:28[c]	20[c]	26[c]
4	**b**	**1**, CuOTf	25	80:20[d]	19[d]	26[d]
5	**c**	$Rh_2(OAc)_4$	35	68:32[b]	<10[b]	<10[b]
6	**c**	**1**, CuOTf	62	75:25[b]	<10[b]	<10[b]
7	**d**	$Rh_2(OAc)_4$	62	85:15[c,d]	33[d]	12[d]
8	**d**	**1**, CuOTf	35	96:04[d,e]	34[d]	02[d]
9	**e**	$Rh_2(OAc)_4$	37	80:20[c]	17[d]	68[d]
10	**e**	**1**, CuOTf	15	85:15[b,d]	02[d]	92[d]

[a] Yields for the isolated mixtures of **3a**–**e** and **4a**–**e**.
[b] Determined by ^{1}H NMR (300 MHz) from the signals of H-1′.
[c] Determined by ^{1}H NMR (300 MHz) from the signals of H-1.
[d] Determined by HPLC using a Chiralpak AD Daicel chiral column (1% *i*-PrOH/ hexane).
[e] Determined by ^{1}H NMR (300 MHz) from the signals of H–3.
[f] Determined by ^{1}H NMR (300 MHz) from the signals of the methoxy group.

responsible for controlling the diastereoselectivity in the cyclopropanation. To the best of our knowledge, this is without precedent and shows that the stereoselectivity of the reaction is not attributed exclusively to the efficiency of the Cu- bis(oxazolines) complexes as chiral catalysts, as depicted in the literature.[10a,11] Furthermore, the results obtained from **2a** in this first report on the use of carbohydrate-based chiral auxiliaries in cyclopropanation with α-diazoacetates show that the chiral auxiliary derived from D-ribose is promising in reactions catalyzed by Cu(I)-fluorous bis(oxazolines) and can be further exploited in organic synthesis.

4. Experimental

4.1. General

Melting points were determined with a Fischer-Johns apparatus and are uncorrected. The optical rotations were recorded with a Perkin–Elmer 243B Polarimeter (sodium lamp at 589 nm). Flash chromatography was performed on silica gel 230–400 mesh (Merck). Infrared spectra were recorded with a Perkin–Elmer FT-IR 1600 spectrophotometer. High-resolution mass spectra (HRMS) were measured on a Hewlett-Packard 5988A spectrometer. The NMR spectra (^{1}H: 300.00 MHz, ^{13}C: 75.00 MHz) were recorded with a Varian Unityplus 300 instrument for solutions in $CDCl_3$ with Me_4Si as the internal standard. The HPLC analyses were performed on a chiral stationary phase (column: Chiralpak AD Daicel; eluent, hexane/*i*-PrOH 99:1; flow rate: 1 mL min^{-1}; $\lambda = 210$ nm).

4.2. Diazo-compounds 2b–f: general procedure

To a stirred solution of the appropriate α-diazo-β-ketoester **5a**–**e** (1 mmol) in CH_3CN (5 mL) was added water (1 mL), $LiOH{\cdot}H_2O$ (1.2 mmol) and the solution was stirred for 24 h. The reaction mixture was then extracted with ethyl acetate (2×10 mL). The combined organic phases were washed with a saturated aqueous sodium chloride solution (10 mL), dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure resulting in a light yellow oil. The products were purified by column chromatography on silica gel flash using hexane/ethyl acetate (95:5) as eluent.

4.2.1. Diazoacetic acid 5-(1-methyl-2,3-*O*-isopropylidene)-β-D-ribofuranose ester 2a. Yellow oil. 85% yield. IR (film) ν_{max} (cm^{-1}): 3101, 2989, 2939, 2836, 2114, 1696, 1455, 1375, 1240, 1192, 1094, 962, 869, 739. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.98 (s, H-1), 4.67 (dd, $J = 5.9$ and 0.6 Hz, H-3), 4.60 (5.9 Hz, H-2), 4.49 (s, COC*H*N$_2$), 4.42 (ddd, $J = 7.3$, 6.7 and 0.6 Hz, H-4), 4.23 (dd, $J = 11.2$ and 7.3 Hz, H-5), 4.16 (dd, $J = 11.2$ and 6.5 Hz, H-5), 3.32 (s, OCH_3), 1.48 (d, $J = 0.6$ Hz, CH_3), 1.32 (d, $J = 0.6$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 166.5 (C=O), 112.8 (C-6), 109.6 (C-1), 85.4 (C-2), 84.5 (C-4), 82.0 (C-3), 65.1 (C-5), 51.1 (OCH_3), 46.5 (CO*C*HN$_2$), 26.6 (CH_3), 25.2 (CH_3). MS (*m*/*z*): 257 (77), 154 (38), 85 (72), 81 (34), 69 (100), 68 (62), 59 (59). HRMS (EI) calcd for $C_{10}H_{13}N_2O_6$ $(M-15)^{+\cdot}$: 257.0774; found, 257.0661. $[\alpha]_D^{20} = -58$ (*c* 1.20, CH_2Cl_2).

4.2.2. Diazoacetic acid 3-(1,2:5,6-di-*O*-isopropylidene)-α-D-glucofuranose ester 2b. Yellow oil, 65% yield. IR (film) ν_{max} (cm^{-1}): 3103, 2989, 2939, 2898, 2116, 1699, 1456, 1384, 1345, 1217, 1164, 1076, 1023, 963, 887, 846, 739. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 5.88 (d, $J = 3.7$ Hz, H-1), 5.32 (d, $J = 2.7$ Hz, H-3), 4.82 (s, OCOC*H*N$_2$) 4.57 (d, $J = 3.7$ Hz, H-2), 4.23 (dd, $J = 7.8$ and 2.9 Hz, H-4), 4.18 (ddd, $J = 7.6$, 5.2 and 4.6 Hz, H-5), 4.07 (dd, $J = 8.5$ and 5.4 Hz, H-6), 4.01 (td, $J = 8.5$ and 4.6 Hz, H-6), 1.52 (s, CH_3), 1.42 (s, CH_3), 1.33 (s, CH_3), 1.31 (s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 166.5 (C=O), 112.1 (C-7), 109.2 (C-8), 104.8 (C-1), 83.1 (C-2), 79.5 (C-4), 76.3 (C-3), 72.2 (C-5), 66.9 (C-6), 46.3 (CO*C*HN$_2$), 26.6 (CH_3), 26.5 (CH_3), 26.0 (CH_3), 25.0 (CH_3). MS (*m*/*z*): 313 (100), 271 (22), 101 (36). HRMS (EI) calcd for $C_{13}H_{17}N_2O_7$ $(M-15)^{+\cdot}$: 313.1036; found, 313.0798. $[\alpha]_D^{20} = -36$ (*c* 1.10, CH_2Cl_2).

4.2.3. Diazoacetic acid 1-(2,3:4,5-di-*O*-isopropylidene)-β-fructopyranose ester 2c. Yellow oil, 63% yield. IR (film) ν_{max} (cm^{-1}): 3102, 2991, 2839, 2115, 1699, 1456, 1384, 1355, 1318, 1252, 1212, 1165, 1105, 1071, 1017, 982, 911, 887, 866, 758, 738. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.82 (s, OCOC*H*N$_2$), 4.61 (dd, $J = 7.8$ and 2.7 Hz, H-4), 4.49 (d, $J = 11.7$ Hz, H-1), 4.30 (d, $J = 2.7$ Hz, H-3), 4.24 (dd, $J = 7.8$ and 1.2 Hz, H-5), 4.15 (d, $J = 11.7$ Hz, H-1), 3.91 (dd, $J = 12.9$ and 1.7 Hz, H-6), 3.77 (dd, $J = 12.9$ and 0.7 Hz, H-6), 1.54 (s, CH_3), 1.49 (s, CH_3), 1.38 (s, CH_3), 1.35 (s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 166.6 (C=O), 109.6 (C-7), 108.7 (C-8), 96.2 (C-2), 70.9 (C-5), 70.6 (C-3), 70.4 (C-4), 66.1 (C-1), 63.7 (C-6), 46.3 (CO*C*HN$_2$), 25.9 (CH_3), 25.8 (CH_3), 24.9 (CH_3), 24.4 (CH_3). MS (*m*/*z*): 328 (37), 169 (34), 125 (39), 113 (100), 100 (69), 81 (28). HRMS (EI) calcd for $C_{14}H_{20}N_2O_7$ $(M^+)^{\cdot}$: 328.1271; found, 328.1288. $[\alpha]_D^{20} = -20$ (*c* 1.50, CH_2Cl_2).

4.2.4. Diazoacetic acid 3-(1,2:4,5-di-*O*-isopropylidene)-β-D-fructopyranose ester 2d. Yellow solid, 50% yield, mp 92.5–93 °C. IR (film) ν_{max} (cm^{-1}): 3101, 2989, 2938, 2889, 2116, 1694, 1456, 1378, 1221, 1113, 1084, 1030, 976, 909, 886, 850, 812, 735. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 5.18 (d, $J = 7.8$ Hz, H-3), 4.82 (s, OCOC*H*N$_2$), 4.29 (dd, $J = 7.8$ and 5.1 Hz, H-4), 4.24 (ddd, $J = 5.1$, 2.2 and 1.0 Hz, H-5), 4.13–4.11 (m, H-6), 3.98 (d, $J = 9.3$ Hz, H-1), 3.91 (d, $J = 9.3$ Hz, H-1), 1.58 (s, CH_3), 1.49 (s, CH_3), 1.38 (s, CH_3), 1.37 (s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 166.1 (C=O), 111.9 (C-7), 109.5 (C-8), 103.6 (C-2), 74.8 (C-5), 73.6 (C-4), 71.5 (C-1), 70.6 (C-3), 60.2 (C-6), 46.3 (CO*C*HN$_2$), 27.7 (CH_3), 26.3 (CH_3), 26.2 (CH_3), 25.8 (CH_3). MS (*m*/*z*): 313 (65), 271 (39), 202 (39), 185 (32), 169 (38), 143 (41), 127 (47), 85 (32), 69 (100), 59 (66), 57 (42). HRMS (EI) calcd for $C_{13}H_{17}N_2O_7$ $(M-15)^{+\cdot}$: 313.1036; found, 313.0601. $[\alpha]_D^{20} = -21$ (*c* 1.80, CH_2Cl_2).

4.2.5. Diazoacetic acid 6-(1,2:3,4-di-*O*-isopropylidene)-α-D-galactopyranose ester 2e. Yellow solid, 60% yield, mp 89–89.5 °C. IR (film) ν_{max} (cm^{-1}): 3126, 2998, 2988, 2939,

2900, 2113, 1691, 1412, 1399, 1354, 1247, 1216, 1183, 1151, 1138, 1099, 1076, 1003, 966, 920, 890, 869, 856, 742. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 5.54 (d, $J = 4.9$ Hz, H-1), 4.82 (s, OCOC*H*N_2), 4.62 (dd, $J = 7.8$ and 2.4 Hz, H-3), 4.37 (dd, $J = 11.7$ and 4.6 Hz, H-6), 4.33 (dd, $J = 4.9$ and 2.4 Hz, H-2), 4.27 (dd, $J = 11.7$ and 7.8 Hz, H-6), 4.24 (dd, $J = 7.8$ and 1.9 Hz, H-4), 4.05 (ddd, $J = 7.1$, 4.6 and 1.9 Hz, H-5), 1.52 (s, CH_3), 1.46 (s, CH_3), 1.34 (s, CH_3), 1.33 (s, CH_3), ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 166.9 (C=O), 109.9 (C-7), 109.0 (C-8), 71.2 (C-4), 96.5 (C-1), 70.9 (C-3), 70.7 (C-2), 66.4 (C-5), 64.0 (C-6), 46.6 (CO*C*HN_2); 26.3 (CH_3), 26.2 (CH_3), 25.2 (CH_3), 24.7 (CH_3). MS (*m*/*z*): 313 (100), 184 (30), 169 (33), 113 (39), 100 (57), 85 (34), 81 (51), 59 (33). HRMS (EI) calcd for $C_{13}H_{17}N_2O_7$ $(M-15)^{+\cdot}$: 313.1036; found, 313.0895. $[\alpha]_D^{20} = -22$ (*c* 1.20, CH_2Cl_2).

4.3. General procedure for the cyclopropanation with 2a–e using Rh(II)

To a mixture of $Rh_2(OAc)_4$ (2.7 mg; 0.61 mol %) and styrene (0.04 g; 0.396 mmol) in dry CH_2Cl_2 (1 mL) under a nitrogen atmosphere was added dropwise a solution of the appropriate α-diazoacetate **2a–e** (0.305 mmol) in dry CH_2Cl_2 (3 mL) over 5 h using a syringe pump and the mixture was stirred at room temperature for 12 h. The volatiles were then evaporated under vacuum to give residues that were purified by flash chromatography (silica gel, 5% AcOEt/hexane) furnishing, in all cases, mixtures of *trans*-**3a–e** and *cis*-**4a–e** as pale yellow oils in yields as that shown in Table 1.

4.4. General procedure for the cyclopropanations with 2a–e using Cu(I)-1

To a mixture of the complex CuOTf·benzene (2×10^{-3} mmol), styrene (0.04 g; 0.396 mmol) and the chiral ligand **1** (4.6 mg; 15 mol %) under a nitrogen atmosphere, was added dropwise a solution of the appropriate α-diazoacetate **2a–e** (0.305 mmol) in dry CH_2Cl_2 (2 mL) over 5 h using a syringe pump and the mixture was stirred at room temperature for 12 h. The volatiles were then evaporated under vacuum to give yellow oils that were purified by flash chromatography (silica gel, 5% AcOEt/hexane) furnishing, in all cases, mixtures of *trans*-**3a–e** and *cis*-**4a–e** as pale yellow oils in yields as that shown in Table 1.

4.4.1. Mixture of 3a and 4a. IR (film) ν_{max} (cm^{-1}): 2989, 2938, 1732, 1459, 1409, 1384, 1174, 1095, 870, 757, 699. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.23–7.01 (m, Ar-H), 4.91 (s, H-1 of the major isomer of **3a**), 4.84 (s, H-1 of the minor isomer of **3a**), 4.83 (s, H-1 of the major isomer of **4a**), 4.82 (s, H-1 of the minor isomer of **4a**), 4.62 (d, $J_{2,3} = 5.4$ Hz, H-2 of the major isomer of **3a**), 4.54 (dd, $J_{2,3} = 6.2$ Hz and $J_{2,4} = 1.5$ Hz, H-2 of the minor isomer of **3a**), 4.42 (d, $J_{2,3} = 6.0$ Hz, H-2 of the minor isomer of **4a**), 4.40 (d, $J_{2,3} = 6.0$ Hz, H-2 of the major isomer of **4a**), 4.34–4.22 (m, H-4 of **3a** and **4a**), 4.16–4.01 (m, H-3 and H-5 of **3a** and **4a**), 3.85–3.66 (m, H-5 of **3a** and **4a**), 3.25 (s, OCH_3 of the major isomer of **4a**), 3.24 (s, OCH_3 of the major isomer of **3a**), 3.17 (s, OCH_3 of the minor isomer of **3a**), 3.10 (s, OCH_3 of the minor isomer of **4a**), 2.59–2.44 (m, H-2′ of **3a** and **4a**), 2.08–2.04 (m, H-1′ of **4a**), 1.88 (ddd, $J_{1',3'} = 8,3$ Hz; $J_{1',3'} = 5,4$ Hz and $J_{1',2'} = 4,0$ Hz, H-1′ of **3a**), 1.70–1.63 (m, H-3′ of **4a**), 1.58–1.52 (m, H-3′ of **3a**), 1.31–1.25 (m, H-3′ of **3a** and **4a**), 1.42 (s, CH_3 of the major isomer of **3a**), 1.40 (s, CH_3 of the minor isomer of **3a**), 1.26 (s, CH_3 of the major isomer of **3a**), 1.23 (s, CH_3 of the minor isomer of **3a**), 1.18 (s, CH_3 of the major isomer of **4a**). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 172.8 (C=O of **3a**), 170.5 (C=O of **4a**), 139.6 (C-4′ of **3a**), 136.3 (C-4′ of **4a**), 134.2, 133.8 and 129.8 (C-5′–C-7′ of the minor isomer of **4a**), 130.0, 129.0 and 126.6 (C-5′–C-7′ of the major isomer of **4a**), 129.1, 128.3 and 126.4 (C-5′–C-7′ of the minor isomer of **3a**), 128.8, 127.9 and 126.0 (C-5′–C-7′ of the major isomer of **3a**), 112.4 (C-6 of the major isomer of **3a**), 112.3 (C-6 of the minor isomer of **3a**), 112.2 (C-6 of the major isomer of **4a**), 112.0 (C-6 of the minor isomer of **4a**), 109.8 (C-1 of **4a**), 109.2 (C-1 of the major isomer of **3a**), 109.0 (C-1 of the minor isomer of **3a**), 88.2 (C-3 of the major isomer of **3a**), 85.6, 84.8, 83.9 and 83.8 (C-2–C-4 of **4a**), 85.1, 85.0, 84.1 and 84.0 (C-2–C-4 of **3a**); 64.3 and 64.2 (C-5 of **3a**), 64.7 and 63.8 (C-5 of **4a**), 55.3 and 54.8 (OCH_3 of **4a**), 54.6 and 54.5 (OCH_3 of **3a**), 31.8 (C-3′ of the minor isomer of **3a**), 29.5 (C-3′ of the major isomer of **4a**), 26.3 (C-2′ of **3a**), 26.1 (C-2′ of **4a**), 26.2 and 24.7 (CH_3 of the major isomer of **3a**), 25.8 and 24.5 (CH_3 of the minor isomer of **4a**), 25.7 and 24.9 (CH_3 of the minor isomer of **3a**), 24.8 and 23.8 (CH_3 of the major isomer of **4a**), 23.7 (C-1′ of **3a**), 21.4 (C-1′ of **4a**), 17.1 (C-3′ major isomer of **3a**), 11.3 (C-3′ of the minor isomer of **4a**). MS (*m*/*z*): 347 (56), 333 (38); 145 (97); 144 (100); 117 (51); 116 (19). HRMS (EI) calcd for $C_{19}H_{23}O_6$ $(M-1)^{+\cdot}$: 347.1495; found, 347.1469.

4.4.2. Mixture of 3b and 4b. IR (film) ν_{max} (cm^{-1}): 2988, 2936, 1735, 1604, 1498, 1456, 1405, 1374, 1259, 1217, 1163, 1176, 1024, 887, 845, 756, 699. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.32–7.20 (m, Ar-H of **3b**), 7.12–7.08 (m, Ar-H of **4b**), 5.91 (d, $J_{1,2} = 3.6$ Hz, H-1 of the minor isomer of **3b**), 5.88 (d, $J_{1,2} = 3.9$ Hz, H-1 of the major isomer of **3b**), 5.55 (d, $J_{1,2} = 3.6$ Hz, H-1 of the major isomer of **4b**), 5.31–5.29 (m, H-3 of the minor isomer of **3b**), 5.28 (d, $J_{3,4} = 2.7$ Hz, H-3 of the major isomer of **3b**), 5.23 (d, $J_{1,2} = 3.9$ Hz, H-1 of the minor isomer of **4b**), 5.02 (d, $J_{3,4} = 1.8$ Hz, H-3 of the minor isomer of **4b**), 4.92 (d, $J_{3,4} = 3.0$ Hz, H-3 of the major isomer of **4b**), 4.53 (d, $J_{2,1} = 4.2$ Hz, H-2 of the minor isomer of **3b**), 4.52 (d, $J_{2,1} = 3.9$ Hz, H-2 of the major isomer of **3b**), 4.30–4.20 (m, H-4 and H-5 of **3b**), 4.20–3.90 (m, H-6 of **3b** and H-4–H 6 of **4b**), 3.42 (d, $J_{2,1} = 3.9$ Hz, H-2 of the minor isomer of **4b**), 3.40 (d, $J_{2,1} = 3.6$ Hz, H-2 of the major isomer of **4b**), 2.68–2.53 (m, H-2′ of **3b** and **4b**), 2.25–2.10 (m, H-1′ of **4b**), 1.96–1.89 (m, H-1′ of **3b**), 1.85–1.80 (m, H-3′ of **4b**), 1.74–1.60 (m, H-3′ of **3b**), 1.52, 1.43, 1.36 and 1.31 (s, CH_3 of the major isomer of **3b**), 1.41, 1.39, 1.33 and 1.32 (s, CH_3 of the minor isomer of **3b**), 1.40, 1.26, 1.15 and 1.14 (s, CH_3 of the major isomer of **4b**), 1.35–1.30 (m, H-3′ of **3b** and **4b**). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 171.8 (C=O of **3b**), 169.0 (C=O of **4b**), 139.4 (C-4′ of the major isomer of **3b**); 139.3 (C-4′ of the minor isomer of **3b**), 136.6 (C-4′ of the minor isomer of **4b**), 135.7 (C-4′ of the major isomer of **4b**), 129.5, 128.8, 128.4, 128.1, 127.8, 126.7, 126.6, 126.5, 126.1 and 125.9 (C-5′–C-7′ of **3b** and **4b**), 111.8

(C-7 of **3b**), 111.6 (C-8 of **3b**), 111.2 (C-7 of **4b**), 111.1 (C-8 of **4b**), 105.3 (C-1 of **3b**), 104.7 (C-1 of **4b**), 83.2 (C-2 of **3b**), 82.6 (C-2 of **4b**), 79.6 (C-4 of **3b**), 79.3 (C-5 of **3b**), 76.2 (C-3 of the major isomer of **3b**), 76.1 (C-3 of the minor isomer of **3b**), 76.0 (C-3 of the major isomer of **4b**), 75.3 (C-3 of the minor isomer of **4b**), 72.3 (C-4 of **4b**), 72.2 (C-5 of **4b**), 67.0 (C-6 of **3b**), 66.9 (C-6 of **4b**), 26.7, 26.6, 26.5 and 26.4 (CH_3 of the major isomer of **3b**), 26.6, 26.4, 26.3 and 26.2 (CH_3 of the minor isomer of **3b**), 26.1, 25.8, 25.7 and 25.5 (CH_3 of the major isomer of **4b**), 26.0 (C-2′ of **4b**), 25.8 (C-2′ of **3b**), 25.2 (C-1′ of the major isomer of **3b**), 25.1 (C-1′ of the minor isomer of **3b**), 23.9 (C-1′ of the major isomer of **4b**), 23.7 (C-1′ of the minor isomer of **4b**), 17.4 (C-3′ of the major isomer of **3b**), 17.2 (C-3′ of the minor isomer of **3b**), 9.8 (C-3′ of the major isomer of **4b**). MS (*m*/*z*): 406 (1,5); 405 (8), 404 (17); 389 (68); 245 (19); 145 (100); 144 (13); 117 (18); 105 (55); 101 (82); 77 (20). HRMS (EI) calcd for $C_{22}H_{28}O_7$ $(M^+)^{\bullet}$: 404.1835; found, 404.1837.

4.4.3. Mixture of 3c and 4c. IR (film) ν_{max} (cm^{-1}): 2990, 2937, 1737, 1457, 1406, 1382, 1252, 1209, 1160, 1105, 1072, 888, 871, 757, 698. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.31–7.20 (m; Ar-H of **3c**), 7.11–7.07 (m, Ar-H of **4c**), 4.61 (dd, $J_{4,5} = 9.0$ Hz; $J_{4,3} = 3.0$ Hz, H-4 of **3c**), 4.56 (d, $J_{1,1} = 9.0$ Hz, H-1 of the major isomer of **4c**), 4.54 (dd, $J_{4,5} = 6.0$ Hz, $J_{4,3} = 3.0$ Hz, H-4 of **4c**), 4.48 (d, $J_{1,1}$=12.0 Hz, H-1 of the major isomer of **3c**), 4.36 (d; $J_{3,4} = 3.0$ Hz, H-3 of **3c**), 4.24–4.19 (m, H-3 of **4c** and H-5 of **3c** and **4c**), 4.17 (d, $J_{1,1} = 9.0$ Hz, H-1 of the minor isomer of **3c**), 4.13 (d, $J_{1,1}$=9.0 Hz, H-1 of the minor isomer of **4c**), 4.11 ppm (d, $J_{1,1}$=9.0 Hz, H-1 of the major isomer of **4c**), 4.09 ppm (d, $J_{1,1} = 9.0$ Hz, H-1 of the minor isomer of **4c**), 4.07 (d, $J_{1,1} = 9.0$ Hz, H-1 of the major isomer of **3c**), 3.94–3.70 (m, H-6 of **3c** and **4c**), 3.90 (d, $J_{1,1} = 12.0$ Hz, H-1 of the minor isomer of **3c**), 2.65–2.53 (m, H-2′ of **3c** and **4c**), 2.20–2.11 (m, H-1′ of **4c**), 1.96–1.90 (m, H-1′ of **3c**), 1.78–1.70 (m, H-3′ of **4c**), 1.68–1.60 (m, H-3′ of **3c**), 1.38–1.33 (m, H-3′ of **3c** and **4c**), 1.55, 1.43, 1.34 and 1.33 (s, CH_3 of the major isomer of **3c**), 1.54, 1.48, 1.45 and 1.44 (s, CH_3 of the major isomer of **4c**), 1.42, 1.39, 1.38 and 1.37 (s, CH_3 of the minor isomer of **3c**). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 172.7 (C═O of **3c**), 170.0 (C═O **4c**), 139.6 (C-4′ of **3c**), 136.0 (C-4′ of **4c**), 129.2, 129.1 and 127.8 (C-5′–C-7′ of **4c**), 128.3, 126.4 and 126.0 (C-5′–C-7′ of **3c**), 109.0 and 101.3 (C-7 and C-8 of the major isomer of **3c**), 108.9 and 101.4 (C-7 and C-8 of the major isomer of **4c**), 108.6 and 101.5 (C-7 and C-8 of the minor isomer of **3c**), 70.6 (C-5 of **3c**), 70.4 (C-5 of **4c**), 70.3 (C-3 of **3c**), 70.2 (C-3 of **4c**), 69.9 (C-4 of **4c**), 69.8 (C-4 of **3c**), 65.3 (C-1 of **3c**), 65.2 (C-1 of **4c**), 65.1 (C-6 of **3c** and **4c**), 61.1 (C-2 of **4c**), 61.0 (C-2 of **3c**), 26.6 (C-2′ of **3c**), 26.5 (C-2′ of **4c**), 26.4, 26.2, 25.7 and 25.0 (CH_3 of the minor isomer of **3c**), 26.3, 25.7, 25.2 and 25.1 (CH_3 of the major isomer of **3c**), 25.9, 25.8, 24.1 and 24.0 (CH_3 the major isomer of **4c**), 23.9 (C-1′ of the major isomer of **3c**), 23.8 (C-1′ of the minor isomer of **3c**), 21.6 (C-1′ of the major isomer of **4c**), 21.2 (C-1′ of the minor isomer of **4c**), 17.2 (C-3′ of the major isomer of **3c**), 17.1 (C-3′ of the minor isomer of **3c**), 11.7 (C-3′ of the major isomer of **4c**), 11.5 (C-3′ of the minor isomer of **4c**). MS (*m*/*z*): 389 (49); 245 (5); 145 (100); 144 (45); 144 (13); 117 (22). HRMS (EI) calcd for $C_{21}H_{25}O_7$ $(M^+-15)^{\bullet}$: 389.1549; found, 389.1494.

4.4.4. Mixture of 3d and 4d. IR (film) ν_{max} (cm^{-1}): 2988, 2935, 1732, 1458, 1405, 1373, 1221, 1189, 1113, 1086, 976, 887, 852, 810, 756, 699. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.31–7.18 (m, Ar-H of **3d**), 7.13–7.09 (m, Ar-H of **4d**), 5.16 (d, $J_{3,4} = 9.0$ Hz, H-3 of **3d**), 4.91 (d, $J_{3,4} = 6.0$ Hz, H-3 of the major isomer of **4d**), 4.90 (d, $J_{3,4} = 6.0$ Hz, H-3 of the minor isomer of **4d**), 4.35–4.28 (m, H-4 of **3d**), 4.26–4.22 (m, H-5 of **3d** and **4d**), 4.18–4.14 (m, H-4 of **4d**), 4.14–4.11 (m, H-6 of **3d**), 4.08–4.00 (m, H-6 of **4d**), 3.98 (d, $J_{1,1} = 9.0$ Hz, H-1 of the major isomer of **3d**), 3.88 (d, $J_{1,1} = 9.0$ Hz, H-1 of the minor isomer of **3d** and H-1 of the major isomer of **4d**), 3.87 (d, $J_{1,1} = 9.0$ Hz, H-1 of the major isomer of **3d**), 3.86 (d, $J_{1,1} = 9.0$ Hz, H-1 of the minor isomer of **3d**), 3.77 (d, $J_{1,1} = 9.0$ Hz, H-1 of the major isomer of **4d**), 3.53 (d, $J_{1,1} = 9.0$ Hz, H-1 of the minor isomer of **4d**), 2.94 (d, $J_{1,1}$=9.0 Hz, H-1 of the minor isomer of **4d**), 2.67–2.55 (m, H-2′ of **3d** and **4d**), 2.26–2.14 (m, H-1′ of **4d**), 2.00–1.93 (m, H-1′ of **3d**), 1.72–1.62 (m, H-3′ of **3d** and **4d**), 1.57, 1.48, 1.37 and 1.35 (s, CH_3 of the major isomer of **3d**), 1.50, 1.46, 1.36 and 1.26 (s, CH_3 of the minor isomer of **3d**), 1.42, 1.41, 1.30 and 1.19 (s, CH_3 of the major isomer of **4d**), 1.40–1.32 (m; H-3′ of **3d** and **4d**). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 172.8 (C═O of **3d**), 172.7 (C═O of **4d**), 139.5 (C-4′ of **3d**), 139.4 (C-4′ of **4d**), 128.3, 126.5 and 126.3 (C-5′–C-7′ of **4d**), 128.2, 126.4 and 126.0 (C-5′–C-7′ of **3d**), 111.9, 109.5 and 103.5 (C-2, C-7 and C-8 of **4d**), 111.8, 109.4 and 103.6 (C-2, C-7 and C-8 of **3d**), 74.7 (C-4 of **4d**), 74.6 (C-4 of **3d**), 73.6 (C-5 of **4d**), 73.5 (C-5 of **3d**), 71.7 (C-1 of **3d**), 71.6 (C-1 of **4d**), 70.3 (C-3 of **4d**), 70.2 (C-3 of **3d**), 60.4 (C-6 of **3d**), 60.3 (C-6 of **4d**), 26.9 (C-2′ of **4d**), 26.0 (C-2′ of **3d**), 27.7, 26.4, 26.3 and 26.0 (CH_3 of **4d**), 27.6, 26.7, 26.2 and 26.1 (CH_3 of **3d**), 23.9 (C-1′ of **3d**), 23.8 (C-1′ of **4d**), 17.4 (C-3′ of **3d**), 16.7 (C-3′ of **4d**). MS (*m*/*z*): 404 (33); 389 (16); 244 (7); 145 (100); 144 (12); 117 (17). HRMS (EI) calcd for $C_{22}H_{28}O_7$ $(M^+)^{\bullet}$: 404.1835; found, 404.1833.

4.4.5. Mixture of 3e and 4e. IR (film) ν_{max} (cm^{-1}): 2988, 2917, 1728, 1456, 1411, 1383, 1256, 1212, 1176, 1071, 1005, 895, 757, 698. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.30–7.17 (m, Ar-H of **3e**), 7.11–7.08 (m Ar-H of **4e**), 5.55 (d, $J_{1,2} = 6.0$ Hz, H-1 of **3e**), 5.49 (d, $J_{1,2} = 6.0$ Hz, H-1 of the minor isomer of **4e**), 5.48 (d, $J_{1,2} = 6.0$ Hz, H-1 of the major isomer of **4e**), 4.63 (dd, $J_{3,2} = 3.0$ Hz and $J_{3,4} = 9.0$ Hz, H-3 of **3e**), 4.52 (dd, $J_{3,4} = 5.5$ Hz and $J_{3,2} = 3.0$ Hz, H-3 of the major isomer of **4e**), 4.49 (dd, $J_{3,4} = 5.4$ Hz and $J_{3,2} = 3.0$ Hz, H-3 of the minor isomer of **4e**), 4.39–4.17 (m, H-4 and H-6 of **3e**), 4.34 (dd, $J_{2,1} = 6.0$ Hz and $J_{2,3} = 3.0$ Hz, H-2 of **3e**), 4.07–4.01 (m, H-5 of **3e** and H-6 of **4e**), 3.91–3.83 (m, H-2 and H-5 of **4e**), 3.82–3.73 (m, H-4 of **4e**), 2.63–2.50 (m, H-2′ of **3e** and **4e**), 2.22–2.11 (m, H-1′ of **4e**), 2.01–1.94 (m, H-1′ of **3e**), 1.74–1.68 (m, H-3′ of **4e**), 1.65–1.58 (m, H-3′ of **3e**), 1.52, 1.51, 1.48 and 1.30 (s, CH_3 of the minor isomer of **3e**), 1.46, 1.34, 1.33 and 1.32 (s, CH_3 of the major isomer of **3e**), 1.40, 1.39, 1.36 and 1.25 (s, CH_3 of the major isomer of **4e**), 1.35–1.30 (m, H-3′ of **3e** and **4e**). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 173.2 (C═O of the major isomer

of **3e**), 173.1 (C=O of the minor isomer of **3e**), 170.7 (C=O of the minor isomer of **4e**), 170.6 (C=O of the major isomer of **4e**), 139.9 (C-4′ of the minor isomer of **3e**), 139.8 (C-4′ of the major isomer of **3e**), 136.4 (C-4′ of the major isomer of **4e**), 136.3 (C-4′ of the minor isomer of **4e**), 129.1, 129.0 and 126.0 (C-5′–C-7′ of the major isomer of **4e**), 128.8, 127.6 and 126.5 (C-5′–C-7′ of the minor isomer of **4e**), 128.3, 128.2 and 126.3 (C-5′–C-7′ of the major isomer of **3e**), 127.9, 127.8 and 126.1 (C-5′–C-7′ of the minor isomer of **3e**), 109.5 (C-7 and C-8 of the major isomer of **3e**), 109.3 and 109.2 (C-7 and C-8 of the major isomer of **4e**), 108.7 and 108.6 (C-7 and C-8 of the minor isomer of **3e**), 108.5 and 108.4 (C-7 and C-8 of the minor isomer of **4e**), 98.8 (C-1 of **3e**), 96.2 (C-1 of **4e**), 71.0, 70.9, 70.6, 70.5, 70.4, 70.3 and 70.2 (C-2–C-4 of **3e** and **4e**), 65.9 (C-5 of the minor isomer of **3e**), 65.8 (C-5 of the major isomer of **3e**), 65.7 (C-5 of the minor isomer of **4e**), 65.3 (C-5 of the major isomer of **4e**), 63.6 (C-6 of the minor isomer of **3e**), 63.5 (C-6 of the major isomer of **3e**), 63.0 (C-6 of the major isomer of **4e**), 62.7 (C-6 of the minor isomer of **4e**), 26.3 (C-2′ of the minor isomer of **3e**), 26.2 (C-2′ of the major isomer of **3e**), 26.1, 25.4, 24.7 and 24.2 (CH_3 of the major isomer of **4e**), 26.0, 25.7, 24.3 and 24.2 (CH_3 of the minor isomer of **3e**), 25.9, 25.8, 24.9 and 24.8 (CH_3 of the major isomer of **3e**), 25.6 (C-2′ of the minor isomer of **4e**), 25.5 (C-2′ of the major isomer of **4e**), 24.0 (C-1′ of the major isomer of **3e**), 23.9 (C-1′ of the minor isomer of **3e**), 21.7 (C-1′ of the minor isomer of **4e**), 21.6 (C-1′ of the major isomer of **4e**), 17.1 (C-3′ of the major isomer of **3e**), 17.0 (C-3′ of the minor isomer of **3e**), 11.6 (C-3′ of the minor isomer of **4e**), 11.3 (C-3′ of the major isomer of **4e**). MS (*m*/*z*): 405 (2,5); 404 (13); 389 (41); 145 (100); 144 (98); 117 (22); 105 (54); 77 (30). HRMS (EI) calcd for $C_{22}H_{28}O_7$ $(M^+)^{\bullet}$: 404.1831; found, 404.1835.

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