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Synthesis of Unsaturated Diesters of Primary, Secondary and Tertiary Diols Derived from Dimethyl (+)-Tartrate and Galactaric Acid

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The preparation of symmetrical unsaturated diesters of dioe first was the reaction of mixed anhydrides, obtained from α,β-unsaturated acids and benzoyl chloride, with diols **3** (primary), **5** (secondary), and **7** (primary), i.e., Yamaguchi–Santa-Lucía's method, however only the symmetrical diacrylates of diols **5** and **7** were obtained quantitatively. In the other ten cases studied the reactions led to mixtures of symmetrical and unsymmetrical diesters that were difficult to separate. The mixed anhydrides did not react with the tertiary diols **4** (TADDOL) and **8**. The average yield obtained in desired symmetrical diesters in the 12 cases studied was 54 %. The acylation of the diols with the anhydrides of the unsaturated acids, was found to be an excellent method, leading to the symmetrical unsaturated diesters of diols **3**, **5**, **7** as the only products of reaction, in an average yield of 83 %. Unfortunately, the method could not be applied to diesters derived from the tertiary diols **4** (TADDOL) and **8**. The third method studied was the reaction between the alkoxides prepared with solutions of *n*BuLi in ether with the unsaturated acid chlorides at –50 °C, i.e., the Kaiser–Woodruff protocol. This was found to be the best of the three methods tested. The method was applied with success to the synthesis of the desired unsaturated diesters derived from diols **3**–**5**, **7**, and **8**. The average yield of the 19 cases studied was 78 %.

Introduction

Unsaturated diesters such as TADDOL dimethacrylate have been synthesized and successfully employed in stereoselective cyclopolymerizations,[1,2] and also in the stereoselective synthesis of optically active macrodiolides through cyclohydrostannation reactions.[3] We have recently reported the synthesis of unsaturated diesters through esterification of TADDOL with α,β-unsaturated carboxylic acid chlorides, in the presence of *n*-butyllithium (*n*BuLi) in *n*-hexane.[4] These reactions lead to mixtures of the corresponding mono- and diesters, the latter in higher yields. The average yields of pure unsaturated diesters using this method were around 72%. It should be mentioned that although the synthesis of TADDOL dimethacrylate (**9**) was reported in 1997,[1] we were not able to find any reference to other unsaturated diesters in the chemical literature other than those of TADDOL reported by us.[4]

To determine the scope of the cyclohydrostannation reactions, we needed a new set of unsaturated systems. This prompted us to carry out a study to establish more convenient protocols for the synthesis of unsaturated diesters of diols derived from dimethyl (*R*,*R*)-tartrate (**1**) and galactaric acid (**2**).

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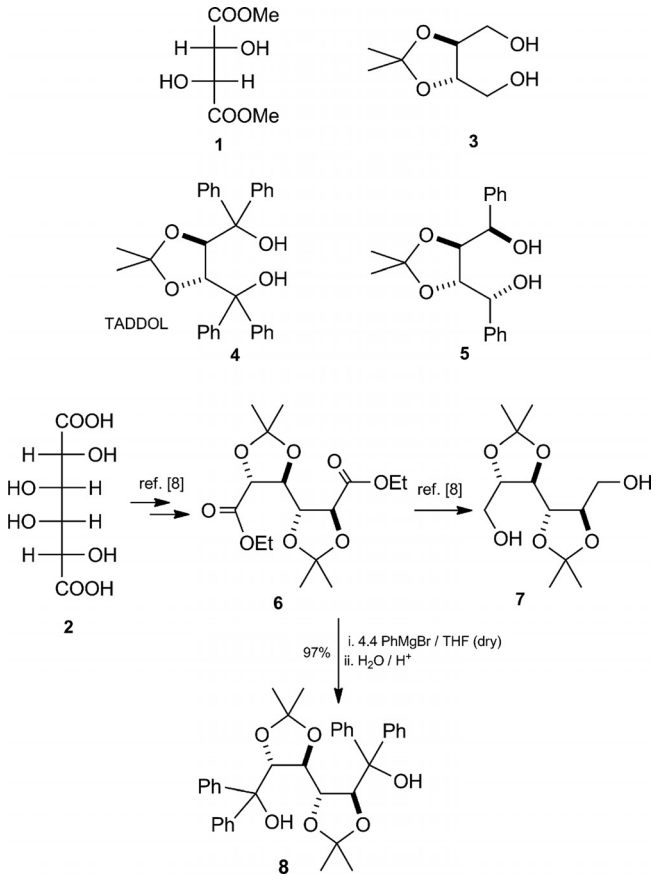
Results and Discussion

Diols **3**,[5] **4**,[6] **5**,[7] **7**,[8] and **8** (Scheme 1) used in the esterification reactions were obtained from commercially available dimethyl (*R*,*R*)-tartrate (**1**) and galactaric acid (**2**) following known procedures.

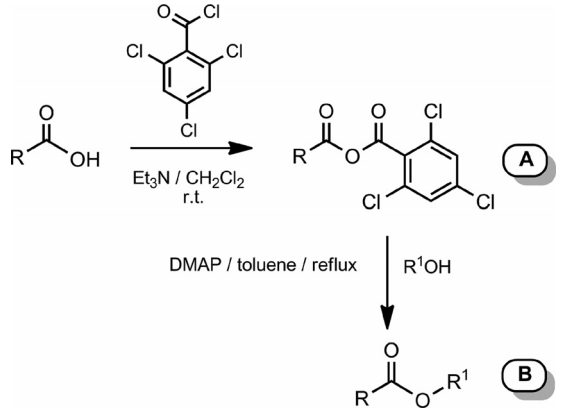
As shown in Scheme 1, diol **8** was obtained in excellent yield from the previously reported diester **6** through addition of an excess of phenylmagnesium bromide in tetrahydrofuran (THF).

First, we studied the esterification of these diols by means of Yamaguchi's method.[9a] The approach involves two steps: (a) the reaction of an aliphatic acid with 2,4,6-trichlorobenzoyl chloride (Yamaguchi's reagent) and isolation of the corresponding mixed anhydride **A**, and (b) reaction of the anhydride with an alcohol in the presence of the nucleophilic catalyst 4-(dimethylamino)pyridine (DMAP) to give ester **B** regioselectively (Scheme 2).

It has recently been reported that through the use of benzoyl chloride instead of the highly hindered 2,4,6-trichlorobenzoyl chloride it was also possible to obtain the mixed esters in excellent yields.[9b] Taking into account the



Scheme 1. Synthesis of diols **3**–**5**, **7** and **8**, starting from dimethyl (*R*,*R*)-tartrate (**1**) or galactaric acid (**2**).



Scheme 2. Yamaguchi reaction.

previous report, we prepared a series of anhydrides through the reaction between α,β-unsaturated acids and benzoyl chloride and then reaction of these mixed anhydrides with primary diol **3**. The results are summarized in Scheme 3.

The α,β-unsaturated carboxylic acid (3 mmol) and benzoyl chloride (3 mmol) were dissolved in anhydrous THF at room temperature. Subsequently, Et_3N (12 mmol) followed by 25% cat. DMAP and diol (1.5 mmol) were added. As shown in Scheme 3, these reactions lead to the formation of mixtures of the symmetrical diesters **I** and the mixed diesters **II**. Unfortunately, we were not able to separate these mixtures either by column chromatography or by crystallization.

Following the same protocol, mixed anhydrides **C** were reacted with primary diol **7**. The results obtained in these reactions are shown in Scheme 4. In this case, using mixed anhydride **C** derived from acrylic acid (**9**), we were able to obtain quantitatively the desired symmetrical diester **21**. Unfortunately, using the mixed anhydrides **C** derived from α,β-unsaturated carboxylic acids **10**–**12**, mixtures of the symmetrical (**III**) and mixed (**IV**) diesters were obtained that, again, could not be separated.

It should be noted that neither in the reactions involving diol **3** nor in those carried out with diol **7**, did the mass spectra of the reaction products show the presence of the diols, indicating that the reactions had reached completion.

Under the same reaction conditions, we also studied the esterification of the secondary diol **5** with the unsaturated acids **9**–**12** following Yamaguchi–SantaLucia's procedure (Scheme 5).

As shown in Scheme 5, symmetrical diester **28** was obtained quantitatively. However, the reactions of **5** with the mixed anhydrides **C** derived from α,β-unsaturated carboxylic acids **10**–**12** gave inseparable mixtures of the symmetrical diesters **V** and the mixed diesters **VI**.

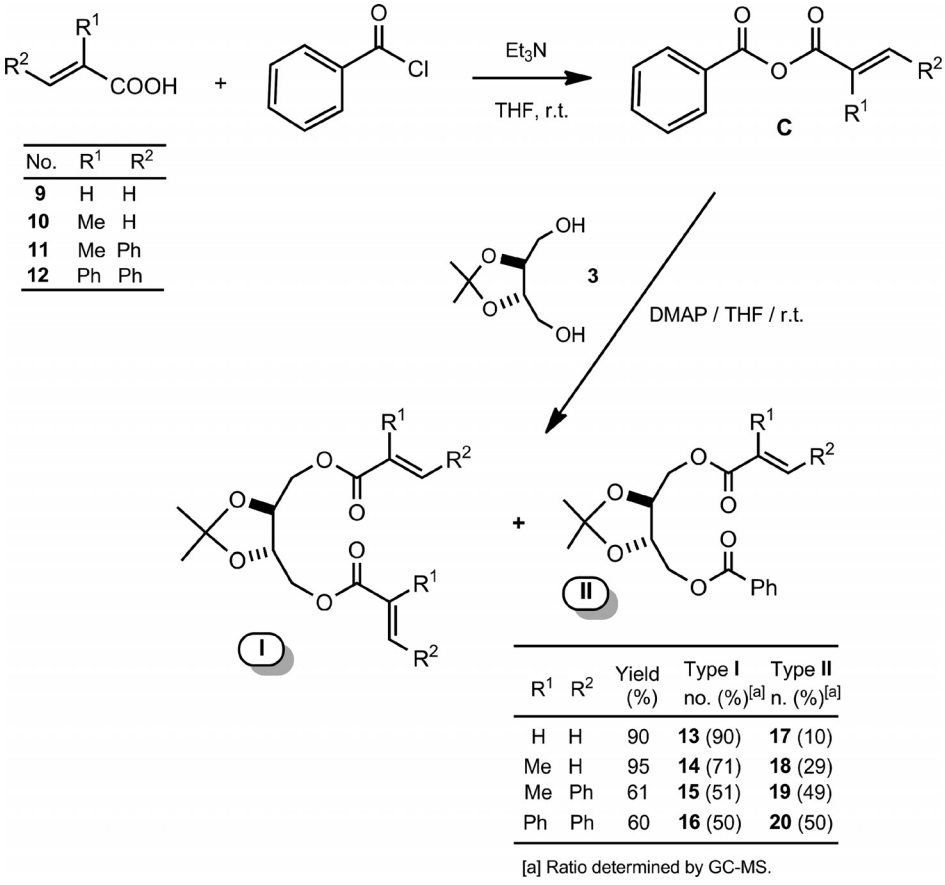
All attempts at the esterification of tertiary diols **4** (TADDOL) and **8** following Yamaguchi–SantaLucia's method failed, probably for steric reasons.

The results described above clearly indicate that Yamaguchi's method is not suitable for the preparation of symmetrical diesters of substituted acrylic acids. Most of the reactions led to inseparable mixtures of symmetrical and mixed diesters, and only the symmetrical unsaturated diesters **21** and **28** could be obtained in pure form. Furthermore, the reactions only take place with primary and secondary diols and not with tertiary alcohols.

Typically, acylation of alcohols is carried out by treatment with acid anhydrides. Therefore, we prepared the symmetric anhydrides of acrylic (**9**) and methacrylic (**10**) acids,[10] and reacted them with diol **3** (Scheme 6). We found that although the only products in both cases were the corresponding symmetrical unsaturated diesters **13** and **14**, respectively, they were formed in very low yields (less than 20%). In the case of unsaturated acids **11** and **12**, no reaction was observed and only starting material was recovered (Scheme 6).

When the same reactions were performed in the presence of DMAP, a dramatic increase in the yields of the symmetrical unsaturated diesters **13** and **14** was found. Taking into account these results, we carried out the "one pot" esterification of diols **3**, **5**, and **7** with the symmetrical anhydrides derived from acids **9**–**12**, according to Scheme 7.

As shown in Scheme 7, in all cases the reactions lead exclusively to the symmetrical unsaturated diesters of both

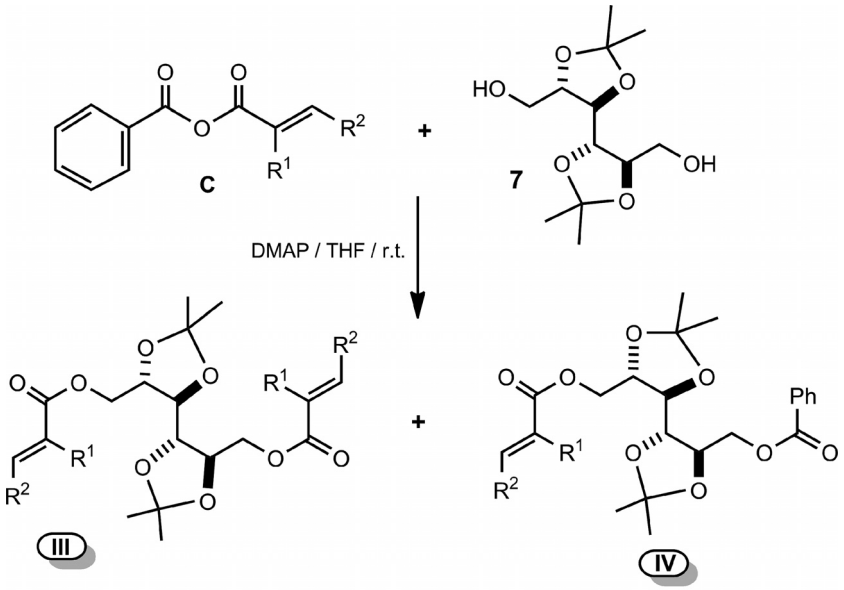


No.	R^1	R^2
9	H	H
10	Me	H
11	Me	Ph
12	Ph	Ph

R^1	R^2	Yield (%)	Type **I** no. (%)[a]	Type **II** n. (%)[a]
H	H	90	**13** (90)	**17** (10)
Me	H	95	**14** (71)	**18** (29)
Me	Ph	61	**15** (51)	**19** (49)
Ph	Ph	60	**16** (50)	**20** (50)

[a] Ratio determined by GC-MS.

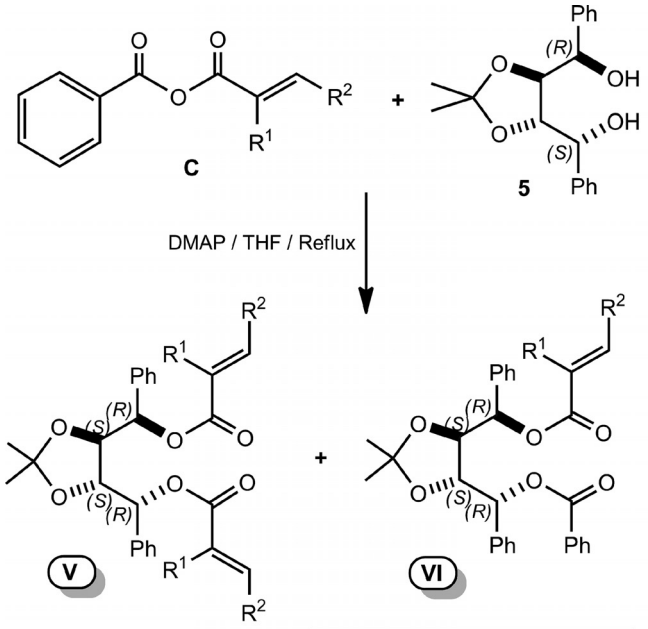
Scheme 3. Yamaguchi–SantaLucia esterification of diol **3**.



R^1	R^2	Yield (%)	Type **III** No. (%)[a]	Type **IV** No. (%)[a]
H	H	100	**21** (100)	–
Me	H	90	**22** (92)	**25** (8)
Me	Ph	51	**23** (53)	**26** (47)
Ph	Ph	45	**24** (49)	**27** (51)

[a] Ratio determined by GC-MS.

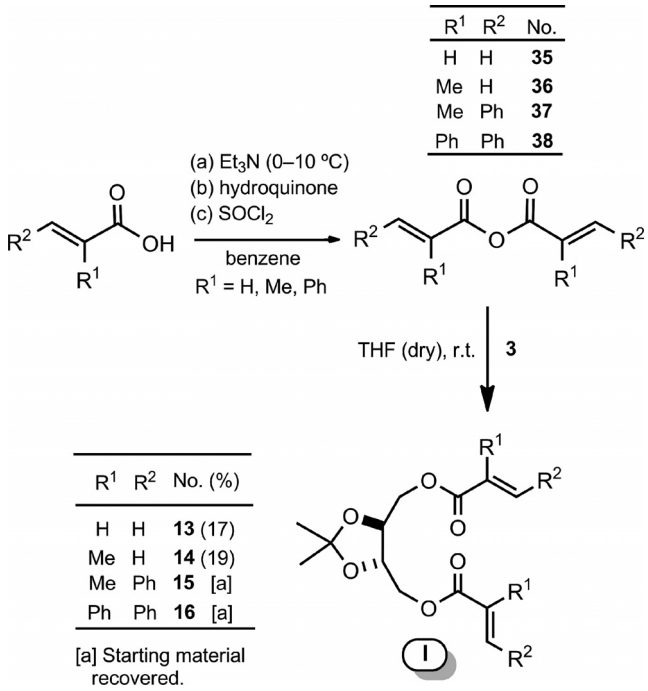
Scheme 4. Yamaguchi–SantaLucía esterification of diol **7**.



R^1	R^2	Yield (%)	Type **V** No. (%)[a]	Type **VI** No. (%)[a]
H	H	100	**28** (100)	–
Me	H	92	**29** (68)	**32** (32)
Me	Ph	53	**30** (51)	**33** (49)
Ph	Ph	49	**31** (49)	**34** (51)

[a] Ratio determined by GC-MS.

Scheme 5. Yamaguchi–SantaLucia esterification of secondary diol **5**.



R^1	R^2	No.
H	H	**35**
Me	H	**36**
Me	Ph	**37**
Ph	Ph	**38**

R^1	R^2	No. (%)
H	H	**13** (17)
Me	H	**14** (19)
Me	Ph	**15** [a]
Ph	Ph	**16** [a]

[a] Starting material recovered.

Scheme 6. Synthesis of symmetrical anhydrides.

primary and secondary diols **3** and **5**, respectively, in high yields. Similarly, acylation of diol **8** using this method led to the corresponding symmetrical unsaturated diesters **21**–**24** in excellent yield (Scheme 7).

Unfortunately, we could not prepare the unsaturated diesters of tertiary alcohols **4** or **8** using this method. However, acylation of primary diols **3** and **7**, and secondary diol **5**, with in situ generated symmetric anhydrides in the presence of DMAP proceeded smoothly to give the corresponding symmetrical unsaturated diesters in very high yields. It should be noted that esters **21**–**24**, obtained from primary diol **5**, were easily isolated because they precipitated in the reaction medium.

In a previous paper,[4] we reported the esterification of TADDOL with α,β-unsaturated carboxylic acid chlorides in THF, using *n*BuLi in *n*-hexane to generate the corresponding alkoxides, following the process developed by Kaiser and Woodruff.[11a] The method leads, in all cases, to mixtures of unsaturated di- and mono esters with the former being generated in higher proportion. These mixtures were separated by column chromatography. We later found that by performing the acylation of TADDOL with the same reagents but working at –50 °C and using diethyl ether as solvent, it was possible to obtain higher yields and, more importantly, the desired unsaturated diesters were the only products.[11b] The results obtained using this method for the esterification of diols **3**–**5** are summarized in Scheme 8. The results obtained in the esterifications of diols **7** and **8** are summarized in Scheme 9.

As shown in Scheme 9, we were not able to obtain the type VIII diester from 2,3-diphenylpropenoic acid (**12**) primarily due to solubility problems.

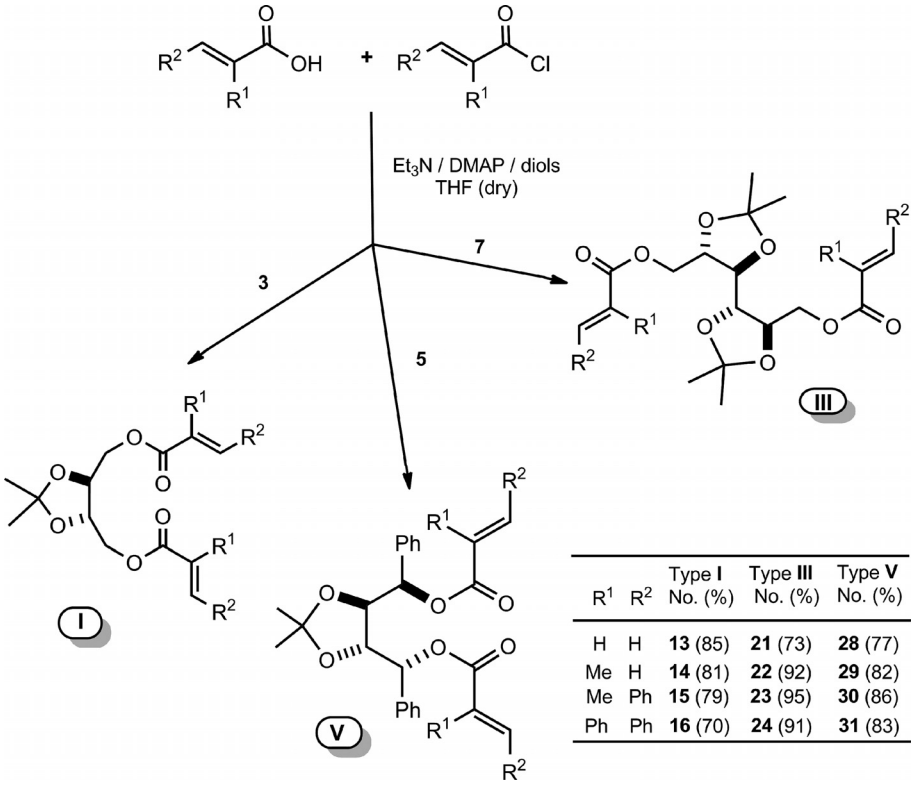
It should be noted that, taking into account that the solutions of *n*BuLi in diethyl ether decompose fairly rapid, the alkoxylation reactions were carried out using freshly prepared solutions of the reagent.

Taking into account the results included in Schemes 8 and 9, this method enables the synthesis of the desired symmetrical diesters of the diols derived from (+)-tartaric acid (diesters of types I, V, and VII) and galactaric acid (type III and VIII diesters) with very good to excellent yields.

A summary of the yields obtained using the three methods studied is enclosed in Table 1. For comparison purposes, some results obtained previously in the esterification with unsaturated acid chlorides of TADDOL (**4**) in THF at 0 °C using BuLi in *n*-hexane to generate the alkoxides have also been included.[4,11b]

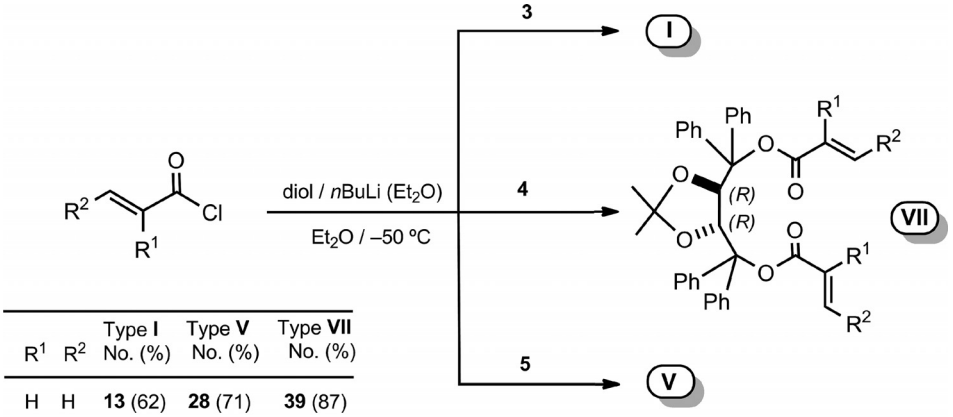
As shown in Table 1, Method B, Yamaguchi–Santa Lucía's protocol, is only useful for the synthesis of diacrylates **21** and **28** derived from diols **7** and **5**, respectively, because the reactions with the other substrates lead, in all cases, to mixtures of symmetrical and unsymmetrical diesters, from which we were not able to separate the desired symmetrical unsaturated diesters in pure form.

Method C (i.e., acylation of the diol with the anhydride of the unsaturated acid; Table 1) was found to be an excellent method for the synthesis of unsaturated diesters of primary and secondary diols. Unfortunately, the approach



R^1	R^2	Type **I** No. (%)	Type **III** No. (%)	Type **V** No. (%)
H	H	**13** (85)	**21** (73)	**28** (77)
Me	H	**14** (81)	**22** (92)	**29** (82)
Me	Ph	**15** (79)	**23** (95)	**30** (86)
Ph	Ph	**16** (70)	**24** (91)	**31** (83)

Scheme 7. Synthesis of unsaturated diesters of diols **3**, **5**, and **7**.

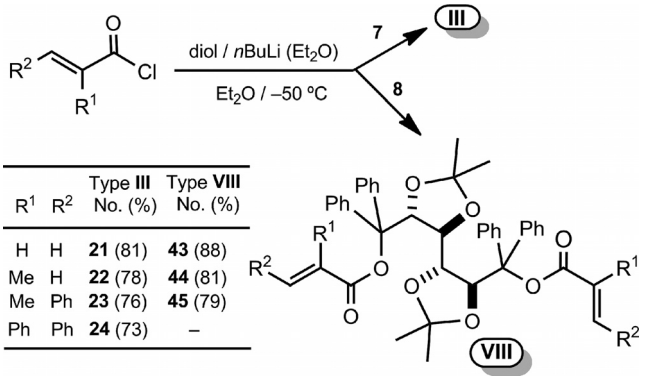


R^1	R^2	Type **I** No. (%)	Type **V** No. (%)	Type **VII** No. (%)
H	H	**13** (62)	**28** (71)	**39** (87)
Me	H	**14** (67)	**29** (77)	**40** (82)
Me	Ph	**15** (76)	**30** (79)	**41** (86)
Ph	Ph	**16** (73)	**31** (75)	**42** (88)

Scheme 8. Synthesis of symmetrical unsaturated diesters of diols **3**–**5**.

could not be applied to the synthesis of diesters derived from tertiary diols, probably for steric reasons. The average yield of the 12 cases studied was of 83%.

On the other hand, Method D (Kaiser and Woodruff protocol; i.e., preparation of the alkoxides at –50 °C using freshly prepared solutions of *n*BuLi in diethyl ether followed by addition of the unsaturated acids chlorides) was found to be the best of the three methods tested. Thus, as shown in Table 1, this method was applied with success to the synthesis of the saturated diesters derived from primary (**3** and **7**), secondary (**5**), and tertiary diols (**4** and **8**). The average yield of the 19 cases studied was 78%.



R^1	R^2	Type III No. (%)	Type VIII No. (%)
H	H	**21** (81)	**43** (88)
Me	H	**22** (78)	**44** (81)
Me	Ph	**23** (76)	**45** (79)
Ph	Ph	**24** (73)	–

Scheme 9. Synthesis of symmetrical unsaturated diesters of diols **7** and **8**.

Table 1. Synthesis of di-unsaturated esters of diols **3**–**5**, **7**, and **8**.[a]

Compd.	Method A[b] Yield [%]	Method B[d] Yield [%]	Method C[e] Yield [%]	Method D[f] Yield [%]
13	62	81	85	62
14	–	67	81	67
15	67	31	79	76
16	–	30	70	73
21	–	100	73	81
22		83	92	78
23	–	27	95	76
24	–	18	91	73
28	58	100	77	71
29	59	62	82	77
30	–	27	86	79
31	–	24	83	75
39	70[c]	–	–	87
40	74[c]	–	–	82
41	57[c]	–	–	86
42	73[c]	–	–	88
43	–	–	–	88
44	–	–	–	81
45	–	–	–	79

[a] Only the symmetrical unsaturated diesters are included. [b] Reaction conditions: diol, unsaturated acid chloride, *n*BuLi (*n*-hexane), THF. [c] See ref.[4]. [d] Yamaguchi–SantaLucia's method; most compounds could not be isolated pure; yields from the mass spectra. [e] Reaction conditions: anhydride, Et_3N, diol, THF. [f] Reaction conditions: diol in Et_2O, *n*BuLi (Et_2O), unsaturated acid chloride.

We have also tested the esterification of the primary and secondary diols with acids **9**–**12** using the *N*,*N*-dicyclohexylcarbodiimide (DCC)/4-(dimethylamino)pyridine (DMAP) method.[12] The yields obtained were poor, and with tertiary diols **4** and **8**, no esterification products were obtained.

The same results were obtained when we attempted the esterification of diols **3**–**5**, **7**, and **8** using Staudinger's reaction with benzylazide.[13]

Conclusions

To establish a general and convenient protocol for the synthesis of unsaturated diesters of diols derived from dimethyl (*R*,*R*)-tartrate (**1**) and galactaric acid (**2**), three methods of esterification were studied. (1) Yamaguchi–SantaLucía's method (Method B, Table 1), i.e., the reaction of mixed anhydrides, obtained from α,β-unsaturated acids and benzoyl chloride, with diols **3**, **5**, and **7**. Although the symmetrical diacrylates of diols **5** and **7** were obtained quantitatively, in all the other cases the reactions led to mixtures of symmetrical and unsymmetrical diesters, which were difficult to separate. Furthermore, the mixed anhydrides do not react with tertiary diols **4** and **8**. Therefore, from a practical point of view, this method is not convenient in general for the synthesis of unsaturated symmetrical diesters. (2) Acylation of the diol with the anhydride of the unsaturated acid, Method **C**, was found to be an excellent method for the synthesis of the desired symmetrical unsaturated diesters of primary and secondary diols. However, also in this case, the anhydrides do not react with tertiary diols **4** or **8**. (3) Finally, the preparation of the alkoxides with *n*BuLi in diethyl ether followed by addition of the unsaturated acid chloride, was found to be the best of the three methods tested. Using this method, reactions of the lithium alkoxides of diols **3**–**5**, **7**, and **8** with the unsaturated acid chlorides led, in all cases, to the corresponding unsaturated diesters in very good yields.

Experimental Section

General: Reactions were monitored by thin-layer chromatography on silica gel plates (60F-254) visualized under UV light and/or using 5% phosphomolybdic acid in ethanol. Column chromatography was performed over silica gel 60 (70–230 mesh). NMR spectra were recorded at 25 °C with a Bruker Avance 300 multinuclear instrument, using $CDCl_3$ as solvent; chemical shifts (δ) are reported in ppm with respect to TMS, ^1H and ^{13}C. IR spectra were recorded with an FTIR Nicolet Nexus 470/670/870 spectrophotometer. Mass spectra were obtained with a Finnigan MAT Incos 50 Galaxy System (DIP-MS) (EI) or a Finnigan MAT 900 (ESI) spectrometer; high-resolution mass spectra were recorded with a Finnigan HSQ-30 (HR-EIMS) or on a Finnigan MAT 900 (HR-ESI-MS) instrument. The method of ionization is given in parentheses. Specific rotations were measured with a Polar L-μP, IBZ Messtechnik instrument. Elemental analyses (C, H) were performed with a Carlo–Erba Instrument. The melting points were determined with a Kofler hot stage apparatus and are not corrected.

All reactions were carried out under an argon atmosphere. Solvents were dried and distilled in accordance with standard procedure. All the solvents and reagents were commercially available and of analytical grade. Diols **3**,[5] **4**,[6] **5**,[7] and **7**,[8] were prepared by know procedures. Compounds **39**–**42** have been reported previously.[4] From a preparative point of view, it should be mentioned that secondary diol **5** was obtained stereoselectively by reduction of the corresponding diketone with $LiAlH_4$. Purification of the resulting diastereomeric mixture of diols afforded pure **5** after column chromatography.

{2,2,2′,2′-Tetramethyl[4,4′-bi(1,3-dioxolane)]-5,5′-diyl}bis(diphenylmethanol) (8): Under an argon atmosphere, magnesium turnings (8.01 g, 0.33 mol) and some iodine crystals were introduced into a dry flask, then 31.4 mL of a solution of bromobenzene (46.92 g, 0.30 mol) in anhydrous THF (120 mL) was added. As soon as the reaction started, the remainder of the THF solution was added at such a rate that gentle reflux was maintained. After complete addition, the reaction was heated to reflux for 1 h by heating with an

oil bath. Finally, the reaction mixture was allowed to cool to room temperature. To the Grignard solution was added with stirring and cooling by an ice bath, a solution of diethyl (2,3:4,5-di-*O*-isopropylidene)galactarate (20.78 g, 0.06 mol) in anhydrous THF (160 mL). The reaction mixture was heated at reflux for 2 h and then cooled to room temperature. Aqueous saturated ammonium chloride solution (500 mL) was carefully added, cooling the mixture with an ice bath, whereupon diol **8** precipitated from the clear solution. Filtration gave the product (33 g, 0.058 mol, 97%) as a white solid; m.p. 233–235 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (s, 6 H), 1.41 (s, 6 H), 3.86 (d, J = 5.1 Hz, 2 H), 3.90 (s, 2 H), 4.63 (d, J = 5.1 Hz, 2 H), 7.26–7.52 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.8, 78.3, 82.7, 110.1, 127.1, 127.2, 127.3, 127.6, 127.8, 128.0, 144.2, 144.3 ppm. FTIR (film): $\tilde{\nu}$ = 3605 (w), 3560 (s), 3081 (w), 3052 (m), 2971 (w), 1885 (w), 1820 (w), 1700 (w), 1598 (m), 1512 (m), 1490 (w), 1453 (m), 1395 (m), 1350 (m), 1160 (m), 1110 (s), 1049 (s), 930 (m), 897 (m), 740 (s), 697 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{36}H_{38}O_6Na$ [M + Na]$^+$ 589.2566; found 589.2561.

Synthesis of Unsaturated Diesters of Diols 3, 4 and 7 (Method A). Typical Procedure for [(4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]-bismethanolyl Diacrylate (13): Under argon, a solution of **3** (1.00 g, 6.17 mmol) in anhydrous THF (27 mL) was cooled to 0 °C and then a solution of *n*BuLi (1.5 M in *n*-hexane, 10 mL, 15 mmol) was added slowly by using a syringe. The mixture was stirred at room temp. for 30 min and cooled to 0 °C, and acryloyl chloride (1.5 mL, 18.5 mmol) was added slowly. A white precipitate (LiCl) formed immediately. The mixture was heated to reflux for 1 h and then stirred at room temp. overnight. The reaction was quenched by the addition of aqueous saturated sodium hydrogen carbonate (90 mL), the organic layer was separated and the aqueous layer was extracted with Et_2O (3× 30 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), and then dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel 60; hexane/EtOAc, 90:10) to give **13** (1.03 g, 3.81 mmol, 62%) as a colorless oil. $[\alpha]_D^{25}$ = –9.95 (c = 0.51, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 3 H); 1.35 (s, 3 H); 4.04–4.33 (m, 6 H); 5.76–5.81 (m, J = 10.4, 1.6 Hz, 2 H), 6.02–6.12 (m, J = 10.4, 17.3 Hz, 2 H), 6.32–6.39 (m, J = 17.3, 1.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.6, 63.5, 75.7, 109.9, 127.6, 131.0, 165.2 ppm. FTIR (Film): $\tilde{\nu}$ = 1165 (m), 1075 (m), 884 (m), 751 (s), 705 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{18}O_6Na$ [M + Na]$^+$ 293.1001; found 293.1007.

Synthesis of Unsaturated Diesters of Diols 3, 5 and 7 (Method B). Typical Procedure for (1*R*,1′*R*)-[(4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]bis(phenylmethanolyl) Bisacrylate (28): Under argon, acrylic acid (0.21 mL, 3 mmol), benzoyl chloride (0.35 mL, 3 mmol) and diol **5** (0.47 g, 1.5 mmol) were suspended in anhydrous THF (15 mL). Triethylamine (1.67 mL, 12 mmol) was added slowly followed by DMAP (0.046 g, 25 mol-%) and the reaction mixture was stirred at 65 °C for 1 h (reaction monitored by TLC). The reaction was quenched by the addition of 10% hydrochloric acid (50 mL) and the solution was extracted with ethyl acetate (2× 60 mL). The combined organic extracts were washed with saturated sodium hydrogen carbonate (2× 50 mL), and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (alumina; hexane/EtOAc, 92:8) to give **28** (0.57 g, 1.35 mmol, 90%) as a white solid; m.p. 88–90 °C; $[\alpha]_D^{25}$ = –6.8 (c = 0.47, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 3 H), 1.35 (s, 3 H), 4.11–4.14 (m, 2 H), 5.40–5.43 (m, 2 H), 5.67 (dd, J = 10.4 Hz, 2 H), 6.01 (dd, J = 10.4, 17.3 Hz, 2 H), 6.30 (dd, J = 17.3 Hz, 2 H), 7.06–7.19 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.3, 75.2, 79.4, 110.9, 127.2, 128.0, 128.4, 131.1, 136.4, 164.7 ppm. FTIR (KBr): $\tilde{\nu}$ = 3057 (w), 3030 (w), 2985 (m), 2940 (w), 1715 (s), 1640 (m), 1615 (w), 1490 (w), 1455 (w), 1294 (w), 1155 (m), 760 (w), 701 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{26}O_6Na$ [M + Na]$^+$ 445.1627; found 445.1622.

Synthesis of Unsaturated Diesters of Diols 3, 5 and 7 (Method C). Typical Procedure for [(4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]-bismethyl Bis(2-methylacrylate) (14): Under argon, methacrylic acid (0.25 mL, 3 mmol), triethylamine (1.67 mL, 12 mmol), methacryloyl chloride (0.29 mL, 3 mmol), DMAP (0.046 g, 25 mol-%) and diol **3** (0.24 g, 1.5 mmol) were suspended in anhydrous THF (15 mL). The reaction mixture was stirred at r.t for 1 h (reaction monitored by TLC). The reaction was quenched by the addition of 10% hydrochloric acid (50 mL). The solution was extracted with ethyl acetate (2× 60 mL), and the combined organic extracts were washed with saturated sodium hydrogen carbonate (2× 50 mL), dried with anhydrous magnesium sulfate, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel 60; hexane/EtOAc, 90:10) to give **14** (0.36 g, 1.2 mmol, 81%) as a colorless oil; $[\alpha]_D^{25}$ = –9.83 (c = 0.58, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (s, 6 H), 1.96 (dd, 6 H), 4.14–4.16 (m, 2 H), 4.26–4.39 (m, 4 H), 5.60 (dd, J = 1.5 Hz, 2 H), 6.15 (dd, J = 1.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2, 26.9, 63.8, 75.9, 110.1, 126.0, 135.8, 166.9 ppm. FTIR (Film): $\tilde{\nu}$ = 3025 (m), 2985 (w), 2917 (m), 1718 (s), 1631 (m), 1493 (m), 1410 (m), 1169 (m), 1074 (m), 803 (m), 748 (s), 608 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{22}O_6Na$ [M + Na]$^+$ 321.1314; found 321.1319.

Synthesis of Unsaturated Diesters of Diols 3, 4, 5, 7 and 8 (Method D). Typical Procedure for [(4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]bis(diphenylmethanolyl) Diacrylate (39): Under argon, a solution of **4** (1.50 g, 3.21 mmol) in anhydrous Et_2O (10 mL) was cooled to –50 °C, then a solution of *n*BuLi (1.3 M in Et_2O, 5.9 mL, 7.70 mmol) was added slowly by using a syringe. The mixture was kept at –50 °C for 1 h and subsequently acryloyl chloride (0.8 mL, 9.63 mmol) was added slowly. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched by the addition of aqueous saturated sodium hydrogen carbonate (25 mL), the organic layer was separated, and the aqueous layer was extracted with Et_2O (3× 25 mL). The combined organic extracts were washed with water (15 mL) and brine (20 mL), and then dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel 60; hexane/Et_2O, 70:30) to give **39** (1.60 g, 2.79 mmol, 87%) as a white solid. The m.p. and spectroscopic characteristics were identical to those reported previously for this compound.[4]

(2*E*,2′*E*)-[(4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]bismethanolyl Bis(2-Methyl-3-phenylacrylate) (15): White solid; m.p. 45–48 °C; $[\alpha]_D^{25}$ = –6.0 (c = 0.50, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 6 H), 2.14 (s, 6 H), 4.21–4.32 (m, 2 H), 4.41–4.53 (m, 4 H), 7.31–7.40 (m, 10 H), 7.70–7.83 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 27.0, 64.2, 76.2, 110.2, 127.8, 128.3, 128.4, 129.6, 135.7, 139.7, 168.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 3092 (w), 3072 (w), 2990 (m), 2945 (w), 1703 (s), 1580 (m), 1454 (m), 1370 (m), 1254 (s), 1111 (s), 771 (m), 698 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{27}H_{30}O_6Na$ [M + Na]$^+$ 450.2042; found 450.2035.

(2*E*,2′*E*)-[(4*S*,5*S*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]bismethanolyl Bis(2,3-diphenylacrylate) (16): White solid; m.p. 113–114 °C; $[\alpha]_D^{25}$ = 94 (c = 0.17, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 6 H), 4.03 (s, 2 H), 4.21–4.33 (m, 4 H), 7.10–7.42 (m, 20 H), 7.91

(s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.7, 63.9, 75.6, 109.8, 127.9, 128.2, 128.7, 129.2, 129.6, 130.7, 132.0, 134.4, 135.6, 141.0, 167.3 ppm. FTIR (KBr): $\tilde{\nu}$ = 3052 (m), 2921 (w), 2852 (w), 1708 (s), 1642 (m), 1389 (s), 1356 (s), 1245 (m), 1172 (m), 755 (m), 714 (s), 694 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{37}H_{34}O_6Na$ [M + Na]$^+$ 597.2253; found 597.2259.

{(4*R*,4′*S*,5*S*,5′*R*)-2,2,2′,2′-Tetramethyl-[4,4′-bi(1,3-dioxolane)]-5,5′-diyl}bis(methylene) Diacrylate (21): White solid; m.p. 79–81 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31 (s, 6 H), 1.34 (s, 6 H), 3.74–3.75 (m, 2 H), 4.12–4.17 (m, 4 H), 4.42–4.45 (m,2 H), 5.79 (dd, *J* = 10.7, 1.4 Hz, 2 H), 6.06–6.15 (m, *J* = 10.7 Hz, 2 H), 6.36–6.41 (dd, *J* = 10.7, 1.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.9, 64.3, 78.3, 78.7, 110.5, 128.1, 131.2, 165.8 ppm. FTIR (KBr): $\tilde{\nu}$ = 3030 (m), 2990 (w), 2931 (m), 1725 (s), 1628 (m), 1480 (m), 1400 (m), 1162 (m), 1065 (m), 881 (m), 745 (s), 699 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{26}O_8Na$ [M + Na]$^+$ 393.1526; found 393.1531.

{(4*R*,4′*S*,5*S*,5′*R*)-2,2,2′,2′-Tetramethyl-[4,4′-bi(1,3-dioxolane)]-5,5′-diyl}bis(methylene) Bis(2-methylacrylate) (22): White solid; m.p. 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 6 H), 1.38 (s, 6 H), 1.94 (s, 6 H), 3.83–3.84 (m, 2 H), 4.19–4.24 (m, 4 H), 4.44–4.49 (m, 2 H), 5.58 (s, 2 H), 6.14 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3, 26.9, 64.2, 78.3, 78.7, 110.4, 125.9, 136.0, 167.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 3033 (m), 2984 (w), 2921 (m), 1720 (s), 1630 (m), 1490 (m), 1403 (m), 1168 (m), 1060 (m), 884 (m), 744 (s), 702 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{30}O_8Na$ [M + Na]$^+$ 421.1839; found 421.1844.

(2*E*,2′*E*)-{(4*R*,4′*S*,5*S*,5′*R*)-2,2,2′,2′-Tetramethyl-[4,4′-bi(1,3-dioxolane)]-5,5′-diyl}bis(methylene) Bis(2-methyl-3-phenylacrylate) (23): White solid; m.p. 124–126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 6 H), 1.36 (s, 6 H), 2.06 (s, 6 H), 3.83–3.84 (m, 2 H), 4.24–4.27 (m, 4 H), 4.45–4.48 (m, 2 H), 7.29–7.33 (m, 10 H), 7.67 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 27.1, 64.7, 78.4, 78.9, 110.5, 128.1, 128.4, 129.7, 135.7, 135.8, 139.5, 168.4 ppm. FTIR (KBr): $\tilde{\nu}$ = 3056 (m), 3027 (m), 2982 (s), 2937 (m), 1703 (s), 1576 (w), 1491 (m), 1450 (m), 1258 (m), 1111 (m), 771 (s), 694 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{38}O_8Na$ [M + Na]$^+$ 573.2465; found 573.2470.

(2*E*,2′*E*)-{(4*R*,4′*S*,5*S*,5′*R*)-2,2,2′,2′-Tetramethyl-[4,4′-bi(1,3-dioxolane)]-5,5′-diyl}bis(methylene) Bis(2,3-diphenylacrylate) (24): White solid; m.p. 194–196 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 6 H), 1.33 (s, 6 H), 3.70–3.72 (m, 2 H), 4.15–4.32 (m, 4 H), 4.51–4.56 (m, 2 H), 7.08–7.37 (m, 20 H), 7.90 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.8, 27.0, 64.3, 77.7, 78.6, 110.2, 127.9, 128.2, 128.6, 129.1, 129.8, 130.6, 132.2, 134.5, 135.8, 140.8, 167.5 ppm. FTIR (KBr): $\tilde{\nu}$ = 3064 (w), 3048 (m), 2986 (m), 2904 (m), 1715 (s), 1625 (m), 1597 (w), 1495 (m), 1446 (m), 1245 (s), 1172 (s), 763 (s), 702 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{42}H_{42}O_8Na$ [M + Na]$^+$ 697.2778; found 697.2783.

(1*R*,1′*R*)-[(4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]bis(phenylmethanolyl) Bis(2-methylacrylate) (29): White solid; m.p. 48–50 °C; $[a]_D^{25}$ = –6.1 (*c* = 0.49, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 6 H), 1.79 (s, 6 H), 4.04–4.10 (m, 2 H), 5.35–5.45 (m, 4 H), 6.04–6.08 (m, 2 H), 7.02–7.15 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2, 27.4, 75.2, 79.5, 110.8, 125.9, 127.2, 128.4, 128.4, 136.0, 136.8, 166.0 ppm. FTIR (Film): $\tilde{\nu}$ = 3068 (w), 3035 (w), 2986 (m), 2937 (w), 1719 (s), 1638 (m), 1621 (w), 1499 (w), 1454 (w), 1298 (w), 1160 (m), 763 (w), 702 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{27}H_{30}O_6Na$ [M + Na]$^+$ 473.1940; found 473.1946.

(2*E*,2′*E*)-(1*R*,1′*S*)-[(4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]bis(phenylmethanolyl) Bis(2-methyl-3-phenylacrylate) (30): White solid; m.p. 45–48 °C; $[a]_D^{25}$ = –6.0 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.5 (s, 6 H), 2.1 (s, 6 H), 4.2–4.3 (m, 2 H), 4.4–4.5 (m, 4 H), 7.3–7.4 (m, 10 H), 7.7–7.8 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 27.6, 75.6, 79.7, 111.1, 127.4, 128.2, 128.3, 128.4, 128.5, 128.6, 129.7, 135.78, 137.0, 167.5 ppm. FTIR (KBr): $\tilde{\nu}$ = 3092 (w), 3072 (w), 2990 (m), 2945 (w), 1703 (s), 1580 (m), 1454 (m), 1370 (m), 1254 (s), 1111 (s), 771 (m), 698 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{39}H_{38}O_6Na$ [M + Na]$^+$ 625.2566; found 625.2570.

(2*E*,2′*E*)-(1*R*,1′*R*)-[(4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl]-bis(phenylmethanolyl) Bis(2,3-diphenylacrylate) (31): White solid; m.p. 112–114 °C. $[a]_D^{25}$ = +9.5 (*c* = 0.85, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (s, 6 H), 4.05 (s, 2 H), 5.51 (s, 2 H), 7.13–7.31 (m, 30 H), 7.70–7.84 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.0, 75.5, 79.1, 110.6, 127.3, 127.8, 128.2, 128.4, 128.7, 129.1, 129.8, 130. 27, 132.3, 134.6, 135.8, 137.0, 141.0, 166.7 ppm. FTIR (KBr): $\tilde{\nu}$ = 3060 (w), 3027 (w), 2962 (m), 2921 (m), 1716 (s), 1495 (m), 1450 (m), 1238 (s), 1168 (s), 800 (w), 760 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{49}H_{42}O_6Na$ [M + Na]$^+$ 749.2879; found 749.2885.

{(4*S*,4′*R*,5*R*,5′*S*)-2,2,2′,2′-Tetramethyl-[4,4′-bi(1,3-dioxolane)]-5,5′-diyl}bis(diphenylmethanolyl) Diacrylate (43): White solid; m.p. 180–182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 12 H), 4.08 (d, 2 H), 5.74–5.86 (m, 4 H), 6.11–6.17 (m, 2 H), 6.25–6.35 (m, 2 H), 7.27–7.53 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1, 27.5, 79.1, 86.4, 109.8, 126.8, 127.4, 128.1, 128.4, 129.2, 130.1, 130.2, 140.4, 143.5, 163.9 ppm. FTIR (KBr): $\tilde{\nu}$ = 3060 (w), 3031 (w), 2974 (m), 2937 (m), 1744 (s), 1634 (m), 1495 (m), 1450 (m), 1266 (m), 1168 (s), 759 (s), 702 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{42}H_{42}O_8Na$ [M + Na]$^+$ 697.2778; found 697.2785.

{(4*S*,4′*R*,5*R*,5′*S*)-2,2,2′,2′-Tetramethyl-[4,4′-bi(1,3-dioxolane)]-5,5′-diyl}bis(diphenylmethanolyl) Bis(2-methylacrylate) (44): White solid; m.p. 191–193 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 6 H), 1.43 (s, 6 H), 1.98 (s, 6 H), 4.13 (m, 2 H), 5.52 (m, 2 H), 5.75 (m, 2 H), 6.13 (s, 2 H), 7.10–7.60 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8, 26.1, 27.6, 78.9, 79.4, 86.5, 110.0, 125.3, 126.9, 127.4, 127.8, 128.4, 129.4, 138.3, 141.0, 144.0, 165.4 ppm. FTIR (KBr): $\tilde{\nu}$ = 3064 (w), 3027 (w), 2982 (m), 2941 (w), 1728 (s), 1634 (m), 1495 (m), 1450 (m), 1249 (m), 1151 (s), 767 (s), 698 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{44}H_{46}O_8Na$ [M + Na]$^+$ 725.3091; found 725.3098.

(2*E*,2′*E*)-{(4*S*,4′*R*,5*R*,5′*S*)-2,2,2′,2′-Tetramethyl-[4,4′-bi(1,3-dioxolane)]-5,5′-diyl}bis(diphenylmethanolyl) Bis(2-methyl-3-phenylacrylate) (45): White solid; m.p. 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (s, 6 H), 1.28 (s, 6 H), 2.14 (s, 6 H), 3.74 (d, 2 H), 4.49 (d, 2 H), 7.20–7.36 (m, 40 H), 7.75 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 26.8, 78.3, 82.8, 110.0, 127.1, 127.3, 127.6, 127.8, 128.0, 128.6, 129.2, 130.0, 135.1, 142.7, 144.2, 144.3, 164.9 ppm. FTIR (KBr): $\tilde{\nu}$ = 3051 (w), 3021 (w), 2960 (m), 2932 (w), 1721 (s), 1625 (m), 1491 (m), 1440 (m), 1130 (m), 1055 (s), 751 (s), 698 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{56}H_{54}O_8Na$ [M + Na]$^+$ 877.3717; found 877.3723.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of the new compounds.

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