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Synthesis of organotin derivatives of optically active eleven-membered macrodiolides

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ABSTRACT

The synthesis and the results obtained in the hydrostannation of eight new TADDOL diacrylates and methacrylates are reported. The addition of triorganotin hydrides, R_3SnH, **12**–**14** (R = *n*Bu, neophyl, Ph, respectively) to diesters **6**–**11** containing different combinations of substituents at the C-2 carbon of the dioxolane ring, led to macrocyclization products in all cases. The cyclohydrostannation of diacrylate **10** proceeded with complete diastereoselectivity. The cyclohydrostannation of diesters **33** and **34** with hydrides **12** and **14** in all cases only afforded one stannylated macrocycle.

1. Introduction

Macrolides, i.e., macrolactones containing more than 8 members, are found in natural products obtained from bacteria, insects, and plants. Taking into account their biological and medicinal activity, a number of synthetic strategies and methodologies have been developed for macrolide synthesis.[1] In many of them, the crucial ring-making reactions proceed with good to excellent yields.[2] However, because most of these syntheses involve many steps, the global yields are very low.[3] We have recently reported a new method which enables the synthesis of 11-membered macrodiolides starting from TADDOL unsaturated diesters via a tandem cyclohydrostannation reaction using triorganotin hydrides and diorganotin chlorohydrides. The new macrocycles were obtained in high overall yields and with very good diastereoselectivy.[4]

Herein we report the results obtained in studies carried out in order to determine the effect on the stereoselectivity of the cyclohydrostannation of TADDOL dipropenoates and di-2-methylpropenoates by (a) varying the substituents attached to carbon C-2 of the dioxolane ring, and (b) replacing the TADDOL four phenyl groups with four bulkier naphthyl groups.

2. Results and discussion

In order to carry out our studies, we had to synthesize a series of unsaturated diesters. The new diesters **6**–**11** were obtained via acylation of known diols **1**–**3**, as shown in Scheme 1.[5] It is important to note that because diols **1** and **2** consist of mixtures of epimers, the corresponding unsaturated diesters **6** and **9** will also be mixtures of the corresponding epimers.

Diols **1**–**3** were esterified following a modified version of Kaiser and Woodruff's method,[6] by preparing the corresponding alkoxides using a freshly prepared solution of *n*-BuLi in dry diethyl ether at −50 °C, followed by the addition of the unsaturated acids chlorides. As shown in Scheme 1, the new unsaturated diesters were obtained in yields similar to those obtained previously in the synthesis of TADDOL unsaturated diesters.[7] The physical characteristics of the new unsaturated diesters including ^1H and ^{13}C NMR spectra are reported in Section 4.

The effect of the substituents attached to C-2 of the dioxolane ring on the stereoselectivity of the cyclohydrostannation reactions, was studied by analysis of the products obtained in the addition of tri-*n*-butyl-**12**, trineophyl-**13**, and triphenyltin **14** hydrides to the unsaturated diesters **6**–**11** under free radical conditions (Scheme 2).

The reactions were performed by adding a solution of the triorganotin hydride in toluene to a mixture of the unsaturated diester and a catalytic amount of azobis(isobutyronitrile) (AIBN) in the same solvent. The hydrostannations were carried out under argon, at 75 °C, and with stirring. The reactions were followed by IR (observing the disappearance of the Sn–H absorption) and ^1H NMR spectroscopy (observing olefin disappearance and product formation). In all cases, the optimum times of the reactions and hydride/olefin ratios required for a quantitative yield (with respect to olefin) were determined.

As shown in Scheme 2, these radical additions could in principle lead to products of diadicion (**II**) and of cyclization (**III**). However, can be seen below, the hydrostannations led in all cases to the products of cyclohydrostannation (**III**) exclusively.

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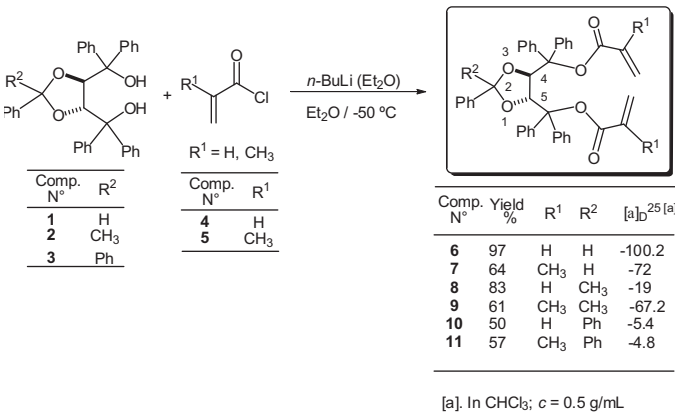
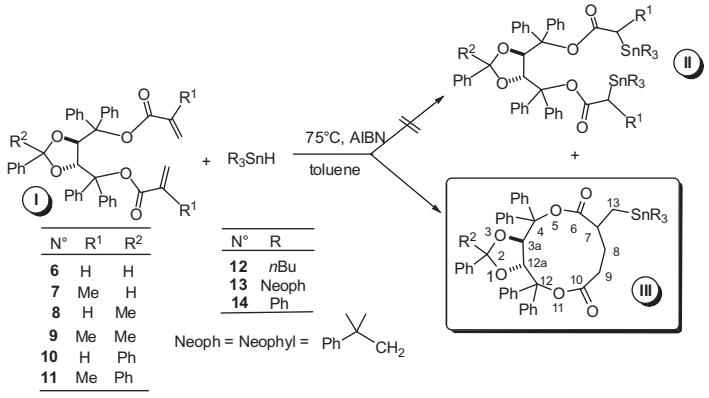


Scheme 1. Synthesis of diesters **6**–**11** at −50 °C.

The results obtained in the hydrostannation of diesters **6** and **7** are summarized in Table 1. Since with these substrates, the cyclohydrostannation led to the creation of one or two new stereogenic centers, a maximum of two or four diastereomers, respectively, are expected. However, taking into account that the starting diesters consist of mixtures of epimers, a maximum of four diastereomers in the case of diester **6**, and of eight diastereomers in the case of **7** should be expected.

The ^{119}Sn NMR spectroscopic analysis of the crude products obtained in the additions of triorganotin hydrides **12**–**14** to diester **6**, showed that in the case of the hydrostannations with hydride **14**, the expected four ^{119}Sn signals were present. On the other hand, the addition of hydride **12** to ester **6** (Table 1) led to a mixture of just three diastereomers We consider it possible that in this case there might be a superposition of signals. In the case of the hydrostannation of **6** with trineophyltin hydride **13**, the ^{119}Sn NMR spectrum showed that a mixture of only two diastereomers was formed. The formation of just two diastereomers could be explained by taking into account that the free radical additions of hydride **13** are slower and thus are more stereoselective than those of organotin hydrides **12** and **14**.[8] As shown in Table 1, the diastereomeric excess (*de*) obtained in the addition of trineophyltin hydride to diester **6** was 36%. It is noteworthy that in the mixtures obtained in the



Scheme 2. Free radical hydrostannation of unsaturated diesters **6**–**11**.

Table 1
Triorganotin hydrides addition to unsaturated diesters **6** and **7**

Ester N°	R_3SnH R	^{119}Sn[a] (δ, ppm)		*D* (%)[b]		Time (h)	Yield (%)[c]	Prod. N°
6	*n*Bu	−9.2		3		4	50	**15ad**
		−9.4		6				
		−12.2		3				
		−12.9		48				
	Neophyl	−41		32		4	60	**16ab**
		−42		68				
	Ph	−101		8		4	30[d]	**17ad**
		−101.2		13				
		−104		35				
		−105		44				
7	*n*-Bu	−15	−22.9	21	8	2	77	**18ah**
		−20.6	−24.8	24	5			
		−20.8	−24.9	28	7			
		−22		7				
	Neophyl	−44.9	−50.0	24	3	2	81	**19ah**
		−45.1	−50.2	22	3			
		−46.4	−52.9	3	18			
		−46.5	−53.0	4	23			
	Ph	−110	−116	27	22	2	83	**20ah**
		−114	−117	12	2			
		−114.3	−117.1	13	3			
		−115		21				

[a] In $CDCl_3$; chemical shifts in ppm with respect to Me_4Sn.
[b] *D* = % of diastereomer in the mixture from the ^{119}Sn NMR spectra of the crude products.
[c] After column chromatography purification.
[d] Most of the diastereomers could not be separated from the hexaphenyldistannane formed in the reaction.

additions of organotin hydrides **12** and **14**, two diastereomers were always present in higher proportion.

The yields of the mixtures of diastereomers obtained in the cyclohydrostannations with hydrides **12** and **13** were reasonable: 50% and 60% respectively. With triphenyltin hydride **14**, we were able to separate only 30% of the diastereomers from the crude mixture of reaction, which also contained hexaphenyldistannane.

As shown in Table 1, the ^{119}Sn NMR spectroscopic analysis of the crude products obtained in the addition of triorganotin hydrides **12**–**14** to diester **7** indicates that for the hydrostannations with triorganotin hydrides **12** and **14**, seven diastereomers were obtained. We considered it possible that this might be due to peak superposition. Only in the addition of trineophyltin hydride **13** were the expected eight diastereomers obtained. The reactions were faster than the hydrostannations of unsaturated diester **6**, and the yields were higher between 77% and 83%.

The structures of the products were established by taking into account the ^{1}H and ^{13}C NMR characteristics of the mixtures **15**–**32**. We assigned the ^{13}C NMR chemical shifts through the analysis of the multiplicity of the signals by means of DEPT experiments and by taking into account the magnitude of $^{n}J(^{13}C,^{119}Sn)$ coupling constants.[9] The use of some key signals in the ^{13}C NMR spectra enabled us to establish that these mixtures consisted exclusively of the products of macrocyclization. Thus, the formation of the cycles gives rise to the existence of two carbonyl signals (C-6 and C-10), with one of them showing $^{3}J(^{119}Sn,^{13}C)$ coupling constants (C-6). Other key signals include those corresponding to the carbons resulting from the ring closure (C-7). These signals show second order $^{2}J(^{119}Sn,^{13}C)$ coupling constants, and the DEPT experiments indicate that these carbons are either tertiary, when the starting diesters are **6**, **8**, and **10**, or quaternary when the starting diesters are **7**, **9**, and **11**.

We next carried out the free radical hydrostannation of the unsaturated diesters **8** and **9** with the triorganotin hydrides **12**–**14**. In Table 2 the results of these additions are shown. In Table 2, the ^{119}Sn NMR spectra of the crude products obtained in the reactions of ester **8** with triorganotin hydrides **12** and **14** indicated the formation of the mixtures of four diastereomers. In the case of the addition of trineophyltin hydride **13**, where only three diastereomers were detected, we considered it possible that there might also be a superposition of ^{119}Sn NMR signals. Here again, the mixtures of adducts **21ad** and **23ad** contained two diastereomers in higher proportions, 91% and 76%, respectively. In the addition of trineophyltin hydride **13**, one of the three peaks shown in the ^{119}Sn NMR spectrum has an area equivalent to 89% of the total. This result supports our assumption that the superposition of signals might explain the lower number of diastereomers detected.

On the other hand, while the additions of hydrides **12** and **13** to diester **9** led to mixtures of the corresponding eight diastereomers, **24ah** and **25ah**, the addition of triphenyltin hydride **14** afforded a mixture of only four diastereomers. The latter might be connected with the fact that hydride **14** would make a faster hydrogen transfer to the macrocyclic radical resulting from the ring closure (radical **B** in Scheme 3) than hydrides **12** and **13**. Again, in the mixtures of products from the hydrostannations of unsaturated diester **9** with triorganotin hydrides **12**–**14**, the formation of two of the four diastereomers in a higher proportion was observed obtained: 68%, 65%, and 68% respectively. The yields were in the range 50–70%.

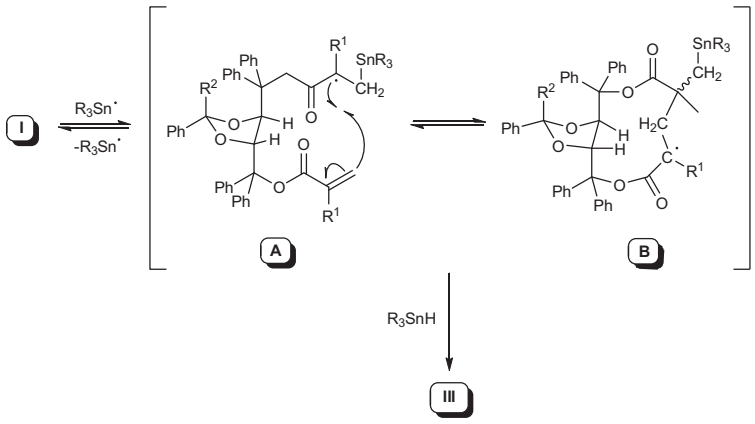
The results obtained in the additions of hydrides **12**–**14** to diesters **10** and **11** are summarized in Table 3. As shown in Table 3, the hydrostannations of diester **10** with the three hydrides led to the corresponding adducts with complete stereoselectivity. Unfortunately, in the case of the addition of triphenyltin hydride **14**, we were unable to completely separate the diastereomer **29** from the hexaphenyldistannane formed in the reaction. The additions to unsaturated diester **11** led to mixtures of the corresponding four diastereomers that, again, we could not separate. Macrodiolide **27** was obtained as a white solid, mp 116–118 °C (EtOH), with a specific rotation $[\alpha]_D^{25} = -20.8$ (*c* 0.77, $CHCl_3$). The compound **28** was obtained pure by column chromatography as a white solid, mp 133–135 °C, $[\alpha]_D^{25} = -6.4$ (*c* 0.77, $CHCl_3$). Both compounds were obtained in very good yields: 80% and 83% respectively.

The ^{13}C NMR characteristics of compounds **27** and **28** are summarized in Table 4. The spectrum of compound **27** showed a signal

Table 2
Triorganotin hydrides addition to unsaturated diesters **8** and **9**

N°	R_3SnH R	^{119}Sn[a] (δ, ppm)		D (%)[b]		Time (h)	Yield (%)[c]	Prod. N°
8	*n*-Bu	−9.2		3		1	60	**21ad**
		−9.4		6				
		−12.2		43				
		−13.9		48				
	Neoph	−40.8		7		4	30	**22ac**
		−40.9		4				
		−42.2		89				
	Ph	−100.5		11		1	d	**23ad**
		−100.8		13				
		−104.8		36				
		−105.7		40				
9	*n*-Bu	−15.7	−22.6	3	8	2	70	**24ah**
		−15.9	−22.9	4	8			
		−20.5	−24.5	32	5			
		−20.7	−24.7	36	4			
	Neoph	−45	−49.8	14	4	16	60	**25ah**
		−45.4	−50.4	13	2			
		−46.6	−52.7	1	29			
		−46.8	−52.9	1	36			
	Ph	−116.4		44		3	50	**26ad**
		−124.5		13				
		−129.1		24				
		−137.8		20				

[a] In $CDCl_3$; chemical shifts in ppm with respect to Me_4Sn.
[b] D = % of diastereomer in the mixture from the ^{119}Sn NMR spectra of the crude products.
[c] After column chromatography purification.
[d] The mixture of diastereomers could not be separated from the hexaphenyldistannane formed in the reaction.



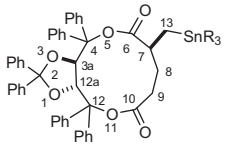
Scheme 3. Mechanism of the free radical cyclohydrostannation of unsaturated diesters.

Table 3
Triorganotin hydrides addition to unsaturated diesters **10** and **11**

Ester N°	R_3SnH R	^{119}Sn[a] (δ, ppm)	*D* (%)[b]	Time (h)	Yield (%)[c]	Prod. N°
10	*n*Bu	−13	100	1	80	**27**
	Neoph	−42	100	1	83	**28**
	Ph	−105	100	2	d	**29**
11	*n*Bu	−16	26	1	54	**30ad**
		−21	46			
		−23	18			
		−25	10			
	Neoph	−45	48	16	42	**31ad**
		−47	6			
		−50	7			
		−53	39			
	Ph	−111	23	1	83	**32ad**
		−115	30			
		−116	44			
		−117	3			

[a] In $CDCl_3$; chemical shifts in ppm with respect to Me_4Sn.
[b] *D* = % of diastereomer in the mixture from the ^{119}Sn NMR spectra of the crude products.
[c] After column chromatography purification.
[d] The mixture of diastereomers could not be separated from the hexaphenyldistannane formed in the reaction.

Table 4
^{13}C NMR characteristics of the new macrodiolides **27** and **28**[a]



R	N°
*n*Bu	**27**
Neoph	**28**

Cycle N°	C-2	C-10	C-8 ^3J(Sn,C)	C-7 ^2J(Sn,C)	C-6 ^3J(Sn,C)
27[b]	112.49	170.93	30.81 (25.1)	43.75 (16.7)	175.55 (33.2)
28[c]	112.30	170.78	30.83 (18.9)	42.79 (13.7)	175.11 (45.7)

[a] In $CDCl_3$; chemical shifts, δ, in ppm with respect to TMS; coupling constants, ^nJ(Sn,C) in Hz (in parentheses).
[b] Other signals: 9.82 (326.2); 12.52 (345.9) (C-13); 14.06; 27.52 (55.2); 29.31 (19.7); 34.93 (C-9); 79.68 and 79.76 (C-3a, C-12a); 87.44 and 87.48 (C-4, C-12); 125.34; 126.18; 126.21; 126.83; 127.00; 127.17; 127.20; 127.45; 127.51; 127.55; 128.53; 128.65; 129.33; 138.86; 139.20; 144.05; 144.08; 144.55.
[c] Other signals: 15.31 (179.5) (C-13); 26.89 (C-9); 32.81; 33.13; 33.50; 34.47; 37.86; 38.09; 39.30 (340.3); 79.52 and 79.60 (C-4, C-12); 87.36 and 87.38 (C-3a, C-12a); 125.22; 125.33; 125.49; 125.89; 125.19; 126.86; 127.00; 127.16; 127.21; 127.54; 128.06; 128.38; 128.50; 128.58; 128.30; 138.80; 139.02; 143.86; 143.90; 144.45; 144.50; 150.48 (21.2); 151.14 (18.0).

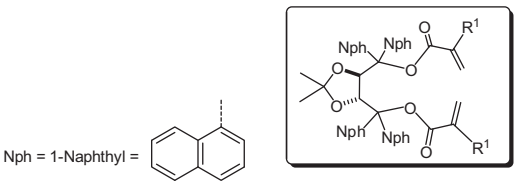
at 43.75 ppm with a $^2J(^{13}C,^{119}Sn)$ coupling constant of 16.7 Hz, and the DEPT indicates that it is a primary C atom. Therefore, this signal should belong to C-7. Of the two signals corresponding to the carbonyl groups at 170.93 ppm and 175.55 ppm, the signal at the lower field has a third order coupling constant $^3J(^{13}C,^{119}Sn)$ of 33.2 Hz, and could be ascribed to C-6. The value of 33.2 Hz for the $^3J(^{119}Sn,C{=}O)$ coupling constant might be associated with dihedral angles of 20/140° between the C=O group (C-6) and the tributylstannyl group.[9]

Similarly, the $^3J(^{119}Sn,C\text{-}8)$ coupling constant of compound **27** is 25.1 Hz, a value which is compatible with the dihedral angles of 45/130° between C-8 and the tributylstannyl group.

In the case of compound **28**, the $^3J(^{119}Sn,C{=}O)$ with a value of 45.7 Hz could be associated with dihedral angles of 20/140°; the $^3J(^{119}Sn,C\text{-}8)$ coupling constant of 18.9 Hz suggests dihedral angles of 60/120°. These data indicate that the structures proposed for compounds **27** and **28** are essentially correct.

Unfortunately, we were unable to obtain crystals suitable for crystallographic analysis. However, comparing the ^{13}C NMR spectra of **27** and **28** with the spectra of the corresponding macrodiolides obtained via hydrostannation of TADDOL's diacrylate with triorganotin hydrides **12** and **13**[4] we can conclude that the configurations could be the same. It should be added that we had previously been able to establish the absolute configuration of this type of molecules.[4b]

The diastereoselectivity observed in the hydroestannation of diester **10** with hydrides **12**–**14**, could be connected with the



Comp. N°	R^1	R^2	$[\alpha]_D^{25}$ [a]
34	H	H	-170.0
35	CH_3	H	-284.2

[a]. In $CHCl_3$; c = 0.5 g/mL.

Figure 1. New unsaturated diesters derived from TADDOL-Naph **33**.

existence of attractive noncovalent interactions (π-stacking) between the phenyl groups attached to C-2 of the dioxolane ring and the *gem* diphenylmethyl units attached to C-4 and C-5 of diester **10**. These interactions could generate a more rigid structure that would force the intermediate alkyl radical formed in the first step of the reaction (radical **A**, Scheme 3) to add to the second olefinic group in a preferential way on one of the faces of the double bond, giving rise to the observed selectivity.

These cyclohydrostannations can be explained by assuming that the triorganotin radical will add to the backbone of one of the unsaturated groups, thus leading to the alkyl radical **A** (Scheme 3) which in turn adds to the less substituted carbon of the other olefinic group leading to the product of endocyclization, i.e., radical **B**. The final step is the hydrogen transfer from the organotin hydride to the cyclic radical to give the product of cyclohydrostannation **III** (Scheme 3).[4]

It is known that this tandem radical cyclization process takes place with very high regio- and diastereoselectivity, with the endocyclization mode being favored.[10] Both polar and steric effects may affect radical cyclization. Since carbon radicals are nucleophilic, the presence of electron-withdrawing substituents activate alkenes toward the addition by such radicals. Steric effects are also critical in determining the ease of carbon radical addition to alkenes, i.e., substitution at the olefin site of radical attack usually reduces the rate of addition.[11]

In the case of unsaturated diesters **6**–**11**, the two factors that dominate the rate of addition to the olefins, i.e., electronic and steric, are both favorable: the alkene substituent (the ester group) is electron withdrawing, and the β-carbon of acrylate and methacrylate esters **6**–**11** is unsubstituted and therefore there is no steric hindrance for the addition.

In order to determine the effect of the change of the steric volume of the diphenylmethyl moieties of TADDOL on the stereoselectivity of the hydrostannation of unsaturated diesters, the four phenyl substituents were replaced by naphthyl groups (Fig. 1).

The esterification of the known α,α,α′,α′-tetranaphtyl-1,3-dioxolan-4,5-dimethanol **33**[12] with acid chlorides **4** and **5** using the protocol described above, led to the new unsaturated diesters **34** and **35** in yields of 86% and 50%, respectively (Fig. 1; TADDOL-Naph denotes the replacement of TADDOL's phenyl substituents by 1-naphthyl groups).

The additions were carried out under the experimental conditions used previously. The results obtained in the hydrostannation of diesters **34** and **35** with triorganotin hydrides **12** and **14** are summarized in Table 5. All attempts to add trineophyltin hydride **13** to **34** and **35** were unsuccessful: after 48 h under free radical conditions, the starting substrates were recovered. The additions of triphenyltin hydride **14** took place with an average yield of 77.5%, while the average yield of the hydrostannations with tri-*n*butyltin hydride **12** was 56.5%. Scheme 4 summarizes the free radical addition of organotin hydrides **12** and **14** to diester **35**.

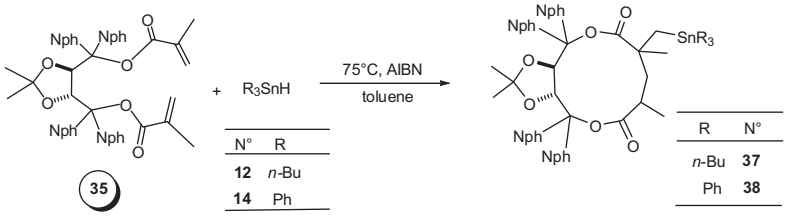
The specific rotations of the new macrocycles included in Table 5, are higher than those of their TADDOL analogues. Thus, the specific rotations of the equivalent macrocyclic adducts of compounds **36**–**39** obtained in the hydrostannation of TADDOL's diacrylates and dimetacrylates are −78, −65, −116, and −100, respectively.

As shown in Table 5, the cyclohydrostannations took place with complete diastereoselectivity. Of the two diastereomers expected in the additions to diacrylate **34**, only one was obtained. Similarly, the hydrostannations of methacrylate **35** with hydrides **12** and **14** that should lead to four stereoisomers with the creation of two new stereocenters, gave just one diastereomer. These results clearly demonstrate that the replacement of TADDOL's four phenyl groups with four bulkier naphthyl groups results in a dramatic increase of the stereoselectivity.

Table 5
Triorganotin hydrides addition to unsaturated diesters **33** and **34**

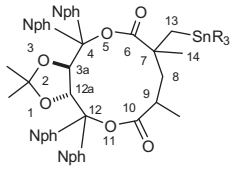
Ester N°	R_3SnH R	^{119}Sn [a] (δ, ppm)	Time (h)	Yield (%)[b]	$[\alpha]_D^{25}$ (*c*, g/mL)[c]	Prod. N°
34	*n*-Bu	−13.6	1	63	−228.5	**36**
	Ph	−102.7	1	78	−105.1	**37**
35	*n*-Bu	−20.3	24	50	−319.6	**38**
	Ph	−116.0	24	77	−136	**39**

[a] In $CDCl_3$; ppm with respect to Me_4Sn.
[b] After column chromatography purification.
[c] In $CHCl_3$; c = 0.77 g/mL.



Scheme 4. Free radical hydrostannation of unsaturated diester **35**.

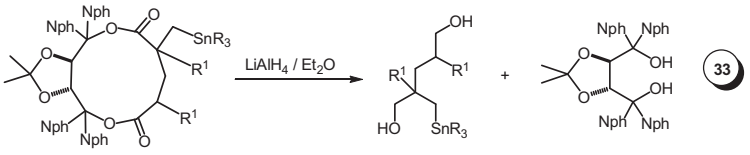
Table 6
^{13}C NMR characteristics of the new macrodiolides **38** and **39**[a]



R	N°
n-Bu	**37**
Ph	**38**

Compd N°	C-10	C-6 ^3J(Sn,C)	C-7 ^2J(Sn,C)	C-8 ^3J(Sn,C)	C-14 ^3J(Sn,C)
38[b]	175.76	175.94 (13.3)	46.97 (21.6)	48.84 (11.6)	30.42 (13.7)
39[c]	175.32	176.33 (14.5)	68.35 (27.8)	46.93 (NO)	30.38 (15.0)

[a] In $CDCl_3$; chemical shifts, δ, in ppm with respect to TMS; coupling constants, ^nJ(Sn,C) in Hz (in parentheses); NO = not observed.
[b] Other signals: 10.51 (327.7); 13.88; 18.89; 21.18 (334.3); 26.15; 26.63; 27.32 (56.5); 29.23 (18.2); 30.26; 36.31; 77.83; 78.74; 87.95; 88.94; 110.44; 123.66; 123.99; 124.17; 124.23; 124.34; 124.40; 124.53; 124.61; 124.97; 125.25; 126.68; 127.58; 127.72; 127.94; 128.04; 128.28; 128.46; 128.81; 129.30; 129.65; 129.67; 129.73; 130.34; 130.63; 133.04; 133.54; 134.07; 134.24; 134.35; 134.38; 136.87; 136.91; 137.17; 139.22.
[c] Other signals: 18.13; 23.40; 23.68 (NO); 26.12; 26.54; 36.01; 77.76; 78.66; 88.17; 89.30; 110.33; 123.70; 123.87; 124.10; 124.31; 124.35; 124.45; 124.60; 124.66; 124.99; 125.16; 126.17; 127.54; 127.75; 128.01; 128.35; 128.54; 128.80; 129.31; 129.54; 129.70; 129.75; 130.27; 130.55; 132.93; 133.27; 134.08; 134.19; 134.35; 136.37; 136.78; 136.88; 137.01; 137.09; 137.25; 139.06; 139.88.



N°	R	R^1
36	*n*-Bu	H
37	Ph	H
38	*n*-Bu	CH_3
39	Ph	CH_3

N°	R	R^1	Yield (%)	$[\alpha]_D^{20}$ (c, g/mL) [a]	^{119}Sn-RMN (δ, ppm) [c]
40	*n*-Bu	H	[b]	[b]	-13
41	Ph	H	75	- 35.2 (0.75)	-100
42	*n*-Bu	CH_3	56	+ 2.4 (0.70)	-15
43	Ph	CH_3	73	- 3.4 (0.70)	-107

[a] In $CHCl_3$. [b] Could not be obtained pure. [c] In $CDCl_3$; in ppm with respect to Me_4Sn.

Scheme 5. Reduction of macrocycles **36**–**39** with $LiAlH_4$.

We then attempted the structural elucidation of compounds **36** and **37** by means of NMR spectrometry. We found that although the ^{119}Sn spectra gave just one sharp signal for each compound, we were unable to obtain well resolved ^{1}H and ^{13}C NMR spectra. The reasons for the low resolution spectra could be ascribed to a saturation of signals due to the great number of peaks especially in the aromatic region. In addition, the observed broad bands and low resolution might be connected with restrictions in the molecular movements due to the bulk of the naphthyl groups. It should be noted that we carried out a series of experiments and varied the concentration of the solutions, the deuterated solvent ($CDCl_3$, DMSO-d_6, acetone-d_6), and the temperature (70 °C in DMSO-d_6) without obtaining good quality spectra. The 2D-spectra and mass spectra were also of no help in these cases.

The ^{1}H and ^{13}C NMR spectra of compounds **38** and **39**, were again of poor quality. However, in this case we were able to obtain enough information for establishing the connectivity between the carbon atoms. The ^{13}C NMR characteristics of the new triorganotin substituted macrodiolides **38** and **39** are included in Table 6.

The presence in **38** and **39** of two carbonyl signals, one of which showed a $^3J(^{119}Sn,^{13}C{=}O)$ coupling constant, indicates that these compounds are the macrocycles product of the cyclohydrostannation of diester **34**. In the DEPT experiments of compounds **37** and **38**, the signals corresponding to the quaternary carbon C-7 disappear, thus confirming the formation of the macrocycle.

Unfortunately, we were unable to obtain crystals suitable for crystallographic analysis of compounds **36**–**39**. In order to establish the structure of these compounds, we carried out the reduction of compounds **36**–**39** with $LiAlH_4$ in ether. The reductions led to mixtures of the corresponding triorganotin diols and α,α,α′,α′-tetranaphthyl-1,3-dioxolan-4,5-dimethanol **33**, as shown in Scheme 5.

The reactions were monitored by TLC and FT-IR, and stirred at rt until the IR spectrum showed no $\nu_{C=O}$ band. The structures of compounds **40**–**43** were confirmed by comparison with authentic samples previously obtained.[4] Diol **40** could not be isolated pure from the chromatography, but we were able to obtain mixtures enriched in **40** that enabled us to achieve its spectroscopic characterization. These results demonstrate that the proposed structures for the starting macrocycles **36**–**39** are essentially correct.

3. Conclusions

In order to study the effect of the introduction of several substituents to TADDOL's dipropenoates and di-2-methylpropenoates on the stereoselectivity of the cyclohydrostannation, we have synthesized and characterized eight new TADDOL unsaturated diesters **6**–**11** and **34**–**35**.

We then studied the hydrostannation of diesters **6**–**11** containing different combinations of substituents at the C-2 carbon of the

TADDOL dioxolane ring. Diesters **6** and **7** (with Ph and H substituents at C-2), **8** and **9** (with Ph and Me), and **10** and **11** (with two Ph groups at C-2) were hydrostannated with tri-*n*butyl-**12**, trineophyl-**13**, and triphenyltin **14** hydrides. The additions led in all cases to products of macrocyclization. The hydrostannation of unsaturated diesters **6**–**9** took place with low diastereoselectivity. Diacrylates **6** and **8** led to four stereoisomers and the dimethacrylates **7** and **9** led to eight diastereomers. The latter was due to the existence of epimers. However, in all cases two stereoisomers were in a higher proportion. On the other hand, for the hydrostannation of diacrylate **10**, the two phenyl groups attached to carbon C-2, with triorganotin hydrides **12**–**14** proceeded with complete diastereoselectivity and in the three cases yielded only one of the two possible diastereomers. In the case of dimethacrylate **11**, the expected formation of the four diastereomers was observed (the creation of two new stereocenters). Here, again, two diastereomers out of the four were formed in higher proportion.

These results suggest that when the substituents are different, the variation of the substituents attached to carbon C-2 of the dioxolane ring does not improve the stereoselectivity of the cyclohydrostannations. When the substituents at C-2 are identical, e.g., TADDOL's unsaturated diesters (two methyl substituents) and diesters **10** and **11** (two phenyl groups), a remarkable increase of the stereoselectivity is observed.

In the case of the unsaturated diesters **34** (diacrylate) and **35** (dimethacrylate), derived from TADDOL-Naph **33**, i.e., the diol in which the four phenyl substituents of TADDOL are replaced by four 1-naphthyl groups, there is a dramatic increase in the stereoselectivity of the cyclohydrostannation. The hydrostannations with both tri-*n*-butyl- **12** and triphenyltin **14** hydrides of diesters **34** and **35** led in all cases to only one stannylated macrocycle, i.e., the reactions took place with complete diastereoselectivity. These results show the magnitude of the increase of the Ingold-Thorpe effect when the phenyl groups are replaced by bulkier naphthyl groups.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere. Solvents were dried and distilled in accordance with standard procedure. 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 on 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 on a FT-IR Nicolet Nexus 470/670/870 spectrophotometer. Mass spectra were obtained on Finnigan MAT Incos 50 Galaxy System (DIP-MS) (EI) or Finnigan MAT 900 (ESI) spectrometers, high resolution mass spectra on a Finnigan HSQ-30 (HR-EIMS) or on a Finnigan MAT 900 (HR-ESI-MS). The method of ionization is given in parentheses. Specific rotations were measured with a Polar L-μP, IBZ Messtechnik instrument. The melting points were determined with a Kofler hot stage apparatus and are not corrected. All the solvents and reagents were commercially available and analytical grade. The diols **1**, **2**, **3**, and **33** were prepared by know procedures.[5,12]

4.2. Synthesis of unsaturated diesters via esterification of diols 1, 2, 3, and 33 with α,β-unsaturated acid chlorides

The same procedure was used in all of the reactions. One experiment is described in detail to illustrate the methods used.

4.2.1. ((4*R*,5*R*)-2-Phenyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethylene) diacrylate 6

A solution of **1** (2.0 g, 3.89 mmol) in dry Et_2O (45 mL) under argon, was cooled to −50 °C and then a solution of *n*-BuLi in Et_2O (5.2 mL, 9.34 mmol, 1.8 M) was added slowly with a syringe. The mixture was kept at −50 °C for 1 h and the acryloyl chloride (0.97 mL, 12 mmol) was added slowly. The mixture was allowed to warm to room temperature and then stirred overnight. The reaction was quenched by the addition of aqueous saturated sodium bicarbonate solution (60 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed once with water (20 mL) and brine (20 mL), and then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The white solid obtained was structurally characterized as the desired product **6** (2.34 g, 3.76 mmol, 97%) without the need for further purification. Mp 129–131 °C.; $[\alpha]_D^{25} = -100$ (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 4.48 (s, 1H), 5.57 (dd, 1H, *J* = 10.2, 1.3 Hz), 5.63 (dd, 1H, *J* = 10.2, 1.3 Hz), 5.82–5.97 (m, 1H), 6.12 (dd, 2H, *J* = 3.9 Hz), 6.17 (dd, 1H, *J* = 1.26 Hz), 6.17–6.18 (m, 1H), 6.65–6.68 (m, 1H), 6.97–7.40 (m, 25H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 78.0, 78.4, 86.7, 87.4, 103.9, 126.6, 126.8, 127.3, 127.4, 127.5, 127.6, 127.8, 127.9, 128.2, 128.5, 129.0, 129.1, 129.3, 130.3, 130.5, 130.7, 130.9, 136.6, 139.7; 141.2; 142.9; 143.4. 164.4, 164.6. FT-IR (KBr): ν = 3052 (m), 3026 (m), 2985 (w), 2930 (m), 1726 (s), 1632 (m), 1497 (m), 1401 (m), 1171 (m), 1075 (m), 887 (m), 747 (s), 7079 (s) cm^{-1}. HRMS (ESI): calcd for $C_{41}H_{34}O_6Na$: 645.2253 $[M+Na]^+$; found: 645.2248.

4.2.2. ((4*R*,5*R*)-2-Phenyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethylene)bis(2-methylacrylate) 7

The title compound was prepared from **1** to give a white solid (1.59 g, 2.46 mmol, 64% yield). Mp 135–137 °C. SiO_2 (hexane/Et_2O = 97:3); $[\alpha]_D^{25} = -72$ (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.70 (s, 3H), 1.74 (s, 3H), 4.55 (s, 1H), 5.41–5.44 (m, 2H), 6.18 (dd, 2H, *J* = 4.8 Hz), 6.40 (dd, 2H, *J* = 7.6 Hz), 7.02–7.37 (m, 25H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2, 77.6, 77.1, 86.9, 87.6, 103.8, 126.8, 127.3, 127.5, 127.7, 127.8, 128.1, 128.3, 128.7, 129.1, 129.2, 129.4, 137.3, 137.4, 127.2, 136,5, 140.4, 141.6, 143.1, 143.7, 165.8, 166.1. FT-IR (KBr): ν = 3023 (m), 2980 (w), 2926 (m), 1723 (s), 1629 (m), 1490 (m), 1401 (m), 1165 (m), 1075 (m), 884 (m), 751 (s), 705 (s) cm^{-1}. HRMS (ESI): calcd for $C_{43}H_{38}O_6Na$: 673.2566 $[M+Na]^+$; found: 673.2561.

4.2.3. ((4*R*,5*R*)-2-Methyl-2-phenyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethylene)diacrylate 8

The title compound was prepared from **2** to give a white solid (2.0 g, 3.10 mmol, 83% yield) without the need of further purification. Mp 138–140 °C; $[\alpha]_D^{25} = -19$ (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.95 (d, 3H), 3.99–4.01 (m, 2H), 5.38–5.42 (m, 2H), 5.91–6.28 (m, 4H), 6.65–7.43 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.8, 79.3, 79.7, 87.3, 87.41, 109.9, 124.6; 126.3; 126.4; 126.9, 127.0, 127.2, 127.3, 127.4, 127.6, 127.7, 128.8, 129.1, 129.2, 130.0, 130.6, 130.9, 131.0, 131.1, 164.3, 164.5. FT-IR (KBr): ν = 3021 (m), 2982 (w), 2923 (m), 1728 (s), 1627 (m), 1492 (m), 1400 (m), 1164 (m), 1071 (m), 882 (m), 750 (s), 707 (s) cm^{-1}. HRMS (ESI): calcd for $C_{42}H_{36}O_6Na$: 659.2410 $[M+Na]^+$; found: 659.2414.

4.2.4. ((4*R*,5*R*)-2-Methyl-2-phenyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethylene)bis(2-methyl-acrylate) 9

The title compound was prepared from **2** to give a white solid (1.50 g, 2.30 mmol, 61% yield). Mp 156–158 °C. SiO_2 (hexane/Et_2O = 95:5); $[\alpha]_D^{25} = -67$ (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.81 (s, 3H), 1.67–1.69 (m, 6H), 5.77 (dd, 4H, *J* = 10.3 Hz), 5.92 (dd, 2H, *J* = 6.0 Hz), 6.73–7.40 (m, 25H). ^{13}C NMR (75 MHz, $CDCl_3$):

δ = 18.3, 18.4, 78.6, 79.1, 87.8, 87.9, 110.8, 124.6, 126.2, 126.9, 127.0, 127.1, 127.5, 127.6, 127.7, 128.7, 129.1, 137.9 138.0, 139.5, 141.1, 143.6, 144.1, 166.1, 166.4. FT-IR (KBr): ν = 3020 (m), 2990 (w), 2925 (m), 1730 (s), 1630 (m), 1495 (m), 1401 (m), 1160 (m), 1073 (m), 881 (m), 748 (s), 705 (s) cm^{-1}. HRMS (ESI): calcd for $C_{44}H_{40}O_6Na$: 664.2825 $[M+Na]^+$; found: 664.2820.

4.2.5. ((4*R*,5*R*)-2,2-Diphenyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethylene)diacrylate 10

The title compound was prepared from **3** to give a white solid (0.88 g, 1.30 mmol, 50% yield) without the need of further purification. Mp 180–182 °C; $[\alpha]_D^{25}$ = −5.4 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 5.80–5.85 (m, 4H), 6.13–6.24 (m, 2H), 6.42 (dd, 2H, *J* = 1.2, 17.1), 6.92–7.60 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 81.3, 87.4, 111.0, 125.42, 126.4, 127.1, 127.2, 127.4, 127.5, 127.7, 128.9, 129.1, 130.5, 131.1, 138.0, 143.0, 143.7, 164.4. FT-IR (KBr): ν = 3025 (m), 2981 (w), 2924 (m), 1721 (s), 1630 (m), 1492 (m), 1403 (m), 1162 (m), 1076 (m), 882 (m), 749 (s), 704 (s) cm^{-1}. HRMS (ESI): calcd for $C_{47}H_{38}O_6Na$: 721.2566 $[M+Na]^+$; found: 721.2561.

4.2.6. ((4*R*,5*R*)-2,2-Diphenyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethylene)bis(2-methylacrylate) 11

The title compound was prepared from **3** to give a white solid (0.70 g, 0.97 mmol, 57% yield) without the need of further purification. Mp 203–205 °C; $[\alpha]_D^{25}$ = −4.8 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.80 (s, 6H); 5.56 (s, 2H); 6.19 (s, 2H); 6.27 (s, 2H); 6.93–7.56 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3, 80.4, 87.9, 112.1, 125.2 126.3, 126.8, 126.9, 127.4, 127.6, 128.9, 137.9, 139.3, 143.9, 144.3, 166.2. FT-IR (KBr): ν = 3022 (m), 2981 (w), 2924 (m), 1729 (s), 1628 (m), 1491 (m), 1402 (m), 1165 (m), 1073 (m), 880 (m), 750 (s), 703 (s) cm^{-1}. HRMS (ESI): calcd for $C_{49}H_{42}O_6Na$: 726.2981 $[M+Na]^+$; found: 726.2985.

4.2.7. ((4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(di(naphthalen-1-yl)-methylene)diacrylate 34

The title compound was prepared from **33** to give a pale yellow solid (1.0 g, 1.30 mmol, 86% yield) without the need of further purification. Mp 145–147 °C; $[\alpha]_D^{25}$ = −170 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 6H); 5.46–5.53 (m, 1H); 5.97–5.95 (m, 3H); 6.39–6.43 (m, 1H); 6.55–6.64 (m, 2H); 6.91–7.02 (m, 4H); 7.12–7.16 (m, 2H); 7.30–7.84 (m, 20H); 7.91–7.94 (m, 1H); 8.22–8.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2, 79.2, 88.1, 110.9, 123.9, 124.3, 124.4, 124.7, 124.9, 125.2, 125.8, 127.7, 127.8, 127.9, 128.0, 128.6, 128.8, 129.6, 129.7, 130.4, 130.6, 130.8, 131.6, 133.2, 134.1, 134.3, 137.3, 137.9, 164.64. FT-IR (KBr): ν = 3022 (m), 3015 (m), 2981 (w), 1731 (s), 1605 (m), 1494 (m), 1401 (m), 1163 (m), 1075 (m), 882 (m), 751 (s), 702 (s) cm^{-1}. HRMS (ESI): calcd for $C_{53}H_{42}O_6Na$: 797.2291 $[M+Na]^+$; found: 797.2295.

4.2.8. ((4*R*,5*R*)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis(di(naphthalen-1-yl)-methylene)bis(2-methylacrylate) 35

The title compound was prepared from **33** to give a white solid (1.2 g, 1.50 mmol, 50% yield). Mp 158–160 °C; SiO_2 (hexane/EtOAc = 96:4); $[\alpha]_D^{25}$ = −284 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.76 (s, 3H); 1.79 (s, 3H); 1.94 (s, 6H); 5.50–5.58 (m, 2H); 6.31–6.41 (m, 2H); 6.81–7.08 (m, 4H); 7.16–8.22 (m, 20H); 8.28–8.97 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.4, 25.2, 79.3, 88.1, 111.2, 124.0, 124.3, 124.4, 124.5, 124.7, 125.2, 126.1, 126.8, 127.4, 127.7, 127.9, 128.0, 128.5, 128.9, 129.0, 129.3, 128.5, 129.7, 130.6, 133.4 134.2, 134.4, 136.3, 137.8, 138.1, 165.8. FT-IR (KBr): ν = 3025 (m), 3019 (m), 2986 (w), 1728 (s), 1603 (m), 1490 (m), 1405 (m), 1161 (m), 1073 (m), 881 (m), 752 (s), 700 (s) cm^{-1}. HRMS (ESI): calcd for $C_{55}H_{46}O_6Na$: 825.3192 $[M+Na]^+$; found: 825.3187.

4.3. Addition of triorganotin hydrides to unsaturated diesters

The same procedure was used in all of the reactions. One experiment is described in detail to illustrate the methods used.

4.3.1. (3a*R*,7*R*,12a*R*)-2,2,4,4,12,12-Hexaphenyl-7-((tributylstannyl)methyl)hexahydro-6*H*-[1,3]dioxolo[4,5-*c*][1,6]dioxacycloundecine-6,10(7*H*)dione 27

Diester **10** (0.12 g, 0.17 mmol) in dry toluene (5 mL) was treated with tributyltin hydride (0.11 g, 0.34 mmol), using AIBN as a radical initiator (0.049 g, 0.3 mmol), under an argon atmosphere at 75 °C for 1 h (optimal time of reaction and adequate excess of organotin hydride were determined in previous runs both by monitoring the reaction by taking samples at intervals and observing the disappearance of the Sn–H absorption and by IR and also by checking that the ^1H NMR spectrum of the reaction mixture did not show the presence of unreacted olefin). The solvent was then distilled off under reduced pressure, and the ^{119}Sn NMR spectrum of the crude product showed that it consisted of only one compound **27**. The crude product thus obtained was purified by recrystallization from ethanol (0.14 g, 0.14 mmol, 80%) as a white solid, mp 115–117 °C. $[\alpha]_D^{25}$ = −20.8 (*c* 0.77, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.63 (t, 4H, $^3J_{H,H}$: 7.6 Hz); 0.81 (t, 9H, $^3J_{H,H}$: 6.9 Hz); 1.16–1.57 (m, 17H); 1.93–2.27 (m, 3H); 2.47–2.61 (m, 2H); 5.94 (d, 1H, $^3J_{H,H}$: 7.1 Hz); 6.00 (d, 1H, $^3J_{H,H}$: 7.1 Hz); 6.63–7.44 (m, 30H). FT-IR (KBr): ν = 3040 (m); 3011 (m); 2946 (w); 2910 (w); 1743 (s); 1600 (m); 1485 (m); 1452 (m); 1240 (m); 1160 (m); 850 (m); 750 (s); 695 (s) cm^{-1}. HRMS (ESI): calcd for $C_{59}H_{66}O_6SnNa$: 1013.3787 $[M+Na]^+$; found: 1013.3782.

4.3.2. (3a*R*,7*R*,12a*R*)-2,2,4,4,12,12-Hexaphenyl-7-((tris(2-methyl-2-phenylpropyl)stannyl)methyl)hexahydro-6*H*-[1,3]dioxolo[4,5-*c*][1,6]dioxacycloundecine-6,10(7*H*)-dione 28

The title compound was prepared from **10** to give a white solid (0.14 g, 0.12 mmol, 83% yield). Mp 130–132 °C; SiO_2 (hexane/Et_2O = 90:10); $[\alpha]_D^{25}$ = −6.4 (*c* 0.77, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.79 (s, 6H, $^2J_{Sn,H}$: 49.2 Hz); 1.07 (s, 9H); 1.13 (s, 9H); 1.65–1.68 (m, 2H); 2.01–2.15 (m, 4H); 2.22–2.30 (m, 1H); 5.92 (d, 1H, $^3J_{H,H}$: 7.3 Hz); 5.98 (d, 1H, $^3J_{H,H}$: 7.3 Hz); 6.80–7.21 (m, 45H). FT-IR (KBr): ν = 3042 (m); 3011 (m); 2940 (w); 2915 (w); 1741 (s); 1602 (m); 1480 (m); 1450 (m); 1242 (m); 1160 (m); 850 (m); 750 (s); 695 (s) cm^{-1}. HRMS (ESI): calcd for $C_{77}H_{78}O_6SnNa$: 1241.4720 $[M+Na]^+$; found: 1241.4725.

4.3.3. (3a*R*,7(*R* or *S*),9(*R* or *S*),12a*R*)-2,2,7,9-Tetramethyl-4,4,12,12-tetra(naphthalen-1-yl)-7-((tributylstannyl)methyl)hexahydro-6*H*-[1,3]dioxolo[4,5-*c*][1,6]dioxacycloundecine-6,10(7*H*)-dione (38)

The title compound was prepared from **35** to give a white solid (0.11 g, 0.10 mmol, 54% yield). Mp 123–125 °C; SiO_2 (hexane/Et_2O = 90:10); $[\alpha]_D^{25}$ = −319 (*c* 0.77, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 3H); 0.12 (s, 2H); 0.46–0.53 (m, 8H); 0.65 (s, 3H); 0.94 (t, 9H); 1.29–1.37 (m, 12 H); 1.47 (s, 3H); 1.56–1.67 (m, 2H); 2.55–2.67 (m, 1H); 2.77–2.88 (m, 1H); 6.38 (d, 1H); 6.59–8.63 (m, 30H). FT-IR (KBr): ν = 3035 (m); 3010 (m); 2935 (w); 2910 (w); 1743 (s); 1601 (m); 1480 (m); 1445 (m); 1242 (m); 1160 (m); 848 (m); 749 (s); 700 (s) cm^{-1}. HRMS (ESI): calcd for $C_{67}H_{74}O_6SnNa$: 1117.4407 $[M+Na]^+$; found: 1117.4412.

4.3.4. (3a*R*,7(*R* or *S*),9(*R* or *S*),12a*R*)-2,2,7,9-Tetramethyl-4,4,12,12-tetra(naphthalen-1-yl)-7-((triphenylstannyl)methyl)hexahydro-6*H*-[1,3]dioxolo[4,5-*c*][1,6]dioxacycloundecine-6,10(7*H*)-dione 39

The title compound was prepared from **35** to give a white solid (0.17 g, 0.15 mmol, 77% yield). Mp 127–129 °C; SiO_2 (hexane/Et_2O = 90:10); $[\alpha]_D^{25}$ = −136 (*c* 0.77, $CHCl_3$); ^1H NMR (300 MHz,

$CDCl_3$): δ = −0.23 (s, 3H); −0.10 (s, 3H); 0.19 (d, 3H); 0.63 (s, 3H); 1.28–1.31 (m, 1H); 1.56–1.60 (m, 1H); 2.18 (d, 1H); 2.40–2.49 (m, 1H); 2.67–2.73 (m, 1H); 6.24 (d, 1H, $^3J_{H,H}$: 6.1 Hz); 6.54 (d, 1H, $^3J_{H,H}$: 6.1 Hz); 1.48–6.62 (m, 4H); 7.79–7.88 (m, 43H). FT-IR (KBr): ν = 3038 (m); 3015 (m); 2941 (w); 2912 (w); 1740 (s); 1600 (m); 1480 (m); 1450 (m); 1240 (m); 1161 (m); 850 (m); 751 (s); 699 (s) cm^{-1}. HRMS (ESI): calcd for $C_{73}H_{62}O_6SnNa$: 1154.3568 $[M+Na]^+$; found: 1154.3572.

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