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Short Communication

Efficient asymmetric TADDOLs-organocatalyzed cycloaddition for the synthesis of allyltin derivatives

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ABSTRACT

We report here the results obtained in the study of organocatalytic asymmetric Diels–Alder reactions to optimize the synthesis of stereo defined allyltin derivatives using (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl)stannane (**1**) as diene and substituted dienophiles in the presence of (4R,5R)-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol (TADDOL, **I**) and analogs (4R,5R)-α,α,α′,α′-tetra(1-naphtyl)-1,3-dioxolane-4,5-dimethanol (**II**) and (4R,5R)-α,α,α′,α′-tetra(9-phenantryl)1,3-dioxolane-4,5-dimethanol (**III**) as chiral catalysts to enhance stereoselectivity through hydrogen bond activation of the dienophile. Catalyst **II** provided excellent results and ultrasonic radiation at low temperature showed the shorter reaction times.

1. Introduction

Asymmetric organocatalysis is one of the three pillars of asymmetric synthesis. Transition metal complexes and enzymes were the most employed catalysts until the exponential growth of the field of organocatalysis in the last decade [1–3]. This subject now plays a valuable role in the synthesis of complex organic compounds and allows more selective, economically and environmentally friendlier transformations [4]. In these reactions, a small amount of an enantiomerically pure organocatalyst is used to produce large quantities of an optically active compound from a precursor that may be chiral or achiral [5]. On the other side, the field of organic synthesis has been greatly benefited since the development of the Diels–Alder reaction, recognized by the award of the Nobel Prize in Chemistry in 1950. With the potential of forming carbon – carbon, carbon – heteroatom and heteroatom – heteroatom bonds, the reaction is a versatile synthetic tool for constructing simple and complex molecules. Undoubtedly, it is one of the most efficient methods for the construction of six member rings built from a conjugated diene and a dienophile [6–9]. During the last 20 years, considerable research work has been made directed toward the development of enantioselective catalytic Diels–Alder reaction [10]. The enormous development of this reaction involves the use of chiral auxiliaries and chiral catalysts to induce enantioselectivity. The advances in both catalyst and substrate have been achieved regarding [4 + 2] cycloadditions. The latter area is based on the activation of the dienophile by hydrogen bonding with a chiral organocatalyst. This interaction blocks one face for the cycloaddition so the reaction occurs stereoselectively through the other face.

2. Experimental

2.1. General

All the reactions were performed under nitrogen or argon as indicated. The solvents used were dried and distilled in accordance with standard procedures. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded in $CDCl_3$ on a Bruker ARX 300 Multinuclear instrument (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C and 111.9 MHz for ^{119}Sn) at 23 °C and calibrated by using signals from solvents referenced to $SiMe_4$ (^{1}H, ^{13}C NMR) and with respect to Me_4Sn in the case of ^{119}Sn NMR spectra. Chemical shifts (δ) are reported in ppm and coupling constants (J) are in Hz. Compounds described in this work (**7**–**11**) were characterized by comparing their ^{1}H, ^{13}C and ^{119}Sn NMR spectra to the previously reported data [11]. The progress of the reaction and the purity of compounds were monitored by TLC analytical silica gel plates (Merck 60 F254). Visualization was accomplished by UV light and phosphomolybdic acid solution in ethanol by heating. Optical rotation measurements were performed

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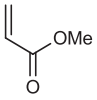
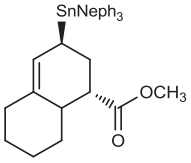
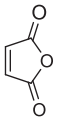
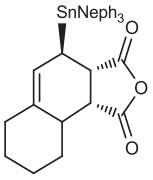
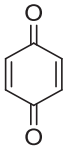
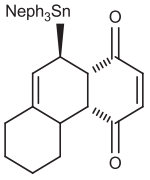
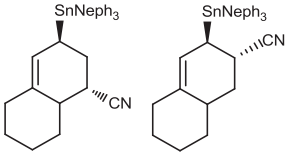
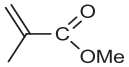
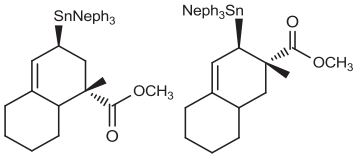
on a digital polarimeter IBZ Messtechnik, Polar L-μP. Gas chromatography (GC) was performed on a Shimadzu GC-14B instrument equipped with a FID detector and an ASTEC capillary column, CHIRALDEX Model, Type B-PM (30 m–0.32 mm i.d., permethyl-β-cyclodextrin as stationary phase). GC conditions are detailed in Supplementary Data. A Cole Parmer 4710 series ultrasonic homogenizer operating at 20 kHz (600 W) provided the high intensity ultrasound. External sonication was carried out using an ultrasonic probe (from Cole-Parmer 4710 series ultrasonic homogenizer of 20 kHz and 375 W) equipped with a 10 mm diameter titanium horn, which was immersed either in a water bath. Reactions were performed under argon in septum lid vials. Column chromatography was performed over neutral aluminum oxide or silica gel 60 70–230 mesh ASTM. All the solvents and reagents were of analytical grade. (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl)stannane (**1**) was prepared as described previously [10]. TADDOL derivatives **I**–**III** were prepared as described in the literature [12–14]. All the reactions with reasonable yields (>40%) according to Table 1 were injected as a dilute sample (1 μL) in order to determine the e.e. by GC-chiral chromatography, except in the case of entry 5, method C, catalyst II which was the only reaction with only one regioisomer despite the low yield (25%).

Table 1
Effect of TADDOL and TADDOL analogs (**I**–**III**) in Diels–Alder reactions (methods **A**–**D**) between diene **1** and some different activated dienophiles (**2**–**6**).

Entry	Dienophile	Method[a] (time, h)[b]	Catalyst	Yield (%)[c] (a:b)[f]	Product[e]
1	 **2**	A (70)	I	45	 **7**
		A (24)	II	80	
		A (70)	III	78	
		B (7)	I	15	
		B (2)	II	38	
		B (8)	III	35	
		C (72)	I	[d]	
		C (62)	II	25	
		C (72)	III	[d]	
		D (48)	$CHCl_3$	5	
2	 **3**	A (48)	I	40	 **8**
		A (24)	II	80	
		A (48)	III	75	
		B (7)	I	90	
		B (7)	II	95	
		B (7)	III	93	
		C (48)	I	92	
		C (12)	II	>99	
		C (48)	III	87	
		D (48)	$CHCl_3$	30	
3	 **4**	A (7)	I	85	 **9**
		A (5)	II	>99	
		A (7)	III	>99	
		B (10)	I	>99	
		B (2)	II	>99	
		B (10)	III	>99	
		C (28)	I	>99	
		C (12)	II	>99	
		C (28)	III	>99	
		D (7)	$CHCl_3$	30	
4	 **5**	A (70)	I	38 (80:20)	 **10** **10′** **(a : b)**
		A (72)	II	42 (>99:<1)	
		A (70)	III	[d]	
		B (10)	I	[d]	
		B (2)	II	49 (>99:<1)	
		B (10)	III	[d]	
		C (24)	I	[d]	
		C (24)	II	[d]	
		C (24)	III	[d]	
		D (48)	$CHCl_3$	[d]	
5	 **6**	A (70)	I	70 (50:50)	 **11** **11′** **(a : b)**
		A (72)	II	75 (75:25)	
		A (70)	III	30 (67:33)	
		B (10)	I	[d]	
		B (2)	II	20 (70:30)	
		B (10)	III	15 (69:31)	
		C (28)	I	[d]	
		C (24)	II	25 (>99:<1)	
		C (24)	III	[d]	
		D (48)	$CHCl_3$	[d]	

[a] Method **A**: organocatalyst, $CHCl_3$, 15 °C; Method **B**: organocatalyst, dry toluene, −30 °C, ultrasound (50–60 Hz); Method **C**: organocatalyst, dry toluene, −30 °C; Method **D**: $CHCl_3$, 15 °C, without organocatalyst.
[b] The optimal reaction time was established by taking samples and monitoring the product formation through TLC, ^{119}Sn and ^{1}H NMR until the reaction showed no changes.
[c] After chromatographic purification of the reaction mixture.
[d] Starting material.
[e] Structure characterization in reference [11].
[f] From ^{119}Sn NMR spectra of the reaction crude product.

The GC-chromatograms and those corresponding to uncatalyzed reactions for entries 1, 2 and 3 are shown in the Supplementary Data. It is important to note that in the cases of entries 4 and 5, the uncatalyzed reaction gives a mixture of regioisomers (**10**–**10′** and **11**–**11′**) that cannot be separated so they were not analyzed by chiral GC.

2.2. Representative procedures for the catalyzed Diels–Alder reactions

2.2.1. Method A

To a solution of the organocatalysts (0.5 mmol) and the corresponding dienophile (2.5 mmol) in dry chloroform (0.5 mL) (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl)stannane (**1**, 1.56 g, 2.5 mmol) was added under argon atmosphere. The solution was stirred at 15 °C for an appropriate time, monitoring the reaction progress by TLC. The solvent was removed *in vacuo* and the crude product was purified by column chromatography with neutral aluminum oxide with hexane/Et2O mixtures for the corresponding characterization.

Methyl-4-trineophylstannylbicyclo[4.4.0]dec-5-ene-2-carboxylate (7): 80% yield after purification, $[\alpha]_D^{25} -83°$ ($c = 0.2$, $CHCl_3$).

2.2.2. Method B

To a solution of the organocatalysts (0.5 mmol) and the corresponding dienophile (2.5 mmol) in dry toluene (0.5 mL) was added (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl)stannane (**1**, 1.56 g, 2.5 mmol) in argon atmosphere. The reaction mixture was exposed to ultrasonic irradiation at −30 °C for an appropriate time, monitoring the reaction progress by TLC. The solvent was removed *in vacuo* and the crude product was purified by column chromatography with neutral aluminum oxide with hexane/Et2O mixtures for the corresponding characterization.

8-Trineophylstannyltricyclo[8.4.0.0^{2,7}]tetradeca-4,9-diene-3,6-dione (9): quantitative yield, $[\alpha]_D^{25} -18.71°$ ($c = 0.7$, $CHCl_3$).

4-Trineophylstannylbicyclo[4.4.0]dec-5-en-2-yl-cyanide (10). 49% yield after purification.

2.2.3. Method C

To a solution of organocatalysts (0.5 mmol) and the corresponding dienophile (2.5 mmol) in dry toluene (0.5 mL) (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl)stannane (**1**, 1.56 g, 2.5 mmol) was added under argon atmosphere. The solution was stirred at −30 °C for an appropriate time, monitoring the reaction progress by TLC. The solvent was removed *in vacuo* and the crude product was purified by column chromatography with neutral aluminum oxide with hexane/Et2O mixtures for the corresponding characterization.

4-Trineophylstannyl-1,3,3a,4,6,7,8,9,9a,9b-decahydrobenzo[e] isobenzofuran-1,3-dione (8): quantitative yield, $[\alpha]_D^{25} -20.17°$ ($c = 0.6$, $CHCl_3$).

Methyl-2-methyl-4-trineophylstannylbicyclo[4.4.0]dec-5-ene-2-carboxilate (11). 25% yield after purification, $[\alpha]_D^{25} -53.0°$ ($c = 0.3$, $CHCl_3$).

2.3. Typical procedure for Diels–Alder reactions using $CHCl_3$ as catalyst (method **D**)

Over a solution of (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl) stannane (**1**, 1.56 g, 2.5 mmol) in dry chloroform (6 mL) under argon atmosphere, the corresponding dienophile (2.5 mmol) was added. The solution was stirred at 15 °C for an appropriate time, monitoring the reaction progress by TLC. The solvent was removed *in vacuo* and the product was isolated by column chromatography with silica-gel 60.

3. Results and discussion

It has been demonstrated that a great number of Lewis acids have been used to promote Diels–Alder reactions with excellent enantioselectivity [15]. In previous work [11] we studied the synthesis of a variety of functionalized allyltin derivatives in high yields through a "one pot" hydrostannation–Diels–Alder reaction as precursors of analogs of non-steroidal compounds acting as selective receptor modulators in the treatment of pathologies such as obesity, diabetes and inflammatory processes. The regio- and stereochemistry of the proposed structures were defined through a detailed spectroscopic analysis and molecular modeling. Stereo defined allyltin derivatives are important tools in organic synthesis because they are useful ligand transfer agents through Stille reactions leading to compounds having proved or potential pharmacological applications [16–20]. Due to the interest of these analogs, the importance of optimmizing the route to obtain these precursors and the increasing interest in asymmetric organocatalysis, we now report the results obtained in catalytic asymmetric Diels–Alder reactions using (**1**) as the precursor diene together with substituted dienophiles in the presence of 20 mol% of (4R,5R)-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanol (TADDOL, **I**) and TADDOL analogs (4R,5R)-α,α,α′,α′-tetra(1-naphtyl)-1,3-dioxolane-4,5-dimethanol (**II**) and (4R,5R)-α,α,α′,α′-tetra(9-phenantryl)1,3-dioxolane-4,5-dimethanol (**III**) as organic catalysts with the aim to improve the efficiency, stereoselectivity and yield of the reaction (Fig. 1). The asymmetric structures of these TADDOL derivatives have been found to have a great influence on both the rate and the enantioselectivity in [4 + 2] cycloadditions. In previous studies, it has been reported the use of (4R,5R)-α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOLs) as a catalyst in Diels–Alder reactions between amino siloxy dienes and substituted acroleins with good yields and enantiomeric excesses up to 92% [21,22]. It is well known that TADDOL catalyzes these reactions *via* a concerted mechanism where the intramolecular hydrogen bridge between the two hydroxylic groups of the catalyst would favor the intermolecular hydrogen bond with the carbonyl group of the dienophiles promoting an increase on the activation of them [23,24]. It is important to consider that this type of catalytic reaction *via* hydrogen bond is not very common in organic synthesis because Lewis acids-metallic salt complexes are used in most of the cases.

In this work, the cycloaddition reactions were carried out under four different reaction conditions (methods **A**, **B**, **C** and **D**) with the catalysts **I**, **II** and **III**, previously mentioned (Fig. 2). It is important to note that no catalyst is used in method **D** in order to study the effect of chloroform as the solvent reaction taking into account that previous studies showed the catalytic effect of this solvent as an increase in the reaction rate compared with those made in aprotic solvents like acetonitrile [25]. The results obtained are shown in Table 1. As can be observed, the reactions that took place with catalyst **II** were, undoubtedly, the best. In the case of entry 1, 80% yield of methyl-4-trineophylstannyl-bicyclo[4.4.0]dec-5-ene-2-carboxylate (**7**) was obtained after 24 h of reaction under method **A** conditions. Similar results were found with the same method using catalyst **III** but after almost 3 days. When the reaction was carried out with dienophile **3** (entry 2), method **C** probed to be excellent for the synthesis of 4-trineophylstannyl-1,3,3a,4,6,7,8,9,9a,9b-decahydrobenzo[e]isobenzofuran-1,3-dione (**8**) in quantitative yield after 12 h. Here, it has to be considered that methods **A** and **B** worked very well too but with slightly minor yields (80 and 95% respectively). In the case of using benzoquinone as dienophile (**4**, entry 3) all three catalysts were extremely efficient and 8-trineophylstannyltricyclo[8.4.0.0^{2,7}]-tetradeca-4,9-diene-3,6-dione (**9**) was obtained quantitatively in all cases except when TADDOL (**I**) was used under method **A** conditions (85%). Besides, when (4R,5R)-α,α,α′,α′-tetra(1-naphtyl)-1,3-dioxolane-4,5-dimethanol (**II**) was used under method **B** conditions, only 2 h of reaction were needed to complete it. In general, all reactions performed under ultrasonic radiation reached equilibrium or were completed in a shorter time, as expected.

In previous studies [11], we obtained 4-trineophylstannylbicyclo [4.4.0]dec-5-en-3-yl cyanide (**10**) and methyl-2-methyl-4-trineophylstannylbicyclo[4.4.0]dec-5-ene-2-carboxilate **(11)** products as enriched mixtures of the "*meta*" adducts that were unable to separate from the *ortho* isomers (**10′** and **11′**). Now, and for our great satisfaction, dienophile **5** gave only one product **10** in the cycloaddition reaction

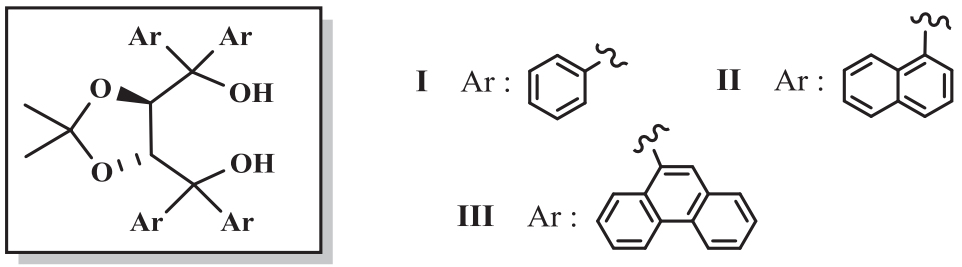


Fig. 1. Organic catalysts **I**–**III** used in the Diels–Alder cycloaddition.

when catalyst **II** was employed under methods **A** and **B**, and methyl-2-methylacrylate (**6**) yielded adduct **11** as the only product with catalyst **II** under method **C** conditions, although in low yields in both cases. Analysis of the ^{119}Sn NMR spectra showed that the "*meta*" adducts **10** and **11** were the unique regioisomers. The lower reactivity of dienophile **6** could be attributed to the presence of a methyl substituent in the alpha position. In the case of acrylonitrile (**5**), very low or no reactivity is observed, probably due to the existence of a weaker H bond between the OH group from TADDOL and the nitrogen atom of acrylonitrile.

After the purification of the corresponding cycloadducts, we intended to determine the enantiomeric excess (e.e.) of the products obtained through the best cycloaddition reactions, that is, those which gave the best performance (yields >40% and/or single products) by gas chromatography (GC) on a commercially available CHIRALDEX B-PM chiral capillary column. The initial parameters were selected based on the information provided in the CHIRALDEX Handbook [26]. In the cases of entries 4 and 5, as the mixtures of **10**–**10′** and **11**–**11′** cannot be separated, only the chiral CG chromatograms corresponding to the cases in which only one regioisomer is obtained are informed (entry 4, method A, catalyst II; entry 4, method B, catalyst II and entry 5, method C, catalyst II). All the optimized GC-traces after varying and testing different chromatography conditions are shown in the Supplementary Data.

In order to compare these results with those previously reported, we registered the chiral GC chromatograms for the products obtained in the cycloadditions reactions under $AlCl_3$ catalysis ($AlCl_3$, CH_2Cl_2, −78 °C) and under thermal conditions (PhH, hydroquinone, 80 °C). These products must be racemic, since no chiral reagent is used, so they are separated into two enantiomers in an approximately 50:50 ratio, as can be seen from the corresponding GC traces. The same chromatographic conditions were now used to study some selected organocatalyzed reactions. In the case of the Diels–Alder reaction between diene **1** and methyl acrylate (entry 1, Table 1), the GC traces were determined for the organocatalyzed reactions using method A ($CHCl_3$ and 15 °C) with organocatalysts **I**, **II** and **III**. In all three cases, there seems to be only one peak corresponding to adduct **7**. Regarding the organocatalyzed cycloadditions between diene **1** and quinone (entry 3, Table 1) and diene **1** with maleic anhydride (entry 2, Table 1), the chiral-GC traces were registered for all the reactions, this is method A ($CHCl_3$ and 15 °C), method B (toluene, −30 °C, ultrasound) and method C (toluene, −30 °C) using the three catalysts (**I**, **II** and **III**) for each reaction conditions. As can be seen from the chromatograms traces, the quality is not so good for those corresponding to adduct **8** (may be except for method A with catalyst **I**). This is probably because the products are coming off the column very fast (*ca.* 1.3 min) and so it is not possible to guarantee that enantioselective separation is taking place. For adduct **9**, almost all cases show seemingly only one straight peak, with the exception of those registered for method B when using catalyst **II** and method C with catalyst **I**, which are rather broad. At this point it is important to say that although the chiral GC traces showed are the best that could be registered after a great number of injections and although it seems to be only one peak in most of the cases, we cannot guarantee that this is a strong evidence of the presence of only one enantiomer because the concentration (regarding the peak areas) that should be used is very high. Because of this, may be the two enantiomers were simply not separated probably due to some column overload. Unfortunately, more diluted samples gave very bad GC traces that were impossible to integrate because of the broadness of the peaks and the jagged base line.

As it was mentioned before, in the case of entry 4, the chromatograms corresponding to method A/catalyst **II** and method B/catalyst **II** were registered for adduct **10**, but the presence of two broad peaks could suggest the existence of more than one stereoisomer. Regarding entry 5, there is only one chiral GC trace registered for the cycloaddition reaction between diene **1** and methyl-2-methylacrilate (method C, catalyst **II**) because adduct **11** was obtained as one stereoisomer (according to ^{119}Sn spectra) just under this unique reaction conditions, but in very low yield. Again, there is one peak in GC trace but too broad to give accurate information. Although different chromatographic conditions were tested in the last two cases, the peaks in the GC traces are too broad and the problem could not be solved efficiently.

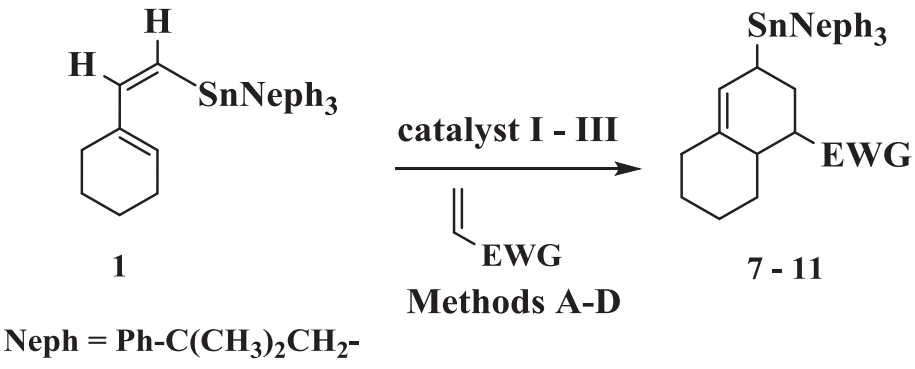


Fig. 2. Diels–Alder cycloaddition between dienylstannane **1** and activated dienophiles **2**–**6** with catalysts **I**–**III**.

Besides, and with the aim of having more information, we determined the corresponding optical rotation of the purified adducts (**7**, **8**, **9** and **11**) obtained in the organocatalyzed Diels–Alder reaction. The fact that they have an optical rotation value different to zero would suggest that the sample is not racemic and that some asymmetric induction is taking place. At this point it is important to note that we assume that there is no mixture of endo/exo adducts because the ^{119}Sn NMR spectra of the organocatalyzed crude reaction showed only one chemical shift value corresponding to the adducts (see Supplementary Data) so it is possible to suggest that the organocatalyzed cycloaddition gave only the *endo* adducts. The existence of a mixture of endo/exo diastereomeric adducts would have shown two different signals in the ^{119}Sn NMR spectra corresponding to the products (although very close regarding the chemical shift values).

These results clearly indicate that the bulky structure of TADDOL (**I**) and TADDOL derivatives **II** and **III** have a strong influence in the regioselectivity of the cycloaddition reaction shown in this study. The presence of a trineophyltin group in the diene together with the coordination of the catalyst with the dienophile induces a transition state where the catalyst and the bulky stannyl group are as far as possible (Fig. 3a). This leads to the "*meta*" adduct as the preferred regioisomer as it was expected from our previous studies but now with better stereoselectivities under milder reaction conditions. Another important consideration is that this type of catalysts promote the course of the reaction in the same way as metal-Lewis acids, this is by coordination with the oxygen or the nitrogen from the carbonyl or nitrile group in the dienophile, lowering the energy in the LUMO. This can be achieved to the reinforcing of the *π–π stacking* interactions with one of the aromatic rings of the catalyst, especially in the case of the naphtyl moiety in TADDOL **II**, and the dienophile caused by the inter- and intramolecular hydrogen bond (Fig. 3b). The less favored stereoisomer could arise through a transition state of higher energy where the dienophile is not pre-organized for catalysis due to lack of π−π* interaction owing to steric clash between their trineophylestannyl groups and the naphthyl groups of the TADDOL catalyst (**II**) which would force the substrate to rotate away from the catalyst. The transition state would display only the corresponding H-bonds to the catalyst without the π−π* interaction leading to the preferred enantiomer. TADDOL catalyst **III** shows, in general, better yields than catalyst **I** but always lower than those observed with catalyst **II**. Even though the existence of a third aromatic ring should increase *π–π stacking* interactions and hence the regioselectivity, it is possible that the restriction in the rotation of the $Csp^3 - Csp^2(Ar)$ bond is a consequence of the important steric hindrance that the big phenantryl group exert, so the stabilizing interactions are disfavored.

Reactions carried out in the absence of catalyst (method **D**) took place with low yields (entries 1, 2 and 3) or no reaction occurred (entries 4 and 5), so in the presented cases, $CHCl_3$ exhibits a negligible catalytic effect.

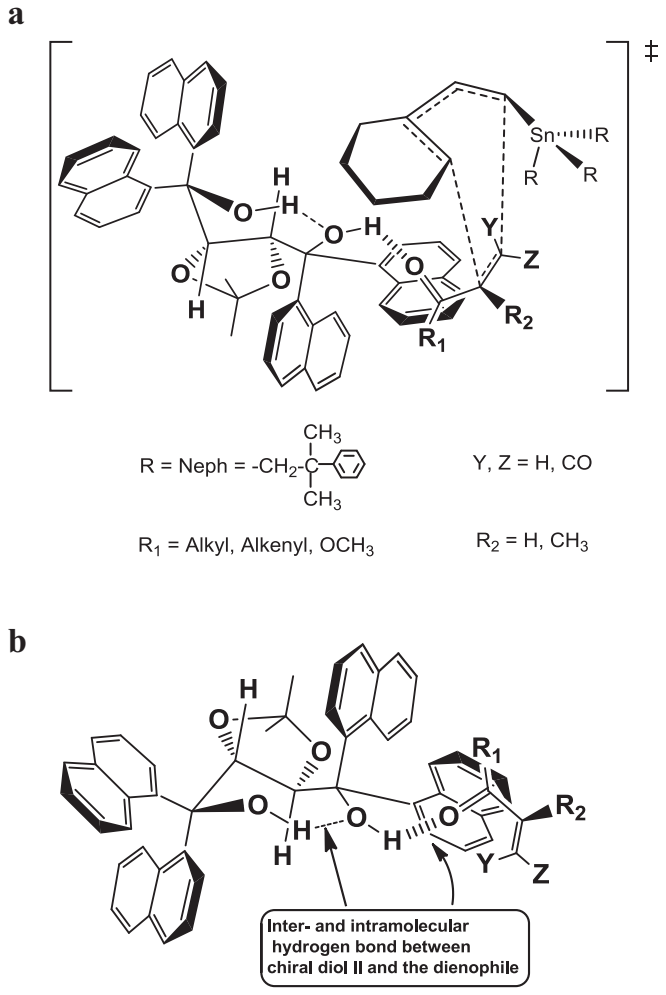


Fig. 3. Postulated transition state for the organocatalyzed Diels–Alder reaction with catalyst **II** (**a**) and hydrogen bond between the dienophile and the catalyst (**b**).

4. Conclusions

We have found that TADDOL (**I**) and TADDOL analogs (**II** and **III**) catalyzed concerted [4 + 2] cycloaddition that leads to the formation of allyltin cycloadducts, precursors of interesting biological compounds, with very good yields, low reaction times and stereoselectivity by reacting (*Z*)-2-(1-cyclohexenyl)-1-ethenyl(trineophyl)stannane (**1**) with several substituted dienophiles. The results clearly show that TADDOL has a significant beneficial effect and the fact that the products have optical rotation, should demonstrate clearly there is asymmetric induction taking place. In most cases, the TADDOL with 1-naphthyl groups (**II**) showed the best yields (>80% in almost all the experiments from entries 2 and 3, Table 1) and the best regioselectivity. Steric interactions between the aromatic rings from the catalyst and the trineophylstannyl group of the substrate together with the strong π−π* interactions and the H bond between the organocatalysts and the dienophile are believe to play a key role in the improvement of the regio- and endoselectivity of the reactions studied in this work. Besides, adducts **10** and **11**, could now be synthesized as the only cycloaddition products when catalyst **II** was employed. Mechanistic studies through computational modeling are actually underway.

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Appendix A. Supplementary data

All relevant supplementary analytical data related to this material is available free of charge *via* the Internet. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.catcom.2014.09.015.

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