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Enantioselective hydrogen transfer reactions from chiral binaphthyl variants of tin hydrides to prochiral radicals

Michael Blumenstein, Matthias Lemmler, Ahlke Hayen and Jürgen O. Metzger*

Department of Chemistry, University of Oldenburg, PO Box 2503, 26111 Oldenburg, Germany

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Abstract—Enantioselective, reagent-controlled radical reductions of prochiral alkyl radicals, mediated by binaphthyl variants of tin hydrides can be carried out in a highly selective fashion: a maximum selectivity of 68% e.e. was reached. Temperature, solvent, Lewis acid and substituent effects are selectivity-controlling elements. The reactions can be conducted catalytically with 1 mol% of chiral information and excess $NaCNBH_3$.

1. Introduction

In the past decade, a growing number of contributions concerning enantioselective radical transformations have been published, proving the potential of this reaction type after highly selective diastereoselective radical reactions had already been receiving great attention and gaining importance as synthetic tools for some time.[1] π-Facial discrimination, which is required for the enantioselective transformation of a prochiral radical or radical trap, can be achieved via two different approaches: In a complex-controlled reaction, an achiral substrate (radical or radical trap) is coordinated by or even covalently attached to a chiral reagent prior to reaction, rendering the faces of the radical diastereotopic and thus allowing the reaction to proceed through diastereomeric transition states with an overall enantioselective reaction outcome after cleavage of the auxiliary if necessary. A reagent-controlled reaction on the other hand involves a prostereogenic radical or radical trap and a chiral reagent. In this strategy, the radical's (or radical trap's) faces become diastereotopic by virtue of their association with the chiral reagent in the transition state.

Examples for complex-controlled enantioselective radical reactions have been reported since 1995,[2] and excellent enantioselectivities have been observed using this strategy, while, in the latter type of transformations, finding suitable chiral reagents as well as selectivity control seem to be more challenging. However, our research has been dedicated to this approach for some time now and we report herein about our progress specifically involving binaphthyl variants of tin hydrides as chiral hydrogen donors in enantioselective hydrogen transfer reactions.

In the history of chiral tin hydride donors, several contributions were based on terpene-derived reagents, where the tin atom was bearing for example a menthyl-group, and alkyl- or aryl-groups in addition to hydrogen.[3–5] None of these compounds were able to reduce the alkyl α-bromo phenylalkanoates, commonly used as model substrate systems with significant enantioselectivity, unless they were used in combination with sterically demanding chiral Lewis acidic auxiliaries.[6] Research in our group has been previously directed towards tin hydrides, bearing chiral 2-[(1-dimethylaminoalkyl)-phenyl] ligands. With these compounds, we demonstrated that the commonly used α-bromo alkanoates could be enantioselectively reduced with enantiomeric excess of up to 25% in radical hydrogen transfer reactions.[7]

2. Results

C_2-Symmetrical compounds have shown excellent performance in various reactions and especially the binaphthyl moiety has evolved as an important tool in stereoselective synthesis. Thus, we decided to direct our focus to the development of enantiomerically pure

* Corresponding author. Tel.: +49 (0) 441-798 3718; fax: +49 (0) 441-798 3329; e-mail: juergen.metzger@uni-oldenburg.de

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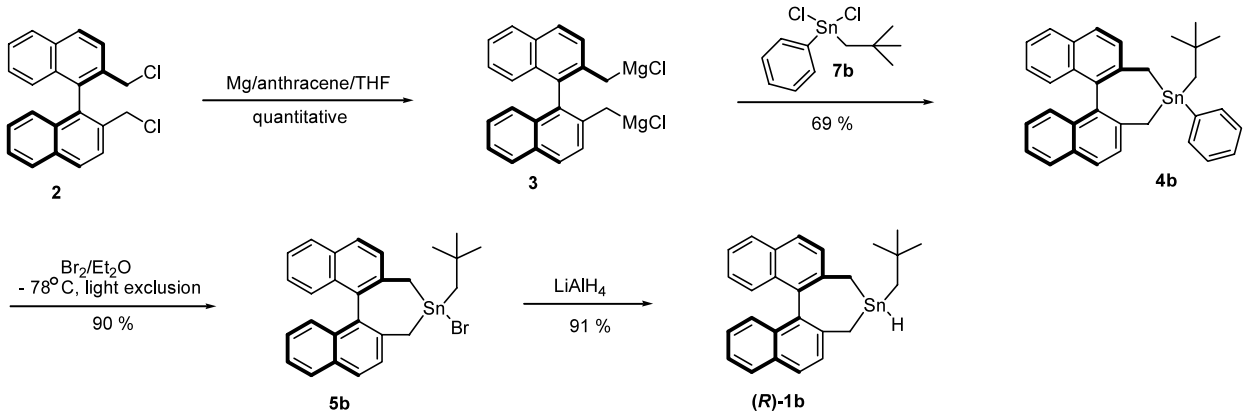


Scheme 1.

binaphthyl tin hydrides and their application in reagent-controlled enantioselective hydrogen transfer reactions. A few tin organic compounds, containing the binaphthyl unit had been described before,[8–10] but tin hydrides remained unknown.

We developed a synthetic route to alkyl-substituted binaphthyl tin hydrides, that basically allows the introduction of any alkyl substituent to the tin atom, as long as the corresponding dichloro alkylphenyl tin compound is available.[11] This method proved to be suitable for the introduction of sterically demanding groups like *tert*-butyl and neopentyl: both enantiomers of 4-*tert*-butyl-4,5-dihydro-3*H*-dinaphtho[2,1-c:1′,2′-e]stannepin **1a** as well as (*R*)-4-neopentyl-4,5-dihydro-3*H*-dinaphtho[2,1-c:1′2′-e]stannepin **1b** were synthesized. The synthetic route is exemplified for the new tin hydride **1b** in Scheme 1.

Starting point for the general synthetic scheme is the chiral ligand (*R*)-2,2′-bis-(chloromethyl)-1,1′-binaphthyl **2**, which we synthesized according to published procedures.[9,12] Enantiomeric separation was achieved by fractionated crystallization with (−)-ephedrine. Although this route might seem rather time consuming, it avoids the use of expensive catalysts. For the following Grignard-activation and reaction of binaphthyl compound **3**, the quality of the activated magnesium [magnesium-anthracene-complex, 9,10-dihydro-9,10-anthracendiyl)-tris-(tetrahydrofuran)-magnesium][13] is crucial and a subsequent successful alkylation of the dichlorotin compound **7** can already be predicted by characteristic colour changes during the reaction. Dichloro neopentylphenyltin **7b** as well as the *tert*-butyl derivative **6a** necessary for the synthesis of **1a**, were synthesized from triphenyltin chloride with neopentyl[14] or *tert*-butyl lithium, respectively, leading to the alkyl triphenyl tin derivatives **6a** and **6b**, which upon treatment with hydrochloric acid then gave **7a** and **7b**.[15] After this ring formation, in the next step the phenyl group of stannepin **4** could be selectively exchanged for bromo if the reaction with bromine was carried out in diethyl ether in high dilution instead of methanol, which is the commonly used solvent for comparable brominations.[4,11] Finally, reduction of 4-bromo-4-neopentyl-4,5-dihydro-3*H*-dinaphtho[2,1-c:1′,2′-e]stannepin **5a** with lithium alanate lead to the desired tin hydride **1b**. Yields for the synthesis of tin hydride **1a** were comparable.

Our efforts coincided with the development of a binaphthyl-derived tin hydride by Curran et al., who gained access to a similar methyl-substituted compound by a different synthetic way.[16]

^{1}H NMR-spectroscopic examination of the new tin hydrides surprisingly revealed that the hydride proton produces a doublet, so obviously coupling with at least one of the methylene protons takes place. This was confirmed by irradiation experiments.

To get a more detailed impression of the structure of the new tin hydrides, molecular modelling, based on the semiempirical PM3 method[17] (RHF—restricted Hartree Fock approach, structures were minimized with the default options available within the MOPAC 93 program package[18]) was carried out, and the result, obtained for tin hydride **1b**, is presented in Figure 1.

The selective potential of all new tin hydrides in enantioselective hydrogen transfer reactions was tested with a system of methyl bromo phenylalkanoates as substrates. Special focus was placed on temperature depen-

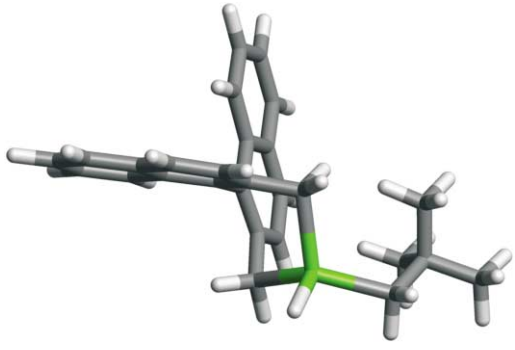
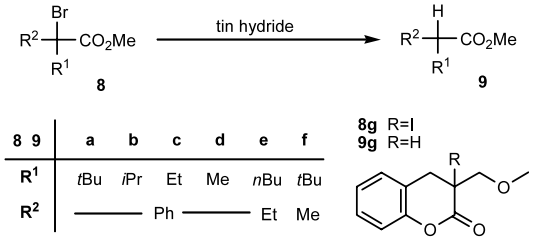


Figure 1. Preferred conformation of stannepin **1b**: the neopentyl group is pointing in the opposite direction relative to the reactive hydrogen.

dence and steric substrate effects, but solvent effects and influence of Lewis acids were examined as well. Finally, the feasibility of a catalytic reaction procedure was investigated. Scheme 2 summarizes the substrates **8** that were employed and the reduction products **9** that resulted.[3,4] The enantioselective reduction of substrate **8g** had been reported for a complex-controlled reaction before and was included here for comparison.[19,20]



Scheme 2.

All reactions at and below room temperature were carried out on an analytical scale in diethyl ether. Enantioselectivity, product yields and degree of conversion of bromo substrates were determined by gas chromatography using dodecane as internal standard. Generally, excellent yields of reduction products were obtained (>90%) and with the exception of substrates **8b** and **8f** only minimum amounts of byproducts were detectable. To ensure a complete conversion of tin hydride and for reasons of practicability, the ratio of **8** to **1a** or **1b** usually was varied between 1:1 and an excess of 3:1. In additional experiments, it had been confirmed that within this range no change in enantioselectivity occurs.[4] The reaction time, until complete conversion of tin hydride had been reached, depended on the reaction temperature and mode of addition of initiators, where applicable. At 0°C and below, the initiator system Et_3B/O_2 was added to accelerate the reaction.

The enantioselectivity of the reduction of bromo ester **8a** by tin hydride **1a** was examined over a temperature range of −110 to 110°C, and all results proved to be reproducible. Neopentyl-substituted tin hydride **1b** was tested at three different temperatures (Table 1). All reactions mediated by (*S*)-configured **1a** showed an (*R*)-selective preference in the product ratio, whereas (*R*)-**1a** and (*R*)-**1b** both favoured the formation of (*S*)-configured **9**. The enantioselectivities observed in the reaction series with **1a** correlate well with the reciprocal temperature: starting with 28% at 110°C, the selectivity increases by lowering the reaction temperature, and finally 64% e.e. are reached at −110°C. At two different temperatures, the enantioselectivities obtained by using (*R*)-**1a** or (*S*)-**1a** while applying the same conditions, respectively, were compared (entries 3/4 and 10/11, respectively). As expected, the use of opposite enantiomers of **1a** resulted in a quantitative reversal of the selectivity observed for reaction products (*R*)-**9a** and (*S*)-**9a**. This outcome also supports the reliability of the analytical determination of enantioselectivities. The results, obtained by using neopentyl-substituted tin hydride (*R*)-**1b**, indicate a somewhat lower inductive potential of this compound relative to **1a** (entries 5–7). At room temperature, only 4% e.e. were observed, whereas at −30°C, as well as at −60°C, 28% e.e. were detected.

Next, differently substituted bromo esters **8b–f** and the iodo lactone **8g** (Scheme 1) were submitted to the same reaction conditions, using tin hydride (*S*)-**1a**. As in the case of *tert*-butyl compound **8a**, for most of the substrates examined here an increase of selectivity was observed by decreasing the reaction temperature; however, selectivities were generally lower than with **8a**.

Table 1. Enantioselectivity of the radical reduction of α-bromo ester **8a**, mediated by tin hydrides **1a** and **1b** at different temperatures

Entry	H-donor	**8a**:**1**[a]	*T* [°C]	*t*[b] [h]	[(*S*)-**9a**]:[(*R*)-**9a**]	Ee %
1	(*S*)-**1a**	3:1	110[c]	3	36:64	28
2	(*S*)-**1a**	3:1	69[d]	3	35:65	30
3	(*S*)-**1a**	2:1	24	22	34:66	32
4	(*R*)-**1a**	2:1	24	16	64:36	28
5	(*R*)-**1b**	[f]	20	5	58:42	16
6[e]	(*R*)-**1b**	[f]	−30	18	64:36	28
7[e]	(*R*)-**1b**	[f]	−60	24	64:36	28
8[e]	(*S*)-**1a**	1.1:1	0	48	30:70	40
9[e]	(*S*)-**1a**	1:1	−15	48	28:72	44
10[e]	(*S*)-**1a**	1.8:1	−78	27	24:76	52
11[e]	(*R*)-**1a**	1.8:1	−78	24	76:24	52
12[e]	(*S*)-**1a**	2:1	−110	30	18:82	64

[a] The conversion of **8a** was quantitative in most cases (with reference to the ratio **8**:**1**), and yields of **9a** were usually ≥90%, referenced to the conversion of **8a**.

[b] Time until complete conversion of tin hydride was reached.

[c] The reaction was carried out in toluene.

[d] Hexane was used as solvent.

[e] Addition of 10 μL of a solution of Et_3B (15%) in hexane (entries 8–12) or diethyl ether (entries 6 and 7) at the beginning and every 4 h.

[f] **8a** was used in excess, conversion and yield were not determined.

Also, the results clearly demonstrate a steric substituent effect: when the sterical demand of alkyl substituents of **8** was reduced (**8b**: *iso*-propyl, Table 2, entries 1 and 7; **8c**: ethyl, entries 2, 8 and **8c**: methyl, entries 3 and 9), enantioselectivity levels decreased. The same applied for compounds **8e** and **8f** (entries 4, 5 and 10), where an alkyl substituent R^1 is combined with a small alkyl group R^2 instead of a phenyl group. For lactone **8g**, the best enantioselectivities in this series of different substrates were found, showing a decent product ratio of 75:25 at −110°C as well as a temperature dependent selectivity (entries 6, 11 and 12). While tin hydride (*S*)-**1a** lead to a preferential formation of (*R*)-configured products **9a**–**c** with alkylphenyl bromo esters **8a**–**c**, for dialkyl substrate **8f** (*S*)-**9** was favoured.

The results presented in Table 3 show, that the reaction and the enantioselectivity can be significantly affected by the solvent. Diethyl ether, methylene chloride and benzene obviously are very comparable, equally suitable solvents for the examined transformation: reaction times and product ratios were very similar (Table 3, entries 1–3). In toluene and hexane, a marginal extension of necessary reaction time to reach complete conversion of **1a** was observed, as well as a small increase in selectivity (entries 4 and 5). Tetrahydrofuran surprisingly is the least suitable solvent for the examined reaction, judging by the obtained product ratio of only 40:60 and although in methanol the best enantioselectivity was found, the extended reaction time of 72 h, which is probably due to the heterogeneity of the reaction caused by insolubility of the tin hydride, disqualifies this solvent (entry 7).

As Lewis acids play such an important role for stereoselectivity in complex-controlled radical reactions mediated by achiral reagents, we decided to test the influence of some of these additives on the outcome of our reactions. In Table 4, the results obtained by adding MgI_2, $MgBr_2$, the chiral, enantiomerically pure tin bromide (*S*)-**5**, or a combination of MgI_2/TMEDA to the usual reaction mixture, containing substrates **8a** or **8g**, and tin hydride (*S*)-**1a** are compiled. Obviously, in the case of substrate **8a**, neither MgI_2, nor $MgBr_2$ exerted an influence on the selectivity (Table 4, entries 2 and 3), whereas an addition of the Lewis-acidic corresponding tin bromide (*S*)-**5a** both significantly influenced reaction time and enantioselectivity: At room temperature, complete conversion was observed after only 15 min, accompanied by a slightly increased selec-

Table 2. Enantioselectivity of the radical reduction of α-bromo esters **8b**–**g**, mediated by tin hydride (*S*)-**1a** at different temperatures

Entry	**8**	**8**:**1**[a]	*T* [°C]	*t*[b] [h]	[(*S*)-**9**]:[(*R*)-**9**]	E.e. %
1	**b**	1.7:1	21	24	39:61	22
2	**c**	2:1	21	24	47:53	6
3	**d**	1.1:1	21	24	50:50	0
4	**e**	2:1	21	22	50:50	0
5	**f**	2:1	21	24	51:49	2
6	**g**	1.4:1	21	7	54:46	8
7	**b**	1:1	−78[c]	48	33:67	34
8	**c**	1.5:1	−78[c]	48	45:55	10
9	**d**	1.1:1	−78[c]	48	52:48	4
10	**f**	1.4:1	−78[c]	45	57:43	14
11	**g**	2:1	−78[c]	19	69:31	38
12	**g**	2.5:1	−110[c]	31	75:25	50

[a] The conversion of **8** was quantitative in most cases (with reference to the ratio **8**:**1**), and yields of **9** were usually ≥90%, referenced to the conversion of **8** [exceptions: entries 1 (55%), 5 (7%), 7 (47%)].
[b] Time until complete conversion of tin hydride was reached.
[c] Addition of 10 μL of a solution of Et_3B (15%) in hexane during the first 4 h of reaction time.

Table 3. Enantioselectivity of the radical reduction of α-bromo ester **8a**, mediated by tin hydride (*S*)-**1a** in different solvents at room temperature

Entry	Solvent	**8a**:**1a**[a]	*t*[b] [h]	[(*S*)-**9a**]:[(*R*)-**9a**]	E.e. %
1	Diethyl ether	2:1	22	34:66[c]	32
2	Methylene chloride	2.5:1	24	34:66	32
3	Benzene	1:1	26	34:66	32
4	Toluene	1:1	28	32:68	36
5	Hexane	1.2:1	28	31:69	38
6	Methanol	0.9:1	72	30:70	40
7	Tetrahydrofurane	2.5:1	24	40:60	20

[a] The conversion of **8a** was quantitative in most cases (with reference to the ratio of **8a**:**1**), and yields of **9** were usually ≥89%, referenced to the conversion of **8a**.
[b] Time until complete conversion of tin hydride was reached.
[c] conf. Table 1, entry 3.

Table 4. Influence of Lewis acidic additives on the enantioselective reduction of selected α-halo esters, mediated by tin hydride (*S*)-**1a** in diethyl ether at room temperature or −78°C

Entry	Additive[c]	**8**	**8**:**1a**[a]	*T* [°C]	*t*[b] [h]	[(*S*)-**9**]:[(*R*)-**9**]	E.e. %
1[d]	–	**a**	2:1	24	22	34:66	32
2	MgI_2	**a**	1.7:1	21	48	34:66	32
3	$MgBr_2$	**a**	2.2:1	21	48	32:68	36
4	(*S*)-**5a**	**a**	1:1	22	0.25[e]	30:70	40
5[d]	–	**a**	1.8:1	−78[f]	27	24:76	52
6	(*S*)-**5a**	**a**	1:1	−78[f]	45	16:84	68
7[d]	–	**g**	2:1	−78[f]	19	69:31	38
8	(*S*)-**5a**	**g**	1:1	−78[f]	45	66:34	32
9	MgI_2, TMEDA	**g**	3.6:1	−78[f]	14	51:49	2

[a] The conversion of **8a** was quantitative in most cases (with reference to the ratio of **8a**:**1**), and yields of **9** were usually ≥90% [exception: entry 9 (81%)], referenced to the conversion of **8a**.
[b] Time until complete conversion of tin hydride was reached.
[c] Molar ratio of additive to substrate app. 1:1.
[d] Conf. Tables 1 and 2.
[e] Complete conversion after 15 min, the enantiomeric ratio was observed for 20 h and did not change.
[f] Addition of 10 μL of a solution of Et_3B (15%) in hexane during the first 3 h of reaction time.

tivity compared to the reaction without additive (entries 1 and 4) and at −78°C, the enantiomeric ratio increased from 24:66 to 16:84 in the presence of tin bromide (*S*)-**5a** (entries 5 and 6). However, substrate **8g** was reduced with lower enantioselectivity upon addition of Lewis acids (entries 7–9). No effect of deracemication was observed when racemic product **9a** was mixed with **5a** under usual experimental conditions. Also, the reduction of bromo ester **8a** by achiral tributyltin hydride in the presence of tin bromide **5a** only lead to racemic products **9a**.

By using the achiral hydride sodium cyanoborohydride we were able to carry out radical reductions enantioselectively with only catalytic amounts of chiral information (<1 mol% catalyst) for the first time (Table 5). During the reaction, chiral tin hydride (*R*)-**1a** was generated or regenerated in situ from catalytic amounts of tin bromide (*R*)-**5a** or tin hydride (*R*)-**1a** with excess $NaCNBH_3$. Curiously, the enantioselectivity level of the reduction of **8a** that could be reached by using only 1 mol% of chiral tin hydride (*R*)-**1a** in combination with excess of achiral hydride $NaCNBH_3$ (entry 2), was lower than in the case where stoichiometric amounts of the chiral reagent had been used (entry 1), while was comparable when a catalytic amount of tin bromide **5a** in connection with $NaCNBH_3$ was used as reduction system (entry 3). As observed for the stoichiometric reactions listed in Table 1, opposite enantiomers of tin bromide **5a** lead to a reversal in selectivity in the reduction of **8a** (entries 3 and 4). When the same reaction was conducted with only 0.01 mol% of tin bromide **5a**, a significantly prolonged reaction time was necessary until complete conversion of substrate **8a** had occurred and also, the enantioselectivity only reached 8% e.e. With *iso*-propyl-substituted bromo compound **8b** and with lactone **8g**, the catalytic (1 mol% tin bromide **5a**) and the stoichiometric pathways lead to comparable results, but in the case of **8b**, again an extended reaction time for complete conversion became necessary (entries 6–9).

Table 5. Enantioselective radical reduction of substrates **8a**, **8b**, and **8g**, mediated by catalytic amounts of tin hydrides (*R*)-**1a** and (*S*)-**1a** in diethyl ether at room temperature

Entry	H-donor system	**8**[a]	*t*[b] [h]	[(*S*)-**9**]:[(*R*)-**9**]	E.e. %
1	(*R*)-**1a**	**a**	16	64:36	28
2	(*R*)-**1a**, $NaCNBH_3$	**a**[c]	16	58:42	16
3	(*R*)-**5a**, $NaCNBH_3$	**a**[d]	16	63:37	26
4	(*S*)-**5a**, $NaCNBH_3$	**a**[d]	16	35:65	30
5	(*S*)-**5a**, $NaCNBH_3$	**a**[e]	48	46:54	8
6	(*R*)-**1a**	**b**	24	39:61	22
7	(*S*)-**5a**, $NaCNBH_3$	**b**[d]	48	38:62	24
8	(*R*)-**1a**	**g**	70	54:46	8
9	(*S*)-**5a**, $NaCNBH_3$	**g**[d]	70	52:48	4

[a] The conversion of **8** was quantitative in most cases, and yields of **9** were usually ≥93% [exception: entry 5 (74%)], referenced to the conversion of **8**.
[b] Time until complete conversion of tin hydride was reached.
[c] The ratio of **8** to **1a** to $NaCNBH_3$ was 100:1:300.
[d] The ratio of **8** to **5a** to $NaCNBH_3$ was 100:1:300.
[e] The ratio of **8** to **5a** to $NaCNBH_3$ was 10000:1:30000.

3. Discussion

Our experimental results show a remarkable potential for enantioselective, reagent-controlled radical reductions: the highest selectivity ever obtained in this kind of transformation was observed in the reactions of tin hydride **1a** and methyl-2-bromo-3,3-dimethyl-2-phenyl-butanoate **8a**: 64% e.e. (Table 1, entry 12) and 68% e.e. (with the addition of tin bromide **5a**; Table 4, entry 6), respectively.

Furthermore—and in contrast to the low yields reported by Nanni and Curran[16] for the enantioselective reduction of 2-bromo-1,2-diphenyl-propane-1-one by a related binaphthyl tin hydride—we generally obtained high yields of >90%, that are common for reductions mediated by achiral tin hydrides. In the case of a bromoketone as radical precursor, the formation of byproducts resulting from carbonyl group reduction seems likely to be responsible, and although we also occasionally observed somewhat lower yields—primarily for reactions involving bromo ester **8f**—we do not think that this is a matter of reduction of the ester function, but rather of subsequent reactions.

A more detailed look into our results reveals, that at room temperature only *tert*-butyl- and *iso*-propyl-substituted bromo esters **8a** and **8b**, respectively, are reduced with enantioselectivities higher than 10% e.e., whereas **8c**–**f** obviously do not fulfill a certain sterical minimum size requirement of substrate for a sufficient selective interaction with the tin hydride (Tables 1 and 2).

Lactone **8g** cannot be directly compared due to its cyclic character, however, for radical precursors **8a**–**f** it can be deducted from the results, that for a sufficient stereodifferentiation certainly all substituents at the radical center need to be as different as possible concerning their sterical demand. Substrate **8f**, carrying a *tert*-butyl, a methyl and an ester group, for example, is reduced almost unselectively, while compound **8a**, that only differs in having a phenyl instead of a methyl group, is the most selectively reduced precursor.

In Figure 2, a likely transition state arrangement for hydrogen transfer from an (*R*)-configured tin hydride **1** to a radical is depicted: the linear alignment of donor, hydrogen and acceptor atoms Sn, H and C should enable a stereodifferentiation between the enantiotopic faces of the radical caused by steric interactions of all substituents. The small group S = COOMe of the radical center will most likely be oriented beneath the binaphthyl substituent and the medium sized substituent M = Ph will probably point backwards, which leaves the least hindered front space for the large substituent L = *t*Bu. In accordance with the experimental results, the situation depicted above will preferentially yield (*S*)-configured product **9**.

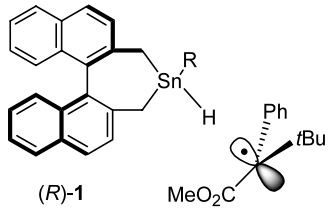


Figure 2.

Neopentyl-derived tin hydride **1b** displays a poorer performance than *tert*-butyl-substituted tin hydride **1a**, when reacted with compound **8a**. Obviously, this also is a matter of sterical factors: although the neopentyl group of **1b** is sterically more demanding overall, it also possesses a certain flexibility, whereas the more compact *tert*-butyl group of **1a** is able and forced to exert a greater influence towards the reaction center by intensifying selective interactions with the substrate (Table 1).

For all compounds investigated, the enantioselectivity increases with a decrease in reaction temperature, although the extent of this dependence differs considerably and is not correlated to the amount of selectivity. Bromo ester **8f**, for instance, exhibits a stronger temperature dependence than the much more selectively reduced substrate **8b** (Table 2). The same is true for bromo ester **8a**, compared to iodo lactone **8g**: although **8a** is reduced with much higher selectivity, the temperature impact on the enantioselectivity is more distinct for **8g**. A comparison of the binaphthyl tin hydride mediated reduction of iodo lactone **8g** with the previously reported [19] tributyl tin hydride mediated variant involving a C_2-symmetrical diamine as chiral auxiliary at −78°C reveals, that the complex-controlled transformation is superior to the reagent-controlled reaction concerning selectivity under these conditions: a ratio of 81:19 (*R*)-**9g**:(*S*)-**9g** was obtained using complex control, while **1a** as reducing agent lead to a ratio of 69:31 (*S*)-**9g**:(*R*)-**9g**.

An examination of the solvent nature with respect to the reaction outcome revealed a strong influence, as shown in Table 3 for the reduction of substrate **8a** by tin hydride (*S*)-**1a**. The highest enantioselectivity was observed in methanol and the lowest in tetrahydrofuran, while other solvents were marginally worse than methanol. The results show, that with methanol and THF on both ends of the enantioselectivity range and hexane in the middle, obviously polar effects cannot be held responsible for these findings. It can rather be assumed, that the complexing properties of the solvent play an important role: Tetrahydrofuran is an excellent complexing solvent for Lewis acids, while diethyl ether is less complexing. Methylene chloride possesses rather weak complexing properties and hexane none. The same goes for methanol, which in this case does not even solubilize tin hydride **1**. With benzene, π-stacking effects allow a small amount of complexation, that is—due to less symmetry—even weaker in toluene. The conclusion must be, that solvents with strong complexing ability for Lewis acids lead to a decrease in enantioselectivity by probably unfavourably interacting with the hydrogen donor.

In Table 4, the results concerning effects of additional Lewis acids on the enantioselectivity of the reduction of several substrates **8** are compiled. Especially the addition of tin bromide **5a** before reaction had a selectivity-enhancing effect, which is particularly pronounced in the reduction of bromo ester **8a** at −78°C (Table 4, entry 6), but can also be observed at rt (entry 4). In contrast, in the reduction of **8g** the enantioselectivity is decreased, compared to the reaction without additive (entries 7 and 8). A subsequent alteration of the reduction product composition by tin bromide **5a** can be ruled out, because no effect was observed when racemic product **9a** was mixed with **5a** under usual experimental conditions. Also, the reduction of bromo ester **8a** by achiral tributyltin hydride in the presence of tin bromide **5a** only lead to racemic products **9a**, so obviously a chiral tin hydride like **1** is mainly responsible for selectivity control, and an additive like tin bromide **5a** merely causes an amplification of enantioselectivity in conjunction with this chiral reducing agent.

Tin bromides like compound **5** possess a weak, Lewis acidic character, and Lewis acids are known for their ability to form complexes with carbonyl groups. Therefore, a coordinating interaction of **5a** with the ester function of substrates **8** can be assumed to take place in our case. As Sibi et al.[21] have found before, organo tin halides can act as weak Lewis acids and can enhance both the chemo- and the diastereoselectivity of a radical reaction. The present work shows for the first time that this probably also applies to enantioselective radical reactions.

Surprisingly, an examination of a mixture of tin bromide **5a** and bromo ester **8a** by NMR neither revealed a complexation of the carbonyl group nor a complexation via π-stacking, so exactly what kind of complexation or interaction actually takes place remains unknown. Based on the missing signal shifts in the NMR spectra, it can be assumed though, that a rather dynamic contact between tin hydride and tin bromide dominates over carbonyl complexation. However, this influence of tin bromide **5** on the tin hydride probably is rather weak, otherwise enantioselectivity would be evident in the reduction of bromo ester **8a** by achiral tributyl tin hydride in conjunction with tin bromide **5a**.

Another important finding of our research was the feasibility of enantioselective radical reductions following catalytic methodology (Table 5). Even if just 1 mol% of chiral 'catalyst' was employed, in most examples no or only a small decrease in enantioselectivity was observed compared to the experiments carried out with stoichiometric amounts of chiral tin hydride and it was even possible to convert preparative amounts of substrate (2.8 g) using the catalytic reaction variant. However, if the quantity of chiral information was further lowered to 0.01 mol% relative to the substrate, a pronounced loss of selectivity was noted.

4. Conclusion

We have developed a synthetic route to enantiomerically pure alkyl-substituted binaphthyl tin hydrides that is suited for the introduction of any kind of alkyl group. With the high yielding syntheses of both enantiomers of a *tert*-butyl variant and one enantiomer of the neopentyl-substituted compound the accessibility of this strategy was demonstrated. These new, chiral tin hydrides were used as hydrogen donors in enantioselective radical reductions, and a variety of interesting results was found. Both the encouragingly high enantioselectivities we obtained as well as the feasibility of conducting the reactions catalytically without loss of selectivity are promising features in the field of reagent controlled enantioselective radical reactions.

5. Experimental

5.1. General procedures

All reactions involving metalloorganic compounds were carried out in standard Schlenk technique under an atmosphere of dry, oxygen free argon. All commercially available reagents were employed as supplied, solvents were dried and distilled according to standard procedures. Analytical GC was performed on a Carlo Erba Vega Series GC 6000 with FID detector and 20 m DB1 capillary column or a Carlo Erba HRGC with FID detector and chiral capillary column [heptakis-(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrine phase diluted in 50% of OV-1701, 25 m or 25% 2,3-dimethyl-6-*tert*-butyl-dimethylsilyl-β-cyclodextrin phase, 30 m]. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AM 300 (^{1}H 300.1 MHz, ^{13}C 75.5 MHz and ^{119}Sn 122 MHz) or a Bruker AM 500 (^{1}H 500.1 MHz and ^{13}C 125.8 MHz) spectrometer at 20°C using TMS (^{1}H NMR), $SnMe_4$, or solvent signals as internal or external standard, respectively. Mass spectra were recorded on a Finnigan MAT 212 or a MAT 95 (HRMS). Elemental analysis was conducted by Analytische Laboratorien 51789 Lindlar. Specific rotations were measured on a Perkin Elmer polarimeter 343. Melting points were determined on a Laboratory Devices Mel-Temp apparatus and are uncorrected. Products were identified by comparison with GC retention times of independently synthesized reference compounds.

5.2. Neopentyltriphenyl tin 6b

Chlorotriphenyltin (10 g, 25.94 mmol) was suspended in 200 mL benzene. Over a time period of 6 h, 40 mL (28.6 mmol) of a solution of neopentyllithium in benzene (0.715 mol L^{-1}) were added dropwise. The mixture was stirred at room temperature overnight, then refluxed for 1 h and allowed to cool. After hydrolysis with 20 mL H_2O and phase separation, the aqueous layer was extracted with benzene and the pooled organics were dried over $MgSO_4$. Evaporation of the solvent yielded 7.65 g (70%) of **6b** as a yellow solid. Mp 52°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (9H, s), 1.75 (2H, s, $^{3}J_{H,Sn(119)} = 29.09$ Hz, $^{3}J_{H,Sn(117)} = 28.54$ Hz), 7.33 (9H,

m), 7.56 (6H, m); ^{13}C NMR (125.7 MHz, C_6D_6) δ 29.71, 31.00, 33.50 ($^3J_{C(13),Sn(117/119)}$ 18.69/18.68 Hz), 128.40 ($^2J_{C(13),Sn(117/119)}$ 23.87/25.65 Hz), 128.62, 137.07 ($^3J_{C(13),Sn(117/119)}$ 17.64/17.65 Hz), 140.18; ^{119}Sn NMR (186.501 MHz, $CDCl_3$) δ 108.51.

5.3. Dichloro *tert*-butylphenyl tin 7a

tert-Butyltriphenyl tin[15] (20 g, 0.05 mol) was heated with concentrated hydrochloric acid to 90°C for 7 min. and the mixture was then cooled immediately. Extraction with dichloro methane was followed by drying over $CaCl_2$. After evaporation of the solvent, a colourless liquid was obtained by distillation in vacuo. Yield: 12 g (74%); bp (0.03 mbar) 97°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.46 (2H, m), 7.10–7.13 (3H, m), 1.18 (9H, s, $^3J_{H,Sn(117/119)}$ = 132 Hz/138 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 138.6, 135.4, 131.5, 129.8, 43.7 [^1J (^{13}C $^{117/119}$Sn) = 545 Hz/571 Hz], 28.4; ^{119}Sn NMR (122 MHz, [D_8]toluene) δ 16.5; HRMS (isobutane, CI) calcd for $C_{10}H_{15}Cl_2Sn$ [MH$^+$] 324.9572, found 324.9567.

5.4. Dichloro neopentylphenyl tin 7b

Same procedure as for **7a**. Yield 70%; bp (0.05 mbar) 112°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (9H, s), 1.70 (2H, s, $^3J_{H,Sn(119)}$ = 36.10 Hz, $^3J_{H,Sn(117)}$ = 30.09 Hz), 7.03 (3H, m), 7.52 (2H, d, $^3J_{H,H}$ = 5.83 Hz, $^3J_{H,Sn(119)}$ = 39.02 Hz, $^3J_{H,Sn(117)}$ = 36.09 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 23.06, 32.64, 45.11, 130.72 ($^2J_{C(13),Sn(117/119)}$ 38.04/38.04 Hz), 131.28, 134.69 ($^3J_{C(13),Sn(117/119)}$ 31.48/31.62 Hz), 141.06; ^{119}Sn NMR (186.501 MHz, $CDCl_3$) δ 38.5; HRMS (isobutane, CI) calcd. for $C_{11}H_{17}Cl_2Sn$ [MH$^+$] 338.9729, found 338.9722.

5.5. 4-*tert*-Butyl-4,5-dihydro-4-phenyl-3*H*-dinaphto-[2,1-c:1′,2′-e]stannepin 4a

2,2′-Bis-(chloromethyl)-1,1′-binaphtyl[9] (**2**, 4.15 g, 11.87 mmol) was dissolved in 80 mL THF and subsequently added to 10 g magnesium-anthracene-THF complex[13] in 40 mL THF at rt over a 1 h period. Stirring was continued for 2 h. In the course of the reaction, the colour of the suspension changed from red-orange to deep green. After complete addition, a yellow suspension was obtained, which was concentrated in vacuo to a volume of 20 mL. 180 mL heptane were added, the remainder of THF was removed in vacuo, and 300 mL benzene were added. The resulting suspension was stirred for 12 h, filtered through a glass frit (P4), and the residue was washed with 100 mL heptane. The yellow solid thus obtained was dissolved in 400 mL THF and dichloride **7a** (3.85 g, 9.5 mmol) was added in one portion. Stirring was continued for 12 h, followed by addition of 500 mL diethyl ether and hydrolysis with 100 mL saturated aqueous NH_4Cl solution. After separation, the organic layer was washed twice with 200 mL H_2O, with 100 mL saturated aqueous Na_2CO_3 solution, with 100 mL brine, and concentrated. Drying over $MgSO_4$ was followed by further concentrating in vacuo, and finally the residue was purified by column chromatography (alumina 90, neutral) with diethyl ether as eluent. Yield: 4.8 g (74%); mp 165–168°C (dec.); (*R*)-**4a** $[\alpha]_D^{20}$ = +245.2 (*c* 2.31, CCl_4); (*S*)-**4a** $[\alpha]_D^{20}$ = −240.5 (*c* 1.12, CCl_4); $[\alpha]_D^{20}$ = −226.9 (*c* 1.48, Et_2O); $[\alpha]_D^{20}$ = −116.1 (*c* 1.45, C_6H_6); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.9–7.9 (17H, m), 2.21 and 2.44 (2H, AB, J_{AB} = 11.0 Hz), 2.19 and 2.56 (2H, AB, J_{AB} = 11.2 Hz), 1.18 (9H, s, $^3J_{(H,Sn(117/119)}$ = 71.1 Hz/74.3 Hz); ^{1}H NMR (300 MHz, C_6D_6) δ 6.9–7.8 (17H, m), 2.38 and 2.55 (2H, AB, J_{AB} = 11.0 Hz), 2.26 and 2.39 (2H, AB, J_{AB} = 11.2 Hz), 1.06 (9H, s, $^3J_{H,Sn(117/119)}$ = 70.4 Hz/73.5 Hz]; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 139.91, 138.35, 138.03, 136.65, 133.18, 133.10, 131.56, 131.40, 131.28, 130.91, 128.62, 128.24, 127.88, 127.73, 127.64, 127.52, 125.90, 125.83, 125.79, 125.70, 124.08, 123.91, 31.10, 30.06, 17.84, 17.07; ^{119}Sn NMR (122 MHz, C_6D_6) δ 31.5; MS (70 eV, EI) *m*/*z* (%) 534 (4) [M^+], 477 (100) [M^+−*t*Bu], 400 (4), 280 (40), 197 (58), 195 (42), 193 (26), 179 (18), 178 (8); HRMS (isobutane, CI): calcd. for $C_{32}H_{31}Sn$ [MH$^+$] 535.1447, found 535.1440; elemental anal. calcd for $C_{32}H_{30}Sn$ (533.3) C, 72.07; H, 5.67; Sn, 22.26; found C, 72.22; H, 5.61; Sn, 22.05.

5.6. (*R*)-4-Neopentyl-4,5-dihydro-4-phenyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]stannepin 4b

Same procedure as described for the synthesis of **4a**. Yield 69%; mp 160°C (dec.); $[\alpha]_D^{20}$ = +170.6 (*c* 0.55, CCl_4); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (9H, s), 1.36 (2H, d, $^2J_{H,H}$ = 11.31 Hz, $^2J_{H,Sn(117/119)}$ 18.47/18.83 Hz), 2.15–2.47 (4H, m), 7.01–7.87 (17H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 19.31, 20.57, 29.71, 32.06, 33.48, 124.04–138.01 (20 C); ^{119}Sn NMR (186.501 MHz, $CDCl_3$) δ 18.1; MS (isobutane, CI) *m*/*z* (%) 604 (100) [M+*i*Bu]$^+$; 470 (28) [M–Ph]$^+$; MS (70 eV, EI) *m*/*z* (%) 548 (32) [M^+] 477 (100) [M–neopentyl]$^+$; HRMS (EI) calcd for $C_{33}H_{32}Sn$ [M^+] 548.1526, found 548.1531.

5.7. 4-Bromo-4-*tert*-butyl-4,5-dihydro-3*H*-dinaphtho[2,1-c:1′,2′-e]stannepin 5a

Stannepin **4a** (1.4 g, 2.6 mmol) was dissolved in 50 mL diethyl ether. The solution was cooled to −78°C and under exclusion of light, bromine (400 mg, 2.5 mmol), diluted in 25 mL diethyl ether was added over a 15 min. period. Stirring at −78°C was continued for 3 h, the reaction mixture was allowed to warm to rt and the solvent was removed in vacuo. Yield: 1.28 g (91%); (*S*)-**5a**: mp 180–185°C (brown), 240–250°C (dec.); (*R*)-**5a** $[\alpha]_D^{20}$ = +74.1 (*c* 0.27, C_6H_6); (*S*)-**5** $[\alpha]_D^{20}$ = −75.3 (*c* 1.2, C_6H_6); ^{1}H NMR (500 MHz, C_6D_6) δ 6.9–7.8 (12H, m), 2.26 and 2.39 (2H, AB, J_{AB} = 11.4 Hz), 2.55 and 2.38 (2H, AB, J_{AB} = 10.8 Hz), 1.02 (9H, s, $^3J_{H,Sn(117/119)}$ = 94.1 Hz/97.9 Hz]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.9–7.9 (12H, m), 2.89 and 2.38 (2H, AB, J_{AB} = 11.3 Hz), 2.62 a. 2.41 (2H, AB, J_{AB} = 11.4 Hz), 1.28 (9H, s, $^3J_{(H,Sn(117/119)}$ = 95.1 Hz/99.4 Hz); ^{13}C NMR (125.7 MHz, C_6D_6) δ 125–136 (20C, m), 29.8, 28.1, 23.6, 21.3; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 125 – 136 (20C, m), 30.0, 28.0, 23.6, 21.2; ^{119}Sn NMR (122 MHz, C_6D_6) δ 120.0; HRMS (isobutane, CI) calcd for $C_{26}H_{26}BrSn$ [MH$^+$] 537.0240, found 537.0221; elemental anal. calcd for $C_{26}H_{25}BrSn$ (535.9) C, 58.28; H, 4.70; Sn, 22.15; found C, 58.06; H, 4.64; Sn, 21.90.

5.8. (*R*)-4-Bromo-4-neopentyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]stannepin 5b

Same procedure as described for the synthesis of **5a**. Yield 90%; mp 151°C (dec.); $[\alpha]_D^{20}=+38.1$ (*c* 0.08, benzene); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (9H, s), 1.41 (2H, d, $^2J_{H,H}=10.82$ Hz), 2.32–2.67 (4H, m), 7.0–7.9 (12H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 23.06, 32.64, 45.11, 130.72 ($^2J_{C(13),Sn(117/119)}$ 38.04/38.04 Hz), 131.28, 134.69 ($^3J_{C(13),Sn(117/119)}$ 31.48/31.62 Hz), 141.06; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.42, 23.33, 29.80, 30, 32, 124.92–136.04 (20 C); ^{119}Sn NMR (186.501 MHz, C_6D_6) $\delta=56.9$ (s); MS (isobutane, CI) *m*/*z* (%) = 606 (100) $[M+i\mathrm{Bu}]^+$; 470 (100) $[M-\mathrm{Br}]^+$; MS (70 eV, EI) *m*/*z* (%): 550 (30) [M^+], 279 (100) [M^+-neopentylSnH], 57 (85); HRMS (EI) calcd. for $C_{27}H_{27}BrSn$ [M^+] 550.0318, found 550.0318.

5.9. 4-*tert*-Butyl-4,5-dihydro-3*H*-dinaphtho[2,1-c:1′,2′-e]stannepin 1a

A solution of tin bromide **5a** (0.76 g, 1.4 mmol) in 20 mL diethyl ether was added to a suspension of $LiAlH_4$ (57 mg, 1.5 mmol) in 10 mL diethyl ether at −10°C and the mixture was stirred subsequently for 6 h at rt. Workup included addition of 0.03 mL H_2O and drying over $MgSO_4$. Yield 602 mg (93%); mp 210–220°C (brown), 290–300°C (dec.); (*R*)-**1a** $[\alpha]_D^{20}=-40$ (*c* 0.1, C_6H_6); (*S*)-**1a** $[\alpha]_D^{20}=+31$ (*c* 0.88, C_6H_6); IR (KBr) $\tilde{\nu}=1790$ cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 6.9–7.8 (12H, m), 6.0 (1H, d, $^3J=5.1$ Hz), 2.0–2.3 (4H, m), 1.01 (9H, s, $^3J_{(H,Sn(117/119)}=75.9$ Hz/78.1 Hz); ^{13}C NMR (75.5 MHz, C_6D_6) δ 125–134 (20C), 31.3, 28.3, 16.6, 16.1; MS (CI, benzene) *m*/*z* (%) = 536.2810 (36) [M^++C_6H_6], 459.4769 (2) [$M\mathrm{H}^+$+H]; HRMS (70 eV, EI) calcd for $C_{26}H_{25}Sn$ [M^+−H] 457.0985, found 457.0981; elemental anal. calcd for $C_{26}H_{26}Sn$ (457.2) C, 68.31; H, 5.73; Sn, 25.96; found C, 68.04; H, 5.60; Sn, 25.65.

5.10. (*R*)-4-Neopentyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]stannepin 1b

Same procedure as described for the synthesis of **1a**. Yield 91%; mp 200°C (brown), 250°C (dec.); $[\alpha]_D^{20}=-34.5$ (*c* 0.15, benzene); IR (KBr) $\tilde{\nu}=1740$ cm^{-1} (SnH); ^{1}H MR (500 MHz, C_6D_6) δ 1.92 (2H, m), 2.06 (9H, s), 2.45–2.51 (2H, m), 2.66–2.74 (2H, m), 5.94 (1H, d, $^3J=4.4$ Hz), 6.79–7.79 (12H, m); ^{13}C NMR (125.7 MHz, C_6D_6) δ 23.31, 24.14, 31.17, 29.27, 30.16, 125.32–138.46 (20 C); MS (isobutane, CI) *m*/*z* (%) = 470 (30) $[M-H_2]^+$; MS (70 eV, EI) *m*/*z* (%): 471 (98) [M^+−H], 279 (100) [$M^+-t\mathrm{BuSnH}$]; HRMS (EI) calcd for $C_{27}H_{27}Sn$ [M^+−H] 471.1134, found 471.1121; elemental anal. calcd for $C_{27}H_{28}Sn$ (471.22) C, 68.82; H, 5.99; found C, 69.75; H, 5.85.

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