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Synthesis of a Bolm's 2,2'-Bipyridine Ligand Analogue and Its Applications

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Abstract: A new method of synthesis of an analogue of Bolm's 2,2'-bipyridine ligand based on the catalytic [2 + 2 + 2] cyclootrimerization of 1-halodiyne with nitriles was developed. Crucial step of the whole synthesis turned out to be homodimerization of a substituted 2-bromopyridine to the corresponding bipyridine, that was studied and optimized. The newly prepared bipyridine (*S,S*)-**2** was then tested as a chiral ligand in metal-catalyzed enantioselective reactions. Out of the studied reactions the most promising results were obtained in epoxide ring opening (82% yield, 98% ee) and Mukaiyama aldol reaction (>96% yield, 99/1 dr, 92% ee). In the case of Mukaiyama-aldol reaction as well as in the Michael addition, novel ligand **2** proved its robustness compared to Bolm's ligand as it was less sensitive to the purity of used reagents.

Keywords: catalysis; enantioselective synthesis; cyclootrimerization; bipyridines; chiral ligands

1 Introduction

2,2'-Bipyridines and their derivatives form an important class of heteroaromatic compounds with application in various fields of chemistry such as supramolecular and macromolecular chemistry, photochemistry and electrochemistry but more significantly, thanks to their unique coordination abilities, as ligands able to complex almost all imaginable metals.^[1] On the contrary to regularly used phosphine or cyclopentadienyl ligands, bipyridine ligands are generally more stable both to moisture and oxidation (air), which is simplifying their synthesis, handling, and storage. In this manner bipyridines have found numerous applications in transition metal-catalyzed racemic and enantioselective reactions. For example, chiral 2,2'-bipyridine ligands have found applications in metal-catalyzed asymmetric reactions such as cyclopropanation of olefins, alkylation and allylation of

aldehydes, hydrosilylation of ketones, allylic oxidation of cycloalkenes.^[2] It is also worth mentioning that the bipyridine scaffold can be found in several natural compounds such as caerulomycins,^[3] orellanine,^[4] lavendermycin,^[5] (\pm)-streptonigrin,^[6] and (+)-complanadine^[7] (Figure 1).

One of the most comprehensively studied member of this class of compounds is diol **1** possessing the 2,2'-bipyridine scaffold (Bolm's ligand) with (*R,R*) configuration (Figure 2) that was designed and synthesized by Bolm *et al.* in 1990.^[8] The synthetic approach was slightly modified by Kobayashi *et al.* in 2005, who prepared (*S,S*)-**1**.^[9] Bolm's ligand **1** proved to be a useful chiral ligand in various types of metal-catalyzed asymmetric reactions as e.g. allylation of aldehydes,^[10] opening of epoxides,^[11,12,13] Michael addition,^[14] Mukaiyama-aldol reaction,^[15] hydroxymethylation,^[16] C–H activation of indols,^[17] and most recently Diels-Alder reaction.^[18] In addition, its complexes with non-

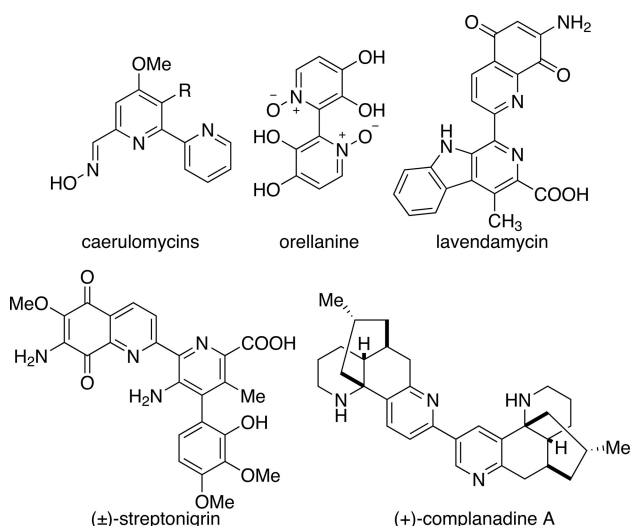


Figure 1. Natural compounds possessing the 2,2'-bipyridine scaffold.

toxic metal salts (e.g. Fe, Bi, Sc) also showed interesting behavior in the aqueous media making it an important player in the field of green chemistry.^[16,19,20]

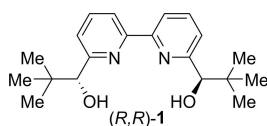


Figure 2. Bolm's 2,2'-bipyridine ligand (R,R).

Despite the abovementioned interesting results, studies of the dependence of the activity of the ligand on changes in its structure have been almost exclusively limited to the variations of the *t*-Bu part of the alcohol moiety in **1** to some other groups (Me, *i*-Pr, Ph, Naph etc.).^[9,11] Only one example of a derivative with substituents in 3,3' position (Me), was efficiently applied in alcoholysis and aminolysis of *meso*-epoxides.^[11,21]

2 Results and Discussion

Ligand design considerations. From the point of view ligand design, further elaboration of the basic skeleton of Bolm's ligand is desirable, because it could lead to development of new ligands capable of producing even higher asymmetric induction. One option is to add additional rings onto the pyridine scaffold that would restrict rotation along the C–C bond connecting the pyridine rings as in the modified Bolm's ligand **2** (Figure 3). This could potentially induce a conformationally dynamic chirality.^[22] If the pyridine rings

cannot lie in one plane, resulting conformational rigidity of the transition state will be higher. This has been already demonstrated in the case of Co^[23] or Re^[24] complexes, and may serve as typical examples. In addition, it is reasonable to expect that the presence of an alkyl group in the 3 and 3' as well as 4 and 4' positions would increase, through its inductive effect, electron density on the nitrogen atom^[25,26] and thus enhance the coordination to a transition metal. In this respect it has been noticed that the presence of alkyl group in the positions 3 and 3' and as well as 4 and 4' of the bipyridine ligand had a positive effect on the performance of Cr-bipyridine catalytic system.^[27]

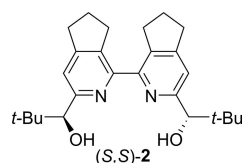
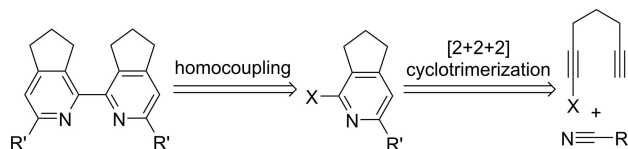


Figure 3. Bolm's ligand analog **2**.

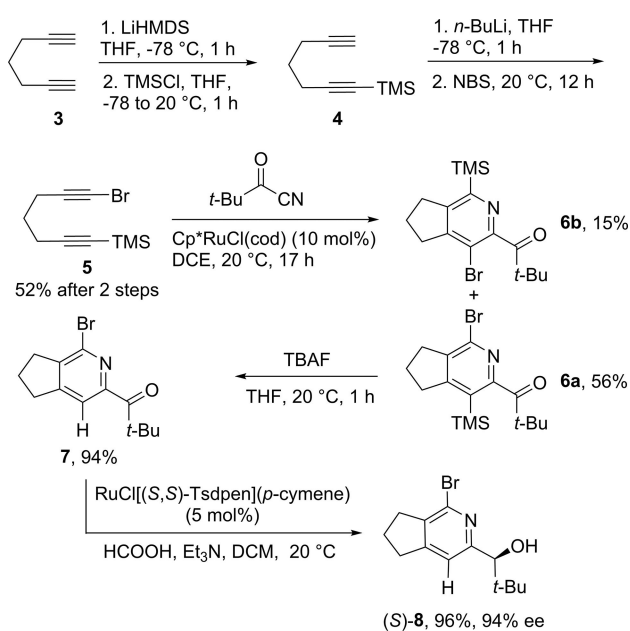
Our intended approach to the modified Bolm's ligand was based on the following retrosynthetic analysis (Scheme 1): a) catalytic homocoupling of a bicyclic 2-halopyridine that in turn could be prepared by b) catalytic cyclotrimerization of 1-halohepta-1,6-diyne with electron-poor nitriles. We have recently developed a new type of Ru-complex catalyzed [2+2+2] cyclotrimerization of halodiyne with electron-poor nitriles,^[28] which would support this approach.



Scheme 1. Retrosynthetic analysis of an approach to a modified Bolm's ligand.

Synthesis of ligand 2. Starting hepta-1,6-diyne **3** was deprotonated with LiHMDS followed by reaction with trimethylsilyl chloride to furnish the monosilylated diyne **4**. Its subsequent deprotonation with *n*-BuLi and reaction with NBS provided diyne **5** in 52% isolated yield after two steps (Scheme 2). It should be noted that the standard conditions for the synthesis of bromoalkynes by using AgNO₃, NBS could not be applied, because of the unwanted removal of the TMS-group during the course of the reaction. Ensuing cyclotrimerization of diyne **5** with pivaloyl cyanide under the standard conditions^[28] (Cp*RuCl(cod) (10 mol%), dichloroethane, 20 °C) provided a mixture

of two regioisomers **6a** and **6b** in 3.5:1 ratio furnishing the former in 56% and the latter in 15% isolated yields. As expected, the desired regioisomer **6a** was formed preferentially. Unfortunately, the use of a simpler starting material such as 1-bromo-1,6-heptadiyne was not feasible, because of undesirable homocyclotrimerization. The TMS-group was then removed by treatment with tetrabutylammonium fluoride yielding ketone **7** (94%). It was necessary to remove the TMS-group prior to the reduction of the carbonyl, because its steric hindrance hampered the reaction. Ketone **7** was then reduced by enantioselective transfer hydrogenation catalyzed by $\text{RuCl}[(S,S)\text{-Tsdpen}](p\text{-cymene})$ ^[9] to the chiral alcohol **8** (96%, 94% ee). Its absolute *S* configuration was unequivocally confirmed by a single crystal X-ray analysis^[29] (Figure 4).



Scheme 2. Synthesis of (*S*)-**8**.

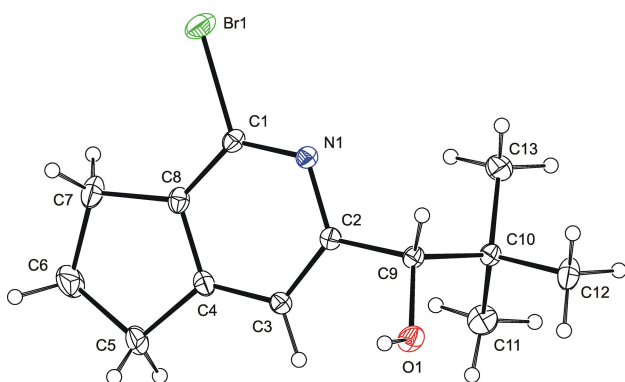


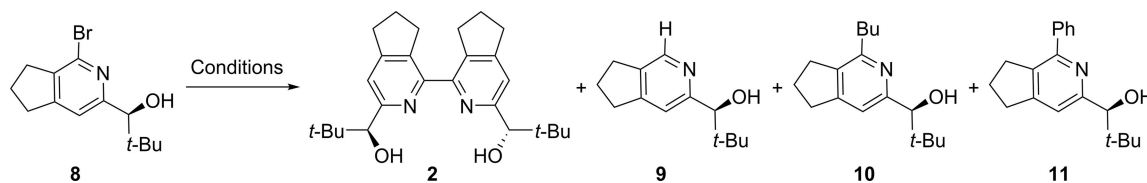
Figure 4. View on the molecule of **8**. Displacement ellipsoids are drawn on 30% probability level.

The crucial step of the whole pathway to bipyridine **2** was the reductive dimerization of (*S*)-**8**. Although, a plethora of various conditions for homocoupling of pyridines has been reported, they mainly deal with simple 2-halopyridines.^[30] Moreover, it was observed that yields were highly dependent on the structure of the starting halopyridine. Out of a number of available reaction conditions four best (in terms of yields) were selected to screen the homocoupling of (*S*)-**8** (Table 1). Among these belong: a) Pd(0)-catalyzed homocoupling by using Pd(II)/tetrakis(dimethylamino)ethylene (TDAE) (Entry 1) the original method used by Kobayashi *et al.* in the synthesis of Bolm's ligand **1**;^[9] b) Pd-catalyzed cross-coupling of the *in situ* generated tributylstannyl pyridine (Entry 2);^[31] c) Ni(0)-catalyzed dimerization by using a mixture of $\text{NiBr}_2(\text{PPh}_3)_2/\text{Zn}/\text{Bu}_4\text{NI}$ in THF (Entry 3);^[32] and finally, d) Ni(0)-catalyzed coupling by using a mixture of $\text{NiCl}_2/\text{Zn}/\text{PPh}_3$ in DMF (Entry 4), the original method used by Bolm *et al.* in the first synthesis of bipyridine **1**.^[8]

In all cases, the main side product was dehalogenated pyridine **9** (Table 1), the formation of this type of product was also observed in most of the published procedures. It should be noted that formation of the side product could be reduced by using carefully degassed solvents. The unexpected products were compounds **10** (formed when method b was used), and **11** (observed in method c) arising after coupling with butyl and phenyl group respectively. The highest HPLC yield (50%) of compound **2** was obtained by Ni(0)-catalyzed homodimerization (Entry 4), but because of the complicated separation, the product was isolated in just 35% yield.

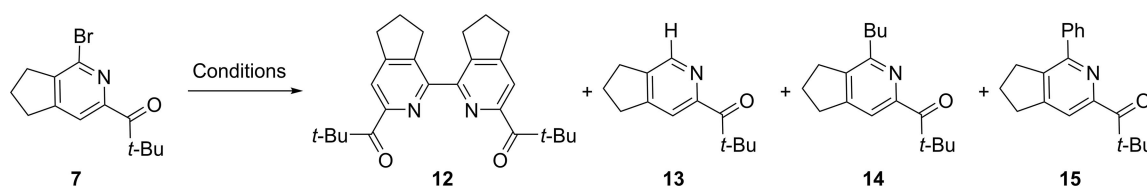
Although in most of the publications studying the dimerization of similar compounds the tolerance of free hydroxyl groups is described, in our hands the reactions proceeded only in low to moderate yields (Entries 1–4 Table 1). We decided to study homocoupling of ketone **7** to diketone **12** with intent to reduce it to the diol afterwards. Homocouplings were carried out under the same reaction conditions as in the above mentioned cases (Table 2). The yields of diketone **12** obtained under the used conditions were improved in all cases and the best yield of **12** (70% HPLC yield, 66% isolated yield) was obtained when the catalytic system composed of a mixture of $\text{NiCl}_2/\text{Zn}/\text{PPh}_3$ was used (Entry 4). Surprisingly, the next step, proved to be more challenging.

Although the racemic reduction of diketone **12** by using NaBH_4 provided a mixture of *rac* and *meso* product in 90% combined isolated yield (See SI), enantioselective reduction turned out to be more challenging (Table 3). Reduction with (–)- Ipc_2BCl brought about no conversion of the starting material (Entry 1). On the other hand, transfer hydrogenation by using 5 mol% of $\text{RuCl}[(S,S)\text{-Tsdpen}](p\text{-cymene})$ ^[9]

Table 1. Reductive dimerization of alcohol (*S*)-**8** to diol (*S,S*)-**2**.

Entry	Catalyst	mol%	Additives 1	Additives 2	Solvent	T (°C)	t (h)	Yield (%) ^[a]			
								2	9	10	11
1	PdCl ₂ (PhCN) ₂	20		TDAE (2 eq.)	DMF	80	120	30	60	ND	ND
2	Pd(PPh ₃) ₄	20+10	(<i>n</i> -Bu) ₆ Sn ₂ (1.15 eq.)	–	toluene	MW 150+180	2+2	10	35	35	ND
3	NiBr ₂ (PPh ₃) ₂	100	Zn (5 eq.)	Bu ₄ Ni (5 eq.)	THF	60	48	20	60	ND	20
4	NiCl ₂	120	Zn (1.3 eq.)	PPh ₃ (4.8 eq.)	DMF	70	15	50 (35)	50	ND	ND

^[a] HPLC-yield (isolated yield). ND – not detected.

Table 2. Reductive dimerization of the ketone **7** to diketone **12**.

Entry	Catalyst	mol%	Additives 1	Additives 2	Solvent	T (°C)	t (h)	Yield (%) ^[a]			
								12	13	14	15
1	PdCl ₂ (PhCN) ₂	20		TDAE (2 eq.)	DMF	80	120	50	50	ND	ND
2	Pd(PPh ₃) ₄	20+10	(<i>n</i> -Bu) ₆ Sn ₂ (1.15 eq.)	–	toluene	MW 150+180	4+2	20	30	20	20
3	NiBr ₂ (PPh ₃) ₂	100	Zn (5 eq.)	Bu ₄ Ni (5 eq.)	THF	60	120	30	60	ND	10
4	NiCl ₂	120	Zn (1.3 eq.)	PPh ₃ (4.8 eq.)	DMF	70	16	70 (66)	30	ND	ND

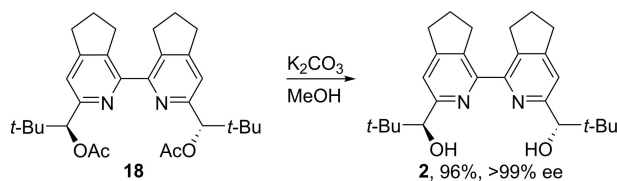
^[a] HPLC-yield (isolated yield). ND – not detected.

and HCOOH/Et₃N mixture at 20 °C gave rise to product **16**, in which only one of the ketone moieties was reduced (Entry 2). Both the higher amount of catalyst (10 mol%, Entry 3) and heating the reaction mixture to 40 °C (Entries 3 and 4) provided compound **16** in higher yields (35% and 50%, respectively), but only with traces of the desired diol **2**. Increasing the temperature to 60 °C along with 10 mol% of the Ru-catalyst finally furnished the diol **2** in excellent enantiomeric excess (97% ee), although only in a moderate yield of 48% (Entry 5).

The next strategy, for the synthesis of diol **2** in high yields, was based on homocoupling of the acetyl-protected alcohol **17**. Chiral alcohol **8** was protected to give **17** in 99% isolated yield under the standard conditions (Ac₂O, pyridine), then was homocoupled under the same four conditions as in the previous cases (Table 4). The best results were obtained again by Ni-catalyzed dimerization (Entry 4) furnishing the diacetate **18** in 68% isolated yield.

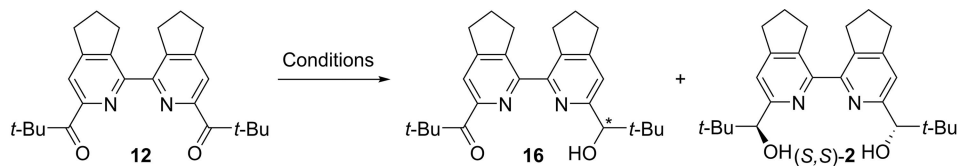
Deprotection of the hydroxyl groups gave the desired bipyridine diol **2** as an optically pure compound after isolation (Scheme 3). The *S,S* stereo-

chemistry of the furnished diol **2** was confirmed by a single crystal X-ray analysis^[29,33] (Figure 5).

**Scheme 3.** Synthesis of the target compound **2** by deprotection of the diacetate **18**.

We intended to determine the rotational barrier in compounds **2** and **12** by ¹H-NMR spectroscopy, because of speculation that the barriers might be close to that of 2,2'-dimethylbiphenyl ($\Delta G^\ddagger = 18.1$ kcal/mol at 25 °C, see Figure SI-19).^[34,35]

Although non-equivalency of the hydrogen atoms of the CH₂ groups in **2** due to diastereotopicity was observed in the spectra of compound **2** (the result of the presence of centers of chirality in the molecule),

Table 3. Transfer hydrogenation of the diketone **12** to diol **2**.

Entry	Catalyst	mol%	Reductant 1	Solvent	T (°C)	t (h)	16	Yield (%) ^[a] (S,S)-2
1	–	20	(–)-Ipc ₂ BCl	THF	20	120	NR	NR
2	RuCl[(<i>S,S</i>)-Tsdpen](<i>p</i> -cymene)	5	HCOOH, Et ₃ N	–	20	48	18	ND
3	RuCl[(<i>S,S</i>)-Tsdpen](<i>p</i> -cymene)	10	HCOOH, Et ₃ N	DCM	20	216	35 ^[b]	traces
4	RuCl[(<i>S,S</i>)-Tsdpen](<i>p</i> -cymene)	10	HCOOH, Et ₃ N	DCM	40	216	50 ^[b]	traces
5	RuCl[(<i>S,S</i>)-Tsdpen](<i>p</i> -cymene)	10	HCOOH, Et ₃ N	DCM	60	96	37	48 (97% ee)

^[a] Isolated yield unless otherwise noted. NR – no reaction; ND – not detected.

^[b] ¹H-NMR yield.

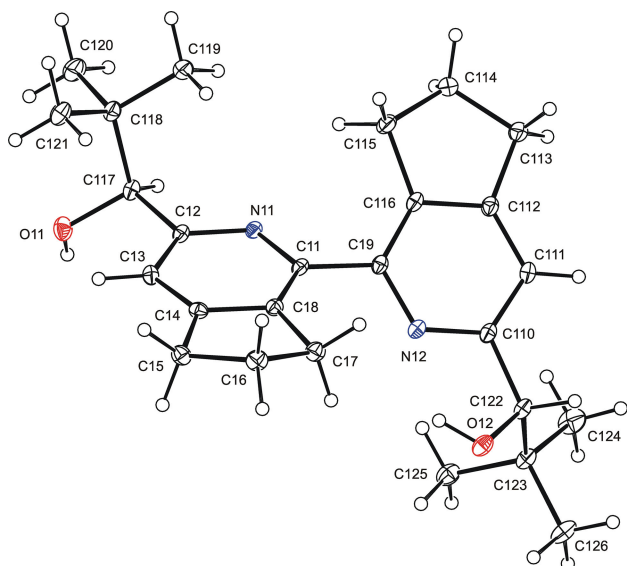


Figure 5. View on the molecule of **2**. Displacement ellipsoids are drawn on 30% probability level.

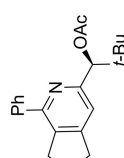
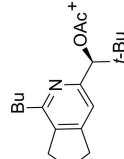
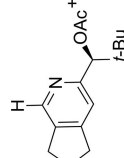
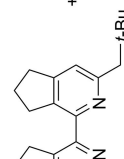
no signal splitting due to the restricted rotation around the axis of chirality in ¹H-NMR spectra of this compound as well as of compound **12** was observed even at –80 °C (Figure SI-19). This observation may be explained either by very low rotational barrier or by very small difference of resonance frequencies of the pairs of diastereotopic hydrogen atoms.

Because the ¹H-NMR determination of rotational barriers in compounds **2** and **12** was not conclusive, we performed density functional theory (DFT) calculations of the barrier in compound **2**. For a validation of the computational method, we included calculations of the rotational barrier in 2,2'-dimethylbiphenyl. An energy scan upon the rotation around the biphenyl/bipyridine main axis revealed a striking difference between compound **2** and 2,2'-dimethylbiphenyl (Fig-

ure SI-20). While 2,2'-dimethylbiphenyl has a clear maximum, which has to be passed to achieve racemization, no such maximum is apparent in the scan of compound **2**. On the other hand, the conformation with planar (antiperiplanar) arrangement of the two pyridine rings has minimal energy. This can be explained by stabilization due to extended conjugation in the planar conformation and at the same time, a decrease of steric hindrance due to missing hydrogen atoms in positions 1 and 1' in bipyridine. These data are in agreement with previously reported calculations regarding rotational barrier of 2,2'-bipyridine.^[36] Optimization of the transition-state structure of the racemization in 2,2'-dimethylbiphenyl provided the rotational barrier of 16.7 kcal/mol, which is reasonably close to the experimental value of 18.1 kcal/mol.^[34]

In order to acquire some information on chiral transition metal pre-catalyst, we tried to crystallize various transition metal salts (FeBr₃, Fe(ClO₄)₂, Bi(OTf)₃, CoCl₂, [RuCl₂(*p*-cymene)]₂, Cu(OTf)₂, Cu(BF₄)₂, CuCl₂, [CuCl(cod)]₂, Cu(MeCN)₄PF₆) with **2**. Out of these attempts only crystallizations with various Cu salts provided partially useful results. However, unlike the previous reports that described Cu complexes with **1** as monomeric species with square pyramidal,^[37] or trigonal bipyramidal^[38] geometry for Cu(II) or Y-shaped planar^[38] geometry for Cu(I), we obtained different types of species. Thus the crystallization of [CuCl(cod)]₂ with **2** provided light green crystals suitable for X-ray analysis. Interestingly, unlike in other cases of Bolm's ligand Cu-complexes, a cluster composed of four Cu atoms and two ligands **2-CuCl** was obtained^[29] (Figure 6). In addition, green crystals **2-CuX1** were obtained from other crystallization attempts with CuCl₂. It was also a cluster, but with tetragonal geometry, in which four Cu atoms were coordinated to the chloride anion (Figure SI-25). In a similar manner blue crystals were obtained by

Table 4. Reductive dimerization of acetate **17** to diacetate **18**.

Entry	Catalyst	mol%	Additives 1	Additives 2	Solvent	T (°C)	t (h)	18	19	20	21
1	PdCl ₂ (PhCN) ₂	20		TDAE (2 eq.)	DMF	80	48		60	ND	ND
2	Pd(PPh ₃) ₄	20+10	(<i>n</i> -Bu) ₆ Sn ₂ (1.15 eq.)	–	toluene	MW	2+2		40	20	30
3	NiBr ₂ (PPh ₃) ₂	100	Zn (5 eq.)	Bu ₄ Ni (5 eq.)	THF	60	48		30	ND	20
4	NiCl ₂	120	Zn (1.3 eq.)	PPh ₃ (4.8 eq.)	DMF	70	14		70 (68)	30	ND

^[a] HPLC-yield (isolated yield). ND – not detected.

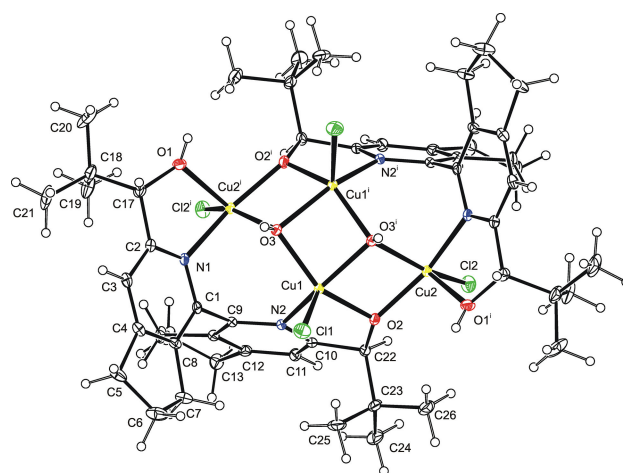


Figure 6. View on the molecule of **2-CuCl**. The displacement ellipsoids are drawn on 30% probability level. The solvating methanol molecules as well as second position of disordered C14 atom are omitted for clarity. The complex exhibits the symmetry of two fold axis of the space group *C*₂, therefore position of half of the atoms are generated via operation with symmetry code (i) 1-x, y, 1-z.

crystallization of **2** with Cu(MeCN)₄PF₆. The crystals showed presence of dimeric complexes **2-CuPF₆**, each Cu atom had square pyramidal geometry coordinating one ligand **2** (Figure SI-27). Unfortunately, the last two examples provided highly disordered crystals that did not allow exact determination of the structure (the obtained parameters did not meet the requirements for structure determination).

Application of **2** in enantioselective catalysis.

Application of ligand **2** in several catalytic enantioselective reactions was examined. For this purpose five typical reactions in which Bolm's ligand **1** proved its activity were chosen: a) Fe(II)-catalyzed Mukaiyama-aldol reaction,^[15,19] b) Bi(III)-catalyzed hydroxymethylation,^[20] c) Sc(III)-catalyzed Michael addition,^[14a] d) Pd(II)-catalyzed C–H activation of indols,^[17] and e) Sc(III)-catalyzed opening of the epoxides.^[13] The conditions from the literature were used without any optimization. In order to ensure comparability of the results obtained with (*S,S*)-Bolm's ligand **1** and our new analogue (*S,S*)-**2**, both of the reactions were done in parallel.

Ligand **2** was applied to iron(II)-catalyzed Mukaiyama-aldol reaction of propiophenone-derived silicon enolate ((*Z*)-trimethyl(1-phenylprop-1-enyloxy)silane) **22** and benzaldehyde, for which were selected three conditions reported by Kobayashi *et al.*^[15] and Ollevier *et al.*^[19] (Table 5). Conditions A used Fe(OTf)₂, pyridine and a ligand, all in catalytic amounts in dimethoxyethane-water mixture (DME/H₂O 9/1) at 0 °C. In conditions B the source of iron was Fe(ClO₄)₂ and benzoic acid was used instead of

pyridine in DME/H₂O 7/3. In conditions C were used Fe(II) dodecylsulfate (Fe(DS)₂), benzoic acid and a ligand in pure water at 20 °C. The reaction under conditions A with ligand **2** proceeded to give the corresponding aldol product **23** in quantitative yield with excellent diastereoselectivity (99/1) and very high enantioselectivity of 92% ee (Entry 3). The results were comparable with the reported results obtained by using Bolm's ligand **1**^[15] (Entry 1) or that carried out by us (Entry 2). The reaction was performed under conditions B by using ligand **2** provided aldol **23** in quantitative yield, good diastereoselectivity (98/2) and a good enantioselectivity of 90% ee (Entry 6) that were almost same as by using Bolm's ligand (Entries 4 and 5). It should be emphasized, that during the course of this study we found that the results of aldol reaction carried out with Bolm's ligand **1** were highly sensitive to the purity of all reactants. In order to achieve reproducible results all reactants had to be meticulously purified prior to the reactions. This can be nicely exemplified by comparison of reactions carried out with the reactants purified (distilled) prior to the reactions (see Entries 1–6) with those used as purchased (see Entries 7–10). Interestingly, the decrease in enantioselectivity was more pronounced in the cases when ligand **1** was used, than in cases when ligand **2** was used.

By using conditions C the published level of selectivity (dr 91/9, 92% ee) with Bolm's ligand **1** was not achieved and **23** was obtained in dr 88/12 and 84% ee (Entries 11 and 12).^[19] This could be attributed to difficulties encountered during the preparation of Fe(DS)₂. Gratifyingly, the use of ligand **2** gave aldol **23** with better diastereoselectivity (93/7) and enantioselectivity (88% ee) (Entry 13).

The second application was Bi(III)-catalyzed hydroxymethylation of the same silicon enolate **22** with formaldehyde (Table 6).^[20] By using ligand **2**, product

Table 6. Bi(III)-catalyzed hydroxymethylation of silicon enolate **22** with formaldehyde in the presence of Bolm's ligand **1** and ligand **2**.

Entry	Ligand	Yield (%) ^[a]	ee (%) ^[b,c]
1 ^[d]	(<i>S,S</i>)- 1	93	91
2	(<i>S,S</i>)- 1	> 96	89
3	(<i>S,S</i>)- 2	> 96	86

^[a] Isolated yields.

^[b] Determined by HPLC with a chiral stationary phase.

^[c] *S* configuration in all cases.

^[d] Data reported in ref. [20].

Table 5. Fe(II)-catalyzed Mukaiyama-aldol reaction of silicon enolate **22** and benzaldehyde in the presence of Bolm's ligand **1** and ligand **2**.

Entry	Cond. ^[a]	Ligand	Yield (%) ^[b]	dr (<i>syn/anti</i>) ^[c]	ee (%) ^[d,e] (<i>syn</i>) ^f
1 ^[f]	A	(<i>S,S</i>)- 1	90	97/3	91
2	A	(<i>S,S</i>)- 1	> 96 ^[c]	97/3	93
3	A	(<i>S,S</i>)- 2	> 96	99/1	92
4 ^[f]	B	(<i>S,S</i>)- 1	85	97/3	88
5	B	(<i>S,S</i>)- 1	95 ^[c]	97/3	91
6	B	(<i>S,S</i>)- 2	> 96	98/2	90
7 ^[g]	A	(<i>S,S</i>)- 1	> 96 ^[c]	95/5	86
8 ^[g]	A	(<i>S,S</i>)- 2	96	97/3	92
9 ^[g]	B	(<i>S,S</i>)- 1	> 96 ^[c]	96/4	76
10 ^[g]	B	(<i>S,S</i>)- 2	90	97/3	83
11 ^[h]	C	(<i>S,S</i>)- 1	80	91/9	92
12	C	(<i>S,S</i>)- 1	88 ^[c]	88/12	84
13	C	(<i>S,S</i>)- 2	87	93/7	88

^[a] Conditions A: Fe(OTf)₂ (3 mol%), pyridine (7.2 mol%), ligand (3.6 mol%), DME/H₂O 9/1, 0 °C.^[15] Conditions B: Fe(ClO₄)₂ (3 mol%), PhCOOH (3.6 mol%), ligand (3.6 mol%), DME/H₂O 7/3, 0 °C.^[15] Conditions C: Fe(DS)₂ (5 mol%), PhCOOH (5 mol%), ligand (15 mol%), H₂O, 20 °C.^[19]

^[b] Isolated yields unless otherwise noted.

^[c] Determined by ¹H-NMR.

^[d] Determined by HPLC with a chiral stationary phase.

^[e] *S,S* configuration in all cases.

^[f] Data reported in ref. [15].

^[g] Reactants were not purified prior to the reaction.

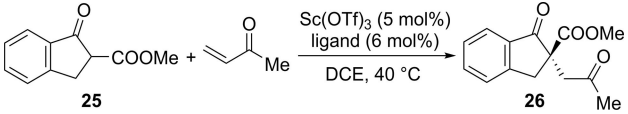
^[h] Data reported in ref. [19].

24 was furnished in quantitative yield and 86% ee (Entry 3) a result similar to the one obtained with Bolm's ligand (Entry 2).

Ligand **2** was also used in Sc(III)-catalyzed Michael addition of β-ketoester **25** to methyl vinyl ketone (MVK) in dichloromethane (Table 7).^[14a] The Michael adduct **26** was obtained in quantitative yield and 81% ee (Entry 3), while using Bolm's ligand **1** its yield was 94% and 90% ee (Entry 2). However, without drying of Sc(III) triflate and distillation of MVK prior to use ee dropped to 67% (Entry 4). On the other hand, under the same conditions using ligand **2** ee remained unchanged at 81% (Entry 5).

Ligand **2** was also tested in C–H activation of indol **27** followed by conjugated addition to **28** catalyzed by Pd(II) in the presence of dodecyl sulfate salt in water (Table 8).^[17] In this case were the yield and ee of product **29** noticeably lower (69%, 72% ee, Entry 3) compared to the use of Bolm's ligand (94%, 89% ee, Entry 2).

Table 7. Sc(III)-catalyzed Michael addition of β -ketoester **25** and MVK in the presence of Bolm's ligand **1** and ligand **2**.



Entry	Ligand	Yield (%) ^[a]	ee (%) ^[b,c]
1 ^[d]	(<i>S,S</i>)- 1	94	92
2	(<i>S,S</i>)- 1	94 ^[e]	90
3	(<i>S,S</i>)- 2	> 96	81
4 ^[f]	(<i>S,S</i>)- 1	> 96	67
5 ^[f]	(<i>S,S</i>)- 2	> 96	81

^[a] Isolated yields unless otherwise noted.

^[b] Determined by HPLC with a chiral stationary phase.

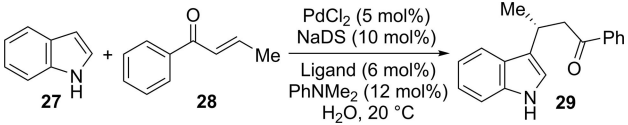
^[c] *R* configuration in all cases.

^[d] Data reported in ref. [14a].

^[e] ¹H-NMR yield.

^[f] Reactants were not purified prior to the reaction.

Table 8. Pd(II)-catalyzed C–H activation of indol **27** in the presence of Bolm's ligand **1** and ligand **2**.



Entry	Ligand	Yield (%) ^[a]	ee (%) ^[b,c]
1 ^[d]	(<i>S,S</i>)- 1	94	92
2	(<i>S,S</i>)- 1	94 ^[e]	89
3	(<i>S,S</i>)- 2	69	72

^[a] Isolated yields unless otherwise noted.

^[b] Determined by HPLC with a chiral stationary phase.

^[c] *R* configuration in all cases.

^[d] Data reported in ref. [17].

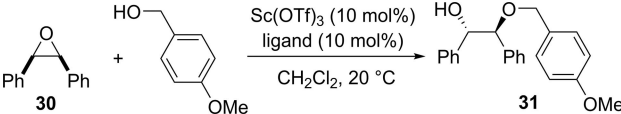
^[e] ¹H-NMR yields.

Last but not least, the activity of ligand **2** was also tested in Sc(III)-catalyzed epoxide ring opening of *cis*-stilbene oxide **30** by *p*-methoxybenzyl alcohol in dichloromethane (Table 9).^[13] By using Bolm's ligand **1**, product **31** was obtained with 90% yield (¹H-NMR) and 95% ee while using ligand **2**, product **31** was obtained in 82% isolated yield and with excellent enantioselectivity of 98%.

3 Conclusion

We have demonstrated that Ru-catalyzed cyclotrimerization of a 1-halodiyne with nitriles is a suitable reaction allowing preparation of substituted pyridines. Specifically, cyclotrimerization of (7-bromohepta-1,6-diyne-1-yl)trimethylsilane with pivaloyl cyanide provides regioselectively 1-bromo-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine that can be easily converted into

Table 9. Sc(III)-catalyzed ring opening of *cis*-stilbene oxide **30** in the presence of Bolm's ligand **1** and ligand **2**.



Entry	Ligand	Yield (%) ^[a]	ee (%) ^[b,c]
1 ^[d]	(<i>R,R</i>)- 1	82	97 ^[e]
2	(<i>S,S</i>)- 1	90 ^[f]	95
3	(<i>S,S</i>)- 2	82	98

^[a] Isolated yields unless otherwise noted.

^[b] Determined by HPLC with a chiral stationary phase.

^[c] *S,S* configuration unless otherwise noted.

^[d] Data reported in ref. [13].

^[e] *R,R* configuration.

^[f] ¹H-NMR yields.

Bolm's ligand analog **2**. One of the crucial steps along the synthetic route was homodimerization of the bromopyridine that was optimized to give a bipyridine intermediate in high yield.

As far as the use of **2** as ligand in enantioselective reactions is concerned, the results indicate its potential applicability. Although the use of **2** in hydroxymethylation, Michael addition, and C–H activation gave products with lower enantioselectivity than the reported values obtained with Bolm's ligand **1**, other reactions were more promising. The use of **2** in aldol reaction gave products within the same range of enantioselectivity as Bolm's ligand **1**. However, it should be pointed out that **2** is more robust, because it gave exactly the same results with reactants that were not purified prior to the reaction. In this instance the use of Bolm's ligand **1** gave products with decreased enantioselectivity by 6–7% ee. Its robustness was also noticed in the case of Michael addition with reactants that were not purified where the product was obtained with enantioselectivity of 81% ee, whereas with **1** the obtained ee was 67%. Gratifyingly, in the ring opening of epoxides it gave products with slightly higher enantioselectivity of 98% ee (95% ee with **1** in our hand, 97% ee the reported value).

Experimental Section

1-(1-Bromo-4-(trimethylsilyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridin-3-yl)-2,2-dimethylpropan-1-one (6a) and 1-(4-bromo-1-(trimethylsilyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridin-3-yl)-2,2-dimethylpropan-1-one (6b). To a dried argon flushed 50 mL flask with Cp**Ru*Cl(COD) (110 mg, 0.29 mmol), DCE (14 mL) followed by pivaloyl cyanide (0.7 mL, 5.8 mmol) were added. Then diyne **5** (700 mg, 2.9 mmol) dissolved in DCE (18 mL) was added slowly by the syringe pump during the course of 1 hour and the reaction mixture was stirred at 20 °C After the consumption of **5** (disappearance of the

respective spot on TLC), volatiles were evaporated under reduced pressure. Column chromatography of the residue on silica gel (gradient 10/1→2/1 hexanes/DCM) provided 566 mg (**6a**, 56%) and 151 mg (**6b**, 15%) of the title compounds as colorless solids.

6a: Mp=65.7 °C. ¹H-NMR (300 MHz, CDCl₃) δ 3.09 (t, *J*=7.6 Hz, 2H, CH₂), 2.92 (t, *J*=7.6 Hz, 2H, CH₂), 2.06 (p, *J*=7.6 Hz, 2H, CH₂), 1.41 (s, 9H, 3×CH₃), 0.28 (s, 9H, 3×CH₃). ¹³C-NMR (75 MHz, CDCl₃) δ 210.59, 162.76, 161.12, 141.90, 137.81, 130.33, 44.17, 36.91, 32.79, 28.31, 23.64, 1.69. IR (drift KBr) ν_{max} 2956, 1681, 1520, 1249, 1054, 919, 901, 845 cm⁻¹. HRMS (ESI) *m/z* calculated for C₁₄H₂₅NOBrSi (M+H) 354.0889, found 354.0889. R_f (20/1 hexane/EtOAc)=0.38.

(S,S)-1-(1-Bromo-6,7-dihydro-5H-cyclopenta[c]pyridin-3-yl)-2,2-dimethylpropan-1-ol (8). To a dried argon flushed 10 mL flask with solution of **7** (332 mg, 1.2 mmol) and RuCl[(*S,S*)-Tsdpen](*p*-cymene) (40 mg, 0.06 mmol) in DCM (1 mL), 2/1 mixture of Et₃N/HCOOH (1.8 mL) was added. After stirring for 3 days at 20 °C, the reaction was quenched with water (10 mL) and extracted with EtOAc (3×30 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. Column chromatography of the residue on silica gel (gradient 10/1→7/1 hexanes/EtOAc) furnished 319 mg (96%, 94% ee) of the title compound **8** as an amorphous solid. Optically pure compound could be obtained by crystallization from CHCl₃ by slow evaporation of solvent.

M.p.= 65.9 °C. ¹H-NMR (400 MHz, CDCl₃) δ 7.01 (s, 1H, Ar-H), 4.27 (s, 1H, CH), 3.60 (brs, 1H, OH), 3.00 (t, *J*=7.6 Hz, 2H, CH₂), 2.92 (t, *J*=7.6 Hz, 2H, CH₂), 2.13 (p, *J*=7.6 Hz, 2H, CH₂), 0.90 (s, 9H, 3×CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ 159.75, 155.84, 140.65, 137.61, 118.37, 80.47, 36.36, 33.91, 32.84, 26.01, 23.75. IR (drift KBr) ν_{max} 2956, 2903, 1598, 1541, 1453, 1415, 1364, 1238, 1108, 1063, 1016 cm⁻¹. HRMS (ESI) *m/z* calculated for C₁₃H₁₈BrNO (M) 283.0572, found 283.0580. R_f (10/1 hexane/EtOAc)=0.28. [α]_D²⁰ = +1.52° (CHCl₃, *c*=2.62 g/100 mL)

(S,S)-(6,6',7,7'-Tetrahydro-5H,5'H-[1,1'-bi(cyclopenta[c]pyridine)]-3,3'-diyl)bis(2,2-dimethylpropane-1,1-diyl) diacetate (18). To a dry argon flushed 100 mL flask with NiCl₂ (305 mg, 2.3 mmol) dry degassed DMF (13.5 mL) was added. The mixture was heated to 70 °C, then PPh₃ (2.4 g, 9.24 mmol) and Zn (166 mg, 2.5 mmol) were added. The reaction mixture was stirred at 70 °C for 1 hour, then **17** (628 mg, 1.9 mmol) in dry degassed DMF (13.5 mL) was added. After stirring for 14 hours at 70 °C, the reaction mixture was quenched with water (25 mL) and extracted with Et₂O (3×100 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. Column chromatography of the residue on silica gel (gradient 20/1→5/1 hexanes/EtOAc) furnished 321 mg (68%) of the title compound **18** as a colorless solid.

Mp=173.6 °C. ¹H-NMR (400 MHz, CDCl₃) δ 7.11 (s, 2H, 2×Ar-H), 5.56 (s, 2H, 2×CH), 3.49–3.38 (m, 2H, 2×CH), 3.14–3.03 (m, 2H, 2×CH), 2.92 (t, *J*=7.6 Hz, 4H, 2×CH₂), 2.12 (s, 6H, 2×CH₃), 2.11–1.94 (m, 4H, 2×CH₂), 1.00 (s, 18H, 6×CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ 170.43, 154.99, 154.63,

152.27, 138.88, 117.76, 84.08, 35.16, 33.01, 32.99, 26.53, 24.99, 21.32. IR (drift KBr) ν_{max} 2959, 2905, 2870, 1735, 1585, 1558, 1427, 1396, 1370, 1244, 1023, 972 cm⁻¹. HRMS (ESI) *m/z* calculated for C₃₀H₄₁N₂O₄ (M+H) 493.30608, found 493.30600. R_f (10/1 hexane/EtOAc)=0.23.

(S,S)-1,1'-(6,6',7,7'-Tetrahydro-5H,5'H-[1,1'-bi(cyclopenta[c]pyridine)]-3,3'-diyl)bis(2,2-dimethylpropan-1-ol) ((S,S)-2). To a solution of 321 mg of **18** (321 mg, 0.65 mmol) in MeOH (5 mL) in 25 mL flask, K₂CO₃ (675 mg, 4.9 mmol) was added. After stirring of the mixture for 5 hours at 20 °C, the reaction was quenched with water and extracted with DCM (4×30 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. Column chromatography of the residue on silica gel (gradient 5/1→3/1 hexanes/EtOAc) provided 254 mg (96%, >99% ee) of the title compound **2** as colorless crystals.

Mp=214.0 °C. ¹H-NMR (400 MHz, CDCl₃) δ 7.09 (s, 2H, 2×Ar-H), 4.71 (brs, 2H, 2×OH), 4.38 (s, 2H, 2×CH), 3.37–3.27 (m, 2H, 2×CH), 3.25–3.15 (m, 2H, 2×CH), 2.97 (t, *J*=7.6 Hz, 4H, 2×CH₂), 2.16–2.05 (m, 4H, 2×CH₂), 0.97 (s, 18H, 6×CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ 156.47, 155.68, 151.06, 138.76, 118.74, 80.50, 36.66, 33.10, 32.89, 26.29, 25.40. IR (drift KBr) ν_{max} 2969, 2870, 1588, 1558, 1435, 1363, 1226, 1066, 1051, 1014 cm⁻¹. HRMS (ESI) *m/z* calculated for C₂₆H₃₇N₂O₂ (M+H) 409.28495, found 409.28521. R_f (3/1 hexanes/EtOAc)=0.33. [α]_D²⁰ = -20.5° (CHCl₃, *c*=0.367 g/100 mL).

(1S,2S)-2-((4-Methoxybenzyl)oxy)-1,2-diphenylethan-1-ol (31). To a solution of Sc(OTf)₃ (15 mg, 0.03 mmol) and (*S,S*)-**2** (13 mg, 0.03 mmol) in dry DCM (1.5 mL) in 4 mL vial under the argon atmosphere were after 5 min of stirring at 20 °C subsequently added *cis*-stilbene oxide **30** (59 mg, 0.3 mmol) and *p*-methoxybenzyl alcohol (86 mg, 0.6 mmol). After 12 hours of stirring at 20 °C, the corresponding spot of stilbene disappeared, so the volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (5/1 hexanes/Et₂O) furnished 83 mg (82%, 98% ee) of the title compound **31** as colorless crystals.

The recorded values were in agreement with the published data.^[13]

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