Chiral Ligands in Hypervalent Iodine Compounds: Synthesis and Structures of Binaphthyl-based λ^3-Iodanes

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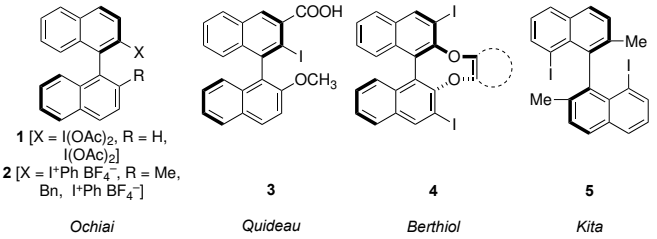
Abstract: Several novel binaphthyl-based chiral hypervalent iodine(III) reagents have been prepared and structurally analyzed. Various asymmetric oxidative reactions were applied to evaluate the reactivities and stereoselectivities of those reagents. Moderate to excellent yields were observed, however, very low stereoselectivities were obtained. The NMR experiments indicate that these reagents are very easily hydrolyzed in either chloroform or DMSO solvents leading to limited stereoselectivities. It is concluded that the use of chiral ligands is an unsuccessful way to prepare efficient stereoselective iodine(III) reagents.

Chiral hypervalent iodine reagents have attracted much attention in asymmetric oxidative reactions,[1] either as stoichiometric reagents where they are directly employed as chiral oxidants or in catalytic reactions in which the precursor iodoarenes are oxidized by a terminal oxidant to generate the hypervalent iodine compounds *in situ*. As a result, extensive efforts have been dedicated to design and synthesize hypervalent iodine compounds.[2] Among them, the introduction of iodine into chiral binaphthyl-based backbones is a strategy for this chemistry which has been pioneered by Ochiai and co-workers in 1990.[3] Binaphthyl-based scaffolds have interesting properties as a result of the orthogonal naphthyl moieties with their restricted rotation about the connecting axis.[4] Thus, they have been studied extensively as chiral catalysts,[5] chemosensors,[6] molecular hosts,[7] and high-performance materials.[8] As chiral catalysts, they can participate in a vast array of chiral transformations including Friedel-Crafts,[9] Aldol,[10] Michael addition,[11] Mannich,[12] Henry,[13] Diels-Alder,[14] Baeyer-Villiger,[15] olefin metathesis,[16] 1,3-dipolar cycloadditions,[17] and others,[18] which makes them one of the most important chiral ligands in stereoselective chemistry.

Ochiai and co-workers achieved the first synthesis of type **1** (Figure 1) and provided evidence for the pseudo-rotation at iodine .[3] They also prepared chiral iodonium salts **2** which were employed in the asymmetric arylation of *β*-keto esters.[19] (*S*)-2,2'-Diiodosyl-1,1'-binaphthalene was used in the aziridination of allylic carbamates by Xu and co-workers, although only moderate yields and low stereoselectivities were observed.[20] In 2009, Quideau and co-workers demonstrated the asymmetric hydroxylative phenol dearomatization induced by an *in situ* generated hypervalent iodine derived from the binaphthyl-based chiral iodoarene **3** with *m*CPBA as an external oxidant.[21] Some years later, Berthiol and co-workers published the synthesis of an array of diiodo-biphenol derivatives **4** (Figure 1), used as catalysts for the *α*-oxytosylation of ketones to deliver target products with moderate yields and enantioselectivities.[22] The Kita group demonstrated the nucleophilic fluorination of *β*-keto esters by using binaphthyl diiodides as catalysts in good yields although with moderate enantioselectivities.[23] The same group also synthesized the chiral 8,8′-diiodobinaphthalene **5** and applied it in the oxidative dearomatizing cyclization of a naphthol carboxylic acid.[24]

Until now, a series of binaphthyl-based chiral hypervalent iodine compounds have been evaluated in oxidative transformations, but most of them offered only moderate enantioselectivity.



1 [X = $I(OAc)_2$, R = H, $I(OAc)_2$]
2 [X = $I^+Ph\ BF_4^-$, R = Me, Bn, $I^+Ph\ BF_4^-$]

3 *Quideau* **4** *Berthiol* **5** *Kita*

Ochiai

Figure 1. Binaphthyl-based chiral hypervalent iodine compounds and iodoarene precursors.

The use of chiral ligands in hypervalent iodine chemistry has very early precedence but also very limited success. In 1986, Imamoto disclosed the asymmetric oxidation of a sulfide induced by hypervalent iodine reagents generated *in situ* by the reaction of *L*-tartaric acid anhydride with iodosobenzene.[25] In 1990, Varvoglis and coworkers prepared a camphoryl-based reagent for the oxidation of carbonyl compounds,[26] which has later been used in the stereoselective synthesis of sulfoxides with low enantioselectivities.[27]

Herein, we present the synthesis, structural elucidation, and applications of several novel chiral hypervalent iodine reagents with binaphthyl-based ligands. We envisioned that the chiral [1,1'-binaphthalene]-2,2'-dicarboxylic acid could react with λ^3-iodanes to form chiral binaphthyl-based hypervalent iodine compounds. [1,1'-Binaphthalene]-2,2'-dicarboxylic acid **6** was synthesized according to Hoshi's method in 80% yield through a lithium–halogen exchange reaction followed by carboxylation of the organolithium intermediate.[28] However, diacid **6** failed to react when exposed to iodosylbenzene, (diacetoxyiodo)benzene or [(bistrifluoroacetoxy)iodo]benzene. Dehydration to the anhydride **7** was achieved in only low yields (36-46%) using thionyl chloride[29] and phosphorus pentoxide,[30] whereas, to our delight, the yield of **7** was dramatically improved to 73% by employing a catalyst produced *in situ* from anhydrous $MgCl_2$ and *di-tert*-butyl dicarbonate (Scheme 1).[31]

The structure of the anhydride **7** was confirmed by X-ray crystallography (Figure 2a) which confirmed that the dehydration oc-

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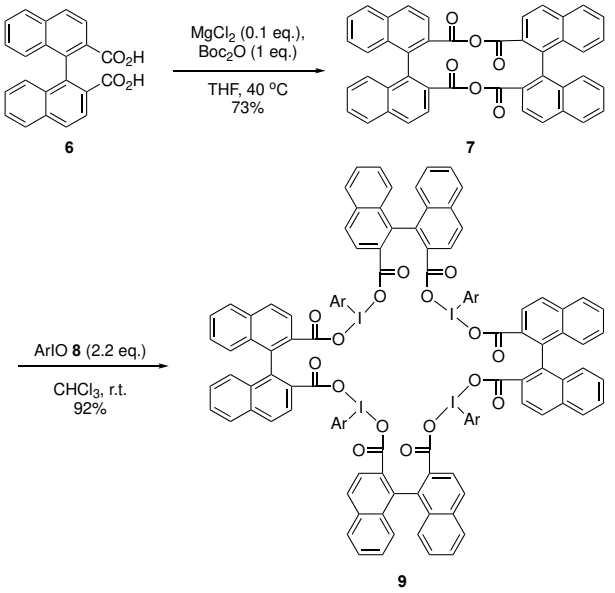
curred intermolecularly rather than intramolecularly. The subsequent reaction with iodosobenzene **8a** was unsuccessful in acetone, acetonitrile and acetic acid (Table 1, entries 1–3). Considering the very poor solubility of **7** and **8a** in these solvents, a grinding method was employed to treat **7** with **8a** directly. After 30 minutes, the desired compound **9a**, which was confirmed by X-ray crystallography (Figure 2b), was obtained in 22% yield (Table 1, entry 4). When the amount of **8a** was increased to 2.2 equivalents, the yield improved to 61% (Table 1, entry 5). Extended grinding times did not further improve the yield (Table 1, entries 6–8). We found that the acid anhydride **7** could be partially dissolved in chlorinated solvents, thus, CH_2Cl_2 and $CHCl_3$ were trialed in this reaction (Table 1, entries 9–10). Surprisingly, the reaction yield was increased to 92% when chloroform was used as a solvent. (Diacetoxyiodo)benzene and [bis(trifluoroacetate)iodo]benzene were not reactive under these reaction conditions (Table 1, entries 11–12).



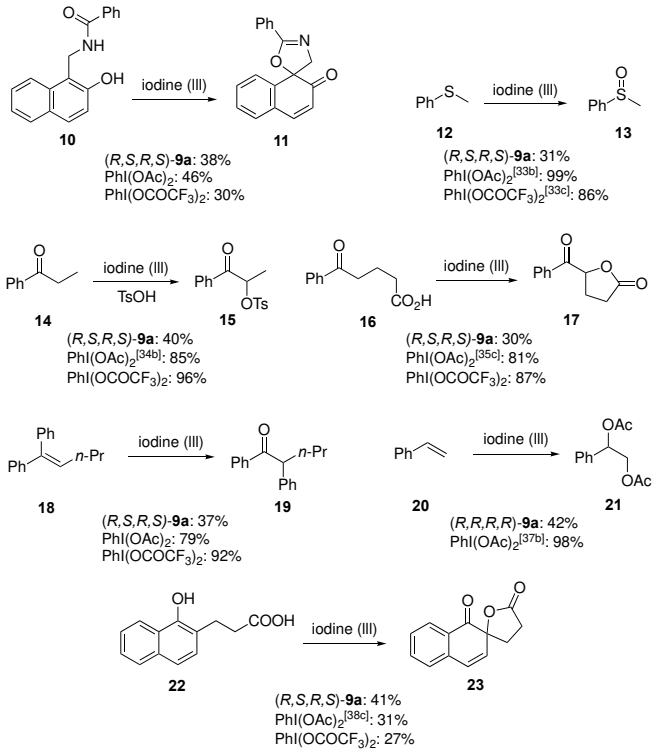
Scheme 1. Synthesis of hypervalent iodine compounds **9**.

Table 1. Optimization of the reaction conditions **7** to **9a**.

Entry	Ratio **7**:**8**	Iodine(III) reagent	Solvent	**9a** Yield [%][a]
1	1:2	Ph-I=O **8a**	acetone	0
2	1:2	Ph-I=O **8a**	CH_3CN	0
3	1:2	Ph-I=O **8a**	CH_3COOH	0
4[b]	1:2	Ph-I=O **8a**	--	22
5[b]	1:2.2	Ph-I=O **8a**	--	61
6[c]	1:2.2	Ph-I=O **8a**	--	62
7[d]	1:2.2	Ph-I=O **8a**	--	64
8[e]	1:2.2	Ph-I=O **8a**	--	65
9	1:2.2	Ph-I=O **8a**	CH_2Cl_2	77
10	1:2.2	Ph-I=O **8a**	$CHCl_3$	92
11	1:2.2	Ph-I(OAc)$_2$	$CHCl_3$	0
12	1:2.2	Ph-I(OCOCF$_3$)$_2$	$CHCl_3$	0

[a] Reactions were carried out using **7** (0.15 mmol) and **8a** (0.33 mmol) in different solvents (2 mL) at room temperature, [b] 30 minutes, [c] 60 minutes, [d] 90 minutes, [e] 120 minutes.

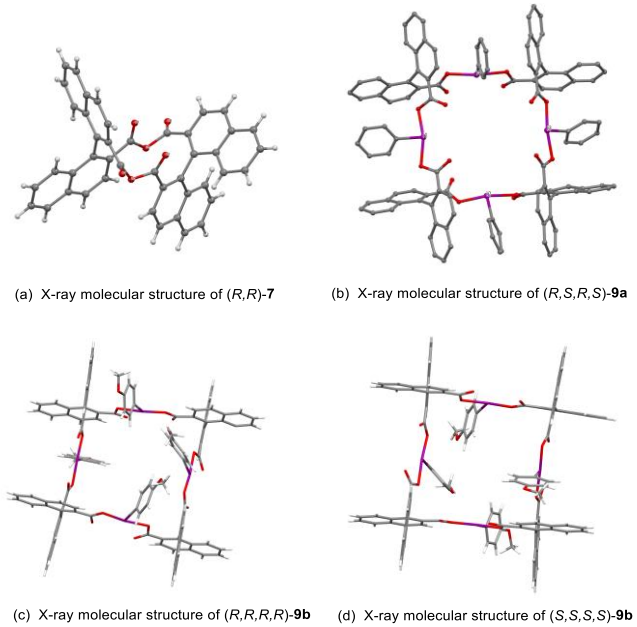
With the racemate **9a** in hand, the dearomatizing cyclization of *N*-((2-hydroxynaphthalen-1-yl)methyl) benzamide **10**[32] was selected to evaluate the reactivity of **9a**. As expected, the desired compound **11** was obtained in 38% yield (Table 3, entry 1). Then, the oxidation of methyl phenyl sulfide **12**,[33] the *α*-oxytosylation of propiophenone **14**,[34] the lactonization of 5-oxo-5-phenylpentanoic acid **16**,[35] the rearrangement of pent-1-ene-1,1-diyldibenzene **18**,[36] the diacetoxylation of styrene **20**,[37] and the dearomative spirolactonization of 3-(1-hydroxynaphthalen-2-yl) propanoic acid **22**[38] were employed to further test the activity of **9a**. Fortunately, all these reactions typical for iodine(III) give rise to the corresponding products in moderate to excellent yields (Scheme 2), which demonstrated that **9a** as a new iodine(III) reagent can promote different oxidative transformations.



Scheme 2. Oxidative transformations mediated by hypervalent iodine(III) compounds.

For the synthesis of enantiopure compound **9a** the enantiomers of the diacid **6** are necessary. (*R*)-**6** was obtained by chemical resolution,[39] where (*R*)-(-)-1-cyclohexylethylamine was used as resolving reagent. Several recrystallizations were necessary to obtain (*R*)-**6** in >99% *ee*. To recover the enantiomer (*S*)-**6** from the residue, (*1R*,*2R*)-diphenylethylene diamine[40] was chosen as resolving reagent. (*R*)-**6** and (*S*)-**6** were obtained in 23% and 22% yield, respectively, with >99% *ee*. When (*R*)-**6** was dehydrated to (*R,R*)-**7** followed by reaction with **8a**, (*R,R,R,R*)-**9a** was obtained in 14% overall yield (Scheme 1). The X-ray crystallography of (*R,R,R,R*)-**9b** and (*S,S,S,S*)-**9b** (Figure 2c and d) further confirmed the structure of these compounds.[41] The structure of the racemate reveals that it consists of two (*R*)- and two (*S*)-diacid moieties in the molecule (Figure 2b).

The single crystals of (*R,S,R,S*)-**9a,** (*R,R,R,R*)-**9b** and (*S,S,S,S*)-**9b** were obtained by crystallization from chloroform. All have monoclinic geometry, with the I–O bond length in these compounds is between 2.136 Å and 2.153 Å, slightly shorter than the average O–I bond length in iodobenzene diacetate (2.153 Å).[42] Their I–C_{Ar} bond length is with 2.017–2.081 Å also slightly shorter than the I–C_{Ph} bond length in (diacetoxyiodo)benzene (2.093 Å). The average of the O–I–O angles in compounds (*R,S,R,S*)-**9a**, (*R,R,R,R*)-**9b** and (*S,S,S,S*)-**9b** is 166.8º, 167.4º and 168.0º, respectively, slightly larger than the O–I–O angle in (diacetoxyiodo)benzene (163.2º). This suggests that the geometry around iodine in **9** is closer to a T-shaped structure which is also confirmed through the slightly larger distance of the carbonyl-oxygen atoms to the iodine (average: 2.828 Å) compared to (diacetoxyiodo)benzene (2.816 Å).



(a) X-ray molecular structure of (*R,R*)-**7** (b) X-ray molecular structure of (*R,S,R,S*)-**9a**

(c) X-ray molecular structure of (*R,R,R,R*)-**9b** (d) X-ray molecular structure of (*S,S,S,S*)-**9b**

Figure 2. X-ray structures of compound (*R,R*)-**7** and compounds **9**.

The transformations shown in Scheme 2 were employed to investigate the enantioinduction of the new hypervalent iodine(III) reagent (*R,R,R,R*)-**9a**. We found that for some reactions, such as the dearomatizing cyclization of **10**, oxidation of **12**, and the rearrangement of **18**, the enantiomeric excess of the products was very low. To potentially improve the enantioinduction in those reactions using **9**, different derivatives of **9a** were synthesized. Both electron-donor substituted iodosylbenzenes such as 4-methoxy- and 4-methyl substituted and electron-withdrawing derivatives with a 4-trifluoromethyl- and 2,3,4,5,6-pentafluoro substituents can react with **7** smoothly to afford the corresponding chiral hypervalent iodine compounds **9** in good yields (Table 2).

Table 2. Synthesis of derivatives **9a**–**9e**.

Entry	Anhydride **7**	Iodine(III) reagent	Product	**9** Yield [%]
1	(*R,R*)-**7**	Ph-I=O **8a**	(*R,R,R,R*)-**9a**	85
2	(*R,R*)-**7**	4-MeO-C_6H_4-I=O **8b**	(*R,R,R,R*)-**9b**	79
3	(*S,S*)-**7**	4-MeO-C_6H_4-I=O **8b**	(*S,S,S,S*)-**9b**	84
4	(*R,R*)-**7**	4-F_3C-C_6H_4-I=O **8c**	(*R,R,R,R*)-**9c**	75
5	(*S,S*)-**7**	4-F_3C-C_6H_4-I=O **8c**	(*S,S,S,S*)-**9c**	87
6	(*R,R*)-**7**	4-Me-C_6H_4-I=O **8d**	(*R,R,R,R*)-**9d**	79
7	(*S,S*)-**7**	4-Me-C_6H_4-I=O **8d**	(*S,S,S,S*)-**9d**	83
8	(*R,R*)-**7**	C_6F_5-I=O **8e**	(*R,R,R,R*)-**9e**	67

The dearomatizing cyclization of **10** was then employed to assess the enantioinduction of these reagents. We found that the reaction of **10** and (*R,R,R,R*)-**9b** in a 3:1 solvent mixture of dichloromethane and methanol at –78 ºC for 4 h yielded the desired compound **11** in 63% yield with 10% *ee* which was the best result in terms of the enantioinduction of chiral reagents **9a-e** (Table 3, entries 2-9). Therefore, (*R,R,R,R*)-**9b** was selected to test other reactions. Like (*R,R,R,R*)-**9a**, some reactions induced by (*R,R,R,R*)-**9b** showed an enantioselectivity to some extent. For example, the rearrangement of **18** and dearomative spirolactonization of **22** gave 2% and 4% *ee* of products **19** and **23**, respectively.

Table 3. Dearomatizing cyclization of **10** to **11** mediated by chiral hypervalent iodine compounds.

Entry	Iodine(III) reagent	**11** Yield [%]	**11** *ee* [%][a]
1	(*R,S,R,S*)-**9a**	38	--
2	(*R,R,R,R*)-**9a**	33	4
3	(*R,R,R,R*)-**9b**	63	1
4	(*R,R,R,R*)-**9c**	77	7
5	(*R,R,R,R*)-**9d**	40	7
6	(*R,R,R,R*)-**9e**	29	0
7	(*S,S,S,S*)-**9b**	77	1
8	(*S,S,S,S*)-**9c**	75	2
9	(*S,S,S,S*)-**9d**	50	1
10	(+)-**35**	67	1
11	(*R*)-**34**	70	0

[a] *ee* was determined by chiral HPLC.

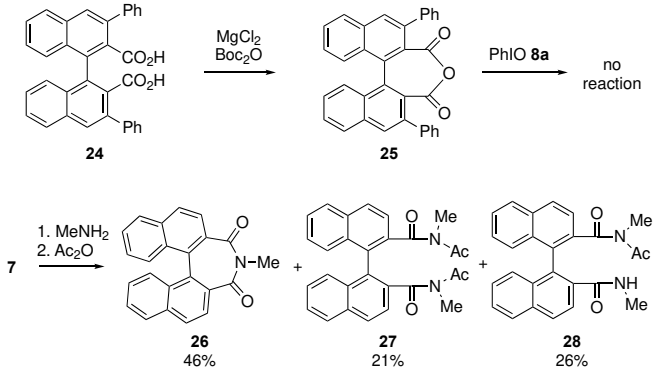
From these results it is apparent that the nature of the aryl group in compounds **9** did not affect the enantioselectivity of the reactions investigated. Therefore, the effect of substituents on the binaphthyl backbone was investigated. The directing abilities of the carboxylic acids in **6** allows a palladium catalyzed *ortho*-functionalization.[43] Phenylation in both *ortho*-position led to 3,3'-diphenyl-[1,1'-binaphthalene]-2,2'-dicarboxylic acid **24**, which dehydrates intramolecularly to anhydride **25** as confirmed by X-ray analysis (see supporting information). Unfortunately, there is no subsequent reaction with iodosylbenzene probably due to steric hindrance.

Due to the poor enantioinduction of chiral reagents **9** it was assumed that **9** may be hydrolyzed during the reaction to diacid **6** and iodosylbenzene **8a**, with the chiral binaphthyl moiety not participating at all in the reaction. To verify this assumption, NMR experiments were carried out with 0.048 mmol of **9a** and 10.0 equivalents water in $CDCl_3$ (4.2 mL) and DMSO-d_6 (0.6 mL). From the carbon NMR spectrums, it was found that after stirring the mixture for 12 hours, **9a** began to be hydrolyzed gradually as a new ^{13}C NMR signal at 93.7 ppm was observed, which is similar to an iodine-linked carbon signal at 94.9 ppm in iodosylbenzene **8a**. To further elucidate this assumption, the hydrolysis of **9a** in DMSO-d_6 was also conducted. Similar results were observed,

with the difference that the hydrolysis of **9a** in DMSO is faster than in chloroform and complete after approx. 60 min (Details see supporting information).

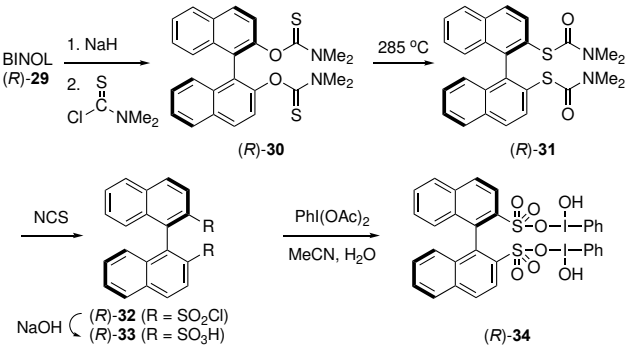
Accordingly, theoretical calculations carried out at the GFN2-xTB level[44] in the xTB 6.4.1 software[45] and using the ALPB[46] (analytical linearized Poisson-Boltzmann) implicit solvent model for chloroform (ε = 4.71) and DMSO (ε = 46.83) indicated a large spontaneity for the hydrolysis of **9a** in solution. The calculated Gibbs free energy was in the order of 119.0 kcal mol^{-1} in chloroform and 99.8 kcal mol^{-1} in DMSO favoring **6** and **8a**, indicating that the hydrolysis is thermodynamically favorable (see the supporting information for the computational details). Given the reported high accuracy of GFN2-xTB[45] when benchmarked to high level *ab*-initio methods as the DLPNO-CCSD(T)/CBS[47] for the calculation of Gibbs free energies of geometries, frequencies and even reaction energies involving large systems (hundreds of atoms), the use of this level seems appropriate to evaluate the Gibbs free energy of hydrolysis of **9a** (200 atoms).

Continuing to explore the binaphthyl based hypervalent iodine reagents, we synthesized nitrogen-containing binaphthyl ligands, as nitrogen atoms can form hydrogen bonds to oxygens linked to the central iodine.[48] Acid anhydride **7** was treated with methylamine and, without isolation, the mixtures were reacted with sodium acetate in anhydrous acetic anhydride to give the imide **26**, diacetylated imine **27** and monoacetylated imine **28** in 46%, 21% and 26% yield, respectively (Scheme 3). Unfortunately, no hypervalent iodine compounds were produced when the individual compounds were treated with iodosylbenzene, (diacetoxyiodo)benzene or [(bistrifluoroacetoxy)iodo]benzene. We speculated that it may not be possible to isolate the nitrogen-containing iodine compounds due to their instablility. Therefore, *in situ* reactions were performed by treatment of **26** with iodosobenzene for 30 min followed by substrate **10**, however, product **11** was not observed.



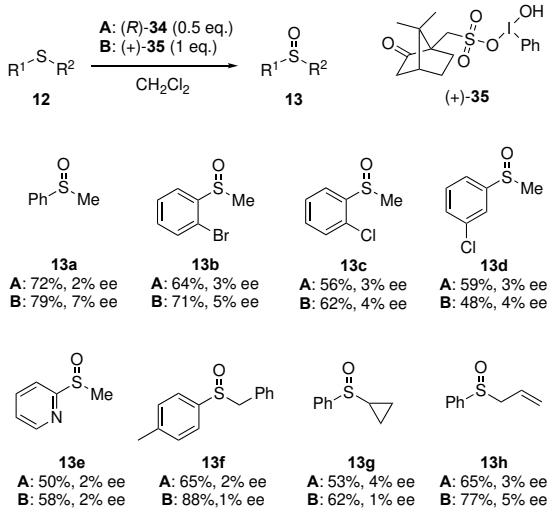
Scheme 3. Synthesis of other binaphthyl ligands.

Recognizing the early attempts by Varvoglis in using chiral sulfonic acids as ligands to iodine(III),[26] a binaphthyl-based Koser's reagent was synthesized. Binol (*R*)-**29** underwent a reaction sequence of nucleophilic substitution, Newman–Kwart rearrangement to (*R*)-**31**, oxidation and hydrolysis to give the binaphthyl-based disulfonic acid (*R*)-**33** in 16% overall yield.[49] The intermediate disulfonylchloride (*R*)-**32** has been characterized also by X-ray structure before.[49b] (*R*)-**33** was transformed to a Koser-type reagent (*R*)-**34** by reaction with (diacetoxyiodo)benzene (Scheme 4).



Scheme 4. Synthesis of bissulfonate binaphthyl ligand **33**.

Although no X-ray structural information on compound (*R*)-**34** could be obtained, an array of sulfides was oxidized with this compound and compared to the original derivative (+)-**35** synthesized by Varvoglis.[26] Some results are shown in Scheme 5, more examples are found in the supporting information. The yields of the sulfoxides are generally good, while the enantioselectivities are only very low or non-existent.



Scheme 5. Stereoselective sulfide oxidations.

In conclusion, several novel binaphthyl-based chiral hypervalent iodine(III) reagents were prepared in good to excellent yields. Their structures were verified by NMR, HRMS and X-ray crystallography. Several stereoselective oxidative reactions were applied to evaluate the reactivities and stereoselectivities of those reagents and although moderate to excellent yields were observed, very low stereoselectivities were obtained. Although the concept of generating enantiopure iodine(III) reagents only with the help of chiral ligands was successful, these reagents are inefficient for stereoselective synthesis due to rapid hydrolysis.

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Keywords: binaphthyl ligands • iodine(III) reagents • ligand synthesis • oxidation • stereoselective synthesis

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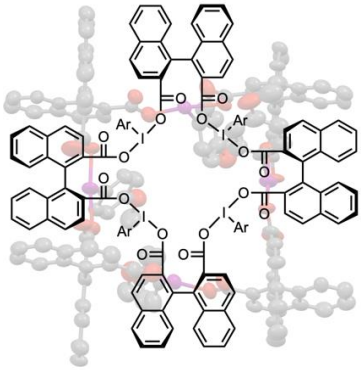
COMMUNICATION

Novel binaphthyl-based chiral hypervalent iodine(III) reagents are presented with the chirality only contained in the ligand. These have been characterized by X-ray analysis and all derivatives show the prominent reactivities of hypervalent iodine reagents. Due to their limited stability in solution they are inefficient chiral iodine(III) derivatives.



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