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VIP Oxidation of BINOLs by Hypervalent Iodine Reagents: Facile Synthesis of Xanthenes and Lactones

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Abstract: Xanthene derivatives have broad applications in medicines, fluorescent probes, dyes, food additives, etc. Therefore, much attention was focused on developing the synthetic methods to prepare these compounds. Binaphthyl-based xanthene derivatives were prepared through the oxidation of BINOLs promoted by the hypervalent iodine reagent iodosylbenzene (PhIO). Nine-membered lactones were obtained through a similar oxidative reaction when iodoxybenzene ($PhIO_2$) was used. Additionally, one-pot reactions of BINOLs, PhIO and nucleophiles such as alcohols and amines were also investigated to provide alkoxylated products and amides in good to excellent yields.

Xanthene is an oxygen-containing heterocycle featuring a dibenzopyran nucleus. Xanthene derivatives have attracted considerable attention due to their applications in fluorescent probes,[1] as laser dyes,[2] in medicines[3] and as food additives.[4] Therefore, these compounds play an important role in pharmaceutical[5] and industry areas.[6] For example, Fluorescein is a common probe for detecting H_2O_2 in living cells,[7] Rhodamine 6G is a classic reference dye to evaluate the efficiency of other dyes,[8] Blumeaxanthene is a traditional Chinese herb to treat gynecological disorders,[9] and Phloxine is generally used as a colorant in sweets, biscuits, ice creams etc. (Figure 1).[4b]

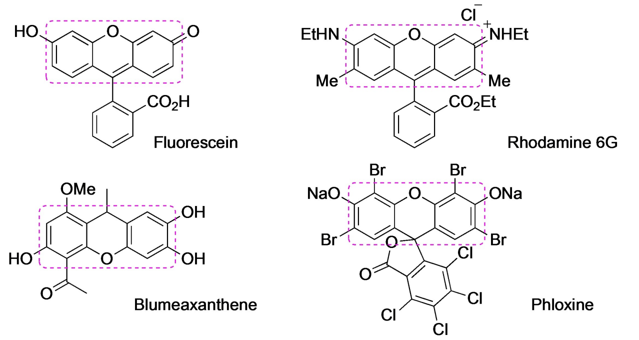

Figure 1. Commercially available xanthene derivatives.

Much attention was focused on exploring synthetic methods to prepare xanthene derivatives. The first one dates back to 1871, in which fluorescein was prepared by the condensation reaction between resorcinol and phthalic anhydride.[10] Since then, various methods have been developed to synthesize these compounds,[11] which mainly focus on exploring different substrates, designing novel catalysts and leveraging new technology. Taking typical research results in the last year as examples, the complex $[(C_6H_6)(PCy_3)(CO)\text{-}RuH]^+BF_4^-$ was used as a catalyst for the reaction of phenols and aldehydes,[12] $In(OTf)_3$ was employed to catalyze the coupling of 1,4-quinones with oxindoles,[13] nano-capsule $Fe_3O_4@Al_2O_3@SiO_2@Fe_2O_3$ were prepared to catalyze the condensation of benzaldehyde and 2-naphthol,[14] $K_2S_2O_8$ was used as a promoter to achieve the reaction of 2-aryloxy phenylacetylenes with phosphine oxides,[15] $TiCl_4$ was used for the cyclization of 2-aryloxybenzaldehydes,[16] $Cu(OAc)_2$ was shown to catalyze the reaction of propargyl amines with 2-hydroxynaphthalene-1,4-diones[17] and others.[18]

Among the synthetic methods to prepare xanthene derivatives, the oxidation of BINOLs mediated by copper salt and amines is a straight way to synthesize binaphthyl-based xanthene derivatives. Xu and coworkers reported the copper salt mediated oxidation of BINOLs in aprotic solvents.[19] In their study, two xanthene derivatives were obtained about 60% yield over 60 h. Six years later, Wulff and coworkers presented a copper-mediated deracemization of the C_2-symmetric compounds while xanthene derivates were isolated as side products in low yields (Scheme 1a).[20] As these methods have several drawbacks, such as low yields and limited substrate scope, it is still necessary to develop better methods for preparing binaphthyl-based xanthene derivatives.

Hypervalent iodine reagents are mild oxidants and enable different functionalizations in an achiral or chiral manner.[21] We are interested in designing and synthesizing chiral hypervalent iodine compounds and using them in asymmetric oxidation transformations.[22] In a recent research, BINOL was used as chiral ligand to react with iodosylbenzene, expecting to obtain

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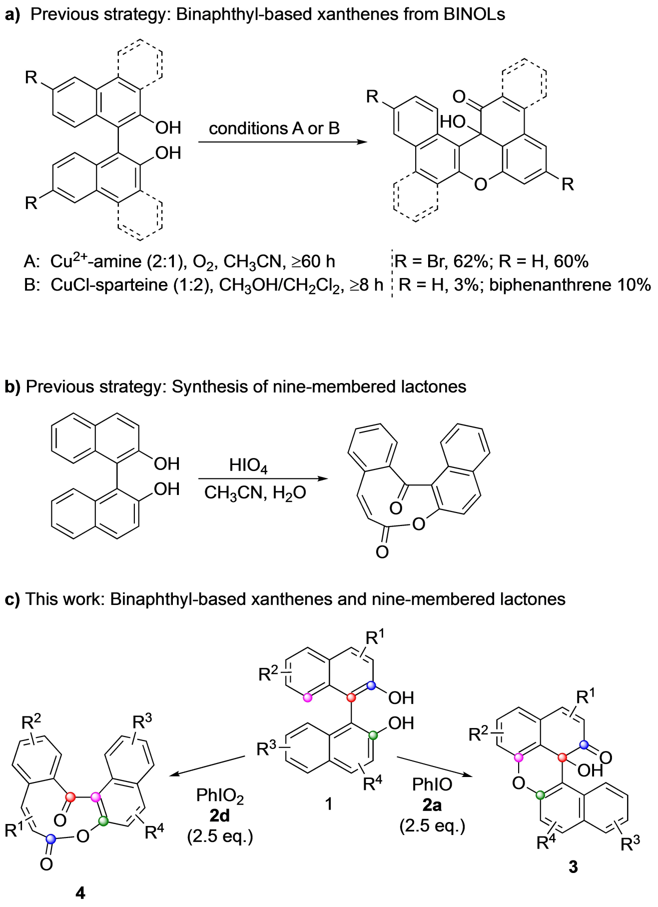
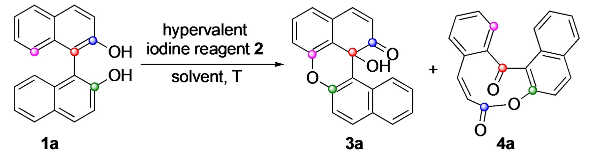


Scheme 1. The oxidation of BINOLs to form xanthene derivatives and lactones.

Table 1. Optimization of the reaction conditions to **3a**.



Entry	Hypervalent reagent **2**	Ratio 1:2	Solvent	Temperature [°C]	**3a** Yield [%][a]
1	Ph–I=O **2a**	1:2.2	$CHCl_3$	20	46
2	Ph–I=O **2a**	1:2.5	$CHCl_3$	20	66
3	Ph–I=O **2a**	1:3	$CHCl_3$	20	28
4	Ph–I=O **2a**	1:1.5	$CHCl_3$	20	64
5	Ph–I=O **2a**	1:1	$CHCl_3$	20	60
6	Ph–I=O **2a**	1:2.5	CH_2Cl_2	20	74
7	Ph–I=O **2a**	1:2.5	THF	20	64
8	Ph–I=O **2a**	1:2.5	Et_2O	20	53
9	Ph–I=O **2a**	1:2.5	CH_3CN	20	47
10	Ph–I=O **2a**	1:2.5	toluene	20	60
11	Ph–I=O **2a**	1:2.5	benzene	20	61
12	Ph–I=O **2a**	1:2.5	acetone	20	74
13	Ph–I=O **2a**	1:2.5	$ClCH_2CH_2Cl$ (DCE)	20	80
14	Ph–I=O **2a**	1:2.5	methanol	20	20
15	Ph–I=O **2a**	1:2.5	ethanol	20	11
16	Ph–I=O **2a**	1:2.5	water	20	0
17	Ph–I=O **2a**	1:2.5	water/DCE	20	53
18	Ph–I(OAc)$_2$ **2b**	1:2.5	DCE	20	45
19	Ph–I(OCOCF$_3$)$_2$ **2c**	1:2.5	DCE	20	40
20	Ph–IO$_2$ **2d**	1:2.5	DCE	20	22[b]
21	Ph–I=O **2a**	1:2.5	DCE	0	47
22	Ph–I=O **2a**	1:2.5	DCE	reflux	29

[a] Reactions were carried out with 0.17 mmol **1a** in 2 mL of solvent. [b] 76% compound **4a** was isolated as well.

a binaphthyl-based chiral hypervalent iodine compound. However, the expected product was not formed, but products **3a** and a nine-membered ketone lactone **4**, which had been reported earlier (Scheme 1b),[23] were observed instead. Herein, we present the oxidation of BINOLs mediated by hypervalent iodine reagents. On the one hand, xanthene derivatives **3** were obtained as the main product when iodosylbenzene **2a** was used as oxidant, on the other hand, nine-membered ketone lactones **4** were generated when iodoxybenzene **2d** was reacted with BINOL (Scheme 1c). In comparison to the former methods, this approach has many valuable merits such as mild reaction conditions, simple operation, short reaction times, high yields, and a broad substrate scope.

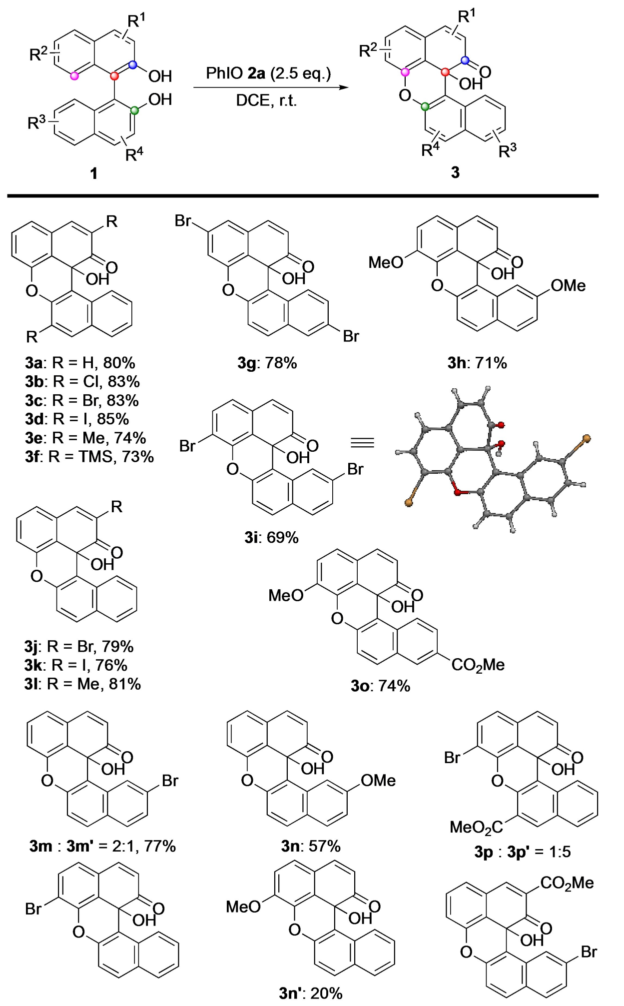
Initially, BINOL **1a** was treated with 2.2 equivalents of iodosylbenzene **2a** at room temperature and xanthene **3a** was obtained in 46% yield accompanied with the formation of the nine-membered lactone **4a**, which was also confirmed by X-ray crystallography (Table entry 3). It was noted that a decrease of the amount of **2a**, **3a** was also obtained in similar yield, but the reaction time was prolonged from 30 minutes to 6 h (Table 1, entries 4–5). Then, different solvents were examined. The reaction occurred well in aprotic solvent such as halogenated solvents, ethers and benzenes (Table 1, entries 6–13). The optimal solvent was 1,2-dichloroethane (DCE) which gave **3a** in 80% yield. When alcohols were used, low yields were observed and the cyclization/alkoxylation product (see Table 4) was isolated as the main product (Table 1, entries 14–15). The reaction cannot occur in water due to the poor solubility of BINOL and **2a**. A mixture solvent of water and DCE was also used, but the yield of **3a** was not increased (Table 1, entries 16–17). Also different hypervalent iodine reagents, such as (diacetoxyiodo)benzene **2b**, [bis(trifluoroacetoxy)iodo]benzene **2c** and iodoxybenzene **2d** were screened, but the yield of **3** was not improved (Table 1, entries 18–20). But when **2d** was used as oxidant, **4a** was obtained as the main product in 76% yield. When the reaction was carried out under either reflux or at 0 °C, reduced yields were observed (Table 1, entries 21–22). Thus, the optimal conditions for the synthesis of **3a** is the treatment of **1a** with 2.5 equivalents of **2a** in DCE for 30 min at room temperature, affording **3a** in 80% yield (Table 1, entry 13).

Next, the generality of substrates **1** was investigated. Firstly, C_2-symmetric BINOLs with substitutions at 3,3′-positions were explored. The corresponding target products **3b**–**3f** were obtained in 73–85% yield. The electronic properties of **1** have an influence on the reaction time and yield. For example, BINOLs with dimethyl and di-TMS groups at 3,3′-positions gave the desired products **3e** and **3f** in 74% and 73% yield, which were lower than these with electron-withdrawing groups such as dibromo, dichloro, diiodo substituents at the same position (Table 2, **3b**–**3f**).

Unfortunately, when 3,3′-diester substituted BINOL was used, the reaction does not occur because of stronger electron withdrawing effects of the ester group. Then, 6,6′-dibromo, 7,7′-dimethoxy and 7,7′-dibromo substituted BINOLs were employed, the target products were generated in 78%, 71% and 69% yield, respectively (Table 2, **3g**–**3i**). The X-ray crystallographic analysis of **3i** further confirmed the structure of the product.[24] Monosubstituted non-C_2-symmetric BINOLs were examined as well. It was found that 3-monosubstituted BINOLs such as 3-bromo, 3-iodo and 3-methyl substituted BINOLs gave the target product **3j**–**3l** in good yields with excellent chemoselectivity (Table 2). The steric hindrance in the *ortho* position will stop the attack of oxygen to the aromatic carbon. On the other hand, when 7-monosubstituted such as 7-bromo, 7-methoxyl BINOLs were used, product mixtures were observed. Due to the steric hindrance in *ortho* position, the ratio of isomers **3m**:**3m′** was 2:1. Similar results were found for isomers **3n** and **3n′** with a 3:1 ratio (Table 2). Disubstituted non-C_2-symmetric BINOLs were also investigated. 7-Methoxyl-6′-ester substituted BINOL gave desired product **3o** in 73% yield exclusively. But 7-bromo-3′-ester BINOL gave an isomer mixture of **3p** and **3p′** in a 1:5 ratio (Table 2).

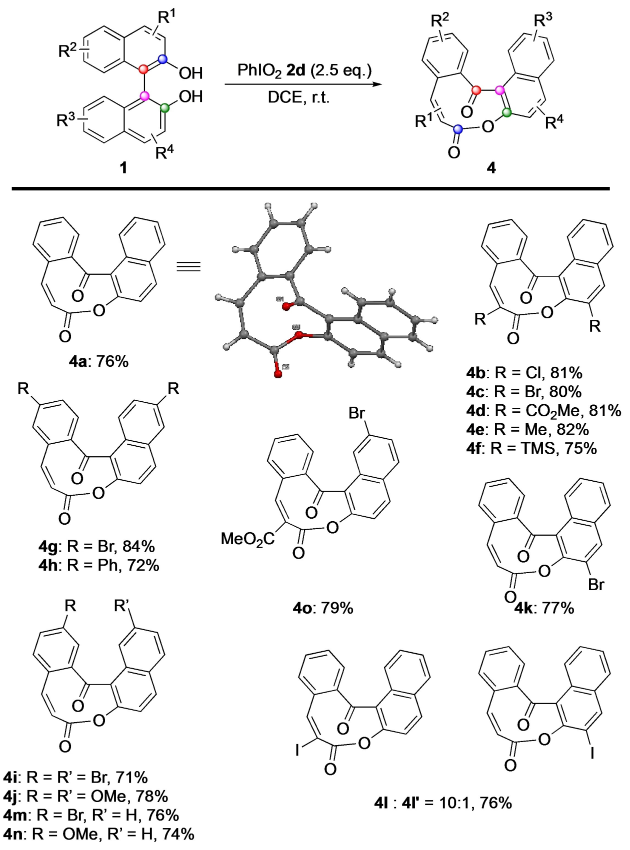
The generality of the oxidative transformation of BINOLs mediated by iodoxybenzene **2d** to form nine-membered lactones was investigated. BINOLs possessing 3,3′-dichloro, dibromo, dimethylester, dimethyl and di-TMS groups gave the target products in good to excellent yield in DCE at room temperature (Table 3, **4b**–**4f**). It was noted that 3,3′-diester substituted BINOL, which cannot be oxidized by **2a**, reacted with **2d** to provide product **4d** in 81% yield, indicating that the electron withdrawing group in BINOLs doesn't greatly affect the oxidation of BINOLs mediated by **2d**. The structure of the product was further confirmed by X-ray crystallography of **4a** and **4e**.[24] 6,6′-Dibromo, 6,6′-diphenyl, 7,7′-dibromo and 7,7′-dimethoxyl substituted BINOLs can also be oxidized by **2d** affording **4g**–**4j** in 71–84% yield (Table 3, **4g**–**4j**). When non-C_2-symmetric BINOLs with different substitute on different position such as 3-bromo, 3-iodo, 7-bromo, 7-methoxyl and 7-bromo-3′-ester were used, all of them gave the corresponding products exclusively except for 3-iodo substituted BINOL which gave the isomeric mixture **4l** and **4l′** in a 10:1 ratio (Table 3, **4k**–**o**).

Table 2. Synthesis of xanthene derivatives **3**.[a]



[a] Reactions were carried out with 0.17 mmol of **1** and 0.43 mmol of **2a** in 2 mL of DCE.

Table 3. Synthesis of nine-membered lactones **4**.[a]



[a] Reactions were carried out with 0.17 mmol of **1** and 0.43 mmol of **2d** in 2 mL of DCE.

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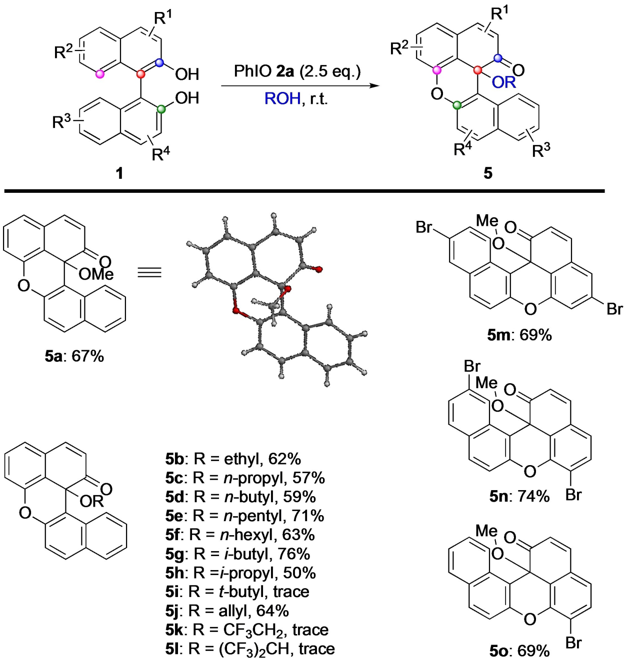
As described in Table 1 (entries 14–15), when BINOL was oxidized by **2 a** in the presence of an alcohol, the cyclization - alkoxylation compounds **5** were obtained as main products. The synthesis of **5** has been reported[25] and some derivatives have been reported to possess bioactivities.[5a,25c] For example, **5 a** and **5 m** exhibit high activities against BEL-7402 cells.[26] Therefore, we turned our attention to investigate the oxidation of BINOLs mediated by **2 a** in the presence of alcohols to form compounds **5**. Treatment of BINOL **1 a** with **2 a** in different alcohols formed the corresponding products **5 a–j** in moderate to good yields (Table 4, **5 a–j**). Specifically, linear primary alcohols from methanol to hexanol can provide the desired product **5 a–f** in 57–71 % yields. The structure of these products was further confirmed by X-ray crystallographic analysis of **5 a** and **5 c**.[24] The chain length of alcohols does not greatly affect the reaction yield. Branched primary alcohols such as isobutyl alcohol also reacted well with BINOL in the presence of **2 a** and compound **5 g** was obtained in 76 % yield. When secondary alcohols such as isopropanol was used, the target compound **5 h** was also produced in 50 % yield. Unfortunately, tertiary alcohols do not provide products due to the steric hindrance. Allyl alcohol also gave the corresponding product **5 j** in good yield. But when electron-poor alcohols such as TFE and HFIP were used, only trace amounts of products were observed (Table 4, **5 k–l**). 6,6′-Dibromo and 7,7′-dibromo substituted BINOLs were selected as C_2-symmetric BINOLs and the desired compounds **5 m** and **5 n** were obtained in 69 % and 74 % yield, respectively. Non-C_2-symmetric 7-bromo substituted BINOL was applied to react with **2 a** in methanol and the target product **5 o** was obtained in 69 % yield.

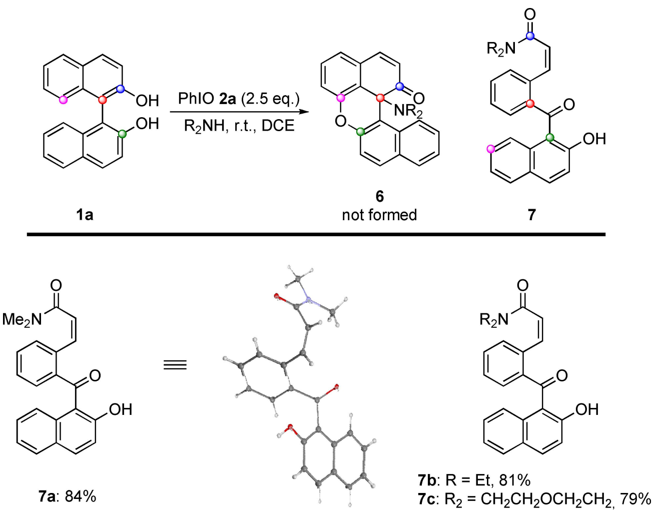
Table 4. Oxidative cyclization and alkoxylation of BINOLs.[a]



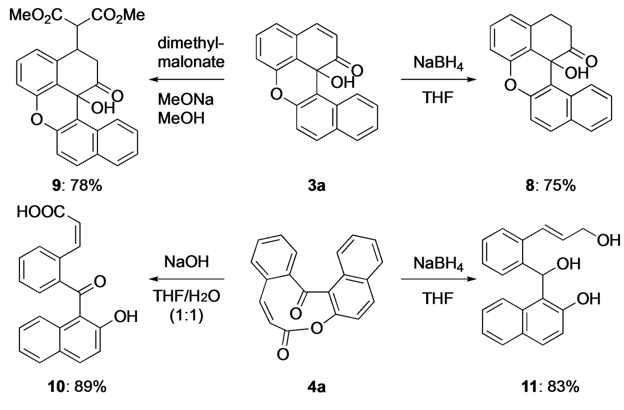
[a] Reactions were carried out with 0.17 mmol of **1** and 0.43 mmol of **2 a** in 2 mL of alcohol.

According to the above results that alcohols can be used as a nucleophile to react with BINOLs in the presence of **2 a** in one-pot manner to afford products **5**, we assumed that amines would also be able to react with BINOL to produce similar products **6**. Thus, dimethylamine, diethyl amine and morpholine were selected as nitrogen-containing nucleophiles to react with **1 a** under the reaction conditions. However, products **6** were not observed but products **7 a–7 c** were formed (Scheme 2). The structures of **7 a** and **7 b** were also confirmed by X-ray crystallography.[24] Products **7** are derived from the oxidation of **1 a** to form **4 a**, followed by hydrolysis under basic condition to yield **10**, which then reacted with the amine to produce amide **7**. Ethanethiol and thiophenol were also selected as possible nucleophiles to react with BINOL mediated by **2 a** but no reactions were observed.

Further transformations of **3 a** and **4 a** are illustrated in Scheme 3. Treatment of **3 a** with $NaBH_4$ in THF allows a selective reduction of the unsaturated ketone in **3 a** and product **8** was obtained in 75 % yield.[24] Due to the existence of the α,β-unsaturated carbonyl skeleton in **3 a**, a Michael addition



Scheme 2. Amines as nucleophile in the oxidation of BINOL with iodosylbenzene **2 a**.

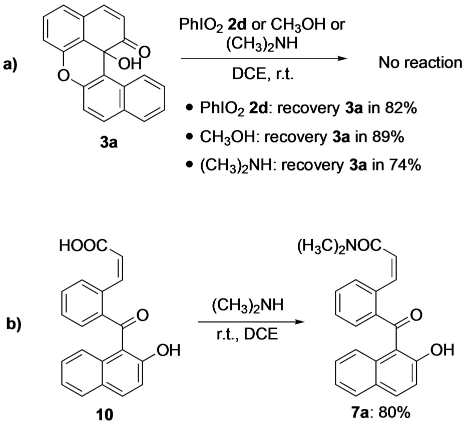


Scheme 3. Synthetic utility of **3 a** and **4 a**.

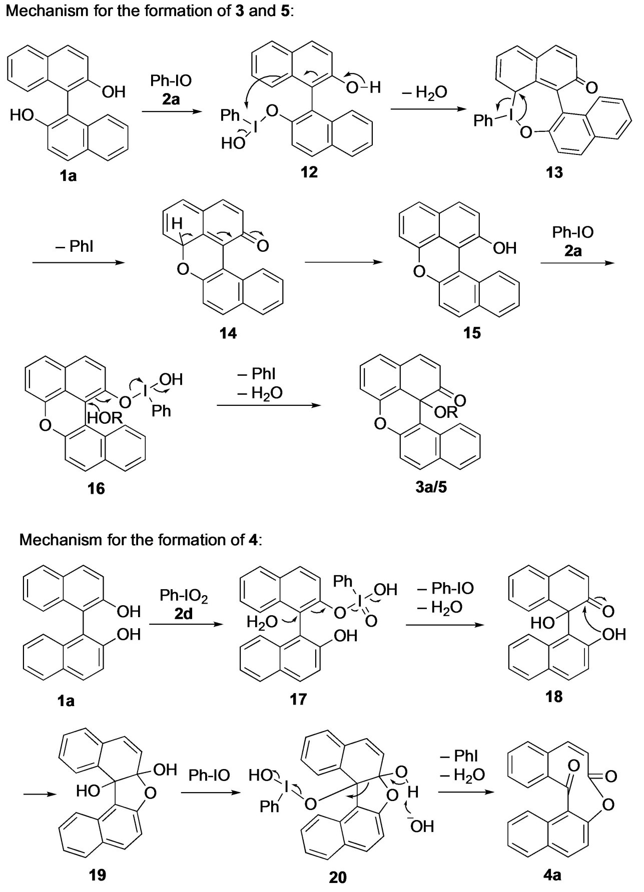
occurred between **3a** and dimethyl malonate under basic reaction conditions to provide product **9** in 78% yield. The synthetic utility of **4a** was also investigated by exposure to a solution of NaOH in THF / water (1:1) and (*Z*)-product **10** was obtained in 89% yield through hydrolysis of **4** by nucleophilic addition to the lactone which doesn't affect the original geometry of C=C bond. Interestingly, treatment of **4a** with $NaBH_4$ in THF formed the (*E*)-product **11** in 83% yield. We assumed that the reduction of **4a** by $NaBH_4$ occurred through the attack of hydride to both carbonyl groups. The initial reduction of the ketone to the secondary alcohol could trigger a subsequent Michael addition to the α,β-unsaturated lactone leading to an isomerization of the C=C double bond to decrease the steric hindrance in **11** during reduction of the lactone.

To gain further insight into the mechanism of the oxidative reaction of BINOLs mediated by hypervalent iodine reagents, several additional experiments were conducted. The target products **3** and **4** cannot be obtained without the hypervalent iodine reagents, but replacing the nitrogen atmosphere with air or adding TEMPO as a radical scavenger did not affect the reaction yield. We could prove that compound **3** is not an intermediate in the formation of **4** and **5** as it does not react with iodoxybenzene **2d** with or without the presence of methanol or dimethylamine. This suggests that **4** and **5** are not derived from **3** (Scheme 4a). However, carboxylic acid **10** can react with dimethyl amine to form **7a** in 80% yield (Scheme 4b).

Based on the control experiments and literature,[21,27] a mechanism for the formation of **3a** and **5** is proposed in Scheme 5. After addition of BINOL **1a** to iodosylbenzene **2a**, iodine(III) intermediate **12** is formed. Iodine(III) intermediate **13** was obtained through intramolecular tautomerism of the enol and addition to iodine. Finally, intermediate **13** underwent reductive elimination to form intermediate **14**, which subsequently aromatises to afford **15**. After addition of **2a** to **15**, iodine(III) intermediate **16** is formed which is then reacting with water or alcohols to deliver products **3a** and **5** accompanied with the elimination of iodobenzene and water. When chiral (*R*)-BINOLs **1** are used as substrates for the reaction with



Scheme 4. Control experiments.



Scheme 5. Proposed mechanisms for the formation of **3**, **4** and **5**.

iodosylbenzene **2a** in either DCE or alcohols (seeing Supporting Information), the resulting products have very low enantioselectivities. As the stereogenic axis of **1** is destroyed in the formation of intermediate **14**, which is reacting with nucleophiles, very low enantiomeric excesses of xanthene derivatives **3** and **5** is obtained.

For the formation of **4a**,[23,28] the addition of **2d** to **1a** gave rise to iodine(V) intermediate **17**, which dearomatized by the attack of water as a nucleophile to form **18**. Intramolecular nucleophilic addition between the naphthyl hydroxyl to the carbonyl group in **18** led to an intermediate diol **19**. Addition to PhIO occured to form iodine(III) intermediate **20**, which was underwent reductive elimination to yield the final nine-membered lactone **4a**.

In conclusion, a novel and facile method for preparing xanthene derivatives and nine-membered lactones through the oxidation of BINOL mediated by hypervalent iodine reagents is presented. Both electron-donating and electron-withdrawing substituted BINOLs, C_2-symmetric and non-C_2-symmetric BINOLs give products **3** and **4** in high yields. Especially for some non-C_2-symmetric cases, excellent chemoselectivities were observed. On the other hand, a one-pot method for the oxidation of BINOLs mediated by iodosylbenzene in the presence of alcohols or amines were explored, various cyclization/alkoxylation product **5** and α,β-unsaturated amides **7** were generated in good to excellent yields. The subsequent synthetic transformations of products **3** and **4** were investigated, showing that these products may become interesting building blocks for organic synthesis.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: BINOL · hypervalent iodine reagents · lactones · oxidation · xanthenes

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