JOC The Journal of Organic Chemistry

ARTICLE

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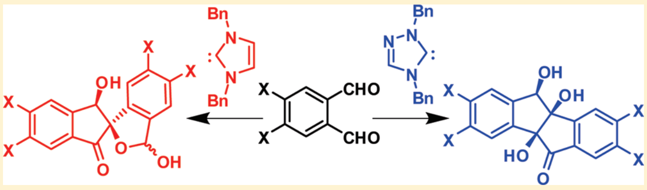
N-Heterocyclic Carbene Catalyzed Reaction of Phthalaldehydes: Controllable Stereoselective Synthesis of Polyhydroxylated Spiro- and Fused Indenones Dictated by the Structure of NHC Catalysts

Ying Cheng,* Jiang-Hua Peng, Yong-Jia Li, Xun-Yu Shi, Ming-Sheng Tang, and Tian-Yu Tan

College of Chemistry, Beijing Normal University, Beijing 100875, China

Supporting Information

ABSTRACT: The *N*-heterocyclic carbene catalyzed stereoselective dimerization reactions of phthalaldehydes produced polyhydroxylated spiro- or fused indenones. The reaction pathways were dictated by the structures of NHC catalysts. Under the catalysis of a imidazole carbene, phthalaldehydes produced dihydroxylspiro[indene-2,1′-isobenzofuran]-3-ones in good to excellent yields, whereas a triazole carbene catalyzed reaction of phthalaldehydes afforded fully *cis*-trihydroxylindeno[2,1-*a*]inden-5-ones in high yields. This work not only provides a highly efficient method for the construction of valuable polyhydroxyl substituted indene derivatives that are not easily assembled by other synthetic means but also reflects the versatility of organocatalysis using *N*-heterocyclic carbenes.



Organic reactions catalyzed by *N*-heterocyclic carbenes (NHCs) have been attracting continued interest in recent years owing to the unique umpolung reaction pathways of carbonyl groups and excellent diversity and selectivity under mild and environmental benign conditions.[1] A large number of NHC-catalyzed inter- and intramolecular benzoin condensation reactions[1,2] and Stetter reactions,[1,3] for example, have been reported to construct various functionalized organic compounds. NHC-catalyzed cross-condensations of α,β-unsaturated aldehydes, which formed homoenolate intermediates, with aldehydes, imines, aziridines, 1,2-diones, and enones constituted another main field in organocatalysis.[1,4] NHCs catalysis has also been employed in [2 + 2], [4 + 2], and [3 + 3] cycloaddition reactions to prepare different heterocycles.[1,5] Most significantly, NHC catalysts have been utilized successfully to furnish multifunctionalized molecules in the total synthesis of natural or bioactive compounds.[6] Although various *N*-heterocyclic carbene catalyzed reactions have been documented in literature, most of them only effect the formation of one or two new chemical bonds. NHC-initiated tandem processes that involved the formation of more than two chemical bonds[7] or the generation of more than two chirogenic centers[8] have been rarely reported.

On the basis of our understandings of the reactivity of nucleophilic carbenes and their versatilities in organic synthesis,[9] we have recently studied NHC-catalyzed reactions. In contrast to intramolecular reactions of bis-functionalized substrates[1,2a,10] and the intermolecular reactions of bis-functionalized compounds such as dialdehyde,[11] 2-ketoaldehyde,[5f] 2-vinylamide,[5a] and 1,2-dione[12] with other reactants, surprisingly, the NHC-catalyzed homoreaction or dimerization of two identical difunctionalized molecules has remained unexplored. We report herein the first example of NHC-catalyzed stereoselective dimerization reactions of phthalaldehydes. Dictated by slight structural variation of NHC catalysts, the reaction produced polyhydroxylated spiro- or fused indenones products in a highly controlled manner.

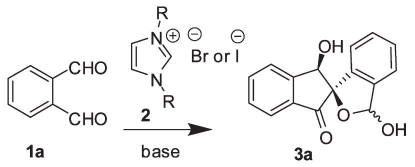
RESULTS AND DISCUSSION

We started with the examination of the NHC-catalyzed reaction of phthalaldehyde **1a** (Table 1). In the presence of *N*,*N*′-dimethylimidazolidene catalyst **2a′**, which was generated in situ from the interaction of *N*,*N*′-dimethylimidazolium salt **2a** (10 mol %) with NaH, phthalaldehyde **1a** underwent an efficient dimerization reaction at ambient temperature in dichloromethane within 3 h to afford a spiro-indenone compound **3a** as the sole product in 87% yield (entry 1, Table 1). Whereas diisopropylimidazolidene **2b′** catalyst gave a slightly lower yield of product **3a**, dibenzylimidazolidene **2c′** catalyzed reaction produced the spiro compound **3a** in 94% within 1 h (entries 2 and 3, Table 1). When catalyst loading was halved to 5 mol % or increased to 20 mol %, **3a** was obtained in 83% or 90% yield, respectively. The reaction was not very sensitive to the temperature used, as almost the same excellent yields were obtained from the reactions both at 0 and at 40 °C; however, a prolonged time caused the product to diminish (entries 6−8, Table 1). The use of other solvents including 1,2-dichloroethane, acetone, THF, and acetonitrile, and other bases such as *t*-BuOK and DBU, led to a slight decrease of the chemical yields of product **3a** (entries 9−13, Table 1).

The generality of the reaction was then investigated under the optimized conditions (Scheme 1, Table 2). The reaction was found to be strongly influenced by the nature and substitution

Received: December 28, 2010
Published: February 22, 2011

Table 1. Imidazole Carbene-Catalyzed Reaction of Phthalaldehyde 1a under Different Conditions



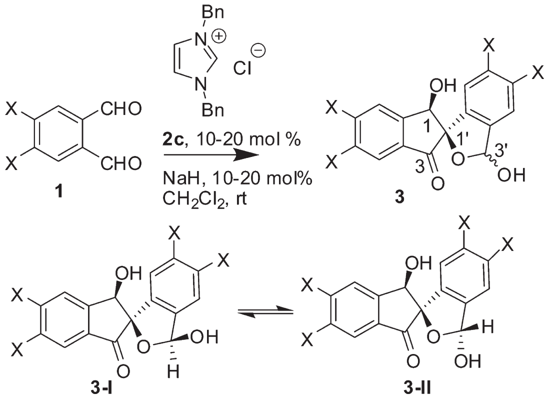
entry	2: R	mol % of 2	base^a	solvent	temp	time (h)	yield of 3a (%)
				reaction conditions^b			
1	**2a**: Me	10	NaH	CH_2Cl_2	rt	3	87
2	**2b**: *i*-Pr	10	NaH	CH_2Cl_2	rt	3	82
3	**2c**: Bn	10	NaH	CH_2Cl_2	rt	1	94
4	**2c**: Bn	5	NaH	CH_2Cl_2	rt	1	83
5	**2c**: Bn	20	NaH	CH_2Cl_2	rt	1	90
6	**2c**: Bn	20	NaH	CH_2Cl_2	rt	12	71
7	**2c**: Bn	10	NaH	CH_2Cl_2	0 °C	2	90
8	**2c**: Bn	10	NaH	CH_2Cl_2	40 °C	1	92
9	**2c**: Bn	10	NaH	$ClCH_2CH_2Cl$	rt	1	88
10	**2c**: Bn	10	NaH	CH_3COCH_3	rt	1	82
11	**2c**: Bn	10	NaH	THF	rt	1.5	89
12	**2c**: Bn	10	NaH	CH_3CN	rt	2	84
10	**2c**: Bn	10	DBU	CH_2Cl_2	rt	5	81
11	**2c**: Bn	10	DBU	$ClCH_2CH_2Cl$	60 °C	6	89
13	**2c**: Bn	10	*t*-BuOK	CH_2Cl_2	rt	6	79

[a] Molar % of base was equal to that of **2**. [b] Molar concentration of reactant **1a** was 0.067 mol/L.

pattern of substituents of phthalaldehydes **1**. For example, symmetrically disubstituted phthalaldehydes including 4,5-dimethyl (**1b**), 4,5-dichloro (**1c**), 4,5-dibromophthalaldehyde (**1d**), and naphthalene-2,3-dicarbaldehyde (**1e**) underwent equally efficient dimerization reaction as **1a** to afford the corresponding spiro products in 77−88% yields (entries 2−5, Table 2). No reaction was observed, however, when 4,5-dimethoxy-substituted substrate **1f** was employed. The inertness of the aldehyde moiety of **1f** toward nucleophilic carbene was most probably due to the electron-donating effect of methoxy groups, which deactivates the aldehydes. In stark contrast, the phthalaldehyde **1g** bearing a strong electron-withdrawing nitro group was unstable under NHC-catalyzed conditions. The reaction led to a dark mass rather than the expected product.

The structures of spiro products were established on the basis of spectroscopic data and single crystal X-ray diffraction analysis. As revealed by NMR spectra, compounds **3a**−**3e** existed as a mixture of epimers **3-I** and **3-II** in solution. The ratio of **3-I**:**3-II** of each compound **3** varied in different deuterated solvents. In deuterated DMSO solution, the ratio between two stereoisomers ranged from 2:1 (**3b**), 3:1 (**3c**), 4:1 (**3d** and **3e**) to 10:1 (**3a**) determined by integration of the intensity of proton signals. Interestingly, the major diastereoisomers **3-I** precipitated from the solution of **3** in THF, and X-ray crystallography identified the structure of **3a-I** unambiguously as (1*R*,1′*R*,3′*S*)- or (1*S*,1′*S*,3′*R*)-1,3′-dihydroxyspiro[indene-2,1′-isobenzofuran]-3-one (see Figure S1 in Supporting Information). To validate the structure of the other diastereoisomer **3-II**, **3a** isolated from the reaction was acylated with pivaloyl chloride in the presence of triethylamine in THF (see Scheme S1 in Supporting Information). The resulting 3′-pivalates **4a-I** and **4a-II** were readily separated by column chromatography, and single crystal X-ray diffraction analyses indicated indeed that **4a-I** and **4a-II** are a pair of epimers with the stereochemistry at hemiacetal carbons inverted (see Figure S2 in Supporting Information).

Scheme 1. Imidazole Carbene-Catalyzed Dimerization Reaction of Phthalaldehydes 1



It was noteworthy that the spiro products **3** obtained from imidazole carbene catalyzed dimerization of phthalaldehydes **1** constitute three stereogenic centers. In all cases, however, the hydroxyl group on the indenone ring is always in a *cis* relationship with the oxygen of tetrahydrofuran ring. No *trans*-configured product was observed. This indicated the stereospecificity of the NHC-catalyzed reaction that produced a *cis* dihydroxyl indenone intermediate. The formation of isomeric structures **3-I** and **3-II** on hemiacetal carbon, on the other hand, reflects the isomerization between hemiacetals **3-I** and **3-II** and aldehyde intermediates.

We also studied the reaction of phthalaldehydes **1** using triazole carbene catalyst. Under the optimized conditions for the formation of spiro indenones **3**, the reaction of **1a** catalyzed by 1,4-dibenzyl-1,2,4-triazole carbene **2d′** (10 mol %) afforded spiro indenone **3a** in 85% yield within 1 h, along with 5% of fused indenone **5a**. The ratio of product **3a** over **5a** changed to ∼1:1 when reaction time was prolonged to 12 h. To our delight, compound **5a** was obtained in 67% yield as the sole product when triazole carbene catalyst loading was increased to 20 mol %. The reaction conditions were further optimized by varying bases, solvents, and reaction temperature. The highest yield (85%) was achieved from the reaction using DBU to generate the carbene catalyst at 60 °C in 1,2-dichloroethane (entry 7, Table 3).

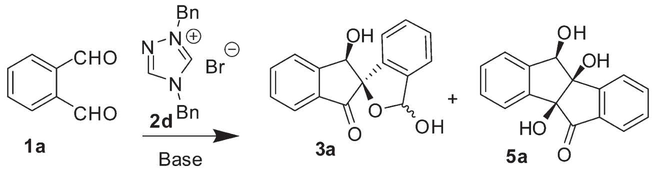
The triazole carbene catalyzed reactions of differently substituted phthalaldehydes **1** were examined under the optimized conditions. As illustrated in Table 4, in the presence of 20 mol % dibenzyltriazole carbene **2d′**, the reaction of phthalaldehydes **1a**−**1d** and naphthalene-2,3-dicarbaldehyde **1e** afforded exclusively the corresponding indeno[2,1-*a*]inden-5-ones **5a**−**5d** and benz[*f*]indeno[2,1-*a*]benz[*f*]inden-6-one **5e**, respectively, in 71−92% yields. The unsymmetrically substituted 4-bromo (**1h**),

Table 2. Imidazole Carbene-Catalyzed Dimerization Reaction of Phthalaldehydes 1 under Optimized Conditions

entry	**1**[a]	X, X	mol % of **2c**[b]	time (h)	**3**	yield of **3** (%)	**3-I**:**3-II**[c]
1	**1a**	H, H	10	1	**3a**	94	10:1
2	**1b**	Me, Me	10	1	**3b**	81	2:1
3	**1c**	Cl, Cl	10	1	**3c**	88	3:1
4	**1d**	Br, Br	10	3	**3d**	87	4:1
5	**1e**	−CH=CH−CH=CH−	20	6	**3e**	77	4:1
6	**1f**	OMe, OMe	20	24	**3e**	NR	
7	**1g**	NO_2, H	10	2	**3f**	*d*	

[a] Molar concentration of reactants **1** was 0.067 mol/L. [b] Molar % of NaH was equal to that of **2c**. [c] The ratios of **3-I**:**3-II** were determined in DMSO-d_6 by ^{1}H NMR spectra. [d] 4-Nitrophthalaldehyde **1f** was unstable under reaction conditions and formed a dark mass with no expected product.

Table 3. Triazole Carbene-Catalyzed Dimerization Reaction of Phthalaldehyde 1a under Different Conditions



			reaction conditions[b]				
entry	mol % of **2d**	base[a]	solvent	temp	time (h)	yield of **3a** (%)	yield of **5a** (%)
1	10	NaH	CH_2Cl_2	rt	1	83	5
2	10	NaH	CH_2Cl_2	rt	12	41	48
3	20	NaH	CH_2Cl_2	rt	12		67
4	20	DBU	CH_2Cl_2	rt	12		69
5	20	DBU	CH_2Cl_2	reflux	3		78
6	20	DBU	$ClCH_2CH_2Cl$	rt	6		80
7	20	DBU	$ClCH_2CH_2Cl$	60 °C	3		85
8	20	DBU	$ClCH_2CH_2Cl$	reflux	3		81
9	20	DBU	CH_3COCH_3	reflux	3		80

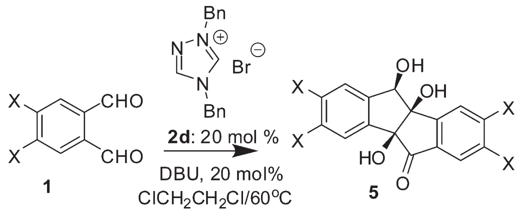
[a] Molar % of base was equal to that of **2d**. [b] Molar concentration of reactant **1a** was 0.067 mol/L.

4-chloro (**1i**), and 4-methoxyphthalaldehyde (**1j**) also reacted efficiently albeit producing a mixture of isomers, which were not separable using column chromatography because of similar polarity (Scheme 2). To determine the structures of isomeric products and clarify the regioselectivity of the reaction, the resulting isomeric mixture **5h**, **5i**, or **5j** was esterified with pivaloyl chloride to form the mixture of isomeric 10-pivalates **6h**, **6i**, or **6j**, respectively (see Scheme S2 in Supporting Information). The ratios of isomeric products **5** were obtained based on the ratios of isomeric pivalates **6** that were determined by ^{1}H NMR spectra. According to the ^{1}H NMR spectra of the mixture of isomeric pivalates **6**, 4-bromophthalaldehyde **1h** produced four isomeric products **5h-I**, **5h-II**, **5h-III**, and **5h-IV** in 45%, 21%, 18%, and 8% yields, respectively, while 4-chlorophthalaldehyde **1i** formed two major isomers **5i-I** and **5i-II** in 44% and 39% yields along with a trace amount of a minor one. The isomeric pivalates **6h-I**, **6h-II**, **6h-III**, and **6h-IV**, or **6i-I** and **6i-II**, were carefully separated by chromatography and were then converted back to **5h-I**, **5h-II**, **5h-III**, and **5h-IV**, or **5i-I** and **5i-II**, by hydrolysis in a refluxing mixture of water and 1,4-dioxane (20:1). In the case of 4-methoxyphthalaldehyde **1j**, two isomers were detected in the form of ester products. However, the methoxy substituted isomers **6j-I** and **6j-II** could not be separated by chromatography. Finally, pure major product **5j-I** was obtained by recrystallization in ethyl acetate and *n*-hexane.

As aforementioned, the reactions of phthalaldehydes **1** catalyzed by an imidazole or triazole carbene under different optimized reaction conditions produced spiro-indenones **3** or fused indenones **5**, respectively. To clarify the controlling effect on the different reaction pathways of phthalaldehydes **1**, we then conducted imidazole or triazole carbene catalyzed reactions of phthalaldehydes **1** under the same conditions. As summarized in Table 5, under the optimized conditions for the formation of fused indenones **5** catalyzed by triazole carbene, all substrates **1a**, **1b**, **1d**, and **1e** produced spiro-indenones **3** in the presence of imidazole carbene. These outcomes demonstrated that it is the nature of catalyst that dictated the pathways of transformation of phthalaldehydes **1**.

The structures of all products **5** were ascertained by spectroscopic methods. To identify the isomeric products beyond doubt, the structures of **5a**, **5j-I**, **6h-I**, **6h-II**, and **6h-III** were determined unambiguously by single crystal X-ray diffraction analysis. As illustrated in Figure S3 in Supporting Information, all three hydroxyl groups on fused indenone skeletons of **5** are *cis*-orientated, which demonstrated that the triazole carbene catalyzed reaction of **1** stereospecifically produced one type of stereoisomer, although compounds **5** have three stereogenic centers. The X-ray molecular structures of pivalates **6h-I**, **6h-II**, and **6h-III** confirmed that those products **5h-I**, **5h-II**, and **5h-III** are regioisomers with the substituents being connected to different positions of benzene rings. X-ray diffraction also indicated that both major products **5h-I** and **5j-I** derived from 4-bromophthalaldehyde **1h** and 4-methoxyphthalaldehyde **1j** are the 3,8-disubstituted products.

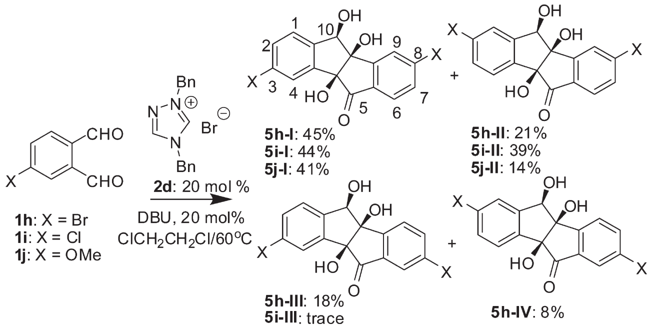
Table 4. Triazole Carbene-Catalyzed Reaction of Phthalaldehydes 1 under Optimized Conditions



entry	1[a]	X, X	time (h)	yield of 5 (%)
1	**1a**	H, H	6	**5a**: 85
2	**1b**	Me, Me	5	**5b**: 71
3	**1c**	Cl, Cl	3	**5c**: 86
4	**1d**	Br, Br	3	**5d**: 92
5	**1e**	−CH=CH−CH=CH−	6	**5e**: 72

[a] Molar concentration of reactants **1** was 0.067 mol/L.

Scheme 2. Triazole Carbene-Catalyzed Reaction of Unsymmetrically Substituted Phthalaldehydes 1h−1j



To account for the formation of spiro-indenones **3** and fused indenones **5** from phthalaldehydes **1**, two cascade reaction mechanisms comprising benzoin and aldol condensations were proposed. As depicted in Scheme 3, phthalaldehydes **1** catalyzed by imidazole or triazole carbene undergo a benzoin condensation via a Breslow intermediate **7** to form α-hydroxylketones **8**. Under the action of a heterocyclic carbene or the base used for generating carbene, intramolecular aldol condensation of **8** stereospecifically affords *cis*-dihydroxylindenones **9**, probably due to the intramolecular hydrogen bonds between the two *cis*-substituted hydroxyl groups. An intramolecular addition of 2-hydroxyl to the aldehyde moiety of **9** forms the hemiacetals of spiro-indenones **3**, which exist as a mixture of epimers **3-I** and **3-II** in solution. Under the catalysis of triazole carbene, hydroxylindenones **9** takes place an intramolecular benzoin condensation between two carbonyl groups to yield the fully *cis*-trihydroxylindeno[2,1-*a*]inden-5-ones **5**. The stereochemical course of the transfromation from intermediate **9** to products **5** should be controlled by the structure of **9**. During the intramolecular benzoin condensation of **9**, the acyl anion equivalent **10** formed from aldehyde group of **9** and triazole carbene can attack the carbonyl group only from the opposite side of the two *cis*-hydroxyl groups due to the steric restriction, which inevitably results in the fully *cis*-trihydroxyl substituted products **5**. In the reactions of 4-bromo (**1h**), 4-chloro (**1i**) and 4-methoxyphthalaldehyde (**1j**), the major products **5-I** were derived from the first benzoin condensation between two aldehydes both *meta* to the halogen or methoxy substituent. This regioselectivity can be best explained by the electronic effects of substituent, because the inductive electron-withdrawing effect of the bromine, chlorine, or oxygen atom activates its *meta* aldehyde, whereas the conjugative electron-donating effect of substituent deactivates its *para* aldehyde when **1h**, **1i**, or **1j** was interacted with nucleophilic carbenes.

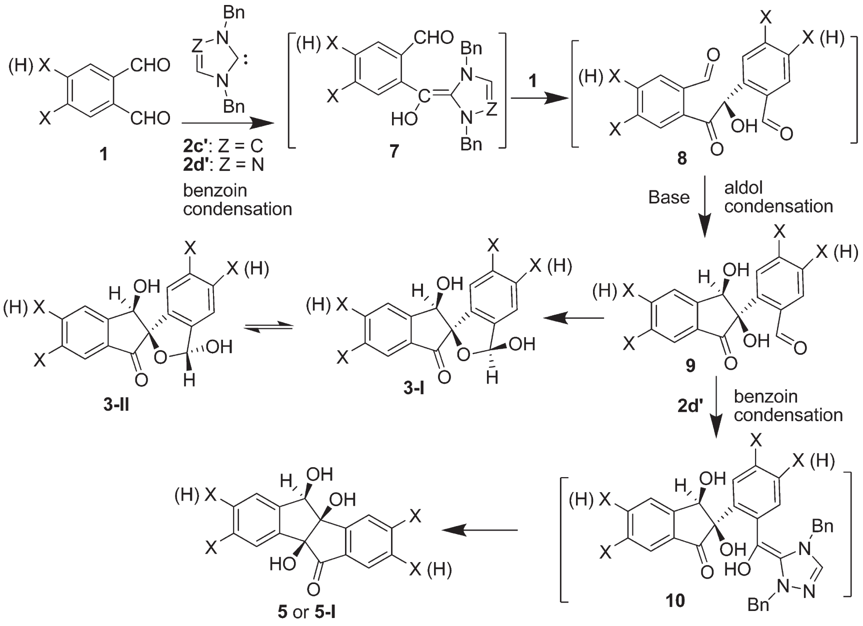
The different transformations of phthalaldehydes **1** under the catalysis of *N*-heterocyclic carbenes were apparently dependent on the divergent reaction pathways of dihydroxylindenone intermediates **9** that were controlled by NHC species employed. According to the literature, triazole carbenes are highly efficient in the catalysis of benzoin condensations or tandem reactions comprising a benzoin process.[1,2a−2d,13] In contrast, imidazole carbene promoted benzoin condensations were very limited and

Table 5. Comparison between Reactions of Phthalaldehydes 1 Catalyzed by Imidazole Carbene 2c′ and Triazole Carbene 2d′ under the Same Conditions

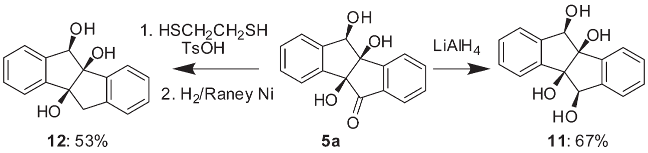
entry	1[a]	2	mol % of 2	reaction conditions	yield of product (%)
1	**1a**	**2c**	20	DBU (20 mol %), $ClCH_2CH_2Cl$, 60 °C, 6 h	**3a**: 91
2	**1a**	**2d**	20	DBU (20 mol %), $ClCH_2CH_2Cl$, 60 °C, 6 h	**5a**: 85
3	**1b**	**2c**	20	DBU (20 mol %), $ClCH_2CH_2Cl$, 60 °C, 5 h	**3b**: 63
4	**1b**	**2d**	20	DBU (20 mol %), $ClCH_2CH_2Cl$, 60 °C, 5 h	**5b**: 71
5	**1d**	**2c**	20	DBU (20 mol %), $ClCH_2CH_2Cl$, 60 °C, 3 h	**3d**:74
6	**1d**	**2d**	20	DBU (20 mol %), $ClCH_2CH_2Cl$, 60 °C, 3 h	**5d**: 92
7	**1e**	**2c**	20	DBU (20 mol %), $ClCH_2CH_2Cl$, 60 °C, 6 h	**3e**: 58
8	**1e**	**2d**	20	DBU (20 mol %), $ClCH_2CH_2Cl$, 60 °C, 6 h	**5e**: 72

[a] Molar concentration of reactants **1** was 0.067 mol/L.

Scheme 3. Proposed Mechanisms for the NHC-Catalyzed Reactions of Phthalaldehydes 1



Scheme 4. Preparation of Tetrahydroindeno[2,1-*a*]indene-4b,5,9b,10-tetraol 11 and Tetrahydroindeno[2,1-*a*]indene-4b,5,9b-triol 12 from 5a



most of them were employed in imidazolium ionic liquids.[14] In 2008, Bode and co-workers undertook a systematic comparison of structurally identical imidazole versus triazole carbene catalysts in a series of reactions of aldehydes or α, β-unsaturated aldehydes known to be catalyzed by *N*-heterocyclic carbenes.[15] They confirmed that the triazole carbene promoted almost exclusively benzoin, Stetter, benzoin-oxy-Cope and aza-benzoin-oxy-Cope reactions, which were via the acyl anion equivalent of Breslow intermediate. On the other hand, imidazole carbene preferentially catalyzed the annulation reactions of α, β-unsaturated aldehydes with electrophiles via the homoenolate equivalent of Breslow intermediate. In the current reactions, both imidazole and triazole carbenes could initiate the first benzoin reaction between two phthalaldehydes **1** because phthalaldehydes were highly reactive toward nucleophiles due to the electron-withdrawing effect of one aldehyde group to another. In the transformation of intermediates **9** to products **5**, however, only triazole carbenes were able to catalyze this intramolecular benzoin condensation, both due to the lower reactivity of ketone carbonyl and the steric hindrance nearby both aldehyde and ketone carbonyls of **9**. Thus, in the imidazole carbene catalyzed reaction of **1**, the intramolecular acetal formation reaction of intermediates **9** afforded spiro products **3**, while in the presence of triazole carbene, the intramolecular cross benzoin condensation of intermediates **9** furnished the fused ring products **5**.

Both spiro- and fused products resulted from the current study provide valuable synthetic intermediates for the preparation of *cis*-polyhydroxylindene derivatives, which may act as unique ligands to complex and chelate metal ions. As a demonstration, we have converted indeno[2,1-*a*]inden-5-one **5a** into fully *cis*-orientated 4b,5,9b,10-tetrahydroindeno[2,1-*a*]indene-4b,5,9b,10-tetraol **11** by means of reduction using $LiAlH_4$. Removal of the carbonyl of **5a** through the formation of a thioketal of **5a** followed by hydrogenation afforded 4b,5,9b,10-tetrahydroindeno[2,1-*a*]-indene-4b,5,9b-triol **12** (Scheme 4).

■ CONCLUSION

In summary, we have reported for the first time the *N*-heterocyclic carbene catalyzed dimerization reaction of phthaldehydes. Under the catalysis of imidazole carbene, phthalaldehydes undergo tandem intermolecular benzoin condensation, intramolecular aldol condensation, and hemiacetal formation reactions to afford spiro-dihydroxylindenones **3**. 1,2,4-Triazole carbene catalyzes consecutively intermolecular benzoin condensation, intramolecular aldol and benzoin condensation to produce stereospecifically fused tetracyclic trihydroxylindeno[2,1-*a*]inden-5-one compounds **5** with three *cis*-configured hydroxyl groups. Further transformations of trihydroxylindeno[2,1-*a*]inden-5-ones **5** extended the applications of current study to the preparation of different *cis*-polyhydroxylindeno[2,1-*a*]indenes. This work not only has provided a highly efficient method for the construction of valuable polyhydroxyl substituted indene derivatives that are not easily assembled by other synthetic means but also has reflected the versatility of organocatalysis using *N*-heterocyclic carbenes.

■ EXPERIMENTAL SECTION

General Procedure for the Reaction of Phthalaldehydes 1 Catalyzed by Imidazole Carbene. Under nitrogen atmosphere and at room temperature (~25 °C), phthalaldehydes **1a**−**1d** (2 mmol) or naphthalene-2,3-dicarbaldehyde **1e** (2 mmol) were mixed with

N,*N*′-dibenzylimidazolium salt **2c** (0.2 mmol for **1a**−**1d** or 0.4 mmol for **1e**) in dichloromethane (30 mL). After the addition of NaH (0.2 mmol for **1a**−**1d** or 0.4 mmol for **1e**), the reaction mixture was stirred at room temperature for 1−3 h. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel column eluting with a mixture of ethyl acetate, petroleum ether, and ethanol (10:10:1) for **3a**−**3d** or a mixture of THF and ethyl acetate (1:2) for **3e** to afford spiroindenones **3** in 77−94% yields.

1,3′-Dihydroxylspiro[indene-2,1′-isobenzofuran]-3-one 3a. Yield: 94%.

(1*R*,1′*R*,3′*S*)- and (1*S*,1′*S*,3′*R*)-3a-I. Mp 150−151 °C; IR ν (cm^{-1}) 3413, 1716; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.94 (t, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.44−7.50 (m, 2H), 7.35 (t, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.48 (d, *J* = 6.4 Hz, 1H), 5.19 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 201.1, 153.5, 140.7, 139.6, 136.2, 133.9, 129.8, 129.2, 128.6, 127.1, 123.7, 123.1, 120.4, 101.4, 92.7, 73.9; MS (TOF-EI) 165 (90), 194 (99), 222 (100), 234 (85), 268 (M$^+$, 10%). Anal. Calcd for $C_{16}H_{12}O_4$: C 71.64, H 4.51. Found: C 71.36, H 4.49.

1,3′-Dihydroxyl-5,5′,6,6′-tetramethylspiro[indene-2,1′-isobenzofuran]-3-one 3b. Yield 81%.

(1*R*,1′*R*,3′*S*)- and (1*S*,1′*S*,3′*R*)-3b-I. Mp 245−246 °C; IR ν (cm^{-1}) 3436, 3354, 1722; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.58 (s, 1H), 7.52 (s, 1H), 7.17 (s, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.38 (s, 1H), 5.20 (d, *J* = 5.8 Hz, 1H), 4.95 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 200.9, 151.5, 146.3, 138.8, 138.3, 138.0, 137.5, 136.8, 132.1, 127.7, 123.8, 123.7, 120.6, 101.3, 92.4, 73.8, 20.4, 19.4; HRMS (ESI+) 347.1250 (M + Na), anal. calcd for $C_{20}H_{20}O_4Na$ 347.1259 (M + Na).

5,5′,6,6′-Tetrachloro-1,3′-dihydroxylspiro[indene-2,1′-isobenzofuran]-3-one 3c. Yield 88%.

(1*R*,1′*R*,3′*S*)- and (1*S*,1′*S*,3′*R*)-3c-I. Mp 179−180 °C; IR ν (cm^{-1}) 3426, 3329, 1732; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.03 (s, 1H), 8.02 (s, 1H), 7.69 (s, 1H), 7.48 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.76 (d, *J* = 7.6 Hz, 1H), 5.25 (d, *J* = 7.5 Hz, 1H). A mixture of tautomers **3c-I** and **3c-II**: ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 198.0, 196.2, 153.5, 153.3, 142.8, 142.0, 139.3, 139.0, 138.9, 138.6, 134.1, 133.5, 133.0, 132.6, 132.0, 131.8, 131.7, 131.6, 128.9, 128.1, 125.4, 125.3, 125.0, 124.3, 123.7, 100.54, 100.47, 92.1, 92.0, 73.6, 72.7. MS (TOF-EI) 370 (80), 372 (100), 404 (M$^+$, 3%). Anal. Calcd for $C_{16}H_8Cl_4O_4$: C 47.33, H 1.99. Found: C 47.28, H 2.29.

5,5′,6,6′-Tetrabromo-1,3′-dihydroxylspiro[indene-2,1′-isobenzofuran]-3-one 3d. Yield 87%.

(1*R*,1′*R*,3′*S*)- and (1*S*,1′*S*,3′*R*)-3d-I. Mp 218−220 °C; IR ν (cm^{-1}) 3422, 3342, 1734; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.18 (s, 1H), 8.12 (s, 1H), 7.83 (s, 1H), 7.63 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.80 (d, *J* = 7.7 Hz, 1H), 5.26 (d, *J* = 7.6 Hz, 1H). A mixture of tautomers **3d-I** and **3d-II**: ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 198.0, 196.2, 153.9, 153.7, 143.6, 142.7, 140.1, 139.7, 134.7, 134.1, 132.6, 132.1, 132.0, 131.2, 128.3, 128.2, 127.5, 126.8, 125.6, 125.2, 124.7, 124.5, 124.3, 124.1, 100.4, 100.3, 92.0, 91.9, 73.5, 72.6; HRMS (ESI−) 578.7081 (M − 1), anal. calcd for $C_{16}H_7Br_4O_4$ 578.7078 (M − 1).

1,3′-Dihydroxylspiro[benz[*f*]indene-2,1′-naphtho[2,3-*c*]furan]-3-one 3e. Yield 77%, mp 300 °C dec.; IR ν (cm^{-1}) 3442, 3337, 1726, 1625. A mixture of tautomers **3e-I** and **3e-II**: ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.47 (s, 1H), 8.32 (s, 0.8H), 8.24 (s, 0.2H), 8.19 (d, *J* = 8.1 Hz, 1H), 8.11 (t, *J* = 8.4 Hz, 1H), 7.92−7.96 (m, 2H), 7.66−7.75 (m, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.35−7.46 (m, 2.2H), 7.29 (d, *J* = 7.6 Hz, 0.8H), 7.16 (d, *J* = 7.4 Hz, 0.2H), 7.07 (s, 0.8H), 6.77 (d, *J* = 7.6 Hz, 0.8H), 6.67 (d, *J* = 7.5 Hz, 0.2H), 5.93 (d, *J* = 7.2 Hz, 0.2H), 5.61 (d, *J* = 6.2 Hz, 0.8H), 5.30 (d, *J* = 6.1 Hz, 0.8H), 5.25 (d, *J* = 7.2 Hz, 0.2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 201.6, 200.3, 146.7, 146.4, 139.9, 139.2, 138.5, 138.3, 137.2, 137.0, 133.4, 133.3, 133.22, 133.19, 133.16, 133.0, 131.9, 131.3, 130.5, 130.4, 129.2, 129.1, 128.5, 128.3, 128.2, 128.0, 127.2, 127.0, 126.4, 126.24, 126.16, 125.3, 125.0, 122.1, 121.9, 119.7, 119.0, 100.8, 92.9, 75.3, 74.5; HRMS (TOF-ESI+) 391.0952 (M + Na$^+$), anal. Calcd for $C_{24}H_{16}O_4Na$ 391.0946 (M + Na$^+$).

General Procedure for the Reaction of Phthalaldehydes 1 Catalyzed by 1,2,4-Triazole Carbene. Phthalaldehydes **1a**−**1d** and **1h**-**1j** or naphthalene-2,3-dicarbaldehyde **1e** (2 mmol), 1,4-dibenzyl-1,2,4-triazolium salt **2d** (0.4 mmol), and DBU (0.4 mmol) were mixed in dichloroethane (30 mL). The reaction mixture was stirred at 60 °C for 1−6 h. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel column eluting with a mixture of ethyl acetate, petroleum ether, and ethanol (10:10:2) for **5a**−**5d** and **5h-5j**, or a mixture of THF and ethyl acetate (1:2) for **5e**, to afford fused indenones **5a**−**5e** in 71−92% yields, or the mixtures of isomeric products **5h-5j** in total yields of 55−92%. The separation of isomeric products **5h-I**, **5h-II**, **5h-III** and **5h-IV**, or **5i-I** and **5i-II** is described in Supporting Information.

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-4b,9b,10-Trihydroxyl-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5a. Yield 85%, mp 201−202 °C; IR ν (cm^{-1}) 3487, 3377, 1710; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.79 (d, *J* = 7.4 Hz, 1H), 7.75 (dt, *J* = 6.8, 1.1 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.49 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.40−7.43 (m, 1H), 7.34−7.37 (m, 1H), 7.28−7.33 (m, 2H), 6.05 (s, 1H), 5.82 (d, *J* = 6.4 Hz, 1H), 5.17 (s, 1H), 4.95 (d, *J* = 5.9 Hz, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 202.6, 154.2, 143.5, 142.7, 136.8, 136.3, 131.0, 130.9, 130.2, 127.4, 127.1, 126.3, 124.1, 86.9, 84.0, 77.9; HRMS (ESI+) 291.0634 (M + Na), anal. calcd for $C_{16}H_{12}O_4Na$ 291.0633 (M + Na).

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-4b,9b,10-Trihydroxyl-2,3,7,8-tetramethyl-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5b. Yield 71%, mp 270−271 °C; IR ν (cm^{-1}) 3509, 3379, 3302, 1703; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.52 (s, 1H), 7.31 (s, 1H), 7.14 (s, 1H), 7.10 (s, 1H), 5.85 (s, 1H), 5.65 (d, *J* = 6.5 Hz, 1H), 4.97 (s, 1H), 4.86 (d, *J* = 6.4 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 202.3, 151.5, 145.7, 140.2, 139.9, 138.8, 138.1, 137.1, 131.7, 127.1, 126.6, 125.4, 123.1, 86.1, 83.0, 76.0, 20.4, 19.5, 19.3; HRMS (ESI−) 323.1281 (M − 1), anal. calcd for $C_{20}H_{19}O_4$ 323.1283 (M − 1).

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-2,3,7,8-Tetrachloro-4b,9b,10-trihydroxyl-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5c. Yield 86%, mp 235−236 °C; IR ν (cm^{-1}) 3417, 1728; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.03 (s, 1H), 7.82 (s, 1H), 7.56 (s, 1H), 7.49 (s, 1H), 6.51 (s, 1H), 5.99 (d, *J* = 6.5 Hz, 1H), 5.68 (s, 1H), 4.90 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 199.6, 153.4, 143.4, 141.1, 139.0, 133.5, 133.0, 132.7, 131.7, 128.5, 128.4, 126.7, 125.1, 85.8, 83.9, 75.7; MS (TOF-EI) 295 (80), 370 (99), 372 (90), 386 (100), 404 (M$^+$, 10%). Anal. Calcd for $C_{16}H_8Cl_4O_4$: C 47.33, H 1.99. Found: C 47.36, H 2.34.

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-2,3,7,8-Tetrabromo-4b,9b,10-trihydroxyl-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5d. Yield 92%, mp 287−288 °C; IR ν (cm^{-1}) 3424, 1726; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.19 (s, 1H), 7.94 (s, 1H), 7.72 (s, 1H), 7.66 (s, 1H), 6.54 (s, 1H), 6.01 (d, *J* = 6.4 Hz, 1H), 5.70 (s, 1H), 4.92 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 199.7, 153.8, 144.1, 141.8, 133.6, 132.6, 131.7, 131.6, 129.8, 128.1, 126.1, 125.4, 124.2, 85.8, 83.8, 75.6; HRMS (ESI−) 578.7078 (M − 1), anal. calcd for $C_{16}H_7Br_4O_4$ 578.7087 (M − 1).

(5b*S*,12b*R*,13*R*)- and (5b*R*,12b*S*,13*S*)-5b,12b,13-Trihydroxyl-12b,13-dihydrobenz[*f*]indeno[2,1-*a*]benz[*f*]inden-6-one 5e. Yield 72%, mp 270 °C dec.; IR ν (cm^{-1}) 3419, 3383, 1728, 1627; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.36 (s, 1H), 8.28 (s, 1H), 8.07 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 9.4 Hz, 3H), 7.86 (brs, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.44−7.46 (m, 2H), 6.29

(s, 1H), 5.88 (d, J = 5.9 Hz, 1H), 5.37 (s, 1H), 5.31 (d, J = 5.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 202.5, 166.8, 141.3, 140.2, 136.9, 134.0, 133.3, 133.1, 131.6, 130.1, 128.8, 128.3, 128.1, 127.9, 127.0, 126.4, 126.2, 125.6, 125.3, 124.4, 124.3, 86.9, 83.7, 76.4; HRMS (TOF-ESI+) 391.0950 (M + Na$^+$), anal. calcd for $C_{24}H_{16}O_4Na$ 391.0946 (M + Na$^+$).

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-3,8-Dibromo-4b,9b,10-trihydroxy-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5h-I. Yield 45%, mp 206−207 °C; IR ν (cm^{-1}) 3436, 1727; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.00 (d, J = 1.4 Hz, 1H), 7.72 (dd, J = 8.1, 1.6 Hz, 1H), 7.51−7.55 (m, 3H), 7.32 (d, J = 8.1 Hz, 1H), 6.36 (s, 1H), 5.91 (d, J = 6.6 Hz, 1H), 5.51 (s, 1H), 4.91 (d, J = 6.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 201.0, 155.9, 143.3, 141.9, 133.4, 132.9, 132.1, 130.3, 129.3, 128.6, 127.6, 125.2, 121.8, 85.9, 83.7, 76.0; MS (ESI+) 446 (M + Na). Anal. Calcd for $C_{16}H_{10}Br_2O_4$: C 45.10, H 2.37. Found: C 45.26, H 2.55.

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-2,8-Dibromo-4b,9b,10-trihydroxy-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5h-II. Yield 21%, mp 233−234 °C; IR ν (cm^{-1}) 3437, 1727; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.99 (d, J = 1.4 Hz, 1H), 7.71 (dd, J = 8.1, 1.5 Hz, 1H), 7.52 (d, J = 6.8 Hz, 3H), 7.35 (d, J = 8.8 Hz, 1H), 6.26 (s, 1H), 5.94 (d, J = 6.6 Hz, 1H), 5.50 (s, 1H), 4.94 (d, J = 6.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 201.0, 155.7, 145.1, 140.3, 133.3, 132.2, 132.1, 130.2, 129.3, 129.2, 127.1, 125.1, 122,9, 85.8, 83.6, 76.1; MS (ESI+) 446 (M + Na). Anal. Calcd for $C_{16}H_{10}Br_2O_4$: C 45.10, H 2.37. Found: C 45.19, H 2.64.

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-3,7-Dibromo-4b,9b,10-trihydroxy-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5h-III. Yield 18%, mp 214−215 °C; IR ν (cm^{-1}) 3393, 3341, 1731; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.98 (dd, J = 8.1, 1.5 Hz, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.52 (s, 1H), 7.35 (d, J = 8.1 Hz, 1H), 6.41 (s, 1H), 5.98 (d, J = 6.6 Hz, 1H), 5.46 (s, 1H), 4.91 (d, J = 6.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 201.0, 152.7, 143.4, 141.9, 138.9, 135.0, 132.9, 128.7, 128.5, 127.6, 125.7, 123.4, 121.8, 86.0, 83.5, 75.9; HRMS (ESI+) 446.8839 (M + Na), anal. calcd for $C_{16}H_{10}Br_2O_4Na$ 446.8838 (M + Na).

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-2,7-Dibromo-4b,9b,10-trihydroxy-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5h-IV. Yield 8%, mp 204−205 °C; IR ν (cm^{-1}) 3388, 1733; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.97 (dd, J = 8.2, 1.3 Hz, 1H), 7.76 (d, J = 8.9 Hz, 2H), 7.54 (d, J = 10.5 Hz, 2H), 7.36 (d, J = 8.1 Hz, 1H), 6.31 (s, 1H), 6.99 (d, J = 6.6 Hz, 1H), 5.45 (s, 1H), 4.93 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 200.9, 152.6, 145.1, 140.3, 138.8, 135.1, 132.1, 129.3, 128.5, 127.1, 125.7, 123.4, 123.0, 85.9, 83.3, 76.0; HRMS (ESI−) 422.8852 (M − 1), anal. calcd for $C_{16}H_9Br_2O_4$ 422.8868 (M − 1).

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-3,8-Dichloro-4b,9b,10-trihydroxy-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5i-I. Yield 44%, mp 215−216 °C; IR ν (cm^{-1}) 3393, 3321, 1735; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.85 (d, J = 1.4 Hz, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.57 (dd, J = 8.2, 1.6 Hz, 1H), 7.37−7.42 (m, 3H), 6.36 (s, 1H), 5.92 (d, J = 6.5 Hz, 1H), 5.51 (s, 1H), 4.93 (d, J = 6.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 200.8, 155.9, 143.1, 141.5, 141.0, 133.4, 131.8, 130.5, 130.1, 128.3, 126.3, 125.2, 124.6, 86.0, 83.8, 75.9; HRMS (ESI+) 337.0019 (M + 1), anal. calcd for $C_{16}H_{11}Cl_2O_4$ 337.0034.

(4b*S*,9b*R*,10*R*)- and (4b*R*,9b*S*,10*S*)-2,8-Dichloro-4b,9b,10-trihydroxy-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5i-II. Yield 39%, mp 205−206 °C; IR ν (cm^{-1}) 3396, 1728; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.87 (s, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.40−7.46 (m, 3H), 6.29 (s, 1H), 5.96 (d, J = 5.4 Hz, 1H), 5.53 (s, 1H), 4.97 (d, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 200.8, 155.7, 144.8, 140.9, 139.9, 134.4, 131.9, 130.5, 129.3, 126.8, 126.3, 126.2, 125.1, 85,8, 83.6, 76.1; MS (ESI+) 359 (M + Na). Anal. Calcd for $C_{16}H_{10}Cl_2O_4$: C 57.00, H 2.99. Found: C 57.07, H 3.37.

(4b*S*,9b*R*,10*R*)- and (4b*S*,9b*R*,10*R*)-4b,9b,10-Trihydroxy-3,8-dimethoxy-9b,10-dihydroindeno[2,1-*a*]inden-5-one 5j-I. Yield 41%, mp 170−171 °C; IR ν (cm^{-1}) 3385, 1701, 1599; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.50 (d, J = 8.5 Hz, 1H), 7.25 (d, J = 9.2 Hz, 1H), 7.24 (s, 1H), 7.03 (dd, J = 8.5, 2.0 Hz, 1H), 6.90 (s, 1H), 7.89 (d, J = 6.8 Hz, 1H), 5.96 (s, 1H), 5.63 (d, J = 6.6 Hz, 1H), 5.09 (s, 1H), 4.90 (d, J = 6.5 Hz, 1H), 3.87 (s, 1H), 3.71 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 200.4, 165.6, 159.9, 157.0, 143.6, 134.5, 127.4, 126.4, 125.0, 117.7, 116.8, 109.4, 108.6, 86.1, 83.4, 75.8, 55.9, 55.2; HRMS (ESI−) 327.0862 (M − 1), anal. calcd for $C_{18}H_{15}O_6$ 327.0869 (M − 1).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Procedures for the acylation of **3a** and **5** and the separation of isomeric products **5-I**, **5-II**, **5-III**, and **5-IV**; the preparation and full characterization of trihydroxyl- and tetrahydroxylindeno[2,1-*a*]indenes **11** and **12**; ORTEP drawing of X-ray structures of compounds **3a-I**, **5a**, **4a-I**, **4a-II**, **6h-I**, **6h-II**, **6h-III**, and **5j-I**; copies of ^{1}H NMR and ^{13}C NMR spectra of products **3**, **5**, **11** and **12**; single crystal data of **3a-I**, **5a**, **4a-I**, **4a-II**, **6h-I**, **6h-II**, **6h-III**, and **5j-I** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ycheng2@bnu.edu.cn.

■ ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No. 20832006), the Ministry of Science and Technology of China (2009ZX09501-006), Beijing Municipal Commission of Education and the Fundamental Research Funds for the Central Universities (2009SC-1).

■ REFERENCES

(1) (a) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606–5655 and references therein. (b) Marion, N.; Diez-Gonzalez, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988–3000 and references therein.

(2) (a) Ema, T.; Oue, Y.; Akihara, K.; Miyazaki, Y.; Sakai, T. *Org. Lett.* **2009**, *11*, 4866–4869. (b) Lathrop, S. P.; Rovis, T. *J. Am. Chem. Soc.* **2009**, *131*, 13628–13630. (c) Enders, D.; Henseler, A. *Adv. Synth. Catal.* **2009**, *351*, 1749–1752. (d) Enders, D.; Grossmann, A.; Fronert, J.; Raabe, G. *Chem. Commun.* **2010**, *46*, 6282–6284. (e) Shimakawa, Y.; Morikawa, T.; Sakaguchi, S. *Tetrahedron Lett.* **2010**, *51*, 1786–1789.

(3) (a) DiRocco, D. A.; Oberg, K. M.; Dalton, D. M.; Rovis, T. *J. Am. Chem. Soc.* **2009**, *131*, 10872–10874. (b) Li, Y.; Shi, F.-Q.; He, Q.-L.; You, S.-L. *Org. Lett.* **2009**, *11*, 3182–3185. (c) Liu, Q.; Rovis, T. *Org. Lett.* **2009**, *11*, 2856–2859. (d) Read de Alaniz, J.; Rovis, T. *Synlett* **2009**, 1189–1207. (e) Liu, Q.; Perreault, S.; Rovis, T. *J. Am. Chem. Soc.* **2008**, *130*, 14066–14067.

(4) (a) Nair, V.; Babu, B. P.; Vellalath, S.; Varghese, V.; Raveendran, A. E.; Suresh, E. *Org. Lett.* **2009**, *11*, 2507–2510. (b) Yadav, L. D. S.; Rai, V. K.; Singh, S.; Singh, P. *Tetrahedron Lett.* **2010**, *51*, 1657–1662. (c) Yang, L.; Tan, B.; Wang, F.; Zhong, G. *J. Org. Chem.* **2009**, *74*, 1744–1746. (d) Kaeobamrung, J.; Bode, J. W. *Org. Lett.* **2009**, *11*, 677–680. (e) Rommel, M.; Fukuzumi, T.; Bode, J. W. *J. Am. Chem. Soc.* **2008**, *130*, 17266–17267. (f) Hirano, K.; Piel, I.; Glorius, F. *Adv. Synth. Catal.* **2008**, *350*, 984–988. (g) Nair, V.; Babu, B. P.; Vellalath, S.; Suresh, E. *Chem. Commun.* **2008**, 747–749.

(5) (a) Lv, H.; Chen, X.-Y.; Sun, L.-H.; Ye, S. *J. Org. Chem.* **2010**, *75*, 6973–6976. (b) Chan, A.; Scheidt, K. A. *J. Am. Chem. Soc.* **2007**, *129*, 5334–5335. (c) He, M.; Uc, G. J.; Bode, J. W. *J. Am. Chem. Soc.* **2006**, *128*, 15088–15089. (d) He, M.; Struble, J. R; Bode, J. W. *J. Am. Chem. Soc.* **2006**, *128*, 8418–8420. (e) Huang, X.-L.; Chen, X.-Y.; Ye, S. *J. Org. Chem.* **2009**, *74*, 7585–7587. (f) He, L.; Lv, H.; Zhang, Y.-R.; Ye, S. *J. Org. Chem.* **2008**, *73*, 8101–8103. (g) Wang, X.-N.; Zhang, Y.-Y.; Ye, S. *Adv. Synth. Catal.* **2010**, *352*, 1892–1895. (h) Lv, H.; You, L.; Ye, S. *Adv. Synth. Catal.* **2009**, *351*, 2822–2826. (i) Wang, X.-N.; Shao, P.-L.; Lv, H.; Ye, S. *Org. Lett.* **2009**, *11*, 4029–4031. (j) Huang, X.-L.; He, L.; Shao, P.-L.; Ye, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 192–195. (k) Zhang, Y.-R.; Lv, H.; Zhou, D.; Ye, S. *Chem.—Eur. J.* **2008**, *14*, 8473–8476.

(6) (a) Candish, L.; Lupton, D. W. *Org. Lett.* **2010**, *12*, 4836–4839. (b) Phillips, E. M.; Roberts, J. M.; Scheidt, K. A. *Org. Lett.* **2010**, *12*, 2830–2833. (c) Gillingham, D. G.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 3860–3864. (d) Galopin, C. C. *Tetrahedron Lett.* **2001**, *42*, 5589–5591. (e) Harrington, P. E.; Tius, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 8509–8514.

(7) (a) Kaeobamrung, J.; Bode, J. W. *Org. Lett.* **2009**, *11*, 677–680. (b) Sánchez-Larios, E.; Holmes, J. M.; Daschner, C. L.; Gravel, M. *Org. Lett.* **2011**, *12*, 5772–5775. (c) Ye, W.; Cai, G.; Zhuang, Z.; Jia, X.; Zhai, H. *Org. Lett.* **2005**, *7*, 3769–3771.

(8) Sánchez-Larios, E.; Gravel, M. *J. Org. Chem.* **2009**, *74*, 7536–7539.

(9) (a) Pan, H.-R.; Li, Y.-J.; Yan, C.-X.; Xing, J.; Cheng, Y. *J. Org. Chem.* **2010**, *75*, 6644–6652. (b) Cheng, Y.; Ma, Y.-G.; Wang, X.-R.; Mo, J.-M. *J. Org. Chem.* **2009**, *74*, 850–855. (c) Cheng, Y.; Wang, B.; Wang, X.-R.; Zhang, J.-H.; Fang, D.-C. *J. Org. Chem.* **2009**, *74*, 2357–2367. (d) Liu, M.-F.; Wang, B.; Cheng, Y. *Chem. Commun.* **2006**, 1215–1217. (e) Cheng, Y.; Liu, M.-F.; Fang, D.-C.; Lei, X.-M. *Chem.—Eur. J.* **2007**, *13*, 4282–4292. (f) Mo, J.-M.; Ma, Y.-G.; Cheng, Y. *Org. Biomol. Chem.* **2009**, *7*, 5010–5019. (g) Li, J.-Q.; Liao, R.-Z.; Ding, W.-J.; Cheng, Y. *J. Org. Chem.* **2007**, *72*, 6266–6269.

(10) Phillips, E. M.; Wadamoto, M.; Chan, A.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 3107–3110.

(11) Sun, F.-G.; Huang, X.-L.; Ye, S. *J. Org. Chem.* **2010**, *75*, 273–276.

(12) Nair, V.; Vellalath, S.; Poonoth, M.; Mohan, R.; Suresh, E. *Org. Lett.* **2006**, *8*, 507–509.

(13) (a) Baragwanath, L.; Rose, C. A.; Zeitler, K.; Connon, S. J. *J. Org. Chem.* **2009**, *74*, 9214–9217. (b) O'Toole, S. E.; Connon, S. J. *Org. Biomol. Chem.* **2009**, *7*, 3584–3593. (c) Ma, Y.; Wei, S.; Wu, J.; Yang, F.; Liu, B.; Lan, J.; Yang, S.; You, J. *Adv. Synth. Catal.* **2008**, *350*, 2645–2651. (d) Enders, D.; Han, J. *Tetrahedron: Asymmetry* **2008**, *19*, 1367–1371. (e) Li, Y.; Feng, Z.; You, S.-L. *Chem. Commun.* **2008**, 2263–2265. (f) Chiang, P.-C.; Kaeobamrung, J.; Bode, J. W. *J. Am. Chem. Soc.* **2007**, *129*, 3520–3521. (g) Enders, D.; Niemeier, O.; Raabe, G. *Synlett* **2006**, 2431–2434. (h) Takikawa, H.; Hachisu, Y.; Bode, J. W.; Suzuki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 3492–3494. (i) Enders, D.; Kallfass, U. *Angew. Chem., Int. Ed.* **2002**, *41*, 1743–1745.

(14) (a) Mavis, M. E.; Yolacan, C.; Aydogan, F. *Tetrahedron Lett.* **2010**, *51*, 4509–4511. (b) Aupoix, A.; Pegot, B.; Vo-Thanh, G. *Tetrahedron* **2010**, *66*, 1352–1356. (c) Orsini, M.; Chiarotto, I.; Elinson, M. N.; Sotgiu, G.; Inesi, A. *Electrochem. Commun.* **2009**, *11*, 1013–1017. (d) Estager, J.; Leveque, J.-M.; Turgis, R.; Draye, M. *Tetrahedron Lett.* **2007**, *48*, 755–759. (e) Estager, J.; Leveque, J.-M.; Turgis, R.; Draye, M. *J. Mol. Catal. A: Chem.* **2006**, *256*, 261–264. (f) Jiang, F. S.; Yu, H.; Gao, G.; Xie, R. G. *Chin. Chem. Lett.* **2005**, *16*, 321–324.

(15) Struble, J. R.; Kaeobamrung, J.; Bode, J. W. *Org. Lett.* **2008**, *10*, 957–960.