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Changing the Reaction Pathway by NHC/Brønsted Base Cooperative Catalysis: Highly Stereoselective Synthesis of Multifunctional Benzo[*a*]fluoren-11-ones from the Dimerization of 2-(Aroylvinyl)arylaldehydes

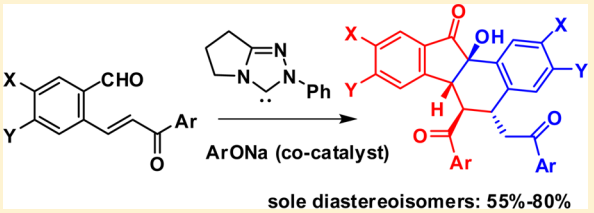
Yuan-feng Tong,[†,‡] Jian-hui Mao,[†] Song Wu,[‡] Yuan Zhao,[†] and Ying Cheng[†,*]

[†]College of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China

[‡]Institute of Materia Medica, Chinese Academy of Medical Sciences & Peking Union Medical College, Beijing 100050, People's Republic of China

Supporting Information

ABSTRACT: The unprecedented NHC/Brønsted base-cocatalyzed dimerization reaction of 2-(aroylvinyl)arylaldehydes was reported. In the presence of a triazole carbene catalyst alone, no reaction of 2-(aroylvinyl)arylaldehydes was observed. However, the combination of triazole carbene and 4-methoxyphenolate efficiently catalyzed the dimerization of 2-(aroylvinyl)arylaldehydes to proceed through a benzoin−Michael−Michael reaction cascade, producing 6-aroyl-5-(aroylmethyl)-11a-hydroxybenzo[*a*]fluoren-11-ones as the sole diastereomers in good yields.



INTRODUCTION

Organocatalysis[1] has been shown to display distinct activation modes of the respective substrates, making the combination of different catalysts in one reaction possible. N-heterocyclic carbenes (NHCs) are versatile Lewis base catalysts that can promote a variety of unconventional transformations, including umpolung of aldehydes,[2] homoenolate generation,[3] oxidative transformations of aldehydes,[4] Brønsted base activated reactions,[5] etc.[6] In recent years, NHC-catalyzed cascade reactions have been attracting continued interest due to the rapid construction of complexity of products.[7] Particularly, a few dual catalytic approaches using NHCs in combination with a second base catalyst have emerged. For example, N-heterocyclic carbene/Brønsted base (a carboxylate salt) cocatalysis enhanced the rate and selectivity of asymmetric acylation of secondary alcohols,[8] and the enantioselective annulation between α,β-unsaturated aldehydes and 2-(bromomethyl)-*o*-(*tert*-butyldimethylsilyl)phenol was activated by combined N-heterocyclic carbene/Lewis base (fluoride) catalysts.[9] In addition, the N-heterocyclic carbene acted as a Brønsted base and a Lewis base catalyst, respectively, in different steps of the cascade rearrangement of cyclopropyl enol esters to dihydropyranones.[10] Furthermore, the N-heterocyclic carbene/Brønsted base cascade catalysis in the reaction of 2-(2-propynyloxy)benzaldehydes with aldehydes led to the formation of benzofuran-3-ones, while the same reaction catalyzed by only NHC afforded chroman-4-ones.[11] These studies have indicated that the cooperative catalysis of N-heterocyclic carbenes and Brønsted or Lewis bases could either improve the reactivity and selectivity of the reaction or regulate the reaction pathways. Therefore, the discovery and development of new synthetic methods utilizing a combined N-heterocyclic carbene/base catalysis strategy are of great importance.

Among the large number of known N-heterocyclic carbene catalyzed reactions, very few have a 2-(aroylvinylaryl)aldehyde as a reactant. For instance, triazole carbene catalyzed annulations of 2-(aroylvinyl)arylaldehydes with nitrosoarenes provided a versatile method for the construction of different types of aromatic ring fused 1,2-oxazinones.[12] On the other hand, the reaction of 2-(aroylvinyl)benzaldehydes with phthalaldehydes produced indene-spiro-indane-1,3-diones under the catalysis of a thiazole carbene.[13] In addition, the imidazole carbene catalyzed intramolecular cyclization of 2-(aroylvinyl)benzaldehydes led to the formation of naphthalenones.[14] In 2010[13a] and 2011,[13b] Gravel and co-workers reported the thiazole carbene catalyzed dimerization reaction of 2-(aroylvinyl)benzaldehydes, which formed spirobi[inden]-1-ones **3** via a Stetter−aldol−Michael cascade (Scheme 1, eq 1). However, our current study on the NHC/base cocatalysis has demonstrated that the dimerization of 2-(aroylvinyl)-benzaldehydes under the catalysis of a triazole carbene in combination with a sodium phenolate proceeded through quite different pathways to produce multifunctional spiro[indene-2,1′-isobenzofuran]-1-ones **4** and benzo[*a*]fluoren-11-one derivatives **5** with high stereoselectivity. Meanwhile, the spiro-indanones **4** can be converted into fused indanones **5** under the reaction conditions (Scheme 1, eq 2). Herein, we report this novel NHC/Brønsted base cooperative catalyzed cascade reaction.

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Scheme 1. Comparison between the Dimerizations of 2-(Aroylvinyl)benzaldehydes 1 under Gravel's Conditions and Those under Our Catalytic Conditions

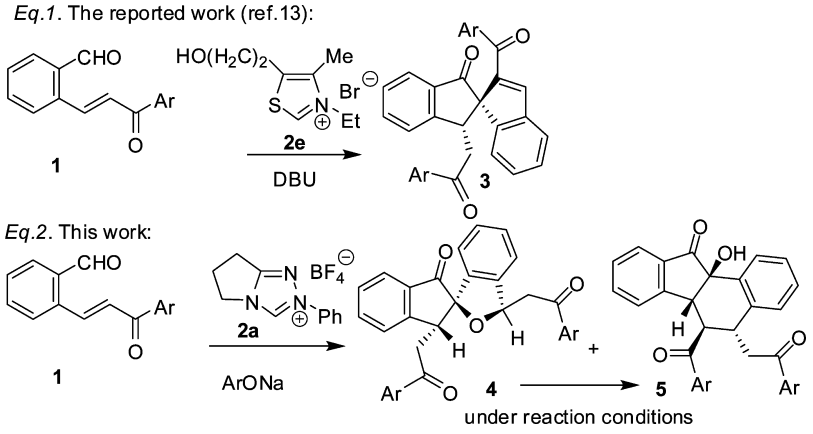
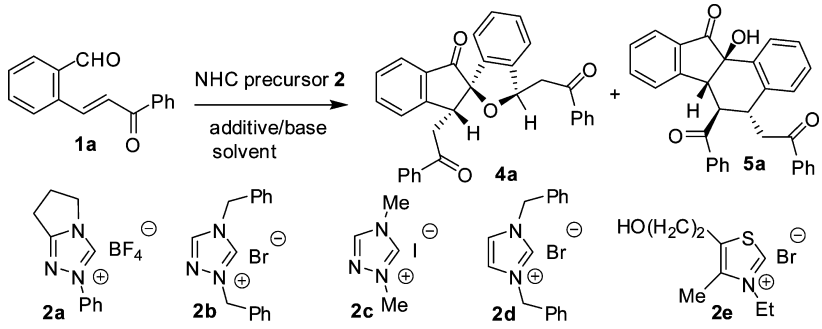


Table 1. Optimization of Reaction Conditions



entry	NHC precursor 2[a]	base (amt (equiv))	additive[b]	solvent	temp (°C)	time (h)	yield (%) 4a	yield (%) 5a
1	**2a**	NaH (0.2)		DCM	room temp	6	*c*	
2	**2a**	NaH (0.2)	benzoic acid	DCM	room temp	6	*d*	
3	**2a**	NaH (0.2)	*o*-chlorobenzoic acid	DCM	room temp	6	*d*	
4	2a	NaH (0.2)	phenol	DCM	room temp	6	25[e]	21
5	**2a**	NaH (1.2)	phenol	DCM	30–35	6	18	59
6	**2a**	**NaH (1.2)**	**4-methoxyphenol**	**DCM**	**30–35**	**6**	**trace**	**73**
7	**2a**	NaH (1.2)	2-(hydroxymethyl)phenol	DCM	30–35	6	trace	70
8	**2a**	NaH (1.2)	4-chlorophenol	DCM	30–35	6	trace	58
9	**2b**	NaH (1.2)	4-methoxyphenol	DCM	30–35	6	trace	58
10	**2c**	NaH (1.2)	4-methoxyphenol	DCM	30–35	6	trace	63
11	**2d**	NaH (1.2)	4-methoxyphenol	DCM	30–35	6	trace	13
12	**2e**	NaH (1.2)	4-methoxyphenol	DCM	30–35	6	*f*	
13	**2a**	NaH (1.2)	4-methoxyphenol	CH_3CN	30–35	6	trace	52
14	**2a**	NaH (1.2)	4-methoxyphenol	benzene	30–35	6	trace	64
15	**2a**	NaH (1.2)	4-methoxyphenol	THF	30–35	6	*d*	
16	**2a**	DBU (1.2)	4-methoxyphenol	DCM	30–35	6	21	12
17	**2a**	Cs_2CO_3 (1.2)	4-methoxyphenol	DCM	30–35	6	15	10

[a]20 mol % of NHC precursors **2** was used. [b]1 equiv of additives was used. [c]No reaction. [d]Messy mixture of products. [e]A byproduct that was derived from one molecule of aldehyde **1a** was detected in the crude product **4a** by ^{1}H NMR, and this byproduct could not be separated from **4a** by TLC. [f]Spiro-indene **3a** (Ar = Ph)[13] was isolated in 25% yield.

RESULTS AND DISCUSSION

At the outset of our study, we examined the reaction of 2-(benzoylvinyl)benzaldehyde (**1a**) in the presence of tetrahydropyrrolo[2,1-*c*][1,2,4]triazole carbene **2a**′, which was generated from the triazolium salt **2a** with NaH in dichloromethane at ambient temperature. No reaction was observed under these conditions (Table 1, entry 1). Since Yamada[8] and Rovis[15] have reported the use of a carboxylate salt or carboxylic acid as a basic or an acidic cocatalyst, respectively, in the NHC catalysis to accelerate the reaction and improve the stereoselectivity, we envisioned that the combined N-heterocyclic carbene/carboxylic acid catalysts could promote the reaction of 2-(benzoylvinyl)benzaldehydes **1**. Disappointingly, however, in the presence of both triazole carbene **2a**′ and a benzoic acid or a *o*-chlorobenzoic acid, the reaction of 2-(benzoylvinyl)-benzaldehyde (**1a**) yielded a messy mixture of products

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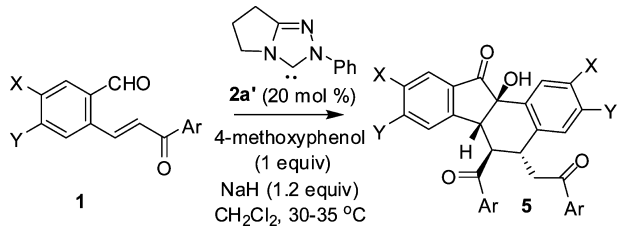
(Table 1, entries 2 and 3). The cocatalysts were further screened by the replacement of carboxylic acids with phenols. To our delight, catalyzed by triazole carbene **2a′** (20 mol %) in the presence of phenol (1 equiv) and NaH (0.2 equiv) in dichloromethane at ambient temperature (about 15−20 °C), the novel multifunctional spiro[indene-2,1′-isobenzofuran]-1-one **4a** and benzo[*a*]fluoren-11-one **5a** were isolated in 25% and 21% yields, respectively (Table 1, entry 4). Monitoring by TLC analysis, we found that the reaction of **1a** gave immediately both spiro[indene-2,1′-isobenzofuran]-1-one **4a** and benzo[*a*]fluoren-11-one **5a** when all of the reactants were mixed in the solvent. During the course of the reaction, the product **4a** underwent isomerization to afford product **5a**. The presence of sodium phenolate was beneficial in accelerating this isomerization. To facilitate the transformation of **4a** to **5a**, the reaction of 2-(benzoylvinyl)benzaldehyde (**1a**) was then conducted employing sodium phenolate, which was generated in situ from phenol (1 equiv) and NaH (1.2 equiv), as a cocatalyst at a higher temperature (30−35 °C). From this reaction, 59% of benzo[*a*]fluoren-11-one **5a** along with 18% of spiro[indene-2,1′-isobenzofuran]-1-one **4a** were isolated (Table 1, entry 5). The reaction conditions were further optimized by varying cocatalytic additives, carbenes, bases, and solvents. As indicated in Table 1, under the catalysis of triazole carbene **2a′** in dichloromethane at 30−35 °C, the replacement of phenol by 4-methoxyphenol or 2-(hydroxymethyl)phenol improved the yield of benzo[*a*]fluoren-11-one **5a** to 70−73%, while the use of 4-chlorophenol led to a yield of **5a** similar to that of phenol (Table 1, entries 6−8). Among the different types of carbene catalysts examined, triazole carbenes **2a′**−**c′** combined with phenolates promoted the reaction efficiently (Table 1, entries 5−10). The reaction catalyzed by imidazole carbene **2d′** or thiazole carbene **2e′** in the presence of phenolates gave a very low yield or virtually none of such products under the same conditions (Table 1, entries 11 and 12). It should also be noted that, under the catalysis of triazole carbene **2a′** and 4-methoxyphenolate, the use of other solvents, including acetonitrile, benzene, and THF, and the employment of other bases such as DBU and Cs_2CO_3 resulted in a decrease in the yields of the products.

With the optimized conditions in hand, we then examined the scope and limitations of the selective synthesis of benzo[*a*]fluoren-11-one derivatives **5**. It was found that, under the catalysis of triazole carbene **2a′**/4-methoxyphenolate, all 2-(aroylvinyl)arylaldehyde substrates **1** tested rapidly underwent a dimerization reaction to form both products **4** and **5**, and then products **4** smoothly isomerized into products **5**. Finally, 55−80% yields of **5** were obtained from the reaction carried out in dichloromethane at 30−35 °C for 6−24 h (Table 2). Notably, the presence of an electron-donating methoxy group on both benzene rings of **1** led to slow reaction velocity (Table 2, entries 2−4 and 8). It was also noteworthy that, irrespective of the electronic features of the substituent on the para position of the aroyl moiety, the reaction of **1a,d−g** produced the corresponding products in good yields (Table 2, entries 1 and 4−7). The variation of the substitution pattern of a methoxy group from para to ortho resulted in a decrease in the chemical yield (55%), while the *m*-methoxy-substituted product was obtained in 69% yield (Table 2, entries 2−4). The chemical yields were only marginally affected by the substituents on the benzaldehyde moiety. For instance, the reaction of substrates **1h−l** that bear either an electron-donating or an electron-withdrawing group afforded products

Table 2. Reaction of 2-(Aroylvinyl)arylaldehydes 1 Catalyzed by Triazole Carbene and 4-Methoxyphenolate at 30−35 °C



entry	1	X	Y	Ar	time (h)	yield of 5 (%)[a,b]
1	**1a**	H	H	Ph	6	73 (**5a**)
2	**1b**	H	H	2-MeOPh	12	55 (**5b**)
3	**1c**	H	H	3-MeOPh	12	69 (**5c**)
4	**1d**	H	H	4-MeOPh	24	60 (**5d**)
5	**1e**	H	H	4-MePh	6	70 (**5e**)
6	**1f**	H	H	4-BrPh	6	73 (**5f**)
7	**1g**	H	H	4-FPh	6	80 (**5g**)
8	**1h**	OMe	H	Ph	12	57 (**5h**)
9	**1i**	Me	H	Ph	6	60 (**5i**)
10	**1j**	F	H	Ph	6	70 (**5j**)
11	**1k**	H	Me	Ph	12	56 (**5k**)
12	**1l**	H	F	Ph	6	63 (**5l**)

[a]Isolated yields. [b]Trace amounts of byproducts that were not the diastereoisomers of **4** or **5** were detected in the reactions.

5h−l in chemical yields ranging from 56% to 70% (Table 2, entries 8−12).

It was noticed that the isomerization of products **4** to **5** slowed down at lower temperature. In order to isolate intermediate products **4** and identify their structures, the reactions of aldehydes **1** catalyzed by triazole carbene **2a′** and 4-methoxyphenolate were conducted at 0 °C and were quenched within 1 h. From these reactions, products **4** were isolated in 20−44% yields along with **5** in 26−49% yields (Scheme 2).

The structures of all isolated products were elucidated on the basis of spectroscopic data. The NMR spectra and mass data indicated evidently that both products **4** and **5** were derived from the addition or dimerization of two molecules of aldehydes **1**. To identify the isomeric products beyond doubt, the structures and stereochemistry of compounds **4f** and **5a** were determined unambiguously to be (1′*R**,3*R**,3′*R**)-3,3′-bis((4-bromobenzoyl)methyl)spiro[indene-2,1′-isobenzofuran]-1-one and (5*R**,6*R**,6a*R**,11a*R**)-6-benzoyl-11a-hydroxy-5-(benzoylmethyl)benzo[*a*]fluoren-11-one, respectively, by single-crystal X-ray diffraction analysis (see Figure S1 in the Supporting Information).

To account for the formations of 3,3′-di(aroylmethyl)spiro-[indene-2,1′-isobenzofuran]-1-ones **4** and 6-aroyl-5-aroylmethyl-11a-hydroxylbenzo[*a*]fluoren-11-ones **5** and the easy conversion of spiro-indanones **4** to fused indanones **5** under triazole carbene/4-methoxyphenolate cocatalytic conditions, we propose the reaction pathways that are illustrated in Scheme 3. The reaction cascade is most likely initiated by the triazole carbene catalyzed intermolecular benzoin condensation of aldehyde reactants **1**. The resulting α-hydroxyl ketone intermediates **6** would undergo base-catalyzed intramolecular oxa-Michael addition to form isobenzofuran intermediates **8**, which are converted to carbanions **9** via proton transfer. The intermediates **9** undergo intramolecular Michael addition to

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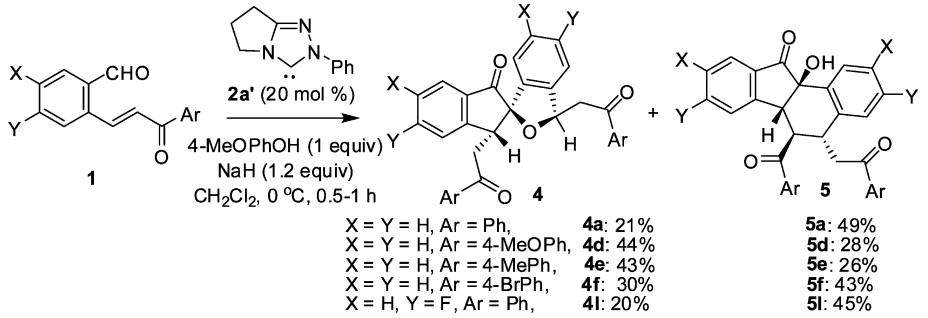
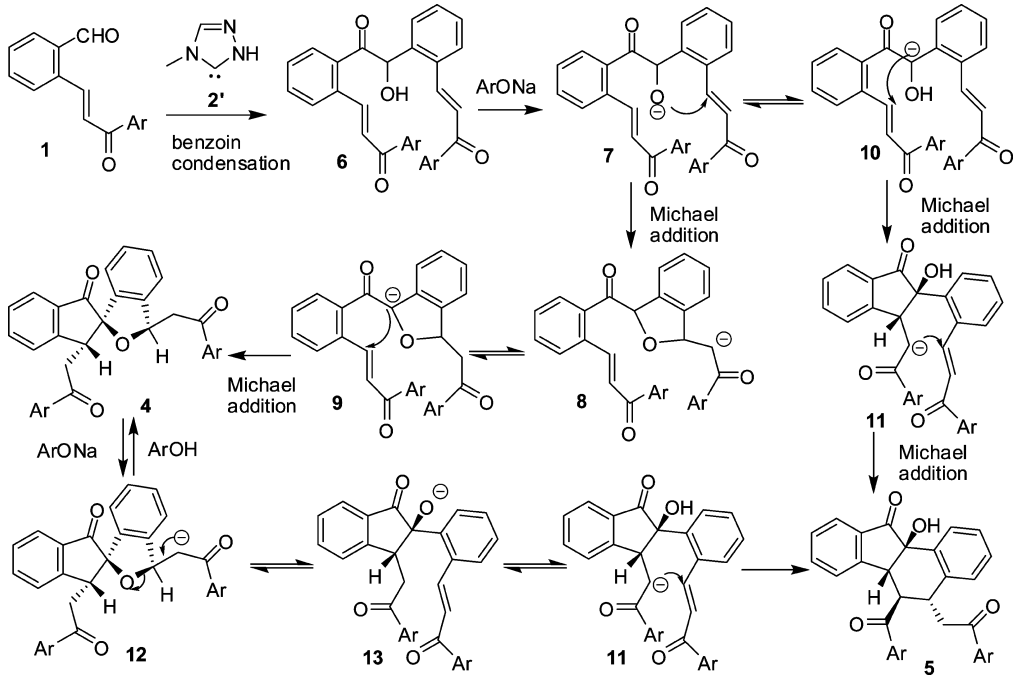
Scheme 2. Reaction of 2-Aroylvinylarylaldehydes 1 Catalyzed by Triazole Carbene and 4-Methoxyphenolate at 0 °C



Scheme 3. Proposed Mechanisms for the Formations of Spiro[indene-2,1′-isobenzofuran]-1-ones 4 and Benzo[*a*]fluoren-11-ones 5 from the Dimerization of 2-(Aroylvinyl)benzaldehydes



afford spiro[indene-2,1′-isobenzofuran]-1-ones **4**. Alternatively, the Benzoin condensation products **6** would also be deprotonated by a base to form carbanions **10**, which undergo sequential Michael addition reactions to produce benzo[*a*]-fluoren-11-one products **5**. The isomerization of products **4** to **5** under the basic conditions probably occurs through deprotonation of **4** by phenolate anion, which triggers the ring opening of tetrahydroisobenzofuran. The thus formed indanone intermediates **13** undergo Michael addition via their tautomers **11** to furnish the formation of benzo[*a*]fluoren-11-ones **5**. The base-catalyzed isomerization of products **4** to **5** has been confirmed by the transformation of pure compound **4a** in the presence of sodium phenolate. The products **4** and **5** have three and four stereocenters, respectively; however, no diastereoisomers of **4** or **5** were found in the reaction. The highly diastereoselective formation of (1′*R**,3*R**,3′*R**)-3,3′-bis(aroylmethyl)spiro[indene-2,1′-isobenzofuran]-1-ones **4** and (5*R**,6*R**,6a*R**,11a*R**)-6-aroyl-11a-hydroxyl-5-(aroylmethyl)-benzo[*a*]fluoren-11-ones **5** can be best explained by the steric effects of the substituents. During the formation of the indane-spiro-isobenzofuran structure of **4**, the two aroylmethyl groups attached to the furan and cyclopentanone rings, respectively, were oriented at the opposite faces of the isobenzofuran ring to reduce their repulsion. On the other hand, in the formation of the benzo[*a*]fluorene ring of **5**, while the cyclohexane was installed *cis* to indane to avoid fused-ring strain, the aroyl group connected to the cyclohexane ring was orientated *trans* to both the aroylmethyl and cyclopentyl groups to reduce steric hindrance among these substituents. As was mentioned earlier, Gravel reported the thiazole carbene catalyzed dimerization of 2-(aroylvinyl)benzaldehydes **1**, which proceeded via a Stetter–aldol–Michael cascade to form spirobi[inden]-1-ones **3** (Scheme 1, eq 1).[13] In this work, however, the dimerization of 2-(aroylvinyl)arylaldehydes **1** catalyzed by a combination catalytic system involving a triazole carbene and a Brønsted base followed the benzoin–Michael–Michael cascade pathway. It is important to address that, although we used an NHC catalyst different from Gravel's carbene catalyst, the triazole carbene was not the sole driving force for the change in reaction pathway, since no reaction of 2-(aroylvinyl)-benzaldehydes **1** was observed in the presence of a triazole carbene catalyst alone. Therefore, it can be concluded that the cooperative actions of triazole carbene and Brønsted base catalysts have promoted the current benzoin–Michael–Michael cascade reaction.

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CONCLUSIONS

In summary, we have shown for the first time the unprecedented NHC/Brønsted base cocatalyzed dimerization reaction of 2-(aroylvinyl)arylaldehydes. Being different from the known thiazole carbene catalyzed dimerization of 2-(aroylvinyl)benzaldehydes that proceeded via a Stetter–aldol–Michael cascade to form spirobi[inden]-1-ones,[13] under the cocatalysis of triazole carbene/phenolate catalysts, the dimerization of 2-(aroylvinyl)arylaldehydes followed a benzoin–Michael–Michael cascade to produce spiro[indene-2,1′-isobenzofuran]-1-one and benzo[*a*]fluoren-11-one derivatives with high diastereoselectivity, and the former can be converted into the latter products under the reaction conditions. It has been demostracted that the cooperative actions of triazole carbene and Brønsted base catalysts changed the reaction pathway of the dimerization of 2-(aroylvinyl)arylaldehydes. Therefore, this work not only provided an efficient method for the diastereoselective synthesis of novel multifunctional benzo[*a*]fluoren-11-ones but also opened up new opportunities for NHC/Brønsted base dual activation in NHC catalysis.

EXPERIMENTAL SECTION

General Procedure for the Selective Synthesis of Benzo[*a*]-fluoren-11-ones 5 from the Reaction of 2-(Aroylvinyl)-arylaldehydes 1 Catalyzed by a Combination of Triazole Carbene and Phenolate at 30–35 °C. Under a nitrogen atmosphere and at ambient temperature, 4-methoxyphenol (0.5 mmol) and NaH (0.6 mmol) were mixed in dry dichloromethane (15 mL) with stirring for 5 min, and then a solid mixture of 2-(aroylvinyl)arylaldehydes **1**[13a] (0.5 mmol) and triazolium salt **2a** (0.1 mmol) was added to this solution of 4-methoxyphenolate in dichloromethane. TLC indicated that both spiro[indene-2,1′-isobenzofuran]-1-ones **4** and benzo[*a*]fluoren-11-ones **5** were formed simultaneously when the reactants and catalysts were mixed in the solvent. The reaction mixture was then kept stirring at 30–35 °C for 6–24 h until products **4** were converted to products **5**. After removal of solvent under vacuum, the residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate (8/1–5/1) as eluent to give benzo[*a*]fluoren-11-ones **5** in 55–80% yields.

(5R,6R*,6aR*,11aR*)-6-Benzoyl-11a-hydroxy-5-(benzoylmethyl)benzo[a]fluoren-11-one (**5a**):* 86 mg, 73%, mp 264–266 °C; IR ν (cm^{-1}) 3491, 1720, 1685, 1672; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.56 (d, *J* = 7.3 Hz, 2H), 8.30 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.13–7.17 (m, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 5.17 (s, 1H), 5.03 (brs, 1H), 4.13 (s, 1H), 3.94 (d, *J* = 8.4 Hz, 1H), 2.68 (dd, *J* = 19.2, 4.1 Hz, 1H), 2.47 (dd, *J* = 19.2, 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.7, 201.8, 198.4, 154.0, 136.2, 136.0, 135.7, 135.0, 134.7, 134.1, 133.9, 133.4, 130.2, 129.8, 128.9, 128.7, 128.4, 128.3, 128.29, 127.7, 127.4, 125.8, 124.4, 75.8, 49.0, 45.7, 44.7, 37.8; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{32}H_{25}O_4$ 473.1747, found 473.1762.

(5R,6R*,6aR*,11aR*)-11a-Hydroxy-6-(2-methoxybenzoyl)-5-((2-methoxybenzoyl)methyl)benzo[a]fluoren-11-one (**5b**):* 73 mg, 55%, mp 208–210 °C; IR ν (cm^{-1}) 3486, 1721, 1674, 1654; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 (d, *J* = 7.9 Hz, 1H), 7.74–7.76 (m, 1H), 7.57 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52 (td, *J* = 8.6, 1.6 Hz, 1H), 7.36–7.42 (m, 3H), 7.32 (td, *J* = 8.0, 1.0 Hz, 1H), 7.22–7.26 (m, 2H), 7.12 (td, *J* = 7.6, 1.1 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 4.99 (s, 1H), 4.61 (s, 1H), 4.21 (s, 1H), 4.04 (s, 3H), 3.90 (t, *J* = 7.1 Hz, 1H), 3.38 (s, 3H), 2.57 (dd, *J* = 18.1, 5.8 Hz, 1H), 2.40 (dd, *J* = 18.2, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 206.3, 202.3, 199.4, 158.5, 158.0, 154.2, 136.2, 135.4, 135.3, 134.4, 133.7, 133.7, 130.7, 130.3, 129.6, 128.3, 128.0, 127.9, 127.74, 127.7, 127.1, 125.3, 124.8, 120.9, 120.4, 111.6, 111.3, 75.8, 55.9, 55.0, 50.7, 50.0, 48.5, 36.8; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{34}H_{29}O_6$ 533.1959, found 533.1953.

(5R,6R*,6aR*,11aR*)-11a-Hydroxy-6-(3-methoxybenzoyl)-5-((3-methoxybenzoyl)methyl)benzo[a]fluoren-11-one (**5c**):* 92 mg, 69%, mp 162–163 °C; IR ν (cm^{-1}) 3483, 1721, 1676, 1597; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.30 (d, *J* = 7.9 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 8.05 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.21 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.14–7.19 (m, 3H), 7.06 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 6.5 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.13 (s, 1H), 5.00 (s, 1H), 4.11 (s, 1H), 3.97 (s, 3H), 3.95 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.79 (s, 3H), 2.66 (dd, *J* = 19.1, 4.1 Hz, 1H), 2.44 (dd, *J* = 19.2, 11.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.5, 201.8, 198.1, 160.1, 159.6, 154.0, 137.5, 136.05, 136.03, 135.8, 135.0, 134.2, 130.1 129.9, 129.3, 128.7, 128.3, 128.3, 127.5, 125.7, 124.4, 122.4, 121.0, 120.3, 119.9, 113.5, 112.0, 75.8, 55.7, 55.5, 49.0, 45.8, 44.8, 38.0; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{34}H_{29}O_6$ 533.1959, found 533.1962.

(5R,6R*,6aR*,11aR*)-11a-Hydroxy-6-(4-methoxybenzoyl)-5-((4-methoxybenzoyl)methyl)benzo[a]fluoren-11-one (**5d**).* 80 mg, 60%, mp 184–185 °C; IR ν (cm^{-1}) 3432, 1721, 1670, 1652; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.58 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.34–7.39 (m, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.07 d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.75–6.78 (m, 3H), 5.20 (s, 1H), 5.10 (s, 1H), 4.09 (s, 1H), 3.92 (s, 3H), 3.91 (dd, *J* = 11.8, 3.6 Hz, 1H), 3.85 (s, 3H), 2.62 (dd, *J* = 19.0, 4.1 Hz, 1H), 2.41 (dd, *J* = 19.0, 11.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.2, 202.0, 197.0, 164.2, 163.8, 154.2, 135.9, 135.8, 135.4, 134.2, 132.2, 130.2, 130.0, 129.3, 128.6, 128.2, 128.1, 127.8, 127.4, 125.6, 124.5, 114.1, 113.6, 75.8, 55.6, 55.5, 49.0, 45.5, 44.5, 38.3; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{34}H_{29}O_6$ 533.1959, found 533.1962.

(5R,6R*,6aR*,11aR*)-11a-Hydroxy-6-(4-methylbenzoyl)-5-((4-methylbenzoyl)methyl)benzo[a]fluoren-11-one (**5e**):* 88 mg, 70%, mp 189–191 °C; IR ν (cm^{-1}) 3455, 1710, 1673, 1599; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.45 (d, *J* = 8.2 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.35–7.37 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.14 (td, *J* = 7.4, 1.2 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.05 (td, *J* = 7.3, 0.9 Hz, 1H), 6.75 (d, *J* = 7.3 Hz, 1H), 5.13 (s, 1H), 5.10 (br, 1H), 4.11 (s, 1H), 3.91 (d, *J* = 7.8 Hz, 1H), 2.63 (dd, *J* = 19.1, 4.2 Hz, 1H), 2.47 (s, 3H), 2.43 (dd, *J* = 19.1, 11.6 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.4, 201.9, 198.0, 154.0, 144.9, 144.3, 136.0, 135.8, 135.2, 134.2, 133.8, 132.3, 130.2, 129.9, 129.6, 129.0, 128.6, 128.3, 128.2, 127.8, 127.4, 125.7, 124.4, 75.8, 49.0, 45.7, 44.7, 38.0, 21.8, 21.6; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{34}H_{29}O_4$ 501.2060, found 501.2064.

(5R,6R*,6aR*,11aR*)-6-(4-Bromobenzoyl)-5-((4-bromobenzoyl)methyl)-11a-hydroxybenzo[a]fluoren-11-one (**5f**):* 115 mg, 73%, mp 229–230 °C; IR ν (cm^{-1}) 3509, 1719, 1676, 1662; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.42 (d, *J* = 7.8 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.29–7.34 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.07 (s, 1H), 4.89 (brs, 1H), 4.12 (s, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 2.64 (dd, *J* = 19.4, 3.0 Hz, 1H), 2.40 (dd, *J* = 19.4, 11.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.2, 200.5, 197.1, 154.5, 136.6, 135.9, 134.9, 134.8, 134.6, 133.2, 131.8, 131.4, 130.7, 129.5, 128.8, 128.4, 127.7, 127.5, 127.3, 127.2, 126.7, 125.9, 124.5, 75.7, 48.7, 46.5, 44.5, 36.0; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{32}H_{23}Br_2O_4$ 628.9958, found 628.9971.

(5R,6R*,6aR*,11aR*)-6-(4-Fluorobenzoyl)-5-((4-fluorobenzoyl)-methyl)-11a-hydroxybenzo[a]fluoren-11-one (**5g**):* 102 mg, 80%, mp 230–232 °C; IR ν (cm^{-1}) 3476, 1722, 1676, 1661; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.62 (dd, *J* =8.8, 5.4 Hz, Hz, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.39 (td, *J* = 8.3, 1.1 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.24–7.29 (m, 2H), 7.14–7.20 (m, 2H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 6.98 (t, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.09 (s, 1H), 4.97 (s, 1H), 4.11 (s,

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1H), 3.88 (dd, J = 11.6, 3.4 Hz, 1H), 2.66 (dd, J = 19.2, 4.0 Hz, 1H), 2.42 (dd, J = 19.2, 11.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.0, 201.6, 196.8, 167.4 (d, J = 39.2 Hz), 164.8 (d, J = 38.6 Hz), 153.9, 135.9, 135.7, 134.7, 134.2, 132.6 (d, J = 9.3 Hz), 132.5 (d, J = 2.8 Hz), 131.0 (d, J = 2.7 Hz), 130.3 (d, J = 9.4 Hz), 130.2, 128.7, 128.41, 128.37, 127.3, 125.9, 124.3, 116.0 (d, J = 21.7 Hz), 115.5 (d, J = 21.8 Hz), 75.7, 48.9, 45.6, 44.6, 37.9; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{32}H_{23}F_2O_4$ 509.1559, found 509.1558.

(5R,6R*,6aR*,11aR*)-6-Benzoyl-11a-hydroxy-2,9-dimethoxy-5-(benzoylmethyl)benzo[a]fluoren-11-one* (**5h**): 76 mg, 57%, mp 207−209 °C; IR ν (cm^{-1}) 3476, 1716, 1679, 1498; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.53 (d, J = 7.4 Hz, 2H), 7.80 (d, J = 2.2 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.59 (t, J = 7.1 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.49 (d, J = 7.9 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.20−7.26 (m, 2H), 6.72 (dd, J = 8.4, 2.4 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.56 (dd, J = 8.4, 2.2 Hz, 1H), 5.08 (s, 1H), 5.02 (s, 1H), 4.03 (s, 1H), 3.90 (s, 3H), 6.89 (d, J = 9.8 Hz, 1H), 3.67 (s, 3H), 2.65 (dd, J = 19.0, 4.2 Hz, 1H), 2.50 (dd, J = 19.0, 11.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.9, 201.6, 198.6, 160.0, 159.4, 146.5, 137.0, 136.4, 135.3, 134.8, 133.9, 133.4, 129.7, 128.9, 128.4, 128.4, 127.6, 127.3, 125.2, 124.8, 116.7, 113.0, 107.4, 76.7, 55.6, 55.5, 48.2, 45.8, 45.0, 37.2; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{34}H_{29}O_6$ 533.1959, found 533.1956.

(5R,6R*,6aR*,11aR*)-6-Benzoyl-11a-hydroxy-2,9-dimethyl-5-(benzoylmethyl)benzo[a]fluoren-11-one* (**5i**): 75 mg, 60%, mp 263−265 °C; IR ν (cm^{-1}) 3473, 1713, 1673, 1654; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.56 (d, J = 7.4 Hz, 2H), 8.10 (s, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.56 (s, 1H), 7.52 (t, J = 7.3 Hz, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.8 Hz, 2H), 7.19 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.66 (d, J = 7.8 Hz, 1H), 5.09 (s, 1H), 4.98 (s, 1H), 4.05 (s, 1H), 3.89 (dd, J = 11.3, 3.4 Hz, 1H), 2.63 (dd, J = 19.2, 4.2 Hz, 1H), 2.46 (dd, J = 19.2, 11.7 Hz, 1H), 2.39 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.8, 202.0, 198.5, 151.3, 138.4, 137.9, 137.4, 136.2, 135.5, 134.7, 134.2, 133.9, 133.3, 132.1, 130.3, 129.7, 129.6, 128.9, 128.2, 127.6, 127.2, 125.6, 124.1, 76.2, 48.6, 45.8, 44.6, 37.4, 21.3, 20.9; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{34}H_{29}O_4$ 501.2060, found 501.2065.

(5R,6R*,6aR*,11aR*)-6-Benzoyl-2,9-difluoro-11a-hydroxy-5-(benzoylmethyl)benzo[a]fluoren-11-one* (**5j**): 89 mg, 70%, mp 239−242 °C; IR ν (cm^{-1}) 3482, 1723, 1673, 1657; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.53 (d, J = 7.4 Hz, 2H), 7.98 (dd, J = 10.0, 2.4 Hz, 1H), 7.68 (t, J = 7.2 Hz, 1H), 7.61 (t, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.50 (d, J = 7.5 Hz, 2H), 7.44 (dd, J = 7.1, 2.1 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.30 (dd, J = 8.2, 4.1 Hz, 1H), 6.87 (td, J = 8.0, 2.4 Hz, 1H), 6.76 (dd, J = 8.1, 5.5 Hz, 1H), 6.67 (td, J = 8.4, 2.2 Hz, 1H), 5.11 (s, 1H), 5.02 (s, 1H), 4.06 (s, 1H), 3.94 (d, J = 8.5 Hz, 1H), 2.68 (dd, J = 19.0, 4.1 Hz, 1H), 2.44 (dd, J = 19.0, 11.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.4, 200.2, 198.0, 163.8 (d, J = 17.2 Hz), 161.3 (d, J = 13.0 Hz), 149.3, 137.8 (d, J = 7.6 Hz), 136.0, 135.7 (d, J = 7.0 Hz), 134.4, 134.1, 133.8, 130.6 (d, J = 2.8 Hz), 129.7, 129.0, 128.9 (d, J = 7.6 Hz), 128.5, 127.5, 126.0 (d, J = 7.9 Hz), 123.8 (d, J = 23.9 Hz), 116.6 (d, J = 19.6 Hz), 116.4 (d, J = 18.9 Hz), 111.5 (d, J = 21.7 Hz), 76.2, 48.3, 45.6, 44.8, 37.3; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{32}H_{23}F_2O_4$ 509.1559, found 509.1545.

(5R,6R*,6aR*,11aR*)-6-Benzoyl-11a-hydroxy-3,8-dimethyl-5-(benzoylmethyl)benzo[a]fluoren-11-one* (**5k**): 70 mg, 56%, mp 238−240 °C; IR ν (cm^{-1}) 3491, 1707, 1674, 1659; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.62 (d, J = 7.4 Hz, 2H), 8.18 (d, J = 8.1 Hz, 1H), 7.60−7.69 (m, 4H), 7.53 (t, J = 7.3 Hz, 1H), 7.49 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.08 (s, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.58 (s, 1H), 5.13 (s, 1H), 5.04 (s, 1H), 4.04 (s, 1H), 3.88 (d, J = 8.5 Hz, 1H), 2.66 (dd, J = 19.3, 4.0 Hz, 1H), 2.54 (dd, J = 19.4, 11.7 Hz, 1H), 2.19 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.8, 201.4, 198.1, 154.4, 148.1, 138.4, 135.8, 134.84, 134.80, 133.9, 133.5, 133.0, 131.8, 130.0, 129.8, 129.6, 129.3, 128.9, 128.4, 127.8, 127.7, 125.7, 124.7, 76.0, 48.8, 45.6, 44.4, 37.8, 21.3, 21.0; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{34}H_{29}O_4$ 501.2060, found 501.2045.

(5R,6R*,6aR*,11aR*)-6-Benzoyl-11a-hydroxy-3,8-difluoro-5-(benzoylmethyl)benzo[a]fluoren-11-one* (**5l**): 80 mg, 63%, mp 241−243 °C; IR ν (cm^{-1}) 3473, 1712, 1676, 1658; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.54 (d, J = 7.4 Hz, 2H), 8.28 (dd, J = 8.8, 5.9 Hz, 1H), 7.80 (dd, J = 8.4, 5.4 Hz, 1H), 7.69 (t, J = 7.1 Hz, 1H), 7.62 (t, J = 7.2 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.09 (td, J = 8.6, 2.4 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 6.81 (t, J = 8.3 Hz, 1H), 6.50 (dd, J = 9.2, 2.3 Hz, 1H), 5.10 (s, 1H), 4.95 (brs, 1H), 4.08 (s, 1H), 3.92 (d, J = 8.6 Hz, 1H), 2.75 (dd, J = 18.9, 4.0 Hz, 1H), 2.48 (dd, J = 19.0, 11.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.2, 199.7, 197.9, 168.0 (d, J = 259.1 Hz), 162.9 (d, J = 247.2 Hz), 156.8 (d, J = 9.4 Hz), 137.1 (d, J = 7.4 Hz), 135.7, 134.3, 134.2, 133.8, 132.5 (d, J = 8.6 Hz), 131.4 (d, J = 2.9 Hz), 130.2, 129.7, 129.0, 128.5, 128.4 (d, J = 10.5 Hz), 127.5, 116.8 (d, J = 23.5 Hz), 115.8 (d, J = 21.1 Hz), 113.5 (d, J = 21.2 Hz), 111.5 (d, J = 22.5 Hz), 75.6, 48.9, 45.3, 44.4, 38.0; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{32}H_{23}F_2O_4$ 509.1559, found 509.1552.

General Procedure for the Reaction of 2-(Aroylvinyl)-arylaldehydes 1 Catalyzed by Triazole Carbene and Phenolate at 0 °C. Under a nitrogen atmosphere, 2-(aroylvinyl)arylaldehydes **1** (0.5 mmol), triazolium salt **2a** (0.1 mmol), 4-methoxyphenol (0.5 mmol), and NaH (0.6 mmol) were mixed in a flask that was cooled in an ice bath. Dry dichloromethane (15 mL), which had been precooled to 0 °C, was added to the cold mixture of reactant and catalysts. The reaction mixture was stirred at 0 °C for 0.5−1 h and was quenched by the addition of a saturated aqueous solution of NaCl (10 mL). The organic layer was washed with aqueous NaOH (0.2 mol/L, 15 mL) to remove 4-methoxyphenol and was then dried over anhydrous $MgSO_4$. After removal of solvent under vacuum, the residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethyl acetate (10/1−5/1) as eluent to give spiro[indene-2,1′-isobenzofuran]-1-ones **4** in 20−44% yields, along with benzo[*a*]-fluoren-11-ones **5** in 26−49% yields.

(1′R,3R*,3′R*)-3,3′-Bis(benzoylmethyl)spiro[indene-2,1′-isobenzofuran]-1-one* (**4a**): 25 mg, 21%, mp 136−138 °C; IR ν (cm^{-1}) 1766, 1724, 1683; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, J = 7.4 Hz, 2H), 7.80 (d, J = 7.2 Hz, 3H), 7.68 (t, J = 7.5 Hz, 1H), 7.52−7.58 (m, 2H), 7.48 (t, J = 7.7 Hz, 4H), 7.41 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 7.5 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 7.6 Hz, 1H), 6.16 (t, J = 6.8 Hz, 1H), 4.44 (dd, J = 7.8, 5.0 Hz, 1H), 4.11 (dd, J = 17.1, 7.3 Hz, 1H), 3.45 (dd, J = 17.1, 5.2 Hz, 1H), 3.13−3.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 201.9, 198.6, 198.3, 152.8, 143.1, 138.0, 137.1, 136.5, 136.1, 134.1, 133.3, 133.2, 129.0, 128.61, 128.59, 128.4, 128.1, 127.9, 125.6, 124.6, 122.7, 121.2, 97.9, 81.4, 48.0, 44.2, 38.7; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{32}H_{25}O_4$ 473.1747, found 473.1741.

(1′R,3R*,3′R*)-3,3′-Bis((4-methoxybenzoyl)methyl)spiro-[indene-2,1′-isobenzofuran]-1-one* (**4d**): 58 mg, 44%, mp 162−164 °C; IR ν (cm^{-1}) 1723, 1673, 1600; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 7.8 Hz, 3H), 7.67 (t, J = 7.4 Hz, 1H), 7.45−7.48 (m, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.29 (t, J = 7.3 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 7.5 Hz, 1H), 6.13 (t, J = 6.0 Hz, 1H), 4.41 (t, J = 6.2 Hz, 1H), 4.06 (dd, J = 16.6, 7.3 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.36 (dd, J = 16.6, 4.8 Hz, 1H), 3.07−3.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.1, 197.1, 196.8, 163.7, 163.6, 152.9, 143.1, 138.0, 136.1, 134.1, 131.0, 130.4, 129.6, 128.9, 128.3, 127.8, 125.7, 124.5, 122.7, 121.2, 113.8, 113.7, 98.0, 81.7, 55.5, 47.7, 44.3, 38.3; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{34}H_{29}O_6$ 533.1959, found 533.1949.

(1′R,3R*,3′R*)-3,3′-Bis((4-methylbenzoyl)methyl)spiro[indene-2,1′-isobenzofuran]-1-one* (**4e**): 54 mg, 43%, mp 168−170 °C; IR ν (cm^{-1}) 1725, 1678, 1601; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.67 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.44 (d, J = 7.4 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 6.47 (d, J = 7.6 Hz, 1H), 6.15 (t, J = 6.6 Hz, 1H), 4.42 (dd, J = 8.2, 4.8 Hz, 1H), 4.08 (dd, J = 17.0, 7.3 Hz, 1H), 3.43 (dd, J = 17.0, 5.3 Hz, 1H), 3.08−3.20 (m, 2H), 2.38 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz,

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$CDCl_3$) δ (ppm) 202.0, 198.2, 197.9, 152.9, 144.1, 144.0, 143.2, 138.0, 136.1, 134.7, 134.1, 134.1, 129.29, 129.26, 128.9, 128.7, 128.3, 128.2, 127.8, 125.7, 124.5, 122.7, 121.2, 97.9, 81.5, 47.9, 44.3, 38.6, 21.7, 21.6; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{34}H_{29}O_4$ 501.2060, found 501.2052.

(1′R,3R*,3R′*)-3,3′-Bis((4-bromobenzoyl)methyl)spiro[indene-2,1′-isobenzofuran]-1-one (**4f**):* 47 mg, 30%, mp 208−210 °C; IR ν (cm^{-1}) 1724, 1682, 1604; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1 H), 7.63 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.26−7.30 (m, 2H), 7.12−7.16 (m, 1H), 6.48 (d, J = 7.6 Hz, 1H), 6.07 (dd, J = 7.6, 4.7 Hz, 1H), 4.40 (t, J = 6.8 Hz, 1H), 4.07 (dd, J = 16.6, 7.7 Hz, 1H), 3.33 (dd, J = 16.7, 4.7 Hz, 1H), 3.09−3.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 201.8, 197.7, 197.2, 152.5, 142.8, 137.8, 136.2, 135.9, 135.1, 134.0, 131.92, 131.89, 130.3, 129.5, 129.1, 128.5, 128.0, 125.4, 124.7, 122.6, 121.2, 97.9, 81.5, 47.9, 44.2, 38.5; HRMS (FTICR-ESI) $[M + H]^+$ calcd for $C_{32}H_{23}Br_2O_4$ 628.9958, found 628.9957.

(1′R,3R*,3R′*)-3,3′-Bis(benzoylmethyl)-5,5′-difluorospiro-[indene-2,1′-isobenzofuran]-1-one (**4l**):* 25 mg, 20%, mp 163−164 °C; IR ν (cm^{-1}) 1716, 1679, 1614, 1590; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 7.7 Hz, 3H), 7.56−7.58 (m, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.13−7.20 (m, 2H), 7.07 (d, J = 7.8 Hz, 1H), 6.87 (t, J = 8.4 Hz, 1H), 6.47 (dd, J = 8.2, 4.6 Hz, 1H), 6.12 (d, J = 6.1 Hz, 1H), 4.41 (t, J = 5.7 Hz, 1H), 4.08 (dd, J = 17.4, 6.8 Hz, 1H), 3.48 (dd, J = 17.4, 5.7 Hz, 1H), 3.11−3.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.0, 198.1, 197.7, 168.1 (d, J = 257.0 Hz), 163.3 (d, J = 246.1 Hz), 155.8 (d, J = 9.7 Hz), 145.6 (d, J = 8.4 Hz), 136.8, 136.2, 133.5, 133.4, 133.3 (d, J = 2.1 Hz), 130.2 (d, J = 2.0 Hz), 128.7, 128.6, 128.5, 128.0, 137.2 (d, J = 10.3 Hz), 122.4 (d, J = 9.0 Hz), 116.7 (d, J = 23.4 Hz), 115.4 (d, J = 23.3 Hz), 113.1 (d, J = 23.0 Hz), 110.4 (d, J = 23.9 Hz), 97.1, 80.9, 47.7, 44.1, 38.5; HRMS (FTICR -ESI): $[M + H]^+$ calcd for $C_{32}H_{23}F_2O_4$ 509.1559, found 509.1556.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^1H NMR and ^{13}C NMR spectra of products **4** and **5** and CIF files giving single-crystal data for **4f** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for Y.C.: ycheng2@bnu.edu.cn.

Notes

The authors declare no competing financial interest.

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