JOC The Journal of Organic Chemistry

Article

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N-Heterocyclic Carbene-Catalyzed Diastereoselective and Enantioselective Reaction of 2-Aroylvinylcinnamaldehydes with α,β-Unsaturated Imines: Complete Control and Switch of Diastereoselectivity by *N*-Substituents of Catalysts

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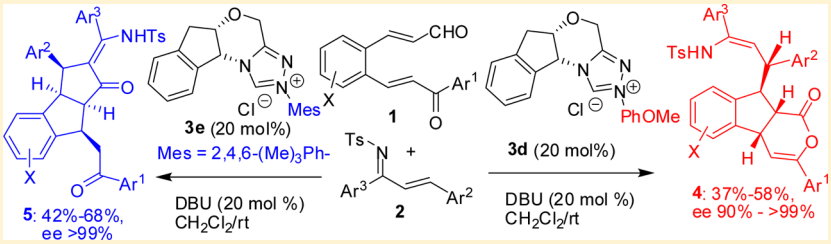
Supporting Information



ABSTRACT: Highly diastereoselective and enantioselective reactions between 2-aroylvinylcinnamaldehydes and α,β-unsaturated imines were achieved under asymmetric catalysis of chiral triazole carbene catalysts. In the presence of *N*-anisylindeno[2,1-*b*]triazolo[4,3-*d*][1,4]oxazinium salt, the reaction of 2-aroylvinylcinnamaldehydes with α,β-unsaturated imines afforded indeno[2,1-*c*]pyran-1-one derivatives **4** with 90%−99% ee, while enantiopure indenocyclopentan-1-ones **5** (>99% ee) were obtained under the catalysis of *N*-mesitylindeno[2,1-*b*]triazolo[4,3-*d*][1,4]oxazinium salt. A slight variation of an *N*-substituent on triazole carbenes was found to switch completely the diastereoselectivity of the reaction for the formation of indeno[2,1-*c*]pyran-1-ones.

INTRODUCTION

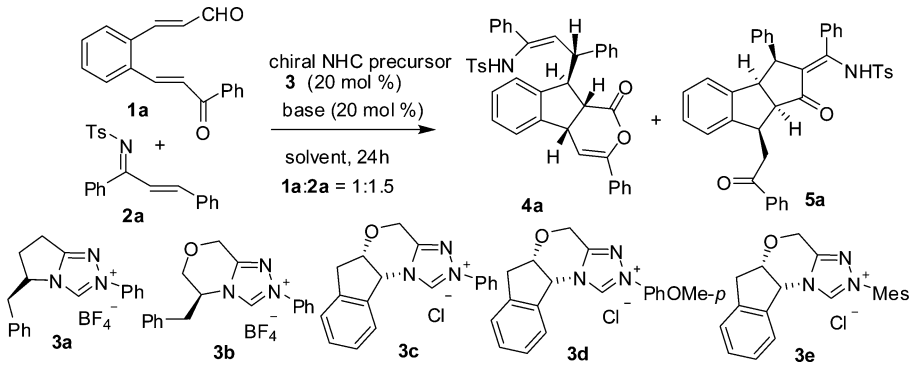
The stereoselective construction of densely functionalized molecules with multiple stereogenic centers is very attractive and challenging in organic synthesis. In the past decade, the asymmetric N-heterocyclic carbene (NHC) catalysis has been developed into a powerful strategy for the enantioselective construction of diverse carbon−carbon and carbon−heteroatom bonds.[1−4] When designed and polyfunctionalized reactants are used, the chiral NHC-catalyzed annulation reactions provide efficient and straightforward routes to multifunctional carbocyclic and heterocyclic molecules in which more than one stereogenic centers are created. For example, the chiral NHC-catalyzed oxodiene Diels−Alder reactions of α,β-unsaturated ketones with enals,[5a−d] α-chloroaldehydes,[5e,f] or ketenes[5g,h] became the efficient methods for the highly enantioselective syntheses of various dihydropyranone derivatives, all with two cis-substituted stereogenic centers. On the other hand, NHC-catalyzed asymmetric azadiene Diels−Alder reactions of α,β-unsaturated imines with enals[6a] or ketenes[6b] produced cis- or trans-substituted dihydropyridinones, respectively. In addition, NHC-catalyzed asymmetric [2 + 2] cycloadditions of ketenes with ketones[7a,b] or imines[7c,d] afforded a direct approach to enantiomerically pure β-lactone or β-lactam derivatives. Furthermore, chiral NHC catalysis and NHC/Lewis acid cocatalysis for the reactions between enals and enones led to the formation of 1,2-disubstituted cyclopentenes[8a,b] or tetrasubstituted cyclopantane derivatives[8c] with excellent enantioselectivity. The results documented in the literature show clearly that both the efficiency and the enantioselectivity are strongly dictated by the structures of chiral NHC catalysts. Variation of the core structures of catalysts, even the modification of substituents of NHC molecules, results in dramatic improvement or reversal of enantioselectivity. However, a complete switch of diastereoselectivity of reactions by modifying the structures of NHC catalysts was scarcely reported. The regulation of diastereoselectivity of reactions appears to be more challenging than to improve enantioselectivity by the means of NHC catalysts.

A few studies on the regulation of reaction pathways by varying chiral NHC catalysts have been reported in recent years. Glorius and co-workers discovered that the reaction between enals and azoalkenes proceeds through a formal [4 + 3] annulation to produce 1,2-diazepine compounds with excellent enantioselectivity in the presence of the chiral *N*-mesitylindeno[2,1-*b*]triazolo[4,3-*d*][1,4]oxazinium salt.[9] The same reactants undergo a [4 + 1] cycloaddition to form pyrazole derivatives when a chiral morpholine-fused triazolium salt is used as a precatalyst.[9] The annulation reaction between enals and 2-arylmethylenebenzofuran-3-ones, on the other

Received: November 22, 2014
Published: January 13, 2015

DOI: 10.1021/jo502668c
J. Org. Chem. 2015, 80, 1727−1734

Table 1. Optimization of Reaction Conditions[a]



entry	NHC precursors **3**	base	solvent	temp	yield of **4a**[b] (%)	ee[c] (%)	yield of **5a**[b] (%)	ee[d] (%)	**4a**/**5a**[e]
1	**3a**	DBU	DCM	rt	29	−88			5:1
2	**3b**	DBU	DCM	rt	36	−95			8:1
3	**3c**	DBU	DCM	rt	42	95			>20:1
4	**3d**	DBU	DCM	rt	50	90			13:1
5	**3e**	DBU	DCM	rt			51	>99	1:10
6	**3d**	DBU	DCM	0	33	96			>20:1
7	**3d**	DBU	DCM	reflux	35	94			17:1
8	**3d**	DBU	benzene	rt	14	96			>20:1
9	**3d**	DBU	acetone	rt	24	95			20:1
10	**3d**	DBU	CH_3CN	rt	39	81			6:1
11	**3d**	DBU	dioxane	rt	30	95			>20:1
12	**3d**	*t*-BuOK	DCM	rt	45	95			10:1
13	**3d**	NaH	DCM	rt	42	88			7:1
14	**3d**	Cs_2CO_3	DCM	rt	35	94			6:1
15	**3e**	DBU	DCM	0			47	>99	1:13
16	**3e**	DBU	DCM	reflux			43	98	1:14
17	**3e**	DBU	benzene	rt			43	>99	1:7
18	**3e**	DBU	acetone	rt			44	>99	1:8
19	**3e**	DBU	CH_3CN	rt			41	97	1:9
20	**3e**	DBU	dioxane	rt			46	99	1:17
21	**3e**	*t*-BuOK	DCM	rt			41	>99	1:14
22	**3e**	NaH	DCM	rt			37	>99	1:20
23	**3e**	Cs_2CO_3	DCM	rt			29	>99	1:20

[a]All reactions were performed for 24 h. [b]Isolated yields. [c]Determined by HPLC analysis on IB column. [d]Determined by HPLC analysis on AD-H column. [e]Determined by ^1H NMR.

hand, forms fused- or spiro-benzofuran derivatives selectively via the O-alkylation or C-alkylation of the intermediates under the catalysis of chiral *N*-mesitylindeno[2,1-*b*]triazolo[4,3-*d*]-[1,4]oxazinium salt or pyrrolidine-fused triazolium salt, respectively.[10] In the *N*-arylindeno[2,1-*b*]triazolo[4,3-*d*][1,4]-oxazinium salt-catalyzed reactions of enals with isatin-derived ketimines, the enals could act either as *β*-carbon nucleophiles (homoenolates) or acyl nucleophiles toward ketimines, leading to the enantioselective formation of pyrrolidinone-spiro-indolinones[11a] or 2-amino-2-acylindolinones,[11b] by varying the *N*-substituents of NHC catalysts. These studies indicate that the chiral NHC catalysis provides not only a general strategy in asymmetric synthesis but also a potential method in divergent synthesis of different products from identical substrates.

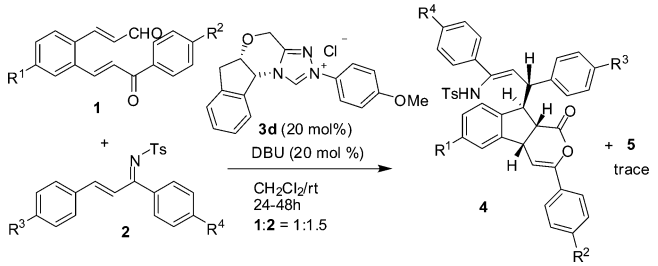
Indane is a common scaffold occurring widely in bioactive and pharmaceutically important molecules.[12] A few chiral N-heterocyclic carbene catalyzed reactions for the enantioselective syntheses of indane derivatives were reported in the last decade.[13] We discovered very recently that the reaction of 2-aroylvinylcinnamaldehydes with *α,β*-unsaturated imines catalyzed by triazole carbenes produced novel 9-(1,3-diaryl-3-tolylsulfonamido)allyl-3-arylindeno[2,1-*c*]pyran-1-ones in good yields.[14] The products were easily converted into different functionalized indane derivatives. To develop a simple method for the synthesis of enantiopure multifunctionalized indeno-[2,1-*c*]pyran-1-ones, useful precursors to chiral 1,2,3-trisubstituted indane derivatives, we undertook the current study on the NHC-catalyzed asymmetric reaction of 2-aroylvinylcinnamaldehydes with *α,β*-unsaturated imines. We were delighted to find out that the structures of chiral NHC catalysts played a paramount role in dictating the reaction pathways. Variation of an *N*-substituent on NHC molecule resulted in the complete switch of diastereoselectivity of the reaction. The reaction produced indeno[2,1-*c*]pyran-1-one or indenocyclopentan-1-one derivatives with excellent enantioselectivity and diastereoselectivity under the catalysis of different *N*-substituted triazole carbene catalysts.

RESULTS AND DISCUSSION

We initiated our study by screening the optimal chiral NHC catalysts for the model reaction of 2-benzoylvinylcinnamalde-

DOI: 10.1021/jo502668c
J. Org. Chem. 2015, 80, 1727−1734

Table 2. Reaction of 2-Aroylvinylcinnamaldehydes 1 with α,β-Unsaturated Imines 2 in the Presence of *N*-Anisyltriazolium Salt 3d and DBU



entry	1	R^1, R^2	2	R^3, R^4	*T* (h)	yield[a] (%)	ee[b] (%)	4/5[c]
1	**1a**	H, H	**2a**	H, H	24/48	**4a**: 50/51	90	13:1
2	**1b**	Me, H	**2a**	H, H	24	**4b**: 45	95	10:1
3	**1c**	OMe, H	**2a**	H, H	24/48	**4c**: 31/37	96	>20:1
4	**1d**	F, H	**2a**	H, H	24	**4d**: 47	94	11:1
5	**1e**	H, Me	**2a**	H, H	24	**4e**: 55	91	17:1
6	**1f**	H, OMe	**2a**	H, H	24	**4f**: 58	95	8:1
7	**1g**	H, Br	**2a**	H, H	24	**4g**: 47	97	8:1
8	**1a**	H, H	**2b**	Me, H	24	**4h**: 46	90	6:1
9	**1a**	H, H	**2c**	OMe, H	24	**4i**: 52	94	17:1
10	**1a**	H, H	**2d**	Br, H	24	**4j**: 45	92	>20:1
11	**1a**	H, H	**2e**	H, Me	24	**4k**: 57	99	7:1
12	**1a**	H, H	**2f**	H, OMe	24	**4l**: 55	92	20:1
13	**1a**	H, H	**2g**	H, Br	24	**4m**: 53	>99	13:1

[a]Isolated yields. [b]Determined by HPLC analysis on IB column, hexane/isopropyl alcohol (IPA) 92:8 to 86:14, flow rate 0.5 mL/min (the details of HPLC separation conditions for each product **4** have been listed in Supporting Information). [c]Determined by ^{1}H NMR.

hyde **1a** with *N*-(*p*-tolylsulfonyl)-1,3-diphenyl-2-propen-1-imine **2a**. On the basis of our previous discovery that the triazole carbenes were able to mediate the reaction while thiazole and imidazole carbenes were inactive catalysts,[14] chiral triazolium salts **3a**−**3e** bearing a different fused ring or a varied *N*-substituent were employed as NHC precursors in this work. The triazole carbenes **3a**′−**3e**′ were generated in situ from the deprotonation of triazolium salts **3a**−**3e** with a base. In the presence of pyrrolidine- (**3a**) or morpholine-fused triazolium salt **3b** (20 mol %) and DBU, the reaction in dichloromethane at ambient temperature gave product **4a** in 29% or 36% yield with good enantioselectivity (88%−95% ee), along with the formation of a trace amount of byproduct **5a** (**4a**/**5a** ≈ 5:1−8:1) (Table 1, entries 1 and 2). When *N*-phenyl- (**3c**) and *N*-anisylindeno[2,1-*b*]triazolo[4,3-*d*][1,4]oxazinium salt **3d** were utilized as precatalysts, both the chemical yields and enantiomeric excess values of **4a** were improved to 42%−50% and 90%−95% ee, respectively (**4a**/**5a** ≈ 13:1−20:1, Table 1, entries 3 and 4). Surprisingly, however, instead of the predominant formation of indeno[2,1-*c*]pyran-1-one **4a**, the reaction using *N*-mesitylindeno[2,1-*b*]triazolo[4,3-*d*][1,4]-oxazinium salt **3e** as precatalyst produced indenocyclopentan-1-one **5a** as the major product in 51% yield with 99% ee (**4a**/**5a** ≈ 1:10) (Table 1, entry 5). Selective formation of two different products **4a** and **5a** under the catalysis of either *N*-anisyl- (**3d**) or *N*-mesityl-substituted triazolium salt **3e** promoted us to further optimize the conditions by varying reaction temperature, solvents, and bases in the presence of triazolium salt **3d** or **3e**. In the *N*-anisyltriazolium salt **3d**-catalyzed reactions, either a decrease of reaction temperature to 0 °C or an increase of temperature to the boiling point of dichloromethane led to the formation of product **4a** in diminished yields (33%−35%) (Table 1, entries 6 and 7). The use of other solvents including benzene, acetone, acetonitrile, and 1,4-dioxane was not beneficial for the formation of product **4a** (Table 1, entries 8−11). Comparable yields of **4a** were obtained when DBU was replaced by *t*-BuOK and NaH, while the use of Cs_2CO_3 as a base apparently decreased the yield of **4a** (Table 1, entries 12−14). On the other hand, under the catalysis of *N*-mesityltriazolium salt **3e**, the yields of product **5a** were marginally affected by the reaction temperature and the nature of the solvents (Table 1, entries 15−20). Noticeably, however, the use of Cs_2CO_3, *t*-BuOK, and NaH all caused the decrease of chemical yields of product **5a** in the **3e**-catalyzed reactions (Table 1, entries 21−23).

Under the optimized conditions for the selective formation of indeno[2,1-*c*]pyran-1-ones **4**, the substrate scopes were surveyed by employing different substituted 2-aroylvinylcinnamaldehydes **1** and *α*,*β*-unsaturated imines **2** in the presence of *N*-anisyltriazolium salt **3d**. First of all, the catalytic process tolerated a range of cinnamaldehyde derivatives **1** and unsaturated imine substrates **2**, as reactants containing either an electron-donating or -withdrawing group proceeded smoothly to form compounds **4** as the major products (Table 2). It is also interesting to note that there was a more pronounced effect of the substituent R^1 than R^2 of cinnamaldehydes **1** on the reaction. When reacted with imine **2a**, cinnamaldehyde **1a**, *p*-methylcinnamaldehyde **1b**, and *p*-fluorocinnamaldehyde **1d** produced the corresponding indeno-[2,1-*c*]pyran-1-ones **4a**, **4b**, and **4d** in 45%−50% yields with 90%−95% ee in 24 h, whereas the *p*-methoxycinnamaldehyde **1c** gave 31% of **4c** (96% ee) (Table 2, entries 1−4). Elongation of reaction time to 48 h slightly improved the yield of **4c** to 37%. On the other hand, cinnamaldehydes **1e** and **1f** attached by *p*-methyl- and *p*-methoxybenzoyl groups afforded slightly higher yields of products **4e** and **4g** (55%−58%, 91%−95% ee) than the **4g** (47% yield, 97% ee) derived from *p*-bromobenzoylvinylcinnamaldehyde **1g** (Table 2, entries 5−7).

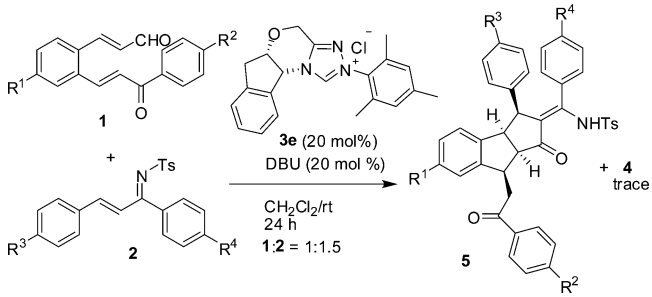
DOI: 10.1021/jo502668c
J. Org. Chem. 2015, 80, 1727−1734

It was noteworthy that the change of two aryl substituents on α,β-unsaturated imines **2** marginally affected the yields and enantioselectivity. For instance, the reactions of enals **1a** with 3-(*p*-tolyl)-, 3-(*p*-anisyl)-, and 3-(*p*-bromophenyl)-2-propenimines **2b**−**2d** produced products **4h**−**4j** in 46%−52% yields with 90%−92% ee (Table 2, entries 8−10), while 1-(*p*-tolyl)-, 1-(*p*-anisyl)-, and 1-(*p*-bromophenyl)-2-propenimines **2e**−**2g** provided products **4k**−**4m** in 53%−57% with 92%−99% ee under the same conditions (Table 2, entries 11−13). The absolute configuration of products **4** was determined to be (*4aS,9S,9aS,1′R*) by X-ray diffraction analysis of **4j**, which contains a bromophenyl group (see Supporting Information for the X-ray structure of **4j**). In all cases, a trace amount of byproducts **5** were detected by ^{1}H NMR in the mixture of crude products (**4**/**5** ≈ 6:1−20:1). Besides the products **4** and **5**, a small amount of byproducts derived from the self-reactions of 2-aroylvinylcinnamaldehydes **1** was also detected in the reaction mixture by TLC analysis. It was also noted that the enals **1** could not be completely consumed in some reactions, although an excess amount of imines **2** was used. Prolonging the reaction time did not effectively improve the chemical yields of products (Table 2, entries 1 and 3).

The generality for the formation of indenocyclopentan-1-ones **5** from the reaction of 2-aroylvinylcinnamaldehydes **1** with α,β-unsaturated imines **2** was also examined utilizing *N*-mesityltriazolium salt **3e** as the precatalyst. It was found that the reactions catalyzed by **3e** and DBU were slightly more reactive than those reactions in the presence of *N*-anisyltriazolium salt **3d** and DBU. The cinnamaldehydes **1a**−**1d** substituted by methyl, methoxy, and fluorine atom on the benzene rings underwent reactions with imine **2a** to produce the corresponding products **5a**−**5d** in similar yields (51%−60%) (Table 3, entries 1−4). The *p*-methyl- and *p*-methoxybenzoyl-substituted cinnamaldehydes **1e** and **1f** afforded higher yields of products **5e** (58%) and **5g** (68%) than that of **5g** (48%) yielded from *p*-bromobenzoylvinylcinnamaldehyde **1g** (Table 3, entries 5−7). When reacted with enal **1a**, 3-tolyl- (**2b**), 3-anisyl- (**2c**), and 3-bromophenyl-2-propenimine **2d** produced the corresponding **5h**−**5j** in similar yields (43%−52%) (Table 3, entries 8−10). However, 1-tolyl-2-propenimine **2e** gave a higher yield of product **5k** (60%) in comparison to 1-anisyl- (**2f**) and 1-bromophenyl-2-propenimine **2g**, which produced **5l** and **5m** in 42%−44% yields (Table 3, entries 11−13). It is worth emphasizing that, under the catalysis of *N*-mesityltriazole carbene **3e′**, all reactions showed outstanding enantioselectivity with enantiomeric excesses being >99%. X-ray diffraction analysis of **5j** confirmed unambiguously that the absolute configuration of products **5** was (*3S,3aS,8R,8aS*) (see Supporting Information for the X-ray structure of **5j**). The ratio of **5**/**4** was in a range of 6:1 to >20:1 based on ^{1}H NMR measurement of the mixtures of crude products. In addition to products **5** and **4**, a small amount of byproducts derived from self-reactions of enals **1** was also found in the reaction.

To account for the selective formations of indeno[2,1-*c*]pyran-1-ones **4** and indenocyclopentan-1-ones **5** from 2-aroylvinylcinnamaldehydes **1** and α,β-unsaturated imines **2**, two cascade reaction pathways were proposed in Scheme 1. The reaction was most likely initiated by an intermolecular Michael addition of the homoenolates **6**, which were derived from enals **1** and carbene catalyst, to α,β-unsaturated imines **2**. The resulting enamine anions **7** underwent isomerization to form enolates **8-A** by proton shift. The enolates **8-A** are tautomerized

Table 3. Reaction of 2-Aroylvinylcinnamaldehydes 1 with α,β-Unsaturated Imines 2 in the Presence of *N*-Mesityltriazolium Salt 3e and DBU[a]



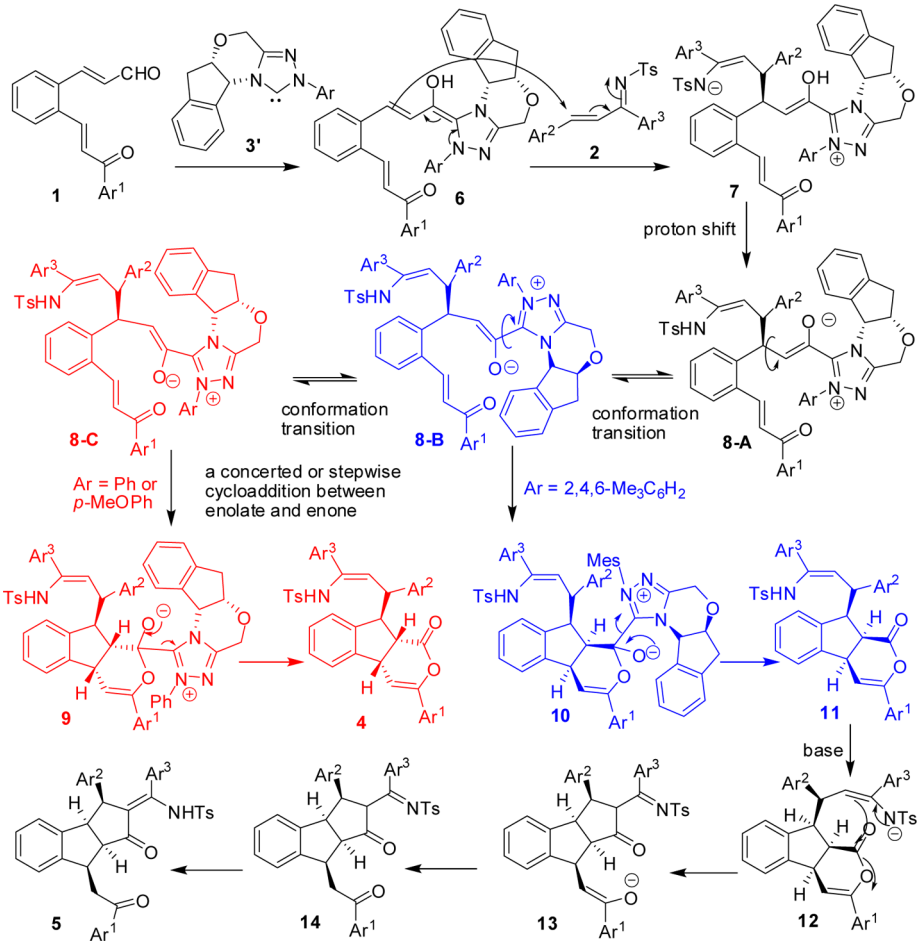
entry	1	R^1, R^2	2	R^3, R^4	yield[b] (%)	ee[c] (%)	5/4[d]
1	**1a**	H, H	**2a**	H, H	**5a**: 51	>99	10:1
2	**1b**	Me, H	**2a**	H, H	**5b**: 59	>99	>20:1
3	**1c**	OMe, H	**2a**	H, H	**5c**: 51	>99	11:1
4	**1d**	F, H	**2a**	H, H	**5d**: 60	>99	>20:1
5	**1e**	H, Me	**2a**	H, H	**5e**: 58	>99	8:1
6	**1f**	H, OMe	**2a**	H, H	**5f**: 68	>99	14:1
7	**1g**	H, Br	**2a**	H, H	**5g**: 48	>99	13:1
8	**1a**	H, H	**2b**	Me, H	**5h**: 46	>99	9:1
9	**1a**	H, H	**2c**	OMe, H	**5i**: 43	>99	9:1
10	**1a**	H, H	**2d**	Br, H	**5j**: 52	>99	11:1
11	**1a**	H, H	**2e**	H, Me	**5k**: 60	>99	10:1
12	**1a**	H, H	**2f**	H, OMe	**5l**: 44	>99	6:1
13	**1a**	H, H	**2g**	H, Br	**5m**: 42	>99	>20:1

[a]All reactions were performed for 24 h. [b]Isolated yields. [c]Determined by HPLC analysis on AD-H column, hexane/IPA 95:5 to 90:10, flow rate 1 mL/min (the details of HPLC separation conditions for each product **5** have been listed in Supporting Information). [d]Determined by ^{1}H NMR.

with comformational isomers **8-A** and **8-B** by conformation transition. The known NHC-catalyzed [4 + 2] cycloaddition reactions between enolates and α,β-unsaturated ketones have been proposed to proceed via either a Diels−Alder reaction[5a,b,f] or a cascade Michael addition and intramolecular lactonization[5d,15] mechanism to afford dihydropyran-2-one derivatives. In 2012, Kozlowski and co-workers reported computational studies on the mechanism of the chiral *N*-mesitylindeno[2,1-*b*]triazolo[4,3-*d*][1,4]oxazinium salt **3e**-catalyzed cycloaddition of α,β-unsaturated aldehydes with α,β-unsaturated ketones.[16] Their calculation indicated a concerted, but highly asynchronous, Diels−Alder reaction rather than the stepwise Michael addition and intramolecular lactonization mechanism. In the current reactions, a concerted or stepwise intramolecular [4 + 2] cycloaddition between the enolate and α,β-unsaturated ketone moieties of enolate intermediates **8** (**8A**, **8B**, or **8C**) leads to the formation of an indeno[2,1-*c*]pyran-1-one core of products. In the *N*-anisyltriazolium salt **3d**-catalyzed reaction, **8-C** is most likely the favorable conformation of enolate intermediates because of the larger indane moiety being away from the 2-aroylvinyl groups. To avoid the steric hindrance of the indane ring, the NHC-substituted enolates of **8-C** probably connect preferentially with the Si-face of α,β-unsaturated ketone species (see Figure 1, structure A), leading to the formation of (*4aS,9S,9aS*)-tetrahydroindeno[2,1-*c*]pyran derivatives **9**. Elimination of the carbene species of **9** affords the final products **4**. When the triazole ring was substituted by a bulky mesityl group, the enolate intermediates probably exist as the

DOI: 10.1021/jo502668c
J. Org. Chem. 2015, 80, 1727−1734

Scheme 1. Proposed Mechanisms for the Formations of Indeno[2,1-*c*]pyran-1-ones 4 and Indenocyclopentan-1-ones 5 from the Reactions of 2-Aroylvinylcinnamaldehydes 1 with *α,β*-Unsaturated Imines 2



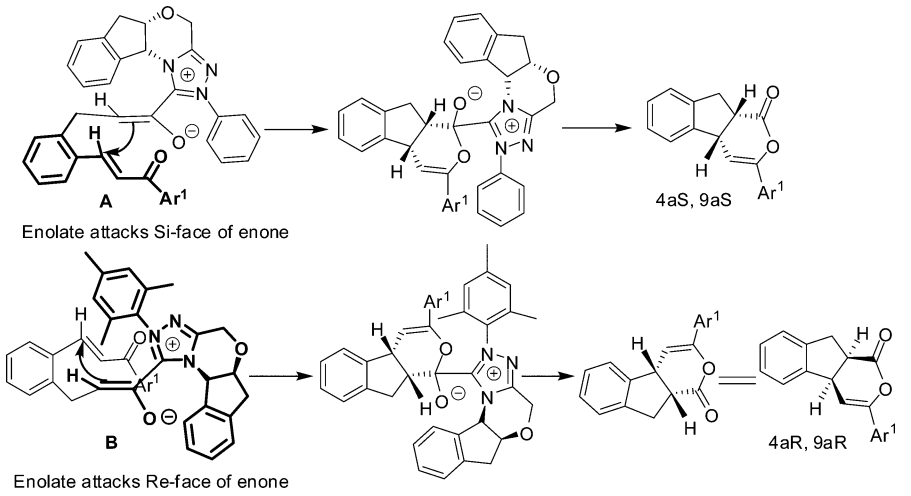


Figure 1. Proposed models for stereochemical outcomes.

conformation **8-B** to avoid the repulsion between the mesityl and 2-aroylvinyl groups. Under this circumstance, the enolates of **8-B** would prefer to attack the Re-face of *α,β*-unsaturated ketones (see Figure 1, structure B) to form (*4aR,9S,9aR*)-indeno[2,1-*c*]pyran-1-ones **11**, one of the diastereomers of products **4**. In the presence of a base catalyst, such as DBU or triazole carbene, diastereomers **11** would isomerize into the indenocyclopentan-1-ones **14** through the intramolecular enaminic addition to the *δ*-lactone moiety. Intermediates **14** then underwent imine−enamine tautomerization to afford the end products **5**. It is very important to address that it is the steric feature of an *N*-substituent on chiral NHC catalyst that governs the diastereoselective formation of isomeric indeno-[2,1-*c*]pyran-1-ones **4** and **11**. The favorable cis-configuration of the enaminic substituent and pyranone moiety of **11** enabled

DOI: 10.1021/jo502668c
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further base-effected ring transformation to furnish the formation of indenocyclopentan-1-one products **5**.

CONCLUSIONS

In summary, we have developed a chiral NHC-catalyzed asymmetric synthesis of functionalized indeno[2,1-*c*]pyran-1-ones and indenocyclopentan-1-one derivatives in excellent enantioselectivity and diastereoselectivity. Remarkably, the pathways of the reaction between 2-aroylvinylcinnamaldehydes and α,β-unsaturated imines were controlled and switched easily by utilizing chiral triazole carbene catalysts, which contained only a different *N*-substituent. The role of triazole carbene catalysts was most likely to control the diastereoselectivity for the formation of *cis*,*cis*- and *cis*,*trans*-9-substituted indeno[2,1-*c*]pyran-1-one structures via a profound steric effect of the *N*-substituents on catalysts. It represented the first example to switch completely the diastereoselectivity of NHC-catalyzed asymmetric reactions by modification of the *N*-substituents on carbene catalysts.

EXPERIMENTAL SECTION

General Procedure for the Enantioselective Synthesis of (*4aS,9S,9aS,1′R*)-9-(1,3-Diaryl-3-(*p*-tolylsulfonamido)allyl)-3-arylindeno[2,1-*c*]pyran-1-ones 4. Under nitrogen atmosphere and at room temperature, 2-aroylvinylcinnamaldehydes **1**[17] (0.5 mmol), *N*-(*p*-tolylsulfonyl)-1,3-diaryl-2-propen-1-imines **2**[18] (0.75 mmol), and *N*-(*p*-anisyl)indeno[2,1-*b*]triazolo[4,3-*d*][1,4]oxazinium salt **3d**[19] (0.1 mmol) were mixed in dry dichloromethane (10 mL), and then DBU (0.1 mmol) was added using a microsyringe. The reaction mixture was stirred at room temperature for 24−48 h. After removal of solvent, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether, dichloromethane, ethyl acetate, and ethanol (PE/DCM/EA/ET = 20:4:1:0.1) to give products **4**, along with a trace amount of byproducts **5**. Products **4** were further purified by chromatography again (PE/DCM/EA = 20:4:1).

(4aS,9S,9aS,1′R,Z)-9-(1,3-Diphenyl-3-(p-tolylsulfonamido)allyl)-3-phenylindeno[2,1-c]pyran-1-one ***4a***. White crystals, 156 mg, 50%, ee 90%, $[\alpha]^{20}_{D}$ = +30.8° (*c* = 0.5, CH_2Cl_2), mp 113−114 °C.

Note: The spectra data of the racemates of compounds **4a**−**4m** have been reported in our previous work.[14]

(4aS,9S,9aS,1′R,Z)-9-(1,3-Diphenyl-3-(p-tolylsulfonamido)allyl)-6-methyl-3-phenylindeno[2,1-c]pyran-1-one ***4b***. White crystals, 137 mg, 43%, ee 95%, $[\alpha]^{20}_{D}$ = +43.2° (*c* = 0.5, CH_2Cl_2), mp 107−108 °C.

(4aS,9S,9aS,1′R,Z)-9-(1,3-Diphenyl-3-(p-tolylsulfonamido)allyl)-6-methoxy-3-phenylindeno[2,1-c]pyran-1-one ***4c***. White crystals, 121 mg, 37%, ee 96%, $[\alpha]^{20}_{D}$ = +74.2° (*c* = 0.5, CH_2Cl_2) mp 99−100 °C.

(4aS,9S,9aS,1′R,Z)-9-(1,3-Diphenyl-3-(p-tolylsulfonamido)allyl)-6-fluoro-3-phenylindeno[2,1-c]pyran-1-one ***4d***. White crystals, 151 mg, 47%, ee 94%, $[\alpha]^{20}_{D}$ = +23.2° (*c* = 0.5, CH_2Cl_2), mp 122−123 °C.

(4aS,9S,9aS,1′R,Z)-9-(1,3-Diphenyl-3-(p-tolylsulfonamido)allyl)-3-(p-methylphenyl)indeno[2,1-c]pyran-1-one ***4e***. White crystals, 175 mg, 55%, ee 91%, $[\alpha]^{20}_{D}$ = +8.8° (*c* = 0.5, CH_2Cl_2), mp 105−106 °C.

(4aS,9S,9aS,1′R,Z)-9-(1,3-Diphenyl-3-(p-tolylsulfonamido)allyl)-3-(p-methoxyphenyl)indeno[2,1-c]pyran-1-one ***4f***. White crystals, 190 mg, 58%, ee 95%, $[\alpha]^{20}_{D}$ = +18.2° (*c* = 0.5, CH_2Cl_2), mp 95−96 °C.

(4aS,9S,9aS,1′R,Z)-9-(1,3-Diphenyl-3-(p-tolylsulfonamido)allyl)-3-(p-bromophenyl)indeno[2,1-c]pyran-1-one ***4g***. White crystals, 165 mg, 47%, ee 97%, $[\alpha]^{20}_{D}$ = +16.0° (*c* = 0.5, CH_2Cl_2), mp 112−113 °C.

(4aS,9S,9aS,1′R,Z)-9-(1-(p-Methylphenyl)-3-phenyl-3-(p-tolylsulfonamido)allyl)-3-phenylindeno[2,1-c]pyran-1-one ***4h***. White crystals, 147 mg, 46%, ee 90%, $[\alpha]^{20}_{D}$ = +13.0° (*c* = 0.5, CH_2Cl_2), mp 104−105 °C.

(4aS,9S,9aS,1′R,Z)-9-(1-(p-Methoxyphenyl)-3-phenyl-3-(p-tolylsulfonamido)allyl)-3-phenylindeno[2,1-c]pyran-1-one ***4i***. White crystals, 170 mg, 52%, ee 94%, $[\alpha]^{20}_{D}$ = +7.8° (*c* = 0.5, CH_2Cl_2), mp 97−98 °C.

(4aS,9S,9aS,1′R,Z)-9-(1-(p-Bromophenyl)-3-phenyl-3-(p-tolylsulfonamido)allyl)-3-phenylindeno[2,1-c]pyran-1-one ***4j***. White crystals, 157 mg, 45%, ee 92%, $[\alpha]^{20}_{D}$ = +16.4° (*c* = 0.5, CH_2Cl_2), mp 115−116 °C.

(4aS,9S,9aS,1′R,Z)-9-(3-(p-Methylphenyl)-1-phenyl-3-(p-tolylsulfonamido)allyl)-3-phenylindeno[2,1-c]pyran-1-one ***4k***. White crystals, 181 mg, 57%, ee 99%, $[\alpha]^{20}_{D}$ = +9.0° (*c* = 0.5, CH_2Cl_2), mp 112−113 °C.

(4aS,9S,9aS,1′R,Z)-9-(3-(p-Methoxyphenyl)-1-phenyl-3-(p-tolylsulfonamido)allyl)-3-phenylindeno[2,1-c]pyran-1-one ***4l***. White crystals, 182 mg, 55%, ee 92%, $[\alpha]^{20}_{D}$ = +25.4° (*c* = 0.5, CH_2Cl_2), mp 102−103 °C.

(4aS,9S,9aS,1′R,Z)-9-(3-(p-Bromophenyl)-1-phenyl-3-(p-tolylsulfonamido)allyl)-3-phenylindeno[2,1-c]pyran-1-one ***4m***. White crystals, 187 mg, 53%, ee >99%, $[\alpha]^{20}_{D}$ = +13.4° (*c* = 0.5, CH_2Cl_2), mp 108−109 °C.

General Procedure for the Enantioselective Synthesis of (*3S,3aS,8R,8aS*)-3-Aryl-8-(aroylmethyl)-2-(aryl(*p*-tolylsulfonamido)methylene)indenocyclopentan-1-ones 5. Under nitrogen atmosphere and at room temperature, 2-aroylvinylcinnamaldehydes **1** (0.5 mmol), *N*-(*p*-tolylsulfonyl)-1,3-diaryl-2-propen-1-imines **2** (0.75 mmol), and *N*-mesitylindeno[2,1-*b*]triazolo[4,3-*d*][1,4]oxazinium salt **3e**[19] (0.1 mmol) were dissolved in dry dichloromethane (15 mL), and then DBU (0.1 mmol) was added using a microsyringe. The reaction mixture was stirred at room temperature for 24 h, and then the solvent was removed under vacuum.The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether, dichloromethane, ethyl acetate, and ethanol (PE/DCM/EA/ET = 20:4:1:0.1) to give products **5**, along with a trace amount of byproducts **4**. Products **5** were further purified by chromatography again (PE/DCM/EA = 20:4:1).

(3S,3aS,8R,8aS,Z)-8-(Benzoylmethyl)-3-phenyl-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5a***. White crystals, 159 mg, 51%, ee >99%, $[\alpha]^{20}_{D}$ = −98.8° (*c* = 0.5, CH_2Cl_2), mp 205−206 °C. IR ν (cm^{-1}) 3431, 1687, 1652. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.31 (s, 1H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.88−6.96 (m, 5H), 6.67−6.79 (m, 5H), 6.54 (t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 2H), 6.33 (d, *J* = 7.4 Hz, 2H), 5.40 (d, *J* = 7.7 Hz, 1H), 4.39 (d, *J* = 9.6 Hz, 1H), 3.95−4.05 (m, 3H), 3.66 (t, *J* = 9.1 Hz,1H), 3.36 (ddd, *J* = 22.8, 9.3, 2.9 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.8, 199.7, 151.2, 145.6, 143.8, 140.7, 140.1, 137.5, 136.9, 133.0, 130.9, 129.6, 129.23, 129.18, 129.0, 128.7, 128.2, 127.7, 127.6, 127.1, 127.0, 126.9, 125.9, 125.8, 122.4, 119.1, 53.6, 48.7, 48.5, 41.1, 39.3, 21.6. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{40}H_{34}NO_4S$: 624.2209; found: 624.2210.

(3S,3aS,8R,8aS,Z)-8-(Benzoylmethyl)-6-methyl-3-phenyl-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5b***. White crystals, 189 mg, 59%, ee >99%, $[\alpha]^{20}_{D}$ = −138.2° (*c* = 0.5, CH_2Cl_2), mp 214−215 °C. IR ν (cm^{-1}) 3430, 1680, 1646. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.41 (s, 1H), 8.17 (d, *J* = 7.0 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.58 (t, *J* = 7.0 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.80−6.92 (m, 6H), 6.62 (d, *J* = 7.2 Hz, 2H), 6.49 (d, *J* = 7.3 Hz, 3H), 5.35 (d, *J* = 7.9 Hz, 1H), 4.51 (d, *J* = 9.4 Hz, 1H), 4.04−4.16 (m, 3H), 3.75 (t, *J* = 8.9 Hz, 1H), 3.42 (ddd, *J* = 24.2, 11.0, 3.9 Hz, 1H), 2.29 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 209.0, 199.8, 151.1, 145.9, 143.8, 139.9, 137.7, 137.5, 136.9, 136.7, 133.0, 131.0, 129.6, 129.3, 129.2, 129.1, 128.7, 128.2, 127.6, 127.4, 127.1, 127.0, 126.9, 125.9, 123.0, 119.0, 54.0, 48.4, 40.9, 39.1, 21.6, 21.2. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{41}H_{36}NO_4S$: 638.2365; found: 638.2356.

(3S,3aS,8R,8aS,Z)- 8-(Benzoylmethyl)-6-methoxy-3-phenyl-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5c***. White crystals, 166 mg, 51%, ee >99%, $[\alpha]^{20}_{D}$ = −169.4° (*c* = 0.5, CH_2Cl_2), mp 224−225 °C. IR ν (cm^{-1}) 3440, 1685, 1651. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.35 (s, 1H), 8.09 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.74−6.85 (m, 5H), 6.55 (d, *J* = 7.3 Hz, 2H), 6.52 (d, *J* = 1.9 Hz, 1H), 6.41 (d, *J* = 7.2 Hz, 2H), 6.16 (dd, *J* = 8.5, 2.2 Hz, 1H), 5.28 (d, *J* = 8.5 Hz, 1H), 4.41 (d, *J* = 9.3 Hz, 1H), 3.95−4.10 (m, 3H), 3.69 (t, *J* = 9.5 Hz, 1H), 3.58

DOI: 10.1021/jo502668c
J. Org. Chem. 2015, 80, 1727−1734

(s, 3H), 3.38 (ddd, J = 24.7, 11.6, 4.1 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 207.9, 198.7, 158.2, 150.2, 146.3, 142.8, 139.0, 136.6, 136.0, 132.0, 131.7, 130.0, 128.6, 128.3, 128.2, 128.1, 127.7, 127.3, 127.2, 126.6, 126.1, 126.0, 124.9, 118.1, 111.1, 106.6, 54.2, 53.2, 47.5, 47.1, 40.2, 38.0, 20.5. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{41}H_{35}NO_5S$: 654.2314; found: 654.2306.

(3S,3aS,8R,8aS,Z)- 8-(Benzoylmethyl)-6-fluoro-3-phenyl-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5d***. White crystals, 191 mg, 60%, ee >99%, $[\alpha]^{20}_D = -97.4°$ (c = 0.5, CH_2Cl_2), mp 228−229 °C. IR ν (cm^{-1}) 3432, 1686, 1648. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.43 (s, 1H), 8.16 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.59 (t, J = 7.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 7.5 Hz, 1H), 6.81−6.93 (m, 5H), 6.75 (d, J = 7.3 Hz, 1H), 6.61 (d, J = 7.3 Hz, 2H), 6.46 (d, J = 7.2 Hz, 2H), 6.36 (td, J = 8.7, 2.0 Hz, 1H), 5.42 (dd, J = 8.1, 5.4 Hz, 1H), 4.50 (d, J = 9.5 Hz, 1H), 4.05−4.17 (m, 3H), 3.81 (t, J = 8.8 Hz, 1H), 3.43 (dd, J = 21.4, 8.9 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.3, 199.3, 162.5 (d, J = 243.6 Hz), 151.6, 147.9 (d, J = 7.7 Hz), 143.8, 140.0, 137.1 (d, J = 38.2 Hz), 136.1, 133.1, 130.8, 129.5, 129.2, 129.1, 128.74, 128.68, 128.2, 127.6, 127.2, 127.0, 126.0, 118.8, 113.0 (d, J = 22.1 Hz), 109.4 (d, J = 22.1 Hz), 54.1, 48.4, 48.0, 41.1, 39.0, 21.5. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{40}H_{33}FNO_4S$: 642.2114; found: 642.2115.

(3S,3aS,8R,8aS,Z)-8-((p-Methylbenzoyl)methyl)-3-phenyl-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5e***. White crystals, 185 mg, 58%, ee >99%, $[\alpha]^{20}_D = -97.0°$ (c = 0.5, CH_2Cl_2), mp 183−184 °C. IR ν (cm^{-1}) 3438, 1670, 1644. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.44 (s, 1H), 8.07 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.02−7.07 (m, 5H), 6.80−6.92 (m, 5H), 6.66 (t, J = 7.1 Hz, 1H), 6.61 (d, J = 7.3 Hz, 2H), 6.46 (d, J = 7.2 Hz, 2H), 5.54 (d, J = 7.6 Hz, 1H), 4.51 (d, J = 9.5 Hz, 1H), 4.05−4.15 (m, 3H), 3.77 (t, J = 8.8 Hz, 1H), 3.46 (dd, J = 16.9, 3.8 Hz, 1H), 2.50 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.8, 199.3, 151.2, 145.8, 143.8, 143.7, 140.7, 140.1, 137.0, 135.0, 130.9, 129.6, 129.34, 129.25, 129.18, 129.0, 128.3, 127.7, 127.6, 127.1, 127.0, 126.9, 125.9, 122.4, 119.2, 53.7, 48.7, 48.5, 41.1, 39.1, 21.7, 21.5. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{41}H_{36}NO_4S$: 638.2365; found: 638.2367.

(3S,3aS,8R,8aS,Z)-8-((p-Methoxybenzoyl)methyl)-3-phenyl-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5f***. White crystals, 225 mg, 68%, ee >99%, $[\alpha]^{20}_D = -78.8°$ (c = 0.5, CH_2Cl_2), mp 194−195 °C. IR ν (cm^{-1}) 3439, 1663, 1640. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.46 (s, 1H), 8.15 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.02−7.07 (m, 7H), 6.80−6.92 (m, 5H), 6.66 (t, J = 7.2 Hz, 1H), 6.61 (d, J = 7.4 Hz, 2H), 6.46 (d, J = 7.2 Hz, 2H), 5.53 (d, J = 7.6 Hz, 1H), 4.51 (d, J = 9.6 Hz, 1H), 4.10−4.15 (m, 2H), 4.06 (t, J = 9.1 Hz, 1H), 3.95 (s, 3H), 3.77 (t, J = 9.2 Hz, 1H), 3.44 (dd, J = 17.2, 4.5 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.8, 198.2, 163.5, 151.2, 145.8, 143.8, 140.7, 140.1, 137.0, 130.9, 130.6, 130.4, 129.6, 129.2, 129.1, 129.0, 127.64, 127.59, 127.1, 127.0, 126.9, 125.84, 125.77, 122.5, 119.1, 113.8, 55.5, 53.8, 48.7, 48.5, 41.2, 38.8, 21.5. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{41}H_{36}NO_5S$: 654.2314; found: 654.2317.

(3S,3aS,8R,8aS,Z)-8-((p-Bromobenzoyl)methyl)-3-phenyl-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5g***. White crystals, 169 mg, 48%, ee >99%, $[\alpha]^{20}_D = -79.0°$ (c = 0.5, CH_2Cl_2), mp 193−194 °C. IR ν (cm^{-1}) 3440, 1673, 1640. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.34 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 6.93−6.98 (m, 5H), 6.72−6.84 (m, 5H), 6.59 (t, J = 7.0 Hz, 1H), 6.52 (d, J = 7.4 Hz, 2H), 6.37 (d, J = 7.2 Hz, 2H), 5.53 (d, J = 7.7 Hz, 1H), 4.44 (d, J = 9.6 Hz, 1H), 4.00−4.08 (m, 2H), 3.95 (t, J = 9.8 Hz, 1H), 3.70 (t, J = 9.2 Hz, 1H), 3.36 (dd, J = 17.6, 4.4 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.7, 198.6, 151.5, 145.4, 143.8, 140.82, 140.75, 140.1, 137.0, 136.2, 132.0, 130.8, 129.7, 129.6, 129.21, 129.17, 129.0, 128.1, 127.8, 127.6, 127.1, 127.0, 126.96, 125.9, 122.3, 118.9, 53.5, 48.6, 48.5, 41.1, 39.2, 21.5. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{41}H_{36}BrNO_4S$: 702.1314; found: 702.1313.

(3S,3aS,8R,8aS,Z)-8-(Benzoylmethyl)-3-(p-methylphenyl)-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5h***. White crystals, 148 mg, 46%, ee >99%, $[\alpha]^{20}_D = -130.0°$ (c = 0.5, CH_2Cl_2), mp 190−191 °C. IR ν (cm^{-1}) 3439, 1681, 1657. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.41 (s, 1H), 8.15 (d, J = 7.1 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.00−7.07 (m, 5H), 6.86 (t, J = 7.9 Hz, 2H), 6.68 (t, J = 7.6 Hz, 1H), 6.62 (d, J = 7.5 Hz, 2H), 6.60 (d, J = 7.0 Hz, 2H), 6.32 (d, J = 7.9 Hz, 2H), 5.61 (d, J = 7.8 Hz, 1H), 4.47 (d, J = 9.5 Hz, 1H), 4.07−4.17 (m, 3H), 3.75 (t, J = 9.1 Hz, 1H), 3.39 (ddd, J = 22.7, 9.9, 3.9 Hz, 1H), 2.36 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.9, 199.8, 151.1, 145.7, 143.8, 140.9, 137.6, 137.0, 136.9, 135.3, 133.0, 131.0, 129.5, 129.3, 129.2, 129.0, 128.7, 128.2, 127.9, 127.7, 127.6, 126.94, 126.92, 125.9, 122.4, 119.4, 53.7, 48.7, 48.1, 41.1, 39.3, 21.6, 20.9. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{41}H_{36}NO_4S$: 638.2365; found: 638.2361.

(3S,3aS,8R,8aS,Z)-8-(Benzoylmethyl)-3-(p-methoxyphenyl)-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5i***. White crystals, 141 mg, 43%, ee >99%, $[\alpha]^{20}_D = -115.0°$ (c = 0.5, CH_2Cl_2), mp 142−143 °C. IR ν (cm^{-1}) 3425, 1685, 1645. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.42 (s, 1H), 8.16 (d, J = 7.3 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.58 (t, J = 7.1 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.02−7.09 (m, 5H), 6.89 (t, J = 7.1 Hz, 2H), 6.71 (t, J = 7.1 Hz, 1H), 6.61 (d, J = 7.4 Hz, 2H), 6.38 (d, J = 9.1 Hz, 2H), 6.35 (d, J = 9.0 Hz, 2H), 5.65 (d, J = 7.7 Hz, 1H), 4.47 (d, J = 9.6 Hz, 1H), 4.08−4.18 (m, 3H), 3.76 (t, J = 9.1 Hz, 1H), 3.67 (s, 3H), 3.48 (ddd, J = 23.1, 10.0, 3.7 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.8, 199.7, 157.6, 151.1, 145.7, 143.7, 140.9, 137.5, 137.0, 132.9, 132.4, 131.0, 130.5, 129.2, 129.1, 129.0, 128.6, 128.2, 127.8, 127.6, 127.0, 126.9, 125.9, 122.4, 119.4, 112.6, 55.2, 53.6, 48.8, 47.7, 41.2, 39.2, 21.5. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{41}H_{36}NO_5S$: 654.2314; found: 654.2306.

(3S,3aS,8R,8aS,Z)-8-(Benzoylmethyl)-3-(p-bromophenyl)-2-(phenyl(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5j***. White crystals, 183 mg, 52%, ee >99%, $[\alpha]^{20}_D = -199.2°$ (c = 0.5, CH_2Cl_2), mp 176−177 °C. IR ν (cm^{-1}) 3440, 1682, 1658. ^{1}H NMR (400 MHz, $CDCl_3$) 12.43 (s, 1H), 8.15 (d, J = 7.3 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 7.2 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 7.03−7.09 (m, 5H), 6.93 (d, J = 8.4 Hz, 2H), 6.89 (t, J = 7.7 Hz, 2H), 6.72 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 7.4 Hz, 2H), 6.31 (d, J = 8.2 Hz, 2H), 5.62 (d, J = 7.7 Hz, 1H), 4.46 (d, J = 9.6 Hz, 1H), 4.12−4.16 (m, 2H), 4.07 (d, J = 9.5 Hz, 1H), 3.78 (t, J = 9.2 Hz, 1H), 3.49 (ddd, J = 24.6, 11.4, 4.0 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.4, 199.5, 151.6, 145.7, 143.9, 140.4, 139.5, 137.5, 136.9, 133.0, 131.3, 130.7, 130.1, 129.2, 129.1, 128.7, 128.2, 127.7, 127.6, 127.2, 126.0, 122.6, 119.6, 118.7, 53.5, 48.3, 48.0, 41.2, 39.1, 21.5. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{40}H_{33}BrNO_4S$: 702.1314; found: 702.1322.

(3S,3aS,8R,8aS,Z)-8-(Benzoylmethyl)-3-phenyl-2-((p-methylphenyl)(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5k***. White crystals, 190 mg, 60%, ee >99%, $[\alpha]^{20}_D = -104.8°$ (c = 0.5, CH_2Cl_2), mp 189−190 °C. IR ν (cm^{-1}) 3439, 1686, 1651. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.40 (s, 1H), 8.17 (d, J = 7.1 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.59 (t, J = 7.7 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.0 Hz, 3H), 7.03 (t, J = 7.6 Hz, 1H), 6.91 (t, J = 7.3 Hz, 1H), 6.82 (t, J = 7.2 Hz, 2H), 6.68 (d, J = 7.8 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 6.53 (d, J = 8.1 Hz, 2H), 6.47 (d, J = 7.2 Hz, 2H), 5.56 (d, J = 7.8 Hz, 1H), 4.53 (d, J = 9.6 Hz, 1H), 4.13−4.19 (m, 2H), 4.09 (d, J = 9.3 Hz, 1H), 3.76 (t, J = 9.2 Hz, 1H), 3.47 (ddd, J = 23.0, 10.0, 3.3 Hz, 1H), 2.38 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.7, 199.7, 151.5, 145.7, 143.8, 140.8, 140.1, 139.3, 137.5, 136.9, 133.0, 129.6, 129.2, 129.1, 128.7, 128.2, 127.7, 127.64, 127.61, 127.0, 126.9, 125.83, 125.8, 122.4, 119.2, 53.6, 48.7, 48.5, 41.1, 39.3, 21.6, 21.3. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{41}H_{36}NO_4S$: 638.2365; found: 638.2371.

(3S,3aS,8R,8aS,Z)-8-(Benzoylmethyl)-3-phenyl-2-((p-methoxyphenyl)(p-tolylsulfonamido)methylene)-indenocyclopentan-1-one ***5l***. White crystals, 145 mg, 44%, ee >99%, $[\alpha]^{20}_D = -99.0°$ (CH_2Cl_2, c = 0.5 g/100 mL), mp 173−174 °C. IR ν (cm^{-1}) 3438, 1675, 1637. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.38 (s, 1H), 8.16 (d, J = 7.1 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.58 (t, J = 7.7 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.6 Hz, 3H), 7.03 (t, J = 7.6 Hz, 1H), 6.92 (t, J = 7.3 Hz, 1H), 6.85 (t, J = 7.0 Hz, 2H), 6.67 (t, J = 7.4 Hz, 1H), 6.60 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 7.2

DOI: 10.1021/jo502668c
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Hz, 2H), 6.40 (d, J = 8.8 Hz, 2H), 5.54 (d, J = 7.7 Hz, 1H), 4.55 (d, J = 9.5 Hz, 1H), 4.09−4.17 (m, 3H), 3.75 (t, J = 8.6 Hz, 1H), 3.69 (s, 3H), 3.47 (dd, J = 21.8, 9.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.5, 199.7, 160.3, 151.2, 145.7, 143.7, 140.7, 139.9, 137.5, 136.9, 132.9, 131.0, 129.6, 129.1, 128.6, 128.2, 127.63, 127.60, 127.1, 126.9, 125.9, 125.8, 123.6, 122.4, 119.1, 112.5, 55.2, 53.6, 48.7, 48.6, 41.1, 39.1, 21.5. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{41}H_{36}NO_5S$: 654.2314; found: 654.2314.

(3S,3aS,8R,8aS,Z)-8-(Benzoylmethyl)-3-phenyl-2-((p-bromophenyl)(p-tolylsulfonamido)methylene)indenocyclopentan-1-one ***5m***. White crystals, 149 mg, 42%, ee >99%, $[\alpha]^{20}_D$ = −145.6° (CH_2Cl_2, c = 0.5 g/100 mL), mp 177−178 °C. IR ν (cm^{-1}) 3439, 1675, 1638. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.23 (s, 1H), 8.07 (d, J = 7.1 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.93−7.02 (m, 4H), 6.90 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 7.3 Hz, 1H), 6.78 (t, J = 7.3 Hz, 2H), 6.59 (t, J = 7.1 Hz, 1H), 6.38 (d, J = 8.4 Hz, 2H), 6.36 (d, J = 6.0 Hz, 2H), 5.49 (d, J = 7.8 Hz, 1H), 4.37 (d, J = 9.6 Hz, 1H), 4.03−4.09 (m, 2H), 3.99 (t, J = 9.6 Hz, 1H), 3.69 (t, J = 9.1 Hz, 1H), 3.41 (dd, J = 16.7, 3.8 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 208.9, 199.6, 149.7, 145.6, 144.1, 140.5, 139.9, 137.5, 136.9, 133.0, 130.8, 130.2, 129.9, 129.7, 129.3, 128.7, 128.2, 127.8, 127.5, 127.2, 127.0, 126.1, 125.9, 123.6, 122.4, 119.7, 53.7, 48.6, 48.5, 41.2, 39.2, 21.5. HRMS (ESI-TOF): $[M + H]^+$ calcd for $C_{40}H_{33}BrNO_4S$: 702.1314; found: 702.1322.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of HPLC chromatographs for all products **4** and **5**, ^{1}H NMR and ^{13}C NMR spectra of new compounds **5**, and single crystal data of **4j** and **5j** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21372030 and 21172021) and the Beijing Municipal Commission of Education.

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