N-Heterocyclic Carbene Catalyzed Reaction of 2-(2-Aroylvinyl)cinnamaldehydes with α,β-Unsaturated Imines: An Efficient Method for the Stereoselective Synthesis of Highly Functionalized Indane Derivatives

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Abstract: The NHC-catalyzed reaction of 2-(2-aroylvinyl)cinnamaldehydes with α,β-unsaturated imines was studied, which produced good yields of novel 3-aryl-9-[1,3-diaryl-3-(4-tolylsulfonamido)allyl]-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-ones with high diastereoselectivity. The products can be easily converted into different highly functionalized indane derivatives via simple operations. Thus, this work provides a simple and efficient method for the stereoselective synthesis of 1,2,3-trisubstituted indane derivatives.

Key words: N-heterocyclic carbene, catalysis, 2-(2-aroylvinyl)cinnamaldehyde, α,β-unsaturated imine, indane

A large number of indane derivatives are known to have a wide spectrum of biological activity. For example, indanes **A** substituted by 4-aminobutyl and benzyl show strong antibacterial activity (Figure 1).[1] 5-(5,6-Dichloroindan-1-yl)-1*H*-tetrazole (**B**) and 5-[(5,6-dichloroindan-1-yl)methyl]-1*H*-tetrazole (**C**) display significant analgesic and anti-inflammatory activity.[2] The indanyl-substituted guanidiniums **D** have been investigated as small-molecule HIV-1 entry inhibitors,[3] and the sulfamides of 1-amino- and 2-aminoindanes **E** and **F** are potential carbonic anhydrase isoenzymes inhibitors.[4] 3-Amino-1-(indan-5-yloxy)propan-2-ol derivatives **G** exhibited blocking activity for Na^+ channels, useful as potent sodium-channel blockers for the treatment of stroke victims.[5] Various indane derivatives **H** derived from 7-aminoindan-4-ol are potent liver-selective thyroid hormone receptor β (TRβ) agonists for the treatment of dyslipidemia,[6] while the 1-aminoindan-2-ol or 2-aminoindan-1-ol derivatives **I** and **J** have highly potent protein kinase C inhibitory activity.[7] Due to their biological, pharmaceutical, and synthetic importance, interest in the synthesis of novel indane derivatives remains undiminished.[2,8]

Cascade reactions catalyzed by N-heterocyclic carbenes (NHCs) have received attention due to the resulting rapid generation of complex products.[9] A few N-heterocyclic carbene catalyzed reactions have been reported to produce different indene or indane derivatives. For example, the cascade reactions of 2-formylcinnamates with imines, phthalaldehydes with imines, and phthalaldehydes with 3-aroylacrylates in the presence of NHC catalysts gave substituted indan-1-ones,[10a–c] while NHC-catalyzed reaction of 3,3′-(1,2-phenylene)bis(1-phenylpropenones) with aldehydes produced 1,2,3-trisubstituted indanes.[10d] Under catalysis by NHCs, the dimerization of *o*-formylchalcones

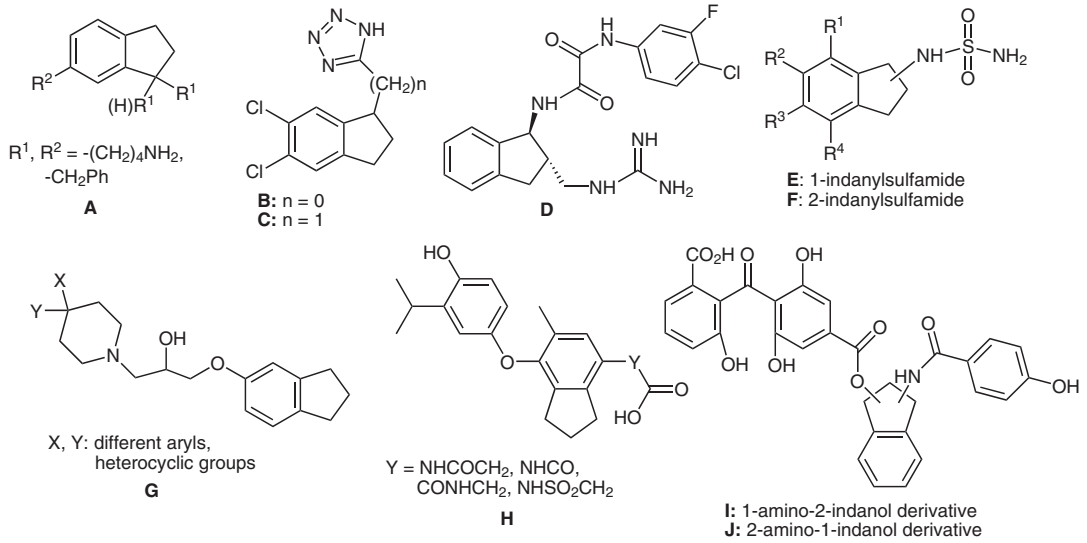

Figure 1 Some bioactive indane derivatives

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or *o*-formylcinnamates, or the reaction of *o*-formylchalcones with phthalaldehydes, afforded indene-spiro-indanone derivatives.[10e] On the other hand, the dimerization of phthalaldehydes catalyzed by a imidazole or triazole carbene produced dihydroisobenzofuran-spiro-indanones or indeno[2,1-*a*]indanone derivatives, respectively.[10f] NHC-catalyzed self-reaction of 2-(2-aroylvinyl)cinnamaldehydes gave indeno[2,1-*c*]pyran-1-ones that were converted into indane-2-carboxylates or indane-2-carboxamides by the addition of alcohols or amines,[11a,b] and the oxidative NHC-catalyzed cascade reaction between 2-(2-aroylvinyl)cinnamaldehydes and β-diketones produced 9-(β-diketones)indeno[2,1-*c*]pyran-1-ones.[11c] Our attention has mainly focused on NHC-catalyzed reactions in recent years.[10f,12] We are interested in NHC-catalyzed reactions of multifunctional reactants in terms of various possible reaction pathways and complex structures of products. We envisioned that the reaction between α,β-unsaturated aldehydes linked with a Michael acceptor and α,β-unsaturated imines might have several different pathways. Thus, we studied the NHC-catalyzed reaction of 2-(2-aroylvinyl)cinnamaldehydes with *N*-sulfonyl ketimines, which provided an efficient and stereoselective method for the synthesis of highly functionalized indane derivatives.

We started this work by studying the reaction employing 2-(2-benzoylvinyl)cinnamaldehyde (**1a**) and 1,3-diphenyl-*N*-tosylprop-2-en-1-imine (**2a**) as model substrates (Table 1). At ambient temperature and in dichloromethane, the reaction of **1a** with **2a** (**1a**/**2a** 1:1.5) was initially catalyzed using 20 mol% of various triazole carbenes **3a′**–**d′** that were generated from triazolium salts **3a**–**d** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). All these reactions produced product **4a**, which was confirmed to be 9-[1,3-diphenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one by spectroscopic and single crystal X-ray diffraction analyses,[13] and the highest yield (66%) of **4a** was obtained from the reaction catalyzed by *N*-(pentafluorophenyl)pyrrolo[2,1-*c*]triazole carbene **3d′** (entries 1–4). Replacement of triazole carbene catalysts with thiazole carbene **3e′** or imidazole carbenes **3f′** and **3g′** resulted in no product or trace yields of product. Under the catalysis of triazole carbene **3d′**, the reaction conditions were further optimized by varying temperature, solvent, and the base used to generate the carbene catalyst. It was found that decreasing reaction temperature to 0 °C improved the yield of **4a** to 78%, however, further decreasing the temperature to –20 °C did not benefit the reaction, while elevating the temperature to the boiling point of dichloromethane led to the formation of product in a lower yield (entries 7–9). At 0 °C, the use of other solvents including benzene, acetone, acetonitrile, and tetrahydrofuran, or other bases like potassium *tert*-butoxide, sodium hydride, and cesium carbonate, all diminished the yield of product (entries 10–16). In addition to the major product **4a**, a small amount of a minor product (below 10%) was detected in the crude product of most reactions by ^{1}H NMR.

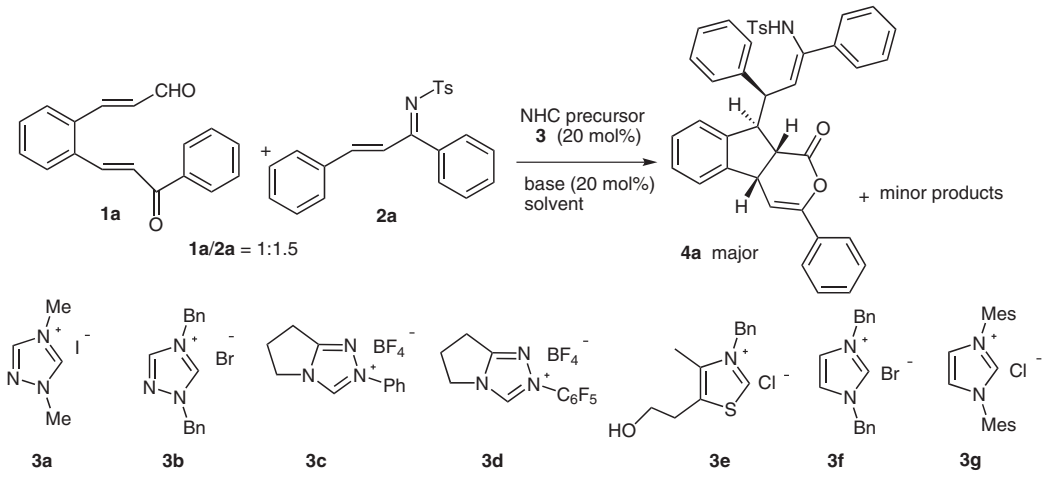
The scope of the reaction was then studied under the optimized conditions using α,β-unsaturated aldehydes **1** and α,β-unsaturated imines **2** that bear different substituents. It was found that the substituents of both reactants have a small influence on the reaction. As illustrated in Table 2, the reaction between 2-(2-aroylvinyl)cinnamaldehyde **1** and α,β-unsaturated imine **2** substituted by either electron-donating or electron-withdrawing groups on any of the four phenyl rings in **1** and **2**, proceeded rapidly and efficiently to furnish products **4** in 69–84% yields in 20 minutes (entries 1–10, 13–15). Since the two phenyl groups of 2-(2-aroylvinyl)cinnamaldehydes **1** and the phenyl on the imine group of ketimines **2** are remote from the site of the reaction between **1** and **2**, we considered that the steric effects of the substituents attached to these three phenyl rings could be ignored. Thus, we only examined the influence of the position of substituent attached to the phenyl group at C3 of ketimine **2**. 3-(4-Methoxyphenyl)prop-2-en-1-imine **2c** and 3-(3-methoxyphenyl)prop-2-en-1-imine **2e** gave higher yields of products (71–79%) than that of 3-(2-methoxyphenyl)prop-2-en-1-imine **2f** (63%) when they reacted with enal **1a** (entries 9, 11, and 12). In addition to the product **4**, the minor product **5** was detected in the crude products by ^{1}H NMR in 3–19% yields (ratio **4**/**5** ~4:1–21:1). Initially, we thought that compounds **5** were diastereomers of products **4**. However, after the isolation of compound **5j**, the spectroscopic characterization and single crystal X-ray diffraction analysis[13] confirmed that **5j** was 8-(benzoylmethyl)-3-(4-bromophenyl)-2-[phenyl(4-tolylsulfonamido)methylene]-3,3a,8,8a-tetrahydrocyclopenta[*a*]inden-1(2*H*)-one, which is derived from the intramolecular transformation of one diastereomer of the major product **4j**. The minor products **5** were difficult to separate from the corresponding major products **4** by chromatography due to the fact that each pair of **4** and **5** has a similar polarity. Thus, with the exception of **5j** which has the highest yield (19%) and the largest difference of polarity to **4j**, other minor products **5** were not isolated. The byproducts **5** can be removed from the major products **4** by recrystallization.

To account for the formation of 3-aryl-9-[1,3-diaryl-3-(4-tolylsulfonamido)allyl]indeno[2,1-*c*]pyran-1-ones **4** and 8-(aroylmethyl)-3-aryl-2-[aryl(4-tolylsulfonamido)methylene]-3,3a,8,8a-tetrahydrocyclopenta[*a*]inden-1(2*H*)-ones **5** from 2-(2-aroylvinyl)cinnamaldehydes **1** and *N*-tosyl ketimines **2**, a cascade reaction mechanism comprising two Michael additions is proposed (Scheme 1). Firstly, the homoenolate **6** derived from enal **1** and carbene **3′** undergoes intermolecular Michael addition to α,β-unsaturated imine **2** to form enamine anion **7**, which isomerizes to enolate **8** by proton transfer. The intramolecular Michael addition of **8** yields diastereomeric indane intermediates **9** and **10**. Intramolecular lactonization of **9** and **10** forms 9-[1,3-diaryl-3-(4-tolylsulfonamido)allyl]indeno[2,1-*c*]pyran-1-ones **4** and **11**, respectively. This reaction occurs by a cascade process to form four stereocenters, however, only the racemates of (4a*S*,9*S*,9a*S*,1′*R*)- and (4a*R*,9*R*,9a*R*,1′*S*)-9-[1,3-diaryl-3-(4-tolylsulfonamido)al-

lyl]indeno[2,1-*c*]pyran-1-ones **4** are found in the reaction. The stereoselective formation of products **4** can be explained by the steric effects of substituents. In the formation of the indane ring of **4**, the substituents attached to the stereocenters at C9 and C9a are arranged in a *trans* configuration to reduce the repulsion of substituents, while the two fused C4a and C9a stereocenters are in a *cis* configuration to avoid fused-ring strain. The minor cyclopenta[*a*]inden-1-one products **5** are derived from the isomerization of minor diastereomers **11** by the intramolecular addition of the enamine to the δ-lactone species of **11** under the catalysis of a base, such as triazole carbene or DBU. However, the major diastereomers **4** could not undergo such a transformation as the enamine and δ-lactone species of **4** are *trans* substituted on the indane ring.

The lactone moiety of indeno[2,1-*c*]pyran-1-ones are known to be easily cleaved by the addition of nucleophiles, such as alcohols or amines.[11a,b] Therefore, it would be possible to convert 9-[3-(sulfonamido)allyl]indeno[2,1-*c*]pyran-1-ones **4** into various highly functionalized indane derivatives. To extend the applications of the current reaction in the synthesis of indane derivatives, the different transformations of 3-aryl-9-[1,3-diaryl-3-(tolyl-

Table 1 Optimization of the Reaction Conditions



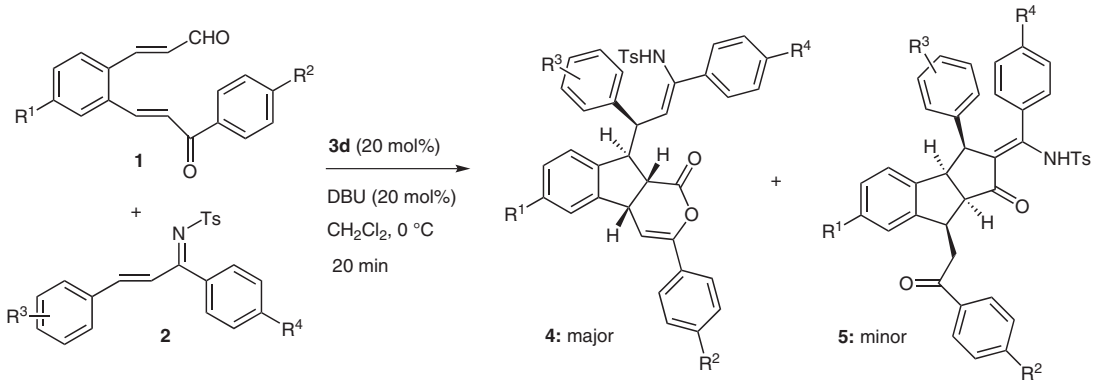
Entry	NHC precursor	Base	Solvent	Temp (°C)	Time	Yield (%) of **4a**
1	**3a**	DBU	CH_2Cl_2	r.t.	5 h	30[a]
2	**3b**	DBU	CH_2Cl_2	r.t.	5 h	19[a]
3	**3c**	DBU	CH_2Cl_2	r.t.	5 h	21[a]
4	**3d**	DBU	CH_2Cl_2	r.t.	20 min	66
5	**3e**	DBU	CH_2Cl_2	r.t.	24 h	trace
6	**3f**	DBU	CH_2Cl_2	r.t.	8 h	–[b]
7	**3g**	DBU	CH_2Cl_2	r.t.	8 h	–[b]
8	**3d**	DBU	CH_2Cl_2	0	20 min	78
9	**3d**	DBU	CH_2Cl_2	–20	30 min	64
10	**3d**	DBU	CH_2Cl_2	reflux	5 min	55
11	**3d**	Cs_2CO_3	CH_2Cl_2	0	2 h	59
12	**3d**	*t*-BuOK	CH_2Cl_2	0	1 h	65
13	**3d**	NaH	CH_2Cl_2	0	2 h	45
14	**3d**	DBU	benzene	0	4 h	46[a]
15	**3d**	DBU	acetone	0	4 h	59
16	**3d**	DBU	MeCN	0	4 h	45[a]
17	**3d**	DBU	THF	0	2 h	65

[a] The enal **1a** was not totally consumed.
[b] Not found.

sulfonamido)allyl]indeno[2,1-*c*]pyran-1-ones **4** were examined. For example, **4a** was converted into methyl 1-(benzoylmethyl)-3-[1,3-diphenyl-3-(4-tolylsulfonamido)allyl]indane-2-carboxylate (**14**) in 82% yield on heating in refluxing methanol. At ambient temperature, the hydrolysis of **4a** with aqueous 30% sodium hydroxide solution followed by saturated aqueous solution of ammonium chloride in tetrahydrofuran afforded 1-(benzoylmethyl)-3-(2-benzoyl-1-phenylethyl)indane-2-carboxylic acid (**15**) in 80% yield. Reduction of **4a** with lithium aluminum hydride in tetrahydrofuran produced 9-[1,3-diphenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-1,4a,9,9a-tetrahydroindeno[2,1-*c*]pyran (**16**) in 70% yield (Scheme 2).

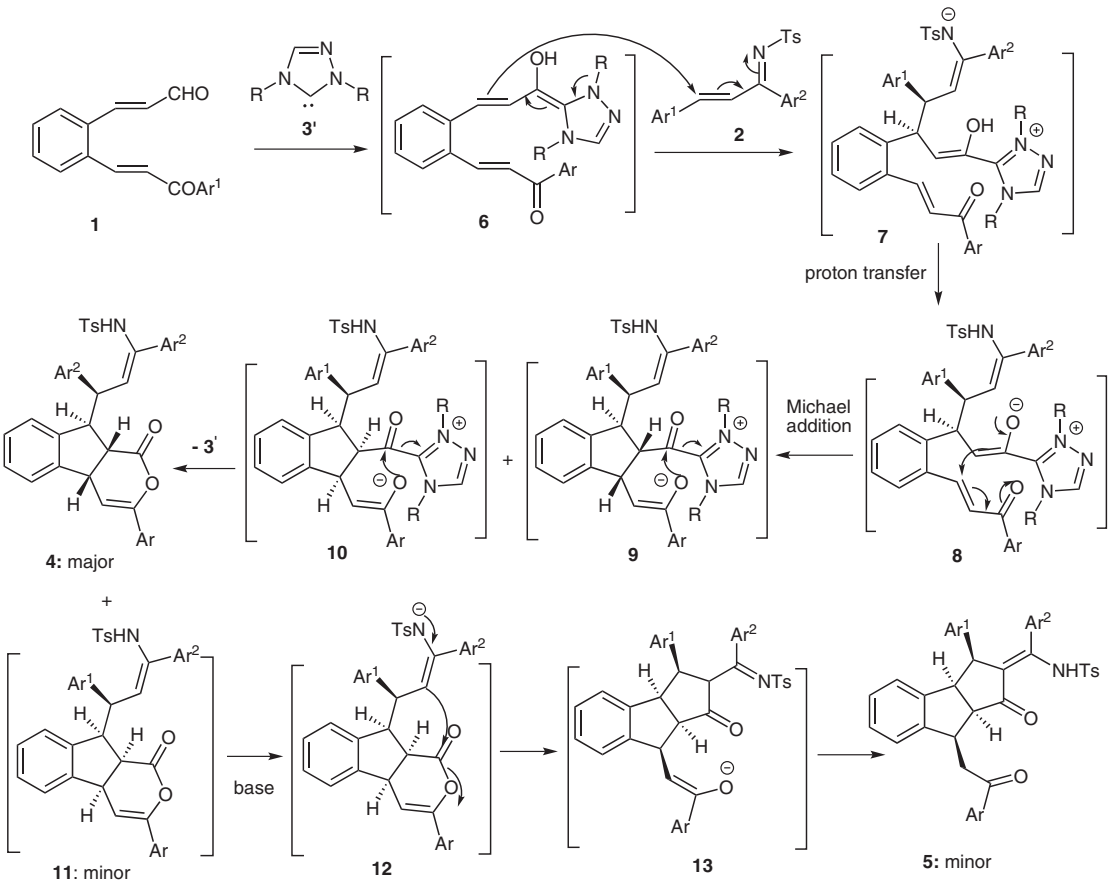
Enantioselective synthesis of 9-[3-(sulfonamido)allyl]indeno[2,1-*c*]pyran-1-ones **4** was also attempted using chiral triazole carbenes. As shown in Scheme 3, while chiral pyrrolo[2,1-*c*]triazole carbene **3h** did not promoted the reaction of enal **1a** with *N*-tosyl ketimine **2a**, a small amount of product **4a** (15%) was obtained from the reaction catalyzed by *N*-(pentafluorophenyl)hexahydroindeno[2,1-*b*]triazolo[3,4-*c*][1,4]oxazine carbene **3i**. However, to our delight, under catalysis by *N*-phenylhexahydroindeno[2,1-*b*]triazolo[3,4-*c*][1,4]oxazine carbene **3j**, the reaction of enal **1a** with ketimine **2a** provided **4a** in 45% yield with high enantioselectivity (90% ee, absolute configuration of **4a** was not determined.) (Scheme 3). This initial study on the asymmetric reaction of 2-(2-benzoylvinyl)cinnamaldehyde (**1a**) with *N*-tosyl ketimine **2a** indi-

Table 2 The Reaction of 2-(2-Aroylvinyl)cinnamaldehydes **1** with 1,3-Diaryl-*N*-tosylprop-2-en-1-imines **2** under Optimized Conditions

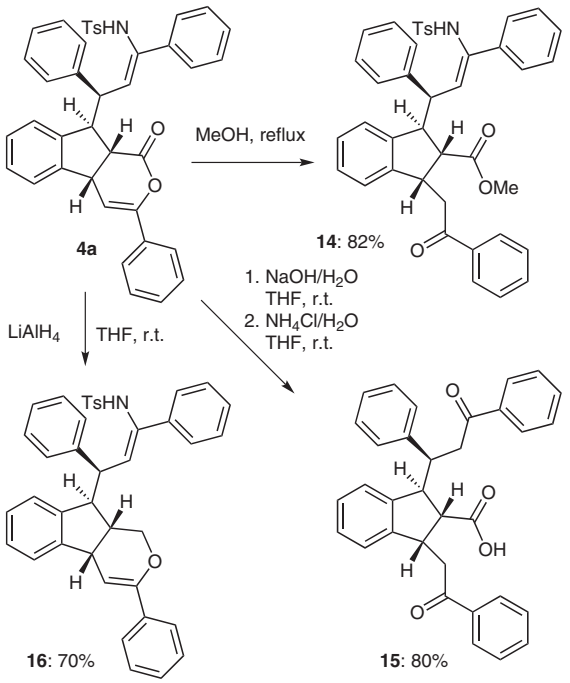


Entry	**1**	R^1	R^2	**2**	R^3	R^4	Yield[a] (%) Total	**4**[b]	**5**[b,c]	Ratio[d] **4**/**5**
1	**1a**	H	H	**2a**	H	H	81	**4a**: 78	**5a**: 3	24:1
2	**1b**	Me	H	**2a**	H	H	84	**4b**: 76	**5b**: 8	10:1
3	**1c**	OMe	H	**2a**	H	H	92	**4c**: 84	**5c**: 8	10:1
4	**1d**	F	H	**2a**	H	H	80	**4d**: 69	**5d**: 11	6:1
5	**1e**	H	Me	**2a**	H	H	82	**4e**: 78	**5e**: 4	20:1
6	**1f**	H	OMe	**2a**	H	H	76	**4f**: 72	**5f**: 4	20:1
7	**1g**	H	Br	**2a**	H	H	77	**4g**: 70	**5g**: 7	10:1
8	**1a**	H	H	**2b**	4-Me	H	79	**4h**: 71	**5h**: 8	9:1
9	**1a**	H	H	**2c**	4-OMe	H	78	**4i**: 71	**5i**: 7	10:1
10	**1a**	H	H	**2d**	4-Br	H	89	**4j**: 70	**5j**: 19	4:1
11	**1a**	H	H	**2e**	3-OMe	H	86	**4k**: 79	**5k**: 7	12:1
12	**1a**	H	H	**2f**	2-OMe	H	76	**4l**: 63	**5l**: 13	5:1
13	**1a**	H	H	**2g**	H	Me	82	**4m**: 74	**5m**: 8	9:1
14	**1a**	H	H	**2h**	H	OMe	80	**4n**: 70	**5n**: 10	7:1
15	**1a**	H	H	**2i**	H	Br	83	**4o**: 74	**5o**: 9	8:1

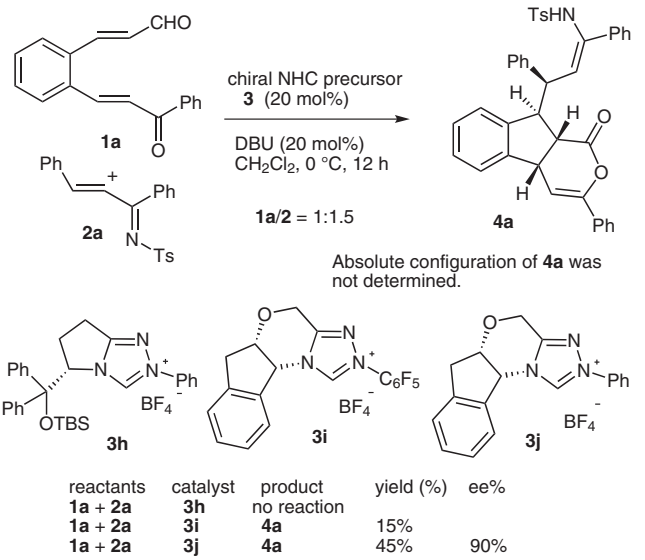
[a] The isolated yields.
[b] The yields of **4** and **5** were calculated based on the ratios of **4**/**5** and the total yields of products.
[c] Except **5j**, other minor products **5** were not isolated and characterized.
[d] The ratios of **4**/**5** were detected by ^{1}H NMR on the crude products.



Scheme 1 The proposed mechanism for the formations of 3-aryl-9-[1,3-diaryl-3-(4-tolylsulfonamido)allyl]indeno[2,1-*c*]pyran-1-ones **4** and 8-(aroylmethyl)-3-aryl-2-[aryl(4-tolylsulfonamido)methylene]-3,3a,8,8a-tetrahydrocyclopenta[*a*]inden-1(2*H*)-ones **5** from the reaction 2-(2-aroylvinyl)cinnamaldehydes **1** with 1,3-diaryl-*N*-tosylprop-2-en-1-imines **2**



Scheme 2 The transformations of 9-[1,3-diphenyl-3-(4-tolylsulfonamido)allyl]-3-phenylindeno[2,1-*c*]pyran-1-one **4a**



reactants	catalyst	product	yield (%)	ee%
1a + **2a**	**3h**	no reaction		
1a + **2a**	**3i**	**4a**	15%	
1a + **2a**	**3j**	**4a**	45%	90%

Scheme 3 Asymmetric reaction of 2-(2-benzoylvinyl)cinnamaldehyde **1a** with *N*-tosyl ketimine **2a** catalyzed by chiral triazole carbenes

cates that the enantioselective synthesis of 9-[3-(sulfonamido)allyl]indeno[2,1-*c*]pyran-1-ones **4** can be achieved using chiral triazole carbene **3j** as the catalyst.

In summary, we have developed an efficient NHC-catalyzed reaction of 2-(2-aroylvinyl)cinnamaldehydes with α,β-unsaturated imines, which produced good yields of novel 3-aryl-9-[1,3-diaryl-3-(4-tolylsulfonamido)allyl]indeno[2,1-*c*]pyran-1-ones with high diastereoselectivity. Indane is a framework that is found in a large number of bioactive and pharmaceutically important molecules. This work provided unique indane derivatives that are amenable to further transformations.

Commercially available chemical reagents were used without further purification. Anhyd CH_2Cl_2 was prepared by distillation over P_2O_5. Melting points are uncorrected. Petroleum ether = PE. ^1H (400 or 500 MHz) and ^{13}C NMR (100 or 125 MHz) were recorded in the indicated solvents using a Bruker instrument. IR spectra were recorded using an AVATAR 360 FT-IR spectrophotometer. Mass spectra were recorded on a Surveyor MSQ Plus (ESI) instrument. Column chromatography was performed using 200–300 mesh silica gel. The 2-(2-aroylvinyl)cinnamaldehydes **1**,[14] 1,3-diaryl-*N*-tosylprop-2-en-1-imines **2**,[15] and NHC precursor **3d**[16] were prepared according to literature methods.

NHC-Catalyzed Reaction of 2-(2-Aroylvinyl)cinnamaldehydes 1 with 1,3-Diaryl-*N*-tosylprop-2-en-1-imines 2; General Procedure

Under N_2 atmosphere and at 0 °C, 2-(2-aroylvinyl)cinnamaldehyde **1** (0.5 mmol), 1,3-diaryl-*N*-tosylprop-2–en-1-imines **2** (0.75 mmol), *N*-(pentafluorophenyl)pyrrolo[2,1-*c*]triazolium salt **3d** (0.1 mmol), and 4-Å molecular sieves (250 mg) were mixed in anhyd CH_2Cl_2 (10 mL). The mixture was stirred for 10 min at 0 °C, and then DBU (0.1 mmol) was added using a microsyringe. The mixture was stirred at 0 °C for ca. 20–30 min until the enal **1** had been consumed. After removal of molecular sieves and the solvent, the residue was purified by flash column chromatography (silica gel, PE–CH_2Cl_2–EtOAc, 16:4:1) to give **4**, which contained a trace amount of by-product **5**. The major product **4** was further purified by recrystallization (*n*-hexane–CH_2Cl_2).

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1,3-Diphenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4a)**

White crystals; yield: 243 mg (0.39 mmol, 78%); mp 180–182 °C.

IR: 3250, 1748, 1628, 1595 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.08 (s, 1 H), 7.68 (d, *J* = 7.0 Hz, 2 H), 7.52–7.54 (m, 2 H), 7.51 (d, *J* = 8.3 Hz, 2 H), 7.42 (t, *J* = 7.7 Hz, 2 H), 7.39 (d, *J* = 6.8 Hz, 1 H), 7.21–7.35 (m, 8 H), 7.16 (d, *J* = 7.7 Hz, 2 H), 7.11 (d, *J* = 7.8 Hz, 2 H), 7.09 (d, *J* = 5.6 Hz, 1 H), 6.85 (d, *J* = 7.5 Hz, 1 H), 6.22 (d, *J* = 5.1 Hz, 1 H), 6.01 (d, *J* = 10.9 Hz, 1 H), 4.22 (t, *J* = 5.0 Hz, 1 H), 4.02–4.06 (m, 2 H), 3.15 (dd, *J* = 8.8, 4.6 Hz, 1 H), 2.23 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.1, 148.9, 144.9, 144.1, 142.1, 142.0, 140.0, 138.6, 137.4, 133.5, 130.4, 129.9, 129.4, 129.2, 128.92, 128.90, 128.8, 128.7, 128.1, 127.9, 127.7, 127.4, 126.2, 125.9, 125.4, 124.9, 101.6, 54.6, 46.5, 45.8, 41.4, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{34}NO_4S$: 624.2209; found: 624.2218.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1,3-Diphenyl-3-(4-tolylsulfonamido)allyl]-6-methyl-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4b)**

White crystals; yield: 242 mg (0.38 mmol, 76%); mp 126–128 °C.

IR: 3335, 1751, 1598 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.09 (s, 1 H), 7.69 (d, *J* = 7.2 Hz, 2 H), 7.52–7.55 (m, 2 H), 7.52 (d, *J* = 8.2 Hz, 2 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.40 (t, *J* = 6.9 Hz, 1 H), 7.25–7.32 (m, 6 H), 7.16 (br s, 3 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.93 (d, *J* = 7.7 Hz, 1 H), 6.71 (d, *J* = 7.8 Hz, 1 H), 6.22 (d, *J* = 5.0 Hz, 1 H), 5.97 (d, *J* = 10.8, 1 H), 4.17 (t, *J* = 5.2 Hz, 1 H), 3.98–4.03 (m, 2 H), 3.12 (dd, *J* = 8.6, 4.6 Hz, 1 H), 2.28 (s, 3 H), 2.25 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.1, 148.8, 145.0, 144.1, 142.2, 140.0, 139.0, 138.6, 138.5, 137.4, 133.6, 130.4, 129.9, 129.4, 129.1, 128.9, 128.87, 128.73, 128.65, 128.2, 127.7, 127.4, 125.9, 125.8, 125.4, 125.3, 101.7, 54.3, 46.8, 45.8, 41.3, 21.5, 21.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{36}NO_4S$: 638.2365; found: 638.2368.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1,3-Diphenyl-3-(4-tolylsulfonamido)allyl]-6-methoxy-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4c)**

White crystals; yield: 284 mg (0.42 mmol, 84%); mp 166–167 °C.

IR: 3298, 1751, 1614, 1593 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.08 (s, 1 H), 7.69 (d, *J* = 7.2 Hz, 2 H), 7.54–7.56 (m, 2 H), 7.52 (d, *J* = 8.3 Hz, 2 H), 7.44 (t, *J* = 7.7 Hz, 2 H), 7.40 (t, *J* = 7.3 Hz, 1 H), 7.23–7.32 (m, 6 H), 7.16 (d, *J* = 6.8 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 6.94 (s, 1 H), 6.71 (d, *J* = 8.4 Hz, 1 H), 6.67 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.22 (d, *J* = 5.0 Hz, 1 H), 5.99 (d, *J* = 10.9 Hz, 1 H), 4.15 (t, *J* = 5.1 Hz, 1 H), 4.02 (dd, *J* = 8.6, 5.1 Hz, 1 H), 3.99 (dd, *J* = 10.9, 5.7 Hz, 1 H), 3.76 (s, 3 H), 3.15 (dd, *J* = 8.7, 4.7 Hz, 1 H), 2.25 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.1, 161.0, 148.9, 146.4, 144.1, 142.2, 140.0, 138.6, 137.4, 133.64, 133.58, 130.4, 129.9, 129.4, 129.1, 128.9, 128.7, 128.2, 127.7, 127.4, 126.8, 125.9, 125.4, 114.0, 110.0, 101.6, 55.7, 54.0, 47.0, 46.0, 41.6, 21.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{41}H_{35}NO_5SNa$: 676.2128; found: 676.2145.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1,3-Diphenyl-3-(4-tolylsulfonamido)allyl]-6-fluoro-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4d)**

White crystals; yield: 225 mg (0.35 mmol, 69%); mp 136–138 °C.

IR: 3189, 1732, 1595 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 8.17 (s, 1 H), 7.69 (d, *J* = 7.2 Hz, 2 H), 7.51–7.52 (m, 4 H), 7.39–7.45 (m, 3 H), 7.27–7.30 (m, 6 H), 7.18 (d, *J* = 6.6 Hz, 2 H), 7.13 (d, *J* = 7.9 Hz, 3 H), 6.89 (br s, 2 H), 6.25 (d, *J* = 5.0 Hz, 1 H), 6.07 (d, *J* = 10.7 Hz, 1 H), 4.20 (t, *J* = 4.3 Hz, 1 H), 4.08 (dd, *J* = 10.3, 5.6 Hz, 1 H), 4.02 (dd, *J* = 7.4, 5.6 Hz, 1 H), 3.24 (dd, *J* = 8.3, 3.3 Hz, 1 H), 2.26 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 170.6, 164.9, 162.5, 149.3, 147.5, 147.4, 144.1, 142.0, 139.9, 138.7, 137.9, 137.3, 133.5, 130.3, 130.0, 129.4, 129.2, 128.9, 128.8, 128.7, 128.1, 127.7, 127.6, 127.5, 126.1, 125.5, 114.9, 114.6, 111.9, 111.6, 100.8, 54.1, 46.8, 46.1, 41.4, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{33}FNO_4S$: 642.2114; found: 642.2102.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1,3-Diphenyl-3-(4-tolylsulfonamido)allyl]-3-(4-methylphenyl)-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4e)**

White crystals; yield: 249 mg (0.39 mmol, 78%); mp 185–187 °C.

IR: 3162, 1727, 1601 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 8.11 (s, 1 H), 7.58 (d, *J* = 8.1 Hz, 2 H), 7.51–7.54 (m, 4 H), 7.31–7.35 (m, 4 H), 7.22–7.28 (m, 6 H), 7.17 (d, *J* = 6.9 Hz, 2 H), 7.12 (d, *J* = 8.1 Hz, 2 H), 7.10 (d, *J* = 8.2 Hz, 1 H), 6.84 (d, *J* = 7.5 Hz, 1 H), 6.17 (d, *J* = 4.9 Hz, 1 H), 6.01 (d, *J* = 10.9 Hz, 1 H), 4.22 (t, *J* = 5.0 Hz, 1 H), 4.02–4.05 (m, 2 H), 3.14 (dd, *J* = 8.7, 4.6 Hz, 1 H), 2.35 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.1, 149.0, 145.0, 144.1, 142.1, 142.0, 140.0, 139.9, 138.7, 137.4, 130.8, 130.4, 130.0, 129.2, 128.9, 128.8, 128.7, 128.2, 127.8, 127.7, 127.4, 126.2, 125.9, 125.4, 124.8, 100.6, 54.7, 46.5, 45.9, 41.4, 21.5, 21.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{36}NO_4S$: 638.2365; found: 638.2371.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1,3-Diphenyl-3-(4-tolylsulfonamido)allyl]-3-(4-methoxyphenyl)-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4f)**

White crystals; yield: 235 mg (0.36 mmol, 72%); mp 180–181 °C.

IR: 3238, 1746, 1604 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.11 (s, 1 H), 7.63 (d, *J* = 8.8 Hz, 2 H), 7.53–7.54 (m, 2 H), 7.52 (d, *J* = 8.3 Hz, 2 H), 7.22–7.34 (m, 8 H), 7.16 (d, *J* = 6.8 Hz, 2 H), 7.12 (d, *J* = 8.1 Hz, 2 H), 7.10 (d, *J* = 10.2 Hz, 1 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 6.84 (d, *J* = 7.5 Hz, 1 H), 6.07 (d, *J* = 5.0 Hz, 1 H), 6.00 (d, *J* = 10.9 Hz, 1 H), 4.20 (t, *J* = 4.9 Hz, 1 H), 4.00–4.05 (m, 2 H), 3.84 (s, 3 H), 3.12 (dd, *J* = 8.7, 4.7 Hz, 1 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.2, 161.4, 148.9, 145.1, 144.1, 142.1, 142.0, 140.0, 138.7, 137.4, 130.4, 129.1, 128.92, 128.86, 128.79, 128.72, 128.1, 127.8, 127.7, 127.4, 126.9, 126.2, 126.0, 125.9, 124.8, 114.8, 99.5, 55.7, 54.6, 46.6, 45.9, 41.4, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{36}NO_5S$: 654.2314; found: 654.2312.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-3-(4-Bromophenyl)-9-[1,3-diphenyl-3-(4-tolylsulfonamido)allyl]-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4g)**

White crystals; yield: 246 mg (0.35 mmol, 70%); mp 206–208 °C.

IR: 3162, 1735, 1598 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.09 (s, 1 H), 7.65 (d, *J* = 8.6 Hz, 2 H), 7.62 (d, *J* = 8.7 Hz, 2 H), 7.50–7.52 (m, 4 H), 7.23–7.35 (m, 8 H), 7.16 (d, *J* = 6.6 Hz, 2 H), 7.13 (d, *J* = 7.5 Hz, 3 H), 6.86 (d, *J* = 7.4 Hz, 1 H), 6.32 (d, *J* = 4.6 Hz, 1 H), 6.02 (d, *J* = 10.7 Hz, 1 H), 4.23 (t, *J* = 4.7 Hz, 1 H), 4.03–4.06 (m, 2 H), 3.18 (dd, *J* = 8.1, 3.9 Hz, 1 H), 2.25 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 170.8, 148.0, 144.6, 144.1, 142.1, 142.0, 139.9, 138.7, 137.4, 132.8, 132.5, 130.4, 129.2, 128.92, 128.86, 128.7, 128.1, 127.9, 127.7, 127.4, 127.3, 126.3, 126.0, 124.8, 123.4, 102.4, 54.7, 46.4, 45.9, 41.5, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{33}BrNO_4S$:702.1314; found: 702.1309.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1-(4-Methylphenyl)-3-phenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4h)**

White crystals; yield: 229 mg (0.36 mmol, 71%); mp 146–147 °C.

IR: 3347, 3282, 1749, 1598 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.05 (s, 1 H), 7.70 (d, *J* = 7.3 Hz, 2 H), 7.53–7.54 (m, 2 H), 7.52 (d, *J* = 8.1 Hz, 2 H), 7.44 (t, *J* = 7.5 Hz, 2 H), 7.40 (t, *J* = 7.0 Hz, 1 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.31–7.32 (m, 3 H), 7.24 (t, *J* = 7.3 Hz, 1 H), 7.11–7.13 (m, 3 H), 7.09 (d, *J* = 8.5 Hz, 2 H), 7.04 (d, *J* = 7.8 Hz, 2 H), 6.88 (d, *J* = 7.5 Hz, 1 H), 6.22 (d, *J* = 4.9 Hz, 1 H), 5.99 (d, *J* = 11.0 Hz, 1 H), 4.18 (t, *J* = 5.0 Hz, 1 H), 4.05 (dd, *J* = 8.3, 5.1 Hz, 1 H), 3.97 (dd, *J* = 10.5, 5.4 Hz, 1 H), 3.15 (dd, *J* = 8.7, 4.9 Hz, 1 H), 2.33 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.1, 148.9, 144.8, 144.1, 142.1, 140.0, 139.1, 138.6, 137.3, 136.8, 133.6, 130.3, 129.9, 129.8, 129.4, 128.9, 128.8, 128.7, 128.1, 127.8, 127.7, 126.2, 126.1, 125.4, 124.9, 101.7, 54.6, 46.5, 45.4, 41.4, 21.5, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{36}NO_4S$:638.2365; found: 638.2371.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1-(4-Methoxyphenyl)-3-phenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4i)**

White crystals; yield: 235 mg (0.36 mmol, 71%); mp 149–151 °C.

IR: 3281, 1745, 1609 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.05 (s, 1 H), 7.69 (d, *J* = 7.3 Hz, 2 H), 7.54 (d, *J* = 7.1 Hz, 2 H), 7.52 (d, *J* = 8.3 Hz, 2 H), 7.44 (t, *J* = 7.0 Hz, 2 H), 7.41 (t, *J* = 7.0 Hz, 1 H), 7.31–7.35 (m, 4 H), 7.24 (t, *J* = 7.2 Hz, 1 H), 7.13 (d, *J* = 8.1 Hz, 2 H), 7.12 (d, *J* = 8.3 Hz, 1 H), 7.06 (d, *J* = 8.5 Hz, 2 H), 6.89 (d, *J* = 7.4 Hz, 1 H), 6.83 (d, *J* = 8.5 Hz, 2 H), 6.23 (d, *J* = 4.9 Hz, 1 H), 5.98 (d, *J* = 10.8 Hz, 1 H), 4.16 (t, *J* = 4.9 Hz, 1 H), 4.02 (dd, *J* = 8.4, 5.3 Hz, 1 H), 3.96 (dd, *J* = 10.5, 5.6 Hz, 1 H), 3.81 (s, 3 H), 3.16 (dd, *J* = 8.6, 4.7 Hz, 1 H), 2.25 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.1, 159.4, 148.9, 144.8, 144.1, 142.2, 140.0, 138.7, 137.2, 133.9, 133.6, 130.4, 129.9, 129.4, 128.8, 128.78, 128.72, 128.1, 127.9, 127.7, 126.3, 126.2, 125.4, 124.8, 114.5, 101.7, 55.5, 54.7, 46.4, 45.1, 41.4, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{36}NO_5S$: 654.2314; found: 654.2310.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1-(4-Bromophenyl)-3-phenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4j)**

White crystals; yield: 245 mg (0.35 mmol, 70%); mp 164–165 °C.

IR: 3278, 1744, 1598 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.24 (s, 1 H), 7.69 (d, *J* = 7.4 Hz, 2 H), 7.55 (d, *J* = 3.7 Hz, 2 H), 7.50 (d, *J* = 7.9 Hz, 2 H), 7.40–7.45 (m, 5 H), 7.31–7.38 (m, 4 H), 7.24 (t, *J* = 7.5 Hz, 1 H), 7.11–7.14 (m, 5 H), 6.86 (d, *J* = 7.5 Hz, 1 H), 6.22 (d, *J* = 4.7 Hz, 1 H), 5.99 (d, *J* = 10.9 Hz, 1 H), 4.22 (t, *J* = 5.2 Hz, 1 H), 4.05–4.08 (m, 2 H), 3.21 (dd, *J* = 8.2, 4.7 Hz, 1 H), 2.26 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.1, 148.9, 144.9, 144.2, 141.7, 141.6, 139.8, 138.6, 137.9, 133.5, 132.1, 131.0, 130.3, 129.9, 129.4, 129.0, 128.9, 128.7, 128.2, 128.0, 127.7, 126.1, 125.4, 125.2, 124.9, 120.9, 101.6, 54.5, 46.5, 45.3, 41.5, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{33}BrNO_4S$ 702.1314; found: 702.1309.

(3*S,3a*S**,8*R**,8a*S**,*Z*)-8-(Benzoylmethyl)-3-(4-bromophenyl)-2-[phenyl(4-tolylsulfonamido)methylene]-3,3a,8,8a-tetrahydrocyclopenta[*a*]inden-1(2*H*)-one (5j)**

White crystals; yield: 70 mg (0.1 mmol, 19%); mp 125–126 °C.

IR: 3436, 1687, 1650, 1570 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 12.44 (s, 1 H), 8.21 (d, *J* = 7.4 Hz, 2 H), 7.71 (t, *J* = 7.4 Hz, 1 H), 7.63 (t, *J* = 7.7 Hz, 2 H), 7.23–7.25 (m, 3 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 7.14 (t, *J* = 7.4 Hz, 1 H), 7.05 (t, *J* = 7.4 Hz, 1 H), 7.01 (d, *J* = 8.3 Hz, 2 H), 6.97 (t, *J* = 7.7 Hz, 2 H), 6.71–6.74 (m, 3 H), 6.54 (d, *J* = 8.0 Hz, 2 H), 5.72 (d, *J* = 7.8 Hz, 1 H), 4.78 (d, *J* = 9.8 Hz, 1 H), 4.28 (t, *J* = 9.6 Hz, 1 H), 4.05–4.14 (m, 2 H), 3.85 (t, *J* = 9.2 Hz, 1 H), 3.68 (d, *J* = 13.8 Hz, 1 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 210.2, 199.4, 147.0, 145.1, 141.8, 141.2, 138.8, 138.1, 133.6, 133.1, 132.6, 132.1, 130.8, 130.3, 130.26, 130.0, 129.5, 128.9, 128.2, 128.1, 128.0, 127.7, 126.6, 123.7, 120.5, 119.9, 54.6, 49.2, 48.5, 42.1, 39.9, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{33}BrNO_4S$: 702.1314; found: 702.1304.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1-(3-Methoxyphenyl)-3-phenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4k)**

White crystals; yield: 261 mg (0.4 mmol, 79%); mp 191–192 °C.

IR: 3255, 1747, 1606 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.06 (s, 1 H), 7.69 (d, *J* = 7.3 Hz, 2 H), 7.55 (d, *J* = 5.1 Hz, 2 H), 7.50 (d, *J* = 7.8 Hz, 2 H), 7.39–7.45 (m, 3 H), 7.31–7.35 (m, 4 H), 7.25 (t, *J* = 7.2 Hz, 1 H), 7.20 (t, *J* = 7.9 Hz, 1 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 6.95 (d, *J* = 7.2 Hz, 1 H), 6.78–6.82 (m, 2 H), 6.66 (s, 1 H), 6.24 (d, *J* = 4.8 Hz, 1 H), 6.06 (d, *J* = 10.8 Hz, 1 H), 4.23 (t, *J* = 4.8 Hz, 1 H), 3.98–4.02 (m, 2 H), 3.74 (s, 3 H), 3.23 (dd, *J* = 8.5, 4.9 Hz, 1 H), 2.25 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 170.1, 159.6, 148.0, 144.0, 143.2, 142.7, 141.3, 139.0, 137.8, 136.4, 132.7, 129.4, 129.2, 128.9, 128.5, 128.0, 127.8, 127.2, 127.0, 126.8, 125.4, 124.5, 123.9, 120.1, 113.8, 112.1, 100.7, 54.5, 53.7, 45.5, 45.1, 40.5, 20.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{36}NO_5S$: 654.2314; found: 654.2313.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[1-(2-Methoxyphenyl)-3-phenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4l)**
White crystals; yield: 209 mg (0.32 mmol, 63%); mp 204–206 °C.

IR: 3203, 1735, 1600 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 7.97 (s, 1 H), 7.68 (d, *J* = 7.2 Hz, 2 H), 7.54–7.57 (m, 2 H), 7.39–7.45 (m, 5 H), 7.37 (d, *J* = 7.4 Hz, 1 H), 7.30–7.33 (m, 4 H), 7.27 (d, *J* = 7.6 Hz, 1 H), 7.23 (t, *J* = 7.4 Hz, 1 H), 7.12 (t, *J* = 7.2 Hz, 1 H), 7.00–7.05 (m, 4 H), 6.96 (t, *J* = 7.5 Hz, 1 H), 6.20 (d, *J* = 5.0 Hz, 1 H), 6.00 (d, *J* = 10.6 Hz, 1 H), 4.35 (t, *J* = 5.8 Hz, 1 H), 4.19 (dd, *J* = 8.2, 5.1 Hz, 1 H), 4.11 (dd, *J* = 10.4, 6.4 Hz, 1 H), 3.91 (s, 3 H), 2.97 (dd, *J* = 8.4, 5.2 Hz, 1 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 169.8, 156.2, 147.2, 143.7, 142.3, 141.3, 138.9, 137.4, 134.8, 132.1, 129.7, 129.0, 128.6, 128.2, 127.8, 127.7, 127.4, 126.6, 126.5, 126.0, 125.96, 125.5, 124.2, 123.5, 120.0, 110.9, 100.8, 55.3, 51.7, 45.9, 40.0, 39.0, 21.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{36}NO_5S$: 654.2314; found: 654.2327.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[3-(4-Methylphenyl)-1-phenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4m)**
White crystals; yield: 236 mg (0.37 mmol, 74%); mp 168–169 °C.

IR: 3268, 1734, 1600 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.05 (s, 1 H), 7.69 (d, *J* = 8.1 Hz, 2 H), 7.51 (d, *J* = 8.1 Hz, 2 H), 7.38–7.45 (m, 5 H), 7.35 (d, *J* = 7.3 Hz, 1 H), 7.22–7.28 (m, 4 H), 7.15 (d, *J* = 6.8 Hz, 2 H), 7.09–7.13 (m, 5 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 6.23 (d, *J* = 5.0 Hz, 1 H), 5.94 (d, *J* = 10.9 Hz, 1 H), 4.22 (t, *J* = 4.9 Hz, 1 H), 4.05 (dd, *J* = 8.7, 4.8 Hz, 1 H), 4.02 (dd, *J* = 11.1, 5.6 Hz, 1 H), 3.14 (dd, *J* = 8.7, 4.7 Hz, 1 H), 2.24 (s, 3 H), 2.07 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.1, 148.9, 144.9, 144.1, 142.2, 138.7, 137.41, 137.38, 137.1, 133.6, 130.4, 129.9, 129.4, 129.1, 128.9, 128.8, 128.1, 127.8, 127.7, 127.4, 126.2, 125.4, 124.8, 124.7, 101.6, 54.7, 46.6, 45.8, 41.4, 21.5, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{36}NO_4S$: 638.2565; found: 638.2371.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[3-(4-Methoxyphenyl)-1-phenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4n)**
White crystals; yield: 229 mg (0.35 mmol, 70%); mp 176–177 °C.

IR: 3173, 1737, 1605 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.02 (s, 1 H), 7.69 (d, *J* = 7.4 Hz, 2 H), 7.50 (d, *J* = 8.1 Hz, 2 H), 7.38–7.47 (m, 5 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.22–7.29 (m, 4 H), 7.16 (d, *J* = 6.8 Hz, 2 H), 7.11 (d, *J* = 7.9 Hz, 2 H), 7.10 (d, *J* = 7.5 Hz, 1 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 6.83 (d, *J* = 7.7 Hz, 1 H), 6.22 (d, *J* = 4.9 Hz, 1 H), 5.87 (d, *J* = 10.8 Hz, 1 H), 4.22 (t, *J* = 5.0 Hz, 1 H), 4.05 (dd, *J* = 8.4, 5.1 Hz, 1 H), 4.02 (dd, *J* = 10.9, 5.7 Hz, 1 H), 3.82 (s, 3 H), 3.15 (dd, *J* = 8.6, 4.7 Hz, 1 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.1, 160.8, 148.9, 144.9, 144.1, 142.3, 142.0, 138.7, 137.2, 133.6, 132.2, 130.3, 129.9, 129.43, 129.41, 129.1, 128.9, 128.8, 127.8, 127.7, 127.3, 126.2, 125.4, 124.8, 123.7, 114.1, 101.7, 55.6, 54.7, 46.6, 45.8, 41.5, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{41}H_{36}NO_5S$: 654.2314; found: 654.2311.

(4a*S,9*S**,9a*S**,1′*R**,*Z*)-9-[-(4-Bromophenyl)-1-phenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-9,9a-dihydroindeno[2,1-*c*]pyran-1(4a*H*)-one (4o)**
White crystals; yield: 259 mg (0.37 mmol, 74%); mp 183–185 °C.

IR: 3441, 1728, 1633, 1595 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.19 (s, 1 H), 7.69 (d, *J* = 7.2 Hz, 2 H), 7.51 (d, *J* = 9.7 Hz, 2 H), 7.45 (br s, 4 H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.40 (t, *J* = 7.3 Hz, 1 H), 7.34 (d, *J* = 7.4 Hz, 1 H), 7.23–7.27 (m, 4 H), 7.12–7.15 (m, 5 H), 6.86 (d, *J* = 7.6 Hz, 1 H), 6.23 (d, *J* = 5.1 Hz, 1 H), 6.09 (d, *J* = 11.0 Hz, 1 H), 4.20 (t, *J* = 5.2 Hz, 1 H), 4.01–4.04 (m, 2 H), 3.17 (dd, *J* = 8.7, 4.5 Hz, 1 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 171.0, 148.9, 144.8, 144.3, 141.9, 141.8, 139.3, 138.4, 136.3, 133.5, 131.8, 130.5, 130.1, 129.9, 129.4, 129.2, 128.9, 128.86, 127.9, 127.7, 127.5, 126.7, 126.2, 125.4, 124.9, 122.4, 101.6, 54.6, 46.4, 45.9, 41.4, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{33}BrNO_4S$: 702.1314; found: 702.1310.

Methyl (1*S,2*R**,3*S**,1′*R**,*Z*)-1-(Benzoylmethyl)-3-[1,3-diphenyl-3-(4-tolylsulfonamido)allyl]indane-2-carboxylate (14)**
Indeno[2,1-*c*]pyran-1-one **4a** (100 mg, 0.16 mmol) was dissolved in MeOH (5 mL) at r.t. The mixture was heated under reflux for about 30 min until **4a** had been consumed. After removal of the solvent under vacuum, the residue was rapidly purified by column chromatography (silica gel, petroleum ether–EtOAc, 5:1) to give **14** as white crystals; yield: 85 mg (0.13 mmol, 82%); mp 90–91 °C.

IR: 3339, 3271, 1723, 1682 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 7.99 (d, *J* = 7.2 Hz, 2 H), 7.62 (t, *J* = 7.3 Hz, 1 H), 7.54 (d, *J* = 8.5 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 2 H), 7.44–7.48 (m, 4 H), 7.12–7.28 (m, 11 H), 7.09 (d, *J* = 6.9 Hz, 2 H), 7.05 (d, *J* = 7.4 Hz, 1 H), 6.03 (d, *J* = 10.4 Hz, 1 H), 4.01 (dd, *J* = 14.1, 8.4 Hz, 1 H), 3.95 (dd, *J* = 14.4, 7.0 Hz, 1 H), 3.83 (t, *J* = 6.6 Hz, 1 H), 3.35 (d, *J* = 8.4 Hz, 1 H), 3.34 (d, *J* = 5.7 Hz, 1 H), 3.29 (s, 3 H), 3.23 (dd, *J* = 8.2, 4.8 Hz, 1 H), 2.31 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 198.8, 174.8, 145.9, 144.1, 144.0, 143.8, 142.4, 140.0, 139.1, 138.2, 136.4, 133.7, 130.4, 129.4, 129.3, 129.1, 128.71, 128.68, 128.13, 128.05, 128.0, 127.7, 127.5, 127.3, 126.1, 124.4, 54.1, 51.8, 51.6, 47.1, 42.0, 41.2, 21.5.

HRMS: *m*/*z* [M + Na]$^+$ calcd for $C_{41}H_{37}NO_5SNa$: 678.2285; found: 678.2271.

(1*S,2*R**,3*S**,1′*S**)-1-(Benzoylmethyl)-3-(2-benzoyl-1-phenylethyl)indane-2-carboxylic Acid (15)**
At r.t., 30% aq NaOH soln (80 mg, 0.6 mmol) was added dropwise to a solution of **4a** (186 mg, 0.3 mmol) in THF (10 mL). The mixture was stirred at r.t. for about 1 h until **4a** had been consumed. The mixture was neutralized with sat. aq NH_4Cl to pH ~ 6–7 and it was then stirred for further 5–6 h at r.t. The mixture was extracted with CH_2Cl_2 (15 × 3 mL), and the combined extracts were dried (anhyd $MgSO_4$) and concentrated under vacuum. The residue was purified by column chromatography (silica gel, PE–EtOH–EtOAc, 40:2:1) to give **15** as white crystals; yield: 117 mg (0.24 mmol, 80%); mp 179–180 °C.

IR: 3438, 1698, 1686, 1679 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.7 Hz, 4 H), 7.45 (d, *J* = 7.3 Hz, 1 H), 7.42 (d, *J* = 7.3 Hz, 1 H), 7.34 (t, *J* = 8.1 Hz, 2 H),

7.29 (t, *J* = 7.6 Hz, 2 H), 7.11–7.18 (m, 4 H), 7.05–7.09 (m, 4 H), 6.95 (d, *J* = 7.4 Hz, 1 H), 3.76–3.82 (m, 2 H), 3.72 (dd, *J* = 14.6, 7.7 Hz, 1 H), 3.46 (d, *J* = 6.0 Hz, 2 H), 3.28 (d, *J* = 8.1 Hz, 1 H), 3.26 (dd, *J* = 15.5, 8.2 Hz, 1 H), 3.17 (dd, *J* = 18.0, 6.1 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 198.5, 179.0, 144.3, 143.4, 141.2, 137.2, 136.9, 133.1, 133.0, 128.5, 128.33, 128.3, 128.0, 127.5, 127.1, 126.8, 125.1, 123.4, 52.7, 50.4, 43.6, 41.9, 40.7, 39.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{33}H_{28}O_4Na$: 511.1880; found: 511.1867.

(4a*R,9*S**,9a*S**,1′*R**,*Z*)-9-[1,3-Diphenyl-3-(4-tolylsulfonamido)allyl]-3-phenyl-1,4a,9,9a-tetrahydroindeno[2,1-*c*]pyran (16)**

Under N_2 atmosphere and at r.t., $LiAlH_4$ (55 mg, 1.44 mmol) was added to a solution of **4a** (300 mg, 0.48 mmol) in anhyd THF (10 mL). The mixture was stirred at r.t. for ca. 1 h until **4a** had been consumed. The reaction was quenched by the addition of 2 M aq HCl (5 mL) under 0 °C. After extraction with CH_2Cl_2 (10 × 3 mL), the product **16** was isolated by rapid column chromatography (silica gel, PE–EtOAc, 5:1).

White crystals; yield: 207 mg (0.34 mmol, 70%); mp 108–110 °C.

IR: 3341, 3276, 1647, 1598 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 7.47 (d, *J* = 7.9 Hz, 2 H), 7.46 (s, 1 H), 7.39 (d, *J* = 8.2 Hz, 2 H), 7.34 (dd, *J* = 7.4, 3.6 Hz, 1 H), 7.15–7.23 (m, 7 H), 7.09–7.13 (m, 6 H), 7.00 (t, *J* = 7.4 Hz, 1 H), 6.95 (dd, *J* = 7.8, 1.9 Hz, 2 H), 6.79 (d, *J* = 7.5 Hz, 1 H), 5.92 (d, *J* = 10.5 Hz, 1 H), 5.82 (d, *J* = 4.9 Hz, 1 H), 3.97 (dd, *J* = 10.6, 5.0 Hz, 1 H), 3.85 (dd, *J* = 10.5, 6.7 Hz, 1 H), 3.39 (t, *J* = 5.9 Hz, 1 H), 3.15 (t, *J* = 11.0 Hz, 1 H), 3.02 (d, *J* = 6.6 Hz, 1 H), 2.32–2.40 (m, 1 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 153.0, 147.9, 144.1, 143.0, 142.5, 140.0, 139.0, 136.6, 136.2, 130.4, 129.1, 128.9, 128.8, 128.72, 128.67, 128.4, 128.0, 127.9, 127.7, 127.2, 127.1, 125.32, 125.27, 99.7, 68.1, 53.7, 47.9, 40.84, 40.8, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{40}H_{36}NO_3S$: 610.2410; found: 610.2394.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis. Included are copies of ^{1}H NMR and ^{13}C NMR spectra of products **4**, **5j**, **14**, **15**, **16**, and the HPLC spectra of **4a**.

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