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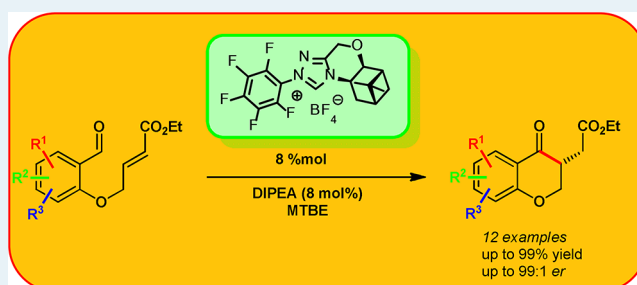
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Supporting Information

ABSTRACT: Novel chiral N-heterocyclic carbenes derived from (–)- β -pinene have been synthesized and used as efficient catalysts for the intramolecular Stetter reaction. Mono-, di-, and trisubstituted 4-chromanone derivatives have been obtained almost quantitatively and with high enantioselectivity up to 99:1 er.

KEYWORDS: Stetter reaction, N-heterocyclic carbenes, organocatalysis, terpenoids, chromanones



The enormous potential of N-heterocyclic carbenes (NHCs) as organocatalysts has become evident in recent years and plays an important role in the growing area of asymmetric organocatalysis. The phenomenal success of NHCs can be attributed primarily to their ability to invert the typical electrophilic nature of aldehydes (“umpolung”).¹ In this context, the Stetter reaction is undoubtedly one of the most important umpolung processes that allows formation of unique 1,4-dicarbonyl compounds and related derivatives, such as ketophosphonates, nitroketones, or ketonitriles.² Various chiral NHCs have been developed, and the triazolium salts 1–3 have proved to be the most efficient precatalysts in numerous asymmetric applications (Figure 1).³

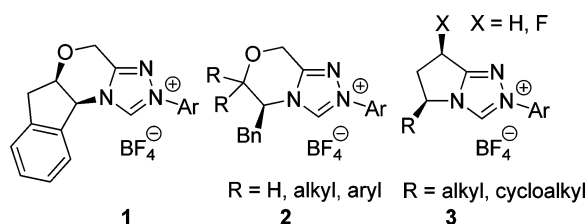


Figure 1. Chiral bi- and tetracyclic triazolium salts.

Deprotonation of the salts generates free carbenes, which react in situ with aldehydes by nucleophilic attack.

In 2008, (1R)-camphor-derived triazolium salts 4 (Figure 2) were applied as efficient catalysts for the intramolecular crossed benzoin condensations and the Michael and Stetter reactions.⁴

To date, these are the only terpenyl triazolium salts combining the reactivity of the NHCs with the selectivity effect of the terpene moiety. Despite the significant progress, only a limited number of reported NHCs backbone scaffolds

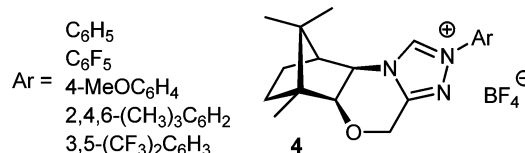


Figure 2. Chiral triazolium salts derived from (1R)-camphor.

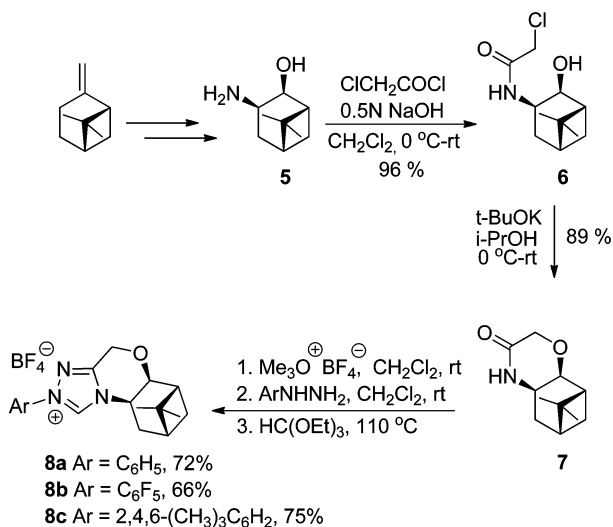
have been effective in highly enantioselective reactions. Many catalysts suffer from a relatively high cost of enantiopure starting materials. Consequently, the design of new NHC catalysts of improved reactivity profiles derived from a readily available chiral precursor is a great challenge.

Except for camphor, no other monoterpenes were used for the synthesis of triazolium carbene catalysts. Therefore, we decided to undertake the synthesis of new terpenyl NHCs. β -Pinene was chosen as a low-priced and readily available chiral precursor, commercially available in both enantiomeric forms.⁵ Chiral auxiliaries and ligands with the pinane backbone are widely used in asymmetric synthesis.⁶ In this communication, we report our preliminary results on the synthesis of novel triazolium salts 8a–c from (–)- β -pinene and their application to the enantioselective intramolecular Stetter reaction, providing chromanone products in almost quantitative yields and excellent enantioselectivity.

We started our investigation by synthesis of triazolium salts from (–)- β -pinene, as outlined in Scheme 1. (–)- β -Pinene was transformed into *cis*-amino alcohol 5 according to the reported method.⁷ Annulation to the lactam 7 proceeded in an overall

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Scheme 1. Synthesis of Triazolium Salts from (–)- β -Pinene

two-step process, using our own procedure based on the reaction of **5** with chloroacetyl chloride, followed by cyclization in the presence of potassium *tert*-butoxide. In the initial attempts, using the literature procedure, the yield of annulation did not exceed 20%.^{4a} With the lactam **7** in hand, the procedure developed by Rovis⁸ was used for its conversion into triazolium salts **8a–c** (Scheme 1). Their preparation does not require chromatographic purification. Evaporation of the solvent followed by washing with diethyl ether or toluene provides pure products that are air- and water-stable solids. The structure of **8a** was established by X-ray crystallographic analysis, as shown in Figure 3.⁹

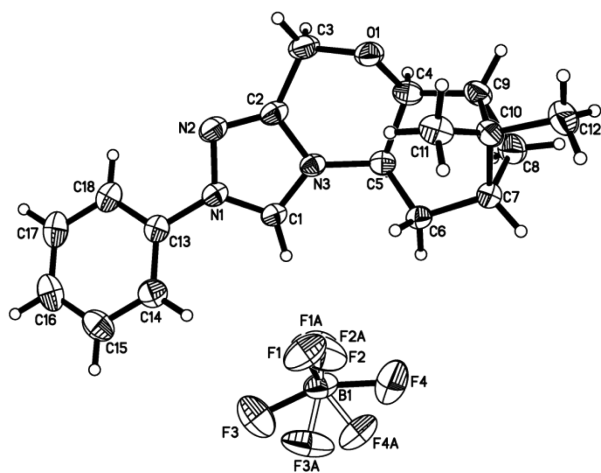


Figure 3. ORTEP drawing of molecular structure of **8a**. Thermal ellipsoids are set at the 30% probability level.

The intramolecular Stetter reaction was chosen as the model reaction to test the catalytic activity of the new triazolium salts. The reaction is highly interesting because it provides an access to 4-chromanone derivatives, widely occurring in many bioactive natural products and used as versatile synthons in organic synthesis.¹⁰

Our initial exploration focused on the examination of triazolium salts **8a–e** in the Stetter cyclization of **9a**. As shown in Table 1, the carbene generated from triazolium salt **8a** proved to be inactive. Using diisopropylethylamine (8 mol %)

Table 1. Screening of the Triazolylidene Catalysts Derived from (–)- β -Pinene and *cis*-1-Amino-2-indanol^a

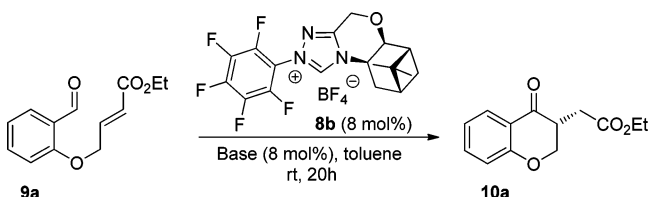
entry	catalyst	yield (%) ^d	er ^e
1	8a	NR	
2	8b	99	97:3
3	8c	31	99:1
4	8d	10	95:5
5	8e	74	96:4
6 ^b	8b	92	96:4
7 ^c	8b	95	95:5

^aReactions were performed in the presence of **8a–e** (8 mol %), DIPEA (8 mol %) in 0.1 M in toluene, and at rt. ^b**8b** (5 mol %) and DIPEA (5 mol %) were used. ^cThe reaction was performed at 0 °C. ^dIsolated yields. ^eDetermined by HPLC using a chiral column (Chiralcel Daicel OD-H).

and triazolylidenes derived from **8b–e**, high selectivity was observed with a catalyst loading of 8 mol %; however, in the case of **8c**, the Stetter product was obtained in low yield. It is worth noting that the reaction catalyzed by amino indanol derived triazolium salts **8d,e** and DIPEA gave the desired product **10a** with excellent enantioselectivity, albeit in low yields (entries 4–5, Table 1). Gratifyingly, the new NHC catalyst generated from **8b** allowed a complete conversion to the desired product with excellent enantioselection of 97:3 er. Lowering the amount of **8b** from 8 to 5 mol % and the reaction temperature to 0 °C also gave excellent yields of the desired cyclization products but with a small erosion of the er value.

The reaction parameters were further examined in the presence of 8 mol % of triazolium salt **8b**. As shown in Table 2, several conventional organic and inorganic bases, such as dicyclohexylethylamine (DCyEA), DBU, Et₃N, KHMDS, DMAP, *tert*-BuOK, and also the commercially available phosphazene bases P₂-Et and P₂-*tert*-Bu, were tested and gave the reaction product in excellent yield and high enantiomeric ratio. Cesium carbonate led to a racemic mixture. A possible explanation of the slight difference in selectivity can be competitive epimerization under the reaction conditions. We also surmise that in the case of cesium carbonate, there is incomplete conversion of triazolium salt to carbene so that the free base might racemize the product. To confirm this, the catalytic process outlined in Table 2, entry 6 was repeated with enantioenriched (*R*)-chromanone **10a** (96% ee) replacing **9a** as the starting material. After stirring for 16 h, the chromanone **10a** was recovered in greatly reduced enantiomeric excess (4% ee) (Scheme 2).

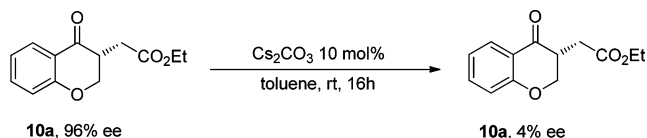
Screening of the various solvents, such as *o*-xylene, CH₂Cl₂, DMF, THF, dimethoxyethane (DME), cyclopentyl methyl ether (CPME), *tert*-amyl methyl ether (TAME), and *tert*-butyl methyl ether (MTBE) showed that they are well tolerated in

Table 2. Screening of Different Bases^a

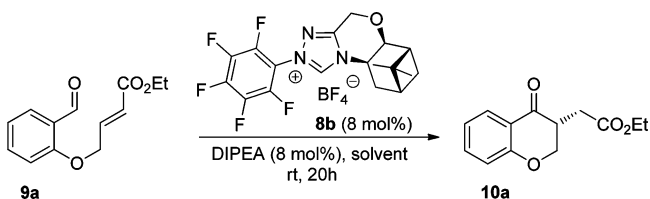
entry	base	yield (%) ^b	er ^c
1	DIPEA	99	97:3
2	DCyEA	99	96:4
3	DBU	99	91:9
4	Et ₃ N	99	92:8
5	KHMDS	97	88:12
6	Cs ₂ CO ₃	91	50:50
7	^t BuOK	97	92:8
8	DMAP	99	91:9
9	P ₂ -Et	97	95:5
10	P ₂ - ^t Bu	98	95:5

^aReactions were performed in the presence of **8b** (8 mol %), base (8 mol %) in 0.1 M in toluene, and at rt. ^bIsolated yields. ^cDetermined by HPLC using chiral column (Chiracel Daicel OD-H).

Scheme 2. Racemization of 10a under the Reaction Condition



this reaction (Table 3); however, the reactions in DMF and DME were not so efficient as in other solvents and provided the product in only 52% and 36% yield, respectively (Table 3, entry 4 and 7). Finally, both the reaction in *tert*-butyl methyl ether and cyclopentyl methyl ether led to the optimal combination of 99% yield and 98:2 er. Taking into account

Table 3. Screening of Different Solvents^a

entry	solvent	yield (%) ^b	er ^c
1	toluene	99	97:3
2	<i>o</i> -xylene	99	96:4
3	THF	98	96.5:3.5
4	DMF	99	88.5:11.5
5	CH ₂ Cl ₂	97	90:10
6	DME	91	93:7
7	MTBE	97	98:2
8	CPME	99	98:2
9	TAME	97	97:3

^aReactions were performed in the presence of **8b** (8 mol %), DIPEA (8 mol %) in 0.1 M in solvent, and at rt. ^bIsolated yields. ^cDetermined by HPLC, using chiral column (Chiracel Daicel OD-H). MTBE = methyl *tert*-butyl ether, CPME = cyclopentyl methyl ether, TAME = *tert*-amyl methyl ether.

the economical aspect, further study was carried out with *tert*-butyl methyl ether.

After identifying both the optimal triazolium catalyst and conditions, the reaction scope was examined using a wide range of substrates with different substitution patterns of the aromatic ring. Various O-tethered mono-, di-, and trisubstituted salicylaldehyde-derived substrates bearing either electron-donating or electron-withdrawing groups were tested (Table 4). For substrates **9b–d**, bearing the electron-donating groups on the salicylaldehyde-structure (5-OMe, 4-OMe, 5-Me, entries 2–4), the products were obtained in excellent yields and with remarkably high enantioselection. Surprisingly, 5-fluoro, and 3-iodo derivatives **9f** and **9g**, were also suitable reaction partners, and the resulting O-tethered chromanones **10f–g** were obtained in a highly selective fashion, albeit for the 3-fluoro **9e** derivative slight erosion of the er value without affecting the reactivity was observed. The enantioselectivity remains at the same level when the substituent on the aryl moiety is either an electron-rich or electron-deficient group (entries 1–4, 6, and 7, Table 4). Di- or trisubstituted substrates led to the formation of di- or trialkylated or dihalogenated chromanones. Cyclization of 4,6-dichloro **9k** also occurred efficiently to give **10k** in a nearly quantitative yield with 98:2 er. Unfortunately, the di-*tert*-butyl-substituted **9h** gave the cyclization product with only 62:38 er, although the yield remained excellent. Selectivity was also affected, when the 5-*tert*-butyl group of **9i** was replaced by the methyl group (entry 9, Table 4). Replacement of the spatially large *tert*-butyl substituents in **9h** by the methyl groups in **9j** significantly enhanced the enantioselectivity. Comparing chromanones **10h–10j** shows that bulky substituents in the 3 and 5 positions decreased the selectivity of the reaction.

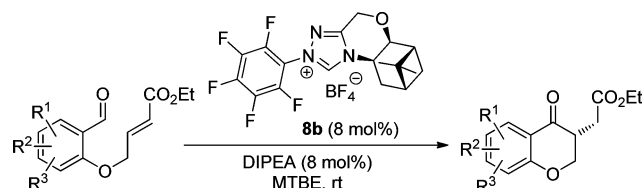
Moreover, trimethyl-substituted O-tethered substrate **9l** was also synthesized and tested in the intramolecular Stetter reaction. The desired product **10l** was obtained in high yield and enantioselectivity, 94:6 er. It is worth noting that 4-chromanone derivatives **10e–10l** are unknown in the literature.

After successfully performing a highly enantioselective intramolecular Stetter reaction on a broad range of aromatic aldehydes, we turn our attention to the potentially more difficult aliphatic aldehyde bearing acidic hydrogens α to the aldehyde. Under the conditions used for the previous aromatic aldehydes **9a–l**, **11** failed to give the reproducible results, and the desired pyrolidinone **12** was obtained in an excellent yield of 98% with a moderate enantioselectivity of 35% ee (Scheme 3).

Furthermore, we also investigated the utility of triazolium salts **8b,c** in the construction of all-carbon quaternary stereogenic centers^{2b,11} (which poses a great challenge)¹² and cyclopentene-forming annulation reaction, respectively.

Cyclization of salicylaldehyde-derived substrate **13** bearing β,β -disubstituted Micheal acceptor occurred very efficiently to give the coumaranone **14** in an excellent yield with 95% ee. Unfortunately, application of triazolium salt **8c** in hydroacylation of an unactivated double bond of **15** failed to catalyze the reaction. To our great delight, with 10 mol % β -pinene-derived triazolium salt **8c** bearing a mesityl group, an enantioselective benzoin-oxy-Cope reaction proceed smoothly, affording the cyclopentene product **16** in 71% yield with 96% ee and 8:2 dr (Scheme 4).

In conclusion, a series of novel tetracyclic triazolium salts was prepared from the readily available (–)- β -pinene. They were used to generate NHC catalysts for the enantioselective synthesis of mono-, di-, and trisubstituted 4-chromanones.

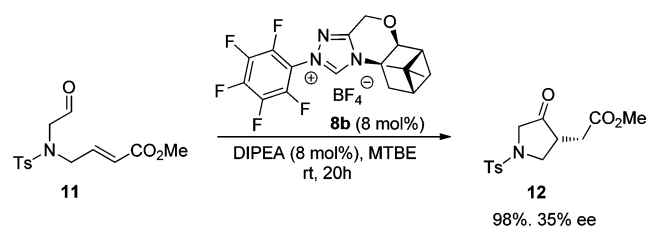
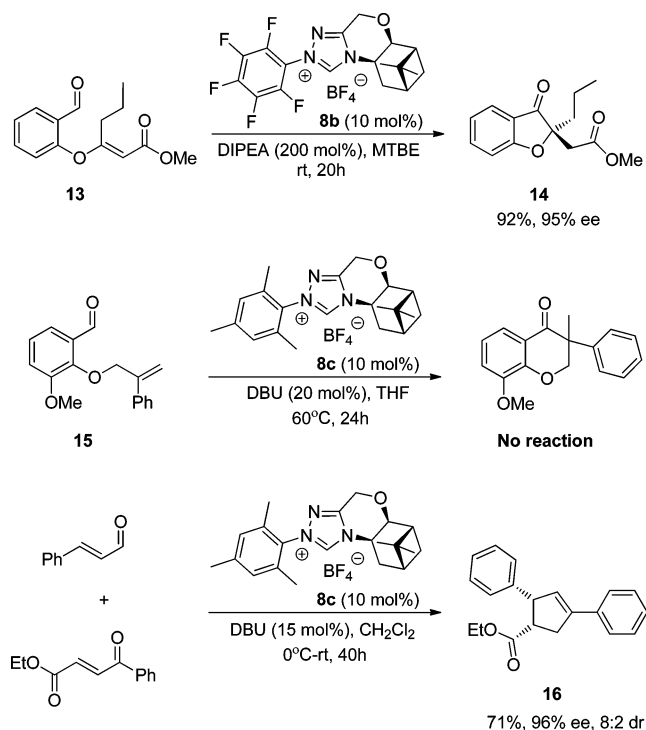
Table 4. Enantioselective Intramolecular Stetter Reaction^a


entry	aldehyde	product	yield (%) ^c	er ^d
1			99	98:2
2			98	96.5:3.5
3			99	99:1
4			98	94:6
5			99	91:9
6			98	94:6
7			99	97:3
8 ^b			94	62:38
9 ^b			97	78.5:21.5
10			98	87:13
11			96	98:2
12			98	94:6

^aReaction conditions: **8b** (8 mol %) and DIPEA (8 mol %) in 0.1 M in MTBE (0.1M) for 20 h, rt. ^bThe reaction was conducted for 48 h. ^cIsolated yields. ^dDetermined by HPLC, using chiral columns (Chiralcel Daicel OD-H, OJ, Lux Cellulose-1).

The chiral triazolium salt **8b** and DIPEA generates a highly efficient and selective carbene catalyst for the intramolecular Stetter reaction, affording the 4-chromanones in excellent yields with up to 99:1 enantiomeric ratio utilizing relatively low catalyst loadings (8 mol %).

Structural diversity of enantiomerically pure monoterpenes, an access to both enantiomeric forms, commercial availability, and a relatively low cost of chiral precursor offers great

Scheme 3. Enantioselective Intramolecular Stetter Reaction of **11**Scheme 4. Application of Triazolium Salts **8b,c** in Other Reactions

opportunities in terms of structural selection and modification of future catalysts. Further applications of these (–)-β-pinene-derived triazolium salts in other asymmetric reactions are currently under way.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization, and crystallographic data for the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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