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NHC catalysis

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Enantioselective N-heterocyclic carbene (NHC) catalysis via the dienyl acyl azolium**

*Rachel M. Gillard, Jared E. M. Fernando and David W. Lupton**

Abstract: *Herein we report the enantioselective N-heterocyclic carbene catalyzed (4 + 2) annulation of the dienyl acyl azolium with enolates. The reaction exploits readily accessible acyl fluorides and TMS enol ethers to give a range of highly enantio- and diastereo-enriched cyclohexenes (most > 97:3 er and >20:1 dr). The reaction was found to require high nucleophilicity NHC catalysts with mechanistic studies supporting a stepwise 1,6-addition/β–lactonization.*

N-Heterocyclic carbenes (NHC) enable diverse transformations via normal and reverse polarity intermediates.[1] In 2006, formation and esterification of the α,β–unsaturated acyl azolium (**1**) was discovered.[2] Subsequent studies demonstrating its use in a broad range of transformations[11,2-5] generally involving (3 + n)[3] or (2 + n)[4] annulations to provide sp^3-rich materials in excellent yield and with high enantiopurity.

While acyl azolium **1** has received significant attention, very little has been directed to the chemistry of higher unsaturated homologs,[6a,b] such as the dienyl acyl azolium (i.e. **2**). The paucity of chemistry involving dienyl acyl azolium **2** is striking and contrasts, for example, iminium organocatalysis which exploits both the α,β–unsaturated iminium and the dienyl iminium (**3**) in many enantioselective tranformations.[6c-g] To the best of our knowledge, the dienyl acyl azolium has only been successfully exploited once, in Chi's synthesis of substituted benzene derivatives **4** (eq. 1).[7] In addition we attempted to access the dienyl acyl azolium from ester **5**, however we found fragmentation was not possible and an olefin isomerization Diels/Alder reaction gave [2.2.2]-bicyclic compounds such as **6** (eq. 2).[8] Herein, we report a new strategy for dienyl acyl azolium formation that has enabled the discovery of an enantioselective (4 + 2) annulation (eq. 3). The reaction allows the highly diastereo- and enantioselective (most >97:3 er and >20:1 dr) synthesis of polycyclic β–lactones (i.e. **7**). In addition to providing a novel approach to β–lactones[9] this is the first example of enantioselective catalysis via the dienyl acyl azolium.

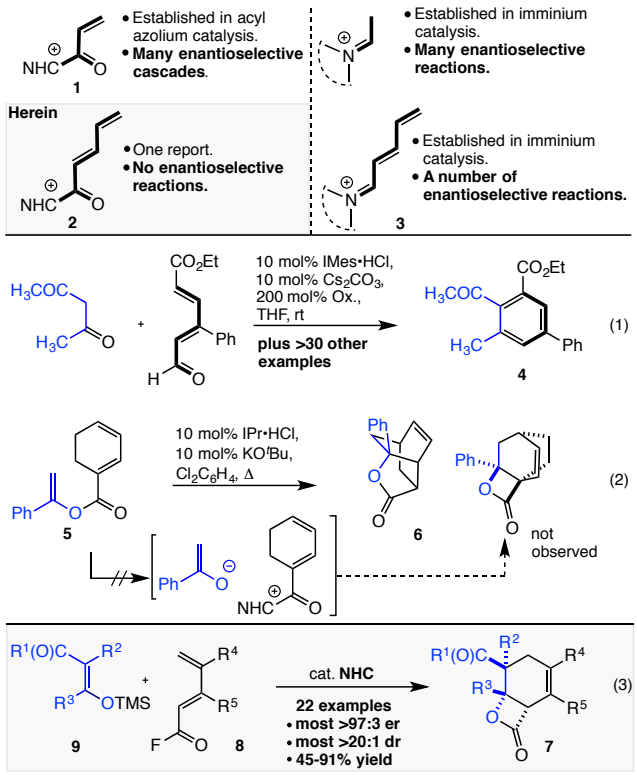

Figure 1.

To avoid the olefin isomerization observed with ester **5** we envisioned using acyl fluorides (i.e. **8**), substrates suited to the generation of unsaturated Lewis base adducts.[10] In addition, deletion of the δ–substituent to favor 1,6-addition, and eliminate olefin isomerization, was deemed desirable. Thus, reaction discovery commenced with dienyl acyl fluoride **8a**, prepared from cyclohexanone in four-steps,[11] and TMS enol ether **9a**, prepared from benzyl acetoacetate in one. Their coupling was expected to provide products bearing three contiguous stereocentres including a quaternary carbon thereby reducing the likelihood of aromatization. When attempted with triazolylidene **A** in THF, β–lactone **7a** formed with modest yield, while the more nucleophilic IMes NHC **B1** gave the same product as a single diasteroisomer (>20:1 dr) and in 74% yield (Table 1, entries 1 and 2). Using IPr (**B2**) a 15% yield of lactone **7a** with little diastereoselectivity was observed (Table 1, entry 3). The outcome with IMes **B1** was not improved using alternate solvents (Table 1, entries 4-6). Development of the enantioselective variant commenced by examining the impact of the N-substituent on reaction outcome (Table 1, entries 7-9). These studies demonstrated that more nucleophilic NHCs, which

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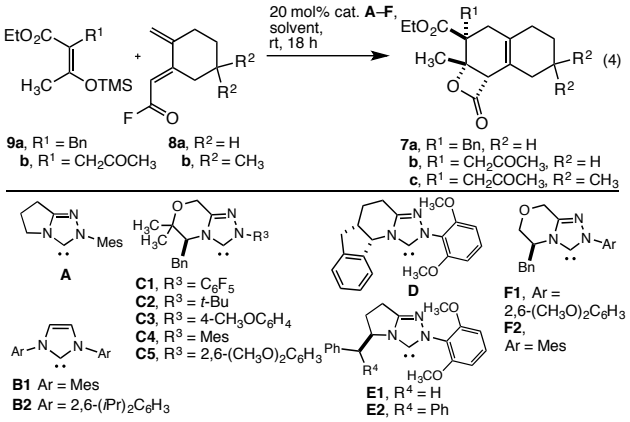
additionally bear *ortho*-disubstitution, were necessary (i.e. **C4** and **5**).[12,13] Of these catalyst **C5**[14] was preferred giving β–lactone **7c** in a >99:1 enantiomeric ratio, albeit with poor diastereoselectivity and yield (Table 1, entry 9). Examining the 2,6-$(CH_3O)_2C_6H_3$ substituent on indanol (**D**) and pyrrolidine scaffolds (**E1** and **2**) failed to improve the outcome, while desmethyl morpholinone catalysts bearing either a 2,6-$(CH_3O)_2C_6H_3$ (**F1**) or Mes (**F2**) N-substituent gave similar outcomes (Table 1, entries 10-14). Although the optimal conditions (Table 1, entries 9 and 14) retain limitations in preparing **7c** this proved to be an outlier with all other β–lactones formed in this study isolated in good yield with excellent enantio-, and diasteropurity (*vide infra*).

Table 1. Selected Optimizations

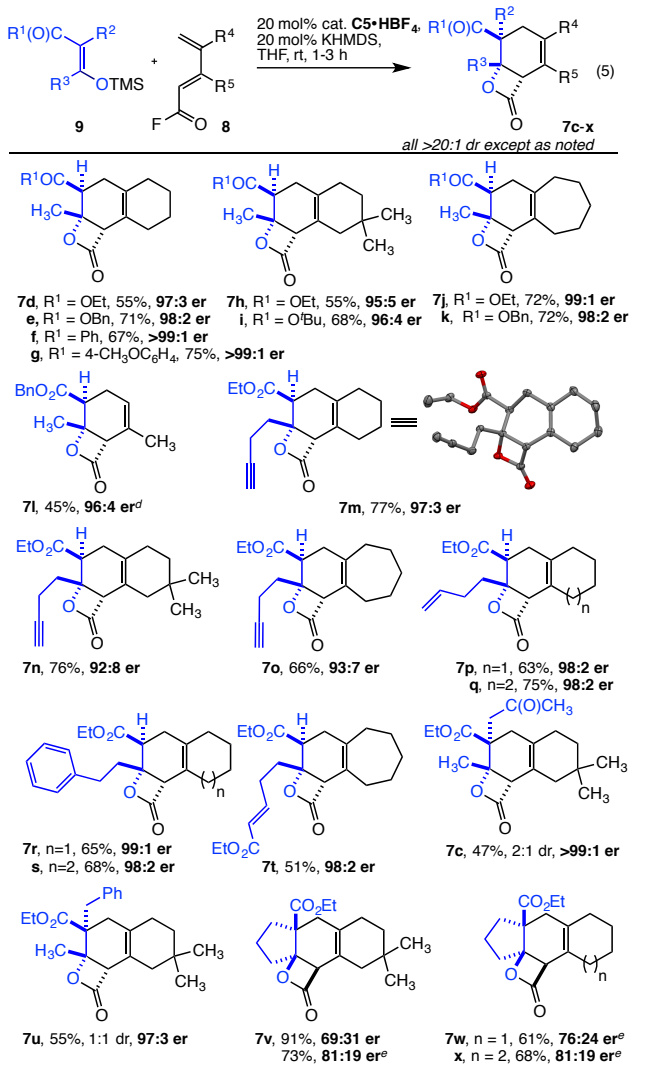


entry	cat[a]	9/8	solvent	yield[b]	dr[c]	er[d]
1[c]	**A**	**a/a**	THF	48	3:1	-
2	**B1**	"	THF	74	>20:1	-
3	**B2**	"	THF	15	2:1	-
4	**B1**	"	DMF	11	2:1	-
5	"	"	$C_6H_5CH_3$	60	19:1	-
6	"	"	dioxane	54	19:1	-
7	**C1-3**	**b/a**	THF	-	-	-
8	**C4**	"	THF	32	3:1	88:12
9	**C5**	**b/b**	**THF**	**47**	**2:1**	**>99:1**
10	**D**	"	THF	20	97:3	98:2
11	**E1**	"	THF	32	7:3	81:19
12	**E2**	"	THF	35	6:1	63:37
13	**F1**	"	THF	35	3:1	91:9
14	**F2**	**"**	**THF**	**30**	**6:1**	**96:4**

[a] NHCs generated with KHMDS [b] Isolated yield of **7** [c] Diastereomeric ratio by ^{1}H-NMR analysis [d] er determined by HPLC over chiral stationary phases.

Reaction generality was examined with fourteen TMS enol ethers of 1,3-diketones or β–ketoesters **9** and four dienyl acyl fluorides **8** (Table 2). TMS enol ethers of ethyl, benzyl and *t*-butyl β–ketoesters when R^2 = H produced six cyclohexyl, dimethylcyclohexyl and cycloheptyl fused β–lactones (**7d, e** and **h–k**) in good yields. TMS enol ethers of 1,3-diketones were also viable giving ketone containing β–lactones **7f** and **g** both in >99:1 er and good yield. In all eight examples high enantiopurity (≥95:5 enantiomeric ratio) with complete diastereoselectivity was observed (>20:1 dr). Indeed, whilst studying generality 20 of the 22 examples formed as single diastereoisomers. The s-cis enforcing annulation (i.e. annulation across R^4 and R^5) has been essential in related NHC catalysed annulations.[4a] Pleasingly in this study acylic dienyl acyl fluoride **8d** (R^4 = H; R^5 = CH_3) could be employed to give cyclohexene **7l** in 96:4 er and with acceptable yield. Next, changes to the R^3-group were examined to produce tricyclic β–lactones bearing alkyne (**7m–o**), alkene (**7p** and **q**), aromatic (**7r** and **s**), and α,β–unsaturated ester (**7t**) functionality. In all cases the enantioselectivity remained high with most products obtained in ≥98:2 enantiomeric ratio. In the case of alkyne **7m** X-ray crystalographic analysis was performed to determine absolute stereochemistry.[15a] As highlighted in the optimization, substrates in which $R^2 \neq$ H allow construction of a challenging quaternary carbon with high enantioselectivity (>99:1 er), although poor diastereoselectivity and yield (Table 1, entry 9). This was further demonstrated with benzyl β–lactone **7u** prepared in 97:3 er, but as a 1:1 mixture of diastereoisomers. In contrast, cyclic TMS enol ethers gave quaternary carbon containing compounds, i.e. tetracycle **7v**, with excellent yield (91%) and diastereoselectivity (>20:1), although modest enantioselectivity (69:31 er). This could be improved using catalyst **F2** at 0 °C, with β–lactone **7v** formed in 81:19 er. These conditions were suitable for the synthesis of **7w** and **x** which formed with similar enantioselectivity and yield. The later

Table 2. Scope of the (4 + 2) annulation[a-c]



[a] Isolated yield [b] Diastereomeric ratio by ^{1}H-NMR analysis [c] er determined by HPLC over chiral stationary phases [d] reaction heated to reflux [e] 20 mol% **F2** at 0 °C.

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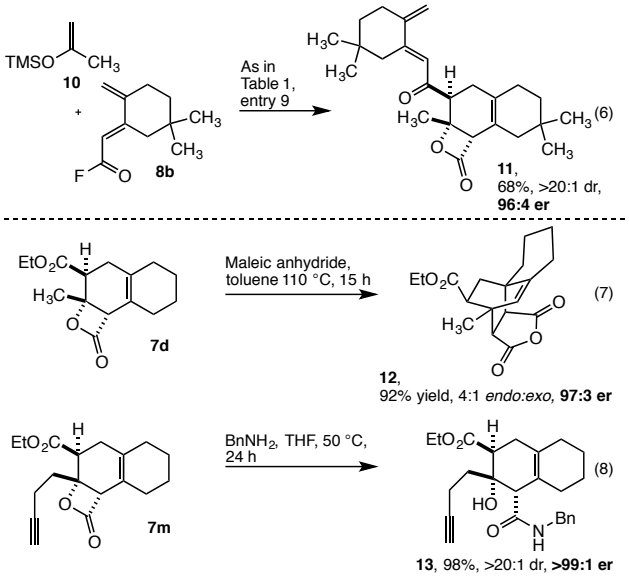
product contains a tetracyclic ring system reminiscent of the yonarolide and scabrolide natural products[16] and is assembled in a concise 4-step sequence from commercial materials.

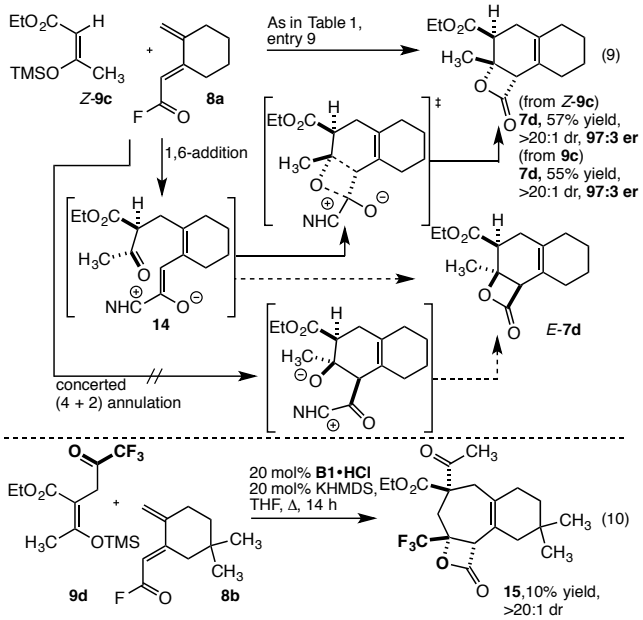
Simple enolates have been sparingly exploited in NHC catalysed reactions of acyl azolium.[3a] When the (4 + 2) annulation was examined with the TMS enol ether of acetone (i.e. **10**) and dienyl acyl fluoride **8b** a Claisen-condensation/(4 + 2) annulation provided **11** in 96:4 er (Scheme 1, eq. 6). This result suggests that the δ–position of the dienyl acyl azolium is less electrophilic than the β–position of the related α,β–unsaturated acyl azolium, thus Claisen condensation is kinetically more favourable than 1,6-addition.

The β–lactone products in this study were expected to have moderate stability due to the presence of unsaturated functionality likely to stabilise the biradicaloid transition state of decarboxylation.[17] Consistent with this prediction, it was found that decarboxylation occurred when the β–lactones were heated at reflux in dimethylformamide. While quaternary carbon containing compounds (i.e. **7a**) gave the expected diene (see SI) substrates lacking this functionality (i.e. **7d**) gave mixtures of olefin containing products. However, when the decarboxylation was performed in the presence of maleic anhydride a 92% yield of [2.2.2]-bicycle **12**[15b] was obtained, as a 4:1 mixture of the separable *endo* and *exo* isomers, indicating that the Diels-Alder reaction is more facile than olefin isomerization. As a consequence of the relatively high stability of the β–lactone β–hydroxy amide **13** could be prepared in 98% yield and >99:1 enantiomeric ratio by simple ring-opening with benzylamine.



Scheme 1. Reaction of TMS enol ether of acetone (**10**) and β–lactone stability.

Mechanistically a stepwise or concerted annulation is potentially viable. To probe these scenarios *Z*-**9c** was prepared and reacted with acyl fluoride **8a** under the standard conditions (Scheme 2, eq. 9). In a concerted reaction *Z*-**9c** should give *E*-**7d**. In the event the product of this reaction was **7d**, with similar yield, and identical stereoselectivity to its formation from **9c**. Thus, the reaction likely proceeds via 1,6-addition to give acyl azolium enolate **14** which undergoes rotation prior to a pseudo-concerted aldol β–lactonization.[17] The likelihood of a stepwise mechanism introduces the possibility for alternate (4 + n) reactions. For example β–lactone **7c** contains a pendant methyl ketone, that could have delivered a (4 + 3) adduct. Failure to observed this product is likely due to a more rapid 6-*exo*-trig cyclization (cf. 7-*exo*-trig) of the acyl azolium enolate intermediate analogous to **14**. To overcome this kinetic bias, and expand the scope of chemistry accessible via dienyl acyl azolium **2**, trifluoro methyl ketone **9d** was prepared. Pleasingly this produced cycloheptane **15** however, despite significant optimization, the yield remained poor (eq. 10).



Scheme 2. Mechanistic studies and (4 + 3) annulation.

Studies reported herein exploit the dienyl acyl azolium in an enantioselective (4 + 2) annulations with enolates. As with the lower homolog (the α,β–unsaturated acyl azolium) good outcomes can be achieved with enolates of β–ketoesters and 1,3-diketones.[3] Pleasingly these are highly abundant materials. The transformation gives rise to a diverse range of bi-, tri-, and tetracyclic β–lactones with high stereochemical purity and yield. In addition to the significant potential of this reaction to deliver enantioenriched building blocks for synthesis these studies demonstrate the first enantioselective reaction of the dienyl acyl azolium. Preliminary studies have demonstrated the viability of a (4 + 3) annulation, however the dienyl acyl azolium could be exploited in a host of alternate reactions by appropriate selection of the coupling partner.

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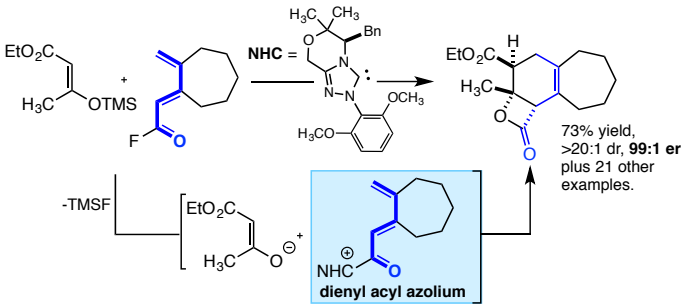
Enantioselective *N*-heterocyclic carbene (NHC) catalysis via the dienyl acyl azoliums.



1,6-Addition of enolates into the dienyl acyl azolium followed by β–lactonization provides a diverse array of polycyclic β–lactones. The reaction proceeds with high enantioselectivity, diastereoselectivity and good yields and represents the first example of enantioselective catalysis using the dienyl acyl azolium, the higher homolog of the α,β–unsaturated acyl azolium.