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Potassium 2-oxo-3-enoates as Effective and Versatile Surrogates for α, β-Unsaturated Aldehydes in NHC-Catalyzed Asymmetric Reactions

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Abstract. Potassium 2-oxo-3-enoates, which are readily prepared at scale and easily stored, have been found to be effective and versatile surrogates for α,β-unsaturated aldehydes in NHC-catalyzed asymmetric reactions. Promoted by chiral N-heterocyclic carbenes combined with LiCl, these easy-to-handle solid salts could release of CO_2 and then undergo asymmetric reactions via homoenolate and α, β-unsaturated acyl azolium intermediate. The reactions have broad substrate scopes with high enantioselectivities.

Keywords: asymmetric catalysis; *N*-heterocyclic carbine; surrogate; α,β-unsaturated aldehyde; 2-oxo-3-enoates

Asymmetric catalysis has attracted extensive and continuous attention in past decades and has proven to be the most efficient strategy for constructing enantiomerically enriched molecules, which are widely applied in biological, pharmaceutical, and material sciences.[1] *N*-Heterocyclic carbenes (NHCs), are among the most important organocatalysts and have been widely used in asymmetric catalysis.[2] α,β-Unsaturated aldehydes are commonly employed precursors that provide access to a range of structurally diverse polyfunctionalized molecules.[3] Especially, numerous bioactive compounds[4] and natural products[5] have been efficiently constructed using α,β-unsaturated aldehydes. Despite the significance of α,β-unsaturated aldehydes, some encounter drawbacks due to their inherent characteristics. For instance, cinnamaldehyde must be purified before use due to being easily oxidized in air. Furthermore, common synthetic approaches to α,β-unsaturated aldehydes suffer from multiple synthetic steps,[6] harsh conditions,[7] or the use of expensive transition metals as catalysts.[8] Additionally, the dimerization of α,β-unsaturated aldehydes cannot be avoided as a side reaction under NHC catalysis.

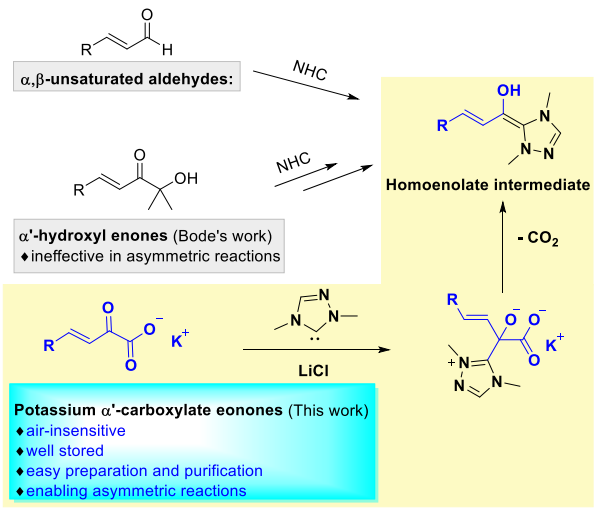

Figure 1. Surrogates for α, β-unsaturated aldehyde promoted by carbene.

Therefore, the development of easily prepared and stable surrogates for α,β-unsaturated aldehydes has long been highly desirable. In 2009, the Bode group[9] developed air-insensitive α′-hydroxyl enones[10] as suitable surrogates for α,β-unsaturated aldehydes, which gave excellent results using a racemic triazolium precatalyst. However, a chiral NHC precursor gave the desired products in lower yields, perhaps due to the sterically bulky group (2-hydroxypropan-2-yl) adjacent to the carbonyl group in the enone hindering attack of the chiral NHC precursor at the carbonyl group. Inspired by this work, we envisioned installing a smaller activated group

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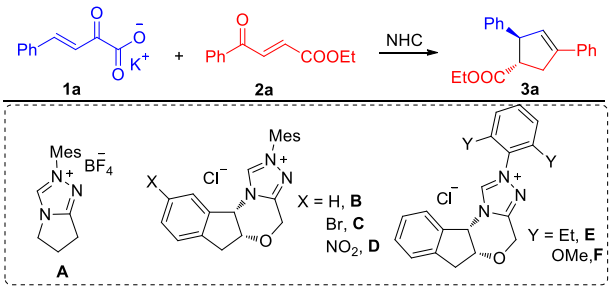
near the reactive site (carbonyl group) to overcome this steric problem. Herein, we develop potassium 2-oxo-3-enoates as outstanding surrogates for α,β-unsaturated aldehydes, especially when applied to chiral NHC-catalyzed asymmetric reactions (Figure 1).

Potassium 2-oxo-3-enoates, of which ester forms are commonly used as Michael acceptors in organic synthesis,[11] can be easily prepared at scale in good to high yields from commercially available aldehyde and pyruvic acid using KOH in MeOH.[12] Notably, these solid salts can be easily purified by recrystallization, with no need for silica gel column chromatography.

Table 1. Screening of reaction conditions for the reaction of **1a** with **2a**. [a]

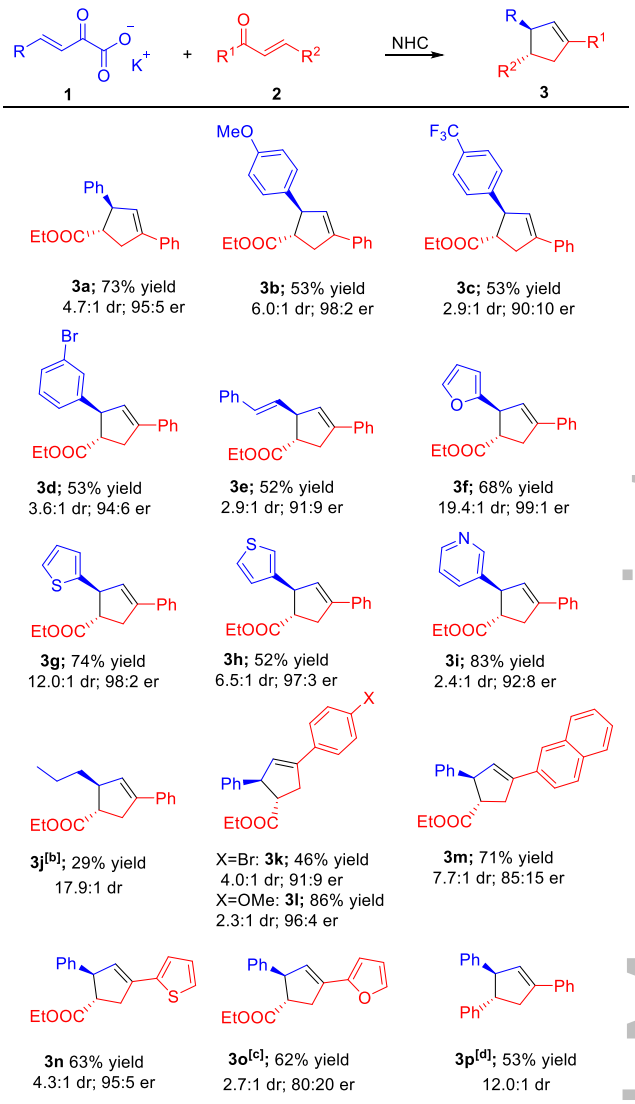


Entry	NHC	Base	Sol.	Yield [%][c]	dr[d]	ee[e]
1[b]	**A**	DBU	THF	nd	-	-
2	**A**	DBU	THF	69	3.2:1	-
3	**B**	DBU	THF	64	1.4:1	98:2
4	**B**	NaOAc	THF	56	1.6:1	99:1
5	**B**	DIPEA	THF	56	1.4:1	99:1
6	**B**	Cs_2CO_3	THF	53	1.5:1	98:2
7	**C**	DBU	THF	51	2.1:1	99:1
8	**D**	DBU	THF	32	2.8:1	98:2
9	**E**	DBU	THF	51	1.9:1	99:1
10	**F**	DBU	THF	60	4.9:1	96:4
11	**F**	DBU	DMF	52	3.9:1	93:7
12	**F**	DBU	Diox.	73	3.4:1	94:6
13	**F**	DBU	THF: Diox. =1:1	73	4.7:1	95:5

[a] Standard condition: NHC precursor (10 mol%), **1a** (1.5 equiv), **2a** (0.2 mmol), DBU (0.5 equiv), LiCl (2.0 equiv), solvent (2.0 mL), $MgSO_4$ (10 mg), 0°C-rt, 40h. [b] Without LiCl. [c] Isolated yields after column chromatography. [d] Diastereomeric ratio of **3a**, determined via ^{1}H NMR analysis of unpurified reaction mixtures. [e] Determined via chiral phase HPLC analysis. Diox.= 1,4-dioxane

We selected the reaction of readily available potassium (*E*)-2-oxo-4-phenylbut-3-enoate (**1a**) and enone[13] **2a** as the model reaction for optimizing conditions. The key results of reaction optimization are summarized in Table 1. Initial attempts were unsuccessful, with no desired product afforded when

Table 2. Scope of salts **1** and enones **2**.[a]



[a] Conditions as in Table 1, entry 13; Yields of isolated products based on **2**. The dr and er of **3** was determined by HPLC analysis on a chiral column. [b] Conditions as in Table 1, entry 2. [c] Conditions as in Table 1, entry 10. [d] Conditions: NHC precursor **A** (30 mol%), DBU (2.0 equiv), LiCl (2.0 equiv), THF (2.0 mL), $MgSO_4$ (10 mg), rt.

triazolium NHC precursor **A** was employed in the presence of DBU in THF at room temperature (entry 1), perhaps due to the low reactivity of **1a**. We envisioned that addition of Lewis acid LiCl[14],[15] could significantly increase the reactivity of the carbonyl group in **1a** via coordination. Indeed, with the addition of two equivalents of LiCl, the reaction proceeded smoothly to give the desired cascade product, cyclopentene **3a**, in 69% yield with 3.2:1 dr. To our delight, when using sterically hindered aminoindanol-derived triazolium NHC precursor **B**, pioneered by Bode,[16] the desired cyclopentene product, **3a**, was obtained in acceptable yield (60%) with excellent enantioselectivity (98:2 er), albeit with lower diastereoselectivity (1.4:1 dr) (entry 3). This result demonstrated that salts **1** could be a suitable surrogate for α,β-unsaturated aldehydes in NHC-catalyzed asymmetric reactions. Next, several bases

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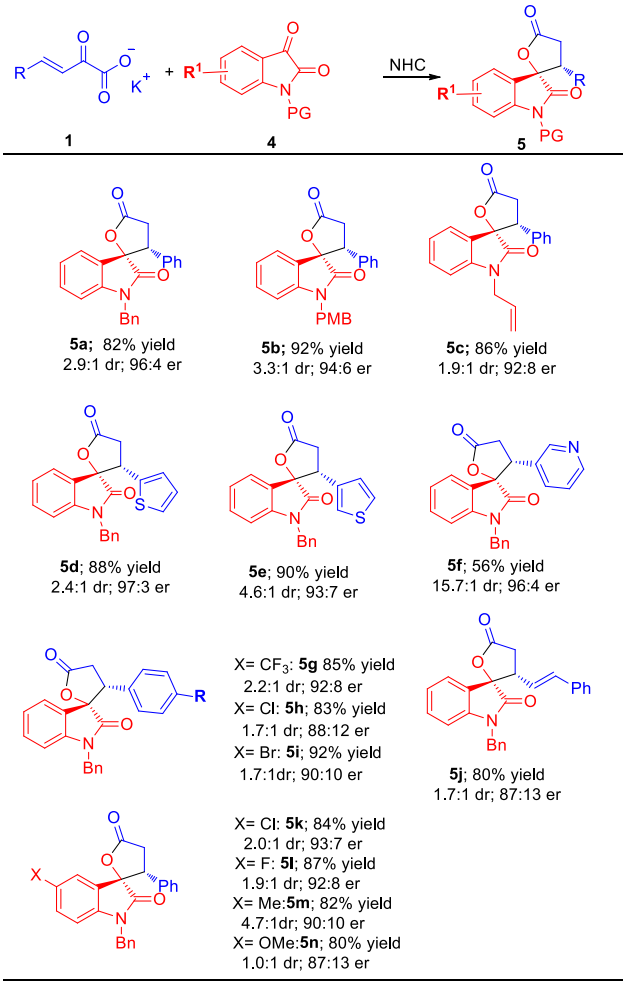
were investigated, with DBU proving to be the best choice (entries 3–6). Furthermore, investigations into triazolium NHC precursors showed that NHC precursor **F**, with an *N*-2,6-diMeOC$_6$H$_4$ moiety,[17] gave the desired product in 60% yield with up to 4.9:1 dr and a small drop in enantioselectivity (entries 6–10). Finally, when using a THF and dioxane (1:1) as a mixed solvent, **3a** was afforded in 73% yield with 4.7:1 dr and 95:5 er.

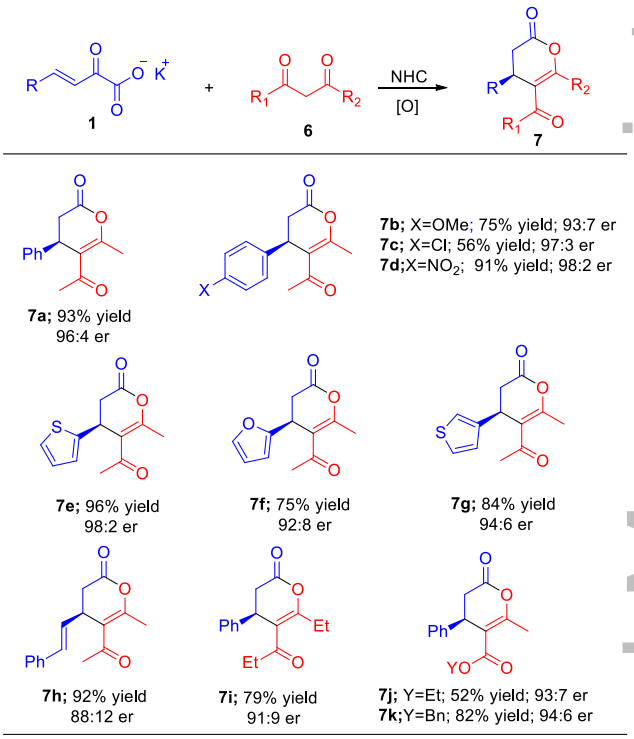
Table 3. Scope of salts **1** and isatins **4**. [a]



[a] Scope of the reaction. Reaction conditions: **1** (1.5 equiv), **4** (0.2 mmol), **B** (20 mol%), DBU (0.5 equiv), LiCl (2 equiv), THF (2 mL), 4Å MS (20 mg), rt. Yields of isolated products based on **4**. The dr and er of **5** was determined by HPLC analysis on a chiral column.

With optimized conditions in hand (Table 1, entry 13), we next evaluated the reaction scope for potassium 2-oxo-3-enoates **1** and enones **2** (Table 2). When salts **1** with γ-aryl substituents were used, both electron-rich and electron-deficient moieties could be placed on the aryl group (**3a**–**j**). Notably, salts **1** bearing γ-heteroaryl substituents were effective, giving higher diastereoselectivities in most cases (**3f**–**i**). Delightingly, a salt with a γ-alkyl substituent was also a suitable substrate for this transformation, albeit achieving a lower yield (**3j**). The yields of products **3** were commonly not that high due to enones **2** easily decomposing under basic conditions. Further investigation of enones **2** also gave products **3** with acceptable yields and enantioselectivities. Gratifyingly, comparably less reactive chalcone also is the suitable substrate to give product **3p** with acceptable outcome. Notably, in contrast to NHC-catalyzed α,β-unsaturated aldehyde reactions, reactions involving salts **1** could be followed clearly by TLC in most cases, and products could be separated easily using silica gel column chromatography.

Table 4. Scope of salts **1** and 1,3-dicarbonyl compounds **6**. [a]

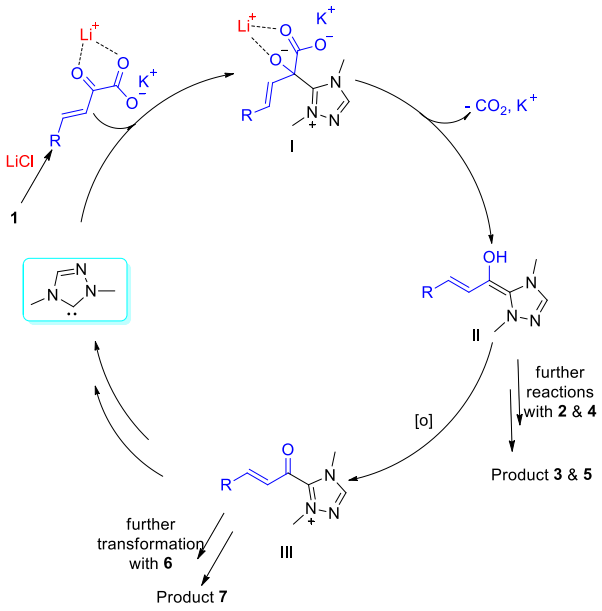


[a] Scope of the reaction. Reaction conditions: **1** (1.5 equiv), **6** (0.2 mmol), **F** (20 mol%), NaOAc (0.5 equiv), LiCl (1 equiv), oxidant (1.2 equiv), dioxane (2 mL), rt, 40h. Yields of isolated products based on **6**. The dr and er of **7** was determined by HPLC analysis on a chiral column.

To demonstrate the generality of potassium 2-oxo-3-enoates as efficient and practical surrogates for α,β-unsaturated aldehydes in NHC-catalyzed asymmetric reactions, we investigated the reactions of potassium β,γ-unsaturated α- ketocarboxylates **1** with isatins **4** via [3+2] cycloaddition to afford spirooxindole lactones **5**,[18] as shown in Table 3. We then examined the asymmetric [3+3] annulation of potassium 2-oxo-3-enoates **1** with 1,3-dicarbonyl compounds **6** to form lactones **7** [19] via oxidative NHC catalysis, as shown in Table 4. Expectedly, salts **1** underwent these asymmetric reactions smoothly, and gave the corresponding products with excellent yields and enantioselectivities.

The proposed pathway for NHC-catalyzed salts **1** acting as surrogates for α,β-unsaturated aldehydes is illustrated in Scheme 1. With the assistance of Lewis

acid LiCl, the addition of NHC to salts **1** gives intermediate **I**, which is liberated of CO_2[20] to form homoenolate intermediate **II**.[21] The addition of homoenolate intermediate **II** to enones or isatins affords cyclopentenes **3** or spirooxindole lactones **5**, respectively, via known processes. Oxidation of homoenolate intermediate **II** could furnish α,β-unsaturated acyl triazolium intermediate **III,**[22] which reacts with 1,3-dicarbonyl compounds **6** to finally give lactones **7** and release the NHC.



Scheme 1. Proposed Mechanism.

In summary, we have demonstrated that potassium 2-oxo-3-enoates are outstanding and practical surrogates for α,β-unsaturated aldehydes in NHC-catalyzed reactions with the assistance of Lewis acid (LiCl). These salts can be readily prepared at scale, easily stored and conveniently handled, to undergo catalytic asymmetric reactions with enones, isatins, and 1,3-dicarbonyl compounds to afford corresponding products with broad substrate scopes and good to excellent enantioselectivities under chiral NHC catalysis. Other reaction models for these salts **1** are currently under investigation in our laboratory.

Experimental Section

General procedure for the synthesis of product 3 (3a as an example): To a dried 10 mL Schlenk tube equipped with a tiny magnetic stir bar under N_2 atmosphere, **1a** (64.2 mg, 0.30 mmol), NHC pre-catalyst **F** (8.8 mg, 0.20 mmol), LiCl (16.8 mg, 0.40 mmol) and oven dried $MgSO_4$ (10 mg) was added. To this mixture was added **(**E)-ethyl 4-oxo-4-phenylbut-2-enoate **2a** (40 μL, 0.20 mmol), followed by the addition of dry THF:Dioxane = 1:1 (2 mL) and DBU (15 μL, 0.1 mmol) via a micro syringe. The reaction mixture was stirred at 0°C to rt until **(**E)-ethyl 4-oxo-4-phenylbut-2-enoate **2a** disappeared, then the reaction mixture was directly applied to silica gel column chromatography (5% v/v ethyl acetate in hexane) to afford **3a** as a colorless gum in 73% yield, 4.7:1 dr and 95:5 er.

General procedure for the synthesis of product 5 (5a as an example):A dry 10 mL Schlenk tube equipped with a magnetic stirring bar was successively charged with **1a** (32.1 mg, 0.15 mmol), 1-benzylindoline-2,3-dione **4a** (23.8 mg, 0.10 mmol), NHC pre-catalyst **B** (7.4 mg, 0.02 mmol), LiCl (8.4 mg, 0.20 mmol) and 4Å Molecular Sieve (beads 200 mg or powder 20 mg). The tube was closed with a septum. To this mixture was added DBU (7.5 μL, 0.05 mmol), followed by the addition of dry THF (2 mL) via a micro syringe. The reaction mixture was stirred at room temperature until 1-benzylindoline-2,3-dione **4a** disappeared, then the reaction mixture was directly applied to silica gel column chromatography (15% v/v ethyl acetate in hexane) to afford **5a** as a white solid in 82% yield, 2.9:1 dr and 96:4 er.

General procedure for the synthesis of product 7 (7a as an example):A dry 10 mL Schlenk tube equipped with a magnetic stirring bar was successively charged with **1a** (64.2 mg, 0.3 mmol), pentane-2,4-dione **6a** (20 uL, 0.20 mmol), NHC pre-catalyst **F** (17.5 mg, 0.04 mmol), NaOAc (8.3 mg, 0.1mmol), LiCl (8.4 mg, 0.2mmol) and oxidant (98.4 mg 0.24 mmol).The tube was closed with a septum. To this mixture was added dry dioxane (2 mL). The reaction mixture was stirred at room temperature until pentane-2,4-dione **6a** disappeared, then the reaction mixture was directly applied to silica gel column chromatography (10% v/v ethyl acetate in hexane) to afford **7a** as a white solid in 93% yield and 96:4 er.

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References

[1] For selected reviews on asymmetric catalysis, see: a) L. Canali, D. C. Sherrington, *Chem. Soc. Rev.* **1999**, *28*, 85; b) L. Ma, C. Abney, W. Lin, *Chem. Soc. Rev.* **2009**, *38*, 1248; c) C. R. Pitts, T. Lectka, *Chem. Rev.* **2014**, *114*, 7930; d) S. Otocka, M. Kwiatkowska, L. Madalinska, P. Kiełbasinski, *Chem. Rev.* **2017**, *117*, 4147; e) L. Klier, F. Tur, P. H. Poulsen, K. A. Jørgensen, *Chem. Soc. Rev.* **2017**, *46*, 1080.

[2] For selected reviews on NHC asymmetric catalysis, see: a) D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, *37*, 534; b) K. Zeitler, *Angew. Chem., Int. Ed.* **2005**, *44*, 7506; c) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606; d) Grossmann, A.; Enders, D. *Angew. Chem., Int. Ed.* **2012**, *51*, 314;e) J. Douglas, G. Churchill, A. D. Smith, *Synthesis* **2012**, *44*, 2295; f) D. T. Cohen, K. A. Scheidt, *Chem. Sci.* **2012**, *3*, 53; g) S. J. Ryan, L. Candish, D. W. Lupton, *Chem. Soc. Rev.* **2013**, *42*, 4906; h) S. D. Sarkar, A. Biswas, R. C. Samanta, A. Studer, *Chem. Eur. J.* **2013**, *19*, 4664; i) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485; j) D. M. Flanigan, F. Romanov-Michailidis, N. A. White, T. Rovis, *Chem. Rev.* **2015**,

115, 9307; k) M. H. Wang, K. A. Scheidt, *Angew. Chem., Int. Ed.* **2016**, *55*, 14912.

[3] a) R. S. Menon, A. T. Biju, V. Nair, *Chem. Soc. Rev.* **2015**, *44*, 5040; b) J. Izquierdo, G. E. Hutson, D. T. Cohen, K.A. Scheidt, *Angew. Chem., Int. Ed.* **2012**, *51*, 11686.

[4] For selected examples, see: a) J. Izquierdo, A. Orue, K. A. Scheidt, *J. Am. Chem. Soc.* **2013**, *135*, 10634; b) Y. Zhang, Y. Du, Z. Huang, J. Xu, X. Wu, Y. Wang, M. Wang, S. Yang, R. D. Webster, Y. R. Chi, *J. Am. Chem. Soc.* **2015**, *137*, 2416; c) X. Wu, B. Liu, Y. Zhang, M. Jeret, H. Wang, P. Zheng, S. Yang, B. Song, Y. R. Chi, *Angew. Chem., Int. Ed.* **2016**, *55*, 12280; d) K. Zhao, D. Enders, *Angew. Chem. Int. Ed.* **2017**, *56*, 3754.

[5] For selected examples, see: a) K. Lee, H. Kim, J. Hong, *Angew. Chem., Int. Ed.* **2012**, *51*, 5735; b) A. K. Singh, R. Chawla, A. Rai, L. D. S. Yadav, *Chem. Commun.*, **2012**, *48*, 3766; c) Q. Jia, J. Wang, *Org. Lett.* **2016**, *18*, 2212; d) C. Zhao, F. Li, J. Wang, *Angew. Chem., Int. Ed.* **2016**, *55*, 1820; e) Y. Wang, M. Tang, Y. Wang, D. Wei, *J. Org. Chem.* **2016**, *81*, 5370.

[6] a) H. Maeta, K. Suzuki, *Tetrahedron* **1993**, *34*, 341; b) G. Battistuzzi, S. Cacchi, G. Fabrizi, *Org. Lett.* **2003**, *5*, 777.

[7] a) B. T. Lee, T. O. Schrader, B. Martín-Matute, C. R. Kauffman, P. Zhang, M. L. Snapper, *Tetrahedron* **2004**, *60*, 7391; b) T. Paul, G. Sirasani, R. B. Andrade, *Tetrahedron Lett.* **2008**, *49*, 3363.

[8] a) R. H. Wollenberg, K. F. Albizati, R. Peries, *R. J. Am. Chem. Soc.* **1977**, *99*, 7365; b) B. Liu, P. Hu, X. Zhou, D. Bai, J. Chang, X. Li, *Org. Lett.* **2017**, *19*, 2086.

[9] P. Chiang, M. Rommel, J. W. Bode, *J. Am. Chem. Soc.* **2009**, *131*, 8714.

[10] a) C. Palomo, M. Oiarbide, E. Arceo, J. M. Garca, R. López, A. González, A. Linden, *Angew. Chem., Int. Ed.* **2005**, *44*, 6187; b) C. Palomo, M. Oiarbidea, J. M. García, *Chem. Soc. Rev.* **2012**, *41*, 4150.

[11] For selected review, see: G. Desimoni, G. Faita, P. Quadrelli, *Chem. Rev.* **2013**, *113*, 5924.

[12] Q. Meng, L. Zhu, Z. Zhang, *J. Org. Chem.* **2008**, *73*, 7209-7212.

[13] For selected exampes, see: (a) V. Nair, S. Vellalath, M. Poonoth, E. Suresh, *J. Am. Chem. Soc.* **2006**, *128*, 8736; b) H. R. Zhang, Z. W. Dong, Y. J. Yang, P. L. Wang, X. P. Hui, *Org. Lett.* **2013**, *15*, 4750; c) Z. Fu, H. Sun, S. Chen, B. Tiwari, G. Li, Y. R. Chi, *Chem. Commun.* **2013**, *49*, 261; d) T. S. Zhu, P. C. Zheng, C. L. Mou, S. Yang, B. A. Song, Y. R. Chi, *Nat. Commun.* **2014**, *5*, 5027.

[14] L. Hong, W. Sun, D. Yang, G. Li, R. Wang, *Chem. Rev.* **2016**, *116*, 4006.

[15] For selected reactions of LiCl as cooperative Lewis acid: (a) E. M. Phillips, M. Riedrich, K. A. Scheidt, *J. Am. Chem. Soc.* **2010**, *132*, 13179; b) J. Dugal-Tessier, E. A. O'Bryan, T. B. H. Schroeder, D. T. Cohen, K. A. Scheidt, *Angew. Chem., Int. Ed.* **2012**, *51*, 4963; c) J. M. Mo, L. Shen, Y. R. Chi, *Angew. Chem., Int. Ed.* **2013**, *52*, 8588; d) S. Bera, R. C. Samanta, C. G. Daniliuc, A. Studer, *Angew. Chem., Int. Ed.* **2014**, *53*, 9622; e) N. A. White, T. Rovis, *J. Am. Chem. Soc.* **2015**, *137*, 10112.

[16] A. G. Kravina, J. Mahatthananchai, J. W. Bode, *Angew. Chem., Int. Ed.* **2012**, *51*, 9433.

[17] N. E. Wurz, C. G. Daniliuc, F. Glorius, *Chem. Eur. J.* **2012**, *18*, 16297.

[18] For selected examples on NHC-catalyzed the reactions of α,β-unsaturated aldehydes and isatins, see: a) L. Sun, L. Shen, S. Ye, *Chem. Commun.* **2011**, *47*, 10136; b) J. Dugal-Tessier, E. A. O'Bryan, T. B. H. Schroeder, D. T. Cohen, K. A. Scheidt, *Angew. Chem., Int. Ed.* **2012**, *51*, 4963; c) J. -L. Li, B. Sahoo, C. G. Daniliuc, F. Glorius, *Angew. Chem., Int. Ed.* **2014**, *53*, 10515; d) S. Mukherjee, S. Joseph, A. Bhunia, R. G. Gonnade, S. R. Yetra, A. T. Biju, *Org. Biomol. Chem.* **2017**, *15*, 2013.

[19] For selected examples on NHC-catalyzed the reactions of α,β-unsaturated aldehydes and 1,3-dicarbonyl compounds, see: a) S. D. Sarkar, A. Studer, *Angew. Chem., Int. Ed.* **2010**, *49*, 9266; b) Z. Rong, M. Jia, S. You, *Org. Lett.* **2011**, *13*, 4080; c) J. Mo, L. Shen, Y. R. Chi, *Angew. Chem., Int. Ed.* **2013**, *52*, 8588; d) L. Ta, A. Axelsson, H. Sundén, *Green Chem.* **2016**, *18*, 686; e) X. Wu, Y. Zhang, Y. Wang, J. Ke, M. Jeret, R. N. Reddi, S. Yang, B. Song, Y. R. Chi, *Angew. Chem., Int. Ed.* **2017**, *56*, 2942.

[20] For examples of α-keto carboxylates activated by carbene, see: a) U. T. Bornscheuer, R. J. Kazlauskas, *Angew. Chem., Int. Ed.* **2004**, *43*, 6032; b) M. C. Myers, A. R. Bharadwaj, B. C. Milgram, K. A. Scheidt, *J. Am. Chem. Soc.* **2005**, *127*, 14675.

[21] For selected reviews on homoenolate intermediates, see: a) V. Nair; S. Vellalath; B. P. Babu *Chem. Soc. Rev.* **2008**, *37*, 2691; b) V. Nair, R. S. Menon, A. T. Biju, C. R. Sinu, R. R. Paul, A. Josea, V. Sreekumar, *Chem. Soc. Rev.* **2011**, *40*, 5336; c) R. S. Menon, A. T. Bijub, V. Nair *Chem. Soc. Rev.* **2015**, *44*, 5040. And some examples in ref. 2. For selected examples, see: a) C. Burstein, F. Glorius, *Angew. Chem., Int. Ed.* **2004**, *43*, 6205; b) M. Rommel, T. Fukuzumi, J. W. Bode, *J. Am. Chem. Soc.* **2008**, *130*, 17266; c) D. E. A. Raup, B. CardinalDavid, D. Holte, K. A. Scheidt, *Nat. Chem.* **2010**, *2*, 766; d) J. Izquierdo, A. Orue, K. A. Scheidt, *J. Am. Chem. Soc.* **2013**, *135*, 10634; e) C. Guo, M. Fleige, D. Janssen-Müller, C. G. Daniliuc, F. Glorius, *Nat. Chem.* **2015**, *7*, 842.

[22] For selected reviews on α,β-unsaturated acyl azolium intermediates, see: (a) J. Mahatthananchai, J. W. Bode, *Acc. Chem. Res.*, **2014**, *47*, 696; b) C. Zhang, J. F. Hooper, D. W. Lupton, *Acs Catal*. **2017**, *7*, 2583. And some examples in ref. 2. For selected examples, see: (a) K. Zeitler, *Org. Lett.* **2006**, *8*, 637; b) S. De Sarkar, S. Grimme, A. Studer, *J. Am. Chem. Soc.* **2010**, *132*, 1190; c) S. J. Ryan, L. Candish, D. W. Lupton, *J. Am. Chem. Soc.* **2011**, *133*, 4694; d) F. G. Sun, L. H. Sun, S. Ye, *Adv. Synth. Catal.* **2011**, *353*, 3134; e) A. G. Kravina, J. Mahatthananchai, J. W. Bode, *Angew.*

10.1002/adsc.201701413

Chem., Int. Ed. **2012**, *51*, 9433; f) L. Candish, D. W. Lupton, *J. Am. Chem. Soc.* **2013**, *135*, 58; g) D. Xie, L. Yang, Y. Lin, Z. Zhang, D. Chen, X. Zeng, G. Zhong, *Org. Lett.* **2015**, *17*, 2318; h) Y. J. Yang, Y. Ji, L. Qi, G. Wang, X. P. Hui, *Org. Lett.* **2017**, *19*, 3271; i) X. Wu, L. Hao, Y. Zhang, M. Rakesh, R. N. Reddi, S. Yang, B. A. Song, Y. R. Chi, *Angew. Chem., Int. Ed.* **2017**, *56*, 4201; j) S. Perveen, Z. Zhao, G. Zhang, J. Liu, M. Anwar, X. Fang, *Org. Lett.* **2017**, *19*, 2470.

10.1002/adsc.201701413

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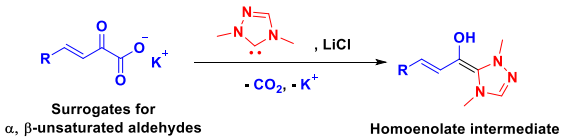

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