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CHEMISTRY AN ASIAN JOURNAL Communication

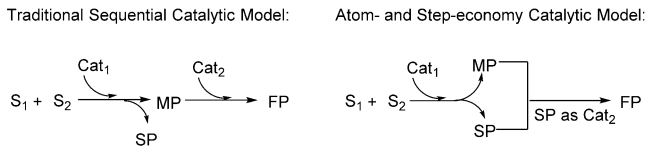
N-Heterocyclic Carbenes

An Upstream By-product from Ester Activation via NHC-Catalysis Catalyzes Downstream Sulfonyl Migration Reaction

Runfeng Han,[a] Liwenze He,[a] Lin Liu,[a] Xingang Xie,[a] and Xuegong She*[a, b]

Abstract: A sequential reaction combining N-heterocyclic carbene (NHC) and N-hydroxyphthalimide (NHPI) catalysis allowed for the upstream by-product NHPI, which was generated in the NHC-catalyzed cycloaddition reaction, to act as the catalyst for a downstream nitrogen-to-carbon sulfonyl migration reaction. Enantiomeric excess of the major product in the cycloaddition reaction remained intact in the follow-up sulfonyl migration reaction.

In organic chemistry, by-products of upstream reactions acting as efficient catalysts for downstream reactions is one of the most challenging subjects in the synthetic community due to the ongoing pursuit of atom- and step-economy. In comparison with the traditional sequential catalytic model, this atom/step-economy catalytic model enables one reaction not only to deliver the final product **FP** but also to realize the reuse of by-products or side-products **SP**; consequently, the atom utilization is obviously improved (Scheme 1). In 1982, Tsuji et al. reported that alkoxides which were generated in the first step acted as Brønsted base to promote the palladium-catalyzed decarboxylative allylation of active methylene compounds.[1a] So far, there have been several reports targeting this concept for the reuse of upstream by-products (HCl, Ph_3PO, CuI, InX_3, I_2, etc.) to promote the next transformation.[1b–k] However, such a catalytic model remains lacking in N-heterocyclic carbene (NHC) chemistry.



Scheme 1. Hypothesis for the catalytic model (S = substrate, Cat = catalyst, MP = main product, SP = side-product, FP = final product).

N-heterocyclic carbenes (NHCs) have emerged as effective organocatalysts for Umpolung of aldehydes.[2] They have also been employed for the activation of esters followed by transesterificaton,[3] polymerization[4] and domino cyclization reactions.[5] The formation of azolium enolates could be achieved by activation of ketenes,[6] α-functionalized aldehydes,[7] enals,[8] and aliphatic aldehydes.[9] Very recently, activation of esters has attracted more and more attention, and several kinds of esters for the domino cyclization have been developed by different groups (Scheme 2). In 2006, Smith and co-workers reported the enol ester activation by NHCs followed by an acyl transfer from oxygen to carbon.[10] Then Lupton's group enclosed the activation of other enol esters (Scheme 2, $\mathbf{A_1}$) by NHCs to get a series of useful skeletons.[11] Recently, Chi's group made significant advancements on the activation of phenol esters by NHC (Scheme 2, $\mathbf{A_2}$) for the asymmetric domino reactions, and they have successfully accomplished α-carbon HOMO activation, β-carbon activation (after activation of the β-carbon of the saturated compounds, this carbon is nucleophilic), β-carbon LUMO activation (after activation, the β-carbon of the unsaturated compounds is electrophilic), and γ-carbon activation in this manner.[12] Furthermore, Smith and co-workers reported that chiral isothiourea behaved as a nucleophlic catalyst for the highly enantioselective synthesis of dihydropyridones.[13] In most cases, the by-product such as 4-nitrophenol generated from NHC activation was discarded. We wondered whether it is possible to utilize such a by-product (**SP** in Scheme 1) as the catalyst to promote subsequent transformations of the product formed in the first step (**MP** in Scheme 1). Application of this concept is of great importance in N-heterocyclic carbene chemistry.

However, activation of substituted phenol esters by NHC for the asymmetric domino Michael addition/lactamization of acetic 4-nitrophenol esters and α,β-unsaturated imines has two drawbacks: (1) high catalyst loading (30%)[12a–d] is needed and (2) the by-product cannot catalyze the next transformation. To overcome these problems, it is highly desirable to explore appropriate esters that can produce the side-product capable to catalyze the next transformation. It has been known that enals could be transformed to esters via NHC-bound enolates and esterification (forward process). Thus, NHC-bound enolates could be obtained via ester activation mode, and this backward process would be interesting and novel in NHC catalysis.

[a] *R. Han, L. He, L. Liu, X. Xie, Prof. Dr. X. She*
State Key Laboratory of Applied Organic Chemistry
College of Chemistry and Chemical Engineering
Lanzhou University
Lanzhou, Gansu, 730000 (P.R. China)
E-mail: shexg@lzu.edu.cn

[b] *Prof. Dr. X. She*
Collaborative Innovation Centre of Chemical Science and Engineering
Tianjin 300071 (P.R. China)

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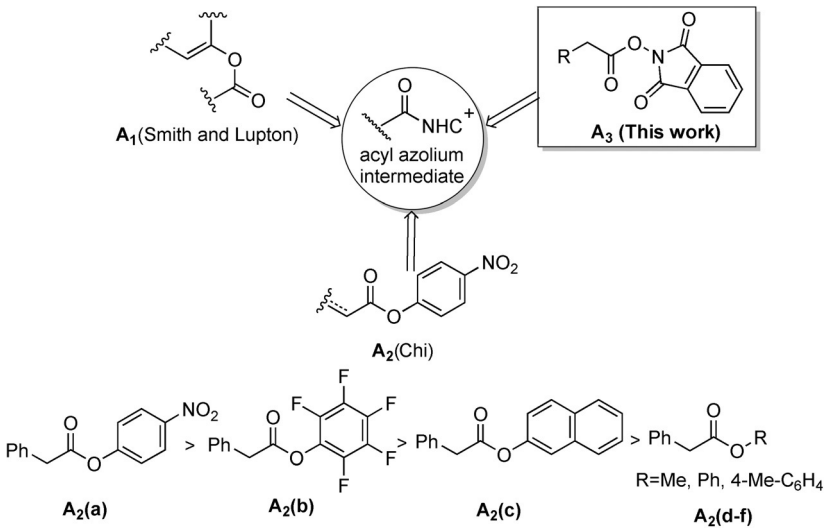


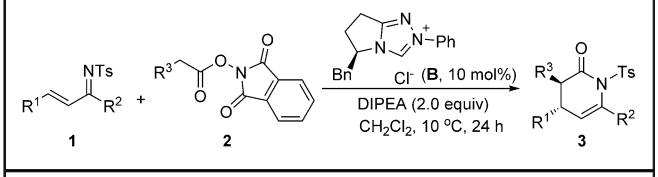
Scheme 2. Esters of acyl azolium precursors for cyclization.

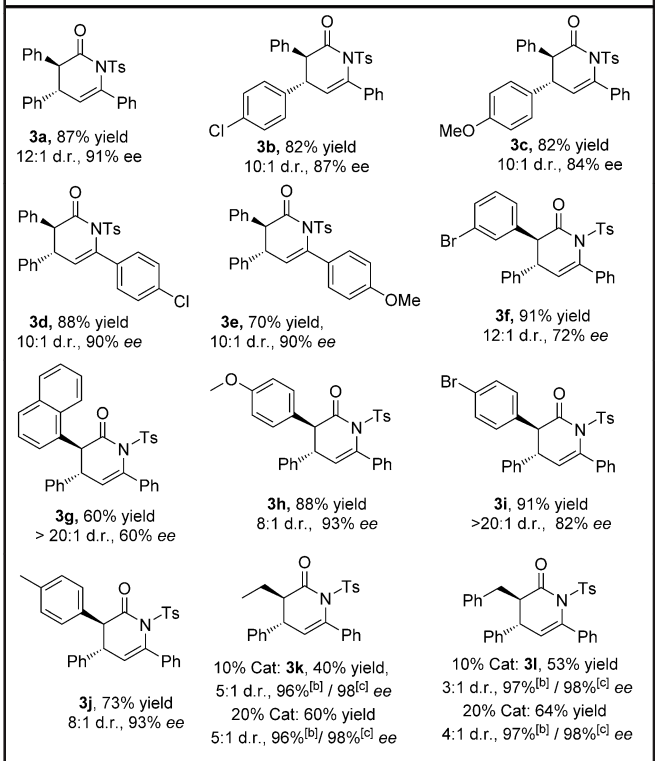
Based on the above considerations, we thought that 1,3-dioxoisoindolin-2-yl 2-phenylacetate $\mathbf{A_3}$ would be the best choice (Scheme 2). In this process, the new catalyst *N*-hydroxyphthalimide (NHPI) is generated from NHC catalysis and then enters another catalytic cycle. Due to the effective role of NHPI, the precursor of phthalimido-*N*-oxyl (PINO) radical for the C–H activation by hydrogen abstraction[14] and aromatic oxidation of heterocyclic compounds,[15] a series of radical reactions of the first product could be performed by this concept. For this, it would be different from the traditional sequential catalytic mode, in which the second catalyst was added sequentially.

In order to verify our design, we initially investigated the enantioselective activation of 1,3-dioxoisoindolin-2-yl 2-phenyl acetate ($\mathbf{A_3}$) via NHC catalysis to react with α,β-unsaturated imines.[15] After screening different reaction conditions (see the Supporting Information), we found that a high yield and selectivity were obtained when 10 mol% NHC precursor **B** was used and CH_2Cl_2 was employed as solvent. Next, the scope and limitation of this system were also explored under the optimized reaction conditions (Table 1). A variety of α,β-unsaturated imines and aryl or alkyl acetic esters were successfully converted into the desired products. We found that the results of this reaction were determined by steric and electronic effects. The yield, diastereoselectivity, and enantioselectivity were all decreased to some extent when the aromatic ring R^1 (-Ph) was replaced by 4-Cl-Ph or 4-OMe-Ph except for the yield with R^2 = 4-Cl-Ph (**3a**–**3e**, Table 1); also the reaction was relatively sensitive to substituents on the aromatic ring R^3 (**3f**–**3j**, Table 1). As for alkyl acetic esters, a stronger base would be necessary due to the weak acidity of the α-position of the acyl azolium intermediate.

A moderate yield and low diastereomeric ratio were obtained when 10% catalyst was used, while a higher yield was obtained to some extent when the catalyst loading was increased to 20%; however, the diastereomeric ratios were still low due to the lower hindrance of the ethyl and benzyl groups

Table 1. Scope of the substrates.[a]



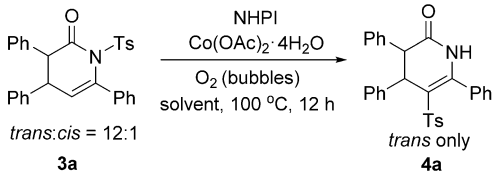


[a] Reaction conditions: **1** (0.10 mmol), **2** (0.15 mmol, 1.5 equiv), solvent (0.5 mL); isolated yield; the diastereomeric ratio was determined by ^{1}H NMR spectroscopic analysis of unpurified reaction mixtures; *ee* value of the major diastereomer as determined by chiral HPLC analysis. [b] DBU was used as the base; *ee* value of the major diastereomer. [c] DBU was used as the base; *ee* value of the minor diastereomer.

compared with the phenyl group (**3k**–**3l**, Table 1). However, excellent and comparable enantioselectivities were detected under 10% and 20% catalyst loadings. It was obvious that when phenol esters were replaced by phthalimide esters, the catalyst loading and base loading could be decreased to 10% and 2.0 equivalents, respectively, and that no further additive was needed. These results revealed that esters **2** exhibited a higher reactivity than 4-nitrophenol esters overall from the point of catalyst loading, amount of base, and additive. As esters as substrates are more stable than enals and more convenient to use, this formal [4+2] annulation provided a series of products containing a single aryl substituent at the lactam α-carbon, while NHC-bound enolates via enals[8a] could not be obtained. On the other hand, this activation mode provided *trans* products, while NHC-bound enolates via enals only provided *cis* products.

Next, we investigated whether NHPI could be used as a new catalyst for the following transformation of the first main product **3a**. Thus, **3a** (12:1 d.r.) was prepared as the substrate for the designed reaction. When **3a** was treated with NHPI and O_2 in $CHCl_3$, the sulfonyl migration product **4a** was obtained in only 16% yield (entry 1, Table 2). A higher yield was obtained

Table 2. Exploring the reaction conditions for the N- to C-sulfonyl migration.[a]

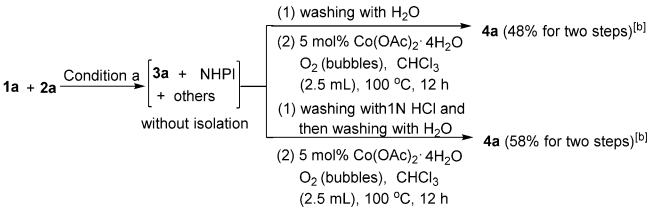


Entry	NHPI	$Co(OAc)_2·4H_2O$	Solvent	Yield [%][b]
1	20%	–	$CHCl_3$	16
2	20%	5%	$CHCl_3$	50
3	–	5%	$CHCl_3$	12
4	50%	5%	$CHCl_3$	58
5[c]	20%	5%	CH_2Cl_2	trace
6	20%	5%	$(CH_2Cl)_2$	trace
7	20%	5%	CH_3CN	n.d.
8	20%	5%	CH_3OH	n.d.

[a] Reaction conditions: **3a** (0.1 mmol), solvent (2.5 mL). [b] Isolated yield; the minor diastereomeric isomer was not detected in all cases. [c] The reaction was performed at 60 °C.

when $Co(OAc)_2·4H_2O$ was added as co-catalyst as the combination of O_2 and Co^{II} could accelerate the formation of a PINO radical (entry 2, Table 2). Control experiments revealed that NHPI is necessary for the transformation (entry 3, Table 2). Pleasingly, increasing the amount of NHPI to 50 mol% gave a higher yield (entry 4, Table 2), and the structure of **4a** was confirmed by X-ray analysis (CCDC 1059049).[16] However, other solvents could not provide improved results (entries 5–8, Table 2).

After the NHC catalytic reaction, $Co(OAc)_2·4H_2O$ was added and the reaction was performed under oxygen atmosphere. However, only trace amounts of **4a** were detected. We speculated that an excess amount of DIPEA and conjugate acid $[DIPEA-H]^+$ may disturb the reaction to some extent. When the mixture of the NHC-catalyzed reaction was washed either with water or 1 N HCl, a satisfactory yield of **4a** was obtained (Scheme 3). However, the yields were decreased sharply either



Scheme 3. Sequential transformation of the two steps.[a] ([a] Condition **a** (achiral catalyst **B′** instead of chiral catalyst **B**): **1** (0.10 mmol), **2** (0.15 mmol, 1.5 equiv), NHC catalyst **B′** (10 mol%), DIPEA (2.0 equiv), CH_2Cl_2 (0.5 mL), r.t. for 24 h; [b] Isolated yield over two steps; the minor diastereomeric isomer was not detected.)

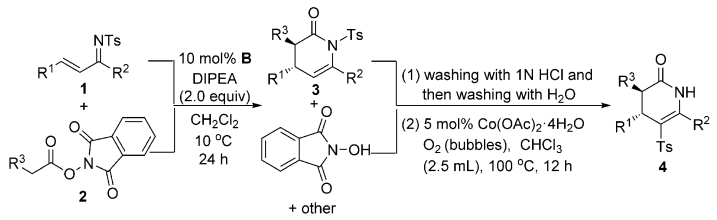
in the absence of Co(II) or by replacement of O_2 (bubbles) with an air atmosphere. This result revealed that the by-product NHPI actually acted as a new catalyst for the second transformation, and this verified our hypothesis (Scheme 1).

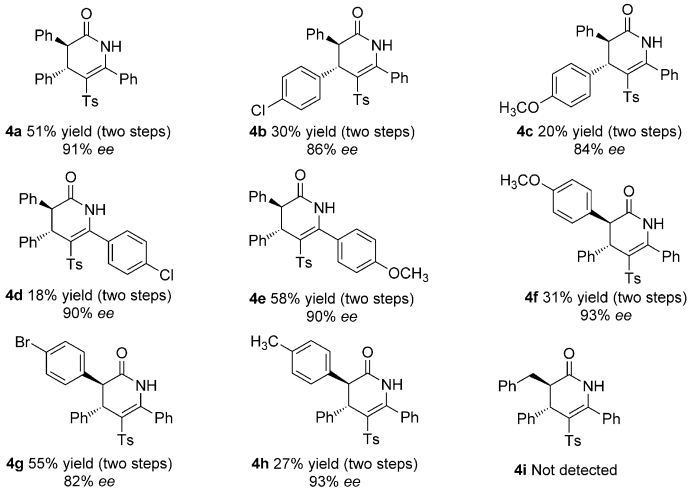
Subsequent studies explored the possibility for the NHC/NHPI catalytic cascade process (Table 3). We found that many substrates could give the desired products successfully, and electronic effects enormously affected the yields of the sulfonyl migration products. When substituents on the aromatic ring R^2 were electron-donating groups (**4d**–**4e**), the migration reaction gave a higher yield; indeed, it is reasonable that an electron-rich system is beneficial for the oxidation process. No obvious interference of the reaction was observed when substituents on the aromatic ring R^1 were different groups (**4b**–**4c**). The inverse trend was observed when different esters were used under the same conditions (**4f**–**4h**). In this process, the enantiomeric excess values of products were all maintained from the upstream products.

This sulfonyl migration reaction may proceed via a radical pathway. In order to support this idea, TEMPO was added to the reaction, and the reaction was completely suppressed. This result provides indirect evidence that the sulfonyl migration reaction proceeds via a radical pathway[17] (Scheme 4).

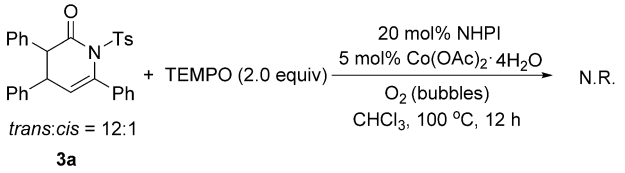
In conclusion, we have developed sequential N-heterocyclic carbene (NHC) catalysis and *N*-hydroxyphthalimide (NHPI) catalysis in which the upstream by-product NHPI acts as the catalyst for a downstream nitrogen-to-carbon sulfonyl migration reaction. In the upstream catalytic system, only a low catalyst loading was needed and no additive was required for the cyclization of enolate azolium with α,β-unsaturated imines, revealing that this kind of esters exhibited a high reactivity. This reaction proceeded to provide a high yield as well as satisfactory enantioselectivity and diastereoselectivity. The downstream catalytic process allowed for sulfonyl migration of the first product, while retaining the enantiomeric excess. Further investigations on the mechanistic studies and other transforma-

Table 3. Substrates for the sulfonyl migration.[a]





[a] The minor diastereomeric isomer was not detected by ^{1}H NMR analysis of the crude mixtures. Isolated yield for two steps.



Scheme 4. Radical capture experiment.

tions by this kind of strategy are being pursued in our laboratory.

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Keywords: ester activation · N-heterocyclic carbenes · N-hydroxyphthalimide · radicals · sulfonyl migration

[1] a) J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, *Tetrahedron Lett.* **1982**, *23*, 4809 – 4812; b) J. Zhou, *Multicatalyst System in Asymmetric Catalysis*, Wiley, New York, **2014**, Chap. 9; c) P. J. Alaimo, R. O'Brien, III., A. W. Johnson, S. R. Slauson, J. M. O'Brien, E. L. Tyson, A.-L. Marshall, C. E. Ottinger, J. G. Chacon, L. Wallace, C. Y. Paulino, S. Connell, *Org. Lett.* **2008**, *10*, 5111 – 5114; d) B.-L. Yang, Z.-T. Weng, S.-J. Yang, S.-K. Tian, *Chem. Eur. J.* **2010**, *16*, 718 – 723; e) H.-H. Li, D.-J. Dong, Y.-H. Jin, S.-K. Tian, *J. Org. Chem.* **2009**, *74*, 9501 – 9504; f) M. Gao, Y. Yang, Y.-D. Wu, C. Deng, W.-M. Shu, D.-X. Zhang, L.-P. Cao, N.-F. She, A.-X. Wu, *Org. Lett.* **2010**, *12*, 4026 – 4029; g) J. Lu, P. H. Toy, *Chem. Asian J.* **2011**, *6*, 2251 – 2254; h) Y. Teng, J. Lu, P. H. Toy, *Chem. Asian J.* **2012**, *7*, 351 – 359; i) F. Portalier, F. Bourdreux, J. Marrot, X. Moreau, V. Coeffard, C. Greck, *Org. Lett.* **2013**, *15*, 5642 – 5645; j) F. Zhu, P.-W. Xu, F. Zhou, C.-H. Wang, J. Zhou, *Org. Lett.* **2015**, *17*, 972 – 975; k) L. Chen, Y. Du, Z.-P. Zeng, T.-D. Shi, F. Zhou, J. Zhou, *Org. Lett.* **2015**, *17*, 1557 – 1560.

[2] For selected reviews on NHC catalysis, see: a) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606 – 5655; b) N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem. Int. Ed.* **2007**, *46*, 2988 – 3000; *Angew. Chem.* **2007**, *119*, 3046 – 3058; c) V. Nair, S. Vellalath, B. P. Babu, *Chem. Soc. Rev.* **2008**, *37*, 2691 – 2698; d) A. T. Biju, N. Kuhl, F. Glorius, *Acc. Chem. Res.* **2011**, *44*, 1182 – 1195; e) K. Hirano, I. Piel, F. Glorius, *Chem. Lett.* **2011**, *40*, 786 – 791; f) D.-C. A. Grossmann, D. Enders, *Angew. Chem. Int. Ed.* **2012**, *51*, 314 – 325; *Angew. Chem.* **2012**, *124*, 320 – 332; g) H. U. Vora, P. Wheeler, T. Rovis, *Adv. Synth. Catal.* **2012**, *354*, 1617 – 1639; h) X. Bugaut, F. Glorius, *Chem. Soc. Rev.* **2012**, *41*, 3511 – 3522; i) D. T. Cohen, K. A. Scheidt, *Chem. Sci.* **2012**, *3*, 53 – 57; j) J. Douglas, G. Churchill, A. D. Smith, *Synthesis* **2012**, 2295 – 2309; k) S. De Sarkar, A. Biswas, R. C. Samanta, A. Studer, *Chem. Eur. J.* **2013**, *19*, 4664 – 4678; l) S. J. Ryan, L. Candish, D. W. Lupton, *Chem. Soc. Rev.* **2013**, *42*, 4906 – 4917; m) J. Mahatthananchai, J. W. Bode, *Acc. Chem. Res.* **2014**, *47*, 696 – 707.

[3] a) E. F. Connor, G. W. Nyce, M. Myers, A. Möck, J. L. Hedrick, *J. Am. Chem. Soc.* **2002**, *124*, 914 – 915; b) G. A. Grasa, R. M. Kissling, S. P. Nolan, *Org. Lett.* **2002**, *4*, 3583 – 3586; c) G. W. Nyce, J. A. Lamboy, E. F. Connor, R. M. Waymouth, J. L. Hedrick, *Org. Lett.* **2002**, *4*, 3587 – 3590; d) Y. Suzuki, K. Yamauchi, K. Muramatsu, M. Sato, *Chem. Commun.* **2004**, 2770 – 2771; e) T. Kano, K. Sasaki, K. Maruoka, *Org. Lett.* **2005**, *7*, 1347 – 1349; f) M. Movassaghi, M. A. Schmidt, *Org. Lett.* **2005**, *7*, 2453 – 2456.

[4] M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, *Chem. Soc. Rev.* **2013**, *42*, 2142 – 2172.

[5] P. Chauhan, D. Enders, *Angew. Chem. Int. Ed.* **2014**, *53*, 1485 – 1487; *Angew. Chem.* **2014**, *126*, 1509 – 1511.

[6] Selected examples for activation of ketenes by NHCs, see: a) Y.-R. Zhang, L. He, X. Wu, P.-L. Shao, S. Ye, *Org. Lett.* **2008**, *10*, 277 – 280; b) N. Duguet, C. D. Campbell, A. M. Z. Slawin, A. D. Smith, *Org. Biomol. Chem.* **2008**, *6*, 1108 – 1113; c) X.-N. Wang, P.-L. Shao, Lv, H. S. Ye, *Org. Lett.* **2009**, *11*, 4029 – 4031; d) X.-L. Huang, X.-Y. Chen, S. Ye, *J. Org. Chem.* **2009**, *74*, 7585 – 7587; e) X.-N. Wang, H. Lv, X.-L. Huang, S. Ye, *Org. Biomol. Chem.* **2009**, *7*, 346 – 350; f) P.-L. Shao, X.-Y. Chen, S. Ye, *Angew. Chem. Int. Ed.* **2010**, *49*, 8412 – 8416; *Angew. Chem.* **2010**, *122*, 8590 – 8594; g) J. Douglas, K. B. Ling, C. Concellón, G. Churchill, A. M. Z. Slawin, A. D. Smith, *Eur. J. Org. Chem.* **2010**, 5863 – 5869; h) T.-Y. Jian, P.-L. Shao, S. Ye, *Chem. Commun.* **2011**, *47*, 2381 – 2383; i) H.-M. Zhang, Z.-H. Gao, S. Ye, *Org. Lett.* **2014**, *16*, 3079 – 3081.

[7] Selected examples for activation of α-functionalized aldehydes by NHCs, see: a) S. S. Sohn, E. L. Rosen, J. W. Bode, *J. Am. Chem. Soc.* **2004**, *126*, 14370 – 14371; b) N. T. Reynolds, J. Read deAlaniz, T. Rovis, *J. Am. Chem. Soc.* **2004**, *126*, 9518 – 9519; c) C. Burstein, F. Glorius, *Angew. Chem. Int. Ed.* **2004**, *43*, 6205 – 6208; *Angew. Chem.* **2004**, *116*, 6331 – 6334; d) N. T. Reynolds, T. Rovis, *J. Am. Chem. Soc.* **2005**, *127*, 16406 – 16407; e) M. He, G. J. Uc, J. W. Bode, *J. Am. Chem. Soc.* **2006**, *128*, 15088 – 15089; f) S. Kobayashi, T. Kinoshita, H. Uehara, T. Sudo, I. Ryu, *Org. Lett.* **2009**, *11*, 3934 – 3937; g) H. U. Vora, T. Rovis, *J. Am. Chem. Soc.* **2010**, *132*, 2860 – 2861; h) Q. Ni, H. Zhang, A. Grossmann, C. C. J. Loh, C. Merkens, D. Enders, *Angew. Chem. Int. Ed.* **2013**, *52*, 13562 – 13566; *Angew. Chem.* **2013**, *125*, 13806 – 13811; i) J. E. Taylor, D. S. B. Daniels, A. D. Smith, *Org. Lett.* **2013**, *15*, 6058 – 6061; j) S. R. Yetra, T. Kaicharla, S. S. Kunte, R. G. Gonnade, A. T. Biju, *Org. Lett.* **2013**, *15*, 5202 – 5205; k) A. T. Davies, J. E. Taylor, J. Douglas, C. J. Collett, L. C. Morrill, C. Fallan, A. M. Z. Slawin, G. Churchill, A. D. Smith, *J. Org. Chem.* **2013**, *78*, 9243 – 9257; l) H.-M. Zhang, H. Lv, S. Ye, *Org. Biomol. Chem.* **2013**, *11*, 6255 –

6257; m) S. R. Yetra, T. Roy, A. Bhunia, D. Porwal, A. T. Biju, *J. Org. Chem.* **2014**, *79*, 4245 – 4251; n) Q. Ni, X. Song, G. Raabe, D. Enders, *Chem. Asian J.* **2014**, *9*, 1535 – 1538; o) H.-M. Zhang, W.-Q. Jia, Z.-Q. Liang, S. Ye, *Asian J. Org. Chem.* **2014**, *3*, 462 – 465.

[8] Selected examples for activation of enals by NHCs, see: a) M. He, J. R. Struble, J. W. Bode, *J. Am. Chem. Soc.* **2006**, *128*, 8418 – 8420; b) M. Wadamoto, E. M. Phillips, T. E. Reynolds, K. A. Scheidt, *J. Am. Chem. Soc.* **2007**, *129*, 10098 – 10099; c) E. M. Phillips, M. Wadamoto, A. Chan, K. A. Scheidt, *Angew. Chem. Int. Ed.* **2007**, *46*, 3107 – 3110; *Angew. Chem.* **2007**, *119*, 3167 – 3170; d) Y. Li, X.-Q. Wang, C. Zheng, S.-L. You, *Chem. Commun.* **2009**, 5823 – 5825; e) J. Kaeobamrung, M. C. Kozlowski, J. W. Bode, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 20661 – 20665; f) V. Nair, R. R. Paul, K. C. Seetha Lakshmi, R. S. Menon, A. Jose, C. R. Sinu, *Tetrahedron Lett.* **2011**, *52*, 5992 – 5994; g) X. Fang, X. Chen, Y. R. Chi, *Org. Lett.* **2011**, *13*, 4708 – 4711; h) J. Mo, L. Shen, Y. R. Chi, *Angew. Chem. Int. Ed.* **2013**, *52*, 8588 – 8591; *Angew. Chem.* **2013**, *125*, 8750 – 8753; i) E. O. McCusker, K. A. Scheidt, *Angew. Chem. Int. Ed.* **2013**, *52*, 13616 – 13620; *Angew. Chem.* **2013**, *125*, 13861 – 13865; j) H. Lv, W.-Q. Jia, L.-H. Sun, S. Ye, *Angew. Chem. Int. Ed.* **2013**, *52*, 8607 – 8610; *Angew. Chem.* **2013**, *125*, 8769 – 8772; k) X.-Y. Chen, F. Xia, J.-T. Cheng, S. Ye, *Angew. Chem. Int. Ed.* **2013**, *52*, 10644 – 10647; *Angew. Chem.* **2013**, *125*, 10838 – 10841; l) J. Izquierdo, A. Orue, K. A. Scheidt, *J. Am. Chem. Soc.* **2013**, *135*, 10634 – 10637; m) M. Wang, Z. Huang, J. Xu, Y. R. Chi, *J. Am. Chem. Soc.* **2014**, *136*, 1214 – 1217; n) X. Dong, J. Sun, *Org. Lett.* **2014**, *16*, 2450 – 2453; o) H. Ikota, T. Ishida, C. Tsukano, Y. Takemoto, *Chem. Commun.* **2014**, *50*, 8871 – 8874; p) X.-W. Fan, Y. Cheng, *Org. Biomol. Chem.* **2014**, *12*, 123 – 131; q) R. C. Johnston, D. T. Cohen, C. C. Eichman, K. A. Scheidt, P. H.-Y. Cheong, *Chem. Sci.* **2014**, *5*, 1974 – 1982.

[9] a) X. Zhao, K. E. Ruhl, T. Rovis, *Angew. Chem. Int. Ed.* **2012**, *51*, 12330 – 12333; *Angew. Chem.* **2012**, *124*, 12496 – 12499; b) J. Mo, R. Yang, X. Chen, B. Tiwari, Y. R. Chi, *Org. Lett.* **2013**, *15*, 50 – 53.

[10] J. E. Thomson, K. Rix, A. D. Smith, *Org. Lett.* **2006**, *8*, 3785 – 3788.

[11] a) S. J. Ryan, L. Candish, D. W. Lupton, *J. Am. Chem. Soc.* **2009**, *131*, 14176 – 14177; b) L. Candish, D. W. Lupton, *Org. Lett.* **2010**, *12*, 4836 – 4839; c) L. Candish, D. W. Lupton, *Org. Biomol. Lett.* **2011**, *9*, 8182 – 8189; d) L. Candish, D. W. Lupton, *Chem. Sci.* **2012**, *3*, 380 – 383; e) L. Candish, A. Levens, D. W. Lupton, *J. Am. Chem. Soc.* **2014**, *136*, 14397 – 14400; f) M. Kowalczyk, D. W. Lupton, *Angew. Chem. Int. Ed.* **2014**, *53*, 5314 – 5317; *Angew. Chem.* **2014**, *126*, 5418 – 5421; g) L. Candish, A. Levens, D. W. Lupton, *Chem. Sci.* **2015**, *6*, 2366.

[12] a) L. Hao, Y. Du, H. Lv, X. Chen, H. Jiang, Y. Shao, Y. R. Chi, *Org. Lett.* **2012**, *14*, 2154 – 2157; b) L. Hao, C. W. Chuen, R. Ganguly, Y. R. Chi, *Synlett* **2013**, 1197 – 1200; c) L. Hao, S. Chen, J. Xu, B. Tiwari, Z. Fu, T. Li, J. Lim, Y. R. Chi, *Org. Lett.* **2013**, *15*, 4956 – 4959; d) S. Chen, L. Hao, Y. Zhang, B. Tiwari, Y. R. Chi, *Org. Lett.* **2013**, *15*, 5822 – 5825; e) Z. Fu, J. Xu, T. Zhu, W. W. Y. Leong, Y. R. Chi, *Nat. Chem.* **2013**, *5*, 835 – 839; f) J. Cheng, Z. Huang, Y. R. Chi, *Angew. Chem. Int. Ed.* **2013**, *52*, 8592 – 8596; *Angew. Chem.* **2013**, *125*, 8754 – 8758; g) J. Xu, Z. Jin, Y. R. Chi, *Org. Lett.* **2013**, *15*, 5028 – 5031; h) Z. Fu, K. Jiang, T. Zhu, J. Torres, Y. R. Chi, *Angew. Chem. Int. Ed.* **2014**, *53*, 6506 – 6510; *Angew. Chem.* **2014**, *126*, 6624 – 6628.

[13] C. Simal, T. Lebl, A. M. Z. Slawin, A. D. Smith, *Angew. Chem. Int. Ed.* **2012**, *51*, 3653 – 3657; *Angew. Chem.* **2012**, *124*, 3713 – 3717.

[14] F. Recupero, C. Punta, *Chem. Rev.* **2007**, *107*, 3800 – 3842.

[15] a) B. Han, Z. Liu, Q. Liu, L. Yang, Z.-L. Liu, W. Yu, *Tetrahedron* **2006**, *62*, 2492 – 2496; b) B. Han, R.-F. Han, Y.-W. Ren, X.-Y. Duan, Y.-C. Xu, W. Zhang, *Tetrahedron* **2011**, *67*, 5615 – 5620.

[16] CCDC 1059049 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[17] Based on a study by Smith and co-workers (ref. 13), **3a** could be transferred to **4a** under photoinduced condition or thermodymic condition(120 °C). When R_3 was β-naphthyl group, sulfonyl migration reaction could be performed under autooxidation condition. Combining with our radical capture experiment (Scheme 4), we considered that this sulfonyl migration reaction may be via radical process. And the possible mechanism is being pursued in our laboratory.

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