



An Unexpected Inactivation of *N*-Heterocyclic Carbene Organic Catalyst by 1-Methylcyclopropylcarbaldehyde and 2,2,2-Trifluoroacetophenone

Yanling Chen[†], Jie Lv[†], Xuling Pan and Zhichao Jin*

State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Guizhou University, Guiyang, China

OPEN ACCESS

Edited by:

Yaqiong Su,
Xi'an Jiaotong University, China

Reviewed by:

Zhen Wang,
Chongqing University, China
Kaizhi Li,
Sichuan University, China

*Correspondence:

Zhichao Jin
zocjin@gzu.edu.cn

[†]These authors have contributed
equally to this work

Specialty section:

This article was submitted to
Organic Chemistry,
a section of the journal
Frontiers in Chemistry

Received: 14 February 2022

Accepted: 18 February 2022

Published: 24 March 2022

Citation:

Chen Y, Lv J, Pan X and Jin Z (2022) An
Unexpected Inactivation of *N*-
Heterocyclic Carbene Organic Catalyst
by 1-Methylcyclopropylcarbaldehyde
and 2,2,2-Trifluoroacetophenone.
Front. Chem. 10:875286.
doi: 10.3389/fchem.2022.875286

An unprecedented inactivation process of the indanol-derived NHC catalysts bearing *N*-C₆F₅ groups is reported. An unexpected multi-cyclic complex product is obtained from the 3-component reaction with the 1-methylcyclopropyl-carbaldehyde, the 2,2,2-trifluoroacetophenone and the NHC catalyst. The absolute structure of the inactivation product is unambiguously assigned *via* X-ray analysis on its single crystals. The formation of the structurally complex product is rationalized through a multi-step cascade cyclization process.

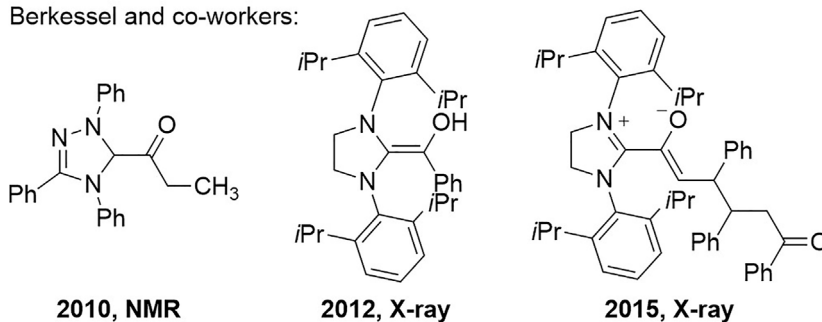
Keywords: catalyst inactivation, *N*-heterocyclic carbene, organocatalysis, 3-component reaction, multi-step cascade cyclization

INTRODUCTION

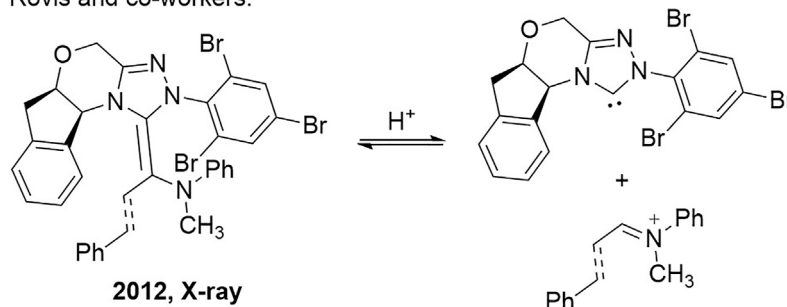
Ever since the first report from Ukai and co-workers on the thiazolium salt promoted benzoin reaction in 1943 (Ukai et al., 1943), *N*-heterocyclic carbene (NHC) has been developed and used as robust organic catalyst for more than 70 years (Breslow, 1958; Sheehan and Hunneman, 1966; Enders et al., 1995; Rovis et al., 2002). Especially, NHC organocatalysis has seen fantastic development within the past two decades (Enders et al., 2007; Lupton et al., 2013; Glorius et al., 2014; Mahatthananchai and Bode, 2014; Nair et al., 2015; Rovis et al., 2015; Scheidt et al., 2018; Chi et al., 2020; Chi et al., 2021; Wang et al., 2017). Numerous catalytic activation modes have been established within this highly active research field with a huge number of reactions realized for quick and selective access to functional molecules with interesting synthetic or biological applications. Functional molecules such as aldehydes, carboxylic acids and their derivatives, imines, ketenes, and activated ketones can be efficiently activated by NHC organic catalysts *via* formation of (*aza*)-Breslow intermediates and go through addition reactions with various electrophiles or nucleophiles through electron-pair-transfer processes (Gu et al., 2017; Yao et al., 2019; Chen et al., 2020; Yao et al., 2020; Fu et al., 2021; Xue and Zheng, 2021). Due to the rich electron densities of the Breslow intermediates formed from the NHC catalysts and the aldehyde substrates, they can be selectively oxidized by external oxidants through single-electron-transfer (SET) processes and furnished radical reactions in both enantioselective and non-chiral fashion. Recently, a couple of carbon- and heteroatom-centered nucleophiles were found to be activated by chiral NHC catalysts *via* non-covalent interactions and smoothly participate in the enantioselective addition reactions with a diversity of electrophiles (Van Halbeek and Poppe, 1991; Enders et al., 1995; Regitz, 1996; Enders,

A Isolable Breslow Intermediates with Full Characterizations:

Berkessel and co-workers:



Rovis and co-workers:

**B Stable NHC-bound Products from NHCs and Electrophiles:**

Rovis and co-workers:

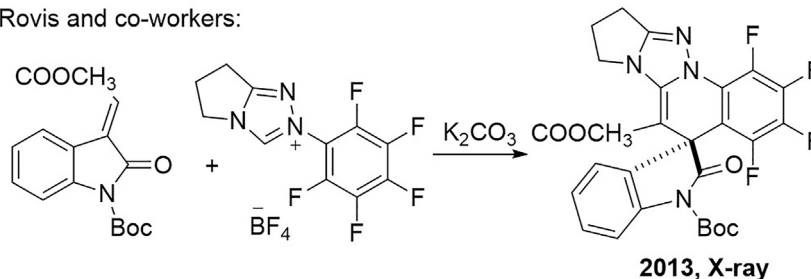
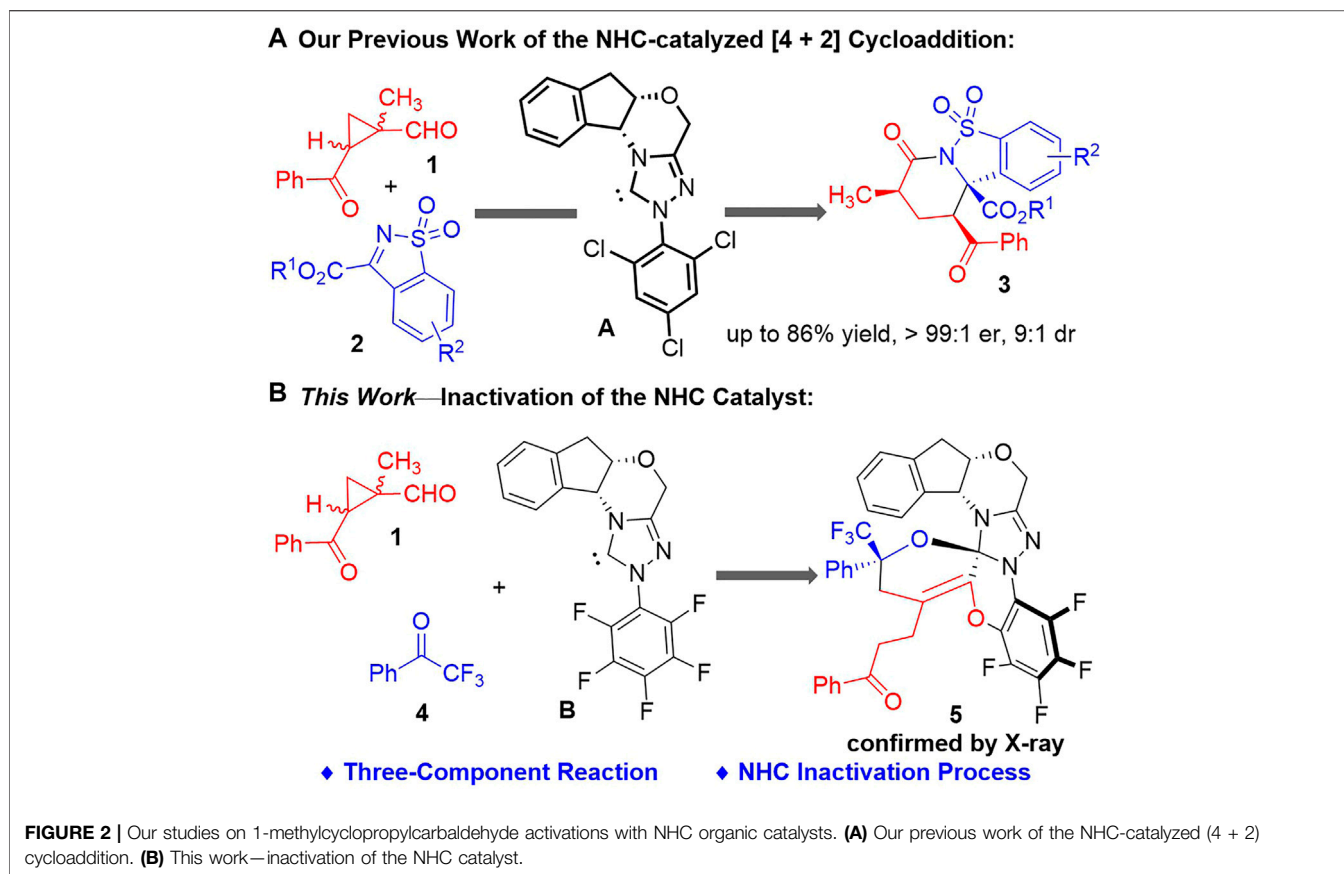


FIGURE 1 | Isolation and characterization of NHC-bound intermediates and products. **(A)** Isolable Breslow intermediates with full characterizations. **(B)** Stable NHC-bound products from NHCs and electrophiles.

2003; Bastin et al., 2019). In all the NHC-catalyzed synthetic transformations we mentioned above, mechanistic studies *via* both experimental and computational methods have played critical roles in the development and innovations of the activation modes. Therefore, the observation and characterization of the critical intermediates and/or side reaction products to provide evidence for mechanistic studies are of great significance.

Investigations into the cross-interactions between the NHC organic catalysts and the reaction substrates are one of the effective approaches for the mechanistic studies in NHC organocatalytic reactions. Continuous endeavour has been made by organic chemists towards the isolation and characterization of the most basic Breslow intermediates since it was hypothesized by Breslow in 1958 (Breslow, 1958) (**Figure 1A**). For example, Berkessel and co-workers reported

in 2010 the full NMR spectra analysis of the ketone form of the Breslow intermediate generated from the triazolium salt-derived NHC catalyst and the propionic aldehyde (Berkessel et al., 2010). They successfully isolated the crystals of the typical Breslow intermediate from an imidazolium-typed NHC catalyst and the benzaldehyde and obtained its X-ray analytical spectrum in 2012 (Berkessel et al., 2012). An advanced reaction intermediate between the α,β -unsaturated Breslow intermediate and the chalcone substrate could also be isolated as stable crystals and their structures were unambiguously assigned *via* X-ray analysis in 2015 (Berkessel et al., 2015). The single crystals of the *aza*-analogues of the Breslow intermediate were obtained by Rovis and co-workers from a chiral indanol-derived NHC catalyst and an iminium salt in 2012 (Rovis et al., 2012). They can also apply the *aza*-Breslow intermediate analogues as the NHC catalyst precursors to



promote an intramolecular Stetter reaction in enantioselective fashion.

The isolation and characterization of the NHC-bounded reaction products from the inactivation of the NHC catalysts in the reaction system can also provide significant information on the cross interactions between the NHC catalysts and the reaction substrates. Although the formation of the NHC-bounded side reaction products might be sometimes observed during the investigations of various NHC organocatalytic transformations, to the best of our knowledge, there has been very limited reports on the characterization of those NHC-bounded reaction products (Berkessel et al., 2013; Berden et al., 2021). A representative study was from Rovis and co-workers in 2013, when they reported a cascade cyclization reaction between the triazolium NHC catalyst bearing an *N*-pentafluorophenyl (*N*-C₆F₅) group and the isatin-derived α,β -unsaturated ester substrate (Rovis et al., 2013) (**Figure 1B**). The spirocyclic product was characterized *via* X-ray analysis on the product crystals.

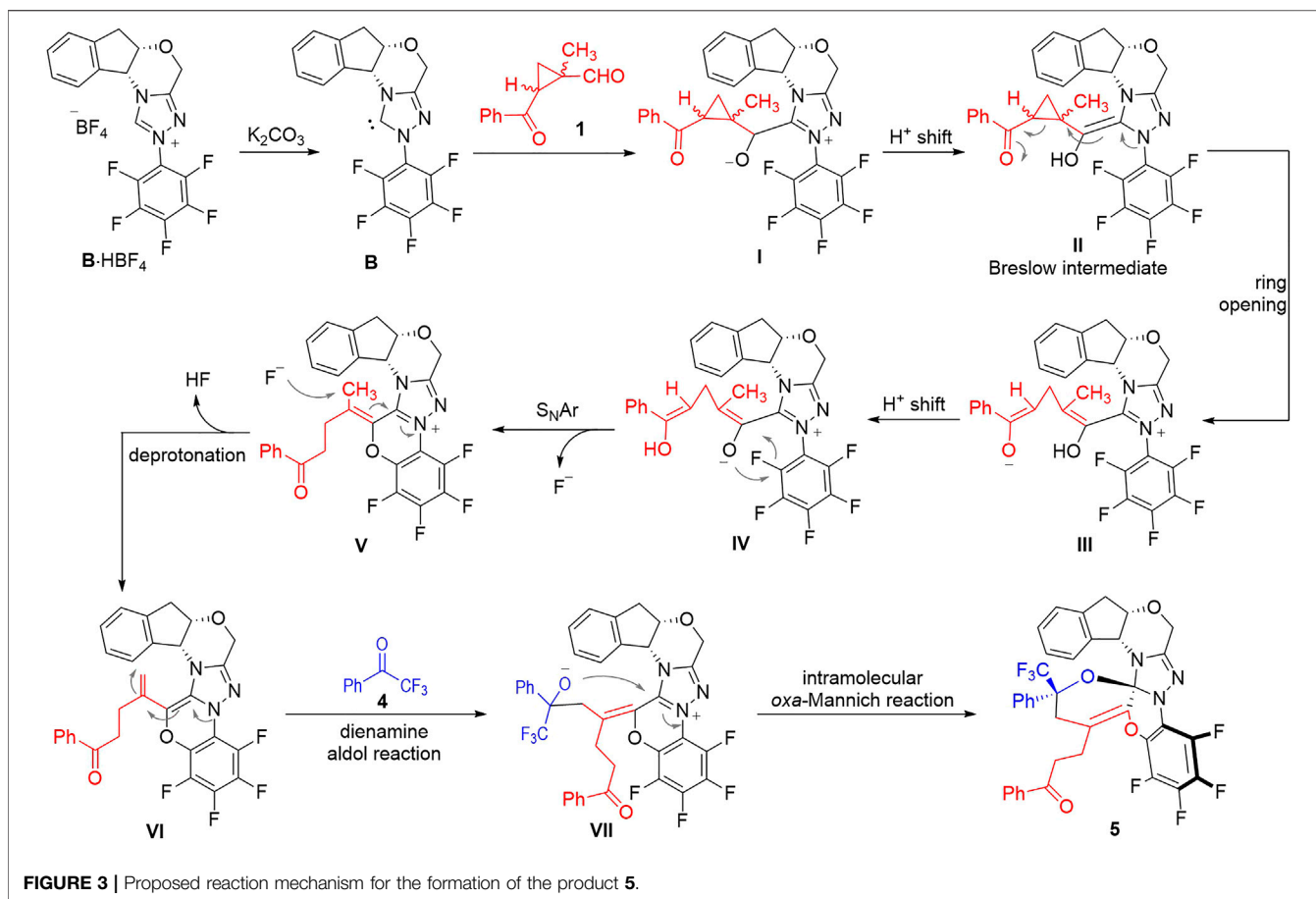
We have previously reported an NHC-catalyzed asymmetric (4 + 2) cycloaddition reaction between 1-methylcyclopropylcarbaldehyde **1** (Chi et al., 2011; Mu et al., 2020; Tong et al., 2021; Wang et al., 2021) and the cyclic sulfonimides **2** (Xu et al., 2013; Wang et al., 2020a; Wang et al., 2020b; Liu et al., 2021) to give a variety of multi-functionalized fused cyclic products **3** in

TABLE 1 | Optimization of reaction conditions^a.

Entry	Base	Equiv. Of base	T (°C)	Solvent	Yield (%) ^b
1	Et ₃ N	1.0	30	THF	12
2	DBU	1.0	30	THF	21
3	Cs ₂ CO ₃	1.0	30	THF	34
4	Cs ₂ CO ₃	1.0	30	DCM	<5
5	Cs ₂ CO ₃	1.0	30	CHCl ₃	<5
6	Cs ₂ CO ₃	1.0	30	MeCN	<5
7	Cs ₂ CO ₃	0.8	30	THF	31
8	Cs ₂ CO ₃	1.5	30	THF	27
9	Cs ₂ CO ₃	1.0	50	THF	34

^aUnless otherwise specified, the reactions were carried using **1** (0.05 mmol), **4** (0.05 mmol), **B**·HBF₄ (0.05 mmol), base, 4 Å MS (50.0 mg), solvent (1.0 ml) at the given temperature for 6 h.

^bIsolated yield of **5**.



moderate to good yields with generally excellent enantio- and diastereoselectivities (Lv et al., 2021) (**Figure 2A**). Indanol-derived NHC catalysts bearing electron-deficient *N*-substituents were found effective for this transformation. However, during the evaluations of different chiral NHC catalysts, we noticed that switching the indanol-derived NHC catalyst **A** (Rovis et al., 2012) to the NHC catalyst **B** (Enders and Balensiefer, 2004) bearing an *N*-C₆F₅ group resulted in a significant drop of the product yields (from 72% with **A** to 36% with **B**), with multiple unidentifiable by-products formed in low yields.

After completion of our studies on the chiral NHC-catalyzed [4 + 2] cycloaddition reactions. We continue to focus on the side products formed with the NHC catalyst **B** bearing an *N*-C₆F₅ group (**Figure 2B**). To our delight, a crystalline product could be isolated from the reaction system consisted of the 1-methylcyclopropyl-carbaldehyde **1**, the 2,2,2-trifluoroaceto-phenone **4** (Su et al., 2017) and the NHC catalyst **B**. An unexpected crystal structure of **5** was assigned by X-ray analysis, with all the three components combined within one molecule.

RESULTS AND DISCUSSION

Having obtained the crystal structure of the NHC-bounded compound **5**, we went on to optimize the reaction condition

in order to improve the yield of the structural complex product **5** (**Table 1**). The raw materials of the 1-methylcyclopropyl-carbaldehyde **1**, the 2,2,2-trifluoroacetophenone **4** and the NHC catalyst **B** were initially stirred in THF at room temperature in the presence of a stoichiometric amount of Et₃N, with the product of **5** obtained in 12% yield (**Table 1**, entry 1). The yield of the target product **5** could be improved when switching Et₃N in to stronger bases such as DBU and Cs₂CO₃ (entries 2-3). Solvents other than THF we tested were not effective for this transformation (e.g., entries 4-6). The attempts to improve the reaction yield by adding more or less amount of basic additives were failed (entries 7-8). Further increasing the reaction temperature resulted in the formation of the target product with the same yield.

The formation of the structurally complex product **5** is rationalized through a multi-step cascade cyclization process among the three components of the 1-methylcyclopropyl-carbaldehyde **1**, the 2,2,2-trifluoroacetophenone **4** and the NHC catalyst **B** (**Figure 3**). After deprotonation of the NHC pre-catalyst, the free NHC **B** can attack the aldehyde **1** to give the adduct **I**, which can isomerize to give the Breslow intermediate **II** via an intramolecular proton shift process. The Breslow intermediate **II** can go through a ring-opening process to give the zwitterionic intermediate **III** that is in equilibrium with the intermediate **IV** through intramolecular proton transfer processes.

The oxide anion of the intermediate **IV** can attack the electron-deficient pentafluorophenyl group to form a 6-membered ring *via* an intramolecular O-addition/elimination (S_NAr) process to give the intermediate **V**. The intermediate **V** bears an α,β -unsaturated iminium ion moiety that can easily be deprotonated by the F^- anion to form the dienamine intermediate **VI**. A dienamine aldol reaction between the intermediate **VI** and the 2,2,2-trifluoroacetophenone **4** gives the adduct **VII**, which can further cyclize to afford the final product **5** *via* an intramolecular *oxa*-Mannich reaction process.

It is worth noting that the formation of the structurally complex compound **5** is a highly stereospecific process. Only one diastereomer is observed in all the experiments we carried out. This is probably due to the steric match/mismatch effects provided by the chiral NHC scaffold we used in this transformation.

CONCLUSION

In summary, we have disclosed an unprecedented inactivation process of NHC organic catalysts bearing $N-C_6F_5$ groups. A structurally complex multi-cyclic compound was obtained from the 3-component reaction of the 1-methylcyclopropyl-carbaldehyde, the 2,2,2-trifluoroacetophenone and the NHC catalyst bearing an $N-C_6F_5$ group. The absolute structure of the complex product was unambiguously assigned *via* X-ray analysis on its single crystals. The current study can provide novel inspections into the possible pathways that are taking place in the reactions promoted by NHC catalysts bearing $N-C_6F_5$ groups. Further investigations into the interactions between the NHC organic catalysts and various reaction substrates are in progress in our laboratories.

REFERENCES

- Bastin, S., Pallova, L., Morantin, M. E., Lafitte, T., Huynh, M., Barthes, C., et al. (2019). N-Heterocyclic Carbenes as Key Intermediates in the Synthesis of Fused, Mesoionic, Tricyclic Heterocycles. *Chem. Eur. J.* 25, 13030–13036. doi:10.1002/chem.201903242
- Berden, G., Peckelsen, K., Thomulka, T., Martens, J., Paul, M., Oomens, J., et al. (2021). Breslow Intermediates (Amino Enols) and Their Keto Tautomers: First Gas-Phase Characterization by IR Ion Spectroscopy. *Chem. Eur. J.* 27, 2662–2669. doi:10.1002/chem.202003454
- Berkessel, A., Elfert, S., Etzenbach-Effers, K., and Teles, J. H. (2010). Aldehyde Umpolung by N-Heterocyclic Carbenes: NMR Characterization of the Breslow Intermediate in its Keto Form, and a Spiro-Dioxolane as the Resting State of the Catalytic System. *Angew. Chem. Int. Edition* 49, 7120–7124. doi:10.1002/anie.200907275
- Berkessel, A., Elfert, S., Yatham, V. R., Neudörfl, J.-M., Schlörer, N. E., and Teles, J. H. (2012). Umpolung by N-Heterocyclic Carbenes: Generation and Reactivity of the Elusive 2,2-Diamino Enols (Breslow Intermediates). *Angew. Chem. Int. Ed.* 51, 12370–12374. doi:10.1002/anie.201205878
- Berkessel, A., Neudörfl, J.-M., Schlörer, N. E., and Yatham, V. R. (2015). Carbene Catalyzed Umpolung of α,β -enals: a Reactivity Study of Diamino Dienols vs. Azolium Enolates, and the Characterization of Advanced Reaction Intermediates. *Chem. Sci.* 6, 3706–3711. doi:10.1039/c5sc01027f
- Berkessel, A., Yatham, V. R., Elfert, S., and Neudörfl, J.-M. (2013). Characterization of the Key Intermediates of Carbene-Catalyzed Umpolung by NMR Spectroscopy and X-ray Diffraction: Breslow Intermediates, Homo-enolates,

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

YC and JL conducted most of the experiments and contributed equally to this work. XP contributed to some work in manuscript writing. ZJ conceptualized and directed the whole project. ZJ drafted the manuscript. All of the authors contributed in scientific discussions.

ACKNOWLEDGMENTS

We acknowledge financial support from the National Natural Science Foundation of China (21961006, 32172459), the Science and Technology Department of Guizhou Province [Qiankehejichu-ZK (2021) Key033], the Program of Introducing Talents of Discipline to Universities of China (111 Program, D20023) at Guizhou University, Frontiers Science Center for Asymmetric Synthesis and Medicinal Molecules, Department of Education, Guizhou Province [Qianjiaohu KY (2020)004] and Guizhou University (China).

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2022.875286/full#supplementary-material>

and Azolium Enolates. *Angew. Chem. Int. Ed.* 52, 11158–11162. doi:10.1002/anie.201303107

Breslow, R. (1958). On the Mechanism of Thiamine Action. IV.1 Evidence from Studies on Model Systems. *J. Am. Chem. Soc.* 80, 3719–3726. doi:10.1021/ja01547a064

Chen, F., Wang, H. J., Zhang, W., and Tang, P. (2020). Asymmetric Catalytic Hydrogenation of Imines and Enamines in Natural Product Synthesis. *Green. Synth. Catal.* 1, 2666–5549. doi:10.1016/j.gresc.2020.05.006

Chi, Y. R., Mo, J., Fang, X., and Lv, H. (2011). Formal Diels-Alder Reactions of Chalcones and Formylcyclopropanes Catalyzed by Chiral N-Heterocyclic Carbenes. *Org. Lett.* 13, 5366–5369. doi:10.1021/ol202250s

Chi, Y. R., Wang, H., Jin, Z., and Chen, X. (2020). N-Heterocyclic Carbene Organocatalysis: Activation Modes and Typical Reactive Intermediates. *Chin. J. Chem.* 38, 1167–1202. doi:10.1002/cjoc.202000107

Chi, Y. R., Wang, H., Jin, Z., and Yang, X. (2021). Development of Green and Low-Cost Chiral Oxidants for Asymmetric Catalytic Hydroxylation of Enals. *Green. Synth. Catal.* 2, 295–298. doi:10.1016/j.gresc.2021.05.002

Dirocco, D. A., and Rovis, T. (2012). Catalytic Asymmetric α -Acylation of Tertiary Amines Mediated by a Dual Catalysis Mode: N-Heterocyclic Carbene and Photoredox Catalysis. *J. Am. Chem. Soc.* 134, 8094–8097. doi:10.1021/ja3030164

Enders, D. (2003). Preparation and Application of 1,3,4-Triphenyl-4,5-Dihydro-1h-1,2,4-Triazol-5-Ylidene, A Stable Carbene. *Synthesis* 2003, 1292–1295. doi:10.1055/s-2003-3940910.1002/chin.200341135

Enders, D., and Balensiefer, T. (2004). Nucleophilic Carbenes in Asymmetric Organocatalysis. *Acc. Chem. Res.* 37, 534–541. doi:10.1021/ar030050j

Enders, D., Breuer, K., Raabe, G., Runsink, J., Teles, J. H., Melder, J.-P., et al. (1995). Preparation, Structure, and Reactivity of 1,3,4-Triphenyl-4,5-Dihydro-1h-1,2,4-Triazol-5-Ylidene, A New Stable Carbene. *Angew. Chem. Int. Ed. Engl.* 34, 1021–1023. doi:10.1002/anie.199510211

- Enders, D., Niemeier, O., and Henseler, A. (2007). Organocatalysis by N-Heterocyclic Carbenes. *Chem. Rev.* 107, 5606–5655. doi:10.1021/cr068372z
- Fu, Z. Q., Guo, J. C., Huang, J., and Zhang, Y. X. (2021). N-heterocyclic Carbene-Catalyzed [4 + 2] Annulation of Acetates and β -Silyl Enones: Highly Enantioselective Synthesis of β -Silyl δ -Lactones. *Chin. J. Org. Chem.* 41, 4467–4475. doi:10.6023/cjoc202105002
- Glorius, F., Richter, C., Schedler, M., and Hopkinson, M. N. (2014). An Overview of N-Heterocyclic Carbenes. *Nature* 510, 485–496. doi:10.1038/nature13384
- Gu, C., Du, G., Zhang, J., and Dai, B. (2017). Strecker Reaction of Ethyl Cyanofornate with Aldimines Catalyzed by N-Heterocyclic Carbene. *Chin. J. Org. Chem.* 37, 914–919. doi:10.6023/cjoc201610029
- Liu, P., Li, X., He, J., Li, W., Yang, Z., Wei, Y., et al. (2021). TBAI-catalyzed Ring-Opening Sulfonylations of Benzothiazoles and Arylsulfonyl Hydrazides. *Green. Synth. Catal.* 2, 381–384. doi:10.1016/j.gresc.2021.08.006
- Lupton, D. W., Candish, L., and Ryan, S. J. (2013). Acyl Anion Free N-Heterocyclic Carbene Organocatalysis. *Chem. Soc. Rev.* 42, 4906–4917. doi:10.1039/c3cs35522e
- Lv, J., Xu, J., Pan, X., Jin, Z., and Chi, Y. R. (2021). Carbene-catalyzed Activation of Cyclopropylcarbaldehydes for Mannich Reaction and δ -lactam Formation: Remote Enantioselectivity Control and Dynamic Kinetic Asymmetric Transformation. *Sci. China Chem.* 64, 985–990. doi:10.1007/s11426-021-9989-1
- Mahatthananchai, J., and Bode, J. W. (2014). On the Mechanism of N-Heterocyclic Carbene-Catalyzed Reactions Involving Acyl Azoliums. *Acc. Chem. Res.* 47, 696–707. doi:10.1021/ar400239v
- Mu, W., Dou, L., and Liu, W. (2020). Recent Progress On[3+2] Ring-Expansion Reaction of Cyclopropane with Unsaturated Compounds. *Chin. J. Org. Chem.* 40, 1150–1176. doi:10.6023/cjoc201910019
- Nair, V., Biju, A. T., and Menon, R. S. (2015). Recent Advances in Employing Homo-enolates Generated by N-Heterocyclic Carbene (NHC) Catalysis in Carbon-Carbon Bond-Forming Reactions. *Chem. Soc. Rev.* 44, 5040–5052. doi:10.1039/c5cs00162e
- Regitz, M. (1996). Nucleophile Carbene: Eine Unglaubliche Renaissance. *Angew. Chem.* 108, 791–794. doi:10.1002/ange.19961080706
- Rovis, T., Glover, G. S., Oberg, K. M., Dalton, D. M., and Zhao, X. (2013). SNAr-Derived Decomposition By-Products Involving Pentafluorophenyl Triazolium Carbenes. *Synlett* 24, 1229–1232. doi:10.1055/s-0033-1338842
- Rovis, T., Oberg, K. M., and Dirocco, D. A. (2012). Isolable Analogues of the Breslow Intermediate Derived from Chiral Triazolylidene Carbenes. *J. Am. Chem. Soc.* 134, 6143–6145. doi:10.1021/ja302031v
- Rovis, T., Read de Alaniz, J., and Kerr, M. S. (2002). A Highly Enantioselective Catalytic Intramolecular Stetter Reaction. *J. Am. Chem. Soc.* 124, 10298–10299. doi:10.1021/ja027411v
- Rovis, T., Romanov-Michailidis, F., White, N. A., and Flanigan, D. M. (2015). Organocatalytic Reactions Enabled by N-Heterocyclic Carbenes. *Chem. Rev.* 115, 9307–9387. doi:10.1021/acs.chemrev.5b00060
- Scheidt, K. A., Jaworski, A. A., and Murauski, K. J. R. (2018). A Continuing challenge: N-Heterocyclic Carbene-Catalyzed Syntheses of γ -butyrolactones. *Chem. Soc. Rev.* 47, 1773–1782. doi:10.1039/c7cs00386b
- Sheehan, J. C., and Hunneman, D. H. (1966). Homogeneous Asymmetric Catalysis. *J. Am. Chem. Soc.* 88, 3666–3667. doi:10.1021/ja00967a049
- Su, Y., Wu, L., Chong, S., Zhang, W., Huang, D., Wang, K., et al. (2017). Chiral Thiourea Catalyzed Asymmetric Henry Reaction: Construction of Stereogenic Center Bearing a CF₃ Group from 2,2,2-Trifluoroacetophenone Substrates. *Chin. J. Org. Chem.* 37, 936–942. doi:10.6023/cjoc201612006
- Tong, M., Zhang, X., Wang, Y., and Wang, Z. (2021). Advances in Reactions of Iodonium Ylides. *Chin. J. Org. Chem.* 41, 126–143. doi:10.6023/cjoc202006021
- Ukai, T., Tanaka, R., and Dokawa, T. (1943). A New Catalyst for the Acyloin Condensation. *J. Pharm. Soc. Jpn.* 63, 296–304. doi:10.1248/yakushi1881.63.6-296
- Van Halbeek, H., and Poppe, L. (1991). Nuclear Magnetic Resonance of Hydroxyl and Amido, Protons of Oligosaccharides in Aqueous Solution: Evidence for A Strong Intramolecular Hydrogen Bond in Sialic Acid Residues. *J. Am. Chem. Soc.* 113, 363–365. doi:10.1021/ja00001a055
- Wang, A., Zhou, Y., Xu, J., and Liu, H. (2017). Progress of Organic Reactions Catalyzed by N-Heterocyclic Carbenes. *Chin. J. Org. Chem.* 37, 2590–2608. doi:10.6023/cjoc201702041
- Wang, H., Gu, S., Yan, Q., Ding, L., and Chen, F.-E. (2020a). Asymmetric Catalysis in Synthetic Strategies for Chiral Benzothiazepines. *Green. Synth. Catal.* 1, 12–25. doi:10.1016/j.gresc.2020.05.005
- Wang, J., Blaszczyk, S. A., and Zhao, C. (2021). Asymmetric Reactions of N-Heterocyclic Carbene (NHC)-Based Chiral Acyl Azoliums and Azolium Enolates. *Green. Synth. Catal.* 2, 198–215. doi:10.1016/j.gresc.2021.03.003
- Wang, P., Zhao, Q., Xiao, W., and Chen, J. (2020b). Recent Advances in Visible-Light Photoredox-Catalyzed Nitrogen Radical Cyclization. *Green. Synth. Catal.* 1, 42–51. doi:10.1016/j.gresc.2020.05.003
- Xu, M.-H., Jiang, T., and Wang, H. (2013). Simple Branched Sulfur-Olefins as Chiral Ligands for Rh-Catalyzed Asymmetric Arylation of Cyclic Ketimines: Highly Enantioselective Construction of Tetrasubstituted Carbon Stereocenters. *J. Am. Chem. Soc.* 135, 971–974. doi:10.1021/ja3110818
- Xue, X.-S., and Zheng, H. (2021). Mechanism and Selectivity of N-Heterocyclic Carbene-Catalyzed Desymmetrizing [4+1] and [4+2] Annulations + 1] and [4 + 2] Annulations. *Chin. J. Org. Chem.* 41, 2530–2531. doi:10.6023/cjoc202100047
- Yao, C. S., Yang, W. H., Luo, X., and Li, S. (2019). An Efficient N-Heterocyclic Carbene (NHC)-Catalyzed Synthesis of Polysubstituted Cyclopentene. *Chin. J. Org. Chem.* 39, 140–1410. doi:10.6023/cjoc201812035
- Yao, C., Xu, J., Luo, X., Yang, W., and Li, S. (2020). Efficient N-Heterocyclic Carbene-Catalyzed Cascade Synthesis of Functionalized Naphthopyranone. *Chin. J. Org. Chem.* 40, 470–547. doi:10.6023/cjoc201905034

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's Note: All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Copyright © 2022 Chen, Lv, Pan and Jin. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.