Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.202000701

Link to VoR: https://doi.org/10.1002/adsc.202000701

10.1002/adsc.202000701

COMMUNICATION

DOI: xxxxxx((will be filled in by the editorial staff))

Diastereoselective Trapping of Transient Carboxylic Oxonium Ylides with α,β-Unsaturated 2-Acyl Imidazoles

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Received: ((will be filled in by the editorial staff))

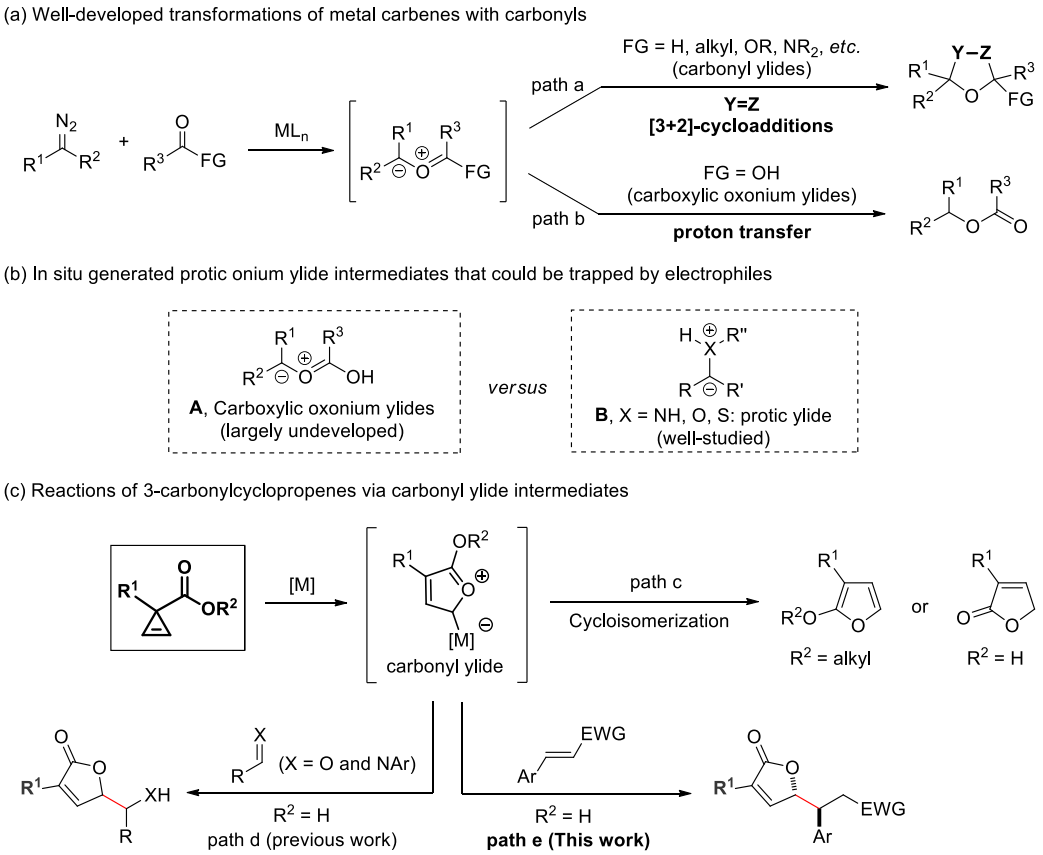
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

Abstract: By developing a diastereoselective reaction of cyclopropene carboxylic acids with α,β-unsaturated 2-acyl imidazoles, we reported here a Michael-type trapping of transient carboxylic oxonium ylides. This transformation provides a direct approach for the construction of valuable γ-butenolide derivatives in good yields (60-99%) with high diastereoselectivities (up to >95:5 dr) under mild reaction conditions.
Keywords: Ylides; Carbenes; Conjugate addition; Green chemistry; Cyclopropene; γ-Butenolide derivatives

Transition-metal-catalyzed reactions of carbenes, such as insertion and cycloaddition reactions, play a pivotal role in carbon-carbon and carbon-heteroatom bond formation.[1] Transient onium ylides, in situ generated from reaction of a metal carbene with a heteroatom in the presence of transition-metal catalysts, are generally considered as the key intermediates in the carbon-heteroatom bond formation process.[1a][1f] Interception of these intermediates could lead to many useful transformations. In this field, carbonyl ylides, one of the most common and important species generated by the interaction of carbenes with the oxygen atom of carbonyl compounds (aldehydes, ketones, esters, and amides), could be trapped by a diverse set of dipolarophiles via 1,3-dipolar cycloaddition reactions. This well-developed transformations afford powerful approaches for the construction of a variety of highly functionalized compounds (Scheme 1a, path a).[2] On the other hand, when using carboxylic acids as the carbonyl nucleophiles, the reaction would result in carboxylic oxonium ylides (Scheme 1b, **A**), which exhibit distinctly different reactivity and could undergo a rapid proton transfer rather than 1,3-dipolar cycloaddition (Scheme 1a, path b).[3] Interception of the carboxylic oxonium ylides with electrophiles would be a desirable task that could offer a direct introduction of an acyloxy moiety or construction of lactone skeletons.

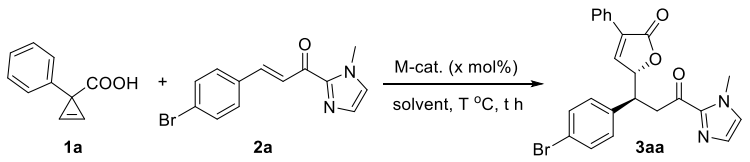
Recently, we demonstrated that transient protic oxonium ylides (Scheme 1b, **B**), formed from metal carbenes and protic heteroatoms, could be trapped by various electrophiles.[4] In this field, a wide range of novel reactions have been developed by our group[5] and others,[6] which has proven to be an efficient methodology for constructing molecular complexity and diversity in atom- and step-economic fashions. However, compared to the well-studied trapping process of protic ammonium and oxonium ylides, the interception of carboxylic oxonium ylides remains largely undeveloped.[7] This may be attributed to the higher acidity of carboxylic acids that would promote the proton transfer process and compromise the stability of this intermediates.[3c]

To facilitate the trapping process, the development of a new strategy to generate stabilized carboxylic oxonium ylides should be a key approach. As emerging synthons, 3-carbonylcyclopropenes have been used for the synthesis multisubstituted *O*-heterocycles.[8] Typically, transition metal-induced cycloisomerization reactions of cyclopropene carboxylates readily give rise to 2-alkoxyfurans, in which the carbon-carbon double bond conjugated cyclic carbonyl ylides were proposed as the key intermediate (Scheme 1c, path c).[8-9] While the use of cyclopropene carboxylic acids as substrates could result in γ-butenolides.[10] Recently, we revealed that cyclopropene carboxylic acids could readily form cyclic carboxylic oxonium ylides, which displayed higher stability than those generated from diazo compounds and carboxylic acids (**A** in Scheme 1) due to stabilizing effect from conjugated C=C moiety, and thus could be trapped by electrophiles with reactive C=X (X = O, NAr) functionality (Scheme 1c, path d) via 1,2-addition.[11] Herein, we reported the first conjugate addition of carboxylic oxonium ylides



Scheme 1. The chemistry of carbonyl ylides.

Table 1. Optimization of the reaction conditions.[a]



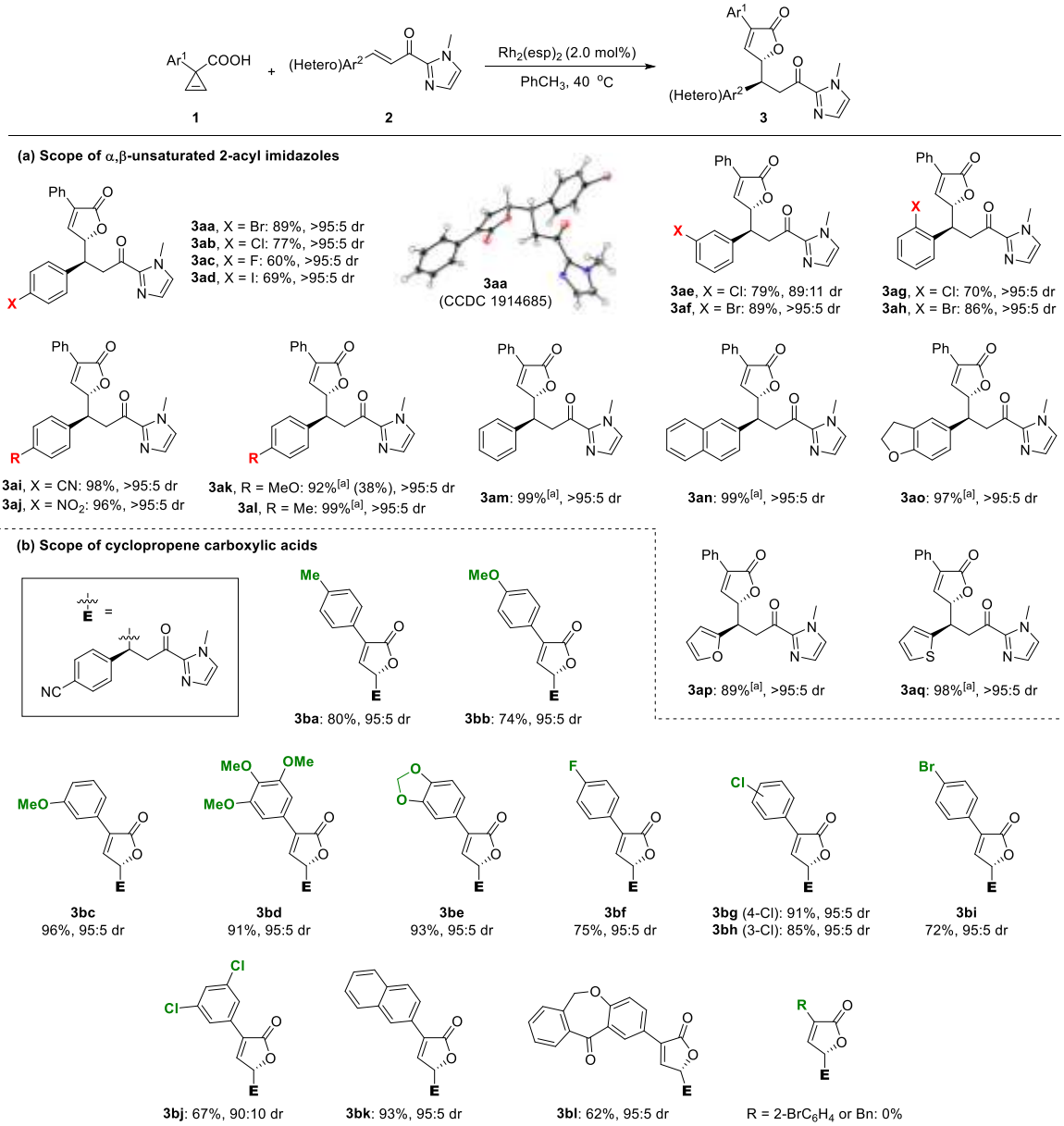
Entry	M-cat. (x)	Solvent	T/℃	t/h	Yield/%[b]	dr[c]
1	JohnPhosAu(MeCN)SbF_6 (5)	CH_2Cl_2	25	72	0	/
2	AgOTf (10)	CH_2Cl_2	25	72	0	/
3	$Cu(OTf)_2$ (10)	CH_2Cl_2	25	72	8	>95:5
4	$Rh_2(OAc)_4$ (5)	CH_2Cl_2	25	72	17	91:9
5	$Rh_2(esp)_2$ (2)	CH_2Cl_2	25	72	82	>95:5
6	$Rh_2(esp)_2$ (2)	DCE	25	72	81	>95:5
7	$Rh_2(esp)_2$ (2)	PhCl	25	72	88	>95:5
8	$Rh_2(esp)_2$ (2)	THF	25	72	27	>95:5
9	$Rh_2(esp)_2$ (2)	EtOAc	25	72	76	>95:5
10	$Rh_2(esp)_2$ (2)	toluene	25	72	87	>95:5
11	$Rh_2(esp)_2$ (2)	toluene	40	6	90 (89[d])	>95:5
12[e]	$Rh_2(esp)_2$ (2)	toluene	40	6	78	>95:5

[a] Unless otherwise indicated, reaction conditions: **1a** (0.15 mmol), **2a** (0.10 mmol), metal catalyst, solvent (1.5 mL). dr: diastereomeric ratio; JohnPhos: di-*tert*-butyl-(2-phenylphenyl)phosphane; $Rh_2(esp)_2$: bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)]; DCE: 1,2-dichloroethane; THF: tetrahydrofuran.
[b] The yields were determined by crude ^{1}H NMR using 1,3,5-trimethoxylbenzene as the internal standard.
[c] *Anti/syn*; the dr values were determined by ^{1}H NMR spectroscopy of the crude reaction mixture.
[d] Isolated yield.
[e] 0.12 mmol **1a**.

with electron-deficient olefins (Scheme 1c, path d), which affords direct construction of γ-butenolide derivatives, the privileged structures shared in numerous pharmaceuticals and natural products.[12]

We commenced the study with the reaction of cyclopropene carboxylic acid (**1a**) and α,β-unsaturated 2-acyl imidazole (**2a**). In the initial attempt, some frequently used metal catalysts in cyclopropene chemistry,[13] including JohnPhosAu(MeCN)SbF_6, $Cu(OTf)_2$, and AgOTf, were tested to promote the reaction, but almost no coupling reaction took place or very low conversion was observed (Table 1, entries 1-3). When we turned to rhodium catalysts,[14] the results revealed that $Rh_2(OAc)_4$ provided desired product **3aa** in 17% yield, while $Rh_2(esp)_2$ significantly improved the yield to 82% and excellent diastereoselectivity (entries 4-5). Subsequently, with using $Rh_2(esp)_2$ as catalyst, the reaction was evaluated in a variety of solvents (entries 6-10). The less toxic toluene was chosen for further optimizations. Since the reaction required long time (72 hours), to enhance the reactivity, the reaction was warmed to 40 °C. The results indicated that reaction time could be reduced down to 6 hours and **3aa** could be obtained in 90% (entry 11). In addition, a reduced stoichiometry in cyclopropene carboxylic acid **1a** resulted in a lower yield (entry 12). Therefore, the conditions listed in Table 1, entry 11 were selected as the optimal ones.

With the optimal reaction conditions in hand, the scope of α,β-unsaturated 2-acyl imidazoles was firstly investigated (Scheme 2a). We were delighted to observe that halide substituents (F, Cl, Br, I) at *para*-

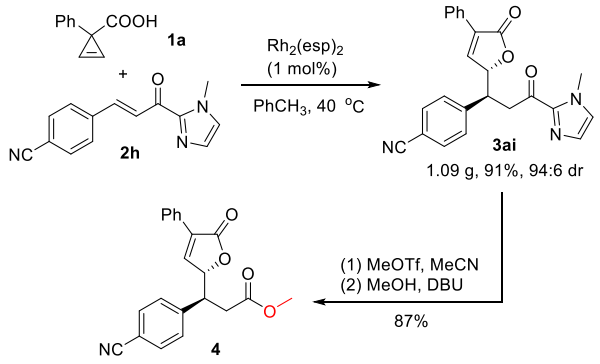


Scheme 2. Scope of substrates. Isolated yields are provided. The dr values were determined by ^{1}H NMR spectroscopy referring to the crude reaction mixture. [a] 3.0 equiv. of **1a** was used.

position (**3aa**-**3ad**), *meta*-position (**3ae**-**3af**), and *ortho*-position (**3ag**-**3ah**) were well tolerated and the corresponding trapping products were obtained in good to high yields (61-89%). In the case of substrates containing a strong electron-withdrawing group (EWG; CN, NO_2) at *para*-position, the corresponding products (**3ai**-**3aj**) could be isolated in excellent yields (96-98%). When switching the substituent from the electron-withdrawing groups to the electron-donating one (EDG; MeO), only moderate yield (38%) of product (**3ak**) was isolated owing to the lower reactivity of substrate, but the yield could be enhanced to 92% by increasing the amount of **1a** to 3.0 equiv. Similarly, other substrates without an EWG also could lead to corresponding products (**3al**-**3ao**) in high yields (up to 99%) by this modification of reaction conditions. Furthermore, heterocyclic substrates also worked well and provided excellent results (**3ap**-**3aq**). Notably, high diastereoselectivities (>95:5 dr) were obtained for most substrates, and the relative configuration was determined by X-Ray single crystal analysis of **3aa**.[15]

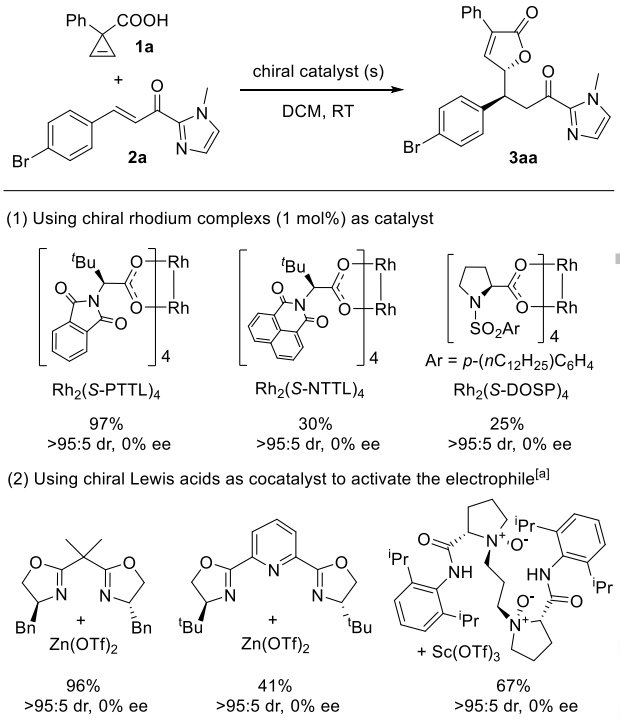
The generality of cyclopropene carboxylic acids was then assessed under the reaction conditions (Scheme 2b). Substrates bearing both EDGs and EWGs at *m*- and *p*-positions proceeded smoothly in the reaction and afforded substituted γ-butenolide derivatives (**3ba**-**3bj**) in good to excellent yields with high diastereoselectivities (>95:5 dr for most cases). As a limitation, the cyclopropene carboxylic acids with an *ortho*-bromide phenyl or a benzyl group didn't work and no reaction took place, probably due to the steric hindrance and low reactivity, respectively.

To illustrate the synthetic utility of this transformation, a gram-scale synthesis was performed with a reduced loading of $Rh_2(esp)_2$ (1.0 mol%), which provided **3ai** in 91% yield (1.09 g) with 94:6 dr (Scheme 3). Furthermore, the imidazole moiety could be removed and transformed into methyl ester under the conditions of MeOTf/MeCN and MeOH/DBU, sequentially, in 87% yield.



Scheme 3. Gram-scale synthesis and transformation of product **3ai**. The dr value was determined by ^{1}H NMR spectroscopy of crude mixture.

We then investigated the catalytic asymmetric reaction of **1a** and **2a** by using several chiral rhodium catalysts. As outlined in Scheme 4, Rh_2(*S*-PTTL)$_4$ could afford **3aa** in 97% yield, while Rh_2(*S*-NTTL)$_4$ and Rh_2(*S*-DOSP)$_4$ were less effective and low yields of desired product were obtained. All chiral rhodium catalysts tested gave high diastereoselectivities, but resulted in racemic products. These results suggested

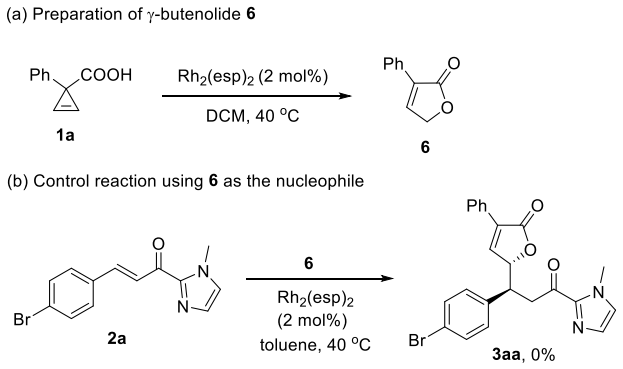


Scheme 4. Attempted asymmetric reactions. The yields were determined by crude ^{1}H NMR using 1,3,5-trimethoxylbenzene as the internal standard; the dr value was determined by ^{1}H NMR spectroscopy of the crude reaction mixture; the ee value was determined by HPLC analysis using a chiral stationary phase. [a] 4 mol% $Rh_2(esp)_2$ was used to activate the cyclopropenes.

that the rhodium catalysts are not involved in the step of nucleophilic addition to α,β-unsaturated 2-acyl imidazole, and the non-metal associated ylide intermediate is more likely. Alternatively, We also tried the asymmetric reaction using in situ-generated chiral Lewis acids to activate α,β-unsaturated 2-acyl imidazole,[16] including chiral bisoxazoline/Zn(OTf)$_2$ complex (Box-Zn), chiral pyridine-2,6-bisoxazolines/Zn(OTf)$_2$ complex (PyBox-Zn), and chiral N,N'-dioxide/Sc(OTf)$_3$ complex, but the strategy also failed to induce asymmetric reaction.[17]

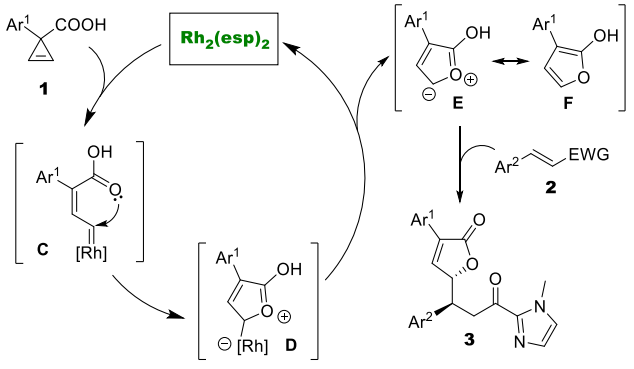
Moreover, to further explore the reaction pathway, we carried out the control experiment using preformed γ-butenolide as nucleophile (Scheme 5). Firstly, in the absence of electrophile **2a**, $Rh_2(esp)_2$ could transform cyclopropene carboxylic acid **1a** into insertion product **6** in 40% yield as an off-white solid.

When **6** and **2a** were subjected to the reaction conditions, **3aa** was not observed, and both **6** and **2a** stayed unreacted. The result indicated that **6** was not the reactive nucleophile, and an active intermediate, such as carboxylic oxonium ylide, was the more likely one.



Scheme 5. Control experiment.

According to the control reaction and previous studies on 3-carbonylcyclopropenes[8-11] as well as the ylide trapping process,[5] a reaction mechanism is outlined in Scheme 6. Rhodium-induced ring-opening of cyclopropenes **1** generates electrophilic vinyl carbene **C**, followed by intramolecular attack by the tethered carboxylic group to give cyclic carboxylic oxonium ylides **D**. Release of the rhodium catalyst will lead to the non-metal associated ylide **E** and its resonance structure **F**, which is captured by the electron-deficient olefins **2** via Michael addition to result in the γ-alkyl γ-butenolides **3**.



Scheme 6. Proposed reaction mechanism.

In summary, we have developed a rhodium-catalyzed trapping process of transient carboxylic oxonium ylides formed from cyclopropene carboxylic acids with a series of α,β-unsaturated 2-acyl imidazoles. Specifically, this reaction affords a de novo access to valuable γ-substituted γ-butenolide derivatives in good to excellent yields (60-99%) with excellent diastereoselectivities (up to >95:5 dr), under very simple, mild reaction conditions. Gram scale synthesis is also performed and the imidazole moiety of the product could be removed. Importantly, this study presents the first trapping of carboxylic oxonium ylides via Michael addition, and provides a new approach for the development of new transformations via interception of transient carboxylic oxonium ylides.

Experimental Section

Experimental procedure for the synthesis of 3aa: 1-phenylcycloprop-2-ene-1-carboxylic acid **1a** (48 mg, 0.30 mmol, 1.5 equiv.), (*E*)-3-(4-bromophenyl)-1-(1-methyl-1*H*-imidazol-2-yl)prop-2-en-1-one **2a** (58.2 mg, 0.20 mmol, 1.0 equiv.) and $Rh_2(esp)_2$ (3.0 mg, 2.0 mol%) were loaded in an oven-dried test tube with a stirring bar. Toluene (3.0 mL) was then added, and the mixture was stirred at 40 °C (oil bath). Upon completion of the reaction monitored by TLC (about 6 h), the mixture was concentrated to give a residue which was subjected to ^{1}H NMR spectroscopy for the determination of diastereoselectivity (dr value). Purification of the crude products by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10/1~3/1) afforded (*S**)-5-((*S**)-1-(4-bromophenyl)-3-(1-methyl-1*H*-imidazol-2-yl)-3-oxopropyl)-3-phenylfuran-2(5*H*)-one **(3aa)** as a white solid (79.8 mg, 89% yield).

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 21901259), Guangdong Basic and Applied Basic Research Foundation (No. 2020A1515011116), and the Program for Guangdong Introducing Innovative and Entrepreneurial Teams (No. 2016ZT06Y337).

References

[1] a) M. P. Doyle, M. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*, *Wiley*, **1998**; b) F. Z. Dorwald, *Metal Carbenes in Organic Synthesis*, *Wiley-VCH*, **1999**; c) G. Bertrand, *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*, *CRC Press*, **2002**; d) R. A. Moss, M. P. Doyle, *Contemporary Carbene Chemistry*, *John Wiley & Sons*, **2014**; e) Y. Xia, D. Qiu, J. Wang, *Chem. Rev.* 2017, **117**, 13810–13889; f) S.-F. Zhu, Q.-L. Zhou, *Acc. Chem. Res.* **2012**, *45*, 1365–1377; g) A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire, M. A. McKervey, *Chem. Rev.* **2015**, *115*, 9981–10080.

[2] a) A. Padwa, S. F. Hornbuckle, *Chem. Rev.* **1991**, *91*, 263–309; b) A. A Padwa, *J. Org. Chem.* **2009**, *74*, 6421–6441; c) A. Padwa, S. Bur, *Recent advances of 1,3-dipolar cycloaddition chemistry for alkaloid synthesis*. In *Advances in Heterocyclic Chemistry*, E. F. V. Scriven, C. A. Ramsden (eds), *Academic Press*, **2016**, Vol. 119; d) D. M. Hodgson, T. Brückl, R. Glen, A. H. Labande, D. A. Selden, A. G. Dossetter, A. J.

Redgrave, *Proc. Natl. Acad. Sci. USA*, **2004**, *101*, 5450–5454; e) A. DeAngelis, M. T. Taylor, J. M. Fox, *J. Am. Chem. Soc.* **2009**, *131*, 1101–1105.

[3] a) S. Bertelsen, M. Nielsen, S. Bachmann, K, A. Jørgensen, *Synthesis.* **2005**, *13*, 2234–2238; b) A. C. Hunter, S. C. Schlitzer, I. Sharma, *Chem. Eur. J.* **2016**, *22*, 16062–16065; c) F. Tan, X. Liu, X. Hao, Y. Tang, L. Lin, X. Feng, *ACS Catal.* **2016**, *6*, 6930−6934; d) Y. Zhang, Y. Yao, L. He, Y. Liu, L. Shi, *Adv. Synth. Catal*. **2017**, *359*, 2754–2761.

[4] a) Y. Wang, Y. Zhu, Z. Chen, A. Mi, W. Hu, M. P. Doyle, *Org. Lett.* **2003**, *5*, 3923–3926; b) C.-D. Lu, H. Liu, Z.-Y. Chen, W.-H. Hu, A.-Q. Mi, *Org. Lett.* **2005**, *7*, 83–86.

[5] a) X. Guo, W. Hu, *Acc. Chem. Res*. **2013**, *46*, 2427–2440; b) D. Zhang, W. Hu, *Chem. Rec*. **2017**, *17*, 739–753; c) D. Zhang, J. Zhou, F. Xia, Z. Kang, W. Hu, *Nat. Commun*. **2015**, *6*, 5801; d) Z. Kang, Y. Wang, D. Zhang, R. Wu, X. Xu, W. Hu, *J. Am. Chem. Soc*. **2019**, *141*, 1473−1478; d) S. Liu, W. Yao, Y. Liu, Q. Wei, J. Chen, X. Wu, F. Xia, W. Hu, *Sci. Adv*. **2017**, *3*: e1602467; e) Z. Kang, D. Zhang, J. Shou, W. Hu, *Org. Lett.* **2018**, *20*, 983–986; f) D. Zhang, W. Hu, *Adv. Synth. Catal*. **2018**, *360*, 2446–2452.

[6] a) C.-Y. Zhou, J.-C. Wang, J. Wei, Z.-J. Xu, Z. Guo, K.-H. Low, & C.-M. Che, *Angew. Chem. Int. Ed.* **2012**, ***51***, 11376–11380; b) S. M. Nicolle, W. Lewis, C. J. Hayes, C. J. Moody, *Angew. Chem. Int. Ed.* **2015**, *54*, 8485–8489; c) S. K. Alamsetti, M. Spanka, C. Schneider, *Angew. Chem. Int. Ed*. **2016**, *55*, 2392–2396; d) W. Yuan, L. Eriksson, K. J. Szabó. *Angew. Chem. Int. Ed.* **2016**, *55*, 8410–8415.

[7] a) C. Zhai, D. Xing, Y. Qian, J. Ji, C. Ma, W. Hu, *Synlett.* **2014**, *25*, 1745–1750; b) T.-S. Zhang, W.-J. Hao, N.-N. Wang, G. Li, D.-F. Jiang, S.-J. Tu, B. Jiang, *Org. Lett.* **2016**, *18*, 3078–3081.

[8] a) M. Rubin, M. Rubina, V. Gevorgyan, *Chem. Rev.* **2007**, *107*, 3117−3179; b) A. V. Gulevich, A. S. Dudnik, N. Chernyak, V. Gevorgyan, *Chem. Rev.* **2013**, *113*, 3084−3213; c) Z.-B. Zhu, Y. Wei, M. Shi, *Chem. Soc. Rev*. **2011**, *40*, 5534–5563; d) P. Li, X. Zhang, M. Shi, *Chem. Commun.* **2020**, *56*, 5457–5471; e) H. Zhang, K. Wang, B. Wang, H. Yi, F. Hu, C. Li, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 13234 –13238.

[9] a) P. Müller, N. Pautex, M. P. Doyle, V. Bagheri, *Helv. Chim. Acta*.**1990**, *73*, 1233–1241; b) P. Müller, C. Gränicher. *Helv. Chim. Acta*, **1993**, *76*, 521–534; c) J. Chen, S. Ma, *Chem. Asian J.* **2010**, *5*, 2415−2421; d) S. Ma, J. Zhang, *J. Am. Chem. Soc.* **2003**, *125*, 12386–12387; e) C. Song, L. Ju, M. Wang, P. Liu, Y. Zhang, J. Wang, Z. Xu. *Chem. Eur. J.* **2013**, *19*, 3584−3589; f) C. Song, S. Dong, L. Feng, X. Peng, M. Wang, J. Wang, Z. Xu, *Org. Biomol. Chem*. **2013**, *11*, 6258–6262; g) C. Song, D. Sun, X. Peng, J. Bai, R. Zhang, S. Hou, J. Wang, Z. Xu, *Chem Commun*. **2013**, *49*, 9167–9169; h) C. Li, Y. Zeng, J. Wang, *Tetrahedron Lett*. **2009**, *50*, 2956–2959; i) X. Xie, Y. Li, J. M. Fox, *Org. Lett*. **2013**, *15*, 1500–1503.; j) J. T. Bauer, M. S. Hadfield, A.-L. Lee, *Chem. Commun*. **2008**, 6405–6407.

[10] Y. S. Rao, *Chem. Rev*. **1976**, *76*, 625–694.

[11] D. Zhang, X. Wang, M. Zhang, Z. Kang, G. Xiao, X. Xu, W. Hu, *CCS Chem*. **2020**, *2*, 432–439; (b) D. Zhang, X. Wang, M. Zhang, W. Hu, *Org. Lett*. **2020**, *22*, 14, 5600–5604.

[12] a) B. Mao, M. Fañanás-Mastral, B. L. Feringa, *Chem. Rev*. **2017**, *117*, 10502−10566; b) R. R. A. Kitson, A. Millemaggi, R. J. K. Taylor, *Angew. Chem. Int. Ed.* **2009**, *48*, 9426−9451; c) P. A. Roethle, D. Trauner, *Nat. Prod. Rep.* **2008**, *25*, 298–317; d) M. D. Delost, D. T. Smith, B. J. Anderson, J. T. Njardarson, *J. Med. Chem.* **2018**, *61*, 10996–11020; e) S. Kitania, K. T. Miyamotoa, S. Takamatsub, E. Herawatia, H. Iguchia, K. Nishitomia, M. Uchidac, T. Nagamitsuc, S. Omurad, H. Ikedab, T. Nihira, Avenolide, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 16410–16415.

[13] a) F. Miege, C. Meyer, J. Cossy, *Beilstein J. Org. Chem.* **2011**, *7*, 717–734; b) R. Vicente, *Synthesis.* **2016**, *48*, 2343–2360; c) D. T. H. Phan, V. M. Dong, *Tetrahedron.* **2013**, *69*, 5726–5731.

[14] a) A. Archambeau, F. Miege, C. Meyer, J. Cossy, *Acc. Chem. Res.* **2015**, *48*, 1021–1031; b) H. Zhang, B. Wang, H. Yi, Y. Zhang, J. Wang, *Org. Lett.* **2015**, *17*, 3322–3325; c) B. Wang, H. Yi, H. Zhang, T. Sun, Y. Zhang, J. Wang, *J. Org. Chem.* **2018**, *83***,** 1026-1032.

[15] CCDC-1914685 for **3aa** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] X. Guan, L. Yang, W. Hu, *Angew. Chem. Int. Ed.* **2010**, *49*, 2190–2192.

[17] Supporting Information contains more results of attempted asymmetric reactions.

10.1002/adsc.202000701

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Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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