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A solid-supported organocatalyst for asymmetric Mannich reaction to construct C2-quaternary indolin-3-ones†

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A simple and novel solid-supported organocatalyst from a 2-chlorotrityl chloride resin-immobilized 4-hydroxyproline was developed, and this organocatalyst has been used for the asymmetric Mannich reaction of 2-aryl-3*H*-indol-3-ones and aldehydes/ketones. A series of C2-quaternary indolin-3-ones were prepared in good yields (up to 83%) and with excellent diastereoselectivities (up to 20 : 1) and enantioselectivities (up to 99% ee). In addition, the organocatalyst can be recovered by simple filtration and also be reused for the asymmetric Mannich reaction without significant loss of catalytic efficiency.

Introduction

Organocatalysis has developed rapidly and become an important strategy in various asymmetric reactions in the past two decades, since organocatalysts are metal-free organic compounds of relatively low molecular weight and simple structure that are able to function as efficient and selective catalysts for a large variety of enantioselective transformations.[1] In 2000, List *et al.* reported the direct asymmetric aldol reaction catalyzed by proline,[2] which has become a research hotspot in the area of asymmetric catalysis because proline is a simple and cheap chiral catalyst. In this context, proline and its derivatives as powerful organocatalysts have been gradually and successfully applied to many asymmetric reactions, such as Robinson annulation,[3] Mannich reactions,[4] Michael reactions,[5] aldol reactions, Diels–Alder reactions,[6] *etc.* However, in order to achieve a high conversion rate within a reasonable reaction time, organocatalysis often requires up to 30 mol% as the loading amount of the catalyst.[7] Moreover, it is difficult to separate the organic catalyst and the product, which is not conducive to recovery and reuse, and renders the isolation wasteful and tedious. To overcome this problem, the development of immobilized, easily recyclable, and reusable organocatalysts seems to be one of the most promising strategies. The significance of using organic catalysts will be even higher if the catalyst could be effectively solid-supported, recycled and reused. As sustainably and environmentally friendly concerns, catalyst recycling and reuse are extremely important to improve the greening process of organocatalysis. Although several solid-supported prolines have been developed for some asymmetric reactions such as aldol reactions,[8] a simple and novel solid-supported proline is still highly needed to explore more asymmetric reactions.

On the other hand, C2-quaternary indolin-3-one skeletons are an important structural motif, which is widely presenting in a variety of natural products and biologically active molecules.[9] Because of its importance in structure and biological activity, there has been extensively studied on the synthetic methods of these valuable C2-quaternary indolin-3-one skeletons.[9e–i,10–15] Till now, some asymmetric synthesis of C2-quaternary indolin-3-ones have been developed from 2-substitued indoles[15] or indolin-3-ones[11–13] as substrates, including our recently developed the combinatorial catalysis of transition metal and organocatlysis to synthesize C2-quaternary indolin-3-ones from 2-substitued indoles,[16] however, most of them require proline as an organocatalyst for this asymmetric Mannich reaction but none of them has been investigated in its solid-supported format to improve this asymmetric Mannich reaction yet (Scheme 1). Therefore, to construct diverse C2-quaternary indolin-3 ketone compounds, it is necessary to further develop environmentally friendly and sustainably solid-supported organocatalysts for this asymmetric Mannich reaction. Based on our previous work, we herein report a simple and cheap synthesis for preparing 2-chlorotrityl chloride resin immobilized 4-hydroxyproline as an organocatalyst, which displayed high catalytic activity and enantioselectivity in the Mannich reaction of 2-aryl-3*H*-indol-3-ones with aldehydes and ketones (Scheme 1). Furthermore, the solid-supported

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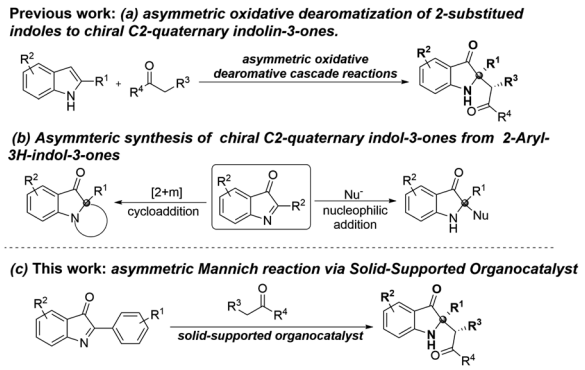


Scheme 1 Strategies for enantioselective synthesis of C2-quaternary indolin-3-ones.

organocatalyst can be conveniently recycled and reused in a green Mannich reaction protocol.

Result and discussion

Usually, a hydroxyproline or its derivative has been used as the solid-supported ligand to be immobilized onto resins by three different strategies (Fig. 1a): direct substitution using the free hydroxy group (A), or two possible combinations of azide (B) and alkyne (C) *via* "click chemistry".[8] However, the simplest method by direct substitution using free hydroxy group rendered the part of proline was too close to the solid phase, resulting in the adverse effect in the catalytic activity. Therefore, we have designed and synthesized four different solid-supported organocatalysts (**6a**, **6b**, **8a** and **8b**) by starting from the esterification of *cis*-4-hydroxyl proline and *trans*-4-hydroxyl proline with succinic anhydride before direct substitution to 2-chlorotrityl chloride resin (Fig. 1b). The detail synthesis of these solid-supported organocatalysts were shown in ESI.† *Trans*-4-hydroxy proline methyl ester **2a** was easily synthesized from the commercially available *trans-N*-Boc-4-hydroxy proline methyl ester **1a**. Compound **2a** was then reacted with *N*-(9 fluorenylmethoxycarbonyloxy)succinimide

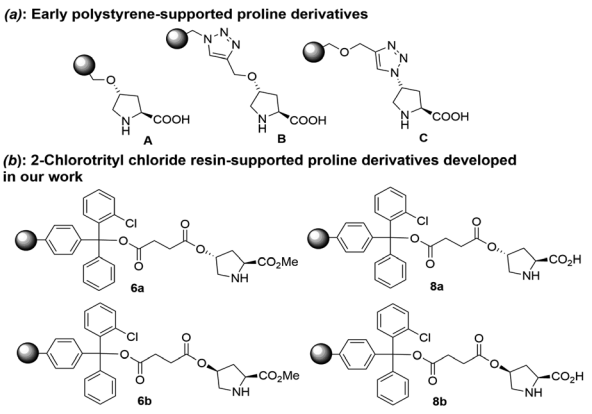
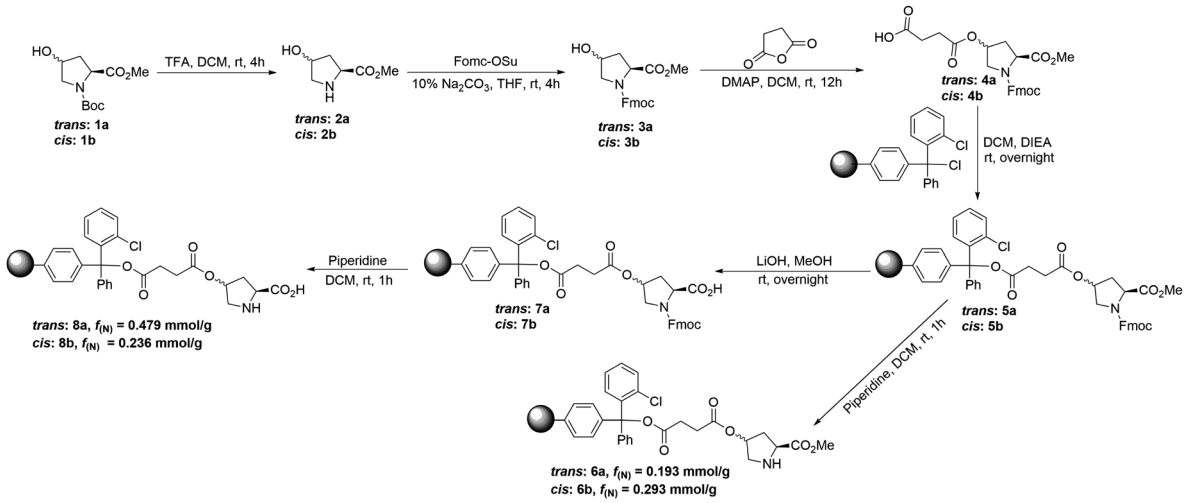


Fig. 1 (a) Early polystyrene-supported proline derivatives. (b) 2-chlorotrityl chloride resin -supported proline derivatives developed in our work.

in THF at room temperature to give the compounds **3a**. Then compound **3a** was reacted with succinic anhydride in anhydrous CH_2Cl_2 at room temperature to give the compounds **4a**, which was immobilized onto the 2-chlorotrityl chloride resin (f = 1.179 mmol g^{-1}) to give solid-supported compound **5a**. Solid-supported compounds **6a** ($f_{(N)}$ = 0.193 mmol g^{-1}) and **8a** ($f_{(N)}$ = 0.497 mmol g^{-1}) were obtained by removing Fmoc or removing Fmoc and methyl ester, respectively (Scheme 2). Using *cis-N*-Boc-4-hydroxy proline methyl ester as starting material, solid-supported compounds **6b** ($f_{(N)}$ = 0.293 mmol g^{-1}) and **8b** ($f_{(N)}$ = 0.238 mmol g^{-1}) were obtained according to the similar procedure (Scheme 2). The loading rate of these solid-supported compounds was determined by elemental analysis in ESI.†

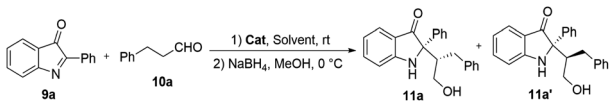
The solid-supported organocatalysts **6a**, **6b**, **8a** and **8b** were tested in the Mannich reaction of 2-aryl-3*H*-indol-3-ones **9a** and phenylpropionaldehyde **10a** and followed by reduction of an aldehyde to give the desired product **11a** (Table 1, entries 1–4). In presence of these solid-supported catalysts, all reactions gave good yields, and the solid-supported organocatalyst **8b** proved to be the best catalyst with 78% yield, 1 : 10.1 dr (*syn* : *anti*) and 93% ee for the desired product **11a** (*syn*). Although catalyst **8a** led to similar yield, diastereoselectivity and ee value for **11a**, catalyst **8b** could give a higher ee value for the diastereomer of **11a′** (Table 1, entry 4 *vs.* entry 2). Therefore, we chose catalyst **8b** to test different solvents to improve the diastereomer selectivity of desired product **11a** (*syn*) under the above conditions (Table 1, entries 5–12). Some common solvents such as DMSO, dioxane, toluene, DMF, MeCN, EtOAc, $CHCl_3$, CH_2Cl_2 and THF were used, and DMF was found to be the optimal choice and the desired product **11a** was also obtained with 66% yield and 95% ee and the *syn*/*anti* ratio was increased to 1 : 1.7. Encouraged by these results, we tested different temperatures to further increase the diastereomer selectivity of desired product **11a** (*syn*) (Table 1, entries 13–14). Experimental results show that the optimal temperature was 0 °C and the desired product **11a** was obtained with up to 81% yield and 98% ee; and the *syn*/*anti* ratio was further increased to 6.6 : 1 (Table 1, entry 13). Finally, the amount of catalyst was also investigated (Table 1, entries 15–16), and the optimal conditions were achieved as: **9a** (1.0 equiv.), **10a** (2.0 equiv.), solid-supported organocatalyst **8b** (10 mol%) and DMF as a solvent at 0 °C. Under the optimal conditions, the desired product **11a** (*syn*) was obtained with up to 79% yield, 6.3 : 1 dr (*syn* : *anti*) and 98% ee (Table 1, entry 16).

With the optimal reaction conditions in hand, we then investigated the reactions of a variety of 2-aryl-3*H*-indol-3-ones **9** and aldehydes **10** catalyzed by the solid-supported organocatalyst **8b** in DMF at 0 °C (Table 2 and 3). In general, the desired C2-quaternary indolin-3-one products **11a–11o** and **12a–12d** were obtained with up to 83% yields, >20 : 1 dr and 99% ee, the absolute configuration and structure of **12d** was unambiguously confirmed by single-crystal X-ray crystallography (Table 3).[16] The reactions of **9a** with aldehydes proceeded smoothly, affording the corresponding 2,2-disubstituted indolin-3-ones (**11a–11e**) in 48–82% yield with 6.3 : 1–11 : 1 dr and 77–98% ee. However, the slightly lower yield and poor ee was obtained for products **11e** may be due to the steric



Scheme 2 Synthesis of 2-chlorotrityl chloride resin-supported catalyst **6a**, **6b**, **8a** and **8b**.

Table 1 Optimization of reaction conditions[a]

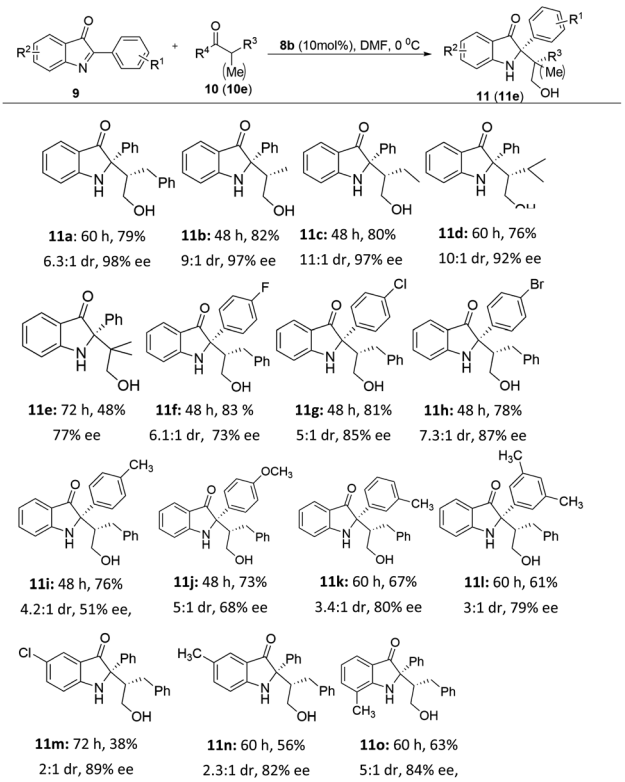


Entry	Cat.	Solvent	*t* (h)	Yield[b] (%)	dr[c] **11a** : **11a′**	ee **11a**[d] (%)	ee **11a′**[d] (%)
1	**6a**	DMSO	60	71	1 : 8.2	57	0
2	**8a**	DMSO	48	76	1 : 7.6	94	0
3	**6b**	DMSO	48	73	1 : 6.8	79	0
4	**8b**	DMSO	48	78	1 : 10.1	93	45
5	**8b**	Dioxane	60	65	1 : 2.3	47	1
6	**8b**	Toluene	48	71	1 : 1.6	39	0
7	**8b**	DMF	60	66	1 : 1.7	95	9
8	**8b**	MeCN	48	59	1 : 1.2	75	11
9	**8b**	EtOAc	48	53	1 : 2.1	81	7
10	**8b**	$CHCl_3$	48	72	1 : 1.9	55	7
11	**8b**	CH_2Cl_2	48	75	1 : 2.5	35	17
12	**8b**	THF	48	47	1.6 : 1	15	25
13[e]	**8b**	DMF	60	81	6.6 : 1	98	9
14[f]	**8b**	DMF	60	59	2.4 : 1	96	37
15[g]	**8b**	DMF	60	79	6.3 : 1	98	39
16[h]	**8b**	DMF	60	58	2.2 : 1	96	7

[a] Unless otherwise specified, the reactions were carried out with **9** (0.10 mmol), **10** (0.20 mmol), catalyst (20 mol%) in solvent (1.0 mL) at room temperature. Then the aldehyde was reduced by $NaBH_4$ was needed to give compounds **11**. [b] Combined yields of all diastereomers after flash column chromatography. [c] Determined by ^1H NMR analysis of the crude products. [d] Determined by chiral HPLC. [e] At 0 °C. [f] At −10 °C. [g] 10 mol% catalyst was used. [h] 5 mol% catalyst was used.

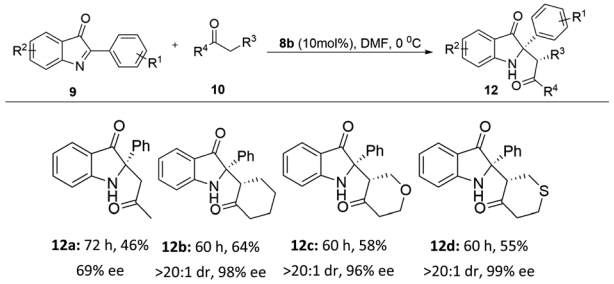
interaction of isobutyraldehyde. We next investigated the effect of different R^1 or R^2 substituent of 2-aryl-3*H*-indol-3-ones **9** on this reaction. 2-aryl-3*H*-indol-3-ones **9** with electron-donating and withdrawing substituents on the aromatic ring of indole were employed to give indolin-3-ones (**11f–11l**) in moderate to good yields (61–83%) with moderate diastereo- (3 : 1–7.3 : 1 dr) and moderate to good enantio- (51–87% ee) selectivities. Compared with electron donating groups (**11i–11j**), substrates with halide groups (**11f–11h**) have slightly higher yield and enantioselectivity. Different R^2 substituents (Cl or Me) on the aromatic ring can give **11m–11o** with 38–63% yield, 2 : 1–5 : 1 dr and 82–89% ee. The electronic effects of the R^2 substituents may have some impact on the experimental results since the yield of the substrate with an electron donating group is higher than that of the one with electron withdrawing group (**11m** *vs.* **11n**). Encouraged by the results of aldehydes, we also investigated different ketones as substrates on this Mannich reaction. Gratifyingly, the reaction of 2-aryl-3*H*-indol-3-ones **9** and ketones **10** catalyzed by the solid-supported organocatalyst **8b** in DMF at 0 °C also can give the desired compounds

Table 2 Scope of aldehydes and 2-aryl-3*H*-indol-3-ones[a]



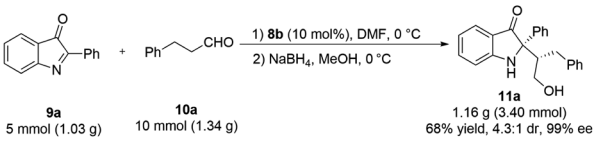
[a] Unless otherwise specified, the reactions were carried out with **9** (0.10 mmol), **10** (0.20 mmol), **8b** (10 mol%) in DMF (1.0 mL) at 0 °C. Then the aldehyde was reduced by $NaBH_4$ was needed to give compounds **11**. Combined yields of all diastereomers after flash column chromatography. The dr values were determined by ^{1}H NMR analysis of the crude products. The ee values were determined by chiral HPLC.

Table 3 Scope of ketones[a]



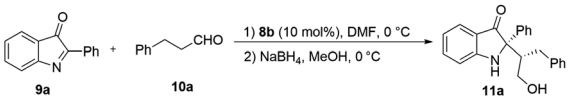
[a] Unless otherwise specified, the reactions were carried out with **9** (0.10 mmol), **10** (0.20 mmol), **8b** (10 mol%) in DMF (1.0 mL) at 0 °C. Combined yields of all diastereomers after flash column chromatography. The dr values were determined by ^{1}H NMR analysis of the crude products. The ee values were determined by chiral HPLC.

12a–12d in yields 46–64% yield with >20 : 1 dr and 69–99% ee (Table 3). These results indicated that our solid-supported organocatalyst **8b** was suitable for the application in this asymmetric Mannich reaction to construct C2-quaternary indolin-3-ones.



Scheme 3 The large-scale synthesis of product **11a**.

Table 4 Recycling and reusing[a]



Cycle	Recovery rate (%)	*t* (h)	Yield[b] (%)	dr[c]	ee[d] (%)
1	—	60	72	5.3 : 1	98
2	95	60	68	4.6 : 1	99
3	93	60	59	3.8 : 1	98
4	92	60	52	3.3 : 1	98

[a] Unless otherwise specified, the reactions were carried out with **9a** (3.87 mmol), **10a** (7.74 mmol), **8b** (10 mol%) in DMF (15 mL) at 0 °C. [b] Combined yields of all diastereomers after flash column chromatography. [c] Determined by ^{1}H NMR analysis of the crude products **11a**. [d] Determined by chiral HPLC.

To further investigate the potential application of the asymmetric Mannich reaction, the large-scale synthesis of chiral C2-quaternary indolin-3-ones **11a** was performed. Under the optimized conditions, the gram scale synthesis of chiral product **11a** can be obtained in 68% yield, 4.3 : 1 dr and 99% ee (Scheme 3). In the four cycles, the recovery rate was between 92–95%. More importantly, the ee value for each cycle rate was between 92–95%. More importantly, the ee value for each cycle was consistent as ~98% ee although the yield and dr value was slightly dropped (Table 4).

Conclusions

In summary, we have developed a simple synthesis method for preparing 2-chlorotrityl chloride resin-immobilized hydroxyproline catalyst, which has been used for the reaction of 2-aryl-3*H*-indol-3-ones with aldehydes or ketones asymmetric Mannich reaction. A series of chiral C2-quaternary indolin-3-ones were obtained *via* this strategy. In addition, the catalyst can be recovered by simple filtration, and it can also be reused at least 3 times without significant loss of catalytic efficiency. To the best of our knowledge, this is the first application of solid-supported catalyst synthesized from 2-chlorotrityl chloride resin and 4-hydroxyl proline for the construction of C2-quaternary indolin-3-one skeleton.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 (*a*) G. Guillena, C. Najera and D. J. Ramon, *Tetrahedron: Asymmetry*, 2007, **18**, 2249; (*b*) H. Pellissier, *Tetrahedron*, 2007, **63**, 9267; (*c*) G. Guillena and D. J. Ramon, *Tetrahedron: Asymmetry*, 2006, **17**, 1465; (*d*) P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2004, **43**, 5138; (*e*) B. List, *Chem. Rev.*, 2007, **107**, 5413; (*f*) R. O. Duthaler, *Angew. Chem., Int. Ed.*, 2003, **42**, 975; (*g*) E. R. Jarvo and S. J. Miller, *Tetrahedron*, 2002, **58**, 2481.

2 B. List, R. A. Lerner and C. F. Barbas III, *J. Am. Chem. Soc.*, 2000, **122**, 2395.

3 (*a*) U. Eder, G. Sauer and R. Wiechert, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 496; (*b*) Z. G. Hajos and D. R. Parrish, *J. Org. Chem.*, 1974, **39**, 161; (*c*) T. Bui and F. Barbas III, *Tetrahedron Lett.*, 2000, **41**, 6951.

4 (*a*) B. List, *J. Am. Chem. Soc.*, 2000, **122**, 9336; (*b*) A. Cordova, W. Notz, G. Zhong, J. M. Betancort and C. F. Barbas III, *J. Am. Chem. Soc.*, 2002, **124**, 1842; (*c*) B. List, P. Pojarliev, W. T. Biller and H. J. Martin, *J. Am. Chem. Soc.*, 2002, **124**, 827; (*d*) W. Notz, F. Tanaka, S. Watanabe, N. S. Chowdari, J. M. Turner, R. Thayumanavan and C. F. Barbas III, *J. Org. Chem.*, 2003, **68**, 9624; (*e*) N. S. Chowdari, J. T. Suri and C. F. Barbas III, *Org. Lett.*, 2004, **6**, 2507; (*f*) Y. Hayashi, W. Tsuboi, I. Ashimine, T. Urushima, M. Shoji and K. Sakai, *Angew. Chem., Int. Ed.*, 2003, **42**, 3677; (*g*) N. S. Chowdari, D. B. Ramachary and C. F. Barbas III, *Synlett*, 2003, **12**, 1906.

5 (*a*) B. List, P. Pojarliev and H. J. Martin, *Org. Lett.*, 2001, **3**, 2423; (*b*) J. M. Betancort and C. F. Barbas III, *Org. Lett.*, 2001, **3**, 3737; (*c*) D. Enders and A. Seki, *Synlett*, 2002, **1**, 26; (*d*) D. Gryko, *Tetrahedron: Asymmetry*, 2005, **16**, 1377; (*e*) I. K. Mangion and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2005, **127**, 3696.

6 (*a*) G. Sabitha, N. Fatima, E. V. Reddy and J. S. Yadav, *Adv. Synth. Catal.*, 2005, **347**, 1353; (*b*) R. Thayumanavan, B. Dhevalapally, K. Sakthivel, F. Tanaka and C. F. Barbas III, *Tetrahedron Lett.*, 2002, **43**, 3817; (*c*) D. B. Ramachary, N. S. Chowdari and C. F. Barbas III, *Tetrahedron Lett.*, 2002, **43**, 6743.

7 R. Martin-Rapffln, X. Fan, S. Sayalero, M. Bahramnejad, F. Cuevas and M. A. Pericas, *Eur. J. Chem.*, 2011, **17**, 8780.

8 (*a*) M. Benaglia, A. Puglisi and F. Cozzi, *Chem. Rev.*, 2003, **103**, 3401; (*b*) F. Cozzi, *Adv. Synth. Catal.*, 2006, **348**, 1367; (*c*) M. Gruttadauria, F. Giacalone and R. Noto, *Chem. Soc. Rev.*, 2008, **37**, 1666; (*d*) M. Benaglia, *New J. Chem.*, 2006, **30**, 1525; (*e*) E. Alza, C. Rodríguez-Escrich, S. Sayalero, A. Bastero and M. A. Pericàs, *Eur. J. Chem.*, 2009, **15**, 10167; (*f*) C. Rodríguez-Escrich and M. A. Pericàs, *Chem. Rec.*, 2019, **19**(9), 1872.

9 (*a*) W. Wu, M. Xiao, J. Wang, Y. Li and Z. Xie, *Org. Lett.*, 2012, **14**, 1624; (*b*) D. S. Bhakuni, M. Silvan, S. A. Matlin and P. G. Sammes, *Phytochemistry*, 1976, **15**, 574; (*c*) D. Stoermer and C. H. Heathcock, *J. Org. Chem.*, 1993, **58**, 564; (*d*) P. S. Baran and E. J. Corey, *J. Am. Chem. Soc.*, 2002, **124**, 7904; (*e*) C. Shu, L. Li, X.-Y. Xiao, Y.-F. Yu, Y.-F. Ping, J.-M. Zhou and L.-W. Ye, *Chem. Commun.*, 2014, **50**, 8689; (*f*) Y.-Q. Zhang, D.-Y. Zhu, Z.-W. Jiao, B.-S. Li, F.-M. Zhang, Y.-Q. Tu and Z. Bi, *Org. Lett.*, 2011, **13**, 3458; (*g*) Y. Goriya and C. V. Ramana, *Chem. Commun.*, 2013, **49**, 6376; (*h*) Z. Xia, J. Hu, Y.-Q. Gao, Q. Yao and W. Xie, *Chem. Commun.*, 2017, **53**, 7485; (*i*) Y.-J. Li, N. Yan, C.-H. Liu, Y. Yu and Y.-L. Zhao, *Org. Lett.*, 2017, **19**, 1160.

10 R. O. Torres-Ochoa, T. Buyck, Q. Wang and J. P. Zhu, *Angew. Chem., Int. Ed.*, 2018, **57**, 5679.

11 R.-R. Liu, S.-C. Ye, C.-J. Lu, G.-L. Zhuang, J.-R. Gao and Y.-X. Jia, *Angew. Chem., Int. Ed.*, 2015, **54**, 11205.

12 (*a*) Q. Ni, X. Song, G. Raabe and D. N. Enders, *Chem. - Asian J.*, 2014, **9**, 1535; (*b*) J. Guo, A.-H. Lin, K.-B. Chen, Y. Xie, A. S. C. Chan, J. Weng and G. Lu, *Org. Chem. Front.*, 2017, **4**, 1400; (*c*) S. Yarlagadda, B. Ramesh, C. Ravikumar Reddy, L. Srinivas, B. Sridhar and B. V. Subba Reddy, *Org. Lett.*, 2017, **19**, 170; (*d*) L.-J. Zhang, Y. Wang, X.-Q. Hu and P.-F. Xu, *Chem.–Asian J.*, 2016, **11**, 834; (*e*) S. Yarlagadda, G. S. Sankaram, S. Balasubramanian and B. V. Subba Reddy, *Org. Lett.*, 2018, **20**, 4195; (*f*) R. Dalpozzo, *Adv. Synth. Catal.*, 2017, **359**, 1772; (*g*) H. Kazahiro, M. Kouhei, K. Tamami, H. Masahiro, S. Masanori and K. Tomomi, *Heterocyles*, 2007, **73**, 641; (*h*) C. Y. Jin, Y. Wang, Y. Z. Liu, C. Shen and P. F. Xu, *J. Org. Chem.*, 2012, **77**, 11307; (*i*) T. G. Chen, P. Fang, X. L. Hou and L. X. Dai, *Synthesis*, 2015, **47**, 134; (*j*) V. P. R. Gajulapallia, E. Jafaria, D. S. Kundua, S. Mahajana, A. Peuronenb, K. Rissanenb and D. Enders, *Synthesis*, 2017, **49**, 4986; (*k*) C. Guo, M. Schedler, C.-G. Daniliuc and F. Glorius, *Angew. Chem., Int. Ed.*, 2014, **53**, 10232; (*l*) S. Yarlagadda, B. Sridhar and B.-V. Subba Reddy, *Chem. - Asian J.*, 2018, **13**, 1327; (*m*) S. Yarlagadda, C.-R. Reddy, B. Ramesh, G. Ravi kumar, B. Sridhar and B.-V.-S. Reddy, *Eur. J. Org. Chem.*, 2018, **2018**, 1364; (*n*) Y.-L. Zhao, W. Yao, J. Cao, Y.-M. Liang and P.-F. Xu, *Org. Lett.*, 2014, **9**, 2438; (*o*) Y.-L. Zhao, X.-H. Fei, Y.-Q. Tang, P.-F. Xu, F.-F. Yang, B. He, X.-Z. Fu, Y.-Y. Yang, M. Zhou, Y.-H. Mao, Y.-X. Dong and C. Li, *J. Org. Chem.*, 2019, **84**, 8168.

13 (*a*) L. Li, M. Han, M. Xiao and Z. Xie, *Synlett*, 2011, **12**, 1727; (*b*) Q. Yin and S.-L. You, *Chem. Sci.*, 2011, **2**, 1344; (*c*) A. Parra, R. Alfaro, L. Marzo, A. Moreno-Carrasco, J. L. GarcíaRuano and J. Aleman, *Chem. Commun.*, 2012, **48**, 9759; (*d*) J.-X. Liu, Q.-Q. Zhou, J.-G. Deng and Y.-C. Chen, *Org. Biomol. Chem.*, 2013, **11**, 8175; (*e*) S. Nakamura, N. Matsuda and M. Ohara, *Eur. J. Chem.*, 2016, **22**, 9478; (*f*) J.-S. Li, Y.-J. Liu, G.-W. Zhang and J.-A. Ma, *Org. Lett.*, 2017, **19**, 6364; (*g*) J.-S. Li, Y.-J. Liu, S. Li and J.-A. Ma, *Chem. Commun.*, 2018, **54**, 9151; (*h*) S.-S. Fang, S.-Y. Jin, R. Ma,

T. Lu and D. Du, *Org. Lett.*, 2019, **21**, 5211; (*i*) M. Rueping, S. Raja and A. Nunez, *Adv. Synth. Catal.*, 2011, **353**, 563.

14 (*a*) C. I. Altinis Kiraz, T. J. Emge and L. S. Jimenez, *J. Org. Chem.*, 2004, **69**, 2200; (*b*) F. Lin, Y. Chen, B. Wang, W. Qin and L. Liu, *RSC Adv.*, 2015, **5**, 37018; (*c*) C. Zhang, S. Li, F. Bures, R. Lee, X. Ye and Z. Jiang, *ACS Catal.*, 2016, **6**, 6853; (*d*) Z. Deng, X. Peng, P. Huang, L. Jiang, D. Ye and L. Liu, *Org. Biomol. Chem.*, 2017, **15**, 442; (*e*) Y. Kong, J. Zhu, Z. Chen and L. Liu, *Can. J. Chem.*, 2014, **92**, 269; (*f*) H. Huang, J. Cai, X. Ji, F. Xiao, Y. Chen and G. Deng, *Angew. Chem., Int. Ed.*, 2016, **55**, 307; (*g*) L. Kong, M. Wang, F. Zhang, M. Xu and Y. Li, *Org. Lett.*, 2016, **18**, 6124; (*h*) X. Jiang, B. Zhu, K. Lin, G. Wang, W. Su and C. Yu, *Org. Biomol. Chem.*, 2019, **17**, 2199; (*i*) M. J. Buller, T. G. Cook and Y. Kobayashi, *Heterocycles*, 2007, **72**, 163; (*j*) W. Ding, Q.-Q. Zhou, J. Xuan, T.-R. Li, L.-Q. Lu and W.-J. Xiao, *Tetrahedron Lett.*, 2014, **55**, 4648.

15 (*a*) X. Ding, C.-L. Dong, Z. Guan and Y.-H. He, *Angew. Chem., Int. Ed.*, 2019, **58**, 118; (*b*) X. Liu, X. Yan, J.-H. Yan, Y.-D. Tang, K. Wang and H. Zhang, *Org. Lett.*, 2019, **21**, 5626; (*c*) F.-Y. Lu, Y.-J. Chen, Y. Chen, X. Ding, Z. Guan and Y.-H. He, *Chem. Commun.*, 2020, **56**, 623; (*d*) C.-L. Dong, X. Ding, L.-Q. Huang, Y.-H. He and Z. Guan, *Org. Lett.*, 2020, **22**, 1076; (*e*) L. Bu, J. Li, Y. Yin, B. Qiao, G. Chai, X. Zhao and Z. Jiang, *Chem.–Asian J.*, 2018, **13**, 2382; (*f*) S. Lerch, L.-N. Unkel and M. Brasholz, *Angew. Chem., Int. Ed.*, 2014, **53**, 6558.

16 Y.-L. Zhao, J.-X. An, F.-F. Yang, X. Guan, X.-Z. Fu, Z.-Q. Li, D.-P. Wang, M. Zhou, Y.-Y. Yang and B. He, *Adv. Synth. Catal.*, 2022, DOI: 10.1002/adsc.202101498.