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Unifying Metal- and Organocatalysis for Asymmetric Oxidative Iminium Activation: A Relay Catalytic System Enabling the Combined Allylic Oxidation of Alcohols and Prolinol Ether Catalyzed Iminium Reactions

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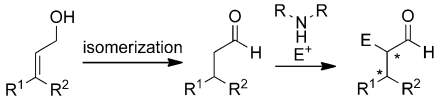
Abstract: A multicatalytic system consisting of tetrapropylammonium perruthenate/*N*-methylmorpholine *N*-oxide (TPAP/NMO) as oxidant, and diarylprolinol TMS-ether as chiral amine catalyst, has been developed and applied in the efficient construction of valuable chiral molecules. The one-pot domino reactions elaborated in the present study are based on the in situ generation of α,β-unsaturated aldehydes from allylic alcohols and their subsequent use in various asymmetric transformations (e.g., cyclopropanation, Michael addition, Michael addition/acetalization). TPAP as a substrate-selective redox catalyst is well tolerated by the amine catalyst and the domino reactions proceed in good yields and high enantioselectivities. The compatibility of metal and organocatalysis presented herein widens the scope of asymmetric iminium catalysis.

Keywords: asymmetric catalysis · cascade reactions · iminium activation · oxidation

Introduction

In organic synthesis costly protecting-group strategies and lengthy purification procedures after each synthetic step remain an obstacle. The desire to circumvent these problems has led to the development of several multi-component domino reactions.[1–2] Asymmetric one-flask combinations of multiple catalytic cycles that allow the formation of complex molecules in a small number of operational steps have attracted considerable interest within the field of organic synthetic chemistry and industrial chemistry. In addition, by designing reaction protocols where several bond forming reactions take place in one flask highly desirable demands such as, time, cost and environmental savings can be met. In this context many highly enantioselective transformations involving the combination of enamine and iminium catalysis have been reported.[1–2] However, the asymmetric one-flask combinations of multiple catalytic cycles based on the combination of a chiral organocatalyst and a achiral metal catalyst still remain a challenge.[3–5] Recently, Alexakis and Mazet reported an elegant catalytic reaction sequence for the highly asymmetric α-functionalization of aldehydes. The strategy involves the achiral iridium catalyzed isomerization of primary alcohols in the first step and the organocatalyzed α-functionalization of the aldehydes in the second step [Eq. (1)].[6] The efficient one-pot, oxidative and enantioselective cross-coupling reaction of aldehydes and nitromethane using 2,3-dichloro-5,6-dicyanoquinone (DDQ) as oxidant and diphenyl-prolinol silyl ether as catalyst has been reported by Hayashi et al. [Eq. (2)].[7] Catalytic enantioselective one-pot domino oxidation procedures where the oxidized intermediate is further elaborated are highly desirable because they offer a potential one-flask-access to demanding and highly functionalized molecules in higher oxidation states.



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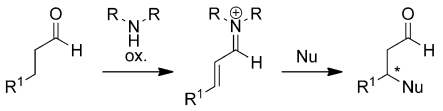

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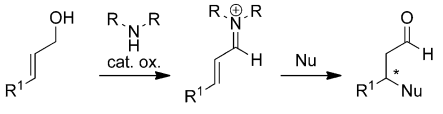

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In a previous investigation on iminium catalysis we and others discovered that trace amounts of acid, abundant in the α,β-unsaturated aldehydes or ketones, have a detrimental effect on both, the reactivity and enantioselectivity.[8] Therefore, the aldehydes have to be distilled or recrystallized prior to use. Hence, we became attracted to the idea of forming the aldehydes in situ. We envisioned that allylic al-

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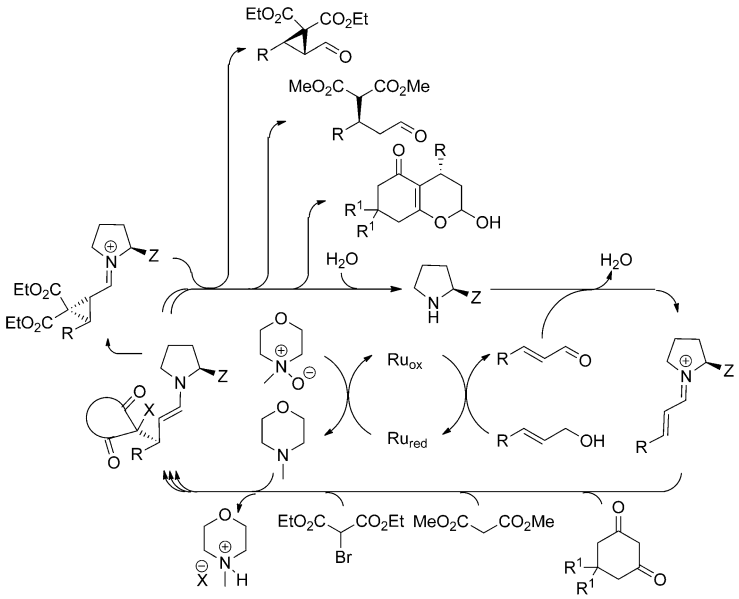
cohols could be oxidized to their aldehyde counterparts with a substrate-selective redox catalyst as a first step in an asymmetric oxidative iminium activation cascade (AOIC) [Eq. (3)].[9]

Results and Discussion

Central to the implementation of an asymmetric oxidative iminium cascade is that the catalytic oxidation is adaptable to the catalytic cycle of the chiral amine catalyst, the chiral amine catalyst is not oxidized, the reactions can be performed at room temperature and the terminal oxidant is mild, cheap and easy to handle. The robust tetrapropylammonium perruthenate TPAP and *N*-methylmorpholine *N*-oxide (NMO) system[10] meets these requirements and therefore became the substrate-selective redox catalyst of choice.

Initial oxidation of the alcohol by the TPAP/NMO system generates the aldehyde and one equiv of *N*-methylmorpholine NMM (Scheme 1). The aldehyde then forms the iminium ion with the amine catalyst and simultaneously NMM acts as a base and activates the nucleophile. The activated nucleophile then adds to the iminium ion upon formation of the chiral enamine. Depending on the nucleophile, several pathways are possible. To survey the scope of the asymmetric oxidative iminium cascade strategy we decided to investigate three reaction types. The domino iminium enamine mechanism was probed using bromo malonate as nucleophile, a Michael addition cyclization reaction with 1,3-diketones[8a–d,h] and a Michael addition using malonates.

In the initial studies, the TPAP/NMO system proved to have good compatibility with the chiral amine catalyst diphenylprolinol TMS-ether (TMS-DPP)[11] without any notable degradation of either TPAP or the TMS-DPP. Furthermore, the NMM formed as a by-product of the sacrificial oxidant had an accelerating effect on the catalytic system. After an optimization of solvent, temperature and catalysts, efficient protocols for the enantioselective formation of formylcyclopropanes, addition cyclization reaction of 1,3-diketones and the Michael addition of malonates were developed.

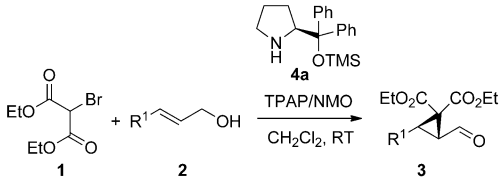


Scheme 1. General overview of the oxidative iminium activation cascade.

The double catalytic asymmetric oxidative formation of formylcyclopropanes[12] from allylic alcohols and diethyl bromomalonate proceeds in high yields with high enantioselectivities in the presence of 1–7 mol% of TPAP, 1.5 equiv of NMO and 10 mol% of amine catalyst **4a** (Table 1, entries 1–8). Cinnamyl alcohol (**2a**) is converted to **3a** in 78% yield with 94% *ee* (Table 1, entry 1). Compounds **3b** and **3c** bearing aryl groups with nitro electron withdrawing groups in the 2- and 4-position can be isolated in 98% yield with 95% *ee* and 72% yield with 92% *ee*, respectively (Table 1, entries 4 and 5).

p-Tolylpropenol is readily converted into the corresponding cyclopropane **3e** in 77% yield with 95% *ee* (Table 1, entry 7). The reactions are finished within 7 h and the products can be obtained after silica gel purification. Moreover the TPAP loading can be decreased to 1 mol% without affecting the stereoselectivity but to the expense of a longer reaction time (Table 1, entry 3).

Table 1. Oxidative enantioselective amine catalyzed formation of formylcyclopropanes.

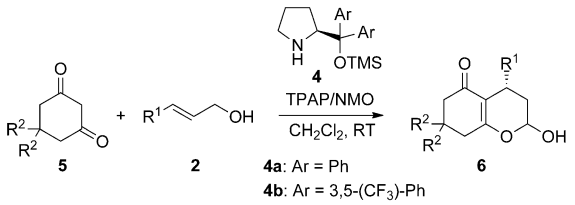


Entry[a]	3	R^1	Yield [%][b]	*ee* [%][c]
1	**3a**	Ph	78	94
2[d]	**3a**	Ph	64	94
3[e]	**3a**	Ph	78	94
4	**3b**	2-NO_2-Ph	89	95
5	**3c**	4-NO_2-Ph	75	92
6	**3d**	4-Br-Ph	66	95
7	**3e**	4-Me-Ph	77	95
8	**3f**	4-CF_3-Ph	70	94

[a] Reactions were performed with diethyl bromomalonate **1** (1.3 equiv), alcohol **2** (1.0 equiv), 10 mol% **4a**, TPAP (0.07 equiv), NMO (1.5 equiv) in CH_2Cl_2 at RT for 6–24 h. [b] Yield of isolated product after column chromatography. [c] *ee* determined by HPLC. [d] Performed with 6 mol% of **4a** (24 h). [e] Performed with 1 mol% of TPAP (36 h).

To further investigate the scope of the asymmetric oxidative iminium cascade, allylic alcohols and 1,3-diketones were subjected to TPAP/NMO and diphenylprolinol ether **4**. The 1,4-addition/cyclization reaction proceeds with high selectivity for both aliphatic and aromatic allylic alcohols (Table 2). Hexenol (**2**, $R^1 = C_3H_7$) affords at room temperature the corresponding 2-hydroxychromenone **6a** in 59% yield with 94% *ee* (Table 2, entry 1). Long alkyl chains are also well tolerated and decenol (**2**, $R^1 = C_7H_{15}$) could be converted to

Table 2. Formation of chromenones through an asymmetric oxidative iminium activation cascade.



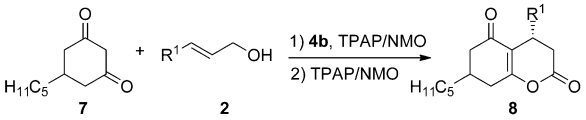
Entry[a]	4	6	R^1	R^2	Yield [%][b]	*ee* [%][c]
1	**4b**	**6a**	C_3H_7	H	59	94
2[d,e]	**4b**	**6b**	C_3H_7	Me	50	90
3	**4b**	**6c**	C_7H_{15}	H	51	96
4[d]	**4a**	**6d**	2-Cl-Ph	H	66	92
5[d,e]	**4a**	**6e**	2-Br-Ph	H	53	80

[a] Reactions were performed with diketone **5** (1.0 equiv), alcohol **2** (5.0 equiv), 20 mol% **4**, TPAP (0.05 equiv), NMO (1.0 equiv) in CH_2Cl_2 at RT for 48 h. [b] Yield of isolated product after column chromatography. [c] *ee* determined by HPLC. [d] Performed at 10 °C. [e] 96 h.

6c in 51% yield with 96% *ee* (Table 2, entry 3). Halo-substituted cinnamyl alcohols were smoothly converted to the heterocyclic enones **6d** and **6e** in good yields and very high selectivities from the double catalytic process (Table 2, entries 4 and 5).

Moreover, the oxidative addition–acetalization process could be further elaborated to yield lactones via a stepwise double oxidative procedure (Table 3). For example, when *meso*-compound **7** and allylic alcohol were treated with TPAP and amine catalyst **4b**, lactones **8a** and **8b** were obtained with 97% *ee* for both diastereomers (Table 3).

Table 3. Catalytic double oxidation/iminium activation to chiral bicyclic lactones.



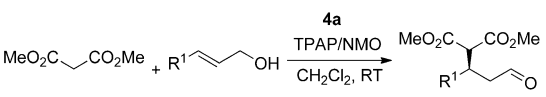
Entry[a]	8	R^1	Yield [%][b]	*ee* [%][c]
1	**8a**	C_3H_7	51	97/97
2	**8b**	C_7H_{15}	50	97/97

[a] 1st[t] step: Reactions were performed with diketone **7** (1.0 equiv), alcohol **2** (5.0 equiv), 20 mol% **4b**, TPAP (0.05 equiv), NMO (1.0 equiv) in CH_2Cl_2 at RT for 72 h; 2nd step: Reactions were performed with isolated lactol (1.0 equiv), TPAP (0.05 equiv), NMO (1.5 equiv) in CH_2Cl_2 at RT for 20 min. [b] Yield of isolated product over 2 steps after column chromatography. [c] *ee* determined by HPLC.

The addition of malonates to allylic alcohols was also successful by applying the asymmetric oxidative iminium cascade, and the products **10**[13] could be isolated in high yields with up to 93% *ee* (Table 4). Cinnamyl alcohol was converted at room temperature into malonate aldehyde **10a** in 61% yield with 93% *ee* (Table 4, entry 1).

Furthermore, the addition of dimethyl malonate to the aromatic allylic alcohols tolerates a variety of functional

Table 4. Oxidative enantioselective amine-catalyzed addition of methyl malonate to allylic alcohols.

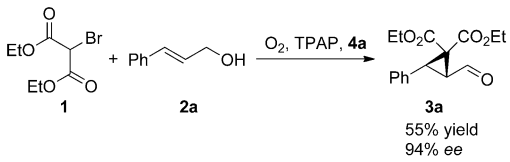


Entry[a]	10	R^1	Yield [%][b]	*ee* [%][c]
1	**10a**	Ph	61	93
2	**10b**	2-NO_2-Ph	73	93
3	**10c**	4-NO_2-Ph	71	86
4	**10d**	4-Br-Ph	63	92
5	**10e**	4-Me-Ph	72	77

[a] Reactions were performed with methyl malonate **9** (3.0 equiv), alcohol **2** (1.0 equiv), 20 mol% **4a**, TPAP (0.07 equiv), NMO (1.5 equiv) in CH_2Cl_2 at RT for 24–48 h. [b] Yield of isolated product after column chromatography. [c] *ee* determined by HPLC.

groups in the *p*- or *o*-position of the aromatic ring. Apart from halogen and alkyl substituents, nitro-aromatics are tolerated well in this reaction giving the addition products in high yields up to 73% and enantioselectivities up to 93% *ee* (Table 4, entries 2 and 3).

The ultimate goal for catalytic oxidations is to use oxygen as the terminal oxidant due to the high efficiency of weight per oxidant and the environmental benefits.[14] Both Ley[15] and Brown[16] have reported that molecular oxygen in addition to NMO can be used in TPAP oxidations, thus, the oxidative cyclopropanation of allylic alcohols was conducted under an oxygen atmosphere to yield cyclopropane **3a** in 55% yield with 94% *ee* (Scheme 2).



Scheme 2. A direct aerobic oxidative iminium cascade.

Conclusion

In summary, we have developed the first catalytic asymmetric oxidative iminium cascade. TPAP as a substrate-selective redox catalyst is well tolerated by the amine catalyst and provides an opportunity to form the α,β-unsaturated aldehydes in situ for further transformations. The generality of this methodology is demonstrated in Tables 1–4. The three fundamentally different reactions applied, proceed in good yields and high enantioselectivities. The reactions are conducted with 6–20% of TMS-prolinol ether and the TPAP loadings can be reduced to 1 mol%. Furthermore, the in situ oxidation can be conducted with environmentally benign terminal oxidants such as O_2. The compatibility of one metal catalyst and one organic catalyst presented here clearly widens the scope of asymmetric iminium catalysis and combined catalysis in general.

Experimental Section

General procedure for the oxidative amine-catalyzed formation of formylcyclopropanes: To a vial containing cinnamyl alcohol (**2**, R^1=Ph, 0.2 mmol, 1.0 equiv) in dichloromethane (1.0 mL) was subsequently added, NMO (0.3 mmol, 1.5 equiv), TPAP (0.014 mmol, 0,07 equiv), diethyl bromomalonate (**1**, 0.26 mmol, 1.3 equiv) and 2-(diphenyl(trimethylsilyloxy)methyl)pyrrolidine (**4a**, 0.1 mmol, 0.1 equiv). The reaction was stirred at room temperature for 6 h and then put on a silica gel column and purified using hexane/ethyl acetate as eluent to give cyclopropane **3a** as a colorless oil. $[\alpha]_D=-49.6$ (c=1.0 in $CHCl_3$, 94% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.45 (d, 1H, J=4.8 Hz), 7.33–7.22 (m, 5H), 4.38–4.20 (m, 2H), 3.93 (dq, 2H, J=7.2, 1.2 Hz), 3.83 (d, 1H, J=7.4 Hz), 3.37 (dd, 1H, J=7.5, 4.8 Hz), 1.30 (t, 3H, J=7.1 Hz), 0.93 ppm (t, 3H, J=7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ=196.0, 166.0, 164.6, 132.2, 128.5, 128.4, 128.0, 62.5, 62.0, 44.7, 38.2, 35.3, 14.0, 13.7 ppm; IR (neat): $\tilde{\nu}$=3425, 2982, 2935, 2872, 1715, 1639, 1448, 1369, 1287, 1216, 1183, 1143, 1020, 744, 698 cm^{-1}; MS-EI: m/z (%): 261.1 (26) $[M-Et]^+$, 216.1 (22), 187.1 (26), 171.1 (17), 170.0 (33), 159.0 (11), 144.1 (16), 130.9 (13), 116.1 (33), 115.1 (100), 105.1 (22), 91.1 (14); HPLC conditions: AS-H column, *n*-hexane/2-propanol 85:15, flow rate=0.6 mL min^{-1}, λ=210 nm; major enantiomer: t_R=11.61 min and minor enantiomer: t_R=13.81 min.

General procedure for the oxidative addition of malonates to allylic alcohols: To a vial containing cinnamyl alcohol (**2**, R^1=Ph, 0.2 mmol, 1.0 equiv) in dichloromethane (1.0 mL) was subsequently added, NMO (0.30 mmol, 1.5 equiv), TPAP (0.014 mmol, 0.07 equiv), dimethyl malonate (**9**, 0.26 mmol, 1.3 equiv) and 2-(diphenyl(trimethylsilyloxy)methyl)-pyrrolidine (**4a**, 0.2 mmol, 0.2 equiv). The reaction was stirred at room temperature for 24 h and then put on a silica gel column and purified using hexane/ethyl acetate as eluent to afford **10a** as colorless oil. $[\alpha]_D=-19.9$ (c=1.0 in $CHCl_3$; 93% *ee*); ^{1}H NMR (300 MHz, $CDCl_3$,): δ=9.59 (t, 1H, J=1.8 Hz), 7.32–7.22 (m, 5H), 4.06–3.98 (m, 1H), 3.74 (d, 1H, J=9.8 Hz) 3.74 (s, 3H), 3.50 (s, 3H), 2.94–2.90 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=199.9, 168.3, 167.8, 139.7, 128.8, 128.0, 127.6, 57.3, 52.7, 52.4, 47.2, 39.5 ppm; IR (neat): $\tilde{\nu}$ = 3427, 3031, 2954, 2846, 1995, 496, 1454, 1434, 1319, 1253, 1197, 1155, 1062, 1022, 767, 701 cm^{-1}; MS-EI: m/z(%): 264.9 (0.1) $[M+H]^+$, 133.1 (12), 132.0 (38), 131.1 (22), 117.1 (12), 115.1 (28), 105.1 (32), 104.1 (48), 103.1 (28), 100.0 (18), 91.1 (15), 78.1 (16), 77.0 (23), 69.0 (21), 59.0 (100); enantioselectivity measured after conversion to the corresponding ester.[13c] HPLC conditions: AD-H column, *n*-hexane/2-propanol 90:10, flow rate=1.0 mL min^{-1}, λ=210 nm. major enantiomer: t_R=12.22 min and minor enantiomer: t_R=14.73 min.

General procedure for the oxidative addition-acetalization: A solution of allylic alcohol (**2**, $R^1=C_3H_7$, 5.00 equiv) in CH_2Cl_2 (0.2 M) was placed in a screw capped test tube equipped with stirring bar and NMO (1.5 equiv) was added to the mixture and stirred for 5 min. TPAP (0.05 equiv) was added and the resulting mixture stirred at the ambient temperature for 15 min. Diketone (**5**, R^2=H, 1.0 equiv) and catalyst **4b** (0.02 equiv) were added and the mixture was stirred for 48 h. The crude reaction mixture was directly charged on silica gel and purified by column chromatography (hexane/EtOAc 5:1 → hexane/EtOAc 1:1) to afford **6a**.[8b]

Acknowledgements

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[1] Reviews on domino reactions: a) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136; b) J.-C. Wasilke, S. J. Obrey, R. T. Baker, G. C. Bazan, *Chem. Rev.* **2005**, *105*, 1001–1020; c) L. F. Tietze, G. Brasche, K. Gericke, *Domino Reactions in Organic Synthesis* Wiley-VCH, Weinheim, **2006**; d) H. Pellissier, *Tetrahedron* **2006**, *62*, 1619–1665; e) H. Pellissier, *Tetrahedron* **2006**, *62*, 2143–2173; f) K. C. Nicolaou, D. J. Edmonds, P. G. Bulger, *Angew. Chem.* **2006**, *118*, 7292–7344; *Angew. Chem. Int. Ed.* **2006**, *45*, 7134–7186; g) C. J. Chapman, C. G. Frost, *Synthesis* **2007**, 1–21.

[2] Reviews on organocatalytic domino reactions: a) D. Enders, C. Grondal, M. R. M. Hüttl, *Angew. Chem.* **2007**, *119*, 1590–1601; *Angew. Chem. Int. Ed.* **2007**, *46*, 1570–1581; b) X. Yu, W. Wang, *Org. Biomol. Chem.* **2008**, *6*, 2037–2046; c) A. N. Alba, X. Companyó, M. Viciano, R. Rios, *Curr. Org. Chem.* **2009**, *13*, 1432–1474; d) C. Grondal, M. Jeanty, D. Enders, *Nat. Chem.* **2010**, *2*, 167–178.

[3] For reviews on the concept of catalysis by combining a transition metal catalyst and an organocatalyst see: a) Z. Shao, H. Zhang, *Chem. Soc. Rev.* **2009**, *38*, 2745–2755; b) M. Klussmann, *Angew. Chem.* **2009**, *121*, 7260–7261; *Angew. Chem. Int. Ed.* **2009**, *48*, 7124–7125; c) P. de Armas, D. Tejedor, F. Garcia-Tellado, *Angew. Chem.* **2010**, *122*, 1029–1032; *Angew. Chem. Int. Ed.* **2010**, *49*, 1013–1016; d) C. Zhong, X. Shi, *Eur. J. Org. Chem.* **2010**, 2999–3025; e) M. Rueping, R. M. Koenigs, I. Atodiresei, *Chem. Eur. J.* **2010**, *16*, 9350–9365.

[4] Selected examples; a) M. Nakoji, T. Kanayama, T. Okino, Y. Takemoto, *Org. Lett.* **2001**, *3*, 3329–3332; b) M. Nakoji, T. Kanayama, T. Okino, Y. Takemoto, *J. Org. Chem.* **2002**, *67*, 7418–7423; c) S. Chercheja, P. Eilbracht, *Adv. Synth. Catal.* **2007**, *349*, 1897–1905; d) S. Mukherjee, B. List, *J. Am. Chem. Soc.* **2007**, *129*, 11336–11337; e) O. Abillard, B. Breit, *Adv. Synth. Catal.* **2007**, *349*, 1891–1895; f) X. Xu, J. Zhou, L. Yang, W. Hu, *Chem. Commun.* **2008**, 6564–6566; g) P. Kukula, V. Matoušek, T. Mallat, A. Baiker, *Chem. Eur. J.* **2008**, *14*, 2699–2708; h) S. Chercheja, T. Rothenbücher, P. Eilbracht, *Adv. Synth. Catal.* **2009**, *351*, 339–344; i) D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, *322*, 77–80; j) D. A. Nagib, M. E. Scott, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2009**, *131*, 10875–10877; k) M. E. Muratore, C. A. Holloway, A. W. Pilling, R. I. Storer, G. Trevitt, D. J. Dixon, *J. Am. Chem. Soc.* **2009**, *131*, 10796–10797; l) Z.-Y. Han, H. Xiao, X.-H. Chen, L.-Z. Gong, *J. Am. Chem. Soc.* **2009**, *131*, 9182–9183; m) S. Chercheja, S. K. Nadakudity, P. Eilbracht, *Adv. Synth. Catal.* **2010**, *352*, 637–643; n) S. Liao, B. List, *Angew. Chem.* **2010**, *122*, 638–641; *Angew. Chem. Int. Ed.* **2010**, *49*, 628–631.

[5] a) M. Rueping, A. P. Antonchick, C. Brinkmann, *Angew. Chem.* **2007**, *119*, 7027–7030; *Angew. Chem. Int. Ed.* **2007**, *46*, 6903–6906; b) M. Rueping, R. M. Koenigs, *Chem. Commun.* **2011**, *47*, 304–306.

[6] A. Quintard, A. Alexakis, C. Mazet, *Angew. Chem.* **2011**, *123*, 2402–2406; *Angew. Chem. Int. Ed.* **2011**, *50*, 2354–2358.

[7] Y. Hayashi, T. Itoh, H. Ishikawa, *Angew. Chem.* **2011**, *123*, 4006–4010; *Angew. Chem. Int. Ed.* **2011**, *50*, 3920–3924.

[8] a) M. Rueping, E. Sugiono, E. Merino, *Angew. Chem.* **2008**, *120*, 3089–3092; *Angew. Chem. Int. Ed.* **2008**, *47*, 3046–3049; b) M. Rueping, E. Sugiono, E. Merino, *Chem. Eur. J.* **2008**, *14*, 6329–6332; c) M. Rueping, E. Merino, E. Sugiono, *Adv. Synth. Catal.* **2008**, *350*, 2127–2131; d) P. T. Franke, B. Richter, K. A. Jørgensen, *Chem. Eur. J.* **2008**, *14*, 6317–6321; e) M. Rueping, A. P. Antonchick, *Angew. Chem.* **2008**, *120*, 10244–10247; *Angew. Chem. Int. Ed.* **2008**, *47*, 10090–10093; f) M. Rueping, A. P. Antonchick, *Angew. Chem.* **2008**, *120*, 5920–5922; *Angew. Chem. Int. Ed.* **2008**, *47*, 5836–5838; g) M. Rueping, A. Kuenkel, F. Tato, J. W. Bats, *Angew. Chem.* **2009**, *121*, 3754–3757; *Angew. Chem. Int. Ed.* **2009**, *48*, 3699–3702; h) M. Rueping, A. Parra, U. Uria, F. Besselivre, E. Merino, *Org. Lett.* **2010**, *12*, 5680–5683; i) M. Rueping, A. Kuenkel, R. Fröhlich, *Chem. Eur. J.* **2010**, *16*, 4173–4176; j) M. Rueping, M.-Y. Lin, *Chem. Eur. J.* **2010**, *16*, 4169–4172; k) M. Rueping, B. J. Nachtsheim, *Synlett* **2010**, 119–122.

[9] For a review of tandem oxidation processes, see: a) R. J. K. Taylor, M. Reid, J. Foot, S. A. Raw, *Acc. Chem. Res.* **2005**, *38*, 851–869; For selected examples of tandem oxidation processes, see: b) M. F. Oswald, S. A. Raw, R. J. K. Taylor, *Org. Lett.* **2004**, *6*, 3997–4000; c) S. A. Raw, C. D. Wilfred, R. J. K. Taylor, *Org. Biomol. Chem.* **2004**, *2*, 788–796; d) M. F. Oswald, S. A. Raw, R. J. K. Taylor, *Chem. Commun.* **2005**, 2253–2255; e) B. E. Maki, A. Chan, E. M. Phillips, K. A. Scheidt, *Org. Lett.* **2007**, *9*, 371–374; f) B. E. Maki, K. A. Scheidt, *Org. Lett.* **2008**, *10*, 4331–4334; g) K. Zeitler, C. A. Rose, *J.*

Org. Chem. **2009**, *74*, 1759–1762; h) B. E. Maki, A. Chan, E. M. Phillips, K. A. Scheidt, *Tetrahedron* **2009**, *65*, 3102–3109; i) H. Kim, Y. Park, J. Hong, *Angew. Chem.* **2009**, *121*, 7713–7717; *Angew. Chem. Int. Ed.* **2009**, *48*, 7577–7581; j) M. Davi, H. Lebel, *Org. Lett.* **2009**, *11*, 41–44; k) S. De Sarkar, S. Grimme, A. Studer, *J. Am. Chem. Soc.* **2010**, *132*, 1190–1191; l) S. De Sarkar, A. Studer, *Org. Lett.* **2010**, *12*, 1992–1995; m) S. De Sarkar, A. Studer, *Angew. Chem.* **2010**, *122*, 9452–9455; *Angew. Chem. Int. Ed.* **2010**, *49*, 9266–9269; n) C. A. Rose, K. Zeitler, *Org. Lett.* **2010**, *12*, 4552–4555; o) B. Maji, S. Vedachalan, X. Ge, S. Cai, X.-W. Liu, *J. Org. Chem.* **2011**, *76*, 3016–3023; p) J. H. Park, S. V. Bhilare, S. W. Youn, *Org. Lett.* **2011**, *13*, 2228–2231; q) B. E. Maki, E. V. Patterson, C. J. Cramer, K. A. Scheidt, *Org. Lett.* **2009**, *11*, 3942–3945.

[10] S. V. Ley, J. Norman, W. P. Griffith, S. P. Marsden, *Synthesis* **1994**, 639–666.

[11] a) M. Marigo, T. C. Wabnitz, D. Fielenbach, K. A. Jørgensen, *Angew. Chem.* **2005**, *117*, 804–807; *Angew. Chem. Int. Ed.* **2005**, *44*, 794–797; b) Y. Hayashi, H. Gotoh, T. Hayashi, M. Shoji, *Angew. Chem.* **2005**, *117*, 4284–4287; *Angew. Chem. Int. Ed.* **2005**, *44*, 4212–4215. Reviews on diphenylprolinol TMS-ether catalysis: c) C. Palomo, A. Mielgo, *Angew. Chem.* **2006**, *118*, 8042–8046; *Angew. Chem. Int. Ed.* **2006**, *45*, 7876–7880; d) A. Mielgo, C. Palomo, *Chem. Asian J.* **2008**, *3*, 922–948.

[12] a) R. Rios, H. Sundén, J. Vesely, G. L. Zhao, P. Dziedzic, A. Córdova, *Adv. Synth. Catal.* **2007**, *349*, 1028–1032; b) H. Xie, L. Zu, H. Li, J. Wang, W. Wang, *J. Am. Chem. Soc.* **2007**, *129*, 10886–10894; c) J. Vesely, G. L. Zhao, A. Bartoszewicz, A. Córdova, *Tetrahedron Lett.* **2008**, *49*, 4209–4212; d) I. Ibrahem, G. L. Zhao, R. Rios, J. Vesely, H. Sundén, P. Dziedzic, A. Córdova, *Chem. Eur. J.* **2008**, *14*, 7867–7879; e) X. Companyó, A.-N. Alba, F. Cárdenas, A. Moyano, R. Rios, *Eur. J. Org. Chem.* **2009**, 3075–3080; f) V. Terrasson, A. van der Lee, R. M. de Figueiredo, J. M. Campagne, *Chem. Eur. J.* **2010**, *16*, 7875–7880; g) U. Uria, J. L. Vicario, D. Badía, L. Carrillo, E. Reyes, A. Pesquera, *Synthesis* **2010**, 701–713.

[13] a) N. Halland, T. Hansen, K. A. Jørgensen, *Angew. Chem.* **2003**, *115*, 5105–5107; *Angew. Chem. Int. Ed.* **2003**, *42*, 4955–4957; b) K. R. Knudsen, C. E. T. Mitchell, S. V. Ley, *Chem. Commun.* **2006**, 66–68; c) S. Brandau, A. Landa, J. Franzen, M. Marigo, K. A. Jørgensen, *Angew. Chem.* **2006**, *118*, 4411–4415; *Angew. Chem. Int. Ed.* **2006**, *45*, 4305–4309; d) Y. Wang, P. Li, X. Liang, J. Ye, *Adv. Synth. Catal.* **2008**, *350*, 1383–1389; e) V. Wascholowski, K. R. Knudsen, C. E. T. Mitchell, S. V. Ley, *Chem. Eur. J.* **2008**, *14*, 6155–6165; f) Y.-Q. Yang, G. Zhao, *Chem. Eur. J.* **2008**, *14*, 10888–10891; g) P. Li, S. Wen, F. Yu, Q. Liu, W. Li, Y. Wang, X. Liang, J. Ye, *Org. Lett.* **2009**, *11*, 753–756; h) Z. Mao, Y. Jia, W. Li, R. Wang, *J. Org. Chem.* **2010**, *75*, 7428–7430.

[14] J. Piera, J. E. Bäckvall, *Angew. Chem.* **2008**, *120*, 3558–3576; *Angew. Chem. Int. Ed.* **2008**, *47*, 3506–3523.

[15] R. Lenz, S. V. Ley, *J. Chem. Soc. Perkin Trans. 1* **1997**, 3291–3292.

[16] I. E. Markó, P. R. Giles, M. Tsukazaki, I. Chellé-Regnaut, C. J. Urch, S. M. Brown, *J. Am. Chem. Soc.* **1997**, *119*, 12661–12662.

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