Communication

Chemodivergent and Diastereoselective Synthesis of #-Lactones and #-Lactams: A Heterogeneous Palladium-Catalyzed Oxidative Tandem Process

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Chemodivergent and Diastereoselective Synthesis of γ-Lactones and γ-Lactams: A Heterogeneous Palladium-Catalyzed Oxidative Tandem Process

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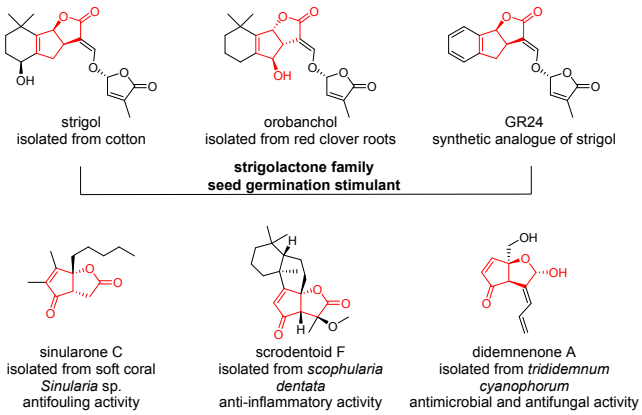
Supporting Information

ABSTRACT: A palladium-catalyzed oxidative tandem process of enallenols was accomplished within a homogeneous/heterogeneous catalysis manifold, setting the stage for highly chemodivergent and diastereoselective synthesis of γ-lactones and γ-lactams under mild conditions.

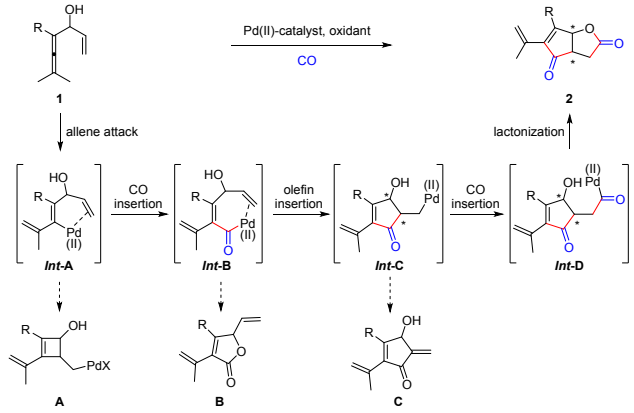
γ-Lactones and γ-lactams are core structures of a large variety of natural and bioactive compounds, as well as versatile intermediates in the synthesis of complex molecules and recyclable polymers.[1] As a result, many studies have been directed toward the selective construction of this structural unit.[2] In most cases, γ-lactones and γ-lactams are fused with other cyclic units to form bicyclic or polycyclic structures with several chiral centers (Figure 1).[1-3] Notable progress was obtained in the past decade.[2,3] Despite these major advances, the procedures reported typically require multistep synthesis with unsatisfactory atom- and step-economy.[1a-d,2a-e,3] Thus, economical and efficient access to ring fused γ-lactones and γ-lactams with high regio- and diastereoselectivity is still of high demand.

Figure 1. Representative bioactive compounds

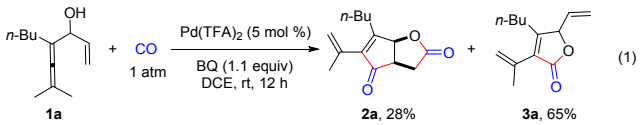


An efficient way to construct complicated molecular structures with high atom- and step-economy is to employ a multistep tandem process, in which a consecutive series of reactions occur via multiple bond formation and cyclization.[4] Following our recent interest in Pd(II)-catalyzed oxidative carbocyclization of allenes for construction of synthetically important carbocyclic skeletons,[5] we have now designed an oxidative tandem route to ring fused γ-lactones (Scheme 1). We envisioned that ***Int*-A** would be generated from the palladium complex of **1** via allene attack on Pd(II). In the presence of carbon monoxide (CO), insertion of CO into the Pd–C bond of ***Int*-A** would produce ***Int*-B**, which could undergo an insertion of the olefin to form ***Int*-C**. A subsequent CO insertion into the Pd–C bond of ***Int*-C** would produce ***Int*-D**, which would be trapped by the hydroxyl group to give cyclopentenone-fused γ-lactone **2** with two chiral centers. This bicyclic skeleton is a structural element of many natural and bioactive compounds (Figure 1).[6] Some typical examples include the strigolactone family[6a-e] members: strigol,[6a] orobanchol[6d] and GR24,[6e] which are new plant hormones that attracted much attention recently. The envisioned tandem process for the construction of this valuable skeleton would undergo selective carbonylation-carbocyclization-carbonylation-lactonization which involves four-step bond formation including twice CO insertion with high atom- and step-economy. In addition, the hydroxyl group of enallenol **1** would potentially act as a directing group to control the diastereoselectivity of the tandem reaction. However, considering the possible side-reactions during each step (Scheme 1), the control of chemoselectivity during the tandem process would be highly challenging.

Scheme 1. Proposed tandem approach for formation of cyclopentenone-fused γ-lactone skeleton

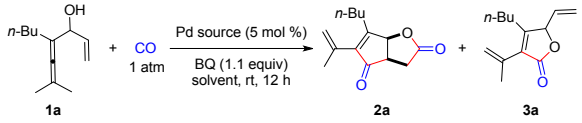


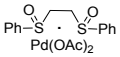
Our initial attempt of the Pd(II)-catalyzed oxidative tandem process began with the reaction of enallenol **1a** in the presence of $Pd(TFA)_2$ (TFA = trifluoroacetate) (5 mol%). To our delight, the cyclopentenone-fused γ-lactone **2a** was obtained in 28% yield as a sole diastereomer (eq 1). Another γ-lactone product **3a** was also formed in 65% yield due to the reaction of acyl palladium with the hydroxyl group (in ***Int*-B**, Scheme 1).



With these inspiring results in hand, we turned to optimize the reaction conditions for the chemoselective formation of cyclopentenone-fused γ-lactone **2a**. However, γ-lactone **3a** was always the major product no matter how the homogeneous reaction conditions were changed (Table 1, entries 1-8, for more details, see Supporting Information, P. S7). We then turned our attention to the heterogeneous Pd catalyst comprising of palladium immobilized on amino-functionalized siliceous mesocellular foam (Pd-AmP-MCF), which is a new heterogeneous palladium catalyst developed by our group.[7] It was used for catalytic hydrogenation of nitro compounds, alkenes and alkynes with H_2, and exhibited excellent reactivity and selectivity compared to homogeneous and other heterogeneous Pd catalyst.[7c-f] Surprisingly, the non-reduced form, Pd^{II}-AmP-MCF, increased the yield of **2a** to 68% and suppressed the yield of **3a** to 20% (Table 1, entry 9). By changing the solvent from DCE to CH_2Br_2, oxidant from BQ to methyl-BQ, and the amount of Pd^{II}-AmP-MCF from 5 mol % to 2 mol %, **2a** was obtained in 80% yield and with a 20:1 chemoselectivity (Table 1, entry 10, for more details, see Supporting Information, P. S8).

Table 1. Optimization of the reaction conditions



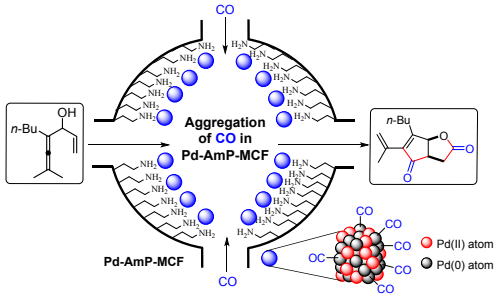
Entry	Pd source	Solvent	Yield of **2a** (%)[a]	Yield of **3a** (%)[a]
1	$Pd(TFA)_2$	DCE	28	65
2	$Pd(OAc)_2$	DCE	17	50
3	$Pd(PPh_3)_2Cl_2$	DCE	12	44
4		DCE	17	35
5	$Pd(TFA)_2$	DCM	28	67
6	$Pd(TFA)_2$	$CHCl_3$	20	70
7	$Pd(TFA)_2$	CH_2Br_2	35	55
8	$Pd(TFA)_2$	THF	26	52
9	Pd^{II}-AmP-MCF	DCE	68	20
10[b]	**Pd^{II}-AmP-MCF**	**CH_2Br_2**	**80**	**4**
11[c]	$Pd(TFA)_2$	CH_2Br_2	15	57
12[d]	**$Pd(TFA)_2$**	**$CHCl_3$**	**3**	**86**

[a]Determined by NMR using anisole as the internal standard. [b]2 mol% of Pd^{II}-AmP-MCF and methyl-BQ was used. [c]15 bar of CO was used. [d]10 mol% of CH_3CO_2H was used.

Despite the elegant work on ligand- and solvent-controlled chemoselective carbonylative reactions developed in homogeneous systems,[8,9] up to now, there are no reports on catalyst-controlled chemo- and diastereoselective carbonylations achieved with heterogeneous palladium catalysts. As a result of its high surface area (500-800 m^2g^{-1}) and large pore sizes (~26 nm), amino-functionalized mesocellular foam (AmP-MCF) could act as ideal support for Pd and excellent host for CO gas.[10] We assume that two factors may lead to the aggregation of CO in Pd-AmP-MCF to favor the formation of **2a** (Figure 2). First, the physical adsorption of CO in the porous AmP-MCF would increase the concentration of CO in the reaction mixture. Control experiments showed that compared to $Pd(TFA)_2$ or $Pd(OAc)_2$, the $Pd(TFA)_2$ + AmP-MCF or $Pd(OAc)_2$ + AmP-MCF catalytic system improved the chemoselectivity of the reaction for formation of cyclopentenone-fused γ-lactone **2a** (see Supporting Information, Table S1, entries 7, 10, and Table S2, entries 4, 5). In addition, an increase of the ratio of **2a**:**3a** from 36:40 to 47:30 was observed with the gradual increase of the amount of AmP-MCF with $Pd(OAc)_2$ as the catalyst (see Supporting Information, p. S8, Table S2, entries 5-7). Second, in the presence of CO, Pd(II) in the heterogeneous catalyst was partially reduced to Pd(0). We observed a mixture of Pd(0) and Pd(II) atoms accommodated in the Pd-AmP-MCF after reaction.[11] The coexistence of Pd(0) and Pd(II) atoms in Pd-AmP-MCF was also detected in our very recent work by using Pd^0-AmP-MCF in Pd-catalyzed carbocyclization, in which the Pd(II) was generataed from the oxidation of Pd(0) by BQ.[7g] The Pd(0) atoms in Pd^{II}-AmP-MCF can adsorb CO efficiently for the next carbonylative step (Figure 2). Control experiments showed that compared to Pd(II) salts, a Pd colloid improved the chemoselectivity of the reaction for formation of cyclopentenone-fused γ-lactone **2a** (see Supporting Information, P. S8, Table S2, entries 11, 12).[12]

On the other hand, the use of $Pd(TFA)_2$ or Li_2PdCl_4 (the precursor of Pd^{II}-AmP-MCF) as the catalyst did not lead to any increase of the chemoselectivity for formation of **2a** with propylamine as the additive (see Supporting Information, Table S1, entry 7, and Table S2, entries 8-10). This observation suggests that coordination of amine to Pd in Pd-AmP-MCF is not causing the switch of the observed chemoselectivity. Based on these results, we propose that Pd-AmP-MCF adsorb CO efficiently to favor selective formation of **2a**. To be noted, **2a** was obtained only in 15% yield with $Pd(TFA)_2$ as the catalyst in the presence of 15 bar of CO (Table 1, entry 11), demonstrating that the chemoselectivity of the reaction for the formation of **2a** cannot be improved by simply increasing the CO pressure in the homogeneous catalytic system. Interestingly, chemoselective formation of γ-lactone **3a** was achieved in 86% yield and with >20:1 chemoselectivity by using 10 mol % of CH_3CO_2H as the additive in the homogeneous catalytic system (Table 1, entry 12).

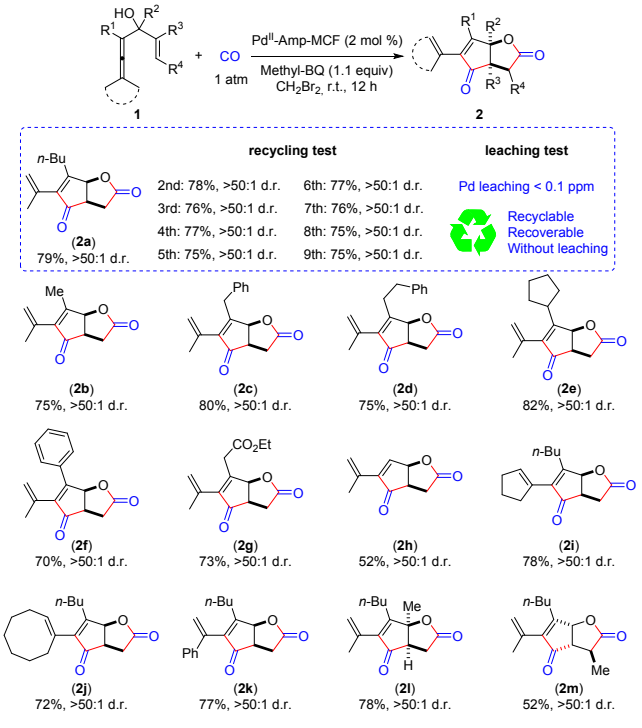
Figure 2. Aggregation of CO in Pd-AmP-MCF for switching chemoselectivity



Under the optimized reaction conditions, we investigated the scope for the chemo- and diastereoselective formation of cyclopentenone-fused γ-lactones **2** (Scheme 2). Enallenols **1a-1h** with an aliphatic, aromatic or hydrogen substituent in the R^1 position worked equally well to give cyclopentenone-fused γ-lactones **2a-2h** in good yields. An ester as functional group was tolerated in the tandem reaction (**2g**). In addition to two methyl substituents, the substrates with cyclopentylidene and

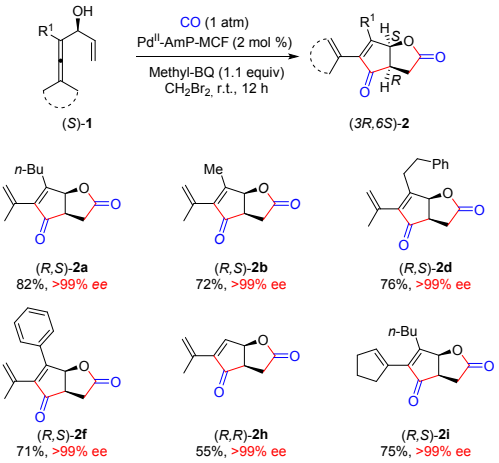
cyclooctylidene substituents on the allene moiety also worked well, affording the corresponding products **2i** and **2j** in good yields. Unsymmetrical enallenol **1k** bearing phenyl and methyl groups afforded **2k** in 77% yield. To our delight, enallenol **1l** bearing a tertiary alcohol led to the corresponding product **2l** with a quaternary carbon stereocenter in good yield, and enallenol **1m** bearing methyl group in R^4 position afforded the corresponding cyclopentenone-fused γ-lactone **2m** as a sole diastereomer with three chiral centers in 52% yield. To be noted, all of the cyclopentenone-fused γ-lactones **2** were obtained as single diastereomers with high diastereoselectivity.[13]

Scheme 2. Scope for selective formation of 2



It is noteworthy that the heterogeneous Pd^{II}-Amp-MCF catalyst used for the selective formation of cyclopentenone-fused γ-lactone **2** can be recovered and recycled many times without any observed loss of activity or selectivity (Scheme 2). Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis of the liquid aliquot after reaction and hot filtration test during reaction (see Supporting Information, P. S18) showed that there was no detectable leached Pd species during or after the reaction, which rule out that leached Pd species catalyze the reaction as a homogeneous catalyst.

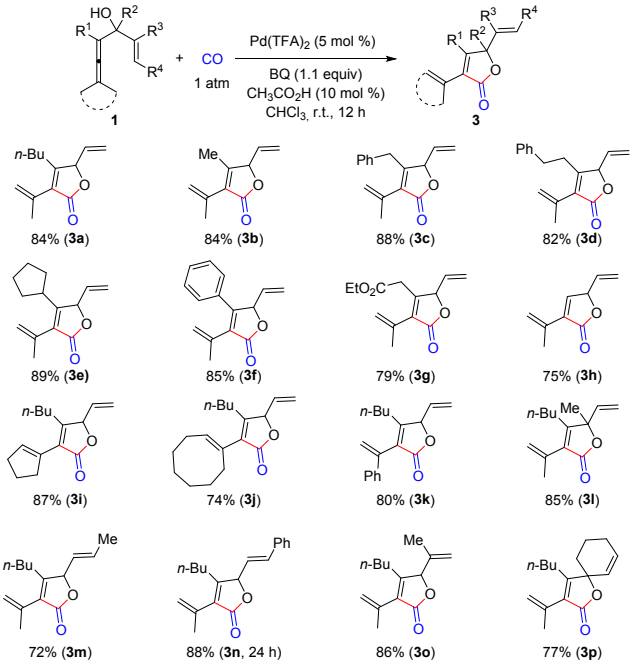
Scheme 3. Synthesis of optically pure 2



Optically pure (>99% ee) cyclopentenone-fused γ-lactones (*R,S*)-**2** were synthesized in high yields (Scheme 3) by using (*S*)-enallenols **1** which were readily obtained from kinetic resolution of enallenols **1** with *Candida antarctica* lipase B (CalB).[14] This strategy provides an efficient way towards chiral cyclopentenone-fused γ-lactones with high step-economy and selectivity.

We next explored the substrate scope for chemoselective formation of γ-lactones **3** (Scheme 4). Enallenols with alkyl, aryl, ester functional groups, and Cyclopentylidene, cyclooctylidene, and unsymmetrical phenyl and methyl substituents worked equally well to afford the γ-lactones **3a-3K** in excellent yields. With alkyl or aromatic substituents in R^2, R^3 and R^4 positions, enallenols **1l-1o** worked equally well to furnish substituted γ-lactones **3l-3o** in good yields. Due to the electronic effect on the olefin moiety, a prolonged reaction time was required for the formation of **3n**. Interestingly, a spiro-γ-lactone **3p** was obtained with good selectivity in 77% yield under the standard homogeneous reaction conditions.

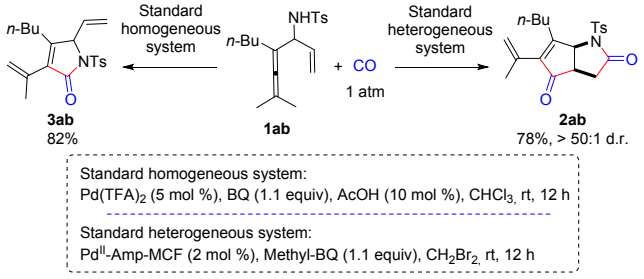
Scheme 4. Scope for selective formation of 3



The strategy for chemodivergent and diastereoselective construction of γ-lactones can be extended to the synthesis of γ-lactams. Using enallenamide **1ab** as starting material, switchable synthesis of cyclopentenone-fused γ-lactam **2ab** and γ-lactam **3ab** were achieved in good yields and excellent

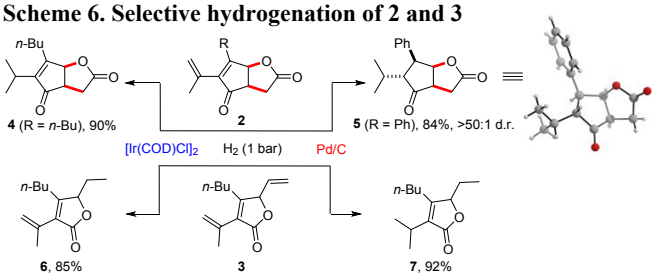
diastereoselectivity under the standard heterogeneous and homogeneous reaction conditions (Scheme 5).

Scheme 5. Chemodivergent and diastereoselective synthesis of γ-Lactams



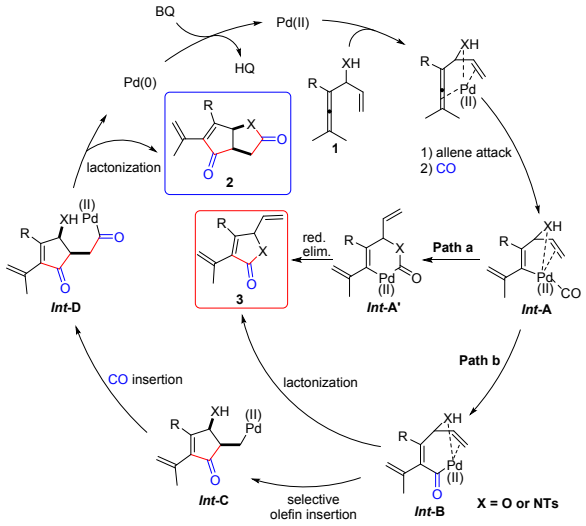
Bearing multiple carbon-carbon double bonds, γ-lactones **2** and **3** were further transformed to their corresponding hydrogenation derivatives selectively. In the presence of 1 bar of H_2, by switching catalyst between $[Ir(COD)Cl]_2$ and Pd/C, we realized the selective hydrogenation of γ-lactones **2** and **3** to mono-hydrogenated products **4** and **6**, and to di-hydrogenated products **5** and **7** in high yield and good selectivity (Scheme 6). To be noted, the hydrogenated product cyclopentanone fused γ-lactone **5** was obtained as a single diastereoisomer with four chiral centers. In addition, the single crystal structure of **5** (Scheme 6, for details, see Supporting Information, P. S35, 36) further confirmed the *cis*-conformation of the cyclopentenone-fused γ-lactone skeleton in product **2**.[13]

Scheme 6. Selective hydrogenation of 2 and 3



Based on the experimental results and our previous work on Pd(II)-catalyzed oxidative carbocyclization of allene derivatives,[5] a plausible mechanism for the chemodivergent and diastereoselective synthesis of γ-lactones and γ-lactams is given in Scheme 7. As the initial step, simultaneous coordination of the hydroxyl group (sulfonamide group), allene and olefin unit to the Pd(II) center would promote the allene attack and then CO coordination to form ***Int*-A**. In the presence of homogeneous Pd, attack by the XH group on coordinated CO would be favored with formation of ***Int*-A´** and give γ-lactones or γ-lactams **3** as the product after reductive elimination (path a), while in the presence of heterogeneous Pd, CO insertion into the Pd–C bond of ***Int*-A** would be favored, affording ***Int*-B** (path b). Lactonization or lactamization of ***Int*-B** could also lead to γ-lactones or γ-lactams **3**, while selective olefin insertion in ***Int*-B** directed by the OH group (for control experiment on diastereoselectivity, see Supporting Information, P. S34) or NHTs group would produce ***Int*-C**. In ***Int*-C** the alkyl palladium and hydroxyl group (sulfonamide group) are on the same side of cyclopentenone moiety. Further CO insertion of ***Int*-C** would produce ***Int*-D**, which would undergo lactonization or lactamization to give cyclopentenone-fused γ-lactones or γ-lactams **2**.

Scheme 7. Proposed mechanism



In conclusion, we have developed an efficient palladium-catalyzed oxidative tandem reaction of eanllenols for the chemodivergent and diastereoselective synthesis of γ-lactone and γ-lactam derivatives. Salient features of our findings include: 1) the catalyst controlled chemodivergent carbonylation is achieved by switching between homogeneous and heterogeneous catalysts, which disclose novel opportunities for control of chemoselectivity in carbonylative reactions. 2) The tandem strategy for synthesis of γ-lactones and γ-lactams is atom- and step-economic with high selectivity, which will be beneficial in synthetic chemistry. 3) Construction of enantioenriched cyclopentenone-fused γ-lactones was realized by employing the heterogeneous Pd-catalyzed tandem process on enantiopure enallenols. Further studies on the use of the heterogeneous Pd-AmP-MCF catalyst for other Pd-catalyzed transformations are currently under way in our laboratory.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and compound characterization data, including the $^1H/^{13}C$ NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) For TEM images and XPS spectra of Pd^{II}-AmP-MCF before and after reaction Supporting Information, P. S9.

(12) In one experiment the use of colloidal palladium afforded 25% yield of **2a** together with 15% yield of **3a** (See Supporting Information, Table S2, entry 12).

(13) The relative stereochemistry of **2** was determined by NOESY spectrum of **2a** (see Supporting Information, P. S10). Single crystal structure of **5** (CCDC 1865456) synthesized by hydrogenation of **2f** (Scheme 6) further confirmed the structure.

(14) For the preparation of (*S*)-**1**, see the Supporting Information, P. S19

Graphic Abstract