ORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Org. Chem. Front.*, 2018, **5**, 1113

Synthesis of chiral sultams with two adjacent stereocenters *via* palladium-catalyzed dynamic kinetic resolution†

Bo Song, [a] Mu-Wang Chen [a] and Yong-Gui Zhou *[a,b]

Received 6th December 2017,
Accepted 16th January 2018

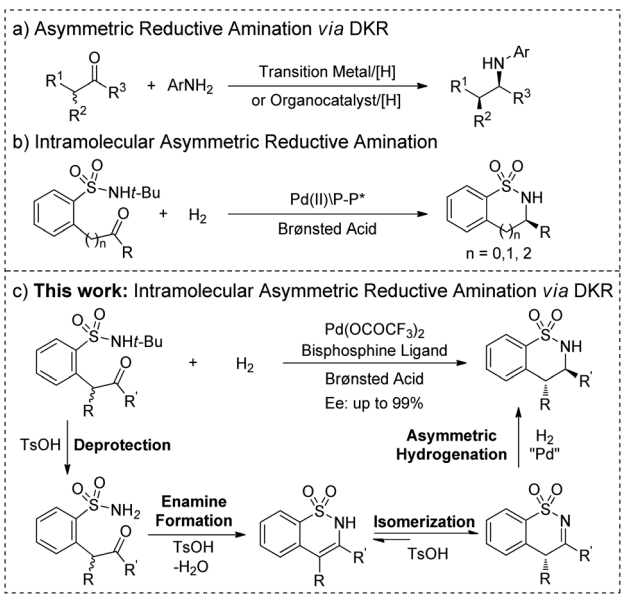
DOI: 10.1039/c7qo01098b

rsc.li/frontiers-organic

A palladium-catalyzed intramolecular asymmetric reductive amination of racemic α-branched ketones bearing the poorly nucleophilic sulfonamides has been successfully developed through dynamic kinetic resolution, providing chiral δ-sultams with two contiguous stereogenic centers with high diastereoselectivity and enantioselectivity.

Chiral δ-sultams represent important structural motifs in natural products and synthetic intermediates, particularly in biologically active molecules targeted as pharmaceuticals.[1] Consequently, a great deal of effort has been dedicated to the development of efficient approaches for their synthesis in an enantioenriched form.[2–4] Although asymmetric hydrogenation[2,3] and transition metal-catalyzed cyclization strategies[4] have been developed and demonstrated to be convenient approaches, the reported examples only concerned the construction of one single stereocenter, and their variants involving multiple contiguous stereocenters are still scarce due to multiselectivity issues such as chemo-, regio-, and stereoselectivity. Therefore, an efficient and atom-economical approach toward the synthesis of chiral δ-sultams possessing two contiguous stereocenters from simple and abundant starting materials is still desirable.

Dynamic kinetic resolution (DKR) has proved to be a highly valuable and particularly efficient strategy to construct multiple contiguous stereocenters, which allows the stereoconvergent transformation of both enantiomers of a racemic substrate into an optically pure product and overcomes the limitation of traditional kinetic resolution.[5] Out of various strategies developed for such transformations,[6–8] asymmetric reductive amination (ARA)[9,10] of racemic α-branched ketones by a fast racemization *via in situ* imine/enamine tautomerization provides an efficient enantioselective synthesis of amines with two contiguous stereogenic centers (Scheme 1a).[8] Recently, we have reported a novel example of intramolecular ARA of ketones with poorly active sulfonamides catalyzed by a chiral palladium-complex in combination with a Brønsted acid, providing a wide range of valuable chiral sultams (Scheme 1b).[3g] Furthermore, we have disclosed that there existed a rapid tautomerization of enesulfonamides to *N*-sulfonylimine intermediates prior to the enantio-determining hydrogenation step of enesulfonamides.[3e,11] In light of these observations, an intriguing premise is the possibility that chiral δ-sultams containing two vicinal stereocenters could be constructed by the intramolecular ARA of the racemic



Scheme 1 The synthesis of chiral amines/sultams through asymmetric reductive amination.

[a]*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China. E-mail: ygzhou@dicp.ac.cn; http://www.lac.dicp.ac.cn/*
[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China*

†Electronic supplementary information (ESI) available: Experimental details, compound characterization, and NMR and HPLC spectra. CCDC 1469313. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7qo01098b

α-branched ketones with sulfonamides through DKR. Although the application of poorly nucleophilic sulfonamides in DKR variants of ARA had no precedence,[3g,12] such a powerful approach would extend the generality of this ARA system. In this communication, we describe our efforts in the synthesis of δ-sultams bearing two adjacent stereocenters by the palladium-catalyzed intramolecular asymmetric reductive amination of the racemic α-branched ketones with sulfonamides in the presence of a Brønsted acid through dynamic kinetic resolution (Scheme 1c).

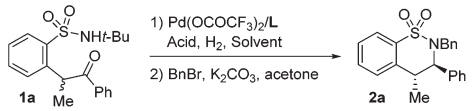
To test the viability of our proposed protocol, readily synthesised *N*-(*tert*-butyl)-2-(1-oxo-1-phenylpropan-2-yl)-benzenesulfonamide (**1a**) was chosen as a model substrate. Gratifyingly, the reaction proceeded smoothly to afford the desired product **2a** in moderate 65% yield and 46% ee in the presence of $Pd(OCOCF_3)_2$/(*R*)-SynPhos and *para*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$) in TFE at 100 °C for 48 h (Table 1, entry 1). Surprisingly, switching to the aprotic solvents (DCE, toluene, and DCM) gave rise to a substantial boost in activity, and good levels of enantiocontrol were also observed (entries 2–4). Next, we further screened several commercially available Brønsted acids; $TsOH{\cdot}H_2O$ was witnessed to be the best (entries 5–9). Finally, employing the electron-rich and steric-demanding ferrocenyl bisphosphine ligand (R,S_p)-*t*-Bu-JosiPhos **L4** resulted in a substantial improvement to 94% ee while maintaining good reactivity (entries 10–12).

With this optimized protocol, we commenced the extension of its substrate scope. The reaction performed well with aryl ketones possessing racemic methyl branched substituents at the α-position regardless of the electronic properties of aryl substituents (Table 2, entries 1, and 3–7). Nevertheless, the sterically bulky *o*-tolyl substituents substantially retarded the reaction rate, and a reoptimization of the reaction conditions resulted in moderate 57% ee in TFE (entry 2). Subsequent investigation with respect to the alkyl substituted substrate **1h** indicated that the diastereofacial control was remarkably deteriorated while minimally varying in high enantioselectivity for both isomers (entry 8); the low diastereoselectivity might be ascribed to the slow tautomerization of alkyl substituted enesulfonamides to *N*-sulfonylimine intermediates. Fortunately, variation of the racemic α-alkyl substituent of ketones to aryl led to high levels of enantiocontrol and diastereocontrol (entries 9 and 10). Furthermore, the introduction of methyl at the 4-position on the phenyl ring of ketosulfonamides did not exert any noticeable effect on the enantioselectivity (entries 1 and 11). The absolute configuration of the product was determined based on single-crystal X-ray diffraction analysis (see the ESI†).

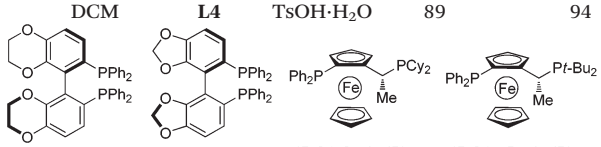
To investigate the detailed reaction pathway, two control experiments were performed (Scheme 2). First, cyclic enesulfonamide **3** can be conveniently synthesized with 95% yield in the presence of toluenesulfonic acid. Next, enesulfonamide **3** was subjected to the above standard conditions, giving the desired product **2a** with identical diastereoselectivity, enantioselectivity and absolute configuration (entry 1, Table 2), which suggested that the enesulfonamide **3** should be an active intermediate of the asymmetric reductive amination process.

According to previous work on the asymmetric hydrogenation of enesulfonamides,[3e,11] a sequential process including

Table 1 Optimization of the reaction conditions[a]

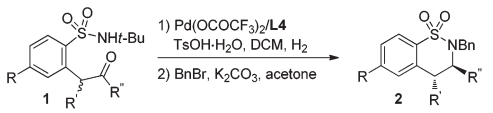


Entry	Solvent	L	Acid	Yield[b] (%)	ee[c] (%)
1	TFE	**L1**	$TsOH{\cdot}H_2O$	65	46
2	Toluene	**L1**	$TsOH{\cdot}H_2O$	83	80
3	DCE	**L1**	$TsOH{\cdot}H_2O$	85	81
4	DCM	**L1**	$TsOH{\cdot}H_2O$	88	80
5	DCM	**L1**	L-CSA	80	71
6	DCM	**L1**	D-CSA	61	77
7	DCM	**L1**	TFA	<5	—
8	DCM	**L1**	D-DDTA	<5	—
9	DCM	**L1**	PhCOOH	<5	—
10	DCM	**L2**	$TsOH{\cdot}H_2O$	92	86
11	DCM	**L3**	$TsOH{\cdot}H_2O$	90	80
12	DCM	**L4**	$TsOH{\cdot}H_2O$	89	94



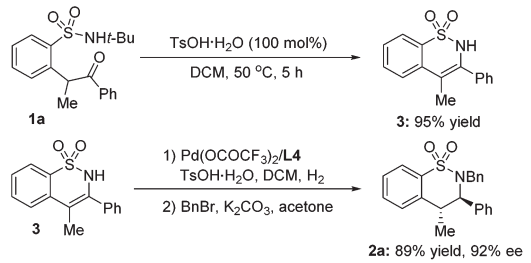
[a] Conditions: **1a** (0.2 mmol), $Pd(OCOCF_3)_2$ (3.0 mol%), ligand (3.3 mol%), acid (100 mol%), H_2 (800 psi), solvent (3.0 mL), 100 °C, 48 h. [b] Isolated yield of its *N*-benzyl protected derivative, dr > 20 : 1, determined by ^{1}H NMR spectroscopy. [c] Determined by the analysis of its *N*-benzyl protected derivative by HPLC.

Table 2 Substrate scope for the synthesis of chiral δ-sultams containing two contiguous stereocenters[a]

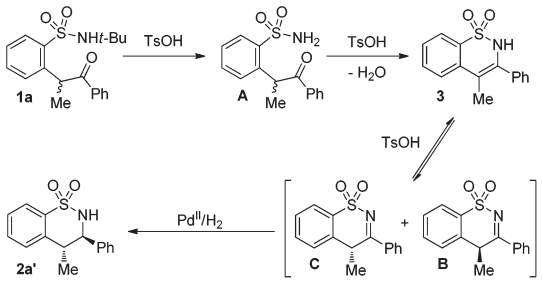


Entry	R	R′	R″	Yield[b] (%)	ee[c] (%)
1	H	Me	Ph	89 (**2a**)	94 (+)
2[d]	H	Me	2-MeC_6H_4	86 (**2b**)	57 (+)
3	H	Me	3-MeC_6H_4	90 (**2c**)	94 (+)
4	H	Me	4-MeC_6H_4	91 (**2d**)	94 (+)
5	H	Me	4-FC_6H_4	96 (**2e**)	95 (+)
6	H	Me	4-ClC_6H_4	89 (**2f**)	92 (+)
7	H	Me	4-BrC_6H_4	85 (**2g**)	90 (+)
8	H	Me	*n*-Bu	92 (**2h**/**2h′**)[e]	85/91[f]
9	H	Ph	Ph	85 (**2i**)	97 (−)
10	H	Ph	*n*-Bu	89 (**2j**)	99 (3*S*,4*R*)
11[g]	Me	Me	Ph	92 (**2k**)	94 (+)

[a] Reaction conditions: **1** (0.20 mmol), $Pd(OCOCF_3)_2$ (3.0 mol%), (R,S_p)-*t*-Bu-JosiPhos (**L1**, 3.3 mol%), $TsOH{\cdot}H_2O$ (100 mol%), H_2 (800 psi), DCM (3.0 mL), 100 °C, 48 h. [b] Isolated yields of two diastereoisomers, dr > 20 : 1, dr was determined by ^{1}H NMR spectroscopy. [c] Determined by chiral HPLC. [d] TFE was used as the solvent. [e] dr = 1.7 : 1 (*trans* : *cis*), determined by ^{1}H NMR spectroscopy. [f] ee values of two diastereoisomers (*trans*/*cis*). [g] The reaction was conducted for 72 h.



Scheme 2 Control experiments.



Scheme 3 A plausible reaction pathway for the synthesis of δ-sultams through dynamic kinetic resolution.

the tautomerization of enesulfonamides to *N*-sulfonylimine intermediates, and the asymmetric hydrogenation of the *N*-sulfonylimine was identified. Based on the above preliminary mechanistic studies and literature precedent,[3e,11] a plausible reaction pathway is depicted in Scheme 3. In this process, Brønsted acid not only promoted the first step of deprotection (removing the *tert*-butyl to give the free sulfonamide) and the following cyclodehydration to form the enesulfonamide **3**, but also simultaneously acted as a promoter for the tautomerization of the enesulfonamide to highly reactive *N*-sulfonylimine intermediates.[13,14] The outcomes of a high level of diastereocontrol provided further insight into the reaction process, and corroborated the dynamic kinetic resolution pathway. Moreover, the phenyl linker should be crucial for the carbonyl group to approach the sulfonamide, which may facilitate the intramolecular reductive amination due to the easy formation of the enesulfonamide intermediate and following the fast isomerization of the enesulfonamide to *N*-sulfonylimine in the presence of a Brønsted acid.

Conclusion

In conclusion, we have successfully developed an unprecedented palladium-catalyzed intramolecular reductive amination of the racemic α-branched ketones with sulfonamides through dynamic kinetic resolution. This transformation delivers a practical and straightforward approach to optically active δ-sultams bearing two adjacent stereocenters with high atom-economy, diastereoselectivity and enantioselectivity. Rudimentary mechanistic investigation demonstrated that a stepwise sequence of deprotection, cyclodehydration, and dynamic kinetic asymmetric hydrogenation promoted by a Brønsted acid was involved. Future studies focused on the development of related sulfonamides involved in amination are ongoing in our laboratory.

Experimental

A typical procedure for the asymmetric intramolecular reductive amination of 1a

Bisphosphine ligand (R,S_p)-*t*-Bu-JosiPhos (3.6 mg, 0.0066 mmol) and $Pd(OCOCF_3)_2$ (2.0 mg, 0.006 mmol) were placed in a dried Schlenk tube under a nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum to give the catalyst. This catalyst was taken into a glove box filled with nitrogen and dissolved in dichloromethane (1.0 mL). To the mixture of ketosulfonamide **1a** (69 mg, 0.2 mmol) and *para*-toluenesulfonic acid monohydrate (38 mg, 0.2 mmol) in dichloromethane was added this catalyst solution, and then the mixture was transferred to an autoclave, which was charged with hydrogen gas (800 psi). The autoclave was stirred under directed conditions (oil bath temperature was shown if it was heated). After the release of hydrogen gas, the autoclave was opened and the reaction mixture was evaporated. To a solution of the crude product in acetone (5.0 mL) was added benzyl bromide (30 μL, 0.25 mmol) and potassium carbonate (69 mg, 0.5 mmol). Then the mixture was heated to reflux overnight. The reaction mixture was evaporated. Purification was performed on silica gel using *n*-hexane/ethyl acetate as the eluent to give the chiral product **2a** as a white solid (64 mg, 89% yield, 94% ee). The enantiomeric excesses were determined by chiral HPLC (AD-H elute: *n*-hexane/i-propanol = 95/5, detector: 254 nm, flow = 0.7 mL min^{--1}), 30 °C, t_1 = 14.7 min, t_2 = 24.6 min (maj).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the National Natural Science Foundation of China (21532006, 21690074), the Chinese Academy of Sciences (QYZDJ-SSW-SLH035), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17020300), and the Dalian Bureau of Science and Technology (2016RD07) is acknowledged.

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