Tetrahedron Letters 53 (2012) 2560–2563

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Enantioselective Pd-catalyzed hydrogenation of tetrasubstituted olefins of cyclic β-(arylsulfonamido)acrylates

Chang-Bin Yu [a], Kai Gao [a], Qing-An Chen [a], Mu-Wang Chen [a], Yong-Gui Zhou [a,b,*]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

ARTICLE INFO

Article history:
Received 27 January 2012
Revised 1 March 2012
Accepted 9 March 2012
Available online 15 March 2012

Keywords:
Tetrasubstituted olefins
Cyclic β-(arylsulfonamido)acrylates
Asymmetric hydrogenation
Palladium complex

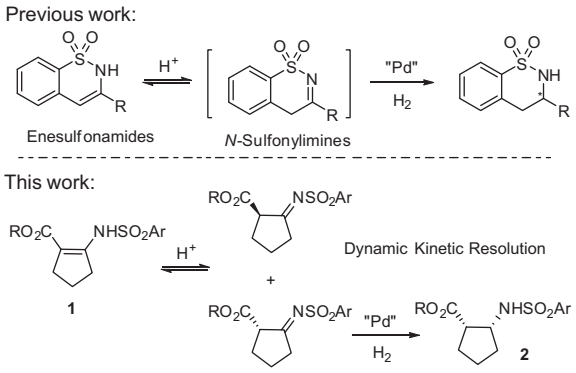
ABSTRACT

Asymmetric hydrogenation of tetrasubstituted olefins of cyclic β-(arylsulfonamido)acrylates produces the corresponding cyclic β-(arylsulfonamido)propionates using $Pd(OCOCF_3)_2$/diphosphine complexes as catalysts in the presence of TFA with up to 96% ee.

Enantiomerically pure β-amino acids and their derivatives are important chiral building blocks for the synthesis of many natural products and biologically active compounds.[1] They are also key structural elements of β-peptides, β-lactams.[2,3] Among them, cyclic β-(arylsulfonamido)propionate acid derivatives drew extreme attention of researchers due to their wide chemical and biological activities.[4] In the past few decades, many methods have been successfully developed to these β-amino acid deriatives.[5] However, despite the importance of β-amino acid derivatives, few researches have been done on the synthesis of chiral cyclic β-(arylsulfonamido) propionates.

According to retrosynthetic analysis of chiral β-(arylsulfonamido)propionates, asymmetric hydrogenation of tetrasubstituted olefins of the corresponding cyclic β-(arylsulfonamido)acrylates is one of the most atom economic and efficient approaches.

Although some examples on the asymmetric hydrogenation of tetrasubstituted unfunctionalized and functionalized olefins have been successfully reported recently,[6] exploring new catalyst system to asymmetric hydrogenation of tetrasubstituted olefins of cyclic β-(arylsulfonamido)acrylates is highly desirable. Recently, the chiral palladium complexes have been successfully applied to asymmetric hydrogenation of imines, ketones, simple indoles and pyrroles by us[7] and other groups.[8] Very recently, we reported the asymmetric hydrogenation of enesulfonamides.[9] The mechanism study showed that the hydrogenation was conducted via Brønsted acid catalyzed tautomerization of enesulfonamides to *N*-sulfonylimine intermediates (Scheme 1). Considering that the cyclic



Scheme 1. Synthesis of chiral cyclic β-amino acids.

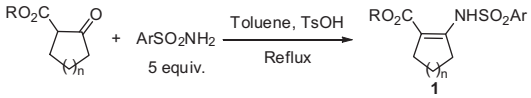
β-(arylsulfonamido)acrylates **1** can be readily transformed into the corresponding sulfonylimine intermediates through isomerization in the presence of Brønsted acid (Scheme 1). We envision that the active imine intermediates should be easily hydrogenated with a proper catalytic system. In this Letter, asymmetric hydrogenation of cyclic β-(arylsulfonamido)acrylates is successfully developed using $Pd(OCOCF_3)_2$/DuanPhos complex as catalysts in the presence of TFA with up to 96% ee.

Cyclic β-(arylsulfonamido)acrylates **1** can be readily synthesized from the corresponding cyclic β-ketoester and substituted arylsulfonamides by slightly modified literature procedures in moderate to good yields (Scheme 2).[10]

Our initial study began with **1i** as the model substrate and $Pd(OCOCF_3)_2$/(R,S_p)-JosiPhos as the catalyst on the basis of our

* Corresponding author. Tel./fax: +86 411 84379220.
E-mail address: ygzhou@dicp.ac.cn (Y.-G. Zhou).

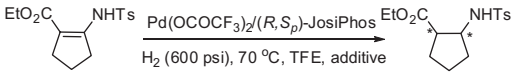
0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.03.035



Scheme 2. Synthesis of β-(arylsulfonamido)acrylates **1**.

previous successful hydrogenation of activated enesulfonamides.[9] However, low conversion (57%) and moderate 64% ee value were observed (Table 1, entry 1). To enhance the activity and enantioselectivity, a number of Brønsted acids were tested, the results are summarized in Table 1. When 1 equiv of L-tartaric acid was added, the conversion was improved and with the almost same enantioselectivity (63% ee, Table 1, entry 2). The chirality of the additive had no influence on the hydrogenation (Table 1, entries 2 vs 3). Other Brønsted acids also were screened, giving incomplete conversions but still with moderate enantioselectivities (Table 1, entries 4–6). When strong acid CF_3CO_2H (TFA) was added, full convention and

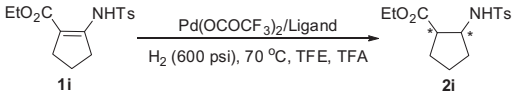
Table 1
The effect of additives on the reactivity and enantioselectivity[a]



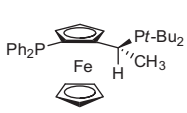
Entry	Additive	Conv[b] (%)	ee[c] (%)
1	—	57	64
2	L-Tartaric acid	70	63
3	D-Tartaric acid	68	63
4	Benzoic acid	80	77
5	4-Nitrobenzoic acid	61	68
6	Phthalic acid	68	76
7	Trifluoro-acetic acid	>95	81
8	2,3,4,5,6-Pentafluorobenzoic acid	28	82
9	2-Hydroxy-3,5-dinitrobenzoic acid	>95	81
10	Morpholine-TFA	27	77

[a] Conditions: 0.125 mmol of **1i**, $Pd(OCOCF_3)_2$ (0.0025 mmol), (R,S_p)-JosPhos (0.003 mmol), H2 (600 psi), additive (100 mol %), 3 mL of TFE, 16 h, 70 °C.
[b] Determined by ^1H NMR on the crude mixture.
[c] Determined by HPLC.

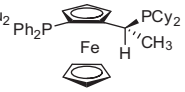
Table 2
Ligand screening for the Pd-catalyzed asymmetric hydrogenation of **1i**[a]



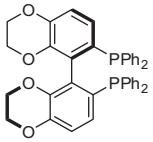
Entry	Ligand	Conv[b] (%)	ee[c] (%)
1	**L1**	>95	47
2	**L2**	>95	81
3	**L3**	64	78
4	**L4**	31	75
5	**L5**	60	68
6	**L6**	29	80
7	**L7**	71	79
8	**L8**	62	58
9	**L9**	>95	77
10	**L10**	71	89
11	**L11**	97[d]	91
12[e]	**L11**	92[d]	90
13[f]	**L11**	95[d]	90
14[g]	**L11**	92[d]	92



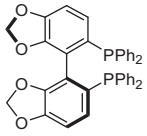
L1: (*R*)-(S)-PPF-P*t*-Bu$_2$



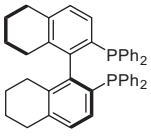
L2: (R,S_p)-JosiPhos



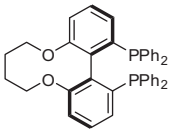
L3: (*R*)-SynPhos



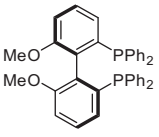
L4: (*S*)-SegPhos



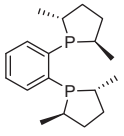
L5: (*S*)-H8-BINAP



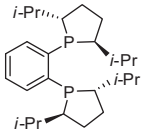
L6: (*R*)-C$_4$-TunePhos



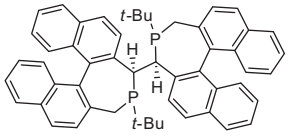
L7: (*S*)-MeO-Biphep



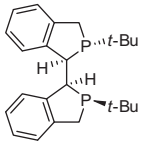
L8: (*R,R*)-Me-DuPhos



L9: (*S,S*)-*i*-Pr-DuPhos



L10: (*S*)-BINAPINE



L11: (1*R*,1'*R*,2*S*,2'*S*)-DuanPhos

[a] The reaction was carried out with **1i** (0.125 mmol), $Pd(OCOCF_3)_2$ (0.0025 mmol), ligand (0.003 mmol), H_2 (600 psi), TFA (100 mol %), and 3 mL TFE under directed condition for 16 h.
[b] Determined by ^1H NMR on the crude mixture.
[c] Determined by HPLC.
[d] Isolated yield.
[e] H_2 (800 psi).
[f] H_2 (400 psi).
[g] H_2 (200 psi).