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SmI_2-promoted imino-Reformatsky reaction for facile synthesis of enantioenriched β-amino acid esters

WANG Li, SHEN Chun & XU Ming-Hua*

Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China

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A facile and efficient method for the stereoselective synthesis of β-amino acid esters via SmI_2-promoted imino-Reformatsky reaction is described. Asymmetric addition of *tert*-butyl bromoacetate to *N-tert*-butanesulfinyl aldimines afforded β-amino acid esters in moderate to high yields with excellent diastereoselectivities. The synthetic utilities of the *tert*-butyl β-amino acid esters were expanded by the preparation of β-lactams and 3-aminoindan-1-ones derivatives.

β-amino acid ester, samarium diiodide, *N-tert*-butanesulfinyl imine, Reformatsky reaction, β-lactam, 3-aminoindan-1-one, asymmetric synthesis

1 Introduction

β-Amino acid structural units are frequently found in nature products and pharmacologically important molecules, such as Cispentacin, (*R*)-β-dopa, Moiramide B, Sperabillins, and Andrimid [1–3]. Furthermore, β-amino acid derivatives are also precursors of many other biologically active compounds, especially β-lactams [4–6]. Due to this importance, the development of the synthetic method to access β-amino acids is of great interest to organic and medicinal chemists. During the last decade, significant effort has been devoted to the stereoselective synthesis of these valuable materials [3, 7]. Of the methods developed, asymmetric addition of Reformatsky-type reagents to imines is known as an attractive strategy for optically active β-amino acid esters preparation. In recent years, a number of different chiral auxiliaries [8–13] as well as catalysts [14] has been introduced to provide the products with high stereoselectivities. Among them, the chiral sulfoxides are found as one of the best auxiliaries for the advantages of good stereodirecting and facile removal [15–19]. In contrast to the classical Zn-induced Reformatsky protocol, the application of other metal salts such as samarium diiodide by diastereoselective samarium enolate addition has received little attention in imino-Reformatsky reaction [9]. As part of our effort to develop efficient new methods for synthesis of diverse structurally important molecules, we herein report our findings on the use of SmI_2 for asymmetric Reformatsky reaction of *N-tert*-butanesulfinyl imine.

We have previously reported SmI_2-induced asymmetric synthesis of optically pure symmetrical and unsymmetrical vicinal diamines and β-amino alcohols by *N-tert*-butanesulfinyl imine-based reductive homocoupling and cross-coupling [20–22]. In these studies, a Sm(III)-*N*-sulfinyl imine chelation model has been proposed to account for the observed excellent reaction stereoselectivities. With this in mind, we envisioned that the similar chelation control might also occur in SmI_2-promoted Reformatsky reactions between α-halo esters and *N-tert*-butanesulfinyl imines, possibly facilitating the formation of β-amino acid ester products with high diastereoselectivities.

*Corresponding author (email: xumh@mail.shcnc.ac.cn)

2 Experimental

2.1 General information

THF was distilled from sodium/benzophenone. CH_2I_2 and *tert*-butyl bromoacetate were distilled in vacuum. Reactions were monitored by thin layer chromatography (TLC) on glass plates coated with silica gel with fluorescent indicator (Huanghai HSGF254). Flash chromatography was performed on silicagel (Huanghai 300–400) with hexane/EtOAc as eluent. Mass spectra were recorded on HP-5989 instrument and HRMS were measured on a Finnigan MA+mass spectrometer. NMR spectra were recorded on a Varian or a Bruker spectrometer (300 MHz), and chemical shifts are reported in δ (ppm) referenced to an internal TMS standard ^{1}HNMR and $CDCl_3$ (77.0 ppm) for ^{13}CNMR.

2.2 Starting materials procedure

Chiral *N*-*tert*-butanesulfinyl imines (**1a–i**) were prepared from the chiral *tert*-butanesulfinamide and the corresponding aldehydes by the known method [23, 24].

2.3 General procedure for asymmetric synthesis of β-amino acid esters and characterization

CH_2I_2 (0.8 mmol) was added at room temperature to a Schlenk flask containing samarium powder (0.8 mmol) and freshly distilled THF (3 mL) under nitrogen. After stirring for 30 min at rt, the dark green colored mixture was cooled to −78 °C. Then *N*-*tert*-butanesulfinyl imine (0.2 mmol) was added, followed by *tert*-butyl bromoacetate (0.4 mmol, dissolved in 1 mL THF) being added dropwise over 10 min. The resulting mixture was stirred at −78 °C for 2 h, quenched with aqueous NH_4Cl, and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography to afford the corresponding β-amino acid esters **3**.

3b ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 9H), 1.41 (s, 9H), 2.79 (d, 2H, J = 6.3 Hz), 4.63 (d, 1H, J = 3.6 Hz), 4.74–4.80 (m, 1H), 7.28–7.36 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 28.0, 43.6, 55.6, 81.6, 127.3, 127.8, 128.5, 140.7, 170.4.

3c ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 9H), 1.39 (s, 9H), 2.43 (s, 3H), 2.73–2.77 (m, 2H), 4.55 (d, 1H, J = 4.5 Hz), 4.50–5.03 (m, 1H), 7.17–7.21 (m, 3H), 7.32–7.35 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.4, 22.6, 27.9, 42.6, 51.5, 55.6, 81.5, 126.1, 126.7, 127.6, 130.6, 135.9, 138.5, 170.5. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{30}N_1O_3S_1$, 340.1939; found, 340.1941.

3d ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 9H), 1.36 (s, 9H), 2.88 (dd, 2H, J = 6.3 Hz, J = 2.7 Hz), 3.87 (s, 3H), 4.74 (d, 1H, J = 7.2 Hz), 5.00–5.07 (m, 1H), 6.87–6.95 (m, 2H), 7.26–7.30 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 24.1, 27.9, 42.1, 52.5, 55.3, 55.7, 81.1, 110.5, 120.3, 128.1, 128.6, 128.9, 156.5, 170.7**.** HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{18}H_{30}N_1O_4S_1$, 356.1883; found, 356.1890.

3e ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 9H), 1.41 (s, 9H), 2.75 (d, 2H, J = 6.3 Hz), 3.80 (s, 3H), 4.63 (d, 1H, J = 2.7 Hz), 4.70–4.75 (m, 1H), 6.81–6.93 (m, 3H), 7.22–7.27 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 28.0, 43.6, 55.2, 55.5, 55.6, 81.7, 112.8, 113.3, 119.6, 129.5, 142.5, 159.7, 170.4. HRMS-ESI *(m/z)*: $[M + H]^+$ calcd for $C_{18}H_{30}N_1O_4S_1$, 356.1883; found, 356.1890.

3f ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 9H), 1.40 (s, 9H), 2.73 (m, 2H), 3.80 (s, 3H), 4.56 (d, 1H, J = 2.7 Hz), 4.68–4.73 (m, 1H), 6.86 (d, 2H, J = 8.7 Hz), 7.25 (d, 2H, J = 8.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 28.0, 43.6, 54.9, 55.2, 55.5, 81.6, 113.8, 128.5, 132.6, 159.1, 170.5. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{18}H_{30}N_1O_4S_1$, 356.1883; found, 356.1890.

3g ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (s, 9H), 1.40 (s, 9H), 2.74 (d, 2H, J = 6.3 Hz), 4.65 (d, 1H, J = 3.9 Hz), 4.66–4.76 (m, 1H), 7.27–7.34 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 28.0, 29.7, 43.3, 55.0, 55.7, 81.9, 128.7, 133.6, 139.3, 170.2. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{17}H_{27}Cl_1N_1O_3S_1$, 360.1400; found, 360.1395.

3h ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (s, 9H), 1.37 (s, 9H), 2.83 (m, 2H, J = 6.0 Hz), 4.74 (d, 1H, J = 4.8 Hz), 4.77–4.83 (m, 1H), 7.27–7.32 (m, 1H), 7.67 (d, 1H, J = 7.2 Hz), 8.55 (d, 1H, J = 4.8 Hz), 8.63 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 27.9, 43.0, 53.6, 55.9, 82.1, 123.4, 135.1, 136.4, 148.9, 149.1, 170.0. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{16}H_{27}N_2O_3S_1$, 327.1738; found, 327.1737.

3i ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (s, 9H), 1.37 (s, 9H), 2.97–3.00 (m, 2H), 4.75 (d, 1H, J = 3.9 Hz), 5.53–5.59 (m, 1H), 7.43–7.59 (m, 4H), 7.79 (d, 1H, J = 8.1 Hz), 7.87 (d, 1H, J = 8.4 Hz), 8.18 (d, 1H, J = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 27.9, 29.7, 42.8, 52.6, 55.8, 81.6, 123.2, 125.0, 125.2, 125.7, 126.3, 128.5, 129.0, 130.7, 133.9, 136.2, 170.6. HRMS-ESI (*m/z*): $[M + H]^+$ calcd for $C_{21}H_{30}N_1O_3S_1$, 376.1956; found, 376.1941.

2.4 General procedure for synthesis of β-lactam 4 and characterization

Compound **3** (0.3 mmol) was added to a solution of HCl in dioxane (4 N, 10 mL) and the mixture was stirred at room temperature for 0.5 h. After removing the solvent in vacuum, the resulting crude product was dissolved in CH_3CN (30 mL), followed by the addition of $NaHCO_3$ (151 mg, 1.8 mmol) and MsCl (92 μL, 1.2 mmol). The mixture was further stirred at 60 °C for 8 h, then quenched with H_2O (10 mL). The solution was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to afford the corresponding β-lactam **4.**

4a (35 mg, yield 80% in two steps) Lit. [25]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.83–2.88 (dd, 1H, J = 15.0 Hz, J = 0.9 Hz), 3.40–3.46 (m, 1H), 4.71–4.73 (m, 1H), 6.72 (br, 1H), 7.32–7.38 (m, 5H). HPLC: Chiracel OD-H Column (250 mm); detected at 220 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; retention times: 13.93 min [(*R*)-enantiomer], 17.09 min [(*S*)-enantiomer].

4b (40 mg, yield 75% in two steps) Lit. [26]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.86–2.91 (dd, 1H, J = 15.0 Hz, J = 2.1 Hz), 3.40–3.48 (m, 1H), 3.82 (s, 3H), 4.70–4.72 (m, 1H), 6.17 (br, 1H), 6.84–6.97 (m, 3H), 7.26–7.33 (m, 1H). HPLC: Chiracel OD-H Column (250 mm); detected at 220 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; retention times: 14.06 min [(*S*)-enantiomer], 14.8 min [(*R*)-enantiomer].

4c (41 mg, yield 76% in two steps) Lit. [25]. $[\alpha]_D^{24}$ = –97.1 (c 0.55, EtOH). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.81–2.89 (m, 1H), 3.41–3.49 (m, 1H), 4.71 (dd, 1H, J = 5.1 Hz, J = 2.4 Hz), 6.43 (br, 1H), 7.28–7.38 (m, 4H). HPLC: Chiracel OD-H Column (250 mm); detected at 220 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; retention times: 11.8 min [(*R*)-enantiomer], 13.0 min [(*S*)-enantiomer].

2.5 General procedure for synthesis of 3-aminoindan-1-one 6 and characterization

Compound **3** (0.5 mmol) was added to a solution of HCl in dioxane (4 N, 10 mL) and the mixture was stirred at room temperature for 0.5 h. After removing the solvent in vacuum, the resulting crude product was dissolved in (CF3CO)2O (1 mL). The solvent was removed in vacuum after stirring at room temperature for 0.5 h. The residue was dissolved in CF_3COOH (2 mL) and stirred at room temperature for 3 h. The solution was poured into sat. aq. $NaHCO_3$, then extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to afford the corresponding 3-aminoindan-1-one **6**.

6a (92 mg, yield 76% in two steps) Lit. [27]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.67–2.74 (dd, 1H, J = 18.6 Hz, J = 3.6 Hz), 3.18–3.27 (dd, 1H, J = 18.6 Hz, J = 7.8 Hz), 5.75–5.82 (m, 1H), 7.55–7.60 (m, 1H), 7.69–7.80 (m, 3H), 9.01 (br, 1H). HPLC: Chiracel AS-H Column (250 mm); detected at 220 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; retention times: 17.2 min [(*S*)-enantiomer], 23.8 min [(*R*)-enantiomer].

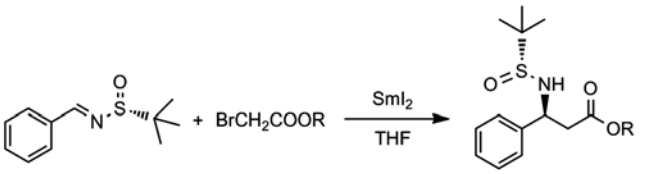
6b (88 mg, yield 65% in two steps) Lit. [28]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.51–2.59 (dd, 1H, J = 19.2 Hz, J = 3.6 Hz), 3.22–3.30 (dd, 1H, J = 19.2 Hz, J = 7.8 Hz), 3.82 (s, 3H), 5.63–5.70 (m, 1H), 6.62 (br, 1H), 7.52–7.55 (m, 3H). HPLC: Chiracel AS-H Column (250 mm); detected at 220 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; retention times: 7.13 min [(*R*)-enantiomer], 9.01 min [(*S*)-enantiomer].

6c (108 mg, yield 78% in two steps) Lit. [27]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59–2.66 (dd, 1H, J = 19.2 Hz, J = 3.3 Hz), 3.27–3.36 (m, 1H), 5.70–5.71 (m, 1H), 6.74 (br, 1H), 7.57 (d, 1H, J = 0.9 Hz) 7.67–7.73 (m, 2H). HPLC: Chiracel AS-H Column (250 mm); detected at 220 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; retention times: 11.78 min [(*R*)-enantiomer], 12.97 min [(*S*)-enantiomer].

3 Results and discussion

We initiated our study by reacting (*R*)-*N*-*tert*-butanesulfinyl imine **1a** with ethyl bromoacetate **2a** in the presence of 5 equiv of SmI_2 in THF at −78 °C (Table 1, entry 1). Unfortunately, only a trace amount of product was observed possibly due to self-addition of **2a** [29–31]. To our delight, the reaction proceeded smoothly and afforded the expected β-amino acid ester product **3b** with excellent diastereoselectivity (93% de) in 66% yield, when *tert*-butyl bromoacetate **2b** was used instead (entry 2). A slightly decreased de value of 88% was obtained when the reaction temperature was raised to −40 °C (entry 3). HMPA was found to have no influence on the reaction diastereoselectivity, but cause deleterious effect on yield when the amount was more than 1 equiv (entries 5–7). Decreasing the amount of *tert*-butyl bromoacetate or SmI_2 resulted in the lower yield of **3b** (20% and 51% respectively, entries 8, 9). Gratifyingly, the reaction

Table 1 Optimization of reaction conditions



Entry [a]	SmI_2 (equiv)	T (°C)	Time (h)	Yield (%) [b]	de (%) [c]
1 [d]	5	–78	2	trace	–
2	5	–78	2	66	93
3	5	–40	2	66	88
4	5	–20	2	40	–
5 [e]	5	–78	4	23	–
6 [f]	5	–78	4	60	93
7 [g]	5	–78	4	65	92
8 [h]	5	–78	2	20	–
9	3	–78	2	51	–
10 [i]	4	–78	2	80	95

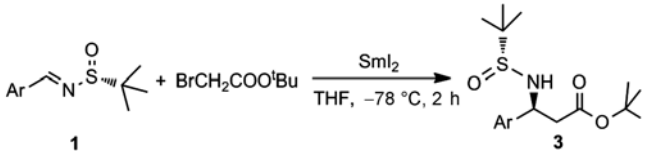
a) Unless otherwise noted, 2 equiv of *tert*-butyl ester **2b** was used, and the concentration of SmI_2 was 0.1 M in the reaction system. b) Isolated yield. c) de was measured as enantiomeric excess for the acetate derivative of **3b** after the removal of the sulfinyl group; determined by HPLC analysis. d) 2 equiv of **2a** was used as additive. e) 2 equiv of HMPA was used as additive. f) 1 equiv of HMPA was added. g) 0.5 equiv of HMPA was added. h) 1.2 equiv of ester **2b** was used. i) **2b** was dissolved in THF and added over 10 minutes.

afforded **3b** in improved yield (80%) at −78 °C when *tert*-butyl bromoacetate **2b** was added to the reaction mixture over 10 minutes as a solution of THF (entry 10).

With the optimized conditions in hand, the scope of this reaction with various aryl-substituted aldimines was explored (Table 2). In all cases, the desired β-amino acid esters with high des (95%–97%) were obtained in moderate to good yields. Substitution groups on the aromatic ring did not seem to affect the reaction rate as well as diastereoselectivity significantly. Moreover, the phenyl substitution could be extended to other aromatics, such as pyridyl and naphthyl.

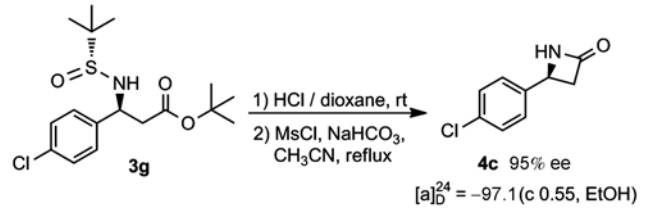
To determine the absolute configuration of the products, compound **3g** was chosen to convert into the known β-lactam for further optical rotation study. As illustrated in Scheme 1, removal of the sulfinyl group and *tert*-butyl ester under acidic conditions, followed by cyclization using the literature procedure [32], afforded the corresponding β-lactam **4c** in good yield. The chirl HPLC analysis of **4c** clearly revealed its excellent enantiomeric excess (95% ee), and the major enantiomer is speculated to has *S* configuration by comparison to literature optical rotation value [25].

Table 2 Asymmetric synthesis of β-amino acid esters



Entry [a]	Ar	Product	Yield (%) [b]	de(%) [c]
1	Ph	**3b**	80	95
2	2-MeC_6H_4	**3c**	74	97
3	2-MeOC_6H_4	**3d**	92	97
4 [d]	3-MeOC_6H_4	**3e**	77	95
5	4-MeOC_6H_4	**3f**	77	97
6	4-ClC_6H_4	**3g**	90	95
7	3-pyridyl	**3h**	65	95
8	1-naphthyl	**3i**	82	95

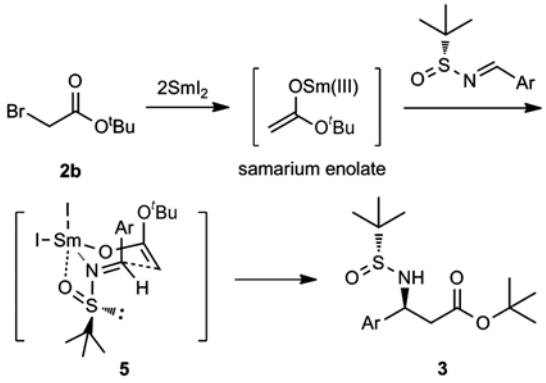
a) Reactions were carried out on a 0.2 mmol scale under N_2 with 2 equiv of ester **2b** and 4 equiv of SmI_2 at −78 °C. b) Isolated yield. c) de was measured as enantiomeric excess for the acetate derivative of **3** after their removal of the sulfinyl group; determined by HPLC analysis. d) de was measured as enantiomeric excess for its β-lactam derivative; determined by HPLC analysis.



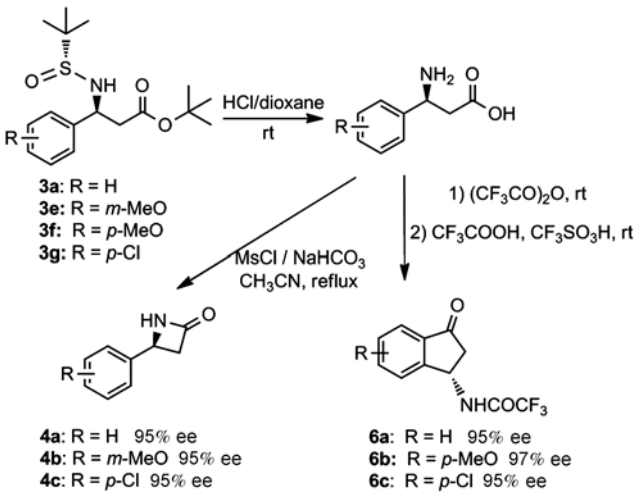
Scheme 1 Determination of the absolute configuration.

A plausible reaction mechanism for the observed stereoselective addition process is presented in Scheme 2. Upon treatment with SmI_2, the *tert*-butyl bromoacetate (**2b**) is reduced to generate samarium enolate [30, 31], which then undergoes intermolecular addition to the C=N bond of the *N*-*tert*-butanesulfinyl imine. Because of the coordination of the sulfinyl moiety in the imine intermediate to the enolate samarium, the Zimmerman-Traxler type six-membered transition state **5** favors approach of the enolate from the *Si*-face of *N*-sulfinyl imine **1** [20, 21, 33]. Therefore, the addition reaction takes place with high stereospecificity to give (*S*)-product.

To highlight the synthetic utility, rapid construction of a series of β-lactams and 3-aminoindan-1-ones was performed. Both of these compounds are valuable intermediates and exhibit interesting biological activities [34, 35]. With the obtained β-amino acid esters, the sulfinyl group and *tert*-butyl ester can be easily cleaved by acidic hydrolysis in one step to give free β-amino acids in high yields, which then undergo further lactamization [32] or Friedel-Crafts acylation [36] conveniently to furnish the corresponding β-lactams (**4**) and 3-aminoindan-1-ones (**6**) without loss of enantioselectivity (Scheme 3).



Scheme 2 Proposed reaction mechanism.



Scheme 3 Access to β-lactams and 3-aminoindan-1-ones.

4 Conclusions

In summary, a facile and efficient method for the asymmetric synthesis of β-amino acid esters via SmI_2-promoted imino-Reformatsky reaction using *N-tert*-butanesulfinyl imine is described. A series of highly enantiomerically enriched β-amino acid esters has been easily accessed in good yields. Moreover, conversion the resulting β-amino acid esters into β-lactams and 3-aminoindan-1-ones were accomplished with ease by taking advantage on the facile sulfinyl removal and ester hydrolysis. Further extension of this methodology is now under investigation in our laboratory.

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1 Davies SG, Smith AD, Price PD. The conjugate addition of nantiomerically pure lithium amidesas homochiral ammonia equivalents: Scope, limitations and synthetic applications. *Tetrahedron: Asymmetry*, 2005, 16: 2833–2891
2 Lui M, Sibi P. Recent advances in the stereoselective synthesis of β-amino acids. *Tetrahedron*, 2002, 58: 7991–8035
3 Juaristi E, Soloshonok VA. *Enantioselective Synthesis of β-Amino Acids*. New York: Wiley-VCH, 2005
4 Murayama T, Kobayashi T, Miura T. A convenient preparative method for β-lactams from β-amino acids using sulfenamide/ triphenylphosphine. *Tetrahedron Lett*, 1995, 36: 3703–3706
5 Escalante J, González-Tototzin MA, Aviña J, Muñoz-Muñiz O, Juaristi E. Synthesis of β-lactams and cyclo-β-dipeptides from β-amino acids: Experimental observations and theoretical analysis. *Tetrahedron*, 2001, 57: 1883–1890
6 Gedey S, Van der Eycken J, Fülöp F, Liquid-phase combinatorial synthesis of alicyclic β-lactams via Ugi four-component reaction. *Org Lett*. 2002, 4: 1967–1969
7 Ma JA, Recent developments in the catalytic asymmetric synthesis of α- and β-amino acids. *Angew Chem Int Ed*, 2003, 42: 4290–4299
8 Brinner K, Doughan B, Poon DJ. Scalable synthesis of β-amino esters via Reformatsky reaction with *N-tert*-butanesulfinyl imines. *Synlett*, 2009, 6: 991–993
9 Concellon JM, Rodriguez-Solla H, Simal C. The use of samarium enolates, a novel alternative in the addition reactions to imines. Synthesis of 3-amino esters, amides and enantiopure 3,4-diamino esters. *Adv Synth Catal*, 2009, 351: 1238–1242
10 Ukaji Y, Takenaka S, Horita Y, Inomata K. Asymmtric addition of Reformatsky-type reagent to imines utilizing diisopropyl tartrate as a chirlauxiliary. *Chem Lett*, 2001, 254–255
11 Marcotte S, Pannecoucke X, Feasson C, Quirion JC. Enantioselective synthesis of α,α-difluoro-β-amino acid and 3,3-difluoroazetidin-2-one via the Reformatsky-type reaction of ethyl bromodifluoroacetate with chiral 1,3-oxazolidines. *J Org Chem*, 1999, 64: 8461–8464
12 Baldoli C, Buttero PD, Licandro E, Papagni A. Tricarbonyi (η^6arene) chromium (0) complexes as chiral auxiliaries: Asymmetric synthesis of β-aminoesters and β-lactams by Reformatsky condensation. *Tetrahedron*, 1996, 52: 4849–4856
13 Shankar BB, Kirkup MP, McCombie SW, Clader JW, Ganguly AK. Synthesis of an optically pure 3-unsubstituted β-lactam using an asymmetric Reformatsky reaction and its conversion to cholesterol absorption inhibitors. *Tetrahedron Lett*, 1996, 37: 4095–4098
14 Cozzi PG, Rivalta E. Highly enantioselective one-pot, three-component imino-Reformatsky reaction. *Angew Chem Int Ed*, 2005, 44: 3600–3603
15 Robak MT, Herbage MA, Ellman JA. Synthesis and applications of *tert*-butanesulfinamide. *Chem Rev*, 2010, 110: 3600–3740
16 Recently, the use of *N*-phosphonyl imines in asymmetric synthesis was proven to be efficient, see lit. [16–19]. Ai T, Li GG. Chiral *N*-phosphonyl imine chemistry: Asymmetric synthesis of α, β-diamino ester by reacting phosphonyl imines with glycine enolates. *Bioorg Med Chem Lett*, 2009, 19: 3967–3969
17 Kaur P, Shakya G, Sun H, Pan Y, Li GG. Chiral *N*-phosphonyl imine chemistry: An efficient asymmetric synthesis of chiral *N*-phosphonyl propargylamines. *Org Biomol Chem*, 2010, 8: 1091–1096
18 Kaur P, Pindi S, Wever W, Rajale T, Li GG. Asymmetric catalytic Strecker reaction of *N*-phosphonyl imines with Et_2AlCN using amino alcohols and BINOLs as catalysts. *Chem Commun*, 2010, 46: 4330–4332
19 Kaur P, Pindi S, Wever W, Rajale T, Li GG. Asymmetric catalytic *N*-phosphonyl imines chemistry: The use of primary free amino acids and Et_2AlCN for asymmetric catalytic Strecker reaction. *J Org Chem*, 2010, 75: 5144–5150
20 Zhong YW, Xu MH, Lin GQ. Samarium diiodide-induced asymmetric synthesis of optically pure unsymmetrical vicinal diamines by reductive cross-coupling of nitrones with *N-tert*-butanesulfinyl imines. *Org Lett*, 2004, 6: 3953–3956
21 Zhong YW, Izumi K, Xu MH, Lin GQ. Highly diastereoselective and enantioselective synthesis of enantiopure C_2-symmetrical vicinal diamines by reductive homocoupling of chiral aromatic *N-tert*-butanesulfinyl imines. *Org Lett*, 2004, 6: 4747–4750
22 Zhong YW, Dong YZ, Fang K, Izumi K, Xu MH, Lin GQ. A highly efficient and direct approach for synthesis of enantiopure β-amino alcohols by reductive cross-coupling of chiral *N-tert*-Butanesulfinyl imines with aldehydes. *J Am Chem Soc*, 2005, 127: 11956–11957
23 Cogan DA, Liu GC, Kim K, Backes BJ, Ellman JA. Catalytic asymmetric oxidation of *tert*-butyl disulfide. Synthesis of *tert*-butanesulfinamides, *tert*-butyl sulfoxides, and *tert*-butanesulfinimines. *J Am Chem Soc*, 1998, 120: 8011–8019
24 Liu GC, Cogan DA, Owens TD, Tang TP, Ellman JA. Synthesis of enantiomerically pure *N-tert*-Butanesulfinyl imines (*tert*-butanesulfinimines) by the direct condensation of *tert*-butanesulfinamide with aldehydes and ketones. *J Org Chem*, 1999, 64: 1278–1284
25 Forro E, Paal T, Tasnadi G, Fulop F. A new route to enantiopure β-aryl-substituted β-amino acids and 4-aryl-substituted β-lactams through lipase-catalyzed enantioselective ring cleavage of β-lactams. *Adv Synth Catal*, 2009, 348: 917–923
26 Frank H, Hans S, Roy H. Chlorosulfonyl isocyanate addition to *o*-dial-kylaminostyrenes: Preparation of 6-(*o*-dialkylaminophenyl) uracils. *Synthesis,* 1982, 8: 662–665
27 Sylvain A, Patrick D, Max R. A simple synthesis of the first 3-amino-1-indanones. *Bull Soc Chim de France*, 1987, 6: 1079–1083
28 Auvray P, Moslemi S, Sourdaine P, Galopin S, Seralini GE, Enguehard C, Dallemagne P, Bureaub R, Sonnetb P, Rault S. Evidence for new non-steroidal human aromatase inhibitorsand comparison with equine aromatase inhibition for an understanding of the mammalian active site. *Eur J Med Chem*, 1998, 33: 451–462
29 Hanessian S, Girard C. Facile access to 3-ulosonic acids via a SmI_2-Mediated Reformatsky reaction on aldonolactones. *Synlett*, 1994, 865–867
30 Park HS, Lee IS, Kim YH. Facile synthesis of β-ketoesters mediated by SmI_2: Reformatsky reaction type selfcondensation. *Tetrahedron Lett*, 1995, 36: 1673–1674
31 Balaux E, Ruel R, Synthesis of succinic diesters via reductive coupling of α-haloesters using samarium (II) iodide and HMPA. *Tetrahedron Lett*, 1996, 37: 801–804
32 Loewe MF, Cvetovich RJ, Hazen GG. An efficient β-amino acid cyclodehydation using methanesulfonyl chloride to thienamycin intermediate 3-[1-hydroxyethyl]-4-[methoxycarbonylmethyl]-azetidin-2-one. *Tetrahedron Lett*, 1991, 32: 2299–2302
33 Tang TP, Ellman JA. The *tert*-butanesulfinyl group: An ideal chiral directing group and boc-surrogate for the asymmetric aynthesis and application of β-amino acids. *J Org Chem*, 1999, 64: 12–13
34 Wasserman HH, Matsuyama H, Robinson RP. β-Lactams as building blocks in the synthesis of macrocyclic spermine and spermidine alkaloids. *Tetrahedron*, 2002, 58: 7177–7190
35 Arefalk A, Wannberg J, Larhed M, Hallberg A, Stereoselective synthesis of 3-aminoindan-1-ones and subsequent incorporation into HIV-1 protease inhibitors. *J Org Chem*, 2006, 71: 1265–1268
36 Dallemagne P, Rault S, Pilo JC, Foloppe MP, Robba M. One-pot scyclization of alkoxy-3-aminoindan-1-ones. *Tetrahedron Lett*, 1991, 32: 6327–6328