RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2014, **4**, 12257

Oxazoline derivatives tagged with tosylated amino acids as recyclable organocatalysts for enantioselective allylation of aldehydes†

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Received 9th December 2013
Accepted 16th January 2014

DOI: 10.1039/c3ra47424k

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A series of amino acid-based oxazoline compounds have been prepared and successfully applied to the enantioselective allylation reaction of aldehydes. The fine-tuning of the structure of the oxazolines led to **(*S*,*S*)-4** as an efficient organocatalyst which gave homoallyl alcohols in good yield (up to 90%) and excellent ee (up to 99%) for a wide range of substrates including aromatic, hetero-aromatic and α,β-unsaturated aldehydes. The chiral organocatalyst was synthesized in three easy steps with an overall 88% yield and successfully recycled for up to three cycles. On the basis of the experimental observations and NMR studies, a probable mechanism was proposed for this reaction.

Introduction

The application of organocatalysts in asymmetric C–C bond formation reactions, especially in asymmetric allylation reactions, is often preferred over metal-based catalysts, particularly in the pharmaceutical sector due to health, environmental, cost and efficiency concerns. For the development of new organocatalysts in asymmetric allylation reactions, various natural and synthetic amino acids as chiral building blocks seem to be most suitable due to their cost-effectiveness and easy availability. Chiral allylation products, *i.e.* homoallyl alcohols and homoallyl amines, are important building blocks for the construction of many biologically active compounds.[1,2] For the production of homoallyl alcohol, allyltrialkylsilanes[2a,c] and stannanes[3] react readily with aldehydes upon the activation of the carbonyl group by a Lewis acid.[2,3] By contrast, allyltrichlorosilane requires activation with a Lewis base that coordinates to the silicon atom. Lewis bases reported in this respect are *N*-oxides,[4] formamides,[5] bisformamides,[6] phosphine oxide,[7] phosphinamides,[8] urea derivatives[9] and catecholates.[10] Oxazoline derivatives as efficient ligands in metal-catalyzed asymmetric allylation reactions has been well documented,[2c,11,12] however, Barrett *et al.*[13] (1997) for the first time demonstrated that bidentate pyridine-linked oxazoline compounds can directly be used as organocatalysts for the allylation of aldehydes. Subsequently, chiral oxazolines appended with chiral sulfoxide[14] and *N*-oxides[4k] have also been registered for their potential as organocatalysts for the asymmetric allylation of aldehydes. However, there are nagging issues, such as the extremely low reaction temperatures, moderate yield and ee, and non-recyclability of these catalysts, which need to be addressed. Bearing in mind the value of oxazolines, overall stability of the catalyst and our previous experience with tosylated amino acids[15] as organocatalysts in the enantioselective allylation reaction of aldehydes, herein we have synthesized a series of oxazoline-based organocatalysts,[16,17] **(*S*,*S*)-1** to **(*S*,*S*,*R*)-5**, featuring sulfonamide groups with varying steric features and two to three chiral centers. Chiral centers in organocatalysts featuring configurations with different permutations and combinations were prepared for their possible role in influencing the product enantioselectivity. In order to know the specific role of the sulfonamide moiety in the organocatalyst on the activity and enantioselectivity of the allylation reaction, we also synthesized a Boc-protected organocatalyst, **(*S*,*S*)-6**.[18] Among these organocatalysts, **(*S*,*S*)-4** (10 mol%) was found to be the most promising, robust and recyclable (3 times) catalyst that gave allylation products in 52–90% yield and 65–99% ee with various substituted aldehydes at 0 °C.

Results and discussion

Recently we have shown that tosylated phenylalanine-based amides are efficient organocatalysts for the enantioselective allylation of aldehydes. Therefore, instinctively we thought of combining tosylated phenylalanine and oxazoline and synthesising organocatalyst **(*S*,*S*)-1** in three simple synthetic steps. The same strategy was used to prepare the remaining

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† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C spectra for all new and the few known compounds, and HPLC chromatograms for the homoallyl alcohols described herein. See DOI: 10.1039/c3ra47424k

organocatalysts **1–5** with varied chirality (Scheme 1).[15,17] We also synthesized catalyst **(*S*,*S*)-6** (Scheme 2) by replacing the tosyl part of the catalyst **(*S*,*S*)-4** with Boc to ascertain the role of the tosyl group in the allylation reaction.

To begin with, catalyst **(*S*,*S*)-1** was evaluated for its efficacy in the asymmetric allylation of aldehydes by using 4-methoxy benzaldehyde (0.5 mmol) as a model substrate with allyltrichlorosilane (1.2 equivalent) as an allylating agent in CH_2Cl_2 at RT. In all of the catalytic reactions, diisopropylethyl amine (DIPEA) as a base additive (2 equiv. with respect to the substrate) was used to facilitate the allylation reaction. Catalyst **(*S*,*S*)-1** showed some hopeful results (Table 1, entry 1; yield 60%, ee 54%). Catalyst **(*R*,*S*)-1** with mismatched chirality gave a product with significantly lower yield (56%) and ee (40%) (entry 2).

The opposite enantiomeric catalyst **(*S*,*R*)-1** gave similar activity (yield 55%) and enantioselectivity (ee 40%) but with the opposite configuration of the allylation product (entry 3).

Based on these results, it can be concluded that the enantioinduction in the product is largely governed by the chirality originating from the phenylalaninol part of the catalyst. In order to improve the efficiency of the organocatalyst, we replaced the (*S*)-phenylalaninol moiety from catalyst **(*S*,*S*)-1** with (*S*)-phenylglycinol and synthesized catalyst **(*S*,*S*)-2**. Unfortunately, there was a significant drop in the product yield (40%) as well as the ee (17%) (entry 4). Catalyst **(*S*,*S*)-3**, which was prepared by replacing the (*S*)-phenylglycinol moiety from catalyst **(*S*,*S*)-2** with (*S*)-*tert*-leucinol, showed relatively better performance (entry 5: yield, 65%; ee, 60%). To our pleasant surprise, substitution of tosylated (*S*)-phenylalanine from catalyst **(*S*,*S*)-3** with tosylated (*S*)-*tert*-leucine to obtain catalyst **(*S*,*S*)-4** resulted in a substantial improvement in the product yield (72%) and ee (70%) (entry 6). For further improvement in the catalyst performance, we varied the steric features in the oxazoline part of the catalyst as in catalysts **(*S*,*R*,*S*)-5** (entry 7) and **(*S*,*S*,*R*)-5** (entry 8), but these could not match the performance of catalyst **(*S*,*S*)-4**. The sulfonamide moiety in organocatalyst **(*S*,*S*)-4** has a specific role, possibly in activating the silicon atom of allyltrichlorosilane through coordination of its sulfonamide oxygen.

To verify this, we prepared catalyst **(*S*,*S*)-6** by replacing the tosyl part of catalyst **(*S*,*S*)-4** by Boc (Scheme 2), and observed a significant drop in both the product yield (55%) and ee (45%) (entry 9).

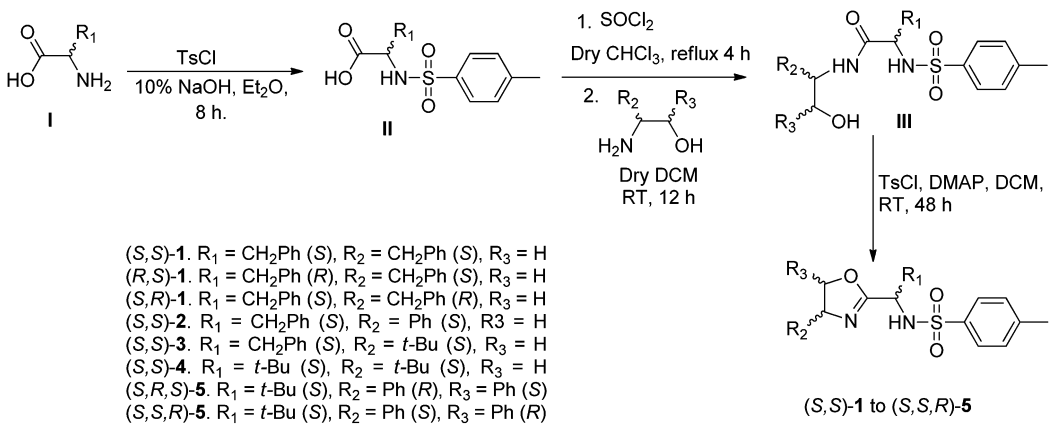
Catalyst **(*S*,*S*)-4**, which was the best performer, was subjected to optimization of the catalytic reaction conditions to further improve the yield and enantioselectivity of the allylation product. The role of additives in the asymmetric allylation reaction is well documented,[2] therefore we first scrutinized the effect of different additives (mostly Lewis bases), *viz.*, DIPEA, Et_3N, 1,8-diazabicycloundec-7-ene (DBU) and tetrabutylammonium iodide (TBAI) (Table 2, entries 2–5), on this reaction by keeping the other parameters constant. It is to be noted that in the absence of an appropriate additive, the catalyst efficiency was significantly lower (Table 2, entry 1). DIPEA was found to be the most suitable (entry 2) among the additives used here.

Even the amount of DIPEA with respect to the substrate amount was found to be crucial for the desired outcome of the reaction, as is evident from the experiments carried out over a range of 1–3 equivalents of DIPEA (entries 2, 6 and 7), with 2 equivalents (entry 2) found to be the optimum. The temperature effect (Table 2, entries 8–10) on this reaction, studied from −40 °C to RT, revealed that at 0 °C the product ee (97%) was highest with 67% yield in 24 h (entry 8).

Further, the catalyst loading of 10 mol%, which was used in the foregoing experiments, was found to be optimum as it was observed that by decreasing the catalyst loading (5 mol%) the product yield (50%) dropped significantly. On the other hand, with an increase in catalyst loading (15 mol%), the reaction was faster but with a marginal drop in the ee (90%) while the product yield remained similar (Table 3, entry 3). Next, solvent variation studies (Table 3, entries 2, 4–7) showed that CH_2Cl_2 was the most suitable solvent among the solvents studied here (Table 3, entry 2).

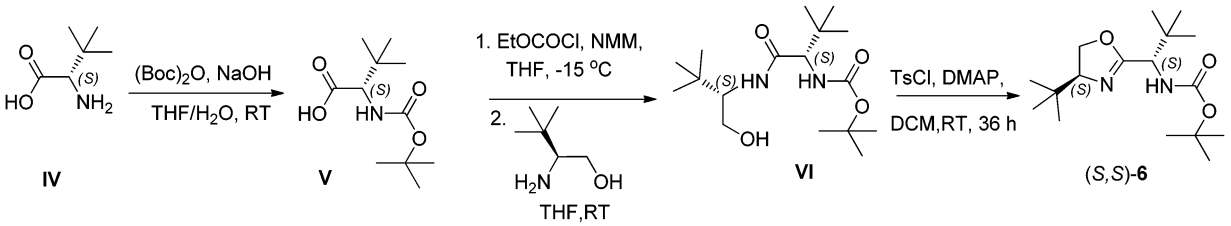
After achieving the optimum reaction conditions (Table 3, entry 2) for the enantioselective allylation reaction, we investigated the efficacy of the catalyst **(*S*,*S*)-4** for various aromatic, hetero-aromatic and aliphatic aldehydes as substrates (Table 4).

Among the different aromatic aldehydes, *m*/*p*-substituted benzaldehydes (Table 4, entries 2–9) gave better ees as



(*S*,*S*)-**1**. R_1 = CH_2Ph (*S*), R_2 = CH_2Ph (*S*), R_3 = H
(*R*,*S*)-**1**. R_1 = CH_2Ph (*R*), R_2 = CH_2Ph (*S*), R_3 = H
(*S*,*R*)-**1**. R_1 = CH_2Ph (*S*), R_2 = CH_2Ph (*R*), R_3 = H
(*S*,*S*)-**2**. R_1 = CH_2Ph (*S*), R_2 = Ph (*S*), R3 = H
(*S*,*S*)-**3**. R_1 = CH_2Ph (*S*), R_2 = *t*-Bu (*S*), R_3 = H
(*S*,*S*)-**4**. R_1 = *t*-Bu (*S*), R_2 = *t*-Bu (*S*), R_3 = H
(*S*,*R*,*S*)-**5**. R_1 = *t*-Bu (*S*), R_2 = Ph (*R*), R_3 = Ph (*S*)
(*S*,*S*,*R*)-**5**. R_1 = *t*-Bu (*S*), R_2 = Ph (*S*), R_3 = Ph (*R*)

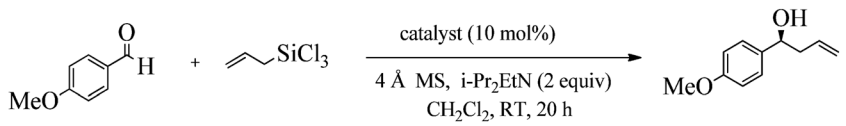
Scheme 1 Synthesis of tosyl-protected organocatalysts.

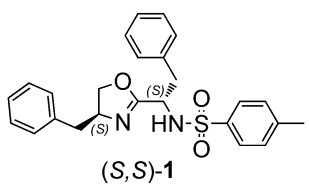


Scheme 2 Synthesis of Boc-protected organocatalyst.

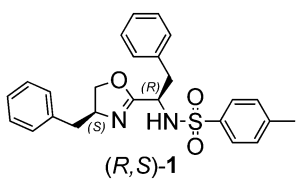
compared to their *o*-counterparts (Table 4, entries 10 and 11). The enantioselectivity was comparatively better for substrates with electron donating substituents (Table 4, entries 2–4) than electron withdrawing substituents (Table 4, entries 6–8). The bulkier aldehydes such as 2-naphthaldehyde, were found to be more reactive in the present catalytic system, which gave a product with higher yield, but with a significantly lower ee (Table 4, entry 12) than benzaldehyde (Table 4, entry 1). The heteroaromatic aldehyde ,thiophene-2-carboxaldehyde (Table 4, entry 13) behaved just like benzaldehyde by giving only a marginally higher yield (82%) and comparable ee (92%). α,β-Unsaturated aldehydes, *viz. trans*-cinnamaldehyde and *trans*-α-methyl cinnamaldehyde, as substrates gave products with good yields and good to excellent ees (Table 4, entries 14 and 15), but with an inverted configuration (*R*) as compared to the products (configuration *S*) obtained with the rest of the aldehydes used in

Table 1 Screening of chiral organocatalysts (*S*,*S*)-**1** to (*S*,*S*)-**6** for the enantioselective allylation reaction[a]

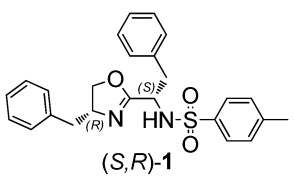



(*S*,*S*)-**1**

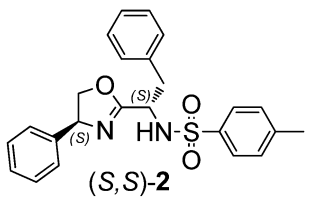
Entry	Yield[b] [%]	ee[c] [%]	Config.[d]
1	60	54	*S*


(*R*,*S*)-**1**

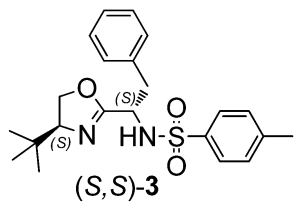
Entry	Yield[b] [%]	ee[c] [%]	Config.[d]
2	56	40	*S*


(*S*,*R*)-**1**

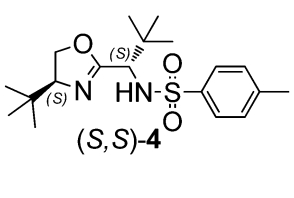
Entry	Yield[b] [%]	ee[c] [%]	Config.[d]
3	55	40	*R*


(*S*,*S*)-**2**

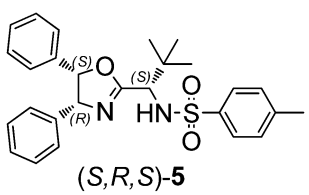
Entry	Yield[b] [%]	ee[c] [%]	Config.[d]
4	40	17	*S*


(*S*,*S*)-**3**

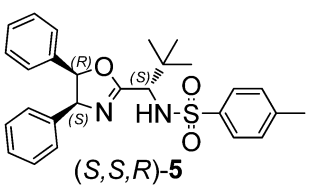
Entry	Yield[b] [%]	ee[c] [%]	Config.[d]
5	65	60	*S*


(*S*,*S*)-**4**

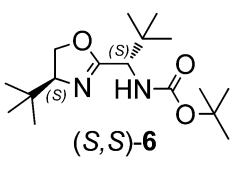
Entry	Yield[b] [%]	ee[c] [%]	Config.[d]
6	72	70	*S*


(*S*,*R*,*S*)-**5**

Entry	Yield[b] [%]	ee[c] [%]	Config.[d]
7	60	20	*R*


(*S*,*S*,*R*)-**5**

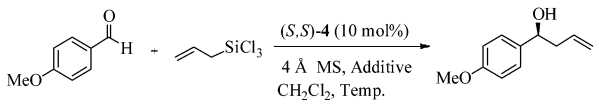
Entry	Yield[b] [%]	ee[c] [%]	Config.[d]
8	63	35	*S*


(*S*,*S*)-**6**

Entry	Yield[b] [%]	ee[c] [%]	Config.[d]
9	55	45	*S*

[a] All the reactions were carried out by using the substrate 4-methoxy benzaldehyde (0.5 mmol), allyltrichlorosilane (0.6 mmol), diisopropylethyl amine (1 mmol) and catalyst (10 mol%) in CH_2Cl_2 at RT. [b] Isolated yields after column chromatography. [c] ee determined by chiral HPLC using a Daicel Chiralcel OD-H column. [d] Absolute configurations were assigned by comparing both the retention time and optical rotation with the reported reliable data.

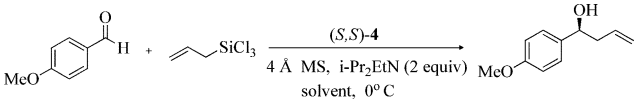
Table 2 Effect of additives and temperature on the asymmetric allylation reaction[a]



Entry	Additive [equiv.]	Temp. [°C]	Time [h]	Yield[b] [%]	ee[c] [%]
1	—	RT	24	40	58
2	DIPEA (2.0)	RT	20	72	70
3	Et_3N (2.0)	RT	20	77	50
4	DBU (2.0)	RT	20	68	41
5	TBAI (2.0)	RT	20	50	30
6	DIPEA (1.0)	RT	20	55	68
7	DIPEA (3.0)	RT	20	71	70
8	DIPEA (2.0)	0	24	67	97
9	DIPEA (2.0)	−20	24	62	96
10	DIPEA (2.0)	−40	36	60	90

[a] Reaction conditions as per Table 1. [b] Isolated yield after column chromatography. [c] ee determined by chiral HPLC using a Daicel Chiralcel OD-H column.

Table 3 Optimization of catalyst loading and effect of the solvent on the asymmetric allylation reaction[a]



Entry	Cat. loading [mol%]	Solvent	Time [h]	Yield[b] [%]	ee[c] [%]
1	5	CH_2Cl_2	24	50	96
2	10	CH_2Cl_2	24	67	97
3	15	CH_2Cl_2	17	68	90
4	10	THF	30	52	67
5	10	CH_2Cl_2 : THF (1 : 1)	24	55	60
6	10	$CHCl_3$	20	60	70
7	10	Toluene	36	40	55

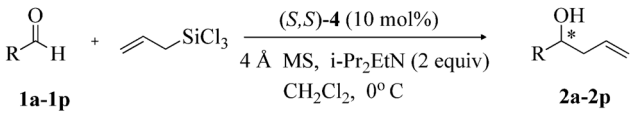
[a] Reaction conditions as per Table 1. [b] Isolated yield after column chromatography. [c] ee determined by chiral HPLC using a Daicel Chiralcel OD-H column.

the present study. Similarly, the inversion of configuration was also observed for the product (configuration *R*) obtained with phenylacetaldehyde, but with a significantly lower yield (52%) and ee (67%).

Reaction mechanism: NMR experiments

A series of NMR experiments were performed for understanding of the mechanism of the allylation reaction operating in the present catalytic system. For this, we looked for any observable changes in the NMR spectra of catalyst **(*S*,*S*)-4** after the sequential addition of allyltrichlorosilane, substrate (benzaldehyde) and DIPEA. The ^{13}C NMR spectra (Fig. 1) showed that the imine carbon peak (163.82 ppm) of catalyst **(*S*,*S*)-4** was

Table 4 Enantioselective allylation of various aldehydes using catalyst (*S*,*S*)-4[a]



Entry	Substrate	Time [h]	Yield[b] [%]	ee[c] [%]	Config.[d]
1	C_6H_5CHO (**1a**)	18	75	93	*S*
2	4-MeO–C_6H_4CHO (**1b**)	24	67	97	*S*
3	4-($C_6H_5CH_2O$)–C_6H_4CHO (**1c**)	24	68	>99	(−)[e]
4	4-$(CH_3)_3C$–C_6H_4CHO (**1d**)	24	70	97	*S*
5	4-Me–C_6H_4CHO (**1e**)	24	65	86	*S*
6	4-NO_2–C $_6H_4CHO$ (**1f**)	20	70	90	*S*
7	4-F–C_6H_4CHO (**1g**)	22	78	75	*S*
8	4-CF_3–C_6H_4CHO (**1h**)	20	75	77	*S*
9	3-MeO–C_6H_4CHO (**1i**)	20	77	93	*S*
10	2-MeO–C_6H_4CHO (**1j**)	20	84	64	*S*
11	2-F–C_6H_4CHO (**1k**)	22	74	69	*S*
12	2-Naphthaldehyde (**1l**)	14	85	81	*S*
13	Thiophene-2-carbaldehyde (**1m**)	14	82	92	*S*
14	(*E*)$C_6H_5CHCHCHO$ (**1n**)	15	77	80	*R*
15	(*E*)$C_6H_5CHC(CH_3)CHO$ (**1o**)	15	90	93	*R*
16	$C_6H_5CH_2CHO$ (**1p**)	24	52	67	*R*

[a] Reaction conditions as per Table 1. [b] Isolated yields after column chromatography. [c] ee determined by chiral HPLC using Daicel Chiralcel and Chiralpak OD-H, AS-H, IA, IB and IC columns according to reported procedures. [d] Absolute configurations were assigned by comparing both the retention time and optical rotation with the reported reliable data. [e] Optical rotation for product **2c** was negative.

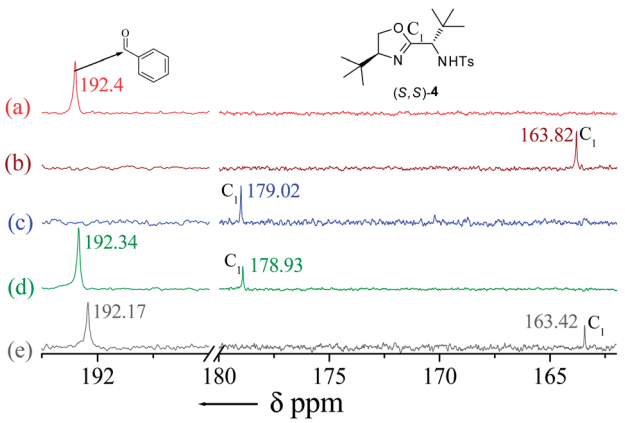
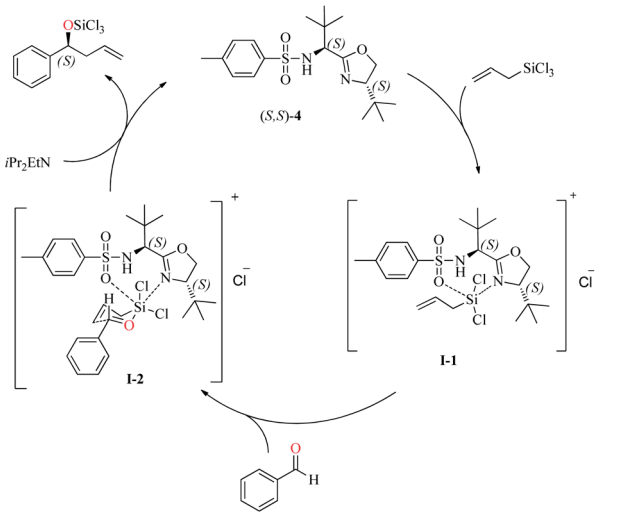


Fig. 1 ^{13}C NMR spectra were taken in $CDCl_3$: (a) benzaldehyde; (b) catalyst **(*S*,*S*)-4**; (c) ^{13}C spectrum of catalyst **(*S*,*S*)-4** after interaction with allyltrichlorosilane; (d) ^{13}C spectrum of catalyst **(*S*,*S*)-4** after interaction with allyltrichlorosilane and benzaldehyde; (e) ^{13}C spectrum of catalyst **(*S*,*S*)-4** after interaction with allyltrichlorosilane, benzaldehyde and DIPEA.

shifted downfield to 179.02 ppm upon the addition of allyltrichlorosilane. This large shifting (15.2 ppm) indicates that there is a strong interaction between the oxazoline nitrogen and silicon of allyltrichlorosilane to form an intermediate **I-1** (Scheme 3).[4l,7c]



Scheme 3 Proposed catalytic cycle for the enantioselective allylation reaction catalysed by (*S*,*S*)-4.

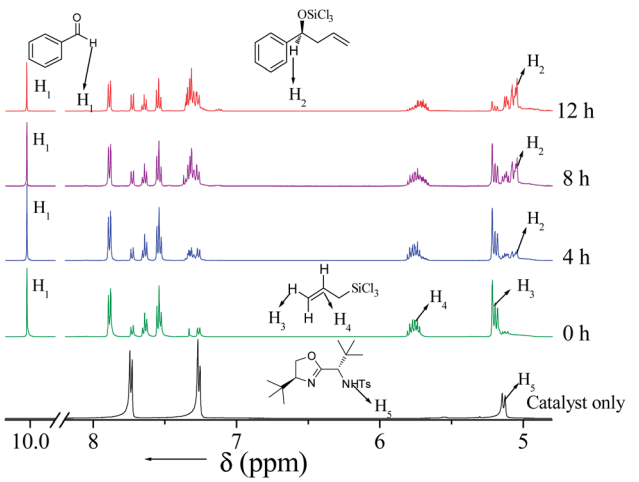


Fig. 2 ^{1}H NMR spectra were recorded in $CDCl_3$ following the general allylation reaction procedure as described in the experimental section, with 0.5 mmol substrate (benzaldehyde), 0.6 mmol allyltrichlorosilane, 1 mmol DIPEA and 10 mol% (*S*,*S*)-4 organocatalyst.

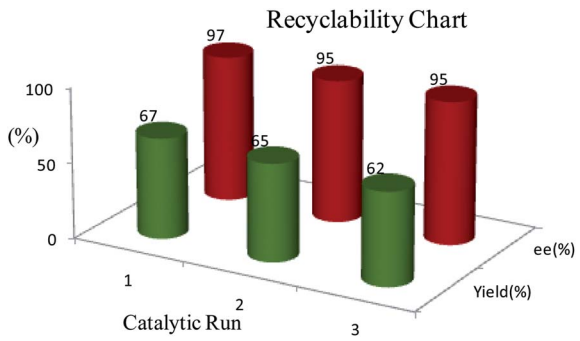


Fig. 3 Recyclability of catalyst (*S*,*S*)-4 using 4-methoxy benzaldehyde as the representative substrate.

After the addition of the substrate, this peak (179.02 ppm) only marginally shifted to appear at 178.93 ppm (spectrum (d), Fig. 1). It is to be noted that on adding DIPEA, product formation takes place (full spectrum in ESI†) with concomitant release of the catalyst[7c,15] (Scheme 3), as evident from spectrum (e) (Fig. 1), where the oxazoline imine carbon peak of the free catalyst at 163.42 ppm was restored (full spectrum in ESI†).

The product formation in the above reaction was followed by ^{1}H NMR experiments. The reaction was conducted in $CDCl_3$ with 10 mol% of catalyst (***S*,*S*)-4** for the allylation of benzaldehyde at RT, and ^{1}H NMR spectra were recorded at 0, 4, 8 and 12 h intervals (Fig. 2). The allylation product peaks at 5.05–5.08 ppm grew over a period of time and became sufficiently visible at ~60% conversion (full spectra in ESI†).

A catalytic cycle (Scheme 3) based on the results obtained during the catalyst screening experiments (Table 1) and NMR study has been proposed here. Accordingly, the catalyst first interacts with allyltrichlorosilane to form an intermediate **I-1**.[4l,7c] The intermediate **I-1** then reacts with the substrate and probably forms intermediate **I-2**,[4l,7c] which reacts with DIPEA to give the desired product and releases the catalyst for the next cycle.

Recyclability of the catalyst

The main problem with homogeneous catalysts is their separation and reuse from the reaction medium in post-catalysis workup. Nevertheless, we have attempted the recycling of catalyst (***S*,*S*)-4** in order to make the present catalytic protocol more cost-effective and also to demonstrate the robust nature of the catalyst under the allylation reaction conditions used. The reuse experiments were conducted using 4-methoxy benzaldehyde as a representative substrate with catalyst (***S*,*S*)-4** and allyltrichlorosilane as the allyl source at 0 °C in CH_2Cl_2 in the presence of DIPEA. After the first catalytic run, the amount of solvent was reduced, and the organocatalyst (***S*,*S*)-4** was precipitated by the addition of an excess amount of hexane. The precipitate contained both organocatalyst (***S*,*S*)-4** and molecular sieves. It was then thoroughly washed with hexane and dissolved in CH_2Cl_2 and immediately filtered. The filtrate was then evaporated under vacuum and dried under an inert atmosphere. It was then used for the subsequent catalytic run without further purification. The recovered catalyst worked well for the three cycles studied (Fig. 3), with only a marginal loss in yield, which is attributed to the physical loss of the catalyst during the recovery process. Moreover, the ^{1}H NMR spectra of the isolated catalyst (see ESI†) showed no change or additional peaks as compared to the fresh catalyst.

Conclusions

A series of oxazoline-based chiral organocatalysts were developed, among which the catalyst (***S*,*S*)-4** showed very good catalytic efficiency in the asymmetric allylation reaction of a wide range of substrates such as aromatic, hetero-aromatic and α,β-unsaturated aldehydes, with allyltrichlorosilane as the allyl source, under mild reaction conditions. The aromatic and

hetero-aromatic aldehydes, in particular, gave allylation products with good yield (up to 90%) and excellent ee (up to 99%). The catalyst was found to be robust and showed excellent recyclability. Also, the mechanism of the asymmetric allylation reaction was proposed based on the experimental observations and evidences obtained from the NMR studies.

Experimental section

The different aldehydes and reagents were used as received. All of the solvents were dried using standard procedures,[19] and were distilled and stored under activated molecular sieves. NMR spectra were obtained with a Bruker F113V spectrometer (200 and 500 MHz) and were referenced internally with tetramethylsilane (TMS). Splitting patterns were reported as s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet; br, broad. Enantiomeric excess (ee) values were determined by HPLC (Shimadzu SCL-10AVP) using Daicel Chiralpak OD-H, AS-H, IA, IB and IC chiral columns with 2-propanol–hexane as the eluent. For the product purification, flash chromatography was performed using silica gel 100–200 mesh.

General procedure for the preparation of catalysts (*S*,*S*)-1 to (*S*,*S*,*R*)-5

The synthesis of tosylated amino acids (II).[15,17,20] To a solution of chiral amino acid (6.05 mmol) dissolved in 15 mL of 1.5 N NaOH, *p*-toluenesulfonyl chloride (7.26 mmol) in diethyl ether (10 mL) was added at room temperature. After 10 h of stirring, the ether layer was separated and the aqueous layer was acidified with conc. HCl up to acidic pH. A white precipitate was thus obtained. Ethyl acetate was then added into the reaction mixture and the aqueous layer was extracted twice with ethyl acetate. In the case of phenylalanine, conc. HCl was added to the reaction mixture until it became homogeneous. The crude product was recrystallized from an ether and ethanol mixture to give pure compound **II** as white crystals (Scheme 1).

The synthesis of amides (III).[15,17,20] To the tosyl-protected amino acid **II** (3.13 mmol) in dry $CHCl_3$, freshly distilled thionyl chloride (341 μL, 4.70 mmol) was added dropwise and the resulting mixture was stirred at room temperature for 1 h. Subsequently, the solution was refluxed for a further 2 h. The clear yellow solution thus obtained was distilled out completely to give a quantitative yield of acid chloride as a yellow solid. The resultant acid chloride was then immediately dissolved in dry CH_2Cl_2 under a nitrogen atmosphere and cooled to 0 °C. To the cooled solution, chiral amino alcohol (3.09 mmol) in CH_2Cl_2 was added dropwise under a nitrogen atmosphere. After stirring for 2 h, the reaction temperature was gradually increased to room temperature and the mixture was allowed to stir at room temperature for 12 h. Then, the solution was extracted with water (50 mL × 5) and dried over anhydrous Na_2SO_4. Consequently, the solvent was removed under reduced pressure, the resulting pale yellow solid was dissolved in the minimum amount of dichloromethane, and an excess amount of hexane was added to precipitate out the desired product. The precipitate was washed twice with hexane, filtered and dried completely to give **III** as a white solid (Scheme 1).

The synthesis of *N*-tosylated oxazolines ((*S*,*S*)-1 to (*S*,*S*,*R*)-5).[16,17] Tosylated chiral amide **III** (2 mmol) was dissolved in dichloromethane (10 mL), and then Et_3N (4 mmol) and DMAP (*N*,*N*-dimethylaminopyridine) (0.2 mmol) were added respectively. To the clear solution, tosyl chloride (3.5 mmol dissolved in 3 mL CH_2Cl_2) was added slowly and the reaction was allowed to stir for 48 h at RT. The solution containing a crystalline solid was diluted with 10 mL of CH_2Cl_2, and upon washing with 20 mL of saturated aqueous NH_4Cl, a white solid formed in the aqueous layer. Water (50 mL) was added, the layers were separated, and the aqueous layer was back-extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with 15 mL of saturated aqueous $NaHCO_3$. The aqueous layer was back-extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered through cotton and concentrated under vacuum to give a yellow-white solid. The resulting pale yellow solid was dissolved in the minimum amount of dichloromethane and an excess amount of hexane was added to precipitate out the desired product. The precipitate was washed twice with hexane, filtered and dried completely to give catalysts **(*S*,*S*)-1** to **(*S*,*S*,*R*)-5** as white solids (Scheme 1).

Typical procedure for preparation of catalyst (*S*,*S*)-6

The synthesis of *N*-Boc-amino acid (V).[18] To a stirred solution of L-*tert*-leucine **IV** (6 mmol, 787.02 mg) in THF–H_2O (5 mL of each solvent) in room temperature was added NaOH (13.2 mmol, 528 mg), followed by Boc_2O (6.6 mmol, 1440.5 mg), and the resulting mixture was stirred for 24 h. THF was removed under vacuum and the aqueous layer was extracted with CH_2Cl_2 (20 mL). The aqueous layer was acidified with HCl (1 M) to pH ∼ 4 and then extracted with CH_2Cl_2 (4 × 15 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The resulting crude product of *N*-Boc-L-*tert*-leucine **V** was used without further purification in the next step (Scheme 2).

The synthesis of *N*-Boc-amide (VI).[18] To the solution of *N*-Boc-L-*tert*-leucine **V** (5.5 mmol, 1.29 g) in freshly dried THF (10 mL) at −15 °C, *N*-methylmorpholine (NMM, 6.6 mmol, 725 μL) and ethylchloroformate (6.6 mmol, 628 μL) were slowly added (a white solid was formed during the addition of EtOCOCl). The reaction mixture was stirred for 45 min at −15 °C, and then L-*tert*-leucinol (5.5 mmol, 644.5 mg) was added and the resulting mixture was stirred at room temperature for another 3 h. The mixture was filtered through silica gel (5 cm × 5 cm) and eluted with ethyl acetate (100 mL). The solvent was concentrated under vacuum and the resulting solid was recrystallized from CH_2Cl_2–*n*-pentane, giving 1.64 g of the pure amide **VI** (Scheme 2).

The synthesis of *N*-Boc-oxazoline ((*S*,*S*)-6). *N*-Boc-amide **VI** (2 mmol) was dissolved in dichloromethane (10 mL) and then Et_3N (4 mmol) and DMAP (0.2 mmol) were added sequentially. To the clear solution, tosyl chloride (3.5 mmol dissolved in 3 mL CH_2Cl_2) was added slowly and the reaction was allowed to stir for 48 h at RT. The solution containing a crystalline solid was diluted with 10 mL of CH_2Cl_2, and upon washing with 20 mL of

saturated aqueous NH_4Cl, a white solid formed in the aqueous layer. Water (50 mL) was added, the layers were separated, and the aqueous layer was back-extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with 15 mL of saturated aqueous $NaHCO_3$. The aqueous layer was back-extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were dried over Na_2SO_4, filtered through cotton and concentrated under vacuum to give a yellow-white solid. The resulting pale yellow solid was dissolved in the minimum amount of dichloromethane and an excess amount of hexane was added to precipitate out the desired product. The precipitate was washed twice with hexane, filtered and dried completely to give catalyst **(*S*,*S*)-6** as a white solid (Scheme 2).

General procedure for the catalytic asymmetric allylation of aldehydes with allyltrichlorosilane using (*S*,*S*)-4 as the organocatalyst

In a N_2 atmosphere glove box, 18.32 mg (0.05 mmol) of catalyst **(*S*,*S*)-4** was weighed out into an oven-dried 5 mL reactor. To this, 15 mg of powdered activated 4 Å molecular sieves was immediately added. Next, 1 mL of dry CH_2Cl_2 was added. The reactor was sealed with a septum and Teflon tape and taken out of the glove box. It was then cooled to 0 °C. To this, allyltrichlorosilane (1.2 equiv. with respect to the aldehyde) was added dropwise. After 2 h, the aldehyde (0.5 mmol) was added over 30 minutes followed by DIPEA (2 equiv. with respect to the aldehyde) was added and the reaction was allowed to stir for 24 h at this temperature. The reaction was quenched with aqueous $NaHCO_3$ (2 mL) and extracted with dichloromethane (3 × 15 mL). The organic layers were washed with brine and dried over Na_2SO_4. The products were purified by flash chromatography using silica gel 100–200 mesh. The products which were confirmed by NMR data corresponded to those published previously.

***N*-Boc-L-*tert*-leucine.**[18] Yield 1.27 g, 92%; White powder; m.p. 116 °C; $[\alpha]_D^{27}$ = +22.8 (c = 0.2, $CHCl_3$); FTIR 3437, 3325, 3180, 2975, 2551, 1744, 1710, 1650, 1513, 1415, 1234, 1162, 1058, 1009, 914, 847, 779, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 1.02 (s, 9H), 1.44 (s, 9H), 4.09 (d, J = 9.6 Hz, 1H), 5.08 (d, J = 8.4 Hz, 1H), 9.64 (br, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.49, 28.26, 34.44, 61.61, 79.99, 155.63, 176.80; TOF-MS (ESI^-) calcd for ($C_{11}H_{21}NO_4$–H^+): 230.15, found: 229.95.

Pre catalyst of (*R*,*S*)-1. Yield 1.27 g, 90%; white solid; m.p. 135 °C; $[\alpha]_D^{30}$ = −220 (c = 0.2, MeOH);[4] FTIR 3324, 3261, 3061, 3032, 2949, 1648, 1539, 1451, 1369, 1328, 1158, 1089, 947, 814, 743, 698, 669 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.64 (m, 4H), 3.24 (d, J = 4 Hz, 2H), 3.76 (q, J = 7 Hz, 1H), 4.11–4.24 (m, 1H), 4.99 (d, J = 7 Hz, 1H), 6.30 (d, J = 8 Hz, 1H) 7.09–7.1 (m, 2H), 6.85–6.87 (m, 2H) 7.10–7.24 (m, 10H), 7.47–7.51 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.51, 36.66, 38.37, 53.17, 58.01, 63.34, 126.69, 127.14, 127.21, 128.63, 128.82, 129.19, 129.28, 129.78, 135.29, 137.31, 143.9, 170.59. Anal. calcd for $C_{25}H_{28}N_2O_4S$: C, 66.35; H, 6.24; N, 6.19; S, 7.09; O, 14.14. Found: C, 66.29; H, 6.38; N, 6.35; S, 7.22; O, 14.40. TOF–MS (ESI^+) calcd for ($C_{25}H_{28}N_2O_4S$–H^+): 451.18, found: 451.14.

Pre catalyst of (*S*,*R*)-1. Yield 1.29 g, 91%; white solid; m.p. 135 °C; $[\alpha]_D^{30}$ = +210 (c = 0.2, MeOH); FTIR 3323, 3262, 3059, 3033, 2947, 1650, 1541, 1450, 1370, 1327, 1160, 1087, 948, 815, 741, 699, 667 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 2.33 (s, 3H), 2.42–2.46 (m, 2H), 2.76–2.80 (m, 1H), 3.05–3.10 (m, H), 3.16–3.20 (m, 1H), 3.67–3.73 (m, 1H), 3.92–3.93 (m, 1H), 4.76 (t, J = 5 Hz, 1H), 7.05–7.06 (m, 2H), 7.13–7.23 (m, 10H), 7.42 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8 Hz, 1H), 7.89 (d, J = 8 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.40, 29.40, 37.69, 38.28, 53.80, 57.6, 65.83, 125.47, 126.63, 126.71, 127.09, 128.40, 128.62, 128.70, 129.56, 129.73, 129.81, 129.93, 130.19, 136.79, 137.74, 138.29, 138.89, 142.98, 170.83. Anal. calcd for $C_{25}H_{28}N_2O_4S$: C, 66.35; H, 6.24; N, 6.19; S, 7.09; O, 14.14. Found: C, 66.30; H, 6.30; N, 6.25; S, 7.19; O, 14.44. TOF-MS (ESI^+) calcd for ($C_{25}H_{28}N_2O_4S$–H^+): 451.18, found: 451.20.

Pre catalyst of (*S*,*S*)-6. Yield 1.62 g, 89%; white crystals; m.p. 155 °C; $[\alpha]_D^{27}$ = −70.2 (c = 0.2, $CHCl_3$); FTIR 3379, 3299, 3088, 2966, 1685, 1654, 1556, 1479, 1392, 1369, 1258, 1176, 1056, 1010, 933, 888, 854, 772, 706, 658 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.94 (s, 9H), 1.04 (s, 9H), 1.43 (s, 9H), 3.5–3.54 (m, 1H), 3.81–3.87 (m, 3H), 5.20 (d, J = 7.5 Hz, 1H), 5.97 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.65, 26.86, 28.24, 33.40, 33.76, 59.67, 62.93, 63.33, 80.17, 156.12, 171.95. Anal. calcd for $C_{17}H_{34}N_2O_4$: C, 61.79; H, 10.37; N, 8.48; O, 19.37. Found: C, 61.71; H, 10.33; N, 8.53; O, 19.48. TOF-MS (ESI^+) calcd for ($C_{17}H_{34}N_2O_4$): 330.25, found: 330.4.

(*S*,*S*)-1. All of the characterization data for catalyst **(*S*,*S*)-1** were well matched with the literature data.[17]

(*R*,*S*)-1. Yield 756 mg, 87%; white crystals; m.p. 118 °C; $[\alpha]_D^{27}$ = −180.3 (c = 0.2, MeOH); FTIR 3379, 3299, 3088, 2966, 1685, 1654, 1556, 1479, 1392, 1369, 1258, 1176, 1056, 1010, 933, 888, 854, 772, 706, 658 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 2.43–2.46 (m, 2H), 2.93–3.07 (m, 3H), 3.85 (q, J = 7 Hz, 1H), 4.12–4.23 (m, 1H), 5.05 (d, J = 8 Hz, 1H), 7.06–7.11 (m, 3H), 7.22–7.23 (m, 4H), 7.29–7.35 (m, 4H), 7.62 (d, J = 8 Hz, 1H), 7.73–7.77 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.51, 22.65, 29.66, 31.88, 36.91, 38.53, 45.77, 50.77, 57.81, 126.96, 127.12, 127.32, 128.74, 128.91, 129.13, 129.29, 129.81, 134.98, 135.73, 136.35, 143.91, 169.68. Anal. calcd for $C_{25}H_{26}N_2O_3S$: C, 69.1; H, 6.03; N, 6.45; S, 7.38; O, 11.05. Found: C, 69.18; H, 6.15; N, 6.51; S, 7.32; O, 11.23. TOF-MS (ESI^+) calcd for ($C_{25}H_{26}N_2O_3S$ + H^+): 435.17, found: 435.66.

(*S*,*R*)-1. Yield 773 mg, 89%; white crystal; m.p. 118 °C; $[\alpha]_D^{27}$ = +185.5 (c = 0.2, MeOH); ^1H NMR (500 MHz, DMSO-d_6): δ = 2.33 (s, 3H), 2.36–2.43 (m, 2H), 2.5–2.55 (m, 2H), 2.74–2.78 (m, 1H), 2.92 (dd, J = 10 Hz, 1H), 3.47–3.5 (m, 1H), 3.66 (dd, J = 8 Hz, 1H), 3.95–4.00 (m, 1H), 6.98–6.99 (m, 2H), 7.12 (d, J = 7 Hz, 2H), 7.16–7.23 (m, 5H), 7.44 (d, J = 8 Hz, 2H), 7.51 (d, J = 8 Hz, 2H), 7.83 (d, J = 8 Hz, 1H), 8.34 (d, J = 9.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 20.92, 36.22, 37.84, 52.38, 57.70, 65.49, 125.97, 126.20, 126.38, 127.93, 128.15, 129.16, 129.26, 137.18, 138.26, 138.94, 142.11, 169.86. Anal. calcd for $C_{25}H_{26}N_2O_3S$: C, 69.1; H, 6.03; N, 6.45; S, 7.38; O, 11.05. Found: C, 69.25; H, 6.08; N, 6.48; S, 7.35; O, 11.3. TOF-MS (ESI^+) calcd for ($C_{25}H_{26}N_2O_3S$): 434.17, found: 434.12.

Catalysts (*S*,*S*)-2, (*S*,*S*)-3, (*S*,*S*)-4, (*S*,*R*,*S*)-5 and (*S*,*S*,*R*)-5. All of the characterization data for these catalysts were well matched with the literature data.[17]

(*S*,*S*)-6. Yield 1.32 g, 86%; white solid; m.p. 110 °C; $[\alpha]_D^{27} = -115.5$ (c = 0.2, $CHCl_3$); FTIR 3413, 2964, 2929, 1709, 1662, 1516, 1367, 1326, 1239, 1175, 1069, 982, 926, 864, 778, 649 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 0.88 (s, 9H), 0.98 (s, 9H), 1.44 (s, 9H), 3.84–3.89 (m, 1H), 4.07–4.21 (m, 3H), 5.13 (d, J = 9.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.84, 26.55, 28.28, 33.56, 34.66, 57.19, 68.50, 75.37, 79.30, 155.55, 166.00. Anal. calcd for $C_{27}H_{32}N_2O_3$: C, 65.35; H, 10.32; N, 8.97; O, 15.36. Found: C, 65.40; H, 10.42; N, 8.90; O, 15.47. TOF-MS (ESI^-) calcd for ($C_{17}H_{32}N_2O_3$–H^+): 311.24, found: 310.94.

Acknowledgements

Authors thank CSIR for the financial support. Debashis Ghosh is thankful to AcSIR for the Ph.D. enrolment. Analytical Discipline and Centralized Instrumental Facility is gratefully acknowledged for providing instrumental facilities.

Notes and references

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