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Ru-Tethered (*R,R*)-TsDPEN with DMAB as an efficient catalytic system for high enantioselective one-pot synthesis of chiral β-aminol *via* asymmetric transfer hydrogenation†

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This work reflects Ru-tethered-TsDPEN as an active chiral catalyst for one pot selective synthesis of optically active α-substituted alcohols and its derivatives from α-bromo ketones in the presence of dimethylamine borane (DMAB) as the hydrogen source. Various Ru-chiral catalysts have been screened and the methodology proceeded *via* a (*R,R*) Ru-tethered TsDPEN catalyst through asymmetric transfer hydrogenation (ATH) of the in-situ formed ketones to the corresponding chiral β-aminol product. Thus, the Ru-tethered TsDPEN-DMAB catalytic system works efficiently with higher yield and high enantiomeric excess over others for the ATH process. Based on a study of *ortho*, *meta* and *para* substituted α-bromo acetophenone derivatives, effective enantioselectivity has been observed for *ortho* substituted β-aminol. The mechanism has been optimized depending on product analysis with the help of its kinetic AT-IR study. This work also focusses on the synthesis of various β-amino alcohol derivatives where the effect of an EWG and EDG on enantio-selectivity has been studied.

Introduction

α-Hetero substituted alcohols are important moieties in pharmaceutical and natural products.[1] Moreover, they are important intermediates in the development of drug molecules.[2] Chiral β-amino alcohols are often used as chiral ligands in asymmetric synthesis for the development of complex chiral catalysts[3] and because of the broad use of chiral β-amino alcohols in asymmetric synthesis they have been synthesized by various synthetic routes, like the reduction of α-amino acids, asymmetric amino hydroxylation of alkenes[4a] with good stereo-control of the β-amino alcohol, and resolution of the racemic starting compound.[4b] The ring opening of epoxides by amines[4c] produced a low yield of the aromatic β-amino alcohols so effective protocols are highly desired for the synthesis of this important class of compounds.[4d–i] Furthermore, the amination of alcohol[5] opens a way for the formation of the C-N bond, which can be used as a synthetic methodology for the synthesis of β-aminols. However, one pot synthesis of β-amino alcohol has also been achieved from a bifunctional base catalyst.[6] Similarly, Yang *et al.* carried out the synthesis of β-amino alcohols *via* amination of 1,2-diols[7] with good enantioselectivity (Scheme 1a). Furthermore, Sekar *et al.* also synthesized β-amino alcohols from α-ketoamides by the application of phosphine ligands along with a Cu salt (Scheme 1b). However, in both these methods hazardous acid and base are used along with the phosphine ligands which hindered the separation and purification of the product, and furthermore the protocol also had limited substrate scope.[8] In addition, Xu *et al.*, also reported the formation of β-amino alcohols from α-aminoketones *via* an ATH process in excellent %ee, by the use of a [Ru-(*p*-cymene) Cl_2]$_2$ catalyst along with (*S,S*)-TsDPEN ligands.[9] However, this protocol showed the opposite configured product with low enantioselectivity. Amongst all the hydrogen sources, DMAB served as a better candidate than the most commonly reported azeotropic mixture of FA : TEA in 5 : 2 ratio. Jung *et al.* reported that DMAB acts as the best hydrogen source along with the Ru catalytic system.[10] Furthermore, Goksu *et al.* reported DMAB as a non-toxic, non-flammable, cheap and easily available hydrogen source which can help in the transfer hydrogenation process of ketone and aldehyde.[11] According to the literature, because of its high volume/mass hydrogen density, two moles of hydrogen gas are produced from one mole of DMAB *via* the dehydrogenative method in the presence of a favourable catalyst.[12] Furthermore, for many years, our lab has also been working effectively in the asymmetric transfer hydrogenation process,[13] encouraged by which here we have designed a methodology for the synthesis of highly enantioselective chiral β-amino alcohols.

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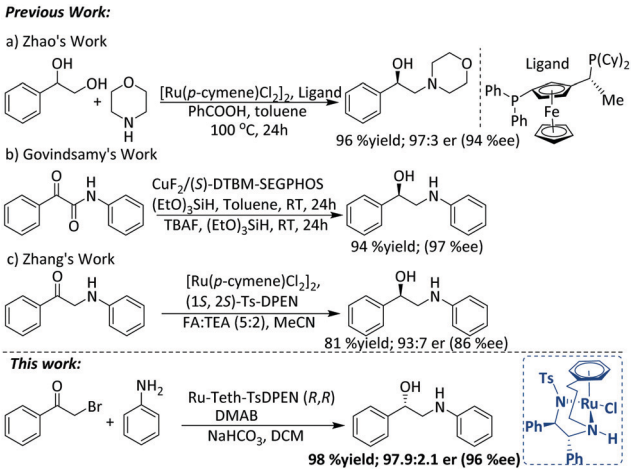
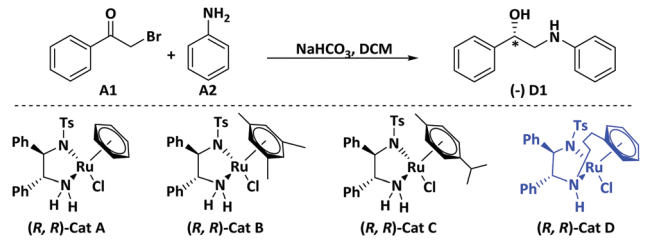


Scheme 1 Ru-Tethered catalysed one pot synthesis of chiral (–) β-aminol.

Herein we report an asymmetric transfer hydrogenation process *via* nucleophilic substitution of a primary amine on the α-carbon of α-bromoketone, where bromine acts as a good leaving group. In the developed protocol, an efficient Ru-tethered catalyst has been explored along with DMAB as an excellent hydrogen source for achieving higher %ee. The reaction involves nucleophilic substitution reaction, which is followed by the ATH process for the synthesis of β-amino alcohols. Although DMAB is highly sensitive to moisture, it acts as a better hydrogen source for forming the hydride catalyst as compared to other hydrogen sources with respect to enantioselectivity achieved.

$$n\mathrm{Me_2NH{\cdot}BH_3} \rightarrow (\mathrm{MeN{=}BH})_n + n\mathrm{H_2}$$

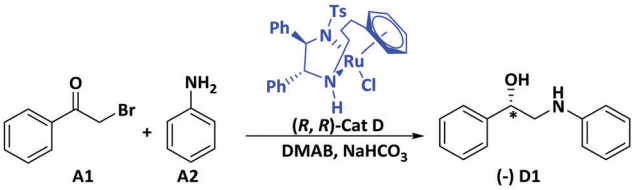
Table 1 Optimisation table of catalyst loading, catalyst and solvent screening for the synthesis of chiral (–) β-aminol[a]



Entry no.	Catalyst	Catalyst loading (mol%)	Hydrogen source	%Yield[b]	%ee[c]
Catalyst screening					
1	(*R*,*R*) A	3	FA : TEA (5 : 2)	94	72
2	(*R*,*R*) B	3	FA : TEA (5 : 2)	92	71
3	(*R*,*R*) C	3	FA : TEA (5 : 2)	94	75
4	(*R*,*R*) D	3	FA : TEA (5 : 2)	95	79
Hydrogen source screening					
5	(*R*,*R*) D	3	FA : TEA (3 : 2)	60	64
6	(*R*,*R*) D	3	FA : TEA (1 : 5)	80	24
7	(*R*,*R*) D	3	DMAB	98	96
8	(*R*,*R*) D	3	IPA	68	65
9	(*R*,*R*) D	3	HCOONa	—	—
10	(*R*,*R*) D	3	H_2O/IPA (1 : 1)	23	12
Catalyst loading					
11	(*R*,*R*) D	2	DMAB	98	96
12	(*R*,*R*) D	1	DMAB	98	96
13	(*R*,*R*) D	0.5	DMAB	91	79

Conditions. [a] 1 mmol of A1′ and A2′ taken with same amt. of base $NaHCO_3$ in 4 mL of DCM for 24 h. [b] %Yield is based on GC-MS analysis. [c] %ee are based on HPLC analysis.

Table 2 Optimisation table of hydrogen source, time scale and temperature screening for the synthesis of chiral (–) β-aminol[a]



Entry no.	Time (h)	Solvent	Temp. (°C)	%Yield[b]	%ee[c]
Solvent screening					
14	24	MeOH	RT (29)	60	64
15	24	EtOH	RT (29)	52	68
16	24	IPA	RT (29)	68	75
17	24	CH_3CN	RT (29)	58	34
18	24	DMF	RT (29)	20	14
19	24	THF	RT (29)	32	30
20	24	Toluene	RT (29)	12	03
Time scale study					
21	12	DCM	RT (29)	11	80
22	48	DCM	RT (29)	98	96
23	72	DCM	RT (29)	98	96
Temperature screening					
24	24	DCM	0	34	92
25	24	DCM	40	76	64
26	24	DCM	50	43	24

Conditions. [a] 1 mmol of A1′ and A2′ taken with 1 mmol of DMAB and 1 mmol of base $NaHCO_3$, 1 mol% of Ru-tethered catalyst dissolved in different solvent. [b] %Yield is based on GC-MS analysis. [c] %ee are based on HPLC analysis.

Results and discussion

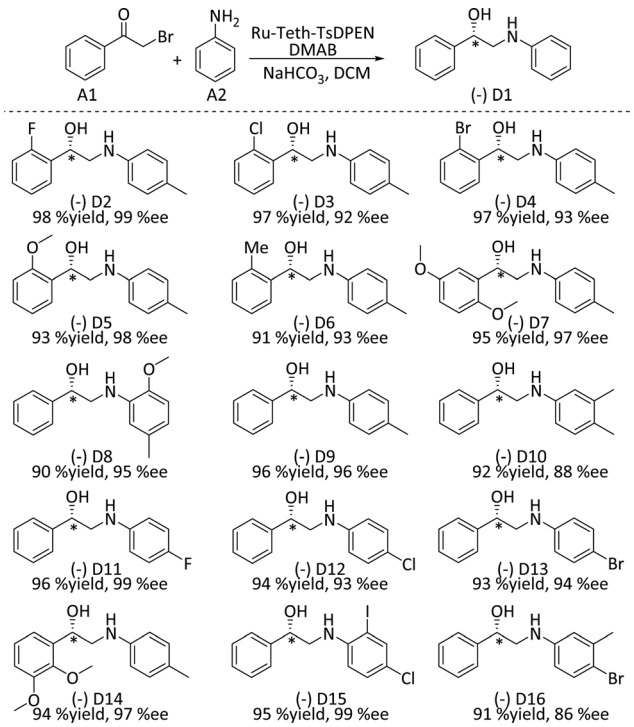
We began our optimization study with 2-bromo-1-phenylethanone (α-bromo ketone) as the model substrate. Initially, the model substrate was screened for one pot asymmetric synthesis by the use of a unique Ru-chiral complex in dichloro methane (DCM) solvent as mentioned in Table 1. Amongst all the chiral catalysts screened, the Ru-tethered catalyst dominates the protocol as compared to untethered catalysts. A high %ee was obtained by (*R*,*R*)-Cat D as compared to (*R*,*R*)-Cat A, B and C (Table 1, entries 1–4). Furthermore, with the perfect catalyst design, the hydrogen source was also screened which showed surprising results. Amongst all the hydrogen sources, different ratios of the azeotropic mixture of formic acid/triethylamine (F/T) (Table 1 entries 4–6), 2-propanol (IPA) (Table 1 entry 8), sodium formate (Table 1, entry 9), and IPA/H_2O (1 : 1) (a mixture of 2-propanol and water) (Table 1, entry10) were optimized for the protocol, and

dimethylamine borane (DMAB) (Table 1 entry 7) shows excellent 96%ee. Again, the catalyst loading was also screened from 3 mol% to 0.5 mol% (Table 1, entries 10–13) amongst which 1 mol% showed better enantioselectivity as compared to other sources (Table 1, entry 12).

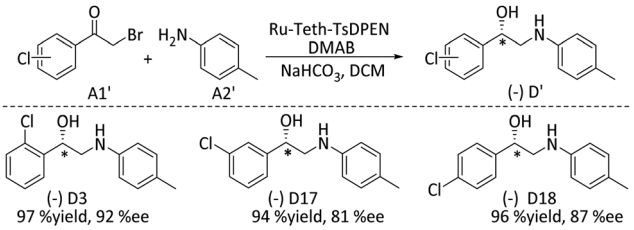
A solvent study was also conducted in the tethered complex which showed that DCM is the most suitable solvent as compared to the others. However, from the solvent study, the relationship between the nature of the solvent and the asymmetricity of the product has been confirmed - for example, for a protic solvent with a lower dielectric constant, a higher %ee is achieved. DCM (ε = 9.1) shows better enantioselectivity than IPA (ε = 17.9), thus the dielectric constant, which signifies the polarity of the solvent,[14] decreases as mentioned below for polar protic solvents: CH_3CN (ε = 37.5) > MeOH (ε = 32.6) > EtOH (ε = 22.4) > IPA (ε = 17.9) > DCM (ε = 9.1), whereas %ee follows the inverse pattern for the given dielectric constant value. DCM shows (96%ee) (Table 1, entry 12) > IPA (75%ee) > EtOH (68%ee) > MeOH (64%ee) > CH_3CN (34%ee) (Table 2, entries 14–17). Similarly, for polar aprotic solvents, THF with a lower dielectric constant shows a higher %ee as compared to the higher dielectric constant of DMF (Table 2, entries 18 and 19). However, toluene having a very low dielectric constant produces a racemic compound rather than a chiral one (Table 2, entry 20), which may be because of its non-polar nature. Thus, a polar aprotic solvent behaves as a better solvent for achieving enantioselectivity as compared to the other solvents.

Furthermore, time scale has been studied where decreasing the time from 24 h to 12 h shows a decrease in the yield from 98% to 11% as well as a decrease in %ee from 96% to 80%, whereas increasing time does not show much fluctuation in %yield and %ee. (Table 2, entries 21–23). Henceforth, the reaction was performed at different temperatures where lower %ee was observed at a higher temperature (Table 2, entries 25 and 26), whereas at lower temperature a small decrease in %ee was observed (Table 2, entry 24). Thus for 1 mmol of substrate, DCM acts as a suitable solvent with 1 mol% of Ru-tethered (*R,R*) catalyst and DMAB as a hydrogen source for obtaining β-aminol at RT after 24 h.

With the optimized parameters in hand, various substrates have been screened where an EWG and EDG are substituted at the aryl ring of both the ketone and amine parts. Various starting materials *viz.* α-bromo ketones have been prepared by the known method[15] which was then taken along with a primary amine for synthesizing different derivatives of β-amino alcohol. It is observed from the substrate study that an EWG showed high %ee because of its electronic effect on the carbonyl functional moiety, whereas an EDG showed good %ee because of the steric effect offered by the *–ortho* functional group. EWGs like –F (D2), –Cl (D3), and –Br (D4) at the *–ortho* position showed higher %ee, which indicates that these electronegative atoms on the substrate favour the adjacent position to η^6-arene of the catalyst, thereby making the carbonyl moiety electronically favourable for the ATH process resulting in higher %ee. Similarly –OMe (D5) and –Me (D6) at the *–ortho* position showed higher %ee, which indicates that these groups exhibit steric hindrance at the adjacent position for the binding of the catalyst with the substrate from one face, thus favouring the interaction of the substrate with the catalyst from the other face resulting in higher %ee. At this stage, the study was further extended to substitution on the aryl ring attached to the amine part, *i.e.*, aryl amine, which signifies no decrease in %ee; rather it yielded a β-amino alcohol with higher %ee. –Me (D9), –F (D11), –Cl (D12) and –Br (D13) at the *para* position showed excellent enantioselectivity with a higher %ee. Again, encouraged by these results, a substrate study with separate di-substitution on both the aryl rings was carried out. Initially, the 2nd and 5th positions of the aryl ketone ring (D7), as well as the 2nd and 3rd positions (D14), got substituted with the –OMe group, wherein both showed 97%ee. Furthermore, di-substitution was carried out at the aryl amine part of the substrate, where the 2nd position substituted by –OMe and the 5th position occupied by –Me group (D8) showed 95%ee. Similarly, when an EWG like –I was substituted at the 2nd position and –Cl at the 4th position (D15), it showed 99%ee. However, when –Me was occupied at the 3rd and 4th position (D10) then it showed 88%ee. Similarly, a small decrease in enantioselectivity to 86%ee was also observed when the 3rd position was occupied by –Me and the 4th position was occupied by a –Br group (D16) which indicates that the 3rd and 4th positions of the aryl ring on the amine part hinder favourable interaction between the substrate and the catalyst, thus resulting in lowering the %ee, whereas –I at the *ortho* position favoured



Scheme 2 Substrate scope for the one pot synthesis of chiral (–) β-aminol. Conditions: 1 mmol of A1′ and 1 mmol of A2′ taken with 1 mmol of DMAB and 1 mmol of base $NaHCO_3$ along with 1 mol% of Ru–tethered catalyst dissolved in 4 mL of DCM. %Yield is based on GC-MS analysis; %ee is based on HPLC analysis.



Scheme 3 Products of ATH of the –*ortho*, –*meta* and –*para* substituted aryl ketones. Conditions: 1 mmol of A1′ and 1 mmol of A2′ taken with 1 mmol of DMAB, 1 mmol of base $NaHCO_3$, and 1 mol% of Ru-tethered catalyst dissolved in 4 mL of DCM. %Yield is based on GC-MS analysis; %ee is based on HPLC analysis.

interaction of the substrate with the catalyst from one face, thus yielding higher %ee of the product (Scheme 2).

Again, to extend the efficiency of the protocol *ortho*, *meta* and *para* substituted ketones have been processed towards ATH which showed some interesting facts as mentioned in Scheme 3.

From the results obtained, D3 containing a –Cl group at the *ortho* position of the aryl ketone showed 92%ee whereas it decreases to 87%ee when a –Cl group occupied the *para* position (D18). Again a –Cl group at the *meta* position (D17) showed a further decrease in enantioselectivity to 81%ee. These results showed good yield but variation in %ee is also observed which indicates that at the –*ortho* position, steric hindrance, as well as the electronic effect, favours the interaction of the carbonyl moiety with the catalyst from one face, whereas a –*para* substituted –Cl group showed smaller hindrance while the same group at the –*meta* position showed more electronic hindrance and as a result %ee decreased to 81% from 92%ee.

Furthermore, a mechanistic investigation was carried out for the one pot asymmetric synthesis of β-amino alcohol. Thus, for tracing the product, GC-MS, as well as AT-IR of the product, was analysed at a different time of reaction (Fig. 1). Initially, an α-bromo keto compound (A1) showed a nucleophilic substitution reaction with aniline (A2) in the presence of base producing active species α-aminoketone (C) which can be confirmed by the AT-IR spectroscopic study. Initially a –C═O peak was observed at 1690 cm^{-1} for compound A1 and an $-NH_2$ peak was observed at 3435 cm^{-1} and 3350 cm^{-1} (peak for primary amine) for compound A2 which after 3 h can be seen decreasing without any disturbance in the –C═O peak. However, after 12 h, it can be observed clearly from AT-IR spectroscopy that the primary amine was converted to a secondary amine, and as a result, conversion of two peaks into one peak was observed at

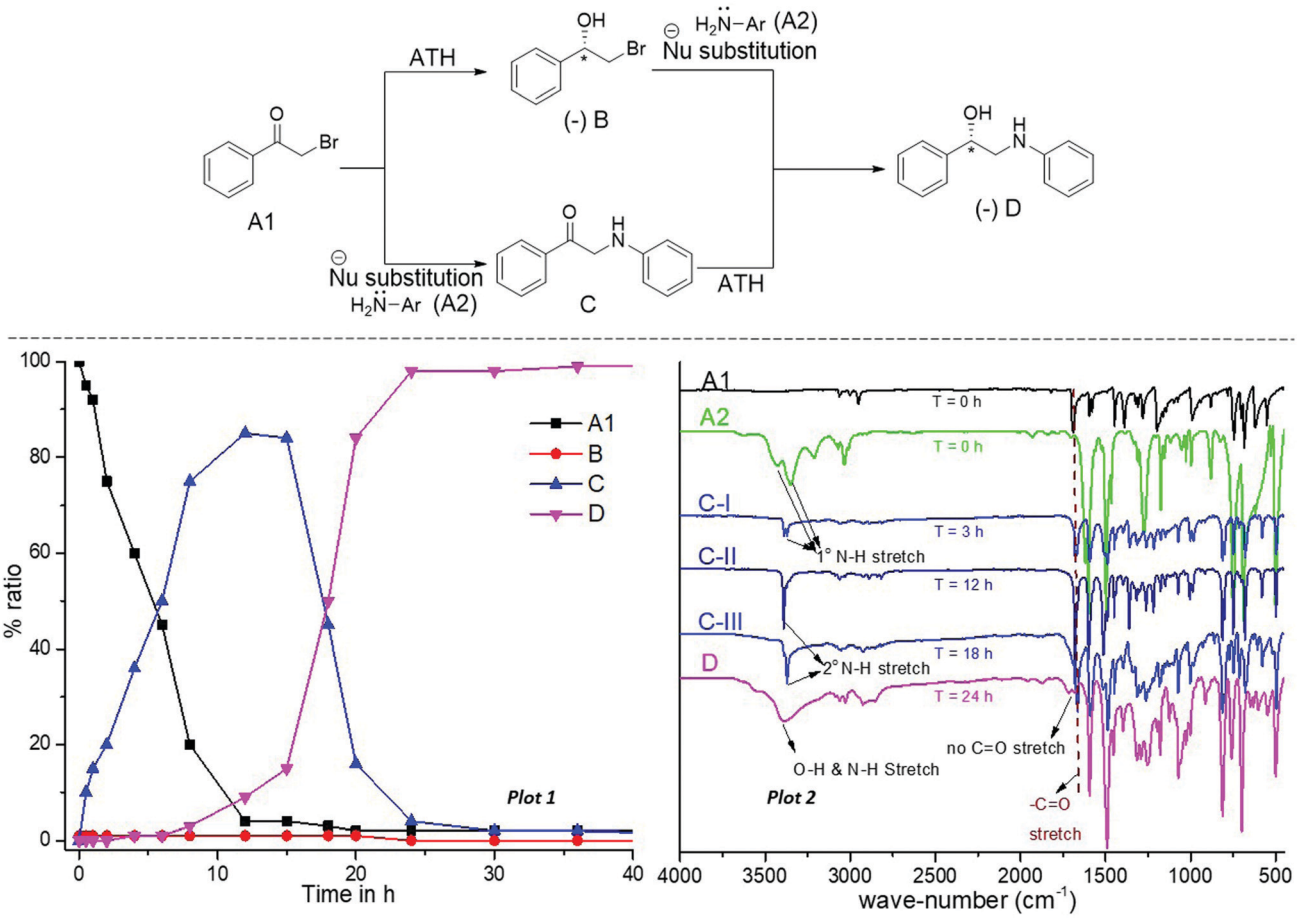
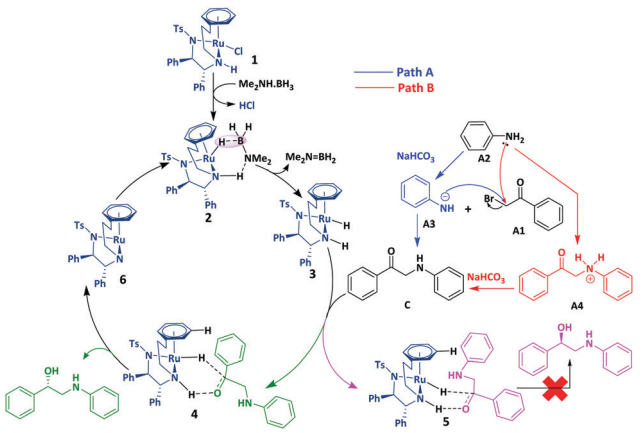


Fig. 1 Represents kinetic study for the consumption of substrate and development of the one pot enantioselective product along with AT-IR spectroscopy.



Scheme 4 Plausible mechanistic pathway for the synthesis of chiral β-aminol.

3394 cm^{-1} with the existence of the –C═O peak at 1685 cm^{-1}. This clearly indicates that one pot synthesis of enantio-selective product "*D*" proceeds *via* "*C*" i.e.; α-aminoketone but not *via* "*B*" as observed in the literature.[16] After 18 h, it can be again visualized that the –C═O peak decreases and it disappears after 24 h along with broadening of the peak observed at 3400 cm^{-1}, which indicates the existence of an –OH bond, thereby confirming the formation of chiral product "(−) *D*".

Based on the obtained results and AT-IR spectroscopic study, a possible mechanism has been proposed (Scheme 4). α-Bromo keto compound (A1) shows nucleophilic substitution reaction with aniline (A2) in the presence of base producing active species α-aminoketone (C). There are two possible pathways for the same either *via* path A in which base $NaHCO_3$ removes a proton from aniline which then attacks the acidic carbon of "A1" producing compound "C" or *via* path B in which the lone-pair of aniline attacks the acidic carbon producing compound "A4" from which loss of a proton yields compound "C". Furthermore, compound (C) fits into the "window" of (*R,R*) Ru-Teth-TsDPEN hydride complex (3) showing favourable "*edge-face*" interaction amongst themselves which leads to generating the targeted product (D) *via* complex "4" whereas complex "5" does not show favourable –CH/π interaction between the aromatic substrate and η^6 aromaticity of the catalyst together with the possibility of steric hindrance. Thus, an "*S*" configured (−) β-amino alcohol is produced which can also be confirmed from its [α] value *i.e.*; optical polarimetry.

Conclusion

In summary, we have developed an efficient protocol for the synthesis of chiral β-amino alcohols where the effect of the (*R,R*) Ru-tethered-TsDPEN catalyst has been investigated over its untethered catalyst. Further, DMAB emerges as an efficient hydrogen source which also favours high %ee as compared to other hydrogen sources. AT-IR study has been performed kinetically, to confirm the change in functional moiety throughout the reaction from which it can be confirmed that nucleophilic attack of the primary amine on the α-carbon of α-bromoketone is preferred followed by an ATH process, which is also confirmed from GC-MS study. Furthermore, the effect of *ortho*, *meta* and *para* substitution towards enantioselectivity has also been studied which confirms that the *ortho* effect is more favourable for high %ee as compared to *meta* and *para*. Different derivatives of β-amino alcohol have been synthesized and characterized by ^{1}H & ^{13}C-NMR spectroscopy, HPLC (on OJ-H & AD-H chiral column) and optical polarimetry. Based on the literature, a possible mechanism and transition state have been deduced to determine the configuration of the product.

Experimental section

General procedure for the asymmetric synthesis of β-aminol

In a 15 ml dried pressure tube cylinder, 1 mmol of 2-bromoacetophenone and its derivatives along with 1 mmol of aniline and its different derivatives are taken along with 1 mol% of catalyst Ru-Teth-TsDPEN (*R,R*) which was then dissolved in 4 ml of DCM along with the addition of 1 mmol of $NaHCO_3$. After 15 min, again 1 mmol of DMAB was added slowly under a nitrogen atmosphere. Furthermore, after 24 h, the presence of the product is assessed by Thin Layer Chromatography (TLC), after which the compound is extracted with DCM and water, and the organic layer is dried over anhydrous Na_2SO_4 followed by filtration and distillation. The final mixture is then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90–10) to obtain pure chiral (−)-β-aminol.

Conflicts of interest

There are no conflicts to declare.

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