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ARTICLE TYPE

Asymmetric Allylation of Sulfonyl Imines Catalyzed by in situ Generated Cu(II) Complexes of Chiral Amino Alcohol Based Schiff Bases

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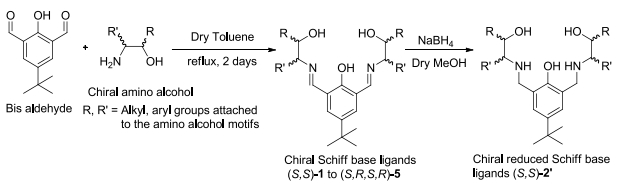
A catalytic route for enantioselective synthesis of homoallyl amines through Cu(II)-Schiff base catalyzed reaction of allyltin with aryl, alkenyl-substituted *N*-sulfonylimines is described. The allylation reaction is promoted by simple *in situ* generated Cu(II)-amino alcohol based Schiff base complex. The addition of allyltin to aldimines delivers the desire products up to 90% yield and 98% enantiomeric excess (ee). Based on experimental observations a probable mechanism was proposed for this reaction. Current methodology was extended to the synthesis of *β*-phenylalanine in good yield and very good enantioselectivity.

Introduction

Asymmetric allylation of carbonyl compounds has been well established[1] and various efficient methods were reported[1,2] in this field. However, asymmetric allylation of imine,[2c,3-8] particularly allylation of sulfonated imines[6d-f,7a-b,8] is comparatively less explored. The allylation products i.e. homoallyl amines are imbedded within various biologically active compounds.[9] Thus synthesis of enantio-enriched homoallyl amines is of current research interest. Transition metal catalyzed allylation of *N*-substituted imines[3-7] is one of the most powerful tools for the preparation of chiral homoallyl amine. However, inexpensive copper catalyzed asymmetric allylation of imines have been rarely explored.[7] Recently A. H. Hoveyda et al., reported (2011) enantioselective allylboration of substituted phosphinoylimines using *N*-heterocyclic carbine (NHC)-Cu complex.[7d] Although this efficient method gave excellent product yield and enantioselectivity, this method used extremely low temperature and required multistep synthesis of NHC-ligand. We thought of a simple *in situ* generated Cu(II)-chiral Schiff base type complex that can work under ambient reaction condition. Synthesis of the ligands follow one step condensation between a bisaldehyde and a chiral amino alcohol.[10,11a] The catalytic efficiency (with respect to both yield and enantioselectivity) is heavily influenced by the substitutions on amino alcohol part. Among various Schiff base ligands, tert-leucinol derived Schiff base ligand was found to be most suitable one in the above catalytic system. Besides this, presence of an additive in an appropriate amount has also influenced the enantioselectivity with a slight change in yield of allylation product. Involvement of the additive in the catalytic cycle was evidenced by UV-vis. as well as mass spectral studies. Our present investigation revealed that a simple chiral Schiff base-Cu(II) complex with a suitable additive is an efficient catalytic system for enantioselective allylation of sulfonyl imine.

Results and Discussion

Chiral Schiff base ligands (*S*,*S*)-**1** to (*S*,*R*,*S*,*R*)-**4** were prepared by the condensation of aromatic bis-aldehyde with different chiral amino alcohols (Scheme 1) by following literature procedure.[10,11a,12] The ligand (*S*,*S*)-**2'** was prepared by the reduction of (*S*,*S*)-**2** with $NaBH_4$ in MeOH (Scheme 1).



Scheme 1. General synthesis of chiral ligands

The required substrates **1a**-**1p** for the synthesis of enantiorich homoallyl sulfonamines **2a**-**2p** can easily be prepared in a single step by the condensation of corresponding aldehydes with cyanuric chloride in good yields.[11a] We began our investigation by using *N*-(4-chlorobenzylidene)-4-methylbenzene sulfonamide (**1b**) as a representative substrate, allyltributyltin as an allylating agent and *in situ* generated chiral Schiff base-Cu(II) complexes of ligands (*S*,*S*)-**1**-**3** and (*S*,*R*,*S*,*R*)-**4** as catalysts in CH_2Cl_2 at RT. The results are summarized in Table 1.

At first we have checked the efficiency of *in situ* generated L-valinol derived ((*S*,*S*)-**1**) Schiff base-Cu(II) complex for the above allylation reaction, where homoallyl sulfonamine was obtained in moderate yield (40%) and low enantioselectivity (ee, 30%) (Table 1, entry 1). Then we have altered the amino alcohol part in the Schiff base ligand by changing L-valinol with L-tert-

leucinol ((*S*,*S*)-**2**) (Figure 1). This modification resulted in a dramatic improvement of product yield (60%) and ee (64%) (entry 2). To get better yield as well as enantioselectivity, we have varied the structural unit of amino alcohol part as in ligands (*S*,*S*)-**3** and (*S*,*R*,*S*,*R*)-**4**, but the results obtained with (*S*,*S*)-**2** were better than other ligands (entries 2,4,5) used in the present study. We have also checked the efficiency of the reduced Schiff base ligand (*S*,*S*)-**2'**, but we got the product in poor yield and ee with this system (entry 3).

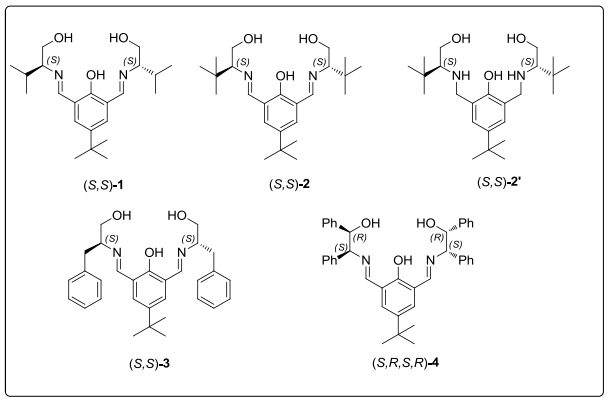
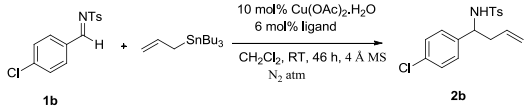


Figure 1. Chiral ligands used in the present study

Table 1. Screening of catalysts for asymmetric allylation reaction of allyltin with *N*-(4-chlorobenzylidene)-4-methylbenzene sulfonamide **(1b)** in CH_2Cl_2 at RT[a]

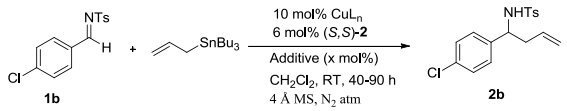


Entry	Ligands	Yield (%)[b]	ee (%)[c]
1	(*S*,*S*)-**1**	40	30
2	(*S*,*S*)-**2**	60	64
3	(*S*,*S*)-**2'**	30	10
4	(*S*,*S*)-**3**	25	20
5	(*S*,*R*,*S*,*R*)-**4**	10	12

[a]All the reactions were carried out by using substrate *N*-(4-chlorobenzylidene)-4-methylbenzene sulfonamide (0.3 mmol), allyltributyltin (0.45 mmol), and catalyst (10 mol%) in CH_2Cl_2 at RT. [b]Isolated yields after column chromatography. [c]ee determined by chiral HPLC using Daicel Chiralcel OD-H column.

A good level of enantioselectivity was already achieved in absence of an additive (Table 2, entry 1) but addition of an additive (10 mol%) among L-tert-leucine, L-valinol and L-tert-leucinol greatly influenced ee of the product (entries 2-4). Among these L-tert-leucinol (10 mol%) had a very positive influence on the allylation reaction. The allylation results were further improved by increasing the amount of L-tert-leucinol to 20 mol% (entry 5), but a further increase in its amount (30 mol%) was of little use (entry 6). It is worth mentioning here that L-tert-leucinol itself can act as ligand, therefore we used it as ligand and conducted the allylation reaction in the absence of (*S*,*S*)-**2** keeping other parameters constant. However, yield as well as ee of the allylation product were found to be poor (entry 7) implying that a combination of L-tert-leucinol and (*S*,*S*)-**2** with copper is forming a highly active and enantioselective catalyst. Furthermore, it is known that different copper salts have variable geometry and reactivity, hence we varied copper sources viz., $Cu(OAc)_2.H_2O$, CuOTf, $Cu(OTf)_2$ and $Cu(acac)_2$ (entries 5, 9-11) and found that $Cu(OAc)_2.H_2O$ was more efficient (entry 5). The optimum reaction must be carried out in presence of 4 Å molecular sieves, in absence of which a large decreased in product yield as well as ee (entry 8) was observed due to the moisture sensitive nature of sulfonyl imine.

Table 2. Optimization study illustrating the effect of cupper salt and additive used in the enantioselective allylation reaction of **1b** at RT[a]

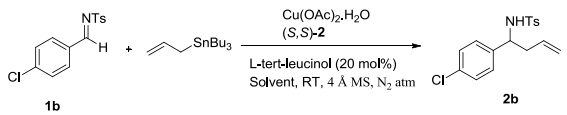


Entry	CuL_n	Additive	Additive amount (mol%)	Yield[b] (%)	ee (%)[c]
1	$Cu(OAc)_2.H_2O$	-	-	60	64
2	$Cu(OAc)_2.H_2O$	L-tert-leucine	10	45	20
3	$Cu(OAc)_2.H_2O$	L-Valinol	10	56	70
4	$Cu(OAc)_2.H_2O$	L-tert-leucinol	10	65	86
5	$Cu(OAc)_2.H_2O$	L-tert-leucinol	20	66	94
6	$Cu(OAc)_2.H_2O$	L-tert-leucinol	30	65	94
7	$Cu(OAc)_2.H_2O$*	L-Tert-leucinol	20	20	16
8	$Cu(OAc)_2.H_2O^{\neq}$	L-tert-leucinol	20	30	60
9	CuOTf.Toluene	L-tert-leucinol	20	35	24
10	$Cu(OTf)_2$	L-tert-leucinol	20	50	40
11	$Cu(acac)_2$	L-tert-leucinol	20	20	16

[a]As per Table 1. [b]Isolated yield after column chromatography. [c]ee determined by chiral HPLC using Daicel Chiralcel OD-H column. *Reaction was done in the absence of ligand (*S*,*S*)-**2**. [≠]Reaction was carried out in absence of 4 Å MS.

The effect of solvent and catalyst loading were evaluated under so far optimized reaction condition (Table 2, entry 5) and the data are summarized in Table 3. Catalytic runs conducted in THF, CH_3CN, $CHCl_3$ or in Toluene were not as effective as those in CH_2Cl_2 (entries 2, 6-10). Further, catalyst loading of 10 mol%, was found to be optimum under the above reaction condition (entries 1-3). Additionally, it appeared that 1:0.6 metal/ligand ratio is the best to achieve highest enantioselectivity (entries 2, 4-5).

Table 3. Influence of the solvent and catalyst loading on allylation reaction[a]



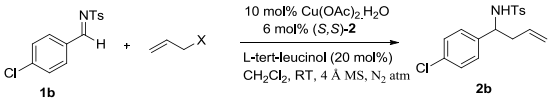
Entry	Cat. Loading (mol%)	$Cu(OAc)_2.H_2O$ /(S,S)-**2**	Solvent	Time (h)	Yield (%)[b]	ee (%)[c]
1	5	1:0.6	CH_2Cl_2	65	50	76
2	10	1:0.6	CH_2Cl_2	46	66	94
3	15	1:0.6	CH_2Cl_2	45	69	88
4	10	1:1	CH_2Cl_2	46	67	90
5	10	1:1.5	CH_2Cl_2	46	66	90
6	10	1:0.6	$CHCl_3$	60	50	60
7	10	1:0.6	THF	72	35	40
8	10	1:0.6	CH_3CN	85	34	46
9	10	1:0.6	Toluene	90	20	30

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

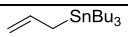
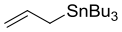
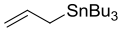
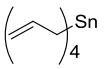
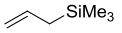
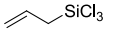
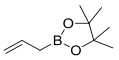
We further examined the chiral Schiff base-Cu(II) complex-promoted allylation reaction of **1b** with other allylating agents (Table 4). Tetra-allyltin showed activity similar to the

allyltributyltin but with significantly lower enantioselectivity (entries 2 and 4). In a marked contrast the reaction using allylsilanes did not proceed at all (entries 4-5). When we used (pinacolato) allylboron as an allylating agent we got homoallyl amine in good yield with very low enantioselectivity (entry 7). After fixing the allylting agent we optimized its amount and the results showed its 1.5 equivalent (with respect to **1b**) was sufficient for getting highest product yield and enantioselectivity (entry 2).

Table 4. Effect of allylating agent on allylation reaction



1b 2b

Entry	Allylating agents	Amount of allylating agents (equiv.)	Yield (%)[b]	ee (%)[c]
1		1	50	90
2		1.5	66	94
3		2	66	92
4		1.5	68	50
5		1.5	20	10
6		1.5	<10	-
7		1.5	70	20

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

The optimal condition established for the enantioselective allylation of *N*-(4-chlorobenzylidene)-4-methylbenzene sulfonamide **1b** (Table 4, entry 2) was applied to other aromatic as well as α,β-unsaturated sulfonyl imines.

Table 5. Chiral Cu (II)-Schiff base catalysed enantioselective allylation of sulfonyl imine[a]

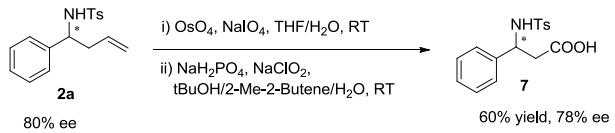
1a-1p 2a-2p

Entry	Substrate	R_1/R_2	Yield (%)[b]	ee (%)[c]
1	Ph	C_6H_5/Me (**1a**)	**2a** (60)	80
2	*p*-ClC_6H_4	*p*-ClC_6H_4/Me (**1b**)	**2b** (66)	94
3	*p*-ClC_6H_4	*p*-ClC_6H_4/H (**1c**)	**2c** (58)	90
4	*p*-ClC_6H_4	*p*-ClC_6H_4/NO_2 (**1d**)	**2d** (68)	78
5	*p*-BrC_6H_4	*p*-BrC_6H_4/H (**1e**)	**2e** (60)	98
6	*p*-FC_6H_4	*p*-FC_6H_4/Me (**1f**)	**2f** (69)	90
7	*p*-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$/Me (**1g**)	**2g** (67)	80
8	*p*-$CF_3C_6H_4$	*p*-$CF_3C_6H_4$/Me (**1h**)	**2h** (65)	76
9	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$/H (**1i**)	**2i** (30)	84
10	*m*-ClC_6H_4	*m*-ClC_6H_4/Me (**1j**)	**2j** (64)	82
11	*o*-ClC_6H_4	*o*-ClC_6H_4/Me (**1k**)	**2k** (70)	66
12	*o*-FC_6H_4	*o*-FC_6H_4/Me (**1l**)	**2l** (65)	78
13	1-naphthyl	1-naphthyl/Me (**1m**)	**2m** (90)	92
14	2-naphthyl	2-naphthyl/Me (**1n**)	**2n** (84)	94
15	*trans*-cinnamyl	(*E*)-C_6H_5CH=CH/Me (**1o**)	**2o** (76)	86
16	alpha-Methyl-*trans*-cinnamyl	(*E*)-C_6H_5CH=C(CH_3)/Me (**1p**)	**2p** (75)	94

[a]All the reactions were carried out by using substrates **1a-1o** (0.3 mmol), allyltributyltin (0.45 mmol), and catalyst (10 mol%) in CH_2Cl_2 at RT. [b]Isolated yields after column chromatography. [c]ee determined by chiral HPLC using OD-H, AD-H, IA chiral column.

The desired homoallyl sulfonamines **2a-2p** were obtained in mostly good yield with high enantioselectivities ranging from 98 to 66% enantiomeric excess (Table 5). *Para-* and *meta-*substituted aromatic imines gave good yield (except electron donating e.g. *p*-methoxy group) and exillent enantioselectivity (entries 2-10) as compared to their *ortho*-counterpart (entries 11-12). The present catalytic system works very well for bulkier aromatic imines (like 1-naphthyl and 2-naphthyl imines; entries 13 and 14) as well as α,β-unsaturated sulfonyl imines (e.g., *trans*-cinnamyl and alpha-methyl-*trans*-cinnamyl imines; entries 15 and 16).

The present asymmetric allylation protocol was successfully extended to the synthesis of enantioenriched β-amino acid **7** (Scheme 2). β-Amino acids[13] are important motifs which serve as precursors to β-lactams, constituents of several medicinally important compounds,[14] and most importantly as monomers in the synthesis of peptidomimetic β-peptides.[15] Compound **2a** was oxidized with $NaIO_4$ in the presence of a catalytic amount of OsO_4 to form the corresponding aldehyde, which without purification was further oxidized to furnish the desired tosyl-protected β-amino acid **7** with an overall yield of 60% with retention of optical purity.



2a 80% ee **7** 60% yield, 78% ee

Scheme 2. Synthesis of enantioriched β-amino acid **7**

Mechanism

To support the mechanism as given in Scheme 3 for the catalytic allylation reaction, a stepwise UV-vis. spectral study was carried out with *N*-(4-chlorobenzylidene)-4-methylbenzene sulfonamide (**1b**) and allyltributyltin in $CHCl_3$ as solvent at RT (Fig. 2A, 2B & 2C).

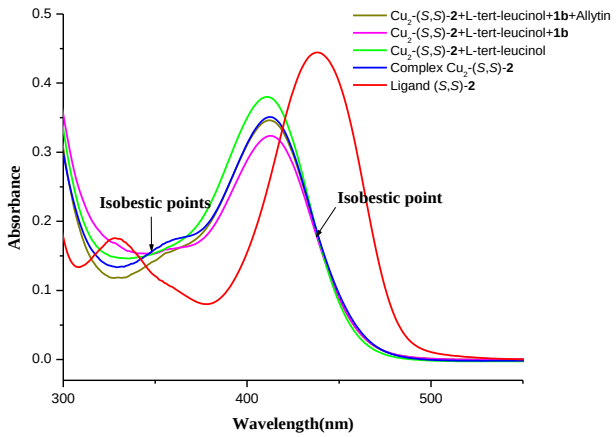


Figure 2A Uv-vis spectra of ligand, *in situ* generate complex and reaction mixture after sequential addition of additive, substrate and allyltributyltin.

Initially, *in situ* formation of the complex was confirmed by UV-vis. (strong blue shift i.e. from 438 nm to 412 nm, Figure 2A) as well as ESI-MS spectral analysis (Figure 3). After the addition of additive (L-tert-leucinol) to the complex solution, the intensity of LMCT band at ~410 nm has increase significantly whereas d-d band was red shifted (from 608 nm to 621 nm) with isobestic

points at ~348 nm and ~438 nm suggests the formation of intermediate **I-1** (Scheme 3).

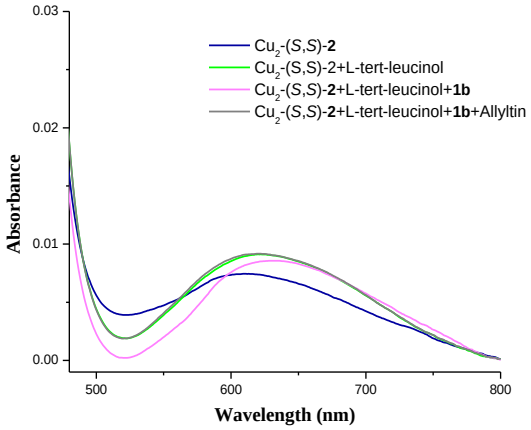


Figure 2B Uv-vis spectra (for d-d transition) of *in situ* generate complex and reaction mixture after sequential addition of additive, substrate and allyltributyltin.

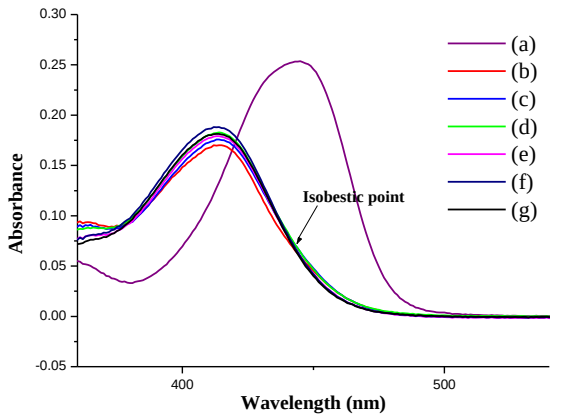


Figure 2C Uv-vis spectra of ligand, *in situ* generate complex and the reaction mixture with varing concentration of tert-leucinol: (a) ligand; (b) *in situ* generate complex; (c) complex:additive (1:0.2); (d) complex:additive (1:0.4); (e) complex:additive (1:0.6); (f) complex:additive (1:0.8); (g) complex:additive (1:1).

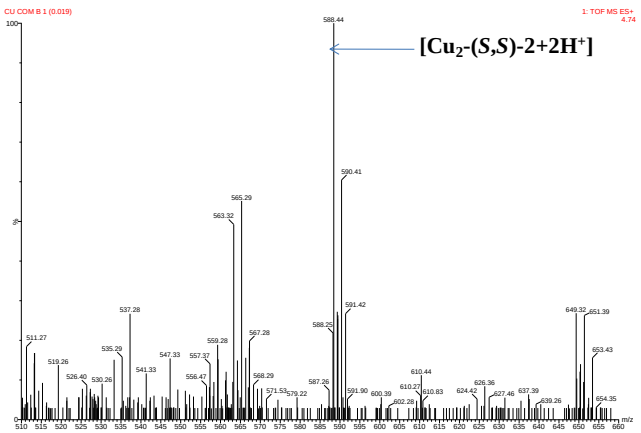


Figure 3 ESI-MS spectum of the in situ generated complex was taken in methanol.

To further confirm this interaction additional experiment on varying the amount of tert-leucinol to the in situ generated copper complex was carried out and was monitored on UV-vis and the spectra (Figure 2C) that clearly show isobestic point at ~441 nm, and thereby additionally supports the formation intermediate **I-1** during the catalytic cycle.

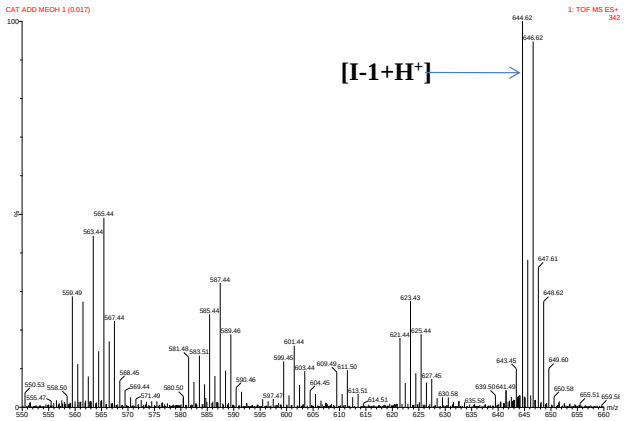
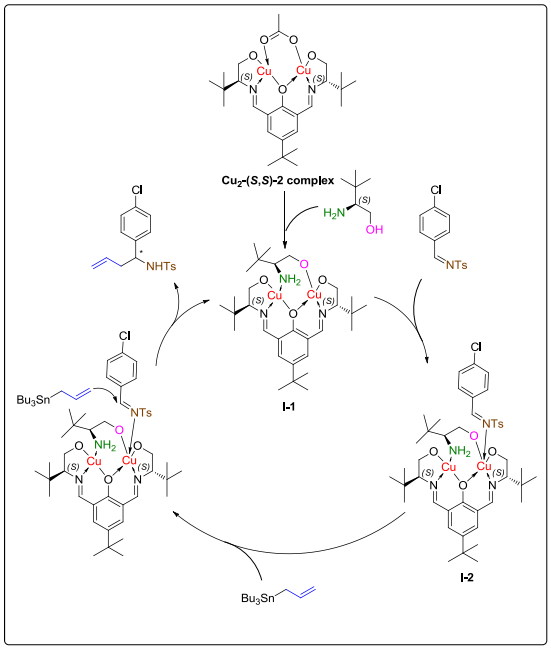


Figure 4 ESI-MS spectum of the in situ generated complex after interaction with additive was recorded in methanol.

This intermediate **I-1** was further confirmed by ESI-MS spectral analysis where new molecular mass peak equivalent to **[I-1+H$^+$]** species (Figure 4) is clearly visible. After the addition of substrate to the above solution, LMCT band maxima slightly diminished with isobestic points at ~348 nm and ~438 nm. A significant red shift in the d-d band (from 621 nm to 631 nm) confirms the direct co-ordination of the substrate to the vacant d orbital of the copper through the lone pair of the nitrogen atom of the *N*-tosylimine. The generation of the isobestic points may be due to the change in geometry of the copper complex and this can be attributed to the attachment of the L-tert-leucinol and the substrate to the complex to form an intermediate **I-2** (Scheme 3).



Scheme 3 Proposed catalytic cycle.

The intermediate **I-2** was further confirmed by ESI-MS spectral analysis where new molecular mass peak corresponding to **[I-2+CH_3OH+H^+]** species (see Figure 1 in Supporting Information).On further addition of allyltributyltin to the reaction mixture there was no observable change in the spectrum. The addition of allyltributyltin follows product formation and regenerates the intermediate **I-1** for the next cycle.

Conclusion

In conclusion, a new copper based catalytic protocol was developed for asymmetric allylation reaction of aryl, alkenyl-substituted *N*-sulfonylimines using allyltributyltin as allylating agent. More importantly, the present catalytic system is simple and works under ordinary reaction condition giving high yields (up to 90%) of the homoallyl amines with excellent enantioselectivities (ee up to 98%) as compared to the other reports. Additionally, the current methodology was extended to the synthesis of *β*-phenylalanine in good and very good enantioselectivity.

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Experimental Section

Different aldehydes and reagents were used as received. The imine substrates (**1a-1o**) were prepared following literature procedure.[11a] All the solvents were dried using standard procedures,[16] distilled and stored under activated molecular sieves. NMR spectra were obtained with a Bruker F113V spectrometer (200 and 500 MHz) and are referenced internally with *tetra*-methylsilane (TMS). Splitting patterns were reported as s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet; br, broad. Enantiomeric ratio (er) values were determined by HPLC (Shimadzu SCL-10AVP) using Daicel Chirl-pak OD-H, AS-H, IA, IB and IC chiral columns with 2-propanol/hexaneas eluent. For the product purification flash chromatography was performed using silica gel 100–200 mesh.

General procedure for preparation of catalysts (*S,S*)-1 to (*S,R,S,R*)-4[11a]

To a solution of 4-*tert*-Butyl-2,6-diformylphenol (300 mg; 1.45 mmol) in dry toluene chiral (*S*)-tert-leucinol (341 mg; 2.91 mmol) was added and the reaction was vigorously stirred for 2 days under reflux condition. In two days yellow coloured precipitate of desired product was formed in the reaction mixture which was filtered, washed twice with cold methanol and dried to get desired ligand (*S,S*)-**2** in sufficient purity (yield, 515 mg; 88%) and was fully characterised by NMR and elemental analysis before its use in catalytic reaction. All other Schiff base ligands (*S,S*)-**1 to** (*S,R,S,R*)-**4** were prepared following the above reaction procedure.

Typical procedure for preparation of ligand (*S,S*)-2'

To the solution of (*S,S*)-**2** (405 mg, 1 mmol) in 20 mL dry methanol $NaBH_4$ (303 mg, 4x2 mmol) was added portion wise in four equal parts. The reaction was monitored by TLC. After completion of the reaction (10 h), solvent was completely removed under reduced pressure. Then the reaction mass was washed by water and extracted with CH_2Cl_2 and dried by Na_2SO_4. Further purification was done by flash column chromatography (EtOAc/hexane = 1:4) using silica gel (100-200 mesh). White solid. yield: 90%; m. p.: 150-152 ^oC. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.91 (s, 18H), 1.19 (s, 9H), 2.35 (m, 2H), 3.52-3.78 (m, 4H), 3.89-4.03 (m, 4H), 4.67 (br, 4H), 6.97 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.24, 29.63, 31.52, 33.99, 52.14, 60.59, 67.65, 123.39, 125.58, 141.46, 154.42. TOF–MS (ESI+) calcd [M + H^+] for ($C_{24}H_{44}N_2O_3$) 409.34, Found: 409.66

General procedure for Cu(II)-Schiff base complex catalyzed asymmetric allylation reaction of tosylimines 1a-1o

To a mixture of $Cu(OAc)_2.H_2O$ (0.03 mmol), ligand (*S,S*-**2**) (0.018 mmol) and 60 mg of powdered activated 4 Å MS in a nitrogen-filled 5 mL reactor, dry DCM (2 mL) was added. After the mixture was stirred at 27 ^oC for 2 h, L-tert-leucinol (0.06 mmol) was added and again stirred for 30 minutes. To it sulfonimines **1a-1o** (0.3 mmol) followed by allyltributyltin (0.45 mmol) were added and the resulting mixture was stirred at same temperature until the reaction was completed as indicated by TLC. After completion of the reaction, the solvent was removed under vacuum and the residue thus obtained was purified by silica gel flash column chromatography with ethyl acetate/hexane as eluent. Products were confirmed by NMR and LCMS data corresponded to those published.

***N*-(1-Phenylbut-3-enyl)-4-methylbenzenesulfonamide 2a[6f]**

The product was isolated as a white solid (yield 57 mg, 60%) after purification by silica gel chromatography (Hexane/EtOAc = 90:10). Optical Rotation: $[\alpha]^{27}_D$ = -71.5 (*c* 0.5, CH_2Cl_2).[6f] ^{1}HNMR ($CDCl_3$, 200 MHz): δ = 2.37-2.45 (m, 5H), 4.37-4.39 (m, 1H), 4.89-5.09 (m, 3H), 5.45-5.53 (m, 1H), 7.09-7.17 (m, 7H), 7.53-7.57 (d, *J* = 7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 23.06, 43.47, 58.66, 120.96, 128.15, 128.75, 128.99, 129.97, 130.92, 134.66, 139.03, 141.91, 144.72. TOF–MS (ESI+) calcd [M + Na^+] for ($C_{17}H_{19}NaNO_2S$) 324.10, Found: 324.40. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 230 nm) t_{major}(*S*) = 19.34 min, t_{minor}(*R*) = 14.31 min.

***N*-(1-(4-Chlorophenyl)but-3-enyl)-4-methylbenzenesulfonamide 2b[6f]**

The product was isolated as a white solid (yield 69 mg, 66%) after purification by silica gel chromatography (Hexane/EtOAc = 88:12). Optical Rotation: $[\alpha]^{27}_D$ = -85.4 (*c* 0.5, CH_2Cl_2).[6f] ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.39-2.44 (m, 5H), 4.29-4.39 (dd, *J* = 6.6 and 13.2 Hz, 1H), 5.01-5.09 (m, 3H), 5.38-5.59 (m, 1H), 6.98-7.17 (m, 6H), 7.51-7.55 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.44, 41.71, 56.56, 119.69, 127.11, 128, 128.42, 129.34, 132.61, 138.82, 143.37. TOF–MS (ESI+) calcd [M + Na^+] for ($C_{17}H_{18}ClNaNO_2S$) 358.06, Found: 358.23. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 230 nm) t_{major} = 22.5 min, t_{minor} = 18.4 min.

***N*-(1-(4-Chlorophenyl)but-3-enyl)benzenesulfonamide 2c**

The product was isolated as a white solid (yield 58.7 mg, 58%) after purification by silica gel chromatography (Hexane/EtOAc = 88:12). Optical Rotation: $[\alpha]^{27}_{D}$ = -80.8 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.40-2.43 (t, *J* = 7 Hz, 2H), 4.37-4.41 (dd, *J* = 7 and 13.5 Hz, 1H), 4.87-4.88 (d, *J* = 6 Hz, 1H), 5.06-5.1 (m, 2H), 5.44-5.51 (m, 1H), 6.99-7.02 (m, 2H), 7.12-7.14 (m, 2H), 7.35-7.38 (m, 2H), 7.48-7.51 (m, 1H), 7.64-7.65 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 41.75, 56.42, 119.88, 127.06, 127.97, 128.5, 128.78, 132.49, 132.53, 138.7, 139.49. TOF–MS (ESI+) calcd [M + Na^+] for ($C_{16}H_{16}ClNaNO_2S$) 344.05, Found: 344.23. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 230 nm) t_{major} = 21.75 min, t_{minor} = 18.4 min.

***N*-(1-(4-Chlorophenyl)but-3-enyl)-4-nitrobenzenesulfonamide 2d**

The product was isolated as a white solid (yield 78 mg, 68%) after purification by silica gel chromatography (Hexane/EtOAc = 85:15). Optical Rotation: $[\alpha]^{27}_{D}$ = -69.4 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.43-2.49 (t, *J* = 7 Hz, 2H), 4.44-4.53 (dd, *J* = 6.4 and 13 Hz, 1H), 5.05-5.17 (m, 3H), 5.44-5.65 (m, 1H), 6.97-7.16 (m, 4H), 7.74-7.78 (d, *J* = 9 Hz, 2H), 8.16-8.2 (d, *J* = 9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 41.66, 56.78, 120.31, 123.9, 128.05, 128.26, 128.67, 132.20, 133.85, 138.01, 146.23, 149.73. TOF–MS (ESI-) calcd [M - H^+] for ($C_{16}H_{14}ClN_2O_4S$) 365.04, Found: 364.82. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 254 nm) t_{major} = 17.78 min, t_{minor} = 14.55 min.

***N*-(1-(4-Bromophenyl)but-3-enyl)benzenesulfonamide 2e**

The product was isolated as a white solid (yield 71 mg, 60%) after purification by silica gel chromatography (Hexane/EtOAc = 84:16). Optical Rotation: $[\alpha]^{27}_{D}$ = -70.7 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.38-2.44 (t, *J* = 7 Hz, 2H), 4.32-4.42 (dd, *J* = 6.4 and 13 Hz, 1H), 4.97-5.11 (m, 3H), 5.42-5.59 (m, 1H), 6.93-6.97 (d, *J* = 8.4 Hz, 2H), 7.3-7.54 (m, 4H), 7.63-7.66 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 41.68, 56.5, 119.87, 127.04, 128.32, 128.79, 131.44, 132.48, 139.22, 140.2. TOF–MS (ESI+) calcd [M + Na^+] for ($C_{16}H_{16}BrNaNO_2S$) 388, Found: 388.13. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 230 nm) t_{major} = 23.6 min, t_{minor} = 20 min.

***N*-(1-(4-Fluorophenyl)but-3-enyl)-4-ethylbenzenesulfonamide 2f[6f]**

The product was isolated as a white solid (yield 69 mg, 69%) after purification by silica gel chromatography (Hexane/EtOAc = 85:15). Optical Rotation: $[\alpha]^{27}_{D}$ = -71.5 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.38 (s, 3H), 2.39-2.43 (m, 2H), 4.34-4.38 (dd, *J* = 6.5 and 13 Hz, 1H), 5-5.06 (m, 3H), 5.44-5.53 (m, 1H), 6.83-6.87 (m, 2H), 7.03-7.07 (m, 2H), 7.15-7.16 (d, *J* = 8 Hz, 2H), 7.53-7.54 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.44, 41.9. 56.4, 115.07, 115.24, 119.6, 127.12, 128.2, 128.26, 129.33, 132.78, 136.12, 137.32, 143.28, 162.95. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 1 mL/min, λ = 220 nm) t_{major} = 17.38 min, t_{minor} = 14.4 min.

***N*-(1-(4-Nitrophenyl)but-3-enyl)-4-methylbenzenesulfonamide 2g**

The product was isolated as a white solid (yield 73 mg, 67%) after purification by silica gel chromatography (Hexane/EtOAc = 88:12). Optical Rotation: $[\alpha]^{27}_{D}$ = -59.4 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.38-2.46 (m, 5H), 4.41-4.51 (dd, *J* = 6.4 and 12.6 Hz, 1H), 5.04-5.15 (m, 3H), 5.36-5.56 (m, 1H), 7.15-7.32 (m, 4H), 7.53-7.57 (d, *J* = 8 Hz, 2H), 8.03-8.07 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 25 MHz): δ = 21.45, 41.59, 56.38, 120.49, 123.55, 127.14, 127.56, 129.48, 131.86, 143.82, 147.9. HPLC (Daicel Chiralcel AD-H, hexanes/2-propanol = 95:5, flow rate = 1 mL/min, λ = 254 nm) t_{major} = 22.5 min, t_{minor} = 23.8 min.

***N*-(1-(4-Trifluoromethylphenyl)but-3-enyl)-4-methylbenzenesulfonamide 2h[6f]**

The product was isolated as a white solid (yield 75 mg, 65%) after purification by silica gel chromatography (Hexane/EtOAc = 82:18). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.38 (s, 3H), 2.41-2.43 (m, 2H), 4.31-4.4 (dd, *J* = 6.4 and 13 Hz, 1H), 4.9-4.93 (d, *J* = 6 Hz, 2H), 5.01-5.09 (m, 2H), 5.39-5.59 (m, 1H), 6.81-6.89 (m, 2H), 7.01-7.17 (m, 4H), 7.51-7.55 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 22.69, 41.66, 56.56, 20.14, 125.23, 127.05, 127.12, 129.32, 132.31, 143.46. HPLC (Daicel Chiralcel IA, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 220 nm) t_{major} = 21.75 min, t_{minor} = 20 min.

***N*-(1-(4-Methoxyphenyl)but-3-enyl)benzenesulfonamide 2i**

The product was isolated as a white solid (yield 28 mg, 30%) after purification by silica gel chromatography (Hexane/EtOAc = 88:12). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.41-2.48 (t, *J* = 7 Hz, 2H), 2.75 (s, 3H), 4.31-4.4 (dd, *J* = 6.6 and 13.2 Hz, 1H), 4.8-4.83 (d, *J* = 5 Hz, 2H), 5.02-5.09 (m, 2H), 5.42-5.62 (m, 1H), 6.67-6.99 (m, 4H), 7.26-7.47 (m, 3H), 7.64-7.68 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 41.82, 55.21, 56.75, 113.71, 119.09, 127.05, 127.71, 128.66, 132.23, 133.2, 140.49, 158.82. HPLC (Daicel Chiralcel ODH, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 254 nm) t_{major} = 28.2 min, t_{minor} = 24.59 min.

***N*-(1-(3-Chlorophenyl)but-3-enyl)-4-methylbenzenesulfonamide 2j[6f]**

The product was isolated as a viscose liquid (yield 68 mg, 64%) after purification by silica gel chromatography (Hexane/EtOAc = 84:16). Optical Rotation: $[\alpha]^{27}_{D}$ = -50.1 (*c* 1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.38-2.44 (m, 5H), 4.31-4.41 (dd, *J* = 6.6 and 13 Hz, 1H), 4.96-5.12 (m, 3H), 5,4-5.57 (m, 1H), 6.95-7.26 (m, 6H), 7.51-7.55 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.44, 41.71, 56.55, 119.82, 124.84, 126.80, 127.08, 127.47, 129.35, 129.61, 132.53, 134.21, 137.13, 142.23, 143.41. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 220 nm) t_{major} = 18.79 min, t_{minor} = 17.14 min.

***N*-(1-(2-Chlorophenyl)but-3-enyl)-4-methylbenzenesulfonamide 2k[6f]**

The product was isolated as a white solid (yield 74 mg, 70%) after purification by silica gel chromatography (Hexane/EtOAc = 85:15). Optical Rotation: $[\alpha]^{27}_{D}$ = -46.1 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.36 (s, 3H), 2.42-2.48 (m, 2H), 4.74-4.84 (dd, *J* = 6.8 and 13.4 Hz, 1H), 5.02-5.14 (m, 3H), 5.38-5.58 (m, 1H), 7,06-7.23 (m, 6H), 7.57-7.21 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.44, 40.23, 54.07, 119.53, 126.76, 127.15, 128.37, 128.42, 129.31, 132.72, 136.78, 137.78, 143.74. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 230 nm) t_{major} = 21.1 min, t_{minor} = 15.1 min.

N-(1-(2-Fluorophenyl)but-3-enyl)-4-methylbenzenesulfonamide 2l

The product was isolated as a white solid (yield 65 mg, 65%) after purification by silica gel chromatography (Hexane/EtOAc = 86:14). Optical Rotation: $[\alpha]^{27}_D$ = -48.6 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.34 (s, 3H), 2.43-2.51 (m, 2H), 4.53-4.64 (dd, *J* = 7.5 and 14.5 Hz, 1H), 5-5.06 (m, 3H), 5.47-5.55 (m, 1H), 6.82-6.86 (m, 1H), 6.93-6.96 (m, 1H), 7.06-7.15 (m, 4H), 7.54-7.56 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.42, 40.65, 52.92, 115.4, 115.57, 119.26, 123.99, 127.02, 127.33, 127.43, 128.72, 128.95, 129.01, 129.28, 132.87, 137.12, 143.13, 158.97, 160.92. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 1 mL/min, λ = 220 nm) t_{major} = 13.5 min, t_{minor} = 10.63 min.

***N*-(1-(1-Naphthyl)but-3-enyl)-4-methylbenzenesulfonamide 2m**

The product was isolated as a white solid (yield 95 mg, 90%) after purification by silica gel chromatography (Hexane/EtOAc = 90:10). Optical Rotation: $[\alpha]^{27}_D$ = -80.4 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.29 (s,3H), 2.58-2.68 (m, 2H), 4.99-5.01 (d, *J* = 6.5 Hz, 1H), 5.08-5.13 (m, 2H), 5.2-5.24 (dd, *J* = 6.5 and 13 Hz, 1H), 5.5-5.58 (m, 1H), 6.99-7 (d, *J* = 8 Hz, 2H), 7.27-7.3 (m, 2H), 7.45-7.48 (m, 4H), 7.66-7.68 (m, 1H), 7.79-7.81 (m, 1H), 7.89-7.91 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.37, 41.16, 53.17, 119.44, 122.37, 124.19, 125.04, 125.54, 126.24, 127.06, 127.96, 128.91, 129.12, 133.11, 143.03. TOF–MS (ESI-) calcd [M - H^+] for ($C_{21}H_{20}NO_2S$) 350.13, Found: 350.19. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 230 nm) t_{major} = 23.1 min, t_{minor} = 19.9 min.

***N*-(1-(2-Naphthyl)but-3-enyl)-4-methylbenzenesulfonamide 2n**

The product was isolated as a white solid (yield 88.2 mg, 84%) after purification by silica gel chromatography (Hexane/EtOAc = 88:12). Optical Rotation: $[\alpha]^{27}_D$ = -89.1 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.2 (s, 3H), 2.49-2.6 (m, 2H), 4.53-4.57 (dd, *J* = 7 and 13.5 Hz, 1H), 5.06-5.1 (m, 3H), 5.47-5.58 (m, 1H), 6.96-6.97 (d, *J* = 8 Hz, 2H), 7.18-7.2 (m, 1H), 7.42-7.43 (m, 3H), 7.49-7.51 (d, *J* = 8 Hz, 2H), 7.63-7.65 (m, 2H), 7.74-7.76 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.25, 41.67, 57.30, 119.37, 124.22, 125.82, 125.89, 126.07, 127.09, 127.47, 127.78, 128.25, 129.13, 132.64, 132.94, 133, 137.31, 143.08. TOF–MS (ESI-) calcd [M - H^+] for ($C_{21}H_{20}NO_2S$) 350.13, Found: 350.20. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 95:5, flow rate = 0.8 mL/min, λ = 220 nm) t_{major} = 27.9 min, t_{minor} = 20.8 min.

(*E*)-*N*-(1-Phenylhexa-1,5-diene-3-yl)-4-methylbenzenesulfonamide 2o[6f]

The product was isolated as a white solid (yield 74 mg, 76%) after purification by silica gel chromatography (Hexane/EtOAc = 90:10). Optical Rotation: $[\alpha]^{27}_D$ = -90.5 (*c* 0.6, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.32-2.43 (m, 5H), 4.03-4.04 (m, 1H), 4.85-4.86 (d, *J* = 6.5 Hz, 1H), 5.05-5.11 (m, 2H), 5.61-5.69 (m, 1H), 5.78-5.62 (m, 1H), 6.27-6.3 (m, 1H), 7.12-7.25 (m, 7H), 7.72-7.74 (d, *J* = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.36, 40.14, 55.18, 119.33, 126.34, 127.29, 127.66,127.92, 128.04, 128.10,m 128.28, 128.35, 128.6, 128.71, 128.93, 129.47, 129.69, 129.78, 131.53, 132.77, 136.14, 137.91, 143.28. TOF–MS (ESI-) calcd [M - H^+] for ($C_{19}H_{20}NO_2S$) 326.13, Found: 326.23. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 96:4, flow rate = 0.8 mL/min, λ = 254 nm) t_{major} = 24.5 min, t_{minor} = 26.05 min.

(*E*)-*N*-(2-methyl-1-phenylhexa-1,5-dien-3-yl)-4-methyl-benzenesulfonamide 2p

The product was isolated as a white solid (yield 76 mg, 75%) after purification by silica gel chromatography (Hexane/EtOAc = 89:11). Optical Rotation: $[\alpha]^{27}_D$ = -94.5 (*c* 0.5, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.56 (s, 3H), 2.28-2.35 (m, 2H), 2.37 (s, 3H), 3.91-3.95 (dd, *J* = 6.5 and 13.5 Hz, 1H), 4.62-4.63 (d, *J* = 6 Hz, 1H), 5.09-5.12 (m, 2H), 5.59-5.67 (m, 1H), 6.25 (s, 1H), 7.01-7.03 (d, *J* = 7.5 Hz, 1H), 7.18-7.22 (m, 3H), 7.28-7.29 (m, 2H), 7.71-7.72 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.45, 38.5, 60.77, 118.92, 126.56, 127.41,127.95, 128.2, 128.83, 129.39, 133.24, 135.38, 136.94, 137.65, 143.22. TOF–MS (ESI-) calcd [M - H^+] for ($C_{20}H_{23}NO_2S$) 340.14, Found: 340.35. HPLC (Daicel Chiralcel OD-H, hexanes/2-propanol = 96:4, flow rate = 0.8 mL/min, λ = 254 nm) t_{major} = 18.96 min, t_{minor} = 20.33 min.

3-(4-methylphenylsulfonamido)-3-phenylpropanoic acid[11a]

The compound **2a** (0.12 mmol, 37 mg) was dissolved in THF/H_2O (320/160 µL) and the reaction vial was covered with an aluminium foil. OsO_4 (0.05 mmol, 2.5 wt% in *t*-BuOH, 81µL) was then added followed by a portion wise addition of $NaIO_4$ (0.3 mmol, 64 mg) over a period of 15 min. After stirring for 4 h at room temperature, the reaction mixture was filtered and the residue was washed with ethyl acetate. The organic solvents were then evaporated and EtOAc and sat. NH_4Cl were added to the reaction mixture. The organic layer was extracted and concentrated to yield the crude aldehyde which was directly used for the next step.

The crude aldehyde was dissolved in *tert*-butanol (700 µL) and 2-methyl-2-butene (0.96 mmol, 100 µL) was added. A solution of $NaClO_2$ (0.90 mmol, 82 mg) and NaH_2PO_4 (0.78 mmol, 93 mg) in H_2O (300 µL) was then slowly added. After stirring the reaction for 12 h at room temperature, conc. HCl (50 µL) was added drop wise and the reaction mixture was extracted with EtOAc. The organic layer was concentrated to yield the crude product which was then purified by column chromatography (1:5, MeOH:DCM as the eluent) to give the desired compound **7** as a white solid. Optical Rotation: $[\alpha]^{27}_D$ = -30.5 (*c* 0.3, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.36 (s, 3H), 2.78-2.93 (m, 2H), 4.7-4.74 (m, 1H), 5.89-5.9 (d, J = 8 Hz, 1H), 7.09-7.18 (m, 7H), 7.57-7.58 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.46, 40.87, 53.99, 126.44, 127.06, 127.84, 128.6, 129.47, 137.05, 138.95, 143.39, 175.22.

Notes and references

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