Synthesis of Enantiopure 1-Aryl-1-butylamines and 1-Aryl-3-butenylamines by Diastereoselective Addition of Allylzinc Bromide to Imines Derived from (*R*)-Phenylglycine Amide

Jan Dalmolen,[a] Marcel van der Sluis,[b] José W. Nieuwenhuijzen,[b] Auke Meetsma,[a] Ben de Lange,[c] Bernard Kaptein,[c] Richard M. Kellogg,*[b] and Quirinus B. Broxterman[c]

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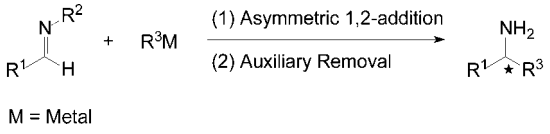
The synthesis of enantiopure 1-aryl-1-butylamines via a highly diastereoselective addition of allylzinc bromide to imines derived from (*R*)-phenylglycine amide is reported. These are synthesised by a three-step procedure, which involves: (a) formation of the chiral imines; (b) asymmetric addition of the allylzinc reagent; (c) removal of the chiral auxiliary by means of a reductive or non-reductive method. The reductive method provides 1-aryl-1-butylamines whereas the non-reductive method preserves the double bond to afford 1-aryl-3-butenylamines.

Introduction

Enantiomerically pure amines with a chiral centre at the α-position are valuable synthons in the synthesis of biologically active natural products and compounds of pharmaceutical interest.[1] One of the strategies used to obtain chiral amines is an asymmetric 1,2-addition of nucleophiles to the electrophilic C=N imino group of chiral aldimines (Scheme 1). Other methods include e.g. catalytic asymmetric addition of dialkylzinc to imines,[2] diastereoselective reduction of chiral imines,[3] enantioselective reduction of prochiral imines[4] and oximes,[5] or use of a transaminase.[6]



Scheme 1. Synthesis of enantiomerically enriched primary amines by asymmetric 1,2-addition

Enantiomerically pure imines can be generated, in most cases fairly easily, by condensation of an enantiopure amine R^2-NH_2 used as a (readily available) chiral auxiliary, with the corresponding carbonyl compound. High asymmetric induction during the addition can be achieved by using imines derived from chiral auxiliaries such as α-arylethylamines,[7] β-amino alcohols, β-alkoxy amines, and α-amino acid esters.[8] A common feature of the latter three auxiliaries is the presence of a second heteroatom, which is capable of rigidifying the transition state of the 1,2-addition through chelation.[7] This effect is also referred to as "chelation control".[9] Drawbacks are the availability, in some cases, of only one enantiomer, high costs, low regioselectivity in the cleavage of the auxiliary, immolative removal and/or the need of removal of these auxiliaries by procedures unsuitable for large-scale preparations, such as oxidation with $[Pb(OAc)_4]$[10] or treatment with $HIO_4/MeNH_2$.[7,8b]

In this paper we report the preparation of easily accessible substituted 1-aryl-1-butylamines and 1-aryl-3-butenylamines, which we intend to use as new families of resolving agents in "Dutch Resolution experiments".[11] A metal-mediated Cope reaction (Figure 1) is a key element of the synthesis. There is extensive precedent for such reactions.[12a,13b,13g]

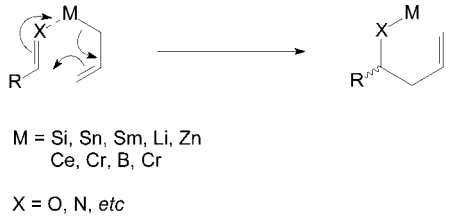


Figure 1. Metal-mediated Cope reaction

[a] University of Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands
[b] Syncom B.V.,
Kadijk 3, 9747 AT Groningen, The Netherlands
E-mail: R.M.Kellogg@syncom.nl
[c] DSM Pharma Chemicals-Advanced Synthesis and Catalysis,
P.O. Box 18, 6160 MD Geleen, The Netherlands

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In a preliminary publication, optically pure (*R*)-phenylglycine amide [(*R*)-PGA (**1**)] was shown to be a highly efficient chiral auxiliary for this process.[12a] (*R*)-PGA (**1**) readily forms imines with aldehydes.[12] These imines, capable of forming rigid chelated intermediates, have been subjected to addition of allylzinc reagents. Both reductive and nonreductive methods for the removal of the chiral auxiliary have been used to obtain the desired substituted enantiomerically pure primary amines. Finally, the selectivity of cleavage of the chiral auxiliary in the reductive removal has been investigated.

Results and Discussion

Diastereoselective Allylation of (*R*)-PGA Aldimines

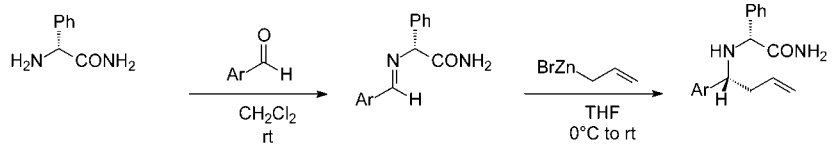
Benzaldimines (*R*)-**2**−**23** are easily obtained in excellent yields and >99% *ee*[14] by stirring a mixture of (*R*)-PGA (**1**) in CH_2Cl_2 with the corresponding substituted benzaldehyde overnight at room temperature (Table 1).[12] No catalyst is required and, in all cases, chemically pure products were obtained. This conclusion is based on the fact that clean singlets for both the proton adjacent to the carboxamide group as well as the imine proton are observed in the ^1H NMR spectra. Imines **2**−**23** are crystalline and have sharp melting points. On the basis of thermodynamic considerations the products should all have the *E*-configuration.

The phenyl-substituted benzaldehydes for the formation of imines **18**−**20** were prepared from the corresponding bromobenzaldehydes by a Suzuki coupling using 10% palladium on carbon as a catalyst.[15]

The addition of benzaldimines (*R*)-**2**−**23** to preformed allylzinc bromide (1.5 equiv.) in THF at 0 °C afforded the (*R*,*R*)-PGA allylamines **24**−**45** in yields of up to 99% or higher and diastereoselectivities of at least 97:3 (Table 1). In all cases, the *dr* could be increased to more than 99:1 by recrystallisation from acetone/hexane (1:20). It has been demonstrated previously for the case of **24** that the addition proceeds without any racemisation of the chiral auxiliary.[12b] Although, this has not been explicitly checked, the *ee*'s of the end products indicate that this is also the case for the other addition products **24**−**45** (vide supra).

The addition reaction has also been performed under Barbier-type[17] conditions with imines **2**−**11** and **18**−**20**, giving similar results. In this procedure the imines are stirred with zinc and allyl bromide in THF at 0 °C and the reaction mixture is allowed to warm to room temperature. This procedure in our experience is considerably easier from an experimental point of view. Imines **12**−**17** undergo partial halogen exchange under these conditions.

Table 1. Formation of (*R*)-PGA imines **2**−**23** by condensation with substituted benzaldehydes and the formation of (*R*,*R*)-PGA allylamines **24**−**45** by addition of allylzinc bromide



(*R*)-PGA, **1** (*R*)-**2**-**23** (*R*,*R*)-**24**-**45**

Entry	Imine	Ar	Yield (%)[a]	Allylamine	Yield (%)[a]	*dr* (*R*,*R*):(*R*,*S*)[b]
1	**2**	C_6H_5	99	**24**	>99	>99:1
2	**3**	*o*-Me-C_6H_4	>99	**25**	93	>99:1
3	**4**	*m*-Me-C_6H_4	97	**26**	>99	>99:1
4	**5**	*p*-Me-C_6H_4	>99	**27**	97	>99:1
5	**6**	*o*-OMe-C_6H_4	93	**28**	98	>99:1
6	**7**	*m*-OMe-C_6H_4	81	**29**	99	>99:1
7	**8**	*p*-OMe-C_6H_4	98	**30**	99	>99:1
8	**9**	*o*-F-C_6H_4	97	**31**	>99	98:2
9	**10**	*m*-F-C_6H_4	96	**32**	97	98:2
10	**11**	*p*-F-C_6H_4	95	**33**	94	99:1
11	**12**	*o*-Cl-C_6H_4	97	**34**	98	97:3
12	**13**	*m*-Cl-C_6H_4	98	**35**	83	98:2
13	**14**	*p*-Cl-C_6H_4	95	**36**	98	>99:1
14	**15**	*o*-Br-C_6H_4	99	**37**	98	>99:1
15	**16**	*m*-Br-C_6H_4	98	**38**	99	>99:1
16	**17**	*p*-Br-C_6H_4	99	**39**	95	>99:1
17	**18**	*o*-Ph-C_6H_4	85	**40**	89	>99:1
18	**19**	*m*-Ph-C_6H_4	89	**41**	85	>99:1
19	**20**	*p*-Ph-C_6H_4	95	**42**	99	>99:1
20	**21**	*o*-NO_2-C_6H_4	97	**43**	>99	>99:1
21	**22**	*m*-NO_2-C_6H_4	98	**44**	96	>99:1
22	**23**	*p*-NO_2-C_6H_4	92	**45**	93	99:1

[a] Isolated yield. [b] Diastereoselectivity values were determined with ^1H NMR spectroscopy.[16]

The high diastereoselectivity of the allylation of the (*R*)-PGA imines can be rationalised by chelation control, as shown in Figure 2.[13] The two heteroatoms of the amide-imine moiety chelate the zinc atom of the allylzinc reagent to form a five-membered ring.[7,9] Simultaneously, a six-membered, chair-like transition state is formed with the allylic system and the C=N double bond of the imine. The *re*-face 1,2-addition proceeds in a concerted fashion via an allylic aza-Cope-like rearrangement. Arguments and experimental evidence in support of this mechanistic model have been given previously.[12a]

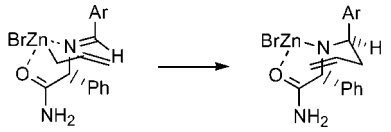


Figure 2. Proposed chelation controlled addition of allylzinc bromide to (*R*)-PGA imines

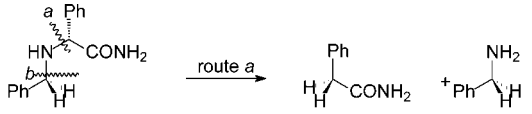
The (*R*,*R*)-configuration of the adducts was unambiguously confirmed by X-ray crystallographic analysis.[12a] The absolute configuration of adducts **24**−**45** was assigned by analogy.

Reductive Removal of the Chiral Auxiliary

The chiral auxiliary can easily be removed by selective catalytic debenzylation using H_2 and 10% palladium on carbon.[18,19] However, since PGA allylamines **24**−**45** are "di-*N*-benzylic", reductive removal of the auxiliary by catalytic hydrogenation may cleave either of the two benzylic C−N bonds via route *a* or route *b* (Scheme 2). In addition, this reductive removal of the chiral auxiliary leads to the loss of the allylic functionality.

Hydrogenolytic cleavage via route *b* leads to the undesired substituted 1-butylbenzene **46**, whereas cleavage via route *a* provides the desired saturated 1-phenylbutylamines (*R*)-**47**−**57**.

There is not much literature precedent to allow prediction whether path *a* or path *b* will dominate, but steric as well as electronic effects might influence the outcome of the hydrogenolysis. With this in mind we began a systematic investigation. Initially 2-(benzylamino)-2-phenylacetamide (**58**)[20] was examined as a model compound (Scheme 3) and we were very much encouraged to observe only benzylamine and phenylacetamide (**59**) (route *a*) and no (*R*)-PGA and toluene (route *b*).



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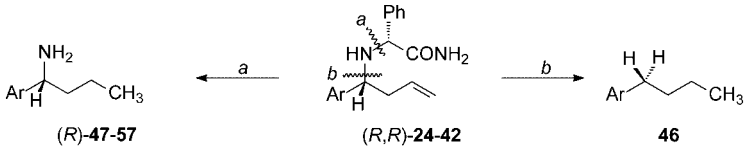
Scheme 3. Regioselectivity in the debenzylation process of **58**; reagents and conditions: Et_2O, H_2, Pd−C (10%)

Most probably the electron-withdrawing carboxamide group withdraws some electron density from the σ-bond involved in path *a* by means of inductive interactions, and one could well expect this σ-bond to be a better hydrogen acceptor.



(*R*)-**47-57** (*R*,*R*)-**24-42** **46**

Scheme 2. Selectivity of cleavage in the catalytic hydrogenation process; reagents and conditions: isopropanol/H_2O/AcOH, H_2, Pd−C (10%)

Table 2. Regioselective cleavage of the chiral auxiliary and generation of primary 1-aryl-1-butylamines **47**−**57** by catalytic hydrogenation

Entry	Allylamine	Ar	Butylamine	Yield (%)[a]	Selectivity *a*:*b*[b]
1	**24**	C_6H_5	**47**	70	91:9
2	**25**	*o*-Me C_6H_4	**48**	95	>99:1
3	**26**	*m*-Me C_6H_4	**49**	92	>99:1
4	**27**	*p*-Me C_6H_4	**50**	91	>99:1
5	**28**	*o*-OMe C_6H_4	**51**	91	>99:1
6	**29**	*m*-OMe C_6H_4	**52**	89	98:2
7	**30**	*p*-OMe C_6H_4	**53**	89	97:3
8	**31**	*o*-F C_6H_4	**54**	88	98:2
9	**32**	*m*-F C_6H_4	**55**	58	>99:1
10	**33**	*p*-F C_6H_4	**56**	79	>99:1
11	**40**	*o*-Ph C_6H_4	**57**	87	97:3
12	**41**	*m*-Ph C_6H_4	**80**	*nd*[c]	>1:99[d]
13	**42**	*p*-Ph C_6H_4	**81**	*nd*	>1:99[d]

[a] Isolated yield. [b] Regioselectivity values determined with ^1H NMR spectroscopy. [c] *nd*: Not determined. [d] Confirmed by mass analysis, ^1H and ^{13}C NMR.

The selectivities (*a*:*b*) for products **24**−**42** were determined by ^{1}H NMR spectroscopy. Analysis of ^{1}H NMR spectra of the reaction mixtures revealed that cleavage according to route *a* gave rise to a characteristic triplet of the benzylic CH group between δ = 3.9−4.2 ppm, and competitive cleavage according to route *b* gave rise to a triplet of the benzylic CH_2 group at approx. δ = 2.5−2.8 ppm. By comparing the ratio of the integrals for both signals, the selectivity for each case could be determined (Table 2). For instance, in the case of the unsubstituted PGA allylamine **24** the selectivity of the cleavage process is 91:9 in favour of path *a* (Figure 3).

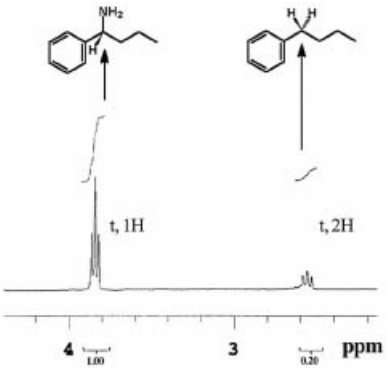


Figure 3. Selectivity of cleavage of homoallylamine **24** after hydrogenation

The PGA allylamines **24**−**33** and **40** showed pleasingly high selectivities in cleavage of the C−N bond of the chiral auxiliary via route *a*. The free primary 1-arylbutylamines (*R*)-**47**−**57** were obtained in yields of up to 95%. The selectivities of the cleavage range from 91:1 up to more than 99:1, depending on the substituent. The earlier work of Baltzly and Russel[18c] showed that the electronic nature of the substituent rather than its position is critical in its effect on the regioselectivity of debenzylation. Most substituents studied here are electron donating and increase the stability of the *N*-benzyl linkage, promoting cleavage according to route *a*.

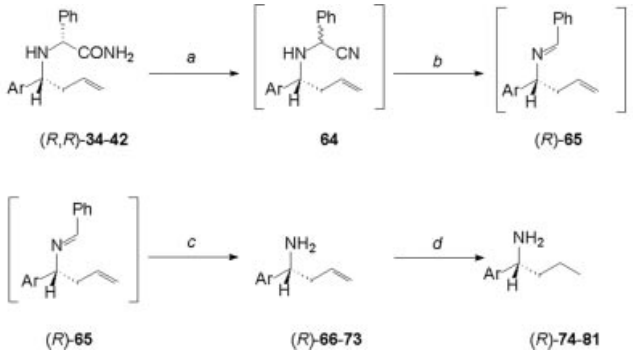
Attempts to convert the chloro- and bromo-substituted PGA allylamines **34**−**39** into the corresponding substituted amines were frustrated by dehalogenation, which occurred prior to debenzylation,[18b,18e] as was established by NMR spectroscopy and mass analysis. In all cases the only product isolated was 1-butyl-1-phenylamine (**47**).

In the cases of the *meta*- and *para*-phenyl-substituted PGA allylamines (entries 12 and 13), the regioselectivity strongly disfavours the desired products. As described by Baltzly and Buck,[18a] for reasons that are still unclear the phenyl group labilizes the nearby *N*-benzyl linkage, which results in the observed regioselectivity towards the unwanted by-product. We postulate that in the case of the *ortho*-phenyl-substituted homoallylamine (**40**, entry 11), the bulky phenyl group shields the nearby benzylic C−N bond and reduction takes place from the less-hindered side, yielding the desired arylbutylamine **57** as the major product.

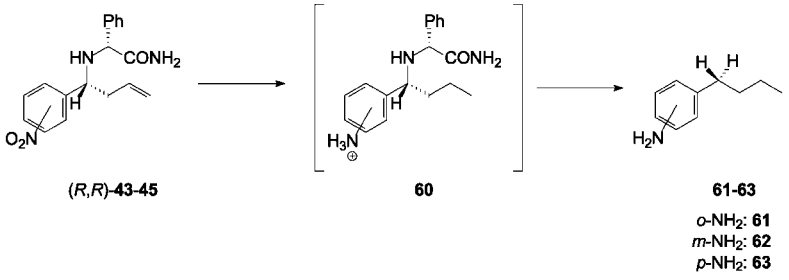
In the case of the catalytic hydrogenation of the nitro-substituted PGA allylamines (*R*,*R*)-**43**−**45**, the only products obtained were the aniline derivatives **61**−**63** (Scheme 4). The NO_2 moiety is reduced prior to debenzylation. Apparently, the electron-withdrawing effect of the cationic NH_3^+ group of intermediate **60**[21] weakens the nearby *N*-benzylic bond, resulting in the observed regioselectivity towards **61**−**63**.

Non-Reductive Removal of the Chiral Auxiliary

The bromo-, chloro-, nitro- and phenyl-substituted PGA allylamines were subjected to a non-reductive deprotection procedure as reported recently.[12a] The conversion of the PGA protected allylamines (*R*,*R*)-**34**−**42** into the nitrile **64** is based on the dehydration of the amide moiety (Scheme 5).[22] This dehydration is performed by treating the amide with Vilsmeier reagent [ClCH=N(CH$_3$)$_2^+$ Cl$^-$]



Scheme 5. Non-reductive removal of the chiral auxiliary; reagents and conditions: (*a*) Vilsmeier reagent [ClCH=N(CH$_3$)$_2^+$Cl$^-$, 1.5 equiv.], CH_2Cl_2, NEt_3 (1 equiv.), 0 °C to room temp.; (*b*) K_2CO_3 (2 equiv.), EtOH, reflux, 2 h; (*c*) $NH_2OH.HCl$, THF/H_2O, room temp., overnight; (*d*) H_2, Pt−C (5%), EtOAc, 1 h



Scheme 4. Regioselectivity of the nitro-substituted PGA allylamines under reductive conditions; reagents and conditions: isopropanol/H_2O/AcOH, H_2, Pd−C (10%)

Table 3. Conversion of the PGA-protected allylamines (*R*,*R*)-**34**−**42** into (*R*)-1-aryl-1-butylamines **74**−**81**

Entry	Allylamine	Ar	Butenylamine	Yield (%)[a]	Butylamine	Yield (%)[b]	*er* (*R*:*S*)
1	**34**	*o*-ClC_6H_4	**66**	51	**74**	91	>99:1[c]
2	**35**	*m*-ClC_6H_4	**67**	42	**75**	>99	>99:1[c]
3	**36**	*p*-ClC_6H_4	**68**	51	**76**	>99	>99:1[c]
4	**37**	*o*-BrC_6H_4	**69**	32	**77**	99	>99:1[c]
5	**38**	*m*-BrC_6H_4	**70**	40	**78**	>99	>99:1[c]
6	**39**	*p*-BrC_6H_4	**71**	48	**79**	85	>99:1[c]
7	**41**	*m*-PhC_6H_4	**72**	40	**80**	93	*nd*[d]
8	**42**	*p*-PhC_6H_4	**73**	49	**81**	95	*nd*

[a] Isolated yield after 3 steps. [b] Isolated yield. [c] For analysis by HPLC[23] the corresponding arylbutylamine was dehalogenated to 1-phenyl-1-butylamine **47** with H_2, Pd−C (10 %). [d] *nd*: Not determined.

in combination with two equivalents of triethylamine. In a general procedure, the Vilsmeier reagent is formed in situ by reaction of DMF with oxalyl chloride in CH_2Cl_2 at 0 °C. A solution of the amide in CH_2Cl_2 is then added dropwise to the Vilsmeier reagent.

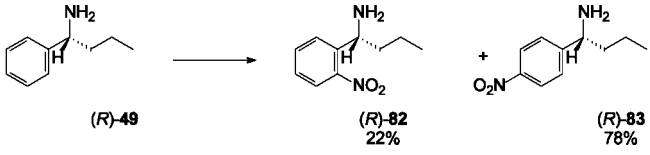
Although the stereocentre of the chiral auxiliary partially epimerises under these conditions, the deprotection proceeds with full retention of configuration at the homoallylic stereocentre — the observation that enantiomerically pure amines are obtained after deprotection makes clear that no racemisation takes place (Table 3, entries 1−6).

The conversion of nitrile **64** into the *N*-benzylidene-protected arylbutenylamine (*R*)-**65** is based on the elimination of HCN in a retro-Strecker fashion. Treating the nitrile with two equivalents of K_2CO_3 for two hours in refluxing ethanol results in full elimination of HCN.[24] Hydroxylamine hydrochloride in aqueous THF[25] is the reagent of choice for the room temperature hydrolysis of the *N*-benzylidene-protected arylbutenylamine **65**. Arylbutenylamines (*R*)-**66**−**73** were obtained in 40−60% overall yields (Table 3). Probably because of the sensitive nature of the NO_2 group, the non-reductive removal failed for all the nitro-substituted substrates.

With satisfactory results for the synthesis of the arylbutenylamines **66**−**73** in hand, we undertook further reduction of the double bond by catalytic hydrogenation with H_2 in the presence of 5% platinum on carbon,[26] which gave the corresponding saturated substituted 1-arylbutylamines (*R*)-**74**−**81** in almost quantitative yields. Samples were taken during the reaction and analysed by ^1H and ^{13}C NMR spectroscopy to follow the reaction: after one hour the uptake of one mol of H_2 was complete. In case of reduction of the bromo-substituted phenylbutylamines (*R*)-**69**−**71** longer reaction times resulted in a considerable amount of the dehalogenated products.

Synthesis of Nitro-Substituted Phenylbutylamines

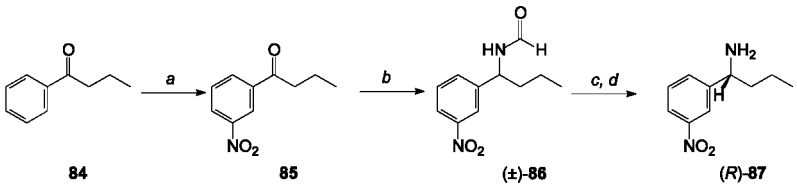
Owing to the failure of other approaches to the nitro-substituted phenylbutylamines an alternative method was examined. Nitration of enantiomerically pure phenylbutylamine (*R*)-**47** with nitric acid[27] provided a mixture containing (*R*)-1-butyl-1-(*ortho*-nitrophenyl)amine [(*R*)-**82**] and (*R*)-1-butyl-1-(*para*-nitrophenyl)amine [(*R*)-**83**] in a ratio of 22:78 (Scheme 6). This mixture of regioisomers was used without further purification.



Scheme 6. Reagents and conditions: HNO_3 (85%), −5 °C, 4 h

The *meta*-nitro-substituted phenylbutylamine (*R*)-**87** was prepared by a Leuckart reductive amination of **85**, followed by resolution of the racemic **87** (Scheme 7). The *m*-nitrobutyrophenone **85** was obtained by nitration of butyrophenone **84** with HNO_3 (85%).[28] The best yield of **85** was obtained by nitration at −5 °C. The main product was the *meta*-nitro compound, which was generally accompanied by a small and variable amount of the *ortho* isomer. From this mixture, the *meta*-nitro compound is easily separated by crystallisation and obtained pure in 55% yield.

In the first step of the Leuckart reaction, the imine is formed in situ with formamide followed by a reduction with formic acid. Formamide **86** is subsequently hydrolysed with 10% HCl and affords the racemic free amine **87** in greater than 99% yield.



Scheme 7. Reagents and conditions: (*a*) HNO_3 (85%), −5 °C, 4 h; (*b*) $HCONH_2/HCO_2H$, Δ; (*c*) HCl, Δ; (*d*) (*S*)-phencyphos **88**, 2-butanone/H_2O, Δ; analysis by HPLC[23]

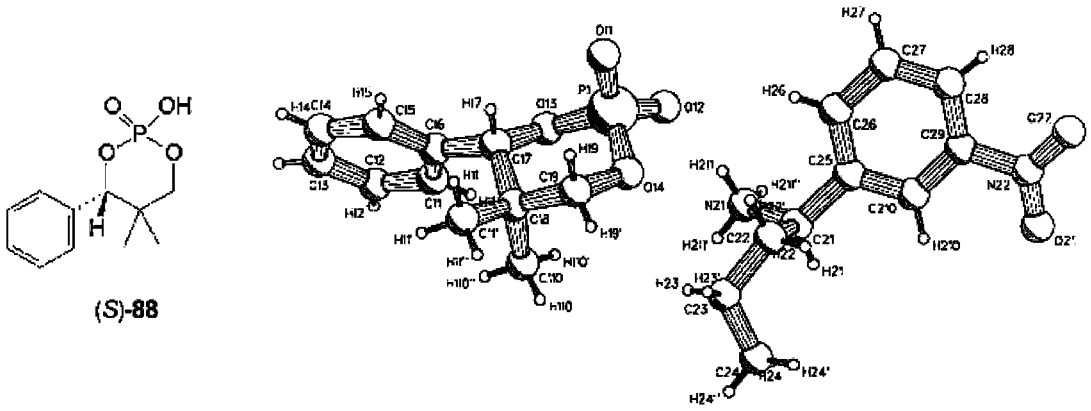


Figure 4. Structure of (*S*)-phencyphos (**88**) and crystal structures of (*S*)-**88** (left) and (*R*)-**87** (right)

Subsequently, the racemic butyl(*meta*-nitrophenyl)amine needed to be resolved. Several 1 mmol test experiments were performed [29] and it turned out that butyl(*meta*-nitrophenyl)amine (**87**) could successfully be resolved with the cyclic phosphoric acid (*S*)-**88**, known by the trivial name of (*S*)-phencyphos.[30]

X-ray crystallographic analysis unambiguously showed that after resolution with (*S*)-**88**, the chiral centre C21 of **87** had the desired (*R*)-configuration. (Figure 4).[31] After liberation, the free amine (*R*)-**87** was obtained in 24% yield and greater than 99% *ee*.

Conclusions

The results presented here further illustrate the versatility of (*R*)-phenylglycine amide (**1**) as a chiral auxiliary for the preparation of enantiomerically pure phenylbutylamines starting from substituted benzaldehydes. Allylation is readily accomplished with allylzinc bromide, prepared in situ from relatively inexpensive allyl bromide. The chiral auxiliary is conveniently removed under either reductive or non-reductive conditions. In the reduction of the bromo-substituted phenylbutenylamines, dehalogenation is a competing reaction. The sensitivity of the nitro group prevented the synthesis of the desired nitro-substituted phenylbutylamines using the reductive- or non-reductive removal of the chiral auxiliary. Alternative routes were used to synthesise these compounds.

Since also (*S*)-phenylglycine amide is readily available, the opposite configuration of the described products can be generated at will. Dutch Resolution experiments with this potential new family of substituted phenylbutylamines, as well as the family based on the unsaturated primary homoallylamines, are currently under investigation.

Experimental Section

General Information: Reagents were purchased from Aldrich Chemical Company and were used without further purification. (*R*)-Phenylglycine amide was provided by DSM (Geleen, The Netherlands). THF was freshly distilled from benzophenone/sodium. Zinc wool was cut prior to use or zinc granules (−30 +100 mesh) were used. Optical rotations were measured at ambient temperatures using a Perkin−Elmer 241 polarimeter. Melting points were measured on a Büchi B-545 or a Mettler FP1 equipped with a Mettler FP-21 microscope, and were uncorrected. ^{1}H NMR spectra were recorded on either a Varian VXR-300 spectrometer (300 MHz) or a Varian Gemini Spectrometer (200 MHz). ^{13}C NMR spectra were recorded on a Varian Gemini 200 (50 MHz). Chemical shifts are denoted in parts per million (δ) and are referenced to the residual protonated solvent. The ^{1}H and ^{13}C NMR spectra of compounds **2**, **24** and **47** were as previously reported.[12a]

Typical Procedure for the Synthesis of (*R*)-PGA-aldimines 2−23: The substituted benzaldehyde (200 mmol) was added to a suspension of (*R*)-phenylglycine amide (200 mmol, 30.0 g) in CH_2Cl_2 (200 mL) at ambient temperature. The reaction mixture was stirred overnight at room temperature. After removal of the CH_2Cl_2, the residual solid was washed with acetone/hexane (1:20) or was recrystallised once from acetone/hexane (1:20). In all cases only the more stable all-*E*-isomer was obtained, as judged from the presence of only one vinyl proton in the ^{1}H NMR spectrum.

(2*R*)-2-{[(*E*)-(2-Methylphenyl)methylidene]amino}-2-phenylacetamide (3): Colourless needles, >99% yield. M.p. 168.0−168.4 °C. ^{1}H NMR (200 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 2.53 (s, 3 H), 4.99 (s, 1 H), 5.91 (br. s, 1 H), 7.01 (br. s, 1 H), 7.19−7.53 (m, 8 H), 7.95 (dd, *J* = 8.0, *J* = 1.7 Hz, 1 H), 8.61 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 17.9 (q), 76.4 (d), 125.0 (d), 126.3 (d), 126.7 (d), 127.2 (d), 129.7 (d), 129.8 (d), 132.4 (s), 137.0 (s), 139.4 (s), 160.3 (d), 171.6 (s) ppm. $C_{16}H_{16}N_2O$ (252.3): calcd. C 76.16, H 6.39, N 11.10; found C 75.78, H 6.37, N 11.09. MS (CI): *m*/*z* = 253 [M + H$^+$].

(2*R*)-2-{[(*E*)-(3-Methylphenyl)methylidene]amino}-2-phenylacetamide (4): Pale yellow needles, 97% yield. M.p. 118.0−118.9 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 4.98 (s, 1 H), 5.67 (br. s, 1 H), 7.05 (br. s, 1 H), 7.26−7.64 (m, 9 H), 8.21 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.9 (q), 74.5 (s), 123.5 (s), 124.7 (d), 125.5 (d), 126.1 (d), 126.2 (d), 126.3 (d), 129.9 (d), 132.9 (s), 136.0 (s), 136.7 (s), 161.0 (d), 171.5 (s) ppm. $C_{16}H_{16}N_2O$ (252.3): calcd. C 75.16, H 6.39, N 11.10; found C 75.09, H 6.30, N 11.11. MS (CI): *m*/*z* = 253 [M + H$^+$].

(2*R*)-2-{[(*E*)-(4-Methylphenyl)methylidene]amino}-2-phenylacetamide (5): Colourless prisms, >99% yield. M.p. 153.9 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 4.96 (s, 1 H), 5.68 (br. s, 1

H), 7.05 (br. s, 1 H), 7.22−7.51 (m, 8 H), 7.69 (d, J = 7.6 Hz, 2 H), 8.27 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.1 (q), 75.4 (d), 125.8 (d), 126.4 (d), 127.0 (d), 127.2 (d), 128.0 (d), 131.4 (s), 137.9 (s), 140.5 (s), 161.6 (d), 173.0 (s) ppm. $C_{16}H_{16}N_2O$ (252.3): calcd. C 75.16, H 6.39, N 11.10; found C 76.06, H 6.41, N 11.09. MS (CI): m/z = 253 [M + H$^+$].

(2*R*)-2-{[(*E*)-(2-Methoxyphenyl)methylidene]amino}-2-phenylacetamide (6): Colourless plates, 93% yield. M.p. 174.3−175.2 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.85 (s, 1 H), 4.98 (s, 1 H), 5.93 (br. s, 1 H), 6.89−7.04 (m, 3 H), 7.26−7.52 (m, 6 H), 8.07 (dd, J = 7.6, J = 1.7 Hz, 1 H), 8.77 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 54.0 (q), 75.9 (d), 109.7 (d), 119.2 (d), 122.4 (s), 125.7 (d), 125.8 (d), 126.3 (d), 127.1 (d), 131.3 (d), 138.1 (s), 157.7 (s), 157.8 (d), 172.9 (s) ppm. $C_{16}H_{16}N_2O_2$ (268.3): calcd. C 71.62, H 6.01, N 10.44; found C 71.54, H 5.97, N 10.47. MS (CI): m/z = 269 [M + H$^+$].

(2*R*)-2-{[(*E*)-(3-Methoxyphenyl)methylidene]amino}-2-phenylacetamide (7): Colourless needles, 81% yield. M.p. 131.9−132.4 °C. ^{1}H NMR (200 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 3.64 (s, 3 H), 4.74 (s, 1 H), 6.07 (br. s, 1 H), 6.78−6.82 (m, 2 H), 6.88 (br. s, 1 H), 7.04−7.27 (m, 6 H), 8.07 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 55.4 (q), 76.9 (d), 112.6 (d), 117.6 (d), 127.0 (d), 127.2 (d), 128.0 (d), 128.7 (d), 129.8 (d), 136.8 (s), 139.2 (s), 159.9 (s), 163.2 (d), 174.1 (s) ppm. $C_{16}H_{16}N_2O_2$ (268.3): calcd. C 71.62, H 6.01, N 10.44; found C 71.62, H 6.09, N 10.41. MS (CI): m/z = 269 [M + H$^+$].

(2*R*)-2-{[(*E*)-(4-Methoxyphenyl)methylidene]amino}-2-phenylacetamide (8): Yellow solid, 98% yield. M.p. 92.5−93.3 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 5.81 (br. s, 1 H), 4.94 (1H), 6.95 (d, J = 8.8 Hz, 2 H), 7.06 (br. s, 1 H), 7.26−7.50 (m, 5 H), 7.75 (d, J = 8.8 Hz, 2 H), 8.23 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 53.9 (q), 75.4 (d), 112.6 (d), 125.8 (d), 126.4 (d), 126.9 (s), 127.2 (d), 128.7 (d), 138.1 (s), 160.8 (s), 161.0 (d), 173.1 (s) ppm. $C_{16}H_{16}N_2O_2$ (268.3): calcd. C 71.62, H 6.01, N 10.44; found C 71.30, H 5.95, N 10.44. MS (CI): m/z = 269 [M + H$^+$].

(2*R*)-2-{[(*E*)-(2-Fluorophenyl)methylidene]amino}-2-phenylacetamide (9): Pale yellow needles, 97% yield. M.p. 153.7−154.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 4.80 (s, 1 H), 6.28 (br. s, 1 H), 6.80 (br. s, 1 H), 6.91 (t, J = 9.3 Hz, 1 H), 7.04 (t, J = 7.3 Hz, 1 H), 7.10−7.30 (m, 6 H), 7.90 (t, J = 7.3 Hz, 1 H), 8.43 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 75.0 (d), 113.4 (d, $^2J_{C,F}$ = 22.0 Hz), 120.5 (s, $^2J_{C,F}$ = 9.8 Hz), 121.8 (d, $^3J_{C,F}$ = 3.7 Hz), 124.7 (d), 125.2 (d, $^4J_{C,F}$ = 2.4 Hz), 125.4 (d), 126.1 (d), 130.7 (d, $^3J_{C,F}$ = 9.8 Hz), 136.7 (s), 154.0 (d, $^3J_{C,F}$ = 4.9 Hz), 159.8 (s, $^1J_{C,F}$ = 253.9 Hz), 171.1 (s) ppm. $C_{15}H_{13}FN_2O$ (256.3): calcd. C 70.30, H 5.10, N 10.90; found C 70.40, H 5.04, N 10.87. MS (CI): m/z = 257 [M + H$^+$].

(2*R*)-2-{[(*E*)-(3-Fluorophenyl)methylidene]amino}-2-phenylacetamide (10): Yellow plates, 96% yield. M.p. 121.6−121.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 4.71 (s, 1 H), 6.39 (br. s, 1 H), 6.74 (br. s, 1 H), 6.91 (d, J = 8.2 Hz, 1 H), 7.02−7.28 (m, 7 H), 7.34 (d, J = 9.2 Hz, 1 H), 8.04 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 74.4 (d), 111.6 (d, $^2J_{C,F}$ = 23.2 Hz), 115.7 (d, $^2J_{C,F}$ = 20.8 Hz), 122.3 (d, $^3J_{C,F}$ = 2.4 Hz), 124.6 (d), 125.3 (d), 126.1 (d), 127.7 (d, $^3J_{C,F}$ = 7.3 Hz), 135.1 (s, $^3J_{C,F}$ = 7.3 Hz), 136.7 (s), 159.1 (d, $^4J_{C,F}$ = 2.4 Hz), 160.3 (s, $^1J_{C,F}$ = 246.6 Hz), 170.9 (s) ppm. $C_{15}H_{13}FN_2O$ (256.3): calcd. C 70.30, H 5.11, N 10.93; found C 70.00, H 5.23, N 10.81. MS (CI): m/z = 257 [M + H$^+$].

(2*R*)-2-{[(*E*)-(4-Fluorophenyl)methylidene]amino}-2-phenylacetamide (11): Colourless plates, 95% yield. M.p. 119.4−120.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.98 (s, 1 H), 5.85 (br. s, 1 H), 6.96 (br. s, 1 H), 7.09−7.50 (m, 10 H), 7.77−7.84 (m, 2 H), 8.28 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 75.4 (d), 114.2 (d), 114.4 (d, $^2J_{C,F}$ = 21.7 Hz), 125.7 (d), 126.5 (d), 127.3 (d), 128.9 (d), 129.0 (d, $^3J_{C,F}$ = 8.8 Hz), 130.2 (s), 137.6 (s), 160.4 (d), 163.3 (s, $^1J_{C,F}$ = 252.5 Hz), 172.6 (s) ppm. $C_{15}H_{13}FN_2O$ (256.3): calcd. C 70.30, H 5.10, N 10.90; found C 70.38, H 5.14, N 10.83. MS (CI): m/z = 257 [M + H$^+$].

(2*R*)-2-{[(*E*)-(2-Chlorophenyl)methylidene]amino}-2-phenylacetamide (12): Colourless needles, 97% yield. M.p. 170.3−171.0 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.05 (s, 1 H), 8.76 (s, 1 H), 8.13 (d, J = 6.1 Hz, 1 H), 7.26−7.51 (m, 8 H), 6.94 (br. s, 1 H), 6.20 (br. s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 75.8 (d), 125.5 (d), 125.7 (d), 126.6 (d), 126.9 (d), 127.3 (d), 128.6 (d), 130.9 (d), 134.5 (s), 137.9 (s), 158.7 (d), 172.4 (s) ppm. $C_{15}H_{13}ClN_2O$ (272.7): calcd. C 66.05, H 4.80, N 10.27; found C 65.92, H 4.81, N 10.31. MS (CI): m/z (%) = 273 (100.0) [M + H$^+$], 275 (34.5) [M + H$^+$].

(2*R*)-2-{[(*E*)-(3-Chlorophenyl)methylidene]amino}-2-phenylacetamide (13): Colourless plates, 98% yield. M.p. 119.4−120.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.94 (s, 1 H), 5.83 (br. s, 1 H), 6.90 (br. s, 1 H), 7.21−7.42 (m, 7 H), 7.56 (d, J = 7.3 Hz, 1 H), 7.80 (s, 1 H), 8.29 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 76.9 (d), 127.1 (d), 127.2 (d), 127.8 (d), 128.1 (d), 128.8 (d), 130.0 (d), 131.5 (d), 124.9 (s), 137.0 (s), 138.9 (s), 161.9 (d), 173.6 (s) ppm. $C_{15}H_{13}ClN_2O$ (272.7): calcd. C 66.05, H 4.80, N 10.27; found C 65.77, H 4.89, N 10.36. MS (CI): m/z = 273 (100.0) [M + H$^+$], 275 (36.1) [M + H$^+$].

(2*R*)-2-{[(*E*)-(4-Chlorophenyl)methylidene]amino}-2-phenylacetamide (14): Pale yellow plates, 95% yield. M.p. 153.4−154.2 °C. ^{1}H NMR (200 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 4.83 (s, 1 H), 6.28 (br. s, 1 H), 6.83 (br. s, 1 H), 7.14−7.36 (m, 7 H), 7.63 (d, J = 8.6 Hz, 2 H), 8.15 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 75.5 (d), 125.7 (d), 126.4 (d), 127.1 (d), 127.4 (d), 128.1 (d), 132.3 (s), 135.8 (s), 137.7 (s), 160.2 (d), 172.1 (s) ppm. $C_{15}H_{13}ClN_2O$ (272.7): calcd. C 66.05, H 4.80, N 10.27; found C 65.76, H 4.93, N 10.25. MS (CI): m/z = 273 (100.0) [M + H$^+$], 275 (34.8) [M + H$^+$].

(2*R*)-2-{[(*E*)-(2-Bromophenyl)methylidene]amino}-2-phenylacetamide (15): Pale yellow needles, 99% yield. M.p. 168.3−168.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 5.02 (s, 1 H), 5.02 (br. s, 1 H), 6.88 (br. s, 1 H), 7.21−7.36 (m, 5 H), 7.43 (d, J = 7.0 Hz, 2 H), 7.54 (d, J = 8.1 Hz, 1 H), 8.07 (dd, J = 7.7, J = 1.8 Hz, 1 H), 8.65 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 76.5 (d), 124.6 (s), 127.4 (d), 127.5 (d), 128.0 (d), 128.4 (d), 129.3 (d), 133.0 (d), 133.1 (d), 133.7 (s), 140.0 (s), 160.9 (d), 172.2 (s) ppm. $C_{15}H_{13}BrN_2O$ (317.2): calcd. C 56.80, H 4.13, N 8.83; found C 56.89, H 4.22, N 9.08. MS (CI): m/z = 317 (100.0) [M + H$^+$], 319 (98.3) [M + H$^+$].

(2*R*)-2-{[(*E*)-(3-Bromophenyl)methylidene]amino}-2-phenylacetamide (16): Colourless plates, 98% yield. M.p. 135.0−136.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.94 (s, 1 H), 5.68 (br. s, 1 H), 6.90 (br. s, 1 H), 7.20−7.33 (m, 5 H), 7.41 (d, J = 7.0 Hz, 1 H), 7.54 (d, J = 8.6 Hz, 1 H), 7.61 (d, J = 7.7 Hz, 1 H), 7.96 (s, 1 H), 8.20 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 74.5 (d), 120.5 (s), 124.7 (d), 125.1 (d), 125.6 (d), 126.3 (d), 127.3 (d), 128.3 (d), 131.9 (d), 134.8 (s), 136.4 (s), 159.3 (d), 171.4 (s) ppm. $C_{15}H_{13}BrN_2O$ (317.2): calcd. C 56.80, H 4.13, N 8.83; found C 56.65, H 4.12, N 8.82. MS (CI): m/z = 317 (100.0) [M + H$^+$], 319 (99.3) [M + H$^+$].

(2*R*)-2-{[(*E*)-(4-Bromophenyl)methylidene]amino}-2-phenylacetamide (17): Colourless prisms, 99% yield. M.p. 164.0−165.3 °C. ^{1}H

NMR (300 MHz, $CDCl_3$/[D_6]DMSO): δ = 4.68 (s, 1 H), 6.37 (br. s, 1 H), 6.69 (br. s, 1 H), 6.98−7.21 (m, 5 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 8.01 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D_6]DMSO): δ = 74.4 (d), 123.0 (s), 124.6 (d), 125.1 (d), 125.9 (d), 127.3 (d), 129.2 (d), 131.7 (s), 136.7 (s), 159.1 (d), 170.8 (s) ppm. $C_{15}H_{13}BrN_2O$ (317.2): calcd. C 56.80, H 4.13, N 8.83; found C 56.70, H 4.22, N 8.86. MS (CI): *m*/*z* = 317 (97.8) [M + H$^+$], 319 (100.0) [M + H$^+$].

(2*R*)-2-{[(*E*)-(1,1′-Biphenyl)-2-ylmethylidene]amino}-2-phenylethanamide (18): White solid, 85% yield. M.p. 152.5−152.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.55 (s, 1 H), 6.27 (br. s, 1 H), 6.81 (br. s, 1 H), 6.97−7.92 (m, 14 H), 7.95 (d, *J* = 6.2 Hz, 1 H), 8.02 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 76.6 (d), 127.8 (d), 127.2 (d), 127.3 (d), 127.3 (d), 127.8 (d), 128.1 (d), 129.3 (d), 129.9 (s), 130.4 (d), 132.4 (s), 138.5 (s), 139.0 (s), 143.0 (s), 161.9 (d), 173.5 (s) ppm. $C_{21}H_{18}N_2O$ (314.4): calcd. C 80.23, H 5.77, N 8.91; found C 80.02, H 5.71, N 8.91. MS (CI): *m*/*z* = 315 [M + H$^+$].

(2*R*)-2-{[(*E*)-(1,1′-Biphenyl)-3-ylmethylidene]amino}-2-phenylethanamide (19): White solid, 89% yield. M.p. 145.7−146.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.99 (s, 1 H), 6.78 (br. s, 1 H), 7.04 (br. s, 1 H), 7.24−7.49 (m, 11 H), 7.59 (dd, *J* = 6.6, *J* = 1.1 Hz, 2 H), 7.66 (d, *J* = 6.6 Hz, 1 H), 7.73 (d, *J* = 6.6 Hz, 1 H), 7.99 (d, *J* = 1.1 Hz, 1 H), 8.31 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 76.8 (d), 126.9 (d), 126.9 (d), 127.0 (d), 127.2 (d), 127.3 (d), 127.6 (d), 127.8 (d), 128.6 (d), 128.8 (d), 129.0 (d), 130.1 (d), 135.8 (s), 139.1 (s), 140.1 (s), 141.6 (s), 163.1 (d), 174.5 (s) ppm. $C_{21}H_{18}N_2O$ (314.4): calcd. C 80.23, H 5.77, N 8.91; found C 80.29, H 5.82, N 8.84. MS (CI): *m*/*z* = 315 [M + H$^+$].

(2*R*)-2-{[(*E*)-(1,1′-Biphenyl)-4-ylmethylidene]amino}-2-phenylethanamide (20): White solid, 95% yield. M.p. 176.5−177.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.96 (s, 1 H), 5.79 (br. s, 1 H), 7.00 (br. s, 1 H), 7.24−7.25 (m, 2 H), 7.31 (t, *J* = 7.3 Hz, 2 H), 7.36−7.46 (m, 4 H), 7.57 (d, *J* = 7.3 Hz, 2 H), 7.62 (d, *J* = 8.1 Hz, 2 H), 7.82 (d, *J* = 8.1 Hz, 2 H), 8.30 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 76.7 (d), 126.6 (d), 126.8 (d), 127.3 (d), 127.5 (d), 128.2 (d), 128.4 (d), 128.5 (d), 129.8 (s), 139.1 (s), 139.5 (s), 143.5 (s), 162.2 (d), 173.5 (s) ppm. $C_{21}H_{18}N_2O$ (314.4): calcd. C 80.23, H 5.77, N 8.91; found C 80.35, H 5.84, N 8.88. MS (CI): *m*/*z* = 315 [M + H$^+$].

(2*R*)-2-{[(*E*)-(2-Nitrophenyl)methylidene]amino}-2-phenylacetamide (21): Pale yellow needles, 97% yield. M.p. 165.0−165.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$/[D_6]DMSO): δ = 4.90 (s, 1 H), 6.43 (br. s, 1 H), 7.14−7.23 (m, 3 H), 7.31 (d, *J* = 7.0 Hz, 2 H), 7.48 (dt, *J* = 7.5 Hz, 1 H), 7.56 (dt, *J* = 7.5 Hz, 1 H), 7.83 (dd, *J* = 7.5, *J* = 0.7 Hz, 1 H), 7.92 (dd, *J* = 7.5, *J* = 0.7 Hz, 1 H), 8.55 (s, 1 H), 6.73 (br. s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D_6]DMSO): δ = 76.9 (d), 123.9 (d), 126.9 (d), 127.7 (d), 127.7 (d), 128.4 (d), 129.5 (s), 129.7 (d), 131.2 (d), 133.0 (d), 138.3 (s), 148.5 (s), 158.7 (d), 172.8 (s) ppm. $C_{15}H_{13}N_3O_3$ (283.3): calcd. C 63.60, H 4.63, N 14.83; found C 63.55, H 4.57, N 14.78. MS (CI): *m*/*z* = 284 [M + H$^+$].

(2*R*)-2-{[(*E*)-(3-Nitrophenyl)methylidene]amino}-2-phenylacetamide (22): Pale yellow plates, 98% yield. M.p. 174.0−174.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$/[D_6]DMSO): δ = 4.73 (s, 1 H), 6.50 (br. s, 1 H), 6.72 (br. s, 1 H), 6.96−7.07 (m, 3 H), 7.16−7.21 (m, 2 H), 7.35 (t, *J* = 8.0 Hz, 1 H), 7.83 (dd, *J* = 8.0, *J* = 1.8 Hz, 1 H), 7.99 (dd, *J* = 8.0, *J* = 1.1 Hz, 1 H), 8.13 (s, 1 H), 8.38 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D_6]DMSO): δ = 75.8 (d), 121.4 (d), 124.3 (d), 126.0 (d), 126.7 (d), 127.4 (d), 128.6 (d), 133.1 (d), 135.7 (s), 137.7 (s), 147.1 (s), 159.4 (d), 171.7 (s) ppm. $C_{15}H_{13}N_3O_3$ (283.3): calcd. C 63.60, H 4.63, N 14.83; found C 63.50, H 4.84, N 14.79. MS (CI): *m*/*z* = 284 [M + H$^+$].

(2*R*)-2-{[(*E*)-(4-Nitrophenyl)methylidene]amino}-2-phenylacetamide (23): Pale yellow prisms, 92% yield. M.p. 168.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.07 (s, 1 H), 5.81 (br. s, 1 H), 6.86 (br. s, 1 H), 7.30−7.46 (m, 3 H), 7.98 (d, *J* = 8.8 Hz, 2 H), 8.30 (d, *J* = 8.8 Hz, 2 H), 8.41 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 77.3 (d), 124.0 (d), 127.2 (d), 128.4 (d), 129.0 (d), 129.2(d), 138.5 (s), 140.6 (s), 149.5 (s), 161.2 (d), 173.1 (s) ppm. $C_{15}H_{13}N_3O_3$ (283.3): calcd. C 63.60, H 4.63, N 14.83; found C 63.36, H 4.62, N 14.83. MS (CI): *m*/*z* = 284 [M + H$^+$].

Typical Procedure for the Allylation of (*R*)-PGA Imines: A solution of allylzinc bromide (1.5 equiv.) was prepared by adding allyl bromide (38.5 mL, 438 mmol) to finely cut zinc wool (28.6 g, 438 mmol) in THF (250 mL). The solution of allylzinc bromide was cooled to room temperature and 292 mmol of the imine in THF (150 mL) was added at 0 °C. The reaction mixture was warmed to room temperature and was then poured into water (500 mL). Ethyl acetate (200 mL) was added and the mixture was stirred vigorously. After filtration through Celite, the organic phase was separated and the water layer was extracted with ethyl acetate (2 × 100 mL). The combined organic phase was dried over sodium sulfate and the ethyl acetate was evaporated to furnish the homoallylamine as a colourless oil, which in some cases crystallised on standing. For compounds **25** and **31**−**35**, the *dr* could be increased to >99:1 by recrystallisation from acetone/hexane (1:20).

Typical Procedure for the Allylation of (*R*)-PGA Imines 2−11 and 18−20 under Barbier Conditions: The imine (292 mmol) and zinc wool (438 mmol, 28.6 g) were added successively to a flask fitted with a cooler and charged with THF (250 mL). Allyl bromide (438 mmol, 38.5 mL, 1.5 equiv.) in 50 mL of THF was added at 0 °C to the stirred mixture. The reaction mixture was allowed to warm to room temperature. Workup was performed as described above.

(2*R*)-2-{[(1*R*)-1-(2-Methylphenyl)-3-butenyl]amino}-2-phenylethanamide (25): Colourless plates, 93% yield, 99:1 *dr*. M.p. 104.3−104.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3 H), 2.31−2.37 (m, 1 H), 3.89 (s, 1 H), 4.01 (d, *J* = 6.2 Hz, 1 H), 5.02−5.11 (m, 2 H), 5.68−5.82 (m, 1 H), 6.12 (br. s, 1 H), 7.10−7.25 (m, 10 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.0 (q), 39.3 (t), 54.2 (d), 62.0 (d), 115.3 (t), 122.5 (d), 123.9 (d), 124.5 (d), 124.8 (d), 125.6 (d), 126.4 (d), 128.1 (d), 132.5 (d), 133.7 (s), 136.9 (s), 138.3 (s), 173.5 (s) ppm. $C_{19}H_{22}N_2O{\cdot}1/2H_2O$: calcd. C 75.22, H 7.64, N 9.23; found C 75.18, H 7.59, N 9.12. MS (CI): *m*/*z* = 295 [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(3-Methylphenyl)-3-butenyl]amino}-2-phenylethanamide (26): Yellow oil, >99% yield, >99:1 *dr*. M.p. 79.0−80.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11 (br. s, 1 H), 2.30 (s, 3 H), 2.39 (d, *J* = 7.0 Hz, 2 H), 3.65 (t, *J* = 7.0 Hz, 1 H), 3.96 (s, 1 H), 5.03−5.10 (m, 2 H), 5.69−5.83 (m, 1 H), 6.96−7.06 (m + br. s, 3 H), 7.11 (br. s, 1 H), 7.16−7.29 (m, 7 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.6 (q), 42.4 (t), 61.5 (d), 64.2 (d), 117.5 (t), 123.8 (d), 127.1 (d), 127.7 (d), 127.8 (d), 128.0 (d), 128.3 (d), 128.6 (d), 134.9 (d), 137.9 (s), 139.3 (s), 142.4 (s), 175.9 (s) ppm. $C_{19}H_{22}N_2O{\cdot}1/2H_2O$: calcd. C 75.22, H 7.64, N 9.23; found C 75.52, H 7.45, N 9.35. MS (CI): *m*/*z* = 295 [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(4-Methylphenyl)-3-butenyl]amino}-2-phenylethanamide (27): Colourless oil, which crystallised on standing, 97% yield, >99:1 *dr*. M.p. 120.3−121.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04 (br. s, 1 H), 2.30 (s, 3 H), 2.38 (d, *J* = 7.0 Hz, 2 H), 3.63 (t, *J* = 7.0 Hz, 1 H), 3.95 (s, 1 H), 5.01−5.08 (m, 2 H),

5.67−5.81 (m, 1 H), 6.12 (br. s, 1 H), 7.05−7.11 (m, 5 H), 7.16−7.24 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.6 (q), 40.0 (t), 59.0 (d), 61.9 (d), 115.2 (t), 124.4 (d), 124.8 (d), 125.6 (d), 126.3 (d), 126.8 (d), 132.6 (d), 134.6 (s), 136.8 (s), 136.9 (s), 173.7 (s) ppm. $C_{19}H_{22}N_2O$ (294.4): calcd. C 77.52, H 7.53, N 9.52; found C 77.43, H 7.42, N 9.34. MS (CI): *m*/*z* = 295 [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(2-Methoxyphenyl)-3-butenyl]amino}-2-phenylethanamide (28): Pale yellow solid, 98% yield, >99:1 *dr*. M.p. 63.1−63.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (d, *J* = 7.0 Hz, 2 H), 3.62 (t, *J* = 7.0 Hz, 1 H), 3.76 (s, 3 H), 3.95 (s, 1 H), 5.00−5.07 (m, 2 H), 5.65−5.79 (m, 2 H), 5.97 (br. s, 1 H), 6.81 (d, *J* = 8.6 Hz, 2 H), 7.03 (br. s, 1 H), 7.07 (d, *J* = 8.6 Hz, 2 H), 7.14−7.26 (m, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.2 (t), 54.9 (q), 64.7 (d), 110.7 (d), 117.1 (t), 120.5 (d), 127.2 (d), 127.9 (d), 128.4 (d), 128.6 (d), 129.5 (s), 135.7 (d), 139.4 (s), 157.3 (s), 176.3 (s) ppm. $C_{19}H_{22}N_2O_2 \cdot 1/2H_2O$: calcd. C 71.45, H 7.26, N 8.77; found C 71.43, H 6.88, N 8.76. MS (CI): *m*/*z* = 311 [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(3-Methoxyphenyl)-3-butenyl]amino}-2-phenylethanamide (29): Pale yellow solid, 99% yield, >99:1 *dr*. M.p. 96.6−97.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08 (br. s, 1 H), 2.38 (d, *J* = 7.0 Hz, 1 H), 3.65 (t, *J* = 7.0 Hz, 1 H), 3.73 (s, 3 H), 3.97 (s, 1 H), 5.02−5.09 (m, 2 H), 5.68−5.81 (m, 1 H), 5.98 (br. s, 1 H), 6.70−6.77 (m, 3 H), 6.99 (br. s, 1 H), 7.17−7.26 (m, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.2 (t), 54.8 (q), 61.3 (d), 64.0(d), 112.4(d), 112.5 (d), 117.4 (t), 119.1 (d), 127.0 (d), 127.7 (d), 128.4 (d), 129.3 (d), 134.7 (d), 139.2 (s), 144.2 (s), 159.5 (s), 175.7 (s) ppm. $C_{19}H_{22}N_2O_2 \cdot 1/2H_2O$: calcd. C 71.45, H 7.26, N 8.77; found C 71.45, H 6.90, N 8.79. MS (CI): *m*/*z* = 311 [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(4-Methoxyphenyl)-3-butenyl]amino}-2-phenylethanamide (30): Pale yellow solid, 99% yield, >99:1 *dr*. M.p. 92.2−92.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (d, *J* = 7.0 Hz, 2 H), 3.62 (t, *J* = 7.0 Hz, 1 H), 3.76 (s, 3 H), 3.95 (s, 1 H), 5.00−5.07 (m, 2 H), 5.65−5.79 (m, 2 H), 5.97 (br. s, 1 H), 6.81 (d, *J* = 8.6 Hz, 2 H), 7.03 (br. s, 1 H), 7.07 (d, *J* = 8.6 Hz, 2 H), 7.14−7.26 (m, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.1 (t), 55.0 (q), 60.9 (d), 63.9 (d), 113.7 (t), 117.4 (t), 127.1 (d), 127.8 (d), 128.0 (d), 128.6 (d), 134.0 (s), 134.7 (d), 138.9 (s), 158.6 (s), 176.0 (s) ppm. $C_{19}H_{22}N_2O_2$ (310.4): calcd. C 73.52, H 7.10, N 9.00; found C 73.70, H 6.95, N 9.04. MS (CI): *m*/*z* = 311 [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(2-Fluorophenyl)-3-butenyl]amino}-2-phenylethanamide (31): Pale yellow oil, which crystallises on standing, >99% yield, 98:2 *dr*. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (br. s, 1 H), 2.46 (dt, *J* = 7.0 Hz, 2 H), 3.94 (s, 1 H), 3.99 (t, *J* = 7.0 Hz, 1 H), 5.02−5.09 (m, 2 H), 5.69−5.83 (m, 1 H), 6.95−7.08 (m, 3 H), 7.13−7.28 (m, 8 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.9 (t), 56.3 (d), 64.6 (d), 115.6 (d, $^2J_{C,F}$ = 22.0 Hz), 117.8 (t), 124.1 (d, $^4J_{C,F}$ = 3.7 Hz), 127.02 (d), 127.9 (d), 128.3 (d, $^3J_{C,F}$ = 4.9 Hz), 128.6 (d), 128.8 (d), 129.2 (s, $^3J_{C,F}$ = 12.2 Hz), 134.6 (d), 139.1 (s), 160.91 (s, $^1J_{C,F}$ = 245.4 Hz), 175.6 (s) ppm. $C_{18}H_{19}FN_2 \cdot 1/2H_2O$: calcd. C 70.34, H 6.56, N 9.11; found C 70.63, H 6.17, N 9.39. MS (CI): *m*/*z* = 299 [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(3-Fluorophenyl)-3-butenyl]amino}-2-phenylethanamide (32): Yellow oil, which crystallises on standing, 97% yield, 98:2 *dr*). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (br. s, 1 H), 2.37 (d, *J* = 7.0 Hz, 2 H), 3.68 (t, *J* = 7.0 Hz, 1 H), 3.92 (s, 1 H), 5.01−5.07 (m, 2 H), 5.63−5.76 (m, 1 H), 6.71 (br. s, 1 H), 6.87−6.95 (m, 4 H), 7.15−7.26 (m, 6 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.3 (t), 61.1 (d), 64.3 (d), 113.7 (d, $^2J_{C,F}$ = 20.8 Hz), 114.2 (d, $^2J_{C,F}$ = 22.0 Hz), 118.0 (t), 122.7 (d, $^3J_{C,F}$ = 2.4 Hz), 127.1 (d), 128.1 (d), 128.8 (d), 130.0 (d, $^3J_{C,F}$ = 8.6 Hz), 134.4 (d), 139.0 (s), 145.5 (s, $^3J_{C,F}$ = 7.3 Hz), 163.0 (s, $^1J_{C,F}$ = 246.6 Hz), 175.6 (s) ppm. $C_{18}H_{19}FN_2$ (282.4): calcd. C 72.46, H 6.42, N 9.39; found C 72.19, H 6.30, N 9.51. MS (CI): *m*/*z* = 299 [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(4-Fluorophenyl)-3-butenyl]amino}-2-phenylethanamide (33): Yellow oil, which crystallises on standing, 94% yield, 99:1 *dr*). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (br. s, 2 H), 2.35 (t, *J* = 7.0 Hz, 2 H), 3.65 (t, *J* = 7.0 Hz, 1 H), 3.88 (s, 1 H), 4.99−5.05 (m, 2 H), 5.58−5.69 (m, 1 H), 6.44 (br. s, 1 H), 6.96 (t, *J* = 8.7 Hz, 2 H), 7.08−7.12 (m, 4 H), 7.18−7.22 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.3 (t), 61.3 (d), 64.3 (d), 115.5 (d, $^2J_{C,F}$ = 13.8 Hz), 118.2 (t), 127.2 (d), 128.3 (d), 128.7 (d, $^3J_{C,F}$ = 5.7 Hz), 134.3 (d), 138.6 (s), 137.7 (s), 162.1 (s, $^1J_{C,F}$ = 162.7 Hz), 175.8 (s) ppm. MS (CI): *m*/*z* = 299 [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(2-Chlorophenyl)-3-butenyl]amino}-2-phenylethanamide (34): Pale yellow oil, which crystallises on standing, 98% yield, 97:3 *dr*. M.p. 110.4−111.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32−2.52 (m + br. s, 3 H), 3.89 (s, 1 H), 4.25 (t, *J* = 6.8 Hz, 1 H), 4.99−5.10 (m, 2 H), 5.68−5.82 (m, 1 H), 6.55 (br. s, 1 H), 7.04 (br. s, 1 H), 7.12−7.30 (m, 9 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.7 (t), 58.2 (d), 64.5 (d), 118.1 (t), 127.0 (d), 127.2 (d), 127.7 (d), 128.1 (d), 128.4 (d), 128.8 (d), 129.9 (d), 133.8 (s), 134.4 (d), 138.9 (s), 139.4 (s), 175.6 (s) ppm. $C_{18}H_{19}ClN_2O$ (314.8): calcd. C 68.67, H 6.08, N 8.90; found C 68.51, H 6.29, N 8.75. MS (CI): *m*/*z* = 315 [M + H$^+$]. MS (CI): *m*/*z* = 315 (100.0) [M + H$^+$], 317 (35.8) [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(3-Chlorophenyl)-3-butenyl]amino}-2-phenylethanamide (35): (white plates, 83% yield, 98:2 *dr*. M.p. 39.2−40.3 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.15 (br. s, 1 H), 2.33 (d, *J* = 6.8 Hz, 2 H), 3.63 (t, *J* = 6.8 Hz, 1 H), 3.88 (s, 1 H), 4.97−5.05 (m, 2 H), 5.55−5.75 (m, 1 H), 6.54 (br. s, 1 H), 6.82 (br. s, 1 H), 6.97−7.24 (m, 8 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.4 (t), 61.3 (d), 64.3 (d), 118.2 (t), 125.2 (d), 127.1 (d), 127.6 (d), 128.2 (d), 128.8 (d), 129.8 (d), 134.2 (d), 134.4 (s), 138.9 (s), 144.8 (s), 175.5 (s) ppm. $C_{18}H_{19}ClN_2O$ (314.8): calcd. C 68.67, H 6.08, N 8.90; found C 68.32, H 6.16, N 8.76. MS (CI): *m*/*z* = 315 (100.0) [M + H$^+$], 317 (35.0) [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(4-Chlorophenyl)-3-butenyl]amino}-2-phenylethanamide (36): Yellow solid, 98% yield, >99:1 *dr*. M.p. 111.3−112.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33−2.47 (m + br. s, 3 H), 3.71 (t, *J* = 7.0 Hz, 1 H), 3.97 (s, 1 H), 5.58−5.72 (m, 2 H), 5.99 (br. s, 1 H), 6.80 (br. s, 1 H), 7.06−7.13 (m, 4 H), 7.21−7.24 (m, 5 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.2 (t), 61.3 (d), 64.3 (d), 118.4 (t), 127.2 (d), 128.4 (d), 128.5 (d), 128.8 (d), 129.0 (d), 133.3 (s), 124.1 (d), 138.5 (s), 175.5 (s), 140.5 (s) ppm. $C_{18}H_{19}ClN_2O$ (314.8): calcd. C 68.67, H 6.08, N 8.90; found C 68.24, H 5.88, N 8.63. MS (CI): *m*/*z* = 315 (100.0) [M + H$^+$], 317 (35.7) [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(2-Bromophenyl)-3-butenyl]amino}-2-phenylethanamide (37): Pale yellow oil, 98% yield, >99:1 *dr*). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24−2.50 (m + br. s, 3 H), 3.88 (s, 1 H), 4.24 (dd, *J* = 8.1, *J* = 5.1 Hz, 1 H), 5.05−5.15 (m, 2 H), 5.71−5.83 (m, 1 H), 6.45 (br. s, 1 H), 6.99 (br. s, 1 H), 7.06 (dt, *J* = 7.5, *J* = 1.8 Hz, 1 H), 7.16−7.24 (m, 7 H), 7.49 (d, *J* = 7.7 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 38.6 (t), 57.7 (d), 62.0 (d), 115.7 (d), 121.9 (d), 124.8 (d), 125.2 (t), 125.5 (d), 125.6 (d), 126.3 (d), 126.3 (d), 130.7 (d), 132.1 (d), 136.8 (s), 138.9 (s), 173.1 (s) ppm. $C_{18}H_{19}BrN_2O$ (359.3): calcd. C 60.18, H 5.33, N 7.80; found C 60.02, H 5.06, N 8.07. MS (CI): *m*/*z* = 359 (39.8) [M + H$^+$], 361 (39.4) [M + H$^+$].

(2*R*)-2-{[(1*R*)-1-(3-Bromophenyl)-3-butenyl]amino}-2-phenylethanamide (38): Pale yellow oil, 99% yield, >99:1 *dr*). ^{1}H NMR

(300 MHz, $CDCl_3$): δ = 2.27 (br. s, 1 H), 2.41 (dt, *J* = 7.0 Hz, 2 H), 3.66 (t, *J* = 7.0 Hz, 1 H), 3.94 (s, 1 H), 5.02−5.13 (m, 2 H), 5.61−5.74 (m, 1 H), 6.26 (br. s, 1 H), 6.84 (br. s, 1 H), 7.08−7.30 (m, 8 H), 7.33 (dd, *J* = 7.7, *J* = 1.1 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.3 (t), 61.4 (d), 64.3 (d), 118.2 (t), 122.7 (s), 124.4 (d), 125.8 (d), 127.2 (d), 128.2 (d), 128.8 (d), 130.1 (d), 130.5 (d), 134.1 (d), 138.7 (s), 144.9 (s), 175.6 (s) ppm. $C_{18}H_{19}BrN_2O$ (359.3): calcd. C 60.18, H 5.33, N 7.80; found C 59.84, H 5.21, N 7.67. MS (CI): *m*/*z* = 359 (100.0) [M + H^+], 361 (99.3) [M + H^+].

(2*R*)-2-{[(1*R*)-1-(4-Bromophenyl)-3-butenyl]amino}-2-phenylethanamide (39): White solid, 95% yield, >99:1 *dr*. M.p. 115.6−116.5 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (br. s, 1 H), 2.31−2.48 (m, 2 H), 3.68 (t, *J* = 6.8 Hz, 1 H), 3.93 (s, 1 H), 5.01−5.07 (m, 2 H), 5.60−5.73 (m, 1 H), 6.30 (br. s, 1 H), 6.84 (br. s, 1 H), 7.03 (d, *J* = 8.2 Hz, 2 H), 7.11−7.14 (m, 2 H), 7.22−7.24 (m, 3 H), 7.39 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.3 (t), 61.3 (d), 64.3 (d), 118.3 (t), 121.2 (s), 127.2 (d), 128.3 (d), 128.85 (d), 128.93 (d), 131.7 (d), 134.2 (d), 138.7 (s), 141.3 (s), 175.6 (s) ppm. $C_{18}H_{19}BrN_2O$ (359.3): calcd. C 60.18, H 5.33, N 7.80; found C 59.75, H 5.37, N 7.72. MS (CI): *m*/*z* = 359 (100.0) [M + H^+], 361 (99.8) [M + H^+].

(2*R*)-2-{[(1*R*)-1-(1,1′-Biphenyl)-2-yl-3-butenyl]amino}-2-phenylethanamide (40): Pale yellow solid, 89% yield, >99:1 *dr*. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.16 (br. s, 1 H), 2.28−2.41 (m, 2 H), 3.99 (dt, *J* = 5.4, *J* = 3.0 Hz, 1 H), 4.01 (s, 1 H), 4.99−5.04 (m, 2 H), 5.64−5.73 (m, 1 H), 5.78 (br. s, 1 H), 7.04 (br. s, 1 H), 7.23−7.25 (m, 5 H), 7.29−7.41 (m, 9 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.9 (t), 64.6 (d), 125.3 (d), 126.7 (d), 127.0 (d), 127.2 (d), 127.8 (t), 128.0 (d), 128.1 (d), 128.7 (d), 129.2 (d), 130.1 (d), 135.0 (d), 139.4 (s), 140.2 (s), 140.7 (s), 142.5 (s), 175.3 (s) ppm. MS (CI): *m*/*z* = 357 [M + H^+].

(2*R*)-2-{[(1*R*)-1-(1,1′-Biphenyl)-3-yl-3-butenyl]amino}-2-phenylethanamide (41): Yellow oil, 85% yield, >99:1 *dr*. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.37 (br. s, 1 H), 2.50 (t, *J* = 6.6 Hz, 2 H), 3.83 (t, *J* = 6.6 Hz, 1 H), 4.08 (s, 1 H), 5.03 −5.16 (m, 2 H), 5.74−5.87 (m, 1 H), 7.19−7.24 (m, 6 H), 7.33−7.45 (m, 5 H), 7.51 (d, *J* = 7.7 Hz, 1 H), 7.57 (dd, *J* = 7.7, *J* = 1.1 Hz, 2 H), 7.00 (br. s, 1 H), 7.08 (br. s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.3 (t), 61.6 (d), 64.2 (d), 117.7 (t), 125.7 (d), 125.8 (d), 126.0 (d), 126.9 (d), 127.1 (d), 127.2 (d), 127.9 (d), 128.5 (d), 128.6 (d), 128.8 (d), 134.6 (d), 139.1 (s), 140.6 (s), 141.2 (s), 143.0 (s), 175.9 (s) ppm. MS (CI): *m*/*z* = 357 [M + H^+].

(2*R*)-2-{[(1*R*)-1-(1,1′-Biphenyl)-4-yl-3-butenyl]amino}-2-phenylethanamide (42): Pale green oil, 99% yield, >99:1 *dr*. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.27 (br. s, 1 H), 2.45 (t, *J* = 6.6 Hz, 2 H), 3.75 (t, *J* = 6.6 Hz, 1 H), 4.02 (s, 1 H), 5.04−5.84 (m, 2 H), 5.73 −5.84 (m, 1 H), 6.75 (br. s, 1 H), 7.04 (br. s, 1 H), 7.22−7.33 (m, 8 H), 7.40 (t, *J* = 7.3 Hz, 2 H), 7.52 (d, *J* = 8.1 Hz, 2 H), 7.56 (d, *J* = 7.3 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.4 (t), 61.2 (d), 64.5 (d), 117.7 (t), 126.8 (d), 127.1 (d), 127.4 (d), 127.9 (d), 128.6 (d), 134.7 (d), 139.2 (s), 140.1 (s), 140.5 (s), 141.5 (s), 175.7 (s) ppm. MS (CI): *m*/*z* = 357 [M + H^+].

(2*R*)-2-{[(1*R*)-1-(2-Nitrophenyl)-3-butenyl]amino}-2-phenylethanamide (43): Orange oil, >99% yield, >99:1 *dr*. ^1H NMR (300 MHz, $CDCl_3$/[D_6]DMSO): δ = 2.49−2.57 (m, 1 H), 2.35−2.45 (m, 1 H), 2.96 (br. s, 1 H), 3.93 (s, 1 H), 4.35 (dd, *J* = 5.1, *J* = 2.9 Hz, 1 H), 5.06−5.12 (m, 2 H), 5.75−5.89 (m, 1 H), 7.00 (br. s, 1 H), 7.19−7.28 (m + br. s, 5 H), 7.39−7.44 (m, 2 H), 7.60 (t, *J* = 7.3 Hz, 1 H), 7.78 (d, *J* = 8.1 Hz, 1 H), 7.86 (d, *J* = 7.3 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$/[D_6]DMSO): δ = 42.0 (t), 54.9 (d), 63.1 (d), 117.8 (t), 123.7 (d), 126.9 (d), 127.2 (d), 128.1 (d), 128.8 (d), 133.0 (d), 134.7 (d), 137.9 (s), 140.0 (s), 149.9 (s), 173.8 (s) ppm. $C_{18}H_{19}N_3O_3$ (325.4): calcd. C 66.45, H 5.89, N 12.91; found C 66.06, H 5.97, N 12.72. MS (CI): *m*/*z* = 326 [M + H^+].

(2*R*)-2-{[(1*R*)-1-(3-Nitrophenyl)-3-butenyl]amino}-2-phenylethanamide (44): Orange oil, which crystallises on standing, 96% yield, >99:1 *dr*. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.46−2.62 (m + br. s, 3 H), 3.92 (t, *J* = 6.8 Hz, 1 H), 4.09 (s, 1 H), 5.06−5.13 (m, 2 H), 5.61−5.82 (m, 1 H), 6.02 (br. s, 1 H), 6.57 (br. s, 1 H), 7.15−7.27 (m, 5 H), 7.42−7.57 (m, 2 H), 8.06−8.11 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.3 (t), 61.4 (d), 64.7(d), 119.0 (t), 122.1 (d), 122.5 (d), 127.3 (d), 128.5 (d), 129.0 (d), 129.5 (d), 133.4 (d), 133.6 (d), 138.3 (s), 144.8 (s), 148.4 (s), 175.0 (s) ppm. $C_{18}H_{19}N_3O_3$ (325.4): calcd. C 66.45, H 5.89, N 12.91; found C 66.21, H 5.80, N 12.82. MS (CI): *m*/*z* = 326 [M + H^+].

(2*R*)-2-{[(1*R*)-1-(4-Nitrophenyl)-3-butenyl]amino}-2-phenylethanamide (45): Orange oil, 93% yield, 99:1 *dr*. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.38−2.47 (m, 1 H), 2.54−2.63 (m, 1 H), 2.75 (br. s, 1 H), 3.93 (t, *J* = 6.2 Hz, 1 H), 4.07 (s, 1 H), 4.97−5.02 (m, 2 H), 5.49−5.63 (m, 1 H), 6.58 (br. s, 1 H), 6.77 (br. s, 1 H), 7.07−7.18 (m, 5 H), 7.29 (d, *J* = 8.6 Hz, 2 H), 8.03 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.8 (t), 61.7 (d), 64.3 (d), 119.1 (t), 123.7 (d), 124.3 (d), 127.4 (d), 128.8 (d), 129.1 (d), 133.0 (d), 137.4 (s), 147.3 (s), 149.1 (s), 176.3 (s) ppm. $C_{18}H_{19}N_3O_3$ (325.4): calcd. C 66.45, H 5.89, N 12.91; found C 66.32, H 5.90, N 12.88. MS (CI): *m*/*z* = 326 [M + H^+].

Typical Procedure for the Catalytic Hydrogenation of (*R*)-PGA Homoallylamines 24−33 and 40: The PGA allylamine (15.0 mmol) was dissolved in isopropyl alcohol (75 mL). Water (75 mL), acetic acid (100 mL), and Pd−C (10%) (0.6 gram, cat) were added successively. After two vacuum/H_2 cycles to remove air from the reaction flask, the stirred mixture of the substrate was hydrogenated at ambient pressure of H_2 and room temperature for 5 days. After filtration, the isopropyl alcohol was evaporated off under reduced pressure. The residue was diluted with water (50 mL) and while acidic, the reaction mixture was washed once with diethyl ether to remove any by-products. The aqueous phase was brought to pH 10 with 10% NaOH and was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phase was washed with brine, dried over sodium sulfate and filtered. After evaporation of the CH_2Cl_2, pentane was added to the residue. Filtration through a glass filter yielded crystalline phenyl acetamide. Evaporation of the pentane yielded the primary substituted (*R*)-phenylbutylamine as an oil.

(1*R*)-1-Butyl-1-(2-methylphenyl)amine (48): Yellow oil, 95% yield. $[\alpha]_D^{25}$ = +32.8 (*c* = 2.08, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3 H), 1.20−1.44 (m, 2 H), 1.52 (br. s, 2 H), 1.46−1.63 (m, 2 H), 2.31 (s, 3 H), 4.14 (t, *J* = 6.6 Hz, 1 H), 7.09 (d, *J* = 4.4 Hz, 2 H), 7.14−7.22 (m, 1 H), 7.37 (d, *J* = 7.3 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (q), 19.6 (t), 21.2 (q), 41.6 (t), 55.7 (d), 123.1 (d), 126.8 (d), 127.3 (d), 128.0 (d), 137.7 (s), 146.5 (s) ppm. $C_{11}H_{17}N$ (163.3): calcd. C 80.93, H 10.50, N 8.58; found C 80.69, H 10.62, N 8.46. MS (CI): *m*/*z* = 164 [M + H^+].

(1*R*)-1-Butyl-1-(3-methylphenyl)amine (49): Yellow oil, 92% yield. $[\alpha]_D^{25}$ = +13.59 (*c* = 1.13, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.3 Hz, 3 H), 1.18−1.38 (m, 2 H), 1.44 (br. s, 2 H), 1.56−1.64 (m, 2 H), 2.31 (s, 3 H), 3.80 (t, *J* = 7.0 Hz, 1 H), 7.00 (d, *J* = 7.5 Hz, 1 H), 7.05 (d, *J* = 7.5 Hz, 1 H), 7.09 (s, 1 H), 7.17 (t, *J* = 7.5 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (q), 19.5 (t), 21.2 (q), 55.7 (t), 123.1 (d), 126.7 (d), 127.3 (d), 128.0 (d), 137.6 (s), 146.6 (s) ppm. MS (CI): *m*/*z* = 164 [M + H^+].

(1*R*)-1-Butyl-1-(4-methylphenyl)amine (50): Yellow oil, which crystallised on standing, 91% yield. M.p. 55.0−56.5 °C. $[\alpha]_D^{25}$ = +19.34 (*c* = 2.23, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.3 Hz, 3 H), 1.13−1.34 (m, 2 H), 1.75−1.50 (m, 2 H), 1.70 (br. s, 2 H), 2.26 (s, 3 H), 3.77 (t, *J* = 7.0 Hz, 1 H), 7.06 (d, *J* = 8.1 Hz, 2 H), 7.13 (d, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.6 (q), 19.3 (t), 20.5 (q), 41.4 (t), 55.2 (d), 125.7 (d), 128.6 (d), 135.7 (s), 143.2 (s) ppm. MS (CI): *m*/*z* = 164 [M + H^+].

(1*R*)-1-Butyl-1-(2-methoxyphenyl)amine (51): Colourless oil, which crystallises on standing, 87% yield. M.p. 56.8−57.6 °C. $[\alpha]_D^{25}$ = +4.49 (*c* = 3.45, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.3 Hz, 3 H), 1.15−1.39 (m, 2 H), 1.53−1.90 (m + br. s, 3 H), 3.76 (s, 3 H), 4.10 (t, *J* = 7.0 Hz, 1 H), 6.80 (d, *J* = 8.1 Hz, 1 H), 6.87 (t, *J* = 7.3 Hz, 1 H), 7.15 (dt, *J* = 8.1, *J* = 1.8 Hz, 1 H), 7.21 (dd, *J* = 7.3, *J* = 1.8 Hz, 1 H), ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (q), 19.9 (t), 39.7 (t), 50.5 (d), 55.1 (q), 110.4 (d), 120.5 (d), 126.6 (d), 127.4 (d), 134.7 (s), 156.8 (s) ppm. $C_{11}H_{17}NO$ (179.3): calcd. C 73.70, H 9.56, N 7.81; found C 73.40, H 9.96, N 7.54. MS (CI): *m*/*z* = 180 [M + H^+].

(1*R*)-1-Butyl-1-(3-methoxyphenyl)amine (52): Pale yellow oil, 89% yield. $[\alpha]_D^{25}$ = +16.4 (*c* = 3.68, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 7.3 Hz, 3 H), 1.12−1.29 (m, 2 H), 1.39 (br. s, 2 H), 1.49−1.56 (m, 2 H), 3.68 (s, 3 H), 3.74 (t, *J* = 7.0 Hz, 1 H), 6.66 (dd, *J* = 8.1, *J* = 1.8 Hz, 1 H), 6.77−6.79 (m, 2 H), 7.12 (t, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7 (q), 19.4 (t), 41.5 (t), 54.7 (d), 55.7 (q), 111.6 (d), 111.7 (d), 118.3 (d), 129.0 (d), 148.3 (s), 159.4 (s) ppm. $C_{11}H_{17}NO$ (179.3): calcd. C 73.70, H 9.56, N 7.81; found C 73.59, H 9.54, N 7.81. MS (CI): *m*/*z* = 180 [M + H^+].

(1*R*)-1-Butyl-1-(4-methoxyphenyl)amine (53): Yellow oil, 89% yield. $[\alpha]_D^{25}$ = +12.57 (*c* = 7.39, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.1 Hz, 3 H), 1.14−1.36 (m, 2 H), 1.44 (br. s, 2 H), 1.50−1.69 (m, 2 H), 3.76 (s, 3 H), 3.82 (t, *J* = 6.8 Hz, 1 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 7.20 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9 (q), 19.6 (t), 41.8 (t), 55.0 (q), 55.2 (d), 113.5 (d), 127.1 (d), 138.8 (s), 158.3 (s) ppm. $C_{11}H_{17}NO$ (179.3): calcd. C 73.70, H 9.56, N 7.81; found C 73.58, H 9.47, N 7.67. MS (CI): *m*/*z* = 180 [M + H^+].

(1*R*)-1-Butyl-1-(2-fluorophenyl)amine (54): Pale yellow oil, 58% yield. $[\alpha]_D^{27}$ = +9.39 (*c* = 3.21, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.3 Hz, 3 H), 1.11−1.36 (m, 2 H), 1.45 (br. s, 2 H), 1.56−1.63 (m, 2 H), 4.10 (t, *J* = 7.0 Hz, 1 H), 6.87−6.93 (m, 1 H), 7.04 (dt, *J* = 7.32, *J* = 1.1 Hz, 1 H), 6.98−7.13 (m, 1 H), 7.27 (dt, *J* = 7.3, *J* = 1.8 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7 (q), 19.5 (t), 40.4 (t), 49.5 (d), 115.1 (d, $^2J_{C,F}$ = 23.2 Hz), 123.9 (d, $^4J_{C,F}$ = 3.7 Hz), 127.3 (d, $^3J_{C,F}$ = 4.9 Hz), 127.8 (d, $^3J_{C,F}$ = 8.5 Hz), 133.4 (s, $^2J_{C,F}$ = 14.7 Hz), 160.3 (s, $^1J_{C,F}$ = 294.2 Hz) ppm. MS (CI): *m*/*z* = 168 [M + H^+].

(1*R*)-1-Butyl-1-(3-fluorophenyl)amine (55): Pale yellow oil, 79% yield. $[\alpha]_D^{25}$ = +16.6 (*c* = 7.21, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 7.1 Hz, 3 H), 1.06−1.32 (m, 2 H), 1.41 (br. s, 2 H), 1.44−1.57 (m, 2 H), 3.77 (t, *J* = 7.0 Hz, 1 H), 6.79 (dt, *J* = 8.1 Hz, 1 H), 6.95 (dt, *J* = 8.3 Hz, 2 H), 7.15 (dd, *J* = 13.9, *J* = 8.1 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.4 (q), 17.0 (t), 39.2 (t), 53.1 (d), 110.6 (d, $^2J_{C,F}$ = 22.97 Hz), 111.0 (d, $^2J_{C,F}$ = 22.0 Hz), 119.5 (d, $^3J_{C,F}$ = 2.4 Hz), 127.2 (d, $^4J_{C,F}$ = 7.3 Hz), 147.1 (s, $^3J_{C,F}$ = 6.1 Hz), 160.5 (s, $^1J_{C,F}$ = 245.4 Hz) ppm. MS (CI): *m*/*z* = 168 [M + H^+].

(1*R*)-1-Butyl-1-(4-fluorophenyl)amine (56): Pale yellow oil, 70% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 7.3 Hz, 3 H), 1.08−1.32 (m, 2 H), 1.50 (br. s, 2 H), 1.45−1.61 (m, 2 H), 3.81 (t, *J* = 7.0 Hz, 1 H), 6.92 (dd, *J* = 8.8, $^2J_{H,F}$ = 8.4 Hz, 2 H), 7.20 (dd, *J* = 5.5, $^3J_{H,F}$ = 8.4 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (q), 19.5 (t), 41.7 (t), 55.1 (d), 114.9 (d, $^2J_{C,F}$ = 21.0 Hz), 127.6 (d, $^3J_{C,F}$ = 7.6 Hz), 142.2 (s, $^4J_{C,F}$ = 3.6 Hz), 161.5 (s, $^1J_{C,F}$ = 244.5 Hz) ppm. MS (CI): *m*/*z* = 168 [M + H^+].

(1*R*)-1-[(1,1′-Biphenyl)-2-yl]butylamine (57): Yellow oil, 87% yield. $[\alpha]_D^{25}$ = +16.17 (*c* = 2.18, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.73 (t, *J* = 7.3 Hz, 3 H), 0.98−1.28 (m, 2 H), 1.47 (br. s, 2 H), 1.52−1.63 (m, 2 H), 4.00 (t, *J* = 7.0 Hz, 1 H), 7.16 (d, *J* = 7.7 Hz, 1 H), 7.20−7.33 (m, 5 H), 7.36 (d, *J* = 7.0 Hz, 2 H), 7.52 (d, *J* = 7.7 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (q), 19.6 (t), 41.5 (t), 50.7 (d), 125.5 (d), 126.2 (d), 126.8 (d), 127.8 (d), 127.9 (d), 129.2 (d), 129.8 (d), 141.2 (s), 141.4 (s), 144.1 (s) ppm. MS (CI): *m*/*z* = 226 [M + H^+].

Typical Procedure for the Non-Reductive Removal of the Chiral Auxiliary:[12a] DMF (48.8, mmol, 3.79 mL) was added to CH_2Cl_2 (450 mL) cooled in an ice bath. Oxalyl chloride (48.8 mmol, 4.60 mL) was then added dropwise. After the formation of gas (CO and CO_2) had ceased, a solution of the (*R*,*R*)-PGA allylamine (32.5 mmol) in 100 mL of CH_2Cl_2 was added all at once. Triethylamine (32.5 mmol, 4.60 mL) was added dropwise over 30 minutes and the reaction was stirred at room temperature for 30 minutes. H_2O (450 mL) was added and the organic phase was separated. The organic layer was dried over Na_2SO_4 and filtered. After evaporation of the solvent, the oily material was dissolved in absolute ethanol (150 mL). After the addition of K_2CO_3 (2 equivalents; 64.9 mmol; 8.97 gram), the reaction mixture was refluxed for two hours. After cooling the reaction mixture to room temperature, the solvent was evaporated. The residue was mixed with water (100 mL) and CH_2Cl_2 (100 mL). The organic phase was separated, dried over Na_2SO_4 and filtered. After removal of the solvent, the crude product was dissolved in a 50% aqueous THF (350 mL), 3 equivalents of $NH_2OH{\cdot}HCl$ (6.80 g, 97.4 mmol) were added and the reaction mixture was stirred overnight at ambient temperature. The THF was evaporated under reduced pressure and the residue was brought to pH 1 with aqueous HCl (30%). The aqueous phase was washed once with CH_2Cl_2 to remove the by-products. The aqueous phase was adjusted to pH 10 with aqueous NaOH (33%) and extracted with CH_2Cl_2. After drying over Na_2SO_4, the solvent was evaporated to furnish the (*R*)-arylbutenylamine as an oily material. If necessary, the 1-aryl-3-butenylamines can be purified by kugelrohr distillation.

(1*R*)-1-Butyl-3-butenyl-1-(2-chlorophenyl)amine (66): Yellow oil, 75% yield, >99:1 *er*. $[\alpha]_D^{25}$ = +61.0 (*c* = 3.44, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.48 (br. s, 2 H), 2.17−2.27 (m, 1 H), 2.42−2.52 (m, 1 H), 4.39 (dd, *J* = 4.6, *J* = 8.2 Hz, 1 H), 4.97−5.09 (m, 2 H), 5.63−5.79 (m, 1 H), 7.08 (dt, *J* = 7.7 *J* = 1.1 Hz, 1 H), 7.17 (d, *J* = 7.7 Hz, 1 H), 7.24 (t, *J* = 8.8 Hz, 1 H), 7.44 (dd, *J* = 7.7, *J* = 1.1 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 41.9 (t), 51.0 (d), 117.7 (t), 126.8 (d), 127.0 (d), 127.7 (d), 129.3 (d), 132.6 (s), 135.0 (d), 142.7 (s) ppm. MS (CI): *m*/*z* = 182 (100.0) [M + H^+], 184 (32.3) [M + H^+].

(1*R*)-1-Butyl-3-butenyl-1-(3-chlorophenyl)amine (67): Yellow oil, 58% yield, >99:1 *er*. $[\alpha]_D^{25}$ = +31.5 (*c* = 2.98, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.55 (br. s, 2 H), 2.21−2.42 (m, 2 H), 3.91 (dd, *J* = 7.9, *J* = 5.1 Hz, 1 H), 5.02−5.08 (m, 2 H), 5.59−5.73 (m, 1 H), 7.12−7.22 (m, 3 H), 7.29 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.9 (t), 54.7 (d), 117.9 (d), 124.4 (d), 126.4 (d), 127.0 (d), 129.5 (d), 134.0 (s), 134.7 (d), 147.8 (s) ppm. MS (CI): *m*/*z* = 182 (100.0) [M + H^+], 184 (33.1) [M + H^+].

(1*R*)-1-Butyl-3-butenyl-1-(4-chlorophenyl)amine (68): Orange oil, 70% yield, >99:1 *er*. $[\alpha]_D^{25}$ = +30.0 (*c* = 2.99, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.59 (br. s, 2 H), 2.18−2.37 (m, 2 H), 3.88 (dd, *J* = 7.7, *J* = 5.5 Hz, 1 H), 4.98−5.05 (m, 2 H), 5.56−5.70 (m, 1 H), 7.16−7.27 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.9 (t), 54.5 (d), 117.8 (t), 127.6 (d), 128.2 (d), 132.3 (s), 134.76 (d), 144.00 (s) ppm. MS (CI): *m*/*z* = 182 (100.0) [M + H^+], 184 (34.3) [M + H^+].

(1*R*)-1-(2-Bromophenyl)-3-butenylamine (69): Red oil, 65% yield, >99:1 *er*. $[\alpha]_D^{25}$ = +39.3 (*c* = 2.40, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.49 (br. s, 2 H), 2.13−2.23 (m, 1 H), 2.42−2.50 (m, 1 H), 4.34 (dd, *J* = 8.4, *J* = 4.4 Hz, 1 H), 4.97−5.09 (m, 2 H), 5.65−5.70 (m, 1 H), 7.00 (t, *J* = 7.7 Hz, 1 H), 7.22 (t, *J* = 7.7 Hz, 1 H), 7.44 (d, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.0 (t), 53.4 (d), 117.7 (t), 123.1 (s), 127.2 (d), 127.4 (d), 128.1 (d), 132.6 (d), 134.9 (d), 144.2 (s) ppm. MS (CI): *m*/*z* = 226 (76.3) [M + H^+], 228 (74.0) [M + H^+].

(1*R*)-1-(3-Bromophenyl)-3-butenylamine (70): Yellow oil, 51% yield, >99:1 *er*. $[\alpha]_D^{25}$ = +29.9 (*c* = 2.84, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.87 (br. s, 2 H), 2.12−2.42 (m, 2 H), 3.90 (dd, *J* = 7.7, *J* = 5.5 Hz, 1 H), 4.97−5.08 (m, 2 H), 5.59−5.72 (m, 1 H), 7.12 (t, *J* = 7.7 Hz, 1 H), 7.20 (d, *J* = 7.7 Hz, 1 H), 7.30 (d, *J* = 7.7 Hz, 1 H), 7.44 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.8 (t), 54.6 (d), 117.8 (t), 124.8 (s), 129.19 (d), 129.68 (d), 134.62 (d), 148.00 (s) ppm. MS (CI): *m*/*z* = 226 (100.0) [M + H^+], 228 (97.4) [M + H^+].

(1*R*)-1-(4-Bromophenyl)-3-butenylamine (71): Pale yellow oil, 48% yield, >99:1 *er*. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.61 (br. s, 2 H), 2.12−2.41 (m, 2 H), 3.92 (t, *J* = 6.4 Hz, 1 H), 5.02−5.08 (m, 2 H), 5.59−5.73 (m, 1 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 44.1 (t), 54.8 (d), 118.0 (t), 120.6 (s), 128.1 (d), 131.4 (d), 134.9 (d), 151.0 (s) ppm. MS (CI): *m*/*z* = 226 (100.0) [M + H^+], 228 (98.0) [M + H^+].

(1*R*)-1-[(1,1′-Biphenyl)-3-yl]-3-butenylamine (72): Yellow oil, 45% yield. $[\alpha]_D^{25}$ = +12.5 (*c* = 0.98, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.96 (br. s, 1 H), 2.28−2.47 (m, 2 H), 3.99 (t, *J* = 6.4 Hz, 1 H), 5.01−5.20 (m, 2 H), 5.65−5.78 (m, 1 H), 7.24−7.42 (m, 6 H), 7.52−7.55 (m, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 44.0 (t), 55.2 (d), 117.5 (t), 125.0 (d), 125.1 (d), 125.6 (d), 126.9 (d), 127.0 (d), 128.5 (d), 128.6 (d), 135.2 (d), 141.0 (s), 141.1 (s), 146.1 (s) ppm. MS (CI): *m*/*z* = 224 [M + H^+].

(1*R*)-1-[(1,1′-Biphenyl)-4-yl]-3-butenylamine (73): Yellow oil, 49% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.85 (br. s, 2 H), 2.28−2.51 (m, 1 H), 2.81−3.00 (m, 1 H), 4.00 (t, *J* = 5.9 Hz, 1 H), 4.98−5.13 (m, 2 H), 5.50−5.80 (m, 1 H), 7.09−7.46 (m, 7 H), 7.53 (t, *J* = 7.3 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 40.0 (t), 55.1 (d), 117.8 (t), 126.9 (d), 127.0 (d), 128.1 (d), 128.7 (d), 130.1 (d), 135.9 (d), 131.1 (s), 139.9 (s), 140.9 (s) ppm. MS (CI): *m*/*z* = 224 [M + H^+].

Typical Procedure for the Catalytic Hydrogenation of Phenylacetamide-Protected Homoallylamines (*R*)-66−73: Homoallylamine (15.0 mmol) was dissolved in 100 mL of EtOAc, and Pt−C (5%) (0.6 gram, cat) was added. After two vacuum/H_2 cycles to remove air from the reaction flask, the stirred mixture of the substrate was hydrogenated at ambient pressure of H_2 and room temperature for 1 hour. After filtration, the EtOAc was evaporated under reduced pressure.

(1*R*)-1-Butyl-1-(2-chlorophenyl)amine (74): Green oil, 91% yield, >99:1 *er*. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.3 Hz, 3 H), 1.21−1.43 (m, 2 H), 1.57−1.72 (m, 2 H), 1.90 (br. s, 2 H), 4.34 (t, *J* = 6.6 Hz, 1 H), 7.09 (t, *J* = 7.7 Hz, 1 H), 7.19 (d, *J* = 7.7 Hz, 1 H), 7.25 (t, *J* = 8.2 Hz, 1 H), 7.41 (d, *J* = 7.3 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7 (q), 19.32 (t), 39.9 (t), 51.4 (d), 126.8 (d), 127.5 (d), 129.2 (d), 132.6 (s), 143.5 (s) ppm. MS (CI): *m*/*z* = 184 (100.0) [M + H^+], 186 (33.1) [M + H^+].

(1*R*)-1-Butyl-1-(3-chlorophenyl)amine (75): Orange oil, >99% yield, >99:1 *er*. $[\alpha]_D^{25}$ = +24.2 (*c* = 3.14, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 7.3 Hz, 3 H), 1.09−1.33 (m, 2 H), 1.46−1.61 (m, 2 H), 1.65 (br. s, 2 H), 3.79 (t, *J* = 6.6 Hz, 1 H), 7.09−7.20 (m, 3 H), 7.24 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9 (q), 19.5 (t), 41.6 (t), 55.5 (d), 124.5 (d), 126.4 (d), 126.8 (d), 129.5 (d), 134.1 (s), 148.8 (s) ppm. MS (CI): *m*/*z* = 184 (100.0) [M + H^+], 186 (33.5) [M + H^+].

(1*R*)-1-Butyl-1-(4-chlorophenyl)amine (76): Yellow oil, >99% yield, >99:1 *er*. $[\alpha]_D^{25}$ = +11.2 (*c* = 6.35, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 7.1 Hz, 3 H), 1.15−1.32 (m, 2 H), 1.49−1.64 (m, 2 H), 2.11 (br. s, 2 H), 3.83 (t, *J* = 6.8 Hz, 1 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7 (q), 19.3 (t), 41.4 (t), 55.1 (d), 127.5 (d), 128.1 (d), 132.0 (s), 144.8 (s) ppm. MS (CI): *m*/*z* = 184 (100.0) [M + H^+], 186 (32.7) [M + H^+].

(1*R*)-1-(2-Bromophenyl)-1-butylamine (77): Dark green oil, 99% yield, >99:1 *er*. $[\alpha]_D^{25}$ = +17.9 (*c* = 3.33, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.3 Hz, 3 H), 1.16−1.38 (m, 2 H), 1.46−1.70 (m, 2 H), 2.00 (br. s, 2 H), 4.28 (t, *J* = 6.8 Hz, 1 H), 7.00 (dt, *J* = 7.7, *J* = 1.5 Hz, 1 H), 7.23 (t, *J* = 7.7 Hz, 1 H), 7.39 (dd, *J* = 7.7, *J* = 1.5 Hz, 1 H), 7.44 (dd, *J* = 7.7, *J* = 1.5 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (q), 19.3 (t), 39.9 (t), 53.8 (d), 123.2 (s), 127.0 (d), 127.5 (d), 127.9 (d), 132.5 (d), 144.9 (s) ppm. MS (CI): *m*/*z* = 228 (63.2) [M + H^+], 230 (61.2) [M + H^+].

(1*R*)-1-(3-Bromophenyl)-1-butylamine (78): Orange oil, >99% yield, >99:1 *er*. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.10 (t, *J* = 7.7 Hz, 1 H), 7.15 (d, *J* = 7.7 Hz, 1 H), 7.15 (d, *J* = 7.7 Hz, 1 H), 7.28 (d, *J* = 7.7 Hz, 1 H), 7.40 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9 (q), 19.5 (t), 41.6 (t), 55.5 (d), 124.5 (d), 126.4 (d), 126.8 (d), 129.5 (d), 134.1 (s), 148.8 (s) ppm. MS (CI): *m*/*z* = 228 (100.0) [M + H^+], 230 (96.6) [M + H^+].

(1*R*)-1-(4-Bromophenyl)-1-butylamine (79): Yellow oil, 85% yield, >99:1 *er*. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7.3 Hz, 3 H), 1.04−1.33 (m, 2 H), 1.43−1.56 (m + br. s, 4 H), 3.78 (t, *J* = 6.8 Hz, 1 H), 7.15 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9 (q), 19.4 (t), 41.6 (t), 55.3 (d), 120.2 (s), 128.2 (d), 131.3 (d), 150.9 (s) ppm. MS (CI): *m*/*z* = 228 (95.8) [M + H^+], 230 (100.0) [M + H^+].

(1*R*)-1-[(1,1′-Biphenyl)-3-yl]butylamine (80): Pale green oil, 93% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.3 Hz, 3 H), 1.15−1.41 (m, 2 H), 1.61−1.73 (m, 2 H), 2.14 (br. s, 2 H), 3.92 (t, *J* = 7.0 Hz, 1 H), 7.25−7.45 (m, 6 H), 7.51 (s, 1 H), 7.59 (d, *J* = 7.0 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.6 (q), 17.3 (t), 39.3 (t), 53.6 (d), 123.0 (d), 122.8 (d), 123.3 (d), 124.7 (d), 124.8 (d), 126.2 (d), 126.4 (d), 138.8 (s), 138.9 (s), 144.5 (s) ppm. MS (CI): *m*/*z* = 226 [M + H^+].

(1*R*)-1-[(1,1′-Biphenyl)-4-yl]butylamine (81): Orange oil, 95% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, *J* = 7.3 Hz, 3 H), 1.20−1.41 (m, 2 H), 1.55−1.68 (m + br. s, 4 H), 3.89 (t, *J* = 7.0 Hz, 1 H), 7.27−7.41 (m, 7 H), 7.54 (t, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (q), 19.4 (t), 41.5 (t), 55.4 (d), 126.5

(d), 126.7 (d), 126.8 (d), 128.4 (d), 139.3 (s), 140.6 (s), 145.6 (s) ppm. MS (CI): m/z = 226 [M + H$^+$].

Synthesis of the Nitro-Substituted Phenylbutylamines (*R*)-82 and (*R*)-83: Enantiomerically pure (*R*)-1-phenylbutylamine (**47**; 35 mmol, 5.22 gram) was cautiously added with continuous stirring during 10 minutes to 30 mL of HNO_3 at −5 °C. Heat was generated, but the temperature was maintained at −5 °C. The reaction was followed by ^{1}H NMR spectroscopy, and the reaction was complete after stirring at −5 °C for 1 hour. The reaction mixture was poured onto 100 g of crushed ice and carefully adjusted to pH 10 with aqueous NaOH (33%). The aqueous layer was extracted with CH_2Cl_2 and dried over sodium sulfate. Removal of the solvent provided a mixture of (*R*)-**82** and (*R*)-**83** in a ratio of 22:78 and this mixture of regioisomers was used without further purification.

(1*R*)-1-Butyl-1-(2-nitrophenyl)amine (82): Yellow oil, 20% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.1 Hz, 3 H), 1.14−1.36 (m, 2 H), 1.55−1.84 (m, 2 H), 1.96 (br. s, 2 H), 3.99 (t, J = 6.8 Hz, 1 H), 7.40−7.63 (m, 2 H), 8.03−8.26 (m, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (q), 19.3 (t), 41.4 (t), 55.3 (d), 121.3 (d), 121.9 (d), 129.2 (d), 132.7 (d), 146.8 (s), 148.2 (s), 153.0 (s) ppm. MS (CI): m/z = 195 [M + H$^+$].

(1*R*)-1-Butyl-1-(4-nitrophenyl)amine (83): Yellow oil, 75% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.1 Hz, 3 H), 1.17−1.34 (m, 2 H), 1.47 (br. s, 2 H), 1.51−1.63 (m, 2 H), 3.98 (t, J = 6.8 Hz, 1 H), 7.44 (d, J = 8.8 Hz, 2 H), 8.12 (t, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.8 (q), 19.3 (t), 41.7 (t), 55.4 (d), 123.5 (d), 127.1 (d), 146.2 (s), 154.3 (s) ppm. MS (CI): m/z = 195 [M + H$^+$].

1-(3-Nitrophenyl)-1-butanone (85): Commercially available butyrophenone (169 mmol, 25.0 g) was cautiously added with continuous stirring during 30 minutes at 150 mL of HNO_3 at −5 °C. Heat was generated, but the temperature was maintained at −5 °C. The reaction was followed by ^{1}H NMR spectroscopy, and the reaction was complete after stirring at −5 °C for 4 hours. When poured onto 500 g of crushed ice, the crude *m*-nitro-compound precipitated as a yellow curdled solid. After suction filtration, the residue was dissolved in 200 mL of diethyl ether and dried over sodium sulfate. After removal of the diethyl ether a yellow oil was obtained, from which the crude *m*-nitro compound separated on standing as yellow plates. After removal of the oil, the yellow plates were recrystallised once from absolute alcohol. Pure **85** was obtained as pale yellow plates (92.9 mmol, 18.0 g, 55% yield. M.p. 60.5 °C (ref.[28a] 61 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.3 Hz, 3 H), 1.63−1.75 (m, 2 H), 2.92 (t, J = 7.1 Hz, 2 H), 7.59 (dt, J = 8.1 Hz, 1 H), 8.19 (d, J = 7.7 Hz, 1 H), 8.28 (d, J = 8.1 Hz, 1 H), 8.63 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.6 (q), 17.2 (t), 40.5 (t), 122.7 (d), 127.0 (d), 129.8 (d), 139.5 (d), 138.1 (s), 148.2 (s), 197.9 (s) ppm. $C_{10}H_{11}NO_3$ (193.2): calcd. C 62.17, H 5.74, N 7.25; found C 62.15, H 5.68, N 7.32. MS (EI): m/z = 193 [M$^+$].

(±)-1-Butyl-1-(3-nitrophenyl)formamide (86): A mixture of 1-(3-nitrophenyl)-1-butanone (**85**; 129 mmol, 25.0 g), 77 mL of formamide and 35 mL of formic acid was heated to reflux. The mixture was refluxed for several hours until the reaction was complete (followed by ^{1}H NMR spectroscopy). After cooling to ambient temperature, 200 mL of water was added and the mixture was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated to furnish a red oil (129 mmol, 28.7 gram, >99% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, J = 7.3 Hz, 3 H), 1.11−1.36 (m, 2 H), 1.58−1.75 (m, 2 H), 4.98 (dd, J = 15.0, J = 7.7 Hz, 1 H), 7.31 (br. s, 1 H), 7.38 (t, J = 8.1 Hz, 1 H), 7.54 (d, J = 7.7 Hz, 1 H), 7.97 (d, J = 8.1 Hz, 1 H), 8.07 (s, 1 H), 8.09 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.4 (q), 19.1 (t), 37.9 (t), 51.8 (d), 121.0 (d), 122.2 (d), 129.5 (d), 133.1 (d), 144.2 (s), 148.2 (s), 162.2 (d) ppm. MS (CI): m/z = 223 [M + H$^+$].

(±)-1-Butyl-1-(3-nitrophenyl)amine (87): A mixture of ±-**86** (129 mmol, 28.7 gram) and 100 mL of aqueous HCl (30%) was heated to reflux. The mixture was refluxed overnight. After cooling to ambient temperature, 200 mL of water was added. The reaction mixture was carefully adjusted to pH 10 with aqueous NaOH (33%) and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated to furnish a red oil.

Resolution of (±)-87 with (*S*)-88: One equivalent of (*S*)-**88** was added to a solution of the racemic substrate (20.3 mmol, 3.95 g) in 40.6 mL of 2-butanone and 20.3 mL of H_2O. The mixture was heated until a clear solution was obtained. While stirring, the solution was allowed to cool to room temperature overnight. The salt was removed by filtration under suction and washed with a little *i*PrOH. The salt obtained was recrystallised twice from *i*PrOH/H_2O (2:1). The salt was shown to contain (*R*)-**87** of >99% *ee* by HPLC analysis.[23] The purified salt was treated with 6 M NaOH solution to liberate the free amine (*R*)-**87** of >99% *ee* in 24% yield from (±)-**87**. $[\alpha]_D^{25}$ = −5.4 (c = 2.15, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.77 (t, J = 7.3 Hz, 3 H), 1.04−1.29 (m, 2 H), 1.47−1.58 (m + br. s, 4 H), 3.91 (t, J = 6.8 Hz, 1 H), 7.35 (t, J = 7.7 Hz, 1 H), 7.55 (d, J = 7.7 Hz, 1 H), 7.92 (d, J = 7.7 Hz, 1 H), 7.92 (d, J = 8.1 Hz, 1 H), 8.06−8.09 (m, 1 H) ppm. ^{13}C NMR (50 MHz,$CDCl_3$): δ = 19.2 (q), 13.7 (t), 41.6 (t), 55.2 (d), 121.2 (d), 121.6 (d), 129.0 (d), 132.6 (d), 148.1 (s), 148.8 (s) ppm. $C_{10}H_{14}N_2O_2{\cdot}C_{11}H_{15}O_4P$: calcd. C 57.79, H 6.70, N 6.42; found C 57.57, H 6.90, N 6.31. MS (CI): m/z = 195 [M + H$^+$].

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[30] IUPAC name of (*R*)-phencyphos: *(R)*-2-hydroxy-5,5-dimethyl-2-oxo-4-phenyl-1,3,2-dioxaphosphorinane.

[31] CCDC-200249 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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