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New chiral amine ligands in the desymmetrization of prochiral phosphine boranes

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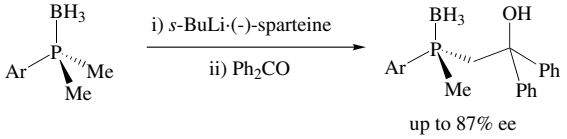
Abstract—P-chirogenic phosphine ligands can be prepared via desymmetrization of prochiral phosphine boranes using *s*-BuLi·(−)-sparteine complexes. One limitation of this method, however, has been that (+)-sparteine is not easily accessible. Herein, we show that derivatives of another alkaloid, (−)-cytisine, are useful surrogates for (+)-sparteine in the desymmetrization of prochiral phenyl-, cyclohexyl- and *tert*-butyl dimethyl phosphine boranes, yielding chiral phosphine boranes in up to 92% ee. Other chiral diamines were also tested but did not give as high enantioselectivity as the (−)-cytisine derivatives.

1. Introduction

P-chirogenic ligands in asymmetric catalysis are a viable alternative to more traditional ligands with chirality situated in the surrounding carbon skeleton.[1] There are several methods available for their preparation. The use of ephedrine as a chiral auxiliary was introduced by Jugé et al., and has proven to be very useful. However, three or four consecutive steps are needed in order to obtain a P-chirogenic phosphine.[2] A route comprising of a one-step protocol to P-chiral compounds is the desymmetrization of prochiral phosphine boranes substrates, developed by Evans et al.[3] Enantioselective deprotonation using a chiral amine–alkyllithium complex is used to differentiate between two prochiral sites in a *meso* compound (Scheme 1).



Scheme 1. Evans' method for the desymmetrization of prochiral phosphine boranes using (−)-sparteine as a chiral ligand.

Livinghouse has further extended this method to allow the dynamic resolution of racemic 2°-phosphine boranes in high enantioselectivities.[4] However, both these methods suffer from the unavailability of (+)-sparteine. Inspired by two publications by O'Brien et al.,[5] we recently reported on the application of (−)-cytisine derivatives **1a** and **1e** (Fig. 1), which work as (+)-sparteine surrogates in the desymmetrization of prochiral phosphine boranes, giving access to the opposite enantiomer as compared to (−)-sparteine.[6] Very recently, O'Brien has also published the application of diamine **1b**, together with two other (−)-cytisine derivatives (R = *n*PrCH$_2$– and *t*-Bu), in a number of different asymmetric transformations, including the dynamic resolution of a secondary phosphine borane.[7]

In spite of the fact that **1a** and **1e** are comparable to or even give better enantioselectivity than (−)-sparteine itself, we felt that other (−)-cytisine derivatives along with new chiral amines had to be screened in this type of desymmetrization. Apart from the cytisine derivatives, which have (−)-sparteine as their natural antipode, all amines should be accessible in both enantiomeric forms, thus giving access to both enantiomers of the P-chiral phosphine product. Herein we report the full details of our study on the desymmetrization of prochiral phosphine boranes.

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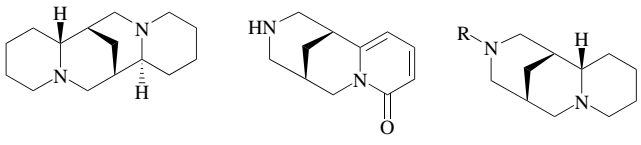


(-)-Sparteine (-)-Cytisine **1a-f**

1a R = Me
1b R = Et
1c R = Bn
1d R = *c*Pr-CH_2-
1e R = *i*Pr
1f R = Cy

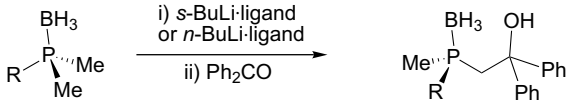
Figure 1.

2. Results and discussion

The cytisine derivatives used in the asymmetric deprotonation of prochiral phosphines were prepared using four different protocols, depending on the nature of the R-substituent (Scheme 2). Compound **1a** was prepared from (−)-cytisine[8] using the procedure published by O'Brien and co-workers,[5] involving the reduction of methyl carbamate **2**. This route could not be applied directly towards the preparation of derivatives **1b**–**f**, but modifications of this method were used instead. Lasne and co-workers have reported the preparation of *N*-acetyl-cytisine **3**.[9] Hydrogenation of **3** with platinum oxide, followed by further reduction of the remaining amide functionalities with $LiAlH_4$, yielded **1b**.

Compound **1c** was prepared via initial hydrogenation of the 2-pyridone ring to form **6**, followed by reductive amination yielding **8d** and finally reduction of the ring amide. **1d**–**f** can be prepared by initial reductive amination, to form **7a**–**c**, followed by reduction with PtO_2 to give **8a**–**c** and then reduction with $LiAlH_4$ as earlier, to yield the desired diamines **1d**–**f**.

Desymmetrization reactions were carried out on three different prochiral phosphine borane substrates, **9a** (R = Ph), **9b** (R = Cy) and **9c** (R = *t*-Bu). For the cytisine derivatives **1a**–**f**, *s*-BuLi was used as the base, subsequently quenching the reaction with benzophenone in order to measure the enantioselectivity in the deprotonation step (Scheme 3).

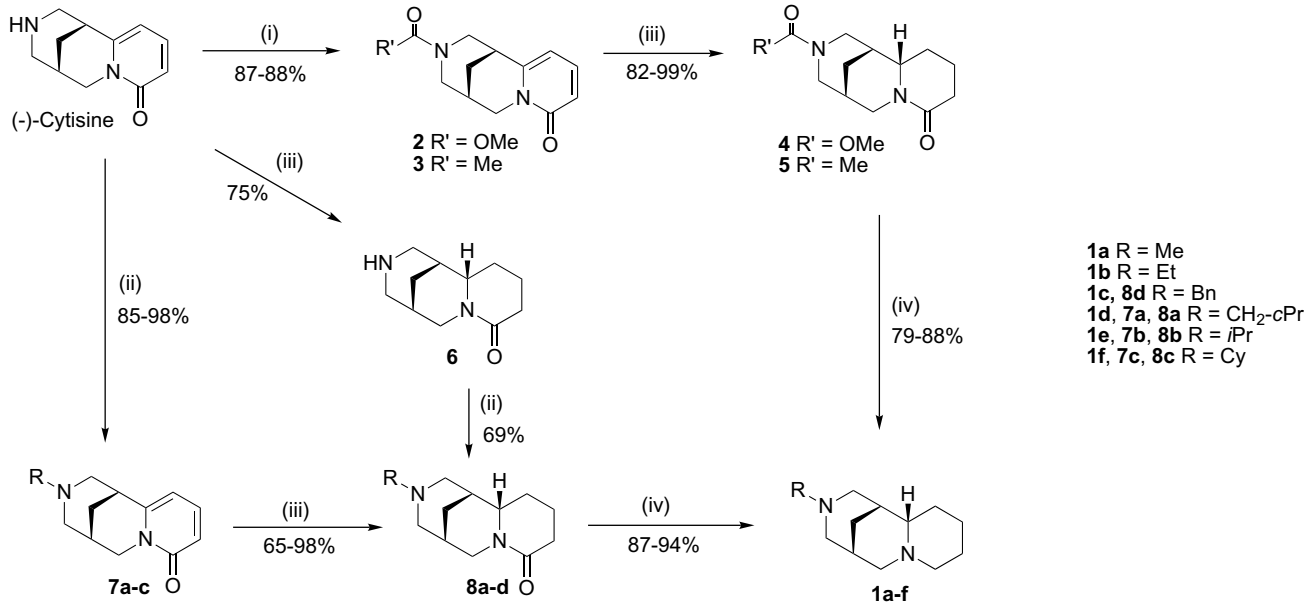


9a-c (*R*)-**10a-c**

a R = Ph
b R = Cy
c R = *t*-Bu

Scheme 3. Desymmetrization of prochiral phosphine boranes using different diamine ligands.

To establish the reaction conditions, the initial desymmetrization reported by Evans was repeated, yielding nearly exactly the same results as the published data. Substituents on the (−)-cytisine skeleton were varied to include both smaller groups like methyl and ethyl, as well as more sterically hindered moieties like isopropyl and cyclohexyl. Results from the reactions with **1a** and **1e** have been reported earlier by us in a preliminary communication,[6] but are included for comparison.



Scheme 2. Preparation of cytisine derivatives **1a**–**f**. Reagents and conditions: (i) **2**: MeO_2CCl, **3**: MeC(O)Cl, DMAP, Et_3N, CH_2Cl_2; (ii) aldehyde or ketone (**7a**: *c*Pr–CH_2–CHO, **7b**: acetone, **7c**: Cy–CHO, **8d**: Ph–CHO), $NaBH(OAc)_3$, THF, rt, 18 h; (iii) PtO_2, H_2, AcOH, rt, 26 h; (iv) $LiAlH_4$, THF, reflux, 18 h.

Results from the desymmetrization reactions using ligands **1a**–**f** are displayed in Table 1.

Table 1. Results from the desymmetrization of phosphine boranes **9a**–**c** using (−)-cytisine derivatives **1a**–**f**

Entry	Ligand	R in **10**	Base	Yield (%)	% Ee (*R*/*S*)
1	(−)-Sparteine	Ph	*s*-BuLi	87	78 (*S*)
2	(−)-Sparteine	Cy	*s*-BuLi	67	70 (*S*)
3	(−)-Sparteine	*t*-Bu	*s*-BuLi	83	76 (*S*)
4	**1a**	Ph	*s*-BuLi	89	67 (*R*)
5	**1a**	Cy	*s*-BuLi	77	74 (*R*)
6	**1a**	*t*-Bu	*s*-BuLi	78	92 (*R*)
7	**1b**	Ph	*s*-BuLi	85	73 (*R*)
8	**1b**	Cy	*s*-BuLi	62	68 (*R*)
9	**1b**	*t*-Bu	*s*-BuLi	82	90 (*R*)
10	**1c**	Ph	*s*-BuLi	16	0 (*R*)
11	**1c**	Cy	*s*-BuLi	24	42 (*R*)
12	**1c**	*t*-Bu	*s*-BuLi	35	50 (*R*)
13	**1d**	Ph	*n*-BuLi	48	26 (*R*)
14	**1d**	Ph	*s*-BuLi	63	56 (*R*)
15	**1d**	Cy	*s*-BuLi	94	66 (*R*)
16	**1d**	*t*-Bu	*n*-BuLi	65	74 (*R*)
17	**1d**	*t*-Bu	*s*-BuLi	76	86 (*R*)
18	**1e**	Ph	*s*-BuLi	82	63 (*R*)
19	**1e**	Cy	*s*-BuLi	86	62 (*R*)
20	**1e**	*t*-Bu	*s*-BuLi	72	75 (*R*)
21	**1f**	Ph	*n*-BuLi	72	60 (*R*)
22	**1f**	Ph	*s*-BuLi	93	59 (*R*)
23	**1f**	Cy	*s*-BuLi	62	60 (*R*)
24	**1f**	*t*-Bu	*n*-BuLi	73	73 (*R*)
25	**1f**	*t*-Bu	*s*-BuLi	79	71 (*R*)

Desymmetrization of the phenyl substituted dimethyl phosphine borane **9a** with different (−)-cytisine derivatives did indeed give the opposite (*R*)-enantiomer as compared to the reactions using (−)-sparteine, where the (*S*)-**10a** enantiomer was produced. The best results were obtained with the ethyl-cytisine derivative **1b** (entry 7), attaining a respectable enantiomeric excess of 73% for (*R*)-**10a** as compared to 78% ee for (−)-sparteine (*S*)-**10a** (entry 1). The methyl cytisine derivative **1a** gave an ee of 67%, while somewhat lower enantioselectivities were obtained for the sterically bulkier isopropyl and cyclohexyl cytisine derivatives (**1e** and **1f**; entries 18 and 22). For **1f**, the reaction was also carried out with *n*-BuLi as we were concerned that the combination of a sterically hindered substrate and bulky diamine ligand might inhibit the approach of the base. The enantioselectivity with *n*-BuLi was nearly the same as that attained with *s*-BuLi (entry 21). Two ligands of intermediate steric hindrance were also included in the study: Benzyl susbstituted diamine **1c** and the methylcyclopropyl cytisine derivative **1d**. The benzyl substituted diamine **1c** gave a racemate, the low yield in this case indicating that some side reaction takes place, probably initiated by deprotonation at the benzylic position of the ligand instead of on the methyl groups (entry 10). For ligand **1d**, the deprotonation was again carried out both with *s*-BuLi and *n*-BuLi. In this case there was quite a large difference between the two reactions, with *s*-BuLi giving by far the better enantioselectivity (56% ee, entry 14) as compared to the reaction with *n*-BuLi (26%, entry 13).

Better enantioselection can be achieved when using alkyl substituted phosphine boranes. Deprotonation of cyclohexyl dimethyl phosphine borane with methyl derivative **1a** gave higher enantioselectivity (74%, entry 5) than the corresponding reaction with (−)-sparteine (70%, entry 2); as earlier the complementary enantiomers were formed. For the other diamine ligands, enantioselectivities were in the range of 60–68% ee (entries 8, 15, 19 and 23), with the exception of diamine **1c**, which gave a rather poor enantioselectivity (42% ee, entry 11). For *tert*-butyl dimethyl phosphine borane **9c**, excellent results were obtained when using the methyl- or the ethyl-substituted ligands **1a** and **1b** (entries 6 and 9), with enantioselectivities of 92% and 90% ee, respectively. In both these cases the enantioselectivities exceed that obtained with (−)-sparteine, which in this specific case gave 76% ee (entry 3). Subsequent deprotonations using the other (−)-cytisine derived ligands also in general gave higher enantioselectivites than for the phenyl or cyclohexyl substrates, in the range of 71–86% ee. As in the earlier examples, using *n*-BuLi instead of *s*-BuLi when using hindered ligands did not offer any great improvements. For the cyclohexyl cytisine derivative **1f**, similar results were obtained irrespective of base (entries 24 and 25), while for the methylcyclopropyl derivative **1e**, *s*-BuLi gave a much better enantioselectivity (entries 16 and 17).

A limited study using other diamines not derived from (−)-cytisine was also carried out (Fig. 2). Diamine **11** was prepared by reaction of (+)-(*R*)-2,2-diamino-1,1-binaphthalene with 1,4-dibromobutane in a 74% yield. Deprotonation of phenyl dimethyl phosphine borane in the presence of **11** and *n*-BuLi, followed by quenching with benzophenone as earlier, gave (*R*)-**10a** in 69% yield but with no enantioselectivity (Table 2, entry 1). *n*-BuLi was used in this case as the ligand is bulky. The related ligand **12**, prepared in a similar manner from (1*S*,2*S*)-(−)-diphenylethylenediamine and 1,4-dibromobutane, gave a modest enantiomeric excess of 17% (entry 2). Both these diamines are new and would be interesting to try in other contexts. Ligand **13** has been used by Heath and Livinghouse in these types of asymmetric

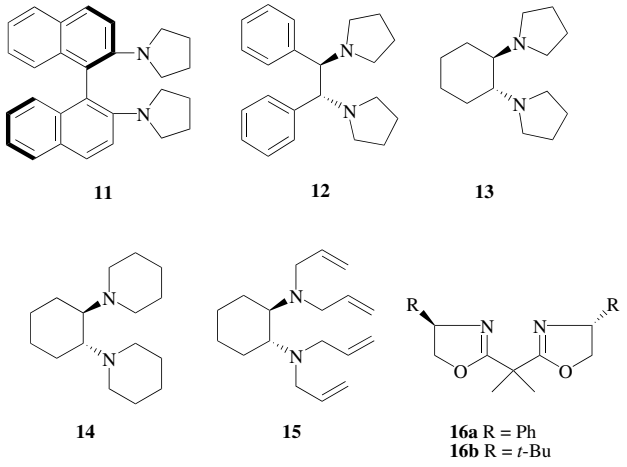


Figure 2.

Table 2. Results from the desymmetrization of phenyl dimethyl phosphine borane (**9a**) using non-cytisine derived diamines **11**–**16**

Entry	Ligand	Base	Yield (%)	% Ee (*RS*)
1	**11**	*n*-BuLi	69	0
2	**12**	*s*-BuLi	69	17 (*R*)
3	**13**	*s*-BuLi	42	53 (*R*)
4	**14**	*s*-BuLi	28	5 (*R*)
5	**15**	*s*-BuLi	34	[a]
6	**16a**	*n*-BuLi	0	0
7	**16b**	*n*-BuLi	33	[a]

[a] (*R*)-**10a** in excess. Not possible to determine exact value for ee due to the overlap with benzhydrol formed as a by-product.

deprotonations.[10] Under our conditions, an enantioselectivity of 53% ee was achieved, better than for **11** and **12** but not as good as for the cytisine-based ligands. Ligand **14**, with a similar structure, was a disappointment however, giving both a low yield and an enantiomeric excess of only 5% (entry 4). Diallylation of cyclohexyldiamine yielded ligand **15**, initially intended for the preparation of ligand **13** via a metathesis reaction. This strategy proved unsuccessful but ligand **15** itself was also tried in an asymmetric deprotonation. A large amount of by-product, benzhydrol, was formed, probably due to migration of the borane group to nitrogen followed by reduction of benzophenone with borane. Some of the desired product was also formed, but could not be separated from the contaminating benzhydrol, rendering the determination of the enantioselectivity difficult, although it could be established that the (*R*)-isomer was in excess.

Chiral bisoxazolines are popular ligands for many different types of reactions. Ligands **16a** and **16b**, both commercially available, were tried in the desymmetrization of **9a**. The use of **16a**, somewhat surprisingly, resulted in no reaction at all, while **16b** yielded a mixture of the desired product and benzhydrol, as in the case of **15** earlier. The (*R*)-isomer was in excess but the exact enantiomeric excess could not be determined.

3. Conclusion

A number of different diamines, many of them new, have been used in the desymmetrization of prochiral boranes with the aim of finding a method of accessing both enantiomers of the desired P-chirogenic phosphine ligands. Derivatives of (−)-cytisine gave enantiomeric excesses of up to 92%, higher than the originally published results using (−)-sparteine but with the formation of the (*R*)-enantiomer as intended, thus forming a complementary technique to the already published methodology using (−)-sparteine, which yields the (*S*)-isomer. Other chiral diamines, available in both enantiomeric forms, were also tried, but did not give as promising results. We are currently applying the developed methodology towards the preparation of combinatorial libraries of P-chirogenic ligands as well as the synthesis of chiral diphosphines for enantioselective organometallic reactions.

4. Experimental

4.1. General information

Optical rotations were measured on a Perkin Elmer 341 LC digital polarimeter with a sodium lamp (D-line, wavelength = 589 nm) and reported as follows: $[\alpha]_D^T$ (*c* g/100 mL of solvent). ^{1}H NMR spectra were recorded on a Varian UNITY-VXR 5000 (400 MHz) spectrometer. Chemical shifts are reported with deuterochloroform as reference (δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constants and integration. ^{13}C NMR spectra were recorded on a Varian UNITY-VXR 5000 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported with deuterochloroform as reference (δ 77.00 ppm). Elemental analyses were conducted by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Exact mass measurements were performed using a Micromass LCT, ECI-TOF-MS. Solvents for extraction and chromatography were HPLC grade. Flash chromatography was performed on Merck silica gel SI-60Å (35–70). Analytical high performance liquid chromatography (HPLC) was performed on a Waters system with Waters 600E system controller, Waters 717 (autosampler) and Waters Photodiode Array Detector, using either Daicel Chiracel AD, OD or OJ columns for chiral analysis or a XTerra C8 column for reversed phase analysis. *n*-BuLi and *sec*-BuLi were titrated using diphenylacetic acid. All experiments were carried out under a nitrogen or argon atmosphere in oven or flame-dried glassware. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl. *Laburnum anagyroides* seeds were purchased from Vilmorin, France, and (−)-cytisine was extracted according Lasne and co-workers.[8] Compounds **2**, **4** and **1a** were prepared according to O'Brien and co-workers.[5] Compound **3** was prepared according to Lasne and co-workers.[8] Phenyl dimethyl phosphine borane **9a** was prepared according to Muci et al.,[3] while phosphine boranes **9b** and **9c** were prepared using the procedure of Imamoto et al.[11] Ligand **13** was prepared according to Corey et al.[12] For the preparation of ligand **14**, see Fraenkel et al.[13] Ligands **16a** and **16b** were purchased from Aldrich.

4.2. General procedure for the reductive amination

(−)-Cytisine (2.05 g, 10.7 mmol) was dissolved in dry THF (30 mL). Cyclopropane-carboxaldehyde (1.6 mL, 21.4 mmol), glacial acetic acid (0.92 mL, 16.1 mmol) and sodium triacetoxyborohydride (3.4 g, 16.1 mmol) were added to the solution in one portion. The reaction mixture was stirred for 18 h under a nitrogen atmosphere and subsequently quenched with aqueous NaOH (1 M), adjusting the pH to ~11. The biphasic mixture was extracted with diethyl ether (3 × 50 mL), and the organic phases concentrated under reduced pressure. The residual oil was acidified to pH 1 using 2 M aqueous HCl. The aqueous phase was removed and the pH adjusted to 11 using 2 M NaOH. The aqueous phase was then extracted using CH_2Cl_2 (3 × 50 mL). The combined

organic phases were dried over Na_2SO_4 and concentrated under reduced pressure to give **7a** as a colourless solid.

4.2.1. Data for (−)-*N*-cyclopropylmethyl-1,2,3,4,5,6-hexahydro-1,5-methano-pyrido[1,2*a*][1,5]diazocin-8-one 7a. Colourless solid, yield 2.23 g (85%). $[\alpha]_D^{20} = -172.4$ (*c* 0.55 in $CHCl_3$); mp 92.5–94.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24 (m, 1H), 6.39 (d, J = 8.8 Hz, 1H), 5.96 (d, J = 7.2 Hz, 1H), 4.00 (d, J = 15.6 Hz, 1H), 3.87 (dd, J = 15.6, 6.8 Hz, 1H), 3.04 (d, J = 10.8 Hz, 1H), 2.97 (d, J = 10.4 Hz, 1H), 2.91 (s, 1H), 2.39 (br s, 1H), 2.29 (d, J = 10.4 Hz, 1H), 2.24 (d, J = 10.8 Hz, 1H), 2.15–2.01 (m, 2H), 1.77 (dd, J = 12.8, 4.4 Hz, 2H), 0.60 (m, 1H), 0.35 (d, J = 7.6 Hz, 2H), −0.07 (d, J = 4.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.9, 152.0, 138.9, 116.5, 104.9, 63.1, 60.6, 60.0, 35.7, 30.4, 28.1, 26.1, 8.1, 4.0, 3.7; IR 2934, 1648, 1546 cm^{-1}. Anal. Calcd for $C_{15}H_{20}N_2O$: C, 73.74; H, 8.25. Found: C, 73.63; H, 8.20.

4.2.2. Data for (−)-*N*-isopropyl-1,2,3,4,5,6-hexahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocin-8-one 7b. Prepared from (−)-cytisine and acetone according to the general procedure for reductive amination. Colourless oil, yield 1.67 g (92%). $[\alpha]_D^{20} = -144.4$ (*c* 2.44 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16 (m, 1H), 6.30 (d, J = 8.8 Hz, 1H), 5.87 (d, J = 6.8 Hz, 1H), 3.86 (d, J = 15.2 Hz, 1H), 3.77 (dd, J = 15.6, 6.4 Hz, 1H), 2.83 (br s, 1H), 2.72 (br t, J = 12.2 Hz, 2H), 2.50–2.35 (m, 3H), 2.31 (br s, 1H), 1.75 (d, J = 12.8 Hz, 1H), 1.65 (d, J = 12.8 Hz, 1H), 0.77 (d, J = 6.8 Hz, 3H), 0.72 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.6, 152.0, 138.6, 116.1, 104.5, 55.8, 55.3, 53.8, 50.0, 35.6, 30.2, 28.0, 26.2, 17.8; IR 2962, 1651, 1547 cm^{-1}. HRMS (ECI) m/z $(M+1)^+$ calcd for $C_{14}H_{21}N_2O$: 233.1654. Found: 233.1679. Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68. Found: C, 72.46; H, 8.54.

4.2.3. Data for (−)-*N*-cyclohexyl-1,2,3,4,5,6-hexahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocin-8-one 7c. Prepared from (−)-cytisine and cyclohexyl-carboxaldehyde according to the general procedure for reductive amination. Colourless oil, yield 2.82 g (98%). $[\alpha]_D^{20} = -173.3$ (*c* 0.45 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26–7.22 (m, 1H), 6.38 (d, J = 9.2 Hz, 1H), 5.94 (d, J = 6.4 Hz, 1H), 3.94 (d, J = 15.2 Hz, 1H), 3.85 (dd, J = 15.2, 6.0 Hz, 1H), 2.85 (dd, J = 25.2, 11.2 Hz, 3H), 2.53 (t, J = 10.4 Hz, 2H), 2.37 (br s, 1H), 2.06 (br s, 1H), 1.77 (dd, J = 44.4, 11.2 Hz, 2H), 1.61–1.45 (m, 5H), 1.05 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.8, 152.3, 138.8, 116.5, 104.5, 63.1, 56.8, 56.3, 53.7, 50.3, 36.1, 28.7, 28.5, 26.6, 26.5, 25.9, 25.8; IR 2927, 1648, 1543 cm^{-1}. HRMS (ECI) m/z $(M+1)^+$ calcd for $C_{17}H_{25}N_2O$: 273.3920. Found: 273.3949. Anal. Calcd for $C_{17}H_{24}N_2O$: C, 74.96; H, 8.88. Found: C, 75.10; H, 8.93.

4.2.4. Data for (−)-*N*-benzyl-decahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocin-8-one 8d. Prepared from **6** and benzaldehyde according to the general procedure for reductive amination. White solid, yield 2.20 g (75%). $[\alpha]_D^{20} = -63.5$ (c = 1.02 in $CHCl_3$); mp 97.5–98.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24 (m, 5H), 4.75 (d, J = 14.0 Hz, 1H), 3.47 (d, J = 17.2 Hz, 1H), 3.44 (d, J = 3.2 Hz, 1H), 3.04 (m, 2H), 2.95 (d, J = 10.8 Hz, 1H), 2.82 (d, J = 14.4 Hz, 1H), 2.45 (d, J = 17.2 Hz, 1H), 2.32 (m, 2H), 2.02 (d, J = 18.4 Hz, 1H), 1.97 (s, 1H), 1.76–1.72 (m, 3H), 1.63–1.44 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.0, 139.2, 129.0, 128.2, 127.0, 63.6, 60.0, 59.2, 46.4, 34.1, 33.6, 33.3, 30.3, 29.5, 28.0, 20.2; IR 2928, 1629, 1444 cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51. Found: C, 75.88; H, 8.45.

4.3. General procedure for the reduction of the 2-pyridone moiety with PtO_2/H_2

Compound **7a** (700 mg, 2.9 mmol) was dissolved in acetic acid (30 mL). PtO_2 (68 mg, 0.29 mmol) was added in one portion under a stream of nitrogen. The flask was evacuated and backfilled with H_2; this procedure was repeated several times. Thereafter the reaction mixture was stirred under an H_2 atmosphere at atmospheric pressure for 26 h. The PtO_2 was filtered off and the reaction concentrated under reduced pressure (toluene was added to ensure complete removal of acetic acid). The residue was dissolved in CH_2Cl_2 (50 mL) and the pH adjusted to ~11 using NaOH (2 M, aq). The organic phase was washed with brine, dried using Na_2SO_4 and concentrated under reduced pressure to give **8a**.

4.3.1. Data for (−)-*N*-cyclopropylmethyl-decahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocin-8-one 8a. White solid, yield 706 mg (98%). $[\alpha]_D^{20} = -58.6$ (*c* 1.1 in $CHCl_3$); mp 52.8–53.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.72 (d, J = 13.6 Hz, 1H), 3.51 (m, 1H), 3.35 (d, J = 12.0 Hz, 1H), 3.00 (d, J = 10.4 Hz, 1H), 2.80 (d, J = 13.2 Hz 1H), 2.43 (d, J = 16.8 Hz, 1H), 2.32–2.18 (m, 3H), 2.08 (dd, J = 12.4, 6.4 Hz, 2H), 2.00 (d, J = 11.6 Hz, 1H), 1.94–1.61 (m, 7H), 0.78 (m, 1H), 0.43 (m, 2H), 0.05 (d, J = 4.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.8, 63.9, 59.6, 59.0, 54.2, 46.7, 34.3, 33.9, 33.4, 29.5, 28.3, 20.3, 9.08, 4.6, 3.5; IR 2922, 1613, 1462 cm^{-1}. Anal. Calcd for $C_{15}H_{24}N_2O$: C, 72.54; H, 9.74. Found: C, 72.62; H, 9.74.

4.3.2. Data for (−)-*N*-acetyl-decahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocin-8-one 5.[6] Prepared from **3** according to the general procedure for the reduction with H_2/PtO_2. Colourless oil, yield 492 mg (99%). Spectroscopic data are in accordance with published data for this compound.[6] $[\alpha]_D^{20} = -214.3$ (*c* 0.6 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.04 (d, J = 12.8 Hz, 1H), 4.88 (d, J = 13.6 Hz, 1H), 3.91 (d, J = 12.8 Hz, 1H), 3.47 (br d, J = 10.8 Hz, 1H), 3.33 (d, J = 13.2 Hz, 1H), 2.80 (d, J = 13.6 Hz, 1H), 2.61 (d, J = 14.0 Hz, 1H), 2.33 (m, 2H), 2.09–1.57 (m, 11H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.2, 169.5, 59.4, 51.5, 45.9, 41.8, 33.6, 32.82, 32.78, 28.1, 27.9, 21.8, 19.9. Anal. Calcd for $C_{13}H_{20}N_2O_2$: C, 66.07; H, 8.53. Found: C, 65.88; H, 8.64.

4.3.3. Data for 1,2,3,4,5,6-hexahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocin-8-one 6. Prepared from (−)-cytisine according to the general procedure for the reduction of the 2-pyridone moiety with H_2/PtO_2 (reaction time 36 h in this case), yielding crude **6** as a white crystalline

solid. Purification by flash chromatography on silica gel using 5% MeOH/NH_3 in CH_2Cl_2 afforded **6** as a single diastereomer, yield: 1.20 g (69%). $[\alpha]_D^{20} = -32.8$ (c 0.97 in $CHCl_3$); mp 59.1–60.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.68 (d, J = 12.0 Hz, 1H), 3.55 (t, J = 6.4 Hz, 1H), 3.35 (d, J = 14.4 Hz, 1H), 3.01 (d, J = 13.6 Hz, 1H), 3.00–2.85 (m, 3H), 2.50 (dd, J = 17.2, 5.2 Hz, 1H), 2.40–2.31 (m, 1H), 2.06–1.67 (m, 8H), 1.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 60.2, 47.2, 47.0, 33.7, 33.4, 33.2, 30.4, 28.7, 28.4, 20.5; IR 2941, 1613 cm^{-1}. Anal. Calcd for $C_{11}H_{18}N_2O$: C, 68.01; H, 9.34; Found: C, 68.10; H, 9.28.

4.3.4. Data for (−)-*N*-isopropyl-decahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocin-8-one 8b. Prepared from **7b** according to the general procedure for the reduction with H_2/PtO_2. Colourless oil, yield 1.35 g (87%). $[\alpha]_D^{20} = -69.9$ (c 0.93 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.68 (d, J = 13.6 Hz, 1H), 3.49 (t, J = 6.4 Hz, 1H), 3.07 (d, J = 11.2 Hz, 1H), 2.83 (dd, J = 18.4, 11.2 Hz, 2H), 2.58–2.34 (m, 3H), 2.30–2.16 (m, 2H), 2.00–1.53 (m, 8H), 0.94 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.8, 58.9, 54.8, 54.0, 48.8, 46.6, 34.0, 33.9, 33.2, 29.4, 28.0, 20.2, 18.8, 17.0; IR 2946, 1613, 1563, 1411 cm^{-1}. HRMS (ECI) m/z $(M+1)^+$ calcd for $C_{14}H_{25}N_2O$: 237.1967. Found: 237.1994. Anal. Calcd for $C_{14}H_{24}N_2O$: C, 71.14; H, 10.23. Found: C, 71.03; H, 10.21.

4.3.5. Data for (−)-*N*-cyclohexyl-decahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocin-8-one 8c. Prepared from **7c** according to the general procedure for the reduction with H_2/PtO_2. Colourless oil, yield 1.98 g (65%). $[\alpha]_D^{20} = -38.6$ (c 0.45 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.68 (d, J = 13.6 Hz, 1H), 3.49 (t, J = 6.4 Hz, 1H), 3.07 (d, J = 11.2 Hz, 1H), 2.83 (dd, J = 18.4, 11.2 Hz, 2H), 2.58–2.34 (m, 3H), 2.30–2.16 (m, 2H), 2.00–1.53 (m, 8H), 0.94 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 63.6, 59.1, 55.5, 49.6, 46.7, 34.3, 34.1, 33.4, 29.6, 29.5, 28.2, 27.8, 26.6, 25.93, 25.89 20.3; IR 2938, 1634, 1562 cm^{-1}. Anal. Calcd for $C_{17}H_{28}N_2O$: C, 73.87; H, 10.21. Found: C, 73.67; H, 10.26.

4.4. General procedure for the reduction of the amide moiety with $LiAlH_4$, exemplified by the formation of 1b

Compound **5** (402 mg, 1.7 mmol) was dissolved in dry THF (10 mL) and cooled to 0 °C. $LiAlH_4$ (0.511 g, 13.5 mmol) was added in one portion. The reaction mixture was refluxed for 18 h, and then cooled to 0 °C. Diethyl ether (10 mL) was added after which saturated aqueous Na_2SO_4 was added dropwise until gas evolution ceased. The crude mixture was filtered through celite and the resulting cake washed with a 9:1 CH_2Cl_2–MeOH mixture. The organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting pale yellow oil was purified by Kugelrohr distillation to give the desired diamine **1b**.

4.4.1. Data for (+)-*N*-ethyl-decahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocine 1b.[6] Prepared from **5** according to the general procedure for the reduction with $LiAlH_4$. Colourless oil, yield 312 mg (88%). Data for **1b** are in accordance with published data for this compound.[6] Bp 75–80 °C (oven temp) at 0.4 mmHg; $[\alpha]_D^{20} = +40.9$ (c 1.10 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.11 (d, J = 11.2 Hz, 1H), 2.93–2.79 (m, 3H), 2.56–2.51 (m, 1H), 2.20 (dt, J = 12.4, 4.0 Hz, 2H), 2.03–1.98 (m, 1H), 1.92–1.46 (m, 11H), 1.32–1.25 (m, 2H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 66.4, 60.7, 59.2, 57.7, 53.7, 52.5, 35.1, 34.4, 30.8, 25.8, 25.4, 12.0, one carbon missing due to overlap; IR 2915 cm^{-1}. HRMS (ECI) m/z $(M+1)^+$ calcd for $C_{13}H_{25}N_2$: 209.2019. Found: 209.2018. Anal. Calcd for $C_{13}H_{24}N_2$: C, 74.94; H, 11.61. Found: C, 75.06; H, 11.73.

4.4.2. Data for (+)-*N*-benzyl-decahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocine 1c. Prepared from **8d** according to the general procedure for reduction with $LiAlH_4$. Colourless oil, which solidified upon cooling, to yield 838 mg (91%). Bp 180–190 °C (oven temp) at 6 mmHg; $[\alpha]_D^{20} = +44.6$ (c 2.79 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (d, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5Hz, 2H), 7.24 (t, J = 7.5 Hz, 1H), 3.73 (d, J = 13.7 Hz, 1H), 3.27 (d, J = 13.7 Hz, 1H), 3.02–2.85 (m, 4H), 2.49 (dd, J = 10.6, 2.8 Hz, 1H), 2.30 (d, J = 10.3 Hz, 1H), 2.07 (dd, J = 11.2, 3.1 Hz, 1H), 1.96 (d, J = 8.9 Hz, 1H), 1.92–1.46 (m, 9H), 1.34–1.25 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.7, 129.0, 128.1, 126.7, 66.3, 63.5, 61.0, 58.7, 57.5, 53.3, 35.3, 34.3, 31.0, 30.8, 26.4, 25.5; IR 2912 cm^{-1}. Anal. Calcd for $C_{18}H_{26}N_2$: C, 79.95; H, 9.69. Found: C, 80.08; H, 9.78.

4.4.3. Data for (+)-*N*-cyclopropylmethyl-decahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocine 1d. Prepared from **8a** according to the general procedure for the reduction with $LiAlH_4$. Colourless oil, yield 0.91 g (94%). Bp 135–140 °C (oven temp) at 0.8 mmHg; $[\alpha]_D^{20} = +21.7$ (c 1.0 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.24 (d, J = 11.2 Hz, 1H), 2.86–2.73 (m, 4H), 2.25 (d, J = 10.8 Hz, 1H), 2.15 (d, J = 11.2 Hz, 1H), 1.92 (d, J = 11.6 Hz, 1H), 1.83 (d, J = 11.2 Hz, 1H) 1.79–1.40 (m, 10H), 1.29–1.16 (m, 2H), 0.87–0.79 (m, 1H), 0.47–0.41 (m, 1H), 0.36–0.30 (m, 1H), 0.04–(−0.02) (m, 1H), −0.04–(−0.10) (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 66.6, 65.0, 60.9, 59.1, 57.8, 53.6, 35.2, 34.3, 31.0, 30.8, 26.0, 25.5, 8.4, 6.0, 2.2; IR 2930 cm^{-1}. Anal. Calcd for $C_{15}H_{26}N_2$: C, 76.87; H, 11.18. Found: C, 76.74; H, 11.26.

4.4.4. Data for (+)-*N*-isopropyl-decahydro-1,5-methano-pyrido[1,2-*a*][1,5]diazocine 1e. Prepared from **8b** according to the general procedure for the reduction with $LiAlH_4$. Colourless oil, yield 0.91 g (94%). Bp 75–80 °C (oven temp) at 0.4 mmHg; $[\alpha]_D^{20} = +31.6$ (c 0.55 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.90 (d, J = 11.2 Hz, 1H), 2.81–2.71 (m, 3H), 2.62–2.51 (m, 2H), 2.20 (s, 1H), 2.16–2.12 (m, 1H), 1.85 (d, J = 11.2 Hz, 1H), 1.80–1.67 (m, 3H), 1.59–1.41 (m, 5H), 1.26–1.18 (m, 3H), 1.03 (d, J = 6.4 Hz, 3H), 0.88 (d, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ

66.5, 61.0, 57.6, 55.0, 54.4, 46.4, 35.0, 34.1, 30.7, 30.5, 25.9, 25.4, 20.6, 15.2; IR 2931 cm^{-1}. Anal. Calcd for $C_{14}H_{26}N_2$: C, 75.62; H, 11.79. Found: C, 75.58; H, 11.86.

4.4.5. Data for (+)-*N*-cyclohexyl-decahydro-1,5-methanopyrido[1,2-*a*][1,5]diazocine 1f. Prepared from **8c** according to the general procedure for the reduction with $LiAlH_4$. Colourless oil, yield 1.62 g (87%). Bp 130–145 °C (oven temp) at 0.4 mmHg; $[\alpha]_D^{20} = +25.6$ (*c* 0.75 in $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 3.55 (br t, $J = 4.6$ Hz, 1H), 2.95 (d, $J = 10.8$ Hz, 1H), 2.83–2.68 (m, 3H), 2.30–2.12 (m, 3H), 1.85–1.69 (m, 8H), 1.62–1.01 (m, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 66.5, 63.4, 61.2, 57.6, 47.1, 35.8, 35.1, 34.0, 30.8, 30.7, 26.9, 26.4, 26.1, 25.7, 25.5, 25.3, 24.4; IR 2930 cm^{-1}. Anal. Calcd for $C_{17}H_{30}N_2$: C, 77.80; H, 11.52. Found: C, 77.73; H, 11.46.

4.5. Preparation of (−)-(*R*)-2,2-bipyrrolidino-1,1-binaphthalene 11

To (+)-(*R*)-2,2-diamino-1,1-binaphthalene (803 mg, 2.82 mmol) dissolved in 8 mL toluene was added *N*-ethyldiisopropylamine (1.60 g, 12.4 mmol) followed by 1,4-dibromobutane (1.34 g, 6.20 mmol). The reaction was stirred at reflux under argon for 28 h. H_2O (95 mL) was added and the solution extracted with 110 mL toluene. The aqueous layer was washed once with toluene (80 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo to a volume of 10 mL. The reaction mixture was purified by chromatography using toluene as the eluent. The solution was concentrated in vacuo and recrystallized from Et_2O, yielding **11** as a pale yellow crystalline solid (665 mg, 74%); $[\alpha]_D^{25} = -1.55$ (*c* 1, $CHCl_3$); mp 182.5–183.5 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, $J = 9.2$ Hz, 2H), 7.71 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 9.0$Hz 2H), 7.15–7.09 (m, 6H), 3.15–3.11 (m, 4H), 2.91–2.89 (m, 4H), 1.67–1.60 (m, 8H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 146.3, 136.6, 128.5, 127.6, 126.9, 126.1, 126.0, 121.4, 117.6, 117.3, 49.7, 26.0; IR 2963, 2862, 1378 cm^{-1}. Exact mass calculated for $C_{28}N_2H_{29}$ requires 392.2252 *m/z*. Found 392.2252 *m/z*.

4.6. Preparation of (1*S*,2*S*)-bis(*N*-pyrrolidino)-1,2-diphenylethylene 12[14]

(1*S*,2*S*)-(−)-1,2-Diphenylethylenediamine (412 mg, 1.94 mmol) was dissolved in dichloromethane (8 mL) under a nitrogen atmosphere. The solution was cooled to 0 °C and triethylamine (825 mg, 8.15 mmol) and 1,4-dibromobutane (881 mg, 4.08 mmol) were added. The reaction was warmed to room temperature under stirring. After 3.5 h, tetrabutylammonium iodide (144 mg, 0.39 mmol) was added. The reaction mixture was stirred for 4 days and subsequently dissolved in pentane, ether and aqueous $NaHCO_3$. The organic layer was washed with H_2O (25 mL) followed by brine (25 mL). The aqueous layer was washed with Et_2O and the combined organic phases dried over $MgSO_4$, filtered and concentrated in vacuo. After recrystallization from MeOH, a white crystalline product **12** was obtained (73 mg, 12%); $[\alpha]_D^{25} = -43.4$ (*c* 0.67, $CHCl_3$); mp 116.6–117.4 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.07 (dd, $J = 7.3$, 2.1 Hz, 6H), 6.92–6.88 (m, 4H), 3.95 (s, 2H), 2.72 (d, $J = 8.4$ Hz, 4H), 2.51 (d, $J = 8.4$ Hz, 4H), 1.80–1.66 (m, 8H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 139.3, 130.1, 127.0, 126.5, 72.3, 52.8, 23.4; IR 2956, 2812, 1492 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_2$: C, 82.54; H, 8.76. Found: C, 82.45; H, 8.81.

4.7. Preparation of (1*R*,2*R*)-*N*,*N*-bisallyldiamine-cyclohexane 15

(2.0 g, 9.5 mmol) of (1*R*,2*R*)-1,2-diammoniumcyclohexane-mono-(+)-tartrate was placed in a 500 mL round flask under nitrogen. THF (300 mL) and K_2CO_3 (10.39 g, 75.2 mmol) were added and the reaction was stirred under nitrogen for 1 h. Allyl bromide (4.78 g, 39.5 mmol) was added in portions and the reaction stirred at reflux under nitrogen for 80 h. The reaction mixture was then cooled to room temperature. After filtration, HCl (250 mL) (5%) was added. The aqueous phase was washed with 3×150 mL Et_2O. Saturated aqueous Na_2CO_3 was then added until the solution attained pH 10. The aqueous layer was extracted with CH_2Cl_2 (3×150 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. Kugelrohr distillation (130 °C, 0.6 mmHg) yielded **15** as a pale yellow oil (2.55 g, 97%); $[\alpha]_D^{25} = -5.5$ (*c* 3.18, $CHCl_3$) ^1H NMR ($CDCl_3$, 400 MHz): δ 5.85 (m, 4H), 5.15 (d, $J = 18.6$ Hz, 2H), 5.02 (d, $J = 10.0$ Hz, 2H), 3.25 (dd, $J = 14.2$, 5.1 Hz, 4H), 2.99 (dd,$J = 14.2$, 7.3 Hz, 4H), 2.66 (m, 2H), 1.86 (m, 2H), 1.69 (m, 2H), 1.09 (m, 4H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 138.9, 115.8, 59.7, 53.1, 27.0, 26.2; IR 2926, 1641, 1448, 1416 cm^{-1}. Anal. Calcd for $C_{18}H_{30}N_2$: C, 78.77; H, 11.02. Found: C, 78.68; H, 10.96.

4.8. General procedure for the asymmetric deprotonation of phosphine boranes 9a–c, followed by trapping with benzophenone

To a cooled (−78 °C) solution of the chiral amine (0.30 mmol) in diethyl ether (1 mL), *s*-BuLi (0.27 mmol, solution in cyclohexane) was added dropwise followed after 10 min by the addition of the dimethyl phosphine borane (**9a**, **b** or **c**, 0.27 mmol) dissolved in diethyl ether (1 mL). After 3 h at −78 °C, benzophenone (55 mg, 0.30 mmol) dissolved in diethyl ether (0.5 mL), was added dropwise. The reaction was warmed to −20 °C, stirred for 4 h and then quenched with HCl (1 mL) (1 M) and diluted with 4 mL ethyl acetate. After phase separation, the aqueous layer was treated once with ethyl acetate (4 mL) and the combined organic phases washed with 1 M HCl, H_2O and aqueous NaCl (1×8 mL in each case). The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo to afford the crude product. Purification by flash chromatography on silica gel using 5% ethyl acetate in petroleum ether (40–60 °C) afforded pure **10a**–**c**, as white crystalline solids. Data for (*R*)-**10a** are in accordance with the published data for the corresponding (*S*)-enantiomer, apart from the sign of the specific rotation.[3]

4.8.1. Data for (*R*)-*P*-(2,2-Diphenyl-2-hydroxyethyl)-*P*-methyl-cyclohexyl-phosphine borane (*R*)-10b. Mp 91.2–92.2 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48–7.45 (m, 4H), 7.33–7.29 (m, 6H), 4.32 (s, 1H), 2.77 (m, 2H), 1.79 (m, 5H), 1.38–1.19 (m, 6H), 0.83 (d, $J = 2.9$ Hz, 3H), 0.82–0.10 (broad q, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.2, 146.2, 128.5, 128.4, 127.5, 127.4, 126.1, 125.7, 77.4, 35.1 (d, $J = 29.6$ Hz), 34.4 (d, $J = 35.7$ Hz), 26.7 (t), 26.3, 26.0 (d), 7.8 (d, $J = 36.5$ Hz), some carbon peaks in the aromatic region overlap. IR 3473, 2918, 2373, 1444 cm^{-1}. Enantiomeric excess was determined by chiral HPLC (Daicel Chiralcel OJ, flow rate 1 mL/min, 20% *i*-PrOH in *n*-hexane): T_R (*R*)-**10b**: 8.0 min, (*S*)-**10b**: 12.5 min. Anal. Calcd for $C_{21}H_{31}BOP$: C, 73.91; H, 9.16. Found: C, 74.23; H, 8.97. A sample of (*R*)-**10b** with 74% ee gave an optical rotation of $[\alpha]_D^{20} = +3.0$ (*c* 0.54 in $CHCl_3$).

4.8.2. Data for (*R*)-*P*-(2,2-Diphenyl-2-hydroxyethyl)-*P*-methyl-*t*-butyl-phosphine borane 10c. Mp 116.5–117.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52–7.50 (m, 4H), 7.36–7.32 (m, 6H), 4.59 (s, 1H), 2.89 (t, 1H), 2.70 (m, 1H), 1.18 (d, $J = 13.5$ Hz, 9H), 0.75 (d, $J = 10.0$ Hz, 3H), 0.73–0.10 (broad q, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.9, 145.4, 128.5, 128.4, 127.4, 126.3, 125.5, 34.4 (d, $J = 23.5$ Hz), 28.2 (d, $J = 38.5$ Hz), 24.9, 6.7 (d, $J = 32.1$ Hz), some carbon peaks in the aromatic region overlap and one carbon overlaps with $CDCl_3$; IR 3473, 2975, 2364, 1444 cm^{-1}. Enantiomeric excess was determined by chiral HPLC (Daicel Chiralcel OD, flow rate 0.5 mL/min, 5% *i*-PrOH in *n*-hexane): T_R (*R*)-**10c**: 9.7 min, (*S*)-**10c**: 11.5 min. Anal. Calcd for $C_{19}H_{28}BOP$: C, 72.63; H, 8.98. Found: C, 72.53; H, 9.02. A sample of (*R*)-**10c** with 92% ee gave a specific rotation of $[\alpha]_D^{20} = -14.7$ (*c* 0.47 in $CHCl_3$).

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