Chinese Chemical Letters 25 (2014) 557–560

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

An easy route to exotic 9-epimers of 9-amino-(9-deoxy) cinchona alkaloids with (8*S*, 9*R*) and (8*R*, 9*S*)-configurations through two inversions of configuration

Jing-Wei Wan, Xue-Bing Ma *, Rong-Xing He, Ming Li *

College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

ARTICLE INFO

Article history:
Received 8 October 2013
Received in revised form 25 November 2013
Accepted 28 November 2013
Available online 7 December 2013

Keywords:
Cinchona alkaloids
9-Amino-(9-deoxy) cinchona alkaloids
Synthesis
Inversion of configuration

ABSTRACT

Four exotic chiral organocatalysts, 9-amino-(9-deoxy) cinchona alkaloids with (8*S*, 9*R*) and (8*R*, 9*S*)-configurations, were conveniently synthesized for the first time in 27–72% total yields through two conversions of configuration at the 9-stereogenic centers of commercially available cinchona alkaloids.

1. Introduction

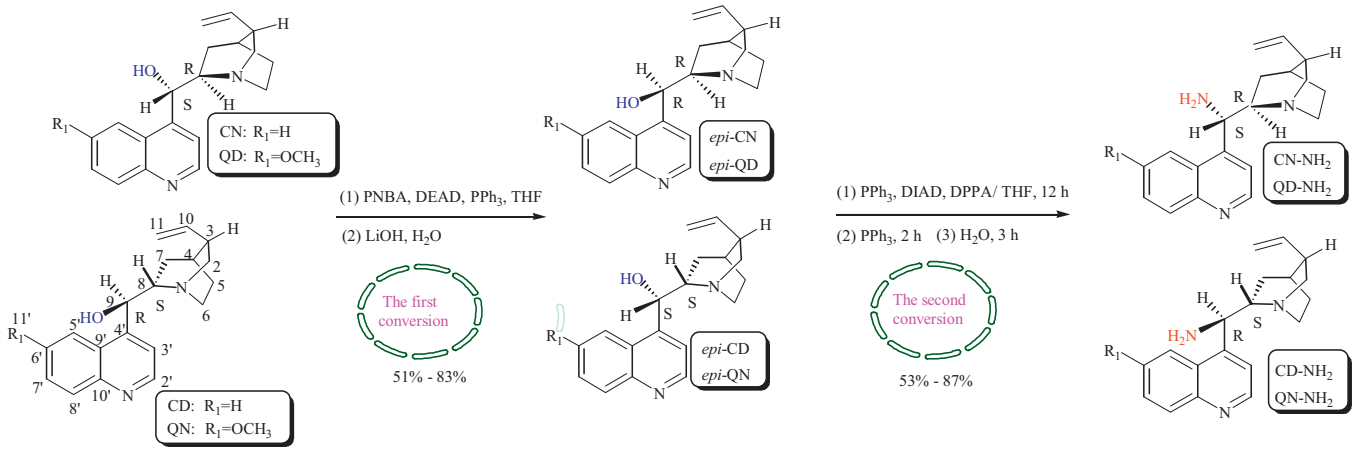
Recent years have witnessed an unthinkable upsurge in potential utility of asymmetric organocatalysis as a tool for the synthesis of enantiopure molecules under mild, environmentally benign conditions [1]. Readily, available cinchona alkaloids, namely cinchonidine (CD), cinchonine (CN), quinine (QN) and quinidine (QD), enjoyed much interest as privileged organocatalysts effective in numerous mechanistically diverse enantioselective transformations [2]. The resulting (8*S*, 9*S*) and (8*R*, 9*R*)-9-amino-(9-deoxy) cinchona alkaloids are employed as attractive and efficient organocatalysts with excellent catalytic properties in asymmetric Aldol addition [3], Diels–Alder reaction [4], Friedel–Crafts reaction [5], Henry reaction [6], Mannich reaction [7], Michael addition [8], hydrogenation [9], epoxidation [10], 1,3-dipolar cycloaddition [11], decarboxylation [12] and methanolytic desymmetrization [13]. In the aforementioned organocatalytic asymmetric reactions, the stereochemistry of catalytic products, to a great extent, generally depended on the configurations of the 8- and 9-stereogenic centers in 9-amino-(9-deoxy) cinchona alkaloids, although the experimental observations occasionally revealed the unexpected hint of enantioselectivity [14]. Considering the influence of stereochemical diversity of the organocatalyst on the stereochemistry of the products, (8*S*, 9*R*) and (8*R*, 9*S*)-9-amino-(9-deoxy) cinchona alkaloids possibly play the different and unthinkable role in determining the spatial structures of catalytic products. However, until now, (8*S*, 9*R*) and (8*R*, 9*S*)-9-amino-(9-deoxy) cinchona alkaloids have not been developed or received considerable attention. Based on the Mitsunobu reaction, in this report, four exotic pseudoenantiomers of (8*S*, 9*R*) and (8*R*, 9*S*)-9-amino-(9-deoxy) cinchona alkaloids were conveniently synthesized for the first time through the two conversions of the configurations at the 9-stereogenic centers in commercially available cinchona alkaloids (Scheme 1).

2. Experimental

General procedure for 9-amino(9-deoxy) cinchona alkaloids: The *epi*-cinchona alkaloids (*epi*-CD, CN, QN and QD) (1.63 mmol) and triphenylphosphine (520 mg, 1.95 mmol) were dissolved in 6 mL of anhydrous THF under an argon atmosphere and added dropwise 2 mL of diisopropyl azidocarboxylate (DIAD) (0.38 mL, 1.95 mmol) and 1 mL THF solution of diphenylphosphoryl azide (DPPA) (0.42 mL, 1.95 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 12 h and 50 °C for 2 h and then triphenylphosphine (563 mg, 2.12 mmol) added in one portion. After the gas evolution had ceased (about 2 h), the reaction mixture was cooled to room temperature, added 0.3 mL of water, stirred for another 3 h and evaporated under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2 and added 5 mL of diluted hydrochloric acid (10%). The aqueous phase was washed with CH_2Cl_2 (3 × 10 mL), alkalinized with an excess of concentrated

* Corresponding authors.
E-mail addresses: zcj123@swu.edu.cn (X.-B. Ma), Liming@swu.edu.cn (M. Li).

1001-8417/$ – see front matter
http://dx.doi.org/10.1016/j.cclet.2013.12.008



Scheme 1. The synthetic route to 9-amino-(9-deoxy) cinchona alkaloids through the two inversions of configuration.

ammonia and extracted with CH_2Cl_2 (3 × 30 mL). The organic phase was dried over anhydrous Na_2SO_4. The concentrated organic phase was purified by silica gel column chromatography using $CHCl_3$–MeOH (40:1, v/v) as an eluent to afford the title compounds as yellowish viscous oils.

CN-NH_2: Yellowish viscous oil, $[\alpha]_D^{20}$ = −56.0 (*c* 0.30, EtOH). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 8.89 (d, 1 H, ^3J = 6.0 Hz, H-2′), 8.21 (d, 1 H, ^3J = 6.0 Hz, H-5′), 8.12 (d, 1 H, ^3J = 6.0 Hz, H-8′), 7.70 (t, 1 H, ^3J = 6.0 Hz, H-7′), 7.57 (t, 1 H, ^3J = 6.0 Hz, H-6′), 7.41 (d, 1 H, ^3J = 3.0 Hz, H-3′), 5.93–6.05 (m, 1 H, H-10), 5.12 (d, 1 H, ^3J = 6.0 Hz, H-11α), 5.08 (d, 1 H, ^3J = 6.0 Hz, H-11β), 4.81 (d, 1 H, ^3J = 9.0 Hz, H-9), 3.18 (q, 1 H, ^3J = 9.0 Hz, H-8), 2.66–2.88 (m, 4 H, H-6α, H-2-exo, H-6β, H-2-endo), 2.25 (q, 1 H, ^3J = 9.0 Hz, H-3), 1.90–1.95 (m, 3 H, NH_2, H-4), 1.80 (d, 2 H, ^3J = 9.0 Hz, H-7α, H-7β), 1.62 (q, 2 H, ^3J = 9.0 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.0 (C-2′), 148.3 (C-10′), 139.3 (C-4′), 130.2 (C-10), 129.1 (C-7′), 128.8 (C-8′), 126.5 (C-9′), 126.3 (C-6′), 122.6 (C-5′), 117.6 (C-3′), 114.9 (C-11), 60.4 (C-8), 52.1 (C-9), 49.1 (C-2), 48.1 (C-6), 38.8 (C-3), 29.4 (C-7), 27.5 (C-4), 25.6 (C-5). Anal. Calcd. for $C_{19}H_{23}N_3$: C, 77.78; H, 7.90; N, 14.32. Found: C, 77.75; H, 9.93; N, 14.27. MS: *m*/*z* 293.8 $[M+H]^+$.

QD-NH_2: Yellowish viscous oil, $[\alpha]_D^{20}$ = −106.7 (*c* 0.79, EtOH). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 8.72 (d, 1 H, ^3J = 6.0 Hz, H-2′), 8.01 (d, 1 H, ^3J = 9.0 Hz, H-8′), 7.42 (s, 1 H, H-5′), 7.31–7.37 (m, 2 H, H-7′, H-3′), 5.93–6.04 (m, 1 H, H-10), 5.04–5.12 (m, 2 H, H-11), 4.73 (d, 1 H, ^3J = 9.0 Hz, H-9), 3.95 (s, 3 H, H-11′), 3.13 (q, 1 H, ^3J = 9.0 Hz, H-8), 2.65–2.92 (m, 4 H, H-6α, H-2-exo, H-6β, H-2-endo), 2.24 (q, 1 H, ^3J = 9.0 Hz, H-3), 2.13 (s, 2 H, NH_2), 1.86 (s, 1 H, H-4), 1.77 (q, 2 H, ^3J = 6.0 Hz, H-7α, H-7β), 1.60 (q, 2 H, ^3J = 9.0 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5 (C-6′), 149.3 (C-2′), 147.6 (C-10′), 144.4 (C-10), 140.2 (C-4′), 131.6 (C-8′), 127.6 (C-9′), 121.2 (C-3′), 118.0 (C-7′), 114.5 (C-11), 101.0 (C-5′), 60.6 (C-8), 55.4 (C-2), 52.8 (C-11′), 49.3 (C-9), 48.4 (C-6), 39.2 (C-3), 27.7 (C-7), 26.1 (C-5), 25.2 (C-4). Anal. Calcd. for $C_{20}H_{25}N_3O$: C, 74.27; H, 7.79; N, 12.99; O, 4.95. Found: C, 74.34; H, 7.81; N, 12.96; O, 4.96. MS: *m*/*z* 324.7 $[M+H]^+$.

CD-NH_2: Yellowish viscous oil, $[\alpha]_D^{20}$ = −55.6 (*c* 1.63, EtOH). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 8.89 (d, 1 H, ^3J = 6.0 Hz, H-2′), 8.22 (d, 1 H, ^3J = 6.0 Hz, H-5′), 8.13 (d, 1 H, ^3J = 9.0 Hz, H-8′), 7.70 (t, 1 H, ^3J = 6.0 Hz, H-7′), 7.57 (t, 1 H, ^3J = 6.0 Hz, H-6′), 7.42 (1 d, H, ^3J = 6.0 Hz, H-3′), 5.86–5.98 (m, 1 H, H-10), 5.03–5.09 (m, 2 H, H-11), 4.76 (d, 1 H, ^3J = 9.0 Hz, H-9), 3.23 (q, 1 H, ^3J = 9.0 Hz, H-8), 2.96–3.07 (m, 2 H, H-6α, H-2-exo), 2.66 (d, 1 H, ^3J = 15.0 Hz, H-6β), 2.55 (td, 1 H, $^3J_1$ = 12.0 Hz, $^3J_2$ = 6.0 Hz, H-2-endo), 2.28 (s, 3 H, NH_2, H-3), 2.16 (m, 1 H, H-4), 1.90 (d, 1 H, H-7β), 1.68 (td, 1 H, $^3J_1$ = 12.0 Hz, $^3J_2$ = 3.0 Hz, H-7α), 1.50–1.56 (q, 2 H, ^3J = 9.0 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.3 (C-2′), 148.6 (C-10′), 141.7 (C-4′), 130.5 (C-10), 129.3 (C-7′), 128.9 (C-8′), 126.6 (C-9′), 126.5 (C-6′), 122.6 (C-5′), 118.0 (C-3′), 114.5 (C-11), 60.6 (C-8), 56.1 (C-2), 53.4 (C-9), 41.8 (C-6), 39.6 (C-3), 27.7 (C-7), 27.6 (C-4), 26.4 (C-5). Anal. Calcd. for $C_{19}H_{23}N_3$: C, 77.78; H, 7.90; N, 14.32. Found: C, 77.72; H, 9.98; N, 14.29. MS: *m*/*z* 293.7 $[M+H]^+$.

QN-NH_2: Yellowish viscous oil, $[\alpha]_D^{20}$ = −42.3 (*c* 1.76, EtOH). ^{1}H-NMR (300 MHz, $CDCl_3$, Me_4Si): δ 8.74 (d, 1 H, ^3J = 6.0 Hz, H-2′), 8.02 (d, 1 H, ^3J = 12.0 Hz, H-8′), 7.44 (d, 1 H, ^3J = 3.0 Hz, H-5′), 7.38 (1 H, d, ^3J = 3.0 Hz, H-7′), 7.35 (d, 1 H, ^3J = 6.0 Hz, H-3′), 5.87–5.99 (1 H, m, H-10), 5.03–5.09 (m, 2 H, H-11), 4.63 (d, 1 H, ^3J = 9.0 Hz, H-9), 3.96 (s, 3 H, H-11′), 3.21 (q, 1 H, ^3J = 9.0 Hz, H-8), 2.95–3.07 (m, 2 H, H-6α, H-2-exo), 2.66 (d, 1 H, ^3J = 12.0 Hz, H-6β), 2.56 (1 H, td, $^3J_1$ = 12.0 Hz, $^3J_2$ = 3.0 Hz, H-2-endo), 2.28 (s, 1 H, H-3), 2.15 (td, 1 H, $^3J_1$ = 9.0 Hz $^3J_2$ = 3.0 Hz, H-4), 1.90 (s, 3 H, NH_2, H-7β,), 1.67 (td, 1 H, $^3J_1$ = 15.0 Hz, $^3J_2$ = 3.0 Hz, H-7α), 1.52 (2 q, H, ^3J = 9.0 Hz, H-5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.7 (C-6′), 149.2 (C-2′), 147.8 (C-10′), 144.7 (C-10), 141.8 (C-4′), 131.9 (C-8′), 127.6 (C-9′), 121.1 (C-3′), 118.3 (C-7′), 114.4 (C-11), 101.1 (C-5′), 60.5 (C-8), 56.1 (C-2), 55.6 (C-11′), 53.7 (C-9), 41.9 (C-6), 39.6 (C-3), 27.8 (C-7), 27.7 (C-4), 26.5 (C-5). Anal. Calcd. for $C_{20}H_{25}N_3O$: C, 74.27; H, 7.79; N, 12.99; O, 4.95. Found: C, 74.32; H, 7.80; N, 12.97; O, 4.98. MS: *m*/*z* 324.9 $[M+H]^+$.

3. Results and discussion

The first conversion of cinchona alkaloids to 9-epimers of cinchona alkaloids was achieved through one-pot inversion of Mitsunobu esterification–saponification [15]. Four cinchona alkaloids (CD, CN, QN and QD) were esterified with 4-nitrobenzoic acid (NBA) and subsequently treated *in situ* with aqueous lithium hydroxide solution. The corresponding 9-*epi*-cinchona alkaloids (*epi*-CD, CN, QN and QD) were easily purified by flash column chromatography using $CHCl_3$/*t*-BuOMe (3:1, v/v) as an eluent to remove Ph_3PO and diethyl hydrazine-1,2-dicarboxylate, and then $CHCl_3$/MeOH/Et_3N (40:1:1, v/v/v) to obtain the target compounds of analytical purity in 51%–83% yield, which were identified by ^{1}H- NMR, ^{13}C NMR, $[\alpha]_D^{20}$ and R_f (Table 1).

According to the reported synthetic procedure [16], four (8*S*, 9*R*) and (8*R*, 9*S*)-9-amino(9-deoxy) cinchona alkaloids (CD-NH_2,

Table 1
Inversion of cinchona alkaloids by Mitsunobu esterification/saponification.[a]

Entry	*epi*-Alkaloid	(R_f)[b]	$[\alpha]_D^{20}$ (*c*, EtOH)	Yield (%)
1	*epi*-CD	0.611	+56.4 (0.86)	68
2	*epi*-QN	0.575	+38.8 (0.81)	83
3	*epi*-CN	0.602	+112.6 (1.47)	51
4	*epi*-QD	0.584	+94.2 (1.23)	78

[a] Reaction conditions: NBA (1.1 equiv.), DEAD (1.2 equiv.), Ph_3P, (1.3 equiv.), then LiOH (5 equiv.).
[b] Eluent: $CHCl_3$–MeOH (10:1, v/v).

Table 2
Inversion of *epi*-cinchona alkaloids to 9-amino(9-deoxy) cinchona alkaloids by Mitsunobu reaction.

Entry	Amino-alkaloid	(R_f)[a]	$[\alpha]_D^{20}$ (*c*, EtOH)	Yield (%)[b]
1	CD-NH_2	0.16	−55.6 (1.63)	81
2	QN-NH_2	0.20	−42.3 (1.76)	87
3	CN-NH_2	0.17	−56.0 (0.30)	53
4	QD-NH_2	0.19	−106.7 (0.79)	75

[a] Eluent: $CHCl_3$–MeOH (10:1, v/v).
[b] Isolated yield.

CN-NH_2, QN-NH_2, QD-NH_2) were conveniently prepared in good yields (53%–87%) [17]. The key step was the Mitsunobu reaction that led to the C_9-azido compound by an S_N2 mechanism. The reduction is performed *in situ* by adding triphenylphosphane. Hydrolysis of the intermediate aminophosphorane yielded free amine. The pure 9-amino(9-deoxy) cinchona alkaloids (CD-NH_2, CN-NH_2, QN-NH_2 and QD-NH_2) were easily separated by silica gel flash column chromatography using $CHCl_3$/MeOH (40:1, v/v) as an eluent to afford yellowish viscous oils, whose structures were identified by ^{1}H NMR, ^{13}C NMR, ^{1}H COSY 2D NMR, ^{1}H NOESY 2D NMR, $[\alpha]_D^{20}$ and R_f (Table 2). It is noteworthy that the $[\alpha]_D^{20}$ values of CD-NH_2, CN-NH_2, QN-NH_2 and QD-NH_2 were converted from positive to negative due to the inversions of the configurations at the 9-hydroxyl groups of *epi*-CD, CN, QN and QD.

Herein, we provided the direct evidence for conformational preference of 9-amino(9-deoxy) cinchona alkaloids (CD-NH_2, CN-NH_2, QN-NH_2 and QD-NH_2) through a combination of ^{1}H NOESY 2D NMR and computational methods. Full geometric optimization calculations were performed in chloroform using the polarized continuum model (PCM) with B3LYP functional and 6-31G(d) basis set, and their minimum energy structures were shown in the Supporting information. For the identification of conformers, the interring NOEs between the quinoline and quinuclidine protons and NOEs involving H_8 and H_9 are most useful. Pointedly, four 9-amino(9-deoxy) cinchona alkaloids appeared to exhibit the hindered rotations around the $C_{4'}$–C_9 and C_9–C_8 bonds and to favor only a narrow range of the available conformational space of the molecule. The ^{1}H NOESY 2D NMR of CN-NH_2 displayed only three cross-peaks related to aromatic hydrogen, indicating close interactions between the $H_{5'}$–H_9, $H_{5'}$–H_8, and $H_{3'}$–H_6 pairs of atoms. These data mainly supported the minimum energy conformation of CN-NH_2, and elucidated that CN-NH_2 favored the open conformation (Fig. 1). Although the NOESY spectrum of CD-NH_2, QN-NH_2 and QD-NH_2 did not directly support their minimum energy conformations, but the favored conformations could be obtained through molecular rotations around the $C_{4'}$–C_9 and C_9–C_8 bonds from their minimum energy structures, in which the $H_{5'}$–H_9 and $H_{3'}$–H_8 pairs of atoms showed close NOE interactions with the closed conformations [18]. Furthermore, ^{1}H NMR and ^{13}C NMR spectra of (8*S*, 9*R*)-CD-NH_2 differed from that of (8*S*, 9*S*)-9-amino-(9-deoxy) cinchona alkaloids (*epi*-CD-NH_2) because of their opposite configurations of carbon atoms at C_9-position. The mixture of 50 wt% (8*S*, 9*R*)-CD-NH_2 and 50 wt% (8*S*, 9*S*)-*epi*-CD-NH_2 showed the more sophisticated ^{1}H NMR and ^{13}C NMR spectra than their own shown in the Supporting information, which provided the indirect evidence to elucidate the different configurations at the C_9-position between (8*S*, 9*R*)-CD-NH_2 and (8*S*, 9*S*)-*epi*-CD-NH_2.

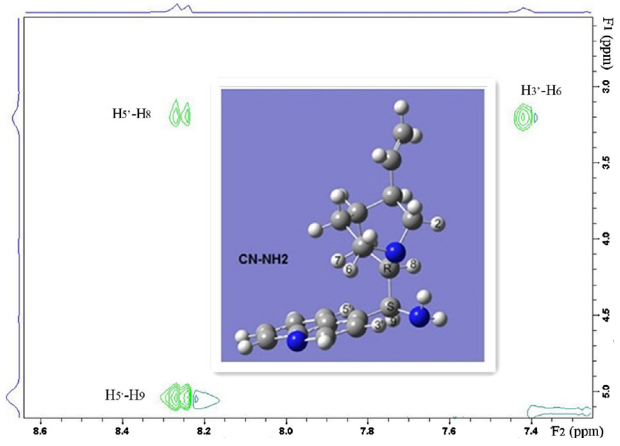


Fig. 1. ^{1}H NOESY 2D NMR and minimum energy conformation of CN-NH_2.

4. Conclusion

In summary, four exotic (8*S*, 9*R*) and (8*R*, 9*S*)-9-amino(9-deoxy) cinchona alkaloids were conveniently synthesized for the first time through the two conversions of the configurations at the 9-stereogenic centers of commercially available cinchona alkaloids. Their catalytic performances in various asymmetric reactions are under investigation.

Acknowledgments

Research support from the National Science Foundation of China (No. 21071116) and Chongqing Scientific Foundation, China (No. 2010BB4126).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2013.12.008.

References

[1] (a) J. Seayad, B. List, Asymmetric organocatalysis, Org. Biomol. Chem. 3 (2005) 719–724;
(b) C.F. Barbas III, Organocatalysis lost: modern chemistry, ancient chemistry, and an unseen biosynthetic apparatus, Angew. Chem. Int. Ed. 47 (2008) 42–47;
(c) W. Notz, F. Tanaka, C.F. Barbas III, Enamine-based organocatalysis with proline and diamines: the development of direct catalytic asymmetric Aldol, Mannich, Michael, and Diels–Alder reactions, Acc. Chem. Res. 37 (2004) 580–591;
(d) H. Chen, R. Jiang, Q.F. Wang, et al., Synthesis of chiral dihydrofuran compounds by thiourea derivatives-catalyzed "interrupted" Feist–Bénary reaction, Chin. Chem. Lett. 21 (2010) 167–170.
[2] (a) S.K. Tian, Y.G. Chen, J.F. Hang, et al., Asymmetric organic catalysis with modified cinchona alkaloids, Acc. Chem. Res. 37 (2004) 621–631;
(b) S.J. Connon, Asymmetric catalysis with bifunctional cinchona alkaloid-based urea and thiourea organocatalysts, Chem. Commun. (2008) 2499–2510;
(c) T. Marcelli, H. Hiemstra, Cinchona alkaloids in asymmetric organocatalysis, Synthesis 8 (2010) 1229–1279.
[3] (a) J. Zhou, V. Wakchaure, P. Kraft, B. List, Primary-amine-catalyzed enantioselective intramolecular aldolizations, Angew. Chem. Int. Ed. 47 (2008) 7656–7658;
(b) B.L. Zheng, Q.Z. Liu, C.S. Guo, X.L. Wang, L. He, Highly enantioselective direct Aldol reaction catalyzed by cinchona derived primary amines, Org. Biomol. Chem. 5 (2007) 2913–2915;
(c) J.Q. Zhou, J.W. Wan, X.B. Ma, W. Wang, Copolymer-supported heterogeneous organocatalyst for asymmetric Aldol addition in aqueous medium, Org. Biomol. Chem. 10 (2012) 4179–4185;
(d) W. Wang, X.B. Ma, J.W. Wan, J. Cao, Q. Tang, Preparation and confinement effect of a heterogeneous 9-amino-9-deoxy-epi-cinchonidine organocatalyst for asymmetric Aldol addition in aqueous medium, Dalton Trans. 41 (2012) 5715–5726.
[4] R.P. Singh, K. Bartelson, Y. Wang, et al., Enantioselective Diels–Alder reaction of simple α,β-unsaturated ketones with a cinchona alkaloid catalyst, J. Am. Chem. Soc. 130 (2008) 2422–2423.
[5] (a) H.M. Li, Y.Q. Wang, L. Deng, Enantioselective Friedel–Crafts reaction of indoles with carbonyl compounds catalyzed by bifunctional cinchona alkaloids, Org. Lett. 8 (2006) 4063–4065;
(b) G. Bartoli, M. Bosco, A. Carlone, et al., Organocatalytic asymmetric Friedel–Crafts alkylation of indoles with simple α,β-unsaturated ketones, Org. Lett. 9 (2007) 1403–1405.
[6] P. Hammar, T. Marcelli, H. Hiemstra, F. Himo, Density functional theory study of the *Cinchona thiourea*-catalyzed Henry reaction: mechanism and enantioselectivity, Adv. Synth. Catal. 349 (2007) 2537–2548.

[7] T.Y. Liu, H.L. Cui, J. Long, et al., Organocatalytic and highly stereoselective direct vinylogous Mannich reaction, J. Am. Chem. Soc. 129 (2007) 1878–1879.
[8] (a) P.F. Li, Y.C. Wang, X.M. Liang, J.X. Ye, Asymmetric multifunctional organocatalytic Michael addition of nitroalkanes to α,β-unsaturated ketones, Chem. Commun. 28 (2008) 3302–3304;
(b) B. Vakulya, S. Varga, A. Csámpai, T. Soós, Highly enantioselective conjugate addition of nitromethane to chalcones using bifunctional cinchona organocatalysts, Org. Lett. 7 (2005) 1967–1969;
(c) J.P. Malerich, K. Hagihara, V.H. Rawal, Chiral squaramide derivatives are excellent hydrogen bond donor catalysts, J. Am. Chem. Soc. 130 (2008) 14416–14417.
[9] H.Y. Jiang, C.F. Yang, C. Li, et al., Heterogeneous enantioselective hydrogenation of aromatic ketones catalyzed by cinchona- and phosphine-modified iridium catalysts, J. Angew. Chem. Int. Ed. 47 (2008) 9240–9244.
[10] (a) X.W. Wang, C.M. Reisinger, B. List, Catalytic asymmetric epoxidation of cyclic enones, J. Am. Chem. Soc. 130 (2008) 6070–6071;
(b) X.J. Lu, Y. Liu, B.F. Sun, B. Cindric, L. Deng, Catalytic enantioselective peroxidation of α,β-unsaturated ketones, J. Am. Chem. Soc. 130 (2008) 8134–8135;
(c) Q.F. Wang, H. Chen, P. Liu, et al., Asymmetric epoxidation of alpha, beta-enones catalyzed by chiral amine salts, Chin. J. Org. Chem. 29 (2009) 1617–1620;
(d) X.D. Liu, X.L. Bai, X.P. Qiu, L.X. Gao, Asymmetric phase-transfer mediated epoxidation of alpha, beta-enones using dendritic catalysts derived from cinchona alkaloids, Chin. Chem. Lett. 16 (2005) 975–978.
[11] W. Chen, W. Du, Y.Z. Duan, et al., Enantioselective 1,3-dipolar cycloaddition of cyclic enones catalyzed by multifunctional primary amines: beneficial effects of hydrogen bonding, Angew. Chem. Int. Ed. 46 (2007) 7667–7670.
[12] H. Brunner, M.A. Baur, α-Amino acid derivatives by enantioselective decarboxylation, Eur. J. Org. Chem. (2003) 2854–2862.
[13] (a) S.H. Oh, H.S. Rho, J.W. Lee, et al., A highly reactive and enantioselective bifunctional organocatalyst for the methanolytic desymmetrization of cyclic anhydrides: prevention of catalyst aggregation, Angew. Chem. Int. Ed. 47 (2008) 7872–7875;
(b) H.S. Rho, S.H. Oh, J.W. Lee, et al., Bifunctional organocatalyst for methanolytic desymmetrization of cyclic anhydrides: increasing enantioselectivity by catalyst dilution, Chem. Commun. (2008) 1208–1210.
[14] M. Bartók, Unexpected inversions in asymmetric reactions: reactions with chiral metal complexes, chiral organocatalysts, and heterogeneous chiral catalysts, Chem. Rev. 110 (2010) 1663–1705.
[15] Ł. Sidorowicz, J. Skarżewski, Easy access to 9-epimers of cinchona alkaloids: one-pot inversion by Mitsunobu esterification–saponification, Synthesis 5 (2011) 708–710.
[16] H. Brunner, J. Bügler, B. Nuber, Enantioselective catalysis 98. Preparation of 9-amino(9-deoxy)cinchona alkaloids, Tetrahedron: Asymmetry 6 (1995) 1699–1702.
[17] C.G. Oliva, A.M.S. Silva, D.I.S.P. Resende, F.A.A. Paz, J.A.S. Cavaleiro, Highly enantioselective 1,4-Michael additions of nucleophiles to unsaturated aryl ketones with organocatalysis by bifunctional cinchona alkaloids, Eur. J. Org. Chem. (2010) 3449–3458.
[18] H. Brunner, P. Schmidt, M. Prommesberger, Enantioselective catalysis. Part 133: Conformational analysis of amides of 9-amino(9-deoxy)epicinchonine, Tetrahedron: Asymmetry 11 (2000) 1501–1502.