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Synthesis, resolution, and absolute configuration of *trans*-1-amino-2-dimethylaminocyclohexane

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Abstract—Racemic *trans*-1-amino-2-dimethylaminocyclohexane was prepared by aziridine ring opening reaction of 7-azabicyclo[4.1.0]-heptane with $HNMe_2$. The resolution of the racemate was accomplished by crystallization as the L-tartrate. The optical purity of this material was checked by NMR after derivatization to the corresponding 10-camphorsulfonamide to be >95% ee. The absolute configuration of the *R*,*R*-enantiomer was confirmed by X-ray single crystal diffraction of a bis(diammine)copper complex.

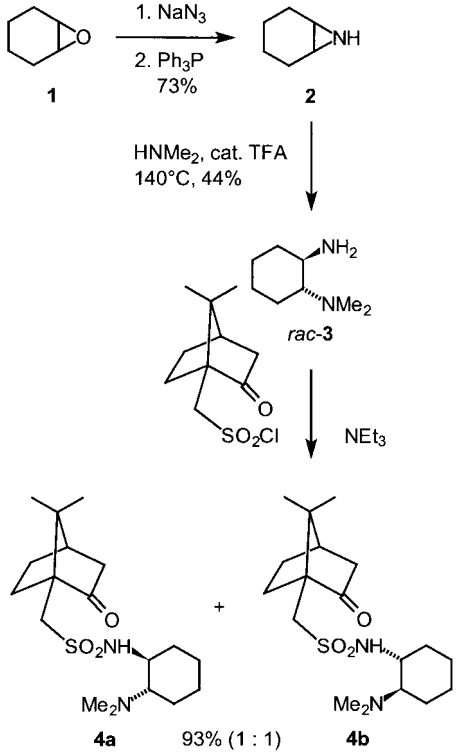
1. Introduction

In the course of our combinatorial catalysis project on asymmetric Michael reactions[1–5] we were able to show that primary amines with an additional tertiary amino or amide donor function are excellent chiral auxiliaries for the construction of quaternary stereocenters at room temperature.[6,7] Optically active *trans*-1,2-diaminocyclohexane—readily available from the racemate by resolution with tartaric acid[8]—is ubiquitous as a building block in a number of chiral ligands,[9–14] whereas the C_1-symmetric *N*,*N*-dimethyl congener **3** (Scheme 1) has not been paid attention to. As mentioned above, optically active **3** fits into our general formula of a useful chiral auxiliary for asymmetric Michael reactions, but was only mentioned once in the literature with the optical purity being uncertain and the absolute configuration being unknown.[15] Herein we wish to report on the synthesis of racemic **3**, its optical resolution and the determination of the absolute configuration.

2. Results and discussion

2.1. Racemic *trans*-1-amino-2-dimethylaminocyclohexane (*rac*-3)

A reasonable precursor of diamine *rac*-**3** seems to be aziridine **2**.[16] We were able to simplify the literature known route to **2** starting from cyclohexene oxide **1** (Scheme 1).[17] A number of reports exists on Lewis-acid catalyzed aziridine opening reactions,[18,19] but in our hands metal promoted conversions of **2** with $HNMe_2$ yielded oligomeric materials



Scheme 1. Synthesis of racemic diamine **3** and derivatization with 10-camphorsulfonyl chloride.

Keywords: amines; copper and compounds; diamines; resolution; stereochemistry.

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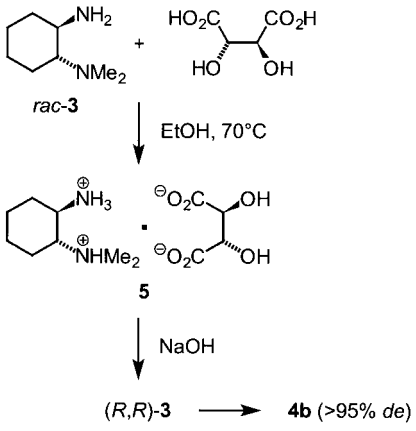

Scheme 2. Resolution of *rac*-**3** as the tartrate.

in all cases. However, the direct conversion of **2** with about 5 equiv. $HNMe_2$ and 0.05 equiv. TFA in an autoclave at 140°C turned out to be a suitable protocol yielding 44% of *rac*-**3** on a multigram scale after distillation.

2.2. Optical resolution of the diamine *rac*-3

Our initial aim was to separate diastereomeric amides derived from the diamine. Racemic *rac*-**3** was converted with 10-camphorsulfonyl chloride to yield an equimolar mixture of the two diastereoisomers **4a** and **4b** (Scheme 1). These isomers were partly separable by column chromatography on SiO_2. At least the less polar isomer **4a** was obtained with >95% de on a gram scale. However, subsequent cleavage of the sulfonamide to yield the diamine (*S*,*S*)-3 turned out to be difficult to accomplish by a number of protocols reported in the literature.[20–27] Presumably two major reasons prevented successful removal of the chiral auxiliary: First, in contrast to, for example, *N*-Tos group the camphor moiety can be reduced at the carbonyl function resulting in a number of unspecified side products. Secondly, the product (*S*,*S*)-**3** is highly polar, to some extent water soluble and volatile. The latter made impossible the separation from by-products as well as from excessive reagents. Only the application of an excess of potassium in refluxing THF provided pure (*S*,*S*)-**3** in 18% yield. Thus we decided not to follow this strategy further but to take a classical way of resolution of the chiral diamine: crystallization as the tartrate.[8] After investigation of a number of chiral acids, solvents and conditions the precipitation from a hot ethanolic solution with L-(+)-tartaric acid yielded the salt **5**, from which the enantiopure (*R*,*R*)-diamine **3** was liberated with aqueous NaOH (Scheme 2). The yield of **5** was relatively low (14%), but — importantly — the supernatant could be worked up and the quantitatively recovered partial-racemic **3** submitted to another tartrate-precipitation. Moreover, no recrystallization was necessary to obtain optically pure material. The optical purity of (*R*,*R*)-**3** was checked by conversion with camphorsulfonyl chloride as outlined in Scheme 2 to yield **4b** with >95% de. The 10-H doublets of the diastereoisomers **4a** and **4b** can be clearly distinguished by ^{1}H NMR spectroscopy.

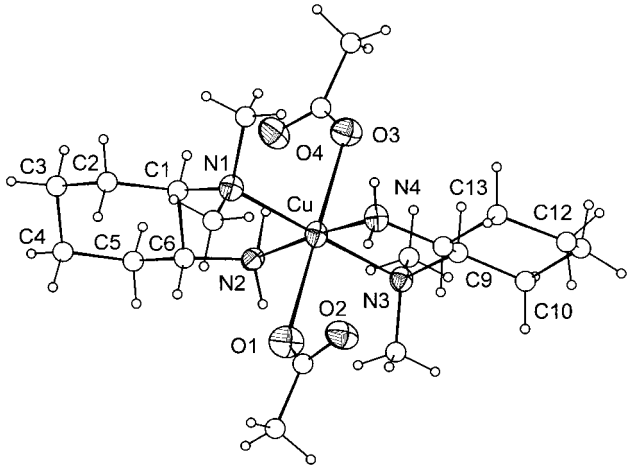

Figure 1. Crystal structure of *trans*,*trans*,*trans*-bis(diammine)copper(II) acetate **6**.

2.3. Absolute configuration of the diamine (*R*,*R*)-3

At that point we assumed the absolute configuration of (−)-**3** to be *R*,*R* by comparison with the nor-compound *trans*-1,2-diaminocyclohexane. To provide proof of that we crystallized 2 equiv. (*R*,*R*)-**3** with $Cu(OAc)_2 \cdot H_2O$ from EtOH–MTB and obtained deep blue single crystals suitable for determination of the absolute configuration by X-ray diffraction. In fact, the structure of the bis-diammine copper(II)-acetate **6** shown in Fig. 1 shows the ligand in *R*,*R*-configuration. Compound **6** crystallized as the *trans*,*trans*,*trans*-stereoisomer. The copper atom is the coordinated distorted octahedral as expected for a d^9-system by four nitrogen atoms of two diamine ligands and two oxygen atoms of two acetate groups. The Cu–N bonds to the nitrogen atoms of the dimethylamino groups are slightly longer than to those of the amino groups (2.14 vs 1.98 Å). The two Cu–O bonds are not equal, too, they are 2.42 and 2.56 Å, respectively. The two hydrogen atoms at N4 could easily be localized from a different Fourier synthesis and refined isotropically. In contrast to that, this was true for only one H atom at N2, the second H site seems to be occupied only partially. It may be assumed, that this H atom is partially localized at N2 and is involved in a hydrogen bond to O4, and partially bound to the oxygen atom O4 of one acetate group.

3. Conclusions

We reported on a straightforward synthesis of racemic *trans*-1-amino-2-dimethylaminocyclohexane (*rac*-**3**) by aziridine ring opening with $HNMe_2$. Optical resolution was conveniently performed by crystallization as the tartrate **5**. The optical purity of **3** can be determined by ^{1}H NMR of the derived 10-camphorsulfonamides **4a** and **4b**. The absolute configuration of (*R*,*R*)-(−)-**3** was established by X-ray single crystal diffraction of the bis(diammine)copper complex **6**.

4. Experimental

4.1. General

Column chromatography was accomplished with Merck

silica gel (Type 60, 0.063–0.200 mm) using *tert*-butyl methyl ether (MTB) and hexanes (PE) as solvents. ^{1}H NMR: Bruker AM 400 (400 MHz) and Bruker AC 200 (200 MHz). ^{13}C NMR: Bruker AC 200 (50 MHz), assignments were made using DEPT experiments. MS (EI, 70 eV): Varian MAT 711 and MAT 955Q (high resolution). IR: Nicolet Magna IR 750. Elemental analyses: Analytik Jena Vario EL. Optical rotations: Perkin–Elmer polarimeter 341; $[\alpha]$ values are given in 10^{-1} deg cm^2 g^{-1}. All starting materials were commercially available. Dimethylamine was purchased from Fluka. Spectroscopic data of **2** were in agreement with the literature.[16]

4.1.1. (*R,*R**)-2-Azidocyclohexanol.** A mixture of oxirane **1** (30.1 g, 0.306 mol) and NaN_3 (50.4 g, 0.775 mol) in H_2O–acetone (330 ml, 1:1) was heated to reflux for 17 h. Acetone was removed under reduced pressure and the residue extracted with MTB (3×160 ml) and CH_2Cl_2 (3×160 ml). The combined extracts were washed with water (2×40 ml) and dried ($MgSO_4$). After filtration removal of the solvent yielded the azido alcohol (40.0 g, 0.283 mol, 93%) as a practically pure yellow oil, which was converted without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.24–1.37 (m, 4H), 1.66–1.75 (m, 2H), 2.00–2.15 (m, 2H), 2.24 (s, 1H; OH), 3.11–3.23 (m, 1H), 3.32–3.43 (m, 1H) ppm.

4.1.2. 7-Azabicyclo[4.1.0]heptane (2). PPh_3 (57.7 g, 0.220 mol) was added within 30 min to a solution of azidocyclohexanol (31.1 g, 0.220 mol) in MTB (250 ml), while N_2 evolved from the mixture. After heating to reflux for 16 h the solvent was stripped through a Vigreux column (20 cm) at 760 mm. Continued distillation under reduced pressure (bp 45°C at 14 mm) yielded the aziridine **2** (16.8 g, 0.173 mol, 79%) as a colorless liquid, which solidified after a few days at ambient temperature; ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.18 (s, br., 1H), 0.96–1.28 (m, 4H), 1.61–1.72 (m, 4H), 1.97–2.04 (m, 2H) ppm.

4.1.3. (*R,*R**)-1-Amino-2-(dimethylamino)cyclohexane (*rac*-3).** CF_3CO_2H (3.37 g, 29.7 mmol) was dropwise added to aziridine **2** (57.7 g, 594 mmol). At about −10°C $HNMe_2$ (134 g, 2.97 mol) was added and the resulting mixture heated to 140°C for 20 h in an autoclave. After the excess of $HNMe_2$ evaporated at ambient temperature the mixture was submitted to distillation through a 25 cm Vigreux column at 14 mm yielding the diamine *rac*-**3** (bp 78°C, 14 mm) as a colorless, hygroscopic liquid (36.8 g, 259 mmol, 44%). IR (ATR): ν=3352, 3213, 2927, 2856, 2823, 2775, 1667, 1449 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.95–1.20 (m, 4H), 1.56–1.74 (m, 3H), 1.64 (s, 2H), 1.83–1.96 (m, 1H), 1.95 (td, *J*=10.3, 3.3 Hz, 1H), 2.17 (s, 6H), 2.50 (td, *J*=10.1, 4.2 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ=20.33 (CH_2), 24.76 (CH_2), 25.25 (CH_2), 34.56 (CH_2), 39.84 (CH_3), 51.03 (CH), 69.30 (CH) ppm. MS (EI, 70 eV), *m*/*z* (%): 142 (50) [M$^+$], 125 (19), 124 (21), 97 (80), 84 (100), 58 (77), 56 (95). $C_8H_{18}N_2$ (142.24): Mol. mass calcd 142.1470, found 142.1470 (HRMS).

4.1.4. (*R,*R**)-1-Amino-2-(dimethylamino)cyclohexane 1-*N*-(1*S*)-(10-camphorsulfonate) (4a and 4b).** (1*S*)-(+)-10-Camphorsulfonyl chloride (1.51 g, 6.04 mmol) was added slowly to a mixture of *rac*-**3** (859 mg, 6.04 mmol), NEt_3 (611 mg, 6.04 mmol) and CH_2Cl_2 (2 ml) at 0°C. After stirring for 18 h at ambient temperature impurities were removed by chromatography of the mixture on SiO_2 with MTB. Finally, elution with MeOH (R_f=0.38) yielded a mixture of **4a** and **4b** as a yellowish solid (2.05 g, 5.61 mmol, 93%), mp 96°C. IR (ATR): ν=3239, 2934, 2863, 1745, 1454, 1391, 1339, 1318, 1145, 1050 cm^{-1}. $C_{18}H_{32}N_2O_3S$ (356.53): Anal. calcd C 60.64, H 9.05, N, 7.86; found C 60.25, H 9.04, N 7.96. Mol. mass calcd 356.2131, found 356.2134 (M$^+$, HRMS).

4.1.5. (*S*,*S*)-1-Amino-2-(dimethylamino)cyclohexane 1-*N*-(1*S*)-(10-camphorsulfonate) (4a). The mixture of **4a** and **4b** was separated by chromatography (SiO_2, MTB/MeOH 1:1) to yield isomer **4a** in a first fraction (R_f=0.27) and subsequently **4b** as the more polar diastereoisomer (R_f=0.15), both as colorless oils. $[\alpha]_D^{20}$=+48, $[\alpha]_{578}^{20}$=+50, $[\alpha]_{546}^{20}$=+58, $[\alpha]_{436}^{20}$=+110, $[\alpha]_{365}^{20}$=+230 (*c* 8.2 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.86 (s, 3H), 1.07 (s, 3H), 1.12–1.21 (m, 2H), 1.21–1.30 (m, 2H), 1.40 (ddd, *J*=3.9, 9.3, 12.8 Hz, 1H), 1.67–1.69 (m, 1H), 1.76–1.83 (m, 3H), 1.90 (d, *J*=18.4 Hz, 1H), 1.97–2.06 (m, 1H), 2.08 (t, *J*=4.5 Hz, 1H), 2.10–2.26 (m, 1H), 2.19 (s, 6H), 2.34 (dt, *J*=18.5, 4.3 Hz, 1H), 2.35–2.47 (m, 2H), 2.97 (d, *J*=14.8 Hz, 1H), 3.91 (td, *J*=10.3, 4.2 Hz, 1H), 3.57 (d, *J*=14.8 Hz, 1H), 6.01 (s, br., 1H) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ=19.72 (CH_3), 19.76 (CH_3), 21.35 (CH_2), 24.47 (CH_2), 25.09 (CH_2), 25.41 (CH_2), 26.98 (CH_2), 33.54 (CH_2), 39.82 (CH_3), 42.72 (CH_2), 42.80 (CH), 48.10 (C), 51.11 (CH_2), 54.31 (CH), 58.96 (C), 66.60 (CH), 215.69 (C=O) ppm.

4.1.6. (*R*,*R*)-1-Amino-2-(dimethylamino)cyclohexane 1-*N*-(1*S*)-(10-camphorsulfonate) (4b). $[\alpha]_D^{20}$=−28, $[\alpha]_{578}^{20}$=−28, $[\alpha]_{546}^{20}$=−30, $[\alpha]_{436}^{20}$=−25, $[\alpha]_{365}^{20}$=+52 (*c* 4.4 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.87 (s, 3H), 1.12 (s, 3H), 1.17–1.32 (m, 4H), 1.40 (ddd, *J*=3.8, 9.3, 12.3 Hz, 1H), 1.63–1.70 (m, 2H), 1.79–1.83 (m, 2H), 1.92 (d, *J*=18.4 Hz, 1H), 1.98–2.05 (m, 1H), 2.08 (t, *J*=4.5 Hz, 1H), 2.11–2.25 (m, 1H), 2.21 (s, 6H), 2.36 (dt, *J*=18.7, 4.2 Hz, 1H), 2.37–2.44 (m, 1H), 2.53 (ddd, *J*=4.0, 11.9, 14.7 Hz, 1H), 2.86 (d, *J*=14.9 Hz, 1H), 3.18 (td, *J*=10.3, 4.2 Hz, 1H), 3.61 (d, *J*=14.9 Hz, 1H), 5.88 (s, br., 1H) ppm. ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ=19.79 (CH_3), 20.04 (CH_3), 21.06 (CH_2), 24.24 (CH_2), 25.07 ($2CH_2$), 26.88 (CH_2), 32.84 (CH_2), 39.80 (CH_3), 42.63 (CH_2), 42.71 (CH), 47.78 (C), 50.83 (CH_2), 54.17 (CH), 58.62 (C), 66.25 (CH), 215.34 (C=O) ppm.

4.1.7. (*R*,*R*)-1-Ammonium-2-(dimethylammonium)cyclohexane *mono*-L-tartrate (5). At 70°C a solution of L-(+)-tartaric acid (12.0 g, 80.0 mmol) in EtOH (20 ml) was added to a stirred solution of *rac*-**3** (22.7 g, 160 mmol) in EtOH (10 ml). After cooling to 23°C the mixture was further stirred for 16 h. The precipitate was collected on a glass frit, washed with MTB and dried in high vacuum to yield the tartrate **5** as a colorless powder (3.50 g, 12.0 mmol, 14%), mp 160°C. From the supernatant the remaining racemic **3** can be almost quantitatively recovered after extraction with aqueous KOH and MTB. $[\alpha]_D^{20}$=+13.7, $[\alpha]_{578}^{20}$=+14.1, $[\alpha]_{546}^{20}$=+16.0, $[\alpha]_{436}^{20}$=+25.7, $[\alpha]_{365}^{20}$=+36.2 (*c* 4.25 in H_2O). IR (ATR): ν=3367,

3029, 2933, 1580, 1348, 1115, 1066, 689 cm^{-1}. ^1H NMR (200 MHz, D_2O): δ=1.12–1.56 (m, 4H), 1.67–1.89 (m, 2H), 2.04–2.20 (m, 2H), 2.79 (s, 6H), 3.31 (td, J=10.6, 4.3 Hz, 1H), 3.48 (td, J=11.1, 3.7 Hz, 1H), 4.27 (s, 2H), 4.72 (s; HDO) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, D_2O): δ= 24.06 (CH_2), 25.24 (CH_2), 25.32 (CH_2), 32.97 (CH_2), 41.90 (CH_3), 51.70 (CH), 68.96 (CH), 76.14 (CH), 180.70 (C=O) ppm. MS (EI, 70 eV), *m/z* (%): 142 (40), 84 (100), 71 (58), 58 (84). $C_{12}H_{24}N_2O_6$ (292.34): Anal. calcd C 49.30, H 8.27, N 9.58; found C 49.11, H 8.47, N 9.60.

4.1.8. (*R*,*R*)-1-Amino-2-(dimethylamino)cyclohexane (*R*,*R*-3). An NaCl-saturated solution of NaOH (1.91 g, 47.8 mmol) in H_2O (25 ml) was dropwise added to a solution of tartrate **5** (3.50 g, 12.0 mmol) in H_2O (5 ml). After stirring for 30 min at ambient temperature the mixture was extracted with CH_2Cl_2 (7×30 ml). The combined extracts were dried ($MgSO_4$). The solvent was evaporated under reduced pressure and the residue submitted to Kugelrohr distillation (175°C oven temperature, 14 mm, receiver flask cooled to −70°C) to yield (*R*,*R*-**3**) as a colorless, hygroscopic liquid (1.31 g, 9.21 mmol, 77%). $[\alpha]_D^{20}$= −36, $[\alpha]_{578}^{20}$=−37, $[\alpha]_{546}^{20}$=−42, $[\alpha]_{436}^{20}$=−64, $[\alpha]_{365}^{20}$=−86 (*c* 5.1 in $CHCl_3$); $[\alpha]_D^{20}$=−51, $[\alpha]_{578}^{20}$= −53, $[\alpha]_{546}^{20}$=−58, $[\alpha]_{436}^{20}$=−91, $[\alpha]_{365}^{20}$=−131 (*c* 0.45 in EtOH); Ref. 15 $[\alpha]_{579}$=−53.2, $[\alpha]_{546}$=−59.7 (*c* 35.62 in EtOH).

4.1.9. *trans*,*trans*,*trans*-Bis-[(*R*,*R*)-1-amino-2-(dimethylamino)cyclohexane]copper(II) acetate (6). A solution of (*R*,*R*)-**3** (10 mg, 0.070 mmol) in EtOH (0.1 ml) was added to a solution of $Cu(OAc)_2 \cdot H_2O$ (11.4 mg, 0.035 mmol) in EtOH (0.1 ml), and the resulting blue solution was filtered through a small pad of cotton. The solvent was gradually displaced with MTB by diffusion through the gas phase and after 10 d blue crystals were collected being suitable for X-ray single crystal diffraction; $[\alpha]_D^{20}$=−42, $[\alpha]_{578}^{20}$=−42, $[\alpha]_{546}^{20}$= −83, $[\alpha]_{436}^{20}$=−330, $[\alpha]_{365}^{20}$=−580 (*c* 0.024 in H_2O).

4.1.10. Crystal data and structure refinement for 6. Formula $C_{20}H_{42}CuN_4O_4$, M=466.12, blue crystal, 0.4× 0.3×0.18 mm^3, monoclinic, space group $P2_1$, temp. 293 K, a=9.5086(3) Å, b=12.5311(4) Å, c=9.9048(3) Å, α=90°, β=100.5200(10)°, γ=90°, V=1160.35(6) $Å^3$, Z=2, ρ_{calcd}= 1.334 g cm^{-3}, abs coeff 0.973 mm^{-1}, scan range 2.09°≤θ≤27.50°, 8802 reflections collected, 4566 independent reflections, refinement method: full-matrix least-squares on F^2, 4566 data, 1 restraints, 282 parameters, goodness-of-fit on F^2: 0.860, final R indices [$I \geq 2\sigma(I)$]: R_1=0.0549, wR_2=0.1090, R indices (all data): R_1=0.0940, wR_2=0.1310, absolute structure parameter 0.03(3), largest diff. peak and hole: 0.386, −0.391e $Å^{-3}$. Data were collected on a Siemens Smart CCD diffractometer using MoKα radiation (λ=0.71069 Å). The structure was solved after *Lp* and absorption correction (SADABS)[28] by direct methods (SHEXS)[29] and refined with anisotropic thermal parameters for the non-hydrogen atoms (SHELXL).[30] Hydrogen positions at the ring atoms were refined with a riding model, the methyl groups were refined as rigid groups, the H atoms of the NH_2 groups were located from Fourier maps and refined isotropically. The refinement converged at R=0.0549. The drawing was created with the DIAMOND[31] program. The compound crystallizes in the acentric space group $P2_1$ with two formula units per unit cell. The absolute structure was determined by means of the Flack parameter. Crystallographic data have been deposited at the Cambridge Data Center and may be obtained without charge on quoting the depository number CCDC 143716 from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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References

1. Christoffers, J.; Rößler, U.; Werner, T. *Eur. J. Org. Chem.* **2000**, 701–705.
2. Christoffers, J.; Mann, A.; Pickardt, J. *Tetrahedron* **1999**, *55*, 5377–5388.
3. Christoffers, J.; Mann, A. *Eur. J. Org. Chem.* **1999**, 1475–1479.
4. Christoffers, J. *J. Prakt. Chem.* **1999**, *341*, 495–498.
5. Christoffers, J.; Rößler, U. *Tetrahedron: Asymmetry* **1999**, *10*, 1207–1215.
6. Christoffers, J.; Mann, A. *Angew. Chem.* **2000**, *112*, 2871–2874 (Angew. Chem. Int. Ed., **2000**, *39*, 2752–2754).
7. Christoffers, J.; Mann, A. *Chem. Eur. J.* **2001** (in press).
8. Larrow, J. F.; Jacobsen, E. N. *Org. Synth.* **1997**, *75*, 1–11.
9. Trost, B. M.; Surivet, J.-P. *J. Am. Chem. Soc.* **2000**, *122*, 6291–6292.
10. Trost, B. M.; Madsen, R.; Guile, S. D.; Brown, B. *J. Am. Chem. Soc.* **2000**, *122*, 5947–5956.
11. Trost, B. M.; Bunt, R. C.; Lemoine, R. C.; Calkins, T. L. *J. Am. Chem. Soc.* **2000**, *122*, 5968–5976.
12. Trost, B. M.; Crawley, M. L.; Lee, C. B. *J. Am. Chem. Soc.* **2000**, *122*, 6120–6121.
13. Brunel, J. M.; Legrand, O.; Reymond, S.; Buono, G. *Angew. Chem.* **2000**, *112*, 2654–2657 (Angew. Chem. Int. Ed. **2000**, *39*, 2554–2557).
14. Saitoh, A.; Achiwa, K.; Tanaka, K.; Morimoto, T. *J. Org. Chem.* **2000**, *65*, 4227–4240.
15. Winternitz, F.; Mousseron, M.; Dennilauler, R. *Bull. Chem. Soc. Fr.* **1956**, 382–391.
16. Beger, J.; Luong, T. T.; Thielemann, C.; Thong, P. D. *J. Prakt. Chem.* **1978**, *320*, 433–451.
17. da Zhang, Z.; Scheffold, R. *Helv. Chim. Acta* **1993**, *76*, 2602–2615.
18. Meguro, M.; Asao, N.; Yamamoto, Y. *Tetrahedron Lett.* **1994**, *35*, 7395–7398.
19. Meguro, M.; Yamamoto, Y. *Heterocycles* **1996**, *43*, 2473–2482.
20. Sabitha, G.; Abraham, S.; Reddy, B. V. S.; Yadav, J. S. *Synlett* **1999**, 1745–1746.
21. Sridhar, M.; Kumar, B. A.; Narender, R. *Tetrahedron Lett.* **1998**, *39*, 2847–2850.
22. Nyasse, B.; Grehn, L.; Ragnarsson, U. *Chem. Commun.* **1997**, 1017–1018.
23. Compagnone, R. S.; Rapoport, H. *J. Org. Chem.* **1986**, *51*, 1713–1719.
24. Holmes, A. B.; Thompson, J.; Baxter, A. J. G.; Dixon, J. *J. Chem. Soc., Chem. Commun.* **1985**, 37–39.

25. Haskell, B. E.; Bowlus, S. B. *J. Org. Chem.* **1976**, *41*, 159–160.
26. Kovacs, J.; Ghatak, U. R. *J. Org. Chem.* **1966**, *31*, 119–121.
27. Snyder, H. R.; Heckert, R. E. *J. Am. Chem. Soc.* **1952**, *74*, 2006–2009.
28. Sheldrick, G. M. *SADABS*: Empirical Absorption Correction Program; Göttingen, 1996.
29. Sheldrick, G. M. *SHELXS-97*: Program for Crystal Structure Solution; Göttingen, 1997.
30. Sheldrick, G.M. *SHELXL-97*: Program for Refinement of Crystal Structures; Göttingen, 1997.
31. Bergerhoff, G.; Brandenburg, K.; Berndt, M. *DIAMOND*: Visuelles Informationssystem für Kristallstrukturen; Bonn, 1996.