Enantioselective Preparation of a Novel Chiral 1,2-Diamine

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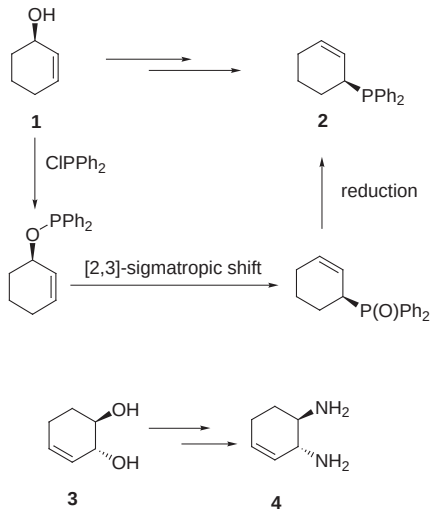
Abstract: A short enantioselective preparation of (1*S*,2*S*)-*trans*-1,2-diamino-3-cyclohexene using a double [3,3]-sigmatropic rearrangement of an allylic bis(imidate) is described (Overman rearrangement). The starting chiral diol is conveniently obtained by enzymatic resolution.

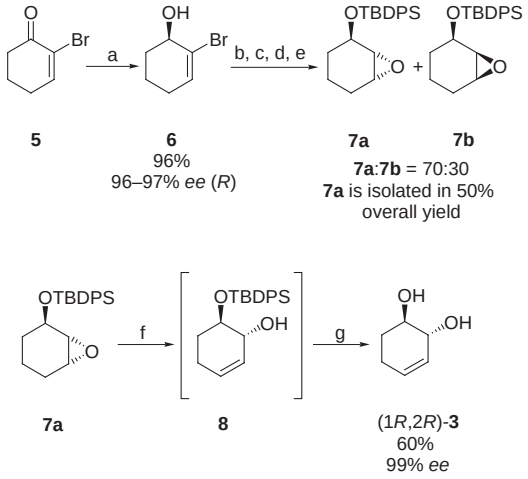
Key words: 1,2-diamines, enzymes, rearrangements, chiral resolution

Chiral diamines are an important class of ligands for asymmetric catalysis.[1,2] Their preparation is always a challenge and only a few practical solutions have been reported.[3] Recently, we have developed a new method based on a [2,3]-sigmatropic rearrangement starting from allylic alcohols of type **1** and allowing the preparation of a chiral phosphine of type **2** after reduction[4] (Scheme 1). This reaction proceeds with complete transfer of the chirality from the alcohol to the phosphine.[4] Herein, we wish to report a related double Overman-rearrangement[5] allowing the practical preparation of (1*S*,2*S*)-1,2-diaminocyclohex-3-ene (**4**) in 9% *ee* starting from (1*R*,2*R*)-1,2-cyclohex-3-enediol (**3**) (Scheme 1).



Scheme 1

The starting 1,2-diol **3** can be prepared in optically pure form using two methods. In the first approach, we have used an asymmetric reduction of 2-bromo-2-cyclohexen-1-one (5)[6] as a key step for introducing the chirality. The CBS-reduction[7] of **5** (BH_3·SMe_2, Me-CBS (15 mol%), THF, –10 °C, 1 hour) provided the chiral allylic alcohol (*R*)-**6** in 96% yield and 96–98% *ee*. The debromination of **6** with *tert*-BuLi[8] (3.2 equivalents, –78 °C, 1 hour) and epoxidation with *m*-chloroperbenzoic acid (*m*-CPBA; 1.4 equivalents) in CH_2Cl_2 at 20 °C for 6 hours furnished a 70:30 mixture of the two diastereoisomeric epoxides **7a** and **7b** as already described in the literature.[9]



Scheme 2 Reagents and conditions: (a) Me-CBS cat. (15 mol%), BH_3·SMe_2 (60 mol%), THF, –10 °C, 1 h; (b) *tert*-BuLi (3.2 equiv), pentane, Et_2O, –78 °C, 1 h; (c) Sat. $NaHCO_3$ solution, –78 °C to r.t.; (d) TBDPS-Cl (1.1 equiv), imidazole (2.2 equiv), DMF, r.t., 12 h; (e) m-CPBA (1.4 equiv), CH_2Cl_2, 0 °C to r.t., 6 h; (f) Et_2NLi (3.5 equiv), Et_2O, hexane, reflux, 17 h; (g) TBAF (1.0 equiv), THF, r.t., 14 h

These two epoxides were readily separated by chromatography (pentane-ether) and the major epoxide **7a** was isolated in 50% overall yield from the allylic alcohol **6**. By treatment with lithium diethylamide (3.5 equivalents) in a mixture of ether and hexane at reflux for 17 hours, the epoxide **7a** underwent a smooth ring opening, affording the selectively protected diol **8**, which was directly used in the next step. After desilylation with tetrabutylammonium fluoride (TBAF) in THF and recrystallization in ethyl acetate, the optically pure diol (1*R*,2*R*)-**3** was obtained in 60% yield and 9% *ee* (Scheme 2).

Alternatively, diol **3** can be prepared using enzymatic resolution. The racemic diacetate **9** was obtained in three steps from cyclohexadiene in 49% overall yield[10] (Scheme 3). By using *Pseudomonas Fluorescens Lipase (PFL)*[11] in a buffered aqueous solution at pH 7, a selective hydrolysis of the racemic diacetate **9** occurred leading to

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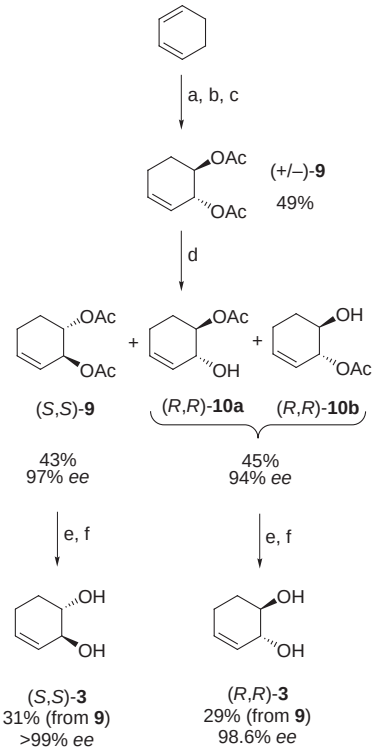
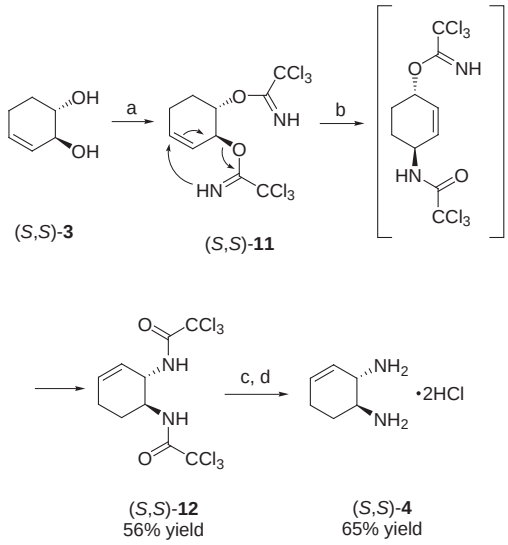
a mixture of the two (*R*,*R*)-monoacetate **10a** and **10b** (45% yield, 94% *ee*) as well as unreacted (*S*,*S*)-diacetate **9** (43% yield; 97% *ee*). The monoacetates (*R*,*R*)-**10** and the unreacted (*S*,*S*)-**9** were readily separated by chromatography (using pentane-ether mixtures; see experimental section). After saponification of **9** and **10** with sodium methoxide in methanol and recrystallization in ethyl acetate, the two chiral diols (1*S*,2*S*)-**3** and (1*R*,2*R*)-**3** were obtained in > 9% *ee* (31% yield) and 98.6% *ee* (29% yield), respectively as determined by HPLC analysis using a Chiralsil-Dex CP column.



Scheme 3 Reagents and conditions: (a) Br_2, $CHCl_3$, 0 °C; (b) 2 M KOH, H_2O, r.t., 4 d; (c) Ac_2O, pyridine; (d) Pseudomonas Fluorescens Lipase, pH 7, buffer; (e) NaOMe, MeOH, r.t., 1 h; (f) recryst. from EtOAc

The reaction of (*S*,*S*)-**3** with trichloroacetonitrile (2 equivalents) and NaH (0.2 equivalent) in THF at 0 °C for 4 hours furnished the intermediate (*S*,*S*)-trichloroimidate derivative **11**. This crude intermediate was heated at reflux in xylene for 6 hours leading by a double Overman-rearrangement[5] to the bis(trichloroacetamide) **12** in 56% yield. The simplicity of the purification step is worth mentioning since the bis(trichloroacetamide) **12** precipitates from the crude reaction mixture at 0 °C, washing with pentane and drying under vacuum was sufficient for obtaining the bis(amide) **12** in an analytically pure form. Deprotection of the diamide with 6 M NaOH at 85 °C for 6 hours provided the desired diamine (1*S*,2*S*)-**4** isolated as its dihydrochloride in 65% yield and 9% *ee*.



Scheme 4 Reagents and conditions: (a) CCl3CN (2 equiv), NaH (0.2 equiv), THF, 0 °C; (b) xylene, reflux, 6 h; (c) 6 M NaOH, 85 °C, 6 h; (d) 37 % HCl, EtOH

In summary, we have reported an enantioselective synthesis to a new chiral diamine. The evaluation of (*S*,*S*)-**4** or simple derivatives of it as ligands for asymmetric metal catalysis is currently underway in our laboratories.

Mps were measured on a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded on a Bruker ARX 200 or ACX 300 instruments. IR spectra were recorded on a Nicolet 510 or a Perkin–Elmer 281 spectrometer. Electron impact (EI) mass spectra were recorded on a Varian MAT CH 7A. All reagents were of commercial quality. *Pseudomonas Fluorescens Lipase* was purchased from FLUKA.

Optically Pure *trans*-1,2-Dihydroxy-3-cyclohexene (3)
Method A: Enzymatic Resolution
Racemic *trans*-1,2-Diacetoxy-3-cyclohexene (9)[10]

A solution of bromine (42 g, 14.5 mL) in $CHCl_3$ (150 mL) was added dropwise to a solution of cyclohexadiene (27 mL, 280 mmol) in $CHCl_3$ (200 mL) at 0 °C. After evaporation of the solvent, the residue was filtered through a short plug of silica with pentane. Following the removal of pentane, the residual oil was treated with 2 N KOH (400 mL) and vigorously stirred for 4 days. After neutralization with concd HCl and solid $NaHCO_3$ to set the pH to 7, all the volatiles were removed in vacuum. The resulting solid was extracted with CH_2Cl_2. After drying ($MgSO_4$) and evaporation of the solvent, crude 1,2-dihydroxy-3-cyclohexene **3** was obtained (20.6 g). Without any further purification, the diol was dissolved in pyridine (300 mL) and treated with acetic anhydride (51 mL, 540 mmol). After stirring at r.t. over night, the solution was poured onto ice/water (600 g), extracted with Et_2O and dried ($MgSO_4$). Removal of the solvent and distillation at reduced pressure gave 25.4 g (49% yield) of the racemic diacetate **9** as a colorless oil.

Bp 126–129 °C (9 mbar).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90 (m, 1H, H-4), 5.58 (dd, 1H, *J* = 9.9, 2.1 Hz, H-3), 5.38 (m, 1H), 5.03 (m, 1H), 2.22 (m, 2H, C*H*$_2$), 2.08 (s, 6H, C*H*$_3$), 1.99 (m, 1H, C*H*$_2$), 1.83 (m, 1H, C*H*$_2$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.9, 170.7, 131.7, 124.6, 71.8, 71.2, 25.8, 23.6, 21.5.

(1*S*,2*S*)-1,2-Dihydroxy-3-cyclohexene (3)

Racemic diacetate **9** (11.9 g, 60 mmol) and phosphate buffer pH 7 (2.4 L) were stirred in a 4 L round bottom flask. The enzyme *Pseudomonas Fluorescens Lipase* (3601U/mg; 15 mg) was added and the reaction mixture was warmed to 38 °C and was allowed to react at this temperature until the ee of the diacetate reached at least 96% (40 h). The progress of the reaction was monitored by GC. After cooling the mixture to r.t., solid NaCl was added until saturation. The solution was then extracted with Et_2O (4 × 800 mL) and the organic layer was dried ($MgSO_4$). The solution was filtered and the solvent was concentrated under vacuum. The resulting oil was purified by flash chromatography on flash silica gel. The (*S*,*S*)-diacetate **9** was first eluted with pentane-Et_2O (4:1) yielding **9** as a colorless oil (5.20 g, 43% yield, 97% *ee*). Then the (*R*,*R*)-monoacetates mixture **10a** and **10b** was eluted with a mixture of pentane-Et_2O-MeOH (10:10:1) yielding **10a** and **10b** as a colorless oil (4.25 g, 45% yield, 94% *ee*).

The *ee* of the diacetate **9** was directly established using chiral GC analysis. The *ee* of the monocetates mixture **10a** and **10b** was determined by chiral GC analysis after converting the monoacetates to the diacetates with acetic anhydride in pyridine for 3 h.

Enantiomeric excess was obtained by chiral capillary GC analysis of the corresponding diacetate using a Chiralsil-Dex CP column (25.0 m × 250 μm × 0.25 μm). Carrier gas: H_2. Internal pressure: 12.12 psi. H_2 flow rate: 2.8 mL min^{-1}. Oven temperature: 40 °C for 10 min, then warming up to 160 °C with a rate of 5 °C·min^{-1} and staying at 160 °C for 20 min. Retention times of the (*R*,*R*) and (*S*,*S*) enantiomers are 27.45 min and 27.63 min respectively.

The (*S*,*S*)-diacetate **9** was then placed in MeOH (20 mL) with solid sodium methoxide (2 equiv) and the reaction mixture was stirred at r.t. for 1 h. Concd HCl was added until pH 5–6, then solid bicarbonate was added. The mixture was concentrated under vacuum, the crude residue was dissolved in EtOAc and the salts were filtered off. The filtrate was concentrated under vacuum and the solid residue was then recrystallized from EtOAc. (*S*,*S*)-Diol **3** was obtained as a colorless crystalline solid (2.1 g, 99.5% *ee*, 31% overall yield from **9**).

The same procedure was applied for the hydrolysis of the (*R*,*R*)-monoacetates mixture **10a** and **10b** using sodium methoxide (1 equiv). The (*R*,*R*)-diol **3** was obtained as a colorless crystalline solid (2.0 g, 98.6% *ee*, 29% overall yield from **9**) (mp 72–73 °C).

Method B

(*R*)-2-Bromo-2-cyclohexen-1-ol (6)

2-Bromo-2-cyclohexen-1-one (**5**) was prepared according to the method of Kowalski.[6] The CBS-reduction of the enone **5** was performed as follows: A solution of the enone **5** (25 g, 143 mmol) in dry THF (150 mL) and a solution of BH_3·SMe_2 (8.6 mL, 86 mmol, 0.6 equiv) in dry THF (100 mL) were simultaneously added dropwise within 1 h to a solution of Me-CBS catalyst (6.0 g, 21 mmol, 0.15 equiv) in dry THF at –10 °C to –15 °C. After the addition, the reaction mixture was stirred at –15 °C for 45 min and quenched with MeOH (50 mL). After evaporating THF and MeOH under vacuum, the residue was dissolved in Et_2O and washed with brine. The organic layer was dried ($MgSO_4$) and Et_2O was evaporated. The crude yellow oil obtained was purified by chromatography on silica gel (Et_2O-pentane, 1:1). (*R*)-2-Bromo-2-cyclohexen-1-ol (**6**) was isolated as a colorless liquid (23.9 g, 95 % yield) with an optical purity of 96–98% *ee*.

IR (KBr): ν = 3371, 1641 cm^{-1}.

$[\alpha]^{20}_D$ +88 (*c* 1.8, $CHCl_3$) (96.8 % *ee*).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.23–6.10 (m, 1H, H-3), 4.25–4.18 (m, 1H, H-1), 3.11 (br s, 1H, OH), 2.12–1.65 (m, 6H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 135.1, 128.3, 72.3, 34.6, 30.4, 20.1

MS (EI): *m/z* (%) = 176.0 (1) [M^+], 97.0 (100) [M^+ – Br], 79.0 (23), 41.0 (50).

Anal. Calcd for C_6H_9BrO (177.04): C, 40.70; H, 5.12. Found: C, 40.70; H, 5.31.

Enantiomeric excess was determined by HPLC with a Chiracel OJ column. Flow rate: 0.7 mL min^{-1}. Temp: 20 °C. Eluent: *n*-heptane-propan-2-ol (99.5:0.5). Retention times of (*R*)- and (*S*)- enantiomers are 31.39 min and 36.94 min, respectively.

(1*R*,2*R*)-1,2-Dihydroxy-3-cyclohexene (3)

A solution of *tert*-BuLi in pentane (1.2 M, 350 mL, 420.0 mmol, 3.2 equiv) was added dropwise to a solution of (*R*)-2-bromo-2-cyclohexen-1-ol (**6**, 23.0 g, 130 mmol) in Et_2O (200 mL) at –78 °C. After the addition, the mixture was stirred for further 10 min at –78 °C and slowly warmed up to –20 °C. Quenching was carefully carried out by addition sat. $NaHCO_3$ (50 mL) and warming up to r.t. After drying the organic layer ($MgSO_4$), the solvents were evaporated under vacuum. The crude 2-cyclohexenol (13.3 g) and imidazole (19.5 g, 286 mmol, 2.2 equiv) were dissolved in DMF (100 mL) and TBDPS-Cl (36.6 mL, 143 mmol, 1.1 equiv) was added dropwise at r.t. After stirring overnight, the crude reaction mixture was poured on water (200 mL) and extracted three times with Et_2O (200 mL). The organic layers were washed successively with 10% HCl, H_2O, and brine. After drying ($MgSO_4$), the solvents were evaporated. The crude protected 2-cyclohexenol was dissolved in CH_2Cl_2 (500 mL) and cooled to 0 °C. Solid *m* -CPBA moistened with 30% H_2O (45 g, 180 mmol, 1.4 equiv) was added over 15 min. The reaction mixture was allowed to warm up to r.t. and was stirred overnight. After filtration of the white precipitate of *m*-CPBA, the organic layer was washed successively with sat. Na_2SO_3, sat. $NaHCO_3$, and brine. After drying ($MgSO_4$), the crude mixture of epoxides **7a** and **7b** (ratio 7:3) was purified by chromatography on silica gel (pentane-Et_2O, 99:1 to 95:5). The epoxide **7a** (23.0 g, 50% yield from **6**) was isolated as a colorless oil, which was used without any further purification in the following step.

A solution of Et_2NLi was prepared by adding BuLi (1.55 M in hexanes, 150 mL, 232 mmol) to a solution of Et_2NH (28.0 mL, 275 mmol) in Et_2O (100 mL) at 0 °C. This solution of Et_2NLi was added to a solution of epoxide **7a** (23.0 g, 65.0 mmol) in Et_2O (150 mL) at r.t. and the reaction mixture was heated to reflux for 17 h. After cooling to 0 °C, the reaction was carefully quenched with H_2O (30 mL). The organic phase was washed successively with 10% HCl, sat. $NaHCO_3$, and brine. After drying ($MgSO_4$), the solvents were evaporated. The crude monoprotected diol **8** was dissolved in THF (30 mL) and TBAF (1 M solution in THF, 65 mL, 1 equiv) was added at r.t. After stirring for 14 h, THF was evaporated and the crude mixture was directly purified by chromatography on silica gel (Et_2O-MeOH, 100:0 to 96:4). After recrystallization from EtOAc, the diol (1*R*,2*R*)-**3** (4.45 g, 60% yield from **7a**) was obtained in optically pure form (> 9% *ee*) as a colorless crystalline solid.

Mp 72–73 °C (racemic mixture recrystallized from EtOAc 76–77 °C).

IR (KBr): ν = 3306 cm^{-1}.

$[\alpha]^{20}_D$ +22.4 (*c* 1.21, $CHCl_3$) (99.5 % *ee*) for the (1*S*,2*S*) enantiomer.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.75–5.70 (m, 1H, H-4), 5.50–5.54 (m, 1H, H-3), 4.12–4.06 (m, 1H, H-2), 3.66–3.59 (m, 1H, H-1), 2.52 (br s, 2H, OH), 2.21–2.14 (m, 2H), 1.99–1.91 (m, 1H), 1.71–1.61 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.6, 128.2, 73.3, 73.2, 28.5, 24.7.

MS (EI): *m/z* (%) = 114.1 (0.32) [M^+], 96.2 (4.6), 70.3 (100), 69.2 (23.4).

Anal. Calcd for $C_6H_{10}O_2$ (114.14): C, 63.14; H, 8.83. Found: C, 62.99; H, 8.84.

(1*S*,2*S*)-*N*,*N*′-Bis(trichloroacetyl)-*trans*-1,2-diamino-3-cyclohexene (12)

NaH (200 mg, 60% dispersion in mineral oil) was added in portions to a solution of (1*S*,2*S*)-1,2-dihydroxy-3-cyclohexene **3** (2.74 g, 24.0 mmol) in dry THF (20 mL) under Ar. The resulting mixture was stirred for 1 h, then cooled in an ice/water bath and a solution of trichloroacetonitrile (6.93 g, 4.8 mL, 48 mmol) in dry THF (20 mL) was added dropwise within 30 min. The resulting brown solution was stirred at r.t. for 3 h. After evaporation of the volatile components in vacuum, the residue was extracted three times with pentane (30 mL) and the combined extracts were evaporated in vacuum to give the colorless crystalline diimidate **11**, which was then dissolved in xylene (30 mL) and refluxed for 6 h. After cooling to 0 °C, the resulting white precipitate was filtered and washed with pentane to give the optically pure bis(trichloroacetamide) **12** (5.40 g, 56% yield) as fine colorless needles.

Mp >290 °C (decomposition).

IR (KBr): ν = 3304, 1686.8, 1528.1 cm^{-1}.

$[\alpha]^{20}_D$ +42.7 (*c* 0.52, MeOH).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.09 (d, 1H, *J* = 8.47 Hz, NH), 8.93 (d, 1H, *J* = 8.52 Hz, NH), 5.87 (m, 1H, H-4), 5.47 (d, 1H, *J* = 9.67 Hz, H-3), 4.73 (m, 1H, H-2), 4.16 (m, 1H, H-1), 2.23 (m, 2H), 2.02–1.88 (m, 2H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 160.9, 160.4, 128.1, 125.9, 92.3, 92.2, 51.2, 50.4, 26.5, 23.7.

MS (EI): *m/z* (%) = 367 (0.4) [M – Cl], 213 (96), 217 (29), 79 (100).

Anal. Calcd for $C_{10}H_{10}N_2O_2Cl_6$ (402.92): C, 29.81; H, 2.50; N, 6.96. Found: C, 29.55; H, 2.51; N, 6.74.

(1*S*,2*S*)-*trans*-1,2-Diamino-3-cyclohexene Dihydrochloride (4)

A slurry of bis(trichloroacetamide) **12** (1.72 g, 4.2 mmol) in 6 M NaOH (10 mL) was stirred at 85 °C for 6 h leading to a yellow solution. After cooling to r.t., the reaction mixture was extracted with dioxane (3 × 30 mL) and the combined organic extracts were dried ($MgSO_4$). Evaporation of the solvent gave a yellow oil (550 mg), which was dissolved in a MeOH-benzene mixture (1:1, 20 mL) and treated with concd HCl (1 mL). Evaporation of the solvents and repeating the previous treatment gave a solid that was washed with EtOH. After drying, the dihydrochloride **4** was obtained as a white solid (510 mg, 65% yield).

Mp >310 °C (decomposition).

IR (KBr): 2912.5, 1604.9, 1524.0 cm^{-1}.

$[\alpha]^{20}_D$ +66.7 (*c* 0.15, H_2O).

^{1}H NMR (300 MHz, D_2O): δ = 6.25 (dd, 1H, *J* = 1.8, 10.1 Hz, H-4), 5.66 (dd, 1H, *J* = 1.8, 10.1 Hz, H-3), 4.69 (s, 6H, NH_3^+), 4.07 (m, 1H, H-2), 3.75 (m, 1H, H-1), 2.29–1.98 (m, 4H).

^{13}C NMR (75 MHz, D_2O): δ = 135.6, 119.0, 48.9, 48.6, 22.8, 21.4.

Anal. Calcd for $C_6H_{14}N_2Cl_2$ (185.09): C, 38.94; H, 7.62; N, 15.13. Found: C, 38.48; H, 7.64; N, 14.83.

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