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Resolution of *ortho*- and *meta*-substituted 1-phenylethylamines with isopropylidene glycerol hydrogen phthalate

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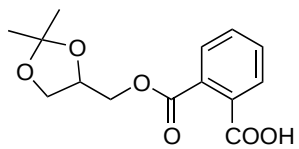
Abstract—The hydrogen phthalate of isopropylidene glycerol **1**, previously reported as an efficient resolving agent of *p*-substituted 1-phenylethylamines, was also found to resolve selected *o*- and *m*-isomers. In particular, the (*S*)-enantiomers of 1-(2-methylphenyl)ethylamine **2**, 1-(3-methylphenyl)ethylamine **3**, 1-(2-chlorophenyl)ethylamine **4** and 1-(3-methoxyphenyl)ethylamine **5** were obtained in good yields and very high enantiomeric excess (e.e.) by selective crystallization of the respective salts with (*S*)- or (*R*)-**1**. The e.e.s of the resolved substrates were determined by chiral HPLC analysis. The (*S*)-configuration of (–)-**3** was established according to Raban's procedure. Optical rotations of non-racemic free amines **2** and **3** are reported. The success of the resolutions presented and of the precedent ones using **1** indicate that the position of the substituent on the 1-phenylethylamine framework does not affect the resolution, showing the uncommon versatility of **1** in the resolution of monosubstituted 1-phenylethylamines.

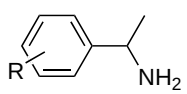
1. Introduction

The hydrogen phthalate of isopropylidene glycerol **1** has proved to efficiently resolve a wide range of amines, including a number of 1-arylalkylamines, 1-phenyl-2-propenylamine, 1-phenyl-2-propynylamine, 1-methyl-allylamine and 1-(1-cyclohexenyl)ethylamine.[1–3] The diastereoisomeric salt between (*S*)-**1** and the (*S*)-isomer of the amine is generally the less soluble and was reported to precipitate from methanol or propan-2-ol, allowing isolation of the (*S*)-amine from the racemate in high yield and e.e. The opposite stereochemical outcome was observed only in the case of 1-phenyl-2-propynylamine, where the enantiomer producing the less soluble diastereomeric salt with (*S*)-**1** had (*R*)-configuration.[3] The effects of structural modification of the parent amine, 1-phenylethylamine, on the resolution process have been examined showing, in particular, that the introduction of *para*-substituents, such as chlorine, bromine, methyl, nitro and methoxyl, or β-substituents, such as one or two methyl residues, does not preclude the resolution by **1**.[1,2]

In this context, it seemed pertinent to extend the investigations on the resolution properties of **1** to *ortho*- and *meta*-substituted 1-phenylethylamines, which have not previously been examined. On the basis of the previous results,[1,2] the resolution of such amines with **1** was likely, but not certain, to succeed as recent resolution studies on 1-phenylethylamines bearing a β-, *p*-, *m*- or *o*-substituent using mandelic acid and its derivatives as resolving agents demonstrated that the position of the substituent on the 1-phenylethylamine (in particular the methyl and methoxy analogues) can dramatically affect the resolution efficiency, sometimes preventing the resolution of the amine.[4–6] Therefore, we selected four substrates, 1-(2-methylphenyl)ethylamine **2**, 1-(3-



1



2 R = 2-Me **4** R = 2-Cl
3 R = 3-Me **5** R = 3-MeO

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methylphenyl)ethylamine **3**, 1-(2-chlorophenyl)ethylamine **4** and 1-(3-methoxyphenyl)ethylamine **5**, as candidates for the resolution with **1**. The three different substituents were chosen out of those present in the previously resolved 1-phenylethylamines so as to allow direct comparisons with the analogous resolutions of the corresponding *p*- or β-substituted amines. In particular, preference was given to methyl, methoxyl and chlorine, considering the ready availability of (±)-**2**–**5** and the recent interest in the preparation of pure enantiomers of these amines.[4–10]

2. Results

The results of the resolutions of **2**–**5** are summarized in Table 1, where the yields and e.e.s are reported. In the case of amines **2**, **4** and **5**, selective precipitation of the (*S*,*S*)-salt took place analogously to the stereochemical course we had observed for all the previously resolved amines, except 1-phenyl-2-propynylamine.

Interestingly, **3** behaved similarly to 1-phenyl-2-propynylamine, (*S*)-**1** giving the less soluble diastereomeric salt with the (*R*)-base. Under the chiral HPLC conditions optimized to determine the e.e.s, the (*R*)-enantiomers of **2**–**5** elute before the (*S*)-enantiomers and so their low percentage in highly (*S*)-enriched samples was more accurately measurable than that of the (*S*)-enantiomers in the reverse case. Therefore, in order to facilitate chromatographic detection of the minor enantiomer in the resolved amine, **3** was treated with (*R*)-**1**, which led to preferential precipitation of the salt of (*S*)-**3**.

Equivalent amounts of racemic amine and enantiopure **1** were used in all experiments, as reported for the precedent resolutions.[1–3] In our study, methanol, which was employed as the solvent in the resolutions of 1-(*p*-methylphenyl)-, 1-(*p*-chlorophenyl)- and 1-(*p*-methoxyphenyl)-ethylamine,[2] was replaced with propan-2-ol due to the high solubility in methanol of the diastereomeric salt mixtures. However, for the second crystallization of the (*R*)-**1**·(*S*)-**3** salt, methanol was preferred to propan-2-ol but was used in a very low ratio to the salt (1.2 mL/g). In this case, despite the similar total efficiencies, recrystallization of the salt of (*S*)-**3** with 31.2% e.e. from propan-2-ol raised the e.e. to only 55.4%, while crystallization from methanol raised the e.e. to 98.9%.

Reversed-phase chiral HPLC analysis of the salts recovered from the first and second crystallizations and of the liberated (*S*)-amines allowed the progress of the resolution to be monitored. Under the chosen chromatographic conditions, the following behavior was observed: (*S*)-**2**, (*S*)-**3**, (*S*)-**4** and (*S*)-**5** eluted after the respective (*R*)-isomers and in the case of directly analyzed diastereomeric salt mixtures, both of the base-resolved enantiomeric pairs were far preceded by (*S*)-**1** or (*R*)-**1**, which exhibited $k'_1 \cong 0$.

The (*R*)-enriched **2**, **3**, **4** and **5** were not isolated from the alcoholic solutions remaining from the original crystallizations of the salts of the respective (*S*)-isomers. Nevertheless, the e.e.s were also determined by HPLC analysis of the residues resulting from the concentration of the mother liquors and found consistent with those expected on the basis of the chemical yield and the diastereomeric composition of the precipitates.

To the best of our knowledge, the optical rotations of both the enantiomers of **2** and **3** are not reported in

Table 1. Preparation of (*S*)-**2**, (*S*)-**3**, (*S*)-**4** and (*S*)-**5** from the corresponding racemates by selective crystallization of the respective salts with enantiopure **1** from propan-2-ol[a]

Entry	Amine	Resolving agent	Yield[b] (%)			e.e.[c] (%)		α_D[d]
			First cryst.[e]	Second cryst.	Recovered amine	First cryst.	Second cryst.	
1	(*S*)-**2**	(*S*)-**1**	73.8	–	68.2	97.7	–	−60.7[f]
2	(*S*)-**3**	(*R*)-**1**	110.5	76.3	–[g]	31.2	55.4	–
3	(*S*)-**3**	(*R*)-**1**	110.5	42.0	40.6	31.2	98.9	−31.0[f]
4	(*S*)-**4**	(*S*)-**1**	88.2	71.5	66.0	91.0	>99.6	−57.4[h]
5	(*S*)-**5**	(*S*)-**1**	67.2	54.5	53.6	92.0	97.5	−22.3[i]

[a] The second crystallization of (*R*)-**1**·(*S*)-**3** (entry 3) was performed from methanol.
[b] Relative to the theoretical amount, i.e. half of starting racemate.
[c] Enantiomeric excess of the amines determined by reversed-phase HPLC analysis on a Chiralcel OD-R column from Daicel ($NaClO_4$ aq./CH_3CN mixtures).
[d] Of the recovered amine.
[e] From the solution containing equivalent amounts of racemic amine and (*S*)- or (*R*)-**1**.
[f] Observed rotation at 25°C; neat.
[g] The salt, resulting from the second crystallization from propan-2-ol and containing (*S*)-**3** with 55.4% e.e., was not decomposed. After being recovered by filtration, it was recombined with the filtrate, propan-2-ol was removed and the resultant solid residue recrystallized from methanol (entry 3).
[h] Observed rotation at 26°C; neat (lit.[7] +55.9, for the (*R*)-isomer).
[i] Specific rotation at 20°C; *c* 2, MeOH (lit.[9] −17.8).

the literature. Therefore, (−)-**2** was converted into the known *levo*-rotatory (*S*)-*N*-[1-(2- methylphenyl)ethyl]-benzamide[11] by treatment with benzoyl chloride and, on the basis of this result, its absolute configuration was established as (*S*). For the elucidation of the absolute stereochemistry of (−)-**3**, it was transformed into the diastereomeric mixture of the corresponding *N*-(2,4-dinitrobenzenesulfenyl)-4-methylbenzenesulfonamide according to Raban's procedure.[12] The product had a positive optical rotation sign, thus establishing that (−)-**3** was of (*S*)-absolute configuration. This assignment was supported by the fact that the (*S*)-enantiomers of the *ortho*- and *para*-isomers of **3** are also *levo*-rotatory and by the elution order of the antipodes on chiral HPLC. In fact, (−)-**3** eluted after (+)-**3**, as did (*S*)-1-phenylethylamine, (*S*)-1-(4-methylphenyl)-ethyl-amine and (*S*)-**2** with respect to the corresponding (*R*)-isomers.

3. Discussion and conclusion

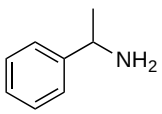
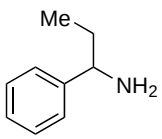
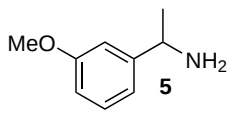
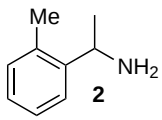
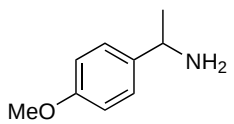
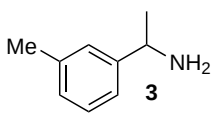
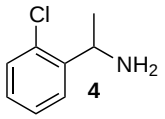
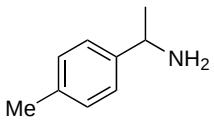
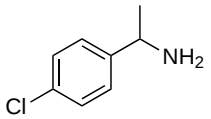
As shown in Table 1 (entries 3–5), amines **3**–**5** were isolated with very high e.e. after simple recrystallization of the respective crude salts of (*S*)-**1**. In this context, **2**, which was recovered from the first formed precipitate with 97.7% e.e. (Table 1, entry 1), represents an exception.

The results obtained for **3**–**5** confirm the trend observed for the previous successful resolutions of 1-arylalkyl-amines using (*S*)-**1**: the separations carried out in propan-2-ol invariably required two crystallizations (in contrast to those in methanol, which gave rise to the precipitation of diastereomerically pure salts directly from the solutions containing equivalent amounts of resolving agent and racemic amine). This can be attributed to the fact that compared to methanol propan-2-ol tends to attenuate the difference in solubility between the two diastereoisomeric salts.

In the case of **3**, recrystallization of the salt containing the amine with 31.2% e.e. from methanol (Table 1, entry 3) was preferable to that from propan-2-ol (Table 1, entry 2). This is consistent with the observations reported for the resolution of **5** with mandelic acid.[9] In fact, according to the authors of this resolution, methanol is better than propan-2-ol in the recrystallization of salts with low d.e.

Comparison between the resolutions of **2**–**5** and the previous ones of the corresponding *p*- or β-substituted 1-phenylethylamines reveals small differences in the total resolution efficiencies between the substrates (see Table 2). The *o*-isomer **2** is more efficiently resolved than 1-(*p*-methylphenyl)ethylamine, while **3**, **4** and **5**

Table 2. Total efficiencies (*E*) observed for the resolutions of 1-phenylethylamine and its methyl-, methoxy- and chloro-substituted analogues with **1**

amine	*E*, [a] %	amine	*E*, [a] %	amine	*E*, [a] %
	81 [b]		60 [c]		53
		 **2**	72		62 [c]
		 **3**	42	 **4**	71
			50 [c]		81 [c]

[a]Total resolution efficiency = chemical yield of the diastereomeric salt (%)×e.e. of the liberated amine (%)/100.
[b]Calculated from the data reported in Ref. 1.
[c]Calculated from the data reported in Ref. 2.

are resolved less efficiently than the respective *p*-isomers. For the four monomethyl substituted 1-phenylethylamines, the resolution efficiencies of **2** and **3** are placed best and worst, respectively. However, all four resolutions reported herein can be considered successful new procedures to obtain enantiomerically pure amines **2**–**5**, the respective efficiencies ranging from a very high 72%, in the case of **2**, to a satisfactory 42%, in the case of **3**. These values can be better appreciated considering that neither mandelic acid nor its recently designed derivatives, namely 2-naphthylglycolic, *p*-methyl- and *p*-methoxymandelic acids, are singly able to resolve all of the methyl- and methoxy-substituted 1-phenylethylamines reported in Table 2.[4–6] Indeed, the additional examples of resolutions described in this paper indicate the high versatility of **1**, which resolves the monomethyl substituted 1-phenylethylamines irrespective of the position of the substituent, and the amines **4** and **5** with efficiencies comparable to those exhibited for the respective *p*-isomers. On the basis of the results presented and previously reported, extension of the application of **1** to the resolution of generically mono-substituted 1-phenylethylamines seems reasonable, though with the limitations previously shown for the β-substitution.[2] Further investigations are required to establish the limits of the resolving properties of enantiopure **1**, which yet untested substrates may reveal.

4. Experimental

^{1}H NMR spectra were recorded on a Bruker 200 (200 MHz) instrument. Optical rotations were measured in a 1 dm cell of 1 mL capacity using a Perking Elmer 241 polarimeter. HPLC analyses were performed on a Chiralcel OD-R column (250×4.6 mm I.D.) from Daicel using a Waters 510 pump and a Pye Unicam PU 4025 UV detector (analytical wavelength 254 nm). Chromatographic data were collected and processed using Maxima 820 software from Waters. Racemic amines **2**–**5** were readily synthesized by the Leuckart reaction from the corresponding ketones according to the experimental procedure described for 1-phenylethylamine.[13] (*S*)-**1** was prepared by resolution of the corresponding racemate with (*S*)-1-phenylethylamine, as previously reported.[1] (*R*)-**1** was obtained by treatment of (*S*)-isopropylideneglycerol with phthalic anhydride in pyridine, as described for the alternative preparation of (*S*)-**1** from (*R*)-isopropylideneglycerol.[1]

4.1. (−)-(*S*)-1-(2-Methylphenyl)ethylamine (*S*)-2

(*S*)-**1** (48.7 g, 173.8 mmol) and (*RS*)-**2** (23.5 g, 173.8 mmol) were combined in propan-2-ol (290 mL) at room temperature. The white precipitate of (*S*)-**1**·(*S*)-**2** salt (26.6 g, 73.8% of the theoretical amount) was collected by filtration and rinsed with cold propan-2-ol: e.e. of (*S*)-**2** 97.7% (by HPLC of the salt; 9/1 0.8 M $NaClO_4/CH_3CN$, 1.6 mL/min); ^{1}H NMR (DMSO-d_6) δ 1.31 (s, 3H), 1.36 (s, 3H), 1.49 (d, 3H), 2.38 (s, 3H), 3.84 (dd, 1H), 4.06 (pseudo t, 1H), 4.20 (d, 2H), 4.37 (m, 1H), 4.56 (q, 1H), 7.22–7.30 (m, 3H), 7.39–7.52 (m, 3H), 7.64 (d, 1H), 7.74 (d, 1H). The salt was decomposed by treatment with 10% HCl in CH_2Cl_2. The aqueous phase was separated, made alkaline with 1N NaOH, and extracted with ethyl acetate. Removal of the solvent from the extract, previously dried over Na_2SO_4, gave a colorless oil (8.22 g), which was distilled under vacuum yielding (*S*)-**2** (8.01 g, 68.2% of the theoretical amount): $\alpha_D^{25} = -60.7$ (neat); e.e. 97.7% (by HPLC under the same conditions as described for (*S*)-**1**·(*S*)-**2** salt); ^{1}H NMR ($CDCl_3$) δ 1.36 (d, 3H), 1.68 (s, 2H), 2.37 (s, 3H), 4.38 (q, 1H), 7.1–7.3 (m, 3H), 7.48 (d, 1H). Benzamide of (*S*)-**2**: $[\alpha]_D^{25} = -17.2$ (*c* 0.4, chloroform) [lit.[11]: $[\alpha]_D^{25} = +19$ (*c* 0.38, chloroform) for the (*R*)-isomer].

4.2. (−)-(*S*)-1-(3-Methylphenyl)ethylamine (*S*)-3

(*R*)-**1** (39.8 g, 142.0 mmol) and (*RS*)-**3** (19.2 g, 142.0 mmol) were combined in propan-2-ol (300 mL) at room temperature. The white precipitate (32.6 g) was collected by filtration, rinsed with cold propan-2-ol, and recrystallized from methanol (40 mL) at 0°C yielding (*R*)-**1**·(*S*)-**3** salt (12.4 g, 42.0% of the theoretical amount): e.e. of (*S*)-**3** 98.9% (31.2% before the recrystallization) (by HPLC of the salts; 85/15 0.4 M $NaClO_4/CH_3CN$, 0.6 mL/min); ^{1}H NMR (DMSO-d_6) δ 1.30 (s, 3H), 1.36 (s, 3H), 1.51 (d, 3H), 2.34 (s, 3H), 3.84 (dd, 1H), 4.06 (pseudo t, 1H), 4.19 (d, 2H), 4.25–4.40 (m, 2H), 7.18 (d, 1H), 7.25–7.50 (m, 6H), 7.75 (d, 1H). The salt was decomposed in the same way as described for (*S*)-**1**·(*S*)-**2** obtaining a colorless oil (3.98 g), whose distillation under vacuum yielded (*S*)-**3** (3.90 g, 40.6% of the theoretical amount): $\alpha_D^{25} = -31.0$ (neat); e.e. 98.9% (by HPLC under the same conditions as described for (*R*)-**1**·(*S*)-**3** salt); ^{1}H NMR ($CDCl_3$) δ 1.39 (d, 3H), 1.63 (s, 2H), 2.35 (s, 3H), 4.09 (q, 1H), 7.0–7.30 (m, 4H).

4.3. (−)-(*S*)-1-(2-Chlorophenyl)ethylamine (*S*)-4

(*S*)-**1** (16.1 g, 57.4 mmol) and (*RS*)-**4** (8.94 g, 57.4 mmol) were combined in propan-2-ol (100 mL) at room temperature. The white precipitate (11.04 g) was collected by filtration, rinsed with propan-2-ol and recrystallized from the same solvent (50 mL) yielding (*S*)-**1**·(*S*)-**4** salt (8.95 g, 71.5% of the theoretical amount): e.e. of (*S*)-**4** >99.6% (91% before the recrystallization) (by HPLC of the salts; 85/15 1 M $NaClO_4/CH_3CN$, 1 mL/min); ^{1}H NMR (DMSO-d_6) δ 1.30 (s, 3H), 1.35 (s, 3H), 1.47 (d, 3H), 3.79 (dd, 1H), 4.06 (pseudo t, 1H), 4.19 (d, 2H), 4.36 (m, 1H), 4.66 (q, 1H), 7.41–7.52 (m, 6H), 7.74–7.82 (m, 2H), 8.0–8.25 (br s, 3H). The salt was decomposed in the same way as described for (*S*)-**1**·(*S*)-**2** obtaining a colorless oil (3.07 g), whose distillation under vacuum yielded (*S*)-**4** (2.95 g, 66.0% of the theoretical amount): $\alpha_D^{26} = -57.4$ (neat) [lit.[7] $\alpha_D^{26} = +55.9$ (neat; for the (*R*)-isomer with 94% e.e.)]; e.e. >99.6% (by HPLC under the same conditions as described for (*S*)-**1**·(*S*)-**4** salt); ^{1}H NMR ($CDCl_3$) δ 1.39 (d, 3H), 1.61 (s, 2H), 4.54 (q, 1H), 7.11–7.35 (m, 3H), 7.52 (dd, 1H).

4.4. (−)-(*S*)-1-(3-Methoxyphenyl)ethylamine (*S*)-5

(*S*)-**1** (7.7 g, 27.5 mmol) and (*RS*)-**5** (4.15 g, 27.5 mmol) were combined in propan-2-ol (20 mL). After cooling to 5°C, the white precipitate (3.98 g) was collected by filtration, rinsed with cold propan-2-ol and recrystallized from the same solvent (10 mL) yielding the (*S*)-**1**·(*S*)-**5** salt (3.23 g, 54.5% of the theoretical amount): e.e. of (*S*)-**5** 97.5% (92% before the recrystallization) (by HPLC of the salts; 85/15 1.5 M $NaClO_4/CH_3CN$, 0.8 mL/min); ^{1}H NMR (DMSO-d_6) δ 1.31 (s, 3H), 1.37 (s, 3H), 1.53 (d, 3H), 3.80 (s, 3H), 3.85 (dd, 1H), 4.07 (pseudo t, 1H), 4.20 (d, 2H), 4.25–4.43 (m, 2H), 6.93 (dd, 1H), 7.09 (d, 1H), 7.18 (s, 1H), 7.27–7.55 (m, 4H), 7.77 (dd, 1H). The salt was decomposed in the same way as described for (*S*)-**1**·(*S*)-**2** obtaining a colorless oil (1.22 g), whose distillation under vacuum yielded (*S*)-**5** (1.11 g, 53.6% of the theoretical amount): $[\alpha]_D^{20} = -22.3$ (*c* 2, methanol) [lit.[9] $[\alpha]_D^{20} = -17.8$ (*c* 2, methanol)]; e.e. 97.5% (by HPLC under the same conditions as described for (*S*)-**1**·(*S*)-**5** salt); ^{1}H NMR ($CDCl_3$) δ 1.38 (d, 3H), 1.57 (s, 2H), 3.81 (s, 3H), 4.09 (q, 1H), 6.74–6.83 (m, 1H), 6.87–6.92 (m, 2H), 7.25 (t, 1H).

4.5. Determination of the absolute configuration of (−)-3 by derivatization as the *N*-(2,4-dinitrobenzenesulfenyl)-4-methylbenzenesulfonamide

(−)-**3** (1 g, 7.4 mmol), *p*-toluenesulfonyl chloride (1.55 g, 8.13 mmol) and triethylamine (1.54 mL, 11.1 mmol) were dissolved in CH_2Cl_2. The solution was heated under reflux for 3 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (el. cyclohexane/ethyl acetate 85/15) yielding the *p*-toluenesulfonamide derivative of (−)-**3** (1.85 g, 86.4%) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.41 (d, 3H), 2.22 (s, 3H), 2.38 (s, 3H), 4.43 (quint., 1H), 4.81 (d, 1H), 6.80–7.23 (m, 6H), 7.62 (d, 2H).

The *p*-toluenesulfonamide (1 g, 3.46 mmol) was dissolved in diethyl ether, LiOH (124 mg, 5.2 mmol) and 2,4-dinitrobenzenesulfenyl chloride (1.22 g, 5.2 mmol) were added and the mixture heated at reflux for 2 h. Subsequent filtration and concentration of the filtrate gave a solid residue (1.65 g), which was purified by column chromatography on silica gel (el. cyclohexane/ethyl acetate 9/1) yielding a 2.7:1 mixture of the two diastereomeric *N*-(2,4-dinitrobenzenesulfenyl)-4-methylbenzenesulfonamide derivatives of (−)-**3** (1.40 g, 83.0%) as a yellow solid: mp 67.2–72.9°C; $[\alpha]_D^{25} = +126.4$ (*c* 0.5, dichloromethane); ^{1}H NMR ($CDCl_3$) δ 1.31 (d, 2.19H), 1.54 (d, 0.81H), 2.15 (s, 0.81H), 2.20 (s, 2.19H), 2.38 (s, 0.81H), 2.51 (s, 2.19H), 5.58 (m, 1H), 6.62 (s, 0.27H), 6.80–7.50 (m, 6.92H), 7.80–8.0 (m, 2.27H), 8.31 (d, 0.27H), 8.57 (dd, 0.27H), 8.92 (d, 0.73H), 9.16 (d, 0.27H). From the positive sign of the optical rotation of the above derivative, (*S*)-configuration was assigned to (−)-**3** according to Ref. 12.

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