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SYNTHESIS AND CRYSTAL STRUCTURE OF (4*S*)-4-BENZYL-3-(4,5-DIMETHOXY-2-METHYLBENZOYL)-2,2-DIMETHYL-1,3-OXAZOLIDINE

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Abstract – The synthesis of (4*S*)-4-benzyl-3-(4,5-dimethoxy-2-methylbenzoyl)-2,2-dimethyl-1,3-oxazolidine **6** was performed in 7 steps starting from veratraldehyde **7**. A new oxidizing system TBHP-ebselen **12** was used for oxidation of 4,5-dimethoxy-2-methylbenzaldehyde **11** into carboxylic acid **13**, being the crucial step of the synthesis. The latter was transformed first to chiral amide **14** using (*S*)-phenylalaninol and then cyclised to oxazolidine **6**. The spatial structure and the absolute configuration of the latter one was confirmed by X-ray study.

Oxazolidines **1**, **2** having at nitrogen atom a chiral auxiliary deriving from commercially available aminoalcohols, e.g. (1*R*,2*R*)-norephedrine, (*S*)- and (*R*)-phenylalaninol, have been used as building blocks in our stereoselective synthesis of 8-oxoberbines **4**, alkaloids which do not possess oxygenated substituents in ring D.[1,2] The key step of the synthesis, in which a new stereogenic centre at C13a was created, involved the addition of laterally lithiated chiral *o*-toluamide type **1** or **2**, to imine **3**. This addition proceeded stereoselectively and led directly to protoberberine alkaloids, type **4** (Figure 1).

To apply the same methodology for the synthesis of protoberberine alkaloids having oxygenated substituents in ring D, e.g. 8-oxoxylopinine **5**,[3] an amide with methoxy-substituents in aromatic ring was needed. Thus, we undertook the synthesis of chiral 4-benzyl-3-(4,5-dimethoxy-2-methylbenzoyl)-2,2-dimethyl-1,3-oxazolidine **6**.

This paper is dedicated to Prof. Isao Kuwajima on the occasion of his 77th birthday.

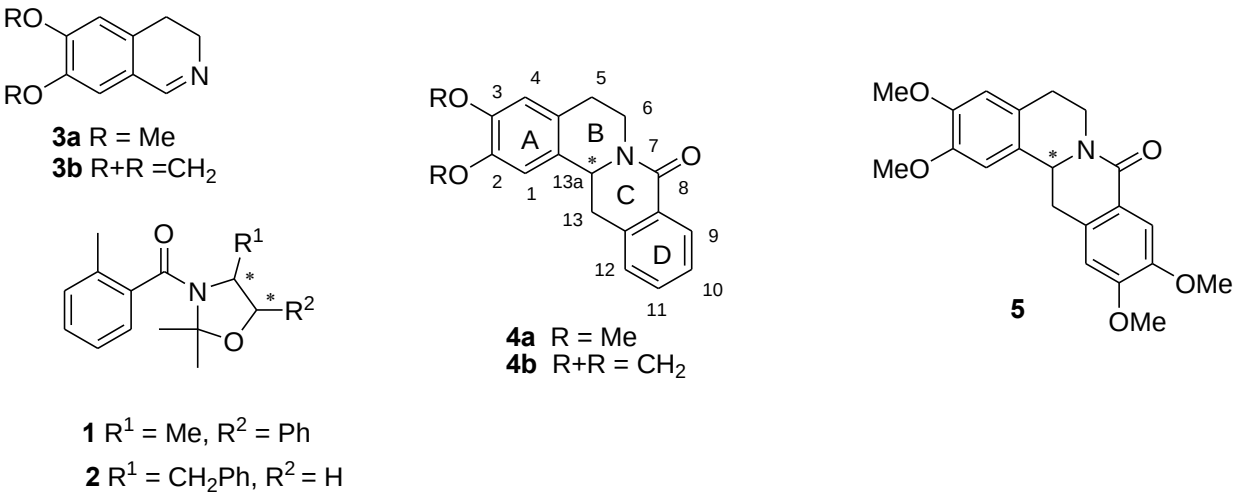
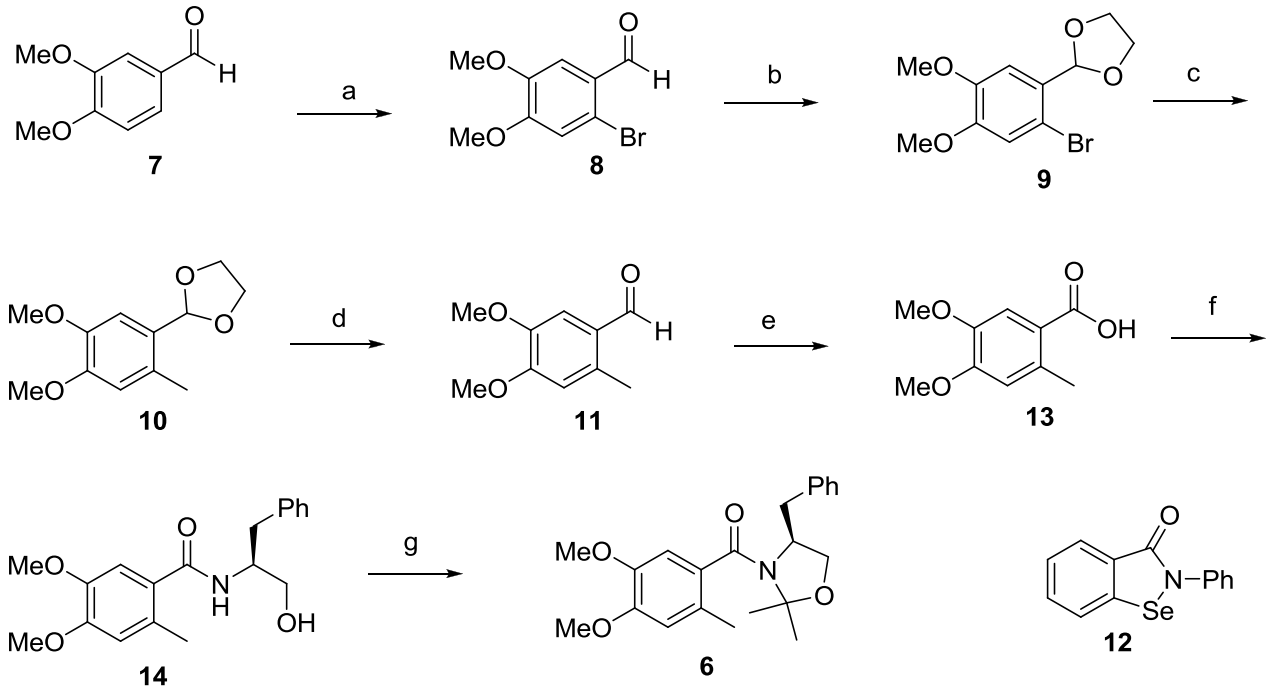


Figure 1. Starting compounds and products in alkaloids synthesis

The performed synthesis of the title compound **6** is presented in Scheme 1. The synthesis started from commercially available veratraldehyde **7**, which was brominated regioselectively using bromine in acetic acid to afford 2-bromo-4,5-dimethoxybenzaldehyde **8**.[4] Extension of the reaction time from 5 h to 24 h increased the yield of product **8** from the literature 80% to quantitative amounts. In the next step the aldehyde function in **8** was protected in the form of cyclic acetal in the reaction with ethylene glycol in the presence of catalytic amounts of *p*-toluenesulfonic acid. Exchange of bromine substituent for methyl group in compound **9** to give methylated derivative **10** was achieved in the reaction with *n*-butyllithium and methyl iodide.[5] Deprotection of the acetal function in compound **10** was performed with 10% HCl in diethyl ether leading to aldehyde **11** in 96% yield. Selective oxidation of 4,5-dimethoxy-2-methylbenzaldehyde **11** to benzoic acid **13** was the crucial step of the synthesis. Looking for environmentally friendly oxidizing agent, to avoid using metal containing agents such as $AgNO_3$/NaOH,[5] we choose *tert*-butyl hydroperoxide (TBHP) with a catalytic amount of selenium compound, 2-phenyl-benzisoselenazol-3(2*H*)-one (ebselen) **12**, introduced by Młochowski *et. al.*[6-8] According to their procedure, to a solution of aldehyde **11** in *tert*-butanol, catalytic amount of ebselen **12** was added followed by *tert*-butyl hydroperoxide and then the mixture was stirred at 70 ºC for 48 h. As a result crude acid **13** was isolated in 93% yield and purified by column chromatography. Treatment of acid **13** with $SOCl_2$ *in situ* and then with (*S*)-phenylalaninol led to amide **14** in 84% yield. It was recrystallised from methanol/diethyl ether to give crystalline amide **14** in the form of white needles showing mp 186 – 188 ºC, $[\alpha]_D$ – 40.12 (c 0.41, $CHCl_3$). The structure of the new amide **14** was confirmed by spectral characteristics and elemental analysis. Oxazolidine **6** was prepared in 49% yield via a reaction of amide **14** with 2,2-dimethoxypropane (DMP), catalyzed by *p*-toluene sulfonic acid, in refluxing benzene under an argon atmosphere. The crude reaction product was purified by column chromatography on silica gel

(hexane/ethyl acetate) and recrystallized from diethyl ether yielding oxazolidine **6** as white crystals with mp 118 – 120 ºC, $[\alpha]_D$ – 46.03 (c 0.315, $CHCl_3$).



Reagents and conditions: (a) Br_2, AcOH; (b) $HOCH_2CH_2OH$, *p*-TsOH, PhH; (c) *n*-BuLi, THF, MeI; (d) 10% HCl; (e) Ebselen **12**, *t*-BuOOH, *t*-BuOH; (f) $SOCl_2$, (*S*)-phenylalaninol, 0.5 M KOH, CH_2Cl_2; (g) DMP, *p*-TsOH, PhH.

Scheme 1. Synthesis of oxazolidine **6**

The correctness of oxazolidine **6** structure was confirmed by spectral characteristics, elemental analysis and crystal X-ray diffraction. The spatial geometry of the molecule of **6** is presented in Figure 2. A summary of data collection and refinement parameters is given in Table 1, while selected geometric parameters are presented in Table 2. The results of the X-ray diffraction study confirmed the absolute configuration 4*S* of the compound studied, by refinement of the Flack parameter.[9] The 4*S* configuration could be postulated also on the basis of the source of chirality – (*S*)-phenylalaninol. The benzyl residue at the stereogenic atom C4 is β-oriented and occupies a pseudo-axial position, as can be seen from the angle between C4–C21 bond vector and Cremer & Pople oxazolidine ring plane normal of 15.11(7)°.[10] Moreover, the conformation of N3–C4 bond is antiperiplanar with respect to C21–C22 bond [torsion angle N3–C4–C21–C22: -170.96(9)°]. The mean plane of the phenyl ring of the benzyl residue is oriented at an angle of 20.45(6)º to the least squares plane of the non-planar oxazolidine ring. Comparable observations have been made for (4*S*)-4-benzyl-2,2-dimethyl-3-*o*-toluoyl-1,3-oxazolidine **2** obtained using a similar method.[11]

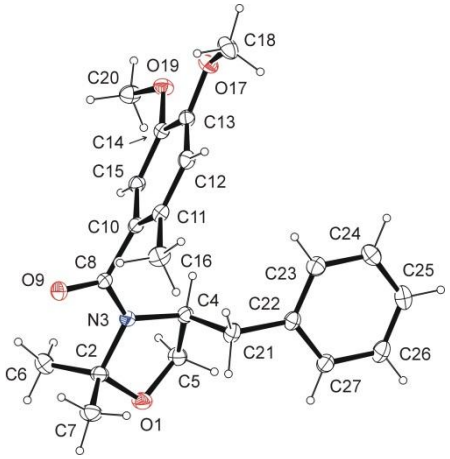


Figure 2. X-Ray crystal structure (ORTEP plot) of **6**

The *o*-tolyl system of the 4,5-dimethoxy-2-methylbenzoyl moiety forms an angle of 71.69(3)º to the approximately planar tertiary amide group (C2/N3/C4/C8/O9, r.m.s. = 0.0443 Å). Orientation of the C11-atom with methyl substituent in the *o*-tolyl system is determined by the torsion angle O9–C8–C10–C11 of 66.36(13)º indicating synclinal (+*sc*) conformation of O9–C8 and C10–C11 bonds. The methoxy groups at C13 and C14 of the 4,5-dimethoxy-2-methylbenzoyl moiety are tilted to a small but statistically significant extent. The vectors of the O17–C18 and O19–C20 bonds are inclined to the mean plane of phenyl ring at the angles of 6.81(8) and 9.18(7)º,[10] respectively.

The C=O group of the amide function is synperiplanar with respect to the C2–N3 bond of oxazolidine ring [torsion angle C2–N3–C8–O9: 1.96(15)°].

In the solid state, the oxazolidine ring has an envelope conformation [puckering parameters[12] Q = 0.3754(11) Å and φ = 322.75(16)°]. The deviation of C5 from the almost planar system formed by the other four atoms of the heterocyclic ring is 0.5748(16) Å.

In conclusion, we have synthesised (4*S*)-4-benzyl-3-(4,5-dimethoxy-2-methylbenzoyl)-2,2-dimethyl-1,3-oxazolidine **6** and fully characterised by physical and spectroscopic data. Compounds **6** can serve as building block in the synthesis of 1-substituted tetrahydroisoquinoline alkaloids, including protoberberines, using the lateral methodology. The absolute configuration of the molecule of oxazolidine **6** was confirmed by X-ray study as 4*S*.

EXPERIMENTAL

Melting points were determined on a Koffler block and are uncorrected. IR spectra: Bruker FT-IR IFS 113V. NMR spectra: Varian Gemini 300, with TMS as the internal standard. Mass spectra: AM D402. Optical rotations: Perkin-Elmer polarimeter 242B at 20 ºC. Elemental analyses: Vario EL III. Analytical

HPLC: Waters HPLC system with Chiralcel OD-H column. Merck DC-Alufolien Kieselgel 60_{254} were used for TLC and Kieselgel 60 (70-230 mesh ASTM) for column chromatography. All compounds were purchased from Aldrich Chemical Co. and used as received.

THF was freshly distilled from $LiAlH_4$, benzene and toluene – from sodium wire.

Table 1. Crystal data and structure refinement for (4*S*)-4-benzyl-3-(4,5-dimethoxy-2-methylbenzoyl)-2,2-dimethyl-1,3-oxazolidine **6**

Formula	$C_{22}H_{27}NO_4$
Formula weight	369.45
Temperature/K	293(2)
Wavelength/Å	1.54178
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	9.90321(17)
b/Å	9.94191(14)
c/Å	20.2832(3)
V/Å^3	1997.02(5)
Z (Z')	4 (1)
D_c/g cm^{-3}	1.229
μ/m m^{-1}	0.678
F(000)	792
Crystal size/mm	0.35*0.30*0.10
Θ range	4.36–76.25º
Max/min. indices *h*, *k*, *l*	$-12 \le h \le 12, -12 \le k \le 12, -25 \le l \le 25$
No. of data collected	29708
Independent Reflections	4189 (R_{int} = 0.0175)
Completeness to θ_{max} = 76.25º /%	100
Restraints/Parameters	4189/0/249
Goodness-of-fit on F^2	1.048
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0277, wR2 = 0.0769
R indices (all data)	R1 = 0.0280, wR2 = 0.0776
Largest diff. peak and hole /eÅ^3	0.088 and -0.145

Table 2. Selected geometric parameters (Å, º) for **6**

Bond lengths	
O(1) – C(5)	1.4264(14)
O(1) – C(2)	1.4331(13)
C(2) – N(3)	1.4855(13)
N(3) – C(4)	1.4690(12)
N(3) – C(8)	1.3535(13)
C(4) – C(5)	1.5146(15)
C(8) – O(9)	1.2295(12)
C(8) – C(10)	1.5023(13)
Bond angles	
C(5) – O(1) – C(2)	108.06(8)
O(1) – C(2) – N(3)	102.44(8)
C(8) – N(3) – C(4)	126.04(8)
C(8) – N(3) – C(2)	122.99(8)
C(4) – N(3) – C(2)	110.54(8)
N(3) – C(4) – C(5)	99.34(8)
O(9) – C(8) – N(3)	122.19(9)
O(9) – C(8) – C(10)	120.71(9)
N(3) – C(8) – C(10)	117.10(8)
O(17) – C(13) – C(12)	124.99(10)
O(17) – C(13) – C(14)	115.39(9)
O(19) – C(14) – C(15)	125.17(9)
O(19) – C(14) – C(13)	115.67(9)
C(13) – O(17) – C(18)	116.58(10)
C(14) – O(19) – C(20)	117.04(8)
Torsion angles	
C(2) – N(3) – C(8) – O(9)	1.96(15)
N(3) – C(4) – C(21) – C(22)	-170.96(9)
N(3) – C(8) – C(10) – C(11)	-114.58(10)
C(4) – C(21) – C(22) – C(23)	82.39(13)
C(4) – C(21) – C(22) – C(27)	-97.54(12)
O(9) – C(8) – C(10) – C(11)	66.36(13)
C(14) – C(13) – O(17) – C(18)	172.70(10)
C(13) – C(14) – O(19) – C(20)	-169.46(9)

2-Bromo-4,5-dimethoxybenzaldehyde (6-bromoveratraldehyde) 8

The veratraldehyde **7** (5.0 g, 30 mmol) was dissolved in acetic acid (30 mL), then the solution of bromine (10.0 g, 63.0 mmol) in acetic acid (20.0 mL) was added dropwise over 15 min. The mixture was stirred at room temperature overnight. Water was added (70 mL) and the mixture was cooled to 4 °C. The product was filtered off and purified by recrystallisation from MeOH/water mixture (6:1 v/v). Product **8** was obtained in quantitative yield (7.35 g), mp 148 – 150 °C (lit.[4] mp 148 – 150 °C). ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 7.06 (s, 1H, ArH), 7.42 (s, 1H, ArH), 10.20 (s, 1H, CHO). ^{1}H NMR spectrum of compound **8** is in agreement with data given in literature.[15]

2-(2-Bromo-4,5-dimethoxyphenyl)-1,3-dioxolane 9

2-Bromo-4,5-dimethoxybenzaldehyde **8** (3.95 g, 16.1 mmol), ethylene glycol (2.0 g, 32.2 mmol) and

p-toluenesufonic acid (0.055 g, 0.3 mmol) were refluxed in benzene under Dean-Stark apparatus over 2 h. The mixture was cooled to room temperature and washed first with 1% NaOH and then with water. Phases were separated; the organic phase was dried over Na_2SO_4 and evaporated to give 4.48 g (96%) of white solid of **9**. ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H, CH_3O), 3.89 (s, 3H, CH_3O), 3.96 – 4.20 (m, 4H, CH_2), 5.99 (s, 1H, CH), 7.02 (s, 1H, ArH), 7.11 (s, 1H, ArH). MS *m/z* 290 (M^+ +1, 44), 289 (M^+, 38), 288 (45), 287 (34), 259 (6), 246 (98), 245 (70), 244 (100), 243 (62), 229 (32), 218 (53), 216 (54), 201 (16), 173 (18), 149 (22), 122 (11), 107 (14), 94 (42), 50 (34). Spectral data of compound **9** are in agreement with data given in literature.[4,16]

2-(4,5-Dimethoxy-2-methylphenyl)-1,3-dioxolane 10

The solution of 2-(2-bromo-4,5-dimethoxyphenyl)-1,3-dioxolane **9** (9.29 g, 32.1 mmol) in dry THF (50 mL) was cooled to – 72 °C under argon atmosphere and *n*-BuLi (22.1 mL of 1.6 M solution in hexane) was added. After 30 min at – 72 °C methyl iodide (21.7 g, 152.9 mmol) solution in THF (10 mL) was added dropwise upon stirring and the mixture was stirred for next 2 h at this temperature. After that time the mixture was allowed to warm up to room temperature and the 20% NH_4Cl was added. Product was extracted with Et_2O (4 x 25 mL). Organic extracts were combined and dried over Na_2SO_4. After evaporation of solvents the crude product was obtained as brown oil in quantitative yield (7.4 g). The crude product was pure enough to be used for the next step of synthesis. The pure analytical sample of **10**, as a white solid, was obtained after chromatography on silica gel (CH_2Cl_2/MeOH, v/v 200:1). ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H, $ArCH_3$), 3.87 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3O), 3.89 – 3.98 (m, 2H, CH_2), 4.02 – 4.22 (m, 2H, CH_2), 5.90 (s, 1H, CH), 6.67 (s, 1H, ArH), 7.09 (s, 1H, ArH). MS *m/z* 225 (M^+ +1, 17), 224 (M^+, 100), 209 (6), 193 (9), 179 (52), 165 (24), 152 (77) 137 (16), 121 (11) 109 (12), 91 (10), 73 (15) 65 (11). ^{1}H NMR spectrum of compound **10** is in agreement with data given in literature.[5]

4,5-Dimethoxy-2-methylbenzaldehyde 11

The crude product **10** (7.4 g) was dissolved in Et_2O (150 mL) and stirred with 10% HCl (30 mL) for 2 h at room temperature. The phases were separated. The aqueous phase was thoroughly extracted with Et_2O (3 x 25 mL). The combined organic layers were dried over Na_2SO_4. Evaporation of solvent gave an oil which solidified on standing. The crude product was chromatographed on silica gel (CH_2Cl_2 and CH_2Cl_2/MeOH, 200:1, v/v) affording 5.55 g (96%) of 4,5-dimethoxy-2-methylbenzaldehyde **11** as an oil, which solidified on standing. The analytical sample of **11** was crystalized from Et_2O mp 71 – 73 °C (lit.[17] mp 73 – 74 °C). IR (KBr) 1677cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.64 (s, 3H, $ArCH_3$), 3.92 (s, 3H, CH_3O), 3.95 (s, 3H, CH_3O), 6.69 (s, 1H, ArH), 7.35 (s, 1H, ArH), 10.22 (s, 1H, CHO). MS *m/z* 181 (M^+ +1, 14), 180 (M^+, 100), 179 (42), 165 (32), 151 (22), 137 (10), 121 (8), 109 (33), 91 (17), 77 (32), 65 (27). Spectral data of compound **11** are in agreement with data given in literature.[5,17]

2-Methyl-4,5-dimethoxybenzoic acid 13

To a solution of 4,5-dimethoxy-2-methylbenzaldehyde **11** (2.37 g, 13.2 mmol) in *t*-butanol (27 mL) the catalyst – ebselen **12** (0.181 g, 0.66 mmol) and then *t*-butyl hydroperoxide (3.3 mL, 70% solution in water) were added upon stirring. The mixture was stirred for 48 h at 70 °C. *t*-Butanol was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (100 mL) and stirred with 5% HCl (52 mL) for 2 h. Phases were separated. The aqueous one was extracted with CH_2Cl_2 (3 x 25 mL). Combined organic extracts were dried over Na_2SO_4 and then evaporated to give an orange solid which was purified by chromatography on silica gel (CH_2Cl_2/MeOH, 150:1, v/v). Acid **13** was recrystallized from EtOAc/hexane yielding 1.19 g (46%) of pure product. Mp 142 – 144 ºC (lit.[5] mp 139 – 141 °C). IR (KBr) 2965, 1690 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.63 (s, 3H, $ArCH_3$), 3.92 (s, 3H, CH_3O), 3.94 (s, 3H, CH_3O), 6.73 (s, 1H, ArH), 7.62 (s, 1H, ArH). MS *m/z* 196 (M^+, 100), 181 (27), 150 (28) 135 (65) 107 (26), 66 (10), 51 (12). Spectral data of compound **13** are in agreement with data given in literature.[5,13,14]

(2*S*)-2-(4,5-Dimethoxy-2-methylbenzamide)-3-phenylpropanol 14

Acid chloride was prepared *in situ* from 2-methyl-4,5-dimethoxybenzoic acid **13** (0.785 g, 4 mmol) by refluxing with $SOCl_2$ (4 mL) and a drop of DMF for 1 h. The excess of $SOCl_2$ was removed in vacuo, affording white precipitate of acid chloride, which was dissolved in CH_2Cl_2 (20 mL) and carefully added to the mixture of (*S*)-(–)-phenylalaninol (0.726 g, 4.8 mmol) in CH_2Cl_2 (150 mL) and 0.5 M KOH (26 mL) at 0 °C. The mixture was stirred vigorously for 1.5 h and precipitated product was filtered off. Addidtional amount of the product was recovered from the filtrate by extraction with CH_2Cl_2 (3 x 30 mL). Organic phases were dried over Na_2SO_4. Solvent was evaporated in vacuo affording white residue, which was combined with precipitate and it was recrystallized from MeOH/Et_2O yielding 1.11 g (84%) of pure product **14**. Mp 186 – 188 °C. $[\alpha]_D$ – 40,12 (c 0.41, $CHCl_3$). IR (KBr) 3334 (NH), 3279 (OH), 1634 (C=O) cm^{-1}.^1H NMR ($CDCl_3$) δ 1.61 (s, 1H, disappears on treatment with D_2O, OH), 2.28 (s, 3H, CH_3), 2.88 – 3.08 (m, 2H, $ArCH_2$), 3.70 – 3.91 (m, 2H, $C\underline{H_2}OH$), 3.78 (s, 3H, CH_3O), 3.87 (s, 3H, CH_3O), 4.34 – 4.43 (m, 1H, CHN), 5.89 (d, J = 7,1 Hz, 1H, NH), 6.64 (s, 1H, ArH), 6.68 (s, 1H, ArH), 7.24 – 7.34 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) δ 19.52 (CH_3Ar), 36.53 (CH_2), 53.51 (CH), 55.87 (CH_3O), 56.04 (CH_3O), 62.21 (CH_2), 110.37 (CH), 113.69 (CH), 126.82 (CH), 127.51(C), 128.8 (2 x CH), 129.16 (C), 129.22 (2 x CH), 137.65 (C), 146.59 (C), 150.00 (C), 170.50 (C=O). MS *m/z* 329 (M^+, 12), 311 (1), 298 (1), 238 (12), 220 (3), 195 (15), 179 (100), 151 (11), 136 (8), 107 (3), 91 (19), 65 (9). Anal. Calcd. for: $C_{19}H_{23}NO_4$ x 1/3 H_2O: C 68.04; H 7.11; N 4.18. Found: C 67.87; H 6.81; N 3.95. HPLC [hexane/propan-2-ol = 15:7, flow rate 0.5 mL/min, t_R = 19.59 min].

(4*S*)-4-Benzyl-3-(4,5-dimethoxy-2-methylbenzoyl)-2,2-dimethyl-1,3-oxazolidine 6

To amide **14** (1.106 g, 3.4 mmol) in dry benzene (70 mL), 2,2-dimethoxypropane (5.6 g, 53.8 mmol) and *p*-toluensulfonic acid monohydrate (5.59 g, 0.87 mmol) were added and the mixture was refluxed for 2 h. It was then cooled to room temperature and washed with 1% NaOH. Organic phase was dried over

Na_2SO_4 and the solvent was evaporated in vacuo. The crude reaction product was chromatographed on silica gel (hexane/EtOAc, 85:15 and 80:20, v/v). Pure oxazolidine **6** as white crystals was obtained in 49% yield (0.616 g) after recrystallization from Et_2O. Mp 118 – 120 °C. $[\alpha]_D$ –46,03 (c 0,315; $CHCl_3$). IR (KBr) 1635 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.71 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.65 – 2.77 (m, 2H, $ArCH_2$), 3.60 – 3.80 (m, 3H, CH_2O, CHN), 3.88 (s, 3H, CH_3O), 3.93 (s, 3H, CH_3O), 6.77 (s, 1H, ArH), 6.84 (s, 1H, ArH), 7.15 – 7.20 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) δ 18.49 ($ArCH_3$), 23.11 (CH_3), 27.03 (CH_3), 40.34 ($ArCH_2$), 56.05 (CH_3O), 56.25 (CH_3O), 61.02 (CH), 66.15 (CH_2), 76.58 (C), 95.40 (C), 109.13 (CH), 113.30 (CH), 126.53 (CH), 128.56 (2 x CH), 128.82 (2 x CH), 129.81 (C), 137.34 (C), 147.03 (C), 149.11 (C), 167.49 (C=O). MS *m/z* 369 (M^+, 4), 311 (1), 278 (4), 220 (2), 179 (100), 151 (7), 121 (3), 91 (5), 65 (4). Anal. Calcd. for $C_{22}H_{27}NO_4$ x 1/8 H_2O: C 71.08; H 7.38; N 3.78. Found: C 71.11; H 7.34; N 3.75. HPLC [hexane/propan-2-ol = 3:1, flow rate 0.5 mL/min, t_R = 22.19 min].

X-Ray structure determination for compound 6

X-Ray diffraction measurements were carried out on a SuperNova Dual Atlas diffractometer.[18] The structure of **6** was solved by direct methods using the SHELXS-97 program.[19] The H atoms were positioned geometrically and were refined using a riding model, with C–H = 0.96 Å (CH_3), 0.97 Å (CH_2), 0.98 Å ($C_{sp}3H$), 0.93 Å ($C_{ar}H$) and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl H atoms. The methyl groups were refined as rigid groups, which were allowed to rotate. The structure was refined by the full-matrix least-squares method on F^2s using the SHELXL-97 program.[19] The crystal data, together with the details concerning the data collection and structure refinement are given in Table 1, and selected geometry parameters in Table 2. Molecular illustration was prepared using ORTEP-3 for Windows.[20] Software used to prepare material for publication was WINGX[20] - and PLATON.[10] The crystallographic data in the CIF form are available as Electronic Supplementary Information from the Cambridge Crystallographic Data Centre, deposition number CCDC 941501; http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.uk).

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