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An Improved Procedure for the Palladium-Catalyzed Oxidative Carbonylation of β-Amino Alcohols to Oxazolidin-2-ones

Bartolo Gabriele,*[,†] Raffaella Mancuso,[‡] Giuseppe Salerno,[‡] and Mirco Costa[§]

Dipartimento di Scienze Farmaceutiche, Università della Calabria, 87036 Arcavacata di Rende, Cosenza, Italy, Dipartimento di Chimica, Università della Calabria, 87036 Arcavacata di Rende, Cosenza, Italy, and Dipartimento di Chimica Organica e Industriale, Università di Parma, Parco Area delle Scienze 17, 43100 Parma, Italy

b.gabriele@unical.it

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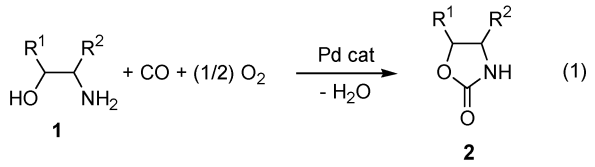
Abstract: A highly efficient oxidative cyclocarbonylation of β-amino alcohols and 2-aminophenol to oxazolidin-2-ones has been achieved by using PdI_2 in conjunction with KI as the catalytic system in DME under relatively mild conditions (100 °C and 20 atm of a 4:1 mixture of CO and air).

We recently reported a new method for the synthesis of 2-oxazolidinones **2** by direct palladium-catalyzed oxidative carbonylation of β-amino alcohols **1** (eq 1).[1] The reaction was carried out in MeOH at 100 °C using a 1/6/5 CO/O_2/air mixture (60 atm total pressure at 25 °C, corresponding to 5 atm of CO and 35 atm of O_2) and was characterized by high to excellent yields (86−100%) and unprecedented catalytic efficiencies for this kind of reaction (860−2000 mol of product per mol of palladium used).

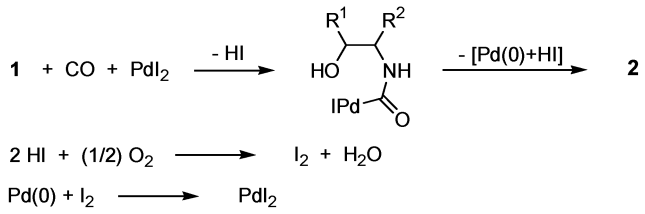


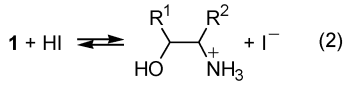
1 **2** (1)

The catalytic system consisted of PdI_2 in conjunction with an excess of KI (200 mol per mol of PdI_2). Reoxidation of Pd(0) ensuing from the cyclocarbonylation process occurred through oxidation of HI (also ensuing from substrate carbonylation) to iodine by oxygen, followed by oxidative addition of I_2 to Pd(0) (Scheme 1; anionic iodide ligands are omitted for clarity).

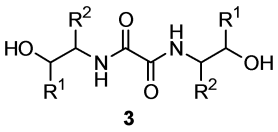
A large excess of both oxygen and iodide anions were essential in order to obtain high yields and high catalytic efficiencies. We interpreted this result as follows. With a basic substrate such as **1**, reoxidation of Pd(0) can be hindered by the acid−base interaction between **1** and HI leading to the corresponding ammonium iodide (eq 2). However, (a) in the presence of a large excess of iodide anions this acid−base equilibrium may be shifted to the left, and (b) a large excess of oxygen in the reaction mixture ensures a fast oxidation of HI to I_2, even in the presence of relatively low concentrations of HI.

SCHEME 1





We have now found that by just changing the reaction solvent from MeOH to 1,2-dimethoxyethane (DME), the oxidative carbonylation of **1** to **2** can be carried out under much milder conditions than those reported above with even higher catalytic efficiencies. In fact, by working in DME the reaction could be effectively performed using only 10 equiv of KI with respect to PdI_2 and under 20 atm of a 4:1 mixture of CO/air (corresponding to 16 atm of CO and only ca. 1 atm of O_2). Some representative results obtained are shown in Table 1. As reported in Table 1, in some cases (entries 3, 6−8) small amounts of oxamide derivatives **3** (corresponding to an oxidative double carbonylation process)[2] were present in the reaction mixtures.



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The reason DME allows the reaction to be carried out under much milder conditions than MeOH can be related again to the effectiveness of Pd(0) reoxidation, which, in turn, depends on the position of the acid−base equilibrium between the substrate and HI (eq 2). DME is an aprotic solvent of low polarity ($\epsilon = 7.54$ at 25 °C, 6.09 at 80 °C),[3] which, however, owing to its coordinating ability, is able to dissolve the PdI_2/KI catalytic system. It is well established that the basicity of amines is significantly reduced in low-polar aprotic solvents with respect to polar protic solvents.[4] This means that a much greater concentration of free HI, necessary for palladium reoxidation, is available in DME rather than MeOH.

The possibility to accomplish the reaction under milder oxidizing conditions has also permitted the application of the methodology to substrates particularly sensitive to oxidizing agents. For example, only traces of benzox-

† Dipartimento di Scienze Farmaceutiche, Università della Calabria.
‡ Dipartimento di Chimica, Università della Calabria.
§ Dipartimento di Chimica Organica e Industriale, Università di Parma.

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TABLE 1. Synthesis of Oxazolidin-2-ones 2 by PdI2/KI-Catalyzed Oxidative Carbonylation of β-Amino Alcohols 1[a]

entry	1	R^1	R^2	1/PdI_2	time (h)	yield of 2 (%)[b]
1[c]	**1a**	H	H	2000	15	96 (90)
2	**1b**[d]	Me	H	2000	15	96 (91)
3	**1c**[d]	Ph	H	2000	8	93 (88)[e]
4	**1d**[d]	H	Me	2000	15	100 (96)
5	**1e**[f]	H	Ph	2000	3	97 (88)
6	**1f**[d]	H	Me_2CH	2000	15	88[g]
7	**1f**[d]	H	Me_2CH	1000	15	94 (87)[h]
8	**1g**[i]	H	$PhCH_2$	2000	15	83[j]
9	**1g**[i]	H	$PhCH_2$	1000	15	90 (81)

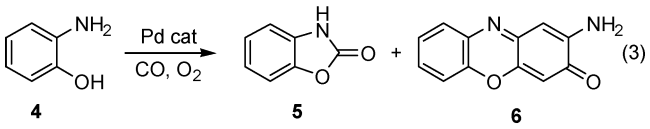
[a] Unless otherwise noted, all reactions were carried out in DME (0.5 mmol/mL DME, 5−10 mmol scale based on **1**) at 100 °C under 20 atm of a 4/1 mixture of CO/air in the presence of PdI_2 in conjunction with 10 equiv of KI. [b] GLC yield (isolated yield) based on **1**. Substrate conversion was practically quantitative in all cases. [c] Substrate concentration was 0.25 mmol/mL DME. The reaction carried out with 0.5 mmol /mL DME led to a lower yield of **2a** (78%, by GLC). [d] Racemic. [e] *N*,*N*-Bis(2-hydroxy-2-phenylethyl)oxalamide **3c** (4%) was also formed. [f] *R* enantiomer. [g] *N*,*N*-Bis(1-hydroxymethyl-2-methylpropyl)oxalamide **3f** was also formed (10%). [h] Oxalamide **3f** was also formed (5%). [i] *S* enantiomer. [j] (*S*,*S*)-*N*,*N*-Bis(1-benzyl-2-hydroxyethyl)oxalamide **3g** (6%) was also formed

TABLE 2. Oxidative Carbonylation of 2-Aminophenol 4 to Benzoxazolidin-2-one 5[a]

entry	solvent	P(CO) (atm)	P(air) (atm)	$P(O_2)$ (atm)	1/KI/PdI_2	mmol 4/mL solvent	yield of 5 (%)[b]	yield of 6 (%)[b]
10	MeOH	5	25	30	2000/200/1	0.5	traces	(62)
11	DME	16	4	-	2000/10/1	0.5	96	traces
12	DME	16	4	-	5000/10/1	0.5	65	traces
13	DME	16	4	-	5000/10/1	1	95 (89)	traces

[a] All reactions were carried out at 100 °C for 15 h, 10−15 mmol scale based on **4**. [b] GLC yield (isolated yield) based on **4**. Substrate conversion was practically quantitative in all cases.

azolin-2-one **5** were obtained from the reaction of 2-aminophenol **4** under the original reaction conditions, while the main reaction product (62% isolated yield, entry 10, Table 2) corresponded to 2-aminophenoxazin-3-one **6** (questiomycin A, an antibiotic)[5] deriving from an oxidative dimerization process without CO incorporation (eq 3).[6] However, under the improved conditions reported in this work, the cyclocarbonylation product **5** was formed with a yield as high as 96%, **6** being present in the reaction mixture just in traces (entry 11). In this latter reaction, catalytic efficiencies up to 4750 mol of **5** per mol of PdI_2 were obtained by using a substrate concentration of 1 rather than 0.5 mmol/mL of DME starting with a **4**/PdI_2 molar ratio of 5000 (entry 13).



4 **5** **6**

In conclusion, we have found that the PdI_2/KI-catalyzed oxidative cyclocarbonylation of β-amino alcohols and 2-aminophenol leading to the corresponding oxazolidin-2-ones can be carried out in high yields and excellent catalytic efficiencies by using a very simple catalytic system (PdI_2 + 10 mol of KI) in DME as the solvent under mildly oxidizing conditions.[7] This atom-economical methodology[8] represents a valuable alternative to the use of diethyl carbonate as an indirect carbonylation agent[9,10] for the synthesis of this very important class of heterocyclic compounds.[11−13]

Experimental Section

General Methods. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, with Me_4Si as internal standard. Chemical shifts and coupling constants (*J*) are given in ppm (δ) and in Hz,

(5) For some recent data on pharmacological activity of **5**, see: Kim, D. S.; Jeong, H. J.; Bhat, K. P. L.; Park, S. Y.; Kang, S. H.; Yoo, E. H.; Lee, M.; Lee, H. W.; Krueger, R. J.; Kim, D. S. H. L. *Planta Med.* **2000**, *66*, 78−79. Igarashi, Y.; Keiichi, K.; Furumai, T. *J. Antibiot.* **1998**, *51*, 915−920.

(6) Formation of **5** from **3** and oxygen has been reported. For recent references, see: (a) Simandi, L. I.; Barna, T.; Nemeth, S. *J. Chem. Soc., Dalton Trans.* **1996**, 473−478. (b) Maruyama, K.; Moriguchi, T.; Mashino, T.; Nishinaga, A. *Chem. Lett.* **1996**, 819−820.

(7) Recently, the Pd(II)-catalyzed oxidative carbonylation of **1** to **2** carried out at room temperature and atmospheric pressure of CO with electrochemical reoxidation of Pd(0) has been reported: Chiarotto, I.; Feroci, M. *Tetrahedron Lett.* **2001**, *42*, 3451−3453. However, very low catalytic efficiencies were obtained (not higher than 9.6 mol of product per mol of Pd used) and the method required the use of an excess of a base such as NaOAc (4 equiv with respect to **1**) in addition to a supporting electrolyte (Bu_4NBF_4).

(8) For a recent review on the importance of the development of new atom-economical processes, see: Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695−705.

(9) Gage, J. R.; Evans, D. A. *Org. Synth.* **1990**, *68*, 77−82. For a review on synthesis of **2**, see Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835−875. For some recent developments in oxazolidin-2-one synthesis, see: Feroci, M.; Gennaro, A.; Inesi, A.; Orsini, M.; Palombi, L. *Tetrahedron Lett.* **2002**, *43*, 5863−5865. Righi, G.; Potini, C.; Bovicelli, P. *Tetrahedron Lett.* **2002**, *43*, 5867−5869. Casado-Bellver, F. J.; Gonzalez-Rosende, M. E.; Asensio, A.; Jorda-Gregori, J. M.; Alvarez-Sorolla, A.; Sepulveda-Arques, J.; Orena, M.; Galeazzi, R. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1650−1654. Kawanami, H.; Ikushima, Y. *Tetrahedron Lett.* **2002**, *43*, 3841−3844. Coelho, F.; Rossi, R. C. *Tetrahedron Lett.* **2002**, *43*, 2797−2800. Tominaga, K.; Sasaki, Y. *Synlett.* **2002**, 307−309. Lei, A. W.; Liu, G. S.; Lu, X. Y. *J. Org. Chem.* **2002**, *67*, 974−980. Overman, L. E.; Remarchuk, T. P. *J. Am. Chem. Soc.* **2002**, *124*, 12−13. Enders, D.; Kallfass, U.; Nolte, B. *Synlett.* **2002**, 33−36. Liu, G. S.; Lu, X. Y. *Org. Lett.* **2001**, *3*, 3879−3882. Bertau, M.; Burli, M.; Hungerbuhler, E.; Wagner, P. *Tetrahedron: Asymm.* **2001**, *12*, 2103-2107. Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Zappia, G. *Org. Lett.* **2001**, *3*, 2539−2541. Ariza, X.; Pineta, O.; Urpi, F.; Vilarrasa, J. *Tetrahedron Lett.* **2001**, *42*, 4995−4999. Yu, C. Z.; Jiang, Y. Y.; Liu, B.; Hu, L. Q. *Tetrahedron Lett.* **2001**, *42*, 1449−1452.

(10) Dialkyl carbonates were initially industrially prepared by the reaction between ROH and phosgene, the latter being in its turn obtained from the reaction between carbon monoxide and chlorine. In the past decades, methods based on oxidative carbonylation of alcohols have been developed (for recent reviews on the production and chemistry of dialkyl carbonates, see: Tundo, P.; Selva, M. *Acc. Chem. Res.* **2002**, *35*, 706−716; Delledonne, D.; Rivetti, F.; Romano, U. *Appl. Catal. A: Gen.* **2001**, *221*, 241−251). Clearly, the possibility to synthesize **2** starting directly from carbon monoxide rather than dialkyl carbonates represents an advantage from the standpoint of atom economy.[8]

(11) Chiral oxazolidin-2-ones are widely used as chiral auxiliaries in many important asymmetric syntheses. For reviews, see: Evans, D. A. *Aldrichim. Acta* **1982**, *15*, 23−32. Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835−875. Ager, D. J.; Prakash, I.; Schaad, D. R. *Aldrichim. Acta* **1997**, *30*, 3−12. For some recent examples, see: Wu, Y. K.; Shen, X.; Tang, C. J.; Chen, Z. L.; Hu, Q.; Shi, W. *J. Org. Chem.* **2002**, *67*, 3802−3810. Wu, Y. K.; Shen, X.; Tang, C. J.; Chen, Z. L. *Helv. Chim. Acta* **2001**, *84*, 3428−3432. Faita, G.; Paio, A.; Quadrelli, P. Rancati, F.; Senesi, P. *Tetrahedron* **2001**, *57*, 8313−8322.

(12) Some molecules containing the oxazolidin-2-one moiety have shown interesting pharmaceutical activity. For recent leading references, see: Ahmed, S.; Adat, S.; Murrells, A.; Owen, C. P. *Biochem. Biophys. Res. Commun.* **2002**, *294*, 380−383. Mai, A.; Artico, M.; Esposito, M.; Sbardella, G.; Massa, S.; Befani, O.; Turini, P.; Giovannini, V.; Mondovi, B. *J. Med. Chem.* **2002**, *45*, 1180−1183; Seki, M.; Mori, K. *Eur. J. Org. Chem.* **1999**, 2965−2967.

respectively. IR spectra were taken on a FT-IR spectrometer. Electronic impact (EI) mass spectra were obtained at 70 eV on a GC-MS apparatus. Electrospray (ES) MS spectra were taken on 1/1 MeOH/H_2O solutions in the presence of 1% AcOH using an ES-MS apparatus. All reactions were analyzed by TLC on silica gel 60 F_{254} or by GLC using capillary columns with polymethylsilicone + 5% phenylsilicone as the stationary phase. R_f in TLC were as follows: **2a**, 0.64 (1:9 hexane/acetone); **2b**, 0.30 (1:1 hexane/acetone); **2c**, 0.36 (1:1 hexane/acetone); **2d**, 0.28 (4:6 hexane/acetone); **2e**, 0.19 (1:1 hexane/AcOEt); **2f**, 0.22 (Et_2O); **2g**, 0.19 (Et_2O); **5**, 0.45 (7:3 hexane/AcOEt); **6**, 0.35 (7:3 hexane/AcOEt). Column chromatography was performed on silica gel 60 (70−230 mesh). Starting materials **1a**−**g** and **4** were commercially available and were used without further purification.

Carbonylation Procedure. Oxidative carbonylation reactions were carried out in a 300 mL stainless steel autoclave with magnetic stirring. In a typical experiment, the autoclave was charged in the presence of air with PdI_2, KI, and a solution of the substrate (5−15 mmol) in DME. The autoclave was pressurized at room temperature with stirring with CO (16 atm) and air (up to 20 atm of total pressure) and then heated at 100 °C with stirring for the required time. Reaction times, substrate/KI/PdI_2 molar ratios, and substrate concentration are indicated in Tables 1 and 2. After cooling, the autoclave was slowly degassed. In some cases (Table 1, entries 3, 6−8) oxamide derivatives **3** were present in suspension as colorless solids; they were easily separated by filtration and purified by washing with cold acetone. After removal of DME by rotary evaporation, crude products **2**, **5**, and **6** were purified as described below.

Separation and Characterization of Products. Crude products **2** were easily purified by column chromatography on silica gel using as eluent hexane/acetone from 1:1 to 4:6 (**2a**, **2c**); 6:4 hexane/acetone (**2b**); 1:1 hexane/acetone (**2d**); hexane/AcOEt from 9:1 to 7:3 (**2e**); hexane/Et_2O from 3:7 to 0:10 (**2f**); hexane/Et_2O from 3:7 to 0:10 (**2g**), and were fully characterized by IR, ^{1}H NMR and ^{13}C spectroscopies, and MS spectrometry. Oxazolidin-2-ones were obtained with a satisfactory degree of purity, as confirmed by elemental analysis, so in the case of solid compounds (**2a**, **2c**, **2e**, **2f**, **2g**) no further purification by crystallization was needed. Products **5**, **6** were separated in this order by column chromatography on silica gel using hexane/AcOEt from 7:3 to 1:1; benzoxazolidin-2-one **5** thus obtained was a pale yellow solid that could be further purified by repeated crystallization from cold Et_2O to give a colorless solid. Compounds **3** were purified as described above. Also products **3**, **5**, and **6** were fully characterized by spectroscopic techniques and elemental analysis.

Oxazolidin-2-one 2a (colorless solid, mp 87−88 °C, lit.[14] 88−89 °C): IR (KBr) 3274, 1731 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.63 (br s, 1 H), 4.42−4.35 (m, 2 H), 3.63−3.56 (m, 2 H); ^{13}C NMR (acetone-d_6) δ 160.8, 65.4, 41.1; MS (EI) *m*/*e* 87 (100, M$^+$), 59 (44), 42 (24). Anal. Calcd for $C_3H_5NO_2$: C, 41.38; H, 5.79; N, 16.09. Found C, 41.48; H, 5.80; N, 16.05.

5-Methyloxazolidin-2-one 2b (pale yellow oil): IR (neat) 3299, 1739 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.61 (br s, 1 H), 4.79−4.66 (m, 1 H), 3.73−3.66 (m, 1 H), 3.20−3.13 (m, 1 H), 1.37 (d, J = 6.4, 3 H); ^{13}C NMR (acetone-d_6) δ 160.2, 73.6, 47.8, 20.7; MS (EI) *m*/*e* 101 (100, M$^+$), 86 (17), 56 (57). Anal. Calcd for $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.85. Found C, 47.47; H, 6.99; N, 13.89.

5-Phenyloxazolidin-2-one 2c (colorless solid, mp 90−91 °C, lit.[14] 90−92 °C): IR (KBr) 3278, 1721 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.46−7.30 (m, 5 H), 6.75 (br s, 1 H), 5.63 (dd, J = 8.8, 7.3, 1 H), 4.00 (td, J = 8.8, 1.0, 1 H), 3.46 (ddd, J = 8.8, 7.3, 1.0, 1 H); ^{13}C NMR (acetone-d_6) 159.8, 140.6, 129.5, 129.3, 126.6, 77.9, 48.7; MS (EI) *m*/*e* 163 (20, M$^+$), 107 (100), 79 (37). Anal. Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58. Found C, 66.31; H, 5.55; N, 8.60.

4-Methyloxazolidin-2-one 2d (pale yellow oil): IR (neat) 3287, 1743 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.82 (br s, 1 H), 4.46 (t, J = 8.3, 1 H), 4.06−3.94 (m, 1 H), 3.89 (dd, J = 8.3, 6.3, 1 H), 1.24 (d, J = 5.9, 3 H); ^{13}C NMR (acetone-d_6) δ 160.0, 71.9, 48.8, 20.8; MS (EI) *m*/*e* 101 (25, M$^+$), 86 (100). Anal. Calcd for $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.85. Found C, 47.58; H, 7.00; N, 13.88.

(*R*)-4-Phenyloxazolidin-2-one 2e (colorless solid, mp 130−131 °C, lit.[14] 131−132 °C): IR (KBr) 3249, 1741, 1706 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.42−7.30 (m, 5 H), 7.16 (br s, 1 H), 5.03 (ddd, J = 8.5, 6.6, 1.0, 1 H), 4.73 (t, J = 8.5, 1 H), 4.06 (dd, J = 8.5, 6.6, 1 H); ^{13}C NMR (acetone-d_6) δ 159.9, 142.0, 129.7, 128.9, 126.9, 72.7, 56.6; MS (EI) *m*/*e* 163 (46, M$^+$), 133 (75), 105 (74), 104 (100). Anal. Calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58. Found C, 66.41; H, 5.56; N, 8.57.

4-Isopropyloxazolidin-2-one 2f (colorless solid, mp 70−71 °C, lit.[15] 69−72 °C): IR (KBr) 3243, 1747 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45 (br s, 1 H), 4.45 (t, J = 8.8, 1 H), 4.10 (dd, J = 8.8, 6.4, 1 H), 3.68−3.59 (m, 1 H), 1.73 (octuplet, J = 6.8, 1 H), 0.97 (d, J = 6.8, 3 H), 0.90 (d, J = 6.8, 3 H); ^{13}C NMR ($CDCl_3$) δ 160.9, 68.7, 58.5, 32.7, 18.0, 17.7; MS (EI) *m*/*e* 129 (4, M$^+$), 86 (100), 85 (39). Anal. Calcd for $C_6H_{11}NO_2$: C, 55.80; H, 8.58; N, 10.84. Found C, 55.71; H, 8.60; N, 10.81.

(*S*)-4-Benzyloxazolidin-2-one 2g (colorless solid, mp 87−88 °C, lit.[16] 87−88 °C): IR (KBr) 3286, 1755, 1710 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.35−7.20 (m, 5 H), 6.84 (br s, 1 H), 4.34 (dd, J = 8.3, 7.8, 1 H), 4.20−4.11 (m, 1 H), 4.07 (distorted dd, J = 8.3, 5.4, 1 H), 2.96−2.81 (m, 2 H); ^{13}C NMR (acetone-d_6) δ 159.7, 137.8, 130.2, 129.4, 127.5, 69.6, 54.2, 41.7; MS (EI) *m*/*e* 177 (3, M$^+$), 92 (100), 91 (65), 86 (79). Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found C, 67.93; H, 6.27; N, 7.92.

***N*,*N*-Bis(2-hydroxy-2-phenylethyl)oxalamide 3c** (colorless solid, mp 166−167 °C): IR (KBr) 3426, 3305, 1654 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.50 (t, J = 5.5, 2 H), 7.36−7.23 (m, 10 H), 5.58 (d, J = 4.4, 2 H), 4.77−4.67 (m, 2 H), 3.41−3.25 (m, 4 H); ^{13}C NMR (DMSO-d_6) δ 159.6, 143.1, 128.0, 127.1, 125.9, 70.5, 46.8; MS (ES) 367 (M + K)$^+$, 351 (M + Na)$^+$, 329 (M + H)$^+$. Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found C, 65.91; H, 6.12; N, 8.51.

***N*,*N*-Bis(1-hydroxymethyl-2-methylpropyl)oxalamide 3f** (colorless solid, mp 186−187 °C): IR (KBr) 3419, 3298, 1640 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.19 (d, J = 9.3, 2 H), 4.74−4.67 (m, 2 H), 3.61−3.42 (m, 6 H), 1.85 (octuplet, J = 6.8, 2 H), 0.88 (d, J = 6.8, 6 H), 0.81 (d, J = 6.8, 6 H); ^{13}C NMR (DMSO-d_6) δ 159.8, 60.9, 56.7, 28.5, 19.5, 18.6; MS (EI) *m*/*e* 260 (2, M$^+$), 229 (47), 72 (100). Anal. Calcd for $C_{12}H_{24}N_2O_4$: C, 55.36; H, 9.29; N, 10.76. Found C, 55.42; N, H, 9.27, N, 10.78.

(*S*,*S*)-*N*,*N*-Bis(1-benzyl-2-hydroxyethyl)oxalamide 3g (colorless solid, mp 217−218 °C, lit.[17] 217−217.5 °C): IR (KBr) 3420, 3301, 1656 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.35 (d, J = 9.3, 2 H), 7.27−7.12 (m, 10 H), 4.89 (t, J = 5.6, 2 H), 4.02−3.87 (m, 2 H), 3.44−3.32 (m, 4 H), 2.85 (distorted dd, J = 13.7, 5.4, 2 H), 2.71 (distorted dd, J = 13.7, 8.8, 2 H); ^{13}C NMR (DMSO-d_6) δ 159.4, 138.7, 128.9, 128.0, 125.9, 62.1, 52.9, 36.0; MS (ES) 395 (M + K)$^+$, 379 (M + Na)$^+$. Anal. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86. Found C, 67.31; H, 6.80, N, 7.86.

3*H*-Benzooxazol-2-one 5 (colorless solid, mp 138−139 °C, lit.[18] 137−139 °C): IR (KBr) 3230, 1776, 1737 cm^{-1}; ^{1}H NMR (CD_3OD) δ 7.20−7.04 (m, 4 H), 5.09 (br s, 1 H); ^{13}C NMR (CD_3OD) δ 157.2, 145.3, 131.5, 125.1, 123.4, 110.9, 110.6; MS (EI)

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m/*e* 135 (100, M^+), 91 (15), 79 (37). Anal. Calcd for $C_7H_5NO_2$: C, 62.22; H, 3.73; N, 10.37. Found C, 62.09; H, 3.73; N, 10.40.

2-Aminophenoxazin-3-one 6 [brown red solid, mp 256−257 °C (dec), lit. 254−256 °C,[6a] 256−258[6b]]: IR (KBr) 3413, 3307, 1587 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.74−7.70 (m, 1 H), 7.54.7.37 (m 3 H), 6.85 (br s, 2 H), 6.37 (s, 1 H), 6.36 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 180.1, 148.8, 148.1, 147.3, 141.8, 133.6, 128.7, 127.9, 125.2, 115.8, 103.3, 98.2; MS (EI) *m*/*e* 212 (100, M^+), 185 (60). Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80, N, 13.20. Found C, 68.09; H, 3.81; N, 13.17.

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