Synthesis of Novel 4-Functionalised Oxazolidin-2-ones

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This paper is dedicated to Prof. Dr. D. Geffken.

Abstract: The synthesis of O-substituted and O-unsubstituted 3-hydroxy-4-thioxo-oxazolidin-2-ones, functionalised 4-imino-oxazolidine-2-ones and 4-phenoxy-imino-oxazolidin-2-one starting from O-substituted and O-unsubstituted 3-hydroxy-4-imino-oxazolidin-2-ones is described. A one-pot protocol for the preparation of 4-methoxyimino-, 4-aralkoxyimino- and 4-phenoxyimino-oxazolidin-2-ones has been developed.

Key words: heterocycles, oxazolidin-2-ones, Dimroth rearrangement, thionation, ring closure

Oxazolidin-2,4-diones and their 4-imino(thioxo) analogues have attracted much attention in medicinal and agricultural chemistry. Famoxadone (Figure 1), a 3-phenylamino-oxazolidin-2,4-dione, is a broad spectrum fungicide, which is particularly active against grape downy mildew and potato and tomato late and early blights.[1] Vinclozolin represents a well known dicarboximide fungicide used for the control of *Botrytis* and *Sclerotina* spp.[2] Trimethadione, is an anticonvulsant for the treatment of epilepsy.[3] Geffken reported the synthesis and fungicidal activity of 4-hydroxyimino-oxazolidin-2-ones, which have been obtained by treatment of 4-alkoxy-3-oxazolin-2-ones with hydroxylamine.[4] Furthermore, in 1992 DuPont described 3-phenylamino-4-imino(thioxo)-oxazolidin-2-ones as novel classes of fungicides.[5] Surprisingly, the corresponding O-substituted and O-unsubstituted 3-hydroxy-4-imino(thioxo)-oxazolidin-2-ones have not been reported so far.

Recently, we reported the first synthesis of O-substituted and O-unsubstituted 3-hydroxy-4-imino-oxazolidin-2-ones **1** and their sodium methoxide-mediated conversion into the corresponding α-hydroxyamidoximes.[6] We now describe the synthetic potential of **1** as precursors in the preparation of novel 4-functionalised oxazolidin-2-one derivatives (Scheme 1).

Thionation of substrates **1a–l** by hydrogen sulfide in anhydrous CH_2Cl_2 in the presence of pyridine afforded previously unreported O-substituted and O-unsubstituted 3-hydroxy-4-thioxo-oxazolidin-2-ones (**2a–l**) in good yields of 75–85% (Scheme 1, Table 1).[5]

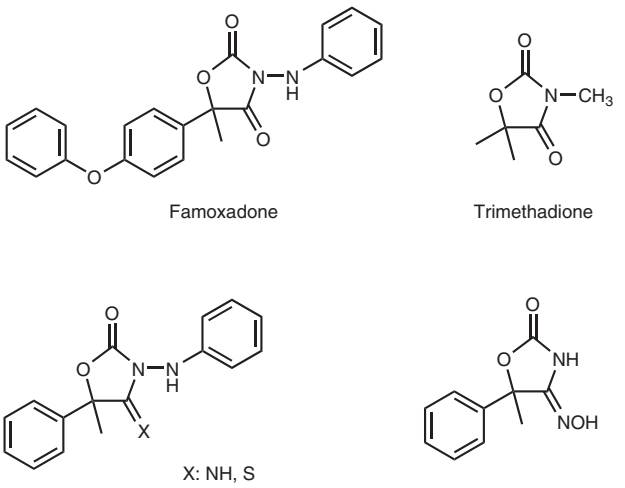
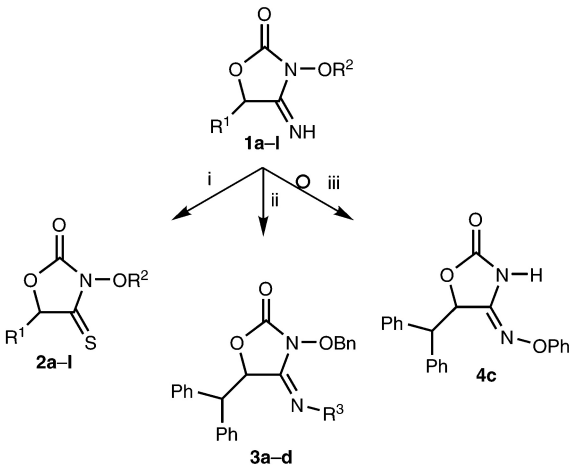


Figure 1 Selected biologically active oxazolidin-2,4-diones and analogues.



Reagents. i: H_2S, pyridine; ii: (a) PhNCO (**3a**, 80%), (b) 4-F-PhNCS (**3b**, 68%), (c) 4-CH_3-$PhSO_2Cl$ (**3c**, 70%), (d) 4-F-PhCOCl (**3d**, 78%), iii: Et_3N, CH_2Cl_2, reflux

Scheme 1 Synthesis of 4-functionalised oxazolidin-2-ones.

Reactions of **1b** with phenyl isocyanate**,** 4-fluorophenyl isothiocyanate, *p*-toluenesulfonyl chloride and 4-fluorobenzoyl chloride furnished the derivatised 4-imino-oxazolidin-2-ones **3a–d** in 68–80% yield (Scheme 1).

Treatment of **1c** with Et_3N in CH_2Cl_2 provided, in accordance with previous studies, the Dimroth rearrangement product **4c** in 93% yield (Scheme 1).[7,8]

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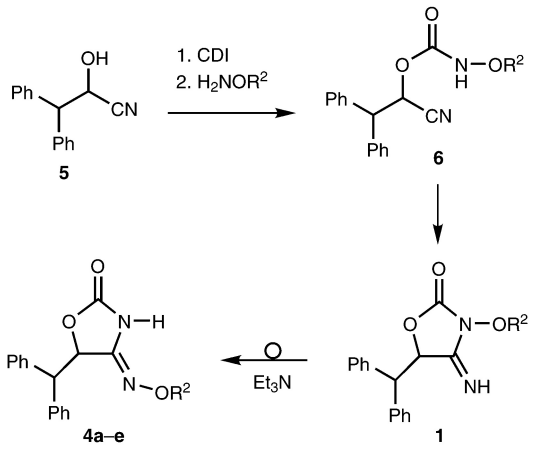
Table 1 3-Alkoxy-, 3-Aralkoxy-, 3-Phenoxy- and 3-Hydroxy-4-thioxo-oxazolidin-2-ones **2a–l**

2	R^1	R^2	Yield (%)
a	Ph_2CH	Me	78
b	Ph_2CH	Bn	85
c	Ph_2CH	Ph	80
d	Ph_2CH	*t*-Bu	75
e	Ph_2CH	$Ph(CH_2)_2$	83
f	Ph_2CH	H	80
g	*t*-Bu	Me	75
h	*t*-Bu	Bn	84
i	*t*-Bu	Ph	75
j	*t*-Bu	*t*-Bu	80
k	*t*-Bu	$Ph(CH_2)_2$	81
l	*t*-Bu	H	75

The smooth conversion of **1c** into **4c** prompted us to develop the first one-pot protocol for the synthesis of 4-methoxyimino-, 4-aralkoxyimino- and 4-phenoxyimino-oxazolidin-2-ones (**4a–e**) (Scheme 2). Successive treatment of cyanohydrins with 1,1′-carbonyldiimidazole (CDI) and O-substituted hydroxylamines furnished intermediates **1,** which upon treatment with Et_3N underwent Dimroth rearrangement to give **4a–e** in good yields of 70–80% (Table 2).[9] Discrimination between the structures of compounds **1** and **4** was accomplished by IR, ^1H and ^{13}C NMR spectroscopy.



Scheme 2 One-pot synthesis of 4-methoxy-, 4-aralkoxy-, and 4-phenoxyimino-oxazolidin-2-ones (**4a–e**).

The structures of all compounds (**2–4**) were elucidated by IR, ^1H, ^{13}C NMR spectroscopy and elemental analysis.

In conclusion, we have synthesised a variety of novel 4-functionalised oxazolidin-2-one derivatives as analogues of existing biologically active oxazolidin-2-ones. Furthermore, we have developed a new and operationally simple one-pot protocol for the synthesis of 4-alkoxyimino-, 4-aralkoxyimino-, and 4-phenoxyimino-oxazolidin-2-ones. This method complements Geffken's multi-step synthesis of 4-hydroxyimino-oxazolidin-2-ones and offers advantages in convenience and yields.

Table 2 4-Methoxyimino-, 4-Aralkoxyimino- and 4-Phenoxyimino-oxazolidin-2-ones (**4a–e**)

4	R^2	Yield (%)
a	Me	70
b	Bn	75
c	Ph	73
d	$Ph(CH_2)_2$	80
e	$Ph(CH_2)_3$	72

Melting points (uncorrected) were determined on a Mettler FP 62 apparatus. Elemental analyses were carried out with a Heraeus CHN-O-Rapid instrument. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AMX 400 spectrometer using TMS as an internal standard and DMSO-d_6 as solvent.

Preparation of 2a–l; General Procedure

H_2S gas was introduced for 30 min to a solution of **1a–l** (3 mmol) in anhyd CH_2Cl_2 (20 mL) and anhyd pyridine (12 mL). After stirring at r.t. for 3 h the reaction mixture was diluted with Et_2O (50 mL) and washed thrice with 20% HCl (15 mL). The organic layer was dried over $MgSO_4$ and the solvent was evaporated to afford **2a–l** as yellow solids, which were recrystallised from Et_2O–hexane.

5-Benzhydryl-3-methoxy-4-thioxo-oxazolidin-2-one (2a)

Yield: 0.73 g (78%); yellow solid; mp 75 °C.

IR (KBr): 1280, 1809 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.45 (s, 3 H), 4.76 (d, *J* = 2.80 Hz, 1 H), 5.84 (d, *J* = 2.54 Hz, 1 H), 7.21–7.43 (m, 10 H).

^{13}C NMR (DMSO-d_6): δ = 54.3, 64.2, 88.1, 127.2, 127.7, 128.4, 128.8, 129.0, 130.1, 137.8, 140.8, 151.2, 192.5.

Anal. Calcd for $C_{17}H_{15}NO_3S$: C, 65.16; H, 4.82; N, 4.47. Found: C, 65.01; H, 5.01; N, 4.35.

5-Benzhydryl-3-benzyloxy-4-thioxo-oxazolidin-2-one (2b)

Yield: 0.99 g (85%); yellow solid; mp 112 °C.

IR (KBr): 1275, 1810 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 4.66 (q, *J* = 9.76 Hz, 2 H), 4.95 (d, *J* = 2.80 Hz, 1 H), 6.15 (d, *J* = 2.54 Hz, 1 H), 7.21–7.44 (m, 15 H).

^{13}C NMR (DMSO-d_6): δ = 53.6, 78.3, 88.2, 126.8, 127.5, 128.2, 128.6, 128.95, 129.02, 129.9, 130.09, 130.11, 132.9, 136.6, 140.0, 151.4, 194.4.

Anal. Calcd for $C_{23}H_{19}NO_3S$: C, 70.93; H, 4.92; N, 3.60. Found: C, 70.80; H, 5.03; N, 3.49.

5-Benzhydryl-3-phenoxy-4-thioxo-oxazolidin-2-one (2c)

Yield: 0.90 g (80%); yellow solid; mp 120 °C.

IR (KBr): 1276, 1815 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 4.82 (d, *J* = 2.81 Hz, 1 H), 6.10 (d, *J* = 2.54 Hz, 1 H), 7.11–7.45 (m, 15 H).

^{13}C NMR (DMSO-d_6): δ = 53.0, 87.9, 126.8, 127.5, 128.2, 128.6, 128.95, 129.02, 129.9, 130.1, 132.9, 136.6, 140.0, 153.6, 194.4.

Anal. Calcd for $C_{22}H_{17}NO_3S$: C, 70.38; H, 4.56; N, 3.73. Found: C, 70.24; H, 4.68; N, 3.55.

5-Benzhydryl-3-*tert*-butoxy-4-thioxo-oxazolidin-2-one (2d)
Yield: 0.80 g (75%); yellow solid; mp 73 °C.

IR (KBr): 1275, 1810 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 0.94 (s, 9 H), 4.66 (d, *J* = 2.81 Hz, 1 H), 5.84 (d, *J* = 2.58 Hz, 1 H), 7.21–7.43 (m, 10 H).

^{13}C NMR (DMSO-d_6): δ = 26.5, 52.6, 79.2, 88.1, 127.2, 127.7, 128.4, 128.8, 129.0, 130.1, 137.8, 140.8, 152.2, 193.9.

Anal. Calcd for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.95; N, 3.94. Found: C, 67.65; H, 6.00; N, 3.85.

5-Benzhydryl-3-phenylethoxy-4-thioxo-oxazolidin-2-one (2e)
Yield: 1.00 g (83%); yellow solid; mp 101 °C.

IR (KBr): 1270, 1815 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 2.95 (t, *J* = 6.87 Hz, 2 H), 4.19 (t, *J* = 7.12 Hz, 2 H), 4.95 (d, *J* = 2.80 Hz, 1 H), 6.15 (d, *J* = 2.54 Hz, 1 H), 7.21–7.44 (m, 15 H).

^{13}C NMR (DMSO-d_6): δ = 35.5, 53.6, 77.4, 88.2, 126.8, 127.5, 128.2, 128.6, 128.95, 129.02, 129.8, 130.09, 130.11, 132.9, 136.6, 140.0, 151.4, 192.8.

Anal. Calcd for $C_{24}H_{21}NO_3S$: C, 71.44; H, 5.25; N, 3.47. Found: C, 71.30; H, 5.45; N, 3.29.

5-Benzhydryl-3-hydroxy-4-thioxo-oxazolidin-2-one (2f)
Yield: 0.72 g (80%); yellow solid; mp 190 °C.

IR (KBr): 1270, 1805 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 4.65 (d, *J* = 2.81 Hz, 1 H), 5.90 (d, *J* = 2.54 Hz, 1 H), 7.00–7.45 (m, 10 H).

^{13}C NMR (DMSO-d_6): δ = 51.2, 88.2, 127.0, 127.5, 128.5, 128.7, 129.8, 137.7, 138.0, 140.8, 151.1, 194.1.

Anal. Calcd for $C_{16}H_{13}NO_3S$: C, 64.20; H, 4.38; N, 4.68. Found: C, 63.95; H, 4.52; N, 4.50.

5-*tert*-Butyl-3-methoxy-4-thioxo-oxazolidin-2-one (2g)
Yield: 0.46 g (75%); yellow solid; mp 67 °C.

IR (KBr): 1280, 1809 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 0.90 (s, 9 H), 3.45 (s, 3 H), 4.66 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 24.6, 34.2, 64.4, 88.6, 152.9, 194.0.

Anal. Calcd for $C_8H_{13}NO_3S$: C, 47.27; H, 6.45; N, 6.89. Found: C, 47.20; H, 6.68; N, 6.63.

3-Benzyloxy-5-*tert*-butyl-4-thioxo-oxazolidin-2-one (2h)
Yield: 0.70 g (84%); yellow solid; mp 60 °C.

IR (KBr): 1273, 1815 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 0.91 (s, 9 H), 4.70 (s, 1 H), 5.07 (q, *J* = 10.68 Hz, 2 H), 7.88–7.55 (m, 5 H).

^{13}C NMR (DMSO-d_6): δ = 24.5, 34.8, 78.5, 84.0, 126.9, 129.7, 120.5, 134.1, 151.8, 194.3.

Anal. Calcd for $C_{14}H_{17}NO_3S$: C, 60.19; H, 6.13; N, 5.01. Found: C, 59.90; H, 6.39; N, 4.85.

5-*tert*-Butyl-3-phenoxy-4-thioxo-oxazolidin-2-one (2i)
Yield: 0.60 g (75%); yellow solid; mp 87 °C.

IR (KBr): 1277, 1816 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 0.92 (s, 9 H), 4.71 (s, 1 H), 7.22–7.50 (m, 5 H).

^{13}C NMR (DMSO-d_6): δ = 27.6, 36.1, 86.6, 126.9, 129.7, 130.5, 134.1, 151.9, 194.0.

Anal. Calcd for $C_{13}H_{15}NO_3S$: C, 58.85; H, 5.70; N, 5.28. Found: C, 58.70; H, 5.93; N, 5.09.

3-*tert*-Butoxy-5-*tert*-butyl-4-thioxo-oxazolidin-2-one (2j)
Yield: 0.60 g (80%); yellow solid; mp 65 °C.

IR (KBr): 1270, 1807 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 0.91 (s, 9 H), 1.10 (s, 9 H), 4.71 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 27.6, 28.0, 36.1, 75.7, 86.6, 153.5, 194.4.

Anal. Calcd for $C_{11}H_{19}NO_3S$: C, 53.85; H, 7.81; N, 5.71. Found: C, 53.90; H, 7.80; N, 5.75.

5-*tert*-Butyl-3-phenylethoxy-4-thioxo-oxazolidin-2-one (2k)
Yield: 0.71 g (81%); yellow solid; mp 93 °C.

IR (KBr): 1275, 1810 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 0.90 (s, 9 H), 2.95 (t, *J* = 6.87 Hz, 2 H), 4.19 (t, *J* = 7.12 Hz, 2 H), 4.73 (s, 1 H), 7.20–7.45 (m, 5 H).

^{13}C NMR (DMSO-d_6): δ = 27.6, 34.4, 36.1, 76.6, 88.3, 126.9, 129.7, 130.5, 134.1, 153.9, 194.0.

Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.35; H, 6.60; N, 4.70.

5-*tert*-Butyl-3-hydroxy-4-thioxo-oxazolidin-2-one (2l)
Yield: 0.43 g (75%); yellow solid; mp 175 °C.

IR (KBr): 1270, 1810 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 0.98 (s, 9 H), 4.78 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 24.6, 34.1, 88.5, 152.9, 193.9.

Anal. Calcd for $C_7H_{11}NO_3S$: C, 44.43; H, 5.86; N, 7.40. Found: C, 44.20; H, 6.00; N, 7.18.

Preparation of 3a,b; General Procedure
Phenyl isocanate or 4-fluorophenyl isothiocyanate (3 mmol) was added to a solution of **1b** (1.11 g, 3 mmol) in anhy THF (5 mL) under ice cooling and the reaction mixture was stirred at r.t. for 3 h. The solvent was evaporated under reduced pressure and the remaining oil was crystallised from EtOAc–hexane to afford **3a**,**b** as colourless solids.

***N*-(5-Benzhydryl-3-benzyloxy-4-oxazolidinylidene)-*N*′-phenylurea (3a)**
Yield: 1.18 g (80%); colourless solid; mp 120 °C.

IR (KBr): 1695, 1720, 1810 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 4.67 (q, *J* = 10.18 Hz, 2 H), 4.75 (d, *J* = 2.90 Hz, 1 H), 5.97 (d, *J* = 2.60 Hz, 1 H), 7.20–7.55 (m, 20 H), 7.66 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 53.6, 78.4, 88.2, 126.8, 127.5, 128.5, 128.6, 128.8, 128.95, 129.01, 129.9, 130.0, 130.2, 132.9, 136.6, 140.0, 151.4, 154.0, 167.0.

Anal. Calcd for $C_{30}H_{25}N_3O_4$: C, 73.31; H, 5.13; N, 8.55. Found: C, 73.20; H, 5.00; N, 8.41.

***N*-(5-Benzhydryl-3-benzyloxy-2-oxo-oxazolidin-4-ylidene)-3-(fluorophenyl)thiourea (3b)**
Yield: 1.07 g (68%); colourless solid; mp 102 °C.

IR (KBr): 1690, 1810 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 4.60 (q, J = 10.18 Hz, 2 H), 4.77 (d, J = 2.90 Hz, 1 H), 5.90 (d, J = 2.61 Hz, 1 H), 7.21–7.50 (m, 19 H), 7.70 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 53.6, 78.3, 87.9, 126.7, 127.0, 128.2, 128.6, 128.8, 129.0, 129.1, 130.0, 130.1, 130.2, 133.0, 136.6, 141.0, 151.5, 154.1, 191.5.

Anal. Calcd for $C_{30}H_{24}FN_3O_3S$: C, 68.56; H, 4.60; N, 7.99. Found: C, 68.42; H, 4.71; N, 7.89.

Preparation of 3c,d; General Procedure

p-Toluenesulfonyl chloride or 4-fluorobenzoyl chloride (3 mmol) was added to a solution of **1b** (1.11 g, 3 mmol) and Et_3N (3 mmol) in anhyd THF (5 mL) under ice cooling. The reaction mixture was stirred at r.t. for 3 h and the solvent was evaporated under reduced pressure. The remaining oil was dissolved in EtOAc (20 mL) and the solution was washed with water. (5 mL). The organic layer was dried over $MgSO_4$, the solvent evaporated and the resulting oil was crystallised from EtOAc–hexane.

***N*-(5-Benzhydryl-3-benzyloxy-2-oxo-oxazolidin-4-ylidene)-4-methylbenzenesulfonamide (3c)**

Yield: 1.11 g (70%); colourless solid; mp 160 °C.

IR (KBr): 1695, 1795 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 3.32 (s, 3 H), 4.62 (q, J = 10.18 Hz, 2 H), 4.70 (d, J = 2.90 Hz, 1 H), 5.97 (d, J = 2.60 Hz, 1 H), 7.18–7.45 (m, 19 H).

^{13}C NMR (DMSO-d_6): δ = 53.7, 78.4, 87.8, 112.1, 126.7, 127.4, 128.5, 128.7, 128.9, 129.0, 129.1, 129.8, 130.1, 130.2, 132.9, 136.7, 140.0, 151.3, 156.0.

Anal. Calcd for $C_{30}H_{26}N_2O_5S$: C, 68.42; H, 4.98; N, 5.32. Found: C, 68.20; H, 5.09; N, 5.23.

***N*-(5-Benzhydryl-3-benzyloxy-2-oxo-oxazolidin-4-ylidene)-4-fluorobenzamide (3d)**

Yield: 1.16 g (78%); colourless solid; mp 173 °C.

IR (KBr): 1670, 1690, 1790 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 4.60 (q, J = 10.17 Hz, 2 H), 4.75 (d, J = 2.90 Hz, 1 H), 5.95 (d, J = 2.60 Hz, 1 H), 7.21–7.50 (m, 19 H).

^{13}C NMR (DMSO-d_6): δ = 53.5, 78.4, 87.9, 111.9, 126.8, 127.4, 128.4, 128.6, 128.8, 128.9, 129.3, 129.9, 130.0, 130.3, 132.9, 136.7, 140.1, 151.4, 154.1, 168.1.

Anal. Calcd for $C_{30}H_{23}FN_2O_4$: C, 70.86; H, 4.69; N, 5.66. Found: C, 72.95; H, 4.80; N, 5.50.

Preparation of 4a–e; General Procedure

A solution of cyanohydrine (5 mmol) in anhyd CH_2Cl_2 (5 mL) was added dropwise over a period of 10 min to a suspension of 1,1′-carbonyldiimidazole (0.89 g, 5.5 mmol) in CH_2Cl_2 (5 mL) under ice cooling. After stirring at r.t. for 10 min a solution of the appropriate *O*-substituted hydroxylamine (5 mmol) in anhyd CH_2Cl_2 (5 mL) was added and the reaction mixture was stirred at r.t. for 1 h. The reaction mixture was concentrated under reduced pressure, Et_3N (3 mL) was added and the mixture was heated to 60–70 °C until two sharp bands in the IR spectrum appeared at 1745–1760 and 1650–1680 cm^{-1}. After cooling to r.t., the reaction mixture was diluted with Et_2O, washed with brine and water. The organic layer was dried over $MgSO_4$, filtered, concentrated and the remaining oil was crystallised from Et_2O–hexane.

5-Benzhydryl-4-methoxyimino-oxazolidin-2-one (4a)

Yield: 1.04 g (70%); colourless solid; mp 101 °C.

IR (KBr): 1755, 1660 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 3.80 (s, 3 H), 4.82 (d, J = 4.71 Hz, 1 H), 6.10 (d, J = 4.59 Hz, 1 H), 7.15–7.49 (m, 10 H), 11.52 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 35.3, 52.7, 66.0, 78.9, 112.6, 120.9, 122.6, 127.3, 129.0, 129.8, 130.1, 140.7, 151.7, 154.0.

Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.95; H, 5.43; N, 9.53.

5-Benzhydryl-4-benzyloxyimino-oxazolidin-2-one (4b)

Yield: 1.40 g (75%); colourless solid; mp 130 °C.

IR (KBr): 1760, 1665 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 4.62 (s, 2 H), 4.91 (d, J = 4.70 Hz, 1 H), 5.90 (d, J = 4.60 Hz, 1 H), 7.15–7.40 (m, 15 H), 11.50 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 53.0, 75.9, 79.0, 112.7, 113.5, 121.0, 122.8, 127.3, 127.8, 128.8, 129.5, 129.8, 130.1, 130.3, 140.5, 151.7, 154.0.

Anal. Calcd for $C_{23}H_{20}N_2O_3$: C, 74.18; H, 5.41; N, 7.52. Found: C, 74.35; H, 5.29; N, 7.33.

5-Benzhydryl-4-phenoxyimino-oxazolidin-2-one (4c)

Yield: 1.31 g (73%); colourless solid; mp 189 °C.

IR (KBr): 1760, 1670 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 4.79 (q, J = 4.70 Hz, 1 H), 6.14 (d, J = 4.60 Hz, 1 H), 7.10–7.50 (m, 15 H), 11.00 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 52.5, 78.4, 112.6, 113.1, 120.9, 122.7, 127.0, 127.6, 128.8, 129.4, 129.7, 130.0, 130.3, 140.8, 151.6, 154.0.

Anal. Calcd for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82. Found: C, 73.82; H, 4.91; N, 7.64.

5-Benzhydryl-4-phenylethyloxyimino-oxazolidin-2-one (4d)

Yield: 1.55 g (80%); colourless solid; mp 110 °C.

IR (KBr): 1758, 1667 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 2.90 (t, J = 6.80 Hz, 2 H), 4.20 (t, J = 6.80 Hz, 2 H), 4.92 (d, J = 4.70 Hz, 1 H), 5.93 (d, J = 4.60 Hz, 1 H), 7.10–7.40 (m, 15 H), 11.23 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 35.5, 51.5, 74.6, 78.8, 112.6, 120.7, 122.6, 127.8, 128.5, 128.8, 129.4, 129.8, 130.2, 137.5, 140.5, 151.6, 154.0.

Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.45; H, 5.83; N, 7.03.

5-Benzhydryl-4-phenylpropyloxyimino-oxazolidin-2-one (4e)

Yield: 1.44 g (72%); colourless solid; mp 107 °C.

IR (KBr): 1760, 1672 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ = 1.90–2.00 (m, 2 H), 2.70 (t, J = 7.56 Hz, 2 H), 4.08 (t, J = 6.5 Hz, 2 H), 4.90 (d, J = 4.70 Hz, 1 H), 6.03 (d, J = 4.60 Hz, 1 H), 7.00–7.39 (m, 15 H), 11.34 (s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 30.6, 31.7, 52.7, 73.7, 79.0, 112.6, 120.7, 122.7, 127.8, 128.5, 128.9, 129.5, 129.8, 130.2, 137.6, 140.3, 151.7, 153.8.

Anal. Calcd for $C_{25}H_{24}N_2O_3$: C, 74.98; H, 6.04; N, 6.99. Found: C, 75.09; H, 5.92; N, 7.20.

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