One-pot Synthesis, Crystal structure, and Bioactivity of *N*-Phenoxyacetyl-2,4,5-trisubstituted-1,3-oxazolidines

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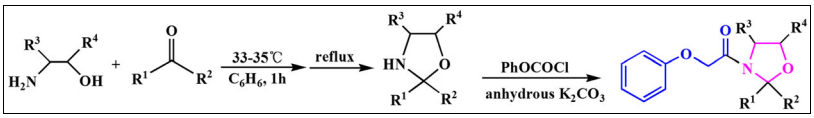

N-phenoxyacetyl-1,3-oxazolidine derivatives were synthesized by the cyclization and acylation with β-amino alcohol, ketone, and phenoxyacetyl chloride as the starting materials. All compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR, ESI-MS, and elemental analysis. The configuration of **4a** was determined by X-ray crystallography. The preliminary biological tests showed that all products could protect soybean against injury caused by 2,4-D butylate to some extent.

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INTRODUCTION

Oxazolidine derivatives have made them attractive targets for synthesis with their structural diversity and biological importance [1]. Oxazolidines are pharmacophores, embedded within the core of potent antitumor tetrahydroisoquinoline natural products [2–4]. They are endowed a large spectrum of biological activities, including remarkable anti-inflammatory, antibacterial agent, antihypertensive, α_1-adrenoceptor antagonists, antiplasmodial, and inhibitors of the epidermal growth factor receptor. 1,3-Oxazolidine derivatives were also widely applied in organic synthesis, chiral auxiliaries, drug design, or prodrugs [5–7]. They also acted as the ligands in asymmetric catalysis and as a host molecule for the incorporation of guest molecules or ions [8–10]. Some reports indicated that *N*-dichloroacetyl oxazolidine derivatives were investigated as herbicide safeners, which effectively protected maize against the injury of thiocarbamate and chloroacetanilide herbicides [11,12]. Structure–activity relationship (SAR) was very important in the search for biological activity because it provided useful information about chemical substituents, which are necessary for the target bioactivity [13,14]. Based on the SAR, isoxadifen-ethyl, which was combined with the structural features of 5-phenyl-4,5-dihydroisoxazole-3-ethyl ester and the safener diphenyl acid, possesses strong security to rice (Scheme 1). Recently, many successful cases using strategies of active substructure combination and bioisosteric replacement have been reported [15].

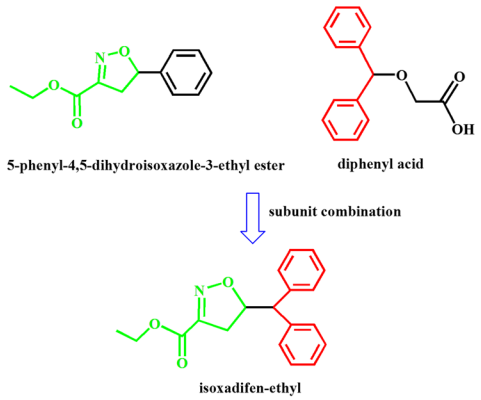
In view of the facts mentioned previously, the novel target molecules *N*-phenoxyacetyl-1,3-oxazolidine derivatives were designed and synthesized based on the SAR [16] and active substructure combination keeping the oxazolidine as the parent skeleton structure (Scheme 2).

1,3-Oxazolidines were usually prepared by condensation of β-amino alcohols with aldehydes or ketones [17–21], the [3 + 2] cycloaddition of azomethine ylides and carbonyl compounds [22–24], palladium catalyzed [3 + 2] cycloaddition reactions, Lewis acid-catalyzed [3 + 2] cycloaddition reactions of aziridines [25,26], or others [27–30]. Recently, Yoon's group has reported an efficient method for establishing 1,3-oxazolidines through iron-catalyzed or copper-catalyzed aminohydroxylation of olefins [31–33]. As part of our work on nitrogen-containing heterocyclic compounds [34–36], herein we reported one-pot synthesis of a series of novel *N*-phenoxyacetyl-1,3-oxazolidines **4** via cyclization and acylation without any expensive reagent or catalyst (Scheme 3). The configuration of **4a** was further determined by X-ray crystallography. The bioactivity determination of the *N*-phenoxyacetyl-1,3-oxazolidine derivatives was carried out on soybean from the injury of 2,4-D butylate.

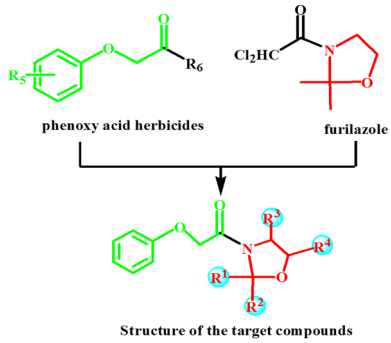
RESULTS AND DISCUSSION

The synthetic route was depicted in Scheme 3. Amino alcohols **1** were cyclization with ketones **2** to generate oxazolidines **3** with benzene as solvent [34]. The acylation of oxazolidine and phenoxyacetyl chloride was achieved by using anhydrous K_2CO_3 as the attaching acid agent at 0–5°C. As oxazolidine easily transformed to Schiff base in the presence of alkali over 18°C [34], anhydrous K_2CO_3 was selected as the attaching acid agent rather than triethylamine. The yields of **4** compounds were obtained in 45–85%. The substitute group structure affected the yields significantly. When R^1 and R^2 were $-CH_3$, the steric hindrance was weak. So the yields of **4b** and **4c** were high, which were 85% and 80%, respectively. The steric hindrance effects caused by R^3 and R^4 are more obvious than effects produced by R^1 and R^2. It can be seen that the yield of **4d** was 45% due to steric hindrance effects caused by the size increasing the of the groups R^3 and

Scheme 1. Design of isoxadifen-ethyl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2. Structure of the target compounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



R^4, which were $-CH_3$ and $-CH_2CH_3$, respectively. It was similar of **4e** with R^3 and R^4 being $-CH_2CH_3$ and $-CH_3$ separately.

The structures of compounds **4a–k** were characterized by infrared (IR), $^1H-$, and ^{13}C NMR, elemental analysis, and MS. In the IR spectra, a characteristic carbonyl band at around 1660 cm^{-1} proved the presence of C=O. The ^1H NMR spectra of **4a–k** exhibited that the aromatic protons appeared at the region 6.88–7.33 ppm, which also confirmed the accomplishment of the acylation. It was the characteristic of oxazolidine. In the ^{13}C NMR spectra of the synthesized compounds, the signals observed in the region were δ 95–100 ppm, δ 60–65 ppm, and δ 45–50 ppm accounting for the signals of the three carbons oxazolidine ring.

The single crystal of **4a** was obtained by dissolving it in ethanol and light petroleum, followed by slow evaporation. The molecular structure and the packing view of **4a** were shown in Figures 1 and 2, respectively. It was obvious that there was π-p-π-p-π large conjunctive effect between C9, N1, C8, N2, C7, O1, and benzene, which resulted in shorter bond length of N1-C9 [1.464(3)], N1-C8 [1.347 (3)] than the typical C-N bond length [1.472(2)Å]. No significant π-π interactions were found in the crystal structure. The compound contained an original benzene ring (plane I) and a new five-member ring, plane II, which were made up of N1, C9, C10, C11, and O3 atoms. Plane I [C1, C2, C3, C4, C5, and C6] made a dihedral angle of 13.4° with plane II. Plane II looked like an envelope shape with C9 deviated from the plane.

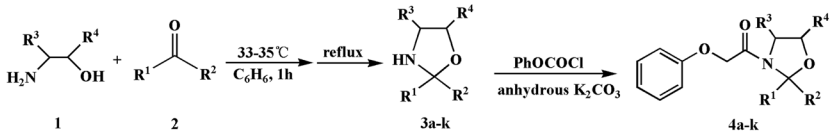
All the novel *N*-phenoxyacetyl oxazolidine derivatives were evaluated for their protection of soybean against the injury of 2,4-D butylate at the concentration of 462 ga.i./hm^2 (Table 1). Compounds **4a–k** showed some recovery rate for plant height, plant fresh weight, root length, and root fresh weight. The recovery rates of the plant index indicated that the synthesized compounds except **4f**, **4g**, and **4i** led to good activity. They might be used as the candidate of herbicide because they are similar as phenoxy acid herbicide. Among the compounds tested, compound **4c** showed the best activity against the injury of 2,4-D butylate. But the activity against the injury of 2,4-D butylate synthesized is inferior to R-28725.

EXPERIMENTAL

Melting points were obtained on a Beijing Taike melting point apparatus (X-4) and are uncorrected. The IR spectra (wave numbers in cm^{-1}) were taken on a KJ-IN-27G infrared spectrophotometer (KBr). The ^1H NMR and ^{13}C NMR spectra were performed on Bruker AVANCE 300 MHz, with $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal standard. Mass spectra were obtained on Finigan Ion trap mass spectrometer. All reagents were of analytical grade.

Preparation of 2,4,5-trisubstituted-3-phenoxyacetyl-1,3-oxazolidines. Amino alcohols **1** (0.03 mol) and ketone (0.03 mol) **2** were added in 35 mL benzene, and the

Scheme 3. The route for synthesis of the title compounds.



a: $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$; b: $R^1 = R^2 = R^4 = CH_3$, $R^3 = H$; c: $R^1 = R^2 = R^3 = R^4 = CH_3$; d: $R^1 = R^2 = R^3 = CH_3$, $R^4 = CH_2CH_3$;
e: $R^1 = R^2 = R^4 = CH_3$, $R^3 = CH_2CH_3$; f: $R^1 = R^2 = CH_3$, $R^3 = CH_2CH_3$, $R^4 = H$; g: $R^1 = CH_3$, $R^2 = R^3 = CH_2CH_3$, $R^4 = H$;
h: $R^1 = R^2 = R^3 = CH_2CH_3$, $R^4 = H$; i: $R^1 = CH_3$, $R^2 = CH_2CH_2CH_3$, $R^3 = CH_2CH_3$, $R^4 = H$;
j: $R^1 = CH_3$, $R^2 = CH_2CH(CH_3)_2$, $R^3 = CH_2CH_3$, $R^4 = H$; k: R^1~$R^2 = (CH_2)_5$, $R^3 = CH_2CH_3$, $R^4 = H$.

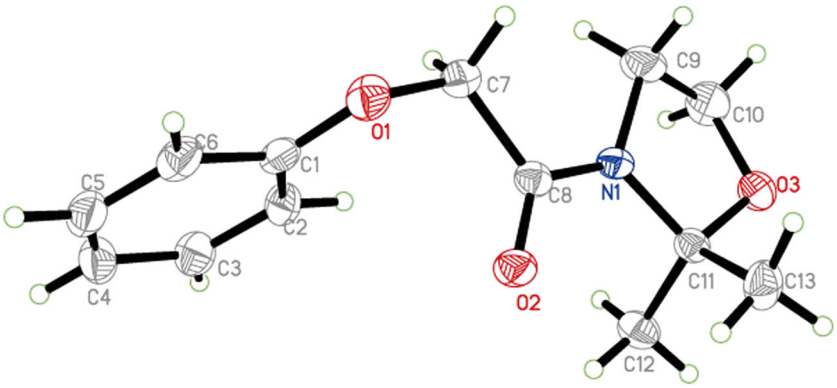


Figure 1. Molecular structure for compound **4a**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

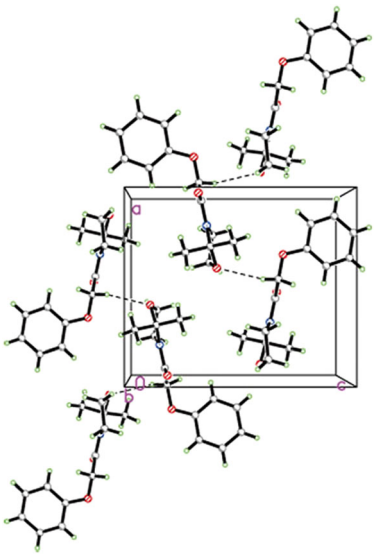


Figure 2. Packing view of the compound **4a**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reaction was stirred for 1 h under 30–35°C. Then, the mixture was heated to reflux until water was stripped off, followed by cooling to 20–25°C and addition of 1 g anhydrous K_2CO_3. Afterwards, 4.2 mL (0.03 mol) of phenoxyacetyl chloride was added dropwise with stirring. Stirring was continued for 1 h. The organic phase was washed until pH = 7. The organic layer was dried over magnesium sulfate anhydrous and vacuum distillation solvent. Compounds **4a**, **4c**, **4d**, **4f**, **4 h**, **4j**, and **4 k** were recrystallized with ethanol and light petroleum until the white crystals were obtained. Compounds **4b**, **4e**, **4i**, and **4 g** were separated on silica gel by column chromatography [*V* (EtOAc):*V* (light petroleum) = 1:3]. The physical and spectra data of the compounds **4a–k** are as follows:

***N*-Phenoxyacetyl-2,2-dimethyl-1,3-oxazolidine (4a)**. White solid. Yield 5.36 g (76%). m.p. 89–90°C. IR: *v* 2880–2979, 1666 (C = O), 1421–1588; ^{1}H NMR ($CDCl_3$): δ 6.88–7.26 (m, 5H, Ar-H), 4.53 (s, 2H, O-CH_2-C = O),

Table 1

Effect of detoxification of compounds **4a–k** to growth index of soybean[a,b,c].

Compound	Recovery of plant height (%)	Recovery of plant weight (%)	Recovery of root length (%)	Recovery of root weight (%)
R-28725	74.46	101.11	67.69	65.49
4a	57.19	65.63	46.67	43.85
4b	47.48	57.45	65.64	6.69
4c	56.47	75.25	125.12	56.64
4d	59.35	65.35	65.64	53.59
4e	44.60	73.64	48.72	27.53
4f	13.67	46.05	−20.51	4.92
4g	1.80	−15.24	1.538	−6.39
4h	59.71	90.60	18.46	14.26
4i	−1.44	15.90	−32.82	18.19
4j	52.52	65.29	51.79	41.89
4k	14.39	79.98	69.74	5.41

[a]Data are means of three replicates.
[b]Recovery Rate(%) $= \frac{\text{Treat with compounds} - \text{Treat with 2,4-D butylate}}{\text{Contrast} - \text{Treat with 2,4-D butylate}}$.
[c]Water treated was used as contrast.

3.95–3.98 (t, J = 2.0 Hz, 2H, C-CH_2-O), 3.59–3.62 (t, J = 1.0 Hz, 2H, N-CH_2-C), 1.54 (s, 6H, 2 × CH_3-C); ^{13}C NMR ($CDCl_3$): δ 164.61, 157.84, 129.60, 129.60, 121.66, 114.57, 114.57, 95.29, 68.59, 63.52, 45.04, 24.26, 24.26. ESI-MS m/z: 236 [M + H^+]. *Anal*. calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95%; Found: C, 66.42; H, 7.35; N, 5.86%.

***N*-phenoxyacety-2,2,5-trimethyl-1,3-oxazolidine (4b)**. White solid. Yield 6.35 g (85%). m.p. 62–63°C. IR: v 2989–2851, 1671 (C = O), 1426–1597. ^{1}H NMR ($CDCl_3$): δ 6.93–7.33 (m, 5H, Ar-H), 4.57 (s, 2H, O-CH_2-C = O), 4.21–4.28 (m, 1H, C-CH-O), 3.77–3.82 (m, 1H, N-CH_2-C),3.14–3.20 (t, J = 2.3 Hz, 1H, N-CH_2-C), 1.58–1.62 (d, J = 3.8 Hz, 6H, 2 × CH_3), 1.33–1.35 (d, J = 1.5 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 164.48, 157.85, 129.64, 129.64, 121.71, 114.60, 114.60, 95.67, 70.64, 68.73, 51.84, 25.80, 23.83, 17.94. ESI-MS *m/z*: 250 [M + 1]. *Anal*. calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62%; Found: C, 67.52; H, 7.55; N, 5.76%.

***N*-phenoxyacety-2,2,4,5-tetramethyl-1,3-oxazolidine (4c)**. White solid. Yield 6.32 g (80%). m.p. 53–54°C. IR: v 2900–2973, 1644–1660 (C = O), 1425–1599. ^{1}H NMR ($CDCl_3$): δ 6.94–7.33 (m, 5H, Ar-H), 4.58–4.71 (d, J = 6.8 Hz, 2H, O-CH_2-C = O), 4.20–4.23 (m, 1H, C-CH-O), 4.03–4.07 (m, 1H, N-CH-C), 1.69 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 1.21–1.27 (m, 6H, 2 × CH_3). ^{13}C NMR ($CDCl_3$): δ 164.24, 157.09, 129.60, 129.60, 121.68, 114.77, 114.77, 94.88, 72.89, 67.96, 55.14, 27.12,23.50,15.64,14.31; ESI-MS *m/z*: 264 [M + 1]. *Anal*. calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32%; Found: C, 68.53; H, 8.14; N, 5.25%.

***N*-phenoxyacety-2,2,4-trimethyl-5-ethyl-1,3-oxazolidine (4d)**. White solid. Yield 3.74 g (45%). m.p. 170–171°C. IR: v 2884–2971, 1646–1661 (C = O), 1422–1599. ^{1}H NMR ($CDCl_3$): δ 6.94–7.32 (m, 5H, Ar-H), 4.58–4.71 (m, 2H, O-CH_2-C = O), 4.03–4.10 (m, 1H, N-CH-C), 3.93–3.98 (m, 1H, C-CH-O), 1.51–1.73 (m, 8H, 2 N-C-CH_3, CH_2-C), 1.20–1.23 (d, J = 2.3 Hz, 3H, N-C-CH_3), 0.98–1.03 (t, J = 1.5 Hz, 3H, O-C-C-CH_3). ^{13}C NMR ($CDCl_3$): δ 164.18, 158.09, 129.61, 129.61, 121.68, 114.78, 114.78, 94.85, 78.80, 67.89, 54.32, 27.11, 23.47, 22.04, 15.50, 10.36. ESI-MS *m/z*: 278 [M + 1]. *Anal*. calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05%; Found: C, 69.21; H, 8.44; N, 5.15%.

***N*-phenoxyacety-2,2,5-trimethyl-4-ethyl-1,3-oxazolidine (4e)**. White solid. Yield 4.16 g (50%). m.p. 50–51°C. IR: v 2983–2937, 1641–1664 (C = O), 1421–1598; ^{1}H NMR ($CDCl_3$): δ 6.93–7.33 (m, 5H, Ar-H), 4.55–4.71 (m, 2H, O-CH_2-C = O), 4.08–4.22 (m, 1H, N-CH-C), 3.66–3.84 (m, 1H, C-CH-O), 1.56–1.65 (m, 8H, 2 × N-C-CH_3, CH_2-C), 1.23–1.32 (m, 3H, O-C-CH_3), 0.96–1.04 (m, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 165.50, 157.80, 129.64, 129.64, 121.72, 114.54, 114.54, 96.11, 68.59, 63.96, 60.54, 27.28, 24.04, 21.24, 14.42, 11.68. ESI-MS *m/z*: 278 [M + 1]. *Anal*. calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05%; Found: C, 69.33; H, 8.48; N, 5.01%.

***N*-phenoxyacety-2,2-dimethyl-4-ethyl-1,3-oxazolidine (4f)**. White solid. Yield 4.11 g (52%). m.p. 64–65°C. IR: v 2891–2977, 1666 (C = O), 1417–1599; ^{1}H NMR ($CDCl_3$): δ 6.94–7.31 (m, 5H, Ar-H), 4.58–4.71 (m, 2H, O-CH_2-C = O), 3.89–3.94 (m, 3H, N-CH-CH_2-O), 1.64–1.79 (m, 5H, N-C-CH_3, CH_2-C), 1.54 (s, 3H, N-C-CH_3), 0.95–0.99 (t, J = 2.0 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 164.54, 158.03, 129.60, 129.60, 121.68, 114.68, 114.68, 95.71, 68.05, 66.97, 58.15, 27.38, 26.47, 22.91, 10.80. ESI-MS *m/z*: 264 [M + 1]. *Anal*. calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32%; Found: C, 68.48; H, 8.12; N, 5.26%.

***N*-phenoxyacety-2-methyl-2,4-diethyl-1,3-oxazolidine (4g)**. White solid. Yield 3.99 g (48%). m.p. 85–87°C. IR: v 2881–2976, 1643–1659 (C = O), 1415–1599; ^{1}H NMR ($CDCl_3$): δ 6.92–7.32 (m, 5H, Ar-H), 4.52–4.71 (m, 2H, O-CH_2-C = O), 3.82–3.97 (m, 3H, N-CH-CH_2-O), 1.97–2.19 (m, 2H, N-C-CH_2-C), 1.61–1.76 (m, 2H, CH_2-C), 1.49 (s, 3H, N-C-CH_3), 0.81–1.06 (m, 6H, 2 × CH_3). ^{13}C NMR ($CDCl_3$): δ 164.59, 158.09, 129.62, 129.62, 121.69, 114.70, 114.70, 98.37, 67.99, 66.92, 58.16, 30.69, 27.76, 21.14, 11.08, 8.28. ESI-MS *m/z*: 278 [M + 1]. *Anal*. calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05%; Found: C, 69.22; H, 8.45; N, 5.13%.

***N*-phenoxyacety-2,2,4-triethyl-1,3-oxazolidine (4h)**. White solid. Yield 5.24 g (60%). m.p. 59–60°C. IR: v 2878–2968, 1647 (C = O), 1421–1599; ^{1}H NMR ($CDCl_3$): δ 6.92–7.32 (m, 5H, Ar-H), 4.58–4.73 (m, 2H, O-CH_2-C = O), 4.98–4.03 (m, 1H, N-CH-C), 3.80–3.89 (m, 2H, O-CH_2-C), 1.68–2.21 (m, 6H, 3CH_2-C), 0.93–0.98 (t, J = 3.0 Hz, 3H, CH_3), 0.81–0.88 (m, 6H, 2 × CH_3). ^{13}C NMR ($CDCl_3$): δ 164.59, 158.03, 129.63, 129.63, 121.66, 114.62, 114.62, 101.09, 67.91, 67.86, 58.06, 28.12, 27.90, 27.49, 11.20, 8.28, 8.18. ESI-MS *m/z*: 292 [M + 1]. *Anal*. calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81%; Found: C, 69.98; H, 8.72; N, 4.77%.

***N*-phenoxyacetyl-2-methyl-2-n-propyl-4-ethyl-1,3-oxazolidine (4i)**. White solid. Yield 5.15 g (59%). m.p. 79–81°C. IR: v 2879–2962, 1642 (C = O), 1420–1598. ^{1}H NMR ($CDCl_3$): δ 6.92–7.33 (m, 5H, Ar-H), 4.57–4.71 (m, 2H, O-CH_2-C = O), 3.84–3.87 (m, 3H, N-CH-CH_2-O), 2.03–1.40 (m, 6H, 3 × CH_2-C), 1.49 (s, 3H, CH_3), 0.88–0.98 (m, 6H, 2 × CH_3). ^{13}C NMR ($CDCl_3$): δ 164.55, 158.08, 129.61, 129.61, 121.68, 114.70, 114.70, 98.01, 67.99, 66.94, 58.14, 40.22, 27.76, 21.36, 17.23, 14.16, 11.08. ESI-MS *m/z*: 292 [M + 1]. *Anal*. calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81%; Found: C, 70.15; H, 8.76; N, 4.70%.

***N*-phenoxyacetyl-2-methyl-2-isobutyl-4-ethyl-1,3-oxazolidine (4j)**. White solid. Yield 5.59 g (61%). m.p. 84–85°C. IR: v 2865–2984, 1649 (C = O), 1415–1598; ^{1}H NMR ($CDCl_3$): δ 6.91–7.32 (m, 5H, Ar-H), 4.56–4.70 (m, 2H, O-CH_2-C = O), 3.80–3.98 (m, 3H, N-CH-CH_2-O), 2.10–2.16 (m,

1H, CH-C), 1.67–1.86 (m, 4H, 2 × CH_2-C), 1.51 (s, 3H, N-C-CH_3), 0.91–0.99 (m, 9H, 3CH_3). ^{13}C NMR ($CDCl_3$): δ 164.64, 158.07, 129.61, 129.61, 121.65, 114.69, 114.69, 98.45, 68.02, 67.05, 57.97, 46.32, 27.61, 24.70, 23.91, 21.46, 11.08. ESI-MS m/z: 306 [M + H$^+$]. *Anal*. calcd for $C_{18}H_{27}NO_3$: C, 70.79; H, 8.91; N, 4.59%; Found: C, 70.86; H, 8.88; N, 4.45%.

***N*-phenoxyacetyl-3-ethyl-1-oxa-4-aza-spiro-4,5-noncane (4k)**. White solid. Yield 6.91 g (76%). m.p. 79–81°C. IR: ν 2865–2954, 1665 (C = O), 1421–1598. ^{1}H NMR ($CDCl_3$): δ 6.92–7.32 (m, 5H, Ar-H), 4.51–4.70 (m, 2H, O-CH_2-C = O), 3.87 (s, 3H, N-CH-CH_2-O), 1.46–2.72 (m, 10H, -$(CH_2)_5$-), 1.21-1.31 (m, 1H, CH_2-C), 0.93–0.98 (t, J = 3.0 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 164.65, 158.11, 129.60, 129.60, 121.63, 114.70, 114.70, 97.28, 68.11, 66.65, 58.12, 34.85, 29.46, 27.61, 24.57, 23.33, 23.23, 10.94. ESI-MS m/z: 304 [M + H$^+$]. *Anal*. calcd for $C_{18}H_{25}NO_3$: C, 71.26; H, 8.31; N, 4.62%; Found: C, 71.18; H, 8.37; N, 4.59%.

X-ray data collection and structure refinement for 4a. The X-ray data were collected on a Bruker AXS II CCD area-detector diffractometer using graphite monochromated Mo *K*a radiation (λ = 0.071073 nm) at 298(2) K. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F^2 using full-matrix least-squares procedures. Minimum and maximum, final electron density were −0.124 and 0.162 eÅ^{-3}. Symmetry equivalent reflections were used to optimize crystal shape and size. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 942879. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk].

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