Generation of Cyclic Ketene-N,X-Acetals (X = O, S) from 2-Alkyl-1,3-oxazolines and 2-Alkyl-1,3-thiazolines. Reactions with Acid Chlorides, 1,3-Diacid Chlorides and N-(Chlorocarbonyl) Isocyanate

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Abstract: 2-Alkyl-1,3-oxazolines, 2-alkyl-1,3-thiazolines, and the corresponding cyclic ketene-N,X-acetals (X = O, S) derived from them were reacted with monoacid chlorides, diacid chlorides, triacid chlorides. A series of these carbon–carbon bond-forming reactions and cyclizations to both substituted 2,3-dihydrooxazolo[3,2-a]pyridine-5,7-diones and 2,3-dihydrothiazolo[3,2-a]pyridine-5,7-diones proceeded under mild reaction conditions. Cyclic ketene-N,X-acetal intermediates play important roles in all these reactions. Related cyclizations with N-(chlorocarbonyl) isocyanate formed substituted 2,3-dihydrooxazolo[3,2-c]pyrimidine-5,7-diones and 2,3-dihydrothiazolo[3,2-c]pyrimidine-5,7-diones.

Key words: 2-alkyl-1,3-oxazolines, 2-alkyl-1,3-thiazolines, cyclic ketene-N,O-acetals, cyclic ketene-N,S-acetals, cyclization reaction

Cyclic ketene acetals have attracted interest due to their nucleophilic reactions with electrophilic compounds1–9 and their ability to undergo rapid cationic homo- and copolymerization.10–16 Cyclic ketene-N,X-acetals (X = O, S) 1 and 2 contain extremely electron-rich double bonds, negatively polarized at their exocyclic carbons. They exhibit high nucleophilicity, exerted through resonance between the exo-methylene group and the two adjacent heteroatoms (N, O or S) (Figure 1). Acetals 1 and 2 contain two nucleophilic contributions within the same functional group, in the form of enamines and vinyl (thio)ether functions. This suggests that they should be explored more thoroughly as a class of carbon nucleophiles for carbon–carbon bond-forming reactions. Heretofore, they have been employed rather sporadically because of their highly reactive and unstable nature.

Figure 1 Resonance structures of N-methyl cyclic ketene-N,X-acetals

Cyclic ketene-N,X-acetals can now be easily made from 2-alkyl-1,3-oxazolines 3 and 2-alkyl-1,3-thiazolines 4.17,18 Oxazolines and thiazolines have been employed in organic synthesis for about 70 years.19–32 Herein, amino alcohols were used as starting materials for 2-alkyl-1,3-oxazolines 3 and 2-alkyl-1,3-thiazolines 4 (Scheme 1), which were converted to cyclic ketene-N,X-acetals.1–3,17,18 Amino alcohols reacted with carboxylic acids to afford 2-alkyl-1,3-oxazolines 3 in 60–80% yield. Amino alcohols reacted with acid chlorides plus triethylamine in CH2Cl2 for one hour to afford hydroxyamides. Treatment with either Lawesson’s reagent in refluxing toluene, or P2S5 in mineral oil at 140 °C generated 2-alkyl-1,3-thiazolines 4. N-Methylation of either 3 or 4 with iodomethane in dry nitromethane afforded N-methyl-2-methyl-1,3-oxazolinium iodides 5 and N-methyl-2-methyl-1,3-thiazolinium iodides 6. Sodium hydride in THF converted 5 and 6 to N-methyl cyclic ketene-N,X-acetals 1 and 2. Compounds 1 and 2 are extremely sensitive to acids, acidic surfaces, and water, so isolation requires basic media or base-treated glassware surfaces.

Scheme 1 Synthesis of N-methyl cyclic ketene-N,X-acetals
2-Methyl-1,3-oxazolines react with two equivalents of an acid chloride, without α-protons, to afford N-acyl-β-keto cyclic ketene-N,O-acetals as shown by Tohda et al.33 Cyclic ketene-N,O-acetals were recently shown to be intermediates in that reaction.17 We now extend this chemistry to 2-alkyl-1,3-thiazolines and other 2-alkyl-1,3-oxazolines (alkyl = ethyl and propyl) upon their reactions with mono-, di-, and triacid chlorides which have no α-protons. Thus, 3 and 4 reacted with acid chloride (2.2 equivalents) and triethylamine (3 equivalents) in refluxing acetonitrile to generate N-acyl-β-keto cyclic ketene-N,X-acetals 7 and 8 in excellent yields (Table 1).

Consumption of one equivalent of acid chloride generates reactive N-acyl cyclic ketene-N,X-acetals intermediates 7 and 8. Subsequent nucleophilic attack by these intermediate N-acyl cyclic ketene-N,X-acetals 7 and 8 on a second equivalent of acid chloride generates the N-acyl-β-keto cyclic ketene-N,X-acetals 9 and 10, where the β-keto group was always cis to the oxygen or sulfur, and R4 was cis to nitrogen (demonstrated by NOESY experiments). High yields of 9 and 10 were achieved when benzoyl and trimethylacetyl chlorides were used. In contrast, the use of propionyl chloride or isobutylchloride, which have α-protons, did not produce the corresponding N-acyl-β-keto cyclic ketene-N,X-acetals. Competing base-catalyzed elimination of HCl from acid chlorides containing α-protons produced ketenes whose further reactions were not studied.

Next, we investigated whether heterocycles 3 and 4 would undergo cyclization through their intermediate N-acyl cyclic ketene-N,X-acetals, when reacted with diacid chlorides which have no α-protons. Could ring closure occur, placing the second keto function cis to N and trans to O? Indeed, the consumption of one acid chloride function of the diacid chloride in the presence of triethylamine generated the expected reactive intermediate N-acyl cyclic ketene-N,X-acetals 11 and 12 (Table 2). Rapid intramolecular nucleophilic attack by the acetal’s nucleophilic carbon on the second acid chloride function generated the 6/5-fused ring 2,3-dihydrooxazolo[3,2-a]pyridine-5,7-diones 13 and 2,3-dihydrothioazolo[3,2-a]pyridine-5,7-diones 14, respectively. For example, one equivalent of α,α-disubstituted malonyl dichloride reacted with one equivalent of 2-alkyl-1,3-oxazolines 3 or 2-alkylthiazolines 4 (Table 2) in refluxing acetonitrile for three hours to give excellent yields of 13a–g and 14a–g, respectively. This facile cyclization is an extremely efficient way to prepare the ring systems 2,3-dihydrooxazolo[3,2-a]pyridine-5,7-diones 13 and 2,3-dihydrothioazolo[3,2-a]pyridine-5,7-diones 14 with a variety of substituents at the 2-, 3-, 6-, and 8-positions.

### Table 1: Reactions of 2-Alkyl-1,3-oxazolines (or 2-Alkyl-1,3-thiazolines) with Acid Chlorides

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Substituents in 3 and 4</th>
<th>R in RCOCl</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
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<tr>
<td>3a</td>
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<td>CH₃</td>
<td>H</td>
<td>H</td>
<td>C₆H₅</td>
</tr>
<tr>
<td>3b</td>
<td>O</td>
<td>CH₃</td>
<td>CH₃</td>
<td>H</td>
<td>C₆H₅</td>
</tr>
<tr>
<td>3c</td>
<td>O</td>
<td>CH₃</td>
<td>CH₃</td>
<td>Et</td>
<td>C₆H₅</td>
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<tr>
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<td>CH₃</td>
<td>H</td>
<td>(CH₃)C</td>
</tr>
<tr>
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<td>S</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>C₆H₅</td>
</tr>
<tr>
<td>4b</td>
<td>S</td>
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<td>H</td>
<td>CH₃</td>
<td>C₆H₅</td>
</tr>
<tr>
<td>4c</td>
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<td>Et</td>
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<td>H</td>
<td>C₆H₅</td>
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<tr>
<td>4d</td>
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<td>CH₃</td>
<td>CH₃</td>
<td>H</td>
<td>C₆H₅</td>
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<td>H</td>
<td>H</td>
<td>(CH₃)C</td>
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<tr>
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<td>H</td>
<td>H</td>
<td>CH₃</td>
<td>(CH₃)C</td>
</tr>
</tbody>
</table>

*The ratio of 3 (or 4)/acid chloride/Et₃N = 1:2.2:3. 
*All yields are isolated yields.
The facile synthesis of ring system 14 reported here is of special interest due to the known biological activities of some of these derivatives. Some 2,3-dihydrothiazolo[3,2-a]pyridine-5,7-diones are known to generate pronounced increases of HDL cholesterol and marked decreases of LDL and VLDL cholesterol, when administered in vivo to rats.34

To expand the scope of this cyclization, N-(chlorocarbonyl) isocyanate was used as the dielectrophile in place of a,a-disubstituted diacid chlorides. N-Acylation should easily occur. Consumption of one equivalent of acid chloride generated reactive N-acyl cyclic ketene-\(N,X\)-acetal intermediates 15 and 16 upon reaction with 3 and 4, respectively. Rapid intramolecular nucleophilic attack by the reactive exocyclic \(\beta\)-carbon of intermediates 15 and 16 on the isocyanate carbon then generated the highly functionalized ring systems of 2,3-dihydrooxazolo[3,2-c]pyrimidine-5,7-diones 17 and 2,3-dihydrothiazolo[3,2-c]pyrimidine-5,7-diones 18 (Table 3). These reactions all proceed in excellent yields. A single similar cyclization has been reported on 2-cyanomethylbenzothiazole in triethylamine–dioxane at ambient temperature with N-(chlorocarbonyl) isocyanate. 35 We are continuing to explore these cyclizations on 2-alkyl-1,3-oxazolines, 2-alkyl-1,3-thiazolines, and 2-alkyl-1,3-oxazines and 2-alkyl-1,3-thiazines without electron-withdrawing substituents on the 2-alkyl group.36

The facile synthesis of ring system 14 is of special interest because biological activity has been demonstrated for derivatives of the latter. They are claimed to be useful for prevention and treatment of diseases involving c-Jun N-terminal kinase (JNK), e.g. cardiac failure, hypertension, rheumatoid arthritis, Alzheimer’s disease, etc.37 JNK is a signaling protein that is capable of initiating the apoptotic cell death process. 38,39

Oxalyl chloride and phthaloyl dichloride (no \(\alpha\)-protons) did not undergo analogous cyclizations with 2-alkyl-1,3-oxazolines 3 or 2-alkyl-1,3-thiazolines 4 to generate the corresponding 5/5- or 7/5-ring fusions (Scheme 2). Similarly, phosgene failed to convert 2-alkyloxazolines or 2-alkylthiazolines to the corresponding ring fusions (Scheme 2).

### Table 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Substituents in 3 and 4</th>
<th>R in RCOCl</th>
<th>Product</th>
<th>Yield (%)b</th>
</tr>
</thead>
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<td>O</td>
<td>H H H H</td>
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<td>13b</td>
<td>94</td>
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<tr>
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<td>O</td>
<td>H H H H</td>
<td>CH₃</td>
<td>13c</td>
<td>92</td>
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<td>CH₃</td>
<td>13d</td>
<td>90</td>
</tr>
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<tr>
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<td>CH₃</td>
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<td>CH₃</td>
<td>14a</td>
<td>94</td>
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<td>4b</td>
<td>S</td>
<td>H H H CH₃</td>
<td>H</td>
<td>14b</td>
<td>92</td>
</tr>
<tr>
<td>4g</td>
<td>S</td>
<td>H H H CH₃</td>
<td>CH₃</td>
<td>14c</td>
<td>92</td>
</tr>
<tr>
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<td>S</td>
<td>H H H CH₃</td>
<td>H</td>
<td>Et</td>
<td>14d</td>
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<td>S</td>
<td>H H H CH₃</td>
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<td>90</td>
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<td>H H H H</td>
<td>-(CH₂)₃⁻</td>
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<td>91</td>
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<tr>
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<td>S</td>
<td>H H H H</td>
<td>-(CH₂)₃⁻</td>
<td>14g</td>
<td>93</td>
</tr>
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</table>

\[a\] The ratio of 3 (or 4)/acid chloride/E₃N = 1:1:3.

\[b\] All yields are isolated yields.
alkylthiazolines to their corresponding 4/5-ring-fusion products (Scheme 2). The failure of oxalyl chloride to generate 20 was disappointing in view of the successful cyclization of oxalyl chloride on a 2-carbethoxythiazoline derivative reported by Shane et al.\textsuperscript{40} at room temperature in CH$_2$Cl$_2$. Oxalyl chloride reacted extremely rapidly and exothermically with 3 and with 4 in acetonitrile, THF, CH$_2$Cl$_2$, or acetone, generating black solutions and black residues. Dropwise additions of oxalyl chloride at 0 °C or –23 °C failed to produce 20. An electron-withdrawing R$_4$ function on 3 or 4 may play a crucial role in this reaction.

Replacement of the N-acyl function with a methyl group in reaction intermediates 7/8, 11/12, and 15/16 should increase the β-carbon’s nucleophilicity. Thus, N-methyl cyclic ketene-N$_X$-acetals 1 and 2 were synthesized (Scheme 1) and reacted with acid chlorides. N-Methyl cyclic ketene-N$_X$-acetals 1 and 2 were used immediately after being prepared and characterized. They reacted with acid chlorides in THF at room temperature in the presence of triethylamine to form the corresponding N-methyl-β-keto cyclic ketene-N$_X$-acetals 22 and 23 in good isolated yields (Table 4).

### Table 3 Preparation of 2,3-Dihydrooxazolo[3,2-c]pyrimidine-5,7-diones 17 and 2,3-Dihydrothiazolo[3,2-c]pyrimidine-5,7-diones 18

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Substituents in 3 or 4</th>
<th>Product</th>
<th>Yield (%)\textsuperscript{b}</th>
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<td>H H H CH$_3$</td>
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<td>94</td>
</tr>
<tr>
<td>4g</td>
<td>S</td>
<td>H H H CH$_3$</td>
<td>18b</td>
<td>92</td>
</tr>
<tr>
<td>4d</td>
<td>S</td>
<td>CH$_3$ CH$_3$ H H</td>
<td>18c</td>
<td>92</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The ratio of 3 (or 4)/N-(chlorocarbonyl)isocyanate/Et$_3$N = 1:1:2.  
\textsuperscript{b}All yields are isolated yields.

### Table 4 The Reaction of N-Methyl Cyclic Ketene-N$_X$-acetals with Acid Chlorides

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Substituents in 1 and 2</th>
<th>R$_X$ in R$/COCl$</th>
<th>Product</th>
<th>Yield (%)\textsuperscript{b}</th>
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</thead>
<tbody>
<tr>
<td>1a</td>
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<td>C$_6$H$_5$ COCl</td>
<td>22a</td>
<td>70</td>
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<tr>
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<td>22b</td>
<td>73</td>
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<tr>
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<td>22c</td>
<td>64</td>
</tr>
<tr>
<td>1a</td>
<td>O</td>
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<td>(CH$_3$)$_2$CH</td>
<td>22d</td>
<td>59</td>
</tr>
<tr>
<td>2a</td>
<td>S</td>
<td>H H H H</td>
<td>C$_6$H$_5$ COCl</td>
<td>23a</td>
<td>78</td>
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<td>2b</td>
<td>S</td>
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<td>C$_6$H$_5$ COCl</td>
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<td>75</td>
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<td>C$_6$H$_5$ COCl</td>
<td>23c</td>
<td>71</td>
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<td>H H H CH$_2$(CH$_3$)$_6$</td>
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\textsuperscript{a}The ratio of 1 (or 2)/acid chloride/Et$_3$N = 1:2:2.5.  
\textsuperscript{b}All yields are isolated yields.

### Scheme 2 Reaction of 2-alkylthiazolines and 2-alkyloxazolines with oxalyl chloride, phthaloyl chloride, and phosgene

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Acid chlorides, with or without α-protons, could be employed in the synthesis of 22 and 23. This demonstrates the much higher nucleophilic reactivity of these cyclic ketene-\(N,\sigma\)-acetals 1 and 2, versus intermediates 7/8, 11/12 and 15/16. The latter could not compete with ketene generation when reacted with acid chlorides. However, 1 and 2 reacted more rapidly with acid chlorides than acid chlorides react with triethylamine to generate ketenes, allowing the use of ambient temperature and shorter reaction times. The reactions to generate 22 and 23 reached completion at room temperature within ten minutes. The successful conversion of 1 and 2 to the corresponding \(N\)-methyl-\(\alpha\)-ketocyclic ketene-\(N,\sigma\)-acetals 22 and 23, using acid chlorides containing α-protons (Table 4), contrasts sharply with the failure to convert 3 and 4 to products 9 and 10 with α-proton-containing acid chlorides. Table 1 contains no reactions with acid chlorides that have α-protons. \(N\)-Methyl cyclic ketene-\(N,\sigma\)-acetals 1 and 2 are clearly stronger carbon nucleophiles than their respective \(N\)-acyl analogues, 7/8, 11/12, and 15/16.

When 2.5 equivalents of either \(N\)-methyl cyclic ketene-\(N,\sigma\)-acetals 1 or 2 were reacted with one equivalent of a diacid chloride having no α-protons (\(a,a\)-disubstituted malonyl dichloride or \(p\)-terephthalic chloride), \(a,a\)-unsaturated ketones 24 and 25 were formed in high yields (Table 5). These reactions were carried out at ambient temperature in THF. However, when diacid chlorides with α-protons (succinyl chloride and glutaryl dichloride) were used, the analogous products were not produced. Instead, extremely rapid reactions occurred in THF, generating black solutions and black residues. Lowering the reaction temperature to −20 °C still did not afford products 24 or 25.

Reactions of 1 and 2 with 1,3,5-benzenetricarbonyl chloride generated the tris-\(a,\beta\)-unsaturated ketones 26 and 27 in high isolated yields (Scheme 3).

Table 5 Reaction of \(N\)-Methyl Cyclic Ketene-\(N,\sigma\)-acetals 1 and 2 with Diacid Chlorides

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substituents in 1 and 2</th>
<th>Product Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>O CH₃ CH₃ H p-C₆H₄</td>
<td>24a 85</td>
</tr>
<tr>
<td>2a</td>
<td>S H H H &gt;C(CH₃)₂</td>
<td>25a 88</td>
</tr>
<tr>
<td>2c</td>
<td>S Et H H &gt;C(CH₃)₂</td>
<td>25b 79</td>
</tr>
<tr>
<td>2a</td>
<td>S H H H p-C₆H₄</td>
<td>25c 80</td>
</tr>
</tbody>
</table>

\(a\) The ratio of 1 (or 2)/diacid chloride/Et₃N = 2.5:1:3.

\(b\) All yields are isolated yields.

Cyclization reactions using 2,4,5-trimethyloxazole 28, 2-methylbenzothiazole 30, and 1,2-dimethylimidazole 32 with diethylmalonyl chloride failed to form 29, 31, and 33, respectively (Scheme 4). Instead, 28, 30, and 32 were recovered. Each of these heterocyclic compounds are aromatic. Therefore, it may be more difficult to produce the corresponding nonaromatic, \(7-\pi\)-electron 1,3-heteroatom cyclic ketene acetals 29, 31, and 33.

Melting points were recorded with a Mel-Temp apparatus. All reactions were carried out under a dried nitrogen atmosphere. MeCN and Et3N were distilled from calcium hydride under nitrogen. THF was distilled from Na metal/benzophenone ketyl. All other commercially obtained reagents were used as received. The silica gel used for the column chromatography was purchased from Aldrich Company (70–230 mesh, 60 Å).

2-(3-Benzoyl-4,4-dimethyloxazolidin-2-ylidene)-1-phenylpropan-1-one (9b)

White solid; yield: 132 mg (90%); mp 120–122 °C.

IR (film): 3062, 2967, 1741, 1675, 1598, 1562, 1414, 1329, 1284, 1022, 900, 727, 698 cm\(^{-1}\).

1H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.18–7.74\) (m, 10 H), 5.04 (s, 1 H), 4.35 (s, 2 H), 1.64 (s, 6 H).

13C NMR (75 MHz, CDCl\(_3\)): \(\delta = 186.4, 168.5, 161.1, 139.8, 134.4, 132.4, 130.9, 128.7, 128.6, 127.7, 126.8, 85.5, 79.5, 62.5, 22.5\).

2-(3-Benzoyl-4,4 dimethyloxazolidin-2-ylidene)-1-phenylbutan-1-one (9c)

White solid; yield: 132 mg (83%); mp 122–124 °C.

IR (film): 3060, 2965, 2926, 2889, 1786, 1735, 1654, 1523, 1450, 1359, 1175, 972, 773, 706 cm\(^{-1}\).

1H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.31–8.11\) (m, 10 H), 3.80 (s, 2 H), 2.14 (s, 3 H), 1.21 (s, 6 H).

13C NMR (75 MHz, CDCl\(_3\)): \(\delta = 186.0, 164.5, 161.6, 134.9, 132.8, 129.7, 128.8, 128.5, 128.0, 127.9, 126.5, 78.4, 66.4, 53.5, 27.8, 16.5.

2-(3-Benzoyl-4,4-dimethyloxazolidin-2-ylidene)-1-phenylbutan-1-one (9d)

White solid; yield: 127 mg (83%); mp 122–124 °C.

IR (film): 3060, 2966, 2930, 2873, 1786, 1735, 1648, 1451, 1356, 1238, 1103, 1065, 972, 773, 706 cm\(^{-1}\).

1H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.34–8.10\) (m, 10 H), 3.81 (s, 2 H), 2.51 (q, \(J = 7.4\) Hz, 2 H), 1.27 (s, 6 H), 1.17 (t, \(J = 7.4\) Hz, 3 H).

13C NMR (75 MHz, CDCl\(_3\)): \(\delta = 185.0, 164.4, 160.7, 134.9, 132.9, 129.8, 128.9, 128.3, 128.2, 128.1, 128.0, 126.5, 78.3, 66.7, 27.9, 23.4, 13.4.

1-[3-(2,2-Dimethylpropionyl)-4,4-dimethyloxazolidin-2-ylidene]-3,3-dimethylbutan-2-one (9e)

White solid; yield: 108 mg (88%); mp 59–60 °C.

IR (film): 3067, 2929, 2870, 1758, 1677, 1644, 1481, 1360, 1106, 1000, 838 cm\(^{-1}\).

1H NMR (300 MHz, CDCl\(_3\)): \(\delta = 5.80\) (s, 1 H), 3.88 (s, 2 H), 1.31 (s, 9 H), 1.27 (s, 6 H), 1.13 (s, 6 H).

13C NMR (75 MHz, CDCl\(_3\)): \(\delta = 174.7, 163.9, 159.6, 102.0, 78.3, 66.1, 39.1, 37.3, 28.1, 27.4, 27.2.

2-(3-Benzoylthiazolidin-2-ylidene)-1-phenylpropan-1-one (10a)

Yellow solid; yield: 125 mg (92%); mp 123–125 °C.

IR (film): 3057, 2962, 2868, 1665, 1511, 1354, 1224, 1157, 1021, 780, 699 cm\(^{-1}\).

1H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.04–7.62\) (m, 10 H), 7.04 (s, 1 H), 4.16 (t, \(J = 6.9\) Hz, 2 H), 3.06 (t, \(J = 6.9\) Hz, 2 H).

13C NMR (75 MHz, CDCl\(_3\)): \(\delta = 187.7, 169.2, 159.4, 138.3, 135.2, 131.7, 131.5, 128.3, 128.2, 127.7, 127.3, 103.4, 52.5, 27.6.

MS (EL, 70 eV); \(m/z\) (%) = 309 [M]+; 308, 204, 105 (100), 77, 51.

2-(3-Benzoyl-5-methylthiazolidin-2-ylidene)-1-phenylpropan-1-one (10b)

Yellow solid; yield: 125 mg (88%); mp 107–110 °C.

IR (film): 3056, 2962, 2869, 1664, 1624, 1597, 1510, 1488, 1327, 1296, 1227, 1172, 1010, 912, 777, 698 cm\(^{-1}\).

1H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.30–7.63\) (m, 10 H), 7.03 (s, 1 H), 4.20 (dd, \(J = 6.1, 10.1\) Hz, 1 H), 3.80 (dd, \(J = 6.9, 11.1\) Hz, 1 H), 3.57 (m, 1 H), 1.41 (d, \(J = 6.7\) Hz, 3 H).

13C NMR (75 MHz, CDCl\(_3\)): \(\delta = 187.6, 169.2, 159.3, 138.3, 135.1, 131.6, 131.3, 128.5, 128.0, 127.5, 127.2, 103.0, 58.8, 37.7, 18.7.

2-(3-Benzoyl-4-ethylthiazolidin-2-ylidene)-1-phenylethanone (10c)
White solid; yield: 108 mg (94%); mp 99–101 °C.
IR (film): 2974, 2926, 2867, 1702, 1436, 1375, 1217, 1175, 984, 938, 679 cm⁻¹.
1H NMR (300 MHz, CDCl3): δ = 4.62 (t, J = 7.8 Hz, 2 H), 4.00 (t, J = 7.8 Hz, 2 H), 1.67 (s, 3 H), 1.32 (s, 6 H).
13C NMR (75 MHz, CDCl3): δ = 196.5, 174.2, 161.4, 88.9, 68.0, 50.6, 42.2, 24.6, 6.7.

6,6,8-Trimethyl-2,3-dihydrooxazolo[3,2-a]pyridine-5,7-dione (13b)
White solid; yield: 108 mg (94%); mp 99–101 °C.
IR (film): 2982, 2935, 2886, 1703, 1376, 1229, 1136, 993, 836, 726 cm⁻¹.
1H NMR (300 MHz, CDCl3): δ = 5.13 (s, 1 H), 4.71 (t, J = 7.0 Hz, 2 H), 4.07 (t, J = 7.0 Hz, 2 H), 1.42 (s, 6 H).
13C NMR (75 MHz, CDCl3): δ = 196.6, 174.5, 164.9, 81.7, 68.4, 50.9, 41.9, 24.4.

6,6-Diethyl-2,3-dihydrooxazolo[3,2-a]pyridine-5,7-dione (13c)
White solid; yield: 106 mg (92%); mp 91–92 °C.
IR (film): 2969, 2935, 1697, 1618, 1445, 1434, 1372, 1200, 1146, 943, 779 cm⁻¹.
1H NMR (300 MHz, CDCl3): δ = 5.27 (s, 1 H), 4.72 (t, J = 8.0 Hz, 2 H), 4.10 (t, J = 8.0 Hz, 2 H), 1.82–2.05 (m, 4 H), 0.77 (t, J = 7.4 Hz, 6 H).
13C NMR (75 MHz, CDCl3): δ = 196.3, 173.7, 165.4, 85.1, 68.3, 61.6, 41.6, 32.7, 9.4.

6,6-Diethyl-2,3-dihydrooxazolo[3,2-a]pyridine-5,7-dione (13d)
White solid; yield: 111 mg (90%); mp 93–95 °C.
IR (film): 2967, 2935, 2877, 1692, 1669, 1605, 1444, 1378, 1203, 1162, 951, 901 cm⁻¹.
1H NMR (300 MHz, CDCl3): δ = 4.70 (t, J = 8.0 Hz, 2 H), 4.10 (t, J = 8.0 Hz, 2 H), 2.05 (m, 4 H), 1.78 (s, 3 H), 0.72 (t, J = 8.0 Hz, 6 H).
13C NMR (75 MHz, CDCl3): δ = 196.1, 173.2, 161.9, 92.4, 68.0, 61.4, 42.0, 32.9, 9.4, 6.5.

6-(1,1-Cyclobutane)-2,3-dihydrooxazolo[3,2-a]pyridine-5,7-dione (13e)
White solid; yield: 105 mg (92%); mp 150–152 °C.
IR (film): 2950, 1695, 1605, 1473, 1441, 1354, 1241, 1131, 927, 818, 582 cm⁻¹.
1H NMR (300 MHz, CDCl3): δ = 5.09 (s, 1 H), 4.72 (t, J = 8.0 Hz, 2 H), 4.09 (t, J = 8.0 Hz, 2 H), 2.45–2.61 (m, 4 H), 2.13–2.24 (m, 2 H).
13C NMR (75 MHz, CDCl3): δ = 194.5, 172.9, 165.1, 81.5, 68.4, 53.8, 41.8, 29.7, 15.3.

6-(1,1-Cyclobutane)-8-methyl-2,3-dihydrooxazolo[3,2-a]pyridine-5,7-dione (13f)
White solid; yield: 120 mg (92%); mp 152–154 °C.
IR (film): 2984, 2935, 2886, 1703, 1376, 1229, 1136, 993, 836, 726 cm⁻¹.
1H NMR (300 MHz, CDCl3): δ = 4.69 (t, J = 8.0 Hz, 2 H), 4.08 (t, J = 8.0 Hz, 2 H), 2.44–2.61 (m, 4 H), 2.13–2.25 (m, 2 H), 1.76 (s, 3 H).
Yellow solid; yield: 112 mg (94%); mp 105–106 °C.

13C NMR (75 MHz, CDCl3): δ = 57.4, 55.2, 29.2, 23.5, 15.1.

IR (film): 3069, 2869, 1687, 1631, 1579, 1391, 1334, 1172, 1039, 1036, 754 cm–1.

White solid; yield: 125 mg (92%); mp 107–108 °C.

1H NMR (300 MHz, DMSO): δ = 4.48 (t, J = 7.2 Hz, 2 H), 3.37 (t, J = 7.2 Hz, 2 H), 2.46–2.62 (m, 4 H), 2.13–2.25 (m, 2 H), 1.85 (s, 3 H), 1.42 (s, 6 H).

13C NMR (75 MHz, DMSO): δ = 194.1, 174.8, 160.6, 98.3, 51.3, 48.8, 27.4, 24.3.

MS (EL, 70 eV): m/z (%) = 197 (100) [M+], 182, 169, 154, 128, 70, 60.

6,6-Diethyl-2,3-dihydrothiazolo[3,2-a]pyridine-5,7-dione (14d)

Yellow solid; yield: 303 mg (86%); mp >250 °C.

1H NMR (300 MHz, DMSO): δ = 8.37–8.39 (m, 2 H), 7.97–8.07 (m, 2 H), 4.00 (t, J = 7.8 Hz, 2 H), 1.84–2.02 (m, 4 H), 0.77 (t, J = 7.4 Hz, 6 H).

13C NMR (75 MHz, DMSO): δ = 194.1, 174.2, 156.7, 105.0, 55.6, 50.8, 38.9, 24.2, 19.7, 12.1.

6,6,6-Tetramethyl-2,3-dihydrothiazolo[3,2-a]pyridine-5,7-dione (14e)

Yellow solid; yield: 122 mg (93%); mp 145–146 °C.

1H NMR (300 MHz, CDCl3): δ = 8.07 (t, J = 7.8 Hz, 2 H), 3.87 (m, 2 H), 2.53 (t, J = 8.0 Hz, 4 H), 2.12–2.25 (m, 2 H), 1.85 (s, 3 H).

13C NMR (75 MHz, CDCl3): δ = 192.7, 173.1, 156.8, 105.7, 54.2, 49.2, 29.9, 27.5, 15.2, 12.4.

8-Methyl-2,3-dihydrothiazolo[3,2-c]pyrimidine-5,7-dione (17a)

Paper procedure.

8-(Methyl-2,3-dihydrothiazolo[3,2-c]pyrimidine-5,7-dione (17b)

White solid; yield: 303 mg (86%); mp >250 °C.

1H NMR (300 MHz, CDCl3): δ = 165.5, 162.8, 147.5, 81.2, 76.4, 45.7, 23.8.
IR (KBr): 3400–3200, 3028, 1715, 1665, 1468, 1374, 1241, 1129, 890, 749 cm⁻¹.

1H NMR (300 MHz, DMSO): δ = 11.10 (s, 1 H), 4.16 (t, J = 7.2 Hz, 2 H), 3.43 (t, J = 7.2 Hz, 2 H), 1.73 (s, 3 H).

13C NMR (75 MHz, DMSO): δ = 162.8, 153.5, 148.6, 99.8, 49.7, 28.2, 12.2.

2.8-Dimethyl-2,3-dihydrothiazolo[3,2-c]pyrimidine-5,7-dione (18b)

Yellow solid; yield: 382 mg (92%); mp 250 °C.

IR (KBr): 3400–3200, 3032, 2825, 1715, 1441, 1385, 1177, 870, 758 cm⁻¹.

1H NMR (300 MHz, DMSO): δ = 10.97 (s, 1 H), 5.85 (s, 1 H), 3.31 (s, 2 H), 1.59 (s, 6 H).

13C NMR (75 MHz, DMSO): δ = 162.3, 158.1, 148.8, 93.1, 68.5, 40.3, 19.9, 12.2.

3,3-Dimethyl-2,3-dihydrothiazolo[3,2-c]pyrimidine-5,7-dione (18c)

Yellow solid; yield: 382 mg (92%); mp 250 °C.

IR (KBr): 3400–3200, 3028, 2828, 1715, 1669, 1470, 1376, 1244, 893, 752 cm⁻¹.

1H NMR (300 MHz, DMSO): δ = 6.6 Hz, 3 H).

1H NMR (300 MHz, DMSO): δ = 10.97 (s, 1 H), 5.58 (s, 1 H), 3.31 (s, 2 H), 1.71 (s, 3 H), 1.40 (d, J = 6.6 Hz, 3 H).

13C NMR (75 MHz, DMSO): δ = 162.7, 153.2, 148.7, 99.9, 55.9, 40.3, 19.9, 12.2.

3,4,4-Trimethyl-2-methyleneoxazolidine (1a)

Colorless liquid; yield: 2.0 g (70%); bp 55–56 °C (9 mmHg).

IR (film): 3057, 2970, 2900, 1627, 1579, 1503, 1435, 1209, 1158, 1018, 914, 864, 733 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 3.80 (s, 2 H), 3.48 and 2.85 (d, J = 3.80 Hz, 2 H), 2.24 (s, 3 H), 1.09 (s, 6 H).

3-Methyl-2-methylenehiazolidine (2a)

AcCl (6.41 g, 81.9 mmol) was added dropwise to a stirred solution of sodium iodide in THF at r.t. Hydrogen evolution was observed during the addition of the sodium iodide. The mixture was stirred for an additional 3 h. Anhyd petroleum ether (200 mL) was added. The reaction mixture separated into a liquid and a solid phase. The clear liquid on the top was transferred to another flask. Distillation of this clear solution gave 2-methylthiazoline (2a).

Colorless liquid; yield: 2.01 g (70%); bp 78 °C (20 mmHg).

1H NMR (300 MHz, CDCl₃): δ = 3.86 (d, J = 6.1 Hz, 2 H), 3.20 (t, J = 6.0 Hz, 2 H), 2.90 (t, J = 5.9 Hz, 2 H), 2.58 (s, 3 H).

13C NMR (75 MHz, CDCl₃): δ = 151.9, 73.8, 57.64, 35.6, 27.9.

3,5-Dimethyl-2-methylenehiazolidine (2b)

Colorless liquid; yield: 2.2 g (68%); bp 82–83 °C (20 mmHg).

1H NMR (300 MHz, CDCl₃): δ = 3.88 (d, J = 4.8 Hz, 2 H), 3.49 (m, 1 H), 3.38 (dd, J = 6.1, 9.2 Hz, 1 H), 2.85 (dd, J = 6.5, 9.2 Hz, 1 H), 2.58 (s, 3 H), 1.23 (d, J = 6.7 Hz, 3 H).

13C NMR (75 MHz, CDCl₃): δ = 152.5, 73.7, 64.7, 38.8, 35.5, 20.3.

4-Ethyl-3-methyl-2-methylenehiazolidine (2c)

Colorless liquid; yield: 2.1 g (64%); bp 93–94 °C (20 mmHg).

1H NMR (300 MHz, CDCl₃): δ = 3.82 (s, 2 H), 3.20 (m, 1 H), 3.22 (dd, J = 6.1, 10.3 Hz, 1 H), 2.68 (dd, J = 6.1, 10.3 Hz, 1 H), 2.56 (s, 3 H), 1.56 (m, 1 H), 1.35 (m, 1 H), 0.76 (t, J = 7.4 Hz, 3 H).

13C NMR (75 MHz, CDCl₃): δ = 151.8, 73.0, 68.3, 35.2, 32.2, 24.6, 10.1.

3,4,4-Trimethyl-2-methyleneoxazolidine (2d)

Colorless liquid; yield: 2.3 g (69%); bp 94–95 °C (20 mmHg).

1H NMR (300 MHz, CDCl₃): δ = 3.89 (d, J = 18.9 Hz, 2 H), 2.79 (s, 2 H), 2.43 (s, 3 H), 1.06 (s, 6 H).

13C NMR (75 MHz, CDCl₃): δ = 151.3, 73.8, 65.2, 41.3, 30.0, 23.3.

1-Phenyl-2-(3,4,4-trimethoxyxazolidin-2-ylidene)ethanone (22a)

Benzyl chloride (450 mg, 3.2 mmol) in THF was added dropwise to the solution of 3,4,4-trimethyl-2-methyleneoxazolidine (2a) (200 mg, 1.6 mmol) and Et₃N (400 mg, 4.0 mmol) in THF at r.t. The mixture was stirred for 20 min. The solid was filtered and the solvent was evaporated. Then the residue was purified by column chromatography with silica gel (hexane–EtOAc, 1:1) to give 22a. The same procedure was used for 22b–f and 23a–o.

White solid; yield: 300 mg (70%); mp 111–113 °C.

IR (film): 3057, 2970, 2900, 1627, 1579, 1503, 1435, 1209, 1158, 1018, 914, 864, 733 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 7.36–7.87 (m, 5 H), 5.10 (s, 1 H), 4.24 (s, 2 H), 2.73 (s, 3 H), 1.24 (s, 6 H).

13C NMR (75 MHz, CDCl₃): δ = 185.5, 165.5, 141.6, 129.6, 127.4, 126.5, 78.2, 72.7, 59.8, 26.2, 22.6.
MS (EI, 70 eV): m/z (%) = 231 [M⁺], 214, 202, 147 (100), 105, 77, 51.

### 3,3-Dimethyl-1-(3,4,4-trimethyloxazolidin-2-ylidene)butan-2-one (22h)

White solid; yield: 246 mg (73%); mp 106–107 °C.

IR (film): 2956, 1634, 1546, 1445, 1260, 1172, 1019, 936, 723 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 4.66 (s, 1 H), 4.21 (s, 2 H), 2.71 (s, 3 H), 1.28 (s, 6 H), 1.15 (s, 9 H).

13C NMR (75 MHz, CDCl₃): δ = 200.8, 165.7, 78.7, 71.0, 59.7, 42.2, 27.9, 26.4, 23.0.

### 1-(3,4,4-Trimethyloxazolidin-2-ylidene)pentan-2-one (22i)

White solid; yield: 273 mg (64%); mp 107–110 °C.

IR (film): 2953, 1733, 1558, 1447, 1167, 1022 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 4.46 (s, 1 H), 4.21 (s, 2 H), 2.71 (s, 3 H), 1.29 (s, 6 H), 1.08 (d, J = 7.0 Hz, 6 H).

13C NMR (75 MHz, CDCl₃): δ = 199.6, 164.8, 78.5, 74.4, 59.7, 39.7, 26.3, 22.8, 19.6.

### 2-(4-Ethyl-3-methylthiazolidin-2-ylidene)-1-phenylethanone (23d)

White solid; yield: 292 mg (74%); mp 120–122 °C.

IR (film): 2967, 2927, 1707, 1596, 1571, 1489, 1421, 1336, 1212, 1153, 892, 735, 708 cm⁻¹.

1H NMR (300 MHz, CDCl₃): δ = 7.92 (m, 2 H), 7.40 (m, 3 H), 5.99 (s, 1 H), 2.91 (s, 2 H), 2.85 (s, 3 H), 1.32 (s, 6 H).

13C NMR (75 MHz, CDCl₃): δ = 185.9, 166.5, 140.1, 130.3, 127.8, 126.9, 87.7, 66.0, 40.7, 30.5, 23.7.

MS (EI, 70 eV): m/z (%) = 247 [M⁺], 230, 218, 170, 105 (70), 77, 51.

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1H NMR (300 MHz, CDCl3); δ = 5.40 (s, 1 H), 3.61 (t, J = 7.7 Hz, 2 H), 3.02 (t, J = 7.7 Hz, 2 H), 2.96 (s, 3 H), 2.32 (t, J = 7.7 Hz, 2 H), 1.65 (m, 2 H), 0.93 (t, J = 7.4 Hz, 3 H).

13C NMR (75 MHz, CDCl3); δ = 185.9, 164.4, 89.6, 66.0, 34.9, 34.7, 27.0, 9.3.

MS (EI, 70 eV); m/z (%) = 185 [M+], 142 (100), 82, 74.

2-(3,4,4-Trimethylthiazolidin-2-ylidene)-1-[4-(2-(3,4,4-trimethylthiazolidin-2-ylidene)acetyl]phenyl}ethanone (24a); Typical Procedure
Terephthaloyl chloride (0.35 g, 1.7 mmol) in THF (60 mL) was added dropwise to the soln of 3,4,4-trimethyl-2-methyleneoxazolidine (0.53 g, 4.2 mmol) and Et3N (0.51 g, 5.1 mmol) in THF at r.t. The mixture was stirred for 20 min. The solid was filtered from the reaction solution and solvent was evaporated. Then the residue was purified by column chromatography with silica gel (hexane–EtOAc, 1:1) to give 24a. The same procedure was applied for the preparation of 25a–c, 26, and 27.

White solid; yield: 0.65 g (85%); mp 238–239 °C.

H NMR (300 MHz, CDCl3); δ = 7.87 (s, 4 H), 5.13 (s, 2 H), 4.28 (s, 4 H), 2.78 (s, 6 H), 1.28 (s, 12 H).

13C NMR (75 MHz, CDCl3); δ = 185.2, 165.7, 143.0, 126.4, 78.7, 73.1, 60.0, 26.3, 22.9.

MS (EI, 70 eV); m/z (%) = 384 [M+], 230 (100), 214, 202, 147, 105, 77, 51.

3,3-Dimethyl-1,5-bis-(3-methylthiazolidin-2-ylidene)pentane-2,4-dione (25a)
Yellow solid; yield: 488 mg (88%); mp 165–167 °C.

IR (film); 2927, 2855, 1604, 1515, 1462, 1422, 1350, 1300, 1102, 1074, 945, 879, 730 cm–1.

1H NMR (300 MHz, CDCl3); δ = 3.60 (t, J = 7.4 Hz, 4 H), 3.05 (t, J = 7.4 Hz, 4 H), 2.92 (s, 6 H), 1.41 (s, 6 H).

13C NMR (75 MHz, CDCl3); δ = 195.0, 165.4, 88.8, 57.8, 55.6, 35.5, 27.4, 23.1.

1,5-Bis-(4-ethyl-3-methylthiazolidin-2-ylidene)-3,3-dimethyl-pentane-2,4-dione (25b)
Yellow solid; yield: 513 mg (79%); mp 173–175 °C.

IR (film); 2926, 2932, 2876, 1605, 1498, 1422, 1348, 1097, 913, 728 cm–1.

1H NMR (300 MHz, CDCl3); δ = 3.73 (m, 2 H), 3.17 (dd, J = 8.8, 11.1 Hz, 2 H), 2.79 (s, 6 H), 2.67 (dd, J = 4.2, 11.1 Hz, 2 H), 1.62 (m, 4 H), 1.35 (s, 6 H), 0.93 (t, J = 7.3 Hz, 6 H).

13C NMR (75 MHz, CDCl3); δ = 195.0, 164.1, 87.4, 66.5, 56.7, 33.3, 30.7, 23.2, 22.6, 8.9.

2-(3-Methylthiazolidin-2-ylidene)-1-[4-(2-(3-methylthiazolidin-2-ylidene)acetyl]phenyl}ethanone (25c)
Yellow solid; yield: 490 mg (80%); mp 262–265 °C.

IR (KBr); 2925, 2859, 1587, 1523, 1460, 1320, 748 cm–1.

1H NMR (300 MHz, CDCl3); δ = 7.87 (s, 4 H), 6.10 (s, 2 H), 3.69 (t, J = 7.7 Hz, 4 H), 3.10 (t, J = 7.4 Hz, 4 H), 3.07 (s, 6 H).

13C NMR (75 MHz, CDCl3); δ = 195.8, 165.4, 88.8, 57.8, 55.6, 35.5, 27.4, 23.1.
White solid; yield: 721 mg (79%); mp 252–255 °C.

1-{3,5-Bis-[2-(3,4,4-trimethyloxazolidin-2-ylidene)acetyl]phenyl}-2-(3-methylthiazolidin-2-ylidene)ethanone (26)

Yellow solid; yield: 749 mg (88%); mp 282–285 °C.

1-{3,5-Bis-[2-(3-methylthiazolidin-2-ylidene)acetyl]phenyl}-2-(3-methylthiazolidin-2-ylidene)ethanone (27)

References