# A New Method for the Generation of α-Nitrosoolefins from Ketooximes and its Application to the Synthesis of 5,6-Dihydro-4*H*-1,2-oxazine Derivatives [1]

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Reaction of ketooximes containing  $\alpha$ -methylene group with chloramine-T followed by treatment with triethylamine leads to the formation of  $\alpha$ -nitrosoolefins *via*  $\alpha$ -nitrosochloride, which can react *in situ* intermolecularly with olefinic compounds to produce 5,6-dihydro-4*H*-1,2-oxazine derivatives in good yield.

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[4+2] Cycloaddition of  $\alpha$ -nitrosoolefins with olefinic compounds are of synthetic interest since the product 5,6dihydro-4H-1,2-oxazines are versatile intermediates for the synthesis of bifunctional compounds [2-4]. The reduced product tetrahydro-4H-1,2-oxazines plays an important role as partial structure in agricultural and horticultural, fungicides, herbicides and broad spectrum of bacteriocides [5]. Compounds possessing the oxazine moiety are also potential glycosidase inhibitors [6]. The usual method of generating them is the elimination of hydrogen halide from  $\alpha$ -monohaloketooximes with triethylamine [7]. However  $\alpha$ -nitrosoolefins are highly reactive and unstable, hence they are usually only generated in situ. The yield of cycloaddition products often is low or side reactions predominate, hence new procedure for the formation of *α*-nitrosoolefins remain of interest.

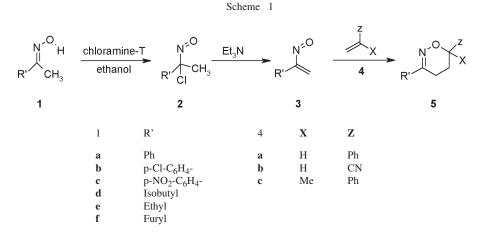
Rai *et al* [8] extensively used chloramine-T for the preparation of biologically active heterocycles *via* [3+2] cycloaddition reaction of 1,3-dipolar species such as nitrile oxides and nitrile imines with olefinic compounds. We have successfully isolated the reactive intermediate nitrile oxides by the oxidation of aldoximes with chloramine-T. During the course of these studies, we have observed that treatment of cyclohexanone oxime with chloramine-T produced a blue colour suggestive of formation of 1-chloro-1-nitrosocyclohexane [6]. With this success, we now report

the use of chloramine-T as a new efficient reagent for the conversion of ketooxime bearing reactive methylene group into  $\alpha$ -nitrosochloride, which is suitable for *in situ* generation of  $\alpha$ -nitrosoolefins during [4+2] cycloaddition to olefins. Typically, the cycloaddition is carried out by refluxing an equimolecular mixture of a ketooxime, chloramine-T trihydrate in ethanol followed by addition of triethylamine and an alkene in ethanol at rt. In general 5,6-dihydro-4*H*-1,2-oxazine derivatives are thus obtained in good yield.

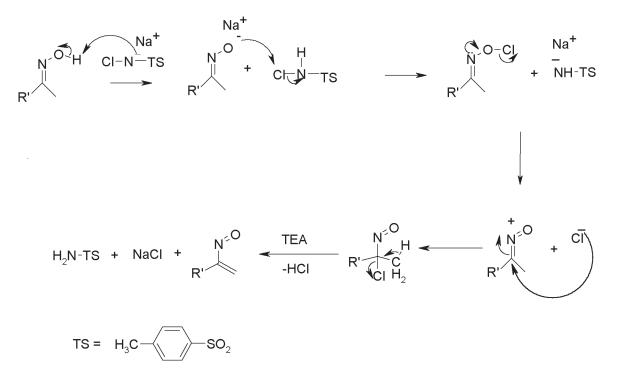
The reaction with chloramine-T proceeds with aromatic as well as aliphatic ketooximes bearing  $\alpha$ -hydrogen (*e.g.* **1a-f**) and with styrene, acrylonitrile and with 1-methyl-styrene.

The probable mechanism for the formation of  $\alpha$ -nitrosoolefins involves the interaction of ketoxime with chloramine-T to form  $\alpha$ -nitrosochloride followed by the elimination of HCl in the presence of triethylamine (Scheme 2).

The structure proof is based on <sup>1</sup>H nmr, <sup>13</sup>C nmr, ms studies and elemental analyses of the 5,6-dihydro-4*H*-1,2oxazine derivatives. As expected, the cycloaddition was regioselective. <sup>1</sup>H nmr indicated the presence of a single isomer in all cases studied. All <sup>1</sup>H nmr spectra of **5** (when X=H), showed the signals due to C<sub>6</sub> as a doublet of doublet in the region 4.5-5.5  $\delta$  ppm while in **5** (when X=CH<sub>3</sub>) shows no signal in the said region and those due to C<sub>5</sub> pro-

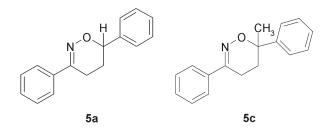






tons a multiplet in the region  $\delta$  1.9–2.5 ppm and those due to C<sub>4</sub> as a triplet in the region  $\delta$  2.0–2.8 ppm.

In the <sup>13</sup>C nmr spectra, all oxazines gave consistent signals for the newly formed ring carbons. For instance, the signals due to C<sub>6</sub> appears in **5** (when X=H) as doublet in the region  $\delta$  70–80 ppm while **5** (when X=CH<sub>3</sub>) appears as singlet in the region  $\delta$  70–80 ppm and those due to C<sub>5</sub> and C<sub>4</sub> appears as triplets in the region  $\delta$  15– 25 ppm and  $\delta$  25–30 ppm repectively. All oxazines show MH<sup>+</sup> as base peak and stable molecular ion peak with relative abundance ranging from 7-20%. The formation of the products was further supported by correct elemental analyses.



In summary we have demonstrated for the first time that oxazines can be easily synthesized by the reaction of ketooximes bearing  $\alpha$ -methylene group with alkenes in presence of chloramine-T and triethylamine in almost 60-83% yield.

The known compounds were identified by the comparison of the spectral data with those described in the literature [9].

## **EXPERIMENTAL**

Melting points were determined on Thomas Hoover melting point apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded on a Bruker AM 300 MHz spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane as internal standard. <sup>13</sup>C NMR spectra were measured on Jeol 400 (100 MHz) instrument. The chemical shifts are expressed in  $\delta$  and following abbreviations were used: s=singlet, d=doublet, t=triplet and m=multiplet. Mass spectra were obtained on a Finnigan 4021 mass spectrometer at an ionizing energy of 35 eV. Elemental analyses were obtained on a Vario-EL instrument. Thin layer chromatography (TLC) was done with pre-coated silica gel G plates using chloroform-acetone (8:2) as eluent.

# 3,6-Diphenyl-5,6-dihydro-4*H*-1,2-oxazine (5a).

## Typical Procedure.

A mixture of 0.50 g (3.7 mmoles) of **1a** and 1.05 g (3.73 mmoles) of chloramine-T trihydrate in ethanol (20 ml) were refluxed for 2 hour. The mixture was cooled to room temperature, triethylamine (1 ml) was added and stirred at room temperature for 15 minutes. After this, solution of 0.39 g (3.75 mmoles) of **4a** in ethanol (5 ml) was added and stirred for 1 hour. It was then concentrated under reduced pressure and the residue is extracted with  $CH_2Cl_2$  (25 ml). This extract was then washed with water (15 ml), with 1 *N* aq. NaOH (2 × 15 ml) and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was evaporated and the remaining pale yellow solid was recrystallized from alcohol-*n*-hexane to gave **5a** 

as a creamy white crystalline solid, yield 0.630 g (72%), mp 159-161 °C (lit. mp 160-162 °C) [9]; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  2.18 (m, 2H, CH<sub>2</sub>), 2.73 (t, 2H, CH<sub>2</sub>), 4.82 (dd, 1H, J=10.3Hz & 2.7Hz, CH), 7.35-7.50 (m, 8H, ArH), 7.72-7.78 (m, 2H, ArH).

Anal. Calcd. for  $C_{16}H_{15}NO$ : C, 80.98; H, 6.37; N, 5.90. Found: C, 80.93; H, 6.44; N, 5.84.

The same procedure was used in all cases.

3-Phenyl-5,6-dihydro-4H-1,2-oxazine-6-carbonitrile (5b).

This compound was obtained from 0.50 g (3.7 mmoles) of **1a**, 0.2 g (3.76 mmol) of **4b**, 1.05 g (3.73 mmoles) of chloramine-T trihydrate and triethylamine as a pale yellow crystalline solid, yield 0.550 g (80%), mp 100-102 °C; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  2.08 (m, 2H, CH<sub>2</sub>), 2.72 (t, 2H, CH<sub>2</sub>), 5.14 (dd, 1H, J=9.6 & 2.4Hz, CH), 7.30-7.50 (m, 5H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  15.1 (t), 27.4 (t), 72.10 (d), 119.6 (s), 128.9 (d), 129.2 (d), 130.6 (d), 132.1 (s), 165.1 (s); ms m/z: 187 (MH+, 100), 186 (M+,6), 117 (10), 103 (13).

Anal. Calcd. for  $C_{11}H_{10}N_2O$ : C, 70.95; H, 5.41; N, 15.04. Found: C, 70.98; H, 5.49; N, 15.01.

6-Methyl-3,6-diphenyl-5,6-dihydro-4*H*-1,2-oxazine (**5c**).

This compound was obtained from 0.50 g (3.7 mmoles) of **1a**, 0.44 g (3.70 mmol) of **4c**, 1.05 g (3.73 mmoles) of chloramine-T trihydrate and triethylamine as a off white crystalline solid, yield 0.620 g (67%), mp 128-130°C (lit mp 128-129°C) [9]; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.59 (s, 3H, CH<sub>3</sub>), 2.12 (t, 2H, CH<sub>2</sub>), 2.42 (t, 2H, CH<sub>2</sub>), 7.17-7.35 (m, 8H, ArH), 7.60-7.76 (m, 2H, ArH).

*Anal.* Calcd. for C<sub>17</sub>H<sub>17</sub>NO: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.22; H, 6.85; N, 5.59.

3-(4-Chlorophenyl)-6-phenyl-5,6-dihydro-4H-1,2-oxazine (5d).

This compound was obtained from 0.50 g (2.94 mmol) of **1b**, 0.31 g (2.98 mmol) of **4a**, 0.84 g (2.95 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil, yield 0.560 g (70%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  2.02 (m, 2H, CH<sub>2</sub>), 2.66 (t, 2H, CH<sub>2</sub>), 4.48 (dd, 1H, J=10.3 & 2.4Hz, CH), 7.20-7.35 (m, 5H, ArH), 7.45 (dd, 2H, ArH), 7.65 (dd, 2H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  22.2 (t), 29.6 (t), 80.2 (d), 125.4 (d), 128.4 (d), 128.6 (d), 129 (d),129.6 (s), 130.8 (d), 134.2 (s), 138.2 (s), 164.1 (s); ms m/z: 272 (MH<sup>+</sup>, 100), 271 (M<sup>+</sup>, 8), 151 (20), 137 (10), 120 (17), 106 (4), 77 (38).

*Anal.* Calcd. for C<sub>16</sub>H<sub>14</sub>ClNO: C, 70.72; H, 5.19; N, 5.15. Found: C, 70.70; H, 5.22; N, 5.17.

3-(4-Chlorophenyl)-5,6-dihydro-4*H*-1,2-oxazine-6-carbonitrile (**5e**).

Obtained from 0.50 g (2.94 mmol) of **1b**, 0.20 g (3.76 mmol) of **4b**, 0.84 g (2.95 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil, yield 0.530 g (81%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  2.11 (m, 2H, CH<sub>2</sub>), 2.74 (t, 2H, CH<sub>2</sub>), 5.22 (dd, 1H, J=10.1 & 2.9Hz, CH), 7.33 (d, 2H ArH), 7.62 (d, 2H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  15.1 (t), 29.2 (t), 71.40 (d), 118.5 (s), 129.6 (d), 130 (s), 131.8 (d), 134.2 (s), 163.6 (s); ms m/z: 221 (MH<sup>+</sup>, 100), 220 (M<sup>+</sup>, 6), 151 (18), 137 (10).

*Anal.* Calcd. for C<sub>11</sub>H<sub>9</sub>ClN<sub>2</sub>O: C, 59.88; H, 4.11; N, 12.70. Found: C, 59.85; H, 4.15; N, 12.68.

3-(4-Chlorophenyl)-6-methyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine) (**5f**).

This compound was obtained from 0.50 g (2.94 mmol) of **1b**, 0.44 g (3.7 mmol) of **4c**, 0.84 g (2.95 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.550 g (65%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.41 (S, 3H, CH<sub>3</sub>), 1.98 (t, 2H, CH<sub>2</sub>), 2.73 (t, 2H, CH<sub>2</sub>), 7.28-7.37 (m, 5H, ArH), 7.51 (dd, 2H, ArH), 7.68 (dd, 2H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  24.6 (q), 27.0 (t), 28.1 (t), 80.4 (s), 123.7 (d), 128.0 (d), 128.6 (d), 129.4 (d), 129.9 (d), 131.2 (s), 137.1 (s), 139.2 (s), 164.1(s); ms m/z: 286 (MH<sup>+</sup>, 100), 285 (M<sup>+</sup>, 11), 151 (15), 137 (11), 134 (8), 120 (18), 77 (40).

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>ClNO: C, 71.45; H, 5.64; N, 4.90. Found: C, 71.48; H, 5.67; N, 4.88.

3-(4-Nitrophenyl)-6-phenyl-5,6-dihydro-4H-1,2-oxazine (5g).

This compound was obtained from 0.50 g (2.77 mmol) of **1c**, 0.29 g (2.78 mmol) of **4a**, 0.79 g (2.81 mmol) of chloramine-T trihydrate and triethylamine as a yellow crystalline solid to yield 0.587 g (75%), mp 186-188 °C (lit mp 188-189 °C) [9]; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  2.16 (m, 2H, CH<sub>2</sub>) 2.74 (t, 2H, CH<sub>2</sub>), 4.78 (dd, 1H, J=10.1 & 2.9Hz, CH), 7.31-7.42 (m, 5H ArH), 7.84 (dd, 2H, ArH ), 8.12 (dd, 2H, ArH).

Anal. Calcd. for  $C_{16}H_{14}N_2O_3$ : C, 68.07; H, 5.0; N, 9.92. Found: C, 68.09; H, 4.98; N, 9.94.

3-(4-Nitrophenyl)-5,6-dihydro-4*H*-1,2-oxazine-6-carbonitrile (**5h**).

This compound was obtained from 0.50 g (2.77 mmol) of **1c**, 0.15 g (2.83 mmol) **4b**, 0.15 g (2.83 mmol), 0.79 g (2.81 mmol) of chloramine-T trihydrate and triethylamine as a yellow oil to yield 0.532 g (83%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  2.07 (m, 2H, CH<sub>2</sub>), 2.73 (t, 2H, CH<sub>2</sub>), 4.89 (dd, 1H, J=9.4 & 2.6 Hz, CH), 7.93 (dd, 2H ArH), 8.13 (dd, 2H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  16.2 (t), 28.6 (t), 71.5 (d), 119.6 (s), 123.1 (d), 128.6 (d), 139.2 (s), 151.4 (s), 162.6 (s); ms m/z: 232 (MH<sup>+</sup>, 100), 231 (M<sup>+</sup>, 8), 162 (14), 148 (02).

*Anal.* Calcd. for C<sub>11</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub>: C, 57.14; H, 3.92; N, 18.17. Found: C, 57.19; H, 3.90; N, 18.16.

6-Methyl-3-(4-nitro-phenyl)-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5**i).

This compound was obtained from 0.50 g (2.77 mmol) of **1c**, 0.33 g (2.78 mmol) **4c**, 0.79 g (2.81 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow crystalline solid to yield 0.575 g (70%), mp 167-169 °C (lit mp 168-172 °C) [9]; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.45 (s, 3H, CH<sub>3</sub>), 1.98 (t, 2H, CH<sub>2</sub>), 2.19 (t, 2H, CH<sub>2</sub>), 7.37-7.5 (m, 5H, ArH), 7.73 (dd, 2H, ArH), 8.19 (dd, 2H, ArH).

Anal. Calcd. for  $C_{17}H_{16}N_2O_3$ : C, 68.44; H, 6.08; N, 9.39. Found: C, 68.49; H, 6.06; N, 9.37.

3-Isobutyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (5j).

This compound was obtained from 0.50 g (4.34 mmol) of **1d**, 0.46 g (4.35mmol) of **4a**, chloramine-T (1.23 g, 4.37 mmol) and triethylamine as a yellow oil to yield 0.594 g (63%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.01 (s, 6H, CH<sub>3</sub>), 1.31-1.37 (m, 4H, CH<sub>2</sub>), 1.84 (m, 1H, CH), 2.02 (m, 2H, CH<sub>2</sub>), 4.53 (dd, 1H, J=9.8 & 2.5 Hz, CH), 7.22-7.64 (m, 5H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  20.4 (d), 22.8 (q), 23.1 (t), 28.5 (t), 43.1 (t), 80.2 (d), 124.8 (d), 127.9 (d), 128.5 (d) 137.6 (s), 163.8(s); ms m/z: 218 (MH<sup>+</sup>, 100), 120 (12), 106 (15), 97 (28), 83 (6), 77 (10).

*Anal.* Calcd. for C<sub>14</sub>H<sub>19</sub>NO: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.32; H, 8.84; N, 6.44.

# 3-Isobutyl-5,6-dihydro-4H-1,2-oxazine-6-carbonitrile (5k).

This compound was obtained from 0.50 g (4.34 mmol) of **1d**, 0.24 g (4.52 mmol) of **4b**, 1.23 g (4.37 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.490 g (69%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.05 (s, 6H, CH<sub>3</sub>), 1.29-1,34 (m, 4H, CH<sub>2</sub>), 1.85 (m, 1H, CH), 2.07 (m, 2H, CH<sub>2</sub>), 4.33 (dd, 1H, J=9.9 & 2.5Hz CH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  18.2 (t), 20.4 (d), 23.4 (q), 27.1 (t), 44.2 (t), 71.4 (d), 119.2 (s), 164.1 (s); ms m/z: 167 (MH<sup>+</sup>, 100), 97 (10), 83 (8).

*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>O: C, 65.03; H, 8.49; N, 16.85. Found: C, 64.99; H, 8.52; N, 16.87.

3-Isobutyl-6-methyl-6-phenyl-5,6-dihydro-4H-1,2-oxazine (5l).

This compound was obtained from 0.50 g (4.34 mmol) of **1d**, 0.52 g (4.40 mmol) of **4c**, 1.23 g (4.37 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.580 g (58%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.04 (s, 6H, CH<sub>3</sub>), 1.33-1.39 (m, 4H, CH<sub>2</sub>), 1.51 (s, 3H, CH<sub>3</sub>), 1.89 (m, 1H, CH), 1.99 (m, 2H, CH<sub>2</sub>), 7.30-7.40 (m, 5H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  20.9 (d), 23.0 (q), 25.8 (q), 26.4 (t), 27.8 (t), 43.2 (t), 80.3 (s), 124.8 (d), 127.9 (d), 128.2 (d), 137.1 (s), 163.5 (s); ms m/z: 232 (MH<sup>+</sup>, 100), 134 (8), 120 (25), 97 (2), 83 (7),77 (11).

*Anal.* Calcd. for C<sub>15</sub>H<sub>21</sub>NO: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.81; H, 9.19; N, 6.07.

#### 3-ethyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5m**).

This compound was obtained from 0.50 g (5.70 mmol) of **1e**, 0.60 g (5.76 mmol) of **4a**, 1.62 g (5.76 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.673 g (63%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.07 (t, 3H, CH<sub>3</sub>), 1.33 (t, 2H, CH<sub>2</sub>), 1.44 (m, 2H, CH<sub>2</sub>), 2.02 (m, 2H CH<sub>2</sub>), 4.53 (dd, 1H, J=10.2 & 2.8Hz, CH), 7.2-7.4 (m, 5H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  7.5 (q), 23.9 (t), 26.9 (t), 27.5 (t), 81.1 (d), 125.4 (d), 127.6 (d), 128.0 (d), 137.2 (s), 163.4 (s); ms m/z: 190 (MH<sup>+</sup>, 100), 189 (M<sup>+</sup>, 7), 106 (20), 77 (30), 69 (6), 55 (10).

*Anal.* Calcd. for C<sub>12</sub>H<sub>15</sub>NO: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.10; H, 8.03; N, 7.44.

3-Ethyl-5,6-dihydro-4H-1,2-oxazine-6-carbonitrile (5n).

This compound was obtained from 0.50 g (5.70 mmol) of **1e**, 0.31 g (5.84 mmol) of **4b**, 1.62 g (5.76 mmol) of chloramine-T trihydrate and triethylamine as a pale yellow oil to yield 0.547 g (69%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.06 (t, 3H, CH<sub>3</sub>), 1.33 (t, 2H, CH<sub>2</sub>), 1.43 (m, 2H, CH<sub>2</sub>), 2.04 (m, 2H, CH<sub>2</sub>), 4.26 (dd, 1H, J=9.9 & 2.6 Hz, CH), 7.23-7.40 (m, 5H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  8.5 (q), 17.2 (t), 27.0 (t), 27.8 (t), 73.3 (d), 118.9 (s), 163.9 (s); ms m/z: 139 (MH<sup>+</sup>, 100), 138 (M<sup>+</sup>, 9) 69 (4), 55 (12).

Anal. Calcd. for  $C_7H_{10}N_2O$ : C, 60.85; H, 7.30; N, 20.27. Found: C, 60.80; H, 7.33; N, 20.30.

3-Ethyl-6-methyl-6-phenyl-5,6-dihydro-4H-1,2-oxazine (50).

This compound was obtained from 0.50 g (5.70 mmol) of **1e**, 0.68 g (5.76 mmol) of **4c**, 1.62 g (5.76 mmol) of chloramine-T trihydrate and triethylamine as pale yellow oil to yield 0.653 g (56%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.07 (t, 3H, CH<sub>3</sub>), 1.30 (t, H, CH<sub>2</sub>), 1.43 (m, 2H, CH<sub>2</sub>), 1.59 (s, 3H, CH3), 1.99 (t, 2H, CH2), 7.28-7.40 (m, 5H, ArH); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$ 

7.9 (q), 24.2 (q), 26.2 (t), 27.0 (t), 27.1 (t), 80.6 (s), 126.1 (d), 128.4 (d), 128.9 (d), 139.9 (s), 165.0 (s); ms m/z: 204 (MH<sup>+</sup>, 100), 203(M<sup>+</sup>, 6), 135 (8),120 (28), 77 (30), 69 (6), 55 (13).

Anal. Calcd. for  $C_{13}H_{17}NO;\ C,\ 76.81;\ H,\ 8.43;\ N,\ 6.89.$  Found: C, 76.75; H, 8.46; N, 6.93.

# 3-Furan-2-yl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (5p).

This compound was obtained from 0.5 g (4.0 mmol) of **1f**, 0.42 g (4.03 mmol) of **4a**, 1.14 g (4.05 mmol) of chloramine-T trihydrate and triethylamine as a yellow oil to yield 0.635 g (70%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.33 (t, 2H, CH<sub>2</sub>), 1.88 (m, 2H, CH<sub>2</sub>), 4.54 (dd, 1H, , J=9.2 & 2.3 Hz, CH), 6.32-6.37 (m, 2H, furyl), 7.20-7.30 (m, 5H, ArH), 7.43 (d, 1H, furyl); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  21.0 (t), 27.1 (t), 80.2 (d), 112.2 (d), 125.1 (d), 128.8 (d), 129.1 (d) 137.8 (s), 140.2 (d), 141 (s), 165.2 (s); ms m/z: 228 (MH<sup>+</sup>, 100), 227 (M<sup>+</sup>, 17), 107 (32), 93(38), 77 (21).

*Anal.* Calcd. for C<sub>14</sub>H<sub>13</sub>NO<sub>2</sub>: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.05; H, 5.74; N, 6.12.

#### 3- Furan-2-yl-5,6-dihydro-4H-1,2-oxazine-6-carbonitrile (5q).

This compound was obtained from 0.5 g (4.0 mmol) of **1f**, 0.22 g (4.15 mmol) of **4b**, 1.14 g (4.05 mmol) of chloramine-T trihydrate and triethylamine as a yellow oil to yield 0.549 g (78%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.32 (t, 2H, CH<sub>2</sub>), 1.87 (m, 2H, CH<sub>2</sub>), 4.23 (dd, 1H, J=9.6 & 2.4Hz, CH), 6.30-6.36 (m, 2H, furyl), 7.42 (d, 1H, furyl); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  15.1 (t), 29.0 (t), 72.1 (d), 112.0 (d), 119.3 (s), 140.2 (d) 143.2 (s), 163.5 (s); ms m/z: 177 (MH<sup>+</sup>, 100), 176(M<sup>+</sup>, 20), 107 (29), 93 (38).

Anal. Calcd. for  $C_9H_8N_2O_2$ : C, 61.36; H, 4.58; N, 15.90. Found: C, 61.30; H, 4.60; N, 15.93.

3-Furan-2-yl-6-methyl-6-phenyl-5,6-dihydro-4*H*-1,2-oxazine (**5r**).

This compound was obtained from 0.5 g (4.0 mmol) of **1f**, 0.51 g (4.32 mmol) of **4c**, 1.14 g (4.05 mmol) of chloramine-T trihydrate and triethylamine as a yellow oil to yield 0.616 g (64%); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.33 (t, 2H, CH<sub>2</sub>), 1.52 (s, 3H, CH<sub>3</sub>), 1.93 (m, 2H, CH<sub>2</sub>), 6.30-6.36 (m, 2H, furyl), 7.19-7.28 (m, 5H, ArH), 7.42 (d, 1H, furyl); <sup>13</sup>C nmr (deuteriochloroform):  $\delta$  24.2 (q), 25.7 (t), 26.7 (t), 79.8 (s), 112.1 (d), 125.1 (d), 128.4 (d), 128.8 (d), 139.4 (d), 142.1 (s), 163.9 (s); ms m/z: 242 (MH<sup>+</sup>, 100), 241 (M<sup>+</sup>, 16), 120 (35), 107 (29),93 (32), 77 (25).

*Anal.* Calcd. for C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.62; H, 6.30; N, 5.79.

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