A Facile Synthesis of [1,2]Oxazinane-3,5-diones

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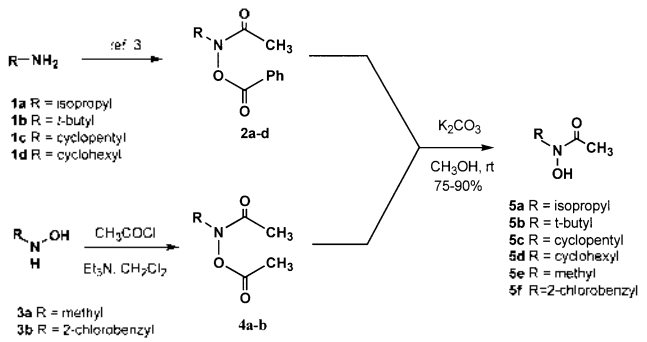
4-Acyl substituted [1,2]oxazinane-3,5-diones have been recently known as herbicides, plant growth regulators, and pesticides, and extensively studied by Shy-Fuh Lee.[1] The preparation of [1,2]oxazinane-3,5-diones involves the reaction of *N*-alkyl-*O*-alkoxycarbonylmethylhydroxylamine and alkyl 3-chloro-3-oxopropionate, followed by the subsequent cyclocondensation and decarboxylation reactions under basic conditions.[1] The resulting [1,2]oxazinane-3,5-diones could be converted to 4-acylated derivatives by *O*-acylation followed by consecutive cyanide catalized rearrangement.[2] The diverse synthesis of [1,2]oxazinane-3,5-dione derivatives has not been studied by limited synthetic methods in spite of their biological potentials. Here we wish to report a facile synthesis of [1,2]oxazinane-3,5-diones starting from readily available amines or hydroxylamines in excellent yields.

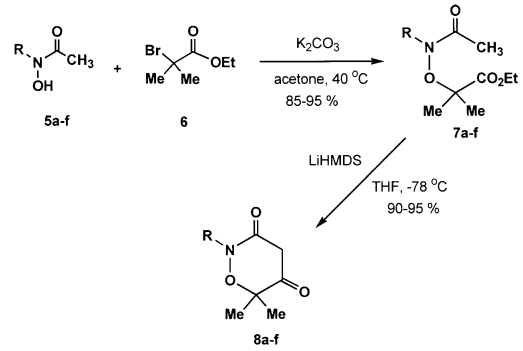
N-Acetyl-*O*-benzoylhydroxylamines **2a-d** were prepared by the known method[3] from amines **1a-d**. *N,O*-Diacetylation of **3a** and **3b** provided **4a** and **4b** respectively in quantitative yields. Selective deprotection of the compounds **2a-d** and **4a-b** by treatment of potassium carbonate in methanol *N*-acetyl hydroxylamines **5a-f** in good yields.

Reaction of the hydroxylamines **5a-f** with ethyl 2-bromoisobutyrate (**6**) in the presence of potassium carbonate in acetone afforded *O*-alkylated products **7a-f** in good yields. Treatment of **7a-f** with lithium bis(trimethylsilyl)amide (LiHMDS) in THF at −78 °C gave [1,2]oxazinane-3,5-diones **8a-f** in excellent yields.

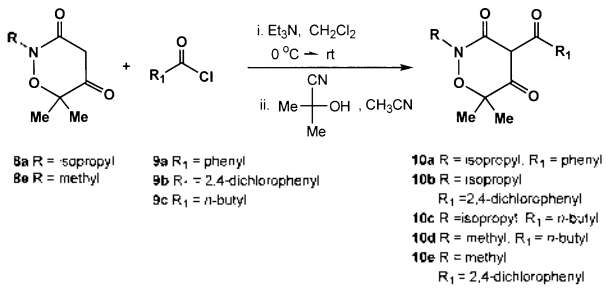
The *O*-acylation of the compounds **8a** and **8b** with aromatic or aliphatic acyl chlorides **9a-c**, followed by the cyanide catalyzed rearrangement[2] provided 4-acyl substituted [1,2]oxazinane-3,5-diones in good yields. All spectroscopic data of compounds **8a-f** and **10a-e** were satisfactory on ^{1}H NMR, ^{13}C NMR, IR, MS, HRMS and some of these showed good agreement with the data described in the literatures.[1]



Scheme 1



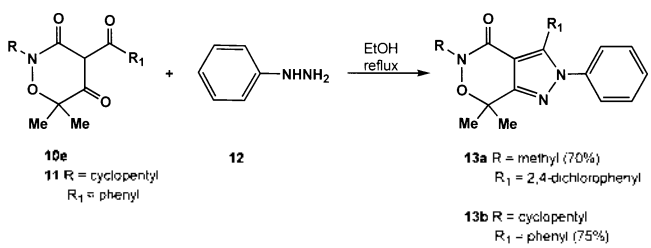
Scheme 2



Scheme 3

As an extended study, new fused heterocyclic compounds were synthesized from the 4-acyl substituted [1,2]oxazinane-3,5-diones (**10**, **11**). The reaction of 4-acyl [1,2]oxazinane-3,5-diones with phenylhydrazine at reflux in ethanol afforded pyrazolate fused bicyclic ring system, 2,7-dihydro-6-oxa-1,2,5-triaza-inden-4-ones, in good yields. The regiochemistry of cyclocondensation was confirmed by NOE experiments. No NOE enhancements between the protons at phenyl ring of phenylhydrazine moiety and those at two methyl groups on the oxazine ring in **13a** and **13b** suggested that the only isomers were formed as shown in Scheme 4.

In summary, a variety of [1,2]oxazinane-3,5-diones were



Scheme 4

synthesized from a hydroxylamine or an amine in a few steps in good yields. Their ester derivatives were prepared and the cyanide ion catalyzed rearrangements were performed to yield 4-acyl substituted derivatives in excellent yields. Treatment of 4-acyl substituted [1,2]oxazinane-3,5-diones with phenylhydrazine afforded 2,7-dihydro-6-oxa-1,2,5-triaza-inden-4-ones in good yields.

Experimental Section

Melting points were measured in capillary tubes with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Schimadzu IR-435 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian GEMINI-200. ^{13}C NMR spectra were recorded on a Bruker AM-300. All chemical shifts are reported in ppm (δ) downfield from internal tetramethylsilane and coupling constants are given in herz (Hz). Mass spectra were recorded on a Shimadzu GCMS-OP 1000 mass spectrometer. Chromatographic separations were carried out on silica gel column (Merck silica gel 230-400). Elemental analysis were performed by Organic Chemistry Research Center at Sogang University in Seoul.

A typical procedure for the preparation of 7a

To a solution of *N*-acetyl-*N*-isopropylhydroxylamine (3.5 g, 29.9 mmol) and ethyl 2-bromoisobutyrate (7.0 g, 35.9 mmol) in acetone (50 mL) was added potassium carbonate (5.0 g, 35.9 mmol) at room temperature. The reaction mixture was warmed up to 40 °C and stirred for 8 h. The white solids were filtered off and the filtrate was concentrated under reduced pressure. The residue was dissolved in ether (150 mL), washed with water (3 × 20 mL) and brine (20 mL). The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (3 : 1) to give *N*-acetyl-*O*-dimethylethoxycarbonylmethyl-*N*-isopropylhydroxylamine (**7a**) as a colorless oil. Yield: 95%; colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.22 (q, J = 7.11 Hz, 2H), 4.05 (h, J = 6.81 Hz, 1H), 2.09 (s, 6H), 1.31 (t, J = 7.11 Hz, 3H), 1.26 (d, J = 6.81 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.89, 83.40, 61.37, 53.85, 23.60, 22.63, 19.44, 14.01, 13.99; FT-IR (cm^{-1}, neat) 2984.4, 2943.0, 1737.5, 1677.9, 1384.2, 1366.8, 1290.6, 1176.6, 1134.3, 1026.5; MS (20 eV) m/z (rel intensity) 232 [(M+1)$^+$, 14.3], 189 (4.7), 174 (1.3), 158 (15.2), 115 (61.1), 100 (6.4), 87 (73.7); HRMS calcd for $C_{11}H_{21}NO_4$ 231.1470, found 231.1468.

***N*-Acetyl-*N*-*t*-butyl-*O*-dimethylethoxycarbonylmethylhydroxylamine (7b).** Yield: 89%; a colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.20 (q, J = 6.10 Hz, 2H), 2.09 (s, 3H), 1.51 (s, 9H), 1.37 (s, 6H), 1.30 (t, J = 7.32 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.21, 172.69, 84.35, 62.21, 61.25, 60.24, 27.90, 26.30, 24.43, 23.74, 20.90, 13.89; FT-IR (cm^{-1}, neat) 3627.3, 3456.5, 2985.7, 2942.4, 1734.4, 1680.8, 1365.1, 1291.4, 1175.2, 1025.5, 823.2; MS (20 eV) m/z (rel intensity) 245 (M$^+$, 0.6), 219 (0.7), 203 (1.8), 188 (0.4), 173 (0.4), 164 (2.2), 125 (7.8), 115 (17.3), 105 (5.6), 87 (19.5); HRMS calcd for $C_{12}H_{23}NO_4$ 245.1627, found 245.1659.

***N*-Acetyl-*N*-cyclopentyl-*O*-dimethylethoxycarbonylmethylhydroxylamine (7c).** Yield: 93%; a colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.22 (q, J = 7.11 Hz, 2H), 3.66 (m, 1H), 2.10 (s, 3H), 1.90-1.38 (m, 8H), 1.50 (s, 6H), 1.32 (t, J = 7.11 Hz, 3H).

***N*-Acetyl-*N*-cyclohexyl-*O*-dimethylethoxycarbonylmethylhydroxylamine (7d).** Yield: 88%; a colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.28-4.15 (m, 3H), 2.09 (s, 3H), 1.95-1.51 (m, 10H), 1.49 (s, 6H), 1.29 (t, J = 7.12 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.62, 128.17, 126.721, 83.38, 62.81, 61.20, 28.21, 23.95, 23.33, 22.19, 13.83; FT-IR (cm^{-1}, neat) 3456.5, 2956.7, 2813.5, 1737.3, 1672.4, 1448.7, 1366.5, 1288.6, 1176.3, 1139.3, 1026.3; MS (20 eV) m/z (rel intensity) 272 [(M+1)$^-$, 0.1], 258 (17.6), 215 (9.8), 184 (14.1), 143 (9.0), 115 (85.5), 101 (63.9), 87 (69.6); HRMS calcd for $C_{14}H_{25}NO_4$ 271.1783, found 271.1796.

***N*-Acetyl-*O*-dimethylethoxycarbonylmethyl-*N*-methylhydroxylamine (7e).** Yield: 85%; a colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.22 (q, J = 7.11 Hz, 2H), 3.17 (s, 3H), 2.12 (s, 3H), 1.50 (s, 6H), 1.30 (t, J = 7.11 Hz, 3H).

***N*-Acetyl-*N*-(2-chlorobenzyl)-*O*-dimethylethoxycarbonylmethylhydroxylamine (7f).** Yield: 91%; a colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41-7.22 (m, 4H), 5.05 (s, 2H), 4.28 (q, J = 7.12 Hz, 2H), 2.13 (s, 3H), 1.51 (s, 6H), 1.32 (t, J = 7.12 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.34, 172.18, 133.54, 132.03, 129.02, 128.03, 127.78, 126.65, 83.64, 61.34, 50.53; FT-IR (cm^{-1}, neat) 3070.5, 2990.0, 2942.4, 1737.2, 1680.6, 1472.9, 1444.9, 1384.9, 1287.3, 1178.0, 1140.9, 1037.1, 752.5; MS (20 eV) m/z (rel intensity) 315 [(M+1)$^+$, 1.4], 314 (M$^+$, 7.6), 278 (27.3), 271 (16.1), 240 (13.6), 164 (31.2), 140 (35.2), 125 (61.6), 115 (98.86), 87 (87.4); HRMS calcd for $C_{15}H_{20}ClNO_4$ 314.1159, found 314.1161.

A typical procedure for the preparation of 8a

To a solution of **7a** (2.9 g, 12.6 mmol) in dry THF (25 mL) was added LiHMDS (25.2 mL, 25.2 mmol) at –78 °C. The reaction mixture was stirred for 0.5 h and allowed to room temperature. The solvent was removed under reduced pressure and quenched with saturated NH_4Cl. The reaction mixture was extracted with ether (3 × 50 mL), washed with water (20 mL) and brine (20 mL). The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (3 : 1) to give 2-isopropyl-6,6-dimethyl-[1,2]oxazinane-3,5-dione (**8a**) as a colorless oil (2.26 g, 97%).

^{1}H NMR (200 MHz, $CDCl_3$) δ 4.62 (h, J = 6.71 Hz, 1H), 3.44 (s, 2H), 1.38 (s, 6H), 1.21 (d, J = 6.71 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.00, 166.44, 85.54, 47.31, 46.80, 21.96, 18.91; FT-IR (cm^{-1}, neat) 3453.8, 3346.3, 2984.4, 2941.5, 2885.9, 1741.8, 1685.0, 1402.6, 1367.8, 1184.0, 1133.4, 906.7; MS (20 eV) m/z (rel intensity) 186 [(M+1)$^-$, 1.3], 185 (M$^+$, 11.0), 170 (2.9), 149 (1.5), 129 (2.6), 111 (13.8), 100 (7.9), 84 (8.2); HRMS calcd for $C_9H_{15}NO_3$ 185.1051, found 185.1056; Anal. calcd for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.39; H,

8.11; N, 7.57.

2-*tert*-Butyl-6,6-dimethyl-[1,2]oxazinane-3,5-dione (8b). Yield: 94%; a colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.42 (s, 2H), 1.44 (s, 9H), 1.38 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.80, 167.80, 85.44, 60.58, 48.47, 27.27, 21.86; FT-IR (cm $^{-1}$, neat) 3198.5, 3102.0, 2955.5, 1735.9, 1565.8, 1449.1, 1301.1, 1137.1, 1017.9, 761.4; MS (20 eV) m/z (rel intensity) 200 [(M+1)$^+$, 2.7], 199 (M$^+$, 16.9), 144 (33.3), 115 (21.4), 100 (2.9), 84 (100.0); HRMS calcd for $C_{10}H_{17}NO_3$ 199.1208, found 199.1206.

2-Cyclopentyl-6,6-dimethyl-[1,2]oxazinane-3,5-dione (8c). Yield: 91%; a colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.32-4.17 (m, 1H), 3.47 (s, 2H), 1.85-1.44 (m, 8H), 1.39 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.64, 166.17, 85.48, 56.33, 46.50, 27.62, 23.51, 21.60; FT-IR (cm $^{-1}$, neat) 3528.1, 3466.2, 2961.7, 2875.8, 2251.3, 1742.7, 1682.1, 1382.7, 1167.7, 917.0, 734.3; MS (20 eV) m/z (rel intensity) 212 [(M+1)$^+$, 40.6], 211 (M$^+$, 44.6), 189 (3.5), 144 (83.7), 125 (3.6), 111 (45.6), 100 (19.4), 83 (27.6); HRMS calcd for $C_{11}H_{17}NO_3$ 211.1208, found 211.1206.

2-Cyclohexyl-6,6-dimethyl-[1,2]oxazinane-3,5-dione (8d). Yield: 93%; a colorless solid; mp, 63-64; ^{1}H NMR (200 MHz, $CDCl_3$) 4.82-4.65 (m, 1H), 3.47 (s, 2H), 1.85-1.45 (m, 10H), 1.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 207.16, 166.13, 85.68, 54.83, 46.87, 29.27, 25.34, 25.09, 22.07; FT-IR (cm^{-1}, neat) 3464.0, 3335.4, 2989.7, 2934.2, 2852.6, 1740.5, 1688.4, 1475.5, 1418.0, 1310.8, 1175.9, 1151.0, 895.2; MS (20 eV) m/z (rel intensity) 226 [(M+1)$^+$, 16.3], 225 (M$^-$, 34.0), 208 (0.5), 182 (0.9), 144 (95.2), 111 (37.2), 98 (11.0), 83 (50.8); HRMS calcd for $C_{12}H_{19}NO_3$ 225.1364, found 225.1371.

2,2,6-Trimethyl-[1,2]oxazinane-3,5-dione (8e). Yield: 95%; a colorless solid; mp, 62-63 °C; ^{1}H NMR (200 MHz, $CDCl_3$) 3.48 (s, 2H), 3.28 (s, 3H), 1.40 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 206.66, 165.43, 86.40, 46.42, 34.61, 21.59, 21.56; FT-IR (cm^{-1}, neat) 3451.5, 3336.3, 2987.6, 2942.5, 2883.4, 1737.5, 1680.4, 1465.1, 1383.5, 1168.3, 917.0, 860.7; MS (20 eV) m/z (rel intensity) 158 [(M+1)$^+$, 21.1], 157 (M$^-$, 74.9), 129 (22.7), 111 (58.0), 83 (37.8), 70 (100.0); HRMS calcd for $C_7H_{11}NO_3$ 157.0738, found 157.0747.

2-(2-Chloro-benzyl)-6,6-dimethyl-[1,2]oxazinane-3,5-dione (8f). Yield: 89%; a pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) 7.38-7.25 (m, 4H), 4.94 (m, 1H), 3.55 (s, 2H), 1.17 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.64, 132.34, 131.37, 129.71, 129.71, 129.60, 128.96, 126.94, 125.56, 86.45, 48.35, 46.57, 26.91, 21.49; FT-IR (cm $^{-1}$, neat) 3528.7, 3443.9, 2986.9, 2934.3, 2254.9, 1742.4, 1680.8, 1467.5, 1381.7, 1167.8, 1098.0, 909.2, 734.8; MS (20 eV) m/z (rel intensity) 268 (M$^+$, 1.2), 257 (0.8), 244 (0.7), 232 (79.5), 190 (3.7), 173 (17.5), 138 (33.5), 125 (100.0), 111 (28.9).

The preparation of 10a-e: refer to the procedure described in reference 1 and 2

4-Benzoyl-5-hydroxy-2-isopropyl-6,6-dimethyl-6H-[1,2]oxazin-3-one (10a). Yield: 82%; a pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.12-7.37 (m, 5H), 4.27 (h, J = 6.72 Hz, 1H), 1.38 (s, 6H), 1.31 (d, J = 6.72 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.43, 164.25, 128.88, 128.37, 128.04, 127.56, 85.48, 47.28, 46.70, 26.78, 21.87, 21.41, 18.84, 18.70; FT-IR (cm $^{-1}$, neat) 2985.0, 2940.0, 1732.0, 1683.8, 1538.7, 1371.5, 1278.6, 1179.7, 768.0; MS (20 eV) m/z (rel intensity) 290 [(M+1)$^+$, 2.4], 289 (M$^+$, 3.9), 231 (5.3), 216 (30.9), 202 (1.2), 188 (2.2), 175 (1.4), 160 (3.2), 138 (7.7), 122 (17.5), 105 (100), 84 (36.4); HRMS calcd for $C_{16}H_{19}NO_4$ 289.1314, found 289.1322; Anal. calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. found: C, 66.38; H, 6.50; N, 4.89.

4-(2,4-Dichloro-benzoyl)-5-hydroxy-2-isopropyl-6,6-dimethyl-6H-[1,2]oxazin-3-one (10b). Yield: 80%; a light brown oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.82-7.19 (m, 3H), 4.72 (h, J = 6.72 Hz, 1H), 1.35 (s, 6H), 1.32 (d, J = 6.72 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.71, 184.28, 168.70, 136.71, 135.08, 132.67, 129.36, 129.17, 127.06, 84.34, 47.27, 46.08, 26.77, 21.27, 20.99, 18.68; FT-IR (cm $^{-1}$, neat) 2985.8, 2941.2, 2255.2, 1689.7, 1591.5, 1564.9, 1470.9, 1178.2, 1103.1, 910.4, 734.6; MS (20 eV) m/z (rel intensity) 358 [(M+1)$^-$, 0.5], 322 (44.4), 280 (13.1), 264 (3.9), 247 (1.9), 215 (1.6), 190 (13.4), 173 (100.0), 145 (29.3), 109 (24.1); HRMS calcd for $C_{16}H_{17}NO_4Cl_2$ 357.0534, found 357.0532.

4-Butyryl-5-hydroxy-2-isopropyl-6,6-dimethyl-6H-[1,2]oxazin-3-one (10c): Yield: 83%; a pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.67 (h, J = 6.71 Hz, 1H), 2.94 (t, J = 7.52 Hz, 2H), 1.79-1.60 (m, 2H), 1.40 (s, 6H), 1.26 (d, J = 6.71 Hz, 6H), 1.01 (t, J = 7.52 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.35, 192.28, 169.59, 163.65, 97.97, 83.79, 46.59, 38.33, 21.16, 19.22, 18.56; FT-IR (cm $^{-1}$, neat) 2981.4, 2939.1, 2877.3, 1680.4, 1469.8, 1376.0, 1181.0, 1049.0, 910.3; MS (20 eV) m/z (rel intensity) 256 [(M+1)$^-$, 18.9], 255 (M$^+$, 39.7), 238 (5.3), 226 (0.3), 199 (3.9), 182 (83.5), 180 (7.1), 154 (20.8), 126 (7.1), 97 (19.9); HRMS calcd for $C_{13}H_{21}NO_4$ 255.1470, found 255.1467.

4-Butyryl-5-hydroxy-2,6,6-trimethyl-6H-[1,2]oxazin-3-one (10d). Yield: 76%; a pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.25 (s, 3H), 2.92 (t, J = 7.32 Hz, 2H), 1.74-1.60 (m, 2H), 1.41 (s, 6H), 1.00 (t, J = 7.32 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.04, 192.39, 164.09, 102.22, 84.57, 38.68, 38.16, 34.27, 21.16, 19.35, 13.92; FT-IR (cm $^{-1}$, neat) 3333.5, 2969.2, 2938.6, 2877.2, 1680.8, 1454.2, 1376.8, 1219.9, 1163.1, 1024.9, 915.7; MS (20 eV) m/z (rel intensity) 228 [(M+1)$^-$, 0.5], 227 (M$^+$, 3.2), 212 (0.6), 181 (1.5), 169 (1.8), 154 (4.5), 126 (9.8), 97 (7.0), 84 (35.1); HRMS calcd for $C_{11}H_{17}NO_4$ 227.1157, found 227.1172.

4-(2,4-Dichloro-benzoyl)-5-hydroxy-2,6,6-trimethyl-6H-[1,2]oxazin-3-one (10e). Yield: 85%; a light brown oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45-7.20 (m, 3H), 3.36 (s, 3H), 1.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.92, 183.49, 169.48, 136.34, 133.96, 132.26, 131.20, 129.34, 127.16, 85.11, 34.53, 26.84, 21.22, 20.96; FT-IR (cm $^{-1}$, neat) 3624.1, 3451.0, 3090.9, 2985.2, 2939.2, 1746.1, 1694.1, 1592.4, 1472.0, 1379.7, 1214.9, 1103.9, 825.2; MS (20eV) m/z (rel intensity) 331 [(M+1)$^+$, 0.5], 330 (M$^-$, 2.6), 294 (100.0), 250 (1.4), 236 (37.0), 208 (34.8), 173 (94.0), 145 (29.9), 123 (13.8), 109 (20.1).

A typical procedure for the the preparation of 13b

A mixture of **11** (0.80 g, 2.54 mmol) and phenylhydrazine (0.28 g, 2.54 mmol) in ethanol (25 mL) was refluxed for 4 h, and then concentrated under reduced pressure. The residue was purified by chromatography on silica gel using hexane/ethyl acetate (3 : 1) to give 5-cyclopentyl-7,7-dimethyl-2,3-diphenyl-2,7-dihydro-6-oxa-1,2,5-triaza-inden-4-one (**13b**) (0.74 g, 75%) as a pale yellow solid. mp 199-200 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.17-8.12 (m, 2H), 7.54-7.38 (m, 8H), 4.46-4.32 (m, 1H), 1.81-1.52 (m, 10H), 1.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.81, 151.29, 150.87, 139.16, 131.35, 129.84, 129.35, 128.95, 128.71, 127.99, 126.99, 108.06, 77.76, 55.42, 29.23, 25.58, 23.97; FT-IR (cm $^{-1}$, neat) 3070.7, 2991.1, 2934.3, 2852.7, 1657.8, 1503.2, 1477.7, 1459.3, 1210.1, 767.0; MS (20 eV) m/z (rel intensity) 387 [(M+1)$^+$, 0.8], 319 (M$^+$, 27.0), 304 (22.0), 287 (100.0), 271 (9.7), 247 (3.5), 218 (2.1), 184 (0.5), 156 (3.7), 129 (4.3), 104 (11.0); HRMS calcd for $C_{24}H_{25}N_3O_2$ 387.1946, found 387.1931; Anal. calcd for $C_{24}H_{25}N_3O_2$: C, 74.39; H, 6.50; N, 10.84, found: C, 74.33; H, 6.64; N, 10.83.

3-(2,4-Dichloro-phenyl)-5,5,7-trimethyl-2-phenyl-2,7-dihydro-6-oxa-1,2,5-triaza-inden-4-one (13a): Yield: 72%; a pale yellow solid; mp 153-154 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.54-7.26 (m, 8H), 3.24 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.49, 150.36, 147.75, 138.83, 135.22, 134.78, 132.66, 130.00, 129.54, 129.44, 126.68, 109.41, 78.71, 33.87, 24.00; FT-IR (cm $^{-1}$, neat) 3059.5, 2985.4, 2936.4, 1673.4, 1596.7, 1503.4, 1365.7, 1105.8, 756.7; MS (20eV) m/z (rel intensity) 402 [(M+1)$^+$, 2.4], 401 (M$^+$, 4.5), 384 (2.3), 366 (80.3), 355 (83.3), 339 (7.2), 321 (49.2), 305 (11.4), 265 (1.2), 242 (1.8), 215 (1.8), 197 (1.5), 178 (5.4), 142 (11.1); HRMS calcd for $C_{20}H_{17}N_3O_2Cl_2$ 401.0697, found 401.0702; Anal. calcd for $C_{20}H_{17}N_3O_2Cl_2$: C, 59.71; H, 4.26; N, 10.45, found: C, 59.77; H, 4.24; N, 10.39

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