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Regioselective Synthesis of Heterocyclic Ketene *N,N*-, *N,O*- and *N,S*-acetals in Aqueous Medium

Langpoklakpam Gellina Chanu, Okram Mukherjee Singh,* Sang Hun Jang,† and Sang-Gyeong Lee†,*

Department of Chemistry, Manipur University, Canchipur-795003, Manipur, India.
†Department of Chemistry and Research Institute of Life Science, Graduate School for Molecular Materials and Nanochemistry, Gyeongsang National University, Jinju 660-701, Korea
**E-mail: leesang@gnu.ac.kr*
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The reactions of ketene dithioacetals with ethane-1,2-diamine, propane-1,3-diamine, 2-aminoethanol, 3-aminopropanol, and 2-aminoethanethiol in ordinary water in the absence of any acid/base catalyst afforded the heterocyclic ketene *N,N*-, *N,O*- and *N,S*-acetals in good yields.

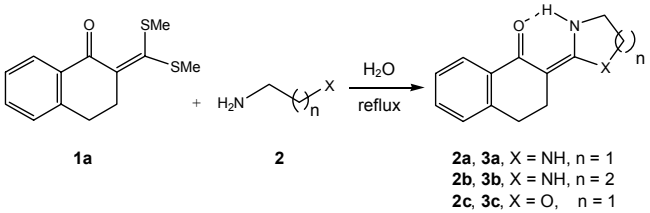
Key Words: Ketene dithioacetals, Heterocyclic ketene acetals, Conjugate addition-elimination reaction

Introduction

Organic reactions in aqueous media have increasingly attracted the attention of synthetic chemists, because water is one of the most abundant, cheapest, non toxic and environmentally friendly solvent.[1] Keeping in our mind this theme of green chemistry, we examined the potential for using alternative benign reaction media for the synthesis of heterocyclic ketene *N,N*-, *N,O*- and *N,S*-acetals. Ketene *N,N*- and *N,S*-acetals are versatile ambident synthetic intermediates, which combine the nucleophilicity of enamines and the electrophilicity of enones. They have been utilized as building blocks for the synthesis of a wide range of heterocycles and natural products.[2,3] *N,N*-Acetals are also of general interest in medicinal and agricultural chemistry because they are possible bioisosteres of thioureas but with extra sites in the ketene that can be derivatised.[4]

Several synthetic methods for *N,N*-, *N,O*- and *N,S*-ketene acetals derived from primary alkyl amines and aromatic amines are available.[5,6] However, the synthetic methods for heterocyclic ketene *N,N*-, *N,O*- and *N,S*-acetals are found to be very few.[7-8] The ketene-dichlorides which were used extensively for the synthesis of heterocyclic ketene acetals, are not very stable compounds.[7] The synthetic methods reported earlier have one or more disadvantages such as the lack of the ease of availability/preparation of necessary starting materials.[8d]

We report herein an easy and efficient synthesis of the heterocyclic ketene acetals by direct displacement of the thiomethyl functional groups of ketene dithioacetals[9] by conjugate addition-elimination reaction with various binucleophiles. The reactions of ketene dithioacetals with ethane-1,2-diamine, propane-1,3-diamine, 2-amino ethanol, 3-aminopropanol and 2-amino ethanethiol in ordinary water in the absence of any acid/base catalyst afforded the dihydroimidazolidines, hexahydropyrimidines, 1,3-oxazolidines, 1,3-oxazines and 1,3-thiazolidines respectively in good to excellent yields (Table 1 and 2).



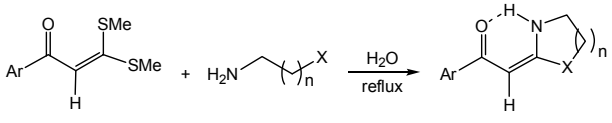
Scheme 1

Results and Discussion

Ketene-*S,S*-acetal (**1a**) derived from tetralone was refluxed with 1 equimolar ethane-1,2-diamine (**2a**) in ordinary water and the isolated product was characterized as 2-(imidazolidin-2-ylidene)-1-phenylethanone (**3a**) on the basis of its spectral and analytical data (Scheme 1). Similarly ketene-*S,S*-acetals (**1a**) was treated with 1,3-diaminopropane and ethanolamine in hot water to yield the corresponding heterocyclic ketene-*N,N*-acetals (**3b**) and *N,O*-acetals (**3c**) in 90 ~ 92% overall yields.

To demonstrate the generality, aroyl ketene-*S,S*-acetals **1b-c** and electron withdrawing group (EWG) substituted ketene-*S,S*-acetals **1d-f** were also treated similarly with various binucleophiles to yield the respective heterocyclic ketene aminals **4a-d**

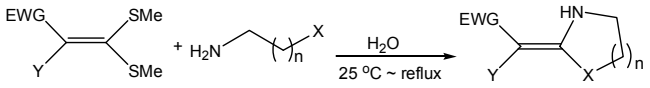
Table 1. The reactions of ketene-*S,S*-acetals (**1**) with ethane-1,2-diamine (**2**) in water[a]



1	Ar	X	n	Product	Yield(%)
1b	C_6H_5	NH	1	**4a**	95[b]
1b	C_6H_5	O	1	**4b**	70[c]
1c	4-$MeOC_6H_5$	O	1	**4c**	73[c]
1b	C_6H_5	NH	2	**4d**	96[b]

[a]*S,S*-acetal (**1**) (5.0 mmol), binucleophile (**2**) (5.0 mmol), water (20 ~ 30 mL). [b]Optimum reaction condition: reflux, 2 ~ 3 h. [c]Optimum reaction condition: reflux, 5 ~ 6 h.

Table 2. The reactions of ketene-*S*,*S*-acetals (**1**) with ethane-1,2-diamine (**2**) in water[a]



1d-h **2** **5a-k**

1	EWG	Y	X	n	Product	Yield (%)
1d	CN	C_6H_5CO	NH	1	**5a**	90[b]
1e	CN	$CO_2C_2H_5$	NH	1	**5b**	93[c]
1g	CO_2CH_3	CO_2CH_3	O	1	**5d**	70[b]
1f	CN	CN	O	1	**5e**	90[b]
1h	CN	CO_2CH_3	O	1	**5f**	93[b]
1h	CN	CO_2CH_3	S	1	**5g**	70[b]
1f	CN	CN	S	1	**5h**	73[b]
1e	CN	CO_2CH_3	NH	2	**5i**	90[c]
1h	CN	CN	NH	2	**5j**	97[c]
1h	CN	CO_2CH_3	O	2	**5k**	90[b]

[a]Reaction conditions: *S*,*S*-acetal (**1**) (5.0 mmol), binucleophile (**2**) (5.1 mmol), H_2O (20 mL), rt ~ reflux. [b]Optimum reaction condition: reflux, 2 ~ 3 h. [c]Optimum reaction condition: rt, 10 ~ 15 min.

and **5a-k**. Thus, ketene-*S*,*S*-acetal (**1b**) was treated with ethane-1,2-diamine in hot water to yield the corresponding heterocyclic ketene-*N*,*N*-aminals (**4a**) in 95% yield. The reaction of ketene-*S*,*S*-acetals **1b-c** with ethanolamine were also examined in order to diversify the synthetic scope of the reaction for the construction of heterocyclic ring systems **4b-c**. The validity of this heterocyclic synthesis was further evaluated by performing the reaction with propane-1,3-diamine, with the aim of synthesizing hexahydropyrimidines. Thus, 1,3-diaminopropane was reacted with ketene-*S*,*S*-acetal (**1b**) to afford the corresponding *N*,*N*-acetal (**4d**) in 96% yield (Table 1).

As expected, electron withdrawing group (EWG) substituted ketene-*S*,*S*-acetals **1d-h** reacts faster than the aroyl substituted dithioacetals with ethane-1,2-diamine, propane-1,3-diamine, ethanolamine and ethanethiol to give the corresponding products **5a-k**. The reactions of **1f-g** with the diamines took only 10 ~ 15 min stirring at ambient temperature to convert fully to the product imidazolidine **5b-c** and hexahydro pyrimidine **5i-j** (monitored by TLC) (Table 2).

α-Oxoketene dithioacetals are well known 1,3-electrophilic three carbon synthons for constructing various heterocyclic ring systems by reacting with various binucleophiles.[9] However, during our investigation, none of the binucleophiles employed react with the α-oxo functionality of the dithioacetals and exclusively the products from the direct displacement of the dithioacetals are obtained. The reaction showed high regioselectivity with excellent yields.

The structural framework of ketene acetals **3a-c** and **4a-d** provides N-C=C-C=O component, which can be utilized for the construction of many heterocyclic rings by reacting with several bis-electrophiles. The electron donating amino groups and electron withdrawing substituents induce the conjugation effect, highly polarizing the double bond and increasing the electron density on the α-carbon, leading to the carbon atom more nucleophilic than the nitrogen atom. These compounds are found to exist in intramolecular hydrogen bonded structures (Scheme 1) as evidenced by the bathochromic shift of the aroyl absorption at ν = 1595 ~ 1625 cm^{-1} in the IR spectra and a hydrogen bonded NH stretching vibration at 3200 ~ 3350 cm^{-1} suggesting its position with the intramolecularly associated hydrogen. ^{1}H NMR spectra of these compounds showed a characteristic chelated NH proton far downfield near δ 9.53 ~ 11 ppm, assigned to the amino group which participated in a strong hydrogen bond with the oxygen of the carbonyl group (NH-O=C) in a six membered, planar chelate.

Similarly, the structures of **5a-k** were established based on the analytical and spectroscopic data. Moreover, it was observed that the chemical shift δ (NH) of **3a-c** and **4a-d** in DMSO-d_6 was at lower field than in $CDCl_3$, presumably indicating a stronger intermolecular hydrogen bonding with the DMSO-d_6.

Conclusion

An easy and efficient green methodology for "on water" mediated highly regioselective synthesis of heterocyclic *N*,*N*-, *N*,*O*- and *N*,*S*-acetals have been described. The general methods described here are very convenient for the synthesis of dihydroimidazoles, hexahydropyrimidines, 1,3-oxazolidines, 1,3-oxazines and 1,3-thiazolidines with readily available starting materials, mild conditions, easy operation, and a broad range of substrates.

Experiment

NMR spectra were recorded on Bruker FT-NMR Avance-400 MHz spectrometer. Chemical shifts δ are in parts per million (ppm) with either $CDCl_3$ or DMSO-d_6 as solvent and are relative to tetramethylsilane (TMS) as the internal reference. The FT-IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer (KBr). Gas chromatography-electron impact mass spectrometry (GC-EIMS) spectra were measured on a Varian SAT2100 TGC3900 spectrometer using ionization by fast atom bombardment (FAB). Melting points were uncorrected. Silica gel 60 (Merck) was used for column separations. TLC was conducted on standard conversion aluminum sheets precoated with a 0.2 mm layer of silica gel. Elemental analyses were measured with LECO Micro Carbon Hydrogen Nitrogen Determinator (CHN-800). Ketene dithioacetals **1a-h** were prepared by earlier reported procedures.[9]

Preparation of *N*,*N*-, *N*,*O*-, *N*,*S*-acetals 3a-c, 4a-d, 5a, 5d-j and 5k. Ketene dithioacetal **1a-e** (10 mmol) were transferred into a round bottom flask. To this the desired binucleophile (**2**) (10 mmol) and 20 mL of water was added. Then the contents were refluxed for about 2 ~ 5 h (monitored by TLC). The reaction flask was cooled at 0 °C, when crystals appeared to adhere on the walls of the flask. The separated solid was filtered through a sintered funnel and dried. It was purified and recrystallized from chloroform and hexane. For compounds **3a-c** and **4b-d**, purification was performed by column chromatography using silica gel and hexane/ethyl acetate as the eluent.

Preparation of 5b-c and 5j-k. Ketene dithioacetal (**1e**) or (**1f**) (10 mmol) was transferred into a round bottom flask. To this the respective diamino compound (10 mmol) and 20 mL of water

was added. The mixture was stirred for 10 ~ 15 min at room temperature (monitored by TLC). The separated solid was filtered through a sintered funnel and washed with 10 mL of diethyl ether. It was purified and recrystallized from ethanol.

3,4-Dihydro-2-(imidazolidin-2-ylidene)naphthalen-1(2*H*)-one (3a): Colourless crystals (chloroform-hexane); mp 219 ~ 220 °C; IR (KBr) 3143, 2808, 1593, 1539 cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.09 (brs, NH, 1H), 7.97-7.99 (m, 1H), 7.26-7.36 (m, 2H), 7.12-7.15 (m, 1H), 4.78 (brs, NH, 1H), 3.78 (t, J = 8.4 Hz, 2H), 3.60 (t, J = 7.6 Hz, 2H), 2.84 (t, J = 7.2 Hz, 2H), 2.45 (t, J = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 180.3, 164.1, 143.2, 136.1, 129.8, 127.0, 126.4, 125.7, 84.5, 44.1, 42.8, 28.9, 23.0; MS *m*/*z* 214 (M^+). Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.80; H, 6.70; N, 13.11.

3,4-Dihydro-2-(tetrahydropyrimidin-2(1*H*)-ylidene)naphthalen-1(2*H*)-one (3b): Colourless crystals (chloroform-hexane); mp 189 ~ 190 °C; IR (KBr) 3195, 2862, 1616, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 12.53 (brs, NH, 1H), 7.92-7.94 (m, 1H), 7.21-7.27 (m, 2H), 7.08-7.10 (m, 1H), 5.40 (brs, NH, 1H), 3.35-3.37 (m, 4H), 2.76 (t, J = 7.2 Hz, 2H), 2.33 (t, J = 7.2 Hz, 2H), 1.88-1.91 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 180.3, 158.7, 139.23, 136.9, 128.9, 126.58, 126.27, 125.05, 86.3, 39.1, 38.0, 28.7, 21.6, 20.2; MS *m*/*z* 228 (M^+). Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.70; H, 7.20; N, 12.51.

3,4-Dihydro-2-(oxazolidin-2-ylidene)naphthalen-1(2*H*)-one (3c): Colourless crystals (chloroform-hexane); mp 120 ~ 122 °C; IR (KBr) 3267, 2837, 1633, 1598, 1527 cm^{-1}; ^1H NMR ($CDCl_3$) δ 14.40 (brs, NH, 1H), 8.03-8.05 (m, 1H), 7.44-7.52 (m, 2H), 7.30-7.34 (m, 1H), 3.58 (t, J = 8.6 Hz, OCH_2, 2H), 3.40 (t, J = 8.4 Hz, NCH_2, 2H), 2.72 (t, J = 7.2 Hz, 2H), 2.47 (t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 183.3, 170.1, 143.2, 136.1, 129.8, 127.0, 126.4, 125.7, 84.5, 44.1, 42.8, 28.9, 20.0. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.80; H 6.20; N 6.41.

2-(Benzoylmethylene)-3,4-dihydroimidazolidine (4a):[8c] Yellow crystals (chloroform-hexane); mp 205 ~ 207 °C; IR (KBr) 3313, 3170, 1606, 1558 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.52 (brs, NH, 1H), 7.78-7.82 (m, 2H), 7.26-7.37 (m, 3H), 5.38 (s, 1H), 5.13 (brs, NH, 1H), 3.54 (t, J = 6.9 Hz, 2H), 3.72 (t, J = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 185.1, 165.6, 141.1, 129.8, 128.0, 126.6, 74.3, 43.7, 42.5; MS *m*/*z* 188 (M^+). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.14; H, 6.38; N, 14.89. Found: C, 70.02; H 5.90; N 14.21.

2-(Benzoylmethylene)-3,4-dihydrooxazolidine (4b): Yellow crystals (chloroform-hexane); mp 172 ~ 174 °C; ^1H NMR ($CDCl_3$) δ 7.85 (brs, NH, 1H), 7.78-7.80 (m, 2H), 7.26-7.37 (m, 3H), 5.10 (s, 1H), 4.76 (t, J = 8.6 Hz, OCH_2, 2H), 3.89 (t, J = 8.4 Hz, NCH_2, 2H); ^{13}C NMR ($CDCl_3$) δ 180.7, 175.9, 137, 134, 124.7, 123.5, 71.0, 43.4, 34.7. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.84; H, 5.90; N, 7.59.

2-(4-Methoxybenzoylmethylene)-3,4-dihydrooxaazolidine (4c): Colourless solid; ^1H NMR ($CDCl_3$) δ 7.80 (brs, NH, 1H), 7.59 (d, J = 6.8 Hz, 2H), 5.10 (s, 1H), 4.76 (t, J = 8.6 Hz, OCH_2, 2H), 3.89 (t, J = 8.4 Hz, NCH_2, 2H), 3.80 (s, OCH_3, 3H); ^{13}C NMR ($CDCl_3$) δ 180.7, 175.9, 165, 134, 130.7, 114.5, 71.0, 43.4, 34.7. Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.84; H, 5.92; N, 6.49.

2-(Benzoylmethylene)hexahydropyrimidine (4d):[8c] mp 210 ~ 212 °C; IR (KBr) 3302, 2953, 1595, 1419 cm^{-1}; ^1H NMR (DMSO-d_6) δ 11.34 (brs, NH, 2H), 7.76-7.79 (m, 2H), 7.28-7.36 (m, 3H), 5.10 (s, vinyl, 1H), 3.30-3.35 (m, CH_2, 4H), 1.92-1.99 (m, CH_2, 2H); ^{13}C NMR (DMSO-d_6) δ 180.2, 159.8, 140, 127, 126, 125, 76.9, 37.5, 20.9; MS *m*/*z* 216 (M^+). Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.28; H, 6. 93; N, 13.86. Found: C, 71.05; H, 6.78; N, 13.56.

2-(Imidazolidin-2-ylidene)-3-oxo-3-phenylpropanenitrile (5a): mp 226-228 °C; IR (KBr) 3230, 2190, 1603, 1556 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.60 (brs, NH, 2H), 7.78-7.82 (m, 2H), 7.20-7.30 (m, 3H), 3.69-3.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 163.2, 133.2, 128, 124.7, 123.5, 116.8, 49.1, 42.4, 41.7; MS *m*/*z* 213 (M^+). Anal. Calcd for $C_{12}H_{11}N_3O$: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.50; H, 5.28; N, 19.70.

Ethyl 2-cyano-2-(imidazolidin-2-ylidene)acetate (5b): mp 210 ~ 212 °C; IR (KBr) 3334, 3261, 2194, 1660, 1600, 1535 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.99 (brs, NH, 1H), 6.34 (brs, NH, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.67-3.90 (m, 4H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 163.2, 133.2, 128, 124.7, 116.8, 49.1, 42.4, 41.7; MS *m*/*z* 181 (M^+). Anal. Calcd for $C_8H_{11}N_3O_2$: C, 53.03; H, 6.12; N, 23.19. Found: C, 53.10; H, 6.48; N, 23.10.

2-(Malononitrilemethylene)imidazolidine (5c): mp 242 °C; IR (KBr) 3267, 2208 (CN), 1597 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.18 (brs, NH, 1H), 3.50-3.54 (m, 4H); ^{13}C NMR (DMSO-d_6) δ 180, 110, 51, 45.5, 45.1; MS *m*/*z* 134 (M^+). Anal. Calcd for $C_6H_6N_4$: C, 53.72; H, 4.51; N, 41.77. Found: C, 53.70; H, 4.48; N, 41.70.

Dimethyl 2-(oxazolidin-2-ylidene)malonate (5d): mp 114 ~ 116 °C; ^1H NMR ($CDCl_3$) δ 9.23 (brs, NH, 1H), 4.65 (t, J = 8.6 Hz, OCH_2, 2H), 3.81 (t, J = 8.3 Hz, NCH_2, 2H), 3.74 (s, OCH_3, 6H); ^{13}C NMR ($CDCl_3$) δ 171.3, 76.2, 69.0, 51.6, 42.3. Anal. Calcd for $C_8H_{11}NO_4$: C, 47.76; H, 5.47; N, 6.97. Found: C, 47.87; H, 5.45; N, 7.06.

2-(Oxazolidin-2-ylidene)malononitrile (5e): mp 172 ~ 174 °C; ^1H NMR ($CDCl_3$) δ 7.75 (brs, NH, 1H), 4.76 (t, J = 8.6 Hz, OCH_2, 2H), 3.89 (t, J = 8.4 Hz, NCH_2, 2H); ^{13}C NMR ($CDCl_3$) δ 173.9, 115.7, 113.5, 71.0, 43.4, 34.7. Anal. Calcd for $C_6H_5N_3O$: C, 53.33; H, 3.70; N, 31.11. Found: C, 52.84; H, 3.92; N, 30.79.

Methyl 2-cyano-2-(oxazolidin-2-ylidene)acetate (5f): mp 152 ~ 154 °C; ^1H NMR ($CDCl_3$) δ 8.56 (brs, NH, 1H), 4.69 (t, J = 8.7 Hz, OCH_2, 2H), 3.89 (t, J = 8.3 Hz, NCH_2, 2H), 3.73(s, OCH_3, 3H); ^{13}C NMR ($CDCl_3$) δ 172.16, 168.5, 116.3, 69.38, 56.14, 51.5, 43.41. Anal. Calcd for $C_7H_8N_2O_3$: C, 50.00; H, 4.76; N, 16.67. Found: C, 50.10; H, 4.83; N, 16.54.

Methyl 2-cyano-2-(thiazolidin-2-ylidene)acetate (5g): mp 98 ~ 100 °C; ^1H NMR ($CDCl_3$) δ 9.16 (brs, NH, 1H), 4.59 (t, J = 8.7 Hz, 2H), 3.75(s, OCH_3, 3H), 3.39 (t, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 175.16, 166.2, 119.1, 69.38, 65.2, 52.4, 51.6. Anal. Calcd for $C_7H_8N_2O_2S$: C, 45.46; H, 4.35; N, 15.22. Found: C, 41.69; H, 4.87; N, 13.88.

2-(Thiazolidin-2-ylidene)malononitrile (5h): mp 195 ~ 200 °C; ^1H NMR ($CDCl_3$) δ 9.85 (brs, NH, 1H), 4.02 (t, J = 7.4 Hz, 2H), 3.51 (t, J = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 177.3, 117.4, 115.5, 52.0, 42.3, 31.8. Anal. Calcd for $C_6H_5N_3S$: C, 47.68; H, 3.31; N, 27.81. Found: C, 47.47; H, 3.42; N, 27.74.

Ethyl 2-cyano-2-(tetrahydropyrimidin-2(1*H*)-ylidene)acetate (5i): mp 130 ~ 132 °C IR (KBr) 3342, 3278, 2204, 1650, 1602; ^1H NMR ($CDCl_3$) δ 9.15 (brs, NH, 1H), 5.91 (brs, NH, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.39 (s, 4H), 1.95-2.00 (m, 2H),

1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 172.3, 164.5, 116.3, 60.1, 52.1, 42.4, 41.7, 14.4; MS *m*/*z* 195 (M^+). Anal. Calcd for $C_9H_{13}N_3O_2$: C, 55.37; H, 6.71; N, 21.52. Found: C, 55.32; H, 6.88; N, 21.50.

2-(Malononitrilemethylene)hexahydropyrimidine (5j): mp 250 °C (dec.); IR (KBr) 3296, 2202, 1568 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 8.15 (brs, NH, 2H), 3.20-3.28 (m, 4H), 2.10-2.20 (m, 2H); ^{13}C NMR (DMSO-d_6) δ 190, 110, 50, 38, 26; MS *m*/*z* 166 (M^+). Anal. Calcd for $C_7H_8N_4$: C, 56.75; H, 5.45; N, 37.81. Found: C, 56.85; H, 5.48; N, 37.86.

Methyl 2-cyano-2-(1,3-oxazinan-2-ylidene)acetate (5k): mp 142 ~ 143 °C; ^{1}H NMR ($CDCl_3$) δ 9.60 (brs, NH, 1H), 4.40 (t, J = 5.0 Hz, OCH_2, 2H), 3.67(s, OCH_3, 3H), 3.46 (t, J = 5.6 Hz, NCH_2, 2H), 2.11 (pentet, J = 5.3 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 169.7, 168.2, 117.4, 66.5, 57.9, 51.1, 37.5, 20.4. Anal. Calcd for $C_8H_{10}N_2O_3$: C, 52.75; H, 5.49; N, 15.38. Found: C, 52.28; H, 5.47; N, 14.78.

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