REGIOSPECIFIC *N*-ALKYLATION OF HETEROCYCLIC KETENE AMINALS WITH METHYL PROPIOLATE

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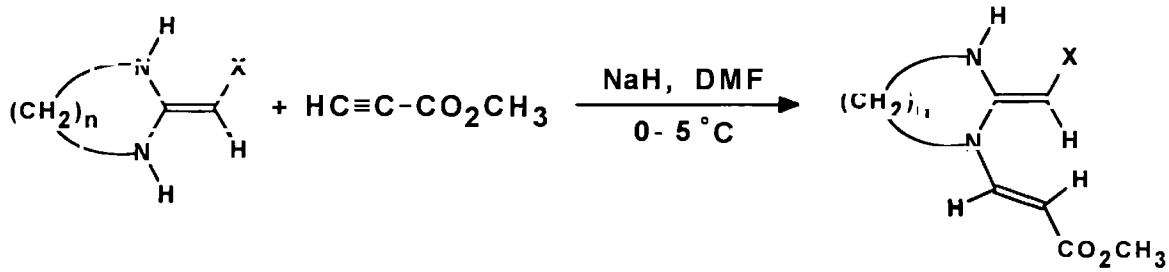
Abstract: Heterocyclic ketene aminals 1 or 2 react with methyl propiolate in the presence of sodium hydride to give *N*-alkylated products, *E*-1-[(*E*)-methoxycarbonylvinyl]-2-[(aroyl)methylene]-imidazolidines 3 or -hexahydropyrimidines 4, in good to excellent yields. Disubstituted heterocyclic ketene aminals 5 or 6 also react smoothly with methyl propiolate in the same conditions to give the *N*-alkylated products 7 or 8.

Introduction

Heterocyclic ketene aminals are important intermediates for the synthesis of a wide variety of new heterocycles and fused heterocycles, therefore, their synthesis and reactions have given rise to much attention (1). Heterocyclic ketene aminals are a kind of ambident nucleophiles, in the case of acyl substituted heterocyclic ketene aminals, the electrophiles may attack in three different ways, *N*-, *C*- and *O*-attack, to give different products. Owing to the conjugation effect of the electron-donating amino groups and electron-withdrawing substituents, the double bond is highly polarized and the α-carbon possesses much higher electron density, leading to greater nucleophilicity at the carbon than at the nitrogen in general cases, and the carbon center always attacks the electropositive site of electrophiles. Thus, alkylation of heterocyclic ketene aminals with alkyl halides or ethyl bromoacetate gave *C*-alkylated products in neutral conditions (2,3). Similarly, alkylation with α, β-unsaturated esters also gave the *C*-alkylated products (4-7). However, the *N*-alkylated products could be obtained by alkylation of heterocyclic ketene aminals with alkyl halides in strongly basic conditions (8-11). The *N*-alkylation of heterocyclic ketene aminals with α, β-unsaturated esters has not been reported yet. Herein we wish to report the results of the regiospecific alkylation of heterocyclic ketene aminals with methyl propiolate to give *N*-alkylated products.

Results and Discussion

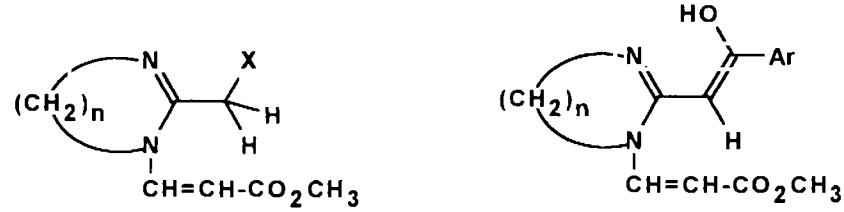
Heterocyclic ketene aminals 1 or 2 react with methyl propiolate in the presence of sodium hydride and anhydrous dimethylformamide (DMF) to give *N*-alkylated products 3 or 4 in good to excellent yields.



1, n = 2
2, n = 3

3, n = 2
4, n = 3

1 - 4	a	b	c	d	e	f
X	CO-Ph	CO-Ph-CH_3	CO-Ph-OCH_3	CO-Ph-Cl	CO-Ph-Br	NO_2

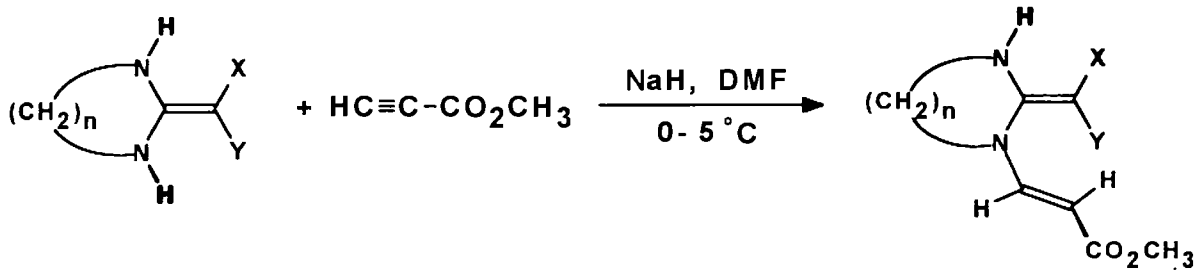


A B

The constitutions of 3 or 4 are determined by the mass spectroscopy and elemental analyses, it is indicated that the alkylated products are the addition products between 1 or 2 and methyl propiolate in 1:1 molar ratio. The structure of products may be *C*-alkylated, or *N*-alkylated, even *O*-alkylated. The presence of one nitrogen proton signal and one ethylenic proton signal in ^{1}H-NMR spectra of products excludes *C*-alkylated products, and the presence of a carbonyl carbon signal in ^{13}C-NMR spectra excludes *O*-alkylated structure for the alkylated products. Therefore, in these reaction conditions, the products are resulted by *N*-alkylation. The spectroscopic data also exclude the tautomeric structure of 3 or 4, the amidine form **A** or amidine enol form **B**. There still remain two stereo problems (*E* or *Z* configuration) in the structure of the products. The *E* configuration for enamine moiety of the products is determined based on the presence of an intramolecular hydrogen bond as indicated by the downfield shift of the nitrogen proton in ^{1}H-NMR spectra and bathochromic shift of the carbonyl absorption in the

IR spectra. The another *E* configuration for methoxycarbonyl vinyl group is determined based on the coupling constants (13.4-13.8 Hz) of the two vinylic protons. Therefore, the *E*, *E*-*N*-alkylated structures 3 or 4 are given for the reaction products.

The reaction between heterocyclic ketene aminals substituted with two electron-withdrawing groups and electrophiles has not been reported yet. In general, such heterocyclic ketene aminals are sluggishly reacted with electrophilic reagents, such as they can not be protonated by acids, while the mono-substituted heterocyclic ketene aminals protonated easily. However, in strong basic reaction conditions, the disubstituted heterocyclic ketene aminals 5 or 6 react smoothly with methyl propiolate, and the *N*-alkylated products are obtained in good yields.



5, n = 2
6, n = 3

7, n = 2
8, n = 3

5 - 8	a	b	c
X	$CO_2C_2H_5$	CN	$CO_2C_2H_5$
Y	CN	CN	$CO_2C_2H_5$

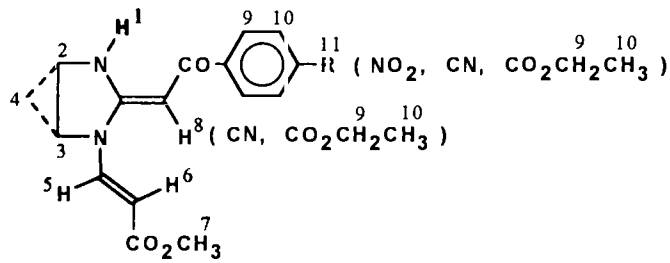
The structure 7 or 8 for the products are coincided with the spectroscopic and elemental analytical data. The *E*, *E*-configurated structure for 7a or 8a and *E*-configurated structure for 7b, c or 8b, c are determined as above. It may be noticed that the two cyano or ethoxy carbonyl groups in 7b, c or 8b, c are not equivalent in crystalline state evidenced by the two different absorptions of these groups in the IR spectra in solid state. It is due to that the one cyano or ethoxy carbonyl group is coplanar with the plane composed by two nitrogen atoms and carbon double bond, and the other is somewhat deviated from this plane (12).

The ^{1}H- and ^{13}C-NMR data are listed in Tables 1 and 2, respectively.

Experimental

Melting points are uncorrected. ^{1}H- and ^{13}C-NMR spectra are recorded with a Varian Unity 200 spectrometer. IR spectra are recorded with a Perkin-Elmer 782 spectrometer. UV spectra are determined with a Hitachi 340 spectrometer. Mass spectra are recorded on a AEI MS-50 instrument. Elemental analyses are performed by the Analytical Laboratory of the Institute.

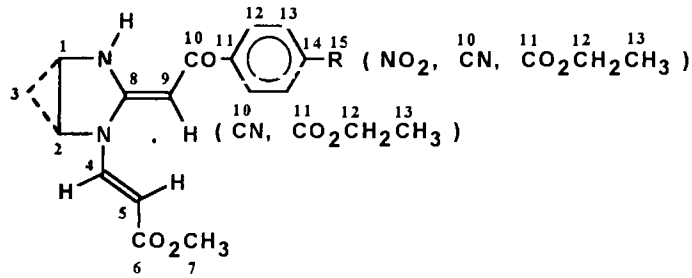
Table 1: ^{1}H-NMR data of 3, 4, 7 and 8 in $CDCl_3$.



	H^1	H^2	H^3	H^4	H^5	H^6	$J_{H5,6}$(Hz)	H^7	H^8	H^9	H^{10}	H^{11}
3a	10.18s	3.65-3.90m			7.92d	5.14d	13.4	3.75s	5.72s	7.38-7.88m		
3b	10.15s	3.64-3.92m			7.94d	5.13d	13.4	3.77s	5.70s	7.79d	7.24d	2.39s
3c	10.10s	3.65-3.90m			7.93d	5.11d	13.6	3.75s	5.67s	7.87d	6.91d	3.83s
3d	10.20s	3.70-3.95m			7.92d	5.16d	13.6	3.78s	5.67s	7.82d	7.40d	
3e	10.18s	3.68-3.95m			7.92d	5.15d	13.6	3.78s	5.64s	7.78d	7.55d	
3f*	9.45s	3.79s			7.69d	5.26d	13.6	3.66s	6.99s			
4a*	12.10s	3.38t	3.50t	1.98quin	7.97d	5.40d	13.4	3.65s	5.55s	7.35-7.80m		
4b	12.30s	3.41t	3.49t	2.10quin	8.10d	5.25d	13.7	3.78s	5.60s	7.75d	7.22d	2.40s
4c	12.20s	3.41t	3.48t	2.10quin	8.10d	5.22d	13.7	3.78s	5.58s	7.83d	6.90d	3.82s
4d	12.22s	3.40t	3.48t	2.10quin	8.05d	5.24d	13.6	3.74s	5.56s	7.76d	7.34d	
4e	12.30s	3.43t	3.49t	2.12quin	8.06d	5.28d	13.8	3.77s	5.56s	7.72d	7.52d	
4f*	10.58s	3.43t	3.53t	2.01quin	7.63d	5.47d	13.6	3.67s	6.65s			
7a	9.17s	3.83s			8.88d	5.19d	13.8	3.74s		4.22q	1.30t	
7b*	9.15s	3.62t	3.92t		8.33d	5.37d	14.2	3.63s				
7c	8.98s	3.82t	3.86t		7.60d	5.12d	14.8	3.72s		4.22q	1.30t	
8a*	9.58s	3.35t	3.52t	2.01quin	7.80d	5.40d	14.7	3.65s		4.11q	1.22t	
8b*	9.06s	3.23t	3.52t	2.00quin	7.80d	5.52d	14.7	3.68s				
8c	9.92s	3.38t	3.48t	2.16quin	7.62d	5.15d	14.8	3.70s		4.14q	1.28t	

* in DMSO-d_6.

Table 2: ^{13}C-NMR data of 3, 4, 7 and 8 in $CDCl_3$.



	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}
3a	41.9	44.8		140.0	97.0	167.5	51.4	159.4	73.4	187.	138.0	128.	126.	130.7	
3b	41.9	44.8		141.0	96.9	167.8	51.4	159.3	73.2	187.	137.5	128.	126.	138.1	21.4
3c	41.9	44.8		138.1	96.8	167.8	51.4	159.1	72.8	186.	132.8	128.	113.	161.8	55.3
3d	41.9	44.8		137.8	97.3	167.5	51.4	159.5	73.2	185.	136.8	128.	128.	138.5	
3e	42.0	44.9		137.8	97.4	167.6	51.5	159.6	73.2	186.	139.0	131.	128.	125.2	
3f*	42.3	45.3		137.8	98.6	166.3	50.7	154.2	96.3						
4a*	37.3	43.8	20.8	142.3	97.2	167.4	51.1	158.1	76.3	183.	140.9	128.	126.	130.1	
4b	37.6	43.8	21.4	142.5	97.3	168.0	51.5	158.2	77.3	185.	138.2	128.	126.	140.5	21.4
4c	37.4	43.6	21.2	142.3	97.0	167.9	51.2	157.9	76.7	185.	133.3	128.	113.	161.3	55.1
4d	37.3	43.4	20.9	141.8	97.5	167.5	51.0	158.1	77.0	184.	135.9	128.	127.	139.0	
4e	37.5	43.6	21.1	142.0	97.7	167.8	51.4	158.3	77.2	184.	139.6	131.	128.	124.6	
4f*	37.7	44.2	20.5	141.7	99.6	166.6	51.0	153.5	95.5						
7a*	41.5	46.4		139.2	98.9	167.3	50.7	159.0	59.3	117.	166.3	59.4	14.1		
7b*	41.6	47.8		138.2	100.4	166.0	50.9	160.9	31.0	116.					
7c	41.4	47.0		142.3	98.4	167.1	51.4	161.2	77.2		168.0	60.4	14.3		
8a	38.6	45.3	22.8	144.9	99.0	167.0	51.6	162.2	60.1	118.	169.9	60.6	14.5		
8b*	38.3	45.3	22.3	144.5	99.5	166.6	51.1	162.3	34.6	117.					
8c	38.3	44.5	23.3	146.2	96.9	167.5	51.5	161.9	80.1		168.4	60.3	14.3		

* in DMSO-d_6.

Heterocyclic ketene aminals 1 and 2 are prepared according to the literature procedure (13, 14), and 5a, b and 6a, b according to literature (12). 5c And 6c are prepared as follows: diethyl malonate reacts in carbon disulfide with sodium hydride and then with methyl iodide in one-spot to give dimethyl bis(ethoxycarbonyl)ketene mercaptal, which reacts with 1,2-ethanediamine or 1,3-propanediamine to give 5c or 6c according to general procedure. 5c: M.p. 91-92 °C. IR (KBr): ν = 3350 (NH), 1612, 1590 (OCO), 1545 cm^{-1}. UV (MeOH): λ_{max} = 246 nm ($\log\varepsilon$ = 4.19). ^{1}H-NMR ($CDCl_3$): δ = 8.55 (s, 2H), 4.16 (q, 4H), 3.68 (s, 4H), 1.31 ppm (t, 6H). ^{13}C-NMR ($CDCl_3$): δ = 169.8, 167.7, 74.3, 59.3, 43.1, 14.4 ppm. MS: *m/z* = 228 (M^+, 33), 183 (22), 156 (34), 84 (100). Anal. Calc. for $C_{10}H_{16}N_2O_4$: C, 52.62; H, 7.07; N, 12.28. Found C, 52.82; H, 7.05, N, 12.38. 6c: M.p. 71.5-72.5 °C. IR (KBr): ν = 3220 (NH), 1620, 1605 cm^{-1}(OCO). UV (MeOH): λ_{max} = 248 nm ($\log\varepsilon$ = 3.93). ^{1}H-NMR ($CDCl_3$): δ = 9.93 (s, 2H), 4.13 (q, 4H), 3.37 (dt, 4H), 1.91 (quin, 2H), 1.29 ppm (t, 6H). ^{13}C-NMR ($CDCl_3$): δ = 171.3, 160.7, 73.5, 59.1, 38.3, 19.9, 14.4 ppm. MS: *m/z* = 242 (M^+, 37), 197 (21), 170 (33), 98 (100). Anal. Calc. for $C_{11}H_{18}N_2O_4$: C, 54.53; H, 7.49; N, 11.57. Found C, 54.56; H, 7.53; N, 11.31.

General Procedure for Synthesis of 3, 4, 7 and 8: 5 mmol of sodium hydride (80 % by weight dispersed in mineral oil and washed with petroleum ether prior to use) is added to an ice-cooled solution of 5 mmol of 1 (2, 5, or 6) in 20 ml of anhydrous dimethylformamide under stirring. The mixture is stirred continuously until no hydrogen gas is evolved. Then a solution of 5 mmol of methyl propiolate in 3 ml of anhydrous dimethylformamide is added dropwise. After stirring for another 10 minutes, the mixture is poured into 150 ml of water and extracted with dichloromethane (3 X 100 ml). The combined extract is dried with anhydrous calcium chloride and the solvent is evaporated. 3, (4, 7, or 8) is obtained by recrystallization of the residue.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(benzoyl)methylene]imidazolidine (3a): 93 %, m.p. 206.5-207.5 °C (methanol-acetone, 10:1). IR (KBr): ν = 3250 (NH), 1700 (OCO), 1625 (CO), 1605, 1575 cm. UV (MeOH): λ_{max} = 344 ($\log\varepsilon$ = 4.62), 281 (4.26), 241 nm (4.11). MS: *m/z* = 272 (M^+, 28), 213 (52), 185 (14), 167 (28), 135 (15), 105 (100). Anal. Calc. for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29. Found C, 66.23; H, 5.81; N, 10.16.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(4-methylbenzoyl)methylene]imidazolidine (3b): 87 %, m.p. 207-208 °C (methanol). IR (KBr): ν = 3250 (NH), 1700 (OCO), 1625 (CO), 1605, 1575 cm^{-1}. UV (MeOH): λ_{max} = 344 ($\log\varepsilon$ = 4.60), 279 nm (4.26). MS: *m/z* = 286 (M^+, 29), 227 (36), 199 (22), 167 (30), 135 (14), 119 (100). Anal. Calc. for $C_{16}H_{18}N_2O_3$: C, 67.11; H, 6.34; N, 9.79. Found C, 67.47; H, 6.35; N, 9.89.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(4-methoxybenzoyl)methylene]imidazolidine (3c): 89 %, m.p. 223-224 °C (methanol-acetone, 10:1). IR (KBr): ν = 3300 (NH), 1700 (OCO), 1623 (CO), 1600,

1570, 1530 cm^{-1}. UV (MeOH): λ_{max} = 348 (logε = 4.64), 278 nm (4.35). MS: *m/z* = 302 (M^+, 31), 243 (18), 215 (19), 167 (23), 135 (100). Anal. Calc. for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27. Found C, 63.51; H, 5.89; N, 9.22.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(4-chlorobenzoyl)methylene]imidazolidine (3d): 95 %, m.p. 198-199 °C (methanol-water, 5:1). IR (KBr): ν = 3260 (NH), 1702 (OCO), 1625 (CO), 1605, 1570, 1530 cm^{-1}. UV (MeOH): λ_{max} = 345 (logε = 4.54), 281 (4.16), 242 nm (4.16). MS: *m/z* = 308 (11), 306 (M^+, 39), 275 (9), 247 (63), 219 (15), 167 (50), 139 (100). Anal. Calc. for $C_{15}H_{15}ClN_2O_3$: C, 58.73; H, 4.93; N, 9.13. Found C, 58.61; H, 4.98; N, 8.91

E-1-[(E)-Methoxycarbonylvinyl]-2-[(4-bromobenzoyl)methylene]imidazolidine (3e): 96 %, m.p. 191.5-192.5 °C (methanol-acetone, 10:1). IR (KBr): ν = 3250 (NH), 1705 (OCO), 1625 (CO), 1600, 1575, 1530 cm^{-1}. UV (MeOH): λ_{max} = 343 (logε = 4.54), 278 (4.25), 241 nm (4.26). MS: *m/z* = 352 (47), 350 (M^+, 43), 291 (77), 263 (16), 183 (90), 167 (100). Anal. Calc. for $C_{15}H_{15}BrN_2O_3$: C, 51.30; H, 4.31; N, 7.98. Found C, 51.38; H, 4.54; N, 7.79.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(nitro)methylene]imidazolidine (3f): 71 %, m.p. 208-209 °C (methanol-acetone, 10:1). IR (KBr): ν = 3310 (NH), 1700 (OCO), 1500, 1360 (NO_2), 1620, 1595 cm^{-1}. UV (MeOH): λ_{max} = 347 (logε = 4.85), 289 (4.32), 231 nm (4.28). MS. *m/z* = 213 (M^+, 41), 182 (20), 167 (62), 135 (37), 107 (57), 28 (100). Anal. Calc. for $C_8H_{11}N_3O_4$: C, 45.07; H, 5.20; N, 19.71. Found C, 45.42; H, 5.32; N, 19.60.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(benzoyl)methylene]hexahydropyrimidine (4a): 81 %, m.p. 111.5-112.5 °C (methanol). IR (KBr): ν = 3400 (NH), 1685 (OCO), 1620 (CO), 1595, 1570, 1520 cm^{-1}. UV (MeOH): λ_{max} = 351 (logε = 4.53), 279 (4.29), 242 nm (4.31). MS: *m/z* = 286 (M^+, 8), 227 (48), 199 (10), 181 (10), 122 (33), 105 (100). Anal. Calc. for $C_{16}H_{18}N_2O_3$: C, 67.11; H, 6.34; N, 9.79. Found C, 67.09; H, 6.40; N, 9.79.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(4-methylbenzoyl)methylene]hexahydropyrimidine (4b): 87 %, m.p. 100-105 °C (ethyl ether-methanol). IR (KBr): ν = 3400 (NH), 1695 (OCO), 1620 (CO), 1600, 1570, 1530 cm^{-1}. UV (MeOH): λ_{max} = 350 (logε = 4.60), 276 (4.40), 233 nm (4.28). MS: *m/z* = 301 ($[M+1]^+$, 26), 241 (100), 213 (36), 181 (29), 91 (55). Anal. Calc. for $C_{17}H_{20}N_2O_3$: C, 67.98; H, 6.71; N, 9.33. Found C, 67.97; H, 6.50; N, 9.22.

E-1-[(E)-Methoxycarbonylvinyl] -2- [(4-methoxybenzoyl)methylene] hexahydropyrimidine (4c): 83%, m.p. 107.5-108.5 °C (ethanol). IR (KBr): ν = 3400 (NH), 1700 (OCO), 1620 (CO), 1590, 1570, 1530 cm^{-1}. UV (MeOH): λ_{max} = 351 (logε = 4.43), 275 nm (4.38). MS: *m/z* = 316 (M^+, 14), 257 (34), 229 (16), 181 (14), 135 (100). Anal. Calc. for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.86. Found C, 64.42; H, 6.40; N, 8.89.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(4-chlorobenzoyl)methylene]hexahydropyrimidine (4d): 84 %, m.p. 147-148 °C (ethanol). IR (KBr): ν = 3400 (NH), 1695 (OCO), 1620 (CO), 1590, 1570, 1525 cm^{-1} UV (MeOH): λ_{max} = 351 ($\log\varepsilon$ = 4.43), 275 nm (4.30). MS: *m/z* = 322 (7), 320 (M^+, 21), 289 (6), 261 (100), 233 (17), 181 (28), 139 (85). Anal. Calc. for $C_{16}H_{17}ClN_2O_3$: C, 59.91; H, 5.34; N, 8.74. Found C, 59.91; H, 5.33; N, 8.54.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(4-bromobenzoyl)methylene]hexahydropyrimidine (4e): 89 %, m.p. 143-144 °C (ethanol). IR (KBr): ν = 3260 (NH), 1705 (OCO), 1630 (CO), 1590, 1570 cm^{-1}. UV (MeOH): λ_{max} = 351 ($\log\varepsilon$ = 4.54), 279 (4.29), 242 nm (4.31). MS: *m/z* = 366 (17), 364 (M^+, 19), 305 (84), 277 (13), 183 (63), 122 (100). Anal. Calc. for $C_{16}H_{17}BrN_2O_3$: C, 52.61, H, 4.69; N, 7.67. Found C, 52.73; H, 4.75; N, 7.59.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(nitro)methylene]hexahydropyrimidine (4f): 83 %, m.p. 184-185 °C (methanol). IR (KBr): ν = 3400 (NH), 1700 (OCO), 1510, 1350 (NO_2), 1620 cm^{-1}. UV (MeOH): λ_{max} = 350 ($\log\varepsilon$ = 4.51), 288 (4.09), 229 nm (4.13). MS: *m/z* = 227 (M^+, 47), 196 (27), 181 (58), 150 (25), 121 (63), 44 (100). Anal. Calc. for $C_9H_{13}N_3O_4$: C, 47.57; H, 5.77; N, 18.49. Found C, 47.93; H, 5.76; N, 18.48.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(cyano)(ethoxycarbonyl)methylene]imidazolidine (7a): 74 %, m.p. 180-181 °C (methanol-acetone, 10:1). IR (KBr): ν = 3300 (NH), 2200 (CN), 1705, 1655 (OCO), 1620, 1580 cm^{-1}. UV (MeOH): λ_{max} = 302 ($\log\varepsilon$ = 4.50), 265 nm (4.38). MS: *m/z* = 265 (M^+, 55), 206 (52), 192 (28), 162 (30), 134 (100). Anal. Calc. for $C_{12}H_{15}N_3O_4$: C, 54.33; H, 5.70; N, 15.84. Found C, 54.85; H, 5.78; N, 15.68.

1-[(E)-Methoxycarbonylvinyl]-2-[(dicyano)methylene]imidazolidine (7b): 76 %, m.p. 248.5-249.5 °C (methanol-acetone, 10:1). IR (KBr): ν = 3240 (NH), 2208, 2198 (CN), 1705 (OCO), 1615, 1600 cm^{-1}. UV (MeOH): λ_{max} = 302 ($\log\varepsilon$ = 4.32), 264 nm (4.24). MS: *m/z* = 218 (M^+, 50), 201 (11), 187 (33), 173 (58), 159 (100). Anal. Calc. for $C_{10}H_{10}N_4O_2$: C, 55.04; H, 4.62; N, 25.68. Found C, 55.28; H, 4.80; N, 25.57.

1-[(E)-Methoxycarbonylvinyl]-2-[bis(ethoxycarbonyl)methylene]imidazolidine (7c): 72 %, m.p. 118-119 °C (methanol-acetone, 10:1). IR (KBr): ν = 3320 (NH), 1700, 1680, 1620 (OCO), 1555, cm^{-1}. UV (MeOH): λ_{max} = 309 ($\log\varepsilon$ = 4.29), 275 (4.26), 230 nm (4.16). MS: *m/z* = 312 (M^+, 99), 297 (13), 281 (19), 267 (29), 253 (86), 181 (57), 135 (79), 95 (100). Anal. Calc. for $C_{14}H_{20}N_2O_6$: C, 53.84; H, 6.45; N, 8.97. Found C, 54.15; H, 6.52; N, 8.56.

E-1-[(E)-Methoxycarbonylvinyl]-2-[(cyano)(ethoxycarbonyl)methylene]hexahydropyrimidine (8a): 84 %, m.p. 166-167 °C (methanol). IR (KBr): ν = 3260 (NH), 2195 (CN), 1700, 1645 (OCO),

1620, 1590 cm^{-1}. UV (MeOH): λ_{max} = 307 (logε = 4.28), 266 nm (4.26). MS: *m/z* = 279 (M^+, 21), 220 (72), 206 (13), 174 (21), 147 (100). Anal. Calc. for $C_{13}H_{17}N_3O_4$: C, 55.90; H, 6.14, N, 15.05. Found C, 56.18; H, 6.07; N, 15.09.

1-[(E)-Methoxycarbonylvinyl]-2-[di(cyano)methylene]hexahydropyrimidine (8b): 80 %, m.p. 211-212 °C (methanol-acetone, 10:1). IR (KBr): ν = 3270 (NH), 2200, 2190 (CN), 1710 (OCO), 1620, 1595 cm^{-1}. UV (MeOH): λ_{max} = 308 (logε = 4.56), 260 (4.71), 232 nm (4.32). MS: *m/z* = 232 (M^+, 21), 201 (12), 187 (12), 173 (100). Anal. Calc. for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.13. Found C, 57.08; H, 5.20; N, 24.06.

1-[(E)-Methoxycarbonylvinyl]-2-[bis(ethoxycarbonyl)methylene]hexahydropyrimidine (8c): 75 %, semi-solid (methanol-acetone, 10:1). IR (KBr): ν = 3260 (NH), 1700, 1670, 1630 (OCO), 1610, 1575 cm^{-1}. UV (MeOH): λ_{max} = 315 (logε = 4.01), 274 (4.34), 248 nm (4.27). MS: *m/z* = 327 ($[M+1]^+$, 38), 296 (9), 282 (28), 268 (100), 248 (33), 194 (51), 149 (61). Anal. Calc. for $C_{15}H_{22}N_2O_6$: C, 55.20; H, 6.80; N, 8.59. Found C, 55.12; H, 6.82; N, 8.48.

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