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β,γ-Unsaturated α-Amino Ester Derivatives by Amination of γ-Silylated α,β-Unsaturated Esters

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Abstract: The reactions of γ-silylated α,β-unsaturated esters **3a-e** and **6** with $NsONHCO_2Et$ and CaO, produce β,γ-unsaturated *N*-(ethoxycarbonyl) α-amino esters **4a-e** and **8**, isolated in 38-66 % yield, through addition of (ethoxycarbonyl)aminic function on the double bond and silyl group elimination. The reactivity increases in presence of α-substituents. © 1997 Elsevier Science Ltd.

INTRODUCTION

β,γ-Unsaturated amino acids arouse wide interest for their antimicrobial and antimicotic properties[1]. They have been shown to be useful in plant growth[2] regulation as photosynthesis stimulators and their use as suicide inhibitors of a great variety of enzymes[3], prompted many researchers to find new and more general procedures for their synthesis[4].

One of the possible synthetic approaches to these compounds is the direct introduction of the aminic function in the right precursor molecule.

For many years our research group has been involved in the study of a particular aminating reagent: the (ethoxycarbonyl)nitrene (NCO_2Et); it can be generated from the ethyl *N*-{[(4-nitrobenzene)sulphonyl]oxy} carbamate ($NsONHCO_2Et$) **1** under basic conditions (Et_3N)[5] in homogeneous solution of CH_2Cl_2.

(Ethoxycarbonyl)nitrene showed good reactivity with electron rich alkenes[6] such as enamines, silyl ketene acetals and allylsilanes. Recently with these latter substrates the use of $NsONHCO_2Et$ permitted the formation of allylamine derivatives through the opening of the addition product and by contemporary elimination of the silyl group.

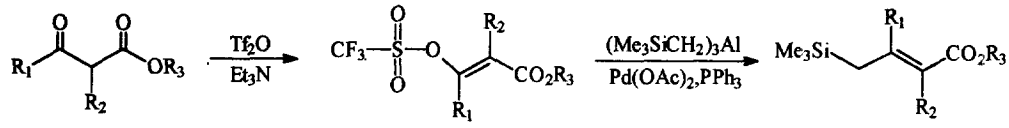
At the same time a new method of introduction of aziridinic function has been developed by us using **1** and inorganic insoluble bases such as CaO, K_2CO_3 in CH_2Cl_2. Under these reaction conditions the introduction of the aziridinic function was also feasible on unactivated olefins such as α,β-unsaturated esters[7] and nitro olefins[8].

We are now interested in providing a new route to β,γ-unsaturated amino acids: our previous experience prompted us to test the reactivity of γ-silylated α,β-unsaturated esters with **1** in the hypothesis that the introduction of the aminic function might first produce the aziridinic ring that, after elimination of the silyl group, would generate the β,γ-unsaturated amino acid derivatives.

RESULTS AND DISCUSSION

Starting from vinyl triflates **2a-e** the substrates **3a-e** were synthesised using a cross-coupling reaction with tris-[(trimethylsilyl)methyl]-aluminum catalysed by Pd (0) according to the method described for compounds **3a** and **3e**[9] (Scheme 1). All the compounds were isolated by flash-chromatography in the reported yields (Table 1).

In the case of the compounds 3b and 3d, the method described by Saulnier and co-workers was partially modified by carrying out the coupling reaction at higher temperatures (50°C) in order to by-pass the problem of steric hindrance.



Scheme 1

The vinyl triflates **2a-e** were derived from the corresponding β-ketoesters. The method, described by Saulnier[9] for **2a** and **2e** was extended to all the substrates giving the vinyl triflates with the reported yields (Table 1).

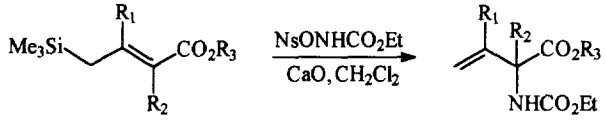
Entry	R_1	R_2	R_3	2 (% yield)	3 (% yield)
a	Me (E)	H	Et	42	46
b	Me (Z)	H	Et	20	29
c	Ph	H	Et	44	88
d	*tert*-butyl	H	Et	15	71
e	$-(CH_2)_3-$		Me	66	70

Table 1. Yields of vinyl triflates **2** and γ-silylated α,β-unsaturated esters **3**.

The amination reactions on substrates **3** using $NsONHCO_2Et$ were carried out using either homogeneous or heterogeneous basic conditions. With all the substrates the classical conditions of generation of the (ethoxycarbonyl)nitrene *i.e.* α-elimination of **1** with Et_3N gave poor yields or no products at all.

Conversely the procedure used in the aziridination of α,β-unsaturated esters, *i.e.* inorganic base (CaO), low solvent amount, 1:7 ratio between substrate and reagent, gave the expected *N*-(ethoxycarbonyl) β,γ-unsaturated amino esters **4a-d** (Scheme 2). All the products were isolated by flash-chromatography on silica gel with the reported yields (Table 2) and the unreacted starting material was recovered.

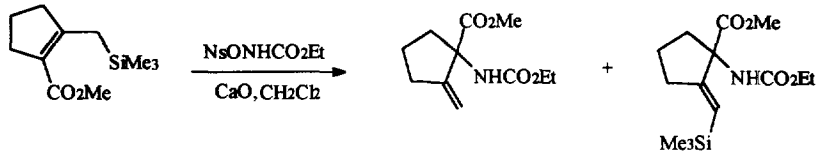
The two isomer **3a** and **3b** give the same *N*-(ethoxycarbonyl) β,γ-unsaturated amino ester **4a** as we expected but **Z** isomer has been shown to be less reactive.



3 **4**

Scheme 2

The reaction of the cyclic γ-silylated α,β-unsaturated ester **3e** with $NsONHCO_2Et$ showed some differences: it needed only five equivalents of reagent for the disappearance of the starting material and gave the β,γ-unsaturated amino ester **4e** isolated in 41 % yield and the γ-silylated β,γ-unsaturated amino ester **5** in 25 % yield (Scheme 3).



3e **4e** **5**

Scheme 3

In order to maximise the yield in β,γ-unsaturated amino ester we completely converted the γ-silylated β,γ-unsaturated amino ester to ester **4e** through a protodesilylation reaction using HI (65 %) in benzene[10].

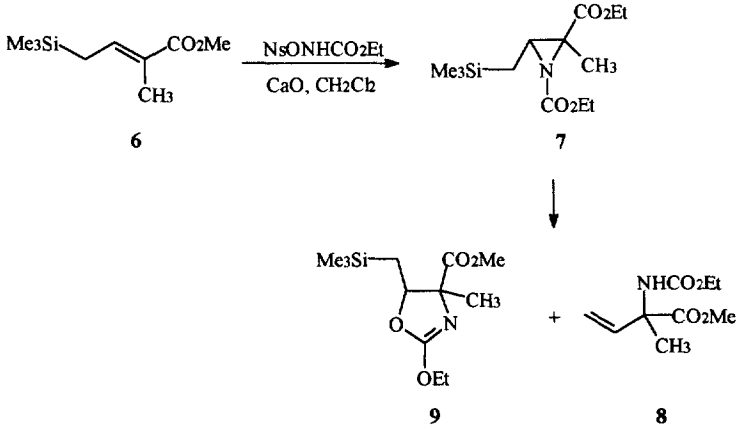
3	3 : $NsONHCO_2Et$	4 (% yield)
a	1:7	65[a]
b	1:7	38[a]
c	1:7	52[a]
d	1:7	53[a]
e	1:5	66[b]

a) yields are based on recovered γ-silylated α,β-unsaturated ester.
b) total yield after conversion of **5**.

Table 2. Addition reaction of γ-silylated α,β-unsaturated ester **3** with $NsONHCO_2Et$.

We also tried the amination reaction on an α-alkylated linear substrate in order to obtain an α-alkylated β,γ-unsaturated amino ester. An attempt to prepare the starting triflate according to the method described for other substrates, completely failed; so we synthesised the methyl 2-methyl-4-(trimethylsilyl)-2-butenoate **6** from tiglic acid[11].

Compound **6**, in the usual reaction conditions, gave a single product that by GC-MS and NMR analysis of the crude material was recognised as the aziridinic structure 7. However, after flash-chromatography purification, three products were obtained: the aziridine **7** (21 %), the β,γ-unsaturated amino ester **8** (27 %) and the oxazoline derivative **9** (20 %) derived from the rearrangement of the aziridine **7** (Scheme 5).



6 **7** **9** **8**

Scheme 5

It is worth stressing that the yields of the three products together reveal the higher reactivity of the α-substituted substrate.

In conclusion in this paper we described a new and general synthesis of linear and cyclic β,γ–unsaturated α-amino acid derivatives. The reactivity of the starting γ-silylated α,β-unsaturated esters appears not to be greatly influenced by the steric hindrance of alkyl groups in β position, while it increases in the presence of α-substituents (compounds **4e** and **6**), even with the production of different addition compounds.

EXPERIMENTAL SECTION

GC analyses were performed on a HP 5890 Series II gas chromatograph with a capillary column (methyl silicone, 12.5 m x 0.2 mm). GC-MS were done on a HP G1800 GDC System with a capillary column (phenyl methyl silicone, 30 m x 0.25 mm) ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Gemini 200 spectrometer, with $CHCl_3$ as internal standard. IR spectra in CCl_4 were done by a Perkin-Elmer 1600 Series FTIR spectrometer. β-Ketoesters are commercially available (Fluka, Aldrich).

Synthesis of triflates ***2a-e***. A solution of β-ketoester (27 mmol), dry Et_3N (32 mmol) in 10 ml of dry CH_2Cl_2, under Argon, was cooled to -78 °C, then trifluoromethanesulfonic anhydride (30 mmol) was added dropwise over 2-3 minutes. The resulting mixture was allowed to warm to -40 °C and then to 0 °C. Finally the solution was magnetically stirred at room temperature for 24 h; the mixture was then washed with a 8% solution of $NaHCO_3$, dried over K_2CO_3 filtered and concentrated *in vacuo*. Purification by chromatography on silica gel (hexane/ ethyl acetate, 9:1) gave the pure products **2** in the reported yields (Table 1).

2a: IR 1731, 1673, 1138 cm^{-1}; ^{1}H NMR δ 1.27 (*t*, 3 H, CH_2CH_3), 2.48 (*d*, 3 H, *J*= 1 Hz, C=CC*H*$_3$), 4.19 (*q*, 2 H, OCH_2), 5.92 (*q*, 1 H, *J*= 1 Hz, C=C*H*); ^{13}C NMR δ 13.86 (CH_2CH_3), 18.22 (C=CCH_3), 61.11 (OCH_2), 113.42 (C=*C*H), 118.54 (*q*, *J*= 319 Hz, CF_3), 162.18 (CH_3C=C), 164.42 (CO); MS *m/z*: 262 (M^+, 11), 234 (15), 217 (51), 216 (29), 153 (14), 87 (41), 85 (14), 84 (33), 69 (100), 59 (25), 45 (12), 43 (45).

2b: IR 1737, 1690, 1138; ^{1}H NMR δ 1.27 (*t*, 3 H, CH_2CH_3), 2.13 (*s*, 3 H, C=CC*H*$_3$), 4.21 (*q*, 2 H, OCH_2), 5.73 (*s*, 1 H, C=C*H*); ^{13}C NMR δ 13.78 (CH_2CH_3), 20.68 (C=CCH_3), 61.15 (OCH_2), 112.90 (C =*C*H), 118.42 (*q*, *J*= 319 Hz, CF_3), 155.23 (C=*C*CH_3), 162.53 (CO); MS *m/z*: 262 (M^+, 1), 233 (15), 216 (55), 215 (29), 153 (12), 87 (45), 85 (18), 84 (30), 69 (100), 59 (28), 45 (11), 43 (46).

2c: IR 1738, 1652, 1138; ^{1}H NMR δ 1.32 (*t*, 3 H, CH_2CH_3), 4.28 (*q*, 2 H, OCH_2), 6.23 (*s*, 1 H, C=C*H*), 7.44 (*m*, 3 H, aromatic CH), 7.55 (*m*, 2 H, aromatic CH); ^{13}C NMR δ 13.78 (CH_2CH_3), 61.27 (OCH_2), 111.77 (C=*C*H), 118.32 (*q*, *J*= 319 Hz, CF_3), 126.57 (aromatic CH), 127.91 (aromatic C), 129.15 (aromatic CH), 131.83 (aromatic CH), 155.24 (C=*C*Ph), 163.24 (CO); MS *m/z*: 324 (M^+, 34), 279 (53), 252 (13), 231 (11), 149 (54), 147 (22), 107 (11), 105 (100), 102 (14), 91 (19), 90 (10), 89 (12), 79 (22), 77 (69), 69 (64), 51 (24).

2d: IR 1736, 1666, 1131; ^{1}H NMR δ 1.20 (*s*, 9 H, $C(CH_3)_3$ *tert*-butyl), 1.27 (*t*, 3 H,CH_2CH_3), 4.21 (*q*, 2 H, OCH_2), 5.80 (*s*, 1H, C=CH); ^{13}C NMR δ 13.75 (CH_2CH_3), 27.69 ($C(CH_3)_3$), 37.39 ($C(CH_3)_3$), 61.18 (OCH_2), 108.93 (C=*C*H), 118.56 (*q*, *J*= 320 Hz, CF_3), 163.59 (CH=*C*), 164.93 (CO); MS *m/z*: 304 (M^+, 1), 259 (22), 155 (33), 129 (30), 127 (29), 126 (12), 115 (12), 111 (18), 109 (18), 101 (17), 87 (14), 83 (22), 81 (31), 69 (100), 57 (48), 55 (11), 43 (31), 41 (45).

2e: IR 1726, 1666, 1138; ^{1}H NMR δ 1.97 (*m*, 2 H, CH_2 ring); 2.66-2.71 (*m*, 4 H, CH_2 ring); 3.74 (*s*, 3 H, OCH_3); ^{13}C NMR δ 18.57 (CH_2 ring), 28.95 (CH_2 ring), 32.54 (CH_2 ring), 51.65 (OCH_3); 118.43 (*q*, *J*= 320 Hz, CF_3), 123.06 (C=*C*CO), 154.18 (TfO*C*=C), 162.86(CO); MS *m/z*: 274 (M^+, 53), 243 (75), 242 (16), 179 (56), 151 (14), 150 (11), 141 (21), 125 (14), 111 (11), 108 (100), 85 (42), 81 (27), 71 (22), 69 (65), 65 (19), 59 (50), 55 (34), 54 (22), 53 (32).

Synthesis of γ-silylated α,β–unsaturated esters ***3a-e***. To a magnetically stirred suspension of $AlCl_3$ (9.1 mmol) in dry 1,2-dichloroethane (55 ml) under argon was added over 10 minutes (trimethylsilyl)methyllithium (1.0 M in pentane, 27.9 mmol). The resulting mixture was stirred at room temperature for 30 min and then treated rapidly by cannula transfer with a solution of the vinyl triflate and the Pd(0) catalyst which was prepared as follows: a solution of $Pd(OAc)_2$ (0.7 mmol) and PPh_3 (2.9 mmol) in dry benzene (30 ml) under argon was treated with *n*-buthyllithium (2.5 M in hexane, 1.46 mmol) followed after 5 min by the addition of the vinyl

triflate (7.6 mmol) in dry benzene (10 ml). This solution was then immediately transferred via cannula as described above and the reaction mixture was stirred for 24 h at room temperature. The workup consisted of dilution with CH_2Cl_2, washing with 0.2 M HCl, H_2O and brine. The crude product was purified by flash-chromatography on silica gel (hexane/ CH_2Cl_2, 8:2).

3a: IR 1707, 1626; ^{1}H NMR δ 0.01 (*s*, 9 H, $SiMe_3$), 1.22 (*t*, 3 H, CH_2CH_3), 1.69 (*s*, 2 H, $SiCH_2$), 2.12 (*m*, 3 H, $C=CCH_3$), 4.07 (*q*, 2 H, OCH_2), 5.44 (*m*, 1 H, $CH=C$); ^{13}C NMR δ 1.63 ($SiMe_3$), 14.14 (CH_2CH_3), 21.28 ($C=CCH_3$), 33.52 ($SiCH_2$), 59.02 (OCH_2), 113.02 (*C*H=C), 160.67 (C=*C*CH_3), 167.11 (CO); MS *m/z*: 200 (M^+, 2), 155 (14), 103 (10), 82 (100), 75 (30), 73 (86), 45(16).

3b: IR 1704, 1623; ^{1}H NMR δ -0.01 (*s*, 9 H, $SiMe_3$), 1.22 (*t*, 3 H, CH_2CH_3), 1.81 (*s*, 3 H, $C=CCH_3$), 2.37 (*s*, 2 H, $SiCH_2$), 4.07 (*q*, 2 H, OCH_2), 5.50 (*s*, 1 H, *CH*=C); ^{13}C NMR δ -1.58 ($SiMe_3$), 14.19 (CH_2CH_3), 27.25 ($SiCH_2$), 27.59 (C=*C*CH_3), 58.97 (OCH_2), 112.31 (*C*H=C), 160.58 (C=*C*CH_3), 167.36 (CO); MS *m/z*: 200 (M^+, 3), 157 (20), 156 (10), 155 (15), 82 (100), 75 (49), 73 (66).

3c: IR 1707, 1607; ^{1}H NMR δ –0.12 (*s*, 9 H, $SiMe_3$), 1.29 (*t*, 3 H, CH_2CH_3), 2.88 (*s*, 2 H, $SiCH_2$), 4.18 (*q*, 2 H, OCH_2), 5.89 (*s*, 1 H, C=C*H*), 7.34 (*m*, 3 H, aromatic CH), 7.41 (*m*, 2 H, aromatic CH); ^{13}C NMR δ -1.16 ($SiMe_3$), 14.42 (CH_2CH_3), 25.06 ($SiCH_2$), 59.42 (OCH_2), 113.48 (C=*C*H), 126.76 (aromatic CH), 128.53 (aromatic CH), 128.80 (aromatic CH), 143.19 (aromatic C), 161.12 (Ph*C*=C), 167.25 (CO); MS *m/z*:262 (M^+, 1), 145 (11), 144 (34), 116 (30), 115 (54), 105 (12), 75 (48), 73 (100), 45 (37), 43 (15).

3d: IR 1701, 1607; ^{1}H NMR δ 0.03 (*s*, 9 H, $SiMe_3$), 1.07 (*s*, 9 H, $C(CH_3)_3$), 1.22 (*t*, 3 H, CH_2CH_3), 2.36 (*s*, 2 H, $SiCH_2$), 4.08 (*q*, 2 H, OCH_2), 5.63 (*s*, 1 H, C=C*H*); ^{13}C NMR δ 0.04 ($SiMe_3$), 14.25 (CH_2CH_3), 21.4 ($SiCH_2$), 29.15 ($C(CH_3)_3$), 37.97 (*C*$(CH_3)_3$), 59.02 (OCH_2), 109.34 (C=*C*H), 168.11 (CH=*C*), 172.87 (CO); MS *m/z*: 242 (M^+, 3), 227 (13), 199 (11), 185 (13), 183 (11), 141 (12), 124 (25), 109 (40), 82 (17), 80 (10), 73 (100), 67 (40), 57 (11), 45(21), 41 (13).

3e: IR 1701, 1619; ^{1}H NMR δ 0.02 (*s*, 9 H, $SiMe_3$), 1.72 (*m*, 2 H, CH_2 ring), 2.21 (*s*, 2 H, $SiCH_2$), 2.38 (*t*, 2 H, CH_2 ring), 2.54 (*t*, 2 H, CH_2 ring), 3.63 (*s*, 3 H, OCH_3); ^{13}C NMR δ -1.15 ($SiMe_3$), 21.59 (CH_2), 23.18 (CH_2), 32.99 (CH_2), 40.91 (CH_2), 50.43 (OCH_3), 123.05 (C=*C*CO), 160.23 (COC=*C*), 167.22 (CO); MS *m/z*: 212 (M^+, 6), 197 (28), 108 (100), 89 (19), 80 (11), 79 (19), 73 (51), 59 (14).

Reaction of 3a-e and 6 with $NsONHCO_2Et$. To a stirred solution of the substrate (2.8 mmol) in 2 ml of CH_2Cl_2 at room temperature, CaO and $NsONHCO_2Et$ were added portionwise, in the molar ratios substrate: $NsONHCO_2Et$: CaO = 1:7:7 for **3a-d** and **6**, 1:5:5 for **3e**. After 20 h of stirring, 10 ml of CH_2Cl_2 and 100 ml of hexane were added. After filtration, the liquid phase was concentrated *in vacuo*. The products were purified by flash chromatography on silica gel (hexane/ ethyl acetate, 8:2) and isolated in the reported yields.

4a: IR 3450, 1730, 1655; ^{1}H NMR δ 1.07 (*t*, 3 H, CH_2CH_3), 1.21 (*t*, 3 H, CH_2CH_3), 1.74 (*s*, 3 H, $C=CCH_3$), 4.03 (*q*, 2 H, OCH_2), 4.18 (*q*, 2 H, OCH_2), 4.75 (*d*, 1 H, NHC*H*), 4.98 (*s*, 1 H, $C=CH_a$), 5.03 (*s*, 1 H, $C=CH_b$), 5.44 (*br*, 1 H, NH); ^{13}C NMR δ 13.84 (CH_2CH_3), 14.31 (CH_2CH_3), 19.1 ($C=CCH_3$), 61.12 (OCH_2), 61.66 (OCH_2), 64.91 (*C*HNH), 115.03 ($C=CH_2$), 124.04 (CH_3C=C), 155.60 (NHCO), 171.06 (*C*CO); MS *m/z*: 215 (M^+, 1), 142 (100), 70 (56).

4c: IR 3424, 1742, 1730; ^{1}H NMR δ 1.14 (*t*, 3 H, CH_2CH_3), 1.20 (*t*, 3 H, CH_2CH_3), 4.14 (*q*, 2 H, OCH_2), 4.27 (*q*, 2 H, OCH_2), 5.26 (*d*, 1 H, C*H*NH), 5.35 (*s*, 1 H, $C=CH_a$), 5.45 (*s*, 1 H, $C=CH_b$), 5.49 (*br*, 1 H, NH), 7.25-7.48 (*m*, 5H, aromatic CH); ^{13}C NMR δ 13.87 (CH_2CH_3), 14.27 (CH_2CH_3), 61.21 (OCH_2), 61.66 (OCH_2), 63.49 (CHNH), 116.48 ($C=CH_2$), 124.02 (Ph*C*=C), 126.83 (aromatic CH), 128.24 (aromatic CH), 128.55 (aromatic CH), 131.11 (aromatic C), 155.94 (NHCO), 171.13 (*C*CO); MS *m/z*: 277 (M^+,9), 205 (14), 204 (100), 132 (67), 131 (17), 130 (28), 117 (30), 115 (11), 103 (18), 77 (16).

4d: IR 3431, 1729, 1690; ^{1}H NMR δ 1.11 (*s*, 9 H, $C(CH_3)_3$), 1.19 (*t*, 3 H, CH_2CH_3), 1.20 (*t*, 3 H, CH_2CH_3), 4.13 (*q*, 2 H, OCH_2), 4.14 (*q*, 2 H, OCH_2), 4.81 (*d*, 1 H, NHC*H*), 5.00 (*br*, 1H, NH), 5.01 (*s*, 1 H, $C=CH_a$), 5.07 (*s*, 1 H, $C=CH_b$); ^{13}C NMR δ 13.95 (CH_2CH_3), 14.52 (CH_2CH_3), 26.62 ($C(CH_3)_3$), 36.51 (*C*$(CH_3)_3$), 53.47 (*C*HNH), 61.24 (2 OCH_2), 91.88 (H_2C=*C*), 111.04 ($C=CH_aH_b$), 155.18 (NHCO), 172.17 (CO); MS *m/z*: 257 (M^+, 1), 184 (100), 112 (26), 57 (21), 56 (38), 41 (15).

4e: IR 3424, 1748, 1695; ^{1}H NMR δ 1.22 (*t*, 3 H, CH_2CH_3), 1.85 (*m*, 2 H, CH_2 ring), 2.25-2.52 (*m*, 4 H, CH_2 ring), 3.72 (*s*, 3 H, OCH_3), 4.09 (*q*, 2 H, OCH_2), 5.11 (*m*, 1 H, $C=CH_a$), 5.15 (*s*,1 H, $C=CH_b$), 5.37 (*br*,

1H, NH); ^{13}C NMR δ 14.29 (CH_2CH_3), 23.66 (CH_2 ring), 32.66 (CH_2 ring), 36.89 (CH_2 ring), 52.71 (OCH_3), 60.79 (OCH_2), 66.69 (CNH), 109.34 (C=CH_2), 122.23 (*C*=CH_2), 153.76 (NHCO), 173.43 (*C*CO); MS *m/z*: 227 (M^+,1), 168 (100), 140 (12), 138 (14), 122 (14), 96 (57), 94 (13), 79 (23), 67 (14), 55 (10), 41 (10).

5: IR 3422, 1741, 1694; ^{1}H NMR δ -0.02 (*s*, 9 H, $SiMe_3$), 1.19 (*t*, 3 H, CH_2CH_3), 1.27 (*m*, 2 H, CH_2 ring), 2.2-2.6 (*m*, 4 H, CH_2 ring), 3.69 (*s*, 3 H, OCH_3), 4.05 (*q*, 2 H, OCH_2), 5.61 (*br*, 2 H, C=CH and NH); ^{13}C NMR δ -1.47 ($SiMe_3$), 14.29 (CH_2CH_3 and CH_2 ring), 30.82 (CH_2 ring), 34.69 (CH_2 ring), 52.61 (OCH_3), 60.53 (OCH_2), 73.54 (CNH), 130.04 (C=*C*H), 138.19 (*C*=CH), 170.23 (NHCO), 174.14 (*C*CO); MS *m/z*: 299 (M^+, 7), 240 (26), 195 (16), 152 (23), 119 (29), 117 (13) ; 107 (17), 106 (38), 105 (11), 94 (14), 91 (13), 89 (14), 79 (21), 78 (10), 77 (13), 75 (24), 73 (100), 59 (19), 45 (21).

7: IR 1741; ^{1}H NMR δ 0.09 (*s*, 9 H,$SiMe_3$), 0.66 (*dd*, 1 H, J_1 = 15 Hz, J_2 = 9 Hz, CH_aSi), 0.79 (*dd*, 1 H, J_1 = 15 Hz, J_2 =5 Hz, CH_bSi), 1.21 (*t*, 3 H, CH_2CH_3), 1.41 (*s*, 3 H, $NCCH_3$), 2.91 (*dd*, 1 H, J_1 = 9 Hz, J_2 = 5 Hz, NCH), 3.70 (*s*, 3 H, OCH_3), 4.11 (*q*, 2 H, OCH_2); ^{13}C NMR δ -1.52 ($SiMe_3$), 14.31 (CCH_3), 14.33 (CH_2CH_3), 15.74 (CH_2Si), 45.73 (CHN), 52.60 (OCH_3), 62.11 (OCH_2), 72.45 (CCH_3), 160.69 (NCO), 170.94 (CO); MS *m/z*: 273 (M^+, 3), 214 (34), 113 (17), 96 (78), 75 (15), 73 (99), 69 (11), 68 (100), 59 (22), 45 (32), 42 (28).

8: IR 3424, 1734; ^{1}H NMR δ 1.23 (*t*, 3 H, CH_2CH_3), 1.65 (*s*, 3 H, $NCCH_3$), 3.76 (*s*, 3 H, OCH_3), 4.09 (*q*, 2 H, OCH_2), 5.24 (*d*, 1 H, *J* = 11 Hz, C=CH_a), 5.28 (*d*, 1 H, *J* = 18 Hz, C=CH_b), 5.46 (*br*, 1 H, NH), 6.05 (*dd*, 1 H, J_1 = 18 Hz, J_2 = 11 Hz, C=CH); ^{13}C NMR δ 14.49 (CH_2CH_3), 23.13 ($NCCH_3$), 45.07 ($NCCH_3$), 52.90 (OCH_3), 60.86 (OCH_2), 115.40 (C=CH_2), 137.77 (C=*C*H), 155.08 (NHCO), 173.11 (CO); MS *m/z*: 201 (M^+, 0.3), 142 (100), 70 (84), 55 (10), 54 (26), 53 (13), 44 (25), 43 (16), 42 (65), 41 (12).

9: IR 1735, 1652; ^{1}H NMR δ 0.04 (*s*, 9 H, $SiMe_3$), 0.74 (*dd*, 1 H, J_1 = 12 Hz, J_2 = 2 Hz, CH_aSi), 0.86 (*m*, 1 H, CH_bSi), 1.28 (*t*, 3 H, CH_2CH_3), 1.30 (*s*, 3 H, $NCCH_3$), 3.71 (*s*, 3 H, OCH_3), 4.22 (*q*, 2 H, OCH_2), 4.89 (*dd*, 1 H, J_1 = 12 Hz, J_2 = 3 Hz, OCH); ^{13}C NMR δ -1.41 ($SiMe_3$), 14.01 (CH_2CH_3), 17.37 (CH_2Si), 20.20 ($NCCH_3$), 52.30 (OCH_3), 66.56 (OCH_2), 73.40 ($NCCH_3$), 84.26 (OCH), 162.56 (C=N), 175.83 (CO); MS *m/z*: 273 (M^+, 0.5), 214 (43), 157 (11), 128 (14), 96 (100), 73 (50), 56 (16).

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