

Electronic Supplementary Information

A Novel, Tandem Construction of C-N and C-C Bonds :

Facile and One-Pot Transformation of the Baylis-Hillman Adducts into 2-Benzazepines

Deevi Basavaiah* and Tummanapalli Satyanarayana

School of Chemistry, University of Hyderabad, Hyderabad-500 046, India

General Remarks: Melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO-FT-IR model 5300 Spectrometer or Perkin-Elmer model 1310 spectrometer using samples as KBr plates (solids) and liquids samples as neat. ¹H NMR (200 MHz) and ¹³C NMR (50 MHz) spectra were recorded in deuteriochloroform (CDCl₃) on a Bruker-AC-200 spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard. Elemental analyses were recorded on a Perkin-Elmer 240C-CHN analyzer. Mass spectra were recorded on Auto Spec or VG70-70H mass spectrometer. The X-ray diffraction measurements were carried out at 293 K on an automated Enraf-Nonious MACH3 diffractometer using graphite monochromated, Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation with CAD4 software.

General procedure for the synthesis of 2-benzazepines (5-15):

To a stirred solution of Baylis-Hillman alcohol (**1e-m**) (2 mmol) in alkanenitrile (aceto- or propionitrile) (5 mL) was added methanesulfonic acid (3 mL) at 60 °C and immediately temperature was raised to 150 °C. After stirring at 150 °C for 6 h, the reaction mixture was brought to room temperature and diluted with water. Aqueous K₂CO₃ solution was added slowly till the acid was neutralized and extracted with ether (3 x 15 mL). The combined organic layer was dried over anhydrous Na₂SO₄. Solvent was evaporated and the residue, thus obtained, was purified by column chromatography (silica gel, 25% EtOAc in hexanes) to furnish the pure compounds (**5-15**).

General procedure for the synthesis of allyl amides (2a-f*, 4a-c):**

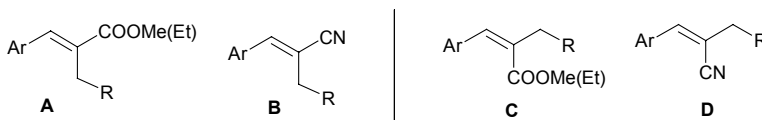
To a stirred solution of Baylis-Hillman alcohol (**1a-d**, **3a-c**) (1 mmol) in alka(e)nenitrile (aceto- or propio- or acrylonitrile) (5 mL) was added methanesulfonic acid (3 mL) at 60 °C and immediately temperature was raised to 110 °C. After stirring for 5 h at 110 °C, reaction mixture was brought to room temperature and diluted with water. Aqueous K₂CO₃ solution was added slowly till the acid was neutralized and extracted with ether (3 x 15 mL). The combined organic layer was dried over anhydrous Na₂SO₄. Solvent was evaporated and the residue, thus obtained, was purified by column chromatography (silica gel, 30% EtOAc in hexanes) to furnish the pure compounds (**2a-f***, **4a-c****).

(E)*-Selectivity in the case of **2a-f

In the ^1H NMR spectra of trisubstituted alkenes (with ester group at α - position) the β -vinylic proton *cis* to the ester group appears downfield while the β -vinylic proton *trans* to ester group appears upfield.¹⁻⁴ ^1H NMR spectra of the crude samples of **2a-f** indicate the presence of 5-12% minor (*Z*)-isomer. The *E/Z* selectivity was determined by the integration ratio of isomeric β -vinylic protons [the β -vinylic proton *cis* to ester group (*E*-isomer) appears at δ 7.76-7.82 while the same proton *trans* to ester group (*Z*-isomer) appears at δ 6.94-7.03].

***(Z)*-Selectivity in the case of **4a-c**

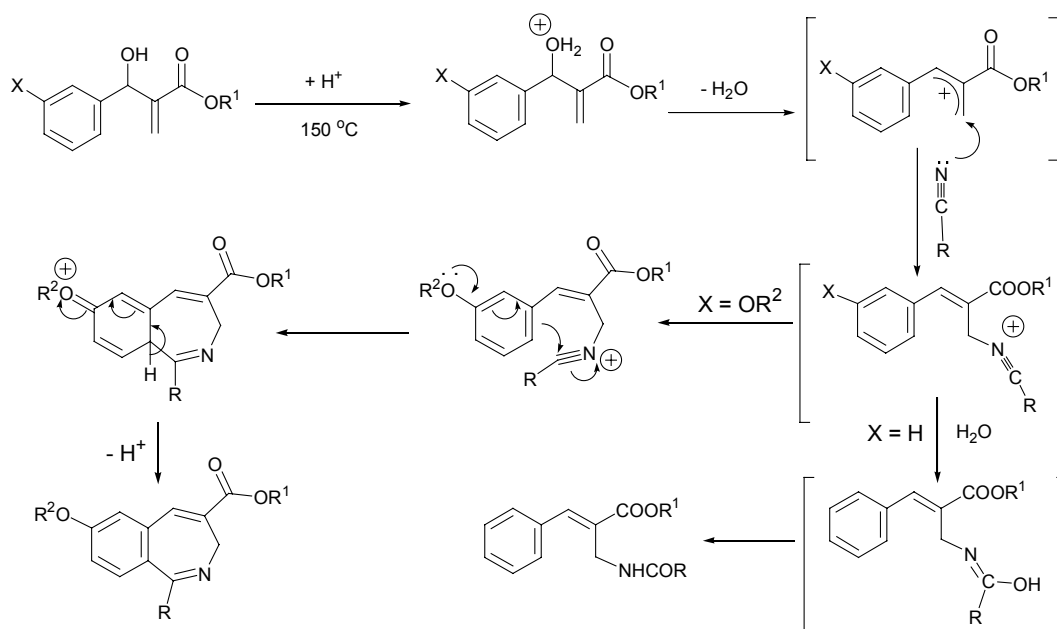
^1H NMR spectra of the crude samples of **4a-c** show at least 95% (*Z*)-selectivity. The (*Z*)-stereochemistry of compounds **4a-c** was assigned on the basis of ^{13}C NMR chemical shift values of allylic methylene carbons (δ 43.42, 43.38 and 43.28) in comparison with that of allylic methylene carbons of **2a-f** (having *E*-stereochemistry) (δ 36.61-36.79) [In the ^{13}C NMR spectra of trisubstituted alkenes, allylic carbon *cis* to aryl group appears upfield while same carbon *trans* to aryl group appears downfield.⁵⁻⁷ We and others⁶⁻¹² observed that the allylic methylene carbons of **A** and **B** derived from (m)ethyl 3-hydroxy(or acetoxy)-3-aryl-2-methylenepropanoates and 3-hydroxy(or acetoxy)-3-aryl-2-methylenepropanenitriles have similar ^{13}C NMR chemical shifts while allylic methylene carbons of **C** and **D** derived from (m)ethyl 3-hydroxy(or acetoxy)-3-aryl-2-methylenepropanoates and 3-hydroxy(or acetoxy)-3-aryl-2-methylenepropanenitriles have similar ^{13}C NMR chemical shifts].



References:

- 1) K. Tanaka, N. Yamagishi, R. Tanikaga, A. Kaji, *Bull. Chem. Soc. Jpn.* 1979, **52**, 3619.
- 2) D. Basavaiah, S. Pandiaraju, M. Krishnamacharyulu, *Synlett* 1996, 747.
- 3) G. L. Larson, de C. F. Kaifer, R. Seda, L. E. Torres, J. R. Ramirez, *J. Org. Chem.* 1984, **49**, 3385.
- 4) P. G. Baraldi, M. Guarneri, G. P. Pollini, D. Simoni, A. Barco, S. Benetti, *J. Chem. Soc., Perkin Trans I* 1984, 2501.
- 5) T. Funabiki, H. Hosomi, S. Yoshida, K. Tarama, *J. Am. Chem. Soc.* 1982, **104**, 1560.
- 6) D. Basavaiah, A. K. D. Bhavani, S. Pandiaraju, P. K. S. Sarma, *Synlett* 1995, 243.
- 7) A. Gruiec, A. Foucaud, *New J. Chem.* 1991, **15**, 943.
- 8) D. Basavaiah, M. Krishnamacharyulu, R. Suguna Hyma, S. Pandiaraju, *Tetrahedron Lett.* 1997, **38**, 2141.
- 9) H. J. Lee, M. R. Seong, J. N. Kim, *Tetrahedron Lett.* 1998, **39**, 6223.
- 10) D. Basavaiah, N. Kumaragurubaran, K. Padmaja, *Synlett* 1999, 1630.
- 11) H. S. Kim, T. Y. Kim, K. Y. Lee, Y. M. Chung, H. J. Lee, J. N. Kim, *Tetrahedron Lett.* 2000, **41**, 2613.
- 12) D. Basavaiah, K. Padmaja, T. Satyanarayana, *Synthesis* 2000, 1662.

Plausible mechanism for the formation of 2-benzazepines and (*E*)-allyl amides:



3-Aza-2-methyl-5-ethoxycarbonyl-9-methoxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (5):

m.p : 86-88 °C

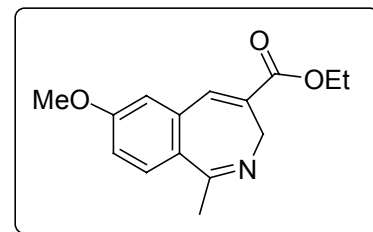
IR (KBr) : 1709, 1630, 1602 cm⁻¹

¹H NMR (CDCl₃) : δ 1.37 (t, 3H, *J* = 7.4 Hz); 2.36 (s, 3H); 3.88 (s, 3H); 3.92 (s, 2H); 4.31 (q, 2H, *J* = 7.4 Hz); 6.91-7.06 (m, 2H); 7.64 (d, 1H, *J* = 8.8 Hz); 7.68 (s, 1H).

¹³C NMR (CDCl₃) : δ 14.23, 26.26, 47.22, 55.39, 61.11, 113.68, 115.21, 130.36, 131.44, 133.69, 137.00, 138.35, 159.59, 165.50, 167.09.

Analysis calcd. for C₁₅H₁₇NO₃ : C, 69.48; H, 6.61; N, 5.40.

Found : C, 69.35; H, 6.63; N, 5.45.

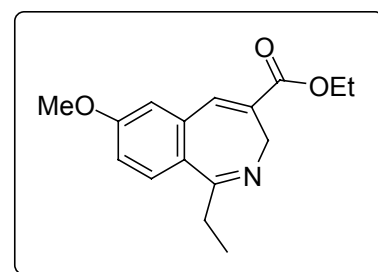


3-Aza-2-ethyl-5-ethoxycarbonyl-9-methoxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (6):

m.p : 89-90 °C

IR (KBr) : 1705, 1618, 1602 cm⁻¹

¹H NMR (CDCl₃) : δ 0.97 (t, 3H, *J* = 7.2 Hz); 1.37 (t, 3H, *J* = 7.0 Hz); 2.69 (q, 2H, *J* = 7.2 Hz); 3.87 (s, 3H); 3.92



(s, 2H); 4.31 (q, 2H, $J = 7.0$ Hz); 6.90-7.06 (m, 2H); 7.63 (d, 1H, $J = 8.6$ Hz); 7.68 (s, 1H).

^{13}C NMR (CDCl_3) : δ 11.69, 14.08, 32.13, 46.89, 55.19, 60.92, 113.36, 115.04, 129.82, 130.69, 133.99, 137.33, 138.24, 159.28, 165.36, 171.09.

MS (m/z) : 273 (M^+), 272 ($\text{M}-1$) $^+$

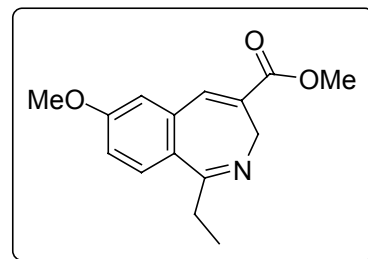
Analysis calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}_3$: C, 70.31; H, 7.01; N, 5.12.

Found : C, 70.39; H, 7.05; N, 5.15.

3-Aza-2-ethyl-5-methoxycarbonyl-9-methoxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (7):

IR (neat) : 1712, 1625, 1602 cm^{-1}

^1H NMR (CDCl_3) : δ 0.93 (t, 3H, $J = 7.5$ Hz); 2.64 (q, 2H, $J = 7.5$ Hz); 3.79 (s, 3H); 3.82 (s, 3H); 3.87 (s, 2H); 6.88-7.02 (m, 2H); 7.58 (d, 1H, $J = 8.6$ Hz); 7.63 (s, 1H).



^{13}C NMR (CDCl_3) : δ 11.75, 32.22, 47.09, 52.00, 55.33, 113.62, 115.22, 129.94, 130.97, 133.90, 137.45, 138.54, 159.51, 165.97, 171.26.

MS (m/z) : 259 (M^+), 258 ($\text{M}-1$) $^+$

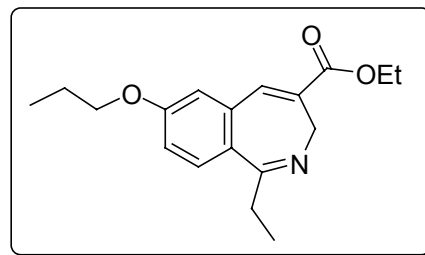
Analysis calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}_3$: C, 69.48; H, 6.61; N, 5.40

Found : C, 69.24; H, 6.56; N, 5.34

3-Aza-2-ethyl-5-ethoxycarbonyl-9-propoxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (8):

IR (neat) : 1711, 1622, 1602 cm^{-1}

^1H NMR (CDCl_3) : δ 0.95 (t, 3H, $J = 7.8$ Hz); 1.04 (t, 3H, $J = 7.8$ Hz); 1.35 (t, 3H, $J = 6.8$ Hz); 1.73-1.94 (m, 2H); 2.68 (q, 2H, $J = 7.8$ Hz); 3.90 (s, 2H); 3.97 (t, 2H, $J = 6.8$ Hz); 4.29 (q, 2H, $J = 6.8$ Hz); 6.88-7.06 (m, 2H); 7.60 (d, 1H, $J = 8.8$ Hz); 7.66 (s, 1H).



^{13}C NMR (CDCl_3) : δ 10.41, 11.86, 14.22, 22.44, 32.26, 46.99, 61.08, 69.69, 114.11, 115.66, 129.95, 130.58, 134.02, 137.49, 138.49, 159.06, 165.56, 171.45.

MS (m/z) : 301 (M^+), 300 ($\text{M}-1$) $^+$

Analysis calcd. for $\text{C}_{18}\text{H}_{23}\text{NO}_3$: C, 71.73; H, 7.69; N, 4.65.

Found : C, 71.50; H, 7.61; N, 4.70.

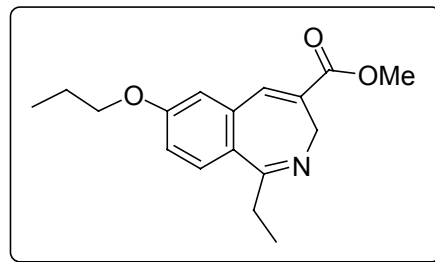
3-Aza-2-ethyl-5-methoxycarbonyl-9-propoxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (9):

IR (neat) : 1714, 1625, 1602 cm^{-1}
 ^1H NMR (CDCl_3) : δ 0.94 (t, 3H, $J = 7.2$ Hz); 1.02 (t, 3H, $J = 7.2$ Hz); 1.68-1.91 (m, 2H); 2.66 (q, 2H, $J = 7.2$ Hz); 3.81 (s, 3H), 3.89 (s, 2H); 3.96 (t, 2H, $J = 6.6$ Hz); 6.87-7.01 (m, 2H), 7.59 (d, 1H, $J = 8.6$ Hz); 7.64 (s, 1H).

^{13}C NMR (CDCl_3) : δ 10.39, 11.84, 22.45, 32.22, 46.98, 52.09, 69.73, 114.19, 115.72, 129.97, 130.60, 133.70, 137.44, 138.71, 159.13, 166.06, 171.59.

Analysis calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_3$: C, 71.06; H, 7.37; N, 4.87.

Found : C, 71.35; H, 7.30; N, 4.81.



3-Aza-2-methyl-5-ethoxycarbonyl-9,11-dimethoxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (10)^S:

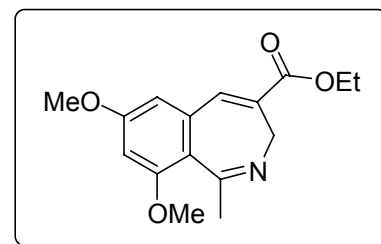
IR (neat) : 1709, 1622, 1599 cm^{-1}
 ^1H NMR (CDCl_3) : δ 1.25 (t, 3H, $J = 7.0$ Hz); 2.18 (s, 3H); 2.84 (d, 1H, $J = 10.8$ Hz); 3.75 (s, 3H); 3.78 (s, 3H); 4.18 (q, 2H, $J = 7.0$ Hz); 4.70 (d, 1H, $J = 10.8$ Hz); 6.43 (s, 2H); 7.53 (s, 1H).

^{13}C NMR (CDCl_3) : δ 14.17, 25.77, 47.48, 55.40, 55.61, 60.99, 99.50, 104.72, 122.63, 135.39, 137.24, 138.23, 159.49, 160.48, 165.48, 165.62.

MS (m/z) : 289 (M^+)

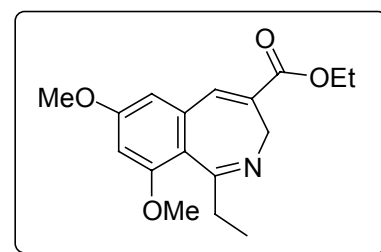
Analysis calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}_4$: C, 66.42; H, 6.62; N, 4.84

Found : C, 66.17; H, 6.68; N, 4.77



3-Aza-2-ethyl-5-ethoxycarbonyl-9,11-dimethoxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (11)^S:

IR (neat) : 1711, 1620, 1599 cm^{-1}
 ^1H NMR (CDCl_3) : δ 0.84 (t, 3H, $J = 7.6$ Hz); 1.32 (s, 3H, $J = 6.8$ Hz); 2.51-2.78 (m, 2H); 2.91 (d, 1H, $J = 10.8$ Hz); 3.82 (s, 3H), 3.84 (s, 3H), 4.15-4.36 (m, 2H), 4.80 (d, 1H, $J = 10.8$ Hz), 6.49 (s, 2H); 7.60 (s, 1H).



^{13}C NMR (CDCl_3) : δ 12.06, 14.21, 31.67, 47.37, 55.45, 55.72, 61.07, 99.47, 104.75, 121.82, 135.91, 137.95, 138.31, 159.45, 160.59, 165.55, 170.90.

MS (m/z) : 303 (M^+)

Analysis calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_4$: C, 67.31; H, 6.98; N, 4.62

Found : C, 67.52; H, 6.95; N, 4.68

3-Aza-2-methyl-5-methoxycarbonyl-9,11-dimethoxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (12)^S:

m.p : 108 $^{\circ}\text{C}$

IR (KBr) : 1703, 1628, 1597 cm^{-1}

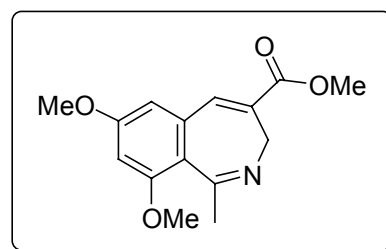
^1H NMR (CDCl_3) : δ 2.29 (s, 3H); 2.97 (d, 1H, $J = 10.8$ Hz); 3.84 (s, 3H); 3.86 (s, 3H), 3.89 (s, 3H), 4.81 (d, 1H, $J = 10.8$ Hz); 6.52 (s, 2H); 7.65 (s, 1H).

^{13}C NMR (CDCl_3) : δ 25.84, 47.60, 52.03, 55.42, 55.65, 99.58, 104.70, 122.76, 135.10, 137.20, 138.49, 159.52, 160.48, 165.63, 166.00.

MS (m/z) : 275 (M^+)

Analysis calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}_4$: C, 65.44; H, 6.22; N, 5.09

Found : C, 65.35; H, 6.20; N, 5.12



3-Aza-2-ethyl-5-methoxycarbonyl-9,10,11-trimethoxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (13)^S:

m.p : 140-141 $^{\circ}\text{C}$

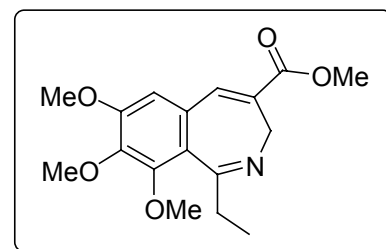
IR (KBr) : 1709, 1624, 1591 cm^{-1}

^1H NMR (CDCl_3) : δ 0.88 (t, 3H, $J = 7.6$ Hz); 2.68 (q, 2H, $J = 7.6$ Hz); 2.93 (d, 1H, $J = 10.8$ Hz); 3.84 (s, 3H); 3.91 (s, 6H); 3.94 (s, 3H); 4.88 (d, 1H, $J = 10.8$ Hz); 6.72 (s, 1H); 7.65 (s, 1H).

^{13}C NMR (CDCl_3) : δ 12.06, 31.88, 47.79, 52.19, 56.05, 61.19, 61.67, 107.80, 126.33, 132.02, 134.10, 138.51, 141.92, 152.47, 153.89, 166.18, 170.20.

Analysis calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_5$: C, 63.94; H, 6.63; N, 4.39

Found : C, 63.80; H, 6.60; N, 4.37



Crystal data : empirical formula, $\text{C}_{17}\text{H}_{21}\text{NO}_5$; formula weight, 319.35; crystal colour, habit: light yellow, rectangular; crystal dimensions, 0.5 x 0.48 x 0.24 mm; crystal system, monoclinic; lattice type,

primitive; lattice parameters, $a = 10.669(6) \text{ \AA}$, $b = 13.041(8) \text{ \AA}$, $c = 12.062(9) \text{ \AA}$; $\beta = 93.18(5)$; $V = 1675.6(18) \text{ \AA}^3$; space group, P21/a:b3 (No. 14); $Z = 4$; $D_{\text{calcd}} = 1.266 \text{ g/cm}^3$; $F_{000} = 680$; (Mo K_{α}) = 0.71073 \AA ; $R = 0.0569$, $wR^2 = 0.1845$.

3-Aza-2-ethyl-5-ethoxycarbonyl-9,10-methylenedioxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (14):

m.p : 78-79 °C

IR (KBr) : 1701, 1630, 1587 cm^{-1}

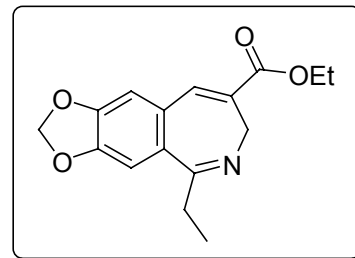
$^1\text{H NMR}$ (CDCl_3) : δ 0.97 (t, 3H, $J = 7.6 \text{ Hz}$); 1.36 (t, 3H, $J = 7.0 \text{ Hz}$); 2.65 (q, 2H, $J = 7.6 \text{ Hz}$); 3.88 (br s, 2H); 4.29 (q, 2H, $J = 7.0 \text{ Hz}$); 6.07 (s, 2H); 6.87 (s, 1H); 7.11 (s, 1H); 7.61 (s, 1H).

$^{13}\text{C NMR}$ (CDCl_3) : δ 11.86, 14.31, 32.47, 47.32, 61.13, 101.93, 107.71, 109.07, 131.39, 131.97, 133.56, 138.10, 147.67, 148.24, 165.69, 170.33.

MS (m/z) : 287 (M^+), 286 ($\text{M}-1$) $^+$

Analysis calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_4$: C, 66.89; H, 5.96; N, 4.87.

Found : C, 66.99; H, 5.94; N, 4.85.



3-Aza-2-ethyl-5-methoxycarbonyl-9,10-methylenedioxybicyclo[5.4.0]undeca-1(7),2,5,8,10-pentaene (15):

m.p : 126-127 °C

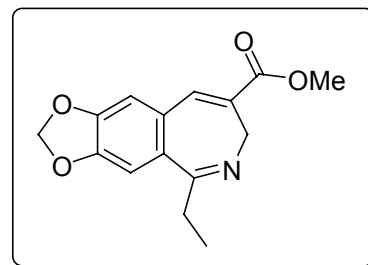
IR (KBr) : 1707, 1630, 1585 cm^{-1}

$^1\text{H NMR}$ (CDCl_3) : δ 0.97 (t, 3H, $J = 7.6 \text{ Hz}$); 2.65 (q, 2H, $J = 7.6 \text{ Hz}$); 3.84 (s, 5H); 6.08 (s, 2H); 6.87 (s, 1H); 7.12 (s, 1H); 7.62 (s, 1H).

$^{13}\text{C NMR}$ (CDCl_3) : δ 11.75, 32.37, 47.28, 52.08, 101.89, 107.61, 108.98, 131.16, 131.42, 133.54, 138.25, 147.64, 148.15, 166.05, 170.18.

Analysis calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_4$: C, 65.93; H, 5.53; N, 5.13

Found : C, 65.76; H, 5.54; N, 5.10



Crystal data : empirical formula, $\text{C}_{15}\text{H}_{15}\text{NO}_4$; formula weight, 273.28; crystal color, habit: light yellow, rectangular; crystal dimensions, 0.47 x 0.42 x 0.40 mm; crystal system, monoclinic; lattice type, primitive; lattice parameters, $a = 8.096(5) \text{ \AA}$, $b = 16.436(8) \text{ \AA}$, $c = 10.159(8) \text{ \AA}$; $\beta = 98.73(5)$; $V =$

1336.1(15) Å³; space group, P21/a:b3 (No. 14); $Z = 4$; $D_{\text{calcd}} = 1.359 \text{ g/cm}^3$; $F_{000} = 576$; (Mo K_{α}) = 0.71073 Å; $R = 0.0441$, $wR^2 = 0.1081$.

[§] It is interesting to note that in the case of compounds **10-13** (having methoxy group at 11 position), one of the ring-allylic methylene protons in ¹H NMR spectra appears as a doublet at δ 2.84-2.97 while the other proton appears as a doublet at δ 4.70-4.88. We have in fact confirmed this assignment in one case (compound **13**) by hydrogen-carbon (hetero) COSY NMR experiment and also by single crystal X-ray data. In the case of all the remaining 2-benzazepine derivatives **5-9**, **14**, **15** (without the methoxy group at 11-position) both the ring allylic methylene protons appear as a singlet at δ 3.84-3.92.

Methyl (2*E*)-2-acetylaminoethyl-3-phenylprop-2-enoate (2a):

m.p : 112-114 °C

IR (KBr) : 3266, 1707, 1639 cm⁻¹

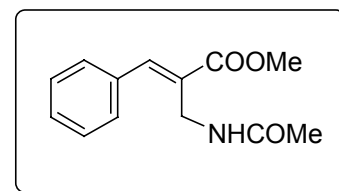
¹H NMR (CDCl₃) : δ 1.98 (s, 3H); 3.86 (s, 3H); 4.35 (d, 2H, $J = 5.7$ Hz); 6.09 (br s, 1H); 7.30-7.60 (m, 5H); 7.80 (s, 1H).

¹³C NMR (CDCl₃) : δ 23.06, 36.74, 52.07, 127.85, 128.60, 129.19, 129.53, 134.12, 142.39, 168.15, 169.61.

MS (m/z) : 233 (M⁺)

Analysis calcd. for C₁₃H₁₅NO₃ : C, 66.94; H, 6.48; N, 6.00

Found : C, 66.75; H, 6.51; N, 6.01



Methyl (2*E*)-2-propionoylaminoethyl-3-phenylprop-2-enoate (2b):

m.p : 93-94 °C

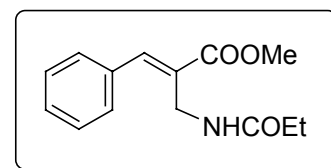
IR (KBr) : 3294, 1714, 1639 cm⁻¹

¹H NMR (CDCl₃) : δ 1.15 (t, 3H, $J = 7.6$ Hz); 2.21 (q, 2H, $J = 7.6$ Hz); 3.85 (s, 3H); 4.37 (d, 2H, $J = 5.7$ Hz); 6.08 (br s, 1H); 7.30- 7.58 (m, 5H); 7.79 (s, 1H).

¹³C NMR (CDCl₃) : δ 9.75, 29.73, 36.76, 52.14, 128.16, 128.73, 129.27, 129.66, 134.30, 142.34, 168.35, 173.25.

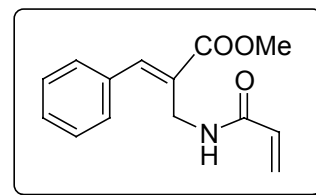
Analysis calcd. for C₁₄H₁₇NO₃ : C, 68.00; H, 6.93; N, 5.66.

Found : C, 68.20; H, 6.95; N, 5.61.



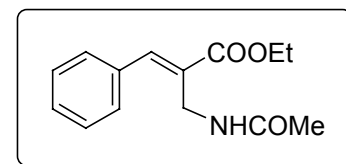
Methyl (2E)-2-acryloylaminoethyl-3-phenylprop-2-enoate (2c):

m.p : 90 °C
IR (KBr) : 3296, 1712, 1655, 1624 cm⁻¹
¹H NMR (CDCl₃) : δ 3.85 (s, 3H); 4.44 (d, 2H, *J* = 5.8 Hz); 5.64 (dd, 1H, *J* = 9.8 Hz, 2.0 Hz); 6.10 (dd, 1H, *J* = 9.8 Hz, 16.6 Hz); 6.21-6.38 (m, 2H); 7.27-7.61 (m, 5H); 7.82 (s, 1H).
¹³C NMR (CDCl₃) : δ 36.61, 51.92, 125.98, 127.52, 128.47, 129.07, 129.40, 130.75, 133.95, 142.48, 165.09, 167.91.
MS (m/z) : 246 (M+H)⁺
Analysis calcd. for C₁₄H₁₅NO₃ : C, 68.56; H, 6.16; N, 5.71.
Found : C, 68.42; H, 6.13; N, 5.75.



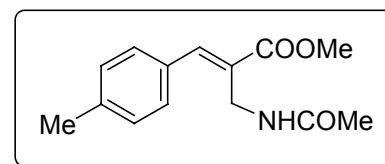
Ethyl (2E)-2-acetylaminoethyl-3-phenylprop-2-enoate (2d):

m.p : 66 °C
IR (KBr) : 3294, 1709, 1649 cm⁻¹
¹H NMR (CDCl₃) : δ 1.37 (t, 3H, *J* = 7.4 Hz); 1.98 (s, 3H); 4.23-4.43 (m, 4H); 6.08 (br s, 1H); 7.30-7.61 (m, 5H); 7.79 (s, 1H).
¹³C NMR (CDCl₃) : δ 14.10, 22.96, 36.67, 60.98, 128.10, 128.50, 129.04, 129.44, 134.13, 142.01, 167.60, 169.61.
Analysis calcd. for C₁₄H₁₇NO₃ : C, 68.00; H, 6.93; N, 5.66.
Found : C, 68.23; H, 6.88; N, 5.70.



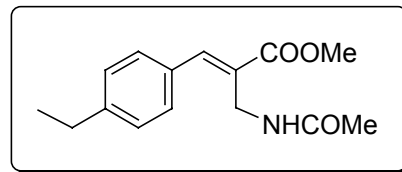
Methyl (2E)-2-acetylaminoethyl-3-(4-methylphenyl)prop-2-enoate (2e):

m.p : 115-116 °C
IR (KBr) : 3254, 1712, 1639 cm⁻¹
¹H NMR (CDCl₃) : δ 1.98 (s, 3H); 2.37 (s, 3H); 3.84 (s, 3H); 4.35 (d, 2H, *J* = 5.8 Hz); 6.06 (br s, 1H); 7.22 (d, 2H, *J* = 8.2 Hz); 7.42 (d, 2H, *J* = 8.2 Hz); 7.77 (s, 1H).
¹³C NMR (CDCl₃) : δ 21.15, 22.95, 36.69, 51.92, 126.77, 129.27, 129.59, 131.19, 139.43, 142.48, 168.19, 169.56.
Analysis calcd. for C₁₄H₁₇NO₃ : C, 68.00; H, 6.93; N, 5.66.
Found : C, 67.86; H, 6.95; N, 5.69.



Methyl (2E)-2-acetylaminoethyl-3-(4-ethylphenyl)prop-2-enoate (2f):

m.p : 78-80 °C
IR (KBr) : 3294, 1716, 1649, 1620 cm⁻¹
¹H NMR (CDCl₃) : δ 1.24 (t, 3H, *J* = 7.6 Hz); 1.98 (s, 3H); 2.66 (q, 2H, *J* = 7.6 Hz); 3.84 (s, 3H); 4.36 (d, 2H, *J* = 5.5 Hz); 6.10 (br s, 1H); 7.24 (d, 2H, *J* = 8.2 Hz); 7.46 (d, 2H, *J* = 8.2 Hz); 7.78 (s, 1H).



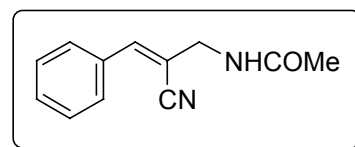
¹³C NMR (CDCl₃) : δ 15.09, 23.05, 28.58, 36.79, 52.01, 126.78, 128.14, 129.77, 131.45, 142.59, 145.80, 168.31, 169.63.

Analysis calcd. for C₁₅H₁₉NO₃ : C, 68.94; H, 7.33; N, 5.36

Found : C, 69.11; H, 7.28; N, 5.34

(2Z)-2-Acetylaminoethyl-3-phenylprop-2-enitrile (4a):

m.p : 98-100 °C
IR (KBr) : 3302, 2216, 1657, 1620 cm⁻¹
¹H NMR (CDCl₃) : δ 2.05 (s, 3H); 4.14 (d, 2H, *J* = 6.0 Hz); 6.13 (br s, 1H); 7.16 (s, 1H); 7.34-7.50 (m, 3H); 7.69-7.81 (m, 2H).



¹³C NMR (CDCl₃) : δ 23.05, 43.42, 107.95, 117.99, 128.86, 130.60, 132.98, 145.30, 170.68.

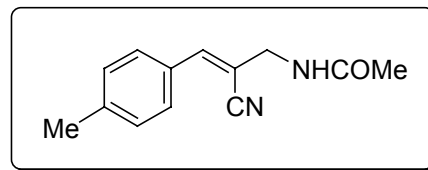
MS (m/z) : 201 (M+H)⁺

Analysis calcd. for C₁₂H₁₂N₂O : C, 71.98; H, 6.04; N, 13.99

Found : C, 72.22; H, 6.07; N, 14.08

(2Z)-2-Acetylaminoethyl-3-(4-methylphenyl)prop-2-enitrile (4b):

m.p : 108-110 °C
IR (KBr) : 3290, 2212, 1649, 1622 cm⁻¹
¹H NMR (CDCl₃) : δ 2.05 (s, 3H); 2.38 (s, 3H); 4.15 (d, 2H, *J* = 6.2 Hz); 6.05 (br s, 1H); 7.13 (s, 1H); 7.21 (d, 2H, *J* = 8.2 Hz); 7.64 (d, 2H, *J* = 8.2 Hz).



¹³C NMR (CDCl₃) : δ 21.41, 22.98, 43.38, 106.68, 118.22, 128.88, 129.54, 130.32, 141.08, 145.17, 170.74.

Analysis calcd. for C₁₃H₁₄N₂O : C, 72.87; H, 6.59; N, 13.07

Found : C, 72.65; H, 6.61; N, 13.17

(2Z)-2-Acetylaminoethyl-3-(4-isopropylphenyl)prop-2-enitrile (4c):

m.p : 76-78 °C

IR (KBr) : 3302, 2212, 1657, 1625 cm⁻¹

¹H NMR (CDCl₃) : δ 1.25 (d, 6H, *J* = 7.8 Hz); 2.05 (s, 3H); 2.93

(sept, 1H, *J* = 7.8 Hz); 4.15 (d, 2H, *J* = 6.0 Hz); 5.99 (br s, 1H); 7.14 (s, 1H); 7.28 (d, 2H, *J* = 7.8 Hz), 7.68 (d, 2H, *J* = 7.8 Hz).

¹³C NMR (CDCl₃) : δ 22.90, 23.54, 33.92, 43.28, 106.62, 118.16, 126.82, 128.91, 130.56, 145.09, 151.81, 170.66.

Analysis calcd. for C₁₅H₁₈N₂O : C, 74.35; H, 7.49; N, 11.56.

Found : C, 74.19; H, 7.45; N, 11.48

