

# Reactions of $\beta$ -amino- $\beta$ -polyfluoroalkylvinyl ketones with diethylenetriamine. Simple synthesis of 1,4,8-triazabicyclo[5.3.0]dec-4-ene derivatives

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$\beta$ -Amino- $\beta$ -polyfluoroalkylvinyl aryl(hetaryl) ketones react with diethylenetriamine to form derivatives of a new 1,4,8-triazabicyclo[5.3.0]dec-4-ene system.

**Key words:**  $\beta$ -amino- $\beta$ -polyfluoroalkylvinyl aryl(hetaryl) ketones, diethylenetriamine, 1,4,8-triazabicyclo[5.3.0]dec-4-ene derivatives.

Recently,<sup>1</sup> we have demonstrated that the reactions of  $\beta$ -amino- $\beta$ -polyfluoroalkylvinyl aryl ketones **1** with ethylenediamine follow two major pathways to form either 2,3-dihydro-1*H*-1,4-diazepines or 2,2-disubstituted imidazolidines. The latter were formed only under conditions of kinetic control and were converted into thermodynamically more stable dihydrodiazepines upon refluxing in ethanol for 3–6 h.

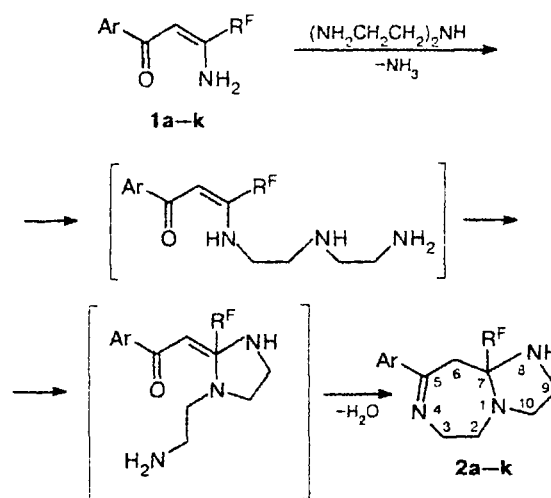
Taking into account these facts, one would expect that the reactions of aminoenones **1** with diethylenetriamine will combine both these pathways, resulting in a new fused triazabicyclo[5.3.0]dec-4-ene system with a common nitrogen atom.

We found that this reaction actually occurs and is typical of aminoenones **1a–k** (for a preliminary communication, see Ref. 2). Compounds **1a–k** reacted with diethylenetriamine at room temperature without a solvent for 4–7 days to form bicycles **2a–k** (Scheme 1). In this case, diethylenetriamine acts as a trinucleophile and its reactions with aminoenones **1a–k** involve the double nucleophilic addition to the  $C_\beta$  atom with elimination of ammonia (analogously to the reactions with ethylenediamine) and the attack at the carbonyl group accompanied by liberation of a water molecule.

Evidently, the presence of a polyfluoroalkyl substituent, which not only increases the electrophilicity of the  $C_\beta$  atom but also stabilizes the imidazolidine ring, favors the reaction, as in the case of amins and aminoketals.<sup>3</sup> However, aminoenones with Ar = Ph and  $R^F$  =  $CF_2H$  or with Ar = 2- $C_4H_3S$  and  $R^F$  =  $CF_2H$  or  $C_3F_7$  did not react with diethylenetriamine under analogous conditions. The nature and the position of the substituent in the benzene ring have no substantial effect on the course of the reaction (bicycles **2** containing 2-hydroxyaryl substituents will be described elsewhere; for a preliminary communication, see Ref. 4).

The reaction of benzil with diethylenetriamine yielding 5,6-diphenyl-1,4,7-triazabicyclo[4.3.0]non-4-ene<sup>5</sup> can be considered as the closest analog of the reaction under consideration.

Scheme 1



1, 2	Ar	$R^F$	1, 2	Ar	$R^F$
a	Ph	$CF_3$	g	4-MeC <sub>6</sub> H <sub>4</sub>	$CF_3$
b	Ph	$(CF_2)_2H$	h	4-ClC <sub>6</sub> H <sub>4</sub>	$CF_3$
c	2-C <sub>4</sub> H <sub>3</sub> S	$CF_3$	i	4-BrC <sub>6</sub> H <sub>4</sub>	$CF_3$
d	2-C <sub>4</sub> H <sub>3</sub> S	$(CF_2)_2H$	j	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	$CF_3$
e	2-C <sub>4</sub> H <sub>3</sub> O	$CF_3$	k	4-MeOC <sub>6</sub> H <sub>4</sub>	$CF_3$
f	2-C <sub>4</sub> H <sub>3</sub> O	$(CF_2)_2H$			

It is significant that compounds **2a–k**, like imidazolidines,<sup>1</sup> were obtained only under conditions of kinetic control because the reactions of aminoenones **1a,b** with diethylenetriamine with heating at 90 °C for 36 h afforded a mixture of 1,5-di(polyfluoroacylamino)-3-azapentanes and *N,N'*-(3-azapentamethylene)bis-(3-amino-1-polyfluoroalkyl-3-phenylprop-2-en-1-ones) in a ratio of 1 : 2.<sup>6</sup> Probably, the last mentioned compounds are the products of further transformations of bicycles **2a,b** under conditions of thermodynamic control rather than a consequence of preliminary isomerization of the starting aminoenones **1a,b** to form

regioisomers containing polyfluoroalkyl and amino groups at the  $\gamma$  positions, as has been suggested previously.<sup>6</sup>

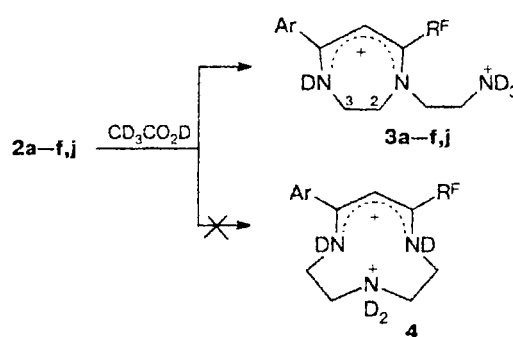
The  $^1\text{H}$  NMR spectra of compounds **2a–k** in  $\text{CDCl}_3$ , which were measured immediately after dissolution and which reflect the structures of the compounds in the crystalline state, have a broadened singlet for the proton of the NH group at  $\delta$  2.0–2.1, which disappears upon addition of  $\text{D}_2\text{O}$ , a signal at  $\delta$  ~3.3 (an AB system of the  $\text{C}(6)\text{H}_2$  group), which overlaps with a multiplet of three methylene groups at positions 9, 10, and 2, and a very characteristic multiplet for the protons of the  $\text{C}(3)\text{H}_2$  group at  $\delta$  ~4 and 4.2 along with signals for the aromatic protons. It should also be noted that the fluorine atoms at the carbon atom directly bound to the asymmetric center in compounds **2b,d,f** are nonequivalent. This leads to splitting of the signal for the proton of the  $\text{CF}_2\text{CF}_2\text{H}$  group (at  $\delta$  ~6.1) into a triplet of doublets of doublets instead of a usual triplet of triplets, which proves that the polyfluoroalkyl substituent is bound to the  $\text{C}(7)$  atom (Fig. 1).

When deuterioacetic acid was added to solutions of compounds **2a–f,j** in  $\text{CDCl}_3$ , their spectra became substantially simplified and contained two triplets of the  $\text{A}_2\text{X}_2$  system instead of complex multiplets of four methylene groups and the AB spectrum of the  $\text{C}(6)\text{H}_2$  group, the low-field triplet being located between two broadened two-proton singlets. Simultaneously, the positions of the signals for the aromatic protons were changed and a singlet for the vinyl proton appeared at  $\delta$  5.80–6.17. The intensity of the latter is lower than 1 H due to partial H/D exchange.

Taking into account the results of studies<sup>1</sup> of the behavior of dihydrodiazepines and imidazolidines in the presence of  $\text{CD}_3\text{CO}_2\text{D}$ , we believe that in the present

case, the addition of deuterioacetic acid led to the cleavage of the  $\text{C}(7)\text{—N}(8)$  bond, giving rise to dication **3**. The latter is a dihydrodiazepinium cation containing the  $\text{CH}_2\text{CH}_2\text{N}^+\text{D}_3$  group at the nitrogen atom nearest to the polyfluoroalkyl substituent. In this case, two triplets should be assigned to the deuterated 2-aminoethyl substituent, whereas the broadened two-proton singlets should be assigned to the methylene groups at positions 2 and 3 of the dihydrodiazepinium cation. An alternative opening of the fused system with cleavage of the  $\text{C}(7)\text{—N}(1)$  bond would afford dication **4** (Scheme 2), whose symmetrical structure is inconsistent with the  $^1\text{H}$  NMR spectral data.

Scheme 2



Based on the above-mentioned data, the 1,4,8-triazabicyclo[5.3.0]dec-4-ene system can be considered as a cyclic form of 2,3-dihydro-1*H*-1,4-diazepines containing the 2-aminoethyl group at the  $\text{N}(1)$  atom. In the

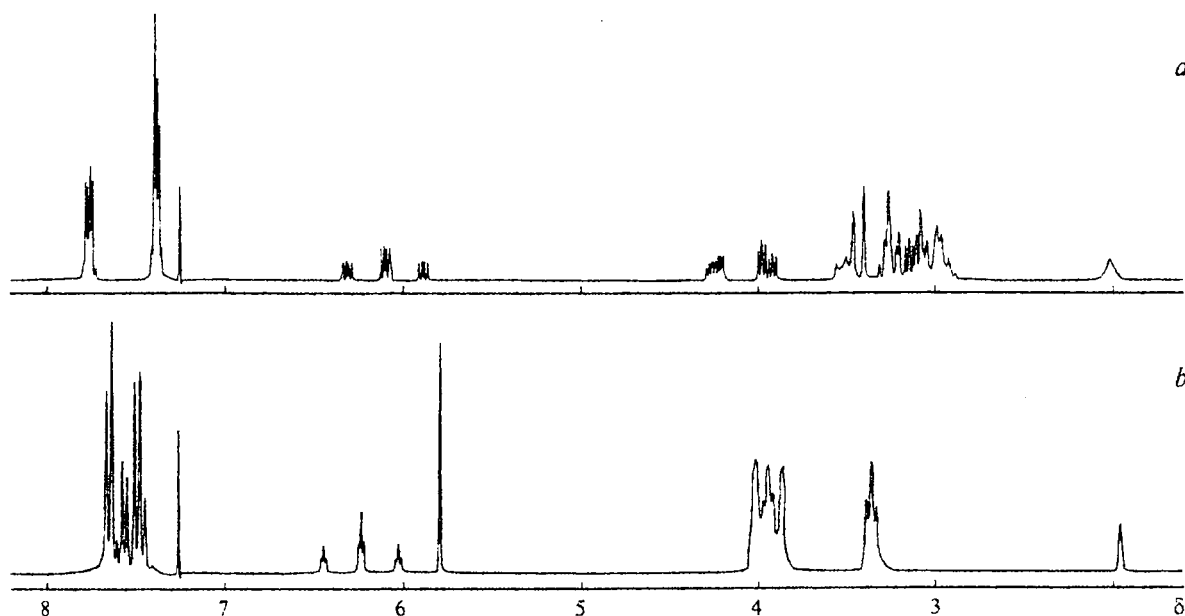


Fig. 1.  $^1\text{H}$  NMR spectrum of compound **2b** in  $\text{CDCl}_3$  (a) and after addition of  $\text{CD}_3\text{CO}_2\text{D}$  (b).

crystalline state and in deuteriochloroform solutions, the reaction products of aminoenones **1** with diethylenetriamine exist only in a bicyclic form **2**, whereas these products in an acidic medium undergo ring opening to form dihydrodiazepine structure **3**. It should also be noted that the  $^1\text{H}$  NMR spectrum of bicycle **2a** recorded for a solution in  $\text{DMSO}-d_6$  has a broadened singlet in the region of ethylene protons (at  $\delta$  5.56), which is apparently indicative of the presence of the monocyclic form (~15%). When  $\text{CF}_3\text{CO}_2\text{D}$  was added to this solution, a one-proton singlet appeared at  $\delta$  5.87. This singlet belongs to the ethylene proton of dication **3** (see Experimental).

Therefore, the reactions of aminoenones **1** with diethylenetriamine under conditions of kinetic control afforded fluorine-containing derivatives of a new 1,4,8-triazabicyclo[5.3.0]dec-4-ene system. These reactions are characterized by simplicity, availability of the starting compounds, and rather high synthetic potentialities, owing to which these reactions are very useful in the synthesis of aza analogs of bicyclo[5.3.0]decane.

### Experimental

The IR spectra were recorded on an IKS-29 instrument in Nujol mulls. The  $^1\text{H}$  NMR spectra were measured on a Bruker WM-250 spectrometer (250 MHz) in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as the internal standard. The  $^{19}\text{F}$  NMR spectrum of compound **2a** was recorded on a Tesla BS-587A spectrometer (75.3 MHz) in  $\text{CDCl}_3$  with  $\text{C}_6\text{F}_6$  as the internal standard. Compounds **2a–i, k** were prepared according to a procedure reported previously.<sup>1</sup> Compound **2j** was isolated after chromatography on  $\text{Al}_2\text{O}_3$  using chloroform as the eluent.

**5-Phenyl-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2a).** Aminoenone **1a** (215 mg, 1 mmol) was dissolved in diethylenetriamine (215  $\mu\text{L}$ , 205 mg, 2 mmol) and the reaction mixture was kept at  $-20^\circ\text{C}$  for 6 days. The crystals of bicycle **2a** that formed were washed with water and recrystallized from hexane. The yield was 210 mg (74%), m.p.  $77\text{--}78^\circ\text{C}$ . Found (%): C, 59.43; H, 5.53; N, 14.85.  $\text{C}_{14}\text{H}_{16}\text{F}_3\text{N}_3$ . Calculated (%): C, 59.36; H, 5.69; N, 14.83. IR,  $\nu/\text{cm}^{-1}$ : 3350 (NH); 1630 (C=N); 1580 (benzene ring).  $^1\text{H}$  NMR,  $\delta$ : 2.08 (br.s, 1 H, NH); 3.04–3.22 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.31 (AB system,  $\Delta\delta = 0.13$ , 2 H, C(6)H<sub>2</sub>,  $J_{\text{AB}} = 15.4$  Hz); 3.43–3.54 (m, 1 H, C(2)HH); 3.99 (dt, 1 H, C(3)HH,  $^2J = 16.1$  Hz,  $^3J = 5.3$  Hz); 4.29 (ddd, 1 H, C(3)HH,  $^2J = 16.1$  Hz,  $^3J = 7.7$  and 4.6 Hz); 7.37–7.40 (m, 3 H, CH arom.); 7.71–7.75 (m, 2 H, CH arom.). After addition of  $\text{CD}_3\text{CO}_2\text{D}$ : **3a**, 3.35 (t, 2 H,  $\text{CH}_2\text{--N}^+\text{D}_3$ ,  $J = 7.1$  Hz); 3.94 (s, 2 H, C(2)H<sub>2</sub>); 4.01 (t, 2 H,  $\text{CH}_2\text{--N}(1)$ ,  $J = 7.1$  Hz); 4.04 (s, 2 H, C(3)H<sub>2</sub>); 5.94 (s, 0.4 H, =CH); 7.47–7.71 (m, 5 H, Ph).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ),  $\delta$ : 2.72–3.45 (m, 8 H, C(2)H<sub>2</sub>, C(6)H<sub>2</sub>, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>); 3.79 (ddd, 1 H, C(3)HH,  $^2J = 16.1$  Hz,  $^3J = 5.6$  and 3.3 Hz); 4.15 (ddd, 1 H, C(3)HH,  $^2J = 16.1$  Hz,  $^3J = 7.4$  and 3.7 Hz); 5.56 (br.s, 0.15 H, =CH of the dihydrodiazepine form); 7.32–7.47 (m, 3 H, CH arom.); 7.71–7.75 (m, 2 H, CH arom.). After addition of  $\text{CF}_3\text{CO}_2\text{D}$ : **3a**, 3.24 (br.s, 2 H,  $\text{CH}_2\text{--N}^+\text{D}_3$ ); 3.92–4.00 (m, 6 H, C(2)H<sub>2</sub>,  $\text{CH}_2\text{--N}(1)$ , C(3)H<sub>2</sub>); 5.87 (s, 1 H, =CH); 7.57–7.76 (m, 5 H, Ph).  $^{19}\text{F}$  NMR,  $\delta$ : 81.85 (s,  $\text{CF}_3$ ).

**5-Phenyl-7-(1,1,2,2-tetrafluoroethyl)-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2b).** The yield was 33%, m.p.  $100\text{--}101^\circ\text{C}$ .

Found (%): C, 57.25; H, 5.52; N, 13.46.  $\text{C}_{15}\text{H}_{17}\text{F}_4\text{N}_3$ . Calculated (%): C, 57.14; H, 5.43; N, 13.33. IR,  $\nu/\text{cm}^{-1}$ : 3400 (NH); 1630 (C=N); 1580 (benzene ring).  $^1\text{H}$  NMR,  $\delta$ : 2.04 (br.s, 1 H, NH); 2.94–3.29 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.35 (AB system,  $\Delta\delta = 0.19$ , 2 H, C(6)H<sub>2</sub>,  $J_{\text{AB}} = 15.1$  Hz); 3.46–3.57 (m, 1 H, C(2)HH); 3.97 (ddd, 1 H, C(3)HH,  $^2J = 15.2$  Hz,  $^3J = 5.7$  and 4.2 Hz); 4.25 (ddd, 1 H, C(3)HH,  $^2J = 15.2$  Hz,  $^3J = 7.8$  and 4.5 Hz); 6.12 (tdd, 1 H,  $\text{CF}_2\text{CF}_2\text{H}$ ,  $^2J_{\text{H,F}} = 53.6$  Hz,  $^3J_{\text{H,F}} = 7.6$  and 4.8 Hz); 7.38–7.43 (m, 3 H, CH arom.); 7.74–7.80 (m, 2 H, CH arom.). After addition of  $\text{CD}_3\text{CO}_2\text{D}$ : **3b**, 3.36 (t, 2 H,  $\text{CH}_2\text{--N}^+\text{D}_3$ ,  $J = 7.0$  Hz); 3.87 (s, 2 H, C(2)H<sub>2</sub>); 3.95 (t, 2 H,  $\text{CH}_2\text{--N}(1)$ ,  $J = 7.0$  Hz); 4.02 (s, 2 H, C(3)H<sub>2</sub>); 5.80 (s, 0.7 H, =CH); 6.25 (tt, 1 H,  $\text{CF}_2\text{CF}_2\text{H}$ ,  $^2J_{\text{H,F}} = 52.7$  Hz,  $^3J_{\text{H,F}} = 3.6$  Hz); 7.46–7.68 (m, 5 H, Ph).

**5-(2-Thienyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2c).** The yield was 64%, m.p.  $140\text{--}141^\circ\text{C}$ . Found (%): C, 49.77; H, 4.68; N, 14.63.  $\text{C}_{12}\text{H}_{14}\text{F}_3\text{N}_3\text{S}$ . Calculated (%): C, 49.82; H, 4.88; N, 14.52. IR,  $\nu/\text{cm}^{-1}$ : 3350 (NH); 3090 (=CH); 1635 (C=N); 1615 (NH); 1530 (thiophene ring).  $^1\text{H}$  NMR,  $\delta$ : 2.10 (br.s, 1 H, NH); 3.03–3.22 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.28 (AB system,  $\Delta\delta = 0.16$ , 2 H, C(6)H<sub>2</sub>,  $J_{\text{AB}} = 15.3$  Hz); 3.44–3.55 (m, 1 H, C(2)HH); 3.93 (dt, 1 H, C(3)HH,  $^2J = 16.5$  Hz,  $^3J = 5.1$  Hz); 4.22 (ddd, 1 H, C(3)HH,  $^2J = 16.5$  Hz,  $^3J = 8.1$  and 4.7 Hz); 7.04 (dd, 1 H, H(4'),  $J_{\text{H(4'),H(5')}} = 5.1$  Hz,  $J_{\text{H(4'),H(3')}} = 3.7$  Hz); 7.30 (dd, 1 H, H(3'),  $J_{\text{H(3'),H(5')}} = 0.9$  Hz); 7.38 (dd, 1 H, H(5')). After addition of  $\text{CD}_3\text{CO}_2\text{D}$ : **3c**, 3.33 (t, 2 H,  $\text{CH}_2\text{--N}^+\text{D}_3$ ,  $J = 7.1$  Hz); 3.89 (s, 2 H, C(2)H<sub>2</sub>); 3.95 (t, 2 H,  $\text{CH}_2\text{--N}(1)$ ,  $J = 7.1$  Hz); 4.01 (s, 2 H, C(3)H<sub>2</sub>); 6.05 (s, 0.6 H, =CH); 7.19 (t, 1 H, H(4'),  $J = 4.5$  Hz); 7.67 (d, 1 H, H(5'),  $J_{\text{H(5'),H(4')}} = 5.1$  Hz); 7.90 (d, 1 H, H(3'),  $J_{\text{H(3'),H(4')}} = 4.0$  Hz).

**7-(1,1,2,2-Tetrafluoroethyl)-5-(2-thienyl)-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2d).** The yield was 25%, m.p.  $110\text{--}111^\circ\text{C}$ . Found (%): C, 48.74; H, 4.60; N, 13.18.  $\text{C}_{13}\text{H}_{15}\text{F}_4\text{N}_3\text{S}$ . Calculated (%): C, 48.59; H, 4.71; N, 13.08. IR,  $\nu/\text{cm}^{-1}$ : 3395 (NH); 3075 (=CH); 1620 (C=N); 1525 (thiophene ring).  $^1\text{H}$  NMR,  $\delta$ : 2.06 (br.s, 1 H, NH); 2.91–3.28 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.29 (AB system,  $\Delta\delta = 0.23$ , 2 H, C(6)H<sub>2</sub>,  $J_{\text{AB}} = 15.0$  Hz); 3.43–3.55 (m, 1 H, C(2)HH); 3.89 (ddd, 1 H, C(3)HH,  $^2J = 15.5$  Hz,  $^3J = 5.5$  and 4.6 Hz); 4.17 (ddd, 1 H, C(3)HH,  $^2J = 15.5$  Hz,  $^3J = 8.2$  and 4.6 Hz); 6.11 (tdd, 1 H,  $\text{CF}_2\text{CF}_2\text{H}$ ,  $^2J_{\text{H,F}} = 53.6$  Hz,  $^3J_{\text{H,F}} = 7.6$  and 4.8 Hz); 7.04 (dd, 1 H, H(4'),  $J_{\text{H(4'),H(5')}} = 5.1$  Hz,  $J_{\text{H(4'),H(3')}} = 3.7$  Hz); 7.31 (dd, 1 H, H(3'),  $J_{\text{H(3'),H(5')}} = 0.9$  Hz); 7.37 (dd, 1 H, H(5')). After addition of  $\text{CD}_3\text{CO}_2\text{D}$ : **3d**, 3.32 (t, 2 H,  $\text{CH}_2\text{--N}^+\text{D}_3$ ,  $J = 7.1$  Hz); 3.77 (s, 2 H, C(2)H<sub>2</sub>); 3.86 (t, 2 H,  $\text{CH}_2\text{--N}(1)$ ,  $J = 7.1$  Hz); 3.99 (s, 2 H, C(3)H<sub>2</sub>); 5.94 (s, 0.6 H, =CH); 6.20 (tt, 1 H,  $\text{CF}_2\text{CF}_2\text{H}$ ,  $^2J_{\text{H,F}} = 52.7$  Hz,  $^3J_{\text{H,F}} = 3.7$  Hz); 7.16 (dd, 1 H, H(4'),  $J_{\text{H(4'),H(5')}} = 4.9$  Hz,  $J_{\text{H(4'),H(3')}} = 4.1$  Hz); 7.62 (d, 1 H, H(5')); 7.83 (d, 1 H, H(3')).

**5-(2-Furyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2e).** The yield was 66%, m.p.  $94\text{--}95^\circ\text{C}$ . Found (%): C, 52.56; H, 5.15.  $\text{C}_{12}\text{H}_{14}\text{F}_3\text{N}_3\text{O}$ . Calculated (%): C, 52.75; H, 5.16. IR,  $\nu/\text{cm}^{-1}$ : 3330 (NH); 3120 (=CH); 1645 (C=N); 1630 br (NH); 1570 (furan ring).  $^1\text{H}$  NMR,  $\delta$ : 2.10 (br.s, 1 H, NH); 3.00–3.20 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.20 (AB system,  $\Delta\delta = 0.15$ , 2 H, C(6)H<sub>2</sub>,  $J_{\text{AB}} = 15.1$  Hz); 3.42–3.54 (m, 1 H, C(2)HH); 3.97 (dt, 1 H, C(3)HH,  $^2J = 16.7$  Hz,  $^3J = 5.0$  Hz); 4.30 (ddd, 1 H, C(3)HH,  $^2J = 16.7$  Hz,  $^3J = 8.4$  and 4.7 Hz); 6.46 (dd, 1 H, H(4'),  $J_{\text{H(4'),H(3')}} = 3.8$  Hz,  $J_{\text{H(4'),H(5')}} = 1.9$  Hz); 6.79 (d, 1 H, H(3')); 7.49 (d, 1 H, H(5')). After addition of  $\text{CD}_3\text{CO}_2\text{D}$ : **3e**, 3.31 (t, 2 H,  $\text{CH}_2\text{--N}^+\text{D}_3$ ,  $J = 7.0$  Hz); 3.86 (s, 2 H, C(2)H<sub>2</sub>); 3.94 (t, 2 H,  $\text{CH}_2\text{--N}(1)$  of the ring); 4.00 (s, 2 H, C(3)H<sub>2</sub>); 6.17 (s, 0.2 H, =CH); 6.62 (dd, 1 H, H(4'),  $J_{\text{H(4'),H(3')}} = 3.7$  Hz,  $J_{\text{H(4'),H(5')}} = 1.6$  Hz); 7.49 (d, 1 H, H(3')); 7.69 (d, 1 H, H(5')).

**5-(2-Furyl)-7-(1,1,2,2-tetrafluoroethyl)-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2f).** The yield was 63%, m.p. 137–138 °C. Found (%): C, 50.98; H, 5.07.  $C_{13}H_{15}F_4N_3O$ . Calculated (%): C, 51.15; H, 4.95. IR,  $\nu/cm^{-1}$ : 3390 (NH); 3185 and 3130 (=CH); 1630 (C=N); 1595 w (NH); 1570 w and 1525 w (furan ring).  $^1H$  NMR,  $\delta$ : 2.00 (br.s, 1 H, NH); 2.87–3.25 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.21 (AB system,  $\Delta\delta = 0.21$ , 2 H, C(6)H<sub>2</sub>,  $J_{AB} = 15.4$  Hz); 3.42–3.53 (m, 1 H, C(2)HH); 3.93 (dt, 1 H, C(3)HH,  $^2J = 15.8$  Hz,  $^3J = 4.9$  Hz); 4.23 (ddd, 1 H, C(3)HH,  $^2J = 15.8$  Hz,  $^3J = 8.2$  and 4.7 Hz); 6.10 (tdd, 1 H, CF<sub>2</sub>CF<sub>2</sub>H,  $^2J_{H,F} = 53.6$  Hz,  $^3J_{H,F} = 7.6$  and 4.9 Hz); 6.46 (dd, 1 H, H(4'),  $J_{H(4'),H(3')} = 3.4$  Hz,  $J_{H(4'),H(5')} = 1.9$  Hz); 6.80 (d, 1 H, H(3')); 7.48 (dd, 1 H, H(5'),  $J_{H(5'),H(3')} = 0.5$  Hz). After addition of CD<sub>3</sub>CO<sub>2</sub>D: 3f, 3.35 (t, 2 H, CH<sub>2</sub>–N<sup>+</sup>D<sub>3</sub>,  $J = 7.2$  Hz); 3.80 (s, 2 H, C(2)H<sub>2</sub>); 3.90 (t, 2 H, CH<sub>2</sub>–N(1)); 3.98 (s, 2 H, C(3)H<sub>2</sub>); 6.03 (s, 0.9 H, =CH); 6.24 (tt, 1 H, CF<sub>2</sub>CF<sub>2</sub>H,  $^2J_{H,F} = 52.5$  Hz,  $^3J_{H,F} = 3.8$  Hz); 6.62 (dd, 1 H, H(4'),  $J_{H(4'),H(3')} = 3.6$  Hz,  $J_{H(4'),H(5')} = 1.9$  Hz); 7.44 (d, 1 H, H(3')); 7.69 (d, 1 H, H(5')).

**5-(4-Tolyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2g).** The yield was 62%, m.p. 84–85 °C. Found (%): C, 60.73; H, 6.11; N, 14.12.  $C_{15}H_{18}F_3N_3$ . Calculated (%): C, 60.60; H, 6.10; N, 14.13. IR,  $\nu/cm^{-1}$ : 3280 (NH); 1630 (C=N); 1610 (NH); 1570 (benzene ring).  $^1H$  NMR,  $\delta$ : 2.07 (br.s, 1 H, NH); 2.37 (s, 3 H, Me); 3.02–3.19 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.30 (AB system,  $\Delta\delta = 0.13$ , 2 H, C(6)H<sub>2</sub>,  $J_{AB} = 15.3$  Hz); 3.43–3.54 (m, 1 H, C(2)HH); 3.97 (dt, 1 H, C(3)HH,  $^2J = 16.2$  Hz,  $^3J = 5.5$  Hz); 4.27 (ddd, 1 H, C(3)HH,  $^2J = 16.2$  Hz,  $^3J = 7.6$  and 4.8 Hz); 7.18 (d, 2 H, H(3'), H(5'),  $J_o = 8.2$  Hz); 7.64 (d, 2 H, H(2'), H(6')).

**5-(4-Chlorophenyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2h).** The yield was 90%, m.p. 66–67 °C. Found (%): C, 53.02; H, 4.78; N, 13.33.  $C_{14}H_{15}ClF_3N_3$ . Calculated (%): C, 52.92; H, 4.76; N, 13.22. IR,  $\nu/cm^{-1}$ : 3285 (NH); 1630 (C=N); 1600 (NH); 1570 (benzene ring).  $^1H$  NMR,  $\delta$ : (br.s, 1 H, NH); 3.03–3.19 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.26 (AB system,  $\Delta\delta = 0.15$ , 2 H, C(6)H<sub>2</sub>,  $J_{AB} = 15.3$  Hz); 3.41–3.52 (m, 1 H, C(2)HH); 3.98 (ddd, 1 H, C(3)HH,  $^2J = 16.2$  Hz,  $^3J = 6.2$  and 4.5 Hz); 4.27 (ddd, 1 H, C(3)HH,  $^2J = 16.2$  Hz,  $^3J = 7.9$  and 4.6 Hz); 7.35 (dt, 2 H, H(3'), H(5'),  $J_o = 8.8$  Hz,  $J_m = J_p = 2.3$  Hz); 7.68 (dt, 2 H, H(2'), H(6')).

**5-(4-Bromophenyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2i).** The yield was 76%, m.p. 73–74 °C. Found (%): C, 46.52; H, 4.16; N, 11.77.  $C_{14}H_{15}BrF_3N_3$ . Calculated (%): C, 46.43; H, 4.17; N, 11.60. IR,  $\nu/cm^{-1}$ : 3285 (NH); 1630 (C=N); 1590 (NH); 1560 (benzene ring).  $^1H$  NMR,  $\delta$ : 2.05 (br.s, 1 H, NH); 3.03–3.19 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.26 (AB system,  $\Delta\delta = 0.15$ , 2 H, C(6)H<sub>2</sub>,  $J_{AB} = 15.3$  Hz); 3.41–3.52 (m, 1 H, C(2)HH); 3.97 (ddd, 1 H, C(3)HH,  $^2J = 16.4$  Hz,  $^3J = 6.3$  and 4.3 Hz); 4.26 (ddd, 1 H, C(3)HH,  $^2J = 16.4$  Hz,  $^3J = 7.8$  and 4.8 Hz); 7.50 (dt, 2 H, H(3'), H(5'),  $J_o = 8.8$  Hz,  $J_m = J_p = 2.2$  Hz); 7.62 (dt, 2 H, H(2'), H(6')).

**5-(4-Nitrophenyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2j).** The yield was 54%, m.p. 91–92 °C.

Found (%): C, 51.22; H, 4.68; N, 17.04.  $C_{14}H_{15}F_3N_4O_2$ . Calculated (%): C, 51.22; H, 4.61; N, 17.07. IR,  $\nu/cm^{-1}$ : 3380 (NH); 1635 (C=N); 1580 (benzene ring); 1515 (NO<sub>2</sub>).  $^1H$  NMR,  $\delta$ : 2.12 (br.s, 1 H, NH); 3.07–3.24 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.31 (AB system,  $\Delta\delta = 0.16$ , 2 H, C(6)H<sub>2</sub>,  $J_{AB} = 15.2$  Hz); 3.44–3.55 (m, 1 H, C(2)HH); 4.05 (dt, 1 H, C(3)HH,  $^2J = 16.5$  Hz,  $^3J = 5.3$  Hz); 4.36 (ddd, 1 H, C(3)HH,  $^2J = 16.5$  Hz,  $^3J = 8.0$  and 4.6 Hz); 7.91 (dt, 2 H, H(2'), H(6'),  $J_o = 8.9$  Hz,  $J_m = J_p = 2.2$  Hz); 8.23 (dt, 2 H, H(3'), H(5')). After addition of CD<sub>3</sub>CO<sub>2</sub>D: 3j, 3.56 (t, 2 H, CH<sub>2</sub>–N<sup>+</sup>D<sub>3</sub>,  $J = 7.3$  Hz); 3.81 (s, 2 H, C(2)H<sub>2</sub>); 3.92 (t, 2 H, CH<sub>2</sub>–N(1)); 4.10 (s, 2 H, C(3)H<sub>2</sub>); 5.87 (s, 0.2 H, =CH); 7.86 (dt, 2 H, H(2'), H(6'),  $J_o = 8.9$  Hz,  $J_m = J_p = 2.2$  Hz); 8.31 (dt, 2 H, H(3'), H(5')).

**5-(2-Methoxyphenyl)-7-trifluoromethyl-1,4,8-triazabicyclo[5.3.0]dec-4-ene (2k).** The yield was 43%, m.p. 98–99 °C. Found (%): C, 57.67; H, 5.90; N, 13.24.  $C_{15}H_{18}F_3N_3O$ . Calculated (%): C, 57.50; H, 5.79; N, 13.41. IR,  $\nu/cm^{-1}$ : 3280 (NH); 1650 (C=N); 1600 (NH); 1585 (benzene ring).  $^1H$  NMR,  $\delta$ : 2.82 (br.s, 1 H, NH); 3.07–3.21 (m, 5 H, C(9)H<sub>2</sub>, C(10)H<sub>2</sub>, C(2)HH); 3.26 (AB system,  $\Delta\delta = 0.06$ , 2 H, C(6)H<sub>2</sub>,  $J_{AB} = 15.9$  Hz); 3.49–3.61 (m, 1 H, C(2)HH); 3.89 (s, 3 H, MeO); 3.95 (dt, 1 H, C(3)HH,  $^2J = 17.3$  Hz,  $^3J = 4.4$  Hz); 4.38 (ddd, 1 H, C(3)HH,  $^2J = 17.3$  Hz,  $^3J = 9.1$  and 4.6 Hz); 6.89 (dd, 1 H, H(3'),  $J_o = 7.8$  Hz,  $J_m = 0.9$  Hz); 6.96 (td, 1 H, H(5'),  $J_o = 7.8$  Hz,  $J_m = 0.9$  Hz); 7.31 (d, 1 H, H(6'),  $J_o = 7.8$  Hz); 7.33 (td, 1 H, H(4'),  $J_o = 7.8$  Hz,  $J_m = 1.7$  Hz).

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