Selective Synthesis and Cycloaddition Reactions of New Azomethine Imines Containing a 1,2,4-Triazine Ring

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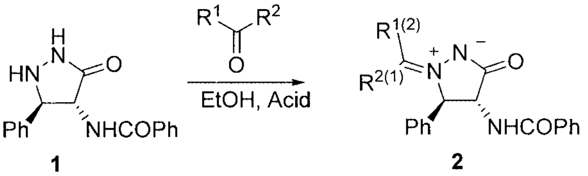
The reactions of 4,5-dihydro[1,2,4]triazolo[3,4-*c*]benzo[1,2,4]triazines with aromatic aldehydes gave stable iminium salts which were deprotonated to give new azomethine imines. These new mesomeric betaines underwent 1,3-dipolar cyclization reactions to yield new tetra- and pentacyclic heterocycles. X-ray analysis and decoupling NMR experiments unambiguously supported the fact that these transformations are regioselective and that the iminium moieties were formed at the N-5 atom in each case.

Introduction

In earlier publications[1–10] it was disclosed that five-membered nitrogen heterocycles containing the NH–NH substructure within the ring can react with aldehydes to give stable cyclic azomethine imines, a group of reactive 1,3-dipoles highly suitable for further transformations, mainly through cycloaddition reactions. For example, tetrahydropyrazolone derivative **1** gave the azomethine imine derivative **2** (Scheme 1).[1] Similar related transformations have also been carried out and a review[11] of this type of transformation has been published. More recently[12] analogous transformations of saturated pyridazines[13,14] and oxadiazinones[15,16] have also been reported.



1 **2**

Scheme 1.

Results

As a continuation of these studies the question arose as to whether unsaturated six-membered heterocycles could be similarly transformed and owing to the results of some earlier intensive investigations on triazines[17–19] we decided to investigate the possible transformations of this ring system. Although partially reduced 1,2,4-triazines and their benzologs (i.e. derivatives containing the required NH–NH moiety) can be obtained relatively easily by treatment of aromatic 1,2,4-triazines with mild reducing agents to yield 1,2-dihydrotriazines, these compounds are extremely air-sensitive and their use as possible starting compounds was, therefore, limited. Earlier we found, however, that tricyclic 4,5-dihydro[1,2,4]triazolo[3,4-*c*]benzo[1,2,4]triazines **4** containing a fused triazole ring at the *c* bond of the triazine ring are readily available from the parent heteroaromatic triazolobenzotriazines **3** and are relatively stable. This stability is obviously due to the fact that after the partial reduction of the central triazine ring the dihydro derivative still contains two aromatic (benzene and triazole) rings. The relatively facile access to such six-membered dihydro compounds prompted us to select these derivatives as model compounds in the planned transformations (Scheme 2).

To this end, four different [1,2,4]triazolobenzo[1,2,4]triazines **3a**–**d** were prepared and transformed into the corresponding 4,5-dihydro derivatives **4a**–**d**. When these compounds were treated with an aldehyde in ethanol in the presence of tetrafluoroboric acid, orange crystals were formed. By using different aryl and arylethenylaldehydes, iminium salts **5a**–**m** were obtained in good yields.

Although elemental analysis and NMR spectroscopic data supported the formation of the expected structure, at this stage of research it was not possible to distinguish between positional [5- (**A**, **B**) and 4-substituted (**C**, **D**) derivatives] and geometric isomers [(*E*) (**B**, **C**) and (*Z*) (**A**, **D**) isomers] (Figure 1). Furthermore, the structural assignment also proved to be difficult because these salts, when dis-

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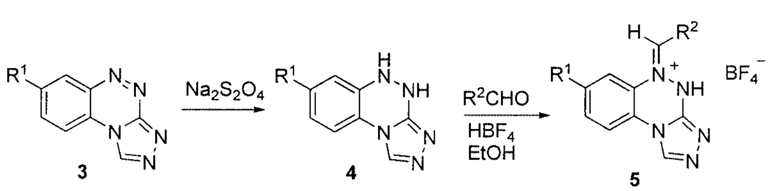


	R^1
a	H
b	Cl
c	CH_3
d	OCH_3

	R^1	R^2
a	H	$4\text{-}CH_3O\text{-}C_6H_4$
b	Cl	$4\text{-}CH_3O\text{-}C_6H_4$
c	Cl	$4\text{-}CH_3\text{-}C_6H_4$
d	Cl	$C_6H_5\text{-}CH{=}CH\text{-}$
e	CH_3	$4\text{-}CH_3O\text{-}C_6H_4$
f	CH_3	$4\text{-}CH_3\text{-}C_6H_4$
g	CH_3	$C_6H_5\text{-}C_6H_4$
h	CH_3	$C_6H_5\text{-}CH{=}CH\text{-}$
i	CH_3	$4\text{-}NO_2\text{-}C_6H_4\text{-}CH{=}CH\text{-}$
j	CH_3	$4\text{-}Cl\text{-}C_6H_4$
k	CH_3	$4\text{-}CH(CH_3)_2\text{-}C_6H_4$
l	OCH_3	$4\text{-}CH_3O\text{-}C_6H_4$
m	OCH_3	$4\text{-}CH_3\text{-}C_6H_4$

Scheme 2.

solved in DMSO for NMR analyses, were slowly hydrolyzed to the starting compounds, and the signals emanating from these impurities made the interpretation of the spectra quite ambiguous. Thus, we decided to continue with the planned synthetic route in the hope that it would be possible to determine the exact structure of through one of the later products.

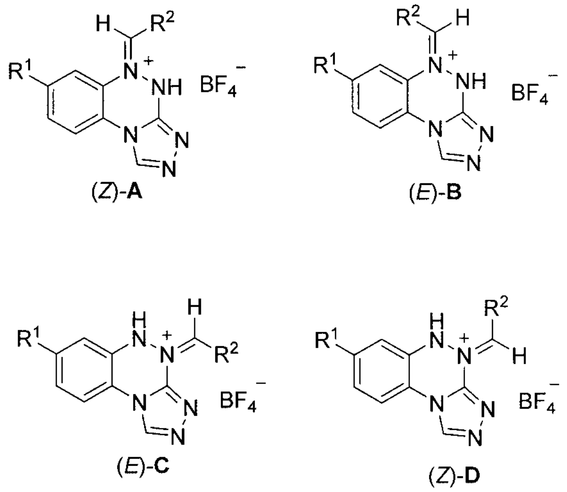


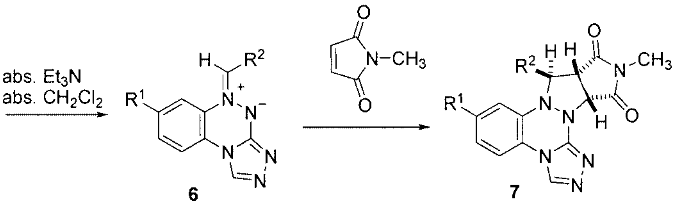
Figure 1. Possible structures of the obtained azomethine iminium salts: positional [5- (**A**, **B**) and 4-substituted (**C**, **D**) derivatives] and geometric isomers [(*E*) (**B**, **C**) and (*Z*) (**A**, **D**) isomers].

Iminium salts **5** when treated with a base (e.g. triethylamine) underwent deprotonation to give the expected mesomeric betaine azomethine imines **6**. We have found that, in contrast to related five-membered heterocycles,[1] these compounds are relatively unstable on storage in the solid form and particularly in solution. In the case of derivative **5e** we found, fortunately, that the product obtained (**6e**) after treatment with a base is isolable as a deep-red solid. Even though our efforts to purify this compound either by chromatography or recrystallization failed, it was pure enough for UV analysis. The significant negative solvatochromism[20] observed in the UV spectra of **6e** recorded in solvents of different polarity convincingly supported the betainic character of this compound (a bathochromic shift of 40 nm was observed by changing the solvent from aqueous ethanol to dichloromethane).

The instability of these mesomeric betaine compounds **6a**,**b**,**e**,**f**,**g**,**h**, however, could easily be circumvented by their in situ preparation and subsequent 1,3-dipolar cycloaddition reactions. Thus, treatment of iminium salts **5a**,**b**, **e**,**f**,**g**,**h** and *N*-methylmaleimide in dichloromethane in the presence of triethylamine successfully yielded the pentacyclic cycloadducts **7a**,**b**,**e**,**f**,**g**,**h** as stable colorless crystals (Scheme 3).

Crystals of derivative **7e** proved to be suitable for X-ray analysis which provided unambiguous details of its structure including its stereochemistry (Figure 2). Selected bond parameters are listed in Table 1.

The C1–N1–C3–C8–N5–N4 triazine has a quasi envelope structure with the N4 atom at the tip. The plane of the C1–N1–C3–C8–N5 atoms makes an angle of 10.8(2)° with the plane of the connecting C1–N1–C2–N2–N3 triazole ring and an angle of 3.2(2)° with the plane of the C3–C4–C5–C6–C7–C8 phenyl ring. The N4–N5–C15–C12–C11 pyrazolidine ring has an envelope structure with the N5 atom at the tip. The plane of this ring is at an angle of 62.0(1)° to the plane of the *N*-methylpyrrolidine (C11–C10–N6–C13–C12) ring. The pyrrolidine ring is fused to the pyrazolidine in a *cis* orientation. The 4-methoxyphenyl substituent on the C15 atom of the pyrazolidine ring assumes an axial position. The inclination angle between the plane of the N4–C11–C12–C15 atoms and that of the phenyl ring is 81.8(1)°. Both N4 and N5 atoms adopt a pyramidal conformation,



	R^1	R^2
a	H	$4\text{-}CH_3O\text{-}C_6H_4\text{-}$
b	Cl	$4\text{-}CH_3O\text{-}C_6H_4\text{-}$
e	CH_3	$4\text{-}CH_3O\text{-}C_6H_4\text{-}$
f	CH_3	$4\text{-}CH_3\text{-}C_6H_4\text{-}$
g	CH_3	$C_6H_5\text{-}C_6H_4\text{-}$
h	CH_3	$C_6H_5\text{-}CH{=}CH\text{-}$

Scheme 3.

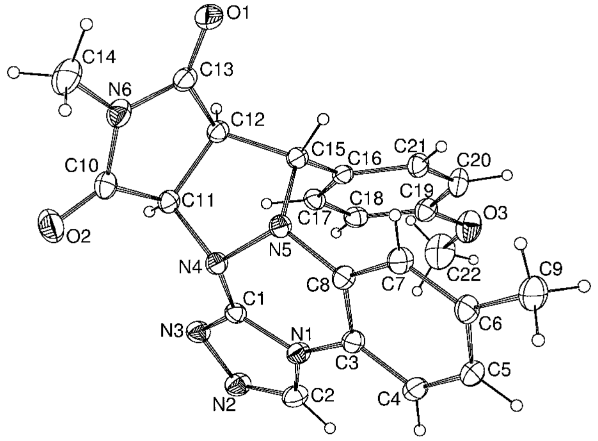


Figure 2. The perspective view of the X-ray structure of **7e** (ellipsoid probability of 20% for better view). An arbitrary numbering is used for an easier interpretation of the structure.

and are 0.409(3) and 0.437(3) Å, respectively, above the plane generated by the three connected atoms.

From this structural elucidation it was finally deduced that only the 5-substituted azomethine imine **6** was involved in the reaction, that is, the parent iminium salt **5** has the 5-substituted structure (i.e. structures **C** and **D** in Figure 1 can be excluded), but it was still necessary to determine whether the (*Z*) or (*E*) geometric isomeric structures (**A** or **B** in Figure 1) were involved. The NOE and ^{1}H–^{13}C HMBC measurements,[21] however, provided unambiguous evidence that the R^{2} group, as shown in the structure of type **5A**, lies in the vicinity of the ring-NH moiety, that is, the (*Z*) isomer is involved.

Significant NOEs (5–8%) were measured between the 6-H and 11-H protons and characteristic correlations transmitted by three bonds were detected between the 11-H/C5a and 9-H/C5a atom pairs (Figure 3). The 9-H doublet was easily assigned as a result of the coupling pattern characteristic of a 1,2,4-trisubstituted benzene ring (in this case condensed to the triazolotriazine moiety). The steric proximity of 9-H and 1-H is reflected by the considerable NOE (11–15%) observed for this proton pair.

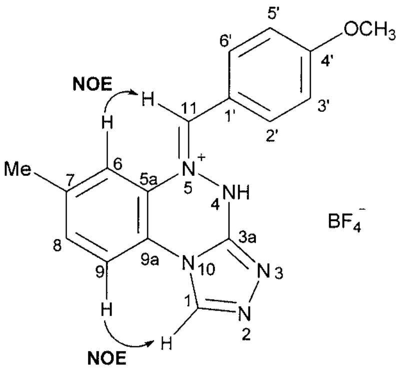
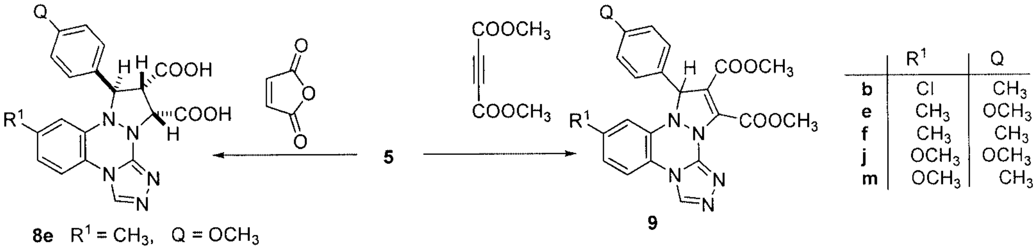


Figure 3. Most important NOE interactions supporting the structure of type **5A**.

Following the assignment of the ^{1}H NMR signals, each nitrogen atom in the [1,2,4]triazolo[3,4-*c*]triazine ring system could be identified by means of ^{1}H–^{15}N HMBC experiments. Three nitrogen signals of the triazole units were detected through correlations with the 1-H proton. The characteristic upfield-shifted signal of N10 (≈148–150 ppm on the scale defined by the reference signal of liquid ammonia at 0 ppm) also correlates with the 9-H proton. The two other triazine nitrogen atoms (N4 and N5) were identified by their correlation with the 11-H proton. It is very important to note that the 6-H proton exhibits a cross peak with

Table 1. Selected bond lengths, angles and torsion angles of **7e**.

Bond lengths [Å]			
N(4)–C(1)	1.384(3)	C(10)–C(11)	1.511(4)
N(4)–C(11)	1.468(3)	C(11)–C(12)	1.540(3)
N(4)–N(5)	1.468(2)	C(12)–C(13)	1.501(3)
N(5)–C(8)	1.437(3)	C(12)–C(15)	1.530(3)
N(5)–C(15)	1.508(3)	C(15)–C(16)	1.505(3)
Angles [°]			
C(1)–N(4)–C(11)	115.7(2)	N(4)–C(11)–C(10)	110.1(2)
C(1)–N(4)–N(5)	116.3(2)	N(4)–C(11)–C(12)	106.2(2)
C(11)–N(4)–N(5)	104.4(2)	C(10)–C(11)–C(12)	114.4(2)
C(8)–N(5)–N(4)	112.7(2)	C(13)–C(12)–C(15)	112.5(2)
C(8)–N(5)–C(15)	116.0(2)	C(13)–C(12)–C(11)	104.5(2)
N(4)–N(5)–C(15)	106.0(2)	C(15)–C(12)–C(11)	106.0(2)
C(10)–N(6)–C(13)	113.5(2)	C(16)–C(15)–N(5)	114.4(2)
N(2)–C(2)–N(1)	111.3(2)	C(16)–C(15)–C(12)	116.1(2)
C(3)–C(8)–N(5)	122.0(2)	N(5)–C(15)–C(12)	99.4(2)
Torsion angles [°]			
C(1)–N(4)–N(5)–C(8)	–38.8(3)	N(4)–N(5)–C(8)–C(3)	23.8(3)
C(11)–N(4)–N(5)–C(8)	–167.7(2)	N(5)–N(4)–C(11)–C(10)	–93.1(2)
C(1)–N(4)–N(5)–C(15)	89.1(2)	N(5)–N(4)–C(11)–C(12)	19.9(2)
C(11)–N(4)–N(5)–C(15)	–39.7(2)	N(4)–C(11)–C(12)–C(15)	6.1(2)
C(11)–N(4)–C(1)–N(1)	155.1(2)	N(4)–N(5)–C(15)–C(12)	42.0(2)
N(5)–N(4)–C(1)–N(1)	32.0(3)	C(11)–C(12)–C(15)–N(5)	–28.4(2)



	R1	Q
b	Cl	CH_3
e	CH_3	OCH_3
f	CH_3	CH_3
j	OCH_3	OCH_3
m	OCH_3	CH_3

Scheme 4.

the signal of the N5 atom in the iminium group (200–220 ppm), which is more downfield shifted than that of N4 (180–190 ppm), thus providing further support for the involvement of structure **A**.

Similar to the above findings we have also found that the cycloaddition reaction of **6** (obtained in situ from iminium salts **5**) can be extended to other dipolarophiles. Thus, its reaction with maleic anhydride gave, after work up in the presence of water, a dicarboxylic acid derivative **8**, whereas its reaction with dimethyl acetylenedicarboxylate (DMAD) yielded partially unsaturated fused pyrazoles **9b**,**e**,**f**,**j**,**m** (Scheme 4).

Conclusions

To the best of our knowledge the new azomethine imines produced in this work are the first examples of such mesomeric betaines containing a triazine moiety. The relative easy access to these reactive compounds, the high yields and the successful cycloaddition reactions indicate the preparative importance of this work. The extension of these transformations to unsymmetrical dipolarophiles, including reagents with cumulated double bonds, is in progress.

Experimental Section

Melting points were determined with a Büchi apparatus and are uncorrected. The IR spectra were recorded with a Thermo Nicolet AVATAR 320 FT-IR spectrophotometer; the NMR spectra were recorded with a Varian UNITY INOVA spectrometer (200 and 400 MHz for ^1H and 100 MHz for ^{13}C) and a Bruker 500 DRX spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C and 50 MHz for ^{15}N).

X-ray Crystal Diffraction of 7e: A colorless, plate crystal of **7e** with approximate dimensions of 0.37 × 0.25 × 0.10 mm was mounted on a glass fibre. All X-ray diffraction measurements were taken with a Rigaku AFC6S diffractometer using graphite monochromated Cu-K_α radiation (λ = 1.54178 Å). Cell constants and the orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 22 carefully centered reflections. The data were collected at a temperature of 293 K using the $\omega/2\theta$ scan technique up to a maximum 2θ value of 150.3°. The backgrounds were measured at half the total time of the peak scans. The intensities of three representative reflections were measured after every 150 reflections. Of the 8380 reflections collected, 3975 were unique (R_{int} = 0.0863). Linear absorption coefficient: μ(Cu-K_α) = 0.788 mm^{-1}. An empirical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.904 and 0.994).[22] The data were corrected for Lorentz and polarization effects.

Data processing was carried out by using the software supplied with the diffractometer. The structure was solved by direct methods.[23] All calculations were performed using the teXsan Crystal Structure Analysis Package[24] except for refinement on F^2, which was performed using the SHELXL-97 program[25] by the full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated based upon geometric evidence and their positions were refined by the riding model. The hydrogen atoms of the two methyl groups (C9 and C14) seem to be disordered.

Crystallographic Data for Compound 7e: $C_{22}H_{20}N_6O_3$, M_w = 416.44, triclinic, space group $P1$, a = 10.764(2), b = 12.582(3), c = 8.205(1) Å, α = 92.71(2), β = 110.44(1), γ = 103.89(2)°, V = 1000.4(3) Å^3, Z = 2, D_c = 1.382 Mg m^{-3}, F(000) = 436. Final R indices are R_1 = 0.0540, wR_2 = 0.1219 for $I > 2\sigma(I)$ and R_1 = 0.1134, wR_2 = 0.1463 for all data. The maximum and minimum peaks on the final difference Fourier map correspond to 0.167 and –0.216 e Å^{-3}, respectively.

CCDC-267920 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[1,2,4]Triazolobenzo[1,2,4]triazines (3a–d) and their 4,5-Dihydro Derivatives 4a–d: These compounds were prepared according to previously reported literature procedures.[19]

General Method for the Preparation of Iminium Salts 5: A mixture of the appropriate 4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4**, 5 mmol), 50% aqueous tetrafluoroboric acid (1.5 mL), an appropriate aldehyde (10 mmol) and ethanol (30 mL) were stirred at room temp. for 10 min, whereupon a yellow colored precipitate was formed. The product was filtered off, dried and stored in an exsiccator over P_2O_5 and NaOH for one day, and recrystallized from acetonitrile to give the pure product.

(5*Z*)-5-(4-Methoxybenzylidene)-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5a): This compound was obtained from 4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4a**, 0.86 g) and anisaldehyde (1.36 g, 1.21 mL): yellow needles (1.675 g, 89% yield). M.p. 239–240 °C. IR (KBr): $\tilde{\nu}$ = 3547, 3326, 3149, 1644, 1592, 1552, 1512, 1430, 1315, 1721, 1175, 1050, 1009, 952, 839, 766, 534 cm^{-1}. ^1H NMR ([D$_6$]DMSO, 500 MHz): δ = 3.91 (s, 3 H, CH_3), 7.18 (d, J = 9.1 Hz, 2 H, 3′-H, 5′-H), 7.63 (t, J = 7.8 Hz, 1 H, 7-H), 7.78 (t, J = 7.8 Hz, 1 H, 8-H), 7.98 (d, J = 7.8 Hz, 1 H, 9-H), 8.27 (d, J = 7.8 Hz, 1 H, 6-H), 8.58 (d, J = 9.1 Hz, 2 H, 2′-H, 6′-H), 8.69 (br. s, 1 H, $N^+=CH$), 9.19 (s, 1 H, 1-H), 13.84 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 56.8 (C–OCH_3), 115.6 (C-3′, C-5′), 117.5 (C-9), 120.5 (C-6), 122.3 (C-1′), 124.5 (C-5a), 126.1 (C-9a), 129.6 (C-7), 132.9

(C-8), 134.4 (C-1), 137.2 (C-2′, C-6′), 140.7 (N$^+$=*C*H), 149.4 (C-3a) ppm. $C_{16}H_{14}BF_4N_5O$ (379.12): calcd. C 50.69, H 3.72, N 18.47; found C 50.55, H 3.42, N 18.33.

(5*Z*)-7-Chloro-5-(4-methoxybenzylidene)-4,5-dihydro[1,2,4]triazolo-[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5b): This compound was obtained from 7-chloro-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4b**, 1.04 g) and anisaldehyde (1.36 g, 1.2 mL): yellow needles (1.99 g, 96% yield). M.p. 240–241 °C. IR (KBr): ṽ = 3307, 3152, 1642, 1598, 1556, 1510, 1264, 1176, 1064, 951, 864, 534 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 3.89 (s, 3 H, CH$_3$), 7.10 (d, *J* = 8.6 Hz, 2 H, 3′-H, 5′-H), 7.81 (br. d, *J* = 8.8 Hz, 1 H, 8-H), 7.94 (d, *J* = 8.8 Hz, 1 H, 9-H), 8.36 (br. s, 1 H, 6-H), 8.46 (d, *J* = 8.6 Hz, 2 H, 2′-H, 6′-H), 8.58 (s, 1 H, N$^+$=C*H*), 9.23 (s, 1 H, 1-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 56.8 (C–CH$_3$), 115.6 (C-3′, C-6′), 119.2 (C-9), 120.3 (C-6), 121.9 (C-1′), 125.0 (C-9a), 125.1 (C-5a), 133.2 (C-8), 133.8 (C-7), 134.3 (C-1), 137.4 (C-2′, C-6′), 141.1 (N$^+$=*C*H), 149.1 (C-3a), 165.2 (C-4′) ppm. $C_{16}H_{13}BClF_4N_5O$ (413.56): calcd. C 46.47, H 3.17, N 16.93; found C 46.84, H 3.32, N 17.21.

(5*Z*)-7-Chloro-5-(4-methylbenzylidene)-4,5-dihydro[1,2,4]triazolo-[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5c): This compound was obtained from 7-chloro-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4b**, 1.04 g) and *p*-tolualdehyde (1.20 g, 1.18 mL): yellow needles (1.732 g, 87% yield). M.p. 239–240 °C. IR (KBr): ṽ = 3237, 3156, 1642, 1506, 1445, 1326, 1068, 951, 862, 500 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 2.43 (s, 3 H, CH$_3$), 7.42 (d, *J* = 8.1 Hz, 2 H, 3′-H, 5′-H), 7.91 (br. d, *J* = 8.8 Hz, 1 H, 8-H), 8.02 (d, *J* = 8.8 Hz, 1 H, 9-H), 8.44 (d, *J* = 8.1 Hz, 2 H, 2′-H, 6′-H), 8.50 (br. s, 1 H, 6-H), 8.72 (s, 1 H, N$^+$=C*H*), 9.23 (s, 1 H, 1-H), 13.67 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 22.5 (C–CH$_3$), 119.3 (C-9), 120.7 (C-6), 125.2 (C-9a), 125.3 (C-5a), 126.9 (C-1′), 130.5 (C-3′, C-5′), 133.2 (C-8), 133.8 (C-7), 134.5 (C-1), 134.6 (C-2′, C-6′), 141.3 (N$^+$=CH), 146.9 (C-4′), 149.1 (C-3a) ppm. $C_{16}H_{13}BClF_4N_5$ (397.57): calcd. N 17.62; found N 17.99.

(5*Z*)-7-Chloro-5-[(2*E*)-3-phenylprop-2-en-1-ylidene]-4,5-dihydro-[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5d): This compound was obtained from 7-chloro-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4b**, 1.04 g) and cinnamaldehyde (1.32 g, 1.26 mL): orange needles (1.908 g, 93% yield). M.p. 238–239 °C. IR (KBr): ṽ = 3266, 3079, 1645, 1584, 1504, 1432, 1224, 1189, 1063, 1003, 948, 759, 687, 628, 525 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 7.47–7.53 (m, 3 H, 3′-H, 4′-H, 5′-H), 7.67 (dd, *J* = 15.8, *J* = 9.3 Hz, 1 H, CH–C*H*=CH), 7.69 (d, *J* = 7.6 Hz, 2 H, 2′-H, 6′-H), 7.75 (d, *J* = 15.8 Hz, 1 H, CH–CH=C*H*), 7.89 (br. d, *J* = 8.3 Hz, 1 H, 8-H), 8.01 (d, *J* = 8.3 Hz, 1 H, 9-H), 8.36 (br. s, 1 H, 6-H), 8.82 (d, *J* = 9.3 Hz, 1 H, N$^+$=C*H*), 9.17 (s, 1 H, 1-H), 13.90 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 118.4 (CH–*C*H=CH), 119.3 (C-9), 119.9 (C-6), 124.8 (C-5a), 125.5 (C-9a), 129.8 (C-2′, C-6′), 130.4 (C-3′, C-5′), 132.9 (C-4′), 133.2 (C-8), 133.8 (C-7), 134.4 (C-1), 135.6 (C-1′), 143.1 (N$^+$=*C*H), 149.1 (C-3a), 152.3 (CH–CH=*C*H) ppm. $C_{17}H_{13}BClF_4N_5$ (409.58): calcd. C 49.85, H 3.20, N 17.10; found C 49.85, H 3.28, N 16.75.

(5*Z*)-5-(4-Methoxybenzylidene)-7-methyl-4,5-dihydro[1,2,4]triazolo-[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5e): This compound was obtained from 7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4c**, 0.94 g) and anisaldehyde (1.36 g, 1.22 mL): yellow needles (1.895 g, 96% yield). M.p. 204–207 °C. IR (KBr): ṽ = 3148, 2931, 1640, 1600, 1271, 1180, 1064, 956 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 2.41 (s, 3 H, CH$_3$), 3.91 (s, 3 H, H–OCH$_3$), 7.14 (d, *J* = 9.1 Hz, 2 H, 3′-H, 5′-H), 7.56 (br. d, *J* = 8.3 Hz, 1 H, 8-H), 7.84 (d, *J* = 8.3 Hz, 1 H, 9-H), 8.06 (br. s, 1 H, 6-H), 8.52 (d, *J* = 9.1 Hz, 2 H, 2′-H, 6′-H), 8.59 (s, 1 H, N$^+$=C*H*), 9.23 (s, 1 H, 1-H), 13.8 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.7 (C–CH$_3$), 56.8 (C–OCH$_3$), 115.6 (C-3′, C-5′), 117.3 (C-9), 120.1 (C-6), 122.2 (C-1′), 123.6 (C-9a), 124.0 (C-5a), 133.5 (C-1), 134.2 (C-8), 137.0 (C-2′, C-6′), 139.5 (N$^+$=*C*H), 140.2 (C-7), 145.6 (C-4′), 149.0 (C-3a) ppm. ^{15}N NMR ([D$_6$]DMSO): δ = 149 (N-10), 165 (N-3), 184 (N-4), 215 (N-5), 272 (N-2) ppm. $C_{17}H_{16}BF_4N_5O$ (393.15): calcd. C 51.94, H 4.10, N 17.81; found C 52.38, H 4.12, N 17.61.

(5*Z*)-7-Methyl-5-(4-methylbenzylidene)-4,5-dihydro[1,2,4]triazolo-[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5f): This compound was obtained from 7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4c**, 0.94 g) and *p*-tolualdehyde (1.20 g, 1.18 mL): yellow needles (1.837 g, 97% yield). M.p. 234–237 °C. IR (KBr): ṽ = 3274, 3157, 1642, 1592, 1553, 1520, 1458, 1187, 1067, 953, 818, 500 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 2.42 (s, 3 H, H–C$_6$H$_4$CH$_3$), 2.43 (s, 3 H, CH$_3$), 7.39 (d, *J* = 8.1 Hz, 2 H, 3′-H, 5′-H), 7.59 (br. d, *J* = 8.3 Hz, 1 H, 8-H), 7.87 (d, *J* = 8.3 Hz, 1 H, 9-H), 8.12 (br. s, 1 H, 6-H), 8.40 (d, *J* = 8.1 Hz, 2 H, 2′-H, 6′-H), 8.62 (s, 1 H, N$^+$=C*H*), 9.16 (s, 1 H, 1-H), 13.92 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.7 (C–CH$_3$), 22.4 (C–C$_6$H$_4$*C*H$_3$), 117.4 (C-9), 120.2 (C-6), 123.6 (C-9a), 124.0 (C-5a), 126.9 (C-1′, C-8), 130.4 (C-3′, C-5′), 133.9 (N$^+$=*C*H), 134.3 (C-2′, C-6′), 139.3 (C-1), 140.2 (C-7), 146.1 (C-4′), 148.8 (C-3a) ppm. ^{15}N NMR ([D$_6$]DMSO): δ = 149 (N-10), 166 (N-3), 187 (N-4), 221 (N-5), 273 (N-2) ppm. $C_{17}H_{16}BF_4N_5$ (377.15): calcd. C 54.14, H 4.28, N 18.57; found C 54.27, H 4.34, N 18.44.

(5Z)-5-(Biphenyl-4-ylmethylene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5g): This compound was obtained from 7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4c**, 0.94 g) and 4-phenylbenzaldehyde (1.82 g): yellow needles (2.073 g, 94% yield). M.p. 238–240 °C. IR (KBr): ṽ = 3143, 1641, 1601, 1545, 1149, 1067, 955, 766 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 2.46 (s, 1 H, CH$_3$), 7.45 (t, *J* = 7.6 Hz, 1 H, 4′′-H), 7.51 (t, *J* = 7.6 Hz, 2 H, 3′′-H, 5′′-H), 7.63 (br. d, *J* = 8.3 Hz, 1 H, 8-H), 7.82 (d, *J* = 7.6 Hz, 2 H, 2′′-H, 6′′-H), 7.91 (d, *J* = 8.3 Hz, 1 H, 9-H), 7.93 (d, *J* = 8.6 Hz, 2 H, 3′-H, 5′-H), 8.20 (br. s, 1 H, 6-H), 8.61 (d, *J* = 8.6 Hz, 2 H, 2′-H, 6′-H), 8.75 (s, 1 H, N$^+$=C*H*), 9.13 (s, 1 H, 1-H), 13.8 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.5 (C–CH$_3$), 117.5 (C-9), 120.3 (C-6), 123.8 (C-9a), 124.1 (C-5a), 127.7 (C-1′), 127.8 (C-3′, C-5′), 128.2 (C-2′′, C-6′′), 129.5 (C-4′′), 130.0 (C-3′′, C-5′′), 134.1 (C-8), 134.8 (C-1), 135.0 (C-2′, C-6′), 138.6 (N$^+$=*C*H), 139.1 (C-1′′), 145.6 (C-4′), 149.0 (C-3a) ppm. ^{15}N NMR ([D$_6$]DMSO): δ = 150 (N-10), 167 (N-3), 189 (N-4), 222 (N-5), 273 (N-2) ppm. $C_{22}H_{18}BF_4N_5$ (439.22): calcd. N 15.95; found N 16.21.

(5*Z*)-7-Methyl-5-[(2*E*)-3-phenylprop-2-en-1-ylidene]-4,5-dihydro-[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5h): This compound was obtained from 7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4c**, 0.94 g) and cinnamaldehyde (1.32 g, 1.26 mL): orange needles (1.86 g, 95% yield). M.p. 221–224 °C. IR (KBr): ṽ = 3291, 3134, 3076, 1643, 1588, 1520, 1454, 1224, 1158, 1064, 954, 756, 686, 627, 525 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 2.39 (s, 3 H, CH$_3$), 7.49–7.44 (m, 3 H, 3′-H, 4′-H, 5′-H), 7.57 (br. d, *J* = 8.3 Hz, 1 H, 8-H), 7.62 (br. d, 2 H, 2′-H, 6′-H), 7.63 (dd, J_1 = 8.8, J_2 = 15.8 Hz, 1 H, CH–C*H*=CH), 7.68 (d, *J* = 15.8 Hz, 1 H, CH–CH=C*H*), 7.97 (br. s, 1 H, 6-H), 8.71 (d, *J* = 8.8 Hz, 1 H, N$^+$=C*H*), 9.11 (s, 1 H, 1-H), 13.88 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.7 (C–CH$_3$), 117.4 (C-9), 118.4 (CH–*C*H=CH), 119.4 (C-6), 123.4 (C-5a), 123.8 (C-9a), 129.5 (C-2′, C-6′), 130.3 (C-3′, C-5′), 132.6 (C-4′), 134.1 (C-8), 134.2 (C-1), 135.6 (C-1′), 140.1 (C-7), 141.0 (N$^+$=*C*H), 148.8 (C-3a), 150.9 (CH–CH=*C*H) ppm. ^{15}N NMR ([D$_6$]DMSO): δ =

149 (N-10), 165 (N-3), 187 (N-4), 217 (N-5), 272 (N-2) ppm. $C_{18}H_{16}BF_4N_5$ (389.16): calcd. C 55.55, N 18.00; found C 55.65, N 17.83.

(5*Z*)-7-Methyl-5-[(2*E*)-3-(4-nitrophenyl)prop-2-en-1-ylidene]-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5i): This compound was obtained from 7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4c**, 0.94 g) and *p*-nitrocinnamaldehyde (1.77 g): deep-red needles (1.94 g, 88% yield). M.p. 227–229 °C. IR (KBr): $\tilde{\nu}$ = 3268, 3131, 3074, 1642, 1593, 1545, 1515, 1451, 1342, 1295, 1225, 1190, 1143, 1069, 1007, 956, 866, 823, 747, 687, 640, 524, 449, 417 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 200 MHz): δ = 2.41 (s, 3 H), 7.67 (d, *J* = 8.8 Hz, 1 H), 7.76 (d, *J* = 16.1 Hz, 1 H), 7.88 (dd, *J* = 9.1, *J* = 16.1 Hz, 1 H), 7.95 (m, 3 H), 8.1 (s, 1 H), 8.29 (d, *J* = 8.8 Hz, 2 H), 8.82 (d, *J* = 9.1 Hz, 1 H), 9.23 (s, 1 H), 14.0 (br.s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.0, 116.9, 118.9, 121.5, 122.9, 123.4, 124.1, 125.0 (2 C), 129.6 (2 C), 129.8, 130.1, 133.7, 137.0, 138.7, 139.4, 141.0, 145.8, 148.2 ppm. $C_{18}H_{15}BF_4N_6O_2$ (434.16): calcd. C 49.80, H 3.48, N 19.36; found C 49.65, H 3.30, N 19.16.

(5*Z*)-5-(4-Chlorobenzylidene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5j): This compound was obtained from 7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4c**, 0.94 g) and 4-chlorobenzaldehyde (1.40 g): yellow needles (1.916 g, 96% yield). M.p. 222–225 °C. IR (KBr): $\tilde{\nu}$ = 3272, 3154, 1638, 1584, 1518, 1457, 1287, 1090, 956, 824, 504 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 2.40 (s, 3 H, CH$_3$), 7.61 (d, *J* = 8.0 Hz, 1 H, 8-H), 7.66 (d, *J* = 8.6 Hz, 2 H, 3′-H, 5′-H), 7.89 (d, *J* = 8.0 Hz, 1 H, 9-H), 8.15 (s, 1 H, 6-H), 8.50 (d, *J* = 8.6 Hz, 2 H, 2′-H, 6′-H), 8.72 (s, 1 H, N$^+$=C*H*), 9.19 (s, 1 H, 1-H), 14.07 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.6 (C–CH$_3$), 117.7 (C-9), 120.6 (C-6), 123.9 (C-9a), 124.2 (C-5a), 130.3 (C-3′, C-5′), 134.6 (C-1, C-8), 135.7 (C-2′, C6′), 138.2 (N$^+$=*C*H), 139.3 (C-4′), 140.2 (C-7), 148.9 (C-3a) ppm. ^{15}N NMR ([D$_6$]DMSO): 150.1 (N-10), 167.2 (N-3), 188.6 (N-4), 224.4 (N-5), 273.2 (N-2) ppm. $C_{16}H_{13}BClF_4N_5$ (397.57): calcd. C 48.34, H 3.30, N 17.62; found C 48.44, H 3.37, N 17.51.

(5*Z*)-5-(4-Isopropylbenzylidene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5k): This compound was obtained from 7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4c**, 0.94 g) and cuminaldehyde (1.48 g, 1.51 mL): yellow needles (1.648 g, 81% yield). M.p. 237–238 °C. IR (KBr): $\tilde{\nu}$ = 3250, 3135, 2971, 1643, 1551, 1520, 1453, 1194, 1067, 953, 838, 557, 520 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 1.27 (d, *J* = 7.1 Hz, 6 H, H–CH(C*H*$_3$)$_2$), 2.46 (s, 3 H, CH$_3$), 3.03 (sept, *J* = 7.1 Hz, 1 H, H–C*H*(CH$_3$)$_2$), 7.53 (d, *J* = 8.3 Hz, 2 H, 3′-H, 5′-H), 7.63 (br. d, *J* = 8.3 Hz, 1 H, 8-H), 7.92 (d, *J* = 8.3 Hz, 1 H, 9-H), 8.20 (br. s, 1 H, 6-H), 8.51 (d, *J* = 8.3 Hz, 2 H, 2′-H, 6′-H), 8.72 (br. s, 1 H, N$^+$=C*H*), 9.21 (s, 1 H, 1-H), 13.97 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.7 (C–CH$_3$), 24.2 (C–CH(*C*H$_3$)$_2$), 34.7 (C–*C*H(CH$_3$)$_2$), 116.8 (C-9), 120.4 (C-6), 123.8 (C-9a), 124.1 (C-5a), 127.4 (C-1′), 127.9 (C-3′, C-5′), 134.0 (C-8), 134.4 (C-1), 134.6 (C-2′, C-6′), 139.8 (N$^+$=*C*H), 140.1 (C-7), 149.0 (C-3a), 156.4 (C-4′) ppm. ^{15}N NMR ([D$_6$]DMSO): δ = 149 (N-10), 166 (N-3), 187 (N-4), 221 (N-5), 273 (N-2) ppm. $C_{19}H_{20}BF_4N_5$ (405.20): calcd. C 56.32, H 4.98, N 17.28; found C 56.72, H 4.92, N 16.90.

(5*Z*)-7-Methoxy-5-(4-methoxybenzylidene)-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5l): This compound was obtained from 7-methoxy-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4d**, 1.02 g) and anisaldehyde (1.36 g, 1.21 mL): yellow needles (1.73 g, 84% yield). M.p. 239–240 °C. IR (KBr): $\tilde{\nu}$ = 3370, 3082, 2938, 1644, 1601, 1554, 1521, 1459, 1335, 1266, 1185, 1084, 956, 837, 534 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 3.93 (s, 6 H, H–OCH$_3$), 7.21 (d, *J* = 9.1 Hz, 2 H, 3′-H, 5′-H), 7.42 (dd, J_1 = 9.1, J_2 = 2.2 Hz, 1 H, 8-H), 7.83 (d, J_2 = 2.2 Hz, 1 H, 6-H), 7.96 (d, J_1 = 9.1 Hz, 1 H, 9-H), 8.61 (d, *J* = 9.1 Hz, 2 H, 2′-H, 6′-H), 8.67 (br. s, 1 H, N$^+$=C*H*), 9.17 (s, 1 H, 1-H), 13.83 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 56.9 (C–C$_6$H$_4$O*C*H$_3$), 57.4 (C–O*C*H$_3$), 105.6 (C-6), 115.6 (C-3′, C-5′), 118.9 (C-8), 119.0 (C-9), 122.4 (C-1′), 125.3 (C-5a), 134.2 (C-1), 137.2 (C-2′, C-6′), 139.9 (N$^+$=*C*H), 149.0 (C-3a), 160.1 (C-7), 164.8 (C-4) ppm. $C_{17}H_{16}BF_4N_5O_2$ (409.15): calcd. C 49.90, H 3.94, N 17.12; found C 49.69, H 3.93, N 16.91.

(5*Z*)-7-Methoxy-5-(4-methylbenzylidene)-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium Tetrafluoroborate (5m): This compound was obtained from 7-methoxy-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine (**4d**, 1.02 g) and *p*-tolualdehyde (1.20 g, 1.18 mL): yellow needles (1.69 g, 86% yield). M.p. 249–251 °C. IR (KBr): $\tilde{\nu}$ = 3317, 3152, 2922, 1642, 1521, 1449, 1328, 1265, 1185, 1049, 954, 820, 500 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 2.44 (s, 3 H, CH$_3$), 3.92 (s, 3 H, H–OCH$_3$), 7.40 (d, *J* = 7.6 Hz, 2 H, 3′-H, 5′-H), 7.43 (br. d, *J* = 8.6 Hz, 1 H, 8-H), 7.79 (br. s, 1 H, 6-H), 7.96 (d, *J* = 8.6 Hz, 1 H, 9-H), 8.44 (d, *J* = 7.6 Hz, 2 H, 2′-H, 6′-H), 8.62 (s, 1 H, N$^+$=C*H*), 9.19 (s, 1 H, 1-H), 13.95 (br. s, 1 H, NH) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 22.4 (C–CH$_3$), 57.3 (C–OCH$_3$), 105.3 (C-6), 119.1 (C-9), 119.4 (C-9a), 119.5 (C-8), 125.1 (C-5a), 126.9 (C-1′), 130.4 (C-3′, C-5′), 134.1 (C-1), 134.3 (C-2′, C-6′), 139.1 (N$^+$=*C*H), 146.6 (C-4′), 148.6 (C-3a), 160.1 (C-7) ppm. $C_{17}H_{16}BF_4N_5O$ (393.15): calcd. C 51.94, H 4.10, N 16.71; found C 51.82, H 4.14, N 16.55.

General Method for the Preparation of Cycloadducts 7, 8 and 9: Triethylamine (TEA) (5 mmol, 0.51 g 0.72 mL) was added dropwise to a mixture of the appropriate iminium salt (**5**, 5 mmol), the appropriate dipolarophile (5.5 mmol) and dichloromethane (20 mL) and the mixture was stirred at room temp. for 3 hours under argon. In the reactions with *N*-methylmaleimide, the crystalline product was filtered off, whereas in the reactions with maleic anhydride and DMAD the reaction mixture was extracted with water, and the organic layer was evaporated, the residue was triturated with diethyl ether to give a suspension, and the solid obtained then filtered off. The crude product was dried and stored in an exsiccator over P_2O_5 and NaOH for 24 h and recrystallized from acetonitrile.

***rel*-(10*R*,10a*S*,13a*R*)-10-(4-Methoxyphenyl)-12-methyl-10a,13a-dihydropyrrolo[3′,4′:3,4]pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine-11,13(10*H*,12*H*)-dione (7a):** This compound was obtained from (5*Z*)-5-(4-methoxybenzylidene)-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5a**) (1.9 g) and *N*-methylmaleimide (0.61 g): white needles (1.67 g, 83.9% yield). M.p. 260–262 °C. IR (KBr): $\tilde{\nu}$ = 2987, 2840, 1785, 1710, 1612, 1548, 1517, 1502, 1433, 1383, 1286, 1259, 1096, 1026, 823, 751, 544 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 3.02 (s, 3 H), 3.07 (s, 3 H), 3.92 (dd, *J* = 2.6, *J* = 8.2 Hz, 1 H), 4.81 (d, *J* = 2.6 Hz, 1 H), 5.70 (d, *J* = 8.2 Hz, 1 H), 6.62 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 6.95–7.21 (m, 4 H), 8.05 (s, 1 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 25.8, 51.5, 55.3, 61.9, 71.0, 114.0 (2 C), 115.5, 122.5, 126.1, 126.4, 126.5, 127.5, 128.8 (2 C), 132.8, 134.3, 135.5, 153.3, 159.7, 170.9, 172.9, 175.7 ppm. $C_{21}H_{18}N_6O_3$ (402.41): calcd. C 62.68, H 4.51, N 20.88; found C 62.57, H 4.37, N 20.68.

***rel*-(10*R*,10a*S*,13a*R*)-7-Chloro-10-(4-methoxyphenyl)-12-methyl-10a,13a-dihydropyrrolo[3′,4′:3,4]pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine-11,13(10*H*,12*H*)-dione (7b):** This compound was obtained from (5*Z*)-5-(4-methoxybenzylidene)-7-chloro-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5b**) (2.2 g) and *N*-methylmaleimide (0.61 g):

white needles (1.56 g, 71.5% yield). M.p. 271–274 °C. IR (KBr): $\tilde{\nu}$ = 3074, 2986, 2837, 1785, 1710, 1611, 1583, 1546, 1518, 1499, 1434, 1383, 1286, 1261, 1224, 1194, 1087, 1029, 996, 964, 881, 818, 803, 725, 627, 556 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO + CDCl$_3$, 200 MHz): δ = 3.03 (s, 3 H), 3.67 (s, 3 H), 3.96 (dd, *J* = 8.2, *J* = 2.9 Hz, 1 H), 4.88 (d, *J* = 2.93 Hz, 1 H), 5.60 (d, *J* = 8.2 Hz, 1 H), 6.62 (d, *J* = 8.6 Hz, 2 H), 6.93 (d, *J* = 8.6 Hz, 2 H), 7.01–7.13 (m, 2 H), 7.39 (d, *J* = 8.42 Hz, 1 H), 8.59 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO + CDCl$_3$): δ = 23.9, 50.2, 53.7, 60.6, 68.3, 112.3 (2 C), 116.0, 120.3, 123.2, 124.3, 125.4, 127.4 (2 C), 130.2, 132.4, 135.4, 151.2, 157.9, 171.5, 173.9 ppm. $C_{21}H_{17}ClN_6O_3$ (436.85): calcd. C 57.74, H 3.92, N 19.24; found. C 57.53, H 3.80, N 18.99.

***rel*-(10*R*,10a*S*,13a*R*)-10-(4-Methoxyphenyl)-7,12-dimethyl-10a,13a-dihydropyrrolo[3′,4′:3,4]pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]-benzotriazine-11,13(10*H*,12*H*)-dione (7e):** This compound was obtained from (5*Z*)-5-(4-methoxybenzylidene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5e**) (1.97 g) and *N*-methylmaleimide (0.61 g): white needles (1.9 g, 91% yield). M.p. 254–257 °C. IR (KBr): $\tilde{\nu}$ = 3374, 2985, 1712, 1611, 1546, 1514, 1435, 1381, 1287, 1255, 1029, 816, 626 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 2.32 (s, 3 H, CH$_3$), 3.16 (s, 3 H, H–NCH$_3$), 3.71 (s, 3 H, H–OCH$_3$), 3.89 (dd, *J* = 8.1, *J* = 2.0 Hz, 1 H, 10a-H), 4.82 (d, 1 H, *J* = 2.0 Hz, 10-H), 5.70 (d, *J* = 8.1 Hz, 1 H, 13a-H), 6.62 (d, *J* = 8.8 Hz, 2 H, 3′-H, 5′-H), 6.83 (d, *J* = 8.8 Hz, 2 H, 2′-H, 6′-H), 6.90 (d, *J* = 8.1 Hz, 1 H, 5-H), 6.92 (br. s, 1 H, 8-H), 6.94 (br. d, *J* = 8.1 Hz, 1 H, 6-H), 7.93 (s, 1 H, 3-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 21.6 (C–CH$_3$), 26.1 (C–NCH$_3$), 51.7 (C-10a), 55.6 (C–OCH$_3$), 62.2 (C-13a), 71.6 (C-10), 114.2 (C-3′, C-5′), 115.5 (C-5), 123.5 (C-8), 124.2 (C-4a), 126.8 (C-1′), 127.3 (C-6), 129.2 (C-2′, C-6′), 132.6 (C-8a), 135.7 (C-3), 138.0 (C-7), 153.4 (C-14a), 159.9 (C-4), 173.2 (C-13), 176.1 (C-11) ppm. $C_{22}H_{20}N_6O_3$ (416.43): calcd. C 63.45, H 4.84, N 20.18; found C 63.52, H 4.84, H 19.89.

***rel*-(10*R*,10a*S*,13a*R*)-7,12-Dimethyl-10-(4-tolyl)-10a,13a-dihydropyrrolo[3′,4′:3,4]pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine-11,13(10*H*,12*H*)-dione (7f):** This compound was obtained from (5*Z*)-5-(4-methylbenzylidene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5f**) (1.9 g) and *N*-methylmaleimide (0.61 g): white needles (1.34 g, 66.8% yield). M.p. 275–278 °C. IR (KBr): $\tilde{\nu}$ = 2985, 1782, 1710, 1548, 1511, 1497, 1432, 1386, 1287, 1220, 1142, 1100, 1037, 880, 823, 807, 624, 516, 405 cm^{-1}. ^{1}H NMR (CDCl$_3$ 200 MHz): δ = 2.21 (s, 3 H), 2.31 (s, 3 H), 3.16 (s, 3 H), 3.91 (dd, *J* = 8.1, *J* = 2.8 Hz, 1 H), 4.81 (d, *J* = 2.8 Hz, 1 H), 5.66 (d, *J* = 8.1 Hz, 1 H), 6.78–6.97 (m, 7 H), 7.94 (s, 1 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 21.1, 21.4, 25.8, 51.6, 61.8, 71.1, 115.2, 122.9, 123.7, 126.9, 127.4 (2 C), 129.3 (2 C), 131.6, 132.6, 135.4, 137.7, 138.5, 153.2, 172.6, 175.7 ppm. HRMS: $C_{22}H_{20}N_6O_2$ (400.43): calcd. 400.1648; found 400.1660.

***rel*-(10*R*,10a*S*,13a*R*)-10-Biphenyl-4-yl-7,12-dimethyl-10a,13a-dihydropyrrolo[3′,4′:3,4]pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine-11,13(10*H*,12*H*)-dione (7g):** This compound was obtained from (5*Z*)-(biphenyl-4-ylmethylene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5g**) (2.2 g) and *N*-methylmaleimide (0.61 g): white needles (1.87 g, 81% yield). M.p. 230–232 °C. IR (KBr): $\tilde{\nu}$ = 3121, 2932, 1779, 1703, 1561, 1514, 1441, 1378, 1293, 1107, 1033, 953, 817, 700, 563 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO + CDCl$_3$, 200 MHz): δ = 2.33 (s, 3 H), 3.12 (s, 3 H), 4.08 (dd, *J* = 8.1, *J* = 2.2 Hz, 1 H), 4.91 (d, *J* = 2.2 Hz, 1 H), 5.72 (d, *J* = 8.1 Hz, 1 H), 6.95 (m, 1 H), 6.96 (s, 1 H), 7.03 (d, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 8.1 Hz, 1 H), 7.33 (d, *J* = 7.8 Hz, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 7.34–7.52 (m, 4 H), 8.27 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO + CDCl$_3$): δ = 20.3, 24.6, 50.4, 61.3, 69.6, 114.7, 121.6, 122.7, 125.7 (2 C), 125.8 (2 C), 126.0, 126.8 (2 C), 127.1 (2 C), 127.9 (2 C), 131.2, 132.8, 135.2, 136.5, 138.8, 139.7, 152.0, 172.0, 174.8 ppm. HRMS: $C_{27}H_{22}N_6O_2$ (462.50): calcd. 462.1804; found 462.1819.

***rel*-(10*R*,10a*S*,13a*R*)-7,12-Dimethyl-10-[(*E*)-2-phenylvinyl]-10a,13a-dihydropyrrolo[3′,4′:3,4]pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]-benzotriazine-11,13(10*H*,12*H*)-dione (7h):** This compound was obtained from (5*Z*)-7-methyl-5-[(2*E*)-3phenylprop-2-en-1-ylidene]4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5h**) (1.95 g) and *N*-methylmaleimide (0.61 g): white needles (1.8 g, 87% yield). M.p. 277–279 °C. IR (KBr): $\tilde{\nu}$ = 3103, 3021, 2950, 1787, 1705, 1456, 1513, 1494, 1436, 1385, 1290, 1222, 1143, 1096, 1057, 1000, 977, 893, 827, 760, 698, 630, 473 cm^{-1}. ^{1}H NMR (CDCl$_3$ + TFA, 200 MHz): δ = 2.4 (s, 3 H), 3.18 (s, 3 H), 3.92 (d, *J* = 8.1 Hz, 1 H), 4.69 (d, *J* = 7.7 Hz, 1 H), 5.57 (dd, *J* = 1.3, *J* = 7.7 Hz, 1 H), 5.86 (ddd, *J* = 1.3, *J* = 8.1, *J* = 15.9 Hz, 1 H), 6.48 (d, *J* = 15.9 Hz, 1 H), 7.00–7.32 (m, 7 H), 7.38 (dd, *J* = 1.5, *J* = 8.4 Hz, 1 H), 9.42 (s, 1 H) ppm. ^{13}C NMR (CDCl$_3$ + TFA): δ = 21.5, 26.3, 50.2, 61.0, 70.0, 116.8, 119.2, 120.1, 126.6 (2 C), 128.6, 129.1 (2 C), 129.8, 132.2, 134.2, 135.9, 138.9, 142.9, 152.0, 173.3, 176.3 ppm. HRMS: $C_{23}H_{20}N_6O_2$ (412.44): calcd. 412.1648; found 412.1656.

***rel*-(10*R*,11*S*,12*R*)-10-(4-Methoxyphenyl)-7-methyl-11,12-dihydro-10*H*-pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine-11,12-dicarboxylic Acid (8e):** This compound was obtained from (5*Z*)-5-(4-methoxybenzylidene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5e**) (1.97 g) and maleic anhydride (0.54 g): yellow needles (1.4 g, 66% yield). M.p. 187–188 °C. IR (KBr): $\tilde{\nu}$ = 3300, 2930, 1744, 1638, 1613, 1569, 1514, 1253, 1179, 1084, 1032, 831 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 500 MHz): δ = 2.08 (s, 3 H, CH$_3$), 3.63 (dd, J_1 = 10.2, J_2 = 8.04 Hz, 1 H, 11-H), 3.73 (s, 3 H, H–OCH$_3$), 4.75 (d, J_1 = 10.2 Hz, 1 H, 12-H), 4.80 (d, J_2 = 8.04 Hz, 1 H, 10-H), 6.38 (br. s, 1 H, 8-H), 6.82 (br. d, *J* = 7.3 Hz, 1 H, 6-H), 6.90 (d, *J* = 8.8 Hz, 2 H, 3′-H, 5′-H), 7.38 (d, *J* = 8.8 Hz, 2 H, 2′-H, 6′-H), 7.43 (d, *J* = 7.3 Hz, 1 H, 5-H), 8.94 (s, 1 H, 3-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 21.9 (C–CH$_3$), 55.9 (C–OCH$_3$), 57.3 (C-11), 61.6 (C-12), 115.0 (C-3′, C-5′), 116.7 (C-8), 116.9 (C-5), 122.7 (C-4a), 124.3 (C-6), 129.0 (C-2′, C-6′), 130.5 (C-1′), 137.5 (C-8a), 137.6 (C-7), 137.8 (C-3), 154.8 (C-13a), 160.1 (C-4′), 169.7 (C$_1$–COOH), 171.1 (C$_2$–COOH) ppm. HRMS (EI): $C_{21}H_{19}N_5O_5$ (421.41): [M – H$_2$O]+ = calcd. 403.1281; found 403.1290.

Dimethyl 7-Chloro-10-(4-methylphenyl)-10*H*-pyrazolo[1,2-*a*]-[1,2,4]triazolo[3,4-c][1,2,4]benzotriazine-11,12-dicarboxylate (9b): This compound was obtained from (5*Z*)-7-chloro-5-(4-methylbenzylidene)-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5b**) (2.26 g) and dimethyl acetylenedicarboxylate (0.78 g, 0.68 mL): white needles (1.98 g, 77% yield). M.p. 208–209 °C. IR (KBr): $\tilde{\nu}$ = 3126, 2955, 2854, 1750, 1708, 1593, 1567, 1510, 1437, 1334, 1306, 1248, 1130, 1021, 847, 801, 560 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 2.35 (s, 3 H, CH$_3$), 3.62 (s, 3 H, H$_1$–COOCH$_3$), 4.07 (s, 3 H, H$_2$–COOCH$_3$), 5.81 (s, 1 H, 10-H), 6.69 (br. s, 1 H, 8-H), 6.95 (br. d, *J* = 8.3 Hz, 1 H, 6-H), 7.13 (d, *J* = 8.3 Hz, 1 H, 5-H), 7.20 (d, *J* = 7.7 Hz, 2 H, 3′-H, 5′-H), 7.49 (d, *J* = 7.7 Hz, 2 H, 2′-H, 6′-H), 8.37 (s, 1 H, 3-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 26.6 (C–CH$_3$), 52.3 (C$_1$–COO*C*H$_3$), 54.5 (C$_2$–COO*C*H$_3$), 69.4 (C-10), 109.2 (C-11), 113.2 (C-8), 116.9 (C-5), 121.0 (C-4a), 123.2 (C-6), 128.5 (C-2′, C-6′), 130.0 (C-3′, C-5′), 134.1 (C-7), 134.9 (C-1′), 135.9 (C-3), 136.3 (C-8a), 136.5 (C-12), 139.5 (C-4′), 146.6 (C-13a), 160.0 (C$_1$–*C*OOCH$_3$), 162.4 (C$_2$–*C*O-OCH$_3$) ppm. $C_{22}H_{18}ClN_5O_4$ (451.81): calcd. C 58.48, H 4.02, N 15.50; found C 58.48, H 4.00, N 15.31.

Dimethyl 10-(4-Methoxyphenyl)-7-methyl-10*H*-pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine-11,12-dicarboxylate (9e): This compound was obtained obtained from (5Z)-5-(4-methoxybenzylidene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5e**) (1.97 g) and dimethyl acetylenedicarboxylate (0.78 g, 0.68 mL): white needles (2.04 g, 91% yield). M.p. 209–211 °C. IR (KBr): $\tilde{\nu}$ = 3114, 3013, 2955, 2819, 1741, 1703, 1613, 1566, 1516, 1429, 1380, 1337, 1300, 1251, 1177, 1127, 1112, 1030, 829, 796, 686, 546 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 2.23 (s, 3 H, CH$_3$), 3.62 (s, 3 H, H$_1$–COOCH3), 3.80 (s, 3 H, H–OCH$_3$), 4.06 (s, 3 H, H$_2$–COOCH$_3$), 5.84 (s, 1 H, 10-H), 6.54 (br. s, 1 H, 8-H), 6.79 (br. d, J = 8.1 Hz, 1 H, 6-H), 6.91 (d, J = 8.8 Hz, 2 H, 3′-H, 5′-H), 7.07 (d, J = 8.1 Hz, 1 H, 5-H), 7.55 (d, J = 8.8 Hz, 2 H, 2′-H, 6′-H), 8.34 (s, 1 H, 3-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 21.9 (C–CH$_3$), 52.2 (C$_1$–COO*C*H$_3$), 54.4 (C$_2$–COO*C*H$_3$), 55.7 (C–OCH$_3$), 69.0 (C-10), 108.8 (C-11), 113.5 (C-8), 114.5 (C-3′, C-5′), 115.7 (C-5), 120.1 (C-4a), 124.0 (C-6), 129.8 (C-2′, C-6′), 130.8 (C-1′), 135.9 (C-3), 135.4 (C-8a), 136.7 (C-12), 138.7 (C-7), 146.8 (C-13a), 160.25 (C$_2$–*C*OOCH$_3$), 160.3 (C-4′), 162.7 (C$_1$–*C*OOCH$_3$) ppm. $C_{23}H_{21}N_5O_5$ (447.44): calcd. C 61.74, H 4.73, N 15.65; found C 61.67, H 4.74, N 15.52.

Dimethyl 7-Methyl-10-(4-methylphenyl)-10*H*-pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine-11,12-dicarboxylate (9f): This compound was obtained from (5*Z*)-5-(4-methylbenzylidene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5f**) (1.89 g) and dimethyl acetylenedicarboxylate (0.78 g, 0.67 mL): pale yellow crystalline compound (2.03 g, 94% yield). M.p. 208–209 °C. IR (KBr): $\tilde{\nu}$ = 3118, 2954, 2818, 1748, 1702, 1627, 1568, 1513, 1429, 1381, 1337, 1300, 1255, 1189, 1127, 1027, 804, 686, 584 cm^{-1}. ^{1}H NMR (CDCl$_3$ 200 MHz): δ = 2.36 (s, 3 H), 2.34 (s, 3 H), 3.62 (s, 3 H), 4.07 (s, 3 H), 5.86 (s, 1 H), 6.55 (s, 1 H), 6.80 (d, J = 7.9 Hz, 1 H), 7.08 (d, J = 7.9 Hz, 1 H), 7.2 (d, J = 7.7 Hz, 2 H), 7.52 (d, J = 7.7 Hz, 2 H), 8.34 (s, 1 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 21.3, 21.6, 51.9, 54.2, 69.1, 108.4, 113.2, 115.4, 119.8, 123.7, 128.2 (2 C), 129.5 (2 C), 135.2, 135.5, 136.5, 138.5, 138.8, 146.5, 159.9, 162.4 ppm. HRMS (EI): $C_{23}H_{21}N_5O_4$ (431.44): calcd. 431.1594; found 431.1582.

Dimethyl 7-Methoxy-10-(4-methoxyphenyl)-10*H*-pyrazolo[1,2-*a*][1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine-11,12-dicarboxylate (9j): This compound was obtained from (5*Z*)-5-(4-methoxybenzylidene)-7-methoxy-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5j**) (2.05 g) and dimethyl acetylenedicarboxylate (0.78 g, 0.67 mL): white crystalline compound (1.97 g, 85% yield). M.p. 201–203 °C. IR (KBr): $\tilde{\nu}$ = 3123, 2953, 2840, 1752, 1709, 1612, 1574, 1512, 1431, 1355, 1313, 1248, 1211, 1173, 1129, 1033, 967, 836, 803, 629 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 3.63 (s, 3 H), 3.70 (s, 3 H), 3.80 (s, 3 H), 4.07 (s, 3 H), 5.82 (s, 1 H), 6.30 (d, J = 2.4 Hz, 1 H), 6.48 (dd, J = 2.4, J = 8.7 Hz, 1 H), 6.91 (d, J = 8.8 Hz, 2 H), 7.12 (d, J = 8.8 Hz, 1 H), 7.54 (d, J = 8.8 Hz, 2 H), 8.32 (s, 1 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 51.9, 54.2, 55.4, 55.7, 68.9, 100.1, 106.8, 108.5, 114.3 (2 C), 115.7, 116.4, 129.5 (2 C), 130.3, 135.4, 136.5, 146.3, 159.3, 159.9, 160.1, 162.4 ppm. $C_{23}H_{21}N_5O_6$ (463.44): calcd. C 59.61, H 4.57, N 15.11; found C 59.49, H 4.49, N 14.90.

Dimethyl 7-Methoxy-10-(4-methylphenyl)-10*H*-pyrazolo[1,2-*a*]-[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazine-11,12-dicarboxylate (9m): This compound was obtained from (5*Z*)-5-(4-methylbenzylidene)-7-methyl-4,5-dihydro[1,2,4]triazolo[3,4-*c*][1,2,4]benzotriazin-5-ium tetrafluoroborate (**5m**) (1.97 g) and dimethyl acetylenedicarboxylate (0.78 g, 0.67 mL): pale yellow crystalline compound (2.24 g, 83.7% yield). M.p. 208–210 °C. IR (KBr): $\tilde{\nu}$ = 3100, 3008, 2953, 2850, 1751, 1738, 1703, 1624, 1573, 1512, 1429, 1354, 1311, 1257, 1209, 1173, 1126, 1045, 1030, 965, 847, 800, 770, 629 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 2.33 (s, 3 H), 3.62 (s, 3 H), 3.69 (s, 3 H), 4.07 (s, 3 H), 5.83 (s, 1 H), 6.30 (d, J = 2.2 Hz, 1 H), 6.47 (dd, J = 2.2, J = 8.7 Hz, 1 H), 7.11 (d, J = 8.8 Hz, 1 H), 7.2 (d, J = 7.9 Hz, 2 H), 7.51 (d, J = 7.9 Hz, 2 H), 8.32 (s, 1 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 21.3, 51.9, 54.1, 55.7, 69.2, 100.0, 106.8, 108.4, 115.6, 116.4, 128.2 (2 C), 129.6 (2 C), 135.4, 135.4, 136.4, 136.5, 138.9, 146.2, 159.3, 159.9, 162.4 ppm. HRMS (EI): $C_{23}H_{21}N_5O_5$ (447.44): calcd. 447.1543; found 447.1546.

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