Synthesis and Reactions of 1,2,3-Triazinium Salts

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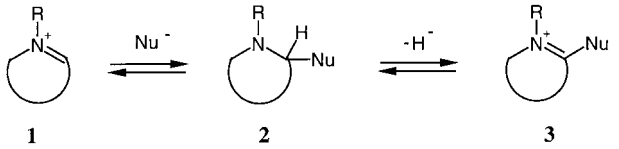
Abstract: The synthesis of monosubstituted 1,2,3-triazinium salts **7**–**9** and their reactivity towards C-nucleophiles is described. The nucleophilic attack at **7**–**9** is regioselective at position 5, isolation of dihydroproducts was possible and an unusual ring contraction was observed.

Key words: 1,2,3-triazines, cations, nucleophilic additions, π-deficient heterocycles, regioselectivity

The concept of nucleophilic aromatic substitution of hydrogen (S_N^H) in azines was introduced by Chupakhin, Charushin and van der Plas et al. and has been successfully used for the introduction of a number of nucleophiles into electrophilic arenes, non-benzoid aromatic systems and hetarenes.[1]

It was shown that the S_N^H-reaction proceeds in a stepwise fashion[2]. The initial attack of a nucleophile at **1** forms a σ-adduct **2** (Scheme 1), which rearomatizes to **3** either by oxidation or by hydride transfer[1]. However, if heterocyclic cations or electron deficient heterocycles are used in S_N^H synthesis, the isolation of the formed dihydro adducts **2** is often possible.[1,3–5]



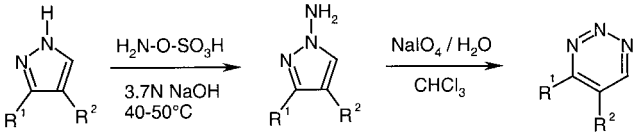
Scheme 1

It was predicted,[1] that electron poor heterocyclic systems should show a high reactivity towards even weak nucleophiles, increasing with the number of aza groups in the aromatic ring. The stability of the primarily formed σ-adduct **2** should increase while lowering the π-electron density in the heterocyclic ring system.

In this connection 1,2,3-triazinium salts[6] are interesting heterocyclic systems which to our knowledge have not yet been studied in S_N^H reactions. In this paper we describe the synthesis of monosubstituted 1,2,3-triazinium salts and their reactivity towards C-nucleophiles.

We concentrated in our work on monosubstituted 1,2,3-triazines with two possible reaction sites. To the best of our knowledge, this is the first time that the activation of monosubstituted 1,2,3-triazines via substitution on *N*-2 and the reactivity of the resulting cations is studied.

1,2,3-Triazines **6** are synthesized from their corresponding pyrazoles **4** (Scheme 2).[7,8] The first step is an electrophilic amination with hydroxylamin-*O*-sulfonic acid followed by a two-phase oxidation using sodium *meta* periodate in the aqueous phase (Table 1).



Scheme 2

Table 1 Reaction Parameters and Overall Yields for the Synthesis of 1,2,3-Triazines **6**

	R^1	R^2	Temp.	Time	Overall Yield (%)
4a	Ph	H	20 °C	5 d	47[8]
4b	H	Ph	20 °C	5 d	49
4c	Me	H	5 °C	72 h	22[8]
4d	H	Me	5 °C	72 h	30[8]

All known procedures for the activation of 4,6-disubstituted 1,2,3-triazines like methyliodide[9] or 1-chloroethyl chloroformate[10] failed with compounds **6**, because of the high reactivity of the formed salts towards nucleophiles. We had to search for an activating reagent, which forms an unreactive anion and succeeded finally by using the Meerwein salt.[11]

Ethylation of the phenyl substituted 1,2,3-triazines **6a**,**b** with triethyloxonium tetrafluoroborate and the methyl substituted 1,2,3-triazines **6c**,**d** with triethyloxonium hexafluorophosphate under argon led to the corresponding 1,2,3-triazinium salts **7** (Scheme 3).

The 2-ethyl-1,2,3-triazinium salts **7** are stable under Ar at 0 °C for only a few days and have to be prepared freshly for further reactions. (^{15}N,^{1}H)-HMBC-NMR studies indicated, that the ethylation took place only at *N*-2 and the EIMS (70eV) spectra show no elimination of nitrogen ($[M^+]$ – 28 peak is missing).

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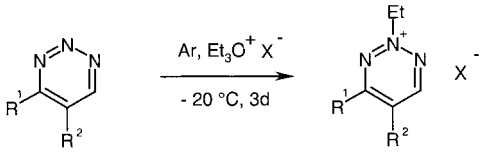


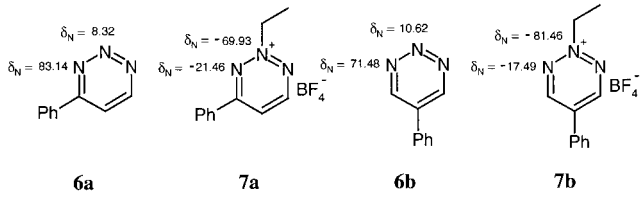
6a[7] R^1 = Ph, R^2 = H — **7a** X^- = BF_4^-, 95%

6b R^1 = H, R^2 = Ph — **7b** X^- = BF_4^-, 98%

6c[7] R^1 = Me, R^2 = H — **7c** X^- = PF_6^-, 56%

6d[7] R^1 = H, R^2 = Me — **7d** X^- = PF_6^-, 57%

Scheme 3



6a **7a** **6b** **7b**

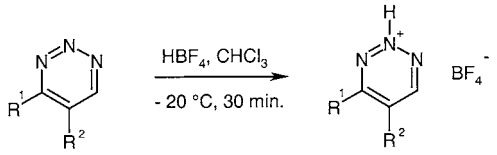
Figure 1

Figure 1 shows the ^{15}N-signals (internal standard nitromethane) of the 1,2,3-triazines **6** and the corresponding 1,2,3-triaziniumsalts **7**. All nitrogen signals shift to a higher field compared to the corresponding 1,2,3-triazines **6** (see experimental for details). For δ = –69.93 (**7a**) and δ = –81.46 (**7b**) one observes ^3J-coupling between N-2 and $–CH_3$ as well as ^3J-coupling N-2/H-6 but no coupling to H-5. For δ = –21.46 (**7a**) and δ = –17.49 (**7b**) N-1/N-3 coupling to H-5, H-6 and the $–CH_2–$ group is observed, making the two nitrogen signals significantly different and clearing the position for the ethyl group.

This evidence is supported by *ab initio* calculations on B3Lyp/6-311G*//HF/6-31G*+0.89ZPE (HF/6-31G*)[12–14] level (Table 2).

The calculation shows, that the *N*-2 substituted 1,2,3-triazine **7** is around 30 kJmol^{-1} more stable than the other isomers. Although the calculated structures refer to the gas phase at 0 K there is at least a significant energy difference between the three possible isomers.

When 1,2,3-triazines **6** were treated with tetrafluoroboric acid, the isolation of protonated 1,2,3-triazinium salts **8** was possible in the case of phenylated 1,2,3-triazines **6a**,**b** (Scheme 4). The methylated 1,2,3-triazines **6c**,**d** decomposed under similar conditions.



6a[7] R^1 = Ph, R^2 = H — **8a**, 92%

6b R^1 = H, R^2 = Ph — **8b**, 88%

Scheme 4

The position of the protonation could not be clarified by ^{1}H NMR studies. We observed a small NOE-effect between N–H and the phenyl ring for the 4-phenylated 1,2,3-triazinium-tetrafluoroborate **8a**, but this result was not satisfying. Due to the poor solubility of **8a**,**b** no ^{15}N-NMR spectra were recorded. By analogy with the ethylated 1,2,3-triazinium salts **7** we assume that the solid 1,2,3-triazinium salt **8** is protonated at N-2 due to thermodynamic effects. *Ab initio* calculations on B3Lyp/6-311G*//HF/6-31G*+0.89ZPE (HF/6-31G*)[12–14] level (Table 3) showed again a thermodynamic energy difference between the three possible isomers.

Table 3 Calculated Relative Energies for the Three Possible Isomers of 1,2,3-Triazinium Salts **8**

	8a	**8b**
N-1 protonated	3.4 kJmol^{-1}	36.5 kJmol^{-1}
N-2 protonated[15]	0 kJmol^{-1}	0 kJmol^{-1}
N-3 protonated	14.7 kJmol^{-1}	–

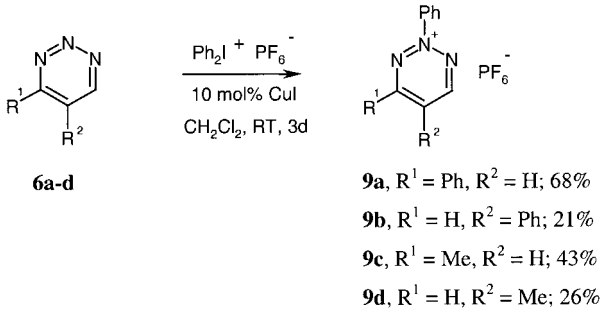
Once more the N-2 substituted isomer is the most stable one, but in the case of 1,2,3-triazinium salt **8a** the energy difference between N-1 and N-2 is so small, that one can assume that a shift of the proton in solution takes place very easily.

Recently, the synthetic utility of hypervalent iodine has been extensively exploited,[16] and diaryliodinium salts have been used to arylate a wide variety of substrates[17]. We report the first arylation of heteroarenes with hypervalent iodonium salts leading to a cationic product.

Kang et al. reported the copper-catalyzed arylation of several amines with hypervalent iodonium salts.[18] We used this method to arylate 1,2,3-triazines **6** leading to *N*-phenylated 1,2,3-triazinium hexafluorophosphates **9** (Scheme 5).

Table 2 Calculated Relative Energies for the Three Possible Isomers of 1,2,3-Triazinium Salts **7**

	7a	**7b**	**7c**	**7d**
N-1 ethylated	12.7 kJmol^{-1}	38.2 kJmol^{-1}	24.4 kJmol^{-1}	33.0 kjmol^{-1}
N-2 ethylated[15]	0 kJmol^{-1}	0 kJmol^{-1}	0 kJmol^{-1}	0 kJmol^{-1}
N-3 ethylated	42.2 kJmol^{-1}	–	31.5 kJmol^{-1}	–



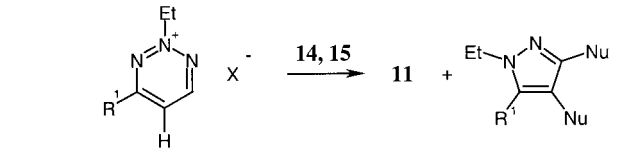
Scheme 5

The resulting 1,2,3-triazinium salts **9** are stable under inert gas for several months. ^{1}H NMR and EIMS (70 eV) studies indicated again that the phenylated 1,2,3-triazines **9** are substituted on N-2 only. Due to their poor solubility no (H,N)-HMBC-NMR studies were possible.

When the prepared 2-ethyl-1,2,3-triazinium salts **7a**–**d** were allowed to react with electron rich heterocyclic systems as weak C-nucleophiles, the expected nucleophilic attack occurred in case of 1,2,3-triazinium salts **7a** and **7c**. Both 5-substituted 2-ethyl-1,2,3-triazinium salts **7b**,**d** did not react. This indicates again, that the 1,2,3-triazinium salts **7** are substituted only at N-2 and because of that, no reaction takes place at the blocked C-5 position. In case of the 4-substituted 2-ethyl-1,2,3-triazinium salts **7a**,**c** only the 4,5-disubstituted products **11** were isolated (Table 4). No reaction occurred at the free C-6 position and no re-aromatization took place leading to the S_N^H-product **13** (Scheme 6). This is in good agreement with the predicted reactivity of π-deficient heterocyclic systems.[1] Oxidation of **11** by air or DDQ in dioxane failed and led only to decomposition products.

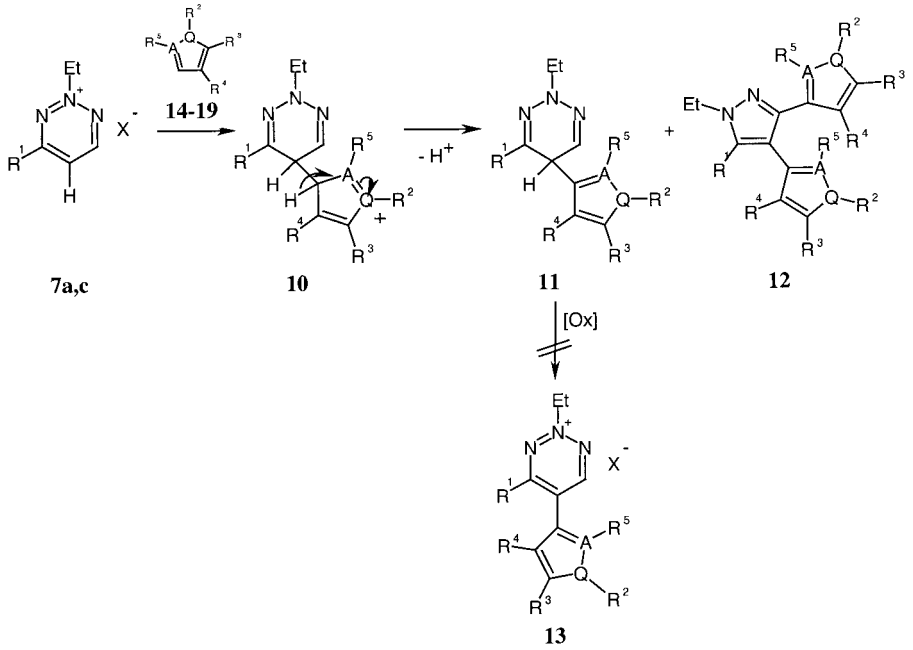
In a typical procedure the 1,2,3-triazinium salt **7a** was dissolved under argon in absolute dichloromethane (or absolute acetonitrile for **7c**) and the C-nucleophile was added at room temperature. The reaction was observed by TLC and stopped when no further changes were detectable. We never observed a complete conversion of the starting material **7**, but failed to recovering the salts **7**. The primarily formed adduct **10** (A = C, Q = N) rearomatizes immediately without any deprotonating agent[1] and the dihydroadducts **11** were isolated by column chromatography and completely characterized. See Table 4 for experimental details, nucleophiles and yields of isolated dihydroadducts **11**.

When 4-phenyl- and 4-methyl-1,2,3-triazinium salts **7a**,**c** were treated with indole (**14**) and pyrole (**15**) an unusual byproduct was observed (Scheme 7).



Scheme 7

A ring contraction took place, leading to these unexpected tetrasubstituted pyrazoles **12**. The position of the ethyl group in pyrazoles **12** was clarified by ^{1}H NMR-NOESY experiments. We were able to prove the existence of am-



Scheme 6

monium tetrafluoroborate in the residue with Nesslers reagent[19] and succeeded in preparing the pyrazole **12a** directly from the corresponding dihydro adduct **11a** by treatment with tetrafluoroboric acid in dichloromethane at room temperature. The ring contraction has to be a secondary reaction of the nucleophilic attack and ammonia is eliminated. We suggest the following mechanism for this reaction (Scheme 8).

Table 4 Parameters and Products of the Reaction of 1,2,3-Triazinium Salts **7** with C-Nucleophiles

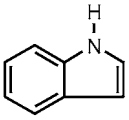
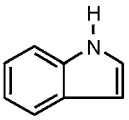
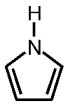
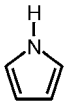
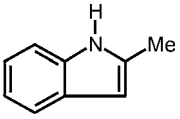
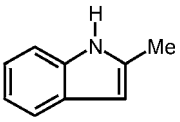
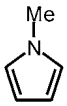
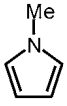
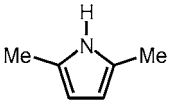
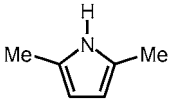
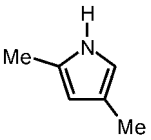
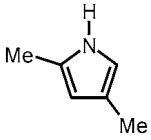
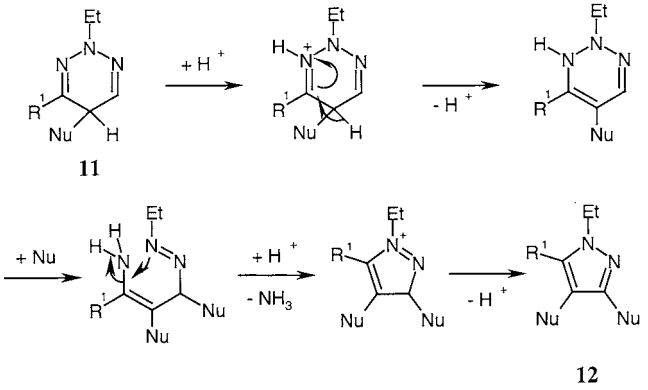
Entry	Solvent[a]	Reaction Time	X^-	Nucleophile	Product **11**, Yield								
						R^1	R^2	R^3	R^4	R^5	A	Q	%
7a	CH_2Cl_2	3 d	BF_4^-	 **14**	**11a**	Ph	H		Ar	H	C	N	15%
7c	CH_3CN	3 d	PF_6^-	 **14**	**11b**	Me	H		Ar	H	C	N	14%
7a	CH_2Cl_2	2 d	BF_4^-	 **15**	**11c**	Ph	H	H	H	H	N	C	23%
					11d	Ph	H	H	H	H	C	N	8%
7c	CH_3CN	1 h	PF_6^-	 **15**	**11e**	Me	H	H	H	H	N	C	5%
7a	CH_2Cl_2	1 d	BF_4^-	 **15**	**11f**	Ph	H		Ar	Me	C	N	21%
7c	CH_3CN	1 d	PF_6^-	 **16**	**11g**	Me	H		Ar	Me	C	N	27%
7a	CH_2Cl_2	1 d	BF_4^-	 **17**	**11h**	Ph	Me	H	H	H	C	N	23%
7c	CH_3CN	1 d	PF_6^-	 **17**	**11i**	Me	H	H	H	Me	N	C	5%
7a	CH_2Cl_2	1 d	BF_4^-	 **18**	**11j**	Ph	H	Me	H	Me	C	N	46%
7c	CH_3CN	16 h	PF_6^-	 **18**	**11k**	Me	H	Me	H	Me	C	N	33%

Table 4 Parameters and Products of the Reaction of 1,2,3-Triazinium Salts **7** with C-Nucleophiles (continued)

Entry	Solvent[a]	Reaction Time	X^-	Nucleophile	Product **11**, Yield	R^1	R^2	R^3	R^4	R^5	A	Q	%
7a	CH_2Cl_2	1 d	BF_4^-	 **19**	**11l**	Ph	H	H	Me	Me	C	N	11%
7c	CH_3CN	16 h	PF_6^-	 **19**	**11m**	Me	H	H	Me	Me	C	N	9%
					11n	Me	H	Me	H	Me	N	C	11%

[a] Absolute CH_2Cl_2 and CH_3CN were used.

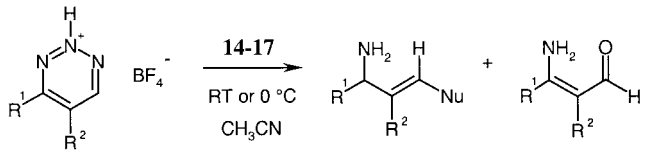


11 **12**

Scheme 8 Proposed reaction mechanism for the formation of **12**.

The initial protonation of **11** at *N*-3 is the key step of this reaction. During the formation of the dihydroadduct **11** (see Scheme 6), tetrafluoroboric acid (or hexafluorophosphoric acid) is formed and this initiates the secondary reaction leading to the pyrazole **12**.

When the protonated 1,2,3-triazinium salts **8** were treated with the nucleophiles **14**–**17**, we could not isolate the expected dihydro adducts. A gas forming reaction took place instantly after the nucleophile was added and only decomposition products **20** and **21** were isolated (Scheme 9).



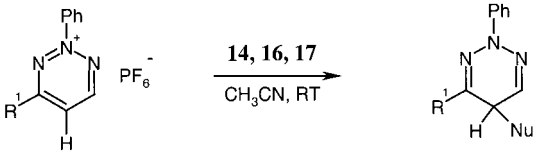
8a R^1 = Ph, R^2 = H **20** **21**

8b R^1 = H, R^2 = Ph

Scheme 9

Noteworthy is the fact, that there is no obvious difference between the 4-phenyl- and 5-phenyl substituted 1,2,3-triazinium salt **8a**,**b**. Both salts led to the same type of products and both decomposed immediately after addition of the nucleophile. This supports our theory, that the position of the proton in solution is not fixed on N-2. If the proton shifts to N-1/N-3 an attack at C-6 is possible leading to the observed products. This is a known reaction for 1,2,3-triazines with nucleophiles like sodium methanolate or sodium hydroxide.[20]

The *N*-phenylated 1,2,3-triazinium salts **9a**,**c** react with indole (**14**), 2-methylindole (**16**) and *N*-methylpyrrole (**17**) in the expected way and form the dihydro adducts **22** (Scheme 10).



9a R^1 = Ph **22a**, Nu = 2'-methylindol-3'-yl; 15%

9c R^1 = Me **22b**, Nu = indol-3'-yl; 16%

9a R^1 = Ph **22c**, Nu = *N*-methyl-pyrrol-3'-yl; 23%

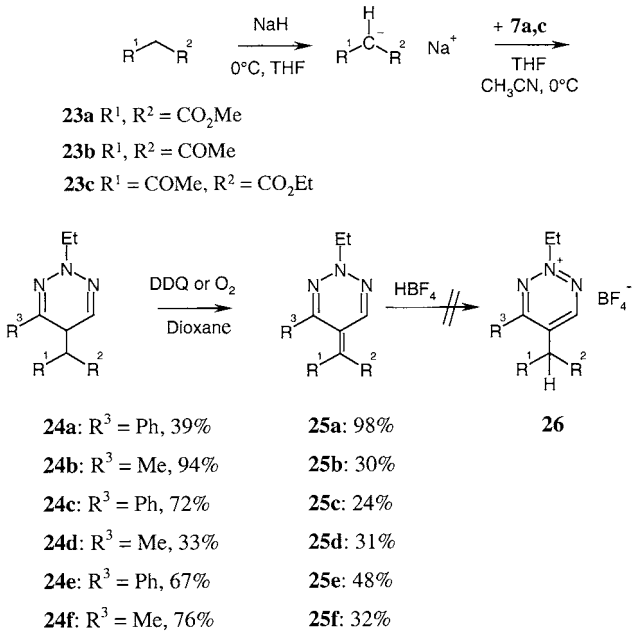
9c R^1 = Me **22d**, Nu = *N*-methyl-pyrrol-3'-yl; 21%

Scheme 10

The reaction was followed by TLC and stopped when no further changes were detectable. Again the transformation of the 1,2,3-triazinium salts **9** was not complete, but this time we could recover the salts **9** in yields up to 30–40%. Similarly to **7**, the nucleophilic attack took place only on C-5. Therefore it can be concluded that the position of the phenyl group is just like the ethyl group in **7** fixed on N-2.

All reactions with these C-nucleophiles suffer from poor yields. This is due to the weak nucleophilicity and the in situ formation of protons, which initiates decomposition or secondary reactions. Therefore we used substances with acidic protons **23**, deprotonated them with sodium hydride and added the 1,2,3-triazinium salts **7a**,**c** (Scheme 11), which is known to work for 4,6-disubstitut-

ed 1,2,3-triazinium salts.[21] A fast reaction was observed by TLC and the expected dihydroadducts **24** were isolated in all cases in moderate to good yields. Oxidation by air or DDQ in dioxane led to the 1,2,3-triazinylidenes **25**. Subsequent protonation with tetrafluoroboric acid did not lead to the completion of the S_N^H-reaction. We only observed slow decomposition even under very mild conditions.



Scheme 11

Ethylation, protonation and phenylation of 1,2,3-triazines **6** occurred only at N-2 of the 1,2,3-triazine ring systems. This was proved for the *N*-ethylated salts **7** by (N,H)-HMBC-NMR studies. Ab initio calculations support our experimental results and indicate, that thermodynamic effects are the reason for this regioselectivity.

Monosubstituted 1,2,3-triazinium salts **7**, **9** showed high reactivity towards weak C-nucleophiles leading to dihydro 1,2,3-triazines **11** and **22** in rather poor yields. No rearomatization took place and also oxidation with DDQ or oxygen failed. If the in situ formation of protons is avoided and stronger nucleophiles are used, one can isolate the expected dihydroadducts **24** in moderate to good yields and functionalize the 1,2,3-triazine system by that method. Oxidation of **24** led to 1,2,3-triazinylidens **25** and not to the completion of the S_N^H-reaction.

All reactions were carried out under Ar atmosphere with purified solvents (p.a. from Merck, VWR International Inc., Darmstadt; dried over molecular sieve). IR spectra were obtained on a Nicolet impact 400 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300, ARX-300 and DRX-500 spectrometer with tetramethylsilane as internal standard. ^{15}N NMR spectra were recorded on a Bruker DRX-500 spectrometer with nitromethane as internal standard. MS were determined on a Varian 212 instrument at 70 eV. Elemental analysis were obtained on a Perkin-Elmer CHN 240 A or 240 B. Silicagel 60 from FLUKA was used for column chromatography.

N-Aminopyrazoles (**5**)[7] and 1,2,3-Triazines (**6a**,**c**,**d**)[6,7] were synthesized by known methods.

4-Phenyl-1,2,3-triazine (6a)

^{15}N-NMR (50.7 MHz, acetone-d_6): δ = 83.14 (N-1, N-3), 8.32 (N-2).

5-Phenyl-1,2,3-triazine (6b)

To a solution of *N*-aminopyrazole **5b** (8.00 g, 51.3 mmol) in $CHCl_3$ (300 mL) was carefully added an aq soln (500 mL) of sodium *meta* periodate (21.5 g, 0.10 mol). The two phase reaction mixture was stirred at r.t. for 5 d. The two phases were seperated and the aqueous layer was extracted with $CHCl_3$ (3 × 200 mL). The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane–EtOAc, 1:1); yield: 4.20 g (54%); yellow needles; mp 145 °C (EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.25 (s, 2 H, 4-H, 6-H), 7.69–7.63 (m, 2 H, Ph), 7.57–7.51 (m, 3 H, Ph).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 147.39, 130.98, 131.42, 130.11, 127.26.

^{15}N-NMR (50.7 MHz, DMSO-d_6): δ = 71.48 (N-1, N-3), 10.62 (N-2).

MS (EI, 70 eV): *m*/*z* (%) = 158 (2) [M^+ + 1], 157 (12) [M^+], 129 (72), 102 (100), 87 (14), 76 (72), 63 (49), 50 (64), 39 (35).

Anal. Calcd for $C_9H_7N_3$: C, 68.78; H, 4.49; N, 26.73. Found: C, 68.81; H, 4.52; N, 26.67.

***N*-Ethylated 1,2,3-Triazinium Salts 7; General Procedure**

Triethyloxonium tetrafluoroborate (650 mg, 3.42 mmol) in $CHCl_3$ (5 mL) or triethyloxonium hexafluorophosphate (840 mg, 3.38 mmol) in CH_2Cl_2 (5 mL) was added to a cooled (0 °C) solution of 1,2,3-triazine **6a**–**d** (2.20 mmol) in $CHCl_3$ (**6a**,**b**) or CH_2Cl_2 (**6c**,**d**) (5 mL) and the mixture kept for 3 d at –20 °C. The crystals that formed were isolated and dried under vacuum.

2-Ethyl-4-phenyl-1,2,3-triazinium Tetrafluoroborate (7a)

Yield: 881 mg (95%); light yellow crystals; mp 130–132 °C ($CHCl_3$).

IR (KBr): 3063, 2925, 1561, 1392, 1067, 787, 685 cm^{-1}.

^{1}H NMR (300 MHz, acetone-d_6): δ = 9.94 (d, 1 H, $^3J_{5,6}$ = 6.2 Hz, 6-H), 9.15 (d, 1 H, $^3J_{5,6}$ = 6.2 Hz, 5-H), 8.45–8.42 (m, 2 H, Ph), 7.84–7.72 (m, 3 H, Ph), 5.46 (q, 2 H, ^3J = 7.2 Hz, –CH_2–), 1.94 (t, 3 H, ^3J = 7.2 Hz, –CH_3).

^{13}C NMR (75.7 MHz, acetone-d_6): δ = 166.80, 159.11, 135.81, 130.93, 129.74, 129.32, 67.96, 14.34.

^{15}N-NMR (50.7 MHz, acetone-d_6): δ = –21.46 (N-1, N-3), –69.93 (N-2).

MS (FD, 15 mA): *m*/*z* (%) = 459 (19) [M + K^+], 186 (100) [K^+], 78 (16).

Anal. Calcd for $C_{11}H_{12}N_3^+ BF_4^-$: C, 48.40; H, 4.06; N, 15.39. Found: C, 48.29; H, 4.16; N, 15.39.

2-Ethyl-5-phenyl-1,2,3-triazinium Tetrafluoroborate (7b)

Yield: 910 mg (98%); colorless crystals; mp 123 °C ($CHCl_3$).

IR (KBr): 3073, 2986, 1591, 1566, 1321, 1056, 766, 695 cm^{-1}.

^{1}H NMR (300 MHz, acetone-d_6): δ = 10.41 (s, 2 H, 4-H, 6-H), 8.28–8.25 (m, 2 H, Ph), 7.84–7.74 (m, 3 H, Ph), 5.32 (q, 2 H, ^3J = 7.3 Hz, –CH_2–), 1.90 (t, 3 H, ^3J = 7.3 Hz, –CH_3).

^{13}C NMR (75.7 MHz, acetone-d_6): δ = 155.17, 138.74, 131.21, 139.70, 128.72, 129.84, 60.78, 15.13.

^{15}N-NMR (50.7 MHz, acetone-d_6): δ = –17.49 (N-1, N-3), –81.46 (N-2).

MS (FD, 20 mA): *m*/*z* (%) = 460 (31) [M + K^+], 186 (100) [K^+], 78 (22).

Anal. Calcd for $C_{11}H_{12}N_3^+ BF_4^-$: C, 48.40; H, 4.06; N, 15.39. Found: C, 48.25; H, 4.24; N, 15.52.

2-Ethyl-4-methyl-1,2,3-triazinium Hexafluorophosphate (7c)
Yield: 510 mg (56%); colorless crystals; mp 78 °C (CH_2Cl_2).

IR (KBr): 3078, 2961, 1591, 1454, 837, 573 cm^{-1}.

^{1}H NMR (300 MHz, CD_3CN): δ = 9.55 (d, 1 H, $^3J_{5,6}$ = 5.8 Hz, 6-H), 8.30 (d, 1 H, $^3J_{5,6}$ = 5.8 Hz, 5-H), 5.15 (q, 2 H, ^3J = 7.3 Hz, –CH_2–), 2.90 (s, 3 H, 4-CH_3), 1.72 (t, 3 H, ^3J = 7.3 Hz, –CH_3).

^{13}C NMR (75.7 MHz, CD_3CN): δ = 172.66, 157.92, 129.01, 67.96, 22.35,14.69.

MS (FD, 15 mA): *m*/*z* (%) = 393 (45) [M + K^+], 124 [K^+] (100).

Anal. Calcd for $C_6H_{10}N_3^+ PF_6^-$: C, 26.78; H, 3.75; N, 15.61. Found: C, 26.93; H, 3.72; N, 15.69.

2-Ethyl-5-methyl-1,2,3-triazinium Hexafluorophosphate (7d)
Yield: 521 mg (57%); violet crystals; mp 152 °C (CH_2Cl_2).

IR (KBr): 3093, 2996, 1586, 1408, 837, 557 cm^{-1}.

^{1}H NMR (300 MHz, CD_3CN): δ = 9.60 (s, 2 H, 4-H, 6-H), 5.16 (q, 2 H, ^3J = 7.3 Hz, –CH_2–), 2.74 (s, 3 H, 5-CH_3), 1.77 (t, 3 H, ^3J = 7.3 Hz, –CH_3).

^{13}C NMR (75.7 MHz, CD_3CN): δ = 159.41, 144.10, 66.70, 17.30, 14.33.

MS (FD, 15 mA): *m*/*z* (%) = 393 (15) [M + K^+], 219 (43), 124 (100) [K^+].

Anal. Calcd for $C_6H_{10}N_3^+ PF_6^-$: C, 26.78; H, 3.75; N, 15.61. Found: C, 26.88; H, 3.65; N, 15.52.

***N*-Protonated 1,2,3-Triazinium Tetrafluoroborates 8a,b; General Procedure**
To a cooled solution (0 °C) of 1,2,3-triazine **6a**,**b** (315 mg, 2.00 mmol) in $CHCl_3$ (5 mL) was slowly added tetrafluoroboric acid (54% in Et_2O, Merck) (0.2 mL) in $CHCl_3$ (5 mL). Shortly after the first addition a solid product is formed. Directly after the last addition the product is filtrated, washed with $CHCl_3$ (2 × 5 mL) and dried under reduced pressure.

***N*-Hydro-4-phenyl-1,2,3-triazinium Tetrafluroborate (8a)**
Yield: 290 mg (92%); colorless crystals; mp 94 °C, dec. ($CHCl_3$).

IR (KBr): 3312, 3052, 2976, 1596, 1571, 1316, 1077, 751 cm^{-1}.

^{1}H NMR (300 MHz, CD_3CN): δ = 13.10 (br s, 1 H, N–H), 8.77 (d, 1 H, $^3J_{5,6}$ = 6.7 Hz, 6-H), 8.33–8.27 (m, 2 H, Ph), 7.72–7.67 (m, 4 H, Ph, 5-H).

^{13}C NMR (75.7 MHz, CD_3CN): δ = 163.53, 149.48, 135.77, 131.05, 130.24, 134.44, 116.96.

MS (FD, 15 mA): *m*/*z* (%) = 159 (6) [K^+ + 1], 158 (18) [K^+], 157 (100) [K^+ – 1], 102 (1), 78 (20).

Due to the hygroscopic nature of the product, no elemental analysis was possible.

***N*-Hydro-5-phenyl-1,2,3-triazinium Tetrafluroborate (8b)**
Yield: 278 mg (88%); light yellow crystals; mp 126 °C ($CHCl_3$).

IR (KBr): 3287, 3037, 1561, 1306, 1067, 781 cm^{-1}.

^{1}H NMR (300 MHz, CD_3CN): δ = 12.60 (br s, 1 H, N–H), 8.15–8.12 (m, 2 H, 4-H, 6-H), 7.86–7.63 (m, 5 H, Ph).

^{13}C NMR (75.7 MHz, CD_3CN): δ = 153.24, 139.93, 132.06, 131.59, 130.56, 131.92.

MS (FD, 15 mA): *m*/*z* (%) = 158 (19) [K^+], 157 (100) [K^+ – 1], 68 (36).

Due to the hygroscopic nature of the product, no elemental analysis was possible.

***N*-Phenylated 1,2,3-Triazinium Salts 9; General Procedure**
To a soln of the 1,2,3-triazines **6a**–**d** (1.50 mmol) and diphenyliodonium hexafluorophosphate (640 mg, 1.50 mmol) in CH_2Cl_2 (8 mL) was added CuI (30.0 mg, 0.15 mmol) and the soln was stirred for 3 d. The formed product is filtrated, washed with CH_2Cl_2 (2 × 5 mL) and dried under reduced pressure.

2,4-Diphenyl-1,2,3-triazinium Hexafluorophosphate (9a)
Yield: 386 mg (68%); light green crystals; mp 206–207 °C (CH_2Cl_2).

IR (KBr): 3134, 3098, 1561, 1403, 1342, 843, 751, 557 cm^{-1}.

^{1}H NMR (300 MHz, CD_3CN): δ = 9.79 (d, 1 H, $^3J_{5,6}$ = 6.1 Hz, 6-H), 8.80 (d, 1 H, $^3J_{5,6}$ = 6.1 Hz, 5-H), 8.57–8.55 (m, 2 H, Ph), 8.43–8.40 (m, 2 H, Ph), 7.93–7.63 (m, 6 H, Ph).

^{13}C NMR (75.7 MHz, CD_3CN): δ = 166.95, 158.96, 136.59, 131.84, 131.32, 130.03, 124.89, 123.90, 148.50, 130.62.

MS (EI, 70 eV): *m*/*z* (%) = 234 (42) [K^+], 107 (50), 77 (100), 51 (22).

MS (FD, 15 mA): *m*/*z* (%) = 613 (4) [M + K^+], 253 (4), 234 (100) [K^+], 78 (2).

Anal. Calcd for $C_{15}H_{12}N_3^+ PF_6^-$: C, 47.51; H, 3.19; N, 11.08. Found: C, 47.62; H, 3.26; N, 11.14.

2,5-Diphenyl-1,2,3-triazinium Hexafluorophosphate (9b)
Yield: 120 mg (29%); colorless crystals; mp >330 °C (CH_2Cl_2).

IR (KBr): 3068, 2930, 1576, 1382, 837, 766, 680, 562 cm^{-1}.

^{1}H NMR (300 MHz, CD_3CN): δ = 10.13 (s, 2 H, 4-H, 6-H), 8.43 (m, 2 H, Ph), 8.25 (m, 2 H, Ph), 8.08 (m, 4 H, Ph), 7.87 (m, 2 H, Ph).

^{13}C NMR (75.7 MHz, CD_3CN): δ = 155.06, 136.83, 135.88, 133.61, 132.20, 131.88, 130.44, 124.09, 134.20, 128.56.

MS (FD, 15 mA): *m*/*z* (%) = 613 (1) [M + K^+], 457 (2), 375 (2), 234 (100) [K^+], 78 (100).

Anal. Calcd for $C_{15}H_{12}N_3^+ PF_6^-$: C, 47.51; H, 3.19; N, 11.08. Found: C, 47.65; H, 3.28; N, 11.10.

4-Methyl-2-phenyl-1,2,3-triazinium Hexafluorophosphate (9c)
Yield: 205 mg (43%); light green crystals; mp 167 °C (CH_2Cl_2).

IR (KBr): 3108, 3073, 1576, 1342, 1311, 837, 751, 680, 557 cm^{-1}.

^{1}H NMR (300 MHz, CD_3CN): δ = 9.67 (d, 1 H, $^3J_{5,6}$ = 5.8 Hz, 6-H), 8.44–8.42 (m, 2 H, Ph), 8.34 (d, 1 H, $^3J_{5,6}$ = 5.8 Hz, 5-H), 7.88–7.87 (m, 1 H, Ph), 7.80–7.76 (m, 2 H, Ph), 3.00 (s, 3 H, 4-CH_3).

^{13}C NMR (75.7 MHz, CD_3CN): δ = 172.59, 157.93, 143.40, 136.33, 131.80, 128.77, 124.72, 22.55.

MS (FD, 18 mA): *m*/*z* (%) = 489 (22) [M + K^+], 341 (7), 172 (100) [K^+], 78 (3).

Anal. Calcd for $C_{10}H_{10}N_3^+ PF_6^-$: C, 37.87; H, 3.18; N, 13.25. Found: C, 37.98; H, 3.28; N, 13.26.

5-Methyl-2-phenyl-1,2,3-triazinium Hexafluorophosphate (9d)
Yield: 124 mg (26%); violet crystals; mp 159 °C (CH_2Cl_2).

IR (KBr): 3078, 1545, 1245, 837, 756, 685, 562 cm^{-1}.

^{1}H NMR (300 MHz, CD_3CN): δ = 9.72 (s, 2 H, 4-H, 6-H), 8.41–8.38 (m, 2 H, Ph), 7.90–7.80 (m, 3 H, Ph), 2.80 (s, 3 H, 5-CH_3).

^{13}C NMR (75.7 MHz, CD_3CN): δ = 171.30, 159.58, 151.25, 135.86, 131.78, 124.19, 17.97.

FDMS (18 mA): *m*/*z* (%) = 489 (3) [M + K^+], 354 (11), 239 (100), 172 (65) [K^+], 95 (14).

Anal. Calcd for $C_{10}H_{10}N_3^+ PF_6^-$: C, 37.87; H, 3.18; N, 13.25. Found: C, 38.02; H, 3.29; N, 13.32.

Reactions of 1,2,3-Triazinium Salts with Electron Rich Heterocycles; General Procedure

To a soln of the *N*-ethyl-1,2,3-triazinium salt **7** (1.00 mmol) in a chlorinated solvent (5 mL) (see Table 4) was added a solution (3 mL of the same solvent) of the heterocycle (1.00 mmol) at r.t. The reaction was followed by TLC and stopped when no further changes were observable. The solvent was removed under reduced pressure and the crude residue purified by column chromatography (for exact experimental details see Table 4).

2-Ethyl-5-(indol-3′-yl)-4-phenyl-2,5-dihydro-1,2,3-triazine (11a) and 1-Ethyl-3,4-bis(indol-3′-yl)-5-phenyl-pyrazole (12a)

Column chromatography with cyclohexane–EtOAc, 1:1.

Fraction 1: **11a** ; yield: 45 mg (15%); red oil.

IR (KBr): 3420, 2966, 1622, 1566, 1454, 748, 702 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (m, 1 H, N–H), 7.70–7.66 (m, 2 H, Ph), 7.33–7.12 (m, 7 H, Ph), 7.06 (d, 1 H, $^3J_{5,6}$ = 4.4 Hz, 6-H), 6.81–6.79 (m, 1 H, Ph), 4.87 (d, 1 H, $^3J_{5,6}$ = 4.4 Hz, 5-H), 4.02 (q, 2 H, ^3J = 7.1 Hz, $–CH_2–$), 1.17 (t, 3 H, ^3J = 7.1 Hz, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 302 (11) [M^+], 287 (11), 260 (43), 245 (100), 217 (10), 187 (25), 172 (10), 144 (19), 130 (17), 117 (33), 102 (88), 89 (11), 77 (34), 51 (19).

HRMS: *m*/*z* calcd for $C_{19}H_{18}N_4$, 302.1531; found, 302.1563.

Fraction 2: **12a**; yield: 60 mg (15%); red oil.

IR (KBr): 3429, 3151, 3029, 2976, 1566, 1459, 1102, 731, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.25 (s, 1 H, N–H), 9.95 (s, 1 H, N–H), 8.55 (m, 1 H, 2′-H Ind.), 7.42–7.31 (m, 7 H, Ph), 7.24–7.21 (m, 1 H, Ph), 7.14–7.10 (m, 4 H, Ph), 7.09 (m, 1 H, Ph), 6.80 (m, 1 H, 2′-H Ind.), 4.19 (q, 2 H, ^3J = 7.1 Hz, $–CH_2–$), 1.50 (t, 3 H, ^3J = 7.1 Hz, -CH_3).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 147.11, 142.98, 137.36, 137.06, 132.02, 130.76, 129.02, 128.84, 127.30, 125.61, 125.44, 124.17, 124.01, 123.38, 122.29, 122.08, 120.53, 120.02, 119.73, 112.20, 112.15, 111.73, 111.08, 111.06, 110.67, 109.31, 45.12, 16.03.

MS (FD, 15 mA): *m*/*z* (%) = 402 (100) [M^+], 202 (3), 78 (62).

HRMS: *m*/*z* calcd for $C_{27}H_{22}N_4$, 402.1844; found, 402.1861.

2-Ethyl-5-(indol-3′-yl)-4-methyl-2,5-dihydro-1,2,3-triazine (11b) and 1-Ethyl-3,4-bis(indol-3′-yl)-5-methyl-pyrazole (12b)

Column chromatography with cyclohexane–EtOAc, 1:1.

Fraction 1: **11b**; yield: 33 mg (14%); red oil.

IR (KBr): 3404, 2971, 1459, 1260, 802, 746 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (br s, 1 H, N–H), 7.47 (m, 1 H, 4′-H or 7′-H), 7.34 (m, 1 H, 4′-H or 7′-H), 7.13 (m, 1 H, 5′-H or 6′-H), 7.05 (m, 1 H, 5′-H or 6′-H), 6.98 (m, 1 H, 2′-H), 6.80 (d, 1 H, $^3J_{5,6}$ = 2.2 Hz, 6-H), 3.10 (q, 2 H, ^3J = 7.1 Hz, $–CH_2–$), 3.51 (d, 1 H, $^3J_{5,6}$ = 2.2 Hz, 5-H), 1.83 (s, 3 H, 4-CH_3), 1.28 (t, 3 H, ^3J = 7.1 Hz, -CH_3).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 142.13, 136.51, 134.51, 126.70, 123.06, 122.61, 120.20, 118.82, 111.59, 54.09, 34.09, 19.99, 12.99.

MS (EI, 70 eV): *m*/*z* (%) = 241 (11) [M^+ + 1], 240 (100) [M^+], 225 (40), 183 (29), 156 (20), 143 (24), 129 (27), 115 (39), 32 (17).

HRMS: *m*/*z* calcd for $C_{14}H_{16}N_4$, 240.1375; found, 240.1385.

Fraction 2: **12b**; yield: 27 mg (8%); red oil.

IR (KBr): 3409, 2966, 1464, 1265, 802, 741 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (br s, 1 H, N–H), 8.14 (m, 1 H, Ph), 7.74 (br s, 1 H, N–H), 7.33–7.25 (m, 2 H, Ph), 7.15–7.01 (m, 6 H, Ph), 6.70 (m, 1 H, Ph), 4.17 (q, 2 H, ^3J = 7.2 Hz, $–CH_2–$), 2.13 (s, 3 H, 5-CH_3), 1.49 (t, 3 H, ^3J = 7.2 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 145.23, 137.21, 136.21, 135.87, 127.85, 126.30, 123.83, 123.29, 122.19, 122.03, 120.80, 120.61, 120.06, 119.67, 109.94, 109.76, 102.66, 44.34, 15.62, 10.13.

MS (EI, 70 eV): *m*/*z* (%) = 340 (1) [M^+], 279 (26), 167 (44), 149 (100), 117 (16), 113 (15), 70 (24), 57 (44), 43 (42).

HRMS: *m*/*z* calcd for $C_{22}H_{20}N_4$, 340.1663; found, 340.1688.

2-Ethyl-4-phenyl-5-(pyrrol-2′-yl)-2,5-dihydro-1,2,3-triazine (11c), 2-Ethyl-4-phenyl-5-pyrrol-3′-yl-2,5-dihydro-1,2,3-triazine (11d) and 1-Ethyl-3,4-bis(pyrrol-2′-yl)-5-phenyl-pyrazole (12c)

Column chromatography with cyclohexane–EtOAc, 1:1.

Fraction 1: **11c**; yield: 57 mg (23%); red oil.

IR (KBr): 3394, 2971, 1632, 1561, 1438, 756, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13 (br s, 1 H, N–H), 7.75–7.64 (m, 2 H, Ph), 7.29–7.24 (m, 3 H, Ph), 7.03 (d, 1 H, $^3J_{5,6}$ = 4.45 Hz, 6-H), 6.50–6.49 (m, 1 H, 5′-H), 6.00–5.99 (m, 1 H, 3′-H or 4′-H), 5.85–5.84 (m, 1 H, 3′-H or 4′-H), 4.67 (d, 1 H, $^3J_{5,6}$ = 4.45 Hz, 5-H), 3.73 (q, 2 H, ^3J = 7.1 Hz, $–CH_2–$), 1.30 (t, 3 H, ^3J = 7.1 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 139.05, 138.21, 134.30, 133.42, 129.47, 128.64, 126.41, 118.31, 108.22, 106.68, 54.57, 31.02, 13.02.

MS (EI, 70 eV, 80 °C): *m*/*z* (%) = 253 (9) [M^+ + 1], 252 (100) [M^+], 223 (10), 195 (30), 175 (19), 168 (31), 92 (29), 79 (12), 65 (20), 39 (11).

HRMS: *m*/*z* calcd for $C_{15}H_{16}N_4$, 252.1375; found, 252.1416.

Fraction 2: **11d**; yield: 20 mg (8%); red oil.

IR (KBr): 3414, 2971, 1566, 1448, 1367, 802, 756, 690 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (br s, 1 H, N–H), 7.75–7.64 (m, 2 H, Ph), 7.30–7.24 (m, 3 H, Ph), 6.98 (d, 1 H, $^3J_{5,6}$ = 4.43 Hz, 6-H), 6.60–6.59 (m, 1 H, 2′-H or 5′-H), 6.50–6.49 (m, 1 H, 2′-H or 5′-H), 6.04–6.03 (m, 1 H, 4′-H), 4.52 (d, 1 H, $^3J_{5,6}$ = 4.43 Hz, 5-H), 3.77 (q, 2 H, ^3J = 7.1 Hz, $–CH_2–$), 1.30 (t, 3 H, ^3J = 7.1 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 138.61, 132.38, 129.48, 128.64, 126.41, 119.88, 118.40, 115.97, 107.83, 54.53, 29.73, 13.21.

MS (EI, 70 eV, 80 °C): *m*/*z* (%) = 253 (12) [M^+ + 1], 252 (100) [M^+], 195 (34), 175 (14), 168 (37), 102 (43), 92 (33), 77 (12), 65 (15), 51 (14), 39 (14).

HRMS: *m*/*z* calcd for $C_{15}H_{16}N_4$, 252.1375; found, 252.1399.

Fraction 3: **12c**; yield: 30 mg (10%); brown oil.

IR (KBr): 3399, 2966, 1566, 1443, 736, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.09 (br s, 1 H, N–H), 8.86 (br s, 1 H, N–H), 7.35–7.30 (m, 2 H, Ph), 7.25–7.21 (m, 3 H, Ph), 6.70–6.65 (m, 2 H, 5′-H), 6.20 (m, 1 H, 3′-H or 4′-H), 6.13–6.05 (m, 2 H, 3′-H or 4′-H), 5.94 (m, 1 H, 3′-H or 4′-H), 4.00 (q, 2 H, ^3J = 7.2 Hz, $–CH_2–$), 1.31 (t, 3 H, ^3J = 7.2 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 150.15, 142.18, 132.36, 130.19, 129.57, 128.50, 118.12, 117.88, 116.98, 116.58, 113.68, 110.60, 109.30, 108.95, 107.09, 44.72, 16.05.

MS (EI, 70 eV): *m*/*z* (%) = 303 (14) [M^+ + 1], 302 (67) [M^+], 237 (15), 197 (9), 168 (12), 102 (100).

HRMS: *m*/*z* calcd for $C_{19}H_{18}N_4$, 302.1531; found, 302.1557.

2-Ethyl-4-methyl-5-(pyrrol-2′-yl)-2,5-dihydro-1,2,3-triazine (11e) and 1-Ethyl-5-methyl-3,4-bis(pyrrol-2′-yl)-pyrazole (12d)
Column chromatography with cyclohexane–EtOAc, 1:1.

Fraction 1: **11e**; yield: 10 mg (5%); red oil.

IR (KBr): 3236, 2961, 1586, 1459, 797, 705 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (br s, 1 H, N–H), 6.85 (d, 1 H, $^3J_{5,6}$ = 3.4 Hz, 6-H), 6.59 (m_c, 1 H, 5′-H), 6.03 (m_c, 1 H, 3′-H or 4′-H), 5.99 (m_c, 1 H, 3′- H, 4′-H), 3.67–3.53 (m, 3 H, $–CH_2–$ and 5-H), 1.93 (s, 3 H, 4-CH_3), 1.21 (t, 3 H, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 191 (7) [M^+ + 1], 190 (69) [M^+], 175 (40), 161 (16), 106 (46), 92 (100), 79 (67), 65 (56), 52 (24), 41 (30), 39 (36).

HRMS: *m*/*z* calcd for $C_{10}H_{14}N_4$, 190.1219; found, 190.1235.

Fraction 2: **12d**; yield: 10 mg (4%); red oil.

IR (KBr): 3399, 3251, 1622, 1489, 802, 731 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.05 (br s, 1 H, N–H), 8.24 (br s, 1 H, N–H), 6.80–6.78 (m, 1 H, 5′-H), 6.69–6.68 (m, 1 H, 5′-H), 6.24–6.21 (m, 1 H, 3′-H or 4′-H), 6.13–6.12, 6.11, 6.07–6.02 (3m, 3 H, 3′-H or 4′-H), 4.07 (q, 2 H, ^3J = 7.2 Hz, $–CH_2–$), 2.18 (s, 3 H, 4-CH_3), 1.39 (t, 3 H, ^3J = 7.2 Hz, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 241 (11) [M^+ + 1], 240 (100) [M^+], 212 (11), 169 (13), 105 (9), 32 (75).

HRMS: *m*/*z* calcd for $C_{14}H_{16}N_4$, 240.1375; found, 240.1398.

2-Ethyl-5-(2′-methylindol-3′-yl)-4-phenyl-2,5-dihydro-1,2,3-triazine (11f)
Column chromatography with cyclohexane–EtOAc, 1:1; yield: 67 mg (21%); violet oil.

IR (KBr): 3409, 2956, 1555, 1459, 751, 695 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.76 (br s, 1 H, N–H), 7.56–7.53 (m, 2 H, Ph), 7.49–7.48 (m, 1 H, 4′-H), 7.17–7.11 (m, 4 H, Ph, 7′-H), 7.06–7.00 (m, 2 H, 5′-H, 6′-H), 6.78 (d, 1 H, $^3J_{5,6}$ = 3.5 Hz, 6-H), 4.56 (d, 1 H, $^3J_{5,6}$ = 3.5 Hz, 5-H), 3.81 (q, 2 H, ^3J = 7.12 Hz, $–CH_2–$), 2.33 (s, 3 H, 2′-CH_3), 1.35 (t, 3 H, ^3J = 7.12 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 137.91, 136.10, 135.08, 134.87, 132.79, 128.74, 128.23, 127.73, 126.31, 121.56, 119.98, 118.18, 110.43, 110.29, 54.31, 28.18, 13.27, 12.14.

MS (EI, 70 eV): *m*/*z* (%) = 317 (23) [M^+ + 1], 316 (100) [M^+], 301 (30), 259 (57), 239 (16), 156 (20), 143 (49), 130 (71), 115 (9), 84 (35), 77 (9), 69 (15), 56 (77), 41 (39), 32 (37).

HRMS: *m*/*z* calcd for $C_{20}H_{20}N_4$, 316.1688; found, 316.1710.

2–Ethyl-4-methyl-5-(2′-methylindol-3′-yl)-2,5-dihydro-1,2,3-triazine (11g)
Column chromatography with cyclohexane–EtOAc, 1:1; yield: 69 mg (27%); violet oil.

IR (KBr): 3261, 2966, 1622, 1510, 1464, 802, 751 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.03 (br s, 1 H, N–H), 7.35–7.24 (m, 2 H, 4′-H, 7′-H), 7.11–6.97 (m, 2 H, 5′-H, 6′-H), 6.71 (d, 1 H, $^3J_{5,6}$ = 1.7 Hz, 6-H), 3.73 (q, 2 H, ^3J = 7.05 Hz, $–CH_2–$), 3.22 (d, 1 H, $^3J_{5,6}$ = 1.7 Hz, 5-H), 2.27 (s, 3 H, 2′-CH_3), 1.71 (s, 3 H, 4-CH_3), 1.35 (t, 3 H, ^3J = 7.05 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 150,67, 142.64, 135.44, 127.90, 135.72, 121.70, 120.06, 118.18, 110.67, 107.47, 54.11, 34.20, 19.53, 13.05, 11.87.

MS (EI, 70 eV): *m*/*z* (%) = 255 (4) [M^+ + 1], 254 (54) [M^+], 239 (28), 197 (22), 156 (11), 130 (26), 121 (11), 88 (30), 86 (93), 84 (100), 47 (47).

HRMS: *m*/*z* calcd for $C_{15}H_{18}N_4$, 254.1532; found, 254.1552.

2-Ethyl-5-(1′-methylpyrrol-3′-yl)-4-phenyl-2,5-dihydro-1,2,3-triazine (11h)
Column chromatography with CH_2Cl_2–EtOAc, 5:1; yield: 61 mg (23%); red oil.

IR (KBr): 2966, 1520, 1443, 1357, 1158, 776, 756, 695 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.76–7.27 (m, 2 H, Ph), 7.30–7.23 (m, 3 H, Ph), 6.96 (d, 1 H, $^3J_{5,6}$ = 4.46 Hz, 6-H), 6.39–6.37 (m, 1 H, 2′-H or 5′-H), 6.30–6.28 (m, 1 H, 2′-H or 5′-H), 5.93–5.91 (m, 1 H, 4-H), 4.46 (d, 1 H, $^3J_{5,6}$ = 4.46 Hz, 5-H), 3.77 (q, 2 H, ^3J = 7.0 Hz, $–CH_2–$), 3.45 (s, 3 H, N–CH_3), 1.32 (t, 3 H, ^3J = 7.0 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 138.78, 134.47, 128.86, 128.47, 126.31, 130.4, 122.13, 119.90, 107.57, 54.35, 36.32, 29.70, 13.19.

MS (EI, 70 eV): *m*/*z* (%) = 266 (29) [M^+], 209 (26), 182 (59), 167 (31), 152 (10), 139 (25), 115 (27), 106 (100), 94 (22), 83 (78), 77 (78), 63 (27), 51 (56), 42 (75), 39 (52), 35 (64).

HRMS: *m*/*z* calcd for $C_{16}H_{18}N_4$, 266.1531; found, 266.1533.

2-Ethyl-4-methyl-5-(1′-methylpyrrol-2′yl)-2,5-dihydro-1,2,3-triazine (11i)
Column chromatography with cyclohexane–EtOAc, 1:1; yield: 10 mg (5%); red oil.

IR (KBr): 2966, 1703, 1566, 1408, 807, 715 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.71 (d, 1 H, $^3J_{5,6}$ = 2.1 Hz, 6-H), 6.57 (m, 1 H, 5′-H), 6.07 (m, 1 H, 3′-H or 4′-H), 5.91 (m, 1 H, 3′-H or 4′-H), 3.59 (q, 2 H, ^3J = 7.2 Hz, $–CH_2–$), 3.50 (s, 3 H, N–CH_3), 3.16 (d, 1 H, $^3J_{5,6}$ = 2.1 Hz, 5-H), 1.87 (s, 3 H, 4-CH_3), 1.25 (t, 3 H, ^3J = 7.2 Hz, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 205 (11) [M^+ + 1], 204 (100) [M^+], 189 (46), 175 (10), 147 (16), 120 (31), 106 (38), 94 (23), 77 (35), 42 (68).

HRMS: *m*/*z* calcd for $C_{11}H_{16}N_4$, 204.1375; found, 204.1390.

(2′,5′-Dimethylpyrrol-3′-yl)-2-ethyl-4-phenyl-2,5-dihydro-1,2,3-triazine (11j)
Column chromatography with cyclohexane–EtOAc, 1:1; yield: 129 mg (46%); red crystals; mp 116 °C (CH_2Cl_2).

IR (KBr): 3424, 3373, 3063, 2981, 2930, 1611, 1448, 1357, 797, 761, 695 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.62 (m, 2 H, Ph), 7.27 (br s, 1 H, N–H), 7.27–7.20 (m, 3 H, Ph), 6.86 (d, 1 H, $^3J_{5,6}$ = 4.18 Hz, 6-H), 5.47 (m, 1 H, 4′-H), 4.27 (d, 1 H, $^3J_{5,6}$ = 4.18 Hz, 5-H), 3.73 (q, 2 H, ^3J = 7.17 Hz, $–CH_2–$), 2.15 (s, 3 H, 2′-CH_3 or 5′-CH_3), 2.05 (s, 3 H, 2′-CH_3 or 5′-CH_3), 1.30 (t, 3 H, ^3J = 7.17 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 138.82, 136.09, 136.53, 134.71, 128.74, 128.39, 126.29, 125.81, 116.63, 106.62, 54.27, 29.36, 13.17, 13.05, 11.47.

MS (EI, 70 eV): *m*/*z* (%) = 281 (9) [M^+ + 1], 280 (84) [M^+], 265 (17), 223 (20), 203 (17), 120 (19), 107 (24), 94 (83), 85 (100), 83 (100), 77 (26), 47 (45).

HRMS: *m*/*z* calcd for $C_{17}H_{20}N_4$, 280.1688; found, 280.1670.

5-(2′,5′-Dimethylpyrrol-3′-yl)-2-ethyl-4-methyl-2,5-dihydro-1,2,3-triazine (11k)
Column chromatography with cyclohexane–EtOAc, 1:1; yield: 72 mg (33%); red oil.

IR (KBr): 3261, 2966, 2915, 1540, 1438, 1377, 812, 741, 680 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (br s, 1 H, N–H), 6.63 (d, 1 H, $^3J_{5,6}$ = 1.9 Hz, 6-H), 5.56 (s, 1 H, 4′-H), 3.63 (q, 2 H, ^3J = 7.1 Hz, $–CH_2–$), 2.96 (d, 1, $^3J_{5,6}$ = 1.9 Hz, 5-H), 2.14, 2.07 (2s, 6 H, 2′-CH_3, 5′-CH_3), 1.78 (s, 3 H, 4-CH_3), 1.22 (t, 3 H, ^3J = 7.1 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 141.85, 134.66, 124.97, 122.17, 114.11, 105.44, 52.90, 33.78, 18.63, 11.91, 11.80, 9.98.

MS (EI, 70 eV): *m*/*z* (%) = 218 (67) [M^+], 203 (62), 134 (28), 120 (29), 107 (26), 94 (100), 77 (15), 42 (29).

HRMS: *m*/*z* calcd for $C_{12}H_{18}N_4$, 218.1532; found, 218.1540.

5-(2′,4′-Dimethylpyrrol-3′-yl)-2-ethyl-4-phenyl-2,5-dihydro-1,2,3-triazine (11l)

Column chromatography with cyclohexane–EtOAc, 1:1; yield: 30 mg (11%); brown oil.

IR (KBr): 3409, 3063, 2971, 2940, 1561, 1443, 1362, 1265, 802, 766, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (br s, 1 H, N–H), 7.65–7.61 (m, 2 H, Ph), 7.45–7.18 (m, 3 H, Ph), 7.21–7.18 (superimposed d, 1 H, 6-H), 6.63 (m, 1 H, 5′-H), 4.38 (d, 1 H, $^3J_{5,6}$ = 4.38 Hz, 5-H), 3.74 (q, 2 H, ^3J = 7.2 Hz, $–CH_2–$), 1.90, 1.89 (2s, 6 H, 2′-CH_3, 4′-CH_3), 1.34 (t, 3 H, ^3J = 7.2 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 138.92, 136.17, 135.28, 129.45, 128.62, 127.04, 129.53, 126.29, 127.42, 107.73, 54.58, 30.96, 29.11, 12.96.

MS (EI, 70 eV): *m*/*z* (%) = 280 [M^+] (16), 265 (12), 186 (11), 107 (16), 98 (11), 84 (100), 77 (10).

HRMS: *m*/*z* calcd for $C_{17}H_{20}N_4$, 280.1688; found, 280.1686.

5-(2′,4′-Dimethylpyrrol-3′-yl)-2-ethyl-4-methyl-2,5-dihydro-1,2,3-triazine (11m)

Column chromatography with cyclohexane–EtOAc, 1:1; yield: 20 mg (9%); red oil.

IR (KBr): 3399, 2966, 2930, 1688, 1545, 1428, 1382, 802, 705 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (br s, 1 H, N–H), 6.87–6.83 (m, 1 H, 5′-H), 6.57 (d, 1 H, $^3J_{5,6}$ = 1.7 Hz, 6-H), 3.64 (q, 2 H, ^3J = 7.12 Hz, $–CH_2–$), 2.92 (d, 1 H, $^3J_{5,6}$ = 1.7 Hz, 5-H), 1.97, 1.87, 1.68 (3s, 9 H, 2′-CH_3, 4′-CH_3, 4-CH_3), 1.25 (t, 3 H, ^3J = 7.12 Hz, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 218 [M^+] (3), 217 [M^+–1] (7), 167 (14), 149 (38), 139 (17), 124 (35), 113 (13), 96 (29), 84 (76), 67 (58), 57 (47), 38 (100), 28 (100).

HRMS: *m*/*z* calcd for $C_{12}H_{18}N_4$, 218.1688; found, 218.1691.

5-(3′,5′-Dimethylpyrrol-2′-yl)-2-ethyl-4-methyl-2,5-dihydro-1,2,3-triazine (11n)

Column chromatography with cyclohexane–EtOAc, 1:1; yield: 24 mg (11%); red oil.

IR (KBr): 3434, 2976, 1448, 802, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (br s, 1 H, N–H), 6.63 (d, 1 H, $^3J_{5,6}$ = 1.5 Hz, 6-H), 5.60–5.59 (m, 1 H, 4′-H), 3.67 (q, 2 H, ^3J = 7.1 Hz, $–CH_2–$), 2.99 (d, 1 H, $^3J_{5,6}$ = 1.5 Hz, 5-H), 2.14, 2.07, 1.76 (3s, 9 H, 3′-CH_3, 5′-CH_3, 4-CH_3), 1.45 (t, 3 H, ^3J = 7.1 Hz, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 218 [M^+] (4), 169 (100), 147 (30), 119 (46), 97 (10), 69 (70), 32 (100).

HRMS: *m*/*z* calcd for $C_{12}H_{18}N_4$, 218.1688; found, 218.1665.

Reactions of *N*-Phenylated 1,2,3-Triazinium Salts 9 with Electron Rich Heterocycles; General Procedure

To a soln of *N*-phenyl-1,2,3-triazinium salt **9** (0.40 mmol) in CH_3CN (5 mL) was added the heterocycle (0.40 mmol) in CH_3CN (5 mL) at r.t. The reaction was observed by TLC and stopped when no further changes were observable. The solvent was removed under reduced pressure and the crude material purified by column chromatography. The insoluble residue (prior to chromatography) is mainly 1,2,3-triazinium salt **9** and can be used for further reactions.

2,4-Diphenyl-5-(2′-methylindol-3′-yl)-2,5-dihydro-1,2,3-triazine (22a)

Reaction time 3 d; column chromatography with cyclohexane–EtOAc, 1:1; yield: 22 mg (15%); violet oil.

IR (KBr): 3404, 3058, 2966, 1606, 1489, 756, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (br s, 1 H, N–H), 7.75–7.71 (m, 4 H, Ph), 7.51–7.48 (m, 1 H, Ind), 7.35–7.30 (m, 3 H, Ind), 7.19–7.15 (m, 3 H, Ph), 7.05–7.01 (m, 3 H, Ph), 6.89 (d, 1 H, $^3J_{5,6}$ = 3.6 Hz, 6-H), 4.82 (d, 1 H, $^3J_{5,6}$ = 3.6 Hz, 5-H), 2.21 (s, 3 H, 2′-CH_3).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 146.09, 137.60, 136.07, 133.43, 127.54, 125.22, 115.40, 134.91, 129.02, 128.38, 126.13, 122.63, 121.72, 120.28, 117.66, 110.61, 27.19, 12.19.

MS (EI, 70 eV): *m*/*z* (%) = 365 (32) [M^+ + 1], 364 [M^+] (100), 349 (35), 336 (18), 287 (15), 272 (33), 260 (34), 246 (14), 234 (24), 217 (13), 182 (10), 169 (17), 143 (79), 130 (77), 115 (12), 91 (12), 77 (50).

HRMS: *m*/*z* calcd for $C_{24}H_{20}N_4$, 364.1688; found, 364.1672.

5-(Indol-3′-yl)-4-methyl-2-phenyl-2,5-dihydro-1,2,3-triazine (22b)

Reaction time 5 d; column chromatography with cyclohexane–EtOAc, 1:1; yield: 18 mg (16%); red oil.

IR (KBr): 3434, 3068, 2971, 2915, 1601, 1510, 1469, 766, 741, 700 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.23 (br s, 1 H), 7.75–7.72 (m, 2 H, Ph), 7.56–7.50 (m, 4 H, Ph), 7.37–7.32 (m, 3 H, Ph), 7.20–7.04 (m, 2 H, 6-H, Ph), 4.79 (m, 1 H, 5-H), 2.14 (s, 3 H, 4-CH_3).

^{13}C NMR (75.7 MHz, DMSO-d_6): δ = 147.10, 143.69, 139.52, 136.19, 127.20, 128.98, 125.62, 123.98, 122.34, 120.97, 119.23, 118.61, 111.58, 38.59, 12.99.

MS (EI, 70 eV): *m*/*z* (%) = 289 [M^+ + 1] (28), 288 [M^+] (100), 246 (18), 219 (12), 144 (11), 77 (23).

HRMS: *m*/*z* calcd for $C_{18}H_{16}N_4$, 288.1375; found, 288.1363.

2,4-Diphenyl-5-(*N*-methylpyrrol-3′-yl)-2,5-dihydro-1,2,3-triazine (22c)

Reaction time 16 h; column chromatography with cyclohexane–EtOAc (1:1); yield: 28 mg (23%); red oil.

IR (KBr): 3052, 2971, 1591, 1494, 751, 695, 608 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.84 (m, 2 H, Ph), 7.74–7.71 (m, 2 H, Ph), 7.33–7.28 (m, 5 H, Ph), 7.10 (d, 1 H, $^3J_{5,6}$ = 4.4 Hz, 6-H), 6.40–6.38 (m, 1 H, 2′-H or 5′-H), 6.32–6.31 (m, 1 H, 2′-H or 5′-H), 5.96–5.94 (m, 1 H, 4′-H), 4.55 (d, 1 H, $^3J_{5,6}$ = 4.4 Hz, 5-H), 3.43 (s, 3 H, N–CH_3).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 146.51, 139.01, 135.48, 135.19, 129.31, 128.89, 128.54, 126.58, 122.73, 122.41, 119.93, 115.74, 120.62, 107.44, 36.32, 29.81.

MS (EI, 70 eV): *m*/*z* (%) = 315 (29) [M^+ + 1], 314 (100) [M^+], 313 (43) [M^+–1], 237 (12), 210 (14), 184 (29), 167 (13), 106 (20), 94 (32), 77 (61).

HRMS: *m/z* calcd for $C_{20}H_{18}N_4$, 314.1531, found, 314.1517.

4-Methyl-5-(*N*-methylpyrrol-3′-yl)-2-phenyl-2,5-dihydro-1,2,3-triazine (22d)
Reaction time 2 h; column chromatography with $CHCl_3$; yield: 21 mg (21%); red oil.

IR (KBr): 2966, 1545, 1418, 797, 705 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.57 (m, 2 H, Ph), 7.28–7.24 (m, 2 H, Ph), 6.98–6.93 (m, 1 H, Ph), 6.81 (d, 1 H, $^3J_{5,6}$ = 2.9 Hz, 6-H), 6.49–6.47 (m, 1 H, 2′-H or 5′-H), 6.38–6.37 (m, 1 H, 2′-H or 5′-H), 5.93–5.92 (m, 1 H, 4′-H), 3.58 (d, 1 H, $^3J_{5,6}$ = 2.9 Hz, 5-H), 3.54 (s, 3 H, N–CH_3), 1.51 (s, 3 H, 4-CH_3).

MS (EI, 70 eV): *m/z* (%) = 253 (1) [M^+ + 1], 252 (10) [M^+], 221 (10), 167 (24), 149 (42), 125 (15), 111 (43), 97 (60), 83 (72), 57 (100), 43 (87).

HRMS: *m/z* calcd for $C_{15}H_{16}N_4$, 252.1375; found, 252.1402.

Reactions with C,H-Acidic Compounds; General Procedure
To a cooled (0 °C) soln of compound **22** (1.20 mmol) in THF (5 mL) was added NaH (29 mg, 1.20 mmol), suspended in THF (2 mL). After 30 min, when no further gas formation was observed, the 1,2,3-triazinium salt **7** (1.00 mmol) in CH_3CN (5 mL) was added. The reaction mixture was warmed to r.t. and stirred for several hours (TLC control). The solvent was removed under reduced pressure and the crude material purified by column chromatography.

Dimethyl 2-(2′-ethyl-4′-phenyl-2′,5′-dihydro-1,2,3-triazin-5′-yl) Malonate (24a)
Reaction time 16 h; column chromatography with CH_2Cl_2–EtOAc, 5:1; yield: 123 mg (39%); yellow oil.

IR (KBr): 3063, 2951, 1739, 1443, 1260, 766, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.68 (m, 2 H, Ph), 7.37–7.24 (m, 3 H, Ph), 6.87 (d, 1 H, $^3J_{6',5'}$ = 4.5 Hz, 6′-H), 4.53 (dd, 1 H, $^3J_{5',6'}$ = 4.5 Hz, $^3J_{5',2}$ = 10.3 Hz, 5′-H), 3.83 (q, 2 H, ^3J = 7.2 Hz, –CH_2–), 3.67 (s, 3 H, –OCH_3), 3.35 (d, 1 H, $^3J_{2,5'}$ = 10.3 Hz, 2-H), 3.20 (s, 3 H, –OCH_3), 1.35 (t, 3 H, ^3J = 7.2 Hz, –CH_3).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 167.65, 149.45, 134.51, 130.36, 129.31, 128.60, 125.93, 54.50, 53.16, 52.67, 46.09, 31.23, 13.40.

MS (EI, 70 eV): *m/z* (%) = 317 [M^+] (11), 186 (100), 158 (20), 115 (20), 104 (28), 77 (14).

HRMS: *m/z* calcd for $C_{16}H_{19}N_3O_4$, 317.1376; found, 317.1359.

Dimethyl 2-(2′-ethyl-4′-methyl-2′,5′-dihydro-1,2,3-triazin-5′-yl) Malonate (24b)
Reaction time 1 h; column chromatography with CH_2Cl_2–EtOAc, 5:1; yield: 240 mg (94%); yellow oil.

IR (film): 2961, 2869, 1739, 1443, 1245, 1026, 975, 843 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.62 (d, 1 H, $^3J_{6',5'}$ = 4.0 Hz, 6′-H), 3.69–3.61 (m, 9 H, 2 × OCH_3, –CH_2–, 5′-H), 3.40–3.32 (d, 1 H, $^3J_{2,5'}$ = 9.9 Hz, 2-H), 1.97 (s, 3 H, 4′-CH_3), 1.23 (t, 3 H, ^3J = 7.1 Hz, –CH_3).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 166.95, 166.47, 136.14, 127.95, 52.97, 51.89, 51.81, 45.10, 34.60, 19.98, 11.90.

MS (EI, 70 eV): *m/z* (%) = 255 [M^+] (4), 181 (9), 164 (10), 124 (100), 96 (11), 85 (19), 83 (21), 42 (18).

HRMS: *m/z* calcd for $C_{11}H_{17}N_3O_4$, 255.1219; found, 255.1233.

3-(2′-Ethyl-4′-phenyl-2′,5′-dihydro-1,2,3-triazin-5′-yl)-pentan-2,4-dione (24c)
Reaction time 3 h; column chromatography with cyclohexane–EtOAc, 1:1; yield: 205 mg (72%); yellow oil.

IR (KBr): 3068, 2981, 2925, 1734, 1708, 1581, 776, 690 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.63 (m, 2 H, Ph), 7.33–7.26 (m, 3 H, Ph), 6.78 (d, 1 H, $^3J_{6',5'}$ = 4.5 Hz, 6′-H), 4.56 (dd, 1 H, $^3J_{5',6'}$ = 4.5 Hz, $^3J_{5',2}$ = 9.5 Hz, 5′-H), 3.86–3.79 (m, 3 H, –CH_2–, 2-H), 2.03 (s, 3 H, –CH_3), 1.88 (s, 3 H, –CH_3), 1.33 (t, 3 H, ^3J = 7.1 Hz, –CH_3).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 202.81, 201.65, 135.31, 134.18, 128.80, 129.69, 126.39, 131.95, 58.28, 53.36, 31.90, 29.78, 30.41, 13.15.

MS (EI, 70 eV): *m/z* (%) = 286 (1) [M^+ + 1], 285 (6) [M^+], 242 (25), 186 (100), 103 (28), 77 (10), 43 (18).

HRMS: *m/z* calcd for $C_{16}H_{19}N_3O_2$, 285.1477; found, 285.1477.

3-(2′-Ethyl-4′-methyl-2′,5′-dihydro-1,2,3-triazin-5′-yl)-pentan-2,4-dione (24d)
Reaction time 1 h; column chromatography with cyclohexane–EtOAc, 1:1; yield: 74 mg (33%); yellow oil.

IR (film): 2966, 2930, 1738, 1714, 1565 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.55–6.52 (m, 1 H, 6′-H), 3.75–3.72 (superimposed q, 2 H, –CH_2–), 3.63 (d, 1 H, $^3J_{2,5'}$ = 9.6 Hz, 2-H), 3.46 (dd, 1 H, $^3J_{5',6'}$ = 4.1 Hz, $^3J_{5',2}$ = 9.6 Hz, 5′-H), 2.13, 2.07, 1.93 (3s, 9 H, 1-CH_3, 5-CH_3, 4′-CH_3), 1.16 (superimposed t, 3 H, –CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.79, 199.58, 148.08, 130.17, 61.26, 58.52, 57.52, 40.02, 34.87, 29.43, 15.77. Superimposition due to a small amount of the enol form.

MS (EI, 70 eV): *m/z* (%) = 224 (2) [M^+ + 1], 223 (12) [M^+], 222 (100) [M^+–1], 179 (24), 124 (38), 43 (18).

HRMS: *m/z* calcd for $C_{11}H_{17}N_3O_2$, 223.1321, found, 223.1267.

Ethyl 2-(2′-ethyl-4′-phenyl-2′,5′-dihydro-1,2,3-triazin-5′-yl)-3-oxobutyrate (24e)
Reaction time 16 h; column chromatography with cyclohexane–EtOAc, 1:1; yield: 212 mg (67%); orange oil.

IR (film): 3068, 2991, 2930, 1729, 1591, 1367, 766, 690 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 13.21 (br s, 0.25 H, -OH of the enol form), 7.72–7.68 (m, 2 H, Ph), 7.30–7.24 (m, 3 H, Ph), 6.85–6.83 (superimposed d, 1 H, 6′-H), 4.59–4.53 (superimposed dd, 1 H, 5′-H), 4.11–4.08 (superimposed d, 1 H, 5′-H, enol), 3.86–3.81 (superimposed q, 2 H, –CH_2–), 3.68–3.61 (superimposed q, 2 H, –CH_2–), 3.54 (d, 1 H, $^3J_{2,5'}$ = 10.2 Hz, 2-H), 2.06 (s, 3 H, 4-CH_3), 1.96 (s, 3 H, 4-CH_3), 1.36 (t, 3 H, –CH_3), 0.75 (t, 3 H, –CH_3).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 202.08, 167.47, 135.03, 134.73, 131.62, 130.88, 129.75, 129.35, 129.09, 128.90, 126.09, 62.00, 61.23, 54.47, 53.99, 52.95, 31.42, 31.27, 30.87, 29,62, 14.08, 13.57, 13.41. The keto/enol forms exist in soln in a 3:1 ratio.

MS (EI, 70 eV): *m/z* (%) = 316 (1) [M^+ + 1], 315 (10) [M^+], 224 (10), 186 (100), 158 (14), 115 (10), 103 (38), 77 (14).

HRMS: *m/z* calcd for $C_{17}H_{21}N_3O_3$, 315.1556; found, 315.1597.

Ethyl 2-(2′-Ethyl-4′-methyl-2′,5′-dihydro-1,2,3-triazin-5′-yl)-3-oxobutyrate (24f)
Reaction time 1 h; column chromatography with cyclohexane–EtOAc, 1:1; yield: 192 mg (76%); red oil.

IR (film): 2986, 2940, 1744, 1713, 1581, 1240, 1016 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.68 (d, 1 H, $^3J_{6',5'}$ = 4.0 Hz, 6′-H), 6.66 (d, 1 H, $^3J_{6',5'}$ = 4.0 Hz, 6′-H), 4.22–4.18 (superimposed q, 4 H, OCH_2–), 3.77–3.61 (m, 8 H, N–CH_2–, 5′-H, 2-H), 2.26 (s, 3 H, 4-CH_3), 2.16 (s, 3 H, 4-CH_3), 2.04, 2.02 (2s, 6 H, 4′-CH_3), 1.32–1.25 (superimposed t, 12 H, –CH_3).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.61, 200.58, 167.60, 167.08, 138.35, 138.18, 130.06, 129.88, 61.08, 54.00, 53.74, 53.44, 35.43,

35.25, 30.69, 29.88, 21.42, 21.21, 14.01, 12.89, 12.87. The keto/enol forms exist in soln in a 1:1 ratio.

MS (EI, 70 eV): *m*/*z* (%) = 254 (1) [M^+ + 1], 253 (7) [M^+], 180 (10), 124 (100), 96 (9).

HRMS: *m*/*z* calcd for $C_{12}H_{19}N_3O_3$, 253.1427; found, 253.1400.

Oxidation of the Dihydroadducts 24; General Procedure

To a soln of the dihydroadduct **24** (0.50 mmol) in dioxane (6 mL) was added DDQ (227 mg, 1.00 mmol) in dioxane (8 mL) at r.t. The reaction mixture was stirred for 2 h (TLC-control). The soln was then concentrated under vacuum and the hydrochinone removed by filtration. The remaining solvent was removed under reduced pressure and the crude product purified by column chromatography (cyclohexane–EtOAc, 1:1).

Dimethyl (2′-Ethyl-4′-phenyl-2′*H*-1,2,3-triazin-5′-yliden) Malonate (25a)

Yield: 155 mg (98%); yellow oil.

IR (KBr): 3007, 2966, 1723, 1683, 1545, 1268, 802, 705 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.14 (s, 1 H, H-6), 7.44–7.39 (m, 2 H, Ph), 7.34–7.28 (m, 3 H, Ph), 4.14 (q, 2 H, ^3J = 7.3 Hz, $–CH_2–$), 3.63 (s, 3 H, OCH_3), 2.90 (s, 3 H, OCH_3), 1.42 (t, 3 H, ^3J = 7.3 Hz, $–CH_3$).

^{13}C NMR (75.7 MHz, $CDCl_3$): δ = 167.43, 166.28, 146.61, 138.29, 136.22, 129.29, 128.56, 126.98, 128.32, 101.49, 56.57, 51.87, 51.28, 14.46.

MS (EI, 70 eV): *m*/*z* (%) = 316 (1) [M^+ + 1], 315 (35) [M^+], 284 (10), 255 (100), 241 (10), 224 (32), 197 (12), 182 (26), 173 (15), 140 (17), 115 (21), 105 (89), 77 (57), 69 (26), 55 (46), 43 (51).

HRMS: *m*/*z* calcd for $C_{16}H_{17}N_3O_4$, 315.1219; found, 315.1231.

Dimethyl (2′-Ethyl-4-methyl-2′*H*-1,2,3-triazin-5′-yliden) Malonate (25b)

Yield: 38 mg (30%); yellow oil.

IR (KBr): 2966, 1729, 1688, 1566, 1438, 1031, 807 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.43 (s, 1 H, 6-H), 4.06 (q, 2 H, ^3J = 7.2 Hz, $–CH_2–$), 3.70, 3.69 (2 s, 6 H, OCH_3), 2.09 (s, 3 H, 4-CH_3), 1.34 (t, 3 H, ^3J = 7.2 Hz, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 254 (6) [M^+ + 1], 253 (79) [M^+], 222 (77), 208 (10), 190 (100), 163 (48), 153 (17), 137 (27), 123 (14), 105 (26), 77 (22), 67 (26), 51 (46).

HRMS: *m*/*z* calcd for $C_{11}H_{15}N_3O_4$, 253.1063; found, 253.1101.

3-(2′-Ethyl-4′-phenyl-2′*H*-1,2,3-triazin-5′-yliden)-pentan-2,4-dione (25c)

Yield: 35 mg (24%); as yellow oil.

IR (KBr): 3013, 2976, 1745, 1716, 1565, 782, 701 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.27 (s, 1 H, 6′-H), 7.46–7.38 (m, 2 H, Ph), 7.31–7.24 (m, 3 H, Ph), 4.04 (q, 2 H, ^3J = 7.1 Hz, $–CH_2–$), 2.10 (s, 3 H, $–CH_3$), 1.96 (s, 3 H, $–CH_3$), 1.27 (t, 3 H, ^3J = 7.1 Hz, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 284 (4) [M^+ + 1], 283 (48) [M^+], 240 (28), 184 (100), 101 (31), 77 (18).

HRMS: *m*/*z* calcd for $C_{16}H_{17}N_3O_2$, 285.1321; found, 285.1344.

3-(2′-Ethyl-4′-methyl-2′*H*-1,2,3-triazin-5′-yliden)-pentan-2,4-dione (25d)

Yield: 34 mg (31%); yellow oil.

IR (film): 2978, 1745, 1721, 1578 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.29 (s, 1 H, 6-H), 3.92 (q, 2 H, ^3J = 7.3 Hz, $–CH_2–$), 2.27, 2.23, 1.85 (3 s, 9 H, 1-CH_3, 5-CH_3, 4′-CH_3), 1.24 (t, 3 H, ^3J = 7.3 Hz, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 222 (1) [M^+ + 1], 221 (27) [M^+], 220 (100) [M^+–1], 178 (27), 122 (17), 43 (37).

HRMS: *m*/*z* calcd for $C_{11}H_{15}N_3O_2$, 221.1164; found, 221.1201.

Ethyl 2-(2′-Ethyl-4′-phenyl-2′*H*-1,2,3-triazin-5′-yliden)-3-oxobutyrate (25e)

Yield: 75 mg (48%); red oil.

IR (film): 3012, 2984, 2941, 1738, 1560, 1348, 775, 701 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.33 (s, 1 H, 6′-H), 7.43–7.35 (m, 2 H, Ph), 7.32–7.24 (m, 3 H, Ph), 4.26 (q, 2 H, ^3J = 7.2 Hz, $–OCH_2–$) 3.95 (q, 2 H, ^3J = 7.2 Hz, $–CH_2–$), 2.10 (s, 3 H, 4-CH_3), 1.86 (t, 3 H, ^3J = 7.2 Hz, $–CH_3$), 1.24 (t, 3 H, ^3J = 7.2 Hz, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 314 (2) [M^+ + 1], 313 (27) [M^+], 222 (14), 184 (100), 156 (20), 101 (45), 77 (37).

HRMS: *m*/*z* calcd for $C_{17}H_{19}N_3O_3$, 313.1426; found, 314.1432.

Ethyl 2-(2′-Ethyl-4′-methyl-2′*H*-1,2,3-triazin-5′-yliden)-3-oxobutyrate (24f)

Yield: 37 mg (48%); red oil.

IR (film): 2993, 2931, 1735, 1567, 1298, 1030 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.02 (s, 1 H, 6′-H), 4.34 (q, 2 H, $–OCH_2–$), 3.58 (q, 2 H, $–CH_2–$), 2.15 (s, 3 H, 4-CH_3), 2.02, (s, 3 H, 4′-CH_3), 1.43–1.36 (superimposed t, 6 H, $–CH_3$).

MS (EI, 70 eV): *m*/*z* (%) = 252 (1) [M^+ + 1], 251 (18) [M^+], 178 (10), 122 (100), 94 (11).

HRMS: *m*/*z* calcd for $C_{12}H_{17}N_3O_3$, 251.1270; found, 251.1258.

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