Non-symmetrical allenyl azines and their transformations leading to new heterocyclic skeletons

Juraj Galeta, Stanislav Man, and Milan Potáček*

Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
E-mail: potacek@chemi.muni.cz

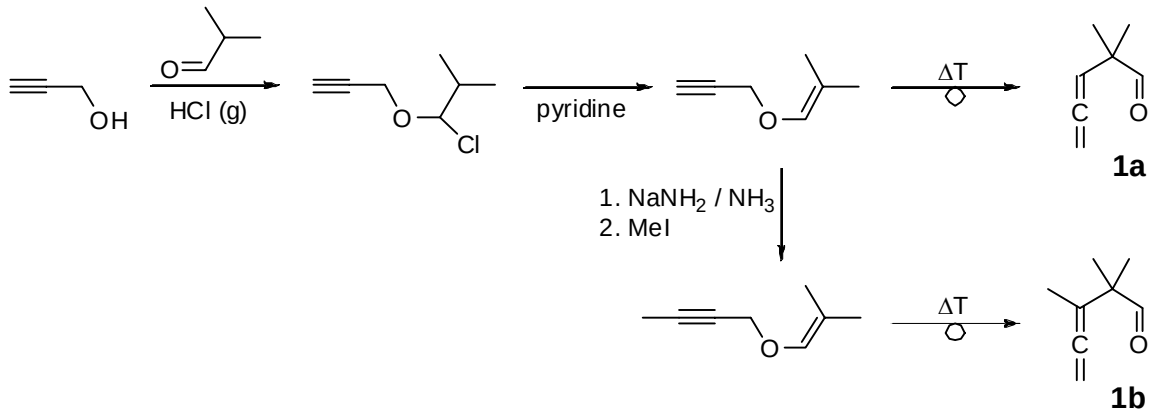
The paper is dedicated to Professor Henk van der Plas on the occasion of his 80th anniversary

Abstract
The preparation of new non-symmetrical allenyl azines **5** with aliphatic and alicyclic substituents and their reactions are described. When aldazines **5** were refluxed in xylene formation of bicyclic products **7** was observed. Compounds **7** appeared as derivatives of isowithasomnine. Combined intra-intermolecular criss-cross cycloadditions of azines **5** afforded heterocyclic products **8** and **9** containing three fused five-membered rings. Structures of all new compounds were elucidated by ^{1}H and ^{13}C NMR, IR and MS measurements and in some cases by X-ray structure analysis.

Keywords: Allene, non-symmetrical azines, 1,3-dipolar cycloadditions, cyclizations, intra-intermolecular criss-cross cycloaddition, isowithasomnine

Introduction

For a long time, the chemistry of the allenyl synthon was neglected in heterocyclic chemistry. Only in the past decade has the number of published papers increased and a survey of its chemical reactivity appeared.[1] However, our laboratory belongs to the working places where the chemistry of allene derivatives was investigated. We have investigated mostly derivatives of homoallenyl aldehyde **1**, because we have developed its improved preparation procedure (Scheme 1).[2] Among all the derivatives symmetrical azines play important role as educts of intramolecular criss-cross cycloadditions.[3] Fused tetracyclic compounds, formed in this fashion, as products of two successive 1,3-dipolar cycloadditions,[4] have been the source of interesting information about the mechanism of their formation and possible further transformations.[5]



Scheme 1. Preparation of homoallenyl aldehydes **1a** and **1b**.

Homoallenyl oxime prepared from compound **1** appeared to be a very fruitful molecule undergoing many further useful transformations *via* a stable nitrone, which underwent further reactions either with preservation of the dipole or with its participation in a 1,3-dipolar cycloaddition and formation of new skeletons.[6] On the other hand non-symmetrical allenyl azines **5,** especially those with an aliphatic and alicyclic substituents are not known. Therefore we concentrated on the preparation of this type of compounds, and then to investigation of their transformations.

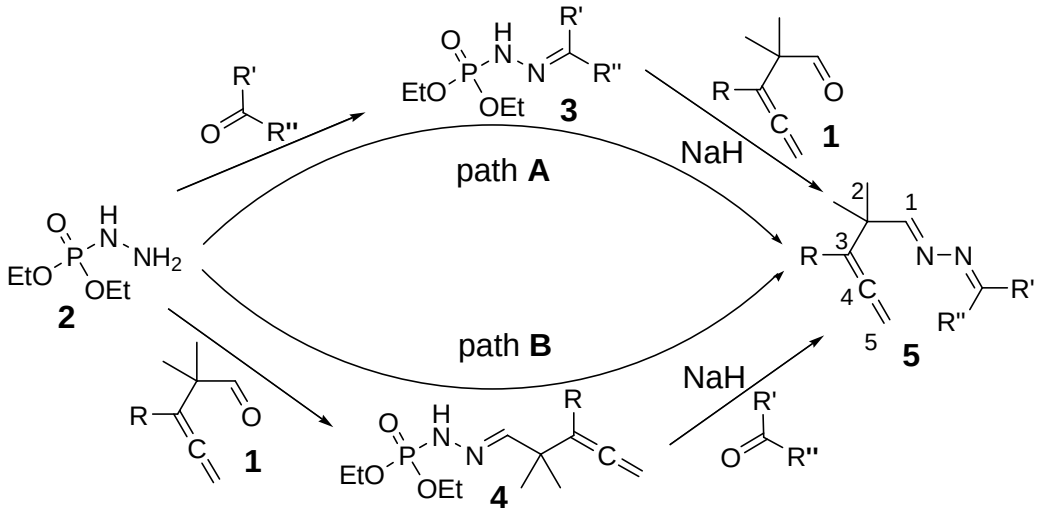
The method published by Zwierzak enabled a comfortable preparation of non-symmetrical azines.[7] In this method the first step consists of one nitrogen of hydrazine molecule protection by the reaction with diethyl phosphite forming diethyl hydrazidophosphate **2**. The intermediate **2** was reacted the usual way with one carbonyl compound to form the protected hydrazones **3** or **4**. Treatment of the hydrazone in the presence of sodium hydride in dry ether with another carbonyl compound yielded the non-symmetrical azine **5** (Scheme 2).

Some of these new non-symmetrical allenyl azines **5** were reacted with different dipolarophiles by thermally initiated combined intra-intermolecular criss-cross cycloaddition (CCC) (Scheme 5). The CCCs reactions may be classified as a special type of [3 + 2] cycloaddition,[8] or 1,3-dipolar cycloaddition. These reactions afforded new heterocycles **8** with three fused five-membered rings. The formation of criss-cross products was first time explained by Huisgen[4] in 1963 as a succession of two successive 1,3-dipolar cycloadditions. This explanation was proven in 1973 when a stable 1,3-dipole was identified by X-ray crystallographic analysis.[9]

Results and Discussion

Preparation of non-symmetrical homoallenyl azines

The synthesis of homoallenyl aldehydes **1a** and **1b** was carried out according the described procedure (Scheme 1).[2] The synthesis of the non-symmetrical allenyl azines **5** from the allenyl aldehyde **1** can be performed by two different pathways (**A** and **B**) as shown at the following Scheme 2. In most of the cases the preparation was carried out *via* aliphatic or alicyclic protected hydrazone **3** from protected hydrazidate **2** and by reaction with homoallenyl aldehyde **1**. The preferred way is (**A**) because in the first step of reaction the less expensive aldehyde or ketone is used. The other path (**B**) consisting of reaction of homoallenyl aldehyde **1** with protected hydrazidate **2** led to the protected homoallenyl hydrazone **4.** Subsequent reaction with the corresponding aliphatic aldehyde or ketone afforded the non-symmetrical azine **5**. Although both pathways could be used for azines **5**, azines **5a**,**b (**where R' and R'' = H) could only be prepared according to path **B.** When preparation was attempted according to path **A,** tar mixtures were isolated.



Scheme 2. Preparation of allenyl azines **5**.

Monitoring of azine **5** formation (Table 1) was carried out by TLC and interestingly also by the odor of reaction mixture because of the typical and strong smell of forming compound **5**. Another important attribute of azines **5** with aliphatic or alicyclic substitution is their rather high stability at room temperature (no decomposition was observed within several weeks).

Table 1. Non-symmetrical allenyl azines **5a-n** and their yields

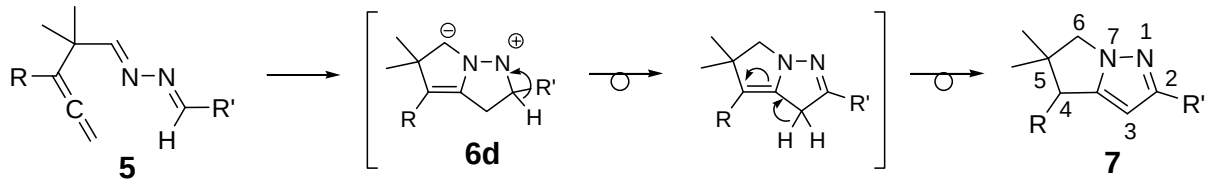
Compound **5**	R	R‘	R“	yield [%]	time [h]
a	H	H	H	89	1
b	Me	H	H	54	1.2
c	H	Me	H	61	3
d	Me	Me	H	70	3
e	H	Et	H	79	2
f	Me	Et	H	54	2.5
g	H	*i*-Pr	H	80	2
h	Me	*i*-Pr	H	78	3.5
i	H	CH=CH-Me	H	89	2
j	Me	CH=CH-Me	H	56	3
k	H	-$(CH_2)_4$-		84	1.5
l	Me	-$(CH_2)_4$-		81	1.5
m	H	-$(CH_2)_5$-		82	1.5
n	Me	-$(CH_2)_5$-		80	1

In the IR spectra, products **5** were characterized by strong C=N vibration (between 1606 – 1659 cm^{-1}) and strong C=C=C vibration (~ 1954 cm^{-1}). The molecular weights of all the products were confirmed by MS by the presence of their molecular ion-peaks.

Absence of a stereogenic centre is typical for all these compounds **5**. Therefore, we can observe only one signal for both of the methyl groups at C2. Characteristic for ^{1}H NMR spectra of compounds with allenyl skeleton C$\underline{H_2}$=C=C$\underline{R}$- is a long distance interaction between protons with coupling constants $^4J_{H,H}$ ~ 6.6 Hz for R = H and $^5J_{H,H}$ ~ 3.0 Hz for R = Me. A similar situation exists with both methyl groups in ^{13}C NMR spectrum.

Reactions of azines 5

In the case that homoallenyl aldazines **5** are refluxed in dry xylene, formation of bicyclic derivatives **7** was observed (Scheme 3, Table 3).



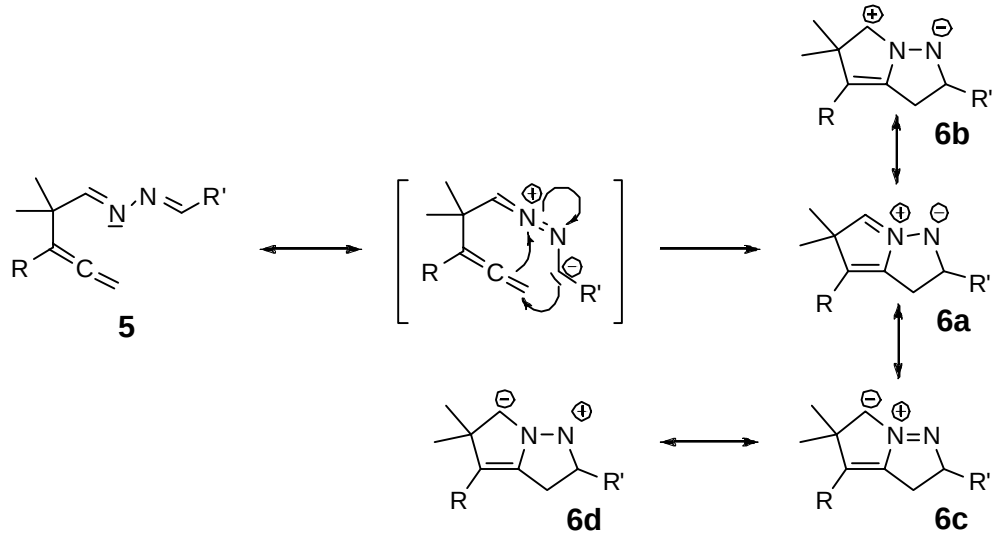
Scheme 3. Formation of bicyclic compounds **7**.

Table 3. Characteristics of bicyclic products **7a-c**

Compound	R	R‘	Yield [%]	Time [h]	Purification
7a	Me	H	35	5	AcOEt/PE (1:3)
7b	Me	Me	~ 50	5	Et_2O
7c	Me	*i*-Pr	94	6	Et_2O/PE (1:1)

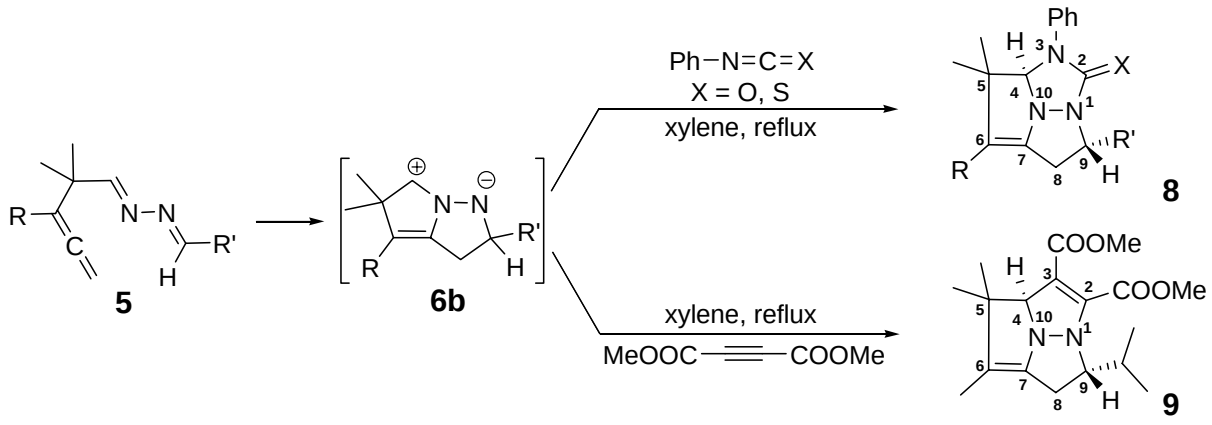
Formation of such structures has already been observed when aromatic homoallenyl azines were heated with low reactive dipolarophiles.[10,11] Compounds **7** prepared in this way are derivatives of isowithasomnine. Products **7** contain an aliphatic chain instead of phenyl in isowithasomnine in position 2. Isowithasomnine differs from withasomnine, a plant alkaloid known as Indian Gin-Seng, by position of the phenyl and was isolated from plants *Withania somnifera Dun,*[12] *Elytraria acaulis*[13] and *Newbouldia laevis.*[14] It has anesthetic and narcotic properties[15] as well as being an inhibitor of malignant growth.[16] Our reaction afforded reasonable yields only in case the applied azine is aldazine. Otherwise a rather complicated mixture of decomposition products is obtained.

When considering the reaction mechanism, the initial step of the process is an intramolecular attack (probably the rate determining step) *via* formation of dipolar intermediate **6,** which may be written in four resonance structures **6a-d** (Scheme 4). Formation of such a product was also predicted in our previous study by *ab initio* calculations.[17] The intermediate **6** then undergoes protons shifts affording compound **7** (Scheme 3).



Scheme 4. Generation of 1,3-dipole **6a-d**, as a reactive intermediate, in dry boiling xylene.

In case we add into reaction mixture a reactive dipolarophile the *in situ* formed dipole reacts to product containing three fused five-membered heterocyclic rings (Scheme 5).



Scheme 5. Intermolecular criss-cross cycloaddition of 1,3-dipole **6b** with dipolarophiles.

This way in so called combined intra-intermolecular criss-cross cycloaddition were prepared new heterocyclic compounds **8** and **9** (Table 4) with three fused five-membered rings (Scheme 5).

Table 4. Overview of prepared compounds **8** and **9** and information for their preparation and purification

Compound	R	R‘	dipolarophile	yield [%]	time [h]	purification	ratio azine/dipolar. [mmol]	solvent [ml]
8a	H	H	PhNCO	50	5	AcOEt/PE (1:4)	2 / 2.4	60
8b	Me	H	PhNCO	61	3	EtOH/Hexan (~2:1)	1 / 1.2	30
8c	H	Me	PhNCO	40	6	AcOEt/PE (1:4)	2.6 / 2.8	80
8d	Me	Me	PhNCO	93	5	AcOEt/PE (1:3)	1 / 1.2	30
8e	H	Et	PhNCO	41	5	AcOEt/PE (1:6)	3.3 / 3.5	100
8f	Me	Et	PhNCO	45	8	Et_2O/PE (~1:1) -10 ºC	1.5 / 1.6	45
8g	H	H	BnNCS	40	3	AcOEt/PE (1:4)	3 / 3	30
8h	H	H	PhNCS	39	4	PE/Et_2O (~5:1)	2 / 2	20
8i	Me	H	PhNCS	78	3	EtOH/Hexane (~2:1)	1 / 1	10
9	Me	*i*-Pr	DAD*	90	5	Et_2O/PE (8:2)	0.6 / 1.2	25

* DAD = dimethylacetylene dicarboxylate; PE = petroleum ether

These structures were elucidated by NMR spectroscopic measurements. In contrast to allenyl azines **5**, compounds **8** contain stereogenic centres. Therefore the methyl groups at the C5 are diastereotopic and we can find their signals as two distinct entities differing by about 0.5 ppm in ^{1}H NMR and by 3 - 5 ppm in ^{13}C NMR spectra. The other signals are presented in the Experimental section. For approval of the structure X-ray diffraction analysis was carried out. The measured compounds appeared as a racemate of one diastereoisomer only (Figure 1).

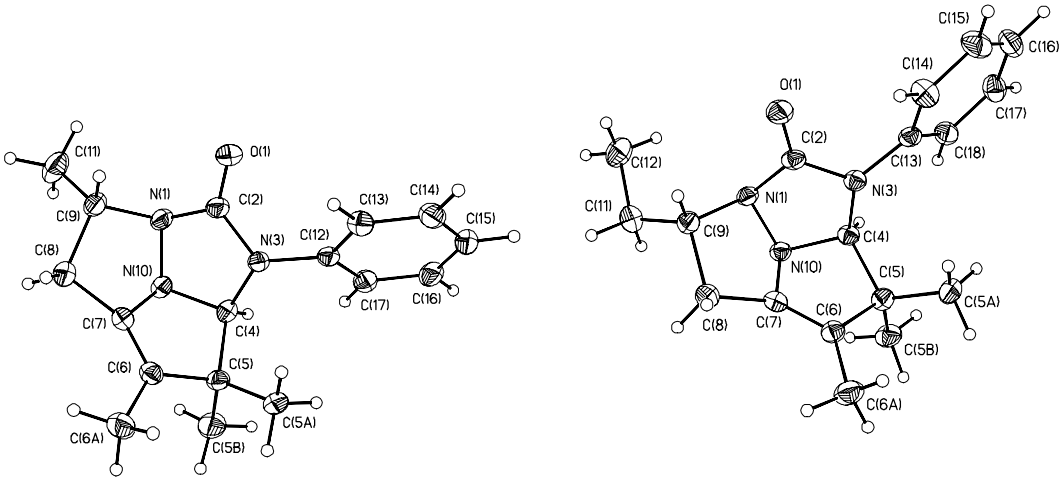


Figure 1. X-ray structure of compounds **8d** and **8f**.

Because of the sterically demanding group R' the dipolarophile is approaching the molecule of 1,3-dipole from one side only and therefore one diastereoisomer is formed.

Conclusions

We have succeeded in synthesising new non-symmetrical homoallenyl azines (aldazines **5a-j** and aldoketazines **5k-n**) in reasonable yields and fully characterise them. When azines **5** were heated without any dipolarophile products **7** belonging to derivatives of isowithasomnine were isolated. Further azines **5** in the presence of reactive dipolarophiles under thermally initiated reaction underwent intra-intermolecular criss-cross cycloaddition *via* formation of 1,3-dipole affording new heterocyclic skeletons **8** and **9,** respectively**,** consisting from three fused five-membered rings.

Experimental Section

General Procedures. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. FT-IR spectra were measured with GENESIS ATI (Unicam) spectrometer. ^{1}H and

^{13}C NMR spectra were recorded on Bruker AVANCE 300 spectrometer in $CDCl_3$. Tetramethylsilane (δ = 0.00 ppm) or $CHCl_3$ (δ = 7.27 ppm) served as an internal standards for ^{1}H NMR (300 MHz) and $CDCl_3$ as an internal standard (δ = 77.23 ppm) for ^{13}C NMR (75.5 MHz). Coupling constants are reported in Hertz [Hz]. MS data were obtained on a FISONS INSTRUMENTS TRIO 1000 spectrometer with EI ionization (30 eV) and GC-MS on SHIMADZU GCMS-QP2010 in EI mode (30 eV). HRMS were taken at Waters-Micromas, Q-Tof Micro (ESSI positive).

X-Ray diffraction data were collected with a Kuma KM-4 four-circle CCD diffractometer and corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by using a SHELXTL program package.[19] The hydrogen atoms were placed in calculated idealized positions. Liquid chromatography was carried out on Horizon HPFC System (Biotage, Inc.) with Biotage Si 12+M and 25+M columns. Xylene (mixture of isomers), benzene and diethylether were dried and distilled from sodium/benzophenone and stored under argon. All reactions were carried out under a dry argon atmosphere and monitored by TLC on plates coated with Merck silica gel F_{254}.

General procedure for the preparation of 5a-b and 5c-n

A mixture of allenyl hydrazone **4** (10 mmol) and paraformaldehyde (20 mmol, equiv. CH_2O) in benzene (30 ml) was slowly added to a suspension of NaH (0.36 g, 15 mmol) in diethylether (30 ml) at 5-10 ºC. Then the reaction mixture was left stirring at room temperature. The solution was filtered and the residue washed with diethylether (3 × 20 ml). The combined organic phases were concentrated in vacuo and the crude product was purified by vacuum distillation using Kugelrohr apparatus to give colorless or yellowish liquid.

The procedure for the preparation of **5c-n** differs in used amounts of reactants only. The reaction mixture contains 10.5 mmol of protected hydrazone **3** and 10 mmol of allenyl aldehyde **1**.

(2,2-Dimethylpenta-3,4-dien-1-ylidene) formaldehyde hydrazone (5a). IR (film) ν_{max} / cm^{-1} 845, 972, 1196, 1362, 1383, 1464, 1606 (C=N), 1637 (C=N), 1954 (=C=), 2866, 2927, 2966. MS m/z (%) 137 (M^++1; 18), 121 (100), 108 (73), 94 (54), 79 (74), 67 (58), 53 (46), 41 (73). ^{1}H NMR δ 1.26 (s, 6H, H_3C-C-CH_3), 4.82 (d, $^4J_{H,H}$ = 6.6; 2H, =CH_2), 5.23 (t, $^4J_{H,H}$ = 6.6; 1H, HC=C), 6.94 (d, $^2J_{H,H}$ = 13.5; 1H, N=CH_2), 7.36 (d, $^2J_{H,H}$ = 13.5; 1H, N=CH_2), 7.64 (s, 1H, HC=N). ^{13}C NMR δ 25.6 ($H_3\underline{C}$-C-$\underline{C}H_3$), 38.1 (H_3C-$\underline{C}$-CH_3), 77.9 (=CH_2), 97.3 (H$\underline{C}$=C), 149.6 (N=CH_2), 169.4 (HC=N), 207.2 (=C=).

(2,2,3-Trimethylpenta-3,4-dien-1-ylidene) formaldehyde hydrazone (5b). IR (film) ν_{max} /cm^{-1} 847, 991, 1109, 1196, 1383, 1456, 1606 (C=N), 1637 (C=N), 1952 (=C=), 2868, 2927, 2970. MS m/z (%) 151 (M^++1; 4), 135 (100), 122 (38), 107 (39), 79 (47), 67 (45), 53 (29), 41 (48). ^{1}H NMR δ 1.25 (s, 6H, H_3C-C-CH_3), 1.67 (t, $^5J_{H,H}$ = 3.0; 3H, =C-CH_3), 4.70 (q, $^5J_{H,H}$ = 3.0; 2H, =CH_2), 6.93 (d, $^2J_{H,H}$ = 13.5; 1H, N=CH_2), 7.35 (d, $^2J_{H,H}$ = 13.5; 1H, N=CH_2), 7.57 (s, 1H, HC=N). ^{13}C NMR δ 15.3 (=C-$\underline{C}H_3$), 24.2 ($H_3\underline{C}$-C-$\underline{C}H_3$), 40.2 (H_3C-$\underline{C}$-CH_3), 76.1 (=CH_2), 103.3 (=$\underline{C}$-CH_3), 149.3 (N=CH_2), 169.1 (HC=N), 206.4 (=C=).

(2,2-Dimethylpenta-3,4-dien-1-ylidene) acetaldehyde hydrazone (5c). IR (film) ν_{max} / cm^{-1} 847, 1147, 1309, 1377, 1433, 1464, 1651 (C=N), 1954 (=C=), 2891, 2929, 2970. ^{1}H NMR δ 1.23 (s, 6H, H_3C-C-CH_3), 2.01 (d, $^3J_{H,H}$ = 5.3; 3H, HC-C$\underline{H}_3$), 4.80 (d, $^4J_{H,H}$ = 6.6; 2H, =CH_2), 5.22 (t, $^4J_{H,H}$ = 6.6; 1H, HC=C), 7.69 (s, 1H, HC=N), 7.87 (q, $^3J_{H,H}$ = 5.5; 1H, $\underline{H}$C-CH_3). ^{13}C NMR δ 18.9 (HC-$\underline{C}H_3$), 25.6 ($H_3\underline{C}$-C-$\underline{C}H_3$), 38.0 (H_3C-$\underline{C}$-CH_3), 77.9 (=CH_2), 97.3 (H$\underline{C}$=C), 161.5 (H$\underline{C}$-CH_3), 169.3 (HC=N), 207.0 (=C=).

(2,2,3-Trimethylpenta-3,4-dien-1-ylidene) acetaldehyde hydrazone (5d). IR (film) ν_{max} / cm^{-1} 845, 1109, 1309, 1375, 1434, 1653 (C=N), 1955 (=C=), 2929, 2972. ^{1}H NMR δ 1.23 (s, 6H, H_3C-C-CH_3), 1.65 (t, $^5J_{H,H}$ = 3.1; 3H, =C-CH_3), 1.95 (d, $^3J_{H,H}$ = 5.3; 3H, HC-C$\underline{H}_3$), 4.68 (q, $^5J_{H,H}$ = 3.0; 2H, =CH_2), 7.62 (s, 1H, HC=N), 7.85 (q, $^3J_{H,H}$ = 5.4; 1H, $\underline{H}$C-CH_3). ^{13}C NMR δ 15.3 (=C-$\underline{C}H_3$), 18.9 (HC-$\underline{C}H_3$), 24.3 ($H_3\underline{C}$-C-$\underline{C}H_3$), 40.1 (H_3C-$\underline{C}$-CH_3), 76.0 (=CH_2), 103.4 (=$\underline{C}$-CH_3), 160.9 (H$\underline{C}$-CH_3), 169.0 (HC=N), 206.4 (=C=).

(2,2-Dimethylpenta-3,4-dien-1-ylidene) propionaldehyde hydrazone (5e). IR (film) ν_{max} / cm^{-1} 847, 901, 1147, 1317, 1363, 1462, 1651 (C=N), 1956 (=C=), 2885, 2935, 2970. MS m/z (%) 165 (M^++1; 84), 149 (91), 135 (62), 108 (100), 94 (88), 81 (66), 67 (51), 53 (38), 41 (64). ^{1}H NMR δ 1.11 (t, $^3J_{H,H}$ = 7.6; 3H, CH_2-C$\underline{H}_3$), 1.22 (s, 6H, H_3C-C-CH_3), 2.32 (dq, $^3J_{H,H}$ = 7.6; $^3J_{H,H}$ = 5.3; 2H, C$\underline{H}_2$-CH_3), 4.79 (d, $^4J_{H,H}$ = 6.7; 2H, =CH_2), 5.21 (t, $^4J_{H,H}$ = 6.7; 1H, HC=C), 7.67 (s, 1H, HC=N), 7.80 (t, $^3J_{H,H}$ = 5.2; 1H, $\underline{H}$C-CH_2). ^{13}C NMR δ 10.5 (CH_2-$\underline{C}H_3$), 25.6 ($H_3\underline{C}$-C-$\underline{C}H_3$), 26.2 ($\underline{C}H_2$-CH_3), 38.0 (H_3C-$\underline{C}$-CH_3), 77.7 (=CH_2), 97.4 (H$\underline{C}$=C), 165.8 (H$\underline{C}$-CH_2), 168.9 (HC=N), 207.1 (=C=).

(2,2,3-Trimethylpenta-3,4-dien-1-ylidene) propionaldehyde hydrazone (5f). IR (film) ν_{max} / cm^{-1} 847, 1034, 1109, 1315, 1373, 1458, 1649 (C=N), 1954 (=C=), 2881, 2937, 2974. MS m/z (%) 179 (M^++1; 49), 163 (77), 149 (54), 122 (100), 108 (96), 97 (48), 81 (49), 67 (64), 55 (45), 41 (64). ^{1}H NMR δ 1.14 (t, $^3J_{H,H}$ = 7.6; 3H, CH_2-C$\underline{H}_3$), 1.25 (s, 6H, H_3C-C-CH_3), 1.67 (t, $^5J_{H,H}$ = 3.0; 3H, =C-CH_3), 2.35 (dq, $^3J_{H,H}$ = 7.5; $^3J_{H,H}$ = 5.1; 2H, C$\underline{H}_2$-CH_3), 4.70 (q, $^5J_{H,H}$ = 3.0; 2H, =CH_2), 7.63 (s, 1H, HC=N), 7.81 (t, $^3J_{H,H}$ = 5.1; 1H, $\underline{H}$C-CH_2). ^{13}C NMR δ 10.5 (CH_2-$\underline{C}H_3$), 15.2 (=C-$\underline{C}H_3$), 24.3 ($H_3\underline{C}$-C-$\underline{C}H_3$), 26.1 ($\underline{C}H_2$-CH_3), 40.0 (H_3C-$\underline{C}$-CH_3), 75.9 (=CH_2), 103.3 (=$\underline{C}$-CH_3), 165.4 (H$\underline{C}$-CH_2), 168.6 (HC=N), 206.3 (=C=).

(2,2-Dimethylpenta-3,4-dien-1-ylidene) isobutyraldehyde hydrazone (5g). IR (film) ν_{max} / cm^{-1} 847,1034, 1363, 1464, 1651 (C=N), 1955 (=C=), 2872, 2931, 2966. MS m/z (%) 179 (M^++1; 75), 163 (55), 135 (45), 108 (100), 94 (69), 79 (44), 67 (29), 53 (34), 41 (51). ^{1}H NMR δ 1.06 (d, $^3J_{H,H}$ = 6.9; 6H, $\underline{H}_3$C-CH-C$\underline{H}_3$), 1.18 (s, 6H, H_3C-C-CH_3), 2.40 – 2.55 (m, 1H, H_3C-C$\underline{H}$-CH_3), 4.74 (d, $^4J_{H,H}$ = 6.6; 2H, =CH_2), 5.17 (t, $^4J_{H,H}$ = 6.6; 1H, HC=C), 7.61 (s, 1H, HC=N), 7.63 (d, $^3J_{H,H}$ = 5.9; 1H, =C$\underline{H}$-CH). ^{13}C NMR δ 19.7 ($H_3\underline{C}$-CH-$\underline{C}H_3$), 25.6 ($H_3\underline{C}$-C-$\underline{C}H_3$), 31.7 (H_3C-$\underline{C}$H-CH_3), 38.0 (H_3C-$\underline{C}$-CH_3), 77.7 (=CH_2), 97.4 (H$\underline{C}$=C), 168.8 (=$\underline{C}$H-CH), 169.2 (HC=N), 207.1 (=C=).

(2,2,3-Trimethylpenta-3,4-dien-1-ylidene) isobutyraldehyde hydrazone (5h). IR (film) ν_{max} / cm^{-1} 847, 1109, 1363, 1466, 1647 (C=N), 1954 (=C=), 2872, 2931, 2968. ^{1}H NMR δ 1.06 (d, $^3J_{H,H}$ = 6.6; 6H, $\underline{H}_3$C-CH-C$\underline{H}_3$), 1.18 (s, 6H, H_3C-C-CH_3), 1.61 (t, $^5J_{H,H}$ = 3.0; 3H, =C-CH_3), 2.40 – 2.55 (m, 1H, H_3C-C$\underline{H}$-CH_3), 4.63 (q, $^5J_{H,H}$ = 2.9; 2H, =CH_2), 7.54 (s, 1H, HC=N), 7.62 (d, $^3J_{H,H}$

= 5.3; 1H, =CH-CH). ^{13}C NMR δ 15.3 (=C-CH_3), 19.7 (H_3C-CH-CH_3), 24.3 (H_3C-C-CH_3), 31.7 (H_3C-CH-CH_3), 40.1 (H_3C-C-CH_3), 75.9 ($=CH_2$), 103.4 (=C-CH_3), 168.4 (=CH-CH), 168.8 (HC=N), 206.4 (=C=).

(2,2-Dimethylpenta-3,4-dien-1-ylidene) crotonaldehyde hydrazone (5i). IR (film) ν_{max} / cm^{-1} 847, 958, 987, 1172, 1298, 1363, 1385, 1444, 1458, 1626 (C=N), 1655 (C=N), 1954 (=C=), 2870, 2929, 2970, 3033. MS m/z (%) 177 (M^++1; 75), 161 (100), 145 (17), 132 (19), 108 (37), 94 (42), 79 (22), 67 (27), 53 (28), 41 (43). ^{1}H NMR δ 1.22 (s, 6H, H_3C-C-CH_3), 1.87 (d, $^3J_{H,H}$ = 4.6; 3H, =CH-CH_3), 4.78 (d, $^4J_{H,H}$ = 6.6; 2H, $=CH_2$), 5.21 (t, $^4J_{H,H}$ = 6.6; 1H, HC=C), 6.11 – 6.36 (m, 2H, CH=CH), 7.71 (s, 1H, HC=N), 8.03 (d, $^3J_{H,H}$ = 8.6; 1H, N=CH-CH). ^{13}C NMR δ 18.6 (=CH-CH_3), 25.4 (CH_3-C-CH_3), 37.8 (CH_3-C-CH_3), 77.5 ($=CH_2$), 97.2 (HC=C), 128.9 (=CH-CH_3), 141.9 (N=CH-CH), 162.7 (N=CH-CH), 169.4 (HC=N), 206.8 (=C=).

(2,2,3-Trimethylpenta-3,4-dien-1-ylidene) crotonaldehyde hydrazone (5j). IR (film) ν_{max} / cm^{-1} 847, 960, 986, 1109, 1373, 1446, 1626 (C=N), 1653 (C=N), 1952 (=C=), 2872, 2929, 2972, 3034. MS m/z (%) 191 (M^++1; 52), 175 (100), 159 (18), 146 (19), 122 (29), 108 (43), 79 (17), 67 (34), 53 (24), 41 (45). ^{1}H NMR δ 1.23 (s, 6H, H_3C-C-CH_3), 1.64 (t, $^5J_{H,H}$ = 3.1; 3H, =C-CH_3), 1.88 (d, $^3J_{H,H}$ = 5.0; 3H, =CH-CH_3), 4.67 (q, $^5J_{H,H}$ = 2.9; 2H, $=CH_2$), 6.10 – 6.34 (m, 2H, CH=CH), 7.66 (s, 1H, HC=N), 8.04 (d, $^3J_{H,H}$ = 8.6; 1H, N=CH-CH). ^{13}C NMR δ 15.3 (=C-CH_3), 18.8 (=CH-CH_3), 24.3 (CH_3-C-CH_3), 40.2 (CH_3-C-CH_3), 76.0 ($=CH_2$), 103.4 (=C-CH_3), 129.2 (=CH-CH_3), 142.1 (N=CH-CH), 162.7 (N=CH-CH), 169.5 (HC=N), 206.4 (=C=).

(2,2-Dimethylpenta-3,4-dien-1-ylidene) cyclopentanone hydrazone (5k). IR (film) ν_{max} / cm^{-1} 847, 1201, 1362, 1383, 1423, 1454, 1466, 1659 (C=N), 1954 (=C=), 2870, 2885, 2937, 2964. MS m/z (%) 191 (M^++1; 100), 175 (86), 120 (12), 108 (75), 94 (39), 82 (25), 67 (30), 55 (29), 41 (22). ^{1}H NMR δ 1.13 (s, 6H, H_3C-C-CH_3), 1.60 – 1.70 (m, 4H, 2×CH_2), 2.25 – 2.40 (m, 4H, 2×CH_2), 4.68 (d, $^4J_{H,H}$ = 6.6; 2H, $=CH_2$), 5.12 (t, $^4J_{H,H}$ = 6.6; 1H, HC=C), 7.38 (s, 1H, HC=N). ^{13}C NMR δ 24.4 (CH_2), 24.6 (CH_2), 25.5 (H_3C-C-CH_3), 29.3 (CH_2), 33.2 (CH_2), 37.9 (H_3C-C-CH_3), 77.3 ($=CH_2$), 97.4 (HC=C), 164.9 (HC=N), 178.5 (N=C), 206.8 (=C=).

(2,2,3-Trimethylpenta-3,4-dien-1-ylidene) cyclopentanone hydrazone (5l). IR (film) ν_{max} / cm^{-1} 847, 1109, 1201, 1371, 1425, 1452, 1657 (C=N), 1954 (=C=), 2872, 2937, 2966. MS m/z (%) 205 (M^++1; 100), 189 (95), 122 (44), 108 (48), 82 (20), 67 (25), 55 (25), 41 (19). ^{1}H NMR δ 1.24 (s, 6H, H_3C-C-CH_3), 1.68 (t, $^5J_{H,H}$ = 3.0; 3H, =C-CH_3), 1.71 – 1.84 (m, 4H, 2×CH_2), 2.37 – 2.52 (m, 4H, 2×CH_2), 4.69 (q, $^5J_{H,H}$ = 3.1; 2H, $=CH_2$), 7.42 (s, 1H, HC=N). ^{13}C NMR δ 15.3 (=C-CH_3), 24.4 (H_3C-C-CH_3), 24.7 (CH_2), 24.8 (CH_2), 29.7 (CH_2), 33.5 (CH_2), 40.3 (H_3C-C-CH_3), 75.8 ($=CH_2$), 103.5 (=C-CH_3), 164.8 (HC=N), 178.4 (N=C), 206.3 (=C=).

(2,2-Dimethylpenta-3,4-dien-1-ylidene) cyclohexanone hydrazone (5m). IR (film) ν_{max} / cm^{-1} 845, 951, 1134, 1244, 1317, 1362, 1383, 1448, 1643 (C=N), 1954 (=C=), 2860, 2889, 2933, 2968. MS m/z (%) 205 (M^++1; 100), 189 (92), 162 (13), 147 (19), 136 (24), 122 (19), 108 (73), 96 (67), 79 (40), 69 (33), 55 (45), 41 (44). ^{1}H NMR δ 1.25 (s, 6H, CH_3-C-CH_3), 1.48 – 1.87 (m, 6H, 3×CH_2), 2.21 – 2.43 (m, 2H, CH_2), 2.46 – 2.71 (m, 2H, CH_2), 4.80 (d, $^4J_{H,H}$ = 6.6; 2H, $=CH_2$), 5.25 (t, $^4J_{H,H}$ = 6.5; 1H, HC=C), 7.50 (s, 1H, HC=N). ^{13}C NMR δ 25.7 (H_3C-C-CH_3),

26.1 (CH_2), 26.5 (CH_2), 27.5 (CH_2), 28.5 (CH_2) 36.0 (CH_2), 38.4 (H_3C-C-CH_3), 77.6 (=CH_2), 97.7 (HC=C), 165.6 (HC=N), 171.4 (N=C), 207.1 (=C=).

(2,2,3-Trimethylpenta-3,4-dien-1-ylidene) cyclohexanone hydrazone (5n). IR (film) ν_{max} / cm^{-1} 847, 1109, 1317, 1371, 1448, 1643 (C=N), 1954 (=C=), 2860, 2889, 2929, 2970. MS m/z (%) 219 (M^++1; 100), 203 (79), 150 (12), 136 (13), 122 (65), 108 (35), 96 (56), 79 (19), 67 (22), 55 (29), 41 (22). ^{1}H NMR δ 1.21 (s, 6H, CH_3-C-CH_3), 1.54 – 1.63 (m, 4H, 2×CH_2), 1.63 (t, $^5J_{H,H}$ = 3.0; 3H, =C-CH_3), 1.65 – 1.78 (m, 2H, CH_2), 2.22 – 2.34 (m, 2H, CH_2), 2.47 – 2.57 (m, 2H, CH_2), 4.64 (q, $^5J_{H,H}$ = 3.0; 2H, =CH_2), 7.38 (s, 1H, HC=N). ^{13}C NMR δ 15.3 (=C-CH_3), 24.3 (H_3C-C-CH_3), 26.0 (CH_2), 26.5 (CH_2), 27.5 (CH_2), 28.5 (CH_2), 35.9 (CH_2), 40.4 (H_3C-C-CH_3), 75.8 (=CH_2), 103.6 (=C-CH_3), 165.0 (HC=N), 170.8 (N=C), 206.3 (=C=).

General procedure for the preparation of 7a-c

A non-symmetrical azine **5** (1 mmol) in dry xylene (20 ml) was heated under reflux and after removal of solvent under vacuum the liquid residue was separated by liquid chromatography on silica gel. In all cases there were isolated brownish liquids.

4,5,5-Trimethyl-5,6-dihydro-4*H*-pyrrolo[1,2-*b*]pyrazole (7a). IR (film) ν_{max} / cm^{-1} 940, 1171, 1341, 1372, 1389, 1464, 1485, 1536, 2873, 2936, 2965. GC-MS m/z (%) 150 (M^+; 14), 135 (14), 109 (11), 95 (100), 83 (19), 65 (12), 41 (18). ^{1}H NMR δ 1.05 (CH_3), 1.16 (d, $^3J_{H,H}$ = 7.3; 3H, HC-CH_3), 1.23 (CH_3), 2.86 (q, $^3J_{H,H}$ = 7.2; 1H, HC-CH_3), 3.80 – 3.90 (m, CH_2), 5.92 (broad s, -C=CH), 7.46 (broad s, N=CH). ^{13}C NMR δ 13.1 (HC-CH_3), 22.7 (CH_3), 26.9 (CH_3), 41.9 (HC-CH_3), 46.4 (-C-$(CH_3)_2$), 60.9 (CH_2), 98.4 (-C=CH), 142.7 (N=CH), 150.0 (N-C=).

2,4,5,5-Tetramethyl-5,6-dihydro-4*H*-pyrrolo[1,2-*b*]pyrazole (7b). IR (film) ν_{max} / cm^{-1} 1009, 1163, 1313, 1369, 1444, 1543, 2872, 2927, 2960. GC-MS m/z (%) 164 (M^+; 27), 149 (27), 123 (25), 109 (100), 79 (15), 41 (12). ^{1}H NMR δ 0.96 (CH_3), 1.05 (d, $^3J_{H,H}$ = 7.3; 3H, HC-CH_3), 1.12 (CH_3), 2.17 (=C-CH_3), 2.72 (q, $^3J_{H,H}$ = 7.2; 1H, HC-CH_3), 3.65 – 3.75 (m, CH_2), 5.62 (broad s, =CH). ^{13}C NMR δ 12.8 (HC-CH_3), 14.1 (=C-CH_3), 22.4 (CH_3), 26.6 (CH_3), 41.7 (HC-CH_3), 45.5 (-C-$(CH_3)_2$), 60.4 (CH_2), 97.6 (=CH), 150.6 (N-C), 151.8 (N=C).

2-Isopropyl-4,5,5-trimethyl-5,6-dihydro-4*H*-pyrrolo[1,2-*b*]pyrazole (7c). IR (film) ν_{max} / cm^{-1} 924, 1082, 1173, 1294, 1377, 1462, 1541, 2870, 2926, 2966. GC-MS m/z (%) 192 (M^+; 48), 177 (100), 164 (12), 149 (12), 137 (43), 121 (30), 95 (16), 41 (11). ^{1}H NMR δ 1.03 (CH_3), 1.13 (d, $^3J_{H,H}$ = 7.3; 3H, HC-CH_3), 1.20 (CH_3), 1.24 (d, $^3J_{H,H}$ = 6.9; 6H, HC-$(CH_3)_2$), 2.81 (q, $^3J_{H,H}$ = 7.2; 1H, HC-CH_3), 2.85 – 3.05 (m, HC-$(CH_3)_2$), 3.75 – 3.85 (m, CH_2), 5.73 (broad s, =CH). ^{13}C NMR δ 13.0 (HC-CH_3), 22.8 (CH_3), 23.1 (CH_3), 23.2 (CH_3), 26.9 (CH_3), 28.6 (HC-$(CH_3)_2$), 42.1 (HC-CH_3), 45.8 (-C-$(CH_3)_2$), 60.8 (CH_2), 94.9 (=CH), 150.4 (N-C), 163.2 (N=C).

General procedure for the preparation of 8a-i and **9**

A mixture of a non-symmetrical azine **5** and dipolarophile in dry xylene was heated to reflux. At the end of the reaction solvent was removed under vacuum. The residue was separated by liquid chromatography on silica gel (**8a,c-e,g, 9**) or recrystallized (**8b,f,h,i**) to give white microcrystals

but in some cases (**8e,g, 9**) there wasn't successful crystallization of these products. More data are provided in Table 4.

5,5-Dimethyl-3-phenyl-1,3,10-triazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-6-en-2-one (8a). MP 139 – 142 ºC. IR ($CHCl_3$) ν_{max} / cm^{-1} 1173, 1311, 1392, 1456, 1500, 1597, 1707 (C=O), 2873, 2908, 2937, 2964. MS m/z (%) 255 (M^+; 85), 240 (100), 185 (24), 135 (28), 119 (16), 108 (32), 104 (47), 77 (65). HRMS calcd. for $C_{15}H_{18}N_3O^+$ 256.1450; found 256.1447. ^{1}H NMR δ 0.82 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 2.50 – 2.68 (m, 2H, =C-CH_2), 3.61 – 3.76 (m, 1H, N-CH_2), 4.16 – 4.28 (m, 1H, N-CH_2), 4.72 (broad s, 1H, =CH), 5.41 (s, N-CH-N), 7.10 – 7.24 (m, 1H, Ph), 7.29 – 7.47 (m, 4H, Ph). ^{13}C NMR δ 23.8 (=C-$\underline{C}H_2$), 24.3 (CH_3), 27.3 (CH_3), 49.6 (N-CH_2), 55.4 ($\underline{C}$-$(CH_3)_2$), 84.8 (N-CH-N), 110.4 (=CH), 122.6 (s, 2×CH, Ph), 125.5 (s, CH, Ph), 129.1 (s, 2×CH, Ph), 138.8 (C, Ph), 149.3 (=$\underline{C}$-CH_2), 162.5 (C=O).

5,5,6-Trimethyl-3-phenyl-1,3,10-triazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-6-en-2-one (8b). MP 144 – 145 ºC. IR ($CHCl_3$) ν_{max} / cm^{-1} 1146, 1294, 1323, 1383, 1439, 1466, 1502, 1599, 1709 (C=O), 2860, 2935, 2966. MS m/z (%) 269 (M^+; 49), 254 (56), 162 (32), 150 (53), 135 (28), 122 (29), 104 (28), 91 (31), 77 (100), 67 (22), 51 (64), 41 (93). HRMS calcd. for $C_{16}H_{20}N_3O^+$ 270.1606; found 270.1590. ^{1}H NMR δ 0.73 (s, 3H, $\underline{H}_3$C-C-CH_3), 1.29 (s, 3H, H_3C-C-C$\underline{H}_3$), 1.50 (dd, $^5J_{H,H}$ = 2.0; $^5J_{H,H}$ = 0.7; 3H, H_3C-C=), 2.37 – 2.65 (m, 2H, =C-CH_2), 3.64 (ddd, $^2J_{H,H}$ = 11.9; $^3J_{H,H}$ = 5.4; $^3J_{H,H}$ = 1.9; 1H, N-CH_2), 4.12 (ddd, $^2J_{H,H}$ = 9.1; $^3J_{H,H}$ = 4.9; $^3J_{H,H}$ = 2.1; 1H, N-CH_2), 5.42 (s, 1H, N-CH-N), 7.10 – 7.20 (m, 1H, Ph), 7.30 – 7.45 (m, 4H, Ph). ^{13}C NMR δ 8.7 ($H_3\underline{C}$-C=), 22.0 (CH_3), 22.6 (=C-$\underline{C}H_2$), 25.5 (CH_3), 49.2 (N-CH_2), 55.8 ($\underline{C}$-$(CH_3)_2$), 84.3 (N-CH-N), 116.2 (H_3C-$\underline{C}$=), 122.8 (s, 2×CH, Ph), 125.5 (s, CH, Ph), 129.0 (s, 2×CH, Ph), 139.2 (C, Ph), 142.7 (=$\underline{C}$-CH_2), 162.3 (C=O).

(4*S, 9*S**)-5,5,9-Trimethyl-3-phenyl-1,3,10-triazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-6-en-2-one (8c).** MP 118 – 119 ºC. IR ($CHCl_3$) ν_{max} / cm^{-1} 1227, 1299, 1380, 1467, 1499, 1599, 1711 (C=O), 2870, 2928, 2970. MS m/z (%) 269 (M^+; 100), 254 (84), 200 (15), 185 (25), 135 (97), 119 (22), 108 (39), 104 (57), 96 (50), 93 (29), 77 (68). HRMS calcd. for $C_{16}H_{20}N_3O^+$ 270.1606; found 270.1595. ^{1}H NMR δ 0.80 (s, 3H, $\underline{H}_3$C-C-CH_3), 1.36 (s, 3H, H_3C-C-C$\underline{H}_3$), 1.45 (d, $^3J_{H,H}$ = 6.8; 3H, HC-C$\underline{H}_3$), 2.18 (ddd, $^2J_{H,H}$ = 15.5; $^3J_{H,H}$ = 4.7; $^4J_{H,H}$ = 2.4; 1H, CH_2), 2.82 (dd, $^2J_{H,H}$ = 15.5; $^3J_{H,H}$ = 8.3; 1H, CH_2), 4.38 – 4.50 (m, 1H, $\underline{H}$C-CH_3), 4.66 (dd, $^4J_{H,H}$ = 2.4; $^4J_{H,H}$ = 1.0; 1H, =CH), 5.39 (s, 1H, N-CH-N), 7.12 – 7.42 (m, 5H, Ph). ^{13}C NMR δ 23.4 (CH_3), 24.3 (CH_3), 27.4 (CH_3), 32.3 (CH_2), 54.9 ($\underline{C}$-$(CH_3)_2$), 59.0 (CH_2-$\underline{C}$H), 85.0 (N-CH-N), 110.0 (=CH), 122.6 (s, 2×CH, Ph), 125.4 (s, CH, Ph), 129.1 (s, 2×CH, Ph), 139.1 (C, Ph), 150.2 (=$\underline{C}$-CH_2), 161.8 (C=O).

(4*S,9*S**)-5,5,6,9-Tetramethyl-3-phenyl-1,3,10-triazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-6-en-2-one (7d).** MP 112 – 113 ºC. IR ($CHCl_3$) ν_{max} / cm^{-1} 1148, 1243, 1297, 1380, 1501, 1598, 1711 (C=O), 2869, 2928, 2968, 3009. MS m/z (%) 284 (M^++1; 100), 269 (38), 149 (50), 122 (26), 110 (18), 107 (19), 104 (19), 91 (19), 77 (35). HRMS calcd. for $C_{17}H_{22}N_3O^+$ 284.1763; found 284.1758. ^{1}H NMR δ 0.81 (s, 3H, $\underline{H}_3$C-C-CH_3), 1.37 (s, 3H, H_3C-C-C$\underline{H}_3$), 1.53 (d, $^3J_{H,H}$ = 6.8; 3H, HC-C$\underline{H}_3$), 1.58 (dd, $^5J_{H,H}$ = 2.1; $^5J_{H,H}$ = 0.7; 3H, H_3C-C=), 2.09 (ddm, $^2J_{H,H}$ = 15.1; $^3J_{H,H}$ = 4.7; 1H, CH_2), 2.81 (dd, $^2J_{H,H}$ = 15.1; $^3J_{H,H}$ = 8.3; 1H, CH_2), 4.35 – 4.46 (m, 1H, $\underline{H}$C-CH_3), 5.42 (s, 1H, N-CH-N), 7.12 – 7.43 (m, 5H, Ph). ^{13}C NMR δ 8.6 ($H_3\underline{C}$-C=), 21.9 (CH_3), 23.3 (CH_3),

25.5 (CH_3), 31.0 (CH_2), 55.2 (C-$(CH_3)_2$), 58.4 (CH_2-CH), 84.5 (N-CH-N), 115.7 (H_3C-C=), 122.8 (s, 2×CH, Ph), 125.4 (s, CH, Ph), 129.0 (s, 2×CH, Ph), 139.0 (C, Ph), 143.4 (=C-CH_2), 162.1 (C=O).

(4*S, 9*S**)-9-Ethyl-5,5-dimethyl-3-phenyl-1,3,10-triazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-6-en-2-one (8e).** IR (film) ν_{max} / cm^{-1} 1128, 1149, 1227, 1300, 1365, 1383, 1460, 1500, 1599, 1718 (C=O), 2873, 2924, 2964. MS m/z (%) 283 (M^+; 100), 268 (46), 165 (47), 149 (27), 135 (19), 106 (27), 93 (36), 84 (88), 65 (19), 47 (65), 43 (37). ^{1}H NMR δ 0.78 (s, 3H, H_3C-C-CH_3), 1.02 (t, $^3J_{H,H}$ = 7.3; 3H, CH_2-CH_3), 1.33 (s, 3H, H_3C-C-CH_3), 1.52 – 1.85 (m, 2H, CH_2-CH_3), 2.19 (dm, $^2J_{H,H}$ = 15.2; 1H, =C-CH_2), 2.73 (dd, $^2J_{H,H}$ = 15.5; $^3J_{H,H}$ = 8.3; 1H, =C-CH_2), 4.04 – 4.20 (m, 1H, HC-CH_2), 4.64 (broad s, 1H, =CH), 5.38 (s, 1H, N-CH-N), 7.05 – 7.16 (m, 1H, Ph), 7.22 – 7.47 (m, 4H, Ph). ^{13}C NMR δ 11.0 (CH_2-CH_3), 24.1 (CH_3), 27.2 (CH_3), 29.9 (CH_2), 30.2 (CH_2), 54.7 (H_3C-C-CH_3), 64.9 (HC-CH_2), 84.6 (N-CH-N), 109.7 (=CH), 122.1 (s, 2×CH, Ph), 125.0 (s, CH, Ph), 128.8 (s, 2×CH, Ph), 139.0 (C, Ph), 149.6 (=C-CH_2), 161.9 (C=O).

(4*S, 9*S**)-9-Ethyl-5,5,6-trimethyl-3-phenyl-1,3,10-triazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-6-en-2-one (8f).** MP 114 – 115 ºC. IR ($CHCl_3$) ν_{max} / cm^{-1} 1149, 1176, 1240, 1294, 1367, 1385, 1394, 1502, 1599, 1707 (C=O), 2877, 2937, 2968. MS m/z (%) 297 (M^+; 85), 282 (62), 202 (35), 162 (22), 149 (100), 110 (32), 107 (24), 104 (24), 77 (42), 41 (15). HRMS calcd. for $C_{18}H_{24}N_3O^+$ 298.1919; found 298.1927. ^{1}H NMR δ 0.74 (s, 3H, H_3C-C-CH_3), 1.04 (t, $^3J_{H,H}$ = 7.3; 3H, CH_2-CH_3), 1.28 (s, 3H, H_3C-C-CH_3), 1.49 (dd, $^5J_{H,H}$ = 1.8; $^5J_{H,H}$ = 0.7; 3H, H_3C-C=), 1.56 – 1.88 (m, 2H, CH_2-CH_3), 2.09 (dm, $^2J_{H,H}$ = 14.9; 1H, =C-CH_2), 2.81 (dd, $^2J_{H,H}$ = 15.0; $^3J_{H,H}$ = 8.3; 1H, =C-CH_2), 4.05 – 4.18 (m, 1H, HC-CH_2), 5.42 (s, 1H, N-CH-N), 7.11 – 7.18 (m, 1H, Ph), 7.30 – 7.44 (m, 4H, Ph). ^{13}C NMR δ 8.6 (H_3C-C=), 11.2 (CH_2-CH_3), 22.0 (CH_3), 25.6 (CH_3), 29.3 (CH_2), 30.1 (CH_2), 55.4 (H_3C-C-CH_3), 64.7 (HC-CH_2), 84.5 (N-CH-N), 115.8 (H_3C-C=), 122.6 (s, 2×CH, Ph), 125.3 (s, CH, Ph), 129.0 (s, 2×CH, Ph), 139.3 (C, Ph), 143.3 (=C-CH_2), 162.5 (C=O).

3-Benzyl-5,5-Dimethyl-1,3,10-triazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-6-en-2-thione (8g). IR (film) ν_{max} / cm^{-1} 847, 1049, 1080, 1128, 1163, 1227, 1282, 1308, 1331, 1385, 1419, 1446, 1495, 1682, 2870, 2926, 2962. MS m/z (%) 285 (M^+; 100), 167 (37), 135 (25), 121 (32), 108 (50), 91 (87), 84 (88), 79 (15), 47 (31). ^{1}H NMR δ 1.21 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 2.46 – 2.61 (m, 2H, =C-CH_2), 3.70 – 3.89 (m, 1H, N-CH_2), 4.26 (d, $^2J_{H,H}$ = 15.2; 1H, CH_2-Ph), 4.43 (s, 1H, N-CH-N), 4.54 – 4.71 (m, 1H, N-CH_2), 4.69 (broad s, 1H, =CH), 5.78 (d, $^2J_{H,H}$ = 15.2; 1H, CH_2-Ph), 7.16 – 7.43 (m, 5H, Ph). ^{13}C NMR δ 23.3 (=C-CH_2), 23.7 (CH_3), 27.5 (CH_3), 51.0 (CH_2), 51.5 (CH_2), 55.7 (C-$(CH_3)_2$), 87.0 (N-CH-N), 109.3 (=CH), 127.9 (s, CH, Ph), 127.9 (s, 2×CH, Ph), 128.7 (s, 2×CH, Ph), 134.7 (C, Ph), 148.1 (=C-CH_2), 187.7 (C=S).

5,5-Dimethyl-3-phenyl-1,3,10-triazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-6-en-2-thione (8h). MP 166–169 ºC. IR ($CHCl_3$) ν_{max} / cm^{-1} 1165, 1257, 1302, 1340, 1402, 1458, 1498, 1597, 1682, 2868, 2927, 2966. MS m/z (%) 271 (M^+; 100), 256 (69), 185 (23), 136 (91), 121 (38), 108 (72), 104 (43), 93 (27), 77 (91), 67 (27), 41 (19). HRMS calcd. for $C_{15}H_{18}N_3S^+$ 272.1221; found 272.1194. ^{1}H NMR δ 0.77 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 2.53 – 2.73 (m, 2H, =C-CH_2), 3.82 – 4.00 (m, 1H, N-CH_2), 4.59 – 4.75 (m, 1H, N-CH_2), 4.76 (broad s, 1H, =CH), 5.34 (s, 1H, N-CH-N),

7.22 – 7.35 (m, 1H, Ph), 7.35 – 7.52 (m, 4H, Ph). ^{13}C NMR δ 23.7 (=C-<u>C</u>H$_2$), 23.8 (CH$_3$), 28.0 (CH$_3$), 53.0 (N-CH$_2$), 56.2 (<u>C</u>-(CH$_3$)$_2$), 90.0 (N-CH-N), 109.9 (=CH), 126.9 (s, 2×CH, Ph), 127.7 (s, CH, Ph), 129.0 (s, 2×CH, Ph), 139.9 (C, Ph), 148.1 (=<u>C</u>-CH$_2$), 187.6 (C=S).

5,5,6-Trimethyl-3-phenyl-1,3,10-triazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-6-en-2-thione (8i). MP 163 – 164 ºC. IR (CHCl$_3$) ν$_{max}$ / cm^{-1} 1169, 1257, 1298, 1342, 1389, 1404, 1437, 1456, 1468, 1498, 1597, 1714, 2860, 2935, 2964. MS m/z (%) 285 (M$^+$; 19), 270 (15), 150 (29), 135 (42), 122 (31), 108 (15), 77 (100), 65 (19), 51 (62), 41 (81). HRMS calcd. for $C_{16}H_{20}N_3S^+$ 286.1378; found 286.1364. ^{1}H NMR δ 0.69 (s, 3H, <u>H</u>$_3$C-C-CH$_3$), 1.25 (s, 3H, H$_3$C-C-C<u>H</u>$_3$), 1.50 (dd, $^5J_{H,H}$ = 2.0; $^5J_{H,H}$ = 0.7; 3H, H$_3$C-C=), 2.42 – 2.70 (m, 2H, =C-CH$_2$), 3.64 (ddd, $^2J_{H,H}$ = 11.9; $^3J_{H,H}$ = 5.7; $^3J_{H,H}$ = 1.9; 1H, N-CH$_2$), 4.62 (ddd, $^2J_{H,H}$ = 9.0; $^3J_{H,H}$ = 4.6; $^3J_{H,H}$ = 1.7; 1H, N-CH$_2$), 5.35 (s, 1H, N-CH-N), 7.25 – 7.35 (m, 1H, Ph), 7.35 – 7.50 (m, 4H, Ph). ^{13}C NMR δ 8.4 (H$_3$<u>C</u>-C=), 21.6 (CH$_3$), 22.6 (=C-<u>C</u>H$_2$), 26.2 (CH$_3$), 52.7 (N-CH$_2$), 56.5 (<u>C</u>-(CH$_3$)$_2$), 89.8 (N-CH-N), 116.0 (H$_3$C-<u>C</u>=), 127.1 (s, 2×CH, Ph), 127.7 (s, CH, Ph), 129.0 (s, 2×CH, Ph), 140.1 (C, Ph), 141.6 (=<u>C</u>-CH$_2$), 187.8 (C=S).

Dimethyl 9-isopropyl-5,5,6-trimethyl-1,10-diazatricyclo[5.2.1^{4,7}.0^{1,10}]dec-2,6-dien-2,3-dicarboxylate (9). IR (film) ν$_{max}$ / cm^{-1} 1128, 1263, 1348, 1437, 1608, 1705 (C=O), 1743 (C=O), 2872, 2956. GC-MS m/z (%) 334 (M$^+$; 27), 207 (30), 153 (22), 107 (100), 94 (22). ^{1}H NMR δ 0.83 (d, $^3J_{H,H}$ = 6.6; 3H, HC-(C<u>H</u>$_3$)$_2$), 0.89 (d, $^3J_{H,H}$ = 6.5; 3H, HC-(C<u>H</u>$_3$)$_2$), 0.96 (s, 3H, CH$_3$), 1.22 (s, 3H, CH$_3$), 1.47 (s, 3H, CH$_3$), 1.60 – 1.75 (m, 1H, N-CH-C<u>H</u>), 2.10 – 2.30 (m, 1H, CH$_2$), 2.50 – 2.63 (m, 1H, CH$_2$), 3.32 – 3.42 (m, 1H, N-C<u>H</u>-CH), 3.61 (s, 3H, OMe), 3.80 (s, 3H, OMe), 4.31 (s, 1H, H<u>C</u>-C=). ^{13}C NMR δ 8.3 (H$_3$<u>C</u>-C=), 18.8 (CH$_3$), 19.4 (CH$_3$), 21.4 (CH$_3$), 27.7 (CH$_2$), 27.7 (CH$_3$), 33.6 (N-CH-<u>C</u>H), 51.2 (OMe), 52.8 (OMe), 54.8 (-<u>C</u>-(CH$_3$)$_2$), 69.4 (N-<u>C</u>H-CH), 76.5 (H<u>C</u>-C=), 106.1 (<u>C</u>-COOMe), 115.8 (H$_3$C-<u>C</u>=), 141.9 (=<u>C</u>-CH$_2$), 152.0 (N-<u>C</u>-COOMe), 164.1 (C=O), 164.3 (C=O).

X-ray analysis data of 8d and 8f

The crystal structures of compounds **8d** and **8f** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 720065 & 720066.

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