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3,4-Diazanorcaradienes and 4,5-Dihydropyridazines as Precursors for New Stable Azomethine Ylides

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Dedicated to Professor Dr. Albrecht Mannschreck on the occasion of his 65th birthday.

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Abstract: The synthesis of a new class of stable coloured azomethine ylides **3** derived from 3,4-diazanorcaradienes is reported, which under acid catalysis are transformed to again coloured stable azomethine ylides **4** containing a five-membered 1-aza-1,3-cyclopentadiene skeleton. Azomethine ylides **3** in boiling methanol rearrange to 3,5-diazahomotropilidenes **8** in good yields.

Keywords: *Azomethine ylides; Diazahomotropilidenes; Rearrangement; Ring transformation*

INTRODUCTION

3,4-Diazanorcaradienes **1** are reactive 4π-systems in Diels-Alder reactions with inverse electron demand, opening an easy route to a large variety of polycyclic, heterocyclic, and carbocyclic compounds [1]. In order to increase the reactivity of the 3,4-diazanorcaradiene system in **1** for cycloadditions we tried to introduce substituents at the nitrogen atoms. The reaction of **1** with tetracyanoethylene oxide (TCNEO, **2**) [2] led to coloured azomethine ylides **3** [3,4]. In protic solvents different reaction paths were followed, either transferring **3** in boiling aqueous acetic acid to a second class of stable azomethine ylides **4** or under mild conditions to 3,5-diazahomotropilidenes **8** [5].

In this communication we give full report on the sythesis of azomethine ylides **3** and **4**, their physical properties, and on the rearrangement of compounds **3** to 3,5-diazahomotropilidines **8**. Azomethine ylides, non stabilized and stable representatives, have been studied quite thoroughly [6,7,8,9,10] in the last two decades. To the best of our knowledge compounds **3** and **4**, isolated in our laboratory, are a new type of stable azomethine ylides.

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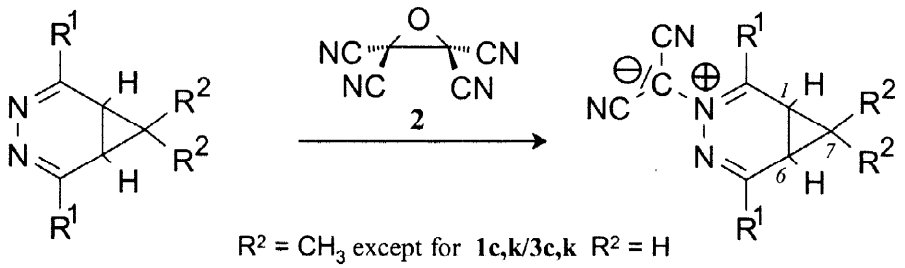
RESULTS AND DISCUSSION

When the yellow solutions of 3,4-diazanorcaradienes **1** in an inert solvent are treated with one equivalent TCNEO **2** at slightly elevated temperature the colour changes to deep red or blue. In most cases, the stable coloured azomethine ylides **3** crystallize from the reaction mixture after cooling and the product can be easily isolated in pure form in fair to reasonable yields (Scheme 1, Table 1), sometimes after some purification steps.



$R^2 = CH_3$ except for **1c,k/3c,k** $R^2 = H$

1 **3**

1/3/4	a	b	c	d	e	f
R^1	4-CH_3O-C_6H_4	4-CH_3-C_6H_4	C_6H_5	C_6H_5	3-Cl-C_6H_4	4-Cl-C_6H_4
1/3/4	**g**	**h**	**i**	**j**	**k**	**l**
R^1	4-CF_3-C_6H_4	2-C_4H_3N-CH_3	2-C_4H_3O	2-C_4H_3S	CH_3-S	CH_3-S

Scheme 1. Reactions of 2,5-disubstituted 3,4-diazanorcaradienes **1** with TCNEO **2**.

Table 1. Data for the reaction of 2,5-disubstituted 3,4-diazanorcaradienes **1** with TCNEO **2**.

R^1	R^2	mmol **1**	mmol **2**	ml, solvent	cond.	% **3**	mp. (°C)
a: 4-CH_3O-C_6H_4	CH_3	2.17	2.17	50, ethyl acetate	50°C/2 min	69 [d]	204-206
b: 4-CH_3-C_6H_4	CH_3	2.32	2.35	50, ethyl acetate	rt/3 h	81 [a]	185
c: C_6H_5	H	6.46	6.70	80, CH_2Cl_2/acetone	50°C/5 min	36 [g]	175-176
d: C_6H_5	CH_3	4.37	4.67	50, ethyl acetate	rt/1 h	85 [a]	196
e: 3-Cl-C_6H_4	CH_3	1.00	1.01	20, CH_2Cl_2	rt/75 min	17 [c]	167-168
f: 4-Cl-C_6H_4	CH_3	1.57	1.58	30, ethyl acetate	60°C/2 h	59 [d]	208-209
g: 4-CF_3-C_6H_4	CH_3	2.80	2.82	100, ethyl acetate	70°C/1 h	9-17 [b]	194
h: 2-C_4H_3N-CH_3	CH_3	3.35	3.37	50, ethyl acetate	reflux/1.5 h	33 [c]	193-194
i: 2-C_4H_3O	CH_3	2.38	2.39	30, ethyl acetate	55°C/1.5 h	50 [h]	179-180
j: 2-C_4H_3S	CH_3	4.12	4.36	160, ethyl acetate	reflux/4 h	68 [e]	187
k: CH_3-S	H	3.42	3.45	20, ethyl acetate	rt/15 min	74 [a]	138-139
l: CH_3-S	CH_3	0.43	0.44	6, ethyl acetate	rt/30 min	67 [f]	145

a) Crystals were filtered and washed with a small amount of chilled ethyl acetate

b) Product was precipitated with petroleum ether (40-60), (crude yield: 48 %); column chromatography (diethyl ether/ethyl acetate (2:1), silica gel 60, i.d.: 25*2.5 cm)
c) Column chromatography (CH_2Cl_2/ ethyl acetate (20:1), silica gel 60, i.d.: 20*2.0 cm)
d) Precipitated as pure product from the reaction mixture, crystals were filtered and washed with a small amount of chilled diethyl ether/ethyl acetate
e) Precipitation was induced with petroleum ether (40-60)/diethyl ether; crystals were filtered and washed with a small amount of chilled diethyl ether
f) Crystals were filtered and washed with a small amount of chilled petroleum ether
g) Precipitation was induced with diethyl ether; crystals were filtered and washed with a small amount of petroleum ether (40-60)
h) Product was precipitated with petroleum ether (40-60), column chromatography (CH_2Cl_2/ethyl acetate (20:1), silica gel 60, i.d.: 25*2.5 cm)

Table 2. $^1H/^{13}C$ NMR data of the azomethine ylides **3** (δ values, CD_3NO_2 (*italic*: $CDCl_3$), 250 or 400 MHz (^1H) and 63 or 101 MHz (^{13}C)).

No. R^1, $R^2 = CH_3$ except for **3k** $R^2 = H$	H-1/C-1	$^3J_{H(1/6)}$ (Hz)	H-6/C-6	*syn*-CH_3	*anti*-CH_3	C-7	$\underline{C}(CN)_2$	CN
3a: 4-CH_3O-C_6H_4	3.23/40.5	7.9	2.76/40.3	0.92/15.3	1.79/26.2	29.5	60.4	121.6
3b: 4-CH_3-C_6H_4	3.25/41.0	7.8	2.78/40.6	0.94/15.6	1.80/26.4	29.5	61.1	121.1
3d: C_6H_5	3.29/41.1	7.8	2.83/40.7	0.99/15.5	1.82/26.2	29.7	≈62	120.8
3e: 3-Cl-C_6H_4	*2.96/39.3*	*8.0*	*2.57/37.8*	*0.95/15.4*	*1.76/26.4*	*28.6*	*62.6*	*117.9*
3f: 4-Cl-C_6H_4 [a]	*2.93/-*	*8.0*	*2.53/-*	*0.96/-*	*1.74/-*	-	-	-
3g: 4-CF_3-C_6H_4	3.40/41.4	7.8	2.90/40.9	1.03/15.6	1.84/26.1	30.4	66.7	119.9
3h: 2-C_4H_3N-CH_3	3.12/≈38	8.1	2.70/≈38	0.93/15.2	1.68/26.3	29.6	60.6	121.6
3i: 2-C_4H_3O	3.33/37.0	8.0	3.15/36.5	0.91/15.3	1.69/26.4	28.8	58.9	120.4
3j: 2-C_4H_3S	3.31/38.2	7.9	3.26/38.0	0.94/15.2	1.76/26.2	29.0	56.8	121.5
3k: CH_3-S	2.98/24.5	7.2	2.66/23.6	0.97 [b]	2.42 [c]	13.8	54.6	121.1
3l: CH_3-S	2.76/18.0	7.6	2.55/25.4	0.92/14.4	1.56/15.0	25.0	54.2	121.1

a) ^{13}C NMR not performed b) syn-H c) anti-H

The correct configuration assignment was demonstrated by an X-ray structure analysis for **3b** and discussed in detail [4]. Both tolyl groups are twisted out of the plane of the diaza cyclohexadiene as well as the dicyanomethylide group (23.7°).

The spectroscopic data in Table 2 prove that all isolated compounds belong to the same azomethine ylide type **3**. The bridgehead protons H-1 and H-6 appear as an AB system with coupling constants between 7-8 Hz. The geminal methyl groups at C-7 show shift differences of about 0.9 ppm for the syn- and anti-position. This effect is even more pronounced for **3k** with a shift difference for syn-H and anti-H of 2.45 ppm at C-7. The ^{13}C-chemical shift for all carbon atoms are normal.

Quite typical for **3** is a very strong IR absorption for the CN groups shifted to low frequencies between 2179-2200 cm^{-1} and 2144-2170 cm^{-1}. The deep colour of azomethine ylides is originated by a strong absorption between 451-570 nm with log ε-values between

3.685-3.971 (ε = 4840-9350). As Figure 1 demonstrates, there exists a pronounced negative solvatochromism, which correlates with the E_T-values of Dimroth and Reichardt [11]. Finally the electronic effect of substituents R^1 in azomethine ylides **3** strongly shows up in the half wave reduction potentials $E_{1/2}$, that range from -1.17 V to -1.62 V.

Table 3. Further characteristic data of the azomethine ylides **3**.

No. R^1, $R^2 = CH_3$ except for **3c,k** $R^2 = H$	$\bar{\nu}_{C\equiv N}$ (cm^{-1})	λ_{max} (nm, log ε) [b]	MS (u)	$E_{1/2}$ (V) [c]
3a: 4-CH_3O-C_6H_4	2179, 2144 [a]	537, 3.920	398.1 [c]	-1.47
3b: 4-CH_3-C_6H_4	2180, 2140	538, 3.886	367 [d]	-1.42
3c: C_6H_5	2200, 2170	534, 3.685	-	-1.31
3d: C_6H_5	2181, 2148 [a]	536, 3.875	339.2 [d]	-1.37
3e: 3-Cl-C_6H_4	2200, 2170	545, 3.872	406 [c]	-
3f: 4-Cl-C_6H_4	2175, 2140	546, 3.875	406 [c]	-1.26
3g: 4-CF_3-C_6H_4	2184, 2151 [a]	552, 3.866	474.2 [c]	-1.17
3h: 2-C_4H_3N-CH_3	2190, 2150	536, 3.966	344.3 [c]	-1.62
3i: 2-C_4H_3O	2200, 2170	540, 3.971	318.2 [c]	-1.25
3j: 2-C_4H_3S	2181, 2142 [a]	570, 3.794	351.1 [d]	-1.17
3k: CH_3-S	2200, 2160	451, 3.774	250.0 [f]	-1.55
3l: CH_3-S	2180, 2140	456, 3.783	278.0 [c]	≈ -1.50

a) KBr; FTIR spectrometer modell 60 SX Nicolet
b) Solvent: 1,4-dioxane
c) FD; CH_2Cl_2
d) FAB; matrix: m-nitrobenzyl alcohol, CH_2Cl_2
e) Reference electrode: 0.1 n $Ag/Ag^{\oplus}$ in CH_3CN
f) EI, 70 eV

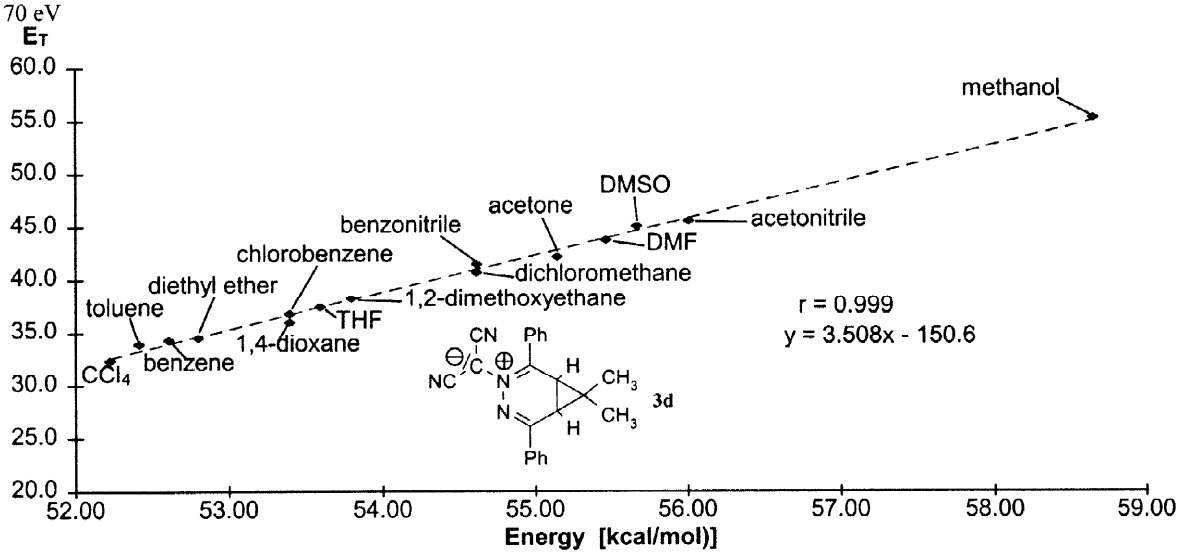
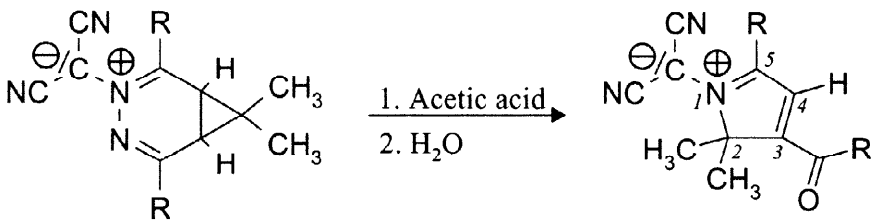


Figure 1. Solvatochromism of azomethine ylide **3d**.

Azomethine ylides possess a rather high dipole moment. In dichloromethane at 25°C dielectric relaxation spectroscopy [12] delivered dipole moments of 13.19 ± 0.03 D for **3b** and 12.5 ± 0.2 D for **3d**.

When azomethine ylides **3** were heated in acetic acid to about 80-100°C until no starting material was detectable by thin layer chromatography, hydrolysis and work-up (see Experimental Section) yielded again coloured, crystalline compounds. X-ray structure analysis for **4d** [4] revealed, that a far reaching transformation had occurred. N,N-breaking in **3** is



3 **4**

Scheme 2. Acid triggered transformation of 2,5-disubstituted azomethine ylides **3** in acetic acid to azomethine ylides **4**.

necessary as well as the opening of the cyclopropane ring; finally a five-membered 1-aza-1,3-cyclopentadiene ring must be closed. As we have not yet performed detailed mechanistic studies we hesitate to write down a speculative mechanism for the transformation **3** → **4**. The azacyclopentadiene ring in **4** is planar. Again, neither the dicyanomethanide (27.5°) nor the phenyl groups are coplanar with the azadiene system as the X-ray shows.

Table 4 summarizes some experimental details for this unexpected transformation which leads to a new class of stable coloured azomethine ylides **4** in fair to medium yields.

Table 4. Reaction conditions for the transformation **3** → **4**.

R	mmol **3**	ml, acetic acid	cond.	% **4**	mp. (°C)
a: 4-CH_3O-C_6H_4	0.43	10	80°C/70 min	41	182-184
b: 4-CH_3-C_6H_4	1.00	20	80°C/60 min	47	199
d: C_6H_5	0.77	15	100°C/20 min	56	224-227
f: 4-Cl-C_6H_4	0.77	15	80°C/90 min	50	215-216
g: 4-CF_3-C_6H_4	- [a]	25	80°C/55 min	40 [b]	187-188
h: 2-C_4H_3N-CH_3	0.60	20	80°C/150 min	16	213-215
i: 2-C_4H_3O	1.68	50	100°C/45 min	37	183-185
j: 2-C_4H_3S	0.35	10	100°C/90 min	68	202-203

a) **3g** was prepared in situ from 0.68 mmol **1g** and 0.83 mmol TCNEO **2** in 30 ml CH_2Cl_2 and used without purification
b) Yield of **4g** refers to **1g**

Again, the spectroscopic data collected in Table 5 and Table 6 prove, that all isolated compounds belong to the same azomethine ylide type **4**. The planar five-membered azacyclopentadiene ring is responsible for the equivalence of the two methyl groups at C-2 in the ^{1}H- and ^{13}C NMR spectra, the signal for the ylide-carbon is slightly shifted to higher field compared to that in azomethine ylide **3** (Table 2).

Table 5. $^{1}H/^{13}C$ NMR data of the azomethine ylides **4** (δ values, $CDCl_3$, 250 or 400 MHz (^{1}H) and 63 or 101 MHz (^{13}C)).

R^1	H-4	CH_3	C=O	Ylid-C	CN	C-2
4a: 4-CH_3O-C_6H_4	7.04	2.01/24.5	187.1	51.6	119.0	85.5
4b: 4-CH_3-C_6H_4	7.03	2.05/24.5	188.1	53.9	118.2	85.6
4d: C_6H_5	7.03	2.11/24.6	188.2	55.5	117.5	85.7
4f: 4-Cl-C_6H_4	6.96	2.09/24.5	186.8	56.1	117.1	86.0
4g: 4-CF_3-C_6H_4 [a]	6.96	2.15/ -	-	-	-	-
4h: 2-C_4H_3N-CH_3	≈ 7	1.94/24.6	177.1	50.0	119.7	84.4
4i: 2-C_4H_3O	8.15	1.99/25.1	173.1	49.0	117.9	85.7
4j: 2-C_4H_3S	7.53	1.93/24.3	179.7	43.7	119.8	85.3

a) ^{13}C NMR not performed

The IR spectra of **4** again show the typical strong absorption for the CN groups between 2177-2200 cm^{-1} and 2135-2175 cm^{-1}, in addition the strong carbonyl absorption between 1610-1657 cm^{-1} (Table 6). The VIS absorption between 537-576 nm with log ε-values 3.781-4.260 is

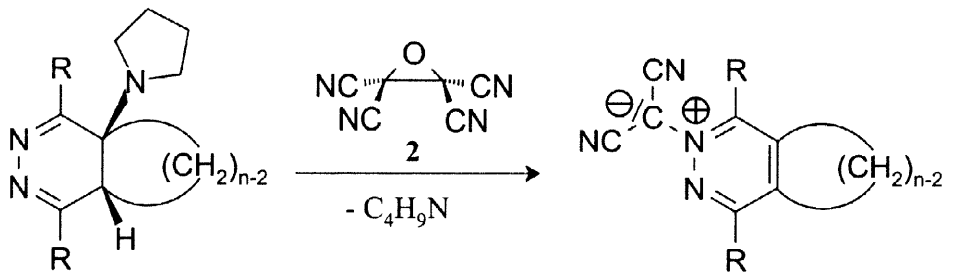
Table 6. Further characteristic data of azomethine ylides **4**.

R^1	$\bar{\nu}_{C\equiv N}$ (cm^{-1})	$\bar{\nu}_{C=O}$ (cm^{-1})	λ_{max} (nm, log ε) [b]	MS (u)	$E_{1/2}$ (V) [d]
4a: 4-CH_3O-C_6H_4	2179, 2142 [a]	1629	560, 4.110	399.1 [c]	-1.04, -1.61
4b: 4-CH_3-C_6H_4	2190, 2160	1640	550, 4.185	367 [c]	-1.00, -1.58
4d: C_6H_5	2182, 2147 [a]	1623	537, 4.217	339.1 [c]	-0.96, -1.53
4f: 4-Cl-C_6H_4	2200, 2160	1640	546, 4.236	407 [c]	-0.91, -1.45
4g: 4-CF_3-C_6H_4	2188, 2152 [a]	1657	538, 4.260	475.3 [c]	-0.85, -1.36
4h: 2-C_4H_3N-CH_3	2190, 2140	1610	571, 3.954	345.3 [e]	-1.12, -1.63
4i: 2-C_4H_3O	2195, 2175	1630	568, 4.093	319.2 [e]	-0.92, -1.48
4j: 2-C_4H_3S	2177, 2135 [a]	1627	576, 3.781	351.1 [c]	-0.92, -1.48

a) KBr; FTIR spectrometer modell 60 SX Nicolet
b) Solvent: 1,4-dioxane
c) FD; CH_2Cl_2
d) Reference electrode: 0.1 n $Ag/Ag^{\oplus}$ in CH_3CN
e) EI, 70 eV

slightly higher than that for azomethine ylide **3**. In contrast, for azomethine ylides **4** two half wave reduction potentials $E_{1/2}$ between -0.91 to -1.12 V and -1.36 to -1.63 V were found. The dipole moments for **4b** and **4d** [12] are distinctly lower compared with those for **3b** and **3d**, but the values of 11.3 ± 0.2 D and 10.82 ± 0.06 D are still rather high.

4,5-Dihydropyridazine derivatives, such as **5**, are easily prepared by [4+2]-cycloaddition of electron-poor 1,2,4,5-tetrazines with N-pyrrolidino cyclopentene and the higher homologous cyclohexene enamine [1,13]. The yellow solution of **5** and TCNEO **2** in an inert solvent turned deep-orange under the conditions of Table 7. Apparently even under quite mild conditions the



5 **6**

Scheme 3. Reactions of 4,5-dihydropyridazines **5** with TCNEO **2**.

Table 7. Data for the reaction of 4,5-dihydropyridazines **5** with TCNEO **2**.

R	n	mmol **5**	mmol **2**	ml, solvent	cond.	% **6**	mp. (°C)
a: 4-CH_3O-C_6H_4	5	0.615	0.632	50, ethyl acetate	70°C/2 h rt/14 h	64 [a]	231-232
b: 4-CH_3-C_6H_4	5	1.56	2.45	50, ethyl acetate	70°C /9 h rt/14 h	63 [b]	217-218
c: C_6H_5	5	1.95 [d]	2.12	40, ethyl acetate	rt/4 h	76 [b]	212-213
d: C_6H_5	6	1.94	2.03	25, CH_2Cl_2	reflux/2.5 h	28 [c]	187-188
g: 4-CF_3-C_6H_4	5	0.861	1.11	25, ethyl acetate	reflux/8 h rt/14 h	27 [c]	211-212
k: CH_3-S	5	5.93	5.95	75, ethyl acetate	rt/19 h	79 [a]	164-165

a) Crystals were filtered and washed with a small amount of petroleum ether, column chromatography (CH_2Cl_2/ethyl acetate (15:1), silica gel 60, i.d.: 25*2.5 cm)
b) Crystals were filtered and washed with a small amount of petroleum ether, column chromatography (CH_2Cl_2/ethyl acetate (20:1), silica gel 60, i.d.: 25*2.5 cm)
c) Crystals were filtered and washed with a small amount of petroleum ether, column chromatography (CH_2Cl_2/ethyl acetate (30:1), silica gel 60, i.d.: 25*2.5 cm)
d) 1,4-Diphenyl-cyclopenta[d]pyridazine as starting material

azomethine ylide formation is followed by β-elimination of pyrrolidine with aromatization and formation of the pyridazinium ylide **6** in low to good yields. Selected spectroscopic data as presented in Table 8 and Table 9 parallel those obtained for the azomethine ylides **3** and **4** and

need no further discussion. The $\pi\pi^*$- absorption of **6** in the visible range near 460 nm is definitely shifted hypsochromically compared to **3** and **4**.

Table 8. $^1H/^{13}C$ NMR data of the azomethine ylides **6** (δ values, $CDCl_3$ (*italic*: CD_2Cl_2), 250 MHz (^1H) and 63 MHz(^{13}C))

No. R	H-5/C-5	H-6/C-6	H-7/C-7	H-8/C-8	$\underline{C}(CN)_2$	CN
6a: 4-CH_3O-C_6H_4 [a]	2.77/-	2.17/-	3.26/-	-/-	-	-
6b: 4-CH_3-C_6H_4	2.79/32.8	2.17/24.9	3.28/33.6	-/-	67.0	117.4
6c: C_6H_5 [a]	2.81/-	2.20/-	3.30/-	-/-	-	-
6d: C_6H_5	2.38/27.7	≈1.72/21.2	≈1.72/21.3	2.75/28.0	66.6	117.1
6g: 4-CF_3-C_6H_4	*2.79/33.1*	*2.21/25.3*	*3.27/33.6*	-/-	*68.1*	*116.6*
6k: CH_3-S	2.90/31.1	2.28/23.5	3.10/33.7	-/-	67.3	117.3

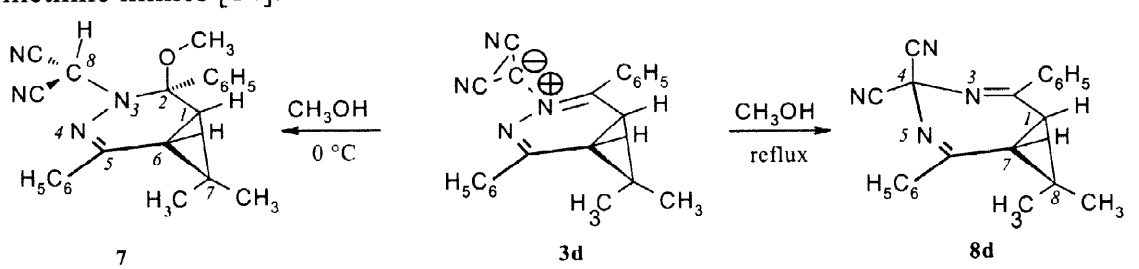
a) ^{13}C NMR not performed

Table 9. Further characteristic data of the azomethine ylides **6**.

No. R	$\bar{\nu}_{C\equiv N}$ (cm^{-1}) [a]	λ_{max} (nm, log ε) [b]	MS (u) [c]	$E_{1/2}$ (V) [d]
6a: 4-CH_3O-C_6H_4	2190, 2160	468, 4.121	397.3	-1.57
6b: 4-CH_3-C_6H_4	2200, 2170	468, 4.250	365.2	-1.54
6c: C_6H_5	2190, 2160	463, 4.199	337.3	-1.52
6d: C_6H_5	2190, 2160	458, 4.228	351.1	-1.56
6g: 4-CF_3-C_6H_4	2185, 2160	462, 4.188	473.3	-1.41
6k: CH_3-S	2200, 2160	468, 4.250	277.0	-1.42

a) KBr
b) Solvent: 1,4-dioxane
c) FAB; matrix: m-nitrobenzyl alcohol, CH_2Cl_2
d) Reference electrode: 0.1 n $Ag/Ag^{\oplus}$ in CH_3CN

While solutions of azomethine ylides **3** in aprotic solvents are stable, the colour of solutions of **3d** in alcohols quickly fades at room temperature. When the reaction is performed at 0°C 73% of **7** could be obtained. Structure proof rests on complete NMR analysis including Nuclear-Overhauser effect demonstrating the proximity of CH_3O and H-1 as well as H-8 [5]. The addition of nucleophiles to the NC-double bond is a well documented reaction in the field of azomethine imines [14].



7 **3d** **8d**

Scheme 4. Reaction of azomethine ylide **3d** in methanol at 0°C and under reflux.

The addition product **7** dissociates in solution on heating. When **3d** is boiled in methanol under reflux a colourless isomer is isolated in 78% yield. ^{1}H- and ^{13}C NMR spectra already indicated the formation of a symmetric compound. X-ray structure analysis [5] revealed the structure of a 3,5-diazahomotropilidene derivative **8d**. The generality of this unexpected rearrangement **3** → **8** is demonstrated by a number of examples in Table 10. The spectroscopic data (^{1}H NMR, ^{13}C NMR) obtained for **8** are in accordance with X-ray analysis and prove the same structural type for all products of this rearrangement.

Table 10. Reaction conditions for the rearrangement **3** › **8**

R	mmol **3**	ml, methanol	time (min)	% **8**	mp. (°C)
a: 4-CH_3O-C_6H_4	0.94	40	120	79 [a]	154
b: 4-CH_3-C_6H_4	0.56	15	150	83 [b]	191-193
d: C_6H_5	0.32	20	70	78 [c]	219-220
e: 3-Cl-C_6H_4	0.53	15	105	48 [d]	234-235
i: 2-C_4H_3O	0.68	15	60	59 [e]	178-179
j: 2-C_4H_3S	0.19	7	240	63 [f]	193
l: CH_3-S	1.37	15	90	37 [g]	187-188

a) Filtered through silica gel 60 (CH_2Cl_2, R_f=0.51); 67% of product crystallized from 5 ml CH_2Cl_2; second crop (12%) from ether/petroleum ether (40-60) (1:1)
b) Recryst.: methanol
c) Filtered through silica gel 60 (CH_2Cl_2, R_f=0.56); recryst.: methanol
d) Filtered through silica gel 60; recryst.: CH_2Cl_2 /petroleum ether (40-60) 3:2
e) Filtered through silica gel 60; recryst.: CH_2Cl_2 /petroleum ether (40-60) 5:2
f) Filtered through silica gel 60 (CH_2Cl_2, R_f=0.53); recryst.: methanol/petroleum ether (40-60)
g) Column chromatography: CH_2Cl_2/petroleum ether (40-60) 1:1

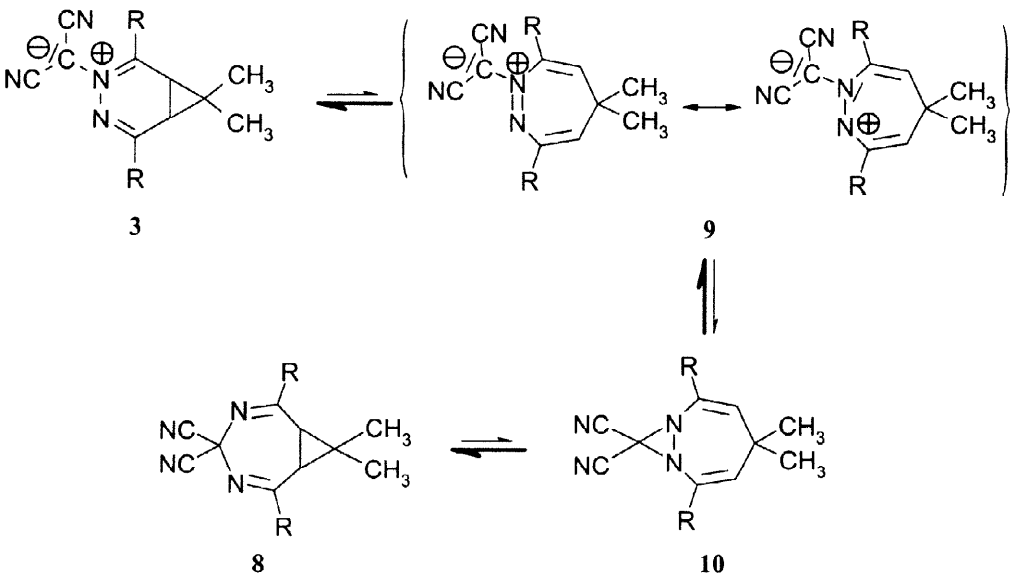
Table 11. ^{1}H/^{13}C NMR data of the diazahomotropilidenes **8** (δ values, $CDCl_3$, 250 or 400 MHz (^{1}H) and 63 or 101 MHz (^{13}C))

No. R	H-1(7) /C-1(7)	*syn*-CH_3	*anti*-CH_3	C-8	C-2(6)	C-4	CN
8a: 4-CH_3O-C_6H_4	2.64/32.5	0.62/18.6	1.67/26.2	24.0	172.4	65.4	114.0, 117.5
8b: 4-CH_3-C_6H_4	2.67/32.6	0.61/18.6	1.67/26.2	24.1	173.2	65.4	113.8, 117.3
8d: C_6H_5	2.72/32.7	0.63/18.6	1.69/26.1	24.3	173.3	65.3	113.5, 117.1
8e: 3-Cl-C_6H_4 [a]	2.71/-	0.64/-	1.70/-	-	-	-	-
8i: 2-C_4H_3O	2.60/32.5	0.80/18.1	1.58/26.3	25.2	164.2	65.1	113.5, 116.6
8j: 2-C_4H_3S	2.69/33.3	0.82/18.7	1.63/26.2	25.0	168.1	64.8	113.6, 116.5
8l: CH_3-S	2.31/14.0	1.05/18.4	1.31/26.4	25.3	178.6	64.5	113.3, 116.6

a) ^{13}C NMR not performed due to lack of solubility in common solvents

How can the isomerization **3** → **8** be rationalized? Still lacking more detailed mechanistic studies, Scheme 5 offers a sequence of valence isomerization, ring closure and Cope rearrangement as a mechanistic proposal.

For the first valence isomerization step **3** ⇌ **9** there is experimental proof for azomethine ylides **3** bearing only one methyl group at the cyclopropane ring [15]. The stereoisomers with syn- respectively anti- methyl group could be separated; already at 21°C in chloroform syn ⇌ anti isomerization occurs to form an equilibrium mixture syn : anti = 20 : 80. An analogous syn ⇌ anti rearrangement was also observed with 7-methyl-3,4-diazanorcaradienes [16].



Scheme 5. Proposed mechanism for the rearrangement **3** → **8**.

Ring closure in **9** could lead to a small equilibrium concentration of 1,7-diazahomotropilidene **10**, which undergoes an almost irreversible Cope rearrangement; breaking of the weak N,N-bond with simultaneous formation of a stronger CC-bond finally shifts the reaction in favour of 3,5-diazahomotropilidene **8**.

Conclusion

3,4-Diazanorcaradienes **1** are the starting point for a number of new azomethine ylides **3** and **4** as well as **6**, all nicely coloured stable compounds, which react as electron-poor 1,3-dipoles with electron-rich 2π-systems to form a variety of interesting cycloadducts [17]. An unexpected isomerization to form 3,4-diazahomotropilidenes **8** makes this interesting bicyclic system easily accessible, too.

EXPERIMENTAL SECTION

General: IR spectra were recorded with a Beckmann Acculab I respectively a 60 SX Nicolet FTIR spectrometer. - NMR spectra were obtained with a Bruker AC250 and ARX400 (250 MHz / 400 MHz for ^{1}H and 63 MHz / 101 MHz for ^{13}C). The degree of substitution of the C atoms was determined by the DEPT-135/90 methods. All NMR spectra were taken in $CDCl_3$ with TMS as an internal standard. - Mass spectra were recorded either with an ionizing voltage of 70 eV by electron impact with a Varian CH90 instrument or by field desorption with a Varian 311A instrument. - Melting points were determined with a Büchi melting point apparatus and are uncorrected. - Elemental analysis were performed in the microanalytical laboratory of the University of Regensburg. - For analytical thin layer chromatography (tlc) precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey-Nagel) were used. Silica gel 60 (particle size 0.040 - 0.063 mm, Merck) was used for flash column chromatography (fcc). The preparative high pressure liquid chromatography (HPLC) was performed with an Orlita MS 30/10 pump, 8300 UVICORD II detector, and a Polygosil column (SiO_2, 7 μm). - The HPLC analysis were carried out with a Bromma LKB 2150 pump, a Spectra 100 UV detector (Thermo Separation Products), recorded with a Spectra-Physics Data Jet Integrator and after data transfer via Labnet treated with the program „Winner on Windows" (Thermo Separation Products). - Solvents for reactions were dried according to standard procedures. Compound **2** was prepared according to literature procedures [2].

General procedure for the synthesis of AMY-I **3a-l**: To a solution of 2,5-di(hetero)arylsubstituted 3,4-diazanorcaradienes **1a-l** (0.43 - 6.46 mmol) was added solid TCNEO **2** (0.44 - 6.70 mmol) at ambient or slightly elevated temperature and allowed to react until no diazanorcaradiene could be detected anymore by tlc. During the reaction in some cases a product precipitation can be observed which is further driven by addition of petroleum ether or diethyl ether and storage of the reaction flask at -18°C. After a filtration and a washing step the crystals are dried in vacuum at 50°C for several hours. Alternatively the product can be purified by column chromatography. Solvent, reaction conditions, and purification method are given in Table 1. Spectroscopic data presented in Table 2 and Table 3 are not repeated anymore below. Elemental analyses are presented in Table 12.

Dicyano(2,5-bis-(4-methoxy-phenyl)-7,7-dimethyl-3,4-diaza-bicyclo[4.1.0]hept-2,4-dien-3-ium-3-yl)methanide (**3a**): Following the *general procedure* **1a** (865 mg, 2.17 mmol) and **2** (313 mg, 2.17 mmol) yielded 549 mg (1.50 mmol, 69%) of **3a**, red crystals, m.p. 204-206°C. - IR (KBr): $\tilde{\nu}$ = 3074-2735, 1603, 1559, 1516, 1425, 1302, 1258, 1176, 1029 cm^{-1}. - ^{1}H NMR (CD_3NO_2, 400 MHz): δ = 3.94 (s, 3 H), 3.95 (s, 3 H), 7.12-7.18 (m, 4 H), 7.90-7.94 (m, 2 H), 8.03-8.07 (m, 2 H) ppm. - ^{13}C NMR (CD_3NO_2, 101 MHz, DEPT 135/90): δ = 56.53 (1 C, +/0), 56.54 (1 C, +/0), 115.75 (2 C, +/+), 115.77 (2 C, +/+), 126.9 (1 C, 0/0), 127.5 (1 C, 0/0), 131.9 (2 C, +/+), 132.6 (2 C, +/+), 144.6 (1 C, 0/0), 162.7 (1 C, 0/0), 163.7 (1 C, 0/0), 165.2 (1 C, 0/0) ppm. - UV/VIS (dioxane) : λ_{max} (ε) = 242 (11600), 270 (11700), 354 (34700) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(7,7-dimethyl-2,5-di-p-tolyl-3,4-diaza-bicyclo[4.1.0]hepta-2,4-dien-3-ium-3-yl)-methanide (**3b**): Following the *general procedure* **1b** (702 mg, 2.32 mmol) and **2** (339 mg,

2.35 mmol) yielded 691 mg (1.88 mmol, 81%) of **3b**, red crystals, m.p. 185°C. - IR (KBr): $\tilde{\nu}$ = 3040, 2990, 2960, 2920, 2870, 1600, 1580, 1410, 1390, 1285, 1180, 805 cm^{-1}. - ^1H NMR (CD_3NO_2, 250 MHz): δ = 2.47 (s, 3 H), 2.48 (s, 3 H), 7.35-7.56 (m, 4 H), 7.80-7.83 (m, 2 H), 7.96-8.00 (m, 2 H) ppm. - ^{13}C NMR (CD_3NO_2, 63 MHz, DEPT 135/90): δ = 21.83 (1 C, +/0), 21.90 (1 C, +/0), 130.04 (2 C, +/+), 130.25 (2 C, +/+), 131.24 (2 C, +/+), 131.26 (2 C, +/+), 132.35 (1 C, 0/0), 132.57 (1 C, 0/0), 144.26 (1 C, 0/0), 144.48 (1 C, 0/0), 145.93 (1 C, 0/0), 164.10 (1 C, 0/0) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 284 (14900), 325 (24000) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(2,5-diphenyl-3,4-diaza-bicyclo[4.1.0]hepta-2,4-dien-3-ium-3-yl)-methanide (**3c**): Following the *general procedure* **1c** (1.59 g, 6.46 mmol) and **2** (966 mg, 6.70 mmol) yielded 717 mg (2.31 mmol, 36%) of **3c**, dark red crystals, m.p. 175-176°C. - IR (KBr): $\tilde{\nu}$ = 3100, 3065, 2940, 1590, 1570, 1480, 1450, 1420, 1365, 1235, 790, 770, 695 cm^{-1}. - UV/VIS (dioxane): λ_{max} (ε) = 282 (13300), 310 (13700) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(7,7-dimethyl-2,5-diphenyl-3,4-diaza-bicyclo[4.1.0]hepta-2,4-dien-3-ium-3-yl)-methanide (**3d**): Following the *general procedure* **1d** (1.20 g, 4.37 mmol) and **2** (673 mg, 4.67 mmol) yielded 1.26 g (3.72 mmol, 85%) of **3d**, red crystals, m.p. 196°C. - IR (KBr): $\tilde{\nu}$ = 3053, 2927, 1592, 1566, 1445, 1405, 1291 1235, 766, 709, 692 cm^{-1}. - ^1H NMR (CD_3NO_2, 250 MHz): δ = 7.55-7.75 (m, 6 H), 7.88-7.92 (m, 2 H), 8.08-8.12 (m, 2 H) ppm. - ^{13}C NMR (CD_3NO_2, 101 MHz, DEPT 135): δ = 130.0 (2 C, +), 130.1 (2 C, +), 130.51 (2 C, +), 130.55 (2 C, +), 133.1 (1 C, +), 134.5 (1 C, +), 135.0 (1 C, 0), 135.1 (1 C, 0), 143.8 (1 C, 0), 164.6 (1 C, 0) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 284 (17500), 290 (16500), 310 (20100) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

(2,5-Bis-(3-chloro-phenyl)-7,7-dimethyl-3,4-diaza-bicyclo[4.1.0]hept-2,4-dien-3-ium-3-yl)dicyanomethanide (**3e**): Following the *general procedure* **1e** (345 mg, 1.00 mmol) and **2** (146 mg, 1.01 mmol) yielded 70.6 mg (0.17 mmol, 17%) of **3e**, dark red crystals, m.p. 167-168°C. - IR (KBr): $\tilde{\nu}$ = 3070, 3050, 2980, 2940, 1565, 1430, 1400, 1290, 1235, 790 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.40-7.70 (m, 6 H), 7.85-8.00 (m, 2 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135/90): δ = 126.04 (1 C, +/+), 126.79 (1 C, +/+), 128.27 (1 C, +/+), 128.52 (1 C, +/+), 130.64 (1 C, +/+), 130.67 (1 C, +/+), 131.70 (1 C, +/+), 133.39 (1 C, +/+), 134.56 (2 C, 0/0), 134.73 (1 C, 0/0), 135.48 (1 C, 0/0), 135.71 (1 C, 0/0), 161.36 (1 C, 0/0) ppm. - FD MS (CH_2Cl_2); *m/z* (%): 812 (4) [M_2^+]. - UV/VIS (dioxane): λ_{max} (ε) = 290 (18800), 386 (3380) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

(2,5-Bis-(4-chloro-phenyl)-7,7-dimethyl-3,4-diaza-bicyclo[4.1.0]hept-2,4-dien-3-ium-3-yl)dicyanomethanide (**3f**): Following the *general procedure* **1f** (540 mg, 1.57 mmol) and **2** (228 mg, 1.58 mmol) yielded 376 mg (0.92 mmol, 59%) of **3f**, dark red crystals, m.p. 208-209°C. - IR (KBr): $\tilde{\nu}$ = 3080, 3060, 3050, 3030, 2970, 2950, 2920, 1580, 1400, 1380, 1280, 1080, 1000 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.47-7.61 (m, 4 H), 7.61-8.74 (m, 2 H), 7.90-8.04 (m, 2 H) ppm. - FD MS (CH_2Cl_2); *m/z* (%): 814 (7), 812 (3) [M_2^+], 787 (17), 408 (64). - UV/VIS (dioxane): λ_{max} (ε) = 282 (18200), 320 (24700) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(7,7-dimethyl-2,5-bis-(4-trifluoromethyl-phenyl)-3,4-diaza-bicyclo[4.1.0]hept-2,4-dien-3-ium-3-yl)methanide (**3g**): Following the *general procedure* **1g** (1.15 g, 2.80 mmol) and **2** (406 mg, 2.82 mmol) yielded 120-226 mg (0.25-0.48 mmol, 9-17%) of **3g**, red crystals, m.p. 194°C. - IR (KBr): $\tilde{\nu}$ = 3059-2935, 1615, 1413, 1326, 1167, 1134, 1112, 1068 cm^{-1}. - ^1H NMR

(CD_3NO_2, 400 MHz): δ = 7.94-7.96 (m, 4 H), 8.06-8.09 (m, 2 H), 8.28-8.30 (m, 2H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135/90): δ = 125.3 (2 C, 0/0), 125.5 (2 C, 0/0), 127.3-127.5 (2 C, +/+), 130.7 (1 C, +/+), 130.8 (1 C, +/+), 133.1 (2 C, 0/0), 135.1 (2 C, 0/0), 138.4 (1 C, 0/0), 138.5 (1 C, 0/0), 140.6 (1 C, 0/0), 164.5 (1 C, 0/0) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 278 (21500), 310 (16300), 378 (3700) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(7,7-dimethyl-2,5-bis-(1-methyl-1H-pyrrol-2-yl)-3,4-diaza-bicyclo[4.1.0]hept-2,4-dien-3-ium-3-yl)methanide (**3h**)*:* Following the *general procedure* **1h** (939 mg, 3.35 mmol) and **2** (486 mg, 3.37 mmol) yielded 384 mg (1.12 mmol, 33%) of **3h**, dark red crystals, m.p. 193-194°C. - IR (KBr): $\bar{\nu}$ = 3120, 3060, 2970, 1560, 1535, 1490, 1430, 1380, 1310, 1260, 1065, 745 cm^{-1}. - ^1H NMR (CD_3NO_2, 250 MHz): δ = 3.88 (s, 3 H), 4.05 (s, 3 H), 6.30 (dd, 1 H, ^3J = 4.1 Hz, 2.6 Hz), 6.38 (dd, 1 H, ^3J = 4.1 Hz, 2.6 Hz), 6.89 (dd, 1 H, ^3J = 4.1 Hz, 1.6 Hz), 7.04 (dd, 1 H, ^3J = 4.1 Hz, 1.6 Hz), 7.10 (m, 2 H) ppm. - ^{13}C NMR (CD_3NO_3, 63 MHz, DEPT 135): δ = 37.1 (1 C, +), 39.2 (1 C, +), 39.6 (1 C, +), 39.7 (1 C, +), 110.8 (1 C, +), 112.3 (1 C, +), 120.2 (1 C, +), 121.7 (1 C, +), 128.0 (1 C, 0), 128.1 (1 C, 0), 131.9 (1 C, +), 133.9 (1 C, +), 135.2 (1 C, 0), 154.6 (1 C, 0) ppm. - EI MS (70 eV); m/z (%): 329 (10) [M^+-CH_3], 317 (11), 302 (10), 280 (41) [M^+-$C(CN)_2$], 266 (44), 250 (100), 238 (29) [M^+- $NCC_4H_3NCH_3$], 223 (19), 210 (11), 196 (11), 173 (24), 160 (38), 146 (32), 124 (18), 122 811), 118 (14), 106 (79) [$NCC_4H_3NCH_3^+$]. - UV/VIS (dioxane): λ_{max} (ε) = 268 (8040), 378 (30400) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(2,5-di-furan-2-yl-7,7-dimethyl-3,4-diaza-bicyclo[4.1.0]hept-2,4-dien-3-ium-3-yl)methanide (**3i**)*:* Following the *general procedure* **1i** (606 mg, 2.38 mmol) and **2** (344 mg, 2.39 mmol) yielded 376 mg (1.18 mmol, 50%) of **3i**, dark red crystals, m.p. 179-180°C. - IR (KBr): $\bar{\nu}$ = 3160-3070, 3000-2940, 1590, 1555, 1470, 1420, 1385, 1100, 1040, 1015, 905, 885, 790, 760 cm^{-1}. - ^1H NMR (CD_3NO_2, 250 MHz): δ = 6.77 (dd, 1 H, ^3J = 3.6 Hz, 1.8 Hz), 6.99 (dd, 1 H, ^3J = 3.9 Hz, 1.7 Hz), 7.43 (dd, 1 H, ^3J = 3.6 Hz, 0.7 Hz), 7.54 (dd, 1 H, ^3J = 3.9 Hz, 0.4 Hz), 7.84 (dd, 1 H, ^3J = 1.8 Hz, 0.7 Hz), 8.01 (dd, 1 H, ^3J = 1.7 Hz, 0.4 Hz) ppm. - ^{13}C NMR (CD_3NO_3, 63 MHz, DEPT 135): δ = 114.5 (1 C, +), 115.8 (1 C, +), 119.6 (1 C, +), 123.8 (1 C, +), 134.1 (1 C, 0), 147.5 (1 C, 0), 149.5 (1 C, +), 149.9 (1 C, 0), 151.0 (1 C, +), 153.9 (1 C, 0) ppm. - EI MS (70 eV); m/z (%): 254 (11) [M^+-$C(CN)_2$], 240 (15), 225 (100) [M^+-NCC_4H_3O], 197 (17), 161 (15), 147 (10), 93 (24) [$NCC_4H_3O^+$]. - UV/VIS (dioxane): λ_{max} (ε) = 266 (9170), 368 (27800) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(7,7-dimethyl-2,5-di-thiophen-2-yl-3,4-diaza-bicyclo[4.1.0]hept-2,4-dien-3-ium-3-yl)methanide (**3j**)*:* Following the *general procedure* **1j** (1.18 g, 4.12 mmol) and **2** (628 mg, 4.36 mmol) yielded 982 mg (2.80 mmol, 68%) of **3j**, dark blue crystals, m.p. 187°C. - IR (KBr): $\bar{\nu}$ = 3083-2927, 1558, 1528, 1505, 1431, 1342, 1082, 857, 734, 718 cm^{-1}. - ^1H NMR (CD_3NO_2, 400 MHz): δ = 7.29 (dd, 1 H, ^3J = 5.1 Hz, 3.8 Hz), 7.37 (dd, 1 H, ^3J = 5.1 Hz, 4.1 Hz), 7.83 (dd, 1 H, ^3J = 5.0 Hz, 1.1 Hz), 7.92 (dd, 1 H, ^3J = 3.8 Hz, 1.1 Hz), 8.15 (dd, 1 H, ^3J = 5.0 Hz, 1.2 Hz), 8.19 (dd, 1 H, ^3J = 4.1 Hz, 1.2 Hz) ppm. - ^{13}C NMR (CD_3NO_3, 101 MHz, DEPT 135/90): δ = 130.0 (1 C, +/+), 130.3 (1 C, +/+), 134.9 (1 C, +/+), 135.1 (1 C, +/+), 135.5 (1 C, 0/0), 139.3 (1 C, 0/0), 139.7 (1 C, +/+), 141.0 (1 C, +/+), 145.5 (1 C, 0/0), 158.3 (1 C, 0/0) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 284 (10500), 372 (21800) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(2,5-bis-methylsulfanyl-3,4-diaza-bicyclo[4.1.0]hept-2,4-dien-3-ium-3-yl)methanide (**3k**)*:* Following the *general procedure* **1k** (636 mg, 3.42 mmol) and **2** (497 mg, 3.45 mmol) yielded 632 mg (2.53 mmol, 74%) of **3k**, yellow crystals, m.p. 138-139°C. - IR (KBr): $\bar{\nu}$ =

3115, 3065, 3020, 2940, 1565, 1505, 1375, 1260, 1120, 920 cm^{-1}. - ^1H NMR (CD_3NO_2, 250 MHz): δ = 0.97 (ddd, 1 H, ^2J = 4.7 Hz, ^3J = 5.6 Hz, 5.0 Hz), 2.42 (ddd, 1 H, ^2J = 4.7 Hz, ^3J = 9.0 Hz, 8.9 Hz), 2.58 (s, 3 H), 2.66 (ddd, 1 H, ^3J = 9.0 Hz, 7.2 Hz, 5.6 Hz), 2.89 (s, 3 H), 2.98 (ddd, 1 H, ^3J = 8.9 Hz, 7.2 Hz, 5.0 Hz) ppm. - ^{13}C NMR (CD_3NO_3, 63 MHz, DEPT 135/90): δ = 14.5 (1 C, +/0), 17.4 (1 C, +/0), 169.5 (1 C, 0/0), 169.8 (1 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 203 (100) [M^+-SCH_3], 129 (19), 124 (21). - UV/VIS (dioxane): λ_{max} (ε) = 316 (13300) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(7,7-dimethyl-2,5-bis-methylsulfanyl-3,4-diaza-bicyclo[4.1.0]hept-2,4-dien-3-ium-3-yl)methanide (**3l**): Following the *general procedure* **1l** (92.1 mg, 0.43 mmol) and **2** (63.3 mg, 0.44 mmol) yielded 80.2 mg (0.29 mmol, 67%) of **3l**, yellow crystals, m.p. 145°C. - IR (KBr): $\bar{\nu}$ = 3060, 3020, 2930, 1550, 1480, 1370 cm^{-1}. - ^1H NMR (CD_3NO_2, 250 MHz): δ = 2.59 (s, 3 H), 2.81 (s, 3 H) ppm. - ^{13}C NMR (CD_3NO_3, 63 MHz, DEPT 135): δ = 34.9 (1 C, +), 35.8 (1 C, +), 167.4 (1 C, 0), 168.5 (1 C, 0) ppm.. - UV/VIS (dioxane): λ_{max} (ε) = 238 (9210), 320 (14000) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Table 12. Data of elemental analyses for azomethine ylides **3a-l**.

No. R^1	Formula	M	C found (calcd)	H	N
3a: 4-CH_3O-C_6H_4	$C_{24}H_{22}N_4O_2$	398.5	72.02 (72.34)	5.71 (5.56)	14.03 (14.06)
3b: 4-CH_3-C_6H_4	$C_{24}H_{22}N_4$	366.5	78.58 (78.66)	6.04 (6.05)	15.19 (15.29)
3d: C_6H_5	$C_{22}H_{18}N_4$	338.4	77.94 (78.08)	5.54 (5.36)	16.44 (16.56)
3e: 3-Cl-C_6H_4	$C_{22}H_{16}N_4Cl_2$	407.3	64.83 (64.87)	4.29 (3.96)	13.60 (13.76)
3f: 4-Cl-C_6H_4	$C_{22}H_{16}N_4Cl_2$	407.3	64.52 (64.87)	3.30 (3.96)	13.52 (13.76)
3g: 4-CF_3-C_6H_4	$C_{24}H_{16}N_4F_6$	474.4	60.51 (60.76)	3.67 (3.40)	11.70 (11.81)
3h: 2-C_4H_3N-CH_3	$C_{20}H_{20}N_6$	344.3	69.64 (69.77)	5.90 (5.85)	24.18 (24.41)
3i: 2-C_4H_3O	$C_{18}H_{14}N_4O_2$	318.3	67.82 (67.94)	4.62, (4.43)	17.42 (17.61)
3j: 2-C_4H_3S	$C_{18}H_{14}N_4S_2$	350.5	61.48 (61.69)	4.04 (4.03)	15.90 (15.99)
3k: CH_3-S	$C_{10}H_{10}N_4S_2$	250.2	47.62 (48.01)	4.35 (4.03)	22.09 (22.39)
3l: CH_3-S	$C_{12}H_{14}N_4S_2$	278.4	51.85 (51.77)	5.28 (5.07)	19.87 (20.13)

General procedure for the synthesis of AMY-II **4**: A solution of azomethine ylide **3** in acetic acid is heated to 80-100°C until no more starting material is detectable by tlc (CH_2Cl_2/ethyl acetate (20:1)). The reaction is hydrolyzed with water (10 vol% of initial acetic acid) and heated at the same temperature until coloured intermediates are no longer detectable. Before CH_2Cl_2 extraction the reaction mixture was again diluted with the equal amount of water. The combined organic layers were neutralized with saturated $NaHCO_3$ solution, washed with water and finally dried with Na_2SO_4. Evaporation of CH_2Cl_2 and column chromatography (CH_2Cl_2/ethyl acetate (20:1)) yielded product **4** which was further purified by recrystallization from CH_2Cl_2/diethyl ether. Reaction conditions are presented in Table 4. Spectroscopic data presented in Table 2 and Table 3 are not repeated anymore below. Elemental analyses are presented in Table 13.

Dicyano(2,2-dimethyl-3-(4-methoxy-benzoyl)-5-(4-methoxy-phenyl)-1-aza-cyclopenta-3,5-dien-1-ium-1-yl)methanide (**4a**): Following the *general procedure* **3a** (171 mg, 0.43 mmol) yielded 70.4 mg (0.18 mmol, 41%) of **4a**, gleaming dark green crystals, m.p. 182-184°C. - IR (KBr): $\bar{\nu}$ = 3077, 3006-2840, 1600, 1463, 1345, 1301, 1258, 1182, 1023, 837 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.91 (s, 6 H), 6.97-7.10 (m, 4 H), 7.73-7.82 (m, 4 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 55.65 (2 C, +), 114.3 (2 C, +), 114.7 (2 C, +), 119.9 (1 C, 0), 130.5 (1 C, 0), 131.3 (2 C, +), 131.4 (2 C, +), 131.8 (1 C, +), 151.2 (1 C, 0), 157.2 (1 C, 0), 163.0 (1 C, 0), 164.2 (1 C, 0) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 248 (16100), 285 (9710), 344 (23300) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(2,2-dimethyl-3-(4-methyl-benzoyl)-5-p-tolyl-1-aza-cyclopenta-3,5-dien-1-ium-1-yl)methanide (**4b**): Following the *general procedure* **3b** (365 mg, 1.00 mmol) yielded 172 mg (0.47 mmol, 47%) of **4b**, gleaming dark green crystals, m.p. 199°C. - IR (KBr): $\bar{\nu}$ = 3030, 2920, 1630, 1615, 1600, 1465, 1455, 1335, 1305, 1180 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.44 (s, 3 H), 2.46 (s, 3 H), 7.28-7.46 (m, 4 H), 7.54-7.71 (m, 4 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 21.65 (1 C, +), 21.87 (1 C, +), 125.15 (1 C, 0), 128.67 (2 C, +), 128.95 (2 C, +), 129.59 (2 C, +), 129.73 (2 C, +), 133.49 (1 C, +), 135.38 (1 C, 0), 143.47 (1 C, 0), 144.33 (1 C, 0), 149.40 (1 C, 0), 155.26 (1 C, 0) ppm. - FD MS (CH_2Cl_2); *m/z* (%): 734 (3) [M_2^+]. - UV/VIS (dioxane): λ_{max} (ε) = 322 (1800) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

(3-Benzoyl-2,2-dimethyl-5-phenyl-1-aza-cyclopenta-3,5-dien-1-ium-1-yl)dicyanomethanide (**4d**): Following the *general procedure* **3d** (259 mg, 0.77 mmol) yielded 146 mg (0.43 mmol, 56%) of **4d**, gleaming green crystals, m.p. 224-227°C. - IR (KBr): $\bar{\nu}$ = 3085-2946, 1461, 1376, 1352, 875, 698 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.49-7.73 (m, 10 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 128.1 (1 C, 0), 128.5 (2 C, +), 128.7 (2 C, +), 128.9 (2 C, +), 129.1 (2 C, +), 132.2 (1 C, 0), 133.1 (1 C, 0), 134.3 (1 C, +), 138.1 (1 C, 0), 147.8 (1 C, 0), 154.1 (1 C, 0) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 280 (12400), 308 (14200), 355 (2730) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

(3-(4-Chloro-benzoyl)5-(4-chloro-phenyl)-2,2-dimethyl-1-aza-cyclopenta-3,5-dien-1-ium-1-yl)dicyanomethanide (**4f**): Following the *general procedure* **3f** (312 mg, 0.77 mmol) yielded 158 mg (0.39 mmol, 50%) of **4d**, red crystals, m.p. 215-216°C. - IR (KBr): $\bar{\nu}$ = 3100, 3010, 2950, 1590, 1470, 1455, 1370, 1340, 1305, 1095, 870 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.44-7.73 (m, 8 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 126.27 (1 C, 0), 129.30 (2 C, +), 129.44 (2 C, +), 129.72 (2 C, +), 130.00 (2 C, +), 133.95 (1 C, +), 136.27 (1 C, 0), 138.39 (1 C, 0), 139.79 (1 C, 0), 145.92 (1 C, 0), 153.48 (1 C, 0) ppm. - EI MS (70 eV); m/z (%): 343 (11), 140 (33), 138 (100) [Cl-C_6H_4-CO^+], 111 (27) [Cl-$C_6H_4^+$], 35 (18) [HCl]. - UV/VIS (dioxane): λ_{max} (ε) = 228 (18300), 284 (13800), 320 (17100), 378 (2550) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

(3-(4-Trifluoromethyl-benzoyl)-5-(4-trifluoromethyl-phenyl)-2,2-dimethyl-1-aza-cyclopenta-3,5-dien-1-ium-1-yl)dicyanomethanide (**4g**): **3g** was prepared in situ from **1g** (279 mg, 0.68 mmol) and **2** (120 mg, 0.83 mmol) in 30 ml CH_2Cl_2 and used without purification for the synthesis - according to the *general procedure* - of 129 mg (0.27 mmol, 40%) **4g**, red crystals, m.p. 187-188°C. - IR (KBr): $\bar{\nu}$ = 3079-2945, 1470, 1370, 1326, 1237, 1167, 1124, 1114, 1065, 845, 772 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.65-7.83 (m, 4 H), 7.79 (s, 4 H) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 280 (14500), 309 (9650), 370 (3130) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(2,2-dimethyl-3-(1-methyl-1H-pyrrol-2-carbonyl)-5-(1-methyl-1H-pyrrol-2-yl)-1-aza-cyclopenta-3,5-dien-1-ium-1-yl)methanide (**4h**): Following the *general procedure* **3h** (205 mg, 0.60 mmol) yielded 32.5 mg (0.09 mmol, 16%) of **4h**, gleaming black crystals, m.p. 213-215°C. - IR (KBr): $\bar{\nu}$ = 3130, 2980, 2940, 1595, 1550, 1400, 840, 760 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.88 (s, 3 H), 3.98 (s, 3 H), 6.20 (dd, 1 H), 6.45 (dd, 1 H), 6.78 (dd, 1 H), 7.00-7.06 (m, 3 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 37.4 (2 C, +), 109.2 (1 C, +), 112.1 (1 C, +), 120.9 (1 C, +), 122.06 (1 C, 0), 122.12 (1 C, +), 129.3 (2 C, +), 130.9 (1 C, 0), 131.8 (2 C, +), 133.6 (2 C, +), 146.3 (1 C, 0), 159.1 (1 C, 0) ppm. - EI MS (70 eV); m/z (%): 281 (17) [M^+-$C(CN)_2$], 266 (21) [M^+-$C(CN)_2$-CH_3], 108 (100) [$CH_3NC_4H_3CO^+$]. - UV/VIS (dioxane): λ_{max} (ε) = 257 (10900), 356 (13800) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(3-(furan-2-carbonyl)-5-furan-2-yl-2,2-dimethyl-1-aza-cyclopenta-3,5-dien-1-ium-1-yl)methanide (**4i**): Following the *general procedure* **3i** (534 mg, 1.68 mmol) yielded 200 mg (0.63 mmol, 37%) of **4i**, bronze gleaming dark crystals, m.p. 183-185°C. - IR (KBr): $\bar{\nu}$ = 3160, 3140, 2950, 1590, 1570, 1500, 1465, 1380, 1350, 1285, 1115, 1030, 830, 760 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 6.69 (dd, 1 H), 6.94 (dd, 1 H), 7.43 (m, 2 H), 7.75 (dd, 1 H), 7.89 (dd, 1 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 113.1 (1 C, +), 114.7 (1 C, +), 120.2 (1 C, +), 123.7 (1 C, +), 130.2 (1 C, +), 142.2 (1 C, 0), 142.7 (1 C, 0), 147.2 (1 C, +), 148.5 (1 C, +), 153.1 (1 C, 0), 155.1 (1 C, 0) ppm. - EI MS (70 eV); m/z (%): 255 (17) [M^+-$C(CN)_2$], 240 (39), 95 (100) [$C_4H_3OCO^+$]. - UV/VIS (dioxane): λ_{max} (ε) = 244 (11800), 272 (7650), 336 (20900) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Dicyano(2,2-dimethyl-3-(thiophene-2-carbonyl)-5-thiophen-2-yl-1-aza-cyclopenta-3,5-dien-1-ium-1-yl)methanide (**4j**): Following the *general procedure* **3j** (123 mg, 0.35 mmol) yielded 83.7 mg (0.24 mmol, 68%) of **4j**, dark blue crystals, m.p. 202-203°C. - IR (KBr): $\bar{\nu}$ = 3099-2987, 1595, 1524, 1413, 1356, 1268, 805, 758, 726 cm^{-1}. - ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (dd, 1 H, ^3J = 5.0 Hz, 3.9 Hz), 7.41 (dd, 1 H, ^3J = 5.0 Hz, 4.1), 7.77 (dd, 1 H, ^3J = 3.9 Hz, 1.1 Hz), 7.87 (dd, 1 H, ^3J = 5.0 Hz, 1.1 Hz), 8.07 (dd, 1 H, ^3J = 4.1 Hz, 1.1 Hz), 8.11 (dd, 1 H, ^3J = 5.0 Hz, 1.1 Hz) ppm. - ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 128.2 (1 C), 128.8 (1 C), 128.9 (1 C), 129.2 (1 C), 134.5 (1 C), 136.5 (1 C), 138.1 (1 C), 139.6 (1 C), 142.8 (1 C), 154.1 (1 C), 160.7 (1 C) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 238 (11400), 266 (10800), 298 (12700), 344 (15500) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Table 13. Data of elemental analyses for azomethine ylides **4**.

No.	R^1	Formula	M	C found (calcd)	H	N
4a	4-CH_3O-C_6H_4	$C_{24}H_{21}N_3O_3$	399.4	72.07 (72.17)	5.51 (5.30)	10.51 (10.52)
4b	4-CH_3-C_6H_4	$C_{29}H_{21}N_3O$	367.3	78.36 (78.45)	5.85 (5.76)	11.38 (11.44)
4d	C_6H_5	$C_{22}H_{17}N_3O$	339.4	77.42 (77.86)	5.04 (5.05)	12.31 (12.38)
4f	4-Cl-C_6H_4	$C_{22}H_{15}Cl_2N_3O$	408.3	64.70 (64.72)	4.09 (3.70)	10.27 (10.29)
4g	4-CF_3-C_6H_4	$C_{24}H_{15}N_3OF_6$	475.4	60.79 (60.64)	3.18 (3.18)	8.93 (8.84)
4h	2-C_4H_3N-CH_3	$C_{20}H_{19}N_5O$	345.4	69.46 (69.55)	5.77 (5.54)	20.16 (20.28)
4i	2-C_4H_3O	$C_{18}H_{13}N_3O_3$	319.3	67.51 (67.71)	4.30 (4.10)	13.07 (13.16)
4j	2-C_4H_3S	$C_{18}H_{13}N_3OS_2$	351.5	61.32 (61.52)	3.83 (3.73)	11.93 (11.96)

General procedure for the synthesis of pyridazinium azomethine ylides **6**: The reactions of 4,5-dihydropyridazines **5** with TCNEO **2** yield (conditions see Table 7) deeply orange coloured reaction mixtures. During the reaction in all cases a product precipitation can be observed. After filtration and a washing step the products are purified (see also Table 7) by flash column chromatography (CH_2Cl_2/ethyl acetate) and then dried in vacuum at 90°C for several hours. Spectroscopic data presented in Table 8 and Table 9 is not repeated anymore below. CHN data are presented in Table 14.

1,4-Bis-(4-methoxy-phenyl)-cyclopenta[d]pyridazinium-2-dicyanomethanide (**6a**): Following the *general procedure* **5a** (248 mg, 0.62 mmol) and **2** (91.4 mg, 0.63 mmol) yielded 159 mg (0.39 mmol, 64%) of **6a**, gleaming orange crystals, m.p. 231-232°C. - IR (KBr): $\bar{\nu}$ = 2970, 2920, 2850, 1605, 1510, 1415, 1405, 1355, 1285, 1255, 1120, 1020, 830 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 3.89 (s, 3 H), 3.90 (s, 3H), 7.05-7.13 (m, 4 H), 7.36-7.42 (m, 2 H), 7.83-7.87 (m, 2 H) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 296 (18400) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

1,4-Di-p-tolyl-cyclopenta[d]pyridazinium-2-dicyanomethanide (**6b**): Following the *general procedure* **5b** (579 mg, 1.56 mmol) and **2** (353 mg, 2.45 mmol) yielded 358 mg (0.98 mmol, 63%) of **6b**, orange crystals, m.p. 217-218°C. - IR (KBr): $\bar{\nu}$ = 3050, 3000-2890, 1600, 1525, 1500, 1415, 1390, 1365, 1345, 1295, 1275, 1230, 1175, 810 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.42 (s, 3 H), 2.45 (s, 3H), 7.27-7.39 (m, 6 H), 7.71-7.76 (m, 2 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 21.5 (1 C, +), 21.7 (1 C, +), 127.5 (1 C, 0), 128.3 (2 C, +), 128.8 (2 C, +), 129.7 (2 C, +), 130.3 (2 C, +), 130.6 (1 C, 0), 138.78 (1 C, 0), 138.83 (1 C, 0), 141.4 (1 C, 0), 141.5 (1 C, 0), 153.7 (1 C, 0), 154.9 (1 C, 0) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 254 (12000), 324 (5870), 468 (17800) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

1,4-Diphenyl-cyclopenta[d]pyridazinium-2-dicyanomethanide (**6c**): Following the *general procedure* **5c** (532 mg, 1.95 mmol) and **2** (305 mg, 2.12 mmol) yielded 499 mg (1.48 mmol, 76%) of **6c**, orange crystals, m.p. 212-213°C. - IR (KBr): $\bar{\nu}$ = 3070, 2990, 1535, 1450, 1415, 1370, 1350, 1310, 1280, 1240, 760, 690 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.42-7.65 (m, 8 H), 7.83-7.91 (m, 2 H) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 261 (21300) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

1,4-Diphenyl-cyclohexa[d]pyridazinium-2-dicyanomethanide (**6d**): Following the *general procedure* **5d** (695 mg, 1.94 mmol) and **2** (292 mg, 2.03 mmol) yielded 190 mg (0.54 mmol, 28%) of **6d**, yellow crystals, m.p. 187-188°C. - IR (KBr): $\bar{\nu}$ = 3080, 2960, 2890, 1520, 1415, 1370, 1305, 1235, 700 cm^{-1}. - ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.34-7.45 (m, 2 H), 7.46-7.53 (m, 4 H), 7.55-7.65 (m, 4 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 128.7 (2 C, +), 129.2 (2 C, +), 129.3 (2 C, +), 129.8 (1 C, 0), 129.9 (2 C, +), 130.3 (1 C, +), 131.4 (1 C, +), 133.2 (1 C, 0), 133.6 (1 C, 0), 140.7 (1 C, 0), 145.1 (1 C, 0), 160.3 (1 C, 0) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 252 (17400) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

1,4-Bis-(4-trifluoromethyl-phenyl)-cyclopenta[d]pyridazinium-2-dicyanomethanide (**6g**): Following the *general procedure* **5g** (413 mg, 0.86 mmol) and **2** (146 mg, 1.11 mmol) yielded 109 mg (0.23 mmol, 27%) of **6g**, orange crystals, m.p. 211-212°C. - IR (KBr): $\bar{\nu}$ = 3100, 3060, 2985-2910, 1615, 1530, 1420, 1405, 1355, 1320, 1230, 1120, 1060, 1015, 840, 760 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 7.63-7.66 (m, 2 H), 7.81-7.89 (m, 4 H), 7.97-8.01 (m, 2 H) ppm. - ^{13}C NMR (CD_2Cl_2, 63 MHz, DEPT 135): δ = 124.1 (1 C, 0), 124.2 (1 C, 0), 126.4 (2 C, +), 127.1 (2 C, +), 129.6 (2 C, +), 129.7 (2 C, +), 133.0 (1 C, 0), 133.1 (1 C, 0), 134.4 (1 C, 0),

137.3 (1 C, 0), 137.3 (1 C, 0), 139.6 (1 C, 0), 154.6 (1 C, 0), 154.9 (1 C, 0) ppm. - UV/VIS (dioxane): λ_{max} (ε) = 258 (22300) nm (l·mol^{-1}·cm^{-1}).

1,4-Bis-methylsulfanyl-cyclopenta[d]pyridazinium-2-dicyanomethanide (**6k**)*:* Following the *general procedure* **5k** (1.68 g, 5.93 mmol) and **2** (858 mg, 5.95 mmol) yielded 1.29 g (4.67 mmol, 79%) of **6k**, orange crystals, m.p. 164-165°C. - IR (KBr): $\tilde{\nu}$ = 2970, 2940, 1540, 1515, 1420, 1355, 1305, 1280, 1170, 1045, 980 cm^{-1}. - ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.54 (s, 3 H), 2.65 (s, 3 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 13.1 (1 C, +), 17.0 (1 C, +), 135.3 (1 C, 0), 138.1 (1 C, 0), 153.8 (1 C, 0), 159.1 (1 C, 0) ppm . - UV/VIS (dioxane): λ_{max} (ε) = 254 (12000), 324 (5870) nm (l·mol^{-1}·cm^{-1}).

Table 14. Data of elemental analyses for azomethine ylides **6**.

No. R	Formula	M	C found (calcd)	H	N
6a: 4-CH_3O-C_6H_4	$C_{24}H_{20}N_4O_2$	396.4	72.36 (72.72)	5.21 (5.08)	14.02 (14.13)
6b: 4-CH_3-C_6H_4	$C_{24}H_{20}N_4$	364.4	78.91 (79.11)	5.58 (5.53)	15.40 (15.38)
6c: C_6H_5	$C_{22}H_{16}N_4$	336.4	78.31 (78.55)	5.01 (4.79)	16.57 (16.66)
6d: C_6H_5	$C_{23}H_{18}N_4$	350.4	78.70 (78.84)	5.17 (5.18)	15.97 (15.99)
6g: 4-CF_3-C_6H_4	$C_{24}H_{14}N_4F_6$	472.4	60.81 (61.02)	2.82 (2.99)	11.72 (11.86)
6k: CH_3-S	$C_{12}H_{12}N_4S_2$	276.3	52.04 (52.17)	4.48 (4.38)	20.30 (20.28)

General procedure for the rearrangement of AMY-I to 3,5-diazahomotropilidenes **8***:* Azomethine ylides **3** are suspended in methanol and heated to reflux, while colour is fading. An initially formed methanol adduct is consumed during the reaction (TLC: CH_2Cl_2) to yield diazahomotropilidenes **8** exclusively. For reaction conditions and purification see Table 10. Spectroscopic data presented in Table 11 are not repeated anymore below. Elemental analyses are presented in Table 15.

8,8-Dimethyl-2,6-bis-(4-methoxy-phenyl)-3,5-diaza-bicyclo[5.1.0]octa-2,5-diene-4,4-dicarbonitrile (**8a**)*:* Following the *general procedure* **3a** (375 mg, 0.94 mmol) yielded 296 mg (0.74 mmol, 79%) of **8a**, colourless crystals, m.p. 154°C. - IR (KBr): $\tilde{\nu}$ = 3050, 2970, 2850, 1650-1550, 1505, 1350, 1250, 1165, 1020, 840 cm^{-1}. - ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.87 (s, 6 H), 6.93-6.98 (m, 4 H), 7.90-7.95 (m, 4 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135): δ = 55.5 (2 C, +), 114.0 (4 C, +), 129.2 (2 C, 0), 129.8 (4 C, +), 163.3 (2 C, 0) ppm. - EI MS (70 eV); m/z (%): 398.4 (55) [M$^+$], 320 (65), 225 (52), 201 (34), 197 (34), 187 (100), 133 (37). - UV/VIS (acetonitrile): λ_{max} (ε) = 226 (15000), 300 (25900), 322 (26900) nm (l·mol^{-1}·cm^{-1}).

8,8-Dimethyl-2,6-di-p-tolyl-3,5-diaza-bicyclo[5.1.0]octa-2,5-diene-4,4-dicarbonitrile (**8b**)*:* Following the *general procedure* **3b** (204 mg, 0.56 mmol) yielded 169 mg (0.46 mmol, 83%) of **8b**, colourless needles, m.p. 191-193°C. - IR (KBr): $\tilde{\nu}$ = 3040, 2980, 2940, 2870, 1620, 1605, 1590, 1565, 1450, 1415, 1360, 1260, 1180, 1050, 830, 785 cm^{-1}. - ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.42 (s, 6 H), 7.26 (m, 4 H), 7.86 (m, 4 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135/90): δ = 21.6 (2 C, +/0), 127.8 (4 C, +/+), 129.5 (4 C, +/+), 133.8 (2 C, 0/0), 143.4 (2 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 366.3 (100) [M$^+$], 351 (22) [M$^+$-CH_3], 324 (16) [M$^+$-CH_3-

HCN], 288 (26), 249 (60), 234 (40), 223 (14), 209 (73), 185 (77), 181 (52), 171 (44), 155 (28), 143 (17), 129 (18), 118 (34), 91 (23). - UV/VIS (**dioxane**): λ_{max} (ε) = 280 (23900) nm (l·mol^{-1}·cm^{-1}).

8,8-Dimethyl-2,6-di-phenyl-3,5-diaza-bicyclo[5.1.0]octa-2,5-diene-4,4-dicarbonitrile (**8d**): Following the *general procedure* **3d** (108 mg, 0.32 mmol) yielded 84.5 mg (0.25 mmol, 78%) of **8d**, colourless needles, m.p. 219-220°C. - IR (KBr): $\tilde{\nu}$ = 2980, 2960, 1730, 1625, 1590, 1570, 1350, 1040, 690 cm^{-1}. - ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.44-7.59 (m, 6 H), 7.96-8.01 (m, 4 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135/90): δ = 127.8 (4 C, +/+), 128.8 (4 C, +/+), 132.7 (2 C, +/+), 136.3 (2 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 338.3 (100) [M$^+$], 227 (33), 235 (60), 220 (43), 218 (37), 195 (42), 171 (81), 167 (55), 157 (30), 141 (41), 115 (44), 104 (37), 103 (39), 77 (44). - UV/VIS (acetonitrile): λ_{max} (ε) = 264 (23200), 310 (5430) nm (l·mol^{-1}·cm^{-1}).

2,6-Bis-(3-chloro-phenyl)-8,8-dimethyl-3,5-diaza-bicyclo[5.1.0]octa-2,5-diene-4,4-dicarbonitrile (**8e**): Following the *general procedure* **3e** (215 mg, 0.53 mmol) yielded 104 mg (0.26 mmol, 48%) of **8e**, colourless crystals, m.p. 234-235°C. - IR (KBr): $\tilde{\nu}$ = 3080, 3010, 2965, 2945, 1625, 1600, 1560, 1420, 1350, 1240, 1120, 1050, 1010, 980, 805, 790, 770, 680 cm^{-1}. - ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.41-7.45 (m, 2 H), 7.52-7.57 (m, 2 H), 7.81-7.85 (m, 2 H), 7.96-7.98 (m, 2H) ppm. - EI MS (70 eV); m/z (%): 407.3 (33) [M$^+$(^{36}Cl)], 406.3 (67) [M$^+$(^{35}Cl)], 286 (39), 254 (31), 234 (28), 229 (81), 205 (100), 201 (53), 190 (28), 155 (24), 137 (42). - UV/VIS (dioxane): λ_{max} (ε) = 264 (16600) nm (l·mol^{-1}·cm^{-1}).

2,6-Di-furan-2-yl-8,8-dimethyl-3,5-diaza-bicyclo[5.1.0]octa-2,5-diene-4,4-dicarbonitrile (**8i**): Following the *general procedure* **3i** (217 mg, 0.68 mmol) yielded 128 mg (0.40 mmol, 59%) of **8i**, colourless needles, m.p. 178-179°C. - IR (KBr): $\tilde{\nu}$ = 3140, 3120, 2960, 1605, 1575, 1560, 1460, 1385, 1160, 1110, 1080, 1030, 1000, 880, 770, 755 cm^{-1}. - ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 6.59 (dd, 2 H, ^3J = 3.6 Hz, 1.7 Hz), 7.10 (dd, 2 H, ^3J = 3.6 Hz, 0.6 Hz), 7.65 (dd, 2 H, ^3J = 1.7 Hz, 0.6 Hz) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135/90): δ = 112.7 (2 C, +/+), 116.4 (2 C, +/+), 146.7 (2 C, +/+), 151.9 (2 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 318.2 (100) [M$^+$], 303 (32) [M$^+$-CH$_3$], 240 (32), 225 (23), 198 (51), 161 (85), 147 (37). - UV/VIS (dioxane): λ_{max} (ε) = 298 (22300), 318 (19300) nm (l·mol^{-1}·cm^{-1}).

8,8-Dimethyl-2,6-di-thiophen-2-yl-3,5-diaza-bicyclo[5.1.0]octa-2,5-diene-4,4-dicarbonitrile (**8j**): Following the *general procedure* **3j** (66.6 mg, 0.19 mmol) yielded 42.0 mg (0.12 mmol, 63%) of **8j**, colourless crystals, m.p. 193°C. - IR (KBr): $\tilde{\nu}$ = 3120, 2980, 1600, 1570, 1520, 1420, 1360, 1105, 1010, 860, 735 cm^{-1}. - ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.13-7.17 (m, 2H), 7.52-7.54 (m, 2 H), 7.58-7.61 (m, 2 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135/90): δ = 128.0 (2 C, +/+), 131.4 (2 C, +/+), 133.0 (2 C, +/+), 142.9 (2 C, 0/0) ppm. - EI MS (70 eV); m/z (%): 350 (100) [M$^+$], 272 (31), 177 (80), 163 (42). - UV/VIS (acetonitrile): λ_{max} (ε) = 270 (15100), 307 (15700), 327 (19200) nm (l·mol^{-1}·cm^{-1}).

8,8-Dimethyl-2,6-bis-methylsulfanyl-3,5-diaza-bicyclo[5.1.0]octa-2,5-diene-4,4-dicarbonitrile (**8l**): Following the *general procedure* **3l** (382 mg, 1.37 mmol) yielded 142 mg (0.51 mmol, 37%) of **8l**, colourless crystals, m.p. 187-188°C. - IR (KBr): $\tilde{\nu}$ = 3035, 2985, 2945, 1600, 1570, 1340, 1135, 1120, 1090, 1040, 1025, 1005 cm^{-1}. - ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.38 (s, 6 H) ppm. - ^{13}C NMR ($CDCl_3$, 63 MHz, DEPT 135/90): δ = 35.7 (2 C, +/0) ppm. - EI MS (70 eV); m/z (%): 278 (11) [M$^+$], 231 (100) [M$^+$-SCH$_3$], 204 (14) [M$^+$-SCH$_3$-HCN], 158

(13), 104 (30), 77 (13). - UV/VIS (dioxane): λ_{max} (ε) = 231 (6050), 257 (10400), 280 (8500) nm ($l \cdot mol^{-1} \cdot cm^{-1}$).

Table 15. Data of elemental analyses for compounds **8**.

No. R	Formula	M	C found (calcd)	H	N
8a: 4-CH_3O-C_6H_4	$C_{24}H_{22}N_4O_2$	398.5	71.02 (72.34)	5.60 (5.56)	13.60 (14.06)
8b: 4-CH_3-C_6H_4	$C_{24}H_{22}N_4$	366.5	78.46 (78.65)	6.02 (6.05)	15.04 (15.29)
8d: C_6H_5	$C_{22}H_{18}N_4$	338.4	77.38 (78.08)	5.35 (5.36)	16.18 (16.56)
8e: 3-Cl-C_6H_4	$C_{22}H_{16}N_4Cl_2$	407.3	64.90 (64.88)	4.11 (3.96)	13.77 (13.76)
8i: 2-C_4H_3O	$C_{18}H_{14}N_4O_2$	318.2	67.93 (67.94)	4.49 (4.43)	17.60 (17.61)
8j: 2-C_4H_3S	$C_{18}H_{14}N_4S_2$	350.5	60.97 (61.69)	4.06 (4.03)	15.65 (15.99)
8l: CH_3-S	$C_{12}H_{14}N_4S_2$	278.4	51.51 (51.77)	5.14 (5.06)	20.06 (20.13)

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