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1,3-Dipolar Cycloaddition Reactions of Stable Bicyclic and Monocyclic Azomethine Ylides: Preparative Aspects

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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Abstract—Stable bicyclic, monocyclic and aromatic azomethine ylides **1**, **13** and **16** add angle-strained, electron-rich and electron-poor alkynes as well as alkenes and heterocumulenes to form 1:1-adducts in highly stereoselective 1,3-dipolar cycloadditions. Unsymmetrical dipolarophiles react in a regiospecific manner.

Introduction

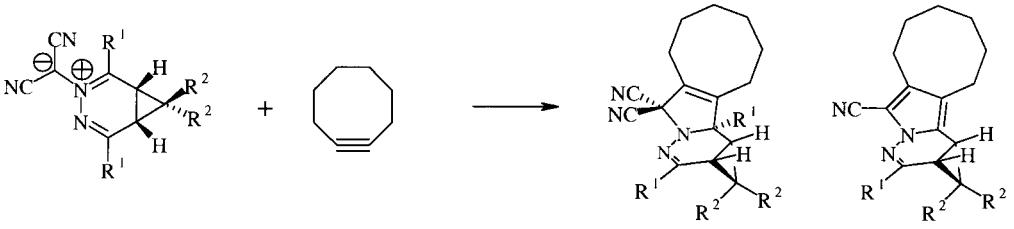
Azomethine ylides, either prepared in situ as reactive intermediates from different precursors or stable representatives, have been studied quite thoroughly during the last two decades.[1–5] The 1,3-dipolar cycloadditions of these azomethine ylides proceed with high regiochemical and stereochemical selectivity yielding pyrroline and pyrrolidine derivatives that can be central skeletons of numerous alkaloids.

Quite recently, we found an easy entrance to a new class of stable bicyclic azomethine ylides derived from diazanorcaradienes which could be transferred to again stable azomethine ylides in an acid-catalyzed rearrangement.[6–9] Using enamines as dipolarophiles we observed nonstereospecific cycloadditions indicating a two-step reaction.[10] In this contribution we report on 1,3-dipolar cycloadditions of these stable azomethine ylides with angle-strained, electron-rich and electron-poor 2π-component systems for which detailed kinetic data have already been presented in a recent paper.[11]

Results

Reactions of bicyclic azomethine ylides 1

Azomethine ylides **1**, **13**, **16** are highly coloured compounds which in the course of 1,3-dipolar cycloadditions are



1a-k **2** **3a-k** **3j',k'**

R^2 = CH_3 except for **1c,j/3c,j/3j'** R^2 = H

1/3	**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	4-Cl-C_6H_4	4-CF_3-C_6H_4

1/3/3'	**g**	**h**	**i**	**j**	**k**
R^1	2-C_4H_3N-CH_3	2-C_4H_3O	2-C_4H_3S	CH_3-S	CH_3-S

Scheme 1. 1,3-Dipolar cycloadditions of bicyclic azomethine ylides **1** with cyclooctyne (**2**).

Keywords: azomethine ylides; 1,3-dipolar cycloadditions; alkynes; alkenes; regiochemistry.
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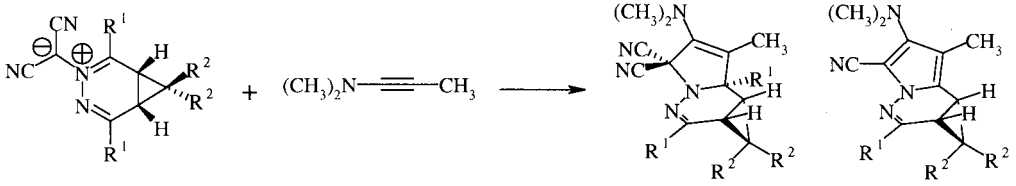
Table 1. Data for the reaction of bicyclic azomethine ylides **1** with cyclooctyne (**2**)

	R^1	R^2	mmol **1**	mmol **2**	ml, Solvent	Cond.	% **3**	mp (°C)
a	4-CH_3O–C_6H_4	CH_3	0.56	4.76	15, Ethyl acetate	70°C/2 min	89[a]	208
b	4-CH_3–C_6H_4	CH_3	0.26	1.85	10, Acetonitrile	70°C/10 min	67[b]	195–196
c	C_6H_5	H	0.55	1.55	20, Ethyl acetate/acetone 3:1	rt/1.5 h	67[c]	208–210
d	C_6H_5	CH_3	0.28	0.49	10, Acetone	Reflux/1.5 h	81[d]	175–177
e	4-Cl–C_6H_4	CH_3	0.30	1.85	10, Acetonitrile	60°C/5 min	95[b]	215–217
f	4-CF_3–C_6H_4	CH_3	0.08	0.16	4, Acetone	rt/75 min	88[e]	197–199
g	2-C_4H_3N–CH_3	CH_3	0.77	1.30	10, Acetonitrile	reflux/2.5 h	69[f]	181–182
h	2-C_4H_3O	CH_3	0.39	1.94	10, Acetonitrile	reflux/30 min	57[g]	150–151
I	2-C_4H_3S	CH_3	0.53	1.18	10, Acetone	reflux/0.5 h	48[h]	194–195
j	CH_3–S	H	0.627	1.05	20, Ethyl acetate	rt/5 h	**3j**: 23[i]	196–197
							3j′: 19[i]	106–107
k	CH_3–S	CH_3	1.48	5.65	50, Ethyl acetate	rt/1.5 h	**3k**: 16[j]	161–162
							3k′: 15[j]	103–104

[a] Washed with petroleum ether (40–60)/diethyl ether, recrystallized from petroleum ether (40–60)/CH_2Cl_2.
[b] Recrystallized from acetonitrile.
[c] Recrystallized from CH_2Cl_2.
[d] Filtered through silica gel 60, recrystallized from petroleum ether (40–60)/CH_2Cl_2.
[e] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from petroleum ether (40–60)/CH_2Cl_2.
[f] Recrystallized from acetonitrile/ethanol 2:1.
[g] Column chromatography (ethanol, silica gel 60), recrystallized from ethanol.
[h] Column chromatography ($CHCl_3$, silica gel 60), recrystallized from petroleum ether (40–60)/ethanol.
[i] Column chromatography (ethyl acetate/petroleum ether (40–60) 1:5), recrystallized from ethyl acetate.
[j] Column chromatography (CH_2Cl_2/petroleum ether (40–60) 1:1), recrystallized from petroleum ether (40–60)/CH_2Cl_2.



1/5	a	b	c	d	e
R^1	4-CH_3O-C_6H_4	4-CH_3-C_6H_4	C_6H_5	C_6H_5	4-Cl-C_6H_4

1/5/5'	f	g	h	i	k
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

Scheme 2. 1,3-Dipolar cycloadditions of bicyclic azomethine ylides **1** with ynamine **4**.

Table 2. Data for the reaction of bicyclic azomethine ylides **1** with ynamine **4**

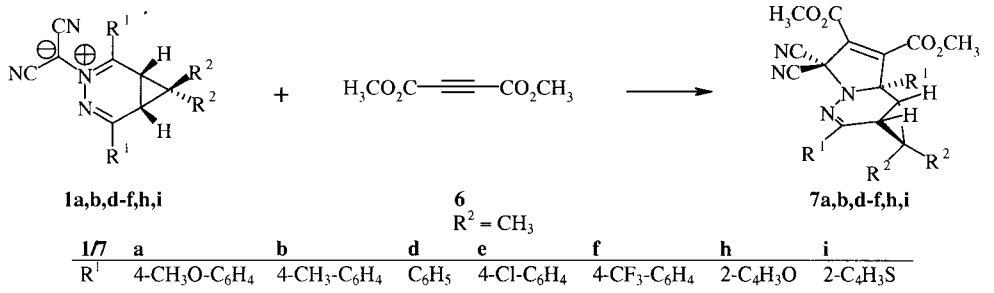
	R^1	R^2	mmol **1**	mmol **4**	ml, Solvent	Cond.	% **5**	mp (°C)
a	4-CH_3O–C_6H_4	CH_3	0.56	4.25	15, Ethyl acetate	rt/2 h	81[a]	184–186
b	4-CH_3–C_6H_4	CH_3	0.27	0.96	10, Acetonitrile	rt/5 min	64[b]	151–156
c	C_6H_5	H	0.32	1.48	10, Ethyl acetate	rt/10 min	40[c]	160–162
d	C_6H_5	CH_3	0.17	0.41	5, Ethyl acetate	rt/20 min	95[d]	171–173
e	4-Cl–C_6H_4	CH_3	0.27	0.72	10, Acetonitrile	rt/5 min	87[e]	196
f	4-CF_3–C_6H_4	CH_3	0.07	0.15	4, Ethyl acetate	rt/5 min	88[f]	199–201
g	2-C_4H_3N–CH_3	CH_3	0.15	0.69	8, Ethyl acetate	55°C/4 h	43[g]	185–186
h	2-C_4H_3O	CH_3	0.44	1.65	10, Ethyl acetate	rt/15 min	54[h]	161–163
I	2-C_4H_3S	CH_3	0.33	1.00	10, Ethyl acetate	rt/3 h	57[i]	194–195
k	CH_3–S	CH_3	0.30	1.25	20, Ethyl acetate	rt/3 h	**5k′**: 28[j]	98–100

[a] Column chromatography (ethyl acetate, silica gel 60), recrystallized from diethyl ether/CH_2Cl_2.
[b] Precipitation induced with petroleum ether (40–60), recrystallized from diethyl ether/petroleum ether (40–60).
[c] Recrystallized from ethyl acetate/diethyl ether 1:4.
[d] No further purification required.
[e] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from petroleum ether (40–60)/ethyl acetate.
[f] Filtered through silica gel 60, recrystallized from petroleum ether (40–60)/CH_2Cl_2.
[g] Recrystallized from ethyl acetate/hexane 2:1.
[h] Recrystallized from ethyl acetate/petroleum ether (40–60) 1:6.
[i] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from diethyl ether/ethyl acetate.
[j] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from petroleum ether (40–60)/CH_2Cl_2.

Table 3. Data for the reaction of bicyclic azomethine ylides **1** with acetylene dicarboxylate **6**

	R^1	R^2	mmol **1**	mmol **6**	ml, Solvent	Cond.	% 7	mp (°C)
a	4-CH_3O–C_6H_4	CH_3	0.47	4.19	10, Acetone	70°C/2.5 h	86[a]	184–185
b	4-CH_3–C_6H_4	CH_3	0.28	0.97	10, Acetonitrile	reflux/2.5 h	69[b]	181–182
d	C_6H_5	CH_3	0.82	3.88	10, Acetone	reflux/5 h	88[c]	184–185
e	4-Cl–C_6H_4	CH_3	0.26	0.97	20, Acetonitrile	reflux/100 min	94[d]	196–197
f	4-CF_3–C_6H_4	CH_3	0.15	0.95	5, Acetone	60°C/4 h	82[e]	156–157
h	2-C_4H_3O	CH_3	0.44	2.41	10, Acetone	reflux/5h, rt/63 h	57[f]	152–153
i	2-C_4H_3S	CH_3	0.47	2.43	10, Acetone	reflux/5 h	70[g]	183–184

[a] Recrystallized from ethanol.
[b] Recrystallized from acetonitrile.
[c] Recrystallized from ethyl acetate/petroleum ether (40–60).
[d] Precipitation induced with diethyl ether. Crystals recrystallized from CH_2Cl_2/petroleum ether (40–60).
[e] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized petroleum ether (40–60).
[f] Column chromatography (ethanol/diethyl ether 1:3, silica gel 60), recrystallized from ethanol/diethyl ether 1:3.
[g] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from petroleum ether (40–60)/ethanol.



Scheme 3. 1,3-Dipolar cycloadditions of bicyclic azomethine ylides **1** with acetylene dicarboxylate **6**.

transformed into colourless 1:1-adducts. So all cycloadditions performed in this contribution could be easily followed by the disappearance of the colour of the starting compounds and/or by thin-layer chromatography.

In order to be able to study the substituent effects of R^1 in the dipoles **1** in our kinetic work[11] according to the Hammett treatment a broader variation of R^1 was necessary; also furan, thiophene and *N*-methylpyrrole as heterocyclic substituents were included in this preparative investigation.

Cyclooctyne (**2**), a highly reactive alkyne in cycloadditions,[12] combines smoothly at slightly elevated temperature with azomethine ylides **1a**–**1k** to form 1:1-adducts **3a**–**3k** (Scheme 1; Table 1). The reactions of **1j** and **1k** in addition to the 'normal' adducts **3j** and **3k** also delivered the aromatic pyrrole derivatives **3j′** and **3k′** in almost equal amounts. Formally CH_3SCN was lost during these reactions. Similar observations were also reported by a Japanese group for [3+2] cycloadditions of pyridazinium dicyanomethylides with substituents OCH_3 and OC_6H_5 instead of SCH_3; in this case loss of ROCN must be postulated.[13] Mechanistic studies to explain these results are still missing.

Also ynamine **4** proved to be a very potent dipolarophile, most reactions already occur at room temperature (Scheme 2; Table 2). With the exception of reaction **1k**+**4**, which again leads to the aromatic pyrrole derivative **5k′** as by-product, 1:1-adducts **5a**–**5i** were isolated in good yields.

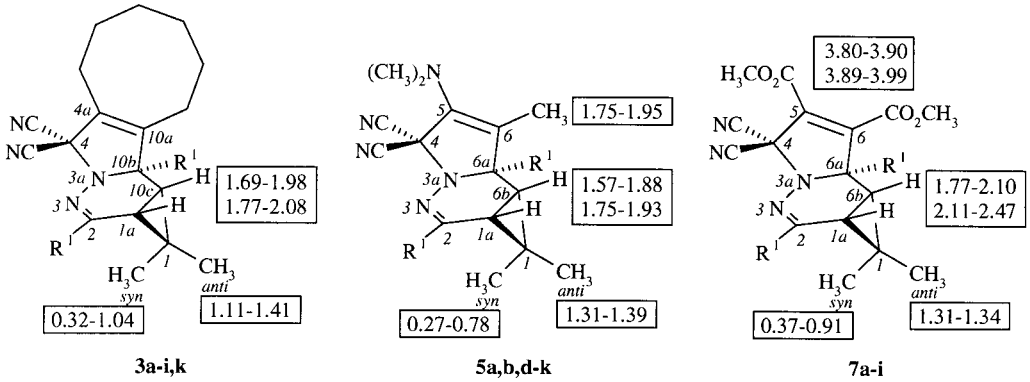
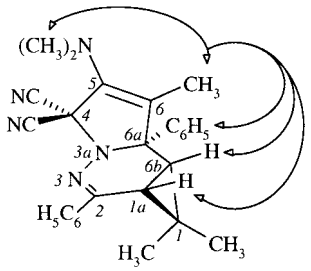


Figure 1. Selected ^{1}H NMR data for cycloadducts **3**, **5** and **7** derived from bicyclic azomethine ylides **1** and acetylene derivatives (δ-values in ppm).



5d

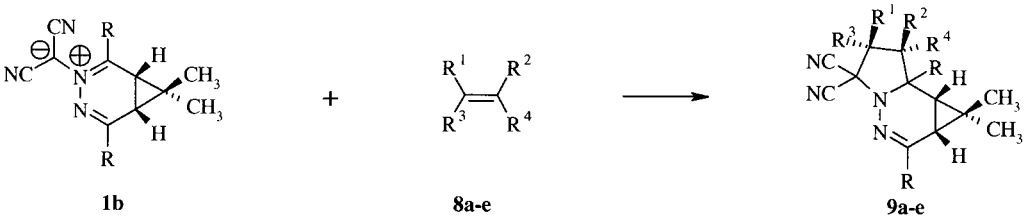
Figure 2. NOE effects found for adduct **5d**.

Already the reaction conditions of Table 3 demonstrate the lower dipolarophilic activity of dimethyl acetylenedicarboxylate (**6**) (Scheme 3) compared with cyclooctyne (**2**) and ynamine **4**. In all cases including **1i** 1:1-adducts are isolated in good yields under more stringent conditions.

All spectroscopic data (see Experimental) are in accord with the structure proposals **3**, **5** and **7** for the 1:1-adducts so only a few arguments need to be discussed here. The very strong and characteristic IR absorption of the cyano groups in dipoles **1** (approximately 2190 and 2150 cm^{-1})[11] have almost disappeared in the 1:1-adducts **3**, **5** and **7**. The presence of the cyclopropane ring is documented by an AB-system of the protons H-1a and H-10c, respectively H-1a and H-6b, with coupling constants between 8 and 9 Hz (Fig. 1). The chemical shift difference between the two cyclopropane protons is quite small. Nevertheless, in a number of cases proton H-1a could be identified by detailed NMR experiments at lower field.[14–16] The two geminal methyl groups at C-1 show two well-separated singlets, the *syn*-CH_3 is shielded by the six-membered ring and absorbing at higher field while the signals for the *anti*-CH_3 show higher δ-values and absorb at lower field. As would be expected, the electronic influence of substituents R^1 on the δ-values is larger for *syn*-CH_3 while the remote *anti*-CH_3 mostly show only minor shift differences when R^1 is varied.

The regiochemistry for the addition step of the unsymmetrical ynamine **4** is proven by NOE experiments (Fig. 2). Irradiation of the $N(CH_3)_2$-signal around 2.8 ppm only enhances the signal of the olefinic methyl group at C-6 (ca. 1.9 ppm) while the irradiation of this methyl signal enhances a number of protons nearby, for instance, those of the aromatic ring at C-6a as well as protons H-6b and H-1a but not the geminal methyl groups at C-1 thus proving the stereochemistry of the complete tricyclic ring system, as Fig. 2 demonstrates. The complete sets for the spectroscopic data of all 1:1-adducts **3**, **5** and **7** are found in Experimental and Refs. 14–16. The ^{13}C chemical shifts for all carbon atoms are normal and in accordance with the structure proposal.

In Schemes 1–3 (Tables 1–3) the substituents R^1 in the dipoles **1** were varied for later kinetic investigations,[11] three different dipolarophiles were used as test 2π-systems, the angle-strained cyclooctyne (**2**), the electron-rich ynamine **4** and the electron-deficient acetylene dicarboxylate **6**. In order to study also the influence of substituents in



1b **8a-e** **9a-e**

R = 4-CH_3-C_6H_4

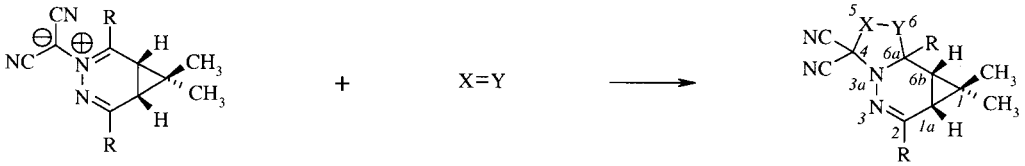
8/9	a	b	c	d	e
R^1	OC_2H_5	$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_2)_4$	CO-$N(CH_3)$-CO
R^2	H	H	H	H	
R^3	OC_2H_5	OC_2H_5	SCH_3	$(CH_2)_4$	H
R^4	H	H	H		H

Scheme 4. 1,3-Dipolar cycloadditions of bicyclic azomethine ylide **1b** with olefinic dipolarophiles **8**.

Table 4. Data for the reaction of bicyclic azomethine ylide **1b** with olefinic dipolarophiles **8**

8/9	R^1	R^2	R^3	R^4	mmol **1b**	mmol **8**	Cond.	% **9**	Mp (°C)
a	OC_2H_5	H	OC_2H_5	H	0.31	1.01	rt/15h, 50°C/4 h	87[a]	177
b	$N(CH_3)_2$	H	OC_2H_5	H	0.48	0.62	rt/fast	100[b]	175–176
c	$N(CH_3)_2$	H	SCH_3	H	0.41	0.74	rt/5 min	100[c]	157
d	$N(CH_2)_4$	H	$(CH_2)_4$		0.36	0.46	rt/72 h	56[d]	175
e	CO–$N(CH_3)$–CO		H	H	0.28	2.78	80°C/9 h	45[e]	238

[a] Column chromatography (ethyl acetate/petroleum ether (40–60), silica gel 60), recrystallized from hexane.
[b] No further purification required.
[c] Washed with diethyl ether.
[d] Column chromatography (ethyl acetate/petroleum ether (40–60), silica gel 60), recrystallized from CH_2Cl_2/hexane.
[e] Excess of **8e** removed by sublimation, further purification by column chromatography (ethyl acetate/petroleum ether (40–60), silica gel 60), recrystallized from CH_2Cl_2/hexane.



R = 4-CH_3-C_6H_4 except for **1d**/**11d** R = C_6H_5

10/11	a	b	c	d
X	Cl_3CCH	O=C	S=C	Cl_2C
Y	O	N-C_6H_5	N-C_6H_5	S

Scheme 5. 1,3-Dipolar cycloadditions of bicyclic azomethine ylides **1** with hetero dipolarophiles **10**.

Table 5. Data for the reaction of bicyclic azomethine ylides **1** with hetero dipolarophiles **10**

	R	X	Y	mmol **1**	mmol **10**	ml, Solvent	Cond.	% **11**	mp (°C)
a	4-CH_3–C_6H_4	Cl_3CCH	O	0.62	10.6	10, Acetonitrile	40°C/8 h	40[a]	151
b	4-CH_3–C_6H_4	O=C	N–C_6H_5	0.29	3.22	10, Acetonitrile	rt/138 h	67[b]	179
c	4-CH_3–C_6H_4	S=C	N–C_6H_5	0.28	3.01	10, Acetonitrile	rt/54d	21[c]	184
d	C_6H_5	Cl_2C	S	0.49	1.05	10, CH_2Cl_2	rt/75 min	65[d]	117

[a] Product precipitates from the reaction mixture. Washed with acetonitrile.
[b] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from diethyl ether/hexane.
[c] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from CH_2Cl_2/hexane.
[d] Recrystallized from petroleum ether (40–60)/ethyl acetate.

the dipolarophiles on the reaction rate[11] we kept R^1 in the azomethine ylides **1** constant and varied the dipolarophile; for practical purposes we used the ditolyl derivative **1b** as 4π-partner. Scheme 4 and Table 4 offer the data for olefinic dipolarophiles, Scheme 5 and Table 5 those for dipolarophiles with hetero double bonds.

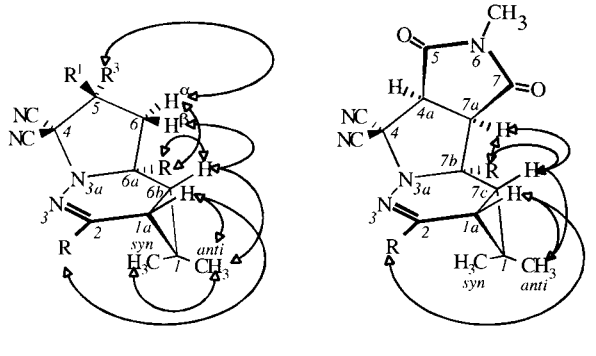
Ketene aminals are superdienophiles in Diels–Alder reactions with inverse electron demand, as demonstrated for 1,2,4,5-tetrazines as dienes by kinetics.[12] Also azomethine ylide **1b** reacts with ketene aminals in a $LUMO_{dipole}$–$HOMO_{dipolarophile}$-controlled reaction.[11] While ketene-*O*,*O*-aminal **8a** after a reaction period of 15 h at room temperature still needs some gentle heating (4 h, 50°C) to bring the reaction to completion, ketene-*N*,*O*-aminal **8b** and ketene-*N*,*S*-aminal **8c** cycloadd to azomethine ylide **1b** almost instantaneously at room temperature. The colourless adducts **9a–c** melt with formation of red liquids, indicating some extent of cycloreversion. In polar solvents **9b** and **9c** form intense red solutions, typical for the free dipole **1b**. In acetonitrile solution of **3b** at 60°C a 5.8-fold excess of cyclooctyne (**2**) traps free **1b** as cyclooctyne adduct **3b** in 52% yield, identical with an authentic sample of **3b**.

Enamine **8d** still proves to be a reactive dipolarophile yielding 56% analytically pure 1:1-adduct **9d**. In contrast the 1,3-dipolar cycloaddition of **1b** with the electron-poor *N*-methylmaleimide (**8e**) needs refluxing acetonitrile for 9 h to give a lower yield of adduct **9e** (45%).

Structure proof for the ketene aminal adducts **9a–c** mainly comes from NMR data (see Experimental).[15] The regiochemistry follows from typical NOE effects especially for H-α and H-β at C-6 (Fig. 3). This technique also demonstrates the *endo*-orientation of the $N(CH_3)_2$-group in **9b** and **9c**.[15] The crystal structure analysis of the enamine adduct **9d** proves the *endo*-configuration also for the pyrrolidin-1-yl substituent, in analogy to the ketene acetal adducts **9b** and **9c**.[17] Finally, the electron-poor *N*-methylmaleimide **8e** prefers the *endo*-configuration in the transition state of the 1,3-dipolar addition, too. Fig. 3 presents some selected NOE effects for **9e** which are only compatible with this structure proposal.

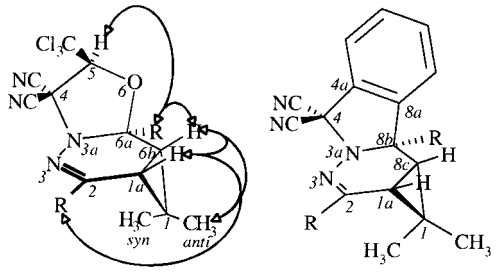
In a limited number of cases we were successful in using hetero double bond systems and heterocumulenes as 2π-components in 1,3-dipolar cycloadditions with azomethine ylides **1b** and **1d**.

Trichloroacetaldehyde (**10a**) formed a 1:1-adduct **11a**, which dropped out from acetonitrile solution in analytically pure form in 40% yield. Phenyl isocyanate (**10b**) and phenyl isothiocyanate (**10c**) reacted with **1b** in acetonitrile at room



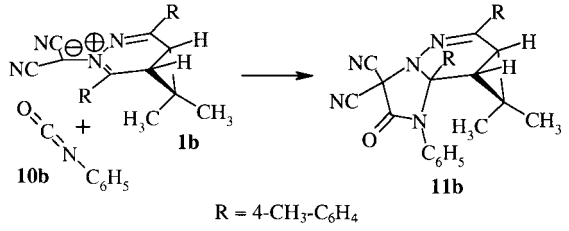
9	R^1	R^3
a	OC_2H_5	OC_2H_5
b	$N(CH_3)_2$	OC_2H_5
c	$N(CH_3)_2$	SCH_3

Figure 3. Selected NOE effects for adducts **9a–c** and **9e** from azomethine ylide **1b** with olefinic dipolarophiles **8** (R=4-CH_3–C_6H_4).



11a **12**

Figure 4. Selected NOE effects for the chloral adduct **11a** and benzyne adduct **12** (R=4-CH_3–C_6H_4).

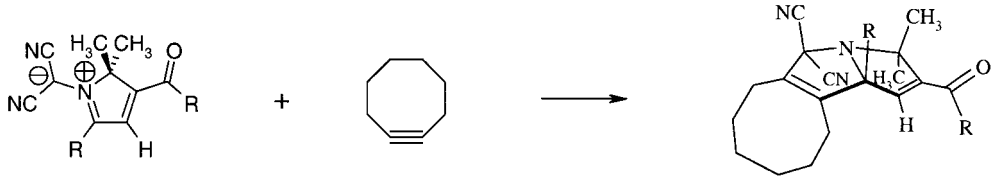


Scheme 6. Addition of phenyl isocyanate (**10b**) to azomethine ylide **1b** with formation of adduct **11b**.

temperature. 67% of **11b** and 21% of **11c** were collected after 138 h, respectively, 54 d as colourless 1:1-adducts. Finally, thiophosgene (**10d**) decolourized a solution of **1d** in dichloromethane at room temperature within 60 min. The faintly pink 1:1-adduct **11d** which was isolated as the only regioisomer in 65% yield melted at 117°C under cycloreversion with formation of a red liquid. Cycloreversion also occurs slowly in solution, so **11d** could only be recrystallized in inert solvents in the presence of an excess of thiophosgene (**10d**).

Again NOE effects in the NMR spectra of **11a** were helpful to assign the stereochemistry of the chloral adduct **11a** which is carrying even the bulky trichloromethyl group in an *endo*-arrangement (Fig. 4). NMR data alone allowed no conclusive decision for the structure assignment of **11b** and **11d** especially with regard to its stereochemistry. Fortunately we were successful in growing single crystals of **11b** suitable for crystal structure analysis.[18] As Scheme 6 demonstrates, phenyl isocyanate approaches the azomethine ylide **1b** in such a way that finally the newly formed five-membered heterocyclic ring appears in a *cis*-arrangement to the cyclopropane ring. Interestingly, this *cis*-arrangement almost cancels the 'normal' dissimilarity of the two methyl groups at C-1 which now appear as two narrow singlets at δ=1.17 and 1.20 ppm; the cyclopropane protons show the usual AB-system at 2.10 and 2.33 ppm with J=9.3 Hz. As we also find the same NMR pattern for the analogue protons of the phenyl isothiocyanate adduct **11c** (AB-system at δ=2.02 and 2.34 ppm, J=9.2 Hz, methyl singlets at δ=1.19 and 1.25 ppm) we propose the same stereochemical arrangement for **11c** as proven for **11b** by crystal structure analysis. Finally having no X-ray data at hand for the thiophosgene adduct **11d** we interpret the NMR data (see Experimental) in favour of regioisomer **11d**.[14]

Benzyne, generated from diazotated anthranilic acid in situ, could be trapped by azomethine ylide **1b** (61% yield **12**, Fig. 4). The colourless 1:1-adduct **12** offers no structural



13a,b,d-f,h **2** **14a,b,d-f,h**

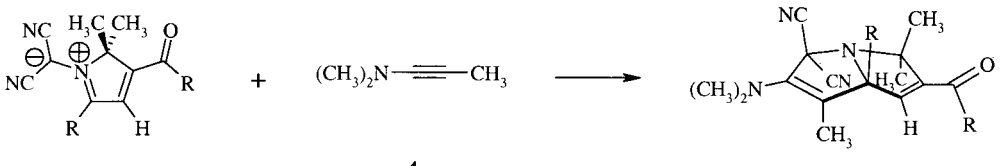
12/14	a	b	d	e	f	h
R	4-CH_3O-C_6H_4	4-CH_3-C_6H_4	C_6H_5	4-Cl-C_6H_4	4-CF_3-C_6H_4	2-C_4H_3O

Scheme 7. 1,3-Dipolar cycloadditions of monocyclic azomethine ylides **13** with cyclooctyne (**2**).

Table 6. Data for the reaction of monocyclic azomethine ylides **13** with cyclooctyne (**2**)

13/14	R	mmol **13**	mmol **2**	ml, Solvent	Cond.	% **14**	Mp (°C)
a	4-CH_3O–C_6H_4	0.32	0.44	10, Acetonitrile	rt/197 h	–[a]	–[b]
b	4-CH_3–C_6H_4	0.25	0.48	15, Acetonitrile	60°C/6 h	85[c]	131–133
d	C_6H_5	0.46	0.79	10, CH_2Cl_2	reflux/3 h	79[d]	166–167
e	4-Cl–C_6H_4	0.19	0.33	10, Acetonitrile	rt/22 h	51[e]	151
f	4-CF_3–C_6H_4	0.09	0.18	5, Acetonitrile	rt/16 h	46[f]	154
h	2-C_4H_3O	0.14	0.71	10, Acetonitrile	60°C/2 h	74[g]	160–161

[a] Column chromatography (CH_2Cl_2, silica gel 60), product could not be crystallized, contains solvent.
[b] Yellowish oil.
[c] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from ethyl acetate/hexane.
[d] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from petroleum ether (40–69)/diethyl ether/CH_2Cl_2.
[e] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from methanol.
[f] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from methanol.
[g] Column chromatography (CH_2Cl_2/petroleum ether (40–60) 5:1, silica gel 60), product washed with hexane/CH_2Cl_2 10:1.



13a,b,d-h **4** **15a,b,d-h**

13/15	a	b	d	e	f	g	h
R	4-CH_3O-C_6H_4	4-CH_3-C_6H_4	C_6H_5	4-Cl-C_6H_4	4-CF_3-C_6H_4	2-C_4H_3N-CH_3	2-C_4H_3O

Scheme 8. 1,3-Dipolar cycloadditions of monocyclic azomethine ylides **13** with ynamine **4**.

Table 7. Data for the reaction of monocyclic azomethine ylides **13** with ynamine **4**

13/15	R	mmol **13**	mmol **4**	ml, Solvent	Cond.	% **15**	Mp (°C)
a	4-CH_3O–C_6H_4	0.20	0.39	10, Acetonitrile	40°C/60 min	65[a]	173–174
b	4-CH_3–C_6H_4	0.26	1.13	10, Acetonitrile	40°C/10 min	56[b]	129–131
d	C_6H_5	0.52	1.20	10, CH_2Cl_2	rt/30 min	50[c]	161
e	4-Cl–C_6H_4	0.19	0.42	10, Acetonitrile	rt/45 min	70[d]	177
f	4-CF_3–C_6H_4	0.16	0.32	10, Acetonitrile	rt/50 min	54[d]	178–180
g	2-C_4H_3N–CH_3	0.14	0.35	10, Acetonitrile	60°C/2 h	37[e]	160–161
h	2-C_4H_3O	0.33	0.80	10, Acetonitrile	60°C/5 min	43[f]	156–157

[a] Column chromatography (ethyl acetate/petroleum ether (40–60), silica gel 60), recrystallized from diethyl ether/hexane.
[b] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from ethanol/water.
[c] Column chromatography (diethyl ether/hexane 1:1, silica gel 60), recrystallized from diethyl ether/hexane.
[d] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from CH_2Cl_2/hexane.
[e] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from ethyl acetate/hexane.
[f] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from ethyl acetate.

problems, ^1H and ^{13}C chemical shifts as well as the coupling constants are as to be expected (see Experimental).[15]

Reactions of monocyclic azomethine ylides 13

Monocyclic azomethine ylides **13** showed similar 1,3-dipolar reactivity compared with the bicyclic representatives **1**. This is clearly documented by the reaction conditions in the following tables and expressed in quantitative data by the rate constants resulting from our kinetic study.[11]

Scheme 7 and Table 6 as well as Scheme 8 and Table 7 summarise the reactions of azomethine ylide **13** with cyclooctyne (**2**) and ynamine **4**. For structure elucidation we again used IR data in combination with ^1H and ^{13}C NMR spectroscopy, NOE effects confirmed the stereochemistry (see Experimental).[14–16]

Also the cycloadditions of **13** with acetylene dicarboxylate **6**, benzyne and ketene-*O*,*O*-aminal **8a** followed the expected route to form 1:1-adducts **19**, **20** and **21** (Fig. 5). Chemical shift data, coupling constants and NOE effects again were helpful tools for the structure elucidation (see Experimental).[14–16]

Reactions of aromatic azomethine ylides 16

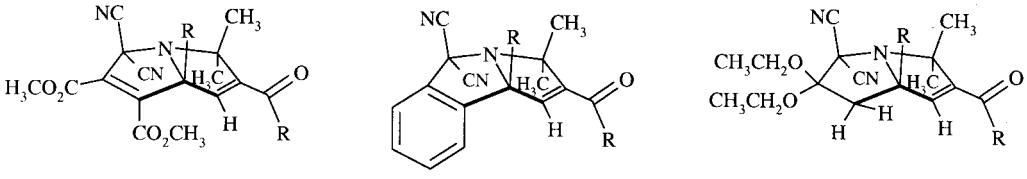
In order to test also the substituent influence on the rate of 1,3-dipolar cycloadditions of aromatic azomethine ylides[11] we included representative dipoles **16** of the pyridazinium type in our investigation.

Scheme 9 and Table 8 as well as Scheme 10 and Table 9 summarize the reactions performed in this contribution. Substituents R were varied to allow the Hammett treatment.[11] The more stringent reaction conditions in Tables 8 and 9 already indicate a definitely lower dipole activity of the aromatic azomethine ylides **16**. In analogy to earlier examples in this paper (see Scheme 1) elimination of CH_3SCN was observed for the reaction of **16f** with cyclooctyne (**2**) leading to the aromatic pyrrole derivative **17f** as the only isolable product in 77% yield.

Structure proof for adducts **17** and **18** again was possible using spectroscopic methods as before (see Experimental).[14–16]

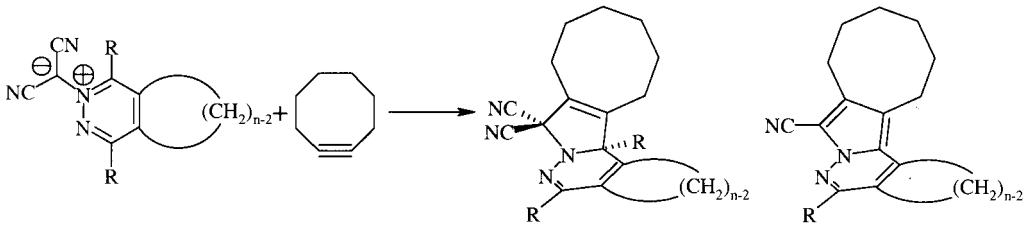
Conclusion

Stable bicyclic, monocyclic and aromatic azomethine ylides



19a,b: R = 4-CH_3-C_6H_4, C_6H_5 **20**: R = 4-CH_3-C_6H_4 **21**: R = 4-CH_3-C_6H_4

Figure 5. 1,3-Dipolar cycloadditions of azomethine ylides **13** with acetylene dicarboxylate **6**, benzyne and ketene-*O*,*O*-aminal **8a** to yield adducts **19**–**21**.



16a-f 2 17a-e 17f

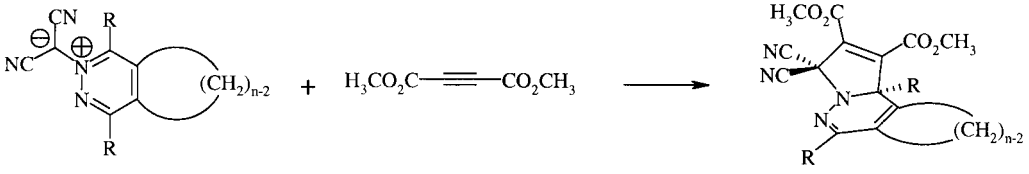
16/17	a	b	c	d	e	f
R	4-CH_3O-C_6H_4	4-CH_3-C_6H_4	C_6H_5	C_6H_5	4-CF_3-C_6H_4	SCH_3
n	5	5	5	6	5	5

Scheme 9. 1,3-Dipolar cycloadditions of aromatic azomethine ylides **16** with cyclooctyne (**2**).

Table 8. Data for the reaction of aromatic azomethine ylides **16** with cyclooctyne (**2**)

16/17	R	*n*	mmol **16**	mmol **2**	ml, Solvent	Cond.	% **17**	Mp (°C)
a	4-CH_3O–C_6H_4	5	0.34	3.37	60, Ethyl acetate	rt/65h, 70°C/24 h	46[a]	146–147
b	4-CH_3–C_6H_4	5	0.34	0.86	10, Acetonitrile	reflux/9 h	55[b]	187–189
c	C_6H_5	5	0.48	1.74	30, Ethyl acetate	reflux/4.5 h	61[c]	175–177
d	C_6H_5	6	0.34	1.87	30, Ethyl acetate	reflux/3 h	67[d]	178–180
e	4-CF_3–C_6H_4	5	0.20	0.62	10, Acetonitrile	reflux/3.5 h	58[e]	132–133
f	SCH_3	5	0.79	3.48	30, Ethyl acetate	70°C/15 min	77[f]	190–191

[a] Column chromatography (ethyl acetate/hexane 1:4, silica gel 60).
[b] Column chromatography (CH_2Cl_2/hexane 2:1, silica gel 60), recrystallized from hexane/ethyl acetate 5:1.
[c] Column chromatography (CH_2Cl_2, silica gel 60), recrystallized from ethyl acetate.
[d] Recrystallized from ethyl acetate.
[e] Recrystallized from hexane/ethyl acetate 10:1.
[f] Column chromatography (CH_2Cl_2/hexane 1:1, silica gel 60), recrystallized from hexane.



16a-e 6 18a-e

16/18	a	b	c	d	e
R	4-CH_3O-C_6H_4	4-CH_3-C_6H_4	C_6H_5	C_6H_5	4-CF_3-C_6H_4
n	5	5	5	6	5

Scheme 10. 1,3-Dipolar cycloadditions of aromatic azomethine ylides **16** with acetylene dicarboxylate **6**.

Table 9. Data for the reaction of aromatic azomethine ylides **16** with acetylene dicarboxylate **6**

16/18	R	*n*	mmol **16**	mmol **6**	ml, solvent	cond.	% **18**	Mp (°C)
a	4-CH_3O–C_6H_4	5	0.14	0.28	15, Acetonitrile	reflux/8 h	85[a]	143–144
b	4-CH_3–C_6H_4	5	0.58	0.86	15, Acetonitrile	reflux/8 h	98[b]	189–190
c	C_6H_5	5	0.61	1.01	10, Acetonitrile	reflux/19 h	75[a]	155–156
d	C_6H_5	6	0.12	0.31	10, Acetonitrile	reflux/2.75 h	77[c]	183–184
e	4-CF_3–C_6H_4	5	0.16	0.33	10, Acetonitrile	reflux/9h, rt/15 h	64[d]	169–170

[a] Column chromatography (CH_2Cl_2/ethyl acetate 40:1, silica gel 60).
[b] Column chromatography (CH_2Cl_2, silica gel 60).
[c] Column chromatography (CH_2Cl_2/hexane 6:1, silica gel 60).
[d] Column chromatography (CH_2Cl_2/petroleum ether (40–60) 3:1, silica gel 60).

1, **13** and **16** are versatile 1,3-dipoles which cycloadd to a variety of dipolarophiles with double and triple bonds as 2π-systems. Hetero double bonds and hetero cumulenes could be included into the bunch of dipolarophiles. All cycloadditions studied proceeded with high regio and stereoselectivity. Influences of substituents in dipoles and dipolarophiles on the reaction rate already show up in the experimental conditions applied and are described in a recent paper.[11]

Experimental

General

IR spectra were recorded with a Beckmann Acculab I. NMR spectra were obtained with a Bruker AC250 and ARX400 (250 MHz/400 MHz for ^1H and 63 MHz/101 MHz for ^{13}C). The degree of substitution of the C atoms was determined by the DEPT-135/90/45 methods. 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 analyses 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). Cycloaddition reactions were carried out under an atmosphere of nitrogen in solvents as presented in Tables 1–9 dried according to standard procedures before use.

All azomethine ylides **1**, **13** and **16** were prepared according to literature procedures.[9,14–16] Amounts of starting materials and products, reaction conditions, yields and melting points are presented in Tables 1–9 and will not be repeated in the Experimental.

General procedure for the cycloadditions

To a solution of **1a–k**, **13a**, **b**,**d–f** or **16a–f** in a dry solvent protected by an atmosphere of nitrogen the dipolarophile was added. The mixture was stirred at ambient or elevated temperature as described in Tables 1–9 until complete discolouration of the solution or until no more reaction could be detected by TLC. After removal of the solvent in vacuo, the crude reaction products were purified as described in Tables 1–9 for the different reactions.

2,10b-Bis-(4-methoxy-phenyl)-1,1-dimethyl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3a). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.42 (s, 3H, *syn*-H_3CCCH_3), 0.97–1.02 (m, 1H, CH_2), 1.26–1.35 (m, 3H, CH_2), 1.38 (s, 3H, *anti*-H_3CCCH_3), 1.44–1.55 (m, 2H, CH_2), 1.77 (s, 2H, cyclopropyl-H), 1.77–1.89 (m, 2H, CH_2), 2.37–2.51 (m, 4H, CH_2), 3.79 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.84–6.88 (m, 2H, aryl-H), 6.91–6.95 (m, 2H, aryl-H), 7.49–7.53 (m, 2H, aryl-H), 7.76–7.79 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=17.4 (*syn*-H_3CCCH_3), 20.5 (cyclopropyl-CH), 23.5 (C-1), 24.3 (CH_2), 25.4 (CH_2), 25.5 (CH_2), 25.6 (cyclopropyl-CH), 25.9 (CH_2), 27.3 (*anti*-H_3CCCH_3), 27.8 (CH_2), 29.4 (CH_2), 55.2 (OCH_3), 55.3 (OCH_3), 68.7, 69.9, 112.3, 113.4, 113.9, 114.1, 125.4, 127.2, 127.4, 129.6, 136.6, 149.2, 152.9, 158.8, 160.9 ppm. IR (KBr): $\tilde{\nu}$=3080–2880, 1610, 1510, 1460, 1300,1170, 1030, 845 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=238 (16 900), 257 (14 700), 275 (14 200), 284 (14 000) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=506.0 (6) [M^+], 439.0 (31), 438 (100), 367.9 (32). $C_{32}H_{34}N_4O_2$ (506.6): calcd C 75.86, H 6.76, N 11.06; found C 75.30, H 6.72, N 11.00.

1,1-Dimethyl-2,10b-di-*p*-tolyl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3b). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.40 (s, 3H, *syn*-H_3CCCH_3), 0.94–1.17 (m, 1H, CH_2), 1.18–1.66 (m, 5H, CH_2), 1.37 (s, 3H, *anti*-H_3CCCH_3), 1.66–1.99 (m, 2H, CH_2), 1.78 (s, 2H, cyclopropyl-H), 2.20–2.60 (m, 4H, CH_2), 2.32 (s, 3H, tolyl-CH_3), 2.37 (s, 3H, tolyl-CH_3), 7.06–7.30 (m, 4H, aryl-H), 7.43–7.56 (m, 2H, aryl-H), 7.65–7.79 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=17.43 (*syn*-H_3CCCH_3), 20.67 (cyclopropyl-CH), 21.00 (tolyl-CH_3), 21.35 (tolyl-CH_3), 23.59 (C-1), 24.44 (CH_2), 25.61 (2C, CH_2), 25.75 (cyclopropyl-CH), 26.07 (CH_2), 27.33 (*anti*-H_3CCCH_3), 27.81 (CH_2), 29.56 (CH_2), 68.89, 70.26, 112.36, 114.12, 125.98, 126.03, 128.91, 129.25, 134.33; 137.13, 139.73, 141.67, 149.04, 152.48 ppm. IR (KBr): $\tilde{\nu}$=3040, 2990, 2940, 2870, 1460, 1450, 1065, 815, 805 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=228 (21 800), 291 (8900) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=474 (19) [M^+], 447 (21) [M^+−HCN], 407 (31), 406 (100), 336 (34), 185 (19) [Ylid$^+$−C_7H_7CN–$C(CN)_2$], 184 (30), 118 (20), 90 (34), 65 (22), 41 (24). $C_{32}H_{34}N_4$ (474.7): calcd C 80.98, H 7.22, N 11.80; found C 80.68, H 7.10, N 11.79.

2,10b-Diphenyl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3c). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.65 (ddd, 1H, ^2J=5.0 Hz, ^3J=5.3 Hz, ^3J=5.6 Hz, *syn*-cyclopropyl-H), 1.18–1.56 (m, 6H, CH_2), 1.36 (ddd, 1H, ^2J=5.0 Hz, ^3J=9.5 Hz, ^3J=8.2 Hz, *anti*-cyclopropyl-H), 1.81–1.87 (m, 2H, CH_2), 1.94 (ddd, 1H, ^3J=5.6 Hz, ^3J=7.8 Hz, ^3J=8.2 Hz, cyclopropyl-H), 2.09 (ddd, 1H, ^3J=5.3 Hz, ^3J=7.8 Hz, ^3J=9.5 Hz, cyclopropyl-H), 2.45–2.60 (m, 4H, CH_2), 7.24–7.53 (m, 8H, aryl-H), 7.88–7.95 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=10.8 (cyclopropyl-CH), 12.3 (C-1), 16.0 (cyclopropyl-H), 24.5 (CH_2), 25.5 (CH_2), 25.8 (CH_2), 26.0 (CH_2), 28.1 (CH_2), 29.2 (CH_2), 66.7, 70.7, 112.4, 113.2, 125.9, 127.4, 127.9, 128.3, 128.5, 128.6, 129.8, 136.5, 142.4, 148.6, 154.9 ppm. IR (KBr): $\tilde{\nu}$=3095, 3070, 3030, 2940, 2870, 1490, 1465, 1450, 1395, 1275, 1160, 1080, 1050, 1035, 1015, 930, 780, 705 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=247 (12 600), 274 (8770) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=418.4 (85) [M^+], 391.4 (100) [M^+−HCN], 348.3 (10), 341.3 (38) [M^+−C_6H_5], 314.3 (57), 232.1 (30), 196.0 (19), 181.0 (23), 142.9 (17), 129.9 (12), 114.9 (10), 103.9 (11), 77.0 (15) [C_6H_5]. $C_{28}H_{26}N_4$ (418.5): calcd C 80.36, H 6.26, N 13.39; found C 79.98, H 6.10, N 13.21.

1,1-Dimethyl-2,10b-diphenyl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3d). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.38 (s, 3H, *syn*-H_3CCCH_3), 0.97–1.03 (m, 1H, CH_2), 1.23–1.37 (m, 3H, CH_2), 1.39 (s, 3H, *anti*-H_3CCCH_3), 1.46–1.56 (m, 2H, CH_2), 1.76–1.90 (m, 2H, CH_2), 1.80 (d, 1H,^3J=8.3 Hz, cyclopropyl-H), 1.84 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.38–2.52 (m, 4H, CH_2), 7.23–7.44 (m, 6H, aryl-H), 7.61–7.64 (m, 2H, aryl-H), 7.81–7.84 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=17.4 (*syn*-H_3CCCH_3), 20.6 (cyclopropyl-CH), 23.6 (C-1), 24.3 (CH_2), 25.4 (cyclopropyl-CH), 25.5 (CH_2), 25.5 (CH_2), 25.9 (CH_2), 27.2 (*anti*-H_3CCCH_3), 27.8 (CH_2), 29.5 (CH_2), 68.7, 70.3, 112.2, 114.0, 126.0, 127.5, 128.2, 128.4, 128.5, 129.6, 136.8, 144.5, 148.9, 152.4 ppm. IR (KBr): $\tilde{\nu}$=3070–2870, 1600, 1445, 1270, 1070, 910, 775, 710 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=222 (21 100), 247 (11 100), 286 (7430) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=447.1 (34), 446.2 (100) [M^+], 419.1 (47), 378.1 (71), 369.1 (37), 171.1 (57), 170.1 (70), 67.1 (33). $C_{30}H_{30}N_4$ (446.6): calcd C 80.68, H 6.77, N 12.55; found C 80.46, H 6.79, N 12.63.

2,10b-Bis-(4-chloro-phenyl)-1,1-dimethyl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3e). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.35 (s, 3H, *syn*-H_3CCCH_3), 0.96–1.11 (m, 1H, CH_2), 1.20–1.45 (m, 3H, CH_2), 1.38 (s, 3H, *anti*-H_3CCCH_3), 1.45–1.63 (m, 2H, CH_2), 1.72–1.93 (m, 2H, CH_2), 1.77 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.82 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.36–2.54 (m, 4H, CH_2), 7.30–7.43 (m, 4H, aryl-H), 7.52–7.61 (m, 2H, aryl-H), 7.71–7.80 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=17.42 (*syn*-H_3CCCH_3), 20.30 (cyclopropyl-CH), 23.60 (C-1), 24.32 (CH_2), 25.20 (cyclopropyl-CH), 25.44 (2C, CH_2), 25.92 (CH_2), 27.12 (*anti*-H_3CCCH_3), 27.68 (CH_2), 29.59 (CH_2), 68.56, 69.88, 111.91, 113.77, 126.46, 127.18, 127.30, 128.47, 128.80, 133.47, 135.03, 135.81, 143.07, 148.27, 151.39 ppm. IR (KBr): $\tilde{\nu}$=2980, 2930, 2860, 1485, 1460, 1450, 1410, 1110, 1085, 1060, 1005, 835, 810 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=231 (25 000), 294 (9600) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=516 (65), 515 (35), 514 (95) [M^+], 499 (11) [M^+-CH_3], 487 (27) [M^+-HCN], 448 (39), 446 (58), 403 (45) [$M^+-C_6H_4Cl$], 206 (32), 205 (54) [Ylid$^+-ClC_6H_4CN-C(CN)_2$], 204 (88), 203 (100), 190 (33), 189 (30), 137 (39), 136 (37), 67 (66), 55 (30), 40 (52), 35 (68). $C_{30}H_{28}Cl_2N_4$ (515.5): calcd C 69.88, H 5.48, N 10.87; found C 69.80, H 5.49, N 10.88.

2,10b-Bis-(4-trifluoromethyl-phenyl)-1,1-dimethyl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3f). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.32 (s, 3H, *syn*-H_3CCCH_3), 1.07–1.24 (m, 1H, CH_2), 1.25–1.41 (m, 3H, CH_2), 1.41 (s, 3H, *anti*-H_3CCCH_3), 1.45–1.75 (m, 2H, CH_2), 1.82–1.93 (m, 2H, CH_2), 1.84 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.91 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.37–2.60 (m, 4H, CH_2), 7.62–7.69 (m, 6H, aryl-H), 7.76–7.95 (m, 2H, aryl-H) ppm. IR (KBr): $\tilde{\nu}$=3010–2870, 2940, 1610, 1415, 1325, 1170, 1120, 1070, 1015, 855 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=226 (22 900), 294 (7720) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=582.9 (24) [M^+], 581.9 (65), 513.8 (35), 238.9 (67), 237.8 (100), 176.9 (32), 67.2 (69), 41.2 (40). $C_{32}H_{28}N_4F_6$ (582.6): calcd C 65.97, H 4.84, N 9.62; found C 65.26, H 4.72, N 9.43.

1,1-Dimethyl-2,10b-bis-(1-methyl-1*H*-pyrrol-2-yl)-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3g). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.34 (s, 3H, *syn*-H_3CCCH_3), 1.11 (s, 3H, *anti*-H_3CCCH_3), 1.44–1.64 (m, 6H, CH_2), 1.75–1.90 (m, 2H, CH_2), 1.98 (d, 1H, ^3J=9.1 Hz, cyclopropyl-H), 2.08 (d, 1H, ^3J=9.1 Hz, cyclopropyl-H), 2.34–2.64 (m, 4H, CH_2), 3.78 (s, 3H, pyrryl-CH_3), 3.91 (s, 3H, pyrryl-CH_3), 5.81 (dd, 1H, pyrryl-H), 6.01 (dd, 1H, pyrryl-H), 6.09 (dd, 1H, pyrryl-H), 6.39 (dd, 1H, pyrryl-H), 6.66–6.70 (m, 2H, pyrryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=15.7 (*syn*-H_3CCCH_3), 22.2 (CH_2), 25.3 (cyclopropyl-CH), 26.5 (CH_2), 26.6 (CH_2), 26.9 (CH_2), 27.0 (CH_2), 28.8 (*anti*-H_3CCCH_3), 31.4 (C-1), 32.3 (CH_2), 35.1 (cyclopropyl-CH), 37.4 (pyrryl-CH_3), 38.2 (pyrryl-CH_3), 58.8, 70.0, 107.2, 107.5, 111.2, 112.2, 114.7, 118.3, 121.4, 126.38, 126.43, 127.5, 129.6, 138.7, 144.1 ppm. IR (KBr): $\tilde{\nu}$=3120, 2940, 2870, 2250, 1610, 1530, 1465, 1440, 1370, 1355, 1330, 1295, 1240, 1100, 1055, 730, 720 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=263 (8610), 308 (12 600) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=452.5 (79) [M^+], 437.5 (11) [M^+-CH_3], 425.5 (45) [M^+-HCN], 384.4 (100), 330.3 (15), 266.2 (27), 227.1 (20), 173.0 (16) 159.9 (21), 122.0 (67), 105.9 (22), 93.9 (10), 81.0 (14). $C_{28}H_{22}N_6$ (452.5): calcd C 74.32, H 7.13, N 18.57; found C 73.90, H 6.94, N 17.84.

2,10b-Di-furan-2-yl-1,1-dimethyl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3h). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.75 (s, 3H, *syn*-H_3CCCH_3), 1.31 (s, 3H, *anti*-H_3CCCH_3), 1.26–1.59 (m, 6H, CH_2), 1.69 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.77–1.86 (m, 2H, CH_2), 1.89 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.43–2.51 (m, 4H, CH_2), 6.33 (dd, 1H, furyl-H), 6.36 (dd, 1H, furyl-H), 6.46 (dd, 1H, furyl-H), 6.78 (dd, 1H, furyl-H), 7.39 (dd, 1H, furyl-H), 7.49 (dd, 1H, furyl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=15.9 (*syn*-H_3CCCH_3), 18.7 (cyclopropyl-CH), 23.7 (cyclopropyl-CH), 24.5 (CH_2), 24.7 (C-1), 25.2 (CH_2), 25.6 (CH_2), 25.9 (CH_2), 27.4 (*anti*-H_3CCCH_3), 27.8 (CH_2), 28.5 (CH_2), 67.3, 69.3, 108.1, 109.3, 110.6, 111.58, 111.60, 113.5, 128.6, 142.0, 142.5, 143.6, 147.0, 151.6, 154.5 ppm. IR (KBr): $\tilde{\nu}$=3160, 3130, 3080, 2940, 2880, 1610, 1495, 1465, 1160, 1070, 1020, 900, 820, 750 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=292 (16 000) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=426.3 (100) [M^+], 411.2 (10) [M^+-CH_3], 358.2 (14), 317.1 (27), 240.0 (19), 160.9 (39), 131.9 (10), 93.9 (15). $C_{26}H_{26}N_4O_2$ (426.4): calcd C 73.24, H 6.15, N 13.14; found C 73.37, H 6.31, N 13.11.

1,1-Dimethyl-2,10b-di-thiophen-2-yl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3i). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.81 (s, 3H, *syn*-H_3CCCH_3), 1.32 (s, 3H, *anti*-H_3CCCH_3), 1.25–1.64 (m, 6H, CH_2), 1.79 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.91 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.77–1.93 (m, 2H, CH_2), 2.43–2.54 (m, 4H, CH_2), 6.92–6.96 (m, 1H, thienyl-H), 7.03–7.06 (m, 2H, thienyl-H), 7.25–7.28 (m, 1H, thienyl-H), 7.32–7.37 (m, 2H, thienyl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=17.1 (*syn*-H_3CCCH_3), 20.8 (cyclopropyl-CH), 24.5 (CH_2), 25.0 (C-1), 25.6 (CH_2), 25.7 (CH_2), 26.0 (CH_2), 27.5 (cyclopropyl-CH), 27.5 (*anti*-H_3CCCH_3), 27.7 (CH_2), 29.5 (CH_2), 68.7, 69.7, 111.8, 113.1, 124.8, 125.5, 126.3, 126.5, 127.1, 127.9, 128.1, 142.5, 147.9, 148.1, 148.4 ppm. IR (KBr): $\tilde{\nu}$=3100–2870, 2930, 1440, 1240, 1065, 845, 720, 710, 700 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=250 (13 800), 306 (9990) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=458.2 (90) [M^+], 390.1 (100), 333.2 (53), 320.1 (45), 262.9 (36), 256.0 (40), 177.3 (51), 176.1 (71), 135.1 (35), 129.1 (44), 110.2 (52), 97.1 (48), 77.0 (31), 67.1 (41), 45.1 (32), 41.1 (57), 39.1 (40). $C_{26}H_{26}N_4S_2$ (458.7): calcd C 68.09, H 5.71, N 12.22; found C 67.88, H 5.67, N 12.21.

2,10b-Bis-methylsulfanyl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]-cyclopropa[*e*]indene-4,4-dicarbonitrile (3j). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.23 (ddd, 1H, *syn*-cyclopropyl-H), 1.45–2.22 (m, 12H, cyclopropyl-H, CH_2), 1.94 (s, 3H, SCH_3), 2.34–2.45 (m, 3H, CH_2), 2.43 (s, 3H, SCH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=12.6 (cyclopropyl-CH),

12.9 (SCH_3), 13.3 (SCH_3), 14.7 (C-1), 16.8 (cyclopropyl-CH), 21.0 (CH_2), 22.3 (CH_2), 23.1 (CH_2), 27.7 (CH_2), 28.4 (CH_2), 33.4 (CH_2), 67.8, 73.0, 110.4, 112.49, 112.54, 136.1, 153.3 ppm. IR (KBr): $\tilde{\nu}$=3100, 3060, 3020, 2990, 2980, 2920, 2850, 1660, 1580, 1440, 1370, 1260, 1175, 1120, 1060, 1040, 1020, 960, cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=273 (10 700) nm ($l\,mol^{-1}\,cm^{-1}$). EI MS (70 eV): *m/z* (%)=358.2 (3) [M^+], 311.2 (100) [M^+-SCH_3], 285.1 (15) [M^+-CH_3SCN]. $C_{18}H_{22}N_4S_2$ (358.4): calcd C 60.32, H 6.19, N 15.63; found C 59.90, H 6.32, N 15.43.

2-Methylsulfanyl-1,1a,5,6,7,8,9,10,10c-nonahydro-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4-carbonitrile (3j′). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.48 (ddd, 1H, *syn*-cyclopropyl-H), 1.41–1.69 (m, 9H, *anti*-cyclopropyl-H,CH_2), 2.02 (ddd, 1H, cyclopropyl-H), 2.48–2.80 (m, 5H, cyclopropyl-H, CH_2), 2.52 (s, 3H, SCH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.5 (C-1), 13.0 (cyclopropyl-CH), 13.1 (SCH_3), 15.6 (cyclopropyl-CH), 22.1 (CH_2), 23.6 (CH_2), 25.5 (CH_2), 25.6 (CH_2), 30.7 (CH_2), 30.8 (CH_2), 99.2, 113.3, 117.9, 121.5, 133.4, 157.2 ppm. IR (KBr): $\tilde{\nu}$=3100, 3060, 3020, 2980, 2900, 2830, 2180, 1545, 1490, 1420, 1395, 1350, 1330, 1300, 1245, 1115, 1085, 1065, 1030, 950, 840, 790, 775, 630 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=249 (9700), 302 (19 000) nm ($l\,mol^{-1}\,cm^{-1}$). EI MS (70 eV): *m/z* (%)=285.1 (100) [M^+], 257.0 (12), 242.0 (14), 238.1 (26), 154.9 (11). $C_{16}H_{19}N_3S$ (285.3): calcd C 67.36, H 6.71, N 14.73; found C 67.12, H 6.91, N 14.54.

1,1-Dimethyl-2,10b-bis-methylsulfanyl-1,1a,5,6,7,8,9,10,10b,10c-decahydro-*cis*-1a-*transoid*-10b,10c-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (3k). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.04 (s, 3H, *syn*-H_3CCCH_3), 1.27 (s, 3H, *anti*-H_3CCCH_3), 1.52–1.66 (m, 7H, CH_2), 1.72 (d, 1H, ^3J=8.0 Hz, cyclopropyl-H), 1.89 (d, 1H, ^3J=8.0 Hz, cyclopropyl-H), 2.00 (s, 3H, SCH_3), 2.02–2.15 (m, 2H, CH_2), 2.27–2.43 (m, 3H, CH_2), 2.44 (s, 3H, SCH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=13.2 (SCH_3), 13.4 (SCH_3), 16.4 (*syn*-H_3CCCH_3), 21.1 (CH_2), 22.6 (CH_2), 23.2 (CH_2), 24.3 (cyclopropyl-CH), 27.1 (*anti*-H_3CCCH_3), 27.8 (CH_2), 28.0 (CH_2), 28.7 (cyclopropyl-CH), 29.0 (C-1), 33.5 (CH_2), 68.0, 72.1, 110.3, 112.5, 112.7, 134.3, 151.0 ppm. IR (KBr): $\tilde{\nu}$=2960, 2930, 2860, 1660, 1570, 1440, 1375, 1260, 1175, 1120, 1060, 1040, 1020, 960, 905, 820, 800 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=282 (10 300) nm ($l\,mol^{-1}\,cm^{-1}$). EI MS (70 eV): *m/z* (%)=386.3 (4) [M^+],339.3 (100) [M^+-SCH_3], 313.8 (28) [M^+-CH_3SCN], 297.2 (12), 266.2 (11). $C_{20}H_{26}N_4S_2$ (386.6): calcd C 62.14, H 6.78, N 14.49; found C 62.15, H 6.81, N 14.42.

1,1-Dimethyl-2-methylsulfanyl-1,1a,5,6,7,8,9,10,10c-nonahydro-3,3a-diaza-cycloocta[*b*]cyclopropa[*e*]indene-4-carbonitrile (3k′). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.68 (s, 3H, *syn*-H_3CCCH_3), 1.32 (s, 3H, *anti*-H_3CCCH_3), 1.40–1.66 (m, 7H, CH_2), 1.80 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.31 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.52 (s, 3H, SCH_3), 2.55–2.58 (m, 2H, CH_2), 2.65–2.70 (m, 3H, CH_2) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=13.0 (SCH_3), 15.1 (*syn*-H_3CCCH_3), 20.4 (C-1), 22.0 (CH_2), 23.7 (CH_2), 25.0 (cyclopropyl-CH), 25.5 (CH_2), 25.6 (CH_2), 25.8 (*anti*-H_3CCCH_3), 27.8 (cyclopropyl-CH), 30.8 (CH_2), 30.9 (CH_2), 98.6, 113.4, 119.0, 119.8, 133.1, 155.7 ppm. IR (KBr): $\tilde{\nu}$=2980, 2940, 2920, 2860, 2215, 1565, 1510, 1440, 1420, 1380, 1350, 1315, 1110, 860 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=251 (10 300), 303 (19 400) nm ($l\,mol^{-1}\,cm^{-1}$). EI MS (70 eV): *m/z* (%)=313.3 (100) [M^+], 298.2 (30) [M^+-CH_3], 285.1 (22), 270.2 (18), 266.2 (14) [M^+-SCH_3], 169.0 (12). $C_{18}H_{23}N_3S$ (313.3): calcd C 68.98, H 7.40, N 13.41; found C 68.89, H 7.41, N 13.32.

2,6a-Bis-(4-methoxy-phenyl)-5-*N*,*N*-dimethylamino-1,1,6-trimethyl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (5a). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.32 (s, 3H, *syn*-H_3CCCH_3), 1.36 (s, 3H, *anti*-H_3CCCH_3), 1.76 (s, 2H, cyclopropyl-H), 1.84 (s, 3H, CH_3), 2.82 (s, 6H, $N(CH_3)_2$), 3.79 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.83–6.96 (m, 4H, aryl-H), 7.43–7.49 (m, 2H, aryl-H), 7.75–7.81 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=11.7 (CH_3), 17.1 (*syn*-H_3CCCH_3), 20.5 (cyclopropyl-CH), 23.6 (C-1), 25.2 (cyclopropyl-CH), 27.3 (*anti*-H_3CCCH_3), 42.7 ($N(CH_3)_2$), 55.2 (OCH_3), 55.3 (OCH_3), 63.9, 67.4, 112.8, 113.5, 113.9, 114.5, 127.1, 127.5, 129.8, 134.7, 134.9, 137.1, 153.2, 158.7, 161.0 ppm. IR (KBr): $\tilde{\nu}$=3080–2840, 1670, 1605, 1510, 1500, 1245, 1170, 1030, 830 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=231 (18 100), 260 (18 400) nm ($l\,mol^{-1}\,cm^{-1}$). EI MS (70 eV): *m/z* (%)=481.0 (18) [M^+], 268.0 (58), 253.0 (29), 187.0 (28), 133.1 (100), 103.1 (63), 90.1 (74), 64.2 (32), 63.2 (40). $C_{29}H_{31}N_5O_2$ (481.6): calcd C 72.33, H 6.49, N 14.54; found C 71.91, H 6.55, 14.40.

5-*N*,*N*-Dimethylamino-1,1,6-trimethyl-2,6a-di-*p*-tolyl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (5b). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.29 (s, 3H, *syn*-H_3CCCH_3), 1.35 (s, 3H, *anti*-H_3CCCH_3), 1.77 (s, 2H, cyclopropyl-H), 1.85 (s, 3H, CH_3), 2.32 (s, 3H, tolyl-CH_3), 2.37 (s, 3H, tolyl-CH_3), 2.82 (s, 6H, $N(CH_3)_2$), 7.09–7.26 (m, 4H, aryl-H), 7.38–7.49 (m, 2H, aryl-H), 7.66–7.80 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.82 (CH_3), 17.14 (*syn*-H_3CCCH_3), 20.49 (cyclopropyl-CH), 20.92 (tolyl-CH_3), 21.32 (tolyl-CH_3), 23.63 (C-1), 25.16 (cyclopropyl-CH), 27.23 (*anti*-H_3CCCH_3), 42.73 ($N(CH_3)_2$), 63.90, 67.65, 112.70, 114.41, 125.78, 125.92, 128.79, 129.18, 134.31, 134.79, 134.95, 136.77, 139.66, 142.05, 152.84 ppm. IR (KBr): $\tilde{\nu}$=3020, 2980, 2950, 2920, 2870, 2800, 1505, 1445, 1125, 1115, 1100, 1075, 1050, 1010, 810 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=225 (21 300), 247 (13 900), 288 (11 800) nm ($l\,mol^{-1}\,cm^{-1}$). EI MS (70 eV): *m/z* (%)=449 (30) [M^+], 434 (17) [M^+-CH_3], 366 (27) [Ylid$^+$], 359 (16), 358 (60) [$M^+-C_7H_7$], 332 (38) [$M^+-C_7H_7CN$], 252 (100), 249 (80), 238 (32), 237 (43), 185 (26) [Ylid$^+$-C_7H_7CN–$C(CN)_2$], 184 (33), 171 (30), 143 (34), 128 (35), 119 (31), 117 (35), 116 (33), 115 (46), 105 (33), 91 (46), 83 (30) [$C_3H_3NMe_2^+$], 42 (36). $C_{29}H_{31}N_5$ (449.6): calcd C 77.47, H 6.95, N 15.58; found C 77.31, H 6.89, N 15.53.

5-*N*,*N*-Dimethylamino-6-methyl-2,6a-diphenyl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (5c). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.38 (ddd, 1H, ^2J=5.1 Hz, ^3J=5.5 Hz, ^3J=5.4 Hz, *syn*-cyclopropyl-H), 1.36 (ddd, 1H, ^2J=5.1 Hz, ^3J=9.7 Hz, ^3J=6.4 Hz, *anti*-cyclopropyl-H), 1.91 (ddd, 1H, ^3J=5.4 Hz, ^3J=7.8 Hz, ^3J=6.4 Hz, cyclopropyl-H), 1.96 (s,

3H, CH_3), 2.66 (ddd, 1H, ^3J=5.5 Hz, ^3J=7.8 Hz, ^3J=9.7 Hz, cyclopropyl-H), 2.87 (s, 6H, $N(CH_3)_2$), 7.21–7.49 (m, 8H, aryl-H), 7.91–7.97 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=10.3 (cyclopropyl-CH), 12.1 (CH_3), 12.5 (C-1), 15.3 (cyclopropyl-CH), 42.8 ($N(CH_3)_2$), 61.9, 68.5, 112.9, 113.6, 125.8, 127.3, 127.6, 128.3, 128.4, 129.8, 132.3, 136.4, 136.8, 142.2, 155.5 ppm. IR (KBr): $\tilde{\nu}$=3110–3010, 2970–2830, 1660, 1485, 1445, 1390, 1360, 1350, 1140, 1080, 1050, 1030, 915, 780, 765, 715, 700 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=247 (12 600), 274 (8770) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=393.3 (36) [M^+], 316.2 (100) [$M^+-C_6H_5$], 232.0 (13), 223.0 (13), 185.0 (13). $C_{25}H_{23}N_5$ (393.3): calcd C 76.35, H 5.89, N 17.81; found C 76.27, H 5.95, N 17.87.

5-*N*,*N*-Dimethylamino-1,1,6-trimethyl-2,6a-diphenyl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (5d). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.27 (s, 3H, *syn*-H_3CCCH_3), 1.37 (s, 3H, *anti*-H_3CCCH_3), 1.79 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.81 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.88 (s, 3H, CH_3), 2.83 (s, 6H, $N(CH_3)_2$), 7.22–7.26 (m, 1H, aryl-H), 7.32–7.43 (m, 5H, aryl-H), 7.55–7.58 (m, 2H, aryl-H), 7.82–7.85 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=11.8 (CH_3), 17.1 (*syn*-H_3CCCH_3), 20.5 (cyclopropyl-CH), 23.7 (C-1), 24.9 (cyclopropyl-CH), 27.1 (*anti*-H_3CCCH_3), 42.7 ($N(CH_3)_2$), 63.8, 67.7, 112.5, 114.2, 125.7, 125.9, 127.1, 128.1, 128.5, 129.6, 134.3, 134.9, 136.8, 144.9, 152.7 ppm. IR (KBr): $\tilde{\nu}$=3080–2800, 1670, 1445, 775, 770, 710, 700 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=220 (19 100), 245 (13 000), 276 (8600) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=421 (27) [M^+], 344.2 (100), 318.4 (42), 241.1 (33), 238.2 (83), 224.1 (36), 223.1 (57), 129.3 (41), 128.3 (37), 115.2 (46), 102.2 (32), 91.3 (35), 77.2 (56), 42.1 (31). $C_{27}H_{27}N_5$ (421.5): calcd C 76.93, H 6.46, N 16.61; found C 77.09, H 6.47, N 16.62.

2,6a-Bis-(4-chloro-phenyl)-5-*N*,*N*-dimethylamino-1,1,6-trimethyl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (5e). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.27 (s, 3H, *syn*-H_3CCCH_3), 1.36 (s, 3H, *anti*-H_3CCCH_3), 1.76 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.81 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.86 (s, 3H, CH_3), 2.83 (s, 6H, $N(CH_3)_2$), 7.28–7.44 (m, 4H, aryl-H), 7.44–7.55 (m, 2H, aryl-H), 7.69–7.83 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=11.74 (CH_3), 17.21 (*syn*-H_3CCCH_3), 20.31 (cyclopropyl-CH), 23.70 (C-1), 24.83 (cyclopropyl-CH), 27.09 (*anti*-H_3CCCH_3), 42.65 ($N(CH_3)_2$), 63.68, 67.46, 112.36, 114.09, 127.08, 127.21, 128.42, 128.80, 132.90, 133.20, 135.19, 135.33, 135.81, 143.52, 151.76 ppm. IR (KBr): $\tilde{\nu}$=2980, 2950, 2910, 2860, 2800, 1480, 1080, 1000, 810 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=228 (22 900), 250 (15 800), 289 (11 500) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=489 (8) [M^+], 474 (3) [M^+-CH_3], 463 (2) [M^+-CN], 406 (5) [Ylid$^+$], 378 (18) [$M^+-C_6H_4Cl$], 352 (7) [$M^+-C_6H_4Cl-CN$], 272 (16), 269 (13), 257 (17), 136 (10), 135 (11), 83 (100), 82 (20) [$Me_2N-C_3H_3$], 35 (14). $C_{27}H_{25}Cl_2N_5$ (490.5): calcd C 66.12, H 5.14, N 14.28; found C 66.09, H 5.22, N 14.26.

2,6a-Bis-(4-trifluoromethyl-phenyl)-5-*N*,*N*-dimethyl-amino-1,1,6-trimethyl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (5f). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.22 (s, 3H, *syn*-H_3CCCH_3), 1.39 (s, 3H, *anti*-H_3CCCH_3), 1.83 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.88 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.89 (s, 3H, CH_3), 2.84 (s, 6H, $N(CH_3)_2$), 7.61–7.71 (m, 6H, aryl-H), 7.93–7.96 (m, 2H, aryl-H), ppm. IR (KBr): $\tilde{\nu}$=3030–2800, 1660, 1410, 1320, 1160, 1120, 1060, 1005, 845 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=222 (24 500), 240 (18 200), 286 (10 900) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=557.9 (5) [M^+], 556.9 (16), 411.9 (100) [$M^+-C_6H_4CF_3$], 305.8 (60), 290.8 (26), 241 (28). $C_{29}H_{25}N_5F_6$ (557.5): calcd C 62.47, H 4.52, N 12.56; found C 62.55, H 4.61, N 12.58.

5-*N*,*N*-Dimethylamino-1,1,6-trimethyl-2,6a-bis-(1-methyl-1*H*-pyrrol-2-yl)-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (5g). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.54 (s, 3H, *syn*-H_3CCCH_3), 1.35 (s, 3H, *anti*-H_3CCCH_3), 1.57 (d, 1H, ^3J=8.4 Hz, H-1a), 1.75 (d, 1H, ^3J=8.4 Hz, H-6b), 1.75 (s, 3H, CH_3), 2.88 (s, 6H, $N(CH_3)_2$), 3.78 (s, 3H, pyrryl-CH_3), 4.00 (s, 3H, pyrryl-CH_3), 5.98 (dd, 1H, aryl-H), 6.09 (dd, 1H, aryl-H), 6.12 (dd, 1H, aryl-H), 6.46–6.49 (m, 2H, aryl-H), 6.71 (dd, 1H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.3 (CH_3), 16.8 (*syn*-H_3CCCH_3), 21.0 (C-6b), 22.3 (C-1), 25.3 (C-1a), 27.4 (*anti*-H_3CCCH_3), 36.5 (pyrryl-CH_3), 38.2 (pyrryl-CH_3), 42.8 ($N(CH_3)_2$), 65.3, 62.5, 106.6, 107.6, 110.6, 113.6, 113.9, 115.0, 124.2, 128.3, 129.1, 132.5, 132.8, 134.0, 157.5 ppm. IR (KBr): $\tilde{\nu}$=3130, 3000–2820, 1675, 1575, 1540, 1480, 1465, 1440, 1380, 1330, 1295, 1120, 1100, 1090, 1060, 1045, 745, 730 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=276 (13 500), 306 (14 700) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=427.5 (100) [M^+], 412.4 (21) [M^+-CH_3], 359.4 (11), 266.2 (12), 226.1 (15), 160.0 (16), 122.0 (14), 104.9 (12), 94.0 (11). $C_{25}H_{29}N_7$ (427.4): calcd C 70.26, H 6.84, N 22.94; found C 70.35, H 6.83, N 22.88.

2,6a-Di-furan-2-yl-5-*N*,*N*-dimethylamino-1,1,6-trimethyl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (5h). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.82 (s, 3H, *syn*-H_3CCCH_3), 1.30 (s, 3H, *anti*-H_3CCCH_3), 1.65 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.89 (s, 3H, CH_3), 1.92 (d, 1H, ^3J=8.4 Hz, cyclopropyl-H), 2.89 (s, 6H, $N(CH_3)_2$), 6.33–6.37 (m, 2H, aryl-H), 6.46 (dd, 1H, aryl-H), 6.79 (dd, 1H, aryl-H), 7.41 (dd, 1H, aryl-H), 7.49 (dd, 1H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.8 (CH_3), 16.2 (*syn*-H_3CCCH_3), 18.8 (cyclopropyl-CH), 24.3 (cyclopropyl-CH), 25.4 (C-1), 27.5 (*anti*-H_3CCCH_3), 42.6 ($N(CH_3)_2$), 64.8, 65.0, 108.3, 109.2, 110.4, 111.6, 111.8, 113.8, 130.1, 138.1, 142.2, 142.6, 143.5, 151.7, 154.6 ppm. IR (KBr): $\tilde{\nu}$=3160, 3140, 3085, 2990–2830, 1605, 1490, 1450, 1160, 1090, 1020, 1000, 770, 745 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=292 (14 700) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=401.3 (100) [M^+], 386.2 (24) [M^+-CH_3], 358.2 (10), 318.1 (18), 308.1 (20), 252.0 (12), 240.0 (30), 228.0 (72), 214.0 (41), 187.9 (16), 160.9 (37), 146.9 (19), 131.9 (13). $C_{23}H_{23}N_5O_2$ (401.5): calcd C 68.84, H 5.78, N 17.45; found C 68.95, H 5.97, N 17.39.

5-*N*,*N*-Dimethylamino-1,1,6-trimethyl-2,6a-di-thiophen-2-yl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-

diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (5i). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.78 (s, 3H, *syn*-H_3CCCH_3), 1.31 (s, 3H, *anti*-H_3CCCH_3), 1.76 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.93 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 1.95 (s, 3H, CH_3), 2.87 (s, 6H, $N(CH_3)_2$), 6.93–6.96 (m, 1H, aryl-H), 7.01–7.05 (m, 1H, aryl-H), 7.21–7.27 (m, 1H, aryl-H), 7.29–7.36 (m, 3H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.9 (CH_3), 17.0 (*syn*-H_3CCCH_3), 20.6 (cyclopropyl-CH), 25.3 (C-1), 27.5 (2C, cyclopropyl-CH, *anti*-H_3CCCH_3), 42.6 ($N(CH_3)_2$), 64.1, 67.0, 112.1, 113.4, 124.7, 125.3, 126.2, 126.4, 127.1, 127.9, 131.8, 136.9, 142.6, 148.1, 148.7 ppm. IR (KBr): $\tilde{\nu}$=3120–2810, 1660, 1440, 1235, 1050, 850, 720 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=248 (15 300), 308 (10 300) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=433.9 (8) [M^+], 432.9 (29), 243.9 (100), 240.9 (29), 229.9 (29), 163.0 (21), 147.0 (22), 129.0 (22), 42.3 (24). $C_{23}H_{23}N_5S_2$ (433.6): calcd C 63.71, H 5.35, N 16.15; found C 63.72, H 5.50, N 16.10.

5-*N*,*N*-Dimethylamino-1,1,6-trimethyl-2-methylsulfanyl-1a,6b-dihydro-1*H*-3,3a-diaza-cyclopropa[*e*]indene-4-carbonitrile (5k′). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.71 (s, 3H, *syn*-H_3CCCH_3), 1.33 (s, 3H, *anti*-H_3CCCH_3), 1.80 (d, 1H, ^3J=8.3 Hz, H-1a), 2.02 (s, 3H, CH_3), 2.27 (d, 1H, ^3J=8.3 Hz, H-6b), 2.51 (s, 3H, SCH_3), 2.90 (s, 6H, $N(CH_3)_2$) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=9.3 (CH_3), 13.1 (SCH_3), 15.2 (*syn*-H_3CCCH_3), 20.3 (C-1), 25.5 (C-6b), 26.0 (*anti*-H_3CCCH_3), 27.9 (C-1a), 43.8 ($N(CH_3)_2$), 91.0, 107.4, 115.2, 121.4, 145.8, 153.9 ppm. IR (KBr): $\tilde{\nu}$=3020, 2970–2810, 2220, 1565, 1525, 1455, 1445, 1430, 1415, 1345, 1315, 1100, 1060, 1040, 980 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=318 (14 000) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=288.2 (100) [M^+], 273.2 (9) [M^+-CH_3], 241.1 (22) [M^+-SCH_3], 227.1 (16), 200.0 (13). $C_{15}H_{20}N_4S$ (288.4): calcd C 62.47, H 6.99, N 19.43; found C 62.30, H 6.78, N 19.45.

4,4-Dicyano-2,6a-bis-(4-methoxy-phenyl)-1,1-dimethyl-1a,4,6a,6b-tetrahydro-1*H*-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-5,6-dicarboxylic acid dimethyl ester (7a). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.40 (s, 3H, *syn*-H_3CCCH_3), 1.32 (s, 3H, *anti*-H_3CCCH_3), 1.91 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.33 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 3.80 (s, 3H, OCH_3), 3.84 (s, 6H, OCH_3), 3.89 (s, 3H, OCH_3), 6.86–6.97 (m, 4H, aryl-H), 7.42–7.48 (m, 2H, aryl-H), 7.74–7.81 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=16.8 (*syn*-H_3CCCH_3), 20.5 (cyclopropyl-CH), 24.0 (C-1), 25.2 (cyclopropyl-CH), 27.0 (*anti*-H_3CCCH_3), 53.3 (OCH_3), 53.3 (OCH_3), 55.3 (OCH_3), 55.4 (OCH_3), 65.1, 69.9, 110.2, 112.2, 114.0, 114.1, 122.9, 127.2, 127.6, 129.2, 133.1, 153.0, 154.1, 159.1, 159.7, 161.3, 163.1 ppm. IR (KBr): $\tilde{\nu}$=3080–2830, 1730, 1720, 1650, 1305, 1290, 1240, 1605, 1510, 1440, 1380, 1035, 840 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ) =225 (25 500), 282 (20 800) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=540.2 (74) [M^+], 201.1 (82), 200.1 (80), 187.1 (56), 186.1 (55), 159.0 (35), 149.1 (100), 134.0 (57), 132.9 (37), 131.9 (34), 120.9 (33), 77.0 (38), 59.0 (36). $C_{30}H_{28}N_4O_6$ (540.6): calcd C 66.66, H 5.22, N 10.36; found C 66.61, H 5.43, N 10.62.

4,4-Dicyano-1,1-dimethyl-2,6a-di-*p*-tolyl-1a,4,6a,6b-tetrahydro-1*H*-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-5,6-dicarboxylic acid dimethyl ester (7b). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.38 (s, 3H, *syn*-H_3CCCH_3), 1.31 (s, 3H, *anti*-H_3CCCH_3), 1.77 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.34–2.38 (m, 7H, tolyl-CH_3, cyclopropyl-H), 3.85 (s, 3H, CO_2CH_3), 3.89 (s, 3H, CO_2CH_3), 7.10–7.30 (m, 4H, aryl-H), 7.35–7.49 (m, 2H, aryl-H), 7.65–7.78 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=16.78 (*syn*-H_3CCCH_3), 20.48 (cyclopropyl-CH), 21.02 (tolyl-CH_3), 21.34 (tolyl-CH_3), 24.05 (C-1), 25.12 (cyclopropyl-CH), 27.00 (*anti*-H_3CCCH_3), 53.25 (CO_2CH_3), 53.30 (CO_2CH_3), 65.17, 70.15, 110.06, 112.12, 123.23, 125.76, 126.03, 129.30, 133.77, 138.19, 138.42, 140.22, 152.57, 153.97, 159.11, 163.11 ppm. IR (KBr): $\tilde{\nu}$=3040, 3020, 3000, 2950, 2910, 1730, 1720, 1660, 1425, 1300, 1260, 1110 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=240 (14 200), 279 (14 300) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=508 (52) [M^+], 493 (25) [M^+-CH_3], 417 (29) [$M^+-C_7H_7$], 185 (100) [Ylid$^+$-C_7H_7CN–$C(CN)_2$], 184 (95), 171 (36), 170 (31), 156 (31), 143 (61), 141 (33), 128 (44), 118 (44), 116 (30), 115 (52), 105 (30), 91 (60), 67 (32), 65 (36), 59 (37). $C_{30}H_{28}N_4O_4$ (508.6): calcd C 70.85, H 5.55, N 11.02; found C 70.85, H 5.46, N 11.04.

4,4-Dicyano-1,1-dimethyl-2,6a-diphenyl-1a,4,6a,6b-tetrahydro-1*H*-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-5,6-dicarboxylic acid dimethyl ester (7d). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.37 (s, 3H, *syn*-H_3CCCH_3), 1.33 (s, 3H, *anti*-H_3CCCH_3), 1.94 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.42 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 3.84 (s, 3H, CO_2CH_3), 3.89 (s, 3H, CO_2CH_3), 7.28–7.49 (m, 6H, aryl-H), 7.52–7.57 (m, 2H, aryl-H), 7.79–7.87 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=16.8 (*syn*-H_3CCCH_3), 20.6 (cyclopropyl-CH), 24.2 (C-1), 25.1 (cyclopropyl-CH), 27.0 (*anti*-H_3CCCH_3), 53.3 (CO_2CH_3), 53.4 (CO_2CH_3), 65.1, 70.3, 110.0, 112.1, 123.4, 125.8, 126.1, 128.6, 128.7, 130.1, 136.4, 141.1, 152.7, 153.7, 159.0, 163.0 ppm. IR (KBr): $\tilde{\nu}$=3080–2890, 1740, 1725, 1660, 1440, 1340–1250, 740, 700, 690 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=215 (26 100), 242 (14 600), 274 (10 600) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=481.2 (33), 480.1 (100) [M^+], 465.1 (52), 403.1 (47), 171.3 (97), 170.1 (71), 128.9 (43). $C_{28}H_{24}N_4O_4$ (480.5): calcd C 69.99, H 5.03, N 11.66; found C 70.05, H 5.07, N 11.67.

2,6a-Bis-(4-chloro-phenyl)-4,4-dicyano-1,1-dimethyl-1a,4,6a,6b-tetrahydro-1*H*-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-5,6-dicarboxylic acid dimethyl ester (7e). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.37 (s, 3H, *syn*-H_3CCCH_3), 1.32 (s, 3H, *anti*-H_3CCCH_3), 1.92 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.38 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 3.87 (s, 3H, CO_2CH_3), 3.91 (s, 3H, CO_2CH_3), 7.30–7.56 (m, 6H, aryl-H), 7.69–7.83 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=16.84 (*syn*-H_3CCCH_3), 20.29 (cyclopropyl-CH), 24.23 (C-1), 24.94 (cyclopropyl-CH), 26.90 (*anti*-H_3CCCH_3), 53.50 (2C, CO_2CH_3), 65.02, 69.79, 109.71, 111.83, 123.94, 127.20, 127.33, 128.93, 128.95, 134.64, 134.80, 136.36, 139.58, 151.53, 152.96, 158.80, 162.79 ppm. IR (KBr): $\tilde{\nu}$=3040, 2980, 2950, 2920, 2870, 1720, 1655, 1485, 1430, 1330, 1285, 1115, 1090, 1070, 1010, 1000 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=222 (24 800), 250 (15 500), 277 (13 300)

nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=550 (31), 548 (43) [M$^+$], 533 (28) [M$^+$−CH_3], 437 (32) [M$^+$−C_6H_4Cl], 207 (34), 206 (38), 205 (100) [Ylid$^+$−ClC_6H_4CN–$C(CN)_2$], 203 (73), 191 (34), 35 (38). $C_{28}H_{22}Cl_2N_4O_4$ (549.4): calcd C 61.21, H 4.04, N 10.20; found C 60.46, H 4.15, N 10.04.

4,4-Dicyano-2,6a-bis-(4-trifluoromethyl-phenyl)-1,1-dimethyl-1a,4,6a,6b-tetrahydro-1*H*-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-5,6-dicarboxylic acid dimethyl ester (7f). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.34 (s, 3H, *syn*-H_3CCCH_3), 1.34 (s, 3H, *anti*-H_3CCCH_3), 1.98 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 2.47 (d, 1H, ^3J=8.3 Hz, cyclopropyl-H), 3.89 (s, 3H, CO_2CH_3), 3.92 (s, 3H, CO_2CH_3), 7.64–7.72 (m, 6H, aryl-H), 7.92–7.95 (m, 2H, aryl-H) ppm. IR (KBr): $\tilde{\nu}$=2960–2880, 1735, 1725, 1660, 1435, 1320, 1280, 1175, 1125, 1065, 1010, 850 cm^{-1}. UV/Vis (dioxane): λ_{max} (ε)=217 (24 700), 242 (16 900), 276 (9350) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=615.9 (26) [M$^+$], 600.8 (50) [M$^+$−CH_3], 470.8 (48) [M$^+$−$C_6H_4CF_3$], 239.0 (100), 238.0 (62), 176.9 (65), 158.9 (44), 67.1 (65), 59.2 (74), 41.2 (34). $C_{30}H_{22}F_6N_4O_4$ (616.5): calcd C 58.45, H 3.60, N 9.09; found C 58.19, H 3.79, N 8.95.

4,4-Dicyano-2,6a-di-furan-2-yl-1,1-dimethyl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]-indene-5,6-dicarboxylic acid dimethyl ester (7h). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.91 (s, 3H, *syn*-H_3CCCH_3), 1.32 (s, 3H, *anti*-H_3CCCH_3), 1.92 (d, 1H, ^3J=8.2 Hz, cyclopropyl-H), 2.11 (d, 1H, ^3J=8.2 Hz, cyclopropyl-H), 3.88 (s, 3H, CO_2CH_3), 3.92 (s, 3H, CO_2CH_3), 6.40 (dd, 1H, aryl-H), 6.49 (dd, 1H, aryl-H), 6.55 (dd, 1H, aryl-H), 6.85 (dd, 1H, aryl-H), 7.48 (dd, 1H, aryl-H), 7.51 (dd, 1H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=16.4 (*syn*-H_3CCCH_3), 18.9 (cyclopropyl-CH), 24.1 (cyclopropyl-CH), 25.5 (C-1), 27.3 (*anti*-H_3CCCH_3), 53.40 (CO_2CH_3), 53.44 (CO_2CH_3), 66.1, 67.1, 109.3, 110.1, 110.6, 110.9, 111.4, 111.8, 127.1, 143.3, 143.6, 144.1, 150.3, 150.9, 151.5, 159.1, 162.3 ppm. IR (KBr): $\tilde{\nu}$=3170, 3130, 3000, 2970, 2940, 1730, 1660, 1440, 1340, 1295, 1130, 1080, 1010, 750 cm^{-1}. UV/Vis (dioxane): λ_{max} (ε)=288 (18 800) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=460.3 (52) [M$^+$], 445.3 (40) [M$^+$−CH_3], 401.2 (10), 351.1 (15), 160.9 (100), 46.9 (13), 131.9 (11), 108.9 (28), 93.9 (13), 55.1 (13). $C_{24}H_{20}N_4O_6$ (460.3): calcd C 62.63, H 4.38, N 12.17; found C 62.72, H 4.67, N 12.04.

4,4-Dicyano-1,1-dimethyl-2,6a-di-thiophen-2-yl-1,1a,6a,6b-tetrahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-5,6-dicarboxylic acid dimethyl ester (7i). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.89 (s, 3H, *syn*-H_3CCCH_3), 1.31 (s, 3H, *anti*-H_3CCCH_3), 2.10 (d, 1H, ^3J=8.2 Hz, cyclopropyl-H), 2.17 (d, 1H, ^3J=8.2 Hz, cyclopropyl-H), 3.90 (s, 3H, CO_2CH_3), 3.99 (s, 3H, CO_2CH_3), 6.96–7.00 (m, 1H, aryl-H), 7.04–7.08 (m, 1H, aryl-H), 7.21–7.23 (m, 1H, aryl-H), 7.37–7.41 (m, 3H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=17.0 (*syn*-H_3CCCH_3), 20.8 (cyclopropyl-CH), 25.6 (C-1), 27.3 (*anti*-H_3CCCH_3), 27.6 (cyclopropyl-CH), 53.4 (CO_2CH_3), 53.5 (CO_2CH_3), 65.4, 69.3, 109.5, 111.1, 125.9, 126.6, 126.8, 127.1, 127.3, 127.3, 128.7, 141.7, 144.3, 148.7, 152.8, 159.2, 162.5 ppm. IR (KBr): $\tilde{\nu}$=3130, 2970, 1740, 1720, 1660, 1435, 1300, 985, 850, 735, 715 cm^{-1}. UV/Vis (dioxane): λ_{max} (ε)=230 (13 800), 250 (13 300), 300 (13 000) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=492.1 (74) [M$^+$], 477.1 (32), 367.0 (33), 203.1 (36), 202.1 (35), 177.1 (100), 176.0 (89), 163.1 (38), 162.1 (36), 147.0 (33), 135.2 (56), 129.2 (84), 125.0 (66), 11.2 (30), 110.1 (54), 109.1 (33), 108.0 (36), 97.1 (51), 91.1 (34), 79.1 (36), 77.0 (35), 67.1 (35), 59.1 (65); 45.1 (46), 41.1 (37), 39.1 (42). $C_{24}H_{20}N_4O_4S_2$ (492.6): calcd C 58.52, H 4.09, N 11.37; found C 58.42, H 4.08, N 11.35.

5,5-Diethoxy-1,1-dimethyl-2,6a-di-*p*-tolyl-1,1a,5,6,6a,6b-hexahydro-*cis*-1a-*transoid*-6a,6b,3,3a-diaza-cyclopropa[*e*]-indene-4,4-dicarbonitrile (9a). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.18 (s, 3H, *syn*-H_3CCCH_3), 0.71 (t, 3H, ^3J=7.0 Hz, *exo*-CH_3CH_2O), 1.19 (s, 3H, *anti*-H_3CCCH_3), 1.25 (t, 3H, ^3J=7.0 Hz, *endo*-CH_3CH_2O), 1.69 (d, 1H, ^3J=8.2 Hz, H-6b), 1.74 (d, 1H, ^3J=8.2 Hz, H-1a), 2.31 (s, 3H, tolyl-CH_3), 2.36 (s, 3H, tolyl-CH_3), 2.47 (dq, 1H, ^2J=8.4 Hz, ^3J=7.1 Hz, *exo*-CH_3CH_2O), 2.64 (d, 1H, ^2J=13.6 Hz, H^β-6), 2.99 (d, 1H, ^2J=13.6 Hz, H^α-6), 3.20 (dq, 1H, ^2J=8.4 Hz, ^3J=7.1 Hz, *exo*-CH_3CH_2O), 3.68–3.88 (m, 2H, *endo*-CH_3CH_2O), 7.07–7.10 (m, 2H, aryl-H), 7.18–7.22 (m, 2H, aryl-H), 7.33–7.37 (m, 2H, aryl-H), 7.69–7.72 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=13.79 (*exo*-CH_3CH_2O), 14.86 (*endo*-CH_3CH_2O), 16.40 (*syn*-H_3CCCH_3), 20.53 (C-1a), 20.90 (tolyl-CH_3), 21.32 (tolyl-CH_3), 23.66 (C-1), 27.13 (*anti*-H_3CCCH_3), 28.75 (C-6b), 48.91 (C-6), 58.67 (*exo*-CH_3CH_2O), 59.60 (*endo*-CH_3CH_2O), 59.78, 68.92, 107.23 (C-5), 112.02, 113.20, 125.84, 126.28, 128.12, 129.15, 134.58, 136.06, 139.39, 143.44, 150.72 ppm. IR (KBr): $\tilde{\nu}$=3060, 3030, 2990, 2940, 2900, 2880, 1510, 1450, 1440, 1305, 1210, 1180, 1120, 1080, 1060, 1045, 820 cm^{-1}. UV/Vis (dioxane): λ_{max} (ε)=222 (18 000), 294 (10 400) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=482 (7) [M$^+$], 437 (2) [M$^+$−OEt], 367 (46), 366 (100) [Ylid$^+$], 365 (13), 351 (11) [Ylid$^+$-CH_3], 250 (14), 249 (71) [Ylid$^+$-C_7H_7CN], 248 (15), 234 (16) [Ylid$^+$-C_7H_7CN–CH_3], 209 (11), 185 (30) [Ylid$^+$–C_7H_7CN–$C(CN)_2$], 184 (21), 181 (12), 171 (14), 170 (15), 157 (14), 155 (11), 143 (13), 142 (12), 118 (13), 117 (17), 116 (11) [$C_2H_2(OEt)_2^+$], 91 (11), 43 (11). $C_{30}H_{34}N_4O_2$ (482.6): calcd C 74.66, H 7.10, N 11.61; found C 74.75, H 7.13, N 11.62.

r-5-Ethoxy-5-*N*,*N*-dimethylamino-1,1-dimethyl-2,c-6a-di-*p*-tolyl-1,1a,5,6,6a,6b-hexahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (9b). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.10 (s, 3H, *syn*-H_3CCCH_3), 0.47 (t, 3H, ^3J=7.0 Hz, OCH_2CH_3), 0.91 (s, 3H, *anti*-H_3CCCH_3), 1.16 (d, 1H, ^3J=8.2 Hz, H-6b), 1.36 (d, 1H, ^3J=8.2 Hz, H-1a), 2.09 (dq, 1H, OCH_2CH_3), 2.10 (s, 3H, tolyl-CH_3), 2.11 (s, 3H, tolyl-CH_3), 2.46 (d, 1H, ^2J=13.2 Hz, H^β-6), 2.48 (s, 6H, $N(CH_3)_2$), 2.54 (d, 1H, ^2J=13.2 Hz, H^α-6), 2.82 (dq, ^2J=8.1 Hz, ^3J=7.0 Hz, OCH_2CH_3), 6.77–6.93 (2H, aryl-H), 6.93–7.06 (m, 2H, aryl-H), 7.14–7.82 (2H, aryl-H), 7.82–7.91 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=13.96 (OCH_2CH_3), 16.47 (*syn*-H_3CCCH_3), 20.52 (C-1a), 20.81 (tolyl-CH_3), 21.19 (tolyl-CH_3), 22.89 (C-1), 26.88 (*anti*-H_3CCCH_3), 28.72 (C-6b), 47.28 (C-6), 58.25 (OCH_2CH_3), 60.33, 70.88, 99.89 (C-5), 113.11, 114.40, 126.18, 128.06, 129.37, 135.20, 135.44, 139.13, 144.82, 149.77 ppm. IR (KBr): $\tilde{\nu}$=3040, 3010, 2970, 2910, 2880, 2800, 1500,

1440, 1120, 1090, 1065, 810 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=222 (18 900), 297 (10 800) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=482 (0.2) [M^+], 366 (5) [$Ylid^+$], 351 (1) [$Ylid^+-CH_3$], 249 (6) [$Ylid^+-C_7H_7CN$], 234 (2) [$Ylid^+-C_7H_7CN-CH_3$], 117 (23), 116 (17), 115 (48) [$C_2H_2OEtNMe_2^+$], 87 (34), 72 (12), 70 (17), 56 (52), 55 (15), 45 (39), 44 (100), 43 (36), 42 (23). $C_{30}H_{35}N_5O$ (481.7): calcd C 74.81, H 7.32, N 14.54; found C 74.77, H 7.40, N 14.56.

5-*N*,*N*-Dimethylamino-1,1-dimethyl-r-5-methylsulfanyl-2,c-6a-di-*p*-tolyl-1,1a,5,6,6a,6b-hexahydro-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (9c). ^1H NMR (400 MHz, CCl_4/d_6-acetone): δ=0.01 (s, 3H, *syn*-H_3CCCH_3), 1.24 (s, 3H, *anti*-H_3CCCH_3), 1.33 (s, 3H, SCH_3), 1.79 (s, 2H, H-1a, H-6b), 2.31 (s, 3H, tolyl-CH_3), 2.38 (s, 3H, tolyl-CH_3), 2.39 (s, 6H, $N(CH_3)_2$), 2.99 (d, 1H, ^2J=13.6 Hz, H^{β}-6), 3.32 (d, 1H, ^2J=13.6 Hz, H^{α}-6), 7.00–7.02 (m, 2H, aryl-H), 7.15–7.17 (m, 2H, aryl-H), 7.20–7.66 (2H, aryl-H), 7.66–7.72 (m, 2H, aryl-H) ppm. IR (KBr): ν=2990, 2960, 2870, 2840, 2800, 1505, 1450, 1430, 1260, 1170, 1110, 1100, 1035, 1010, 810 cm^{-1}. UV/Vis (dioxane): (λ_{max} (ϵ)=248 (13 000), 305 (7780) nm (l mol^{-1} cm^{-1}). FD MS (solvent CCl_4): *m/z* (%)=966 (6) [M_2^+], 849 (1) [$M_2^+-C_2H_2SMeNMe_2$], 732 (1) [$M_2^+-2\times C_2H_2SMeNMe_2$], 483 (100) [$M^+$], 366 (46) [$M^+-C_2H_2SMeNMe_2$]. $C_{29}H_{33}N_5S$ (483.7): calcd C 72.01, H 6.88, N 14.48; found C 71.75, H 7.06, N 14.51.

1,1-Dimethyl-4a-pyrrolidin-1-yl-2,8b-di-*p*-tolyl-1,1a,4a,5,6,7,8,8a,8b,8c-decahydro-*cis*-1a-*cis*-4a-transoid-8a,8b-transoid-8b,8c-3,3a-diaza-cyclopropa[*c*]fluorene-4,4-dicarbonitrile (9d). ^1H NMR (400 MHz, $CDCl_3$): δ=0.01 (s, 3H, *syn*-H_3CCCH_3), 0.06–0.24 (m, 1H, cyclohexyl-H), 1.00–1.10 (m, 1H, cyclohexyl-H), 1.17–1.45 (m, 2H, cyclohexyl-/pyrrolidyl-H), 1.27 (s, 3H, *anti*-H_3CCCH_3), 1.60–2.08 (m, 6H, cyclohexyl-/pyrrolidyl-H), 1.77 (s, 2H, cyclopropyl-H), 2.08–2.27 (m, 2H, cyclohexyl-/pyrrolidyl-H), 2.32 (s, 3H, tolyl-CH_3), 2.36 (s, 3H, tolyl-CH_3), 2.91–4.00 (m, 5H, cyclohexyl-/pyrrolidyl-H), 7.00–7.15 (m, 2H, aryl-H), 7.18–7.20 (m, 2H, aryl-H), 7.27–7.40 (m, 1H, aryl-H), 7.46–7.60 (m, 1H, aryl-H), 7.70–7.79 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=16.20 (*syn*-H_3CCCH_3), 19.06 (CH_2), 19.78 (CH_2), 20.69 (cyclopropyl-CH), 20.94 (tolyl-CH_3), 21.34 (tolyl-CH_3), 22.48 (C-1), 22.57 (CH_2), 25.44 (2C, CH_2), 27.30 (*anti*-H_3CCCH_3), 28.96 (CH_2), 31.37 (cyclopropyl-CH), 45.53 (CH_2), 53.63 (C-8a), 63.30, 67.00, 72.24, 113.31, 115.25, 125.86, 127.35, 128.20, 128.42, 129.06, 134.10, 136.58, 139.64, 142.04, 155.43 ppm. IR (KBr): $\tilde{\nu}$=3030, 2960, 2930, 2880, 1510, 1450, 1180, 1170, 1120, 1015, 820 cm^{-1}. UV/Vis (dioxane): (λ_{max} (ϵ)=223 (22 100), 252 (13 900), 306 (9740) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=517 (0.1) [M^+], 366 (5) [$Ylid^+$], 185 (11) [$Ylid^+-C_7H_7CN-C(CN)_2$], 184 (12), 152 (13), 151 (100), 150 (76), 136 (84), 123 (67), 122 (59), 117 (23), 116 (18), 108 (43), 96 (11), 95 (51), 94 (35), 81 (15), 80 (18), 79 (16), 77 (10), 70 (25), 68 (10), 67 (13), 55 (12), 54 (19), 53 (12), 41 (20). $C_{34}H_{39}N_5$ (517.7): calcd C 78.88, H 7.59, N 13.53; found C 78.89, H 7.63, N 13.48.

1,1,6-Trimethyl-5,7-oxo-2,7b-di-*p*-tolyl-1,1a,4a,7a,7b,7c-hexahydro-*cis*-1a-*cis*-4a-*cisoid*-7a,7b-*transoid*-7b,7c-3,3a,6-triaza-cyclopenta[*b*]cyclopropa[*e*]indene-4,4-dicarbonitrile (9e). ^1H NMR (400 MHz, $CDCl_3$): δ=1.08 (s, 3H, *syn*-H_3CCCH_3), 1.13 (s, 3H, *anti*-H_3CCCH_3), 1.90 (d, 1H, ^3J=8.1 Hz, H-1a), 2.22 (d, 1H, ^3J=8.1 Hz, H-7c), 2.37 (s, 3H, tolyl-CH_3), 2.38 (s, 3H, tolyl-CH_3), 2.65 (s, 3H, NCH_3), 3.82 (d, 1H, ^3J=7.9 Hz, H-4a), 4.18 (d, 1H, ^3J=7.9 Hz, H-7a), 7.19–7.21 (m, 2H, aryl-H), 7.23–7.25 (m, 2H, aryl-H), 7.50–7.58 (m, 2H, aryl-H), 7.58–7.60 (m, 2H, aryl-H). ^{13}C NMR (101 MHz, $CDCl_3$): δ=16.99 (*syn*-H_3CCCH_3), 21.06 (tolyl-CH_3), 21.33 (tolyl-CH_3), 22.32 (C-1a), 25.43 (NCH_3), 28.09 (*anti*-H_3CCCH_3), 29.15 (C-1), 35.98 (C-7c), 54.23 (C-7a), 55.06 (C-4a), 62.30, 68.16, 109.75, 112.75, 125.93, 126.35, 129.33, 129.41, 133.67, 138.56, 138.70, 140.36, 152.20, 170.47, 173.63 ppm. IR (KBr): $\tilde{\nu}$=3030, 3000, 2960, 2920, 2880, 1780, 1705, 1430, 1370, 1280 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=281 (14 300) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=478 (23), 477 (67) [M^+], 434 (23), 387 (26), 386 (100) [$M^+-C_7H_7$], 366 (20) [$Ylid^+$], 365 (14), 344 (26), 303 (10), 186 (14), 185 (25) [$Ylid^+-C_7H_7CN-C(CN)_2$], 184 (45), 170 (15), 143 (10), 118 (25), 117 (16), 116 (12), 91 (19), 67 (12). $C_{29}H_{27}N_5O_2$ (477.6): calcd C 72.94, H 5.70, N 14.67; found C 72.88, H 5.77, N 14.59.

1,1-Dimethyl-2,6a-di-*p*-tolyl-*trans*-5-trichloromethyl-1,1a,6a,6b-tetrahydro-6-oxa-*cis*-1a-*transoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (11a). ^1H NMR (400 MHz, $CDCl_3$): δ=1.16 (s, 3H, *syn*-H_3CCCH_3), 1.22 (s, 3H, *anti*-H_3CCCH_3), 2.01 (d, 1H, ^3J=8.1 Hz, H-6b), 2.08 (d, 1H, ^3J=8.1 Hz, H-1a), 2.40 (s, 3H, tolyl-CH_3), 2.42 (s, 3H, tolyl-CH_3), 4.76 (s, 1H, H-5), 7.20–7.27 (m, 2H, aryl-H), 7.29–7.31 (m, 2H, aryl-H), 7.56–7.59 (m, 2H, aryl-H), 7.69–7.77 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=16.72 (*syn*-H_3CCCH_3), 21.27 (tolyl-CH_3), 21.37 (tolyl-CH_3), 21.58 (cyclopropyl-CH), 24.44 (C-1), 27.49 (*anti*-H_3CCCH_3), 33.25 (cyclopropyl-CH), 64.62, 92.36 (C-5), 93.54, 95.77, 108.18, 113.19, 126.21, 126.36, 129.41, 129.84, 133.96, 134.28, 140.23, 140.31, 151.20 ppm. IR (KBr): $\tilde{\nu}$=3060, 3020, 3000, 2960, 2920, 2860, 1175, 1010, 950, 825, 810 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=270 (17 300) nm (l mol^{-1} cm^{-1}). FD MS (solvent CH_2Cl_2): *m/z* (%)=512 (100) [M^+]. $C_{26}H_{23}Cl_3N_4O$ (513.9): calcd C 60.77, 4.51, 10.90; found C 60.68, H 4.58, N 10.93.

1,1-Dimethyl-5-oxo-6-phenyl-2,6a-di-*p*-tolyl-1,1a,5,6,6a,6b-hexahydro-*cis*-1a-*cisoid*-6a,6b-3,3a,6-triaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (11b). ^1H NMR (250 MHz, $CDCl_3$): δ=1.17 (s, 3H, H_3CCCH_3), 1.20 (s, 3H, H_3CCCH_3), 2.10 (d, 1H, ^3J=9.3 Hz, cyclopropyl-H), 2.33 (s, 3H, tolyl-CH_3), 2.36 (d, 1H, ^3J=9.3 Hz, cyclopropyl-H), 2.40 (s, 3H, tolyl-CH_3), 7.10–7.50 (m, 11H, aryl-H), 7.65–7.68 (m, 2H, aryl-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ=15.19 (H_3CCCH_3), 21.02 (tolyl-CH_3), 21.32 (tolyl-CH_3), 26.71 (cyclopropyl-CH), 28.51 (H_3CCCH_3), 29.76, 37.23 (cyclopropyl-CH), 56.01, 79.31, 110.10, 110.25, 124.73, 125.63, 125.74, 128.08, 129.33, 129.51, 129.91, 133.85, 134.11, 136.35, 139.96, 140.05, 151.07, 157.17 ppm. IR (KBr): $\tilde{\nu}$=3040, 2960, 2920, 2870, 1740 1505, 1495, 1485, 1405, 1370, 1350, 1300, 1290, 1170, 1150, 800, 740 cm^{-1}. UV/Vis (dioxane): λ_{max}(ϵ)=227 (23 000), 306 (14 500) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=485 (2) [M^+], 366 (2) [$Ylid^+$], 119 (100)

[PhNCO$^+$], 118 (70), 117 (14), 91 (87), 86 (11), 84 (22), 65 (11), 64 (40), 63 (18), 51 (12), 49 (16), 41 (13), 39 (12). $C_{31}H_{27}N_5O$ (485.6): calcd C 76.68, H 5.60, N 14.42; found C 75.95, H 5.79, N 14.22.

1,1-Dimethyl-5-thioxo-6-phenyl-2,6a-di-*p*-tolyl-1,1a,5,6,6a,6b-hexahydro-*cis*-1a-*cisoid*-6a,6b-3,3a,6-triaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (11c). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.19 (s, 3H, H_3CCCH_3), 1.25 (s, 3H, H_3CCCH_3), 2.02 (d, 1H, ^3J=9.2 Hz, cyclopropyl-H), 2.34 (d, 1H, ^3J=9.2 Hz, cyclopropyl-H), 7.12–7.32 (m, 6H, aryl-H), 7.35–7.60 (m, 5H, aryl-H), 7.60–7.75 (m, 2H, aryl-H) ppm. IR (KBr): $\tilde{\nu}$=3070, 3040, 2960, 2930, 2880, 1420, 1410, 1375, 1270, 1230 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=219 (28 900), 295 (24 800) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%) =501 (7) [M$^+$], 366 (23) [Ylid$^+$], 302 (14), 249 (25), 185 (19) [Ylid$^+$−C_7H_7CN−$C(CN)_2$], 184 (22), 135 (100) [PhNCS$^+$], 117 (12), 116 (11), 91 (11), 77 (61), 51 (30), 50 (12). $C_{31}H_{27}N_5S$ (501.6): calcd C 74.23, H 5.43, N 13.96; found C 74.08, H 5.56, N 13.90.

1,1-Dimethyl-6-thia-5,5-dichloro-2,6a-diphenyl-1,1a,5,6,6a,6b-hexahydro-*cis*-1a-*cisoid*-6a,6b-3,3a-diaza-cyclopropa[*e*]indene-4,4-dicarbonitrile (11d). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.95 (s, 3H, *syn*-H_3CCCH_3), 1.18 (s, 3H, *anti*-H_3CCCH_3), 2.05 (d, 1H, ^3J=8.1 Hz, cyclopropyl-H), 2.11 (d, 1H, ^3J=8.1 Hz, cyclopropyl-H), 7.35–7.50 (m, 6H, aryl-H), 7.60–7.64 (m, 2H, aryl-H), 7.79–7.84 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=17.0 (*syn*-H_3CCCH_3), 21.2 (cyclopropyl-CH), 27.3 (*anti*-H_3CCCH_3), 28.7 (C-1), 36.6 (cyclopropyl-CH), 79.9, 82.5, 96.6, 108.9, 109.6, 126.0, 126.3, 128.3, 128.8, 129.3, 130.2, 136.2, 142.4, 149.7 ppm. IR (KBr): $\tilde{\nu}$=3070–2880, 1610, 1440, 1360, 1005, 835, 765, 745, 695 cm^{-1}. FD MS (solvent CH_2Cl_2): *m/z* (%)=452.1 (100) [M$^+$], 338.3 (63) [Ylid$^+$], 274.2 (15) [Ylid$^+$−$C(CN)_2$]. $C_{23}H_{18}Cl_2N_4S$ (453.4): calcd C 60.93, H 4.00, N 12.36; found C 60.93, H 3.98, N 12.41.

2-(4-Methoxy-benzoyl)-3a-(4-methoxy-phenyl)-1,1-dimethyl-1,3a,4,5,6,7,8,9-octahydro-10a-aza-cycloocta[*a*]-pentalene-10,10-dicarbonitrile (14a). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.80–1.00 (m, 1H, CH_2), 1.16 (s, 3H, CH_3), 1.35–1.70 (m, 5H, CH_2), 1.80–2.20 (m, 4H, CH_2), 1.98 (s, 3H, CH_3), 2.43–2.70 (m, 2H, CH_2), 3.79 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.75 (s, 1H, olefinic-CH), 6.79–6.90 (m, 2H, aryl-H), 6.90–7.08 (m, 2H, aryl-H), 7.14–7.25 (m, 2H, aryl-H), 7.84–7.99 (m, 2H, aryl-H) ppm. IR (KBr): $\tilde{\nu}$=3080, 3010, 2940, 2870, 1640, 1600, 1510, 1305, 1250, 1170 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=233 (27 300), 293 (14 300) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=507 (12) [M$^+$], 481 (11) [M$^+$−HCN], 135 (100) [$MeOC_6H_4CO^+$]. $C_{32}H_{33}N_3O_3$ (507.6): calcd C 75.71, H 6.55, N 8.28; found C 74.22, H 6.75, N 7.65, solvent could not be removed completely from the oily compound.

1,1-Dimethyl-2-(4-methyl-benzoyl)-3a-*p*-tolyl-1,3a,4,5,6,7,8,9-octahydro-10a-aza-cycloocta[*a*]pentalene-10,10-dicarbonitrile (14b). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.74–1.00 (m, 1H, CH_2), 1.14 (s, 3H, CH_3), 1.32–1.70 (m, 5H, CH_2), 1.77–2.20 (m, 4H, CH_2), 2.00 (s, 3H, CH_3), 2.31 (s, 3H, tolyl-CH_3), 2.43 (s, 3H, tolyl-CH_3), 2.47–2.70 (m, 2H, CH_2), 6.80 (s, 1H, olefinic-H), 7.03–7.23 (m, 4H, aryl-H), 7.23–7.34 (m, 2H, aryl-H), 7.77–7.80 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.06 (CH_3), 21.30 (CH_3), 21.60 (CH_3), 24.99 (2C, CH_2), 25.22 (CH_2), 26.08 (CH_2), 27.41 (CH_2), 27.79 (CH_2), 31.79 (CH_3), 62.20, 69.56, 88.14, 115.26, 116.12, 126.24, 129.23, 129.40, 130.05, 135.81, 137.85, 138.18 (olefinic-CH), 140.29, 143.70, 144.14, 149.38, 192.29 ppm. IR (KBr): $\tilde{\nu}$=3070, 3020, 3000, 2950, 2880, 1640, 1600, 1460, 1450, 1325, 1250, 1180, 830, 755 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=226 (20 200), 264 (12 200) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=475 (12) [M$^+$], 460 (16) [M$^+$−CH_3], 448 (4) [M$^+$−HCN], 384 (31) [M$^+$−C_7H_7], 119 (100) [$C_7H_7CO^+$], 91 (18) [$C_7H_7^+$]. $C_{32}H_{33}N_3O$ (475.6): calcd C 80.81, H 6.99, N 8.84; found C 79.55, H 7.30, N 8.28, solvent could not be removed completely from the oily compound.

1,1-Dimethyl-2-benzoyl-3a-phenyl-1,3a,4,5,6,7,8,9-octahydro-10a-aza-cycloocta[*a*]pentalene-10,10-dicarbonitrile (14d). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.71–0.88 (m, 1H, CH_2), 1.14 (s, 3H, CH_3), 1.37–1.50 (m, 3H, CH_2), 1.55–1.62 (m, 2H, CH_2), 1.77–2.17 (m, 4H, CH_2), 2.03 (s, 3H, CH_3), 2.46–2.68 (m, 2H, CH_2), 6.84 (s, 1H, olefinic-H), 7.21–7.35 (m, 5H, aryl-H), 7.45–7.52 (m, 2H, aryl-H), 7.56–7.63 (m, 1H, aryl-H), 7.85–7.90 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.3 (CH_3), 25.0 (CH_2), 25.0 (CH_2), 25.2 (CH_2), 26.1 (CH_2), 27.4 (CH_2), 27.7 (CH_2), 31.8 (CH_3), 62.3, 69.6, 88.3, 115.2, 116.1, 126.3, 128.1, 128.6, 128.6, 129.2, 130.4, 132.9, 138.4, 138.6 (olefinic-CH), 143.2, 143.9, 149.5, 192.6 ppm. IR (KBr): $\tilde{\nu}$=3090–2870, 2840, 1640, 1590, 1445, 1320, 1175, 730, 700 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=212 (20 400), 220 (19 000), 252 (14 300) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=447.0 (3) [M$^+$], 432.9 (2), 420.0 (2), 369.9 (14) [M$^+$−C_6H_5], 105.0 (100) [$C_6H_5CO^+$], 77.1 (29) [$C_6H_5^+$], 43.3 (43). $C_{30}H_{29}N_3O$ (447.6): calcd C 80.51, H 6.53, N 9.39; found C 79.93, H 6.67, N 9.37.

2-(4-Chloro-benzoyl)-3a-(4-chloro-phenyl)-1,1-dimethyl-1,3a,4,5,6,7,8,9-octahydro-10a-aza-cycloocta[*a*]pentalene-10,10-dicarbonitrile (14e). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.75–1.00 (m, 1H, CH_2), 1.14 (s, 3H, CH_3), 1.33–1.74 (m, 5H, CH_2), 1.78–2.20 (m, 4H, CH_2), 2.01 (s, 3H, CH_3), 2.43–2.70 (m, 2H, CH_2), 6.76 (s, 1H, olefinic-H), 7.16–7.38 (m, 4H, aryl-H), 7.40–7.55 (m, 2H, aryl-H), 7.73–7.90 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.18 (CH_3), 24.97 (CH_2), 25.02 (CH_2), 25.16 (CH_2), 26.04 (CH_2), 27.32 (CH_2), 27.80 (CH_2), 31.83 (CH_3), 62.15, 69.76, 87.85, 114.86, 115.92, 127.69, 128.90, 128.95, 130.56, 131.00, 134.23, 136.45, 137.68 (olefinic-CH), 139.58, 141.73, 143.41, 149.83, 191.15 ppm. IR (KBr): $\tilde{\nu}$=3100, 3070, 3010, 2930, 2860, 1650, 1640, 1580, 1480, 1455, 1450, 1390, 1310, 1275, 1240, 1175, 1080, 1010, 840, 830 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=228 (26 200), 262 (16 100) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=515 (7) [M$^+$], 502 (13), 500 (18) [M$^+$−CH_3], 406 (12), 405 (9), 404 (33) [M$^+$−C_6H_4Cl], 141 (33), 140 (8), 139 (100) [$C_6H_4ClCO^+$]. $C_{30}H_{27}Cl_2N_3O$ (516.5): calcd C 69.77, H 5.27, N 8.14; found C 69.58, H 5.42, N 8.09.

2-(4-Trifluoromethyl-benzoyl)-3a-(4-trifluoromethyl-phenyl)-1,1-dimethyl-1,3a,4,5,6,7,8,9-octahydro-10a-

aza-cycloocta[a]pentalene-10,10-dicarbonitrile (14f). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.73–0.96 (m, 1H, CH_2), 1.12 (s, 3H, CH_3), 1.32–1.75 (m, 5H, CH_2), 1.80–2.20 (m, 4H, CH_2), 2.05 (s, 3H, CH_3), 2.44–2.74 (m, 2H, CH_2), 6.82 (s, 1H, olefinic-H), 7.42–7.45 (m, 2H, aryl-H), 7.57–7.61 (m, 2H, aryl-H), 7.76–7.79 (m, 2H, aryl-H), 7.95–7.99 (m, 2H, aryl-H) ppm. IR (KBr): $\tilde{\nu}$=3090, 3020, 2950, 2880, 1660, 1325, 1170, 1130 1070 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=226 (19 900), 248 (16 000) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=583 (1) [M^+], 568 (8) [M^+-CH_3], 438 (15) [$M^+-C_6H_4CF_3$], 173 (100) [$F_3CC_6H_4CO^+$], 145 (20) [$C_6H_4CF_3^+$]. $C_{32}H_{27}F_6N_3O$ (583.6): calcd C 65.86, H 4.66, N 7.20; found C 65.83, H 4.37, N 7.23.

2-(Furan-2-carbonyl)-3a-furan-2-yl-1,1-dimethyl-1,3a,4,5,6,7,8,9-octahydro-10a-aza-cycloocta[*a*]pentalene-10,10-dicarbonitrile (14h). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.05–1.18 (m, 1H, CH_2), 1.30 (s, 3H, CH_3), 1.44–1.72 (m, 5H, CH_2), 1.83–1.95 (m, 2H, CH_2), 1.98 (s, 3H, CH_3), 2.06–2.25 (m, 2H, CH_2), 2.45–2.66 (m, 2H, CH_2), 6.22 (dd, 1H, ^3J=3.3 Hz, ^4J=0.9 Hz, aryl-H), 6.34 (dd, 1H, ^3J=3.3 Hz, ^3J=1.8 Hz, aryl-H), 6.56 (dd, 1H, ^3J=3.6 Hz, ^3J=1.7 Hz, aryl-H), 6.92 (s, 1H, olefinic-H), 7.23 (dd, 1H, ^3J=3.6 Hz, ^4J=0.8 Hz, aryl-H), 7.40 (dd, 1H, ^3J=1.8 Hz, ^4J=0.9 Hz, aryl-H), 7.56 (dd, 1H, ^3J=1.7 Hz, ^4J=0.8 Hz, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.5 (CH_3), 24.8 (CH_2), 25.0 (CH_2), 25.3 (CH_2), 26.0 (CH_2), 27.3 (CH_2), 27.4 (CH_2), 31.3 (CH_3), 61.5, 70.0, 84.4, 108.3, 110.7, 112.4, 114.8, 115.6, 120.0, 131.4, 134.8 (olefinic-CH), 141.8, 142.6, 147.3, 149.2, 152.6, 153.6, 178.4 ppm. IR (KBr): $\tilde{\nu}$=3160, 3120, 3080, 2990, 2940, 2865, 1640, 1605, 1465, 1390, 1330, 1270, 1230, 1190, 1160, 1025, 905, 890, 760, 750 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=228 (15 400), 290 (12 200) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=427.3 (42) [M^+], 412.2 (97) [M^+-CH_3], 332.2 (27) [M^+−furan-2-carbonyl], 291.1 (15), 94.8 (100) [furan-2-carbonyl$^+$]. $C_{26}H_{25}N_3O$ (427.5): calcd C 73.05, H 5.89, N 9.83; found C 72.83, H 6.04, N 9.71.

6-(4-Methoxy-benzoyl)-7a-(4-methoxy-phenyl)-2-*N*,*N*-dimethylamino-1,5,5-trimethyl-5,7a-dihydro-pyrrolizine-3,3-dicarbonitrile (15a). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.14 (s, 3H, CH_3), 1.49 (s, 3H, olefinic-CH_3), 1.95 (s, 3H, CH_3), 2.96 (s, 6H, $N(CH_3)_2$), 3.78 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.77 (s, 1H, olefinic-H), 6.80–6.88 (m, 2H, aryl-H), 6.94–7.04 (m, 2H, aryl-H), 7.12–7.23 (m, 2H, aryl-H), 7.88–8.00 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.96 (olefinic-CH_3), 21.13 (CH_3), 31.57 (CH_3), 42.72 ($N(CH_3)_2$), 55.24 (OCH_3), 55.49 (OCH_3), 58.38, 69.55, 85.29, 113.85, 113.97, 115.34, 116.81, 124.95, 127.38, 131.20, 131.62, 136.15, 136.84 (olefinic-CH), 138.76, 149.05, 159.27, 163.63, 191.30 ppm. IR (KBr): $\tilde{\nu}$=3070, 3040, 3010, 2950, 2880, 2850, 2810, 1670, 1650, 1635, 1590, 1565, 1500, 1465, 1455, 1450, 1440, 1300, 1245, 1180, 1170, 1130, 1020, 840, 830, 770, 760 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=231 (26 400), 287 nm (16 900) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=483 (11), 482 (33) [M^+], 467 (12) [M^+-CH_3], 455 (7) [M^+-HCN], 399 (9) [$M^+-(CH_3)_2NC_3H_3$], 375 (12) [$M^+-C_6H_4OMe$], 347 (7) [$M^+-MeOC_6H_4CO$], 267 (11), 135 (100) [$MeOC_6H_4CO^+$]. $C_{29}H_{30}N_4O_3$ (482.6): calcd C 72.18, H 6.27, N 11.61; found C 72.09, H 6.38, N 11.57.

2-*N*,*N*-Dimethylamino-1,5,5-trimethyl-6-(4-methyl-benzoyl)-7a-*p*-tolyl-5,7a-dihydro-pyrrolizine-3,3-dicarbonitrile (15b). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.12 (s, 3H, CH_3), 1.47 (s, 3H, olefinic-CH_3), 1.97 (s, 3H, CH_3), 2.31 (s, 3H, tolyl-CH_3), 2.43 (s, 3H, tolyl-CH_3), 2.96 (s, 6H, $N(CH_3)_2$), 6.81 (s, 1H, olefinic-H), 7.04–7.18 (m, 4H, aryl-H), 7.28–7.31 (m, 2H, aryl-H), 7.80–7.83 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.93 (olefinic-CH_3), 21.05 (CH_3), 21.15 (CH_3), 21.61 (CH_3), 31.55 (CH_3), 42.70 ($N(CH_3)_2$), 58.42, 69.47, 85.46, 115.34, 116.72, 124.77, 126.09, 129.23, 129.27, 129.41, 135.89, 137.65, 137.96 (olefinic-CH), 138.82, 141.18, 143.60, 149.04, 192.32 ppm. IR (KBr): $\tilde{\nu}$=3070, 3050, 3010, 2950, 2880, 2820, 1675, 1645, 1600, 1325, 1180 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=222 (22 400), 264 (17 900) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=450 (5) [M^+], 435 (5) [M^+-CH_3], 367 (3) [$M^+-(CH_3)_2NC_3H_3$], 359 (10) [$M^+-C_7H_7$], 120 (10), 119 (100) [$C_7H_7CO^+$], 91 (30) [$C_7H_7^+$]. $C_{29}H_{30}N_4O$ (450.6): calcd C 77.30, H 6.71, N 12.43; found C 77.00, H 6.77, N 12.55.

2-*N*,*N*-Dimethylamino-1,5,5-trimethyl-6-benzoyl-7a-phenyl-5,7a-dihydro-pyrrolizine-3,3-dicarbonitrile (15d). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.11 (s, 3H, CH_3), 1.48 (s, 3H, olefinic-CH_3), 2.00 (s, 3H, CH_3), 2.97 (s, 6H, $N(CH_3)_2$), 6.86 (s, 1H, olefinic-H), 7.23–7.32 (m, 5H, aryl-H), 7.48–7.52 (m, 2H, aryl-H), 7.58–7.62 (m, 1H, aryl-H), 7.89–7.92 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=12.0 (olefinic-CH_3), 21.0 (CH_3), 31.4 (CH_3), 42.6 ($N(CH_3)_2$), 58.4, 69.3, 85.5, 115.1, 116.6, 123.5, 126.1, 127.9, 128.5, 128.6, 129.2, 132.8, 138.3, 138.6 (olefinic-CH), 138.7, 144.1, 148.9, 192.6 ppm. IR (KBr): $\tilde{\nu}$=3080–2810, 1680, 1600, 1450, 1325, 1130, 720, 695 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=206 (11 500), 212 (20 700), 250 (18 500) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=422.2 (8) [M^+], 345.1 (22), 104.9 (100), 77.0 (37). $C_{27}H_{26}N_4O$ (422.5): calcd C 76.75, H 6.20, N 13.26; found C 76.70, H 6.32, N 13.19.

6-(4-Chloro-benzoyl)-7a-(4-chloro-phenyl)-2-*N*,*N*-dimethylamino-1,5,5-trimethyl-5,7a-dihydro-pyrrolizine-3,3-dicarbonitrile (15e). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.12 (s, 3H, CH_3), 1.49 (s, 3H, olefinic-CH_3), 1.98 (s, 3H, CH_3), 2.97 (s, 6H, $N(CH_3)_2$), 6.78 (s, 1H, olefinic-H), 7.14–7.24 (m, 2H, aryl-H), 7.24–7.33 (m, 2H, aryl-H), 7.43–7.53 (m, 2H, aryl-H), 7.80–7.90 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.94 (olefinic-CH_3), 21.00 (CH_3), 31.59 (CH_3), 42.53 ($N(CH_3)_2$), 58.29, 69.59, 85.21, 114.91, 116.52, 122.15, 127.54, 128.90, 128.96, 130.60, 133.95, 136.53, 137.59 (olefinic-CH), 139.14, 139.47, 142.71, 149.31, 191.19 ppm. IR (KBr): $\tilde{\nu}$=3100, 3070, 3000, 2940, 2800, 1665, 1640, 1315, 1085, 1010 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=223 (23 800), 262 (19 400) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=492 (16), 491 (7), 490 (24) [M^+], 475 (11) [M^+-CH_3], 407 (8) [$M^+-Me_2N-C_3H_3$], 381 (14), 380 (10), 379 (40) [$M^+-C_6H_4Cl$], 351 (10) [$M^+-C_6H_4ClCO$], 141 (33), 140 (8) 139 (100) [$C_6H_4ClCO^+$], 111 (5) [$C_6H_4Cl^+$], 83 (13) [$(CH_3)_2N-C_3H_3^+$]. $C_{27}H_{24}Cl_2N_4O$ (491.4): calcd C 65.99, H 4.92, N 11.40; found C 66.03, H 5.08, N 11.35.

6-(4-Trifluoromethyl-benzoyl)-7a-(4-trifluoromethyl-

phenyl)-2-*N*,*N*-dimethylamino-1,5,5-trimethyl-5,7a-dihydro-pyrrolizine-3,3-dicarbonitrile (15f). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.10 (s, 3H, CH_3), 1.49 (s, 3H, olefinic-CH_3), 2.02 (s, 3H, CH_3), 2.98 (s, 6H, $N(CH_3)_2$), 6.85 (s, 1H, olefinic-H), 7.38–7.41 (m, 2H, aryl-H), 7.56–7.60 (m, 2H, aryl-H), 7.77–7.80 (m, 2H, aryl-H), 7.98–8.02 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.91 (olefinic-CH_3), 20.95 (CH_3), 31.59 (CH_3), 42.45 ($N(CH_3)_2$), 58.32, 69.64, 85.39, 114.72, 116.41, 120.97, 123.62 (q, ^1J=272.7 Hz, CF_3), 123.85 (q, ^1J=272.1 Hz, CF_3), 125.71 (q, ^3J=3.6 Hz), 126.52, 129.43, 130.44 (q, ^2J=32.7 Hz), 134.33 (q, ^2J=32.9 Hz), 138.18 (olefinic-CH), 139.42, 141.08 (^5J=1.3 Hz), 148.15 (^5J=1.3 Hz), 149.62, 191.27 ppm. IR (KBr): $\tilde{\nu}$=3070, 3010, 2940, 2800, 1650, 1320, 1160, 1120, 1060 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=244 nm (17 900) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m*/*z* (%)=559 (14), 558 (39) [M^+], 543 (9) [M^+-CH_3], 539 (5) [M^+-F], 414 (11), 413 (43) [$M^+-C_6H_4CF_3$], 385 (14) [$M^+-F_3CC_6H_4CO$], 173 (100) [$F_3CC_6H_4CO^+$], 145 (14) [$C_6H_4CF_3^+$], 83 (25) [$(CH_3)_2N-C_3H_3^+$]. $C_{29}H_{24}F_6N_4O$ (558.5): calcd C 62.36, H 4.33, N 10.03; found C 63.00, H 4.64, N 9.51.

2-*N*,*N*-Dimethylamino-1,5,5-trimethyl-6-(1-methyl-1*H*-pyrrol-2-carbonyl)-7a-(1-methyl-1*H*-pyrrol-2-yl)-5,7a-dihydro-pyrrolizine-3,3-dicarbonitrile (15g). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.27 (s, 3H, CH_3), 1.57 (s, 3H, olefinic-CH_3), 1.93 (s, 3H, CH_3), 2.97 (s, 6H, $N(CH_3)_2$), 3.70 (s, 3H, NCH_3), 3.97 (s, 3H, NCH_3), 5.85 (dd, 1H, ^3J=3.7 Hz, ^3J=1.8 Hz, aryl-H), 5.95 (dd, 1H, ^3J=3.7 Hz, ^4J=2.7 Hz, aryl-H), 6.15 (dd, 1H, ^3J=4.1 Hz, ^3J=2.5 Hz, aryl-H), 6.58 (dd, 1H, ^4J=2.7 Hz, ^3J=1.8 Hz, aryl-H), 6.65 (s, 1H, olefinic-H), 6.90 (dd, 1H, ^3J=2.5 Hz, ^4J=1.7 Hz, aryl-H), 7.01 (dd, 1H, ^3J=4.1 Hz, ^4J=1.7 Hz, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.8 (olefinic-CH_3), 21.5 (CH_3), 30.4 (CH_3), 35.2 (NCH_3), 37.2 (NCH_3), 42.8 ($N(CH_3)_2$), 58.0, 69.8, 82.2, 106.3, 108.4, 109.0, 115.1, 116.3, 122.4, 122.9, 124.8, 130.3, 131.3, 132.0, 134.7 (olefinic-CH), 139.1, 149.5, 182.0 ppm. IR (KBr): $\tilde{\nu}$=3130, 3010, 2950, 2820, 1670, 1610, 1590, 1405, 1375, 1355, 1240, 1140, 1060, 790, 740, 705 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=228 (16 300), 306 (14 700) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m*/*z* (%)=428.3 (42) [M^+], 413.3 (18) [M^+-CH_3], 320.2 (12), 107.9 (100), 93.9 (20). $C_{25}H_{28}N_6O$ (428.5): calcd C 70.08, H 6.59, N 19.61; found C 69.62, H 6.80, N 19.27.

2-*N*,*N*-Dimethylamino-6-(furan-2-carbonyl)-7a-furan-2-yl-1,5,5-trimethyl-5,7a-dihydro-pyrrolizine-3,3-dicarbonitrile (15h). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.30 (s, 3H, CH_3), 1.62 (s, 3H, olefinic-CH_3), 1.95 (s, 3H, CH_3), 2.97 (s, 6H, $N(CH_3)_2$), 6.20 (dd, 1H, ^3J=3.3 Hz, ^4J=0.8 Hz, aryl-H), 6.33 (dd, 1H, ^3J=3.3 Hz, ^3J=1.8 Hz, aryl-H), 6.56 (dd, 1H, ^3J=3.6 Hz, ^3J=1.7 Hz, aryl-H), 6.92 (s, 1H, olefinic-H), 7.28 (dd, 1H, ^3J=3.6 Hz, ^4J=0.8 Hz, aryl-H), 7.41 (dd, 1H, ^3J=1.8 Hz, ^4J=0.8 Hz, aryl-H), 7.68 (dd, 1H, ^3J=1.7 Hz, ^4J=0.8 Hz, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=11.5 (olefinic-CH_3), 21.4 (CH_3), 31.1 (CH_3), 42.6 ($N(CH_3)_2$), 57.9, 69.9, 82.0, 108.4, 110.5, 112.3, 114.9, 116.2, 120.1, 121.4, 134.8 (olefinic-CH), 139.9, 142.7, 147.3, 148.7, 152.6, 154.2, 178.5 ppm. IR (KBr): $\tilde{\nu}$=3140, 3020, 2940, 2880, 2830, 1675, 1645, 1470, 1395, 1325, 1195, 1150, 1030, 790, 780, 760 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=228 (16 800), 288 (13 500) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m*/*z* (%)=402.5 (34) [M^+], 387.3 (28) [M^+-CH_3], 319.4 (28) [$M^+-(CH_3)_2NC_3H_3$], 307.3 (17) [M^+−furan-2-carbonyl], 240.1 (49), 94.9 (100) [furan-2-carbonyl$^+$]. $C_{23}H_{22}N_4O_3$ (402.4): calcd C 68.65, H 5.51, N 13.92; found C 68.24, H 5.89, N 13.43.

1,9b-Bis-(4-methoxy-phenyl)-4,5,6,7,8,9,9b,10,11,12-decahydro-3*H*-2,2a-diaza-cycloocta[*a*]*as*-indacene-3,3-dicarbonitrile (17a). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.70–0.79 (m, 1H, CH_2), 1.46–1.67 (m, 5H, CH_2), 1.92–2.60 (m, 10H, CH_2), 2.82–3.09 (m, 2H, CH_2), 3.76 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.80–6.87 (m, 4H, aryl-H), 7.26–7.29 (m, 2H, aryl-H), 7.54–7.58 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=23.4 (CH_2), 24.5 (CH_2), 25.3 (CH_2), 26.06 (CH_2), 26.08 (CH_2), 27.4 (CH_2), 28.0 (CH_2), 33.0 (CH_2), 34.8 (CH_2), 55.27 (OCH_3), 55.30 (OCH_3), 65.1, 74.4, 112.5, 113.6, 113.8, 114.0, 127.6, 127.7, 128.6, 129.1, 129.8, 133.8, 138.7, 145.7, 153.7, 159.6, 160.4 ppm. IR (KBr): $\tilde{\nu}$=3020, 2940, 2875, 1610, 1515, 1465, 1365, 1330, 1305, 1260, 1180, 1030, 850 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=234 (25 600), 267 (13 600), 336 (5550) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m*/*z* (%)=504.4 (26) [M^+], 371.2 (100) [$M^+-H_3COC_6H_4CN$], 343.2 (18), 330.2 (51), 316.2 (13), 280.1 (59), 225.0 (64), 133.9 (30), 118.9 (13), 107.9 (8) [$C_6H_4OCH_3^+$]. $C_{32}H_{32}N_4O_2$ (504.6): calcd C 76.17, H 6.39, N 10.40; found C 75.95, H 6.56, N 10.95.

1,9b-Di-*p*-tolyl-4,5,6,7,8,9,9b,10,11,12-decahydro-3*H*-2,2a-diaza-cycloocta[*a*]*as*-indacene-3,3-dicarbonitrile (17b). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.72–0.76 (m, 1H, CH_2), 1.44–1.61 (m, 5H, CH_2), 1.90–2.61 (m, 10H, CH_2), 2.29 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.80–3.09 (m, 2H, CH_2), 7.07–7.14 (m, 4H, aryl-H), 7.22–7.25 (m, 2H, aryl-H), 7.47–7.50 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.0 (CH_3), 21.3 (CH_3), 23.5 (CH_2), 24.5 (CH_2), 25.3 (CH_2), 26.05 (CH_2), 26.07 (CH_2), 27.4 (CH_2), 28.0 (CH_2), 32.9 (CH_2), 34.8 (CH_2), 65.2, 75.1, 112.5, 113.9, 126.3, 127.6, 127.7,128.8, 129.1, 129.9, 133.1, 138.1, 138.6, 138.9, 139.0, 145.8, 153.0 ppm. IR (KBr): $\tilde{\nu}$=3050, 2940, 2875, 1615, 1510, 1460, 1450, 1410, 1370, 1330, 1295, 1250, 1220, 1185, 1130, 1025, 960, 820, 730 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=237 (24 500), 253 (20 800), 344 (4990) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m*/*z* (%)=472.4 (6) [M^+], 381.3 (100) [$M^+-C_7H_7$], 311.2 (20), 299.2 (15), 90.9 (19), [$C_7H_7^+$]. $C_{32}H_{32}N_4$ (472.6): calcd C 81.33, H 6.82, N 11.85; found C 81.22, H 6.73, N 11.87.

1,9b-Di-phenyl-4,5,6,7,8,9,9b,10,11,12-decahydro-3*H*-2,2a-diaza-cycloocta[*a*]*as*-indacene-3,3-dicarbonitrile (17c). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.65–0.74 (m, 1H, CH_2), 1.39–1.85 (m, 2H, CH_2), 1.89–2.61 (m, 13H, CH_2), 2.82–2.95 (m, 1H, CH_2), 2.99–3.14 (m, 1H, CH_2), 7.21–7.35 (m, 8H, aryl-H), 7.39–7.44 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=23.5 (CH_2), 24.5 (CH_2), 25.3 (CH_2), 26.0 (CH_2), 26.1 (CH_2), 27.5 (CH_2), 28.0 (CH_2), 32.8 (CH_2), 34.9 (CH_2), 65.3, 75.3, 112.4, 113.8, 126.3, 127.7, 127.9, 128.2, 128.4, 128.5 129.0, 129.9, 135.8, 138.6, 141.9, 145.6, 153.7 ppm. IR (KBr): $\tilde{\nu}$=3060, 3020, 2920, 2860, 1485, 1440, 1350, 1320, 1070, 1045, 1020, 775,

695 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=242 (19 200), 329 (4410) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=444.4 (4) [M^+], 367.3 (100) [$M^+-C_6H_5$], 297.1 (11). $C_{30}H_{28}N_4$ (444.6): calcd C 81.05, H 6.35, N 12.60; found C 80.98, H 6.36, N 12.62.

1,9b-Diphenyl-4,5,6,7,8,9,9b,10,11,12,13-undecahydro-2,2a-diaza-cycloocta[*b*]cyclohexa[*e*]indene-3,3-dicarbonitrile (17d). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.50–0.59 (m, 1H, CH_2), 1.40–2.75 (m, 19H, CH_2), 7.21–7.35 (m, 8H, aryl-H), 7.39–7.44 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=22.26 (CH_2), 22.3 (CH_2), 24.9 (CH_2), 25.0 (CH_2), 26.4 (CH_2), 27.0 (CH_2), 27.4 (CH_2), 27.6 (CH_2), 28.6 (CH_2), 28.9 (CH_2), 63.5, 74.0, 112.4, 113.5, 124.5, 126.8, 128.1, 128.2, 128.3, 128.4 128.6, 129.0, 132.0, 135.0, 140.9, 145.9, 159.2 ppm. IR (KBr): $\tilde{\nu}$=3095, 3070, 3040, 2940, 2870, 1450, 1325, 1175, 1100, 1075, 1030, 770, 750, 730, 700 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=234 (15 300), 321 (3940) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=458.5 (7) [M^+], 432.4 (5) [M^+-HCN], 381.4 (100) [$M^+-C_6H_5$]. $C_{31}H_{30}N_4$ (458.6): calcd C 81.19, H 6.59, N 12.22; found C 80.96, H 6.68, N 12.14.

1,9b-Bis-(4-trifluoromethyl-phenyl)-4,5,6,7,8,9,9b,10,11,12-decahydro-3*H*-2,2a-diaza-cycloocta[*a*]*as*-indacene-3,3-dicarbonitrile (17e). ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.63–0.85 (m, 1H, CH_2), 1.43–1.72 (m, 5H, CH_2), 1.95–2.64 (m, 10H, CH_2), 2.84–2.96 (m, 1H, CH_2), 3.04–3.17 (m, 1H, CH_2), 7.48–7.51 (m, 2H, aryl-H), 7.58–7.62 (m, 4H, aryl-H), 7.70–7.77 (m, 2H, aryl-H) ppm. IR (KBr): $\tilde{\nu}$=3070, 2945, 2875, 1620, 1445, 1410, 1330, 1170, 1130, 1080, 1020, 850, 780 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=242 (21 000), 254 (23 600), 346 (5180) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=580.4 (3) [M^+], 561 (3) [M^+-F], 435.3 (100) [$M^+-C_6H_4CF_3$], 365.2 (25). $C_{32}H_{26}F_6N_4$ (580.4): calcd C 66.22, H 4.51, N 9.65; found C 66.26, H 4.70, N 9.66.

1-Methylsulfanyl-4,5,6,7,8,9-octahydro-12*H*-2,2a-diaza-cycloocta[*a*]*as*-indacene-3-carbonitrile (17f). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.32–1.47 (m, 4H, CH_2), 1.56–1.75 (m, 4H, CH_2), 2.22 (qu, 2H, CH_2), 2.62 (s, 3H, SCH_3), 2.75–2.85 (m, 6H, CH_2), 3.16 (t, 2H, CH_2) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=12.5 (SCH_3), 22.5 (CH_2), 23.3 (CH_2), 24.1 (CH_2), 25.5 (CH_2), 25.8 (CH_2), 29.9 (CH_2), 31.1 (CH_2), 31.6 (CH_2), 31.8 (CH_2), 98.0, 112.2, 113.6, 125.5, 128.2, 134.7, 139.7, 151.0 ppm. IR (KBr): $\tilde{\nu}$=2940, 2860, 2210, 1600, 1540, 1440, 1310, 1265, 1170, 1125, 980 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=265 (14 800), 277 (26 200), 287 (37 400), 341 (2160) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=311.2 (100) [M^+], 283.2 (36), 268.1 (33), 256.1 (18). $C_{18}H_{21}N_3S$ (311.4): calcd C 69.43, H 6.80, N 13.49; found C 69.31, H 6.76, N 13.40.

3,3-Dicyano-5,8b-bis-(4-methoxy-phenyl)-6,7,8,8b-tetrahydro-3*H*-3a,4-diaza-*as*-indacene-1,2-dicarboxylic acid dimethyl ester (18a). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.98–2.24 (m, 2H, CH_2), 2.51–2.62 (m, 1H, CH_2), 2.72–2.97 (m, 3H, CH_2), 3.74 (s, 3H, CO_2CH_3), 3.77 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.98 (s, 3H, CO_2CH_3), 6.83–6.91 (m, 4H, aryl-H), 7.20–7.26 (m, 2H, aryl-H), 7.53–7.59 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=23.3 (CH_2), 33.1 (CH_2), 34.1 (CH_2), 53.2 (CO_2CH_3), 53.6 (CO_2CH_3), 55.29 (OCH_3), 55.34 (OCH_3), 61.0, 74.7, 110.7, 112.1, 113.6, 114.1, 125.4, 127.8, 128.0, 129.2, 130.6, 130.8, 137.5, 151.4, 153.4, 158.9, 160.2, 160.7, 162.0 ppm. IR (KBr): $\tilde{\nu}$=3020, 2970, 2860, 1740, 1730, 1610, 1510, 1440, 1285, 1260, 1180, 1035, 835, 750 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=228 (28 200), 277 (12 700), 320 (6960) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=538.5 (20) [M^+], 431.3 (100) [$M^+-C_6H_4OCH_3$], 107.9 (37) [$C_6H_4OCH_3^+$]. $C_{30}H_{26}N_4O_6$ (538.5): calcd C 66.91, H 4.87, N 10.40; found C 66.72, H 5.01, N 10.30.

3,3-Dicyano-5,8b-di-*p*-tolyl-6,7,8,8b-tetrahydro-3*H*-3a,4-diaza-*as*-indacene-1,2-dicarboxylic acid dimethyl ester (18b). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.97–2.26 (m, 2H, CH_2), 2.31 (s, 3H, tolyl-CH_3), 2.34 (s, 3H, tolyl-CH_3), 2.39–2.61 (m, 1H, CH_2), 2.73–2.95 (m, 3H, CH_2), 3.75 (s, 3H, CO_2CH_3), 3.97 (s, 3H, CO_2CH_3), 7.12–7.24 (m, 6H, aryl-H), 7.47–7.50 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.1 (CH_3), 21.3 (CH_3), 23.3 (CH_2), 33.0 (CH_2), 34.1 (CH_2), 53.2 (CO_2CH_3), 53.6 (CO_2CH_3), 61.1, 75.1, 110.7, 112.1, 125.5, 126.2, 127.6, 129.0, 129.5, 130.8, 132.6, 135.8, 137.4, 139.3, 139.5, 151.4, 153.4, 158.9, 162.0 ppm. IR (KBr): $\tilde{\nu}$=3070, 3040, 2960, 2930, 2870, 1720, 1640, 1610, 1435, 1330, 1290, 1150, 1050, 1020, 980, 830, 730 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=240 (19 100), 324 (4200) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=506.5 (22) [M^+], 415.4 (100) [$M^+-C_7H_7$], 91.0. $C_{30}H_{26}N_4O_4$ (506.5): calcd C 71.14, H 5.17, N 11.06; found C 70.89, H 5.47, N 11.00.

3,3-Dicyano-5,8b-diphenyl-6,7,8,8b-tetrahydro-3*H*-3a,4-diaza-*as*-indacene-1,2-dicarboxylic acid dimethyl ester (18c). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.99–2.27 (m, 2H, CH_2), 2.49–2.62 (m, 1H, CH_2), 2.75–2.98 (m, 3H, CH_2), 3.73 (s, 3H, CO_2CH_3), 3.98 (s, 3H, CO_2CH_3), 7.25–7.41 (m, 8H, aryl-H), 7.55–7.63 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=23.3 (CH_2), 32.9 (CH_2), 34.2 (CH_2), 53.2 (CO_2CH_3), 53.7 (CO_2CH_3), 61.2, 75.3, 110.6, 112.0, 125.6, 126.2, 127.7, 128.3, 128.8, 129.3, 129.4, 130.8, 135.2, 137.5, 138.8, 151.2, 153.5, 158.8, 161.9 ppm. IR (KBr): $\tilde{\nu}$=3090, 3060, 3040, 2960, 2920, 2860, 1740, 1650, 1490, 1440, 1360, 1340, 1325, 1280, 1150, 1130, 1080, 1030, 980, 940, 775, 745, 695 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=238 (22 300), 324 (4120) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=478.4 (5) [M^+], 401.3 (100) [$M^+-C_6H_5$], 343.3 (13). $C_{28}H_{22}N_4O_4$ (478.5): calcd C 70.28, H 4.63, N 11.71; found C 70.14, H 4.90, N 11.61.

3,3-Dicyano-5,9b-diphenyl-3,6,7,8,9,9b-hexahydro-pyrrolo[2,1-*a*]phthalazine-1,2-dicarboxylic acid dimethyl ester (18d). ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.49–1.65 (m, 1H, CH_2), 1.70–2.02 (m, 4H, CH_2), 2.27–2.50 (m, 3H, CH_2), 3.71 (s, 3H, CO_2CH_3), 4.00 (s, 3H, CO_2CH_3), 7.28–7.44 (m, 10H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.8 (CH_2), 22.1 (CH_2), 27.5 (CH_2), 28.0 (CH_2), 53.2 (CO_2CH_3), 53.7 (CO_2CH_3), 60.1, 74.5, 110.7, 111.7, 125.5, 126.8, 127.1, 128.2, 128.5, 129.0, 129.3, 131.3, 135.1, 138.0, 151.4, 158.5, 158.9, 162.2 ppm. IR (KBr): $\tilde{\nu}$=3100, 3080, 3040, 2970, 2940, 2880, 1740, 1650, 1450, 1435, 1320, 1275, 1205, 1155, 1125, 1090, 1035, 1000, 770, 750, 700 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=236 (19 600), 316 (3550) nm (l mol^{-1} cm^{-1}). EI MS

(70 eV): *m/z* (%)=492.4 (13) [M^+], 415.4 (100) [$M^+-C_6H_5$], 357.3 (12). $C_{29}H_{24}N_4O_4$ (492.5): calcd C 70.72, H 4.91, N 11.38; found C 70.43, H 4.97, N 11.23.

3,3-Dicyano-5,8b-bis-(4-trifluoromethyl-phenyl)-6,7,8,8b-tetrahydro-3*H*-3a,4-diaza-*as*-indacene-1,2-dicarboxylic acid dimethyl ester (18e). ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.05–2.30 (m, 2H, CH_2), 2.51–2.63 (m, 1H, CH_2), 2.79–2.97 (m, 3H, CH_2), 3.79 (s, 3H, CO_2CH_3), 4.01 (s, 3H, CO_2CH_3), 7.43–7.46 (m, 2H, aryl-H), 7.62–7.74 (m, 6H, aryl-H) ppm. IR (KBr): $\tilde{\nu}$=3080, 2970, 2940, 2860, 1740, 1730, 1660, 1645, 1615, 1440, 1410, 1325, 1280, 1165, 1130, 1070, 1020, 850 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=242 (25 300), 324 (4400) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=614.4 (4) [M^+], 469.4 (100) [$M^+-C_6H_4CF_3$]. $C_{30}H_{20}F_6N_4O_4$ (614.5): calcd C 58.64, H 3.28, N 9.12; found C 58.40, H 3.38, N 9.00.

Following the general procedure, 0.21 mmol **13b** and 0.69 mmol **6** were heated in 5 ml acetonitrile at 80°C for 35 h. Fcc (CH_2Cl_2, silica gel 60) and recrystallization from CH_2Cl_2/hexane yielded 0.17 mmol (82%) **3,3-dicyano-5,5-dimethyl-6-(4-methyl-benzoyl)-7a-*p*-tolyl-5,7a-dihydro-pyrrolizine-1,2-dicarboxylic acid dimethyl ester (19a)**, mp 191°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.20 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.32 (s, 3H, tolyl-CH_3), 2.44 (s, 3H, tolyl-CH_3), 3.59 (s, 3H, CO_2CH_3), 3.95 (s, 3H, CO_2CH_3), 7.03 (s, 1H, olefinic-H), 7.07–7.24 (m, 4H, aryl-H), 7.30–7.33 (m, 2H, aryl-H), 7.81–7.85 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.13 (CH_3), 21.17 (CH_3), 21.66 (CH_3), 31.73 (CH_3), 53.04 (CO_2CH_3), 53.45 (CO_2CH_3), 58.41, 70.79, 86.71, 113.47, 113.88, 125.68, 126.22, 129.42, 129.49, 129.67, 135.19, 136.24, 136.61, 139.15, 144.26, 149.75, 150.41, 158.61, 162.10, 191.62 ppm. IR (KBr): $\tilde{\nu}$=3090, 3030, 3000, 2960, 2930, 1725, 1650, 1640, 1320, 1270, 1175 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=241 (16 900), 270 (14 900) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=509 (9) [M^+], 494 (17) [M^+-CH_3], 418 (6) [$M^+-C_7H_7$], 119 (100) [$C_7H_7CO^+$], 91 (14) [$C_7H_7^+$]. $C_{30}H_{27}N_3O_5$ (509.6): calcd C 70.71, H 5.34, N 8.25; found C 70.57, H 5.00, N 8.29.

Following the general procedure, 0.36 mmol **13d** and 2.39 mmol **6** were heated in 10 ml acetone at 80°C for 16 h. Recrystallization from petroleum ether (40–60)/diethyl ether/CH_2Cl_2 yielded 0.27 mmol (75%) **3,3-dicyano-5,5-dimethyl-6-benzoyl-7a-phenyl-5,7a-dihydro-pyrrolizine-1,2-dicarboxylic acid dimethyl ester (19b)**, mp 193–194°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.21 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 3.57 (s, 3H, CO_2CH_3), 3.95 (s, 3H, CO_2CH_3), 7.08 (s, 1H, olefinic-H), 7.28–7.37 (m, 5H, aryl-H), 7.50–7.54 (m, 2H, aryl-H), 7.61–7.65 (m, 1H, aryl-H), 7.91–7.94 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.1 (CH_3), 31.6 (CH_3), 53.1 (CO_2CH_3), 53.6 (CO_2CH_3), 58.3, 70.7, 86.7, 113.3, 113.6, 125.6, 126.2, 128.7, 129.0, 129.2, 129.3, 133.3, 136.7, 137.6, 139.4, 149.6, 150.4, 158.7, 162.1, 191.9 ppm. IR (KBr): $\tilde{\nu}$=3100–2970, 1760, 1730, 1640, 1595, 1445, 1350–1250, 1150, 730, 700 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=204 (9590), 212 (22 000), 242 (17 600) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=481.9 (0.7) [M^+], 433.9 (4), 403.9 (5), 105.0 (100) [$C_6H_5CO^+$], 77.1 (32), 51.2 (6). $C_{28}H_{23}N_3O_5$ (481.5): calcd C 69.85, H 4.81, N 8.73; found C 69.58, H 4.97, N 8.77.

To a boiling suspension of 0.30 mmol **13b** in 8 ml CH_2Cl_2 benzene diazonium-2-carboxylate (suspension in CH_2Cl_2) was added until a colourless solution was obtained. After evaporation of the solvent fcc (CH_2Cl_2, silica gel 60) and recrystallization from ethanol/water yielded 0.10 mmol (32%) **3,3-dimethyl-2-(4-methyl-benzoyl)-9b-*p*-tolyl-3,9b-dihydro-pyrrolo[2,1-*a*]isoindole-5,5-dicarbonitrile (20)**, mp 177°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.29 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.30 (s, 3H, tolyl-CH_3), 2.39 (s, 3H, tolyl-CH_3), 6.95 (s, 1H, olefinic-H), 7.03–7.90 (m, 12H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=21.04 (CH_3), 21.59 (CH_3), 21.86 (CH_3), 31.12 (CH_3), 57.61, 70.43, 84.47, 115.22, 116.04, 122.42, 124.98, 125.90, 129.24, 129.41, 129.46, 129.80, 131.75, 134.15, 135.61, 137.92, 139.39, 142.16, 143.06, 143.79, 149.67, 191.95 ppm. IR (KBr): $\tilde{\nu}$=3010, 2960, 2940, 2880, 1640, 1600, 1320, 750 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=225 (25 300), 267 (14 600) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=443 (2) [M^+], 428 (6) [M^+-CH_3], 352 (5) [$M^+-C_7H_7$], 119 (100) [$C_7H_7CO^+$], 91 (34) [$C_7H_7^+$], 65 (10) [$C_5H_5^+$]. $C_{30}H_{25}N_3O$ (443.6): calcd C 81.24, H 5.68, N 9.47; found C 80.91, H 5.88, N 9.41.

Following the general procedure, 0.20 mmol **13b** and 1.47 mmol 1,1-bis-ethoxy-ethene (**8a**) in 2 ml acetonitrile were stirred at rt for 96 h. Fcc (CH_2Cl_2, silica gel 60) and recrystallization from CH_2Cl_2/hexane yielded 0.11 mmol (56%) **2,2-bis-ethoxy-5,5-dimethyl-6-(4-methyl-benzoyl)-7a-*p*-tolyl-1,2,5,7a-tetrahydro-pyrrolizine-3,3-dicarbonitrile (21)**, mp 180–181°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.19 (t, 3H, ^3J=7.0 Hz, CH_3CH_2O), 1.28 (s, 3H, CH_3), 1.30 (t, 3H, ^3J=7.0 Hz, CH_3CH_2O), 2.00 (s, 3H, CH_3), 2.30 (s, 3H, tolyl-CH_3), 2.43 (s, 3H, tolyl-CH_3), 2.60 (d, 1H, ^2J=14.1 Hz, CH_2), 2.77 (d, 1H, ^2J=14.1 Hz, CH_2), 2.97 (dq, 1H, ^2J=8.7 Hz, ^3J=7.0 Hz, CH_3CH_2O), 3.42 (dq, 1H, ^2J=8.7 Hz, ^3J=7.0 Hz, CH_3CH_2O), 3.88–4.00 (m, 2H, CH_3CH_2O), 6.78 (s, 1H, olefinic-H), 7.07–7.09 (m, 2H, aryl-H), 7.27–7.29 (m, 2H, aryl-H), 7.32–7.34 (m, 2H, aryl-H), 7.75–7.85 (m, 2H, aryl-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ=14.28 (CH_3CH_2O), 15.05 (CH_3CH_2O), 20.81 (CH_3), 20.95 (tolyl-CH_3), 21.61 (tolyl-CH_3), 31.41 (CH_3), 44.31 (CH_2), 59.02 (CH_3CH_2O), 59.43 (CH_3CH_2O), 61.64, 70.97, 76.56, 108.86, 114.47, 115.61, 125.64, 128.93, 129.20, 129.41, 136.18, 136.97, 142.27, 142.83 (olefinic-CH), 143.62, 146.58, 192.57 ppm. IR (KBr): $\tilde{\nu}$=3080, 3050, 3000, 2950, 2920, 1635, 1605, 1330, 1315, 1300, 1250, 1190, 1150, 1125, 1095, 1045, 820, 760 cm^{-1}. UV/Vis (dioxane): λ_{max} (ϵ)=265 (14 400) nm (l mol^{-1} cm^{-1}). EI MS (70 eV): *m/z* (%)=483 (0.2) [M^+], 468 (2) [M^+-CH_3], 368 (13), 367 (46) [$M^+-(EtO)_2C_2H_2$], 288 (12) [Ylid$^+$-$(CN)_2$C-Me], 120 (10), 119 (100) [$C_7H_7-CO^+$], 91 (16) [$C_7H_7^+$]. $C_{30}H_{33}N_3O_3$ (483.6): calcd C 74.51, H 6.88, N 8.69; found C 74.20, H 6.88, N 8.63.

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18. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144200. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].