[4+2] Cycloadditions of 1,2,4,5-Tetrazines and Cyclopropenes − Synthesis of 3,4-Diazanorcaradienes and Tetracyclic Aliphatic Azo Compounds

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Dedicated to Prof. Siegfried Hünig on the occasion of his 80th birthday

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1,2,4,5-Tetrazines **1** readily react with cyclopropenes **2** to form 3,4-diazanorcaradienes **3**, **4**, **7** and **8** in a cycloaddition – cycloelimination sequence. Compounds **3** and **4** still act as 1,3-dienes with cyclopropenes **2**, producing aliphatic azo compounds **5** and **6**, versatile starting compounds in thermolysis and photolysis reactions.

Introduction

Forty years have passed since the first report on the diene activity of 1,2,4,5-tetrazines was published.[1] In the meantime this heterocyclic system has proved to be a valuable electron-poor diene in [4+2] cycloadditions with angle-strained and electron-rich dienophiles.[2] A large variety of heterocyclic and carbocyclic compounds are accessible in a few steps; examples include 3,4-diazanorcaradienes,[3] homotropilidenes,[4−6] *syn*-bis-σ-homobenzenes[7] and semibullvalenes.[8,9] Here we give a full report on the synthesis of 3,4-diazanorcaradienes **3**, **4**, **7** and **8**, as well as for the aliphatic azo compounds **5** and **6**. Diazanorcaradienes **3** and **4** were also needed for a detailed kinetic study.[10]

Results and Discussion

Schemes 1 and 2 summarize all reactions performed. As already indicated, [4+2] cycloaddition reactions between tetrazines **1** and cyclopropenes **2** occur readily. After the addition step, the sequence is completed by loss of nitrogen in a cycloelimination, with diazanorcaradienes **3**, **4**, **7** and **8** being formed in reasonable yields, mostly between 70 and 90%. The cyano derivatives **5c** and **6c** could not be obtained directly from the labile dicyanotetrazine **1c**, so we instead used the conventional transformations **5a/6a** → **5b/6b** → **5c/6c**. The highly reactive cyclopropene (**2a**)[11] was introduced into a solution of tetrazine **1** in a stream of nitrogen at −78 °C; the reaction can be monitored by the disappearance of the tetrazine colour [General Procedure (1)]. 3,3-Dimethylcyclopropene (**2b**) is far less reactive, by a factor of approximately 5000−6000 in rate constants (dioxane, 20 °C).[11] The fading of the colour here again indicates the progress of the reaction at room temperature [General Procedure (2)].

3,4-Diazanorcaradienes **3** and **4** are much less reactive dienes than 1,2,4,5-tetrazines, by a factor of 10^3 to 10^4 for the rate constants derived from kinetic data.[2] Consequently, only those diazadienes **3** and **4** with electron-withdrawing substituents R^1 react readily with an excess of cyclopropene (**2a**) at −78 °C, forming the so-called "bisadducts" **5** and **6**. The reaction can be driven to final completion by warming the reaction mixture to room temperature. Again, the disappearance of the tetrazine or diazanorcaradiene colour is a simple indicator that the reaction is successfully going to completion [General Procedure (3)]. For the less reactive 3,3-dimethylcyclopropene (**2b**), more forcing conditions were required: high pressure (up to 8 kbar) and slightly elevated temperatures (56−100 °C) [General procedure (4)]. The highly negative $\Delta V^{\neq}$ values, well known in concerted cycloaddition reactions, are responsible for the accelerating pressure effect.[12] We were unsuccessful, however, in forcing 3,4-diazanorcaradienes **7** and **8** to undergo addition reactions to form "bisadducts" of type **5** and **6**. In this cycloaddition step, the resonance energy of one or two imino ester units has to be sacrificed.

NMR spectra provided structural proof for all compounds obtained. Tables 1 and 2 show selected ^{1}H NMR spectroscopic data for 3,4-diazanorcaradienes **3** and **4**, while the corresponding values for the tetracyclic azo compounds **5** and **6** are to be found in Tables 2 and 3. The typical pronounced chemical shift difference between 7-H_{syn} and 7-H_{anti} in **3**, in conjunction with the characteristic set of coupling constants for the ABX_2 spin system,[3] is in accordance with the diazanorcaradiene structure (Figure 1). Simpler ^{1}H NMR spectra were observed for the dimethyl derivatives **4**, with the chemical shift differences between methyl groups, *syn* and *anti*, again being considerable. Detailed analysis of the ^{1}H NMR spectroscopic data for the "bisadducts" **5** and **6**, including chemical shifts and coup-

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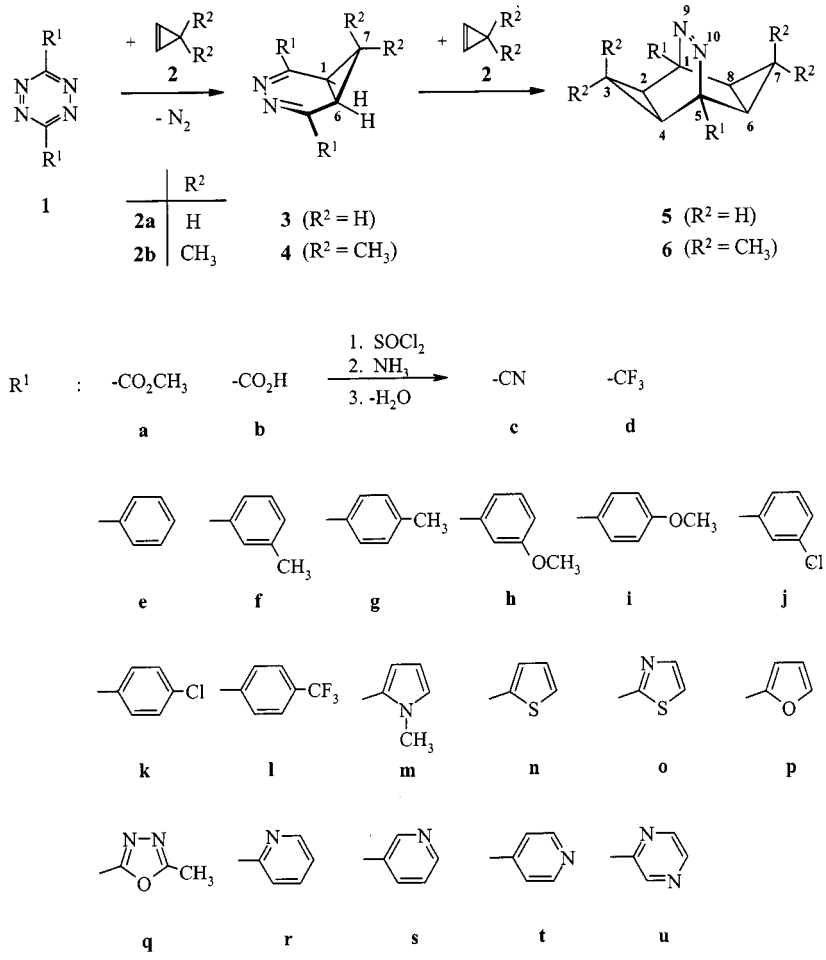
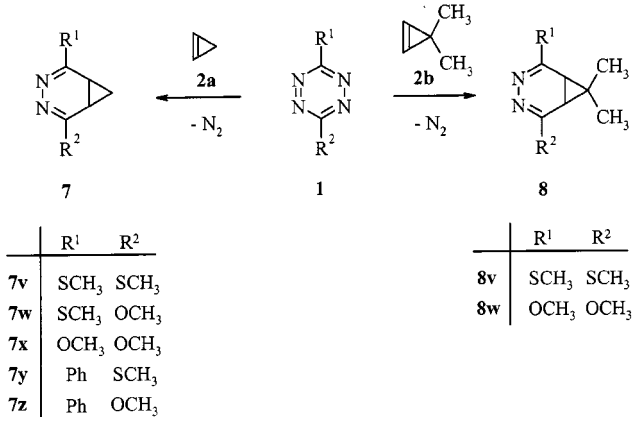


Scheme 1. Cycloadditions between 1,2,4,5-tetrazines **1a**−**1u** and cyclopropenes **2**, giving 3,4-diazanorcaradienes **3** and **4**, with subsequent formation of tetracyclic azo compounds **5** and **6**



Scheme 2. Cycloadditions between 1,2,4,5-tetrazines **1v**−**1z** and cyclopropenes **2**, giving 3,4-diazanorcaradienes **7** and **8**

ling constants (Tables 2 and 3), proves the *syn*,*syn* arrangement, relative to the azo bridge, in both cyclopropane units.

As ^{13}C NMR spectra did not change dramatically over compounds **3**−**8**, ^{13}C NMR spectra were measured only for a limited number of compounds (see Exp. Sect.).

Table 1. ^{1}H NMR chemical shifts (δ values, $CDCl_3$/TMS, 80 or 250 MHz) and coupling constants $^{n}J(^{1}H,^{1}H)$ [Hz] of 3,4-diazanorcaradienes **3** and **7**

Cmpd.	7-H_{syn}	7-H_{anti}	1-H, 6-H	$^{3}J_{7s,1/6}$	$^{3}J_{7a,1/6}$	$^{2}J_{7,7}$
3a[a][3]	−0.03 (dt)	2.28 (dt)	3.05 (dd)	4.8	8.9	3.8
3d[b]	0.32−0.41 (m)	2.41−2.51 (m)	2.71 (m)	–	–	–
3e	0.35 (dt)	2.16 (dt)	2.71(dd)	4.9	9.0	3.8
3f	0.31 (dt)	2.15 (dt)	2.68 (dd)	4.9	9.0	3.8
3g	0.27 (dt)	2.09 (dt)	2.63 (dd)	4.9	9.0	3.8
3h	0.33 (dt)	2.15 (dt)	2.70 (dd)	4.9	9.1	3.8
3i	0.30 (dt)	2.08 (dt)	2.48 (dd)	4.9	9.0	3.8
3j	0.35 (dt)	2.22 (dt)	2.69 (dd)	4.9	9.1	3.9
3k	0.36 (dt)	2.19 (dt)	2.71 (dd)	4.9	9.0	3.9
3l	0.41 (dt)	2.28 (dt)	2.77 (dd)	4.9	9.0	3.9
3n	0.41 (dt)	2.04 (dt)	2.74 (dd)	4.9	9.0	4.1
3o	0.43 (dt)	2.27 (dt)	3.39 (dd)	4.8	9.1	4.0
3q	0.40 (dt)	2.40 (dt)	3.35 (dd)	4.8	9.1	4.7
3r	0.29 (dt)	2.32 (dt)	3.48 (dd)	4.8	9.2	3.6
3s	0.43 (dt)	2.31 (dt)	2.80 (dd)	4.9	9.0	3.9
3t	0.38 (dt)	2.30 (dt)	2.78 (dd)	4.9	9.0	4.0
3u	0.27 (dt)	2.29 (dt)	3.42 (dd)	4.7	9.1	3.6
7v	0.42 (dt)	1.73 (dt)	2.21 (dd)	4.7	8.9	4.5
7x	0.51 (dt)	1.49 (dt)	2.14 (dd)	4.6	9.1	4.6

[a] At 248 K. – [b] At 233 K.

Table 2. ^{1}H NMR chemical shifts (δ values, $CDCl_3$/TMS, 80 or 250 MHz) of 3,4-diazanorcaradienes **4**, **8** and tetracyclic azo compounds **6**

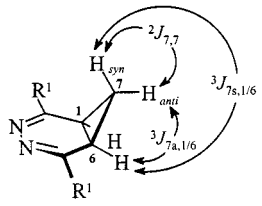
	3,4-Diazanorcaradienes **4** and **8**				Tetracyclic azo compounds **6**		
Cmpd.	7-CH_3-*syn*	7-CH_3-*anti*	1-H, 6-H	Cmpd.	7-CH_3-*syn*	7-CH_3-*anti*	2,4,6,8-H
4a[a][3]	0.59 (s)	1.55 (s)	2.88 (s)	**6a**[b]	0.92 (s)	1.01 (s)	1.78 (s)
4d	0.69 (s)	1.53 (s)	2.49 (s)	**6b**[c]	0.93 (s)	0.97 (s)	1.88 (s)
4e	0.63 (s)	1.61 (s)	2.45 (s)	**6c**	1.02 (s)	1.10 (s)	1.86 (s)
4g	0.68 (s)	1.66 (s)	2.46 (s)	**6d**	0.96 (s)	1.02 (s)	1.72 (s)
4i	0.67 (s)	1.67 (s)	2.45 (s)	**6e**	1.11 (s)	1.23 (s)	1.75 (s)
4k	0.70 (s)	1.68 (s)	2.43 (s)	**6o**	0.91 (s)	1.08 (s)	2.20 (s)
4l	0.79 (s)	1.80 (s)	2.61 (s)	**6q**[b]	1.02 (s)	1.09 (s)	1.99 (s)
4m	0.65 (s)	1.51 (s)	2.35 (s)	**6r**	0.92 (s)	1.08 (s)	2.18 (s)
4n	0.72 (s)	1.80 (s)	2.55 (s)				
4o	0.80 (s)	1.76 (s)	3.28 (s)				
4p	0.70 (s)	1.56 (s)	2.58 (s)				
4q	0.72 (s)	1.65 (s)	3.17 (s)				
4r	0.67 (s)	1.68 (s)	3.33 (s)				
4s	0.74 (s)	1.72 (s)	2.58 (s)				
4t	0.71 (s)	1.71 (s)	2.57 (s)				
4u	0.68 (s)	1.68 (s)	3.26 (s)				
8v	0.67 (s)	1.27 (s)	1.94 (s)				
8w	0.67 (s)	1.20 (s)	1.90 (s)				

[a] At 253 K. − [b] Solvent CD_2Cl_2. − [c] Solvent CD_3OD.

Table 3. ^{1}H NMR chemical shifts (δ values, $CDCl_3$/TMS, 80 or 250 MHz) and coupling constants $J(^1H,^1H)$ [Hz] of tetracyclic azo compounds **5**

Cmpd.	3,7-H_{syn}	3,7-H_{anti}	2,4,6,8-H	$^3J_{3s,2/4}$	$^3J_{3a,2/4}$	$^2J_{3,3}$
5a[3]	0.13 (dt)	0.56 (dt)	1.93 (dd)	3.7	7.4	6.8
5b[a]	0.00 (dt)	0.55 (dt)	2.00 (dd)	3.6	7.6	7.2
5c	0.37 (m)	0.85 (m)	2.07 (m)	−	−	−
5d	0.10 (dt)	0.60 (dt)	1.80 (dd)	3.6	7.7	7.2
5o	0.27 (dt)	0.55 (dt)	2.29 (dd)	3.6	7.7	7.0
5q[b]	0.33 (dt)	0.79 (dt)	2.12 (dd)	3.6	7.7	7.0
5r	0.21 (dt)	0.54 (dt)	2.22 (dd)	3.6	7.7	6.4
5s	0.49 (dt)	0.90 (dt)	1.95 (dd)	3.7	7.7	6.5
5t	0.43 (dt)	0.83 (dt)	1.93 (dd)	3.7	7.7	6.6

[a] Solvent CD_3OD. − [b] Solvent CD_2Cl_2.



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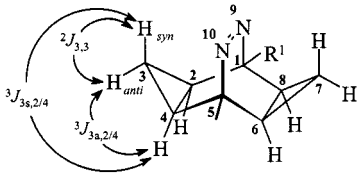

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Figure 1. Significant coupling constants $^nJ(^1H,^1H)$ observed for 3,4-diazanorcaradienes **3** and tetracyclic azo compounds **5**

Conclusion

3,4-Diazanorcaradienes such as **3**, **4**, **7** and **8**, and also the "bisadducts" **5** and **6**, required for preparative and kinetic studies, are accessible in good yields in wide structural variety with the aid of simple [4+2] cycloadditions. The reaction conditions required vary from −78 °C at normal pressure to +100 °C at 8 kbar, depending on the reactivity of the 4π and 2π components.

Experimental Section

General Remarks: IR spectra were recorded with a Beckman Acculab 1 machine and UV/Vis spectra with a Carl Zeiss Specord M500 UV spectrophotometer. − NMR spectra were obtained with Bruker AW 80 and AC 250 machines (80 MHz/250 MHz for ^{1}H and 63 MHz for ^{13}C); δ values are reported in ppm downfield from tetramethylsilane; s, d, dd, dt and m indicate singlet, doublet, doublet of doublets, doublet of triplets and multiplet. The degree of substitution of the C atoms was determined by DEPT-135 and DEPT-90 methods and indicated as quat. C, =CH, $-CH_2-$, $-CH_3$. − Mass spectra were measured with a Varian MAT311A instrument by electron impact, at an ionizing voltage of 70 eV. − Melting points were determined either with a Büchi melting point apparatus (< 280 °C) or with a copper block (> 280 °C) and are uncorrected. − Elemental analyses were performed in the microanalytical laboratory of the University of Regensburg with Heraeus Mikro U/E and CHN-Rapid instruments. In some cases − such as for **3d**, **3e**, **4d** and **4e** − correct elemental analyses could not be obtained. − For analytical thin layer chromatography, precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey−Nagel & Co.) were used. − Silica gel 60 (particle size 0.040−0.063 nm, Merck) was used for flash column chromatography (FC). − Reactions were carried out under nitrogen. Solvents for reactions were dried according to standard procedures. The petroleum ether (PE) used had a boiling range of 40−60 °C.

Synthesis of 3,4-Diazanorcaradienes and Tetracyclic Azo Compounds

General Procedure (1) for the Synthesis of 3,4-Diazanorcaradienes 3d−3l, 3n, 3o, 3q−3u and 7v−7z, and Tetracyclic Azo Compounds 5d, 5o and 5q: A ca. 30-fold excess of gaseous cyclopropene (**2a**), generated using an optimized procedure by Closs and Krantz,[13] was condensed (ca. 6 h) into a trap maintained at dry ice temperature and containing a stirred suspension of tetrazine **1** in an inert solvent (vide infra). The trap was allowed to warm to room temperature and stirring was continued until the red colour of the tetrazine **1** had disappeared (reaction times: see below). After completion of the reaction, the solvent was removed in vacuo and the crude reaction product was purified as described below.

General Procedure (2) for the Synthesis of 7,7-Dimethyl-3,4-diazanorcaradienes 4d, 4e, 4g, 4i, 4k−4u, 8v and 8w, and Tetracyclic Azo Compounds 6a and 6d: The tetrazine **1** was dissolved in an inert solvent (vide infra). The dienophile 3,3-dimethylcyclopropene (**2b**) synthesized using a procedure described by Huber and Sauer,[14] was added and the reaction mixture was stirred until the characteristic red colour of the tetrazine **1** had disappeared (reaction times: see below). The solution was concentrated to dryness and the crude product was purified as described below.

General Procedure (3) for the Synthesis of Tetracyclic Azo Compounds 5r−5t: A ca. 100-fold excess of gaseous cyclopropene (**2a**) was generated according to General Procedure (1) and condensed (ca. 6 h) into a trap maintained at dry ice temperature.[13] A solution of diazanorcaradiene **3** in CH_2Cl_2 was added and the reaction mixture was stirred for 3 h at −78 °C. The mixture was then allowed to warm to room temperature and stirring was continued for 24 h until the colour of **3** had disappeared (vide infra). After removal of the solvent the colourless residue was purified as described below.

General Procedure (4) for the High-Pressure Synthesis of Tetracyclic Azo Compounds 6e, 6o, 6q and 6r: The diazanorcaradiene **4** was dissolved in CH_2Cl_2 or CH_3CN (4−6 mL) in a high-pressure vessel. After addition of 3,3-dimethylcyclopropene (**2b**), the reaction vessel was pressurized to max. 8.0 kbar at a temperature of 56−100 °C until completion of the reaction (reaction times: see below). After evaporation of the solvent, the crude material was purified as described below.

Synthesis of the 3,4-Diazanorcaradienes 3d−3l, 3n, 3o, 3q−3u and 7v−7z

2,5-Bis(trifluoromethyl)-3,4-diazanorcaradiene (3d): This compound was prepared according to General Procedure (1). Compounds **1d** (530 mg, 2.43 mmol) and **2a**, after stirring in CCl_4 (10 mL) at room temp. overnight, yielded **3d**, which was purified by bulb-tube distillation (50 °C/0.01 Torr) to give extremely moisture-sensitive yellow crystals. No yield, melting point or elemental analysis could be determined. − IR (CCl_4): $\tilde{\nu}$ = 1400, 1305, 1290, 1205, 1135, 1090, 1070, 1050, 900 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$, θ = 233.1 K): δ = 0.32−0.41 (m, 1 H, 7-H_{syn}), 2.41−2.51 (m, 1 H, 7-H_{anti}), 2.71 (m, 2 H, 1-H, 6-H). − MS (EI, 70 eV): *m/z* (%) = 230 (36) [M^+].

2,5-Diphenyl-3,4-diazanorcaradiene (3e): This compound was prepared according to General Procedure (1). Compounds **1e** (3.00 g, 12.8 mmol) and **2a**, after stirring in CH_2Cl_2 (50 mL) at 0 °C for 6 h, purification by FC (CH_2Cl_2 → CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/EtOAc), yielded **3e** (2.65 g, 10.8 mmol, 84%) as yellow crystals, m.p. 198 °C (ref.[15] m.p. 196 °C). − IR (KBr): $\tilde{\nu}$ = 3090, 3040, 1530, 1490, 1410, 1385, 1045, 1015, 765, 680 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.35 (dt, ^2J = 3.8, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.16 (dt, ^2J = 3.8, ^3J = 9.0 Hz, 1 H, 7-H_{anti}), 2.71 (dd, ^3J = 4.9, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.45−7.53 (m, 6 H, Ar-H), 8.13−8.19 (m, 4 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 312 (21400) nm.

2,5-Bis(*m*-tolyl)-3,4-diazanorcaradiene (3f): This compound was prepared according to General Procedure (1). Compounds **1f** (3.00 g, 11.4 mmol) and **2a**, after stirring in CH_2Cl_2 (80 mL) at −78 °C for 10 min, purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/EtOAc), yielded **3f** (1.90 g, 6.90 mmol, 61%) as yellow crystals, m.p. 132 °C. − IR (KBr): $\tilde{\nu}$ = 3040, 2980, 1610, 1590, 1550, 1515, 1430, 1400, 1280, 1200, 805, 715, 685 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.31 (dt, ^2J = 3.8, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.15 (dt, ^2J = 3.8, ^3J = 9.0 Hz, 1 H, 7-H_{anti}), 2.44 (s, 6 H, Ar-CH_3), 2.68 (dd, ^3J = 4.9, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.30−8.00 (m, 8 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 317 (21400) nm. − $C_{19}H_{18}N_2$ (274.4): calcd. C 83.18, H 6.61, N 10.21; found C 83.14, H 6.64, N 10.23.

2,5-Bis(*p*-tolyl)-3,4-diazanorcaradiene (3g): This compound was prepared according to General Procedure (1). Compounds **1g** (3.00 g, 11.4 mmol) and **2a**, after stirring in CH_2Cl_2 (80 mL) at 0 °C for 1 h and purification by FC (CH_2Cl_2/EtOAc = 1:1), yielded **3g** (1.82 g, 6.60 mmol, 58%) as yellow crystals, m.p. 224 °C. − IR (KBr): $\tilde{\nu}$ = 3040, 2910, 1605, 1530, 1400, 1385, 1180, 1170, 1040, 1010, 810, 710 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.27 (dt, ^2J = 3.8, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.09 (dt, ^2J = 3.8, ^3J = 9.0 Hz, 1 H, 7-H_{anti}), 2.41 (s, 6 H, Ar-CH_3), 2.63 (dd, ^3J = 4.9, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.26−8.05 (m, 8 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 321 (25700) nm. − $C_{19}H_{18}N_2$ (274.4): calcd. C 83.18, H 6.61, N 10.21; found C 83.41, H 6.35, N 10.22.

2,5-Bis(*m*-methoxyphenyl)-3,4-diazanorcaradiene (3h): This compound was prepared according to General Procedure (1). Compounds **1h** (3.00 g, 10.2 mmol) and **2a**, after stirring in CH_2Cl_2 (80 mL) at 0 °C for 2 h and purification by FC (CH_2Cl_2/Et_2O/PE = 1:1:1), yielded **3h** (2.60 g, 8.50 mmol, 83%) as yellow crystals, m.p. 117 °C. − IR (KBr): $\tilde{\nu}$ = 3040, 2990, 2940, 2830, 1590, 1500, 1280, 1215, 1040, 850, 790, 700 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.33 (dt, ^2J = 3.8, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.15 (dt, ^2J = 3.8, ^3J = 9.1 Hz, 1 H, 7-H_{anti}), 2.70 (dd, ^3J = 4.9, ^3J = 9.1 Hz, 2 H, 1-H, 6-H), 3.89 (s, 6 H, OCH_3), 7.05−7.81 (m, 8 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 320 (19500) nm. − $C_{19}H_{18}N_2O_2$ (306.4): calcd. C 74.49, H 5.92, N 9.14; found C 74.18, H 6.00, N 9.05.

2,5-Bis(*p*-methoxyphenyl)-3,4-diazanorcaradiene (3i): This compound was prepared according to General Procedure (1). Compounds **1i** (3.00 g, 10.2 mmol) and **2a**, after stirring in CH_2Cl_2 (80 mL) at 0 °C for 1 h, purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/EtOAc), yielded **3i** (3.02 g, 9.90 mmol, 97%) as yellow crystals, m.p. 224 °C. − IR (KBr): $\tilde{\nu}$ = 3040, 3000, 2940, 2840, 1600, 1535, 1510, 1415, 1395, 1300, 1250, 1170, 1030, 840, 640 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.30 (dt, ^2J = 3.8, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.08 (dt, ^2J = 3.8, ^3J = 9.0 Hz, 1 H, 7-H_{anti}), 2.48 (dd, ^3J = 4.9, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 3.87 (s, 6 H, OCH_3), 6.96−8.12 (m, 8 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 335 (27500) nm. − $C_{19}H_{18}N_2O_2$ (306.4): calcd. C 74.49, H 5.92, N 9.14; found C 74.42, H 5.84, N 9.21.

2,5-Bis(*m*-chlorophenyl)-3,4-diazanorcaradiene (3j): This compound was prepared according to General Procedure (1). Compounds **1j** (3.00 g, 9.90 mmol) and **2a**, after stirring in CH_2Cl_2 (80 mL) at 0 °C for 1.5 h, purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrys-

tallization (CH_2Cl_2/EtOAc), yielded **3j** (1.53 g, 4.90 mmol, 49%) as yellow crystals, m.p. 191 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 1580, 1510, 1435, 1400, 1260, 1030, 810, 790, 720, 700, 670 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.35 (dt, ^2J = 3.9, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.22 (dt, ^2J = 3.9, ^3J = 9.1 Hz, 1 H, 7-H_{anti}), 2.69 (dd, ^3J = 4.9, ^3J = 9.1 Hz, 2 H, 1-H, 6-H), 7.40−8.14 (m, 8 H, Ar-H). − UV/Vis (1,4-dioxane): λ_{max} (ε) = 317 (18200) nm. − $C_{17}H_{12}Cl_2N_2$ (315.2): calcd. C 64.78, H 3.84, N 8.89; found C 64.87, H 4.09, N 8.81.

2,5-Bis(*p*-chlorophenyl)-3,4-diazanorcaradiene (3k): This compound was prepared according to General Procedure (1). Compounds **1k** (3.00 g, 9.90 mmol) and **2a**, after stirring in CH_2Cl_2 (80 mL) at 0 °C for 1.5 h, purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **3k** (2.97 g, 9.42 mmol, 95%) as yellow crystals, m.p. 256 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 1590, 1535, 1490, 1425, 1400, 1090, 1080, 1045, 1010, 985, 830, 720, 655 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$,): δ = 0.36 (dt, ^2J = 3.9, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.19 (dt, ^2J = 3.9, ^3J = 9.0 Hz, 1 H, 7-H_{anti}), 2.71 (dd, ^3J = 4.9, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.45−8.12 (m, 8 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 320 (22900) nm. − $C_{17}H_{12}Cl_2N_2$ (315.2): calcd. C 64.78, H 3.84, N 8.89; found C 64.67, H 3.63, N 8.89.

2,5-Bis(*p*-trifluoromethylphenyl)-3,4-diazanorcaradiene (3l): This compound was prepared according to General Procedure (1). Compounds **1l** (3.00 g, 8.10 mmol) and **2a**, after stirring in CH_2Cl_2 (80 mL) at 0 °C for 1 h, purification by FC (CH_2Cl_2/*n*-hexane = 1:1) and recrystallization (CH_2Cl_2/EtOAc), yielded **3l** (2.02 g, 5.03 mmol, 65%) as yellow crystals, m.p. 244 °C. − IR (KBr): $\tilde{\nu}$ = 3070, 2940, 1615, 1420, 1330, 1170, 1130, 1070, 1030, 860, 850, 710, 690 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.41 (dt, ^2J = 3.9, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.28 (dt, ^2J = 3.9, ^3J = 9.0 Hz, 1 H, 7-H_{anti}), 2.77 (dd, ^3J = 4.9, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.76−8.29 (m, 8 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 7.5 (−CH_2−, 1 C), 18.4 (=CH, 2 C), 123.9 (quat. C, 2 C), 125.4 (=CH, 4 C), 128.0 (=CH, 4 C), 132.8 (quat. C, 2 C), 139.5 (quat. C, 2 C), 158.7 (quat. C, 2 C). − UV/Vis (CH_3CN): λ_{max} (ε) = 315 (11500) nm. − $C_{19}H_{12}F_6N_2$ (382.3): calcd. C 59.69, H 3.16, N 7.33; found C 59.92, H 3.23, N 7.38.

2,5-Bis(2-thienyl)-3,4-diazanorcaradiene (3n): This compound was prepared according to General Procedure (1). Compounds **1n** (2.46 g, 10.0 mmol) and **2a**, after stirring in CH_2Cl_2 (70 mL) at room temp. for 24 h, purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **3n** (1.90 g, 7.36 mmol, 74%) as yellow crystals, m.p. 169−170 °C. − IR (KBr): $\tilde{\nu}$ = 3090, 3060, 2850, 1530, 1485, 1430, 1380, 1250, 1225, 1060, 1045, 1020, 840, 815, 790, 690 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.41 (dt, ^2J = 4.1, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.04 (dt, ^2J = 4.1, ^3J = 9.0 Hz, 1 H, 7-H_{anti}), 2.74 (dd, ^3J = 4.9, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.13 (dd, ^3J = 3.7, ^3J = 5.1 Hz, 2 H, Ar-H), 7.48 (dd, ^3J = 5.1, ^4J = 1.1 Hz, 2 H, Ar-H) 7.64 (dd, ^3J = 3.7, ^4J = 1.1 Hz, 2 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 273 (13800), 365 (32700) nm. − $C_{13}H_{10}N_2S_2$ (258.3): calcd. C 60.44, H 3.90, N 10.84; found C 60.33, H 3.88, N 10.78.

2,5-Bis(2-thiazolyl)-3,4-diazanorcaradiene (3o): This compound was prepared according to General Procedure (1). Compounds **1o** (154 mg, 10.0 mmol) and **2a**, after stirring in *n*-hexane (25 mL) at room temp. for 12 h, purification by FC (CH_2Cl_2/ethanol = 15:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **3o** (133 mg, 0.511 mmol, 81%) as yellow crystals, m.p. 171−173 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 3070, 3050, 2995, 1530, 1475, 1420, 1260, 1050, 1115, 865, 760, 730 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.43 (dt, ^2J = 4.0, ^3J = 4.8 Hz, 1 H, 7-H_{syn}), 2.27 (dt, ^2J = 4.0, ^3J = 9.1 Hz, 1 H, 7-H_{anti}), 3.39 (dd, ^3J = 4.8, ^3J = 9.1 Hz, 2 H, 1-H, 6-H), 7.56 (d, ^3J = 3.2 Hz, 2 H, Ar-H), 8.03 (d, ^3J = 3.2 Hz, 2 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 8.3 (−CH_2−, 1 C), 19.6 (=CH, 2 C), 123.4 (=CH, 2 C), 144.6 (=CH, 2 C), 158.1 (quat. C, 2 C), 166.3 (quat. C, 2 C). − MS (EI, 70 eV): *m/z* (%) = 260 (91) [M^+]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 252 (4790), 294 (4970), 377 (17000) nm. − $C_{11}H_8N_4S_2$ (260.4): calcd. C 50.74, H 3.10, N 21.52; found C 50.99, H 3.60, N 21.33.

2,5-Bis(2-methyl-1,3,4-oxadiazol-5-yl)-3,4-diazanorcaradiene (3q): This compound was prepared according to General Procedure (1). Compounds **1q**[16] (198 mg, 0.804 mmol) and **2a**, after stirring in *n*-hexane (15 mL) at room temp. for 12 h, purification by FC (CH_2Cl_2/EtOAc/ethanol = 15:1:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **3q** (156 mg, 0.603 mmol, 75%) as yellow crystals, m.p. 219−221 °C. − IR (KBr): $\tilde{\nu}$ = 3095, 3040, 2995, 1555, 1410, 1340, 1245, 1105, 1055, 1040, 990, 755 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.40 (dt, ^2J = 4.7, ^3J = 4.8 Hz, 1 H, 7-H_{syn}), 2.40 (dt, ^2J = 4.7, ^3J = 9.1 Hz, 1 H, 7-H_{anti}), 2.70 (s, 6 H, Ar-CH_3), 3.35 (dd, ^3J = 4.8, ^3J = 9.1 Hz, 2 H, 1-H, 6-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 8.2 (−CH_2−, 1 C), 11.2 (−CH_3, 2 C), 20.0 (=CH, 2 C), 151.4 (quat. C, 2 C), 162.6 (quat. C, 2 C), 166.2 (quat. C, 2 C). − MS (EI, 70 eV): *m/z* (%) = 258 (74) [M^+]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 263 (10400), 324 (19600) nm. − $C_{11}H_{10}N_6O_2$ (258.4): calcd. N 32.54; found N 32.28.

2,5-Bis(2-pyridyl)-3,4-diazanorcaradiene (3r): This compound was prepared according to General Procedure (1). Compounds **1r** (2.36 g, 10.0 mmol) and **2a**, after stirring in CH_2Cl_2 (60 mL) at 0 °C for 5 h, purification by FC (CH_2Cl_2/ethanol = 15:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **3r** (1.93 g, 7.77 mmol, 78%) as yellow crystals, m.p. 165−168 °C. − IR (KBr): $\tilde{\nu}$ = 3050, 3000, 2920, 1580, 1560, 1535, 1500, 1455, 1425, 1380, 1100, 1035, 940, 890, 730, 670 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.29 (dt, ^2J = 3.6, ^3J = 4.8 Hz, 1 H, 7-H_{syn}), 2.32 (dt, ^2J = 3.6, ^3J = 9.2 Hz, 1 H, 7-H_{anti}), 3.48 (dd, ^3J = 4.8, ^3J = 9.2 Hz, 2 H, 1-H, 6-H), 7.38−7.43 (m, 2 H, Ar-H), 7.78−7.85 (m, 2 H, Ar-H), 8.50−8.54 (m, 2 H, Ar-H), 8.73−8.76 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 240 (11600), 323 (24400) nm. − $C_{15}H_{12}N_4$ (248.3): calcd. C 72.56, H 4.87, N 22.56; found C 72.48, H 4.88, N 22.45.

2,5-Bis(3-pyridyl)-3,4-diazanorcaradiene (3s): This compound was prepared according to General Procedure (1). Compounds **1s** (2.36 g, 10.0 mmol) and **2a**, after stirring in CH_2Cl_2 (70 mL) at room temp. for 24 h, purification by FC (CH_2Cl_2/ethanol = 7:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **3s** (1.47 g, 5.92 mmol, 59%) as yellow crystals, m.p. 191−192 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 1595, 1580, 1510, 1480, 1440, 1410, 1205, 1075, 1050, 820, 720 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.43 (dt, ^2J = 3.9, ^3J = 4.9 Hz, 1 H, 7-H_{syn}), 2.31 (dt, ^2J = 3.9, ^3J = 9.0 Hz, 1 H, 7-H_{anti}), 2.80 (dd, ^3J = 4.9, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.42−7.48 (m, 2 H, Ar-H), 8.46−8.51 (m, 2 H, Ar-H), 8.75−8.77 (m, 2 H, Ar-H), 9.30−9.32 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) =240 (11600), 323 (24400) nm. − $C_{15}H_{12}N_4$ (248.3): calcd. C 72.56, H 4.87, N 22.56; found C 72.46, H 4.74, N 22.31.

2,5-Bis(4-pyridyl)-3,4-diazanorcaradiene (3t): This compound was prepared according to General Procedure (1). Compounds **1t** (2.36 g, 10.0 mmol) and **2a**, after stirring in CH_2Cl_2 (60 mL) at 0 °C for 5 h, purification by FC (CH_2Cl_2/ethanol = 10:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **3t** (1.54 g, 5.87 mmol, 71%) as yellow crystals, m.p. 204−207 °C. − IR (KBr): $\tilde{\nu}$ = 3110, 3080, 3030, 2980, 1585, 1550, 1525, 1490, 1410, 1390, 1050, 990, 825, 700, 675 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.38 (dt, ^2J =

4.0, ^3J = 4.9 Hz, 1 H, 7-H$_{syn}$), 2.30 (dt, ^2J = 4.0, ^3J = 9.0 Hz, 1 H, 7-H$_{anti}$), 2.78 (dd, ^3J = 4.9, ^3J = 9.0 Hz, 2 H, 1-H, 6-H), 7.97−8.00 (m, 4 H, Ar-H), 8.79−8.81 (m, 4 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 225 (12200), 305 (14400) nm. − $C_{15}H_{12}N_4$ (248.3): calcd. C 72.56, H 4.87, N 22.56; found C 72.54, H 4.97, N 22.39.

2,5-Bis(2-pyrazyl)-3,4-diazanorcaradiene (3u): This compound was prepared according to General Procedure (1). Compounds **1u** (414 mg, 1.74 mmol) and **2a**, after stirring in CH_2Cl_2 (25 mL) at room temp. for 12 h and purification by FC (CH_2Cl_2/EtOAc = 2:1), yielded **3u** (342 mg, 1.37 mmol, 79%) as yellow crystals, m.p. 204−205 °C. − IR (KBr): $\tilde{\nu}$ = 3070, 2990, 1460, 1410, 1370, 1165, 1105, 1055, 1030, 1005, 845, 780, 750 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.27 (dt, ^2J = 3.6, ^3J = 4.7 Hz, 1 H, 7-H$_{syn}$), 2.29 (dt, ^2J = 3.6, ^3J = 9.1 Hz, 1 H, 7-H$_{anti}$), 3.42 (dd, ^3J = 4.7, ^3J = 9.1 Hz, 2 H, 1-H, 6-H), 8.67−8.69 (m, 4 H, Ar-H), 9.62−9.64 (m, 2 H, Ar-H). − MS (EI, 70 eV): *m/z* (%) = 250 (100) [M$^+$]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 261 (5440), 337 (19500) nm. − $C_{13}H_{10}N_6$ (250.3): calcd. N 33.58; found N 33.31.

2,5-Bis(methylthio)-3,4-diazanorcaradiene (7v): This compound was prepared according to General Procedure (1). Compounds **1v** (510 mg, 2.93 mmol) and **2a**, after stirring in Et_2O (15 mL) at room temp. for 6 h, yielded **7v** (321 mg, 1.70 mmol, 58%) as a colourless precipitate, m.p. 125−127 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 3015, 2960, 1540, 1370, 1320, 1120, 1090, 1070 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.42 (dt, ^2J = 4.5, ^3J = 8.9 Hz, 7-H$_{syn}$), 1.73 (dt, ^2J = 4.5, ^3J = 4.7 Hz, 1 H, 7-H$_{anti}$), 2.21 (dd, ^3J = 8.9, ^3J = 4.7 Hz, 2 H, 1-H, 6-H), 2.53 (s, 6 H, SCH_3). − MS (HR): calcd: 186.0285, found 186.0281.

2-Methoxy-5-methylthio-3,4-diazanorcaradiene (7w): This compound was prepared according to General Procedure (1). Compounds **1w** (364 mg, 2.30 mmol) and **2a**, after stirring in Et_2O (15 mL) at room temp. for 5 h, yielded **7w** (317 mg, 1.86 mmol, 81%) as a colourless precipitate, m.p. 78−80 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 3020, 3000, 2950, 2940, 1590, 1455, 1390, 1370, 1260, 1060, 995 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.44 (ddd, 1 H, ^3J = 9.0, ^3J = 9.1, ^2J = 4.5 Hz, 7-H$_{syn}$), 1.60 (ddd, ^3J = 4.7, ^3J = 4.7, ^2J = 4.5 Hz, 1 H, 7-H$_{anti}$), 2.08 (ddd, ^3J = 7.7, ^3J = 9.1, ^3J = 4.7 Hz, 1 H, 1-H), 2.26 (ddd, ^3J = 7.7, ^3J = 9.0, ^3J = 4.7 Hz, 1 H, 6-H), 2.50 (s, 3 H, SCH_3), 3.89 (s, 3 H, OCH_3). − MS (HR): calcd: 170.0514, found 170.0511.

2,5-Dimethoxy-3,4-diazanorcaradiene (7x): This compound was prepared according to General Procedure (1). Compounds **1x** (283 mg, 1.99 mmol) and **2a**, after stirring in Et_2O (15 mL) at room temp. for 4.5 h, yielded **7x** (270 mg, 1.75 mmol, 88%) as a colourless precipitate, m.p. 67−69 °C. − IR (KBr): $\tilde{\nu}$ = 3120, 3083, 2995, 2555, 1620, 1590, 1460, 1390, 1250, 1050, 1015, 1000, 775 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.51 (dt, ^2J = 4.6, ^3J = 9.1 Hz, 1 H, 7-H$_{syn}$), 1.49 (dt, ^2J = 4.6, ^3J = 4.6 Hz, 1 H, 7-H$_{anti}$), 2.14 (dd, ^3J = 9.1, ^3J = 4.6 Hz, 2 H, 1-H, 6-H), 3.86 (s, 6 H, OCH_3). − MS (HR): calcd: 154.0742, found 154.0745.

2-Methylthio-5-phenyl-3,4-diazanorcaradiene (7y): This compound was prepared according to General Procedure (1). Compounds **1y** (320 mg, 1.57 mmol) and **2a**, after stirring in Et_2O (10 mL) at room temp. for 4 h, yielded **7y** (161 mg, 0.744 mmol, 47%) as a colourless precipitate, m.p. 138−141 °C. − IR (KBr): $\tilde{\nu}$ = 3055, 3000, 2925, 1540, 1505, 1450, 1395, 1380, 1130, 1090, 1060, 780, 700 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.39 (ddd, ^3J = 9.0, ^3J = 9.2, ^2J = 4.0 Hz, 1 H, 7-H$_{syn}$), 1.95 (ddd, ^3J = 4.9, ^3J = 4.9, ^2J = 4.0 Hz, 1 H, 7-H$_{anti}$), 2.35 (ddd, ^3J = 7.7, ^3J = 9.2, ^3J = 4.9 Hz, 1 H, 1-H), 2.56 (ddd, ^3J = 7.7, ^3J = 9.0, ^3J = 4.9 Hz, 1 H, 6-H), 2.60 (s, 3 H, SCH_3), 7.41−7.48 (m, 3 H, Ar-H), 8.03−8.07 (m, 2 H, Ar-H). − MS (HR): calcd: 216.0721, found 216.0726.

2-Methoxy-5-phenyl-3,4-diazanorcaradiene (7z): This compound was prepared according to General Procedure (1). Compounds **1z** (417 mg, 2.17 mmol) and **2a**, after stirring in Et_2O (15 mL) at room temp. for 5 h, yielded **7z** (233 mg, 1.16 mmol, 54%) as a colourless precipitate, m.p. 106−107 °C. − IR (KBr): $\tilde{\nu}$ = 3050, 3030, 3000, 2955, 1575, 1450, 1390, 1240, 1000, 770, 690 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.41 (ddd, ^3J = 9.0, ^3J = 9.2, ^2J = 4.4 Hz, 1 H, 7-H$_{syn}$), 1.79 (ddd, ^3J = 4.6, ^3J = 4.7, ^2J = 4.4 Hz, 1 H, 7-H$_{anti}$), 2.20 (ddd, ^3J = 7.8, ^3J = 9.2, ^3J = 4.7 Hz, 1 H, 1-H), 2.63 (ddd, ^3J = 7.8, ^3J = 9.0, ^3J = 4.7 Hz, 1 H, 6-H), 3.98 (s, 3 H, OCH_3), 7.43−7.46 (m, 3 H, Ar-H), 7.99−8.03 (m, 2 H, Ar-H). − MS (HR): calcd: 200.0950, found 200.0945.

Synthesis of 7,7-Dimethyl-3,4-diazanorcaradienes 4d, 4e, 4g, 4i, 4k−4u, 8v and 8w

7,7-Dimethyl-2,5-bis(trifluoromethyl)-3,4-diazanorcaradiene (4d): This compound was prepared according to General Procedure (2). Compounds **1d** (890 mg, 4.08 mmol) and **2b** (830 mg, 12.2 mmol), after stirring in CCl_4 (2 mL) at room temp. until the red colour of the tetrazine had disappeared and purification by bulb-tube distillation (70 °C/0.01 Torr), yielded **4d** (845 mg, 3.87 mmol, 95%) as yellow crystals. − IR (film): $\tilde{\nu}$ = 3060, 2980, 2940, 2880, 1570, 1425, 1400, 1380, 1325, 1285, 1200, 1140, 1080, 1060, 1040, 960, 750 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.69 (s, 3 H, 7-CH_3-*syn*), 1.53 (s, 3 H, 7-CH_3-*anti*), 2.49 (s, 2 H, 1-H, 6-H). − Because of the high moisture sensitivity, no correct elemental analysis for compound **4d** could be obtained.

7,7-Dimethyl-2,5-diphenyl-3,4-diazanorcaradiene (4e): This compound was prepared according to General Procedure (2). Compounds **1e** (1.98 g, 8.46 mmol) and **2b** (3.50 g, 51.4 mmol), after stirring in Et_2O (20 mL) at room temp. for 4 weeks and purification by recrystallization (Et_2O/*n*-hexane), yielded **4e** (2.21 g, 7.32 mmol, 86%) as yellow crystals, m.p. 153−154 °C, ref. m.p. 156−157 °C.[17] − IR (KBr): $\tilde{\nu}$ = 3060, 3020, 2930, 1535, 1500, 1440, 1390, 770, 720, 690 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.63 (s, 3 H, 7-CH_3-*syn*), 1.61 (s, 3 H, 7-CH_3-*anti*), 2.45 (s, 2 H, 1-H, 6-H), 7.0−8.0 (m, 10 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.5 (quat. C, 1 C), 15.0 (−CH_3, 1 C), 25.9 (−CH_3, 1 C), 31.9 (=CH, 2 C), 127.7 (=CH, 4 C), 128.5 (=CH, 4 C), 130.8 (=CH, 2 C), 137.3 (quat. C, 2 C), 157.6 (=CH, 2 C). − UV/Vis (CH_3CN): λ_{max} (ε) = 269 (22000), 326 (14900) nm.

7,7-Dimethyl-2,5-bis(*p*-tolyl)-3,4-diazanorcaradiene (4g): This compound was prepared according to General Procedure (2). Compounds **1g** (2.00 g, 5.15 mmol) and **2b** (2.00 g, 29.4 mmol), after stirring in CH_2Cl_2 (20 mL) under reflux for 40 h and purification by FC (CH_2Cl_2/EtOAc = 1:1), yielded **4g** (1.90 g, 6.20 mmol, 83%) as yellow crystals, m.p. 204−205 °C. − IR (KBr): $\tilde{\nu}$ = 3050, 2950, 2890, 1625, 1545, 1400, 1190, 1125, 840, 780, 730 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.68 (s, 3 H, 7-CH_3-*syn*), 1.66 (s, 3 H, 7-CH_3-*anti*), 2.42 (s, 6 H, Ar-CH_3), 2.46 (s, 2 H, 1-H, 6-H), 7.26−7.96 (m, 8 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 260 (9100), 325 (14100) nm. − $C_{21}H_{22}N_2$ (302.4): calcd. C 83.40, H 7.33, N 9.26; found C 83.15, H 7.13, N 9.27.

2,5-Bis(*p*-methoxyphenyl)-7,7-dimethyl-3,4-diazanorcaradiene (4i): This compound was prepared according to General Procedure (2). Compounds **1i** (3.00 g, 10.2 mmol) and **2b** (2.00 g, 29.4 mmol), after stirring in CH_2Cl_2 (80 mL) under reflux for 7 d, purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/EtOAc), yielded **4i** (630 mg, 1.90 mmol, 53%) as yellow crystals,

m.p. 196 °C. − IR (KBr): $\tilde{\nu}$ = 3010, 2940, 2850, 1600, 1510, 1410, 1390, 1300, 1250, 1170, 840, 800 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.67 (s, 3 H, 7-CH_3-*syn*), 1.67 (s, 3 H, 7-CH_3-*anti*), 2.45 (s, 2 H, 1-H, 6-H), 3.87 (s, 6 H, OCH_3), 7.00−8.00 (m, 8 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 268 (8320), 336 (23400) nm. − $C_{21}H_{22}N_2O_2$ (334.4): calcd. C 75.42, H 6.63, N 8.38; found C 75.36, H 6.60, N 8.33.

2,5-Bis(*p*-chlorophenyl)-7,7-dimethyl-3,4-diazanorcaradiene (4k): This compound was prepared according to General Procedure (2). Compounds **1k** (2.00 g, 4.76 mmol) and **2b** (2.00 g, 29.4 mmol), after stirring in CH_2Cl_2 (20 mL) under reflux for 7 d, purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/EtOAc), yielded **4k** (1.35 g, 5.10 mmol, 75%) as yellow crystals, m.p. 238 °C. − IR (KBr): $\tilde{\nu}$ = 3080, 2960, 2930, 1590, 1570, 1390, 1090, 1010, 860, 840, 740, 610 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.70 (s, 3 H, 7-CH_3-*syn*), 1.68 (s, 3 H, 7-CH_3-*anti*), 2.43 (s, 2 H, 1-H, 6-H), 7.10−8.00 (m, 8 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 260 (7760), 325 (20900) nm. − $C_{19}H_{16}Cl_2N_2$ (343.3): calcd. C 66.48, H 4.70, N 8.16; found C 66.70, H 4.74, N 8.16.

7,7-Dimethyl-2,5-bis(*p*-trifluoromethylphenyl)-3,4-diazanorcaradiene (4l): This compound was prepared according to General Procedure (2). Compounds **1l** (2.00 g, 5.40 mmol) and **2b** (760 mg, 11.2 mmol), after stirring in CH_2Cl_2 (20 mL) under reflux for 20 h and purification by recrystallization (CH_2Cl_2/PE), yielded **4l** (1.98 g, 4.80 mmol, 89%) as yellow crystals, m.p. 234−235 °C. − IR (KBr): $\tilde{\nu}$ = 3050, 2950, 1625, 1550, 1420, 1330, 1185, 1130, 1075, 860, 710 cm^{-1}. − ^1H NMR (60 MHz, $CDCl_3$): δ = 0.79 (s, 3 H, 7-CH_3-*syn*), 1.80 (s, 3 H, 7-CH_3-*anti*), 2.61 (s, 2 H, 1-H, 6-H), 7.76−8.31 (m, 8 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 254 (18100), 322 (15200) nm. − $C_{21}H_{16}F_6N_2$ (410.4): calcd. C 61.47, H 3.93, N 6.83; found C 61.52, H 3.98, N 6.82.

7,7-Dimethyl-2,5-bis(1-methyl-1*H*-pyrrol-2-yl)-3,4-diazanorcaradiene (4m): This compound was prepared according to General Procedure (2). Compounds **1m** (500 mg, 2.08 mmol) and **2b** (845 mg, 12.4 mmol), after stirring in $CHCl_3$ (10 mL) under reflux for 20 h and another 114 h at room temp., purification by FC (CH_2Cl_2/EtOAc = 1:2) and recrystallization (EtOAc/PE), yielded **4m** (430 mg, 1.53 mmol, 74%) as yellow crystals, m.p. 133−134 °C. − IR (KBr): $\tilde{\nu}$ = 3120, 3020, 2970, 1550, 1450, 1430, 1315, 1245, 1090, 1065, 1030, 1010, 990, 960, 735, 725, 720 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.65 (s, 3 H, 7-CH_3-*syn*), 1.51 (s, 3 H, 7-CH_3-*anti*), 2.35 (s, 2 H, 1-H, 6-H), 4.09 (s, 6 H, NCH_3), 6.21 (dd, ^3J = 3.9, ^3J = 2.6 Hz, 2 H, Ar-H), 6.67 (dd, ^3J = 3.9, ^4J = 1.8 Hz, 2 H, Ar-H), 6.78 (dd, ^4J = 1.8, ^3J = 2.6 Hz, 2 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.7 (−CH_3, 1 C), 15.2 (quat. C, 1 C), 25.9 (−CH_3, 1 C), 30.2 (=CH, 2 C), 38.2 (−CH_3, 2 C), 108.1 (=CH, 2 C), 115.9 (=CH, 2 C), 128.7 (=CH, 2 C), 130.7 (quat. C, 2 C), 149.4 (quat. C, 2 C). − MS (EI, 70 eV): *m*/*z* (%) = 280 (100) [M^+]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 298 (3270), 366 (30300) nm. − $C_{17}H_{20}N_4$ (280.4): calcd. C 72.82, H 7.19, N 19.98; found C 72.81, H 7.25, N 19.73.

7,7-Dimethyl-2,5-bis(2-thienyl)-3,4-diazanorcaradiene (4n): This compound was prepared according to General Procedure (2). Compounds **1n** (1.89 g, 7.67 mmol) and **2b** (1.07 g, 15.7 mmol), after stirring in CH_2Cl_2 (50 mL) at room temp. for 24 h, purification by FC (CH_2Cl_2/ethanol = 7:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **4n** (1.47 g, 5.13 mmol, 67%) as yellow crystals, m.p. 170−172 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 3080, 3030, 2980, 2950, 2870, 1530, 1510, 1430, 1380, 1250, 1235, 1075, 1050, 845, 830, 765, 700 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.72 (s, 3 H, 7-CH_3-*syn*), 1.80 (s, 3 H, 7-CH_3-*anti*), 2.55 (s, 2 H, 1-H, 6-H), 6.98−7.25 (m, 2 H, Ar-H), 7.35−7.66 (m, 4 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 277 (16000), 365 (30200) nm. − $C_{15}H_{14}N_2S_2$ (286.4): calcd. C 62.90, H 4.92, N 9.78; found C 62.95, H 4.85, N 9.80.

7,7-Dimethyl-2,5-bis(2-thiazolyl)-3,4-diazanorcaradiene (4o): This compound was prepared according to General Procedure (2). Compounds **1o** (900 mg, 3.62 mmol) and **2b** (820 mg, 12.0 mmol), after stirring in CH_2Cl_2 (70 mL) at room temp. for 1 h and purification by recrystallization (CH_2Cl_2/*n*-hexane), yielded **4o** (620 mg, 2.15 mmol, 59%) as yellow crystals, m.p. 136−137 °C. − IR (KBr): $\tilde{\nu}$ = 3130, 3100, 2970, 2940, 2870, 1540, 1480, 1425, 1285, 1195, 1105, 1065, 1030, 970, 880, 790, 760, 745 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.80 (s, 3 H, 7-CH_3-*syn*), 1.76 (s, 3 H, 7-CH_3-*anti*), 3.28 (s, 2 H, 1-H, 6-H), 7.60 (d, ^3J = 3.2 Hz, 2 H, Ar-H), 8.08 (d, ^3J = 3.2 Hz, 2 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 240 (5930), 289 (6910), 376 (16900) nm. − $C_{13}H_{12}N_4S_2$ (288.4): calcd. C 54.14, H 4.19, N 19.43; found C 53.75, H 4.18, N 19.19.

2,5-Bis(2-furanyl)-7,7-dimethyl-3,4-diazanorcaradiene (4p): This compound was prepared according to General Procedure (2). Compounds **1p** (436 mg, 2.04 mmol) and **2b** (580 mg, 8.52 mmol), after stirring in CH_2Cl_2 (8 mL) under reflux for 11 h followed by 51 h at room temp. and purification by FC (EtOAc), yielded **4p** (416 mg, 1.64 mmol, 80%) as yellow crystals, m.p. 159−160 °C. − IR (KBr): $\tilde{\nu}$ = 3135, 3035, 2960, 2940, 2880, 1580, 1525, 1480, 1470, 1410, 1230, 1160, 1060, 1020, 965, 910, 890, 770, 750 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.70 (s, 3 H, 7-CH_3-*syn*), 1.56 (s, 3 H, 7-CH_3-*anti*), 2.58 (s, 2 H, 1-H, 6-H), 6.56 (dd, ^3J = 3.5, ^3J = 1.8 Hz, 2 H, Ar-H), 7.14 (dd, ^3J = 3.5, ^4J = 0.8 Hz, 2 H, Ar-H), 7.61 (dd, 2 H, ^3J = 1.8, ^4J = 0.8 Hz, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.9 (−CH_3, 1 C), 15.3 (quat. C, 1 C), 26.0 (−CH_3, 1C), 31.0 (=CH, 2 C), 112.3 (=CH, 2 C), 112.4 (=CH, 2 C), 145.2 (quat. C, 2 C), 149.4 (quat. C, 2 C), 152.6 (quat. C, 2 C). − MS (EI, 70 eV): *m*/*z* (%) = 254 (100) [M^+]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 291 (4300), 360 (22400) nm. − $C_{15}H_{14}N_2O_2$ (254.3): calcd. C 70.87, H 5.55, N 11.02; found C 70.87, H 5.63, N 11.06.

7,7-Dimethyl-2,5-bis(2-methyl-1,3,4-oxadiazol-5-yl)-3,4-diazanorcaradiene (4q): This compound was prepared according to General Procedure (2). Compounds **1q** (126 mg, 0.512 mmol) and **2b** (109 mg, 1.60 mmol), after stirring in CH_2Cl_2 (10 mL) at room temp. for 1 h, purification by FC (CH_2Cl_2/ethanol = 20:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **4q** (142 mg, 0.496 mmol, 97%) as yellow crystals, m.p. 195−197 °C. − IR (KBr): $\tilde{\nu}$ = 3015, 2940, 2920, 1550, 1345, 1240, 1185, 1025, 975 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.72 (s, 3 H, 7-CH_3-*syn*), 1.65 (s, 3 H, 7-CH_3-*anti*), 2.70 (s, 6 H, Ar-CH_3), 3.17 (s, 2 H, 1-H, 6-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 11.3 (−CH_3, 2 C), 14.9 (−CH_3, 1 C), 16.1 (quat. C, 1 C), 25.4 (−CH_3, 1 C), 33.5 (=CH, 2 C), 149.5 (quat. C, 2 C), 163.0 (quat. C, 2 C), 166.1 (quat. C, 2 C). − MS (EI, 70 eV): *m*/*z* (%) = 286 (3) [M^+]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 275 (13100), 329 (11600) nm. − $C_{13}H_{14}N_6O_2$ (286.3): calcd. C 54.54, H 4.93, N 29.35; found C 54.32, H 5.20, N 29.21.

7,7-Dimethyl-2,5-bis(2-pyridyl)-3,4-diazanorcaradiene (4r): This compound was prepared according to General Procedure (2). Compounds **1r** (1.89 g, 8.00 mmol) and **2b** (1.64 g, 24.1 mmol), after stirring in CH_2Cl_2 (70 mL) at 0 °C for 3 h and purification by recrystallization (CH_2Cl_2/*n*-hexane), yielded **4r** (1.97 g, 7.13 mmol, 89%) as yellow crystals, m.p. 162−164 °C. − IR (KBr): $\tilde{\nu}$ = 3050, 3000, 2960, 2930, 2870, 1580, 1560, 1540, 1495, 1455, 1425, 1375, 1140, 1090, 990, 775, 740 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$):

δ = 0.67 (s, 3 H, 7-CH_3-*syn*), 1.68 (s, 3 H, 7-CH_3-*anti*), 3.33 (s, 2 H, 1-H, 6-H), 7.34−7.40 (m, 2 H, Ar-H), 7.75−7.82 (m, 2 H, Ar-H), 8.49−8.54 (m, 2 H, Ar-H), 8.70−8.73 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 269 (22200), 326 (14900) nm. − $C_{17}H_{17}N_4$ (276.3): calcd. C 73.89, H 5.84, N 20.27; found C 74.03, H 5.67, N 20.12.

7,7-Dimethyl-2,5-bis(3-pyridyl)-3,4-diazanorcaradiene (4s): This compound was prepared according to General Procedure (2). Compounds **1s** (1.86 g, 7.87 mmol) and **2b** (1.32 g, 19.4 mmol), after stirring in CH_2Cl_2 (50 mL) at room temp. for 24 h, purification by FC (CH_2Cl_2/ethanol = 5:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **4s** (1.43 g, 5.18 mmol, 66%) as yellow crystals, m.p. 159−160 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 3020, 2970, 2950, 2920, 2870, 1590, 1565, 1530, 1495, 1400, 1385, 1180, 1000, 955, 815, 720, 690 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.74 (s, 3 H, 7-CH_3-*syn*), 1.72 (s, 3 H, 7-CH_3-*anti*), 2.58 (s, 2 H, 1-H, 6-H), 7.42−7.47 (m, 2 H, Ar-H), 8.41−8.46 (m, 2 H, Ar-H), 8.74−8.77 (m, 2 H, Ar-H), 9.17−9.18 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 247 (12800), 320 (13500) nm. − $C_{17}H_{16}N_4$ (276.3): calcd. C 73.89, H 5.84, N 20.27 found C 74.09, H 5.64, N 20.20.

7,7-Dimethyl-2,5-bis(4-pyridyl)-3,4-diazanorcaradiene (4t): This compound was prepared according to General Procedure (2). Compounds **1t** (1.89 g, 8.00 mmol) and **2b** (1.54 g, 22.6 mmol), after stirring in CH_2Cl_2 (70 mL) at 0 °C for 24 h, purification by FC (CH_2Cl_2/ethanol = 7:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **4t** (1.60 g, 5.79 mmol, 72%) as yellow crystals, m.p. 202−205 °C. − IR (KBr): $\tilde{\nu}$ = 3010, 2930, 2900, 2850, 1580, 1520, 1480, 1400, 1380, 1110, 1050, 980, 820, 780, 690 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.71 (s, 3 H, 7-CH_3-*syn*), 1.71 (s, 3 H, 7-CH_3-*anti*), 2.57 (s, 2 H, 1-H, 6-H), 7.72−8.03 (m, 4 H, Ar-H), 8.66−8.92 (m, 4 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 241 (22200), 320 (14900) nm. − $C_{17}H_{14}N_4$ (276.3): calcd. C 73.89, H 5.84, N 20.27; found C 73.78, H 5.85, N 20.25.

7,7-Dimethyl-2,5-bis(2-pyrazinyl)-3,4-diazanorcaradiene (4u): This compound was prepared according to General Procedure (2). Compounds **1u** (477 mg, 2.00 mmol) and **2b** (544 mg, 8.00 mmol), after stirring in CH_2Cl_2 (15 mL) at room temp. for 12 min and purification by recrystallization (CH_2Cl_2/*n*-hexane), yielded **4u** (537 mg, 1.93 mmol, 97%) as yellow crystals, m.p. 173−175 °C. − IR (KBr): $\tilde{\nu}$ = 3035, 2975, 2955, 2850, 1540, 1505, 1450, 1415, 1360, 1160, 1145, 1070, 1045, 1005, 840, 790, 750 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.68 (s, 3 H, 7-CH_3-*syn*), 1.68 (s, 3 H, 7-CH_3-*anti*), 3.26 (s, 2 H, 1-H, 6-H), 8.67 (m, 4 H, Ar-H), 9.72 (m, 2 H, Ar-H). − ^{13}C NMR: (63 MHz, $CDCl_3$): δ = 15.0 (−CH_3, 1 C), 15.5 (quat. C, 1 C), 25.9 (−CH_3, 1 C), 33.5 (=CH, 2 C), 143.5 (=CH, 2 C), 144.1 (=CH, 2 C), 145.4 (=CH, 2 C), 149.9 (quat. C, 2 C), 159.4 (quat. C, 2 C). − MS (EI, 70 eV): *m*/*z* (%) = 278 (4) [M^+]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 290 (11300), 345 (15000) nm. − $C_{15}H_{14}N_6$ (278.3): calcd. N 30.20; found N 29.90.

7,7-Dimethyl-2,5-bis(methylthio)-3,4-diazanorcaradiene (8v): This compound was prepared according to General Procedure (2). Compounds **1v** (830 mg, 4.76 mmol) and **2b** (1.00 g, 14.7 mmol), after stirring in Et_2O (20 mL) at room temperature for 6 weeks and washing with *n*-pentane, yielded **8v** (570 mg, 2.65 mmol, 56%) as colourless crystals, m.p. 86.5−87.5 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 3015, 2960, 1540, 1370, 1320, 1120, 1090, 1070 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.67 (s, 3 H, 7-*CH₃-syn*), 1.27 (s, 3 H, 7-*CH₃-anti*), 1.94 (s, 2 H, 1-H, 6-H), 2.44 (s, 6 H, SCH_3). − $C_9H_{14}N_2S_2$ (214.3): calcd. C 50.44, H 6.58, N 13.14; found C 50.20, H 6.66, N 13.07.

2,5-Dimethoxy-7,7-dimethyl-3,4-diazanorcaradiene (8w): This compound was prepared according to General Procedure (2). Compounds **1w** (309 mg, 2.17 mmol) and **2b** (500 mg, 7.34 mmol), after stirring in Et_2O (20 mL) at room temperature for 6 weeks, yielded **8w** (260 mg, 1.42 mmol, 66%) as a colourless precipitate, m.p. 55.5−56.5 °C. − IR (KBr): $\tilde{\nu}$ = 2960, 1600, 1575, 1450, 1370, 1230, 1010, 965, 770 cm^{-1}. − ^1H NMR (250 MHz, nitrobenzene-d_5): δ = 0.67 (s, 3 H, 7-*CH₃-syn*), 1.20 (s, 3 H, 7-*CH₃-anti*) 1.90 (s, 2 H, 1-H, 6-H), 3.78 (s, 6 H, OCH_3). − $C_9H_{14}N_2O_2$ (182.2): calcd. C 59.33, H 7.74, N 15.46; found C 59.02, H 7.79, N 15.49.

Synthesis of the Tetracyclic Azo Compounds 5b−5d, 5o, 5q and 5r−5t

***exo,exo*-9,10-Diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarboxylic Acid (5b):** Hydrolysis of the ester **5a** (5.00 g, 20.0 mmol) with KOH (3.90 g, 70.0 mmol) in aqueous methanol (60 mL, H_2O/methanol = 1:2) and subsequent acidification with conc. HCl yielded, after recrystallization (EtOAc), **5b** (3.42 g, 15.4 mmol, 78%) as colourless crystals, m.p. 218−219 °C. − IR (KBr): $\tilde{\nu}$ = 3600−2500, 1735 cm^{-1}. − ^1H NMR (80 MHz, CD_3OD): δ = 0.00 (dt, ^2J = 7.2, ^3J = 3.6 Hz, 2 H, 3,7-H_{syn}), 0.55 (dt, ^2J = 7.2, ^3J = 7.6 Hz, 2 H, 3,7-H_{anti}), 2.00 (dd, ^3J = 3.6, ^3J = 7.6 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 5.05 (s, 2 H, COO*H*). − MS (EI, 70 eV): *m*/*z* (%) = 193 (35) [M^+ − N_2H]. − UV/Vis (methanol): λ_{max} (ε) = 370 (62) nm. − $C_{10}H_{10}N_2S_4$ (222.2): calcd. C 54.05, H 4.54, N 12.60; found C 53.99, H 4.48, N 12.57.

***exo,exo*-9,10-Diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarbonitrile (5c):** Acid **5b** (0.46 g, 2.10 mmol) and $SOCl_2$ (4.95 g, 41.2 mmol) were stirred at room temp. for 3 h. After removal of excess $SOCl_2$, addition of conc. ammonia (20 mL) in acetone (6 mL) then gave the amide (0.20 g, 0.91 mmol, 41%) as colourless crystals. A suspension of the latter and freshly distilled $POCl_3$ (8.60 g, 5.00 mL, 5.50 mmol) in 1,2-dichloroethylene (50 mL) was heated under reflux for 22 h. After concentration to dryness, the crude material was purified by recrystallization (methanol), affording **5c** (1.37 g, 7.43 mmol, 55%) as colourless crystals, m.p.168 °C. − IR (KBr): $\tilde{\nu}$ = 3100−3000, 2240 cm^{-1}. − ^1H NMR (80 MHz, $CDCl_3$): δ = 0.37 (m, 2 H, 3,7-H_{syn}), 0.85 (m, 2 H, 3,7-H_{anti}), 2.07 (m, 4 H, 2-H, 4-H, 6-H, 8-H). − MS (EI, 70 eV): *m*/*z* (%) = 155 (69) [M^+ − N_2H]. − UV/Vis (methanol): λ_{max} (ε) = 368 (83) nm. − $C_{10}H_8N_4$ (184.2): calcd. C 65.20, H 4.38, N 30.42; found C 64.98, H 4.04, N 30.28.

***exo,exo*-1,5-Bis(trifluoromethyl)-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (5d):** This compound was prepared according to General Procedure (1). Compounds **1d** (1.35 g, 6.19 mmol) and **2a**, after stirring in CCl_4 (5 mL) at room temp. for 3 h, purification by recrystallization (cyclohexane) and bulb-tube distillation (75 °C/0.01 Torr), yielded **5d** (780 mg, 2.89 mmol, 47%) as colourless crystals, m.p. 120−122 °C. − IR (KBr): $\tilde{\nu}$ = 3040, 1450, 1360, 1305, 1200, 1160, 1140, 1090, 1070, 1040, 1010, 980, 930, 920, 780 cm^{-1}. − ^1H NMR (80 MHz, $CDCl_3$): δ = 0.10 (dt, ^2J = 7.2, ^3J = 3.6 Hz, 2 H, 3,7-H_{syn}), 0.60 (dt, ^2J = 7.2, ^3J = 7.7 Hz, 2 H, 3,7-H_{anti}), 1.80 (dd, ^3J = 3.6, ^3J = 7.7 Hz, 4 H, 2-H, 4-H, 6-H, 8-H). − UV/Vis (CCl_4): λ_{max} (ε) = 366 (89) nm. − $C_{10}H_8F_6N_2$ (270.2): calcd. C 44.46, H 2.96, N 10.37; found C 44.40, H 3.09, N 10.32.

***exo,exo*-1,5-Bis(2-thiazolyl)-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (5o):** This compound was prepared according to General Procedure (1). Compounds **1o** (221 mg, 0.890 mmol) and **2a**, after stirring in CH_2Cl_2 (20 mL) at room temp. for 12 h, purification by FC (CH_2Cl_2/ethanol = 15:1) and washing with dry Et_2O, yielded **5o** (92 mg, 0.308 mmol, 35%) as yellow crystals, m.p. 163−164 °C. − IR (KBr): $\tilde{\nu}$ = 3110, 3070, 3040, 3020, 2995, 1490, 1435, 1285, 1220, 1160, 1150, 990, 915, 855, 730, 710 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.27 (dt, ^2J = 7.0, ^3J = 3.6 Hz, 2

H, 3,7-H$_{syn}$), 0.55 (dt, ^2J = 7.0, ^3J = 7.7 Hz, 2 H, 3,7-H$_{anti}$), 2.29 (dd, ^3J = 3.6, ^3J = 7.7 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 7.48 (d, ^3J = 3.3 Hz, 2 H, Ar-H), 7.95 (d, ^3J = 3.3 Hz, 2 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 6.0 (−CH_2−, 2 C), 19.2 (=CH, 4 C), 74.2 (quat. C, 2 C), 120.1 (=CH, 2 C), 143.2 (=CH, 2 C), 171.6 (quat. C, 2 C). − MS (EI, 70 eV): *m*/*z* (%) = 271 (97) [M$^+$ − N_2H]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 252 (11400), 387 (43) nm. − $C_{14}H_{12}N_4S_2$ (300.4): calcd. C 55.98, H 4.03, N 18.65; found C 55.68, H 4.23, N 18.39.

***exo,exo*-1,5-Bis(2-methyl-1,3,4-oxadiazol-5-yl)-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (5q):** This compound was prepared according to General Procedure (1). Compounds **1q** (165 mg, 0.670 mmol) and **2a**, after stirring in CH_2Cl_2 (20 mL) at room temp. for 1 h, purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **5q** (180 mg, 0.603 mmol, 90%) as a colourless solid, m.p. 183 °C. − IR (KBr): $\tilde{\nu}$ = 2995, 1580, 1560, 1380, 1235, 1090, 1070, 1020, 935, 790, 675 cm^{-1}. − ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 0.33 (dt, ^2J = 7.0, ^3J = 3.6 Hz, 2 H, 3,7-H$_{syn}$), 0.79 (dt, ^2J = 7.0, ^3J = 7.7 Hz, 2 H, 3,7-H$_{anti}$), 2.12 (dd, ^3J = 3.6, ^3J = 7.7 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 2.63 (s, 6 H, Ar-CH_3). − ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 6.8 (−CH_2−, 2 C), 11.3 (−CH_3, 2 C), 15.9 (=CH, 4 C), 69.1 (quat. C, 2 C), 165.7 (quat. C, 2 C), 166.7 (quat. C, 2 C). − MS (EI, 70 eV): *m*/*z* (%) = 269 (100) [M$^+$ − N_2H]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 383 (30) nm. − $C_{14}H_{14}N_6O_2$ (298.4): calcd. C 56.35, H 4.73, N 28.16; found C 56.15, H 5.10, N 27.71.

***exo,exo*-1,5-Bis(2-pyridyl)-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (5r):** This compound was prepared according to General Procedure (3). Compounds **3r** (838 mg, 3.37 mmol) and **2a**, after stirring in CH_2Cl_2 (25 mL) at room temp. for 24 h, purification by FC (CH_2Cl_2/EtOAc/*n*-hexane = 1:5:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **5r** (576 mg, 2.00 mmol, 59%) as a colourless solid, m.p. 168−170 °C. − IR (KBr): $\tilde{\nu}$ = 3070, 3020, 2940, 1595, 1575, 1475, 1440, 1325, 1155, 1100, 1075, 1050, 1040, 825, 795, 780, 760, 705, 625 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.21 (dt, ^2J = 6.4, ^3J = 3.6 Hz, 2 H, 3,7-H$_{syn}$), 0.54 (dt, ^2J = 6.4, ^3J = 7.7 Hz, 2 H, 3,7-H$_{anti}$), 2.22 (dd, ^3J = 3.6, ^3J = 7.7 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 7.29−7.35 (m, 2 H, Ar-H), 7.80−7.87 (m, 2 H, Ar-H), 8.12−8.16 (m, 2 H, Ar-H), 8.73−8.76 (m, 2 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 6.1 (−CH_3, 2 C), 17.9 (=CH, 4 C), 75.0 (quat. C, 2 C), 122.3 (=CH, 2 C), 122.6 (=CH, 2 C), 136.6 (=CH, 2 C), 149.3 (=CH, 2 C), 161.6 (quat. C, 2 C). − UV/Vis (CH_3CN): λ_{max} (ε) = 259 (7430), 379 (58) nm. − $C_{18}H_{16}N_4$ (288.4): calcd. C 74.98, H 5.59, N 19.43; found C 75.17, H 5.52, N 19.38.

***exo,exo*-1,5-Bis(3-pyridyl)-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (5s):** This compound was prepared according to General Procedure (3). Compounds **3s** (750 mg, 3.02 mmol) and **2a**, after stirring in CH_2Cl_2 (25 mL) at room temp. for 24 h, purification by FC (CH_2Cl_2/ethanol = 10:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **5s** (200 mg, 0.693 mmol, 23%) as a colourless solid, m.p. 134−137 °C. − IR (KBr): $\tilde{\nu}$ = 3080, 3030, 2970, 1570, 1515, 1475, 1410, 1315, 1065, 1015, 810, 800, 710 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.49 (dt, ^2J = 6.5, ^3J = 3.7 Hz, 2 H, 3,7-H$_{syn}$), 0.90 (dt, ^2J = 6.5, ^3J = 7.7 Hz, 2 H, 3,7-H$_{anti}$), 1.95 (dd, ^3J = 3.7, ^3J = 7.7 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 7.47−7.52 (m, 2 H, Ar-H), 8.17−8.22 (m, 2 H, Ar-H), 8.73−8.77 (m, 2 H, Ar-H), 9.12−9.13 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 266 (7100), 383 (90) nm. − $C_{18}H_{16}N_4$ (288.4): calcd. C 74.96, H 5.59, N 19.42; found C 74.75, H 5.66, N 18.97.

***exo,exo*-1,5-Bis(4-pyridyl)-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (5t):** This compound was prepared according to General Procedure (3). Compounds **3t** (1.00 g, 4.03 mmol) and **2a**, after stirring in CH_2Cl_2 (25 mL) at room temp. for 24 h, purification by FC (CH_2Cl_2/ethanol = 10:1) and recrystallization (CH_2Cl_2/*n*-hexane), yielded **5t** (1.90 g, 7.36 mmol, 74%) as a colourless solid, m.p. 160−162 °C. − IR (KBr): $\tilde{\nu}$ = 3080, 3040, 2920, 1585, 1550, 1520, 1485, 1410, 1400, 1380, 1310, 1265, 1055, 1035, 990, 805, 770, 670, 620 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.43 (dt, ^2J = 6.6, ^3J = 3.7 Hz, 2 H, 3,7-H$_{syn}$), 0.83 (dt, ^2J = 6.6, ^3J = 7.7 Hz, 2 H, 3,7-H$_{anti}$), 1.93 (dd, ^3J = 3.6, ^3J = 7.7 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 7.79−7.82 (m, 4 H, Ar-H), 8.80−8.83 (m, 4 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 250 (6890), 405 (73) nm. − $C_{18}H_{16}N_4$ (288.4): calcd. C 74.98, H 5.59, N 19.42; found C 74.24, H 5.54, N 18.90.

Synthesis of Tetramethyl-Substituted Tetracyclic Azo Compounds 6a−6e, 6o, 6q and 6r

Dimethyl *exo,exo*-3,3,7,7-Tetramethyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarboxylate (6a): This compound was prepared according to General Procedure (2). Compounds **1a** (2.80 g, 14.1 mmol) and **2b** (3.81 g, 55.9 mmol), after stirring in CH_3CN (30 mL) at room temp. for 96 h, purification by FC (CH_2Cl_2) and recrystallization (methanol), yielded **6a** (2.73 g, 8.91 mmol, 63%) as colourless crystals, m.p. 149−150 °C. − IR (KBr): $\tilde{\nu}$ = 3020, 2840, 1740, 1720 cm^{-1}. − ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 0.92 (s, 6 H, 3,7-CH_3-*syn*), 1.01 (s, 6 H, 3,7-CH_3-*anti*), 1.78 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 4.01 (s, 6 H, OCH_3). − MS (EI, 70 eV): *m*/*z* (%) = 263 (42) [M^+ − N_2 − CH_3]. − UV/Vis (methanol): λ_{max} (ε) = 372 (134) nm. − $C_{16}H_{22}N_2O_4$ (306.2): calcd. C 62.72, H 7.24, N 9.14; found C 62.94, H 7.19, N 9.30.

***exo,exo*-3,3,7,7-Tetramethyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]-dec-9-ene-1,5-dicarboxylic Acid (6b):** Hydrolysis of ester **6a** (5.10 g, 16.7 mmol) with KOH (3.90 g, 70.0 mmol) in aqueous methanol (90 mL, H_2O/methanol = 1: 2) and subsequent acidification with conc. HCl (water/ice bath) gave **6b** (4.50 g, 16.2 mmol, 97%) as colourless crystals, m.p. 273−275 °C. − IR (KBr): $\tilde{\nu}$ = 1715 cm^{-1}. − ^{1}H NMR (80 MHz, CD_3OD): δ = 0.93 (s, 6 H, 3,7-CH_3-*syn*), 0.97 (s, 6 H, 3,7-CH_3-*anti*), 1.88 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 5.02 (s, broad, 2 H, COO*H*). − MS (EI, 70 eV): *m*/*z* = 278 [M$^+$]. − UV/Vis (methanol): λ_{max} (ε) = 373 (130) nm. − $C_{14}H_{18}N_2O_4$ (278.3): calcd. C 60.41, H 6.53, N 10.07; found C 60.38, H 6.52, N 10.10.

***exo,exo*-3,3,7,7-Tetramethyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]-dec-9-ene-1,5-dicarbonitrile (6c):** Dicarboxylic acid **6b** (4.00 g, 14.4 mmol) and $SOCl_2$ (24.8 g, 206 mmol) were stirred at room temp. for 3 h. After removal of excess $SOCl_2$, addition of 33% aqueous ammonia (75 mL) then gave the amide (3.70 g, 13.4 mmol, 93%) as colourless crystals. Trifluoroacetic anhydride (3.28 mL, 23.6 mmol) in 1,4-dioxane (8 mL) was added dropwise to a solution of the amide (2.00 g, 7.20 mmol) in 1,4-dioxane (20 mL) and dry pyridine (3.48 mL, 43.0 mmol). After 19 h of stirring at room temp., the crude material was isolated. Recrystallisation (methanol) yielded **6c** (1.50 g, 62.5 mmol, 86%) as colourless crystals, m.p. 229−231 °C. − IR (KBr): $\tilde{\nu}$ = 2235, 2250 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 (s, 6 H, 3,7-CH_3-*syn*), 1.10 (s, 6 H, 3,7-CH_3-*anti*), 1.86 (s, 4 H, 2-H, 4-H, 6-H, 8-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 18.6 (−CH_3, 2 C), 24.7 (quat. C, 2 C), 30.1 (−CH_3, 2 C), 35.8 (=CH, 4 C), 66.2 (quat. C, 2 C), 118.9 (quat. C, 2 C). − MS (EI, 70 eV): *m*/*z* = 240 [M$^+$]. − UV/Vis (methanol): λ_{max} (ε) = 371 (226) nm. − $C_{14}H_{16}N_4$ (240.3): calcd. C 69.96, H 6.72, N 23.52; found C 69.90, H 6.78, N 23.06.

***exo,exo*-3,3,7,7-Tetramethyl-1,5-bis(trifluoromethyl)-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (6d):** This compound was prepared according to General Procedure (2). Compounds **1d** (1.03 g,

4.72 mmol) and **2b** (650 mg, 9.56 mmol), after stirring in CCl_4 (7 mL) under reflux for 8 h and recrystallization (methanol), yielded **6d** (835 mg, 2.56 mmol, 54%) as colourless crystals, m.p. 163−164 °C. − IR (KBr): $\tilde{\nu}$ = 3040, 2980, 2940, 2880, 1455, 1360, 1300, 1190, 1170, 1155, 1080, 1050, 1020, 910, 730 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.96 (s, 6 H, 3,7-CH_3-*syn*), 1.02 (s, 6 H, 3,7-CH_3-*anti*), 1.72 (s, 4 H, 2-H, 4-H, 6-H, 8-H). − UV/Vis (CCl_4): λ_{max} (ε) = 369 (187) nm. − $C_{14}H_{16}F_6N_2$ (326.3): calcd. C 51.50, H 4.97, N 8.58; found C 51.24, H 5.17, N 8.40.

***exo,exo*-3,3,7,7-Tetramethyl-1,5-diphenyl-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (6e):** This compound was prepared according to General Procedure (4). A solution of **4e** (500 mg, 1.82 mmol) and **2b** (1.20 g, 17.6 mmol) in CH_3CN (4 mL) was pressurized in a suitable reaction vessel to 8.0 kbar at 100 °C for 65 h. Purification by FC (Et_2O/PE = 1:1) and recrystallization (methanol) yielded **6e** (155 mg, 0.453 mmol, 25%) as colourless crystals, m.p. 180−182 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 3040, 3000, 2960, 2930, 2880, 1600, 1580, 1515, 1490, 1445, 1375, 1315, 1255, 1175, 1130, 1020, 945, 820, 750, 695, 670 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.11 (s, 6 H, 3,7-CH_3-*syn*), 1.23 (s, 6 H, 3,7-CH_3-*anti*), 1.75 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 7.50−7.57 (m, 6 H, Ar-H), 7.72−7.75 (m, 4 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.3 (−CH_3, 2 C), 24.4 (quat. C, 2 C), 30.9 (−CH_3, 2 C), 38.1 (=CH, 4 C), 78.2 (quat. C, 2 C), 127.8 (=CH, 2 C), 128.1 (=CH, 4 C), 128.7 (=CH, 4 C), 143.5 (quat. C, 2 C). − MS (EI, 70 eV): *m*/*z* (%) = 314 (14) [M^+ − N_2H]. − UV/Vis (CH_3CN): λ_{max} (ε) = 339 (138), 387 (172) nm. − $C_{24}H_{26}N_2$ (342.5): calcd. C 84.17, H 7.65, N 8.18; found C 84.05, H 7.68, N 8.19.

***exo,exo*-3,3,7,7-Tetramethyl-1,5-bis(2-thiazolyl)-9,10-diaza-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (6o):** This compound was prepared according to General Procedure (4). A solution of **4o** (574 mg, 1.99 mmol) and **2b** (272 mg, 4.00 mmol) in CH_2Cl_2 (4 mL) was pressurized in a suitable reaction vessel to 7.6 kbar at 56 °C for 5 days. Purification by FC ($CHCl_3$/ethanol = 1:1) and recrystallization (CH_2Cl_2/*n*-hexane) yielded **6o** (518 mg, 1.47 mmol, 74%) as colourless crystals, m.p. 220 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 3075, 2995, 2975, 2870, 1490, 1290, 1220, 1340, 1150, 1135, 1110, 1050, 960, 890, 850, 725 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.91 (s, 6 H, 3,7-CH_3-*syn*), 1.08 (s, 6 H, 3,7-CH_3-*anti*), 2.20 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 7.49 (d, ^3J = 3.2 Hz, 2 H, Ar-H), 7.49 (d, ^3J = 3.2 Hz, 2 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 18.6 (−CH_3, 2 C), 24.2 (quat. C, 2 C), 30.5 (−CH_3, 2 C), 39.3 (=CH, 4 C), 77.5 (quat. C, 2 C), 120.0 (=CH, 2 C), 143.3 (=CH, 2 C), 173.0 (quat. C, 2 C). − MS (EI, 70 eV): *m*/*z* (%) = 315 (11) [M^+ − N_2 − CH_3]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 242 (12200), 378 (132) nm. − $C_{18}H_{20}N_4S_2$ (356.5): calcd. C 60.73, H 5.66, N 15.72; found C 60.76, H 5.59, N 15.75.

***exo,exo*-3,3,7,7-Tetramethyl-1,5-bis(2-methyl-1,3,4-oxadiazol-5-yl)-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (6q):** This compound was prepared according to General Procedure (4). A solution of **4q** (80.9 mg, 0.283 mmol) and **2b** (272 mg, 4.00 mmol) in CH_2Cl_2 (4 mL) was pressurized to 7.3 kbar in a suitable reaction vessel at 55 °C for 5 d. Purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/*n*-hexane) yielded **6q** (88.0 mg, 0.248 mmol, 88%) as colourless crystals, m.p. 201−202 °C. − IR (KBr): $\tilde{\nu}$ = 2950, 2920, 2870, 1585, 1520, 1380, 1340, 1235, 1110, 1080, 1050, 1020, 965 cm^{-1}. − ^1H NMR (250 MHz, CD_2Cl_2): δ = 1.02 (s, 6 H, 3,7-CH_3-*syn*), 1.09 (s, 6 H, 3,7-CH_3-*anti*), 1.99 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 2.65 (s, 6 H, Ar-CH_3). − ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 11.4 (−CH_3, 2 C), 19.1 (−CH_3, 2 C), 24.8 (quat. C, 2 C), 30.5 (−CH_3, 2 C), 36.3 (=CH, 4 C), 72.2 (quat. C, 2 C), 165.8 (quat. C, 2 C), 167.6 (quat. C, 2 C). − MS (EI, 70 eV), *m*/*z* (%) = 311 (100) [M^+ − N_2 − CH_3]. − UV/Vis (1,4-dioxane): λ_{max} (ε) = 386 (203) nm. − $C_{18}H_{22}N_6O_2$ (354.4): calcd. C 61.00, H 6.26, N 23.71; found C 60.88, H 6.22, N 23.42.

***exo,exo*-3,3,7,7-Tetramethyl-1,5-bis(2-pyridyl)-9,10-diaza-tetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (6r):** This compound was prepared according to General Procedure (4). A solution of **4r** (587 mg, 2.12 mmol) and **2b** (1.29 g, 18.9 mmol) in CH_2Cl_2 (3 mL) was pressurized to 7.6 kbar in a suitable reaction vessel at 60 °C for 5 d. Purification by FC (CH_2Cl_2/ethanol = 15:1) and recrystallization (CH_2Cl_2/*n*-hexane) yielded **6r** (540 mg, 1.57 mmol, 74%) as colourless crystals, m.p. 226−227 °C. − IR (KBr): $\tilde{\nu}$ = 3050, 3000, 2950, 2930, 2870, 1580, 1570, 1465, 1430, 1315, 1120, 1095, 1035, 1000, 775, 750, 700, 615 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.92 (s, 6 H, 3,7-CH_3-*syn*), 1.08 (s, 6 H, 3,7-CH_3-*anti*), 2.18 (s, 4 H, 2-H, 4-H, 6-H, 8-H), 7.25−7.45 (m, 2 H, Ar-H), 7.74−8.00 (m, 2 H, Ar-H), 8.16−8.35 (m, 2 H, Ar-H), 8.68−8.79 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ_{max} (ε) = 260 (7960), 392 (132) nm. − $C_{22}H_{24}N_4$ (344.5): calcd. C 76.71, H 7.02, N 16.26; found C 76.67, H 7.01, N 16.14.

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