The Cycloaddition-Cycloelimination Pathway to Homotropilidenes − Synthesis and Properties of Homotropilidenes

Jürgen Sauer,*[a] Peter Bäuerlein,[a] Wolfgang Ebenbeck,[a] Rainer Dyllick-Brenzinger,[a] Charalampos Gousetis,[a] Heinz Sichert,[a] Theodor Troll,[a] and Uwe Wallfahrer[a]

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

Keywords: Azo compounds / Cycloadditions / Kinetics / Photolysis / Rearrangements / Substituent effects

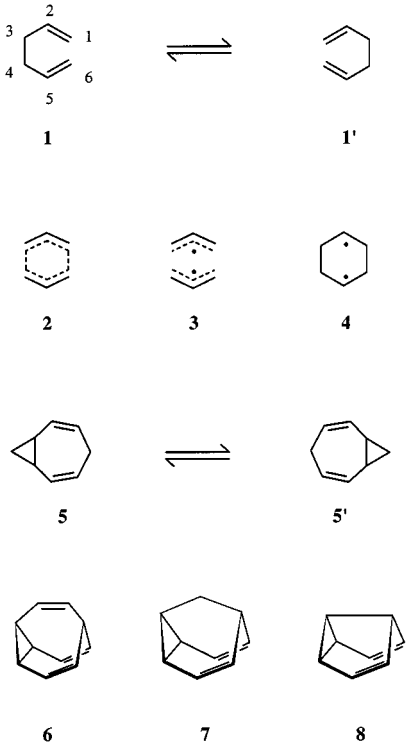
The cycloaddition-cycloelimination reaction sequence between 3,6-disubstituted 1,2,4,5-tetrazines **9** and various cyclopropenes **10** provides 3,4-diazanorcaradienes **11**, which undergo [4+2] cycloadditions with additional cyclopropenes **10** to form tetracyclic azo compounds **12**. Photolysis of these compounds, with accompanying loss of nitrogen, affords homotropilidenes (bicyclo[5.1.0]octa-2,5-dienes) **13**–**26**. Substituents at various positions of the homotropilidene skeleton have been observed to exert significant influences on the Cope rearrangement rate and, in cases of unsymmetrically substituted homotropilidenes, on the equilibrium positions.

Introduction

In 1940 Cope reported the first examples of thermally induced rearrangements of 1,5-hexadienes.[1] This [3,3]-sigmatropic rearrangement, by Woodward−Hoffmann nomenclature,[2,3] not only turned out to be of tremendous synthetic value,[4−6] but its mechanism has been the topic of heated discussion for nearly 50 years. In two remarkable contributions, Doering quite recently offered a critical discussion of all mechanistic aspects.[7,8] Houk summarized all relevant articles to show how quantum mechanical calculations have been used to analyse and predict the rates and mechanisms of this and other pericyclic reactions.[9,10]

Historically, as illustrated in Scheme 1, three models have been the focus of mechanistic attention, as demonstrated for the *degenerate* Cope rearrangement of the parent system **1** ⇄ **1′**. One possible pathway is a single-step, concerted mechanism, involving an aromatic-type transition state **2**. Two alternatives are represented by intermediates **3** and **4**: Either a bond fission of 1,5-hexadiene **1** between C-3 and C-4 may produce two allyl radicals, shown as **3,** or bond formation between C-1 and C-6 may produce a cyclohexa-1,4-diyl diradical **4**.

A logical but nevertheless ingenious extension of the Cope rearrangement of **1** was the synthesis of homotropilidene (**5**), bullvalene (**6**), barbaralane (**7**) and semibullvalene (**8**), all of which display the phenomenon of the *degenerate* [3,3]-sigmatropic rearrangement. The same mechanistic dichotomy also exists in principle for these compounds, as described for **1** ⇄ **1′,** with either a concerted reaction (transition state analogous to **2**) or two-step rearrangements involving biradical intermediates analogous to **3** or **4**.



Scheme 1. The Cope rearrangement of 1,5-hexadienes

In this contribution, we give a full report on our investigations of the synthesis of symmetrically and unsymmetrically substituted homotropilidenes by means of a cycloaddition-cycloelimination sequence utilizing 1,2,4,5-tetrazines and cyclopropenes as starting materials.[11−16]

Results and Discussion

Homotropilidene (**5**) itself was first synthesized in Doering's group,[17,18] by cyclopropanation of 1,3,5-cyclohepta-

[a] Institut für Organische Chemie der Universität Regensburg, Universitätsstrasse 31, 93040 Regensburg, Germany
Fax: (internat.) + 49-(0)941/943−4946
E-mail: rudolf.vasold@chemie.uni-regensburg.de

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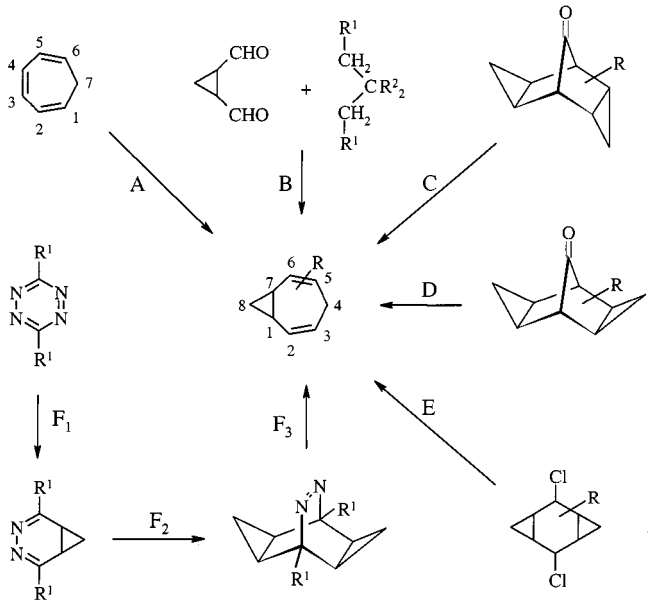
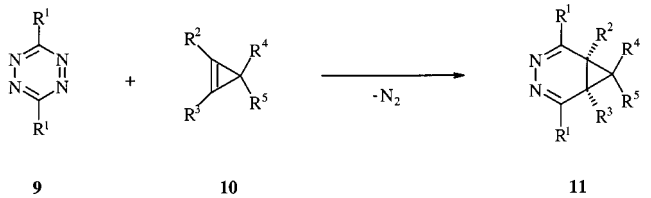
triene at the 3- and 4-positions and subsequent separation from other isomers by GC (Scheme 2, path A). However, this pathway is limited as cyclopropanation preferentially takes place at the 1- and 2-positions, affording isomeric mixtures. Similarly, the cyclocondensation, as outlined in pathway B, can only be performed in few cases.[19,20] Reaction sequences C, D, E and F all include a 1,4-elimination step (CO, Cl_2, N_2) from a suitable precursor with concomitant ring opening of one cyclopropane unit. Pathway F offers the greatest potential for variation, because substituents on the 1,2,4,5-tetrazine and the cyclopropene can be varied for the initial [4+2] cycloaddition step. As 3,4-diazanorcaradienes can, in principle, be isolated, a variety of different cyclopropenes can also be employed in the cycloaddition steps F_1 and F_2, thus producing unsymmetrically substituted azo compounds, which represent precursors for unsymmetrical homotropilidenes.[11−16,21,22] The value of this synthetic approach is illustrated in the following sections.



Scheme 2. Synthetic pathways leading to homotropilidenes

Synthesis of 3,4-Diazanorcaradienes 11 and Azo Compounds 12

By virtue of their high angle strain, cyclopropenes **10** in general act as very reactive 2π components in [4+2] cycloadditions with the extremely electron poor 1,2,4,5-tetrazines **9**, to form 3,4-diazanorcaradienes **11** in good to excellent yields (Scheme 3 and Exp. Sect.).[22,23] Depending on the reactivities of the two components, the cycloaddition step can be performed by introducing gaseous cyclopropenes at −78 °C or at ambient temperature. The reaction can be monitored conveniently by the disappearance of the tetrazine colour, with the reaction mixture turning, for example, from purple (tetrazine) to yellow or orange-yellow (diazanorcaradiene).



9 **10** **11**

9	R^1	Ref.
a	CO_2CH_3	[22]
b	CN	[22]
c	Ph	[22]
d	2-Py	[22]
e	5-Oxa	[22]
f	2-Thia	[22]

10	R^2	R^3	R^4	R^5	Ref.
a	H	H	H	H	[22]
b	CH_3	H	H	H	[54]
c	H	H	CH_3	H	[54]
d	H	H	*t*Bu	H	[56][57]
e	H	H	CH_3	CH_3	[22]
f	Ph	Ph	H	H	[58]

11	R^1	R^2	R^3	R^4	R^5	Ref.
a	CO_2CH_3	H	H	H	H	[21]
b	CO_2CH_3	CH_3	H	H	H	[21]
c	CO_2CH_3	H	H	CH_3	H	[21]
d	CO_2CH_3	H	H	*t*Bu	H	this work
e	CO_2CH_3	H	H	CH_3	CH_3	[21]
f	CO_2CH_3	Ph	Ph	H	H	this work
g	Ph	H	H	H	H	[22]
h	Ph	H	H	CH_3	H	this work
i	2-Py	H	H	H	H	[22]
j	2-Py	CH_3	H	H	H	this work
k	2-Py	H	H	CH_3	H	this work
l	2-Py	H	H	CH_3	CH_3	[22]
m	5-Oxa	H	H	H	H	[22]
n	5-Oxa	H	H	CH_3	CH_3	[22]
o	2-Thia	H	H	H	H	[22]

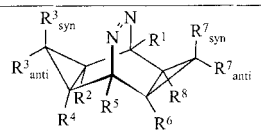
Scheme 3. Synthesis of 3,4-diazanorcaradienes **11** (Ph = phenyl, 2-Py = 2-pyridyl, 2-Thia = 1,3-thiazol-2-yl, 5-Oxa = 2-methyl-1,3,4-oxadiazol-5-yl)

The dienophilic activity of cyclopropene is influenced remarkably by methyl substitution on **10**. While the introduction of one methyl group at position 3 of compound **10** slightly increases the rate, the introduction of a second methyl group sharply reduces the reactivity: 3,3-Dimethylcyclopropene (**10e**) is less reactive (in terms of rate constants) than **10a** by a factor of approximately 5000−6000 (reaction with **9a**, 20 °C, 1,4-dioxane).[24] Interestingly enough, the diphenyl derivative **10f** was quite sluggish in reactivity.

3,4-Diazanorcaradienes **11** are still quite reactive dienes in Diels−Alder reactions with inverse electron demand. The diene activity drops considerably in the 1,2,4,5-tetrazine → 1,2,4-triazine → 3,4-diazanorcaradiene series;[23] the rate constants for the same dienophile are reduced by a factor of more than 1000 for each nitrogen atom fewer in this six-membered heterocycle series. When cyclopropenes are used as dienophiles, the tetracyclic azo compounds **12** are formed in good to very good yields from 3,4-diazanorcaradienes **11**. More active dienes **11** readily add to cyclopropenes **10** at room temperature or slightly elevated temperature; sluggish systems, however, can be accelerated by

working at higher temperatures and/or using high pressure (up to 8 kbar). For the synthesis of symmetrical azo compounds **12**, the intermediate 3,4-diazanorcaradienes **11** do not need to be isolated and azo compounds **12** can be obtained in a one-pot synthesis. Table 1 offers a collection of azo compounds **12**, representing precursors for homotropilidenes **13**−**26**. For the synthesis of the dicyano derivative **12i**−**12o** we applied traditional transformation sequences $R^1 = CO_2CH_3 \rightarrow CO_2H \rightarrow COCl \rightarrow CONH_2 \rightarrow CN$.

Table 1. Substituted tetracyclic azo compounds **12**



12

12	R^1/R^5	R^3_{syn}	R^3_{anti}	R^2	R^4	R^7_{syn}	R^7_{anti}	R^8	R^6	Ref.
a	CO_2CH_3	H	H	H	H	H	H	H	H	[21]
b	CO_2CH_3	H	CH_3	H	H	H	H	H	H	this work
c	CO_2CH_3	H	H	CH_3	H	H	H	H	H	this work
d	CO_2CH_3	H	CH_3	H	H	H	CH_3	H	H	this work
e	CO_2CH_3	H	tBu	H	H	H	tBu	H	H	this work
f	CO_2CH_3	H	H	CH_3	H	H	H	H	CH_3	this work
g	CO_2CH_3	H	CH_3	H	H	H	H	H	CH_3	this work
h	CO_2CH_3	H	H	Ph	Ph	H	H	H	H	this work
i	CN	H	H	H	H	H	H	H	H	[22]
j	CN	H	CH_3	H	H	H	H	H	H	this work
k	CN	H	H	CH_3	H	H	H	H	H	this work
l	CN	H	CH_3	H	H	H	CH_3	H	H	this work
m	CN	H	tBu	H	H	H	tBu	H	H	this work
n	CN	H	H	CH_3	H	H	H	H	CH_3	this work
o	CN	H	H	Ph	Ph	H	H	H	H	this work
p	Ph	H	H	H	H	H	H	H	H	this work
q	Ph	H	CH_3	H	H	H	H	H	H	this work
r	Ph	H	CH_3	H	H	H	CH_3	H	H	this work
s	2-Py	H	H	H	H	H	H	H	H	[22]
t	2-Py	H	CH_3	H	H	H	H	H	H	this work
u	2-Py	H	H	CH_3	H	H	H	H	H	this work
v	2-Py	CH_3	CH_3	H	H	H	H	H	H	this work
w	2-Py	H	CH_3	H	H	H	CH_3	H	H	this work
x	2-Py	H	H	CH_3	H	H	H	H	CH_3	this work
y	2-Py	H	CH_3	H	H	H	H	H	CH_3	this work
z	2-Py	CH_3	CH_3	H	H	H	CH_3	H	H	this work
$\mathbf{a_1}$	5-Oxa	H	H	H	H	H	H	H	H	[22]
$\mathbf{b_1}$	5-Oxa	H	H	H	H	CH_3	CH_3	H	H	this work
$\mathbf{c_1}$	2-Thia	H	H	H	H	H	H	H	H	[22]

The obvious alternative synthetic approach, starting from 3,6-dicyano-1,2,4,5-tetrazine (**9b**), is impracticable because the very sensitive dicyanotetrazine **9b** can only be obtained in small amounts and stored for a limited time at low temperature in the solid state.[25,26] Compound **9b** surpasses the diester tetrazine **9a** in reactivity: The rate constants for the [4+2] cycloaddition with 1-methoxycyclohexene, for instance, have been determined as **9b**:**9a** = 970:1 (20 °C, dioxane)[27] and parallel the half-wave reduction potentials of the tetrazines.[28]

^{1}H and ^{13}C NMR spectra unequivocally corroborate the correct structures for **11** and **12** (see Exp. Sect.). In particular, the chemical shifts of the protons and carbon atoms of the cyclopropane units, in combination with the proton-proton coupling constants (ABX_2 spin systems), are conclusive[21−23] and need no further detailed discussion. The characteristic azo chromophore in **12** ($\lambda \approx 350$ nm) shows low extinction coefficients for the forbidden n-π^* transition (see Exp. Sect.).

Photolysis of Azo Compounds 12 to Homotropilidenes 13−26

Aliphatic azo compounds are valuable precursors for the synthesis of energy-rich intermediates, such as alkyl radicals, as well as a variety of aliphatic compounds with interesting and unusual structures. The reactions are usually initiated by thermolysis or photolysis of the corresponding azo compounds.[29−32]

Tetracyclic azo compounds **12** offer a rather simple route to homotropilidenes, and in most cases studied the photolytic pathway was a successful one. Photolysis of azo compounds **12** was carried out either in an immersion well photoreactor or on an optical bench (for details, see Exp. Sect.). Inert solvents such as benzene, acetonitrile or dichloromethane were used. Depending on the structure of **12**, its concentration, the solvent used and the photochemical conditions, the nitrogen extrusion was usually completed within a few hours and the reactions could easily be monitored by thin layer chromatography. Only in a few cases was the yield of homotropilidene lower than 50%.

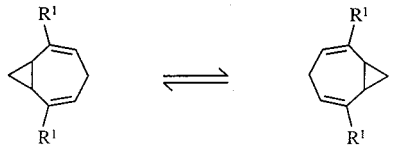
Homotropilidenes − Structure and Equilibrium Position

In this study homotropilidene substitution was varied in two ways, as depicted in Schemes 4 to 8:

i. Variation at positions 2 and 6: CO_2CH_3, CN, Ph, 2-Py (2-pyridyl), 2-Thia (1,3-thiazol-2-yl), 5-Oxa [2-methyl-(1,3,4-oxadiazol-5-yl)].

ii. Hydrogen was exchanged for methyl, phenyl and *tert*-butyl to yield symmetrical and unsymmetrical monoalkyl-, dialkyl-, and trialkyl-substituted homotropilidenes. Substituents at positions 2 and 6 were also in part varied.

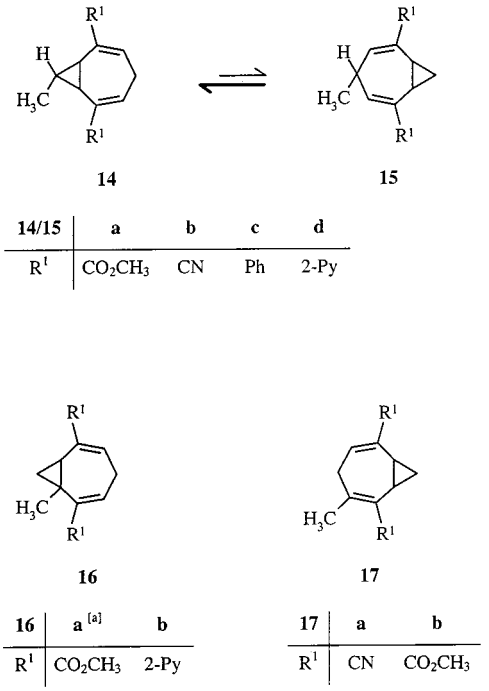
The structural confirmation of the homotropilidenes **13**−**26** shown in Scheme 4 to 8 relies on the ^{1}H NMR spectra obtained at low temperature when the Cope rearrangement is slow. Table 2 summarizes typical values for chemical shifts of protons at the cyclopropane moiety, the seven-membered ring and the methyl groups at different positions, together with the ^2J and ^3J coupling constants for geminal protons and those in adjacent positions. Chemical shift data and coupling constants convincingly establish both the structure and the existence of the *trans* conformation of homotropilidenes **13**−**26**.



13 **13'**

13/13'	a	b	c	d	e	f
R^1	CO_2CH_3	CN	Ph	2-Py	2-Oxa	2-Thia

Scheme 4. 2,6-Disubstituted homotropilidenes **13**/**13'**



Scheme 5. Monomethyl derivatives of 2,6-disubstituted homotropilidenes **14**−**17**: [a] **16a** was observed as the major Cope isomer (> 95%)

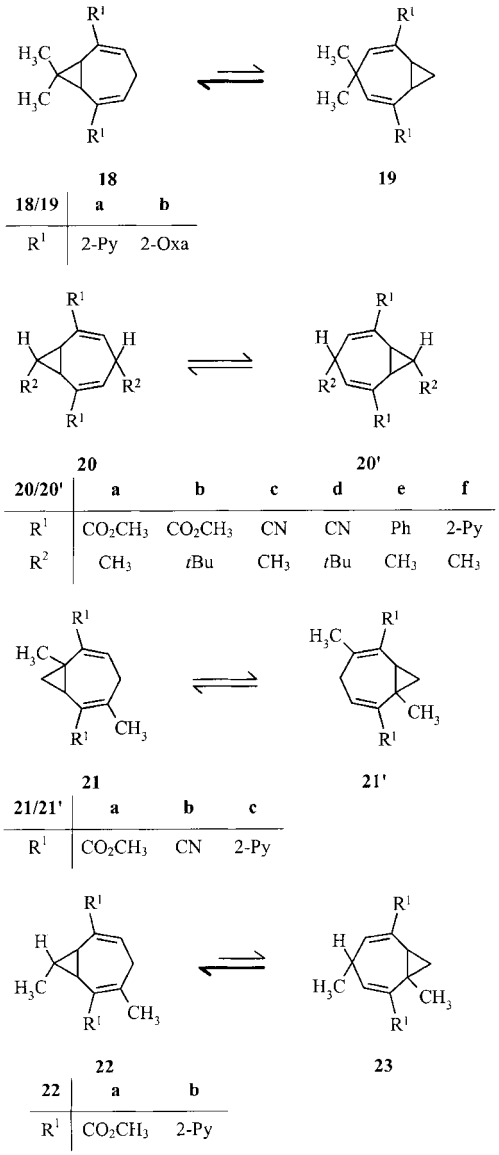
Symmetrical Homotropilidenes 13 ⇄ 13′, 20 ⇄ 20′ and 21 ⇄ 21′

On photolysis, symmetrically substituted azo compounds **12** yield symmetrical homotropilidenes, which can undergo *degenerate* Cope rearrangement at elevated temperature. 2,6-Disubstituted homotropilidenes **13/13′a**−**f**, together with the 4,8-dialkyl derivatives **20/20′a**−**f** and the 1,5-dimethyl homotropilidenes **21/21′a**−**c** are easily obtained in good yields (Schemes 4 and 6). At temperatures below −30 °C, the [3,3]-sigmatropic rearrangement is slow on the NMR timescale in all cases. A typical ^{1}H NMR spectrum shows the signals of protons for the cyclopropane unit and the protons of the seven-membered ring, with the anticipated values for chemical shifts, multiplicity and coupling constants confirming the homotropilidene structure and *trans* conformation (Table 2).

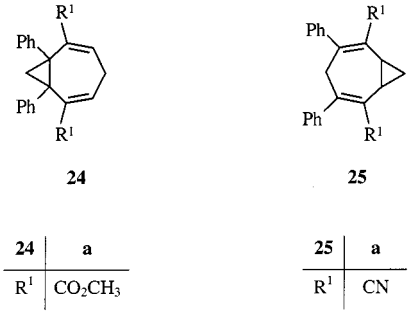
At elevated temperatures, the ^{1}H NMR spectra became temperature-dependant, and on passing a coalescence point a fast equilibrium is reached (vide infra) during which protons and/or substituents at position 4/8, and also 1/3 or 5/7, become equivalent.

Unsymmetrical Alkyl-Substituted Homotropilidenes 14, 16/17, 18, 22/23 and 26

Unsymmetrical substitution on the homotropilidene skeleton gives rise to two nonequivalent Cope tautomers. The analysis of the ^{1}H NMR spectra for monomethyl homotropilidenes (Table 2) convincingly confirms the existence of the 8-methyl isomer for **14a**−**14d** (Scheme 5). In the case of a single methyl group at position 1/3, the 1-isomer is favoured for **16a** and **16b**, while the 3-isomer **17a** is preferred for the dicyano derivative (Scheme 5). As is to be expected, the two geminal methyl groups prefer position 8 (**18a** and

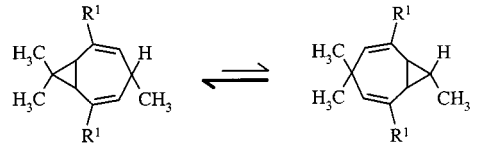


Scheme 6. Dialkyl derivatives of 2,6-disubstituted homotropilidenes **18**−**23**



Scheme 7. Diphenyl derivatives of 2,6-disubstituted homotropilidenes **24/25**

18b in Scheme 6), whereas in the competition between two methyl groups in positions 3/8 versus 1/4, the isomer **22** (**22a** and **22b** in Scheme 6), with the substituents in positions 3/8 of the homotropilidene skeleton, seems to be the more stable isomer. Finally, for a trisubstitution pattern, the 3,8,8-combination **26** is preferred over the alternative 4,4,8-arrangement **27** (Scheme 8).



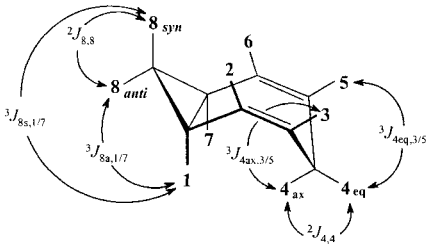
26	a
R^1	2-py

Scheme 8. Trimethyl derivatives of 2,6-disubstituted homotropilidenes **26/27**

Unsymmetrical Diphenyl-Substituted Homotropilidenes 24a and 25a

Only one case of unsymmetrical disubstitution with two phenyl groups can be presented. While we find the two phenyl substituents at position 1/7 for the diester derivative **24a**, the dicyano derivative **25a** prefers the phenyl rings in position 3/5, in conjugation with the cyano groups (Scheme 7). A detailed discussion of all equilibrium phenomena is given, together with the kinetic data (vide infra).

Table 2. ^{1}H NMR chemical shifts (δ values, $CDCl_3$/TMS, 60, 90, 250 or 400 MHz) and coupling constants $^nJ(^1H,^1H)$ [Hz] of 3,4-homotropilidenes **13a**−**26a**



Cmpd.	8-H$_{syn}$	8-H$_{anti}$	4-H$_{eq}$	4-H$_{ax}$	1-H/7-H	3-H/5-H	$^2J_{8,8}$	$^3J_{8s,1/7}$	$^3J_{8a,1/7}$	$^2J_{4,4}$	$^3J_{4eq,3/5}$	$^3J_{4ax,3/5}$
13a[a]	0.13 (dt)	1.34 (dt)	1.92 (dt)	2.62 (dt)	1.78 (dd)	6.91 (dd)	3.5	6.0	9.0	16.0	8.5	4.0
13b[b]	–0.19 (dt)	0.49 (dt)	1.28 (dt)	2.00 (dt)	0.81 (dd)	5.42 (dd)	3.5	6.0	9.0	18.0	8.0	4.0
13c	0.25–0.30 (m)	1.46–1.55 (m)	2.67 (dt)	3.51 (m)	2.14 (m)	6.44–6.48 (m)	n/a	n/a	n/a	15.2	8.0	n/a
13d	0.21–0.22 (m)	1.49–1.57 (m)	2.79–2.92 (m)	3.54–3.61 (m)	2.24–2.30 (m)	7.08–7.31 (m)	n/a	n/a	n/a	n/a	n/a	n/a
13e[c]	0.41 (dt)	1.63 (dt)	2.94 (dt)	3.58 (dtt)[d]	2.28 (ddd)[d]	6.94 (dd)	4.1	6.2	9.3	16.4	8.6	4.1
13f[c]	0.47 (dt)	1.63 (dt)	2.84 (dt)	3.55 (dtt)[d]	2.30 (ddd)[d]	7.12 (dd)	3.7	6.1	9.1	15.4	8.8	4.4
16a	0.37 (dd)	1.17 (dd)	2.08 (dt)	2.82 (dt)	1.45 (dd)	7.02 (dd)	4.5	6.0	10.0	14.2	8.5	5.0
16b	0.54 (dd)	1.92–1.99 (m)	2.82 (dt)	3.41–3.51 (m)	1.39 (dd)	7.55–7.66 (m)/ 7.23–7.33 (m)	6.5	3.8	9.3	14.0	8.6	n/a
17a	0.57 (dt)	1.27 (dt)	2.48 (dd)	3.57–3.87 (m)	1.83–2.17 (m)	6.79 (dd)	4.7	5.8	9.0	14.7	8.6	5.4
21a[e]	0.40 (dd)	0.97 (dd)	1.91 (dd)	3.25 (dd)	1.55 (qdd)[d]	7.17 (dd)	4.5	6.0	9.2	13.0	8.5	6.0
21b	0.67 (dd)	1.03 (dd)	2.45 (dd)	3.53 (dd)	1.72 (qdd)[d]	6.69 (dd)	4.6	5.8	8.8	14.2	8.6	5.4
21c	0.41 (dd)	1.00 (dd)	2.43 (dd)	3.69 (dd)	2.05–2.13 (m)	7.46 (dd)	3.9	6.3	9.3	13.2	8.6	6.1
24a	1.31 (d)	2.82 (d)	2.97 (dt)	3.96 (dt)	–	7.45 (dd)	6.5	–	–	14.0	8.8	5.0
25a	0.82 (dt)	1.2–1.7 (m)	3.21 (d)	4.63 (dt)[d]	2.28 (ddd)[d]	–	5.2	6.0	9.1	13.3	–	–
		8-CH$_3$-*anti*										
14a	0.59 (tq)	1.30 (d)	2.74 (dt)	3.0–3.5 (m)	1.73 (dd)	6.93 (dd)	–	5.5	–	18.0	8.0	4.0
14b[f]	1.02 (tq)	1.33 (d)	2.87 (dt)	3.42 (dtt)[d]	1.73 (dd)[d]	6.65 (dd)	–	5.4	–	18.1	8.1	3.7
14c	0.54–0.63 (m)	1.44 (d)	2.59–2.78 (m)	3.46 (d)	1.82 (d)	6.43 (dd)	–	4.5	–	16.5	7.8	3.9
14d	0.49–0.55 (m)	1.51 (d)	2.87 (dt)	3.52 (dt)	1.92 (d)	7.18 (dd)	–	4.7	–	15.5	8.4	4.2
22a	0.40 (dt)	1.25 (d)	2.30 (dd)	3.47–3.80 (m)	1.58 (d)	7.18 (dd)		6.0	–	13.5	8.0	5.2
22b	0.44–0.49 (m)	1.18 (d)	2.41 (dd)	3.83 (dd)	1.79–2.05 (m)	7.11 (dd)	–	n/a	–	13.9	8.7	5.2
	8-CH$_3$-*syn*	8-CH$_3$-*anti*										
18a	0.59 (s)	1.53 (s)	2.95 (dt)	3.52 (dt)	2.05 (s)	7.18 (dd)	–	–	–	16.5	8.6	4.0
18b	0.77 (s)	1.47 (s)	2.96 (dt)	3.51 (dtt)[d]	2.05 (dt)[d]	6.86 (ddt)[d]	–	–	–	17.7	8.5	3.7
		8-CH$_3$-*anti*		4-CH$_3$-*anti*								
20a[g]	0.67 (tq)	1.24 (d)	3.12 (tq)	1.36 (d)	1.67 (d)	7.06 (d)	–	5.5	–	–	8.0	–
20b[h]	0.49 (t)	–	3.00 (t)	–	1.92 (d)	6.95 (d)	–	6.0	–	–	8.0	–
20c[i]	1.16 (tq)	1.29 (d)	3.08 (tq)	1.36 (d)	1.73 (d)	6.67 (d)	–	5.1	–	–	8.1	–
20d[j]	0.96 (t)	–	2.98 (t)	–	1.85 (d)	6.50 (d)	–	6.0	–	–	8.0	–
20e[k]	0.65 (tq)	1.46 (d)	3.06 (tq)	1.50 (d)	1.84 (d)	6.53 (d)	–	5.6	–	–	8.5	–
20f[l]	0.70 (tq)	1.56 (d)	3.18 (tq)	1.56 (d)	1.96 (d)	7.42 (d)	–	5.6	–	–	9.3	–
	8-CH$_3$-*syn*	8-CH$_3$-*anti*		4-CH$_3$-*anti*								
26a	0.63 (s)	1.54 (s)	3.18–3.34 (m)	1.51 (d)	2.04 (s)	7.32 (d)	–	–		–	8.5	–

[a] Solvent [D$_8$]toluene at 214 K. – [b] Solvent [D$_8$]toluene at 226 K. – [c] Solvent CD_2Cl_2 at 223 K. – [d] Observed ^nJ (^{1}H,^{1}H) long-range couplings (see Exp. Sect.). – [e] Solvent [D$_8$]toluene. – [f] At 235 K. – [g] Solvent CD_2Cl_2/CS_2 (2:1) at 188 K. – [h] Solvent CD_2Cl_2 at 227 K. – [i] Solvent CD_2Cl_2 at 216 K. – [j] Solvent CD_2Cl_2 at 233 K. – [k] Solvent CD_2Cl_2. – [l] Solvent CD_2Cl_2 at 220 K.

^{1}H NMR Spectroscopic Temperature Dependence in Symmetrical Homotropilidenes 13 ⇄ 13′, 20 ⇄ 20′ and 21 ⇄ 21′

As already mentioned, symmetrical homotropilidenes have temperature-dependant ^{1}H NMR spectra. At lower temperature (−76 °C to +110 °C), depending on the structure of the homotropilidenes, the Cope rearrangement is "frozen" and the ^{1}H NMR spectra can easily be analysed (Table 2). At elevated temperatures, the signals belonging to exchangeable positions (4/8, 1/3, 5/7) broaden and, finally, at still higher temperatures (+40 °C to +200 °C) the area of fast exchange is reached.

We measured the ^{1}H NMR spectra in such inert solvents as CD_2Cl_2, $CDCl_3$, $C_2D_2Cl_4$, CS_2, [D_8]toluene or mixtures (Table 5, Exp. Sect.), depending on the homotropilidene structure and the rate of the *degenerate* Cope rearrangement (which varied considerably). In a number of cases, it was possible to measure ^{1}H NMR spectra over a large temperature range ($\Delta T \approx 80-120$ °C) and spectra were usually taken at more than 10−15 different temperatures. Rate constants at different temperatures were obtained by complete line-shape analysis using the RSHKUBO program.[33−35] Calculations for $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are based on the Eyring equation (see Table 4 and 5 and Figure 2).[36]

In addition, $\Delta G^{\neq}$ values for the *degenerate* Cope rearrangement were available for a number of homotropilidenes, from the coalescence temperatures of signals for the appropriate substituents (Table 5). These data obtained for activation parameters are given in Table 4, together with corresponding data from the literature.

Substituents Effects on Equilibria and Rates of Cope Rearrangement of Homotropilidenes

Figure 1 illustrates the current stage of mechanistic discussion of *degenerate* Cope rearrangements of homotropilidenes, together with the corresponding energy profile for this sequence. Results obtained from NMR studies,[37] photoelectron spectroscopy[38] and force field calculations[39] suggest that the parent structure of homotropilidene **5** prefers the energetically favoured *trans* conformation $\mathbf{5}_{trans}$ with the minimum conformational strain, due to an observed dihedral angle of 80° between the substituents in position 1/2 and 6/7.[37] In contrast, the corresponding *cis* conformation $\mathbf{5}_{cis}$ exists in an almost eclipsed conformation with a reduced dihedral angle of 5−10°, and is therefore less favoured,[37] with a difference in free energy of ΔG.

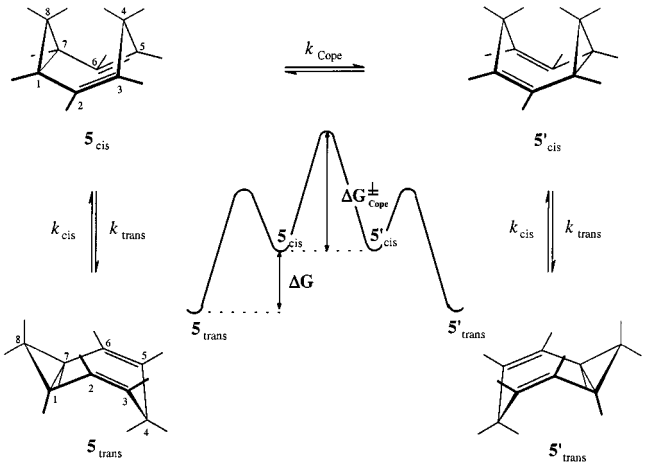


Figure 1. Valence isomerization energy profile of homotropilidene **5**

The mechanism for the *degenerate* Cope rearrangement given in Figure 1 proceeds through the *cis* conformation $\mathbf{5}_{cis}$ by a concerted pathway involving an aromatic transition state **2**. The sigmatropic rearrangement is then followed by a conformational change to form the more stable *trans* conformer $\mathbf{5'}_{trans}$. Hence, the experimental free activation energy $\Delta G^{\neq}_{exp}$ for the total sequence is determined as the sum of the difference in free energies ΔG between the two conformers ($\mathbf{5}_{trans}$ and $\mathbf{5}_{cis}$) and the activation energy $\Delta G^{\neq}_{Cope}$ required for the Cope rearrangement [Equation (1)].

$$\Delta G^{\neq}_{exp} = \Delta G + \Delta G^{\neq}_{Cope} \quad (1)$$

Steric and electronic effects of substituents in different positions of the homotropilidene system have a considerable influence both on the conformational equilibrium $\mathbf{5}_{trans} \rightleftarrows \mathbf{5}_{cis}$ and on the rate of the sigmatropic rearrangement $\mathbf{5}_{cis} \rightleftarrows \mathbf{5'}_{cis}$, making accurate mechanistic predictions difficult. Unsymmetrically substituted homotropilidenes, represented by the two *trans* Cope isomers $\mathbf{5}_{trans}$ and $\mathbf{5'}_{trans}$, differ in their energies, and so their ratios are different from 1:1. Again, these substituents are expected to influence the equilibrium by means of steric and electronic factors. A collection of unsymmetrical homotropilidenes synthesized in our group is given in Table 3, and also includes the known 3-methylhomotropilidene (**28**)[40] for comparative discussion. It is important to note that the exclusively formed or dominant Cope isomer is shown in Table 3.

A number of symmetrical homotropilidenes, including both those synthesized by us and those obtained according to the literature, gave $\Delta G^{\neq}_{exp}$ values obtained from coalescence measurements or NMR line-shape analysis; these are displayed in Table 4. Apart from a very few exceptions, the corresponding $\Delta G^{\neq}_{exp}$ values relate to 298 K. Some of the activation parameters from coalescence measurements were obtained at slightly different temperatures; however, this still allows for direct comparison.

The question that now arises is, how do substituents in unsymmetrical homotropilidenes influence the equilibrium of Cope isomers? Table 3 gives a selection of compounds with symmetrical substitution patterns in positions 2/6 (R^1 = CO_2CH_3, CN, 2-Py, 2-Oxa, Ph or H) and bearing methyl or phenyl groups in various positions around the homotropilidene skeleton. Predictions about the preferred positions of alkyl groups are based on the Schleyer rule,[41] EHT calculations by Hoffmann and Stohrer[42] and MNDO/2-calculations by Dewar and Lo.[43] As outlined in the following sequence, a methyl group prefers an olefinic position over a cyclopropane position over an sp^3-carbon atom.

Table 3. Preferred structural isomer of unsymmetrically substituted homotropilidenes (percentage of isomer)

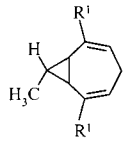
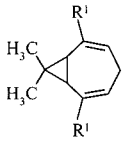
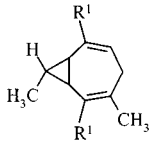
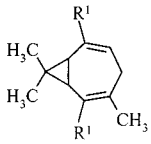
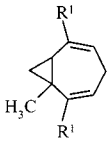
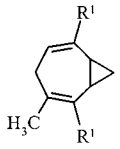
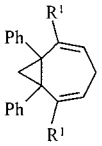
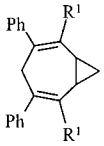
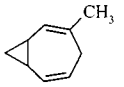
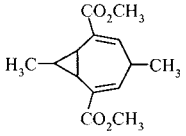
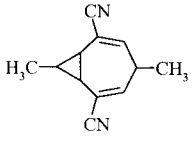
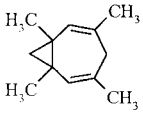
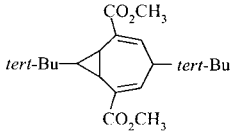
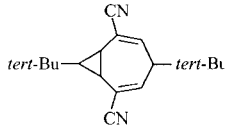
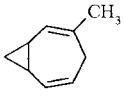
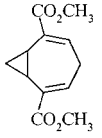
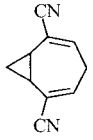
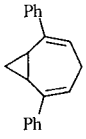
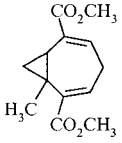
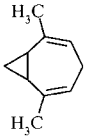
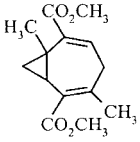
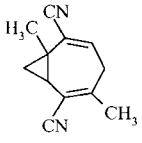
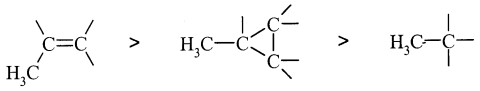
Structure	R^1	Cmpd. (%)	Structure	R^1	Cmpd. (%)	Structure	R^1	Cmpd. (%)
	CO_2CH_3, CN, Ph, 2-Py	**14a–d** (100)		2-Py, 2-Oxa	**18a,b** (100)		CO_2CH_3, 2-Py	**22a–b** (100)
	2-Py	**26a** (100)		CO_2CH_3, 2-Py	**16a,b** (> 95, 100)		CN, CO_2CH_3	**17a,b** (100, < 5)
	CO_2CH_3	**24a** (100)		CN	**25a** (100)		H	**28**[40] (87)

Table 4. $\Delta G^{\neq}_{298}$ values (kcal/mol; 298 K) for the Cope rearrangement of homotropilidenes

Structure	Cmpd.	$\Delta G^{\neq}_{298}$	Ref.	Structure	Cmpd.	$\Delta G^{\neq}_{298}$	Ref.	Structure	Cmpd.	$\Delta G^{\neq}_{298}$	Ref.
	**5**	14.1	[37,40,48]		**20a**	11.8	this work		**20c**	12.4[a]	this work
	**31**	13.6[a]	[49]		**20b**	13.3[b]	this work		**20d**	14.4	this work
	**28** **29**	3-CH_3: 14.9 1-CH_3: 13.8	[40]		**13a**	13.9	this work		**13b**	15.1	this work
	**13c**	16.5	[46,59]		**16a** **17b**	1-CH_3: 17.5 3-CH_3: 16.5	this work				
	**30**	18.0	[46,59]		**21a**	20.7	this work		**21b**	17.5	this work

[a] $\Delta G^{\neq}_{274}$ at 274 K. – [b] $\Delta G^{\neq}_{320}$ at 320 K.



The homotropilidenes **14**, **18**, **22** and **26** exactly follow the Schleyer rule, as shown by comparison of these compounds with their alternative structural isomers in previous schemes. These results are consistent with those obtained

by Maas[44,45] using simple 4,8-dialkyl-substituted homotropilidenes unsubstituted at position 2/6. In all these compounds, alkyl and phenyl substituents prefer the cyclopropane position at C-8 rather than the sp^3-carbon atom at C-4.

An interesting substituent effect was observed with homotropilidenes **16** and **17**. In contrast to **17a** and 3-methylhomotropilidene (**28**),[40] the elucidated structures of **16a** and **16b** are in disagreement with the Schleyer rule. We assume that this outcome is the result mainly of steric effects. Possibly because of a large dihedral angle between the methyl group and the substituent R^1 (R^1 = CO_2CH_3 or 2-Py), the steric interaction in the unexpected Cope isomer **16a** and **16b** is minimal,[37] whereas in their alternative structural isomer **17** (R^1 = CO_2CH_3/2-Py) a substantial steric strain would be invoked.

The dicyano derivative **17a** displays no steric interaction between the substituents in position 2 and 3, because of the small steric demand of the nonbulky cyano group. The equilibrium of compound **17a** is thus not dictated by steric effects and this is therefore consistent with the Schleyer rule.

Similar steric effects have been found to be responsible for the opposite equilibria observed for compounds **24a** and **25a**. Introduction of bulky phenyl groups adjacent to the ester substituents in position 2/6 raises the steric congestion dramatically and the sterically less hindered isomer **24a**, with phenyl groups attached to the cyclopropane ring in positions 1 and 7, is subsequently formed. In the corresponding dicyano derivative **25a**, the steric interactions are reduced for reasons already mentioned above. Furthermore, additional conjugative factors (Ph in position 3/5 adjacent to CN in position 2/6) favour the formation of isomer **25a**, and this is found to be consistent with the Schleyer rule.

Earlier kinetic studies investigating the Cope rearrangement of homotropilidenes have been carried out by Kessler,[39,46,47] Guenther,[37,48] Winstein[49] and Maas.[44,45] These results are given in Table 4 and are compared with kinetic data obtained from our compounds. As already indicated, mechanistic interpretation of the $\Delta G^{\neq}_{exp}$ values is complicated by the fact that both the conformational equilibrium $\mathbf{5}_{trans} \rightleftarrows \mathbf{5}_{cis}$ and the Cope rearrangement $\mathbf{5}_{cis} \rightleftarrows \mathbf{5'}_{cis}$ are influenced by substituents attached to the parent homotropilidene skeleton, through steric and electronic effects. Even in bridged homotropilidene derivatives, the effects of substituents on the rate of rearrangement are not fully understood, as shown by an excellent kinetic study on barbaralanes and semibullvalenes by Jackman and Quast.[50] Opposing substituent effects, for instance, have been observed within different classes of bridged homotropilidenes. Consequently, discussion of our results is limited to expressing trends rather than drawing absolute conclusions.

Substituents such as methyl, attached to the parent homotropilidene **5** in position 1/3/5 or 7 (see **28**, **29**, **31** in Table 4), have a minor effect on the free activation energy $\Delta G^{\neq}_{exp}$, while introduction of phenyl groups and − in particular − methyl groups at position 2/6, increase the energy barrier for the *degenerate* Cope rearrangement (see compounds **13c** and **30** in Table 4). Electronic effects aside, the influence of substituents on the conformational equilibrium has to be taken into account as well. As shown for barbaralanes and semibullvalenes, methyl and phenyl groups in these positions significantly reduced the rate of the *degenerate* Cope rearrangement.[50]

The disubstituted homotropilidenes **13a** and **13b** exhibit only slightly different $\Delta G^{\neq}_{exp}$ values compared to the parent system **5**. Within this pair of compounds, however, the dicyano derivative **13b** is slower in rate than the corresponding diester derivative **13a**. This trend has also been found to be operative for both the homotropilidene analogues **20a/20c** and **20b/20d**. These observed relatively insignificant substituent effects, which are based on experimental $\Delta G^{\neq}_{exp}$ values involving two processes, are not regarded as having further relevance.

A simpler explanation can be given for the increase in rate of the *degenerate* Cope rearrangement induced by alkyl disubstitution in positions 4/8. Calculations on the effect of substituents on the stability of cyclopropane bonds[42] and analogous kinetic studies on semibullvalenes[51] confirmed this result. According to this, the electron-donating alkyl groups in position 4/8, residing on the opposite side of the cyclopropane bond, weaken this bond and facilitate an enhanced sigmatropic rearrangement rate. Furthermore, a change in the conformational equilibrium, as initially assumed, favouring the *cis* conformer over the *trans* conformer because of steric interaction between the pseudoaxial substituents in position 4 and the hydrogen atoms on the cyclopropane unit (position 1 and 7), is not believed to occur. It has been shown that the rate of rearrangement for the *tert*-butyl-substituted homotropilidenes **20b** and **20d** is slower than for the corresponding methyl derivatives **20a** and **20c**.

The opposite trend in reactivity has been observed for compounds **21a/21b**, an effect which is generated by steric interactions. The enhanced steric interaction between the methyl substituents in position 1 and 5 and the ester groups in position 2 and 6 shifts the conformational equilibrium towards the *trans* conformer, thus reducing the rate of rearrangement. As expected, steric interactions are lessened in homotropilidene **21b**, due to small steric demand from the corresponding cyano groups in position 2 and 6, and so an enhanced rate of rearrangement was observed for the dicyano derivative **21b** as compared to diester derivative **21a**.

Unfortunately, our kinetic data do not allow us to conclude whether the individual Cope rearrangement occurs through a concerted mechanism or a nonconcerted one. According to an article by Doering et al.[7,8] and calculations (Becke3LYP/6−31G* level) by Borden and Houk[52,53] on 1,5-hexadienes bearing cyano and vinyl groups in different positions, these systems are specified as the so-called "chameleonic" transition states for the Cope rearrangement. The relative importance of the cyclohexane-1,4-diyl (**4**) and bis(allyl) radical (**3**) resonance contributors can be altered by substituents, depending on the carbon atoms to which the substituents are attached. There is no doubt that similar effects have to be considered in our systems.

Conclusion

Symmetrical and unsymmetrical homotropilidenes were prepared by photolysis of substituted tetracyclic azo compounds **12**. Substituents attached to different positions of the homotropilidene skeleton show strong effects on the equilibria of unsymmetrical homotropilidenes, as well as on the rate of the *degenerate* Cope rearrangement for symmetrical homotropilidenes. Electronic substituent effects aside, steric interactions have been shown to influence both equilibrium position and reaction rates. Steric substituent effects are mainly responsible for the change of the conformational equilibrium $\mathbf{5}_{trans} \rightleftarrows \mathbf{5}_{cis}$ initiating the sigmatropic rearrangement.

Experimental Section

General Remarks: IR spectra were recorded with a Beckman Acculab 1, and UV/Vis spectra with a Beckman Model 24 and a Carl Zeiss Specord M500 UV spectrophotometer. − NMR spectra were obtained with a Varian T 60 and Bruker WH 90, AC 250 and ARX 400 machines (60, 90, 250 and 400 MHz for ^{1}H, 22.63, 63 and 100 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 is indicated as quat. C, =CH, $-CH_2-$, $-CH_3$. − Mass spectra were measured by electron impact at an ionizing voltage of 70 eV, with Varian MAT 90 and MAT311A instruments. − 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, for oily compounds in particular, no correct elemental analysis could be obtained, such as for **12q**, **16b**, **21c**, **22a** and **22b**. − For analytical thin layer chromatography, precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey & Nagel) 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 synthesis of dienophiles **10a**,[22] **10b**,[54] **10c**,[54] **10d**,[55,56,57] **10e**,[22] **10f**[58] and tetrazines **9a** − **9f**[22] were performed according to published procedures. − The petroleum ether (PE) used had a boiling range of 40−60 °C. − Activation parameters and experimental kinetic parameters are listed in Table 5 and 6, Arrhenius plots are shown in Figure 2.

Synthesis of 3,4-Diazanorcaradienes. − General Procedure (1) for the Synthesis of 3,4-Diazanorcaradienes 11h, 11j and 11k: A stirred suspension of tetrazine **9** in an inert solvent (vide infra) was cooled to −78 °C under Ar. The corresponding cyclopropene **10a**−**10c** was generated in situ according to the literature procedure and passed through the cooled suspension. The reaction mixture was allowed to warm to room temp. and stirring was continued until the red colour of the tetrazine had disappeared. After completion of the reaction, the solvent was evaporated and the crude product was purified as described below.

Synthesis of Tetracyclic Azo Compounds. − General Procedure (2) for the Synthesis of Tetracyclic Azo Compounds 12d−12f: Tetrazine **9** was dissolved at room temp. in an inert solvent (vide infra) and a large excess of the corresponding cyclopropene **10c**−**10f** was added to the solution. The reaction mixture was stirred until the characteristic red colour of the tetrazine had disappeared (reaction times: see below). After completion of the reaction, as indicated by TLC analysis, the solvent was evaporated and the crude product was purified as described below.

General Procedure (3) for the Synthesis of Tetracyclic Azo Compounds 12b, 12c, 12g, 12p−12r, 12t, 12u and 12w−12y: A stirred suspension of 3,4-diazanorcaradiene **11** in an inert solvent (vide infra) was cooled to −78 °C under Ar. The corresponding cyclopropene **10a**−**10c** was generated in situ and transferred in a weak nitrogen stream into the reaction flask, maintained at dry ice temperature. The reaction mixture was allowed to warm to room temp. and stirring was continued until the reaction was complete (reaction times: see below). After evaporation of the solvent, the crude material was purified as described below.

General Procedure (4) for the Synthesis of Tetracyclic Azo Compound 12h: 3,4-Diazanorcaradiene **11** was dissolved at room temperature in an inert solvent (vide infra) and a large excess of the corresponding cyclopropene **10d**−**10f** was added to the solution. Stirring of the reaction mixture was continued until the reaction

Table 5. Activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ for the Cope rearrangement of homotropilidenes

Cmpd.	$\Delta H^{\neq}_{298}$ (kcal/mol)	$\Delta S^{\neq}_{298}$ (eu)	$\Delta G^{\neq}_{298}$ (kcal/mol)	$\Delta G^{\neq}_{T}$ (kcal/mol)	$T^{\neq}_{T}$ (K)	Solvent	Ref.
5	12.3 ± 0.3	−5.9 ± 0.5	14.1 ± 0.1		237–420	$CDCl_3$/ [D_5]bromobenzene	[37,40,48]
13a	11.3 ± 0.1	−8.9 ± 0.3	13.9 ± 0.2		267–368	[D_8]toluene	this work
13b	12.3 ± 0.1	−9.4 ± 0.2	15.1 ± 0.1		282–417	[D_8]toluene	this work
13c	14.5 ± 0.3	−6.8 ± 0.5	16.5 ± 0.1	16.9[a]	303–413	$C_2D_2Cl_4$	[46]
16a	15.5 ± 0.2	−6.6 ± 0.6	17.5 ± 0.4		334–435	[D_8]toluene	this work
17b	14.3 ± 0.2	−7.3 ± 0.5	16.5 ± 0.4		334–435	[D_8]toluene	this work
20a	8.6 ± 0.1	−10.6 ± 0.3	11.8 ± 0.3		197–314	CD_2Cl_2/CS_2	this work
20b			13.3 ± 0.4[b]		298		this work
20c				12.4 ± 0.5[b]	274		this work
20d				14.4 ± 0.4[b]	320		this work
21a	20.5 ± 0.15	−0.9 ± 0.4	20.7 ± 0.3		384–473	[D_8]toluene	this work
21b	16.1 ± 0.2	−4.5 ± 0.6	17.5 ± 0.4		316–448	[D_8]toluene	this work
28			14.9 ± 0.2[c]				[40]
29			13.8 ± 0.2[c]				[40]
30	18.2 ± 0.5	0.7 ± 0.8	18.0 ± 0.1	18.0[a]	289–410		[46]
31				13.6[b]	274[b]		[59]

[a] At 353 K. − [b] Determined at the coalescence temperature. − [c] The methyl group prefers the 3-position by 1.1 kcal/mol.

Table 6. Experimental kinetic parameter for the *degenerate* Cope rearrangement of homotropilidenes **13a**, **13b**, **16a**, **17b**, **20a**, **21a** and **21b**

13a T (K)	$10^{-2}\,k$ [s^{-1}]	**13b** T (K)	$10^{-2}\,k$ [s^{-1}]	**16a** T (K)	$10^{-2}\,k$ [s^{-1}]	**17b** T (K)	$10^{-2}\,k$ [s^{-1}]	**20a** T (K)	$10^{-2}\,k$ [s^{-1}]	**21a** T (K)	$10^{-2}\,k$ [s^{-1}]	**21b** T (K)	$10^{-2}\,k$ [s^{-1}]
267.3	0.390	282.2	0.170	334.0	0.170	334.0	0.640	197.0	0.042	383.6	0.115	316.3	0.050
282.2	1.10	292.4	0.380	344.0	0.430	344.0	1.62	208.2	0.170	392.4	0.190	327.3	0.120
292.4	2.60	302.1	0.800	355.1	0.750	355.1	2.66	215.7	0.400	395.6	0.250	340.9	0.390
302.3	4.90	312.6	1.60	359.4	1.10	359.4	3.90	224.2	1.10	403.1	0.440	352.4	0.900
312.6	9.00	322.8	2.75	379.4	3.80	379.4	12.0	226.4	1.30	407.1	0.550	361.0	1.50
322.9	17.5	334.0	5.75	391.2	7.00	391.2	22.0	234.6	2.40	411.7	0.750	370.3	2.50
333.7	32.0	344.0	10.5	393.2	7.50	393.2	24.0	244.7	5.50	416.3	1.00	382.7	4.00
343.9	53.0	355.1	19.0	399.5	10.0	399.5	27.5	254.8	12.0	419.0	1.22	392.8	9.00
355.1	100.0	367.8	37.0	414.1	24.0	414.1	65.0	264.4	19.0	421.0	1.30	401.6	16.0
367.8	165.0	377.3	57.0	433.1	50.0	434.0	135.0	277.4	40.0	424.5	1.65	412.9	32.0
		391.2	105.0	454.7	120.0	454.7	295.0	286.2	81.0	427.4	1.90	426.5	45.0
		399.5	145.0					296.7	130.0	432.1	2.50	436.4	90.0
		417.1	288.0					306.9	210.0	441.7	3.90	448.2	150.0
								314.2	270.0	450.1	6.75		
										452.9	7.20		
										458.6	10.5		
										472.8	21.0		

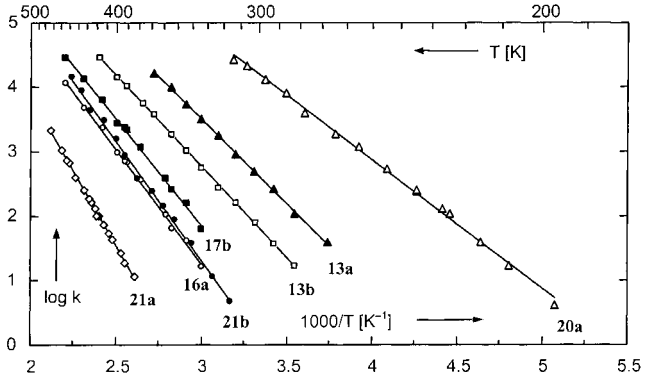


Figure 2. Arrhenius plots for the Cope rearrangements of homotropilidenes **13a**, **13b**, **16a**, **17b**, **20a**, **21a**, **21b**

was complete (reaction times: see below). After evaporation of the solvent, the crude material was purified as described below.

General Procedure (5) for the High-Pressure Synthesis of Tetracyclic Azo Compounds 12v, 12z and 12b$_1$: The 3,4-diazanorcaradiene **11** was dissolved in CH_2Cl_2 (3−4 mL) and transferred into a high-pressure vessel. After addition of the cyclopropene **10e**, the reaction vessel was pressurized to max. 8.0 kbar at a temperature of 52−60 °C until completion of the reaction was indicated by TLC analysis (reaction times: see below). After evaporation of the solvent, the crude material was purified as described below.

Synthesis of 3,4-Homotropilidenes. − General Procedure (6) for the Photolysis of Tetracyclic Azo Compounds 13a, 14a−14b, 16a, 17a, 20a−20c, 21a−21b and 25a: The photolysis was carried out in a water-cooled immersion well photoreactor constructed from quartz. The photoreactor was provided with a medium-pressure mercury lamp (HPK 125 W, Philips) and a Pyrex filter. The photoactive compound was dissolved in an inert solvent (vide infra) and photolyzed with magnetic stirring (reaction times: see below).

General Procedure (7) for the Photolysis of Tetracyclic Azo Compounds 13b−13f, 14c−14d, 16b, 18a−18b, 20d−20f, 21c, 22a−22b and 26a: The photochemical reaction was carried out on an optical bench arrangement, utilizing a focused high-pressure lamp (type HBO-500 W; Osram) and a glass filter (λ_{max} = 280 nm; Schott). The reactant was dissolved in an inert solvent (vide infra) and irradiated with stirring in a water-cooled quartz cell (reaction times: see below).

Synthesis of 3,4-Diazanorcaradienes

Dimethyl 1,6-Diphenyl-3,4-diazanorcaradiene-2,5-dicarboxylate (11f): Compound **10f** (1.00 g, 5.20 mmol) was added in portions at room temp. to a stirred solution of **9a** (800 mg, 4.00 mmol) in CH_2Cl_2 (20 mL), and stirring was continued until the red colour of the tetrazine had disappeared. Purification by recrystallization (CCl_4) afforded **11f** (1.05 g, 2.90 mmol, 72%) as yellow crystals; m.p. 172−174 °C. − IR (KBr): $\tilde{\nu}$ = 3080−2960, 1720 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$, θ = 248 K): δ = 0.96 (d, ^2J = 5.0 Hz, 1 H, 7-H$_{syn}$), 3.60 (d, ^2J = 5.0 Hz, 1 H, 7-H$_{anti}$), 3.63 (s, 6 H, OCH_3), 7.03 (s, broad, 10 H, Ar-H). − UV/Vis (CH_2Cl_2): λ (ε) = 252 (6300). − $C_{21}H_{18}N_2O_4$ (362.4): calcd. C 69.60, H 5.00, N 7.73; found C 69.28, H 5.21, N 7.77.

7-Methyl-2,5-diphenyl-3,4-diazanorcaradiene (11h): Compounds **9c** (1.30 g, 5.55 mmol) and **10c** were stirred in CH_2Cl_2 (80 mL) at room temp. overnight according to General Procedure (1). Purification by recrystallization (CH_2Cl_2/EtOAc) afforded **11h** (1.40 g, 5.40 mmol, 98%) as yellow crystals; m.p. 135 °C. − IR (KBr): $\tilde{\nu}$ = 3040, 2925, 1530, 1495, 1450, 1440, 1390, 755, 680 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.73 (m, 1 H, 7-H$_{syn}$), 1.60 (d, ^3J = 6.1 Hz, 3 H, 7-CH_3-*anti*), 2.47 (d, ^3J = 4.4 Hz, 2 H, 1-H, 6-H), 7.41−8.34 (m, 10 H, Ar-H). − UV/Vis (CH_3CN): λ (ε) = 315 (17780). − $C_{18}H_{16}N_2$ (260.3): calcd. C 83.04, H 6.20, N 10.76; found C 83.33, H 6.38, N 10.57.

1-Methyl-2,5-bis(2-pyridyl)-3,4-diazanorcaradiene (11j): Compounds **9d** (2.30 g, 9.73 mmol) and **10b** were stirred at room temp. overnight in CH_2Cl_2 (60 mL) and toluene (40 mL) according to General Procedure (1). Purification by FC (CH_2Cl_2/ethanol = 10:1) and recrystallization (CH_2Cl_2/*n*-hexane) afforded **11j** (1.60 g, 6.10 mmol, 63%) as yellow crystals; m.p. 139−142 °C. − IR (KBr): $\tilde{\nu}$ = 3090, 3060, 3000, 2940, 1585, 1565, 1550, 1460, 1430, 1390, 1380, 1350, 1040, 1020, 995, 970, 790, 740, 705 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.60 (dd, ^2J = 3.8, ^3J = 5.2 Hz, 1 H, 7-H$_{syn}$), 1.56 (s, 3 H, CH_3), 2.23 (dd, ^2J = 3.8, ^3J = 9.7 Hz, 1 H, 7-H$_{anti}$), 3.13 (dd, ^3J = 5.2, ^3J = 9.7 Hz, 1 H, 6-H), 7.36−7.43 (m, 2 H, Ar-H), 7.79−7.86 (m, 2 H, Ar-H), 8.05−8.09 (m, 1 H, Ar-H), 8.50−8.54 (m, 1 H, Ar-H), 8.73−8.76 (m, 2 H, Ar-H). − $C_{16}H_{14}N_4$ (262.3): calcd. C 73.26, H 5.38, N 21.26; found C 72.83, H 5.16, N 21.24.

7-Methyl-2,5-bis(2-pyridyl)-3,4-diazanorcaradiene (11k): Compounds **9d** (2.30 g, 9.73 mmol) and **10c** were stirred in CH_2Cl_2 (70 mL) and toluene (40 mL) at room temp. overnight according

to General Procedure (1). Purification by FC (DMF/CH_2Cl_2/toluene = 1:2:3) and recrystallization (CH_2Cl_2/*n*-hexane) afforded **11k** (1.95 g, 7.43 mmol, 76%) as yellow crystals; m.p. 165−166 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 3020, 2960, 2920, 2875, 1580, 1560, 1530, 1490, 1470, 1385, 1260, 1150, 1120, 1100, 990, 785, 745 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.65 (dd, ^3J = 5.9, ^3J = 4.2 Hz, 1 H, 7-H_{syn}), 1.58 (d, ^3J = 5.9 Hz, 3 H, 7-CH_3-*anti*), 3.31 (d, ^3J = 4.2 Hz, 2 H, 1-H, 6-H), 7.35−7.42 (m, 2 H, Ar-H), 7.76−7.84 (m, 2 H, Ar-H), 8.47−8.57 (m, 2 H, Ar-H), 8.71−8.74 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ (ε) = 248 (12200), 323 (15800). − $C_{16}H_{14}N_4$ (262.3): calcd. N 21.26; found N 21.27.

Synthesis of Tetracyclic Azo Compounds

Dimethyl *exo*,*exo*-3-Methyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarboxylate (12b): This compound was synthesized according to General Procedure (3); **11a** (2.50 g, 11.9 mmol) and **10c**, after stirring in benzene (30 mL) at room temp. for 15 min and purification by recrystallization (methanol), yielded **12b** (2.18 g, 8.25 mmol, 69%) as colourless crystals, m.p. 70−71 °C. − IR (KBr): $\tilde{\nu}$ = 1735 cm^{-1}. − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.10 (dt, ^2J = 7.6, ^3J = 3.8 Hz, 1 H, 7-H_{syn}), 0.5 (m, ^3J = 5.9, ^3J = 3.1 Hz, 1 H, 3-H_{syn}), 0.5 (m, ^2J = 7.6, ^3J = 7.6 Hz, 1 H, 7-H_{anti}), 0.96 (d, ^3J = 5.9 Hz, 3 H, 3-CH_3-*anti*), 1.67 (d, ^3J = 3.1 Hz, 2 H, 2-H, 4-H), 1.89 (dd, ^3J = 3.8, ^3J = 7.6 Hz, 2 H, 6-H, 8-H). − UV/Vis (1,4-dioxane): λ (ε) = 372 (68). − $C_{13}H_{16}N_2O_4$ (264.3): calcd. C 59.08, H 6.10, N 10.60; found C 59.01, H 6.03, N 10.74.

Dimethyl *exo*,*exo*-2-Methyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarboxylate (12c): This compound was synthesized according to General Procedure (3); **11b** (5.00 g, 23.8 mmol) and **10a**, after stirring in CH_2Cl_2 (30 mL) at room temp. for 15 min and purification by recrystallization (methanol), yielded **12c** (4.50 g, 17.0 mmol, 71%) as colourless crystals, m.p. 98−99 °C. − IR (KBr): $\tilde{\nu}$ = 1740 cm^{-1}. − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.08 (ddd, ^2J = 7.8, ^3J = 3.6, ^3J = 3.6 Hz, 1 H, 7-H_{syn}), 0.32 (dd, ^2J = 6.7, ^3J = 4.8 Hz, 1 H, 3-H_{syn}), 0.40 (dd, ^2J = 6.7, ^3J = 6.8 Hz, 1 H, 3-H_{anti}), 0.58 (ddd, ^2J = 7.8, ^3J = 7.8, ^3J = 7.8 Hz, 1 H, 7-H_{anti}), 1.19 (s, 3 H, CH_3), 1.60 (dd, ^3J = 6.8, ^3J = 4.8 Hz, 1 H, 4-H), 1.88 (dd, ^3J = 7.8, ^3J = 3.6 Hz, 1 H, 6-H), 2.08 (dd, ^3J = 7.8, ^3J = 3.6 Hz, 1 H, 8-H), 3.96 (s, 6 H, OCH_3). − UV/Vis (1,4-dioxane): λ (ε) = 371 (72). − $C_{13}H_{16}N_2O_4$ (264.3): calcd. C 59.08, H 6.10, N 10.60; found C 59.38, H 6.21, N 10.69.

Dimethyl *exo*,*exo*-3,7-Dimethyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarboxylate (12d): This compound was synthesized according to General Procedure (2); **9a** (7.20 g, 36.4 mmol) and **10c**, after stirring in CH_2Cl_2 (30 mL) at room temp. for 15 min and purification by recrystallization (methanol), yielded **12d** (6.70 g, 24.1 mmol, 66%) as colourless crystals; m.p. 110−111 °C. − IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1}. − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.37 (tq, ^3J = 6.0, ^3J = 3.0 Hz, 2 H, 3,7-H_{syn}), 0.93 (d, ^3J = 6.0 Hz, 6 H, 3,7-CH_3-*anti*), 1.63 (d, ^3J = 3.0 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 3.97 (s, 6 H, OCH_3). − UV/Vis (1,4-dioxane): λ (ε) = 371 (79). − $C_{14}H_{18}N_2O_4$ (278.3): calcd. C 60.42, H 6.52, N 10.07; found C 60.65, H 6.57, N 10.25.

Dimethyl *exo*,*exo*-3,7-Di-*tert*-butyl-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarboxylate (12e): This compound was synthesized according to General Procedure (2); **9a** (1.00 g, 5.05 mmol) and **10d** (1.25 g, 13.0 mmol) were stirred in CH_2Cl_2 (10 mL) at room temp. overnight. Purification of the crude product by FC (Et_2O) gave **12e** (213 mg, 0.59 mmol, 12%) as colourless crystals, m.p. 124−125 °C. − IR (KBr): $\tilde{\nu}$ = 2960, 1740 cm^{-1}. − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.33 (t, ^3J = 4.0 Hz, 2 H, 3-H_{syn}, 7-H_{syn}), 0.80 (s, 18 H, *t*Bu-H), 1.73 (d, ^3J = 4.0 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 3.97 (s, 6 H, OCH_3). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 18.7 (=CH, 4 C, 2-C, 4-C, 6-C, 8-C), 28.2 (−CH_3, 6 C, CH_3), 29.1 (=CH, 2 C, 3-C, 7-C), 29.1 (quat. C, 2 C, *t*Bu-C), 52.8 (−CH_3, 2 C, OCH_3), 74.6 (quat. C, 2 C, 1-C, 5-C), 172.1 (quat. C, 2 C, C=O). − UV/Vis (1,4-dioxane): λ (ε) = 275 (356), 283 (294), 295 (322), 332 (36), 372 (50). − $C_{20}H_{30}N_2O_4$ (362.5): calcd. C 66.27, H 8.34, N 7.73; found C 66.26, H 8.26, N 7.51.

Dimethyl *exo*,*exo*-2,6-Dimethyl-19,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]-dec-9-ene-1,5-dicarboxylate (12f): This compound was synthesized according to General Procedure (2); **9a** (7.10 g, 35.9 mmol) and **10b** in CH_2Cl_2 (20 mL), after purification by recrystallization (methanol), gave **12f** (7.50 g, 26.9 mmol, 75%) as colourless crystals; m.p. 158−159 °C. − IR (KBr): $\tilde{\nu}$ = 1730 cm^{-1}. − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.12−0.63 (m, ^2J = 7.5, ^3J = 4.5, ^3J = 8.0 Hz, 4 H, 3,7-H_{syn}, 3,7-H_{anti}), 1.23 (s, 6 H, 2,6-CH_3), 1.81 (dd, ^3J = 8.0, ^3J = 4.5 Hz, 2 H, 4-H, 8-H), 4.00 (s, 6 H, OCH_3). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 13.4 (−CH_2−, 2 C, 3-C, 7-C), 16.9 (−CH_3, 2 C, 2,6-*C*H_3), 18.5 (=CH, 2 C, 4-C, 8-C), 20.8 (quat. C, 2 C, 4-C, 8-C), 52.8 (−CH_3, 2 C, O*C*H_3), 78.5 (quat. C, 2 C, 1-C, 5-C), 171.1 (quat. C, 2 C, C=O). − UV/Vis (1,4-dioxane): λ (ε) = 368 (68). − $C_{14}H_{18}N_2O_4$ (278.3): calcd. C 60.42, H 6.52, N 10.07; found C 60.45, H 6.65, N 10.03.

Dimethyl *exo*,*exo*-3,6-Dimethyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]-dec-9-ene-1,5-dicarboxylate (12g): This compound was synthesized according to General Procedure (3); **11b** (2.40 g, 10.7 mmol) and **10c** in benzene (30 mL), after recrystallization (methanol), yielded **12g** (2.26 g, 8.13 mmol, 76%) as colourless crystals; m.p. 107−108 °C. − IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1}. − ^1H NMR (60 MHz, $CDCl_3$): δ = 0.20−0.54 (m, 3 H, 3/7-H_{syn}, 3-H_{anti}), 0.96 (d, ^3J = 6.6 Hz, 3 H, 3-CH_3-*anti*), 1.20 (s, 3 H, 6-CH_3), 1.72 (dd, ^3J = 3.6, ^3J = 7.4 Hz, 1 H, 8-H), 1.38−1.95 (m, ^3J = 2.6, ^3J = 8.0 Hz, 2 H, 2-H, 4-H), 4.00 (s, 6 H, OCH_3). − UV/Vis (1,4-dioxane): λ (ε) = 370 (71). − $C_{14}H_{18}N_2O_4$ (278.3): calcd. C 60.42, H 6.52, N 10.07; found C 60.47, H 6.43, N 10.14.

Dimethyl *exo*,*exo*-2,4-Diphenyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]-dec-9-ene-1,5-dicarboxylate (12h): This compound was synthesized according to General Procedure (4); **11a** (4.00 g, 19 mmol) and **10f** (3.60 g, 18.7 mmol) were stirred in CH_2Cl_2 (70 mL) at reflux for 40 h. Purification of the crude product by recrystallization (methanol) gave **12h** (4.80 g, 11.9 mmol, 63%) as colourless crystals; m.p. 181−182 °C. − IR (KBr): $\tilde{\nu}$ = 1774, 1745 cm^{-1}. − ^1H NMR (60 MHz, $CDCl_3$): δ = 0.15 (dt, ^2J = 7.0, ^3J = 3.5 Hz, 1 H, 7-H_{syn}), 0.73 (dt, ^2J = 7.0, ^3J = 7.0 Hz, 1 H, 7-H_{anti}), 1.33 (s, 2 H, 3-H_{syn}, 3-H_{anti}), 2.59 (dd, ^3J = 7.0, ^3J = 3.5 Hz, 2 H, 6-H, 8-H), 3.59 (s, 6 H, OCH_3), 7.02−7.53 (m, 10 H, Ar-H). − UV/Vis (1,4-dioxane): λ (ε) = 370 (117). − $C_{24}H_{22}N_2O_4$ (402.4): calcd. C 71.62, H 5.51, N 6.96; found C 71.43, H 5.52, N 6.85.

***exo*,*exo*-3-Methyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarbonitrile (12j):** Hydrolysis of the carboxylic ester **12b** (13.0 g, 49.2 mmol) with KOH (7.80 g, 140 mmol) in aqueous methanol (120 mL, H_2O/methanol = 1:2) and acidification with conc. HCl yielded, after recrystallization (H_2O), the dicarboxylic acid (10.0 g, 42.2 mmol, 86%). This (9.50 g, 40.2 mmol) was stirred with $SOCl_2$ (94.8 g, 58.0 mL, 797 mmol) at room temperature for 3.5 h; addition of conc. ammonia (300 mL) in acetone (100 mL) then produced the amide (7.00 g, 29.9 mmol, 74%) as colourless crystals after recrystallization (H_2O/ethanol = 1:10). A suspension of the amide (6.60 g, 28.2 mmol) and freshly distilled $POCl_3$ (6.61 g, 4.02 mL, 43.1 mmol) in 1,2-dichloroethylene (150 mL) was heated at reflux for 18 h. After evaporation of the solvent, the crude material was purified by recrystallization (CH_3CN), affording **12j** (2.40 g, 12.1 mmol, 43%) as colourless crystals, m.p. 175−176 °C.

– IR (KBr): $\tilde{\nu}$ = 2250 cm^{-1}. – ^1H NMR (90 MHz, [D_6]DMSO, θ = 323 K): δ = 0.04 (dt, ^2J = 7.6, ^3J = 3.6 Hz, 1 H, 7-H_{syn}), 0.45 (tq, ^3J = 6.2, ^3J = 3.1 Hz, 1 H, 3-H_{syn}), 0.74 (dt, ^2J = 7.6, ^3J = 7.6 Hz, 1 H, 7-H_{anti}), 0.95 (d, ^3J = 6.2 Hz, 3 H, 3-CH_3-*anti*), 2.13 (d, ^3J = 3.1 Hz, 2 H, 2-H, 4-H), 2.29 (dd, ^3J = 3.6, ^3J = 7.6 Hz, 2 H, 6-H, 8-H). – UV/Vis (methanol): λ (ε) = 368 (78). – $C_{11}H_{10}N_4$ (198.2): calcd. C 66.65, H 5.09, N 28.27; found C 66.82, H 5.15, N 28.35.

***exo*,*exo*-2-Methyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarbonitrile (12k):** Hydrolysis of the carboxylic ester **12c** (10.0 g, 37.8 mmol) with KOH (6.00 g, 108 mmol) in aqueous methanol (90 mL, H_2O/methanol = 1:2) and acidification with conc. HCl yielded, after recrystallization (H_2O), the dicarboxylic acid (7.30 g, 30.9 mmol, 82%). This (7.10 g, 30.1 mmol) was stirred with $SOCl_2$ (70.9 g, 43.5 mL, 596 mmol) at room temp. for 2.5 h, and after removal of excess $SOCl_2$, addition of conc. ammonia (230 mL) in acetone (60 mL) then gave the amide (3.60 g, 15.5 mmol, 51%) as colourless crystals, after recrystallization (H_2O/ethanol = 3:10). A suspension of the amide (3.40 g, 14.5 mmol) and freshly distilled $POCl_3$ (3.41 g, 2.07 mL, 22.2 mmol) in 1,2-dichloroethylene (70 mL) was heated at reflux for 1 d. After evaporation of the solvent, the crude material was purified by recrystallization (methanol), affording **12k** (1.50 g, 7.57 mmol, 52%) as colourless crystals, m.p. 128–130 °C. – IR (KBr): $\tilde{\nu}$ = 2250 cm^{-1}. – ^1H NMR (60 MHz, $CDCl_3$): δ = 0.32 (ddd, ^2J = 5.9, ^3J = 3.7, ^3J = 3.7 Hz, 1 H, 7-H_{syn}), 0.48 (dd, ^2J = 6.1, ^3J = 3.8 Hz, 1 H, 3-H_{syn}), 0.63 (dd, ^3J = 7.3, ^2J = 6.1 Hz, 1 H, 3-H_{anti}), 0.83 (ddd, ^3J = 7.8, ^3J = 7.8, ^2J = 5.9 Hz, 1 H, 7-H_{anti}), 1.43 (s, 3 H, CH_3), 1.77 (dd, ^3J = 7.3, ^3J = 3.8 Hz, 1 H, 4-H), 2.00 (ddd, ^3J = 7.8, ^3J = 7.8, ^3J = 3.7 Hz, 1 H, 6-H or 8-H), 2.15 (ddd, ^3J = 7.8, ^3J = 7.8, ^3J = 3.7 Hz, 1 H, 8-H or 6-H). – UV/Vis (methanol): λ (ε) = 367 (77). – $C_{11}H_{10}N_4$ (198.2): calcd. C 66.65, H 5.09, N 28.27; found C 67.14, H 5.26, N 28.00.

***exo*,*exo*-3,7-Dimethyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarbonitrile (12l):** Hydrolysis of the carboxylic ester **12d** (6.50 g, 23.4 mmol) with KOH (3.80 g, 68.1 mmol) in aqueous methanol (60 mL, H_2O/methanol = 1:2) and acidification with conc. HCl yielded, after recrystallization (H_2O), the dicarboxylic acid (5.80 g, 23.2 mmol, 99%). This (5.50 g, 22.0 mmol) was stirred with $SOCl_2$ (65.2 g, 40.0 mL, 548 mmol) at room temp. for 3 h; after removal of excess $SOCl_2$, addition of conc. ammonia (150 mL) in acetone (50 mL) then gave the amide (5.00 g, 20.2 mmol, 92%) as colourless crystals, after recrystallization (H_2O/ethanol = 1:1). A suspension of the amide (4.60 g, 18.5 mmol) and freshly distilled $POCl_3$ (4.38 g, 2.66 mL, 28.6 mmol) in 1,2-dichloroethylene (120 mL) was heated at reflux for 2 d. After evaporation of the solvent, the crude material was purified by recrystallization (methanol), affording **12l** (2.50 g, 11.8 mmol, 64%) as colourless crystals, m.p. 170–173 °C. – IR (KBr): $\tilde{\nu}$ = 2260 cm^{-1}. – ^1H NMR (60 MHz, CD_2Cl_2): δ = 0.53 (tq, ^3J = 5.9, ^3J = 3.2 Hz, 2 H, 3,7-H_{syn}), 1.00 (d, ^3J = 5.9 Hz, 6 H, 3,7-CH_3-*anti*), 1.72 (d, ^3J = 3.2 Hz, 4 H, 2-H, 4-H, 6-H, 8-H). – ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 13.5 (=CH, 2 C, 3-C, 7-C), 15.4 (–CH_3, 2 C, 3,7-*C*H_3-*anti*), 23.5 (=CH, 4 C, 2-C, 4-C, 6-C, 8-C), 64.0 (quat. C, 2 C, 1-C, 5-C), 118.4 (quat. C, 2 C, CN). – UV/Vis (1,4-dioxane): λ (ε) = 367 (81). – $C_{12}H_{12}N_4$ (212.2): calcd. C 67.90, H 5.70, N 26.40; found C 67.82, H 5.66, N 26.36.

***exo*,*exo*-3,7-Di-*tert*-butyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarbonitrile (12m):** Hydrolysis of the carboxylic ester **12e** (2.50 g, 6.91 mmol) with KOH (2.00 g, 35.8 mmol) in aqueous methanol (40 mL, H_2O/methanol = 1:2) and acidification with conc. HCl yielded, after recrystallization (H_2O), the dicarboxylic acid (2.10 g, 6.29 mmol, 91%). This (1.80 g, 5.39 mmol) was stirred with $SOCl_2$ (16.3 g, 10.0 mL, 137 mmol) at room temp. for 3.5 h; after removal of excess $SOCl_2$, addition of conc. ammonia (50 mL) in acetone (30 mL) then gave the amide (1.03 g, 3.10 mmol, 58%) as colourless crystals after recrystallization (CH_3CN). A suspension of the amide (1.60 g, 4.82 mmol) and freshly distilled $POCl_3$ (1.25 g, 0.76 mL, 8.15 mmol) in 1,2-dichloroethylene (20 mL) was heated at reflux for 20 h. After evaporation of the solvent, the crude material was purified by FC (CH_2Cl_2) and recrystallization (CH_2Cl_2/*n*-hexane), affording **12m** (0.77 g, 2.60 mmol, 54%) as colourless crystals, m.p. 165–167 °C. – IR (KBr): $\tilde{\nu}$ = 3070, 2965, 2910, 2875, 2245 cm^{-1}. – ^1H NMR (90 MHz, $CDCl_3$): δ = 0.40 (t, ^3J = 4.0 Hz, 2 H, 3,7-H_{syn}), 0.87 (s, 18 H, *t*Bu-H), 1.85 (d, ^3J = 4.0 Hz, 4 H, 2-H, 4-H, 6-H, 8-H). – ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 19.4 (=CH, 4 C, 2-C, 4-C, 6-C, 8-C), 28.0 (–CH_3, 6 C, CH_3), 29.0 (quat. C, 2 C, *t*Bu-C), 29.3 (=CH, 2 C, 3-C, 7-C), 64.4 (quat. C, 2 C, 1-C, 5-C), 118.2 (quat. C, 2 C, CN). – UV/Vis (methanol): λ (ε) = 369 (39), 350 (22), 333 (22). – $C_{18}H_{24}N_4$ (296.4): calcd. C 72.94, H 8.16, N 18.90; found C 72.61, H 8.00, N 18.99.

***exo*,*exo*-2,6-Dimethyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarbonitrile (12n):** Hydrolysis of the carboxylic ester **12f** (7.50 g, 27.0 mmol) with KOH (5.30 g, 94.6 mmol) in aqueous methanol (90 mL, H_2O/methanol = 1:2) and acidification with conc. HCl yielded, after recrystallization (H_2O), the dicarboxylic acid (6.00 g, 24.0 mmol, 89%). This (2.50 g, 10.0 mmol) was stirred with $SOCl_2$ (32.6 g, 20.0 mL, 274 mmol) at room temp. for 3 h; after removal of excess $SOCl_2$, addition of conc. ammonia (75 mL) in acetone (18 mL) then gave the amide (1.30 g, 5.20 mmol, 52%) as colourless crystals after recrystallization (ethanol). A suspension of the amide (2.80 g, 11.3 mmol) and freshly distilled $POCl_3$ (2.50 g, 1.52 mL, 16.3 mmol) in 1,2-dichloroethylene (70 mL) was heated at reflux for 1 d. Purification of the crude product by recrystallization (methanol) afforded **12n** (1.37 g, 6.46 mmol, 57%) as colourless crystals, m.p. 159–160 °C. – IR (KBr): $\tilde{\nu}$ = 2250 cm^{-1}. – ^1H NMR (60 MHz, $CDCl_3$): δ = 0.40 (dd, ^2J = 7.3, ^3J = 4.0 Hz, 2 H, 3,7-H_{syn}), 0.65 (dd, ^2J = 7.3, ^3J = 7.2 Hz, 2 H, 3,7-H_{anti}), 1.44 (s, 6 H, 2,6-CH_3), 1.81 (dd, ^3J = 7.2, ^3J = 4.0 Hz, 2 H, 4-H, 8-H). – UV/Vis (methanol): λ (ε) = 366 (71). – $C_{12}H_{12}N_4$ (212.2): calcd. C 67.90, H 5.70, N 26.40; found C 67.89, H 5.66, N 26.14.

***exo*,*exo*-2,4-Diphenyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-1,5-dicarbonitrile (12o):** Hydrolysis of the carboxylic ester **12h** (2.30 g, 5.70 mmol) with KOH (1.20 g, 21.5 mmol) in aqueous methanol (60 mL, H_2O/methanol = 1:2) and acidification with conc. HCl yielded, after recrystallization (H_2O), the dicarboxylic acid (2.10 g, 5.60 mmol, 98%). This (2.10 g, 5.60 mmol) was stirred with $SOCl_2$ (16.3 g, 10.0 mL, 137 mmol) at room temp. for 2 h. After removal of excess $SOCl_2$, addition of conc. ammonia (75 mL) in acetone (18 mL) then gave the amide (1.60 g, 4.30 mmol, 77%) as colourless crystals after recrystallization (ethanol). A suspension of the amide (1.50 g, 4.00 mmol) and freshly distilled $POCl_3$ (1.50 g, 4.00 mmol) in 1,2-dichloroethylene (70 mL) was heated at reflux for 2 d. Purification of the crude product by recrystallization (methanol) afforded **12o** (120 mg, 0.36 mmol, 9%) as colourless crystals, m.p. 192–194 °C. – IR (KBr): $\tilde{\nu}$ = 2250 cm^{-1}. – ^1H NMR (60 MHz, CD_2Cl_2): δ = 0.43 (dt, ^2J = 7.6, ^3J = 3.6 Hz, 1 H, 7-H_{syn}), 0.93 (dt, ^2J = 7.6, ^3J = 7.6 Hz, 1 H, 7-H_{anti}), 1.26 (d, ^2J = 7.5 Hz, 1 H, 3-H_{syn}), 1.52 (d, ^2J = 7.5 Hz, 1 H, 3-H_{anti}), 2.62 (dd, ^3J = 7.6, ^3J = 3.6 Hz, 2 H, 6-H, 8-H), 7.22–7.61 (m, 10 H, Ar-H). – $C_{22}H_{16}N_4$ (336.4): calcd. C 78.54, H 4.80, N 16.66; found C 78.49, H 4.99, N 16.69.

***exo*,*exo*-1,5-Diphenyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (12p):** Compounds **11g** (1.66 g, 5.79 mmol) and **10a** were

stirred in CH_2Cl_2 (50 mL) at 35 °C overnight, according to General Procedure (3). After purification by FC (EtOAc/*n*-hexane = 2:1) and recrystallization (Et_2O), a mixture of two azo compounds was obtained as colourless crystals containing **12p** (479 mg, 1.67 mmol, 29%) in a 3:2 ratio (determined by analytical HPLC: LiChrosorb RP 18, methanol/H_2O = 90:10). Subjection of this mixture to photolysis according to General Procedure (7) gave a mixture of the corresponding homotropilidenes, which could then be separated by preparative HPLC (LiChroprep. RP 8, methanol/H_2O = 93:7). Analytical data for **12p** obtained from the inseparable mixture: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.16−0.81 (m, 4 H, 3,7-H_{syn}, 3,7-H_{anti}), 1.83 (dd, ^3J = 7.7, ^3J = 3.7 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 7.24−7.56 (m, 6 H, Ar-H), 7.77−7.86 (m, 4 H, Ar-H).

***exo*,*exo*-3-Methyl-1,5-diphenyl-9,10-diazatetracyclo[3.3.2.0^{2,4}.0^{6,8}]-dec-9-ene (12q):** Compounds **11g** (2.50 g, 10.1 mmol) and **10c** were stirred in CH_2Cl_2 (50 mL) at 35 °C for 15 h according to General Procedure (3). Purification by FC (EtOAc/*n*-hexane = 2:1) and recrystallization (Et_2O) afforded **12q** (1.43 g, 4.77 mmol, 51%) as colourless crystals, m.p. 106−108 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 3030, 2950, 2920, 1600, 1490, 1440, 1315, 1050, 1020, 750, 680 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.35 (dt, ^2J = 6.2, ^3J = 3.4 Hz, 1 H, 3-H_{syn}), 0.66−0.77 (m, 2 H, 7-H_{syn}, 7-H_{anti}), 1.11 (d, ^3J = 6.1 Hz, 3 H, 3-CH_3-*anti*), 1.57 (d, ^3J = 3.4 Hz, 2 H, 2-H, 4-H), 1.77 (dd, ^3J = 7.7 Hz; ^3J = 3.6 Hz, 2 H, 6-H, 8-H), 7.23−7.52 (m, 6 H, Ar-H), 7.78−7.81 (m, 4 H, Ar-H). − UV/Vis (CH_3CN): λ (ε) = 224 (6890), 386 (66).

***exo*,*exo*-3,7-Dimethyl-1,5-diphenyl-9,10-diazatetracyclo]-[3.3.2.0^{2,4}.0^{6,8}dec-9-ene (12r):** Compounds **11h** (2.85 g, 10.9 mmol) and **10c** were stirred in CH_2Cl_2 (50 mL) at 35 °C for 15 h according to General Procedure (3). Purification by FC (EtOAc/*n*-hexane = 2:1) and recrystallization (Et_2O) afforded **12r** (1.44 g, 4.80 mmol, 44%) as colourless crystals, m.p. 141−143 °C. − IR (KBr): $\tilde{\nu}$ = 3070, 3040, 3010, 2950, 1600, 1490, 1445, 1210, 1070, 1025, 755, 700 cm^{-1}. − ^{1}H NMR (60 MHz, $CDCl_3$): δ = 0.65 (m, 2 H, 2-H, 3,7-H_{syn}), 1.11 (d, ^3J = 6.1 Hz, 6 H, 3,7-CH_3-*anti*), 1.52 (d, ^3J = 3.2 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 7.23−7.53 (m, 6 H, Ar-H), 7.63−7.82 (m, 4 H, Ar-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 13.7 (=CH, 2 C, 3-C, 7-C), 16.3 (−CH_3, 2 C, 3,7-*C*H$_3$-*anti*), 25.8 (=CH, 4 C, 2-C, 4-C, 6-C, 8-C), 74.1 (quat. C, 2 C, 1-C, 5-C), 127.3 (=CH, 2 C, Ar-C), 127.8 (=CH, 2 C, Ar-C), 128.5 (=CH, 2 C, Ar-C), 142.9 (quat. C, 2 C, Ar-C). − UV/Vis (CH_3CN): λ (ε) = 29 (8895), 385 (62). − $C_{22}H_{22}N_2$ (300.3): calcd. N 8.97; found N 8.60.

***exo*,*exo*-3-Methyl-1,5-bis(2-pyridyl)-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (12t):** Compounds **11i** (1.50 g, 6.04 mmol) and **10c** were stirred in CH_2Cl_2 (50 mL) and toluene (35 mL) at room temp. for 2 d according to General Procedure (3). Purification of the crude product by FC (CH_2Cl_2/ethanol = 15:1) and recrystallization (CH_2Cl_2/*n*-hexane) afforded **12t** (576 mg, 1.90 mmol, 47%) as colourless crystals, m.p. 147−149 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 3010, 2970, 2940, 2890, 1580, 1565, 1530, 1465, 1430, 1315, 1150, 1095, 1070, 1050, 1035, 1000, 990, 820, 780, 755, 710, 700, 650, 620 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11 (dt, ^2J = 6.4, ^3J = 3.6 Hz, 1 H, 7-H_{syn}), 0.41−0.54 (m, ^3J = 3.0, ^3J = 6.1 Hz, 1 H, 3-H_{syn}), 0.41−0.54 (m, ^2J = 6.4, ^3J = 7.8 Hz, 1 H, 7-H_{anti}), 0.91 (d, ^3J = 6.1 Hz, 3 H, 3-CH_3-*anti*), 1.94 (d, ^3J = 3.0 Hz, 2 H, 2-H, 4-H), 2.18 (dd, ^3J = 3.6, ^3J = 7.8 Hz, 2 H, 6-H, 8-H), 7.28−7.33 (m, 2 H, Ar-H), 7.79−7.86 (m, 2 H, Ar-H), 8.12−8.16 (m, 2 H, Ar-H), 8.72−8.75 (m, 2 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 5.2 (−CH_2−, 1 C, 7-C), 13.2 (−CH_3, 1 C, 3-*C*H$_3$-*anti*), 16.4 (=CH, 1 C, 3-C), 17.6 (=CH, 2 C, 6-C, 8-C), 26.4 (=CH, 2 C, 2-C, 4-C), 75.1 (=CH, 2 C, 1-C, 5-C), 122.1 (=CH, 2 C, Ar-C), 122.4 (=CH, 2 C, Ar-C), 136.4 (=CH, 2 C, Ar-C), 149.2 (=CH, 2 C, Ar-C), 161.8 (quat. C, 2 C, Ar-C). − UV/Vis (CH_3CN): λ (ε) = 259 (7310), 379 (111). − $C_{19}H_{18}N_4$ (302.4): calcd. C 75.47, H 6.00, N 18.53; found C 75.66, H 6.14, N 18.45.

***exo*,*exo*-2-Methyl-1,5-bis(2-pyridyl)-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (12u):** Compounds **11i** (1.00 g, 4.03 mmol) and **10b** were stirred in CH_2Cl_2 (55 mL) and toluene (70 mL) at room temp. for 4 h according to General Procedure (3). Purification of the crude product by FC (CH_2Cl_2/ethanol = 15:1) and recrystallization (CH_2Cl_2/*n*-hexane) afforded **12u** (780 mg, 2.58 mmol, 63%) as colourless crystals, m.p. 134−135 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 3010, 2970, 2930, 2870, 1585, 1565, 1465, 1430, 1070, 1035, 990, 880, 870, 855 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12−0.15 (m, 1 H, 7-H_{syn}), 0.38 (dd, ^2J = 6.2, ^3J = 7.8 Hz, 1 H, 3-H_{anti}), 0.48 (dd, ^2J = 6.2, ^3J = 3.6 Hz, 1 H, 3-H_{syn}), 0.61−0.66 (m, 1 H, 7-H_{anti}), 0.98 (s, 3 H, 2-CH_3), 1.88 (dd, ^3J = 3.6, ^3J = 7.8 Hz, 1 H, 4-H), 2.13−2.18 (m, 1 H, 6-H), 2.52−2.57 (m, 1 H, 8-H), 7.25−7.30 (m, 2 H, Ar-H), 7.76−7.85 (m, 3 H, Ar-H), 8.10−8.12 (m, 1 H, Ar-H), 8.69−8.72 (m, 2 H, Ar-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.1 (−CH_2−, 1 C, 7-C), 12.1 (=CH, 1 C, 8-C), 13.4 (−CH_2−, 1 C, 3-C), 17.1 (=CH, 1 C, 6-C),17.5 (−CH_3, 1-C, 2-*C*H$_3$), 23.1 (quat. C, 1 C, 2-C), 24.9 (=CH, 1 C, 4-C), 75.5 (quat. C, 1 C, 5-C), 78.6 (quat. C, 1 C, 1-C), 122.1 (=CH, 1 C, Ar-C), 122.4 (=CH, 1 C, Ar-C), 122.6 (=CH, 1 C, Ar-C), 123.2 (=CH, 1 C, Ar-C), 136.4 (=CH, 1 C, Ar-C), 136.5 (=CH, 1 C, Ar-C), 148.7 (=CH, 1 C, Ar-C), 149.1 (=CH, 1 C, Ar-C), 160.4 (quat. C, 1 C, Ar-C), 161.4 (quat. C, 1 C, Ar-C). − UV/Vis (CH_3CN): λ (ε) = 255 (7210), 260 (7450), 348 (16.6), 362 (29.4), 380 (59.3). − $C_{19}H_{18}N_4$ (302.4): calcd. C 75.47, H 6.00, N 18.53; found C 75.34, H 6.00, N 18.54.

***exo*,*exo*-3,3-Dimethyl-1,5-bis(2-pyridyl)-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (12v):** Compounds **11i** (638 mg, 2.56 mmol) and **10e** (940 mg, 13.8 mmol) in CH_2Cl_2 (3 mL) were pressurized in a reaction vessel to 8.0 kbar at 60 °C for 3 d according to General Procedure (5). Purification by FC (CH_2Cl_2/ethanol = 15:1) and recrystallization (EtOAc) afforded **12v** (549 mg, 1.74 mmol, 68%) as pink crystals, m.p. 159−160 °C. − IR (KBr): $\tilde{\nu}$ = 3060, 3010, 2970, 2930, 2880, 1585, 1570, 1470, 1430, 1320, 1120, 1100, 1065, 1040, 1005, 820, 780, 735, 700, 620 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.14 (dt, ^2J = 6.5, ^3J = 3.6 Hz, 1 H, 7-H_{syn}), 0.53 (dt, ^2J = 6.5, ^3J = 7.7 Hz, 1 H, 7-H_{anti}), 0.93 (s, 3 H, 3-CH_3-*syn*), 1.13 (s, 3 H, 3-CH_3-*anti*), 2.10 (s, 2 H, 2-H, 4-H), 2.25 (dd, ^3J = 3.6, ^3J = 7.7 Hz, 2 H, 6-H, 8-H), 7.29−7.35 (m, 2 H, Ar-H), 7.81−7.88 (m, 2 H, Ar-H), 8.15−8.19 (m, 2 H, Ar-H), 8.74−8.77 (m, 2 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 5.9 (−CH_2−, 1 C, 7-C), 18.0 (=CH, 2 C, 6-C, 8-C), 19.2 (−CH_3, 1 C, 3-*C*H$_3$-*syn*), 23.6 (quat. C, 1 C, 3-C), 30.6 (−CH_3, 1 C, 3-*C*H$_3$-*anti*), 37.8 (=CH, 2 C, 2-C, 4-C), 76.6 (quat. C, 2 C, 1-C, 5-C), 122.2 (=CH, 2 C, Ar-C), 122.8 (=CH, 2 C, Ar-C), 139.4 (=CH, 2 C, Ar-C), 149.3 (=CH, 2 C, Ar-C), 162.0 (quat. C, 2 C, Ar-C). − UV/Vis (CH_3CN): λ (ε) = 213 (6270), 382 (92). − $C_{20}H_{20}N_4$ (316.4): calcd. C 75.92, H 6.37, N 17.71; found C 76.23, H 6.34, N 17.68.

***exo*,*exo*-3,7-Dimethyl-1,5-bis(2-pyridyl)-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (12w):** Compounds **11k** (600 mg, 2.29 mmol) and **10c** were stirred in CH_2Cl_2 (50 mL) at room temp. overnight according to General Procedure (3). Purification by FC (EtOAc/*n*-hexane = 3:1) and recrystallization (CH_2Cl_2/*n*-hexane) afforded **12w** (489 mg, 1.54 mmol, 67%) as colourless crystals, m.p. 167−168 °C. − IR (KBr): $\tilde{\nu}$ = 3070, 3030, 2980, 2940, 2880, 1585, 1570, 1530, 1455, 1430, 1310, 1145, 1095, 1060, 1045, 995, 770, 750, 700 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.40 (tq, ^3J = 6.2, ^3J = 3.0 Hz, 2 H, 3,7-H_{syn}), 0.88 (d, ^3J = 6.2 Hz, 6 H, 3,7-CH_3-

anti), 1.93 (d, ^3J = 3.0 Hz, 4 H, 2-H, 4-H, 6-H, 8-H), 7.27−7.33 (m, 2 H, Ar-H), 7.79−7.86 (m, 2 H, Ar-H), 8.15−8.19 (m, 2 H, Ar-H), 8.72−8.75 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ (ε) = 258 (8000), 380 (54). − $C_{20}H_{20}N_4$ (316.4): calcd. C 75.92, H 6.37, N 17.71; found C 76.08, H 6.28, N 17.67.

***exo*,*exo*-2,6-Dimethyl-1,5-bis(2-pyridyl)-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (12x):** Compounds **11j** (890 mg, 3.39 mmol) and **10b** were stirred in CH_2Cl_2 (60 mL) and toluene (40 mL) at room temp. overnight according to General Procedure (3). Purification of the crude product by FC (CH_2Cl_2/*n*-hexane/ethanol = 10:1:2) and recrystallization (CH_2Cl_2/*n*-hexane) afforded **12x** (460 mg, 1.45 mmol, 43%) as colourless crystals, m.p. 154−155 °C. − IR (KBr): ṽ = 3050, 3010, 2950, 2930, 2870, 1585, 1560, 1465, 1425, 1300, 1145, 1080, 1035, 985, 795, 785, 765 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.45 (dd, ^2J = 6.2, ^3J = 3.8 Hz, 2 H, 3,7-H$_{syn}$), 0.54 (dd, ^2J = 6.2, ^3J = 7.9 Hz, 2 H, 3,7-H$_{anti}$), 1.01 (s, 6 H, 2,6-C*H*$_3$), 2.29 (dd, ^3J = 3.8, ^3J = 7.9 Hz, 2 H, 4-H, 8-H), 7.29−7.33 (m, 2 H, Ar-H), 7.80−7.88 (m, 4 H, Ar-H), 8.71−8.73 (m, 2 H, Ar-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 (−CH_2−, 2 C, 3-C, 7-C), 17.6 (−CH_3, 2 C, CH_3), 19.5 (=CH, 2 C, 4-C, 8-C), 22.7 (quat. C, 2 C, 2-C, 6-C), 79.5 (quat. C, 2 C, 1-C, 5-C), 122.7 (=CH, 2 C, Ar-C), 123.4 (=CH, 2 C, Ar-C), 136.6 (=CH, 2 C, Ar-C), 148.7 (=CH, 2 C, Ar-C), 160.6 (quat. C, 2 C, Ar-C). − UV/Vis (CH_3CN): λ (ε) = 260 (6910), 342 (13), 361 (28), 390 (55). − $C_{20}H_{20}N_4$ (316.4): calcd. C 75.92, H 6.37, N 17.71; found C 75.67, H 6.42, N 17.55.

***exo*,*exo*-3,6-Dimethyl-1,5-bis(2-pyridyl)-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (12y):** Compounds **11k** (910 mg, 3.47 mmol) and **10b** were stirred in CH_2Cl_2 (60 mL) at room temp. overnight according to General Procedure (3). Purification by FC (CH_2Cl_2/*n*-hexane/ethanol = 15:2:1) and recrystallization (CH_2Cl_2/*n*-hexane) afforded **12y** (531 mg, 1.68 mmol, 48%) as colourless crystals, m.p. 159−161 °C. − IR (KBr): ṽ = 3060, 3010, 2980, 2940, 2880, 1585, 1565, 1465, 1430, 1310, 1080, 1045, 1035, 995, 775, 760, 750 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.33 (dd, ^2J = 6.2, ^3J = 7.7 Hz, 2 H, 7-H$_{anti}$), 0.41−0.43 (m, ^2J = 6.1, ^3J = 2.9, ^3J = 3.1 Hz, 1 H, 3-H$_{syn}$), 0.46 (dd, ^2J = 6.2, ^3J = 3.7 Hz, 1 H, 7-H$_{syn}$), 0.99 (s, 3 H, 6-C*H*$_3$), 1.02 (d, ^3J = 6.1 Hz, 3 H, 3-C*H*$_3$-*anti*), 1.86 (dd, ^3J = 3.7, ^3J = 7.7 Hz, 1 H, 8-H), 1.90 (dd, ^3J = 2.9, ^3J = 8.0 Hz, 1 H, 2-H or 4-H), 2.29 (dd, ^3J = 3.1, ^3J = 8.0 Hz, 1 H, 4-H or 2-H), 7.27−7.34 (m, 2 H, Ar-H), 7.78−7.87 (m, 3 H, Ar-H), 8.13−8.17 (m, 1 H, Ar-H), 8.71−8.76 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ (ε) = 260 (7450), 342 (17), 364 (31), 380 (58). − $C_{20}H_{20}N_4$ (316.4): calcd. C 75.92, H 6.37, N 17.71; found C 75.43, H 6.78, N 17.45.

***exo*,*exo*-3,3,7-Trimethyl-1,5-bis(2-pyridyl)-9,10-diazatetracyclo-[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene (12z):** Compounds **11k** (684 mg, 2.61 mmol) and **10e** (1.00 g, 14.7 mmol) in CH_2Cl_2 (3 mL) were pressurized in a reaction vessel to 8.0 kbar at 60 °C for 3 d according to General Procedure (5). Purification by FC (CH_2Cl_2/EtOAc/*n*-hexane = 3:1:1) and recrystallization (EtOAc) afforded **12z** (641 mg, 1.94 mmol, 74%) as colourless crystals, m.p. 201−203 °C. − IR (KBr): ṽ = 3060, 3020, 2960, 2930, 2870, 1585, 1565, 1535, 1465, 1430, 1315, 1150, 1095, 1065, 1040, 1000, 780, 755, 705, 600 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.41 (tq, ^3J = 6.1, ^3J = 3.0 Hz, 1 H, 7-H$_{syn}$), 0.88 (s, 3 H, 3-C*H*$_3$-*syn*), 0.89 (d, ^3J = 6.1 Hz, 3 H, 7-C*H*$_3$-*anti*), 1.07 (s, 3 H, 3-C*H*$_3$-*anti*), 2.00 (d, ^3J = 3.0 Hz, 2 H, 6-H, 8-H), 2.08 (s, 2 H, 2-H, 4-H), 7.28−7.34 (m, 2 H, Ar-H), 7.80−7.87 (m, 2 H, Ar-H), 8.19−8.23 (m, 2 H, Ar-H), 8.73−8.76 (m, 2 H, Ar-H). − UV/Vis (CH_3CN): λ (ε) = 261 (91), 381 (8830). − $C_{21}H_{22}N_4$ (330.4): calcd. C 76.33, H 6.71, N 16.96; found C 76.33, H 6.47, N 16.86.

***exo*,*exo*-3,3-Dimethyl-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 (12b$_1$):** Compounds **11m** (99.4 mg, 0.385 mmol) and **10e** (272 mg, 4.40 mmol) in CH_2Cl_2 (4 mL) were pressurized in a reaction vessel to 7.2 kbar at 52 °C for 3 d, according to General Procedure (5). Purification by recrystallization (CH_2Cl_2/*n*-hexane) afforded **12b$_1$** (71.8 mg, 0.220 mmol, 57%) as colourless crystals, m.p. 163−164 °C. − IR (KBr): ṽ = 3050, 3010, 2960, 2930, 2870, 1585, 1560, 1445, 1385, 1345, 1240, 1080, 1030, 965, 940, 820 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.36 (dt, ^2J = 7.5, ^3J = 3.7 Hz, 1 H, 7-H$_{syn}$), 0.80 (dt, ^2J = 7.5, ^3J = 7.7 Hz, 1 H, 7-H$_{anti}$), 1.06 (s, 3 H, 3-C*H*$_3$-*syn*), 1.17 (s, 3 H, 3-C*H*$_3$-*anti*), 2.00 (s, 2 H, 2-H, 4-H), 2.13 (dd, ^3J = 7.7, ^3J = 3.7 Hz, 6-H, 8-H), 2.68 (s, 6 H, Ar-C*H*$_3$). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 6.6 (−CH_2, 1 C, 7-C), 11.2 (−CH_3, 2 C, Ar-*C*H$_3$), 16.0 (−CH_2, 2 C, 6-C, 8-C), 19.1 (−CH_3, 1 C, 3-*C*H$_3$-*syn*), 24.4 (quat.C, 1 C, 3-C), 30.3 (−CH_3, 1 C, 3-*C*H$_3$-*anti*), 35.3 (−CH, 2 C, 2-C, 4-C), 70.1 (quat. C, 2 C, 1-C, 5-C), 165.3 (quat. C, 2 C, Ar-C), 166.7 (quat. C, 2 C, Ar-C). − UV/Vis (CH_3CN): λ (ε) = 385 (140). − MS (EI, 70 eV): *m*/*z* (%) = 298 (23), 297 (83), 283 (11), 201 (100), 187 (30). − $C_{16}H_{18}N_6O_2$ (326.4): calcd. C 58.88, H 5.56, N 25.75; found C 58.93, H 5.83, N 25.31.

Synthesis of 3,4-Homotropilidenes

Dimethyl 3,4-Homotropilidene-2,6-dicarboxylate (13a): Compound **12a** (500 mg, 2.00 mmol), after photolysis in benzene (200 mL) at room temp. for 15 min according to General Procedure (6) and purification by distillation at 0.001 Torr, yielded **13a** (351 mg, 1.58 mmol, 79%) as an colourless oil. − IR (film): ṽ = 1715 cm^{-1}. − ^{1}H NMR (100 MHz, [D$_8$]toluene, θ = 214 K): δ = 0.13 (dt, ^2J = 3.5, ^3J = 6.0 Hz, 1-H, 8-H$_{syn}$), 1.34 (dt, ^2J = 3.5, ^3J = 9.0 Hz, 1 H, 8-H$_{anti}$), 1.78 (dd, ^3J = 6.0, ^3J = 9.0 Hz, 2 H, 1-H, 7-H), 1.92 (dt, ^2J = 16.0, ^3J = 8.5 Hz, 1 H, 4-H$_{eq}$), 2.62 (dt, ^2J = 16.0, ^3J = 4.0 Hz, 1 H, 4-H$_{ax}$), 3.76 (s, 6 H, OC*H*$_3$), 6.91 (dd, ^3J = 8.5, ^3J = 4.0 Hz, 2 H, 3-H, 5-H). − UV/Vis (1,4-dioxane): λ (ε) = 286 (1150). − $C_{12}H_{14}O_2$ (222.2): calcd. C 64.85, H 6.35; found C 65.01, H 6.47.

3,4-Homotropilidene-2,6-dicarbonitrile (13b): Compound **12i** (400 mg, 2.20 mmol), after photolysis in benzene (50 mL) at room temp. for 7 h according to General Procedure (7) and purification by filtration and evaporation of the solvent, yielded **13b** (344 mg, 2.20 mmol, quant.) as a colourless oil. − IR (KBr): ṽ = 3090, 2990, 2220, 1630 cm^{-1}. − ^{1}H NMR (100 MHz, [D$_8$]toluene, θ = 226 K): δ −0.19 (dt, ^2J = 3.5, ^3J = 6.0 Hz, 1-H, 8-H$_{syn}$), 0.49 (dt, ^2J = 3.5, ^3J = 9.0 Hz, 1 H, 8-H$_{anti}$), 0.81 (dd, ^3J = 6.0, ^3J = 9.0 Hz, 2 H, 1-H, 7-H), 1.28 (dt, ^2J = 18.0, ^3J = 8.0 Hz, 1 H, 4-H$_{eq}$), 2.00 (dt, ^2J = 18.0, ^3J = 4.0 Hz, 1 H, 4-H$_{ax}$), 5.42 (dd, ^3J = 8.0, ^3J = 4.0 Hz, 2 H, 3-H, 5-H). − UV/Vis (methanol): λ (ε) = 270 (1745). − MS (EI, 70 eV): *m*/*z* (%) = 156 (61) [M^+], 128 (100). − $C_{10}H_8N_2$ (156.2): calcd. C 76.90, H 5.16, N 17.94; found C 76.98, H 5.18, N 18.11.

2,6-Diphenyl-3,4-homotropilidene (13c): An inseparable mixture of two azo compounds containing 60% of **12p** (287 mg, 1.00 mmol) was photolyzed in CH_3CN (15 mL) at room temp. for 15 min according to General Procedure (7). Separation by preparative HPLC (LiChroprep. RP 8, methanol/H_2O = 93:7) afforded the desired homotropilidene **13c** (245 mg, 0.95 mmol, 95%) as colourless crystals; m.p. 100−101 °C, ref. m.p. 101 °C.[39][59] − IR (KBr): ṽ = 3050, 3010, 1590, 1485, 1440, 825, 750, 685 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.25−0.30 (m, broad, 1 H, 8-H$_{syn}$), 1.46−1.55 (m, broad, 1 H, 8-H$_{anti}$), 2.14 (m, broad, ^3J = 7.2 Hz, 2 H, 1-H, 7-H), 2.67 (dt, broad, ^2J = 15.2, ^3J = 8.0 Hz, 1 H, 4-H$_{eq}$), 3.51 (m, broad, ^2J = 15.2 Hz, 1 H, 4-H$_{ax}$), 6.44−6.48 (m, broad, 2 H, 3-H, 5-H), 7.18−7.34 (m, 6 H, Ar-H), 7.55−7.60 (m, 4 H, Ar-

H). − MS (EI, 70 eV): *m/z* (%) = 259 (19) [M^+], 238 (100). − UV/Vis (CH_3CN): λ (ε) = 267 (11750), 246 (13580), 220 (15260).

2,6-Bis(2-pyridyl)-3,4-homotropilidene (13d): Compound **12s** (302 mg, 1.05 mmol) was photolyzed in CH_3CN (45 mL) at room temp. for 5 h, according to General Procedure (7). Purification by FC (CH_2Cl_2/ethanol = 15:1) and recrystallization (methanol/H_2O) afforded **13d** (83.3 mg, 0.320 mmol, 30%) as brown crystals, m.p. 70−72 °C. − IR (KBr): ṽ = 3060, 3010, 2980, 2860, 1660, 1585, 1565, 1470, 1430, 1155, 995, 790, 780, 750 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.21−0.22 (m, 1 H, 8-H_{syn}), 1.49−1.57 (m, 1 H, 8-H_{anti}), 2.24−2.30 (m, 2 H, 1-H, 7-H), 2.79−2.92 (m, 1 H, 4-H_{eq}), 3.54−3.61 (m, 1 H, 4-H_{ax}), 7.08−7.31 (m, 4 H, 3-H, 5-H, Ar-H), 7.44−7.82 (m, 4 H, Ar-H), 8.53−8.61 (m, 2 H, Ar-H). − $C_{18}H_{16}N_2$ (260.3). calcd. C 83.06, H 6.20, N 10.76; found C 83.08, H 6.62, N 10.66.

2,6-Bis(2-methyl-1,3,4-oxadiazol-5-yl)-3,4-homotropilidene (13e): Compound **12a$_1$** (98 mg, 0.328 mmol) was photolyzed in CH_2Cl_2 (20 mL) at room temp. for 3.5 h according to General Procedure (7). Purification by FC ($CHCl_3$/ethanol = 15:1) and recrystallization (CH_2Cl_2/*n*-pentane) afforded **13e** (69.0 mg, 0.255 mmol, 78%) as colourless crystals, m.p. 160−161 °C. − IR (KBr): ṽ = 3080, 3010, 2960, 2895, 1650, 1575, 1520, 1220, 1050, 1030, 1010, 970, 905, 810, 720, 670 cm^{-1}. − ^1H NMR (400 MHz, CD_2Cl_2, θ = 223 K): δ = 0.41 (dt, ^2J = 4.1, ^3J = 6.2 Hz, 1-H, 8-H_{syn}), 1.63 (dt, ^2J = 4.1, ^3J = 9.3 Hz, 1 H, 8-H_{anti}), 2.28 (ddd, ^3J = 9.3, ^3J = 6.2, ^5J = 1.9 Hz, 2 H, 1-H, 7-H), 2.54 (s, 6 H, Ar-CH_3), 2.94 (dt, ^2J = 16.4, ^3J = 8.6 Hz, 1 H, 4-H_{eq}), 3.58 (dtt, ^2J = 16.4, ^3J = 4.1, ^5J = 1.9 Hz, 1 H, 4-H_{ax}), 6.94 (dd, ^3J = 8.6, ^3J = 4.1 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR: (63 MHz, CD_2Cl_2, θ = 223 K): δ = 11.1 (−CH_3, 2 C, Ar-*C*H_3), 14.2 (−CH_2−, 1 C, 8-C), 16.6 (=CH, 2 C, 1-C, 7-C), 25.5 (−CH_2−, 1 C, 4-C), 126.1 (quat. C, 2 C, 2-C, 6-C), 135.0 (=CH, 2 C, 3-C, 5-C), 163.2 (quat. C, 2 C, Ar-C), 165.3 (quat. C, 2 C, Ar-C). − UV/Vis (1,4-dioxane): λ (ε) = 233 (15400). − MS (EI, 70 eV): *m/z* (%) = 271 (10) [M^+], 270 (62), 269 (86), 243 (17), 229 (23), 228 (55), 212 (27), 187 (41), 186 (28), 185 (19), 173 (20), 161 (29), 160 (20), 145 (19), 135 (100), 131 (20), 117 (14), 116 (13), 115 (24), 105 (13), 104 (14), 103 (25), 91 (12), 90 (14), 83 (18), 77 (28),43 (81), 39 (12). − $C_{14}H_{14}N_4O_2$ (270.4): calcd. C 62.19, H 5.22, N 20.72; found C 61.88, H 5.10, N 20.52.

2,6-Bis(2-thiazolyl)-3,4-homotropilidene (13f): Compound **12c$_1$** (104 mg, 0.345 mmol) was photolyzed in CH_2Cl_2 (30 mL) at room temp. for 9 h according to General Procedure (7). Purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/*n*-pentane) afforded **13f** (60.9 mg, 0.224 mmol, 65%) as colourless crystals, m.p. 79−80 °C. − IR (KBr): ṽ = 3100, 3080, 3060, 3030, 2970, 1620, 1475, 1305, 1220, 1130, 1050, 950, 910, 850, 825, 730, 650, 620 cm^{-1}. − ^1H NMR (400 MHz, CD_2Cl_2, θ = 223 K): δ = 0.47 (dt, ^2J = 3.7, ^3J = 6.1 Hz, 1 H, 8-H_{syn}), 1.63 (dt, ^2J = 3.7, ^3J = 9.1 Hz, 1 H, 8-H_{anti}), 2.30 (ddd, ^3J = 9.1, ^3J = 6.1, ^5J = 2.0 Hz, 2 H, 1-H, 7-H), 2.84 (dt, ^2J = 15.4, ^3J = 8.8 Hz, 1 H, 4-H_{eq}), 3.55 (dtt, ^2J = 15.4, ^3J = 4.4, ^5J = 2.0 Hz, 1 H, 4-H_{ax}), 7.12 (dd, ^3J = 8.8, ^3J = 4.4 Hz, 2 H, 3-H, 5-H), 7.33 (d, ^3J = 3.2 Hz, 2 H, Ar-H), 7.78 (d, ^3J = 3.2 Hz, 2 H, Ar-H). − ^{13}C NMR: (63 MHz, CD_2Cl_2, θ = 223 K): δ = 13.9 (−CH_2−, 1 C, 8-C), 19.0 (=CH, 2 C, 1-C, 7-C), 25.1 (−CH_2−, 1 C, 4-C), 118.1 (=CH, 2 C, Ar-C), 131.3 (=CH, 2 C, 3-C, 5-C), 133.1 (quat. C, 2 C, 2-C, 6-C), 142.8 (=CH, 2 C, Ar-C), 169.9 (quat. C, 2 C, Ar-C). − UV/Vis (1,4-dioxane): λ (ε) = 270 (13800), 282 (15800), 295 (16300). − MS (EI, 70 eV): *m/z* (%) = 273 (21) [M^+], 272 (74), 271 (100), 257 (27), 245 (36), 188 (21), 187 (17), 186 (20), 174 (16), 173 (14), 162 (16), 136 (23), 123 (11), 59 (27), 58 (49). − $C_{14}H_{12}N_2S_2$ (272.4): calcd. C 61.73, H 4.44, N 10.28; found C 61.46, H 4.74, N 10.14.

Dimethyl 8-Methyl-3,4-homotropilidene-2,6-dicarboxylate (14a): Compound **12b** (792 mg, 3.00 mmol), after photolysis in benzene (300 mL) at room temp. for 10 min according to General Procedure (6) and purification by distillation at 0.001 Torr, yielded **14a** (560 mg, 2.37 mmol, 79%) as a colourless oil. − IR (film): ṽ = 1710 cm^{-1}. − ^1H NMR (100 MHz, $CDCl_3$): δ = 0.59 (tq, ^3J = 5.5, ^3J = 5.5 Hz, 1 H, 8-H_{syn}), 1.30 (d, ^3J = 5.5 Hz, 3 H, 8-CH_3-*anti*), 1.73 (d, ^3J = 5.5 Hz, 2 H, 1-H, 7-H), 2.74 (td, ^2J = 18.0, ^3J = 8.0 Hz, 1 H, 4-H_{eq}), 3.0−3.5 (m, ^2J = 18.0, ^3J = 4.0 Hz, 1 H, 4-H_{ax}), 3.85 (s, 6 H, OCH_3), 6.93 (dd, ^3J = 8.0, ^3J = 4.0 Hz, 2 H, 3-H, 5-H). − UV/Vis (1,4-dioxane): λ (ε) = 290 (1500). − $C_{13}H_{16}O_4$ (236.2): calcd. C 66.08, H 6.83; found C 66.02, H 6.72.

8-Methyl-3,4-homotropilidene-2,6-dicarbonitrile (14b): Compound **12j** (800 mg, 4.04 mmol) was photolyzed in benzene (300 mL) at room temp. for 3.5 h according to General Procedure (6). Purification by recrystallization (benzene/PE) afforded **14b** (650 mg, 3.80 mmol, 96%) as yellow crystals, m.p. 64−70 °C. − IR (KBr): ṽ = 2215 cm^{-1}. − ^1H NMR (90 MHz, $CDCl_3$, θ = 235 K): δ = 1.02 (tq, ^3J = 5.9, ^3J = 5.4 Hz, 1 H, 8-H_{syn}), 1.33 (d, ^3J = 5.9 Hz, 3 H, 8-CH_3-*anti*), 1.73 (dd, ^3J = 5.4, ^5J = 1.8 Hz, 2 H, 1-H, 7-H), 2.87 (dt, ^2J = 18.1, ^3J = 8.1 Hz, 1 H, 4-H_{eq}), 3.42 (dtt, ^2J = 18.1, ^3J = 3.7, ^5J = 1.8 Hz, 1 H, 4-H_{ax}), 6.65 (dd, ^3J = 8.1, ^3J = 3.7 Hz, 2 H, 3-H, 5-H). − UV/Vis (1,4-dioxane): λ (ε) = 257 (980). − MS (EI, 70 eV): *m/z* (%) = 170 (18) [M^+], 142 (100). − $C_{11}H_{10}N_2$ (170.2): calcd. C 77.62, H 5.92, N 16.46; found C 77.73, H 5.76, 16.48.

8-Methyl-2,6-diphenyl-3,4-homotropilidene (14c): Compound **12q** (450 mg, 1.50 mmol), after photolysis in acetonitrile (15 mL) at room temp. for 15 min according to General Procedure (7) and purification by recrystallization (methanol), yielded **14c** (346 mg, 1.27 mmol, 85%) as colourless needles, m.p. 89−90 °C. − IR (KBr): ṽ = 3050, 2960, 1630, 1590, 1445, 830, 760, 750, 690 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.54−0.63 (m, 1 H, 8-H_{syn}), 1.44 (d, ^3J = 5.9 Hz, 3 H, 8-CH_3-*anti*), 1.82 (d, broad, ^3J = 4.5 Hz, 2 H, 1-H, 7-H), 2.59−2.78 (m, broad, 1 H, 4-H_{eq}), 3.46 (d, broad, ^2J = 16.5 Hz, 1 H, 4-H_{ax}), 6.43 (dd, broad, ^3J = 7.8, ^3J = 3.9 Hz, 2 H, 3-H, 5-H), 7.18−7.34 (m, 6 H, Ar-H), 7.50−7.58 (m, 4 H, Ar-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 19.4 (−CH_3, 1 C, 8-*C*H_3), 21.5 (=CH, 1 C, 8-C), 26.3 (−CH_2−, 1 C, 4-C), 27.7 (=CH, 2 C, 1-C, 7-C), 124.3 (=CH, 2 C), 126.7 (=CH, 2 C), 127.8 (=CH, 2 C), 128.1 (=CH, 2 C), 139.0 (quat. C, 2 C), 142.0 (quat. C, 2 C). − MS (EI, 70 eV): *m/z* (%) = 273 (25) [M^+], 272 (100). − UV/Vis (CH_3CN): λ (ε) = 268 (11840), 244 (14350), 225 (13470). − $C_{21}H_{20}$ (272.2): calcd. C 92.66, H 7.40; found C 92.74, H 7.40.

8-Methyl-2,6-bis(2-pyridyl)-3,4-homotropilidene (14d): Compound **12t** (316 mg, 1.05 mmol), after photolysis in CH_3CN (45 mL) at room temp. for 4.5 h according to General Procedure (7) and purification by recrystallization (methanol), yielded **14d** (208 mg, 0.756 mmol, 72%) as colourless crystals, m.p. 122−124 °C. − IR (KBr): ṽ = 3090, 3050, 3000, 2950, 2920, 2860, 1635, 1585, 1565, 1470, 1440, 1155, 990, 790, 775, 745 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.49−0.55 (m, ^3J = 5.9, ^3J = 4.7 Hz, 1 H, 8-H_{syn}), 1.51 (d, ^3J = 5.9 Hz, 3 H, 8-CH_3-*anti*), 1.92 (d, broad, ^3J = 4.7 Hz, 2 H, 1-H, 7-H), 2.87 (dt, broad, ^2J = 15.5, ^3J = 8.4 Hz, 1 H, 4-H_{eq}), 3.52 (dt, broad, ^2J = 15.5, ^3J = 4.2 Hz, 1 H, 4-H_{ax}), 7.11−7.14 (m, 2 H, Ar-H), 7.18 (dd, broad, ^3J = 8.4, ^3J = 4.2 Hz, 2 H, 3-H, 5-H), 7.47−7.50 (m, 2 H, Ar-H), 7.62−7.69 (m, 2 H, Ar-H), 8.53−8.56 (m, 2 H, Ar-H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.3 (−CH_3, 1 C, 8-*C*H_3), 21.2 (=CH, 1 C, 8-C), 26.1 (−CH_2−, 1 C, 4-C), 26.5 (=CH, 2 C, 1-C, 7-C), 119.5 (=CH, 2C, Ar-C), 121.5

(=CH, 2 C, Ar-C), 131.5 (=CH, 2 C, 3-C, 5-C), 136.3 (=CH, 2 C, Ar-C), 138.3 (quat. C, 2 C, 2-C, 6-C), 148.9 (=CH, 2 C, Ar-C), 158.5 (quat. C, 2 C, Ar-C). − $C_{19}H_{18}N_2$ (274.4): calcd. C 83.17, H 6.61, N 10.21; found C 83.04, H 6.54, N 10.22.

Dimethyl 1-Methyl-3,4-homotropilidene-2,6-dicarboxylate (16a): Compound **12c** (450 mg, 1.70 mmol), after photolysis in benzene (200 mL) at room temp. for 15 min according to General Procedure (6) and purification by distillation at 0.001 Torr, yielded **16a** (333 mg, 1.41 mmol, 83%) as a colourless oil. − IR (film): $\tilde{\nu}$ = 1715 cm^{-1}. − ^1H NMR (100 MHz, $CDCl_3$): δ = 0.37 (dd, ^2J = 4.5, ^3J = 6.0 Hz, 1-H, 8-H_{syn}), 1.17 (dd, ^2J = 4.5, ^3J = 10.0 Hz, 1 H, 8-H_{anti}), 1.21 (s, 3 H, 1-CH_3), 1.45 (dd, ^3J = 6.0, ^3J = 10.0 Hz, 2 H, 7-H), 2.08 (dt, ^2J = 14.2, ^3J = 8.5 Hz, 1 H, 4-H_{eq}), 2.82 (dt, ^2J = 14.2, ^3J = 5.0 Hz, 1 H, 4-H_{ax}), 3.82 (s, 6 H, OCH_3), 7.02 (dd, ^3J = 8.5, ^3J = 5.0 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 19.3 (−CH_3, 1 C, 1-CH_3), 21.1 (quat. C, 1 C, 1-C), 23.9 (=CH, 1 C, 7-C), 25.3 (−CH_2−, 1 C, 8-C or 4-C), 25.6 (−CH_2−, 1 C, 4-C or 8-C), 51.5 (−CH_3, 1 C, OCH_3), 51.6 (−CH_3, 1 C, OCH_3), 134.4 (quat. C, 1 C, 2-C or 6-C), 136.8 (quat. C, 1 C, 6-C or 2-C), 141.8 (=CH, 1 C, 3-C or 5-C), 142.2 (=CH, 1 C, 3-C or 5-C), 167.1 (quat. C, 1 C, C=O), 167.7 (quat. C, 1 C, C=O). − UV/Vis (1,4-dioxane): λ (ε) = 250 (3400). − $C_{13}H_{16}O_4$ (236.2): calcd. C 66.08, H 6.83; found C 66.00, H 7.01.

1-Methyl-2,6-bis(2-pyridyl)-3,4-homotropilidene (16b): Compound **12u** (511 mg, 1.69 mmol) was photolyzed in acetonitrile (30 mL) at room temp. for 4.5 h according to General Procedure (7). Purification by FC (CH_2Cl_2/*n*-hexane/ethanol = 15:2:1) afforded **16b** (434 mg, 1.58 mmol, 93%) as a yellow oil. − IR (film): 3070, 3020, 2970, 2910, 2860, 1635, 1580, 1565, 1470, 1430, 1270, 1155, 1095, 1000, 910, 700 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.54 (dd, ^2J = 6.5, ^3J = 3.8 Hz, 1 H, 8-H_{syn}), 1.39 (dd, ^3J = 3.8, ^3J = 9.3 Hz, 1 H, 7-H), 1.43 (s, 3 H, 1-CH_3), 1.92−1.99 (m, ^2J = 6.5, ^3J = 9.3 Hz, 1 H, 8-H_{anti}), 2.82 (dt, ^2J = 14.0, ^3J = 8.6 Hz, 1 H, 4-H_{eq}), 3.41−3.51 (m, ^2J = 14.0 Hz, 1 H, 4-H_{ax}), 7.07−7.12 (m, 2 H, Ar-H), 7.23−7.33 (m, 3 H, 5-H, Ar-H), 7.55−7.66 (m, 3 H, 3-H, Ar-H), 8.53−8.55 (m, 2 H, Ar-H). − The isolated compound contained about 10% of an inseparable impurity (according to ^1H NMR).

3-Methyl-3,4-homotropilidene-2,6-dicarbonitrile (17a): Compound **12k** (1.30 g, 6.56 mmol), after photolysis in benzene (250 mL) at room temp. for 24 h according to General Procedure (6) and purification by distillation at 0.001 Torr, yielded **17a** (1.10 g, 6.46 mmol, 98%) as a colourless oil. − IR (film): $\tilde{\nu}$ = 2220 cm^{-1}. − ^1H NMR (90 MHz, $CDCl_3$): δ = 0.57 (dt, ^2J = 4.7, ^3J = 5.8 Hz, 1 H, 8-H_{syn}), 1.27 (dt, ^2J = 4.7, ^3J = 9.0 Hz, 1 H, 8-H_{anti}), 1.83−2.17 (m, ^3J = 5.8, ^3J = 9.0 Hz, 2 H, 1-H, 7-H) and 2.10 (s, 3 H, 3-CH_3), 2.48 (dd, ^2J = 14.7, ^3J = 8.6 Hz, 1 H, 4-H_{eq}), 3.57−3.87 (m, ^2J = 14.7, ^3J = 5.4 Hz, 1 H, 4-H_{ax}), 6.79 (dd, ^3J = 8.6, ^3J = 5.4 Hz, 1 H, 5-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 10.7 (−CH_2−, 1 C, 8-C), 18.6 (=CH, 1 C, 1-C or 7-C), 18.7 (=CH, 1 C, 7-C or 1-C), 24.9 (−CH_3, 1 C, 3-CH_3), 32.5 (−CH_2−, 1 C, 4-C), 108.9 (quat. C, 1 C, 2-C or 6-C), 115.8 (quat. C, 1 C, 6-C or 2-C), 118.3 (quat. C, 1 C, CN), 118.6 (quat. C, 1 C, CN), 146.0 (=CH, 1 C, 5-C), 157.9 (quat. C, 1 C, 3-C). − UV/Vis (1,4-dioxane): λ (ε) = 243 (2270). − MS (EI, 70 eV): *m/z* (%) = 170 (63) [M^+], 155 (100). − $C_{11}H_{10}N_2$ (170.2): calcd. C 77.62, H 5.92, N 16.46; found C 77.53, H 5.65, 16.59.

8,8-Dimethyl-2,6-bis(2-pyridyl)-3,4-homotropilidene (18a): Compound **12v** (255 mg, 0.807 mmol), after photolysis in CH_3CN (45 mL) at room temp. for 4.5 h according to General Procedure (7) and purification by FC (CH_2Cl_2/ethanol = 15:1), yielded **18a** (204 mg, 0.707 mmol, 88%) as a red oil. − IR (oil): $\tilde{\nu}$ = 3060, 3010, 2960, 2880, 1635, 1585, 1520, 1270, 1160, 1060, 995, 880, 795, 780, 750 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.59 (s, 3H, 8-CH_3-*syn*), 1.53 (s, 3 H, 8-CH_3-*anti*), 2.05 (s, 2 H, 1-H, 7-H), 2.95 (dt, ^2J = 16.5, ^3J = 8.6 Hz, 1 H, 4-H_{eq}), 3.52 (dt, ^2J = 16.5, ^3J = 4.0 Hz, 1 H, 4-H_{ax}), 7.09−7.14 (m, 2 H, Ar-H), 7.18 (dd, ^3J = 8.6, ^3J = 4.0 Hz, 2 H, 3-H, 5-H), 7.37−7.42 (m, 2 H, Ar-H), 7.60−7.71 (m, 2 H, Ar-H), 8.53−8.56 (m, 2 H, Ar-H). − $C_{20}H_{20}N_2$ (288.4): calcd. C 83.29, H 6.99, N 9.71; found C 83.49, H 6.76, N 9.63.

8,8-Dimethyl-2,6-bis(2-methyl-1,3,4-oxadiazol-5-yl)-3,4-homotropilidene (18b): Compound **12b$_I$** (68.0 mg, 0.208 mmol) was photolyzed in CH_3CN (30 mL) at room temp. for 5 h according to General Procedure (7). Purification by FC (CH_2Cl_2/EtOAc = 1:1) and recrystallization (CH_2Cl_2/*n*-hexane) afforded **18b** (56.0 mg, 0.188 mmol, 90%) as colourless crystals, m.p. 96−97 °C. − IR (film): $\tilde{\nu}$ = 3010, 2960, 2940, 2910, 1630, 1570, 1520, 1440, 1430, 1420, 1345, 1220, 1115, 1040, 1010, 990, 905, 875, 830, 735, 705 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, 8-CH_3-*syn*), 1.47 (s, 3 H, 8-CH_3-*anti*), 2.05 (dt, ^5J = 2.0, ^4J = 0.5 Hz, 2 H, 1-H, 7-H), 2.54 (s, 6 H, Ar-CH_3), 2.96 (dt, ^2J = 17.7, ^3J = 8.5 Hz, 1 H, 4-H_{eq}), 3.51 (dtt, ^2J = 17.7, ^3J = 3.7, ^5J = 2.0 Hz, 1 H, 4-H_{ax}), 6.86 (ddt, ^3J = 3.7, ^3J = 8.5, ^4J = 0.5 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR: (63 MHz, $CDCl_3$): δ = 11.0 (−CH_3, 2 C, Ar-CH_3), 15.6 (−CH_3, 1 C, 8-CH_3), 23.7 (quat. C, 1 C, 8-C), 26.6 (−CH_2−, 1 C, 4-C), 27.1 (−CH_3, 1 C, 8-CH_3), 28.5 (=CH, 2 C, 1-C, 7-C), 125.3 (quat. C, 2 C, 2-C, 6-C), 132.8 (=CH, 2 C, 3-C, 5-C), 162.9 (quat. C, 2 C, Ar-C), 165.8 (quat. C, 2 C, Ar-C). − UV/Vis (1,4-dioxane): λ (ε) = 235 (20600). − MS (EI, 70 eV): *m/z* (%) = 298 (49) [M^+], 297 (92), 202 (13), 201 (100), 187 (22), 173 (56), 172 (18), 132 (14), 130 (14), 129 (12), 128 (14), 116 (15), 115 (22), 104 (22), 103 (22), 91 (18), 89 (12), 77 (33), 56 (11), 43 (49), 41 (12). − $C_{16}H_{18}N_4O_2$ (298.4): calcd. C 64.40, H 6.08, N 18.78; found C 64.10, H 6.18, N 18.45.

Dimethyl 4,8-Dimethyl-3,4-homotropilidene-2,6-dicarboxylate (20a): Compound **12d** (834 mg, 3.00 mmol), after photolysis in benzene (300 mL) at room temp. for 15 min according to General Procedure (6) and purification by distillation at 0.001 Torr, yielded **20a** (548 mg, 2.19 mmol, 73%) as a colourless oil. − IR (film): $\tilde{\nu}$ = 1720, 1705 cm^{-1}. − ^1H NMR [90 MHz, CD_2Cl_2/CS_2 (2:1), θ = 188 K]: δ = 0.67 (tq, ^3J = 6.0, ^3J = 5.5 Hz, 1-H, 8-H_{syn}), 1.24 (d, ^3J = 6.0 Hz, 3 H, 8-CH_3-*anti*), 1.36 (d, ^3J = 7.0 Hz, 3 H, 4-CH_3-*anti*), 1.67 (d, ^3J = 5.5 Hz, 2 H, 1-H, 7-H), 3.12 (tq, ^3J = 7.0, ^3J = 8.0 Hz, 1 H, 4-H_{eq}), 3.78 (s, 6 H, OCH_3), 7.06 (d, ^3J = 8.0 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR (22.63 MHz, CD_2Cl_2, θ = 200 K): δ = 19.0 (−CH_3, 1 C, 8-CH_3 or 4-CH_3), 21.0 (−CH_3, 1 C, 4-CH_3 or 8-CH_3), 24.8 (=CH, 2 C), 31.7 (=CH, 2 C), 52.6 (−CH_3, 2 C, OCH_3), 131.7 (quat. C, 2 C, 2-C, 6-C), 144.5 (=CH, 2 C, 3-C, 5-C, 168.8 (quat. C, 2 C, C=O). − UV/Vis (1,4-dioxane): λ (ε) = 297 (2500). − $C_{14}H_{18}O_4$ (250.3): calcd. C 67.18, H 7.25; found C 66.85, H 7.23.

Dimethyl 4,8-Di-*tert*-butyl-3,4-homotropilidene-2,6-dicarboxylate (20b): Compound **12e** (145 mg, 0.400 mmol), after photolysis in methanol (100 mL) at room temp. for 110 min according to General Procedure (6) and purification by recrystallization (CH_2Cl_2), yielded **20b** (77.6 mg, 0.232 mmol, 58%) as colourless crystals; m.p. 91−94 °C. − IR (KBr): $\tilde{\nu}$ = 2970, 2950, 2870, 1715, 1655 cm^{-1}. − ^1H NMR (60 MHz, CD_2Cl_2, θ = 227 K): δ = 0.49 (t, ^3J = 6.0 Hz, 1 H, 8-H_{syn}), 0.93 (s, 9 H, *t*Bu-H), 1.00 (s, 9 H, *t*Bu-H), 1.92 (d, ^3J = 6.0 Hz, 2 H, 1-H, 7-H), 3.00 (t, ^3J = 8.0 Hz, 1 H, 4-H_{eq}), 3.73 (s, 6 H, OCH_3), 6.95 (d, ^3J = 8.0 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR (22.63 MHz, $C_2D_2Cl_4$, θ = 413 K): δ = 27.7 (−CH_3, 6 C, *t*Bu-CH_3), 34.2 (quat. C, 2 C, *t*Bu-*C*), 47.4 (=CH, 2 C, 4-C, 8-C), 50.7 (−CH_3, 2 C, OCH_3), 80.1 (broad, 1-C, 7-C, 3-C, 5-C),

132.9 (quat. C, 2 C, 2-C, 6-C), 167.7 (quat. C, 2 C, C=O). − UV/Vis (1,4-dioxane): λ (ε) = 217 (17060). − $C_{20}H_{30}O_4$ (334.4): calcd. C 71.82, H 9.04; found C 71.73, H 8.80.

4,8-Dimethyl-3,4-homotropilidene-2,6-dicarbonitrile (20c): Compound **12l** (1.00 g, 4.72 mmol) was photolyzed in benzene (250 mL) at room temp. for 4 h according to General Procedure (6). Purification by recrystallization (methanol), cooling to −78 °C, afforded **20c** (440 mg, 2.39 mmol, 51%) as colourless crystals, m.p. 77−79 °C. − IR (film): 2220 cm^{-1}. − ^1H NMR (90 MHz, CD_2Cl_2, θ = 216 K): δ = 1.16 (tq, ^3J = 6.0, ^3J = 5.1 Hz, 1 H, 8-H_{syn}), 1.29 (d, ^3J = 6.0 Hz, 3 H, 8-CH_3-*anti*), 1.36 (d, ^3J = 7.4 Hz, 3 H, 4-CH_3-*anti*), 1.73 (d, ^3J = 5.1 Hz, 2 H, 1-H, 7-H), 3.08 (tq, ^3J = 7.4, ^3J = 8.1 Hz, 1 H, 4-H_{eq}), 6.67 (d, ^3J = 8.1 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$, θ = 233 K): δ = 18.3 (−CH_3, 1 C, 8-*C*H_3 or 4-*C*H_3), 20.7 (−CH_3, 1 C, 4-*C*H_3 or 8-*C*H_3), 25.6 (=CH, 2 C, 1-C, 7-C), 27.0 (=CH, 1 C, 4-C or 8-C), 33.6 (=CH, 8-C or 4-C), 113.9 (quat. C, 2 C, 2-C, 6-C), 119.4 (quat. C, 2 C, CN), 149.2 (=CH, 2 C, 3-C, 5-C). − UV/Vis (1,4-dioxane): λ (ε) = 280 (2860). − MS (EI, 70 eV): *m*/*z* (%) = 183 (39) [M^+], 169 (100). − $C_{12}H_{12}N_2$ (182.4): calcd. N 15.21; found N 15.16.

4,8-Di-*tert*-butyl-3,4-homotropilidene-2,6-dicarbonitrile (20d): Compound **12m** (208 mg, 0.70 mmol), after photolysis in methanol (30 mL) at room temp. for 100 min according to General Procedure (7) and purification by recrystallization (methanol), yielded **20d** (114 mg, 0.43 mmol, 61%) as colourless crystals; m.p. 120−122 °C. − IR (KBr): ṽ = 2970, 2870, 2220, 1640 cm^{-1}. − ^1H NMR (60 MHz, CD_2Cl_2, θ = 233 K): δ = 0.96 (t, ^3J = 6.0 Hz, 1 H, 8-H_{syn}), 0.97 (s, 9 H, *t*Bu-H), 1.03 (s, 9 H, *t*Bu-H), 1.85 (d, ^3J = 6.0 Hz, 2 H, 1-H, 7-H), 2.98 (t, ^3J = 8.0 Hz, 1 H, 4-H_{eq}), 6.50 (d, ^3J = 8.0 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$, θ = 233 K): δ = 23.7 (=CH, 2 C, 1-C, 7-C), 27.7 (−CH_3, 3 C, *C*H_3), 28.2 (−CH_3, 3 C, *C*H_3), 30.0 (quat. C, 1 C, *t*Bu-*C*), 40.5 (quat. C, 1 C, *t*Bu-*C*), 45.7 (=CH, 1 C, 8-C), 50.8 (=CH, 1 C, 4-C), 115.0 (quat. C, 2 C, C-2, C-6), 119.5 (quat. C, 2 C, CN), 145.9 (=CH, 2 C 3-C, 5-C). − $C_{18}H_{24}N_2$ (268.4): calcd. C 80.55, H 9.01, N 10.44; found C 80.31, H 9.07, N 10.39.

4,8-Dimethyl-2,6-diphenyl-3,4-homotropilidene (20e): Compound **12r** (455 mg, 1.45 mmol), after photolysis in CH_3CN (15 mL) at room temp. for 15 min according to General Procedure (7) and purification by recrystallization (methanol), yielded **20e** (320 mg, 1.12 mmol, 77%) as colourless needles, m.p. 91−92 °C. − IR (KBr): ṽ = 3060, 2960, 2900, 1635, 1595, 1495, 1450, 860, 840, 760, 690 cm^{-1}. − ^1H NMR (250 MHz, CD_2Cl_2): δ = 0.65 (tq, ^3J = 5.9, ^3J = 5.6 Hz, 1 H, 8-H_{syn}), 1.46 (d, ^3J = 5.9 Hz, 3 H, 8-CH_3-*anti*), 1.50 (d, ^3J = 5.5 Hz, 3 H, 4-CH_3-*anti*), 1.84 (d, ^3J = 5.6 Hz, 2 H, 1-H, 7-H), 3.06 (tq, ^3J = 5.5, ^3J = 8.5 Hz, 1 H, 4-H_{eq}), 6.53 (d, ^3J = 8.5 Hz, 2 H, 3-H, 5-H), 7.20−7.35 (m, 6 H, Ar-H), 7.51−7.59 (m, 4 H, Ar-H). − MS (EI, 70 eV): *m*/*z* (%) = 287 (20) [M^+], 244 (100). − UV/Vis (CH_3CN): λ (ε) = 264 (12110), 247 (14930), 225 (16480). − $C_{22}H_{22}$ (286.3): calcd. C 92.21, H 7.75; found C 91.93, H 7.93.

4,8-Dimethyl-2,6-bis(2-pyridyl)-3,4-homotropilidene (20f): Compound **12w** (180 mg, 0.568 mmol), after photolysis in CH_3CN (45 mL) at room temp. for 4.5 h according to General Procedure (7) and purification by recrystallization (CH_2Cl_2/*n*-hexane), yielded **20f** (133 mg, 0.462 mmol, 81%) as colourless crystals, m.p. 88−91 °C. − IR (KBr): ṽ = 3050, 3000, 2920, 2900, 2860, 1640, 1580, 1560, 1470, 1425, 1260, 1165, 1090, 880, 780, 745, 700 cm^{-1}. − ^1H NMR (250 MHz, CD_2Cl_2, θ = 220 K): δ = 0.70 (tq, ^3J = 5.6, ^3J = 5.6 Hz, 1 H, 8-H_{syn}), 1.56 (d, ^3J = 5.6 Hz, 3 H, 8-CH_3-*anti*), 1.56 (d, ^3J = 5.6 Hz, 3 H, 4-CH_3-*anti*), 1.96 (d, ^3J = 5.6 Hz, 2 H, 1-H, 7-H), 3.18 (tq, ^3J = 5.6, ^3J = 9.3 Hz, 1 H, 4-H_{eq}), 7.09−7.29 (m, 2 H, Ar-H), 7.42 (d, ^3J = 9.3 Hz, 2 H, 3-H, 5-H), 7.54−7.93 (m, 4 H, Ar-H), 8.43−8.64 (m, 2 H, Ar-H). − $C_{20}H_{20}N_2$ (288.4): calcd. N 9.71; found N 9.57.

Dimethyl 1,5-Dimethyl-3,4-homotropilidene-2,6-dicarboxylate (21a): Compound **12f** (556 mg, 2.00 mmol) was photolyzed in benzene (200 mL) at room temp. for 15 min according to General Procedure (6). Evaporation of the solvent afforded **21a** (135 mg, 0.540 mmol, 27%) as a colourless oil. − IR (film): 1710 cm^{-1}. − ^1H NMR (90 MHz, [D_8]toluene): δ = 0.40 (dd, ^3J = 6.0, ^2J = 4.5 Hz, 1 H, 8-H_{syn}), 0.97 (dd, ^3J = 9.2, ^2J = 4.5 Hz, 1 H, 8-H_{anti}), 1.22 (s, 3 H, 1-CH_3), 1.55 (qdd, ^3J = 6.0, ^3J = 9.2, ^5J = 2.2 Hz, 1 H, 7-H), 1.91 (dd, ^2J = 13.0, ^3J = 8.5 Hz, 1 H, 4-H_{eq}), 2.01 (d, ^5J = 2.2 Hz, 3 H, 5-CH_3), 3.25 (dd, ^2J = 13.0, ^3J = 6.0 Hz, 1 H, 4-H_{ax}), 3.81 (s, 6 H, OCH_3), 7.17 (dd, ^3J = 8.5, ^3J = 6.0 Hz, 1 H, 3-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 17.6 (−CH_2−, 1 C, 8-C or 4-C), 21.8 (quat. C, 1 C, 1-C), 23.1 (=CH, 1 C, 7-C), 25.5 (−CH_3, 2 C, 1-*C*H_3, 5-*C*H_3), 34.5 (−CH_2−, 1 C, 4-C or 8-C), 51.2 (−CH_3, 1 C, O*C*H_3), 51.4 (−CH_3, 1 C, O*C*H_3), 127.4 (quat. C, 1 C, 2-C or 6-C), 136.1 (quat. C, 1 C, 6-C or 2-C), 142.7 (=CH, 1 C, 3-C), 151.7 (quat. C, 1 C, 5-C), 166.8 (quat. C, 1 C, C=O), 168.9 (quat. C, 1 C, C=O). − UV/Vis (1,4-dioxane): λ (ε) = 257 (2320). − $C_{14}H_{18}O_4$ (250.3): calcd. C 67.18, H 7.25; found C 66.77, H 7.10.

1,5-Dimethyl-3,4-homotropilidene-2,6-dicarbonitrile (21b): Compound **12n** (1.00 g, 4.72 mmol) was photolyzed in benzene (250 mL) at room temp. for 8 h according to General Procedure (6). Purification by recrystallization (methanol), cooling to −78 °C, afforded **21b** (400 mg, 2.17 mmol, 46%) as colourless crystals, m.p. 75−76 °C. − IR (KBr): ṽ = 2210 cm^{-1}. − ^1H NMR (60 MHz, $CDCl_3$): δ = 0.67 (dd, ^3J = 5.8, ^2J = 4.6 Hz, 1 H, 8-H_{syn}), 1.03 (dd, ^3J = 8.8, ^2J = 4.6 Hz, 1 H, 8-H_{anti}), 1.36 (s, 3 H, 1-CH_3), 1.72 (qdd, ^3J = 5.8, ^3J = 8.8, ^5J = 1.8 Hz, 1 H, 7-H), 2.10 (d, ^5J = 1.8 Hz, 3 H, 5-CH_3), 2.45 (dd, ^2J = 14.2, ^3J = 8.6 Hz, 1 H, 4-H_{eq}), 3.53 (dd, ^2J = 14.2, ^3J = 5.4 Hz, 1 H, 4-H_{ax}), 6.69 (dd, ^3J = 8.6, ^3J = 5.4 Hz, 1 H, 3-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 17.5 (−CH_2−, 1 C, 8-C), 24.5 (quat. C, 1 C, 1-C), 24.7 (=CH, 1 C, 7-C), 26.2 (−CH_3, 2 C, 1-*C*H_3, 5-*C*H_3), 32.2 (−CH_2−, 1 C, 4-C), 110.0 (quat. C, 2 C, 2-C, 6-C), 118.5 (quat. C, 1 C, CN), 120.5 (quat. C, 1 C, CN), 145.5 (=CH, 1 C, 3-C), 159.0 (quat. C, 1 C, 5-C). − UV/Vis (1,4-dioxane): λ (ε) = 248 (2290). − MS (EI, 70 eV): *m*/*z* (%) = 184 (40) [M^+], 169 (100). − $C_{12}H_{12}N_2$ (184.2): calcd. C 78.23, H 6.57, N 15.21; found C 78.01, H 6.93, N 14.96.

1,5-Dimethyl-2,6-bis(2-pyridyl)-3,4-homotropilidene (21c): Compound **12x** (369 mg, 1.17 mmol), after photolysis in CH_3CN (30 mL) at room temp. for 5.5 h according to General Procedure (7) and purification by FC [CH_2Cl_2/PE/ethanol = 10:2:1], yielded **21c** (343 mg, 1.15 mmol, 98%) as a colourless oil. − IR (KBr): ṽ = 3050, 2990, 2940, 2920, 2850, 1575, 1550, 1460, 1420, 1370, 1265, 1140, 1080, 1040, 1020, 1005, 985, 960, 900, 770, 720 cm^{-1}. − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.41 (dd, ^3J = 6.3, ^2J = 3.9 Hz, 1 H, 8-H_{syn}), 1.00 (dd, ^2J = 3.9, ^3J = 9.3 Hz, 1 H, 8-H_{anti}), 1.34 (s, 3 H, 1-CH_3), 1.78 (d, ^5J = 0.5 Hz, 3 H, 5-CH_3), 2.05−2.13 (m, ^3J = 6.3, ^3J = 9.3 Hz, 1 H, 7-H), 2.43 (dd, ^2J = 13.2, ^3J = 8.6 Hz, 1 H, 4-H_{eq}), 3.69 (dd, ^2J = 13.2, ^3J = 6.1 Hz, 1 H, 4-H_{ax}), 7.05−7.12 (m, 3 H, Ar-H), 7.46 (dd, ^3J = 8.6, ^3J = 6.1 Hz, 1 H, 3-H), 7.58−7.63 (m, 3 H, Ar-H), 8.54−8.61 (m, 2 H, Ar-H).

Dimethyl 3,8-Dimethyl-3,4-homotropilidene-2,6-dicarboxylate (22a): Compound **12g** (975 mg, 3.50 mmol), after photolysis in benzene (150 mL) at room temp. for 20 min according to General Procedure (6) and purification by distillation at 0.001 Torr, yielded **22a** (680 mg, 2.72 mmol, 78%) as a colourless oil. − IR (film): ṽ = 1715 cm^{-1}. − ^1H NMR (60 MHz, $CDCl_3$): δ = 0.40 (dt, ^3J = 6.0, ^3J = 6.0 Hz, 1 H, 8-H_{syn}), 1.25 (d, ^3J = 6.0 Hz, 3 H, 8-CH_3-*anti*),

1.58 (d, ^3J = 6.0 Hz, 2 H, 1-H, 7-H), 2.07 (s, 3 H, 3-CH_3), 2.30 (dd, ^3J = 8.0, ^2J = 13.5 Hz, 1 H, 4-H_{eq}), 3.47−3.80 (m, ^3J = 6.0, ^2J = 13.5 Hz, 1 H, 4-H_{ax}), 3.73 (s, 6 H, OCH_3), 7.18 (dd, ^3J = 8.0, ^3J = 6.0 Hz, 1 H, 5-H). − UV/Vis (1,4-dioxane): λ (ε) = 274 (1150).

3,8-Dimethyl-2,6-bis(2-pyridyl)-homotropilidene (22b): Compound **12y** (430 mg, 1.36 mmol), after photolysis in CH_3CN (35 mL) at room temp. for 5 h according to General Procedure (7) and purification by FC (CH_2Cl_2/PE/ethanol = 15:2:1), yielded **22b** (237 mg, 0.822 mmol, 60%) as a yellow oil. − IR (KBr): ṽ = 3060, 3010, 2960, 2940, 2910, 2870, 2585, 2560, 1470, 1430, 1375, 1150, 1000, 910, 775, 730 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.44−0.49 (m, ^3J = 5.9 Hz, 1 H, 8-H_{syn}), 1.18 (d, ^3J = 5.9 Hz, 3 H, 8-CH_3-*anti*), 1.73 (d, ^3J = 1.7 Hz, 3 H, 3-CH_3), 1.79−2.05 (m, 2 H, 1-H, 7-H), 2.41 (dd, ^2J = 13.9, ^3J = 8.7 Hz, 4-H_{eq}), 3.83 (dd, ^2J = 13.9, ^3J = 5.2 Hz, 1 H, 4-H_{ax}), 7.11 (dd, 1 H, ^3J = 5.2, ^3J = 8.7 Hz, 1 H, 5-H), 7.09−7.15 (m, 2 H, Ar-H) 7.36−7.40 (m, 1 H, Ar-H), 7.46−7.48 (m, 1 H, Ar-H), 7.57−7.68 (m, 2 H, Ar-H), 8.53−8.60 (m, 2 H, Ar-H).

Dimethyl 1,7-Diphenyl-3,4-homotropilidene-2,6-dicarboxylate (24a): A suspension of **12h** (240 mg, 0.64 mmol) in tetrachloroethylene (2.5 mL) was heated at 120 °C for 41 h. Purification by recrystallization (methanol) afforded **24a** (170 mg, 0.45 mmol, 71%) as colourless crystals; m.p. 163−165 °C. − IR (KBr): ṽ = 1700 cm^{-1}. − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 1.31 (d, ^2J = 6.5 Hz, 1 H, 8-H_{syn}), 2.82 (d, ^2J = 6.5 Hz, 1 H, 8-H_{anti}), 2.97 (dt, ^2J = 14.0, ^3J = 8.8 Hz, 1 H, 4-H_{eq}), 3.61 (s, 6 H, OCH_3), 3.96 (dt, ^2J = 14.0, ^3J = 5.0 Hz, 1 H, 4-H_{ax}), 6.89−7.30 (m, 10 H, Ar-H), 7.45 (dd, ^3J = 8.8, ^3J = 5.0 Hz, 2 H, 3-H, 5-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 20.5 (−CH_2−, 1 C, 8-C or 4-C), 25.7 (−CH_2−, 1 C, 4-C or 8-C), 36.5 (quat. C, 2 C, 1-C, 7-C), 51.5 (−CH_3, 2 C, O*C*H_3), 126.2 (=CH, 4 C, Ar-C), 128.1 (=CH, 2 C, Ar-C), 128.9 (=CH, 4 C, Ar-C), 137.8 (quat. C, 2 C, Ar-C or 2-C, 6-C), 139.1 (quat. C, 2 C, 2-C, 6-C or Ar-C), 141.5 (=CH, 2 C, 3-C, 5-C), 166.6 (quat. C, 2 C, C=O). − UV/Vis (1,4-dioxane): λ (ε) = 257 (5550). − MS (EI, 70 eV): *m*/*z* (%) = 374 (89) [M^+], 255 (100). − $C_{22}H_{22}O_4$ (374.5): calcd. C 76.97, H 5.93; found C 76.94, H 6.02.

3,5-Diphenyl-3,4-homotropilidene-2,6-dicarbonitrile (25a): Compound **12o** (400 mg, 1.19 mmol), after photolysis in acetone (400 mL) at room temp. for 8 h according to General Procedure (6) and purification by recrystallization (methanol), yielded **25a** (230 mg, 0.75 mmol, 63%) as colourless crystals, m.p. 189−191 °C. − IR (KBr): ṽ = 2205 cm^{-1}. − ^{1}H NMR (90 MHz, $CDCl_3$): δ = 0.82 (dt, ^2J = 5.2, ^3J = 6.0 Hz, 1 H, 8-H_{syn}), 1.2−1.7 (m, 1 H, 8-H_{anti}), 2.28 (ddd, ^3J = 9.1, ^3J = 6.0, ^5J = 1.3 Hz, 2 H, 1-H, 7-H), 3.21 (d, ^2J = 13.3 Hz, 1 H, 4-H_{eq}), 4.63 (dt, ^2J = 13.3, ^5J = 1.3 Hz, 1 H, 4-H_{ax}), 7.2−7.5 (m, 10 H, Ar-H). − ^{13}C NMR (22.63 MHz, $CDCl_3$): δ = 9.9 (−CH_2−, 1 C, 8-C), 20.4 (=CH, 2 C, 1-C, 7-C), 40.2 (−CH_2−, 1 C, 4-C), 109.7 (quat. C, 2 C, 2-C, 6-C), 118.7 (quat. C, 2 C, CN), 127.3 (=CH, 4 C, Ar-C), 128.8 (=CH, 2 C, Ar-C), 129.7 (=CH, 4 C, Ar-C), 138.2 (quat. C, 2 C, Ar-C), 159.8 (quat. C, 2 C, 3-C, 5-C). − UV/Vis (1,4-dioxane): λ (ε) = 258 (18350). − MS (EI, 70 eV): *m*/*z* (%) = 308 (100) [M^+]. − $C_{22}H_{16}N_2$ (308.4): calcd. C 85.67, H 5.24, N 9.09; found C 85.76, H 5.23, N 8.99.

4,8,8-Trimethyl-2,6-bis(2-pyridyl)-3,4-homotropilidene (26a): Compound **12z** (176 mg, 0.531 mmol) was photolyzed in CH_3CN (45 mL) at room temp. for 4.5 h according to General Procedure (7). Purification by FC (CH_2Cl_2/*n*-hexane/ethanol = 10:2:1) afforded **26a** (170 mg, 0.531 mmol, quant.) as a yellow oil. − IR (film): ṽ = 3070, 3040, 2950, 2910, 2850, 1630, 1570, 1555, 1455, 1415, 770, 730 cm^{-1}. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.63 (s, 3 H, 8-CH_3-*syn*), 1.51 (d, ^3J = 7.2 Hz, 3 H, 4-CH_3-*anti*), 1.54 (s, 3 H, 8-CH_3-*anti*), 2.04 (s, 2 H, 1-H, 7-H), 3.18−3.34 (m, ^3J = 7.2, ^3J = 8.5 Hz, 1 H, 4-H_{eq}), 7.09−7.14 (m, 2 H, Ar-H), 7.32 (d, ^3J = 8.5 Hz, 2 H, 3-H, 5-H), 7.37−7.42 (m, 2 H, Ar-H), 7.62−7.69 (m, 2 H, Ar-H), 8.54−8.57 (m, 2 H, Ar-H). − $C_{21}H_{22}N_2$ (302.4): calcd. C 83.41, H 7.33, N 9.26; found C 83.47, H 7.12, N 9.26.

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