1-Vinyltricyclo[4.1.0.0^{2,7}]heptanes: Synthesis and Reactions with Electrophilic Dienophiles

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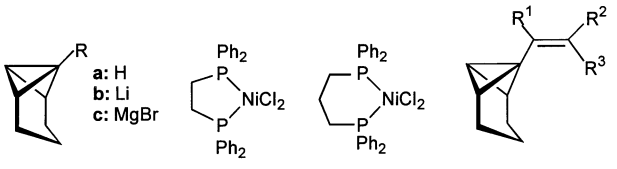
A series of 1-vinyltricyclo[4.1.0.0^{2,7}]heptanes **4** has been obtained by Ni^0-catalyzed cross-coupling reactions of the corresponding Grignard reagent with vinyl halides or via reaction of **4b** with various electrophiles. Selected model compounds **4** were treated with tetracyanoethylene (TCNE), *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD), and dimethyl acetylenedicarboxylate (DMAD). Product studies revealed that TCNE and PTAD attacked the CC double bond forming a zwitterion, which in most cases underwent several carbenium ion rearrangements until internal bond formation of the ionic centers took place. The main reaction path of DMAD and **4** led via attack at the bicyclo[1.1.0]butane bridgehead to a biradical of type **38**, which after H abstraction and CC bond formation gave rise to the tricyclic system **37**.

For more than two decades it has been known that the central bond of bicyclo[1.1.0]butanes is formed by interaction of 2p orbitals of the bridgehead carbon atoms leading to a considerable π orbital character of this bond[3a][3b]. There have been several attempts to add electron-deficient olefins or alkynes to the central bond of bicyclobutanes, and the results have been reviewed[4]. Some time ago we showed that cross-coupling reactions of 1-tricyclo[4.1.0.0^{2,7}]heptylmagnesium bromide (**1**) with vinyl chlorides or bromides in the presence of Ni^{II} catalysts of type **2** (Kumada coupling[5]) afforded 1-vinyltricyclo[4.1.0.0^{2,7}]-heptanes **3** in reasonable yields[6][7]. In these 1-vinylbicyclo-[1.1.0]butanes, a CC double bond is in conjugation with the bicyclobutane central bond and one might ask if there is an analogy between these molecules and 1,3-butadienes. Therefore, a series of model bicyclobutane compounds was prepared and subsequently reacted with tetracyanoethylene (TCNE), phenyltriazolinedione (PTAD), and dimethyl acetylenedicarboxylate (DMAD). It seemed of interest to find out where the primary attack of the electrophile took place, i.e. at the CC double bond or at the bicyclo[1.1.0]butane bridgehead position.

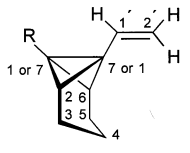


1 **2a** **2b**

3	**a**	**b**
R^1	Me	H
R^2	H	Me
R^3	H	Me

A. Synthesis of Model Compounds 4

The parent 1-vinyltricyclo[4.1.0.0^{2,7}]heptane (**4a**) was obtained by reaction of **1c**, prepared from hydrocarbon **1a** by metallation with *n*-butyllithium (BuLi) followed by transmetallation with anhydrous $MgBr_2$, with vinyl chloride in the presence of 1% of catalyst **2a**. The second bridgehead position of **4a** could also be lithiated with BuLi in diethyl ether to afford a suspension of **4b**, which was an intermediate in the preparation of several further vinyltricycloheptanes **4**.



4

4	R	**4**	R
a:	H	**g:**	Br (41%)
b:	Li	**h:**	Ph (21%)
c:	MgBr	**i:**	$CH{=}CH_2$ (57%)
d:	$SiMe_3$ (58%)	**j:**	$CH{=}CH{-}CH{=}CH_2$ (67%)
e:	Me (39%)	**k:**	$C(=CH_2){-}CH{=}CH_2$ (38%)
f:	Cl (42%)		

Reaction of **4b** with chlorotrimethylsilane, iodomethane, *p*-toluenesulfonyl chloride, and *p*-toluenesulfonyl bromide led to **4d**−**g** in yields of 58, 39, 42, and 41%, respectively. The syntheses of **4h**−**k** also started from **4b**, which by treatment with anhydrous $MgBr_2$ was converted into the Grignard reagent **4c**. This was then reacted with bromobenzene, vinyl chloride, 1-chloro-1,3-butadiene and 2-chloro-1,3-butadiene, in each case in the presence of catalytic amounts

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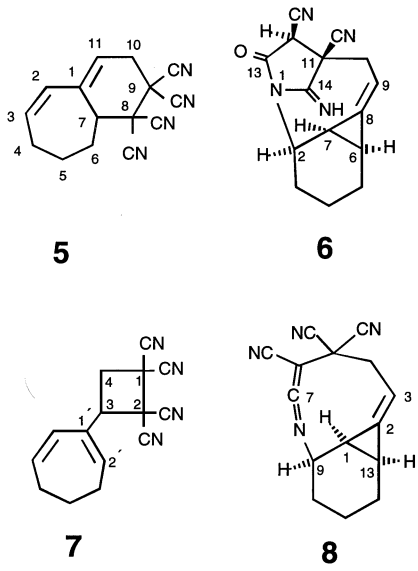


of nickel complex **2a** or **2b**, to afford **4h**−**k** in yields of 21, 67, 67, and 38%, respectively.

The structures of products **4** are based on their NMR spectra. At room temperature, all compounds were liquids, showing a strong propensity towards polymerization. Therefore, in some cases, combustion analyses could not be undertaken.

B. Reactions of TCNE with 1-Vinyltricyclo[4.1.0.0^{2,7}]-heptanes

The reactions of TCNE with **4a** and **4d**−**g** were carried out in dichloromethane at room temperature. Column chromatographic work-up of the reaction mixture with **4a** afforded two main products **5** and **6** and two side products **7** and **8**, in yields of 23 and 34%, and 3.2 and 2.0%, respectively.

Clearly, **6** was formed by reaction of **8** with water. Work-up of a second experiment under anhydrous conditions improved the isolated yield of **8** to 9%. The structures of **6** and **8** were established by single-crystal X-ray analyses. The computer-generated ORTEP plots are shown in Figures 1 and 2.

Compound **8** consists of a cyclic ketene imine in a nine-membered ring. As a consequence, the C=C=N unit in **8** is bent, with an NCC angle of 172.2°. The C=C=N bond lengths amount to 1.341(5) and 1.172(5) Å. Recently, Huisgen has shown that the ketene imine unit can even be incorporated into a seven-membered ring. Compound **9** exhibits an NCC ketene imine angle of 163.8° and C=C=N bond lengths of 1.33 and 1.20 Å[8].

Although **6** was found to exist as a single compound in the solid state, this was not the case in solution. The ^{1}H-NMR spectrum of **6** in $CDCl_3$ at room temperature revealed a 15:5:4 mixture of three compounds. Presumably, **6** is in equilibrium with the enol **10** and the diastereomer **11**.

The structures of **5** and **7** are based on their NMR spectra. For **5**, the connectivity was determined by a 2D INADEQUATE experiment.

Figure 1. ORTEP plot of **6**

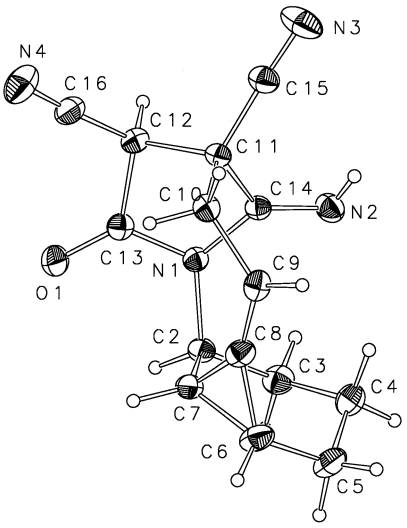
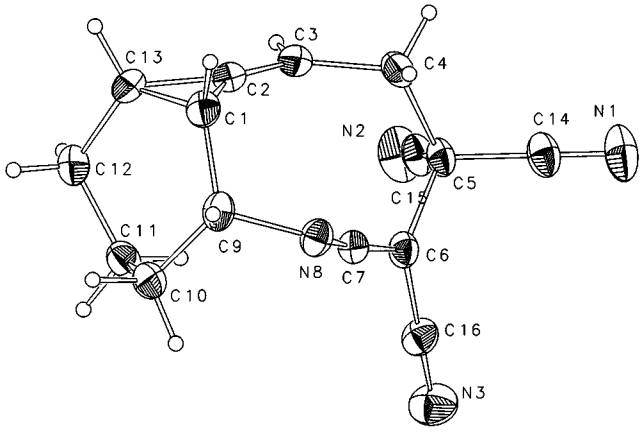
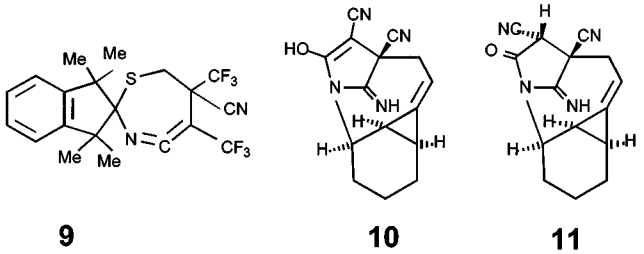


Figure 2. ORTEP plot of **8**

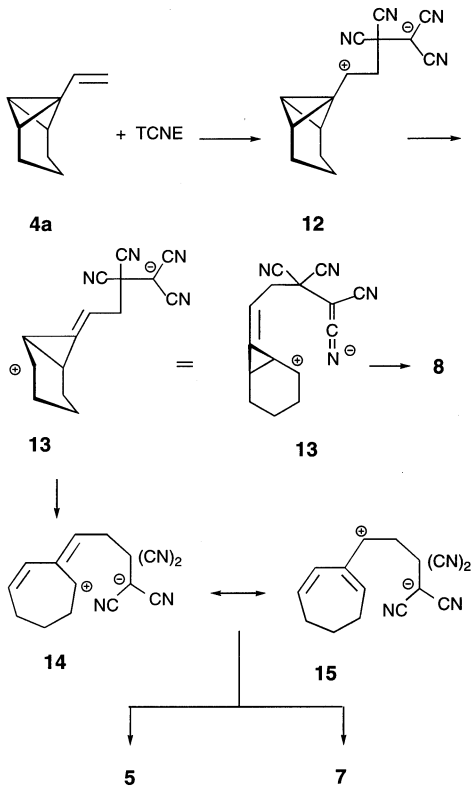




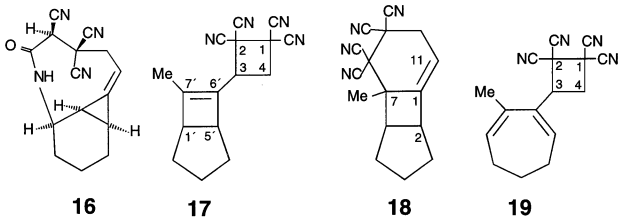
A possible mechanism for the formation of the products is depicted in Scheme 1[9]. The reaction sequence depicted in Scheme 1 is based on recent results of Wiberg concerning

the energy of the 1-bicyclo[1.1.0]butylcarbinyl cation and the 3-methylenecyclobutyl cation[10].

Scheme 1

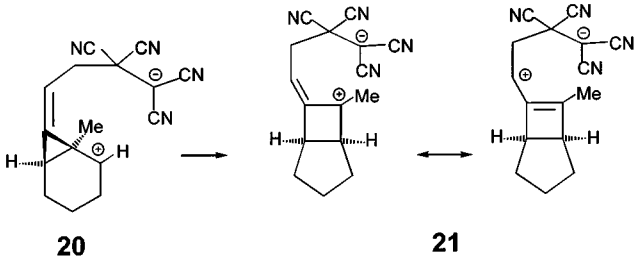


From the structures of products **5**, **7**, and **8** it follows that the initial attack of TCNE takes place at the methylene carbon atom of the CC double bond to form the zwitterion **12**, which opens a bicyclo[1.1.0]butane side bond to afford zwitterion **13**. Intermediate **13** either cyclizes to ketene imine **8** or undergoes a cyclopropylcarbinyl-homoallyl rearrangement to the allylic cation charaterized by resonance structures **14** and **15**, from which the final products **5** and **7** are formed. In the presence of water, **8** is converted into the amide **16**, which then undergoes closure of the five-membered ring to give the amidine **6**.



The results of the reaction of 1-methyl-7-vinyltricyclo[4.1.0.0^{2,7}]heptane **4e** with TCNE were disappointing in that the total yield of recovered material was very low. Column chromatographic work-up afforded products **17**, **18**, and **19** in yields of 4.4, 2.5, and 4.2%, respectively. The structures are based on the NMR spectra.

Whereas the formation of **19** should follow the route for **7** (Scheme 1), one further rearrangement of **20**, the analogue of **13**, is necessary to account for structures **17** and **18**. A Wagner-Meerwein shift of **20** leads to **21**, which then cyclizes to **17** or **18**. Again, the products indicate that TCNE attacks **4e** at the olefinic site.



Reactions of 1-chloro- and 1-bromo-7-vinyltricyclo[4.1.0.0^{2,7}]heptane (**4f** and **g**) with TCNE led to **22a** and **b** as the main products in yields of 25 and 49%. Small amounts (1.5 and 4.5%) of **23a** and **24b** were also isolated. Again, the structures of the products are based on the NMR spectra. For **24b**, an X-ray analysis was carried out (see Figure 3).

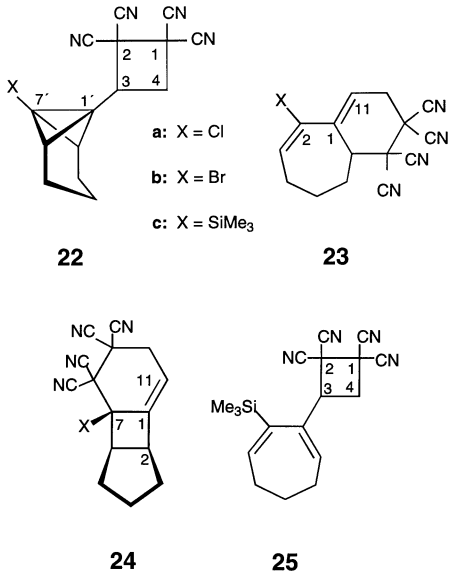
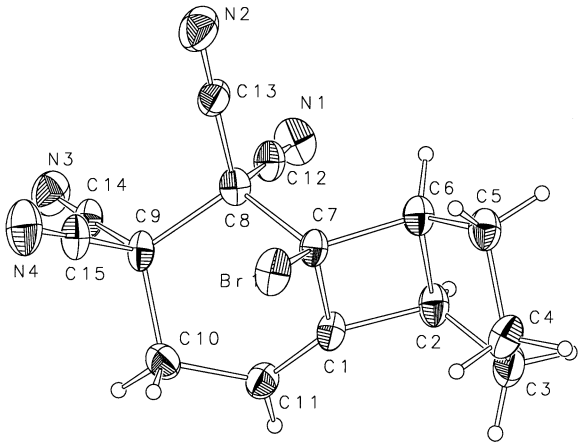


Figure 3. ORTEP plot of **24b**



Concerning the formation of **22**, it can readily be seen that if a halide is connected to the second bridgehead posi-

tion of the bicyclobutane subunit of zwitterion **12**, then the rate of the **12** → **13** conversion is decreased and cyclization to **22** becomes a competitive process (see Scheme 1). The formation of **23a** and **24b** follows routes that have already been discussed.

The reaction of **4d** with TCNE led to the generation of **22c** as the main product (yield 26−32%). In addition, **23c** and **25** were formed in yields of 7.7% and 7.4%. The structures of **22c** and **25** were confirmed by X-ray analyses (see Figures 4 and 5).

Figure 4. ORTEP plot of **22c**

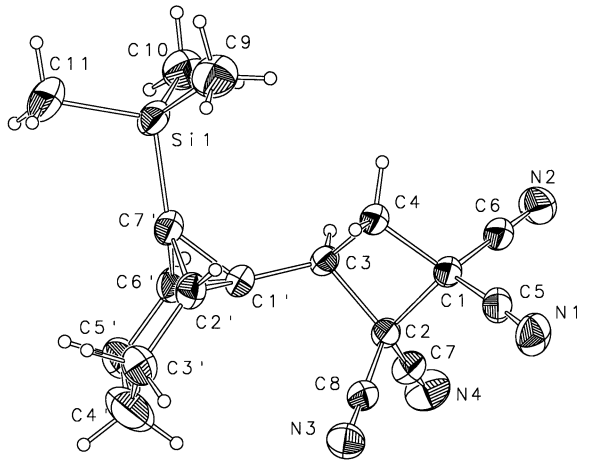
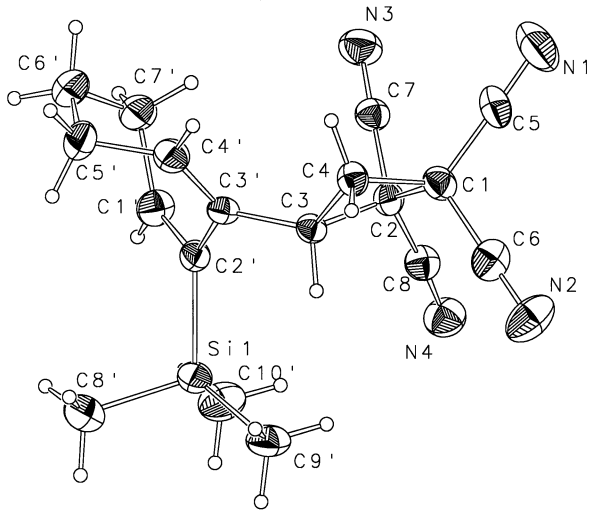


Figure 5. ORTEP plot of **25**



The formula of the fourth product **26** (yield 8.5%) is $C_{19}H_{21}N_5Si$; in addition to TCNE, hydrogen cyanide has also been incorporated into this compound. The structure **26** is consistent with the results of the recorded 2D NMR spectra. A possible mechanism is depicted in Scheme 2. The formation of HCN in reactions of TCNE has been reported previously[11].

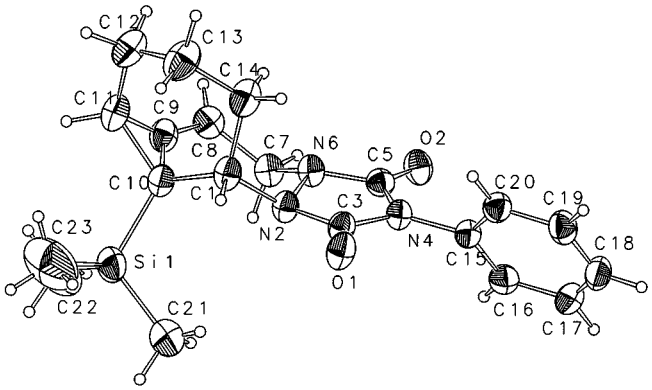
The interesting feature of Scheme 2 is that TCNE also attacks the substituted bicyclo[1.1.0]butane **4d** at the bridgehead position. The seven-membered ketene imine intermediate **29** could not be isolated, but was trapped by the nucleophilic reagents present in the reaction mixture. Cation **27** should have a non-classical structure with a short diagonal distance of the C atoms of the four-membered ring[12].

C. 4-Phenyl-1,2,4-triazoline-3,5-dione

4a and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) were reacted for 4 h at room temperature in dichloromethane to afford a 34% yield of a single product **31a**. The structure was established by NMR spectroscopy, specifically by a 2D INADEQUATE experiment. **31a** is formed by a mechanism analogous to that outlined in Scheme 1 for TCNE as the electrophilic reagent.

Reaction of the trimethylsilyl derivative **4d** with PTAD led to low yields of three products, **31b**, **32b**, and **33b** (2.0, 6.8, and 5.4%, respectively). Their structures followed from their NMR spectra. For **31b**, the structure was confirmed by X-ray analysis of a single crystal (see Figure 6). In all cases, the attack of the electrophile took place at the CC double bond.

Figure 6. ORTEP plot of **31b**

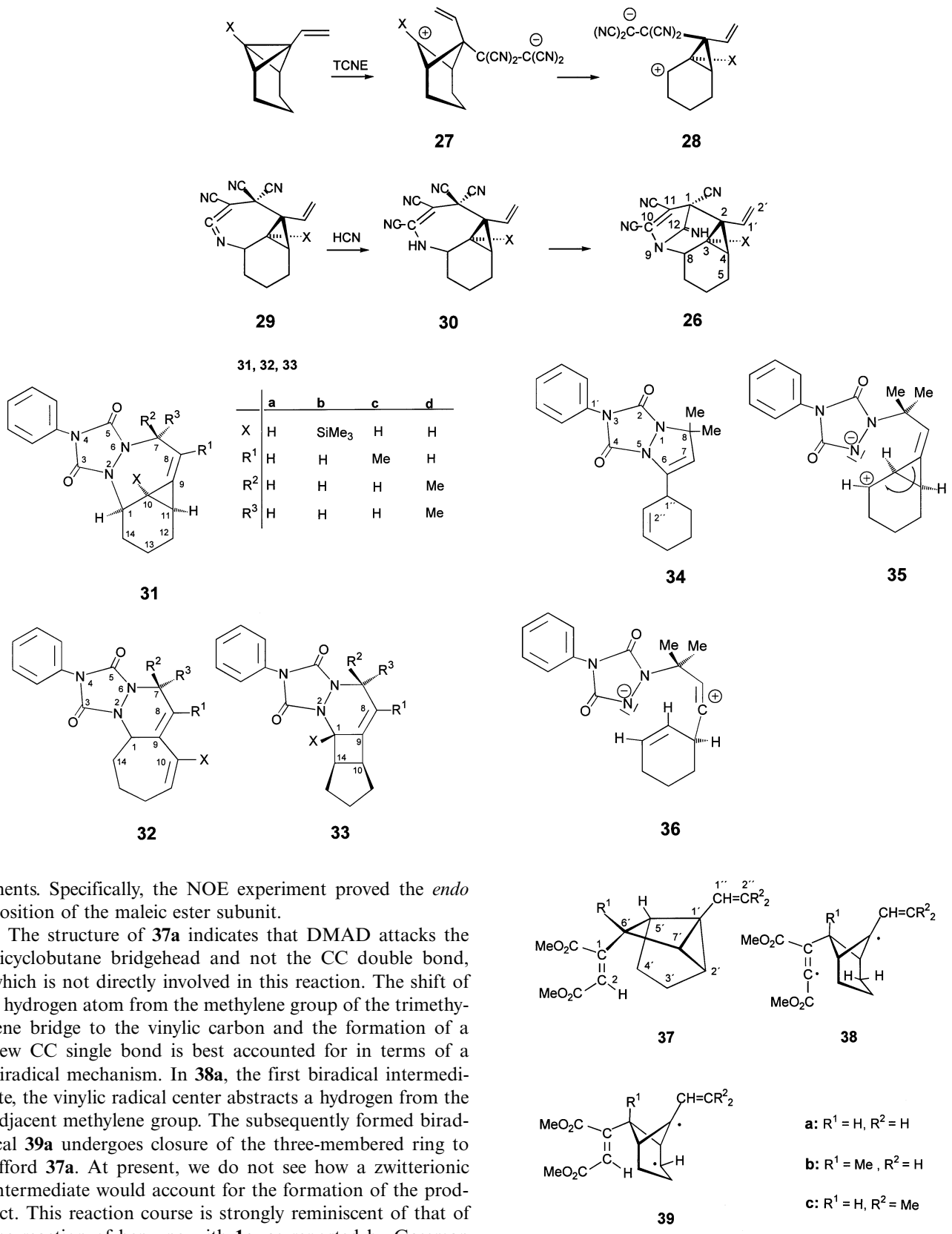


Besides **4a** and **d**, PTAD was also reacted with **3a** and **b**. In both cases, the yields were also low. With **3a**, a 4.5% yield of **32c** was isolated; with **3b**, a complex reaction mixture was formed, from which **31d** and **32d** could be isolated in yields of 10 and 2.9% by column chromatography. In addition, a 5.2% yield of **34** was obtained. The carbon skeleton of **34** was not observed at any other instance in the course of our investigations. Its formation can probably be explained in terms of isomerization of intermediate **35** to give **36**. **35** is an analogue of **20**, the generation of which has already been discussed. Although in **36** a vinyl cation is invoked, its formation could profit from the relief of strain of the methylenecyclopropane subunit.

D. Dimethyl Acetylenedicarboxylate

Reactions of **4a** with dimethyl acetylenedicarboxylate (DMAD) in dichloromethane at room temperature followed by column chromatographic work-up led to a 1:1 adduct **37a** in greatly varying yields (14−87%). Reproducible results (yield 51%) were obtained when the reaction was carried out in 1,4-dioxane. The structure of **37a** was established by 2D INADEQUATE and NOESY NMR experi-

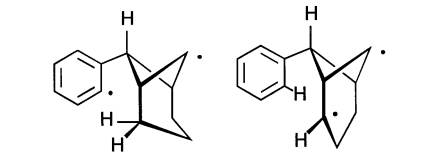
Scheme 2. X = $SiMe_3$



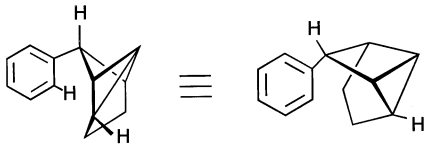
ments. Specifically, the NOE experiment proved the *endo* position of the maleic ester subunit.

The structure of **37a** indicates that DMAD attacks the bicyclobutane bridgehead and not the CC double bond, which is not directly involved in this reaction. The shift of a hydrogen atom from the methylene group of the trimethylene bridge to the vinylic carbon and the formation of a new CC single bond is best accounted for in terms of a biradical mechanism. In **38a**, the first biradical intermediate, the vinylic radical center abstracts a hydrogen from the adjacent methylene group. The subsequently formed biradical **39a** undergoes closure of the three-membered ring to afford **37a**. At present, we do not see how a zwitterionic intermediate would account for the formation of the product. This reaction course is strongly reminiscent of that of the reaction of benzyne with **1a**, as reported by Gassman and Richmond, in which hydrocarbon **42** was generated via diradicals **40** and **41**[13]. Moreover, reaction of dicyanoacetylene with **1a** gave an analogous product in 46% yield[13].

Substitution of the bicyclobutane bridgehead position would be expected to render the approach of DMAD more



40 **41**



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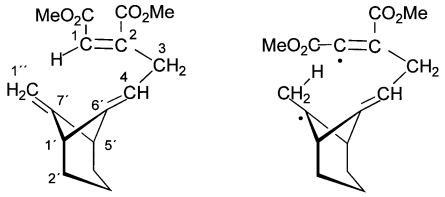
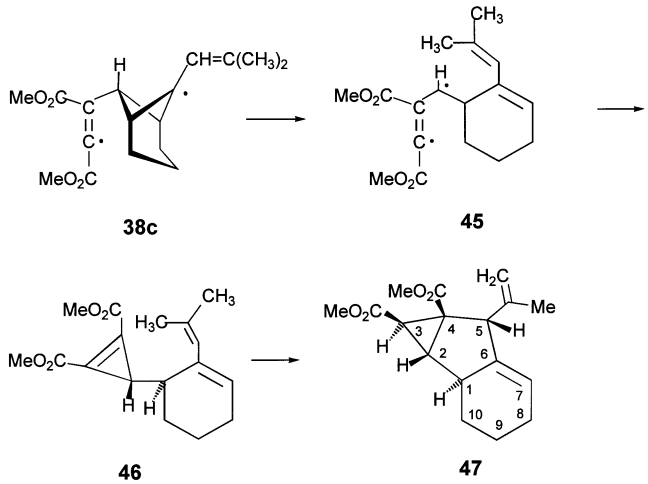
difficult because of steric hindrance. Indeed, in the reaction with **4e**, the yield of adduct **37b** dropped to 3.2%. A by-product **43** was isolated in 1.9% yield, indicating that attack of DMAD on the double bond is possible. Clearly, biradical **44** is stabilized by hydrogen abstraction from the methyl group. It should be pointed out that the reaction temperature was much higher is this experiment (90°C versus room temperature).



43 **44**

Whereas **4d** and **4g** were unreactive towards DMAD, reaction of vinylbicyclobutane **3b** led to two 1:1 adducts **37c** and **47**, in yields of 2.4 and 33%, respectively. The formation of the minor product **37c** follows the outlined mechanism, but the origin of the generated **47** is less obvious. In Scheme 3, a mechanism is proposed in which the key steps are the ring-opening of biradical **38c** to the biradical **45**, ring-closure of **45** to give the cyclopropene **46**, and its ene reaction to afford the final tricyclic system **47**. It should be noted that alternative mechanisms with zwitter-ionic intermediates could also explain the formation of **47**. The structure of **47** is based on a 2D NMR INADEQUATE experiment.

Scheme 3



38c **45**

46 **47**

E. Concluding Remarks

This investigation was oriented towards structure elucidation of the products derived from the reaction of 1-vinyltricyclo[4.1.0.0^{2,7}]heptanes with electrophilic alkenes and alkynes. The formation of products with several rather different structures made mechanistic interpretations necessary. Whenever this had to be carried out, care was taken to ensure that the proposed reaction paths had precedent in previous investigations. Therefore, we believe that the intermediates are realistic, although we are aware that full mechanistic proof of the course of the reactions has not been provided. This, however, was not the aim of the present work.

We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support of this investigation.

Experimental Section

For analytical instruments and general procedures, see ref.[14].

I. Starting Materials

The following compounds were synthesized according to published procedures: [1,2-Bis(diphenylphosphanyl)ethane]nickel dichloride (**2a**)[15], [1,2-bis(diphenylphosphanyl)propane]nickel dichloride (**2b**)[15], *p*-toluenesulfonyl bromide (TsBr)[16], 1-isopropenyltricyclo[4.1.0.0^{2,7}]heptane (**3a**)[7], 1-(2-methyl-1-propenyl)tricyclo[4.1.0.0^{2,7}]heptane (**3b**)[7], and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD)[17].

n-Butyllithium (BuLi) was purchased from Chemetall as a 1.60 M solution in *n*-hexane. Tetracyanoethylene (TCNE) and dimethyl acetylenedicarboxylate (DMAD) were commercial products.

II. 1-Vinyltricyclo[4.1.0.0^{2,7}]heptanes **4**

1. *1-Vinyltricyclo[4.1.0.0^{2,7}]heptane* **4a**: A suspension of 1-tricyclo[4.1.0.0^{2,7}]heptyllithium **1b**, obtained by reaction of **1a** (28.2 g, 300 mmol) with BuLi (200 ml, 1.60 M, 320 mmol) in diethyl ether according to ref.[7], was reacted with anhydrous $MgBr_2$ (55.2 g, 300 mmol) in ether to give **1c**. This solution was added dropwise with stirring to a solution of vinyl chloride (29.1 g, 466 mmol) and catalyst **2a** (1.60 g, 3.03 mmol) in diethyl ether (200 ml) at −78°C. The temperature was raised to −30°C and stirring was continued for 4 h. The reaction mixture was then slowly warmed to room temperature, and the excess vinyl chloride distilled off was destroyed by passage through a solution of potassium permanganate. Stirring was continued for 18 h at 20°C and then 1,4-dioxane (79.3 g, 900 mmol) was added to the solution. The resulting precipitate was filtered off and washed several times with diethyl ether. The filtrate was hydrolyzed with ammonia (350 ml of a 2 N aqueous solution) and the organic phase washed four times with an aqueous solution of Titriplex. The ethereal layer was dried with $MgSO_4$, filtered, and the solvent was removed by distillation through a 15-cm Vigreux column at 760 Torr. The remaining oil was purified by distillation to give **4a** (20.5 g, 57%) as a colorless liquid of b.p. 40−45°C/12

Torr. On contact with air, the liquid polymerized to form a colorless solid.

A second experiment starting from **1a** (17.6 g, 187 mmol), BuLi (188 mmol), $MgBr_2$ (34.6 g, 188 mmol), and vinyl chloride (15.3 g, 245 mmol) afforded 17.3 g (77%) of **4a**. − UV (*n*-hexane): λ_{max} (log ε) = 228 nm (4.065). − IR (film): $\tilde{\nu}$= 3087 cm^{-1}, 2986, 2926, 2857, 1622, 1484, 1442, 980, 883, 813, 757, 647, 628. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25−1.43 (m, 7 H, 3-, 4-, 5-H_2, 7-H), 2.65−2.72 (m, 2 H, 2-, 6-H), 4.86 [ddd, *J*(2′-H, 7-H) = 0.5 Hz, *J* = 10.3 Hz, *J* = 1.9 Hz, 1 H, 2′-H_{cis}], 5.06 (dd, *J* = 16.9 Hz, *J* = 1.9 Hz, 1 H, 2′-H_{trans}), 6.08 (dd, *J* = 16.9 Hz, *J* = 10.3 Hz, 1 H, 1′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.74 (d), 20.68 (t, 2 C), 20.95 (t), 23.24 (s), 43.11 (d, 2 C), 110.79 (t), 137.61 (d). − MS (70 eV), *m*/*z* (%): 120 (35) [M$^+$], 105 (100), 92 (42), 91 (86), 79 (56), 77 (44). − C_9H_{12} (120.2): calcd. C 89.94, H 10.06; found C 90.38, H 10.43; C_9H_{12}: calcd. 120.094; found 120.096 (HRMS).

2. *General Procedure for the Generation of 7-Vinyltricyclo[4.1.0.0^{2,7}]hept-1-yllithium* **4b** *and 7-Vinyltricyclo[4.1.0.0^{2,7}]hept-1-ylmagnesium Bromide* **4c**: At 12 Torr and with a bath temperature of up to 40°C, the solvent was removed from a solution of BuLi in *n*-hexane (1.00 equiv. of a 1.60 M solution). With cooling in an ice-bath, the oily residue was redissolved in a volume of diethyl ether to give a 1.60 M solution of BuLi in this solvent. At 0°C, **4a** (0.90 to 0.95 equiv.) was added and the mixture was stirred under nitrogen for 48 h at room temperature, after which the metallation of **4a** to give **4b** as a colorless suspension was complete. For the transmetallation of **4b** into **4c**, anhydrous magnesium bromide (0.90 to 0.95 equiv.) was added in portions to the stirred suspension of **4b** at 0°C (bath temp.) and the mixture was stirred for 12 h at room temperature under nitrogen. The green solution of **4c** was used for further reactions.

3. *1-Trimethylsilyl-7-vinyltricyclo[4.1.0.0^{2,7}]heptane* **4d**: To a suspension of **4b**, prepared from **4a** (6.00 g, 49.9 mmol) and BuLi (56.0 mmol) according to procedure II.2., freshly distilled chlorotrimethylsilane (5.40 g, 49.7 mmol) in diethyl ether (25 ml) was added dropwise under stirring at 0°C and stirring was continued for 1 h at this temperature. The mixture was then stirred for 2 d at room temperature, and NaOH (40 ml of an aqueous 2 N solution) was added. Standard work-up of the organic layer followed by distillation of the oily organic residue through a 10-cm Vigreux column afforded **4d** (5.59 g, 58%) as a colorless liquid of b.p. 70−80°C/12 Torr, which polymerized slowly on contact with air to form a white solid. − UV (cyclohexane): λ_{max} (log ε) = 231 nm (4.077). − IR (film): $\tilde{\nu}$= 2977 cm^{-1}, 2955, 2933, 2856, 1628, 1494, 1443, 1248, 1179, 1015, 980, 945, 887, 863, 837, 797, 756, 746, 663, 643. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.01 (s, 9 H, Me), 1.22−1.50 (m, 6 H, 3-, 4-, 5-H_2), 2.43-2.46 (m, 2 H, 2-, 6-H), 4.91 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1 H, 2′-H_{cis}), 5.08 (dd, *J* = 17.0 Hz, *J* = 2.0 Hz, 1 H, 2′-H_{trans}), 6.09 (dd, *J* = 10.4 Hz, *J* = 17.0 Hz, 1 H, 1′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.57 (q, 3 C), 16.13 (s), 21.03 (t, 3 C), 30.74 (s), 42.91 (d, 2 C), 111.80 (t), 137.29 (d). In C_6D_6, the signals of the trimethylene bridge appear at δ = 21.35 (t, 2 C), 21.40 (t). − MS (70 eV), *m*/*z* (%): 192 (22) [M$^+$], 149 (13), 118 (16), 117 (15), 109 (14), 73 (100), 59 (21). − $C_{12}H_{20}Si$ (192.4): calcd. C 74.92, H 10.48; found C 75.62, H 10.57; $C_{12}H_{20}Si$: calcd. 192.133; found 192.133 (HRMS).

4. *1-Methyl-7-vinyltricyclo[4.1.0.0^{2,7}]heptane* **4e**: To a suspension of **4b**, prepared from **4a** (6.00 g, 49.9 mmol) and BuLi (56.0 mmol) according to procedure II.2., iodomethane (12.5 g, 88.1 mmol) in diethyl ether (15 ml) was added dropwise under stirring at 0°C. Subsequently, stirring was continued for 1 h at 0°C and for 2 h at room temperature. By this stage the suspension had turned to an olive-green solution. It was then hydrolyzed by addition of 40 ml of 2 N NaOH. Standard work-up of the organic layer followed by distillation of the oily organic residue through a 10-cm Vigreux column afforded **4e** (2.64 g, 39%) as a colorless liquid of b.p. 54°C/20 Torr, which polymerized quickly on contact with air to form a white solid. − UV (cyclohexane): λ_{max} (log ε) = 235 nm (3.910). − IR (film): $\tilde{\nu}$= 2940 cm^{-1}, 2864, 1624, 1444, 1378, 1020, 979, 880, 674, 637. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 3 H, Me), 1.29−1.41 (m, 6 H, 3-, 4-, 5-H_2), 2.38 (m, 2 H, 2-, 6-H), 4.90 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1 H, 2′-H_{cis}), 4.94 (dd, *J* = 16.9 Hz, *J* = 2.0 Hz, 1 H, 2′-H_{trans}), 6.83 (dd, *J* = 10.4 Hz, *J* = 16.9 Hz, 1 H, 1′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.57 (q), 20.96 (t, 2 C), 21.03 (t), 24.20, 25.41 (2 s), 45.26 (d, 2 C), 111.23 (t), 135.74 (d). − MS (70 eV), *m*/*z* (%): 134 (83) [M$^+$], 119 (89), 106 (29), 105 (47), 93 (31), 91 (100), 79 (31), 77 (29). − $C_{10}H_{14}$ (134.2): calcd. C 89.49, H 10.51; found C 89.59, H 10.51; $C_{10}H_{14}$: calcd. 134.110; found 134.114 (HRMS).

5. *1-Chloro-7-vinyltricyclo[4.1.0.0^{2,7}]heptane* **4f**: To a suspension of **4b**, prepared from **4a** (8.50 g, 70.7 mmol) and BuLi (80.0 mmol) according to procedure II.2., *p*-toluenesulfonyl chloride (13.0 g, 68.2 mmol) in diethyl ether (50 ml) was added dropwise under stirring at 0°C and stirring was continued for 18 h at room temperature. The reaction mixture was then hydrolyzed by addition of 100 ml of 2 N NaOH. Standard work-up of the organic layer followed by distillation of the oily organic residue through a 10-cm Vigreux column afforded **4f** (4.41 g, 42%) as a colorless oil of b.p. 73°C/16 Torr. On contact with air, polymerization of **4f** to a white solid occurred within minutes. Therefore, all work-up procedures had to be carried out under nitrogen. − UV (acetonitrile): λ_{max} (log ε) = 230 nm (3.860). − IR (film): $\tilde{\nu}$= 3089 cm^{-1}, 2935, 2858, 1626, 1498, 1458, 1443, 1426, 1172, 1107, 1048, 1016, 988, 976, 944, 893, 852, 792, 598, 528. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24−1.59 (m, 6 H, 3-, 4-, 5-H_2), 2.92 (narrow m, 2 H, 2-, 6-H), 5.14−5.19 (m, 2 H, 2′-H_2), 5.89 (dd, *J* = 10.7 Hz, *J* = 16.8 Hz, 1 H, 1′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.16 (t, 2 C), 20.34 (t), 26.90, 42.62 (2 s), 48.58 (d, 2 C), 115.70 (t), 131.79 (d). − MS (70 eV), *m*/*z* (%): 156 (14), 154 (41) [M$^+$], 119 (63), 117 (29), 103 (36), 91 (100), 77 (32). − $C_9H_{11}Cl$ (154.6): calcd. C 69.90, H 7.17; found C 71.08, H 7.79; $C_9H_{11}{}^{35}Cl$: calcd. 154.055; found 154.054 (HRMS).

6. *1-Bromo-7-vinyltricyclo[4.1.0.0^{2,7}]heptane* **4g**: To a suspension of **4b**, prepared from **4a** (7.12 g, 59.2 mmol) and BuLi (65.2 mmol) according to procedure II.2., *p*-toluenesulfonyl bromide (13.9 g, 59.1 mmol) was added in portions under stirring at 0°C and stirring was continued for 3 h at room temperature. The reaction mixture was then hydrolyzed by addition of 100 ml of 2 N NaOH. Standard work-up of the organic layer followed by short-path distillation of the oily organic residue afforded **4g** (4.82 g, 41%) as a colorless oil of b.p. 50−60°C (bath)/0.01 Torr. − UV (acetonitrile): λ_{max} (log ε) = 229 nm (3.793). − IR (film): $\tilde{\nu}$= 2931 cm^{-1}, 2857, 1629, 1442, 1158, 1048, 1016, 975, 896. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26−1.59 (m, 6 H, 3-, 4-, 5-H_2), 2.91 (narrow m, 2 H, 2-, 6-H), 5.17 (dd, *J* = 17.0 Hz, *J* = 1.7 Hz, 2 H, 2′-H_{trans}), 5.22 (dd, *J* = 10.7 Hz, *J* = 1.7 Hz, 1 H, 2′-H_{cis}), 5.89 (dd, *J* = 17.0 Hz, *J* = 10.7 Hz, 1 H, 1′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.23 (t, 2 C), 20.25 (t), 26.50, 31.07 (2 s), 49.82 (d, 2 C), 115.78 (t), 132.82 (d). − MS (70 eV), *m*/*z* (%): 200 (12), 198 (12) [M$^+$], 119 (51), 117 (26), 91 (100), 41 (25). − $C_9H_{11}{}^{79}Br$: calcd. 198.004; found 198.015 (HRMS).

7. *1-Phenyl-7-vinyltricyclo[4.1.0.0^{2,7}]heptane* **4h**: To a suspension of **4b**, prepared from **4a** (7.10 g, 59.1 mmol) and BuLi (67.2 mmol) according to procedure II.2., anhydrous $MgBr_2$ (12.0 g, 65.2 mmol)

was added in portions under stirring at 0°C and stirring was continued for 18 h at room temperature. The reaction mixture was then charged with catalyst **2a** (312 mg, 0.591 mmol) and bromobenzene (9.28 g, 59.1 mmol) in diethyl ether (100 ml) was added dropwise. The solution was heated to reflux for 1 h and then stirred at room temperature for 3 d. 1,4-Dioxane (13.4 g, 152 mmol) was added, the resulting precipitate was filtered off, and the filtrate was treated as described under II.1. Distillation of the yellow oily material obtained after removal of the solvent afforded **4h** (2.42 g, 21%) as a pale-yellow oil of b.p. 50−70°C (bath)/10^{-3} Torr. − UV (acetonitrile): λ_{max} (log ε) = 264 nm (3.774). − IR (film): $\tilde{\nu}$= 3030 cm^{-1}, 2980, 2931, 2856, 1622, 1603, 1520, 1485, 1447, 1312, 1123, 1044, 1024, 988, 976, 932, 886, 765, 693, 645. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39−1.64 (m, 6 H, 3-, 4-, 5-H_2), 3.19 (narrow m, 2 H, 2-, 6-H), 4.90 (dd, *J* = 10.3 Hz, *J* = 1.8 Hz, 1 H, 2′′-H_{trans}), 5.09 (dd, *J* = 1.8 Hz, *J* = 16.8 Hz, 1 H, 2′′-H_{cis}), 5.59 (dd, *J* = 16.8 Hz, *J* = 10.3 Hz, 1 H, 1′′-H), 7.07−7.12, 7.21−7.26 (m, 5 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.97 (t), 21.00 (t, 2 C), 32.94, 36.82 (2 s), 43.16 (d, 2 C), 113.39 (t), 124.90 (d), 125.12, 128.09 (2 d, 2 C each), 134.18 (d), 137.48 (s). − MS (70 eV), *m/z* (%): 196 (91) [M^+], 181 (59), 168 (56), 167 (100), 166 (39), 165 (54), 155 (41), 154 (33), 153 (52), 141 (37), 128 (40), 91 (31). − $C_{15}H_{16}$ (196.3): calcd. C 91.78, H 8.22; found C 92.24, H 8.39; $C_{15}H_{16}$: calcd. 196.125; found 196.134 (HRMS).

8. *1,7-Divinyltricyclo[4.1.0.0^{2,7}]heptane* **4i**: To a suspension of **4b**, prepared from **4a** (6.04 g, 50.3 mmol) and BuLi (80.0 mmol) according to procedure II.2., anhydrous $MgBr_2$ (14.7 g, 79.8 mmol) was added in portions under stirring at 0°C and stirring was continued for 18 h at room temperature. The reaction mixture was then charged with catalyst **2a** (500 mg, 0.947 mmol), cooled to −78°C, and vinyl chloride (6.32 g, 101 mmol) was condensed into the mixture, which was subsequently allowed to warm slowly to room temperature. Stirring was continued for 18 h at room temperature. 1,4-Dioxane (20.7 g, 235 mmol) was then added, the resulting precipitate was filtered off, and the filtrate was treated as described under II.1. Distillation of the oily material obtained after removal of the solvent afforded **4i** (4.91 g, 67%) as a colorless liquid of b.p. 58−62°C (bath)/18 Torr, which polymerized within several hours, even at −30°C.− IR (film): $\tilde{\nu}$= 3088 cm^{-1}, 2979, 2929, 2858, 1621, 990, 885. − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.40 (broad s, 6 H, 3-, 4-, 5-H_2), 2.83 (narrow m, 2 H, 2-, 6-H), 4.95 (m, 4 H, CH=CH_2), 5.73 (dd, *J* = 17.0 Hz, *J* = 9.6 Hz, 2 H, C*H*=CH_2). − ^{13}C NMR (20 MHz, $CDCl_3$): δ = 20.93 (t), 21.08 (t, 2 C), 33.95 (s, 2 C), 44.83 (d, 2 C), 112.55 (t), 134.39 (d). − MS (70 eV), *m/z* (%): 146 (31) [M^+], 131 (58), 117 (63), 91 (100), 79 (63).

9. *1-[(E)-1,3-Butadien-1-yl]-7-vinyltricyclo[4.1.0.0^{2,7}]heptane* **4j**: To a suspension of **4b**, prepared from **4a** (2.04 g, 17.0 mmol) and BuLi (17.0 mmol) according to procedure II.2., anhydrous $MgBr_2$ (3.13 g, 17.0 mmol) was added in portions under stirring at 0°C and stirring was continued for 18 h at room temperature. The reaction mixture was then charged with catalyst **2b** (100 mg, 0.184 mmol), cooled to 0°C, and 1-chloro-1,3-butadiene (1.50 g, 16.9 mmol) was added dropwise. The mixture was then allowed to warm slowly to room temperature and stirring was continued for 18 h. 1,4-Dioxane (4.67 g, 53 mmol) was then added, the resulting precipitate was filtered off, and the filtrate was treated as described under II.1. Distillation of the oily material obtained after removal of the solvent afforded **4j** (1.96 g, 67%) as a colorless liquid of b.p. 80°C (bath)/10^{-3} Torr, which polymerized even in solution in degassed pentane after three hours at −30°C. − IR (film): $\tilde{\nu}$= 3085 cm^{-1}, 2929, 2857, 1623, 1457, 982. − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.46 (broad s, 6 H, 3-, 4-, 5-H_2), 2.86 (narrow m, 2 H, 2-, 6-H), 4.68−5.25 (m, 4 H, CH=CH_2), 5.48−6.23 (m, 4 H, vinylic H). − ^{13}C NMR (20 MHz, $CDCl_3$): δ = 20.69 (t), 21.23 (t, 2 C), 34.32, 36.14 (2 s), 45.49 (d, 2 C), 112.98 (t), 113.71 (2 t), 129.91, 130.79, 134.18, 136.82 (4 d). − MS (70 eV), *m/z* (%): 172 (27) [M^+], 131 (44), 129 (100), 115 (53), 91 (97), 79 (50), 77 (39).

10. *1-(1,3-Butadien-2-yl)-7-vinyltricyclo[4.1.0.0^{2,7}]heptane* **4k**: To a suspension of **4b**, prepared from **4a** (1.65 g, 13.7 mmol) and BuLi (13.8 mmol) according to procedure II.2., anhydrous $MgBr_2$ (2.53 g, 13.7 mmol), catalyst **2b** (100 mg, 0.184 mmol), and 2-chloro-1,3-butadiene (1.22 g, 13.8 mmol) were combined as described in the case of II.9. The work-up was carried out by addition of 1,4-dioxane (3.51 g, 39.8 mmol), filtering off the precipitate and treating the filtrate as described under II.1. Distillation of the oily material obtained after removal of the solvent afforded **4k** (900 mg, 38%) as a colorless liquid of b.p. 80°C (bath)/10^{-3} Torr. **4k** was prone to polymerization, leading in some cases to a glassy mass in the distillation receiver. − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.45 (broad s, 6 H, 3-, 4-, 5-H_2), 2.84 (narrow m, 2 H, 2-, 6-H), 4.88−5.13 (m, 4 H, C=CH_2), 5.35 (dd, *J* = 10.0 Hz, *J* = 1.8 Hz, 2 H, C=CH_2), 5.85 (dd, *J* = 10.0 Hz, *J* = 9.6 Hz, 1 H, C=C*H*), 6.19 (dd, *J* = 10.0 Hz, *J* = 9.6 Hz, 1 H, C=C*H*). − ^{13}C NMR (20 MHz, $CDCl_3$): δ = 20.81 (t), 20.93 (t, 2 C), 21.32, 22.96 (2 s), 44.13 (d, 2 C), 110.68 (t), 113.19 (t), 115.25 (t), 134.06 (d), 137.21 (d), 142.99 (s). − MS (70 eV), *m/z* (%): 172 (5) [M^+], 146 (5), 120 (74), 105 (100), 91 (99), 79 (74).

III. Reactions of 1-Vinyltricyclo[4.1.0.0^{2,7}]heptanes **4** *with TCNE*

1. *TCNE and* **4a**: A stirred solution of **4a** (2.00 g, 16.6 mmol) in dichloromethane (CH_2Cl_2) (50 ml), cooled in an ice-bath, was charged with TCNE (2.13 g, 16.6 mmol) in several portions and then stirred for 18 h at room temperature (r.t.). The solution was then concentrated under reduced pressure and the residue was subjected to flash silica gel chromatography (fsgc) with CH_2Cl_2 as eluent. Fraction 1 consisted of bicyclo[5.4.0]undeca-1(11),2-diene-8,8,9,9-tetracarbonitrile **5** (965 mg, 23%) as a colorless oil, which solidified to a white resin. The second fraction contained 3-(cyclohepta-1,6-dien-1-yl)cyclobutane-1,1,2,2-tetracarbonitrile **7** (132 mg, 3.2%) as the major product, which was obtained as a viscous liquid contaminated with minor components that could not be removed by a second flash chromatography. From the third fraction, 8-azatricyclo[7.4.0.0^{2,13}]trideca-2,6,7-triene-5,5,6-tricarbonitrile **8** (83.0 mg, 2.0%) was isolated as a colorless solid, m.p. 120°C (dec.). With ethyl acetate as eluent, 1-aza-14-imino-13-oxotetracyclo-[9.2.1.0^{2,7}.0^{6,8}]tetradec-8-ene-11,12-dicarbonitrile **6** (1.95 g) was isolated, which after crystallization from ethyl acetate/petroleum ether furnished **6** (1.50 g, 34%) as a yellow solid, m.p. 150°C (dec.). For X-ray analysis, the compound was further purified by crystallization from chloroform.

5: UV (cyclohexane): λ_{max} (log ε) = 240 nm (3.934). − IR (film): $\tilde{\nu}$= 2980 cm^{-1}, 2875, 1645, 1440, 918, 740. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17−1.80 (m, 4 H, 5-, 6-H_2), 1.90−2.00 (m, 2 H, 4-H_2), 2.32 (dd, *J* = 5.1 Hz, *J* = 18.8 Hz, 1 H, 10-H), 2.56 (d, *J* = 18.8 Hz, 1 H, 10-H), 3.04 (d, *J* = 10 Hz, 1 H, 7-H), 4.91−4.95 (m, 1 H, 11-H), 5.44 (m, 1 H, 3-H), 5.62 (d, *J* = 12.3 Hz, 1 H, 2-H). − ^{13}C NMR [100 MHz, $CDCl_3$, ^{1}*J*(CC) by INADEQUATE]: δ = 25.29 [t, *J*(C4-C5) = 33.8 Hz, *J*(C5-C6) = 34.2 Hz, C-5], 27.65 [t, *J*(C3-C4) = 40.7 Hz, C-4], 29.59 [t, *J*(C6-C7) = 34.2 Hz, C-6], 31.74 [t, *J*(C9-C10) = 31.2 Hz, *J*(C10-C11) = 40.0 Hz, C-10], 38.60 [s, *J*(C8-C9) = 34.2 Hz, *J*(C9-C14) = 67.9 Hz, *J*(C9-C15) = 68.3 Hz, C-9], 43.65 [d, *J*(C1-C7) = 39.6 Hz, *J*(C7-C8) = 30.5 Hz, C-7], 45.49 [s, *J*(C8-C12) = 67.6 Hz, *J*(C8-C13) = 68.3 Hz, C-8], 109.54 (s, C-12 or C-13), 110.99 (s, C-14 or C-15), 111.97 (s, C-15 or C-14), 112.36 (s, C-13 or C-12), 120.10 [d, *J*(C1-C11) = 71.2 Hz, C-11], 129.17 [d, *J*(C1-C2) = 55.6 Hz, *J*(C2-C3) = 70.5 Hz,

C-2], 131.78 (d, C-3), 135.82 (s, C-1). − MS (70 eV), *m/z* (%): 248 (100) [M$^+$], 120 (98), 105 (56), 91 (99), 77 (55). − $C_{15}H_{12}N_4$ (248.3): calcd. C 72.56, H 4.87, N 22.57; found C 72.09, H 4.96, N 22.40; $C_{15}H_{12}N_4$ calcd. 248.106; found 248.108 (HRMS).

7: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88−1.98 (m, 2 H, 4′-H_2), 2.26−2.50 (m, 4 H, 3′-, 5′-H_2), 3.04 (dd, *J* = 8.2 Hz, *J* = 12.3 Hz, 1 H, 4-H), 3.16 (t, *J* = 12.3 Hz, 1 H, 4-H), 3.96−4.04 (m, 1 H, 3-H), 5.62 (dd, *J* = 11.8 Hz, *J* = 1.6 Hz, 1 H, 7′-H), 5.82 (m, 1 H, 6′-H), 6.14 (m, 1 H, 2′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.12 (t), 29.64 (t), 31.47 (t), 32.78 (s), 34.49 (t), 42.90 (s), 49.28 (d), 108.39, 109.89, 110.28, 110.81 (4 s), 122.41 (d), 129.68 (s), 134.76 (d), 139.53 (d).

8: UV (acetonitrile): λ_{max} (log ε) = 242 nm (4.142), 310 (2.582). − IR (KBr): ṽ= 2963 cm^{-1}, 2953, 2865, 2214, 2067, 1446, 1440, 1362, 1184, 906, 855, 686. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35−1.55 (m, 2 H, 11-H_2), 1.65−1.84 (m, 3 H, 10-H_2, 12-H), 1.99 (m, 1 H, 12-H), 2.08 (m, 1 H, 13-H), 2.41 (m, 1 H, 1-H), 2.82 (dd, *J* = 12.1 Hz, *J* = 15.5 Hz, 1 H, 4-H), 3.23 (m, 1 H, 4-H), 4.36 (m, 1 H, 9-H), 6.10 (m, 1 H, 3-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.81 (t), 18.44 (d), 20.53 (d), 21.45 (t), 29.47 (t), 37.44 (s), 38.66 (t), 42.41 (s), 57.08 (d), 111.47 (d), 111.79, 112.44, 113.89 (3 s), 137.58 (s), 165.36 (s). − MS (70 eV), *m/z* (%): 248 (8) [M$^+$], 120 (84), 119 (47), 105 (100), 92 (44), 91 (58). − $C_{15}H_{12}N_4$ (248.3): calcd. C 72.56, H 4.87, N 22.57; found C 72.80, H 4.86, N 22.47; $C_{15}H_{12}N_4$: calcd. 248.106; found 248.118 (HRMS).

6: IR (KBr): ṽ= 3265 cm^{-1}, 2923, 2902, 2857, 1755, 1676, 1386, 1353, 1336, 1300, 1197, 1149, 1129, 1073, 896, 874, 865, 819. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38−2.32 (m, 8 H, 3-, 4-, 5-H_2, 6-, 7-H), 2.86 and 3.18 (2 dd, *J* = 7.0 Hz, *J* = 14.5 Hz for both dd, 2 H, 10-H_2), 4.13 (s, 1 H, 12-H), 4.80 (t, *J* = 8 Hz, 1 H, 2-H), 5.94 (m, 1 H, 9-H), 9.05 (s, 1 H, NH). In addition, the NMR spectrum shows further signals of low intensity, assignable to the isomers **10** and **11**. − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.10 (d), 17.31 (t), 18.05 (d), 19.90 (t), 23.86 (t), 36.67 (t), 44.71 (d), 48.24 (d), 50.48 (s), 110.83 (d), 111.63, 115.82 (2 s), 137.03 (s), 161.78 (s), 166.27 (s). − MS (70 eV), *m/z* (%): 266 (31) [M$^+$], 265 (58), 238 (32), 119 (59), 118 (31), 117 (44), 91 (100). − $C_{15}H_{14}N_4O$ (266.3): calcd. C 67.65, H 5.30, N 21.04; found C 67.63, H 5.54, N 21.09; $C_{15}H_{14}N_4O$: calcd. 265.109; found 265.098 (HRMS).

In a second reaction of **4a** (3.28 g, 27.3 mmol) with TCNE (3.50 g, 27.3 mmol), the chromatographic work-up was carried out with anhydrous solvents, which afforded the ketene imine **8** in 9% yield.

2. *TCNE and* **4d**: Compound **4d** (1.34 g, 6.97 mmol) and TCNE (0.892 g, 6.96 mmol) were allowed to react as described under III.1. Fsgc work-up using petroleum ether/ethyl acetate (1:1) as eluent afforded in the first fraction 3-(7-trimethylsilyltricyclo[4.1.0.0^{2,7}]hept-1-yl)cyclobutane-1,1,2,2-tetracarbonitrile **22c**, which was crystallized from the same solvent mixture to afford 720 mg (32%) of a crystalline solid of m.p. 120°C (dec.). Fraction 2 contained a mixture of 3 components, which were subjected to a second chromatographic separation with petroleum ether/ethyl acetate (7:1) as eluent. This separation furnished 134 mg (6%) of a 1:1 mixture of **22c** and 2-trimethylsilylbicyclo[5.4.0]undeca-1(11),2-diene-8,8,9,9-tetracarbonitrile **23c**, which could not be separated, and 3-[7-trimethylsilylcyclohepta-1,6-dien-1-yl]cyclobutane-1,1,2,2-tetracarbonitrile **25** (165 mg, 7.4%) as a colorless solid, m.p. 140°C (dec.). Fraction 3 afforded 9-aza-12-imino-3-trimethylsilyl-2-vinyltetracyclo[7.2.1.0^{2,4}.0^{3,8}]dodec-10-ene-1,10,11-tricarbonitrile **26** as a pale-yellow powder (380 mg), which after crystallization from petroleum ether/ethyl acetate gave 205 mg of **26** (8.5%) of m.p. 200°C (dec.). − **22c**: IR (KBr): ṽ= 2983 cm^{-1}, 2937, 2860, 1447, 1266, 1251, 990, 944, 900, 888, 855, 841, 798, 761, 744, 723. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 9 H, $SiMe_3$), 1.20−1.35 (m, 2 H, 4′-H_2), 1.40−1.67 (m, 4 H, 3′-, 5′-H_2), 2.24 and 2.37 (2 m, 1 H each, 2′-, 6′-H), 2.88 (dd, *J* = 9.3 Hz, *J* = 12.0 Hz, 1 H, 4-H, *trans* to 3-H), 2.92 (dd, *J* = 9.3 Hz, *J* = 12.0 Hz, 1 H, 4-H, *cis* to 3-H), 3.69 (t, *J* = 9.3 Hz, 1 H, 3-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.23 (q), 13.02 (s), 20.29, 20.38, 20.57 (3 t), 25.66 (s), 33.03 (s), 34.09 (t), 41.40 (d), 42.99 (s), 44.26 (d), 48.88 (d), 109.68, 110.03, 110.32, 110.75 (4 s). − MS (70 eV), *m/z* (%): 320 (2) [M$^+$], 228 (19), 227 (100), 78 (22), 73 (51). − $C_{18}H_{20}N_4Si$ (320.5): calcd. C 67.46, H 6.29, N 17.48; found C 67.46, H 6.24, N 17.44; $C_{18}H_{20}N_4Si$: calcd. 320.146; found 320.150 (HRMS).

25: IR (KBr): ṽ= 2993 cm^{-1}, 2956, 2898, 2860, 1447, 1265, 1246, 961, 872, 840, 754, 718, 685, 644, 626. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 9 H, $SiMe_3$), 1.85 and 2.00−2.36 (m, 1 H, and m, 5 H, 3′-, 4′-, 5′-H_2), 3.01 (dd, *J* = 12.1 Hz, *J* = 7.9 Hz, 4-H *trans* to 3-H), 3.25 (t, *J* = 12.1 Hz, 1 H, 4-H *cis* to 3-H), 4.11 (dd, *J* = 12.1 Hz, *J* = 7.9 Hz, 1 H, 3-H), 6.21 (m, 1 H, 2′-H), 6.76 (t, *J* = 7.3 Hz, 1 H, 6′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.09 (q), 25.42 (t), 27.06 (t), 33.27 (s), 34.56 (t), 37.15 (t), 43.82 (s), 47.77 (d), 109.30, 109.82, 109.85, 110.81 (4 s), 133.36 (d), 136.15 (s), 141.01 (s), 148.68 (d). − MS (70 eV), *m/z* (%): 320 (11) [M$^+$], 227 (82), 177 (27), 78 (24), 73 (100), 59 (24). − $C_{18}H_{20}N_4Si$ (320.5): calcd. C 67.46, H 6.29, N 17.48; found C 67.74, H 6.36, N 17.22; $C_{18}H_{20}N_4Si$: calcd. 320.146; found 320.151 (HRMS).

26: IR (KBr): ṽ= 3424 cm^{-1}, 2953, 2215, 1606, 1520, 1435, 1255, 881, 842. − ^{1}H NMR (400 MHz, $CDCl_3$): (assignment by DQF-COSY and HETCOR measurements): δ = 0.10 (s, 9 H, $SiMe_3$), 0.80 (m, 1 H, 6-H), 1.38−1.46 (m, 2 H, 4-, 6-H), 1.49 (dt, *J* = 13.6 Hz, *J* = 2.7 Hz, 1 H, 7-H), 1.80 (m, 1 H, 7-H), 1.89 (m, 1 H, 5-H), 2.02 (dd, *J* = 15.0 Hz, *J* = 6.0 Hz, 1 H, 5-H), 4.62 (t, *J* = 2.7 Hz, 1 H, 8-H), 5.32 (d, *J* = 10.3 Hz, 1 H, 2′-H *cis* to 1′-H), 5.37 (d, *J* = 17.0 Hz, 1 H, 2′-H *trans* to 1′-H), 5.75 (dd, *J* = 10.3 Hz, *J* = 17.0 Hz, 1 H, 1′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.09 (q), 13.38 (s), 14.30 (t), 17.73 (t), 22.32 (d), 29.35 (t), 45.04 (s), 49.32 (d), 74.43 (s), 102.01 (s), 104.64 (s), 109.43, 110.50, 112.07 (3 s), 117.38 (t), 137.79 (d), 145.89 (s). − MS (70 eV), *m/z* (%): 348 (27), 347 (100) [M$^+$], 346 (22) 332 (33), 73 (90). − $C_{19}H_{21}N_5Si$ (347.5): calcd. C 65.67, H 6.09, N 20.15; found C 66.08, H 6.32, N 20.07; $C_{19}H_{21}N_5Si$: calcd. 347.157; found 347.162 (HRMS).

In a second experiment, **4d** (1.76 g, 9.15 mmol) and TCNE (1.17 g, 9.13 mmol) were allowed to react at r.t. for 18 h in acetonitrile (100 ml). The usual work-up by flash chromatography using petroleum ether/ethyl acetate as eluent furnished **23c** (225 mg, 7.7%) as a colorless solid of m.p. 154−156°C.

23c: IR (KBr): ṽ= 2954 cm^{-1}, 2896, 2874, 1606, 1463, 1446, 1424, 1428, 1123, 970, 959, 946, 895, 866, 844, 813, 758, 693, 639. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.14 (s, 9 H, $SiMe_3$), 1.78 (m, 1 H), 1.98 (m, 1 H), 2.10−2.24 (m, 2 H), 2.28 (m, 1 H) and 2.43 (m, 1 H, 4-, 5-, 6-H_2 in unknown order), 3.19−3.24 (m, 2 H, 10-H_2), 3.28 (m, 1 H, 7-H), 5.50 (m, 1 H, 11-H), 6.15 (m, 1 H, 3-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.69 (q), 21.01 (t), 27.75 (t), 31.00 (t), 32.76 (t), 37.79 (s), 43.74 (d), 44.38 (s), 109.90, 111.02, 111.35, 111.66 (4 s), 116.21 (d), 138.27 (s), 141.06 (s), 142.31 (d). − MS (70 eV), *m/z* (%): 320 (33) [M$^+$], 305 (68), 177 (100), 73 (58). − $C_{18}H_{20}N_4Si$ (320.5): calcd. C 67.46, H 6.29, N 17.48; found C 67.68, H 6.33, N 17.21; $C_{18}H_{20}N_4Si$: calcd. 320.146; found 320.148 (HRMS).

3. *TCNE and* **4e**: Compound **4e** (2.42 g, 18.0 mmol) and TCNE (2.30 g, 18.0 mmol) were allowed to react as described under III.1. for 16 h at r.t. Fsgc work-up using petroleum ether/ethyl acetate (1:1) as eluent afforded in the first fraction 3-(7-methylbicyclo[3.2.0]hept-6-en-6-yl)cyclobutane-1,1,2,2-tetracarbonitrile **17** (210

mg, 4.4%) as a 2.8:1 mixture of diastereomers, which could not be separated. The second fraction was further purified by fsgc (eluent petroleum ether/ethyl acetate/CH_2Cl_2, 7:1:4) and afforded in the faster moving fraction 7-methyltricyclo[5.4.0.0^{2,6}]undec-1(11)-ene-8,8,9,9-tetracarbonitrile **18** (120 mg, 2.5%) as colorless crystals of m.p. 96−97°C. From the next fraction, 3-[7-methylcyclohepta-1,6-dien-1-yl]cyclobutane-1,1,2,2-tetracarbonitrile **19** (200 mg, 4.2%) was isolated as colorless crystals of m.p. 114−116°C.

Diastereomeric mixture **17**: ^{13}C NMR (100 MHz, $CDCl_3$): major component δ = 12.80 (q), 23.09 (t), 24.06 (t), 26.20 (t), 33.77 (s), 35.52 (t), 41.97 (d), 42.56 (s), 44.98 (d), 47.48 (d), 109.31, 109.94, 110.05, 110.72 (4 s), 129.71 (s), 151.37 (s); minor component δ = 13.12 (q), 23.03 (t), 23.81 (t), 25.03 (t), 33.92 (s), 35.29 (t), 41.93 (s), 42.52 (d), 44.27 (d), 47.79 (d), 109.09, 109.87, 110.08, 110.67 (4 s), 129.89 (s), 148.98 (s). − MS (70 eV), *m/z* (%): 262 (5) [M$^+$], 134 (99), 119 (100), 106 (35). − $C_{16}H_{14}N_4$ (262.3): calcd. C 73.26, H 5.38, N 21.36; found C 73.49, H 5.66, N 21.27; $C_{16}H_{14}N_4$ calcd. 262.122; found 262.105 (HRMS).

18: IR (KBr): ṽ= 2990 cm^{-1}, 2970, 2949, 2898, 1635, 1476, 1398, 1152, 1043, 914, 878, 850, 811, 651, 555, 482. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 3 H, Me), 1.81−2.01 (m, 6 H, 3-, 4-, 5-H_2), 3.17−3.21 (m, 2 H, 10-H_2), 3.24 (m, 1 H, 6-H), 3.60 (m, 1 H, 2-H), 5.71−5.75 (m, 1 H, 11-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.82 (q), 27.61 (t), 28.57 (t), 30.72 (t), 33.72 (t), 37.85 (s), 49.48 (s), 49.51 (d), 49.78 (d), 49.98 (s), 110.09, 110.74, 112.79, 112.94 (4 s), 113.85 (d), 147.74 (s). − MS (70 eV), *m/z* (%): 262 (15) [M$^+$], 220 (31), 184 (48), 183 (86), 169 (100), 157 (38), 156 (63), 134 (38), 119 (50). − $C_{16}H_{14}N_4$ (262.3): calcd. C 73.26, H 5.38, N 21.36; found C 73.58, H 5.36, N 21.04; $C_{16}H_{14}N_4$ calcd. 262.122; found 262.109 (HRMS).

19: IR (KBr): ṽ= 3005 cm^{-1}, 2936, 2862, 1653, 1636, 1448, 1383, 1249, 1148, 1051, 1037, 839, 700, 649, 620, 533, 462, 417. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 3 H, Me), 1.93−2.16 (m, 6 H, 3′-, 4′-, 5′-H_2), 3.08 (dd, *J* = 8.0 Hz, *J* = 12.2 Hz, 1 H, 4-H), 3.26 (t, *J* = 12.2 Hz, 1 H, 4-H), 4.23 (m, 1 H, 3-H), 6.11 (m, 1 H, 6′-H), 6.22 (m, 1 H, 2′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.51 (q), 25.25 (t), 25.93 (t), 33.19 (s), 34.34 (t), 36.69 (t), 42.77 (s), 46.15 (d), 109.01, 109.85, 110.00, 110.83 (4 s), 132.24 (s), 134.58 (d), 135.18 (d), 135.50 (s). − MS (70 eV), *m/z* (%): 262 (42) [M$^+$], 134 (100), 119 (97), 106 (39), 105 (31), 91 (43). − $C_{16}H_{14}N_4$ (262.3): calcd. C 73.26, H 5.38, N 21.36; found C 72.88, H 5.32, N 21.14; $C_{16}H_{14}N_4$ calcd. 262.122; found 262.109 (HRMS).

4. *TCNE and* **4f**: Compound **4f** (2.89 g, 18.7 mmol) and TCNE (2.39 g, 18.7 mmol) were allowed to react as described under III.1. for 16 h at r.t. Fsgc work-up using petroleum ether/ethyl acetate (4:1) as eluent afforded in the first fraction 3-(7-chlorotricyclo[4.1.0.0^{2,7}]hept-1-yl)cyclobutane-1,1,2,2-tetracarbonitrile **22a** (1.30 g, 25%) as a crystalline powder of m.p. 118°C (dec.). The second fraction was further purified by fsgc (eluent CH_2Cl_2) and afforded 2-chlorobicyclo[5.4.0]undeca-1(11),2-diene-8,8,9,9-tetracarbonitrile **23a** (80.0 mg, 1.5%) as a pale-yellow oil, which solidified to a yellow resin.

22a: IR (KBr): ṽ= 2948 cm^{-1}, 2863, 1506, 1444, 1183, 1061, 993, 856, 795, 710. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35−1.70 (m, 6 H, 3′-, 4′-, 5′-H_2), 2.93 (m, 1 H, 2′- or 6′-H), 2.98−3.06 (m, 2 H, 4-H, 6′- or 2′-H), 3.12 (dd, *J* = 9.3 Hz, *J* = 12.7 Hz, 1 H, 4-H), 3.73 (t, *J* = 9.3 Hz, 1 H, 3-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.59 (s), 19.62 (t), 19.70 (t), 19.79 (t), 33.97 (s), 34.13 (t), 40.03 (s), 43.40 (s), 46.22 (d), 48.21 (d), 51.50 (d), 109.38, 109.80, 109.81, 110.40 (4 s). − MS (70 eV), *m/z* (%): 284 (8), 282 (21) [M$^+$], 204 (39), 189 (34), 169 (100), 168 (43), 142 (54), 115 (52), 78 (61), 77 (40), 51 (45). − $C_{15}H_{11}ClN_4$ (282.7): calcd. C 63.72, H 3.92, Cl 12.54, N 19.82; found C 63.74, H 4.01, Cl 12.35 N 19.81; $C_{15}H_{11}{}^{35}ClN_4$: calcd. 282.067; found 282.066 (HRMS).

23a: IR (KBr): ṽ= 2957 cm^{-1}, 2874, 1714, 1635, 1461, 1438, 1356, 1257, 1191, 1163, 1122, 1078, 933, 913, 889, 871, 785, 731. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92−2.50 (m, 6 H, 4-, 5-, 6-H_2), 3.27−3.31 (m, 1 H, 10-H_2), 3.36 (m, 1 H, 7-H), 6.27 (dd, *J* = 5.6 Hz, 9.3 Hz, 1 H, 3-H), 6.41 (narrow m, 1 H, 11-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.80 (t), 24.21 (t), 28.03 (t), 32.57 (t), 37.88 (s), 41.30 (d), 44.98 (s), 108.75, 110.36, 111.05, 111.36 (4 s), 121.75 (d), 130.21 (s), 130.76 (d), 134.51 (s). − MS (70 eV), *m/z* (%): 284 (31), 282 (91) [M$^+$], 247 (100), 220 (42), 193 (31), 154 (81), 119 (64). − $C_{15}H_{11}ClN_4$ (282.7): calcd. N 19.82; found N 19.81; $C_{15}H_{11}{}^{35}ClN_4$: calcd. 282.067; found 282.061 (HRMS).

5. *TCNE and* **4g**: Compound **4g** (3.88 g, 19.5 mmol) and TCNE (2.49 g, 19.4 mmol) were allowed to react as described under III.1. for 48 h at r.t. After aqueous work-up, the crude material was analyzed by NMR spectroscopy, which indicated the presence of 3-(7-bromotricyclo[4.1.0.0^{2,7}]hept-1-yl)cyclobutane-1,1,2,2-tetracarbonitrile **22b** (49%) and 7-bromotricyclo[5.4.0.0^{2,6}]undec-1(11)-ene-8,8,9,9-tetracarbonitrile **24b** (14%). Fsgc purification using petroleum ether/ethyl acetate (6:1) as eluent afforded in the first fraction **22b** (1.75 g, 28%) as a microcrystalline powder of m.p. 125°C (dec.) and in the second fraction **24b** (294 mg, 4.5%), which was further crystallized from petroleum ether/ethyl acetate to give quadratic crystals of m.p. 160°C (dec.). This material was used for a single-crystal X-ray analysis.

22b: IR (KBr): ṽ= 2947 cm^{-1}, 2859, 1496, 1437, 1176, 1052, 993, 856, 795, 705. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38−1.70 (m, 6 H, 3′-, 4′-, 5′-H_2), 2.89 (m, 1 H, 2′- or 6′-H), 2.98−3.05 (m, 2 H, 4-H, 6′- or 2′-H), 3.16 (dd, *J* = 9.0 Hz, *J* = 12.9 Hz, 1 H, 4-H), 3.73 (t, *J* = 9.0 Hz, 1 H, 3-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.58 (s), 19.65 (t), 19.69 (t), 19.77 (t), 26.39 (s), 33.74 (t), 33.88 (s), 43.19 (s), 47.18 (d), 49.27 (d), 52.62 (d), 109.43, 109.83 (2 C), 110.43 (3 s). − MS (70 eV), *m/z* (%): 328 (2), 326 (3) [M$^+$], 169 (54), 142 (40), 119 (80), 115 (65), 91 (100), 78 (53), 77 (39), 51 (58). − $C_{15}H_{11}BrN_4$ (327.2): calcd. C 55.07, H 3.39, Br 24.42, N 17.12; found C 54.98, H 3.50, Br 24.36, N 17.03; $C_{15}H_{11}{}^{79}BrN_4$: calcd. 326.017; found 326.007 (HRMS).

24b: IR (KBr): ṽ= 2970 cm^{-1}, 2941, 2864, 1442, 1435, 1331, 1296, 1284, 1213, 1144, 938, 914, 893, 845, 820, 806, 790, 719, 569. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68−2.30 (m, 6 H, 3-, 4-, 5-H_2), 3.30 (dd, *J* = 7.2 Hz, *J* = 16.5 Hz, 1 H, 10-H), 3.40 (dt, *J* = 16.5 Hz, *J* = 3.4 Hz, 1 H, 10-H), 3.53 (narrow m, 1 H, 2-H or 6-H), 3.70 (narrow m, 6-H or 2-H), 6.03 (m, 1 H, 11-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.45 (t), 31.29 (t), 32.63 (t), 33.04 (t), 39.21 (s), 49.82 (d), 51.22 (s), 51.50 (d), 61.61 (s), 109.40, 109.73, 112.06, 112.57 (4 s), 118.75 (d), 148.13 (s). − MS (70 eV), *m/z* (%): 248 (17) [M$^+$ − Br], 247 (100). − $C_{15}H_{11}BrN_4$ (327.2): calcd. C 55.07, H 3.39, Br 24.42, N 17.12; found C 54.48, H 3.39, Br 23.58, N 16.91

IV. Reactions of 1-Vinyltricyclo[4.1.0.0^{2,7}]heptanes 4 with 4-Phenyl-1,2,4-triazoline-3,5-dione (PTDA)

1. *PDTA and* **4a**: Compound **4a** (3.06 g, 25.5 mmol) and PTDA (4.46 g, 25.5 mmol, freshly sublimed) were allowed to react as described under III.1. for 4 h at r.t. Fsgc work-up using petroleum ether/ethyl acetate (1:1) as eluent afforded 2,4,6-triaza-4-phenyltetracyclo[8.4.0.0^{2,6}.0^{9,11}]tetradec-8-ene-3,5-dione **31a** (2.53 g, 34%) as the sole product in the form of a microcrystalline yellow powder of m.p. 121°C.

31a: IR (KBr): ṽ= 2939 cm^{-1}, 2854, 1710, 1700, 1496, 1424, 1420, 1150, 756, 732, 694. − ^{1}H NMR (400 MHz, $CDCl_3$): δ =

1.21 (m, 1 H), 1.48-1.61 (m, 3 H), 1.68 (m, 1 H), 1.86 (m, 1 H), 2.03 (m, 1 H) and 2.45 (m,1 H), (assignment of these 6 m uncertain), 4.38 and 4.59−4.70 (2 m, 1 H and 2 H, 1-H and 7-H_2), 6.04 (m, 1 H, 8-H), 7.35−7.59 (m, 5 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$, ^1J(CC) by INADEQUATE): δ = 13.45 [d, C-10, J(C1-C10) = 45.3 Hz, J(C9-C10) = 15.1 Hz, J(C10-C11) = 7.3 Hz], 19.55 [t, C-13, J(C12-C13) = 33.9 Hz, J(C13-C14) = 32.9 Hz], 19.90 [d, C-11, J(C9-C11) = 28.4 Hz, J(C11-C12) = 40.3 Hz], 21.09 (t, C-12), 24.46 [t, C-14, J(C1-C14) = 36.6 Hz], 50.92 [t, C-7, J(C7-C8) = 48.0 Hz], 55.39 (d, C-1), 110.90 [d, C-8, J(C8-C9) = 95.2 Hz], 124.99 [d, C-2′, -6′, J(C2′-C3′) = 56.7 Hz, J(C1′-C2′) not detected], 127.53 [d, C-4′, J(C3′-C4′) = 55.8 Hz], 128.60 (d, C-3′, C-5′), 131.38 (s, C-1′), 134.55 (s, C-9), 154.06, 154.09 (2 s, C-3, C-5). − MS (70 eV), *m/z* (%): 295 (100) [M$^+$], 119 (38), 105 (40), 91 (52). − $C_{17}H_{17}N_3O_2$ (295.3): calcd. C 69.14, H 5.80; found C 69.91, H 5.72. $C_{17}H_{17}N_3O_2$: calcd. 295.131; found 295.128 (HRMS).

2. *PDTA and* **4d**: Compound **4d** (1.76 g, 9.15 mmol) and PTDA (1.60 g, 9.14 mmol, freshly sublimed) were allowed to react as described under III.1. for 18 h at r.t. Fsgc work-up using petroleum ether/ethyl acetate/CH_2Cl_2 (5:1:2) as eluent afforded in the first fraction unreacted **4d** (420 mg, 24%). The second fraction contained a colorless oil, from which 2,4,6-triaza-4-phenyl-10-trimethylsilyltricyclo[7.5.0.0^{2,6}]tetradeca-8,10-diene-3,5-dione **32b** (230 mg, 6.8%) was isolated after crystallization from diethyl ether as colorless crystals of m.p. 158−161°C. The third fraction contained two solids, which were separated by fractional crystallization from petroleum ether/ethyl acetate, leading to 2,4,6-triaza-4-phenyl-1-trimethylsilyltetracyclo[7.5.0.0^{2,6}.0^{10,14}]tetradec-8-ene-3,5-dione **33b** (181 mg, 5.4%) as a crystalline solid of m.p. 197−199°C, and 2,4,6-triaza-4-phenyl-1-trimethylsilyltetracyclo[8.4.0.0^{2,6}.0^{9,11}]tetradec-8-ene-3,5-dione **31b** (68 mg, 2.0%) as crystalline solid of m.p. 94−95°C. Crystals of **31b** were submitted to an X-ray structural analysis.

32b: IR (KBr): ṽ= 2954 cm^{-1}, 2918, 1768, 1717, 1503, 1494, 1464, 1425, 1305, 1246, 1237, 1136, 877, 842, 770, 751, 724, 694. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.13 (s, 9 H, Me), 1.64 (1 H), 1.74−1.87 (2 H) and 2.15−2.38 (3 H) (3 m, assignment uncertain), 4.12 (dt, J = 2.3 Hz, J = 16.9 Hz, 1 H, 7-H), 4.35 (m, 1 H, 1-H), 4.42 (dd, J = 3.3 Hz, J = 16.9 Hz, 1 H, 7-H), 5.56 (t, J = 3.3 Hz, 1 H, 8-H), 6.28 (t, J = 5.8 Hz, 1 H, 11-H), 7.33−7.55 (m, 5 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.97 (q), 24.22 (t), 29.92 (t), 33.31 (t), 43.83 (t), 55.42 (d), 114.89 (d), 125.36 (d), 127.98 (d), 129.08 (d), 131.36 (s), 138.47 (s), 142.90 (s), 143.13 (d), 151.33 (s), 153.12 (s). − MS (70 eV), *m/z* (%): 367 (100) [M$^+$], 73 (34). − $C_{20}H_{25}N_3O_2Si$ (367.5): calcd. C 65.36, H 6.86, N 11.43; found C 65.56, H 6.90, N 11.33. $C_{20}H_{25}N_3O_2Si$: calcd. 367.172; found 367.171 (HRMS).

33b: IR (KBr): ṽ= 2938 cm^{-1}, 2899, 2862, 1763, 1694, 1503, 1494, 1452, 1423, 1293, 1250, 1129, 943, 841, 750, 694, 646, 511. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 9 H, Me), 1.29−1.46 and 1.77−2.06 (2 m, 2 H and 4 H, 11-, 12-, 13-H_2), 3.02 (m, 1 H, 10-H), 3.80 (dd, J = 9.6 Hz, J = 11.0 Hz, 1 H, 7-H), 3.97−4.03 (m, 2 H, 7-H, 14-H), 5.53 (narrow m, 1 H, 8-H), 7.30−7.46 (m, 5 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.03 (q), 20.94 (t), 24.76 (t), 25.11 (t), 46.71 (t), 51.78 (d), 56.76 (d), 59.61 (s), 119.13 (d), 125.49 (d, 2 C), 127.74 (d), 128.92 (d, 2 C), 132.06 (s), 135.30 (s), 149.26 (s), 149.99 (s). − MS (70 eV), *m/z* (%): 368 (20), 367 (70) [M$^+$], 206 (66), 73 (100). − $C_{20}H_{25}N_3O_2Si$ (367.5): calcd. C 65.36, H 6.86, N 11.43; found C 65.61, H 6.78, N 11.21. $C_{20}H_{25}N_3O_2Si$: calcd. 367.172; found 367.171 (HRMS).

31b: IR (KBr): ṽ= 2949 cm^{-1}, 1769, 1714, 1503, 1457, 1421, 1360, 1251, 1124, 1150, 840, 769, 748, 730, 690, 645. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 9 H, Me), 1.06, 1.48−1.68 and 1.84 (3 m, 1 H, 4 H, 1 H, 12-, 13-, 14-H_2), 2.28 (dd, J = 6.5 Hz, J = 0.9 Hz, 1 H, 11-H), 4.38 and 4.54 (AB system, J = 15.9 Hz, each line further split by small couplings, 7-H_2), 4.64 (dd, J = 8.5 Hz, J = 6.6 Hz, 1 H, 1-H), 6.02 (narrow m, 1 H, 8-H), 7.32−7.52 (m, 5 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.66 (q), 15.01 (s), 20.28 (t), 21.70 (t), 23.98 (d), 25.07 (t), 50.81 (t), 56.98 (d), 108.62 (d), 125.49 (d, 2 C), 128.03 (d), 129.05 (d, 2 C), 131.52 (s), 139.56 (s), 153.97 (s), 154.44 (s). − MS (70 eV), *m/z* (%): 367 (11) [M$^+$], 190 (48), 175 (89), 159 (43), 73 (100). − $C_{20}H_{25}N_3O_2Si$ (367.5): calcd. C 65.36, H 6.86, N 11.43; found C 65.22, H 6.66, N 11.58. $C_{20}H_{25}N_3O_2Si$: calcd. 367.172; found 367.170 (HRMS).

3. *PDTA and* **3a**: Compound **3a** (1.20 g, 8.94 mmol) and PTDA (1.56 g, 8.91 mmol, freshly sublimed) were allowed to react as described under III.1. for 14 h at r.t. Fsgc work-up using petroleum ether/ethyl acetate/CH_2Cl_2 (5:1:2) as eluent afforded 2,4,6-triaza-8-methyl-4-phenyltricyclo[7.5.0.0^{2,6}]tetradeca-8,10-diene-3,5-dione **32c** (283 mg, 10%) as the sole product. This was further purified by crystallization from petroleum ether/ethyl acetate leading to colorless crystals (125 mg, 4.5%) of m.p. 166−169°C.

32c: ṽ= 2938 cm^{-1}, 1717, 1714, 1502, 1457, 1415, 1294, 1265, 1133, 767, 753, 742, 716, 690, 644. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60−1.90 and 2.21−2.40 (2 m, 9 H, 12-, 13-, 14-H_2, Me), 3.95 and 4.25 (AB system, J = 16.8 Hz, 7-H_2), 4.71 (dd, J = 9.8 Hz, J = 6.4 Hz, 1 H, 1-H), 5.92 (m, 1 H, 11-H), 6.32 (d, J = 11.6 Hz, 1 H, 10-H), 7.33−7.48 (m, 5 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.08 (q), 23.83 (t), 27.84 (t), 30.35 (t), 47.87 (t), 55.47 (d), 123.33 (s), 125.28 (d, 2 C), 126.38 (d), 127.77 (s), 127.93 (d), 129.04 (d, 2 C), 131.34 (s), 133.59 (d), 151.16 (s), 153.12 (s). − MS (70 eV), *m/z* (%): 310 (21), 309 (100) [M$^+$], 119 (23), 91 (33). − $C_{18}H_{19}N_3O_2$ (309.4): calcd. C 69.88, H 6.19, N 13.58; found C 70.35, H 6.38, N 13.53. $C_{18}H_{19}N_3O_2$: calcd. 309.148; found 309.155 (HRMS).

4. *PDTA and* **3b**: Compound **3b** (1.10 g, 7.42 mmol) and PTDA (1.30 g, 7.42 mmol, freshly sublimed) were allowed to react as described under III.1. for 2 d at r.t. Fsgc work-up using petroleum ether/ethyl acetate (4:1) as eluent afforded in the first fraction 2,4,6-triaza-7,7-dimethyl-4-phenyltetracyclo[8.4.0.0^{2,6}.0^{9,11}]tetradec-8-ene-3,5-dione **31d** (241 mg, 10%) as colorless crystals of m.p. 137−143°C. From the second fraction, 2,4,6-triaza-7,7-dimethyl-4-phenyltricyclo[7.5.0.0.^{2,6}]tetradeca-8,10-diene-3,5-dione **32d** (70.0 mg, 2.9%) was isolated as colorless crystals of m.p. 105−109°C. The third fraction contained 1,2,5-triaza-6-(2-cyclohexenyl)-8,8-dimethyl-3-phenylbicyclo[3.3.0]oct-6-ene-2,4-dione **34** (125 mg, 5.2%) as a colorless solid of m.p. 152−153°C.

31d: ṽ= 2973 cm^{-1}, 2935, 2866, 1767, 1712, 1503, 1456, 1420, 1363, 1351, 1244, 1160, 1013, 773, 755, 740, 691, 646. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21−1.29, 1.46−1.81, 1.95−2.03, 2.18−2.26 (4 m, 1 H, 4 H, 1 H, 2 H, 10-, 11-H, 12-, 13-, 14-H_2 in unknown order), 1.44 and 1.87 (2 s, each 3 H, Me), 4.35 (m, 1 H, 1-H), 5.57 (t, J = 2.0 Hz, 1 H, 8-H), 7.32−7.46 (m, 5 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.07 (d), 15.58 (t), 12.52 (d), 21.03 (t), 22.03 (q), 28.38 (t), 28.95 (q), 61.28 (d), 70.86 (s), 123.95 (d), 125.66 (d, 2 C), 126.14 (s), 127.97 (d), 128.88 (d, 2 C), 131.26 (s), 157.05 (s), 157.70 (s). − MS (70 eV), *m/z* (%): 324 (22), 323 (100) [M$^+$], 308 (46), 119 (32). − $C_{19}H_{21}N_3O_2$ (323.4): calcd. C 70.57, H 6.55, N 12.99; found C 71.48, H 7.09, N 12.98. $C_{19}H_{21}N_3O_2$ calcd. 323.163; found 323.165 (HRMS).

32d: ṽ= 2936 cm^{-1}, 1766, 1707, 1705, 1502, 1457, 1417, 1283, 1143, 771, 740, 726, 689. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43, 1.75 (2 s, each 3 H, Me), 1.63−1.76, 1.90, 2.40, 2.30−2.44 (4 m, 2 H, 1 H, 1 H, 2 H, 12-, 13-, 14-H_2 in unknown order), 4.76

(dd, J = 10.0 Hz, J = 6.7 Hz, 1 H, 1-H), 5.42 (s, 1 H, 8-H), 5.87 (m, 1 H, 11-H), 6.10 (dd, J = 11.5 Hz, J = 2.5 Hz, 1 H, 10-H), 7.30−7.54 (m, 5 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.73 (q), 24.18 (t), 27.03 (q), 27.10 (t), 28.95 (t), 54.94 (d), 59.17 (s), 125.37 (d, 2 C), 127.88 (d), 128.96 (d, 2 C), 129.10 (d), 131.11 (d), 131.33 (s), 132.21 (s), 133.80 (d), 151.37 (s), 153.13 (s). − MS (70 eV), *m/z* (%): 324 (16), 323 (78) [M^+], 308 (100), 189 (19), 91 (18). − $C_{19}H_{21}N_3O_2$ (323.4): calcd. C 70.57, H 6.55, N 12.99; found C 70.59, H 6.69, N 13.13. $C_{19}H_{21}N_3O_2$: calcd. 323.163; found 323.163 (HRMS).

34: ṽ= 2929 cm^{-1}, 1762, 1714, 1503, 1494, 1457, 1398, 1364, 1295, 1129, 755, 743, 690, 637. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.64, 1.67 (2 s, each 3 H, Me), 1.65−1.82, 2.02−2.21 (2 m, each 3 H, 4′′-, 5′′-, 6′′-H_2 in unknown order), 3.62 (narrow m, 1 H, 1′′-H), 4.96 (d, J = 1.6 Hz, 1 H, 7-H), 5.69 (m, 1 H, 2′′-H), 5.90 (m, 1 H, 3′′-H), 7.32−7.54 (m, 5 H, arom. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.65 (t), 24.97 (t), 25.28 (q), 27.03 (q), 27.17 (t), 32.16 (d), 66.89 (s), 115.93 (d), 125.29 (d), 125.60 (d, 2 C), 127.88 (d), 128.94 (d, 2 C), 130.20 (d), 131.65 (s), 139.46 (s), 146.37 (s), 149.05 (s). − MS (70 eV), *m/z* (%): 324 (3), 323 (14) [M^+], 309 (18), 308 (100), 161 (10). − $C_{19}H_{21}N_3O_2$ (323.4): calcd. C 70.57, H 6.55, N 12.99; found C 70.36, H 6.50, N 13.10. $C_{19}H_{21}N_3O_2$ calcd. 323.163; found 323.165 (HRMS).

V. Reactions of 1-Vinyltricyclo[4.1.0.0^{2,7}]heptanes **4** *with Dimethyl Acetylenedicarboxylate (DMAD)*

1. *DMAD and* **4a**: Compound **4a** (3.60 g, 30.0 mmol) and DMAD (4.26 g, 30.0 mmol) were allowed to react in CH_2Cl_2 as described under III.1. for 4 d at r.t. Fsgc work-up using CH_2Cl_2 as eluent gave dimethyl *endo*-(*Z*)-1-(1-vinyltricyclo[3.2.0.0^{2,7}]hept-6-yl)ethene-1,2-dicarboxylate **37a** (1.06 g, 13%) as the sole product in the form of a colorless liquid. In a second experiment, reaction of **4a** (1.20 g, 9.98 mmol) and DMAD (1.42 g, 9.99 mmol) afforded 2.28 g (87%) of **37a** after 2 d in CH_2Cl_2 and the usual work-up. Reproducible yields of **37a** of 51% were obtained when the reaction of **4a** and DMAD was carried out in 1,4-dioxane for 4 d at r.t.

37a: UV (cyclohexane): λ_{max} (log ε) = 211 nm (4.283). − IR (film): ṽ= 2952 cm^{-1}, 1725, 1485, 1259, 1168, 989. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68−2.04 (m, 6 H, 2′-, 7′-H, 3′-, 4′-H_2), 2.90 (m, 1 H, 5′-H), 3.30 (m, 1 H, 6′-H), 3.73 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 5.01 (dd, J = 10.5 Hz, J = 1.7 Hz, 1 H, 2′′-H *cis* to 1′′-H), 5.05 (dd, J = 17.3 Hz, J = 1.7 Hz, 1 H, 2′′-H *trans* to 1′′-H), 5.83 (dd, J = 17.3 Hz, J = 10.5 Hz, 1 H, 1′′-H), 5.93 (d, J = 2.1 Hz, 1 H, 2-H). − ^{13}C NMR [100 MHz, $CDCl_3$, ^1J(CC) by INADEQUATE]: δ = 25.06 [t, C-3′, J(C2′-C3′) = 39.9 Hz, J(C3′-C4′) = 33.4 Hz], 25.29 [d, C-7′, J(C1′-C7′) = 5.6 Hz, J(C2′-C7′) = 15.8 Hz, J(C6′-C7′) = 38.0 Hz], 30.05 [t, C-4′, J(C4′-C5′) = 32.9 Hz], 32.33 [d, C-2′, J(C1′-C2′) = 15.8 Hz], 38.73 [d, C-6′, J(C1-C6′) = 40.8 Hz, J(C5′-C6′) = 27.8 Hz], 39.39 [s, C-1′, J(C1′-C5′) = 35.3 Hz, J(C1′-C1′′) not detected], 43.37 (d, C-5′), 51.83 (q), 52.23 (q), 112.06 [t, C-2′′, J(C1′′-C2′′) = 70.0 Hz], 121.39 [d, C-2, J(C1-C2) = 75.1 Hz, J(C2-CO) = 75.6 Hz], 135.90 (d, C-1′′), 150.99 [s, C-1, J(C1-CO) = 69.6 Hz], 165.52 (s), 168.57 (s). − MS (70 eV), *m/z* (%): 262 (3) [M^+], 202 (58), 174 (38), 171 (38), 169 (57), 143 (100), 142 (37), 141 (40), 128 (67), 115 (54), 111 (77), 105 (43), 91 (57), 59 (39). − $C_{15}H_{18}O_4$ (262.3): calcd. C 68.69, H 6.92; found C 68.10, H 6.84. $C_{15}H_{18}O_4$: calcd. 262.121; found 262.122 (HRMS).

2. *DMAD and* **4e**: Compound **4e** (2.00 g, 14.9 mmol) and DMAD (2.12 g, 14.9 mmol) were allowed to react in dimethoxyethane as described under III.1. for 4 h at 90°C, and thereafter for 10 d at r.t. Fsgc work-up using petroleum ether/ethyl acetate (7:1) as eluent afforded dimethyl *endo*-(*Z*)-1-(6-methyl-1-vinyltricyclo[3.2.0.0^{2,7}]hept-6-yl)ethene-1,2-dicarboxylate **37b** (410 mg), which was further purified by fsgc to give 130 mg (3.2%) of **37b** as a colorless liquid. From the second fraction, dimethyl (*Z*)-4-(7-methylenebicyclo[3.1.1]hept-6-ylidene]but-1-ene-1,2-dicarboxylate **43** (80 mg, 1.9%) was obtained as a colorless oil.

37b: UV (acetonitrile): λ_{max} (log ε) = 211 nm (4.244). − IR (film): ṽ= 2953 cm^{-1}, 2874, 1733, 1628, 1435, 1350, 1285, 1262, 1240, 1196, 1167, 1048, 1018, 988, 962, 885, 852, 833. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (s, 3 H, Me), 1.68−1.98 (m, 6 H, 2′-, 7′-H, 3′-, 4′-H_2), 2.43 (t, J = 3.2 Hz, NOE with 6′-Me, 1 H, 5′-H), 3.70 (s, 3 H, OMe), 3.78 (s, 3 H, OMe), 4.98 (dd, J = 10.5 Hz, J = 1.7 Hz, 1 H, 2′′-H *cis* to 1′′-H), 5.05 (dd, J = 17.3 Hz, J = 1.7 Hz, 1 H, 2′′-H *trans* to 1′′-H), 5.83 (s, 1 H, 2-H), 5.87 (dd, J = 17.3 Hz, J = 10.5 Hz, 1 H, 1′′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.45 (t), 27.27 (q), 29.98 (t), 31.98 (d), 34.93 (d), 39.57 (s), 42.99 (s), 50.86 (d), 51.74 (q), 52.00 (q), 111.76 (t), 120.13 (d), 137.16 (d), 155.08 (s), 165.52 (s), 168.13 (s). − MS (70 eV), *m/z* (%): 276 (9) [M^+], 216 (66), 185 (34), 184 (37), 183 (100), 170 (63), 157 (85), 156 (36), 142 (33), 129 (35). − $C_{16}H_{20}O_4$ (276.3): calcd. C 69.54, H 7.30; found C 68.30, H 7.07. $C_{16}H_{20}O_4$: calcd. 276.136; found 276.124 (HRMS).

43: IR (film): ṽ= 2949 cm^{-1}, 2862, 1724, 1642, 1437, 1262, 1273, 1225, 1203, 1176, 1110, 1092, 1020, 871, 787. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.56−1.69 (m, 2 H, 3′-H_2), 2.02−2.15 (m, 4 H, 2′-, 4′-H_2), 3.17 (m, 1 H, 1′-H), 3.44 (dd, J = 7.3 Hz, J = 13.3 Hz, 1 H, 3-H), 3.50 (m, 1 H, 5′-H), 3.58 (dd, J = 7.1 Hz, J = 13.3 Hz, 1 H, 3-H), 3.76 (s, 3 H, OMe), 3.78 (s, 3 H, OMe), 4.66 (s, 1 H, 1′′-H_{trans}), 4.68 (s, 1 H, 1′′-H_{cis}), 5.12 (t, J = 7.3 Hz, 1 H, 4-H), 6.70 (s, 1 H, 1-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.78 (t), 27.64 (t), 35.23 (t), 36.04 (t), 50.56 (d), 51.70 (q), 52.44 (d), 52.45 (q), 97.08 (t), 109.36 (d), 125.60 (d), 144.95 (s), 146.54 (s), 153.05 (s), 166.00 (s), 167.19 (s). − MS (70 eV), *m/z* (%): 276 (100) [M^+], 244 (62), 217 (40), 216 (75), 185 (55), 157 (96), 129 (54), 128 (44), 119 (38), 115 (40), 95 (54), 91 (70). − $C_{16}H_{20}O_4$ (276.3): calcd. C 69.54, H 7.30; found C 69.41, H 7.62. $C_{16}H_{20}O_4$: calcd. 276.136; found 276.122 (HRMS).

3. *DMAD and* **3b**: Compound **3b** (1.50 g, 10.1 mmol) and DMAD (1.44 g, 10.1 mmol) were allowed to react in CH_2Cl_2 as described under III.1. for 3 d at r.t. Fsgc work-up using petroleum ether/ethyl acetate (9:1) as eluent afforded in the first fraction dimethyl *endo*-(*Z*)-1-(2-methyl-1-propenyltricyclo[3.2.0.0^{2,7}]hept-6-yl)ethene-1,2-dicarboxylate **37c** (377 mg), which was further purified by fsgc (petroleum ether/ethyl acetate/CH_2Cl_2, 12:1:3) to give 70 mg (2.4%) of **37c** as a colorless liquid. From the second fraction, dimethyl 5-isopropenyltricyclo[4.4.0.0^{2,4}]dec-6-ene-3,4-dicarboxylate **47** (1.27 g) was obtained as a colorless oil, which was purified by a second fsgc (petroleum ether/ethyl acetate, 4:1) to give 980 mg (33%) of **47**.

37c: IR (film): ṽ= 2951 cm^{-1}, 2931, 2873, 1726, 1436, 1374, 1352, 1342, 1268, 1261, 1225, 1161, 1110, 1084, 1066, 1036. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (t, J = 4.5 Hz, 1 H, 7′-H), 1.68, 1.71 (2 d, J = 0.5 Hz each, 3 H each, Me), 1.69−2.03 (m, 5 H, 2′-H, 3′-, 4′-H_2), 2.76 (m, 1 H, 5′-H), 3.37 (m, 1 H, 6′-H), 3.72 (s, 3 H, OMe), 3.78 (s, 3 H, OMe), 5.32 (m, 1 H, 1′′-H), 5.92 (d, J = 2.0 Hz, 1 H, 2-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.75 (q), 23.53 (d), 25.13 (t), 25.90 (q), 30.41 (t), 31.18 (d), 35.33 (s), 39.12 (d), 47.55 (d), 51.77 (q), 52.18 (q), 121.11 (d), 121.13 (d), 134.92 (s), 151.57 (s), 165.56 (s), 168.78 (s). − MS (70 eV), *m/z* (%): 290 (19) [M^+], 230 (89), 215 (42), 202 (49), 187 (57), 171 (75), 170 (43), 169 (89), 155 (44), 143 (48), 142 (33), 141 (39), 133 (43), 129 (78), 128 (64), 117 (34), 115 (57), 105 (44), 91 (100), 79 (41),

Table 1. Crystal data of **6**, **8**, **24b**, **22c**, **25**, and **31b**

Compound	**6**	**8**	**24b**	**22c**	**25**	**31b**
formula	$C_{15}H_{14}N_4O$	$C_{15}H_{12}N_4$	$C_{15}H_{11}BrN_4$	$C_{18}H_{20}N_4Si$	$C_{18}H_{20}N_4Si$	$C_{20}H_{25}N_3O_2Si$
formula weight	266.30	248.29	327.19	320.47	320.47	367.52
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [pm]	982.9(1)	654.2(2)	1144.9(3)	1140.4(3)	1581.9(8)	925.2(2)
b [pm]	1040.5(2)	1109.2(2)	1011.0(2)	956.4(2)	980.4(3)	696.7(1)
c [pm]	1242.1(2)	1773.7(6)	1233.3(3)	1712.8(5)	1182.2(7)	3195.8(6)
β [deg]	91.25(9)	99.07(2)	98.369(7)	91.15(2)	91.50(3)	96.93(2)
V [nm^3]	1.2700	1.2710	1.4123	1.8677	1.8328	2.0449
Z	4	4	4	4	4	4
D [g/cm^3]	1.393	1.298	1.539	1.140	1.16	1.194
crystal size [mm]	0.2×0.3×0.6	0.33×0.47×0.53	0.27×0.53×0.53	0.20×0.40×0.53	0.13×0.40×0.53	0.46×0.30×0.64
temperature [K]	296	296	296	298	294	296
reflections collected	1860	2295	2068	3447	2387	3061
indp. reflections	1760	2220	1960	3289	2248	2856
obsd. reflections	1489; [$I>2\sigma(I)$]	1981; [$I>2\sigma(I)$]	1464; [$I>2\sigma(I)$]	2692; [$I>2\sigma(I)$]	1697; [$I>2\sigma(I)$]	2262; [$I>2\sigma(I)$]
scan range	4°<2Θ<46°	4°<2Θ<50°	4°<2Θ<46°	4°<2Θ<50°	4°<2Θ<44°	4°<2Θ<46°
number of parameters	182	172	181	211	211	238
R	0.0343	0.0981	0.0604	0.0514	0.0609	0.0598
wR2	0.0832	0.3349	0.1704	0.1780	0.1737	0.1763
residual e-density	0.205/	0.404/	0.711/	0.624/	0.242/	0.338
[e 10^6 pm^{-3}]	−0.131	−0.480	−0.894	−0.320	−0.316	−0.216

77 (61), 59 (50). − $C_{17}H_{22}O_4$ (290.4): calcd. C 70.32, H 7.64; found C 69.42, H 7.84. $C_{17}H_{22}O_4$: calcd. 290.152; found 290.154 (HRMS).

47: IR (film): $\tilde{\nu}$= 2950 cm^{-1}, 2932, 2858, 1737, 1439, 1410, 1374, 1353, 1289, 1271, 1254, 1211, 1199, 1155, 1124, 1064, 1044, 901. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10, 1.47 (2 m, 1 H each, 9-H_2), 1.76 (m, 1 H, 10-H), 1.79 (d, J = 0.9 Hz, 3 H, Me), 1.86 (d, J = 4.5 Hz, 1 H, 3-H), 1.90−2.05 (m, 3 H, 8-H_2, 10-H), 2.38 (t, J = 4.5 Hz, 1 H, 2-H), 2.77 (broad m, 1 H, 1-H), 3.66 (s, 3 H, OMe), 3.68 (s, 3 H, OMe), 3.79 (m, 1 H, 5-H), 4.91 and 4.98 (2 m, 1 H each, 2′H_2), 5.38 (m, 1 H, 7-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.70 (q), 21.58 (t), 24.58 (t), 26.11 (t), 26.15 (d), 32.26 (d), 39.67 (d), 39.90 (s), 51.88 (q), 51.93 (q), 54.36 (d), 115.16 (t), 122.55 (d), 137.75 (s), 142.07 (s), 170.63 (s), 170.67 (s). − MS (70 eV), *m/z* (%): 290 (30) [M$^+$], 258 (31), 231 (100), 199 (55), 171 (55). − $C_{17}H_{22}O_4$ (290.4): calcd. C 70.32, H 7.64; found C 70.06, H 7.83. − $C_{17}H_{22}O_4$: calcd. 290.152; found 290.153 (HRMS).

VI. Crystal Data

The crystal data of compounds **6**, **8**, **24b**, **22c**, **25**, and **31b** are given in Table 1[16].

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[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-407475, -407476, -407477, -407478, -407479, and -407480. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; e-mail: deposit@chemcrys.cam.ac.uk].

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