The Effect of High Pressure on the Diastereoselectivity of Intermolecular All-Carbon Diels–Alder Reactions

Lutz F. Tietze,*[a] Marielouise Henrich,[a] Anja Niklaus,[b] and Michael Buback*[b]

Abstract: The influence of high pressure on the diastereoselectivity of the intermolecular all-carbon Diels–Alder reaction of the phenylbutadienes **1a–c** with the dicyanoethylenes **2a–d** to give the cyclohexenes **3–8** is described. The differences in activation volume, $\Delta\Delta V^{\neq}$, for the two pathways leading to *cis* and *trans* diastereomers range from $-(0.7\pm0.8)$ to $-(6.4\pm0.6)$ cm^{3}mol^{-1}, indicating a pressure-induced increase of diastereoselectivity in favour of the *cis* adducts **3a–d**, **5a–d** and **7b–d**.

Keywords: activation volume · asymmetric synthesis · cycloadditions · diastereoselectivity · high pressure chemistry

Introduction

The Diels–Alder reaction is one of the most important in synthesis, since it provides an efficient route not only to carbocycles, but also to a multitude of heterocycles.[1] In many cases the cycloadditions can be accelerated markedly by applying high pressure[1a, 2] since both the intermolecular and intramolecular Diels–Alder reactions are associated with large negative volumes of activation, between -25 to -45 cm^{3}mol^{-1},[3, 4] and with large negative reaction volumes. In contrast, synthetically useful improvements of stereoselectivity under high pressure have been found only for a very few systems so far, for example for the intermolecular hetero-Diels–Alder reaction of enamino ketones with enol ethers to give dihydropyrans with a difference in activation volume of up to $\Delta\Delta V^{\neq} = -7.3$ cm^{3}mol^{-1}.[5, 6]

In this paper we present the first synthetically useful examples of a pressure-induced increase of diastereoselectivity for all-carbon Diels–Alder reactions. It is the aim of this work to show that the application of high pressure in organic transformations is not only useful for the acceleration of reactions for which $\Delta V^{\neq}$ is negative, but also for the improvement of diastereoselectivity. For this purpose, we have determined the $\Delta\Delta V^{\neq}$ value of the described cycloadditions in a laborious procedure; this allows a prediction of the selectivity over a wide range of pressures up to 10 kbar.

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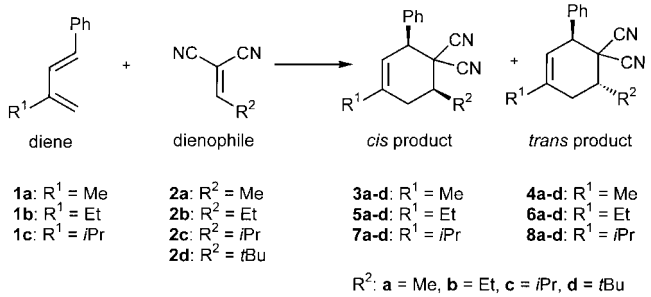
Results and Discussion

The phenylbutadienes **1a–c** and the dicyanoethylenes **2a–d** were allowed to react to yield the *cis* and *trans* cycloadducts **3a–d**, **5a–d**, **7a–d** and **4a–d**, **6a–d**, **8a–d**, respectively (Scheme 1). Assuming a pressure-dependent



Scheme 1. Diels–Alder reactions of **1a–c** and **2a–d**.

diastereoselectivity to be primarily due to differences in steric interaction of the two diastereomeric transition structures and not to a change in reaction mechanism,[2d] we expected an increase in $-\Delta\Delta V^{\neq}$ with increasing bulkiness of the substituents R^1 and R^2.

The dienes **1a–c** were easily prepared in a three-step sequence starting from *trans*-cinnamaldehyde **9** (Scheme 2). Alkylation of **9** with MeLi and with the Grignard reagents of

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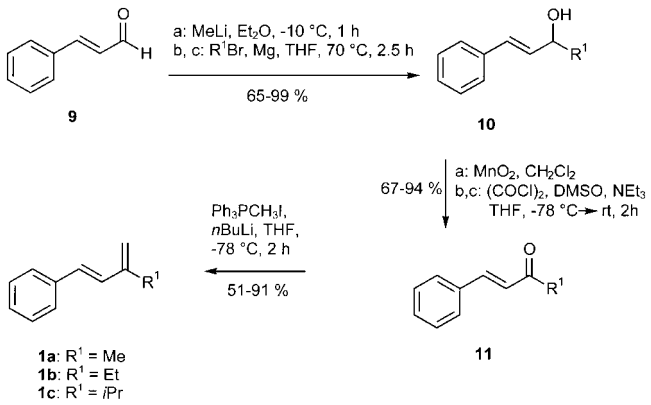


Scheme 2. Synthesis of the 1,3-butadienes **1a–c**.

bromoethane and 2-bromopropane, respectively, led to the alcohol **10**, which, after oxidation to the ketone **11**, gave the desired butadienes **1a–c** in good overall yields on Wittig reaction with methyltriphenylphosphonium iodide.

The cycloadditions of **1a–c** to **2a–d** were carried out in toluene at 120 °C for 12–48 h at ambient pressure to give the cyclohexenes **3–8** as a mixture of two diastereomers. Under these conditions, the reactions of the bulkier substrates to give the cycloadducts **5d/6d**, **7c/8c** and **7d/8d** gave only low yield. However, the yields could be easily improved by running the cycloadditions of **1b** and **2d**, of **1c** and **2c** and of **1c** and **2d** under high pressure; for example, at 10 kbar yields between 31 and 98 % were achieved.[7]

The diastereomers of **3–8** could partially be separated by column chromatography. The relative configuration of the diastereomers was deduced either from the $^1H-^1H$ NOSY spectra or from X-ray analysis. The ratio of the diastereomers was determined from the crude product mixture by GC, with the exception of the cycloadducts **7a** and **8a**, for which ^{13}C NMR spectra of the product mixture were analysed.

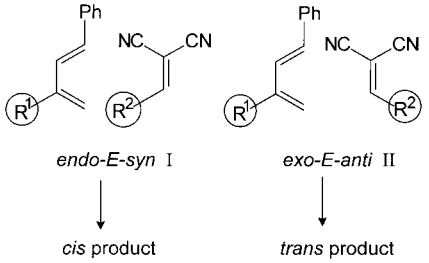
The obtained ratios of the *cis* to *trans* diastereomer of **3–8** at ambient pressure clearly depend on the steric demand of the substituents R^1 and R^2 (Table 1). With R^1 and R^2 being methyl or ethyl (entries 1–2, 5–6), and with $R^1 = i$Pr and R^2 = Me (entry 9) the formation of the *cis* adducts is favoured.

Table 1. Yields and diastereoselectivities of the Diels–Alder reactions of **1a–c** and **2a–d**.

Entry	Diene	Dienophile	Method[a]	Time [h]	Products	Yield [%]	Selectivity[b] *cis*/*trans*
1	**1a**	**2a**	IV	12	**3a/4a**	70	1.86:1
2	**1a**	**2b**	IV	12	**3b/4b**	80	1.56:1
3	**1a**	**2c**	IV	12	**3c/4c**	66	1.18:1
4	**1a**	**2d**	IV	48	**3d/4d**	90	1:5.56
5	**1b**	**2a**	IV	12	**5a/6a**	73	1.17:1
6	**1b**	**2b**	IV	12	**5b/6b**	95	1.13:1
7	**1b**	**2c**	IV	24	**5c/6c**	69	1:1.56
8	**1b**	**2d**	V	48	**5d/6d**	96	1:5.88
9	**1c**	**2a**	IV	12	**7a/8a**	54	≈2:1[c]
10	**1c**	**2b**	IV	24	**7b/8b**	98	1:1.89
11	**1c**	**2c**	V	36	**7c/8c**	31	1:3.33
12	**1c**	**2d**	V	24	**7d/8d**	70	< 1:99

[a] General procedure IV: reaction in toluene at 120 °C and ambient pressure; general procedure V: reaction in dichloromethane at 50 °C and 10 kbar. [b] Determined by GC. [c] Determined by ^{13}C NMR.

With increasing bulkiness of the substituents on either the diene or dienophile ($R^1 = i$Pr or/and $R^2 = i$Pr, *t*Bu; entries 3–4, 7–8, 11–12), the amount of the *cis* product decreases significantly. Thus, the cycloaddition of the substrates **1c** and **2d** leads exclusively to the *trans* product **8d** (entry 12). These results are in agreement with the expectation that the *cis* diastereomers are formed via an *endo-E-syn* transition structure **I**, which is energetically favoured unless the substituents R^1 and R^2 are too bulky (Scheme 3). Under conditions of a strong steric interaction the *exo-E-anti* transition structure **II** is preferred.



Scheme 3. Transition structures for the Diels–Alder reactions of **1** and **2**.

The cycloadditions of **1a–c** and **2a–d** under high pressure were carried out in dichloromethane with a large excess of the diene (30 equiv). The experimental set-up, including the high-pressure cell, has already been described.[5g, 8]

It should be noted that 1) the Diels–Alder reactions of **1a–c** with **2a–d** are kinetically controlled and 2) isomerization of the double bond in the butadienes **1a–c** and in the products does not take place under reaction conditions. For the cycloadditions two effects have to be discussed, namely steric and electronic influences on the Diels–Alder reaction. The cycloaddition belongs to the normal type, for which the overlap of the LUMO of the dienophile and the HOMO of the diene is dominating. Whereas steric hindrance obviously increases for the diene and the dienophile when going from methyl to ethyl, isopropyl and *tert*-butyl substituents, the electronic effects are different for the diene and the dienophile. As a consequence of the interaction between the $+I$ effect of the alkyl substituents with the relevant molecular orbitals, the reaction rate decreases from dienophile **2a** to dienophile **2d** for the same diene and increases from diene **1a** to diene **1c** for the same dienophile. Furthermore, the electronic effect on the reaction rate should be more obvious for the formation of the *trans* product, whereas the formation of the *cis* product should be influenced by steric interaction to a higher extent.

The differences in activation volume, $\Delta\Delta V^{\neq} = \Delta V^{\neq}_{cis} - \Delta V^{\neq}_{trans}$, were derived from the pressure dependence of the product ratios c_{cis}/c_{trans} (Table 2).

Figures 1–3 show plots of $\ln(c_{cis}/c_{trans})$ against the El'yanov parameter Ψ[9] for the cycloaddition reactions of dienes **1a–c** with dienophiles **2a–d** in dichloromethane solution at pressures from 250 to 3000 bar.

As can be seen from Table 2, $\Delta\Delta V^{\neq}$ is negative for the entire set of cycloadditions. According to the well-established rule that high pressure favours sterically hindered processes, this

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Table 2. Differences in activation volume $\Delta\Delta V^{\neq} = \Delta V^{\neq}_{cis} - \Delta V^{\neq}_{trans}$ determined from product ratios of the Diels–Alder reactions of phenylbutadienes **1a–c** with dicyanoethylenes **2a–d** in dichloromethane solution.

Reactants	T [°C][a]	$\Delta\Delta V^{\neq}$ [cm^{3}mol^{-1}]
1a + **2a**	30	$-(1.9\pm0.1)$
1a + **2b**	30	$-(1.9\pm0.2)$
1a + **2c**	70	$-(4.3\pm0.3)$
1a + **2d**	90	$-(6.4\pm0.6)$
1b + **2a**	30	$-(1.3\pm0.1)$
1b + **2b**	30	$-(1.6\pm0.1)$
1b + **2c**	50	$-(2.9\pm0.3)$
1b + **2d**	70	$-(3.9\pm0.3)$
1c + **2a**[a]	30	–
1c + **2b**	30	$-(0.7\pm0.8)$
1c + **2c**	70	$-(1.9\pm0.4)$
1c + **2d**[b]	70	–

[a] The *cis*/*trans* product ratio could not be determined. [b] The *cis* adduct could not be detected.

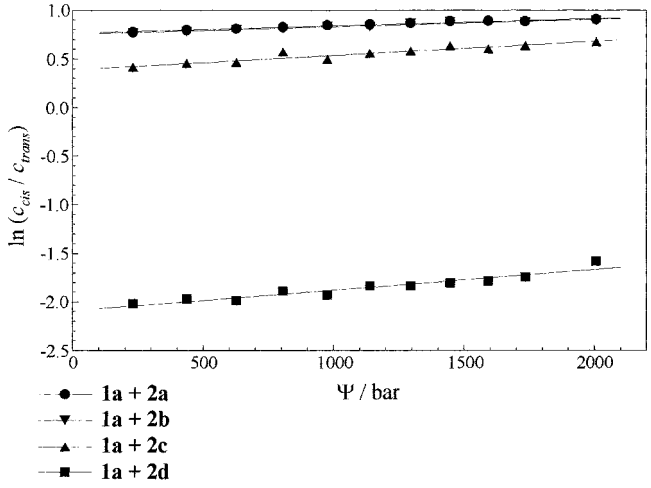

Figure 1. Dependence of the product ratio c_{cis}/c_{trans} on the El'yanov parameter Ψ for the cycloaddition reactions of phenylbutadiene **1a** with the dicyanoethylenes **2a–d** at 30 °C.

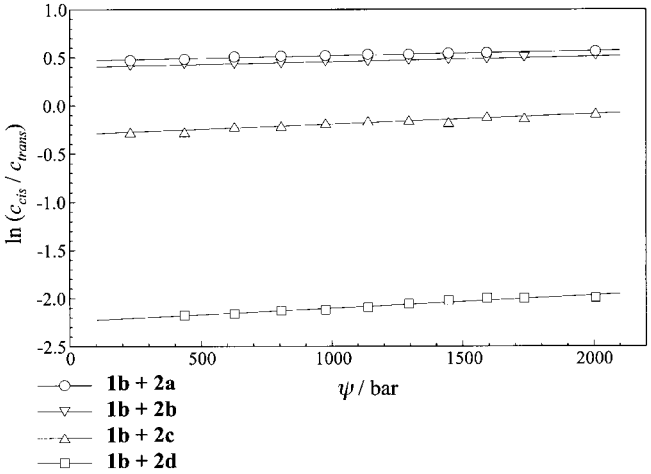

Figure 2. Dependence of the product ratio c_{cis}/c_{trans} on the El'yanov parameter Ψ for the cycloaddition reactions of phenylbutadiene **1b** with the dicyanoethylenes **2a–d** at 30 °C.

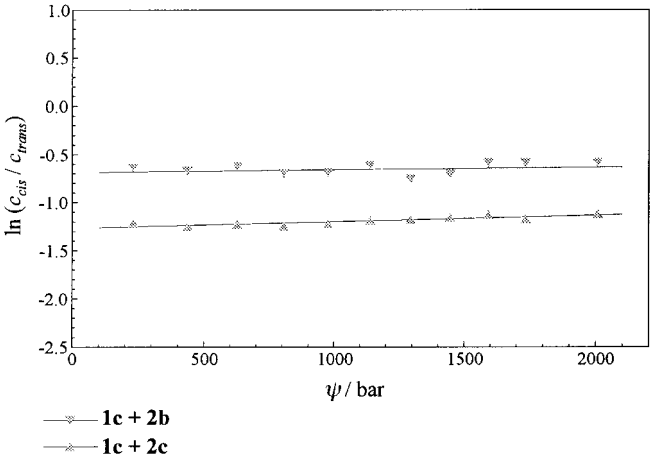

Figure 3. Dependence of the product ratio c_{cis}/c_{trans} on the El'yanov parameter Ψ for the cycloaddition reactions of phenylbutadiene **1c** with the dicyanoethylenes **2b** and **2c** at 30 °C.

indicates that steric hindrance is greater for cycloadditions via an *endo* transition structure than for the reaction via an *exo* transition structure. A corresponding pressure-induced selectivity in favour of the *cis* adduct is what one would expect.

Fully consistent with this argument is the clear increase of $-\Delta\Delta V^{\neq}$ with steric bulkiness of the substituent at the dienophile. Thus, for the cycloaddition of **1a** (R^1 = Me) with **2a** (R^2 = Me), **2b** (R^2 = Et), **2c** (R^2 = *i*Pr), and **2d** (R^2 = *t*Bu) a significant increase in $-\Delta\Delta V^{\neq}$, from (1.9 ± 0.1) to (6.4 ± 0.6) cm^{3}mol^{-1}, is found. The same trend is observed within the series of cycloadditions of **1b** (R^1 = Et) with dienophiles **2a–d**, where $-\Delta\Delta V^{\neq}$ continuously increases from (1.3 ± 0.1) to (3.9 ± 0.3) cm^{3}mol^{-1}. For the cycloadditions of **1c** (R^1 = *i*Pr), too, an enhancement of $-\Delta\Delta V^{\neq}$ is found with increasing steric bulkiness, (0.7 ± 0.8) cm^{3}mol^{-1} for **1c** + **2b** and (1.9 ± 0.4) cm^{3}mol^{-1} for **1c** + **2c**.

However, an important point to note from the data in Table 2 is that the attempts to increase steric hindrance by adding bulky substituents on both diene and dienophile do not yield $-\Delta\Delta V^{\neq}$ values that exceed, for example, the number found for the **1a** + **2d** cycloaddition. For a particular dienophile, **2b** or **2c**, variation of the diene from **1a** to **1c** leads to a decrease in $-\Delta\Delta V^{\neq}$ although the steric demand of the transition structures would be expected to increase. The values of $-\Delta\Delta V^{\neq}$ are (1.9 ± 0.2), (1.6 ± 0.1) and (0.7 ± 0.8) cm^{3}mol^{-1} for the respective cycloadditions of **2b**. For the cycloadditions of **1a** + **2c**, **1b** + **2c** and **1c** + **2c** they are (4.3 ± 0.3), (2.9 ± 0.3) and (1.9 ± 0.4) cm^{3}mol^{-1}. These data indicate that sterically overloading the transition structure may lead to a situation where the geometries with favourable interactions characteristic of *endo* transition structures cannot be organized. We argue that this is the reason that a *cis* product does not result from the cycloaddition of **1c** + **2d.**

It must be assumed that the expression *endo* transition structure and perhaps also *exo* transition structure does not refer to well-defined species, such as a set of species with identical geometry at the reactive site. The activation volume data indicate that, depending on the type of substitution at the diene and the dienophile, the overlap of the dominating orbitals varies, in particular in the *endo* transition structure.

The effect of an interchange of the substituents R^1 and R^2 at the diene and dienophile, as indicated by the differences of the activation volumes, for example, for the reactions of **1c** + **2b** ($\Delta\Delta V^{\neq} = -(0.7 \pm 0.8)$ cm^{3}mol^{-1}) and of **1b** + **2c** ($\Delta\Delta V^{\neq} = -(2.9 \pm 0.3)$ cm^{3}mol^{-1}), demonstrates that the endo transition structure of the cycloaddition of **1c** + **2b** having the bulky *i*Pr substituent as R^1 at the diene is of "lower quality". It is thus only within a series in which the diene remains unchanged that the numerical size of the $\Delta\Delta V^{\neq}$ value, which corresponds to a pressure-induced enhancement of diastereoselectivity, increases towards larger steric hindrance. This is seen in the series in which the substituent R^2 at the dienophile increases in steric size. The measured differences in activation volume are fairly large, $\Delta\Delta V^{\neq}$ up to $-(6.4 \pm 0.7)$ cm^{3}mol^{-1}, which may allow for applications in selective synthesis. It should be noted that the results of our previous investigations on hetero Diels–Alder reactions[5] also apply to the all-carbon Diels–Alder reactions of the present study.[10]

Conclusion

The Diels–Alder reactions of the phenylbutadienes **1a–c** and the dicyanoethylenes **2a–d** with substituents R^1 and R^2 of different size clearly demonstrate that under high pressure an *endo* transition structure to give the *cis* products is increasingly stabilized with increasing bulkiness of R^2 at the dienophile. Thus, for the cycloaddition of **1a** (R^1 = Me) with **2a** (R^2 = Me), **2b** (R^2 = Et), **2c** (R^2 = *i*Pr), and **2d** (R^2 = *t*Bu) a significant enlargement in $-\Delta\Delta V^{\neq}$, from (1.9 ± 0.1) to (6.4 ± 0.6) cm^{3}mol^{-1}, in favour of the *cis* adducts is found. However, this effect is limited by steric overload, which can prevent the formation of a proper *endo* transition structure. Thus, increasing the bulkiness of R^1 at the diene results in a decrease of $-\Delta\Delta V^{\neq}$; indeed, for the cycloadditions of **2c** (R^2 = *i*Pr) with **1a** (R^1 = Me), **1b** (R^1 = Et) and **1c** (R^1 = *i*Pr) $-\Delta\Delta V^{\neq}$ is found to be (4.3 ± 0.3), (2.9 ± 0.3), and (1.9 ± 0.4) cm^3/mol, respectively. Thus, we have shown for the first time that a steric overload phenomena in pressure dependent diastereoselectivity exists. We are confident that the observed effects are not associated with a change in the reaction mechanism where the *exo* adduct is formed by a concerted and the *endo* adduct by a two-step pathway. That such a change in mechanism is possible has been demonstrated by Klärner[2d, 11] for the dimerisation of 1,3-cyclohexadiene.

Experimental Section

General: The high-pressure cells and details of the experimental set-up and procedures have already been described.[5g, 8] The experimental pressures were determined to better than ±10 bar. The uncertainty in temperature was below ±0.5 °C. GC: Varian Star 3400 CX with a Merck–Hitachi Integrator D-2000. Column SGE BPX-5, 0.22 mm × 30 m. ^{1}H NMR and ^{13}C NMR: Varian XL-200, Bruker AMX-300, Varian XL-500; multiplicities were determined with APT pulse sequence. MS: Varian MAT 311A; high resolution: Varian MAT 731. IR: Bruker IFS 25. UV: Perkin Elmer Lambda 9. Elemental analyses were carried out in the analytical laboratory of the university. All solvents were distilled prior to use. Reagents and materials were obtained from commercial suppliers and were used without further purification. All reactions were carried out under argon pressure and monitored by TLC (Macherey–Nagel, Polygram SIL G/UV$_{254}$). Products were isolated by column chromatography on silica gel (Silica gel 60, particle size 0.04–0.063 mm, Merck).

3-Hydroxy-1-phenyl-1-butene (**10a**): A solution of methyl lithium in diethyl ether (1.6 M, 39.7 mmol, 24.8 mL) was added to a solution of cinnamaldehyde (**9**, 5.00 g, 37.8 mmol) in 50 mL THF at −10 °C. After stirring of the mixture for 1 h at RT, aqueous saturated ammonium chloride solution (50 mL) was added and the organic phase was separated. The aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined organic phases were washed with brine, dried with $MgSO_4$, filtered and evaporated in vacuo. Distillation of the residue afforded 5.41 g of the alcohol **16a** (97 %) as a colourless oil. R_f = 0.22 (petroleum ether/ethyl acetate 6:1); b.p. 80 °C (0.5 mbar); UV (CH_3CN): λ_{max} (lg ε) = 204 nm (4.193), 251 (4.081); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.21 (d, J = 6.0 Hz, 3 H, 4-H), 1.55 (s, 1 H, OH), 4.42 (quint, J = 6.0 Hz, 1 H, 3-H), 6.19 (dd, J = 15.8, 6.3 Hz, 1 H, 2-H), 6.48 (d, J = 15.8 Hz, 1 H, 1-H), 7.20–7.41 (m, 5 H, Ph-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 23.39 (C-4), 68.89 (C-3), 126.4, 127.6, 128.5, 129.3, 133.5 (Ph-C, C-1, C-2), 136.6 (Ph-C$_i$); MS (70 eV): m/z (%) = 43 (52) [$C_3H_7^+$], 77 (23) [$C_6H_5^+$], 91 (44) [$C_7H_7^+$], 105 (100) [$M^+ - C_3H_7$], 115 (22) [$C_9H_7^+$], 133 (26) [$C_9H_8OH^+$], 148 (62) [M^+]; $C_{10}H_{12}O$ (148.2): calcd 148.0888, found 148.0888 (HRMS).

General procedure I. Grignard reaction of 9: A 2.0 M solution of the alkyl magnesium bromide (100 mmol) in THF was added dropwise to a solution of cinnamaldehyde (**9**, 100 mmol) in 15 mL THF at 0 °C. The reaction mixture was heated to 70 °C for 2.5 h and then cooled to RT. The mixture was poured into an identical volume of ice-water and hydrolysed by addition of 6 N HCL (until pH reached 7). The aqueous phase was extracted with diethyl ether (3 × 50 mL), and the combined organic extracts were washed with aqueous saturated sodium bicarbonate solution and brine. The resulting solution was dried with Na_2SO_4, the solvents were evaporated and the crude product purified by distillation.

3-Hydroxy-1-phenyl-1-pentene (**10b**): Grignard reaction of **9** (10.0 g, 75.7 mmol) and ethyl bromide (8.20 g, 75.7 mmol) according to General Procedure I gave 12.3 g of the alcohol **10b** (quant). R_f = 0.29 (petroleum ether/ethyl acetate 5:1); IR (film): = 3360 cm^{-1} (OH), 966, 694 (monosubstituted aromatic); UV (CH_3CN): λ_{max} (lg ε) = 191 nm (4071), 204 (4110), 252 (3980); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.2 Hz, 3 H, 5-H), 1.70 (s, 1 H, OH), 1.69 (quint, J = 7.2 Hz, 2 H, 4-H), 4.21 (q, J = 7.2 Hz, 1 H, 3-H), 6.20 (dd, J = 16.0, 7.2 Hz, 1 H, 2-H), 6.60 (d, J = 16.0 Hz, 1 H, 1-H), 7.20–7.41 (m, 5 H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 9.75 (C-5), 30.19 (C-4), 74.35 (C-3), 126.4, 127.5, 128.5, 130.3, 132.2 (Ph C, C-1, C-2), 136.7 (Ph C$_i$); MS (70 eV): m/z (%) = 77 (65) [$C_6H_5^+$], 91 (42) [$C_7H_7^+$], 115 (50) [$C_9H_7^+$], 133 (100) [$C_9H_8OH^+$], 162 (30) [M^+]; $C_{11}H_{14}O$ (162.2), calcd C 81.44, H 8.70; found C 81.62, H 8.75.

3-Hydroxy-4-methyl-1-phenyl-1-pentene (**10c**): Grignard reaction of **9** and 2-bromopropane (12.6 mL, 100 mmol) with isopropylmagnesium bromide (50 mL of a 2.0 M solution in THF) according to General Procedure I gave 11.5 g of the alcohol **10c** (65 %). R_f = 0.35 (petroleum ether/ethyl acetate 4:1); b.p. 70 °C (0.2 mbar); IR (film): = 3404 cm^{-1} (OH), 968, 696 (monosubstituted aromatic); UV (CH_3CN): λ_{max} (lg ε) = 192 nm (4.124), 204 (3.976); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92, 0.99 (2d, J = 7.5 Hz, 6 H, 2 × CH_3), 1.62 (s, 1 H, OH), 1.82 (hept, J = 7.5 Hz, 2 H, 4-H), 4.10 (t, J = 7.2 Hz, 1 H, 3-H), 6.21 (dd, J = 16.0, 7.5 Hz, 1 H, 2-H), 6.54 (d, J = 16.0 Hz, 1 H, 1-H), 7.21–7.42 (m, 5 H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 37.92, 35.94 (2 × CH_3), 78.11 (C-3), 126.4, 127.6, 128.5, 130.8, 131.1 (Ph C, C-1, C-2), 136.8 (Ph C$_i$); MS (70 eV): m/z (%) = 43 (4) [$C_3H_7^+$], 77 (12) [$C_6H_5^+$], 91 (8) [$C_7H_7^+$], 115 (19) [$C_9H_7^+$], 133 (100) [$C_9H_8OH^+$], 176 (12) [M^+]; $C_{12}H_{16}O$ (176.3), calcd 176.1201, found 176.1201 (HRMS).

1-Phenylbut-1-ene-3-one (**11a**): To a solution of alcohol **10a** (4.90 g, 33.3 mmol) in 10 mL dichloromethane was added MnO_2 (28.9 g, 333 mmol, 10 equiv). After stirring for 12 h at RT the mixture was filtered, the solvent evaporated, and the crude product (4.21 g, 29.0 mmol, 87 %) used in the olefination without further purification. R_f = 0.37 (petroleum ether/ethyl acetate 6:1); b.p. 92 °C (2.5 mbar); IR (film): = 3004 cm^{-1} (C–H), 1610 (C=O), 976, 692 (monosubstituted aromatic); UV (CH_3CN): λ_{max} (lg ε) = 282 nm (4.167); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 6.72 (d, J = 16.0 Hz, 1 H, 2-H), 7.36–7.60 (m, 5 H, Ph H), 7.44 (d, J = 16.0 Hz, 1 H, 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 27.49 (C-1), 127.1, 128.9, 130.5 (Ph C, C-2), 134.4 (Ph C$_i$), 143.4 (C-1), 198.0 (C=O); MS (70 eV): m/z (%) = 77 (31) [$C_6H_5^+$], 103 (69) [$C_8H_7^+$], 131 (100) [$M^+ - C_3H_7$], 146 (12) [M^+]; $C_{10}H_{10}O$ (146.2): calcd C 82.16, H 6.25; found C 82.00, H 6.96.

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General procedure II. Swern oxidation of 10: A cooled solution of DMSO (4.5 M, 3.2 equiv) in dry dichloromethane was added to a 0.5 M solution of oxalyl chloride (1.6 equiv) in dry dichloromethane at a temperature below −78 °C. After stirring for 10 min, a solution of the alcohols **10** (1.0 equiv) in dichloromethane (4.0 mL) was added dropwise over 30 min. After continued stirring for 2 h at −78 °C, triethylamine (6.4 equiv) was added. The resulting mixture was stirred for another 5 min, then slowly warmed to 0 °C and poured onto an identical volume of ice-water. After separation of the organic layer, the aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phases were washed with water and aqueous saturated sodium chloride solution, and dried with Na_2SO_4. After filtration, the solvent was removed in vacuo to afford the crude ketone, which was purified by distillation.

1-Phenylpent-1-ene-3-one (**11b**): Reaction of **10b** (6.00 g, 37.0 mmol) with oxalyl chloride (7.50 g, 59.2 mmol, 1.6 equiv), DMSO (9.25 g, 118 mmol, 3.2 equiv) and triethylamine (24.0 g, 237 mmol, 6.4 equiv) according to General Procedure II gave 3.97 g of the ketone **11b** (67 %). $R_f = 0.24$ (petroleum ether/ethyl acetate 10:1); b.p. 80 °C (0.6 mbar); IR (film): = 1666 cm^{-1} (C=O), 980, 692 (monosubstituted aromatic); UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 282 nm (4.031); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.19$ (t, $J = 8.0$ Hz, 3H, CH_3), 2.70 (q, $J = 8.0$ Hz, 2H, 4-H), 6.72 (d, $J = 16.0$ Hz, 1H, 2-H), 7.33–7.53 (m, 5H, Ph H), 7.54 (d, $J = 16.0$ Hz, 1H, 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 8.14$ (CH_3), 33.94 (C-4), 125.9, 128.1, 128.5, 128.8, 130.2 (Ph C, C-2), 134.5 (Ph C_i), 142.1 (C-1), 200.7 (C=O); MS (70 eV): *m*/*z* (%) = 103 (100) [$C_8H_7^+$], 131 (80) [$M^+ - C_3H_7$], 160 (17) [M^+]; $C_{11}H_{12}O$ (160.2): calcd 160.0888, found 160.0888 (HRMS).

4-Methyl-1-phenylpent-1-ene-3-one (**11c**): Treatment of **10c** (5.00 g, 28.4 mmol) according to General Procedure II gave 4.65 g of the ketone **11c** (94 %) as a pale yellow oil. $R_f = 0.29$ (petroleum ether/ethyl acetate 50:1); b.p. 73 °C (0.5 mbar); IR (film): = 2970 cm^{-1} (C–H), 1612 (C=O), 984, 686 (monosubstituted aromatic); UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 285 nm (4.089); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.20$ (d, $J = 7.2$ Hz, 6H, 2 × CH_3), 2.95 (hept, 1H, 4-H), 6.82 (d, $J = 16.0$ Hz, 1H, 2-H), 7.20–7.41 (m, 5H, Ph H), 7.62 (d, $J = 16.0$ Hz, 1H, 1-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.50$ (2 × CH_3), 39.29 (C-4), 124.4, 128.2, 128.9 (Ph C, C-2), 134.7 (Ph C_i), 142.4 (C-1), 203.8 (C=O); MS (70 eV): *m*/*z* (%) = 77 (34) [$C_6H_5^+$], 103 (46) [$C_8H_7^+$], 131 (100) [$M^+ - C_3H_7$], 174 (12) [M^+]; $C_{12}H_{14}O$ (174.2): calcd 174.1044, found 174.1044 (HRMS).

General procedure III. Wittig reaction of 11: A 0.5 M suspension of methyl triphenylphosphonium iodide (7.18 mmol, 1.0 equiv) in THF was added to 2.4 M *n*BuLi in hexane (7.90 mmol, 1.1 equiv) at −78 °C and stirred for 30 min at 0 °C and for a further 30 min at RT. Subsequently, a 0.5 M solution of ketone **11** (5.74 mmol, 0.8 equiv) in 10 mL THF was added at −78 °C, the mixture was stirred for 15 min at −78 °C and then allowed to warm to RT. The reaction mixture was stirred until the reaction was complete (TLC) and then poured onto an identical volume of ice-water. Pentane (50 mL) and water (10 mL) were added, and the aqueous phase was extracted twice with pentane. The combined organic phases were washed with water and aqueous saturated sodium potassium tartrate solution, dried with $MgSO_4$, filtered and evaporated in vacuo. The residue was distilled to give the butadienes **1a–c**.

3-Methyl-1-phenylbuta-1,3-diene (**1a**): According to General Procedure III, ketone **11a** (4.00 g, 27.6 mmol, 0.8 equiv) was transformed into the butadiene **1a** (2.01 g, 14.1 mmol, 51 %) by means of methyl triphenylphosphonium iodide (13.9 g, 34.5 mmol, 1.0 equiv); b.p. 74 °C (6.5 mbar); IR (film): = 2982, 2934 cm^{-1} (C–H), 748, 694 (monosubstituted aromatic), 962 (RHC=CHR); UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 281 nm (4.155); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.98$ (s, 3H, CH_3), 5.07, 5.12 (2s, 2H, 4-H), 6.52 (d, $J = 15.0$ Hz, 1H, 2-H), 6.89 (d, $J = 15.0$ Hz, 1H, 1-H), 7.20–7.43 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.58$ (CH_3), 117.3 (C-4), 126.4 (Ph C_o), 127.4, 128.6 (Ph C, C-2), 131.6 (C-1), 137.3 (Ph C_i), 142.0 (C-3); MS (70 eV): *m*/*z* (%) = 115 (11) [$C_9H_7^+$], 129 (100) [$M^+ - C_3H_7$], 144 (44) [M^+]; $C_{11}H_{12}$ (144.2): calcd 144.0939, found 144.0939 (HRMS).

3-Ethyl-1-phenylbuta-1,3-diene (**1b**): Ketone **11b** (3.85 g, 24.0 mmol, 0.80 equiv) was transformed into the butadiene **1b** (2.16 g, 13.7 mmol, 57 %) according to General Procedure III by means of methyl triphenylphosphonium iodide (12.1 g, 30.0 mmol, 1.00 equiv). B.p. 80 °C (4 mbar); IR (film): = 2968, 2936 cm^{-1} (C–H), 754, 694 (monosubstituted aromatic), 962 (RHC=CHR); UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 282 nm (4.217); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.18$ (t, $J = 7.2$ Hz, 3H, CH_3), 2.36 (q, $J = 7.2$ Hz, 2H, 1′-H), 5.08, 5.14 (2d, $J = 1.5$ Hz, 2H, 4-H), 6.59 (d, $J = 16.0$ Hz, 1H, 2-H), 6.83 (d, $J = 16.0$ Hz, 1H, 1-H), 7.18–7.50 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 12.75$ (CH_3), 24.71 (C-1′), 115.1 (C-4), 126.6 (Ph C_o), 127.3, 127.7, 128.5 (Ph C, C-2), 131.1 (C-1), 137.4 (Ph C_i), 147.6 (C-3); MS (70 eV): *m*/*z* (%) = 51 (23) [$C_4H_3^+$], 77 (38) [$C_6H_5^+$], 115 (62) [$C_9H_7^+$], 129 (100) [$C_{10}H_9^+$], 143 (30) [$M^+ - C_{11}H_{11}$], 158 (82) [M^+]; $C_{12}H_{15}$ (159.3): calcd C 91.08, H 8.92; found C 91.20, H 8.93.

1-Phenyl-3-isopropylbuta-1,3-diene (**1c**): Ketone **11c** (1.00 g, 5.74 mmol, 0.80 equiv) was transformed into the butadiene **1c** (0.99 g, 5.22 mmol, 91 %) according to General Procedure III by means of methyl triphenylphosphonium iodide (2.90 g, 7.18 mmol, 1.0 equiv). B.p. 60 °C (2 mbar); IR (film): = 2964 cm^{-1} (C–H), 754, 692 (monosubstituted aromate), 962 (RHC=CHR); UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 282 nm (4.116); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.15$ (d, $J = 6.4$ Hz, 6H, 2 × CH_3), 2.80 (hept, J = 6.4 Hz, 1H, C-1′), 5.05, 5.15 (2s, 2H, 4-H), 6.65 (d, $J = 15.0$ Hz, 1H, 2-H), 6.78 (d, $J = 15.0$ Hz, 1H, 1-H), 7.15–7.50 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 22.34$ (2 × CH_3), 29.25 (C-1′), 112.8 (C-4), 126.4 (Ph C_o), 127.3, 127.4, 128.5 (Ph C, C-2), 130.9 (C-1), 137.4 (Ph C_i), 152.6 (C-3); MS (70 eV): *m*/*z* (%) = 115 (6) [$C_9H_7^+$], 129 (100) [$M^+ - C_3H_7$], 172 (20) [M^+]; $C_{13}H_{16}$ (172.3): calcd 172.1252, found 172.1252 (HRMS).

General procedure IV. Diels–Alder reaction under ambient pressure: A solution of the butadiene **1a**, **1b** or **1c** (0.58 mmol) and the dienophile **2a**, **2b**, **2c** or **2d** (0.58 mmol) in 5 mL of toluene was heated at 120 °C for 12–48 h in a pressure flask. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel (petroleum ether/diethyl ether 20:1).

General procedure V. Diels–Alder reaction under high pressure: A solution of diene **1b** or **1c** (0.58 mmol) and dienophile **2c** or **2d** (0.58 mmol) in dichloromethane (2.5 mL) was filled by syringe into a teflon tube. The tube was sealed and placed in a high-pressure cell[7] at 50 °C, 10 kbar for 24–48 h. Afterwards, the solvent was evaporated and the residue purified by column chromatography on silica gel (petroleum ether/diethyl ether 20:1).

1,1-Dicyano-4,6-dimethyl-2-phenylcyclohex-3-ene (**3/4a**): Diene **1a** (200 mg, 1.38 mmol) and dienophile **2a** (128 mg, 1.38 mmol) were cyclized according to General Procedure IV at 120 °C in 5 mL toluene over 12 h. The ratio of **3a** to **4a** was 1.86:1 (GC). Column chromatography gave 43.0 mg of **3a**, 13.0 mg of **4a** and 170 mg of a mixture of **3a**/**4a** (70 %). ***trans*-1,1-Dicyano-4,6-dimethyl-2-phenylcyclohex-3-ene** (**4a**): $R_f = 0.21$ (petroleum ether/ethyl acetate 30:1); IR (film): = 2928 cm^{-1} (C–H), 2242 (C≡N), 1452 (Ar–C=C), 700, 762 (monosubstituted aromatic); UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 191 nm (4.189); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, $J = 6.5$ Hz, 3H, CH_3), 1.88 (br s, 3H, CH_3), 2.07 (m_c, 1H, 5-H), 2.35–2.51 (m, 2H, 6-H, 5-H), 3.97 (m_c, 1H, 2-H), 5.48 (m_c, 1H, 3-H), 7.31–7.41 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 17.23$, 23.30 (2 × CH_3), 31.53 (C-5), 34.55 (C-6), 43.27 (C-1), 47.12 (C-2), 114.6, 115.0 (C≡N), 118.3 (C-3), 128.5, 128.9, 130.2 (Ph C), 135.4, 135.9 (C-4, Ph C_i); MS (70 eV): *m*/*z* (%) = 129 (100) [diene − CH_3^+], 144 (80) [diene$^+$], 236 (8) [M^+]; R_t (180 °C, 1 °C min^{-1}) = 13.4 min; $C_{16}H_{16}N_2$ (236.3): calcd 236.1313, found 236.1313 (HRMS). ***cis*-1,1-Dicyano-4,6-dimethyl-2-phenylcyclohex-3-ene** (**3a**): $R_f = 0.19$ (petroleum ether/ethyl acetate 30:1); IR (film): = 2934 cm^{-1} (C–H), 2252 (C≡N), 1456 (Ar–C=C), 700, 764 (monosubstituted aromatic); UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 242 nm (3.164); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 1.41$ (d, $J = 6.5$ Hz, 3H, CH_3), 1.82 (br s, 3H, CH_3), 2.10–2.32 (m_c, 2H, 5-H_2), 2.46 (quintd, $J = 11.2$, 6.5 Hz, 1H, 6-H), 3.91 (m_c, 1H, 2-H), 5.42 (m_c, 1H, 3-H), 7.38–7.47 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 18.23$, 23.06 (2 × CH_3), 34.86 (C-5), 37.30 (C-6), 46.02 (C-1), 50.06 (C-2), 112.4, 115.4 (C≡N), 120.0 (C-3), 128.7, 128.8, 129.1 (Ph C), 136.3, 137.3 (C-4, Ph C_i); MS (70 eV): *m*/*z* (%) = 129 (100) [diene − CH_3^+], 144 (90) [diene$^+$], 236 (12) [M^+]; R_t (180 °C, 1 °C min^{-1}) = 13.6 min; $C_{16}H_{16}N_2$ (236.3): calcd C 81.32, H 6.82; found C 81.25, H 6.82.

1,1-Dicyano-6-ethyl-4-methyl-2-phenylcyclohex-3-ene (**3/4b**): Diene **1a** (124 mg, 0.87 mmol) and dienophile **2b** (92.0 mg, 0.87 mmol) were cyclized according to General Procedure IV at 120 °C in 5 mL toluene over 12 h. The ratio of **3b**/**4b** was 1.56:1 (GC). Column chromatography gave 105 mg of **3b** (49 %) and 68 mg of **4b** (31 %). ***trans*-1,1-Dicyano-6-ethyl-4-methyl-2-phenylcyclohex-3-ene** (**4b**): $R_f = 0.44$ (petroleum ether/ethyl acetate 30:1); IR (film): = 2932, 2970 cm^{-1} (C–H), 2246 (C≡N), 702, 766 (monosubstituted aromatic); UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 191 nm (4.215); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.0$ Hz, 3H, CH_2CH_3), 1.36–1.50 (m,

1H, CH_2CH_3), 1.75 – 1.90 (m, 1H, CH_2CH_3), 1.92 – 2.14 (m, 1H, 5-H_{ax}), 2.06 (m_c, 1H, 6-H), 2.42 (br d, J = 16.0 Hz, 1H, 5-H_{eq}), 3.90 (br s, 1H, 2-H), 5.41 (br s, 1H, 3-H), 7.38 – 7.46 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.18 (CH_2CH_3), 23.40 (CH_3), 24.63 (CH_2CH_3), 31.41 (C-5), 37.51 (C-6), 45.81 (C-1), 47.46 (C-2), 114.6, 115.2 (C≡N), 118.4 (C-3), 128.5, 130.2 (Ph C), 135.3, 135.9 (C-4, Ph C_i); MS (70 eV): m/z (%) = 129 (90) [diene – CH_3^+], 144 (100) [diene$^+$], 251 (15) [M^+]; R_t (150 °C, 5 °C min^{-1}) = 15.2 min; $C_{17}H_{18}N_2$ (250.3). ***cis*-1,1-Dicyano-6-ethyl-4-methyl-2-phenylcyclohex-3-ene** (**3b**): R_f = 0.40 (petroleum ether/ethyl acetate 30:1); IR (film): = 2934, 2970 cm^{-1} (C–H), 2248 (C≡N), 702, 772 (monosubstituted aromatic); UV (CH_3CN): λ_{max} (lg ε) = 191 nm (4.188); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (t, J = 7.5 Hz, 3H, CH_2CH_3), 1.50 – 1.65 (m, 2H, 6-H, CH_2CH_3), 1.85 (br s, 3H, CH_3), 2.00 – 2.30 (m, 3H, 5-H, CH_2CH_3, 6-H), 3.90 (m_c, 1H, 2-H), 5.43 (m_c, 1H, 3-H), 7.38 – 7.46 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 10.95 (CH_2CH_3), 23.19 (CH_3), 25.97 (CH_2CH_3), 31.94 (C-5), 43.25 (C-6), 45.81 (C-1), 50.29 (C-2), 112.7, 115.5 (C≡N), 120.1 (C-3), 128.7, 128.8, 129.1 (Ph C), 136.1, 137.2 (C-4, Ph C_i); MS (70 eV): m/z (%) = 129 (100) [diene – CH_3^+], 144 (80) [diene$^+$], 251 (10) [M^+]; R_t (150 °C, 5 °C min^{-1}) = 15.8 min; $C_{17}H_{18}N_2$ (250.3): calcd 250.1470, found 250.1470 (HRMS).

1,1-Dicyano-6-isopropyl-4-methyl-2-phenylcyclohex-3-ene (**3**/**4c**): Diene **1a** (150 mg, 1.04 mmol) and dienophile **2c** (125 mg, 1.04 mmol) were cyclized according to General Procedure IV at 120 °C in 5 mL toluene over 12 h. The ratio of **3c** to **4c** was 1.18:1 (GC). Column chromatography gave 20.0 mg of **4c** and 181 mg of a mixture of **3c**/**4c** (66 %). ***trans*-1,1-Dicyano-6-isopropyl-4-methyl-2-phenylcyclohex-3-ene** (**4c**): R_f = 0.20 (petroleum ether/ethyl acetate 50:1); IR (film, mixture with **3c**): = 2970 cm^{-1} (C–H), 2248 (C≡N), 706, 762 (monosubstituted aromatic); UV (CH_3CN, mixture with **3c**): λ_{max} (lg ε) = 191 nm (4.241); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09, 1.11 (2d, J = 7.0 Hz, 6H, 2 × CH_3), 2.09 – 2.19 (m, 2H, 6-H, $HCMe_2$), 2.20 – 2.28 (m, 2H, 5-H_2), 4.06 (br d, J = 4.5 Hz, 1H, 2-H), 5.47 (m_c, 1H, 3-H), 7.37 – 7.43 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 16.21, 21.91, 23.41 (3 × CH_3), 26.98 (C-5), 29.09 (CMe_2), 39.26 (C-1), 41.46 (C-6), 50.00 (C-2), 114.4, 116.2 (C≡N), 118.3 (C-3), 128.5, 129.0, 130.7 (Ph C), 136.5 (C-4, Ph C_i); MS (70 eV, mixture with **3c**): m/z (%) = 129 (72) [diene – CH_3^+], 144 (100) [diene$^+$], 264 (10) [M^+]; R_t (180 °C, 5 °C min^{-1}) = 11.6 min; $C_{18}H_{19}N_2$ (263.4): calcd C 81.78, H 7.62; found C 81.70, H 7.60. ***cis*-1,1-Dicyano-6-isopropyl-4-methyl-2-phenylcyclohex-3-ene** (**3c**): R_f = 0.16 (petroleum ether/ethyl acetate 50:1); IR see **4c**; UV see **4c**; ^{1}H NMR (500 MHz, $CDCl_3$, 1:1 mixture with **4c**): δ = 0.70, 1.09 (2d, J = 7.0 Hz, 6H, 2 × CH_3), 2.09 – 2.19 (m, 1H, 6-H), 2.29 – 2.39 (m, 2H, 5-H_2), 2.46 (d sept, J = 7.0, 3.0 Hz, 1-H, $HCMe_2$), 3.94 (m_c, 1H, 2-H), 5.42 (m_c, 1H, 3-H), 7.34 – 7.43 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 16.11, 21.94, 23.35 (3 × CH_3), 26.74 (C-5), 29.86 (CMe_2), 44.97 (C-1), 46.99 (C-6), 51.89 (C-2), 113.4, 115.0 (C≡N), 120.1 (C-3), 128.6, 128.8, 129.3 (Ph C), 136.4 (C-4), 137.0 (Ph C_i); MS see **4c**; R_t (180 °C, 5 °C min^{-1}) = 12.3 min; $C_{18}H_{19}N_2$ (263.4).

6-*tert*-Butyl-1,1-dicyano-4-methyl-2-phenylcyclohex-3-ene (**3**/**4d**): Diene **1a** (200 mg, 1.40 mmol) and dienophile **2d** (187 mg, 1.40 mmol) were cyclized according to General Procedure IV at 120 °C in 5 mL toluene over 48 h. The ratio of **3d** to **4d** was 1:5.56 (GC). Column chromatography gave 20.0 mg of **3d** (containing 20 % **4d**), 90.0 mg of **4d** and 216 mg of a mixture **3d**/**4d** (90 %). ***trans*-6-tert-Butyl-1,1-dicyano-4-methyl-2-phenylcyclohex-3-ene** (**4d**): R_f = 0.23 (petroleum ether/ethyl acetate 30:1); IR (film): = 2936 cm^{-1} (C–H), 2244 (C≡N), 704, 756 (monosubstituted aromatic); UV (CH_3CN): λ_{max} (lg ε) = 258 nm (2.100); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 9H, *t*Bu), 1.89 (s, 3H, CH_3), 2.10 (t, J = 8.0 Hz, 1H, 5-H_{ax}), 2.30 (br d, J = 8.0 Hz, 2H, 6-H, 5-H_{eq}), 4.06 (br d, J = 5.0 Hz, 1H, 2-H), 5.48 (br d, J = 5.0 Hz, 1H, 3-H), 7.38 – 7.42 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 23.24 (CH_3), 28.49 (*t*Bu); 30.99 (C-5), 33.40 (CMe_3), 39.08 (C-6), 43.21 (C-1), 51.87 (C-2), 116.4, 116.5 (C≡N), 118.4 (C-3), 128.3, 128.9, 130.9 (Ph C), 135.3 (C-4), 136.5 (Ph C_i); MS (70 eV): m/z (%) = 129 (58) [diene – CH_3^+], 144 (100) [diene$^+$], 278 (8) [M^+]; R_t (180 °C, 5 °C min^{-1}) = 17.9 min; $C_{19}H_{22}N_2$ (278.4): calcd 278.1782, found 278.1782 (HRMS). ***cis*-6-*tert*-Butyl-1,1-dicyano-4-methyl-2-phenylcyclohex-3-ene** (**3d**): R_f = 0.19 (petroleum ether/ethyl acetate 30:1); IR (film): = 2940, 2966 cm^{-1} (C–H), 2246 (C≡N), 702 (monosubstituted aromatic); UV (CH_3CN): λ_{max} (lg ε) = 252 nm (1.948); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 9H, *t*Bu), 1.82 (s, 3H, CH_3), 2.26 (dd, J = 12.5, 4.5 Hz, 1H, 6-H), 2.31 (br dd, J = 17.0, 12.5 Hz, 1H, 5-H_{ax}), 2.43 (br d, J = 17.0 Hz, 1H, 5-H_{eq}), 3.87 (m_c, 1H, 2-H), 5.37 (m_c, 1H, 3-H), 7.35 – 7.48 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 23.18 (CH_3), 28.79 (*t*Bu); 30.73 (C-5), 34.13 (CMe_3), 41.51 (C-6), 51.12 (C-1), 53.27 (C-2), 113.8, 116.4 (C≡N), 120.4 (C-3), 128.4, 128.9, 129.8 (Ph C), 136.4 (C-4), 137.0 (Ph C_i); MS (70 eV): m/z (%) = 91 (9) [$C_7H_7^+$], 77 (6) [$C_6H_5^+$], 129 (65) [diene – CH_3^+], 144 (100) [diene$^+$], 278 (18) [M^+]; R_t (180 °C, 5 °C min^{-1}) = 16.5 min; $C_{19}H_{22}N_2$ (278.4): calcd C 81.97, H 7.96; found C 81.77, H 7.76.

1,1-Dicyano-4-ethyl-6-methyl-2-phenylcyclohex-3-ene (**5**/**6a**): Diene **1b** (150 mg, 0.95 mmol) and dienophile **2a** (105 mg, 1.14 mmol, 1.2 equiv) were cyclized according to General Procedure IV at 120 °C in 5 mL toluene over 12 h. The ratio of **5a**/**6a** was determined to be 1.17:1 (GC). Column chromatography gave 18.0 mg of **5a**, 18.0 mg of **6a** and 174 mg of a mixture **5a**/**6a** (73 %). ***trans*-1,1-Dicyano-4-ethyl-6-methyl-2-phenylcyclohex-3-ene** (**6a**): R_f = 0.52 (petroleum ether/ethyl acetate 10:1); IR (film, mixture with **5a**): = 2968 cm^{-1} (C–H), 2248 (C≡N), 1458 (Ph C=C), 768, 702 (monosubstituted aromatic); UV (CH_3CN, mixture with **5a**): λ_{max} (lg ε) = 191 nm (4.247); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.10 (t, J = 7.2 Hz, 3H, CH_2CH_3), 1.28 (d, J = 6.5 Hz, 3H, CH_3), 2.00 – 2.21 (m, 5H, 5-H_2, CH_2CH_3, 6-H), 2.35 – 2.55 (m, 1H, CH_2CH_3), 3.99 (br s, 1H, 2-H), 5.46 (br s, 1H, 3-H), 7.28 – 7.45 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 12.15, 17.22 (2 × CH_3), 29.82, 32.91 (C-5, CH_2CH_3), 31.50 (C-6), 43.42 (C-1), 46.97 (C-2), 114.6, 114.9 (C≡N), 116.6 (C-3), 128.6, 128.9, 130.1 (Ph C), 136.0 (C-4), 140.7 (Ph C_i); MS (70 eV, mixture with **5a**): m/z (%) = 129 (100) [diene – $C_2H_5^+$], 158 (62) [diene$^+$], 250 (10) [M^+]; R_t (190 °C, 1 °C min^{-1}) = 13.0 min; $C_{17}H_{18}N_2$ (250.3), calcd C 81.56, H 7.25; found C 81.52, H 7.33. ***cis*-1,1-Dicyano-4-ethyl-6-methyl-2-phenylcyclohex-3-ene** (**5a**): R_f = 0.46 (petroleum ether/ethyl acetate 10:1); IR see **6a**; UV see **5a**; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.15 (t, J = 7.0 Hz, 3H, CH_2CH_3), 1.48 (d, J = 7.5 Hz, 3H, CH_3), 2.01 – 2.58 (m, 5H, 5-H_2, CH_2CH_3, 6-H), 2.35 – 2.55 (m, 1H, CH_2CH_3), 3.89 (m_c, 1H, 2-H), 5.41 (m_c, 1H, 3-H), 7.28 – 7.45 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 12.03, 18.29 (2 × CH_3), 29.62, 33.38 (C-5, CH_2CH_3), 37.32 (C-6), 46.21 (C-1), 50.02 (C-2), 112.4, 115.4 (C≡N), 118.3 (C-3), 128.7, 128.8, 129.1 (Ph C), 137.5 (C-4), 141.7 (Ph C_i); MS see **6a**; R_t (190 °C, 1 °C min^{-1}) = 13.4 min; $C_{17}H_{18}N_2$ (250.3): calcd 250.1470, found 250.1470 (HRMS).

1,1-Dicyano-4,6-diethyl-2-phenylcyclohex-3-ene (**5**/**6b**): Diene **1b** (150 mg, 0.95 mmol) and dienophile **2b** (121 mg, 1.14 mmol, 1.2 equiv) were cyclized according to General Procedure IV at 120 °C in 5 mL toluene over 12 h. The ratio of **5b** to **6b** was 1.13:1 (GC). Column chromatography gave 12.0 mg of **5b**, 18.0 mg of **6b** and 209 mg of a mixture **5b**/**6b** (95 %). ***trans*-1,1-Dicyano-4,6-diethyl-2-phenylcyclohex-3-ene** (**6b**): R_f = 0.54 (petroleum ether/ethyl acetate 10:1); IR (film, mixture with **5b**): = 2934, 2968 cm^{-1} (C–H), 2248 (C≡N), 1456 (Ar–C=C), 702, 766 (monosubstituted aromatic); UV (CH_3CN, mixture with **5b**): λ_{max} (lg ε) = 192 nm (4.199); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01, 1.10 (t, J = 7.0 Hz, 6H, 2 × CH_3), 1.40 – 1.57 (m, 1H, CH_2CH_3), 1.80 – 1.96 (m, 1H, CH_2CH_3), 2.00 – 2.20 (m, 4H, CH_2CH_3, 6-H, 5-H), 2.44 – 2.55 (m, 1H, 5-H), 3.95 (br s, 1H, 2-H), 5.46 (br s, 1H, 3-H), 7.39 – 7.43 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.23, 12.17 (2 × CH_3), 25.56 (C-5), 29.75, 29.94 (CH_2CH_3), 37.66 (C-6), 43.41 (C-1), 47.33 (C-2), 114.6, 115.2 (C≡N), 116.9 (C-3), 128.6, 128.9, 130.2 (Ph C), 136.1 (C-4), 140.7 (Ph C_i); MS (70 eV): m/z (%) = 129 (100) [diene – $C_2H_5^+$], 158 (36) [diene$^+$], 264 (8) [M^+]; R_t (180 °C, 5 °C min^{-1}) = 12.4 min; $C_{18}H_{20}N_2$ (264.4): calcd C 81.78, H 7.62; found C 81.73, H 7.63. ***cis*-1,1-Dicyano-4,6-diethyl-2-phenylcyclohex-3-ene** (**5b**): R_f = 0.50 (petroleum ether/ethyl acetate 10:1); IR see **6b**; UV see **6b**; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08, 1.09 (t, J = 7.0 Hz, 6H, 2 × CH_3), 1.50 – 1.61 (m, 1H, CH_2CH_3), 2.00 – 2.27 (m, 1H, CH_2CH_3, 5-H, 6-H), 2.40 (m_c, 1H, 5-H), 3.90 (m_c, 1H, 2-H), 5.40 (m_c, 1H, 3-H), 7.35 – 7.42 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 10.95, 12.01 (2 × CH_3), 26.00 (C-5), 29.70, 30.46 (CH_2CH_3), 43.25 (C-6), 45.97 (C-1), 50.21 (C-2), 112.7, 115.5 (C≡N), 118.4 (C-3), 128.7, 128.8, 129.1 (Ph C), 137.4 (C-4), 141.5 (Ph C_i); MS (70 eV): m/z (%) = 129 (100) [diene – $C_2H_5^+$], 158 (24) [diene$^+$], 264 (3) [M^+]; R_t (180 °C, 5 °C min^{-1}) = 12.8 min; $C_{18}H_{20}N_2$ (264.4) calcd 264.1626, found 264.1626 (HRMS).

1,1-Dicyano-4-ethyl-6-isopropyl-2-phenylcyclohex-3-ene (**5**/**6c**): Diene **1b** (150 mg, 0.95 mmol) and dienophile **2c** (137 mg, 1.14 mmol, 1.2 equiv) were cyclized according to General Procedure IV at 120 °C in 5 mL toluene over 24 h. The ratio of **5c** to **6c** was 1:1.56 (GC). Column chromatography gave 40.0 mg of **5c**, 46.0 mg of **6c** and 96.0 mg of a mixture **5c**/**6c** (69 %). ***trans*-1,1-Dicyano-4-ethyl-6-isopropyl-2-phenylcyclohex-3-ene** (**6c**): R_f = 0.31 (petroleum ether/ethyl acetate 20:1); IR (KBr, mixture with **5c**): = 2928, 2966 cm^{-1} (C–H), 2244 (C≡N), 1464 (Ar–C=C), 700, 760 (monosubstituted aromatic); UV (CH_3CN, mixture with **5c**): λ_{max} (lg ε) = 191 nm (4.152); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98, 1.10, 1.15 (d, J = 6.8 Hz, 9H,

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3 × CH_3), 2.08–2.30 (m, 6H, 4-H_2, 5-H, CH_3CH_2, $HCMe_2$), 4.08 (m_c, 1H, 2-H), 5.48 (m_c, 1H, 3-H), 7.29–7.45 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 12.24, 16.21, 21.89 (3 × CH_3), 25.33, 29.98 (C-5, CH_3CH_2), 29.11 (CMe_2), 39.16 (C-6), 41.58 (C-1), 49.81 (C-2), 114.4, 116.1 (C≡N), 116.6 (C-3), 128.4, 128.9, 130.6 (Ph C), 135.6 (C-4), 141.8 (Ph C_i); MS (70 eV): *m*/*z* (%) = 129 (100) [diene – $C_2H_5^+$], 158 (38) [diene$^+$], 278 (4) [M^+]; R_t (180 °C, 5 °C min^{-1}) = 12.2 min; $C_{19}H_{22}N_2$ (278.4): calcd C 81.97, H 7.96; found C 81.84, H 7.86. ***cis*-1,1-Dicyano-4-ethyl-6-isopropyl-2-phenylcyclohex-3-ene (5c)**: R_f = 0.28 (petroleum ether/ethyl acetate 20:1); IR see **6c**; UV see **6c**; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10, 1.12 (d, *J* = 7.0 Hz, 6H, 2 × CH_3), 1.11 (t, *J* = 7.0 Hz, 3H, CH_2CH_3), 2.10–2.52 (m, 6H, 4-H_2, 6-H, CH_3CH_2, $HCMe_2$), 3.93 (m_c, 1H, 2-H), 5.41 (m_c, 1H, 3-H), 7.37–7.46 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 12.08, 16.12, 21.95 (3 × CH_3), 25.24 (C-5) 29.88 (CH_3CH_2), 29.91 (CMe_2), 44.23 (C-1), 46.96 (C-6), 51.79 (C-2), 113.4, 115.0 (C≡N), 118.3 (C-3), 128.6, 128.9, 129.3 (Ph C), 137.1 (C-4), 142.4 (Ph C_i); MS (70 eV): *m*/*z* (%) = 129 (100) [diene – $C_2H_5^+$], 158 (28) [diene$^+$], 278 (3) [M^+]; R_t (180 °C, 5 °C min^{-1}) = 12.9 min; $C_{19}H_{22}N_2$ (278.4): calcd 278.1783, found 278.1783 (HRMS).

6-*tert*-Butyl-1,1-dicyano-4-ethyl-2-phenylcyclohex-3-ene (5/6d): Diene **1b** (100 mg, 0.63 mmol) and dienophile **2d** (254 mg, 2.00 mmol, 3 equiv) were cyclized according to General Procedure V at 50 °C, 10 kbar in 2.5 mL dichloromethane over 48 h. The ratio of **5d** to **6d** was 1:5.88 (GC). Column chromatography gave 39.0 mg of **6d** and 85 mg of a mixture **5d**/**6d** (96%). ***trans*-6-*tert*-Butyl-1,1-dicyano-4-ethyl-2-phenylcyclohex-3-ene (6d)**: R_f = 0.36 (petroleum ether/ethyl acetate 30:1); IR (KBr, mixture with **5d**): = 2968 cm^{-1} (C–H), 2242 (C≡N) 700, 754 (monosubstituted aromatic); UV (CH_3CN, mixture with **5d**): λ_{max} (lg ε) = 191 nm (4.142); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 9H, *t*Bu), 2.08 (dd, *J* = 9.0, 8.0 Hz, 1H, 5-H_{ax}), 2.18 (br q, *J* = 7.0 Hz, 2H, CH_2CH_3), 2.33 (br d, *J* = 8.0 Hz, 2H, 5-H_{eq}, 6-H), 4.09 (m_c, 1H, 2-H), 5.49 (m_c, 1H, 3-H), 7.29–7.45 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 12.20 (CH_3), 28.50 (*t*Bu), 29.93, 29.78 (C-5, CH_3CH_2), 33.42 (CMe_3), 39.22 (C-6), 43.15 (C-1), 51.73 (C-2), 116.4, 116.5 (C≡N), 116.8 (C-3), 128.3, 128.9, 130.9 (Ph C), 135.4 (C-4), 141.9 (Ph C_i); MS (70 eV, mixture with **5d**): *m*/*z* (%) = 129 (100) [diene – $C_2H_5^+$], 158 (45) [diene$^+$], 292 (10) [M^+]; R_t (180 °C, 5 °C min^{-1}) = 12.5 min; $C_{20}H_{24}N_2$ (292.4): calcd C 82.43, H 7.95; found C 82.51, H 8.07. ***cis*-6-*tert*-Butyl-1,1-dicyano-4-ethyl-2-phenylcyclohex-3-ene (5d)**: R_f = 0.30 (petroleum ether/ethyl acetate 30:1); IR see **6d**; UV see **6d**; ^{13}C NMR (50.3 MHz, $CDCl_3$, mixture with **6d**): δ = 12.07 (CH_3), 28.78 (*t*Bu), 29.27, 29.69 (C-5, CH_3CH_2), 34.15 (CMe_3), 41.65 (C-6), 51.05 (C-1), 53.11 (C-2), 113.8 (C≡N), 118.7 (C-3), 128.4, 128.8, 129.8 (Ph C), 136.8 (C-4), 142.4 (Ph C_i); MS see **6d**; R_t (180 °C, 5 °C min^{-1}) = 13.1 min; $C_{20}H_{24}N_2$ (292.4).

1,1-Dicyano-6-ethyl-4-isopropyl-2-phenylcyclohex-3-ene (7–8b): Diene **1c** (100 mg 113, 0.58 mmol) and dienophile **2b** (61.5 mg, 0.58 mmol) were cyclized according to General Procedure IV at 120 °C in 5 mL toluene within 24 h. The ratio of **7b**/**8b** was determined to be 1:1.89 (GC). Column chromatography gave 3.0 mg of **7b**, 14.0 mg of **8b** and 148 mg of a mixture **7b**/**8b** (98%). ***trans*-1,1-Dicyano-6-ethyl-4-isopropyl-2-phenylcyclohex-3-ene (8b)**: R_f = 0.23 (petroleum ether/ethyl acetate 20:1); IR (film, mixture with **7b**): = 2966 cm^{-1} (C–H), 2248 (C≡N) 702, 768 (monosubstituted aromatic); UV (CH_3CN, mixture with **7b**): λ_{max} (lg ε) = 191 nm (4.188); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 0.96 (d, *J* = 6.8 Hz, 6H, 2 × CH_3), 1.34–1.52 (m, 1H, CH_2CH_3), 1.72–1.93 (m, 1H, CH_2CH_3), 1.96–2.10 (m, 2H, 5-H, 6-H), 2.31 (sept, *J* = 6.8 Hz, 1H, $HCMe_2$), 3.90 (br d, *J* = 4.0 Hz, 1H, 2-H), 5.39 (m_c, 1H, 3-H), 7.21–7.39 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.28 (CH_2CH_3), 21.21, 21.42 (2 × CH_3), 24.47 (CH_2CH_3), 27.41 (C-5), 34.90 (CMe_2), 37.74 (C-6), 43.50 (C-1), 47.13 (C-2), 114.7, 115.2 (C≡N), 116.1 (C-3), 128.6, 128.9, 130.2 (Ph C), 136.2 (C-4), 144.8 (Ph C_i); MS (70 eV, mixture with **8d**): *m*/*z* (%) = 129 (100) [diene – $C_3H_7^+$], 172 (24) [diene$^+$], 278 (2) [M^+]; R_t (180 °C, 5 °C min^{-1}) = 11.9 min; $C_{19}H_{22}N_2$ (278.4): calcd C 81.97, H 7.96; found C 82.12, H 7.99. ***cis*-1,1-Dicyano-6-ethyl-4-isopropyl-2-phenylcyclohex-3-ene (7b)**: R_f = 0.19 (petroleum ether/ethyl acetate 20:1); IR see **8b**; UV see **8b**; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.09, 1.10 (2d, *J* = 6.8 Hz, 6H, 2 × CH_3), 1.11 (t, *J* = 7.0 Hz, 3H, CH_2CH_3), 1.55–1.60 (m, 1H, CH_2CH_3), 2.06–2.24 (m, 3H, 6-H, 5-H, CH_2CH_3), 2.34 (sept, *J* = 6.8 Hz, 1H, $HCMe_2$), 3.90 (m_c, 1H, 2-H), 5.44 (m_c, 1H, 3-H), 7.39–7.42 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 10.99 (CH_2CH_3), 21.11, 21.50 (2 × CH_3), 26.08 (CH_2CH_3), 28.31 (C-5), 34.68 (CMe_2), 43.20 (C-6), 46.01 (C-1), 50.01 (C-2), 112.6, 115.5 (C≡N), 117.5 (C-3), 128.5, 128.8, 129.1 (Ph C), 137.4 (C-4), 145.7 (Ph C_i); MS see **8b**; R_t (180 °C, 5 °C min^{-1}) = 12.2 min; $C_{19}H_{22}N_2$ (278.4).

1,1-Dicyano-4,6-diisopropyl-2-phenylcyclohex-3-ene (7/8c): Diene **1c** (100 mg, 0.58 mmol) and dienophile **2c** (70 mg, 0.58 mmol) were cyclized according to General Procedure V at 50 °C, 10 kbar in 2.5 mL dichloromethane within 36 h. The ratio of **7c**/**8c** was determined to be 1:3.33 (GC). Column chromatography gave 37.0 mg of **8c** and 16 mg of a mixture **7c**/**8c** (31%). ***trans*-1,1-Dicyano-4,6-diisopropyl-2-phenylcyclohex-3-ene (8c)**: R_f = 0.28 (petroleum ether/ethyl acetate 30:1); IR (KBr, mixture with **7c**): = 2964 cm^{-1} (C–H), 2248 (C≡N) 702, 764 (monosubstituted aromatic); UV (CH_3CN, mixture with **7c**): λ_{max} (lg ε) = 191 nm (4.183); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01, 1.11, 1.14, 1.16 (4d, *J* = 6.5 Hz, 12H, 4 × CH_3), 2.02–2.34 (m, 4H, 5-H_2, 6-H, $HCMe_2$), 2.42 (sept, *J* = 6.5 Hz, 1H, $HCMe_2$), 4.08 (br d, *J* = 5.0 Hz, 1H, 2-H), 5.49 (m_c, 1H, 3-H), 7.20–7.42 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 16.29, 21.20, 21.64, 21.91 (4 × CH_3), 23.15 (C-5), 29.20, 35.04 (2 × CMe_2), 39.18 (C-6), 41.70 (C-1), 49.67 (C-2), 115.8 (C-3), 114.4, 116.0 (C≡N), 128.5, 128.9, 130.6 (Ph C), 135.7 (C-4), 146.0 (Ph C_i); MS (70 eV, mixture with **7c**): *m*/*z* (%) = 129 (100) [diene – *i*Pr$^+$], 172 (55) [diene$^+$], 292 (10) [M^+]; R_t (180 °C, 3 °C min^{-1}) = 16.8 min; $C_{20}H_{24}N_2$ (292.4): calcd C 82.14, H 8.27; found C 82.05, H 8.28. ***cis*-1,1-Dicyano-4,6-diisopropyl-2-phenylcyclohex-3-ene (7c)**: R_f = 0.26 (petroleum ether/ethyl acetate 30:1); IR see **8c**; UV see **8c**; ^{1}H NMR (300 MHz, $CDCl_3$ δ = 0.94, 1.02, 1.10, 1.18 (4d, *J* = 6.5 Hz, 12H, 4 × CH_3), 2.04–2.50 (m, 5H, 5-H_2, 6-H, 2 × $HCMe_2$), 3.95 (m_c, 1H, 2-H), 5.44 (br s, 1H, 3-H), 7.20–7.43 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 16.19, 21.20, 21.64, 21.91 (4 × CH_3), 23.15 (C-5), 30.01, 34.90 (2 × CMe_2), 44.31 (C-1), 47.01 (C-6), 51.77 (C-2), 113.3, 115.1 (C≡N), 117.6 (C-3), 128.3, 128.7, 128.9 (Ph C), 137.1 (C-4), 146.6 (Ph C_i); MS see **8c**; R_t (180 °C, 3 °C min^{-1}) = 18.3 min; $C_{20}H_{24}N_2$ (292.4): calcd 292.1939, found 292.1939 (HRMS).

***trans*-6-*tert*-Butyl-1,1-dicyano-4-isopropyl-2-phenylcyclohex-3-ene (8d)**: Diene **1c** (100 mg, 0.63 mmol) and dienophile **2d** (84.8 mg, 0.63 mmol) were cyclized according to General Procedure V at 50 °C, 10 kbar in 2.5 mL dichloromethane over 24 h. Column chromatography gave 39 mg of **8d** as a single product (96%). Traces of the cycloadduct **7d** may have been determined by GC, **8d**:**7d** > 99:1). R_f = 0.37 (petroleum ether/ethyl acetate 20:1); IR (KBr): = 2968 cm^{-1} (C–H), 2242 (C≡N) 702, 770 (monosubstituted aromatic); UV (CH_3CN): λ_{max} (lg ε) = 191 nm (4.170); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 9H, *t*Bu), 1.13, 1.15 (2d, *J* = 6.5 Hz, 6H, 2 × CH_3), 2.05 (dd, *J* = 10.0, 6.5 Hz, 1H, 5-H_{ax}), 2.33 (td, *J* = 10.0, 1.0 Hz, 1H, 5-H_{eq}), 2.35 (br d, *J* = 6.5, 1.0 Hz, 1H, 6-H), 2.38 (sept, *J* = 6.5 Hz, 1H, $HCMe_2$), 4.08 (br d, *J* = 4.0 Hz, 1H, 2-H), 5.50 (m_c, 1H, 3-H), 7.31–7.45 (m, 5H, Ph H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.17, 21.67 (2 × CH_3), 27.23 (C-5), 28.25 (*t*Bu), 33.48 (CMe_3), 34.82 (CMe_2), 39.29 (C-1), 39.29 (C-6), 43.11 (C-6), 51.55 (C-2), 115.9 (C-3), 116.3, 116.5 (C≡N), 128.3, 128.9, 130.9 (Ph C), 135.4 (C-4), 146.1 (Ph C_i); MS (70 eV): *m*/*z* (%) = 129 (100) [diene – *i*Pr$^+$], 172 (41) [diene$^+$], 306 (12) [M^+]; $C_{21}H_{26}N_2$ (306.5): calcd C 82.27, H 8.55; found C 82.37, H 8.70.

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