Competing Michael and Knoevenagel reactions of terpenoids with malononitrile on basic Cs-beta zeolite

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Abstract

Basic cesium-beta (Cs-beta) zeolite has been synthesized. It proved to be an effective catalyst in reactions of a number of α,β-unsaturated carbonyl compounds with malononitrile. It is shown that the process is either the Michael or Knoevenagel reaction, or tandem transformations generally initiated by the Michael reaction, which depends on steric hindrance at the carbonyl group and the β-position of the carbon=carbon (C=C) double bond adjacent to the carbonyl group.
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1. Introduction

Application of heterogeneous catalysts including zeolites to fine chemicals synthesis is one of the most important fields in modern organic chemistry [1]. Although it started to develop more than a dozen years ago, only some recent publications have dealt with the application of basic zeolites to catalysis of synthetically important reactions of CH-acids with carbonyl compounds (Michael and Knoevenagel reactions) [2–5]. In all cases, the acceptors were either aromatic aldehydes or simple α,β-unsaturated carbonyl compounds, whose reaction routes were known beforehand. On the other hand, we have previously shown that the use of terpenoids in intermolecular reactions catalyzed by acid aluminosilicate catalysts often leads to unusual processes [6,7]. In the case of

basic zeolites, the complex structure of terpenoids ensures a nucleophilic attack at the carbon=carbon (C=C) double bond (Michael reaction) or at the carbonyl group (Knoevenagel reaction). The aim of the present work is to examine the effect of the structure of some terpenoids on the route of their reactions with malononitrile occurring in the presence of basic-beta zeolite and hence on the synthetic utility of such reactions in environmentally friendly conditions.

We have studied the reactions of some terpenoids containing an α,β-unsaturated carbonyl group with malononitrile in the presence of a basic cesium-beta (Cs-beta) zeolite prepared by impregnation of Cs-beta with Cs formate. It was found that the reaction route mainly depends on steric hindrances created by substituents at the double bond and carbonyl group. A number of new compounds have been synthesized which are the products of Michael or Knoevenagel reactions or both.

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2. Results and discussion

The basic Cs-beta zeolite catalyst was prepared by impregnating Cs-beta with an aqueous solution of cesium formate. The XRD patterns of the impregnated Cs-beta catalyst and the ion-exchanged Cs-beta zeolite, which is the intermediate product in the preparation of the basic Cs-beta catalyst, are shown in Fig. 1.

The XRD powder diffraction pattern of the ion-exchanged form of Cs-beta corresponds to that of beta zeolite in every detail [8], indicating that no structural changes take place in the zeolite framework during the exchange process. Analysis of the XRD powder pattern of the basic-beta catalyst (Fig. 1c) shows several features.

First, there are no indications to the presence of any crystalline phases (i.e. cesium formate) other than the beta phase. Thus, it may be concluded that a crust of solid CsOOCH is not formed on the surface of the zeolite crystal.

Second, the characteristic broad intense low-angle reflection of beta zeolite at $7.5°$ (2θ) disappears. Low-angle reflections are most strongly affected by non-framework species [9]. The absence of the corresponding peak on the XRD pattern of the basic Cs-beta catalyst indicates that cesium formate molecules occupy the zeolite channels.

Third, the intensities of the peaks decrease by a factor of 2.5 compared to those of Cs-beta (Fig. 1a). This may be attributed to the increased mass transfer coefficient of the sample owing to the high content of the cesium salt [10]. Because of the neutral nature of the cesium formate reagent and the low temperature of impregnation, generation of any structural defects at this stage is rather improbable. On the other hand, activation of the basic Cs-beta catalyst at $500°C$ in air led to a further decrease in the diffraction intensities (Fig. 1d). This may be explained not only by the conversion of cesium formate to denser cesium carbonate and cesium oxide (and hence to increased mass transfer coefficient), but also by the possible interaction of the Cs_2O product with the zeolite framework (amorphization process). The presence of Cs^+ ions at the cationic sites does not affect the thermal stability of beta zeolite, as can be seen from the comparison of the diffraction patterns of the Cs-beta sample and the Cs-beta sample calcined at $500°C$ (Fig. 1a and b).

Thermal activation of the basic Cs-beta zeolite catalyst (further denoted as Cs-beta) leads to decomposition of the occluded cesium formate molecules in
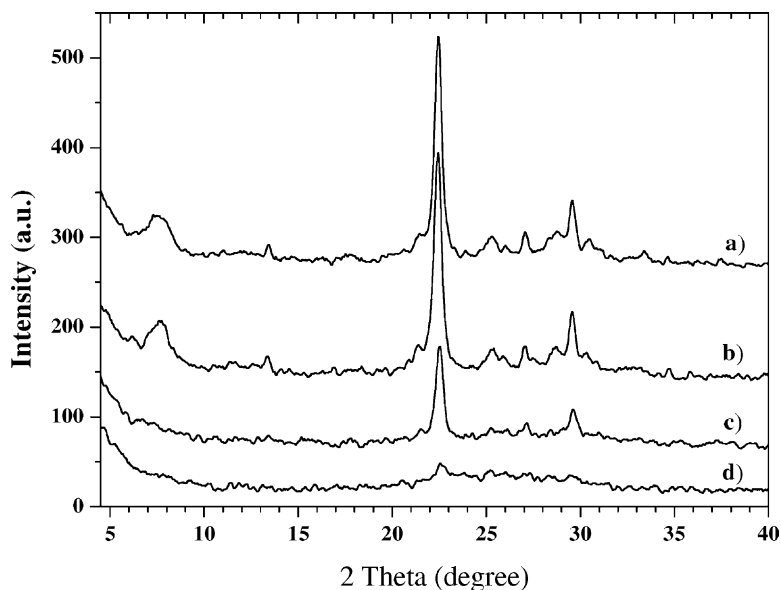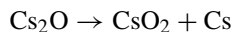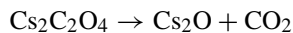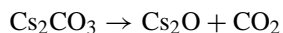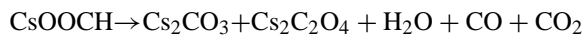

Fig. 1. XRD powder patterns of Cs-beta zeolite (a), Cs-beta zeolite calcined at $500°C$ (b), basic Cs-beta catalyst (c), and basic Cs-beta catalyst calcined at $500°C$ in air (d).

accordance with the following scheme:

$$CsOOCH \rightarrow Cs_2CO_3 + Cs_2C_2O_4 + H_2O + CO + CO_2$$

$$Cs_2CO_3 \rightarrow Cs_2O + CO_2$$

$$Cs_2C_2O_4 \rightarrow Cs_2O + CO_2$$

$$Cs_2O \rightarrow CsO_2 + Cs$$

The most important reaction in this scheme seems to be the last one, according to which the cesium oxide product decomposes to elemental cesium and cesium dioxide CsO_2. The latter is volatile at $500\,°C$, enriching the catalyst with cesium, which might be a basic catalyst itself.

The spectrum of the impregnated Cs-beta sample is presented in Fig. 2. The spectrum is characterized by rather low signal-to-noise ratio and probably consists of one line at 35 ppm with a width of 4 kHz. According to the chemical shift and width of the observed resonance, it can be assigned to neither different cesium–oxygen binary phases [11] or those supported on such carriers as alumina and silica [12] nor isolated cesium cations in ion-exchange positions of zeolite lattice with typical NMR line width not exceeding 2 kHz [13]. The pronounced broadening and unique chemical position of the signal points to a high dispersion of the impregnated cesium-bearing guest inside the pores of beta zeolite.

Wong et al. [14] presented the correlation of [133]Cs chemical shifts in different cesium complexes with crown ethers and cryptands with the number of oxygen atoms surrounding the central cation. Using that correlation the coordination number of cesium by oxygen atoms is 7 ± 1 in our impregnated Cs-beta sample.

Before starting to examine the reactions of malononitrile with terpenoids, whose structure favors both Michael and Knoevenagel reactions, we decided to check the activity of the basic zeolite sample using simpler models. Thus, the reaction of malonic ester with acrylonitrile (Scheme 1) gave the expected products of the Michael reaction [15]–compounds **1** and **2**, as well as compound **3**, never obtained previously in this reaction. The possibility of the Knoevenagel reaction was verified by performing the reaction of citronellal **4** with malononitrile (Scheme 2). While storage of citronellal on Cs-beta leads to the product of aldol condensation (**5**), the reaction of citronellal with malononitrile gives compound **6** as the sole product. These products were previously obtained in homogeneous reactions [16,17]. The successful verification of these transformations in the presence of Cs-beta zeolite has demonstrated the basic properties
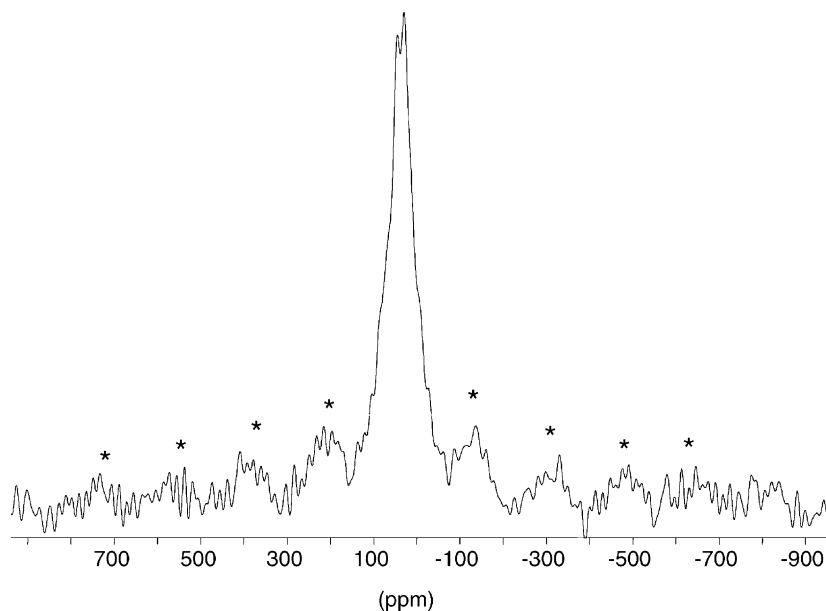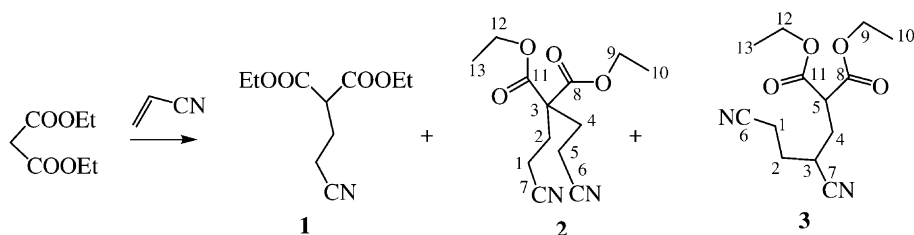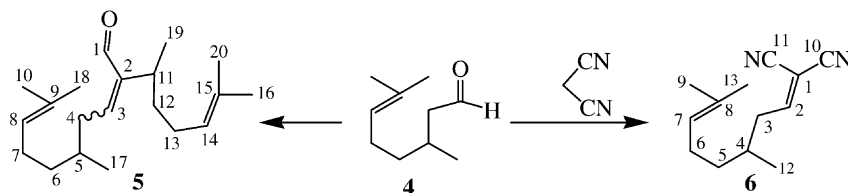

Fig. 2. The [133]Cs MAS NMR spectrum of the impregnated Cs-beta sample. Asterisks denote spinning sidebands.

Scheme 1.

Scheme 2.

of the latter and permitted us to start investigating the reactions of malononitrile with terpenoids containing an α,β-unsaturated carbonyl group with various substituents.

The investigation was started from citral **7**. This compound was often employed as donor in Knoevenagel reactions, which generally occurred non-trivially, leading to complex mixtures of products [18,19]. In our case, the reaction of citral **7** (a mixture of *cis*- and *trans*-isomers, 1:1) with malononitrile in the presence of Cs-beta zeolite in diethyl ether gave a mixture of *cis*- and *trans*-isomers **8a,b** (in ratio 1:1) (Scheme 3). It is interesting that in the absence of a solvent the reaction proceeded much faster, but the yield of trienes **8a,b** dropped from 41 to 13%. As donors hereinafter we used ketones, which are less reactive than aldehydes and do not react with malononitrile in diethyl ether; therefore all subsequent reactions were conducted in dry solvent-free media.
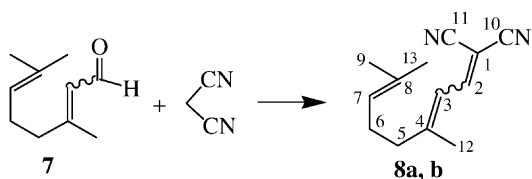
It was shown [18] that β,β-disubstituted enals react with malonic ester and its derivatives exclusively at the carbonyl group (Knoevenagel reaction) in conditions of phase transfer catalysis. Therefore, we performed reactions between malononitrile and ketones **9** and **10**, containing only one, though bulky, substituent in the β-position of the double bond at the carbonyl group (Scheme 4). The major products of these reactions were compounds **11** and **12**, which are Knoevenagel reaction products. Moreover, we have unexpectedly isolated unusual compounds **13** and **14**, apparently produced by tandem Michael and Knoevenagel reactions with further intramolecular carbocyclization and nucleophilic substitution of the nitrile group by the hydroxy group. The suggested sequence and mechanism of formation of compounds **13** and **14** is supported by the fact that storage of **11** with malononitrile under reaction conditions did not form any products and the starting dinitrile **11** was recovered unchanged. Thus, in the case of ketones **9** and **10**, the competing Knoevenagel and Michael reactions led to different products. The Michael reaction initiates tandem transformations forming complex polyfunctional compounds **13** and **14** with various reactive functional groups. Nitriles **15** and **16** (Fig. 3) as well as dinitrile **11** do not interact with malononitrile on Cs-beta. When the reaction of ketone **9** with malononitrile was carried out in the presence of calcined cesium formate instead
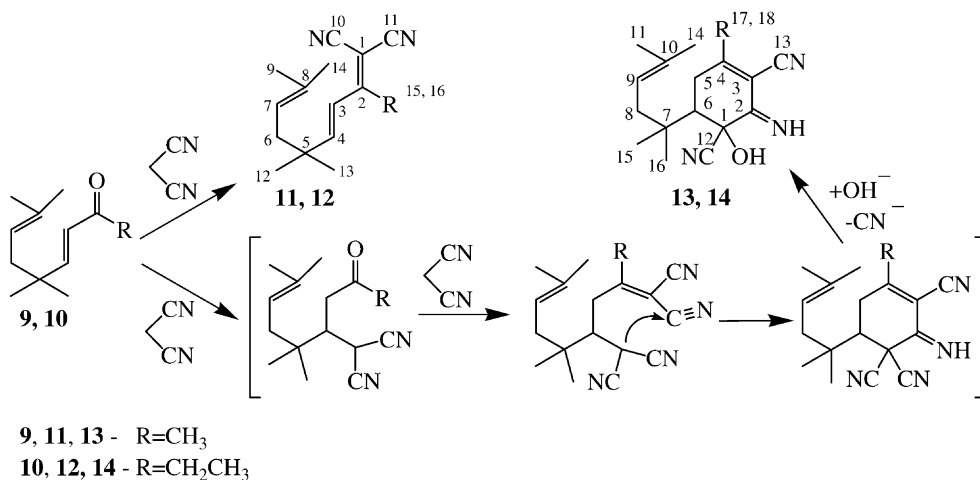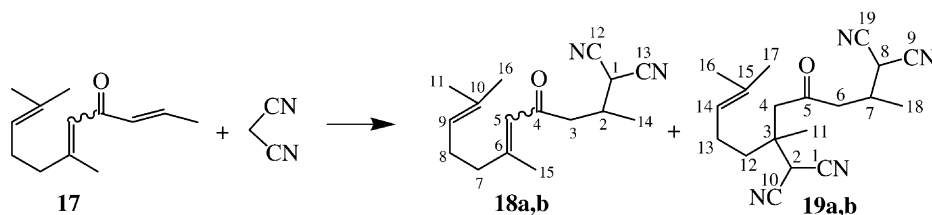

Scheme 3.

Scheme 4.
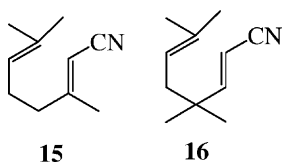
Fig. 3. Structures of nitriles **15** and **16**.

of zeolite the conversions increased from 73 to 100%, but overall yield decreased from 47 to 30%; the only product in this reaction was dinitrile **11**. Thereby, use of Cs-beta zeolite leads not only to easy treatment of reaction mixture and ecologically friendly process, but also to the formation of new interesting compounds.

The sterically uncrowded position of the carbonyl group is also essential to the reaction route. The reaction of φ-damascone **17** (cis + trans-isomer mixture 1:1) with malononitrile (Scheme 5) yielded compounds **18a,b** (in a 1:1 ratio) as the major products,

which are the products of the Michael reaction. Further reaction of **18a,b** with malononitrile, however, led to an attack at the olefinic double bond with two substituents in the β-position relative to the carbonyl group, but not to an attack at the carbonyl group, as would be expected by analogy with ketones **9** and **10**, and gave a 1:1 mixture of diastereomers **19a,b**. Thus, when an attack at the carbonyl group encounters steric hindrances, the reaction of malononitrile with a β-disubstituted double bond can lead to a product of Michael reaction.

The reaction of malononitrile with α-ionone **20**, containing (analogously to **9** and **10**) only one substituent in the β-position of the double bond near the carbonyl group, leads to formation of compound **21**, which is the product of the Knoevenagel reaction (Scheme 6). It seems that the absence of Michael reaction products in this case is explained by the extremely large size of substituent in the β-position of the double bond.

Scheme 5.
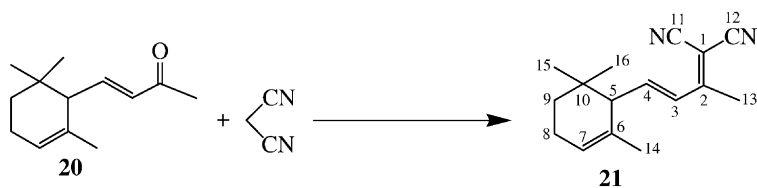
Scheme 6.
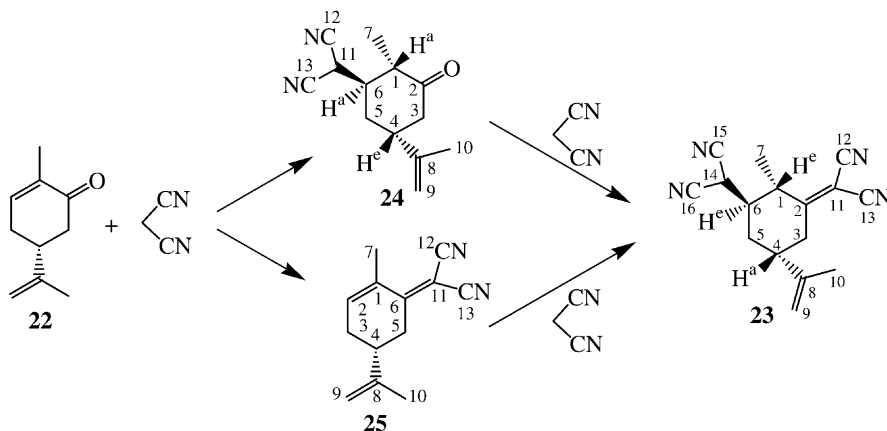
Scheme 7.

Carvone **22** has a relatively readily accessible β-position of the double bond at the carbonyl group. It is not surprising therefore that this is one of the most widespread terpenoids used as an acceptor in Michael reactions [20–22]. The compounds formed from carvone **22** in these reactions are valuable intermediates in chiral syntheses of natural products and their analogs.

We showed that the reaction of carvone **22** ($[\alpha]_D^{20} = -61°$ (neat)) with malononitrile on Cs-beta forms an unusual compound **23**, which the product of tandem Michael and Knoevenagel reactions (Scheme 7). To examine which of the two possible intermediates–the product of an attack at the double bond or at the carbonyl group—leads to compound **23** we performed a reaction of carvone with a small amount of malononitrile. Both Michael (**24**) and Knoevenagel (**25**) reaction products were isolated along with compound **23**, indicating that the reaction proceeds via both intermediates. Although compound **24** was isolated with a higher yield than **25**, it is currently impossible to infer which intermediate leads to compound **23** as the

major product, since the rates of the reactions of **24** and **25** with malononitrile are unknown. Previously, compounds **23**–**25** were supposed to be intermediates in the reaction of carvone with malononitrile in the presence of KF [23], but were not isolated.

All the three products are formed stereoselectively and optically active. Increased interest in such tandem transformations arises from the possibility of formation of several bonds and structure complexation in one reaction [24].

In all cases, we used catalytic amounts of zeolite; zeolite is easy recoverable by calcinations at 500 °C and can be reusable without lost activity; compounds **3**, **11**–**14**, **18a,b**, **19a,b**, **21**, and **23**–**25** were not reported in the literature, and their structure was established by ^{1}H and ^{13}C NMR, MS and IR spectroscopy.

3. Conclusions

Thus we have synthesized basic Cs-beta zeolite and showed that this is an effective catalyst for reactions

of a number of terpenoid α,β-unsaturated carbonyl compounds with malononitrile leading to products of either Michael or Knoevenagel reactions or both. The structure of the product depends on steric crowdedness of both the β-position of the C=C bond lying near the carbonyl group and of the carbonyl group itself.

4. Experimental

Cs-beta was prepared by three ion-exchange treatment. Beta zeolite in hydrogen form (Si/Al = 13.3, lab preparation [25]) was treated with 0.5 M aqueous $CsNO_3$ (solid/solution = 1 g/10 ml, 50 °C, 10 h) with a subsequent interval between the exchange procedures and the final vacuum filtration, after which the solid product was washed and dried at 90 °C.

The basic Cs-beta zeolite catalyst was prepared by impregnation of Cs-beta with aqueous 2 M cesium formate. Cs-beta was impregnated by mixing zeolite powder (37 g) with aqueous 2 M HCOOCs (55 ml, 19.6 g HCOOCs). The resulting paste was dried at 90 °C. The product was characterized by X-ray powder diffraction (HZG-4 diffractometer, Cu Kα radiation), elemental analysis (BAIRD ICP spectrometer), and argon adsorption at 77 K. The specific surface area of the sample calcined at 500 °C in air was 51 m^2/g. Single-quantum solid state ^{133}Cs MAS NMR spectrum of the impregnated Cs-beta sample was recorded at 52.458 MHz (magnetic field of 9.4 T) on a Bruker MSL-400 spectrometer. The experimental conditions were: pulse length of 3 ms, repetition time of 5 s, spinning rate of 10 kHz, 16,000 transients. 0.001 M CsNO3 water solution was used as an external chemical-shift standard. Chemical analysis of the basic Cs-beta zeolite catalyst showed 1.39% Al, 19.27% Si, and 33.93% Cs, giving the formula $Cs_{4.47}[Al_{4.47}Si_{59.53}O_{128}]\cdot17.7CsCHOO\cdot60.8H_2O$ for the zeolite unit cell.

The composite catalyst was calcined at 500 °C for 2 h immediately before use.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer with operating frequencies of 400.13 and 100.61 MHz, respectively, for CDCl$_3$ or 1:1 (v:v) CCl$_4$–CDCl$_3$ solutions of the substances. Deuterochloroform (δ_H 7.24 ppm, δ_C 76.90 ppm) was used as an internal standard. The structure of the compounds was elucidated by analyzing the geminal, vic-

inal, and long-range proton spin–spin coupling constants in ^{1}H–^{1}H double resonance spectra and by considering ^{13}C NMR spectra using proton off-resonance saturation, ^{13}C–^{1}H 2D-COSY ($^1J_{C-H}$ = 135 Hz), and ^{13}C–^{1}H 1D-LRJMD (J_{C-H} = 10 Hz) spectra. Tables 2 and 3 lists the ^{13}C NMR spectral data. High-resolution mass spectra were recorded on a Finnigan MAT 8200 instrument. Chromatomass-spectra were measured on an HPG 1800 A instrument. IR spectra were obtained on a Bruker Vector 22 instrument. Specific rotation was measured on a Polamat A spectrometer for CHCl$_3$ solutions. The purity of the starting substances was checked and the products were analyzed by GLC on a 3700 chromatograph with a flame-ionization detector (glass capillary column 17,000 mm × 0.25 mm, stationary phase VC-30, column temperature 60–190 °C, helium gas carrier pressure 2 atm).

4.1. General procedure

To a suspension of Cs-beta was added a solution of malononitrile in diethyl ether (2 ml). The ether was distilled off, and the terpenoid was added dropwise. The reaction mixture was allowed to stay at room temperature, and then extracted with diethyl ether and acetone. The catalyst was removed by filtration. The solvent was distilled off. The products were separated by column chromatography on silica gel (40–100 μm, 1–95% hexane solution of ether as eluent). The experimental conditions and results are given in Table 1.

4.2. Interaction of malonic ester with acrylonitrile

To Cs-beta (200 mg) was added malonic ester (300 mg) and acrylonitrile (400 mg). The mixture was allowed to stay at room temperature for 72 h. After extraction with diethyl ether, the mixture was separated by column chromatography on silica gel (30–95% hexane solution of ether as eluent). This gave 120 mg of compound **1** (yield 30%) and 80 mg of a 1.5:1 mixture of compounds **2** and **3** (total yield 16%).

4.2.1. 2,2-bis-(2-Cyanoethyl)-malonic acid diethyl ester (**2**)

^{1}H NMR, δ, J (Hz): 1.267 (t, J = 7, 6H, C^{10}H3, C^{13}H$_3$), 2.20 (t, J = 7.5, 4H, 2H^2, 2H^4), 2.40 (t, J = 7.5, 4H, 2H^1, 2H^5), 4.22 (q, J = 7, 4H, 2H^9, 2H^{12}).

Table 1
Experimental conditions

Terpenoid number, mass (mg)	Malononitrile (mg)	Zeolite (mg)	Reaction time (h)	Conversion (%)	Product, mass (mg)	Yield[a] (%)	$[\alpha]_{580}^{20}$ (c, g/100 ml)
4, 140		80	90	100	**5**, 33	13	
4, 140	300	20	20	100	**6**, 70	38	
7, 68	100	25	48[b]	100	**8a,b**, 37	41	
7, 150	200	30	18	100	**8a,b**, 25	13	
9, 200	300	80	48	73	**11**, 74	40	
					13, 16	7	
9, 200	300	80[c]	48	100	**11**, 77	30	
10, 250	200	40	115	40	**12**, 57	46	
					14, 6	4	
17, 500	600	140	24	70	**18a,b**, 289	62	
					19a,b, 52	9	
20, 800	600	140	120	70	**21**, 493	71	
22, 150	150	40	168	65	**23**, 89	52	+24 (8.9)
22, 150	60	40	168	55	**23**, 56	39	+25 (3.4)
					24, 25	21	+20 (0.3)
					25, 3	3	−167 (0.2)

[a] Yield given based on the changed terpenoid.

[b] The reaction was carried out in diethyl ether (5 ml).

[c] The catalyst was cesium formate calcined at 500 °C for 2 h.

4.2.2. 2-(2,4-Dicyanobutyl)-malonic acid diethyl ester (3)

^{1}H NMR, δ, J (Hz): 1.265 and 1.273 (t, $J = 7$, 6H, $C^{10}H_3$, $C^{13}H_3$), 1.98 (m, $2H^2$), 2.06–2.19 (m, $2H^4$), 2.51 (dt, $J_{1,1'} = 17$, $J_{1,2} = 8$, $1H^1$) and 2.59 (ddd, $J = 17$, $J_{1',2} = 8$, $J_{1',2'} = 6$, $1H^{1'}$)—AB-system, 2.84 (m, $1H^3$), 3.52 (dd, $J_{5,4} = 9$, $J_{5,4'} = 6$, $1H^5$), 4.18 and 4.19 (q, $J = 7$, 4H, $2H^9$, $2H^{12}$).

4.2.3. 2-(1,5-Dimethylhex-4-enyl)-5,9-dimethyldeca-2,8-dienal (5)

m/e for $C_{20}H_{34}O$: calc. 290.26095, obs. 290.26065. ^{1}H NMR, δ, J (Hz): 0.91 (d, $J_{17,5} = 6.5$, 3H, $C^{17}H_3$), 1.11 (d, $J_{19,11} = 7$, 3H, $C^{19}H_3$), 1.22 and 1.36 (m, $2H^6$), 1.47–1.73 (m, 3H, $1H^5$, $2H^{12}$), 1.51 and 1.57 (br s, 6H, $C^{18}H_3$, $C^{20}H_3$), 1.63 (br s, 3H) and 1.65 (m, 6H, $C^{10}H_3$, $C^{16}H_3$), 1.79 (m, $2H^{13}$), 1.88–2.05 (m, $2H^7$), 2.16 (ddd, $J_{4,4'} = 15$, $J_{4,3} = 8$, $J_{4,5} = 7.5$, $1H^4$) and 2.29 (ddd, $J = 15$, $J_{4',3} = 7$, $J_{4',5} = 5.5$, $1H^{4'}$)—AB-system, 2.65 (m, $J_{11,12} = 8$, $J_{11,12'} = 7$, $J_{11,19} = 7$, $J_{11,1} = 2$, $1H^{11}$), 5.00 and 5.03 (tqq, $J = 7$, 1.5, 1.5, 2H, $1H^8$, $1H^{14}$), 6.35 (dd, $J = 8$, 7, $1H^3$), 9.30 (d, $J = 2$, $1H^1$).

4.2.4. 2-(3,7-Dimethyloct-6-enylidene)-malononitrile (6)

m/e for $C_{13}H_{18}N_2$: calc. 202.14699, obs. 202.14663. ^{1}H NMR, δ, J (Hz): 0.96 (d, $J_{12,4} = 6.5$, 3H, $C^{12}H_3$), 1.22–1.40 (m, $2H^5$), 1.58 (br s, 3H, $C^{13}H_3$), 1.67 (m, 3H, C^9H_3), 1.77 (m, $J_{4,3} = 7.5$, $J_{4,12} = 6.5$, $J_{4,3'} = 5.5$, $1H^4$), 1.99 (m, $2H^6$), 2.43 (ddd, $J_{3,3'} = 14.5$, $J_{3,2} = 8$, $J = 7.5$, $1H^3$) and 2.57 (ddd, $J = 14.5$, $J_{3',2} = 7.5$, $J = 5.5$, $1H^{3'}$)—AB-system, 5.02 (tqq, $J_{7,6} = 7$, $J_{7,9} = 1.5$, $J_{7,13} = 1.5$, $1H^7$), 7.31 (dd, $J = 8$, 7.5, $1H^2$).

The ^{13}C NMR spectrum of compound **6** recorded in this work is identical to the spectrum reported in the literature [26]. In the ^{1}H NMR spectrum (recorded in deuterochloroform), the chemical shifts of some signals differ essentially from the data of [26] evidently because the latter were given for a deuterobenzene solution.

4.2.5. 2-(3,7-Dimethylocta-2,6-dienylidene)-malononitrile (8a,b)

m/e for $C_{13}H_{16}N_2$: calc. 200.13134, obs. 200.13142. ^{1}H NMR for *cis*-isomer **8a**, δ, J (Hz): 1.58 (br s, 3H, $C^{13}H_3$), 1.69 (br s, 3H, C^9H_3), 2.08 (d, $J_{12,3} = 1.2$, 3H, $C^{12}H_3$), 2.17 (br td, $J_{6,5} = 7$, $J_{6,7} = 7$, $2H^6$),

2.37 (t, $J = 7$, 2H[5]), 5.00 (tqq, $J = 7$, $J_{7,9} = 1.5$, $J_{7,13} = 1.5$, 1H[7]), 6.47 (dq, $J_{3,2} = 12$, $J = 1.2$, 1H[3]), 7.62 (d, $J = 12$, 1H[2]); ^{1}H NMR for *trans*-isomer **8b**, δ, J (Hz): 1.60 (br s, 3H, C[13]H$_3$), 1.68 (br s, 3H, C[9]H$_3$), 2.01 (d, $J_{12,3} = 1.2$, 3H, C[12]H$_3$), 2.21 (br td, $J_{6,5} = 7$, $J_{6,7} = 7$, 2H[6]), 2.33 (t, $J = 7$, 2H[5]), 5.01 (tqq, $J = 7$, $J_{7,9} = 1.5$, $J_{7,13} = 1.5$, 1H[7]), 6.46 (dq, $J_{3,2} = 12$, $J = 1.2$, 1H[3]), 7.70 (d, $J = 12$, 1H[2]).

4.2.6. 2-(1,4,4,7-Tetramethylocta-2,6-dienylidene)-malononitrile (11)

m/e for $C_{15}H_{20}N_2$: calc. 228.16264, obs. 228.16324. ^{1}H NMR, δ, J (Hz): 1.08 (s, 6H, C[12]H$_3$, C[13]H$_3$), 1.56 (br s, 3H, C[14]H$_3$), 1.69 (br s, 3H, C[9]H$_3$), 2.06 (br d, $J_{6,7} = 7.5$, 2H[6]), 2.31 (s, 3H, C[15]H$_3$), 5.01 (tqq, $J = 7.5$, $J_{7,9} = 1.5$, $J_{7,15} = 1.5$, 1H[7]), 6.59 and 6.62 (d, $J = 16$, 2H, 1H[3], 1H[4])—AB-system.

4.2.7. 2-(1-Ethyl-4,4,7-trimethylocta-2,6-dienylidene)-malononitrile (12)

m/e for $C_{16}H_{22}N_2$: calc. 242.17829, obs. 242.17844. ^{1}H NMR, δ, J (Hz): 1.10 (s, 6H, C[12]H$_3$, C[13]H$_3$), 1.19 (t, $J_{16,15} = 7$, 3H, C[16]H$_3$), 1.58 (br s, 3H, C[14]H$_3$), 1.70 (dt, $J_{9,7} = 1.5$, $J_{9,6} = 1.5$, 3H, C[9]H$_3$), 2.08 (br d, $J_{6,7} = 7.5$, 2H[6]), 2.70 (q, $J = 7$, 2H[15]), 5.02 (tqq, $J = 7.5$, 1.5, $J_{7,16} = 1.5$, 1H[7]), 6.51 (d, $J_{4,3} = 16$, 1H[4]) and 6.59 (d, $J = 16$, 1H[3])—AB-system.

4.2.8. 1-Hydroxy-2-imino-4-methyl-6-(1,1,4-trimethylpent-3-enyl)-cyclohex-3-ene-1,3-dicarbonitrile (13)

m/e for $C_{17}H_{23}N_3$ ($M - 16$): calc. 269.18919, obs. 269.18927. ^{1}H NMR, δ, J (Hz): 0.76 and 0.86 (s, 6H, C[15]H$_3$, C[16]H$_3$), 1.57 (d, $J_{14,9} = 1.5$, 3H, C[14]H$_3$), 1.70 (dt, $J_{11,9} = 1.5$, $J_{11,8} = 1.5$, 3H, C[11]H$_3$), 1.88 (br d, $J_{8,9} = 7.5$, 2H[8]), 2.23 (d, $J_{17,5'} = 1.5$, 3H, C[17]H$_3$), 2.31 (dd, $J_{6,5'} = 9$, $J_{6,5} = 2.5$, 1H[6]), 2.48 (dd, $J_{5,5'} = 18.5$, $J = 2.5$, 1H[5]) and 2.55 (ddq, $J = 18.5$, 9, 1.5, 1H[5']) —AB-system, 4.77 (br s, 2H, OH, NH), 5.09 (tqq, $J = 7.5$, 1.5, 1.5, 1H[9]). IR (CCl$_4$): δ_{N-H} 1580 cm^{-1}, $\nu_{C=N}$ 1647 cm^{-1}, $\nu_{C\equiv N}$ 2188, 2220 cm^{-1}, ν_{O-H}, ν_{N-H} 3357, 3400, 3480 cm^{-1}.

4.2.9. 4-Ethyl-1-hydroxy-2-imino-6-(1,1,4-trimethyl-pent-3-enyl)-cyclohex-3-ene-1,3-dicarbonitrile (14)

m/e for $C_{18}H_{25}N_3$ ($M - 16$): calc. 283.20484, obs. 283.20437. ^{1}H NMR, δ, J (Hz): 0.78 and 0.87 (s, 6H, C[15]H$_3$, C[16]H$_3$), 1.19 (t, $J_{18,17} = 7$, 3H, C[18]H$_3$), 1.58

(br s, 3H, C[14]H$_3$), 1.70 (dt, $J_{11,9} = 1.5$, $J_{11,8} = 1.5$, 3H, C[11]H$_3$), 1.90 (br s, $J_{8,9} = 7.5$, 2H[8]), 2.35 (dd, $J_{6,5} = 8.5$, $J_{6,5'} = 2.5$, 1H[6]), 2.51 (dd, $J_{5,5'} = 18.5$, $J = 8.5$, 1H[5]) and 2.58 (dd, $J = 18.5$, 2.5, 1H[5'])— AB-system, 2.50–2.64 (m, 2H[17]), 4.72 (br s, 2H, OH, NH), 5.11 (tqq, $J = 7.5$, 1.5, $J_{9,14} = 1.5$, 1H[9]). IR (CCl$_4$): δ_{N-H} 1579 cm^{-1}, $\nu_{C=N}$ 1642 cm^{-1}, $\nu_{C\equiv N}$ 2188, 2220 cm^{-1}, ν_{O-H}, ν_{N-H} 3355, 3400, 3500 cm^{-1}.

4.2.10. 2-(1,5,9-Trimethyl-3-oxodeca-4,8-dienyl)-malononitrile (18a,b)

m/e for $C_{16}H_{22}N_2O$: calc. 258.17320, obs. 258.17370. ^{1}H NMR for *trans*-isomer **18a**, δ, J (Hz): 1.25 (d, $J_{14,2} = 6.5$, 3H, C[14]H$_3$), 1.57 (d, $J_{16,9} = 1.5$, 3H, C[16]H$_3$), 1.65 (br s, 3H, C[11]H$_3$), 2.11 (d, $J_{15,5} = 1.5$, 3H, C[15]H$_3$), 2.12 (m, 4H, 2H[7], 2H[8]), 2.60 (m, 2H[3]), 2.64 (m, 1H[2]), 4.32 (d, $J_{1,2} = 4$, 1H[1]), 5.00 (m, 1H[9]), 5.98 (m, 1H[5]); ^{1}H NMR for *cis*-isomer **18b**, δ, J (Hz): 1.24 (d, $J_{14,2} = 6.5$, 3H, C[14]H$_3$), 1.58 (br s, 3H, C[16]H$_3$), 1.65 (br s, 3H, C[11]H$_3$), 1.88 (d, $J_{15,5} = 1.5$, 3H, C[15]H$_3$), 2.08 (td, $J_{8,7} = 7$, $J_{8,9} = 7$, 2H[8]), 2.50–2.61 (m, 4H, 2H[7], 2H[3]), 2.64 (m, 1H[2]), 4.32 (d, $J_{1,2} = 4$, 1H[1]), 5.07 (tqq, $J_{9,8} = 7$, $J_{9,11} = 1.5$, $J_{9,16} = 1.5$, 1H[9]), 5.98 (m, 1H[5]). Since the 2H[7], 2H[8], 2H[3], and H[2] signals of the *trans*-isomer and the H[2] signal of the *cis*-isomer overlap in the ^{1}H NMR spectrum, the centers of multiplets were taken from the 2D-COSY ([13]C–[1]H) spectrum recorded for an isomer mixture.

4.2.11. 2,8-Dicyano-3,7-dimethyl-3-(4-methylpent-3-enyl)-5-oxononanedinitrile (19a,b)

m/e for $C_{19}H_{24}N_4O$: calc. 324.19500, obs. 324.19497. ^{1}H NMR, δ, J (Hz): 1.262 (d, $J_{18,7} = 7$, 6H, 2C[18]H$_3$[18]H$_3$), 1.268 and 1.274 (s, 6H, 2C[11]H$_3$), 1.60 (br s, 6H, 2C[17]H$_3$), 1.68 (br s, 6H, 2C[16]H$_3$), 1.55–1.76 (m, 4H[12]), 1.83–2.06 (m, 4H[13]), 2.57 and 2.77 (d, $J_{4,4'} = 18$, 2H[4])—AB-system, 2.67 and 2.72 (d, $J = 18$, 2H[4])—AB-system, 2.62–2.71 (m, 6H, 2H[7], 4H[6]), 4.03 and 4.05 (d, $J_{8,7} = 4.5$, 2H[8]), 4.63 and 4.64 (s, 2H[2]), 5.02 (tqq, $J_{14,13} = 7$, $J_{14,16} = 1.5$, $J_{14,17} = 1.5$, 2H[14]).

4.2.12. 2-[1-Methyl-3-(2,6,6-trimethylcyclohex-2-enyl)-allylidene]-malononitrile (21)

m/e for $C_{16}H_{20}N_2$: calc. 240.16264, obs. 240.16277. ^{1}H NMR, δ, J (Hz): 0.83 and 0.94 (s, 3H, C[15]H$_3$

and s, 3H, $C^{16}H_3$), 1.25 (dt, $J_{9,9'} = 13$, $J_{9,8} = 5$, 1H[9]), 1.42 (dt, $J = 13$, $J_{9',8} = 8$, 1H[9']), 1.56 (td, $J_{14,8} = 1.5$, $J_{14,7} = 1.5$, 3H, $C^{14}H_3$), 2.06 (m, 2H[8]), 2.33 (s, 3H, $C^{13}H_3$), 2.38 (br d, $J_{5,4} = 10$, $J_{5,8} = 1.5$, 1H[5]), 5.52 (m, $J_{7,8} = 3.5$, $J = 1.5$, 1H[7]), 6.42 (dd, $J_{4,3} = 15.5$, $J = 10$, 1H[4]), 6.71 (d, $J = 15.5$, 1H[3]).

4.2.13. 2-(3-Dicyanomethyl-5-isopropenyl-2-methylcyclohexylidene)-malononitrile (23)

m/e for $C_{16}H_{16}N_4$: calc. 264.13749, obs. 264.13820. ^{1}H NMR, δ, J (Hz): 1.42 (d, $J_{7,1} = 7$, 3H, C^7H_3), 1.80 (br s, 3H, $C^{10}H_3$), 2.00 (ddd, $J_{5a,5e} = 15$, $J_{5a,4a} = 13$, $J_{5a,6e} = 4.5$, 1H[5a]) and 2.10 (dm, $J = 15$, $J_{5e,4a} = 3.5$, $J_{5e,6e} = 2.5$, $J_{5e,3e} = 1.5$, 1H[5e])—AB-system, 2.25 (dddd, $J_{4a,3a} = 13$, $J = 13$, $J_{4a,3e} = 4$, $J = 3.5$, 1H[4a]), 2.42 (dd, $J_{3a,3e} = 15$, $J = 13$, 1H[3a]), 2.57 (dm, $J_{6e,14} = 10.5$, $J = 4.5$, 2.5, $J_{6e,1e} = 1.5$, 1H[6e]), 2.98 (dm, $J = 15$, 4, 1.5, $J_{3e,1e} = 1$, 1H[3e]), 3.45 (br q, $J = 7$, 1H[1e]), 3.75 (d, $J = 10.5$, 1H[14]), 4.86 and 4.92 (br s, 2H[9]).

4.2.14. 2-(5-Isopropenyl-2-methyl-3-oxocyclohexyl)-malononitrile (24)

m/e for $C_{13}H_{16}N_2O$: calc. 216.12626, obs. 216.12603. ^{1}H NMR, δ, J (Hz): 1.11 (d, $J_{7,1} = 7$, 3H, C^7H_3), 1.75 (dd, $J_{10,9'} = 1.5$, $J_{10,4} = 1$, 3H, $C^{10}H_3$), 2.08 (ddd, $J_{5a,5e} = 12$, $J_{5a,6a} = 12$, $J_{5a,4e} = 4.5$, 1H[5a]) and 2.15 (dddd, $J = 12$, $J_{6a,1a} = 12$, $J_{6a,11} = 3.5$, $J_{6a,5e} = 2.5$, 1H[6a])—AB-system, 2.37 (dqd, $J = 12$, 7, $J_{1a,3a} = 1.2$, 1H[1a]), 2.39 (dddd, $J = 12$, $J_{5e,4e} = 3.5$, $J = 2.5$, $J_{5e,3e} = 2.5$, 1H[5e]), 2.56 (ddd, $J_{3a,3e} = 15$, $J_{3a,4e} = 6$, $J = 1.2$, 1H[3a]) and 2.74 (ddd, $J = 15$, $J_{3e,4e} = 3$, $J = 2.5$, 1H[3e])—AB-system, 2.87 (br s, 1H[4e]), 3.95 (d, $J = 3.5$, 1H[11]), 4.67 (br s, 1H[9]), 4.92 (br s, 1H[9']).

The axial position of H[4] and the equatorial positions of H[1] and H[6] in compound **23** follow from the values of the vicinal constants of spin–spin coupling with the neighboring protons: there are two $^3J = 13$ Hz (for coupling with H[3a] and H[5a]) in the first case, and all constants are smaller than 5 Hz for both H[1e] and H[6e] in the second case. For H[1], its equatorial position is also confirmed by its long-range coupling with H[3e] (W: constant $J_{1e,3e} \sim 1$ Hz). In compound **24**, the axial positions of H[1] and H[6] and the equatorial position of H[4] are additionally inferred from analysis of the vicinal constants of spin–spin coupling with neighboring protons. Based on the above treatment, one can conclude that in both compounds, **23** and **24**, the H[1] and H[4] protons

Table 2
^{13}C NMR data for compounds **2**, **3**, **5**, **8a**,**b**, **11**–**14**, δ_C (chemical shifts are given in ppm)[a]

Number	2	3	5	8a	8b	11	12	13	14
1	12.87 t	15.11 t	194.82 d	81.45 s	81.75 s	83.14 s	82.50 s	72.01 s	72.14 s
2	29.43 t	28.31 t	147.58 s	155.13 s	155.45 s	169.15 s	175.07 s	147.48 s	147.65 s
3	55.44 s	28.79 d	154.32 d	122.42 d	121.50 d	123.29 d	121.81 d	104.89 s	103.87 s
4	29.43 t	30.57 t	36.06 t	163.68 s	164.16 s	158.62 d	158.14 d	163.48 s	169.23 s
5	12.87 t	49.21 d	32.77 d	34.06 t	40.98 t	38.69 s	38.78 s	32.21 t	30.84 t
6	118.10 s	117.30 s	36.98 t	26.78 t	26.09 t	40.40 t	40.66 t	39.86 d	39.60 d
7	118.10 s	118.89 s	25.54 t	121.89 d	122.11 d	119.23 d	119.38 d	40.29 s	40.28 s
8	168.84 s	167.70[a] s	124.53[a] d	134.32 s	133.38 s	134.49 s	134.52 s	37.54 t	37.51 t
9	62.11 t	61.86[b] t	131.40[b] s	25.70 q	25.62 q	25.84 q	25.97 q	119.84 d	119.70 d
10	13.87 q	13.94 q	25.68 q	113.63[a] s	113.68[a] s	112.82[a] s	112.61[a] s	133.85 s	133.91 s
11	168.84 s	167.66[a] s	31.27 d	111.39[a] s	111.47[a] s	111.84[a] s	111.98[a] s	26.13 q	26.01 q
12	62.11 t	61.81[b] t	34.20 t	25.54 q	18.80 q	26.08 q	26.21 q	120.45 s	120.74 s
13	13.87 q	13.94 q	26.52 t	17.80 q	17.75 q	26.08 q	26.21 q	113.77 s	113.84 s
14			124.26[a] d			17.82 q	17.93 q	18.00 q	17.90 q
15			131.16[b] s			17.91 q	25.18 t	24.65[a] q	24.14[a] q
16			25.68 q				14.25 q	24.30[a] q	24.65[a] q
17			19.66 q					23.69 q	29.71 t
18			17.65 q						11.82 q
19			18.67 q						
20			17.65 q						

[a] The values of the chemical shifts denoted with the same letter may be exchanged within the column.

Table 3
^{13}C NMR data for compounds **18a,b**, **19a,b**, **21**, **23**, **24**, **25**, δ_C (chemical shifts are given in ppm)[a]

Number	18a	18b	19a,b	21	23	24	25
1	27.53 d	27.53 d	111.55 s	83.67 s	38.55 d	46.94 d	131.73 s
2	31.24 d	31.24 d	32.17 d, 32.10 d	167.82 s	180.32 s	207.38 s	144.99 d
3	46.03 t	45.94 t	39.75 s, 39.72 s	127.98 d	34.31 t	43.56 t	32.19 t
4	196.75 s	196.19 s	46.86 t	150.10 d	39.51 d	39.16 d	40.78 d
5	122.15 d	122.84 d	206.21 s, 206.17 s	55.47 d	27.22 t	29.80 t	36.76 t
6	161.47 s	162.14 s	46.17 t, 46.09 t	131.44 s	43.15 t	41.04 d	168.43 s
7	41.20 t	34.05 t	30.85 d, 30.81 d	123.29 d	19.57 q	11.39 q	21.46 q
8	25.90 t	26.55 t	27.86 d, 27.84 d	22.97 t	144.70 s	144.89 s	145.35 s
9	122.57 d	123.28 d	111.16[a] s	31.33 t	112.00 t	113.76 t	111.81 t
10	132.54 s	132.15 s	111.55 s	32.95 s	20.45 q	21.86 q	20.57 q
11	25.53 q	25.53 q	22.49 q, 22.33 q	112.60[a] s	86.93 s	26.81 d	81.00 s
12	112.19 s	111.33 s	37.12 t, 36.79 t	111.69[a] s	110.72[a] s	111.72[a] s	113.17[a] s
13	112.19 s	111.33 s	22.66 t, 22.61 t	18.01 q	110.46[a] s	110.42[a] s	113.08[a] s
14	16.80 q	16.80 q	122.28 d, 122.21 d	22.80 q	26.17 d		
15	19.61 q	25.68 q	133.32 s, 133.26 s	28.05[b] q	111.64[b] s		
16	17.56 q	17.49 q	25.69 q	26.77[b] q	111.00[b] s		
17			17.73 q				
18			17.01 q				
19			111.55[a] s				

[a] The values of the chemical shifts denoted with the same letter may be exchanged within the column.

are *cis* relative to each other and *trans* relative to the H^1 signal relative to the characteristic position of the allyl protons (1.9–2.8 ppm) may be explained by the effect of the triple bond of the C^{12}N group. As follows from Dreiding's models, the anisotropic effect is maximal when H^1 is equatorial in the cyclohexane ring (whose conformation is slightly distorted by the exo-double bond at C^2 if at all). The difference between the chemical shifts of the C^{7}H$_3$ signals in the ^{1}H NMR spectra of **23** and **24** is probably explained by the screening effect of the C=O group on the methyl group in addition to the effect of the nitrile groups of the substituents at the C^6 atoms in **24**, leading to a diamagnetic shift of the C^{7}H$_3$ signal.

4.2.15. 2-(5-Isopropenyl-2-methyl-cyclohex-2-enylidene)-malononitrile (*25*)

m/e for $C_{13}H_{14}N_2$: calc. 198.11569, obs. 198.11633. ^{1}H NMR, δ, J (Hz): 1.77 (br s, 3H, C^{10}H$_3$), 2.24 (m, 1H^3), 2.27 (br d, $J_{7,2}$ = 1.5, 3H, C^{7}H$_3$), 2.38–2.55 (m, 3H, 1H$^{3'}$, 1H^4, 1H^{5a}), 3.06 (dm, $J_{5e,5a}$ = 14, 1H^{5e}), 4.78 (br s) and 4.85 (m) (2H^9), 6.35 (m, $J_{2,3'}$ = 5, $J_{2,3}$ = 3, $J_{2,7}$ = 1.5, 1H^2) (Tables 2 and 3).

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