Synthesis of 1-alkynyl-2-dialkylaminocyclopropanes and 1-alkynyl-2-diazolylcyclopropanes by reactions of 1-alkynyl-1-chlorocyclopropanes with amines and their lithium derivatives*

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Reactions of 1-alkynyl-1-chlorocyclopropanes with lithium dialkylamides gave previously unknown 1-alkynyl-2-dialkylaminocyclopropanes. 1-(Alk-1-ynyl)-2-diazolylcyclopropanes were obtained by reactions of 1-alkynyl-1-chlorocyclopropanes with diazoles in the presence of KOH in DMSO at 100 °C. These reactions passed through the formation of conjugated alkynylcyclopropenes and reversible addition of amide anions to them. The regioselectivity and stereoselectivity of these transformations depend on the substituents in the starting chlorocyclopropanes and amines.

Key words: cyclopropanes, cyclopropenes, alkynes, amines, pyrazoles, imidazoles, elimination, nucleophilic addition.

1-Alkynyl-1-halocyclopropanes, notably 1-alkynyl-1-chlorocyclopropanes, are convenient and accessible cyclopropane synthetic units easily prepared by [1+2] cycloaddition of alkynylchlorocarbenes to alkenes[2,3] or by reactions of *n*-BuLi with trichlorovinyl(chloro)cyclopropanes followed by hydrolysis.[4] The currently known numerous transformations of 1-alkynyl-1-chlorocyclopropanes include metalation at the Cl atom followed by reactions with various electrophiles,[4,5] the Pauson—Khand cycloaddition,[4] and the synthesis of nitrogen-containing heterocycles[6] and conjugated alkynyl- and iminoalkylcyclopropenes.[1,7]

Another class of polyfunctional cyclopropanes with a high synthetic potential is constituted by alkynylcyclopropanes with electron-donating substituents in position 2 of the cyclopropane ring,[8] which have been subjected to hydrogenation,[9] cross-coupling at the triple bond,[10] and metalation at the methine H atom of the cyclopropane ring at the alkynyl substituent.[11] In addition, they were successfully used for the synthesis of unsaturated polycyclic alcohols[11] and ketones.[9] Among the compounds of this class, 2-alkoxy-1-(alk-1-ynyl)cyclopropanes are used most widely, probably because of their accessibility. These compounds can be obtained by addition of ethynylcarbenes (generated from appropriate diazoalkynes or 3*H*-pyrazoles) to vinyl ethers,[12,13] intramolecular cyclization of 4-alkoxy-5-haloalk-1-ynes[11] and 4-alkoxy-5-tosyloxyalk-1-ynes[9] in the presence of strong bases, and reactions of 2,2-dichloro-[14] and 2,2-dibromovinyl(alkoxy)cyclopropanes[15] with organometallic compounds.

However, other alkynylcyclopropanes with electron-donating substituents in position 2 (*e.g.*, 1-alkynyl-2-aminocyclopropanes) have not been documented hitherto. At the same time, they can be of equal interest because the aminocyclopropane fragment is found in a great number of biologically active natural compounds and drugs.[16—18]

The present work is devoted to a detailed study of transformations of 1-alkynyl-1-chlorocyclopropanes under the action of secondary amines and their lithium derivatives that lead to 1-alkynyl-2-dialkylaminocyclopropanes and 1-alkynyl-2-diazolylcyclopropanes, new cyclopropylacetylene compounds with nitrogen-containing substituents in position 2.

Most part of our work was done using easily accessible[2] 1-alkynyl-1-chloro-2,2-dimethylcyclopropanes **1a—c** as starting materials because the presence of two geminal methyl groups in the cyclopropane ring dictates the only pathway of HCl elimination and prevents further isomerization of the resulting cyclopropene intermediates.

Reactions of chlorocyclopropanes **1a—c** with a fourfold excess of lithium derivatives of dimethylamine, diethylamine, *N*-benzyl-*N*-methylamine, and cyclic amines such as morpholine, pyrrolidine, piperidine, and piperazine in THF at 20—40 °C afforded 1-(alk-1-ynyl)-2-dialkylaminocyclopropanes **3a—m** in 33—71% yields (Scheme 1, Table 1).

Reactions of chlorocyclopropane **1a** bearing the electron-withdrawing phenylethynyl substituent with lithium

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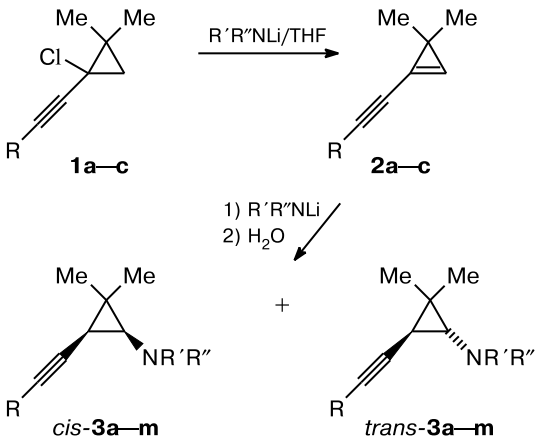
Scheme 1

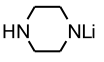
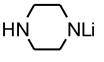
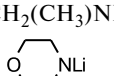


derivatives of morpholine, dimethylamine, piperazine, pyrrolidine, piperidine, and *N*-benzyl-*N*-methylamine gave a mixture of the *trans*- and *cis*-isomers of cyclopropanes **3a,c—g** in ratios from 2.5 : 1 to 3.7 : 1. With sterically slightly more hindered lithium diethylamide as the nucleophile, only a *trans*-isomer of compound **3b** was obtained. Analogously, chlorocyclopropanes **1b** and **1c** with bulky electron-donating *tert*-butyl and adamantyl substituents at the triple bond always yielded only *trans*-isomers of the corresponding aminocyclopropanes **3h—m**. Therefore, this reaction is highly sensitive to the steric and electronic properties of the substituents in both the starting chlorocyclopropane **1** and lithium dialkylamide.

The nature of the substituent at the triple bond substantially influences the rates of the reactions under study. For instance, compound **1a** with the phenylethynyl substituent is consumed completely within 30 min in room-temperature reactions with all the lithium amides used, while in the case of its alkylethynyl analogs **1b** and **1c**, heating at 40 °C for 1 h is required to complete these reactions.

In contrast to other similar transformations, a reaction of cyclopropane **1b** with lithium diethylamide for 1 h gave cyclopropene **2b** as a major product rather than aminocyclopropane **3h** (GLC and NMR data). Using sequential treatment of the reaction mixture with water and 5% HCl, we isolated compound **2b** (>90% purity) in 45% yield.

Table 1. Synthesis of 1-(alk-1-ynyl)-2-aminocyclopropanes **3a—m** from 1-(alk-1-ynyl)-1-chloro-2,2-dimethylcyclopropanes and lithium dialkylamides in THF

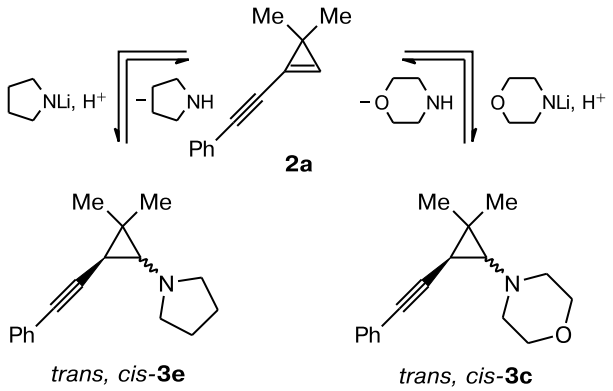
Starting cyclopropane[a]		R′R″NLi	*t*/h	*T*/°C	Reaction product	Yield[b] (%)	Ratio of the *trans*/*cis* isomers[c]
1	R						
1a	Ph	Me_2NLi	0.5	20	**3a**	62	3.5 :1
	Ph	Et_2NLi	0.5	20	**3b**	52	—[d]
	Ph		0.5	20	**3c**	66	2.5 : 1
	Ph		0.5	20	**3d**	51	2.6 : 1
	Ph		0.5	20	**3e**	71	3.2 : 1
	Ph		0.5	20	**3f**	69	3.7 : 1
	Ph	$PhCH_2(CH_3)NLi$	0.5	20	**3g**	53	3.3 : 1
1b	Bu^t	Et_2NLi	24	20	**3h**	33	—[d]
	Bu^t		1	40	**3i**	70	—[d]
	Bu^t		1	40	**3j**	63	—[d]
	Bu^t		1	40	**3k**	65	—[d]
	Bu^t	$PhCH_2(CH_3)NLi$	1	40	**3l**	50	—[d]
1c	Ad		1	40	**3m**	60	—[d]

[a] In all the experiments, the molar ratio of the starting cyclopropane (2 mmol) to lithium dialkylamide is 1 : 4.
[b] Isolated by column chromatography.
[c] According to NMR data for the products isolated.
[d] The *trans*-isomer is formed only.

With an increase in the reaction time to 24 h, cyclopropene **2b** disappeared completely and product **3h** was obtained in 33% yield. Apparently, the formation of aminocyclopropanes **3a—m** results from addition of the anions R´R″N$^-$ to *in situ* generated cyclopropenes **2**. Because the C=C bond is polarized by the alkynyl substituent, the amide ions add selectively at the unsubstituted C atom of the cyclopropene ring.

Interestingly, a reaction of pyrrolidinocyclopropane **3e** with excess lithium morpholide in THF gave a 1 : 3.5 mixture of the starting compound with the corresponding morpholine derivative **3c** (Scheme 2). Obviously, compound **3c** results from a sequence of reversible reactions: elimination of lithium pyrrolidide and addition of the morpholide ion at the double bond of cyclopropene **2a**.

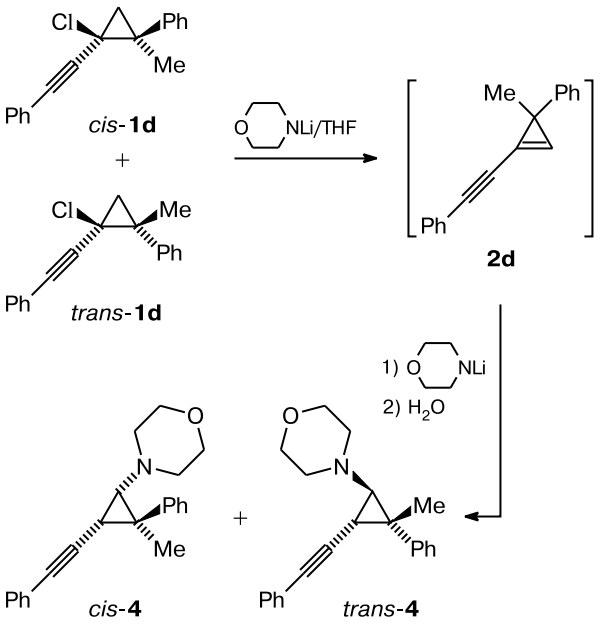
Scheme 2



To estimate the influence of the electronic and spatial structure of the substituent in the cyclopropane ring on the regio- and stereoselectivity of the reaction, we studied the behavior of asymmetrically substituted chloro(phenyl)-cyclopropanes **1d—f** in the transformations under discussion (Schemes 3, 4). According to NMR date, a room-temperature reaction of compound **1d** with lithium morpholide in THF affords only two (out of four possible) stereoisomers of morpholinocyclopropane **4** with the *cis*- and *trans*-arrangement of the morpholine and phenylethynyl substituents in a ratio of 1.0 : 1.2 and a total yield of 58% (see Scheme 3). This reaction seems to be highly sensitive to steric factors since its products include no isomers in which the morpholine and phenyl substituents are *cis* to each other.

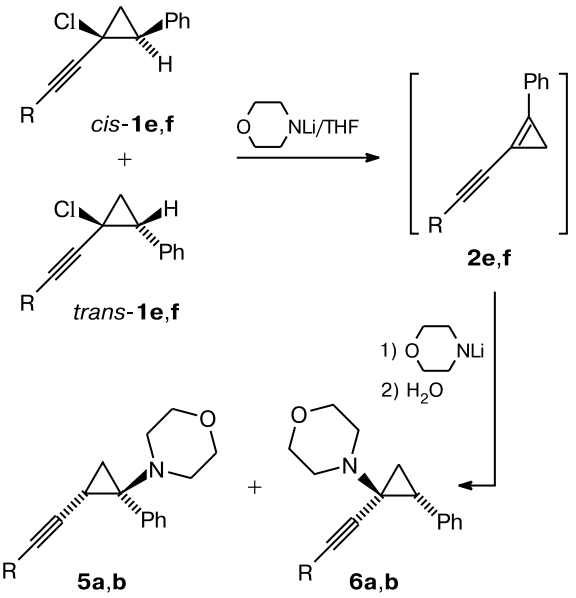
A reaction of 1-(*tert*-butylethynyl)-1-chloro-2-phenylcyclopropane **1e** with lithium morpholide gave a 1 : 2.5 mixture of two regioisomeric morpholinocyclopropanes **5a** and **6a** with different relative positions of the ethynyl and morpholine fragments in a total yield of 48% (see Scheme 4). Structurally similar products **5b** and **6b** were obtained in a total yield of 37% by a reaction of lithium morpholide with chlorocyclopropane **1f**. However, in this case, compound **5b**, in which the phenyl group and the

Scheme 3



morpholine ring are attached to the same C atom, is the major product of the reaction (**5b** : **6b** = 2 : 1). Note that −10 °C is a preferred reaction temperature since at 20 °C, the yields of amines **5b** and **6b** decrease sharply and many by-products are formed.

Scheme 4



R = Bu^t (**1e**, **2e**, **5a**, **6a**), Ph (**1f**, **2f**, **5b**, **6b**)

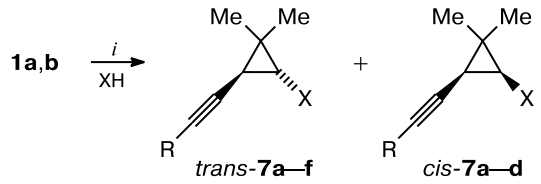
Apparently, the double bond in intermediate cyclopropenes **2e,f** is only slightly polarized because of the nearly

equal electronegativities of the alkynyl and phenyl substituents. As the result, compounds **2e,f** react with amide ions at both carbon atoms of the endocyclic double bond to give regioisomeric products **5** and **6**. As expected, the ratio **5** : **6** increases with an increase in the electronegativity of the substituent R (Ph > Bu^t).

Azole salts, which are weaker bases than lithium dialkylamides, do not react with compounds **1a—f** under the conditions studied. For instance, chlorocyclopropane **1a** remains unchanged in reactions with a fourfold excess of lithium imidazolide (room temperature, THF) or sodium imidazolide (100 °C, DMF).

However, in the presence of a stronger base (KOH in DMSO) used earlier for the synthesis of cyclopropenes from chlorocyclopropanes,[19] 1-alkynyl-1-chloro-2,2-dimethylcyclopropanes **1a—b** react with pyrazole, 2,5-dimethylpyrazole, imidazole, and 2-methylimidazole to produce the corresponding 1-(alk-1-ynyl)-2-diazolylcyclopropanes **7a—f** in 23—72% yields (Scheme 5, Table 2).

Scheme 5



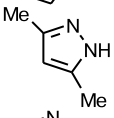
i. KOH/DMSO, 100 °C.

As in the reactions of alkynylcyclopropanes **1** with lithium dialkylamides, chlorocyclopropane **1b** containing a bulky electron-donating *tert*-butyl substituent forms the corresponding azolylcyclopropanes **7e,f** as *trans*-isomers only, while phenyl derivative **1a** yields a mixture of *trans*- and *cis*-isomers of cyclopropanes **7a—d** in a ratio from 3.2 : 1 to 7 : 1.

Using the system KOH—DMSO, we also obtained dialkylaminocyclopropanes **3b**, **3c**, and **3f** from chlorocyclopropane **1a** and diethylamine, morpholine, and piperidine in 30, 50, and 45% yields, respectively. However, cyclopropane **1b** does not form with morpholine the expected product **3i**, probably because of the low reactivity of cyclopropene **2b** toward the amines and its polymerization under these conditions.

To sum up, we developed the methods for the synthesis of various aminocyclopropanes containing an alkynyl substituent. The methods involve reactions of 1-alkynyl-1-chlorocyclopropanes with lithium dialkylamides in THF and with diazoles in the presence of KOH in DMSO. We demonstrated that the reactions studied follow an elimination—addition mechanism and found out how their regio- and stereoselectivity depends on the substituents in the starting compounds.

Table 2. Synthesis of 1-alkynyl-2-diazolylcyclopropanes **7a—f** from 1-(alk-1-ynyl)-1-chloro-2,2-dimethylcyclopropanes **1a,b** and diazoles (XH) in DMSO in the presence of KOH at 100 °C

Starting cyclopropane[a]	Diazole (XH)	t[b]/h	Product	Yield (%)[c]	*trans*/*cis* ratio[d]
1a		1	**7a**	52	3.2 : 1
		1	**7b**	58	4 : 1
		1	**7c**	69	4.5 : 1
		1	**7d**	72	7 : 1
1b		6	**7e**	38	—[e]
		6	**7f**	23	—[e]

[a] In all the experiments, the molar ratio starting cyclopropane (2 mmol) : diazole : KOH is 1 : 4 : 5.
[b] The reaction time.
[c] The products were isolated by column chromatography.
[d] Determined from the NMR spectra of the products isolated.
[e] The *trans*-isomer is formed only.

Experimental

The reagents and the products were analyzed by GLC on a Hewlett-Packard 5890 Series II instrument fitted with an HP-1 capillary column (30 000×0.153 mm) and a Hewlett-Packard 3396A automatic integrator. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200p spectrometer in $CDCl_3$ with $SiMe_4$ as the internal standard. Mass spectra were measured on a Finnigan MAT INCOS-50 GC-MS spectrometer.

The starting 1-(alk-1-ynyl)-1-chlorocyclopropanes **1** were prepared by cycloaddition (alk-1-ynyl)chlorocarbenes to appropriate alkenes (2-methylpropene, styrene, and 2-phenylprop-1-ene) as described earlier.[2,3]

Reactions of 1-(alk-1-ynyl)-1-chloro-2,2-dimethylcyclopropanes (1a—c) with lithium dialkylamides (general procedure). A 1.6 *M* solution of BuLi (5 mL, 8 mmol) in hexane was added at 0 °C to a solution of an appropriate secondary amine (8 mmol) in anhydrous THF (5 mL). To the resulting solution of lithium dialkylamide, a solution of (alk-1-ynyl)chlorocyclopropane (2 mmol) in THF (1 mL) was added. The reaction mixture was kept at the specified temperature (the reaction temperatures and times are given in Table 1). After the reaction was completed, water (5 mL) and ether (10 mL) were added and the organic layer was separated. Organic material from the aqueous layer was extracted with ether three times. The combined organic extracts were washed with water, dried with $MgSO_4$, and concentrated. The product was isolated from the residue by column chromatography in light petroleum—Et_2O (10 : 1). This procedure was used to obtain dimethyl(2,2-dimethyl-3-phenylethynylcyclopropyl)amine (**3a**), diethyl(2,2-dimethyl-3-phenylethynyl-

cyclopropyl)amine (**3b**), 4-(2,2-dimethyl-3-phenylethynylcyclopropyl)morpholine (**3c**), 1-(2,2-dimethyl-3-phenylethynylcyclopropyl)piperazine (**3d**), 1-(2,2-dimethyl-3-phenylethynylcyclopropyl)pyrrolidine (**3e**), 1-(2,2-dimethyl-3-phenylethynylcyclopropyl)piperidine (**3f**), benzyl(2,2-dimethyl-3-phenylethynylcyclopropyl)methylamine (**3g**), [3-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropyl]diethylamine (**3h**), 4-[3-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropyl]morpholine (**3i**), 1-[3-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropyl]piperazine (**3j**), 1-[3-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropyl]pyrrolidine (**3k**), benzyl[3-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropyl]methylamine (**3l**), and 4-(3-adamantylethynyl-2,2-dimethylcyclopropyl)morpholine (**3m**). The yields and the ratios of isomers of the products are given in Table 1. Their spectroscopic characteristics are presented in Tables 3 and 4.

Under similar conditions, aminocyclopropane **4** was obtained as a 1 : 1.2 mixture of *cis*- and *trans*-isomers in 58% yield from 1-chloro-2-methyl-2-phenyl-1-phenylethynylcyclopropane (**1d**, *trans* : *cis* = 2.3 : 1) and morpholine and a 1 : 2.5 mixture of products **5a** and **6a** was obtained in a total yield of 48% from 1-(*tert*-butylethynyl)-1-chloro-2-phenylcyclopropane **1e** and morpholine.

A reaction of cyclopropane **1f** with lithium morpholide was carried out at both −10 °C and room temperature. In the former case, a 2 : 1 mixture of products **5b** and **6b** was isolated by column chromatography; in the latter case, the final reaction mix-

Table 3. NMR spectra of 2-(alk-1-ynyl)-1-dialkylamino-3,3-dimethylcyclopropanes **3a—m**

Compound	H NMR ($CDCl_3$, 200 MHz, δ, *J*/Hz)					^{13}C NMR ($CDCl_3$, 50 MHz, δ)			
	R	R′, R″	2 Me at the ring (s, 3 H)	C≡CC<u>H</u> (d, 1 H)	R′R″—NC<u>H</u> (d, 1 H)	R	R′, R″	*cyclo*-C_3, 2 Me	C≡C
trans-**3a**	7.35—7.46 (m, 5 H, Ph)	2.35 (s, 6 H, NMe_2)	1.30; 1.32	1.29 (*J* = 3.8)	1.66 (*J* = 3.8)	124.2 (C(1)); 127.2, 128.0, 131.5	45.2 ($N(\underline{C}H_3)_2$);	19.1, 21.5, 22.1 (2 Me, <u>C</u>HC≡C); 26.9 (<u>C</u>Me_2); 60.4 (<u>C</u>HNMe_2)	78.9, 90.0
cis-**3a**	The same	2.40 (s, 6 H, NMe_2)	1.13; 1.38	1.40 (*J* = 7.0)	1.58 (*J* = 7.0)	124.5 (C(1)); 127.1, 127.9, 131.7	45.1 ($N(\underline{C}H_3)_2$)	15.7, 20.1, 25.9 (2 Me, <u>C</u>HC≡C); 24.5 (<u>C</u>Me_2); 56.2 (<u>C</u>HNMe_2)	80.1, 88.3
trans-**3b**	7.35—7.50 (m, 5 H, Ph)	1.13 (t, 6 H, $N(CH_2\underline{Me})_2$, *J* = 7.2); 2.68 (q, 4 H, $N(C\underline{H}_2Me)_2$, *J* = 7.2)	1.30; 1.31	1.29 (*J* = 4.2)	1.87 (*J* = 4.2)	124.3 (C(1)); 127.2, 128.1, 131.5	11.8 (2 Me); 47.9 (2 CH_2);	19.8, 21.8, 22.0 (2 Me, <u>C</u>HC≡C); 26.4 (<u>C</u>Me_2); 57.2 (<u>C</u>HNEt_2)	78.8, 90.3
trans-**3c**	7.30—7.46 (m, 5 H, Ph)	2.40—2.65 (m, 4 H, CH_2NCH_2); 3.68 (t, 4 H, CH_2OCH_2, *J* = 4.7)	1.28; 1.30	1.26 (*J* = 3.8)	1.74 (*J* = 3.8)	124.0 (C(1)); 127.2, 128.0, 131.4 (Ph)	53.1 ($\underline{C}H_2N\underline{C}H_2$); 66.8 ($\underline{C}H_2O\underline{C}H_2$)	19.0, 20.5, 22.0 (2 Me, <u>C</u>HC≡C); 26.4 (<u>C</u>Me_2); 58.6 (<u>C</u>HN)	78.9, 89.7
cis-**3c**	The same	2.55—2.81 (m, 4 H, CH_2NCH_2); 3.72 (t, 4 H, CH_2OCH_2, *J* = 4.7)	1.11; 1.32	1.38 (*J* = 6.9)	1.69 (*J* = 6.9)	124.5 (C(1)); 127.1, 128.0, 131.3 (Ph)	52.9 ($\underline{C}H_2N\underline{C}H_2$); 67.0 ($\underline{C}H_2O\underline{C}H_2$)	14.1, 19.4, 25.8 (2 Me, <u>C</u>HC≡C); 24.4 (<u>C</u>Me_2); 53.8 (<u>C</u>HN)	79.8, 88.2
trans-**3d**	7.14—7.40 (m, 5 H, Ph)	2.23 (br.s, 1 H, NH); 2.35—2.65 (m, 4 H, CH_2NCH_2); 2.80 (t, 4 H, CH_2NCH_2, *J* = 4.8)	1.20; 1.22	1.18 (*J* = 3.9)	1.68 (*J* = 3.9)	124.0 (C(1)); 127.2, 128.0, 131.4 (Ph)	45.7, 53.9 (4 $\underline{C}H_2$)	19.0, 20.5, 22.0 (2 Me, <u>C</u>HC≡C); 26.4 (<u>C</u>Me_2); 58.9 (<u>C</u>HN)	78.7, 90.0
cis-**3d**	The same	2.23 (br.s, 1 H, NH); 2.35—2.65 (m, 4 H, CH_2NCH_2); 2.83 (t, 4 H, CH_2NCH_2, *J* = 4.8)	1.03; 1.27	1.30 (*J* = 6.7)	1.64 (*J* = 6.7)	124.6 (C(1)); 127.0, 128.0, 131.3 (Ph)	45.8, 53.7 (4 $\underline{C}H_2$)	15.7, 19,4, 25,8 (2 Me, <u>C</u>HC≡C); 24.5 (<u>C</u>Me_2); 54.1 (<u>C</u>HN)	79.6, 88.4

(*continued*)

Table 3 (*continued*)

Compound	H NMR ($CDCl_3$, 200 MHz, δ, *J*/Hz)					^{13}C NMR ($CDCl_3$, 50 MHz, δ)			
	R	R′, R″	2 Me at the ring (s, 3 H)	C≡CC<u>H</u> (d, 1 H)	R′R″—N—C<u>H</u> (d, 1 H)	R	R′, R″	*cyclo*-C_3, 2 Me	C≡C
trans-**3e**	7.25—7.52 (m, 5 H, Ph)	1.70—1.85 (m, 4 H, CH_2CH_2); 2.62—2.75 (m, 4 H, CH_2NCH_2)	1.27; 1.31	1.27 (*J* = 3.8)	1.72 (*J* = 3.8)	124.4 (C(1)); 127.1, 128.1, 131.6 (Ph)	24.5 ($\underline{C}H_2\underline{C}H_2$); 54.9 ($\underline{C}H_2N\underline{C}H_2$)	19.2, 21.2, 22.4 (2 Me, $\underline{C}HC{\equiv}C$); 25.8 ($\underline{C}Me_2$); 59.8 ($\underline{C}HN$)	78.8, 90.2
cis-**3e**	7.25—7.52 (m, 5 H, Ph)	1.70—1.85 (m, 4 H, CH_2CH_2); 2.62—2.75 (m, 4 H, CH_2NCH_2)	1.12; 1.37	1.38 (*J* = 6.7)	1.64 (*J* = 6.7)	124.7 (C(1)); 126.9, 128.3, 131.8 (Ph)	23.8 ($\underline{C}H_2\underline{C}H_2$); 53.5 ($\underline{C}H_2N\underline{C}H_2$)	15.8, 19.9, 24.9 (2 Me, $\underline{C}HC{\equiv}C$); 24.3 ($\underline{C}Me_2$); 54.3 ($\underline{C}HN$)	79.3, 89.3
trans-**3f**	7.20—7.47 (m, 5 H, Ph)	1.41—1.64 (m, 6 H, 2 CH_2); 2.40—2.62 (m, 4 H, CH_2NCH_2)	1.26; 1.30	1.24 (*J* = 3.8)	1.69 (*J* = 3.8)	124.3 (C(1)); 127.2, 128.1, 131.5 (Ph)	24.5 (CH_2); 25.9 (2 CH_2); 54.3 (CH_2NCH_2)	19.1, 20.9, 22.3 (2 Me, $\underline{C}HC{\equiv}C$); 26.0 ($\underline{C}Me_2$); 59.6 ($\underline{C}HN$)	78.7, 90.5
cis-**3f**	The same	The same	1.11; 1.33	1.34 (*J* = 6.7)	1.65 (*J* = 6.7)	124.8 (C(1)); 127.0, 128.2, 131.6 (Ph)	26.1 (CH_2); 26.7 (2 CH_2); 54.0 (CH_2NCH_2)	15.7, 19.7, 24.7 (2 Me, $\underline{C}HC{\equiv}C$); 24.6 ($\underline{C}Me_2$); 54.8 ($\underline{C}HN$)	79.5, 88.9
trans-**3g**	2.27 (s, 3 H, Me); 3.69 (s, 2 H, $C\underline{H}_2Ph$); 7.30—7.50 (m, 10 H, 2 Ph)		1.29; 1.34	1.33 (*J* = 3.9)	1.89 (*J* = 3.9)	41.5 (Me); 61.8 ($\underline{C}H_2Ph$); 124.2 (C(1), PhC≡C); 127.0, 127.4, 128.2, 128.3, 129.2, 131.6 (2 Ph); 138.2 (C(1), Ph)		19.3, 21.7, 22.0 (2 Me, $\underline{C}HC{\equiv}C$); 27.5 ($\underline{C}Me_2$); 59.1 ($\underline{C}HN$)	79.0, 90.1
cis-**3g**	2.23 (s, 3 H, CH_3); 3.50 (d, 1 H, $C\underline{H}_2Ph$, *J* = 13.2); 3.96 (d, 1 H, $C\underline{H}_2Ph$, *J* = 13.2); 7.30—7.50 (m, 10 H, 2 Ph)		1.18; 1.41	1.32 (*J* = 6.6)	1.88 (*J* = 6.6)	41.2 (Me); 61.4 ($\underline{C}H_2Ph$); 124.1 (C(1), PhC≡C); 126.8, 127.2, 128.1, 128.5, 129.1, 131.7 (2 Ph); 139.1 (C(1), Ph)		15.9, 20.4, 25.9 (2 Me, $\underline{C}HC{\equiv}C$); 25.2 ($\underline{C}Me_2$); 54.8 ($\underline{C}HN$)	80.3, 88.6
trans-**3h**	1.19 (s, 9 H, Bu^t)	1.02 (t, 6 H, 3 Me, *J* = 7.2); 2.59 (q, 4 H, CH_2NCH_2, *J* = 7.2)	1.10; 1.14	0.97 (*J* = 4.0)	1.53 (*J* = 4.0)	27.5 ($\underline{C}Me_3$); 31.6 (3 Me)	11.8 (2 Me); 48.1 ($\underline{C}H_2N\underline{C}H_2$)	19.9, 21.2, 22.7 (2 Me, $\underline{C}HC{\equiv}C$); 24.8 ($\underline{C}Me_2$); 56.9 ($\underline{C}HN$)	78.2, 87.3
trans-**3i**	1.11 (s, 9 H, Bu^t)	2.32—2.56 (m, 4 H, CH_2NCH_2); 3.56 (t, 4 H, CH_2OCH_2, *J* = 4.6)	1.04; 1.10	0.88 (*J* = 3.8)	1.41 (*J* = 3.8)	27.3 ($\underline{C}Me_3$); 31.4 (3 Me)	53.2 ($\underline{C}H_2N\underline{C}H_2$); 66.8 ($\underline{C}H_2O\underline{C}H_2$)	19.1, 19.7, 21.7 (2 Me, $\underline{C}HC{\equiv}C$); 24.9 ($\underline{C}Me_2$); 58.2 ($\underline{C}HN$)	77.7, 87.2
trans-**3j**	1.12 (s, 9 H, Bu^t)	1.78 (br.s, 1 H, NH); 2.30—2.52 (m, 4 H, 2 CH_2); 2.75 (t, 4 H, 2 CH_2, *J* = 4.9)	1.03; 1.11	0.87 (*J* = 3.8)	1.39 (*J* = 3.8)	27.4 ($\underline{C}Me_3$); 31.5 (3 Me)	45.9 (2 CH_2); 54.2 (2 CH_2)	19.1, 20,0, 21.8 (2 Me, $\underline{C}HC{\equiv}C$); 24.9 ($\underline{C}Me_2$); 58.6 ($\underline{C}HN$)	77.8, 87.1
trans-**3k**	1.16 (s, 9 H, Bu^t)	1.66—1.75 (m, 4 H, CH_2CH_2); 2.50—2.61 (m, 4 H, CH_2NCH_2)	1.07; 1.10	0.99 (*J* = 3.7)	1.40 (*J* = 3.7)	27.5 ($\underline{C}Me_3$); 31.5 (3 Me)	23.8 ($\underline{C}H_2\underline{C}H_2$); 53.7 ($\underline{C}H_2N\underline{C}H_2$)	19.5, 20.6, 21.8 (2 Me, $\underline{C}HC{\equiv}C$); 24.6 ($\underline{C}Me_2$); 56.9 ($\underline{C}HN$)	78.1, 87.1
trans-**3l**	1.26 (s, 9 H, Bu^t)	2.21 (s, 3 H, Me); 3.65 (s, 2 H, $C\underline{H}_2Ph$); 7.30—7.50 (m, 5 H, Ph)	1.18; 1.27	1.08 (*J* = 3.8)	1.52 (*J* = 3.8)	27.6 ($\underline{C}Me_3$); 31.6 (3 Me)	41.6 (Me); 61.9 ($\underline{C}H_2Ph$); 127.0, 128.1, 129.4 (Ph); 138.3 (C(1), Ph)	19.4, 21.2, 21.9 (2 Me, $\underline{C}HC{\equiv}C$); 26.2 ($\underline{C}Me_2$); 58.6 ($\underline{C}HN$)	78.0, 87.5

(*continued*)

Table 3 (*continued*)

Compound	H NMR ($CDCl_3$, 200 MHz, δ, *J*/Hz)					^{13}C NMR ($CDCl_3$, 50 MHz, δ)			
	R	R′, R″	2 Me at the ring (s, 3 H)	C≡CC<u>H</u> (d, 1 H)	R′R″—N<u>C</u>H (d, 1 H)	R	R′, R″	*cyclo*-C_3, 2 Me	C≡C
trans-**3m**	1.60—1.70 (m, 6 H, 3 CH_2); 1.75—1.84 (m, 6 H, 3 CH_2); 1.90—1.98 (m, 3 H, 3 CH)	2.38—2.62 (m, 4 H, CH_2NCH_2); 3.61 (t, 4 H, CH_2OCH_2, *J* = 4.7)	1.09; 1.17	0.94 (*J* = 3.8)	1.45 (*J* = 3.8)	28.1 (3 CH); 29.6 (C(1)); 36.5 (3 CH_2), 43.5 (3 CH_2)	53.4 ($\underline{C}H_2N\underline{C}H_2$); 67.0 ($\underline{C}H_2O\underline{C}H_2$)	19.2, 20.1, 21.9 (2 Me, <u>C</u>HC≡C); 25.0 (<u>C</u>Me_2); 58.4 (<u>C</u>HN)	78.1, 87.5

ture contained many by-products (NMR data) and no target compounds were isolated.

***trans*-3-Methyl-1-morpholino-3-phenyl-2-phenylethynylcyclopropane (*trans*-4).** ^1H NMR, δ: 1.63 (s, 3 H, Me); 1.67 (d, 1 H, CH_2, *J* = 3.2 Hz); 2.44 (d, 1 H, CH_2, *J* = 3.2 Hz); 2.42—2.97 (m, 4 H, CH_2NCH_2); 3.81 (t, 4 H, CH_2NCH_2, *J* = 4.5 Hz); 7.05—7.50 (m, 10 H, 2 Ph). ^{13}C NMR, δ: 21.1, 21.4 (Me, C≡C<u>C</u>H); 36.5 (<u>C</u>MePh); 53.3 ($\underline{C}H_2N\underline{C}H_2$); 67.1 ($\underline{C}H_2O\underline{C}H_2$); 81.0, 87.2 (C≡C); 123.8 (C(1), <u>Ph</u>C≡C); 126.6, 127.4, 128.0, 128.2, 129.3, 131.2 (2 Ph); 145.8 (C(1), Ph). MS, *m/z*: 317 $[M^+]$.

***cis*-3-Methyl-1-morpholino-3-phenyl-2-phenylethynylcyclopropane (*cis*-4).** ^1H NMR, δ: 1.68 (s, 3 H, Me); 2.00 (d, 1 H, CH_2, *J* = 7.2 Hz); 2.25 (d, 1 H, CH_2, *J* = 7.2 Hz); 2.42—2.97 (m, 4 H, CH_2NCH_2); 3.80 (t, 4 H, CH_2NCH_2, *J* = 4.5 Hz); 7.05—7.50 (m, 10 H, 2 Ph). ^{13}C NMR, δ: 17.1, 20.0 (Me, C≡C<u>C</u>H); 33.4 (<u>C</u>MePh); 52.9 ($\underline{C}H_2N\underline{C}H_2$); 66.8 ($\underline{C}H_2O\underline{C}H_2$); 81.6, 89.5 (C≡C); 124.2 (C(1), <u>Ph</u>C≡C); 126.5, 127.5, 127.8, 128.3, 128.6, 131.6 (2 Ph); 148.8 (C(1), Ph). MS, *m/z*: 317 $[M^+]$.

Table 4. Mass spectra and elemental analysis data for compounds **3a—m**

Compound	MS, *m/z*	Found / Calculated (%)		
		C	H	N
trans-**3a**,	213 $[M]^+$	<u>84.38</u>	<u>9.05</u>	<u>6.42</u>
cis-**3a**		84.46	8.98	6.57
trans-**3b**	241 $[M]^+$	<u>84.41</u>	<u>9.68</u>	<u>5.63</u>
		84.59	9.60	5.80
trans-**3c**,	255 $[M]^+$	<u>79.85</u>	<u>8.19</u>	<u>6.21</u>
cis-**3c**		79.96	8.29	6.27
trans-**3d**,	254 $[M]^+$	<u>80.12</u>	<u>8.70</u>	<u>10.89</u>
cis-**3d**		80.27	8.72	11.01
trans-**3e**,	239 $[M]^+$	<u>85.32</u>	<u>8.69</u>	<u>5.71</u>
cis-**3e**		85.30	8.84	5.85
trans-**3f**,	253 $[M]^+$	<u>85.23</u>	<u>9.18</u>	<u>5.42</u>
cis-**3f**		85.32	9.15	5.53
trans-**3g**,	289 $[M]^+$	<u>86.98</u>	<u>8.05</u>	<u>4.75</u>
cis-**3g**		87.15	8.01	4.84
trans-**3h**	221 $[M]^+$	<u>81.42</u>	<u>12.39</u>	<u>6.15</u>
		81.38	12.29	6.33
trans-**3i**	235 $[M]^+$	<u>76.42</u>	<u>10.76</u>	<u>5.99</u>
		76.55	10.71	5.95
trans-**3j**	235 $[M]^+$	<u>76.96</u>	<u>11.03</u>	<u>11.87</u>
		76.87	11.18	11.95
trans-**3k**	219 $[M]^+$	<u>82.25</u>	<u>11.42</u>	<u>6.21</u>
		82.13	11.49	6.39
trans-**3l**	269 $[M]^+$	<u>84.41</u>	<u>10.23</u>	<u>5.36</u>
		84.70	10.10	5.20
trans-**3m**	313 $[M]^+$	<u>80.59</u>	<u>9.85</u>	<u>4.96</u>
		80.46	9.97	5.10

2-(3,3-Dimethylbut-1-ynyl)-1-morpholino-1-phenylcyclopropane (5a). ^1H NMR, δ: 1.00 (s, 9 H, Bu^t); 1.23—1.44 (m, 2 H, CH_2); 1.77 (dd, 1 H, C≡CC<u>H</u>, *J* = 9.3 Hz, *J* = 5.8 Hz); 2.50—2.59 (m, 4 H, CH_2NCH_2); 3.57—3.65 (m, 4 H, CH_2OCH_2); 7.15—7.4 (m, 5 H, Ph). ^{13}C NMR, δ: 15.9 (C≡C<u>C</u>H); 23.9 (CH_2); 27.1 (<u>C</u>Me_3); 30.7 (3 Me); 54.6 (Ph<u>C</u>, *cyclo*-C_3H_3); 49.7 ($\underline{C}H_2N\underline{C}H_2$); 67.1 ($\underline{C}H_2O\underline{C}H_2$); 78.8, 89.2 (C≡C); 127.1, 127.2, 132.0 (Ph); 132.7 (C(1), Ph). MS, *m/z*: 283 $[M^+]$.

1-Morpholino-1-phenyl-2-phenylethynylcyclopropane (5b). ^1H NMR, δ: 1.13 (dd, 1 H, CH_2, *J* = 5.9 Hz, *J* = 4.1 Hz); 1.38 (dd, 1 H, CH_2, *J* = 9.4 Hz, *J* = 4.1 Hz); 1.91 (dd, 1 H, C≡CC<u>H</u>, *J* = 9.4 Hz, *J* = 5.9 Hz); 2.37—2.47 (m, 4 H, CH_2NCH_2); 3.50 (t, 4 H, CH_2OCH_2, *J* = 4.5 Hz); 7.0—7.4 (m, 10 H, 2 Ph). ^{13}C NMR, δ: 16.6 (C≡C<u>C</u>H); 24.4 (CH_2); 50.0 ($\underline{C}H_2N\underline{C}H_2$); 55.4 (Ph<u>C</u>, *cyclo*-C_3H_3); 67.2 ($\underline{C}H_2O\underline{C}H_2$); 80.8, 90.3 (C≡C); 123.8 (C(1), <u>Ph</u>C≡C); 127.3, 127.4, 127.6, 128.0, 131.2, 131.9 (2 Ph); 137.5 (C(1), Ph). MS, *m/z*: 303 $[M^+]$.

2-(3,3-Dimethylbut-1-ynyl)-2-morpholino-1-phenylcyclopropane (6a). ^1H NMR, δ: 1.05 (s, 9 H, Bu^t); 1.30 (dd, 1 H, CH_2, *J* = 7.2 Hz, *J* = 4.8 Hz); 1.39 (dd, 1 H, CH_2, *cyclo*-C_3H_3, *J* = 9.4 Hz, *J* = 4.8 Hz); 2.32 (dd, 1 H, PhC<u>H</u>, *J* = 9.4 Hz, *J* = 7.2 Hz); 2.70—2.78 (m, 4 H, CH_2NCH_2); 3.69—3.76 (m, 4 H, CH_2OCH_2); 7.15—7.4 (m, 5 H, Ph). ^{13}C NMR, δ: 22.4 (CH_2, *cyclo*-C_3H_3); 27.2 (<u>C</u>Me_3); 30.9 (3 Me); 33.0 (<u>C</u>HPh, *cyclo*-C_3H_3); 45.2 (C≡C<u>C</u>, *cyclo*-C_3H_3); 50.1 ($\underline{C}H_2N\underline{C}H_2$); 67.0 ($\underline{C}H_2O\underline{C}H_2$); 73.3, 95.3 (C≡C); 126.0, 127.5, 128.3 (Ph); 138.0 (C(1), Ph). MS, *m/z*: 283 $[M^+]$.

Table 5. NMR spectra of 2-(alk-1-ynyl)-1-diazolyl-3,3-dimethylcyclopropanes **7a—f**

Compound	^{1}H NMR ($CDCl_3$, 200 MHz, δ, *J*/Hz)					^{13}C NMR ($CDCl_3$, 50 MHz, δ)			
	R	X	2 Me at the ring (s, 3 H)	C≡CC<u>H</u> (d, 1 H)	XC<u>H</u> (d, 1 H)	R	X	*cyclo*-C_3, 2 Me	C≡C
trans-**7a**	7.20—7.45 (m, 5 H, Ph)	6.91 (br.s, 1 H, CH); 7.01 (br.s, 1 H, CH); 7.52 (br.s, 1 H, CH)	0.98, 1.39	1.92 (*J* = 4.0)	3.28 (*J* = 4.0)	122.9 (C(1)); 128.1, 128.2, 131.5	119.9, 128.0, 137.6 (3 CH)	19.8, 20.9, 21.2 (2 Me, <u>C</u>HC≡C); 26.0(<u>C</u>Me$_2$); 45.9 (<u>C</u>HN)	80.6, 86.4
cis-**7a**	The same	7.02 (br.s, 1 H, CH); 7.2—7.25* (m, 1 H, CH); 7.66 (br.s, 1 H, CH)	1.14, 1.26	1.93 (*J* = 7.4)	3.17 (*J* = 7.4)	122.8 (C(1)); 128.15, 129.0, 131.2	120.2, 127.8, 138.2 (2 CH)	16.9, 20.7, 25.2 (2 Me, <u>C</u>HC≡C); 25.1 (<u>C</u>Me$_2$); 41.7 (<u>C</u>HN)	84.0, 84.7
trans-**7b**	7.15—7.43 (m, 5 H, Ph)	2.34 (s, 3 H, Me); 6.72 (d, 1 H, CH, *J* = 1.4); 6.81 (d, 1 H, CH, *J* = 1.4)	0.93, 1.38	1.84 (*J* = 4.0)	3.08 (*J* = 4.0)	122.9 (C(1)); 127.8, 128.0, 131.5	13.2 (Me); 119.2, 126.6 (2 CH); 146.2 (<u>C</u>Me)	19.4, 20.8, 21.2 (2 Me, <u>C</u>HC≡C); 26.5(<u>C</u>Me$_2$); 46.0 (<u>C</u>HN)	80.6, 86.3
cis-**7b**	The same	2.39 (s, 3 H, Me); 6.82 (d, 1 H, CH, *J* = 1.4); 7.11 (d, 1 H, CH, *J* = 1.4)	1.12, 1.27	1.90 (*J* = 7.4)	3.00 (*J* = 7.4)	123.0 (C(1)); 127.8, 128.0, 131.2	13.4 (Me); 1 19.8, 125.9 (2 CH); 146.6 (<u>C</u>Me)	16.7, 20.5, 25.2 (2 Me, <u>C</u>HC≡C); 24.9 (<u>C</u>Me$_2$); 41.9 (<u>C</u>HN)	83.6, 84.8
trans-**7c**	7.20—7.45 (m, 5 H, Ph)	6.22 (dd, 1 H, CH, *J* = 2.3, *J* = = 1.9); 7.35—7.45* (m, 1 H, CH); 7.49 (dd, 1 H, CH, *J* = 1.8, *J* = 0.7)	0.96, 1.42	2.21 (*J* = 3.9)	3.53 (*J* = 3.9)	123.2 (C(1)); 127.5, 128.1, 131.4	105.4, 130.0, 139.3 (3 CH)	19.4, 20.7, 20.8 (2 Me, <u>C</u>HC≡C); 26.7 (<u>C</u>Me$_2$); 50.3 (<u>C</u>HN)	80.2, 87.0
cis-**7c**	The same	6.19 (dd, 1 H, CH, *J* = 2.3, *J* = 1.9); 7.35—7.45* (m, 1 H, CH); 7.52 (dd, 1 H, CH, *J* = 1.8, *J* = 0.7)	1.17, 1.21	1.93 (*J* = 7.1)	3.40 (*J* = 7.1)	122.6 (C(1)); 127.9, 131.0, 131.2	104.4, 130.0, 139.5 (3 CH)	16.7, 20.6, 25.1 (2 Me, <u>C</u>HC≡C); 25.9 (<u>C</u>Me$_2$); 45.9 (<u>C</u>HN)	83.6, 85.6
trans-**7d**	7.20—7.45 (m, 5 H, Ph)	2.20 (s, 3 H, Me); 2.22 (br.s, 3 H, Me); 5.81 (br.s, 1 H, CH)	0.94, 1.41	2.43 (*J* = 3.9)	3.22 (*J* = 3.9)	123.5 (C(1)); 127.6, 128.1, 131.5	11.0, 13.5 (2 Me); 105.4 (CH); 140.5, 146.9 (2 <u>C</u>Me)	19.2, 20.5, 20.8 (2 Me, <u>C</u>HC≡C); 26.7(<u>C</u>Me$_2$); 48.6 (<u>C</u>HN)	80.0, 87.6
cis-**7d**	The same	2.25 (br.s, 3 H, Me); 2.38 (br.s, 3 H, Me); 5.78 (br.s, 1 H, CH)	1.30, 1.39	1.90 (*J* = 7.0)	3.16 (*J* = 7.0)	123.9 (C(1)); 127.4, 128.3, 131.3	11.4, 13.6 (2 Me); 105.0 (CH); 142.1, 147.3 (2 <u>C</u>Me)	18.2, 22.0, 25.8 (2 Me, <u>C</u>HC≡C); 25.3 (<u>C</u>Me$_2$); 44.7 (<u>C</u>HN)	82.3, 86.2
trans-**7e**	1.20 (s, 9 H, 3 Me)	6.19 (dd, 1 H, CH, *J* = 2.3, *J* = =1.8); 7.38 (d, 1 H, CH, *J* = 2.3); 7.45 (br.d, 1 H, CH, *J* = 1.8)	0.86, 1.29	1.92 (*J* = 3.9)	3.31 (*J* = 3.9)	27.4 (<u>C</u>Me$_3$); 31.2 (3 Me)	105.2, 130.0, 139.4 (3 CH)	19.5, 20.5, 20.7 (2 Me, <u>C</u>HC≡C); 25.7 (<u>C</u>Me$_2$); 50.3 (<u>C</u>HN)	75.4, 89.1
trans-**7f**	1.20 (s, 9 H, 3 Me)	2.34 (s, 3 H, Me); 6.73 (d, 1 H, CH, *J* = 0.9); 6.81 (d, 1 H, CH, *J* = 0.9)	0.89, 1.30	1.62 (*J* = 4.0)	2.91 (*J* = 4.0)	27.4 (<u>C</u>Me$_3$); 31.2 (3 Me)	13.3 (Me); 119.4, 126.5 (2 CH); 146.1 (<u>C</u>Me)	19.5, 20.7, 20.8 (2 Me, <u>C</u>HC≡C); 25.5 (<u>C</u>Me$_2$); 46.0 (<u>C</u>HN)	74.5, 89.6

* Overlap with the signals for the Ph group.

Table 6. Mass spectra and elemental analysis data for compounds **7a—f**

Compound	MS, *m/z*	Found / Calculated (%)		
		C	H	N
trans-**7a**,	236 $[M]^+$	81.13	6.89	11.61
cis-**7a**		81.32	6.82	11.85
trans-**7b**,	250 $[M]^+$	81.63	7.15	11.31
cis-**7b**		81.56	7.25	11.19
trans-**7c**,	236 $[M]^+$	81.53	6.65	11.78
cis-**7c**		81.32	6.82	11.85
trans-**7d**,	264 $[M]^+$	81.89	7.73	10.42
cis-**7d**		81.78	7.63	10.60
trans-**7e**	216 $[M]^+$	77.65	9.46	12.73
		77.73	9.32	12.95
trans-**7f**	230 $[M]^+$	78.29	9.75	12.02
		78.21	9.63	12.16

2-Morpholino-1-phenyl-2-phenylethynylcyclopropane (6b). ^{1}H NMR, δ: 1.14 (dd, 1 H, CH_2, J = 7.5 Hz, J = 4.2 Hz); 1.41 (dd, 1 H, CH_2, *cyclo*-C_3H_3, J = 9.1 Hz, J = 4.2 Hz); 2.36 (dd, 1 H, PhC<u>H</u>, J = 9.1 Hz, J = 7.5 Hz); 2.70—2.78 (m, 4 H, CH_2NCH_2); 3.62 (t, 4 H, CH_2OCH_2, J = 4.5 Hz); 7.0—7.4 (m, 10 H, 2 Ph). ^{13}C NMR, δ: 22.7 (CH_2, *cyclo*-C_3H_3); 33.7 (<u>C</u>HPh, *cyclo*-C_3H_3); 45.8 (C≡C<u>C</u>, *cyclo*-C_3H_3); 50.3 (<u>C</u>H_2N<u>C</u>H_2); 67.1 (<u>C</u>H_2O<u>C</u>H_2); 85.5, 86.6 (C≡C); 123.2 (C(1), <u>Ph</u>C≡C); 126.4, 127.8, 128.3, 130.6, 131.4, 132.4 (2 Ph); 136.0 (C(1), Ph). MS, *m/z*: 303 $[M^+]$.

Reaction of aminocyclopropane 3e with lithium morpholide. A 1.6 *M* solution of BuLi (5 mL, 8 mmol) in hexane was added at 0 °C to a solution of morpholine (870 mg, 10 mmol) in anhydrous THF (10 mL). To the resulting solution a solution of aminocyclopropane **3e** (*trans* : *cis* = 3.2 : 1; 480 mg, 2 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. After the reaction was completed, water (5 mL) and ether (10 mL) were added and the organic layer was separated. Organic material from the aqueous layer was extracted with ether three times. The combined organic extracts were washed with water, dried with $MgSO_4$, and concentrated. The liquid residue contained the starting reagent **3e** (*trans* : *cis* = 3 : 1) and cyclopropane **3c** (*trans* : *cis* = 2.8 : 1) in a ratio of 1 : 3.5 and no other compounds at all (NMR and GLC data).

Synthesis of 2-alkynyl-1-diazolylcyclopropanes (7a—f) by reactions of 1-(alk-1-ynyl)-1-chloro-2,2-dimethylcyclopropanes 1a—c with diazoles in DMSO in the presence of KOH (general procedure). Powdered KOH (560 mg, 10 mmol) was added to a solution of an appropriate diazole (8 mmol) in anhydrous DMSO (10 mL). Then a solution of chlorocyclopropane (2 mmol) in DMSO (2 mL) was added. The reaction mixture was stirred at 100 °C (the reaction time is specified in Table 2). Then water (20 mL) and diethyl ether (20 mL) were added and the organic layer was separated. Organic material from the aqueous layer was extracted with ether (20 mL). The combined organic extracts were washed with water three times, dried with $MgSO_4$, and concentrated. The product was isolated from the residue by column chromatography (dichloromethane—acetonitrile, 10 : 1—1 : 1). This procedure was used to obtain 1-(2,2-dimethyl-3-phenylethynylcyclopropyl)-1*H*-imidazole (**7a**), 1-(2,2-dimethyl-3-phenylethynylcyclopropyl)-2-methyl-1*H*-imidazole (**7b**), 1-(2,2-dimethyl-3-phenylethynylcyclopropyl)-1*H*-pyrazole (**7c**), 1-(2,2-dimethyl-3-phenylethynylcyclopropyl)-3,5-dimethyl-1*H*-pyrazole (**7d**), 1-[3-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropyl]-1*H*-pyrazole (**7e**), and 1-[3-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropyl]-2-methyl-1*H*-imidazole (**7f**). The yields and ratios of isomers of products **7** are given in Table 2. Their spectroscopic characteristics are presented in Tables 5 and 6.

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