Organocopper reagents undergo conjugate addition to (1,3-diphenyl- and (1-methyl-3-phenyl-2-propynylidene)morpholinium triflates 1a and 1b. The resulting morpholinoallenes can be isolated if the allenic unit bears no CH substituent. Allenes bearing a R^1R^2 CH substituent at C-3 can be isolated in some cases; their thermal isomerization yields 4-(1,3-diphenyl-1,3-alkadienyl)morpholines 9. Allenes resulting from salt 1b spontaneously isomerize to 2-morpholino-1,3-butadienes 12. Reaction of allyl copper with 1a yields 4-[(3Z and 3E)-1,3-diphenyl-1,3,5-hexatrienyl]morpoline (8).

(3-Phenyl-2-propynylidene)morpholinium triflates 1 (R^1 = Ph, Me) are easily obtained from the appropriate enaminoketone and triflic anhydride in two steps. The resonance-stabilized cations display ambident behavior towards nucleophiles; bond connection can either occur at the iminium carbon atom to form propargymorpholines 2 or at the acetylenic position to form morpholinoallenes 3 (Scheme 1). Either possibility has been realized with heteronucleophiles such as amines, thiols, and their respective anions. Furthermore, we have already reported in formaldehyde that organo-, silyl-, and stannylicuprates add to 1 in a conjugate manner to form morpholinoallenes 5, whereas organolithium and Grignard reagents yield propargymorpholines 4 predominantly or exclusively.

So far, diaalkylaminoallenes constitute a rather small and little-known subset of the class of electron-rich allenes. Presumably, this is due in part to the low stability of the unsubstituted diaalkylaminoallenes (such as dimethylamino-6,7 diethylamino-8, and morpholinoallene-6,7), which are prone to dimerization and polymerization. Diallylallenes bearing a R^1R^2 substituent at C-1 or C-3 have a tendency to isomerize, by a formal 1,3-hydrogen shift to the central allenic carbon atom, to 2-or 1-diaalkylamino-1,3-butadienes; this reaction occurs readily in basic media and at elevated temperatures.

The conjugate addition of organocopper reagents to 4-(2-propynylidene)morpholinium salts 1 offers the opportunity to synthesize highly substituted and functionalized morpholinoallenes. In this paper, we report on scope and limitation of this novel synthesis. The 1,4-addition of organocopper reagents [including organocopper compounds (RCu), lower-order and higher-order organocuprates, Grignard reagents in the presence of catalytic or stoichiometric amounts of copper(I) salts] has been widely used in organic synthesis. Similarly, the S_n2-type addition of the same reagents to propargylic compounds (R^1 R^2 CX−C≡C−X being a leaving group) has been used to synthesize a broad range of allenes. Since 4-(2-propynylidene)morpholinium cations closely resemble the two organic substrates mentioned except for the full positive charge, a similar reactivity towards organocopper reagents was anticipated. In fact, when salt 1a is allowed to react with the higher-order cyanocuprates 6a,c,e,f, prepared in situ from organolithium and copper(I) cyanide in a 2:1 ratio, morpholinoallenes 7a,c,e,f are obtained as the only isolable products (Scheme 2, Table 1). Analogously, reaction of 1a with the lower-order cuprate (s-Bu)3CuLi (6b) (a Gilman reagent), prepared from two equivalents of sec-butyllithium and one equivalent of copper(I) bromide, or with (CH_2=CH)_2CuMgBr (6d) [obtained from two equivalents of vinylmagnesium bromide and one equivalent of copper(I) cyanide], provided morpholinoallenes 7b and 7d, respectively. By the same strategy, higher-order silyl- and stannylicuprates 6g–i were used to synthesize 1-morpholino-3-silyl (or 3-stannylic)allenes 7g–i by small variations of the reaction temperature (Table 1), the yields of 7g,h could be improved as compared to our published procedure. Table 1 illustrates the generality of our synthesis of morpholinoallenes, in that sp^2, sp^3- and sp-centered carbon nucleophiles as well as silyl and stannyl groups can all be delivered at the beta-acetylenic position of salt 1a. Steric hindrance at the nucleophile does not affect adversely the efficiency of the bond connection (7c,g–i).
### Table 1. Morpholinoallenes 7 Prepared

<table>
<thead>
<tr>
<th>Product</th>
<th>Cuprate 6</th>
<th>Reaction Conditions*</th>
<th>Yield (%)</th>
<th>mp (°C) (solvent)</th>
<th>Molecular Formulaa</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>Bu₂Cu(CN)Li₂</td>
<td>-70°C, 0.5 h → -20°C, 1 h, → r.t.</td>
<td>64</td>
<td>61</td>
<td>C₁₃H₁₇NO (333.5)</td>
</tr>
<tr>
<td>7b</td>
<td>s-Bu₂CuLi</td>
<td>-70°C, 0.5 h → -45°C, 1 h, → r.t.</td>
<td>72</td>
<td>oil</td>
<td>C₁₃H₁₇NO (333.5)</td>
</tr>
<tr>
<td>7c</td>
<td>t-Bu₂Cu(CN)Li₂</td>
<td>-70°C, 0.5 h → 0°C, 1 h, → r.t.</td>
<td>73</td>
<td>71 (MeCN)</td>
<td>C₁₃H₁₇NO (333.5)</td>
</tr>
<tr>
<td>7d</td>
<td>(CH₂=CH)₂CuMgBr</td>
<td>-70°C, 0.5 h → 0°C, 1 h, → r.t.</td>
<td>52</td>
<td>oil</td>
<td>C₁₃H₁₇NO (303.4)</td>
</tr>
<tr>
<td>7e</td>
<td>Ph₂Cu(CN)Li₂</td>
<td>-70°C, 0.5 h → 0°C, 1 h, → r.t.</td>
<td>53</td>
<td>80 (MeCN)</td>
<td>C₁₃H₁₇NO (353.5)</td>
</tr>
<tr>
<td>7f</td>
<td>(Ph=C=Cl)₂Cu(CN)Li₂</td>
<td>-70°C, 0.5 h → 0°C, 1 h, → r.t.</td>
<td>17</td>
<td>oilb</td>
<td>C₁₃H₁₇NO (380.0)</td>
</tr>
<tr>
<td>7g</td>
<td>(t-BuPh₂)₂Cu(CN)Li₂</td>
<td>-70°C, 0.5 h → 0°C, 1 h, → r.t.</td>
<td>67</td>
<td>123 (MeCN)</td>
<td>C₁₃H₁₇NO (515.8)</td>
</tr>
<tr>
<td>7h</td>
<td>(Ph₂Si)₂Cu(CN)Li₂</td>
<td>-70°C, 0.5 h → 0°C, 1 h, → r.t.</td>
<td>52</td>
<td>146</td>
<td>C₁₃H₁₇NO (555.8)</td>
</tr>
<tr>
<td>7i</td>
<td>(Ph₂Sn)₂Cu(CN)Li₂</td>
<td>-70°C, 0.5 h → 0°C, 1 h, → r.t.</td>
<td>31</td>
<td>149</td>
<td>C₁₃H₁₇NO (626.4)</td>
</tr>
</tbody>
</table>

*a Solvent: THF (for 7g–i); THF/hexane (for 7a–c,f); THF/Et₂O (for 7d); THF/cyclohexane/Et₂O (for 7e).
b Satisfactory microanalysis obtained for 7a-g (C ± 0.54, H ± 0.06, N ± 0.2 (2e: -0.46)); for microanalyses of 7g-i, Ref. 3.

### Table 2. Spectral Data for Morpholinoallenes 7a–f

<table>
<thead>
<tr>
<th>Product</th>
<th>IR * (cm⁻¹)</th>
<th>¹H-NMR (CDCl₃/TMS)</th>
<th>Other Signals</th>
<th>¹³C-NMR (CDCl₃/TMS)</th>
<th>Other Signals</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>1927/1960</td>
<td>2.78 (me) 3.75 (pseudo-t)</td>
<td>0.80 (t, CH₃), 1.00–1.80 (m, CH₂-CH₂, CH₃), 2.53 (t, =C–CH₂), 7.00–7.50 (m, Ph)</td>
<td>127.64</td>
<td>197.93, 121.10</td>
</tr>
<tr>
<td>7b</td>
<td>1926/1960</td>
<td>2.53–2.99 3.78 (pseudo-t)</td>
<td>0.76–1.90 (m, CH₂-CH₂, CH–CH₂), 7.06–7.60 (m, Ph)</td>
<td>127.77</td>
<td>197.99, 121.34</td>
</tr>
<tr>
<td>7c</td>
<td>1935</td>
<td>2.56–2.75 3.70 (pseudo-t)</td>
<td>1.11 (t, s-Bu), 7.10–7.43 (m, Ph)</td>
<td>124.4 or 124.1</td>
<td>195.9, 124.9 or 124.1</td>
</tr>
<tr>
<td>7d</td>
<td>1890/1945</td>
<td>2.79 (pseudo-t) 3.77 (pseudo-t)</td>
<td>5.25–5.28, 5.39–5.44 (AB part of ABX, =CH₁), 6.58 (X-part of ABX, =CH₁), 7.21–7.50 (m, Ph)</td>
<td>127.1</td>
<td>202.0, 116.0</td>
</tr>
<tr>
<td>7e</td>
<td>1905/1945</td>
<td>2.83 (pseudo-t) 3.76 (pseudo-t)</td>
<td>7.16–7.63 (m, Ph)</td>
<td>130.2</td>
<td>202.2, 118.7</td>
</tr>
<tr>
<td>7f</td>
<td>1880f</td>
<td>2.93 (pseudo-t) 3.83 (pseudo-t)</td>
<td>7.20–7.80 (m, Ph)</td>
<td>122.9</td>
<td>207.1, 101.0</td>
</tr>
</tbody>
</table>

*a KBr pellets (for 7a,c,e) or film (for 7b,d,f).
b 90 MHz (for 7a,b,e,f) or 400 MHz (for 7c,d).
c Two diastereomers in 1:1 ratio (according to ¹³C-NMR).

In contrast to unsubstituted dialkylallenoates (see introduction), morpholinoallenes 7 (except for 7f) show no tendency to oligomerize or polymerize. They are, however, sensitive to hydrolysis of their enamine function, and can therefore not be isolated or purified by column chromatography on silica gel. Their isolation is usually achieved by repeated extraction of the reaction mixture with pentane. Whereas the solid products so obtained can be purified by recrystallization, attempts to purify the oily allenes 7b,d,f by distillation results in thermal isomerization (7b,d; see below for 7b) or polymerization (for 7f); however, the latter allenes are already sufficiently pure according to their spectra and elemental analyses.

In the IR spectrum of 7a–f, the C=C=C asymmetric stretching vibration appears as a broad, weak or medium-strong absorption at ν = 1935–1890 cm⁻¹ (Table 2). In most cases, a distinct, less intense band is observed at higher wavenumbers (ca. 30–55 cm⁻¹), as well as a shoulder at lower wavenumbers. As expected, the
Asymmetric stretching vibration of the allenones bearing π substituents, 7d–f, is shifted to lower wavenumbers. In the 13C-NMR spectra (Table 2), the central allenic carbon atom appears at δ = 195.9–207.1. Since the substituents are such that their influence on the chemical shifts of this carbon atom is small (and in part of opposite sign), the δ values found are not much different from that of dimethylaminoallene (δ = 204.22).

Since the allene moiety of 7a–d,f is chiral, the CH₂ protons of the morpholine ring become diastereotopic. Provided that the morpholine ring is freely rotating and inverting, the 1H-NMR signal of NCH₂ is expected to have an AB pattern in which each line is split into a triplet by coupling with the OCH₂ protons (which are too far away from the chiral center to be magnetically inequivalent). This pattern is observed nicely in the spectrum of 7c.

In order to transfer an allyl group to propyne iminium ion 1a, we decided to utilize allyl copper rather than an allylcuprate. Although allyl copper reagents in general are rather unreactive in those coupling reactions usually carried out with “ate” complexes, allyl copper has been used repeatedly with good success (e.g. conjugate addition to propargyl esters, addition to imines). Furthermore, allyl copper reagents in the presence of chloro- or bromoethylene have only recently been found to add to α,β-unsaturated ketones cleanly and consistently in the 1,4-mode, in contrast to higher-order diallyl-cyanocuprates and simple diallylcuprates.

Addition of salt 1a to a suspension of allyl copper (prepared from equimolar amounts of allylmagnesium chloride and copper(I) bromide–dimethyl sulfide complex at −45 °C) in tetrahydrofuran produced, after work-up, 1-morpholino-1,3,5-hexatriene 8. According to 1H- and 13C-NMR spectra, only two isomers are present; based on the difference of δ values for 4-H, 5-H, and 2-H (δ = 0.22, 0.38, and 0.07 ppm, respectively) it can be concluded, that the 3,4-diastereomers are present (3Z/3E, 3:1). In the 13C-NMR spectrum, an upfield shift of the olefinic 2 position is observed, as expected (γ-effect) for the 3E-isomer (δ = −5.5 ppm).

Obviously, 1,3,5-hexatriene 8 is formed from 1-morpholino-1,2,5-hexatriene 7j by a spontaneous prototropic shift. The proton-activating influence of the vinyl group is certainly responsible for the reduced stability of 7j as compared to the other allenones bearing R₂R’CH substituents at C-3, 7a and 7b. However, the latter allenones are isomerized as well under thermal impact, and 1-morpholino-1,3-butadienes 9a,b are obtained. According to NMR spectra, at least three of the four possible diastereomers are formed for 9a (isomer ratio 47:42:11), whereas only two isomers are seen for 9b (67:33).

Mild hydrolysis converts the dienamines into β,γ-unsaturated ketones 10. Since virtually the same diastereomer ratios are found (Scheme 4) in 10a,b as in 9a (two major isomers) or 9b, respectively, it may be concluded that hydrolysis does not alter the configuration at the C-3–C-4 double bond of dienamines 9 and that only one (or mainly one, for 9a) C-1–C-2 diastereomer is present. The same conclusion has been reached for hexatriene 8, as discussed above. The structural assignment of the two isomers of 10a is based on NMR data, such as NOE experiments (irradiation at the resonance of =CH) and the observation of a significant upfield shift of δ(CO–CH₂) in (E)-(10a) (γ-effect). For 10b, it was assumed that the proton resonance of the olefinic β-substituents is shifted upfield when they are cis to the phenyl ring. This was also the case for δ(=CH) in (E)-10a, it implies that the phenyl ring is tilted against the olefinic plane. The effect of a shift reagent [Eu(dpm)]₃ on the NMR spectrum of the mixture of isomers confirmed the configurational assignment.

Scheme 2

Scheme 3

Scheme 4
The higher-order cyanocuprates 6c,e,g also undergo conjugate addition to the 1-methyl-substituted 4-(2-propynylidene)morpholinium salt 1b (Scheme 5). However, the expected morpholinoallenes 11 isomerize under the reaction conditions by a prototropic 1,3-shift, and the 2-morpholino-1,3-butadienes 12a–c are isolated (Table 3). [A minor byproduct, which was detected in the crude products obtained immediately after workup (1H-NMR: δ (Me) = 1.96) but had disappeared a few hours later, may be the allene 11c]. For 12a and 12c, diastereomers are possible; immediately after workup, isomer A is the major (for 12a) or exclusive (for 12c) diastereomer found.

Both 12aA and 12cA are transformed quantitatively to their respective isomers 12bB and 12cB even at room temperature (near or in solution, see experimental part). For sterically hindered, the latter isomers are expected to be more stable. Thus, the prototropic step 11 → 12A yields mainly the kinetically favored butadiene which is transformed subsequently into the thermodynamically favored diastereomer 12B. Since the isomerization 11 → 12 is likely to be a base-catalyzed process in which a second allene molecule acts as the base, a proton must be delivered at the central allenic carbon in a bimolecular reaction on the way to 12. Clearly, approach of the conjugate acid of 11 is less hindered from the side of the phenyl ring which is less bulky than tert-butyl or tert-butylidiphenylsilyl, and the butadiene isomer 12A is formed. The ease of the cis → trans isomerization (12A → 12B) is quite surprising. It is assumed that it occurs by a sequence of two conrotatory electrocyclic reactions (butadiene → cyclobutene → butadiene); an acid-catalyzed process is excluded based on the observation, that 12aA isomerizes at the same rate in benzene or chloroform solution. Thermal electrocyclizations of butadienes occur for highly substituted derivatives, and an equilibrium between a substituted butadiene and a cyclobutene maintained at room temperature is even more rare. Several monosubstituted 1-diakylaminocyclobutanes have been reported to be stable at room temperature and above, whereas in other cases, electrocyclic ring-opening has been observed at ca. 50–100°C. 2-Morpholino-1,3-butadienes 12a,b are likely to exist in a configuration close to s-cis, since a

![Scheme 5](image)

### Table 3. 2-Morpholino-1,3-butadienes 12a–c Prepared

<table>
<thead>
<tr>
<th>Product</th>
<th>Ratio A/B after work-up</th>
<th>Yield (%)</th>
<th>1H-NMR (CDCl₃/TMS)δ</th>
<th>13C-NMR (CDCl₃/TMS)δ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>after equilibration</td>
<td></td>
<td>Isomer A</td>
<td>Isomer B</td>
</tr>
<tr>
<td>12a</td>
<td>79:21 (3:97)</td>
<td>73d</td>
<td>1.19 (s, t-Bu, 2.97)</td>
<td>1.12 (s, t-Bu, 2.71)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(NCH₃), 3.71 (OCH₃),</td>
<td>(NCH₃), 3.57 (OCH₃),</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.98, 3.99 (2s, =CH=)</td>
<td>3.98, 3.87 (2s, =CH=)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.68 (pseudo-t, =CH)</td>
<td>6.00 (d, J = 0.8, =CH)</td>
</tr>
<tr>
<td>12b</td>
<td>53</td>
<td></td>
<td>2.86 (NCH₃), 3.43 (OCH₃), 4.10, 4.12 (2s, CH₃=), 6.43 (s, CH=), 7.24–7.46 (m, Ph)</td>
<td>48.9 (NCH₃), 66.0 (OCH₃), 92.5 (CH₃=), 126.2–130.3 (CH=, C=CH), 140.3, 143.5, 144.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1350, 1245, 1105, 690</td>
<td>=C=CH, C=CH, =C=CH, =C=CH, =C=CH</td>
</tr>
<tr>
<td>12c</td>
<td>&gt; 97:3 (3:97)</td>
<td>59d</td>
<td>0.76 (s, t-Bu, 2.53)</td>
<td>0.95 (s, t-Bu, 2.73)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(NCH₃), 3.20 (1H, =CH=), 3.57 (OCH₃), 3.90, 3.99 (2s, CH₃=), 3.86 (1H, =CH=), 6.83 (m, CH=)</td>
<td>19.0 (C=CH), 28.6 (C=CH), 48.8 (NCH₃), 66.4 (OCH₃), 92.7 (CH₃=), 125.7 (d), 127.5–129.2 (m, 1350, 1355, 1425, 1427, 1431 (s), 152.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.52 (s, CH=), 6.93–7.60 (m, Ph)</td>
<td></td>
</tr>
</tbody>
</table>

* Values are given for 12aB (film), 12bK (KBr pellet), and 12cB (film).

**a** 100.6 MHz spectra.

**b** 400 MHz spectra. The signals of NCH₃ and OCH₃ are pseudotriplets in all cases.
strong steric interaction between the morpholine ring and a substituent at C-4 should favor the s-trans configuration. 23 Thus, the termini of the 1,3-diene unit are already in a geometrical position suitable for electrolytic ring closure, a fact which explains the low activation energy for the isomerization process 12A → 12B.

The E or Z configurations of compounds 12a and 12c were deduced from 1H-NMR data (Table 3). In all cases, the phenyl ring at C-4 of the butadiene unit must be strongly tilted against the plane containing the C-3–C-4 double bond because of the bulky group R. Thus, 3-H in 12aA is expected to be shielded with respect to 3-H in 12aB; this is indeed observed (δ = −0.32). Conversely, since the s-cis conformation shown in Scheme 5 is assumed for both isomers and on steric grounds (see above), the olefinic protons at C-1 appear at higher field in 12aB, where they are in the shielding cone of the phenyl ring at C-1. For the pair 12ca/12cB, the olefinic proton at C-3 is shielded more when it is cis to the tert-butyldiphenylsilyl)group (12cB) rather than to the phenyl ring. This has been proven on an alkene closely related to 12c, where the constitution of one diastereomer could be established by X-ray analysis. 32

In conclusion, we have shown that the reaction of 4-(2-propynylene)morpholinium triflates with organocopper reagents is a versatile route to highly substituted and functionalized morpholinolamines. Allenes bearing a methyl group at C-1 cannot be isolated, since they rapidly isomerize to 2-morpholino-1,3-butenedienes. The stability of morpholinolamines bearing a R1R2CH substituent at C-3 towards prototropic isomerization is more balanced; however, quantitative rearrangement to 1-morpholino-1,3-butenedienes is only a matter of temperature.

We consider the synthesis of 8, 9, and 12 as a valuable addition to already existing strategies producing acyclic 1-dienamines [e.g. addition of sec-amines to α,β-unsaturated aldehydes 23 or ketones 24 (in the latter case, 2-dienamines may be formed instead), thermal reaction of propargyl alcohols with carbamidocetals 25] and 2-dienamines (e.g. mercury(II)-catalyzed addition of sec-amines to 3-buten-1-yne 36). Because of the incorporated enamine function, all three classes of title compounds are of interest for further synthetic transformations, especially addition of electrophiles and cycloaddition reactions (for reactions of 1- and 2-dienamines, see Ref. 24; for recent cycloaddition reactions of 2-dienamines, see Ref. 37).

All reactions (except for the hydrolyses) were carried out in rigorously dried glassware under an Ar atmosphere. THF and Et2O were dried (KOH), distilled over LiAlH4, and stored under Ar. Petroleum ether (distilled at 40–60°C) and toluene were refluxed with Na, distilled, and stored over molecular sieves (4 Å) under an Ar atmosphere. Melting points were determined in a copper block and are not calibrated. 1H-NMR spectra: Varian EM 390 (90 MHz) and Bruker AMX 400 (400 MHz), TMS as internal standard. 13C-NMR spectra: Bruker WP 200 (50.3 MHz) and Bruker AMX 400 (100.6 MHz), TMS as internal standard. IR spectra: Perkin-Elmer Infrared Spectrophotometer 397, Beckmann IR 20A. Microanalyses: Perkin-Elmer EA 240 and EA 2400.

Synthesis of Solutions of Organocuprates 6b– E 28

Lithium Di-sec-butylcuprate (1) (6b): Two equivalents of a solution of s-BuLi in cyclohexane/hexane (98:8, v/v) (1.3 M, 7.6 mL, 9.9 mmol) are added dropwise at −70°C to a magnetically stirred suspension of CuBr · Me2S (1 equiv, 1.01 g, 4.9 mmol) in THF (25 mL). The mixture is brought to −45°C, stirred for 30 min, and recooled to −70°C for further use.

Lithium Di-tert-butyl(cyclo)cuprate (1) (6c): A solution of t-BuLi (2 equiv) in hexane (1.5 M, 4.9 mL, 7.4 mmol) is added at −70°C to a magnetically stirred suspension of CuCN (0.33 g, 3.7 mmol) in THF (30 mL). The yellow mixture is brought to 0°C within 30 min. After 5 min at 0°C, a colorless solution has been formed which is cooled to −70°C for further use.

Magnesium Bromide (Divinyl)cuprate (1) (6d): A solution of (CH2=CH)2MgBr (2 equiv) in THF (1.0 M solution, 11.5 mL, 11.5 mmol) is added dropwise at −70°C to a magnetically stirred suspension of CuCN (1 equiv, 0.52 g, 5.80 mmol) in Et2O (10 mL). The mixture is brought to 0°C within 15 min, stirred for 3 min, and the brown suspension is recooled to −70°C for further use.

Lithium Cyano(diphenyl)cuprate (1) (6e): A solution of PhLi in cyclohexane/Et2O (70:30, v/v) (2 equiv, 2 M, 3.1 mL, 6.1 mmol) is added at 0°C to a magnetically stirred solution of CuCN (0.29 g, 3.2 mmol) in THF (25 mL). After 30 min at 0°C, a faintly yellow homogeneous solution is obtained, which is cooled to −70°C for further use.

Lithium Bis(phenylethynyl)cycano(cuprate (1)) (6f): To a solution of phenylecetylene (0.82 g, 8.0 mmol) in THF (20 mL), BuLi (1.6 M solution in hexane, 5 mL, 8.0 mmol) is added. After 30 min, the solution is cooled to 0°C, CuCN (3.7 g, 4.10 mmol) is added, and after stirring for 30 min, the solution is cooled to −70°C for further use.

4-(1,3-Diphenyl-1,2-heptadienyl)morpholine (7a); Typical Procedure: A solution of BuLi in hexane (1.6 M, 5.88 mL, 9.40 mmol) is added dropwise at −70°C to a magnetically stirred suspension of CuCN (1.01 g, 9.43 mmol) in THF (25 mL). The mixture is brought to −20°C within 30 min, stirred for 10 min, and the dark-brown solution is recooled to −70°C. A suspension of salt 1a (2.00 g, 4.70 mmol) in THF (25 mL) is gradually added. After additional stirring at −70°C for 30 min, the mixture is brought to −25°C, stirred for 1 h, and warmed to r.t. within 30 min. The solvent is removed at 0.003 mbar, and the residue is extracted with petroleum ether (3 × 65 mL). The combined extracts yield, after evaporation of the solvent, a yellow powder; yield: 1.00 g (64%); mp 61°C. C23H23NO calc. C 82.84 H 8.16 N 4.20 (333.5) found 82.3 8.1 4.0

Spectral data: Table 2.

Morpholinolamines 7b–i are prepared analogously (Table 1). The synthesis of 7e by this procedure has already been described. 3

4-(3Z and 3E)-1,3-Diphenyl-1,3,5-hexatrienyl)morpholine (8): A round-bottom flask is placed in an ice bath and charged with Mg turnings (3.85 g, 15.4 mmol), an i-Pr, and THF (30 mL). Allyl chloride (0.79 g, 10.4 mmol) is added dropwise. When the exothermic reaction is over, the mixture is filtered into a three-necked round-bottom flask cooled to −70°C. CuBr · Me2S (2.13 g, 10.4 mmol) is added in several portions, and the resulting yellow-brown suspension is then stirred at −45°C for 30 min. After recooling to −70°C, a suspension of salt 1a (2.00 g, 4.70 mmol) in THF (25 mL) is added. The mixture is brought to −45°C, stirred for 1 h, then allowed to come to r.t. within 30 min. The solvent is evaporated at 0.003 mbar, and the residue is extracted with petroleum ether (3 × 65 mL). After removing the solvent from the combined extracts, a viscous orange-colored oil is left, which cannot be purified further by column chromatography (hydrolysis) or distillation (polymerization): yield: 1.00 g (72%), diastereomer ratio: 32/3E = 3:1. A correct microanalysis was not obtained.

IR (film): ν = 1580, 1438, 1257, 1215, 1118, 695 cm−1.
1H-NMR (CDCl₃, 400 MHz): δ = 2.85/2.93 (NCH₂), 3.69/3.76 (OCH₂), 4.77/4.96 (dd, J = 10.0, 2.0 Hz, 6-H, cis to 5'-H), 4.90/5.08 (dd, J = 16.4, 2.0 Hz, 6'-H, trans to 5'-H), 5.38/5.45 (s, 2'-H), 5.90/6.13 (d, J = 11.2 Hz, 4'-H), 6.27/6.65 (dd, J = 16.4, 11.2 Hz, 5'-H). The first of the two values are obtained for a slat refers to the (3'S)-isomer.

13C-NMR (CDCl₃, 100.6 MHz): δ = 49.5/50.0 (NCH₂), 66.9 (OCH₂), 108.6/103.1 (C-2'), 115.0/116.2 (C-6'), 126.3/131.7 (C arom), C dref, 134.8/134.9 (d, C-4' or C-5'), 137.0/139.5 (s), 140.4/142.4 (s), 152.2/154.0 (C-1').

4-(1,3-Diphenyl-1,3-hexadienyl)morpholine (9a): A solution of 7a (0.50 g, 1.50 mmol) in toluene (25 mL) is heated for 1 h at 130 °C in a tightly closed thick-walled Schlenk tube. The solvent is removed at 25 °C/0.003 mbar, and the residual oil is subjected to bulb-to-bulb distillation at 230 °C/0.02 mbar; yellow oil, mixture of at least three diastereomers (isomer ratio determined by 1H-NMR: 47:42:11); yield: 0.49 g (98%).

C₁₉₂H₂₆N₂O calc. C 82.84 H 8.16 N 4.20 (333.5) found 82.7 8.0 3.8

IR (film): ν = 1603, 1448, 1120, 695 cm⁻¹.

1H-NMR (benzene-d₆, 400 MHz): δ = 0.82/0.62/0.93~1.12 (t, CH₃), 1.15/0.97/1.49 (mc, CH₂CH₃), 1.80~1.86/2.27/1.80~1.83 (mc, =C-CH₃), 2.78/2.87 (pseudo-t, NCH₂), 3.73/3.66/3.43 (pseudo-t, OCH₂), 5.50/5.17/5.92 (t, J = 7.4 Hz, =CH-CH₃), 5.31/5.26 (s, N-C=CH₂), 7.06~7.56 (m, PH). (Values are given for each isomer in the order of decreasing percentage; some signals of the third isomer are covered by one of the other two isomers. The following 13C-NMR data are presented in the same way.)

13C-NMR (benzene-d₆, 100.6 MHz): δ = 13.0/12.7 (CH₃), 21.2/21.8/21.6 (CH₂CH₃), 30.8/30.4/31.3 (CH₂CH₂CH₃), 49.2/48.6/48.1 (NCH₂), 66.2/66.0/66.3 (OCH₂), 103.1/108.2/105.0 (N-C=CH₂), 151.7/149.6/150.0 (N-C=CH). At 70 °C, the mixture is quantitatively transformed into the (3S)-isomer 12a, b; by bulb-to-bulb distillation at 170 °C/0.03 mbar, isomerization is incomplete. Yield 12a: 4.20 g (73%).

C₁₉₂H₂₆N₂O calc. C 79.66 H 9.28 N 5.16 (271.4) found 79.8 9.3 5.1

Spectral data: Table 3

2-Morpholin-4,4-diphenyl-1,3-butadiene (12b): To a magnetically stirred solution of 6c, prepared as described above from t-BuLi [24.9 mL (42.4 mmol) of a 1.7 M solution in hexane] and CuCN (2.0 g, 22.2 mmol) in THF (25 mL), is added gradually at 70 °C a suspension of salt 1b' (7.69 g, 21.2 mmol) in THF (25 mL). The dark-red suspension is brought to 10 °C within 30 min, stirred for 1 h, brought to r.t. (30 min) and stirred for 30 min. The solvent is removed at 0.003 mbar, and the residue is extracted with petroleum ether (3 × 65 mL). After removal of the solvent from the combined extracts at 0.003 mbar, a yellow-orange oil is left which consists of 12a and 12b (73:27). In solution (benzene or CHCl₃, 24 h, r.t. or 60 °C, 1 h), this mixture is quantitatively transformed into the (3S)-isomer 12a, b; by bulb-to-bulb distillation at 170 °C/0.03 mbar, isomerization is incomplete. Yield 12a: 4.20 g (73%).

C₉₈H₇₂NO calc. C 79.66 H 9.28 N 5.16 (271.4) found 79.8 9.3 5.1

Spectral data: Table 3

4-tert-Butyl(diphenylsilyl)-2-morpholin-4-phenyl-1,3-butadiene (12c): To a magnetically stirred solution of 6g, prepared from t-BuPh₂SiCl (5.68 g, 20.6 mmol), Li (0.83 g, 120.0 mmol), and CuCN (0.93 g, 10.3 mmol) in THF (25 mL), is added gradually at 70 °C a suspension of salt 1b' (3.00 g, 8.3 mmol) in THF (25 mL). The mixture is warmed to −10 °C within 30 min, stirred for 1 h, brought to r.t. and stirred for 30 min. The solvent is evaporated at 22 °C/0.003 mbar, and the residue is extracted with petroleum ether/Et₂O (2.5:1 v/v, 3 × 65 mL). The combined extracts are concentrated at 22 °C/0.003 mbar to a volume of ca 10 mL. After 12 h at −78 °C, the deposited yellow powder is quickly filtered off in a cooled funnel; yield: 0.75 g (53%); mp 70 °C.

C₉₈H₇₂NO calc. C 82.44 H 7.26 N 4.81 (291.4) found 82.7 7.3 5.0

Spectral data: Table 3
C_{60}H_{35}NOSi calc. C 78.93  H 7.73  N 3.07  
(456.5) found  78.2   7.5   2.1
Spectral data: Table 3

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(20) For a discussion of whether higher-order cyanocuprates, \( R_5Cu(CN)Li \), "are real or not", see:
(31) For other 2-morpholino-1,3-butadienes having s-cis conformation, see:
(32) Maas, G.; Mayer, T. unpublished work.
Opitz, G.; Merz, W. Liebig’s Ann. Chem. 1962, 652, 139.
(38) The following organocuprates have been synthesized in analogy to published procedures, except for the indicated changes: