Palladium(0)-Catalyzed Coupling Reactions of 2-Alkoxy-1-ethynylcyclopropanes with Aryl and Ethenyl Halides: Preparation of Cyclopropyl Substituted Ethynylarenes, Eneynes and Enediynes[1]

Gregory McGaffin, Armin de Meijere*
Institut für Organische Chemie der Georg-August-Universität Göttingen, Tammannstraße 2, D-37077 Göttingen, Germany

Received 25 October 1993

Dedicated to Professor Christoph Rückardt on the occasion of his 65th birthday

2-Alkoxy-1-ethynylcyclopropanes **1-R^1**, readily available in diastereo- and enantiopure form,[2,3] undergo facile palladium-catalyzed cross-coupling reactions with various mono- and oligohaloarenes **2(a–c)-X, 4, 6, 9, 12**, haloalkenes **14a–d** and (*E*/*Z*)-1,2-dihaloethenes [(*E*/*Z*)-**18-X**]. The *trans*- and *trans*/*cis*-(2-alkoxycyclopropyl)-ethynyl derivatives **3(a–c)-R^1, 5, 7, 10, 13, 15a–d** and (*E*)-**19(22)** were exclusively obtained in good to excellent yields. The coupling reaction thus opens the first direct access to configurationally uniform (2-alkoxycyclopropyl)ethynyl substituted arenes, and 2-alkoxycyclopropyl substituted eneynes and enediynes. Catalytic hydrogenation of ethynylarenes **3(a–c)-R^1, 10**, and **13** smoothly afforded the corresponding (*E*/*Z*)-[(2-alkoxycyclopropyl)ethenyl]arenes **24(a–c)-R^1, 25** and **26**, which are not directly accessible by palladium(0)-catalyzed coupling reactions of (*E*)-2-alkoxy-1-ethenylcyclopropanes with haloarenes.

Palladium(0)-catalyzed cross-coupling reactions have been developed into eminently important preparative methods during the past 20 years, and are now some of the simplest and most effective methods in forming new C–C bonds.[4] Among these, facile palladium-catalyzed alkynylations of haloarenes and haloalkenes have emerged as a powerful synthetic tool and have become a focus of major interest,[5] in particular due to their possible applications in the preparation of new liquid crystalline compounds (e.g. oligoethynylarenes)[6] and, more recently, antitumor antibiotics (enediynes).[7]

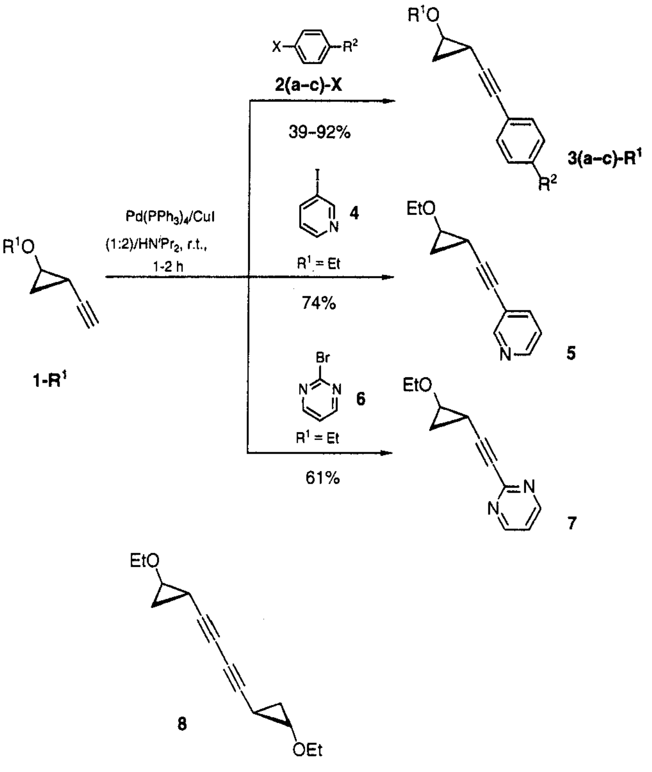
In pursuit of suitable synthetic approaches to model representatives of novel liquid crystalline ethynylarenes with configurationally uniform 2-alkoxycyclopropane wing groups, recently developed accesses[2,3] to stereopure *trans*-2-alkoxy-1-ethynylcyclopropanes **1-R^1** were employed, and the resulting materials subjected to palladium(0)-catalyzed coupling reactions with aryl and alkenyl halides under various conditions.

Aryl and Hetaryl Halide Coupling Reactions

trans-[(2-Alkoxycyclopropyl)ethynyl]arenes and -hetarenes **3(a–c)-R^1, 5** and **7** were easily obtained by applying a catalytic system consisting of $Pd(PPh_3)_4$ and CuI[8] (1 : 2) to a solution of one equivalent each of **1-R^1** and iodo- or bromo(het)arenes **2(a–c)-X, 4** and **6** in diisopropylamine (39–92%, Scheme 1 and Table 1). Yields were consistently better with iodo(het)arenes, as frequently observed. All reactions were performed at room temperature, i.e. under mild conditions as may be required for sensitive and fairly volatile (e.g. **1-Et**) ethynylcyclopropanes **1-R^1**, and were complete within 1 h. Diisopropylamine[9] proved to be superior to the more commonly used triethylamine, and 4-(*trans*-ethoxycyclopropylethynyl)biphenyl **(3b-Et)** was isolated in 92% yield.

A diastereomeric mixture of *trans*/*cis*-2-*tert*-butyldimethylsilyloxy-1-ethynylcyclopropane (**1-SiMe$_2$*t*-Bu**, *trans*/*cis* = 2 : 1) was coupled with iodobenzene **(2a-I)** under these conditions to give the *trans* and *cis* diastereomers of **3a-SiMe$_2$*t*-Bu** (85%), which were easily separated by column chromatography.

Similarly, **1-Et** was coupled with 3-iodopyridine **(4)** and 2-bromo-1,3-pyrimidine **(6)**, affording the *trans*-[(2-ethoxycyclopropyl)ethynyl]heteroarenes **5** (74%) and **7** (61%), respectively.[10]



Scheme 1. For details see Table 1

Table 1. Coupling of 2-Alkoxy-1-ethynylcyclopropanes **1-Et** and **1-SiMe$_2$*t*-Bu** with Aryl Halides **2, 4, 6** (see Scheme 1)

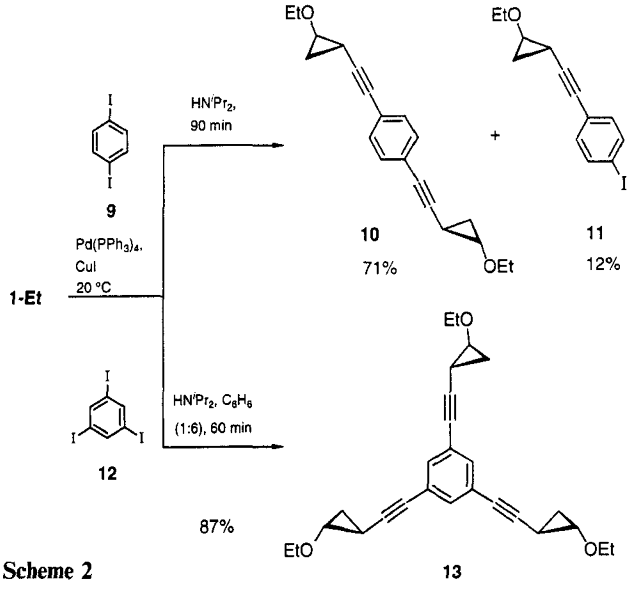
Starting Materials 1-R^1	Haloarene	X	R^2	Product 3-R^1	Yield (%)[a]
1-Et	**2a-I**	I	H	**3a-Et**	91
1-Et	**2b-I**	I	Ph	**3b-Et**	87 (92)
1-Et	**2c-Br**	Br	C_6H_4-*p*-Br	**3c-Et**	33 (39)
1-SiMe$_2$*t*-Bu[b]	**2a-I**	I	Ph	**3a-SiMe$_2$*t*-Bu**[b]	85
1-Et	**4**	I	–	**5**	74
1-Et	**6**	Br	–	**7**	61

[a] Yields in parentheses are based on consumed starting materials **2-X**.

[b] *trans*/*cis* mixture (2 : 1).

In triethylamine, compound **3b-Et**, the coupling product of **1-Et** with **2b-I**, was obtained in only 9 % yield besides 34 % of the terminal homocoupled bisacetylene **8**,[11] although the reaction had been carried out under inert gas (as in all performed reactions). The attempted $Pd(PPh_3)_4$ catalyzed cross-coupling[12] of *trans*-2-ethoxycyclopropylethynylzinc chloride with bromo- and iodobenzene (**2a-I**) gave lower yields of *trans*-[(2-ethoxycyclopropyl)ethynyl]benzene (**3a-Et**) (31 and 47 %, respectively), also accompanied by **8** (up to 10 % with bomobenzene and a trace with **2a-I**).

Symmetrical oligo(ethylnylaryl)benzenes have received considerable attention because of their recently discovered calamitic and nematodiscotic liquid crystalline properties.[13] In close analogy, therefore, the cross-coupling reactions of *trans*-2-ethoxy-1-ethynylcyclopropane (**1-Et**) was also carried out with symmetrical oligoiodobenzenes. Thus, the reaction of **1-Et** with 1,4-diiodobenzene (**9**) gave, after facile chromatographic separation from monoalkynylated **11** (12 %), the low melting bisalkynylated solid **10** (mp 29 °C) in 71 % isolated yield. An analogous treatment of 1,3,5-triiodobenzene (**12**) exclusively afforded the C_3-symmetrical 1,3,5-tris(*trans*-2-ethoxycyclopropylethynyl)benzene (**13**) in 87 % isolated yield (Scheme 2).



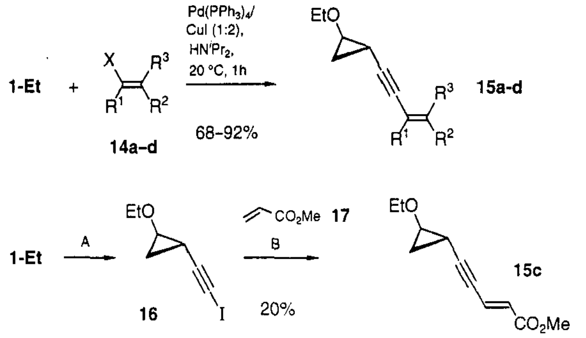
Scheme 2

Alkenyl Halide Coupling Reactions

The forementioned reaction conditions were also successfully applied to couple **1-Et** with bromoalkenes **14a–c** and iodoalkene **14d**[5,14] to configurationally uniform 2-alkoxycyclopropyl substituted eneynes **15a–d** (Scheme 3, Table 2).

In these cases yields were equally high with bromo- as well as iodoalkenes, and moreover, virtually no homocoupled **8** was observed. In fact, the highest yield (92 %) was obtained for (*E*)-[4-(*trans*-2-ethoxycyclopropyl)but-1-en-3-ynyl]benzene (**15a**) from **1-Et** and β-bromostyrene (**14a**). Even 1-bromocyclooct-1-ene (**14b**) and **1-Et** gave the eneyne **15b** in good yield (68 %).

Eneyne **15c** was alternatively prepared by the palladium(II)-catalyzed cross-coupling[15] of *trans*-2-ethoxy-1-(iodoethynyl)cyclopropane (**16**), prepared from **1-Et** according to a general procedure by Brandsma,[16] and methyl acrylate (**17**), but the yield was only 20 %.



Scheme 3. For more details see Table 2. A: 1, BuLi, THF, – 78 °C, 15 min; 2, I_2, – 20 °C, 20 min. B: $Pd(OAc)_2$, K_2CO_3, Bu_4NBr, DMF, – 20 °C, 12 h

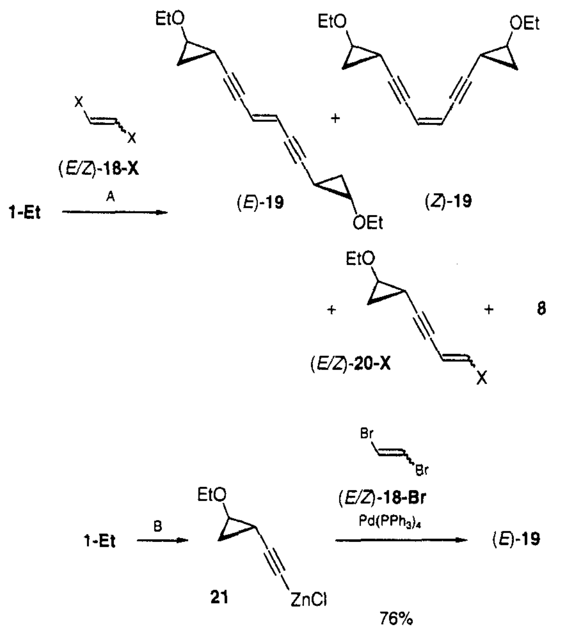
Table 2. Coupling Reactions of *trans*-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) with Haloalkenes **14a–d** (see Scheme 3)

14	Haloalkene X	R^1	R^2	R^3	Product 15	Yield (%)
a	Br	H	Ph	H	a	92
b	Br	$–(CH_2)_6–$		H	b	68
c	Br	H	CO_2Me	H	c	79
d	I	H	H	CO_2Me	d	84

Although double cross-couplings between acetylenes (trimethylsilyl- and phenylethyne) and diastereopure (*E*)- and (*Z*)-1,2-dichloroethane [(*E*)- and (*Z*)-**18-Cl**] have previously been reported[17] to yield the corresponding *E* and *Z* enediynes under the above mentioned conditions (in benzene/$BuNH_2$), analogous experiments with (*E*)-**18-Cl**, (*Z*)-**18-Cl** and **1-Et** did not give the expected (*E*)- and (*Z*)-1,6-(2-ethoxycyclopropyl)hex-3-ene-1,5-diynes [(*E*)- and (*Z*)-**19**], but only monocoupled chloroeneyne (*E*)-**20-Cl** (12 %) and (*Z*)-**20-Cl** (11 %), respectively, together with 30 % (33 %) of homocoupled bisacetylene **8** (Scheme 4, Table 3). Yields depended drastically on the solvent: in benzene/*i*-Pr_2NH (14 : 1), (*Z*)-**20-Cl** was isolated in 34 % yield, accompanied by 40 % of diyne **8**.

Under the same conditions a mixture of (*E*)- and (*Z*)-1,2-dibromoethene [(*E*/*Z*)-**18-Br**, *E*/*Z* = 1 : 1.56 (GC, NMR)] gave the enediynes (*E*)- and (*Z*)-**19**, but only in 19 and 24 % yield, respectively. Although the isomers (*E*)- and (*Z*)-**19** could be separated by chromatography, (*E*)-**19** and the diyne **8** (47 %) coeluted as a mixture (Table 3).

Rossi et al.[18] have reported a high-yielding palladium(0)-catalyzed coupling of trimethylsilyl- and alkylethynylzinc chlorides with commercially available (*E*/*Z*)-1,2-dibromoethene [(*E*/*Z*)-**18-Br**] to yield pure (*E*)-enediynes. Similarly, when *trans*-2-ethoxycyclopropylethynylzinc chloride (**21**) was generated from **1-Et** by deprotonation with butyllithium at – 78 °C in THF and subsequent addition of $ZnCl_2$ at 0 °C, and treated with (*E*/*Z*)-**18-Br** in the presence of $Pd(PPh_3)_4$, symmetrical all-*trans*-ene-



Scheme 4. A: Pd(PPh$_3$)$_4$, CuI, HN*i*-Pr$_2$, 20°C. B: 1, BuLi, THF, −78°C, 15 min; 2, ZnCl$_2$, 0°C

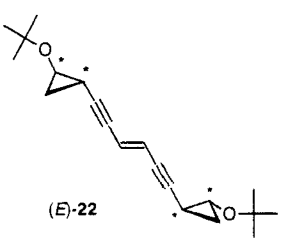
Table 3. Coupling Reactions of **1-Et** with (*E*)- and (*Z*)-1,2-Dihaloethenes **18-X** (for Details see Scheme 4)

18-X X	Method[a]	Yield (%)[b] (*E*)-**19**	 (*Z*)-**19**	 (*E*)-**20-X**	 (*Z*)-**20-X**	 **8**
(*E*)-Cl	A	0	–	12	–	30
(*Z*)-Cl	A	–	0	–	11	33
(*Z*)-Cl	A[c]	–	0	–	34	40
(*Z*)-Cl	B	–	0	–	0	26
(*E*/*Z*)-Br	A	19[d]	24[e]	0	0	47
(*E*/*Z*)-Br	B	76	0	0	0	0

[a] See Scheme 4.
[b] Yields based on proportion of (*E*)- and (*Z*)-alkene in the mixture (X = Br).
[c] In benzene/*i*-Pr$_2$NH (14 : 1).
[d] Isolated together with coeluting **8** (NMR).
[e] Isolated with minor impurities.

diyne (*E*)-**19** was solely isolated analytically pure (76 %), without any detectable quantities of mono- or homocoupled products (Table 3).

Because of the complete stereoselectivity in this reaction, enantiopure 1,6-bis[(*1R*,*2R*)-2-*tert*-butoxycyclopropyl]-hex-3-ene-1,5-diyne [(*E*)-**22**] was prepared from enantiopure **1-*t*-Bu**[3] under identical conditions, and was isolated in 81 % yield as a colorless solid. Recrystallization from pentane afforded (*E*)-**22** in large cubic crystals {$[\alpha]_D^{20} = -288.5$ (c = 1.17, EtOH)}.



(*E*)-**22**

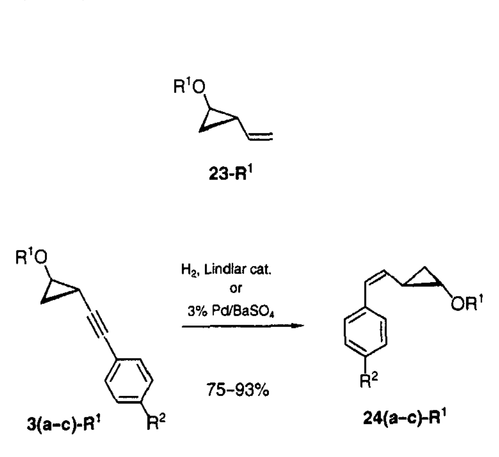
The all-*trans* configuration both in (*E*)-**19** and (*E*)-**22** was confirmed by the vicinal coupling constants $^{3}J_{3,4}$ = 16 Hz observed in the ^{13}C satellite spectra. Further evidence was provided by the IR and Raman spectra. Neither (*E*)-**19** nor (*E*)-**22** showed IR absorptions for the C=C stretching vibration, whereas the Raman spectrum for (*E*)-**22** exhibited a distinct band at 1592 cm^{-1} (C=C), in accord with the selection rules for C_{2h} molecular symmetry.

Catalytic Hydrogenation of [(2-Alkoxycyclopropyl)-ethynyl]arenes

Application of typical Heck coupling conditions [Pd(OAc)$_2$, PPh$_3$, KOAc, Bu$_4$NCl in DMF, 3 d at 80 °C] to ethenylcyclopropane and *o*-iodophenol has been reported not to give (*E*)-(cyclopropylethenyl)phenol, but only 2-(1-propenyl)-2,3-dihydrobenzofuran, with ring-opening of the cyclopropane moiety.[19] The attempted coupling of 2-ethoxy-1-ethenylcyclopropane (**23-Et**) with iodobenzene (**2a-I**) under the same conditions led to an intractable mixture of compounds, from which no cyclopropane derivative could be isolated. In addition, the attempted hydroalumination of **1-Et** with diisobutylaluminum hydride and subsequent palladium(0)-catalyzed coupling reactions[20] of the resulting ethenylaluminane with haloarenes also failed to yield the configurationally uniform (*E*)-(*trans*-2-alkoxycyclopropylethenyl)arenes.

However, the direct partial catalytic hydrogenation[21] of diastereopure [(2-alkoxycyclopropyl)ethynyl]arenes **3-R**^{1} prepared from **1-R**^{1} and haloarenes proved to be a feasible synthetic alternative to Heck reactions of **23-R**^{1} with haloarenes **2-X**.

All ethynylarenes **3-R**^{1} were hydrogenated to the corresponding ethenylarenes **24-R**^{1} in high yields, applying commercially available and appropriately deactivated Pd-catalysts (Scheme 5, Table 4).



Scheme 5

Under similar conditions, partial hydrogenations of di- and tri(cyclopropylethynyl)benzenes **10** and **13** to the symmetrical di- and tri(cyclopropylethenyl)benzenes **25** and **26** were successful, but occurred consistently more slowly, and the products were more prone to side reactions (e.g. complete hydrogenation). Nevertheless, care-

Table 4. Catalytic Hydrogenation of [(2-Alkoxy-1-cyclopropyl)-ethynyl]arenes to [(2-Alkoxy-1-cyclopropyl)ethenyl]arenes

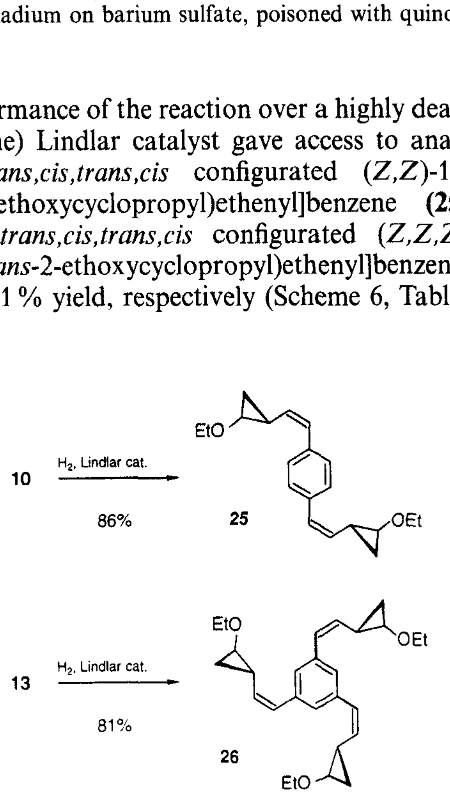
Starting Material	R^2	Product	Amount of Cat. (mol%)	Time (h)	Yield (%)
3a-Et	H	**24a-Et**	1.2[a]	48	79
3b-Et	Ph	**24b-Et**	1.0[a]	36	76
3c-Et	C_6H_4-*p*-Br	**24c-Et**	1.2[a]	36	81
3a-SiMe$_2$*t*-Bu[b]	Ph	**24a-SiMe$_2$*t*-Bu**[b]	0.5[c]	120	93
10	–	**25**	2.0[a]	120	86
13	–	**26**	1.7[a]	168	81

[a] Lindlar Catalyst (5% palladium on calcium carbonate, poisoned with lead and additionally with quinoline).

[b] *trans/cis* mixture (2 : 1).

[c] 3% Palladium on barium sulfate, poisoned with quinoline.

ful performance of the reaction over a highly deactivated (quinoline) Lindlar catalyst gave access to analytically pure *trans,cis,trans,cis* configurated (*Z,Z*)-1,4-bis[2-(*trans*-2-ethoxycyclopropyl)ethenyl]benzene (**25**) and *trans,cis,trans,cis,trans,cis* configurated (*Z,Z,Z*)-1,3,5-tris[2-(*trans*-2-ethoxycyclopropyl)ethenyl]benzene (**26**) in 86 and 81% yield, respectively (Scheme 6, Table 4).



Scheme 6

Thus, the forementioned coupling reactions e.g. with enantiopure ethynylcyclopropanes **1-R^1** (e.g. **1-*t*-Bu**) do not only lead to model systems for novel liquid crystalline compounds.[22] Upon enantioselective cyclopropanation[23] of derivatives such as (*E*)-**22**, **25** or **26** the resulting configurationally defined compounds may serve as useful model substrates for the unravelling of the unknown relative configuration of recently discovered naturally occuring oligocyclopropyl chains,[24] and for the construction of oligo(bicyclopropyl)arenes.

^{1}H NMR spectra were recorded on Bruker AW 250 (250 MHz), AM 250 (250 MHz) or Varian VXR 500 S (500 MHz) spectrometers; $\delta = 0$ for tetramethylsilane, 7.26 for chloroform. Characterization of signal multiplicity: d = doublet, (nd)d = n-fold doublet (n = 2, 3, 4, 5), t = triplet, dt = double triplet, q = quartet, dq = double quartet, pt = pseudo triplet, m = multiplet, s = singlet. ^{13}C NMR spectra were also recorded on Bruker AW 250 (62.9 MHz), AM 250 (62.9 MHz) or Varian VXR 500 S (125.7 MHz) spectrometers. IR spectra were run on a Perkin-Elmer 399 spectrophotometer. Mass spectra were measured with Varian MAT CH-7 and MAT 311 A (high resolution) instruments. Optical rotations were measured on a Perkin-Elmer-243 polarimeter. Merck Kieselgel 60 (200–400 mesh) and petroleum ether bp 60–80°C (PE) was used for column chromatographic separations. Melting points were determined on a Büchi instrument and are uncorrected. Elemental analyses wer performed by the Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Georg-August-Universität Göttingen.

Racemic and enantiopure starting materials 2-alkoxy-1-ethynylcyclopropanes **1-R^1** {**1-*t*-Bu**: optical purity > 95%, determined by analytical GC [chiral column heptakis(6-*O*-methyl-2,3-di-*O*-pentyl)-*β*-cyclodextrin]}, were prepared according to recently published procedures.[2,3] Bromo- and iodoalkenes(arenes) are, except for the following, of commercial origin and were freshly distilled or recrystallized prior to use. 4-Iodobiphenyl (**2b-I**) was prepared according to Cheng et al.,[25] 1,3,5-triiodobenzene (**12**) according to Willgerodt et al.[26] and 1-bromocyclooct-1-ene (**14b**) according to Tietze–Eicher.[27] (*E*)-*β*-Bromostyrene (**14a**) was prepared according to Takai et al.,[28] (*E*)-3-bromoacrylic acid according to Houben-Weyl[29] (methyl ester by standard procedures[30]) and methyl (*Z*)-3-iodoacrylate according to the procedure of Lu et al.[31]

2-Alkoxy-1-ethynylcyclopropyl Substituted Arenes and Eneynes; General Procedure:

To a stirred suspension of $Pd(PPh_3)_4$ (0.05 mmol) and CuI (0.10 mmol) in *i*-Pr_2NH (5 mL) was added the haloarene(alkene) (1.00 mmol). After stirring for 15 min at 20°C and after the appearance (in most cases) of a deep-green color, 2-alkoxy-1-ethynylcyclopropane **1-R^1** (1.00 mmol) in *i*-Pr_2NH (2 mL) was added. Precipitation of *i*-Pr_2NH_2X usually occurred within minutes and was accompanied by a characteristic change of color of the solution, indicating complete conversion. The suspension was stirred for 1–2 h, then filtered and the filtrate concentrated. The residue was purified by column chromatography on silica gel and recrystallized (compound **3c-Et**) to give the pure products.

(*trans*-2-Ethoxycyclopropyl)ethynylbenzene (3a-Et):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (1.00 g, 9.08 mmol), $Pd(PPh_3)_4$ (523 mg, 0.45 mmol), CuI (172 mg, 0.90 mmol), and iodobenzene (**2a-I**) (1.85 g, 9.07 mmol) gave 1.55 g (91%) of **3a-Et** as a colorless oil (50 g of silica gel, column 3 × 30 cm; PE/Et_2O, 40:1; $R_f = 0.27$).

4-[(*trans*-2-Ethoxycyclopropyl)ethynyl]biphenyl (3b-Et):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (100 mg, 0.91 mmol), $Pd(PPh_3)_4$ (52 mg, 0.04 mmol), CuI (17 mg, 0.09 mmol), and 4-iodobiphenyl (**2b-I**) (255 mg, 0.91 mmol) gave 15 mg (0.05 mmol) of recovered **2b-I** (fraction I) and 208 mg (92% based on consumed **2b-I**) of **3b-Et** as a colorless oil (fraction II) (10 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 40:1, $R_f = 0.25$).

4'-Bromo-4-[2-(*trans*-2-ethoxycyclopropyl])ethynyl]biphenyl (3c-Et):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (300 mg, 2.72 mmol), $Pd(PPh_3)_4$ (60 mg, 0.05 mmol), CuI (20 mg, 0.11 mmol), and 4,4'-dibromobiphenyl (**2c-Br**) (1250 mg, 4.01 mmol) gave 614 mg (1.97 mmol) of recovered **2c-Br** (fraction I) and 272 mg (39% based on consumed **2c-Br**) of **3c-Et** as a yellow solid (fraction II) (50 g of silica gel, column 3 × 30 cm; PE/Et_2O, 40:1; $R_f = 0.23$); mp 106°C (MeOH).

4-[(*cis/trans*-2-*tert*-Butyldimethylsilyloxycyclopropyl)ethynyl]-benzene (3a-SiMe$_2$*t*-Bu):
cis/trans-2-*tert*-Butyldimethylsilyloxy-1-ethynylcyclopropane (**1-SiMe$_2$*t*-Bu**) [981 mg, 5.00 mmol (*cis/trans*, 2:1)], $Pd(PPh_3)_4$ (289 mg, 0.25 mmol), CuI (95 mg, 0.50 mmol), and iodobenzene (**2a-I**) (1020 mg, 5.00 mmol) gave 556 mg (41%) of diastereopure *trans*-**3a-SiMe$_2$*t*-Bu** (fraction I, $R_f = 0.28$), 302 mg (22%) of a mixture of *trans/cis*-**3a-SiMe$_2$*t*-Bu** (fraction II) and 300 mg (22%) of diastereopure *cis*-**3a-SiMe$_2$*t*-Bu** (fraction III, $R_f = 0.25$) (50 g of silica gel, column 3 × 30; PE/Et_2O, 200:1) as colorless oils.

Table 5. Physical Properties of New Compounds

Product	mp (°C)	IR (neat) ν (cm^{-1})	MS (70 eV) m/z (%)
3a-Et[a]	–	3120, 2228	186 (5), 157 (88), 129 (95), 128 (100), 77 (14)
3b-Et[a]	–	3031, 2222	262 (12), 233 (26), 128 (100), 77 (26)
3c-Et[b]	106	3090, 2157, 765	342/340 (26/26), 313/311 (55/55), 297/295 (5/5), 204 (100), 176 (12), 152 (19), 77 (9)
3a-SiMe$_2$*t*-Bu[a, c]	–	3079, 2929, 2857, 2224, 1385, 1361	272 (3), 215 (77), 141 (54), 115 (24), 77 (7), 73 (100)
5[a]	–	3120, 2976, 2873, 2227	187 (22), 158 (66), 130 (100)
7[a]	–	3081, 2976, 2874, 2228	188 (4), 159 (50), 143 (3), 131 (100), 79 (12)
8	–	2977, 2874, 2156	218 (100), 189 (42), 173 (1)
10[a]	29	2976, 2871, 2225	294 (100), 265 (74), 249 (6)
13[b]	–	3050, 2976, 2872, 2224	402 (8), 373 (12)
15a[a]	–	3020, 2967, 2207	212 (76), 183 (62), 167 (58), 165 (66), 155 (100), 77 (18)
15b[a]	–	3080, 2976, 2927, 2850, 2214, 1627	218 (21), 189 (19), 173 (2), 109 (7), 91 (100)
15c	–	2978, 2209, 1729, 1617	194 (13), 179 (17), 165 (78), 149 (4), 135 (13), 109 (20), 105 (98), 77 (100)
15d[a]	–	2968, 2179, 1730, 1610	194 (1), 179 (27), 165 (95), 149 (4), 135 (10), 109 (21), 105 (100)
(*E*)-**19**[a]	–	3080, 2976, 2873, 2216	244 (10), 215 (7), 199 (3), 128 (68), 115 (100)
(*Z*)-**20-Cl**[a]	–	–	172/170 (2/9), 143/141 (5/14), 127/125 (< 1/2), 115/113 (3/11), 79/77 (38/100)
(*E*)-**22**[a]	75–76	2976, 2216, 1439, 1365, 1317	300 (< 1), 57 (100)
24a-Et[a]	–	3120, 3030, 1636	188 (37), 159 (8), 143 (12), 131 (39), 129 (50), 128 (33), 116 (21), 115 (100), 91 (61), 77 (9)
24b-Et[a]	–	–	264 (31), 235 (3), 219 (13), 206 (5), 191 (57), 179 (18), 165 (36), 153 (4), 115 (36), 91 (46), 77 (25), 57 (59), 55 (73), 43 (100), 41 (87)
24c-Et	–	–	–
24a-SiMe$_2$*t*-Bu[d]	–	3125, 3050, 2857, 1637, 1373	–
25[a]	–	3030, 2974, 2870, 1637	298 (30), 269 (4), 253 (12), 223 (38), 213 (2), 208 (28), 206 (37), 193 (97), 187 (46), 181 (56), 180 (42), 179 (91), 167 (68), 165 (71), 153 (49), 143 (53), 141 (78), 129 (52), 128 (63), 83 (100)
26[b]	–	3042, 2974, 2870, 1636	408 (< 1), 379 (< 1), 316 (29), 287 (23), 257 (63), 229 (48), 217 (48), 205 (80), 178 (71), 164 (65), 140 (24), 111 (32), 82 (100), 57 (31)

[a] Gave satisfactory microanalyses: C, H ± 0.2%.
[b] Gave satisfactory HRMS: m/z ± 0.0000.
[c] (*E*)-isomer.
[d] (*Z*)-isomer.

3-[(*trans*-2-Ethoxycyclopropyl)ethynyl]pyridine (5):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (100 mg, 0.91 mmol), $Pd(PPh_3)_4$ (52 mg, 0.04 mmol), CuI (17 mg, 0.09 mmol), and 3-iodopyridine (**4**) (185 mg, 0.90 mmol) gave 5 mg (0.02 mmol) of recovered **4** (fraction I) and 122 mg (74% based on consumed **4**) of **5** as a colorless oil (fraction II) (10 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 2:1; R_f = 0.37).

2-[(*trans*-2-Ethoxycyclopropyl)ethynyl]pyrimidine (7):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (150 mg, 1.36 mmol), $Pd(PPh_3)_4$ (78 mg, 0.07 mmol), CuI (26 mg, 0.14 mmol), and 2-bromopyrimidine (**6**) (216 mg, 1.36 mmol) gave 157 mg (61%) of **7** as a colorless oil (15 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 1:1; R_f = 0.32).

1,4-Bis[(*trans*-2-ethoxycyclopropyl)ethynyl]benzene (10):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (400 mg, 3.63 mmol), $Pd(PPh_3)_4$ (209 mg, 0.18 mmol), CuI (68 mg, 0.36 mmol), and 1,4-diiodobenzene (**9**) (498 mg, 1.51 mmol) gave 58 mg (12%) of monoalkynylated 1-iodo-4-[(2-ethoxycyclopropyl)ethynyl]benzene (**11**) (fraction I, R_f = 0.24) and 315 mg (71 %) of **10** as a slow-solidifying oil (fraction II) (30 g of silica gel, column 3 × 30 cm; PE/Et_2O, 20:1; R_f = 0.16); mp 29 °C.

1,3,5-Tris[(*trans*-2-ethoxycyclopropyl)ethynyl]benzene (13):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (469 mg, 4.26 mmol), $Pd(PPh_3)_4$ (251 mg, 0.22 mmol), CuI (82 mg, 0.43 mmol), and 1,3,5-triiodobenzene (**12**) (496 mg, 1.09 mmol) gave 381 mg (87%) of **13** as a colorless oil (30 g of silica gel, column 3 × 30 cm; PE/Et_2O, 20:1, R_f = 0.24).

(*E*)-[4-(*trans*-2-Ethoxycyclopropyl)but-1-en-3-ynyl]benzene (15a):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (100 mg, 0.91 mmol), $Pd(PPh_3)_4$ (52 mg, 0.04 mmol), CuI (18 mg, 0.09 mmol), and β-bromostyrene (**14a**)[28] (167 mg, 0.91 mmol) gave 177 mg (92%) of **15a** as a colorless oil (10 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 30:1; R_f = 0.29).

1-[(*trans*-2-Ethoxycyclopropyl)ethynyl]cyclooct-1-ene (15b):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (100 mg, 0.91 mmol), $Pd(PPh_3)_4$ (52 mg, 0.04 mmol), CuI (18 mg, 0.09 mmol), and 1-bromocyclooct-1-ene (**14b**) (143 mg, 0.76 mmol) gave 113 mg (68%) of **15b** as a colorless oil (15 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 30:1, R_f = 0.29).

Methyl (*E*)-5-(*trans*-2-Ethoxycyclopropyl)pent-2-en-4-ynoate (15c):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (200 mg, 1.82 mmol), $Pd(PPh_3)_4$ (104 mg, 0.09 mmol), CuI (34 mg, 0.18 mmol), and methyl (*E*)-3-bromoacrylate (**14c**) (297 mg, 1.80 mmol) gave 276 mg (79%) of **15c** as a colorless oil (15 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 10:1; R_f = 0.28).

Methyl (*Z*)-5-(*trans*-2-Ethoxycyclopropyl)pent-2-en-4-ynoate (15d):
trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (200 mg, 1.82 mmol), $Pd(PPh_3)_4$ (104 mg, 0.09 mmol), CuI (34 mg, 0.18 mmol), and methyl (*Z*)-3-iodoacrylate (**14d**) (320 mg, 1.51 mmol) gave 246 mg (84%) of **15d** as a colorless oil (20 g of silica gel, column 3 × 30 cm; PE/Et_2O 10:1; R_f = 0.32).

***trans*-1-[(*Z*)-4-Chlorobut-3-en-1-ynyl]-2-ethoxycyclopropane [(*Z*)-20-Cl]:**
According to the general procedure, but with benzene/*i*-Pr_2NH (14:1) as solvent, *trans*-2-ethoxy-1-ethynylcyclopropane (**1-Et**)

Table 6. Spectroscopic Data of New Compounds

Product	^{1}H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$) δ
3a-Et	1.00 (ddd, $^3J_{3''(trans),2''} = 6.7$, $^3J_{3''(trans),1''} = 6.3$, $^2J = 5.6$, 1H, 3″-H$_{trans}$), 1.18 (ddd, $^3J_{3''(cis),1''} = 9.9$, $^2J = 5.6$, $^3J_{3''(cis),2''} = 3.8$, 1H, 3″-H$_{cis}$), 1.22 (t, 3H, $OCH_2C\underline{H}_3$), 1.59 (ddd, $^3J_{1'',3''(cis)} = 9.9$, $^3J_{1'',3''(trans)} = 6.3$, $^3J_{1'',2''} = 2.7$, 1H, 1″-H), 3.50 (ddd, $^3J_{2'',3''(trans)} = 6.7$, $^3J_{2'',3''(cis)} = 3.8$, $^3J_{2'',1''} = 2.7$, 1H, 2″-H), 3.64 (q, 2H, $OC\underline{H}_2CH_3$), 7.30 (m, 5H, Ar-H)	8.40 (C-1″), 15.00 ($OCH_2\underline{C}H_3$), 16.38 (C-3″), 60.46 (C-2″), 66.31 ($O\underline{C}H_2CH_3$), 76.61 (C-1′), 90.54 (C-2′), 123.64 (C-1), 127.52 (C-4), 128.12 [C-3(5)], 131.52 [C-2(6)]
3b-Et	1.03 (ddd, $^3J_{3'''(trans),2'''} = 6.7$, $^3J_{3'''(trans),1'''} = 6.3$, $^2J = 5.6$, 1H, 3‴-H$_{trans}$), 1.20 (ddd, $^3J_{3'''(cis),1'''} = 9.9$, $^2J = 5.6$, $^3J_{3'''(cis),2'''} = 3.8$, 1H, 3‴-H$_{trans}$), 1.23 (t, 3H, $OCH_2C\underline{H}_3$), 1.60 (ddd, $^3J_{1''',3'''(cis)} = 9.9$, $^3J_{1''',3'''(trans)} = 6.3$, $^3J_{1''',2'''} = 2.7$, 1H, 1‴-H), 3.52 (ddd, $^3J_{2''',3'''(trans)} = 6.7$, $^3J_{2''',3'''(cis)} = 3.8$, $^3J_{2''',1'''} = 2.7$, 1H, 2‴-H), 3.66 (q, 2H, $OC\underline{H}_2CH_3$), 7.50 (m, 9H, Ar-H)	8.54 (C-1‴), 15.05 ($OCH_2\underline{C}H_3$), 16.50 (C-3‴), 60.57 (C-2‴), 66.38 ($O\underline{C}H_2CH_3$), 76.59 (C-1″), 91.31 (C-2″), 122.61 (C-4), 126.84 [C-2′(6′)], 126.92 [C-2(6)], 127.46 (C-4′), 128.78 [C-3′(5′)], 131.97 [C-3(5)], 140.28 (C-1), 140.41 (C-1′)
3c-Et	1.03 (ddd, $^3J_{3'''(trans),2'''} = 6.7$, $^3J_{3'''(trans),1'''} = 6.4$, $^2J = 5.5$, 1H, 3‴-H$_{trans}$), 1.20 (ddd, $^3J_{3'''(cis),1'''} = 9.3$, $^2J = 5.5$, $^3J_{3'''(cis),2'''} = 3.5$, 1H, 3‴-H$_{cis}$), 1.23 (t, 3H, $OCH_2C\underline{H}_3$), 1.61 (ddd, $^3J_{1''',3'''(cis)} = 9.3$, $^3J_{1''',3'''(trans)} = 6.4$, $^3J_{1''',2'''} = 2.9$, 1H, 1‴-H), 3.52 (ddd, $^3J_{2''',3'''(trans)} = 6.7$, $^3J_{2''',3'''(cis)} = 3.5$, $^3J_{2''',1'''} = 2.9$, 1H, 2‴-H), 3.67 (q, 2H, $OC\underline{H}_2CH_3$), 7.45 (m, 8H, Ar-H)	8.55 (C-1‴), 15.08 ($OCH_2\underline{C}H_3$), 16.54 (C-3‴), 60.58 (C-2‴), 66.45 ($O\underline{C}H_2CH_3$), 77.22 (C-1″), 91.70 (C-2″), 121.70 (C-4′), 123.10 (C-4), 126.66 [C-3(5)], 128.53 [(C-2(6)], 131.94 [C-2′(6′)], 132.11 [C-3′(5′)], 139.09 (C-1), 139.37 (C-1′)
3a-SiMe$_2$*t*-Bu[a]	0.11 [s, 6H, $Si(CH_3)_2$], 0.62 (ddd, $^2J = 6.2$, $^3J_{3''(cis),1''} = 6.2$, $^3J_{3''(cis),2''} = 3.7$, 1H, 3″-H$_{cis}$), 0.92 [s, 9H, $C(CH_3)_3$], 1.04 (ddd, $^3J_{3''(trans),1''} = 9.2$, $^3J_{3''(trans),2''} = 6.3$, $^2J = 6.2$, 1H, 3″-H$_{trans}$), 1.85 (dddd, $^3J_{1'',2'} = 9.9$, $^3J_{1'',3''(trans)} = 9.2$, $^3J_{1'',3''(cis)} = 6.2$, $^3J_{1'',2''} = 6.2$, 1H, 1″-H), 3.61 (ddd, $^3J_{2'',3''(trans)} = 6.3$, $^3J_{2'',1''} = 6.2$, $^3J_{2'',3''(cis)} = 3.7$, 1H, 2″-H), 5.58 (dd, $^3J_{2',1'} = 11.6$, $^3J_{2',1''} = 9.9$, 1H, 2′-H), 6.49 (d, $^3J_{1',2'} = 11.6$, 1H, 1′-H), 7.30 (m, 5H, Ar-H)	−5.04 [$Si(CH_3)_2$], −4.89 [$Si(CH_3)_2$], 16.43 (C-3″), 17.61 (C-1″), 18.15 [$\underline{C}(CH_3)_3$], 25.84 [$C(\underline{C}H_3)_3$], 52.88 (C-2″), 126.26 (C-2′), 128.16 [C-2(6)], 128.39 (C-4), 128.62 (C-1′), 130.48 [C-3(5)], 138.21 (C-1)
5	1.03 (ddd, $^3J_{3''(trans),2''} = 6.8$, $^3J_{3''(trans),1''} = 6.2$, $^2J = 5.7$, 1H, 3″-H$_{trans}$), 1.21 (ddd, $^3J_{3''(cis),1''} = 9.5$, $^2J = 5.7$, $^3J_{3''(cis),2''} = 3.8$, 1H, 3″-H$_{cis}$), 1.22 (t, 3H, $OCH_2C\underline{H}_3$), 1.61 (ddd, $^3J_{1'',3''(cis)} = 9.5$, $^3J_{1'',3''(trans)} = 6.2$, $^3J_{1'',2''} = 2.7$, 1H, 1″-H), 3.51 (ddd, $^3J_{2'',3''(trans)} = 6.8$, $^3J_{2'',3''(cis)} = 3.8$, $^3J_{2'',1''} = 2.7$, 1H, 2″-H), 3.65 (q, 2H, $OC\underline{H}_2CH_3$), 7.19 (ddd, $^3J_{5,4} = 7.9$, $^3J_{5,6} = 4.9$, $^5J_{5,2} = 0.9$, 1H, 5-H), 7.63 (ddd, $^3J_{4,5} = 7.9$, $^4J_{4,2} = 2.0$, $^4J_{4,6} = 1.6$, 1H, 4-H), 8.47 (dd, $^3J_{6,5} = 4.9$, $^4J_{6,4} = 1.6$, 1H, 6-H), 8.59 (dd, $^4J_{2,4} = 2.0$, $^5J_{2,5} = 0.9$, 1H, 2-H)	8.32 (C-1″), 14.95 ($OCH_2\underline{C}H_3$), 16.46 (C-3″), 60.44 (C-2″), 66.37 ($O\underline{C}H_2CH_3$), 73.43 (C-1′), 94.16 (C-2′), 120.76 (C-3), 122.77 (C-5), 138.33 (C-4), 147.86 (C-6), 152.29 (C-2)
7	1.18 (ddd, 1H, 3″-H$_{trans}$), 1.21 (t, 3H, $OCH_2C\underline{H}_3$), 1.28 (ddd, $^3J_{3''(cis),1''} = 9.5$, $^2J = 5.7$, $^3J_{3''(cis),2''} = 3.2$, 1H, 3″-H$_{cis}$), 1.63 (ddd, $^3J_{1'',3''(cis)} = 9.5$, $^3J_{1'',3''(trans)} = 6.2$, $^3J_{1'',2''} = 2.9$, 1H, 1″-H), 3.62 (ddd, 1H, 2″-H), 3.63 (q, 2H, $OC\underline{H}_2CH_3$), 7.19 (t, $^3J_{5,4(6)} = 4.9$, 1H, 5-H), 8.65 [d, $^3J_{4(6),5} = 4.9$, 2H, 4(6)-H]	7.95 (C-1″), 14.76 ($OCH_2\underline{C}H_3$), 16.47 (C-3″), 60.42 (C-2″), 66.33 ($O\underline{C}H_2CH_3$), 75.93 (C-1′), 90.82 (C-2′), 119.17 (C-5), 152.86 (C-2), 156.95 [C-4(6)]
8	0.93 (ddd, $^3J_{3'(trans),2'} = 6.6$, $^3J_{3'(trans),1'} = 6.3$, $^2J = 5.9$, 2H, 3′-H$_{trans}$), 1.10 (ddd, $^3J_{3'(cis),1'} = 9.8$, $^2J = 5.9$, $^3J_{3'(cis),2'} = 3.9$, 2H, 3′-H$_{cis}$), 1.18 (t, 6H, $OCH_2C\underline{H}_3$), 1.39 (ddd, $^3J_{1',3'(cis)} = 9.8$, $^3J_{1',3'(trans)} = 6.3$, $^3J_{1',2'} = 2.5$, 2H, 1′-H), 3.40 (ddd, $^3J_{2',3'(trans)} = 6.6$, $^3J_{2',3'(cis)} = 3.9$, $^3J_{2',1'} = 2.5$, 2H, 2′-H), 3.57 (dq, 4H, $OC\underline{H}_2CH_3$)	8.22 (C-1′), 14.92 ($OCH_2\underline{C}H_3$), 16.35 (C-3′), 60.41 (C-2′), 61.71 [C-2(3)], 66.44 ($O\underline{C}H_2CH_3$), 77.51 [C-1(4)]
10	0.99 (ddd, $^2J = 5.6$, $^3J_{3''(trans),1''} = 6.3$, $^3J_{3''(trans),2''} = 6.7$, 2H, 3″-H$_{trans}$), 1.19 (ddd, $^3J_{3''(cis),2''} = 3.8$, $^2J = 5.6$, $^3J_{3''(cis),1''} = 9.9$, 2H, 3″-H$_{cis}$), 1.21 (t, 6H, $OCH_2C\underline{H}_3$), 1.58 (ddd, $^3J_{1'',3''(cis)} = 9.9$, $^3J_{1'',3''(trans)} = 6.3$, $^3J_{1'',2''} = 2.7$, 2H, 1″-H), 3.48 (ddd, $^3J_{2'',1''} = 2.7$, $^3J_{2'',3''(trans)} = 6.7$, $^3J_{2'',3''(cis)} = 3.8$, 2H, 2″-H), 3.64 (q, 4H, $OC\underline{H}_2CH_3$), 7.25 [s, 4H, 2(3,5,6)-H]	8.48 (C-1″), 15.02 ($OCH_2\underline{C}H_3$), 16.50 (C-3″), 60.54 (C-2″), 66.38 ($O\underline{C}H_2CH_3$), 76.49 (C-2′), 92.23 (C-1′), 122.84 [C-1(4)], 131.34 [C-2(3,5,6)]
13	0.97 (ddd, $^2J = 5.6$, $^3J_{3''(trans),1''} = 6.4$, $^3J_{3''(trans),2''} = 6.8$, 3H, 3″-H$_{trans}$), 1.17 (ddd, $^3J_{3''(cis),2''} = 3.9$, $^2J = 5.6$, $^3J_{3''(cis),1''} = 9.8$, 3H, 3″-H$_{cis}$), 1.21 (t, 9H, $OCH_2C\underline{H}_3$), 1.55 (ddd, $^3J_{1'',3''(cis)} = 9.8$, $^3J_{1'',3''(trans)} = 6.4$, $^3J_{1'',2''} = 2.9$, 3H, 1″-H), 3.45 (ddd, $^3J_{2'',1''} = 2.9$, $^3J_{2'',3''(trans)} = 6.8$, $^3J_{2'',3''(cis)} = 3.9$, 3H, 2″-H), 3.63 (q, 6H, $OC\underline{H}_2CH_3$), 7.23 [s, 3H, 2(4,6)-H]	8.34 ($OCH_2\underline{C}H_3$), 15.00 (C-1″), 16.45 (C-3″), 60.51 (C-2″), 66.39 ($O\underline{C}H_2CH_3$), 75.38 (C-2′), 91.47 (C-1′), 123.96 [C-1(3,5)], 133.55 [C-2(4,6)]
15a	0.98 (ddd, $^3J_{3''(trans),2''} = 6.5$, $^3J_{3''(trans),1''} = 6.5$, $^2J = 5.8$, 1H, 3″-H$_{trans}$), 1.18 (ddd, $^3J_{3''(cis),1''} = 9.5$, $^2J = 5.8$, $^3J_{3''(cis),2''} = 3.9$, 1H, 3″-H$_{cis}$), 1.21 (t, 3H, $OCH_2C\underline{H}_3$), 1.55 (dddd, $^3J_{1'',3''(cis)} = 9.5$, $^3J_{1'',3''(trans)} = 6.5$, $^3J_{1'',2''} = 2.9$, $^5J_{1'',2'} = 2.0$, 1H, 1″-H), 3.46 (ddd, $^3J_{2'',3''(trans)} = 6.5$, $^3J_{2'',3''(cis)} = 3.9$, $^3J_{2'',1''} = 2.9$, 1H, 2″-H), 3.62 (q, 2H, $OC\underline{H}_2CH_3$), 6.10 (dd, $^3J_{2',1'} = 16.2$, $^5J_{2',1''} = 2.0$, 1H, 2′-H), 6.85 (d, $^3J_{1',2'} = 16.2$, 1H, 1′-H), 7.30 (m, 5H, Ar-H)	8.65 (C-1″), 14.98 ($OCH_2\underline{C}H_3$), 16.51 (C-3″), 60.57 (C-2″), 66.30 ($O\underline{C}H_2CH_3$), 76.05 (C-3′), 93.17 (C-4′), 108.45 [C-3(5)], 125.95 [C-2(6)], 128.21 (C-4), 128.57 (C-2′), 136.41 (C-1), 140.23 (C-1′)
15b	0.88 (ddd, $^3J_{3''(trans),2''} = 6.7$, $^3J_{3''(trans),1''} = 6.4$, $^2J = 5.8$, 1H, 3″-H$_{trans}$), 1.09 (ddd, $^3J_{3''(cis),1''} = 9.6$, $^2J = 5.8$, $^3J_{3''(cis),2''} = 3.9$, 1H, 3″-H$_{trans}$), 1.20 (t, 3H, $OCH_2C\underline{H}_3$), 1.50 [m, 9H, 1″-H and 4(5,6,7)-H], 2.11 (m, 2H, 3-H), 2.20 (t, 2H, 8-H), 3.39 (ddd, $^3J_{2'',3''(trans)} = 6.7$, $^3J_{2'',3''(cis)} = 3.9$, $^3J_{2'',1''} = 2.7$, 1H, 2″-H), 3.60 (q, 2H, $OC\underline{H}_2CH_3$), 5.96 (t, $^3J_{2,3} = 8.4$, 1H, 2-H)	8.46 (C-1″), 15.03 ($OCH_2\underline{C}H_3$), 16.41 (C-3″), 25.80 (C-3), 26.37 (C-8), 26.91 (C-4), 28.39 (C-7), 29.74 (C-6), 30.15 (C-5), 60.54 (C-2″), 66.25 ($O\underline{C}H_2CH_3$), 79.14 (C-1′), 87.10 (C-2′), 123.84 (C-1), 136.38 (C-2)

Table 6. continued

Product	^1H NMR ($CDCl_3$) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ
15c	1.01 (ddd, $^3J_{3'(trans),2'} = 6.7$, $^3J_{3'(trans),1'} = 6.4$, $^2J = 5.4$, 1H, 3'-H_{trans}), 1.20 (t, 3H, $OCH_2C\underline{H}_3$), 1.21 (ddd, 1H, 3'-H_{cis}), 1.54 (dddd, $^3J_{1',3'(cis)} = 9.8$, $^3J_{1',3'(trans)} = 6.4$, $^3J_{1',2'} = 2.5$, $^5J_{1',3} = 2.3$, 1H, 1'-H), 3.48 (ddd, $^3J_{2',3'(trans)} = 6.7$, $^3J_{2',3'(cis)} = 4.2$, $^3J_{2',1'} = 2.5$, 1H, 2'-H), 3.61 (q, 2H, $OC\underline{H}_2CH_3$), 3.74 (s, 3H, CO_2CH_3), 6.11 (d, $^3J_{2,3} = 15.8$, 1H, 2-H), 6.71 (dd, $^3J_{3,2} = 15.8$, $^5J_{3,1'} = 2.3$, 1H, 3-H)	8.78 (C-1'), 14.98 ($OCH_2\underline{C}H_3$), 16.93 (C-3'), 51.72 (C-2'), 60.84 ($CO_2\underline{C}H_3$), 66.51 ($O\underline{C}H_2CH_3$), 74.36 (C-5), 101.40 (C-4), 126.02 (C-3), 128.58 (C-2), 166.53 (C-1)
15d	1.09 (ddd, $^3J_{3'(trans),2'} = 6.6$, $^3J_{3'(trans),1'} = 6.2$, $^2J = 5.9$, 1H, 3'-H_{trans}), 1.20 (t, 3H, $OCH_2C\underline{H}_3$), 1.26 (ddd, $^3J_{3'(cis),1'} = 9.7$, $^2J = 5.9$, $^3J_{3'(cis),2'} = 4.1$, 1H, 3'-H_{cis}), 1.61 (dddd, $^3J_{1',3'(cis)} = 9.7$, $^3J_{1',3'(trans)} = 6.2$, $^3J_{1',2'} = 2.6$, $^5J_{1',3} = 2.4$, 1H, 1'-H), 3.53 (ddd, $^3J_{2',3'(trans)} = 6.6$, $^3J_{2',3'(cis)} = 4.1$, $^3J_{2',1'} = 2.6$, 1H, 2'-H), 3.62 (q, 2H, $OC\underline{H}_2CH_3$), 3.74 (s, 3H, CO_2CH_3), 6.01 (d, $^3J_{2,3} = 11.5$, 1H, 2-H), 6.10 (dd, $^3J_{3,2} = 11.5$, $^5J_{3,1'} = 2.4$, 1H, 3-H)	9.12 (C-1'), 14.92 ($OCH_2\underline{C}H_3$), 17.27 (C-3'), 51.21 (C-2'), 61.18 ($CO_2\underline{C}H_3$), 66.43 ($O\underline{C}H_2CH_3$), 74.39 (C-5), 105.03 (C-4), 123.95 (C-3), 126.64 (C-2), 165.21 (C-1)
(*E*)-**19**	0.92 (ddd, $^3J_{3'(trans),2'} = 6.6$, $^3J_{3'(trans),1'} = 6.3$, $^2J = 5.8$, 2H, 3'-H_{trans}), 1.14, (ddd, $^3J_{3'(cis),1'} = 9.8$, $^2J = 5.8$, $^3J_{3'(cis),2'} = 4.0$, 2H, 3'-H_{cis}), 1.20 (t, 6H, $OCH_2C\underline{H}_3$), 1.49 (ddd, $^3J_{1',3'(cis)} = 9.8$, $^3J_{1',3'(trans)} = 6.3$, $^3J_{1',2'} = 2.6$, 2H, 1'-H), 3.40 (ddd, $^3J_{2',3'(trans)} = 6.6$, $^3J_{2',3'(cis)} = 4.0$, $^3J_{2',1'} = 2.6$, 2H, 2'-H), 3.60 (dq, 4H, $OC\underline{H}_2CH_3$), 5.80 [pt, $^5J_{3(4),1'} = 0.8$, $^6J_{4(3),1'} = 0.6$, 2H, 3(4)-H]	8.59 (C-1'), 14.93 ($OCH_2\underline{C}H_3$), 16.52 (C-3'), 60.54 (C-2'), 66.29 ($O\underline{C}H_2CH_3$), 75.40 [C-1(6)], 95.49 [C-2(5)], 120.06 [C-3(4)]
(*Z*)-**20-Cl**	1.00 (ddd, $^3J_{3(trans),2} = 6.5$, $^3J_{3(trans),1} = 6.3$, $^2J = 5.5$, 1H, 3-H_{trans}), 1.19 (ddd, $^3J_{3(cis),1} = 9.8$, $^2J = 5.5$, $^3J_{3(cis),2} = 4.0$, 1H, 3-H_{cis}), 1.21 (t, 3H, $OCH_2C\underline{H}_3$), 1.57 (dddd, $^3J_{1,3(cis)} = 9.8$, $^3J_{1,3(trans)} = 6.3$, $^3J_{1,2} = 2.5$, $^5J_{1,3'} = 2.0$, 1H, 1-H), 3.48 (ddd, $^3J_{2,3(trans)} = 6.5$, $^3J_{2,3(cis)} = 4.0$, $^3J_{2,1} = 2.5$, 1H, 2-H), 3.62 (q, 2H, $OC\underline{H}_2CH_3$), 5.80 (dd, $^3J_{3',4'} = 7.5$, $^5J_{3',1} = 2.0$, 1H, 3'-H), 6.28 (d, $^3J_{4',3'} = 7.5$, 1H, 4'-H)	8.66 (C-1), 14.99 ($OCH_2\underline{C}H_3$), 16.76 (C-3), 60.72 (C-2), 66.41 ($O\underline{C}H_2CH_3$), 70.85 (C-1'), 99.56 (C-2'), 112.20 (C-3'), 126.93 (C-4')
(*E*)-**22**	0.93 (ddd, $^3J_{3'(trans),2'} = 6.8$, $^3J_{3'(trans),1'} = 6.3$, $^2J = 5.6$, 2H, 3'-H_{trans}), 1.07, (ddd, $^3J_{3'(cis),1'} = 9.8$, $^2J = 5.6$, $^3J_{3'(cis),2'} = 4.0$, 2H, 3'-H_{cis}), 1.24 [s, 18H, $C(CH_3)_3$], 1.43 (dddt, $^3J_{1',3'(cis)} = 9.8$, $^3J_{1',3'(trans)} = 6.3$, $^3J_{1',2'} = 2.7$, $^5J_{1',3(4)} = 0.8$, 2H, 1'-H), 3.35 (ddd, $^3J_{2',3'(trans)} = 6.8$, $^3J_{2',3'(cis)} = 4.0$, $^3J_{2',1'} = 2.7$, 2H, 2'-H), 5.82 [pt, $^5J_{4(3),1'} = 0.8$, $^6J_{3(4),1'} = 0.6$, 2H, 3(4)-H]	10.08 (C-1'), 15.81 (C-3'), 28.06 [$C(\underline{C}H_3)_3$], 54.46 (C-2'), 75.50 [$\underline{C}(CH_3)_3$], 75.52 [C-1(6)], 95.59 [C-2(5)], 120.09 [C-3(4)]
24a-Et	0.71 (ddd, $^3J_{3''(trans),2''} = 6.4$, $^3J_{3''(trans),1''} = 6.2$, $^2J = 5.6$, 1H, 3''-H_{trans}), 1.14, (ddd, $^3J_{3''(cis),1''} = 9.7$, $^2J = 5.6$, $^3J_{3''(cis),2''} = 3.8$, 1H, 3''-H_{cis}), 1.19 (t, 3H, $OCH_2C\underline{H}_3$), 2.07 (dddd, $^3J_{1'',2'} = 10.0$, $^3J_{1'',3''(cis)} = 9.7$, $^3J_{1'',3''(trans)} = 6.2$, $^3J_{1'',2''} = 2.7$, 1H, 1''-H), 3.29 (ddd, $^3J_{2'',3''(trans)} = 6.4$, $^3J_{2'',3''(cis)} = 3.8$, $^3J_{2'',1''} = 2.7$, 1H, 2''-H), 3.56 (q, 2H, $OC\underline{H}_2CH_3$), 5.03 (dd, $^3J_{2',1'} = 11.5$, $^3J_{2',1''} = 10.0$, 1H, 2'-H), 6.35 (d, $^3J_{1',2'} = 11.5$, 1H, 1'-H), 7.30 (m, 5H, Ar-H)	15.06 ($OCH_2\underline{C}H_3$), 15.76 (C-3''), 19.47 (C-1''), 61.21 (C-2''), 66.03 ($O\underline{C}H_2CH_3$), 126.49 [C-2(4,6)], 128.14 [C-3(5)], 128.62 (C-1'), 132.56 (C-2'), 137.51 (C-1)
24b-Et	0.75 (ddd, $^3J_{3'''(trans),2'''} = 6.8$, $^3J_{3'''(trans),1'''} = 6.3$, $^2J = 5.4$, 1H, 3'''-H_{trans}), 1.18, (ddd, $^3J_{3'''(cis),1'''} = 9.2$, $^2J = 5.4$, $^3J_{3'''(cis),2'''} = 4.0$, 1H, 3'''-$H_{cis}$), 1.20 (t, 3H, $OCH_2C\underline{H}_3$), 2.12 (dddd, $^3J_{1''',2''} = 10.0$, $^3J_{1''',3'''(cis)} = 9.2$, $^3J_{1''',3'''(trans)} = 6.3$, $^3J_{1''',2'''} = 3.0$, 1H, 1'''-H), 3.31 (ddd, $^3J_{2''',3'''(trans)} = 6.8$, $^3J_{2''',3'''(cis)} = 4.0$, $^3J_{2''',1'''} = 3.0$, 1H, 2'''-H), 3.58 (q, 2H, $OC\underline{H}_2CH_3$), 5.07 (dd, $^3J_{2'',1''} = 11.5$, $^3J_{2'',1'''} = 10.0$, 1H, 2''-H), 6.39 (d, $^3J_{1'',2''} = 11.5$, 1H, 1''-H), 7.45 (m, 9H, Ar-H)	15.13 ($OCH_2\underline{C}H_3$), 15.93 (C-3'''), 19.69 (C-1'''), 61.35 (C-2'''), 66.14 ($O\underline{C}H_2CH_3$), 126.90 (C-4'*), 126.95 (C-1''*), 127.19 [C-3(5)], 127.79 [C-2(6)], 128.75 [C-2'(6')], 129.11 (C-2''), 132.85 [C-3'(5')], 136.63 (C-1), 139.30 (C-4), 140.84 (C-1')
24c-Et	0.75 (ddd, $^3J_{3'''(trans),2'''} = 6.5$, $^3J_{3'''(trans),1'''} = 6.3$, $^2J = 5.7$, 1H, 3'''-H_{trans}), 1.20 (m, 4H, $OCH_2C\underline{H}_3$ and 3'''-H_{cis}), 2.20 (dddd, $^3J_{1''',2''} = 9.3$, $^3J_{1''',3'''(cis)} = 9.8$, $^3J_{1''',3'''(trans)} = 6.3$, $^3J_{1''',2'''} = 2.5$, 1H, 1'''-H), 3.41 (ddd, $^3J_{2''',3'''(trans)} = 6.5$, $^3J_{2''',3'''(cis)} = 3.8$, $^3J_{2''',1'''} = 2.5$, 1H, 2'''-H), 3.59 (q, 2H, $OC\underline{H}_2CH_3$), 5.09 (dd, $^3J_{2'',1''} = 10.4$, $^3J_{2'',1'''} = 9.3$, 1H, 2''-H), 6.38 (d, $^3J_{1'',2''} = 10.4$, 1H, 1''-H), 7.50 (m, 8H, Ar-H)	15.01 ($OCH_2\underline{C}H_3$), 15.09 (C-3'''), 15.88 (C-1'''), 61.49 (C-2'''), 66.05 ($O\underline{C}H_2CH_3$), 121.69 (C-4'), 126.59 (C-1''), 127.57 [C-3(5)], 128.41 (C-2''), 129.16 [C-2(6)], 131.78 [C-2'(6')], 133.05 [C-3'(5')], 136.96 (C-4), 137.88 (C-1), 139.61 (C-1')
24a-SiMe$_2$*t*-Bu[b]	0.11 [s, 6H, $Si(CH_3)_2$], 0.62 (ddd, $^2J = 6.2$, $^3J_{3''(cis),1''} = 6.2$, $^3J_{3''(cis),2''} = 3.7$, 1H, 3''-H_{cis}), 0.92 [s, 9H, $C(CH_3)_3$], 1.04 (ddd, $^3J_{3''(trans),1''} = 9.2$, $^3J_{3''(trans),2''} = 6.3$, $^2J = 6.2$, 1H, 3''-H_{trans}), 1.85 (dddd, $^3J_{1'',2'} = 9.9$, $^3J_{1'',3''(trans)} = 9.2$, $^3J_{1'',3''(cis)} = 6.2$, $^3J_{1'',2''} = 6.2$, 1H, 1''-H), 3.61 (ddd, $^3J_{2'',3''(trans)} = 6.3$, $^3J_{2'',1''} = 6.2$, $^3J_{2'',3''(cis)} = 3.7$, 1H, 2''-H), 5.58 (dd, $^3J_{2',1'} = 11.6$, $^3J_{2',1''} = 9.9$, 1H, 2'-H), 6.49 (d, $^3J_{1',2'} = 11.6$, 1H, 1'-H), 7.30 (m, 5H, Ar-H)	−5.04 [$Si(CH_3)_2$], −4.89 [$Si(CH_3)_2$], 16.43 (C-3''), 17.61 (C-1''), 18.15 [$\underline{C}(CH_3)_3$], 25.84 [$C(\underline{C}H_3)_3$], 52.88 (C-2''), 126.26 (C-2'), 128.16 [C-2(6)], 128.39 (C-4), 128.62 (C-1'), 130.48 [C-3(5)], 138.21 (C-1)
25	0.72 (ddd, $^3J_{3''(trans),2''} = 6.4$, $^3J_{3''(trans),1''} = 6.2$, $^2J = 5.4$, 2H, 3''-H_{trans}), 1.16 (ddd, $^3J_{3''(cis),1''} = 9.7$, $^2J = 5.4$, $^3J_{3''(cis),2''} = 3.8$, 2H, 3''-H_{cis}), 1.19 (t, 6H, $OCH_2C\underline{H}_3$), 2.10 (ddddd, $^3J_{1'',1'} = 10.0$, $^3J_{1'',3''(cis)} = 9.7$, $^3J_{1'',3''(trans)} = 6.2$, $^3J_{1'',2''} = 2.7$, $^4J_{1'',2'} = 0.8$, 2H, 1''-H), 3.30 (ddd, $^3J_{2'',3''(trans)} = 6.4$, $^3J_{2'',3''(cis)} = 3.8$, $^3J_{2'',1''} = 2.7$, 2H, 2''-H), 3.58 (q, 4H, $OC\underline{H}_2CH_3$), 5.03 (dd, $^3J_{1',2'} = 11.5$, $^3J_{1',1''} = 10.0$, 2H, 1'-H), 6.33 (dd, $^3J_{2',1'} = 11.5$, $^4J_{2',1''} = 0.8$, 2H, 2'-H), 7.40 [s, 4H, 2(3,5,6)-H]	15.06 ($OCH_2\underline{C}H_3$), 15.83 (C-3''), 19.61 (C-1''), 61.27 (C-2''), 66.04 ($O\underline{C}H_2CH_3$), 127.90 (C-1'), 128.49 (C-2'), 132.47 [C-2(3,5,6)], 135.83 [C-1(4)]
26	0.72 (ddd, $^3J_{3''(trans),2''} = 6.4$, $^3J_{3''(trans),1''} = 6.1$, $^2J = 5.8$, 3H, 3''-H_{trans}), 1.17 (m, 12H, 3''-H_{cis} and $OCH_2C\underline{H}_3$), 2.10 (dddd, $^3J_{1'',1'} = 11.5$, $^3J_{1'',3''(cis)} = 9.4$, $^3J_{1'',3''(trans)} = 6.1$, $^3J_{1'',2''} = 2.9$, 3H, 1''-H), 3.28 (ddd, $^3J_{2'',3''(trans)} = 6.4$, $^3J_{2'',3''(cis)} = 3.8$, $^3J_{2'',1''} = 2.9$, 3H, 2''-H), 3.57 (q, 6H, $OC\underline{H}_2CH_3$), 5.05 (dd, $^3J_{1',2'} = 11.6$, $^3J_{1',1''} = 11.5$, 3H, 1'-H), 6.35 (d, $^3J_{2',1'} = 11.6$, 3H, 2'-H), 7.38 [s, 3H, 2(4,6)-H]	15.08 ($OCH_2\underline{C}H_3$), 15.73 (C-3''), 19.60 (C-1''), 61.35 (C-2''), 66.09 ($O\underline{C}H_2CH_3$), 127.30 (C-2'), 128.10 (C-1'), 132.78 [C-2(4,6)], 137.39 [C-1(3,5)]

[a] *trans*-Isomer

[b] *cis*-Isomer

(300 mg, 2.72 mmol), $Pd(PPh_3)_4$ (85 mg, 0.07 mmol), CuI (33 mg, 0.17 mmol), and (*Z*)-1,2-dichloroethene [(*Z*)-**18-Cl**] (110 mg, 1.13 mmol) gave 66 mg (34%) of (*Z*)-**20-Cl** as a colorless oil (fraction I, $R_f = 0.31$).

HRMS: *m*/*z* $C_9H_{11}ClO$ calc. 170.0498; found 170.0498.

Additionally, 120 mg (40%) of 1,4-bis(*trans*-2-ethoxycyclopropyl)-buta-1,3-diyne (**8**) (fraction II, $R_f = 0.22$) was isolated (15 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 40 : 1).

2-Alkoxy-1-ethynylcyclopropyl Substituted Enediynes; General Procedure:

To a stirred solution of 2-alkoxy-1-ethynylcyclopropane **1-R**^{1} (1.00 mmol) in THF (5 mL) was added a solution of butyllithium (1.10 mmol, 466 μL of a 2.36 M solution in *n*-hexane) at −78 °C and stirring was continued for 15 min. The mixture was warmed to 0 °C over 1 h and $ZnCl_2$ (1.15 mmol) in THF (2 mL) was added. After a further 20 min, $Pd(PPh_3)_4$ (0.05 mmol) was added, followed by (*E*/*Z*)-1,2-dibromoethene [(*E*/*Z*)-**18-Br**] [1.06 mmol, *E*/*Z* = 1 : 1.56 (GC, NMR); 0.41 mmol *E* isomer]. The mixture was warmed to 20 °C over 1 h and stirred for 1 h. Pentane and sat. aq NH_4Cl (20 mL each) were added and the mixture was extracted with pentane (3 × 20 mL). The organic layer was filtered through a short Celite pad, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel and recrystallized [compound (*E*)-**22**] to give the pure products.

(*E*)-1,6-Bis(*trans*-2-ethoxycyclopropyl)hex-3-ene-1,5-diyne [(*E*)-19]:

trans-2-Ethoxy-1-ethynylcyclopropane (**1-Et**) (200 mg, 1.82 mmol), butyllithium (844 μl, 1.99 mmol), $ZnCl_2$ (284 mg, 2.08 mmol), $Pd(PPh_3)_4$ (105 mg, 0.09 mmol) and (*E*/*Z*)-1,2-dibromoethene [(*E*/*Z*)-**18-Br**] (357 mg, 1.92 mmol; 0.75 mmol *E* isomer) gave 139 mg (76%) of (*E*)-**19** as a colorless oil (15 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 30 : 1, $R_f = 0.26$).

^1H-^{13}C satellite spectrum for ethylenic signals H-3 and H-4 ($\delta = 5.80$): $^1J_{3(4)H,C} = 166.8$, $^3J_{3(4),4(3)} = 15.9$ Hz.

1,6-Bis-[(1*R*,2*R*)-2-*tert*-butoxycyclopropyl]hex-3-ene-1,5-diyne [(*E*)-22]:

(1*R*,2R)-2-*tert*-Butoxy-1-ethynylcyclopropane (**1-*t*-Bu**) (750 mg, 5.43 mmol), butyllithium (2530 μL, 5.97 mmol), $ZnCl_2$ (851 mg, 6.24 mmol), $Pd(PPh_3)_4$ (314 mg, 0.27 mmol), and (*E*/*Z*)-1,2-dibromoethene [(*E*/*Z*)-**18-Br**] (1071 mg, 5.76 mmol; 2.25 mmol *E* isomer) gave 545 mg (81%) of (*E*)-**22** as a colorless solid (80 g of silica gel, column 4 × 30 cm; PE/Et_2O, 30 : 1, $R_f = 0.29$); mp 75–76 °C (pentane); $[\alpha]_D^{20} = -288.5$ (*c* = 1.17, EtOH).

Raman: $\nu = 1592\ cm^{-1}$ (C=C).

^1H-^{13}C satellite spectrum for ethylenic signals H-3 and H-4 ($\delta = 5.82$): $^1J_{3(4)H,C} = 166.7$, $^3J_{3(4),4(3)} = 15.8$ Hz.

Hydrogenation of [(2-Alkoxycyclopropyl)ethynyl]arenes; General Procedure:

To a stirred suspension of 1.00 mmol of [(2-alkoxycyclopropyl)-ethynyl]arene and 0.27–7.14 mol% of a Lindlar catalyst (or a catalyst containing 3% Pd on barium sulfate) in *n*-pentane (5 mL) was added 0.20–4.04 mol% of quinoline at 20 °C. The reaction flask was flushed with N_2 at a low flow rate for several minutes. The mixture was set under a hydrogen atmosphere (slightly pressurized by a rubber balloon) and the reaction initiated by vigorous stirring. The reaction was checked by TLC and NMR at intervals of approximately 6–12 h until the conversion was complete, after which stirring was immediately stopped. The mixture was filtered through a Celite pad and concentrated. The residue was purified by column chromatography on silica gel to give the pure products.

(*Z*)-[2-(*trans*-2-Ethoxycyclopropyl)ethenyl]benzene (24a-Et):

[(*trans*-2-Ethoxycyclopropyl)ethynyl]benzene (**3a-Et**) (340 mg, 1.83 mmol), 1.2 mol% of Lindlar catalyst, and quinoline (1.1 μl, 0.50 mol%) gave after 48 h 272 mg (79%) of **24a-Et** as a colorless oil (18 g of silica gel, column 3 × 30 cm; PE/Et_2O, 70 : 1; $R_f = 0.28$).

(*Z*)-4-[2-(*trans*-2-Ethoxycyclopropyl)ethenyl]biphenyl (24b-Et):

4-[(*trans*-2-Ethoxycyclopropyl)ethynyl]biphenyl (**3b-Et**) (36 mg, 0.14 mmol), 1.0 mol% of Lindlar catalyst, and quinoline (0.1 μl, 0.06 mol%) gave after 36 h 28 mg (76%) of **24b-Et** as a colorless oil (5 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 40 : 1; $R_f = 0.28$).

(*Z*)-4′-Bromo-4-[2-(*trans*-2-ethoxycyclopropyl)ethenyl]biphenyl (24c-Et):

4′-Bromo-4-[2-(*trans*-2-ethoxycyclopropyl)ethynyl]biphenyl (**3c-Et**) (220 mg, 0.64 mmol), 1.2 mol% of Lindlar catalyst, and quinoline (0.1 μl, 0.13 mol%) gave after 36 h 179 mg (81%) of **24c-Et** as a slow-solidifying oil (20 g of silica gel, column 3 × 30 cm; PE/Et_2O, 20 : 1; $R_f = 0.24$).

(*Z*)-[2-(*trans*/*cis*-2-*tert*-Butyldimethylsilyloxycyclopropyl)ethenyl]-benzene (24a-SiMe$_2$*t*-Bu):

[2-(*trans*/*cis*-2-*tert*-Butyldimethylsilyloxycyclopropyl)ethynyl]benzene (**3a-SiMe$_2$*t*-Bu**) [500 mg, 1.84 mmol (*E*/*Z*, 2 : 1), 0.50 mol% of catalyst (3% Pd on $BaSO_4$), and quinoline (2 μL, 0.91 mol%) gave after 120 h and chromatography (70 g of silica gel, column 3 × 30 cm; PE/Et_2O, 300 : 1) 156 mg (31%) of diastereopure (*Z*)-**24a-SiMe$_2$*t*-Bu** (fraction I, $R_f = 0.25$) and 313 mg (62%) of diastereopure (*E*)-**24a-SiMe$_2$*t*-Bu** (fraction II, $R_f = 0.20$) as a slow-solidifying oil.

1,4-Bis[(*Z*)-2-(*trans*-2-ethoxycyclopropyl)ethenyl]benzene (25):

1,4-Bis[(*trans*-2-ethoxycyclopropyl)ethynyl]benzene (**10**) (100 mg, 0.34 mmol), 2.0 mol% of Lindlar catalyst, and quinoline (0.5 μl, 1.24 mol%) gave after 120 h 87 mg (86%) of **25** as a colorless oil (10 g of silica gel, column 1.5 × 30 cm; PE/Et_2O, 20 : 1, $R_f = 0.29$).

1,3,5-Tris[(*Z*)-2-(*trans*-2-ethoxycyclopropyl)ethenyl]benzene (26):

1,3,5-Tris[(*trans*-2-ethoxycyclopropyl)ethynyl]benzene (**13**) (100 mg, 0.25 mmol), 1.7 mol% of Lindlar catalyst, and quinoline (0.3 μl, 1.01 mol%) gave after 168 h 83 mg (81%) of **26** as a colorless oil (10 g of silica gel, column 1.5 × 20 cm; PE/Et_2O, 15 : 1; $R_f = 0.25$).

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Generous gifts of chemicals from Hoechst AG, Degussa AG and Chemetall GmbH are gratefully acknowledged. The authors are indebted to Dr. B. Knieriem, Göttingen, for his careful proofreading of the manuscript.

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