Synthesis of 1,4-Diethynyl- and 1,1,4,4-Tetraethynylbutatrienes

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In this paper, we report the synthesis and opto-electronic properties of differentially substituted 1,4-diethynyl- and 1,1,4,4-tetraethynylbuta-1,2,3-trienes. These novel chromophores greatly extend the series of building modules for oxidative coupling, which includes 1,2-diethynyl- and 1,1,2,2-tetraethynylethenes and 1,3-diethynylallenes (*Fig. 1*). A general synthesis of 1,1,4,4-tetraethynylbutatrienes, which tolerates a significant number of peripheral substituents, starts from pentadiynols that are oxidized to the corresponding dialkynyl ketones, followed by *Corey–Fuchs* dibromo-olefination, and transition metal mediated dimerization (*Schemes 2* and *3*). A similar protocol, including oxidation of propargyl aldehydes, dibromo-olefination, and dimerization yields the less stable 1,4-diethynylbutatrienes (*Scheme 4*). Attempts to prepare 1,1,4,4-tetraethynylbutatrienes with four terminal electron-donor-substituted aryl groups failed so far, mainly due to difficulties in the dibromoolefination step (*Scheme 6*). *cis-trans*-Isomerization of differentially substituted 1,1,4,4-tetraethynylbutatrienes is remarkably facile, with barriers to rotation in the range of those for peptide bond isomerization ($\Delta G^{\neq} \approx 20$ kcal mol^{-1}). Barriers to rotation of 1,4-diethynylbutatrienes are higher ($\Delta G^{\neq} \approx 25$ kcal mol^{-1}), allowing in some cases the isolation of pure isomers. Both UV/VIS spectroscopy (*Figs. 2* and *3*) and electrochemical studies (*Table*) demonstrate that the all-C-cores in diethynyl- and tetraethynylbutatrienes have strong electron-acceptor properties that are greatly enhanced with respect to those of diethynyl- and tetraethynylethenes with two C(sp)-atoms less. Substitution with peripheral electron donor groups leads to efficient intramolecular charge-transfer interactions, as evidenced by intense, bathochromically shifted longest-wavelength bands in the UV/VIS spectra.

1. Introduction. – The synthesis and study of conjugated organic scaffolds as sources of advanced materials for opto-electronic applications continue to attract large interest in the chemical community [1–3]. In this context, much effort has been directed towards the preparation of small acetylenic building blocks as precursors for the assembly – *via* oxidative coupling – of well-defined molecular architectures extending into one, two, and three dimensions [4][5]. Starting from (*E*)-diethynylethenes (DEEs, (*E*)-hex-3-ene-1,5-diynes) or tetraethynylethenes (TEEs, 3,4-diethynylhex-3-ene-1,5-diynes; *Fig. 1*), monodisperse conjugated poly(triacetylene) oligomers measuring up to 18 nm in length [6] and organometallic rods featuring insulating Pt^{II} σ-bis(acetylide) connectors [7] were prepared. TEE Building blocks also provided access to perethynylated dehydroannulenes [8][9], expanded radialenes [10], and radiaannulenes [9][11]. These strongly electron-withdrawing, conjugated macrocycles display

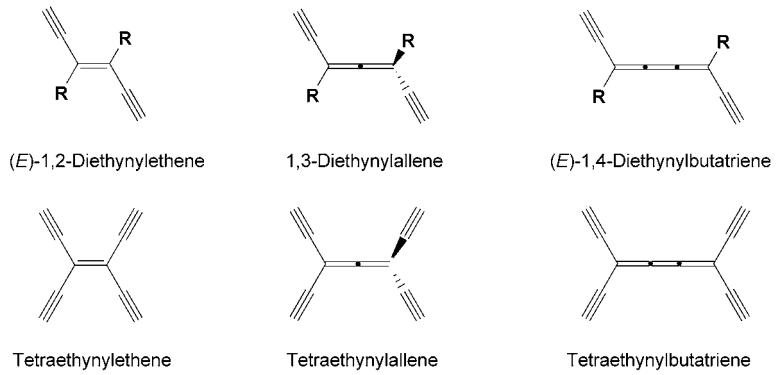


Fig. 1. *C-Rich building blocks for acetylenic scaffolding*

intense intramolecular charge-transfer bands when substituted with *N,N*-dialkylanilino donor groups at the periphery.

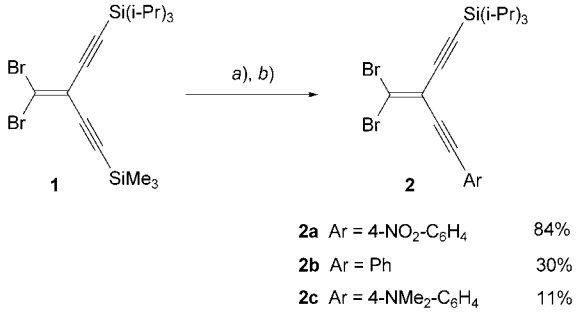
Extension of the central olefinic core in DEEs and TEEs leads to diethynyl- and tetraethynylallenes (*Fig. 1*). While methods for the preparation of 1,3-diethynylallenes by regioselective Pd^0-catalyzed cross-coupling of substrates bearing bispropargylic leaving groups with silyl-protected alkynes have recently been developed [12][13], the corresponding tetraethynylallenes remain elusive [13][14]. Similarly, further expansion of the central cumulenic fragment towards diethynyl- and tetraethynylbutatrienes (*Fig. 1*) has only been investigated scarcely. Prior to this project, only the preparation of two symmetrical 1,1,4,4-tetrakis[(trialkylsilyl)ethynyl]butatrienes had been reported [15]. In contrast, alkyl- and aryl-substituted butatrienes have been investigated to a greater extent (for a survey of butatriene synthesis, see [16]; for recent examples, see [17]). Thus, tetraarylated butatrienes were cyclo-oligomerized into [4]- and [6]radialenes [18][19], whereas dialkyl- or diaryl-substituted butatrienes were found to polymerize under radical-free conditions to yield substituted poly(acetylene)s [20–22]. On the other hand, developing an access to partially deprotected diethynyl- and tetraethynylbutatrienes would subsequently allow the preparation, *via* oxidative coupling, of a novel class of acetylenic molecular rods and macrocycles with potentially unusual properties.

Here, we describe the synthesis of a series of 1,4-diethynyl- and 1,1,4,4-tetraethynylbutatrienes by dimerization of appropriate dibromo olefins. Moreover, we show that these compounds exhibit interesting opto-electronic properties as well as an unexpectedly low barrier for *cis-trans* isomerization (for an experimental and theoretical study concerning this isomerization process, see [23]).

2. Results and Discussion. – 2.1. *Synthesis of Tetraethynyl and Diethynylbutatrienes.* 1,1-Dibromoethenes have previously been shown to dimerize to butatrienes when reacted with appropriate transition metal complexes [24]. Consequently, di- and tetraethynylated butatrienes should be obtained starting from the corresponding alkynylated 1,1-dibromoethenes.

For the preparation of 1,1,4,4-tetraalkynylbutatrienes, diethynylated **1** was synthesized as described in [25] *via* addition of $(i\text{-}Pr)_3Si-C\equiv CH$ to $Me_3Si-C\equiv C-CHO$, followed by oxidation of the resulting alcohol to the bispropargylic ketone with pyridinium chlorochromate (PCC) and *Corey–Fuchs* dibromo-olefination with CBr_4/Ph_3P. Deprotection with K_2CO_3 in THF/MeOH furnished the mono-deprotected alkyne that was directly subjected to *Sonogashira* cross-coupling [26] with various iodoarenes under standard conditions ($[Pd(PPh_3)_2Cl_2]$/CuI/$HN(i\text{-}Pr)_2$) to give **2a–2c** (*Scheme 1*). However, yields were disappointing except for electron-deficient iodoarenes such as 4-nitro-iodobenzene (**2a**: 84%). Attempts to improve the yields in the coupling of electron-rich iodo-arenes by using other catalyst systems ($[Pd_2(dba)_3]$/$AsPh_3$ in Et_3N or $[Pd(MeCN)_2Cl_2]$/CuI in $EtN(i\text{-}Pr)_2$) failed. As the coupling to **2b** and **2c** proceeds very slowly, decomposition of mono-deprotected **1** in solution becomes a competitive pathway.

Scheme 1. Sonogashira *Cross-Coupling between Iodoarenes and Mono-Deprotected* **1**

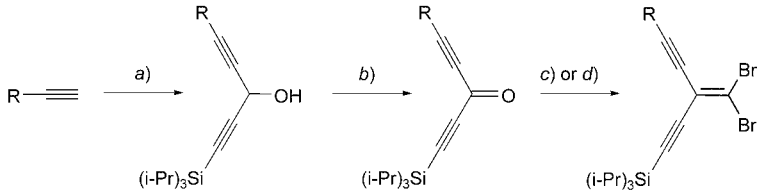


a) K_2CO_3, THF/MeOH. *b*) $[Pd(PPh_3)_2Cl_2]$, CuI, $(i\text{-}Pr)_2NH$, ArI (yields over both steps).

The synthesis of the gem-dibromo olefins **2b–2g** was finally achieved by a less direct but more efficient route. Addition of aryl-, ferrocenyl-, or alkyl-substituted lithium acetylide to $(i\text{-}Pr)_3Si-C\equiv C-CHO$ gave the pentadiynols **3b–3g** in good yields, and subsequent oxidation with MnO_2 provided the corresponding ketones **4b–4g** (*Scheme 2*). Two different sets of conditions were employed in the dibromo-olefination step: compounds **2b–2d** were obtained by reacting ketones **4b–4d** with CBr_4 (1.3 equiv.) and Ph_3P (2.6 equiv.) in benzene at room temperature, whereas the presence of Zn was required for the preparation of **2e–2g** (CBr_4 (2 equiv.), Ph_3P (2 equiv.), and Zn (2 equiv.) in CH_2Cl_2 at room temperature). Our problems encountered with the dibromo-olefination of dialkynyl ketones resemble those already pointed out by *Tykwinsky* and co-workers [27]. Nevertheless, the presented methodology allowed the preparation of **2b–2g** in moderate-to-good overall yields (19–58% starting from $(i\text{-}Pr)_3$-protected propargyl aldehyde).

The gem-dibromo olefins **2b–2g** were subsequently treated with 1 equiv. of BuLi at $-110°$ in Et_2O, followed by addition of 1 equiv. of $[CuI\cdot PBu_3]$ (prepared according to [28]) at $-85°$ to deliver the corresponding highly colored tetraethynylbutatrienes **5b–5g** (*Scheme 3*). Not unexpectedly, the dimerization of the electron-deficient NO_2 derivative **2a** did not proceed successfully, due to the enhanced instability of the elusive butatriene **5a** caused by the presence of two strongly electron-accepting entities

Scheme 2. *Synthesis of Dialkynylated 1,1-Dibromoethenes* **2b**–**2g**

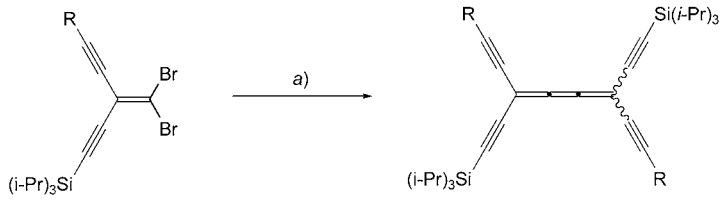


R = Ph	**3b** (66%)	**4b** (95%)	**2b** (38%)
R = 4-NMe_2-C_6H_4	**3c** (60%)	**4c** (97%)	**2c** (49%)
R = 3,5-(t-Bu)$_2$$C_6H_3$	**3d** (59%)	**4d** (95%)	**2d** (56%)
R = 4-MeO-C_6H_4	**3e** (66%)	**4e** (85%)	**2e** (83%)
R = Fc	**3f** (66%)	**4f** (85%)	**2f** (35%)
R = t-Bu	**3g** (74%)	**4g** (98%)	**2g** (85%)

a) BuLi, THF, $-10°$; then (i-Pr)$_3$Si–C≡C–CHO. *b*) MnO_2, Et_2O, 20°. *c*) CBr_4, Ph_3P, benzene, 20°. *d*) CBr_4, PPh_3, Zn, CH_2Cl_2, 20°. Fc = ferrocenyl.

(the cumulenic core and the $NO_2C_6H_4$ groups) in the molecule. In contrast, yields were particularly high in the presence of electron-donating groups (*e.g.*, **5c**: 80%). On the other hand, the yields of donor-substituted **5f** and **5g** were substantially lower due to difficulties with purification, which required both regular column (SiO_2) and gel-permeation chromatography (*Bio-Beads SX-1*) to separate the desired butatrienes from 2,2-dialkynylated 1-bromo alkenes formed as side products.

Scheme 3. *Synthesis of 1,1,4,4-Tetraethynylbutatrienes*



2a-g

		Yield	Color
5a	R = 4-NO_2-C_6H_4	-	-
5b	R = Ph	(62%)	brown
5c	R = 4-NMe_2-C_6H_4	(80%)	purple
5d	R = 3,5-(t-Bu)$_2$$C_6H_3$	(69%)	orange
5e	R = 4-MeO-C_6H_4	(56%)	red
5f	R = Fc	(37%)	green
5g	R = t-Bu	(24%)	yellow

a) BuLi, Et_2O, $-110°$, then [CuI . PBu_3], $-85° \rightarrow 20°$. The colors of solutions in CH_2Cl_2 are indicated.

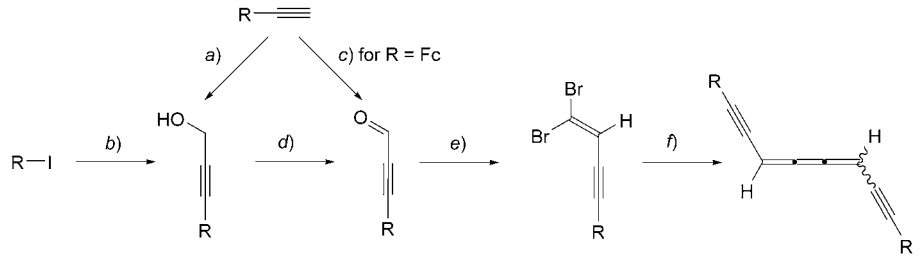
In the dimerization of **2b**–**2g** to **5b**–**5g**, respectively, the high solubility of the Cu complex employed [24] seems to be particularly beneficial, since it allows the reaction to take place at very low temperature, thus preventing any decomposition of starting material and product. Accordingly, protocols for similar dimerization processes at

room temperature [29] did not lead to any isolable tetraethynylbutatrienes. All butatrienes **5b**–**5g** were obtained as inseparable mixtures of *cis*- and *trans*-isomers as demonstrated by ^{1}H- and ^{13}C-NMR spectroscopy, with the characteristic central cumulenic resonance appearing at *ca.* 150 ppm in the ^{13}C-NMR spectra. The IR spectra of these compounds displayed weak bands around 2200 and 1530 cm^{-1}, corresponding to C≡C and C=C bond stretches, respectively. The obtained tetraethynylbutatrienes **5c**–**5g** are surprisingly stable and can be stored for prolonged time periods in the solid state at −30°; only **5b** decomposes with time, even at low temperatures.

To evidence the potential of the (i-Pr)$_3$Si-protected tetraethynylbutatrienes as building blocks for acetylenic scaffolding, deprotection of the anilino derivative **5c** was attempted in the presence of Bu_4NF (2 equiv.) and 2-nitrophenol (2 equiv.) in THF at 0°. Complete deprotection was observed by TLC after 2 h, and the solution seems stable enough for performing subsequent *in situ* oxidative couplings. Decomposition, however, occurs upon evaporation of the solvent.

1,4-Diethynylbutatrienes had not been described prior to this work. On the way to these new building modules, the substituted propargylic alcohols **6a**–**6d** were prepared either by nucleophilic addition of the corresponding lithium acetylide to paraformaldehyde [30] or *via* Pd-catalyzed cross-coupling between propargyl alcohol and the appropriate aryl iodide (*Scheme 4*) [31][32]. Subsequent oxidation afforded the propargyl aldehydes **7a**–**7d** in high yield [14][31][32]. In the case of the ferrocenyl derivative **7e**, a direct synthesis *via* lithiation of ethynylferrocene, followed by addition of dimethylformamide (DMF), was very efficient giving rise to the formation of **7e** in 90% yield. Dibromo-olefination (CBr_4, Ph_3P, and Zn in CH_2Cl_2 at room temperature) afforded the gem-dibromo olefins **8a**–**8e**.

Scheme 4. *Synthesis of 1,4-Diethynylbutatrienes*



a) BuLi, THF, −10°, then $(HCHO)_x$. *b*) HC≡C−CH_2OH, [$Pd(PPh_3)_2Cl_2$], CuI, HN(i-Pr)$_2$. *c*) BuLi, THF, −78°, then DMF, −78° → 20°. *d*) CBr_4, Ph_3P, Zn, CH_2Cl_2, 20°. *e*) BuLi, Et_2O, −110°, then [CuI·PBu_3], −85° → 20°.

The subsequent dimerization was not successful in all cases. Whereas the reaction of the (i-Pr$_3$)Si, *N,N*-dimethylanilino, and ferrocenyl derivatives, **8a**, **8b**, and **8e**, respectively, provided the desired 1,4-diethynylbutatrienes **9a**, **9b**, and **9e**, respectively,

the synthesis of the 3,5-di(tert-butyl)phenyl and 4-methoxyphenyl derivatives, **9c** and **9d**, respectively, was not successful. This may reflect a higher instability of 1,4-diethynylbutatrienes under the reaction conditions as compared to 1,1,4,4-tetraethynylbutatrienes. All three butatrienes were obtained as a mixture of *cis*- and *trans*-isomers (NMR). While one isomer of **9a** could be separated and isolated in pure form, compounds **9b** and **9e** were obtained as inseparable isomeric mixtures. The ^{13}C-NMR resonances of the two central C(sp)-atoms in the cumulene fragment of **9b** and **9e** appear at *ca.* 155 ppm, whereas this signal appears in the spectrum of **9a** at 160.9 ppm.

2.2. cis-trans *Isomerization.* Based on the published data for butatrienes, [16][33], we expected the isomerization barriers to be high enough to allow separation of *cis*- and *trans*-1,1,4,4-tetraethynylbutatrienes **5b**–**5g** at room temperature. However, all attempts to separate the two isomers either by gravity or high-performance liquid chromatography failed. A subsequent determination of the activation parameters for the *cis-trans* isomerization process by ^{1}H-NMR techniques revealed a remarkably low rotational barrier $\Delta G^{\neq}$ for 1,1,4,4-tetraethynylbutatrienes **5d** and **5f** of *ca.* 20 kcal mol^{-1}, in the range of those observed for rotation about peptide bonds [23]. This facile isomerization process explains the failure of all our attempts to separate the *cis*- and *trans*-isomers.

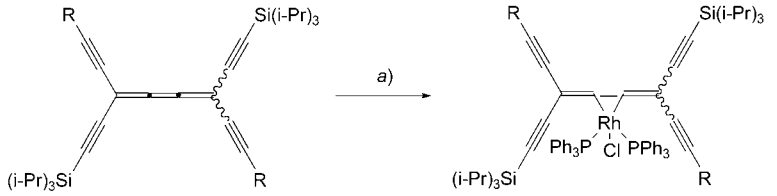
In contrast, the isolation of a pure isomer was possible for **9a**, showing that isomerization is less facile in the case of 1,4-diethynylbutatrienes. ^{1}H-NMR Investigations allowed estimation of the barrier for thermal *cis-trans* isomerization of **9a** as $\Delta G^{\neq} \approx 25$ kcal mol^{-1} [23]. On the other hand, all attempts to separate the isomers of **9b** and **9e** remained unsuccessful. Possibly, increased extension of conjugation through the terminal aromatic rings further reduces the barrier for rotation in these cumulenes, thereby rendering isomer separation impossible at room temperature (for elegant investigations on the dependence of the barrier for *cis-trans* isomerization in olefins as a function of conjugation length, see [34]).

Detailed computational studies by *Houk*, *Jarowski*, and co-workers [23] confirmed the stabilizing effect of alkynyl substituents on the proposed but-2-yne-1,4-diyl singlet diradical transition state of the *cis-trans* isomerization in 1,4-diethynyl- and 1,1,4,4-tetraethynylbutatrienes and accurately reproduced the experimentally determined rotational barriers.

2.3. *Rh^I Coordination.* Previous reports concerning the coordination of the central double bond in [3]cumulenes to Rh^I under formation of stable η^2-complexes [15][35–37] prompted us to investigate this complexation mode for the new tetraethynylated butatrienes **5c** and **5d**. Reaction with $[Rh(PPh_3)_3Cl]$ in CH_2Cl_2 at room temperature proceeded rapidly in the case of **5c**, whereas the corresponding conversion of **5d** was very slow, presumably due to steric hindrance (*Scheme 5*).

The resulting η^2-complexes **10c** and **10d** were obtained as mixtures of isomers. However, their high instability towards SiO_2 or Al_2O_3 precluded any chromatographic purification. In the course of attempted purifications, it appeared that **5c** and **5d** only acted as poor ligands for Rh^I, since they underwent smooth decomplexation during column chromatography. Finally, the η^2-complexes were separated from starting material by gel-permeation chromatography (GPC), thereby furnishing **10c** and **10d** in 13 and 72% yield, respectively. The anilino-substituted complex **10c** was found to be substantially less stable than **10d**, and full characterization by NMR spectroscopy was

Scheme 5. *Synthesis of η^2-Rh^I Complexes*



5c,d

10c R = 4-Me_2N-C_6H_4 (13%)
10d R = 3,5-(t-Bu)$_2$$C_6H_3$ (72%)

a) [Rh(PPh_3)$_3$Cl], CH_2Cl_2, 20°.

not possible due to rapid degradation in solution. Separation of the *cis*- and *trans*-isomers of the η^2-Rh^I complexes was also not possible due to the limited stability of these species.

2.4. *Electronic Absorption Spectroscopy.* The UV/VIS spectra of tetraethynylbutatrienes **5b**–**5g** (CH_2Cl_2; *Fig. 2*) revealed strong chromophoric properties. The spectra of the aryl-substituted tetraethynylbutatrienes **5b**, **5d**, and **5e** are very similar with an end-absorption around 550 nm and a longest-wavelength absorption maximum λ_{max}

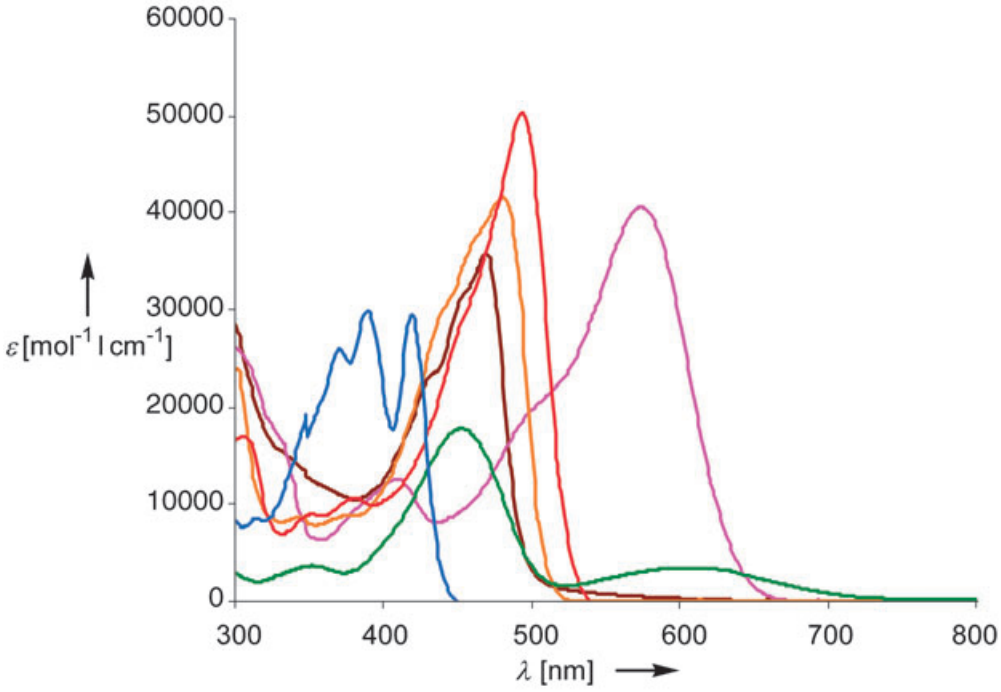


Fig. 2. *Electronic absorption spectra of* **5b** (*brown*), **5c** (*pink*), **5d** (*orange*), **5e** (*red*), **5f** (*green*), *and* **5g** (*blue*) *in* CH_2Cl_2

around 480 nm (**5b**: $\lambda_{max} = 469$ nm, $\varepsilon = 35700$ mol^{-1} l cm^{-1}; **5d**: $\lambda_{max} = 481$ nm, $\varepsilon = 41600$ mol^{-1} l cm^{-1}; **5e**: $\lambda_{max} = 494$ nm, $\varepsilon = 50400$ mol^{-1} l cm^{-1}). When replacing the aryl rings by alkyl groups (in **5g**) the longest-wavelength band is hypsochromically shifted to $\lambda_{max} = 419$ nm ($\varepsilon = 29400$ mol^{-1} l cm^{-1}).

Introduction of strongly electron-donating dialkylanilino groups in **5c** led to an intense longest-wavelength band at 573 nm, which is bathochromically shifted by more than 100 nm (0.48 eV) as compared to the phenyl derivative **5b**. The reversible quenching of this absorption band upon acidification with TsOH and subsequent neutralization with Et_3N identifies it as a charge-transfer resulting from intramolecular charge-transfer interactions between the anilino donor group and the electron-accepting cumulenic core. It is worth comparing the UV/VIS spectra of anilino-substituted tetraethynylbutatriene **5c** ($\lambda_{max} = 573$ nm) and the corresponding tetra-ethynylethene derivative ($\lambda_{max} = 459$ nm) [38]. Introduction of the two additional C(sp)-atoms into the central core of **5b** leads to a strong red-shift of the intramolecular charge-transfer band ($\Delta\lambda = 114$ nm, $\Delta E = 0.53$ eV), thus highlighting a strong increase of the electron-acceptor potential of the C-core.

Introduction of ferrocenyl substituents (*i.e.*, **5f**) shifts the longest-wavelength band λ_{max} bathochromically to 602 nm, presumably due to the intramolecular charge-transfer character of this transition. On the other hand, the molar extinction coefficient of this band is remarkably reduced ($\varepsilon = 3450$ mol^{-1} l cm^{-1}), for which we do not have a good explanation. The second absorption band at 452 nm ($\varepsilon = 17800$ mol^{-1} l cm^{-1}) may be due to metal-to-ligand charge transfer.

The UV/VIS spectra (CH_2Cl_2) of the dialkynylated butatrienes **9a**, **9b**, and **9e** are depicted in *Fig. 3*. The reduction of the conjugated all-C-chromophore as compared to the tetraalkynylated analogs is clearly evident from the position of the longest-wavelength band, which appears at $\lambda_{max} = 419$ nm in the *t*-Bu-substituted tetraethynyl derivative **5g** and at $\lambda_{max} = 356$ nm in (i-Pr)$_3$Si-substituted diethynylbutatriene **9a**. The

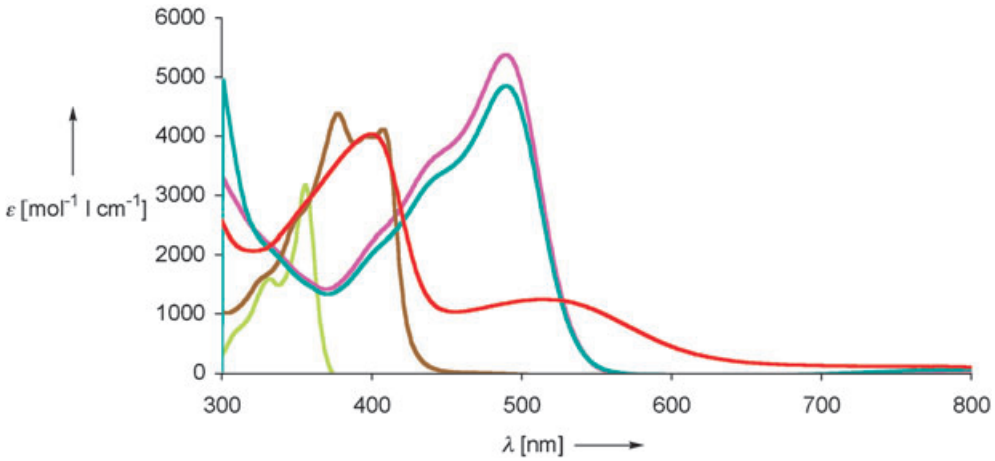


Fig. 3. *Electronic absorption spectra* **9a** (*yellow*), **9b** (*pink*), *and* **9e** (*red*) in CH_2Cl_2. Also shown are the spectra of **9b** after addition of TsOH (brown) and subsequent neutralization with Et_3N (*green*).

spectrum of ferrocenyl derivative **9e** resembles the one of the tetraethynylated analog **5f** (*Fig. 2*), featuring two absorption bands, with the longest-wavelength band – presumably with high charge-transfer character – appearing at $\lambda_{max} = 516$ nm ($\varepsilon = 140$ mol^{-1} l cm^{-1}) as compared to $\lambda_{max} = 602$ nm in the spectrum of **5f**.

The decrease in chromophoric extension and electron-acceptor strength upon removal of two C≡C bonds is also visible in the comparison between the two dimethylanilino-substituted derivatives, diethynylated **9b** ($\lambda_{max} = 489$ nm, $\varepsilon = 5400$ mol^{-1} l cm^{-1}) and tetraethynylated **5c** ($\lambda_{max} = 573$ nm, $\varepsilon = 40500$ mol^{-1} l cm^{-1}): the longest-wavelength band of the diethynylated derivative features both a strong hypsochromic shift and a large hypochromism. Addition of TsOH caused a color change of the solution of **9b** in CH_2Cl_2 from purple to yellow, reflecting the disappearance of the intramolecular charge-transfer band in the UV/VIS spectrum (*Fig. 3*). Again, the original spectrum of **9b** was completely recovered upon subsequent neutralization with Et_3N, albeit with a slight reduction in absorption intensity presumably due to a slight degradation of the compound upon acidification.

2.5. *Electrochemistry.* The electrochemical properties of tetraethynylbutatrienes **5c**–**5f** were investigated by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). The redox potentials *vs.* Fc$^+$/Fc (ferricinium/ferrocene couple) are listed in the *Table*.

Table. *Cyclic Voltammetry (CV) and Rotating-Disk Voltammetry (RDV) Data in CH_2Cl_2 (+ 0.1M Bu_4NPF_6)*. Potentials are given *vs.* Fc$^+$/Fc. Working electrode: glassy-C electrode; counter electrode: Pt; reference electrode: Ag/AgCl electrode.

	Cyclic voltammetry[a])			Rotating-disk voltammetry	
	E°[b]) [V]	ΔE_p[c]) [mV]	E_p[d]) [V]	$E_{1/2}$[e]) [V]	Slope[f]) [mV]
5c	+0.28[g])	60		+0.28	80
	−1.38	60		−1.38	70
			−1.82	−1.88	120
5d			+1.03[h])	+1.01	80
	−1.28	80		−1.27	75
			−1.78	−1.83	100
5e			+0.84	+0.84	125
	−1.34	60		−1.33	80
			−1.80		
5f	+0.18	120		0.22	90
	−1.41	80		−1.41	95
			−1.91		

[a]) Scan rate 0.1 V s^{-1}. [b]) $E^{\circ} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c]) ΔE_p is the peak potential difference at $v = 0.1$ V s^{-1}. [d]) Peak potential E_p for irreversible electron transfer. [e]) Half-wave potential $E_{1/2}$. [f]) Slope of the linearized plot of E *vs.* $\log [I/(I_{lim} - I)]$. [g]) Unresolved two-electron oxidation. [h]) The electron transfer becomes reversible at scan higher than 5 V s^{-1}.

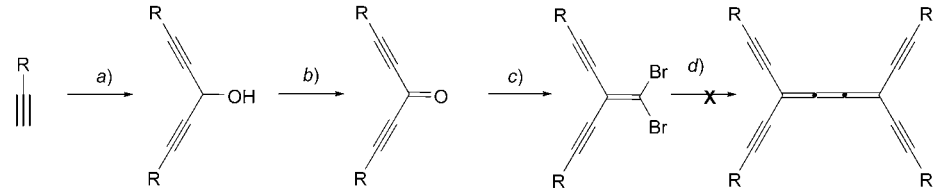
All tetraethynylbutatrienes exhibit two reduction steps; the first one is a reversible one-electron transfer, whereas the second one is irreversible. These two reductions take place at the conjugated backbone. Reductions in compounds **5c**–**5f** occur at potentials between −1.28 and −1.41 V for the first one, and −1.78 to −1.91 V for the second one. These values are in good agreement with the reduction potentials measured for

tetrakis[tri(isopropylsilyl)ethynyl]butatriene ($E_{red} = -1.30$ and -1.84 V *vs.* Fc^+/Fc) [39]. Comparatively, the one-electron reduction of the tetraethynylethene (TEE) core in tetrakis(phenylethynyl)ethene occurs at a more negative potential around -1.80 V [40]. As expected, introduction of electron-donating groups shifts the first reduction potential of tetraethynylbutatrienes cathodically from -1.28 V for **5d** to -1.34 V for **5e**, -1.38 V for **5c**, and -1.41 V for **5f**. This is consistent with a more-difficult reduction for electron-richer molecules.

The conjugated backbone in **5d** is oxidized irreversibly at 1.03 V. However, for **5c** and **5e** the first oxidation occurs at the anilino or methoxyphenyl substituents at 0.28 and 0.84 V, respectively, since these groups are electroactive [41]. Comparison with the corresponding tetraethynylethenes is difficult, since data are scarce, nevertheless, the oxidation of the anilino group in the tetraethynylethene analog of **5c** was measured at 0.39 V [40]. As the first oxidation potential shifts anodically going from tetraethynylbutatriene to tetraethynylethene, the presence of the [3]cumulenic acceptor fragment does not make the oxidation of the anilino group more difficult, which may indicate that there is almost no communication between the anilino substituent and the C(sp)-core fragment at the HOMO level. Moreover, the ferrocenyl derivative **5f** gives a single reversible two-electron transfer, the characteristics of which denote overlap of the two reversible one-electron transfers. The peak potential difference is equal to 120 mV and remains constant for scan rates up to 1 V s^{-1}. Analysis of the peaks allowed the determination of the potential difference between the two ferrocene units at 80 mV, the oxidation potentials being $E_{ox1} = +0.14$ and $E_{ox2} = +0.22$ V. It is worth comparing the results obtained for **5f** with those published for 1,4-diferrocenyl-1,4-diphenylbutatriene [17b]. In the latter system, two reversible steps occur at $+0.41$ and $+0.61$ V *vs.* SCE (standard calomel electrode), and an irreversible one at $+1.45$ *vs.* SCE. As the two ferrocenyl substituents are directly connected to the cumulenic core, potential splitting is observed. In our case, the distance between the two ferrocenyl units is larger, so that the electrostatic interactions between the two oxidized ferrocenyl units are reduced. Under these conditions, there are less interactions through the conjugated backbone, so that the two oxidation potentials are very close ($+0.14$ and $+0.22$ V *vs.* Fc^+/Fc).

2.6. *Synthetic Approaches towards Tetrakis(arylethynyl)butatrienes.* Since the central C-core of tetraethynylbutatrienes proved to have strong electron-acceptor properties (*Sect. 2.4*), we became interested in the synthesis of derivatives bearing four donor groups to further enhance the intramolecular charge-transfer interactions. For this purpose, pentadiynols **11a**–**11c** were prepared by nucleophilic addition of donor-substituted acetylides to HCO_2Et. Deprotonation of the alkyne was first performed using BuLi at $-78°$, but after addition of the electrophile the expected alcohol was formed together with the corresponding aldehyde resulting from mono-addition. Chromatographic separation of the two products was tedious, since the aldehyde proved to be sensitive to SiO_2. Finally, we found that deprotonation of the alkyne using EtMgBr in Et_2O at 40° followed by addition of HCO_2Et was a more efficient procedure, delivering **11a** (R = 4-MeO–C_6H_4), **11b** (R = 4-Me_2N–C_6H_4), and **11c** (R = Fc) in 59, 45, and 49% yield, respectively (*Scheme 6*). Subsequent oxidation by MnO_2 proceeded smoothly, furnishing ketones **12a**–**12c**. On the other hand, dibromoolefination of these ketones bearing two donor groups was difficult. The transformation

Scheme 6. *Synthetic Attempts towards Tetrakis(arylethynyl)butatrienes*



R = 4-MeO-C_6H_4	**11a** (59%)	**12a** (94%)	**13a** (52%)
R = 4-Me_2N-C_6H_4	**11b** (45%)	**12b** (92%)	**13b** (9%)
R = Fc	**11c** (49%)	**12c** (73%)	**13c** (-)

a) EtMgBr, Et_2O, 40°, then HCO_2Et. *b*) MnO_2, Et_2O, 20°. *c*) CBr_4, Ph_3P, PhH or CH_2Cl_2, 20°. *d*) BuLi, Et_2O, −110°, then [CuI·PBu_3], −85° → 20°.

of the 4-MeO–C_6H_4 derivative **12a** into dibromo olefin **13a** proceeded in 52% yield, under the conditions described above (*Sect. 2.1*). For ketones **12b** and **12c**, featuring the stronger dimethylanilino and ferrocenyl donor groups, these reaction conditions were not efficient: **13b** was isolated in only 9% yield, while **13c** was not formed at all. A variety of reaction conditions were employed to prepare **13b** in higher yield, including a recent procedure that requires the formation of a hydrazone intermediate, [42], albeit none of them were successful. The dimerization of dibromo olefin **13a** was subsequently attempted using the conditions described above (*Sect. 2.1*). Unfortunately, no butatriene could be isolated; rather the forming product seems to become unstable when warming the solution to room temperature. This lower stability of tetrakis(arylethynyl)butatrienes may be explained by the absence of steric protection of the cumulenic core, which, in case of the tetraethynylbutatrienes **5b**–**5f**, was provided by the lateral $(i\text{-}Pr)_3Si$ groups. Further efforts towards the preparation and characterization of the targeted tetrakis(arylethynyl)butatrienes are underway.

3. Conclusions. – With the differentially substituted 1,4-diethynylated and 1,1,4,4-tetraethynylated butatrienes reported in this paper, the series of cumulenic building blocks for acetylenic scaffolding, which hitherto included diethynyl- and tetraethynylethenes (DEEs and TEEs) and 1,3-diethynylallenes, has been substantially extended. Their synthesis *via* transition-metal-mediated coupling of alkynylated gem-dibromoethenes proves to be quite versatile, tolerating a large number of substituents on the alkyne groups. On the other hand, the preparation of the gem-dibromo-ethenes *via* *Corey–Fuchs* dibromo-olefination has been found problematic at instances, in agreement with other literature reports [27]. *cis-trans* Isomerization of differentially substituted 1,1,4,4-tetraethynylbutatrienes *via* a singlet diradical transition state is remarkably facile, and the rotational barrier was determined in ^{1}H-NMR investigations as $\Delta G^{\neq} \approx 20$ kcal mol^{-1}, similar to the barrier for rotation about a peptide bond [23]. The barriers for 1,4-diethynylbutatrienes are higher, around 25 kcal mol^{-1}, allowing, in some cases, the isolation of pure isomers. UV/VIS Spectroscopy and electrochemical studies demonstrate that the electron-accepting power of the central all-C-core is greatly increased upon changing from tetraethynylethenes to tetraethynylbutatrienes. Introduction of peripheral aryl donor groups such as *N,N*-dimethylanilino residues

leads to compounds (*e.g.*, **5c**) featuring intense, bathochromically shifted intramolecular charge-transfer bands. Attempts to introduce four peripheral donor groups into tetraethynylbutatrienes failed so far; these compounds will be the subject of further investigations. Preliminary work shows that 1,1,4,4-tetraethynylbutatrienes with two terminal free alkyne groups in positions 1 and 4 of the cumulenic core can be prepared by removal of $(i\text{-}Pr)_3Si$-protecting groups. The reasonable stability of the deprotected derivatives in solution should allow, in future work, the construction by oxidative coupling of novel linear oligomers and macrocycles with unprecedented all-C-skeletons and unusual opto-electronic properties.

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Experimental Part

General. All reactions were carried out under an inert atmosphere (Ar or N_2) by applying a positive pressure. Chemicals were purchased from commercial suppliers and used as received. Compounds **6a** [30] , **6b** and **6d** [31][32], and **7a**, **7b**, and **7d** [14][31][32] were prepared according to literature protocols. THF was freshly distilled from sodium benzophenone ketyl, and CH_2Cl_2 was freshly distilled from CaH_2. Et_2O on molecular sieves from *Fluka* was used for dimerization reactions. Evaporation *in vacuo* was performed using a membrane pump at a pressure of 20–50 Torr. TLC: alumina sheets precoated with 0.25-mm *Macherey–Nagel* SiO_2, with fluorescent indicator. Column chromatography (CC): SiO_2 *60* (particle size 0.04–0.063 mm, 230–400 mesh) from *Fluka* and distilled technical solvents. Size-exclusion chromatography (GPC): *Bio-Beads S-X3* and *S-X1* from *Bio-Rad* using distilled technical solvents. M.p. in open capillaries with a *Büchi 540* apparatus, uncorrected; 'dec.' refers to decomposition. UV/VIS Spectra: *Varian CARY 500 Scan* spectrophotometer, λ_{max} in nm and ε in $mol^{-1}\ l\ cm^{-1}$. IR Spectra: *Perkin-Elmer FT1600* spectrometer; selected absorption bands in wavenumbers (cm^{-1}). ^{1}H- (300 MHz) and ^{13}C-NMR (75 MHz) spectra: *Varian Gemini 300* spectrometers; Chemical shifts are indicated in ppm downfield from Me_4Si using the solvent peak as internal reference ($CDCl_3$: $\delta(H) = 7.25$, $\delta(C) = 77.2$); coupling constants J are indicated in Hz. MS: *VG-Tribid* instrument operating at 70 eV (EI-MS) or on an *IonSpec Ultra* instrument (MALDI-MS), with 2,5-dihydroxybenzoic acid (DHB) or 2-{(*E*)-3-[(4-*tert*-butyl)phenyl]-2-methyl-2-propenylidene}malonitrile (DCTB) as a matrix. Elemental analyses were performed by the *Mikrolabor* at the *Laboratorium für Organische Chemie* at *ETH-Zürich*.

Electrochemistry. Electrochemical measurements were carried out in CH_2Cl_2 containing 0.1M Bu_4NPF_6 in a classical three-electrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). The working electrode was a glassy-C disk (2 mm in diameter), the auxiliary electrode a Pt wire, and the reference electrode an aq. Ag/AgCl electrode. All potentials are given *vs.* Fc^+/Fc as internal reference.

3-(Dibromomethylidene)-1-(4-nitrophenyl)-5-(triisopropylsilyl)penta-1,4-diyne (**2a**). K_2CO_3 (0.276 g, 2 mmol) was added to a soln. of **1** (0.460 g, 1.0 mmol) in THF (10 ml) and MeOH (10 ml). After stirring for 30 min, CH_2Cl_2 (30 ml) was introduced, and the mixture was filtered through SiO_2. Evaporation *in vacuo* left an orange oil to which $(i\text{-}Pr)_2NH$ (15 ml) and 4-nitro-1-iodobenzene (0.249 mg, 1 mmol) were added. This soln. was extensively purged with Ar for 1 h, after which $[Pd(PPh_3)_2Cl_2]$ (0.035 g, 0.05 mmol) and CuI (0.010 g, 0.05 mmol) were introduced. The mixture turned brown. After stirring for 1 h, CH_2Cl_2 was added and the mixture filtered over SiO_2. Evaporation *in vacuo* and CC (SiO_2; hexane) afforded **2a** (0.429 g, 84%). Yellow solid. R_f (hexane/CH_2Cl_2 7:3) 0.47. M.p. 88.0°. IR (CCl_4): 2944*s*, 2892*m*, 2866*s*, 1596*s*, 1525v*s*, 1491*w*, 1462*m*, 1344v*s*, 1166*w*, 1107*w*, 1010*w*, 997*w*, 922*m*, 883*m*, 868*s*, 855*s*, 803v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*m*, 21 H); 7.64 (*d*, $J = 9$, 2 H); 8.50 (*d*, $J = 9$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 147.7; 132.6; 129.2; 123.9; 114.2; 111.1; 101.6; 101.0; 93.2; 90.9; 18.8; 11.4. EI-MS: 511.0 (15, M^+), 468.0 (100, $[M - i\text{-}Pr]^+$). HR-EI-MS: 511.0051 (M^+, $C_{21}H_{25}Br_2NO_2Si^+$; calc. 511.0001); 467.9496 (100, $[M - i\text{-}Pr]^+$, $C_{18}H_{18}Br_2NO_2Si^+$; calc. 467.9453). Anal. calc. for $C_{21}H_{25}NO_2SiBr_2$ (511.33): C 49.33, H 4.93, N 2.74; found: C 49.44, H 5.05, N 2.90.

1-Phenyl-5-(triisopropylsilyl)penta-1,4-diyn-3-ol (**3b**). BuLi (1.5M in hexanes, 2 ml, 3 mmol) was added to ethynylbenzene (0.329 ml, 3 mmol) in freshly distilled THF (30 ml) at 0°. After stirring for 1 h at this temp., 3-(triisopropylsilyl)propynal (0.631 g, 3 mmol) was introduced. After stirring for 1 h, the reaction was quenched by adding sat. aq. NH_4Cl soln. (20 ml). The mixture was extracted twice with Et_2O (30 ml), the combined org. phases were washed with H_2O and sat. aq. NH_4Cl soln. (20 ml), and dried ($MgSO_4$). Evaporation *in vacuo* and

CC (SiO_2; hexane/CH_2Cl_2 7:3 then 1:1) afforded **3b** (0.318 g, 66 %). Brown oil. R_f (hexane/CH_2Cl_2 1:1) 0.29. IR (CCl_4): 3601*s*, 2890*w*, 3470*w* (br.), 2944v*s*, 2892v*s*, 2866v*s*, 2235*w*, 2174*w*, 1670*w*, 1600*w*, 1490v*s*, 1463v*s*, 1443*s*, 1383*m*, 1367*m*, 1294*m*, 1231*w*, 1070*m*, 2030v*s*, 1017v*s*, 998v*s*, 915*m*, 903*m*, 883v*s*, 809v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*m*, 21 H); 2.23 (*d*, *J* = 8, 1 H); 5.34 (*d*, *J* = 8, 1 H); 7.32 (*m*, 3 H); 7.45 (*dd*, *J* = 8, 2, 2 H). ^{13}C-NMR (75 MHz, CD_3OD): 132.5; 129.6; 129.3; 123.5; 106.5; 87.8; 85.1; 84.0; 52.9; 18.9; 12.2. EI-MS : 312.3 (21, M^+), 295.1 (29, $[M - OH]^+$), 267.2 (77, $[M - OH - i\text{-}Pr]^+$), 253.2 (20, $[M - OH - i\text{-}Pr - Me]^+$), 239.1 (57, $[M - i\text{-}Pr - 2\ Me]^+$), 225,1 (28, $[M - 2i\text{-}Pr]^+$), 213.1 (91, $[M - 2\ i\text{-}Pr - Me]^+$), 183.1 (71, $[M - 3\ i\text{-}Pr]^+$), 169.1 (100, $[M - OH - 3\ i\text{-}Pr]^+$), 139.1 (64, $[M - Si(i\text{-}Pr)_3 - OH]^+$). Anal. calc. for $C_{20}H_{28}OSi$ (312.53): C 76.86, H 9.03; found: C 76.84, H 8.87.

1-[4-(Dimethylamino)phenyl]-5-(triisopropylsilyl)penta-1,4-diyn-3-ol (**3c**). 4-Ethynyl-*N,N*-dimethylaniline (0.508 g, 3.5 mmol), BuLi (1.5M in hexanes, 2.33 ml, 3.5 mmol), and 3-(triisopropylsilyl)propynal (0.737 g, 3.5 mmol) were reacted according to the procedure described for **3b** to give **3c** (0.746 g, 60%) after flash chromatography (FC; SiO_2; hexane/CH_2Cl_2 1:2, then hexane/AcOEt: 4:3). Yellow oil with properties identical to those described in [43]. R_f (hexane/CH_2Cl_2 3:7) 0.29. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.08 (*m*, 21 H); 2.20 (*d*, *J* = 7.5, 1 H); 2.98 (*s*, 6 H); 5.32 (*d*, *J* = 7.5, 1 H); 6.62 (*d*, *J* = 9, 2 H); 7.32 (*d*, *J* = 9, 2 H).

*1-[3,5-Di(*tert*-butyl)phenyl]-5-(triisopropylsilyl)penta-1,4-diyn-3-ol* (**3d**). 3,5-Di(*tert*-butyl)phenylacetylene (0.643 g, 3 mmol), BuLi (1.5M in hexanes, 2.0 ml, 3 mmol), and 3-(triisopropylsilyl)propynal (0.632 g, 3 mmol) were reacted according to the procedure described for **3b** to give **3d** (0.752 g, 59%) after CC (SiO_2; hexane/CH_2Cl_2 1:1). Brown oil. R_f (hexane/CH_2Cl_2 1:1) 0.11. IR (CCl_4): 3602*m*, 2965v*s*, 2866*s*, 2362*w*, 2336*w*, 2226*w*, 1590*m*, 1463*m*, 1364*m*, 1248*m*, 1055*m*, 1030*s*, 944*w*, 878*m*, 815v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*m*, 21 H); 1.27 (*s*, 18 H); 2.22 (*d*, *J* = 8, 1 H); 5.34 (*d*, *J* = 8, 1 H); 7.31 (*d*, *J* = 2, 2 H); 7.40 (*t*, *J* = 2, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 151.1; 126.3; 123.4; 121.3; 104.6; 86.3; 85.6; 85.3; 53.4; 35.0; 31.5; 18.0; 11.4. EI-MS: 424.4 (13, M^+), 381.2 (17, $[M - i\text{-}Pr]^+$), 351.2 (20, $[M - i\text{-}Pr - 2\ Me]^+$), 339.3 (15, $[M - 2\ i\text{-}Pr]^+$), 325.3 (100, $[M - i\text{-}Pr - t\text{-}Bu]^+$), 273.2 (24, $[M - OH\text{-}(i\text{-}Pr)_3Si]^+$), 211.2 (16, $[M - CCC_6H_3(C_4H_9)_2]^+$). Anal. calc. for $C_{28}H_{44}OSi$ (424.74): C 79.18, H 10.44; found: C 79.11, H 10.39.

1-(4-Methoxyphenyl)-5-(triisopropylsilyl)penta-1,4-diyn-3-ol (**3e**). (4-Methoxyphenyl)acetylene (0.632 g, 4.79 mmol), BuLi (1.3M in hexanes, 3.19 ml, 4.79 mmol), and 3-(triisopropylsilyl)propynal (1.051 g, 5 mmol) were reacted according to the procedure described for **3b** to give **3e** (1.081 g, 66%) after CC (SiO_2; hexane/CH_2Cl_2 1:1). Brown oil. R_f (hexane/CH_2Cl_2 1:1) 0.26. IR (CCl_4): 3588*m*, 3366*w*, 3008*m*, 2945v*s*, 2893*s*, 2866v*s*, 2253*w*, 2231*m*, 2174*w*, 1607*s*, 1572*w*, 1510v*s*, 1464*s*, 1442*m*, 1383*m*, 1368*m*, 1368*m*, 1290*s*, 1250v*s*, 1221v*s*, 1181*m*, 1173*s*, 1107*w*, 1034v*s*, 913*s*, 904.3*s*, 883*s*, 884*s*, 801*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*s*, 21 H); 2.20 (*d*, *J* = 8, 1 H); 3.81 (*s*, 3 H); 5.32 (*d*, *J* = 8, 1 H); 6.84 (*d*, *J* = 9, 2 H); 7.38 (*d*, *J* = 9, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.1; 135.6; 114.5; 114.2; 104.8; 86.0; 85.4; 84.3; 55.5; 53.3; 18.8; 11.4. EI-MS: 342.1 (12, M^+), 297.0 (12, $[M - H - i\text{-}Pr]^+$), 283.1 (32, $[M - H - i\text{-}Pr - Me]^+$), 269.1 (19, $[M - H - i\text{-}Pr - 2\ Me]^+$), 255.1 (27, $[M - H - 2\ i\text{-}Pr]^+$), 241.0 (41, $[M - H - 2\ i\text{-}Pr - Me]^+$), 225.1 (40, $[M - 2\ i\text{-}Pr - 2\ Me]^+$), 213.1 (54, $[M - 2\ i\text{-}Pr]^+$), 169.1 (100, $[M - OH - (i\text{-}Pr)_3Si]^+$). Anal. calc. for $C_{21}H_{30}O_2Si$ (342.55): C 73.63, H 8.83; found: C 73.69, H 8.83.

1-Ferrocenyl-5-(triisopropylsilyl)penta-1,4-diyn-3-ol (**3f**). Ethynylferrocene (0.840 g, 4.00 mmol), BuLi (1.5M in hexanes, 2.80 ml, 4.12 mmol), and 3-(triisopropylsilyl)propynal (1.11 g, 4.12 mmol) were reacted according to the procedure described for **3b** to give **3f** (1.109 g, 66%) after CC (SiO_2; hexane/CH_2Cl_2 1:1). Brown oil. R_f (hexane/CH_2Cl_2 1:1) 0.18. IR ($CHCl_3$): 3588*m*, 3155*m*, 2945v*s*, 2892*m*, 2866v*s*, 2253v*s*, 2233*s*, 1817*w*, 1793*m*, 1645*w*, 1463*s*, 1382*s*, 1295*m*, 1106*s*, 1098*s*, 1066*w*, 1026*s*, 1006v*s*, 903v*s*, 825*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.11 (*s*, 21 H); 2.25 (*d*, *J* = 6, 1 H); 4.19 (*t*, *J* = 2, 2 H); 4.21 (*s*, 4 H), 4.19 (*m*, 2 H); 5.32 (*d*, *J* = 6, 1 H); 5.24 (*d*, *J* = 6, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 104.4; 87.7; 83.3; 82.7; 71.7; 71.5; 70.0; 68.9; 53.3; 18.7; 11.3. MALDI-MS (DHB): 420.16 (100, M^+), 403.15 (17, $[M - OH]^+$). HR-MALDI-MS: 420.1572 (100, M^+, $C_{24}H_{32}FeOSi^+$; calc. 420.1572). Anal. calc. for $C_{24}H_{32}FeOSi$ (420.45): C 68.56, H 7.67; found: C 68.32, H 7.72.

2,2-Dimethyl-7-(triisopropylsilyl)hepta-3,6-diyn-5-ol (**3g**). 3,3-Dimethylbut-1-yne (0.616 ml, 5.0 mmol), BuLi (1.5M in hexanes, 3.74 ml, 5.5 mmol), and 3-(triisopropylsilyl)propynal (1.157 g, 5.5 mmol) were reacted according to the procedure described for **3b** to give **3g** (1.081 g, 74%) after CC (SiO_2; hexane/CH_2Cl_2 7:3). Brown oil. R_f (hexane/CH_2Cl_2 7:3) 0.11. IR ($CHCl_3$): 3591v*s*, 3384*w* (br.), 3156*w*, 2967v*s*, 2864v*s*, 2717*w*, 2726*w*, 2253v*s*, 2175*m*, 1794*w*, 1463v*s*, 1383*s*, 1364v*s*, 1293*s*, 1263*s*, 1215*m*, 1217*s*, 10121*s*, 1219*s*, 1207v*s*, 1074*s*, 1024v*s*, 997*s*, 909v*s*, 884v*s*, 832*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.11 (*s*, 21 H); 1.21 (*s*, 9 H); 2.05 (*d*, *J* = 7.5, 1 H); 5.07 (*d*, *J* = 7.5, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 105.4; 93.3; 85.3; 76.7; 52.9; 30.8; 27.5; 18.7; 11.4. MALDI-MS (DHB): 275.2 ($[M - OH]^+$). HR-MALDI-MS: 275.2139 ($[M - OH]^+$, $C_{18}H_{31}Si^+$; calc. 275.2195).

1-Phenyl-5-(triisopropylsilyl)penta-1,4-diyn-3-one (**4b**). MnO_2 (0.416 g, 4.84 mmol) was added to **3b** (0.432 g, 1.38 mmol) in Et_2O (20 ml), and the soln. was stirred for 12 h. CH_2Cl_2 was added, and the mixture was filtered through a plug (SiO_2) to afford **4b** (0.407 g, 95%). Orange oil. R_f (hexane/CH_2Cl_2 1:1) 0.43. IR (CCl_4):

2946v*s*, 2893*s*, 2867v*s*, 2208v*s*, 2175*m*, 2142*s*, 1630v*s*, 1598*m*, 1490*s*, 1463*s*, 1444*m*, 1385*w*, 1368*w*, 1293*m*, 1278v*s*, 1237*w*, 1179*w*, 1124v*s*, 1070*m*, 1026*w*, 1019*m*, 999*s*, 920*m*, 876*s*, 805*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*m*, 21 H); 7.40 (*dd*, *J* = 7.5, 7, 2 H); 7.47 (*tt*, *J* = 7.5, 1.5, 1 H); 7.47 (*dd*, *J* = 7, 1.5, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.4; 133.5; 131.5; 128.9; 119.7; 105.4; 97.6; 91.7; 89.7; 18.7; 11.3. EI-MS: 310.3 (11, M^+), 267.2 (90, [M – i-Pr]$^+$), 239.1 (63, [M – i-Pr – Me]$^+$), 223.0 (16, [M – 2 i-Pr]$^+$), 211.1 (71, [M – 2 i-Pr – Me]$^+$), 195,1 (51, [M – 2 i-Pr – 2 Me]$^+$), 183.1 (100, [M – 3 i-Pr]$^+$), 169.0 (77, [M – $C_{10}H_5O$]$^+$), 129.1 (37, [M – C≡CSi(i-Pr)$_3$]$^+$). Anal. calc. for $C_{20}H_{26}OSi$ (310.51): C 77.36, H 8.44; found: C 77.49, H 8.51.

1-[4-(Dimethylamino)phenyl]-5-(triisopropylsilyl)penta-1,4-diyn-3-one (**4c**). Alcohol **3c** (1.85 g, 5.2 mmol) was oxidized with MnO_2 (1.57 g, 18.2 mmol) according to the procedure described for **4b** to give **4c** (1.79 g, 97%), exhibiting properties similar to those described in [43]. Yellow oil. R_f (CH_2Cl_2) 0.57. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*m*, 21 H); 3.00 (*s*, 6 H); 6.63 (*d*, *J* = 9, 2 H); 7.47 (*d*, *J* = 9, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.5; 152.2; 135.8; 111.8; 104.9; 97.2; 95.9; 94.9; 91.8; 40.2; 18.6; 11.3.

1-[3,5-Di(tert-*butyl)phenyl]-5-(triisopropylsilyl)penta-1,4-diyn-3-one* (**4d**). Alcohol **3d** (0.734 g, 1.73 mmol) was oxidized with MnO_2 (0.521 g, 6.06 mmol) according to the procedure described for **4b** to give **4d** (0.697 g, 95%). Red oil. R_f (hexane/CH_2Cl_2 1:1) 0.45. IR (CCl_4): 3020*s*, 2967v*s*, 2905*s*, 2868v*s*, 2728*w*, 2253*m*, 2210v*s*, 2184v*s*, 2149*s*, 2728*w*, 2253*m*, 2210v*s*, 2184v*s*, 2149*s*, 1620v*s*, 1590*s*, 1463v*s*, 1426*s*, 1395*m*, 1385*m*, 1365*s*, 1248v*s*, 1142v*s*, 1127v*s*, 1072*m*, 1019*m*, 998*s*, 958*s*, 909v*s*, 882v*s*, 830*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.16 (*m*, 21 H), 1.33 (*s*, 18 H); 7.45 (*d*, *J* = 1.5, 2 H), 7.55 (*t*, *J* = 1.5, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.7; 151.6; 128.0; 126.1; 118.8; 105.6; 97.6; 93.8; 89.3; 35.1; 31.4; 18.7; 11.3. EI-MS: 422.4 (14, M^+), 379.4 (30, [M – i-Pr]$^+$), 351.3 (100, [M – i-Pr – 2 Me]$^+$), 323.3 (82, [M – 2 i-Pr – O]$^+$), 309.3 (87, M – 2 *t*-Bu]$^+$), 295.2 (73, [M – 3 i-Pr]$^+$), 281.2 (44, [M – 2 *t*-Bu – 2 Me]$^+$). Anal. calc. for $C_{28}H_{42}OSi$ (422.72): C 79.56, H 10.01; found: C 79.49, H 10.15.

1-(4-Methoxyphenyl)-5-(triisopropylsilyl)penta-1,4-diyn-3-one (**4e**). Alcohol **3e** (0.902 g, 2.59 mmol) was oxidized with MnO_2 (1.11 g, 12.95 mmol) according to the procedure described for **4b** to give **4e** (0.751 g, 85%). Orange oil. R_f (hexane/CH_2Cl_2 1:1) 0.44. IR (CCl_4): 3200*w*, 3032*w*, 3009*m*, 2946v*s*, 2893*s*, 2867v*s*, 2842*s*, 2728*w*, 2591*w*, 2558*w*, 2253*m*, 2203v*s*, 2164v*s*, 2147v*s*, 2051*w*, 1605v*s*, 1597v*s*, 1569*s*, 1509v*s*, 1463v*s*, 1442*s*, 1385*m*, 1368*m*, 1305v*s*, 1287v*s*, 1254v*s*, 1226*s*, 1218v*s*, 1215*s*, 1210v*s*, 1207v*s*, 1182*s*, 1175*s*, 1126v*s*, 1030v*s*, 998*s*, 907v*s*, 883v*s*, 835v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*m*, 21 H); 3.80 (*s*, 3 H); 6.86 (*d*, *J* = 9, 2 H); 7.56 (*d*, *J* = 9, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 162.4; 160.4; 135.7; 114.7; 111.3; 105.5; 96.9; 93.3; 90.1; 55.6; 18.7; 11.3. EI-MS: 340.2 (5, M^+), 297.1 (59, [M – i-Pr]$^+$), 269.1 (100, [M – i-Pr – Me – CH]$^+$), 253.1 (12, [M – 2 i-Pr]$^+$), 241.1 (77, [M – 2 i-Pr – Me]$^+$), 213.1 (71, [M – 3 i-Pr]$^+$), 159.1 (38, [M – C≡CSi(i-Pr)$_3$]$^+$). Anal. calc. for $C_{21}H_{28}O_2Si$ (340.54): C 74.07, H 8.29; found: C 73.93, H 8.29.

1-Ferrocenyl-5-(triisopropylsilyl)penta-1,4-diyn-3-one (**4f**). Alcohol **3f** (1.04 g, 2.47 mmol) was oxidized with MnO_2 (1.25 g, 14.82 mmol) according to the procedure described for **4b** to give **4f** (0.887 g, 85%). Red oil. R_f (hexane/CH_2Cl_2 1:1) 0.44. IR ($CHCl_3$): 3101*w*, 2946v*s*, 2893*s*, 2867v*s*, 2219*s*, 2181v*s*, 2149*s*, 1608v*s*, 1462*s*, 1413*w*, 1385*w*, 1368*w*, 1287v*s*, 1147v*s*, 1107*m*, 1072*w*, 1037v*s*, 1019*w*, 998*m*, 932*m*, 883*s*, 8839*s*, 827*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*m*, 21 H); 4.28 (*s*, 5 H); 4.43 (*d*, *J* = 2, 2 H); 4.62 (*d*, *J* = 2, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.0; 105.4; 96.3; 96.2; 88.6; 73.3; 71.3; 70.6; 59.4; 18.6; 11.2. MALDI-MS (DHB): 418.14 (100, M^+). HR-MALDI-MS: 418.1421 (100, M^+, $C_{24}H_{30}FeOSi^+$; calc. 418.1415).

2,2-Dimethyl-7-(triisopropylsilyl)hepta-3,6-diyn-5-one (**4g**). Alcohol **3g** (1.07 g, 3.70 mmol) was oxidized with MnO_2 (1.84 g, 21.19 mmol) according to the procedure described for **4b** to give **4g** (1.056 g, 98%). Yellow oil. R_f (hexane/CH_2Cl_2 7:3) 0.52. IR ($CHCl_3$): 3155*m*, 2947*s*, 2867*s*, 2253v*s*, 2229*m*, 2191*m*, 2156*w*, 1817*m*, 1793*m*, 1626*s*, 1463*s*, 1382*s*, 1271*m*, 1175*m*, 1097*m*, 991*m*, 903v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.11 (*m*, 21 H); 1.29 (*s*, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): 161.1; 105.5; 103.0; 96.6; 81.3; 30.0; 29.1; 18.6; 11.3. MALDI-MS (DHB): 313.1 ([M + Na]$^+$). HR-MALDI-MS: 313.1958 ([M + Na]$^+$, $C_{18}H_{30}NaOSi^+$: calc. 313.1964).

3-(Dibromomethylidene)-1-phenyl-5-(triisopropylsilyl)penta-1,4-diyne (**2b**). CBr_4 (0.542 g, 1.64 mmol) and Ph_3P (0.860 g, 3.28 mmol) were added to a soln. of **4b** (0.391 g, 1.26 mmol) in benzene (40 ml). After stirring for 3 d at 20°, hexane (200 ml) was added, and the suspension was filtered through a plug (SiO_2; hexane). Evaporation *in vacuo* and CC (SiO_2; hexane) afforded **2b** (0.223 g, 38%). Brown oil. R_f (hexane) 0.51. IR (CCl_4): 2944*m*, 2866*m*, 2203*w*, 2151*w*, 1488*w*, 1462*w*, 1317*w*, 1164*w*, 1119*w*, 1070*w*, 921*m*, 883*m*, 865*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*m*, 21 H); 7.36 (*m*, 3 H); 7.50 (*dd*, *J* = 2, 7.5, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 131.9; 129.4; 128.6; 122.5; 114.8; 108.7; 102.2; 99.9; 95.8; 86.4; 18.9; 11.4. EI-MS: 466.1 (19, M^+), 423.0 (58, [M – i-Pr]$^+$), 395.0 (16, [M – i-Pr – 2 Me]$^+$), 381.0 (6, [M – 2 i-Pr]$^+$), 368.9 (10, [M – 2 i-Pr – Me]$^+$), 202.9 (37, [M – Br – C≡CSi(i-Pr)$_3$]$^+$), 177.1 (100, [M – 2 Br – 3 i-Pr]$^+$). Anal. calc. for $C_{21}H_{26}Br_2Si$ (466.33): C 54.09, H 5.62; found: C 53.89, H 5.86.

3-(Dibromomethylidene)-1-[4-(dimethylamino)phenyl]-5-(triisopropylsilyl)penta-1,4-diyne (**2c**). CBr_4 (0.430 g, 1.3 mmol) and Ph_3P (0.683 g, 2.60 mmol) were reacted with **4c** (0.353 g, 1.00 mmol) as described for

2b to deliver **2c** (0.248, 49%) after CC (SiO_2; hexane/CH_2Cl_2 1:1). Brown solid. R_f (hexane/CH_2Cl_2 7:3) 0.40. M.p. 55.5°. IR (CCl_4): 2958*m*, 2866*m*, 2197*w*, 1608*s*, 1525*w*, 1361*w*, 1156*w*, 908*w*, 883*w*, 864*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*m*, 21 H); 2.99 (*s*, 6 H); 6.62 (*d*, $J = 9$, 2 H); 7.38 (*d*, $J = 9$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.8; 133.1; 115.2; 111.9; 108.9; 106.2; 102.7; 99.01; 97.9; 85.2; 40.4; 18.9; 11.4. EI-MS: 509.0 (100, M^+), 464.0 (2, [M – i-Pr]$^+$), 429.1 (4, [M – Br]$^+$), 387.1 (62, [$M - C_6H_4N(CH_3)_2$]$^+$), 359.0 (21, [$M - C_6H_4N(CH_3)_2) - 2$ Me]$^+$). Anal. calc. for $C_{23}H_{31}Br_2NSi$ (507.06): C 54.86, H 6.71, N 2.67; found: C 54.95, H 6.62, N 2.58.

*3-(Dibromomethylidene)-1-[3,5-di(*tert*-butyl)phenyl]-5-(triisopropylsilyl)penta-1,4-diyne* (**2d**). CBr_4 (0.562 g, 2.15 mmol) and Ph_3P (1.42 g, 4.29 mmol) were reacted with **4d** (0.697 g, 1.65 mmol) as described for **2b** to give **2d** (0.534 g, 56%). Brown solid. R_f (hexane/CH_2Cl_2 7:3) 0.71. M.p. 73.5°. IR (CCl_4): 2964v*s*, 2866v*s*, 2336*w*, 2205*m*, 1589*s*, 1463*s*, 1427*w*, 1384*w*, 1364*m*, 1332*w*, 1264*w*, 1248*m*, 1216*s*, 1171*m*, 1072*w*, 1019*w*, 997*m*, 977*m*, 920*w*, 899*w*, 878v*s*, 811v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*m*, 21 H); 1.33 (*s*, 18 H); 7.35 (*d*, $J = 2$, 2 H); 7.45 (*t*, $J = 2$, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 151.2; 126.1; 124.0; 121.5; 115.0; 108.1; 102.5; 99.7; 97.2; 85.3; 35.0; 31.5; 18.9; 11.4. EI-MS: 576.2 (4, M^+), 535.2 (100, [M – i-Pr]$^+$), 507.3 (2, [M – i-Pr – 2 Me]$^+$), 479.1 (10, [$M - 2$ *t*-Bu]$^+$), 304.4 (4, [$M - 2$ *t*-Bu – (i-Pr)$_3$Si]$^+$). Anal. calc. for $C_{29}H_{42}Br_2Si$ (578.54): C 60.21, H 7.32; found: C 60.19, H 7.14.

3-(Dibromomethylidene)-1-(4-methoxyphenyl)-5-(triisopropylsilyl)penta-1,4-diyne (**2e**). CBr_4 (1.46 g, 4.4 mmol), Ph_3P (1.16 g, 4.4 mmol), and Zn (0.288 g, 4.4 mmol) were suspended in CH_2Cl_2 (5 ml). The soln. was stirred for 45 min at 20°, then ketone **4d** (0.717 g, 2.1 mmol) was added. After stirring for 12 h at 20°, hexane (50 ml) was added, and the suspension was filtered, the precipitate obtained was dissolved in CH_2Cl_2 and re-precipitated with hexane. The combined filtrates were concentrated *in vacuo*, and the resulting oil was purified by CC (SiO_2; hexane/CH_2Cl_2 7:3) to afford **2e** (0.858 g, 83%). Clear yellow oil. R_f (hexane/CH_2Cl_2 7:3) 0.44. IR ($CHCl_3$): 3020*m*, 3011*m*, 2945v*s*, 2892*m*, 2866v*s*, 2841*m*, 2249*w*, 2200*m*, 2151*w*, 1606v*s*, 1573*w*, 1515*s*, 1505*s*, 1465*s*, 1442*m*, 1384*w*, 1304*m*, 1290*s*, 1226*s*, 1221v*s*, 1216*s*, 1212*m*, 1208v*s*, 1206*m*, 1203*w*, 1191*m*, 1108*w*, 1072*w*, 1032*s*, 997*m*, 923*s*, 883*s*, 865v*s*, 834v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*s*, 21 H); 3.82 (*s*, 3 H); 6.86 (*d*, $J = 9$, 2 H); 7.44 (*d*, $J = 9$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.2; 133.1; 114.7; 114.2; 114.0; 107.4; 102.2; 99.3; 96.0; 85.2; 55.3; 18.8; 11.3. EI-MS: 496.0 (22, M^+), 452.9 (64, [M – i-Pr]$^+$), 424.9 (30, [M – i-Pr – 2 Me]$^+$), 412.9 (19, [$M - 2$ i-Pr]$^+$), 316.0 (21, [$M - C{\equiv}CSi(i\text{-}Pr)_3$]$^+$), 207.2 (100, [$M - C{\equiv}CSi(i\text{-}Pr)_3 - C_6H_4(OMe)$]$^+$). Anal. calc. for $C_{22}H_{28}Br_2OSi$ (496.36): C 53.24, H 5.69; found: C 53.41, H 5.89.

3-(Dibromomethylidene)-1-ferrocenyl-5-(triisopropylsilyl)penta-1,4-diyne (**2f**). CBr_4 (1.38 g, 4.17 mmol), Ph_3P (1.09 g, 4.17 mmol), Zn (0.273 g, 4.17 mmol), and **4f** (0.871 g, 2.08 mmol) were reacted according to the procedure described for **2e** to afford **2f** (0.415 g, 35%) after CC (SiO_2; hexane/CH_2Cl_2 1:1). Brown oil. R_f (hexane/CH_2Cl_2 1:1) 0.73. IR ($CHCl_3$): 3690*m*, 3023*s*, 3018*s*, 3016*s*, 2944*m*, 2866*m*, 2337*w*, 2207*m*, 1463*w*, 1226*w*, 1224*s*, 1219*s*, 1215*m*, 1210*s*, 1207v*s*, 1203*w*, 1186*w*, 998*w*, 947*w*, 882*m*, 825*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.12 (*s*, 21 H); 4.24 (*s*, 5 H); 4.27 (*d*, $J = 2$, 2 H); 4.50 (*d*, $J = 2$, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 114.9; 106.8; 102.4; 99.0; 95.9; 82.5; 71.7; 70.2; 69.4; 63.6; 18.8; 11.3. MALDI-MS (DHB): 574.0 (100, M^+). HR-MALDI-MS: 573.9803 (100, M^+, $C_{25}H_{30}Br_2FeSi^+$; calc. 573.9812).

5-(Dibromomethylidene)-2,2-dimethyl-7-(triisopropylsilyl)hepta-3,6-diyne (**2g**). CBr_4 (3.00 g, 9.06 mmol), Ph_3P (2.38 g, 9.06 mmol), Zn (0.592 g, 9.06 mmol) and **4f** (1.31 g, 4.53 mmol) were reacted according to the procedure described for **2e** to give **2g** (1.710 g, 85%) after CC (SiO_2; hexane) Yellow oil. R_f (hexane) 0.69. IR ($CDCl_3$): 3020*s*, 2945*m*, 2866*m*, 1642*w*, 1364*w*, 1295*w*, 871*m*, 822*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*s*, 21 H); 1.27 (*s*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 115.0; 107.1; 105.8; 102.9; 98.8; 76.8; 30.6; 28.6; 18.8; 11.4. EI-MS: 446.05 (27, M^+), 403.0 (100, [M – i-Pr]$^+$). HR-EI-MS: 446.0473 (26, M^+, $C_{19}H_{30}Br_2Si^+$; calc. 446.0463) 402.9964 ([M – i-Pr]$^+$, $C_{16}H_{23}Br_2Si^+$; calc. 402.9915).

1,8-Diphenyl-3,6-bis[(triisopropylsilyl)ethynyl]octa-3,4,5-triene-1,7-diyne (**5b**). BuLi (1.5M in hexanes, 0.50 ml, 0.76 mmol) was added to **2b** (0.353 g, 0.76 mmol) in Et_2O (6 ml) at −110°. The mixture was stirred for 1 h at −100°, then a soln. of [CuI · PBu_3] (0.299 g, 0.76 mol) in Et_2O (6 ml) was introduced. The resulting red soln. was stirred for 1 h at −85°, after which it was allowed to warm to 20° within 5 h. After stirring for 12 h at 20°, the soln. was filtered through SiO_2. Evaporation *in vacuo* afforded a red solid, which was purified by CC (SiO_2: hexane) to give **5b** (0.145 g, 62%). Brown solid, mixture of *cis*- and *trans*-isomers (slowly equilibrating on the NMR time scale) in a 43:57 ratio (^{1}H-NMR, without configurational assignment). R_f (hexane) 0.09. M.p. 90° (dec.). UV/VIS (CH_2Cl_2): 469 (35700), 450 (sh, 30300), 427 (sh, 22100). IR (CCl_4): 2957*m*, 2944*s*, 2892*m*, 2866*s*, 2184*w*, 1489*w*, 1463*m*, 1384*w*, 1318*w*, 1233*w*, 1187*w*, 1148*w*, 1069*w*, 1019*w*, 996*w*, 908*m*, 883*m*, 814v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 1.13 (*m*, 42 H); 7.34 (*m*, 6 H); 7.52 (*dd*, $J = 7.5$, 2, 4 H); minor isomer: 1.13 (*m*, 42 H); 7.34 (*m*, 6 H); 7.48 (*dd*, $J = 7.5$, 2, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.5, 149.3; 132.1, 132.0; 129.4; 128.6; 122.5; 104.3; 100.7, 100.4; 96.8, 96.7; 88.9, 88.8; 87.7; 18.8; 11.5.

1,8-Bis[4-(dimethylamino)phenyl]-3,6-bis[(triisopropylsilyl)ethynyl]octa-3,4,5-triene-1,7-diyne (**5c**). BuLi (1.5M in hexanes, 0.8 ml, 1.2 mmol), **2c** (0.608 g, 1.2 mmol), and [CuI · PBu_3] (0.471 g, 1.2 mmol) were reacted as described for **5b** to give **5c** (0.279 g, 80%) after CC (SiO_2; hexane/CH_2Cl_2 7:3). Purple solid, mixture of slowly equilibrating *cis*- and *trans*-isomers in a 44:56 ratio (^{1}H-NMR, without configurational assignment). R_f (hexane/CH_2Cl_2 7:3) 0.13. M.p. 103–104°. UV/VIS (CH_2Cl_2): 573 (40500), 503(sh, 20100), 489 (17500), 409 (12600). IR (CCl_4): 2959*m*, 2943*m*, 2892*w*, 2865*m*, 2174*m*, 2129*w*, 2001*w*, 1605*s*, 1538*m*, 1531*m*, 1463*w*, 1445*w*, 1362*m*, 1331*w*, 1196*w*, 1182*w*, 1143*w*, 1112*w*, 1071*w*, 947*w*, 897*w*, 883*w*, 801vs. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 1.13 (*m*, 42 H); 3.00 (*s*, 12 H); 6.61 (*d*, *J* = 9, 4 H); 7.33 (*d*, *J* = 9, 4 H); minor isomer: 1.13 (*m*, 42 H); 3.00 (*s*, 12 H); 6.63 (*d*, *J* = 9, 4 H); 7.38 (*d*, *J* = 9, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.9; 150.8; 146.6, 146.4; 133.6, 133.5; 111.9; 109.3; 105.1, 105.0; 99.3, 99.2; 98.8, 98.4; 89.0, 88.9; 86.5; 40.3; 18.9; 11.6. MALDI-MS (DCTB): 698 (100, M^+), 349 (6, M^{++}). HR-MALDI-MS: 698.4439 (M^+, $C_{46}H_{62}N_2Si_2^+$; calc. 698.4452).

1,8-Bis[3,5-di(tert-*butyl)phenyl]-3,6-bis[(triisopropylsilyl)ethynyl]octa-3,4,5-triene-1,7-diyne* (**5d**). BuLi (1.5M in hexanes, 0.53 ml, 0.8 mmol), **2d** (0.461 g, 0.8 mmol), and [CuI · PBu_3] (0.314 g, 0.8 mmol) were reacted as described for **5b** to give **5d** (0.235 g, 69%) after CC (SiO_2; hexane/CH_2Cl_2 9:1). Orange solid; mixture of slowly equilibrating *cis*- and *trans*-isomers in a 39:61 ratio (^{1}H-NMR, without configurational assignment). R_f (hexane) 0.16. M.p. 122° (dec.). UV/VIS (CH_2Cl_2): 481 (41600), 456 (sh, 35500), 443 (sh, 30600). IR (CCl_4): 2964vs, 2866*s*, 2187*m*, 1866*s*, 1589*m*, 1539*w*, 1463*m*, 1427*w*, 1394*w*, 1364*m*, 1248*w*, 1184*w*, 1158*w*, 904*w*, 878*m*, 833*w*, 812vs. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 1.15 (*m*, 42 H); 1.33 (*s*, 36 H); 7.38 (*d*, *J* = 2, 4 H); 7.43 (*t*, *J* = 2, 2 H); minor isomer: 1.16 (*m*, 42 H); 1.33 (*s*, 36 H); 7.34 (*d*, *J* = 2, 4 H); 7.43 (*t*, *J* = 2, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 151.2, 151.0; 149.1, 149.0; 126.5, 126.4; 124.0; 121.6, 121.5; 104.8, 104.7; 100.4, 100.0; 98.4, 98.2; 88.0; 87.6; 35.0; 31.5; 18.8, 18.7; 11.7, 11.6. MALDI-MS (DCTB): 837 (100, M^+), 794 (20, [M – i-Pr]$^+$). HR-MALDI: 836.6117 (M^+, $C_{58}H_{84}Si_2^+$; calc. 836.6112).

1,8-Bis(4-methoxyphenyl)-3,6-bis[(triisopropylsilyl)ethynyl]octa-3,4,5-triene-1,7-diyne (**5e**). BuLi (1.5M in hexanes, 0.667 ml, 1 mmol), **2e** (0.494 g, 1 mmol), and [CuI · PBu_3] (0.393 g, 1 mol) were reacted as described for **5b** to give **5e** (0.188 g, 56%) after CC (SiO_2; hexane/CH_2Cl_2 8:2). Red solid, mixture of slowly equilibrating *cis*- and *trans*-isomers in a 41:59 ratio (^{1}H-NMR, without configurational assignment). R_f (hexane/CH_2Cl_2 8:2) 0.20. M.p. 100°. UV/VIS (CH_2Cl_2): 494 (50600), 459 (sh, 31000), 381 (10600). IR ($CHCl_3$): 3687*w*, 3643*m*, 3005*m*, 2958*s*, 2868*m*, 1603*m*, 1509*w*, 1481*w*, 1467*m*, 1432*s*, 1509*w*, 1432*s*, 1362*w*, 1314*w*, 1249*w*, 1157*m*, 1121*w*, 864*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 1.10 (*m*, 42 H); 3.83 (*s*, 6 H); 6.87 (*d*, *J* = 9, 4 H); 7.41 (*d*, *J* = 9, 4 H); minor isomer: 1.14 (*m*, 42 H); 3.82 (*s*, 6 H); 6.86 (*d*, *J* = 9, 4 H); 7.47 (*d*, *J* = 9, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.6; 148.4, 148.3; 133.8, 133.7; 114.7; 114.4; 104.5; 100.0, 99.7; 97.3, 97.2; 88.4, 88.3; 87.3; 55.6; 18.8; 11.6. MALDI (DCTB): 672 (M^+). HR-MALDI-MS: 672.3805 (M^+, $C_{44}H_{56}O_2Si_2^+$; calc. 672.3819).

1,8-Diferrocenyl-3,6-bis[(triisopropylsilyl)ethynyl]octa-3,4,5-triene-1,7-diyne (**5f**). BuLi (1.5M in hexanes, 0.467 ml, 0.70 mmol), **2f** (0.402 g, 0.70 mmol), and [CuI · PBu_3] (0.275 g, 0.70 mol) were reacted as described for **5b** to give **5f** (0.188 g, 37%) after CC (SiO_2; hexane/CH_2Cl_2 9:1) and GPC (CH_2Cl_2). Green solid, mixture of slowly equilibrating *cis*- and *trans*-conformers in a 40:60 ratio (^{1}H-NMR, without configurational assignment). R_f (hexane/CH_2Cl_2 9:1) 0.17. M.p. 105°. UV/VIS (CH_2Cl_2): 602 (3450), 452 (17800). IR ($CDCl_3$): 2959*s*, 2945*s*, 2891*m*, 2866*s*, 2184*m*, 2134*w*, 2003*w*, 1605*w*, 1542*w*, 1464*m*, 1412*w*, 1380*w*, 1301*w*, 1265*w*, 1226vs, 1106*w*, 997*w*, 935*w*, 883*w*, 825*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 1.13 (*s*, 42 H); 4.26 (*s*, 10 H); 4.31 (*t*, *J* = 2, 4 H); 7.41 (*t*, *J* = 2, 4 H); minor isomer: 1.14 (*m*, 42 H); 4.25 (*s*, 10 H); 4.31 (*t*, *J* = 2, 4 H); 4.50 (*t*, *J* = 2, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 147.6, 147.5; 104.7, 104.6; 99.1, 98.8; 97.4, 97.3; 86.5; 85.8, 85.7; 71.9, 71.8; 70.3; 70.1, 69.8; 64.2, 64.1; 18.8; 11.5. MALDI (DCTB): 828 (100, M^+). HR-MALDI-MS: 828.2918 (M^+, $C_{50}H_{60}Fe_2Si_2^+$; calc. 828.2932).

2,2,11,11-Tetramethyl-5,8-bis[(triisopropylsilyl)ethynyl]dodeca-5,6,7-triene-3,9-diyne (**5g**). BuLi (1.15M in hexanes, 0.690 ml, 0.81 mmol), **2f** (0.355 g, 0.81 mmol), and [CuI · PBu_3] (0.318 g, 0.81 mol) were reacted as described for **5b** to yield **5g** (0.056 g, 24%) after CC (SiO_2; hexane) and GPC (CH_2Cl_2). Yellow oil, mixture of slowly equilibrating *cis*- and *trans*-isomers in a 45:55 ratio (^{1}H-NMR, without configurational assignment). R_f (hexane) 0.32. UV/VIS (CH_2Cl_2): 419 (29400), 390 (29800), 370 (25900), 346 (18100). IR ($CDCl_3$): 2945*m*, 2866*m*, 2253*m*, 2202*w*, 1463*m*, 1383*w*, 1363*w*, 1288*w*, 1216*s*, 1096*w*, 996*w*, 816*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 1.10 (*m*, 42 H); 1.26 (*s*, 18 H); minor isomer: 1.08 (*m*, 42 H); 1.25 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.5, 150.2; 106.0, 105.8; 105.2; 98.9, 98.7; 87.3; 78.3, 78.2; 30.7; 28.7; 18.8; 11.5. MALDI-MS (DCTB): 351 (100, [M + Na – 5 i-Pr – 2 Me]$^+$), 573 (20, M^+), 595 (21, [M + Na]$^+$). HR-MALDI-MS: 572.4201 (M^+, $C_{38}H_{60}Si_2^+$; calc. 572.4234); 595.4119 ([M + Na]$^+$, $C_{38}H_{60}NaSi_2^+$; calc. 595.4131).

3-[3,5-Di(tert-*butyl)phenyl]prop-2-yn-1-ol* (**6c**). BuLi (1.5M in hexanes, 1.02 ml, 1.52 mmol) was added to [3,5-di(*tert*-butyl)phenyl]acetylene (0.326 g, 1.52 mmol) in THF (8 ml) at –10°, and the orange soln. was stirred for 30 min. Paraformaldehyde (0.055 g, 1.82 mmol) was added, and stirring was continued for 4 h, while the

temp. reached 20°. Sat. aq. NH_4Cl soln. (10 ml) was added, the mixture was extracted with Et_2O (2 × 30 ml), and the combined org. phases were washed with sat. aq. NH_4Cl soln. (10 ml) and dried ($MgSO_4$). Evaporation *in vacuo*, followed by CC (SiO_2; hexane/CH_2Cl_2 1:1), provided **6c** (0.308 g, 83%). Yellow oil. R_f (hexane/CH_2Cl_2 1:1) 0.17. IR ($CHCl_3$): 3684*w*, 3619*m*, 3461*w*, 3019v*s*, 2975*s*, 2896*m*, 2405*m*, 2400*s*, 1521*w*, 1476*m*, 1424*m*, 1394*m*, 1218v*s*, 1045*s*, 910v*s*, 878*s*, 851*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.31 (*s*, 18 H); 1.62 (*t*, *J* = 6, 1 H); 4.50 (*d*, *J* = 6, 2 H); 7.30 (*d*, *J* = 2, 2 H); 7.38 (*t*, *J* = 2, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.7; 125.9; 122.9; 121.3, 86.9; 85.9; 51.8; 34.9; 31.4. EI-MS: 244.2 (25, M^+), 229.1 (100, [M – OH]$^+$), 153.0 (29, [M – *t*-Bu – OH]$^+$), 115.1 (14, [M – 2 *t*-Bu – OH]$^+$). Anal. calc. for $C_{17}H_{24}O$ (244.18): C 82.73, H 6.25; found: C 82.56, H 6.13.

3-[3,5-Di(tert-*butyl)phenyl]propynal* (**7c**). MnO_2 (0.223 g, 2.59 mmol) was added to **6c** (0.181 g, 0.74 mmol) in CH_2Cl_2. After stirring for 24 h at 20°, the mixture was filtered through *Celite*, and the solvent was evaporated *in vacuo*. The product (0.152 g, 85%), the purity of which was controlled by NMR, was directly used for further conversions. R_f (hexane/CH_2Cl_2 1:1) 0.32. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.32 (*s*, 18 H); 7.46 (*d*, *J* = 2, 2 H); 7.55 (*t*, *J* = 2, 1 H); 9,43 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 177.2; 151.7; 128.0; 126.2; 118.7; 97.2; 88.1; 35.1; 31.4.

3-Ferrocenylpropynal (**7e**). BuLi (1.1M in hexanes, 7.13 ml, 7.7 mmol) was added to a soln. of ethynylferrocene (1.47 g, 7 mmol) in THF (35 ml) cooled to −78°. After stirring the darkened soln. for 1 h at this temp., DMF (1.46 ml, 19.0 mmol) was added. Stirring was continued for 1 h at −78°, then the mixture was warmed to 20° and poured into ice-cold H_2O (50 ml) containing conc. HCl (8 ml). The purple soln. was neutralized with aq. $NaHCO_3$ soln and turned red. The org. phase was extracted with Et_2O, washed with H_2O, dried ($MgSO_4$), and filtered through *Celite*. The red oil obtained after evaporation was purified by CC (SiO_2; hexane/CH_2Cl_2 8:2 → 5:5) to give **7e** (1.503 g, 90%) with properties identical to those described in [44]. Red crystals. R_f (hexane/CH_2Cl_2 7:3) 0.16. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.25 (*s*, 5 H); 4.43 (*t*, *J* = 2, 2 H,); 4.61 (*t*, *J* = 2, 2 H); 9.28 (*s*, 1 H).

1,1-Dibromo-4-(triisopropylsilyl)but-1-en-3-yne (**8a**). CBr_4 (1.32 g, 4 mmol), Ph_3P (1.05 g, 4 mmol), and Zn (0.262 g, 4 mmol) were suspended in CH_2Cl_2 (5 ml). The soln. was stirred for 45 min at 20°, then **7a** (0.420 g, 2 mmol) was added. After stirring for 5 h at 20°, hexane (50 ml) was added, and the suspension was filtered, the obtained precipitate was dissolved in CH_2Cl_2 and re-precipitated with hexane. The combined filtrates were concentrated *in vacuo*, and the resulting oil was purified by CC (SiO_2; hexane) to afford **8a** (0.470 g, 65%). Clear yellow oil. R_f (hexane) 0.66. IR ($CHCl_3$): 3010*m*, 3021*m*, 2946v*s*, 2891v*s*, 2865v*s*, 2759*w*, 2726*w*, 2166*m*, 2118*m*, 1646*w*, 1562*m*, 1463v*s*, 1384*s*, 1367*s*, 1260*s*, 1220v*s*, 1070v*s*, 1018*s*, 997v*s*, 954*w*, 919*s*, 883v*s*, 846v*s*, 824*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*s*; 21 H); 6.61 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 120.2; 103.2; 102.7; 101.0; 18.8; 11.4. EI-MS: 365.9 (38, M^+), 322.9 (81, [M – i-Pr]$^+$), 282.8 (26, [M – 2 i-Pr]$^+$), 266.8 (33, [M – 2 i-Pr – Me]$^+$), 252.7 (36, [M – 2 i-Pr – 2 Me]$^+$), 202.8 (62, [M – 2 i-Pr – Br]$^+$), 159.0 (65, [M – 3 i-Pr – Br]$^+$), 76.9 (100, [M – 2 i-Pr – 2 Br]$^+$). Anal. calc. for $C_{13}H_{22}Br_2Si$ (366.21): C 42.64, H 6.05; found: C 42.72, H 5.93.

1-(4,4-Dibromobut-3-en-1-ynyl)-4-(dimethylamino)benzene (**8b**). CBr_4 (0.662 g, 2 mmol), Ph_3P (0.526 g, 2 mmol), Zn (0.131 g, 2 mmol), and **7b** (0.212 g, 1 mmol) were reacted as described for **8a** to deliver **8b** (0.109 g, 33%) after CC (SiO_2; hexane/CH_2Cl_2 8:2). Yellow solid. R_f (hexane/CH_2Cl_2 1:1) 0.63. M.p. 69°. IR ($CHCl_3$): 3012*m*, 2191*m*, 1608v*s*, 1566*w*, 1520*s*, 1446*w*, 1364*m*, 1226v*s*, 1215*m*, 1211v*s*, 1210*m*, 1205*w*, 1192*m*, 1170*w*, 1127*w*, 1028*w*, 945*w*, 848*w*, 819*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.99 (*s*, 6 H); 6.62 (*d*, *J* = 9, 2 H); 6.75 (*s*, 1 H); 7.36 (*d*, *J* = 9, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.4; 132.7; 120.1; 11.7; 111.5; 108.8; 99.0; 84.9; 40.2. MALDI-MS (DHB): 329.9 (100, MH$^+$), 328.9 (48, M^+). HR-MALDI-MS: 329.9306 (100, MH$^+$, $C_{12}H_{11}Br_2N^+$; calc. 329.9316).

1-(4,4-Dibromobut-3-en-1-ynyl)-3,5-di(tert-*butyl)benzene* (**8c**). CBr_4 (0.404 g, 1.22 mmol), Ph_3P (0.321 g, 1.22 mmol), Zn (0.080 g, 1.22 mmol), and **7c** (0.147 g, 0.61 mmol) were reacted as described for **8a** to give **8c** (0.138 g, 57%) after CC (SiO_2; hexane). White solid. R_f (hexane) 0.76. M.p. 88°. IR ($CHCl_3$): 3023*s*, 3020v*s*, 3016*s*, 2966*m*, 2905*w*, 2869*w*, 2200*w*, 1478*w*, 1395*w*, 1227*w*, 1223*m*, 1211*m*, 1205v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.32 (*s*, 18 H); 6.78 (*s*, 1 H); 7.33 (*d*, *J* = 2, 2 H); 7.44 (*d*, *J* = 2, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.9; 125.7; 123.5; 121.3; 119.7; 101.2; 98.4; 85.0; 34.9; 31.4. EI-MS: 398.0 (50, M^+), 383.0 (68, [M – Me]$^+$), 238.1 (6, [M – 2 Br]$^+$), 223.1 (20, [M – 2 Br – Me]$^+$), 191.0 (15, [M – C_4HBr_2]$^+$). Anal. calc. for $C_{18}H_{22}Br_2$ (398.18): C 54.30, H 5.57; found: C 54.05, H 5.65.

1-(4,4-Dibromobut-3-en-1-ynyl)-4-methoxybenzene (**8d**). CBr_4 (2.09 g, 6.32 mmol), Ph_3P (1.66 g, 6.32 mmol), Zn (0.413 g, 6.32 mmol), and **7d** (0.506 g, 3.16 mmol) were reacted as described for **8a** to provide **8d** (0.734 g, 74%) after CC (SiO_2; hexane/CH_2Cl_2 8:2). Yellow solid. R_f (hexane/CH_2Cl_2 7:3) 0.65. M.p. 54–55°. IR ($CHCl_3$): 3011*m*, 2962*w*, 2937*w*, 2840*m*, 2549*w*, 2200v*s*, 2047*w*, 1607v*s*, 1568*s*, 1507v*s*, 1465*s*, 1442*s*, 1415*w*, 1295*s*, 1279*s*, 1250v*s*, 1223*s*, 1218v*s*, 1217*w*, 1214*s*, 1209*w*, 1205*m*, 1181*s*, 1173v*s*, 1108*m*, 1036v*s*, 1022*m*, 1006*w*, 850v*s*, 834v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.82 (*s*, 3 H); 6.75 (*s*, 1 H); 6.85 (*d*, *J* = 9, 2 H); 7.42 (*d*, *J* = 9, 2 H).

^{13}C-NMR (75 MHz, $CDCl_3$): 160.0; 133.0; 119.7; 114.4; 114.0; 105.6; 97.4; 85.2; 55.4. EI-MS: 315.9 (65, M^+), 300.9 (37, $[M-Me]^+$), 156.0 (41, $[M-2\ Br]^+$), 141.0 (42, $[M-2\ Br-Me]^+$), 127.9 (15, $[M-CBr_2-Me]^+$), 113.0 (100, $[M-CBr_2-OMe]^+$). Anal. calc. for $C_{11}H_8Br_2$ (313.89): C 41.81, H 2.55; found: C 41.79, H 3.00.

(4,4-Dibromobut-3-en-1-ynyl)ferrocene (**8e**). CBr_4 (4.18 g, 12.63 mmol), Ph_3P (3.31 g, 12.63 mmol), Zn (0.826 g, 12.63 mmol), and **7e** (1.503 g, 6.31 mmol) were reacted as described for **8a** to afford **8e** (1.883 g, 76%) after CC (SiO_2; hexane). Orange solid. R_f (hexane/CH_2Cl_2 1:1) 0.67. M.p. 58°. IR ($CHCl_3$): 3101*w*, 3016*w*, 2983*w*, 2929*w*, 2483*w*, 2203v*s*, 1472*m*, 1465*m*, 11437*w*, 11419*w*, 1394*s*, 1387*s*, 1277*w*, 1257*w*, 1216*w*, 1204*w*, 1107*s*, 1098*m*, 1074*w*, 1051*w*, 1026*w*, 1004*m*, 826*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.24 (*s*, 5 H); 4.26 (*t*, $J=2$, 2 H); 4.48 (*t*, $J=2$, 2 H); 6.65 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 120.0; 99.8; 97.3; 82.6; 71.5; 70.2; 69.4; 63.9. MALDI-MS (DCTB): 394 (100, M^+). HR-MALDI-MS: 393.8498 (M^+, $C_{14}H_{10}Br_2Fe^+$; calc. 393.8498). Anal. calc. for $C_{14}H_{10}Br_2Fe$ (393.89): C 42.69, H 2.56; found: C 42.90, H 2.85.

1,8-Bis(triisopropylsilyl)octa-3,4,5-triene-1,7-diyne (**9a**). BuLi (1.5M in hexanes, 0.707 ml, 1.06 mmol) was added to **8a** (0.386 g, 1.06 mmol) in Et_2O (7 ml) at −110°. The mixture was stirred for 1 h at −100°, then a soln. of $[CuI\cdot PBu_3]$ (0.416 g, 1.06 mol) in Et_2O (5 ml) was added. The resulting red soln. was stirred for 1 h at −85°, after which it was allowed to warm to 20° within 5 h. After stirring for 12 h at 20°, the now orange soln. was filtered through SiO_2. Evaporation *in vacuo* afforded a brown oil, which was purified by CC (SiO_2; hexane) to give **9a** (0.131 g, 60%) as a mixture of *cis*- and *trans*-isomers in a 31:69 ratio (^{1}H-NMR). Clear oil. From this mixture, one isomer (A) was obtained in pure form (0.029 g, 13%). Isomer A: R_f (hexane) 0.65. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.09 (*m*, 42 H); 5.74 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 161.6; 104.1; 101.0; 92.3; 18.7, 11.4. Isomer B: R_f (hexane) 0.67. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.09 (*m*, 42 H); 5.66 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 161.3; 104.3; 100.9; 92.1; 18.7; 11.4. Isomeric mixture: UV/VIS (CH_2Cl_2): 356 (3150), 332 (1600). IR ($CHCl_3$): 3683*w*, 3018*m*, 3015*w*, 2944v*s*, 2891*m*, 2865v*s*, 2182*w*, 1602*m*, 1464*m*, 1315*w*, 1228*m*, 1224v*s*, 1221v*s*, 1219*w*, 1216*s*, 1212v*s*, 1210*s*, 1207v*s*, 1204*m*, 997*w*, 884*m*. EI-MS: 412.3 (14, M^+), 370.2 (60, $[M-i\text{-}Pr]^+$), 327.2 (37, $[M-2\ i\text{-}Pr]^+$), 285 (100, $[M-3\ i\text{-}Pr]^+$), HR-EI-MS: 413.2968 (MH^+, $C_{26}H_{44}Si_2^+$; calc. 413.2982).

1,8-Bis[4-(dimethylamino)phenyl]octa-3,4,5-triene-1,7-diyne (**9b**). BuLi (1.5M in hexanes, 0.534 ml, 0.8 mmol), **8b** (0.262 g, 0.8 mmol), and $[CuI\cdot PBu_3]$ (0.314 g, 0.8 mmol) were reacted as described for **9a** to provide **9b** (0.025 g, 19%) after CC (SiO_2; hexane/CH_2Cl_2 7:3). Red solid, mixture of *cis*- and *trans*-isomers in a 72:28 ratio (^{1}H-NMR, without configurational assignment). R_f (hexane/CH_2Cl_2 6:4) 0.22. M.p. 70–73°. UV/VIS (CH_2Cl_2): 489 (5400), 439 (3600). IR ($CHCl_3$): 3019*w*, 2170*w*, 1795*w*, 1606*w*, 1214*s*, 1097*w*, 996*w*, 816*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 2.99 (*s*, 12 H); 5.84 (*s*, 2 H); 6.62 (*d*, $J=9$, 4 H); 7.34 (*d*, $J=9$, 4 H); minor isomer: 3.00 (*s*, 12 H); 5.79 (*s*, 2 H); 6.64 (*d*, $J=9$, 4 H); 7.37 (*d*, $J=9$, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 155.9; 150.2; 133.0, 132.9; 111.7; 109.6, 109.4; 99.7, 99.6; 90.3, 90.2; 87.8, 87.7; 40.2. MALDI-MS (DCTB): 338.2 (100, M^+). HR-MALDI-MS: 338.1774 (100, M^+, $C_{24}H_{22}N_2^+$; calc. 338.1783).

1,8-Bis(ferrocenyl)octa-3,4,5-triene-1,7-diyne (**9e**). BuLi (1.5M in hexanes, 0.647 ml, 1 mmol), **8e** (0.395 g, 1 mmol), and $[CuI\cdot PBu_3]$ (0.393 g, 1 mmol) were reacted as described for **9a** to yield **9e** (0.210 g, 45%) after CC (SiO_2; hexane/CH_2Cl_2 9:1). Red solid, mixture of *cis*- and *trans*-isomers in a 52:48 ratio (^{1}H-NMR, without configurational assignment). R_f (hexane/CH_2Cl_2 1:1) 0.42. M.p. 51–53°. UV/VIS (CH_2Cl_2): 516 (1150), 408 (4100). IR (neat): 2940*w*, 2862*w*, 1590*s*, 1511*s*, 1446*w*, 1365*w*, 1321*m*, 1302*m*, 1285*m*, 1252*m*, 1196*s*, 1173*s*, 1147*s*, 1070*w*, 1015*m*, 996v*s*, 936*w*, 922*w*, 862*s*, 825v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): major isomer: 4.25 (*s*, 10 H); 4.30 (*m*, 4 H); 4.51 (*t*, $J=2$, 4 H); 5.75 (*s*, 2 H); minor isomer: 4.26 (*s*, 10 H); 4.30 (*m*, 4 H); 4.48 (*t*, $J=2$, 4 H); 5.78 (*s*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 156.7, 156.3; 97.5, 97.2; 89.6; 84.9; 70.6, 70.5; 69.1; 68.7, 68.6; 63.9, 63.8. MALDI-MS (DCTB): 468. 3 (60, M^+); 467.0 (100, $[M-H]^+$). HR-MALDI-MS: 468.0254 (M^+, $C_{28}H_{20}Fe_2^+$; calc. 468.0258).

4,5-η²-[1,8-Bis[3,5-di(tert-*butyl)phenyl]-3,6-bis[(triisopropylsilyl)ethynyl]octa-3,4,5-triene-1,7-diyne](chloro)-bis(triphenylphosphine)rhodium(I)* (**10d**). $[RhCl(PPh_3)_3]$ in CH_2Cl_2 (3 ml) was added to **5d** (0.060 g, 0.072 mmol) in CH_2Cl_2 (3 ml), and the mixture was stirred for 3 d at 20°. The mixture was filtered through *Celite*, and the solvent was removed *in vacuo*. The crude product was purified by CC (SiO_2; hexane/CH_2Cl_2 7:3), providing, besides recovered starting material (17%), a green solid, which was further purified by GPC to give **10d** (isomeric mixture; 0.078 g, 72%). R_f (hexane/CH_2Cl_2 1:1) 0.32. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.10 (*m*, 84 H); 1.44, 1.43, 1.36, 1.34, 1.30, 1.29 (*s*, 72 H); 7.26–7.35 (*m*, 36 H); 7.42 (*m*, 2 H); 7.48 (*d*, $J=2$, 2 H); 7.52 (*d*, $J=2$, 2 H); 7.56 (*m*, 2 H); 7.62–7.70 (*m*, 24 H); 7.77 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 151.3; 151.2; 150.4; 149.9; 135.2*m*; 131.8 (*t*, J(P,C) = 21); 130.5; 130.3; 130.2; 130.0; 128.0 (*d*, J(P,C) = 4); 126.9; 126.0; 125.9; 123.5; 123.0; 122.2; 115.2; 115.0; 106.4; 104.0; 103.0; 98.1; 97.6; 97.4; 94.9; 91.5; 91.2; 90.7; 88.9; 88.7; 80.6; 35.1; 34.9; 34.7; 31.5; 31.4; 31.3; 31.2; 18.9; 18.8; 18.7; 11.8; 11.7; 11.6; 11.4. MALDI-MS (DHB): 1238 (41, $[M-PPh_3]^+$), 1202 (30, $[M-PPh_3-Cl]^+$), 1160 (6, $[M-PPh_3-Cl-i\text{-}Pr]^+$), 1118 (41, $[M-Ph_3P-Cl-2\ i\text{-}Pr]^+$), 1075 (100,

$[M - Ph_3P - Cl - 3\ i\text{-}Pr]^+$), 662 (15, $[Rh(PPh_3)_2Cl]^+$), 627 (51, $[Rh(Ph_3)_2)]^+$). HR-MALDI-MS: 1236.5739 ($[M - PPh_3]^+$, $C_{76}H_{99}ClPRhSi_2^+$; calc. 1236.5766).

1,5-Bis(ferrocenyl)penta-1,4-diyn-3-ol (**11c**). EtMgBr in THF (2.2 ml, 2.2 mmol) was added to ethynylferrocene (0.420 g, 2 mmol) in Et_2O (3 ml), and the red soln. was heated to 45° for 90 min. After cooling to 0°, ethyl formate (0.077 ml, 0.921 mmol) was added, and stirring was pursued for 5 h at 20°. Sat. aq. NH_4Cl soln. (10 ml) was added, and the phases were separated. The aq. phase was extracted again with Et_2O. The combined org. phases were washed with sat. aq. $NaHCO_3$ soln. (20 ml) and H_2O, and dried ($MgSO_4$). Evaporation *in vacuo* gave a residue, which was purified by CC (hexane/CH_2Cl_2 3:7) to deliver **11c** (0.202 g, 49%). Brown solid. R_f (hexane/CH_2Cl_2 3:7) 0.26. M.p. 65°. IR ($CHCl_3$): 3683*w*, 3604*w*, 3439*w* (br.), 3020v*s*, 3013*m*, 2399*w*, 2231*w*, 1602*w*, 1227*w*, 1225*w*, 1222*w*, 1217*s*, 1214v*s*, 1212*s*, 1210v*s*, 1207*m*, 1204*w*, 1106*w*, 1004*m*, 823*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.21 (*d*, *J* = 7.5, 1 H); 4.21 (*t*, *J* = 2, 2 H); 4.24 (*s*, 5 H); 4.47 (*t*, *J* = 2, 2 H); 5.55 (*d*, *J* = 7.5, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 83.5; 83.0; 71.6; 70.0; 69.0; 63.8; 53.6. MALDI-MS (DHB): 448.0 (80, M^+), (100, $[M - OH]^+$). HR-MALDI-MS: 448.0208 (80, M^+, $C_{25}H_{20}Fe_2O^+$; calc. 448.0213); 431.0174 (100, $[M - OH]^+$, $C_{25}H_{19}Fe_2^+$; calc. 431.0186).

1,5-Bis(4-methoxyphenyl)penta-1,4-diyn-3-ol (**11a**). 4-Ethynylanisole (0.265 g, 2 mmol), EtMgBr (2.2 ml, 2.2 ml), and HCO_2Et (0.077 ml, 0.921 mmol) were reacted as described for **11c** to give **11a** (0.159 g, 59%) with properties identical to those described in [45]. Orange solid. R_f (CH_2Cl_2) 0.38. M.p. 90° ([45]: 90.5°). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.32 (*d*, *J* = 8, 1 H); 3.82 (*s*, 6 H); 5.55 (*d*, *J* = 8, 1 H); 6.85 (*d*, *J* = 9, 4 H); 7.43 (*d*, *J* = 9, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.8; 133.3; 133.0; 113.8; 84.9; 84.4; 55.3; 53.3.

1,5-Bis[4-(dimethylamino)phenyl]penta-1,4-diyn-3-ol (**11b**). 4-Ethynyl-*N,N*-dimethylaniline (0.290 g, 2 mmol), EtMgBr (2.2 ml, 2.2 ml), and HCO_2Et (0.077 ml, 0.921 mmol) were reacted as described for **11c**, to give **11b** (0.131 g, 45%) with properties identical to those described in [46]. Brown solid. R_f (CH_2Cl_2) 0.21. M.p. 141° ([46]: 143–145). ^{1}H-NMR (300 MHz, $CDCl_3$): 2.30 (*d*, *J* = 7.5, 1 H); 2.98 (*s*, 12 H); 5.56 (*d*, *J* = 7.5, 1 H); 6.61 (*d*, *J* = 9, 4 H); 7.80 (*d*, *J* = 7.5, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.2; 132.9; 111.6; 108.8; 85.3; 84.6; 53.5; 40.2.

1,5-Bis(ferrocenyl)penta-1,4-diyn-3-one (**12c**). MnO_2 (0.294 g, 3.42 mmol) was added to **11c** (0.200 g, 0.44 mmol) in Et_2O. After stirring for 12 h at 20°, the mixture was filtered through *Celite*, and the solvent was removed *in vacuo* to deliver **12c** (0.143 g, 73%). Red powder. M.p. 70°. R_f (hexane/CH_2Cl_2 3:7) 0.47. IR ($CHCl_3$): 3689*w*, 3014*w*, 2183v*s*, 1300*s*, 1227*m*, 1224*w*, 1221*s*, 1214v*s*, 1209v*s*, 1206*s*, 1204*w*, 1129*s*, 1107*w*, 1029*s*, 1003*w*, 821*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.30 (*s*, 10 H); 4.43 (*t*, *J* = 2, 4 H); 4.66 (*t*, *J* = 2, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 159.9; 94.7; 88.4; 73.3; 71.1; 70.6; 59.9. MALDI-MS (DHB): 447.0 (100, MH^+), 446.0 (86, M^+). HR-MALDI-MS: 446.0059 (M^+, $C_{25}H_{18}Fe_2O^+$; calc. 446.0056).

1,5-Bis(4-methoxyphenyl)penta-1,4-diyn-3-one (**12a**). MnO_2 (0.294 g, 3.42 mmol) and **11a** (0.166 g, 0.59 mmol) were reacted as described for **12c** to deliver **12a** (0.691 g, 94%) with properties identical to the ones previously described in [42]. Orange powder. R_f (CH_2Cl_2) 0.43. M.p. 117–119° ([42]: 124–125°) ^{1}H-NMR (300 MHz, $CDCl_3$): 3.86 (*s*, 3 H); 6.92 (*d*, *J* = 9, 4 H); 7.61 (*d*, *J* = 9, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 161.8; 160.7; 135.3; 114.3; 111.3; 92.5; 89.7; 55.5.

1,5-bis[4-(dimethylamino)phenyl]penta-1,4-diyn-3-one (**12b**). MnO_2 (0.185 g, 2.15 mmol) and **11b** (0.136 g, 0.43 mmol) were reacted as described for **12c** to deliver **12b** (0.124 g, 92%) after CC (SiO_2; CH_2Cl_2/hexane 1:1 then 1:0). Red solid with properties identical to those described in [43]. R_f (CH_2Cl_2) 0.3. M.p. 140–142° ([43]: 143–145°). ^{1}H-NMR (300 MHz, $CDCl_3$): 3.04 (*s*, 12 H); 6.63 (*d*, *J* = 9, 4 H); 7.41 (*d*, *J* = 9, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 161.0; 152.1; 135.6; 111.8; 105.4; 95.6; 91.3; 40.2.

3-(Dibromomethylidene)-1,5-bis(4-methoxyphenyl)penta-1,4-diyne (**13a**). CBr_4 (1.58 g, 4.76 mmol), Ph_3P (1.25 g, 4.76 mmol), and Zn (0.311 g, 4.76 mmol) were suspended in a CH_2Cl_2 (10 ml), and the soln. was stirred for 90 min at 20°. Ketone **12a** (0.690 g, 2.38 mmol) was added, and the darkened soln. was stirred for 3 d at 20°. Hexane (100 ml) was added, and the suspension was filtered. The precipitate was dissolved in CH_2Cl_2 and reprecipitated with hexane. The combined filtrates were concentrated *in vacuo*, and the obtained yellow solid was purified by short CC (SiO_2; hexane/CH_2Cl_2 7:3) to afford **13a** (0.553 g, 52%). Clear yellow solid. R_f (CH_2Cl_2) 0.5. M.p. 127–128°. IR ($CHCl_3$): 3028*w*, 3017*m*, 3014*w*, 2840*w*, 2197*m*, 1606*s*, 1512*s*, 1465*w*, 1442*w*, 1291*m*, 1251*s*, 1227*m*, 1223v*s*, 1221*w*, 1215v*s*, 1211*s*, 1208*s*, 1204*s*, 1181*w*, 1173*m*, 1124*w*, 1108*w*, 1031*m*, 834*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.84 (*s*, 6 H); 6.87 (*d*, *J* = 9, 4 H); 7.48 (*d*, *J* = 9, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 160.2; 133.2; 114.5; 114.2; 114.0; 105.8; 95.9; 85.2; 55.4. EI-MS: 445.9 (23, M^+), 286.2 (100, $[M - 2\ Br]^+$), 271.2 (61, $[M - 2\ Br - Me]^+$), 256.1 (8, $[M - 2\ Br - 2\ Me]^+$), 243.2 (20, $[M - 2\ Me - CBr_2]^+$). Anal. calc. for $C_{20}H_{14}Br_2O$ (446.14): C 53.84, H 3.16; found: C 53.72, H 3.24.

3-(Dibromomethylidene)-1,5-bis[4-(dimethylamino)phenyl]penta-1,4-diyne (**13b**). CBr_4 (0.431 g, 1.35 mmol), and Ph_3P (0.683 g, 2.6 mmol) were added to **12b** (0.142 g, 0.45 mmol) in benzene (30 ml). The

darkening soln. was stirred for 2 d at 20°, then hexane (100 ml) was added, and the formed suspension was filtered through a plug (SiO_2; hexane). Evaporation *in vacuo* and CC (SiO_2; hexane/CH_2Cl_2 7:3 → 1:1) afforded **13b** (0.019 g, 9%). Clear yellow solid. R_f (hexane/CH_2Cl_2 1:1) 0.71. M.p. 187° (dec.). IR (CCl_4): 3155*w*, 3053*m*, 2685*w*, 2305*m*, 2253*s*, 2188*m*, 1795*w*, 1607*s*, 1524*m*, 1465*m*, 1423*w*, 1378*m*, 1264v*s*, 1224v*s*, 1212v*s*, 1120*w*, 1097*w*, 906v*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.99 (*s*, 12 H); 6.63 (*d*, $J = 9$, 4 H); 7.41 (*d*, $J = 9$, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 150.8; 133.2; 114.7; 111.9; 110.1; 103.4; 97.4; 85.2; 40.4. MALDI-MS (DHB): 472 (64, M^+), 471.0 (100, $[M-H]^+$). HR-MALDI-MS (DHB): 471.9965 (M^+, $C_{22}H_{20}Br_2N_2^+$; calc. 471.9973).

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