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Mori–Hiyama versus Hay Coupling for Higher Polyynes

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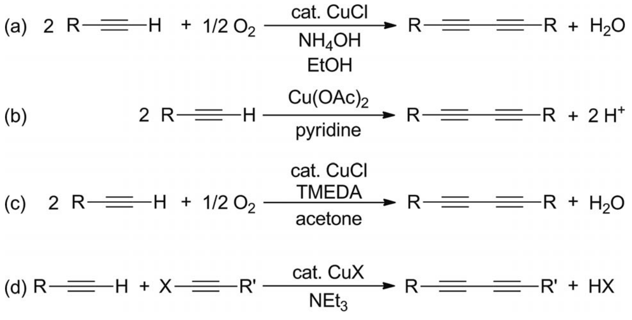
Dimerizations of C_4 precursors RC≡CC≡CTMS [R = C_6H_5 (**1**), *p*-$CH_3C_6H_5$, (**2**), 4-*n*-$C_5H_{11}C_6H_4$ (**3**), C_6H_9 (**4**), *p*-$CH_3OC_6H_4$ (**5**), *p*-$C_6H_5COC_6H_4$ (**6**), *p*-$NO_2C_6H_4$ (**7**), and *p*-NCC_6H_4 (**8**)] by Hay coupling with in situ deprotection gave stable octatetraynes R(C≡C)$_4$R (**1**–**8**-C_8-**1**–**8**) in 42–80 % yields as light yellow to brown powders. The same tetraynes were next synthesized from the same C_4 precursors by an alternative Mori–Hiyama method that typically utilizes trimethylsilyl-substituted alkynes without prior deprotection. The latter protocol proved useful and gave the expected products but with lower yields of 8–74 %. The resulting tetraynes were characterized by spectroscopic methods and in some cases by X-ray crystallography. In the cases of **1**-C_8-**1** and **3**-C_{12}-**3**, close analysis of the crystal data showed high degrees of carbon chain linearity, with % contraction indexes of 0.13 % and 0.19 %, respectively. The chains were more strained in the cases of **6**-C_8-**6** (0.34 %) and **3**-C_8-**3** (0.68 %). Deeper analysis of packing motifs revealed **3**-C_{12}-**3** to be a very promising candidate for topochemical 1,4-polymerization.

Introduction

Over the last three decades, conjugated oligo- and polyynes have continued to attract unabated attention. This has been due to their salient application potential as carbon-rich building blocks both in organic syntheses and as material precursors in different technological areas.[1] For instance, organic polyynes (especially diynes) are important precursors of numerous types of polymers, including those that result from topochemical crystal-to-crystal polymerization.[2] Thanks to the presence of redox-active end-groups, organometallic and metal-containing polyynes are regarded as extremely useful in molecular nanoelectronics as parts of molecular-scale devices such as wires and switches.[3] This group of compounds includes organometallic complexes of type $L_mMC_xML_m$,[4] as well as metal-containing species in which metal atoms are not bound directly to the carbon atoms of polyyne chains. The latter group mostly includes ferrocene derivatives,[5] although other types of compounds are known.[6] Moreover, the polyyne motif is ubiquitous in many natural organic products, which often show remarkable biological activities.[7]

Unlike the compounds with odd-carbon chains, symmetrical even-carbon chain polyynes of C_{2n} type are quite straightforward to synthesize. The typical pathway involves the introduction of an acetylene moiety, followed by chain elongation. For the latter step, the most commonly used procedures include not only classical Glaser/Hay/Eglinton–Galbraith,[8–10] or Cadiot–Chodkiewicz[8b,11] reactions (shown in Scheme 1), but also other approaches/modifications that have been developed over the last years.[12]



Scheme 1. Syntheses of diynes by (a) Glaser, (b) Eglinton–Galbraith, (c) Hay, and (d) Cadiot–Chodkiewicz couplings.

Most of the methods mentioned above utilize terminal alkynes, which are often only of moderate stability towards isolation and purification and tend to decompose under ambient conditions.[13] This inexpedient "property", which also applies for long-chain disubstituted polyynes, can be greatly mitigated by application of bulky end-groups.[4e,4g,4h,12i,14]

Terminal alkynes are usually synthesized from much more stable trialkylsilyl-substituted precursors by different deprotection procedures, so in 2000 Mori and Hiyama (M–H) successfully employed silyl-protected alkynes to test a new coupling method that proceeded without the desilylation step.[15] A while later, pathways with in situ depro-

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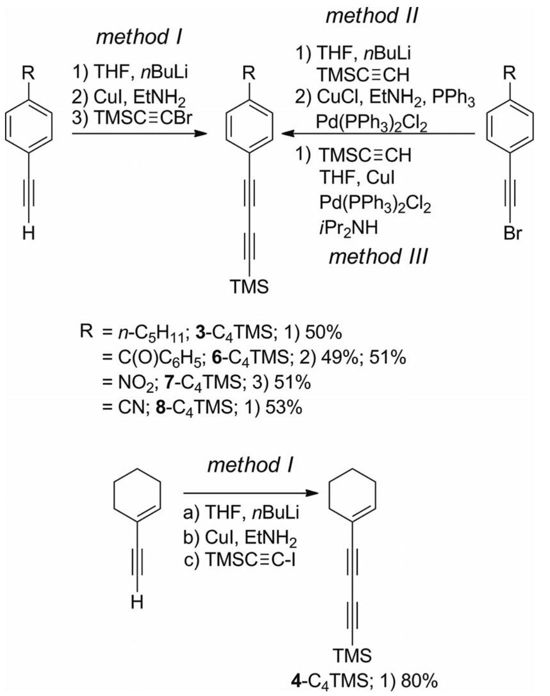
tection were introduced, although some of the reaction conditions had to be chosen in a particularly astute manner.[16]

A number of butadiynes were obtained by the Mori–Hiyama method, which has proven to give good results for different types of end-groups. Here we have extended this method for the synthesis of organic octatetraynes and compared the Mori–Hiyama yields with those of Hay coupling with in situ deprotection. The resulting tetraynes were fully characterized by spectroscopic methods and in some cases by X-ray crystallography.

Results and Discussion

Syntheses of Diacetylenes

Syntheses of the diacetylenic derivatives $C_6H_5C{\equiv}CC{\equiv}CTMS$ (**1**-C_4TMS),[17] p-$CH_3C_6H_4C{\equiv}CC{\equiv}CTMS$ (**2**-C_4TMS),[18] 4-n-$C_5H_{11}C_6H_4C{\equiv}CC{\equiv}CTMS$ (**3**-C_4TMS), $C_6H_9C{\equiv}CC{\equiv}CTMS$ (**4**-C_4TMS), p-$CH_3OC_6H_4C{\equiv}CC{\equiv}CTMS$ (**5**-C_4TMS),[19] p-$C_6H_5COC_6H_4C{\equiv}CC{\equiv}CTMS$ (**6**-C_4TMS), p-$NO_2C_6H_4C{\equiv}CC{\equiv}CTMS$ (**7**-C_4TMS), and p-$NCC_6H_4C{\equiv}CC{\equiv}CTMS$ (**8**-C_4TMS) was by the already classical Cadiot–Chodkiewicz procedure[11] as shown in Scheme 2. In the cases of the new **3**-C_4TMS, **4**-C_4TMS, and **8**-C_4TMS the reactions were performed by starting from aryl- or cyclohexenyl-substituted terminal acetylenes, which were treated with TMSC≡CBr or TMSC≡CI (Method I in Scheme 2). In the cases of **6**-C_4TMS and **7**-C_4TMS the aryl-substituted bromoalkynes p-$C_6H_5COC_6H_4C{\equiv}CBr$ (**6**-C_2Br)[20] and p-$NO_2C_6H_4C{\equiv}CBr$[21] were treated with TMSC≡CH (Methods II and III in Scheme 2) in the presence of palladium(II)/Cu^I catalyst. Compound **6**-C_4TMS was obtained by the use of two different catalytic systems (see Exp. Sect.), which gave nearly identical yields (49–51 %).



Scheme 2. Syntheses of TMS end-capped diynes.

Workup by column chromatography gave the targeted butadiynes, including the new **3**-C_4TMS (oil), **4**-C_4TMS (brown liquid), **6**-C_4TMS (beige solid), **7**-C_4TMS (light yellow powder), and **8**-C_4TMS (yellow solid) in 49–80 % yields. All of the compounds were soluble in common polar and nonpolar organic solvents such as CH_2Cl_2, acetone, THF, and hexanes.

All resulting diynes were characterized by ^1H and ^{13}C NMR spectroscopy and gave correct elemental analysis. Although the ^1H and ^{13}C NMR spectroscopic data were routine, we performed HMBC analysis for selected diynes in order to assign the carbon signals unambiguously. The results are presented in Table 1 and the representative HMBC spectrum for **3**-C_4TMS is shown in Figure 1.

Table 1. ^{13}C NMR shifts for chain carbon atoms in diynes $RC{\equiv}CC{\equiv}CTMS$.[a]

Compound	R	Yield [%]	C(1)	C(2)	C(3)	C(4)
1-C_4TMS[17]	C_6H_5[17]	95	76.6	74.3	88.0	90.3
2-C_4TMS[18]	p-$CH_3C_6H_4$[18]	85[18b]	–[18a]	73.6	88.0	90.1
3-C_4TMS	4-n-$C_5H_{11}C_6H_4$	50	77.3	73.8	88.3	90.3
4-C_4TMS	C_6H_9	80	79.2	71.9	88.4	89.4
5-C_4TMS	p-$CH_3OC_6H_4$	36	–[b][19]	73.2	88.3	90.1
6-C_4TMS	p-$C_6H_5COC_6H_4$	51	77.1	75.8	87.6	92.7
7-C_4TMS	p-$NO_2C_6H_4$	52	79.2	74.4	87.1	94.4
8-C_4TMS	p-$N{\equiv}CC_6H_4$	53	78.4	74.6	87.1	93.9

[a] All spectra were measured in $CDCl_3$. [b] The signal overlies with the solvent signal.

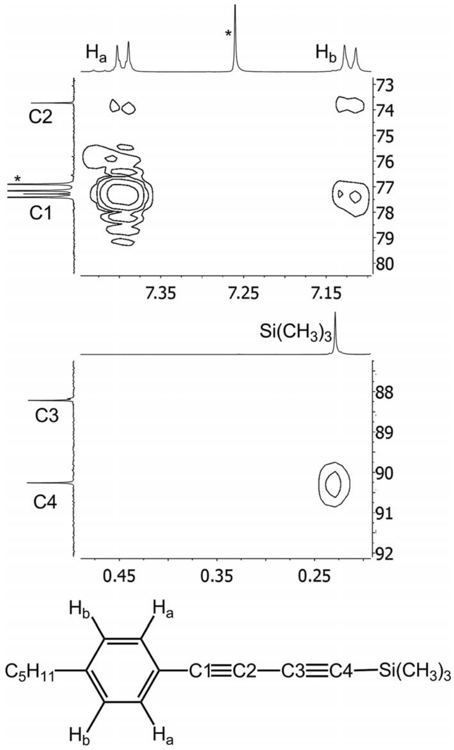


Figure 1. Partial HMBC spectrum for **3**-C_4TMS.

As shown in Table 1, for all the compounds the most strongly downfield-shifted signal belongs to the C(4) carbon, which is α to the trimethylsilyl group. The next are the C(3) carbons, which lie in the narrow range between δ = 87.1 and 88.4 ppm. This range becomes slightly wider for C(2) carbons (75.8–71.9 ppm; 3.9 ppm) as well as for C(1) atoms (79.2–76.6 ppm; 2.6 ppm). The signals in C_6D_6 (measured for **3**-C_4TMS and **7**-C_4TMS) are shifted only slightly relative to those in $CDCl_3$, as shown in the Experimental Section.

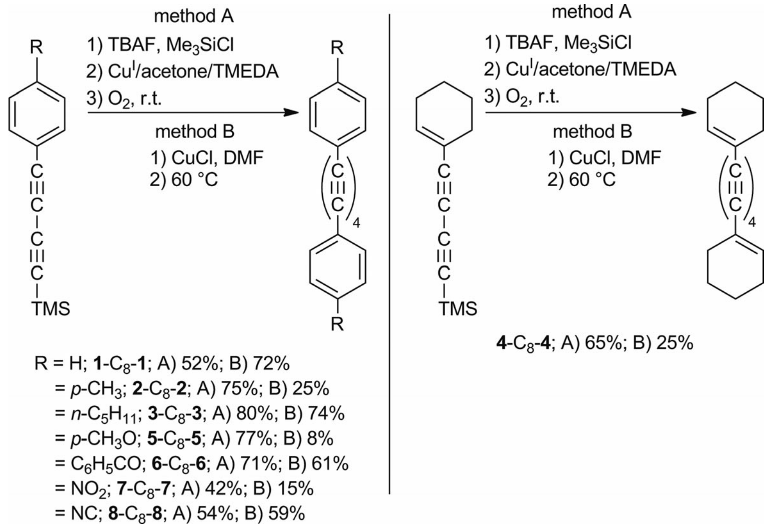
Proton spectra revealed the signals of the TMS groups at 0.24 (**3**-C_4TMS, 0.11 in C_6D_6), 0.20 (**4**-C_4TMS), 0.25 (**6**-C_4TMS), 0.25 (**7**-C_4TMS, 0.11 in C_6D_6), and 0.24 (**8**-C_4TMS) ppm. The signal of the carbonyl group carbon in **6**-C_4TMS was at δ = 195.8 ppm.

Synthesis of Tetraynes

Organic and organometallic tetraynes have been objects of intense research over the last two decades. To date, numerous aryl-end-capped organic C_8 polyynes have been obtained and characterized. The compounds are interesting from different perspectives. Perfluorophenyl-substituted polyynes, for instance, form solid admixture with unique properties with benzene.[22] Benzaldehyde-end-capped tetraynes were used for the synthesis of tetraynic porphyrins.[23] It was noticed that some of the C_8 and longer polyynes possess higher dipole moments, as well as first- and second-order hyperpolarizabilities.[24] The pharmaceutical potential of a few natural tetraynes is also worth mentioning.[25]

A straightforward synthesis and characterization of the series of symmetric tetraynes R(C≡C)$_4$R (**1**–**8**-C_8-**1**–**8**) directly from TMS-end-capped diynes was a major goal of this research. For comparison, two synthetic strategies – a) Hay coupling with in situ deprotection, and b) the Mori–Hiyama approach – were tested. The latter, as mentioned already, has successfully been employed for the synthesis of symmetrical diynes,[15] so we were curious as to whether or not the protocol would work equally well for tetraynes as it did for diynes, with which the yields exceeded 70%.

As shown in Scheme 3 the Hay coupling was performed by the standard procedures, with wet TBAF as the deprotecting agent, ClSiMe$_3$ as the F$^-$ ion scavenger, and Cu^I/TMEDA/acetone or CH_3CN as the oxidation catalytic system. Workups on silica gel columns gave analytically pure target tetraynes **1**–**8**-C_8-**1**–**8** in 42–80% yields (see Table 2)



Scheme 3. Syntheses of tetraynes.

Table 2. Yields and spectroscopic data for **1**–**8**-C_8-**1**–**8**.[a]

Compound	**1**-C_8-**1**	**2**-C_8-**2**[18b]	**3**-C_8-**3**	**4**-C_8-**4**	**5**-C_8-**5**	**6**-C_8-**6**	**7**-C_8-**7**	**8**-C_8-**8**
Hay yield [%]	72	75	80	65	77	71	42	54
M–H yield [%]	52	25	74	25	8	61	15	59
IR [cm^{-1}]	2202	2198	2198	2192	2197	2200	2205	2202
	2098	2094	2075	2100	2074	(not observed)	2105	2102
^{13}C NMR; C≡CC≡*C*Ar	75.8	78.7	80.9	80.2	76.1	77.8	78.2	77.6
^{13}C NMR; C≡C*C*≡CAr	74.8	74.7	74.9	73.1	73.5	77.0	74.3	74.1
^{13}C NMR; C≡*C*C≡CAr	70.5	67.8	68.0	67.3	71.4	68.8	73.4	73.8
^{13}C NMR; *C*≡CC≡CAr	65.6	64.7	64.8	64.5	68.9	64.8	67.6	67.7

[a] The chemical shifts are in ppm. Spectra were recorded in C_6D_6.

as light yellow to brown solids readily soluble in most common organic solvents. The compounds are stable in the solid state and in solution for extended periods (weeks to months).

Compounds **1**–**8**-C_8-**1**–**8** were characterized by IR and by ^1H and ^{13}C NMR spectroscopy and gave correct microanalyses. The IR spectra showed a set of two $\nu_{C\equiv C}$ absorptions for each compound at frequencies ranging from 2205 to 2192 cm^{-1} (vs) and from 2105 to 2074 cm^{-1} (variable intensities). The latter band was not observed in the case of **6**-C_8-**6**.

Similarly as for C_4 compounds, HMBC spectra were recorded for selected compounds in order to assign carbon chain signals unambiguously. The spectrum of **3**-C_8-**3** is shown in part in Figure 2.

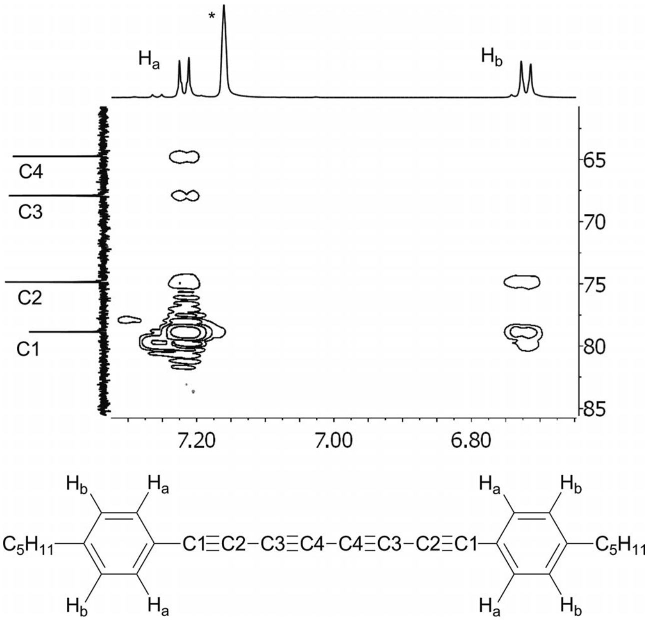


Figure 2. Partial HMBC spectrum of **3**-C_8-**3**.

From these data, we assigned carbon chain signals for each compound. The most strongly downfield-shifted signals, ranging from 75.8 ppm for **1**-C_8-**1** to 80.9 ppm for **3**-C_8-**3**, were assigned to carbons adjacent to end-groups. Along the carbon chain towards its middle point the signals for each compound moved upfield. The detail analysis is presented in Table 2 and in the Experimental Section.

The Mori–Hiyama protocol was next tested. The reactions were performed in DMF at 60 °C with the use of CuCl as catalyst and C_4TMS precursor as shown in Scheme 3 (Method B). Workup gave the target tetraynes in 8–74% yields, showing the protocol to be useful. Nevertheless, as can easily be seen in Table 2, the yields achieved in the Hay couplings substantially surpass the Mori–Hiyama results. This is particularly apparent in the case of **5**-C_8-**5**, but in some cases (**3**-C_8-**3**, **6**-C_8-**6**, and **8**-C_8-**8**) Mori–Hiyama coupling gave similar yields. With this in mind and in view of the simplicity of the method it would always be smart not to exclude the approach from a strategy for a longer chain synthesis.

Although no thermal analysis was performed for the majority of the compounds, **2**-C_8-**2** revealed interesting behavior. The compound melted without decomposition at 120 °C, giving a nematic phase, and then polymerized at 156 °C. Figure 3 shows the thermal transformations of **2**-C_8-**2**.

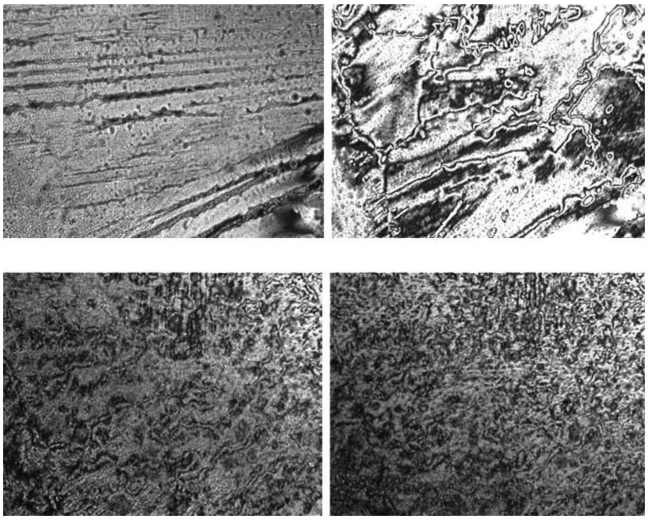


Figure 3. Melting and polymerization of **2**-C_8-**2**: crystalline phase (top left), nematic phase (top right), disappearance of nematic phase (bottom left), and polymerization (bottom right).

Crystal Structures of Tetraynes

The crystal structures of **1**-C_8-**1**, **3**-C_8-**3**, **3**-C_{12}-**3**, and **6**-C_8-**6** were determined as outlined in Tables 3 and 4 and described in the Experimental Section.

Table 3. X-ray data for tetraynes **1**-C_8-**1**, **3**-C_8-**3**, and **6**-C_8-**6** and for hexayne **3**-C_{12}-**3**.

Complex	**1**-C_8-**1**	**3**-C_8-**3**	**3**-C_{12}-**3**	**6**-C_8-**6**
Formula	$C_{20}H_{10}$	$C_{30}H_{30}$	$C_{34}H_{30}$	$C_{34}H_{18}O_2$
Formula weight	250.28	390.54	438.58	458.51
T [K]	100(2)	100(2)	100(2)	100(2)
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	10.808(6)	7.704(4)	4.936(4)	51.66(2)
b [Å]	3.871(3)	8.974(4)	9.892(7)	3.889(3)
c [Å]	16.768(9)	16.297(8)	13.545(9)	11.380(4)
α [°]	90.0	90.90(5)	87.91(4)	90.0
β [°]	106.03(5)	91.21(5)	79.40(4)	96.38(3)
γ [°]	90.0	92.54(5)	82.78(4)	90.0
V [Å^3]	674.3(7)	1125.2(9)	644.9(8)	2272(2)
Z	2	2	1	4
ρ [g cm^{-3}]	1.233	1.153	1.131	1.340
μ (Mo-K_α) [mm^{-1}]	0.070	0.065	0.478	0.082
R_1 [%] (>2σ)	0.0636	0.1139	0.0658	0.0603
wR_2 [%] (>2σ)	0.1218	0.2389	0.1769	0.1507

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Table 4. Interatomic distances and angles for **1**-C_8-**1**, **3**-C_8-**3**, **3**-C_{12}-**3**, and **6**-C_8-**6**.

Complex	**1**-C_8-**1**	**3**-C_8-**3**	**3**-C_{12}-**3**	**6**-C_8-**6**
Interatomic distances [Å]				
C(11)–C(1)	1.435(2)	1.431(7)	1.4318(19)	1.4299(19)
C(1)–C(2)	1.2072(19)	1.196(6)	1.2088(19)	1.2075(19)
C(2)–C(3)	1.367(2)	1.367(7)	1.3600(19)	1.363(2)
C(3)–C(4)	1.213(2)	1.217(7)	1.2168(19)	1.2107(19)
C(4)–C(4a)	1.363(3)	–	–	1.360(3)
C(4)–C(5)	–	1.355(6)	1.3507(19)	–
C(5)–C(6)	–	1.202(6)	1.2206(18)	–
C(6)–C(6a)	–	–	1.350(3)	–
C(6)–C(7)	–	1.375(7)	–	–
C(7)–C(8)	–	1.202(6)	–	–
C(8)–C(21)	–	1.422(6)	–	–
C(1)-C(X)[a] sum	8.937	8.914	14.0638	8.9224
C(1)–C(X)[a] dist	8.934	8.878	14.045	8.916
% contraction	0.03	0.41	0.13	0.07
C(11)–C(Y)[b] sum	11.807	11.767	16.9275	11.7822
C(11)–C(Y)[b] dist	11.792	11.688	16.895	11.742
% contraction	0.13	0.68	0.19	0.34
Interatomic angles [°]				
C(11)–C(1)–C(2)	176.69(15)	177.6(6)	178.02(14)	173.06(15)
C(1)–C(2)–C(3)	177.87(16)	177.6(6)	178.24(15)	177.40(15)
C(2)–C(3)–C(4)	177.84(16)	178.7(6)	178.22(15)	176.98(16)
C(3)–C(4)–C(4a)	179.3(2)	–	–	179.6(2)
C(3)–C(4)–C(5)	–	176.2(6)	177.47(15)	–
C(4)–C(5)–C(6)	–	176.8(6)	178.05(15)	–
C(5)–C(6)–C(6a)	–	–	179.9(2)	–
C(5)–C(6)–C(7)	–	177.8(6)	–	–
C(6)–C(7)–C(8)	–	177.8(5)	–	–
C(7)–C(8)–C(21)	–	177.2(5)	–	–
av. Angle	177.93	177.46	178.32	176.76

[a] C(X) represents the last atom in carbon chain opposite to C(1).
[b] C(Y) represents the atom from the end-group that bounds to the carbon chain.

In the case of the structure of **1**-C_8-**1**, data for two polymorphs of this compound have already been published,[26] but only space group and unit cell characteristics were reported, with no interatomic angles or atomic coordinates. For that reason we decided to grow crystals of this compound and to solve and refine its structure to fill out an important gap in the CCDC data and to provide additional information for a future structural analysis.[4a,4b]

Crystals of hexayne **3**-C_{12}-**3** were obtained by chance when one of the **3**-C_8-**3** mixtures (from Hay coupling) was set for crystallization. It has been documented that longer or shorter polyynes can spontaneously form in small quantities during chain elongation processes.[27] Subsequent dimerization of such mixture without prior separation gives mixture of symmetrical polyynes. This method is sometimes used for the formation of C_{4n+2} compounds.[28]

As depicted in Figure 4 the centrosymmetric molecule of **1**-C_8-**1** is almost ideally planar. The two phenyl rings are coplanar, which is a consequence of the fact that the molecule lies at the symmetry center. The interatomic distances in the carbon chain are 1.2072(19) and 1.213(2) Å for the triple C(1)≡C(2) and C(3)≡C(4) bonds and 1.367(2) and 1.363(3) Å for the single C(2)–C(3) and C(4)–C(4a) bonds, respectively, and are similar to those found for other tetraynes.[4a,4b] An analogous situation applies for centrosymmetric **3**-C_{12}-**3**, which crystallizes in the *C*2/*c* space group. Also in this case the terminal phenyl rings are coplanar, as shown in Figure 5.

Figure 4. ORTEP views of **1**-C_8-**1**.

Slightly lower degrees of planarity are observed for **3**-C_8-**3** and **6**-C_8-**6**, although in the latter case this is caused by the bulky end-groups. The two molecules are shown in Figures 6 and 7, respectively, and the bottom views illustrate their planarity.

In **3**-C_8-**3** the angle between the phenyl rings is 4.8°. In **6**-C_8-**6** it is 0°, but the phenyl rings of the C_6H_5CO substituents form an angle of 49.2° with the rings that are adjacent to the carbon chain. The value is almost identical with the analogous one in diyne $C_6H_5COC_6H_4C{\equiv}CC{\equiv}CC_6H_4$-$COC_6H_5$ (49.8°).[15] Each C=O group [defined by C(5), C(14), C(21), and O(1) atoms] lies at an angle of 37.9° to the terminal phenyl ring and of 16.2° to the C_6H_4 ring.

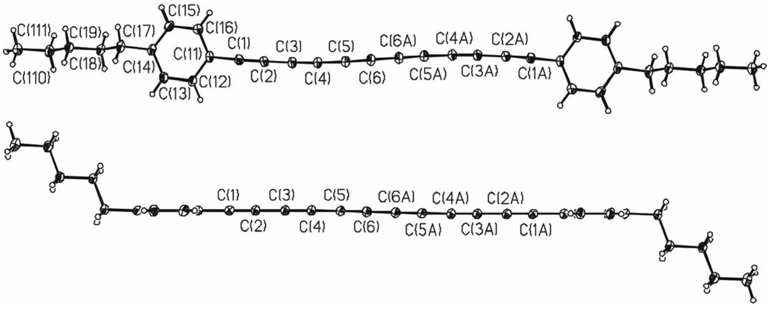

Figure 5. ORTEP views of **3**-C_{12}-**3**.

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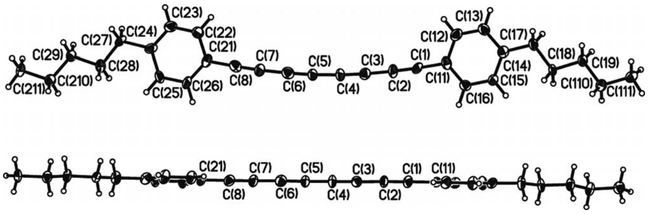

Figure 6. ORTEP views of **3**-C_8-**3**.

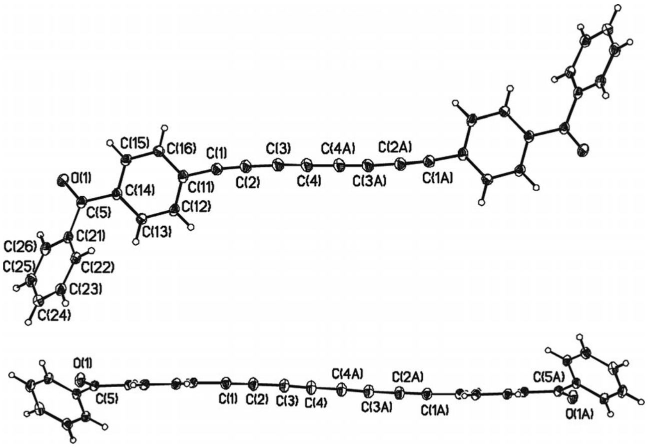

Figure 7. ORTEP views of **6**-C_8-**6**.

These values are also similar to the corresponding ones in $C_6H_5COC_6H_4C{\equiv}CC{\equiv}CC_6H_4COC_6H_5$ (38.4° and 15.1°, respectively).

The interatomic distances and angles within carbon chains (see Table 4) were next analyzed. The shortest C≡C distances are 1.196(6) Å and 1.202(6) Å, both for **3**-C_8-**3**, and they are shorter than the C≡C distances in ethyne[29] (1.2033 Å) and butadiyne (1.217–1.20964 Å).[30] The longest C≡C distance of 1.2206(18) Å belongs to internal triple bond in **3**-C_{12}-**3** and is slightly longer than the average value of this bond in the other crystallographically characterized C_8 compounds.[4a,4b]

Because C_8 chains are long enough to exhibit distinctive bending, we inspected the chains in order to estimate the degree of deformation for each compound. As can be seen from the top sections of Figures 4–7, compounds **1**-C_8-**1**, **3**-C_{12}-**3**, and **6**-C_8-**6** can be regarded as S-shaped, whereas **3**-C_8-**3** represents a slightly unsymmetrical bow. These easily perceptible deformations from linearity are further supported by the non-zero % contraction values, which range (those calculated for chain carbon-carbon bonds only) from as low as 0.03 for **1**-C_8-**1** through 0.07 and 0.013 for **6**-C_8-**6** and **3**-C_{12}-**3**, respectively, to the highest value of 0.41 for **3**-C_8-**3**. Interestingly, the average value for the C-C–C angles is the lowest for **6**-C_8-**6** and the highest for **3**-C_{12}-**3**.

Packing Motifs and Reactivity Implications

The four structures crystallize in the monoclinic system in the $P2_1/n$ (**1**-C_8-**1**) and $C2/c$ (**6**-C_8-**6**) space groups and in the triclinic system in the $P\bar{1}$ (**3**-C_8-**3** and **3**-C_{12}-**3**) space group. As a consequence, molecules **1**-C_8-**1** and **6**-C_8-**6** are packed to form two non-parallel sets of parallel chains. These sets form angles of 14.0° in **1**-C_8-**1** and 15.2° in **6**-C_8-**6**. Figures 8 and 9 show packing diagrams for **1**-C_8-**1** and **6**-C_8-**6** with nearly perpendicular sets of molecules.

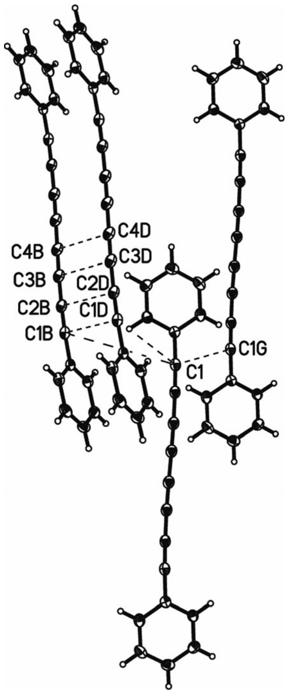

Figure 8. Packing diagram for **1**-C_8-**1** with the shortest chain–chain distances for parallel and non-parallel neighbors. The distances [Å] are: C(1B)–C(1D), C(2B)–C(2D), etc., 3.871; C(1)–C(1B) and C(1)–C(1D), 5.119; C(1)–C(1G), 4.369. Symmetry operations for related atoms are (B): 0.5 – *x*, 0.5 + *y*, 1.5 – *z*; (D): 0.5 – *x*, 0.5 + *y*, 1.5 – *z*; (G): –*x*, 1 – *y*, 1 – *z*.

The closest chain–chain separation was then analyzed. As defined earlier,[4a,4b,16] we approximate the closest chain–chain distance as the closest carbon-carbon distance from two neighboring carbon chains. Accordingly, the nearest chains with parallel orientation for **1**-C_8-**1** are only 3.871 Å apart and this separation is slightly larger than the sum of the van der Waals radii (3.56 Å) and very similar to that found for TMS(C≡C)$_4$TMS (3.853 Å).[31]

Despite the bulkier end-group the distance is similarly short for **6**-C_8-**6** (3.889 Å), whereas for **3**-C_8-**3**, with less bulky (relative to **6**-C_8-**6**) end-groups, it is longer (4.524 Å). Additionally, for **6**-C_8-**6** the chain–chain distance between non-parallel chains is even shorter than that for parallel chains and reaches 3.652 Å.

Not surprisingly, the value for **3**-C_{12}-**3** (Figure 10) is much shorter (3.484 Å), which can be attributed to the longer chain. This value is even smaller than that for MeTe-(C≡C)$_4$TeMe (3.486 Å), which had previously been regarded as the one possessing the shortest carbon–carbon chain distance out of all the X-ray-characterized compounds.[4a,4b,32]

1,*n*-Topochemical polymerization is one of the most widely recognized transformations that can take place in relation to organic polyynes.[2] The geometric requirements

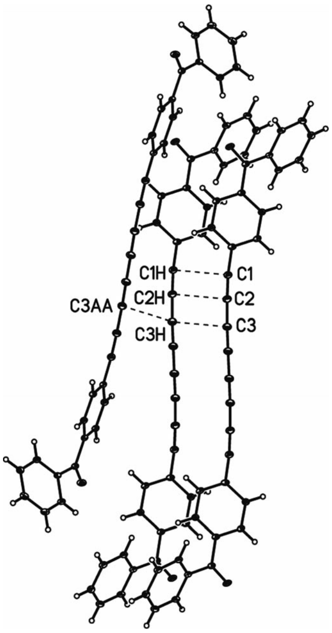

Figure 9. Packing diagram for **6**-C_8-**6** with the shortest chain–chain distances for parallel and non-parallel neighbors. The distances [Å] are: C(1)–C(1H), C(2)–C(2H), etc., 3.889; C(3H)–C(3AA), 3.652. Symmetry operations for related atoms are (H): $-x$, $-1 + y$, z; (AA): $-x$, $-1 + y$, $1.5 - z$.

for such process for diynes (1,4-polymerization) are fulfilled when the nearest parallel chains are separated by ca. 3.5 Å and the angle ϕ is close to 45° (see Figure 11).

The corresponding values for triynes and tetraynes are 3.5 Å and 28° (1,6-polymerization) and 3.5 Å and 21° (1,8-polymerization), respectively.[4a,4b] On searching for such values, it can easily be seen (see Table 5) that there is no good candidate for 1,8-polymerization. Although structures **1**-C_8-**1** and **6**-C_8-**6** present more ladder-type architectures (ϕ = 83.0° and 82.4°; for ideal ladder type ϕ = 90°), compound **3**-C_{12}-**3** seems as an ideal candidate for 1,4-polymerization.

Conclusions

In summary, we have demonstrated the utility of the Mori–Hiyama protocol for the synthesis of longer polyynes. Although the received yields were lower than those of more "traditional" Hay coupling with in situ deprotection, the simplicity of the procedure might in specific cases be more useful than the resulting yield. The Mori–Hiyama approach also seems advantageous in cases when one needs to avoid isolation or even formation of terminal alkynes. The resulting octatetraynes are stable solids that can be stored for long periods (weeks to months) at reduced temperatures. They were fully characterized by spectroscopic methods and for some compounds HMBC experiments were conducted in order to assign the signals of carbons from unsaturated chains unambiguously. Structural analysis of crystallographically characterized compounds showed high degrees of chain linearity. In the case of **3**-C_{12}-**3**, a side product of **3**-C_8-**3** synthesis, the insight into packing motifs showed a great potential for topochemical (crystal-to-crystal) 1,4-polymerization.

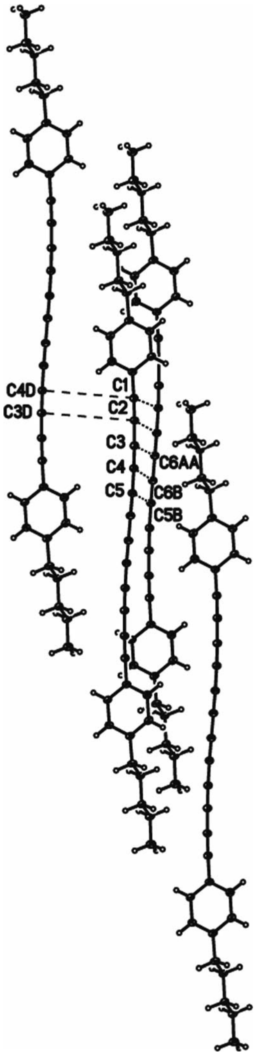

Figure 10. Packing diagram for **3**-C_{12}-**3** with the shortest chain–chain distances. The distances [Å] are: C(1)–C(4D), 5.032; C(2)–C(3D), 5.095; C(3)–C(6AA), 3.567; C(4)–C(6B), 3.625; C(5)–C(5B), 3.625. Symmetry operations for related atoms are: (AA): $1 + x$, y, z; (B) $2 - x$, $1 - y$, $1 - z$; (D): $2 - x$, $2 - y$, $1 - z$.

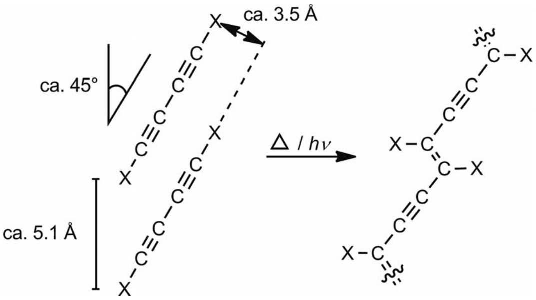

Figure 11. Topochemical 1,4-polymerization of crystalline diynes.

Table 5. Packing parameters for tetraynes **1**-C_8-**1**, **3**-C_8-**3**, **3**-C_{12}-**3**, and **6**-C_8-**6**.

Complex	**1**-C_8-**1**	**3**-C_8-**3**	**3**-C_{12}-**3**	**6**-C_8-**6**
Chain–chain contact [Å, parallel] [°][33]	3.871	4.524	3.484	3.889
	83.0	29.1	45.3	82.4
Offset distance [Å][33]	0.47	8.90	11.88	0.51
Fractional offset	0.04	0.76	0.70	0.06
Angle between nonparallel chains [°]	14.0	–	–	15.2
Chain–chain contact [Å, nonparallel]	5.119	–	–	3.652

Experimental Section

General: All reactions were conducted under N_2 with use of standard Schlenk techniques. Solvents were treated as follows: hexanes and Et_2O were distilled from Na, THF was predried with NaOH and then distilled from Na/benzophenone, CH_2Cl_2 and acetone were distilled from P_2O_5, and CH_3CN (HPLC grade) and DMF (Aldrich, 99.8% anhydrous) were used as received.

$TMSC\equiv CH$ (98%, Aldrich), $Pd(PPh_3)_2Cl_2$ (99%, Aldrich), CuI (99.999%, Aldrich), CuCl (99.995%, Aldrich), BuLi (1.6 M in hexane, Aldrich), *N*-bromosuccinimide (NBS, 99%, Aldrich), *N*-iodosuccinimide (NIS, 97%, Fluka), AgF (99.9%, Aldrich), $EtNH_2$ (2.0 M in THF, Aldrich), diisopropylamine (99.95%, Aldrich), ethynylcyclohexene (99%, Aldrich), tetrabutylammonium fluoride (TBAF, 1.0 M in THF, Aldrich), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, 99%, distilled from KOH, Aldrich), phenylacetylene (98%, Aldrich), 4-ethynyltoluene (97%, Aldrich), 4-ethynylbenzonitrile (97%, Aldrich), 4-ethynylpentylbenzene (97%, Aldrich), PPh_3 (99%, Merck), $ClSiMe_3$ (97%, Riedel–de Haen), Na_2SO_4 (POCh), NaCl (POCh), and $MgSO_4$ (POCh) were used without further purification unless stated otherwise.

$TMSC\equiv CI$, $TMSC\equiv CBr$,[34] $C_6H_5(C\equiv C)_2TMS$,[17] $p\text{-}CH_3C_6H_5(C\equiv C)_2TMS$,[18b] $p\text{-}CH_3OC_6H_4(C\equiv C)_2TMS$,[19] $p\text{-}C_6H_5COC_6H_4C\equiv CTMS$,[16] and $p\text{-}NO_2C_6H_4C\equiv CBr$,[16,35] were prepared by the known protocols.

Infrared spectra were recorded in a KBr cell with a Bruker 66/s FTIR spectrophotometer. TG-DTA analyses were recorded with a Setaram SETSYS 16/18 instrument. NMR spectra were obtained with BRUKER ESP 300E and 500 spectrometers. GC–MS analyses were recorded with a gas chromatograph, a mass detector (HP 5971A), and an infrared detector (HP5965B, Hewlett–Packard). Microanalyses were conducted with an ARL Model 3410 + ICP spectrometer (Fisons Instruments) and a VarioEL III CHNS (both in-house).

$C_6H_5(C\equiv C)_4C_6H_5$ (1-C_8-1)

Method A: A Schlenk flask was charged with CuCl (1.32 g, 13.3 mmol), acetone (5 mL), and TMEDA (0.781 mL, 5.21 mmol). The mixture was stirred for 30 min and a blue supernatant formed over a green solid. It was filtered off and the filtrate was kept under N_2. In a separate flask, $C_6H_5(C\equiv C)_2TMS$[17] (0.258 g, 1.30 mmol) was dissolved in acetone (10 mL). The solution was purged with N_2 for 10 min and TBAF (0.260 mL, 0.260 mmol, 20 mol-%) was added. After 20 min, $ClSiMe_3$ (0.168 mL, 1.33 mmol) was introduced and after another 15 min O_2 began to be bubbled through the solution. The blue filtrate was then added to the solution in several portions. After the last portion had been added, bubbling of O_2 was continued for an additional 3.5 h. After this time the solvent was evaporated under oil pump vacuum. The residue was dissolved in hexanes/CH_2Cl_2 (5 mL, 1:1, v/v) and passed through a Al_2O_3 plug (10 cm) and then through a silica plug (3 cm). Solvents were evaporated under oil pump vacuum to give **1**-C_8-**1** as a light yellow crystalline solid in 72% yield (0.117 g, 0.467 mmol).

Method B: $C_6H_5(C\equiv C)_2TMS$ (0.250 g, 1.26 mmol) was added to a suspension of CuCl (0.120 g, 1.21 mmol) in DMF (5 mL). The mixture was heated to 60 °C and kept at this temperature for 3 h. HCl (1 M, 30 mL) was then added to the warm solution. The water layer was extracted with Et_2O (5 × 20 mL). The combined organic layers were rinsed with saturated NaCl solution and dried with Na_2SO_4. The solution was next filtered and reduced in volume to ca. 30 mL under oil pump vacuum. It was chromatographed on a silica gel column (25 × 2.5 cm, hexanes) to give **1**-C_8-**1** in 52% yield (0.082 g, 0.328 mmol) as a light yellow solid.

^1H NMR (300 MHz, C_6D_6): δ = 7.20–6.80 (m, 10 H of 2 × C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 133.1 (s, 4 C-*ortho* of 2 × C_6H_5), 129.6 (s, 4 C-*meta* of 2 × C_6H_5), 128.0 (s, 2 C-*para* of 2 × C_6H_5), 120.9 (s, 2 C-*ipso*[36] of 2 × C_6H_5), 75.8 (s, 2 C, $C_6H_5\mathit{C}\equiv CC\equiv C$), 74.8 (s, 2 C, $C_6H_5C\equiv \mathit{C}C\equiv C$), 70.5 (2 C, $C_6H_5C\equiv C\mathit{C}\equiv C$), 65.6 (2 C, $C_6H_5C\equiv CC\equiv \mathit{C}$) ppm. IR (KBr): $\tilde{\nu}$ = 2202 (C≡C), 2098 (C≡C) cm^{-1}. MS: *m/z* = 250 $[M]^+$. $C_{20}H_{10}$ (250.30): calcd. C 95.97, H 4.03; found C 96.13, H 4.08.

$p\text{-}CH_3C_6H_4(C\equiv C)_4\text{-}p\text{-}C_6H_4CH_3$ (2-C_8-2):[18b] A) As described in ref.[18b] B) $p\text{-}CH_3C_6H_5(C\equiv C)_2TMS$ (0.220 g, 1.04 mmol), CuCl (0.101 g, 1.02 mmol), and DMF (5 mL) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method B) to give **2**-C_8-**2** as a light yellow powder in 25% yield (0.036 g. 0.129 mmol) with NMR characteristics congruent with those reported. M.p. 120 °C.

$p\text{-}C_5H_{11}C_6H_4(C\equiv C)_2TMS$ (3-C_4TMS): A Schlenk flask was charged with $p\text{-}C_5H_{11}C_6H_4C\equiv CH$ (1.00 mL, 0.858 g, 4.98 mmol) and THF (20 mL). The solution was cooled to –45 °C and *n*BuLi (3.44 mL, 5.50 mmol, 1.1 equiv.) was added with stirring. After 15 min CuI (0.949 g, 4.98 mmol) was added. The temperature was slowly raised to ca. –10 °C. After 10 min the solution was again cooled to –45 °C and $EtNH_2$ (3 mL) and $TMSC\equiv CBr$ (0.863 g, 4.88 mmol) were added. After 15 min the cold bath was removed and the mixture was stirred for 1 h at room temperature. The solvent was removed under oil pump vacuum. The residue was passed through a 5 cm silica gel plug (rinsed with hexanes/CH_2Cl_2, 1:1, v/v) and solvent was removed under oil pump vacuum. The residue was flash chromatographed (silica gel, hexanes) to give **3**-C_4TMS as an oily liquid in 50% yield (0.666 g, 2.48 mmol). ^1H NMR (600 MHz, C_6D_6): δ = 7.30 (d, $J_{H,H}$ = 8.3 Hz, 2 H of C_6H_4), 6.73 (d, $J_{H,H}$ = 8.3 Hz, 2 H of C_6H_4), 2.27 (t, $J_{H,H}$ = 7.8 Hz, 2 H of CH_2), 1.31–1.38 (m, 2 H of CH_2), 1.15–1.22 (m, 2 H of CH_2), 1.06–1.13 (m, 2 H of CH_2), 0.83 (t, $J_{H,H}$ = 7.4 Hz, 3 H of CH_3), 0.11 (s, 9 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ = 144.8 (s, C-*para* of C_6H_4), 133.0 (s, 2 C-*ortho* of C_6H_4), 128.9 (s, 2 C-*meta* of C_6H_4), 119.0 (s, C-*ipso* of C_6H_4), 90.5 (s, 1 C, $C\equiv CC\equiv \mathit{C}TMS$), 89.5 (s, 1 C, $C\equiv C\mathit{C}\equiv CTMS$), 77.9 (s, 1 C, $\mathit{C}\equiv CC\equiv CTMS$), 74.9 (s, 1 C, $C\equiv \mathit{C}C\equiv CTMS$), 36.1 (s, 1 C, $C_6H_4\mathit{C}H_2CH_2$), 31.7 (s, 1 C, $\mathit{C}H_2CH_2CH_3$), 31.0 (s, 1 C, $\mathit{C}H_2CH_2CH_2CH_3$), 22.8 (s, 1 C, $\mathit{C}H_2CH_3$), 14.2 (s, 1 C, $\mathit{C}H_3$), –0.4 (s, 3 C, $SiMe_3$) ppm. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40 (d, $J_{H,H}$ = 8.3 Hz, 2 H of C_6H_4), 7.13 (d, $J_{H,H}$ = 8.3 Hz, 2 H of C_6H_4), 2.60 (t, $J_{H,H}$ = 7.8 Hz, 2 H of CH_2), 1.57–1.63 (m, 2 H of CH_2), 1.30–1.35 (m, 4 H of CH_2), 0.89 (t, $J_{H,H}$ = 7.4 Hz, 3 H of CH_3), 0.24 (s, 9 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 144.9 (s, C-*para* of C_6H_4), 132.8 (s, 2 C-*ortho* of C_6H_4), 128.7 (s, 2 C-*meta* of C_6H_4), 118.6 (s, C-*ipso* of C_6H_4), 90.3 (s, 1 C, $C\equiv CC\equiv \mathit{C}TMS$), 88.3 (s, 1 C, $C\equiv C\mathit{C}\equiv CTMS$), 77.3 (s, 1 C, $\mathit{C}\equiv CC\equiv CTMS$), 73.8 (s, 1 C, $C\equiv \mathit{C}C\equiv CTMS$), 36.2 (s, 1 C, $C_6H_4\mathit{C}H_2CH_2$), 31.6 (s, 1 C, $\mathit{C}H_2CH_2CH_3$), 31.0 (s, 1 C, $\mathit{C}H_2CH_2CH_2CH_3$), 22.7 (s, 1 C,

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CH_2CH_3), 14.2 (s, 1 C, CH_3), –0.2 (s, 3 C, $SiMe_3$) ppm. $C_{18}H_{24}Si$ (262.43): calcd. C 82.38, H 9.22; found C 82.46, H 9.16.

p-$C_5H_{11}C_6H_4(C\equiv C)_4$-*p*-$C_6H_4C_5H_{11}$ (3-C_8-3)

Method A: Compound **3**-C_4TMS (0.212 g, 0.790 mmol), TBAF (0.158 mL, 0.158 mmol), $ClSiMe_3$ (0.102 mL, 0.790 mmol), CuCl (0.799 g, 7.900 mmol), and TMEDA (0.474 mL, 3.16 mmol) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method **A**). The analogous workup gave **3**-C_8-**3** as a light yellow, crystalline powder in 80% yield (0.123 g, 0.316 mmol).

Method B: Compound **3**-C_4TMS (0.200 g, 0.745 mmol), CuCl (0.076 g, 0.745 mmol), and DMF (10 mL) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method **B**) to give **3**-C_8-**3** as a light yellow powder in 74% yield (0.107 g, 0.274 mmol).

^{1}H NMR (600 MHz, C_6D_6): δ = 7.22 (d, $J_{H,H}$ = 8.3 Hz, 4 H of 2 × C_6H_4), 6.73 (d, $J_{H,H}$ = 8.3 Hz, 4 H of 2 × C_6H_4), 2.27 (t, $J_{H,H}$ = 7.8 Hz, 4 H of 2 × CH_2), 1.31–1.38 (m, 4 H of 2 × CH_2), 1.16–1.24 (m, 4 H of 2 × CH_2), 1.06–1.14 (m, 4 H of 2 × CH_2), 0.84 (t, $J_{H,H}$ = 7.3 Hz, 6 H of 2 × CH_3) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ = 145.6 (s, 2 C-*para* of 2 × C_6H_4), 133.6 (s, 4 C-*ortho* of 2 × C_6H_4), 128.9 (s, 4 C-*meta* of 2 × C_6H_4), 118.0 (s, 2 C-*ipso* of 2 × C_6H_4), 80.9 (s, 2 C, $C_6H_4C\equiv CC\equiv C$), 74.9 (s, 2 C, $C_6H_4C\equiv CC\equiv C$), 68.0 (s, 2 C, $C_6H_4C\equiv CC\equiv C$), 64.8 (s, 2 C, $C_6H_4C\equiv CC\equiv C$), 36.2 (s, 2 C, $C_6H_4CH_2CH_2$), 36.1 (s, 2 C, $CH_2CH_2CH_3$), 31.7 (s, 2 C, $CH_2CH_2CH_2CH_3$), 22.8 (s, 2 C, CH_2CH_3), 14.2 (s, 2 C, CH_3) ppm. IR (KBr): $\tilde{\nu}_{C\equiv C}$ = 2198 (vs), 2075 (w) cm^{-1}. MS: *m/z* = 391 [M]$^+$. $C_{30}H_{30}$ (390.57): calcd. C 92.26, H 7.74; found C 92.05, H 7.58.

$C_6H_9(C\equiv C)_2TMS$ (4-C_4TMS): $C_6H_9C\equiv CH$ (0.200 mL, 1.701 mmol), *n*BuLi (0.828 mL, 1.87 mmol, 1.1 equiv.), CuI (0.356 g, 1.87 mmol), $EtNH_2$ (6 mL), and TMSC≡CI (0.287 mL, 1.87 mmol) were combined in a procedure analogous to that used for **3**-C_4TMS. The analogous workup gave **4**-C_4TMS as a brown liquid in 80% yield (0.275 g, 1.36 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.31–6.27 (m, 1 H, HC=), 2.13–2.03 (m, 4 H of C_6H_9), 1.65–1.55 (m, 4 H of C_6H_9), 0.20 (s, 9 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 139.6 (s, 1 C, $CH=C$), 119.6 (s, 1 C, $CH=C$), 89.4 (s, 1 C, $C_6H_9C\equiv CC\equiv C$), 88.4 (s, 1 C, $C_6H_9C\equiv CC\equiv C$), 79.2 (s, 1 C, $C_6H_9C\equiv CC\equiv C$), 71.9 (s, 1 C, $C_6H_9C\equiv CC\equiv C$), 28.7 (s, 1 C, $CH_2CH=C$), 26.1 (s, 1 C, $CH=CCH_2$), 22.2 (s, 1 C, $CH=CCH_2CH_2$), 21.4 (s, 1 C, $CH_2CH_2CH=C$), –0.1 (s, 3 C, $SiMe_3$) ppm. $C_{13}H_{18}Si$ (202.37): calcd. C 77.16, H 8.97; found C 77.24, H 9.06. GC–MS: *m/z* = 202 [M]$^+$.

$C_6H_9(C\equiv C)_4C_6H_9$ (4-C_8-4)

Method A: Compound **4**-C_4TMS (0.337 g, 1.67 mmol), TBAF (0.333 mL, 0.333 mmol), $ClSiMe_3$ (0.216 mL, 1.67 mmol), CuCl (1.65 g, 16.7 mmol), and TMEDA (0.999 mL, 6.66 mmol) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method A). The analogous workup gave **4**-C_8-**4** as a pale yellow-brown powder in 65% yield (0.140 g, 0.541 mmol).

Method B: Compound **4**-C_4TMS (0.150 g, 0.760 mmol), CuCl (0.080 g, 0.812 mmol), and DMF (5 mL) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method B) to give **4**-C_8-**4** as a pale yellow-brown powder in 25% yield (0.036 g. 0.128 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): 6.38–6.33 (m, 4 H, =CH), 2.12–2.06 (m, 8 H, C_6H_9), 1.66–1.54 (m, 8 H, C_6H_9) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 141.8 (s, 2 C, $CH=C$), 119.3 (s, 2 C, $CH=C$), 80.2 (s, 2 C, $C_6H_9C\equiv CC\equiv C$), 73.1 (s, 2 C, $C_6H_9C\equiv CC\equiv C$), 67.3 (s, 2 C, $C_6H_9C\equiv CC\equiv C$), 64.5 (s, 2 C, $C_6H_9C\equiv CC\equiv C$), 28.2 (s, 2 C, $CH_2CH=C$), 25.8 (s, 2 C, $CH=CCH_2$), 22.1 (s, 2 C, $CH=CCH_2CH_2$), 21.3 (s, 2 C, $CH_2CH_2CH=C$) ppm. IR (KBr): $\tilde{\nu}_{C\equiv C}$ = 2192 (vs), 2100 (s) cm^{-1}. MS: *m/z* = 258 [M]$^+$. $C_{20}H_{18}$ (258.36): calcd. C 92.98, H 7.02; found C 92.55, H 7.17.

p-$CH_3OC_6H_4(C\equiv C)_4$-*p*-$C_6H_4OCH_3$ (5-C_8-5)

Method A: *p*-$CH_3OC_6H_4(C\equiv C)_2TMS$[19] (0.070 g, 0.310 mmol), TBAF (0.061 mL, 0.061 mmol), $ClSiMe_3$ (0.040 mL, 0.309 mmol), CuCl (0.030 g, 0.309 mmol), and TMEDA (0.018 mL, 0.12 mmol) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method A). THF was used instead of acetone. The analogous workup gave **7**-C_8-**7** as a light yellow, crystalline powder in 77% yield (0.037 g, 0.12 mmol).

Method B: *p*-$CH_3OC_6H_4(C\equiv C)_2TMS$ (0.054 g, 0.24 mmol), CuCl (0.023 g, 0.23 mmol), and DMF (5 mL) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method B) to give 7-C_8-7 as a light yellow powder in 8% yield (0.008 g. 0.026 mmol).

^{1}H NMR (500 MHz, C_6D_6): δ = 7.21 (d, $J_{H,H}$ = 8.9 Hz, 2 H of C_6H_4), 6.40 (d, $J_{H,H}$ = 8.9 Hz, 2 H of C_6H_4), 3.08 (s, 3 H of OCH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 160.9 [s, 2 C-*para* (CH_3OC) of 2 × C_6H_4], 134.7 (s, 4 C-*ortho* of 2 × C_6H_4), 114.4 (s, 4 C-*meta* of 2 × C_6H_4), 113.2 (s, 2 C-*ipso* of 2 × C_6H_4), 76.1 (s, 2 C, $C_6H_4C\equiv CC\equiv C$), 73.5 (s, 2 C, $C_6H_4C\equiv CC\equiv C$), 71.4 (s, 2 C, $C_6H_4C\equiv CC\equiv C$), 68.9 (s, 2 C, $C_6H_4C\equiv CC\equiv C$), 54.6 (s, 1 C, OCH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2197 (C≡C), 2074 (C≡C) cm^{-1}. $C_{22}H_{14}O_2$ (310.35): calcd. C 85.14, H 4.55; found C 85.21, H 4.55.

***p*-$C_6H_5COC_6H_4C\equiv CBr$ (6-C_2Br):** A 50 mL Schlenk flask was charged with *p*-$C_6H_5COC_6H_4C\equiv CTMS$[16] (0.880 g, 3.16 mmol) and acetonitrile (25 mL). It was wrapped with aluminum foil and AgF (0.440 g, 3.47 mmol) was added. After 30 min NBS (0.720 g, 4.10 mmol) was added. The mixture was stirred for 28 h, after which time a solid precipitated. It was filtered off and solvent was evaporated from the filtrate. The crude product was extracted with diethyl ether, which was then washed with water. The organic fraction was dried with $MgSO_4$. After removal of Et_2O the product was additionally purified by flash chromatography (silica gel, CH_2Cl_2) to yield **6**-C_2Br (0.612 g, 69%) as a beige solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78 (d, $J_{H,H}$ = 7.5 Hz, 2 H of C_6H_5), 7.76 (d, $J_{H,H}$ = 8.6 Hz, 2 H of C_6H_4), 7.60 (t, $J_{H,H}$ = 7.5 Hz, 1 H of C_6H_5), 7.55 (d, $J_{H,H}$ = 8.6 Hz, 2 H of C_6H_4), 7.49 (t, $J_{H,H}$ = 7.5 Hz, 2 H of C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 196.0 (s, 1 C, C=O), 137.8 (s, 1 C-*ipso* of C_6H_5), 137.5 (s, 1 C-*para* of C_6H_4), 132.8 (s, 1 C-*para* of C_6H_5), 132.1 (s, 2 C-*ortho* of C_6H_4), 130.2 (s, 2 C-*ortho* of C_6H_5), 130.1 (s, 2 C-*meta* of C_6H_4), 128.6 (s, 2 C-*meta* of C_6H_5), 127.0 [s, 1 C-*ipso* ($CC\equiv CBr$) of C_6H_4], 79.6 ($C\equiv CBr$), 53.6 ($\equiv CBr$) ppm. IR (KBr): $\tilde{\nu}$ = 2195 (C≡C), 1652 (C=O) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_9OBrNa$ 306.9729 [M + Na]$^+$; found 306.9735. $C_{15}H_9BrO$ (285.14): calcd. C 63.18, H 3.18; found C 62.72, H 3.04.

p-$C_6H_5COC_6H_4(C\equiv C)_2TMS$ (6-C_4TMS):

Method A: A 50 mL Schlenk flask was charged with TMSC≡CH (0.110 mL, 0.78 mmol) and THF (15 mL). The solution was cooled to –45 °C and *n*BuLi (2.53 M solution in hexanes, 0.320 mL, 0.81 mmol) was added with stirring. After 15 min, CuCl (0.083 g, 0.84 mmol) was added. The cold bath was removed and after 10 min **6**-C_2Br (0.210 g, 0.736 mmol), $EtNH_2$ (1 mL, 2.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.026 g, 0.037 mmol), and PPh_3 (0.019 g, 0.072 mmol) were added with stirring. The mixture was left at room temperature for 10 min and the solvent was removed under oil pump vacuum. The residue was flash chromatographed (CH_2Cl_2/hexanes 2:1, v/v) to give **6**-C_4TMS as a beige solid in 49% yield (0.108 g, 0.36 mmol).

Method B: A Schlenk flask was charged with **6**-C_2Br (0.776 g, 2.72 mmol) and THF (30 mL). $\mathrm{TMSC{\equiv}CH}$ (0.580 mL, 4.10 mmol), CuI (0.010 g, 0.050 mmol), and $Pd(PPh_3)_2Cl_2$ (0.038 g, 0.054 mmol) were added. Diisopropylamine (0.960 mL, 6.79 mmol) was then added in portions over a period of a few min. The mixture was stirred at room temperature for 20 h. It was then treated with saturated NaCl (20 mL) and extracted with Et_2O (3 × 30 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under oil pump vacuum. The residue was flash chromatographed (silica gel, CH_2Cl_2/hexanes 2:1, v/v) to give **6**-C_4TMS as a beige solid in 51% yield (0.422 g, 1.40 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, $J_{H,H}$ = 7.6 Hz, 2 H of C_6H_5), 7.75 (d, $J_{H,H}$ = 8.6 Hz, 2 H of C_6H_4), 7.59 (t, $J_{H,H}$ = 7.6 Hz, 1 H of C_6H_5), 7.58 (d, $J_{H,H}$ = 8.6 Hz, 2 H of C_6H_4), 7.48 (t, $J_{H,H}$ = 7.6 Hz, 2 H of C_6H_5), 0.25 (s, 9 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 195.8 (s, 1 C, $C\mathrm{=O}$), 137.9 (s, 1 C-*ipso* of C_6H_5), 137.3 (s, 1 C-*para* of C_6H_4), 132.9 (s, 1 C-*para* of C_6H_5), 132.7 (s, 2 C-*ortho* of C_6H_4), 130.1 (s, 2 C-*ortho* of C_6H_5), 130.1 (s, 2 C-*meta* of C_6H_4), 128.6 (s, 2 C-*meta* of C_6H_5), 125.8 [s, 1 C-*ipso* ($C\mathrm{C{\equiv}C}$) of C_6H_4], 92.7 (s, 1 C, $\mathrm{C_6H_4C{\equiv}CC{\equiv}}C$), 87.6 (s, 1 C, $\mathrm{C_6H_4C{\equiv}C}C\mathrm{{\equiv}C}$), 77.1 (s, 1 C, $\mathrm{C_6H_4}C\mathrm{{\equiv}CC{\equiv}C}$), 75.8 (s, 1 C, $\mathrm{C_6H_4C{\equiv}}C\mathrm{C{\equiv}C}$), –0.3 (s, 3 C, $SiMe_3$) ppm. IR (Nujol mull): $\tilde{\nu}$ = 2204 ($\mathrm{C{\equiv}C}$), 2104 ($\mathrm{C{\equiv}C}$), 1651 (C=O) cm^{-1}. GC–MS: m/z = 302 $[M]^+$. $C_{20}H_{18}OSi$ (302.45): calcd. C 79.42, H 6.00; found C 77.56, H 6.02.

p-$C_6H_5COC_6H_4(C{\equiv}C)_4$-*p*-$C_6H_4COC_6H_5$ (**6**-C_8-**6**)

Method A: Compound **6**-C_4TMS (0.073 g, 0.240 mmol), TBAF (0.048 mL, 0.048 mmol), $ClSiMe_3$ (0.031 mL, 0.24 mmol), CuCl (0.024 g, 0.024 mmol), and TMEDA (0.014 mL, 0.09 mmol) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method A). THF was used instead of acetone. The analogous workup gave **6**-C_8-**6** as a light yellow-brown, crystalline powder in 71% yield (0.039 g, 0.085 mmol).

Method B: Compound **6**-C_4TMS (0.028 g, 0.092 mmol), CuCl (0.009 g, 0.091 mmol), and DMF (5 mL) were combined in a procedure analogous to that used for **1** (Method B) to give **6**-C_8-**6** as a light brown powder in 61% yield (0.013 g. 0.028 mmol).

^{1}H NMR (500 MHz, C_6D_6): δ = 7.59 (d, $J_{H,H}$ = 7.7 Hz, 2 H, H_{Ar}), 7.38 (d, $J_{H,H}$ = 8.5 Hz, 2 H, C_6H_4), 7.12 (t, $J_{H,H}$ = 7.7 Hz, 1 H, C_6H_5), 7.08 (d, $J_{H,H}$ = 8.5 Hz, 2 H, C_6H_5), 7.02 (t, $J_{H,H}$ = 7.7 Hz, 2 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 194.5 (s, 2 C, 2 C=O), 138.8 (s, 2 C-*ipso* of 2 × C_6H_5), 137.5 (s, 2 C-*para* of 2 × C_6H_4), 133.2 (s, 2 C-*para* of 2 × C_6H_5), 132.4 (s, 4 C-*ortho* of 2 × C_6H_4), 130.1 (s, 4 C-*ortho* of 2 × C_6H_5), 130.0 (s, 4 C-*meta* of 2 × C_6H_4), 128.4 (s, 4 C-*meta* of 2 × C_6H_5), 124.0 [s, 2 C-*ipso* ($C\mathrm{C{\equiv}C}$) of 2 × C_6H_4], 77.8 (s, 2 C, $\mathrm{C_6H_4}C\mathrm{{\equiv}CC{\equiv}C}$), 77.0 (s, 2 C, $\mathrm{C_6H_4C{\equiv}}C\mathrm{C{\equiv}C}$), 68.8 (s, 2 C, $\mathrm{C_6H_4C{\equiv}C}C\mathrm{{\equiv}C}$), 64.8 (s, 2 C, $\mathrm{C_6H_4C{\equiv}CC{\equiv}}C$) ppm. IR (KBr): $\tilde{\nu}_{C\equiv C}$ = 2200 (s) cm^{-1}.

***p*-$NO_2C_6H_4(C{\equiv}C)_2$TMS (7-C_4TMS):** 1-(Bromoethynyl)-4-nitrobenzene[16,35] (1.26 g, 5.57 mmol), $\mathrm{TMSC{\equiv}CH}$ (1.19 mL, 8.42 mmol), $Pd(PPh_3)_2Cl_2$ (0.079 g, 0.11 mmol), CuI (0.021 g, 0.11 mmol), diisopropylamine (1.98 mL, 14.0 mmol), and THF (80 mL) were combined in a procedure analogous to that used for **6**-C_4TMS (Method B). The analogous workup gave **7**-C_4TMS as a light yellow, crystalline powder in 52% yield (0.714 g, 0.293 mmol). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.55 (d, $J_{H,H}$ = 9.0 Hz, 2 H of C_6H_4), 6.88 (d, $J_{H,H}$ = 9.0 Hz, 2 H of C_6H_4), 0.11 (s, 9 H of $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 147.7 [s, 1 C, C-*para* ($\mathrm{O_2N}C$) from C_6H_4], 133.2 (s, 2 C-*ortho* of C_6H_4), 127.6 (s, 1 C-*ipso* of C_6H_4), 123.5 (s, 2 C-*meta* of C_6H_4), 94.1 (s, 1 C, $\mathrm{C_6H_4C{\equiv}CC{\equiv}}C$), 88.0 (s, 1 C, $\mathrm{C_6H_4C{\equiv}C}C\mathrm{{\equiv}C}$), 79.2 (s, 1 C, $\mathrm{C_6H_4}C\mathrm{{\equiv}CC{\equiv}C}$), 74.9 (s, 1 C, $\mathrm{C_6H_4C{\equiv}}C\mathrm{C{\equiv}C}$), –0.7 (s, 3 C, $SiMe_3$) ppm. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19 (d, $J_{H,H}$ = 9.0 Hz, 2 H of C_6H_4), 7.62 (d, $J_{H,H}$ = 9.0 Hz, 2 H of C_6H_4), 0.25 (s, 9 H of $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 147.8 [s, 1 C, C-*para* ($\mathrm{O_2N}C$) from C_6H_4], 133.6 (s, 2 C-*ortho* of C_6H_4), 128.6 (s, 1 C-*ipso* of C_6H_4), 123.9 (s, 2 C-*meta* of C_6H_4), 94.4 (s, 1 C, $\mathrm{C_6H_4C{\equiv}CC{\equiv}}C$), 87.1 (s, 1 C, $\mathrm{C_6H_4C{\equiv}C}C\mathrm{{\equiv}C}$), 79.2 (s, 1 C, $\mathrm{C_6H_4}C\mathrm{{\equiv}CC{\equiv}C}$), 74.4 (s, 1 C, $\mathrm{C_6H_4C{\equiv}}C\mathrm{C{\equiv}C}$), –0.4 (s, 3 C, $SiMe_3$) ppm. GC–MS: m/z = 243 $[M]^+$. $C_{13}H_{13}NO_2Si$ (243.34): calcd. C 64.17, H 5.38; found C 63.82, H 5.33.

p-$NO_2C_6H_4(C{\equiv}C)_4$-*p*-$C_6H_4NO_2$ (7-C_8-7)

Method A: Compound **7**-C_4TMS (0.062 g, 0.254 mmol), TBAF (0.050 mL, 0.050 mmol), $ClSiMe_3$ (0.032 mL, 0.25 mmol), CuCl (0.025 g, 0.25 mmol), and TMEDA (0.015 mL, 0.10 mmol) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method A). THF was used instead of acetone. The analogous workup gave **7**-C_8-**7** as a light yellow-brown, crystalline powder in 42% yield (0.018 g, 0.053 mmol).

Method B: Compound **7**-C_4TMS (0.029 g, 0.12 mmol), CuCl (0.012 g, 0.12 mmol), and DMF (5 mL) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method B) to give 7-C_8-**7** as a light yellow solid in 15% yield (0.003 g. 0.009 mmol).

^{1}H NMR (500 MHz, C_6D_6): δ = 7.45 (d, $J_{H,H}$ = 8.9 Hz, 2 H of C_6H_4), 6.75 (d, $J_{H,H}$ = 8.90 Hz, 2 H of C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ = 147.8 [s, 2 C-*para* ($\mathrm{O_2N}C$) from 2 × C_6H_4], 133.2 (s, 4 C-*ortho* of 2 × C_6H_4), 127.0 (s, 2 C-*ipso* of 2 × C_6H_4), 123.4 (s, 4 C-*meta* of 2 × C_6H_4), 78.2 (s, 2 C, $\mathrm{C_6H_4}C\mathrm{{\equiv}CC{\equiv}C}$), 74.3 (s, 2 C, $\mathrm{C_6H_4C{\equiv}}C\mathrm{C{\equiv}C}$), 73.4 (s, 2 C, $\mathrm{C_6H_4C{\equiv}C}C\mathrm{{\equiv}C}$), 67.6 (s, 2 C, $\mathrm{C_6H_4C{\equiv}CC{\equiv}}C$) ppm. IR (KBr): $\tilde{\nu}_{C\equiv C}$ = 2205 (vs), 2105 (s) cm^{-1}.

***p*-$NCC_6H_4(C{\equiv}C)_2$TMS (8-C_4TMS):** 4-Ethynylbenzonitrile (0.294, 0.294 g, 2.24 mmol), THF (15 mL), *n*BuLi (2.53 M solution in THF, 0.975 mL, 1.1 equiv.), CuCl (0.222 g, 2.24 mmol), $\mathrm{IC{\equiv}CTMS}$ (0.553 g, 2.467 mmol), and Et_2NH (1.5 mL) were combined in a procedure analogous to that used for **3**-C_4TMS. The analogous workup gave **8**-C_4TMS as a yellow solid in 53% yield (0.268 g, 1.20 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 7.26 ppm): δ = 7.62–7.59 (m, 2 H of C_6H_4), 7.54–7.57 (m, 2 H of C_6H_4), 0.24 (s, 9 H of $SiMe_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.2 (s, 2 C-*ortho* of C_6H_4), 132.2 (s, 2 C-*meta* of C_6H_4), 126.6 (s, 1 C-*ipso* of C_6H_4), 118.3 (s, 1 C, $C\mathrm{{\equiv}N}$), 112.7 (s, 1 C-*para* of C_6H_4), 93.9 (s, 1 C, $\mathrm{C_6H_4C{\equiv}CC{\equiv}}C$), 87.1 (s, 1 C, $\mathrm{C_6H_4C{\equiv}C}C\mathrm{{\equiv}C}$), 78.4 (s, 1 C, $\mathrm{C_6H_4}C\mathrm{{\equiv}CC{\equiv}C}$), 74.6 (s, 1 C, $\mathrm{C_6H_4C{\equiv}}C\mathrm{C{\equiv}C}$), –0.4 (s, 3 C, $SiMe_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2106 ($\mathrm{C{\equiv}C}$), 2108 ($\mathrm{C{\equiv}C}$), 2231 ($\mathrm{C{\equiv}N}$) cm^{-1}. GC–MS: m/z = 223 $[M]^+$. $C_{14}H_{13}NSi$ (223.35): calcd. C 75.29, H 5.87; found C 75.30, H 6.02.

p-$NCC_6H_4(C{\equiv}C)_4$-*p*-C_6H_4CN (8-C_8-8)

Method A: Compound **8**-C_4TMS (0.046 g, 0.206 mmol), TBAF (0.206 mL, 0.206 mmol), $ClSiMe_3$ (0.027 mL, 0.207 mmol), CuCl (0.020 g, 0.206 mmol), and TMEDA (0.012 mL, 0.080 mmol) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method A). THF was used instead of acetone. The analogous workup gave **8**-C_8-**8** as a light yellow, crystalline powder in 54% yield (0.017 g, 0.056 mmol).

Method B: Compound **8**-C_4TMS (0.038 g, 0.170 mmol), CuCl (0.017 g, 0.172 mmol), and DMF (5 mL) were combined in a procedure analogous to that used for **1**-C_8-**1** (Method B) to give **8**-C_8-**8** as a light yellow powder in 59% yield (0.015 g. 0.050 mmol).

^{1}H NMR (500 MHz, C_6D_6): δ = 6.69–6.72 (m, 4 H of 2 × C_6H_4), 6.59–6.62 (m, 4 H of 2 × C_6H_4) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 133.0 (s, 4 C-*ortho* of 2 × C_6H_4), 131.9 (s, 4 C-*meta* of 2 × C_6H_4), 125.2 (s, 2 C-*ipso* of 2 × C_6H_4), 118.0 (s, 2 C, 2 × $\mathrm{C{\equiv}N}$), 113.3 (s, 2 C-*para* of 2 × C_6H_4), 77.6 (s, 2 C, $\mathrm{C_6H_4}C\mathrm{{\equiv}CC{\equiv}C}$), 74.1

(s, 2 C, $C_6H_4C{\equiv}\mathit{C}C{\equiv}C$), 73.8 (s, 2 C, $C_6H_4C{\equiv}C\mathit{C}{\equiv}C$), 67.7 (s, 2 C, $C_6H_4C{\equiv}CC{\equiv}\mathit{C}$) ppm. IR (KBr): $\tilde{\nu}_{C\equiv C}$ = 2202 (vs), 2102 (s) cm^{-1}. $C_{22}H_8N_2$ (300.32): calcd. C 87.99, H 2.68; found C 87.81, H 2.74.

Details of X-ray Data Collection and Reduction: X-ray diffraction data were collected with a KUMA KM4 CCD (ω scan technique) diffractometer with an Oxford Cryosystem-Cryostream cooler.[37] The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix, least-squares on F^2 by use of the SHELXTL Package.[38] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined.

CCDC-876314 (for **1**-C_8-**1**), -876313 (for **3**-C_8-**3**), -876315 (for **3**-C_{12}-**3**) and -876312 (for **6**-C_8-**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): NMR spectra of the new butadiynes and octatetraynes.

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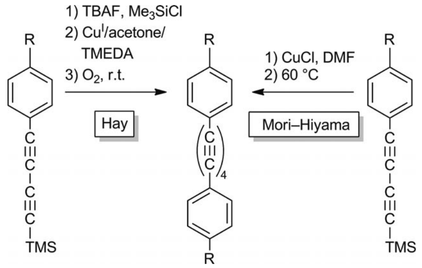
Topochemical 1,*n*-Polymerization

A series of diaryloctatetraynes was synthesized by Mori–Hiyama and Hay protocols. Target compounds were isolated and spectroscopically characterized. Crystalline samples were analyzed by X-ray diffraction methods and the structures were closely scrutinized to reveal potential for topochemical 1,*n*-polymerization.



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Mori–Hiyama versus Hay Coupling for Higher Polyynes

Keywords: Polyynes / Cross-coupling / X-ray diffraction / Topochemistry / Polymerization