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Protection/Deprotection-Free Syntheses and Structural Analysis of (Keto-aryl)diynes

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The reactions of precursors 4-BrC_6H_4COR with TMSC≡CH (Sonogashira coupling) followed by in situ deprotection and subsequent dimerization gave thermally stable dimeric keto-diynes $RCOC_6H_4(C{\equiv}C)_2C_6H_4COR$ (**8**–**11**) as yellow powders in 25–85 % yields without the necessity of carbonyl group protection/deprotection steps. Compounds **8**–**11** were also synthesized by an alternative method that utilized α-haloalkynes previously obtained directly from TMS-protected 4-$RCOC_6H_4C{\equiv}CTMS$ alkynes. The resulting diynes were characterized by spectroscopic methods and in most cases by X-ray crystallography. Careful analysis of the crystal data revealed a surprisingly high degree of chain curvature. Moreover, compounds **9** (R = Me) and **10** (R = Et) were extremely flat, which greatly facilitates electronic communication throughout the whole molecule. Deeper analysis of the packing motifs showed **9** to have a great potential for topochemical 1,4-polymerization.

Introduction

Conjugated organic, organometallic and metal-containing polyynes have attracted a great deal of attention from several standpoints. The polyyne[1] motif is, for instance, ubiquitous in many natural organic products,[2] which often show remarkable biological activities.[3] Organic diynes are also useful precursors for different types of conjugated polymers,[4] including those that result from topochemical crystal-to-crystal polymerization.[5] Polyynes that bear redox-active moieties are another group of compounds that are envisioned to be highly useful in nanotechnology as molecular-scale devices like wires and switches.[6] This group of compounds includes organometallic complexes of the $L_mMC_xML_m$ type[7] as well as metal-containing species in which the metal atom is not bound directly to the carbon atoms of a polyyne chain. The latter group mostly includes ferrocene derivatives[8] although other types of compounds are known.[9]

There are now many synthetic strategies that enable the introduction of a C≡C fragment as well as unsaturated carbon-chain elongation.[10] These range from an already historical Glaser-type coupling to new modifications of the Cadiot–Chodkiewicz cross-coupling protocols. Nevertheless, the great majority of these methods involve the use of terminal alkynes, which for longer chains are often of moderate-to-low stability, which, as a consequence, lowers the yield of the final product.

In 2000 Mori, Hiyama and co-workers described a new method of coupling of alkynylsilanes that did not involve a deprotection step.[11] Later, similar pathways with in situ deprotection were introduced although some of the reaction conditions have to be chosen in a particularly astute manner.

All the above-mentioned methods are largely chemoselective and tolerate many substituents within an alkyne end-group. To our surprise we have found just a few reports that deal with carbonyl-containing (aldehydes or ketones) end-groups, which are, unarguably, one of the most versatile functionalities. The combination of their functional versatility and activity renders them an ideal "anchor" for further transformations especially in asymmetric synthesis. From that standpoint the synthesis of carbonyl-containing polyynes in a simple manner would open the door to chiral polyyne derivatives.

Alkynones are very interesting compounds. For instance, α-alkynones undergo cyclization by Ni-catalyzed cyanation to give hydroxy lactams.[12] They can also be added organocatalytically to β-dicarbonyl compounds[13] or used for the synthesis of pyroglutamic acid derivatives.[14] They also find use in the synthesis of organometallic ketovinylidenes.[15] Further separation of C=O and C≡C groups allows the synthesis of interesting and practically very important heterocycles.[16]

In the examined multistep syntheses of different alkynones the carbonyl group is usually created from a hydroxy group at the final stage of the synthesis. For instance, in the synthesis of an oxidized derivative of panaxytriol,[17] the major constituent responsible for the biological activity of red ginseng that helped to establish the relative and absolute

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configuration of panaxytriol, the carbonyl group was introduced in the last synthetic step by oxidation of a hydroxy group at the 3-position. Very often it comes from acetal hydrolysis which protects the carbonyl group through the whole synthetic procedure. This approach usually lowers the final yield as conjugated triple bonds are sensitive towards electrophilic attack.[18,19]

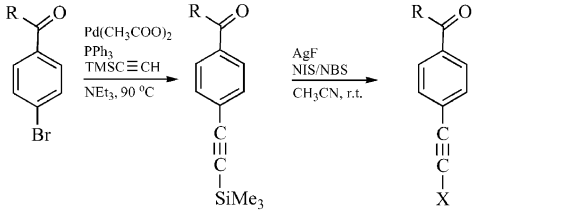
In some other cases the carbonyl group was introduced into the already formed oligoacetylene, for instance, in the excellent work of Frauenrath and co-workers on diacetylene copolymers[5g] or in a more general acylation of trimethylsilyl-substituted[20] or terminal alkynes.[21]

Although the published procedures are claimed to be general we have found the homocoupling reaction of aryl aldehydes and ketones to be quite tricky. This is probably due to the common use of primary and secondary amines in the majority of synthetic protocols which are known to easily react with the C=O group. In this paper, we report the successful synthesis of a series of diynes with aryl aldehyde/ketone containing end-groups. The presented strategies involve no protection/deprotection steps.

Results and Discussion

Synthesis of $RCOC_6H_4C{\equiv}CTMS$ (R = C_2H_5, C_6H_5)

Following the previously described procedure for $HCOC_6H_4C{\equiv}CTMS$ (**1**) and $CH_3COC_6H_4C{\equiv}CTMS$ (**2**),[22] the trimethylsilylacetylenic derivatives $C_2H_5COC_6H_4C{\equiv}CTMS$ (**3**) and $C_6H_5COC_6H_4C{\equiv}CTMS$ (**4**) were synthesised as shown in Scheme 1. Work-up by column chromatography gave **3** (brown oily solid) and **4** (pale yellow powder) in 90 and 98% yields, respectively. Both compounds are readily soluble in CH_2Cl_2, acetone and THF and poorly soluble in hexanes.



1: R = H[22]
2: R = CH_3[22]
3: R = C_2H_5, 90 %
4: R = C_6H_5, 98 %

5-I: R = H, X = I, 90 %
5-Br: R = H, X = Br, 94 %
6-I: R = CH_3, X = I, 87 %
6-Br: R = CH_3, X = Br, 97 %
7-I: R = C_2H_5, X = I, 80 %
7-Br: R = C_2H_5, X = Br, 95 %

Scheme 1. Synthesis of aryl trimethylsilylacetylenic and haloacetylenic derivatives.

Compounds **3** and **4** were characterized by ^1H and ^{13}C NMR spectroscopy and gave the correct elemental analysis. The ^1H and ^{13}C NMR spectroscopic data were routine. The ^1H NMR spectra revealed signals of the TMS group at δ = 0.20 and 0.25 ppm for **3** and **4**, respectively. The signals of the carbonyl carbon atoms were at 199.6 (**3**) and 195.9 ppm (**4**).

Synthesis of $RCOC_6H_4C{\equiv}CX$ (R = H, CH_3, C_2H_5; X = Br or I)

α-Haloalkynes are important starting materials in numerous organic transformations. The specific properties of a triple bond modified by a halo atom make them very susceptible to the addition of nucleophilic agents.[23] More interestingly they are excellent substrates for simultaneous addition/substitution reactions.[24] Traditionally, α-haloalkynes are key substrates in heterocoupling reactions in the synthesis of asymmetric polyynes.[25] They are also used in the synthesis of 1-bromovinylboranes, which, by transmetallation followed by C=O addition in one pot, are transformed into (*Z*)-substituted allylic alcohols[26] and are great substrates for the synthesis of α-keto acid esters.[27] From our perspective an important paper was published in 2003 by Lee and co-workers that described the successful homocoupling reaction of 1-iodoalkynes.[28]

Syntheses of α-haloalkynes are usually based on the use of terminal alkynes as starting materials. These are often unstable, which lowers the final yield. Lately, the syntheses of α-haloalkynes directly from R_3Si-protected alkynes have been published.[29] These protocols obviate the need of deprotection and, as a consequence, save one preparation step.

Bromo- and iodo-derivatives **5**–**7** were obtained in the reaction of trimethylsilyl-substituted precursors **1**–**3** with NBS or NIS, as shown in Scheme 1. Work-up gave the analytically pure target α-iodo- (**5**–**7-I**) and α-bromoalkynes (**5**–**7-Br**) in 80–90 and 94–97% yields, respectively. Interestingly, this method did not allow the substitution of **4**, which surprisingly has also proven resistant to other halogenation methods.[30] Compounds **5**–**7-X** are yellow powders that are soluble in most common organic solvents. In the solid state they are stable for extended periods, but in solution iodoalkynes partially decompose over a period of a few days.

These compounds were characterized by ^1H and ^{13}C NMR spectroscopy, which gave routine spectra. The signals of the acetylenic α-carbon atoms of **5**–**7-Br** were shifted by around 23 ppm to lower values compared with the iodo derivatives. Signals from the β-carbon atoms were observed at values lower by ca. 14 ppm, as shown in the Exp. Sect.

Synthesis of $RCOC_6H_4(C{\equiv}C)_2C_6H_4COR$ (R = H, CH_3, C_2H_5 or C_6H_5)

The straightforward synthesis and characterization of symmetric ketodiynes formed a major goal of our research. One obvious route would require the deprotection of **1**–**4** and subsequent dimerization. This approach was tested for ethynylbenzaldehyde and gave target $HCOC_6H_4(C{\equiv}C)_2C_6H_4CHO$ (**8**) in 66% yield.[31] Although this protocol has proven useful we were looking for other expedient syntheses that would give satisfactory yields and exclude the deprotection step. First, in accord with the report of Mori, Hiyama and co-workers,[11] we tried the homocoupling of trimethylsilyl-protected (keto-aryl)acetylenes **1** and **2** in DMF at 60 °C catalyzed by CuCl. Although this approach gave ex-

cellent results for alkyl- and phenyl-substituted acetylenes[11] and diacetylenes,[32] the resulting yields were as low as 15% and most of the starting material was recovered.

In another thrust, we tried two alternative approaches. The first one utilized $SiMe_3$-protected **1**–**4**, which were subjected to homocoupling with in situ deprotection by using TBAF followed immediately by the addition of Me_3SiCl (as an F^- ion scavenger) and the Cu^I/TMEDA/acetone catalytic system. Although this approach gave targets **8**–**11**, the yields were considerably obscured (in the cases of **1**–**3** they were less than 10%) by the aldol side-reaction of the starting aldehyde or ketone with acetone, presumably promoted by the Lewis acidic Me_3SiCl. The products of this reaction were unambiguously identified by GC–MS. Modification of the catalytic system by exchanging acetone for THF allowed the synthesis of **9**–**11** in yields of 75–85% as yellow powders (Table 1). Surprisingly, this approach repeatedly gave a much lower yield (25% best) for **8**, which might be related to the possible oxidation of the aldehyde by TBAF.[33]

Table 1. Yields and spectroscopic data for **8**–**11**.

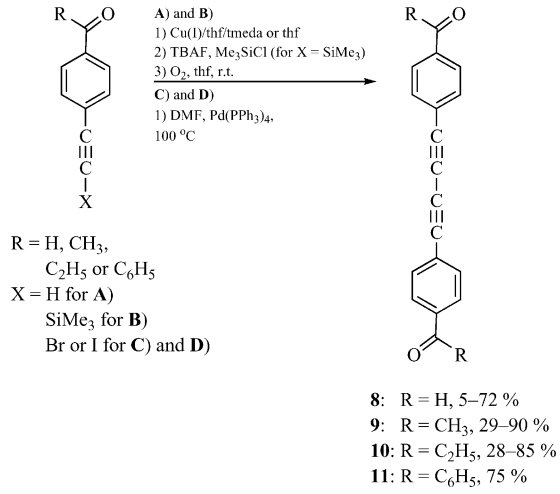
Complex	**8**	**9**	**10**	**11**
Yield from C≡CTMS [%]	25	75	85	75
Yield from C≡CI [%]	5	29	28	–
Yield from C≡CBr [%]	72	90	85	–
IR [cm^{-1}]	2210	2213	2213	2105
	1928	1934	1936	1941
	1697	1677	1685	1650
^{13}C NMR of C=O [ppm]	191.2	197.0	199.7	195.6
^{13}C NMR of C≡*C*Ph [ppm]	82.1	82.0	81.8	81.8
^{13}C NMR of *C*≡CPh [ppm]	76.4	76.5	76.3	76.3

An alternative approach was next tried. This was based on the protocol of Lee and co-workers who utilized 1-iodoalkynes for the homocoupling.[28] In a typical reaction, one of the halogen-terminated **5**–**7-X** (X = I or Br) was placed in DMF and $[Pd(PPh_3)_4]$ was added as the catalyst.[28] The reactions proceeded at 100 °C. Work-up gave analytically pure **8**–**10** in 72–90% yields when **5**–**7-Br** were used as the substrates (Scheme 2). Surprisingly, the yields were much lower (5–29%) with the iodoalkynes **5**–**7-I**.

Compounds **8**–**11** are stable, light-yellow solids that are readily soluble in most common organic solvents. All the diynes were characterized by IR, ^1H and ^{13}C NMR spectroscopy and mass spectrometry and the data are summarized in the Exp. Sect.

Compounds **9**–**11** melted without decomposition at 176, 156 and 185 °C, respectively, whereas **8** melted with decomposition at 123 °C. The mass spectra in each case showed strong parent ions and fragmentation of the carbonyl substituent.

The IR spectra for each compound showed two weak $\nu_{C\equiv C}$ bands at $\tilde{\nu}$ = 2210, 2213, 2213 and 2105 cm^{-1} and 1928, 1934, 1936 and 1941 cm^{-1} for **8**–**11**, respectively. Also $\nu_{C\equiv O}$ bands were observed at $\tilde{\nu}$ = 1697, 1677, 1685 and 1650 cm^{-1}.



Scheme 2. Synthesis of (keto-aryl)diynes.

The ^{13}C NMR spectra showed C≡C–C≡C signals ($CDCl_3$) at δ = 82.1, 82.0, 81.8 and 81.8 ppm for C*C*Ph and at δ = 76.4, 76.5, 76.3 and 76.3 ppm for *C*CPh for **8**–**11**, respectively. These values are in accord with the chemical shifts of other diynes.

Crystal Structures of 9–11

The crystal structures of **9**–**11** were determined as outlined in Table 2 and Table 3 and described in the Exp. Sect. Figure 1 presents two views of the centrosymmetric molecule of **9**. As can be seen in the bottom view the molecule is almost planar. Both phenyl rings as well as the two planes

Table 2. Bond lengths [Å] and angles [°] for **9**–**11**.

Complex	**9**	**10**	**11**
C(11)–C(1)	1.439(2)	1.430(1)	1.428(4)
C(1)–C(2)	1.205(2)	1.212(1)	1.208(3)
C(2)–C(2′)	1.369(3)	1.367(2)	1.384(6)
C(3)–O(1)	1.227(2)	1.223(1)	1.234(3)
C(11)–C(1)–C(2)	176.3(2)	176.6(1)	174.3(4)
C(1)–C(2)–C(2′)	179.0(2)	179.7(1)	179.5(6)
O(1)–C(3)–C(14)	120.7(2)	119.7(1)	119.4(3)

Table 3. Crystallographic data for **9**–**11**.

Complex	**9**	**10**	**11**
Chemical formula	$C_{20}H_{14}O_2$	$C_{22}H_{18}O_2$	$C_{30}H_{18}O_2$
Formula weight	286.31	314.36	410.44
Temp. [K]	100(2)	100(2)	100(2)
Space group	$P2_1/c$	$P2_1/c$	$C2/c$
a [Å]	5.409(2)	9.807(4)	45.52(3)
b [Å]	4.942(2)	12.142(5)	3.902(3)
c [Å]	27.23(2)	7.103(3)	11.399(8)
β [°]	90.12(5)	97.36(3)	93.74(5)
V [$Å^3$]	727.9(7)	838.8(6)	2020(2)
Z	2	2	4
P [$g\,cm^{-3}$]	1.306	1.245	1.349
M(Mo-K_α) [mm^{-1}]	0.083	0.078	0.083
R_1 ($>2\sigma$)	0.0647	0.0574	0.0752
wR_2 ($>2\sigma$)	0.1312	0.1464	0.0737

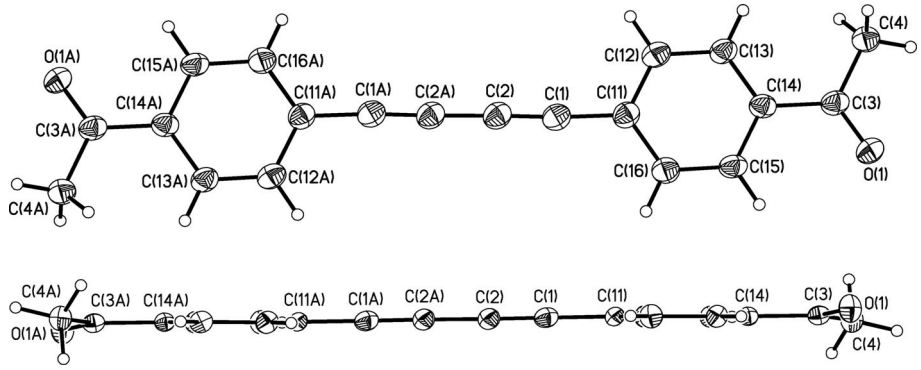


Figure 1. Crystal structure of **9**.

of the carbonyl groups, defined by C(14)C(3)C(4)O(1) and C(14a)C(3a)C(4a)O(1a) atoms, are mutually coplanar, which is a consequence of the fact that the molecule lies on a symmetry centre, but the plane of the carbonyl group is twisted by 6.2° from the plane of the adjacent phenyl ring. The bond lengths within the carbon chain are 1.205(2) Å for C(1)≡C(2) and 1.369(3) Å for C(2)–C(2A) and are similar to those found in other diynes.[34]

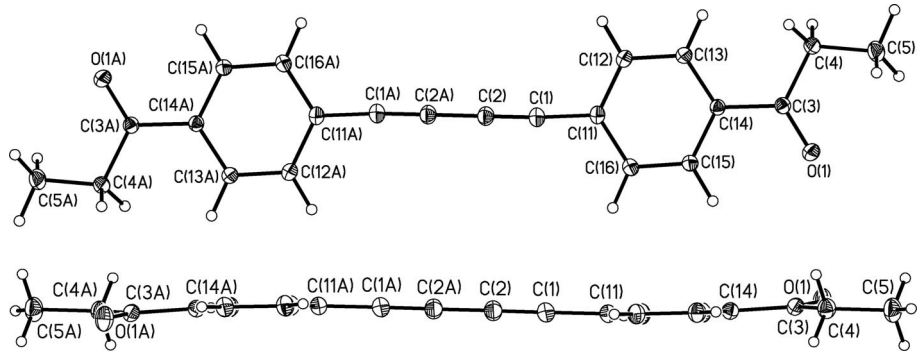


Figure 2. Crystal structure of **10**.

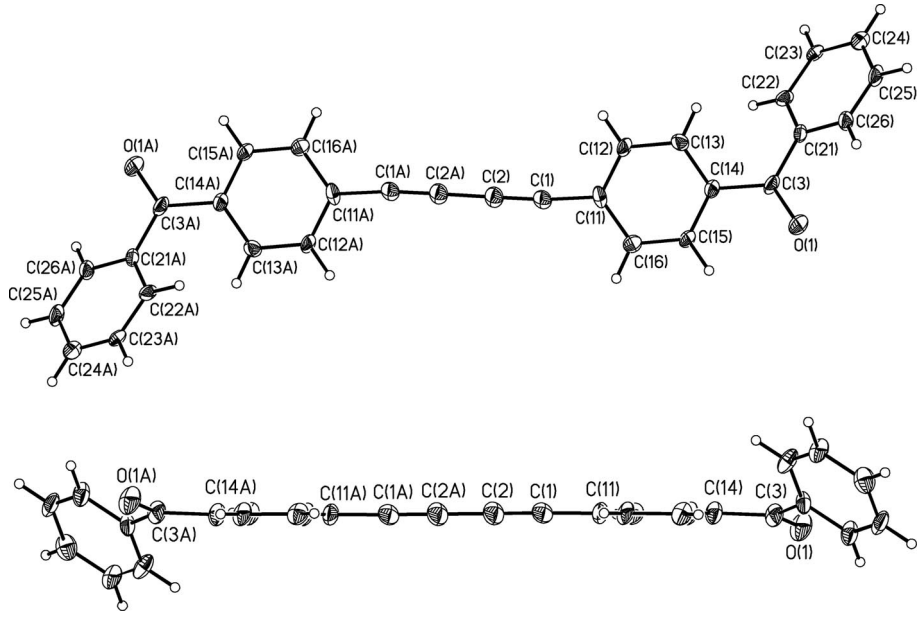


Figure 3. Crystal structure of **11**.

A similar situation is observed for **10** and **11**. The structures of the two molecules are shown in Figures 2 and 3, respectively. The bottom views illustrate their high degree of planarity although the carbonyl group in **11** is a little more twisted out of the plane and forms an angle of 15.1° with the phenyl ring that bears the carbon chain. The angle between the C=O group and the second phenyl is 38.4° (the phenyl rings of one end-group are twisted by 49.8°). The planarity of **10** is almost identical to that of **9** with the C=O/phenyl angle of 5.4°. The bond lengths within the carbon chain are 1.212(1) (**10**) and 1.208(3) Å (**11**) for C(1)≡C(2) and 1.367(2) (**10**) and 1.384(6) Å (**11**) for the C(2)–C(2A) single bond.

Although the C_4 chains are believed to be too short to have a distinctive bending, closer inspection shows perceptible deformation. This is confirmed by an analysis of the carbon chain bond angles C11–C1–C2 and C1–C2–C2A. These values for **9** are 176.3(2) and 178.96(17)° (average 177.7°), which is unexpectedly low. The corresponding bond angles in **10** are 176.6(1) and 179.7(1)° (average 178.1°) and they are 174.3(4) and 179.5(6)° for **11** (average 176.9°). Note that these values are often even higher for much longer chains.[7c] Based on the bond angles and visualization of the molecules, the chain conformations for **9**–**11** can be described as kinked.[7c]

Packing Motifs

The three structures **9**–**11** crystallize in the monoclinic system in the $P2_1/c$ (**9** and **10**) and $C2/c$ (**11**) space groups. As a consequence, the molecules pack to form two non-parallel sets of parallel chains. These sets form an angle of 88.9° in **9**, 36.0° in **10** and 23.4° in **11**. Figure 4 shows the packing diagram for **9** with nearly perpendicular sets of molecules.

The closest chain–chain separation was analyzed. As deformation of chains takes place we understand the closest chain–chain distance to be the closest carbon–carbon distance between two neighbouring carbon chains.[7c] Accordingly, the closest chains with parallel orientation for **9** are only 3.527 Å apart and this separation is slightly smaller than the sum of the van der Walls radii (3.56 Å). Interestingly, of the longer chain examples analyzed to date,[7c] only two have a shorter chain–chain distance: tellurium Me-Te(C≡C)$_4$TeMe (3.486 Å)[35] and ferrocenyl Fc(C≡C)$_6$Fc (3.512 Å).[36]

In spite of the bulkier end-group the distance is similarly low for **11** (3.814 Å, Figure 5). Surprisingly, it is significantly different for **10** even though it has a structure very similar to **9** (7.036 Å) and it is even longer than the separation for the closest non-parallel chains (5.993 Å). Table 4 summarizes all the geometrical data for **9**–**11**. Figure 5 shows the closest chain–chain distances in **11**.

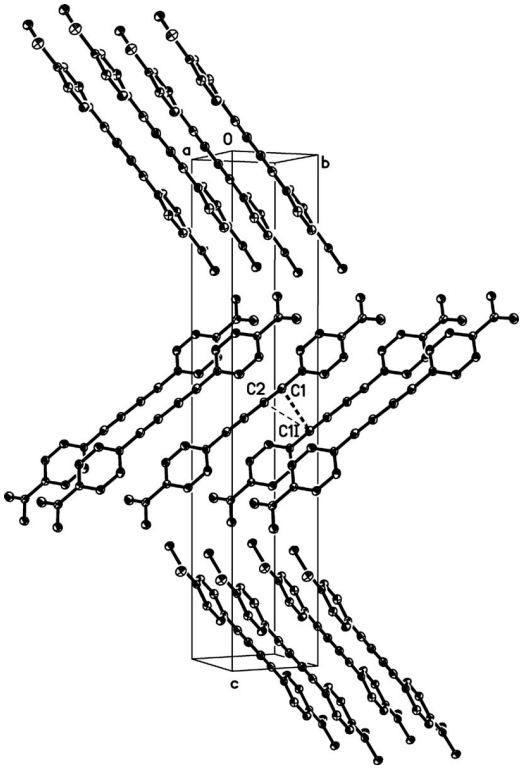


Figure 4. Packing diagram and shortest chain–chain contacts for **9**. The distances are 3.527 Å for C(1)–C(1I) and 3.623 Å for C(2)–C(1I). Symmetry operation for C(1I): 1 – x, 2 – y, 1 – z.

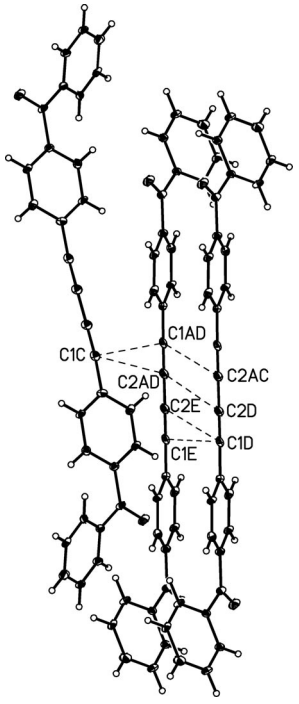


Figure 5. Shortest chain–chain distances for parallel and non-parallel neighbours of **11**. The distances [Å] are: C(1AD)–C(2AC), 3.815; C(2AD)–C(2D), 3.825; C(2E)–C(1D), 3.814; C(1E)–C(1D), 3.902 Å; C(1C)–C(1AD), 4.296; C(1C)–C(2AD), 4.473. Symmetry operations for related atoms are: C(1C): 0.5 – x, 0.5 + y, 0.5 – z; C(1D) and C(2D): 0.5 – x, 0.5 – y, 1 – z; C(2AC): x – 0.5, y – 0.5, z; C(1AD) and C(2AD): x – 0.5, y + 0.5, z; C(1E) and C(2E): 0.5 – x, 1.5 – y, 1 – z.

Table 4. Packing parameters for diynes **9**–**11**.

Complex	**9**	**10**	**11**
Chain–chain contact (parallel) [Å]	3.527	7.036	3.814
Angle between parallel chains [°]	45.5	33.4	78.3
Offset distance [Å]	4.66	8.19	0.79
Fractional offset	0.70	1.23	0.12
Angle between non-parallel chains [°]	88.9	36.0	23.4
Chain–chain contact (non-parallel) [Å]	12.233	5.993	4.296

Next, we calculated the offset values,[7c] which is a measure of the mutual position of the neighbouring molecules/carbon chains. These values are 4.663 Å for **9**, 8.187 Å for **10** and 0.791 Å for **11**, which correspond to fractional offsets[7c] (an offset divided by the C11–C11A distance) of 0.70 for **9**, 1.23 for **10**, and 0.12 for **11**.

Implications for Reactivity

1,4-Topochemical polymerization is one of the possible transformations that organic diynes or polyynes in general can undergo. As illustrated in Figure 6 this occurs most readily when the closest parallel chains are separated by around 3.5 Å and the ϕ angle is close to 45°. These requirements fulfil the need of a close geometric match of the butadiyne and polybutadiyne crystal lattices. By screening the geometrical properties of **9**–**11** it can easily be seen that **9** is an example of an ideal candidate for such polymerization (chain–chain separation: 3.527 Å and ϕ = 45.5°; Figure 7).

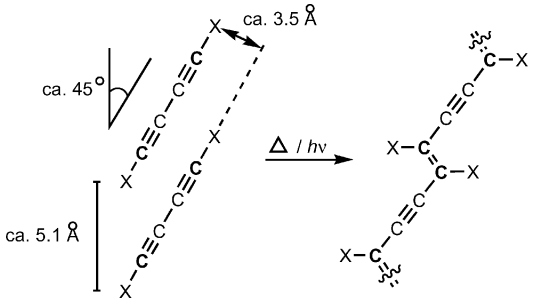


Figure 6. Geometrical conditions for 1,4-topochemical polymerization.

Compound **11**, although it possesses an appropriate chain–chain separation, has a much more ladder-type structure (ϕ = 78.3°; for an ideal ladder-type structure, ϕ = 90°). Compound **10**, however, is far from the required geometry. It is worth adding that even though **9** crystallizes in the *C*2/*c* space group, which creates two sets of parallel chains, the additional translational requirement in this case is also met.

Conclusions

We have demonstrated that (keto-aryl)diynes can easily be synthesized in good-to-high yields without protection/deprotection steps by two methods: (1) from trimethylsilylacetylene and (2) from bromoacetylene by palladium-catalyzed homocoupling. A little to our surprise, iodoacetylenes gave the desired products with much lower yields. The resulting diynes are stable solids with a high degree of planarity, as evidenced by X-ray crystallography. Owing to this feature and the presence of carbonyl groups they form a group of attractive ligands for different metals. Their complexes would most likely allow electronic communication between the metal atoms, which is of great interest for nanoscale electronics. This will certainly be the subject of ongoing investigations.

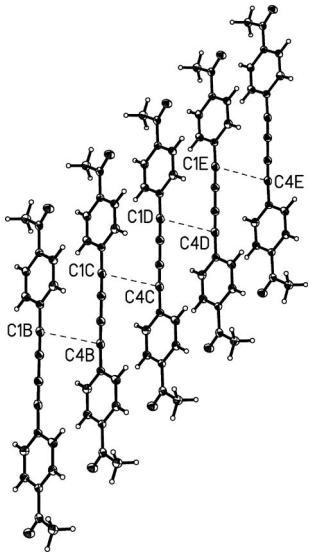


Figure 7. The mutual orientation of molecules of **9** in the crystal lattice. Symmetry operation for related atoms: *x*, *y* + 1, *z*.

Experimental Section

General: All reactions were conducted under N_2 by using standard Schlenk techniques. The solvents were treated as follows: hexanes, distilled from Na; CH_2Cl_2 and acetone, distilled from P_2O_5; THF and Et_2O, predried with NaOH and then distilled from Na/benzophenone; DMF, distilled from CaH_2 and degassed; NEt_3, distilled from NaOH; CH_3CN, used as received. $CDCl_3$, vacuum transferred from CaH_2; C_6D_6, vacuum transferred from Na.

4-Bromobenzaldehyde (99%), 4-bromoacetophenone (98%), 4-bromopropiophenone (97%), 4-bromobenzophenone (98%), *N*-bromosuccinimide (NBS; 99%), $Pd(CH_3COO)_2$ (99.9+%), [Pd(PPh_3)$_4$] (99%), TMSC≡CH (98%), AgF (99.9+%), CuCl (99.995+%), PPh_3 (99%), tetramethylethylenediamine (TMEDA; 99%; distilled from NaOH) and tetrabutylammonium fluoride (TBAF; 1.0 M in THF) were obtained from Aldrich and used without further purification unless stated otherwise. *N*-Iodosuccinimide (NIS; Fluka; 97%), Na_2SO_4 (AppliChem, pure), $AgNO_3$ (POCh, pure by analysis) and Me_3SiCl (Fluka, 99%) were used as received. 4-(Trimethylsilylethynyl)benzaldehyde, 4-ethynylbenzaldehyde and 4-(trimethylsilylethynyl)acetophenone were prepared according to the literature.[22]

Infrared spectra were recorded in a KBr cell with a Bruker 66/s FTIR spectrometer. TG-DTA analyses were carried out with a Setaram SETSYS 16/18 spectrometer. NMR spectra were obtained with Bruker ESP 300E and 500 spectrometers. GC–MS analyses were performed with a gas chromatograph equipped with a mass detector HP 5971A or an infrared detector HP5965B (Hewlett–Packard). Microanalyses were conducted with an ARL Model 3410

+ ICP spectrometer (Fisons Instruments) and a VarioEL III CHNS instrument (both in-house).

$C_2H_5COC_6H_4C{\equiv}CTMS$ (3): 4-Bromopropiophenone (0.500 g, 2.347 mmol) and PPh_3 (0.018 g, 0.070 mmol) were dissolved in NEt_3 (50 mL). Next $Pd(CH_3COO)_2$ (0.005 g, 0.023 mmol; 1 mol-%) and trimethylsilylacetylene (0.497 mL, 3.520 mmol) were added. The solution was heated at reflux and the reaction was monitored by TLC. After 6 h the mixture was filtered to remove $NEt_3{\cdot}HBr$ (0.418 g, 98%) and solvent was removed under oil-pump vacuum leaving a brown oil. This was dissolved in a mixture of hexane/CH_2Cl_2 (5 mL; v/v 1:1) and passed through a silica gel plug (2 cm). The solvent was removed under oil-pump vacuum to give **3** as a brown sticky solid (90%; 0.487 g, 2.114 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.45 (d, J_{HH} = 8 Hz, 2 H, Ph), 2.88 (q, J_{HH} = 7 Hz, 2 H, CH_2), 1.14 (t, J_{HH} = 7 Hz, 3 H, CH_3), 0.20 [s, 9 H, $Si(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 199.6 (s, 1 C, *C*O), 136.0 (s, 1 C, *p*-Ph), 131.9 (s, 2 C, *o*-Ph), 127.6 (s, 2 C, *m*-Ph), 127.5 (s, 1 C, *i*-Ph), 104.0 (s, 1 C, C*C*Ph), 97.7 (s, 1 C, *C*CPh), 31.6 (s, 1 C, *C*H_2), 8.0 (s, 1 C, *C*H_3), –0.3 [s, 3 C, $Si(CH_3)_3$] ppm. $C_{14}H_{18}OSi$ (230.381): calcd. C 72.99, H 7.88; found C 73.14, H 7.66.

$C_6H_5COC_6H_4C{\equiv}CTMS$ (4): Benzophenone (1.000 g, 3.830 mmol), PPh_3 (0.030 g, 0.115 mmol), $Pd(CH_3COO)_2$ (0.017 g, 0.0757 mol; 2 mol-%) and (trimethylsilyl)acetylene (0.812 mL, 5.745 mmol) were combined in a procedure analogous to that for **3**. Analogous work-up gave **4** as a pale-yellow powder in 98% yield (1.045 g, 3.753 mmol). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.41 (m, 9 H, Ph), 0.25 [s, 9 H, $Si(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 195.9 (s, 1 C, *C*O), 137.4 (s, 1 C, *i*′-Ph), 137.0 (s, 1 C, *p*-Ph), 132.5 (s, 1 C, *p*′-Ph), 131.8 (s, 2 C, *o*-Ph), 129.9 (s, 2 C, *o*′-Ph), 129.9 (s, 2 C, *m*-Ph), 128.3 (s, 2 C, *m*′-Ph), 127.3 (s, 1 C, *i*-Ph), 104.1 (s, 1 C, C*C*Ph), 97.8 (s, 1 C, *C*CPh), –0.2 [s, 3 C, Si-(*C*H_3)$_3$] ppm. $C_{18}H_{18}OSi$ (278.425): calcd. C 77.65, H 6.53; found C 77.34, H 6.45.

$CHOC_6H_4C{\equiv}CI$ (5-I). Method A: 4-(Trimethylsilylethynyl)benzaldehyde (0.300 g, 1.482 mmol) and AgF (0.188 g, 1.482 mmol) was placed in round-bottomed flask and CH_3CN (15 mL) was added. The flask was wrapped in aluminium foil and NIS (0.333 g, 1.482 mmol) was added. The mixture was stirred for 5 h at room temperature after which time it was passed through a 2cm plug of silica gel. The solvent was removed by rotary evaporation. The resulting residue was dissolved in Et_2O and washed with H_2O (2 × 5 mL). The organic part was separated and dried with Na_2SO_4. The solution was filtered, the Na_2SO_4 was rinsed with Et_2O (2 × 5 mL) and the solvent was removed under oil-pump vacuum to give **5-I** in 90% yield (0.341 g, 1.334 mmol).

Method B: Ethynylbenzaldehyde (0.140 g, 1.076 mmol) was dissolved in acetone (10 mL) and $AgNO_3$ (0.055 g, 0.323 mmol) was added. After 0.5 h Et_2O (30 mL) and NIS (0.242 g, 1.076 mmol) were added. The mixture was stirred for 12 h after which time it was filtered and washed with ice-cold H_2O (30 mL). The organic layer was separated. The aqueous layer was washed with Et_2O (2 × 5 mL) and the combined organic parts were dried with Na_2SO_4. The solvent was removed under oil-pump vacuum and the residue was purified by chromatography on silica gel (20 cm; hexane/CH_2Cl_2 v/v, 1:1) to give **5-I** as a yellow powder in 90% yield (0.248 g, 0.968 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.96 (s, 1 H, CHO), 7.80 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.55 (d, J_{HH} = 8 Hz, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.3 (s, 1 C, *C*O), 135.7 (s, 1 C, *p*-Ph), 132.9 (s, 2 C, *o*-Ph), 129.4 (s, 2 C, *m*-Ph), 129.3 (s, 1 C, *i*-Ph), 93.3 (s, 1 C, C*C*Ph), 77.2 (s, 1 C, *C*CPh) ppm. C_9H_5IO (256.041): calcd. C 42.22, H 1.97; found C 42.66, H 1.87.

$CHOC_6H_4C{\equiv}CBr$ (5-Br):[36] 4-(Trimethylsilylethynyl)benzaldehyde (0.200 g, 0.988 mmol), AgF (0.125 g, 0.988 mmol) and NBS (0.176 g, 0.988 mmol) were combined in a procedure analogous to Method A for **5-I**. Analogous work-up gave **5-Br** as a yellow powder in 94% yield (0.194 g, 0.929 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.95 (s, 1 H, CHO), 7.78 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.53 (d, J_{HH} = 8 Hz, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.2 (s, 1 C, *C*O), 135.6 (s, 1 C, *p*-Ph), 132.5 (s, 2 C, *o*-Ph), 129.4 (s, 2 C, *m*-Ph), 128.7 (s, 1 C, *i*-Ph), 79.2 (s, 1 C, C*C*Ph), 54.6 (s, 1 C, *C*CPh) ppm. C_9H_5BrO (209.041): calcd. C 51.71, H 2.41; found C 51.89, H 2.32.

$CH_3COC_6H_4C{\equiv}CI$ (6-I): 4-(Trimethylsilylethynyl)acetophenone (0.210 g, 0.971 mmol), AgF (0.123 g, 0.971 mmol) and NIS (0.218 g, 0.971 mmol) were combined in a procedure analogous to Method A for **5-I**. Analogous work-up gave **6-I** as a yellow powder in 87% yield (0.228 g, 0.845 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.50 (d, J_{HH} = 8 Hz, 2 H, Ph), 2.59 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 197.1 (s, 1 C, *C*O), 136.6 (s, 1 C, *p*-Ph), 132.4 (s, 2 C, *o*-Ph), 128.1 (s, 2 C, *m*-Ph), 128.0 (s, 1 C, *i*-Ph), 93.3 (s, 1 C, C*C*Ph), 76.7 (s, 1 C, *C*CPh), 26.5 (s, 1 C, *C*H_3) ppm. $C_{10}H_7IO$ (270.068): calcd. C 44.47, H 2.61; found C 45.14, H 2.49.

$CH_3COC_6H_4C{\equiv}CBr$ (6-Br):[36] 4-(Trimethylsilylethynyl)acetophenone (0.130 g, 0.601 mmol), AgF (0.076 g, 0.601 mmol) and NBS (0.107 g, 0.601 mmol) were combined in a procedure analogous to Method A for **5-I**. Analogous work-up gave **6-Br** as a yellow powder in 97% yield (0.130 g, 0.583 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.49 (d, J_{HH} = 8 Hz, 2 H, Ph), 2.56 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 197.2 (s, 1 C, *C*O), 136.6 (s, 1 C, *p*-Ph), 132.2 (s, 2 C, *o*-Ph), 128.2 (s, 2 C, *m*-Ph), 127.5 (s, 1 C, *i*-Ph), 79.4 (s, 1 C, C*C*Ph), 53.8 (s, 1 C, *C*CPh), 26.6 (s, 1 C, *C*H_3) ppm. $C_{10}H_7BrO$ (223.069): calcd. C 53.85, H 3.16; found C 53.44, H 3.36.

$C_2H_5COC_6H_4C{\equiv}CI$ (7-I): 4-(Trimethylsilylethynyl)propiophenone (0.215 g, 0.933 mmol), AgF (0.118 g, 0.933 mmol) and NIS (0.210 g, 0.933 mmol) were combined in a procedure analogous to Method A for **5-I**. Analogous work-up gave **7-I** as a yellow powder in 80% yield (0.210 g, 0.746 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.83 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.43 (d, J_{HH} = 8 Hz, 2 H, Ph), 2.91 (q, J_{HH} = 7 Hz, 2 H, CH_2), 1.15 (t, J_{HH} = 7 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 199.7 (s, 1 C, *C*O), 136.3 (s, 1 C, *p*-Ph), 132.3 (s, 2 C, *o*-Ph), 127.7 (s, 2 C, *m*-Ph), 127.6 (s, 1 C, *i*-Ph), 93.3 (s, 1 C, C*C*Ph), 76.7 (s, 1 C, *C*CPh), 31.7 (s, 1 C, *C*H_2), 8.1 (s, 1 C, *C*H_3) ppm. $C_{11}H_9IO$ (284.096): calcd. C 46.51, H 3.19; found C 46.39, H 3.15.

$C_2H_5COC_6H_4C{\equiv}CBr$ (7-Br): 4-(Trimethylsilylethynyl)propiophenone (0.150 g, 0.651 mmol), AgF (0.082 g, 0.651 mmol) and NBS (0.116 g, 0.651 mmol) were combined in a procedure analogous to Method A for **5-I**. Analogous work-up gave **7-Br** as a yellow powder in 95% yield (0.146 g, 0.618 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.49 (d, J_{HH} = 8 Hz, 2 H, Ph), 2.95 (q, J_{HH} = 7 Hz, 2 H, CH_2), 1.19 (t, J_{HH} = 7 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 199.9 (s, 1 C, *C*O), 136.3 (s, 1 C, *p*-Ph), 132.1 (s, 2 C, *o*-Ph), 127.9 (s, 2 C, *m*-Ph), 127.2 (s, 1 C, *i*-Ph), 79.4 (s, 1 C, C*C*Ph), 53.6 (s, 1 C, *C*CPh), 31.8 (s, 1 C, *C*H_2), 8.1 (s, 1 C, *C*H_3) ppm. $C_{11}H_9BrO$ (237.095): calcd. C 55.72, H 3.83; found C 55.53, H 3.83.

$CHOC_6H_4(C{\equiv}C)_2C_6H_4CHO$ (8). Method A: A Schlenk flask was charged with CuCl (0.010 g, 0.101 mmol) and TMEDA (0.009 mL, 0.060 mmol). THF (6 mL) was added and the mixture was stirred for 0.5 h. A blue supernatant formed over the green solid. In a separate flask 4-ethynylbenzaldehyde (0.064 g, 0.492 mmol) was

dissolved in THF (15 mL). O_2 was bubbled through the solution for 15 min and the blue supernatant was added in portions. After 4 h the solvent was evaporated by oil pump vacuum. The residue was treated with a 1:1 mixture of hexane/CH_2Cl_2 (5 mL) and the solution was filtered through a 5 cm plug of alumina. The solvent was evaporated by oil-pump vacuum to give **8** as a yellow solid in 66% yield (0.042 g, 0.162 mmol).

Method B: A Schlenk flask was charged with **1** (0.200 g, 0.988 mmol) and THF (10 mL) was added. The solution was purged with N_2 and wet TBAF (1.0 M solution in THF, 0.198 mL, 20 mol-%) was added dropwise. After 20 min Me_3SiCl (0.125 mL, 0.988 mmol) was added. After 15 min O_2 was bubbled through the solution for 10 min. In a separate Schlenk flask CuCl (0.098 g, 0.989 mmol) and TMEDA (0.059 mL, 0.390 mmol) were mixed in THF (5 mL). The blue supernatant that emerged after 0.5 h was added in portions to the first Schlenk flask. O_2 was bubbled through the reaction. After 5 h the solvent was removed by oil pump vacuum. The residue was dissolved in a minimum of CH_2Cl_2 and filtered through a 5 cm plug of alumina and then through a 3 cm plug of silica gel. The solvent was removed by oil-pump vacuum to give a yellow solid residue in 25% yield (0.032 g, 0.123 mmol).

Method C: 5-I (0.080 g, 0.312 mmol) was dissolved in DMF (2 mL). Next $[Pd(PPh_3)_4]$ (0.014 g, 0.012 mmol, 4 mol-%) was added. The mixture was heated at 100 °C for around 14 h. DMF was evaporated under oil-pump vacuum and the residue was dissolved in CH_2Cl_2 (1 mL) and filtered through a silica plug (ca. 6 cm). The second fraction was pure **8** (5% yield, 0.002 g, 0.008 mmol).

Method D: 5-Br (0.060 g, 0.287 mmol) was dissolved in DMF (2 mL). Next $[Pd(PPh_3)_4]$ 0.013 g, 0.011 mmol, 4 mol-%) was added. The mixture was heated at 100 °C for around 20 h. DMF was evaporated under oil-pump vacuum and the residue was dissolved in CH_2Cl_2 (1 mL) and filtered through a silica plug (ca. 6 cm) to give **8** as a yellow powder in 72% yield (0.027 g, 0.103 mmol). M.p. 123 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.01 (s, 1 H, CHO), 7.85 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.67 (d, J_{HH} = 8 Hz, 2 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 191.2 (s, 1 C, *C*O), 136.2 (s, 1 C, *p*-Ph), 133.1 (s, 2 C, *o*-Ph), 129.6 (s, 2 C, *m*-Ph), 127.5 (s, 1 C, *i*-Ph), 82.1 (s, 1 C, C*C*Ph), 76.4 (s, 1 C, *C*CPh) ppm. IR (KBr): $\tilde{\nu}$ = 2210 (w, $\nu_{C\equiv C}$), 1928 (w, $\nu_{C=O}$) 1697 (s) cm^{-1}. MS: *m*/*z* = 258 $[M]^+$, 229 $[M - HCO]^+$, 200 $[M - 2HCO]^+$. $C_{18}H_{10}O_2$ (258.068): calcd. C 83.70, H 3.91; found C 83.54, H 3.87.

$CH_3COC_6H_4(C\equiv C)_2C_6H_4COCH_3$ (9). Method B: 2 (0.230 g, 1.063 mmol), wet TBAF (0.213 mL, 1.0 M solution in THF, 20 mol-%), $SiMe_3SiCl$ (0.134 mL, 1.063 mmol), CuCl (0.421 g, 4.252 mmol) and TMEDA (0.257 mL, 1.700 mmol) were combined in a procedure analogous to that for **8** (Method B). Analogous work-up gave **9** as a yellow powder in 75% yield (0.114 g, 0.398 mmol).

Method C: 6-I (0.065 g, 0.241 mmol) and $[Pd(PPh_3)_4]$ (0.011 g, 0.010 mmol, 4 mol-%) were combined in a procedure analogous to that for **8** (Method C). Analogous work-up gave **9** as a yellow powder in 29% yield (0.010 g, 0.035 mmol).

Method D: 6-Br (0.082 g, 0.368 mmol) and $[Pd(PPh_3)_4]$ (0.017 g, 0.015 mmol, 4 mol-%) were combined in a procedure analogous to that for **8** (Method D). Analogous work-up gave **9** as a yellow powder in 90% yield (0.047 g, 0.165 mmol). M.p. 176 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.59 (d, J_{HH} = 8 Hz, 2 H, Ph), 2.59 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 197.0 (s, 1 C, *C*O), 137.1 (s, 1 C, *p*-Ph), 132.6 (s, 2 C, *o*-Ph), 128.3 (s, 2 C, *m*-Ph), 126.2 (s, 1 C, *i*-Ph), 82.0 (s, 1 C, C*C*Ph), 76.5 (s, 1 C, *C*CPh), 26.6 (s, 1 C, *C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2213 (w, $\nu_{C\equiv C}$), 1934 (w, $\nu_{C=O}$) 1677 (s) cm^{-1}. MS: *m*/*z* = 286 $[M]^+$, 271 $[M - CH_3]^+$, 243 $[M - CH_3 - CO]^+$, 228 $[M - 2CH_3 - CO]^+$, 200 $[M - 2CH_3 - 2CO]^+$. $C_{20}H_{14}O_2$ (286.329): calcd. C 83.90, H 4.93; found C 83.67, H 4.87.

$C_2H_5COC_6H_4(C\equiv C)_2C_6H_4COC_2H_5$ (10). Method B: Compound **3** (0.360 g, 1.563 mmol), wet TBAF (0.313 mL, 1.0 M solution in THF, 20 mol-%), Me_3SiCl (0.197 mL, 1.559 mmol), CuCl (0.155 g, 1.563 mmol) and TMEDA (0.094 mL, 0.625 mmol) were combined in a procedure analogous to that for **8** (Method B). Analogous work-up gave **10** as a yellow powder in 85% yield (0.209 g, 0.664 mmol). Method C: **7-I** (0.203 g, 0.714 mmol) and $[Pd(PPh_3)_4]$ (0.033 g, 0.028 mmol, 4 mol-%) were combined in a procedure analogous to that for **8** (Method C). Analogous work-up gave **10** as a yellow powder in 28% yield (0.031 g, 0.100 mmol).

Method D: 7-Br (0.065 g, 0.274 mmol) and $[Pd(PPh_3)_4]$ (0.013 g, 0.011 mmol, 4 mol-%) were combined in a procedure analogous to that for **8** (Method D). Analogous work-up gave **9** as a yellow powder in 85% yield (0.037 g, 0.116 mmol). M.p. 156 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, J_{HH} = 8 Hz, 2 H, Ph), 7.58 (d, J_{HH} = 8 Hz, 2 H, Ph), 2.97 (q, J_{HH} = 7 Hz, 2 H, CH_2), 1.20 (t, J_{HH} = 7 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 199.7 (s, 1 C, *C*O), 136.8 (s, 1 C, *p*-Ph), 132.5 (s, 2 C, *o*-Ph), 127.8 (s, 2 C, *m*-Ph), 125.9 (s, 1 C, *i*-Ph), 81.8 (s, 1 C, C*C*Ph), 76.3 (s, 1 C, *C*CPh), 31.8 (s, 1 C, *C*H$_2$), 8.0 (s, 1 C, *C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2213 (w, $\nu_{C\equiv C}$), 1936 (w, $\nu_{C=O}$) 1685 (s) cm^{-1}. MS: *m*/*z* = 314 $[M]^+$, 285 $[M - CH_2CH_3]^+$, 228 $[M - 2CH_2CH_3 - CO]^+$, 200 $[M - 2CH_2CH_3 - 2CO]^+$. $C_{22}H_{18}O_2$ (314.382): calcd. C 84.05, H 5.77; found C 83.87, H 5.67.

$C_6H_5COC_6H_4(C\equiv C)_2C_6H_4COC_6H_5$ (11). Method B: Compound **3** (0.300 g, 1.077 mmol), wet TBAF (0.216 mL, 1.0 M solution in THF, 20 mol-%), Me_3SiCl (0.136 mL, 1.077 mmol), CuCl (0.106 g, 1.077 mmol) and TMEDA (0.064 mL, 0.424 mmol) were combined in a procedure analogous to that for **8** (Method B). Analogous work-up gave **11** as a yellow powder in 75% yield (0.166 g, 0.404 mmol). M.p. 185 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.50 (m, 9 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 195.6 (s, 1 C, *C*O), 137.7 (s, 1 C, *i*′-Ph), 137.0 (s, 1 C, *p*-Ph), 132.7 (s, 1 C, *p*′-Ph), 132.3 (s, 2 C, *o*-Ph), 130.0 (s, 2 C, *o*′-Ph), 129.8 (s, 2 C, *m*-Ph), 128.3 (s, 2 C, *m*′-Ph), 125.5 (s, 1 C, *i*-Ph), 81.8 (s, 1 C, C*C*Ph), 76.3 (s, 1 C, *C*CPh) ppm. IR (KBr): $\tilde{\nu}$ = 2105 (w, $\nu_{C\equiv C}$), 1941 (w, $\nu_{C=O}$), 1650 (s) cm^{-1}. $C_{30}H_{18}O_2$ (410.470): calcd. C 87.78, H 4.42; found C 87.32, H 4.51.

Details of X-ray Data Collection and Reduction: X-ray diffraction data were collected by using a KUMA KM4 CCD (ω scan technique) diffractometer equipped 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 using 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-682769 (for **9**), CCDC-682770 (for **10**), and CCDC-682771 (for **11**) 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.

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[1] In this paper the term polyyne is used for compounds with two or more conjugated C≡C bonds.
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