ChemPubSoc Europe
DOI: 10.1002/chem.201502737
CHEMISTRY A European Journal
Full Paper

Polyynes

# Synthesis of Long, Palladium End-Capped Polyynes through the Use of Asymmetric 1-Iodopolyynes

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**Abstract:** The synthesis of a unique series of long, asymmetric 1-iodopolyynes (**1**-$C_n$I and **2**-$C_n$I) with the sp-hybridized carbon chain up to a decapentayne is reported. These compounds were then used as substrates in reactions with $Pd(PPh_3)_4$ leading to another series of palladium end-capped polyynes, which were unstable in solution. Organometallic octatetraynes **1**-$C_8$[Pd]I, **2**-$C_8$[Pd]I, and decapentayne **1**-$C_{10}$[Pd]I are palladium end-capped polyyne compounds with the longest carbon chains reported so far. All the complexes as well as their organic precursors were fully characterized by NMR, HRMS(ESI), IR, TGA-DTA, and UV/Vis techniques, and the X-ray crystal structures of two silyl-protected precursors and one palladium complex are presented. The synthetic approach for palladium species is envisioned as a general route for the synthesis of labile organometallic polyynes.

## Introduction

Organic, organometallic, and metal-containing polyynes have attracted interest from the scientific community for more than half a century.[1] Such species may be regarded as model compounds of the hypothetical linear allotropic form of carbon—carbyne—however, polyynes also possess considerable potential for a number of applications. Such molecules have been explored as molecular wires and switches in nanoelectronics,[2] as materials for optoelectronics because of their nonlinear optical response[3] or as precursors for conducting polymers.[4] It is also noteworthy that polyynes and cyanopolyynes are among the largest molecules that have been found in interstellar matter.[5]

Organometallic polyynes are an important class of polyynes[6] and, to date, the most intense research has concerned rhenium,[7] ruthenium,[8] iron,[9] and especially platinum[10] complexes. Alkynyl palladium complexes are well known and have been studied for many years; this is because such compounds may be regarded as key intermediates in many coupling reactions[11] and are known as active catalysts for living polymerization of isocyanides.[12] Recently, the use of palladium end-capped butadiynes as highly active initiators for this reaction was reported.[12c] Moreover, organometallic polymers with a PdC≡C moiety exhibit nonlinear optical, luminescence, and liquid crystalline properties, all of which make them attractive for use in numerous commercial applications.[13] Despite the extensive and ongoing studies of polyynic palladium complexes, they are rarely reported and, before this report, only a few examples of compounds with butadiyne carbon chain were known.[14] Recently, we reported the use of 1-halopolyynes (mostly 1-bromobutadiynes) as substrates for palladium end-capped polyynes with a carbon chain up to the hexatriyne.[15] To date, this reported palladium compound with a $C_6$ carbon chain is the only known palladium end-capped hexatriyne.

The lack of long palladium polyynes is a consequence of the fact that it is impossible to use the most common synthetic strategy leading to polyynes; that is, chain elongation starting, for instance, from an ethynyl complex. Alkynyl palladium complexes have proven to be highly unstable in solution because of ligand exchange[15] and, therefore, it is not possible to carry out C(sp)–C(sp) cross-coupling reactions for σ-alkynyl palladium complexes. This is why long, palladium end-capped polyynes are not reported whereas their platinum analogues are well explored. For this reason, the synthetic approach in which the polyyne chain with the target length is attached to the metal in the final step seems to be the only rational way to approach such unstable organometallic polyynes. Moreover, palladium end-capped polyynes may be a versatile starting material for numerous new coupling products.

In this work, we present the synthesis of a series of unique, fully conjugated 1-iodopolyynes with carbon chain up to the decapentayne and describe their use as substrates for the synthesis of palladium end-capped polyynes.[15–16] This approach led to the longest known palladium end-capped polyynes with a carbon chain up to $C_{10}$. The new compounds were characterized by $^1$H, $^{13}$C, $^{31}$P NMR, IR, TGA-DTA, UV/Vis and HRMS (ESI) techniques. Furthermore, the X-ray crystal structures of hexatriyne **2**-$C_6$[Pd]I and silyl-protected precursors **1**-$C_8$TMS and **1**-$C_{10}$-TIPS are presented.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201502737.

## Results and Discussion

### Synthesis of long 1-halopolyynes

1-Iodopolyynes and 1-halopolyynes in general are a rare class of compounds that exhibit several fascinating properties. The history of 1-halopolyynes begins in the second half of the 19th century with von Baeyer's synthesis of diiodobutadiyne.[17] However, the synthesis of longer homologues was not achieved until $I(C{\equiv}C)_nI$ ($n=3$, 4, 5) carbon rods were obtained in Goroff's group (see Figure 1) from which $I(C{\equiv}C)_{10}I$ is the longest known 1-halopolyyne to date.[18] 1-Halopolyynes may be used as precursors of an interesting group of carbon-rich molecules. It has been shown that diiodobutadiyne and dibromobutadiyne may be substrates for easy preparation of tetrahalobutatrienes[19] but the most fascinating example of their reactivity is topochemical crystal-to-crystal polymerization of diiodobutadiyne yielding the conducting poly(diiododiacetylene) (PIDA).[4,20] Furthermore, PIDA undergoes carbonization under treatment of Lewis bases, giving conducting carbon nanofibers.[21] Another interesting reactivity of 1-halopolyynes is a unique single-crystal-to-single-crystal topochemical dimerization.[22] Moreover, 1-halopolyynes are used in the iterative synthesis of longer polyynes by Negishi[23] or Stille reaction[18b] or in the synthesis of butadiyne-substituted pyrroles.[24] Despite sparse experimental data on their synthesis, modern computational studies of halogen end-capped polyynes are fairly numerous.[25]

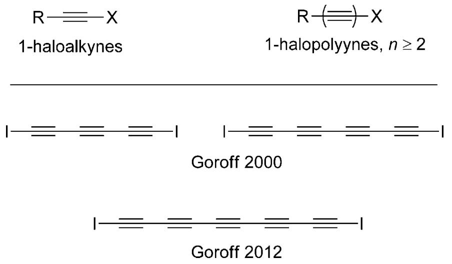
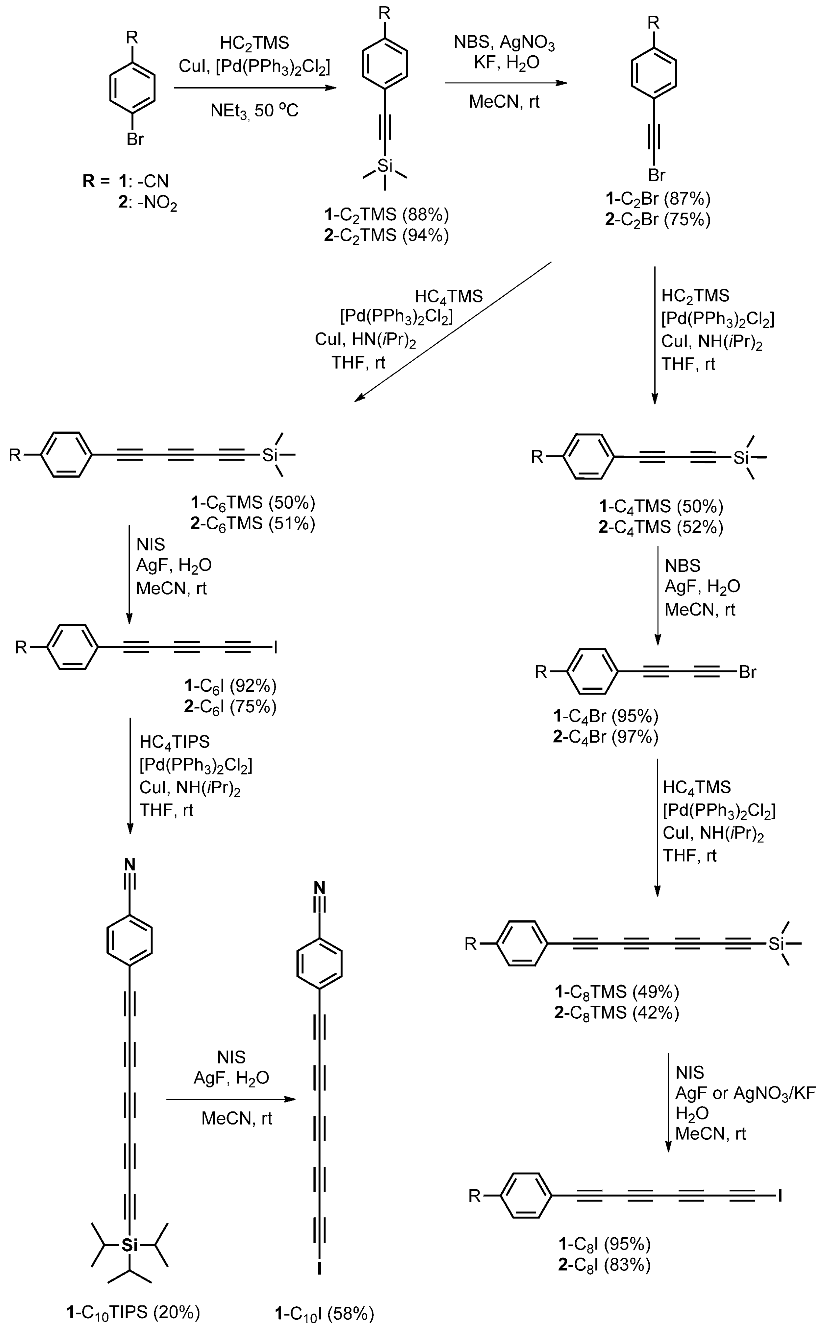


**Figure 1.** 1-Haloalkynes, 1-halopolyynes (top), and examples of 1,*n*-diiodopolyynes from Goroff's group (bottom).

Accordingly, the initial step of our research strategy was the synthesis of long, fully conjugated 1-halopolyynes. During our previous work with 1-halopolyynes we noted that iodides are usually more stable than the corresponding chlorides and bromides upon chain elongation, although no clear evidence for this has been reported. We suppose that the reason may be lower polarization of the polyyne chain or the size of the halogen atom. To investigate this observation in more detail, we performed TGA-DTA measurements for a series of known[15,26] 4-(halobutadiynyl)benzonitriles. The data have shown the decomposition temperatures for chloride, bromide, and iodide derivatives to be 128, 147, and 183 °C, respectively. With this result in mind, we selected iodides as targets for the synthesis of long 1-halopolyynes, and compounds with carbon chains up to decapentayne were obtained by using an iterative procedure with the Cadiot–Chodkiewicz cross-coupling as the carbon chain elongation step. As mentioned in the introduction, long 1-halopolyynes are extremely rare and the only known examples are octatetrayne $I(C{\equiv}C)_8I$[18a] and decapentayne $I(C{\equiv}C)_{10}I$.[18b]

All of our syntheses started from *para*-bromonitrobenzene or *para*-bromobenzonitrile according to the synthetic strategy involving Sonogashira cross-coupling in the first step, followed by bromination with deprotection in situ and Cadiot–Chodkiewicz cross-coupling with TMSC$_2$H or TMSC$_4$H, as shown in Scheme 1 (TMSC$_4$H was obtained according to a reported procedure;[27] synthetic route to **1**-C$_4$Br, **2**-C$_4$Br, and **1**-C$_6$TMS was reported in our previous work;[15,28] compound **2**-C$_6$TMS was obtained as described for **1**-C$_6$TMS). The choice of aryl substituents was based on the greater stability of 1-iodopolyynes with these groups compared with, for instance, *para*-fluorophenyl or perfluorophenyl groups. Polar end-groups such as nitro and nitrile groups also allowed column chromatography after coupling reactions to be performed more easily. Cadiot–Chodkiewicz cross-coupling of **1**-C$_4$Br and **2**-C$_4$Br with TMSC$_4$H gave new octatetraynes **1**-C$_8$TMS and **2**-C$_8$TMS. Iodination of all TMS-protected polyynes gave new 1-iodohextatriynes (**1**-C$_6$I and **2**-C$_6$I) and 1-iodooctatetraynes (**1**-C$_8$I and **2**-C$_8$I) with good yields (75–95 %). Synthesis of the C$_{10}$I type compound presented a greater challenge. We have noticed that elongation of the carbon chain strongly decreases the solubility of 1-iodopolyynes. Compound **2**-C$_8$I was very poorly soluble in CH$_2$Cl$_2$, CHCl$_3$, tetrahydrofuran (THF), and MeCN, and consequently its use in further chain elongation was challenging. The solubility of compounds with a benzonitrile end-group was better, so we attempted to obtain the silyl-protected precursor of **1**-C$_{10}$I. In the first thrust, Cadiot–Chodkiewicz cross-coupling of **1**-C$_8$I with TMSC$_2$H was performed, but we observed only traces of the desired product in the $^1$H NMR spectrum. Analogous reaction with TESC$_2$H (triethylsilylacetylene) gave **1**-C$_{10}$TES with low yields (5–7 %). Finally, we stepped down with chain length to maintain a better solubility and performed a reaction of **1**-C$_6$I with TIPSC$_4$H (triisopropylsilylbutadiyne) to finally obtain **1**-C$_{10}$TIPS in 20 % yield. TIPSC$_4$H is a known compound[29] but for its synthesis we designed a modified, very effective synthetic procedure (starting from TMSC$_4$TMS; see the Supporting Information). Iodination of **1**-C$_{10}$TIPS proceeded smoothly and gave **1**-C$_{10}$I in good yield (58 %).

The unsymmetrical 1-iodopolyynes reported in this work are significantly more stable than those previously described. The only known octatetrayne $I(C{\equiv}C)_8I$ explodes at 85 °C[18a] and the only known decapentayne $I(C{\equiv}C)_{10}I$ decomposes rapidly above 0 °C and explodes above 55–56 °C,[18b] so both must be stored in solution below 0 °C. The newly synthesized **1**–**2**-C$_8$I decompose rapidly at 125 °C (**1**-C$_8$I) and 129 °C (**2**-C$_8$I) and longer **1**-C$_{10}$I decomposes at 98 °C. Moreover, **1**-C$_{10}$I may be handled at room temperature for several hours without significant decomposition and may be stored for months as a solid at temperatures below −25 °C. Although diiodopolyynes have been reported to be explosive,[18b] we did not experience any dangerous incident during our work with the 1-iodopolyynes reported in this work. However, careful handling and small-scale syn-

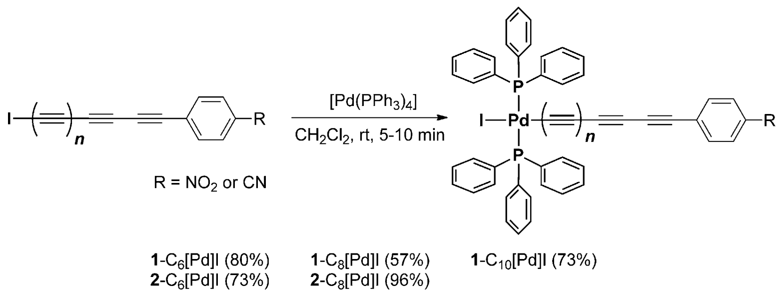


**Scheme 1.** Synthesis of 1-iodohexatriynes, 1-iodooctatetraynes, and 1-iododecapentayne.

thesis should always be applied when working with 1-halopolyynes.

## Synthesis of palladium complexes

With 1-iodopolyynes in hand, their reactions with [Pd(PPh$_3$)$_4$] in CH$_2$Cl$_2$ were then carried out. Oxidative addition gave palladium(II) end-capped polyynes in good to excellent yields, as shown in Scheme 2, but it was necessary to avoid reaction times longer than 5 to 10 min. As was noted previously, alkynyl palladium complexes are highly unstable in solution[15] and longer reaction times initiate the formation of byproducts and a black tar-like precipitate. Notably, the use of 1-iodopolyynes instead of 1-bromopolyynes allowed the formation and isolation of compounds with longer carbon chains, but the stability of resulting complexes with iodine in solution was lower than the stability of analogous complexes with bromine.[15] None of the complexes in the solid form exhibited significant sensitivity towards air or moisture.



**Scheme 2.** Synthesis of palladium end-capped polyynes.

## Characterization of 1-iodopolyynes and palladium complexes

All 1-iododopolyynes and palladium complexes were characterized through the use of $^1$H and $^{13}$C NMR, IR and UV/Vis spectroscopy, and by using TGA-DTA and HRMS (ESI) techniques. Moreover, for all the complexes, $^{31}$P NMR spectra were obtained. $^1$H NMR spectra of 1-iodopolyynes are quite simple, with only multiplets from the *para* substituted phenyl groups being observed. The $^{13}$C NMR spectra contained much more structural information. The $^{13}$C NMR spectra of **1**-C$_n$I ($n=3$–5) are shown in Figure 2 and all the data for carbon spectra of 1-iodopolyynes and palladium complexes (acetylenic range) are given in Table 1. The carbon atoms directly attached to the iodine are shifted strongly upfield and exhibit chemical shifts that are unusual for acetylenes (in $CDCl_3$ slightly above 0 ppm); this phenomenon has also been reported for 1-iodopolyynes.[30] For instance, chemical shifts of the I**C**≡C carbon for $IC_nI$ ($n=3$–5) are 0.9, 1.9, and 2.3 ppm (in $CDCl_3$), respectively.[18] Compound **2**-$C_8I$ was almost insoluble in $CDCl_3$ and the carbon NMR spectrum was recorded in [$D_6$]DMSO. Due to the different Lewis basicity of [$D_6$]DMSO, the chemical shift of I**C**≡C carbon for this compound changed dramatically to 20.7 ppm. It is known for 1-iodoalkynes that in Lewis-base solvents, the chemical shift of the alpha carbon is shifted strongly downfield because of the formation of Lewis acid–base complex.[30] For comparison, the $^{13}C$ NMR spectrum of **1**-$C_8I$ in [$D_6$]DMSO is also presented (I**C**≡C resonance: 20.4 ppm). Full assignment of acetylenic signals was problematic, but HMBC data recorded in $CDCl_3$ suggested that signals at 73.5–74.7 ppm may be assigned to Ar**C**≡C carbon centers. A comparison with the literature data for $IC_nI$ suggests that the most downfield shifted signals arise from IC≡**C** carbon atoms. An upfield shift of I**C**≡C signals is visible as the length of the carbon rods is increased for the **1**-$C_nI$ series (4.2 ppm for **1**-$C_6I$, 3.7 ppm for **1**-$C_8I$, 3.6 ppm for **1**-$C_{10}I$) and these data are consistent with the chemical shift of the I**C**≡C signal (6.5 ppm) of **1**-$C_4I$ reported previously.[15]

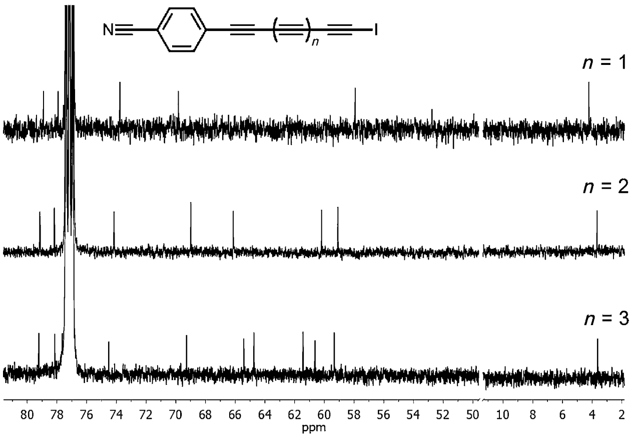
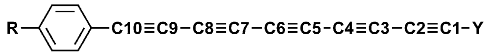


**Figure 2.** $^{13}C$ NMR spectra (acetylene range) of **1**-$C_nI$ ($n=6$, 8, 10) in $CDCl_3$.

**Table 1.** $^{13}C$ NMR spectra (acetylenic range) of 1-iodopolyynes and palladium complexes in $CDCl_3$.[a]



R = CN, **1**; $NO_2$, **2**
Y = I or[$Pd(PPh_3)_2I$]

| Compound | C1 | C2 | C3 to C9 | | | | | | | CX–Ar |
|---|---|---|---|---|---|---|---|---|---|---|
| **1**-$C_6I$ | 4.2 | 78.9 | 57.9 | 69.8 | 77.9 | | | | | 73.8 |
| **2**-$C_6I$ | 4.6 | 78.9 | 57.9 | 70.2 | 78.7 | | | | | 73.5 |
| **1**-$C_8I$ | 3.7 | 79.1 | 59.1 | 60.2 | 66.1 | 69.0 | 78.2 | | | 74.2 |
| **1**-$C_8I$[b] | 20.4 | 76.6 | 57.3 | 59.6 | 66.2 | 68.1 | 76.5 | | | 75.0 |
| **2**-$C_8I$[b] | 20.7 | 77.2 | 57.2 | 59.6 | 66.4 | 68.5 | 76.6 | | | 74.7 |
| **1**-$C_{10}I$ | 3.6 | 79.2 | 59.3 | 60.6 | 61.4 | 64.8 | 65.4 | 69.3 | 78.2 | 74.5 |
| | C1 | C2 | C3 | C4 to C9 | | | | | | CX–Ar |
| **1**-$C_6$[Pd]I | 107.0 | 90.8 | 72.4 | 80.7 | 55.6 | | | | | 71.9 |
| **2**-$C_6$[Pd]I | 107.6 | 90.8 | 73.0 | 81.7 | 55.6 | | | | | 71.7 |
| **1**-$C_8$[Pd]I | 107.3 | 90.5 | 68.4 | 79.7 | 72.7 | 58.1 | 57.0 | | | 71.8 |
| **2**-$C_8$[Pd]I | 107.7 | 90.5 | 68.7 | 80.5 | 72.5 | 58.0 | 57.0 | | | 72.3 |
| **1**-$C_{10}$[Pd]I | 107.5 | 90.4 | 67.0 | 79.1 | 73.5 | 68.2 | 59.5 | 59.1 | 57.3 | 70.8 |

[a] All chemical shifts are given in ppm. [b] Spectrum recorded in [$D_6$]DMSO. [c] Unambiguous assignment is possible only for carbon atoms near to the end-groups.

The $^1H$ NMR spectra of the palladium complexes also provide very little structural information, and the $^{13}C$ NMR spectra are much more informative. Resonances of the Pd**C**≡C carbon atoms resonate as strongly downfield shifted triplets ($J$(C,P) = 14.3–14.5 Hz) with chemical shift between 107.0 (**1**-$C_6$[Pd]I) and 107.7 ppm (**2**-$C_8$[Pd]I). Triplets ($J$(C,P) = 6.5–6.7 Hz) of PdC≡**C** carbon atoms exhibit chemical shifts between 90.4 and 90.8 ppm. It is also possible to assign the signals of PdC≡**C**C≡C carbon atoms (from 67.0 ppm for **1**-$C_{10}$[Pd]I to 71.9 ppm for **1**-$C_6$[Pd]I) due to a weak $J$(C,P) coupling constant (2.3–2.4 Hz). The acetylenic range of the $^{13}C$ NMR spectra of **1**-$C_n$[Pd]I series is shown in Figure 3. Full assignment of resonances of carbon atoms from polyyne chain was once again not possible. Three signals (*ipso*, *ortho*, and *meta*) of the phosphine groups are split into triplets. Such phenomena was described previously as a 'virtual coupling' and is known for *trans* square planar complexes.[31] In the phosphorus NMR spectra we observed only one resonance near 22 ppm, which confirmed the *trans* configuration of products and is typical for σ-alkynyl bis(triphenylphosphine)palladium complexes.[32] Nevertheless, it should be noted that the *cis* product is likely initially generated during oxidative addition, which isomerizes over time to the final *trans* coordination.

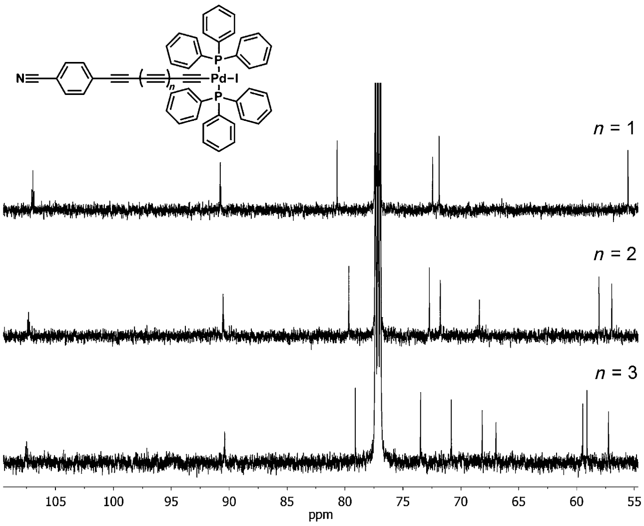


**Figure 3.** $^{13}C$ NMR spectra (acetylene range) of **1**-$C_n$[Pd]I ($n=3$,4,5); $CDCl_3$, 300 K, 151 MHz.

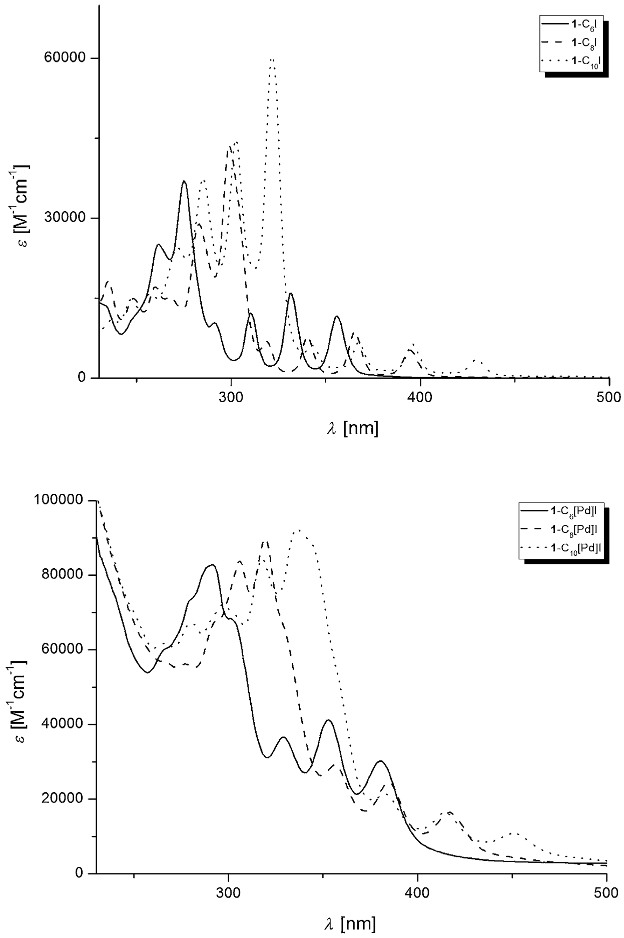


**Figure 4.** UV/Vis spectra of **1**-$C_n$I (top) and **1**-$C_n$[Pd]I (bottom) compounds.

Example UV/Vis spectra of 1-iodopolyynes and the corresponding Pd complexes are shown in Figure 4 (for all UV/Vis spectra see the Supporting Information). Vibronic structure is clearly visible and a series of narrow peaks can be observed, especially for the benzonitrile derivatives. A bathochromic shift in $\lambda_{max}$ is clearly visible as the length of the carbon rods is increased (as well as a hyperchromic shift), which is a known dependence for polyynes.[3a] The spectra of the Pd complexes are slightly more bathochromic shifted than the spectra of 1-iodopolynes and have higher molar absorptivity values (17 000–93 000 $M^{-1}cm^{-1}$).

IR C≡C stretching bands for all palladium complexes and the 1-iodopolyynes are within the typical acetylenic range (see the Experimental Section). These data are in good agreement with those of the previously reported palladium complexes and 1-halopolyynes.[15] The HRMS characterization of the palladium complexes was relatively straightforward. The signals from $[M-I]^+$ with a characteristic palladium isotope pattern could be observed with the use of an ESI ion source. The thermal stability of the palladium complexes was investigated by using TGA-DTA techniques. The complexes possess high thermal stability, ranging from 177 °C for **1**-$C_{10}$[Pd]I to 208 °C for **2**-$C_8$[Pd]I. High decomposition temperatures were previously noted for shorter palladium end-capped polyynes.[15] It is not surprising that 1-iodopolyynes are less stable and that their decomposition temperatures decrease as the length of the carbon chain increases. Hexatriynes decompose near 160 °C (161 °C for **1**-$C_6$I, 158 °C for **2**-$C_6$I), octatetraynes decompose below 130 °C (125 °C for **1**-$C_8$I, 129 °C for **2**-$C_8$I), and decapentayne **1**-$C_{10}$I decomposes at 98 °C. We did not observe noticeable light-sensitivity for any reported polyyne; however, all compounds were stored in the dark.

## X-ray Crystallography

As noted above, polyyne palladium complexes are unstable in solution[15] and therefore single crystals suitable for X-ray analysis are extremely difficult to obtain. If the crystallization time is too long (several hours) only the decomposition products ($Pd(PPh_3)_2I_2$, most probably $Pd(PPh_3)_2((C{\equiv}C)_nR)_2$ and some other unidentified compounds) are observed. Nevertheless, in case of **2**-$C_6$[Pd]I, our efforts were eventually successful. Clearly, silyl-protected precursors are far more stable and their crystallization was much easier.

X-ray crystal structures of two silyl-protected polyynes **1**-$C_8$TMS and **1**-$C_{10}$TIPS and one palladium complex **2**-$C_6$[Pd]I were solved. Crystals of **1**-$C_8$TMS and **1**-$C_{10}$TIPS were obtained by slow evaporation of their solutions in *n*-hexane and **2**-$C_6$[Pd]I was crystallized from a mixture of *n*-hexane and $CH_2Cl_2$. **1**-$C_8$TMS crystallizes in the *Pbcma* space group in the orthorhombic system with $Z=4$, whereas **1**-$C_{10}$TIPS and **2**-$C_6$[Pd]I crystallize in the $P\bar{1}$ space group in the triclinic system with $Z=4$ and $Z=2$, respectively (for further details see the Supporting Information). Molecular structures of the compounds are given in Figure 5 and Figure 6.

Selected bond lengths of the compounds are given in the Table 2. The Pd–C bond in **2**-$C_6$[Pd] (1.971(7) Å) is in a lower region of a typical range for neutral σ-alkynyl palladium complexes (usually 1.94–2.07 Å)[32–33] and is consistent with our pre-

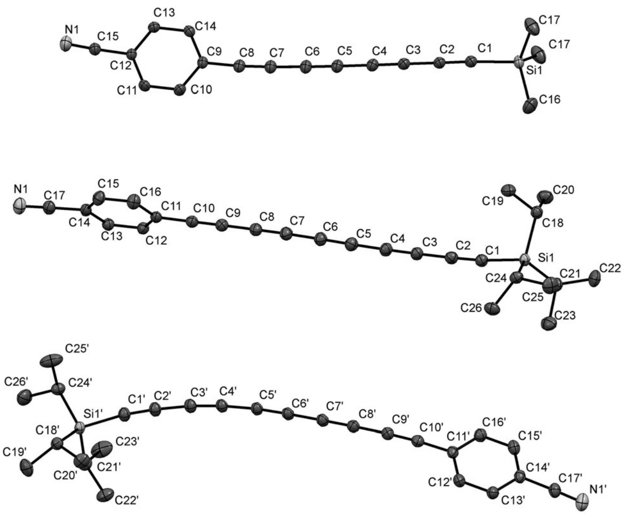


**Figure 5.** Molecular structures of silyl-protected polyynes **1**-$C_8$TMS and **1**-$C_{10}$TIPS. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50% probability. In the case of **1**-$C_{10}$TIPS, there are two different molecules in the asymmetric unit.

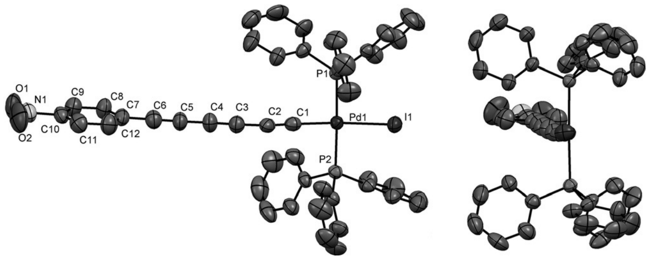


**Figure 6.** Molecular structure of **2**-$C_6$[Pd]I. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn with 50 % probability.

**Table 3.** Contraction coefficients for **1**-$C_8$TMS, **1**-$C_{10}$TIPS, and **2**-$C_6$[Pd]I compounds.

| | Contraction[a] C1–Cx [%] | Contraction[b] X–$C_{Ar}$ [%] |
|---|---|---|
| **1**-$C_8$TMS | 0.00 | 0.60 |
| **1**-$C_{10}$TIPS[b] | 0.19 | 0.61 |
| **1**-$C_{10}$TIPS[b] | 1.01 | 1.98 |
| **2**-$C_6$[Pd]I | 0.09 | 0.19 |

[a] Contraction C1–Cx = (C1–Cx sum of bond lengths–C1–Cx distance)/C1–Cx sum of bond lengths × 100 %. [b] Contraction X–$C_{Ar}$ = (X–$C_{Ar}$ sum of bond lengths–X-$C_{Ar}$ distance)/X–$C_{Ar}$ sum of bond lengths × 100 %. [c] X = Si, Pd.

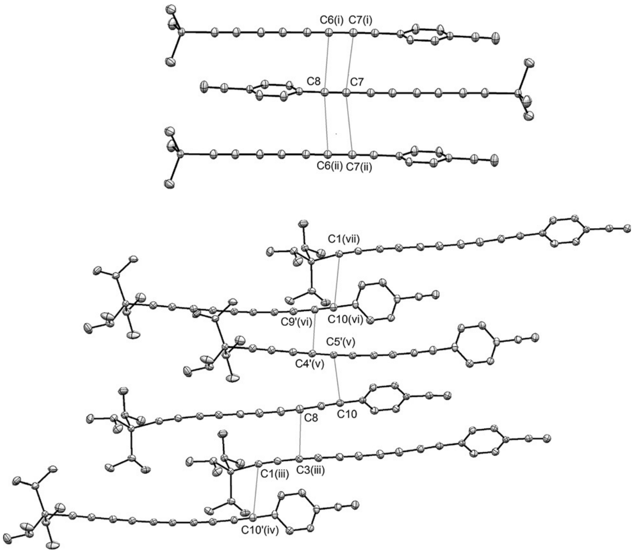


**Figure 7.** Packing motifs for **1**-$C_8$TMS (top) and **1**-$C_{10}$TIPS (bottom). The distances [Å] for **1**-$C_8$TMS are: C8–C6(i) 3.530, C7–C7(i) 3.540. Symmetry operations for related atoms are: (i) −*x*, 1/2 + *y*, −*z*; (ii): −*x*. −1/2 + *y*, −z. The distances [Å] for **1**-$C_{10}$TIPS are: C8–C3(iii) 4.193, C1–C10(iv) 5.334, C10–C5′(v) 3.462, C4′(v)–C9′(vi) 3.681, C10′(vi)–C1(vii) 5.334. Symmetry operations for related atoms are: (iii): −1 + *x*, 1−*y*, 1−*z*, (iv): 2−*x*, 1−*y*, 1−*z*, (v): 1−*x*, 2−*y*, 1−*z*, (vi): 2−*x*, 2−*y*, 1−*z*, (vii): −1 + *x*, 1 + *y*, *z*.

vious work.[15] In all the compounds the length of triple bonds are usually below 1.22 Å, which is a typical value for polyynes with a carbon chain of such a length.[6]

The conformations of the polyyne chains were then analyzed. In the case of **1**-$C_{10}$TIPS it is possible to observe conformational flexibility of the carbon chain that is known for longer polyynes.[6] Two molecules in the asymmetric unit possess different conformation of the carbon chain and different contraction coefficients (see Table 3). The molecule with the bigger distortion from linearity possesses 'unsymmetrical bow' conformation, whereas the second is 'S-shaped'. The carbon chains in **1**-$C_8$TMS and **2**-$C_6$[Pd]I are only slightly distorted from linearity.

The packing motifs for all the reported structures were analyzed (two packings are shown in Figure 7). As mentioned before, polyynes have great potential for 1,*n*-topochemical polymerization[4,34] so we analyzed the packing diagrams in search for good candidates for such a process. Compound **1**-$C_8$TMS crystallizes in the *Pnma* space group with 0.5 molecule in the asymmetric unit so, consequently, its molecules form two sets of parallel chains (with head-to-tail orientation within a set). Instead, **1**-$C_{10}$TIPS and **2**-$C_6$[Pd]I crystallize in $P\bar{1}$ space group. There are two molecules in the asymmetric unit for **1**-$C_{10}$TIPS, which means that the compound also forms two sets of parallel chains (head-to-head within each set) and only **2**-$C_6$[Pd]I forms one set of parallel chains (with head to-tail orientation).

The closest chain–chain separation was then analyzed for each structure, which was understood as the closest carbon–carbon distance from two neighboring carbon chains. In the case of **2**-$C_6$[Pd]I, the geometrical parameters appeared far from those necessary for topochemical polymerization (3.5 Å)[6] and the closest carbon–carbon contact was as high as 5.04 Å, which is most probably an effect of the bulky end-group. Instead, as revealed by a detailed analysis (see Figure 6), the closest distances between two chain carbon atoms for **1**-$C_8$TMS (3.53 Å) and **1**-$C_{10}$TIPS (3.46 Å) were slightly lower than the sum of van der Waals radii (3.56 Å). Nevertheless, only in the case of **1**-$C_8$TMS was it possible to define an infinite chain with such short contacts. In the case of **1**-$C_{10}$TIPS, the shortest carbon–carbon distances formed between atoms from two chain sets whereas contacts within one set were much longer (5.33 Å) than is necessary for topochemical polymerization.

**Table 2.** Selected bond lengths for **1**-$C_8$TMS, **1**-$C_{10}$TIPS, and **2**-$C_6$[Pd]I polyynes.

| | X[c]–C1 | C1–C2 | C2–C3 | C3–C4 | C4–C5 | C5–C6 | C6–C7 | C7–C8 | C8–C9 | C9–C10 | ≡C–Ar |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-$C_8$TMS | 1.8507(14) | 1.216(2) | 1.369(2) | 1.210(2) | 1.361(2) | 1.212(2) | 1.364(2) | 1.207(2) | | | 1.428(2) |
| 1-$C_{10}$TIPS[b] | 1.849(2) | 1.214(2) | 1.373(2) | 1.209(2) | 1.360(2) | 1.213(2) | 1.357(2) | 1.210(2) | 1.364(2) | 1.204(2) | 1.429(2) |
| 1-$C_{10}$TIPS[b] | 1.845(2) | 1.213(2) | 1.370(2) | 1.211(2) | 1.357(2) | 1.213(2) | 1.355(2) | 1.214(2) | 1.364(2) | 1.206(2) | 1.424(2) |
| 2-$C_6$[Pd]I | 1.971(7) | 1.167(8) | 1.387(10) | 1.220(9) | 1.360(9) | 1.202(9) | | | | | 1.439(10) |

[a] All lengths in Å. [b] Two molecules in the asymmetric unit. [c] X = Si, Pd.

Based on the analysis, only **1**-C$_8$TMS could be considered as a good candidate for 1,*n*-topochemical polymerization.

## Conclusion

We have described the synthesis of a series of fully conjugated long 1-iodopolyynes with carbon chains up to the decapentayne by using an iterative procedure with Cadiot–Chodkiewicz cross-couplings and halogenations with deprotection in situ. The development of **1**-C$_8$I, **2**-C$_8$I, and **1**-C$_{10}$I significantly enriches the family of known 1-halopolyynes. The oxidative addition of Pd(PPh$_3$)$_4$ to resulting 1-iodopolyynes was then carried out and the corresponding palladium end-capped polyynes were obtained. To our knowledge, decapentayne **1**-C$_{10}$[Pd]I is the palladium polyynyl complex with the longest carbon chain for this class of compounds reported to date. All the complexes were characterized by using $^1$H, $^{13}$C, $^{31}$P NMR, IR, HRMS(ESI), TGA-DTA and UV/Vis techniques. Moreover, X-ray crystal structures of two silyl protected precursors (**1**-C$_8$TMS and **1**-C$_{10}$TIPS) and one palladium complex (**2**-C$_6$[Pd]I) were determined.

## Experimental Section

### Experimental details

For full details, including additional experimental procedures, copies of $^1$H, $^{13}$C and $^{31}$P NMR spectra and X-ray crystallography details, see the Supporting Information. CCDC 1056226 (**1**-C$_8$TMS), 1056227 (**1**-C$_{10}$TIPS), and 1056228 (**2**-C$_6$[Pd]I) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

### General

All reactions were conducted under N$_2$ by using standard Schlenk techniques. Glassware was pre-dried at 120 °C. Solvents were treated as follows: hexane was distilled from Na, THF was distilled from Na/benzophenone, CH$_2$Cl$_2$ was distilled from P$_2$O$_5$, and CH$_3$CN (HPLC grade) was used as received. Pd(PPh$_3$)$_4$ (Aldrich, 99%), *N*-iodosuccinimide (NIS) (Alfa Aesar, 97%), AgF (Alfa Aesar, 98%) were used as received. **2**-C$_2$Br, **1**-C$_4$Br, **2**-C$_4$Br, **1**-C$_6$TMS, and TMSC$_4$H were obtained according to the known procedures.[15,27]

$^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded with Bruker Avance 500 and Avance III 600 MHz spectrometers. For all the $^1$H NMR spectra, the chemical shifts are given in ppm relative to the solvent residual peaks (CDCl$_3$, $^1$H: 7.26 ppm, $^{13}$C: 77.2 ppm; [D$_6$]DMSO, $^1$H: 2.50 ppm, $^{13}$C: 39.5 ppm,). For the $^{31}$P NMR spectra, H$_3$PO$_4$(aq) (85%) was used as an external standard (0 ppm). Coupling constants are given in Hz. HRMS spectra were recorded with Bruker apex ultra FT-ICR and MicOTOF-Q spectrometers with ESI ion source. IR spectra were recorded with a Bruker 66s FTIR spectrometer. UV/Vis spectra were recorded with an Agilent Cary 60 spectrophotometer. TGA-DTA data were collected with a Setaram SETSYS 16/18 thermal analyzer. Microanalyses were conducted with an Elementar CHNS Vario EL III analyzer.

### Details of X-ray data collection and reduction

X-ray diffraction data were collected with a KUMA KM4 CCD ($\omega$ scan technique) diffractometer. 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.[35] 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.

### General procedure for Cadiot–Chodkiewicz cross-coupling

**Trimethyl((4-nitrophenyl)hexa-1,3,5-triyn-1-yl)silane (2-C$_6$TMS)**: Under a N$_2$ atmosphere 1-(bromoethynyl)-4-nitrobenzene (**2**-C$_2$Br; 655 mg, 2.90 mmol) was dissolved in anhydrous THF (25 mL). Buta-1,3-diyn-1-yltrimethylsilane (533 mg, 4.36 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (102 mg, 0.145 mmol), and CuI (28 mg, 0.147 mmol) were added and the mixture was degassed by using the freeze-pump-thaw technique. Diisopropylamine (1.02 mL, 7.25 mmol) was then added and the mixture was stirred for 40 min. Solvent was removed and the product was purified by silica gel chromatography (hexane/CH$_2$Cl$_2$, 3:1 v/v) to give the product. Yield: 398 mg (1.49 mmol, 51%); yellow solid. $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta$ = 8.22–8.18 (m, 2H), 7.69–7.64 (m, 2H), 0.24 ppm (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta$ = 147.9 (s, *C*NO$_2$), 134.0 (s, *C*H of C$_6$H$_4$), 128.0 (s, $C_{Ar}C\equiv C$), 123.8 (s, *C*H of C$_6$H$_4$), 91.3 (s, $C\equiv C$), 87.7 (s, $C\equiv C$), 79.2 (s, $C\equiv C$), 74.3 (s, $C\equiv C$), 69.5 (s, $C\equiv C$), 60.6 (s, $C\equiv C$), −0.5 ppm (SiMe$_3$); elemental analysis calcd (%) for C$_{15}$H$_{13}$NO$_2$Si: C 67.50, H 4.90, N 5.24; found: C 67.41, H 4.85, N 5.15.

### Typical procedure for iodination of silyl-protected polyynes

**4-(Iodohexa-1,3,5-triyn-1-yl)benzonitrile (1-C$_6$I)**: Under a N$_2$ atmosphere **1**-C$_6$TMS (751 mg, 3.04 mmol), AgF (393 mg, 3.01 mmol), NIS (845 mg, 3.64 mmol), and H$_2$O (109 μL) were dissolved in MeCN (40 mL). The flask was wrapped with aluminum foil and the mixture was stirred for 5.5 h. After this time the solvent was removed under reduced pressure. The crude product was purified by elution through a silica gel plug (hexane/CH$_2$Cl$_2$, 1:1 v/v) to give the product. Yield: 840 mg (2.79 mmol, 92%); yellow solid; decomposition: 161 °C; $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta$ = 7.64–7.58 ppm (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta$ = 133.8 (s, *C*H of C$_6$H$_4$), 132.3 (s, *C*H of C$_6$H$_4$), 125.8 (s, $CC\equiv N$), 118.2 (s, $C\equiv N$), 113.2 (s, $C_{Ar}C\equiv C$), 78.9 (s, $C\equiv C$), 77.9 (s, $C\equiv C$), 73.76 (s, $C\equiv C$), 69.8 (s, $C\equiv C$), 57.9 (s, $C\equiv C$), 4.2 ppm (s, $C\equiv CI$). IR (fluorinated oil mull): $\tilde{\nu}$ = 1920 ($C\equiv C$), 2072 ($C\equiv C$), 2159 ($C\equiv C$), 2237 cm$^{-1}$ ($C\equiv N$). UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 356 (11 000), 332 (16 000), 310 (12 000), 291 (10 000), 275 (37 000), 262 nm (25 000). HRMS (ESI): *m/z* calcd for C$_{13}$H$_4$INAg: 407.8434 [*M*+Ag]$^+$; found: 407.8417.

**1-(Iodohexa-1,3,5-triyn-1-yl)-4-nitrobenzene (2-C$_6$I)**: According to the general procedure for iodination of silyl-protected polyynes, **2**-C$_6$TMS (166 mg, 0.621 mmol), NIS (173 mg, 0.746 mmol), AgF (82 mg, 0.63 mmol), and MeCN (20 mL) were used. Time: 2 h. Workup on silica gel plug (hexane/CH$_2$Cl$_2$, 1:1 v/v) gave the product. Yield: 149 mg (0.464 mmol, 75%); yellow solid; decomposition: 158 °C; $^1$H NMR (600 MHz, CDCl$_3$, 25 °C): $\delta$ = 8.23–8.17 (m, 2H), 7.70–7.64 ppm (m, 2H); $^{13}$C NMR (151 MHz, CDCl$_3$, 25 °C): $\delta$ = 148.0 (s, *C*NO$_2$), 134.1 (s, *C*H of C$_6$H$_4$), 127.7 (s, $C_{Ar}C\equiv C$), 123.9 (s, *C*H of C$_6$H$_4$), 78.9 (s, $C\equiv C$), 78.7 (s, $C\equiv C$), 73.5 (s, $C\equiv C$), 70.2 (s, $C\equiv C$), 57.9 (s, $C\equiv C$), 4.6 ppm (s, $C\equiv CI$); IR (fluorinated oil mull): $\tilde{\nu}$ = 1931 ($C\equiv C$), 2075 ($C\equiv C$), 2162 cm$^{-1}$ ($C\equiv C$); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 367 (8000), 342 (9000), 319 (8000), 292 (9000), 279 (8000), 237 nm (18 000); HRMS (ESI) *m/z* calcd for C$_{12}$H$_4$INNa: 343.9185 [*M*+Na]$^+$; found: 343.9188.

**4-((Trimethylsilyl)octa-1,3,5,7-tetrayn-1-yl)benzonitrile (1-C$_8$TMS)**: According to the general procedure for Cadiot–Chodkiewicz cross-coupling, **1**-C$_4$Br (200 mg, 0.869 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (32 mg, 0.046 mmol), CuI (9 mg, 0.047 mmol), TMSC$_4$H (163 mg, 1.33 mmol), NH(*i*Pr)$_2$ (0.30 mL, 2.12 mmol), and anhydrous THF (20 mL) were used. Time: 20 min. Silica gel chromatography (hexane/CH$_2$Cl$_2$, 1:1 v/v) gave the product. Yield: 116 mg (0.427 mmol, 48 %); yellow solid. $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta = 7.64$–7.58 (m, 4H), 0.23 ppm (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta = 133.8$ (s, *C*H of $C_6H_4$), 132.4 (s, *C*H of $C_6H_4$), 125.7 (s, *C*C≡N), 118.2 (s, C≡N), 113.4 (s, $C_{Ar}$C≡C), 90.1 (s, *C*≡C), 87.8 (s, *C*≡C), 78.4 (s, C≡C), 74.5 (s, C≡C), 69.5 (s, C≡C), 65.4 (s, C≡C), 61.9 (s, C≡C), 61.0 (s, C≡C), −0.5 ppm (s, SiMe$_3$); HRMS (ESI) *m*/*z* calcd for $C_{18}H_{14}NSi$: 272.0890 [*M*+H]$^+$; found: 272.0892.

**Trimethyl((4-nitrophenyl)octa-1,3,5,7-tetrayn-1-yl)silane (2-C$_8$TMS)**: According to the general procedure for Cadiot–Chodkiewicz cross-coupling, **2**-C$_4$Br (542 mg, 2.17 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (30 mg, 0.043 mmol), CuI (15 mg, 0.079 mmol), TMSC$_4$H (318 mg, 2.60 mmol), NH(*i*Pr)$_2$ (0.76 mL, 5.38 mmol), and anhydrous THF (15 mL) were used. Time: 3 h. Silica gel chromatography (hexane/CH$_2$Cl$_2$, 1:1 v/v) gave the product. Yield: 267 mg (0.916 mmol, 42 %); yellow solid. $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta = 8.22$–8.19 (m, 2H; $C_6H_4$), 7.69–7.66 (m, 2H; $C_6H_4$), 0.23 ppm (s, 9H; SiMe$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta = 148.1$ (s, *C*NO$_2$), 134.1 (s, *C*H of $C_6H_4$), 127.6 (s, $C_{Ar}$C≡C), 123.9 (s, *C*H of $C_6H_4$), 90.3 (s, C≡C), 87.7 (s, C≡C), 79.1 (s, C≡C), 74.2 (s, C≡C), 69.8 (s, C≡C), 65.6 (s, C≡C), 61.7 (s, C≡C), 60.9 (s, C≡C), −0.5 ppm (s, SiMe$_3$); HRMS (ESI) *m*/*z* calcd for $C_{17}H_{13}NO_2SiNa$: 314.0619 [*M*+Na]$^+$; found: 314.0617.

**4-(Iodoocta-1,3,5,7-tetrayn-1-yl)benzonitrile (1-C$_8$I)**: According to the general procedure for iodination of silyl-protected polyynes, **1**-C$_8$TMS (100 mg, 0.368 mmol), AgNO$_3$ (19 mg, 0.112 mmol), KF (22 mg, 0.379 mmol), NIS (103 mg, 0.444 mmol), H$_2$O (14 μL), and MeCN (10 mL) were used. Time: 2 h. Workup on silica gel plug (hexane/CH$_2$Cl$_2$, 1:1 v/v) gave the product. Yield: 114 mg (0.351 mmol, 95 %); yellow solid; decomposition: 125 °C; $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta = 7.64$–7.59 ppm (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta = 133.9$ (s, *C*H of $C_6H_4$), 132.3 (s, *C*H of $C_6H_4$), 125.5 (s, *C*C≡N), 118.1 (s, C≡N), 113.4 (s, $C_{Ar}$C≡C), 79.1 (s, C≡C), 78.2 (s, C≡C), 74.2 (s, C≡C), 69.0 (s, C≡C), 66.1 (s, C≡C), 60.2 (s, C≡C), 59.1 (s, C≡C), 3.7 ppm (s, C≡CI); IR (fluorinated oil mull): $\tilde{\nu}$ = 2058 (C≡C), 2122 (C≡C), 2190 (C≡C), 2234 cm$^{-1}$ (C≡N); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 394 (5000), 365 (9000), 340 (8000), 319 (7000), 300 (44 000), 283 nm (29 000); HRMS (ESI) *m*/*z* calcd for $C_{15}H_5IN$: 325.9461 [*M*+H]$^+$; found: 325.9458.

**1-(Iodoocta-1,3,5,7-tetrayn-1-yl)-4-nitrobenzene (2-C$_8$I)**: According to the general procedure for iodination of silyl-protected polyynes, **2**-C$_8$TMS (100 mg, 0.343 mmol), AgF (44 mg, 0.347 mmol), NIS (95 mg, 0.410 mmol), H$_2$O (12 μL), and MeCN (30 mL) were used. Time: 4 h. Workup on silica gel plug (CH$_2$Cl$_2$) gave the product. Yield: 98 mg (0.284 mmol, 83 %); yellow solid; decomposition: 129 °C; $^1$H NMR (500 MHz, DMSO, 25 °C): $\delta = 8.28$–8.24 (m, 2H), 7.95–7.91 ppm (m, 2H); $^{13}$C NMR (126 MHz, DMSO, 25 °C): $\delta = 148.0$ (s, *C*NO$_2$), 134.8 (s, *C*H of $C_6H_4$), 125.6 (s, $C_{Ar}$C≡C), 124.0 (s, *C*H of $C_6H_4$), 77.2 (s, C≡C), 76.6 (s, C≡C), 74.7 (s, C≡C), 68.5 (s, C≡C), 66.4 (s, C≡C), 59.6 (s, C≡C), 57.2 (s, C≡C), 20.7 ppm (s, C≡CI); IR (fluorinated oil mull): $\tilde{\nu}$ = 1930 (C≡C), 2119 (C≡C), 2192 cm$^{-1}$ (C≡C); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 400 (7000), 370 (13 000), 345 (14 000), 318 (18 000), 303 (19 000), 289 (15 000), 263 (23 000), 252 (24 000), 242 nm (23 000); HRMS (ESI): *m*/*z* calcd for $C_{14}H_4INO_2Na$: 367.9190 [*M*+Na]$^+$; found: 367.9191.

**4-((Triisopropylsilyl)deca-1,3,5,7,9-pentayn-1-yl)benzonitrile (1-C$_{10}$TIPS)**: According to the general procedure for Cadiot–Chodkiewicz cross-coupling, **1**-C$_6$I (193 mg, 0.641 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (9 mg, 0.013 mmol), CuI (2.4 mg, 0.013 mmol), TIPSC$_4$H (199 mg, 0.964 mmol), NH(*i*Pr)$_2$ (0.23 mL, 1.63 mmol), and anhydrous THF (15 mL) were used. Time: 30 min. Silica gel chromatography (hexane/CH$_2$Cl$_2$, 1:1 v/v) gave the product. Yield: 48 mg (0.126 mmol, 20 %); yellow solid; $^1$H NMR (500 MHz, CDCl$_3$, 25 °C): $\delta = 7.65$–7.59 (m, 4H; $C_6H_4$), 1.08–1.10 ppm (m, 21H; TIPS); $^{13}$C NMR (126 MHz, CDCl$_3$, 25 °C): $\delta = 133.9$ (s, *C*H of $C_6H_4$), 132.3 (s, *C*H of $C_6H_4$), 125.5 (s, *C*C≡N), 118.1 (s, C≡N), 113.5 (s, $C_{Ar}$C≡C), 89.5 (s, C≡C), 88.0 (s, C≡C), 78.3 (s, C≡C), 74.5 (s, C≡C), 69.6 (s, C≡C), 66.0 (s, C≡C), 64.4 (s, C≡C), 61.8 (s, C≡C), 61.1 (s, C≡C), 60.7 (s, C≡C), 18.6 (s, CH(*C*H$_3$)), 11.4 ppm (s, *C*H(CH$_3$)); HRMS (ESI): *m*/*z* calcd for $C_{26}H_{26}NSi$: 402.1654 [*M*+H]$^+$; found: 402.1661.

**4-(Iododeca-1,3,5,7,9-pentayn-1-yl)benzonitrile (1-C$_{10}$I)**: According to the general procedure for iodination of silyl-protected polyynes, **1**-C$_{10}$TIPS (21 mg, 0.055 mmol), AgF (7.2 mg, 0.056 mmol), NIS (15 mg, 0.067 mmol), and MeCN (5 mL) were used. Time: 4 h. Workup on silica gel plug (hexane/CH$_2$Cl$_2$, 1:1) gave the product. Yield: 11 mg (0.032 mmol, 58 %); yellow solid; decomposition: 98 °C; $^1$H NMR (600 MHz, CDCl$_3$, 25 °C): $\delta = 7.65$–7.60 ppm (m, 4H); $^{13}$C NMR (151 MHz, CDCl$_3$, 25 °C): $\delta = 133.9$ (s, *C*H of $C_6H_4$), 132.3 (s, *C*H of $C_6H_4$), 125.3 (s, *C*C≡N), 118.1 (s, C≡N), 113.6 (s, $C_{Ar}$C≡C), 79.2 (s, C≡C), 78.2 (s, C≡C), 74.5 (s, C≡C), 69.3 (s, C≡C), 65.4 (s, C≡C), 64.8 (s, C≡C), 61.4 (s, C≡C), 60.6 (s, C≡C), 59.3 (s, C≡C), 3.6 ppm (s, C≡CI); IR (fluorinated oil mull): $\tilde{\nu}$ = 1919 (C≡C) (weak), 2044 (C≡C), 2087 (C≡C), 2169 (C≡C), 2235 cm$^{-1}$ (C≡N); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 430 (3000), 396 (6000), 367 (7000), 343 (6000), 322 (60 000), 302 (45 000), 285 (38 000), 272 nm (25 000); HRMS (ESI): *m*/*z* calcd for $C_{17}H_5IN$: 349.9461 [*M*+H]$^+$; found: 349.9465.

### Typical procedure for the synthesis of palladium complexes

***trans*-Iodo((4-cyanophenyl)hexatriynyl)bis(triphenyphosphine)palladium (1-C$_6$[Pd]I)**: Under a N$_2$ atmosphere, **1**-C$_6$I (57 mg, 0.189 mmol) was added to a solution of [Pd(PPh$_3$)$_4$] (222 mg, 0.190 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL). The mixture was stirred for 5 min and then part of the solvent was removed under reduced pressure. A solid was precipitated with hexane and then filtered off. The crude product was dissolved in CH$_2$Cl$_2$ and reprecipitated with hexane to give the product. Yield: 141 mg (0.151 mmol, 80 %); yellow solid; decomposition: 186 °C; $^1$H NMR (600 MHz, CDCl$_3$, 25 °C): $\delta = 7.71$ (dd, *J* = 12.5, 5.9 Hz, 12H; PPh$_3$), 7.53 (d, *J* = 8.4 Hz, 2H; $C_6H_4$), 7.47–7.38 ppm (m, 20H; PPh$_3$ and $C_6H_4$); $^{13}$C NMR (151 MHz, CDCl$_3$, 25 °C): $\delta = 135.1$ (t, *J* = 6.3 Hz; *ortho* of PPh$_3$), 133.1 (s, *C*H of $C_6H_4$), 132.0 (s, *C*H of $C_6H_4$), 131.9 (t, *J* = 25.8 Hz; *ipso* of PPh$_3$), 130.7 (s, *para* of PPh$_3$), 128.2 (t, *J* = 5.4 Hz; *meta* of PPh$_3$), 127.6 (s, *C*C≡N), 118.5 (s, C≡N), 111.7 (s, $C_{Ar}$C≡C), 107.0 (t, *J* = 14.3 Hz, C≡CPd), 90.8 (t, *J* = 6.7 Hz; C≡CPd), 80.7 (s, C≡C), 72.4 (t, *J* = 2.3 Hz; *C*C≡CPd), 71.9 (s, C≡C), 55.6 ppm (s, C≡C); $^{31}$P NMR (243 MHz, CDCl$_3$, 25 °C): $\delta = 22.2$ ppm (s); IR (fluorinated oil mull): $\tilde{\nu}$ = 2034 (C≡C), 2135 (C≡C), 2162 (C≡C), 2225 cm$^{-1}$ (C≡N); UV/Vis (CH$_2$Cl$_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 380 (30 000), 352 (41 000), 329 (37 000), 292 nm (83 000); HRMS (ESI): *m*/*z* calcd for $C_{49}H_{34}NP_2Pd$: 804.1201 [*M*−I]$^+$; found: 804.1211.

***trans*-Iodo((4-nitrophenyl)hexatriynyl)bis(triphenyphosphine)palladium (2-C$_6$[Pd]I)**: **2**-C$_6$I (40 mg, 0.13 mmol), [Pd(PPh$_3$)$_4$] (144 mg, 0.123 mmol), and CH$_2$Cl$_2$ (10 mL) were used according to the general procedure for the synthesis of palladium complexes. Time: 10 min. Workup gave the product as a yellow solid (73 %, 90 mg, 0.095 mmol); decomposition: 186 °C; $^1$H NMR (600 MHz, CDCl$_3$, 25 °C): $\delta = 8.14$–8.10 (m, 2H; $C_6H_4$), 7.73–7.68 (m, 12H; PPh$_3$), 7.52–7.49 (m, 2H; $C_6H_4$), 7.47–7.38 ppm (m, 18H; PPh$_3$); $^{13}$C NMR (151 MHz, CDCl$_3$, 25 °C): $\delta = 147.1$ (s, *C*NO$_2$), 135.1 (t, *J* = 6.3 Hz; *ortho* of PPh$_3$), 133.4 (s, *C*H of $C_6H_4$), 131.9 (t, *J* = 25.8 Hz; *ipso* of PPh$_3$), 130.7 (s, *para* of PPh$_3$), 129.7 (s, *C*C≡C), 128.2 (t, *J* = 5.4 Hz; *meta* of PPh$_3$), 123.7 (s, *C*H of $C_6H_4$), 107.6 (t, *J* = 14.4 Hz; C≡CPd), 90.8 (t, *J* = 6.5 Hz; C≡CPd), 81.7 (s, C≡C), 73.0 (t, *J* = 2.3 Hz; *C*C≡

CPd), 71.7 (s, $C{\equiv}C$), 55.6 ppm (s, $C{\equiv}C$); $^{31}$P NMR (243 MHz, $CDCl_3$, 25 °C): $\delta = 22.2$ ppm (s); IR (fluorinated oil mull): $\tilde{\nu} = 2037$ ($C{\equiv}C$), 2137 cm$^{-1}$ ($C{\equiv}C$); UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 400 (16 000), 373 nm (17 000); HRMS (ESI): *m/z* calcd for $C_{48}H_{34}NO_2P_2Pd$: 824.1099 $[M{-}I]^+$; found: 824.1102.

***trans*-Iodo((4-cyanophenyl)octatetraynyl)bis(triphenyphosphine)-palladium (1-$C_8$[Pd]I)**: **1**-$C_8$I (9.0 mg, 0.028 mmol), $[Pd(PPh_3)_4]$ (32 mg, 0.027 mmol), and $CH_2Cl_2$ (10 mL) were used according to the general procedure for the synthesis of palladium complexes. Time: 5 min. Workup gave the product as a beige solid (15 mg, 0.016 mmol, 57 %). Decomposition: 185 °C; $^1$H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 7.69$ (dd, $J = 12.5$, 5.9 Hz, 12 H; $PPh_3$), 7.57 (d, $J = 8.4$ Hz, 2 H; $C_6H_4$), 7.52 (d, $J = 8.4$ Hz, 2 H; $C_6H_4$), 7.47–7.36 ppm (m, 18 H; $PPh_3$); $^{13}$C NMR (151 MHz, $CDCl_3$, 25 °C): $\delta = 135.1$ (t, $J = 6.2$ Hz; *ortho* of $PPh_3$), 133.5 (s, *C*H of $C_6H_4$), 132.2 (s, *C*H of $C_6H_4$), 131.8 (t, $J = 25.8$ Hz; *ipso* of $PPh_3$), 130.8 (s, *para* of $PPh_3$), 128.2 (t, $J = 5.4$ Hz; *meta* of $PPh_3$), 126.7 (s, $CC{\equiv}N$), 118.4 (s, $C{\equiv}N$), 112.5 (s, $C_{Ar}C{\equiv}C$), 107.3 (t, $J = 14.5$ Hz; $C{\equiv}CPd$), 90.5 (t, $J = 6.7$ Hz; $C{\equiv}CPd$), 79.7 (s, $C{\equiv}C$), 72.7 (s, $C{\equiv}C$), 71.8 (s, $C{\equiv}C$), 68.4 (t, $J = 2.0$ Hz; $CC{\equiv}CPd$), 58.1 (s, $C{\equiv}C$), 57.0 ppm (s, $C{\equiv}C$); $^{31}$P NMR (243 MHz, $CDCl_3$, 25 °C): $\delta = 22.1$ ppm (s); IR (fluorinated oil mull): $\tilde{\nu} = 2032$ ($C{\equiv}C$), 2097 ($C{\equiv}C$), 2133 ($C{\equiv}C$), 2226 cm$^{-1}$ ($C{\equiv}N$); UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 417 (16 000), 385 (24 000), 356 (29 000), 319 (90 000), 306 nm (84 000); HRMS (ESI): *m/z* calcd for $C_{51}H_{34}NP_2Pd$: 828.1201 $[M{-}I]^+$; found: 828.1210.

***trans*-Iodo((4-nitrophenyl)octatetraynyl)bis(triphenyphosphine)-palladium (2-$C_8$[Pd]I)**: **2**-$C_8$I (9.5 mg, 0.028 mmol), $[Pd(PPh_3)_4]$ (32 mg, 0.027 mmol), and $CH_2Cl_2$ (10 mL) were reacted according to the general procedure for the synthesis of palladium complexes. Time: 5 min. Workup gave the product as a yellow solid (26 mg, 0.027 mmol, 96 %). Decomposition: 208 °C; $^1$H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 8.16$ (d, $J = 8.8$ Hz, 2 H; $C_6H_4$), 7.69 (dd, $J = 12.6$, 5.9 Hz, 12 H; $PPh_3$), 7.59 (d, $J = 8.8$ Hz, 2 H; $C_6H_4$), 7.47–7.38 ppm (m, 18 H; $PPh_3$); $^{13}$C NMR (151 MHz, $CDCl_3$, 25 °C): $\delta = 147.6$ (s, $CNO_2$), 135.1 (t, $J = 6.2$ H, *ortho* of $PPh_3$), 133.7 (s, *C*H of $C_6H_4$), 131.8 (t, $J = 25.8$ Hz; *ipso* of $PPh_3$), 130.8 (s, *para* of $PPh_3$), 130.4 (s, $C_{Ar}C{\equiv}C$), 128.2 (t, $J = 5.4$ Hz; *meta* of $PPh_3$), 123.8 (s, *C*H of $C_6H_4$), 107.7 (t, $J = 14.5$ Hz; $C{\equiv}CPd$), 90.5 (t, $J = 6.5$ Hz; $C{\equiv}CPd$), 80.5 (s, $C{\equiv}C$), 72.5 (s, $C{\equiv}C$), 72.3 (s, $C{\equiv}C$), 68.7 (t, $J = 2.4$ Hz; $CC{\equiv}CPd$), 58.0 (s, $C{\equiv}C$), 57.0 ppm (s, $C{\equiv}C$); $^{31}$P NMR (243 MHz, $CDCl_3$, 25 °C) $\delta = 22.1$ ppm (s); IR (fluorinated oil mull): $\tilde{\nu} = 2122$ ($C{\equiv}C$), 2195 ($C{\equiv}C$), 2186 cm$^{-1}$ ($C{\equiv}C$); UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 428 (26 000), 394 (36 000), 330 (63 000), 311 (63 000), 278 nm (77 000); HRMS (ESI): *m/z* calcd for $C_{50}H_{34}NO_2P_2Pd$: 848.1099 $[M{-}I]^+$; found: 848.1099.

***trans*-Iodo((4-cyanophenyl)decapentaynyl)bis(triphenylphosphine)palladium (1-$C_{10}$[Pd]I)**: **1**-$C_{10}$I (13 mg, 0.037 mmol), $[Pd(PPh_3)_4]$ (42 mg, 0.036 mmol), and $CH_2Cl_2$ (10 mL) were reacted according to the general procedure for the synthesis of palladium complexes. Time: 5 min. Workup gave the product as a yellow solid (26 mg, 0.027 mmol, 73 %). Decomposition: 177 °C; $^1$H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta = 7.69$ (dd, $J = 12.4$, 6.0 Hz, 12 H; $PPh_3$), 7.61 (d, $J = 8.4$ Hz, 2 H; $C_6H_4$), 7.58 (d, $J = 8.3$ Hz, 2 H; $C_6H_4$), 7.48–7.38 ppm (m, 18 H; $PPh_3$); $^{13}$C NMR (151 MHz, $CDCl_3$, 25 °C): $\delta = 135.1$ (t, $J = 6.2$ Hz; *ortho* of $PPh_3$), 133.7 (s, *C*H of $C_6H_4$), 132.2 (s, *C*H of $C_6H_4$), 131.7 (t, $J = 25.8$ Hz; *ipso* of $PPh_3$), 130.8 (s, *para* of $PPh_3$), 128.2 (t, $J = 5.4$ Hz; *meta* of $PPh_3$), 126.1 (s, $CC{\equiv}N$), 118.2 (s, $C{\equiv}N$), 113.0 (s, $C_{Ar}C{\equiv}C$), 107.5 (t, $J = 14.5$ Hz; $C{\equiv}CPd$), 90.4 (t, $J = 6.5$ Hz; $C{\equiv}CPd$), 79.1 (s, $C{\equiv}C$), 73.5 (s, $C{\equiv}C$), 70.8 (s, $C{\equiv}C$), 68.2 (s, $C{\equiv}C$), 67.0 (t, $J = 2.4$ Hz; $CC{\equiv}CPd$), 59.5 (s, $C{\equiv}C$), 59.1 (s, $C{\equiv}C$), 57.3 ppm (s, $C{\equiv}C$); $^{31}$P NMR (243 MHz, $CDCl_3$, 25 °C): $\delta = 22.1$ ppm (s); IR (fluorinated oil mull): $\tilde{\nu} = 2015$ ($C{\equiv}C$), 2067 ($C{\equiv}C$), 2145 ($C{\equiv}C$), 2122 ($C{\equiv}C$), 2226 cm$^{-1}$ ($C{\equiv}N$); UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\varepsilon$, dm$^3$ mol$^{-1}$ cm$^{-1}$) = 451 (11 000), 415 (16 000), 383 (21 000), 336 (93 000), 318 (84 000), 297 (72 000), 279 nm (67 000); HRMS (ESI): *m/z* calcd for $C_{53}H_{34}NP_2Pd$: 852.1201 $[M{-}I]^+$; found: 828.1199.

## Acknowledgements

The authors would like to thank the National Science Centre (Grants UMO-2012/05/N/ST5/00665 and UMO-2013/08M/ST5/00942) for support of this research.

**Keywords:** alkynes · cross-coupling · hyperconjugation · iodine · palladium

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Received: July 12, 2015