

# Highly Practical and General Synthesis of Monodisperse Linear $\pi$ -Conjugated Oligoenynes and Oligoenediynes with Either *trans*- or *cis*-Olefin Configuration

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**Abstract:** Efficient and practical synthesis of a variety of 1-iodo-4-(trimethylsilyl)but-1-en-3-yne derivatives **1** and **2** with *trans*- and *cis*-olefin configuration was described. Their repeated use as building blocks allowed the facile synthesis of *trans*- and *cis*-oligoenynes, respectively. Development of a highly practical method for preparing monodisperse *trans*- and *cis*-oligoenediynes having the effective conjugation length was also accomplished by using **5** and **4**, which can be readily prepared from **1** and **2**, respectively.

## Introduction

Recently, a number of  $\pi$ -conjugated polymers have attracted much interest as advanced materials for electronic and photonic applications from both academic and industrial research laboratories.<sup>1</sup> The direct analytical characterization and physical study of extended  $\pi$ -chain polymers with high molecular weight, however, are often hampered by the low solubility of these compounds. Soluble, monodisperse  $\pi$ -conjugated oligomers as finite model systems offer the possibility to attain, by extrapolation, specific information concerning the electronic, thermal, and morphological properties of their corresponding high-molecular weight analogues.<sup>2</sup> Moreover, the oligomers having the effective conjugation length,<sup>3</sup> i.e. the shortest oligomers which would have the same properties as the polymers, might be used as a more processable substitute to the corresponding insoluble polymers. The second interest in monodisperse  $\pi$ -conjugated oligomers of defined length and constitution arises from their potential to act as molecular wires in molecular-scale electronics and nanotechnological devices.<sup>4</sup>

Linear  $\pi$ -conjugated oligomers having an ene scaffold may be viewed as model compounds for polyacetylene which has been widely explored for its interesting material properties, in

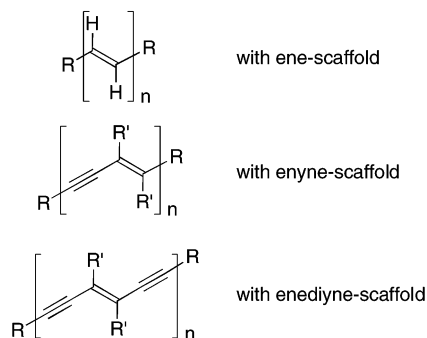


Figure 1.  $\pi$ -Conjugated polymers and oligomers.

particular for its high electrical conductivity upon doping.<sup>1a,4a,5</sup> Unfortunately, an oligoene compound without an olefin substituent has insoluble character, and thus it is difficult to prepare a model compound to investigate the properties of polyacetylene. Substitution of the ethylenic hydrogen atoms by an alkyl group for improving the solubility, however, results in distortion of the  $\pi$ -conjugated backbone out of planarity due to severe steric interactions resulting in a loss of conjugation. Oligomers having an enyne- or enediyne scaffold with an olefin substituent have a  $\pi$ -conjugated backbone, and thus, considerable effort has been devoted to their synthesis and characterization, which provide much useful information concerning the properties of linear  $\pi$ -conjugated polymers with an all-carbon backbone not composed of aromatic rings, including polyacetylene (Figure 1). Since variations in their molecular structure such as the chain length, olefin geometry, olefin substituent, and end-capping group can result in significant modifications of their properties, the development of synthetic methodology which allows access to a wide range of each of these  $\pi$ -conjugated compounds is

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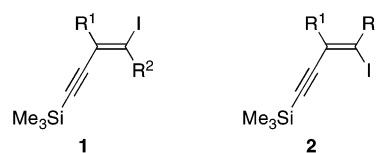
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important.<sup>2,6</sup> The synthetic methods developed thus far, however, have some drawbacks, more or less, such as lack of generality or low yield, or are not applicable to prepare in quantity.

Polymers and oligomers having an enyne scaffold can be prepared by topochemical solid-state polymerization of suitably prearranged and substituted buta-1,3-dienes,<sup>7</sup> a requirement, however, which severely limits their accessibility. Wudl and Biter reported a synthetic method for preparing a systematic series of *trans*-oligoenynes using coupling reaction of an alkynylmetal compound with *trans*-1,2-dihalo ethylene as the key reaction.<sup>8</sup> However, extension of this coupling method for synthesizing oligoenynes having olefin substituent(s) failed,<sup>9</sup> and thus far, a model compound of polymers obtained by polymerization of substituted buta-1,3-dienes has not been prepared. An iterative approach to *cis*-oligoenynes using the Sonogashira coupling as the key reaction was reported by Hirsch and co-workers which allowed preparation of some kinds of oligoenyne with up to four triple and three double bonds, albeit the overall yield was rather low.<sup>10</sup>

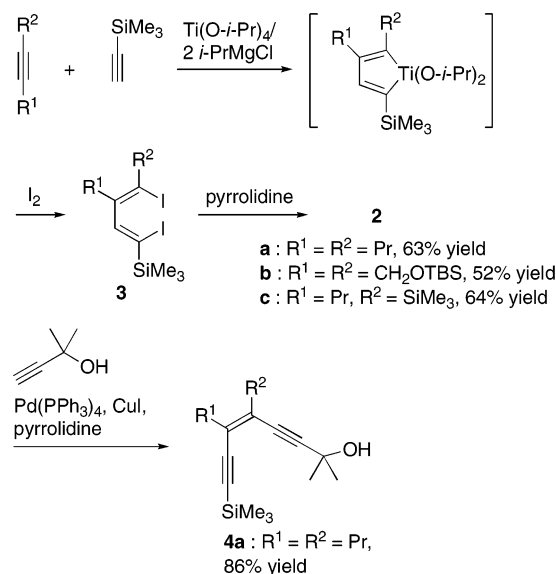
Preparation of monodisperse oligomers having an enediyne scaffold with *trans*-olefin configuration was reported by Diederich et al. They prepared the oligomers with extended size by a statistical deprotection–oxidative Hay oligomerization protocol which enabled them to carry out comprehensive structure–property studies.<sup>11</sup> On the basis of their study, the effective conjugation length could be revealed to comprise 9–11 monomer units, which corresponds to a total of 27–33 double and triple bonds.<sup>11a</sup> The multinanometer-long  $\pi$ -conjugated oligomers having an enediyne scaffold thus prepared have been shown to work as potential components of future molecular-scale electronic devices. The synthetic method, however, was not selective, and the yield of the oligomers decreased notably in proportion to the increase of the number of monomer units. Moreover, isolation of the resulting oligomers required the use of preparative size-exclusion chromatography and/or gel-permeation chromatography. It should also be noted that no general entry to oligoenedynes having *cis*-olefin configuration has been developed thus far.

Herein we report a practical synthetic method to prepare monodisperse  $\pi$ -conjugated oligomers containing an enyne- or enediyne scaffold with either *trans*- or *cis*-olefin configuration, including oligoenedynes having the effective conjugation length.<sup>12</sup>



**Figure 2.** Building blocks **1** and **2** for the synthesis of oligoenynes.

#### Scheme 1



## Results and Discussion

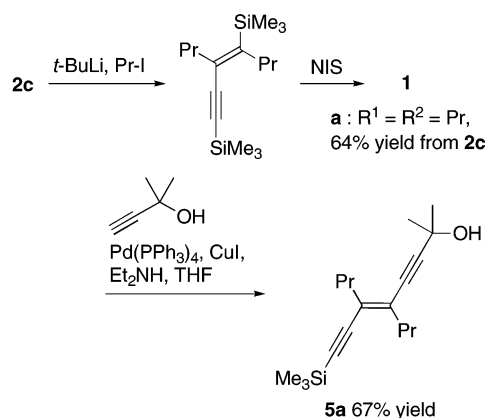
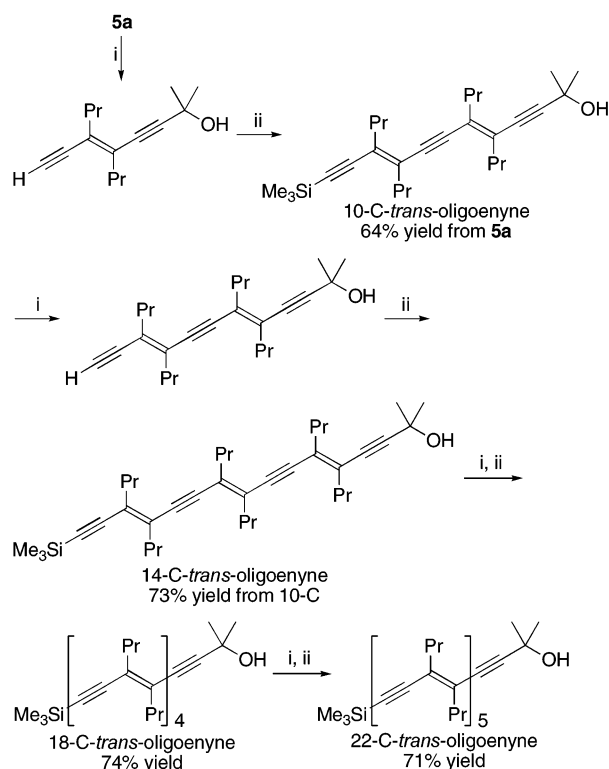
**Synthesis of Oligoenynes.** Our synthetic method for preparing oligoenynes includes efficient and practical synthesis of a variety of 1-iodo-4-(trimethylsilyl)but-1-en-3-yne derivative with *trans*- and *cis*-olefin configuration, i.e., **1** and **2** shown in Figure 2, and repeated use of **1** and **2** as building blocks, for the synthesis of *trans*- and *cis*-oligoenynes, respectively, using the Sonogashira coupling reaction<sup>13</sup> as the key carbon-elongation reaction.

Recently, we have developed a one-pot method for synthesizing 1-trimethylsilyl-1,4-diiodo-1,3-alkadienes **3** via regioselective coupling of internal acetylenes and ethynyltrimethylsilane mediated by a divalent titanium reagent  $\text{Ti}(\text{O}-i\text{-Pr})_4/2 i\text{-PrMgCl}$ , and the following reaction of the resulting titanacyclopentadienes with  $\text{I}_2$ .<sup>14,15</sup> We have now found that treatment of crude **3** with pyrrolidine afforded **2** in high overall yield as shown in Scheme 1. Meanwhile, enynes **1** can be synthesized from **2** obtained using 1-trimethylsilyl-1-alkynes as the internal alkyne by the conventional reaction sequence, as exemplified by the production of **1a** from **2c** as shown in Scheme 2. As also shown in Schemes 1 and 2, the Sonogashira coupling of **2** or **1** thus obtained with 3-methyl-1-butyne-3-ol provided enedynes **4** and

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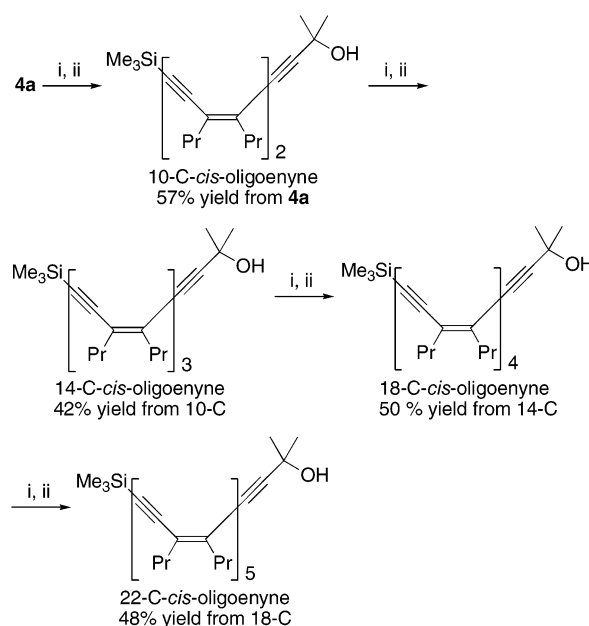
Scheme 2

Scheme 3. Synthesis of *trans*-Oligoenynes<sup>a</sup>

<sup>a</sup> Reagents: (i) K<sub>2</sub>CO<sub>3</sub>, THF, MeOH, H<sub>2</sub>O (ii) **1a**, Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, Et<sub>2</sub>NH, THF.

**5**, respectively, which can be utilized as the terminal unit for synthesizing oligoenynes (vide infra).

Using **1a** and **5a** thus obtained, we carried out the synthesis of the corresponding *trans*-oligoenynes by sequential reactions which involve the Sonogashira coupling of **1a** with a terminal alkyne, and removal of the trimethylsilyl group of the resulting product affording a new terminal alkyne which can be used for the next coupling with **1a**. Thus, oligoenyne with a 10-carbon atom backbone was prepared in 64% yield from **1a** and **5a** which, in turn, was converted into oligoenyne having a 14-carbon backbone in 73% yield by coupling, after desilylation, with **1a**. Applying these sequential reactions, oligoenynes with an 18- and a 22-carbon atom backbone were also prepared in good yield, respectively, as shown in Scheme 3. In the step of the Sonogashira coupling of **1a** with the terminal acetylenes, we used two equivalents of **1a** to suppress production of the

Scheme 4. Synthesis of *cis*-Oligoenynes<sup>a</sup>

<sup>a</sup> Reagents: (i) K<sub>2</sub>CO<sub>3</sub>, THF, MeOH, H<sub>2</sub>O (ii) **2a**, Pd<sub>2</sub>(dba)<sub>3</sub>, dppb, CuI, pyrrolidine.

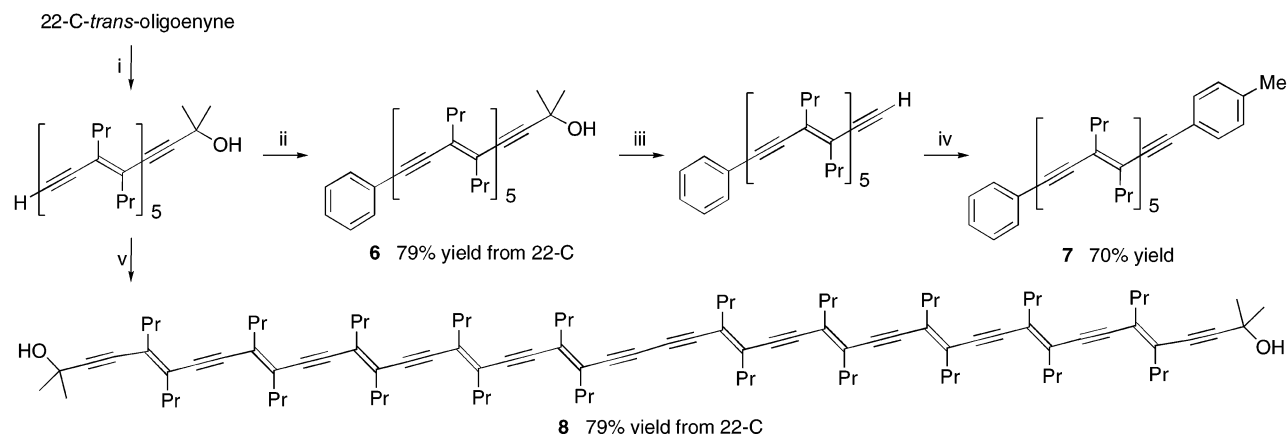
homocoupling product of the terminal acetylenes. Even under these reaction conditions, 10–20% of the homocoupling product was always coproduced; however, the homocoupling product, which is a diol derivative, and the cross-coupling product, that is a monoal derivative, and the starting non-polar **1a** could be readily separated by column chromatography, and **1a** used in excess amount was recovered in excellent yield.

Using a similar reaction strategy, *cis*-oligoenynes having up to a 22-carbon atom backbone were prepared starting from **2a** and **4a** in the yields shown in Scheme 4. It should be noted that the Sonogashira coupling of **2a** with **4a** using the reagent shown in Scheme 3 afforded almost equal amounts of the cross- and homocoupling products; however, use of Pd<sub>2</sub>(dba)<sub>3</sub>-dppb-CuI as the reagent improved the ratio of the cross- and homocoupling products to 65:35. Thus, we used the latter reagent for the Sonogashira coupling for the synthesis of *cis*-oligoenynes. In these reactions the resulting cross- and homocoupling products also can be readily separated by column chromatography.

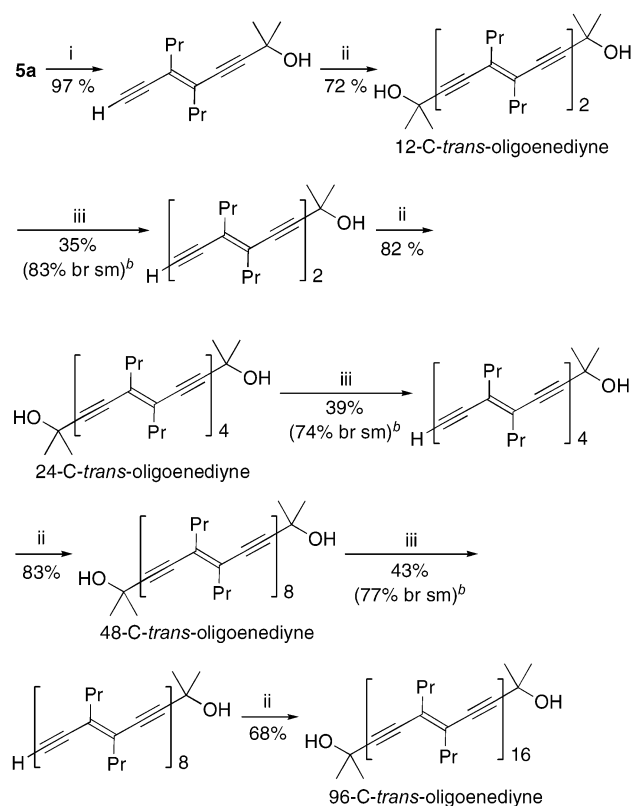
Oligoenynes thus obtained can be readily manipulated as exemplified by the transformation of 22-C-*trans*-oligoenynes shown in Scheme 5. Oligoenynes **7** having a different aryl end cap can be readily synthesized by the successive deprotection of the trimethylsilyl group and 2-hydroxyisopropyl group and the Sonogashira coupling, respectively, with an aryl iodide. The homocoupling reaction of the oligoenyne under Hay conditions<sup>16</sup> after desilylation afforded poly  $\pi$ -conjugated oligomer **8** with 12 triple and 10 double bonds.

**Synthesis of Oligoenediynes.** Oligoenediynes with either *trans*- or *cis*-olefin configuration can also be prepared starting from **5** (Scheme 2) or **4** (Scheme 1), respectively. We prepared *trans*-oligoenediyne dimer (12-C-), tetramer (24-C-), octamer (48-C-), and hexadecamer (96-C-oligoenediyne) from *trans*-**5a**

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**Scheme 5.** Manipulation of 22-C-*trans*-Oligoenyne<sup>a</sup>

<sup>a</sup> Reagents: (i) K<sub>2</sub>CO<sub>3</sub>, MeOH, THF, H<sub>2</sub>O (ii) PhI, Pd(PPh<sub>3</sub>)<sub>4</sub>, pyrrolidine (iii) NaOH, toluene (iv) 4-iodotoluene, Pd(PPh<sub>3</sub>)<sub>4</sub>, pyrrolidine (v) CuCl, TMEDA, O<sub>2</sub>

**Scheme 6.** Synthesis of *trans*-Oligoenediynes<sup>a</sup>

<sup>a</sup> Reagents: (i) K<sub>2</sub>CO<sub>3</sub>, THF, MeOH, H<sub>2</sub>O; (ii) CuCl, TMEDA, O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>; (iii) NaOH, toluene. <sup>b</sup>Yield shown in parentheses is based on recovered starting material.

according to the procedure shown in Scheme 6. The synthetic method relies on the selective deprotection of one of the two 2-hydroxyisopropyl groups connected at both of the terminal carbons of the oligoenediyne, and acetylene–acetylene coupling under oxidative Hay conditions.<sup>16</sup> As the latter reaction was expected to proceed in almost quantitative yield, when we planned the synthetic strategy shown in Scheme 6, our concern was the efficiency of mono-deprotection of one of the two 2-hydroxyisopropyl groups, and to our satisfaction, we found that it could be easily attained by treatment with NaOH (50 equiv) in toluene (bath temperature, 85 to 90 °C).<sup>17</sup> When we monitored the progression of the reaction by thin-layer chro-

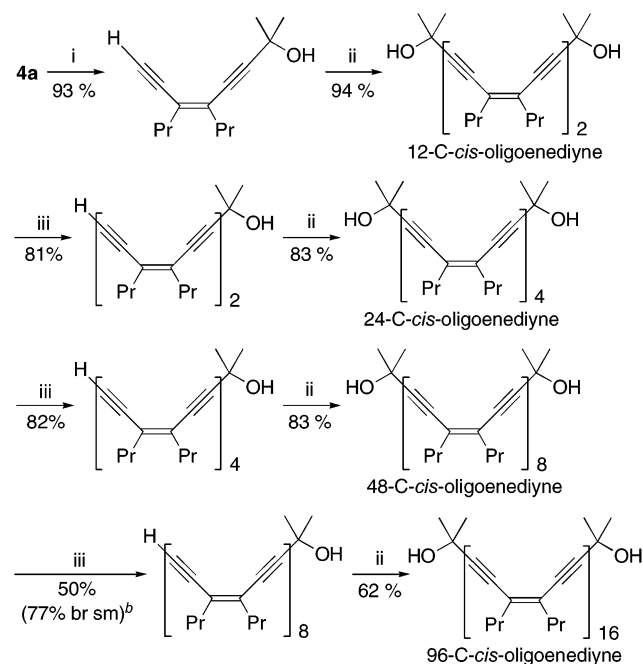
matography, the bis-deprotected product was not essentially detected before 50% conversion in every case, and according to further reaction progress, the bis-deprotected compound appeared gradually. These facts strongly indicated that generation of the  $\alpha,\omega$ -dianion of oligoenediyne is rather difficult due to the electronic effect through communication across the  $\pi$ -bonds along the oligomeric backbone. As the polarity of the starting compound, the mono-deprotected product, and the bis-deprotected product differs from one another in every case because they are, respectively, diol, monool, and hydrocarbon derivatives, they are readily separated and isolated by column chromatography at least up to an octamer. Actually, we terminated most of the deprotection reactions at around 50% conversion and isolated the desired mono-deprotected compound and recovered the starting substrate by column chromatography. The yield of the mono-deprotected product based on the recovered starting material (br sm) in addition to actual isolated yield, therefore, is indicated in parentheses in Scheme 6 and is very high. The Hay coupling reaction proceeded in essentially quantitative yield as expected; thus, in conclusion, the present method for synthesizing oligoenediynes is highly efficient and practical, allowing preparation of *trans*-oligoenediynes in amount.

Similarly, *cis*-oligoenediyne dimer, tetramer, octamer, and hexadecamer were prepared starting from *cis*-4a as shown in Scheme 7. In this case, deprotection reaction of the diol of dimer and tetramer was carried out until the starting diol almost disappeared, and thus, high isolated yield of the mono-deprotected product based on the starting diol (not br sm) was obtained, respectively, as shown in Scheme 7. It should be noted that this is the first general method to access oligoenediynes having *cis*-olefin configuration.

**Electronic Absorption Spectra of the Oligomers.** The electronic absorption spectra of several oligoenynes and oligoenediynes thus prepared were measured in hexane or chloroform at room temperature. The longest wavelength absorption maxima  $\lambda_{\text{max}}$  and  $\epsilon$  are summarized in Table 1. From Table 1, the following trend can be seen for oligoenynes, namely, that the longest energy electronic absorption in the series 10- to 14- to 18- to 22-C-oligoenynes goes from 346 to 385 to 386 to 400 nm for *trans*-oligoenynes, respectively, while for *cis*-oligoenynes,

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**Scheme 7.** Synthesis of *cis*-Oligoenediynes<sup>a</sup>

<sup>a</sup> Reagents: (i) K<sub>2</sub>CO<sub>3</sub>, THF, MeOH, H<sub>2</sub>O; (ii) CuCl, TMEDA, O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>; (iii) NaOH, toluene. <sup>b</sup>Yield shown in parentheses is based on recovered starting material.

the conjugated lengths had already reached saturation, and essentially the  $\lambda_{\max}$  values for each of these *cis*-oligoenynes remained similar values around 345 nm.

For the *trans*-oligoenediynes, the trend of the change in these values according to the variation of the conjugated chain length coincides well with that reported by Diederich<sup>11b</sup> despite the difference in the olefin substituent. For the *cis*-oligoenediynes, the values of  $\lambda_{\max}$  and  $\epsilon$  of each oligomer are smaller than those of the corresponding *trans*-oligoenediynes, and the conjugated length seems to reach saturation at around the 48-C-oligoenediynes which has a total of 24 double and triple bonds.

## Conclusions

An efficient and practical method for synthesizing monodisperse  $\pi$ -conjugated oligomers containing an enyne- or enediynes scaffold with either *trans*- or *cis*-olefin configuration has been developed. The characteristic features of the synthetic method include (1) an easy synthesis of 1-iodo-4-(trimethylsilyl)but-1-

**Table 1.** UV/Vis Data of Oligoenynes and Oligoenediynes with Either *trans*- or *cis*-Olefin Configuration

	cmpd	$\lambda_{\max}$ [nm] <sup>a</sup> ( $\epsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ]) <sup>b</sup>	
		<i>trans</i> -oligomer	<i>cis</i> -oligomer
oligoenynes <sup>c</sup>	10-C	346 (24 700)	343 (16 500)
	14-C	385 (35 200)	348 (24 700)
	18-C	386 (65 900)	351 (31 000)
	22-C	400 (67 700)	340 (17 600)
	<b>6</b>	401 (25 500)	
	<b>7</b>	402 (21 600)	
oligoenediynes <sup>d</sup>	<b>8</b>	427 (68 200)	
	12-C	369 (27 600)	364 (15 500)
	24-C	397 (76 900)	390 (27 500)
	48-C	425 (111 600)	416 (85 000)
	96-C	429 (301 300)	417 (175 900)

<sup>a</sup> Longest-wavelength absorption. <sup>b</sup> Molar extinction coefficient. <sup>c</sup> Measured in hexane at room temperature. <sup>d</sup> Measured in CHCl<sub>3</sub> at room temperature for oligoenediynes having a 2-hydroxyisopropyl group at both terminal positions.

en-3-yne derivative with *trans*- and *cis*-olefin configuration, i.e., **1** and **2**, (2) repeated use of **1** and **2** as building blocks for the preparation of *trans*- and *cis*-oligoenynes, respectively, using the Sonogashira coupling reaction as the key carbon-elongation reaction, and (3) use of **5** and **4**, readily prepared from **1** and **2**, respectively, as the starting compounds for preparation of *trans*- and *cis*-oligoenediynes, respectively, where the oxidative Hay coupling reaction is the key reaction for carbon-elongation reaction.

Although we prepared oligoenynes and oligoenediynes using **1a** and **2a** as building blocks, a variety of **1** and **2** are accessible as shown in Schemes 1 and 2, and therefore, the present synthetic method might allow access to oligoenynes and oligoenediynes with the designed structure.

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**Supporting Information Available:** Experimental procedures, spectroscopic data, and physical properties of **2a**, **2c**, **4a**, **1a**, **5a**, **6**, **7**, **8**, oligoenynes, and oligoenediynes (PDF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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