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Stereoselective Iterative Convergent Synthesis of *Z*-Oligodiacetylenes from Propargylic Dithioacetals

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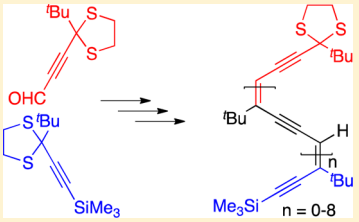
Supporting Information

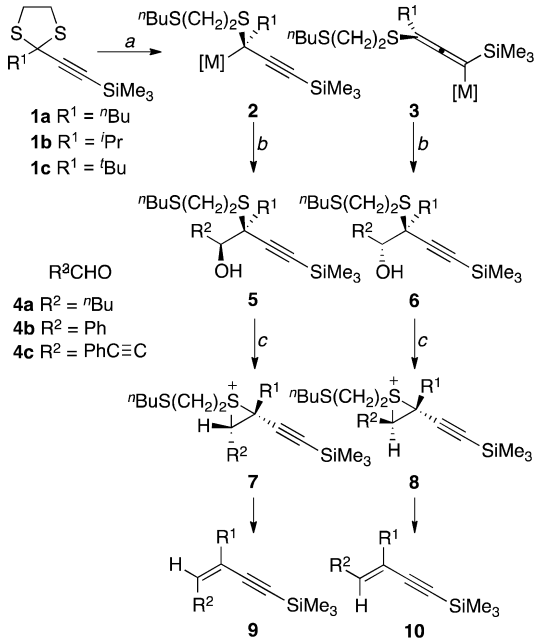
ABSTRACT: A series of ^{t}Bu-substituted *Z*-oligodiacetylenes (*Z*-ODAs) are synthesized from the reactions of allenyl/propargylic zinc reagents, obtained from the corresponding propargylic dithiolanes and BuLi, with dithiolane-substituted propargylic aldehydes followed by stereospecific elimination of *β*-thioalkoxy alcohols under Mitsunobu conditions. The stereochemical assignments are based on NOE experiments. The X-ray structure of the hexamer further supports the *Z* configuration for each of the double bonds in these ODAs. The photophysical properties of these *Z*-ODAs have been examined and are compared with known related *E*- and *Z*-ODAs with different substituents.



INTRODUCTION

Polydiacetylenes (PDAs) are conjugated polymers with alternating carbon−carbon double bonds and triple bonds.[1,2] They are synthesized by irradiation of substituted butadiynes in single-crystal form[1] or in self-assembled morphologies.[2] These polymers show a color change (blue to red) upon external stimulation, and the blue-phase PDAs are nonfluorescent, whereas emission is observed from the excited state of the red-phase analogues. These unique properties have enabled PDAs to serve in various sensing applications.[1−3] In the past three decades, extensive effort has been put forth on the synthesis of various oligodiacetylenes (ODAs), or oligoenynes, with well-defined chain lengths and stereochemistry of the double bonds to mimick PDAs.[4−9] Most *E*-[4,5] and *Z*-ODAs[5a,b,6,7] are synthesized stereospecifically by cross-coupling reactions from the corresponding vinyl halides and acetylenyl nucleophiles. Enyne metathesis gives exclusively *Z*-ODAs.[8] On the other hand, photolysis of a single crystal of diarylbutadiyne furnishes a mixture of ODAs in which all of the double bonds are suggested to be in the *Z* configuration.[9] It is interesting to note that the double bonds in these ODAs are either disubstituted[4,6] or tetrasubstituted,[5,7−9] and no ODAs with trisubstituted double bonds have been disclosed. We recently reported that the reaction of a propargylic dithioacetal **1** having an alkyl substituent at C2 of the dithiolane group with ^{n}BuLi and then with an aldehyde **4** gives the corresponding diastereomeric mixture of *β*-thioalkoxy alcohols **5** and **6**.[10−12] The reaction may presumably proceed via propargylic (**2**) and allenyl (**3**) organolithium intermediates (M = Li), which are allowed to react with **4** to give **5** and **6**. Upon treatment with Mitsunobu reagent, **5** and **6** undergo stereospecific *trans* elimination of the *β*-thioalkoxy alcohol moiety, yielding the corresponding enynes **9** and **10**, respectively (Scheme 1), via episulfonium ion intermediates **7** and **8**. It is worth mentioning that trisubstituted double bonds are formed selectively in these conjugated enynes. Organocopper reagents **2** and **3** (M = Cu) behave similarly in these transformations.[10c,11] The regio- and

Scheme 1. Synthesis of 9 and 10 from 1[a]



[a]Conditions: (*a*) ^{n}BuLi; (*b*) **4**; (*c*) ^{i}PrO$_2$CN=NCO$_2$Pr^i (DIAD), PPh$_3$.

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stereoselectivity of the reaction of propargylic and allenyl organometallic intermediates **2** and **3** with a carbonyl electrophile **4** has been shown to be dependent on the nature of the substituents of both the electrophile and nucleophile and on the metallic species.[10−13] It was envisaged that if **5** or **6** could be formed diastereoselectively, then the synthesis of conjugated enynes **9** or **10** with trisubstituted double bonds would be achieved accordingly. Here we report a stereoselective iterative convergent synthesis of ODAs with all trisubstituted double bonds in *Z* configuration from the corresponding propargylic dithioacetals **1c**.

RESULTS AND DISCUSSION

Diastereoselectivities of the Reactions of 2 and 3 (M = Zn) with Aldehydes. In the beginning of this research, organozinc reagents **2** and **3** (M = Zn) were prepared from the reactions of parpargylic dithioacetals **1**[10] and ^{n}BuLi in THF at −78 followed by treatment with a stoichiometric amount of $ZnCl_2$.[13g] A range of different aldehydes **4** was used as electrophiles to afford the corresponding diastereomeric mixture of *β*-thioalkoxyalcohols **5** and **6**.[14,15] Conjugated enynes **9** and **10** were obtained by the stereospecific elimination of *β*-thioalkoxyalcohol moiety in **5** and **6** under Mitsunobu conditions (diisopropyl azodicarboxylate (DIAD), Ph_3P).[12] The results are summarized in Table 1. The

Table 1. Synthesis of 9 and 10 from 1 and 4 via the Corresponding Organozinc Reagents 2 and 3 (M = Zn)[15]

entry	**1** (R^1)	**4** (R^2)	**5**/**6**[a]		**9**/**10**[a]	yield (%)[b]
1	**1a** (^{n}Bu)	**4a** (^{n}Bu)	26/74	**a**	28/72	58
2		**4b** (Ph)	23/77	**b**	24/77	63
3		**4c** (PhC≡C)	31/69	**c**	30/70	69
4	**1b** (^{i}Pr)	**4a** (^{n}Bu)	8/92	**d**	6/94	45
5		**4b** (Ph)	14/86	**e**	16/84	55
6		**4c** (PhC≡C)	4/96	**f**	5/95	62
7	**1c** (^{t}Bu)	**4a** (^{n}Bu)	84/16	**g**	85/15	51[c]
8		**4b** (Ph)	24/76	**h**	27/73	36[c]
9		**4c** (PhC≡C)	91/9	**i**	90/10	47

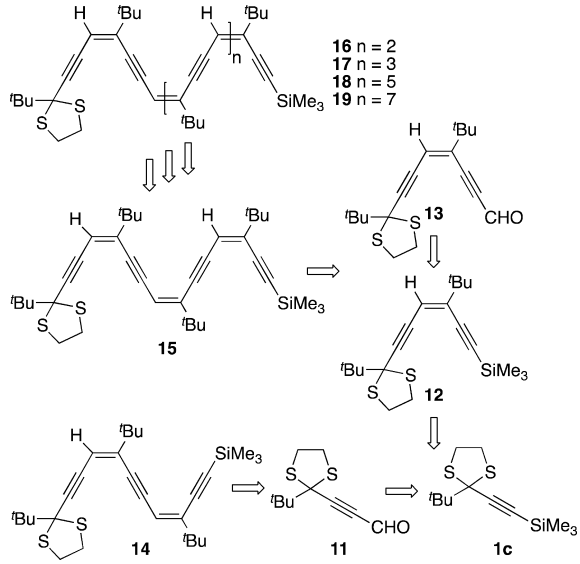
[a]Ratios of the crude mixtures before chromatographic purification.[14] [b]Overall yields of **9** and **10** from **1**. [c]Bu_3P was used in place of Ph_3P.

stereochemical assignments of **9** and **10** were based on NOE experiments,[14] and the ratios of the diastereomers **5** and **6** were thus determined.

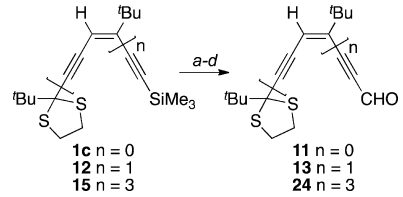
As shown in Table 1, reactions of **1a** with aldehydes **4a−c** under these conditions gave mixtures of **5a−c** and **6a−c** nonselectively (entries 1−3). When the *n*-butyl substituent in **1a** was replaced by the isopropyl group in **1b**, the reactions with aldehydes **4a−c** gave the corresponding products **5d−f** and **6d−f** with much better stereoselectivity, favoring **6** over **5** (entries 4−6). It is striking to note that when the *tert*-butyl-substituted substrate **1c** was employed, the diastereoselectivity for **5** and **6** was reversed when **4a** or **4c** was used as the electrophile (entries 7 and 9). Although the actual mode for this discrepancy remains to be clarified, the results appear to be useful for the stereoselective synthesis of conjugated enynes. It was therefore envisioned that a convergent synthesis of ODAs could be achieved stereoselectively by adopting this protocol. The strategy is outlined in Scheme 2.

Stereoselective Synthesis of *Z*-ODAs. Propargylic aldehyde **11** was obtained in overall 52% yield from **1c** according to Scheme 3. Treatment of organozinc species **2** and **3** (M = Zn,

Scheme 2. Synthetic Strategy for *Z*-ODAs 12 and 14−19



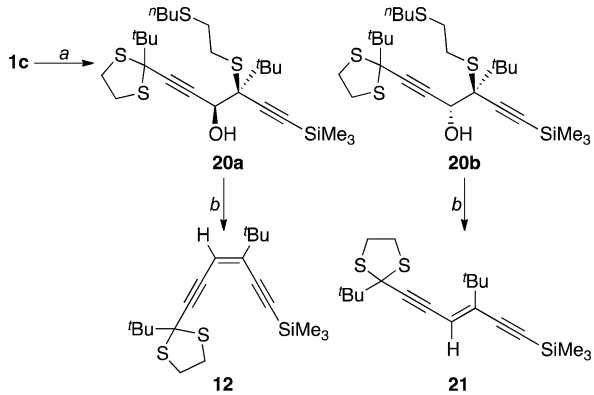
Scheme 3. Conversions of Acetylenylsilanes into Acetylenyl Aldehydes[a]



[a]Conditions: (*a*) K_2CO_3, 80% from **1c**, 85% from **12**, and 90% from **15**; (*b*) MeMgI, then $(CH_2O)_n$, 78% from **1c**, 65% from **12**, and 71% from **15**; (*c*) PCC, 85% to **11**; (*d*) MnO_2, 67% to **13** and 69% to **24**.

$R^1 = {}^t$Bu, $R^2 = Me_3Si$), obtained from the reaction of **1c** and ^{n}BuLi at −78 °C followed by addition of $ZnCl_2$, with **11** gave a 95% yield of a mixture of diastereomers **20a** and **20b** in a ratio of 89:11 (Scheme 4). The two diastereomers were separated by column

Scheme 4. Synthesis of 12 and 21 from 1c[a]



[a]Conditions: (*a*) (1) ^{n}BuLi, (2) $ZnCl_2$, (3) **11**, (**20a**:**20b** = 89:11); (*b*) DIAD, Ph_3P.

chromatography. Reaction of **20a** under Mitsunobu reaction conditions (DIAD, Ph_3P) gave **12** in 75% yield. Similarly, **21** was obtained from **20b** in 83% yield (Scheme 4). The results are outlined in Table 2, entry 1.

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Table 2. Synthesis of ODAs

entry	dithioacetal–trimethylsilane	dithioacetal–aldehyde	diastereomeric ratio of β-thioalkoxy alcohol	ODA	overall yield (%)
1	**1c**	**11**	**20a**:**20b** = 89:11	**12**	63
2	**12**	**11**	**22a**:**22b** = 92:8	**14**	51
3	**12**	**13**	**23a**:**23b** = 93:7	**15**	45
4	**15**	**11**	–[a]	**16**	36
5	**15**	**13**	–[a]	**17**	33
6	**15**	**24**	–[b]	**18**	30
7	**17**	**24**	–[b]	**19**	27

[a]Minor isomers were not detected by crude NMR analysis. [b]The characteristic peaks in the ^{1}H NMR spectra were overlapped with peaks due to other impurities. No attempts were made to get the diastereomeric ratio.

Compound **12**, having a *tert*-butyl-substituted dithiolane group at one end and a trimethylsilyl group at the other, can be considered as an enyne homologue of **1c**. Base-promoted removal of the Me_3Si group followed by treatment with MeMgI and paraformaldehyde and then oxidation with MnO_2 furnished **13** in 36% overall yield (Scheme 3). Again, **13** can be taken as an enyne homologue of **11**. It was envisioned that the route shown in Scheme 5 using reactions of homologues of **1c**, a dithioacetal–trimethylsilane, and homologues of **11**, a dithioacetal–aldehyde, could be adopted for the iterative convergent synthesis of *Z*-ODAs stereoselectively.

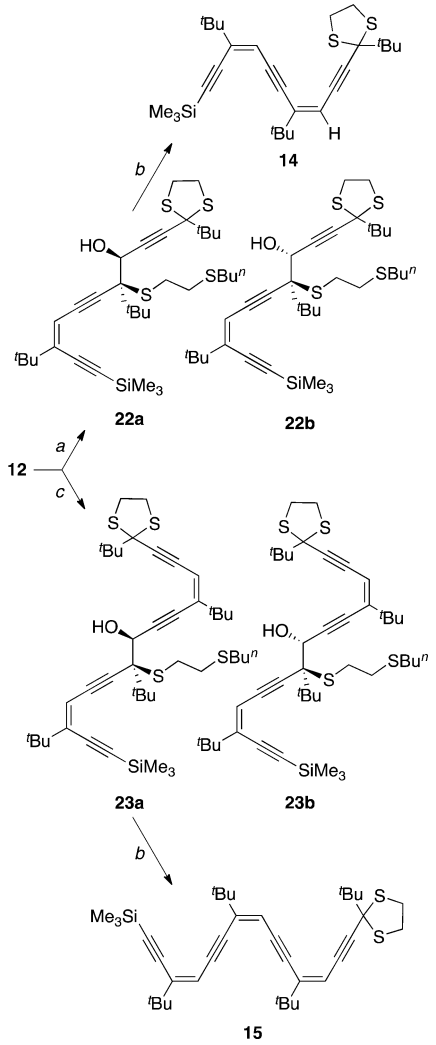
Under similar conditions, the reaction of **12** with ^{n}BuLi, $ZnCl_2$, and then with **11** afforded **22a** and **22b** (92:8). Pure **22a** was isolated in 70% yield after chromatographic separation. Elimination of the β-thioalkoxy alcohol moiety in **22a** under Mitsunobu conditions gave **14** in 73% yield (Table 2, entry 2 and Scheme 5).

Tetramer **15** was obtained in 45% yield from the reactions of **12** and **13** following the same sequence as described in Scheme 4. It is worth mentioning that no attempts were made to separate the two diastereomers **23a** and **23b**. The direct reaction of **23** under Mitsunobu conditions afforded **15** after chromatographic separation (Table 2, entry 3 and Scheme 5). Under the same conditions as those described for the preparation of **13**, **24** was obtained in 44% yield from **15** (Scheme 3).

By means of the same protocol, a combination of the reactions involving a dithioacetal–trimethylsilane (**15** or **17**) with a dithioacetal–aldehyde (**11**, **13**, or **24**) afforded *Z*-ODAs **16**–**19** selectively (Schemes 6 and 7). The results are summarized in Table 2, entries 4–7, and the details are described in the Experimental Section.

X-ray Structure of 17. The stereochemical assignments were based NOE experiments.[14] In particular, the X-ray structure of **17** shows unambiguously that every double bond is in *Z* configuration and that the conjugated enyne framework is almost planar (Figure 1a). The through-space distances between olefinic carbons and methyl carbons of nonadjacent ^{t}Bu groups in **17** (C14 and C32, C18 and C36, and C22 and C40) range from 3.96 to 4.31 Å. The dihedral angles between adjacent triple bonds attached to the same double bonds range from 0.35 to 2.48° in **17**. The dihedral angles for the related *Z*-ODA **29** (Chart 1) determined by X-ray diffraction, however, are 0°.[7a] These results indicate that **17** is somewhat less planar than **29**. Presumably, the presence of bulky *tert*-butyl groups in **17** slightly perturbs the planar conformation. In addition, the bond lengths for carbon–carbon single bonds in **17** are 1.41–1.43 Å, which are a little bit longer than those in **29** (1.40–1.41 Å). Moreover, the bond lengths for carbon–carbon double bonds in **17** (1.34–1.35 Å)

Scheme 5. Transformations of 12 into 22 and 23, Which Were Then Converted into 14 and 15, Respectively[a]



[a]Conditions: (*a*) (1) ^{n}BuLi, (2) $ZnCl_2$, (3) **11**, (**22a**: **22b** = 92:8), 70%; (*b*) DIAD, Ph_3P, 73% for **14**, 71% for **15**; (*c*) (1) ^{n}BuLi, (2) $ZnCl_2$, (3) **13**, (**23a**: **23b** = 93:7), 63%.

are shorter than those in **29** (1.35–1.36 Å). These comparisons suggest that **17** is less conjugated than **29**.

In the crystal packing, there are four molecules per unit cell (Figure 1b). The closest intermolecular carbon–carbon distance between a *tert*-butyl group of **17** and an alkynyl carbon of another molecule is 3.66 Å. This distance may be responsible for the deviation from a planar structure in **17** and reflect the unusual solid-state absorption properties, which will be discussed in the next section.

Photophysical Properties of ODAs. The absorption and emission spectra of **12** and **14**–**19** are shown in Figure 2, and the photophysical properties are summarized in Table 3. As expected, both λ_{max} (from 286 to 398 nm) and the molar absorptivity increase with increasing chain length (Figure 2a). The λ_{max} values for *Z*-ODAs in this study appear at shorter wavelengths in comparison with, for example, those of *E*-ODAs **30** with a similar number of conjugated enyne moieties (Chart 1).[5d] As discussed above, the X-ray structure of **17** appears to deviate slightly from a planar structure. The bond lengths for the carbon–carbon double bonds in **17** are somewhat shorter than those in **29**, and the bond lengths for the carbon–carbon single bonds in **17** are

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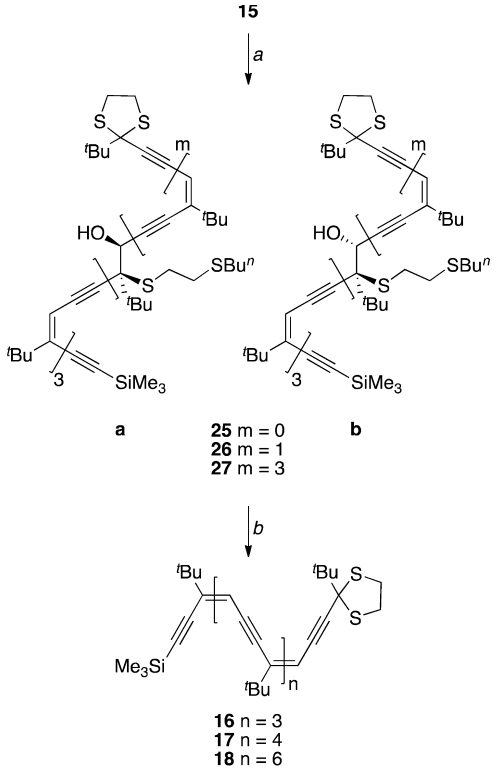
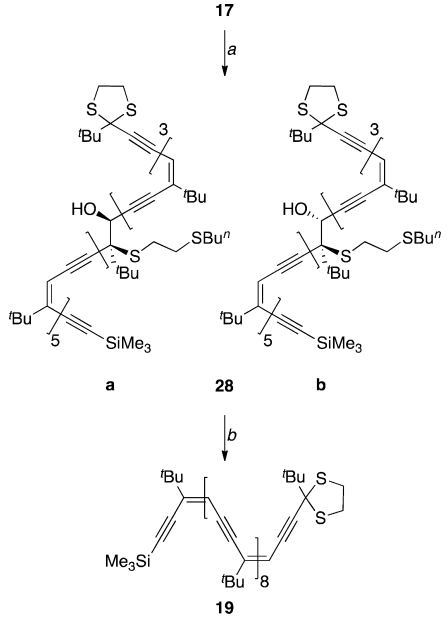
Scheme 6. Transformations of 15 into 25−27, Which Were Then Converted into 16−18[a]



[a]Conditions: (*a*) (1) ^{n}BuLi, (2) $ZnCl_2$, (3) **11** or **13** or **24**; (*b*) DIAD, Ph_3P. Overall yields: 36% for **16**, 33% for **17**, and 30% for **18**.

Scheme 7. Transformation of 17 into 28, Which Was Then Converted into 19[a]



[a]Conditions: (*a*) (1) ^{n}BuLi, (2) $ZnCl_2$, (3) **24**; (*b*) DIAD, Ph_3P. Overall yield: 27%.

slightly longer than those in **29**. The conjugation lengths for *Z*-ODAs in this study could be somewhat affected by this small deviation, although no X-ray structure for **30** is known. A plot of the energy gap corresponding to λ_{max} against $1/m$, where m is

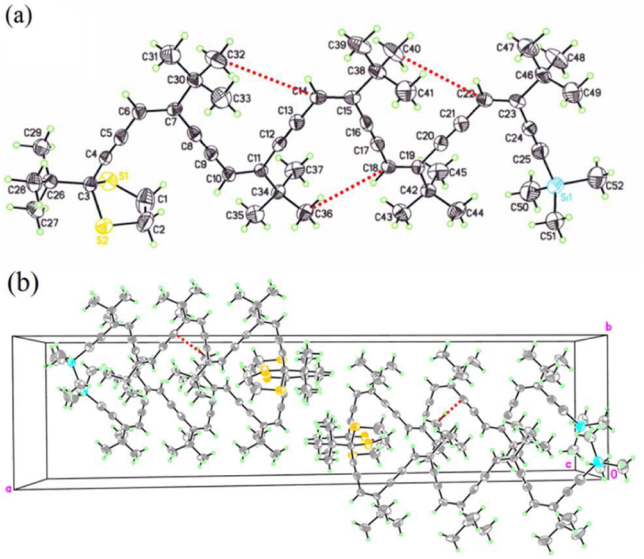
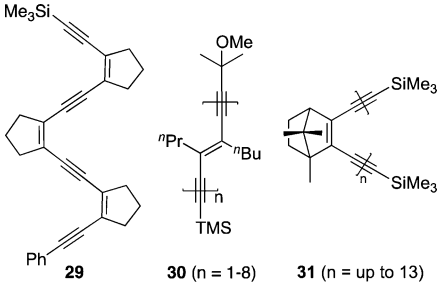


Figure 1. (a) ORTEP structure (50%) of **17**. Each dotted red line indicates the through-space distance between a methyl carbon atom in a *tert*-butyl group and an olefinic carbon atom. (b) Crystal packing of **17** in a unit cell. Each dotted red line indicates the closest through-space distance between a methyl carbon atom in a *tert*-butyl group in **17** and an alkynyl carbon atom in another molecule of **17**.

Chart 1. Selected *Z*- and *E*-ODAs from the Literature[5d,7a,b]



the total number of unsaturated bonds along the *Z*-ODA chain, gives a straight line (Figure 3). Like those of related conjugated systems,[7b,16] when the conjugation length is increased, the energy gap for **19** slightly deviates from the linearly extrapolated value based on this plot.

As mentioned above, PDAs exhibit color changes upon external stimulation.[1−3,17] It is believed that aggregation may be responsible for such color variations.[1−3,17] The λ_{max} value for **19** is 398 nm in cyclohexane and 402 nm in DCM. In contrast to *E*-ODAs,[5d−g] λ_{max} for **19** shows a blue shift in MeOH/DCM mixed solvents. Thus, it appeared at 388 nm when the sample was dissolved in 75:25 MeOH/DCM. Additional amounts of methanol may cause aggregation of **19**. Indeed, when 90:10 MeOH/DCM was used, λ_{max} further shifted to 370 nm and also exhibited strong tailing beyond 470 nm. The intensity of such tailing became stronger with increasing methanol content (Figure S1 in the Supporting Information). It seems likely that such tailing may arise from light scattering because it was also observed in the absorption spectrum of a thin film of **19**.[14]

The absorption spectrum for the solid film of **19** is also shown in Figure 2b. A significant shift to shorter wavelength (363 nm) together with scattering of light was observed. As mentioned in the previous section, a *tert*-butyl group in **17** is quite close to an alkynyl carbon in another molecule of **17** (3.66 Å) in a unit cell of the single crystal. This observation suggests that there might be

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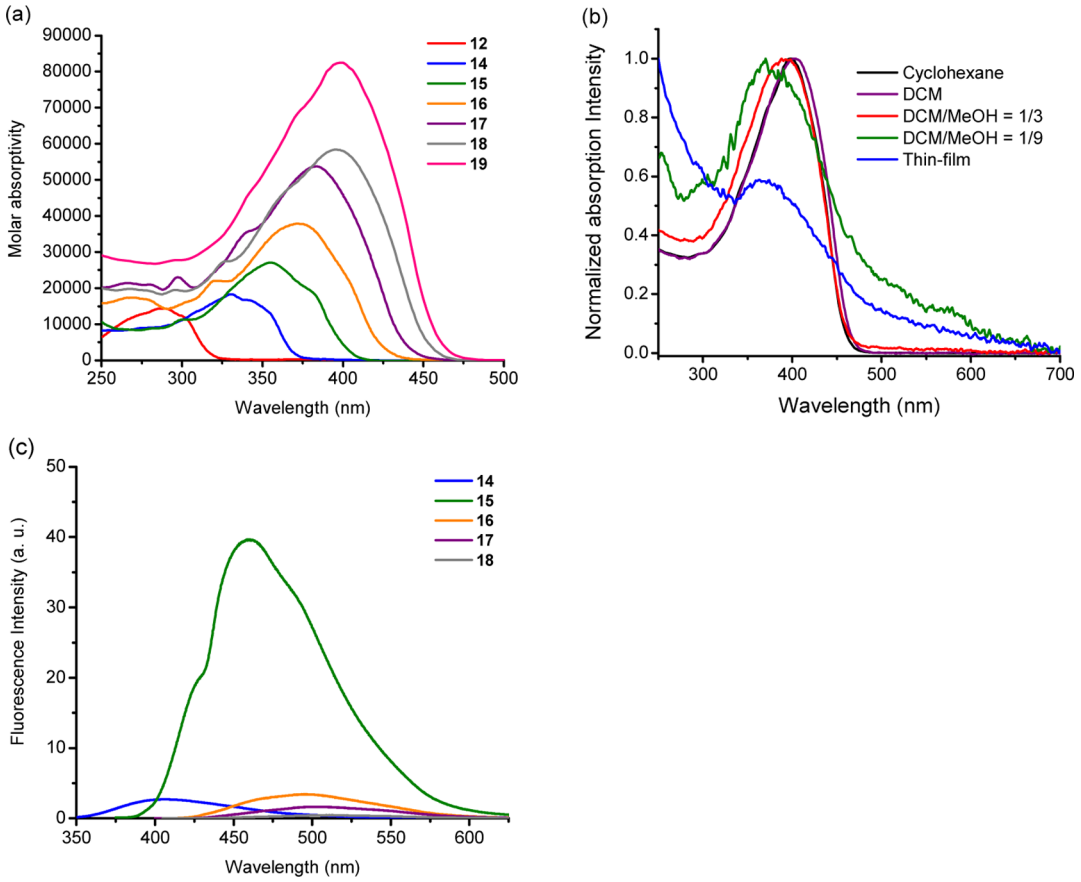

Figure 2. (a) Absorption spectra of *Z*-ODAs **12** and **14**–**19** in cyclohexane. (b) Absorption spectra of *Z*-ODA **19** in different solvents and as a thin film. (c) Fluorescence spectra of *Z*-ODAs **14**–**18** in cyclohexane.

Table 3. Photophysical Properties of ODAs[a]

ODA	m[b]	λ_{max} (log ε)[c]	λ_{em}[d] (Φ_f[e])	τ (ps)[f]
12	3	286 (4.16)	–[g]	
14	5	331 (4.26)	406 (0.007)	390
15	7	355 (4.43)	459 (0.065)	480
16	9	372 (4.58)	495 (0.005)	150
17	11	383 (4.73)	502 (0.003)	60
18	15	395 (4.77)	512 (0.0007)	40
19	19	398 (4.92)	–[g]	

[a]Absorption and fluorescence spectra were measured in cyclohexane. [b]m is the total number of unsaturated bonds along the ODA chain. [c]λ_{max} in nm and ε in M^{-1} cm^{-1}. [d]In nm. λ_{max} was used as the excitation wavelength in each of the emission spectra. [e]Coumarin 1 in EtOAc (Φ_f = 0.99) was used as the reference for the measurements of quantum yield (Φ_f) . [f]Fluorescence lifetimes measured by time-resolved spectroscopy. [g]No emission was detected.

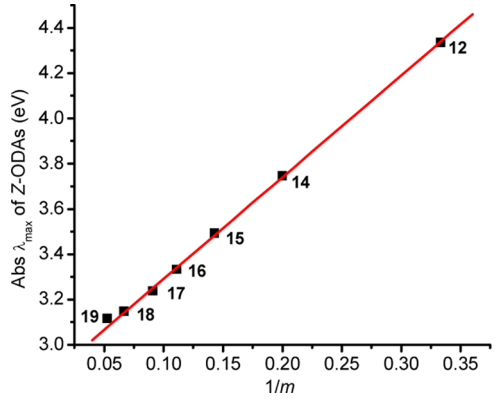

Figure 3. Plot of the energy gap corresponding to λ_{max} against $1/m$, where m is the number of unsaturated bonds along the conjugated chain.

interactions between the *tert*-butyl group of a molecule of **17** and the alkenyl group of another molecule of **17** in the solid state, which might lead to discrepancies from a planar structure. As a result, the absorption shifts toward the blue in the solid state in comparison with that in solution.

It is noteworthy that large hypsochromic shifts have been observed for similar *Z*-ODAs **31** (Chart 1).[7b] The λ_{max} values for *Z*-ODAs in the presence of fused strained rings, such as norbornene in **31**, are significantly perturbed, appearing at longer wavelengths than those in **12** and **14**–**19**.[7b,18]

The λ_{em} values for **14**–**18** appear from 406 to 512 nm (Figure 2c), whereas **12** and **19** are nonfluorescent. As shown in Table 3, the fluorescence quantum yields for **14**–**18** are relatively low. It is interesting to note that the quantum yield for **15** is the highest among this series. A similar observation was found in the emission spectra of **30**, the quantum yield being highest for n = 3.[5d] The fluorescence lifetimes (τ) for **13**–**18** increase in going from **14** to **15** but decrease after **15** with increasing chain length. A similar trend was observed in *E*-ODAs.[5d–g,19]

CONCLUSION

We have demonstrated a convenient stereoselective convergent iterative synthesis of a series of *Z*-ODAs from propargylic dithioacetal **1c** and aldehyde **11** and from their homologues. The

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key to the success of this protocol relies on the stereoselective formation of β-thioalkoxy alcohols when the propargylic dithioacetal substrates contain *tert*-butyl substituent(s) and the stereospecific formation of *Z* double bonds under Mitsunobu reaction coditions. The photophysical properties have been compared with those of related substituted *E*-ODAs. It is worth mentioning that *Z*-ODAs exibit hypsochromic shifts in poor solvents, whereas red shifts are found in *E*-ODAs. It seems likely that aggregation of ODAs may perturb the absorption maxima in either direction. Nevertheless, the photophysical features of the oligomers so far obtained in this study and reported in the literature appear to be incompatible with those of PDAs.

EXPERIMENTAL SECTION

General Information. High-resolution mass spectrometry was performed by the EI method with a magnetic sector analyzer, MALDI with a TOF analyzer, or ESI with TOF analyzer. Absorption and emission spectra were measured on a Hitachi U-3310 spectrometer and a Hitachi F-4500 fluorescence spectrometer, respectively, and the molar concentrations of the sample solutions were about 10^{-5} M. The thin film was obtained by spin-coating (2000 rpm) of a solution of **19** in toluene (1 mg/mL, 0.25 mL) on quartz (1 cm^2) and dried under vacuum for 2 h before measurement. The fluorescence quantum yields were obtained by the Parker−Reas method using coumarin I in EtOAc as the reference.[20]

Time-resolved fluorescence experiments were performed using a mode-locked Ti:sapphire laser (repetition rate = 76 MHz; pulse width < 200 fs) that was passed through an optical parametric amplifier to produce the desired wavelength. The fluorescence of the sample was reflected by a grating (150 grooves/mm; BLZ = 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 0.3 ps. The sample was prepared with a concentration of 1.0×10^{-5} M in a cuvette. The signal was collected 10 times to decrease the signal-to-noise ratio.

General Procedure for the Preparation of Enynes 9 and 10. Under an atmosphere of N_2, ^{n}BuLi (0.25 mL, 2.5 M in hexane, 0.63 mmol, 1.25 equiv) was added dropwise to a THF solution (10 mL) of **1** (0.5 mmol, 1.0 equiv) at −78 °C, and the mixture was stirred at −78 °C for 1 h. A THF solution (5 mL) of $ZnCl_2$ (100 mg, 1.47 equiv) was then added. After 15 min of stirring, a THF solution (5 mL) of **4** (0.75 mmol, 1.5 equiv) was added dropwise at −100 °C. The mixture was gradually warmed to rt, quenched with saturated NH_4Cl (10 mL), and extracted with ether (25 mL). The organic layer was washed with brine (10 mL), dried ($MgSO_4$), and filtered, and the filtrate was evaporated in vacuo to give crude homopropargylic alcohols **5** and **6**.

To a THF solution (5 mL) of crude homopropargylic alcohols **5** and **6** was added dropwise a mixture of DIAD (0.25 mL, d = 1.027 g/mL, 1.27 mmol) and Ph_3P (300 mg, 1.15 mmol) or Bu_3P (225 mg, 1.11 mmol) in THF (15 mL) at −78 °C. The mixture was gradually warmed to rt, stirred for 16 h, and evaporated in vacuo to give the residue, which was chromatographed on silica gel (hexane) to give **9** and **10**.

*3-Butyl-1-trimethylsilyloct-3Z-en-1-yne/3-Butyl-1-trimethylsilyloct-3E-en-1-yne (**9a/10a**).* In a manner similar to that described in the general procedure, **1a**[10b] (129 mg), **4a** (65 mg), and Ph_3P were transformed into **9a** and **10a** (69 mg, 58%, **9a**:**10a** = 33:67). ^{1}H NMR (400 MHz, $CDCl_3$) for **10a**: δ 0.18 (s, 9H), 0.86−0.94 (m, 6H), 1.24−1.40 (m, 6H), 1.43−1.53 (m, 2H), 2.04−2.14 (m, 4H), 5.92 (t, J = 7.4 Hz, 1H). Characteristic ^{1}H NMR signals for **9a** (400 MHz, $CDCl_3$): δ 0.19 (s, 9H), 2.26 (q, J = 7.2 Hz, 2H), 5.68 (t, J = 7.2 Hz, 1H). HRMS (EI, M^+): calcd for $C_{15}H_{28}Si$, 236.1960; found, 236.1957.

*1-Trimethylsilyl-3-butyl-4-phenylbut-3Z-en-1-yne/1-Trimethylsilyl-3-butyl-4-phenylbut-3E-en-1-yne (**9b/10b**).* In a manner similar to that described in the general procedure, **1a**[10b] (129 mg), **4b** (80 mg), and Ph_3P were transformed into **9b** and **10b** (81 mg, 63%, **9b**:**10b** = 23:77). ^{1}H NMR (400 MHz, $CDCl_3$) for **10b**: δ 0.23 (s, 9H), 0.90 (t, J = 7.2 Hz, 3H), 1.37 (sext, J = 7.2 Hz, 2H), 1.55−1.66 (m, 2H), 2.37 (t, J = 6.9 Hz, 2H), 6.90 (s, 1H), 7.21−7.27 (m, 3H), 7.28−7.38 (m, 2H). Characteristic ^{1}H NMR signals for **9b** (400 MHz, $CDCl_3$): δ 0.24 (s, 9H), 0.94 (t, J = 7.4 Hz, 3H), 2.30 (q, J = 7.2 Hz, 2H), 6.54 (s, 1H), 7.85 (d, J = 7.2 Hz, 2H). HRMS (EI, M^+): calcd for $C_{17}H_{24}Si$, 256.1647; found, 256.1642.

*1-Trimethylsilyl-3-butyl-6-phenylhex-3Z-en-1,5-diyne/1-Trimethylsilyl-3-butyl-6-phenylhex-3E-en-1,5-diyne (**9c/10c**).* In a manner similar to that described in the general procedure, **1a**[10b] (129 mg), **4c** (98 mg), and Ph_3P were transformed into **9c** and **10c** (97 mg, 69%, **9c**:**10c** = 32:68). ^{1}H NMR (400 MHz, $CDCl_3$) for **10c**: δ 0.21 (s, 9H), 0.96 (t, J = 7.2 Hz, 3H), 1.30−1.46 (m, 2H), 1.50−1.64 (m, 2H), 2.48 (t, J = 7.6 Hz, 2H), 6.03 (s, 1H), 7.28−7.38 (m, 3H), 7.40−7.46 (m, 2H). Characteristic ^{1}H NMR signals for **9c** (400 MHz, $CDCl_3$): δ 0.25 (s, 9H), 0.93 (t, J = 6.4 Hz, 3H), 2.25 (t, J = 7.4 Hz, 2H), 5.88 (s, 1H). HRMS (EI, M^+): calcd for $C_{19}H_{24}Si$, 280.1647; found, 280.1640.

*1-Trimethylsilyl-3-isopropyloct-3Z-en-1-yne/1-Trimethylsilyl-3-isopropyloct-3E-en-1-yne (**9d/10d**).* In a manner similar to that described in the general procedure, **1b**[10b] (122 mg), **4a** (65 mg), and Ph_3P were transformed into **9d** and **10d** (50 mg, 45%, **9d**:**10d** = 6:94). ^{1}H NMR (400 MHz, $CDCl_3$) for **10d**: δ 0.18 (s, 9H), 0.89 (t, J = 7.2 Hz, 3H), 1.05 (d, J = 6.8 Hz, 6H), 1.28−1.40 (m, 4H), 2.10 (q, J = 7.2 Hz, 2H), 2.72 (hept, J = 6.8 Hz, 1H), 5.83 (t, J = 7.2 Hz, 1H). Characteristic ^{1}H NMR signals for **9d** (400 MHz, $CDCl_3$): δ 1.06 (d, J = 6.4 Hz, 6H), 2.26 (q, J = 7.2 Hz, 2H), 2.31 (hept, J = 6.4 Hz, 1H), 5.70 (t, J = 7.2 Hz, 1H). HRMS (EI, M^+): calcd for $C_{14}H_{26}Si$, 222.1804; found, 222.1806.

*1-Trimethylsilyl-3-isopropyl-4-phenylbut-3Z-en-1-yne/1-Trimethylsilyl-3-isopropyl-4-phenylbut-3E-en-1-yne (**9e/10e**).* In a manner similar to that described in the general procedure, **1b**[10b] (122 mg), **4b** (80 mg), and Ph_3P were transformed into **9e** and **10e** (67 mg, 55%, **9e**:**10e** = 15:85). ^{1}H NMR (400 MHz, $CDCl_3$) for **10e**: δ 0.24 (s, 9H), 1.14 (d, J = 6.4 Hz, 6H), 3.03 (hept, J = 6.4 Hz, 1H), 6.83 (s, 1H), 7.20−7.28 (m, 3H), 7.29−7.37 (m, 2H). Characteristic ^{1}H NMR signals for **9e** (400 MHz, $CDCl_3$): δ 0.25 (s, 9H), 1.18 (d, J = 7.2 Hz, 6H), 2.55 (hept, J = 7.2 Hz, 1H), 6.57 (s, 1H), 7.87 (d, J = 7.6 Hz, 6H). HRMS (EI, M^+): calcd for $C_{16}H_{22}Si$, 242.1491; found, 242.1496.

*1-Trimethylsilyl-3-isopropyl-6-phenylhex-3Z-en-1,5-diyne/1-Trimethylsilyl-3-iso-propyl-6-phenylhex-3E-en-1,5-diyne (**9f/10f**).* In a manner similar to that described in the general procedure, **1b**[10b] (122 mg), **4c** (98 mg), and Ph_3P were transformed into **9f** and **10f** (83 mg, 62%, **9f**:**10f** = 5:95). ^{1}H NMR (400 MHz, $CDCl_3$) for **10f**: δ 0.22 (s, 9H), 1.13 (d, J = 6.8 Hz, 6H), 3.19 (hept, J = 6.8 Hz, 1H), 5.96 (s, 1H), 7.28−7.36 (m, 3H), 7.41−7.46 (m, 2H). Characteristic ^{1}H NMR signals for **9f** (400 MHz, $CDCl_3$): δ 0.25 (s, 9H), 2.51 (hept, J = 6.8 Hz, 1H), 5.91 (s, 1H). HRMS (EI, M^+): calcd for $C_{18}H_{22}Si$, 266.1491; found, 266.1495.

*1-Trimethylsilyl-3-tert-butyloct-3Z-en-1-yne/1-Trimethylsilyl-3-tert-butyloct-3E-en-1-yne (**9g/10g**).* In a manner similar to that described in the general procedure, **1c**[10a] (129 mg), **4a** (65 mg), and ^{n}Bu_3P were transformed into **9g** and **10g** (60 mg, 51%, **9g**:**10g** = 81:19). ^{1}H NMR (400 MHz, $CDCl_3$) for **9g**: δ 0.20 (s, 9H), 0.91 (t, J = 7.2 Hz, 3H), 1.10 (s, 9H), 1.27−1.43 (m, 4H), 2.82 (q, J = 7.2 Hz, 2H), 5.72 (t, J = 7.3 Hz, 1H). Characteristic ^{1}H NMR signals for **10g** (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 0.90 (t, J = 6.8 Hz, 3H), 1.22 (s, 9H), 5.91 (t, J = 7.8 Hz,1H). HRMS (EI, M^+): calcd for $C_{15}H_{28}Si$, 236.1960; found, 236.1952.

*1-Trimethylsilyl-3-tert-butyl-4-phenylbut-3Z-en-1-yne/1-Trimethylsilyl-3-tert-butyl-4-phenyl- but-3E-en-1-yne (**9h/10h**).* In a manner similar to that described in the general procedure, **1c**[10a] (129 mg), **4b** (80 mg), and ^{n}Bu_3P were transformed into **9h** and **10h** (51 mg, 36%, **9h**:**10h** = 29:71). ^{1}H NMR (400 MHz, $CDCl_3$) for **10h**: δ 0.23 (s, 9H), 1.08 (s, 9H), 7.07 (s, 1H), 7.12−7.17 (m, 2H), 7.19−7.34 (m, 3H). Characteristic ^{1}H NMR signals for **9h** (400 MHz, $CDCl_3$): δ 0.24 (s, 9H), 1.24 (s, 9H), 6.61 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H). HRMS (ESI, $[M + Na]^+$): calcd for $C_{17}H_{24}NaSi$, 279.1545; found, 279.1539.

*1-Trimethylsilyl-3-tert-butyl-6-phenylhex-3Z-en-1,5-diyne/1-Trimethylsilyl-3-tert-butyl-6- phenylhex-3E-en-1,5-diyne (**9i/10i**).* In a manner similar to that described in the general procedure, **1c**[10a] (129 mg), **4c** (98 mg), and Ph_3P were transformed into **9i** and **10i** (66 mg, 47%, **9i**:**10i** = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) for **9i**: δ 0.25 (s, 9H), 1.19 (s, 9H), 5.95 (s, 1H), 7.26−7.40 (m, 2H), 7.40−7.50 (m, 3H). Characteristic ^{1}H NMR signals for **10i** (400 MHz, $CDCl_3$): δ 0.21 (s, 9H), 1.38 (s, 9H), 6.15 (s, 1H). HRMS (EI, M^+): calcd for $C_{19}H_{24}Si$, 280.1647; found, 280.1648.

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2-*tert*-Butyl-2-(2-formylethynyl)-1,3-dithiolane (11). Under a nitrogen atmosphere, a solution of **1c**[10b] (12.9 g, 50 mmol) and K_2CO_3 (27.6 g, 200 mmol) in methanol (500 mL) was stirred for 20 h at rt. Water (300 mL) and hexane (200 mL) were then added, and the mixture was separated. The aqueous phase was extracted with hexane (2 × 200 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was evaporated in vacuo to give a residue that was chromatographed on silica gel (hexane) to afford corresponding terminal alkyne as a white solid (7.4 g, 80%).

Under an atmosphere of N_2, MeMgI (150 mL, 1.0 M Et_2O solution prepared from Mg and MeI, 150 mmol) was added dropwise to a THF solution (500 mL) of the terminal alkyne (18.6 g, 100 mmol) at −78 °C. After 0.5 h of stirring at this temperature, a powder of paraformaldehyde (12.0 g, 400 mmol) was added. The mixture was gradually warmed to rt and stirred for 4 h, quenched with saturated NH_4Cl, and filtered through a Celite bed (10 cm). Ether (200 mL) and brine (200 mL) were added. The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was evaporated in vacuo to give a residue that was chromatographed on silica gel (hexane/Et_2O = 3:1) to yield the corresponding alcohol as a colorless liquid (16.8 g, 78%).

To a solution of the alcohol (10.8 g, 50 mmol) in CH_2Cl_2 (200 mL) was slowly added a mixture of PCC (15.1 g, 70 mmol) and Celite (15.0 g) under vigorous stirring at 0 °C. The reaction mixture was stirred at room temperature for 12 h and then passed through a silica gel bed (5 cm) and washed with Et_2O (100 mL). The combined filtrate was evaporated in vacuo to give a residue that was chromatographed on silica gel (hexane/Et_2O = 10:1) to afford **11** as a colorless oil (9.1 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9H), 3.34−3.44 (m, 2H), 3.47−3.56 (m, 2H), 9.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.7, 39.9, 40.6, 70.2, 84.1, 98.7, 175.9. IR (KBr) ν: 2968, 2928, 2867, 2186, 1660, 1460, 1365, 1279, 1142, 872, 641 cm^{-1}. HRMS (EI, M$^+$): calcd for $C_{10}H_{14}OS_2$, 214.0486; found, 214.0481.

4-(1,4-Dithiaoctyl)-4-*tert*-butyl-1-(2-*tert*-butyl-1,3-dithiolan-2-yl)-6-(trimethylsilyl)hexa-1,5- diyn-3-ol (20). Under an atmosphere of N_2, ^{n}BuLi (0.75 mL, 1.6 M hexane solution, 1.20 mmol) was added dropwise to a THF solution (15 mL) of **1c**[10a] (284 mg, 1.10 mmol) at −78 °C. After 1 h of stirring at this temperature, a solution of $ZnCl_2$ (170 mg, 1.25 mmol) in THF (5 mL) was added. After 15 min of stirring, a THF solution (5 mL) of **11** (214 mg, 1.00 mmol) was added dropwise at −100 °C. The mixture was gradually warmed to rt, stirred for 6 h, and then quenched with saturated NH_4Cl (25 mL). The mixture was extracted with Et_2O (50 mL) and brine (50 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was evaporated in vacuo to give the residue of **20** (**20a**:**20b** = 89:11), which was chromatographed on silica gel (hexane/Et_2O = 50:1) to give **20a** as a pale-yellow liquid (451 mg, 85%) along with **20b** (16 mg, 3%).

Data for **20a**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.20 (s, 9H), 0.92 (t, J = 7.2 Hz, 3H), 1.20 (s, 9H), 1.27 (s, 9H), 1.35−1.46 (m, 2H), 1.52−1.62 (m, 2H), 2.55 (t, J = 7.4 Hz, 2H), 2.67 (d, J = 8.8 Hz, 1H), 2.72−2.81 (m, 2H), 3.04 (t, J = 8.2 Hz, 2H), 3.30−3.38 (m, 2H), 3.45−3.53 (m, 2H), 4.65 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0, 13.7, 21.9, 27.5, 27.6, 31.7, 31.8, 32.7, 33.1, 39.1, 39.9, 40.1, 63.5, 67.5, 71.2, 83.9, 89.4, 94.4, 102.1. IR (KBr) ν: 3438, 2958, 2928, 2871, 2160, 1460, 1392, 1364, 1249, 1202, 1154, 1043, 1015, 844, 760, 699 cm^{-1}. HRMS (MALDI, [M + Na]$^+$): calcd for $C_{26}H_{46}NaOSiS_4$, 553.2099; found, 503.2114.

Data for **20b**: ^{1}H NMR: δ 0.19 (s, 9H), 0.89 (t, J = 7.2 Hz, 3H), 1.17 (s, 9H), 1.27 (s, 9H), 1.33−1.44 (m, 2H), 1.50−1.60 (m, 2H), 2.54 (dt, J = 1.3, 7.4 Hz, 2H), 2.65−2.73 (m, 1H), 2.76−2.84 (m, 1H), 2.94 (d, J = 11.2 Hz, 1 H), 3.09−3.16 (m, 1H), 3.18−3.26 (m, 1H), 3.26−3.34 (m, 2H), 3.43−3.51 (m, 2H), 4.82 (d, J = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0, 13.7, 21.9, 27.3, 27.5, 31.7, 31.8, 32.6, 32.7, 39.4, 40.0, 40.2, 63.0, 66.4, 66.5, 71.1, 84.6, 87.8, 93.6, 102.9. IR (KBr) ν: 3446, 2957, 2925, 2870, 2158, 1460, 1392, 1364, 1249, 1202, 1154, 1046, 1023, 844, 760, 695 cm^{-1}. HRMS (MALDI, [M + Na]$^+$): calcd for $C_{26}H_{46}NaOSiS_4$, 553.2099; found, 553.2124.

1-Trimethylsilyl-3-*tert*-butyl-6-(2-*tert*-butyl-1,3-dithiolan-2-yl)hex-3*Z*-en-1,5-diyne (12). Under a nitrogen atmosphere, a THF solution (10 mL) of **20a** (531 mg, 1.0 mmol) was added dropwise to a THF solution (10 mL) of DIAD (0.43 mL, d = 1.027 g/mL, 2.2 mmol) and PPh_3 (524 mg, 2.0 mmol) at −78 °C. The mixture was gradually warmed to rt and stirred for 16 h, and the solvent was evaporated in vacuo to give a residue that was chromatographed on silica gel (hexane/Et_2O = 100:1) to give **12** as a white solid (274 mg, 75%). Mp: 33−34 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, 9H), 1.13 (s, 9H), 1.32 (s, 9H), 3.32−3.41 (m, 2H), 3.50−3.59 (m, 2H), 5.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.1, 27.9, 29.1, 36.4, 40.1, 40.3, 72.2, 83.2, 97.6, 102.3, 103.1, 112.0, 143.7. IR (KBr) ν: 2966, 2927, 2902, 2868, 2137, 1478, 1459, 1392, 1363, 1278, 1249, 1215, 1097, 878, 840, 759, 637 cm^{-1}. HRMS (MALDI, [M + H]$^+$): calcd for $C_{20}H_{33}SiS_2$, 365.1793; found, 365.1806.

1-Trimethylsilyl-3-*tert*-butyl-6-(2-*tert*-butyl-1,3-dithiolan-2-yl)hex-3*E*-en-1,5-diyne (21). Under a nitrogen atmosphere, a THF solution (10 mL) of **20b** (531 mg, 1.0 mmol) was added dropwise to a THF solution (10 mL) of DIAD (0.43 mL, 2.2 mmol) and PPh_3 (524 mg, 2.0 mmol) at −78 °C. The mixture was gradually warmed to rt and stirred for 16 h, and the solvent was evaporated in vacuo to give a residue that was chromatographed on silica gel (hexane/Et_2O = 100:1) to give **21** as a colorless oil (303 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.19 (s, 9H), 1.25 (s, 9H), 1.30 (s, 9H), 3.31−3.40 (m, 2H), 3.43−3.51 (m, 2H), 6.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.1, 27.7, 29.7, 35.7, 40.2, 40.3, 72.5, 82.8, 98.3, 103.8, 106.5, 115.2, 143.4. IR (KBr) ν: 2957, 2924, 2868, 2130, 1459, 1393, 1363, 1249, 1215, 1178, 1130, 1026, 843, 758, 697 cm^{-1}. HRMS (MALDI, [M + H]$^+$): calcd for $C_{20}H_{33}SiS_2$, 365.1793; found, 365.1808.

1-(2-*tert*-Butyl-1,3-dithiolan-2-yl)-4-(1,4-dithiaoctyl)-4,8-di-*tert*-butyl-10-(trimethylsilyl)dec-7*Z*-en-1,5,9-triyn-3-ol (22). In a manner similar to that described in the synthesis of compound **20**, a mixture of **12** (401 mg, 1.10 mmol), ^{n}BuLi (0.75 mL, 1.6 M hexane solution, 1.20 mmol), $ZnCl_2$ (170 mg, 1.25 mmol), and **1** (214 mg, 1.00 mmol) was transformed into **22** (**22a**:**22b** = 92:8), which was chromatographed on silica gel (hexane/Et_2O = 50:1) to give **22a** as pale-yellow liquid (446 mg, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.21 (s, 9H), 0.91 (t, J = 7.2 Hz, 3H), 1.15 (s, 9H), 1.25 (s, 9H), 1.26 (s, 9H), 1.30−1.46 (m, 2H), 1.48−1.62 (m, 2H), 2.55 (t, J = 7.2 Hz, 2H), 2.68−2.84 (m, 2H), 2.89 (d, J = 9.0 Hz, 1H), 3.06 (t, J = 8.0 Hz, 2H), 3.28−3.38 (m, 2H), 3.44−3.54 (m, 2H), 4.69 (d, J = 9.0 Hz, 1H), 5.77 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0, 13.8, 22.1, 25.7, 27.7, 27.9, 29.1, 31.9, 33.1, 36.6, 39.5, 39.9, 40.0, 64.2, 68.1, 68.2, 71.6, 84.4, 88.2, 89.5, 91.7, 103.4, 110.9, 145.3. IR (KBr) ν: 3500, 2958, 2926, 2869, 2136, 1460, 1392, 1363, 1249, 1201, 1150, 1098, 1017, 877, 841, 760 cm^{-1}. HRMS (MALDI, [M + H]$^+$): calcd for $C_{34}H_{57}OS_4Si$, 637.3062; found, 637.3079. Characteristic ^{1}H NMR signals for **22b** (400 MHz, $CDCl_3$): δ 4.87 (d, J = 11.2 Hz, 1H, RR′*H*COH).

1-Trimethylsilyl-3,7-di-*tert*-butyl-10-(2-*tert*-butyl-1,3-dithiolan-2-yl)deca-3*Z*,7*Z*-dien-1,5,9- triyne (14). In a manner similar to that described in the synthesis of compound **12**, a mixture of **22a** (319 mg, 0.50 mmol), DIAD (0.22 mL, 1.10 mmol), and PPh_3 (262 mg, 1.00 mmol) was transformed into **14** as a white solid (274 mg, 73%). Mp: 87−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, 9H), 1.17 (s, 9H), 1.21 (s, 9H), 1.33 (s, 9H), 3.32−3.41 (m, 2H), 3.50−3.60 (m, 2H), 5.79 (s, 1H), 5.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.1, 27.8, 29.2, 29.5, 36.5, 36.6, 40.1, 40.2, 72.4, 83.9, 93.9, 95.8, 97.7, 103.2, 103.3, 111.6, 112.3, 144.3, 144.8. IR (KBr) ν: 2963, 2926, 2868, 2136, 1477, 1460, 1392, 1362, 1249, 1191, 1160, 1098, 878, 841, 759, 637 cm^{-1}. HRMS (FAB, [M + H]$^+$): calcd for $C_{28}H_{43}SiS_2$, 471.2575; found, 471.2570.

4-*tert*-Butyl-7-(2-*tert*-butyl-1,3-dithiolan-2-yl)hept-4*Z*-en-2,6-diyn-1-al (13). In a manner similar to that described in the synthesis of compound **11**, a mixture of **12** (3.65 g, 10 mmol) and K_2CO_3 (5.52g, 40 mmol) was transformed into the corresponding terminal alkyne as a white solid (2.48 g, 85%).

A mixture of the alkyne (1.46 g, 5.0 mmol), MeMgI (7.5 mL, 1.0 M Et_2O solution, 7.5 mmol), and paraformaldehyde (0.6 g, 20 mmol) was transformed into corresponding alcohol as a colorless liquid (1.05 g, 65%).

Under an atmosphere of N_2, a CH_2Cl_2 solution (10 mL) of the alcohol (0.97 g, 3.0 mmol) was added to a suspension of MnO_2 (10.4 g, 120 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C and monitored by TLC. Extra MnO_2 (2.6 g, 30 mmol) was added to the mixture every 30 min until the reaction was complete. After completion of the reaction, the mixture was filtered through a silica

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gel bed (10 cm) and washed with Et_2O (100 mL). The filtrate was dried ($MgSO_4$) and evaporated in vacuo, and the residue was chromatographed on silica gel (hexane/Et_2O = 3:1) to give **13** as a pale-yellow liquid (0.64 g, 67%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 9H), 1.31 (s, 9H), 3.35−3.44 (m, 2H), 3.52−3.60 (m, 2H), 6.11 (s, 1H), 9.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.9, 29.3, 36.5, 40.1, 40.5, 72.0, 82.3, 93.5, 94.7, 101.3, 118.5, 140.8, 175.6. IR (KBr) ν: 2964, 2920, 2867, 2174, 1658, 1460, 1391, 1363, 1185, 1137, 971, 742 cm^{-1}. HRMS (MALDI, $[M + H]^+$): calcd for $C_{18}H_{25}OS_2$, 321.1347; found, 321.1356.

1-(2-*tert*-Butyl-1,3-dithiolan-2-yl)-4,8,12-tri-*tert*-butyl-8-(1,4-dithiaoctyl)-14-(trimethylsilyl)tetradeca-3*Z*,11*Z*-dien-1,5,9,13-tetrayn-7-ol (23). In a manner similar to that described in the synthesis of compound **20a**, a mixture of **12** (401 mg, 1.10 mmol), ^{n}BuLi (0.75 mL, 1.6 M hexane solution, 1.20 mmol), $ZnCl_2$ (170 mg, 1.25 mmol), and **13** (321 mg, 1.00 mmol) was transformed into **23** (**23a**:**23b** = 93:7), which was chromatographed on silica gel (hexane/Et_2O = 50:1) to give **23a** as pale-yellow liquid (470 mg, 63%). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.20 (s, 9H), 0.90 (t, J = 7.4 Hz, 3H), 1.14 (s, 9H), 1.15 (s, 9H), 1.27 (s, 9H), 1.31 (s, 9H), 1.34−1.42 (m, 2H), 1.48−1.58 (m, 2H), 2.52 (t, J = 7.2 Hz, 2H), 2.68−2.82 (m, 2H), 2.96−3.10 (m, 3H, embodied a doublet at δ 3.06 (J = 8.4 Hz, 1H)), 3.30−3.40 (m, 2H), 3.50−3.62 (m, 2H), 4.80 (d, J = 8.8 Hz, 1H), 5.78 (s, 1H), 5.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.1, 13.9, 22.1, 27.8, 27.9, 29.1, 29.2, 31.8, 31.9, 33.0, 33.2, 36.6, 36.8, 39.6, 40.1, 40.2, 40.3, 64.3, 68.3, 72.4, 83.3, 85.8, 88.2, 91.8, 96.8, 97.4, 103.3, 103.4, 110.1, 112.0, 143.7, 145.2. IR (KBr) ν: 3480, 2956, 2916, 2849, 2140, 1732, 1456, 1358, 1249, 1199, 906, 876, 841, 730 cm^{-1}. HRMS (MALDI, $[M + Na]^+$): calcd for $C_{42}H_{66}NaOS_4Si$, 765.3665; found, 765.3689. Characteristic ^1H NMR signals for **23b** (400 MHz, $CDCl_3$): δ 4.98 (d, J = 10.4 Hz, 1H, RR′*H*COH).

1-Trimethylsilyl-3,7,11-tri-*tert*-butyl-14-(2-*tert*-butyl-1,3-dithiolan-2-yl)tetradeca-3*Z*,7*Z*,11*Z*- trien-1,5,9,13-tetrayne (15). In a manner similar to that described in the synthesis of compound **12**, a mixture of **23a** (744 mg, 1.0 mmol), DIAD (0.43 mL, 2.2 mmol), and PPh_3 (524 mg, 2.0 mmol) was transformed into the crude product, which was recrystallized in Et_2O/MeOH to obtain **15** as a white solid (410 mg, 71%). Mp: 109−110 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 9H), 1.15 (s, 9H), 1.19 (s, 9H), 1.23 (s, 9H), 1.32 (s, 9H), 3.30−3.40 (m, 2H), 3.50−3.60 (m, 2H), 5.78 (s, 1H), 5.87 (s, 1H), 5.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.1, 27.8, 29.1, 29.2, 29.5, 36.5, 36.6, 36.8, 40.1, 40.2, 72.4, 83.9, 93.8, 93.9, 96.4, 96.5, 97.7, 103.2, 103.4, 111.2, 111.8, 112.3, 144.5, 144.9, 145.3. IR (KBr) ν: 2963, 2934, 2898 2875, 2134, 1457, 1366, 1249, 1199, 1100, 878, 841 cm^{-1}. HRMS (MALDI, $[M + H]^+$): calcd for $C_{36}H_{53}S_2Si$, 577.3358; found, 577.3358.

4,8,12-Tri-*tert*-butyl-15-(2-*tert*-butyl-1,3-dithiolan-2-yl)-pentadeca-4*Z*,8*Z*,12*Z*-trien-2,6,10,14- tetrayn-1-al (24). By the same procedure as described in the synthesis of compound **13**, a mixture of **15** (400 mg, 0.69 mmol) and K_2CO_3 (400 mg, 2.90 mmol) was transformed into the terminal alkyne as a white solid (315 mg, 90%). A mixture of the terminal alkyne (300 mg, 0.52 mmol), MeMgI (1.0 mL, 1.0 M Et_2O solution, 1.0 mmol), and paraformaldehyde (72 mg, 2.4 mmol) was then transformed into the corresponding alcohol as a white solid (198 mg, 71%). A mixture of the alcohol (175 mg, 0.33 mmol) and MnO_2 (600 mg, 6.9 mmol) was transformed into **24** as a pale-yellow oil (120 mg, 69%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 9H), 1.19 (s, 9H), 1.23 (s, 9H), 1.31 (s, 9H), 3.32−3.41 (m, 2H), 3.50−3.58 (m, 2H), 5.80 (s, 1H), 5.94 (s, 1H), 6.19 (s, 1H), 9.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.7, 29.1, 29.2, 29.3, 36.5, 36.6, 36.7, 40.1, 40.2, 72.4, 83.7, 93.3, 94.6, 95.1, 95.2, 95.9, 97.0, 98.0, 111.8, 113.2, 118.6, 141.5, 144.4, 144.5, 176.1. IR (KBr) ν: 2965, 2929, 2868, 2176, 1660, 1477, 1460, 1391, 1362, 1252, 1195, 1136, 968, 837, 745, 650 cm^{-1}. HRMS (ESI, $[M + Na]^+$): calcd for $C_{34}H_{44}ONaS_2$, 555.2731; found, 555.2750.

1-Trimethylsilyl-3,7,11,15-tetra-*tert*-butyl-18-(2-*tert*-butyl-1,3-dithiolan-2-yl)octadeca-3*Z*,7*Z*,11*Z*,15*Z*-tetraen-1,5,9,13,17-pentayne (16). In a manner similar to that described in the synthesis of **20**, a mixture of **15** (120 mg, 0.21 mmol), ^{n}BuLi (0.15 mL, 1.6 M hexane solution, 0.24 mmol), $ZnCl_2$ (34 mg, 0.25 mmol), and **11** (54 mg, 0.25 mmol) was transformed into the homopropargylic alcohol as an orange-yellow oil (122 mg, 68%). In a manner similar to that described in the synthesis of **12**, a mixture of the homopropargylic alcohol, DIAD (0.22 mL, 1.1 mmol), and PPh_3 (262 mg, 1.0 mmol) was transformed into the crude product, and subsequent chromatographic separation on silica gel (hexane/Et_2O = 50:1) and recrystallization in Et_2O/MeOH afforded **16** as pale-yellow solid (52 mg, 36% for two steps). Mp: 135−136 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 9H), 1.16 (s, 9H), 1.20 (s, 9H), 1.22 (s, 9H), 1.23 (s, 9H), 1.32 (s, 9H), 3.32−3.42 (m, 2H), 3.50−3.60 (m, 2H), 5.77 (s, 1H), 5.86 (s, 1H), 5.88 (s, 1H), 5.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.1, 27.7, 29.0, 29.1, 29.2, 29.4, 36.5, 36.6, 36.7, 40.0, 40.1, 72.5, 84.0, 93.9, 96.5, 96.7, 97.3, 97.7, 103.3, 103.5, 111.3, 111.5, 111.9, 112.3, 144.7, 145.1, 145.5, 145.7. IR (KBr) ν: 2962, 2930, 2873, 2136, 1480, 1457, 1395, 1361, 1250, 1198, 1152, 1101, 1032, 878, 841 cm^{-1}. HRMS (MALDI, $[M + H]^+$): calcd for $C_{44}H_{63}S_2Si$, 683.4141; found, 683.4161.

1-Trimethylsilyl-3,7,11,15,19-penta-*tert*-butyl-22-(2-*tert*-butyl-1,3-dithiolan-2-yl)docosa-3*Z*,7*Z*,11*Z*,15*Z*,19*Z*-pentaen-1,5,9,13,17,21-hexayne (17). In a manner similar to that described in the synthesis of **20**, a mixture of **15** (120 mg, 0.21 mmol), ^{n}BuLi (0.15 mL, 1.6 M hexane solution, 0.24 mmol), $ZnCl_2$ (34 mg, 0.25 mmol), and **13** (80 mg, 0.25 mmol) was transformed into the homopropargylic alcohol as an orange-yellow oil (127 mg, 63%). In a manner similar to that described in the synthesis of compound **12**, a mixture of the homopropargylic alcohol, DIAD (0.22 mL, 1.1 mmol), and PPh_3 (262 mg, 1.0 mmol) was transformed into the crude product, and subsequent chromatographic separation on silica gel (hexane/Et_2O = 50:1) and recrystallization in Et_2O/MeOH afforded **17** as a yellow solid (55 mg, 33% for two steps). Mp: 180 °C (dec.). ^1H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 9H), 1.16 (s, 9H), 1.20 (s, 9H), 1.22 (s, 9H), 1.23 (br s, 18H), 1.25 (s, 9H), 1.32 (s, 9H), 3.32−3.42 (m, 2H), 3.50−3.60 (m, 2H), 5.77 (s, 1H), 5.85 (s, 1H), 5.86 (s, 1H), 5.87 (s, 1H), 5.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.1, 27.8, 29.0, 29.1, 29.2, 29.3, 29.5, 36.6, 36.7, 36.8, 40.1, 40.2, 72.5, 83.9, 93.9, 96.5, 96.6, 97.2, 97.3, 97.6, 103.2, 103.5, 111.1 111.4 111.5 111.7, 112.2, 144.8, 145.1, 145.6, 145.8. IR (KBr) ν: 2963, 2972, 2904, 2865, 2140, 1483, 1456, 1395, 1364, 1256, 1202, 1152, 1105, 881, 840 cm^{-1}. HRMS (MALDI, $[M + H]^+$): calcd for $C_{52}H_{73}S_2Si$, 789.4923; found, 789.4952.

1-Trimethylsilyl-3,7,11,15,19,23,27-hepta-*tert*-butyl-30-(2-*tert*-butyl-1,3-dithiolan-2-yl)triaconta-3*Z*,7*Z*,11*Z*,15*Z*,19*Z*,23*Z*,27*Z*-heptaen-1,5,9,13,17,21,25,29-octayne (18). In a manner similar to that described in the synthesis of **20**, a mixture of **15** (120 mg, 0.21 mmol), ^{n}BuLi (0.15 mL, 1.6 M hexane solution, 0.24 mmol), $ZnCl_2$ (34 mg, 0.25 mmol), and **24** (133 mg, 0.25 mmol) was transformed into the homopropargylic alcohol as an orange-yellow solid (149 mg, 61%). In a manner similar to that described in the synthesis of compound **12**, a mixture of the homopropargylic alcohol, DIAD (0.22 mL, 1.1 mmol), and PPh_3 (262 mg, 1.0 mmol) was transformed into the crude product, and subsequent chromatographic separation on silica gel (hexane/Et_2O = 50:1) and recrystallization in Et_2O/MeOH afforded **18** as a yellow solid (64 mg, 30% for two steps). Mp: 180 °C (dec.). ^1H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, 9H), 1.16 (s, 9H), 1.20 (s, 9H), 1.22 (s, 9H), 1.23 (s, 9H), 1.24 (br s, 27H), 1.33 (s, 9H), 3.32−3.42 (m, 2H), 3.52−3.60 (m, 2H), 5.77 (s, 1H), 5.85 (s, 1H), 5.86 (br s, 3H), 5.87 (s, 1H), 5.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.1, 27.7, 29.1, 29.2, 29.4, 36.5, 36.6, 36.7, 40.0, 40.1, 72.5, 84.0, 93.9, 94.0, 94.1, 96.5, 96.7, 97.4, 97.5, 97.7, 103.3, 103.5, 111.2, 111.4, 111.5, 111.8, 112.3, 144.8, 145.1, 145.6, 145.8, 145.9, 150.0. IR (KBr) ν: 2966, 2954, 2931, 2904, 2873, 2140, 1478, 1460, 1399, 1360, 1253, 1152, 1098, 1024, 878, 841 cm^{-1}. HRMS (MALDI, $[M + H]^+$): calcd for $C_{68}H_{93}S_2Si$, 1001.6488; found, 1001.6527.

1-Trimethylsilyl-3,7,11,15,19,23,27,31,35-nona-*tert*-butyl-38-(2-*tert*-butyl-1,3-dithiolan-2-yl)octatriaconta-3*Z*,7*Z*,11*Z*,15*Z*,19*Z*,23*Z*,27*Z*,31*Z*,35*Z*-nonaen-1,5,9,13,17,21,25,29,33,37-decayne (19). In a manner similar to that described in the synthesis of compound **20**, a mixture of **17** (100 mg, 0.13 mmol), ^{n}BuLi (0.10 mL, 1.6 M hexane solution, 0.16 mmol), $ZnCl_2$ (30 mg, 0.22 mmol), and **24** (100 mg, 0.19 mmol) was transformed into the homopropargylic alcohol as an orange-yellow solid (105 mg, 59%). In a manner similar to that described in the synthesis of compound **12**, a mixture of the homopropargylic alcohol, DIAD (0.22 mL, 1.1 mmol), and PPh_3 (262 mg, 1.0 mmol) was transformed into the crude product, and subsequent chromatographic

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separation on silica gel (hexane/Et_2O = 50:1) and recrystallization in Et_2O/MeOH twice and hexane twice afforded **19** as a yellow solid (42 mg, 27% for two steps). Mp: 180 °C (dec.). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.20 (s, 9H), 1.16 (s, 9H), 1.21 (s, 9H), 1.22 (s, 9H), 1.23 (br s, 54H), 1.30 (s, 9H), 3.32−3.41 (m, 2H), 3.48−3.57 (m, 2H), 5.79 (s, 1H), 5.87 (s, 1H), 5.88 (br s, 4H), 5.89 (s, 1H), 5.90 (s, 1H), 5.91 (s, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 0.1, 28.0, 29.4, 29.5, 29.7, 31.4, 37.1, 37.3, 40.5, 40.8, 72.9, 84.3, 94.5, 97.1, 97.3, 98.1, 98.7, 103.8, 104.3, 111.8, 112.0, 112.4, 112.7, 145.7, 146.4, 146.7. IR (KBr) ν: 2964, 2920, 2867, 2174, 1658, 1460, 1391, 1363, 1185, 1137, 971, 742 cm^{-1}. HRMS (MALDI, $[M + Na]^+$): calcd for $C_{84}H_{112}NaS_2Si$, 1235.7866; found, 1235.7828.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01626.

^{1}H and ^{13}C NMR spectra of new compounds and/or NOE spectra of **9**, **10**, **12**, and **14**−**19**, absorption spectra of **19** in mixed DCM/MeOH solvents, and time-resolved fluorescence profiles for **14**−**18** (PDF)

X-ray crystal data for **17** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For reviews, see: (a) Chu, B.; Xu, R. *Acc. Chem. Res.* **1991**, *24*, 384−389. (b) Sarkar, A.; Okada, S.; Matsuzawa, H.; Matsuda, H.; Nakanishi, H. *J. Mater. Chem.* **2000**, *10*, 819−828. (c) Lauher, J. W.; Fowler, F. W.; Goroff, N. S. *Acc. Chem. Res.* **2008**, *41*, 1215−1229. (d) Ahn, D. J.; Lee, S.; Kim, J.-M. *Adv. Funct. Mater.* **2009**, *19*, 1483−1496. (e) Yarimaga, O.; Jaworski, J.; Yoon, B.; Kim, J.-M. *Chem. Commun.* **2012**, *48*, 2469−2485. (f) Chen, X.; Zhou, G.; Peng, X.; Yoon, J. *Chem. Soc. Rev.* **2012**, *41*, 4610−4630. (g) Hill, S. C.; Htet, Y.; Kauffman, J.; Han, I. Y.; Dawson, P. L.; Pennington, W. T.; Hanks, T. W. *ACS Symp. Ser.* **2013**, *1138*, 137−154.

(2) For reviews, see: (a) Okada, S.; Peng, S.; Spevak, W.; Charych, D. *Acc. Chem. Res.* **1998**, *31*, 229−239. (b) Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* **2005**, *41*, 3245−3258. (c) Reppy, M. A.; Pindzola, B. A. *Chem. Commun.* **2007**, *43*, 4317−4338. (d) Zhou, W.; Li, Y.; Zhu, D. *Chem. - Asian J.* **2007**, *2*, 222−229. (e) Ahn, D. J.; Kim, J.-M. *Acc. Chem. Res.* **2008**, *41*, 805−816. (f) Yoon, B.; Lee, S.; Kim, J.-M. *Chem. Soc. Rev.* **2009**, *38*, 1958−1968. (g) Sun, X.; Chen, T.; Huang, S.; Li, L.; Peng, H. *Chem. Soc. Rev.* **2010**, *39*, 4244−4257. (h) Gravel, E.; Ogier, J.; Arnauld, T.; Mackiewicz, N.; Ducongé, F.; Doris, E. *Chem. - Eur. J.* **2012**, *18*, 400−408. (i) Jelinek, R.; Ritenberg, M. *RSC Adv.* **2013**, *3*, 21192.

(3) For selected recent examples, see: (a) Wang, X.; Sun, X.; Hu, P. A.; Zhang, J.; Wang, L.; Feng, W.; Lei, S.; Yang, B.; Cao, W. *Adv. Funct. Mater.* **2013**, *23*, 6044−6050;(b) *Adv. Funct. Mater.* **2013**, *23*, 6044−6050. (c) Zou, G.; Hu, W.; Taguchi, D.; Manaka, T.; Iwamoto, M. *Chem. Commun.* **2013**, *49*, 8105−8107. (d) Rondeau-Gagné, S.; Néabo, J. R.; Desroches, M.; Levesque, I.; Daigle, M.; Cantin, K.; Morin, J.-F. *Chem. Commun.* **2013**, *49*, 9546−9548. (e) Assali, M.; Cid, J.-J.; Fernández, I.; Khiar, N. *Chem. Mater.* **2013**, *25*, 4250−4261. (f) Xu, Q.; Lee, S.; Cho, Y.; Kim, M. H.; Bouffard, J.; Yoon, J. *J. Am. Chem. Soc.* **2013**, *135*, 17751−17754. (g) Banerjee, S.; König, B. *J. Am. Chem. Soc.* **2013**, *135*, 2967−2970. (h) Gravel, E.; Thézé, B.; Jacques, I.; Anilkumar, P.; Gombert, K.; Ducongé, F.; Doris, E. *Nanoscale* **2013**, *5*, 1955−1960. (i) Yan, X.; An, X. *Nanoscale* **2013**, *5*, 6280−6283. (j) Lee, S.; Lee, J.; Lee, M.; Cho, Y. K.; Baek, J.; Kim, J.; Park, S.; Kim, M. H.; Chang, R.; Yoon, J. *Adv. Funct. Mater.* **2014**, *24*, 3699−3705. (k) Park, D.-H.; Hong, J.; Park, I. S.; Lee, C. W.; Kim, J.-M. *Adv. Funct. Mater.* **2014**, *24*, 5186−5193. (l) Hu, W.; Chen, Y.; Jiang, H.; Li, J.; Zou, G.; Zhang, Q.; Zhang, D.; Wang, P.; Ming, H. *Adv. Mater.* **2014**, *26*, 3136−3141. (m) Xu, Y.; Jiang, H.; Zhang, Q.; Wang, F.; Zou, G. *Chem. Commun.* **2014**, *50*, 365−367. (n) Yang, G.; Han, L.; Jiang, H.; Zou, G.; Zhang, Q.; Zhang, D.; Wang, P.; Ming, H. *Chem. Commun.* **2014**, *50*, 2338−2340. (o) Lee, S.; Cho, Y.; Ye, B. U.; Baik, J. M.; Kim, M. H.; Yoon, J. *Chem. Commun.* **2014**, *50*, 12447−12449. (p) Guo, H.; Zhang, J.; Porter, D.; Peng, H.; Löwik, D. W. P. M.; Wang, Y.; Zhang, Z.; Chen, X.; Shao, Z. *Chem. Sci.* **2014**, *5*, 4189−4195. (q) Lee, J.; Chang, H. T.; An, H.; Ahn, S.; Shim, J.; Kim, J.-M. *Nat. Commun.* **2013**, *4*, 2461. (r) Lee, J.; Pyo, M.; Lee, S.-h.; Kim, J.; Ra, M.; Kim, W.-Y.; Park, B. J.; Lee, C. W.; Kim, J.-M. *Nat. Commun.* **2014**, *5*, 3736. (s) Gou, M.; Qu, X.; Zhu, W.; Xiang, M.; Yang, J.; Zhang, K.; Wei, Y.; Chen, S. *Nat. Commun.* **2014**, *5*, 3774.

(4) (a) Wudl, F.; Bitler, S. P. *J. Am. Chem. Soc.* **1986**, *108*, 4685−4687. (b) Lindsell, W. E.; Preston, P. N.; Tomb, P. J. *J. Organomet. Chem.* **1992**, *439*, 201−212. (c) Giesa, R.; Schulz, R. C. *Polym. Int.* **1994**, *33*, 43−60. (d) Crousse, B.; Alami, M.; Linstrumelle, G. *Tetrahedron Lett.* **1995**, *36*, 4245−4248. (e) Polhuis, M.; Hendrikx, C. C. J.; Zuilhof, H.; Sudhölter, E. J. R. *Tetrahedron Lett.* **2003**, *44*, 899−901.

(5) (a) Takayama, Y.; Delas, C.; Muraoka, K.; Sato, F. *Org. Lett.* **2003**, *5*, 365−368. (b) Takayama, Y.; Delas, C.; Muraoka, K.; Uemura, M.; Sato, F. *J. Am. Chem. Soc.* **2003**, *125*, 14163−14167. (c) Barluenga, J.; de Sáa, D.; Gómez, A.; Ballesteros, A.; Santamaría, J.; de Prado, A.; Tomás, M.; Suárez-Sobrino, A. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6225−6228. (d) Pilzak, G. S.; van Lagen, B.; Hendrikx, C. C. J.; Sudhölter, E. J. R.; Zuilhof, H. *Chem. - Eur. J.* **2008**, *14*, 7939−7950. (e) Pilzak, G. S.; van Lagen, B.; Sudhölter, E. J. R.; Zuilhof, H. *Tetrahedron Lett.* **2008**, *49*, 4949−4952. (f) Pilzak, G. S.; Baggerman, J.; van Lagen, B.; Posthumus, M. A.; Sudhölter, E. J. R.; Zuilhof, H. *Chem. - Eur. J.* **2009**, *15*, 2296−2304. (g) Pilzak, G. S.; van Gruijthuijsen, K.; van Doorn, R. H.; van Lagen, B.; Sudhölter, E. J. R.; Zuilhof, H. *Chem. - Eur. J.* **2009**, *15*, 9085−9096.

(6) (a) Bharucha, K. N.; Marsh, R. M.; Minto, R. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 3120−3121. (b) Lin, C.-F.; Wu, M.-J. *J. Org. Chem.* **1997**, *62*, 4546−4548. (c) Wu, H.-J.; Lin, C.-F.; Lee, J.-L.; Lu, W.-D.; Lee, C.-Y.; Chen, C.-C.; Wu, M.-J. *Tetrahedron* **2004**, *60*, 3927−3934.

(7) (a) Kosinski, C.; Hirsch, A.; Heinemann, F. W.; Hampel, F. *Eur. J. Org. Chem.* **2001**, *2001*, 3879−3890. (b) Chernick, E. T.; Börzsönyi, G.; Steiner, C.; Ammon, M.; Gessner, D.; Frühbeißer, S.; Gröhn, F.; Maier, S.; Tykwinski, R. R. *Angew. Chem., Int. Ed.* **2014**, *53*, 310−314.

(8) Kim, M.; Lee, D. *J. Am. Chem. Soc.* **2005**, *127*, 18024−18025.

(9) Coates, G. W.; Dunn, A. R.; Henling, L. M.; Dougherty, D. A.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 248−251.

(10) (a) Huang, L.-F.; Lee, C.-F.; Tseng, J.-C.; Luh, T.-Y. *Synlett* **2006**, *2006*, 3173−3175. (b) Huang, L.-F.; Chen, C.-W.; Luh, T.-Y. *Org. Lett.* **2007**, *9*, 3663−3665. (c) Tseng, H.-R.; Luh, T.-Y. *J. Org. Chem.* **1997**, *62*, 4568−4569.

(11) For reviews of the synthetic applications of propargylic dithioacetals, see: (a) Luh, T.-Y. *J. Organomet. Chem.* **2002**, *653*, 209−214. (b) Luh, T.-Y. *Pure Appl. Chem.* **2005**, *77*, 1213−1219. (c) Luh, T.-Y.; Lee, C.-F. *Eur. J. Org. Chem.* **2005**, *2005*, 3875−3885.

(12) Chen, C.-W.; Luh, T.-Y. *J. Org. Chem.* **2008**, *73*, 8357−8363.

(13) (a) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31−48. (b) Marshall, J. A. *Chem. Rev.* **2000**, *100*, 3163−3185. (c) Ma, S.-M.; Zhang, A.-B. *Pure Appl. Chem.* **2001**, *73*, 337−341. (d) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-i., Ed.; Wiley-VCH: New York, 2002; p 3279. (e) Marshall, J. A.; Gung, B. W.; Grachan, M. L. In *Modern Allene Chemistry*; Krause, N., Hashmi, A. S. K., Eds.; Wiley-VCH: Weinheim, Germany, 2004; pp 493−592. (f) Ma, S. *Eur. J. Org.*

DOI: 10.1021/acs.joc.5b01626
J. Org. Chem. 2015, 80, 8772−8781

Chem. **2004**, *2004*, 1175−1183. (g) Gung, B. W. *Org. Reactions* **2004**, *64*, 1−113. (h) Marshall, J. A. In *The Chemistry of Organozinc Compounds*; Rappoport, Z., Marek, I., Eds; Wiley: Chichester, U.K., 2006; pp 421−455. (i) Hegedus, L. S.; Ranslow, P.; Achmatowicz, M.; de los Rios, C.; Hyland, C.; Garcia-Frutos, E. M.; Salman, S. *Pure Appl. Chem.* **2006**, *78*, 333−339. (j) Ding, C.-H.; Hou, X.-L. *Chem. Rev.* **2011**, *111*, 1914−1937. (k) Wisniewska, H. M.; Jarvo, E. R. *J. Org. Chem.* **2013**, *78*, 11629−11636.

(14) See the Supporting Information for details.

(15) The diastereoselectivities of the coupling reactions depend on the metal counterion used. Reactions involving organozinc reagents **2** and **3** (M = Zn) gave different selectivities than those using organolithium species **2** and **3** (M = Li, cf. ref 12).

(16) (a) Kauffmann, T.; Lexy, H.; Kriegesmann, R. *Chem. Ber.* **1981**, *114*, 3667−3673. (b) Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* **1989**, *30*, 3461−3464. (c) Distefano, G.; Jones, D.; Guerra, M.; Favaretto, L.; Modelli, A.; Mengoli, G. *J. Phys. Chem.* **1991**, *95*, 9746−9753. (d) Bäuerle, P.; Fischer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 303−307. (e) Becker, R. S.; Seixas de Melo, J.; Maçanita, A. L.; Elisei, F. *J. Phys. Chem.* **1996**, *100*, 18683−18695. (f) Martin, R. E.; Günter, P.; Bosshard, C.; Gubler, U.; Gramlich, V.; Gross, M.; Boudon, C.; Gisselbrecht, J.-P.; Diederich, F. *Chem. - Eur. J.* **1997**, *3*, 1505−1512. (g) Saadeh, H.; Goodson, T., III; Yu, L. *Macromolecules* **1997**, *30*, 4608−4612. (h) Martin, R. E.; Mäder, T.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 817−821. (i) Roncali, J. *Acc. Chem. Res.* **2000**, *33*, 147−156. (j) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791−804. (k) Hicks, R. G.; Nodwell, M. B. *J. Am. Chem. Soc.* **2000**, *122*, 6746−6753. (l) Seixas de Melo, J.; Elisei, F.; Gartner, C.; Aloisi, G. G.; Becker, R. S. *J. Phys. Chem. A* **2000**, *104*, 6907−6911. (m) Sakamoto, Y.; Komatsu, S.; Suzuki, T. *J. Am. Chem. Soc.* **2001**, *123*, 4643−4644. (n) Sakurai, S. I.; Goto, H.; Yashima, E. *Org. Lett.* **2001**, *3*, 2379−2382. (o) Izumi, T.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2003**, *125*, 5286−5287. (p) Edder, C.; Fréchet, J. M. J. *Org. Lett.* **2003**, *5*, 1879−1882. (q) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480−13501. (r) Miyata, Y.; Nishinaga, T.; Komatsu, K. *J. Org. Chem.* **2005**, *70*, 1147−1153. (s) Tam, I. W.; Yan, J.; Breslow, R. *Org. Lett.* **2006**, *8*, 183−185. (t) Chou, C.-M.; Chen, W.-Q.; Chen, J.-H.; Lin, C.-L.; Tseng, J.-C.; Lee, C.-F.; Luh, T.-Y. *Chem. - Asian J.* **2006**, *1*, 46−55. (u) Gierschner, J.; Cornil, J.; Egelhaaf, H.-J. *Adv. Mater.* **2007**, *19*, 173−191. (v) Karsten, B. P.; Viani, L.; Gierschner, J.; Cornil, J.; Janssen, R. A. J. *J. Phys. Chem. A* **2008**, *112*, 10764−10773. (w) Tanaka, T.; Osuka, A. *Chem. Soc. Rev.* **2015**, *44*, 943−969.

(17) (a) Wenz, G.; Müller, M. A.; Schmidt, M.; Wegner, G. *Macromolecules* **1984**, *17*, 837−850. (b) Lim, K. C.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 522−530. (c) Li, Y.; Chu, B. *Macromolecules* **1991**, *24*, 4115−4122.

(18) (a) Pilling, G. M.; Sondheimer, F. *J. Am. Chem. Soc.* **1968**, *90*, 5610−5611. (b) Pilling, G. M.; Sondheimer, F. *J. Am. Chem. Soc.* **1971**, *93*, 1977−1984. (c) Hopf, H.; Theurig, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1099−1100. (d) Hopf, H.; Theurig, M.; Jones, P. G.; Bubenitschek, P. *Liebigs Ann.* **1996**, 1301−1311. (e) Kaneko, T.; Takahashi, M.; Hirama, M. *Angew. Chem., Int. Ed.* **1999**, *38* (9), 1267−1268.

(19) Hendrikx, C. C. J.; Polhuis, M.; Pul-Hootsen, A.; Koehorst, R. B. M.; van Hoek, A.; Zuilhof, H.; Sudhölter, E. J. R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 548−553.

(20) (a) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999. (b) Fery-Forgues, S.; Lavabre, D. *J. Chem. Educ.* **1999**, *76*, 1260−1264. (c) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991−1024.

DOI: 10.1021/acs.joc.5b01626
J. Org. Chem. 2015, 80, 8772−8781