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Palladium-Catalyzed S_N2'-Cyclization of Ambivalent (Bromoalkadienyl)malonates: Preparation of Medium- to Large-Membered Endocyclic Allenes

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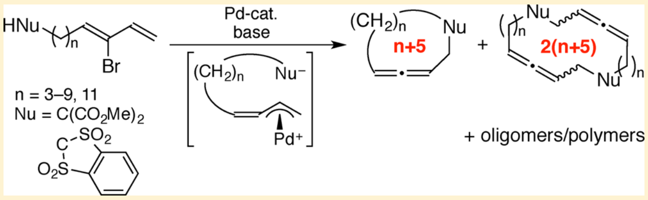
Supporting Information

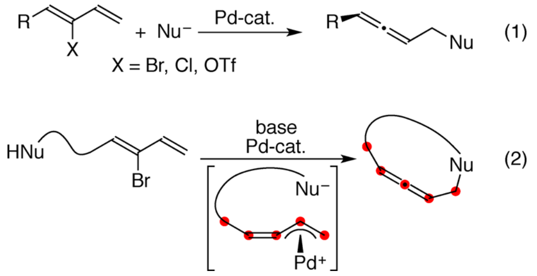
ABSTRACT: A palladium-catalyzed reaction for preparing various endocyclic allenes was developed. The substrates for the reaction were readily available ω-(pronucleophile-tethered)-3-bromo-1,3-alkadienes, and a palladium-catalyst facilitated their unimolecular S_N2'-cyclization in the presence of potassium *tert*-butoxide to give the corresponding 9- to 16-membered endocyclic allenes in fair yields of up to 67% together with the dimeric 16- to 32-membered endocyclic bis-allenes and other oligomeric/polymeric intermolecular reaction products. For higher yields of the monomeric endocyclic allenes, the reaction needed to be conducted under high-dilution conditions. Using a chiral palladium catalyst, axially chiral endocyclic allenes were obtained in up to 70% ee.



■ INTRODUCTION

Allenes are a class of compounds characterized by two cumulated carbon−carbon double bonds. Because of their propadiene structures, they show distinctive steric and electronic properties and have emerged as highly interesting target molecules in organic synthesis.[1,2] Incorporation of an allenic substructure into a carbocycle creates a peculiar topological property.[3] Although various endocyclic allenes have been prepared and reported so far, most of their synthetic methods construct an allenic motif within a preformed carbocycle precursor.[4−6] Two of the most widely applicable methods in the synthesis of endocyclic allenes, namely the ring enlargement of cycloalkenes via the corresponding *gem*-dibromobicyclo[*n*.1.0]alkenes by the Doering−Moore−Skattebøl reaction[4] and dehydrohalogenation of 1-halocycloalkenes,[5] are also classified in this category. Another approach to the endocyclic allenes is cyclization of preformed acyclic allenes.[7] This approach, however, is not applicable to the synthesis of relatively smaller ring cyclic allenes. The third category of the endocyclic allene synthesis is simultaneous construction of both allenic and cyclic structures by a single process, but the reported examples in this category are very rare.[8] Since 2000, we have developed a palladium-catalyzed reaction of preparing functionalized allenes starting with 2-halo 1,3-dienes and appropriate soft nucleophiles (eq 1 in Scheme 1).[9] The reaction was extended into an asymmetric counterpart by the use of a chiral Pd catalyst, and enantiomerically enriched axially chiral allenes were obtained in up to 94% ee.[10] We also demonstrated that the palladium-catalyzed reaction could be used for the synthesis of a series of endocyclic allenes starting with cycloalkenones.[9b]

Scheme 1. Palladium-Catalyzed Reaction of 2-Halo 1,3-Dienes with a Soft Nucleophile



In this report, we describe a novel method of preparing various endocyclic allenes utilizing the Pd-catalyzed reaction. The two reactants of the palladium-catalyzed reaction, namely a 2-bromo-1,3-diene and a soft nucleophile, are incorporated into a single molecule, and the S_N2'-cyclization of the "ambivalent" substrates proceeds primarily intramolecularly to afford various endocyclic allenes in fair yields.

The allenic substructure, which is with two cumulated orthogonal carbon−carbon double bonds, suppresses the relative motion among the five consecutive atoms (marked in red; eq 2 in Scheme 1). Similarly, the relative orientation of the five atoms is fastened in the (alkylidene-π-allyl)palladium

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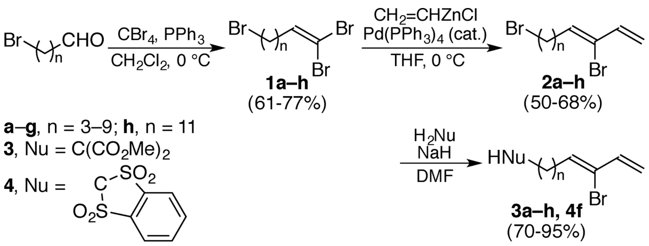
intermediate of the palladium-catalyzed reaction.[11] These rigid substructures in the palladium intermediates as well as in the allenic products may lead to the unusual preference/selectivity in the present cyclization reactions. Indeed, the cyclization process could provide various medium to large carbocycles in reasonable yields. It should be mentioned that formation of five- to seven-membered carbocycles, which are easy to assemble in typical cyclization processes, are impractical by the present method because thermodynamically stable endocarbocyclic allenes are usually nine-membered or larger.[12] Although a few kinetically stabilized eight-membered carbocyclic allenes were reported to be isolable,[13] endocyclic allenes with a seven-membered or a smaller carbocycle exist only as transient reactive intermediates.

■ RESULTS AND DISCUSSION

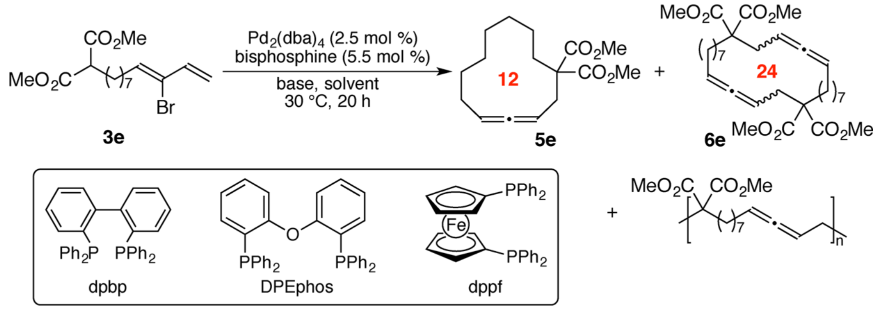
Preparation of Pronucleophile-Tethered 3-Bromo 1,3-Diene Derivatives 3 and 4. The substrates for our endocyclic allene synthesis are pronucleophile-tethered 3-bromo 1,3-dienes (**3a−h** and **4f**), and they are prepared from *ω*-bromoalkanals by the simple three-step sequence as depicted in Scheme 2. Readily available *ω*-bromoalkanals were converted into the corresponding 1,1,*ω*-tribromoalkenes **1a−i** in 61−77% yields by the standard Wittig dibromoolefination (Ramirez olefination).[14] The palladium-catalyzed cross-coupling of **1** with vinylzinc chloride proceeded at the sterically less congested alkenyl-Br (i.e., C═C*Br* *trans* to the *ω*-bromoalkyl group) selectively to give the corresponding (*Z*)-3,*ω*-dibromo-1,3-dienes **2a−h** in 50−68% yields.[15] Alkylation of dimethyl malonate or benzodithiole tetraoxide (BDT) with **2** furnished designed substrates **3a−h** and **4f** in pure form (70−95%).

Scheme 2. Preparation of Pronucleophile-Tethered 3-Bromo 1,3-Dienes



Palladium-Catalyzed Reactions of Pronucleophile-Tethered 3-Bromo 1,3-Diene Derivatives 3 and 4. Substrates **3** and **4** prepared as in Scheme 2 were subjected to the palladium-catalyzed reaction. At the outset, the conditions for the palladium-catalyzed reaction were optimized using **3e** ($n = 7$) as a model substrate, and the results of the optimization studies are summarized in Table 1. The reaction of **3e** was efficiently catalyzed by 5 mol % of a palladium complex generated in situ from $Pd_2(dba)_4$ and dpbp[16] (1.1 equiv to Pd) in THF in the presence of potassium *tert*-butoxide (1.1 equiv to **3e**). Under the rather standard conditions, i.e., with the initial concentration of substrate **3e** being 1.4×10^{-2} mol/L, **3e** was completely consumed within 20 h at 30 °C. However, to our disappointment, the yield of the desired 12-membered endocyclic allene **5e** was only 9% (entry 1). Complete consumption of **3e** and the low yield of **5e** indicated that intermolecular processes giving oligomeric/polymeric products competed with the unimolecular cyclization reaction. Indeed, reactions under dilute conditions facilitated the desired intramolecular pathway leading to the higher yields of **5e** (entries 2 and 3). When the initial concentration of **3e** was 1.4×10^{-3} mol/L, **5e** was isolated in 31% yield (entry 3). It should be mentioned that the reactions in entries 1−3 produced dimeric endocyclic bis-allene **6e** in 11−19% yields together with **5e**. Endocyclic bis-allene **6e** was obtained as a mixture of

Table 1. Optimization of Reaction Conditions for Palladium-Catalyzed S_N2'-Cyclization of 3e[a]



entry	solvent	base	ligand	concn of **3e** (mol/L)	yield of **5e** (%)	yield of **6e**[b] (%)
1	THF	KO^{t}Bu	dpbp	1.4×10^{-2}	9^{c}	13^{c}
2	THF	KO^{t}Bu	dpbp	1.4×10^{-2}	22^{c}	11^{c}
3	THF	KO^{t}Bu	dpbp	4.6×10^{-3}	31^{c}	19^{c}
4	DMF	KO^{t}Bu	dpbp	1.4×10^{-3}	8^{d}	nd[e]
5	toluene	KO^{t}Bu	dpbp	1.4×10^{-3}	7^{d}	nd[e]
6	CH_2Cl_2	KO^{t}Bu	dpbp	1.4×10^{-3}	0^{d}	nd[e]
7	THF	NaOMe	dpbp	1.4×10^{-3}	31^{c}	15^{c}
8	THF	CsO^{t}Bu	dpbp	1.4×10^{-3}	16^{d}	nd[e]
9	THF	Cs_2CO_3	dpbp	1.4×10^{-3}	0	nd[e]
10	THF	NaOMe	DPEphos	1.4×10^{-3}	23^{d}	nd[e]
11	THF	NaOMe	dppf	1.4×10^{-3}	25^{d}	nd[e]

[a] The reaction was carried out with **3f** (140 μmol) and a base (154 μmol) in the given solvent at 30 °C for 20 h in the presence of a palladium catalyst (5 mol %) generated from $Pd_2(dba)_4$ and a bisphosphine ligand. [b] Obtained as *dl*/*meso*-diastereomeric mixtures.[17] [c] Isolated yield by recycle HPLC. [d] Determined by GC analysis. [e] Not determined.

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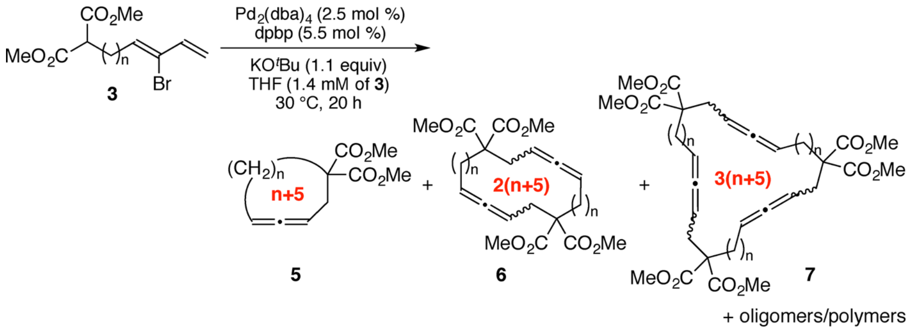
Table 2. Influences of Ring Size in Palladium-Catalyzed S_N2' Cyclization of 3[a]



entry	substrate **3**	yield of **5**[b] (%)	yield of **6**[b−d] (%)	yield of **7**[b−d] (%)
1	**3a** (*n* = 3)	0 (**5a**)	30 (**6a**)	10 (**7a**)
2	**3b** (*n* = 4)	23 (**5b**)	16 (**6b**)	*e*
3	**3c** (*n* = 5)	11 (**5c**)	24 (**6c**)	7 (**7c**)
4	**3d** (*n* = 6)	18 (**5d**)	27 (**6d**)	9 (**7d**)
5	**3e** (*n* = 7)	31 (**5e**)	19 (**6e**)	*e*
6	**3f** (*n* = 8)	52 (**5f**)	14 (**6f**)	*e*
7	**3g** (*n* = 9)	42 (**5g**)	21 (**6g**)	*e*
8	**3h** (*n* = 11)	33 (**5h**)	10 (**6g**)	*e*

[a]The reaction was carried out with **3** (350 μmol) and a base (385 μmol) in THF (250 mL) at 30 °C for 20 h in the presence of a palladium catalyst (5 mol %) generated from $Pd_2(dba)_4$ and dppb. [b]Isolated yield by recycle HPLC. [c]Calculated on the basis of **3**. [d]Obtained as diastereomeric mixtures.[17] [e]Not determined or <5% yield.

dl- and *meso*-diastereomers with respect to the allenic axial chirality; two allenic central sp-C signals were detected at δ 205.8 and 205.9 in the ^{13}C NMR spectrum (see the Experimental Section).[17] THF was the best solvent examined so far. Reactions in DMF, toluene, or dichloromethane gave **5e** in much lower yields ranging from 0 to 8% (entries 4−6). The choice of a proper base drastically influences the yield of **5e**; while the reactions with KO^{t}Bu or NaOMe afforded the monomeric endocyclic allene in 31% yield (entries 3 and 7), the yield of **5e** declined to 16% with the use of CsO^{t}Bu (entry 8), and the reaction using Cs_2CO_3 did not provide **5e** at all (entry 9). On the other hand, the effects of the bisphosphine ancillary ligands were minor, and the reactions with DPEphos[18] (1.1 equiv to Pd) or dppf gave **5e** in 23% and 25% yields, respectively (entries 10 and 11).

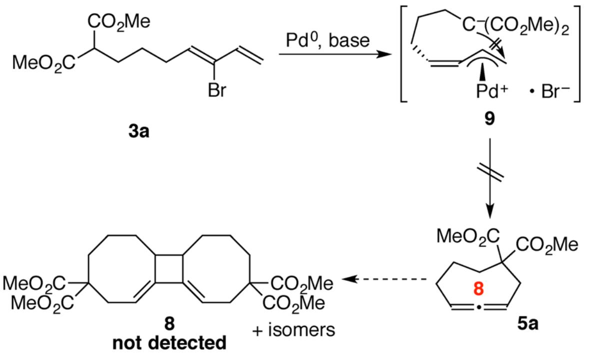
The reaction conditions shown in entry 3 of Table1 were selected as "optimized conditions", and they were applied to the other substrates in the same way. The results of the palladium-catalyzed reaction are summarized in Table 2.

While the substrates with more than three methylene units (i.e., **3b** and the longer ones) afforded the corresponding monomeric endocyclic allenes **5b−h** in moderate yields by the palladium-catalyzed reaction, the reaction of **3a** did not provide eight-membered endocyclic allene **5a** (entry 1). The highest yield of **5** was achieved for the reaction of **3f** giving 13-membered monomeric endocyclic allene **5f** in 52% yield (entry 6). With a longer polymethylene chain in **3g** (*n* = 9) and **3h** (*n* = 11), the yields of **5g** (42%) and **5h** (33%) were slightly lower (entries 7 and 8). Likewise, shorter substrates **3b−e** afforded the corresponding monomeric endocyclic allenes **5b−e** in lower yields ranging from 11% to 31% (entries 2−5). In all cases including the reaction of **3a**, substrates **3** were completely consumed under these conditions, and the formation of dimeric endocyclic bis-allenes **6**, which were isolated in 10−30% yields by the HPLC separation, was observed. Homologous trimeric endocyclic tris-allenes **7a**, **7c**, and **7d** were also isolated in 10%, 7%, and 9% yields, respectively, in the reactions giving **6** in relatively higher yields (entries 1, 3, and 4). Since bis-allenes **6** and tris-allenes **7** possess multiple allenic axially chiral elements, they were obtained as diastereomeric mixtures.[17]

Whereas eight-membered endocarbocyclic allenes are generally too reactive to be isolated without appropriate kinetically stabilizing bulky substituents,[3a,e,13] it was rational that **5a** was not detected in the reaction of **3a**. However, the absence of **5a** should not be ascribed to its high reactivity. Once highly reactive **5a** was generated in situ, it was expected to undergo [2 + 2]cycloaddition[19] giving an isomeric mixture of homodimers such as **8**, but **8** and/or related isomeric species were not detected in the reaction mixture. The key intermediate of the palladium-catalyzed reaction of **3a** is (alkylidene-π-allyl) palladium species **9**. Due to the short trimethylene chain in **9**, the nucleophilic malonate moiety is not capable of attacking the CH_2 π-allyl terminus intramolecularly, and thus, the formation of **5a** could not be realized (Scheme 3).

The cyclization reaction of **4f** was also examined. Substrate **4f** possesses a benzo[1,3]dithiole tetraoxide (BDT) substructure as a pronucleophilic moiety. The palladium-catalyzed reaction of **4f** was conducted essentially in the same way as in Table 2

Scheme 3



Scheme 4. Palladium-Catalyzed S_N2' Cyclization of BDT-Tethered Substrate 4f

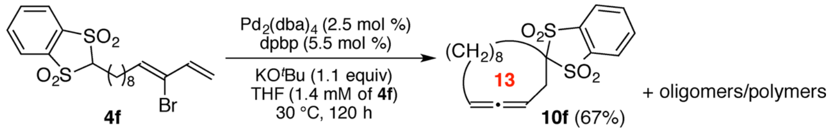
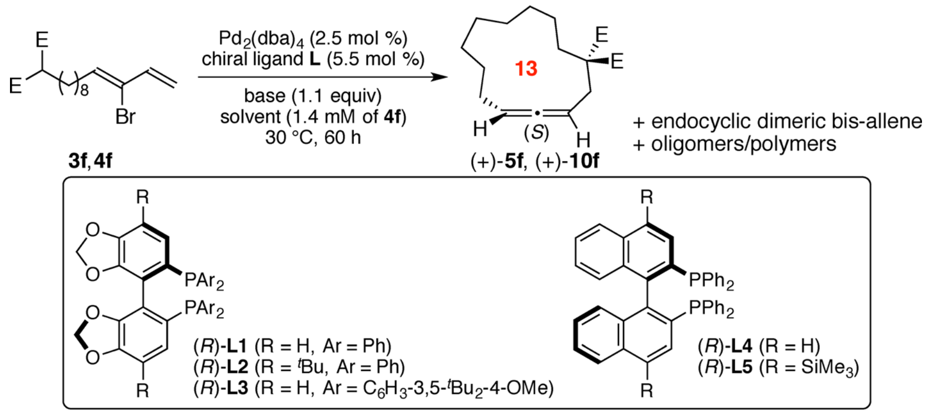


Table 3. Palladium-Catalyzed Asymmetric Synthesis of Axially Chiral Endocyclic Allenes 5f/10f[a]



entry	substrate	chiral ligand	base	solvent	yield[b] (%)	% ee (config)[c,d]
1	**3f**	(*R*)-**L1**	KO^{t}Bu	THF	50 (**5f**)	65 (*S*)
2	**3f**	(*R*)-**L1**	KO^{t}Bu	dioxane	5 (**5f**)	11 (*S*)
3	**3f**	(*R*)-**L1**	KO^{t}Bu	CH$_2$Cl$_2$	nd[e]	
4	**3f**	(*R*)-**L1**	NaOMe	THF	13 (**5f**)	59 (*S*)
5	**3f**	(*R*)-**L1**	CsO^{t}Bu	THF	35 (**5f**)	55 (*S*)
6	**3f**	(*R*)-**L2**	KO^{t}Bu	THF	42 (**5f**)	45 (*S*)
7	**3f**	(*R*)-**L3**	KO^{t}Bu	THF	25 (**5f**)	70 (*S*)
8	**3f**	(*R*)-**L4**	KO^{t}Bu	THF	34 (**5f**)	55 (*S*)
9	**3f**	(*R*)-**L5**	KO^{t}Bu	THF	54 (**5f**)	50 (*S*)
10	**4f**	(*R*)-**L3**	KO^{t}Bu	THF	29 (**10f**)	51 (*S*)

[a] The reaction was carried out with **3f** or **4f** (100 μmol) and a base (110 μmol) in a given solvent (70 mL) at 30 °C for 60 h in the presence of a palladium catalyst (5 mol %) generated from Pd$_2$(dba)$_4$ and a chiral ligand **L**. [b] Isolated yield by recycle HPLC. [c] Determined by chiral HPLC analysis (see the Experimental Section for details). [d] The absolute configurations were deduced by the Lowe–Brewster rule.[20] [e] Not determined.

except for the reaction time. Due probably to the lower nucleophilicity of BDT, the reaction took longer time (120 h) for completion, and monomeric endocyclic allene **10f** was obtained in the highest yield of 67% (Scheme 4). The formation of the corresponding endocyclic dimeric bis-allene and trimeric tris-allene was minor (<5%) in this reaction. The BDT moiety in **4f** is sterically more compact than the malonate moiety in **3f**, which may facilitate the intramolecular cyclization in the palladium-catalyzed process.

Palladium-Catalyzed Asymmetric Synthesis of Axially Chiral Endocyclic Allenes 5f and 10f. Endocyclic allenes **5** and **10** obtained as in Table 2 and Scheme 4 are axially chiral but racemic. Using **3f** as a representative substrate, palladium-catalyzed enantioselective synthesis of **5f** was examined according to our previous studies;[10] that is, with a palladium catalyst (5 mol %) generated from Pd$_2$(dba)$_4$ and (*R*)-segphos ((*R*)-**L1**) in THF at 30 °C in the presence of KO^{t}Bu, (+)-**5f** was obtained in 50% yield with 65% ee (Table 3, entry 1). Among the various solvents and bases examined, the combination of THF and KO^{t}Bu showed the highest yield and the highest enantioselectivity for the reaction of **3f** (entries 1–5). While (*R*)-**L2**, (*R*)-**L4**, and (*R*)-**L5** showed lower enantioselectivity than (*R*)-**L1** with 45–55% ee (entries 6, 8, and 9), the enantioselectivity was improved to 70% ee by the use of (*R*)-**L3** although the chemical yield of (+)-**5f** was considerably lower (entry 7). The enantioselective reaction of **4f** was conducted as in entry 7, and (+)-**10f** was obtained in 51% ee and 29% yield (entry 10). The absolute configurations of dextrorotatory (+)-**5f** and (+)-**10f** were deduced to be (*S*) by the Lowe–Brewster rule.[20]

■ CONCLUSIONS

In summary, we have developed a general method of preparing various endocyclic allenes of a 9- to 16-membered carbocycle utilizing the palladium-catalyzed reaction. Readily available ω-(pronucleophile-tethered)-3-bromo-1,3-alkadienes **3** and **4** undergo the unimolecular S_N2'-cyclization in the presence of an appropriate palladium catalyst to give the corresponding endocyclic allenes **5**/**10** in fair yields together with the dimeric endocyclic bis-allenes and higher oligomers/polymers. The highest yield of 67% was achieved for the preparation of the 13-membered cyclic allene. Due probably to the rigid substructures in the allenic C=C=C products as well as in the (alkylidene-π-allyl)palladium intermediates, the medium- to large-membered carbocyclic compounds are accessible in reasonable yields by the present cyclization reaction. By the use of a chiral palladium catalyst, axially chiral endocyclic allenes were obtained in up to 70% ee.

■ EXPERIMENTAL SECTION

General Methods. All anaerobic and/or moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 100 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. The HRMS measurements were carried out by the EI method with a TOF analyzer. Tetrahydrofuran (from benzophenone-ketyl) and dichloromethane (from CaH_2) were distilled under nitrogen prior to use. $Pd(PPh_3)_4$,[21] $Pd_2(dba)_4$,[22] dpbp,[16] (*R*)-**L1**,[23] (*R*)-**L2**,[24] (*R*)-**L4**,[25] (*R*)-**L5**,[26] and 1,3-benzodithiole-1,1,3,3-tetraoxide (BDT)[27] were prepared according to the reported methods. All of the other chemicals were obtained from commercial sources and used as received unless otherwise noted.

Preparation of *ω*-Bromoalkanals. The *ω*-bromoalkanals were prepared from the corresponding commercially available *ω*-bromo-1-alkanols according to the reported procedure,[28] in which the preparation of 8-bromooctanal (n = 7 in Scheme 2) was described in detail. All the *ω*-bromoalkanals used in this study are known compounds and were characterized by comparison of their NMR spectra with those reported previously (n = 3,[29] n = 4,[29] n = 5,[30] n = 6,[31] n = 7,[28] n = 8,[32] n = 9,[32] n = 11[33]).

Preparation of 1,1,*ω*-Tribromo-1-alkenes (1a−h). To a CH_2Cl_2 (ca. 2 mL/*ω*-bromoalkanal 1 mmol) solution of CBr_4 (1.5 equiv to *ω*-bromoalkanal) was added PPh_3 (3.0 equiv to *ω*-bromoalkanal) portionwise at 0 °C, and the solution was allowed to stir at this temperature for 20 min. A solution of *ω*-bromoalkanal (1 equiv) in CH_2Cl_2 (ca. 1 mL/*ω*-bromoalkanal 2 mmol) was added dropwise at 0 °C, and the mixture was stirred at the same temperature for 10 min. After the reaction mixture was quenched with a small amount of water (ca. 1 mL), the mixture was concentrated under reduced pressure. Addition of hexane (ca. 5 mL/*ω*-bromoalkanal 1 mmol) to the concentrated solution precipitated triphenylphosphine oxide as pale yellow solid, which was removed by filtration. The filtrate was evaporated, and the residue was purified by silica gel column chromatography (with hexane). The characterization data of **1a**−**h** are given below.

*1,1,5-Tribromo-1-pentene (**1a**; n = 3).* Colorless liquid. Yield: 6.27 g (63%) starting with 4-bromobutanal (4.90 g; 32.5 mmol). ^{1}H NMR ($CDCl_3$): δ 1.96−2.03 (m, 2H), 2.25−2.31 (m, 2H), 3.42 (t, J = 6.6 Hz, 2H), 6.40 (t, J = 7.3 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.8, 31.7, 32.5, 90.5, 136.7. EI-HRMS: calcd for $C_5H_7Br_3$ 303.8098, found 303.8101.

*1,1,6-Tribromo-1-hexene (**1b**; n = 4).* Colorless liquid. Yield: 5.78 g (61%) starting with 5-bromopentanal (4.90 g; 29.7 mmol). ^{1}H NMR ($CDCl_3$): δ 1.56−1.64 (m, 2H), 1.86−1.93 (m, 2H), 2.12−2.17 (m, 2H), 3.42 (t, J = 6.7 Hz, 2H), 6.39 (t, J = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.3, 31.9, 32.1, 33.3, 89.5, 137.9. EI-HRMS: calcd for $C_6H_9Br_3$ 317.8254, found 317.8251.

*1,1,7-Tribromo-1-heptene (**1c**; n = 5).* Colorless liquid. Yield: 3.96 g (65%) starting with 6-bromohexanal (3.26 g; 18.2 mmol). ^{1}H NMR ($CDCl_3$): δ 1.41−1.52 (m, 4H), 1.84−1.91 (m, 2H), 2.09−2.14 (m, 2H), 3.41 (t, J = 6.8 Hz, 2H), 6.39 (t, J = 7.3 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.0, 27.6, 32.5, 32.8, 33.6, 89.1, 138.3. EI-HRMS: calcd for $C_7H_{11}Br_3$ 331.8411, found 331.8405.

*1,1,8-Tribromo-1-octene (**1d**; n = 6).* Colorless liquid. Yield: 1.78 g (61%) starting with 7-bromoheptanal (1.62 g; 8.39 mmol). ^{1}H NMR ($CDCl_3$): δ 1.31−1.38 (m, 2H), 1.41−1.49 (m, 4H), 1.83−1.90 (m, 2H), 2.07−2.13 (m, 2H), 3.41 (t, J = 6.8 Hz, 2H), 6.38 (t, J = 7.3 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.6, 27.9, 28.2, 32.7, 32.9, 33.9, 88.8, 138.6. EI-HRMS: calcd for $C_8H_{13}Br_3$ 345.8567, found 345.8570.

*1,1,9-Tribromo-1-nonene (**1e**; n = 7).* Colorless liquid. Yield: 5.64 g (77%) starting with 8-bromooctanal (4.18 g; 20.2 mmol). ^{1}H NMR ($CDCl_3$): δ 1.31−1.47 (m, 8H), 1.82−1.89 (m, 2H), 2.07−2.12 (m, 2H), 3.41 (t, J = 6.8 Hz, 2H), 6.38 (t, J = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.7, 28.1, 28.5, 28.8, 32.7, 32.9, 34.0, 88.7, 138.7. EI-HRMS: calcd for $C_9H_{15}Br_3$ 359.8724, found 359.8718.

*1,1,10-Tribromo-1-decene (**1f**; n = 8).* Colorless liquid. Yield: 4.66 g (63%) starting with 9-bromononanal (4.34 g; 19.6 mmol). ^{1}H NMR ($CDCl_3$): δ 1.28−1.47 (m, 10H), 1.82−1.89 (m, 2H), 2.06−2.12 (m, 2H), 3.41 (t, J = 6.8 Hz, 2H), 6.39 (t, J = 7.3 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.8, 28.1, 28.7, 28.9, 29.2, 32.8, 33.0, 34.1, 88.6, 138.9. EI-HRMS: calcd for $C_{10}H_{17}Br_3$ 373.8880, found 373.8881.

*1,1,11-Tribromo-1-undecene (**1g**; n = 9).* Colorless liquid. Yield: 3.06 g (66%) starting with 10-bromodecanal (2.79 g; 11.9 mmol). ^{1}H NMR ($CDCl_3$): δ 1.26−1.43 (m, 12H), 1.82−1.89 (m, 2H), 2.06−2.12 (m, 2H), 3.41 (t, J = 6.9 Hz, 2H), 6.38 (t, J = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.8, 28.1, 28.7, 29.0, 29.2, 29.3, 32.8, 33.0, 34.1, 88.5, 138.9. EI-HRMS: calcd for $C_{11}H_{19}Br_3$ 387.9037, found 387.9037.

*1,1,13-Tribromo-1-tridecene (**1h**; n = 11).* Colorless liquid. Yield: 4.68 g (68%) starting with 12-bromododecanal (4.32 g; 16.4 mmol). ^{1}H NMR ($CDCl_3$): δ 1.26−1.46 (m, 16H), 1.82−1.89 (m, 2H), 2.06−2.11 (m, 2H), 3.41 (t, J = 6.9 Hz, 2H), 6.38 (t, J = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.8, 28.2, 28.8, 29.1, 29.3, 29.4, 29.49, 29.50, 32.9, 33.0, 34.1, 88.5, 138.9. EI-HRMS: calcd for $C_{13}H_{23}Br_3$ 415.9350, found 415.9356.

Preparation of (*Z*)-3,*ω*-Dibromo-1,3-alkadienes (2a−h). To a suspension of ($CH_2{=}CH$)ZnCl in THF, prepared from dry $ZnCl_2$ (28 mmol) and vinylmagnesium chloride (2.0 M THF solution; 12 mL; 24 mmol), was added a solution of 1,1,*ω*-tribromo-1-alkene **1** (8.0 mmol) and $Pd(PPh_3)_4$ (0.20 mmol) in THF (16 mL) at 0 °C. After the mixture was stirred for 4.5 h at room temperature, it was diluted with hexane, filtered, and evaporated to dryness. The residue was purified by silica gel chromatography (with hexane) and further purified by recycle HPLC to give the title compound. The characterization data of **2a**−**h** are given below.

*(Z)-3,7-Dibromo-1,3-heptadiene (**2a**; n = 3).* Colorless liquid. Yield: 1.10 g (54%). ^{1}H NMR ($CDCl_3$): δ 1.99−2.06 (m, 2H), 2.46−2.52 (m, 2H), 3.43 (t, J = 6.8 Hz, 2H), 5.20 (d, J = 10.4 Hz, 1H), 5.56 (d, J = 16.3 Hz, 1H), 5.98 (t, J = 7.2 Hz, 1H), 6.32 (dd, J = 16.3 and 10.4 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 30.3, 31.5, 32.9, 118.2, 127.4, 132.7, 135.7. EI-HRMS: calcd for $C_7H_{10}Br_2$ 251.9149, found 251.9144.

*(Z)-3,8-Dibromo-1,3-octadiene (**2b**; n = 4).* Colorless liquid. Yield: 1.16 g (54%). ^{1}H NMR ($CDCl_3$): δ 1.58−1.66 (m, 2H), 1.87−1.94 (m, 2H), 2.34−2.39 (m, 2H), 3.43 (t, J = 6.7 Hz, 2H), 5.19 (d, J = 10.5 Hz, 1H), 5.55 (d, J = 16.3 Hz, 1H), 5.97 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.3 and 10.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.9, 30.6, 32.2, 33.6, 117.7, 126.6, 134.0, 135.7. EI-HRMS: calcd for $C_8H_{12}Br_2$ 265.9306, found 265.9303.

*(Z)-3,9-Dibromo-1,3-nonadiene (**2c**; n = 5).* Colorless liquid. Yield: 1.17 g (52%). ^{1}H NMR ($CDCl_3$): δ 1.47−1.50 (m, 4H), 1.85−1.92 (m, 2H), 2.31−2.36 (m, 2H), 3.41 (t, J = 6.8 Hz, 2H), 5.17 (d, J = 10.5 Hz, 1H), 5.54 (d, J = 16.3 Hz, 1H), 5.98 (t, J = 7.2 Hz, 1H), 6.31 (dd, J = 16.3 and 10.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.5, 27.8, 31.3, 32.6, 33.7, 117.5, 126.2, 134.5, 135.8. EI-HRMS: calcd for $C_9H_{14}Br_2$ 279.9462, found 279.9467.

*(Z)-3,10-Dibromo-1,3-decadiene (**2d**; n = 6).* Colorless liquid. Yield: 1.21 g (51%). ^{1}H NMR ($CDCl_3$): δ 1.32−1.51 (m, 6H), 1.83−1.90 (m, 2H), 2.30−2.35 (m, 2H), 3.41 (t, J = 6.9 Hz, 2H), 5.17 (d, J = 10.5 Hz, 1H), 5.53 (d, J = 16.3 Hz, 1H), 5.97 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.3 and 10.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.0, 28.2, 28.4, 31.4, 32.7, 34.0, 117.3, 126.1, 134.9, 135.8. EI-HRMS: calcd for $C_{10}H_{16}Br_2$ 293.9619, found 293.9617.

*(Z)-3,11-Dibromo-1,3-undecadiene (**2e**; n = 7).* Colorless liquid. Yield: 1.56 g (63%). ^{1}H NMR ($CDCl_3$): δ 1.31−1.49 (m, 8H), 1.82−1.89 (m, 2H), 2.29−2.34 (m, 2H), 3.41 (t, J = 6.9 Hz, 2H), 5.16 (d, J = 10.5 Hz, 1H), 5.53 (d, J = 16.3 Hz, 1H), 5.98 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.3 and 10.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.1, 28.2, 28.6, 29.0, 31.5, 32.8, 34.0, 117.2, 126.0, 135.0, 135.8. EI-HRMS: calcd for $C_{11}H_{18}Br_2$ 307.9775, found 307.9777.

*(Z)-3,12-Dibromo-1,3-dodecadiene (**2f**; n = 8).* Colorless liquid. Yield: 1.30g (50%). ^{1}H NMR ($CDCl_3$): δ 1.26−1.46 (m, 10H), 1.82−1.89 (m, 2H), 2.28−2.34 (m, 2H), 3.41 (t, J = 6.8 Hz, 2H), 5.16 (d, J = 10.5 Hz, 1H), 5.53 (d, J = 16.3 Hz, 1H), 5.98 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.3 and 10.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.2, 28.3, 28.7, 29.15, 29.24, 31.5, 32.8, 34.1, 117.2, 125.9, 135.2, 135.9. EI-HRMS: calcd for $C_{12}H_{20}Br_2$ 321.9932, found 321.9931.

*(Z)-3,13-Dibromo-1,3-tridecadiene (**2g**; n = 9).* Colorless liquid. Yield: 1.84 g (68%). ^{1}H NMR (CDCl$_3$): δ 1.30−1.34 (m, 8H), 1.39−1.46 (m, 4H), 1.82−1.89 (m, 2H), 2.28−2.34 (m, 2H), 3.41 (t, J = 6.9 Hz, 2H), 5.16 (d, J = 10.5 Hz, 1H), 5.53 (d, J = 16.3 Hz, 1H), 5.98 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.3 and 10.5 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 28.1, 28.3, 28.7, 29.2, 29.28, 29.32, 31.5, 32.8, 34.1, 117.1, 125.8, 135.2, 135.9. EI-HRMS: calcd for $C_{13}H_{22}Br_2$ 336.0088, found 336.0091.

*(Z)-3,15-Dibromo-1,3-pentadecadiene (**2h**; n = 11).* Colorless liquid. Yield: 1.64 g (56%). ^{1}H NMR (CDCl$_3$): δ 1.28−1.47 (m, 16H), 1.82−1.89 (m, 2H), 2.28−2.34 (m, 2H), 3.41 (t, J = 6.9 Hz, 2H), 5.15 (d, J = 10.5 Hz, 1H), 5.52 (d, J = 16.3 Hz, 1H), 5.98 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.3 and 10.5 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 28.2, 28.4, 28.8, 29.3, 29.450, 29.455, 29.53 (2C), 31.6, 32.9, 34.1, 117.1, 125.8, 135.3, 135.9. EI-HRMS: calcd for $C_{15}H_{26}Br_2$ 364.0401, found 364.0404.

Preparation of Malonate-Tethered Bromodienes 3a−h. A general procedure is given below. To a solution of NaH (4.9 mmol) in DMF (10 mL) was added dimethyl malonate (4.9 mmol) at 0 °C. After gas evolution ceased, dibromoalkadiene **2** (4.0 mmol) was added to the solution by means of syringe under nitrogen. The mixture was stirred at room temperature for 20 h. After being quenched with saturated NH_4Cl_{aq}, the reaction mixture was extracted with Et_2O twice and the combined organic layer was washed with H_2O and $NaCl_{aq}$, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel chromatography (hexane/ethyl acetate = 4/1) to afford the malonate-tethered bromodiene **3**. The characterization data of **3a−h** are given below.

*Dimethyl 2-((Z)-5-Bromo-4,6-heptadienyl)-1,3-propanedioate (**3a**; n = 3).* Colorless liquid. Yield: 854 mg (70%). ^{1}H NMR (CDCl$_3$): δ 1.43−1.53 (m, 2H), 1.92−1.98 (m, 2H), 2.33−2.38 (m, 2H), 3.39 (t, J = 7.5 Hz, 1H), 3.74 (s, 6H), 5.18 (d, J = 10.4 Hz, 1H), 5.54 (d, J = 16.3 Hz, 1H), 5.96 (t, J = 7.1 Hz, 1H), 6.30 (dd, J = 16.3 and 10.4 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 26.1, 28.4, 31.1, 51.5, 52.6, 117.7, 126.6, 133.8, 135.7, 169.8. ESI-HRMS: calcd for $C_{12}H_{17}BrO_4Na$ 327.0208 (M + Na), found 327.0220. Anal. Calcd for $C_{12}H_{17}BrO_4$: C, 47.23; H, 5.61. Found: C, 47.23; H, 5.57.

*Dimethyl 2-((Z)-6-Bromo-5,7-octadienyl)-1,3-propanedioate (**3b**; n = 4).* Colorless liquid. Yield: 1.02 g (80%). ^{1}H NMR (CDCl$_3$): δ 1.32−1.40 (m, 2H), 1.45−1.52 (m, 2H), 1.90−1.96 (m, 2H), 2.30−2.35 (m, 2H), 3.37 (t, J = 7.5 Hz, 1H), 3.74 (s, 6H), 5.17 (d, J = 10.5 Hz, 1H), 5.53 (d, J = 16.3 Hz, 1H), 5.96 (t, J = 7.3 Hz, 1H), 6.31 (dd, J = 16.3 and 10.5 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 27.0, 27.9, 28.7, 31.2, 51.6, 52.6, 117.5, 126.3, 134.5, 135.8, 169.9. EI-HRMS: calcd for $C_{13}H_{19}BrO_4$: 318.0467, found 318.0468. Anal. Calcd for $C_{13}H_{19}BrO_4$: C, 48.92; H, 6.00. Found: C, 48.77; H, 5.97.

*Dimethyl 2-((Z)-7-Bromo-6,8-nonadienyl)-1,3-propanedioate (**3c**; n = 5).* Colorless liquid. Yield: 1.00 g (75%). ^{1}H NMR (CDCl$_3$): δ 1.29−1.50 (m, 6H), 1.88−1.93 (m, 2H), 2.28−2.33 (m, 2H), 3.36 (t, J = 7.6 Hz, 1H), 3.74 (s, 6H), 5.16 (d, J = 10.6 Hz, 1H), 5.52 (d, J = 16.3 Hz, 1H), 5.96 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.3 and 10.6 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 27.1, 27.9, 28.69, 28.71, 31.3, 51.6, 52.4, 117.2, 126.0, 134.7, 135.8, 169.9. Anal. Calcd for $C_{14}H_{21}BrO_4$: C, 50.46; H, 6.35. Found: C, 50.37; H, 6.29. ESI-HRMS: calcd for $C_{14}H_{21}BrO_4Na$ 355.0515 (M + Na), found 355.0516.

*Dimethyl 2-((Z)-8-Bromo-7,9-decadienyl)-1,3-propanedioate (**3d**; n = 6).* Colorless liquid. Yield: 1.01 g (73%). ^{1}H NMR (CDCl$_3$): δ 1.29−1.34 (m, 6H), 1.40−1.47 (m, 2H), 1.87−1.93 (m, 2H), 2.28−2.33 (m, 2H), 3.36 (t, J = 7.5 Hz, 1H), 3.74 (s, 6H), 5.16 (d, J = 10.3 Hz, 1H), 5.53 (d, J = 16.3 Hz, 1H), 5.97 (t, J = 7.2 Hz, 1H), 6.31 (dd, J = 16.3 and 10.3 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 27.3, 28.2, 28.8, 28.9, 29.0, 31.5, 51.7, 52.5, 117.2, 126.0, 135.0, 135.9, 170.0. EI-HRMS: calcd for $C_{15}H_{23}BrO_4$ 346.0780, found 346.0781. Anal. Calcd for $C_{15}H_{23}BrO_4$: C, 51.88; H, 6.68. Found: C, 51.72; H, 6.60.

*Dimethyl 2-((Z)-9-Bromo-8,10-undecadienyl)-1,3-propanedioate (**3e**; n = 7).* Colorless liquid. Yield: 1.37 g (95%). ^{1}H NMR (CDCl$_3$): δ 1.26−1.32 (m, 8H), 1.39−1.47 (m, 2H), 1.87−1.92 (m, 2H), 2.28−2.33 (m, 2H), 3.36 (t, J = 7.6 Hz, 1H), 3.74 (s, 6H), 5.16 (d, J = 10.4 Hz, 1H), 5.53 (d, J = 16.3 Hz, 1H), 5.97 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.3 and 10.4 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 27.3, 28.3, 28.8, 29.09, 29.11 (2C), 31.5, 51.7, 52.5, 117.2, 125.9, 135.2, 135.9, 170.0. EI-HRMS: calcd for $C_{16}H_{25}BrO_4$ 360.0936, found 360.0936. Anal. Calcd for $C_{16}H_{25}BrO_4$: C, 53.19; H, 6.97. Found: C, 52.66; H, 6.91.

*Dimethyl 2-((Z)-10-Bromo-9,11-dodecadienyl)-1,3-propanedioate (**3f**; n = 8).* Colorless liquid. Yield: 1.20 g (80%). ^{1}H NMR (CDCl$_3$): δ 1.26−1.33 (m, 10H), 1.39−1.47 (m, 2H), 1.87−1.92 (m, 2H), 2.28−2.33 (m, 2H), 3.36 (t, J = 7.6 Hz, 1H), 3.74 (s, 6H), 5.16 (d, J = 10.5 Hz, 1H), 5.53 (d, J = 16.4 Hz, 1H), 5.98 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.4 and 10.5 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 27.4, 28.3, 28.9, 29.18, 29.21, 29.22, 29.3, 31.5, 51.8, 52.5, 117.2, 125.9, 135.2, 135.9, 170.0. EI-HRMS: calcd for $C_{17}H_{27}BrO_4$ 374.1093, found 374.1093. Anal. Calcd for $C_{17}H_{27}BrO_4$: C, 54.41; H, 7.25. Found: C, 54.48; H, 7.27.

*Dimethyl 2-((Z)-11-Bromo-10,12-tridecadienyl)-1,3-propanedioate (**3g**; n = 9).* Colorless liquid. Yield: 1.42 g (91%). ^{1}H NMR (CDCl$_3$): δ 1.28−1.33 (m, 12H), 1.40−1.47 (m, 2H), 1.87−1.92 (m, 2H), 2.28−2.33 (m, 2H), 3.36 (t, J = 7.6 Hz, 1H), 3.74 (s, 6H), 5.15 (d, J = 10.4 Hz, 1H), 5.52 (d, J = 16.3 Hz, 1H), 5.98 (t, J = 7.3 Hz, 1H), 6.31 (dd, J = 16.3 and 10.4 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 27.3, 28.3, 28.8, 29.16, 29.21, 29.25, 29.34, 29.38, 31.5, 51.7, 52.4, 117.1, 125.8, 135.2, 135.9, 170.0. EI-HRMS: calcd for $C_{18}H_{29}BrO_4$ 388.1249, found 388.1247. Anal. Calcd for $C_{18}H_{29}BrO_4$: C, 55.53; H, 7.51. Found: C, 55.60; H, 7.39.

*Dimethyl 2-((Z)-13-Bromo-12,14-pentadecadienyl)-1,3-propanedioate (**3h**; n = 11).* Colorless liquid. Yield: 1.29 g (77%). ^{1}H NMR (CDCl$_3$): δ 1.26−1.35 (m, 16H), 1.40−1.47 (m, 2H), 1.87−1.92 (m, 2H), 2.28−2.34 (m, 2H), 3.36 (t, J = 7.6 Hz, 1H), 3.74 (s, 6H), 5.15 (d, J = 10.4 Hz, 1H), 5.52 (d, J = 16.3 Hz, 1H), 5.98 (t, J = 7.1 Hz, 1H), 6.31 (dd, J = 16.3 and 10.4 Hz, 1H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 27.4, 28.4, 28.9, 29.2, 29.29, 29.32, 29.4, 29.51, 29.54, 29.6, 31.6, 51.8, 52.5, 117.1, 125.8, 135.3, 135.9, 170.0. ESI-HRMS: calcd for $C_{20}H_{33}BrO_4Na$ 439.1454 (M + Na), found 439.1449. Anal. Calcd for $C_{20}H_{33}BrO_4$: C, 57.55; H, 7.97. Found: C, 57.69; H, 7.84.

*2-((Z)-10-Bromo-9,11-dodecadienyl)-1,3-benzodithiole 1,1,3,3-Tetraoxide (**4f**).* To a mixture of NaH (26 mg, 1.1 mmol) and BDT (240 mg, 1.1 mmol) in DMF (4.5 mL) was added dibromododecadiene **2f** (274 mg, 844 μmol) by means of syringe under nitrogen. After the mixture was stirred for 16 h at 80 °C, it was extracted with ethyl acetate twice, and the combined organic layer was washed with H_2O and $NaCl_{aq}$, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by recycle HPLC to afford **4f** (263 mg, 570 mol, 68%) as a white solidMp: 67−69 °C. ^{1}H NMR (CDCl$_3$): δ 1.33−1.50 (m, 10H), 1.75−1.80 (m, 2H), 2.30−2.34 (m, 4H), 4.36 (t, J = 7.1 Hz, 1H), 5.16 (d, J = 10.4 Hz, 1H), 5.53 (d, J = 16.3 Hz, 1H), 5.99 (t, J = 7.0 Hz, 1H), 6.32 (dd, J = 16.3 and 10.4 Hz, 1H) 7.91−7.94 (m, 2H), 8.02−8.05 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 22.1, 25.8, 28.2, 28.8, 29.00, 29.04, 29.1, 31.4, 73.7, 117.1, 122.5, 125.8, 135.1, 135.78, 135.79, 137.6. EI-HRMS: calcd for $C_{19}H_{25}BrO_4S_2$ 460.0378, found 460.0367. Anal. Calcd for $C_{19}H_{25}BrO_4S_2$: C, 49.46; H, 5.46. Found: C, 49.80; H, 5.40.

Palladium-Catalyzed Reaction of Malonate-Tethered Bromodienes 3a−h. A general procedure is given below. To a mixture of $Pd_2(dba)_4$ (17.5 μmol), dppb (19.2 μmol), and KO^{t}Bu (385 μmol) in THF (250 mL) was added malonate-tethered bromodiene **3** (350 μmol, 1.4 mM) by means of syringe under nitrogen. After the mixture was stirred for 20 h at 30 °C, it was concentrated, filtered through a short pad of silica gel, and evaporated to dryness. The crude product was purified by recycle HPLC to afford the corresponding endocyclic allenes **5**, **6**, and **7**. The characterization data of the cyclic allenic products (**5**, **6**, and **7**) are listed below.

*Dimethyl 2,2-(2,3-Octadiene-1,8-diyl)-1,3-propanedioate (**5b**; n = 4).* Colorless liquid. Yield: 19.2 mg (23%). ^{1}H NMR (CDCl$_3$): δ 1.42−1.58 (m, 4H), 1.93−2.06 (m, 3H), 2.36−2.46 (m, 1H), 2.57−2.63 (m, 1H), 2.81−2.87 (m, 1H), 3.71 (s, 3H), 3.72 (s, 3H), 4.94−5.01 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 18.9, 24.1, 24.8, 28.4, 31.6, 52.5, 52.6, 57.0, 85.3, 87.4, 172.2, 172.6, 209.8. ESI-HRMS: calcd for $C_{13}H_{18}O_4Na$: 261.1103 (M + Na), found 261.1106.

*Dimethyl 2,2-(2,3-Nonadiene-1,9-diyl)-1,3-propanedioate (**5c**; n = 5).* Colorless liquid. Yield: 9.7 mg (11%). ^{1}H NMR (CDCl$_3$): δ 1.29−1.84 (m, 7H), 1.88−1.96 (m, 1H), 2.04−2.11 (m, 1H), 2.32−

2.41 (m, 1H), 2.61–2.72 (m, 2H), 3.72 (s, 3H), 3.73 (s, 3H), 4.98–5.05 (m, 1H), 5.29–5.32 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.0, 20.6, 28.3, 29.7, 29.8, 32.6, 52.5, 52.6, 55.5, 87.0, 92.9, 172.0, 172.7, 205.9. EI-HRMS: calcd for $C_{14}H_{20}O_4$ 252.1362, found 252.1363.

*Dimethyl 2,2-(2,3-Decadiene-1,10-diyl)-1,3-propanedioate (**5d**; n = 6).* Colorless liquid. Yield: 16.8 mg (18%). ^1H NMR ($CDCl_3$): δ 1.18–1.62 (m, 8H), 1.78–1.96 (m, 2H), 2.04–2.15 (m, 2H), 2.59 (dd, J = 14.1 and 11.6 Hz, 1H), 2.79 (dt, J = 14.1 and 4.4 Hz, 1H), 3.71 (s, 3H), 3.74 (s, 3H), 5.01–5.08 (m, 1H), 5.26–5.31 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.4, 26.0, 26.1, 26.4, 26.8, 30.9, 34.0, 52.5, 52.6, 57.2, 87.4, 91.4, 171.8, 172.2, 206.0. EI-HRMS: calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1516.

*Dimethyl 2,2-(2,3-Undecadiene-1,11-diyl)-1,3-propanedioate (**5e**; n = 7).* Colorless liquid. Yield: 30.4 mg (31%). ^1H NMR ($CDCl_3$): δ 0.97–1.59 (m, 10H), 1.74–1.82 (m, 1H), 1.93–2.17 (m, 3H), 2.55 (dd, J = 13.9 and 11.6 Hz, 1H), 2.68–2.73 (m, 1H), 3.71 (s, 3H), 3.74 (s, 3H), 4.61–4.67 (m, 1H), 4.89–4.96 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.1, 21.4, 22.3, 25.9, 26.48, 26.54, 27.3, 32.1, 52.5, 52.6, 56.8, 83.8, 89.2, 171.7, 171.8, 208.4. EI-HRMS: calcd for $C_{16}H_{24}O_4$ 280.1675, found 280.1675. Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.28; H, 8.74.

*Dimethyl 2,2-(2,3-Dodecadiene-1,12-diyl)-1,3-propanedioate (**5f**; n = 8).* Colorless liquid. Yield: 53.6 mg (52%). ^1H NMR ($CDCl_3$): δ 1.06–1.15 (m, 1H), 1.26–1.62 (m, 11H), 1.90–2.12 (m, 4H), 2.55 (dd, J = 14.6 and 11.4 Hz, 1H), 2.77 (dtd, J = 14.6, 4.4, and 1.2 Hz, 1H), 3.71 (s, 3H), 3.73 (s, 3H), 4.74–4.81 (m, 1H), 5.12–5.17 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.7, 25.0, 26.1, 26.9, 27.2, 27.9, 28.6, 30.8, 31.7, 52.45, 52.51, 57.4, 85.7, 91.4, 171.8 (2C), 206.1. EI-HRMS: calcd for $C_{17}H_{26}O_4$ 294.1831, found 294.1824. Anal. Calcd for $C_{17}H_{26}O_4$: C, 69.36; H, 8.90. Found: C, 69.28; H, 9.05.

*Dimethyl 2,2-(2,3-Tridecadiene-1,13-diyl)-1,3-propanedioate (**5g**; n = 9).* Colorless liquid. Yield: 45.3 mg (42%). ^1H NMR ($CDCl_3$): δ 0.73–0.90 (m, 1H), 1.14–1.57 (m, 13H), 1.87–2.04 (m, 4H), 2.58 (dd, J = 14.5 and 11.6 Hz, 1H), 2.78 (dtd, J = 14.5, 4.4, and 0.9 Hz, 1H), 3.72 (s, 3H), 3.73 (s, 3H), 4.63–4.70 (m, 1H), 5.02–5.08 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.7, 23.2, 23.9, 26.0, 26.37, 26.40, 27.16, 27.18, 31.6, 32.4, 52.5, 52.6, 57.2, 84.5, 91.3, 171.8, 171.9, 206.1. EI-HRMS: calcd for $C_{18}H_{28}O_4$ 308.1988, found 308.1989. Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.00; H, 9.11.

*Dimethyl 2,2-(2,3-Pentadecadiene-1,15-diyl)-1,3-propanedioate (**5h**; n = 11).* Colorless liquid. Yield: 38.9 mg (33%). ^1H NMR ($CDCl_3$): δ 1.07–1.43 (m, 18H), 1.82–2.03 (m, 4H), 2.56 (dd, J = 14.2 and 9.8 Hz, 1H), 2.71 (ddd, J = 14.2, 6.0, and 3.2 Hz, 1H), 3.72 (s, 3H), 3.73(s, 3H), 4.69–4.71 (m, 1H), 5.07–5.13 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.6, 24.2, 24.4, 25.9, 26.0, 26.2, 26.3, 27.4, 27.5, 29.0, 31.9, 32.9, 52.41, 52.44, 57.3, 84.6, 91.2, 171.81, 171.84, 206.2. EI-HRMS: calcd for $C_{20}H_{32}O_4$ 336.2301, found 336.2302.

*5,5,13,13-Tetra(methoxycarbonyl)cyclohexadeca-1,2,9,10-tetraene (**6a**; n = 3).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 23.5 mg (30%). ^1H NMR ($CDCl_3$): δ 1.02–1.10 (m, 1H), 1.17–1.41 (m, 3H), 1.79–2.12 (m, 8H), 2.49–2.55 (m, 2H), 2.66–2.72 (m, 2H), 3.70–3.72(s, 12H), 4.63–4.81 (m, 2H), 4.97–5.10 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.9, 24.8, 29.7, 31.0, 31.1, 31.5, 31.8, 32.1, 52.5, 52.57, 52.64, 57.0, 84.3, 84.8, 90.5, 90.6, 171.51, 171.55, 171.60, 171.62, 205.7, 206.0. EI-HRMS: calcd for $C_{24}H_{32}O_8$ 448.2097, found 448.2098. Anal. Calcd for $C_{24}H_{32}O_8$: C, 64.27; H, 7.19. Found: C, 64.08; H, 7.25.

*5,5,14,14-Tetra(methoxycarbonyl)cyclooctadeca-1,2,10,11-tetraene (**6b**; n = 4).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 13.3 mg (16%). ^1H NMR ($CDCl_3$): δ 0.94–1.70 (m, 8H), 1.82–2.08 (m, 8H), 2.50–2.57 (m, 2H), 2.68–2.73 (m, 2H), 3.72–3.75 (m, 12H), 4.65–4.80 (m, 2H), 5.04–5.15 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.7, 24.1, 28.4, 29.0, 30.2, 30.8, 31.7, 31.9, 32.6, 32.9, 52.50, 52.54, 52.6, 57.0, 57.1, 84.6, 85.5, 90.7, 90.9, 171.6, 171.7, 205.7, 206.0. EI-HRMS: calcd for $C_{26}H_{36}O_8$ 476.2410, found 476.2414. Anal. Calcd for $C_{26}H_{36}O_8$: C, 65.53; H, 7.61. Found: C, 65.81; H, 7.77.

*5,5,15,15-Tetra(methoxycarbonyl)cycloeicosa-1,2,11,12-tetraene (**6c**; n = 5).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 21.2 mg (24%). ^1H NMR ($CDCl_3$): δ 0.96–1.12 (m, 2H), 1.16–1.45 (m, 10H), 1.82–2.07 (m, 8H), 2.51–2.56 (m, 2H), 2.68–2.72 (m, 2H), 3.72–3.73 (m, 12H), 4.65–4.75 (m, 2H), 5.01–5.09 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.0, 24.1, 29.3, 29.5, 29.8, 30.1, 30.6, 30.7, 31.6, 31.7, 32.18, 32.22, 52.55, 52.60, 57.1, 57.2, 84.4, 84.8, 90.8, 90.9, 171.7, 205.8, 205.9. EI-HRMS: calcd for $C_{28}H_{40}O_8$ 504.2723, found 504.2724. Anal. Calcd for $C_{28}H_{40}O_8$: C, 66.65; H, 7.99. Found: C, 66.49; H, 8.12.

*5,5,16,16-Tetra(methoxycarbonyl)cyclodocosa-1,2,12,13-tetraene (**6d**; n = 6).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 25.2 mg (27%). ^1H NMR ($CDCl_3$): δ 0.96–1.38 (m, 16H), 1.84–2.02 (m, 8H), 2.50–2.56 (m, 2H), 2.68–2.74 (m, 2H), 3.72–3.73 (m, 12H), 4.65–4.77 (m, 2H), 5.03–5.13 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.3, 24.4, 29.0, 29.6, 29.87, 29.92, 30.3, 30.4, 30.6, 31.9, 32.6, 32.7, 52.50, 52.54, 57.11, 57.13, 84.6, 85.0, 90.99, 91.04, 171.8, 205.78, 205.82. EI-HRMS: calcd for $C_{30}H_{44}O_8$ 532.3036, found 532.3037. Anal. Calcd for $C_{30}H_{44}O_8$: C, 67.64; H, 8.33. Found: C, 67.44; H, 8.38.

*5,5,17,17-Tetra(methoxycarbonyl)cyclotetracosa-1,2,13,14-tetraene (**6e**; n = 7).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 18.6 mg (19%). ^1H NMR ($CDCl_3$): δ 0.97–1.43 (m, 20H), 1.83–2.05 (m, 8H), 2.51–2.57 (m, 2H), 2.66–2.72 (m, 2H), 3.72 (s, 6H), 3.73(s, 6H), 4.66–4.75 (m, 2H), 5.02–5.10 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.1, 24.3, 29.4, 29.7, 29.75, 29.82, 29.9, 30.3, 30.38, 30.43, 30.8, 31.6, 31.7, 31.8, 32.3, 52.5, 52.6, 57.18, 57.23, 84.5, 84.6, 91.0, 91.1, 171.8, 205.8, 205.9. EI-HRMS: calcd for $C_{32}H_{48}O_8$ 560.3349, found 560.3353. Anal. Calcd for $C_{32}H_{48}O_8$: C, 68.54; H, 8.63. Found: C, 68.78; H, 8.83.

*5,5,18,18-Tetra(methoxycarbonyl)cyclohexacosa-1,2,14,15-tetraene (**6f**; n = 8).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 14.4 mg (14%). ^1H NMR ($CDCl_3$): δ 1.02–1.37 (m, 24H), 1.86–2.03 (m, 8H), 2.50–2.57 (m, 2H), 2.67–2.72 (m, 2H), 3.71–3.73 (m, 12H), 4.68–4.76 (m, 2H), 5.04–5.11 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.2, 24.3, 29.2, 29.6, 29.8, 30.0, 30.17, 30.21, 30.3, 30.4, 30.5, 30.6, 31.9, 32.6, 52.49, 52.52, 57.2, 84.6, 84.8, 91.1, 171.8, 205.8. EI-HRMS: calcd for $C_{34}H_{52}O_8$ 588.3662, found 588.3658. Anal. Calcd for $C_{34}H_{52}O_8$: C, 69.36; H, 8.90. Found: C, 69.30; H, 9.09.

*5,5,19,19-Tetra(methoxycarbonyl)cyclooctacosa-1,2,15,16-tetraene (**6g**; n = 9).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 22.7 mg (21%). ^1H NMR ($CDCl_3$): δ 1.01–1.37 (m, 28H), 1.86–2.05 (m, 8H), 2.56 (dd, J = 14.3 and 9.8 Hz, 2H), 2.68 (ddd, J = 14.3, 6.1, and 3.3 Hz, 2H), 3.71 (s, 6H), 3.72(s, 6H), 4.68–4.76 (m, 2H), 5.04–5.10 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.0, 24.1, 29.3, 29.5, 29.67, 29.72, 29.8, 29.97, 30.03, 30.1, 30.2, 30.3, 30.5, 31.8, 32.4, 52.5, 57.2, 84.58, 84.64, 91.1, 171.8, 205.8. EI-HRMS: calcd for $C_{36}H_{56}O_8$ 616.3975, found 616.3978. Anal. Calcd for $C_{36}H_{56}O_8$: C, 70.10; H, 9.15. Found: C, 70.08; H, 9.01.

*5,5,21,21-Tetra(methoxycarbonyl)cyclodotriaconta-1,2,17,18-tetraene (**6h**; n = 11).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 11.8 mg (10%). ^1H NMR ($CDCl_3$): δ 1.04–1.41 (m, 36H), 1.86–2.05 (m, 8H), 2.55 (ddd, J = 14.3, 9.6, and 1.2 Hz, 2H), 2.67 (ddd, J = 14.3, 6.2, and 3.3 Hz, 2H), 3.71 (s, 6H), 3.72(s, 6H), 4.70–4.78 (m, 2H), 5.04–5.10 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.0, 29.20, 29.24, 29.57, 29.63, 29.7, 29.8, 29.85, 29.94, 30.02, 30.07, 30.2, 30.3, 31.8, 32.4, 52.5, 57.3, 84.7, 91.1, 171.9, 205.8. EI-HRMS: calcd for $C_{40}H_{64}O_8$ 672.4601, found 672.4602. Anal. Calcd for $C_{40}H_{64}O_8$: C, 71.39; H, 9.59. Found: C, 70.96; H, 9.56.

*5,5,13,13,21,21-Hexa(methoxycarbonyl)cyclotetracosa-1,2,9,10,17,18-hexaene (**7a**; n = 3).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 7.8 mg (10%). ^1H NMR ($CDCl_3$): δ 1.19–1.35 (m, 6H), 1.86–2.08 (m, 12H), 2.56–2.67 (m, 6H), 3.71–3.74 (m, 18H), 4.79–4.871 (m, 3H), 4.98–5.06 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.9, 29.4, 31.4, 32.6, 52.5, 57.3, 84.8, 90.3, 171.6, 205.8, 205.9, 206.0. EI-HRMS: calcd for $C_{36}H_{48}O_{12}$ 672.3146, found 672.3148.

*5,5,15,15,25,25-Hexa(methoxycarbonyl)cyclotriaconta-1,2,11,12,21,22-hexaene (**7c**; n = 5).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 6.2

mg (7%). ^{1}H NMR (CDCl$_3$): δ 1.11−1.43 (m, 18H), 1.86−1.98 (m, 12H), 2.55−2.66 (m, 6H), 3.71−3.72 (m, 18H), 4.78−4.85 (m, 3H), 5.03−5.08 (m, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 23.6, 28.7, 28.9, 29.2, 31.8, 32.5, 52.5, 57.5, 84.9, 90.8, 171.8, 205.8. EI-HRMS: calcd for $C_{42}H_{60}O_{12}$ 756.4085, found 756.4085.

*5,5,16,16,27,27-Hexa(methoxycarbonyl)cyclotritriaconta-1,2,12,13,23,24-hexaene (**7d**; n = 6).* Diastereomeric mixture (^{13}C NMR signals not completely resolved).[17] Colorless liquid. Yield: 8.4 mg (9%). ^{1}H NMR (CDCl$_3$): δ 1.10−1.41 (m, 24H), 1.86−1.98 (m, 12H), 2.55−2.66 (m 6H), 3.715 (s, 9H), 3.718 (s, 9H), 4.79−4.86 (m, 3H), 5.03−5.09 (m, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 23.8, 28.7, 28.8, 29.1, 29.6, 31.9, 32.5, 52.5, 57.5, 84.9, 90.9, 171.8, 205.8. EI-HRMS: calcd for $C_{45}H_{66}O_{12}$ 798.4554, found 798.4552.

*2,2-(Dodecadiene-1,12-diyl)-1,3-benzodithiole 1,1,3,3-Tetraoxide (**10f**).* To a mixture of Pd$_2$(dba)$_4$ (5.5 mg, 11 μmol), dpbp (6.0 mg, 12 μol), and KO^{t}Bu (23.6 mg, 210 μmol) in THF (150 mL) was added **4f** (96.9 mg, 210 μmol, 1.4 mM) by means of syringe under nitrogen. After the mixture was stirred for 120 h at 30 °C, the reaction mixture was concentrated, filtered through a short pad of silica gel, and evaporated to dryness. The crude product was purified by recycle HPLC to afford **10f** (53.2 mg, 140 μmol, 67%) as a colorless liquid. ^{1}H NMR (CDCl$_3$): δ 1.21−1.86 (m, 12H), 2.02−2.15 (m, 2H), 2.26−2.38 (m, 2H), 2.88 (dt, J = 15.3 and 4.3 Hz, 1H), 2.99 (dd, J = 15.3 and 10.6 Hz, 1H), 5.22−5.28 (m, 1H), 5.43−5.50 (m, 1H) 7.88−7.93 (m, 2H), 7.98−8.04 (m, 2H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 21.1, 25.3, 25.7, 26.1, 26.6, 26.7, 27.5, 29.0, 29.7, 79.5, 83.4, 92.6, 123.1, 123.2, 135.1, 135.2, 135.8, 136.3, 207.1. EI-HRMS: calcd for $C_{19}H_{24}O_4S_2$ 380.1116, found 380.1121. Anal. Calcd for $C_{19}H_{24}O_4S_2$: C, 59.97; H, 6.36. Found: C, 60.04; H, 6.36.

Palladium-Catalyzed Asymmetric Synthesis of Axially Chiral 5f and 10f. The asymmetric reactions were conducted in the same way as with the nonasymmetric reaction described above except a chiral ligand was used instead of achiral dpbp (see Table 3 for details). (*S*)-**5f** (entry 7, Table 3): $[\alpha]^{25}_{D}$ = +93.1 (c 0.73, CHCl$_3$ for the sample of (*S*)-70% ee). Chiral HPLC analysis conditions: Chiralpak IC; eluent, hexane/^{i}PrOH = 200/1; flow rate, 1.0 mL/min; t_1 [(*R*)-enantiomer] = 20.8 min, t_2 [(*S*)-enantiomer] = 40.7 min. (*S*)-**10f** (entry 10, Table 3): $[\alpha]^{25}_{D}$ = +56.9 (c 0.37, CHCl$_3$ for the sample of (*S*)-51% ee). Chiral HPLC analysis conditions: Chiralpak IC; eluent, hexane/^{i}PrOH = 9/1; flow rate, 1.0 mL/min; ; t_1 [(*S*)-enantiomer] = 20.0 min, t_2 [(*R*)-enantiomer] = 31.9 min.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01204.

^{1}H- and ^{13}C NMR spectra for all the new compounds and chiral HPLC chromatograms of (+)-**5f** and (+)-**10f** (PDF)

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Notes

The authors declare no competing financial interest.

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