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Headline Articles

Dimerization–Carbostannylation of Alkynes Catalyzed by a Palladium–Diimine Complex: Regioselectivity, Stereoselectivity and Mechanism

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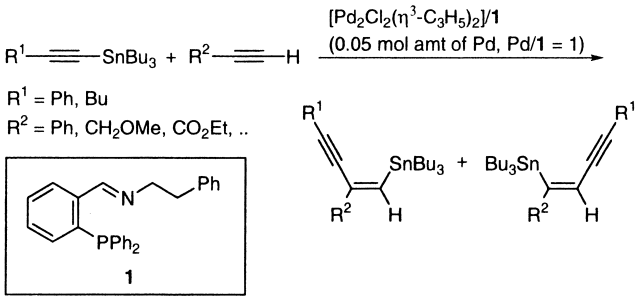
Double insertion of alkynes into the C–Sn bond of an alkynyl-, alkenyl-, allyl- or arylstannane proceeded in the presence of a palladium–diimine complex to afford highly conjugated alkenylstannanes with exclusive *syn* selectivity. Perfect regioselectivities were observed in the dimerization–carbostannylation of ethyl propiolate with a palladium–1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene complex, which allowed regio- and stereoselective synthesis of stannyl-substituted muconic acid derivatives. The π-conjugation of the dimerization–carbostannylation products was further extended through a cross-coupling or homocoupling reaction. A palladacyclopentadiene is proposed as an intermediate species.

Carbostannylation of alkynes has become a powerful synthetic tool owing to the novel synthetic transformation: C–C and C–Sn bonds are simultaneously introduced across a triple bond of alkynes in a *syn*-manner to give alkenylstannanes, which can be converted into variously substituted ethenes with retention of configuration through the Migita–Kosugi–Stille coupling reaction.[1] Furthermore, high chemoselectivity and mild reactivity of organostannanes as compared with other organometallic reagents make the carbostannylation and subsequent reactions extremely useful and applicable to a wide variety of substrates. Although allylstannylation of alkynes, in particular, has been shown to be mediated by a Lewis acid,[2] radical initiator,[3] nickel complex[4] or palladium complex,[5] alkynylstannanes and acylstannanes also are demonstrated to participate in the carbostannylation of alkynes in the presence of a nickel[4] or palladium[6] catalyst.[7,8,9,10]

In the palladium-catalyzed alkynylstannylation of alkynes, the nature of a ligand influences significantly the catalytic activity. Thus, a palladium complex coordinated by *N*-(2-diphenylphosphinobenzylidene)phenylethylamine (**1**) efficiently catalyzes the reaction (Scheme 1), whereas such phosphorus ligands as triphenylphosphine and 1,3-bis(diphenylphosphino)propane were ineffective, suggesting that the imino moiety of **1** plays an important role in the catalysis.[6] Since then we directed our research to the improvement of the efficiency of the palladium-catalyzed carbostannylation, and found that a dimerization–carbostannylation reaction of alkynes was triggered by a palladium complex consisting of a rigid diimine ligand, i.e., 1,2-bis(arylimino)acenaphthene (**2**).



Scheme 1. Pd–iminophosphine-catalyzed alkynylstannylation of alkynes.

We describe herein the scope and limitations of the palladium-catalyzed dimerization–carbostannylation of alkynes, demonstrating that the novel catalytic process provides a convenient method to produce a variety of highly π-conjugated alkenylstannanes with three to six covalent bonds being generated in one pot.[11]

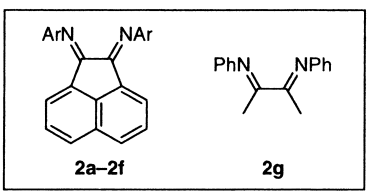
Results and Discussion

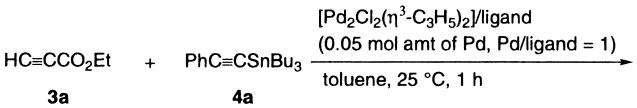
Reaction Conditions for Dimerization–Carbostannylation. First we investigated the reaction of ethyl propiolate (**3a**) with tributyl(phenylethynyl)tin (**4a**) in toluene at 25 °C for 1 h using a palladium–1,2-bis(phenylimino)acenaphthene (**2a**) complex to observe that diethyl (2*E*,4*Z*)-2-(phenylethynyl)-5-(tributylstannyl)-2,4-hexadienedioate (**5a**) was produced as the sole product in 89% conversion (Scheme 2, entry 1 of Table 1).

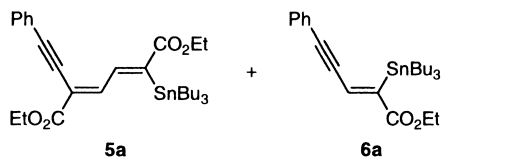
Table 1. Palladium-Catalyzed Dimerization–Carbostannylation of Ethyl Propiolate (**3a**) with Tributyl(phenylethynyl)tin (**4a**)[a)]

Entry	Ligand (Ar in **2**)		Solvent	Conversion %[b)]	Product(s)
1	Ph	(**2a**)	toluene	89	**5a**
2	Ph	(**2a**)	THF	71	**5a**
3	Ph	(**2a**)	dioxane	70	**5a**
4	Ph	(**2a**)	$CHCl_3$	70	**5a**
5	Ph	(**2a**)	DME	64	**5a**
6	Ph	(**2a**)	DMF	53	**5a**
7	Ph	(**2a**)	octane	< 5	**5a**
8	4-$CF_3C_6H_4$	(**2b**)	toluene	80	**5a**
9	3,5-$(CF_3)_2C_6H_3$	(**2c**)	toluene	49	**5a**
10	4-$MeOC_6H_4$	(**2d**)	toluene	68	**5a**
11	4-MeC_6H_4	(**2e**)	toluene	89	**5a**
12	2,6-(*i*-Pr)$_2C_6H_3$	(**2f**)	toluene	< 5	**5a**
13	—	(**2g**)	toluene	31	**5a**, **6a**[c)]
14	—	(**1**)	toluene	84	**6a**[d)]
15	none		toluene	20	**6a**[e)]

a) The reaction was carried out in a solvent (3mL) at 25 °C using **3a** (1.0 mmol) and **4a** (0.34 mmol) for 1 h in the presence of $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ (8.2 μmol) and a ligand (16 μmol). b) Determined by ^{119}Sn NMR. c) **5a**/**6a** = 54/46. d) The regioisomer of **6a** was also detected (**6a**/isomer = 4/1). e) Regioisomer was not detected.

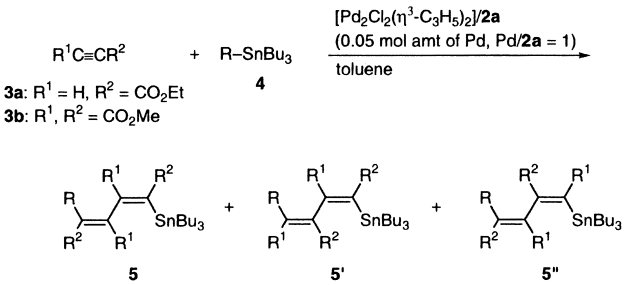






Scheme 2. Reaction of **3a** with **4a** in the presence of Pd–**2** complexes.

The product formation is ascribed to addition of the C–Sn bond in **4a** to **3a** accompanied by dimerization of the alkyne. Results of the reaction of **3a** with **4a** using other solvents and ligands are summarized in Table 1. In a polar solvent such as THF, dioxane, DME or DMF, the reaction using the Pd–**2a** catalyst was slow (entries 2–6); in octane, the reaction did not proceed at all, probably due to low solubility of the catalyst (entry 7). Diimines having an electron-withdrawing or -donating substituent on Ar did not accelerate the reaction (entries 8–11). Bulky diimine **2f** was totally ineffective (entry 12). Palladium complex with acyclic diimine ligand **2g** gave a mixture of the 2:1 and 1:1 carbostannylation products (entry 13).



Scheme 3. Dimerization–carbostannylation of alkynes catalyzed by Pd–**2a**.

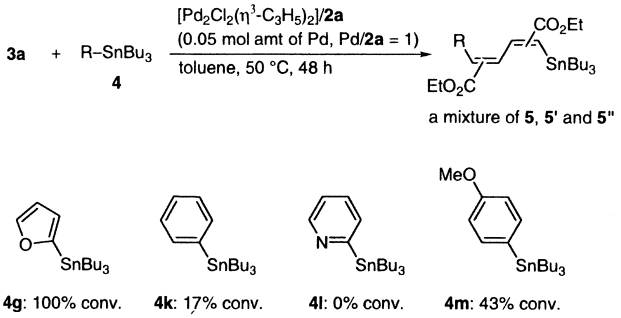
Only 1:1 carbostannylation product **6a** was obtained with the palladium–**1** catalyst, as we disclosed before (entry 14).[6] The reaction without any ligand was extremely sluggish (entry 15).

Dimerization–Carbostannylation Catalyzed by Pd–2a. We next examined the dimerization–carbostannylation of various organostannanes and alkynes using the Pd–**2a** catalyst (Scheme 3, Table 2). As mentioned above, the reaction of **3a** with **4a** proceeded smoothly to afford **5a** in 77% yield in a period of 40 min (entry 1). Tributyl(1-hexynyl)tin (**4b**) and tributyl(trimethylsilylethynyl)tin (**4c**) also reacted effectively with **3a** with perfect regioselectivities (entries 2 and 3). Alkenylstannanes **4d**, **4e** and **4f** were more reactive towards **3a** than alkynylstannanes and gave rise to the corresponding conjugated (stannyl)trienes consisting of two regioisomers **5** and **5′** (entries 4–6). The reaction of heteroarylstannanes such as tributyl(2-furyl)tin (**4g**) and tributyl(2-thienyl)tin (**4h**) with **3a** also proceeded; yields of regioisomer **5′** predominated over those of **5** and **5″** (entries 7 and 8). In all cases, the addition of organostannanes to **3a** occurred with exclusive *syn* selectivity (*vide infra*). The reaction was also applicable to dimethyl acetylenedicarboxylate (**3b**), giving **5i**–**5q**[12] in a stereoselective manner

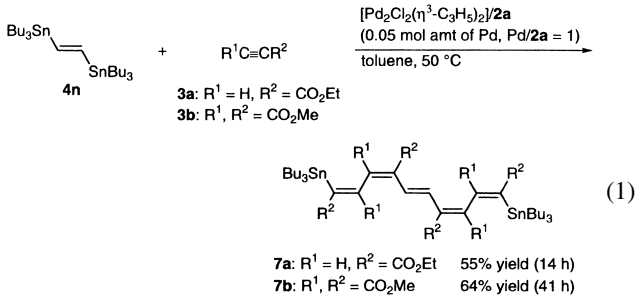
Table 2. Dimerization–Carbostannylation of Alkynes Catalyzed by Palladium–Diimine **2a**[a)]

Entry	Alkyne	R		Temp °C	Time h	Yield %[b)]	Product(s)	Ratio **5**:**5′**:**5″**[c)]
1	**3a**	PhC≡C	(**4a**)	50	0.7	77	**5a**	100:0:0
2		BuC≡C	(**4b**)	30	3	93	**5b**	100:0:0
3		TMSC≡C	(**4c**)	20	0.5	75	**5c**	100:0:0
4		CH_2=CH	(**4d**)	50	0.7	72	**5d**, **5′d**	79:21:0
5		(*E*)-PhCH=CH	(**4e**)	50	1	78	**5e**, **5′e**	89:11:0
6		(*E*)-HexCH=CH	(**4f**)	50	1	76	**5f**, **5′f**	71:29:0
7		2-furyl	(**4g**)	50	14	81	**5g**, **5′g**, **5″g**	30:63:7
8		2-thienyl	(**4h**)	50	12	42	**5h**, **5′h**, **5″h**	13:69:18
9	**3b**	PhC≡C	(**4a**)	70	2	77	**5i**	—
10		BuC≡C	(**4b**)	90	19	32	**5j**	—
11		TMSC≡C	(**4c**)	90	2	52	**5k**	—
12		CH_2=CH	(**4d**)	50	2	76	**5l**	—
13		(*E*)-PhCH=CH	(**4e**)	50	1	75	**5m**	—
14		(*E*)-HexCH=CH	(**4f**)	50	8	75	**5n**	—
15		2-furyl	(**4g**)	50	19	63	**5o**	—
16		2-benzofuryl	(**4i**)	50	26	75	**5p**	—
17		(*E*)-PhCH=CHCH$_2$	(**4j**)	50	1	86	**5q**[d)]	—

a) The reaction was carried out in toluene (3mL) at 50 °C using an alkyne (1.0 mmol) and an organostannane (0.34 mmol) in the presence of $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ (8.2 μmol) and **2a** (16 μmol). b) Isolated yield based on the organostannane is given. c) Determined by ^{119}Sn NMR. d) A 1:1 carbostannylation product (**6b**) was also obtained in 4% yield.



Scheme 4. Dimerization–carbostannylation of arylstannanes.



(1)

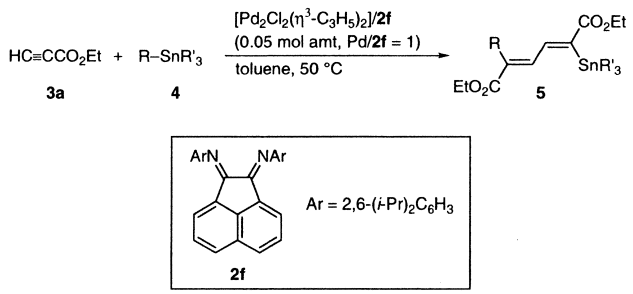
(entries 9–16). Tributyl[(*E*)-cinnamyl]tin (**4j**) can participate in the dimerization–carbostannylation with **3b** (entry 17). Ester substituent on acetylene seems to be essential for successful reaction: neither phenylacetylene, 1-octyne, nor 1-butyn-3-one gave the corresponding carbostannylation product.

In contrast to five-membered heteroarylstannanes, tributyl(phenyl)tin (**4k**) gave a dimerization–carbostannylation product with **3a** only in 17% conversion after 48 h, and tributyl(2-pyridyl)tin (**4l**) was totally unreactive (Scheme 4). Such an electron-donating group as methoxy on the phenyl in **4k** assisted the reaction: with **4m**, conversion increased to 43%. Thus the reactivity scale of arylstannanes is 2-furyl (**4g**) ≫ 4-$MeOC_6H_4$ (**4m**) > Ph (**4k**) > 2-pyridyl (**4l**), indicating that electron-richer arylstannanes are more subject to the reaction.

Application of the dimerization–carbostannylation to an organostannane containing two C–Sn bonds provided highly conjugated polyenylstannanes: the reaction of (*E*)-1,2-bis(tributylstannyl)ethene (**4n**) with alkynes **3a** and **3b** afforded α,ω-distannyldecapentaenes **7a** and **7b**, respectively, forming six new covalent bonds all in one pot (Eq.1).

High regioselectivity observed in the reaction of **4n** with **3a** compared with alkenylstannanes **4d**–**4f** can be attributed to the low reactivity of **4n**, as discussed later.

Regioselective Synthesis of Stannyl-Substituted Muconic Acid Derivatives. Although palladium complex coordinated by bulky diimine ligand, 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (**2f**), did not catalyze the reaction of **3a** with **4a** at 25 °C as stated above, this complex was found to promote the reaction at 50 °C, giving a single isomer regardless of organostannanes employed (Scheme 5).



Scheme 5. Pd–**2f**-catalyzed dimerization–carbostannylation.

Table 3. Pd–**2f**-Catalyzed Dimerization–Carbostannylation of Ethyl Propiolate (**3a**)[a)]

Entry	R	R′		Time / h	Yield / %[b)]	Product
1	CH_2=CH	Bu	(**4d**)	1	72	**5d**
2	2-furyl	Bu	(**4g**)	13	78	**5g**
3	2-thienyl	Bu	(**4h**)	22	68	**5h**
4	2-benzofuryl	Bu	(**4i**)	23	79	**5r**
5	3-thienyl	Bu	(**4o**)	21	80	**5s**
6	Ph	Me	(**4′k**)	27	42	**5t**
7	4-$MeOC_6H_4$	Me	(**4′m**)	19	64	**5u**

a) The reaction was carried out in toluene (3mL) at 50 °C using **3a** (1.0 mmol) and an organostannane (0.34 mmol) in the presence of $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ (8.2 μmol) and **2f** (16 μmol). b) Isolated yield based on the organostannane is given.

The dimerization–carbostannylation of **3a** in the presence of Pd–**2f** offers a straightforward method to synthesize variously substituted *trans,trans*-muconic acid derivatives. The results are summarized in Table 3. Tributyl(vinyl)tin (**4d**) smoothly reacted to afford **5d** as the sole product in 72% yield (entry 1). It is noteworthy that the Pd–**2f** catalyst allowed a variety of five-membered heteroarylstannanes to give **5** exclusively (entries 2–5), whereas with the Pd–**2a** catalyst and the heteroarylstannanes the reactions gave **5′** as major products (entries 7 and 8 of Table 2). Phenyl- and *p*-methoxyphenylstannanes could participate in the reaction, when $-SnBu_3$ in **4k** and **4m** was replaced by $-SnMe_3$, affording desired products **5t** and **5u** in moderate yields (entries 6 and 7).

Structure Determination of Dimerization–Carbostannylation Products. Configuration of **5a**–**5h** and **5r**–**5u** was determined based on coupling constants in NMR.[13] Products **5′d–5′h**, **5″g** and **5″h** were confirmed to be regioisomers of **5d**–**5h**, respectively, by the corresponding coupling constants between olefinic protons as well as between tin and olefinic proton and/or by NOE experiments. Typical examples of **5a**, **5′h** and **5″h** are shown in Fig. 1.

Catalytic Cycle. In the course of the present study, no trace of a 1:1 carbostannylation product was observed except for the case of tributyl[(*E*)-cinnamyl]tin (**4j**).[5,6] Furthermore, neither trimerization–carbostannylation products nor higher oligomers were produced. Consequently, the present reaction should be initiated not by oxidative addition of a C–Sn bond of an organostannane to a Pd(0)–diimine complex,[6] but by formation of palladacyclopentadiene (**8** or **9**) from a Pd(0)–diimine complex and 2 mol of an alkyne.[14] In order to confirm that the palladacyclopentadiene would be involved in the dimerization–carbostannylation, we monitored the reaction by ^{1}H NMR, choosing **2e** as a ligand, because the methyl substituent gave distinct information. ^{1}H NMR spectra of the reaction of **3b** with **4d** showed no other peaks than those of palladacycle **8a** in addition to those of the substrate and the expected product (Fig. 2). Furthermore, palladacycle **8b** was prepared from Pd(0)–**2a** and allowed to react with three equimolar amounts of **4d** to give carbostannylation product **5l** in a good yield, and **8b** was shown to be an equally active catalyst (Scheme 6). All these observations suggest that the catalytic cycle should be initiated by formation of the palladacyclopentadiene intermediate, followed by reaction with an organostannane, although subsequent steps of the catalytic cycle remain yet to be studied.

The different regioselectivities observed in the reaction of ethyl propiolate (**3a**) can be explained as follows (Scheme 7). Formation of three regioisomeric products **5**, **5′** and **5″** upon

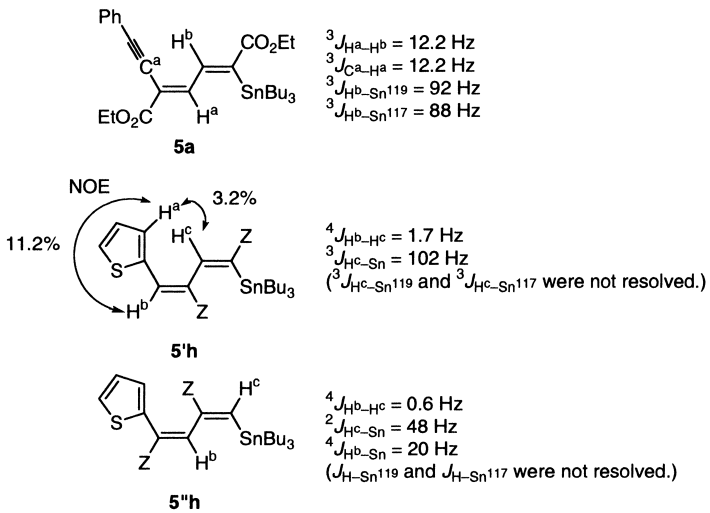
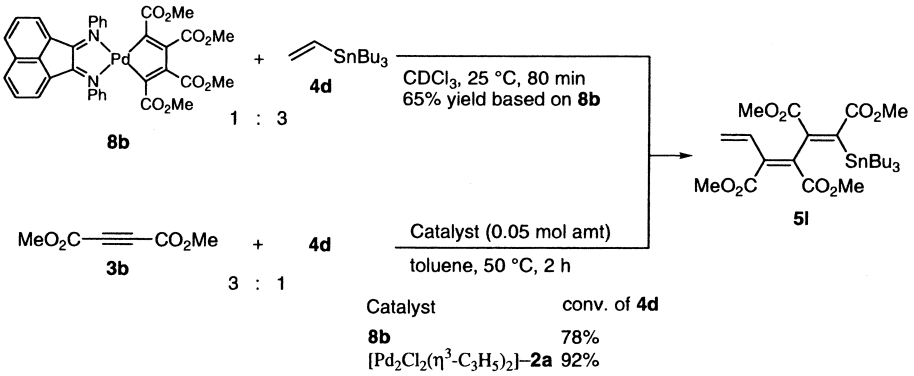


Fig. 1. Structure determination of dimerization–carbostannylation products.



Scheme 6. Reactions using palladacycle **8b**.

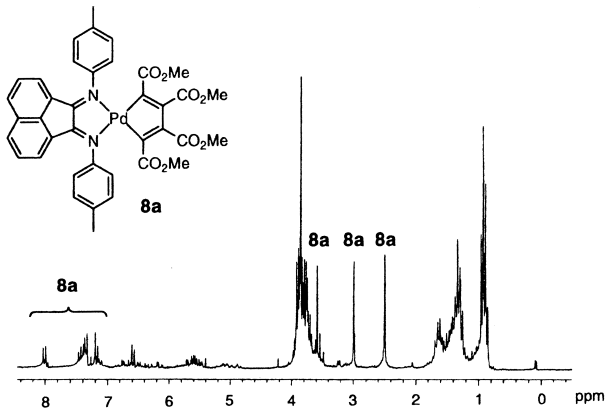
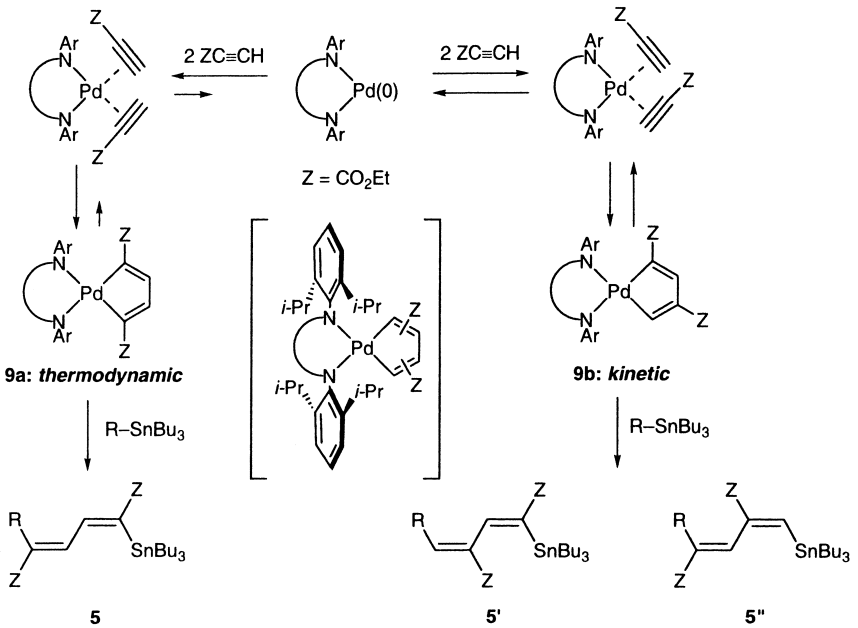
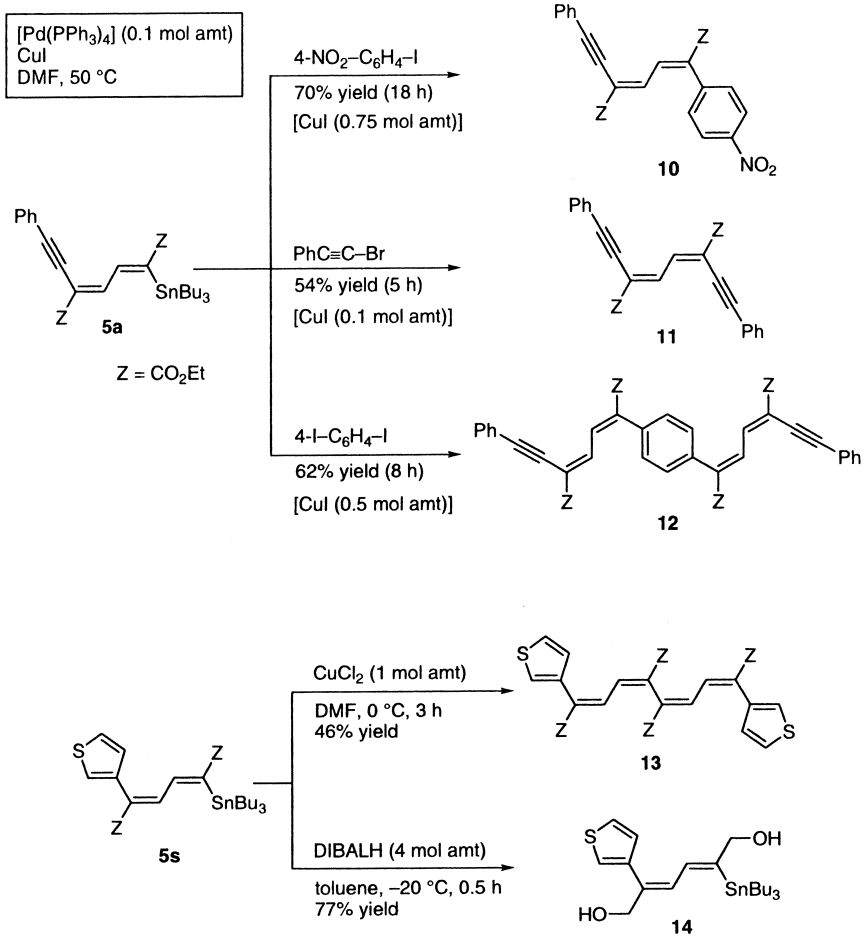


Fig. 2. ^{1}H NMR (200 MHz) spectrum of the reaction mixture (at ca. 31% conversion) in the reaction of **3b** with **4d** in the presence of $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$–**2e** complex (0.2 mol amt of Pd, Pd/**2e** = 1) in $CDCl_3$ at 25 °C.

use of Pd–**2a** is attributed to palladacycle intermediates, **9a** and **9b**, which might be equilibrated with each other via a palladium(0)–diimine complex, since product ratios are considerably influenced by the structure of the organostannane despite use of an identical catalyst system (see Table 2). Among these palladacycles, **9a** should be thermodynamically stable, because two electron-withdrawing ester groups are attached to carbons next to the palladium atom.[15] In contrast, formation of **9b** would be kinetically favored due to less steric repulsion between the aryl groups of the diimine ligand and the ester groups of **3a**. According to this mechanism, an organostannane with low reactivity towards palladacycle **9** should afford **5** predominantly, because kinetically generated palladacycle **9b** should isomerize to thermodynamically stable **9a** prior to reaction with the organostannane. Indeed, exclusive formation of a dimerization–carbostannylation product via **9a** (**5** or **7a**) was observed using such a less reactive organostannane as alkynylstannanes **4a**–**4c** or (*E*)-1,2-bis(tributylstannyl)ethene (**4n**) (entries 1–3 of Table 2 or Eq. 1), whereas the reaction of



Scheme 7. Plausible catalytic cycle of the dimerization–carbostannylation.



Scheme 8. Transformation of dimerization–carbostannylation products.

more reactive alkenylstannanes **4d**–**4f** gave mixtures of isomers (entries 4–6 of Table 2). In use of bulky diimine **2f**, the two isopropyl groups would prevent an organostannane from coordinating to an apical position of the palladacycle as in Scheme 7,[16] leading to slow reaction of the palladacycle with organostannanes (entry 1 vs 12 of Table 1), which resulted in the exclusive production of **5** irrespective of the organostannane used (Table 3). Although examples to support the reversibility of **9** remain yet to be found,[17] this catalytic cycle rationally explains the results. At present, the reason why five-membered heteroarylstannanes **4g** and **4h**, which react with **3a** most slowly in the presence of Pd–**2a** catalyst, give three regioisomeric products (entries 7 and 8 of Table 2) is unclear.

Transformation of Dimerization–Carbostannylation Products. Utility of the dimerization–carbostannylation reaction is demonstrated by transformation to more conjugated compounds through cross-coupling reaction (Scheme 8). Thus, cross-coupling reaction of **5a** with 4-iodonitrobenzene, 1-bromo-2-phenylethyne or 1,4-diiodobenzene in the presence of Pd(0)/CuI[18] gave **10**, **11** or **12**, respectively. Moreover, the π-conjugate system in **5s** could be extended by oxidative homocoupling reaction with $CuCl_2$ to afford **13** in 46% yield. Ester groups in **5s** could be reduced with diisobutylaluminum hydride to give stannyl-substituted allylic alcohol **14**.

Conclusion. The palladium–diimine complex has been disclosed to effectively catalyze the dimerization–carbostannylation of alkynes and to give highly conjugated (*Z*)-alkenylstannanes stereoselectively. Furthermore, regio- and stereoselective dimerization–carbostannylation of ethyl propiolate has been achieved in the presence of a palladium complex coordinated by bulky diimine **2f**, providing a simple and convenient approach to stannyl-substituted muconic acid derivatives. The π-system of the dimerization–carbostannylation products can be further extended to highly conjugated system through cross- or homocoupling reaction, proving that the dimerization–carbostannylation reaction offers a novel entry to the synthesis of various π-conjugated molecules.

Experimental

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through a BASF-Catalyst R3-11 column at 80 °C). Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz; ^{119}Sn, 101 MHz) spectrometer or a Varian Mercury 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz) spectrometer using tetramethylsilane (^{1}H) as an internal standard and tetramethyltin (^{119}Sn) as an external standard. The preparative recycling gel permeation chromatography was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). High-resolution mass spectra were obtained with a Bruker Bio APEX 70e spectrometer. All melting

points were measured with a Yanagimoto Micro Melting Point apparatus without correction. R_f values were measured by TLC analyses using Merck Kieselgel 60 F_{254}. Unless otherwise noted, commercially available reagents were used without purification. Solvents were distilled from a suitable drying reagent as follows: sodium/benzophenone ketyl for toluene, THF, dioxane, DME and octane; diphosphorus pentaoxide for chloroform; calcium hydride for DMF. *N*-(2-Diphenylphosphinobenzylidene)phenylethylamine (**1**),[6] 1,2-bis(phenylimino)acenaphthene (**2a**),[19] 1,2-bis[(4-trifluoromethylphenyl)imino]acenaphthene (**2b**),[19] 1,2-bis{[3,5-bis(trifluoromethyl)phenyl]imino}acenaphthene (**2c**),[19] 1,2-bis[(*p*-methoxyphenyl)imino]acenaphthene (**2d**),[19] 1,2-bis[(*p*-tolyl)imino]acenaphthene (**2e**),[19] 1,2-bis[(2,6-diisopropylphenyl)imino]-acenaphthene (**2f**),[19] 2,3-bis(phenylimino)butane (**2g**),[20] tributyl-(phenylethynyl)tin (**4a**),[21] tributyl(1-hexynyl)tin (**4b**),[21] tributyl-(trimethylsilylethynyl)tin (**4c**),[21] tributyl(vinyl)tin (**4d**),[22] tributyl-[(*E*)-styryl]tin (**4e**),[23] tributyl[(*E*)-1-octenyl]tin (**4f**),[24] tributyl(2-furyl)tin (**4g**),[25] tributyl(2-thienyl)tin (**4h**),[26] 2-benzofuryl(tributyl)tin (**4i**),[27] tributyl[(*E*)-cinnamyl]tin (**4j**),[28] tributyl(phenyl)tin (**4k**),[29] tributyl(2-pyridyl)tin (**4l**),[30] tributyl(*p*-methoxyphenyl)tin (**4m**),[31] (*E*)-1,2-bis(tributylstannyl)ethene (**4n**),[32] tributyl(3-thienyl)tin (**4o**)[33] and *p*-methoxyphenyl(trimethyl)tin (**4′m**)[34] were prepared according to literature procedures.

Dimerization–Carbostannylation of Alkynes. A General Procedure. A solution of **2** (16 μmol), $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ (3.0 mg, 8.2 μmol) and an alkyne (1.0 mmol) in toluene (3 mL) was degassed by four freeze-thaw cycles. To this solution was added an organostannane (0.34 mmol); each mixture was stirred at the specified temperature for the specified period indicated in Table 2 and 3. Concentration in vacuo followed by GPC purification gave the corresponding dimerization–carbostannylation products. Yields are listed in Table 2 and 3.

Diethyl (2*E*,4*Z*)-2-(Phenylethynyl)-5-(tributylstannyl)-2,4-hexadienedioate (5a). A brown oil, R_f 0.35 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.70–1.83 (m, 33 H), 4.24 (q, J = 7.2 Hz, 2 H), 4.32 (q, J = 7.2 Hz, 2 H), 7.15–7.74 (m, 6 H), 8.30 (d, J = 12.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.6, 14.2, 14.3, 27.2, 28.9, 61.0, 61.8, 83.4, 100.8, 121.3, 122.6, 128.4, 129.0, 131.8, 144.3, 147.8, 153.0, 164.5, 171.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −42.8. Found: C, 61.60; H, 7.60%. Calcd for $C_{30}H_{44}O_4Sn$: C, 61.34; H, 7.55%.

Diethyl (2*E*,4*Z*)-2-(1-Hexynyl)-5-(tributylstannyl)-2,4-hexadienedioate (5b). A brown oil, R_f 0.38 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.72–1.72 (m, 40 H), 2.49 (t, J = 6.9 Hz, 2 H), 4.08–4.36 (m, 4 H), 7.53 (d, J = 11.9 Hz, 1 H), 8.17 (d, J = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.59, 13.64, 14.2, 14.3, 19.6, 21.9, 27.2, 28.9, 30.5, 60.9, 61.6, 74.6, 102.8, 121.8, 143.6, 148.0, 151.8, 164.9, 171.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −43.3. Found: C, 59.12; H, 8.31%. Calcd for $C_{28}H_{48}O_4Sn$: C, 59.27; H, 8.53%.

Diethyl (2*E*,4*Z*)-5-(Tributylstannyl)-2-(trimethylsilylethynyl)-2,4-hexadienedioate (5c). A brown oil, R_f 0.43 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 0.71–1.73 (m, 33 H), 4.22 (q, J = 7.1 Hz, 2 H), 4.27 (q, J = 7.1 Hz, 2 H), 7.59 (d, J = 12.1 Hz, 1 H), 8.18 (d, J = 12.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −0.2, 11.9, 13.6, 14.1, 14.3, 27.2, 28.9, 61.0, 61.7, 98.1, 107.1, 121.1, 145.7, 147.7, 153.6, 164.3, 171.2; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −42.8. Found: C, 55.66; H, 8.55%. Calcd for $C_{27}H_{48}O_4SiSn$: C, 55.58; H, 8.29%.

Diethyl (2*E*,4*Z*)-2-Ethenyl-5-(tributylstannyl)-2,4-hexadienedioate (5d). A brown oil, R_f 0.38 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.82–1.74 (m, 33 H), 4.21 (q, J = 7.1 Hz, 2 H), 4.27 (q, J = 7.1 Hz, 2 H), 5.54 (dd, J = 11.5, 1.6 Hz, 1 H), 5.74 (dd, J = 17.6, 1.6 Hz, 1 H), 6.71 (dd, J = 17.6, 11.5 Hz, 1 H), 7.24 (d, J = 12.7 Hz, 1 H), 8.15 (d, J = 12.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.6, 14.25, 14.29, 27.2, 29.0, 60.9, 61.0, 122.7, 128.9, 134.7, 136.9, 146.6, 149.7, 166.6, 171.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −44.4. Found: C, 56.01; H, 8.24%. Calcd for $C_{24}H_{42}O_4Sn$: C, 56.16; H, 8.25%.

Diethyl 4-[(*E*)-2-Propenylidene]-2-(tributylstannyl)-(*Z*)-2-pentenedioate (5′d). A brown oil, R_f 0.32 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.69–1.78 (m, 33 H), 4.22 (q, J = 7.1 Hz, 2 H), 4.24 (q, J = 7.1 Hz, 2 H), 5.50 (d, J = 10.1 Hz, 1 H), 5.67 (d, J = 17.6, 1 H), 6.63 (ddd, J = 17.6, 11.2, 10.1 Hz, 1 H), 7.24 (d, J = 11.2 Hz, 1 H), 7.89 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.3, 27.3, 29.0, 60.9, 61.0, 126.5, 130.9, 132.9, 141.0, 144.2, 148.1, 166.3, 170.6; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −47.3. Found as a mixture of **5d** and **5′d**: C, 56.27; H, 8.22%. Calcd for $C_{24}H_{42}O_4Sn$: C, 56.16; H, 8.25%.

Diethyl 2-[(*E*)-Styryl]-5-(tributylstannyl)-(2*E*,4*Z*)-2,4-hexadienedioate (5e). A brown oil, R_f 0.33 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.76 (m, 33 H), 4.23 (q, J = 7.1 Hz, 2 H), 4.32 (q, J = 7.1 Hz, 2 H), 7.15–7.60 (m, 8 H), 8.29 (d, J = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.3, 27.2, 29.0, 60.9, 61.1, 120.5, 127.0, 128.4, 128.6, 134.3, 136.1, 136.5, 137.0, 146.5, 149.3, 166.8, 171.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −44.1. Found: C, 60.87; H, 7.80%. Calcd for $C_{30}H_{46}O_4Sn$: C, 61.13; H, 7.87%.

Diethyl 4-{(*E*)-[(*E*)-Cinnamylidene]}-2-(tributylstannyl)-(*Z*)-2-pentenedioate (5′e). A brown oil, R_f 0.24 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.68–1.50 (m, 33 H), 4.26 (q, J = 7.1 Hz, 4 H), 6.95–7.02 (m, 2 H), 7.28–7.50 (m, 6 H), 8.00 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.6, 14.3, 27.3, 29.0, 60.90, 60.95, 124.2, 127.4, 128.7, 129.2, 129.8, 136.0, 141.3, 141.5, 144.0, 148.6, 166.4, 170.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −47.3. Found as a mixture of **5e** and **5′e**: C, 61.35; H, 7.77%. Calcd for $C_{30}H_{46}O_4Sn$: C, 61.13; H, 7.87%.

Diethyl 2-[(*E*)-1-Octenyl]-5-(tributylstannyl)-(2*E*,4*Z*)-2,4-hexadienedioate (5f). A brown oil, R_f 0.47 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.77 (m, 44 H), 2.22 (q, J = 6.8 Hz, 2 H), 4.21 (q, J = 7.1 Hz, 2 H), 4.26 (q, J = 7.1 Hz, 2 H), 6.21 (dt, J = 15.7, 6.8 Hz, 1 H), 6.40 (d, J = 15.7 Hz, 1 H), 7.11 (d, J = 11.9 Hz, 1 H), 8.17 (d, J = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.7, 13.6, 14.1, 14.2, 14.3, 22.6, 27.2, 28.89, 28.94, 29.0, 31.6, 33.9, 60.8, 60.9, 122.0, 134.8, 135.1, 140.7, 147.3, 147.7, 167.0, 171.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −45.0. Found as a mixture of **5f** and **5'f**: C, 60.30; H, 8.93%. Calcd for $C_{30}H_{54}O_4Sn$: C, 60.31; H, 9.11%.

Diethyl 4-{(*E*)-[(*E*)-2-Nonenylidene]}-2-(tributylstannyl)-(*Z*)-2-pentenedioate (5′f). A brown oil, R_f 0.32 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.69–1.75 (m, 44 H), 2.17 (q, J = 6.8 Hz, 2 H), 4.22 (q, J = 7.2 Hz, 2 H), 4.23 (q, J = 7.1 Hz, 2 H), 6.18 (dt, J = 15.2, 6.6 Hz, 1 H), 6.33 (dd, J = 15.2, 10.3 Hz, 1 H), 7.23 (d, J = 10.3 Hz, 1 H), 7.91 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.0, 14.3, 22.6, 27.3, 28.9, 29.0, 31.7, 33.5, 60.8, 126.6, 127.7, 141.7, 143.1, 146.4, 148.8, 166.6, 170.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −47.9. Found as a mixture of **5f** and **5′f**: C, 60.30; H, 8.93%. Calcd for $C_{30}H_{54}O_4Sn$: C, 60.31; H, 9.11%.

Diethyl (2*E*,4*Z*)-2-(2-Furyl)-5-(tributylstannyl)-2,4-hexadienedioate (5g). A brown oil, R_f 0.30 (hexane–ethyl acetate= 7:1). ^{1}H NMR ($CDCl_3$) δ 0.73–1.75 (m, 33 H), 4.22 (q, J = 7.1 Hz, 2 H), 4.32 (q, J = 7.1 Hz, 2 H), 6.48 (dd, J = 3.5, 1.8 Hz, 1 H), 6.90 (d, J = 3.1 Hz, 1 H), 7.30 (d, J = 12.1 Hz, 1 H), 7.56 (dd, J = 1.8, 0.4 Hz, 1 H), 8.55 (d, J = 12.1 Hz, 1 H); ^{13}C NMR

($CDCl_3$) δ 11.8, 13.7, 14.3, 27.2, 29.0, 60.9, 61.4, 111.5, 114.4, 125.6, 135.6, 143.8, 148.5, 149.4, 151.3, 165.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −45.4. Found: C, 56.26; H, 7.75%. Calcd for $C_{26}H_{42}O_5Sn$: C, 56.44; H, 7.65%.

Diethyl 4-[(*E*)-(2-Furyl)methylene]-2-(tributylstannyl)-(*Z*)-2-pentenedioate (5′g). A brown oil, R_f 0.28 (hexane–ethyl acetate = 7:1). ^1H NMR ($CDCl_3$) δ 0.67–1.73 (m, 33 H), 4.247 (q, J = 7.1 Hz, 2 H), 4.254 (q, J = 7.1 Hz, 2 H), 6.44–6.54 (m, 1 H), 6.73 (d, J = 3.5 Hz, 1 H), 7.53 (d, J = 1.7 Hz, 1 H), 7.56 (d, J = 1.8 Hz, 1 H), 7.99 (d, J = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.29, 14.32, 27.3, 29.0, 60.8, 61.2, 112.7, 117.0, 126.0, 128.1, 143.9, 145.1, 148.1, 151.0, 166.2, 171.3; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −46.1. Found: C, 56.22; H, 7.41%. Calcd for $C_{26}H_{42}O_5Sn$: C, 56.44; H, 7.65%.

Diethyl 2-(2-Furyl)-4-[(*E*)-(tributylstannyl)methylene]-(*E*)-2-pentenedioate (5″g). A brown oil, R_f 0.24 (hexane–ethyl acetate = 7:1). ^1H NMR ($CDCl_3$) δ 0.52–1.66 (m, 33 H), 4.16 (q, J = 7.0 Hz, 2 H), 4.18 (q, J = 7.1 Hz, 2 H), 6.41 (dd, J = 3.5, 1.8 Hz, 1 H), 6.62 (d, J = 3.5 Hz, 1 H), 7.44 (d, J = 1.7 Hz, 1 H), 7.57 (s, 1 H), 7.93 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.7, 13.6, 14.2, 14.3, 27.3, 28.9, 60.8, 61.0, 112.1, 115.8, 127.8, 128.0, 143.2, 144.6, 150.8, 151.8, 164.7, 166.9; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −57.7. Found as a mixture of **5g**, **5′g** and **5″g**: C, 56.59; H, 7.42%. Calcd for $C_{26}H_{42}O_5Sn$: C, 56.44; H, 7.65%.

Diethyl (2*E*,4*Z*)-2-(2-Thienyl)-5-(tributylstannyl)-2,4-hexadienedioate (5h). A brown oil, R_f 0.35 (hexane–ethyl acetate = 7:1). ^1H NMR ($CDCl_3$) δ 0.73–1.71 (m, 33 H), 4.19 (q, J = 7.1 Hz, 2 H), 4.32 (q, J = 7.1 Hz, 2 H), 7.07 (dd, J = 4.9, 3.5 Hz, 1 H), 7.15 (dd, J = 3.5, 1.3 Hz, 1 H), 7.46 (dd, J = 4.9, 1.3 Hz, 1 H), 7.52 (d, J = 11.6 Hz, 1 H), 8.07 (d, J = 11.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.3, 27.2, 29.0, 60.9, 61.6, 126.6, 128.4, 130.7, 131.0, 134.7, 138.0, 148.0, 150.8, 166.4, 171.4; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −44.0. Found: C, 54.88; H, 7.57%. Calcd for $C_{26}H_{42}O_4SSn$: C, 54.85; H, 7.43%.

Diethyl 4-[(*E*)-(2-Thienyl)methylene]-2-(tributylstannyl)-(*Z*)-2-pentenedioate (5′h). A brown oil, R_f 0.28 (hexane–ethyl acetate = 7:1). ^1H NMR ($CDCl_3$) δ 0.65–1.76 (m, 33 H), 4.25 (q, J = 7.1 Hz, 2 H), 4.26 (q, J = 7.1 Hz, 2 H), 7.02–7.14 (m, 1 H), 7.33 (d, J = 3.3 Hz, 1 H), 7.48 (d, J = 5.1 Hz, 1 H), 7.87 (d, J = 1.7 Hz, 1 H), 8.00 (d, J = 1.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.3, 27.3, 29.0, 60.8, 61.2, 126.4, 127.5, 131.4, 133.3, 133.7, 138.5, 146.1, 147.9, 166.3, 170.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −45.7. Found: C, 54.95; H, 7.69%. Calcd for $C_{26}H_{42}O_4SSn$: C, 54.85; H, 7.43%.

Diethyl 2-(2-Thienyl)-4-[(*E*)-(tributylstannyl)methylene]-(*E*)-2-pentenedioate (5″h). A brown oil, R_f 0.22 (hexane–ethyl acetate = 7:1). ^1H NMR ($CDCl_3$) δ 0.53–1.65 (m, 33 H), 4.20 (q, J = 7.1 Hz, 2 H), 4.22 (q, J = 7.1 Hz, 2 H), 6.99–7.07 (m, 1 H), 7.22–7.41 (m, 2 H), 7.93 (d, J = 0.6 Hz, 1 H), 8.11 (d, J = 0.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.8, 13.6, 14.2, 14.3, 27.3, 29.0, 60.9, 127.0, 128.1, 130.3, 133.4, 134.0, 138.4, 142.7, 156.0, 164.5, 166.9; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −58.1. Found: C, 54.57; H, 7.18%. Calcd for $C_{26}H_{42}O_4SSn$: C, 54.85; H, 7.43%.

Tetramethyl (1*E*,3*Z*)-6-Phenyl-1-(tributylstannyl)-1,3-hexadien-5-yne-1,2,3,4-tetracarboxylate (5i). A brown oil, R_f 0.39 (hexane–ethyl acetate = 2:1). ^1H NMR ($CDCl_3$) δ 0.73–1.83 (m, 27 H), 3.71 (s, 3 H), 3.77 (s, 3 H), 3.86 (s, 3 H), 3.93 (s, 3 H), 7.16–7.65 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.5, 27.2, 28.6, 51.6, 52.7, 53.2, 84.1, 104.9, 121.4, 128.4, 129.5, 129.9, 132.0, 132.5, 135.0, 137.1, 161.0, 163.0, 164.7, 172.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −26.1. Found: C, 56.92; H, 6.63%. Calcd for $C_{32}H_{44}O_8Sn$: C, 56.91; H, 6.57%.

Tetramethyl (1*E*,3*Z*)-1-(Tributylstannyl)-1,3-decadien-5-yne-1,2,3,4-tetracarboxylate (5j). A brown oil, R_f 0.45 (hexane–ethyl acetate = 2:1). ^1H NMR ($CDCl_3$) δ 0.71–1.72 (m, 34 H), 2.32 (t, J = 7.1 Hz, 2 H), 3.68 (s, 3 H), 3.71 (s, 3 H), 3.77 (s, 3 H), 3.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 12.4, 13.5, 13.7, 19.7, 22.0, 27.2, 28.8, 30.1, 51.4, 52.5, 52.9, 75.3, 105.8, 127.9, 135.8, 136.0, 162.4, 164.9, 165.5, 166.7, 171.2; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −35.0. Found: C, 55.04; H, 7.46%. Calcd for $C_{30}H_{48}O_8Sn$: C, 54.98; H, 7.38%.

Tetramethyl (1*E*,3*Z*)-1-(Tributylstannyl)-6-(trimethylsilyl)1,3-hexadien-5-yne-1,2,3,4-tetracarboxylate (5k). A brown oil, R_f 0.62 (hexane–ethyl acetate = 2:1). ^1H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 0.81–1.73 (m, 27 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 3.80 (s, 3 H), 3.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ −0.7, 11.1, 13.6, 27.2, 28.6, 51.4, 52.5, 52.7, 53.1, 97.7, 112.3, 129.0, 134.7, 139.2, 160.6, 162.5, 164.4, 172.3; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −27.4. Found: C, 51.86; H, 7.00%. Calcd for $C_{29}H_{48}O_8SiSn$: C, 51.87; H, 7.21%.

Tetramethyl (1*E*,3*Z*)-1-(Tributylstannyl)-1,3,5-hexatriene-1,2,3,4-tetracarboxylate (5l). A brown oil, R_f 0.42 (hexane–ethyl acetate = 2:1). ^1H NMR ($CDCl_3$) δ 0.80–1.82 (m, 27 H), 3.70 (s, 3 H), 3.74 (s, 3H), 3.83 (s, 3 H), 3.92 (s, 3 H), 5.54 (d, J = 17.4 Hz, 1 H), 5.60 (d, J = 10.8 Hz, 1 H), 6.96 (dd, J = 17.4, 10.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.6, 27.2, 28.6, 51.7, 52.5, 52.7, 125.2, 127.6, 130.9, 134.6, 145.5, 161.1, 163.3, 165.2, 167.4, 172.4; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −26.5. Found: C, 51.82; H, 7.11%. Calcd for $C_{26}H_{42}O_8Sn$: C, 51.93; H, 7.04%. Found: C, 51.82; H, 7.11%.

Tetramethyl (1*E*,3*Z*,5*E*)-6-Phenyl-1-(tributylstannyl)-1,3,5-hexatriene-1,2,3,4-tetracarboxylate (5m). A brown oil, R_f 0.40 (hexane–ethyl acetate = 2:1). ^1H NMR ($CDCl_3$) δ 0.70–1.58 (m, 27 H), 3.69 (s, 3 H), 3.73 (s, 3 H), 3.85 (s, 3 H), 3.97 (s, 3 H), 6.75 (d, J = 16.2 Hz, 1 H), 6.96 (d, J = 16.2 Hz, 1 H), 7.20–7.54 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.5, 27.1, 28.6, 51.7, 52.4, 52.6, 52.7, 122.0, 126.4, 127.7, 128.8, 129.7, 134.9, 135.2, 139.5, 145.9, 161.3, 163.5, 165.4, 168.0, 172.6; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −30.3. Found: C, 56.62; H, 7.04%. Calcd for $C_{32}H_{46}O_8Sn$: C, 56.74; H, 6.84%.

Tetramethyl (1*E*,3*Z*,5*E*)-1-(Tributylstannyl)-1,3,5-dodecatriene-1,2,3,4-tetracarboxylate (5n). A brown oil, R_f 0.46 (hexane–ethyl acetate = 2:1). ^1H NMR ($CDCl_3$) δ 0.78–1.64 (m, 38 H), 2.16 (q, J = 7.0 Hz, 2 H), 3.67 (s, 3 H), 3.70 (s, 3 H), 3.81 (s, 3 H), 3.89 (s, 3 H), 6.00 (dt, J = 15.9, 6.8 Hz, 1 H), 6.23 (d, J = 15.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.6, 14.0, 22.5, 27.2, 28.5, 28.6, 28.9, 31.5, 33.7, 51.6, 52.3, 52.4, 52.6, 124.5, 134.9, 144.6, 146.1, 160.7, 163.5, 165.5, 168.0, 172.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −27.7. Found: C, 55.88; H, 7.98%. Calcd for $C_{32}H_{54}O_8Sn$: C, 56.07; H, 7.94%.

Tetramethyl (1*E*,3*Z*)-1-(2-Furyl)-4-(tributylstannyl)-1,3-butadiene-1,2,3,4-tetracarboxylate (5o). A brown solid, mp 86–88 °C. ^1H NMR ($CDCl_3$) δ 0.67–1.49 (m, 27 H), 3.67 (s, 3 H), 3.76 (s, 3 H), 3.85 (s, 3 H), 3.97 (s, 3 H), 6.49 (dd, J = 3.7, 1.8 Hz, 1 H), 6.79 (dd, J = 3.7, 0.7 Hz, 1 H), 7.53 (dd, J = 1.8, 0.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.6, 13.6, 27.2, 28.5, 51.6, 52.6, 52.9, 112.8, 117.6, 122.9, 135.1, 136.0, 145.6, 148.0, 159.5, 163.4, 165.5, 166.6, 172.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ −29.3. Found: C, 52.25; H, 6.73%. Calcd for $C_{28}H_{42}O_9Sn$: C, 52.44; H, 6.60%.

Tetramethyl (1*E*,3*Z*)-1-(2-Benzofuryl)-4-(tributylstannyl)-1,3-butadiene-1,2,3,4-tetracarboxylate (5p). A brown oil, R_f 0.38 (hexane–ethyl acetate = 2:1). ^1H NMR ($CDCl_3$) δ 0.64–1.40 (m, 27 H), 3.69 (s, 3 H), 3.79 (s, 3 H), 3.89 (s, 3 H), 4.02 (s, 3 H), 7.07 (d, J = 0.9 Hz, 1 H), 7.17–7.64 (m, 4 H); ^{13}C NMR ($CDCl_3$)

δ 10.6, 13.4, 27.1, 28.5, 51.6, 52.7, 52.8, 53.1, 111.9, 113.5, 122.1, 123.7, 125.9, 127.1, 127.5, 135.2, 136.1, 147.3, 149.4, 155.5, 159.0, 163.4, 165.4, 172.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −28.7. Found: C, 55.30; H, 6.55%. Calcd for $C_{32}H_{44}O_9Sn$: C, 55.59; H, 6.41%.

Tetramethyl (1*E*,3*Z*,6*E*)-7-Phenyl-1-(tributylstannyl)-1,3,6-heptatriene-1,2,3,4-tetracarboxylate (5q). A brown oil, R_f 0.65 (hexane–ethyl acetate = 2:1). ^{1}H NMR ($CDCl_3$) δ 0.82–1.67 (m, 27 H), 3.60 (s, 3 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 3.83 (s, 3 H), 6.04 (dt, J = 15.7, 7.0 Hz, 1 H), 6.43 (d, J = 15.7 Hz, 1 H), 7.14–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.0, 13.5, 27.2, 28.6, 35.6, 51.6, 52.3, 52.45, 52.54, 122.7, 126.2, 127.5, 128.4, 130.3, 133.5, 135.0, 136.8, 145.4, 159.7, 163.3, 165.4, 168.6, 172.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −28.3. Found: C, 57.07; H, 7.27%. Calcd for $C_{33}H_{48}O_8Sn$: C, 57.32; H, 7.00%.

Diethyl (2*E*,4*Z*)-2-(2-Benzofuryl)-5-(tributylstannyl)-2,4-hexadienedioate (5r). A brown oil, R_f 0.41 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.68–1.75 (m, 33 H), 4.23 (q, J = 7.1 Hz, 2 H), 4.36 (q, J = 7.1 Hz, 2 H), 7.15–7.70 (m, 6 H), 8.69 (d, J = 12.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.7, 14.3, 27.2, 29.0, 61.0, 61.6, 110.7, 111.3, 121.7, 123.1, 125.4, 125.7, 128.2, 138.4, 148.1, 153.2, 155.1, 165.6, 165.7, 174.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −45.0. Found: C, 59.98; H, 7.41%. Calcd for $C_{30}H_{44}O_5Sn$: C, 59.72; H, 7.35%.

Diethyl (2*E*,4*Z*)-2-(3-Thienyl)-5-(tributylstannyl)-2,4-hexadienedioate (5s). A brown oil, R_f 0.37 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.67 (m, 33 H), 4.17 (q, J = 7.1 Hz, 2 H), 4.29 (q, J = 7.1 Hz, 2 H), 7.13 (dd, J = 4.5, 1.8 Hz, 1 H), 7.29–7.36 (m, 2 H), 7.50 (d, J = 11.7 Hz, 1 H), 7.91 (d, J = 11.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.3, 27.2, 29.0, 60.9, 61.3, 124.8, 126.9, 129.6, 133.0, 134.1, 138.1, 148.0, 150.1, 166.7, 171.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −44.2. Found: C, 54.84; H, 7.72%. Calcd for $C_{26}H_{42}O_4SSn$: C, 54.85; H, 7.43%.

Diethyl (2*E*,4*Z*)-2-Phenyl-5-(trimethylstannyl)-2,4-hexadienedioate (5t). A brown oil, R_f 0.26 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 9 H), 1.25 (t, J = 7.1 Hz, 3 H), 1.32 (t, J = 7.1 Hz, 3 H), 4.14 (q, J = 7.1 Hz, 2 H), 4.27 (q, J = 7.1 Hz, 2 H), 7.17–7.45 (m, 5 H), 7.65 (d, J = 11.9 Hz, 1 H), 7.72 (d, J = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −6.7, 14.2, 60.9, 61.3, 128.0, 128.3, 130.3, 134.0, 137.8, 138.9, 148.1, 149.5, 166.9, 170.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −38.1. Found: C, 52.41; H, 6.07%. Calcd for $C_{19}H_{26}O_4Sn$: C, 52.21; H, 6.00%.

Diethyl (2*E*,4*Z*)-2-(4-Methoxyphenyl)-5-(trimethylstannyl)-2,4-hexadienedioate (5u). A brown oil, R_f 0.17 (hexane–ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9 H), 1.25 (t, J = 7.1 Hz, 3 H), 1.32 (t, J = 7.1 Hz, 3 H), 3.83 (s, 3 H), 4.14 (q, J = 7.1 Hz, 2 H), 4.26 (q, J = 7.1 Hz, 2 H), 6.91 (d, J = 8.6 Hz, 2 H), 7.19 (d, J = 8.6 Hz, 2 H), 7.60 (d, J = 11.9 Hz, 1 H), 7.77 (d, J = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ −6.8, 14.1, 55.2, 60.8, 61.2, 113.4, 126.2, 131.6, 137.0, 138.4, 148.5, 148.6, 159.6, 167.1, 170.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −38.5. Found: C, 51.67; H, 6.12%. Calcd for $C_{20}H_{28}O_5Sn$: C, 51.42; H, 6.04%.

Dimerization–Carbostannylation of Alkynes with (*E*)-1,2-Bis(tributylstannyl)ethene. A solution of 1,2-bis(phenylimino)acenaphthene (**2a**) (5.5 mg, 16 μmol), [$Pd_2Cl_2(\eta^3$-$C_3H_5)_2$] (3.0 mg, 8.2 μmol) and an alkyne (1.0 mmol) in toluene (3 mL) was degassed by four freeze-thaw cycles. To this solution was added (*E*)-1,2-bis(tributylstannyl)ethene (**4n**) (0.10 g, 0.17 mmol), and the mixture was stirred at 50 °C. After the time specified in Eq.1, the solvent was evaporated. GPC purification of the residue gave the corresponding dimerization–carbostannylation product.

Tetraethyl (1*Z*,3*E*,5*E*,7*E*,9*Z*)-1,10-Bis(tributylstannyl)-1,3,5,7,9-decapentaene-1,4,7,10-tetracarboxylate (7a). A brown oil, R_f 0.69 (hexane–ethyl acetate = 2:1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.81 (m, 66 H), 4.20 (q, J = 7.1 Hz, 4 H), 4.31 (q, J = 7.1 Hz, 4 H), 7.26 (d, J = 12.1 Hz, 2 H), 7.32 (s, 2 H), 8.17 (d, J = 12.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.25, 14.29, 27.2, 29.0, 60.9, 61.2, 127.8, 134.0, 138.0, 145.9, 151.0, 166.5, 171.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −44.0. Found: C, 55.35; H, 7.88%. Calcd for $C_{46}H_{80}O_8Sn_2$: C, 55.33; H, 8.08%.

Octamethyl (1*E*,3*Z*,5*E*,7*Z*,9*E*)-1,10-Bis(tributylstannyl)-1,3,5,7,9-decapentaene-1,2,3,4,7,8,9,10-octacarboxylate (7b). A brown solid, mp 91–92 °C. ^{1}H NMR ($CDCl_3$) δ 0.69–1.93 (m, 54 H), 3.67 (s, 6 H), 3.73 (s, 6 H), 3.82 (s, 6 H), 3.94 (s, 6 H), 6.54 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.6, 27.1, 28.6, 51.6, 52.6, 52.7, 52.8, 130.7, 131.9, 134.3, 144.5, 162.1, 162.9, 164.8, 166.5, 172.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −25.9. Found: C, 50.93; H, 6.89%. Calcd for $C_{50}H_{80}O_{16}Sn_2$: C, 51.13; H, 6.86%.

Cross-Coupling of 5a with 4-Iodonitrobenzene. A solution of **5a** (50 mg, 85 μmol) in DMF (1.5 mL) was degassed by three freeze-thaw cycles. To this solution was added 4-iodonitrobenzene (21 mg, 85 μmol), [$Pd(PPh_3)_4$] (9.8 mg, 8.5 μmol) and CuI (12 mg, 64 μmol). The mixture was stirred at 50 °C for 18 h and then diluted with diethyl ether (25 mL). The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was diluted with diethyl ether (10 mL) and stirred for 30 min with a 1 M (= 1 mol dm^{-3}) KF aqueous solution (2 mL). Filtration through a Celite plug was followed by extraction with diethyl ether (20 mL). The organic layer was washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave diethyl (2*E*,4*E*)-2-(4-nitrophenyl)-5-(phenylethynyl)-2,4-hexadienedioate (**10**) (25 mg, 70% yield) as a yellow solid: mp 147–149 °C. ^{1}H NMR ($CDCl_3$) δ 1.26 (t, J = 7.1 Hz, 3 H), 1.27 (t, J = 7.1 Hz, 3 H), 4.21 (q, J = 7.1 Hz, 2 H), 4.24 (q, J = 7.1 Hz, 2 H), 7.09–7.75 (m, 8 H), 8.11 (d, J = 12.3 Hz, 1 H), 8.22 (d, J = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.09, 14.13, 61.9, 62.1, 83.4, 102.1, 122.2, 123.3, 123.5, 128.5, 129.4, 131.3, 131.9, 136.5, 137.5, 138.9, 140.9, 147.8, 164.0, 165.6. HRMS (ESI) Found: *m*/*z* 442.1261. Calcd for $C_{24}H_{21}NO_6Na$: M^++Na, 442.1261.

Cross-Coupling of 5a with 1-Bromo-2-phenylethyne. A solution of **5a** (65 mg, 0.11 mmol) in DMF (1.5 mL) was degassed by three freeze-thaw cycles. To this solution was added 1-bromo-2-phenylethyne (20 mg, 0.11 mmol), [$Pd(PPh_3)_4$] (13 mg, 11 μmol) and CuI (2.1 mg, 11 μmol). The mixture was stirred at 50 °C for 5 h and then diluted with diethyl ether (25 mL). The organic layer was washed with water and dried over anhydrous magnesium sulfate; then it was concentrated in vacuo. The residue was diluted with diethyl ether (10 mL) and stirred for 30 min with a 1 M KF aqueous solution (2 mL). Filtration through a Celite plug was followed by extraction with diethyl ether (20 mL). The organic layer was washed successively with water and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave diethyl (2*E*,4*E*)-2,5-Bis(phenylethynyl)-2,4-hexadienedioate (**11**) (24 mg, 54% yield) as a red solid: mp 112–114 °C. ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.1 Hz, 6 H), 4.02 (q, J = 7.1 Hz, 4 H), 6.82 (s, 2 H), 7.13–7.45 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 60.5, 117.3, 125.4, 127.8, 129.2, 131.2, 154.4, 154.8, 165.1. HRMS (ESI) Found: *m*/*z* 421.1414. Calcd for $C_{26}H_{22}O_4Na$: M^++Na, 421.1410.

Cross-Coupling of 5a with 1,4-Diiodobenzene. A solution of **5a** (48 mg, 81 μmol) in DMF (1.5 mL) was degassed by three freeze-thaw cycles. To this solution was added 1,4-diiodobenzene

(13 mg, 41 μmol), [$Pd(PPh_3)_4$] (9.4 mg, 8.1 μmol) and CuI (7.7 mg, 41 μmol). The mixture was stirred at 50 °C for 8 h and then diluted with diethyl ether (25 mL). The organic layer was washed with water, dried over anhydrous magnesium sulfate; then it was concentrated in vacuo. The residue was diluted with diethyl ether (10 mL) and stirred for 30 min with a 1 M KF aqueous solution (2 mL). Filtration through a Celite plug was followed by extraction with diethyl ether (20 mL). The organic layer was washed successively with water and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave 2,2′-(*p*-phenylene)bis[diethyl(2*E*,4*E*)-5-phenylethynyl-2,4-hexadienedioate] (**12**) (17 mg, 62% yield) as an orange solid: mp 164–167 °C. ^{1}H NMR ($CDCl_3$) δ 1.33 (t, J = 7.2 Hz, 6 H), 1.36 (t, J = 7.1 Hz, 6 H), 4.29 (q, J = 7.2 Hz, 4 H), 4.33 (q, J = 7.1 Hz, 4 H), 7.15–7.73 (m, 16 H), 8.12 (d, J = 12.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.2, 61.6, 61.9, 83.8, 101.3, 122.1, 122.5, 128.4, 129.1, 130.1, 131.8, 134.5, 135.2, 139.2, 140.6, 164.3, 166.6. HRMS (ESI) Found: *m/z* 693.2464. Calcd for $C_{42}H_{38}O_8Na$: M^++Na, 693.2459.

Homocoupling of 5s. To a solution of **5s** (29 mg, 52 μmol) in DMF (1.0 mL) was added $CuCl_2$ (6.9 mg, 52 μmol), and the mixture was stirred at 0 °C for 3 h. Saturated aqueous NH_4Cl–NH_3 (pH 8, 2 mL) was added, and the mixture was stirred under an aerial atmosphere until the color became deep blue. The mixture was extracted with diethyl ether (10 mL). The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave tetraethyl (1*E*,3*E*,5*E*,7*E*)-1,8-di(3-thienyl)-1,3,5,7-octatetraene-1,4,5,8-tetracarboxylate (**13**) (6.6 mg, 46% yield) as a yellow oil: R_f 0.37 (hexane–ethyl acetate = 2:1). ^{1}H NMR ($CDCl_3$) δ 1.24 (t, J = 7.1 Hz, 12 H), 4.22 (q, J = 7.1 Hz, 8 H), 7.12–7.48 (m, 8 H), 7.67 (d, J = 11.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.2, 61.4, 61.5, 125.2, 127.6, 129.5, 132.5, 133.5, 134.1, 135.0, 138.2, 165.8, 166.2. Found: C, 60.04; H, 5.65%. Calcd for $C_{28}H_{30}O_8S_2$: C, 60.20; H, 5.41%.

Reduction of 5s. To a solution of **5s** (19 mg, 33 μmol) in toluene (1.0 mL) was added diisobutylaluminum hydride (0.9 M in hexanes, 0.15 mL, 0.13 mmol); then the mixture was stirred at −20 °C for 30 min. Saturated aqueous NH_4Cl (3 mL) was added, and the resulting mixture was extracted with ethyl acetate (10 mL). The organic layer was separated, dried over anhydrous magnesium sulfate; then it was concentrated in vacuo. GPC purification of the residue gave (2*E*,4*E*)-2-(3-thienyl)-5-(tributylstannyl)-2,4-hexadiene-1,6-diol (**14**) (12 mg, 77%) as a yellow oil: R_f 0.51 (hexane–ethyl acetate = 2:1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.75 (m, 27 H), 4.28 (d, J = 4.8 Hz, 2 H), 4.41 (d, J = 5.5 Hz, 2 H), 6.32 (d, J = 11.0 Hz, 1 H), 7.00–7.44 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 10.5, 13.7, 27.3, 29.2, 67.7, 70.3, 123.8, 125.4, 128.2, 135.9, 136.7, 138.1, 152.6; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −52.3. Found: C, 54.43; H, 7.61%. Calcd for $C_{22}H_{38}O_2SSn$: C, 54.45; H, 7.89%.

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