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Efficient Cyclotrimerization of Bicyclic *vic*-Bromostannylalkenes Promoted by Copper(I) Thiophen-2-carboxylate

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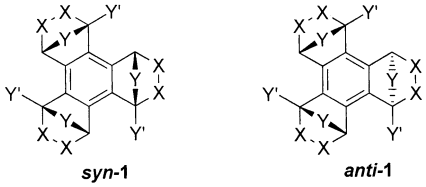
Abstract: Copper(I) thiophen-2-carboxylate was successfully employed in the trimerization of [2.2.1] bicyclic *vic*-bromotrimethyltin olefins (in their racemic composition), bearing different functionalities, to invariably obtain almost quantitative yields of the syn and anti tris-annelated benzenes. The two isomers come in different ratios, smaller than or equal to the statistical 1:3 ratio, depending on the steric hindrance opposed by the functionalities. In the case of enantiopure (3-bromo-4,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)trimethylstannane, the 1:9 ratio found with $Cu(NO_3)_2 \cdot 3H_2O$ increases to 1:6.

The cyclotrimerization of doubly functionalized cyclo- or bicycloalkenes, via a coupling mechanism, is a powerful method for the preparation of tris-annelated benzenes. We have pursued in our laboratory the synthesis of molecules annelated with [2.2.1] bicyclic systems.[1] These molecules possess two configurations: *syn*-**1** (when the methano bridges point the same direction) and *anti*-**1**. The syn configuration, as a dome-shaped molecule with functions at the edge, presents interesting structural characteristics, which may allow further applications or synthetic developments. The method adopted in our



syn-**1** *anti*-**1**

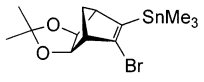
a: X–X =  ; Y= CH_2; Y'= H

b: X–X =  ; Y= CH_2; Y'= H

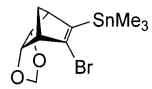
c: X–X = HC=CH; Y= CH_2; Y'= H

d: X–X = H_2C-CH_2; Y= $C(Me)_2$; Y'= Me

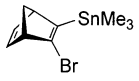
laboratory is based on the reaction of *vic*-bromotrimethylstannyl[2.2.1] bicyclic olefins **2a**–**d** mediated by copper salts.[1] The preparation of the monomeric substrates **2c**[1c] and **2d**[1e] is described elsewhere. The substrates **2a** and **2b** have been synthesized as outlined in Schemes 1 and 2 and detailed in the Experimental Section. The trimerization reaction with inorganic copper



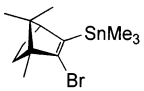
2a



2b



2c



2d

salts is, however, plagued by low reactivity and by the production of uninteresting side products. For example, the reaction of the *exo*-dihydroxynorbornene acetal **2a** with $Cu(NO_3)_2 \cdot 3H_2O$ leads to the formation (cf. Scheme 3 and Table 1) of the trimers *syn*-**1a** and *anti*-**1a** in low yields, of the protodestannylated species **5a**, and of the two dibromodimers **9** (with C_s and C_2 symmetry).[5] No reaction was observed with CuI in the presence of LiCl.[1g] The different reactivities may be attributed, as suggested by Liebeskind,[6a] to the reversibility of the transmetalation step from tin to copper, and to the different sequestering abilities of the anion toward the trialkyltin group (greater in the case of trialkyltin nitrates[7] than in the case of trialkyltin halogenides).

Actually, with use of the water-free promoter "$CuNO_3$" (generated in situ by stirring a slurry of dry CuI with 1 equiv of $AgNO_3$) the trimers are again obtained, with no trace of the protodestannylated derivative; the C_s and C_2 dimers are, however, still generated in disturbingly low yield. This result also suggests that the formation of the protodestannylated species may be due to the water cocrystallized with the $Cu(NO_3)_2$ catalyst.

We then tried the promoter introduced by Liebeskind, copper(I) thiophene-2-carboxylate (CuTC).[6] This species,

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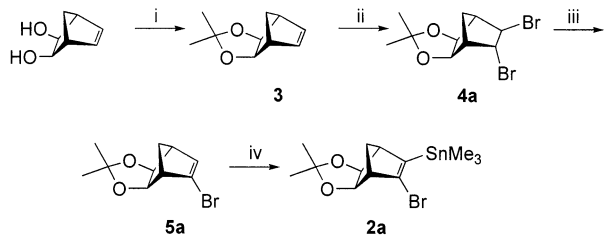
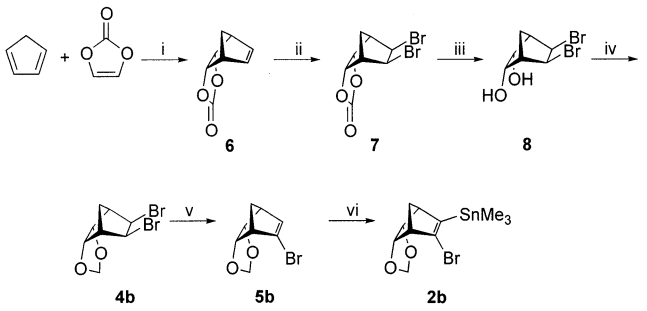
SCHEME 1[a]



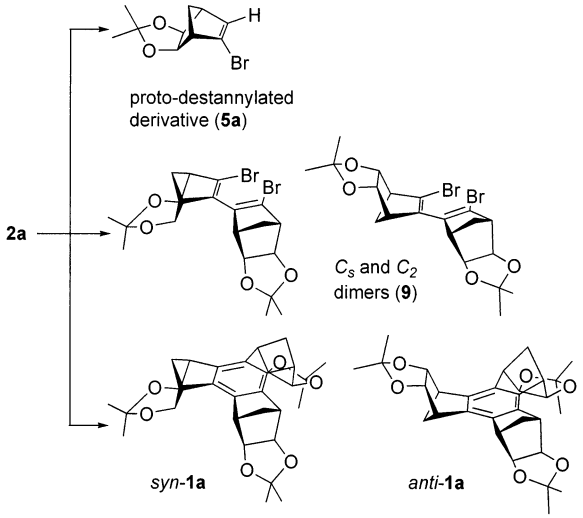
[a] Reagents, conditions and (yields): (i) DMP;[2] (ii) Br_2, CCl_4 (90%); (iii) *t*-BuOK, THF, reflux (80%); (iv) LDA, Me_3SnCl, THF, rt (98%).

SCHEME 2[a]



[a] Reagents, conditions and (yields): (i) toluene, 110 °C, (98%);[3] (ii) Br_2, CCl_4 (98%); (iii) K_2CO_3, THF, MeOH, H_2O,[4] rt (99%); (iv) DMM, hexane, reflux, (99%); (v) *t*-BuOK, THF, reflux (87%); (vi) LDA, Me_3SnCl, THF, rt (70%).

SCHEME 3



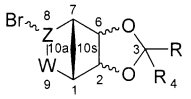
which offers practical advantages (inexpensive, air stable, nonhygroscopic), mediates the selective couplings between vinyl bromides and trialkylvinylstannanes, giving almost quantitative yields of the conjugated dienes.[6a] When applied to our substrates, where the bromide and trimethylstannyl functions occupy the cis positions of the same vinyl moiety, CuTC gives the following results: (i) as expected, the reaction occurs at milder conditions (cf. Table 1); and (ii) as anticipated, the yield of trimers *syn*-**1a** and *anti*-**1a** is almost quantitative, and neither the protodestannylated derivatives nor the dibromodimers **9** are observed.

Similar encouraging results have been achieved with the *endo*-dihydroxynorbornene acetal **2b**, with norbornadiene **2c**, and with enantiopure **2d**, a camphor derivative (cf. Table 1). Using CuTC we obtained the **1d** trimers almost quantitatively, compared with the 50% yield obtained with $Cu(NO_3)_2 \cdot 3H_2O$.[1e]

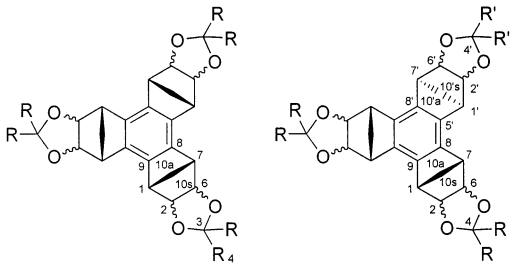
Only in the case of unhindered substrate **2c** does the ratio of syn to anti isomers of trimers **1c** correspond to that expected from a statistical distribution of products. The ratio is significantly smaller for the other substrates, because of the steric hindrance opposed by the substitution patterns. In the case of the particularly hindered substrate **2b**, the ratio is 1:8. This situation is rather disappointing, as the *syn*-**1b** trimer (where the 6 oxygen atoms point toward the inner endo direction, so it might, therefore, be considered a new brand of crown ether with the bottom side occluded by a benzene ring) is obtained in a too low overall yield. The ratio seems also to depend on other factors. For example, the 1:9 ratio of cyclotrimers **1d** observed when the reaction is promoted by $Cu(NO_3)_2 \cdot 3H_2O$[1e] is increased to 1:6 with CuTC. Therefore we are presently examining experimental conditions which will improve the yield of the more valuable syn trimers at least to the limit of the statistical ratio.

Experimental Section

General. The ^1H and ^{13}C NMR spectra for new compounds were taken in $CDCl_3$ with the solvent peak as internal standard. The signal assigments and the structural determinations could be accomplished via bidimensional COSY, NOESY, HMQC, and HMBC spectroscopies. The assignments refer to the numbering reported below. The products **3** and **6** have been synthesized following literature procedures.[2,3] The monomers **2c**,**d** and the trimers *syn*-**1c**,**d** and *anti*-**1c**,**d** are described elsewhere.[1a,c,e,h]



2a,b; 4a,b; 5a,b; 7; 9



***exo*-8,*endo*-9-Dibromo-*exo*-4,4-dimethyl-3,5-dioxatricyclo-[5.2.1.0^{2,6}]decane (4a).** A solution of Br_2 (1.65 mL, 32 mmol) in CCl_4 (30 mL) was added dropwise to a solution of **3**[2] (5.3 g, 32 mmol) in CCl_4 (40 mL) at room temperature and stirred 1 h. The mixture was quenched with saturated solutions of $Na_2S_2O_3$ and $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by FC (eluant 1:9 AcOEt/hexanes) giving **4a** (9.2 g, 28.4 mmol, 88%) as a yellow oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 4.62 (1H, H_2, d, J = 5.3 Hz), 4.34 (1H, H_9, t, J = 4.0 Hz), 4.12 (1H, H_6, dm, J = 5.7 Hz), 3.68 (1H, H_8, t, J = 3.1 Hz), 2.56 (1H, H_1, d, J = 4.6 Hz), 2.51 (1H, H_7, s), 1.89 (1H, H_{10s}, dm, J = 11.3 Hz), 1.79 (1H, H_{10a}, dquint, J = 11.3, 1.5 Hz), 1.45 (3H, Me_4, s), 1.32 (3H, Me_4, s); ^{13}C NMR ($CDCl_3$,

TABLE 1. Results of the Cyclotrimerization Reactions with Different Copper Salts

substrate	copper salt	solvent	time	temp, °C	% trimers **1** (syn:anti ratio)	% protodestannylated deriv. **5**	% C_s and C_2 dimers **9**
2a	$Cu(NO_3)_2 \cdot 3H_2O$	THF	20 min	25	10 (1:4)	70	20
2a	CuI (+LiCl)	DME−DMF	24 h	25		no reaction	
2a	"$CuNO_3$" [a]	DME−DMF	20 min	−15	70 (1:4)		30
2a	CuTC	NMP	20 min	−15	98 (1:4)		
2b	CuTC	NMP	12 h	−15→25	70 (1:8)[b]		
2c	$Cu(NO_3)_2 \cdot 3H_2O$	THF	25 min	25	78 (1:3)[b,c]		
2c	CuTC	NMP	25 min	−20	94 (1:3)		
2d	$Cu(NO_3)_2 \cdot 3H_2O$	THF	25 min	25	50 (1:9)[b,d]	20	20
2d	CuTC	NMP	40 min	−20	98 (1:6)		

[a] Generated in situ from CuI and $AgNO_3$. [b] The remnant is unidentified material. [c] Reference 1c. [d] Reference 1e.

100 MHz) δ 110.14 (C_4), 78.98 (C_6), 78.35 (C_2), 55.65 (C_9), 53.31 (C_8), 51.25 (C_7), 47.58 (C_1), 29.72 (C_{10}), 25.43 (Me_4), 24.18 (Me_4).

8-Bromo-*exo*-4,4-dimethyl-3,5-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene (5a). A solution of *t*-BuOK (4.7 g, 42 mmol) in 20 mL of dry THF was added dropwise at room temperature to a solution of **4a** (9.2 g, 28.2 mmol) in 40 mL of dry THF. The mixture was stirred and refluxed 8 h, quenched with water, and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The reaction crude was purified by FC (eluant 1:9 AcOEt/hexanes), giving **5a** (5.78 g, 23.5 mmol, 83%) as a yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.10 (1H, H_9, m), 4.36 (1H, H_6, dm, J = 4.9 Hz), 4.31 (1H, H_2, dm, J = 4.9 Hz), 2.81 (2H, H_1, H_7, m), 2.00 (1H, H_{10s}, dt, J = 9.1, 1.7 Hz), 1.93 (1H, H_{10a}, dquint, J = 9.1, 1.6 Hz), 1.47 (3H, s, Me_4), 1.35 (3H, s, Me_4); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.87 (C_9), 127.62 (C_8), 114.42 (C_4), 80.70 (C_2), 79.72 (C_6), 53.47 (C_1 or C_7), 46.89 (C_7 or C_1), 42.52 (C_{10}), 26.01 (Me_4), 24.44 (Me_4).

***exo*-8,*exo*-9-Dibromo-*endo*-3,5-dioxatricyclo[5.2.1.0^{2,6}]decan-4-one (7).** A solution of Br_2 (3.6 mL, 67 mmol) in 30 mL of CCl_4 was added dropwise to a solution of **6** [3] (10.0 g, 67 mmol) in 70 mL of CCl_4 and stirred 1 h at room temperature. Some **7** precipitated as a brown solid and was filtered off. The residual was quenched with saturated solutions of $Na_2S_2O_3$ and $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The second portion of **7** was recrystallized from MeOH (total yield: 19.9 g, 28.4 mmol, 88%): mp 112.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.82 (2H, H_2, H_6, m), 4.60 (2H, H_8, H_9, d, J = 1.8 Hz), 3.07 (2H, H_1, H_7, m), 2.53 (1H, H_{10a}, dt, J = 12.4, 1.8 Hz), 1.53 (1H, H_{10s}, dquint, J = 12.4, 1.8 Hz).

***exo*-5,*exo*-6-Dibromobicyclo[2.2.1]heptane-*endo*-2,*endo*-3-diol (8).** A solution of **7** (8.7 g, 27.9 mmol) and K_2CO_3 (0.2 g, 1.3 mmol) in 1500 mL of a 5:7:1 mixture of THF, MeOH, and H_2O was stirred for 48 h at room temperature. After dilution with water the organic solvent was removed in vacuo and the residual aqueous solution was extracted with AcOEt. The extract was dried with $MgSO_4$, the solvent removed in vacuo, and the residue recrystallized from MeOH, giving **8** as a brown solid (7.6 g, 28.4 mmol, 97%): mp 126.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.80 (2H, H_5, H_6, d, J = 1.8 Hz), 4.01 (2H, H_2, H_3, m), 2.78 (2H, H_1, H_4, m), 2.70 (2H, OH, br s), 2.22 (1H, H_{7a}, dt, J = 11.8, 2.0 Hz), 1.32 (1H, H_{7s}, dquint, J = 11.8, 1.8 Hz).

***exo*-8,*exo*-9-Dibromo-*endo*-3,5-dioxatricyclo[5.2.1.0^{2,6}]decane (4b).** A solution in 600 mL of hexane of **8** (8.0 g, 28.4 mmol) and DMM (260 mL, 2.7 mol) with a trace of *p*-toluenesulfonic acid was refluxed 72 h under stirring in an apparatus equipped for continuous water removal. The mixture was extracted with CH_2Cl_2 and washed with a solution of $NaHCO_3$. The organic layers were dried over $MgSO_4$ and concentrated in vacuo and the residue recrystallized from MeOH, giving **4b** as a brown solid (7.1 g, 24.0 mmol, 85%): mp 62.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.31 (1H, H_4, s), 4.91 (1H, H_4, s), 4.81 (2H, H_8, H_9, d, J = 1.9 Hz), 4.33 (2H, H_2, H_6, dd, J = 3.0, 2.4 Hz), 2.82 (2H, H_1, H_7, m), 2.46 (1H, H_{10a}, dt, J = 11.8, 1.7 Hz), 1.71 (1H, H_{10s}, dq, J = 11.8, 1.9 Hz).

8-Bromo-*endo*-3,5-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene (5b). A solution of *t*-BuOK (4.1 g, 36.3 mmol) in 75 mL of dry THF was added dropwise at room temperature to a solution of **4b** (7.1 g, 23.9 mmol) in 75 mL of dry THF and refluxed 8 h under stirring. The mixture was quenched with water and extracted with Et_2O, and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The reaction crude was recrystallized from MeOH, giving **5b** (4.5 g, 24.04 mmol, 88%) as a white solid: mp 74.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.21 (1H, H_9, d, J = 3.3 Hz), 5.14 (1H, H_4, s), 5.00 (1H, H_4, s), 4.81 (1H, H_6, dd, J = 6.9, 3.9 Hz), 4.71 (1H, H_2, dd, J = 6.9, 3.8 Hz), 3.12 (1H, H_7, m), 3.10 (1H, H_1, m), 1.91 (1H, H_{10a}, dt, J = 9.9, 2.0 Hz), 1.45 (1H, H_{10s}, dquart, J = 9.9, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.54 (C_9), 124.29 (C_8), 100.80 (C_4), 82.03 (C_6), 81.39 (C_2), 53.61 (C_7), 47.39 (C_1), 46.65 (C_{10}).

General Procedure for the Synthesis of *vic*-Bromotrimethylstannyl[2.2.1]bicyclic Olefins 2a−d. A 2.5 M solution of *n*-BuLi in hexane (25 mL, 62 mmol) was added dropwise to a solution of diisopropylammine (8.6 mL, 62 mmol) in 20 mL of dry THF at 0 °C under Ar atmosphere and stirred 15 min. A solution of the bromo[2.2.1]bicyclic olefin **5a**−**d** (23.5 mmol) in 40 mL of dry THF was then added dropwise and stirred 30 min. Finally, trimethyltin chloride (4.7 g, 23.5 mmol) was added portionwise and the mixture was stirred 12 h. The crude was washed with water and extracted with Et_2O, and the combined ethereal extracts were dried over $MgSO_4$ and concentrated in vacuo. In the case of **2a**,**c**,**d** the crude was purified by FC. The product **2b** was recrystallized from MeOH.

8-Bromo-9-trimethylstannyl-*exo*-4,4-dimethyl-3,5-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene (2a): oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.34 (1H, H_6, dt, J = 5.5, 1.5 Hz), 4.12 (1H, H_2, ddd, J = 5.5, 1.6, 1.0 Hz), 2.86 (1H, H_1, m), 2.82 (1H, H_7, m), 1.94 (1H, H_{10s}, dt, J = 9.2, 1.6 Hz), 1.88 (1H, H_{10a}, dt, J = 9.2, 1.7 Hz), 1.47 (3H, Me_4, s), 1.36 (3H, Me_4, s), 0.24 (9H, trimethylstannyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.50 (C_9), 138.83 (C_8), 114.12 (C_4), 80.00 (C_2), 79.34 (C_6), 55.09 (C_7), 51.76 (C_1), 42.21 (C_{10}), 26.20 (Me_4), 24.54 (Me_4), −9.72 (trimethylstanniyl).

8-Bromo-9-trimethylstannyl-*endo*-3,5-dioxatricyclo-[5.2.1.0^{2,6}]dec-8-ene (2b): white crystals, mp 75.8 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.08 (1H, H_4, d, J = 0.8 Hz), 4.96 (1H, H_4, d, J = 0.8 Hz), 4.75 (1H, H_6, dd, J = 6.7, 3.8 Hz), 4.65 (1H, H_2, dd, J = 6.7, 3.8 Hz), 3.15 (1H, H_1, m), 3.13 (1H, H_7, m), 1.88 (1H, H_{10a}, dt, J = 9.8, 2.1 Hz), 1.43 (1H, H_{10s}, dt, J = 9.8, 1.4 Hz), 0.25 (9H, trimethylstannyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.56 (C_9), 135.39 (C_8), 100.61 (C_4), 82.39 (C_6), 81.45 (C_2), 55.45 (C_7), 52.09 (C_1), 46.61 (C_{10}), −9.42 (trimethylstannyl).

Reaction of 2a with $Cu(NO_3)_2 \cdot 3H_2O$. Copper nitrate trihydrate (78 mg, 0.36 mmol) was added portionwise to a solution of **2a** (130 mg, 0.36 mmol) in 1 mL of THF. The blue solution turned brown in 30 min; 10 mL of 10% aqueous NH_3 was then added. The mixture was extracted with Et_2O and the combined ethereal extracts were dried over $MgSO_4$. The crude product was purified by FC (eluant 1:4 AcOEt/hexanes). The protodestannylated monomer **5a** (70%), the dibromo dimers **9** (20%), and the trimers *syn*-**1a** and *anti*-**1a** (10%) were eluted in this order.

Reaction of 2a with "$Cu(NO_3)_2$". Anhydrous "$CuNO_3$" was generated in situ by stirring a slurry of dry CuI with 1 equiv of $AgNO_3$ in 4:1 DMF/DME. After decantation of precipitated AgI, the supernatant was transferred by syringe to a 4:1 DMF/DME solution of **2a** (130 mg, 0.32 mmol) kept at room temperature,

and 10 mL of 10% aqueous NH_3 was then added. The mixture was extracted with Et_2O and the combined ethereal extracts were dried over $MgSO_4$. The crude product was purified by FC (eluant 1:4 AcOEt/hexanes). The dibromo dimers **9** (30%) and the trimers *syn*-**1a** ant *anti*-**1a** (70%) were eluted in this order.

***C*$_s$ and *C*$_2$ Isomers of 8,8′-Dibromo-4,4,4′,4′-tetramethyl-[9,9′]bis[3,5-dioxatricyclo[5.2.1.0^{2,6}]decyl]-8,8′-diene (9). First isomer:** oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.56 (2H, C_2 or C_6, dt, J = 5.5, 1.2 Hz), 4.36 (2H, C_6 or C_2, dt, J = 5.5, 1.4 Hz), 3.43 (2H, C_1 or C_7, m), 2.87 (2H, C_7 or C_1, m), 1.98 (2H, C_{10s}, dt, J = 9.2, 1.7 Hz), 1.91 (2H, C_{10a}, dquint, J = 9.2, 1.6 Hz), 1.48 (6H, Me), 1.37 (6H, Me). **Second isomer:** oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.41 (2H, C_2 or C_6, dm, J = 5.4 Hz), 4.39 (2H, C_6 or C_2, dm, J = 5.4 Hz), 3.46 (2H, C_1 or C_7, m), 2.87 (2H, C_7 or C_1, m), 2.00 (2H, C_{10s}, dt, J = 9.2, 1.7 Hz), 1.92 (2H, C_{10a}, dquint, J = 9.2, 1.7 Hz), 1.48 (6H, Me), 1.36 (6H, Me).

General Procedure for the Reaction with CuTC. CuTC (1.5 equiv) was added portionwise to a solution of *vic*-bromostannylalkene **2a**−**d** (0.35 mmol) in 2 mL of dry NMP kept at −20 °C under Ar atmosphere. The mixture was stirred for the time indicated in Table 1 and 10 mL of 10% aqueous NH_3 was added. The mixture was extracted with Et_2O and the combined ethereal extracts were dried over $MgSO_4$ and concentrated in vacuo. The isomer *anti*-**1a**,**b** was separated by crystallization from MeOH. The isomer *syn*-**1a**,**b** was purified by FC (eluant 1:4 AcOEt/hexanes). The cyclotrimers *syn*-**1c**,**d** and *anti*-**1c**,**d** were separated by FC (eluant hexanes).

***syn*-2,3,6,7,10,11-Triisopropylidenedioxy-1,4;5,8;9,12-trimethanotrifenilene (*syn*-1a):** white solid, mp 237.6 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.08 (6H, H_2, H_6, d, J = 1.5 Hz), 3.26 (6H, H_1, H_7, t, J = 1.5 Hz), 2.25 (3H, dt, H_{10s}, J = 9.5, 1.5 Hz), 1.87 (3H, H_{10a}, dquint, J = 9.6, 1.5 Hz), 1.52 (9H, Me_4, s), 1.31 (9H, Me_4, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.10 (C_8, C_9), 112.58 (C_4), 81.55 (C_2, C_6), 45.28 (C_1, C_7), 42.60 (C_{10}), 25.88 (Me_4), 24.40 (Me_4).

***anti*-2,3,6,7,10,11-Triisopropylidenedioxy-1,4;5,8;9,12-trimetanotriphenylene (*anti*-1a):** white solid, mp 279.3 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.18 (2H, H_2 or H_6, dm, J = 5.4 Hz), 4.17 (2H, $H_{2'}$, $H_{6'}$, m), 4.08 (2H, H_6 or H_2, dm, J = 5.4 Hz), 3.27 (2H, H_1 or H_7, m), 3.24 (2H, H_7 or H_1, m), 3.24 (2H, $H_{1'}$, $H_{4'}$, m), 2.25 (2H, H_{10s}, dt, J = 9.5, 1.3 Hz), 2.25 (1H, $H_{10's}$, dt, J = 9.5, 1.3 Hz), 1.82 (2H, H_{10a}, dquint, J = 9.5, 1.5 Hz), 1.76 (1H, $H_{10'a}$, dquint, J = 9.5, 1.5 Hz), 1.52 (3H, s, Me_4), 1.52 (6H, s, $Me_{4'}$), 1.31 (6H, s, Me_4), 1.30 (3H, s, $Me_{4'}$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.31, 136.21 and 136.21 (C_8, C_9, $C_{8'}$, and $C_{9'}$), 112.58 (C_4, $C_{4'}$), 81.50, 81.37 and 81.35 (C_2, C_6, $C_{2'}$, and $C_{6'}$), 45.38, 45.22, 45.10 (C_1, C_7, $C_{1'}$, and $C_{7'}$), 42.37 (C_{10}), 42.05 ($C_{10'}$), 25.87, 25.87, 24.38 and 24.34 (Me_4 and $Me_{4'}$).

***syn*-2,3,6,7,10,11-Trimethylidenedioxy-1,4;5,8;9,12-trimethanotrifenilene (*syn*-1b):** white solid, mp 230.2 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.86 (6H, H_2, H_6, m), 4.76 (3H, H_4, s), 4.05 (3H, H_4, s), 3.56 (6H, H_1, H_7, m), 1.97 (1H, dt, H_{10a}, J = 10.2, 1.6 Hz), 1.87 (1H, H_{10s}, J = 10.2, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.98 (C_8, C_9), 99.13 (C_4), 80.75 (C_2, C_6), 48.18 (C_{10}), 45.72 (C_1, C_7).

***anti*-2,3,6,7,10,11-Trimethylidenedioxy-1,4;5,8;9,12-trimethanotrifenilene (*anti*-1b):** white solid, mp 250.2 °C dec; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.87−4.82 (6H, H_2,H_6, $H_{2'}$,$H_{6'}$, multiplets), 4.71 (2H, H_4, d, J = 0.7 Hz), 4.64 (1H, $H_{4'}$, d, J = 1.5 Hz), 3.77 (2H, H_4, d, J = 0.7 Hz), 3.56 (6H, $H_{1'}$, $H_{7'}$, H_1, H_7, m), 2.93 (1H, $H_{4'}$, d, J = 1.5 Hz), 1.92 (1H, $H_{10'a}$, dt, J = 10.2, 2.0 Hz), 1.89 (2H, H_{10a}, dt, J = 10.2, 1.9 Hz), 1.84 (2H, H_{10s}, dt, J = 10.2, 1.4 Hz), 1.74 (1H, $H_{10's}$, dt, J = 10.2, 1.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.51 and 136.44 (C_8, C_9), 135.75 ($C_{8'}$, $C_{9'}$), 99.36 ($C_{4'}$), 99.11 (C_4), 80.96, 80.86 and 80.46 (C_2, C_6, $C_{2'}$, and $C_{6'}$), 47.57 (C_{10}), 45.80, 45.71 and 45.67 (C_1, C_7, $C_{1'}$, and $C_{7'}$), 45.41 ($C_{10'}$).

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Supporting Information Available: Copies of ^{1}H, ^{13}C, HMQC, and HMBC spectra of compounds *syn*-**1a**,**b** and *anti*-**1a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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