Stereoconvergent Generation of a Contrasteric *syn*-Bicyclopropylidene (=*syn*-Cyclopropylidenecyclopropane) by *Stille*-Like Coupling

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Stereoisomerically pure *endo*- and *exo*-7-halo-7-(trimethylstannyl)benzonorcar-3-enes (=*endo*- and *exo*-(1-halo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-1-yl)trimethylstannane) **4** and **6** were selectively obtained by lithium–tin or magnesium–tin transmetalation in good yields (*Scheme 2* and *3*). The reaction of these compounds with copper(I) thiophene-2-carboxylate (CuTC) produced in both cases the corresponding C_S-symmetric bicyclopropylidene (=cyclopropylidenecyclopropane) *syn*-**1**, a single diastereoisomer (*Schemes 5* and *6*). The structure of *syn*-**1** was undoubtedly elucidated by X-ray single crystal diffraction. The coupling mechanism of the carbenoid cyclopropane is discussed (*Scheme 7*).

Introduction. – Bicyclopropylidenes (=cyclopropylidenecyclopropanes) display a wide reactivity, ranging from the expected reactions of a tetrasubstituted olefin with electrophiles to the intriguing cascade-reaction recently reported by *de Meijere* and co-workers. [1]. Many procedures for the preparation and derivatization of bicyclopropylidenes are reported [1][2], including coupling of carbenes generated *in situ* from gemminally dihalo-substituted cyclopropanes [3], which, in turn, can be obtained by dihalocarbene insertion in C=C bonds. The research groups have, for a long time, been involved in the study of coupling reactions promoted by copper salts [4], and recently our attention focused on the masked carbene functionality of gemminally-bromo(-trimethylstannyl)-substituted cyclopropanes. In this article, we describe an efficient and highly stereoselective synthetic methodology for the preparation of the contrasteric *syn*-1a,1′a,2, 2′,7, 7′,7a,7′a-octahydro-1,1′-bi[cyclopropa[*b*]naphthalenylidene] (*syn*-**1**)[1]) (*Fig. 1*). This compound has been previously synthesized by *Banwell* and co-workers, as a mixture of *syn*- and *anti*-**1** in 7 and 11% yield, respectively [5].

[1]) The terms *syn*/*anti* in names and key numbers mean that a compound has a cage-like/stair-like overall gross structure, *cf. Fig. 1*.

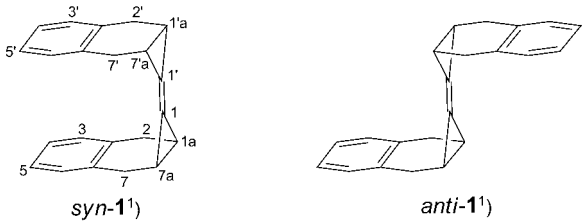
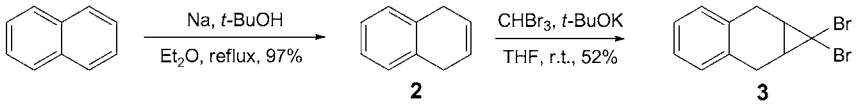


Fig. 1. *The two possible isomers of bicyclopropylidene* **1**

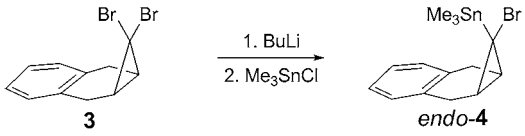
Results and Discussion. – The starting material **3** was readily obtained in two steps from naphthalene, which was selectively reduced at the 1,4 positions [6] followed by dibromocyclopropanation with tribromomethane and potassium *tert*-butoxide (*Scheme 1*) [7].

Scheme 1. *Synthesis of the Dibromo Adduct* **3**



Although the formation of bicyclopropylidenes can be accomplished by the use of simple metalating agents [8], the yields and diastereoselectivities of these reactions are not very good [3b][3i][5][9]. The use of bromostannanes with copper(I) as promoter of the coupling reaction can provide milder conditions with an efficiency improvement. When 7,7-dibromobenzonorcar-3-ene (=1,1-dibromo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene; **3**) was treated with BuLi at $-78°$, and the resulting anion was quenched with chlorotrimethyltstannane, the *endo*-trimethylstanyl derivative *endo*-**4**[2]) was isolated as the sole product in 90% yield (*Scheme 2*). The configuration was confirmed by a NOESY experiment: the scalar correlation between the Me groups and the *endo* benzylic H-atoms was in good agreement with distances observed in minimized models (MacSpartan Plus, semi-empirical, PM3 basis set), which resulted in 2.32 and 4.29 Å for the *endo*- and *exo*-(trimethylstannyl) derivatives, respectively. The remarkable diastereoselectivity observed with substrate **3** matched the previously reported results obtained with 2-oxa-7,7-dibromonorcarane [10], 7,7-dibromonorcarane [9d][11], and 7,7-dibromonorcar-2-ene [12].

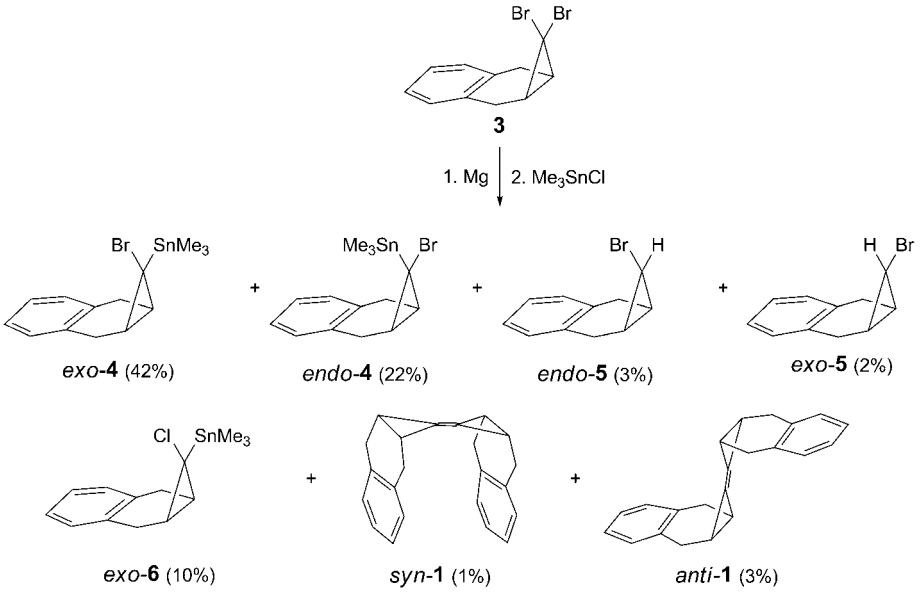
Scheme 2. *Reaction of Dibromonorcarane Derivative* **3** *with BuLi/Me*$_3$*SnCl*



[2]) The terms *endo*/*exo* in names and key numbers mean that the senior of the geminal substitutents is on the concave/convex side of the molecule, cf. *Schemes 2–4* and *7*.

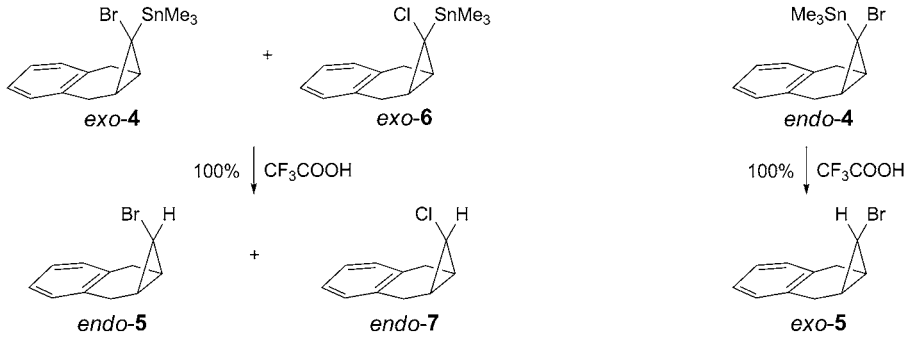
However, the use of Mg as the metalating agent in the reaction of dibromonorcar-3-ene derivative **3** with Me_3SnCl produced a complex mixture consisting of *exo*-stannyl isomer *exo*-**4** as the major product along with products similar to those obtained by treatment of 7,7-dibromonorcarane with an organomagnesium reagent (*Scheme 3*) [13]. The *endo*-product *endo*-**4** was formed in 22% yield, the reduction products *endo*- and *exo*-**5** in 3 and 2% yield, respectively, and the coupling product, *syn*- and *anti*-**1** in 1 and 3% yield. Compound *exo*-**4** was isolated as a mixture with *exo*-**6**; all attempts (chromatography, crystallization) to separate this mixture failed. However, the protodestannylation reaction of all stannylated products, *i.e.*, of *endo*-**4**, *exo*-**4**, and *exo*-**6**, with CF_3COOH resulted in the formation of the corresponding reduced products *exo*-**5** [14], *endo*-**5** [14], and *endo*-**7** [15] which allowed us to characterize the isolated products (*Scheme 4*). The attribution of the configuration of the monohalo-substituted structures was also confirmed by the coupling constants between the H-atoms of the cyclopropane moieties (J_{cis} was typically 8 Hz, while J_{trans} was typically 4 Hz) [16].

Scheme 3. *Reaction of Dibromonorcarane Derivative* **3** *with Mg/Me_3SnCl*

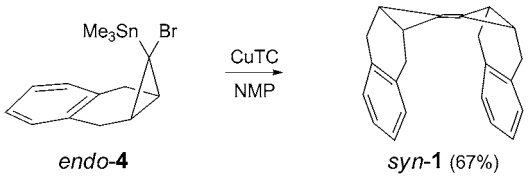


Copper(I) thiophene-2-carboxylate (CuTC) is a reagent successfully employed either for couplings between unsaturated halides and stannanes [17], or between two unsaturated halides [18] or stannanes [19]. Furthermore, it is one of the most efficient reagents for the preparation of benzocyclotrimers from vicinally-bromo(stannyl)-substituted olefins [4][20]. Treatment of *endo*-**4** with a slight excess of CuTC in dry *N*-methylpyrrolidin-2-one (NMP) at $-20°$ afforded the *syn*-coupling product *syn*-**1** as the sole isomer in 67% yield (*Scheme 5*). Careful analysis of the crude reaction mixture (^{1}H-NMR, GC/MS) did not reveal the formation of any trace of other products such as a trimer, which may be formed by further addition of the carbene to *syn*-**1**.

Scheme 4. *Protodestannylation of the Halo(trimethylstannyl) Compounds* exo-**4**, endo-**4**, *and* exo-**6** *to Confirm the Exact Configurations*



Scheme 5. *Reaction of* endo-**4** *with Copper(I) Thiophene-2-carboxylate* (CuTC) *in* N-*Methylpyrrolidin-2-one* (NMP)



The configuration of *syn*-**1** was established by X-ray crystallography that revealed also peculiar and interesting structural features. The compound crystallized in a monoclinic centrosymmetric space group $P2_1/n$ with four molecules in the unit cell. The structure contains two 1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene fragments connected by a C=C (C(11)–C(12) = 1.302 Å) bond. The tetrahydronaphthalene moieties are folded onto each other, as shown in the structure reported in *Fig. 2*. The interplanar and centroid-to-centroid distances between the cofacial pair of benzene moieties are 4.157(3) Å and 4.247(3) Å, respectively, and the dihedral angle between the planes is 17.7(2)°. The cyclohexene fragments are also partially folded along the C(15)···C(18) and C(7)···C(10) axis. The hinge angles between the cyclopropane C(15)–C(14)–C(13)–C(18) and C(7)–C(8)–C(9)–C(10) planes are 112.0(2)° and 112.3(1)°, respectively. The molecular packing of *syn*-**1** as viewed along the *a*-axis is shown in *Fig. 2*. Translation symmetry in the crystal structure may be easily seen in the unit cell along the diagonal axis.

Surprisingly, treatment of the mixture *exo*-**4**/*exo*-**6** (ratio 4.2 : 1) with CuTC under the same reaction conditions afforded also formation of *syn*-**1** as a major product (64%) beside the isomeric *anti*-**1** (2%) (*Scheme 6*).

After having observed a strong selectivity in the coupling reaction of both substrates *exo*- and *endo*-**4**, we propose the following mechanism for the formation of the products. Copper–tin transmetalation is the most likely step to start the coupling process, as previously observed in the case of vicinally-bromo(stannyl)-substituted olefins [19]. In principle, the geminally subtituted-bromocuprates *exo*- and *endo*-**8** can eliminate CuBr to afford a carbene, which may undergo the dimerization reaction.

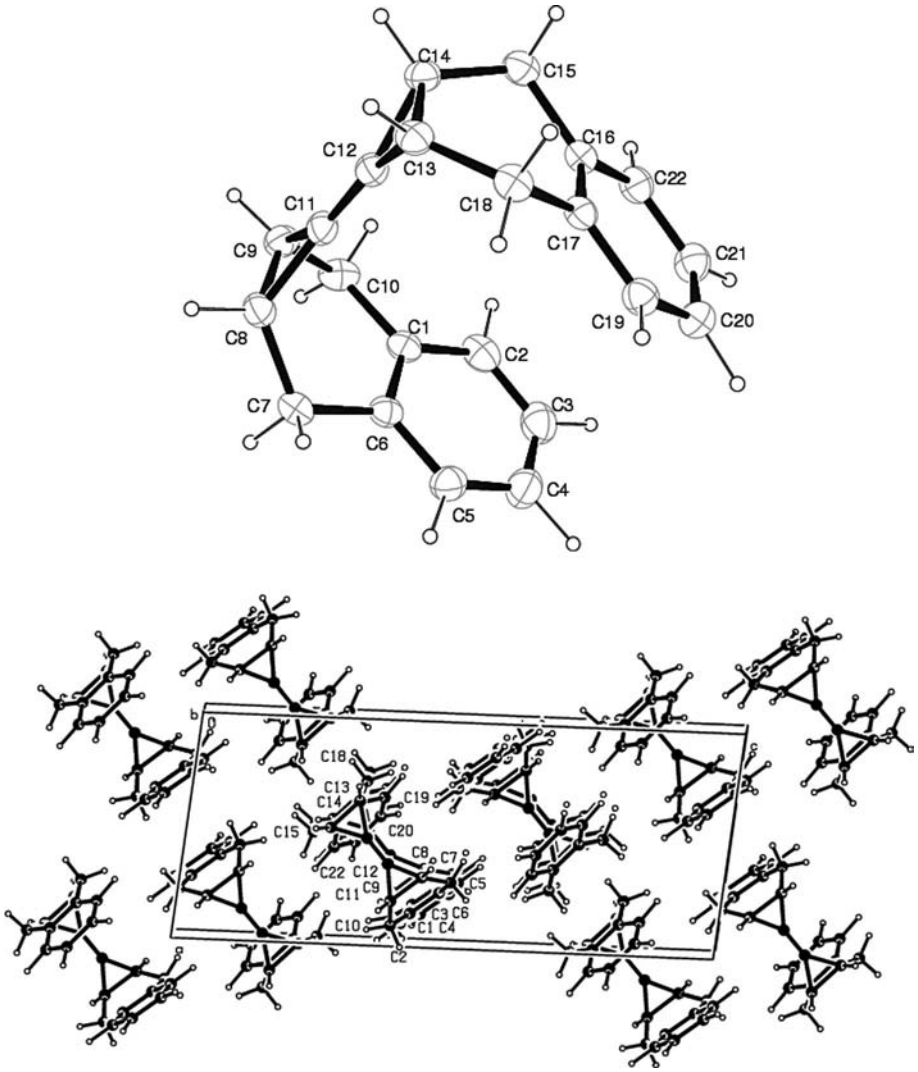
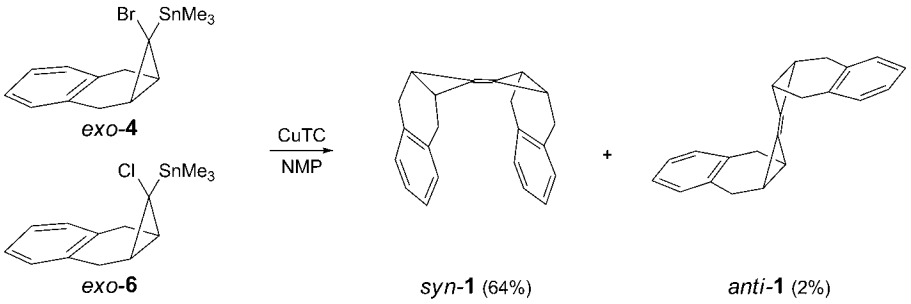


Fig. 2. *Molecular structure of* syn-**1** *and molecular packing in* syn-**1** *crystals viewed along the* a-*axis.* Thermal ellipsoids are drawn at the 40% probability level. Arbitrary atom numbering.

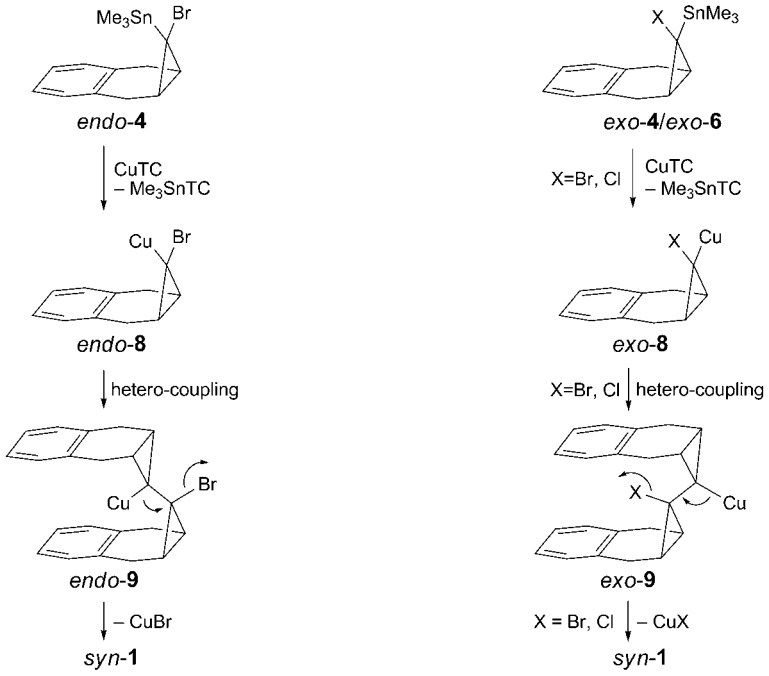
However, in this case, a diastereoselectivity would not be expected. The fact that *syn*-**1** (which is the more sterically congested isomer) is formed in the coupling reaction of *endo*-**4** as the sole product indicates that a stepwise process is involved. We assume that a hetero-coupling between two molecules of *endo*-**8** takes place to form *endo*-**9** with a defined configuration by eliminating only one molecule of CuBr. Removal of a second molecule of CuBr then gives *syn*-**1** with the expected configuration (*Scheme 7*).

In conclusion, the results show that *endo*-**4** and *exo*-**4**/*exo*-**6** undergo stereoselective reactions in which the Cu/Sn exchange is the preferred process. *anti*-Periplanar

Scheme 6. *Reaction of* exo-**4**/exo-**6** *with Copper(I) Thiophene-2-carboxylate* (CuTC) *in* N-*methylpyrrolidin-2-one* (NMP)



Scheme 7. *Formation Mechanism of the Major Product* syn-**1**



elimination of CuBr or CuCl furnishes the corresponding coupling product *syn*-**1** nearly as single diastereoisomer, where the configuration of the stannylated halo compounds determine the configuration of the coupling products. The present study represents a viable synthesis of the contrasteric bicyclopropylidene *syn*-**1** and confirms the ability of CuTC to promote Sn–Sn (preferentially) coupling process.

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Experimental Part

General. All reactions were carried out under Ar and monitored by TLC and/or ^{1}H-NMR. All solvents were dried and distilled before use. Flash column chromatography (FC): silica gel (SiO_2, 60 mesh; *Merck*). TLC: *Merck* 0.2 mm silica gel *60* F_{254} on anal. aluminium plates. M.p.: uncorrected. ^{1}H- and ^{13}C-NMR Spectra [3]): *Varian-400* or *Bruker-400* spectrometer; δ in ppm rel. to Me_4Si as internal standard, J in Hz. All new compounds gave satisfactory elemental analyses.

endo-*(1-Bromo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-1-yl)trimethylstannane* (*endo*-**4**). To a soln. of dibromide **3** [7] (1.0 g, 3.31 mmol) in dry THF (10 ml) at $-78°$, 2.5M BuLi in hexanes (1.32 ml, 3.31 mmol) was added dropwise, and the resulting mixture was stirred for 1 h at $-78°$. Chlorotrimethylstannane (660 mg, 3.31 mmol) was added portionwise within 60 min. The mixture was stirred for 2 h at $-78°$. Then, the temp. was allowed to rise to r.t. overnight. The reaction was quenched with H_2O (50 ml), the mixture extracted with Et_2O (3 × 30 ml), the combined extract dried ($MgSO_4$) and concentrated, and the residue purified by FC (hexane): *endo*-**4** (1.15 g, 90%). Colorless oil. IR (KBr): 3062, 3020, 2906, 2883, 1496, 1454, 1430, 1187, 1056, 1040, 773, 745. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.16–7.01 (*AA′BB′*, 4 arom. H); 3.18 (br. *d*, *A* of *AB*, J(2*syn*,2*anti*) = J(7*syn*,7*anti*) = 17.3, 1 H–C(2), 1 H–C(7)); 3.03 (br. *d*, *B* of *AB*, J(2*syn*,2*anti*) = J(7*syn*,7*anti*) = 17.3, 1 H–C(2), 1 H–C(7)); 2.05 (br. *d*, J(1a,2*anti*) = J(7a,7*anti*) = 3.5, H–C(1a), H–C(7a)); −0.04 (*s*, Me_3Sn). ^{13}C-NMR (100 MHz, $CDCl_3$): 134.4; 130.6; 127.3; 32.4; 29.4; 28.3; −5.3.

Mixture of exo- *and* endo-**4**/exo- *and* endo-**5**/exo-**6**/syn- *and* anti-**1**. Mg (1.09 g, 44.90 mmol) was added to a soln. of dibromide **3** (11.3 g, 37.42 mmol) in dry THF (100 ml) at r.t. in an ultrasonic bath. Chlorotrimethylstannane (7.53 g, 37.79 mmol) was added portionwise. The mixture was stirred for 1 h at r.t. The reaction was quenched with sat. NH_4Cl soln. (95 ml) and the mixture extracted with Et_2O (3 × 80 ml). The combined extract was dried ($MgSO_4$) and concentrated and the crude residue subjected to column chromatography (neutral Al_2O_3 (450 g) hexane): *endo*-**4** (3.2 g, 22%; see above, *exo*-**5** (167 mg, 2%), *exo*-**4**/*exo*-**6** 4.2 : 1 (7.35 g; by ^{1}HNMR: *exo*-**4** (6.07 g, 42%) and *exo*-**6** (1.28 g, 10%), *endo*-**5** (250 mg, 3%), *syn*-**1** (53 mg, 1%; see below), and *anti*-**1** (160 mg, 3%), in this order.

exo-*1-Bromo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene* (*exo*-**5**): Colorless liquid. IR (KBr): 3021, 2888, 2833, 1455, 1323, 1282, 1217, 1024, 749, 675. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.14 (*AA′* of *AA′BB′*, 2 arom. H); 7.02 (*BB′* of *AA′BB′*, 2 arom. H); 3.15 (br. *d*, *A* of *AB*, J(2*syn*,2*anti*) = J(7*syn*,7*anti*) = 15.8, 1 H–C(2), 1 H–C(7)); 3.06 (br. *d*, *B* of *AB*, J(2*syn*,2*anti*) = J(7*syn*,7*anti*) = 15.8, 1 H–C(2), 1 H–C(7)); 2.63 (*t*, J(1,1a) = J(1,7a) = 3.0, H–C(1)); 1.77 (*m*, H–C(1a), H–C(7a)). ^{13}C-NMR (100 MHz, $CDCl_3$): 134.0; 129.3; 126.8; 28.6; 22.0; 19.3. Anal. calc. for $C_{11}H_{11}Br$ (223.11): C 59.22, H 4.97; found: C 59.77, H 4.96.

exo-(*1-Bromo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-1-yl)trimethylstannane* (*exo*-**4**): From the mixture *exo*-**4**/*exo*-**6** 4.2 : 1: ^{1}H-NMR (400 MHz, $CDCl_3$): 7.14–7.08 (*AA′BB′*, 4 arom. H); 3.21 (*ddd*, A of *AB*, J(2*syn*,2*anti*) = J(7*syn*,7*anti*) = 16.5, J(*syn*,1a) = J(7*syn*,7a) = 5.5, J(2*syn*,7a) = J(7*syn*,1a) = 2.6, 1 H–C(2), 1 H–C(7)); 2.70 (br. *d*, *B* of *AB*, J(2*syn*, 2*anti*) = J(7*syn*,7*anti*) = 16.5, 1 H–C(2), 1 H–C(7)); 1.38 (*m*, H–C(1a), H–C(7a)); 0.19 (*s*, Me_3Sn). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.4; 128.2; 125.6; 27.6; 24.9; 18.1; −9.7.

exo-*(1-Chloro-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-1-yl)trimethylstannane* (*exo*-**6**): From the mixture *exo*-**4**/*exo*-**6** 4.2 : 1 (only non-overlapped signals): ^{1}H-NMR (400 MHz, $CDCl_3$): 3.12 (*ddd*, *A* of *AB*, J(2*syn*, 2*anti*) = J(7*syn*,7*anti*) = 16.5, J(2*syn*,1a) = J(7*syn*,7a) = 5.5, J(2*syn*,7a) = J(7*syn*,1a) = 2.7, 1 H–C(2); 1 H–C(7)); 2.68 (br. *d*, *B* of *AB*, J(2*syn*,2*anti*) = J(7*syn*,7*anti*) = 16.5, 1 H–C(2), 1 H–C(7)). ^{13}C-NMR (100 MHz, $CDCl_3$): 125.5; 37.2; 18.6; −10.1.

endo-*1-Bromo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene* (*endo*-**5**): Colorless oil. IR (KBr): 3061, 3019, 2939, 2894, 2840, 1495, 1455, 1429, 1257, 743, 646. ^{1}H-NMR (400 MHz, $CDCl_3$):

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[3]) The lable *syn* or *anti* refers to the position of a H-atom on the concave or convex side of a molecule.

7.16–7.11 (*AA′BB′*, 4 arom. H); 3.53 (*t*, *J*(1,1a) = *J*(1,7a) = 7.5, H–C(1); 3.21 (*ddd*, *A* of *AB*, *J*(2*syn*,2*anti*) = *J*(7*syn*,7*anti*) = 16.5, *J*(2*syn*,1a) = *J*(7*syn*,7a) = 5.3, *J*(2*syn*,7a) = *J*(7*syn*,1a) = 2.8, 1 H–C(2), 1 H–C(7)); 2.68 (br. *d*, *B* of *AB*, *J*(2*syn*,2*anti*) = *J*(7*syn*,7*anti*) = 16.5, 1 H–C(2), 1 H–C(7)); 1.55 (*m*, H–C(1a), H–C(7a)). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.0; 128.5; 126.0; 33.6; 26.3; 14.5. Anal. calc. for $C_{11}H_{11}Br$: C 59.22, H 4.97; found: C 59.56, H 4.80.

anti-*1a,1′a,2,2′,7,7′,7a,7′a-Octahydro-1,1′-bi[1*H*-cyclopropa[*b*]naphthalenylidene]* (= anti-*1a,2,7,7a-Tetrahydro-1-(1a,2,7,7a-tetrahydro-1*H*-cyclopenta[b]naphtalen-1-ylidene)-1*H*-cyclopropa[b]naphthalene*; *anti*-**1**)[1]): Colorless crystals from CH_2Cl_2/hexane 1:3. M.p. 239–240° ([5]: M.p. 228–232°). IR (KBr): 2964, 2924, 2844, 1260, 1094, 1021, 864, 799, 748. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.06–6.95 (*AA′BB′*, 8 arom. H); 2.99 (*m*, 2 H–C(2), 2 H–C(2′), 2 H–C(7), 2 H–C(7′)); 1.63 (*m*, H–C(1a), H–C(7a), H–C(1′a), H–C(7′a)). ^{13}C-NMR (100 MHz, $CDCl_3$): 135.8; 128.7; 125.8; 118.0; 29.6; 14.4. Anal. calc. for $C_{22}H_{20}$: C 92.91, H 7.09; found: C 92.89, H, 6.27.

syn-*1a,1′a,2,2′,7,7′,7a,7′a-Octahydro-1,1′-bi[1*H*-cyclopropa[*b*]naphthalenylidene]* (= syn-*1a,2,7,7a-Tetrahydro-1-(1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-1-ylidene)-1*H*-cyclopropa[*b*]naphthalene; syn*-**1**)[1]). To copper(I) thiophene-2-carboxylate (CuTC; 1.73 g, 9.07 mmol) in a flask purged with Ar and capped with a septum, dry NMP (25 ml) and bromo(stannyl) derivative *endo*-**4** (1.0 g, 2.59 mmol) were added consecutively *via* syringe at −20°. The mixture was stirred for 1 h at −20° and for 3 h at r.t. (TLC monitoring). After completion of the reaction, 10% aq. NH_3 soln. (20 ml) was added, and the slurry was stirred until the brown solid disappeared. The mixture was extracted with Et_2O (3 × 20 ml), the combined org. extract dried ($MgSO_4$) and concentrated, and the residue purified by FC (hexane): *syn*-**1** (248 mg, 67%). Colorless crystals from CH_2Cl_2/hexane 1:3. M.p. 155–156° ([5]: M.p. 144–157°). IR (KBr) 3058, 3019, 2991, 2966, 2911, 2889, 2829, 1493, 1454, 1435, 1300, 1113, 1041, 1004, 753, 739. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.82–6.73 (*AA′BB′*, 8 arom. H), 2.97 (br. *d*, *A* of *AB*, *J*(2*syn*,2*anti*) = *J*(7*syn*,7*anti*) = *J*(2′*syn*,2′*anti*) = *J*(7′*syn*,7′*anti*) = 15.0, 1 H–C(2), 1 H–C(2′), 1 H–C(7), 1 H–C(7′)); 2.50 (br. *d*, *B* of *AB*, *J*(2*syn*,2*anti*) = *J*(7*syn*,7*anti*) = *J*(2′*syn*,2′*anti*) = *J*(7′*syn*,7′*anti*) = 15.0, 1 H–C(2), 1 H–C(2′), 1 H–C(7), 1 H–C(7′)); 1.90 (*m*, H–C(1a), H–C(7a), H–C(1′a), H–C(7′a)). ^{13}C-NMR (100 MHz, $CDCl_3$) 135.5; 128.3; 126.0; 118.8; 29.5; 14.7. EI-MS (70 eV): 285 (M^+, 5), 267 (7), 240 (9), 180 (37), 153 (29), 142 (65), 129 (82), 116 (100), 105 (21), 91 (43), 66 (10).

X-Ray Crystal-Structure Determination of syn-**1**[4]). For the crystal structure determination, the single crystal of *syn*-**1** was used for data collection on a four-circle *Rigaku-R-AXIS-RAPID-S* diffractometer equipped with a two-dimensional area IP detector. The graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) and oscillation-scans technique with $\Delta\omega = 5°$ for one image were used for data collection. Images for *syn*-**1** were taken successfully by varying ω with three sets of different χ and φ values. The 108 images for six different runs covering *ca.* 99.7% of the *Ewald* spheres were performed. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for *Lorentz* and polarization effects, and cell refinement was performed with CrystalClear (*Rigaku/MSC Inc.*, 2005) software [21]. The structure was solved by direct methods SHELXS-97 [22], and non-H-atoms were refined by the full-matrix least-squares method with anisotropic temperature factors SHELXL-97 [22]. Crystal data: $C_{22}H_{20}$; crystal system monoclinic; space group $P2_1/n$ (no.14); unit cell dimensions: $a = 8.8709(2)$, $b = 8.5274(2)$, $c = 21.1090(3)$ Å, $\beta = 95.92(2)°$; volume 1588.3(1) Å^3; $Z = 4$; $D_x = 1.19$ Mg/m^3; absorption coefficient 0.067 mm^{-1}; $F(000)$ 608; θ range for data collection 2.4–30.7°; refinement method: full-matrix least-square on F^2; data and parameters, 4877 and 212; goodness-of-fit on F^2 1.025; final R indices ($I > 2\sigma(I)$): $R_1 = 0.070$, $wR_2 = 0.183$; R indices (all data): $R_1 = 0.130$, $wR_2 = 0.218$; largest diff. peak and hole 0.160 and −0.182 e Å^{-3}.

Reaction of exo-**4**/exo-**6** *4.2*:1 *with CuTC.* As described for *syn*-**1**, with CuTC (1.74 g, 9.10 mmol), NMP (25 ml), and halo(stannyl) derivatives *exo*-**4**/*exo*-**6** 4.2:1 (790 mg of *exo*-**4** + 188 mg of *exo*-**6**, total 2.60 mmol). FC (hexane) yielded *syn*-**1** (236 mg, 64%) and *anti*-**1** (7 mg, 2%) in this order.

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[4]) CCDC-643590 contains the supplementary crystallographic data for this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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