

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

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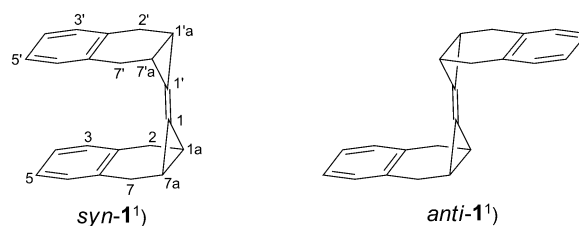
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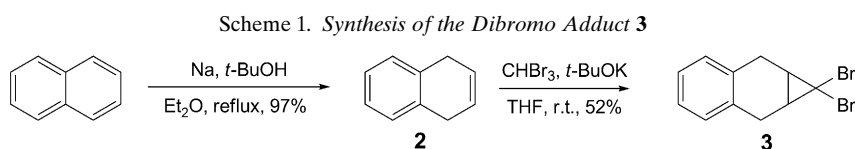
Stereoisomerically pure *endo*- and *exo*-7-halo-7-(trimethylstannyl)benzonorcar-3-enes (= *endo*- and *exo*-(1-halo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalen-1-yl)trimethylstannane) **4** and **6** were selectively obtained by lithium–tin or magnesium–tin transmetalation in good yields (*Scheme 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*]naphthalenyldiene] (*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].

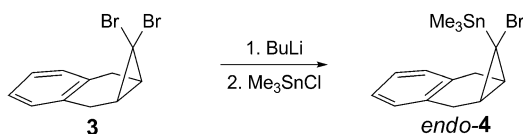
¹⁾ The terms *syn/anti* in names and key numbers mean that a compound has a cage-like/stair-like overall gross structure, cf. *Fig. 1*.

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].



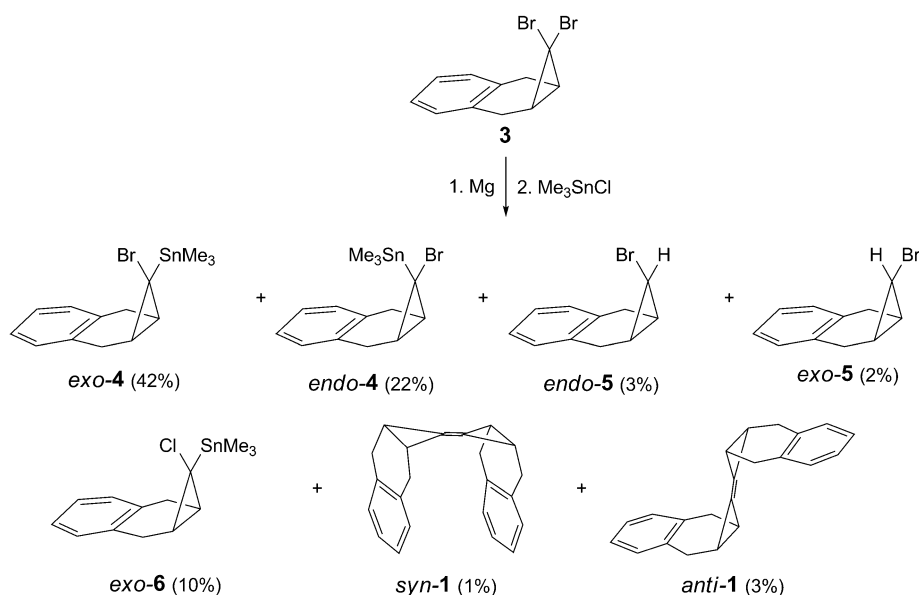
Although the formation of bicyclopropylidenes can be accomplished by the use of simple metalating agents [8], the yields and diastereoselectivities of these reactions are not very good [3b][3i][5][9]. The use of bromostannanes with copper(I) as promoter of the coupling reaction can provide milder conditions 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 chlorotrimethylstannane, the *endo*-trimethylstannyl 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/Me₃SnCl

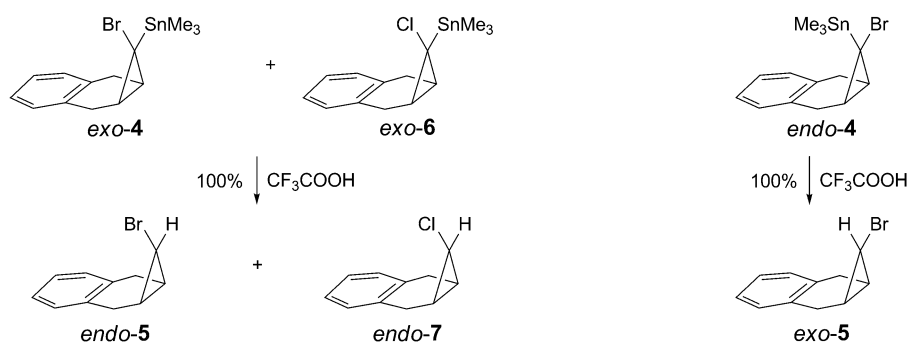
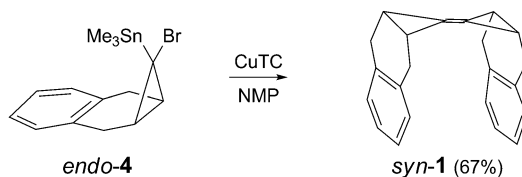
²⁾ The terms *endo/exo* in names and key numbers mean that the senior of the geminal substituents is on the concave/convex side of the molecule, cf. Schemes 2–4 and 7.

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-5* 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 $\text{Mg}/\text{Me}_3\text{SnCl}$



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 ($^1\text{H-NMR}$, 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 ConfigurationsScheme 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 substituted-bromocuprates *exo*- and *endo*-8 can eliminate CuBr to afford a carbene, which may undergo the dimerization reaction.

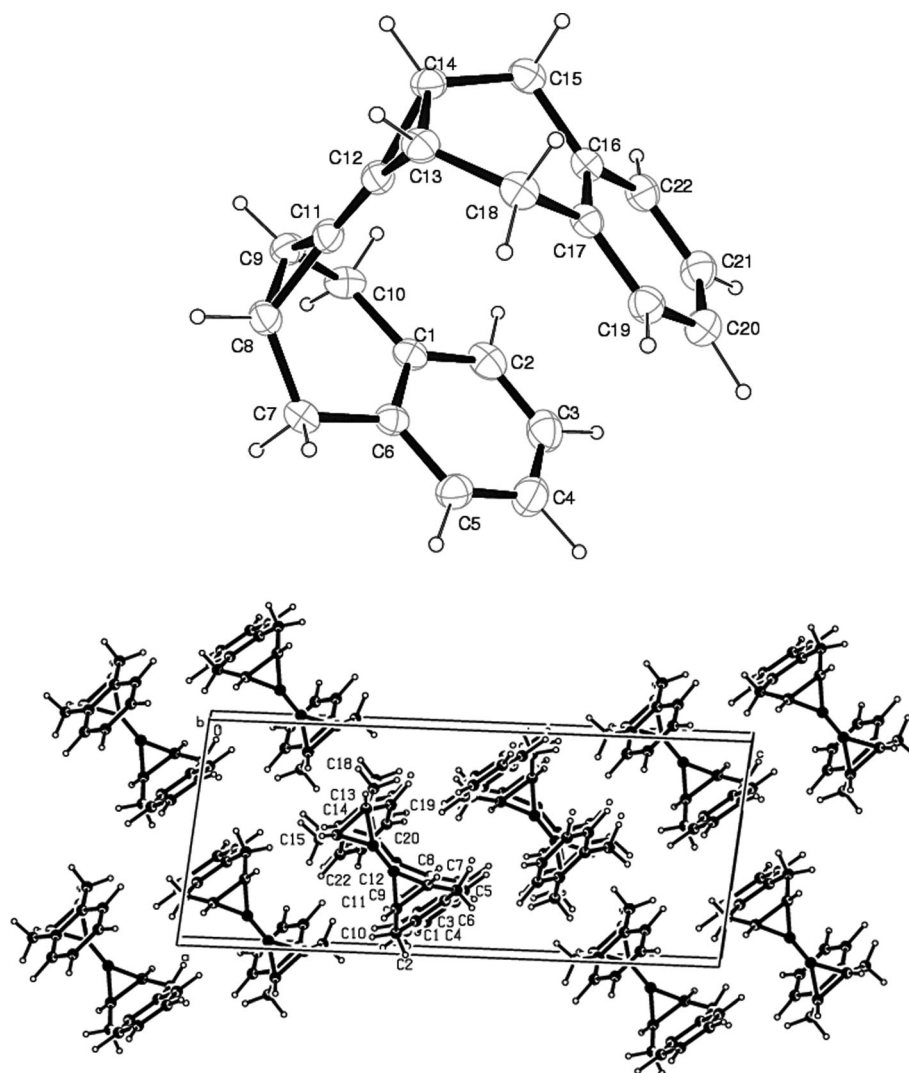
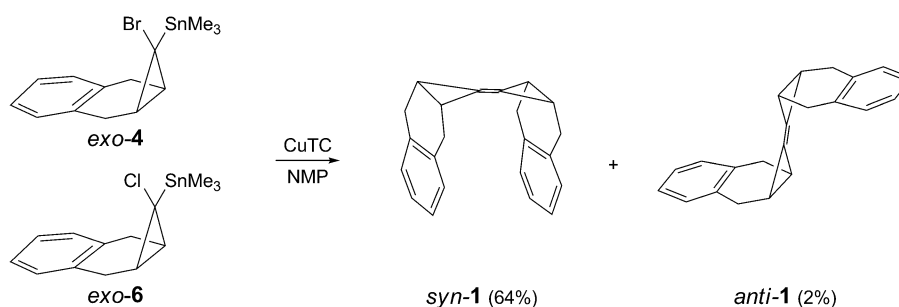


Fig. 2. Molecular structure of *syn-1* and molecular packing in *syn-1* crystals viewed along the *a*-axis. Thermal ellipsoids are drawn at the 40% probability level. Arbitrary atom numbering.

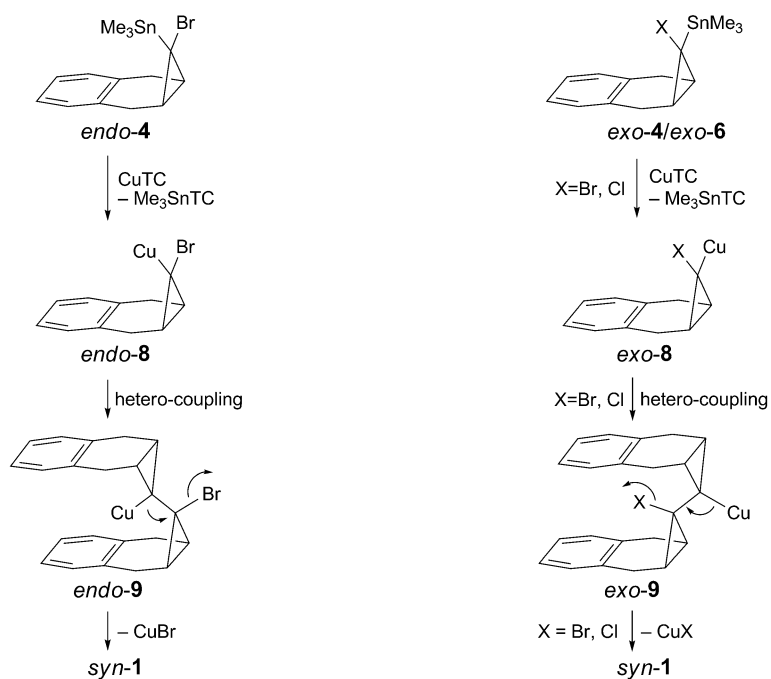
However, in this case, a diastereoselectivity would not be expected. The fact that *syn-1* (which is the more sterically congested isomer) is formed in the coupling reaction of *endo-4* as the sole product indicates that a stepwise process is involved. We assume that a hetero-coupling between two molecules 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 ^1H -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. ^1H - 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-1H-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. ^1H -NMR (400 MHz, CDCl_3): 7.16–7.01 (AA'BB', 4 arom. H); 3.18 (br. d, A of AB, $J(2\text{syn},2\text{anti})=J(7\text{syn},7\text{anti})=17.3$, 1 H–C(2), 1 H–C(7)); 3.03 (br. d, B of AB, $J(2\text{syn},2\text{anti})=J(7\text{syn},7\text{anti})=17.3$, 1 H–C(2), 1 H–C(7)); 2.05 (br. d, $J(1a,2\text{anti})=J(7a,7\text{anti})=3.5$, 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 ^1H NMR: **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-1H-cyclopropa[b]naphthalene (exo-5): Colorless liquid. IR (KBr): 3021, 2888, 2833, 1455, 1323, 1282, 1217, 1024, 749, 675. ^1H -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, $J(2\text{syn},2\text{anti})=J(7\text{syn},7\text{anti})=15.8$, 1 H–C(2), 1 H–C(7)); 3.06 (br. d, B of AB, $J(2\text{syn},2\text{anti})=J(7\text{syn},7\text{anti})=15.8$, 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 $\text{C}_{11}\text{H}_{11}\text{Br}$ (223.11): C 59.22, H 4.97; found: C 59.77, H 4.96.

exo-(1-Bromo-1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-yl)trimethylstannane (exo-4): From the mixture **exo-4/exo-6** 4.2 : 1: ^1H -NMR (400 MHz, CDCl_3): 7.14–7.08 (AA'BB', 4 arom. H); 3.21 (ddd, A of AB, $J(2\text{syn},2\text{anti})=J(7\text{syn},7\text{anti})=16.5$, $J(\text{syn},1a)=J(7\text{syn},7a)=5.5$, $J(2\text{syn},7a)=J(7\text{syn},1a)=2.6$, 1 H–C(2), 1 H–C(7)); 2.70 (br. d, B of AB, $J(2\text{syn},2\text{anti})=J(7\text{syn},7\text{anti})=16.5$, 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-1H-cyclopropa[b]naphthalen-1-yl)trimethylstannane (exo-6): From the mixture **exo-4/exo-6** 4.2 : 1 (only non-overlapped signals): ^1H -NMR (400 MHz, CDCl_3): 3.12 (ddd, A of AB, $J(2\text{syn},2\text{anti})=J(7\text{syn},7\text{anti})=16.5$, $J(2\text{syn},1a)=J(7\text{syn},7a)=5.5$, $J(2\text{syn},7a)=J(7\text{syn},1a)=2.7$, 1 H–C(2), 1 H–C(7)); 2.68 (br. d, B of AB, $J(2\text{syn},2\text{anti})=J(7\text{syn},7\text{anti})=16.5$, 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-1H-cyclopropa[b]naphthalene (endo-5): Colorless oil. IR (KBr): 3061, 3019, 2939, 2894, 2840, 1495, 1455, 1429, 1257, 743, 646. ^1H -NMR (400 MHz, CDCl_3):

³⁾ The label *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*, $J(2syn,2anti) = J(7syn,7anti) = 16.5$, $J(2syn,1a) = J(7syn,7a) = 5.3$, $J(2syn,7a) = J(7syn,1a) = 2.8$, 1 H–C(2), 1 H–C(7)); 2.68 (*br. d*, *B* of *AB*, $J(2syn,2anti) = J(7syn,7anti) = 16.5$, 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 $\text{C}_{11}\text{H}_{11}\text{Br}$: 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[1H-cyclopropa[b]naphthalenylidene] (= *anti-1a,2,7,7a-Tetrahydro-1-(1a,2,7,7a-tetrahydro-1H-cyclopenta[b]naphthalen-1-ylidene)-1H-cyclopropa[b]naphthalene; anti-1*)⁴: 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. ^1H -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 $\text{C}_{22}\text{H}_{20}$: 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[1H-cyclopropa[b]naphthalenylidene] (= *syn-1a,2,7,7a-Tetrahydro-1-(1a,2,7,7a-tetrahydro-1H-cyclopropa[b]naphthalen-1-ylidene)-1H-cyclopropa[b]naphthalene; syn-1*)⁴: 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. ^1H -NMR (400 MHz, CDCl_3): 6.82–6.73 (*AA'BB'*, 8 arom. H), 2.97 (*br. d*, *A* of *AB*, $J(2syn,2anti) = J(7syn,7anti) = J(2'syn,2'anti) = J(7'syn,7'anti) = 15.0$, 1 H–C(2), 1 H–C(2'), 1 H–C(7), 1 H–C(7')); 2.50 (*br. d*, *B* of *AB*, $J(2syn,2anti) = J(7syn,7anti) = J(2'syn,2'anti) = J(7'syn,7'anti) = 15.0$, 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-RAXIS-RAPID-S* diffractometer equipped with a two-dimensional area IP detector. The graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) and oscillation-scans technique with $\Delta\omega = 5^\circ$ 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/MSI 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: $\text{C}_{22}\text{H}_{20}$; 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, $\beta = 95.92(2)^\circ$; volume 1588.3(1) Å³; $Z = 4$; $D_x = 1.19$ Mg/m³; 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.

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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