

Molybdenum-Catalyzed Stannylations as Key Steps in **Heterocyclic Synthesis**

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THF/carbonyl complexes of molybdenum and tungsten are suitable precursors for the synthesis of the corresponding monoisonitrile carbonyl complexes. Whereas complexes with electron-rich isonitriles are suitable for regioselective hydrostannations, complexes with electron-poor isonitriles are efficient catalysts for distannations, without reduction of aromatic halides. This allows for the synthesis of halogenated distannylated allyl ethers, which can be subjected to intramoleculare Stille couplings giving rise to heterocycles, which can be further modified at the remaining stannyl group.

Introduction

Condensed heterocycles are widespread in nature, and many of these compounds show interesting biological activity. The benzofurane skeleton is a common feature in the large group of furocumarines and aflatoxines, which are known for their cancerogenity.¹ Others, such as 1, show antibiotic activity and are therefore interesting from a pharmaceutical point of view.² The ring-enlarged chromanes are found in vitamin E, cannabinol, and related structures, and therefore many syntheses have been developed for compounds of this type.³ In contrast, the preparation of the isomeric isochromanes has been less well investigated, despite the fact that these compounds also show an interesting pharmaceutical profile. For example, **2** and analogues, which are found in roots and barks of several plants,⁴ show antifungal activity⁵ and inhibit lipid peroxidation in microsomes.⁶



A common strategy, suitable for the synthesis of both classes of natural products, is the cyclization of allylic or propargylic ethers of o-iodophenols (yielding benzofuranes) or halogenated benzyl alcohols (providing isochromanes). These cyclizations can be carried out via radical intermediates⁷ or in the presence of transition metal catalysts. Propargylic ethers can be cyclized under chromium(II)-mediated nickel(II)-catalyzed conditions8 or in the presence of palladium catalysts.⁹ Palladium also can be used for cyclizations via π -allylintermediates¹⁰ or for intramolecular Heck reactions of the corresponding allyl ethers.¹¹ The critical step of the Heck reaction in general is the last one of the catalytic cycle, the β -hydride elimination, which often can occur in different directions, giving mixtures of isomeric products. This is definitely a limitation of this protocol. Other approaches such as intramolecular Stille couplings are more suitable, especially because the olefin geometry of the vinylstannane in general can be transferred into the product,¹² but under certain circumstances cine substitution products¹³ can be found, as reported by Quayle et al.14.

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Results and Discussion

On the basis of our interest in the selective synthesis of vinylstannanes we developed a molybdenum isonitrile complex 3 (MoBl₃) that allows regioselective hydrostannations of terminal alkynes with Bu₃SnH. In principle, Mo(CO)₆ can be used for hydrostannations as well, but the yields and selectivities obtained were moderate. Replacing three CO ligands by isoelectronic isonitrile ligands resulted in a significant increase of the yield and the selectivity as well. tert-Butylisonitrile was chosen for steric reasons, with the expectation that the sterically demanding tert-butyl groups may have an influence on the regioselective outcome of the reaction. Indeed, MoBI₃ transfers the stannane to the sterically more hindered position of the triple bond.¹⁵ An additional isonitrile ligand (MoBI₄)¹⁶ has no positive effect on the reaction. In contrast, the yields obtained are somewhat lower, although this decrease is not significant in most cases. The lower yield might result from the lower stability of $M_0(CO)_2(CNtBu)_4$ (MoBI₄) in comparison to that of MoBI₃. In contrast to the later complex, which is perfectly stable at room temperature even under air, MoBI₄ decomposes during storage even under argon at -18 °C. Obviously, three isonitrile ligands are the optimum not only for the yield and selectivity but also the stability of the catalyst.

Very recently we were able to develop a new catalyst 4 based on tungsten that allows the distannation of alkynes, also by using Bu₃SnH.¹⁷ So, depending on the catalyst used, we can obtain both hydro- or distannylated products from the same starting materials.

$$\frac{Mo(CO)_3(CNtBu)_3}{3} \quad W(CO)_5(CNC_6H_4-pNO_2)}{4}$$

The different reaction behavior of these two complexes probably results from the different electronic properties of the isonitrile ligands. Replacement of CO ligands by tert-butylisonitrile as an electron-rich ligand results in a reduced metal-CO bond (1.989-1.994 Å)¹⁸ in comparison to that of $Mo(CO)_6$ (2.053–2.065 Å).¹⁹ This clearly indicates that *tert*-butylisonitrile acts preferentially as a σ -donor and less as a π -acceptor. Obviously the isonitrile is the ligand that dissociates from the metal, opening free coordinations sites for the additions of the tin hydride and the alkyne. This would explain the higher reactivity of $MoBI_3$ (3) in comparison to that of $Mo(CO)_6$. On the other hand, the isonitrile stays in solution and, after the reaction is finished, can recoordinate to the molybdenum, regenerating the catalyst. This is in aggreement with the observation that MoBI₃ can be recovered in most cases in high yield without loss of activity. With respect to the fact that molybdenum and tungsten can easily enlarge their coordination sphere, we assume that (probably two) of the isonitrile ligands dissociate from the catalyst, the alkyne coordinates to a free coordination site, and oxidative addition of the tin hydride gives rise to complex A. Insertion of the alkyne into the molybdenum tin bond occures in such a way that the sterically more demanding molybdenum moiety is located at the sterically least hindered position (**B**). Reductive elimination than gives rise to the hydrostannation product and the catalyst is recycled by recoordination of the isonitrile ligands.

Quite different is the situation in the case of the tungsten complex 4. IR and Raman spectra show an increase of the C-O bond energy in comparison to that of W(CO)₆, which is equivalent to a reduced metal-CO π -back-bonding. The electron-poor isonitrile obviously is tightly bond to the tungsten, and in this case the CO probably is the ligand that dissociates from the metal. This is also in good agreement with the observation that the electron-poor isonitrile complex 4 cannot be recovered in contrast to **3**. We assume that the tungsten complex 4 behaves differently from the molybdenum complex 3. Oxidative additon of 2 equiv of tin hydride and subsequent reductive elimination of H₂ probably gives rise to distannane complex C. Insertion of the alkyne (D) and reductive elimination then provides the distannated product. Distannane complexes similar to C were characterized by Schubert et al.²⁰Alternatively one might propose that the decomposition of the tin hydride via elimination of H₂ and formation of the distannane competes with the hydrostannation. This would explain the formation of the distannylated product as a metalcatalyzed addition of an in situ prepared distannane to an alkyne. Decompositions of this type are well-known for palladium-catalyzed reactions,²¹ and palladium complexes also catalyze the addition of distannanes to alkynes.²² Only a few months ago, Lautens et al. described distannations using palladium isonitrile complexes.23

To verify our mechanistic hypothesis we tried to react hexabutyldistannane with an alkyne in the presence of our molybdenum catalysts, but in no case were we able to isolate any stannylated product. Obviously a "free" distannane is not the reagent for the addition, but the "decomposition" must take place in the coordination sphere of the metal, probably in the presence of coordinated alkyne.

Both catalysts are mixed CO and isonitrile complexes and can be prepared by ligand exchange from the homoleptic carbonyl complexes according to Coville and Albers (Scheme 1).²⁴ The protocol is especially suitable for complexes with electron-rich isonitriles such as the Mo(CO)₃(CN*t*Bu)₃ (MoBl₃) catalyst (3)¹⁶ but shows deficits with electron-poor isonitriles, such as *p*-nitrophenylisoni-

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FIGURE 1. Mechanistic rationals for hydrostannations and distannations.





trile (5).²⁵ In contrast to $MoBl_3$ (3), which was obtained in excellent yield with only a slight excess of *tert*butylisonitrile, the corresponding trisisonitrile complex with ligand 5 could not be obtained. Instead a mixture of the mono- and bisisonitrile complexes 6/7 and 4/8 are formed independent of the metal carbonyl used and in reasonably good yields.

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SCHEME 2. Stannation of Propargyl Acetate 9



TABLE 1. Stannation of Propargyl Acetate 9

entry	catalyst	yield, %		
		10	11	12
1	3	88 ^a	3	
2	4	1	1	87
3	6	2	1	51
4	7	22	1	41
5	8	6	5	57

All catalysts were tested in the hydrostannation/ distannation of propargyl acetate **9** (Scheme 2, Table 1). This substrate was chosen because it is known that molybdenum complexes such as $MoBl_3$ (**3**) and $MoBI_4$ can be used as catalysts in allylic alkylations, ¹⁶ but we were interested to develop selective catalysts that do not undergo these "side reactions".

The reactions were carried out in toluene at 60 $^{\circ}C$, ²⁶ and hydroquinone was added to suppress the hydrostan-

⁽²⁶⁾ In general, the best results for hydrostannations with ${\bf 3}$ are obtained in THF at 55 °C (see Experimental Section).

SCHEME 3. Formation of Monoisonitrile Complexes

Mo(CO) ₆	<u>THF</u> 24h, ∆	(THF)Mo(CO) ₅	5 THF, ∆ 67%	Mo(CO) ₅ (CNC ₄ H ₄ NO ₂) 6
W(CO) ₆	THF 24h, hv -78°→0°C	(THF)W(CO) ₅	5 THF, ∆ 88%	W(CO) ₅ (CNC ₄ H ₄ NO ₂) 4





nation via a radical pathway. In general, this occurs at higher temperature and results in a higher amount of β -substituted product **11** as a E/Z mixture;²⁷ however, obviously this side reaction does not play a significant role. According to our previous observations made with propargylic ethers, $MoBl_3$ (3) gave the α -stannylated product **10**, whereas with the monoisonitrile complexes 4 and 6 the distannylated product 12 was obtained nearly exclusively. The tungsten complex 4 again showed a reactivity higher than that of the molybdenum complex 6. Unfortunately, these highly selective complexes are only the minor products in the ligand exchange reaction, and therefore we were interested to find an alternative approach toward their synthesis. The yields could dramatically be increased after conversion of the homoleptic carbonyl complexes into the corresponding mono-THF complexes (Scheme 3). In the case of the molybdenum complex this was accomplished by refluxing $Mo(CO)_6$ in THF;²⁵ for the tungsten complex irradiation at low temperature was necessary.²⁸ Compound 5 was added, and the monoisonitrile complexes were obtained after refluxing in THF in good to excellent overall yield.

After the development of a straightforward synthesis for the required complexes, we focused on applications of this synthetic protocol toward the synthesis of heterocycles via intramolecular Stille couplings. First of all we investigated the reaction of the propargylic *O*-bromobenzyl ether **13** with our catalysts **3** and **4** (Scheme 4). Although **3** gave the expected hydrostannation product **14** in moderate yield as a single regioisomer, the results SCHEME 5. Intramolecular Stille Couplings of Stannylated Allyl Ethers



with our "highly reactive" tungsten catalyst **4** were even worse in this reaction. We found previously that the yields in hydrostannations and distannations increase with the electron-withdrawing properties of substituents on the alkyne moiety; therefore propargylic ethers are normally less reactive than, e.g., propargylic esters. Obviously this effect is more significant in the case of the tungsten than the molybdenum complexes.

Unfortunately all attempts to subject 14 to intramolecular Stille coupling failed, and we switched to the more reactive *o*-iodobenzyl ether 16. The results obtained with **3** and **4** were comparable those of to the previous reaction. Again the tungsten complex provided the expected product 18 in only 9% yield. To proof the influence of the central metal we have also investigated the corresponding molybdenum complex 6. Indeed, the yield could be increased dramatically, and 18 could be obtained nearly exclusively (only 3% 17) in good yield. No reduction of the halide was observed in all experiments.²⁹ This underlines our observation that 4 is an excellent catalyst for electronpoor alkynes but fails with electron-rich substrates, while the molybdenum complex 6 is less sensitive regarding the electronic properties of the substrate.

After the successful synthesis of the stannylated iodides 17 and 18, we turned back to the intramolecular Stille reactions. In the cyclization of 17 we made an interesting observation (Scheme 5). If the reaction was carried out at 90 °C, not the expected Stille product 19 was obtained, but the isomerization product 20. Obviously under these reaction conditions the exocyclic double bond migrates to the thermodynamically more stable position. On the other hand, by decreasing the temperature to 75 °C, this isomerization could be nearly suppressed, and the expected coupling product 19 was obtained in good yield, with only traces of 20. A similar observation was made by Heck^{11a} and Overman et al.,^{11b} who found **20** as side product in the corresponding Heck reaction. They performed their reactions in refluxing acetonitrile (bp 81.5 °C), and probably the temperature difference in our experiments was responsible for the complete isomerization.

In general, the terminal stannane in vinyldistannanes is the more reactive one, allowing the selective coupling of the terminal in the presence of an internal tin substituent.³⁰ On the other hand, in distannylated products such as **15** and **18** the internal stannane should be

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SCHEME 6. Intramolecular Stille Couplings of Distannylated Allyl Ethers



SCHEME 7. Synthesis of Benzofurane Derivatives



the preferred one for intramolecular couplings, while the terminal group should give di- or oligomers. To avoid isomerization processes we performed the cyclization at 75 °C as reported above (Scheme 6). Indeed, both stannylated ethers could be cyclized, while the more reactive iodo derivative **18** gave better yields, and no intermolecular coupling product or *cine* product was obtained.¹⁴ The stannylated methylidene isochromane **21** formed is a suitable substrate for further modifications. Exemplarily, **21** was converted into the corresponding lithio derivative via metal-metal exchange with *n*-BuLi, which was trapped with ethylchloroformiate to give the ester **22**. However, other types of electrophiles should be applicable as well.

The intramolecular Stille coupling, as well as the further modification, proceeds with clean retention of the olefin geometry as determined by NOESY experiments. Strong couplings are observed between the vinylic hydrogen and the adjacent methylene group, as well as between the aromatic ring and butyl groups (21) or the ethyl ester group (22). To enlarge the synthetic potential of this protocol, we transferred this method also to the corresponding benzofurane system. Distannation of phenyl ether 23 gave the distannylated product 24 (besides 7% hydrostannylated α -product), and subsequent Stille coupling at 70 °C gave rise to the benzofurane derivative 25 in good yield. We expected that the *exo* double bond should show a high tendency to isomerize to the heteroaromatic ring system. Therefore we performed the same reaction also at 90 °C. Surprisingly, not the expected product was obtained, but a mixture of the reduced (26) and the protodestannylated product (27). The observation that the double bond is reduced at higher temperatures was also made by Echavarren et al. in the coupling of (E)-1,2-bis(tributylstannyl)ethene with acid

chlorides.³¹ They assume the transfer of a butyl group (from the tributyl halide formed in the Stille coupling) onto the palladium and a subsequent formation of a palladium hydride species, which is responsible for the reduction step. A similar process is probably responsible for our observation.

In conclusion, we have shown that molybdenumcatalyzed stannylation reactions can be used for the construction of interesting heterocylic ring systems via subsequent intramolecular Stille couplings, because aromatic halides are not affected by the metalation step. Further synthetic applications and mechanistic questions are currently under investigation.

Experimental section

Preparation of Isonitrile Ligand 5.32 A solution of p-nitroformanilide (1.02 g, 6.13 mmol) and triethylamine (2.6 mL, 18.65 mmol) was stirred in 60 mL of DCM at room temperature for 3 h. The solution was cooled to 0 °C before phosphoroxychloride (1.43 g, 9.29 mmol) was added in 15 mL of DCM. The icebath was removed, and the mixture was stirred 2 h at room temperature. After cooling to 0 °C, a saturated Na₂CO₃ solution (7.44 g, 60 mmol) was added slowly (strong CO₂ evolution). After the emulsion stirred vigorously for 3 h, the layers were separated, and the aqueous layer was extracted twice with DCM. The combined organic layers were dried over Na₂SO₄, and the solvent was evaporated in vacuo. The crude product was purified by flash chromatography on silica (hexanes/ethyl acetate 7/3) giving rise to 830 mg (5.610 mmol, 92%) of **5** as a yellow-green solid, mp \approx 110 °C (dec). This solid is stable at room temperature for a short time but should be stored in the fridge below 4 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.57 (d, J = 8.7 Hz, 2H), 8.30 (d, J = 8.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 125.0, 127.5, 131.0, 147.5, 169.8. IR (KBr, cm⁻¹): ν 3108, 3077 (w, C_{Aryl-H vs)}, 2130 (s, C–N vs), 1610, 1595, 1489 (m, C=C vs), 1531, 1348 (s, N-O vs), 860 (s, C-NO2 vs), 747 (m, CArvl-H). MS (EI+): 148.11 (M+), 102.08, 75.04, 51.01, 29.96, 26.98.

(4-Nitrophenylisocyano)tungsten Pentacarbonyl 4. A suspension of W(CO)6 (775 mg, 2.20 mmol) in 10 mL of absolute THF was cooled in an oven-dried irradiation apparatus to -78 °C under Ar and was irradiated with a sodium steam lamp for 12 h. During that time the solution was slowly warmed to 0 °C. The pale-yellow solution was transferred via cannula into an oven-dried three-neck flash with reflux condenser. A solution of isonitrile 5 (258 mg, 1.74 mmol) in 3 mL of absolute THF was added via syringe at room temperature under Ar. The mixture was stirred for 30 min, before it was refluxed for 3 h. During that time the color of the solution turned dark orange and finally deep red. The solvent was evaporated in vacuo, and the residue was purified by flash chromatography on silica (DCM/hexanes 1/1). Yield: 726 mg (1.54 mmol, 88%) of 4 as a yellow-orange solid. ¹H NMR (300 MHz, CDCl₃): δ 7.55 (d, J = 9.1 Hz, 2H), 8.32 (d, J = 9.1 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 125.3, 127.3, 132.4, 147.0, 166.3, 193.4, 195.0. IR (KBr, cm⁻¹): v 2135, 2048, 1925 (s, C-O vs), 1972 (m, C-N vs), 1638, 1606, 1589 (w, C=C vs), 1524, 1344 (s, N–O vs), 859 (m, C–NO₂ vs). Raman (cm⁻¹): ν = 2135, 2043, 1981, 1923 (s, C-O vs), 1586, 1341 (s, N-O vs). HRMS (FAB⁺) m/e: C₁₂H₄N₂O₇¹⁸⁶W [M]⁺ calcd 473.9563; found 473.9581. $C_{12}H_4N_2O_7^{184}W$ [M]⁺ calcd 471.9528; found 471.9535. C₁₂H₄N₄O₇¹⁸²W [M]⁺ calcd 469.9501, found 469.9515. Anal. Calcd for C₁₂H₄N₂O₇W (472.02): C, 30.53; H, 0.85; N, 5.93. Found: C, 30.28; H, 1.04; N, 5.68.

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(4-Nitrophenylisocyano)molybdenum Pentacarbonyl 6. A solution of Mo(CO)₆ (570 mg, 2.15 mmol) in 10 mL of absolute THF was refluxed in an oven-dried apparatus for 24 h under Ar. After the heating bath was removed, isonitrile 5 (254 mg, 1.71 mmol) in 3 mL of absolute THF was added to the yellow solution, and the solution was refluxed for further 3 h. The solution darkened via red to black. The solvent was evaporated in vacuo, and the crude product was purified by flash chromatography on silica (DCM/hexanes 1/1). Complex 6 was isolated as a red solid (440 mg, 1.15 mmol, 67%). 1 H NMR (300 MHz, CDCl₃): δ 7.52 (d, J = 9.0 Hz, 2H), 8.31 (d, J = 8.9 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 125.3, 127.3, 132.7, 147.0, 173.8, 203.3, 205.8. 95 Mo NMR (20 MHz, toluene): δ –1836. IR (KBr, cm⁻¹): ν 2138, 2062, 1939 (s, C–O vs), 1956 (m, C-N vs), 1637, 1593 (w, C=C vs), 1593, 1490 (s, N-O vs), 850 (w, C-NO₂ vs). Raman (cm⁻¹): v 2139, 2058, 1995, 1937 (s, C-O vs), 1591, 1466 (s, N-O vs). HRMS (FAB+) m/e: C12H4N2O798Mo [M]+ calcd 385.9073; found 385.9060. C₁₂H₄N₂O₇⁹⁶Mo [M]⁺ calcd 385.9065; found 383.9035. C₁₈H₈-N₄O₈95Mo [M]⁺ calcd 382.9077, found 382.9048. Anal. Calcd for C₁₂H₄N₂O₇Mo (384.11): C, 37.52; H, 1.05; N, 7.29. Found: C, 37.34; H, 1.18; N, 7.46.

General Procedure for Hydrostannations. In an ovendried Schlenk tube were dissolved 1 equiv of alkyne and 2 mol % of catalyst 3 in absolute THF under Ar together with 1 mol % of hydroquinone. The solution was heated to 55 °C before 2 equiv of Bu_3SnH was added. After 4 h at this temperature 1 equiv of Bu_3SnH was added, and the mixture was stirred for 2 h at this temperature. After cooling to room temperature, the solvent was evaporated in vacuo, and the crude product was purified by flash chromatography on silica using a hexane/ ethyl acetate mixture containing 1% NEt₃.

General Procedure for Distannations. In an oven-dried Schlenk tube were dissolved 1 equiv of the alkyne, 0.5-2.5 mol % of catalyst **4** or **6**, and a point of a spatula of hydroquinone in dry toluene and heated for 15 min at 60 °C. After addition of 3.5-4 equiv of tributyl tinhydride heating was continued for 12 h at 60 °C. After removal of the solvent the crude product was chromatographed over silica gel. First hexabutyldistannane and tributyl tinhydride were eluated with pure hexane, and then the product could be isolated using a hexane/ethyl acetate mixture containing 1% NEt₃.

2-Tributylstannyl-2-propenyl Acetate 10. Acetate 10 was prepared according to the general procedure for hydrostannations from propargyl acetate (620 mg, 6.30 mmol) with catalyst 3 (51 mg, 0.12 mmol) and Bu₃SnH (5.0 mL, 18.9 mmol) in 20 mL of THF. Flash chromatography (hexanes/ethyl acetate/NEt₃ 95/4/1) gave rise to 10 as a colorless liquid (2.22 g, 5.72 mmol, 91%) and a mixture of regioisomers (α/β 96/4). ¹H NMR (300 MHz, CDCl₃): δ 0.80–1.05 (m, 15H), 1.32 (m, 6H), 1.47 (m, 6H), 2.06 (s, 3H), 4.71 (t, J = 2.0 Hz, 2H), 5.30 (dt, J = 1.9 Hz, 1.7 Hz, $J_{H.Sn} = 59.3$ Hz, 1H), 5.85 (dt, J = 1.8Hz, 1.7 Hz, $J_{H,Sn} = 121.1$ Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 9.3, 13.6, 20.8, 27.1, 29.0, 71.2, 125.2, 148.7, 170.2. $^{119}\mathrm{Sn}$ NMR (112 MHz, CDCl₃): δ –42.2. Selected signals of the minor isomer 11: ¹H NMR (300 MHz, CDCl₃): δ 6.02 (dt, J = 19.0Hz, 5.3 Hz, 1H), 6.26 (d, J = 19.0 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 73.7, 131.8, 145.5. ¹¹⁹Sn NMR (112 MHz, CDCl₃): δ -48.1. Anal. Calcd for C₁₇H₃₄O₂Sn (389.14): C, 52.48; H, 8.74. Found: C, 52.23; H, 8.78.

2,3-Bis(tributylstannyl)allyl Acetate 12. According to the general procedure for distannations, **12** was obtained from propargyl acetate (100 mg, 1.02 mmol), Bu₃SnH (1.0 mL, 3.8 mmol), and catalyst **4** (3 mg, 6 μ mol) in 3 mL of toluene after flash chromatography (hexanes/ethyl acetate/NEt₃ 95/4/1) as a colorless liquid (601 mg, 0.89 mmol, 87%). ¹H NMR (300 MHz, CDCl₃): δ 0.81–0.98 (m, 30H), 1.32 (m, 12H), 1.48 (m, 12H), 2.07 (s, 3H), 4.65 (d, J = 1.5 Hz, 2H), 6.80 (t, J = 1.4 Hz, $J_{H,Sn} = 173.5$ Hz, $J_{H,Sn} = 71.2$ Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 10.5, 10.8, 13.6, 21.0, 27.4, 27.5, 29.1, 29.2, 79.0, 145.2, 160.5, 170.4. ¹¹⁹Sn NMR (112 MHz, CDCl₃): δ –64.8,

-53.1. Anal. Calcd for $C_{29}H_{60}O_2Sn_2$ (678.17): C, 51.36; H, 8.92. Found: C, 51.34; H, 8.80.

2-Bromobenzyl-2-tributylstannylallyl Ether 14. Ether 14 was obtained according to the general procedure for hydrostannations from 2-bromobenzylpropargyl ether 13 (98 mg, 0.43 mmol) and Bu₃SnH (0.35 mL, 1.32 mmol) using catalyst 3 (5 mg, 0.012 mmol) after flash chromatography (hexanes/NEt₃ 99/1) as a colorless liquid (71 mg, 0.14 mmol, 32%). ¹H NMR (300 MHz, CDCl₃): $\delta \bar{0}.80-1.07 (m, 15H, 1H)$, 1.21-1.34 (m, 6H), 1.41 - 1.59 (m, 6H), 4.23 (m, $J_{H,Sn} = 33.8$ Hz, 2H), 4.53 (s, 2H), 5.29 (m, $J_{H,Sn} = 61.4$ Hz, 1H), 5.91 (m, $J_{\rm H,Sn} = 129.5$ Hz, 1H), 7.11 (m, 1H), 7.29 (m, 1H), 7.51 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 9.4, 13.4, 27.1, 28.9, 71.1, 77.7, 122.2, 124.7, 127.0, 128.4, 128.6, 132.1, 137.8, 152.4. 119-Sn NMR (112 MHz, CDCl₃): δ -46.3. HRMS (FAB⁺) m/e: $C_{18}H_{28}O^{81}Br^{120}Sn \ [M - Bu]^+ \ calcd \ 461.0325; \ found \ 461.0346.$ $C_{18}H_{28}O^{81}Br^{118}Sn [M - Bu]^+$ calcd 459.0319; found 459.0348. $C_{18}H_{28}O^{81}Br^{116}Sn\ [M-{\it n}\mathchar`Bu]^+\ calcd\ 457.0320,\ found\ 457.0360.$

2,3-Bis(tributylstannyl)allyl-(2-bromobenzyl)ether 15. According to the general procedure for distannations, **15** was obtained from 2-bromobenzylpropargyl ether **13** (81 mg, 0.36 mmol), Bu₃SnH (0.4 mL, 1.5 mmol), and catalyst **4** (3 mg, 6 μ mol) in 2 mL of toluene after flash chromatography (hexanes/ ethyl acetate/NEt₃ 98/1/1) as a colorless liquid (32 mg, 0.039 mmol, 11%). ¹H NMR (300 MHz, CDCl₃): δ 0.79–0.97 (m, 30H), 1.31 (m, 12H), 1.49 (m, 12H), 4.22 (d, J = 1.1 Hz, 2H), 4.52 (s, 2H), 6.94 (s, $J_{\rm H,Sn} = 173.8$ Hz, 72.4 Hz, 1H), 7.12 (dt, J = 7.7 Hz, 1.5 Hz, 1H), 7.30 (dt, J = 7.5 Hz, 1.2 Hz, 1H), 7.12 (dt, J = 7.9 Hz, 1.2 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 10.5, 10.8, 13.6, 27.4, 27.5, 29.3, 70.8, 83.1, 122.2, 127.6, 128.1, 128.2, 132.2, 138.0, 144.0, 164.2. ¹¹⁹Sn NMR (112 MHz, CDCl₃): δ -65.2, -55.0. Anal. Calcd for C₃₄H₆₃BrOSn₂ (805.16): C, 50.72; H, 7.89. Found: C, 50.87; H, 7.69.

2-Iodobenzyl-2-tributylstannylallyl Ether 17. Ether **17** was obtained according to the general procedure for hydrostannations from 2-iodobenzylpropargyl ether **16** (253 mg, 0.93 mmol) and Bu₃SnH (0.75 mL, 2.83 mmol) using catalyst **3** (10 mg, 0.023 mmol) after flash chromatography (hexanes/NEt₃ 99/1) as a colorless liquid (183 mg, 0.32 mmol, 35%). ¹H NMR (300 MHz, CDCl₃): δ 0.79–0.93 (m, 15 H, 1-H), 1.20–1.33 (m, 6H), 1.41–1.54 (m, 6H), 4.22 (s, $J_{\rm H,Sn}$ = 34.2 Hz, 2H), 4.44 (s, 2H), 5.30 (d, J = 2.4 Hz, $J_{\rm H,Sn}$ = 66.2 Hz, 1H), 5.92 (d, J = 2.4 Hz, $J_{\rm H,Sn}$ = 130.8 Hz, 1H), 6.96 (m, 1H), 7.32 (m, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): 9.6, 13.7, 27.4, 29.1, 75.9, 79.3, 125.0, 128.1, 128.4, 128.9, 139.0, 140.9, 156.3, 152.6. ¹¹⁹Sn NMR (112 MHz, CDCl₃): δ –46.1. Anal. Calcd for C₂₂H₃₇IOSn (563.12): C, 46.92; H, 6.62. Found: C, 47.21; H, 6.75.

2,3-Bis(tributylstannyl)allyl-(2-iodobenzyl)ether 18. According to the general procedure for distannations, **18** was obtained from 2-iodobenzylpropargyl ether **16** (331 mg, 1.22 mmol), Bu₃SnH (1.0 mL, 3.8 mmol), and catalyst **6** (11 mg, 0.029 mmol) in 3 mL of toluene after flash chromatography (hexanes/ethyl acetate/NEt₃ 98/1/1) as a colorless liquid (683 mg, 0.80 mmol, 66%). ¹H NMR (300 MHz, CDCl₃): δ 0.82–0.97 (m, 30H), 1.31 (m, 12H), 1.49 (m, 12H), 4.27 (d, J = 1.7 Hz, 2H), 4.60 (s, 2H), 6.94 (s, $J_{H,Sn} = 173.8$ Hz, $J_{H,Sn} = 67.8$ Hz, 1H), 6.98 (dt, J = 9.6 Hz, 1.5 Hz, 1H), 7.34 (dd, J = 7.3 Hz, 3.0 Hz, 1H), 7.45 (dt, J = 7.7 Hz, 0.9 Hz, 1H), 7.80 (dd, J = 7.9 Hz, J = 3.3 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 10.5, 10.8, 13.7, 27.4, 27.5, 29.2, 29.3, 75.4, 83.0, 97.2, 128.0, 128.4, 128.8, 138.9, 140.9, 144.1, 164.2. Anal. Calcd for C₃₄H₆₃IOSn₂ (852.16): C, 47.92; H, 7.45. Found: C, 47.99; H, 7.44.

4-Methylenisochroman 19.^{11a,b} $Pd(PPh_3)_4$ (75 mg, 0.052 mmol) was dissolved in a oven-dried Schlenk tube in 2.5 mL of absolute toluene under Ar. A solution of **17** (270 mg, 0.52 mmol) in 1 mL of toluene was added, and the mixture was heated to 75 °C for 48 h. Saturated KF solution was added, and the mixture was stirred vigorously for 12 h. Precipitated Bu₃SnF was filtered off, and the solvent was evaporated in vacuo. The residue was dissolved in ethyl acetate and filtered again. The crude product was purified by flash chromatogra-

phy on silica (hexane/ethyl acetate 98/2) giving rise to **19** as a colorless oil (52 mg, 0.36 mmol, 68%).¹H NMR (300 MHz, CDCl₃): δ 4.44 (s, 2H), 4.80 (s, 2H), 5.00 (s, 1H), 5.60 (s, 1H), 7.00–7.69 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 68.7, 70.7, 106.6, 123.2, 124.4, 126.7, 127.8, 130.8, 134.3, 138.1. MS (EI⁺) *m/e*: C₁₀H₁₀O 146.0 (M⁺, 39), 115.0 (100), 91.1 (40.2).

4-Methylisochromen 20.^{11a,b} According to the preparation of **19** isomerzation product **20** was obtained from **17** (152 mg, 0.30 mmol) at 90 C. The reaction was stopped after 18 h, because the catalyst was precipitated as elemental Pd. Workup as described provided **20** (34 mg, 0.23 mmol, 79% d. Th.) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 1.92 (d, J = 1.4 Hz, 3H), 4.99 (s, 2H), 6.47 (d, J = 1.4 Hz, 1H), 6.45 – 7.28 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 13.1, 68.2, 111.4, 120.3, 123.7, 126.6, 128.1, 128.7, 132.4, 142.3. MS (EI⁺) *m/e*: C₁₀H₁₀O: 146.1 (M⁺, 86), 117.1 (100), 91.0 (42.7).

(E)-4-(Tributylstannylmethyliden)isochroman 21. According to the preparation of 19 the stannylated analogue 21 was obtained from 18 (340 mg, 0.40 mmol) in the presence of Pd(PPh₃)₄ (24 mg, 0.021 mmol) in 6 mL of toluene at 75 °C. Flash chromatography on silica (hexanes/ethyl acetate 98/2) gave 21 (153 mg, 0.352 mmol, 88%) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 0.79 – 0.98 (m, 15H), 1.26 (m, 6H), 1.46 (m, 6H), 4.46 (d, J = 1.4 Hz, 2H), 4.81 (s, 2H), 6.32 (t, J= 1.1 Hz, $J_{\rm H,Sn}$ = 43.7 Hz, 1H), 7.04 (dd, J = 6.9 Hz, 1.5 Hz, 1H), 7.17–7.34 (m 2H), 7.48 (dd, J = 7.1 Hz, 2.1 Hz, 1H).¹³C NMR (75 MHz, CDCl₃): δ 11.0, 13.6, 27.2, 29.0, 68.8, 74.3, 124.3, 124.4, 125.1, 126.4, 127.9, 134.3, 135.7, 147.7. HRMS (FAB⁺) m/e: C₁₈H₂₇O¹²⁰Sn [M - Bu]⁺ calcd 379.1084; found 379.1101. $C_{18}H_{27}O^{118}Sn \ [M - Bu]^+$ calcd 377.1078; found 377.1083. C₁₈H₂₇O¹¹⁶Sn [M - Bu]⁺ calcd 375.1079, found 375.1083. Anal. Calcd for C22H36OSn (435.22): C, 60.71; H, 8.34. Found: C, 61.41; H, 8.38.

(E)-4-(Ethylcarboxymethyliden)isochroman 22. A solution of 1.6 M n-BuLi (0.1 mL, 0.16 mmol) was added to a solution of 21 (51 mg, 0.117 mmol) in 2 mL of absolute THF at - 78 °C under Ar. During the addition the solution turned deep blue and after 30 min at -78 °C became deep red. This red mixture was added to a solution of ethyl chloroformate in 1 mL of THF at -78 °C, and the color dissappeared immediately. The resulting yellow solution was allowed to warm to room temperature, before a solution of TBAF·H₂O (182 mg, 0.7 mmol) in 4 mL of an ether/water emulsion was added. The mixture was stirred for 8 h, before further ether and water was added and the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed twice with water and once with brine. After drying (Na₂SO₄) and evaporation of the organic solvent in vacuo, the crude product was purified by flash chromatography on silica (hexanes/ethyl acetate 9/1). Compound 22 was isolated as a yellow liquid (16 mg, 0.073 mmol, 62%). ¹H NMR (300 MHz, CDCl₃): δ 1.29 (t, J = 7.0 Hz, 3H), 4.23 (q, J = 7.1 Hz, 2H), 4.38 (d, J = 1.1 Hz, 2H), 4.83 (s, 2H), 5.81 (t, J = 1.1 Hz, 1H), 7.07 (dd, J = 7.4 Hz, 0.9 Hz, 1H), 7.19-7.38 (m, 2H), 7.99 (d, J = 7.6 Hz, 1H).¹³C NMR (75 MHz, CDCl₃): δ 14.1, 60.5, 68.8, 72.0, 115.0, 124.2, 126.3, 129.3, 129.4, 129.8, 136.6, 143.8, 166.6. HRMS (EI⁺) m/e: C₁₃H₁₄O₃ [M]⁺ calcd 218.0943; found 218.0957.

2,3-Bis(tributylstannyl)allyl-(2-iodophenyl)ether 24. According to the general procedure for distannations, **24** was obtained from 2-iodophenylpropargyl ether **23** (226 mg, 0.876 mmol), Bu₃SnH (1.0 mL, 3.8 mmol), and catalyst **6** (5 mg, 0.013 mmol) in 3 mL of toluene after flash chromatography (hexanes/ ethyl acetate/NEt₃ 98/1/1) as colorless liquid (386 mg, 0.46 mmol, 53%). ¹H NMR (300 MHz, CDCl₃): δ 0.79–1.10 (m, 30H), 1.31 (m, 12H), 1.48 (m, 12H), 4.71 (d, J = 1.3 Hz, 2H), 6.66 (dt, J = 7.5 Hz, 1.1 Hz, 1H), 6.75 (dd, J = 8.2 Hz, 1.3 Hz, 1H), 7.11 (s, $J_{H,Sn}$ = 167.4 Hz, 66.3 Hz, 1H), 7.22 (dt, J = 7.7 Hz, 1.5 Hz, 1H), 7.76 (dd, J = 7.9 Hz, 1.4 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 10.6, 10.7, 13.6, 27.4, 27.5, 29.1, 29.3, 80.1, 86.3, 112.7, 122.1, 129.1, 139.5, 144.4, 157.3, 161.2. ¹¹⁹Sn NMR (112 MHz, CDCl₃): δ -63.20, -54.93. Anal. Calcd for C₃₃H₆₁-IOSn₂ (838.13): C, 47.29; H, 7.34; I, 15.14. Found: C, 47.33; H, 7.28; I, 15.12.

(*E*)-3-Tributylstannylmethyliden-2*H*-benzo[*b*]furan 25. According to the preparation of **19** the stannylated furane **25** was obtained from **24** (99 mg, 0.118 mmol) in the presence of Pd(PPh₃)₄ (3 mg, 0.003 mmol) in 2 mL of toluene at 70 °C. Flash chromatography on silica (hexanes/ethyl acetate 98/2) gave **25** (39 mg, 0.093 mmol, 79%) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 0.84–0.96 (m, 15H), 1.35 (m, 6H), 1.61 (m, 6H), 5.36 (s, 2H), 6.32 (d, *J* = 1.1 Hz, *J*_{H,Sn} = 43.8 Hz, 1H), 6.90 (dt, *J* = 8.3 Hz, 1.7 Hz, 1H), 7.30 (dd, *J* = 7.4 Hz, 1.5 Hz, 1H), 7.22 (dt, *J* = 7.2 Hz, 1.6 Hz, 1H), 7.76 (dd, *J* = 7.1 Hz, 1.7 Hz, 1H).¹³C NMR (75 MHz, CDCl₃): δ 7.9, 13.6, 26.6, 29.1, 79.1, 111.3, 119.4, 124.0, 134.0, 138.1, 139.5, 141.3, 159.6. HRMS (CI⁺) *m/e*: C₂₁H₃₄O¹²⁰Sn [M]⁺ calcd 422.1626; found 420.1777. C₂₁H₃₄O¹¹⁶Sn [M]⁺ calcd 418.1627, found 418.1617.

3-Tributylstannylmethyl-2*H*,3*H*-benzo[*b*]furan 26 and 3-Methylen-2H-benzo[b]furan 27. According to the preparation of 19 the stannylated furanes 26 and 27 were obtained from 24 (125 mg, 0.149 mmol) in the presence of Pd(PPh₃)₄ (14 mg, 0.012 mmol) in 4 mL of toluene at 90 °C. Flash chromatography on silica (hexanes/ethyl acetate 99/1) gave 26 (29 mg, 0.069 mmol, 46%) and 27 (8 mg, 0.061 mmol, 41%) as colorless liquids. **Data for 26:** ¹H NMR (300 MHz, CDCl₃): δ 0.74–0.92 (m, 15H), 1.11 (dd, J = 13.3 Hz, 9.6 Hz, 1H), 1.29 (m, 6H), 1.35 (dd, J = 13.3 Hz, 4.5 Hz, 1H), 1.44 (m, 6H), 3.73 (m, 1H), 3.97 (dd, J = 8.6 Hz, 8.4 Hz, 1H), 4.66 (dd, J = 8.6Hz, 8.6 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 6.86 (t, J = 7.4 Hz, 1H), 7.13 (t, J = 7.4 Hz, 1H), 7.76 (d, J = 7.1 Hz, 1H).¹³C NMR (75 MHz, CDCl₃): δ 7.9, 9.4, 13.6, 27.4, 29.2, 40.3, 79.4, 111.3, 120.5, 123.7, 127.8, 141.3, 159.5. HRMS (FAB+) m/e: C₁₇H₂₇O¹²⁰-Sn $[M - Bu]^+$ calcd 367.1083; found 367.1096. $C_{17}H_{27}O^{118}Sn$ $[M - Bu]^+$ calcd 365.1078; found 365.1083. $C_{17}H_{27}O^{116}Sn$ [M - Bu]⁺ calcd 363.1079, found 363.1098. Anal. Calcd for C₂₁H₃₆-OSn (421.19): C, 59.60; H, 8.57. Found: C, 59.67; H, 8.54. **Data for 27:** ¹H NMR (300 MHz, CDCl₃): δ 4.99 (t, J = 2.7Hz, 1H), 5.10 (t, J = 3.0 Hz, 2H), 5.40 (t, J = 3.2 Hz, 1H), 6.86 (dd, J = 7.2 Hz, 1.0 Hz, 1H), 6.90 (dt, J = 7.4 Hz, 1.0 Hz, 1H),7.20 (dt, J = 8.0 Hz, 1.2 Hz, 1H), 7.41 (dd, J = 7.6 Hz, 1.3 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 74.9, 99.4, 110.6, 120.6, 120.9, 125.8, 130.4, 143.9, 163.8. HRMS (EI+) m/e: C₉H₈O [M]+ calcd 132.0575; found 132.0592.

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