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Molybdenum-Catalyzed α-Hydrostannations of Propargylamines as the Key Step in the Synthesis of N-Heterocycles

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Dedicated to the memory of Professor Peter Welzel

Keywords: Hydrostannation / Indoles / Molybdenum / Nitrogen heterocycles / Stille couplings / Stannanes

The Mo-catalyzed hydrostannation of propargylic amines and amides gave rise to functionalized vinylstannanes in good yield. The α-stannylated products were formed preferentially, which are interesting synthetic building blocks. If halogenated aromatic amines were subjected to this protocol, the products obtained could be converted into indole and isoquinoline derivatives through intramolecular Stille couplings.

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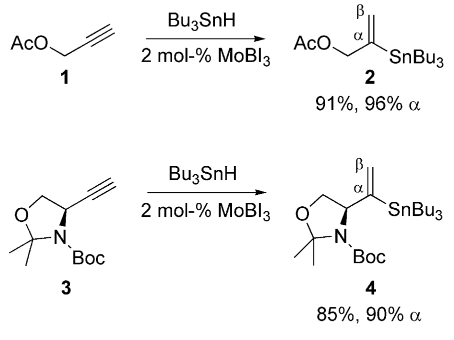
Introduction

Vinylstannanes are interesting building blocks in organic synthesis and are easily available, for example, through the hydrostannations of alkynes. In general, these hydrometallations can be carried out under radical or transition-metal-catalyzed conditions.[1] The major drawbacks of these methods result from difficulties in controlling the regioselectivity of the tin hydride addition to unsymmetrical alkynes, although the transition-metal-catalyzed version has the advantage of a clean *cis* addition, based on the reaction mechanism.[2] In the case of terminal alkynes, catalytic hydrometallations generally give rise to the terminal (*E*)-vinylmetal compounds, species which can also be obtained by stannylcupration.[3] Interestingly, the corresponding (*Z*) isomers can be obtained in the presence of Lewis acids, as reported by Yamamoto et al.,[4] or by a (*Z*)-selective hydrotelluration/transmetallation approach, according to Williams et al.[5] Hale et al. described the regioselective, radical hydrostannation of propargyl alcohol derivatives, which occurred preferentially at the α position. If internal alkynes were used, the (*Z*) isomers were formed preferentially.[6]

Recently, our group has developed a new catalyst based on Mo. $Mo(CO)_3(CNtBu)_3$ ($MoBI_3$) was found to be an excellent catalyst for the highly regio- and stereoselective hydrostannations of functionalized alkynes, such as propargylic esters **1**, to afford the α-stannylated products **2** preferentially.[7] The stannylated allylic esters are excellent building blocks, undergoing Pd-catalyzed allylic alkylations or Claisen rearrangements, and can be used for the synthesis of stannylated amino acids.[8] These can be further modified by a wide range of Stille couplings.[9] In general, the regioselectivity towards the α products increases with the electron-withdrawing properties of the substituents adjacent to the triple bond.

For example, propargylic esters are more reactive and selective than are propargylic ethers.[10] Therefore, other electron-withdrawing groups such as sulfones[11] or phosphonates[12] are also suitable substrates. Recently, we showed that propargylic amides **3** can also be subjected to Mo-catalyzed hydrostannations (Scheme 1). Probably because of the weaker electron-withdrawing properties of amines and amides, the regioselectivities were slightly worse with these substrates but were still in the preparatively useful range.[13]



Scheme 1. Regioselective Mo-catalyzed hydrostannations.

Results and Discussion

To evaluate the synthetic potential and the scope and limitations of this reaction, we investigated the hydrostan-

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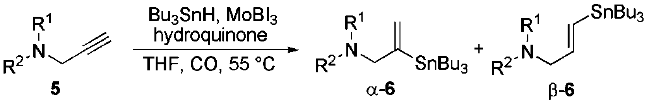
nations of several other propargylic amines and amides. The reactions were carried out in the presence of hydroquinone (to suppress radical hydrostannations) and under an CO (which prolongs the lifetime of the catalyst). The results are shown in Table 1. In contrast to the reaction of unprotected propargylamine (Table 1, Entry 1), which afforded the hydrostannation product in only 10% yield without significant α regioselectivity, the singly protected propargylamines gave rise to acceptable yields and moderate α regioselectivities (Table 1, Entries 2–5). The best α selectivity was obtained with the *N*-benzoylated propargylamine (Table 1, Entry 5). The significant improvement in yield obtained by switching from an unprotected to a monoprotected propargylamine forced us to investigate disubstituted amines, bearing various combinations of aryl/alkyl and acyl protecting groups (Table 1, Entries 6–10). Nearly independent of the substitution pattern, we obtained the hydrostannation products in good yields of 80–85% with α selectivities from 86–92% (Table 1, Entries 6–9). These results fit perfectly with those obtained previously in that electron-withdrawing groups increased not only the reactivity and yield but also the regioselectivity. Increasing the steric bulk of the substituent (replacing the NH by an *N*-alkyl or -aryl group) also contributed positively to the selectivity. A further increase of the electron-withdrawing properties (e.g. by introducing the phthaloyl protecting group) caused no further improvement (Table 1, Entry 10).[9d,10]

Table 1. Hydrostannation of various propargylamines **5**.

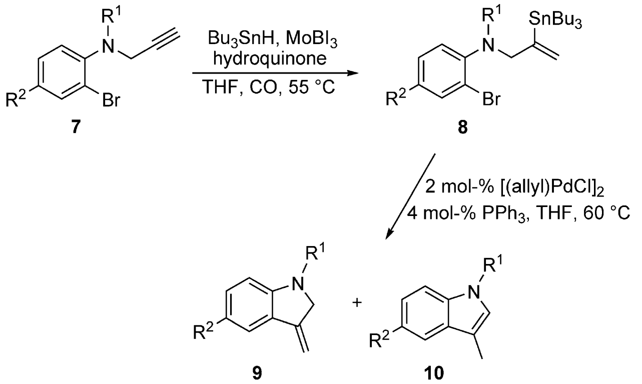


Entry	Amine	R^1	R^2	Product	Yield [%][a]	α-**6**/β-**6**
1	**5a**	H	H	**6a**	<10	60:40
2	**5b**	Boc	H	**6b**	74	78:22
3	**5c**	Bn	H	**6c**	65	65:35
4	**5d**	Ph	H	**6d**	75	79:21
5	**5e**	Bz	H	**6e**	69	84:16
6	**5f**	COOEt	Ph	**6f**	81	86:14
7	**5g**	Boc	Bn	**6g**	79	86:14
8	**5h**	Ac	Bn	**6h**	85	91:9
9	**5i**	Bz	Bn	**6i**	84	92:8
10	**5k**	Phth		**6k**	87	89:11

[a] Isolated yields of the α product.

Based on these good results obtained with the doubly protected propargylamines, we next focused on an application of this protocol towards the synthesis of N-heterocycles. In principle, if suitable precursors are used, the hydrostannation can be combined with an intramolecular Stille coupling.[14] Although the regioisomeric vinylstannanes can be separated easily by flash chromatography, such an approach has the great advantage that only the α-stannanes can undergo cyclization,[15] and therefore, a separation of the isomers is not absolutely necessary.

Substituted indoles should be accessible by such an approach with *o*-brominated aniline derivatives **7** (Scheme 2). The introduction of an electron-withdrawing bromine atom should also influence the yield and selectivity of vinylstannane **8** formation positively. Subsequent intramolecular Stille coupling should provide methylene-substituted indole derivative **9** first, which might isomerize to the heteroaromatic indole **10** under the reaction conditions used. The results of these investigations are summarized in Table 2.



Scheme 2. Synthesis of indoles by a hydrostannation/Stille coupling sequence.

The hydrostannation of a range of different protected propargylanilines proceeded in preparatively useful yields (60–72%) and with consistently good α selectivity (86 ± 1%). The only exception was the internal alkyne **7d** (Table 2, Entry 4) which gave only a marginal yield and moderate selectivity, even after a reaction time of 2 d. In this case also, we used 5 mol-% $MoBI_3$ (instead of the 2 mol-% used generally). Obviously, these substituted propargylamines were unsuitable substrates.

With these stannanes **8** in hand, we next focused on the intramolecular Stille couplings. The reaction of **8a** gave rise to the cyclization product **9a** in 84% yield (Table 2, Entry 1), whereas under the same reaction conditions, **8b** afforded the corresponding product **9b**, accompanied by 6% of the double-bond-migration product **10b** (Table 2, Entry 2). We observed the same results with the second acetylamide **8c**. We chose **8c** because the Stille coupling should easily differentiate between the two bromo substituents, and the brominated indole obtained should be a good candidate for further modifications by several types of cross couplings. This substrate showed an even higher isomerization tendency, and the two isomeric products **9c** and **10c** formed as an approximately 2:1 mixture. Because the isomerization occurs after the cyclization, we prolonged the reaction time for the Stille coupling to 20 h and were able to obtain nearly complete double-bond migration and indole **10c** in high yield. We note that **9a** did not undergo this isomerization. Even after 20 h, only traces of the corresponding indole **10a** formed. Obviously, the *N*-protecting group (and probably also the substitution pattern of the aromatic ring) had a significant influence on product formation. It seems that the more electron-withdrawing acyl group favored isomerization more than the carbamates did. Also, we observed no bond migration for substituted vinylstannane **8d** (Table 2, Entry 4), even after 48 h.

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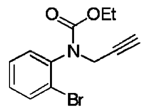
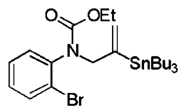
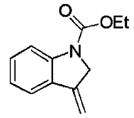
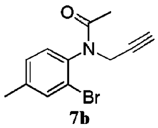
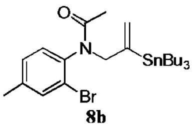
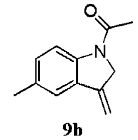
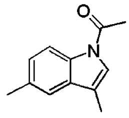
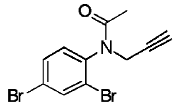
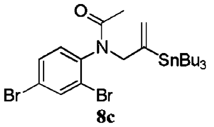
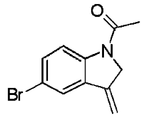
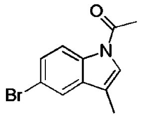
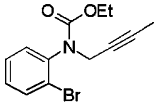
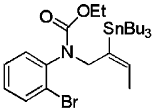
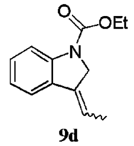
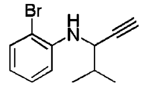
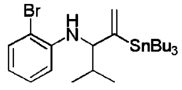
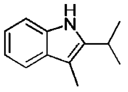
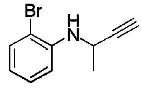
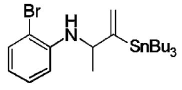
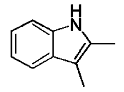
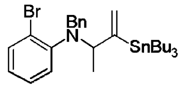
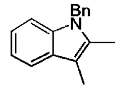
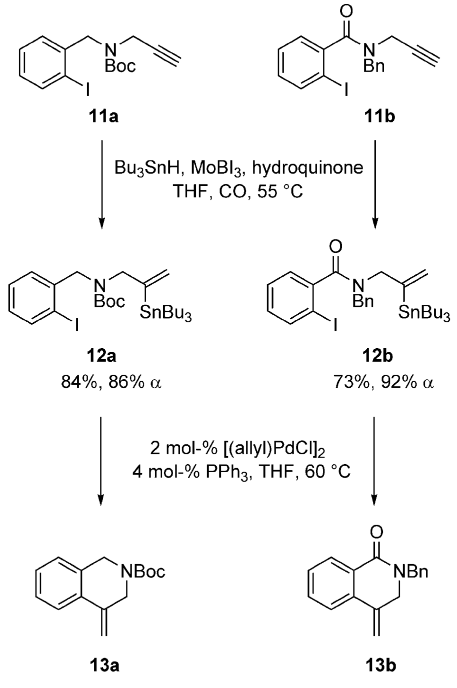
Table 2. Synthesis of indoles by a hydrostannation/Stille coupling sequence.

Entry	Substrate	Hydrostannation Product			Indole derivative			
	7	8	Yield [%][a]	α-8/β-8	9	Yield [%]	10	Yield [%]
1	 **7a**	 **8a**	65[b]	87:13	 **9a**	84[c]	**10a**	traces[e]
2	 **7b**	 **8b**	61[b]	85:15	 **9b**	86[d]	 **10b**	7
3	 **7c**	 **8c**	72[b]	87:13	 **9c**	56[c] 8[e]	 **10c**	26 82
4	 **7d**	 **8d**	12[f]	75:25	 **9d**	58[f]	–	–
5	 **7e**	 **8e**	65[b]	87:13	–	–	 **10e**	<10[f]
6	 **7f**	 **8f**	60[b]	86:14	–	–	 **10f**	<10[f]
7	–	 **8g**	–	–	–	–	 **10g**	65[f]

[a] Isolated yields of the α product. [b] Reaction time: 12 h. [c] Reaction time: 4 h. [d] Reaction time: 2 h. [e] Reaction time: 20 h. [f] Reaction time: 48 h.

As a different class of substrates, we also investigated the cyclization of the unprotected secondary amines **8e** and **8f** (Table 2, Entries 5 and 6). Whereas the hydrostannation gave comparable results to those of the acylated derivatives, the intramolecular Stille couplings nearly failed. We obtained less than 10% of the cyclization product (exclusively the indoles **10**), even after prolonged reaction times. The substituent at the allyl position did not seem to have a strong influence, and the free NH is probably responsible for this breakdown in the yield. To validate this hypothesis, we also submitted the *N*-benzylated derivative **8g** (obtained by the benzylation of **8f**) to our reaction conditions. And indeed, we obtained indole derivative **10g** in 65% yield.

To determine if this synthetic protocol can also be applied to the synthesis of the ring-enlarged isoquinoline derivatives, we investigated the reactions of *N*-(*o*-iodobenzyl)-*N*-propargyl amide **11a** and the *o*-iodobenzoylated amine **11b** (Scheme 3). Both alkynes gave the corresponding hydrostannation products **12** in good yield and α selectivity. The subsequent Stille coupling proceeded slower and in slightly lower yield than did the analogous 5-membered rings, but were still in a preparatively useful range. Interestingly, we observed no isomerization of **13** in these cases, even after 2 d.



Scheme 3. Synthesis of isoquinoline derivatives by a hydrostannation/Stille coupling sequence.

Conclusions

We showed that doubly protected propargylamines are good substrates for Mo-catalyzed hydrostannations. If *o*-halogenated aromatic derivatives are used, the α-stannylated allylic amines or amides can undergo an intramolecular Stille cyclization, giving rise to 5- or 6-membered heterocycles. Further applications of this protocol are currently under investigation.

Experimental Section

General Remarks: All reactions were carried out in oven-dried glassware (100 °C). All solvents were dried before use. THF was freshly distilled from sodium/benzophenone. The products were purified by flash chromatography on silica gel. Mixtures of EtOAc and hexane or diethyl ether and hexane were generally used as the eluents. TLC: commercially precoated Polygram® SIL-G/UV 254 plates. Visualization was accomplished with UV light and $KMnO_4$ solution. Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ with a Bruker DRX 400 NMR spectrometer. Selected signals in the NMR spectra for the minor isomers were extracted from the spectra of the isomeric mixture. CI-MS analyses were performed with a Finnigan MAT 95. Elemental analyses were carried out at the Department of Chemistry, Saarland University.

General Procedures for Hydrostannations with $MoBI_3$: The corresponding alkyne (2.0 mmol), hydroquinone (11.2 mg, 0.1 mmol) and $MoBI_3$ (17.2 mg, 0.04 mmol, 2 mol-%) were dissolved in THF (1.6 mL) in a Schlenk tube under CO. The mixture was warmed to 60 °C, and Bu_3SnH (1.1 mL, 4 mmol) was added slowly. After the mixture had been stirred at this temperature overnight and cooled to room temperature, the reaction mixture was subjected to flash chromatography. Excess Bu_3SnH was removed with hexane as the eluent. Changing the eluent to diethyl ether/hexane (1:100, v/v) allowed for the separation of the regioisomeric vinylstannanes to provide the required α products in pure form.

***tert*-Butyl *N*-[2-(tributylstannyl)allyl]carbamate (α-6b):** According to the general procedure for hydrostannations, α-**6b** (646 mg, 1.48 mmol, 74%) was obtained from **5b** (350 mg, 2.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.2 Hz, 9 H), 0.93 (m, 6 H), 1.31 (m, 6 H), 1.44 (s, 9 H), 1.48 (m, 6 H), 3.89 (s, 2 H), 4.55 (s, 1 H), 5.21 (dd, J = 2.0, 1.2, $J_{Sn,H}$ = 59.5 Hz, 1 H), 5.79 (dd, J = 2.0, 1.6, $J_{Sn,H}$ = 127.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.3, 13.6, 27.3, 28.4, 29.0, 49.2, 79.1, 124.8, 151.6, 155.5 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –44.1 ppm. HRMS: calcd. for $C_{20}H_{41}NO_2Sn$ $[M - C_4H_9]^+$ 390.1455; found 390.1484.

(Benzyl)[2-(tributylstannyl)allyl]amine (α-6c): According to the general procedure for hydrostannations, α-**6c** (851 mg, 1.95 mmol, 65%) was obtained from **5c** (436 mg, 3.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.2 Hz, 9 H), 0.94 (m, 6 H), 1.34 (m, 6 H), 1.52 (m, 6 H), 3.44 (dd, J = 1.6, 1.6, $J_{Sn,H}$ = 39.6 Hz, 2 H), 3.78 (s, 2 H), 5.25 (dd, J = 2.0, 1.6, $J_{Sn,H}$ = 68.8 Hz, 1 H), 5.87 (dd, J = 1.6, 1.6, $J_{Sn,H}$ = 136.3 Hz, 1 H), 7.26 (m, 1 H), 7.31–7.36 (m, 4 H) ppm; NH signal not found. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 13.7, 27.4, 29.2, 53.5, 58.8, 124.5, 126.7, 128.1, 128.2, 140.7, 154.9 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –47.3 ppm. HRMS: calcd. for $C_{22}H_{39}NSn$ $[M]^+$ 437.2105; found 437.2123.

***N*-[2-(Tributylstannyl)allyl]aniline (α-6d):** According to the general procedure for hydrostannations, α-**6d** (953 mg, 2.26 mmol, 75%) was obtained from **5d** (363 mg, 3.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.8 Hz, 9 H), 0.94 (m, 6 H), 1.33 (m, 6 H), 1.52 (m, 6 H), 3.79 (s, 1 H), 3.95 (s, $J_{Sn,H}$ = 32.0 Hz, 2 H), 5.32 (dd, J = 1.6, 1.2, $J_{Sn,H}$ = 61.1 Hz, 1 H), 5.98 (dd, J = 2.0, 1.6, $J_{Sn,H}$ = 131.2 Hz, 1 H), 6.62 (dd, J = 8.4, 1.2 Hz, 2 H), 6.72 (td, J = 7.2, 1.2 Hz, 1 H), 7.18 (dd, J = 8.8 7.2, Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.5, 13.7, 27.4, 29.2, 53.1, 113.0, 117.3, 125.3, 129.1, 148.3, 153.0 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –44.9 ppm. HRMS: calcd. for $C_{21}H_{37}NSn$ $[M - C_4H_{10}]^+$ 365.1165; found 365.1160.

***N*-[2-(Tributylstannyl)allyl]benzamide (α-6e):** According to the general procedure for hydrostannations, α-**6e** (543 mg, 1.38 mmol, 69%) was obtained from **5e** (318 mg, 2.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.2 Hz, 9 H), 0.93 (m, 6 H), 1.28 (m, 6 H), 1.47 (m, 6 H), 4.22 (d, J = 1.2, $J_{Sn,H}$ = 30.7 Hz, 2 H), 5.29 (d, J = 1.2, $J_{Sn,H}$ = 58.7 Hz, 1 H), 5.88 (d, J = 1.2, $J_{Sn,H}$ = 125.2 Hz, 1 H), 6.29 (s, 1 H), 7.40 (dt, J = 1.2, 7.2 Hz, 2 H), 7.47 (tt, J = 7.2, 1.2 Hz, 1 H), 7.78 (dt, J = 7.2, 1.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4, 13.6, 27.3, 29.0, 48.3, 125.6, 126.8, 128.4, 131.3, 134.5, 150.6, 166.7 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –42.6 ppm. HRMS: calcd. for $C_{22}H_{37}NOSn$ $[M - C_4H_9]^+$ 394.1193; found 394.1213.

Ethyl *N*-[2-(Tributylstannyl)allyl]phenylcarbamate (α-6f): According to the general procedure for hydrostannations, α-**6f** (794 mg, 1.61 mmol, 81%) was obtained from **5f** (406 mg, 2.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.6 Hz, 9 H), 0.95 (m, 6 H), 1.25 (t, J = 7.2 Hz, 3 H), 1.33 (m, 6 H), 1.49 (m, 6 H), 4.65 (q, J = 7.2 Hz, 2 H), 4.65 (dd, J = 1.6, 1.6, $J_{Sn,H}$ = 23.2 Hz, 2 H), 5.31 (dd, J = 1.6, 1.6, $J_{Sn,H}$ = 61.2 Hz, 1 H), 5.81 (dd, J = 2.4, 2.0, $J_{Sn,H}$ = 127.0 Hz, 1 H), 7.17 (m, 1 H), 7.24–7.35 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.3, 13.6, 14.5, 27.3, 29.0, 58.4, 61.6, 124.4, 125.5, 125.6, 128.4, 142.7, 149.4, 155.4 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –43.1 ppm. HRMS: calcd. for $C_{24}H_{41}NO_2Sn$ $[M]^+$ 495.2159; found 495.2174.

***tert*-Butyl *N*-benzyl-*N*-[2-(tributylstannyl)allyl]carbamate (α-6g):** According to the general procedure for hydrostannations, α-**6g** (848 mg, 1.58 mmol, 79%) was obtained from **5g** (491 mg, 2.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.2 Hz, 9 H), 0.93 (m, 6 H), 1.33 (m, 6 H), 1.48 (s, 9 H), 1.49 (m, 6 H), 3.92 (m, 1 H), 4.03 (m, 1 H), 4.34 (m, 1 H), 4.42 (m, 1 H), 5.33 (s, $J_{Sn,H}$ = 59.8 Hz, 1 H), 5.73 (s, $J_{Sn,H}$ = 127.1 Hz, 1 H), 7.17–7.29 (m, 3 H), 7.30–7.36 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.2, 16.7, 27.4, 28.4, 29.1, 48.8, 53.8, 79.7, 124.1, 127.1, 127.9, 128.4, 138.3, 149.2, 150.3 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –44.3 ppm. HRMS calcd. for $C_{27}H_{47}NO_2Sn$ $[M - C_4H_9]^+$ 480.1925; found 480.1924.

***N*-Benzyl-*N*-[2-(tributylstannyl)allyl]acetamide (α-6h):** According to the general procedure for the hydrostannations, α-**6h** (889 mg, 1.86 mmol, 85%) was obtained from **5h** (375 mg, 2.0 mmol) as a colorless oil. Mixture of rotamers: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 9 H), 0.93 (m, 6 H), 1.31 (m, 6 H), 1.48 (m, 6 H), 2.10 (s, 2 H), 2.16 (s, 1 H), 3.95 (dd, J = 2.4, 1.6, $J_{Sn,H}$ = 13.5 Hz, 1.33 H), 4.18 (s, $J_{Sn,H}$ = 31.4 Hz, 0.67 H), 4.45 (s, 0.67 H), 4.57 (s, 1.33 H), 5.33 (dd, J = 1.6, 1.6, $J_{Sn,H}$ = 58.8 Hz, 0.33 H), 5.35 (dd, J = 2.4, 1.6, $J_{Sn,H}$ = 60.4 Hz, 0.67 H), 5.68 (dd, J = 2.0, 1.6, 1 H, $J_{Sn,H}$ = 126.5 Hz, 0.33 H), 5.76 (dd, J = 2.0, 2.0, $J_{Sn,H}$ = 125.4 Hz, 0.67 H), 7.17 (d, J = 7.2 Hz, 0.67 H), 7.21–7.40 (m, 4.33 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.3, 13.6, 21.2, 27.2, 29.0, 48.4, 54.8, 123.5, 127.3, 128.3, 128.5, 137.8, 147.6, 171.2 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –42.2 ppm. Selected signals of the minor rotamer: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4, 13.7, 21.5, 27.3, 29.0, 50.4, 52.9, 126.3, 126.4, 127.5, 128.9, 136.7, 141.9, 170.5 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –42.7 ppm. HRMS: calcd. for $C_{24}H_{41}NOSn$ $[M]^+$ 479.2210; found 479.2202.

_N_-Benzyl-_N_-[2-(tributylstannyl)allyl]benzamide (α-6i): According to the general procedure for hydrostannations, **α-6i** (909 mg, 1.68 mmol, 84%) was obtained from **5i** (500 mg, 2.0 mmol) as a colorless oil. Mixture of rotamers: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77–1.03 (m, 15 H), 1.23 (m, 6 H), 1.35 (m, 6 H), 3.94 (s, 1.4 H), 4.29 (s, 0.6 H), 4.50 (s, 0.6 H), 4.79 (s, 1.4 H), 5.04 (s, $J_{Sn,H}$ = 54.0 Hz, 0.3 H), 5.47 (s, $J_{Sn,H}$ = 60.2 Hz, 0.7 H), 5.78 (s, $J_{Sn,H}$ = 110.0 Hz, 0.3 H), 5.99 (s, $J_{Sn,H}$ = 124.0 Hz, 0.7 H), 7.15 (d, J = 6.8 Hz, 0.7 H), 7.23–7.45 (m, 7.3 H), 7.50 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.1, 13.5, 27.1, 28.9, 47.6, 55.0, 124.2, 126.3, 127.3, 128.0, 128.3, 128.5, 129.5, 136.1, 137.4, 148.8, 172.2 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –41.7 ppm. Selected signals of the minor rotamer: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4, 13.6, 27.3, 29.0, 51.3, 51.5, 126.1, 126.7, 126.8, 128.0, 128.3, 128.7, 129.4, 136.3, 136.7, 148.1, 171.7 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –42.1 ppm. HRMS: calcd. for $C_{29}H_{43}NOSn$ $[M - C_4H_9]^+$ 484.1662; found 484.1682.

Ethyl _N_-(2-Bromophenyl)-_N_-[2-(tributylstannyl)allyl]carbamate (8a): According to the general procedure for hydrostannations, **8a** (745 mg, 1.30 mmol, 65%) was obtained from **7a** (318 mg, 2.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.2 Hz, 9 H), 0.94 (m, 6 H), 1.45 (t, J = 7.2 Hz, 3 H), 1.29 (m, 6 H), 1.47 (m, 6 H), 3.65 (m, 1 H), 4.23 (m, 2 H), 4.93 (m, 1 H), 5.30 (d, J = 1.2, $J_{Sn,H}$ = 60.1 Hz, 1 H), 5.75 (s, $J_{Sn,H}$ = 111.0 Hz, 1 H), 7.10–7.21 (m, 2 H), 7.26 (dd, J = 7.6, 7.2 Hz, 1 H), 7.62 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.5, 13.7, 14.6, 27.3, 29.1, 58.0, 61.8, 123.6, 126.6, 127.7, 128.6, 130.8, 133.2, 141.0, 149.1, 155.3 ppm. HRMS: calcd. for $C_{24}H_{40}BrNO_2Sn$ $[M - C_4H_{10}]^+$ 515.0482; found 515.0452.

_N_-(2-Bromo-4-methylphenyl)-_N_-[2-(tributylstannyl)allyl]acetamide (8b): According to the general procedure for hydrostannations, **8b** (1.02 g, 1.83 mmol, 61%) was obtained from **7b** (796 mg, 3.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.2 Hz, 9 H), 0.94 (m, 6 H), 1.30 (m, 6 H), 1.47 (m, 6 H), 1.81 (s, 3 H), 2.37 (s, 3 H), 3.46 (d, J = 15.6, $J_{Sn,H}$ = 46.8 Hz, 1 H), 5.19 (ddd, J = 15.2, 2.0, 1.2, $J_{Sn,H}$ = 17.2 Hz, 1 H), 5.31 (dd, J = 1.2, 1.2, $J_{Sn,H}$ = 60.1 Hz, 1 H), 5.67 (dd, J = 1.2, 1.2, $J_{Sn,H}$ = 127.4 Hz, 1 H), 7.06 (d, J = 8.4 Hz, 1 H), 7.12 (dd, J = 8.0, 1.6 Hz, 1 H), 7.51 (d, J = 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6, 13.6, 20.7, 22.2, 27.3, 29.0, 56.4, 123.2, 127.2, 128.9, 130.8, 134.1, 139.3, 139.9, 148.5, 170.1 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –42.3 ppm. HRMS: calcd. for $C_{24}H_{40}BrNOSn$ $[M - C_4H_9]^+$ 500.0611; found 500.0511.

_N_-(2,4-Dibromophenyl)-_N_-[2-(tributylstannyl)allyl]acetamide (8c): According to the general procedure for hydrostannations, **8c** (1.11 g, 1.78 mmol, 72%) was obtained from **7c** (820 mg, 2.477 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.2 Hz, 9 H), 0.94 (m, 6 H), 1.30 (m, 6 H), 1.47 (m, 6 H), 1.82 (s, 3 H), 3.44 (d, J = 15.2, $J_{Sn,H}$ = 46.8 Hz, 1 H), 5.19 (ddd, J = 15.2, 2.0 1.6,, $J_{Sn,H}$ = 16.7 Hz, 1 H), 5.32 (dd, J = 1.6, 1.2, $J_{Sn,H}$ = 58.0 Hz, 1 H), 5.65 (dd, J = 1.2, 1.2, $J_{Sn,H}$ = 121.7 Hz, 1 H), 7.06 (d, J = 8.8 Hz, 1 H), 7.46 (dd, J = 8.4, 2.4 Hz, 1 H), 7.86 (d, J = 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 13.7, 22.3, 27.3, 29.1, 56.3, 122.5, 124.7, 127.6, 131.5, 132.3, 136.3, 141.1, 148.3, 169.5 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –41.7 ppm. HRMS: calcd. for $C_{23}H_{37}BrNOSn$ $[M - C_4H_9]^+$ 563.9560; found 563.9520.

Ethyl _N_-(2-Bromophenyl)-_N_-[(2_E_)-2-(tributylstannyl)-2-butenyl]carbamate (8d): According to the general procedure for hydrostannations, **8d** (117 mg, 0.20 mmol, 12%) was obtained from **7d** (500 mg, 1.69 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.6 Hz, 9 H), 0.92 (m, 6 H), 1.15 (t, J = 6.8 Hz, 3 H), 1.26 (d, J = 6.8, $J_{Sn,H}$ = 16.5 Hz, 3 H), 1.33 (m, 6 H), 1.48 (m, 6 H), 3.96–4.27 (m, 3 H), 4.75 (m, 1 H), 5.79 (q, J = 6.4, $J_{Sn,H}$ = 70.0 Hz, 1 H), 7.07 (d, J = 7.6 Hz, 1 H), 7.15 (ddd, J = 8.0, 7.2, 2.0 Hz, 1 H), 7.25 (ddd, J = 7.6, 7.2, 1.6 Hz, 1 H), 7.61 (dd, J = 8.0, 1.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6, 13.7, 14.1, 14.7, 27.5, 29.2, 48.5, 61.7, 123.9, 127.5, 128.7, 131.7, 133.1, 138.7, 140.0, 140.3, 155.3 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –38.7 ppm. HRMS: calcd. for $C_{25}H_{42}BrNO_2Sn$ $[M - C_4H_{10}]^+$ 529.0638; found 529.0640.

_o_-Bromo-_N_-[2-(tributylstannyl)-4-methylpent-1-en-3-yl]aniline (8e): According to the general procedure for hydrostannations, **8e** (973 mg, 1.79 mmol, 65%) was obtained from **7e** (756 mg, 3.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.6 Hz, 9 H), 0.89 (m, 6 H), 1.0 (d, J = 6.4 Hz, 3 H), 1.06 (d, J = 6.8 Hz, 3 H), 1.27 (m, 6 H), 1.42 (m, 6 H), 1.79 (m, 1 H), 3.59 (dd, J = 6.8, 6.4, $J_{Sn,H}$ = 54.9 Hz, 1 H), 4.53 (d, J = 6.0 Hz, 1 H), 5.38 (dd, J = 0.8, 1.2, $J_{Sn,H}$ = 62.1 Hz, 1 H), 5.88 (dd, J = 0.8, 1.2, $J_{Sn,H}$ = 133.2 Hz, 1 H), 6.52 (ddd, J = 8.0, 7.6, 1.2 Hz, 1 H), 6.58 (dd, J = 8.4, 1.2 Hz, 1 H), 7.10 (ddd, J = 8.4, 7.6, 1.2 Hz, 1 H), 7.40 (dd, J = 8.0, 1.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.1, 13.6, 18.7, 20.6, 27.4, 29.0, 32.4, 69.3, 109.7, 112.3, 117.1, 126.6, 128.1, 132.1, 144.6, 157.1 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –47.1 ppm. HRMS: calcd. for $C_{24}H_{42}BrNSn$ $[M - C_4H_9]^+$ 486.0818; found 486.0776.

_o_-Bromo-_N_-[2-(tributylstannyl)but-1-en-3-yl]aniline (8f): According to the general procedure for hydrostannations, **8f** (1.39 g, 2.69 mmol, 60%) was obtained from **7f** (600mg, 4.14 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.2 Hz, 9 H), 0.91 (m, 6 H), 1.27 (m, 6 H), 1.36 (d, J = 6.8 Hz, 3 H), 1.42 (m, 6 H), 4.08 (m, 1 H), 4.36 (d, J = 5.6 Hz, 1 H), 5.29 (s, $J_{Sn,H}$ = 62.3 Hz, 1 H), 5.96 (s, $J_{Sn,H}$ = 131.0 Hz, 1 H), 6.54 (ddd, J = 8.4, 7.2, 1.6 Hz, 1 H), 6.63 (dd, J = 8.4, 1.2 Hz, 1 H), 7.11 (ddd, J = 8.4, 7.2, 1.2 Hz, 1 H), 7.41 (dd, J = 8.0, 1.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.0, 13.6, 22.9, 27.4, 29.0, 57.9, 109.6, 112.6, 117.5, 124.6, 128.1, 132.2, 144.3, 160.0 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –46.7 ppm. HRMS: calcd. for $C_{22}H_{38}BrNSn$ $[M - C_4H_9]^+$ 458.0505; found 458.0466.

_o_-Bromo-_N_-benzyl-_N_-[2-(tributylstannyl)but-1-en-3-yl]aniline (8g): Compound **8f** (515 mg, 1.0 mmol) was dissolved in DMF (3 mL) in a Schlenk tube under N_2. The mixture was cooled to 0 °C before NaH (60 mg, 1.5 mmol, 60% in oil) was added. After the mixture had been stirred at 0 °C for 30 min, benzyl bromide (178 µL, 1.5 mmol) was added. The mixture was stirred at the same temperature for another 6 h before the reaction was quenched with saturated aq. NH_4Cl (5 mL). The product was extracted with diethyl ether (3 × 20 mL), and the combined organic layers were washed with brine (2 × 10 mL) and dried ($NaSO_4$), and the solvent was evaporated. The crude product was purified by flash chromatography (silica gel; diethyl ether/hexane, 1:50) to give **8g** (356 mg, 0.588 mmol, 59%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.2 Hz, 9 H), 0.99 (m, 6 H), 1.17 (d, J = 6.8 Hz, 3 H), 1.35 (m, 6 H), 1.52 (m, 6 H), 4.12 (q, J = 6.8, $J_{Sn,H}$ = 41.1 Hz, 1 H), 4.24 (d, J = 15.2 Hz, 1 H), 4.28 (d, J = 14.8 Hz, 1 H), 5.40 (s, $J_{Sn,H}$ = 63.4 Hz, 1 H), 6.21 (s, $J_{Sn,H}$ = 135.2 Hz, 1 H), 6.86 (ddd, J = 7.2, 6.4, 2.0 Hz, 1 H), 6.88 (dd, J = 7.2, 1.2 Hz, 1 H), 7.07 (ddd, J = 8.0, 6.8, 1.2 Hz, 1 H), 7.10–7.22 (m, 5 H), 7.55 (dd, J = 8.0, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.3, 13.7, 19.2, 27.4, 29.1, 52.5, 65.1, 122.9, 124.8, 126.1, 126.6, 126.9, 127.1, 127.7, 128.9, 133.7, 137.9, 147.6, 157.2 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –43.6 ppm. HRMS: calcd. for $C_{29}H_{44}BrNSn$ $[M - H]^+$ 604.1601; found 604.1596.

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General Procedures for the Intramolecular Stille Couplings: The corresponding vinylstannane (0.5 mmol) was dissolved in dry THF (2 mL) in a Schlenk tube under N_2. A solution of allylpalladium chloride dimer (3.7 mg, 0.01 mmol) and PPh_3 (5.3 mg, 0.02 mmol) in THF (2 mL) was added, and the mixture was warmed to 60 °C overnight. After removal of the solvent, the residue was dissolved in ethyl acetate (2 mL), saturated aq. KF (2 mL) was added, and the emulsion was stirred overnight. The mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic phases were washed with water (2 × 10 mL) and dried ($NaSO_4$), and the solvent was evaporated. The crude product was purified by flash chromatography (silica gel; ethyl acetate/hexane, 1: 20).

***N*-(Ethoxycarbonyl)-3-methyleneindoline (9a):** According to the general procedure for the Stille coupling, **9a** (85 mg, 0.42 mmol, 84%) was obtained from **8a** (287 mg, 0.5 mmol) as colorless crystals, m.p. 41–43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (m, 3 H), 4.30 (m, 2 H), 4.63 (s, 2 H), 5.07 (s, 1 H), 5.48 (dd, J = 3.2, 2.0 Hz, 1 H), 7.00 (ddd, J = 8.0, 7.6, 0.8 Hz, 1 H), 7.27 (dd, J = 7.6, 7.0 Hz, 1 H), 7.45 (d, J = 7.6 Hz, 1 H), 7.58 (m, 0.3 H), 7.97 (m, 0.7 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6, 53.1, 61.4, 101.4, 115.4, 120.3, 122.6, 128.9, 129.9, 141.2, 145.2, 152.4 ppm. HRMS: calcd. for $C_{12}H_{13}NO_2$ $[M]^+$ 203.0946; found 203.0974.

***N*-Acetyl-5-methyl-3-methyleneindoline (9b):** According to the general procedure for the Stille coupling, **9b** (81 mg, 0.43 mmol, 86%) was obtained from **8b** (279 mg, 0.5 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3 H), 2.34 (s, 3 H), 4.66 (dd, J = 3.2, 2.4 Hz, 2 H), 5.04 (dd, J = 2.8, 2.4 Hz, 1 H) 5.48 (dd, J = 3.2, 2.8 Hz, 1 H), 7.09 (d, J = 7.2 Hz, 1 H), 7.26 (s, 1 H), 8.17 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1, 24.0, 54.5, 101.3, 117.3, 120.5, 129.4, 130.8, 133.3, 140.6, 143.2, 167.7 ppm. HRMS: calcd. for $C_{12}H_{13}NO$ $[M]^+$ 187.0997; found 187.0986.

***N*-Acetyl-3,5-dimethylindole (10b):** According to the general procedure for the Stille coupling, **10b** (7 mg, 0.037 mmol, 7%) was obtained from **8b** (279 mg, 0.5 mmol) as a side product and a white solid, m.p. 64–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 2.48 (s, 3 H), 2.59 (s, 3 H), 7.16 (s, 1 H), 7.18 (dd, J = 8.4, 1.2 Hz, 1 H), 7.29 (dd, J = 0.8, 0.8 Hz, 1 H), 8.27 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 21.4, 23.8, 116.2, 118.1, 118.8, 122.2, 126.3, 131.6, 132.9, 134.0, 168.0 ppm. HRMS: calcd. for $C_{12}H_{13}NO$ $[M]^+$ 187.0997; found 187.0997.

***N*-Acetyl-5-bromo-3-methyleneindoline (9c):** According to the general procedure for the Stille coupling, **9c** (70 mg, 0.279 mmol, 56%) was obtained as the major product from **8c** (220 mg, 0.375 mmol) (reaction time: 4 h) as a white solid, m.p. 92–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3 H), 4.69 (dd, J = 2.8, 5.6 Hz, 2 H), 5.13 (t, J = 2.8 Hz, 1 H), 5.52 (t, J = 6.4 Hz, 1 H), 7.75 (dd, J = 8.8, 2.4 Hz, 1 H), 7.54 (d, J = 2.0 Hz, 1 H), 8.19 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9, 54.3, 103.2, 116.4, 118.8, 123.2, 131.4, 132.6, 139.2, 144.1, 168.0 ppm. HRMS: calcd. for $C_{11}H_{10}BrNO$ $[M]^+$ 250.9946; found 250.9859.

***N*-Acetyl-5-bromo-3-methylindole (10c):** According to the general procedure for the Stille coupling, **10c** (32 mg, 0.127 mmol, 26%) was obtained as the major product from **8c** (311 mg, 0.5 mmol) (reaction time: 20 h) as a white solid, m.p. 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 3 H), 2.55 (s, 3 H), 7.11 (s, 1 H), 7.40 (dd, J = 8.8, 2.0 Hz, 1 H), 7.57 (d, J = 2.0 Hz, 1 H), 8.25 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4, 23.7, 116.6, 117.7, 117.8, 121.5, 123.2, 127.7, 133.0, 134.3, 168.0 ppm. HRMS: calcd. for $C_{11}H_{10}BrNO$ $[M]^+$ 250.9946; found 250.9818.

***N*-(Ethoxycarbonyl)-3-ethylideneindoline (9d):** According to the general procedure for the Stille coupling, **9d** (58 mg, 0.214 mmol, 58%) was obtained from **8d** (220 mg, 0.375 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (m, 3 H), 1.78 (d, J = 7.0 Hz, 3 H), 4.30 (m, 2 H), 4.56 (s, 2 H), 5.96 (m, 1 H), 6.97 (dd, J = 7.5, 7.5 Hz, 1 H), 7.19 (m, 1 H), 7.36 (d, J = 7.5 Hz, 1 H), 7.55 (m, 0.4 H), 7.94 (m, 0.6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6, 17.7, 51.3, 61.4, 112.9, 115.2, 119.3, 122.6, 128.7, 129.6, 133.7, 144.3, 152.5 ppm. HRMS: calcd. for $C_{13}H_{15}NO_2$ $[M]^+$ 217.1103; found 217.1149.

***N*-Benzyl-2,3-dimethylindole (10g):** According to the general procedure for the Stille coupling, **10g** (64 mg, 0.276 mmol, 65%) was obtained from **8g** (256 mg, 0.423 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 2.32 (s, 3 H), 5.32 (s, 2 H), 7.00 (d, J = 7.2 Hz, 2 H), 7.08–7.16 (m, 2 H), 7.19–7.32 (m, 4 H), 7.56 (dd, J = 4.8, 4.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.9, 10.2, 46.5, 107.0, 108.8, 118.0, 118.8, 120.8, 126.0, 127.1, 128.6, 128.7, 132.4, 136.4, 138.3 ppm. HRMS: calcd. for $C_{17}H_{17}N$ $[M]^+$ 235.1361; found 235.1348.

***tert*-Butyl *N*-(*o*-iodobenzyl)-*N*-[2-(tributylstannyl)allyl]carbamate (12a):** According to the general procedure for hydrostannations, **12a** (793 mg, 1.20 mmol, 84%) was obtained from **11a** (527 mg, 1.42 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 9 H), 0.94 (m, 6 H), 1.33 (m, 6 H), 1.48 (s, 9 H), 1.51 (m, 6 H), 3.96 (m, 1 H), 4.07 (m, 1 H), 4.30 (m, 1 H), 4.44 (m, 1 H), 5.31 (m, 1 H), 5.72 (s, $J_{Sn,H}$ = 128.6 Hz, 1 H), 6.96 (dd, J = 7.2, 7.2 Hz, 1 H), 7.16 (m, 1 H), 7.33 (m, 1 H), 7.82 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.3, 13.7, 27.3, 28.3, 29.1, 54.2, 54.3, 79.9, 98.4, 126.6, 126.8, 128.2, 128.6, 139.4, 39.9, 149.9, 155.4 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –43.9 ppm. Selected signals of the minor rotamer: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 54.6, 100.0, 124.0, 127.6, 128.4, 148.7, 155.9 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –43.6 ppm. HRMS: calcd. for $C_{27}H_{46}INO_2Sn$ $[M - C_4H_9]^+$ 606.0891; found 606.0915.

***N*-Benzyl-*o*-iodo-*N*-[2-(tributylstannyl)allyl]benzamide (12b):** According to the general procedure for hydrostannations, **12b** (973 mg, 1.46 mmol, 73%) was obtained from **11b** (750 mg, 2.0 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, J = 7.2 Hz, 9 H), 0.88 (m, 6 H), 1.20 (m, 6 H), 1.29 (m, 6 H), 3.75 (s, 2 H), 4.04 (m, 1 H), 5.57 (m, 1 H), 5.39 (dd, J = 1.6, 2.0, $J_{Sn,H}$ = 61.1 Hz, 1 H), 5.92 (dd, J = 1.6, 2.0, $J_{Sn,H}$ = 125.3 Hz, 1 H), 7.03 (dd, J = 7.6, 6.8 Hz, 1 H), 7.22–7.40 (m, 6 H), 7.49 (dd, J = 1.6, 6.4 Hz, 1 H), 7.80 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.1, 13.6, 27.2, 28.9, 47.5, 54.1, 92.5, 123.8, 127.2, 127.6, 127.7, 128.4, 129.4, 130.1, 136.6, 139.1, 141.9, 147.8, 171.3 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –41.1 ppm. Selected signals of the minor rotamer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.69 (t, J = 7.2 Hz, 9 H), 1.46 (m, 6 H), 4.21 (m, 1 H), 4.30–4.48 (m, 3 H), 6.10 (dd, J = 2.4, 2.0, $J_{Sn,H}$ = 128.0 Hz, 1 H), 7.16 (dd, J = 6.8, 1.6 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.5, 13.7, 27.3, 29.1, 50.2, 51.6, 93.0, 125.1, 127.2, 128.0, 128.4, 128.6, 129.4, 130.2, 135.9, 139.7, 142.5, 147.1, 170.7 ppm. ^{119}Sn NMR (150 MHz, $CDCl_3$): δ = –42.1 ppm. HRMS: calcd. for $C_{29}H_{42}INOSn$ $[M + H]^+$ 668.1411; found 668.1378.

***N*-(*tert*-Butoxycarbonyl)-4-methylenetetrahydroisoquinoline (13a):** According to the general procedure for the Stille coupling, **13a** (57 mg, 0.232 mmol, 47%) was obtained from **12a** (332 mg, 0.50 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51 (s, 9 H), 4.42 (s, 2 H), 4.64 (s, 2 H), 5.12 (s, 1 H), 5.57 (s, 1 H), 7.14 (dd, J = 6.8, 1.6 Hz, 1 H), 7.20–7.29 (m, 2 H), 7.64 (dd, J = 6.8, 2.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.4, 46.1, 48.8, 80.0, 109.0, 124.2, 126.3, 126.7, 128,1, 132.7, 133.6, 138.2, 154.6 ppm. Selected signals of the minor rotamer: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.6, 47.6, 108.8 ppm. HRMS: calcd. for $C_{15}H_{19}NO_2$ $[M + H]^+$ 246.1494; found 246.1457.

***N*-Benzyl-3,4-dihydro-4-methyleneisoquinolin-1-one (13b):** According to the general procedure for the Stille coupling, **13b** (77 mg, 0.314 mmol, 63 %) was obtained from **12b** (333 mg, 0.5 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.14 (s, 2 H), 4.83 (s, 2 H), 5.15 (s, 1 H), 5.57 (s, 1 H), 7.29 (m, 1 H), 7.31–7.39 (m, 4 H), 7.41–7.59 (m, 3 H), 8.24 (dd, J = 7.6, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.2, 51.7, 112.2, 123.0, 127.4, 127.7, 128.0, 128.6, 128.7, 128.9, 132.0, 135.7, 136.5, 136.8, 163.4 ppm. HRMS: calcd. for $C_{17}H_{15}NO$ $[M]^+$ 249.1154; found 249.1136.

Supporting Information (see also the footnote on the first page of this article): NMR spectra of all new compounds.

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[15] Stille couplings of vinylstannanes generally proceed with retention of the olefin geometry. In the case of the (*E*)-β-stannylated products formed here, an intramolecular Stille coupling would give rise to a 6-membered ring with an (*E*) double bond.

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