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Diaryliodonium Salt-Based Synthesis of *N*-Alkoxyindolines and Further Insights into the Ishikawa Indole Synthesis

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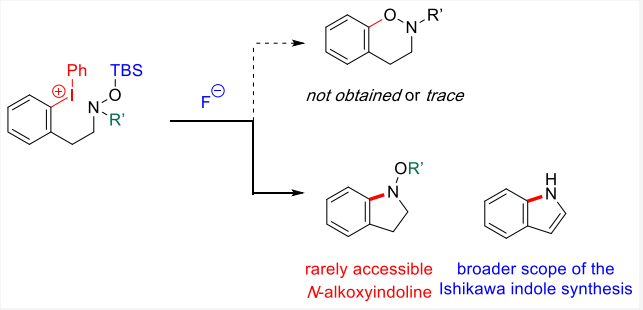
ABSTRACT: A diaryliodonium salt-based strategy enabled the first systematic synthesis of rarely accessible *N*-alkoxyindolines. Mechanistic analyses suggested that the reaction likely involves reductive elimination of iodobenzene from iodaoxazepine via a four-membered transition state, followed by Meisenheimer rearrangement. Substrates with *N*-carbamate protection afforded indole in a manner similar to that of the Ishikawa indole synthesis. Preinstallation of a stannyl group as an iodonium salt precursor greatly expanded the substrate scope, and further mechanistic insights are discussed.



INTRODUCTION

Diaryliodonium salts have emerged as precursors for new bond formation strategies due to their high reactivity, sufficient stability, and low toxicity.[1−10] Various reactions are enabled by metal catalysts,[11−13] whereas diaryliodonium salts are useful for metal-free carbon−heteroatom bond formation, offering an attractive metal-free alternative to the Buchwald−Hartwig reaction.[14] A variety of reactions using the iodonium salt have been developed for *O*-arylation with aliphatic alcohols,[15−19] carboxylic acids,[20−23] and phenols,[16,23−26] as well as *N*-arylation with amines,[27−29] amides,[30−33] anilines,[20,26,34,35] and heteroaromatics.[36−40]

Intramolecular aryl−heteroatom bond formation is particularly practical and enables efficient construction of bicyclic heterocycles. Chemoselectivity is often a problem with asymmetric diaryliodonium salts[41] but can be minimized due to the strong tendency to give the cyclic product over its linear counterpart. The Chi group reported the metal-free intramolecular *N*-arylation of diaryliodonium salts (Scheme 1A).[42] Copper-mediated intramolecular C−O bond formation from the diaryliodonium salt generated in situ was achieved by the Zakarian group (Scheme 1B).[43] Very recently, Ishikawa and co-workers reported an elegant indole synthesis using boron-masked *N*-hydroxyamides utilizing the diaryliodonium salt generated in situ (Scheme 1C).[44] Although the substrate scope of this strategy is limited to electron-rich aromatic derivatives, this efficient one-pot procedure afforded indoles in good yield.

In this context, we initially intended to synthesize benzoxazine via diaryliodonium salt-based C−O bond formation (Scheme 1D). However, treatment of diaryliodonium salts with a fluorine source resulted in the synthesis of *N*-alkoxyindolines, which are rarely synthesized hydrogenated congeners of *N*-alkoxyindoles, via C−N bond formation. Further examination of this strategy revealed that indoles could be obtained by changing the substituent on the nitrogen atom, vastly expanding the utility of the Ishikawa indole synthesis. We describe the details of these findings below.

RESULTS AND DISCUSSION

The substrate was prepared as shown in Scheme 2. Commercially available 2-(2-bromophenyl)ethyl alcohol (**1**) was converted to stannane **2a** and condensed with a hydroxylamine derivative[45,46] by the Mitsunobu reaction to afford **3a** after the removal of the Ns group.[47] The resulting amine was benzylated, and **4a** was subsequently treated with the Koser reagent[48] to afford iodonium salt **5a** as the sole product.[49] Other substrates were similarly synthesized, although the corresponding iodonium salts are unstable upon storage even in a freezer and should be used immediately for the next reaction.

With the substrate in hand, **5a** was treated with tetrabutylammonium fluoride (TBAF). Contrary to our initial expectation, a small amount of *N*-benzyloxyindoline **6a** was obtained along with a trace amount of a compound that was likely benzoxazine **7a** (Table 1, entry 1).[50] Mild heating of the reaction mixture improved the yield of **6a** to 48% (entry 2). Solvent and reagent screening revealed that the initially chosen

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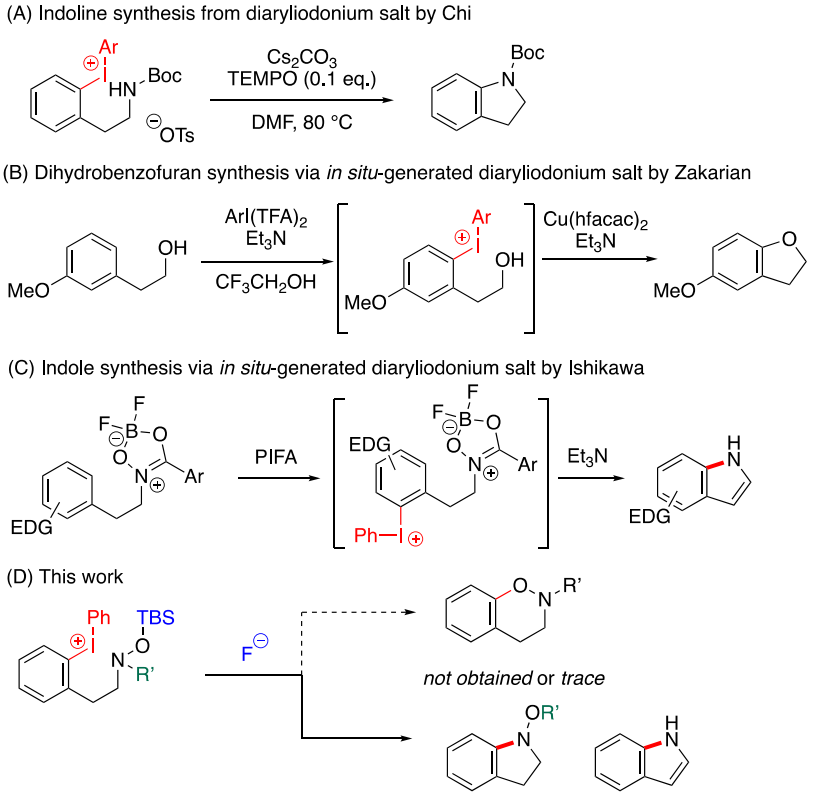
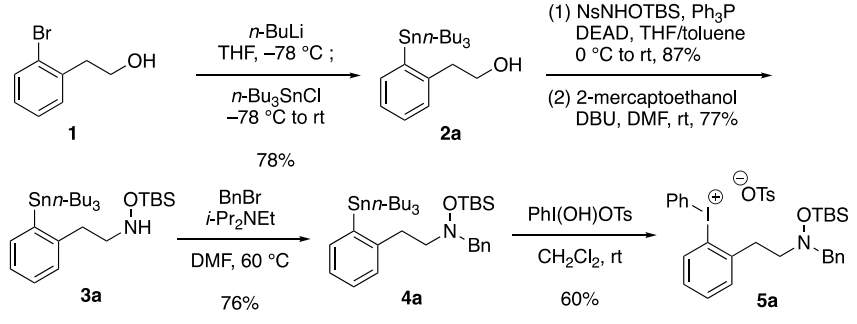
Scheme 1. Diaryliodonium Salt-Based Indole/Indoline Synthesis



Scheme 2. Substrate Preparation



*Summary of preparation of the substrates **5**.*

Mitsunobu reaction / benzylation	denosylation / iodoniumization	(yield)
Sn n-Bu3, Me — **2b-5b**	53%	quant.
	84%	69%
Sn n-Bu3, Me — **2c-5c**	93%	82%
	quant.	74%
Sn n-Bu3, MeO — **2d-5d**	93%	80%
	quant.	62%
Sn n-Bu3, Cl — **2e-5e**	quant.	74%
	89%	24%
Sn n-Bu3, F — **2f-5f**	quant.	71%
	quant.	42%

combination of TBAF and dimethylformamide (DMF) worked best (entries 3−9). The addition of molecular sieves (MS) did not improve the yield (entry 10). Despite their very simple structure, 2-unsubstituted-*N*-alkoxyindolines have rarely been synthesized[51,52] as the oxidation of indolines easily leads to aromatization to indoles or over-oxidation to nitrones and hydroxamic acids.[53] Although *N*-alkoxyindoline **6a** gradually converted to indole during silica gel purification, isolated **6a** could be stored at room temperature (rt) as a $CDCl_3$ solution for 1 week or for more than 2 months in a freezer without decomposition. The reason for the difference in stability between *N*-alkoxyindolines and *N*-hydroxyindolines[54] remains

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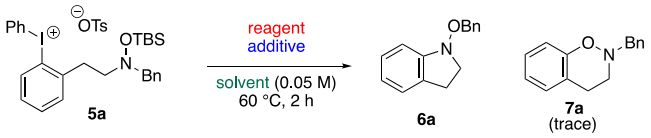
Table 1. Optimization for *N*-Alkoxyindoline Synthesis



entry	reagent (equiv)	additive (equiv)	solvent	yield of **6a** (%)[a]
1[b]	TBAF (1.5)		DMF	2
2	TBAF (1.5)		DMF	48
3	TBAF (1.5)		THF	29
4	TBAF (1.5)		toluene	18
5[c]	TBAF (1.5)		CH_2Cl_2	18
6	CsF (1.5)		DMF	17
7	NH_4F (1.5)		DMF	28
8	TASF (1.5)		DMF	45
9	PPTS (1.5)		DMF	0
10	TBAF (1.5)	MS 4 Å (500 g/mol)	DMF	34

[a]Isolated yield. [b]rt, 6 h. [c]Reflux.

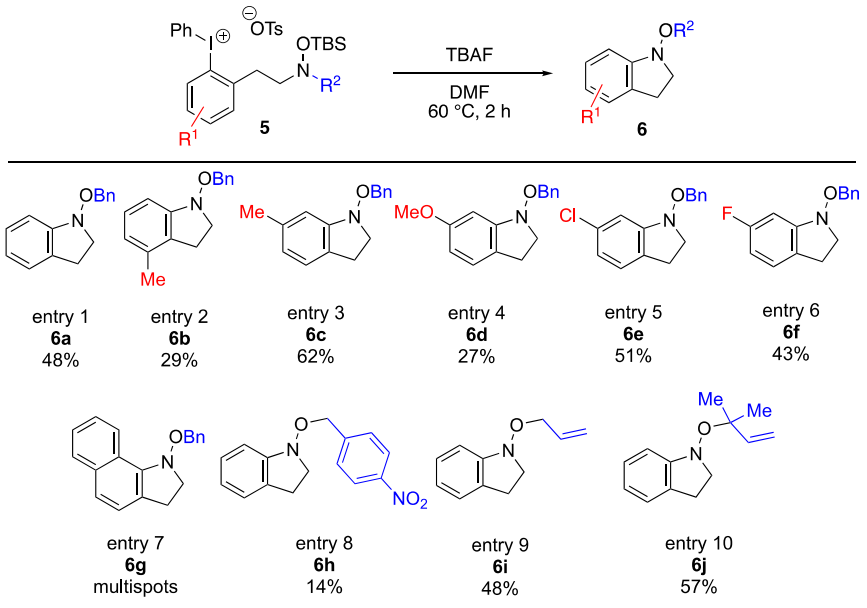
unclear but could be related to known differences between *N*-alkoxyindoles and *N*-hydroxyindoles.[55,56]

Having optimized the reaction conditions, we moved on to investigate the substrate scope (Table 2). Substitutions on benzene were tolerated, but substitution with an electron-donating methoxy group gave lower yield (entry 4), which might be attributed to the instability of the product **6d** to oxidation due to the increased electron density of the benzene ring. The use of a naphthyl ring as the main core leads to multiple spots on thin-layer chromatography (TLC), possibly due to complex radical recombination (entry 7; the reaction mechanism is discussed below). We also screened substitutions on the nitrogen. The use of a *p*-nitrobenzyl group led to lower yield, apparently due to instability of the substrate (entry 8). *N*-Allyl substitution worked well and afforded the corresponding product (entry 9). Remarkably, the *N*-prenylated substrate afforded *O*-reverse-prenylated **6j** as the sole product (entry 10). In contrast to previous hypervalent iodine-based syntheses of *N*-alkoxyanilines,[57−61] our method does not require electron-withdrawing group incorporation on the nitrogen atom of the final product.

We propose that the reaction proceeds as described in Scheme 3A. After deprotection of the hydroxy group, the oxygen atom attacks the iodine center to afford iodaoxazepine **B**. This proposed attack is supported by computational analysis of a model compound since the corresponding six-membered iodazine *N*-oxide (*N*-attack product) is more unstable by 50 kJ/mol (Scheme 3B, also see the Supporting Information (SI)). Subsequently, intramolecular ipso-attack by nitrogen leads to the four-membered ring transition state **C**, which undergoes the elimination of iodobenzene to afford the five-membered *N*-oxide intermediate **D** (also, see time-course analysis in the SI). Calculations using the model compound suggested that although *N*-oxide is thermodynamically unfavorable compared with benzoxazine, a four-membered ring transition state is strongly advantageous over a three-membered ring transition state (Scheme 3B).[62] Subsequent *N*-to-*O* benzyl migration likely proceeds via a radical-mediated [1,2]-Meisenheimer rearrangement pathway[63,64] since the addition of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) remarkably inhibited the reaction and benzylated TEMPO **8** was obtained instead (Scheme 3A, also the Experimental Section). [2,3]-Meisenheimer rearrangement of *N*-allyl or *N*-prenyl substrates (**5i** and **5j**) is likely sigmatropic.

With this mechanism in mind, we envisaged that decreasing the electron density on the nitrogen atom would favor conversion to the initially expected benzoxazine, and we therefore synthesized *N*-Boc-protected diaryliodonium salt **9a** (see the preparation in the Experimental Section). Treatment with TBAF, however, afforded indole **10a** in 73% yield, without the formation of benzoxazine **11a** (Table 3, entry 1), and a stoichiometric amount of iodobenzene was generated. Interestingly, a small amount (ca. 10%) of 5-substituted indoline **12a** was detected during each optimization reaction (discussed below). The solvent screening revealed that DMF is the optimum solvent, likely due to the good solubility of the iodonium salt (entries 2−4). We next examined fluoride

Table 2. Substrate Scope for *N*-Alkoxyindoline Synthesis



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Scheme 3. Proposed Reaction Mechanism

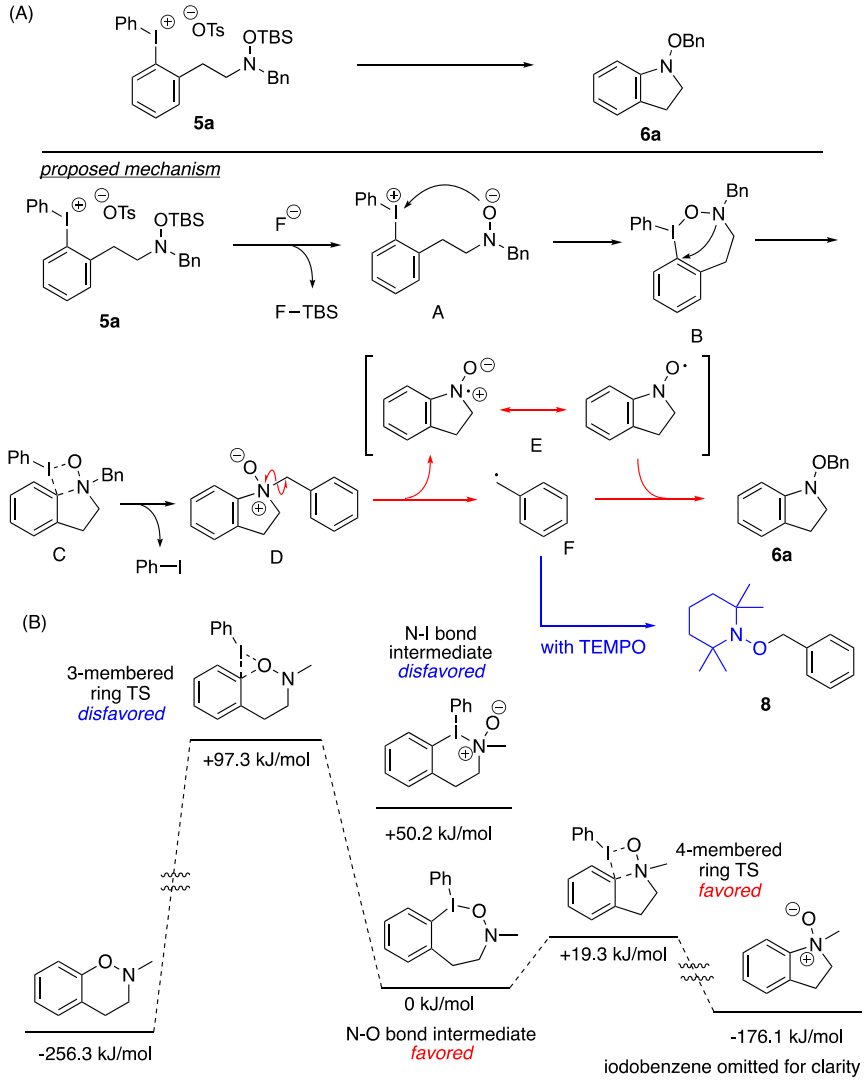
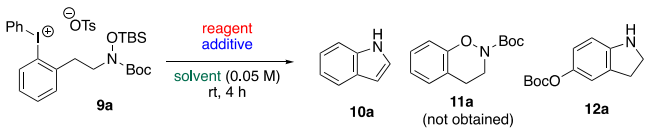


Table 3. Optimization for Indole Synthesis



				yield (%)[a]	
entry	reagent (equiv)	additive (equiv)	solvent	10a	12a
1	TBAF (1.2)		DMF	73	6
2	TBAF (1.2)		THF	58	20
3	TBAF (1.2)		toluene	60	2
4	TBAF (1.2)		CH_2Cl_2	71	17
5	CsF (1.5)		DMF	23	3
6	NH_4F (1.2)		DMF	62	5
7	TASF (1.2)		DMF	83	6
8	TASF (1.2)	MS 4 Å (500 g/mol)	DMF	87	–[b]
9	TBAF (1.2)	MS 4 Å (500 g/mol)	DMF	89	–[b]

[a]Isolated yield. [b]Obtained as an inseparable mixture with unidentified by-products.

sources and found that tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) provided the best result (entries 5–7). The addition of molecular sieves improved the yield, giving an excellent yield with TBAF and TASF (entries 8 and 9). For operational simplicity, we chose a combination of TBAF and MS 4 Å as the optimal conditions (entry 9).

With the optimized conditions in hand, we next examined the substrate scope (Table 4). Various indoles with substituents at the 4-, 5-, and 6-positions were obtained, showing the robustness of this transformation. In particular, the electron-donating methoxy group and electron-withdrawing fluorine group were both tolerated (entries 4–6). Interestingly, benzoindole **10g** and biaryl-type indole **10h** were also obtained in good yield (entries 7 and 8). 3-Substitution resulted in lower yield (entry 9). The *N*-Cbz-protected substrate afforded indole in moderate yield (entry 10). It is important to note that while diaryliodonium salt-based indole synthesis was originally discovered by Ishikawa and co-workers,[44] their substrate scope has been limited to electron-rich aromatic substrates because in situ nucleophilic aromatic substitution is required to prepare the diaryliodonium salt. The stepwise preparation of diaryliodonium salts via stannane developed herein allowed great expansion of the substrate scope of the indole synthesis via diaryliodonium salts. Additionally to note, we were unable to prepare iodonium salts from acyl-protected substrates (*N*-Ac or *N*-Piv), which are

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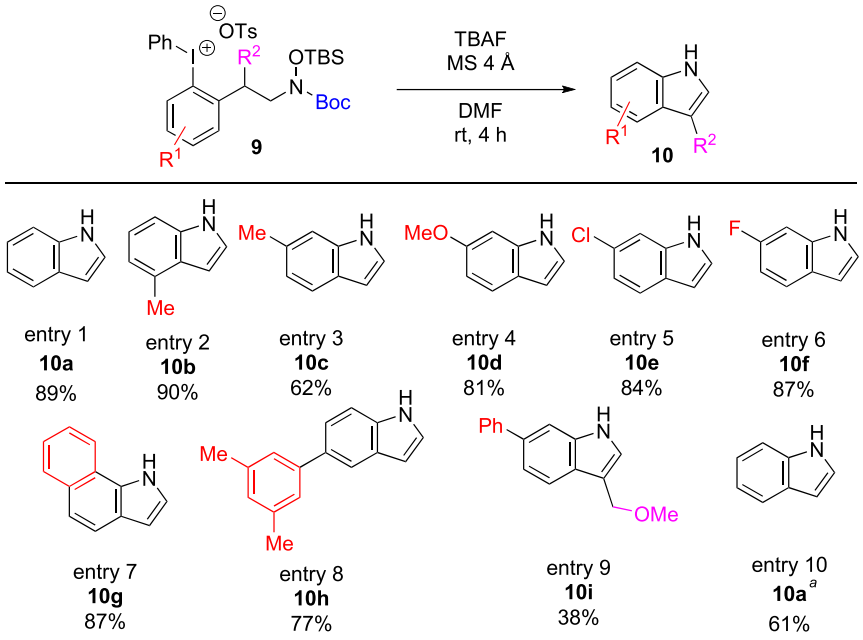
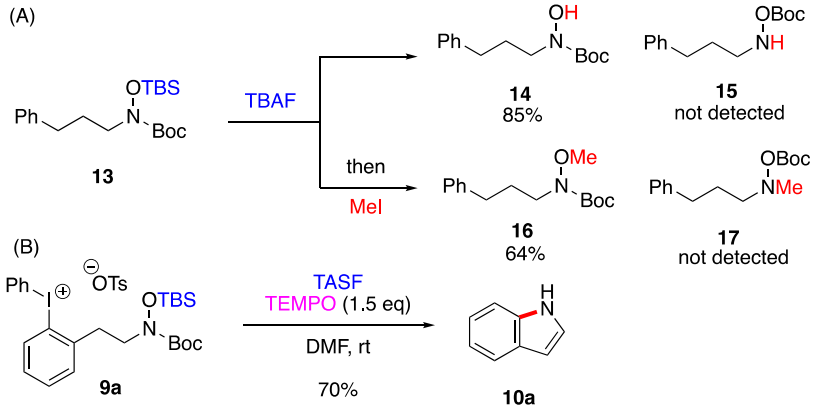
Table 4. Substrate Scope for Indole Synthesis



[a]From the *N*-Cbz-protected substrate.

Scheme 4. Control Experiments



direct congeners for Ishikawa's original substrates, likely due to rapid decomposition during purification.

We performed several control reactions to clarify the reaction mechanism (Scheme 4). When protected hydroxylamine **13** was treated with TBAF, **14** was isolated as the sole product and the corresponding *O*-Boc product **15** was not detected (Scheme 4A). One-pot methylation afforded only *O*-Me product **16**. This is in accord with our brief calculation with a model compound (see the SI), showing essentially no equilibrium between the *N*-carbamate and the corresponding *O*-carbonate due to the large energy difference (see the SI). These results suggest that *N*-to-*O* acyl migration[65] is unlikely to be involved in the initiation step of the reaction. Furthermore, the addition of TEMPO had little effect on yield and no prominent new by-products were observed, showing that the reaction is unlikely to be mediated by radical chemistry (Scheme 4B).

From the above results and comparison with Ishikawa's hypothesis,[44] we propose the reaction mechanism shown in Scheme 5. Upon deprotection of the oxygen atom, intramolecular attack of the anionic oxygen on the iodine center leads to seven-membered ring intermediate **H**. The recombination of the chemical bond is accompanied by reductive elimination of iodobenzene to afford **I**,[29,62,66,67] which undergoes *N*-to-*O* acyl migration to provide *O*-Boc intermediate **J**.[57,68] Subsequent intramolecular hydrogen subtraction affords **K**, which isomerizes quickly to indole **10a**. Although direct decomposition of *N*-Boc intermediate **I** to *N*-hydroxyindoline **L** can also be postulated, successful transformation of Cbz-protected hydroxylamine is inconsistent with a mechanism involving β-hydrogen elimination. This is further supported by gas chromatography (GC) analysis: a nearly equal amount of *tert*-butyl alcohol was detected in the reaction mixture, which cannot be generated by a β-elimination pathway. It should be emphasized that the formation of side product **12a** can be accounted for by sequential [3,3]-sigmatropic rearrangements via **M**[69] or **N**,[70] which also strongly indicates the presence of acyl migration intermediate **J**.[57] The role of molecular sieves can be attributed to the removal of water, which could hydrolyze intermediates such as **I** or **J**.

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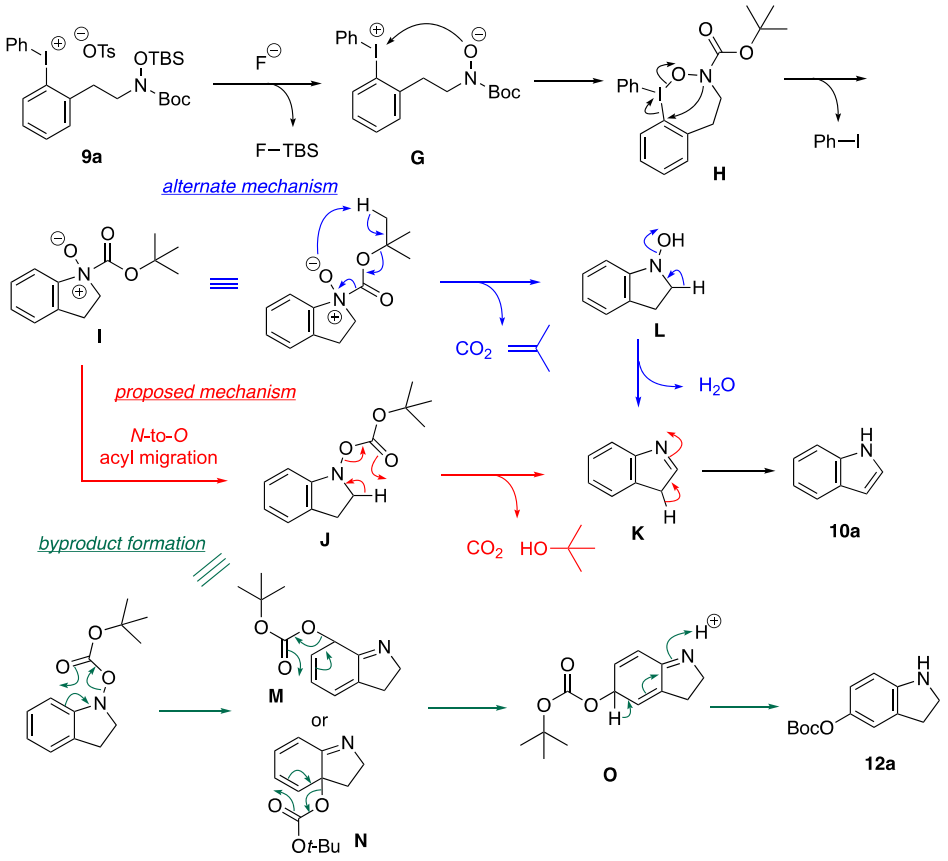
Scheme 5. Proposed Reaction Mechanism



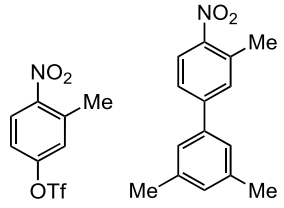
CONCLUSIONS

In conclusion, we have discovered a novel method for the synthesis of rarely accessible *N*-alkoxyindolines via diaryliodonium salt-based transformation. This is the first systematic synthetic study of *N*-alkoxyindolines to date, despite their simple structures. Further examination greatly expands both the substrate scope of the Ishikawa indole synthesis and the understanding of its mechanism. Our method is characterized by operational simplicity and a broad substrate scope. Application of this strategy to other heteroaromatics, as well as further mechanistic analyses, will be reported in due course.

EXPERIMENTAL SECTION

General Methods. The reactions were carried out under Ar unless otherwise noted. Melting points are uncorrected. ^{1}H HMR spectra were recorded at 400 or 500 MHz with tetramethylsilane as an internal standard on a JEOL JNM-ECS400 (400 MHz), JEOL JNM-ECZ400 (400 MHz), or JEOL JNM-ECA500 (500 MHz) spectrometer unless otherwise noted. ^{13}C{^{1}H} NMR spectra were recorded at 100 or 125 MHz. High-resolution mass spectra (HRMS) were measured by the electrospray ionization (ESI) mode (TOF analyzer) on a Waters LCT Premier XE spectrometer. Thin-layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} plates. An oil bath was used as the heating source for the reactions that require heating. The crude reaction mixtures and extracted materials were purified by chromatography on silica gel (Fuji Silysia, PSQ-100B) or PTLC (Merck). Combined organic extracts were dried over anhydrous Na_2SO_4. Solvents were removed from the reaction mixture and the combined organic extracts by concentration under reduced pressure using an evaporator with a water bath at 35−45 °C.

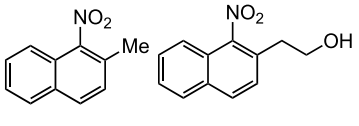
*3,3′,5′-Trimethyl-4-nitro-1,1′-biphenyl (**S2a**).*



S1 **S2a**

To a stirred solution of **S1**[71] (1.61 g, 5.66 mmol), (3,5-dimethylphenyl)boronic acid (933 mg, 6.22 mmol), and K_2CO_3 (1.80 g, 13.0 mmol) in 1,2-dimethoxyethane (DME) (50 mL) was added tetrakis(triphenylphosphine)palladium (144 mg, 0.124 mmol). After being stirred at 70 °C for 12 h, the mixture was diluted with H_2O (100 mL) and extracted with EtOAc (50 mL × 3). The combined extracts were washed with saturated brine (50 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:19−1:2) to provide 1.39 g (quant.) of **S2a** as a white solid: TLC R_f 0.74 (EtOAc/hexane, 1:6); IR (neat) 1584, 1515, 1335, 846, 831, 694 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, 1H, J = 8.0 Hz), 7.52 (d, 1H, J = 8.0 Hz), 7.52 (s, 1H), 7.21 (s, 2H), 7.07 (s, 1H), 2.69 (s, 3H), 2.40 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.9, 146.5, 139.0, 138.8 (2C), 134.4, 131.5, 130.4, 125.6, 125.5, 125.3 (2C), 21.5 (2C), 21.2; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{15}NO_2$ 242.1181; found 242.1180.

*2-(1-Nitronaphthalen-2-yl)ethan-1-ol (**S3a**).*



S2b **S3a**

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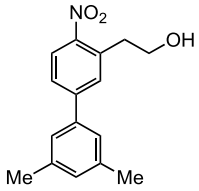
To a cooled (0 °C) stirred solution of 2-methyl-1-nitronaphthalene (**S2b**) (4.00 g, 21.3 mmol) and formalin (35% solution, 3.80 mL, 36.1 mmol) in dimethyl sulfoxide (DMSO) (40 mL) was added aqueous KOH (17.9 M solution, 2.02 mL, 36.1 mmol). After being stirred at 0 °C for 30 min and at room temperature for 30 min, the mixture was quenched with saturated aqueous NH_4Cl (40 mL), diluted with H_2O (20 mL), and extracted with EtOAc (70 mL × 4). The combined extracts were washed with saturated brine (100 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:1) to provide 3.31 g (71%) of **S3a** as yellow crystals: mp 79−84 °C; TLC R_f 0.32 (EtOAc/hexane, 1:1); IR (neat) 3546, 1523, 1361, 1056, 818, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, 1H, J = 8.0 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.72 (d, 1H, J = 8.4 Hz), 7.63 (td, 1H, J = 8.0, 1.2 Hz), 7.57 (td, 1H, J = 8.0, 1.2 Hz), 7.46 (d, 1H, J = 8.4 Hz), 3.98 (q, 2H, J = 6.4 Hz), 3.03 (t, 2H, J = 6.4 Hz), 1.61 (t, 1H, J = 6.4 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.5, 132.7, 130.8, 128.8, 128.4, 128.1, 127.6, 127.2, 124.7, 121.6, 62.8, 35.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{12}H_{11}NNaO_3$ 240.0637; found 240.0643.

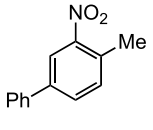
*2-(3′,5′-Dimethyl-4-nitro-[1,1′-biphenyl]-3-yl)ethan-1-ol (**S3b**).*



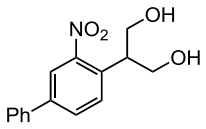
S3b

To a suspension of **S2a** (2.03 g, 8.41 mmol) in DMSO (80 mL) were added formalin (35%, 1.44 mL, 16.8 mmol), aqueous KOH (1.68 M solution, 5.0 mL, 8.4 mmol), and tetrahydrofuran (THF) (5 mL) successively under air. After being stirred at room temperature for 12 h, the mixture was quenched with saturated aqueous NH_4Cl (10 mL), diluted with H_2O (100 mL), and extracted with EtOAc (100 mL × 3). The combined extracts were washed with H_2O (100 mL) and saturated brine (100 mL) sequentially, dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:9−2:1) to provide 1.41 g (62%) of **S3b** as a yellow solid: TLC R_f 0.12 (EtOAc/hexane, 1:6); IR (neat) 3306, 1582, 1517, 1339, 1041, 840 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, 1H, J = 8.0 Hz), 7.60 (d, 1H, J = 2.0 Hz), 7.58 (dd, 1H, J = 8.0, 2.0 Hz), 7.21 (s, 2H), 7.06 (s, 1H), 4.01 (q, 2H, J = 6.0 Hz), 3.27 (t, 2H, J = 6.0 Hz), 2.40 (s, 6H), 1.60 (t, 1H, J = 6.0 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 148.4, 146.6, 138.9 (2C), 138.8, 134.6, 131.6, 130.6, 126.3, 125.8, 125.4 (2C), 63.0, 36.7, 21.5 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}NO_3$ 272.1287; found 272.1296.

*2-(3-Nitro-[1,1′-biphenyl]-4-yl)propane-1,3-diol (**S3c**).*



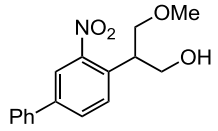
S2c



S3c

To a cooled (0 °C) stirred solution of **S2c**[72] (4.17 g, 19.6 mmol) in DMSO (100 mL) and THF (10 mL) were added aqueous KOH (3.92 M solution, 5.0 mL, 20 mmol) and formalin (35%, 3.3 mL, 39.1 mmol) under air. After being stirred at room temperature for 12 h, the mixture was quenched with saturated aqueous NH_4Cl (10 mL), diluted with H_2O (100 mL), and extracted with EtOAc (100 mL × 3). The combined extracts were washed with H_2O (100 mL) and saturated brine (100 mL) sequentially, dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:1−1:0) to provide 3.08 g (58%) of **S3c** as a yellow oil: TLC R_f 0.41 (EtOAc); IR (neat) 3343, 1529, 1355, 1037, 760, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 1H, J = 2.0 Hz), 7.79 (dd, 1H, J = 8.2, 2.0 Hz), 7.63 (d, 1H, J = 8.2 Hz), 7.58 (dd, 1H, J = 7.0, 2.6 Hz), 7.48 (t, 2H, J = 7.0 Hz), 7.42 (tt, 1H, J = 7.0, 2.6 Hz), 4.09 (d, 4H, J = 6.0 Hz), 3.64 (quin, 1H, J = 6.0 Hz), 2.20 (br s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.2, 141.3, 138.4, 132.8, 131.2, 129.7, 129.3 (2C), 128.6, 127.1 (2C), 123.0, 65.0 (2C), 43.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}NO_4$ 274.1079; found 274.1073.

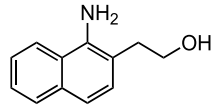
*3-Methoxy-2-(3-nitro-[1,1′-biphenyl]-4-yl)propan-1-ol (**S4**).*



S4

To a cooled (0 °C) stirred solution of **S3c** (3.08 g, 11.3 mmol) in DMF (56 mL) was added NaH (60% in oil, 452 mg, 11.3 mmol). The mixture was stirred at room temperature for 30 min, and MeI was added. After being stirred at room temperature for 12 h, the mixture was cooled to 0 °C, quenched with saturated aqueous NH_4Cl (5 mL), diluted with H_2O (100 mL), and extracted with EtOAc (100 mL × 3). The combined extracts were washed with H_2O (100 mL) and saturated brine (100 mL) sequentially, dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:2−1:1) to provide 2.06 g (63%) of **S4** as a yellow oil: TLC R_f 0.64 (EtOAc); IR (neat) 3398, 1529, 1356, 1116, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 1H, J = 2.0 Hz), 7.77 (dd, 1H, J = 8.4, 2.0 Hz), 7.63 (d, 1H, J = 8.4 Hz), 7.58 (dd, 2H, J = 7.2, 1.4 Hz), 7.48 (tt, 2H, J = 7.2, 1.4 Hz), 7.41 (tt, 1H, J = 7.2, 1.4 Hz), 4.07 (m, 1H), 3.99 (m, 1H), 3.81 (m, 2H), 3.73 (m, 1H), 3.40 (s, 3H), 2.66 (t, 1H, J = 6.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.1, 141.5, 138.5, 133.1, 131.1, 130.0, 129.3 (2C), 128.6, 127.1 (2C), 122.9, 74.7, 65.2, 59.3, 41.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}NO_4$ 288.1236; found 288.1228.

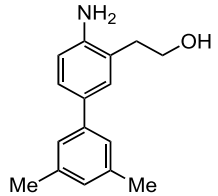
*2-(1-Aminonaphthalen-2-yl)ethan-1-ol (**S5a**).*



S5a

To a stirred solution of **S3a** (1.22 g, 5.61 mmol) in EtOH/H_2O (4:1, 55 mL) were added iron powder (1.76 g, 31.6 mmol) and NH_4Cl (312 mg, 5.83 mmol). The mixture was stirred at 70 °C for 22 h under air. The insoluble materials were removed by filtration through a pad of Celite and washed well with CH_2Cl_2. The combined filtrate and washings were concentrated under reduced pressure. The residue was washed with saturated aqueous $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (30 mL × 4). The combined extracts were washed with saturated brine (20 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 2:1) to provide 784 mg (75%) of **S5a** as light brown crystals: mp 75−78 °C; TLC R_f 0.23 (EtOAc/hexane, 1:1); IR (neat) 3406, 3019, 1384, 1217, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 1H, J = 8.0 Hz), 7.78 (dd, 1H, J = 8.0, 1.6 Hz), 7.46 (td, 1H, J = 8.0, 1.6 Hz), 7.42 (td, 1H, J = 8.0, 1.6 Hz), 7.30 (d, 1H, J = 8.4 Hz), 7.21 (d, 1H, J = 8.4 Hz), 3.99 (t, 2H, J = 6.4 Hz), 2.99 (t, 2H, J = 6.4 Hz), 1.65 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.2, 133.5, 129.1, 128.6, 125.4, 125.2, 123.9, 120.6, 118.9, 117.8, 63.4, 35.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}NO$ 188.1075; found 188.1068.

*2-(4-Amino-3′,5′-dimethyl-[1,1′-biphenyl]-3-yl)ethan-1-ol (**S5b**).*

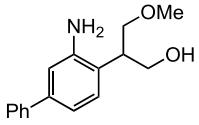


S5b

https://doi.org/10.1021/acs.joc.1c00820
J. Org. Chem. 2021, 86, 10067−10087

To a stirred solution of **S3b** (1.42 g, 5.23 mmol) in EtOH (44 mL) and H_2O (12 mL) were added NH_4Cl (401 mg, 7.50 mmol) and iron powder (2.92 g, 52.3 mmol). The mixture was stirred at 70 °C for 2 days under air, and NH_4Cl (200 mg, 3.74 mmol) and iron powder (1.60 g, 28.7 mmol) were added. The mixture was further stirred at 70 °C for 12 h under air. The insoluble materials were removed by filtration through a pad of Celite and washed well with EtOAc and H_2O. A saturated aqueous solution (5 mL) of NaOH (1 g) and saturated brine (100 mL) were added to the combined filtrate and washings, and the mixture was extracted with EtOAc (100 mL × 3). The combined extracts were washed with saturated brine (50 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:2−1:0) to provide 409 mg (32%) of **S5b** as a black oil: TLC R_f 0.38 (EtOAc); IR (neat) 3374, 2921, 1600, 1505, 1384, 1212, 1034, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2H), 7.15 (br s, 2H), 6.93 (br s, 1H), 6.76 (d, 1H, J = 8.0 Hz), 3.95 (t, 2H, J = 6.0 Hz), 2.86 (t, 2H, J = 6.0 Hz), 2.36 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.6, 141.2, 138.3 (2C), 132.5, 129.5, 128.1, 126.5, 124.5 (3C), 116.7, 63.6, 35.1, 21.6 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NO$ 242.1545; found 242.1542.

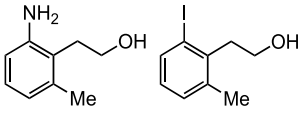
*2-(3-Amino-[1,1′-biphenyl]-4-yl)-3-methoxypropan-1-ol (**S5c**).*



S5c

To a stirred solution of **S4** (2.06 g, 7.17 mmol) in EtOH (60 mL) and H_2O (15 mL) were added NH_4Cl (384 mg, 7.17 mmol) and iron powder (4.00 g, 71.7 mmol). The mixture was stirred at 70 °C for 12 h under air. The insoluble materials were removed by filtration through a pad of Celite and washed well with EtOAc and H_2O. Saturated aqueous $NaHCO_3$ (5 mL) and saturated brine (100 mL) were added to the combined filtrate and washings, and the mixture was extracted with EtOAc (100 mL × 3). The combined extracts were washed with saturated brine (50 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:1−1:0) to provide 1.37 g (74%) of **S5c** as pale red crystals: mp 128−130 °C; TLC R_f 0.11 (EtOAc/hexane, 1:1); IR (neat) 3357, 2925, 1633, 1384, 1212, 1113, 764, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, 2H, J = 7.2 Hz), 7.41 (t, 2H, J = 7.2 Hz), 7.32 (t, 1H, J = 7.2 Hz), 7.07 (d, 1H, J = 8.0 Hz), 6.99 (dd, 1H, J = 8.0, 1.6 Hz), 6.93 (d, 1H, J = 2.0 Hz), 4.04 (dd, 1H, J = 10.4, 9.2 Hz), 3.90 (dd, 1H, J = 11.2, 5.6 Hz), 3.80 (t, 1H, J = 9.2 Hz), 3.70 (dd, 1H, J = 11.2, 5.6 Hz), 3.41 (s, 3H), 3.26 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.3, 141.1, 140.9, 128.8 (2C), 127.7, 127.3, 127.1 (2C), 123.9, 118.1, 115.3, 75.8, 65.7, 59.3, 42.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NO_2$ 258.1494; found 258.1493.

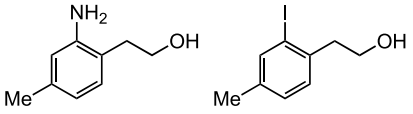
*2-(2-Iodo-6-methylphenyl)ethan-1-ol (**S6a**).*



S5d **S6a**

To a stirred solution of $TsOH{\cdot}H_2O$ (7.55 g, 39.7 mmol) in CH_3CN (28 mL) was added **S5d**[73] (1.99 g, 13.2 mmol). The mixture was stirred at room temperature for 15 min and at 0 °C for 15 min, and aqueous $NaNO_2$ (6.60 M solution, 4.00 mL, 26.3 mmol) was added. The mixture was stirred at 0 °C for 40 min, and aqueous KI (8.25 M solution, 4.00 mL, 33.0 mmol) was added. After being stirred at 0 °C for 10 min and at room temperature for 4 h, the mixture was quenched with saturated aqueous $NaHCO_3$ (20 mL), 20 wt % aqueous $Na_2S_2O_3$ (20 mL), and extracted with EtOAc (80 mL × 3). The combined extracts were washed with saturated brine (50 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:2) to provide 2.58 g (75%) of **S6a** as yellow crystals: mp 110−113 °C; TLC R_f 0.43 (EtOAc/hexane, 1:2); IR (neat) 3280, 2953, 1444, 1384, 1038, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 1H, J = 7.6 Hz), 7.12 (d, 1H, J = 7.6 Hz), 6.80 (t, 1H, J = 7.6 Hz), 3.81 (t, 2H, J = 7.2 Hz), 3.13 (t, 2H, J = 7.2 Hz), 2.43 (s, 3H), 1.44 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.0, 138.5, 137.9, 130.7, 128.4, 102.6, 61.6, 41.0, 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_9H_{11}INaO$ 284.9752; found 284.9763.

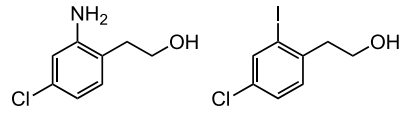
*2-(2-Iodo-4-methylphenyl)ethan-1-ol (**S6b**).*



S5e **S6b**

As described for the preparation of **S6a**, compound **S5e**[74] (2.07 g, 13.7 mmol) was converted to 2.88 g (80%) of **S6b**. Compound **S6b** was obtained as an orange oil: TLC R_f 0.37 (EtOAc/hexane, 1:2); IR (neat) 3357, 2951, 2923, 1486, 1217, 1039, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.13 (d, 1H, J = 7.6 Hz), 7.09 (d, 1H, J = 7.6 Hz), 3.82 (br s, 2H), 2.97 (t, 2H, J = 6.8 Hz), 2.28 (s, 3H), 1.53 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.2, 138.4, 138.0, 130.1, 129.3, 100.8, 62.5, 43.3, 20.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{12}IO$ 262.9933; found 262.9942.

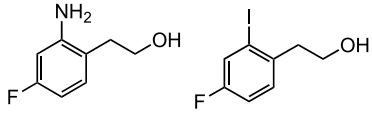
*2-(4-Chloro-2-iodophenyl)ethan-1-ol (**S6c**).*



S5f **S6c**

As described for the preparation of **S6a**, compound **S5f**[73] (2.14 g, 12.5 mmol) was converted to 2.61 g (74%) of **S6c**. Compound **S6c** was obtained as a red oil: TLC R_f 0.37 (EtOAc/hexane, 1:2); IR (neat) 3332, 2933, 2878, 1579, 1465, 1034, 815, 798 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 1H, J = 1.6 Hz), 7.27 (dd, 1H, J = 8.0, 1.6 Hz), 7.18 (d, 1H, J = 8.0 Hz), 3.84 (t, 2H, J = 6.8 Hz), 2.98 (t, 2H, J = 6.8 Hz), 1.50 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.9, 138.9, 133.0, 130.9, 128.6, 100.6, 62.2, 43.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for C_8H_9ClIO 282.9387; found 282.9380.

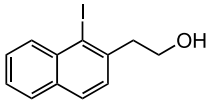
*2-(4-Fluoro-2-iodophenyl)ethan-1-ol (**S6d**).*



S5g **S6d**

As described for the preparation of **S6a**, compound **S5g**[73] (1.86 g, 12.0 mmol) was converted to 2.53 g (80%) of **S6d**. Compound **S6d** was obtained as a red oil: TLC R_f 0.37 (EtOAc/hexane, 1:2); IR (neat) 3364, 2954, 1593, 1482, 1221, 1042, 862, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, 1H, J = 8.4, 2.8 Hz), 7.22 (dd, 1H, J = 8.4, 6.0 Hz), 7.02 (td, 1H, J = 8.4, 2.8 Hz), 3.82 (t, 2H, J = 6.8 Hz), 2.98 (t, 2H, J = 6.8 Hz), 1.61 (br, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8 (d, J = 249.1 Hz), 137.1 (d, J = 2.9 Hz), 130.8 (d, J = 7.6 Hz), 126.5 (d, J = 23.0 Hz), 115.4 (d, J = 20.1 Hz), 99.7 (d, J = 7.7 Hz), 62.3, 42.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for C_8H_9FIO 266.9682; found 266.9669.

*2-(1-Iodonaphthalen-2-yl)ethan-1-ol (**S6e**).*



S6e

As described for the preparation of **S6a**, compound **S5a** (1.39 g, 7.44 mmol) was converted to 1.82 g (82%) of **S6e**. Compound **S6e** was obtained as orange crystals: mp 72−75 °C; TLC R_f 0.43 (EtOAc/hexane, 1:2); IR (neat) 3406, 3017, 1499, 1216, 1039, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, 1H, J = 8.4 Hz), 7.76 (d, 2H, J =

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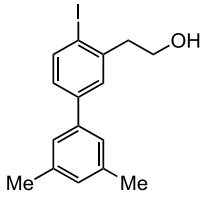
J. Org. Chem. 2021, 86, 10067−10087

8.0 Hz), 7.57 (t, 1H, J = 8.0 Hz), 7.48 (t, 1H, J = 8.0 Hz), 7.39 (d, 1H, J = 8.4 Hz), 3.97 (q, 2H, J = 6.4 Hz), 3.34 (t, 2H, J = 6.4 Hz), 1.46 (t, 1H, J = 6.4 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.7, 135.3, 133.1, 132.9, 128.9, 128.3, 128.1, 128.0, 126.3, 106.0, 62.7, 45.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{12}IO$ 298.9933; found 298.9922.

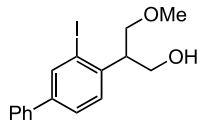
*2-(4-Iodo-3′,5′-dimethyl-[1,1′-biphenyl]-3-yl)ethan-1-ol (**S6f**).*



S6f

As described for the preparation of **S6a**, compound **S5b** (427 mg, 1.77 mmol) was converted to 328 mg (62%) of **S6f**. Compound **S6f** was obtained as a light brown oil: TLC R_f 0.41 (EtOAc/hexane, 1:2); IR (neat) 3381, 2919, 1604, 1384, 1042, 900, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, 1H, J = 8.4 Hz), 7.46 (d, 1H, J = 2.4 Hz), 7.17 (br s, 2H), 7.14 (dd, 1H, J = 8.4, 2.0 Hz), 7.01 (br s, 1H), 3.91 (q, 2H, J = 6.4 Hz), 3.08 (t, 2H, J = 6.8 Hz), 2.38 (s, 6H), 1.42 (t, 1H, J = 6.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 141.4, 140.0 (2C), 138.6 (2C), 129.5, 129.2, 127.3, 125.0 (2C), 99.3, 62.5, 43.9, 21.5 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}IO$ 353.0402; found 353.0397.

*2-(3-Iodo-[1,1′-biphenyl]-4-yl)-3-methoxypropan-1-ol (**S6g**).*



S6g

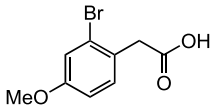
As described for the preparation of **S6a**, compound **S5c** (1.27 g, 4.95 mmol) was converted to 1.67 g (92%) of **S6g**. Compound **S6g** was obtained as a yellow oil: TLC R_f 0.27 (EtOAc/hexane, 1:2); IR (neat) 3406, 2926, 2878, 1596, 1538, 1474, 1376, 1116, 1033, 762, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.53 (d, 3H, J = 8.0 Hz), 7.44 (t, 2H, J = 7.6 Hz), 7.36 (t, 1H, J = 7.6 Hz), 7.29 (d, 1H, J = 8.0 Hz), 4.04−3.91 (m, 2H), 3.78−3.71 (m, 2H), 3.60 (tt, 1H, J = 7.6, 6.4 Hz), 3.43 (s, 3H), 2.50 (t, 1H, J = 5.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 140.8, 139.2, 138.5, 129.0 (2C), 127.9 (2C), 127.3, 127.1 (2C), 102.7, 75.3, 65.4, 59.3, 50.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}IO_2$ 369.0352; found 369.0366.

*2-(2-Tributylstannylphenyl)ethan-1-ol (**2a**).* To a cooled (−78 °C) stirred solution of 2-(2-bromophenyl)ethyl alcohol (**1**) (2.70 mL, 20.0 mmol) in THF (50 mL) was added n-BuLi (2.6 M solution in hexane, 19.5 mL, 50.7 mmol). The mixture was stirred at −78 °C for 1 h, and n-Bu_3SnCl (7.50 mL, 27.6 mmol) was added. After being stirred at −78 °C for 1 h and at room temperature for 5.5 h, the mixture was quenched with saturated aqueous NH_4Cl (25 mL), diluted with H_2O (25 mL), and extracted with EtOAc (50 mL × 3). The combined extracts were washed with saturated brine (50 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to provide 6.44 g (78%) of **2a** as a colorless oil: TLC R_f 0.46 (EtOAc/hexane, 1:10); IR (neat) 3356, 2957, 2926, 1464, 1377, 1217, 1045, 757, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, 1H, J = 6.8, 0.9 Hz), 7.30−7.24 (m, 2H), 7.19 (td, 1H, J = 7.2, 2.0 Hz), 3.83 (q, 2H, J = 6.8 Hz), 2.87 (t, 2H, J = 6.8 Hz), 1.54−1.44 (m, 6H), 1.39−1.29 (m, 6H), 1.16−0.99 (m, 6H), 0.89 (t, 9H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.0, 143.0, 137.3, 128.7, 128.6, 126.1, 64.2, 42.3, 29.3 (3C), 27.6 (3C), 13.8 (3C), 10.6 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{37}OSn$ 413.1866; found 413.1873.

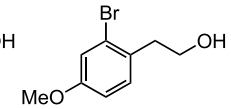
*2-[2-Methyl-6-(tributylstannyl)phenyl]ethan-1-ol (**2b**).* To a cooled (−78 °C) stirred solution of **S6a** (1.21 g, 4.60 mmol) in THF (11 mL) was added n-BuLi (2.69 M solution in hexane, 4.10 mL, 11.0 mmol). The mixture was stirred at −78 °C for 0.5 h, and n-Bu_3SnCl (1.75 mL, 6.45 mmol) was added. After being stirred at −78 °C for 30 min and at room temperature for 8 h, the mixture was quenched with saturated aqueous NH_4Cl (5 mL), diluted with H_2O (5 mL), and extracted with EtOAc (10 mL × 3). The combined extracts were washed with saturated brine (10 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to provide 875 mg (45%) of **2b** as a yellow oil: TLC R_f 0.58 (EtOAc/hexane, 1:2); IR (neat) 3429, 2958, 2927, 1457, 1216, 1030, 759, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 1H), 7.16−7.14 (m, 2H), 3.72 (br q, 2H, J = 8.0 Hz), 2.97 (t, 2H, J = 8.0 Hz), 2.41 (s, 3H), 1.62−1.49 (m, 6H), 1.43−1.31 (m, 6H), 1.21−1.04 (m, 6H), 0.93 (t, 9H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.9, 142.8, 136.5, 135.0, 130.9, 126.3, 63.1, 40.2, 29.2 (3C), 27.6 (3C), 20.5, 13.8 (3C), 10.9 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{39}OSn$ 427.2023; found 427.2028.

*2-[4-Methyl-2-(tributylstannyl)phenyl]ethan-1-ol (**2c**).* As described for the preparation of **2b**, compound **S6b** (877 mg, 3.35 mmol) was converted to 481 mg (34%) of **2c**. Compound **2c** was obtained as a yellow oil: TLC R_f 0.58 (EtOAc/hexane, 1:2); IR (neat) 3421, 2958, 2929, 1464, 1381, 1216, 1044, 758, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (br s, 1H), 7.15 (d, 1H, J = 8.0 Hz), 7.08 (d, 1H, J = 8.0 Hz), 3.80 (t, 2H, J = 7.2 Hz), 2.84 (t, 2H, J = 7.2 Hz), 2.31 (s, 3H), 1.56−1.46 (m, 6H), 1.37−1.30 (m, 6H), 1.11−1.02 (m, 6H), 0.89 (t, 9H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.6, 141.9, 138.0, 135.2, 129.4, 128.6, 64.3, 41.7, 29.3 (3C), 27.6 (3C), 21.1, 13.8 (3C), 10.6 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{39}OSn$ 427.2023; found 427.2014.

*2-[4-Methoxy-2-(tributylstannyl)phenyl]ethan-1-ol (**2d**).*



S7



S8

To a cooled (0 °C) stirred solution of 2-bromo-4-methoxyphenylacetic acid (**S7**) (1.12 g, 4.76 mmol) in THF (15 mL) were added $NaBH_4$ (437 mg, 11.6 mmol) and $BF_3{\cdot}OEt_2$ (0.720 mL, 5.73 mmol). After being stirred at 60 °C for 1 h, the mixture was quenched with MeOH (5 mL) and stirred at room temperature for 30 min. The mixture was diluted with H_2O (10 mL) and extracted with EtOAc (25 mL × 4). The combined extracts were washed with saturated brine (25 mL), dried, and concentrated under reduced pressure to provide crude **S8**, which was used in the next step without further purification.

To a cooled (−78 °C) stirred solution of crude **S8** obtained above in THF (13 mL) was added n-BuLi (2.69 M solution in hexane, 3.60 mL, 9.68 mmol). The mixture was stirred at −78 °C for 40 min, and n-Bu_3SnCl (1.50 mL, 5.53 mmol) was added. After being stirred at −78 °C for 20 min and at room temperature for 2.5 h, the mixture was quenched with saturated aqueous NH_4Cl (10 mL), diluted with H_2O (10 mL), and extracted with EtOAc (20 mL × 4). The combined extracts were washed with saturated brine (20 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:8) to provide 1.25 g (60% for two steps from **S7**) of **2d** as a yellow oil: TLC R_f 0.67 (EtOAc/hexane, 1:2); IR (neat) 3445, 2958, 2928, 1589, 1465, 1216, 1041, 758, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, 1H, J = 8.6 Hz), 6.98 (d, 1H, J = 2.6 Hz), 6.82 (dd, 1H, J = 8.6, 2.6 Hz), 3.80 (s, 3H), 3.78 (q, 2H, J = 6.8 Hz), 2.82 (t, 2H, J = 6.8 Hz), 1.59−1.48 (m, 6H), 1.40−1.27 (m, 6H), 1.18−1.00 (m, 6H), 0.89 (t, 9H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.5, 144.4, 136.9, 129.5, 122.9, 113.3, 64.4, 55.3, 41.2, 29.2 (3C), 27.5 (3C), 13.8 (3C), 10.7 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{39}O_2Sn$ 443.1972; found 443.1986.

*2-[4-Chloro-2-(tributylstannyl)phenyl]ethan-1-ol (**2e**).* As described for the preparation of **2b**, compound **S6c** (1.50 g, 5.32 mmol) was converted to 651 mg (27%) of **2e**. Compound **2e** was obtained as a red oil: TLC R_f 0.43 (EtOAc/hexane, 1:2); IR (neat)

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J. Org. Chem. 2021, 86, 10067−10087

3375, 2957, 2926, 1462, 1377, 1046, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, 1H, J = 2.0 Hz), 7.24−7.17 (m, 2H), 3.80 (q, 2H, J = 6.8 Hz), 2.83 (t, 2H, J = 6.8 Hz), 1.55−1.48 (m, 6H), 1.38−1.29 (m, 6H), 1.18−1.01 (m, 6H), 0.90 (t, 9H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.6, 143.3, 136.4, 132.4, 129.9, 128.4, 64.0, 41.5, 29.2 (3C), 27.5 (3C), 13.8 (3C), 10.7 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{36}ClOSn$ 447.1477; found 447.1479.

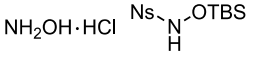
*2-[4-Fluoro-2-(tributylstannyl)phenyl]ethan-1-ol (**2f**).* As described for the preparation of **2b**, compound **S6d** (1.50 g, 5.63 mmol) was converted to 733 mg (30%) of **2f**. Compound **2f** was obtained as a red oil: TLC R_f 0.43 (EtOAc/hexane, 1:2); IR (neat) 3375, 2957, 2927, 1577, 1474, 1214, 1045, 875, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, 1H, J = 8.4, 5.2 Hz), 7.11 (dd, 1H, J = 8.4, 2.4 Hz), 6.94 (td, 1H, J = 8.4, 2.4 Hz), 3.80 (t, 2H, J = 6.8 Hz), 2.85 (t, 2H, J = 6.8 Hz), 1.62−1.43 (m, 6H), 1.39−1.27 (m, 6H), 1.19−1.00 (m, 6H), 0.90 (t, 9H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J = 247.2 Hz), 145.6 (d, J = 1.9 Hz), 140.5 (d, J = 2.8 Hz), 129.9 (d, J = 5.8 Hz), 123.1 (d, J = 17.3 Hz), 115.1 (d, J = 21.8 Hz), 64.2, 41.3, 29.2 (3C), 27.5 (3C), 13.8 (3C), 10.7 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{36}FOSn$ 431.1772; found 431.1771.

*2-[1-(Tributylstannyl)naphthalen-2-yl]ethan-1-ol (**2g**).* As described for the preparation of **2b**, compound **S6e** (988 mg, 3.31 mmol) was converted to 404 mg (26%) of **2g**. Compound **2g** was obtained as a yellow oil: TLC R_f 0.68 (EtOAc/hexane, 1:2); IR (neat) 3428, 2958, 2927, 1457, 1383, 1216, 1043, 816, 758, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, 1H, J = 8.4, 1.6 Hz), 7.81 (dd, 1H, J = 8.4, 1.6 Hz), 7.77 (d, 1H, J = 8.4 Hz), 7.46 (td, 1H, J = 8.4, 1.6 Hz), 7.42 (td, 1H, J = 8.4, 1.6 Hz), 7.35 (d, 1H, J = 8.4 Hz), 3.86 (q, 2H, J = 6.8 Hz), 3.08 (t, 2H, J = 6.8 Hz), 1.62−1.45 (m, 6H), 1.38−1.29 (m, 6H), 1.27−1.15 (m, 6H), 0.87 (t, 9H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.4, 142.7, 139.7, 132.5, 129.8, 129.2, 128.9, 127.7, 125.7, 125.0, 64.7, 42.3, 29.3 (3C), 27.5 (3C), 13.8 (3C), 13.3 (3C); HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{24}H_{38}NaOSn$ 485.1842; found 485.1853.

*2-(3′,5′-Dimethyl-4-(tributylstannyl)-[1,1′-biphenyl]-3-yl)ethan-1-ol (**2h**).* As described for the preparation of **2b**, compound **S6f** (272 mg, 0.773 mmol) was converted to 151 mg (38%) of **2h**. Compound **2h** was obtained as a pale yellow oil: TLC R_f 0.54 (EtOAc/hexane, 1:2); IR (neat) 3332, 2956, 2925, 1604, 1463, 1383, 1217, 1045, 823, 759, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.40 (m, 3H), 7.21 (br s, 2H), 6.99 (br s, 1H), 3.87 (q, 2H, J = 6.8 Hz), 2.94 (t, 2H, J = 6.8 Hz), 2.38 (s, 6H), 1.62−1.49 (m, 6H), 1.44−1.28 (m, 6H), 1.19−1.02 (m, 6H), 0.90 (t, 9H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.4, 141.60, 141.55, 141.2, 138.4 (2C), 137.6, 129.1, 127.5, 125.2 (2C), 124.8, 64.3, 42.3, 29.3 (3C), 27.6 (3C), 21.6 (2C), 13.8 (3C), 10.7 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{45}OSn$ 517.2492; found 517.2488.

*3-Methoxy-2-{3-(tributylstannyl)-[1,1′-biphenyl]-4-yl}propan-1-ol (**2i**).* As described for the preparation of **2b**, compound **S6g** (1.67 g, 4.55 mmol) was converted to 792 mg (33%) of **2i**. Compound **2i** was obtained as a yellow oil: TLC R_f 0.71 (EtOAc/hexane, 1:2); IR (neat) 3448, 2956, 2925, 1466, 1376, 1115, 1081, 1034, 765, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (br s, 1H), 7.55 (d, 2H, J = 8.4 Hz), 7.50−7.42 (m, 3H), 7.34 (td, 1H, J = 7.6, 0.8 Hz), 7.25 (d, 1H, J = 8.4 Hz), 4.05 (m, 1H), 3.83 (m, 1H), 3.78 (t, 1H, J = 8.8 Hz), 3.65 (dd, 1H, J = 8.8, 4.4 Hz), 3.41 (s, 3H), 3.11 (m, 1H), 2.72 (dd, 1H, J = 8.0, 3.6 Hz), 1.66−1.47 (m, 6H), 1.40−1.28 (m, 6H), 1.23−1.05 (m, 6H), 0.90 (t, 9H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 144.6, 141.3, 139.3, 136.0, 128.9 (2C), 127.5, 127.2 (3C), 126.4, 77.9, 67.7, 59.4, 50.8, 29.3 (3C), 27.6 (3C), 13.8 (3C), 10.7 (3C); HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{45}O_2Sn$ 533.2442; found 533.2448.

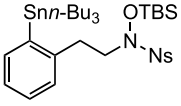
*N-(tert-Butyldimethylsilyloxy)-2-nitrobenzenesulfon-amide (**S10**).*



S9 **S10**

To a cooled (0 °C) stirred solution of hydroxylamine hydrochloride (**S9**) (1.45 g, 22.5 mmol) in DMF (50 mL) were added *tert*-butyldimethylchlorosilane (3.40 g, 22.5 mmol) and Et_3N (10.5 mL, 75.0 mmol). The mixture was stirred at room temperature for 11 h and 2-nitrobenzenesulfonyl chloride (3.34 g, 15.1 mmol) was added at 0 °C. After being stirred at room temperature for 6.5 h, the mixture was quenched with H_2O (50 mL) and extracted with EtOAc/hexane (1:4, 100 mL × 4). The combined extracts were washed with H_2O (100 mL × 2) and saturated brine (60 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to provide 3.20 g (64%) of **S10**[75] as white crystals: TLC R_f 0.33 (EtOAc/hexane, 1:3); ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, 1H, J = 6.8, 2.0 Hz), 7.90 (dd, 1H, J = 7.2, 1.6 Hz), 7.84−7.76 (m, 2H), 7.65 (br s, 1H), 0.88 (s, 9H), 0.25 (s, 6H).

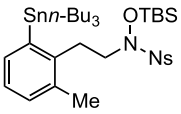
*N-(tert-Butyldimethylsilyloxy)-2-nitro-N-[2-(tributyl-stannyl)-phenethyl]benzenesulfonamide (**S11a**).*



S11a

To a cooled (0 °C) stirred solution of **2a** (5.88 g, 14.3 mmol), **S10** (3.73 g, 11.2 mmol), and PPh_3 (5.87 g, 22.4 mmol) in THF/toluene (1:3, 44 mL) was slowly added diethyl azodicarboxylate (2.2 M solution in toluene, 7.70 mL, 16.9 mmol). After being stirred at 0 °C for 1 h and at room temperature for 2 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/hexane, 1:8) to provide 7.06 g (87% from **S10**) of **S11a** as pale yellow crystals: mp 39−41 °C; TLC R_f 0.31 (EtOAc/hexane, 1:6); IR (neat) 2956, 2929, 1550, 1464, 1378, 1180, 845, 758, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08, (dd, 1H, J = 8.0, 1.6 Hz), 7.76 (td, 1H, J = 8.0, 1.6 Hz), 7.68 (td, 1H, J = 8.0, 1.6 Hz), 7.55 (dd, 1H, J = 8.0, 1.6 Hz), 7.38 (d, 1H, J = 7.2 Hz), 7.24 (m, 1H), 7.19−7.15 (m, 2H), 3.37 (t, 2H, J = 8.0 Hz), 2.96 (t, 2H, J = 8.0 Hz), 1.53−1.40 (m, 6H), 1.36−1.27 (m, 6H), 1.14−1.02 (m, 6H), 0.98 (s, 9H), 0.87 (t, 9H, J = 7.6 Hz), 0.23 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.8, 144.9, 142.6, 137.2, 134.8, 133.0, 130.8, 128.6, 128.5, 126.4, 126.1, 123.8, 57.1, 37.0, 29.3 (3C), 27.5 (3C), 26.2 (3C), 18.5, 13.8 (3C), 10.5 (3C), −4.1 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{55}N_2O_5SSiSn$ 727.2623; found 727.2603.

*N-(tert-Butyldimethylsilyloxy)-N-[2-methyl-6-(tributyl-stannyl)-phenethyl]-2-nitrobenzenesulfonamide (**S11b**).*



S11b

As described for the preparation of **S11a**, compounds **2b** and **S10** (357 mg, 1.07 mmol) were converted to 421 mg (53% from **S10**) of **S11b**. Compound **S11b** was obtained as a yellow oil: TLC R_f 0.56 (EtOAc/hexane, 1:2); IR (neat) 2957, 2929, 1550, 1380, 1258, 1181, 827, 753, 562 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, 1H, J = 8.0 Hz), 7.75 (t, 1H, J = 8.0 Hz), 7.67 (td, 1H, J = 8.0, 1.2 Hz), 7.51 (dd, 1H, J = 8.0, 1.2 Hz), 7.25 (m, 1H), 7.13−7.08 (m, 2H), 3.16 (t, 2H, J = 8.0 Hz), 2.97 (t, 2H, J = 8.0 Hz), 2.25 (s, 3H), 1.57−1.40 (m, 6H), 1.37−1.27 (m, 6H), 1.18−1.05 (m, 6H), 1.03 (s, 9H), 0.89 (t, 9H, J = 7.6 Hz), 0.34 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.8, 143.5, 142.7, 136.3, 135.2, 134.8, 132.6, 131.1, 130.8, 126.6, 126.2, 123.8, 55.2, 35.6, 29.3 (3C), 27.5 (3C), 26.4 (3C), 20.5, 18.6, 13.8 (3C), 10.7 (3C), −3.6 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{57}N_2O_5SSiSn$ 741.2779; found 741.2743.

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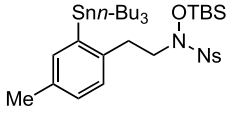
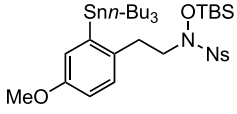
*N-(tert-Butyldimethylsilyloxy)-N-[4-methyl-2-(tributyl-stannyl)-phenethyl]-2-nitrobenzenesulfonamide (**S11c**).*



S11c

As described for the preparation of **S11a**, compounds **2c** and **S10** (329 mg, 0.989 mmol) were converted to 682 mg (93% from **S10**) of **S11c**. Compound **S11c** was obtained as white crystals: mp 83−85 °C; TLC R_f 0.45 (EtOAc/hexane, 1:3); IR (neat) 2957, 2929, 1550, 1379, 1181, 829, 758, 579 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, 1H, J = 8.0, 0.9 Hz), 7.75 (td, 1H, J = 8.0, 0.9 Hz), 7.67 (td, 1H, J = 8.0, 0.9 Hz), 7.54 (dd, 1H, J = 8.0, 0.9 Hz), 7.18 (br s, 1H), 7.09−7.07 (m, 2H), 3.35 (t, 2H, J = 8.0 Hz), 2.92 (t, 2H, J = 8.0 Hz), 2.29 (s, 3H), 1.53−1.40 (m, 6H), 1.37−1.28 (m, 6H), 1.15−1.01 (m, 6H), 0.98 (s, 9H), 0.88 (t, 9H, J = 7.2 Hz), 0.25 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.8, 142.4, 141.7, 137.8, 135.3, 134.8, 133.0, 130.8, 129.4, 128.3, 126.5, 123.8, 57.2, 36.4, 29.3 (3C), 27.5 (3C), 26.3 (3C), 21.2, 18.5, 13.8 (3C), 10.4 (3C), −4.1 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{57}N_2O_5SSiSn$ 741.2779; found 741.2806.

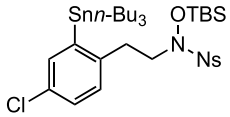
*N-(tert-Butyldimethylsilyloxy)-N-[4-methoxy-2-(tributyl-stannyl)-phenethyl]-2-nitrobenzenesulfonamide (**S11d**).*



S11d

As described for the preparation of **S11a**, compounds **2d** and **S10** (858 mg, 2.58 mmol) were converted to 1.82 g (93% from **S10**) of **S11d**. Compound **S11d** was obtained as white crystals: mp 85−87 °C; TLC R_f 0.30 (EtOAc/hexane, 1:6); IR (neat) 2956, 2930, 1550, 1379, 1180, 828, 748, 585 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, 1H, J = 8.0, 0.9 Hz), 7.76 (td, 1H, J = 8.0, 0.9 Hz), 7.68 (td, 1H, J = 8.0, 0.9 Hz), 7.54 (dd, 1H, J = 8.0, 0.9 Hz), 7.12 (d, 1H, J = 8.4 Hz), 6.94 (d, 1H, J = 2.8 Hz), 6.78 (dd, 1H, J = 8.4, 2.8 Hz), 3.78 (s, 3H), 3.33 (t, 2H, J = 8.0 Hz), 2.90 (t, 2H, J = 8.0 Hz), 1.56−1.40 (m, 6H), 1.36−1.27 (m, 6H), 1.15−1.04 (m, 6H), 0.98 (s, 9H), 0.88 (t, 9H, J = 7.6 Hz), 0.24 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.5, 149.6, 144.0, 136.8, 134.8, 133.0, 130.8, 129.3, 126.3, 123.8, 122.7, 113.4, 57.3, 55.2, 36.0, 29.3 (3C), 27.5 (3C), 26.2 (3C), 18.5, 13.8 (3C), 10.5 (3C), −4.1 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{57}N_2O_6SSiSn$ 757.2729; found 757.2739.

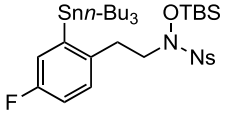
*N-(tert-Butyldimethylsilyloxy)-N-[4-chloro-2-(tributyl-stannyl)-phenethyl]-2-nitrobenzenesulfonamide (**S11e**).*



S11e

As described for the preparation of **S11a**, compounds **2e** and **S10** (300 mg, 0.901 mmol) were converted to 759 mg (quant. from **S10**) of **S11e**. Compound **S11e** was obtained as pale red crystals: mp 75−77 °C; TLC R_f 0.72 (EtOAc/hexane, 1:3); IR (neat) 2956, 2929, 1550, 1381, 1180, 827, 770, 583, 563 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, 1H, J = 8.0, 1.2 Hz), 7.77 (td, 1H, J = 8.0, 1.2 Hz), 7.69 (td, 1H, J = 8.0, 1.2 Hz), 7.55 (dd, 1H, J = 8.0, 1.2 Hz), 7.31 (d, 1H, J = 2.4 Hz), 7.20 (dd, 1H, J = 8.0, 2.4 Hz), 7.11 (d, 1H, J = 8.0 Hz), 3.34 (t, 2H, J = 7.2 Hz), 2.93 (t, 2H, J = 7.2 Hz), 1.54−1.40 (m, 6H), 1.36−1.27 (m, 6H), 1.16−0.99 (m, 6H), 0.97 (s, 9H), 0.88 (t, 9H, J = 7.6 Hz), 0.21 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.8, 145.3, 143.1, 136.4, 134.9, 133.2, 132.5, 130.8, 129.7, 128.5, 126.1, 123.8, 56.9, 36.2, 29.2 (3C), 27.5 (3C), 26.2 (3C), 18.4, 13.8 (3C), 10.6 (3C), −4.2 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{54}ClN_2O_5SSiSn$ 761.2233; found 761.2262.

*N-(tert-Butyldimethylsilyloxy)-N-[4-fluoro-2-(tributyl-stannyl)-phenethyl]-2-nitrobenzenesulfonamide (**S11f**).*



S11f

As described for the preparation of **S11a**, compounds **2f** and **S10** (341 mg, 1.03 mmol) were converted to 996 mg (quant. from **S10**) of **S11f**. Compound **S11f** was obtained as pale red crystals: mp 68−71 °C; TLC R_f 0.72 (EtOAc/hexane, 1:3); IR (neat) 2957, 2930, 1578, 1474, 1379, 1255, 1180, 845, 749, 583 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, 1H, J = 8.0, 1.2 Hz), 7.77 (td, 1H, J = 8.0, 1.2 Hz), 7.69 (td, 1H, J = 8.0, 1.2 Hz), 7.55 (dd, 1H, J = 8.0, 1.2 Hz), 7.15 (dd, 1H, J = 8.4, 5.2 Hz), 7.07 (dd, 1H, J = 8.4, 2.8 Hz), 6.91 (td, 1H, J = 8.4, 2.8 Hz), 3.33 (t, 2H, J = 8.0 Hz), 2.93 (t, 2H, J = 8.0 Hz), 1.52−1.44 (m, 6H), 1.36−1.27 (m, 6H), 1.15−1.00 (m, 6H), 0.97 (s, 9H), 0.88 (t, 9H, J = 7.6 Hz), 0.21 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J = 247.2 Hz), 149.8, 145.4 (J = 1.9 Hz), 140.4 (J = 2.9 Hz), 134.9, 133.2, 130.8, 129.8 (d, J = 6.7 Hz), 126.1, 123.7, 123.0 (d, J = 17.3 Hz), 115.2 (d, J = 20.1 Hz), 57.2, 36.1, 29.2 (3C), 27.5 (3C), 26.2 (3C), 18.4, 13.8 (3C), 10.5 (3C), −4.2 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{54}FN_2O_5SSiSn$ 745.2529; found 745.2492.

*O-(tert-Butyldimethylsilyl)-N-[2-(tributylstannyl)phenethyl]-hydroxylamine (**3a**).* To a cooled (0 °C) stirred solution of **S11a** (3.21 g, 4.42 mmol) in DMF (25 mL) were added 2-mercaptoethanol (0.930 mL, 13.3 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.00 mL, 13.4 mmol). After being stirred at room temperature for 3 h, the mixture was quenched with H_2O (30 mL) and extracted with EtOAc/hexane (1:4, 50 mL × 3). The combined extracts were washed with saturated brine (50 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:20) to provide 1.83 g (77%) of **3a** as a yellow oil: TLC R_f 0.66 (EtOAc/hexane, 1:8); IR (neat) 2956, 2928, 1464, 1252, 864, 837, 780, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, 1H, J = 7.2 Hz), 7.26−7.22 (m, 2H), 7.16 (m, 1H), 5.10 (br s, 1H), 3.10 (t, 2H, J = 8.0 Hz), 2.82 (t, 2H, J = 8.0 Hz), 1.53−1.42 (m, 6H), 1.37−1.28 (m, 6H), 1.16−0.99 (m, 6H), 0.93 (s, 9H), 0.88 (t, 9H, J = 7.2 Hz), 0.12 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.4, 142.5, 137.1, 128.5 (2C), 125.7, 56.2, 36.8, 29.3 (3C), 27.6 (3C), 26.5 (3C), 18.2, 13.8 (3C), 10.6 (3C), −5.2 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{52}NOSiSn$ 542.2840; found 542.2855.

*O-(tert-Butyldimethylsilyl)-N-[2-methyl-6-(tributyl-stannyl)-phenethyl]hydroxylamine (**3b**).* As descried for the preparation of **3a**, compound **S11b** (120 mg, 0.162 mmol) was converted to 101 mg (quant.) of **3b** (a mixture of rotamer). Compound **3b** was obtained as a yellow oil: TLC R_f 0.65 (EtOAc/hexane, 1:10); IR (neat) 2957, 2928, 1463, 1253, 838, 759, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, 1H, J = 6.0, 2.8 Hz), 7.17−7.09 (m, 2H), 5.09 (br s, 1H), 3.09 (t, 2H × 1/6, J = 7.2 Hz), 3.00−2.96 (m, 2H × 5/6), 2.87−2.83 (m, 2H), 2.36 (s, 3H × 5/6), 2.33 (s, 3H × 1/6), 1.60−1.44 (m, 6H), 1.40−1.29 (m, 6H), 1.16−0.99 (m, 6H), 0.94 (s, 9H × 5/6), 0.93 (s, 9H × 1/6), 0.89 (t, 9H, J = 7.2 Hz), 0.13 (s, 6H × 5/6), 0.11 (s, 6H × 1/6); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) for major rotamer δ 144.6, 143.1, 136.3, 134.9, 130.9, 126.1, 55.1, 35.4, 29.3 (3C), 27.6 (3C), 26.5 (3C), 20.3, 18.2, 13.8 (3C), 10.8 (3C), −5.2 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{54}NOSiSn$ 556.2997; found 556.2997.

*O-(tert-Butyldimethylsilyl)-N-[4-methyl-2-(tributyl-stannyl)-phenethyl]hydroxylamine (**3c**).* As described for the preparation of **3a**, compound **S11c** (575 mg, 0.778 mmol) was converted to 355 mg (82%) of **3c**. Compound **3c** was obtained as a yellow oil: TLC R_f 0.59 (EtOAc/hexane, 1:10); IR (neat) 2956, 2928, 1463, 1250, 837, 779 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, 1H, J = 1.4 Hz), 7.16 (d, 1H, J = 8.0 Hz), 7.09 (dd, 1H, J = 8.0, 1.4 Hz), 5.11 (br s, 1H), 3.10 (t, 2H, J = 7.2 Hz), 2.79 (t, 2H, J = 7.2 Hz), 2.32 (s, 3H), 1.62−1.43 (m, 6H), 1.39−1.30 (m, 6H), 1.17−0.99 (m, 6H), 0.94 (s, 9H), 0.90 (t, 9H, J = 7.2 Hz), 0.13 (s, 6H); $^{13}C\{^1H\}$ NMR (100

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J. Org. Chem. 2021, 86, 10067−10087

MHz, $CDCl_3$) δ 143.3, 142.2, 137.8, 134.9, 129.3, 128.3, 56.3, 36.2, 29.3 (3C), 27.6 (3C), 26.5 (3C), 21.2, 18.2, 13.8 (3C), 10.5 (3C), −5.2 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{54}NOSiSn$ 556.2997; found 556.2978.

*O-(tert-Butyldimethylsilyl)-N-[4-methoxy-2-(tributyl-stannyl)-phenethyl]hydroxylamine (**3d**).* As described for the preparation of **3a**, compound **S11d** (1.74 g, 2.30 mmol) was converted to 1.05 g (80%) of **3d**. Compound **3d** was obtained as a yellow oil: TLC R_f 0.67 (EtOAc/hexane, 1:10); IR (neat) 2956, 2928, 1590, 1464, 1385, 1241, 1044, 837, 759, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, 1H, J = 8.8 Hz), 6.97 (d, 1H, J = 2.8 Hz), 6.81 (dd, 1H, J = 8.8, 2.8 Hz), 5.10 (br s, 1H), 3.80 (s, 3H), 3.07 (t, 2H, J = 7.2 Hz), 2.78 (t, 2H, J = 7.2 Hz), 1.63−1.44 (m, 6H), 1.39−1.30 (m, 6H), 1.18−1.01 (m, 6H), 0.94 (s, 9H), 0.90 (t, 9H, J = 7.2 Hz), 0.13 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.3, 143.9, 138.3, 129.2, 122.6, 113.3, 56.3, 55.2, 35.7, 29.3 (3C), 27.6 (3C), 26.5 (3C), 18.2, 13.8 (3C), 10.6 (3C), −5.2 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{54}NO_2SiSn$ 572.2946; found 572.2930.

*O-(tert-Butyldimethylsilyl)-N-[4-chloro-2-(tributyl-stannyl)-phenethyl]hydroxylamine (**3e**).* As described for the preparation of **3a**, compound **S11e** (317 mg, 0.417 mmol) was converted to 177 mg (74%) of **3e**. Compound **3e** was obtained as a yellow oil: TLC R_f 0.67 (EtOAc/hexane, 1:10); IR (neat) 2958, 2929, 1463, 1384, 1216, 839, 758, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, 1H, J = 2.4 Hz), 7.22 (dd, 1H, J = 8.4, 2.4 Hz), 7.17 (d, 1H, J = 8.4 Hz), 5.08 (br s, 1H), 3.08 (t, 2H, J = 7.2 Hz), 2.80 (t, 2H, J = 7.2 Hz), 1.59−1.42 (m, 6H), 1.39−1.28 (m, 6H), 1.18−1.03 (m, 6H), 0.93 (s, 9H), 0.90 (t, 9H, J = 7.6 Hz), 0.12 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 144.6, 136.3, 132.0, 129.8, 128.4, 56.0, 36.1, 29.2 (3C), 27.5 (3C), 26.4 (3C), 18.2, 13.8 (3C), 10.6 (3C), −5.2 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{51}ClNOSiSn$ 576.2450; found 576.2439.

*O-(tert-Butyldimethylsilyl)-N-[4-fluoro-2-(tributyl-stannyl)-phenethyl]hydroxylamine (**3f**).* As described for the preparation of **3a**, compound **S11f** (310 mg, 0.417 mmol) was converted to 165 mg (71%) of **3f**. Compound **3f** was obtained as a yellow oil: TLC R_f 0.62 (EtOAc/hexane, 1:10); IR (neat) 2958, 2929, 1577, 1473, 1384, 1216, 872, 838, 759, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, 1H, J = 8.4, 5.2 Hz), 7.08 (dd, 1H, J = 8.4, 2.8 Hz), 6.93 (td, 1H, J = 8.4, 2.8 Hz), 5.08 (br s, 1H), 3.08 (t, 2H, J = 7.2 Hz), 2.80 (t, 2H, J = 7.2 Hz), 1.61−1.42 (m, 6H), 1.38−1.29 (m, 6H), 1.18−1.01 (m, 6H), 0.93 (s, 9H), 0.89 (t, 9H, J = 7.2 Hz), 0.12 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J = 246.2 Hz), 145.1 (d, J = 2.0 Hz), 141.8 (d, J = 2.9 Hz), 129.7 (d, J = 6.7 Hz), 122.9 (d, J = 17.2 Hz), 115.1 (d, J = 21.1 Hz), 56.2, 35.9, 29.2 (3C), 27.5 (3C), 26.4 (3C), 18.2, 13.8 (3C), 10.6 (3C), −5.2 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{51}FNOSiSn$ 560.2746; found 560.2751.

*N-Benzyl-O-(tert-butyldimethylsilyl)-N-[2-(tributyl-stannyl)-phenethyl]hydroxylamine (**4a**).* To a stirred solution of **3a** (873 mg, 1.62 mmol) in DMF (8 mL) were added BnBr (0.290 mL, 2.42 mmol) and *N*,*N*-diisopropylethylamine (0.560 mL, 3.22 mmol). After being stirred at 60 °C for 34 h, the mixture was quenched with H_2O (10 mL) and extracted with EtOAc/hexane (1:4, 20 mL × 4). The combined extracts were washed with saturated brine (20 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$/hexane, 1:5:200) to provide 775 mg (76%) of **4a** as a yellow oil. A small amount of **4a** was further purified by preparative TLC (EtOAc/hexane, 1:50): TLC R_f 0.82 ($MeOH/CH_2Cl_2$/hexane, 1:5:160), 0.62 (EtOAc/hexane, 1:50); IR (neat) 2957, 2928, 2855, 1463, 1254, 1217, 890, 837, 759, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.29 (m, 5H), 7.24−7.11 (m, 4H), 4.02 (br, 1H), 3.76 (br, 1H), 2.83 (br, 4H), 1.50−1.36 (m, 6H), 1.34−1.25 (m, 6H), 0.94 (s, 9H), 1.09−0.92 (m, 6H), 0.87 (t, 9H, J = 6.8 Hz), 0.08 (br, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.1, 142.3, 137.3, 136.9, 129.9 (2C), 128.7, 128.5, 128.4 (2C), 127.5, 125.5, 65.7, 62.1, 36.9, 29.2 (3C), 27.5 (3C), 26.4 (3C), 18.0, 13.9 (3C), 10.4 (3C), −4.4 (br, 2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{58}NOSiSn$ 632.3310; found 632.3297.

*N-Benzyl-O-(tert-butyldimethylsilyl)-N-[2-methyl-6-(tributylstannyl)phenethyl]hydroxylamine (**4b**).* As described for the preparation of **4a**, compound **3b** (48.8 mg, 88.0 μmol) was converted to 47.8 mg (84%) of **4b** (a mixture of rotamer). Compound **4b** was obtained as a yellow oil: TLC R_f 0.40 (EtOAc/hexane, 1:50); IR (neat) 2956, 2928, 2855, 1462, 1254, 891, 836, 759, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.22 (m, 5H), 7.18 (dd, 1H, J = 5.6, 2.8 Hz), 7.10−7.02 (m, 2H), 4.10 (br, 1H), 3.66 (br, 1H), 3.07 (br, 1H), 2.78 (br, 3H), 2.28 (s, 3H × 5/6), 2.26 (s, 3H × 1/6), 1.52−1.35 (m, 6H), 1.32−1.23 (m, 6H), 0.97 (s, 9H), 0.88 (t, 9H, J = 7.6 Hz), 0.95−0.86 (m, 6H), 0.22 (br, 3H), 0.12 (br, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) for major rotamer δ 145.0, 143.1, 137.3, 136.4, 134.8, 130.9, 129.7 (2C), 128.4 (2C), 127.5, 126.0, 66.3, 60.1, 35.5, 29.3 (3C), 27.5 (3C), 26.4 (3C), 20.3, 18.0, 13.9 (3C), 10.7 (3C), −3.8 (br), −4.5 (br); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{60}NOSiSn$ 646.3466; found 646.3435.

*N-Benzyl-O-(tert-butyldimethylsilyl)-N-[4-methyl-2-(tributylstannyl)phenethyl]hydroxylamine (**4c**).* As described for the preparation of **4a**, compound **3c** (224 mg, 0.404 mmol) was converted to 262 mg (quant.) of **4c** (a mixture of rotamer). Compound **4c** was obtained as a yellow oil: TLC R_f 0.37 (EtOAc/hexane, 1:50); IR (neat) 2956, 2928, 2855, 1462, 1384, 1253, 890, 836, 779, 759, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.24 (m, 5H), 7.14 (br s, 1H), 7.08−7.03 (m, 2H), 4.01 (br, 1H), 3.76 (br, 1H), 2.81 (br, 4H), 2.31 (s, 3H × 1/6), 2.28 (s, 3H × 5/6), 1.55−1.41 (m, 6H), 1.37−1.26 (m, 6H), 1.16−0.94 (m, 6H), 0.94 (s, 9H), 0.88 (t, 9H, J = 7.6 Hz), 0.10 (br, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) for major rotamer δ 144.0, 142.1, 137.5, 137.3, 134.7, 129.9 (2C), 129.3, 128.5, 128.3 (2C), 127.5, 65.7, 62.3, 36.4, 29.3 (3C), 27.5 (3C), 26.4 (3C), 21.2, 18.0, 13.9 (3C), 10.4 (3C), −4.3 (br, 2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{60}NOSiSn$ 646.3466; found 646.3481.

*N-Benzyl-O-(tert-butyldimethylsilyl)-N-[4-methoxy-2-(tributylstannyl)phenethyl]-hydroxylamine (**4d**).* As described for the preparation of **4a**, compound **3d** (466 mg, 0.816 mmol) was converted to 621 mg (quant.) of **4d**. Compound **4d** was obtained as a yellow oil: TLC R_f 0.71 ($MeOH/CH_2Cl_2$/hexane, 1:5:320); IR (neat) 2956, 2929, 2855, 1590, 1473, 1230, 1044, 909, 891, 837, 780, 734, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.28 (m, 5H), 7.13 (d, 1H, J = 8.8 Hz), 6.95 (d, 1H, J = 2.4 Hz), 6.80 (dd, 1H, J = 8.8, 2.4 Hz), 4.06 (br, 1H), 3.80 (br, 1H), 3.80 (s, 3H), 2.85 (br, 4H), 1.61−1.42 (m, 6H), 1.39−1.30 (m, 6H), 1.16−1.02 (m, 6H), 0.99 (s, 9H), 0.92 (t, 9H, J = 8.0 Hz), 0.13 (br, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.2, 143.6, 139.0, 137.3, 129.9 (2C), 129.4, 128.3 (2C), 127.5, 122.3, 113.3, 65.7, 62.4, 55.2, 35.9, 29.3 (3C), 27.5 (3C), 26.4 (3C), 18.0, 13.9 (3C), 10.5 (3C), −4.2 (br, 2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{60}NO_2SiSn$ 662.3415; found 662.3446.

*N-Benzyl-O-(tert-butyldimethylsilyl)-N-[4-chloro-2-(tributylstannyl)phenethyl]hydroxylamine (**4e**).* As described for the preparation of **4a**, compound **3e** (103 mg, 0.179 mmol) was converted to 106 mg (89%) of **4e**. Compound **4e** was obtained as a yellow oil: TLC R_f 0.43 (EtOAc/hexane, 1:50); IR (neat) 3020, 2958, 2929, 1463, 1384, 1216, 891, 837, 758, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.25 (m, 6H), 7.16 (dd, 1H, J = 8.0, 2.4 Hz), 7.07 (d, 1H, J = 8.0 Hz), 4.02 (br, 1H), 3.74 (br, 1H), 2.77 (br, 4H), 1.53−1.39 (m, 6H), 1.35−1.25 (m, 6H), 1.12−0.98 (m, 6H), 0.94 (s, 9H), 0.88 (t, 9H, J = 7.2 Hz), 0.09 (br, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.3, 144.9, 137.1, 136.0, 131.7, 129.9, 129.8 (2C), 128.4 (2C), 128.3, 127.6, 65.7, 61.9, 36.2, 29.2 (3C), 27.4 (3C), 26.3 (3C), 18.0, 13.8 (3C), 10.5 (3C), −4.4 (br, 2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{57}ClNOSiSn$ 666.2920; found 666.2900.

*N-Benzyl-O-(tert-butyldimethylsilyl)-N-[4-fluoro-2-(tributylstannyl)phenethyl]hydroxylamine (**4f**).* As described for the preparation of **4a**, compound **3f** (95.7 mg, 0.171 mmol) was converted to 111 mg (100%) of **4f**. Compound **4f** was obtained as a yellow oil: TLC R_f 0.46 (EtOAc/hexane, 1:50); IR (neat) 2957, 2928, 2855, 1577, 1473, 1361, 1216, 877, 837, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.25 (m, 5H), 7.11 (dd, 1H, J = 8.4, 0.9 Hz),

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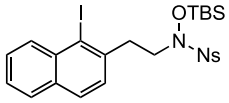
J. Org. Chem. 2021, 86, 10067−10087

7.02 (dd, 1H, J = 8.4, 2.8 Hz), 6.88 (td, 1H, J = 8.4, 2.8 Hz), 4.04 (br, 1H), 3.74 (br, 1H), 2.80 (br, 4H), 1.55−1.36 (m, 6H), 1.34−1.25 (m, 6H), 1.13−0.98 (m, 6H), 0.94 (s, 9H), 0.88 (t, 9H, J = 7.2 Hz), 0.10 (br, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.0 (d, J = 236.7 Hz), 144.9 (d, J = 1.9 Hz), 142.5 (d, J = 2.8 Hz), 137.2, 129.9 (2C), 129.8, 128.4 (2C), 127.6, 122.5 (d, J = 17.3 Hz), 115.0 (d, J = 21.1 Hz), 65.7, 62.1, 36.1, 29.2 (3C), 27.5 (3C), 26.3 (3C), 18.0, 13.8 (3C), 10.5 (3C), −4.2 (br, 2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{57}FNOSiSn$ 650.3215; found 650.3245.

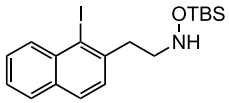
*N-(tert-Butyldimethylsilyloxy)-N-[2-(1-iodonaphthalen-2-yl)-ethyl]-2-nitrobenzenesulfonamide (**S12**).*



S12

To a cooled (0 °C) stirred solution of **S6e** (1.11 g, 3.71 mmol), **S10** (1.12 g, 3.37 mmol), and PPh_3 (1.31 g, 5.01 mmol) in THF/toluene (1:3, 11 mL) was slowly added diethyl azodicarboxylate (2.2 M solution in toluene, 2.30 mL, 5.06 mmol). After being stirred at 0 °C for 30 min and at room temperature for 4.5 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/hexane, 1:2) to provide 1.80 g (87%) of **S12** as yellow crystals: mp 150−152 °C; TLC R_f 0.42 (EtOAc/hexane, 1:2); IR (neat) 2954, 2930, 1547, 1383, 1179, 827, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, 1H, J = 8.0 Hz), 8.12 (d, 1H, J = 8.0 Hz), 7.78−7.75 (m, 3H), 7.70 (t, 1H, J = 8.0 Hz), 7.56 (t, 2H, J = 8.4 Hz), 7.47 (t, 2H, J = 8.4 Hz), 3.54 (t, 2H, J = 6.8 Hz), 3.38 (t, 2H, J = 6.8 Hz), 0.97 (s, 9H), 0.19 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.5, 135.2, 134.9, 133.3, 133.1, 132.9, 130.9, 129.2, 128.4, 128.04, 127.96 (2C), 126.40, 126.37, 123.7, 105.9, 55.2, 40.4, 26.2 (3C), 18.3, −4.3 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{30}IN_2O_5SSi$ 613.0689; found 613.0681.

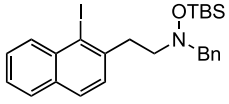
*O-(tert-Butyldimethylsilyl)-N-[2-(1-iodonaphthalen-2-yl)ethyl]-hydroxylamine (**S13**).*



S13

To a cooled (0 °C) stirred solution of **S12** (1.60 g, 2.61 mmol) in DMF (9 mL) were added 2-mercaptoethanol (0.550 mL, 7.88 mmol) and DBU (1.17 mL, 7.84 mmol). After being stirred at room temperature for 3.5 h, the mixture was quenched with H_2O (20 mL) and extracted with EtOAc/hexane (1:4, 50 mL × 6). The combined extracts were washed with H_2O (100 mL × 2) and saturated brine (100 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:60) to provide 958 mg (86%) of **S13** as a yellow oil: TLC R_f 0.50 (EtOAc/hexane, 1:10); IR (neat) 3255, 3051, 2954, 2928, 2855, 1620, 1471, 1252, 1048, 881, 838, 780, 747 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (br d, 1H, J = 8.4 Hz), 7.75 (br d, 2H, J = 8.4 Hz), 7.56 (td, 1H, J = 8.4, 1.6 Hz), 7.48 (td, 1H, J = 8.4, 1.6 Hz), 7.39 (d, 1H, J = 8.4 Hz), 5.11 (br s, 1H), 3.29 (t, 2H, J = 6.8 Hz), 3.21 (t, 2H, J = 6.8 Hz), 0.94 (s, 9H), 0.13 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 135.3, 132.94, 132.88, 128.8, 128.3, 127.93, 127.89, 126.2, 105.7, 54.2, 40.4, 26.5 (3C), 18.2, −5.2 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{27}INOSi$ 428.0907; found 428.0893.

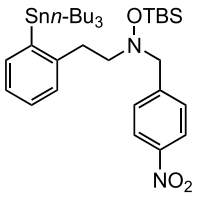
*N-Benzyl-O-(tert-butyldimethylsilyl)-N-[2-(1-iodonaphthalen-2-yl)ethyl]hydroxylamine (**S14**).*



S14

To a stirred solution of **S13** (884 mg, 2.07 mmol) in DMF (20 mL) were added BnBr (0.380 mL, 3.18 mmol) and *N,N*-diisopropylethylamine (0.720 mL, 4.13 mmol). After being stirred at 60 °C for 38 h, the mixture was quenched with H_2O (30 mL) and extracted with EtOAc/hexane (1:4, 75 mL × 4). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:40) to provide 1.12 g (quant.) of **S14** as white crystals: mp 65−67 °C; TLC R_f 0.31 (EtOAc/hexane, 1:50); IR (neat) 3030, 2954, 2855, 1461, 1385, 1253, 884, 836, 780, 750, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (br d, 1H, J = 8.4 Hz), 7.72 (t, 2H, J = 8.8 Hz), 7.55 (td, 1H, J = 8.0, 1.2 Hz), 7.46 (td, 1H, J = 8.0, 1.2 Hz), 7.39 (d, 2H, J = 6.8 Hz), 7.36−7.27 (m, 4H), 4.00 (br, 2H), 3.31 (br, 2H), 2.99 (br, 2H), 0.96 (s, 9H), 0.09 (br, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.6, 137.4, 135.2, 132.9, 132.8, 130.1 (2C), 128.9, 128.34 (2C), 128.24, 127.8, 127.7, 127.5, 126.1, 105.6, 64.6, 59.3, 39.5, 26.4 (3C), 18.0, −4.6 (br, 2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{33}INOSi$ 518.1376; found 518.1401.

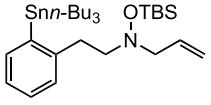
*O-(tert-Butyldimethylsilyl)-N-(4-nitrobenzyl)-N-[2-(tributylstannyl)phenethyl]hydroxylamine (**S15**).*



S15

To a stirred solution of **3a** (273 mg, 0.505 mmol) in DMF (3 mL) were added 4-nitrobenzyl bromide (163 mg, 0.756 mmol) and *N,N*-diisopropylethylamine (0.175 mL, 1.00 mmol). The mixture was stirred at 60 °C for 16.5 h, and 4-nitrobenzyl bromide (122 mg, 0.566 mmol) and *N,N*-diisopropylethylamine (0.130 mL, 0.746 mmol) were added. After being stirred at 60 °C for 13.5 h, the mixture was quenched with H_2O (5 mL) and extracted with EtOAc/hexane (1:4, 5 mL × 6). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:50) to provide 280 mg (82%) of **S15** as a yellow oil. A small amount of **S15** was further purified by preparative TLC (EtOAc/hexane, 1:50): TLC R_f 0.62 (EtOAc/hexane, 1:50); IR (neat) 2957, 2928, 2856, 1607, 1525, 1464, 1347, 1255, 893, 851, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, 2H, J = 8.4 Hz), 7.50 (d, 2H, J = 8.4 Hz), 7.36 (d, 1H, J = 7.6 Hz), 7.27−7.23 (m, 1H), 7.18−7.13 (m, 2H), 3.98 (br, 2H), 2.85 (br, 4H), 1.56−1.38 (m, 6H), 1.36−1.26 (m, 6H), 1.12−0.99 (m, 6H), 0.94 (s, 9H), 0.88 (t, 9H, J = 7.2 Hz), 0.07 (br, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.5, 146.5, 144.8, 142.1, 137.0, 130.7 (2C), 128.7, 128.6, 125.8, 123.6 (2C), 64.7, 62.6, 36.9, 29.3 (3C), 27.5 (3C), 26.2 (3C), 17.9, 13.8 (3C), 10.5 (3C), −4.4 (br, 2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{57}N_2O_3SiSn$ 677.3160; found 677.3188.

*N-Allyl-O-(tert-butyldimethylsilyl)-N-[2-(tributyl-stannyl)-phenethyl]hydroxylamine (**S16**).*



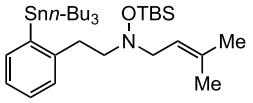
S16

To a stirred solution of **3a** (264 mg, 0.489 mmol) in DMF (2 mL) were added 3-bromopropene (54 μL, 0.64 mmol) and *N,N*-diisopropylethylamine (0.130 mL, 0.746 mmol). After being stirred at 60 °C for 39.5 h, the mixture was quenched with H_2O (8 mL) and extracted with EtOAc/hexane (1:4, 10 mL × 8). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:50) to provide 138 mg (49%) of **S16** as a yellow oil. A small amount of **S16** was further purified by preparative TLC (EtOAc/hexane, 1:50): TLC R_f 0.58 (EtOAc/hexane, 1:50); IR (neat) 3053, 2957, 2928, 2856, 1723, 1464, 1253, 1217, 992, 889, 837, 759, 668

https://doi.org/10.1021/acs.joc.1c00820
J. Org. Chem. 2021, 86, 10067−10087

cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, 1H, J = 6.8, 0.8 Hz), 7.29−7.22 (m, 2H), 7.16 (td, 1H, J = 6.8, 2.0 Hz), 5.93 (m, 1H), 5.18 (br d, 1H, J = 14.8 Hz), 5.13 (br d, 1H, J = 8.0 Hz), 3.42 (br, 2H), 2.87 (br, 4H), 1.62−1.43 (m, 6H), 1.39−1.30 (m, 6H), 1.18−1.01 (m, 6H), 0.95 (s, 9H), 0.90 (t, 9H, J = 7.2 Hz), 0.17 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.2, 142.2, 136.9, 133.8, 128.8, 128.5, 125.6, 118.5, 64.3, 62.0, 37.2, 29.3 (3C), 27.6 (3C), 26.3 (3C), 18.0, 13.8 (3C), 10.5 (3C), −4.3 (br, 2C); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{29}H_{56}NOSiSn$ 582.3153; found 582.3167.

*O-(tert-Butyldimethylsilyl)-N-(3-methylbut-2-en-1-yl)-N-[2-(tributylstannyl)phenethyl]-hydroxylamine (**S17**).*



S17

To a stirred solution of **3a** (172 mg, 0.319 mmol) in DMF (2 mL) were added 1-bromo-3-methyl-2-butene (57 μL, 0.49 mmol) and *N*,*N*-diisopropylethylamine (0.110 mL, 0.631 mmol). After being stirred at 60 °C for 42 h, the mixture was quenched with H_2O (2 mL) and extracted with EtOAc/hexane (1:4, 5 mL × 4). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:50) to provide 65.3 mg (34%) of **S17** as a yellow oil. A small amount of **S17** was further purified by preparative TLC (EtOAc/hexane, 1:50): TLC R_f 0.37 (EtOAc/hexane, 1:50); IR (neat) 2958, 2929, 1463, 1384, 1256, 1216, 893, 836, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, 1H, J = 6.8 Hz), 7.26−7.22 (m, 2H), 7.15 (td, 1H, J = 6.8, 2.0 Hz), 5.26 (t, 1H, J = 7.2 Hz), 3.36 (br, 2H), 2.79 (br, 4H), 1.71 (s, 3H), 1.62 (s, 3H), 1.58−1.43 (m, 6H), 1.38−1.29 (m, 6H), 1.17−1.00 (m, 6H), 0.94 (s, 9H), 0.89 (t, 9H, J = 7.6 Hz), 0.15 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.4, 142.3, 136.9, 135.5, 128.8, 128.5, 125.5, 120.0, 62.1, 59.1, 37.3, 29.3 (3C), 27.6 (3C), 26.4 (3C), 26.1, 18.4, 18.0, 13.9 (3C), 10.5 (3C), −4.2 (2C); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{31}H_{60}NOSiSn$ 610.3466; found 610.3447.

*1-(Benzyloxy)indoline (**6a**).* To a stirred solution of **4a** (192 mg, 0.305 mmol) in CH_2Cl_2 (3 mL) was added PhI(OH)OTs (Koser reagent, 180 mg, 0.460 mmol). After being stirred at room temperature in the dark for 15 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (MeOH/CH_2Cl_2, 1:10) to provide **5a**, containing a small amount of tin-derived impurities, as a yellow oil. To remove impurities, the obtained oil was treated with hexane (50 mL), sonicated for 30 min, and filtered through a filter paper to afford white crystals, which were recrystallized from Et_2O (50 mL), sonicated for 30 min, and filtered through a filter paper to give 131 mg (60%) of pure **5a** as white crystals: mp 132−134 °C (decomposition); TLC R_f 0.13 (MeOH/CH_2Cl_2, 1:10); IR (neat) 2954, 2978, 1471, 1194, 1131, 1044, 1015, 887, 836, 753, 691, 573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 1H, J = 8.4 Hz), 7.68 (dd, 2H, J = 8.4, 0.9 Hz), 7.57−7.55 (m, 2H), 7.49−7.44 (m, 2H), 7.34−7.25 (m, 8H), 7.17 (t, 1H, J = 7.6 Hz), 7.03 (d, 2H, J = 8.0 Hz), 3.86 (br, 2H), 3.08 (t, 2H, J = 7.6 Hz), 2.78 (br, 2H), 2.30 (s, 3H), 0.88 (s, 9H), −0.03 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.7, 142.9, 139.4, 138.0, 136.7, 134.2 (2C), 133.1, 131.9 (2C), 131.7, 131.5, 130.0 (2C), 129.9, 128.7 (2C), 128.6 (2C), 127.8, 126.1 (2C), 120.3, 115.0, 64.4, 59.3, 35.4, 26.3 (3C), 21.4, 17.9, −4.7 (br, 2C); HRMS (ESI-TOF) calcd for m/z: [M-OTs]$^+$ $C_{27}H_{35}INOSi$ 544.1533; found 544.1545.

To a stirred solution of **5a** (44.7 mg, 63.3 μmol) in DMF (1 mL) was added TBAF (1.0 M solution in THF, 95 μL, 95 μmol). After being stirred at 60 °C for 2 h, the mixture was quenched with saturated aqueous NH_4Cl (2 mL), diluted with H_2O (6 mL), and extracted with EtOAc/hexane (1:4, 8 mL × 6). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by preparative TLC (EtOAc/hexane, 1:10) to provide 6.9 mg (48%) of **6a** as a brown oil: TLC R_f 0.57 (EtOAc/hexane, 1:10); IR (neat) 3030, 2954, 2919, 2859, 1608, 1476, 1365, 1240, 1016, 746, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2H, J = 6.8 Hz), 7.41−7.32 (m, 3H), 7.12 (d, 2H, J = 8.0 Hz), 6.91 (t, 2H, J = 8.0 Hz), 5.02 (s, 2H), 3.48 (t, 2H, J = 8.0 Hz), 2.88 (t, 2H, J = 8.0 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.0, 138.0, 129.2 (2C), 128.6 (2C), 128.2, 128.1, 127.4, 124.7, 122.8, 113.6, 77.1, 58.1, 27.9; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{15}H_{16}NO$ 226.1232; found 226.1226.

*1-(Benzyloxy)-4-methylindoline (**6b**).* As described for the preparation of **5a**, compound **4b** (47.8 mg, 74.1 μmol) was converted to 37.5 mg (69%) of **5b**. Since compound **5b** was unstable and difficult to store even in the freezer, the obtained **5b** was immediately used in the next step.

As described for the preparation of **6a**, compound **5b** (25.5 mg, 34.9 μmol) was converted to 2.4 mg (29%) of **6b**. Compound **6b** was obtained as a yellow oil: TLC R_f 0.43 (EtOAc/hexane, 1:10); IR (neat) 3011, 2924, 2854, 1599, 1455, 1379, 1216, 1025, 757, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, 2H, J = 7.6 Hz), 7.40−7.32 (m, 3H), 7.04 (t, 1H, J = 8.0 Hz), 6.74 (dd, 2H, J = 8.0, 2.4 Hz), 5.00 (s, 2H), 3.47 (t, 2H, J = 7.6 Hz), 2.80 (t, 2H, J = 7.6 Hz), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.7, 138.0, 134.1, 129.2 (2C), 128.5 (2C), 128.2, 127.5, 126.8, 123.8, 111.0, 77.2, 57.8, 26.6, 18.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{18}NO$ 240.1388; found 240.1395.

*1-(Benzyloxy)-6-methylindoline (**6c**).* As described for the preparation of **5a**, compound **4c** (189 mg, 0.293 mmol) was converted to 158 mg (74%) of **5c**. Since compound **5c** was unstable and difficult to store even in the freezer, the obtained **5c** was immediately used in the next step.

As described for the preparation of **6a**, compound **5c** (31.3 mg, 42.9 μmol) was converted to 6.4 mg (62%) of **6c**. Compound **6c** was obtained as a yellow oil: TLC R_f 0.48 (EtOAc/hexane, 1:10); IR (neat) 3012, 2925, 2855, 1591, 1454, 1216, 1024, 757, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2H, J = 6.8 Hz), 7.41−7.32 (m, 3H), 6.99 (d, 1H, J = 7.6 Hz), 6.72 (d, 1H, J = 7.6 Hz), 6.72 (br s, 1H), 5.02 (s, 2H), 3.45 (t, 2H, J = 7.6 Hz), 2.82 (t, 2H, J = 7.6 Hz), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.1, 138.0, 137.3, 129.1 (2C), 128.5 (2C), 128.2, 125.2, 124.4, 123.6, 114.2, 77.2, 58.4, 27.6, 21.6; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{18}NO$ 240.1388; found 240.1387.

*1-(Benzyloxy)-6-methoxyindoline (**6d**).* As described for the preparation of **5a**, compound **4d** (301 mg, 0.455 mmol) was converted to 210 mg (62%) of **5d**. Since compound **5d** was unstable and difficult to store even in the freezer, the obtained **5d** was immediately used in the next step.

As described for the preparation of **6a**, compound **5d** (27.3 mg, 36.6 μmol) was converted to 2.5 mg (27%) of **6d**. Compound **6d** was obtained as a yellow oil: TLC R_f 0.40 (EtOAc/hexane, 1:10); IR (neat) 2918, 2850, 1595, 1493, 1384, 1283, 1208, 1027, 754, 613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, 2H, J = 7.6 Hz), 7.41−7.34 (m, 3H), 6.98 (d, 1H, J = 8.4 Hz), 6.45 (dd, 1H, J = 8.4, 2.0 Hz), 6.36 (br s, 1H), 4.99 (s, 2H), 3.71 (s, 3H), 3.48 (t, 2H, J = 8.0 Hz), 2.81 (t, 2H, J = 8.0 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.9, 154.2, 137.9, 129.3 (2C), 128.6 (2C), 128.2, 125.0, 120.0, 108.7, 99.4, 77.2, 58.6, 55.6, 27.1; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{18}NO_2$ 256.1338, found 256.1335.

*1-(Benzyloxy)-6-chloroindoline (**6e**).* As described for the preparation of **5a**, compound **4e** (69.8 mg, 0.104 mmol) was converted to 19.2 mg (24%) of **5e**. Since compound **5e** was unstable and difficult to store even in the freezer, the obtained **5e** was immediately used in the next step.

As described for the preparation of **6a**, compound **5e** (15.8 mg, 21.1 μmol) was converted to 2.8 mg (51%) of **6e**. Compound **6e** was obtained as a yellow oil: TLC R_f 0.50 (EtOAc/hexane, 1:10); IR (neat) 3031, 2958, 2858, 1725, 1603, 1476, 1216, 1023, 884, 756, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, 2H, J = 7.2 Hz), 7.41−7.33 (m, 3H), 7.00 (d, 1H, J = 7.6 Hz), 6.85 (d, 1H, J = 7.6 Hz), 6.82 (br s, 1H), 4.98 (s, 2H), 3.47 (t, 2H, J = 7.6 Hz), 2.82 (t, 2H, J = 7.6 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.1, 137.6, 133.1, 129.2 (2C), 128.6 (2C), 128.4, 126.5, 125.5, 122.6, 113.7, 77.2, 58.5, 27.4;

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J. Org. Chem. 2021, 86, 10067−10087

HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}ClNO$ 260.0842; found 260.0831.

*1-(Benzyloxy)-6-fluoroindoline (**6f**).* As described for the preparation of **5a**, compound **4f** (60.5 mg, 93.3 μmol) was converted to 28.7 mg (42%) of **5f**. Since compound **5f** was unstable and difficult to store even in the freezer, the obtained **5f** was immediately used in the next step.

As described for the preparation of **6a**, compound **5f** (23.2 mg, 31.6 μmol) was converted to 3.3 mg (43%) of **6f**. Compound **6f** was obtained as a yellow oil: TLC R_f 0.47 (EtOAc/hexane, 1:10); IR (neat) 3017, 2923, 2858, 1615, 1488, 1216, 1022, 887, 756, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, 2H, J = 8.0, 1.2 Hz), 7.41−7.35 (m, 3H), 7.00 (dd, 1H, J = 8.0, 5.2 Hz), 6.60−6.52 (m, 2H), 4.98 (s, 2H), 3.49 (t, 2H, J = 7.6 Hz), 2.82 (t, 2H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.2, 154.5 (d, J = 15.3 Hz), 137.6, 129.2 (2C), 128.6 (2C), 128.4, 125.2 (d, J = 9.5 Hz), 123.1, 109.0 (d, J = 23.0 Hz), 101.2 (d, J = 26.8 Hz), 77.2, 58.7, 27.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}FNO$ 244.1138; found 244.1145.

*1-(4-Nitrobenzyloxy)indoline (**6h**).* As described for the preparation of **5a**, compound **S15** (185 mg, 0.274 mmol) was converted to 185 mg (89%) of **5h**. Since compound **5h** was unstable and difficult to store even in the freezer, the obtained **5h** was immediately used in the next step.

As described for the preparation of **6a**, compound **5h** (23.8 mg, 31.3 μmol) was converted to 1.2 mg (14%) of **6h**. Compound **6h** was obtained as a yellow oil: TLC R_f 0.46 (EtOAc/hexane, 1:6); IR (neat) 2926, 2855, 1523, 1347, 1216, 853, 758, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, 2H, J = 8.8 Hz), 7.64 (d, 2H, J = 8.8 Hz), 7.17−7.13 (m, 2H), 6.95 (t, 1H, J = 7.2 Hz), 6.88 (d, 1H, J = 7.2 Hz), 5.10 (s, 2H), 3.49 (t, 2H, J = 7.6 Hz), 2.90 (t, 2H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.7, 152.5, 145.4, 129.5 (2C), 128.2, 127.5, 124.9, 123.8 (2C), 123.3, 113.5, 75.6, 58.2, 27.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}N_2O_3$ 271.1083; found 271.1090.

*1-(Allyloxy)indoline (**6i**).* As described for the preparation of **5a**, compound **S16** (73.1 mg, 0.126 mmol) was converted to 71.0 mg (85%) of **5i**. Since compound **5i** was unstable and difficult to store even in the freezer, the obtained **5i** was immediately used in the next step.

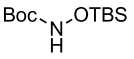
As described for the preparation of **6a**, compound **5i** (25.1 mg, 37.7 μmol) was converted to 3.2 mg (48%) of **6i**. Compound **6i** was obtained as a brown oil: TLC R_f 0.47 (EtOAc/hexane, 1:8); IR (neat) 2923, 2852, 1723, 1384, 1262, 1022, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, 1H, J = 7.8 Hz), 7.13 (br d, 1H, J = 7.8 Hz), 6.99 (d, 1H, J = 7.8 Hz), 6.93 (td, 1H, J = 7.8, 0.8 Hz), 6.11 (m, 1H), 5.37 (dd, 1H, J = 17.2, 1.6 Hz), 5.27 (dd, 1H, J = 10.4, 0.8 Hz), 4.50 (d, 2H, J = 6.0 Hz), 3.56 (t, 2H, J = 7.6 Hz), 2.92 (t, 2H, J = 7.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.0, 134.8, 128.2, 127.5, 124.7, 122.8, 118.5, 113.5, 75.9, 58.1, 27.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}NO$ 176.1075; found 176.1081.

*1-[(2-Methylbut-3-en-2-yl)oxy]indoline (**6j**).* As described for the preparation of **5a**, compound **S17** (63.3 mg, 0.104 mmol) was converted to 42.7 mg (59%) of **5j**. Since compound **5j** was unstable and difficult to store even in the freezer, the obtained **5j** was immediately used in the next step.

As described for the preparation of **6a**, compound **5j** (23.5 mg, 33.9 μmol) was converted to 3.9 mg (57%) of **6j**. Compound **6j** was obtained as a brown oil: TLC R_f 0.50 (EtOAc/hexane, 1:10); IR (neat) 2979, 2930, 2859, 1609, 1477, 1359, 1237, 1145, 995, 923, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, 1H, J = 7.6 Hz), 7.10 (d, 1H, J = 7.6 Hz), 6.94 (d, 1H, J = 7.6 Hz), 6.89 (t, 1H, J = 7.6 Hz), 6.14 (dd, 1H, J = 17.6, 10.8 Hz), 5.37 (d, 1H, J = 17.6 Hz), 5.13 (d, 1H, J = 10.8 Hz), 3.52 (br, 2H), 2.90 (br, 2H), 1.44 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.9, 144.1, 128.0, 127.3, 124.5, 122.2, 113.7, 113.5, 80.3, 60.3, 27.9 (2C), 25.6 (br); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{18}NO$ 204.1388; found 204.1380.

*1-(Benzyloxy)-2,2,6,6-tetramethylpiperidine (**8**).* To a stirred solution of **5a** (20.6 mg, 28.8 μmol) in DMF (0.6 mL) were added TBAF (1.0 M solution in THF, 44 μL, 44 μmol) and TEMPO (7.0 mg, 45 μmol). After being stirred at 60 °C for 2 h, the mixture was quenched with saturated aqueous NH_4Cl (2 mL), diluted with H_2O (2 mL), and extracted with EtOAc/hexane (1:4, 5 mL × 6). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by preparative TLC (EtOAc/hexane, 1:10) to provide 0.6 mg (9%) of **6a** and 1.3 mg (18%) of **8**.[76] Compound **8** was obtained as a yellow oil: TLC R_f 0.71 (EtOAc/hexane, 1:10); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.32 (m, 5H), 4.82 (s, 2H), 1.52−1.49 (m, 6H), 1.26 (s, 6H), 1.15 (s, 6H).

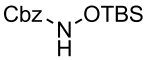
*tert-Butyl (tert-Butyldimethylsilyloxy)carbamate (**S18**).*



S18

To a cooled (0 °C) stirred solution of hydroxylamine hydrochloride (**S9**) (1.03 g, 15.6 mmol) in DMF (30 mL) were added *tert*-butyldimethylchlorosilane (2.80 g, 18.6 mmol) and Et_3N (12.0 mL, 86.0 mmol). The mixture was stirred at room temperature for 2.5 h, and *tert*-butyldimethylchlorosilane (498 mg, 3.31 mmol) was added. The mixture was stirred at room temperature for 1 h, and Boc_2O (4.06 g, 18.6 mmol) was added at 0 °C. After being stirred at room temperature for 4 h, the mixture was quenched with H_2O (30 mL) and extracted with EtOAc/hexane (1:4, 30 mL × 4). The combined extracts were washed with saturated brine (60 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to provide 3.67 g (92%) of **S18**[77] as a colorless oil: TLC R_f 0.82 (EtOAc/hexane, 1:2); ^1H NMR (400 MHz, $CDCl_3$) δ 6.66 (br s, 1H), 1.48 (s, 9H), 0.95 (s, 9H), 0.17 (s, 6H).

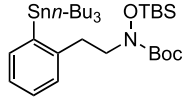
*Benzyl (tert-Butyldimethylsilyloxy)carbamate (**S19**).*



S19

To a cooled (0 °C) stirred solution of hydroxylamine hydrochloride (**S9**) (203 mg, 3.14 mmol) in DMF (16 mL) were added *tert*-butyldimethylchlorosilane (575 mg, 3.81 mmol) and Et_3N (2.40 mL, 17.2 mmol). The mixture was stirred at room temperature for 12 h, and benzyl chloroformate (0.500 mL, 3.56 mmol) was added at 0 °C. After being stirred at room temperature for 9.5 h, the mixture was quenched with H_2O (50 mL) and extracted with EtOAc/hexane (1:4, 50 mL × 4). The combined extracts were washed with H_2O (50 mL) and saturated brine (50 mL), dried, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:20) to provide 144 mg (16%) of **S19**[77] as a yellow oil: TLC R_f 0.32 (EtOAc/hexane, 1:10); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.32 (m, 5H), 6.89 (br s, 1H), 5.17 (s, 2H), 0.94 (s, 9H), 0.16 (s, 6H).

*tert-Butyl (tert-Butyldimethylsilyloxy)-[2-(tributyl-stannyl)-phenethyl]carbamate (**S20a**).*



S20a

To a cooled (0 °C) stirred solution of **2a** (2.18 g, 5.30 mmol), **S18** (1.00 g, 4.04 mmol), and PPh_3 (2.12 g, 8.08 mmol) in THF/toluene (1:3, 14 mL) was slowly added diethyl azodicarboxylate (2.2 M solution in toluene, 3.70 mL, 8.14 mmol). After being stirred at 0 °C for 1 h and at room temperature for 6 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:60) to provide 805 mg (44% from **S18**) of **S20a** as a colorless oil: TLC R_f 0.68 (EtOAc/hexane, 1:10); IR (neat) 2957, 2857, 1705, 1463, 1367, 1254, 1164, 1074, 839, 757, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, 1H, J = 6.4 Hz), 7.25−7.23 (m, 2H), 7.15 (td, 1H, J = 7.2, 1.6 Hz), 3.63 (t, 2H, J = 7.6 Hz), 2.93 (t, 2H, J = 7.6 Hz), 1.53−1.47 (m, 6H), 1.46 (s, 9H), 1.37−1.28 (m, 6H), 1.17−1.05 (m, 6H), 0.99 (s, 9H), 0.88 (t. 9H, J = 7.2 Hz), 0.17 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz,

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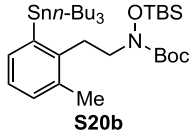
J. Org. Chem. 2021, 86, 10067−10087

$CDCl_3$) δ 157.9, 146.1, 142.4, 136.9, 128.7, 128.6, 125.8, 81.3, 54.6, 35.2, 29.3 (3C), 28.4 (3C), 27.5 (3C), 26.1 (3C), 18.0, 13.9 (3C), 10.5 (3C), −4.9 (2C); HRMS (ESI-TOF) m/z: $[M + K]^+$ calcd for $C_{31}H_{59}KNO_3SiSn$ 680.2923; found 680.2953.

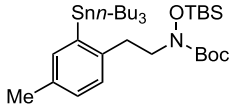
*tert-Butyl (tert-Butyldimethylsilyloxy)-[2-methyl-6-(tributylstannyl)phenethyl]carbamate (**S20b**).*



S20b

To a stirred solution of **2b** (92.4 mg, 0.217 mmol) and **S18** (48.1 mg, 0.194 mmol) in toluene (2 mL) was added cyanomethylenetributylphosphorane (80 μL, 0.31 mmol). After being stirred at 100 °C for 15 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:70) to provide 57.3 mg (45% from **S18**) of **S20b** (a mixture of rotamer) as a yellow oil: TLC R_f 0.56 (EtOAc/hexane, 1:10); IR (neat) 2957, 2929, 2857, 1703, 1462, 1367, 1253, 1164, 1071, 893, 841, 759, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (m, 1H), 7.13−7.09 (m, 2H), 3.56 (t, 2H × 1/6, J = 8.0 Hz), 3.47 (t, 2H × 5/6, J = 8.0 Hz), 2.97 (t, 2H, J = 8.0 Hz), 2.39 (s, 3H × 5/6), 2.35 (s, 3H × 1/6), 1.50 (s, 9H), 1.53−1.45 (m, 6H), 1.37−1.28 (m, 6H), 1.20−1.03 (m, 6H), 0.99 (s, 9H), 0.88 (t. 9H, J = 7.2 Hz), 0.16 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) for major rotamer δ 158.3, 143.9, 143.3, 136.7, 135.0, 131.0, 126.2, 81.5, 53.4, 33.0, 29.3 (3C), 28.4 (3C), 27.6 (3C), 26.1 (3C), 20.4, 18.0, 13.9 (3C), 10.9 (3C), −4.8 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{62}NO_3SiSn$ 656.3521; found 656.3551.

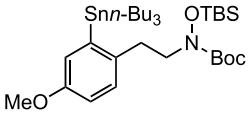
*tert-Butyl (tert-Butyldimethylsilyloxy)-[4-methyl-2-(tributylstannyl)phenethyl]carbamate (**S20c**).*



S20c

As described for the preparation of **S20a**, compounds **2c** and **S18** (144 mg, 0.581 mmol) were converted to 51.1 mg (14% from **S18**) of **S20c**. Compound **S20c** was obtained as a colorless oil: TLC R_f 0.64 (EtOAc/hexane, 1:10); IR (neat) 2957, 2929, 2857, 1705, 1463, 1368, 1254, 1163, 1080, 841, 759, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17−7.07 (m, 3H), 3.60 (t, 2H, J = 8.0 Hz), 2.89 (t, 2H, J = 8.0 Hz), 2.30 (s, 3H), 1.53−1.47 (m, 6H), 1.46 (s, 9H), 1.37−1.30 (m, 6H), 1.17−1.02 (m, 6H), 0.98 (s, 9H), 0.88 (t. 9H, J = 7.2 Hz), 0.17 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.0, 143.0, 142.2, 137.6, 134.9, 129.5, 128.5, 81.3, 54.8, 34.7, 29.3 (3C), 28.4 (3C), 27.5 (3C), 26.1 (3C), 21.2, 18.0, 13.9 (3C), 10.5 (3C), −4.9 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{62}NO_3SiSn$ 656.3521; found 656.3549.

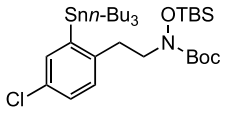
*tert-Butyl (tert-Butyldimethylsilyloxy)-[4-methoxy-2-(tributylstannyl)phenethyl]carbamate (**S20d**).*



S20d

As described for the preparation of **S20a**, compounds **2d** and **S18** (404 mg, 1.63 mmol) were converted to 341 mg (31% from **S18**) of **S20d**. Compound **S20d** was obtained as a yellow oil: TLC R_f 0.66 (EtOAc/hexane, 1:10); IR (neat) 2957, 2930, 2857, 1704, 1591, 1464, 1368, 1251, 1164, 1079, 841, 759, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, 1H, J = 8.4 Hz), 6.94 (d, 1H, J = 2.8 Hz), 6.80 (dd, 1H, J = 8.4, 2.8 Hz), 3.78 (s, 3H), 3.59 (t, 2H, J = 7.6 Hz), 2.87 (t, 2H, J = 7.6 Hz), 1.54−1.47 (m, 6H), 1.45 (s, 9H), 1.37−1.28 (m, 6H), 1.17−1.03 (m, 6H), 0.99 (s, 9H), 0.88 (t. 9H, J = 7.2 Hz), 0.17 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 157.3, 143.8, 138.0, 129.5, 122.5, 113.4, 81.2, 55.3, 54.8, 34.2, 29.3 (3C), 28.4 (3C), 27.5 (3C), 26.1 (3C), 18.0, 13.9 (3C), 10.6 (3C), −4.9 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{62}NO_4SiSn$ 672.3470; found 672.3484.

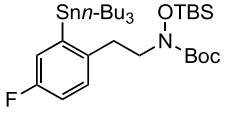
*tert-Butyl (tert-Butyldimethylsilyloxy)-[4-chloro-2-(tributylstannyl)phenethyl]carbamate (**S20e**).*



S20e

As described for the preparation of **S20b**, compounds **2e** and **S18** (57.6 mg, 0.233 mmol) were converted to 85.9 mg (55% from **S18**) of **S20e**. Compound **S20e** was obtained as a yellow oil: TLC R_f 0.47 (EtOAc/hexane, 1:10); IR (neat) 2957, 2929, 2857, 1704, 1463, 1368, 1252, 1162, 1079, 840, 759, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, 1H, J = 2.4 Hz), 7.20 (dd, 1H, J = 8.0, 2.4 Hz), 7.15 (d, 1H, J = 8.0 Hz), 3.59 (t, 2H, J = 7.6 Hz), 2.88 (t, 2H, J = 7.6 Hz), 1.56−1.47 (m, 6H), 1.43 (s, 9H), 1.37−1.28 (m, 6H), 1.19−1.04 (m, 6H), 0.98 (s, 9H), 0.89 (t. 9H, J = 7.2 Hz), 0.17 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.8, 144.9, 144.3, 136.0, 132.1, 130.0, 128.4, 81.4, 54.2, 34.3, 29.2 (3C), 28.4 (3C), 27.5 (3C) 26.1 (3C), 17.9, 13.8 (3C), 10.6 (3C), −4.8 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{31}H_{59}ClNO_3SiSn$ 676.2975; found 676.3005.

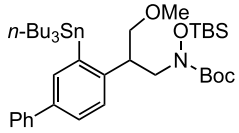
*tert-Butyl (tert-Butyldimethylsilyloxy)-[4-fluoro-2-(tributylstannyl)phenethyl]carbamate (**S20f**).*



S20f

As described for the preparation of **S20b**, compounds **2f** and **S18** (52.7 mg, 0.213 mmol) were converted to 81.6 mg (58% from **S18**) of **S20f**. Compound **S20f** was obtained as a yellow oil: TLC R_f 0.54 (EtOAc/hexane, 1:10); IR (neat) 2957, 2929, 2857, 1704, 1474, 1368, 1253, 1215, 1163, 1078, 840, 759, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, 1H, J = 8.4, 5.2 Hz), 7.06 (dd, 1H, J = 8.4, 2.0 Hz), 6.91 (td, 1H, J = 8.4, 2.0 Hz), 3.59 (t, 2H, J = 7.6 Hz), 2.89 (t, 2H, J = 7.6 Hz), 1.56−1.46 (m, 6H), 1.43 (s, 9H), 1.37−1.28 (m, 6H), 1.18−1.01 (m, 6H), 0.98 (s, 9H), 0.88 (t. 9H, J = 7.2 Hz), 0.17 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.8, 145.1, 141.5, 130.0 (d, J = 5.7 Hz), 122.8, 122.6, 115.2 (d, J = 21.1 Hz), 81.3, 54.5, 34.3, 29.2 (3C), 28.4 (3C), 27.5 (3C), 26.1 (3C), 18.0, 13.8 (3C), 10.6 (3C), −4.8 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{31}H_{59}FNO_3SiSn$ 660.3270, found 660.3256.

*tert-Butyl (tert-Butyldimethylsilyloxy)-{3-methoxy-2-[3-(tributylstannyl)-[1,1′-biphenyl]-4-yl]propyl}carbamate (**S20i**).*



S20i

As described for the preparation of **S20b**, compounds **2i** and **S18** (79.8 mg, 0.323 mmol) were converted to 63.8 mg (26% from **S18**) of **S20i**. Compound **S20i** was obtained as a yellow oil: TLC R_f 0.64 (EtOAc/hexane, 1:10); IR (neat) 2956, 2928, 2857, 1730, 1703, 1464, 1366, 1251, 1170, 1108, 840, 763, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 2H, J = 8.0 Hz), 7.53 (br s, 1H), 7.48 (d, 1H, J = 8.0 Hz), 7.45−7.37 (m, 3H), 7.32 (t, 1H, J = 6.8 Hz), 3.98 (dd, 1H, J = 14.8, 6.4 Hz), 3.80 (dd, 1H, J = 14.8, 6.0 Hz), 3.60 (t, 1H, J = 8.0 Hz), 3.52 (t, 1H, J = 8.0 Hz), 3.28 (m, 1H), 3.28 (s, 3H), 1.55−1.51 (m, 6H), 1.39−1.31 (m, 6H), 1.31 (s, 9H), 1.22−1.05 (m, 6H), 0.94 (s, 9H), 0.89 (t. 9H, J = 7.2 Hz), 0.17 (s, 3H), 0.15 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.8, 146.6, 144.5, 141.8, 138.8, 135.6, 128.8 (2C), 127.5, 127.2 (3C), 127.0, 80.7, 76.0, 59.1, 53.6, 46.9, 29.4 (3C), 28.2 (3C), 27.6 (3C), 26.1 (3C), 18.0, 13.9 (3C), 10.8 (3C), −4.6, −4.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{39}H_{68}NO_4SiSn$ 762.3940; found 762.3911.

https://doi.org/10.1021/acs.joc.1c00820
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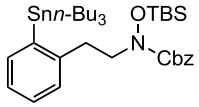
*Benzyl (tert-Butyldimethylsilyloxy)-[2-(tributylstannyl)-phenethyl]carbamate (**S21**).*



S21

To a cooled (0 °C) stirred solution of **2a** (678 mg, 1.64 mmol), **S19** (388 mg, 1.38 mmol), and PPh_3 (867 mg, 3.31 mmol) in THF/toluene (1:3, 5 mL) was slowly added diethyl azodicarboxylate (2.2 M solution in toluene, 31.5 mL, 3.30 mmol). After being stirred at 0 °C for 1 h and at room temperature for 3 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:70) to provide 539 mg (58% from **S19**) of **S21** as a colorless oil: TLC R_f 0.56 (EtOAc/hexane, 1:10); IR (neat) 2956, 2929, 2857, 1709, 1463, 1390, 1252, 1075, 836, 756, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, 1H, J = 6.8, 2.0 Hz), 7.35−7.30 (m, 5H), 7.24−7.19 (m, 2H), 7.15 (td, 1H, J = 6.8, 2.0 Hz), 5.06 (s, 2H), 3.67 (t, 2H, J = 7.6 Hz), 2.94 (t, 2H, J = 7.6 Hz), 1.52−1.41 (m, 6H), 1.35−1.26 (m, 6H), 1.14−1.00 (m, 6H), 0.96 (s, 9H), 0.87 (t, 9H, J = 7.2 Hz), 0.13 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.5, 145.8, 142.4, 137.0, 136.0, 128.9, 128.5 (4C), 128.3 (2C), 125.9, 67.9, 54.5, 35.3, 29.3 (3C), 27.5 (3C), 26.0 (3C), 18.0, 13.8 (3C), 10.5 (3C), −4.9 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{58}NO_3SiSn$ 676.3208; found 676.3242.

*1H-Indole (**10a**).* To a stirred solution of **S20a** (538 mg, 0.839 mmol) in CH_2Cl_2 (8 mL) was added PhI(OH)OTs (Koser reagent, 498 mg, 1.27 mmol). After being stirred at room temperature in the dark for 14 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$, 1:10) to provide 404 mg (67%) of **9a** as a yellow amorphous: TLC R_f 0.13 ($MeOH/CH_2Cl_2$, 1:10); IR (neat) 2956, 2929, 1699, 1384, 1201, 1130, 1044, 755, 689, 572 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, 3H, J = 8.0 Hz), 7.65 (d, 2H, J = 7.6 Hz), 7.55−7.50 (m, 3H), 7.39 (t, 2H, J = 8.0 Hz), 7.22 (m, 1H), 7.08 (d, 2H, J = 8.0 Hz), 3.74 (t, 2H, J = 6.8 Hz), 3.19 (t, 2H, J = 6.8 Hz), 2.32 (s, 3H), 1.31 (s, 9H), 0.96 (s, 9H), 0.16 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.5, 143.0, 141.9, 139.1, 138.1, 134.5 (2C), 132.7, 132.1, 131.6 (2C), 131.4, 130.0, 128.4 (2C), 126.1 (2C), 120.6, 115.9, 81.6, 51.9, 35.2, 28.2 (3C), 25.9 (3C), 21.3, 17.8, −5.0 (2C); HRMS (ESI-TOF) m/z: $[M - OTs]^+$ calcd for $C_{25}H_{37}INO_3Si$ 554.1587; found 554.1598.

To a stirred solution of **9a** (25.9 mg, 35.7 μmol) and dried molecular sieves 4 Å powder (17.8 mg) in DMF (0.7 mL) was added TBAF (1.0 M solution in THF, 44 μL, 44 μmol). After being stirred at room temperature for 4 h, the mixture was quenched with saturated aqueous NH_4Cl (2 mL), diluted with H_2O (2 mL), and extracted with EtOAc/hexane (1:4, 6 mL × 5). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by preparative TLC (EtOAc/hexane, 1:4) to provide 4.1 mg (89%) of **10a**[78] as light brown crystals; TLC R_f 0.30 (EtOAc/hexane, 1:4); ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (br, 1H), 7.65 (d, 1H, J = 8.0 Hz), 7.41 (dd, 1H, J = 8.0, 0.8 Hz), 7.23 (td, 1H, J = 8.0, 0.8 Hz), 7.23−7.18 (m, 2H), 6.57 (br s, 1H).

Data for a trace amount of by-product **12a**: brown crystals; mp 58−60 °C; TLC R_f 0.18 (EtOAc/hexane, 1:4); IR (neat) 3383, 2928, 2852, 1754, 1493, 1370, 1275, 1154, 886, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.92 (br d, 1H, J = 0.8 Hz), 6.78 (dd, 1H, J = 8.0, 0.8 Hz), 6.57 (d, 1H, J = 8.0 Hz), 3.57 (t, 2H, J = 8.0 Hz), 3.03 (t, 2H, J = 8.0 Hz), 1.54 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.0, 149.5, 143.9, 130.7, 119.9, 118.1, 109.3, 83.2, 48.0, 30.1, 27.9 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{18}NO_3$ 236.1287; found 236.1294.

*4-Methyl-1H-indole (**10b**).* As described for the preparation of **9a**, compound **S20b** (80.2 mg, 0.123 mmol) was converted to 61.8 mg (68%) of **9b**. Since compound **9b** was unstable and difficult to store even in the freezer, the obtained **9b** was immediately used in the next step.

As described for the preparation of **10a**, compound **9b** (30.0 mg, 40.6 μmol) was converted to 4.8 mg (90%) of **10b**.[78] Compound **10b** was obtained as a brown oil: TLC R_f 0.25 (EtOAc/hexane, 1:4); ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (br, 1H), 7.25 (d, 1H, J = 7.2 Hz), 7.21 (t, 1H, J = 2.8 Hz), 7.11 (t, 1H, J = 7.2 Hz), 6.92 (d, 1H, J = 7.2 Hz), 6.58 (br s, 1H), 2.57 (s, 3H).

*6-Methyl-1H-indole (**10c**).* As described for the preparation of **9a**, compound **S20c** (50.3 mg, 76.8 μmol) was converted to 43.1 mg (76%) of **9c**. Since compound **9c** was unstable and difficult to store even in the freezer, the obtained **9c** was immediately used in the next step.

As described for the preparation of **10a**, compound **9c** (22.6 mg, 30.5 μmol) was converted to 2.5 mg (62%) of **10c**.[79] Compound **10c** was obtained as brown crystals: TLC R_f 0.39 (EtOAc/hexane, 1:4); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (br, 1H), 7.52 (d, 1H, J = 8.4 Hz), 7.20 (br s, 1H), 7.14 (t, 1H, J = 2.8 Hz), 6.95 (d, 1H, J = 8.4 Hz), 6.50 (br s, 1H), 2.47 (s, 3H).

*6-Methoxy-1H-indole (**10d**).* As described for the preparation of **9a**, compound **S20d** (233 mg, 0.347 mmol) was converted to 134 mg (51%) of **9d**. Since compound **9d** was unstable and difficult to store even in the freezer, the obtained **9d** was immediately used in the next step.

As described for the preparation of **10a**, compound **9d** (26.6 mg, 35.2 μmol) was converted to 4.2 mg (81%) of **10d**.[80] Compound **10d** was obtained as brown crystals: TLC R_f 0.40 (EtOAc/hexane, 1:3); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (br, 1H), 7.51 (d, 1H, J = 8.8 Hz), 7.10 (t, 1H, J = 2.8 Hz), 6.89 (d, 1H, J = 2.4 Hz), 6.80 (dd, 1H, J = 8.8, 2.4 Hz), 6.48 (br s, 1H), 3.85 (s, 3H).

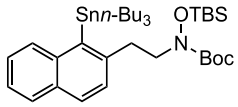
*6-Chloro-1H-indole (**10e**).* As described for the preparation of **9a**, compound **S20e** (78.3 mg, 0.116 mmol) was converted to 47.5 mg (54%) of **9e**. Since compound **9e** was unstable and difficult to store even in the freezer, the obtained **9e** was immediately used in the next step.

As described for the preparation of **10a**, compound **9e** (26.2 mg, 34.5 μmol) was converted to 4.4 mg (84%) of **10e**.[81] Compound **10e** was obtained as brown crystals: TLC R_f 0.37 (EtOAc/hexane, 1:4); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (br, 1H), 7.54 (d, 1H, J = 8.4 Hz), 7.40 (br s, 1H), 7.21 (t, 1H, J = 2.8 Hz), 7.09 (dd, 1H, J = 8.4, 2.0 Hz), 6.54 (br s, 1H).

*6-Fluoro-1H-indole (**10f**).* As described for the preparation of **9a**, compound **S20f** (73.3 mg, 0.111 mmol) was converted to 43.6 mg (53%) of **9f**. Since compound **9f** was unstable and difficult to store even in the freezer, the obtained **9f** was immediately used in the next step.

As described for the preparation of **10a**, compound **9f** (27.1 mg, 36.4 μmol) was converted to 4.3 mg (87%) of **10f**.[78] Compound **10f** was obtained as brown crystals: TLC R_f 0.34 (EtOAc/hexane, 1:4); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (br, 1H), 7.55 (dd, 1H, J = 8.8, 6.2 Hz), 7.19 (t, 1H, J = 2.0 Hz), 7.08 (dd, 1H, J = 9.6, 2.4 Hz), 6.89 (td, 1H, J = 8.8, 2.4 Hz), 6.53 (br s, 1H).

*1H-Benzo[g]indole (**10g**).*



S20g

As described for the preparation of **S20b**, compounds **2g** and **S18** (66.2 mg, 0.268 mmol) were converted to 120 mg (65% from **S18**) of **S20g**. Since compound **S20g** was unstable due to protodestanylation, the obtained **S20g** was immediately used in the next step.

As described for the preparation of **9a**, compound **S20g** (43.7 mg, 63.2 μmol) was converted to 34.1 mg (69%) of **9g**. Since compound **9g** was unstable and difficult to store even in the freezer, the obtained **9g** was immediately used in the next step.

As described for the preparation of **10a**, compound **9g** (20.3 mg, 26.2 μmol) was converted to 3.8 mg (87%) of **10g**.[82] Compound **10g** was obtained as yellow crystals: TLC R_f 0.33 (EtOAc/hexane, 1:4); ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (br, 1H), 8.01 (d, 1H, J = 8.0

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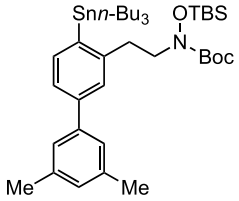
J. Org. Chem. 2021, 86, 10067−10087

Hz), 7.93 (d, 1H, J = 8.6 Hz), 7.73 (d, 1H, J = 8.6 Hz), 7.54 (t, 1H, J = 8.0 Hz), 7.52 (d, 1H, J = 8.0 Hz), 7.43 (t, 1H, J = 8.0 Hz), 7.29 (t, 1H, J = 2.4 Hz), 6.71 (br s, 1H).

*5-(3,5-Dimethylphenyl)-1H-indole (**10h**).*



S20h

As described for the preparation of **S20b**, compounds **2h** (110 mg, 0.213 mmol) and **S18** were converted to 121 mg (76% from **2h**) of **S20h**. Since compound **S20h** was unstable due to protodestanylation, the obtained **S20h** was immediately used in the next step.

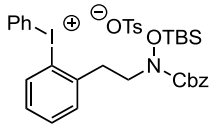
As described for the preparation of **9a**, compound **S20h** (121 mg, 0.162 mmol) was converted to 107 mg (79%) of **9h**. Since compound **9h** was unstable and difficult to store even in the freezer, the obtained **9h** was immediately used in the next step.

As described for the preparation of **10a**, compound **9h** (30.6 mg, 36.9 μmol) was converted to 6.3 mg (77%) of **10h**. Compound **10h** was obtained as a yellow oil: TLC R_f 0.37 (EtOAc/hexane, 1:4); IR (neat) 3415, 3019, 2918, 1601, 1458, 1413, 1307, 1217, 1094, 882, 850, 762, 727 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (br, 1H), 7.85 (s, 1H), 7.44 (s, 2H), 7.28 (br s, 2H), 7.24 (br s, 1H), 6.97 (br s, 1H), 6.60 (br s, 1H), 2.40 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.7, 138.2 (2C), 135.4, 133.8, 128.5, 128.1, 125.5 (2C), 124.8, 122.2, 119.4, 111.2, 103.1, 21.6 (2C); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{16}N$ 222.1283; found, 222.1292.

*3-(Methoxymethyl)-6-phenyl-1H-indole (**10i**).* As described for the preparation of **9a**, compound **S20i** (46.0 mg, 60.5 μmol) was converted to 31.7 mg (62%) of **9i**. Since compound **9i** was unstable and difficult to store even in the freezer, the obtained **9i** was immediately used in the next step.

As described for the preparation of **10a**, compound **9i** (28.0 mg, 33.1 μmol) was converted to 6.3 mg (38%) of **10i**. Compound **10i** was obtained as pale yellow crystals: mp 105−108 °C; TLC R_f 0.36 (EtOAc/hexane, 1:2); IR (neat) 3378, 2924, 2858, 1446, 1384, 1091, 1055, 822, 752, 690, 545 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (br, 1H), 7.77 (d, 1H, J = 8.4 Hz), 7.64 (d, 2H, J = 7.6 Hz), 7.58 (s, 1H), 7.46−7.41 (m, 3H), 7.32 (br t, 1H, J = 8.4 Hz), 7.23 (br s, 1H), 4.70 (s, 2H), 3.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.4, 137.1, 136.1, 128.8 (2C), 127.5 (2C), 126.8, 126.6, 124.4, 120.1, 119.6, 113.5, 109.8, 66.6, 57.7; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{16}H_{16}NO$ 238.1232; found 238.1236.

*1H-Indole (**10a**) from the Diaryliodonium Salt (**S22**).*

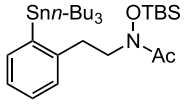


S22

As described for the preparation of **9a**, compound **S21** (251 mg, 0.373 mmol) was converted to 251 mg (89%) of **S22**. Since compound **S22** was unstable and difficult to store even in the freezer, the obtained **S22** was immediately used in the next step.

As described for the preparation of **10a**, compound **S22** (26.7 mg, 35.1 μmol) was converted to 2.5 mg (61%) of **10a**.

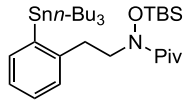
*N-(tert-Butyldimethylsilyloxy)-N-[2-(tributylstannyl)-phenethyl]-acetamide (**S23**).*



S23

To a cooled (0 °C) stirred solution of **3a** (50.3 mg, 93.1 μmol) in CH_2Cl_2 (1 mL) were added Ac_2O (18 μL, 0.19 mmol) and 4-dimethylaminopyridine (DMAP) (2.6 mg, 21 μmol). After being stirred at room temperature for 2 h, the mixture was quenched with H_2O (2 mL) and extracted with EtOAc (2 mL × 4). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by preparative TLC (EtOAc/hexane, 1:20) to provide 33.2 mg (61%) of **S23** as a yellow oil: TLC R_f 0.35 (EtOAc/hexane, 1:20); IR (neat) 2956, 2929, 2857, 1678, 1464, 1383, 1254, 1071, 836, 784, 755, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, 1H, J = 7.2, 1.2 Hz), 7.25−7.15 (m, 3H), 3.80 (br, 2H), 2.94 (t, 2H, J = 7.2 Hz), 2.07 (br, 3H), 1.57−1.42 (m, 6H), 1.38−1.29 (m, 6H), 1.20−1.05 (m, 6H), 1.01 (s, 9H), 0.88 (t, 9H, J = 7.2 Hz), 0.24 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.7, 142.5, 137.1 (2C), 128.5, 125.9, 51.8 (br), 35.2 (br), 29.3 (3C), 27.5 (3C), 26.0 (3C), 21.4, 18.0, 13.8 (3C), 10.5 (3C), −4.4 (2C); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{28}H_{54}NO_2SiSn$ 584.2946; found 584.2957.

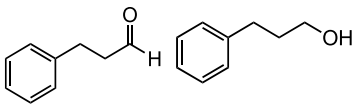
*N-(tert-Butyldimethylsilyloxy)-N-[2-(tributylstannyl)-phenethyl]-pivalamide (**S24**).*



S24

To a cooled (0 °C) stirred solution of **3a** (186 mg, 0.344 mmol) in CH_2Cl_2 (4 mL) were added PivCl (64 μL, 0.53 mmol) and Et_3N (72 μL, 0.52 mmol). After being stirred at room temperature for 23 h, the mixture was quenched with H_2O (4 mL) and extracted with CH_2Cl_2 (4 mL × 4). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/hexane, 1:2) to provide 177 mg (82%) of **S24** as a yellow oil: TLC R_f 0.30 (MeOH/CH_2Cl_2/hexane, 1:5:60); IR (neat) 2957, 2929, 1652, 1464, 1254, 1168, 838, 784, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, 1H, J = 7.2 Hz), 7.29−7.16 (m, 3H), 3.91 (t, 2H, J = 8.0 Hz), 3.00 (t, 2H, J = 8.0 Hz), 1.61−1.45 (m, 6H), 1.39−1.30 (m, 6H), 1.21 (s, 9H), 1.12−1.06 (m, 6H), 1.02 (s, 9H), 0.89 (t, 9H, J = 7.2 Hz), 0.25 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.8, 145.4, 142.7, 137.1, 128.6, 127.9, 125.9, 53.8, 39.1, 35.4, 29.3 (3C), 27.9 (3C), 27.5 (3C), 26.4 (3C), 18.6, 13.8 (3C), 10.5 (3C), −4.0 (2C); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{31}H_{60}NO_2SiSn$ 626.3415; found 626.3385.

*tert-Butyl (tert-Butyldimethylsilyloxy)(3-phenylpropyl)-carbamate (**13**).*



S25 **S26**

To a cooled (0 °C) stirred solution of 3-phenylpropion-aldehyde (**S25**) (0.265 mL, 2.01 mmol) in MeOH (20 mL) was added $NaBH_4$ (117 mg, 3.09 mmol) under air. After being stirred at 0 °C for 5 min, the mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (20 mL × 2). The combined extracts were washed with saturated brine (40 mL), dried, and concentrated under reduced pressure to provide crude **S26**, which was used in the next step without further purification.

To a cooled (0 °C) stirred solution of crude **S26** obtained above, **S18** (395 mg, 1.60 mmol), and PPh_3 (1.05 g, 4.00 mmol) in THF/toluene (1:3, 8 mL) was slowly added diethyl azodicarboxylate (2.2 M solution in toluene, 1.55 mL, 3.41 mmol). After being stirred at 0 °C for 1 h and at room temperature for 1 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:20) to provide 158 mg (27%) of **13** as a yellow oil: TLC R_f 0.57 (EtOAc/hexane, 1:8); IR (neat) 2953, 2931, 2858, 1702, 1455, 1367, 1252, 1164, 1098, 1024, 894, 840, 784, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.26 (m, 2H), 7.20−7.18 (m, 3H), 3.45 (t, 2H, J = 7.6 Hz), 2.62 (t, 2H, J =

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J. Org. Chem. 2021, 86, 10067−10087

7.6 Hz), 1.98 (quint, 2H, J = 7.6 Hz), 1.46 (s, 9H), 0.93 (s, 9H), 0.12 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.1, 141.8, 128.4 (3C), 125.9 (2C), 81.2, 52.1, 33.1, 28.4 (3C), 27.5, 26.0 (3C), 17.9, −5.0 (2C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{36}NO_3Si$ 366.2464, found 366.2461.

*tert-Butyl Hydroxy(3-phenylpropyl)carbamate (**14**).* To a stirred solution of **13** (18.4 mg, 50.3 μmol) in DMF (1 mL) was added TBAF (1.0 M solution in THF, 61 μL, 61 μmol). After being stirred at room temperature for 1 h, the mixture was quenched with saturated aqueous NH_4Cl (2 mL) and extracted with EtOAc/hexane (1:4, 4 mL × 3). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by preparative TLC (EtOAc/hexane, 1:4) to provide 10.7 mg (85%) of **14** as a pale yellow oil: TLC R_f 0.23 (EtOAc/hexane, 1:4); IR (neat) 3279, 2930, 1693, 1385, 1163, 1112, 756, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, 2H, J = 7.6 Hz), 7.21−7.17 (m, 3H), 6.51 (br, 1H), 3.51 (t, 2H, J = 7.4 Hz), 2.66 (t, 2H, J = 7.4 Hz), 1.97 (quint, 2H, J = 7.4 Hz), 1.46 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.1, 141.7, 128.6 (2C), 128.5 (2C), 126.0, 82.0, 49.5, 32.9, 28.6, 28.5 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{22}NO_3$ 252.1600; found 252.1602.

*tert-Butyl Methoxy(3-phenylpropyl)carbamate (**16**).* To a stirred solution of **13** (29.4 mg, 80.4 μmol) in DMF (2 mL) was added TBAF (1.0 M solution in THF, 100 μL, 100 μmol). The mixture was stirred at room temperature for 0.5 h, and MeI (6 μL, 96 μmol) was added. After being stirred at room temperature for 1 h, the mixture was quenched with saturated aqueous NH_4Cl (2 mL) and extracted with EtOAc/hexane (1:4, 4 mL × 4). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by preparative TLC (EtOAc/hexane, 1:4) to provide 13.6 mg (64%) of **16** as a pale yellow oil: TLC R_f 0.60 (EtOAc/hexane, 1:4); IR (neat) 3019, 2981, 2936, 1700, 1369, 1216, 1162, 757, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30−7.27 (m, 2H), 7.20−7.17 (m, 3H), 3.68 (s, 3H), 3.47 (t, 2H, J = 7.2 Hz), 2.65 (t, 2H, J = 7.2 Hz), 1.94 (quint, 2H, J = 7.2 Hz), 1.49 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.5, 141.8, 128.5 (3C), 126.0 (2C), 81.3, 62.4, 48.8, 33.2, 28.9, 28.5 (3C); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{24}NO_3$ 266.1756, found 266.1768.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00820.

Supporting experimental procedures; computational methods; and spectral data of new compounds (PDF)

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This manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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J. Org. Chem. 2021, 86, 10067−10087