Stereoselective Synthesis of Exocyclic Allylsilanes by Intramolecular Reductive Heck Cyclisation of Propargylsilanes

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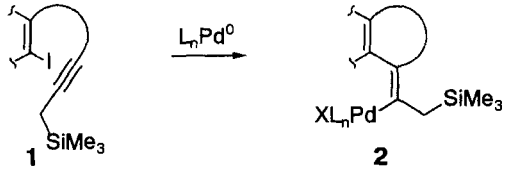
The stereoselective palladium-catalysed synthesis of the heterocycles **13**–**15** with a (Z)-exocyclic allylsilane moiety is described. Alkylation of the secondary amides **5a**, **5b**, **9a**, and **9b** and the phenol **11** containing an iodoaryl moiety with the propargyl iodide **6** leads to the propargylsilanes **7a**, **7b**, **10a**, **10b**, and **12**, which are allowed to react with a catalyst system of $Pd(OAc)_2/PPh_3/NPr_4Br$ and sodium formate as a hydride source. The (Z) configuration of the cyclisation products is confirmed by NOESY spectra and a single-crystal X-ray structure of **13b**.

Allylsilanes have increasingly attracted the attention of organic chemists in the last two decades, due to the importance of these allyl derivatives in synthetic organic chemistry. Their unique characteristics make them a powerful tool in allylation processes with a great variety of electrophiles[1]. Quite recently we have shown that allylsilanes may also be used in an enantioselective Heck reaction allowing the formation of tertiary benzylic carbon centers with an *ee* up to 90%[2]. Although very efficient procedures for the preparation of allylsilanes are already known[3], a main problem is always the stereoselective formation of the double bond, especially in the case of exocyclic allylsilanes[4]. The synthesis of these compounds is usually performed by a Wittig reaction of cyclic ketones, such as cyclopentanone or cyclohexanone or their derivatives, which in most cases leads to mixtures of (*E*/*Z*) isomers. An additional disadvantage of this procedure is its restriction to cyclic substrates. A more flexible and efficient way would be the use of acyclic precursors in which the cyclisation and the formation of the exocyclic allylsilane moiety takes place in one step. In this paper we describe a procedure by a stereoselective intramolecular Heck reaction of iodobenzene derivatives **1** carrying a propargylsilane moiety followed by a reductive replacement of palladium in the intermediately formed vinylpalladium species **2** using sodium formate. Thus, starting from **7a**, **7b**, **10a**, **10b**, and **12** we obtained the exocyclic allylsilanes **13a**, **13b**, **14a**, **14b**, and **15** as single isomers with (*Z*) configuration and mostly in good yields. Heck cyclisations with alkynes and a hydride source have also been applied to the synthesis of exocyclic vinylsilanes[5], and, with different kinds of organometallics, to the synthesis of exocyclic alkenes[6]. Another related methodology is the intramolecular capture of a vinylpalladium species, which is an intermediate in all Heck cyclisations with alkynes. This has been demonstrated in some elegant sequential transformations[7,8].



Results

The synthesis of the substrates **7a**, **7b**, **10a**, **10b**, and **12** was performed in the following way: Homoveratrylamine (**3**) was converted into the amide **4** by acylation with mesitylenesulfonyl chloride in the presence of triethylamine and a catalytic amount of 4-(dimethylamino)-pyridine (DMAP) in dichloromethane in 86% yield. Regioselective iodination of **4** was accomplished by refluxing with iodine and iodic acid in a mixture of methanol and water to give **5a** in 92% yield. Alkylation of **5a** and **5b**[9] with sodium hydride and propargyl iodide **6**[10] in dimethylformamide afforded the propargylsilanes **7a** and **7b** in 87 and 88% yield, respectively.

The known compounds **9a**[11] and **9b**[12] could be obtained by treating the amines **8a** and **8b** with trifluoroacetic anhydride and triethylamine in tetrahydrofuran in 88 and 93% yield, respectively. Subsequent alkylation, as described for **5a** and **5b**, led to propargylsilanes **10a** and **10b** in 80 and 83% yield. Compound **12** was synthesised by alkylation of 2-iodophenol (**11**) with **6** in the presence of sodium methoxide in methanol under reflux in 66% yield. Surprisingly, the alkylation in the presence of so-

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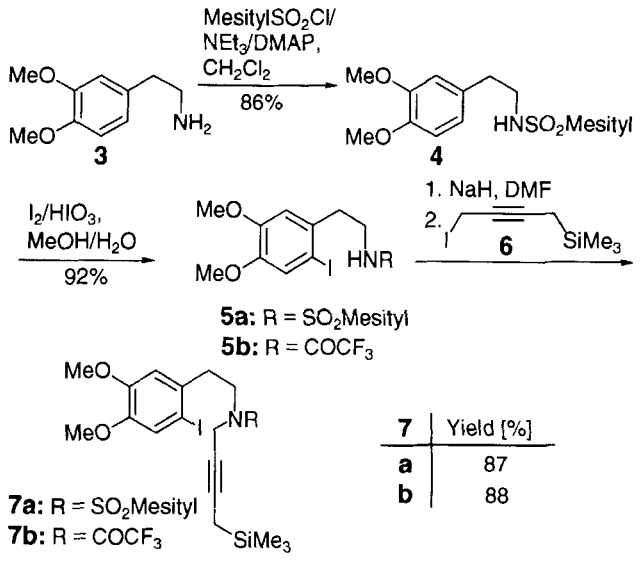
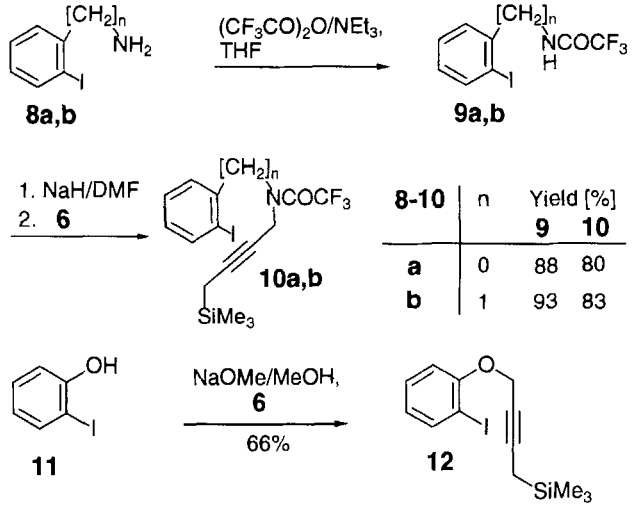
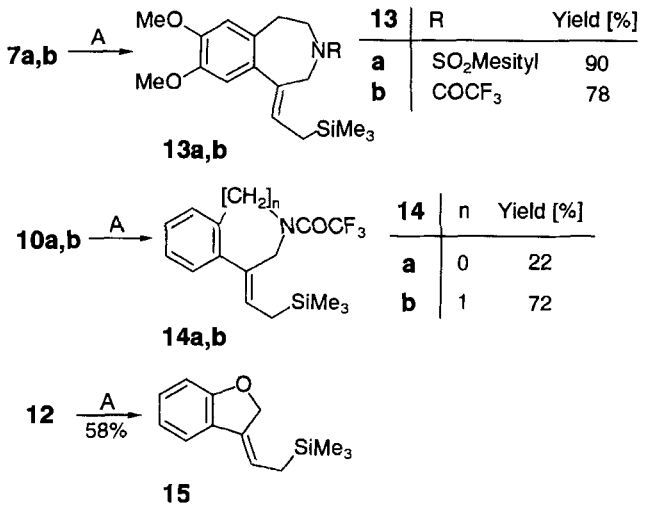


dium hydride in dimethylformamide or potassium carbonate in acetone[13] failed.



The cyclisation of the propargylsilanes was performed with a catalyst system containing 5 mol-% of palladium(II) acetate, 10 mol-% of triphenylphosphane, one equivalent of tetrapropylammonium bromide, and three equivalents of sodium formate in dimethylformamide at temperatures between 75 and 85°C within 2 to 3 h. The reaction of **7a** with formation of **13a** proceeded smoothly in 90% yield. In contrast, the aniline derivative **10a** afforded **14a** in only 22% yield. The low yield is caused by desilylation of the starting material and by the low stability of the *N*-trifluoroacetamide moiety in the product leading to an indoline, from which a complex mixture of compounds is formed. The isoquinoline **14b** and the benzofuran **15** were obtained in yields of 72 and 58%, respectively. Compounds **14a**, **14b**, and **15** are not very stable and must be stored at temperatures below −18°C, whereas **13a** and **13b** are stable at room temperature.



The structure of the exocyclic allylsilanes **13**–**15** was determined mainly by ^{1}H-NMR spectroscopy. Table 1 shows the resonance signals of the olefinic protons at the exocyclic double bond and for the endocyclic methylene protons adjacent to the double bond as well as their ^4J coupling constants.

Table 1. ^{1}H-NMR resonance signals of olefinic and methylene protons adjacent to the double bond as well as their coupling constants for compounds **13**–**15**

Compound	δ (C=C*H*)	δ (HC=CC*H*$_2$)	^4J [Hz]	Ring size
13a	5.62	3.97	1.0	7
13b[a]	5.70, 5.79	4.32, 4.34	1.5, 2.0	7
14b[a]	6.21, 6.23	4.42, 4.47	2.0, 2.0	6
14a	6.08	4.80	3.0	5
15	5.90	5.08	3.0	5

[a] The two sets of signals are due to the existence of rotamers at room temp.

The (*Z*) configuration in the products was proven for **13b** by single-crystal X-ray crystallography[14]. In addition, NOESY spectra of **13a**, **14a**, and **14b** clearly confirmed the proposed structure.

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Experimental

^{1}H and ^{13}C NMR: Varian XL-200, Bruker AMX-300, Varian XL-500; multiplicities were determined with APT pulse sequence. – MS: Varian MAT 311 A, high resolution. Varian MAT 731. – IR: Bruker IFS 25. – UV: Perkin Elmer Lambda 9. – Melting points: Kofler hot stage or Mettler FP 61. – Elemental analyses: Analytical laboratory of the university. – All solvents were distilled prior to use. Reagents and materials were obtained from commercial suppliers and were used without further purification. All reactions were carried out under a positive pressure of argon and monitored by TLC (Macherey-Nagel & Co., Polygram SIL G/UV$_{254}$). Products were isolated by column chroma-

tography on silica gel (Silica gel 60, particle size 0.04–0.063 mm, Merck).

N[-2-(3,4-Dimethoxyphenyl)ethyl]mesitylenesulfonamide (**4**): To a solution of homovertarylamine (**3**) (1.81 g, 10.0 mmol), triethylamine (1.01 g, 10.0 mmol), and 4-(dimethylamino)pyridine (61 mg, 0.5 mmol) in dichloromethane (60 ml) was added mesitylenesulfonyl chloride (2.19 g, 10.0 mmol) in small portions at 0°C. After warming to room temp. and completion of the reaction the solution was washed with aqueous HCl (1 M, 20 ml), water (30 ml), and brine (20 ml), dried (Mg_2SO_4, and concentrated in vacuo to give a pale yellow solid. Recrystallization yielded **4** (3.63 g, 8.60 mmol, 86%) as colourless crystals. R_f = 0.39 (petroleum ether/ethyl acetate, 1:1), m.p. 154°C (ether/methanol). – IR (KBr): $\tilde{\nu}$ = 3258 cm^{-1} (NH), 2982, 2934, 2840 (CH), 1604, 1592 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 201 nm (4.857), 232 (4.176), 281 (3.540). – ^1H NMR ($CDCl_3$): δ = 2.30 (s, 3H, mesityl-4-CH_3), 2.51 (s, 6H, mesityl-2,6-CH_3), 2.72 (t, *J* = 6.5 Hz, 2H, 2-H), 3.14 (dt, *J* = 6.5, 6.5 Hz, 2H, 1-H), 3.80 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.38 (t, *J* = 6.5 Hz, 1H, NH), 6.54 (d, *J* = 2.0 Hz, 1H, Ar-2-H), 6.63 (d, *J* = 8.0, 2.0 Hz, 1H, Ar-6-H), 6.77 (d, *J* = 8.0 Hz, 1H, Ar-5-H), 6.92 (s, 2H, mesityl-3,5-H). – ^{13}C NMR ($CDCl_3$): δ = 20.73 (mesityl-4-CH_3), 22.63 (mesityl-2,6-CH_3), 34.86 (C-2), 43.57 (C-1), 55.53, 55.74 (OCH_3), 111.1, 111.3 (Ar-C-2,5), 120.6 (Ar-C-6), 130.1 (Ar-C-1), 131.7 (mesityl-C-3,5), 133.2 (mesityl-C-4), 138.9 (mesityl-C-2,6), 142.0 (mesityl-C-1), 147.7, 148.9 (Ar-C-3,4). – MS (70 eV), *m/z* (%): 363 (42) [M^+], 212 (13) [$M^+ - C_9H_{11}O_2$], 183 (53) [$C_9H_{11}SO_2^+$], 164 (45) [$C_{10}H_{12}O_2^+$], 151 (100) [$C_9H_{11}O_2^+$], 119 (82) [$C_9H_{11}^+$]. – $C_{19}H_{25}NO_4S$ (363.5): calcd. C 62.78, H 6.93; found C 62.95, H 6.87.

N-[2-(2-Iodo-4,5-dimethoxyphenyl)ethyl]mesitylenesulfonamide (**5a**): To a solution of sulfonamide **4** (1.31 g, 3.60 mmol) and iodine (366 mg, 1.44 mmol) in methanol (40 ml) was added a solution of iodic acid (134 mg, 0.76 mmol) in water (10 ml), and the reaction mixture was refluxed with the exclusion of light for 48 h. After removal of the solvent in vacuo the residue was dissolved in dichloromethane (20 ml) and the obtained solution was washed with diluted aqueous Na_2SO_3 (5 ml), water (5 ml), and brine (10 ml). The organic phase was dried (Mg_2SO_4) and the solvent removed in vacuo. Chromatography (petroleum ether/ethyl acetate, 1:1) of the residue yielded **5a** (1.62 g, 3.31 mmol, 92%) as colourless crystals. R_f = 0.41 (petroleum ether/ethyl acetate, 1:1), m.p. 141°C. – IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1}, 3298 (NH), 2972, 2940, 2920, 2846 (CH), 1630, 1600 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 206 nm (4.849), 236 (4.314), 284 (3.652). – ^1H NMR ($CDCl_3$): δ = 2.30 (s, 3H, mesityl-4-CH_3), 2.59 (s, 6H, mesityl-2,6-CH_3), 2.85 (t, *J* = 6.0 Hz, 2H, 2-H), 3.14 (dt, *J* = 6.0, 6.0 Hz, 2H, 1-H), 3.82 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.50 (t, *J* = 6.0 Hz, 1H, NH), 6.66 (s, 1H, Ar-6-H), 6.92 (s, 2H, mesityl-3,5-H), 7.16 (s, 1H, Ar-3-H). – ^{13}C NMR ($CDCl_3$): δ = 20.89 (mesityl-4-CH_3), 22.96 (mesityl-2,6-CH_3), 39.99 (C-2), 42.52 (C-1), 55.85, 56.12 (OCH_3), 87.83 (Ar-C-2), 112.7 (Ar-C-6), 121.6 (Ar-C-3), 131.9 (mesityl-C-3,5), 132.9 (Ar-C-1), 133.4 (mesityl-C-4), 139.0 (mesityl-C-2,6), 142.1 (mesityl-C-1), 148.3, 149.3 (Ar-C-4,5). – MS (70 eV), *m/z* (%): 489 (79) [M^+], 290 (17) [$C_{10}H_{11}IO_2^+$], 277 (100) [$C_9H_{10}IO_2^+$], 183 (66) [$C_9H_{11}SO_2^+$]. – $C_{19}H_{24}INO_4S$ (489.4): calcd. C 46.63, H 4.94; found C 46.63, H 4.93.

General Procedure I. – Preparation of Trifluoroacetamides **9a** *and* **9b**: To a solution of the amine **8a** and **8b** (10.0 mmol), respectively, and triethylamine (10.0 mmol) in tetrahydrofuran (50 ml) trifluoroacetic anhydride was added dropwise at −15°C. After warming up to room temp. the mixture was stirred for 2 h. Then, water (50 ml) was added and the aqueous layer extracted with ether (3 × 10 ml). The combined organic phases were washed with water (10 ml), brine (20 ml), and dried ($MgSO_4$). After removal of the solvent in vacuo the residue was purified by crystallisation (ether/methanol).

2,2,2-Trifluoro-N-(2-iodophenyl)acetamide (**9a**): According to general procedure I, **8a** (2.19 g, 10.0 mmol) was transformed into **9a** (2.77 g, 8.80 mmol, 88%) as colourless crystals. Compound **9a** is mentioned in the literature[11], but physical and spectroscopical data were not reported. R_f = 0.29 (petroleum ether/ether, 20:1), m.p. 102°C. – IR (KBr): $\tilde{\nu}$ = 3212 cm^{-1} (NH), 3064, 2964, 2920, 2880 (CH), 1712 (C=O), 1578 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 221 nm (4.167). – ^1H NMR ($CDCl_3$): δ = 6.98 (ddd, *J* = 8.0, 8.0, 1.5 Hz, 1H, 4-H), 7.42 (ddd, *J* = 8.0, 8.0, 1.5 Hz, 1H, 5-H), 7.84 (dd, *J* = 8.0, 1.5 Hz, 1H, 6-H), 8.21 (dd, *J* = 8.0, 1.5 Hz, 1H, 3-H), 8.28 (sbr, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 90.28 (C-2), 115.6 (q, *J* = 289 Hz, $COCF_3$), 122.1 (C-6), 127.9 (C-4), 129.6 (C-5), 135.6 (C-1), 139.2 (C-3), 154.8 (q, *J* = 37.7 Hz, $COCF_3$). – MS (70 eV), *m/z* (%): 315 (37) [M^+], 188 (100) [$M^+ - I$]. – $C_8H_5F_3INO$: calcd. 314.9368; found 314.9366 (HRMS).

2,2,2-Trifluoro-N-(2-iodobenzyl)acetamide (**9b**): According to general procedure I, **8b** (2.33 g, 10.0 mmol) was transformed into **9b** (3.06 g, 9.30 mmol, 93%) as colourless crystals. M.p. 75°C (ref.[13]: Yield 46%, m.p. 74–76°C).

General Procedure II. – Preparation of Propargylsilanes **7a**, **7b**, **10a** *and* **10b**: To a suspension of sodium hydride (1.1 equiv. washed with *n*-pentane) and dimethylformamide the amides **5a**, **5b**, **9a**, and **9b**, respectively, were added in small portions (to give a 0.15 M solution) at 0°C under argon, and the obtained mixture was stirred until hydrogen evolution had ceased. After warming to room temp., propargyl iodide **6** (1.1 equiv.) was added. The temp. may be raised to 50°C to accelerate the alkylation. After completion of the reaction water (equal volume as dimethylformamide) and ether (double the volume of dimethylformamide) were added, the phases were separated, and the aqueous layer was extracted with ether (3 ×). The combined organic phases were washed with water and brine, dried (Na_2SO_4), the solvent was evaporated in vacuo, and the residue was purified by chromatography.

N-[2-(2-Iodo-4,5-dimethoxyphenyl)ethyl]-N-[4-(trimethylsilyl)but-2-ynyl]mesitylenesulfonamide (**7a**): According to general procedure II, **5a** (1.20 g, 2.45 mmol) was transformed into **7a** (1.31 g, 2.13 mmol, 87%) as a colourless oil after chromatography (petroleum ether/ethyl acetate, 4:1). R_f = 0.26 (petroleum ether/ethyl acetate, 4:1). – IR (film): $\tilde{\nu}$ = 2954 cm^{-1}, 2866, 2848 (CH), 2216 (C≡C), 1600 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 203 nm (4.814), 237 (4.276), 285 (3.621). – ^1H NMR ($CDCl_3$): δ = 0.11 [s, 9H, $Si(CH_3)_3$], 1.45 (t, *J* = 2.5 Hz, 2H, 4-H), 2.29 (s, 3H, mesityl-4-CH_3), 2.59 (s, 6H, mesityl-2,6-CH_3), 2.92 (t, *J* = 7.5 Hz, 2H, $ArCH_2CH_2$), 3.45 (t, *J* = 7.5 Hz, 2H, $ArCH_2CH_2$), 3.83 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.09 (t, *J* = 2.5 Hz, 2H, 1-H), 6.66 (s, 1H, Ar-6-H), 6.89 (s, 2H, mesityl-3,5-H), 7.12 (s, 1H, Ar-3-H). – ^{13}C NMR ($CDCl_3$): δ = −1.95 [$Si(CH_3)_3$], 7.17 (4-C), 20.91 (mesityl-4-CH_3), 22.89 (mesityl-2,6-CH_3), 35.90 (Ar-CH_2CH_2), 38.30 ($ArCH_2CH_2$), 45.69 (C-1), 55.77, 56.08 (OCH_3), 72.37 (C-2), 83.45 (C-3), 87.62 (Ar-C-2), 112.5 (Ar-C-6), 121.5 (Ar-C-3), 131.8 (mesityl-C-3,5), 132.7 (Ar-C-1), 133.7 (mesityl-C-4), 140.2 (mesityl-C-2,6), 142.2 (mesityl-C-1), 148.1, 149.2 (Ar-C-4,5). – MS (70 eV), *m/z* (%): 613 (24) [M^+], 336 (57) [$M^+ - C_9H_{10}IO_2$], 284 (100), 277 (22)

$[C_9H_{10}IO_2^+]$, 73 (45) $[C_3H_9Si^+]$. – $C_{26}H_{36}INO_4SSi$ (613.6): calcd. C 50.89, H 5.91; found C 50.97, H 5.87.

2,2,2-Trifluoro-N-[2-(2-iodo-4,5-dimethoxyphenyl)ethyl]-N-[4-(trimethylsilyl)but-2-ynyl]acetamide (**7b**): According to general procedure II, **5b** (1.25 g, 3.10 mmol) was transformed into **7b** (1.44 g, 2.73 mmol, 88%) as a colourless oil after chromatography (petroleum ether/ethyl acetate, 7:1). R_f = 0.23 (petroleum ether/ethyl acetate, 7:1). – IR (film): $\tilde{\nu}$ = 3002 cm^{-1}, 2956, 2906, 2842 (CH), 2222 (C≡C), 1694 (C=O), 1596 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 211 nm (4.682), 239 (4.145), 286 (3.539). – ^1H NMR ($CDCl_3$): δ = 0.06 [s, 9H, $Si(CH_3)_3$], 1.44 (t, J = 2.5 Hz, 1.2H, 4-H), 1.46 (t, J = 2.5 Hz, 0.8 Hz, 4-H), 2.96–3.04 (m, 2H, $ArCH_2CH_2$), 3.68 (t, J = 8.0 Hz, 1.2H, $ArCH_2CH_2$), 3.69 (t, J = 7.5 Hz, 1H, $ArCH_2CH_2$), 3.82, 3.84, 3.85 (3 s, 6H, OCH_3), 3.98 (sbr, 1.3H, 1H), 4.26 (t, J = 2.5 Hz, 0.7H, 1-H), 6.67 (s, 0.3H, Ar-6-H), 6.72 (s, 0.7H, Ar-6-H), 7.19 (s, 1H, Ar-3-H). – ^{13}C NMR ($CDCl_3$): δ = −2.03, −2.09 [$Si(CH_3)_3$], 7.00, 7.10 (C-4), 36.91, 37.24 ($Ar\text{-}CH_2CH_2$), 38.66 (q, J = 4.2 Hz, $ArCH_2CH_2$), 39.34 ($ArCH_2CH_2$), 46.90 (q, J = 3.0 Hz, C-1), 47.04 (C-1), 55.84, 55.93, 56.09, 56.13 (OCH_3), 71.63, 71.81 (C-3), 83.60, 83.80 (C-2), 87.,64, 87.76 (Ar-C-2), 112.4, 112.6 (Ar-C-6), 116.2 (q, J = 288 Hz, $COCF_3$), 121.6, 121.8 (Ar-C-3), 132.5), 133.0 (Ar-C-1), 148.4, 148.6, 149.5, 149.7 (Ar-C-4,5), 156.4 (q, J = 36.0 Hz, $COCF_3$). – MS (70 eV), *m/z* (%): 527 (33) $[M^+]$, 290 (60) $[C_{10}H_{11}IO_2^+]$, 277 (39) $[C_9H_{10}IO_2^+]$, 73 (100) $[C_3H_9Si^+]$. – $C_{19}H_{25}F_3INO_3Si$ (527.4): calcd. C 43.27, H 4.78; found C 43.38, H 4.82.

2,2,2-Trifluoro-N-(2-iodophenyl)-N-[4-(trimethylsilyl)but-2-ynyl]acetamide (**10a**): According to general procedure II, **9a** (2.20 g, 6.98 mmol) was transformed into **10a** (2.45 g, 5.58 mmol, 80%) as a colourless oil after chromatography (petroleum ether/ether, 20:1). R_f = 0.26 (petroleum ether/ether, 20:1). – IR (film): $\tilde{\nu}$ = 2958 cm^{-1}, 2898 (CH), 2224 (C≡C), 1710 (C=O). – UV (CH_3CN): λ_{max} (lg ε) = 225 nm (4.103). – ^1H NMR ($CDCl_3$): δ = 0.01 [s, 9H, $Si(CH_3)_3$], 1.40 (t, J = 2.5 Hz, 2H, 4-H), 3.90 (dt, J = 17.0, 2.5 Hz, 1H, 1-H_a), 5.03 (dt, J = 17.0, 2.5 Hz, 1H, 1-H_b), 7.12 (ddd, J = 8.0, 8.0, 2.0 Hz, 1H, Ar-4-H), 7.36 (d br., J = 8.0 Hz, 1H, Ar-6-H), 7.40 (ddd, J = 8.0, 8.0, 1.5 Hz, 1H, Ar-5-H), 7.91 (dd, J = 8.0, 1.5 Hz, 1H, Ar-3-H). – ^{13}C NMR ($CDCl_3$): δ = −2.06 [$Si(CH_3)_3$], 7.02 (C-4), 40.43 (C-1), 70.88 (C-3), 84.69 (C-2), 99.47 (Ar-C-2), 115.8 (q, J = 289 Hz, $COCF_3$), 128.7 (Ar-C-6), 130.9 (Ar-C-4), 131.2 (Ar-C-5), 139.8 (Ar-C-3), 140.3 (Ar-C-1), 156.1 (q, J = 36.4 Hz, $COCF_3$). – MS (70 eV), *m/z* (%): 439 (9) $[M^+]$, 424 (10) $[M^+ - CH_3]$, 387 (96), 73 (100) $[C_3H_9Si^+]$. – $C_{15}H_{17}F_3INOSi$ (439.3): calcd. C 41.01, H 3.90; found C 41.00, H 3.87.

2,2,2-Trifluoro-N-(2-iodobenzyl)-N-[4-(trimethylsilyl)but-2-ynyl]acetamide (**10b**): According to general procedure II, **9b** (1.70 g, 5.17 mmol) was transformed into **10b** (1.94 g, 4.29 mmol, 83%), as a colourless oil after chromatography (petroleum ether/ethyl acetate, 20:1). R_f = 0.29 (petroleum ether/ethyl acetate, 20:1). – IR (film): $\tilde{\nu}$ = 2958 cm^{-1}, 2898 (CH), 2222 (C≡C), 1700 (C=O). – ^1H NMR ($CDCl_3$): δ = 0.07 [s, 3.6H, $Si(CH_3)_3$], 0.10 [s, 5.4H, $Si(CH_3)_3$], 1.50 (t, J = 2.5 Hz, 2H, 4-H), 4.10 (sbr, 0.8H, 1-H), 4.21 (t, J = 2.5 Hz, 1.2H, 1-H), 4.76 (s, 0.8H, $ArCH_2N$), 4.82 (s, 1.2H, $ArCH_2N$), 6.99–7.17 (m, 2H, Ar-4,6-H), 7.35 (ddd, J = 8.5, 8.5, 1.5 Hz, 0.4H, Ar-5-H), 7.38 (ddd, J = 8.5, 8.5, 1.5 Hz, 0.6H, Ar-5-H), 7.88 (dd, J = 8.5, 1.5 Hz, 0.4H, Ar-3-H), 7.89 (dd, J = 8.5, 1.5 Hz, 0.6H, Ar-3-H). – ^{13}C NMR ($CDCl_3$): δ = −2.01 [$Si(CH_3)_3$], 7.04, 7.13 (C-4), 36.74 ($Ar\text{-}CH_2N$), 37.49 (q, J = 4.2 Hz, $Ar\text{-}CH_2N$), 53.60 (C-1), 54.74 (q, J = 3.7 Hz, C-1), 70.97, 71.23 (C-3), 84.43, 84.47 (C-2), 97.44, 98.72 (Ar-C-2), 116.3, 116.4 (q, J = 288 Hz, $COCF_3$), 126.6, 128.4, 128.6, 128.7 (Ar-C-4, Ar-C-5), 129.5, 129.6 (Ar-C-6), 136.8, 137.0 (Ar-C-1), 139.8 (Ar-C-3), 156.4 (q, J = 36.0 Hz, $COCF_3$). – MS (70 eV), *m/z* (%): 453 (7) $[M^+]$, 217 (100) $[C_7H_6I^+]$, 73 (67) $[C_3H_9Si^+]$. – $C_{16}H_{19}F_3INOSi$: calcd. 453.0233; found 453.0231 (HRMS).

1-Iodo-2-[4-(trimethylsilyl)but-2-ynyloxy]benzene (**12**): To a solution of sodium methoxide (300 mg, 5.45 mmol) in methanol (30 ml) were added **11** (1.00 g, 4.55 mmol) and propargyl iodide **6** (1.38 g, 5.45 mmol), and the mixture was refluxed for 12 h. After removal of the solvent in vacuo the residue was dissolved in ether (15 ml), and the resulting solution was washed with water (10 ml), brine (10 ml), and dried (Mg_2SO_4). Evaporation of the solvent in vacuo and chromatography (petroleum ether/ethyl acetate, 7:1) of the residue yielded **12** (1.03 g, 3.00 mmol, 66%) as a pale yellow oil. R_f = 0.52 (petroleum ether/ethyl acetate, 7:1). – IR (film): $\tilde{\nu}$ = 2956 cm^{-1}, 2888 (CH), 2220 (C≡C), 1580 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 203 nm (4.528), 228 (4.011), 277 (3.429), 284 (3.396). – ^1H NMR (C_6D_6): δ = 0.03 [s, 9H, $Si(CH_3)_3$], 1.33 (t, J = 2.5 Hz, 2H, 4-H), 4.45 (t, J = 2.5 Hz, 2H, 1-H), 6.48 (ddd, J = 8.0, 8.0, 1.5 Hz, 1H, Ar-4-H), 6.79 (dd, J = 8.0, 1.5 Hz, 1H, Ar-6-H), 7.07 (ddd, J = 8.0, 8.0, 2.0 Hz, 1H, Ar-5-H), 7.78 (dd, J = 8.0, 2.0 Hz, 1H, Ar-3-H). – ^{13}C NMR (C_6D_6): δ = −1.71 [$Si(CH_3)_3$], 7.66 (C-4), 57.92 (C-1), 74.41 (C-3), 87.29 (C-2), 87.60 (Ar-C-2), 113.6 (Ar-C-6), 123.4 (Ar-C-4), 129.7 (Ar-C-5), 140.4 (Ar-C-3), 157.5 (Ar-C-1). – MS (70 eV), *m/z* (%): 344 (1) $[M^+]$, 277 (93), 73 (100), $[C_3H_9Si^+]$. – $C_{13}H_{17}IOSi$ (344.3): calcd. C 45.36, H 4.98; found C 45.34, H 5.05.

General Procedure III. – Preparation of Allylsilanes **13**–**15**: To a stirred suspension of sodium formate (3.0 equiv.), tetrapropylammonium bromide (1.0 equiv.), palladium(II) acetate (5 mol-%), triphenylphosphane (10 mol-%), and degassed dimethylformamide the propargylsilanes **7a**, **7b**, **10a**, **10b**, and **12**, respectively, were added (to give a 0.05 M solution). The mixture was heated to 75–85°C with vigorous stirring (TLC, hexane/ether, 3:1). After completion of the reaction the unsoluble material was filtered off, then water (equal volume as dimethylformamide) and ether (double the volume of dimethylformamide) were added, the phases were separated, and the aqueous layer was extracted with ether (3×). The combined organic phases were washed with water and brine, dried (Na_2SO_4), the solvent was evaporated in vacuo and the residue was purified by chromatography.

2,3,4,5-Tetrahydro-3-(mesitylsulfonyl)-7,8-dimethoxy-[(Z)-2-(trimethylsilyl)ethylidene]-1H-3-benzazepine (**13a**): According to general procedure III, **7a** (900 mg, 1.47 mmol) was transformed into **13a** (644 mg, 1.32 mmol, 90%) as colourless crystals after chromatography (hexane/ether, 3:1). R_f = 0.36 (hexane/ether, 3:1), m.p. 116°C. – IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1}, 2950, 2874, 2830 (CH), 1632, 1604 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 203 nm (4.711), 257 (4.060). – ^1H NMR ($CDCl_3$): δ = 0.00 [s, 9H, $Si(CH_3)_3$], 1.38 [d, J = 9.0 Hz, 2H, $CH_2(Si(CH_3)_3$], 2.28 (s, 3H, mesityl-4-CH_3), 2.44 (s, 6H, mesityl-2,6-CH_3), 2.85 (t, J = 5.8 Hz, 2H, 5-H), 3.49 (t, J = 5.8 Hz, 2H, 4-H), 3.84 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.97 (sbr, 2H, 2-H), 5.62 (tt, J = 9.0, 1.0 Hz, 1H, $C=CHCH_2$), 6.56 (s, 2H, 6-H, 9-H), 6.86 (s, 2H, mesityl-3,5-H). – ^{13}C NMR ($CDCl_3$): δ = −1.78 [$Si(CH_3)_3$], 19.32 [$CH_2(Si(CH_3)_3$], 20.82 (mesityl-4-CH_3), 22.59 (mesityl-2,6-CH_3), 33.59 (C-5), 45.39 (C-4), 45.52 (C-2), 55.92, 55.96 (OCH_3), 111.6, 112.1 (C-6,9), 128.0 ($C=CHCH_2$), 131.6 (mesityl-C-3,5), 132.1 (mesityl-C-4), 134.0, 135.0 (C-5a,9a), 140.4 (mesityl-C-2,6), 142.2 (mesityl-C-1), 147.4, 147.7 (C-7,8). – MS (70 eV), *m/z*

(%): 487 (12) [M^+], 87 (100) [$C_4H_{11}Si^+$]. – $C_{26}H_{37}NO_4SSi$ (487.7): calcd. C 64.03, H 7.65; found C 64.27, H 7.64.

2,3,4,5-Tetrahydro-7,8-dimethoxy-N-(trifluoroacetyl)-[(Z)-2-(trimethylsilyl)ethylidene]-1H-3-benzazepine (**13b**): According to general procedure III, **7b** (3.25 g, 6.16 mmol) was transformed into **13b** (1.93 g, 4.81 mmol, 78%) as colourless crystals after chromatography (petroleum ether/ethyl acetate, 5:1). R_f = 0.21 (petroleum ether/ethyl acetate, 5:1), m.p. 102°C. – IR (KBr): $\tilde{\nu}$ = 2998 cm^{-1}, 2954, 2834 (CH), 1692 (C=O), 1634, 1606 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 211 nm (4.534), 260 (4.197), 291 (3.770). – ^1H NMR ($CDCl_3$): δ = 0.07 [s, 9H, $Si(CH_3)_3$], 1.58 [d, J = 9.0 Hz, 0.8H, $CH_2(Si(CH_3)_3)$], 1.73 [d, J = 9.0 Hz, 1.2H, $CH_2(Si(CH_3)_3)$], 2.89 (t, J = 6.0 Hz, 2H, 5-H), 3.74 (t, J = 6.0 Hz, 1.2H, 4-H), 3.83 (s, 3H, OCH_3), 3.86 (t, J = 6.0 Hz, 0.8H, 4-H), 3.86 (s, 3H, OCH_3), 4.33 (sbr, 2H, 2-H), 5.70 (tt, J = 9.0, 2.0 Hz, 0.4H, C=$CHCH_2$), 5.79 (tt, J = 9.0, 1.5 Hz, 0.6H, C=$CHCH_2$), 6.57, 6.69, 6.71 (3 s, 1H, 0.4H, 0.6H, 6,9-H). – ^{13}C NMR ($CDCl_3$): δ = −1.60 [$Si(CH_3)_3$], 19.73, 20.07 [$CH_2(Si(CH_3)_3)$], 31.51, 34.00 (C-5), 45.34 (C-4), 45.98 (C-2), 46.73 (q, J = 3.4 Hz, C-4), 47.10 (q, J = 3.0 Hz, C-2), 55.87, 55.91, 56.03 (OCH_3), 111.7, 111.8, 112.2 (C-6,9), 116.5 (q, J = 288 Hz, $COCF_3$), 126.8 (C=$CHCH_2$), 126.9, 127.1 (C-1), 129.6 (C=$CHCH_2$), 133.1, 133.9, 134.3 (C-5a,9a), 147.8, 148.0, 148.4 (C-7,8), 156.6 (q, J = 35.2 Hz, $COCF_3$). – MS (70 eV), *m/z* (%): 401 (34) [M^+], 73 (86) [$C_3H_9Si^+$], 43 (100). – $C_{19}H_{26}F_3NO_3Si$ (401.5): calcd. C 56.84, H 6.53; found C 57.05, H 6.52.

2,3-Dihydro-1-(trifluoroacetyl)-3-[(Z)-2-(trimethylsilyl)ethylidene]-1H-indole (**14a**): According to general procedure III, **10a** (800 mg, 1.82 mmol) was transformed into **14a** (124 mg, 0.40 mmol, 22%) as a pale yellow oil after chromatography (petroleum ether/ether, 30:1). R_f = 0.35 (petroleum ether/ether, 30:1). – IR (film): $\tilde{\nu}$ = 2956 cm^{-1}, 2898 (CH), 1702 (C=O), 1664, 1598 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 227 nm (4.115), 242 (4.194), 251 (4.235), 259 (4.214), 289 (4.078). – ^1H NMR ($CDCl_3$): δ = 0.10 [s, 9H, $Si(CH_3)_3$], 1.60 [d, J = 9.0 Hz, 2H, $CH_2(Si(CH_3)_3)$], 4.80 (t, J = 3.0 Hz, 2H, 2-H), 6.08 (tt, J = 9.0, 3.0 Hz, 1H, C=$CHCH_2$), 7.16 (ddd, J = 8.0, 8.0, 1.0 Hz, 1H, 6-H), 7.25 (ddd, J = 8.0, 8.0, 1.5 Hz, 1H, 5-H), 7.38 (dd, J = 8.0, 1.5 Hz, 1H, 7-H), 8.28 (dd, J = 8.0, 1.0 Hz, 1H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = −1.55 [$Si(CH_3)_3$], 21.44 [$CH_2(Si(CH_3)_3)$], 51.32 (q, J = 4.2 Hz, C-2), 116.0 (q, J = 288 Hz, $COCF_3$), 117.6 (C=$CHCH_2$), 118.3 (C-7), 125.9 (C-6), 128.3 (C-4), 128.7 (C-3a), 131.0 (C-3), 142.9 (C-7a). – MS (70 eV), *m/z* (%): 313 (68) [M^+], 298 (4) [$M^+ - CH_3$], 229 (22), 73 (100) [$C_3H_9Si^+$]. – $C_{15}H_{18}F_3NOSi$: calcd. 313.1110; found 313.1109 (HRMS).

1,2,3,4-Tetrahydro-2-(trifluoroacetyl)-4-[(Z)-2-(trimethylsilyl)-ethylidene]isoquinoline (**14b**): According to general procedure III, **10b** (1.00 g, 2.21 mmol) was transformed into **14b** (520 mg, 1.59 mmol, 72%) as a colorless oil after chromatography (petroleum ether/ether, 50:1). R_f = 0.23 (petroleum ether/ether, 50:1). – IR (film): $\tilde{\nu}$ = 2956 cm^{-1}, 2924, 2854 (CH), 1694 (C=O). – UV (CH_3CN): λ_{max} (lg ε) = 205 nm (4.229), 264 (4.009). – ^1H NMR ($CDCl_3$): δ = 0.06 [s, 9H, $Si(CH_3)_3$], 1.71 [d, J = 9.0 Hz, 1H, $CH_2(Si(CH_3)_3)$], 1.77 [d, J = 9.0 Hz, 1H, $CH_2(Si(CH_3)_3)$], 4.42 (sbr, 1H, 3-H), 4.47 (sbr, 1H, 3-H), 4.67 (s, 1H, 1-H), 4.78 (s, 1H, 1-H), 6.21 (dt, J = 9.0, 2.0 Hz, 0.5H, C=$CHCH_2$), 6.23 (dt, J = 9.0, 2.0 Hz, 0.5H, C=$CHCH_2$), 7.10–7.31 (m, 3H, 6,7,8-H), 7.50 (dd, J = 7.5, 1.5 Hz, 0.5H, 5-H), 7.51 (dd, J = 7.5, 1.5 Hz, 0.5H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = −1.60 [$Si(CH_3)_3$], 19.82, 20.24 [$CH_2(Si(CH_3)_3)$], 43.32 (C-1), 44.18 (q, J = 3.7 Hz, C-1), 45.94 (C-3), 47.73 (q, J = 3.8 Hz, C-3), 116.5 (q, J = 288 Hz, $COCF_3$), 123.2, 123.5 (C=$CHCH_2$), 124.6 (C-5), 125.3 (C-4), 125.4 (C-5), 125.7, 126.5 (C-7), 126.9, 127.0, 127.5, 128.0 (C-6,8), 130.4 (C-4a), 134.1, 134.9 (C-8a), 155.9 (q, J = 37.0 Hz, $COCF_3$). – MS (70 eV), *m/z* (%): 327 (3) [M^+], 255 (98) [$M^+ - C_3H_9Si$], 128 (100), 73 (10) [$C_3H_9Si^+$]. – $C_{16}H_{20}F_3NOSi$ (327.4): calcd. C 58.69, H 6.16; found C 58.59, H 6.20.

2,3-Dihydro-3-[(Z)-2-(trimethylsilyl)ethylidene]benzofuran (**15**): According to general procedure III, **12** (900 mg, 2.90 mmol) was transformed into **15** (368 mg, 1.68 mmol, 58%) as a pale yellow oil after chromatography (hexane/ether, 100:1). R_f = 0.22 (hexane/ether, 100:1). – IR (film): $\tilde{\nu}$ = 2954 cm^{-1}, 2916, 2896, 2872 (CH), 1660, 1608, 1596 (C=C). – UV (CH_3CN): λ_{max} (lg ε) = 212 nm (4.220), 231 (4.047), 262 (3.797), 317 (4.041), 330 (4.043). – ^1H NMR ($CDCl_3$): δ = 0.08 [s, 9H, $Si(CH_3)_3$], 1.51 [dt, J = 9.0, 1.5 Hz, 2H, $CH_2(Si(CH_3)_3)$], 5.08 (dt, J = 3.0, 1.5 Hz, 2H, 2-H), 5.90 (tt, J = 9.0, 3.0 Hz, 1H, C=$CHCH_2$), 6.83 (dd, J = 7.5, 1.0 Hz, 1H, 7-H), 6.87 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H, 5-H), 7.11 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H, 6-H), 7.32 (dd, J = 7.5, 1.5 Hz, 1H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 0.00 [$Si(CH_3)_3$], 22.92 [$CH_2(Si(CH_3)_3)$], 75.33 (C-2), 111.6 (C-7), 115.8 (C=$CHCH_2$), 121.0 (C-5), 122.0 (C-6), 128.3 (C-3a), 130.0 (C-4), 134.6 (C-3), 164.3 (C-7a). – MS (70 eV), *m/z* (%): 218 (23) [M^+], 203 (12) [$M^+ - CH_3$], 145 (13) [$M^+ - C_3H_9Si$], 73 (100) [$C_3H_9Si^+$]. – $C_{13}H_{18}OSi$ (218.4): calcd. C 71.50, H 8.31; found C 71.41, H 8.37.

X-ray Crystal-Structure Analysis of **13b**[14]: Colourless crystals from hexane. – Crystal data: $C_{19}H_{26}F_3NO_3Si$ (401.50); monoclinic; space group $P2_1/c$; a = 1055.3(2), b = 1952.2(4), c = 1033.9(2) pm, α = 90, β = 94.99(2), γ = 90°; Z = 4; $d_{calcd.}$ = 1.257 mg m^{-3}. – Data collection: Stoe Siemens AED four-circle diffractometer; Mo-K_α radiation (λ = 71.073 pm, ω/2Θ-scan technique); graphite monochromator; crystal size 0.60 × 0.40 × 0.20 mm; Θ = 3.56 to 22.45°; index ranges $0 \leq h \leq 11$, $-19 \leq k \leq 0$, $-11 \leq l \leq 11$; 4051 measured reflections, 2702 independent reflections (R_{int} = 0.0227); absorption coefficient 0.154 mm^{-1}. – Structure solution and refinement: Full-matrix least-squares on F^2. Atomic scattering factors from International Tables for X-ray Crystallography[15]. Data-to-parameter ratio 10.92; final R indices [$I > 2\sigma(I)$] $R1$ = 0.0629, $wR2$ = 0.1376. Programme used for structure solution: SHELXS-90. Programme used for structure refinement: SHELXL-92.

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