Jan Horstmann, Stefanie Reger, Beate Neumann, Hans-Georg Stammler and Norbert W. Mitzel*

One-pot desilylation-Sonogashira coupling

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Abstract: Coupling of diethynyldiphenylsilane (**1**) with aryl halides under Sonogashira conditions affords the symmetrical diarylacetylenes bis(2-methylpyridin-5-yl)acetylene (**2**), bis(4-fluorophenyl)acetylene (**3**) and bis(4-trifluoromethylphenyl)acetylene (**4**) in 60% to 82% yield. In the case of **2**, the by-product bis(2-methylpyridin-5-yl)butadiyne (**2a**) was isolated in 12% yield. The occurring desilylation reaction was investigated by treating bis(phenylethynyl)diphenylsilane (**5**) under the same conditions. The formation of 1-fluoro-4-(phenylethynyl)benzene (**6**), 1-trifluoromethyl-4-(phenylethynyl)benzene (**7**) and (tetrafluoropyridin-4-yl)ethynylbenzene (**8**) in 70 to 84% yield and the cleavage of hexaphenylcyclotrisiloxane were observed in all cases.

Keywords: desilylation; diarylacetylene; Songogashira coupling.

1 Introduction

Since Sonogashira and Hagihara reported Pd- and Cu-catalyzed reactions of aryl halides with terminal acetylenes in 1975, this cross coupling reaction is used extensively for the syntheses of acetylenic compounds [1, 2]. It is the most popular and widely used procedure for alkynylation of aryl halides (simply known as Sonogashira coupling). A wide range of conditions concerning the Pd catalyst, phosphorus ligand, amine solvent and the alkynylation reagent has been used over the years depending on the substrates [3].

Using alkyne protecting groups, the synthesis of internal alkynes is mostly carried out in stepwise procedures of coupling, deprotection and coupling again. Only a few one-pot reaction protocols for diarylacetylenes using palladium nanoparticles [4], alkyne metathesis [5] or by addition of deprotection reagents, e.g. CuCl or DBU and H_2O, have been published [6–9]. Multiple Sonogashira coupling cycles can also be used for the syntheses of oligomers [10] and polymers [11]. In 2005, Kunugi et al. used diethynyldibutylsilane and dibromoarenes to generate copolymers and observed a hydrolytic desilylation in wet triethylamine. Converting 1-bromonaphtalene with diethynyldibutylsilane and thousand equivalents of water provides dinaphthylacetylene [12].

Herein we present an efficient method for the synthesis of diarylacetylenes using diethynyldiphenylsilane as acetylene source, standard substrates and catalysts [ArBr, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH] without any other additions. In a one-pot synthetic procedure, Sonogashira-coupled diethynyldiphenylsilanes undergo a desilylation to terminal alkynes, which are coupled *in situ* again with hexaphenylcyclotrisiloxane being formed after hydrolysis. This was proven by the desilylation-Sonogashira coupling of bis(phenylethynyl)diphenylsilane at 100°C in diisopropylamine. In all cases, both alkynyl units of diethynyldiphenylsilane (**1**) and bis(phenylethynyl)diphenylsilane (**5**) can be transferred, as is indicated by the yields (>50%).

2 Results and discussion

During our investigations in the field of host-guest complexes, we synthesized new bidentate Lewis acids and bases [13]. Di- and triethinylsilanes were intended to provide the necessary backbones for corresponding functionalization. The treatment of diethynyldiphenylsilane (**1**) with 5-bromo-2-methylpyridine under Sonogashira conditions [$PdCl_2(PPh_3)_2$, CuI, diisopropylamine] did not afford the desired product bis[(6-methylpyridin-3-yl)ethynyl]diphenylsilane. After hydrolysis we found bis(2-methylpyridin-5-yl)acetylene (**2**), bis(2-methylpyridin-5-yl)butadiyne (**2a**) and hexaphenylcyclotrisiloxane to be the major components of the crude product by GC/MS analysis (Scheme 1).

Diethynyldiphenylsilane (**1**) is a crystalline, air and moisture stable solid that can easily be synthesized and handled [14, 15]. However, when **1** was converted under Sonogashira conditions in diisopropylamine, desilylation took place. First, when the Sonogashira coupling of

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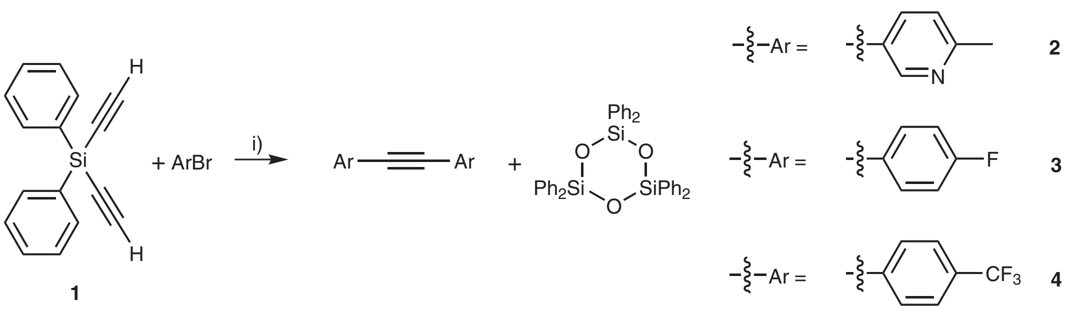
***Corresponding author: Norbert W. Mitzel,** Chair of Inorganic and Structural Chemistry, Faculty of Chemistry and Center for Molecular Materials CM_2, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany, Fax: Int +(0)521 106 6026,
E-mail: mitzel@uni-bielefeld.de
Jan Horstmann, Stefanie Reger, Beate Neumann and Hans-Georg Stammler: Chair of Inorganic and Structural Chemistry, Faculty of Chemistry and Center for Molecular Materials CM_2, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany



Scheme 1: Syntheses of symmetrical diarylacetylenes **2**, **3** and **4** *via* Sonogashira and desilylation reactions of **1**. Reagents and conditions: (i) ArBr (2.3–6.0 eq.), $PdCl_2(PPh_3)_2$ (3.0–4.1 mol%), CuI (3.4–5.9 mol%), *i*-Pr_2NH, reflux, 14–95 h, 60–82%.

Table 1: One-pot syntheses of symmetrical diarylacetylenes from **1** (for Ar see Scheme 1).

Compound	Equiv. ArBr[a]	$PdCl_2(PPh_3)_2$ (mol%)[b]	CuI (mol%)[b]	Time (h)	Yield (%)[c]
2	2.3	3.3	5.9	14	63[d]
3	5.0	4.1	4.1	95	60
3	5.0	4.1	4.1	24	57
4	6.0	3.4	3.4	21	82

[a] Based on **1**; [b] based on ArBr; [c] isolated yield based on **1**; [d] based on ArBr.

1 was conducted in diisopropylamine, only 2.3 equivalents of 5-bromo-2-methylpyridine were introduced (Table 1). Nevertheless, compound **2** could be isolated by sublimation in 63% yield, based on the insufficient amount of aryl bromide. When trimethylsilylacetylene was used instead of **1**, no desilylation of the trimethylsilyl group was observed, and 2-methyl-5-(trimethylsilylethynyl)pyridine was formed almost quantitatively. Further reactions of **1** were carried out using an excess of 25% (5 equiv.) or 50% (6 equiv.) of aryl bromides. Fluoro- and trifluoromethyl-substituted aryl bromides were used to verify the formation of the corresponding diarylacetylene in solution *via* ^{19}F NMR spectra before hydrolysis of the reaction mixture.

The crude product of **3** was analyzed by ^{19}F NMR spectroscopy. The spectrum displays only the signals of product **3** [$\delta = -110.8$ ppm (tt)] and of residual 4-fluorobromobenzene [$\delta = -115.3$ ppm (tt)] after 95 h. A reaction time of 95 h does not substantially increase the yield. A reaction time of 24 h affords a slightly lower yield of 57% under the same reaction conditions. Grieco et al. could isolate **3** in 89% yield, using the aryl iodide, trimethylsilylacetylene, double molar catalyst ratio, water and six equivalents of DBU at 60°C after 18 h. Although our yield is lower, it shows the application width of the desilylation-Sonogashira coupling. In case of the trifluoromethyl compound **4** [$\delta(^{19}F) = -62.9$ ppm], a good yield of 82% could be achieved even after a reaction time of only 21 h. 1,2-Bis(4-trifluoromethylphenyl)butadiyne [$\delta(^{19}F) = -63.0$ ppm] was isolated as a second product in 8% yield. In the literature, the synthesis of **4** is usually described by multistep couplings or alkyne metathesis (max. yield 49% overall) [5].

The excess of alkynyl units (only 2.3 equiv. of ArBr) in the reaction mixture of **2** leads to the mentioned second product bis(2-methylpyridin-5-yl)butadiyne (**2a**) in 12% yield. Single crystals suitable for X-ray diffraction experiments of this compound were obtained by slow evaporation of a concentrated solution in benzene (Fig. 1).

Bis(2-methylpyridin-5-yl)butadiyne (**2a**) crystallizes in the triclinic space group $P\bar{1}$, with one molecule per unit cell. The C≡C bond lengths are 1.202(2) Å, and the adjacent single bonds to the pyridine are longer [1.431(1) Å] than C(1)–C(1′) between the C≡C bonds [1.373(2) Å], which is typical for bispyridinylbutadiyne derivatives [16]. The butadiyne unit of **2a** is linear, as indicated by the

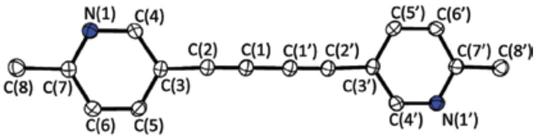
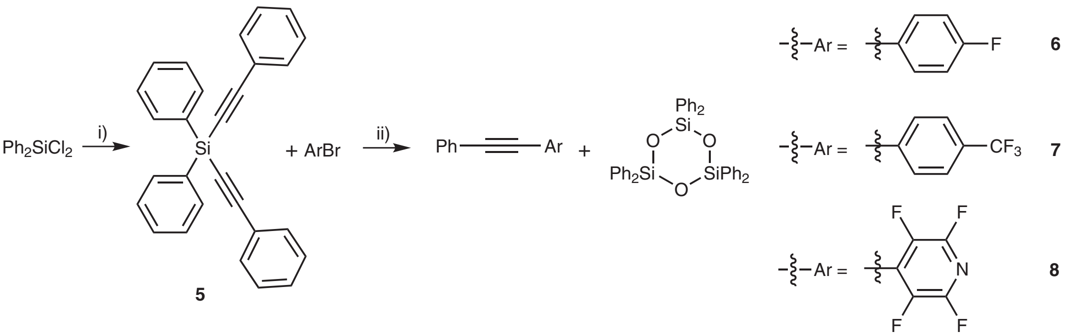


Fig. 1: Molecular structure of bis(2-methylpyridin-5-yl)butadiyne (**2a**) in the crystalline state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–C(1′) 1.373(2), C(1)–C(2) 1.202(2), C(2)–C(3) 1.431(1); C(1′)–C(1)–C(2) 179.2(2), C(1)–C(2)–C(3) 177.6(1). Symmetry equivalent atoms are generated by the operation $1-x$, $2-y$, $1-z$.



Scheme 2: Syntheses of unsymmetrical phenylacetylenes **6**, **7** and **8** *via* desilylation reactions of **5**. Reagents and conditions: (i) 2.1 eq. phenylacetylene, 2.1 eq. *n*-BuLi, THF, −78°C to r. t., 90% (ii) 2.8–3.0 eq. ArX [X = Br (**6**, **7**), X = I (**8**)], $PdCl_2(PPh_3)_2$ (2.8–4.4 mol%), CuI (4.5–6.1 mol%), *i*-Pr_2NH, reflux, 16–70 h, 70 to 84%.

centroid(pyridine)-center[C(1)–C(1′)]-centroid(pyridine) angle of 180° [13].

To clarify, whether the desilylation took place before or after the first Sonogashira coupling, we synthesized the phenyl substituted diethynyldiphenylsilane **5** *via* salt elimination, in order to avoid the formation of diphenylacetylene when using bromobenzene in a Sonogashira coupling (Scheme 2). Similar to compound **1** bis(phenylethynyl)diphenylsilane (**5**) is a crystalline air and moisture stable solid. Single crystals suitable for X-ray diffraction experiments were obtained by slow evaporation of a concentrated *n*-hexane solution (Fig. 2).

Bis(phenylethynyl)diphenylsilane (**5**) crystallizes in the monoclinic space group *Pc*, with two molecules per unit cell. The Si(1)–C bonds toward the ethynyl substituents are slightly shorter than the Si(1)–C bonds toward the phenyl substituents [C(21)–Si(1) 1.829(2) Å vs. C(1)–Si(1) 1.868(2) Å]. The C≡C bonds are of normal length [C(13)–C(14) 1.206(3) Å and C(21)–C(22) 1.202(3) Å] [11] and the centroid(phenyl)-center[C(1)–C(1′)]-centroid(phenyl) angle is compressed to 106.1(1)°. In contrast to other diethynyldiphenylsilane derivatives, the angle between the ethynyl units is also shortened to 107.5° [C(21)–Si(1)–C(13)] while C(1)–Si(1)–C(7) [112.5(1)°] is widened [17].

Compound **5** was converted with aryl halides under the Sonogahira conditions mentioned above. Compound **5** first undergoes a desilylation reaction toward the phenylacetylene unit, which is directly substituted in a Sonogashira coupling with the aryl substrate (Scheme 2).

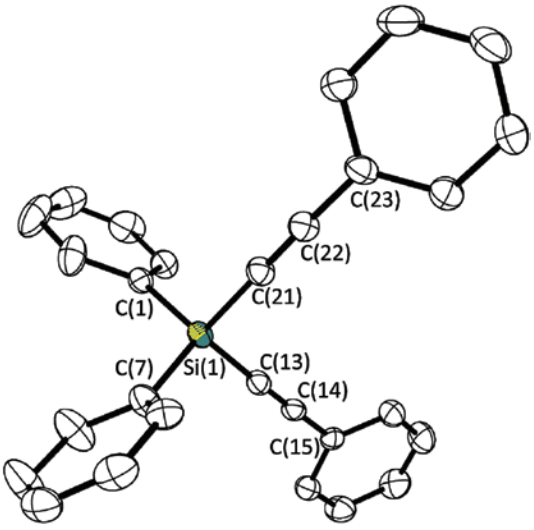


Fig. 2: Molecular structure of bis(phenylethynyl)diphenylsilane (**5**) in the crystalline state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–Si(1) 1.868(2), C(7)–Si(1) 1.863(2), C(21)–Si(1) 1.829(2), C(13)–Si(1) 1.830(2), C(13)–C(14) 1.206(3), C(14)–C(15) 1.436(3), C(21)–C(22) 1.202(3), C(22)–C(23) 1.438(3); C(1)–Si(1)–C(7) 112.5(1), C(21)–Si(1)–C(13) 107.5(1), Si(1)–C(13)–C(14) 177.8(2), C(13)–C(14)–C(15) 179.0(2), Si(1)–C(21)–C(22) 179.7(2), C(21)–C(22)–C(23) 178.3(2).

We converted **5** with three different fluorine substituted aryl halides (Table 2). Using 4-fluorobromobenzene, 1-fluoro-4-phenylethynylbenzene (**6**) could be isolated in 76% yield. This proves that **5** is a transfer reagents for two equivalents of phenylacetylene under Sonogashira coupling conditions. Although phenylacetylene could be used instead of **5** under these conditions, this desilylation opens new possibilities in the synthesis of unsymmetrically arylphenylacetylenes. The formation of tetrafluoropyridinyl-4-ethynylbenzene (**8**) indicates that a reaction time of 16 h might be sufficient (**6** and **7** were refluxed over the weekend). 1-Bromo-4-trifluoromethylbenzene can be converted in a good yield of 70% into **7** without formation of other products than hexaphenylcyclotrisiloxane, which can be easily separated by column chromatography. Single crystals of compound **7** suitable for X-ray diffraction experiments were obtained by slow evaporation of a concentrated solution in DCM (Fig. 3).

Table 2: Syntheses of unsymmetrical aryl-phenylacetylenes **6**, **7** and **8** from **5** (for Ar see Scheme 2).

Compound	Equiv. ArX[a]	$PdCl_2(PPh_3)_2$ (mol%)[b]	CuI (mol%)[b]	Time (h)	Yield (%)[c]
6	3.0	4.4	5.0	65	76
7	2.8	4.2	4.5	70	70
8	2.6	2.8	6.1	16	84

[a][X = Br (**6**, **7**), X = I (**8**)], based on **5**; [b]based on ArBr; [c]isolated yield based on **5**.

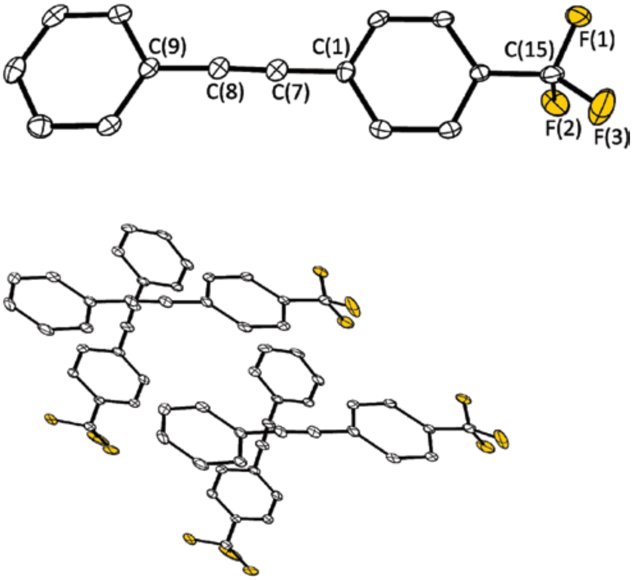


Fig. 3: Molecular structure of 1-trifluoromethyl-4-phenylethynylbenzene (**7**) (above) and its packing in the crystalline state (below). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(15)–F(1) 1.337(2), C(15)–F(2) 1.345(2), C(15)–F(3) 1.338(2), C(9)–C(8) 1.437(2), C(8)–C(7) 1.198(2), C(7)–C(1) 1.434(2); F(1)–C(15)–F(2) 105.8(1), F(1)–C(15)–F(3) 106.6(1), F(2)–C(15)–F(3) 106.3(1), C(9)–C(8)–C(7) 177.4(2), C(8)–C(7)–C(1) 178.2(2).

1-Trifluoromethyl-4-(phenylethynyl)benzene (**7**) crystallizes in the orthorhombic space group *Pbcn*, with eight molecules per unit cell. All C–F bonds are of the same length within experimental error. The observed compressed F–C(15)–F angles [F(1)–C(15)–F(2) 105.8(1)°, F(1)–C(15)–F(3) 106.6(1)° and F(2)–C(15)–F(3) 106.3(1)°] agree well with predictions of the VSEPR model. The C≡C bond is 1.198(2) Å long and the centroid(phenyl)-center[C(1)–C(1′)]-centroid(phenyl) angle is close to linearity [178.9(1)°].

3 Conclusion

With diethynyldiphenylsilane (**1**), we present a stable and easily accessible reagent for the synthesis of symmetrical diarylacetylenes in yields up to 82% under standard Sonogashira conditions [ArX, $PdCl_2(PPh_3)_2$, CuI, *i*-Pr_2NH, reflux] without any further additives. In a one-pot protocol, two Sonogashira coupling reactions and a desilylation of the primarily coupled bis(arylethynyl)diphenylsilane take place. This sequence could be clarified by using bis(phenylethynyl)diphenylsilane (**5**) to generate phenyl-substituted diarylacetylenes in up to 84% yields. In all cases, both alkynyl units could be transferred, and hexaphenylcyclotrisiloxane was identified as a second product after hydrolysis.

4 Crystal structure determinations

Suitable crystals of compounds **5** and **7** were obtained by cooling saturated *n*-hexane solutions to −30°C, **2a** from saturated benzene solution. The crystals were coated with paratone-N oil, selected, mounted on a glass fiber and transferred onto the goniometer into the cryostream of the diffractometer. Data collections were performed at 100.0(2) K on a SuperNova diffractometer, using monochromated Cu-Kα radiation.

Using OLEX2, the structures were solved by Direct Methods and refined by full-matrix least-squares cycles (program SHELX-97) [18, 19]. Crystal and refinement details as well as CCDC numbers are provided in Table 3.

CCDC 1528756–1528758 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

5 Experimental section

5.1 Materials and methods

The syntheses and structures of diethynyldiphenylsilane (**1**) [14, 15] and bis(2-methylpyridin-5-yl)acetylene (**2**) [13] have been described elsewhere. All reactions were performed under an anhydrous, inert atmosphere of nitrogen

Table 3: Crystallographic data for **2a**, **5** and **7**.

	2a	**5**	**7**
Empirical formula	$C_{16}H_{12}N_2$	$C_{28}H_{20}Si$	$C_{15}H_9F_3$
M_r	232.28	384.53	246.22
$F(000)$, e	122	404	1008
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	Pc	$Pbcn$
a, Å	6.1877(6)	10.16959(14)	14.5263(5)
b, Å	6.5036(5)	9.31545(9)	5.85100(19)
c, Å	7.6239(8)	12.29851(14)	27.2283(10)
α, deg	87.694(7)	90	90
β, deg	77.641(9)	108.9004(13)	90
γ, deg	89.608(7)	90	90
V, Å^3	299.45(5)	1102.27	2314.22(14)
Z	1	2	8
$\rho_{calcd.}$, g cm^{-3}	1.29	1.16	1.41
μ, mm^{-1}	0.6	1.0	1.0
θ_{max}, deg	144.6	144.5	152.3
Index ranges	$-7 \le h \le 7$	$-11 \le h \le 12$	$-18 \le h \le 14$
h, k, l	$-8 \le k \le 8$	$-11 \le k \le 11$	$-7 \le k \le 5$
	$-9 \le l \le 8$	$-15 \le l \le 15$	$-33 \le l \le 31$
Reflexes collected	4269	18048	6221
Independent reflexes	1176	4155	2367
R_{int}	0.0194	0.0262	0.0342
Observed refl. ($I > 2\,\sigma(I)$)	963	4107	1950
Ref. parameters	83	282	199
R_1 ($I > 2\sigma(I)$)	0.0411	0.0273	0.0429
wR_2 ($I > 2\sigma(I)$)	0.1173	0.0708	0.1148
R_1 (all data)	0.0479	0.0276	0.0524
wR_2 (all data)	0.1245	0.0712	0.1251
Flack parameter x	–	−0.001(8)	–
GoF	1.088	1.072	1.042
$\Delta\rho_{max}/\rho_{min}$, e Å^{-3}	0.18/−0.22	0.20/−0.14	0.27/−0.31
CCDC	1528756	1528757	1528758
Remarks	–	[a]	–

[a] Disorder of C(8), C(9) and C(10) over two sites (58:42); disorder of C(26), C(27) and C(28) over two sites (77:23).

or argon by using Schlenk or glovebox techniques and freshly dried and distilled solvents (benzene dried with Na/K alloy, THF dried with K, pentane, *n*-hexane and Et_2O dried with $LiAlH_4$). Diisopropylamine (99%) was purchased from Merck KGaA (Darmstadt). Bis(triphenylphosphine) palladium(II) dichloride (from Fluorochem), CuI (from Merck), phenylacetylene (from Aldrich), 4-fluorobromobenzene (from Merck), 5-bromo-2-methylpyridine (from fluorochem) and 4-trifluoromethylbromobenzene (from Lancaster) were used as purchased. NMR spectra were recorded on a Bruker DRX 500 and a Bruker Avance III 500 HD instrument. The chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$: ^1H NMR, $\delta = 7.26$ ppm, ^{13}C NMR, $\delta = 77.16$ ppm) or referenced externally (^{29}Si: $SiMe_4$, ^{19}F: $CFCl_3$). EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by push rod in aluminum crucibles. Ions were accelerated by 8 kV. Elemental analyses were performed with CHNS elemental analyzer HEKAtech EURO EA.

5.2 Bis(2-methylpyridin-5-yl)butadiyne (2a)

Diethynyldiphenylsilane (1.0 g, 4.3 mmol) and 5-bromo-2-methylpyridine (1.6 g, 10 mmol) were dissolved in diisopropylamine (30 mL), and the solution was degassed two times. $PdCl_2(PPh_3)_2$ (230 mg, 0.33 mmol) and CuI (110 mg, 0.59 mmol) were added, and the yellow solution was refluxed for 14 h. The reaction was quenched with sat. aqueous NH_4Cl solution (30 mL) and extracted with DCM (40 mL). The organic phases were dried over $MgSO_4$, and all volatile compounds were removed in vacuum. Sublimation (100°C, 10^{-2} mbar) provided **2a** as a colorless solid. Yield 140 mg (0.60 mmol, 12%). – ^1H NMR (500 MHz, C_6D_6): $\delta = 8.71$ (s, 2H, 2-*H*), 7.31 (d, $J = 7.9$, 2H, 4-*H*), 6.36 (d, $J = 8.0$ Hz, 2H, 5-*H*), 2.25 (s, 6H, CH_3) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta = 159.2$, 153.0, 139.2, 122.5, 115.9, 80.1, 76.9, 24.5 ppm. – EI-MS (70 eV): $m/z = 232.2$, 208.2, 180.1.

5.3 Bis(4-fluorophenyl)acetylene (3)

Diethynyldiphenylsilane (100 mg, 0.44 mmol) and 1-bromo-4-fluorobenzene (0.24 mL, 2.2 mmol) were dissolved in diisopropylamine (15 mL). The solution was degassed two times and CuI (17 mg, 0.09 mmol) and $PdCl_2(PPh_3)_2$ (62 mg, 0.09 mmol) were added. The yellow solution was heated to 100°C for 95 h, then quenched with sat. aqueous NH_4Cl solution (15 mL) and extracted with DCM (40 mL). The organic phases were dried over $MgSO_4$, and all volatile compounds were removed in vacuum. Sublimation (50°C, 6×10^{-2} mbar) gave bis(4-fluorophenyl) acetylene as a colorless solid. Yield: 110 mg (0.53 mmol, 60%). – ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.50$ (m, 4H, *o*-Ph*H*), 7.05 (m, 4H, *m*-Ph*H*) ppm. – $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta = 162.7$ (d, $J = 249.7$ Hz), 133.6 (d, $J = 8.4$ Hz), 119.3 (d, $J = 3.5$ Hz), 115.8 (d, $J = 22.1$ Hz), 88.1 ppm. – ^{19}F NMR (470 MHz, $CDCl_3$): $\delta = -110.8$ (tt, $J = 8.6$, 5.4 Hz) ppm.

5.4 Bis(4-trifluoromethylphenyl)acetylene (4)

Diethynyldiphenylsilane (0.12 mg, 0.52 mmol) and 1-bromo-4-trifluoromethylbenzene (0.46 mL, 3.2 mmol) were dissolved in diisopropylamine (15 mL). The solution was degassed two times, and CuI (21 mg, 0.11 mmol) and $PdCl_2(PPh_3)_2$ (68 mg, 0.10 mmol) were added. The solution was heated to 100°C for 21 h then quenched with sat. aqueous NH_4Cl solution (15 mL) and extracted with DCM (40 mL). The organic phases were dried over $MgSO_4$, and all volatile compounds were removed in vacuum. Column chromatography (pentane) afforded 1,2-bis(4-trifluoromethylphenyl)acetylene as a colorless solid. Yield: 0.27 g (0.85 mmol, 82%). – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.64$ (m, Ar*H*) ppm. – ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): $\delta = 133.0$, 132.1, 130.7 (q, *J* = 33.2 Hz), 125.5 (q, *J* = 3.9 Hz), 124.0 (q, *J* = 272.1 Hz), 90.3 ppm. – ^{19}F NMR (470 MHz, $CDCl_3$): $\delta = -62.9$ ppm.

5.5 Bis(phenylethynyl)diphenylsilane (5)

Phenylacetylene (0.88 mL, 8.0 mmol) was dissolved in THF (15 mL), and *n*-BuLi (5.0 mL, 1.6 M in *n*-hexane, 8.0 mmol) was added dropwise at –78°C. The clear solution was warmed to ambient temperature, dichlorodiphenylsilane (0.80 mL, 3.8 mmol) was added and the yellow solution was stirred for 1 h. The reaction was quenched with sat. aqueous NH_4Cl solution (5 mL) and extracted with Et_2O (20 mL). The organic phases were dried over $MgSO_4$, and all volatile compounds were removed in vacuum. Column chromatography (pentane-DCM 1:1) provided bis(phenylethynyl)diphenylsilane as a crystalline solid. Yield: 1.3 g (3.4 mmol, 90%). – ^{1}H NMR (500 MHz, C_6D_6): $\delta = 7.89$ (m, 4H, *o*-Ph*H*), 7.60 (m, 4H, *o*-Ph*H*), 7.45 (m, 6H, *m*/*p*-Ph*H*), 7.35 (m, 6H, *m*/*p*-Ph*H*) ppm. – ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): $\delta = 135.1$, 133.2, 132.5, 130.4, 129.4, 128.4, 128.2, 122.6, 108.9, 87.8 ppm. – ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6): $\delta = -48.1$ ppm. – EI-MS (70 eV): *m*/*z* = 384.0, 307.1, 205.0, 129.0, 105.0, 77.0. – Elemental analysis calcd. (%) for $C_{28}H_{20}Si$ (*M* = 384.54): C 87.45, H 5.24; found C 87.50, H 5.45.

5.6 1-Fluoro-4-phenylethynylbenzene (6)

Bis(phenylethynyl)diphenylsilane (200 mg, 0.53 mmol) and 1-bromo-4-fluorobenzene (0.17 mL, 1.6 mmol) were dissolved in diisopropylamine (15 mL). The solution was degassed twice, and CuI (15 mg, 0.08 mmol) and $PdCl_2(PPh_3)_2$ (48 mg, 0.07 mmol) were added. The yellow solution was heated to 100°C for 65 h then quenched with sat. aqueous NH_4Cl solution (10 mL) and extracted with DCM (40 mL). The organic phases were dried over $MgSO_4$, and all volatile compounds were removed in vacuum. Sublimation (2×10^{-2} mbar, 40°C) gave 1-fluoro-4-phenylethynylbenzene as a colorless solid. Yield: 160 mg (0.80 mmol, 76%). – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.52$ (m, 4H, *o*-Ph*H*, 3-*H*/5-*H*), 7.35 (m, 3H, *m*/*p*-Ph*H*), 7.05 (m, 2H, 2-*H*/6-*H*) ppm. – ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): $\delta = 162.5$ (d, *J* = 249.6 Hz), 133.6 (d, *J* = 8.3 Hz), 131.8, 128.5, 128.5, 123.4, 119.5 (d, *J* = 3.7 Hz), 115.8 (d, *J* = 22.1 Hz), 89.5, 88.4 ppm. – ^{19}F NMR (470 MHz, $CDCl_3$): $\delta = -111.0$ (tt, *J* = 8.6, 5.4 Hz) ppm.

5.7 1-Trifluoromethyl-4-phenylethynylbenzene (7)

Bis(phenylethynyl)diphenylsilane (200 mg, 0.53 mmol) and 1-bromo-4-trifluoromethylbenzene (0.21 mL, 1.5 mmol) were dissolved in diiospropylamine (15 mL). The solution was degassed two times, and CuI (13 mg, 0.07 mmol) and $PdCl_2(PPh_3)_2$ (44 mg, 0.06 mmol) were added. The yellow solution was heated to 100°C for 70 h, then quenched with sat. aqueous NH_4Cl solution (10 mL) and extracted with DCM (40 mL). The organic phases were dried over $MgSO_4$, and all volatile compounds were removed in vacuum. Column chromatography (pentane) gave 1-trifluoromethyl-4-phenylethynylbenzene as a colorless solid. Yield: 180 mg (0.74 mmol, 70%). – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.62$ (m, 4H, 2-*H*/3-*H*/5-*H*/6-*H*), 7.56 (m, 2H, *o*-Ph*H*), 7.38 (m, 3H, *m*/*p*-*H*) ppm. – ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): $\delta = 132.7$, 132.0, 131.9, 130.1 (q, *J* = 32.7 Hz), 129.0, 128.6, 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.1 Hz), 122.7, 91.9, 88.1 ppm. – ^{19}F NMR (470 MHz, $CDCl_3$): $\delta = -62.8$ ppm.

5.8 (Tetrafluoropyridin-4-ylethynyl)-benzene (8)

Bis(phenylethynyl)diphenylsilane (166 mg, 0.43 mmol) and 4-iodotetrafluoropyridine (300 mg, 1.1 mmol) were dissolved in diisopropylamine (20 mL). CuI (15 mg, 0.08 mmol) and $PdCl_2(PPh_3)_2$ (25 mg, 0.04 mmol) were added, and the yellow solution was heated to 100°C for 16 h then quenched with sat. aqueous NH_4Cl solution (10 mL) and extracted with DCM (20 mL). The organic phases were dried over $MgSO_4$, and all volatile compounds were removed in vacuum. Column chromatography (pentane) afforded (tetrafluoropyridin-4-yl)ethynylbenzene as a colorless crystalline solid. Yield: 180 mg (0.72 mmol, 84%). – ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.63$ (m, 2H, *o*-Ph*H*), 7.48 (m, 1H, *p*-Ph*H*), 7.43 (m, 2H, *m*-Ph*H*) ppm. – ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): $\delta = 143.9$, 141.8, 132.5, 130.8, 129.4, 128.8, 120.7, 117.5, 106.8 ppm. – ^{19}F NMR (470 MHz, $CDCl_3$): $\delta = -90.5$ (3-*F*/5-*F*), –138.3 (2-*F*/6-*F*) ppm.

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