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Fluoride-ion-mediated reactions of trimethylsilylacetylene with carbonyl compounds and terminal acetylenes

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Abstract

Fluoride-ion-mediated reaction of trimethylsilylacetylene with carbonyl compounds has been thoroughly studied. The products of addition to the C=O bond were obtained in 15–66% yield, their subsequent silylation and addition to the second molecule of the carbonyl compound being observed. It has been found that terminal aryl and hetaryl acetylenes undergo silylation in a two-phase-system $Me_3SiC{\equiv}CH$/CsF/18-crown-6 to afford aryl(hetaryl) trimethylsilylacetylenes with up to 100% yields. Combining these two reactions, a novel one-pot fluoride-ion-mediated method for the synthesis of 1-trimethylsiloxy-3-aryl(hetaryl)-2-propynes from trimethylsilylacetylene, terminal aryl or hetaryl acetylenes and carbonyl compounds has been elaborated.

Keywords: Trimethylsilylacetylene; Fluoride ion; Carbonyl compounds; Aryl and hetaryl acetylenes

1. Introduction

At present the reactions of organosilicon compounds catalyzed by nucleophiles are under extensive study. In the majority of cases a fluoride ion acting as a nucleophilic reagent is used for the activation of silicon bonds [1,2]. Among these reactions the synthesis of 1-trimethylsiloxy-3-aryl-2-propynes was described. It was realized by the addition of 1-phenyl-2-(trimethylsilyl)acetylene or other terminal silylacetylenes to carbonyl compounds in the Bu_4NF/THF [3,4], KF/18-crown-6/CH_2Cl_2 or THF [5], KF/DMF [6], $Ph_4P^+HF_2^-$/DMF [7], $Bu_4N^+HF_2^-$ [8] systems. An intramolecular addition of silylacetylene to aldehyde in the system CsF/18-crown-6/THF was also reported [9]. Derivatives of 1-trimethylsiloxy-2-propynes can be also prepared by $InCl_3$-promoted addition of alkynyl stannanes to aldehydes in the presence of trimethylchlorosilane [10]. However, trimethylsilylacetylene was used only in the fluoride-ion-mediated reaction with 4-*t*-butylcyclohexanone [3]. Therefore, the detailed study of fluoride catalyzed reaction of trimethylsilylacetylene with carbonyl compounds in nonpolar media was one of the present work goals.

Aryl and hetaryl trimethylsilylacetylenes were usually obtained in the reactions of aryl (hetaryl) acetylene with BuLi/Me_3SiCl or EtMgBr/Me_3SiCl [11], ArCu with trimethylsilyl-iodoacetylene [12] as well as in Pd catalyzed alkynylation of aryl triflates [13] or halides [14]. Phenyltrimethylsilylacetylene was also a result of the reaction of phenylacetylene in ethyl trimethylsilylacetate/Bu_4NF/THF [15] and trimethylsilylacetylene/KF-Al_2O_3 [16] systems.

The investigation of CsF-mediated reaction of terminal aryl and hetaryl acetylenes with trimethylsilylacetylene in low-polarity media was the second goal of the present work.

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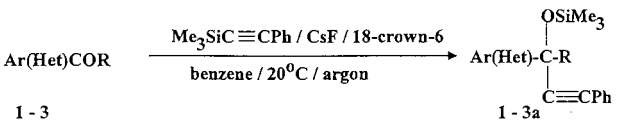
2. Results and discussion

2.1. Reactions of phenyltrimethylsilylacetylene with carbonyl compounds in the presence of fluoride ion

We found that the reactions of aromatic and heteroaromatic ketones **1**–**3** with phenyl trimethylsilylacetylene readily proceed in the phase-transfer-catalytic (PTC) system CsF/18-crown-6/benzene at room temperature. The yields of silyl ethers **1**–**3a** were quantitative. High efficiency of PTC system CsF/18-crown-6/benzene or CH_2Cl_2 was also recently demonstrated in the hydrosilylation reaction [17] (Scheme 1, Table 1).



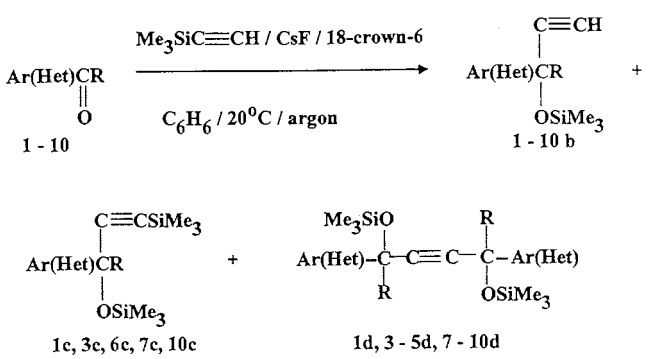
Scheme 1.

2.2. Reactions of trimethylsilylacetylene with carbonyl compounds in the presence of fluoride ion

The reactions of aromatic and heterocyclic aldehydes and ketones **1**–**10** with trimethylsilylacetylene were carried out in the presence of a catalytic amount of CsF as a fluoride ion source and 18-crown-6 in benzene. A total of 50 mol. % of CsF to carbonyl compounds **1**–**10** were found to be optimum quantity of the fluoride ion source. The trimethylsilylacetylene adducts to the C=O double bond **1b**, **3**–**5b**, **7**–**10b** and the corresponding desilylated products **2b**, **6b** were obtained as main products (15–66% yield) in all reactions. The silylated adducts **1c**, **3c**, **6c**, **7c** and **1d**, **3**–**5d**, **7**–**10d** were formed as by-products in the reaction of **1**–**10b** with trimethylsilylacetylene or with trimethylsilylacetylene and carbonyl compounds, respectively (Scheme 2, Table 2).

Table 1
Addition of phenyltrimethylsilylacetylene to ketones in the presence of CsF under the PTC conditions at room temperature (Ar(Het)COMe:$Me_3SiC{\equiv}CPh$:CsF:18-crown-6/1:1.5:0.2:0.1)

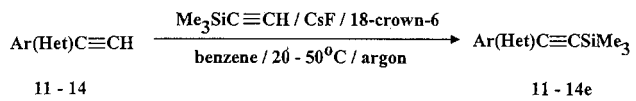
Starting ketone	Ar(Het)	Reaction time (h)	Product	Isolated yield (%)
1	Ph	2	**1a**	100
2	2-Pyridyl	2	**2a**	100
3	2-Thienyl	15	**3a**	100



Scheme 2.

2.3. Reactions of trimethylsilylacetylene with terminal aryl and hetaryl acetylenes in the presence of CsF

The silylation of terminal aryl and hetaryl acetylenes **11**–**14** with trimethylsilylacetylene readily proceeds in the presence of 20 mol. % of CsF and 10 mol. % of 18-crown-6 in benzene. Formation of **11**–**14e** was selective and reached 57–100% (Scheme 3, Table 3).

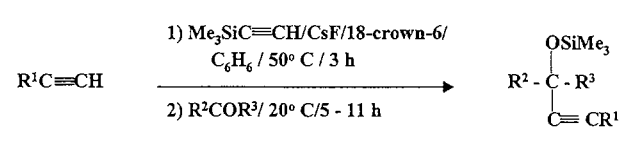


Scheme 3.

2.4. CsF-mediated one-pot synthesis of 1-trimethylsiloxy-3-aryl(hetaryl)-2-propynes **1a**, **3a**, **15**–**25a** from trimethylsilylacetylene, terminal aryl or hetaryl acetylene and carbonyl compound

Combining the reactions discussed in Sections 2.1, 2.2 and 2.3, we have developed a new simple method to prepare 1-trimethylsiloxy-3-aryl(hetaryl)-2-propynes **1a**, **3a**, **15**–**25a** from trimethylsilylacetylene, terminal aryl or hetaryl acetylene and carbonyl compound. Carbonyl compounds were added to 1-aryl(hetaryl)-2-trimethylsilylacetylene that resulted in situ from aryl(hetaryl)acetylenes and trimethylsilylacetylene in the presence of the fluoride ion. The experiments showed that 20 mol% of CsF to substrates **11**, **13** was an optimal amount of the catalyst (Scheme 4).

Usually the formation of **1a**, **3a**, **15**–**25a** occurred selectively, sometimes affording also small quantities (up to 10%) of trimethylsilylacetylene adducts to carbonyl compounds ($R^2R^3C(OSiMe_3)C{\equiv}CH$). Products **1a**, **3a**, **15**–**25a** were separated by column chromatography and identified by ^{1}H-NMR and mass spectra (Table 4).



Scheme 4.

Table 2
Trimethylsilylethynylation of aryl and hetaryl aldehydes and ketones (**1**–**10**) promoted by CsF at room temperature (Ar(Het)COR:$Me_3SiC{\equiv}CH$:CsF:18-crown-6/1:1.1:0.5:0.1)

Carbonyl compound	Ar(Het)	R	Reaction time (h)	Products	GC yields (%)
1	Ph	Me	1	**1b**	52
				1c**	15
				1d	19
2*	2-Pyridyl	Me	5	**2b*****	17
3	2-Thienyl	Me	5	**3b**	51
				3c**	6
				3d**	6
4	3-Pyridyl	Me	1	**4b**	15
				4d**	7
5	4-Pyridyl	Me	2	**5b**	54
				5d**	17
6	2-Methyl-5-thienyl	Me	5	**6b*****	69
				6c**	16
7	2-Furyl	Me	5	**7b**	53
				7c**	5
				7d**	20
8	Ph	H	2	**8b**	66
				8d**	22
9	2,3-$(MeO)_2C_6H_3$	H	1	**9b**	62
				9d	26
10	2-Thienyl	H	1	**10b**	57
				10d	34

* Reaction temperature was 0–10°C.
** Product was detected by MS.
*** Products **2b** and **6b** were isolated as corresponding alcohols.

3. Experimental

^{1}H-NMR spectra were recorded on a Varian 200 Mercury spectrometer (200 MHz) using $CDCl_3$ as a solvent and HMDSO as a secondary internal standard. Mass spectra were registered on a GC–MS HP 6890 (70 eV) apparatus. GC analysis was performed on a Chrom-5 instrument equipped with a flame-ionization detector using a glass column packed with 5% OV-101/Chromosorb W-HP (80–100 mesh, 1.2 m × 3 mm). Carbonyl compounds (Aldrich) and trimethylsilylacetylene (Acros) were used without additional purification. Benzaldehyde (**8**) was purified by distillation in vacuo prior to use. CsF was calcined at ca. 200°C during 1 h. Benzene was dried with 4Å molecular sieves.

*3.1. The reaction of carbonyl compounds **1**–**3** with phenyltrimethylsilylacetylene in the presence of fluoride ion. General procedure of the synthesis of compounds **1**–**3a***

Freshly calcined CsF (0.03 g, 0.2 mmol) was added to a mixture of **1**–**3** (1 mmol) and 18-crown-6 (0.026 g, 0.1 mmol) in 1.5 ml of dry benzene under argon atmosphere. The mixture was stirred for 5 min, then phenyltrimethylsilylacetylene (0.295 ml, 1.5 mmol) was added. Reaction was carried out at room temperature (r.t.) (GC control at 170–250°C) for 2–15 h. The reaction mixture was filtered over a thin layer of silica gel and evaporated at reduced pressure. The residue was chromatographed on a silica gel column (eluents: benzene for **1a**; 1:1 benzene–petroleum ether for **2a**; 4:1 benzene–ethyl acetate for **3a**).

^{1}H-NMR ($CDCl_3$, HMDSO) and MS spectra data for the compounds obtained. (**1a**) ^{1}H-NMR δ (ppm): 0.15 (s, 9H, $SiMe_3$), 1.87 (s, 3H, CH_3), 7.2–7.7 (m, 10H, Ph). MS: m/z (I, %) 294 (M^+, 13), 279 (M^+–Me, 89), 217 (15), 205 (35), 189 (16), 178 (9), 159 (22), 127 (23), 105 (100), 73 (79), 45 (31).

(**2a**) ^{1}H-NMR δ (ppm): 0.25 (s, 9H, $SiMe_3$), 1.92 (s, 3H, CH_3), 7.18 (m, 1H, H-5), 7.29 (m, 5H, Ph), 7.45 (m, 1H, H-3), 7.72 (m, 1H, H-4), 8.61 (m, 1H, H-6). MS: m/z (I, %): 295 (M^+, 18), 294 (18), 281 (M^+–Me, 14), 280 (55), 265 (10), 220 (20), 218 (24), 217 (66), 206 (29), 205 (11), 204 (41), 178 (49), 159 (21), 150 (26), 149 (60), 132 (37), 106 (20), 78 (51), 77 (15), 75 (28), 74 (13), 73 (100), 51 (18), 45 (32), 43 (28).

(**3a**) ^{1}H-NMR δ (ppm): 0.28 (s, 9H, $SiMe_3$), 2.04 (s, 3H, CH_3), 7.00 (m, 1H, H-4), 7.27 (m, 1H, H-5), 7.30–7.50 (m, 5H, Ph), 7.59 (m, 1H, H-3). MS: m/z (I, %) 300 (M^+, 12), 285 (M^+–Me, 100), 233 (6), 211 (49), 184 (7), 159 (13), 127 (21), 111 (70), 73 (65), 45 (30).

Table 3
Synthesis of trimethylsilylacetylenes **11**–**14e** promoted by cesium fluoride (Ar(Het)C≡CH:Me_3SiC≡CH:CsF:18-crown-6/1:1.5:0.2:0.1)

Starting ketone	Ar(Het)	Reaction temperature (°C)	Reaction time (min)	Product	Isolated yield (%)
11	Ph	50	180	**11e**	100
12	2-Pyridyl	50	180	**12e**	57
13	2-Methyl-5-pyridyl	50	210	**13e**	74
14	2-Thienyl	20	5	**14e**	100

*3.2. The reaction of carbonyl compounds **1**–**10** with trimethylsilylacetylene in the presence of fluoride ion. General procedure of the synthesis of compounds **1**–**10b***

Freshly calcined CsF (0.075 g, 0.5 mmol) was added to a mixture of **1**–**10** (1 mmol) and 18-crown-6 (0.026 g, 0.1 mmol) in 1.5 ml of dry benzene under argon atmosphere. The mixture was stirred for 5 min, then trimethylsilylacetylene (0.139 ml, 1 mmol) was added. Reaction was carried out at r.t. (GC control at 170–250°C) for 1–5 h. The reaction mixture was filtered over a thin layer of silica gel and evaporated at reduced pressure. The residue was chromatographed on silica gel column (eluents: benzene for **1b**, **6b**, **8b**; 4:1 benzene–ethyl acetate for **2b**, **4b**; 2:1 benzene–petroleum ether for **3b**; 20:9 benzene–ethyl acetate for **5b**; 10:1 benzene–ethyl acetate for **7b**; 30:0.02 benzene–ethyl acetate for **9b**; 1:1 benzene–petroleum ether for **10b**). ^{1}H-NMR ($CDCl_3$, HMDSO) and MS spectra data for the compounds obtained.

(**1b**) ^{1}H-NMR δ (ppm): 0.13 (s, 9H, $SiMe_3$), 1.73 (s, 3H, CH_3), 2.67 (s, 1H, C≡CH), 7.25–7.60 (m, 5H, Ph). MS: m/z (I, %): 218 (M^+, <1), 203 (M^+–Me, 100).

(**1c**) MS: m/z (I, %): 275 (M^+–Me, 100), 105 (PhCO, 65), 73 ($SiMe_3$, 61).

(**1d**) ^{1}H-NMR δ (ppm): 0.13 and 0.20 (both s, 9H, $SiMe_3$), 1.68 (s, 6H, both CH_3), 7.25–7.60 (m, 10H, both Ph). MS: m/z (I,%): 410 (M^+, <1), 395 (M^+–Me, 43), 105 (PhCO, 22), 73 (100).

(**2b**) MS: m/z (I, %): 219 (M^+, 8), 204 (M^+–Me, 100), 189 (M^+–2Me, 44), 130 (M^+–$OSiMe_3$, 27), 73 ($SiMe_3$, 50). ^{1}H-NMR of the corresponding alcohol, δ (ppm): 1.79 (s, 3H, CH_3), 2.55 (s, 1H, C≡CH), 5.55 (s, 1H, OH), 7.27 (m, 1H, H-5), 7.64 (m, 1H, H-3), 7.76 (m, 1H, H-4), 8.52 (m, 1H, H-6). MS of the corresponding alcohol: m/z (I, %): 147 (M^+, 47), 130 (M^+–OH, 100).

(**3b**) ^{1}H-NMR δ (ppm): 0.18 (s, 9H, $SiMe_3$), 1.72 (s, 3H, CH_3), 2.54 (s, 1H, C≡CH), 6.96 (m, 1H, H-4), 7.44 (m, 1H, H-5), 7.96 (m, 1H, H-3). MS: m/z (I, %): 209 (M^+–Me, 100), 135 (M^+–$OSiMe_3$, 41), 73 ($SiMe_3$, 39).

(**3c**) MS: m/z (I, %): 281 (M^+–Me, 100), 207 (M^+–$OSiMe_3$, 12), 73 ($SiMe_3$, 45).

(**3d**) MS: m/z (I, %): 407 (M^+–Me, 43), 73 ($SiMe_3$, 100).

(**4b**) ^{1}H-NMR δ (ppm): 0.16 (s, 9H, $SiMe_3$), 1.74 (s, 3H, CH_3), 2.64 (s, 1H, C≡CH), 7.26 (m, 1H, H-5), 7.87 (m, 1H, H-4), 8.52 (m, 1H, H-6), 8.85 (m, 1H, H-2). MS: m/z (I, %): 219 (M^+, <1), 204 (M^+–Me, 100), 130 (M^+–$OSiMe_3$, 28), 73 ($SiMe_3$, 37).

(**4d**) MS: m/z (I, %): 412 (M^+, 2), 73 ($SiMe_3$, 100).

(**5b**) ^{1}H-NMR δ (ppm): 0.18 (s, 9H, $SiMe_3$), 1.70 (s, 3H, CH_3), 2.71 (s, 1H, C≡CH), 7.50 (dd, 2H, $J_1 = 4.8$ Hz, $J_2 = 1.8$ Hz, H-3, H-5), 8.58 (dd, 2H, $J_1 = 4.8$ Hz, $J_2 = 1.8$ Hz, H-2, H-6). MS: m/z (I, %): 219 (M^+, <1), 204 (M^+–Me, 100), 130 (M^+–$OSiMe_3$, 23), 73 ($SiMe_3$, 40).

(**5d**) MS: m/z (I, %): 412 (M^+, 1), 397 (M^+–Me, 62), 73 ($SiMe_3$, 100).

(**6b**) MS: m/z (I, %): 238 (M^+, 6), 223 (M^+–Me, 100), 149 (M^+–$OSiMe_3$, 47), 134 (M^+–Me–$OSiMe_3$, 12), 73 ($SiMe_3$, 36). ^{1}H-NMR of corresponding alcohol, δ (ppm): 1.94 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 2.58 (s, 1H, C≡CH), 6.73(m, 1H, H-4), 7.56 (m, 1H, H-3). MS of corresponding alcohol: m/z (I, %): 166 (M^+, 21), 151 (M^+–Me, 100), 149 (M^+–OH, 14).

(**6c**) MS: m/z (I, %): 295 (M^+–Me, 100), 221 (M^+–$OSiMe_3$, 18), 73 ($SiMe_3$, 48).

(**7b**) MS: m/z (I, %): 208 (M^+, 2), 193 (M^+–Me, 100), 119 (M^+–$OSiMe_3$, 44), 73 ($SiMe_3$, 36).

(**7c**) MS: m/z (I, %): 265 (M^+–Me, 100), 191 (M^+–$OSiMe_3$, 24), 73 ($SiMe_3$, 64).

(**7d**) MS: m/z (I, %): 375 (M^+–Me, 47), 73 ($SiMe_3$, 100).

(**8b**) ^{1}H-NMR δ (ppm): 0.07 (s, 9H, $SiMe_3$), 2.58 (d, 1H, C≡CH), 5.48 (d, 1H, CH), 7.65 (m, 5H, Ph). MS: m/z (I, %): 204 (M^+, 31), 189 (M^+–Me, 53), 115 (100), 105 (PhCO, 10), 73 ($SiMe_3$, 29).

(**8d**) MS: m/z (I, %): 383 (M^+, <1), 292 (13), 202 (10), 179 (20), 147 (35), 102 (21), 75 (15), 73 ($SiMe_3$, 100), 45 (22).

(**9b**) ^{1}H-NMR δ (ppm): 0.18 (s, 9H, $SiMe_3$), 2.51 (d, 1H, $J = 2.2$ Hz, C≡CH), 3.86 (s, 3H, OMe), 3.89 (s, 3H, OMe), 5.84 (d, 1H, $J = 2.2$ Hz, CH), 6.87 (dd, 1H, $J_1 = 8.2$ Hz, $J_2 = 1.4$ Hz, H-6), 7.08 (t, 1H, $J = 8.2$ Hz, H-5), 7.26 (dd, 1H, $J_1 = 8.2$ Hz, $J_2 = 1.4$ Hz, H-4). MS: m/z (I, %): 264 (M^+, 36), 249 (M^+–Me, 74), 234 (M^+–2Me, 32), 233 (M^+–OMe, 32), 219 (M^+–3Me, 12), 175 (M^+–$OSiMe_3$, 39), 73 (100).

(**9d**) ^{1}H-NMR δ (ppm): 0.15 and 0.17 (both s, 9H, $SiMe_3$), 3.86 (m, 12H, OMe), 5.91 (s, 2H, CH), 6.90,

Table 4
Fluoride-ion-mediated synthesis of silyl ethers **1a**, **3a**, **15–25a** from trimethylsilylacetylene, aryl acetylene and carbonyl compound ($R^1C{\equiv}CH{:}Me_3SiC{\equiv}CH{:}CsF{:}18\text{-crown-}6{:}R^2COR^3/1{:}1{:}0.2{:}0.1{:}1$)

R^1	R^2	R^3	Reaction time (h)	Product	Isolated yield (%)
Ph	Ph	Me	8	**1a**	61
Ph	2-Thienyl	Me	11	**3a**	47
Ph	Et	Me	5	**15a**	57
Ph	Ph	H	6	**16a**	61
Ph	3-Pyridyl	Me	8	**17a**	58
Ph	4-Pyridyl	Me	5	**18a**	51
2-Methyl-5-pyridyl	Et	Me	6	**19a**	65
2-Methyl-5-pyridyl	Ph	H	6	**20a**	61
2-Methyl-5-pyridyl	Ph	Me	9	**21a**	58
2-Methyl-5-pyridyl	2-Thienyl	Me	6	**22a**	57
2-Methyl-5-pyridyl	2-Pyridyl	Me	6	**23a**	58
2-Methyl-5-pyridyl	3-Pyridyl	Me	9	**24a**	55
2-Methyl-5-pyridyl	4-Pyridyl	Me	5	**25a**	55

7.10 and 7.30 (m, 2H, protons of Ph). MS: m/z (I, %): 502 (M^+, 5), 73 (100).

(**10b**) ^{1}H-NMR δ (ppm): 0.22 (s, 9H, $SiMe_3$), 2.63 (s, 1H, C≡CH), 5.70 (m, 1H, CH), 6.95 (m, 1H, H-4), 7.12 (m, 1H, H-3), 7.27 (m, 1H, H-5). MS: m/z (I, %): 210 (M^+, 34), 195 (M^+-Me, 18), 121 ($M^+-OSiMe_3$, 100), 73 ($SiMe_3$, 35).

(**10d**) MS: m/z (I, %): 394 (M^+, 7), 73 ($SiMe_3$, 100).

*3.3. The reactions of terminal aryl and hetaryl acetylenes **11–14** with trimethylsilylacetylene in the presence of the fluoride ion. General procedure of the synthesis of aryl and hetaryl trimethylsilylacetylenes **11–14e***

Freshly calcined CsF (0.03 g, 0.2 mmol) was added to a mixture of **11–14** (1 mmol) and 18-crown-6 (0.026 g, 0.1 mmol) in 1.5 ml of dry benzene under argon atmosphere. After 5 min stirring the trimethylsilylacetylene (0.207 ml, 1.5 mmol) was added. Reaction was carried out for 5–210 min (GC control, 130°C). The reaction mixture was filtered over a thin layer of silica gel and evaporated at reduced pressure. The residue was chromatographed on silica gel column using 10:1 petroleum ether–benzene (**11e**), 6:1 benzene–ethyl acetate (**12e**), 5:1 benzene–ethyl acetate (**13e**) and 2:1 benzene–petroleum ether (**14e**) as eluents.

^{1}H-NMR and MS data for the compounds isolated.

(**11e**) ^{1}H-NMR, δ ppm: 0.31 (s, 9H, $SiMe_3$), 7.44 (m, 5H, Ph). MS: m/z (I, %): 174 (M^+, 17), 160 (16), 159 (M^+-Me, 100), 129 (8), 105 (8), 79 (5), 77 (3), 53 (6), 43 (9).

(**12e**) ^{1}H-NMR, δ ppm: 0.27 (s, 9H, $SiMe_3$), 7.22 (m, 1H, H–3), 7.45 (m, 1H, H-4), 7.63 (m, 1H, H-5), 8.56 (m, 1H, H-6). MS: m/z (I, %): 175 (M^+, 24), 160 (M^+-Me, 100), 145 (M^+-2Me, 4), 132 (11), 106 (12), 43 (8).

(**13e**) ^{1}H-NMR, δ ppm: 0.06 (s, 9H, $SiMe_3$), 2.33 (s, 3H, CH_3), 6.87 (d, 1H, $J=8$ Hz, H-3), 7.42 (dd, 1H, $J_1=8$ Hz, $J_2=2$ Hz, H-4), 8.39 (d, 1H, $J=8$ Hz, H-6). MS: m/z (I, %): 189 (M^+, 18), 175 (16), 174 (M^+-Me, 100), 144 (5), 77 (5), 73 (3), 53 (5), 43 (7).

(**14e**) ^{1}H-NMR, δ ppm: 0.20 (s, 9H, $SiMe_3$), 6.69 (m, 1H, H-4), 6.95 (s, 1H, H-5), 7.00 (s, 1H, H-3). MS: m/z (I,%): 180 (M^+, 23), 167 (10), 166 (14), 165 (M^+-Me, 100), 135 (M^+-3Me, 6), 77 (8), 75 (6), 53 (6), 43 (9).

*3.4. General procedure for the one-pot fluoride-ion-mediated synthesis of 1-trimethylsiloxy-3-aryl(hetaryl)-2-propynes **1a**, **3a**, **15–25a** from trimethylsilylacetylene, terminal acetylene and carbonyl compound*

Freshly calcined CsF (0.0302 g, 0.2 mmol) and trimethylsilylacetylene (0.139 ml, 1 mmol) were added to a solution of terminal acetylene (phenyl acetylene (**11**) or 2-methyl-5-ethynylpyridine (**13**), 1 mmol) and 18-crown-6 (0.026 g, 0.1 mmol) in dry benzene (1.5 ml). The reaction mixture was heated at 50°C for 3 h under argon. Then the reaction mixture was cooled to r.t. The carbonyl compound (1 mmol) was added and the reaction mixture was stirred for 5–11 h at r.t. (GLC control). The reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography (eluent: benzene for compounds **1a**, **3a**, **15a**, **16a,** or benzene–ethyl acetate in different ratios for compounds **17–25a**).

^{1}H-NMR and MS data for compounds isolated.

(**15a**) ^{1}H-NMR δ (ppm): 0.18 (s, 9H, $SiMe_3$), 0.98 (t, 3H, $J=7.0$ Hz, CH_2CH_3), 1.46 (s, 3H, CCH_3), 1.62 (q, 2H, $J=7.0$ Hz, CH_2CH_3), 7.24 (m, 5H, Ph). MS: m/z (I, %) 245 (M^+-1, <1), 231 (11), 217 (100), 159 (19), 141 (9), 129 (14), 115 (11), 73 (57), 57 (10), 43 (25).

(**16a**) ^{1}H-NMR δ (ppm): 0.13 (s, 9H, $SiMe_3$), 7.10–7.70 (m, 11H, Ph and CH). MS: m/z (I, %) 280 (M^+,

35), 265 (M^+–Me, 14), 206 (15), 191 (100), 159 (40), 129 (7), 105 (14), 73 (82), 45 (29).

(**17a**) ^{1}H-NMR δ (ppm): 0.16 (s, 9H, $SiMe_3$), 1.77 (s, 3H, CH_3), 7.24 (m, 6H, Ph and H-5), 7.73 (m, 1H, H-4), 8.42 (m, 1H, H-6), 8.93 (m, 1H, H-2). MS: m/z (I, %) 295 (M^+, 10), 294 (15), 280 (M^+–Me, 98), 217 (11), 206 (36), 178 (10), 159 (29), 127 (11), 106 (49), 73 (100), 45 (33).

(**18a**) ^{1}H-NMR δ (ppm): 0.16 (s, 9H, $SiMe_3$), 1.69 (s, 3H, CH_3), 7.25 (m, 5H, Ph), 7.40 (m, 2H, H-3 and H-5), 8.49 (m, 2H, H-2 and H-6). MS: m/z (I, %) 295 (M^+, 11), 280 (M^+–Me, 96), 217 (21), 206 (25), 178 (15), 159 (40), 106 (15), 73 (100), 45 (29).

(**19a**) ^{1}H-NMR δ (ppm): 0.16 (s, 9H, $SiMe_3$), 0.96 (t, 3H, $J = 7.2$ Hz, CH_2CH_3), 1.47 (s, 3H, CCH_3), 1.64 (q, 2H, $J = 7.2$ Hz, CH_2CH_3), 2.49 (s, 3H, CH_3 in ring), 7.04 (m, 1H, H-3), 7.47 (m, 1H, H-4), 8.44 (m, 1H, H-6). MS: m/z (I, %) 261 (M^+, 1), 246 (M^+–Me, 11), 232 (100), 190 (63), 174 (15), 144 (8), 129 (9), 73 (64), 45 (21).

(**20a**) ^{1}H-NMR δ (ppm): 0.29 (s, 9H, $SiMe_3$), 2.28 (s, 3H, CH_3), 7.11 (m, 1H, H-3), 7.47 (m, 1H, H-4), 7.50–7.90 (m, 6H, Ph and CH), 8.51 (m, 1H, H-6). MS: m/z (I, %) 295 (M^+, 43), 280 (M^+–Me, 26), 221 (21), 206 (93), 190 (10), 174 (50), 152 (11), 139 (21), 105 (13), 89 (9), 73 (100), 45 (27).

(**21a**) ^{1}H-NMR δ (ppm): 0.17 (s, 9H, $SiMe_3$), 1.79 (s, 3H, CCH_3), 2.50 (s, 3H, CH_3 in ring), 7.16 (m, 1H, H-3), 7.56 (m, 1H, H-4), 8.51 (m, 1H, H-6). MS: m/z (I, %) 310 (M^+, 3), 308 (13), 294 (84), 220 (36), 204 (10), 174 (18), 142 (9), 105 (100), 73 (88), 45 (29).

(**22a**) ^{1}H-NMR δ (ppm): 0.28 (s, 9H, $SiMe_3$), 2.06 (s, 3H, CCH_3), 2.71 (s, 3H, CH_3 in ring), 7.01 (m, 1H, H′-4), 7.22 (m, 1H, H-3), 7.33 (m, 1H, H′-5), 7.64 (m, 1H, H′-3), 7.80 (m, 1H, H-4), 8.73 (m, 1H, H-6). MS: m/z (I, %) 315 (M^+, 16), 300 (M^+–Me, 100), 226 (51), 210 (7), 174 (13), 142 (10), 111 (93), 73 (97), 45 (36).

(**23a**) ^{1}H-NMR δ (ppm): 0.09 (s, 9H, $SiMe_3$), 1.64 (s, 3H, CCH_3), 2.31 (s, 3H, CH_3 in ring), 7.09 (m, 2H, H-3 and H′-5), 7.42 (m, 3H, H-4, H′-3 and H′-4), 8.34 (m, 2H, H-6 and H′-6). MS: m/z (I, %) 310 (M^+, 27), 309 (34), 295 (M^+–Me, 67), 280 (12), 232 (56), 221 (31), 205 (12), 190 (61), 178 (49), 149 (58), 140 (30), 106 (25), 78 (43), 73 (100), 45 (32).

(**24a**) ^{1}H-NMR δ (ppm): 0.16 (s, 9H, $SiMe_3$), 1.73 (s, 3H, CH_3), 2.49 (s, 3H, CH_3 in ring), 7.04 (m, 1H, H-3), 7.24 (m, 6H, Ph, H′-5), 7.56 (m, 1H, H-4), 7.80 (m, 1H, H′-4), 8.49 (m, 2H, H-6 and H′-6), 8.85 (m, 1H, H′-2). MS: m/z (I, %) 310 (M^+, 10), 309 (20), 295 (M^+–Me, 100), 232 (9), 221 (30), 205 (9), 190 (9), 174 (23), 106 (51), 73 (97), 45 (32).

(**25a**) ^{1}H-NMR δ (ppm): 0.16 (s, 9H, $SiMe_3$), 1.73 (s, 3H, CCH_3), 2.53 (s, 3H, CH_3 in ring), 7.02 (m, 1H, H-3), 7.48 (m, 2H, H′-3 and H′-5), 7.62 (m, 1H, H-4), 8.51 (m, 3H, H-6, H′-2 and H′-6). MS: m/z (I, %) 310 (M^+, 9), 309 (12), 295 (M^+–Me, 100), 232 (15), 221 (24), 190 (13), 174 (35), 106 (16), 73 (99), 45 (27).

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