

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

Edgars Abele, Kira Rubina, Ramona Abele, Juris Popelis, Ilona Mazeika,
Edmunds Lukevics *

Latvian Institute of Organic Synthesis, 21 Aizkraukles Street, Riga, LV-1006, Latvia

Received 12 March 1999; received in revised form 4 May 1999

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 $\text{Me}_3\text{SiC}\equiv\text{CH}/\text{CsF}/18\text{-crown-6}$ 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. © 1999 Elsevier Science S.A. All rights reserved.

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 $\text{Bu}_4\text{NF}/\text{THF}$ [3,4], $\text{KF}/18\text{-crown-6}/\text{CH}_2\text{Cl}_2$ or THF [5], KF/DMF [6], $\text{Ph}_4\text{P}^+\text{HF}_2^-/\text{DMF}$ [7], $\text{Bu}_4\text{N}^+\text{HF}_2^-$ [8] systems. An intramolecular addition of silylacetylene to aldehyde in the system $\text{CsF}/18\text{-crown-6}/\text{THF}$ 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 $\text{BuLi}/\text{Me}_3\text{SiCl}$ or $\text{EtMgBr}/\text{Me}_3\text{SiCl}$ [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/ $\text{Bu}_4\text{NF}/\text{THF}$ [15] and trimethylsilylacetylene/ $\text{KF}-\text{Al}_2\text{O}_3$ [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.

* Corresponding author. Tel.: +7-371-7551822; fax: +7-371-7821038.

E-mail address: kira@osi.lanet.lv (E. Lukevics)

Scheme 4.

Table 2
Trimethylsilylethynylation of aryl and hetaryl aldehydes and ketones (**1–10**) promoted by CsF at room temperature (Ar(Het)COR:Me₃SiC≡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 1c** 1d	52 15 19
2*	2-Pyridyl	Me	5	2b***	17
3	2-Thienyl	Me	5	3b 3c** 3d**	51 6 6
4	3-Pyridyl	Me	1	4b 4d**	15 7
5	4-Pyridyl	Me	2	5b 5d**	54 17
6	2-Methyl-5-thienyl	Me	5	6b*** 6c**	69 16
7	2-Furyl	Me	5	7b 7c** 7d**	53 5 20
8	Ph	H	2	8b 8d**	66 22
9	2,3-(MeO) ₂ C ₆ H ₃	H	1	9b 9d	62 26
10	2-Thienyl	H	1	10b 10d	57 34

* Reaction temperature was 0–10°C.

** Product was detected by MS.

*** Products **2b** and **6b** were isolated as corresponding alcohols.

3. Experimental

¹H-NMR spectra were recorded on a Varian 200 Mercury spectrometer (200 MHz) using CDCl₃ 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 (eluent: benzene for **1a**; 1:1 benzene–petroleum ether for **2a**; 4:1 benzene–ethyl acetate for **3a**).

1a ¹H-NMR (CDCl₃, HMDSO) and MS spectra data for the compounds obtained. (**1a**) ¹H-NMR δ (ppm): 0.15 (s, 9H, SiMe₃), 1.87 (s, 3H, CH₃), 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 ¹H-NMR δ (ppm): 0.25 (s, 9H, SiMe₃), 1.92 (s, 3H, CH₃), 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 ¹H-NMR δ (ppm): 0.28 (s, 9H, SiMe₃), 2.04 (s, 3H, CH₃), 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:Me₃SiC≡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**).

¹H-NMR (CDCl₃, H₂MSO) and MS spectra data for the compounds obtained.

(1b) ¹H-NMR δ (ppm): 0.13 (s, 9H, SiMe₃), 1.73 (s, 3H, CH₃), 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 (SiMe₃, 61).

(1d) ¹H-NMR δ (ppm): 0.13 and 0.20 (both s, 9H, SiMe₃), 1.68 (s, 6H, both CH₃), 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⁺–OSiMe₃, 27), 73 (SiMe₃, 50). ¹H-NMR of the corresponding alcohol, δ (ppm): 1.79 (s, 3H, CH₃), 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) ¹H-NMR δ (ppm): 0.18 (s, 9H, SiMe₃), 1.72 (s, 3H, CH₃), 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⁺–OSiMe₃, 41), 73 (SiMe₃, 39).

(3c) MS: *m/z* (I, %): 281 (M⁺–Me, 100), 207 (M⁺–OSiMe₃, 12), 73 (SiMe₃, 45).

(3d) MS: *m/z* (I, %): 407 (M⁺–Me, 43), 73 (SiMe₃, 100).

(4b) ¹H-NMR δ (ppm): 0.16 (s, 9H, SiMe₃), 1.74 (s, 3H, CH₃), 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⁺–OSiMe₃, 28), 73 (SiMe₃, 37).

(4d) MS: *m/z* (I, %): 412 (M⁺, 2), 73 (SiMe₃, 100).

(5b) ¹H-NMR δ (ppm): 0.18 (s, 9H, SiMe₃), 1.70 (s, 3H, CH₃), 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⁺–OSiMe₃, 23), 73 (SiMe₃, 40).

(5d) MS: *m/z* (I, %): 412 (M⁺, 1), 397 (M⁺–Me, 62), 73 (SiMe₃, 100).

(6b) MS: *m/z* (I, %): 238 (M⁺, 6), 223 (M⁺–Me, 100), 149 (M⁺–OSiMe₃, 47), 134 (M⁺–Me–OSiMe₃, 12), 73 (SiMe₃, 36). ¹H-NMR of corresponding alcohol, δ (ppm): 1.94 (s, 3H, CH₃), 2.54 (s, 3H, CH₃), 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⁺–OSiMe₃, 18), 73 (SiMe₃, 48).

(7b) MS: *m/z* (I, %): 208 (M⁺, 2), 193 (M⁺–Me, 100), 119 (M⁺–OSiMe₃, 44), 73 (SiMe₃, 36).

(7c) MS: *m/z* (I, %): 265 (M⁺–Me, 100), 191 (M⁺–OSiMe₃, 24), 73 (SiMe₃, 64).

(7d) MS: *m/z* (I, %): 375 (M⁺–Me, 47), 73 (SiMe₃, 100).

(8b) ¹H-NMR δ (ppm): 0.07 (s, 9H, SiMe₃), 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 (SiMe₃, 29).

(8d) MS: *m/z* (I, %): 383 (M⁺, < 1), 292 (13), 202 (10), 179 (20), 147 (35), 102 (21), 75 (15), 73 (SiMe₃, 100), 45 (22).

(9b) ¹H-NMR δ (ppm): 0.18 (s, 9H, SiMe₃), 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⁺–OSiMe₃, 39), 73 (100).

(9d) ¹H-NMR δ (ppm): 0.15 and 0.17 (both s, 9H, SiMe₃), 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) 1H -NMR δ (ppm): 0.22 (s, 9H, $SiMe_3$), 2.63 (s, 1H, $C\equiv CH$), 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.

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

(11e) 1H -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) 1H -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) 1H -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) 1H -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**).

1H -NMR and MS data for compounds isolated.

(15a) 1H -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) 1H -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 ($M^+ - \text{Me}$, 14), 206 (15), 191 (100), 159 (40), 129 (7), 105 (14), 73 (82), 45 (29).

(17a) $^1\text{H-NMR}$ 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 ($M^+ - \text{Me}$, 98), 217 (11), 206 (36), 178 (10), 159 (29), 127 (11), 106 (49), 73 (100), 45 (33).

(18a) $^1\text{H-NMR}$ 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 ($M^+ - \text{Me}$, 96), 217 (21), 206 (25), 178 (15), 159 (40), 106 (15), 73 (100), 45 (29).

(19a) $^1\text{H-NMR}$ 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 ($M^+ - \text{Me}$, 11), 232 (100), 190 (63), 174 (15), 144 (8), 129 (9), 73 (64), 45 (21).

(20a) $^1\text{H-NMR}$ 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 ($M^+ - \text{Me}$, 26), 221 (21), 206 (93), 190 (10), 174 (50), 152 (11), 139 (21), 105 (13), 89 (9), 73 (100), 45 (27).

(21a) $^1\text{H-NMR}$ 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) $^1\text{H-NMR}$ 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 ($M^+ - \text{Me}$, 100), 226 (51), 210 (7), 174 (13), 142 (10), 111 (93), 73 (97), 45 (36).

(23a) $^1\text{H-NMR}$ 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 ($M^+ - \text{Me}$, 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) $^1\text{H-NMR}$ 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 ($M^+ - \text{Me}$, 100), 232 (9), 221 (30), 205 (9), 190 (9), 174 (23), 106 (51), 73 (97), 45 (32).

(25a) $^1\text{H-NMR}$ 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 ($M^+ - \text{Me}$, 100), 232 (15), 221 (24), 190 (13), 174 (35), 106 (16), 73 (99), 45 (27).

References

- [1] C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, *Chem. Rev.* 93 (1993) 1371.
- [2] G.G. Furin, O.A. Vyazankina, B.A. Gostevsky, N.S. Vyazankin, *Tetrahedron* 44 (1988) 2675.
- [3] I. Kuwajima, E. Nakamura, K. Hashimoto, *Tetrahedron* 39 (1983) 975.
- [4] E. Nakamura, I. Kuwajima, *Angew. Chem. Int. Ed. Engl.* 15 (1976) 498.
- [5] A.B. Holmes, C.L.D. Jennings-White, A.H. Schulthess, B. Akinde, D.R.M. Walton, *J. Chem. Soc. Chem. Commun.* (1979) 840.
- [6] (a) M.D. Stadnichuk, E.V. Komissarova, *Zh. Obshch. Khim.* 64 (1994) 694. (b) M.D. Stadnichuk, E.V. Komissarova, *Chem. Abstr.* 122 (1995) 105316y.
- [7] A. Bohsako, C. Asakura, T. Shiori, *Synlett* (1995) 1033.
- [8] A. Mori, A. Fujita, K. Ikegashira, Y. Nishihara, T. Hiyama, *Synlett* (1997) 693.
- [9] T. Nishikawa, S. Shibuya, M. Isobe, *Synlett* (1994) 482.
- [10] M. Yusuda, T. Miyai, I. Shibata, A. Baba, *Tetrahedron Lett.* 36 (1995) 9497.
- [11] C. Eaborn, D.R.M. Walton, *J. Organomet. Chem.* 2 (1964) 95.
- [12] R. Oliver, D.R.M. Walton, *Tetrahedron Lett.* (1972) 5209.
- [13] T. Okita, M. Isobe, *Synlett* (1994) 589.
- [14] A. Carpita, R. Rossi, C.A. Veracini, *Tetrahedron* 41 (1985) 1919.
- [15] E. Nakamura, T. Murofushi, M. Shimizu, I. Kuwajima, *J. Am. Chem. Soc.* 98 (1976) 2346.
- [16] T. Baba, A. Kato, H. Yuasa, F. Toriyama, H. Handa, Y. Ono, *Catal. Today* 44 (1998) 271.
- [17] Yu. Goldberg, E. Abele, M. Shymanska, E. Lukevics, *J. Organomet. Chem.* 410 (1991) 127.