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Synthesis of Arylsilanes via Palladium(0)-Catalyzed Silylation of Aryl Halides with Hydrosilane

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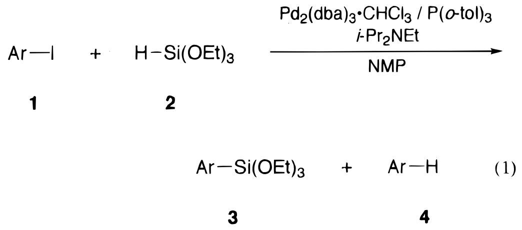
Arylsilanes are both valuable intermediates in organic synthesis[1] and useful cross-linking agents.[2] Accordingly, much attention has been paid to their synthesis.[3] Among others, the catalytic cross-coupling reaction of organic halides using disilanes as silicon sources has proven to be a versatile method for synthesizing functionalized organosilanes.[4] Kunai and Ishikawa have recently reported on a $PdCl_2$-catalyzed Si−H/C−I exchange reaction that formed an Si−I bond as well as an Si−C bond,[5] indicating the potential use of hydrosilanes as silylating reagents in the presence of palladium catalyst. To our knowledge, however, there has been no report of palladium-catalyzed silicon−aryl carbon bond formation using hydrosilane derivatives with high chemical selectivity. We describe here the first and advantageous example of a specific silylation of aryl iodides **1** with triethoxysilane $(EtO)_3SiH$ (**2**) as a silicon source and affording the corresponding arylsilanes **3** in high yield (eq 1).



$$\underset{\mathbf{1}}{\text{Ar—I}} + \underset{\mathbf{2}}{\text{H−Si(OEt)}_3} \xrightarrow[\text{NMP}]{\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3\ /\ \text{P}(o\text{-tol})_3,\ i\text{-Pr}_2\text{NEt}} \underset{\mathbf{3}}{\text{Ar−Si(OEt)}_3} + \underset{\mathbf{4}}{\text{Ar−H}} \quad (1)$$

Preliminary investigations indicated that the combination of **2** as hydrosilane and a tertiary amine was highly efficient for this silylation of aryl iodides. It is known that the $Cl_3SiH−Et_3N$ combination greatly facilitates the silylation of allyl[6] or benzyl chlorides.[7] However, the present use of Cl_3SiH was not suitable in the presence of palladium complex, under which condition it merely recovered the starting aryl halide. Furthermore, the trialkylsilanes usually used as reducing reagents, such as Et_3SiH, tended to form a C−H bond in preference to a C−Si bond.[8,9]

The results of the reaction of 4-iodoanisole (**1**) with 1.5 equiv of $(EtO)_3SiH$ (**2**) for 1 h at room temperature under various conditions are listed in Table 1. The products were contaminated with the normal cross-coupling product,[1c,9] anisole (**4**), in each case as a result of a hydridic behavior of **2**. Although we were unable to completely control the selectivity of the products, the $(EtO)_3SiH$−base combination provided the predominant formation of 4-(triethoxysilyl)anisole (**3**). As for the base, the tertiary amines, such as Et_3N and *i*-Pr_2NEt, proved to be highly effective (entries 2 and 3). In the absence of a base or in the presence of other types of bases, the reactions occurred insufficiently (entries 1, 4, and 5), even though the cited simultaneous silylation and reduction of alkyl iodides using Et_2SiH_2 was caused in the absence of base.[5] The use of amide solvents, such as NMP, DMF, and DMA, is also essential for this silylation (entries 3 and 6). The reactions in other kind of solvents, such as DMSO, MeCN, dioxane, and toluene, resulted in quite low yields (entries 7 and 8).

The reaction was efficiently catalyzed by $Pd_2(dba)_3{\cdot}CHCl_3$ with 2 equiv (for Pd atom) of P(*o*-tol)$_3$ (entry 2). The palladium complex having bulky phosphines may effectively accelerate the oxidative addition step by ready formation of a coordinatively unsaturated species.[10] The ratio of $Pd_2(dba)_3{\cdot}CHCl_3$ to a phosphine ligand affected the rate of the silylation; that is, more than 2 equiv of P(*o*-tol)$_3$ slowed the reaction rate extremely. And the monodentate phosphine ligand was recognized to be more effective than the bidentate ligand (entries 9 and 10).

Table 2 summarizes the results of the silylation of representative aryl halides **1** with **2**, which was conducted in a manner similar to that above. Since the desired **3** and reduced arenes **4** were purely and easily separated by bulb-to-bulb distillation, although **3** was contaminated with **4** in each case, the present reaction should provide a simple and available procedure for synthesizing arylsilanes **3**. The rate of the silylation was also affected by the sort of aryl halides used; that is, aryl iodides **1** usually exhibited higher reactivity than aryl bromides (entries 1 and 2). The presence of functional groups such as $MeCO_2$ in the starting **1** did not interfere with the outcome of the present reaction, since the reactants were inert to many functional groups (entry 5). However, although both aryl iodides **1** having electron-donating groups and heteroaromatic iodides were very readily silylated with **2** (entries 1, 3−7, 10, and 11), the presence of electron-withdrawing groups significantly decreased the yields and the selectivity of this silylation (entries 8 and 9). Namely, aryl iodides having the latter groups had a strong tendency to produce competitively reduced arenes **4** (52 and 60%, GLC yields) as a result of the respective acceleration both of the oxidative addition

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[1] For the cross-coupling reaction with organic electrophiles, see: (a) Hatanaka, Y.; Hiyama, T. *Chem. Lett.* **1989**, 2049. (b) Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Chem. Lett.* **1989**, 1771. (c) For a recent review, see: Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845.

[2] For examples, see: (a) Loy, D. A.; Shea, K. J. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 1431. (b) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 1409.

[3] (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic: New York, 1988; p 39. (b) Colvin, E. W. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1987; Vol. 4, p 562.

[4] (a) Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 4715. (b) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 1653. (c) Matsumoto, H.; Kasahara, M.; Takahashi, M.; Arai, T.; Nakao, T.; Nagai, Y. *J. Organomet. Chem.* **1983**, *250*, 99. (d) Eaborn, C.; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331.

[5] Kunai, A.; Sakurai, T.; Toyoda, E.; Ishikawa, M.; Yamamoto, Y. *Organometallics* **1994**, *13*, 3233.

[6] Furuya, N.; Sukawa, T. *J. Organomet. Chem.* **1975**, *96*, C1.

[7] Benkeser, R. A.; Gaul, J. M.; Smith, W. E. *J. Am. Chem. Soc.* **1969**, *91*, 3666.

[8] A mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.015 mmol), P(*o*-tol)$_3$ (0.06 mmol), Et_3SiH (1.5 mmol), iodobenzene (1.0 mmol), and *i*-Pr_2NEt (3.0 mmol) in NMP (4 mL) was stirred at room temperature for 2 h. The GLC analysis of the reaction mixture indicated the formation of the corresponding phenylsilane (34% yield).

[9] Boukherroub, R.; Chatgilialoglu, C.; Manuel, G. *Organometallics* **1996**, *15*, 1508 and references therein.

[10] Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585.

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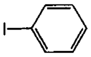
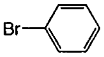
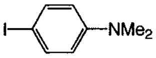
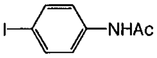
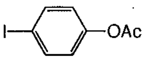
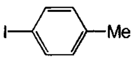
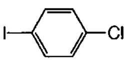
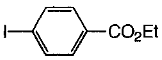
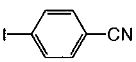
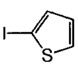
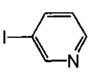
Table 1. Reaction of 4-Iodoanisole under Various Conditions[a]

entry	ligand	base	solvent	yield (%)[b] 3	4
1	P(*o*-tol)$_3$	none	NMP	5	4
2	P(*o*-tol)$_3$	Et$_3$N	NMP	88	6
3	P(*o*-tol)$_3$	*i*-Pr$_2$NEt	NMP	92	7
4	P(*o*-tol)$_3$	pyridine	NMP	4	5
5	P(*o*-tol)$_3$	KOAc	NMP	72	23
6	P(*o*-tol)$_3$	*i*-Pr$_2$NEt	DMF	82	17
7	P(*o*-tol)$_3$	*i*-Pr$_2$NEt	DMSO	31	19
8	P(*o*-tol)$_3$	*i*-Pr$_2$NEt	toluene	6	5
9	PPh$_3$	*i*-Pr$_2$NEt	NMP	76	19
10	dppe	*i*-Pr$_2$NEt	NMP	0	1

[a] Reactions of 4-iodoanisole (**1**) (1.0 mmol) with **2** (1.5 mmol) were carried out at room temperature for 1 h in 4 mL of solvent by using 0.015 mmol of Pd$_2$(dba)$_3$·CHCl$_3$, phosphine ligand (0.06 mmol), and base (3 mmol). [b] GLC yields are based on **1** used.

Table 2. Palladium-Catalyzed Silylation of Aryl Halides[a]

entry	aryl halide 1	time (h)	yield of **3** (%)[b]
1		1	83
2		16	9[c]
3		1	(81)
4		1	(72)
5		1	(77)
6		1	(82)
7		4	(72)
8		16	23
9		16	20
10		1	(84)
11		1	(56)[d]

[a] Reactions of aryl halide **1** (1.0 equiv) with **2** (1.5 equiv) were carried out at room temperature in NMP by using Pd$_2$(dba)$_3$·CHCl$_3$ (1.5 mol %), P(*o*-tol)$_3$ (6 mol %), and ^{i}Pr$_2$NEt (3 equiv). [b] GLC yields are based on **1** used. Those in parentheses are isolated yield. [c] The reaction was carried out at 50 °C. [d] At 80 °C.

to form an Ar−Pd^{II}−X and the following transmetalation with the hydride.[11]

Bearing in mind the previously described result,[12] a hydrosilane as well as an aryl halide can add oxidatively to palladium(0) complexes. Chatgilialoglu presented that the organic halides were the first to be added oxidatively to the palladium(0) complexes, forming an R−Pd^{II}−X intermediate in preference to the hydrosilane.[9] However, the present treatment of isolated Ar−Pd^{II}−X with (EtO)$_3$SiH (**2**) and Et$_3$N gave neither **3** nor **4**.[13,14] Consequently, a mechanism involving oxidative addition of aryl halides **1** can effectively be ruled out in the present reaction. On the other hand, Kunai and Ishikawa proposed a mechanism for the Si−H/C−I exchange involving oxidative addition of the hydrosilane followed by σ-bond metathesis between an Si−Pd bond and a C−I bond.[5] In analogy with this mechanism, the oxidative addition of (EtO)$_3$SiH (**2**) must be a key step in the present silylation.

In conclusion, we found a new and useful synthesis of arylsilanes **3** in which (EtO)$_3$SiH (**2**) acted specifically as a silicon source for the coupling reaction with aryl iodides **1** in the presence of the palladium catalyst and the tertiary amine. Investigations for further mechanistic studies and silylations with other organic halides are currently in progress in our laboratory.

Experimental Section

General. All the experiments were carried out under an argon atmosphere. NMP was distilled from CaH$_2$ before use. A commercial triethoxysilane was used directly. NMR spectra were recorded on a JEOL JNM-FX-200 spectrometer (^{1}H, 199.5 MHz; ^{13}C, 50.1 MHz). EI mass spectra were obtained at an ionization potential of 70 eV with a JEOL JMS-SX102 spectrometer. **CAUTION!** A hood should be worn while handling triethoxysilane and all contact with the eyes avoided.[16]

Synthesis of triethoxyphenylsilane.[17] **Typical Procedure.** Triethoxyphenylsilane synthesis is used to illustrate the general procedure for synthesizing arylsilanes. To a solution of Pd$_2$(dba)$_3$·CHCl$_3$ (80 mg, 0.08 mmol) and P(*o*-tol)$_3$ (91 mg, 0.3 mmol) in NMP (20 mL) were added iodobenzene (1.00 g, 4.90 mmol), *i*-Pr$_2$NEt (2.6 mL, 15 mmol), and triethoxysilane (1.24 g, 7.5 mmol). After being stirred for 1 h at room temperature, the mixture was extracted with benzene. The extract was washed three times with water to remove NMP, dried over MgSO$_4$, and concentrated. The residue was purified by Kugelrohr distillation to give 846 mg (72% yield) of analytically and spectroscopically pure triethoxyphenylsilane: ^{1}H NMR (CDCl$_3$) δ 1.25 (t, $J = 7.0$ Hz, 9 H), 3.88 (q, $J = 7.0$ Hz, 6 H), 7.3−7.5 (m, 3 H), 7.6−7.8 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 18.12, 58.68, 127.78, 130.22, 131.08, 134.74; MS (*m/z*) 240 (16), 195 (38), 181 (13), 162 (28), 147 (100), 139 (33), 135 (33); HRMS for $C_{12}H_{20}O_3Si$ calcd 240.1182, found 240.1141.

4-(Triethoxysilyl)anisole:[17c,d] IR (neat) 2975, 2360, 1598, 1567, 1506, 1459, 1390, 1282, 1250 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.24 (t, $J = 7.0$ Hz, 9 H), 3.86 (q, $J = 7.0$ Hz, 6 H), 6.92 (d, $J = 8.6$ Hz, 2 H), 7.61 (d, $J = 8.6$ Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 18.12, 54.89, 58.55, 113.57, 122.00, 136.37, 161.37; MS (*m/z*) 270 (52), 255 (53), 225 (38), 211 (25), 181 (28), 169 (27), 149 (22), 147 (100), 135 (32); HRMS for $C_{13}H_{22}O_4Si$ calcd 270.1287, found 270.1261.

4-(Triethoxysilyl)-*N,N*-dimethylaniline:[17c] IR (neat) 2973, 2884, 1600, 1517, 1389, 1360, 1167, 1077 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.23 (t, $J = 7.0$ Hz, 9 H), 2.97 (s, 3 H), 3.85 (q, $J = 7.0$ Hz, 6 H), 6.71 (d, $J = 8.8$ Hz, 2 H), 7.53(d, $J = 8.8$ Hz, 2 H); ^{13}C NMR

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(12) For a recent review of Pd-catalyzed hydrosilylation, see: Horn, K. A. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 1317.

(13) Benkeser proposed that a silyl anion species was generated by the Et$_3$N−hydrosilane system.[7] It is believed that transmetalation between an R−Pd^{II}−X and a silyl anion analogue provides the formation of an Si−C bond.[4a]

(14) To a solution of (4-MeO-C$_6$H$_4$)PdI(PPh$_3$)$_2$[15] (0.050 mmol) in DMF (1 mL) were added Et$_3$N (0.30 mmol) and (EtO)$_3$SiH (0.098 mmol). After being stirred at 50 °C for 6 h, the GLC analysis indicated neither the formation of the corresponding arylsilane nor that of anisole.

(15) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.

(16) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 7, p 5083.

(17) (a) Chappelow, C. C.; Elliott, R. L.; Goodwin, J. T., Jr. *J. Org. Chem.* **1960**, *25*, 435. (b) Sobolevskii, M. V.; Kleshchevnikova, S. I.; Rumyantseva, E. I.; Abramova, E. A; Dubrovskaya, G. A. *Plast. Massy* **1971**, 9. (c) Lutskii, A. E.; Abukhova, E. M.; Voronkov, M. G.; Alksne, V. *Teor. Eksp. Khim.* **1973**, *9*, 123. (d) Ernst, C. R.; Spialter, L.; Buell, G. R.; Wilhite, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 5375. (e) Chuy, N. D.; Chvalovsky, V.; Schraml, J.; Magi, M.; Lippmaa, E. *Collect. Czech. Chem. Commun.* **1974**, *40*, 875.

($CDCl_3$) δ 18.16,39.90, 58.43, 111.57, 115.69, 135.96, 151.76; MS (*m*/*z*) 283 (100), 238 (12), 182 (8), 166 (13), 147 (29), 122 (12); HRMS for $C_{14}H_{25}O_3NSi$ calcd 283.1604, found 283.1630.

4-(Triethoxysilyl)acetanilide: IR (neat) 3307, 2975, 1669, 1593, 1525, 1392, 1318, 1291 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, $J = 6.8$ Hz, 9 H), 2.18 (s, 3 H), 3.85 (q, $J = 6.8$ Hz, 6 H), 7.52 (d, $J = 8.3$ Hz, 2 H), 7.64 (d, $J = 8.3$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.18, 24.46, 58.71, 119.11, 128.64, 135.67, 140.10, 168.97; MS (*m*/*z*) 297 (10), 252 (68), 205 (100), 176 (31), 162 (15), 147 (48); HRMS for $C_{14}H_{23}O_4NSi$ calcd 297.1396, found 297.1399.

4-Acetoxy(triethoxysilyl)benzene: IR (neat) 2976, 2887, 1767, 1593, 1499, 1392 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, $J = 6.8$ Hz, 9 H), 2.28 (s, 3 H), 3.84 (q, $J = 6.8$ Hz, 6 H), 7.09 (d, $J = 8.3$ Hz, 2 H), 7.67 (d, $J = 8.3$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.11, 20.98, 58.68, 120.98, 128.55, 136.06, 152.48, 169.00; MS (*m*/*z*) 298 (3), 256 (100), 210 (51), 183 (17), 155 (27), 147 (62); HRMS for $C_{14}H_{22}O_5Si$ calcd 298.1237, found 298.1238.

4-(Triethoxysilyl)toluene:[17c,d] IR (neat) 2975, 2926, 2360, 1604, 1443, 1390, 1295, 1167 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, $J = 7.0$ Hz, 9 H), 2.36 (s, 3 H), 3.86 (q, $J = 7.0$ Hz, 6 H), 7.19 (d, $J = 7.9$ Hz, 2 H), 7.57(d, $J = 7.9$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.16, 21.50, 58.59, 127.41, 128.59, 134.82, 140.20; MS (*m*/*z*) 254 (23), 209 (38), 181 (5), 165 (16), 162 (30), 153 (19), 147 (100), 135 (17); HRMS for $C_{13}H_{22}O_3Si$ calcd 254.1363, found 254.1338.

4-Chloro(triethoxysilyl)benzene:[17d] IR (neat) 2975, 2888, 2360, 1699, 1583, 1557, 1485, 1443, 1389, 1296, 1261 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (t, $J = 7.0$ Hz, 9 H), 3.79 (q, $J = 7.0$ Hz, 6 H), 7.28 (d, $J = 8.5$ Hz, 2 H), 7.54 (d, $J = 8.5$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.12, 58.75, 128.06, 129.53, 136.13, 136.70; MS (*m*/*z*) 274 (3), 239 (27), 229 (44), 185 (15), 173 (25), 162 (31), 147 (100), 135 (9); HRMS for $C_{12}H_{19}O_3ClSi$ calcd 274.0792, found 274.0792.

Ethyl 4-(Triethoxysilyl)benzoate: IR (neat) 2977, 2928, 2361, 1720, 1558, 1445, 1391, 1367, 1279, 1101 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, $J = 7.0$ Hz, 9 H), 1.47 (t, $J = 7.0$ Hz, 3 H), 3.88 (q, $J = 7.0$ Hz, 6 H), 4.39 (q, $J = 7.0$ Hz, 2 H), 7.74 (d, $J = 8.2$ Hz, 2 H), 8.04 (d, $J = 8.2$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.29, 14.16, 54.84, 56.96, 124.55, 128.05, 130.70, 132.94, 162.63; MS (*m*/*z*) 312 (5), 267 (100), 253 (15), 239 (61), 223 (16), 195 (22), 183 (17), 163 (25), 147 (20), 135 (8); HRMS for $C_{15}H_{24}O_5Si$ calcd 312.1393, found 312.1392.

4-(Triethoxysilyl)benzonitrile: IR (neat) 2977, 2231, 1444, 1390, 1296 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, $J = 7.0$ Hz, 9 H), 3.88 (q, $J = 7.0$ Hz, 6 H), 7.65 (d, $J = 8.3$ Hz, 2 H), 7.78 (d, $J = 8.3$ Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.16, 59.04, 113.93, 131.12, 135.23, 137.88, 159.74; MS (*m*/*z*) 265 (43), 250 (17), 220 (100), 206 (46), 192 (20), 176 (34), 164 (62); HRMS for $C_{13}H_{19}O_3NSi$ calcd 265.1134, found 265.1144.

2-(Triethoxysilyl)thiophene:[18] IR (neat) 2976, 2888, 1695, 1501, 1442, 1407, 1391, 1296, 1216, 1167 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, $J = 7.0$ Hz, 9 H), 3.90 (q, $J = 7.0$ Hz, 6 H), 7.22 (dd, $J = 3.3$, 4.5 Hz, 1 H), 7.48 (d, $J = 3.3$ Hz, 1 H), 7.66 (d, $J = 4.5$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.42, 60.26, 129.37, 130.63, 133.15, 138.12; MS (*m*/*z*) 246 (52), 213 (6), 201 (34), 187 (7), 167 (7), 158 (13), 147 (100), 135 (34); HRMS for $C_{10}H_{18}O_3SiS$ calcd 246.0765, found 246.0746.

3-(Triethoxysilyl)pyridine:[19] ^{1}H NMR ($CDCl_3$) δ 1.26 (t, $J = 6.8$ Hz, 9 H), 3.90 (q, $J = 6.8$ Hz, 6 H), 7.2−7.3 (m, 1 H), 7.95 (d, $J = 5.9$ Hz, 1 H), 8.65 (d, $J = 4.9$ Hz, 1 H), 8.83 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.04, 58.80, 123.07, 126.55, 142.36, 151.05, 154.99; MS (*m*/*z*) 241 (54), 240 (100), 226 (18), 212 (27), 196 (88), 147 (29), 182 (25); HRMS for $C_{11}H_{19}O_3NSi$ calcd 241.1134, found 241.1112.

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