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SYNTHESIS AND BIOLOGICAL ACTIVITY OF NEW 2-[(3-AMINOPROPYL)DIMETHYL-SILYL]-5-TRIALKYLGERMYLFURANS

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New highly cytotoxic 3-aminopropyl derivatives of 2-dimethylsilyl-5-trialkylgermylfuran (IC_{50} 1–3 $\mu g \cdot ml^{-1}$) have been prepared by hydrosilylation of heterocyclic N-allylamines with the corresponding hydrosilane in the presence of Speier's catalyst. The influence of the amine structure and alkyl substituent at the germanium atom on the cytotoxicity has been investigated.

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The heterocyclic amines are important building blocks for the creation of anticancer drugs [1, 2]. In some cases the benzene ring has been substituted for thiophene or furan to enhance the activity and increase the therapeutic index. Examples are the thiophene-containing folate analogue *Raltitrexed* [3], the antimetastatic agent *Batimastat* [4], and the furan-containing anticancer agent *Lapatinib* [5].

Our previous investigations have demonstrated that hetarylaminoalkyl(siloxy)silanes, containing an alkyl(or siloxy) group attached to the silicon atom, have anticancer, neurotropic, and bacteriostatic activity [6–8]. On the other hand, toxicological studies have demonstrated that most tested organogermanium compounds were less toxic than the corresponding organosilicon analogs [9].

Taking into consideration the information gained from the fragment analysis of known anticancer drugs as well as the fact that silylation and germylation increase the lypophilicity of the compounds and can change their metabolism [10–12] we decided to combine in one molecule the fragments of germylated furan and silylated heterocyclic amine and to test their cytotoxicity.

The starting 2-dimethylsilyl-5-trimethyl(ethyl)germylfurans **1** and **12** have been prepared from the furan by two consecutive organolithium syntheses. These compounds were used for the hydrosilylation of heterocyclic allylamines in the presence of Speier's catalyst (Scheme 1). Hydrosilylation of all studied

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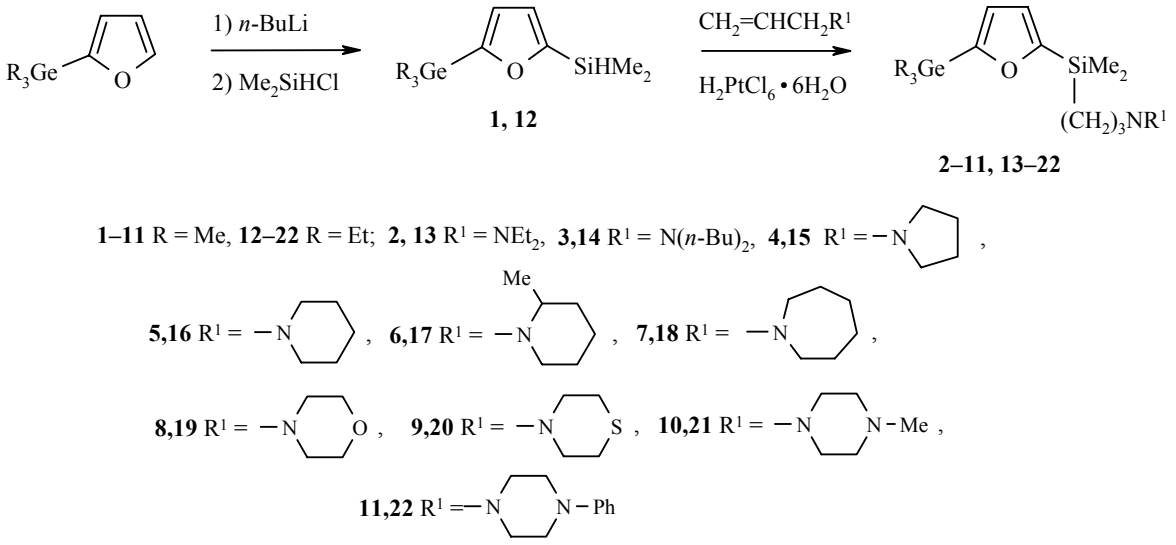
allylamines by hydrosilanes **1**, **12** occurred smoothly during 1 h heating of the mixture of compounds with a drop of catalyst. The reaction afforded a series of silylamines **2**–**11** and **13**–**22** containing two different heterocycles in good or moderate yield. The ^{13}C and ^{29}Si NMR spectra are given in Table 1.



1, 12

2–11, 13–22

1–11 R = Me, **12–22** R = Et; **2, 13** $R^1 = NEt_2$, **3,14** $R^1 = N(n\text{-}Bu)_2$, **4,15** R^1 = ,

5,16 R^1 = , **6,17** R^1 = , **7,18** R^1 = ,

8,19 R^1 = , **9,20** R^1 = , **10,21** R^1 = ,

11,22 R^1 =

The cytotoxicity of silylamines **2–11** and **13–22** *in vitro* has been investigated on tumor cells HT-1080 (human fibrosarcoma), MG-22A (mouse hepatoma) and normal mouse fibroblasts 3T3 to determine the effect of the amine on the antitumor activity. The experimental evaluation of cytotoxic properties is presented in Table 2. Most of the studied compounds (**2**, **4–8, 10, 13, 15–18, 21**) exhibited high cytotoxic activity (IC_{50} 1–3 μg·ml^{-1}). The amines **6**, **16**, **17** and **21** showed high cytotoxic activity in cancer cells accompanied by the highest cytotoxic activity on normal cells 3T3 (IC_{50} 0.3 μg·ml^{-1}). This means that the therapeutic index for these compounds is low. In the case of morpholino derivative **19** some selectivity has been found: amine **19** is less cytotoxic against human fibrosarcoma (IC_{50} 6 μg·ml^{-1}) but is highly cytotoxic against mouse hepatoma (IC_{50} 2 μg·ml^{-1}).

Morpholino derivatives **8** and **19** were more active for both cancer cell lines and less cytotoxic for normal fibroblasts than thiomorpholino derivatives **9** and **20.** The N-methylpiperazino derivatives **10** and **21** showed high cytotoxic activity in both cancer cell lines, but compound **21** was very cytotoxic for normal fibroblasts (IC_{50} 0.3 μg·ml^{-1}). Amines **8** and **10** are more promising compounds among morpholino and N-methylpiperazino derivatives. Substitution of the N-methyl group for the N-phenyl led to the loss of cytotoxic activity in the case of germanium derivatives **11**, **22**; at the same time, derivative **11** is very toxic for normal fibroblasts (IC_{50} 1 μg·ml^{-1}).

Substitution of three methyl group for three ethyl groups at the germanium atom leads to a further increase in cytotoxicity (comparing compounds **10** and **21**), but at the same time compound **21** exhibits very high cytotoxicity on normal cells 3T3 (IC_{50} 0.3 μg·ml^{-1}) and high toxicity (LD_{50} 72 mg·kg^{-1}).

The morpholino derivative **8** and N-methylpiperazino derivative **10** are the most promising compounds in this series of amines: moderate toxicity (LD_{50} 307-333 mg·kg^{-1}), high cytotoxicity on both cancer cell lines (IC_{50} 2–4 μg·ml^{-1}), and low cytotoxicity on normal fibroblasts (IC_{50} 8–10 μg·ml^{-1}). All compounds **2**–**11** and **13**–**22** have low $NO^{\cdot}$ generation ability (Table 2).

Thus, by variations in the substituent (germanium or silicon [8] atom, different alkyl groups) and type of amine, one can achieve a high cytotoxicity against cancer cells and cytoselectivity in furylsilylamines.

TABLE 1. Spectral Characteristics of 2-[(3-Aminopropyl)dimethylsilyl]-5-trimethyl(ethyl)germylfurans **2-11** and **13-22**

Compound	^{13}C NMR, δ, ppm					^{29}Si NMR, δ, ppm
	C(4)	C(3)	C(5)	C(2)	R_3Ge- , $Si(CH_3)_2CH_2CH_2CH_2R^1$	
2	122.93	120.51	168.59	166.46	59.72, 50.15, 24.56, 16.33, 14.97, 1.42	-9.72
3	122.86	120.48	168.58	166.55	60.96, 57.19, 32.55, 24.56, 24.02, 17.33, 1.41, -0.02	-9.70
4	122.99	120.56	168.65	166.46	63.20, 57.45, 26.68, 26.62, 16.51, 1.48, 3.42, 0.001	-9.69
5	122.98	120.54	168.68	166.42	66.14, 57.84, 29.17, 27.71, 24.32, 16.40, 1.45, -0.05	-9.70
6	122.91	120.50	168.60	166.43	60.90, 59.02, 55.52, 37.96, 29.48, 27.40, 22.76, 16,41, 1.41, 0.03, -0.003	-9.75
7	122.88	120.47	168.57	166.46	64.91, 58.75, 31.15, 30.23, 24.84, 16.22, 1.40, -0.004	-9.77
8	123.05	120.56	168.72	166.27	70.25, 65.59, 56.89, 24.07, 16.22, 1.46, -0.002	-9.72
9	123.01	120.54	168.68	166.24	65.87, 58.23, 31.23, 23.97, 16.20, 1.45, -0.001	-9.76
10	123.02	120.55	168.69	166.33	65.26, 58.44, 56.48, 49.35, 24.43, 16.30, 1.46, -0.003	-9.71
11	123.04	122.85	168.74	166.31	154.64, 132.33, 120.55, 119.26, 65.24, 56.51, 52.39, 24.41, 16.31, 1.46, 0.00	-9.65
13	122.75	121.61	167.02	166.47	59.79, 50.19, 24.57, 16.45, 15.00, 12.21, 7.90, 0.001	-9.83
14	122.67	121.57	166.97	166.55	61.05, 57.23, 32.64, 24.61, 24.08, 17.40, 16.35, 12.19, 7.90, -0.001	-9.82
15	122.79	121.64	167.07	166.49	63.27, 57.49, 26.74, 26.67, 16.61, 12.26, 7.95, -0.002	-9.79
16	122.74	121.60	167.05	166.47	66.32, 57.92, 29.33, 27.84, 24.48, 16.54, 12.22, 7.91, -0.006	-9.72
17	122.75	121.60	167.03	166.45	60.97, 59.09, 55.60, 38.01, 29.52, 27.44, 22.77, 16.55, 12.21, 7.91, 0.06, -0.005	-9.82
18	122.66	121.55	166.98	166.50	65.09, 58.83, 31.28, 30.29, 24.93, 16.35, 12.18, 7.87, -0.006	-9.81
19	122.85	121.65	167.15	166.31	70.35, 65.70, 57.06, 24.18, 16.34, 12.24, 7.93, -0.004	-9.70
20	122.82	121.63	167.13	166.29	66.01, 58.29, 31.31, 24.07, 16.34, 12.23, 7.91, -0.002	-9.76
21	122.82	121.64	167.10	166.34	65.36, 58.51, 56.54, 49.42, 24.54, 16.43, 12.25, 7.93, -0.002	-9.78
22	122.83	121.63	167.14	166.32	154.70, 132.38, 122.91, 119.31, 65.33, 56.56, 52.45, 24.50, 16.42, 12.24, 7.92, -0.005	-9.78

EXPERIMENTAL

Materials and methods. IR spectra (KBr) were registered on a Shimadzu Prestige-21 spectrometer. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian 200 Mercury instrument at 200, 50, and 40 MHz, respectively, in $CDCl_3$ as solvent, $(Me_3Si)_2O$ as standard for ^{1}H, TMS (external) as standard for ^{29}Si, and

TABLE 2. Cytotoxicity (IC_{50}) and Toxicity (LD_{50}) of Compounds **2-11** and **13-22**

Compound	IC_{50}, μg·ml^{-1}*							LD_{50}, mg·kg^{-1}
	HT-1080			MG-22A			3T3	
	CV	MTT	NO·	CV	MTT	NO·	NR	
2	1	1	250	1	1	250	3	178
3	10	12	200	10	10	200	2	165
4	1	2	250	1	3	250	2	142
5	2	3	200	1	2	200	2	147
6	2	2	200	1	3	100	0.3	76
7	2	2	150	1	3	75	3	191
8	4	3	200	2	3	200	10	333
9	6	10	250	4	6	250	5	232
10	2	3	250	2	3	200	8	307
11	29	35	100	18	28	100	1	134
13	2	2	250	1	1	250	1	120
14	22	20	100	10	11	250	1	136
15	3	3	200	1	1	200	1	119
16	3	3	150	2	1	150	0.3	82
17	3	3	200	2	3	100	0.3	120
18	2	3	150	1	1	150	1	128
19	6	6	150	2	2	150	7	288
20	16	22	200	8	10	200	14	385
21	1	1	200	1	1	200	0.3	72
22	31	27	75	17	23	167	30	585

* IC_{50} providing 50% cell killing effect [CV– crystal violet coloration, action on cell membranes; MTT – 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide coloration, influence on the activity of mitochondrial enzymes]; NR – neutral red; NO· – concentration.

the signal on the residual proton of the solvent (δ 77.05 ppm) for ^{13}C. The mass spectra were recorded under electron impact conditions on a GC-MS Agilent Technologies 7890 GC system with 5975C EI/CI MSD (70 eV) on capillary column HP-5. All solvents were dried on CaH_2, and distilled prior to use. Thin-layer chromatography (TLC) was performed on a Merck silica gel 60 F_{254} with various eluents. Column chromatography was performed on Silica gel (0.060–0.200 mm, pore diameter 6 nm, "Acros"). 2-Trimethylgermyl- and 2-triethylgermylfuran have been prepared by the known method [13].

Cytotoxicity *in vitro*. Monolayer tumor cell lines MG-22A (mouse hepatoma), HT-1080 (human fibrosarcoma), and NIH 3T3 (normal mouse fibroblasts) were cultivated for 72 h in standard Dulbecco's modified Eagle's medium (Sigma) without indicator and antibiotics [14]. After the ampoule was thawed, not more than four passages were performed. The control cells and cells with the tested substances in the range of (2–5) × 10^4 cells/ml concentration (depending on line nature) were placed on separate 96-well plates. Solutions containing the test compounds were diluted and added in the wells to give final concentrations of 50, 25, 12.5, and 6.25 μg·ml^{-1}. The control cells were treated in the same manner only in the absence of test compounds. Plates were cultivated for 72 h. The quantity of surviving cells was determined using CV, NR, or MTT coloration, which was assayed by a multiscan spectrophotometer Tetretek Multiscan MCC/340. The quantity of living cells on the control plate was taken in calculations for 100% (IC_{50} determination) [14, 15]. The concentration of NO was determined according to [15]. The mean lethal dose (LD_{50}) was determined on NIH

3T3 cells (alternative to LD_{50} *in vivo* test) according to the protocols of the Interagency Coordinating Committee on the Validation of Alternative Methods and the National Toxicology Program of the Interagency Center for the Evaluation of Alternative Toxicological Methods [16].

2-Dimethylsilyl-5-trimethylgermylfuran (1). A solution of 2-trimethylgermylfuran (5.6 g, 30 mmol) in dry ether (43 ml) was placed in a three-necked flask fitted with a reflux condenser, a thermometer, a magnetic stirrer, and a rubber stopper in a stream of argon. The flask with the solution was cooled to -30°C, and 12 ml (30 mmol) of a 2.5 N solution of *n*-BuLi in hexane was added dropwise slowly to maintain the temperature below -25°C. When all the *n*-BuLi had been added, the mixture was stirred for 1 h at -10°C, and for 2 h at 10°C. Then dimethylchlorosilane (2.82 g, 20 mmol) was added dropwise at -25°C. After the addition of chlorosilane the mixture was stirred for 10 min at -25°C, the temperature was slowly raised to room temperature, and the mixture was stirred for 12 h. The precipitate was filtered off through Al_2O_3, the solvents evaporated and the residue distilled under reduced pressure at 64-65°C (7.5 mm Hg), to give 4.8 g (66%) of the compound **1**. IR spectrum, ν_{Si-H}, cm^{-1}: 2131.8. ^1H NMR, δ, ppm (*J*, Hz): 0.37-0.39 (6H, m, $Si(CH_3)_2$); 0.45 (9H, s, $Ge(CH_3)_3$); 4.42-4.52 (1H, m, SiH); 6.60 (1H, d, *J* = 3.6, H-3); 6.73 (1H, d, *J* = 3.6, H-4). ^{29}Si NMR, δ, ppm: -28.36. GC-MS, *m/z* (*I*, %): 244 $[M]^+$ (15), 229 $[M^+–Me]$ (100), 179 (51), 163 (10), 119 $[Me_3Ge]$ (25), 104 (9), 89 (29), 73 (59), 59 (44).

2-[(3-Diethylaminopropyl)dimethylsilyl]-5-trimethylgermylfuran (2). A solution of silane **1** (0.2 g, 0.8 mmol) and N,N-diethylallylamine (0.09 g, 0.8 mmol) and one drop of $H_2PtCl_6 \cdot 6H_2O$ (0.1% in 2-PrOH) were placed in a flask with a reflux condenser, a thermometer, and a magnetic stirrer. The mixture was heated at 90°C for 1 h, afterwards cooled and analyzed by GC-MS. Separation by column chromatography (CH_2Cl_2–MeOH, 20:1) gave 0.17 g (56%) of compound **2**. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.39 (9H, s, $Ge(CH_3)_3$); 0.67-0.71 (2H, m, $SiCH_2$); 0.98-1.02 (6H, t, *J* = 7.2, CH_3); 1.47-1.55 (2H, m, CH_2); 2.37-2.41 (2H, m, CH_2N); 2.47-2.53 (4H, m, CH_2N); 6.50 (1H, d, *J* = 3.2, H-3); 6.61 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 357 $[M]^+$ (4), 342 $[M^+$-Me] (5), 238 (45), 213 (6), 193 (6), 163 (7), 142 (17), 119 $[Me_3Ge]$ (16), 95 (7), 86 (100), 73 (15), 58 (22).

Compounds 3-11 were prepared and isolated in the same manner as described for compound **2**. The ^{13}C and ^{29}Si NMR data for compounds **2-11** are given in Table 1.

2-[(3-Dibutylaminopropyl)dimethylsilyl]-5-trimethylgermylfuran (3) was prepared from compound **1** and N,N-dibutylallylamine. Yield 53%. ^1H NMR, δ, ppm (*J*, Hz): 0.25 (6H, s, $Si(CH_3)_2$); 0.40 (9H, s, $Ge(CH_3)_3$); 0.68-0.72 (2H, m, $SiCH_2$); 0.88-0.92 (6H, t, *J* = 7.2, CH_3); 1.23-1.54 (10H, m, CH_2); 2.36-2.39 (6H, t, *J* = 7.6, CH_2N); 6.51 (1H, d, *J* = 3.2, H-3); 6.62 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 414 $[M]^+$ (3), 294 (17), 199 (25), 170 (9), 156 (8), 142 (100), 119 $[Me_3Ge]$ (9), 100 (20), 83 (5), 73 (5), 57 (8).

2-[Dimethyl(3-pyrrolidinopropyl)silyl]-5-trimethylgermylfuran (4) was prepared from compound **1** and N-allylpyrrolidine. Yield 46%. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.39 (9H, s, $Ge(CH_3)_3$); 0.73-0.77 (2H, m, $SiCH_2$); 1.53-1.61 (2H, m, CH_2); 1.74-1.79 (4H, m, CH_2); 2.38–2.49 (6H, m, CH_2N); 6.50 (1H, d, *J* = 3.2, H-3); 6.61 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 355 $[M]^+$ (3), 340 $[M^+$-Me] (5), 236 (62), 208 (13), 168 (20), 141(22), 119 $[Me_3Ge]$ (21), 99 (6), 73 (10), 55 (33).

2-[Dimethyl(3-piperidinopropyl)silyl]-5-trimethylgermylfuran (5) was prepared from compound **1** and N-allylpiperidine. Yield 37%. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.39 (9H, s, $Ge(CH_3)_3$); 0.67-0.72 (2H, m, $SiCH_2$); 1.40-1.48 (2H, m, CH_2); 1.52-1.62 (6H, m, CH_2); 2.26-2.40 (6H, m, CH_2N); 6.50 (1H, d, *J* = 3.4, H-3); 6.61 (1H, d, *J* = 3.4, H-4). GC–S, *m/z* (*I*, %): 354 $[M^+$-Me] (6), 250 (63), 222 (13), 182 (15), 155 (15), 124 (28), 98 (100), 55 (49).

2-{Dimethyl-[3-(2-methylpiperidino)propyl]silyl}-5-trimethylgermylfuran (6) was prepared from compound **1** and N-allyl-2-methylpiperidine. Yield 49%. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.39 (9H, s, $Ge(CH_3)_3$); 0.63-0.69 (2H, m, $SiCH_2$); 1.02-1.03 (3H, d, *J* = 6.0, CH_3); 1.23-1.30 (2H, m, CH_2); 1.46-1.64 (6H, m, CH_2); 2.09-2.36 (3H, m, CH_2N, CH); 2.59-2.84 (2H, m, CH_2N); 6.50 (1H, d, *J* = 3.2, H-3); 6.61 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 383 $[M]^+$ (3), 368 $[M^+$-Me] (15), 353 $[M^+$-2Me] (6), 264 (62), 236 (12), 213 (9), 193 (15), 176 (13), 163 (10), 154 (8), 138 (14), 149 (37), 112 (100), 95 (14), 83 (34), 73 (23), 55 (60).

2-[(3-Hexamethyleneiminopropyl)dimethylsilyl]-5-trimethylgermylfuran (7) was prepared from compound **1** and N-allylhexamethyleneimine. Yield 45%. ^{1}H NMR, δ, ppm (*J*, Hz): 0.25 (6H, s, $Si(CH_3)_2$); 0.40 (9H, s, $Ge(CH_3)_3$); 0.68-0.72 (2H, m, $SiCH_2$); 1.50-1.62 (10H, m, CH_2); 2.43-2.47 (2H, m, CH_2N); 2.60-2.62 (4H, m, CH_2N); 6.55 (1H, d, *J* = 3.2, H-3); 6.62 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 383 $[M]^+$ (3), 368 [M^+-Me] (6), 264 (61), 236 (10), 213 (7), 196 (13), 169 (11), 154 (6), 138 (14), 112 (100), 83 (26), 58 (69).

2-[Dimethyl(3-morpholinopropyl)silyl]-5-trimethylgermylfuran (8) was prepared from compound **1** and N-allylmorpholine. Yield 42%. ^{1}H NMR, δ, ppm (*J*, Hz): 0.25 (6H, s, $Si(CH_3)_2$); 0.39 (9H, s, $Ge(CH_3)_3$); 0.70-0.74 (2H, m, $SiCH_2$); 1.51-1.59 (2H, m, CH_2); 2.28–2.34 (6H, m, CH_2N); 3.68–3.70 (4H, m, CH_2O); 6.50 (1H, d, *J* = 3.2, H-3); 6.61 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 371 $[M]^+$ (3), 356 [M^+-Me] (5), 252 [M^+-$GeMe_3$] (100), 224 (10), 209 (9), 193 (9), 184 (10), 157 (19), 142 (29), 128 (14), 119 [Me_3Ge] (25), 100 (100), 83 (16), 73 (19), 56 (30).

2-[Dimethyl(3-thiomorpholinopropyl)silyl]-5-trimethylgermylfuran (9) was prepared from compound **1** and N-allylthiomorpholine. Yield 46%. ^{1}H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.39 (9H, s, $Ge(CH_3)_3$); 0.67-0.71 (2H, m, $SiCH_2$); 1.50-1.58 (2H, m, CH_2); 2.31-2.35 (2H, m, CH_2N); 2.65 (8H, s, CH_2); 6.50 (1H, d, *J* = 3.4, H-3); 6.61 (1H, d, *J* = 3.4, H-4). GC-MS, *m/z* (*I*, %): 387 $[M]^+$ (3), 372 [M^+-Me] (5), 268 (60), 240 (7), 200 (9), 173 (18), 158 (30), 142 (10), 128 (28), 116 (100), 95 (5), 88 (43), 73 (18), 59 (21).

2-{[3-Dimethyl(4-methylpiperazino)propyl]silyl}-5-triethylgermylfuran (10) was prepared from compound **1** and N-allyl-4-methylpiperazine. Yield 47%. ^{1}H NMR, δ, ppm (*J*, Hz): 0.22 (6H, s, $Si(CH_3)_2$); 0.37 (9H, s, $Ge(CH_3)_3$); 0.67-0.72 (2H, m, $SiCH_2$); 1.49-1.57 (2H, m, CH_2); 2.26 (3H, s, CH_3); 2.28-2.42 (10H, m, CH_2N); 6.48 (1H, d, *J* = 3.2, H-3); 6.59 (1H, d, *J* = 3.2, H-4). GC–MS, *m/z* (*I*, %): 384 $[M]^+$ (5), 265 (33), 142 (5), 113 (100), 95 (5), 70 (42).

2-{[3-Dimethyl(4-phenylpiperazino)propyl]silyl}-5-triethylgermylfuran (11) was prepared from compound **1** and N-allyl-4-phenylpiperazine. Yield 58%. ^{1}H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.38 (9H, s, $Ge(CH_3)_3$); 0.71-0.75 (2H, m, $SiCH_2$); 1.54-1.62 (2H, m, CH_2); 2.34 (2H, m, CH_2N); 2.55-2.57 (4H, m, CH_2); 3.16-3.19 (4H, m, CH_2); 6.49 (1H, d, *J* = 3.2, H-3); 6.60 (1H, d, *J* = 3.2, H-4); 6.82-6.92 (3H, m, C_6H_5); 7.22-7.25 (2H, m, C_6H_5). GC-MS, *m/z* (*I*, %): 446 $[M]^+$ (5), 327(21), 207 (5), 175(100), 132 (16), 104(12), 70 (25).

2-Dimethylsilyl-5-triethylgermylfuran (12). A solution of 2-triethylgermylfuran (2.55 g, 11 mmol) in dry ether (20 ml) was placed in a three-necked flask fitted with a reflux condenser, a thermometer, a magnetic stirrer, and a rubber stopper in a stream of argon. The flask with the solution was cooled to -30°C, and 4.5 ml (11 mmol) of 2.5 N solution of *n*-BuLi in hexane was added, dropwise slowly to maintain the temperature below -25°C. When all the *n*-BuLi had been added, the mixture was stirred for 1 h at -10°C, and for 2 h at 20°C. Then 1.05 g (11 mmol) of dimethylchlorosilane was added dropwise at -25°C. After the addition of chlorosilane, the mixture was stirred for 10 min at -25°C, the temperature was slowly raised to room temperature, and the mixture was stirred for 12 h. The precipitate was filtered off through Al_2O_3, the solvents evaporated, and the residue distilled under reduced pressure at 79-80°C (7 mm Hg), to give 2.2 g (69%) of the compound **12**. IR spectrum, ν_{Si-H}, cm^{-1}: 2131.8. ^{1}H NMR, δ, ppm (*J*, Hz): 0.38 (6H, s, $Si(CH_3)_2$); 1.00-1.16 (15H, m, $Ge(C_2H_5)_3$); 4.47-4.51 (1H, m, SiH); 6.57 (1H, d, *J* = 3.3, H-3); 6.73 (1H, d, *J* = 3.3, H-4). ^{29}Si NMR, δ, ppm: -28.45. GC-MS, *m/z* (*I*, %): 286 $[M]^+$ (5), 257 [M^+-Et] (100), 229 (31), 201 (26), 171 (5), 148 (8), 130 (12), 111 (23), 103 (30), 83 (30), 59 (100).

2-[(3-Diethylaminopropyl)dimethylsilyl]-5-triethylgermylfuran (13). A solution of silane **12** (0.2 g, 0.7 mmol) and N,N-diethylallylamine (0.08 g, 0.7 mmol), and one drop of $H_2PtCl_6 \cdot 6H_2O$ (0.1% in 2-PrOH) were placed in a flask with a reflux condenser, a thermometer, a magnetic stirrer. The mixture was heated at 90°C during 1 h, cooled, and analyzed by GC-MS. Separation by column chromatography (CH_2Cl_2–MeOH, 20:1) gave 0.18 g (64%) of compound **13**. ^{1}H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.66-0.70 (2H, m, $SiCH_2$); 0.93-1.10 (21H, m, $Ge(C_2H_5)_3$, CH_3); 1.46-1.54 (2H, m, CH_2); 2.37-2.41 (2H, m, CH_2); 2.47-2.52 (4H, m, CH_2N); 6.50 (1H, d, *J* = 3.2, H-3); 6.61 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 399 $[M]^+$ (3), 238 (45), 213 (25), 199 (5), 171 (5), 148 (8), 133 (6), 112 (6), 86 (100), 58 (34).

Compounds 14–22 were prepared and isolated in the same manner as described for compound **13**. The ^{13}C and ^{29}Si NMR data for compounds **13–22** are given in Table 1.

2-[(3-Dibutylaminopropyl)dimethylsilyl]-5-triethylgermylfuran (14) was prepared from compound **12** and N,N-dibutylallylamine. Yield 67%. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.67-0.71 (2H, m, $SiCH_2$); 0.88-1.11 (21H, m, $Ge(C_2H_5)_3$, CH_3); 1.23-1.53 (12H, m, CH_2); 2.35-2.39 (6H, m, CH_2N); 6.51 (1H, d, *J* = 3.4, H-3); 6.62 (1H, d, *J* = 3.4, H-4). GC-MS, *m/z* (*I*, %): 409 $[M]^+$ (7), 394 $[M^+-Me]$ (3), 195 (34), 170 (9), 142 (100), 125(5), 100 (14), 59 (10).

2-[Dimethyl(3-pyrrolidinopropyl)silyl]-5-triethylgermylfuran (15) was prepared from compound **12** and N-allylpyrrolidine. Yield 51%. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.72-0.76 (2H, m, $SiCH_2$); 0.93-1.10 (15H, m, $Ge(C_2H_5)_3$); 1.52-1.60 (2H, m, CH_2); 1.73 (4H, m, CH_2); 2.38-2.45 (6H, m, CH_2N); 6.50 (1H, d, *J* = 3.6, H-3); 6.61 (1H, d, *J* = 3.6, H-4). GC-MS, *m/z* (*I*, %): 396 $[M]^+$ (3), 236 (59), 208 (13), 168 (21), 141 (23), 128 (10), 110 (10), 84 (100), 59 (17).

2-[Dimethyl(3-piperidinopropyl)silyl]-5-triethylgermylfuran (16) was prepared from compound **12** and N-allylpiperidine. Yield 53% .^1H NMR, δ, ppm (*J*, Hz): 0.23 (6H, s, $Si(CH_3)_2$); 0.64-0.72 (2H, m, $SiCH_2$); 0.89-1.14 (15H, m, $Ge(C_2H_5)_3$); 1.39-1.62 (8H, m, CH_2); 2.22-2.33 (6H, m, CH_2N); 6.50 (1H, d, *J* = 3.2, H-3), 6.62 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 382 $[M^+-Me]$ (3), 250 (40), 222 (9), 182 (8), 155 (7), 124 (5), 96 (100), 83 (10), 69 (7), 55 (15).

2-{[Dimethyl-3-(2-methylpiperidino)propyl]silyl}-5-triethylgermylfuran (17) was prepared from compound **12** and N-allyl-2-methylpiperidine. Yield 73%. ^1H NMR, δ, ppm (*J*, Hz): 0.23 (6H, s, $Si(CH_3)_2$); 0.62-0.67 (2H, m, $SiCH_2$); 0.93-1.10 (18H, m, $Ge(C_2H_5)_3$, CH_3); 1.23-1.32 (2H, m, CH_2); 1.46-1.65 (6H, m, CH_2); 2.09-2.36 (3H, m, CH_2N, CH); 2.59-2.85 (2H, m, CH_2N); 6.50 (1H, d, *J* = 3.2, H-3); 6.61 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 425 $[M]^+$ (3), 397 (6), 264 (16), 236 (5), 196 (5), 162 (5), 112 (100), 98 (6), 83 (11), 55 (20).

2-[(3-Hexamethyleneiminopropyl)dimethylsilyl]-5-triethylgermylfuran (18) was prepared from compound **12** and N-allylhexamethyleneimine. Yield 56%. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.66-0.70 (2H, m, $SiCH_2$); 0.94-1.10 (15H, m, $Ge(C_2H_5)_3$); 1.48-1.61 (8H, m, CH_2); 2.42-2.45 (2H, m, CH_2N); 2.58-2.61 (4H, m, CH_2N); 6.50 (1H, d, *J* = 3.2, H-3); 6.62 (1H, d, *J* = 3.2, H-4). GC–MS, *m/z* (*I*, %): 396 (5), 264 (50), 236 (10), 196 (11), 169 (14), 149 (7), 138 (10), 112 (100), 101 (8), 83 (18), 58 (35).

2-[Dimethyl(3-morpholinopropyl)silyl]-5-triethylgermylfuran (19) was prepared from compound **12** and N-allylmorpholine. Yield 52%. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.69-0.73 (2H, m, $SiCH_2$); 0.93-1.10 (15H, m, $Ge(C_2H_5)_3$); 1.50-1.58 (2H, m, CH_2); 2.28-2.39 (6H, m, CH_2N); 3.68-3.71 (4H, m, CH_2O); 6.50 (1H, d, *J* = 3.2, H-3), 6.62 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 398 $[M^+-Me]$ (3), 252 (30), 224 (5), 184 (7), 157 (13), 142 (20), 128 (8), 100 (100), 83 (10), 56 (15).

2-[Dimethyl(3-thiomorpholinopropyl)silyl]-5-triethylgermylfuran (20) was prepared from compound **12** and N-allylthiomorpholine. Yield 58%. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.66-0.70 (2H, m, $SiCH_2$); 0.93-1.00 (15H, m, $Ge(C_2H_5)_3$); 1.48-1.56 (2H, m, CH_2); 2.30-2.34 (2H, m, CH_2); 2.66 (8H, s, CH_2N, CH_2S); 6.51 (1H, d, *J* = 3.2, H-3); 6.61 (1H, d, *J* = 3.2, H-4). GC–MS, *m/z* (*I*, %): 414 $[M^+-Me]$ (3), 399 $[M^+-2Me]$ (3), 268 (38), 240 (6), 227 (6), 199 (10), 173 (15), 158 (20), 142 (10), 128 (20), 116 (100), 103 (8), 88 (16), 59 (13).

2-{[Dimethyl-3-(4-methylpiperazino)propyl]silyl}-5-triethylgermylfuran (21) was prepared from compound **12** and N-allyl-4-methylpiperazine. Yield 69%. ^1H NMR, δ, ppm (*J*, Hz): 0.22 (6H, s, $Si(CH_3)_2$); 0.66-0.71 (2H, m, $SiCH_2$); 0.93-1.08 (15H, m, $Ge(C_2H_5)_3$); 1.48-1.57 (2H, m, CH_2); 2.26 (3H, m, CH_3); 2.28-2.42 (13H, m, CH_2, CH_2N, CH_3); 6.48 (1H, d, *J* = 3.2, H-3), 6.60 (1H, d, *J* = 3.2, H-4). GC-MS, *m/z* (*I*, %): 426 $[M]^+$ (3), 265 (42), 237 (5), 197 (10), 142 (15), 128 (16), 113 (100), 98 (12), 83 (10), 70 (92), 59 (12).

2-{[Dimethyl-3-(4-phenylpiperazino)propyl]silyl}-5-triethylgermylfuran (22) was prepared from compound **12** and N-allyl-4-phenylpiperazine. Yield 56%. ^1H NMR, δ, ppm (*J*, Hz): 0.24 (6H, s, $Si(CH_3)_2$); 0.70-0.74 (2H, m, $SiCH_2$); 0.95-1.08 (15H, m, $Ge(C_2H_5)_3$); 1.53-1.62 (2H, m, CH_2N); 2.33–2.37 (2H, m, CH_2N);

2.54-2.57 (4H, m, CH_2); 3.16-3.18 (4H, m, CH_2); 6.50 (1H, d, J = 3.2, H-3); 6.61 (1H, d, J = 3.2, H-4); 6.81-6.92 (3H, m, C_6H_5); 7.22-7.24 (2H, m, C_6H_5). GC-MS, *m/z* (*I*, %): 488 $[M]^+$ (8), 460(5), 327 (42), 259 (10), 231 (5), 207 (10), 175(100), 160 (10), 142 (15), 132(30), 105 (22), 77 (11), 70 (43), 59 (10).

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