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# The ruthenium-catalyzed silylation of aromatic C–H bonds with triethylsilane

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## Abstract

The Ru<sub>3</sub>(CO)<sub>12</sub>-catalyzed reaction of aromatic compounds such as arylazoles, arylimines, and arylpyridines with triethylsilane (**2**) gave silylation products in good to excellent yields. Amide and ester groups could also be used as a directing group. In nearly all cases, C–Si bond formation took place at a position *ortho* to the directing groups. This coupling reaction is tolerant of both electron-donating and -withdrawing groups such as methoxy, fluoro, and trifluoromethyl groups. We expected that the use of 2-naphthyl-3-methylpyridine would not result in the formation of a coupling product, because the severe steric repulsion between the methyl group and the peri-hydrogen at the 8-position would strongly inhibit the attainment of a co-planar geometry. Interestingly, however, the reaction of 2-naphthyl-3-methylpyridine afforded the corresponding silylation product in quantitative yield. This observation indicates that the formation of metalacycle intermediate is not essential for the catalytic reaction to proceed. When a deuterium-labeling experiment using phenyloxazoline-*d*<sub>5</sub> was carried out in the absence of olefin, partial H/D scrambling occurred between the *ortho* positions of the phenyloxazoline and the Si–H of triethylsilane. This labeling experiment indicates that C–H bond cleavage is not the rate-determining step and that a rapid equilibrium prior to C–Si bond formation (i.e. the reductive elimination step) occurs in this catalytic reaction.

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**Keywords:** Ruthenium catalysts; C–H bond cleavage; Aromatic C–H bonds; Triorganosilane; C–H/SiR<sub>3</sub> coupling

## 1. Introduction

During the last decade, the catalytic use of otherwise unreactive carbon–hydrogen bonds has become one of the most attractive areas in organic synthesis [1–4]. In particular, catalytic conversions of C–H bonds to C–C bonds such as C–H/olefin [4–18], C–H/acetylene [4,19–21], and C–H/CO/olefin coupling [22–24], which are now maturing as a useful synthetic tool in organic synthesis, have been studied. In addition to these reactions, the catalytic conversion of C–H bonds to C–Si bonds has recently attracted the attention of investigation.

To date, several studies of the catalytic silylation of C–H bonds have been reported. In 1982, Curtis

reported, to the best of our knowledge, the first example of the catalytic silylation of C–H bonds [25]. Unfortunately, in this case, the silylation product was obtained in low yield and a mixture of several products was formed. Tanaka subsequently reported another type of silylation reaction of arenes using bis(dimethylsilyl)benzene as a silylating reagent [26]. Berry reported the (*p*-cymene)Ru(H)<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub>-catalyzed silylation of aromatic compounds having electron-withdrawing substituents such as F and CF<sub>3</sub> groups on the aromatic ring using triethylsilane [27]. Hexaorganodisilanes can also be used to replace triorganosilanes as a silylating reagent. Ishikawa reported the Ni(cod)<sub>2</sub>-catalyzed silylation of arenes with four-membered cyclic disilanes [28]. A major drawback of the above silylation reactions is their low regioselectivity. Therefore, when substituted arenes are used in silylation reactions, multiple regioisomers are produced. To carry out such reactions in a highly

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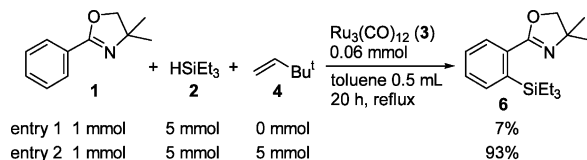
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regioselective manner, one of the most reliable protocols involves the use of chelation-assisted C–H bond cleavage. This protocol has recently become popular for regioselective C–C bond formation via C–H bond cleavage [1–24]. In 1995, Tanaka reported the Pt<sub>2</sub>(dba)<sub>3</sub>-catalyzed regioselective silylation of aromatic imines using hexaorganodisilanes [29,30]. The key to this regioselective silylation is believed to be the coordination of the imino nitrogen to the platinum center. However, in this case, only hexamethyl- and diphenyltetramethyldisilane were examined as silylating reagents and a limited number of aromatic compounds containing an electron-withdrawing group on the aromatic ring showed reactivity. In 2000, we reported the Ru<sub>3</sub>(CO)<sub>12</sub>-catalyzed regioselective silylation of heteroaromatic compounds with vinylsilanes, giving the corresponding silylation products [31]. In this case, triorganovinylsilane worked as a silylating reagent and as a hydrogen scavenger. We recently reported that the Ru<sub>3</sub>(CO)<sub>12</sub>-catalyzed silylation of aryloxazolines, benzylamines, and aryl pyridyl ethers with hydrosilanes give the *ortho* silylation products in good to excellent yields [32,33]. These studies suggest that the coordination of the sp<sup>2</sup> or sp<sup>3</sup> nitrogen atom might be central to such silylation reactions. The applicability of our method for regioselective silylation of aromatic compounds is still obscure. As a result, we investigated the chelation-assisted silylation of arenes with hydrosilanes more extensively. In this paper, we report on the scope and limitations of the Ru<sub>3</sub>(CO)<sub>12</sub>-catalyzed silylation of aromatic C–H bonds using hydrosilanes as well as a mechanistic study of this reaction.

## 2. Results and discussions

In the initial screening to determine reaction conditions, phenyloxazoline (**1**) (4,4-dimethyl-2-phenyl-4,5-dihydro-oxazole) was used as a test substrate for a silylation reaction. When the reaction of **1** with triethylsilane (**2**) using Ru<sub>3</sub>(CO)<sub>12</sub> (**3**) as a catalyst was conducted in the absence of a hydrogen scavenger, the expected *ortho* silylation product was obtained in only a 7% yield (entry 1, Eq. (1)). We attribute the reason for this low efficiency to the failure in the reductive elimination of molecular hydrogen, which should be generated by the reaction of phenyloxazoline **1** with silane **2**, from the ruthenium center. The dissociation of molecular hydrogen (H<sub>2</sub>) from the dihydride-ruthenium seems unlikely since the dissociation of H<sub>2</sub> from RuH<sub>2</sub>L<sub>4</sub> (L = CO or PR<sub>3</sub>) is known to thermally unfavorable process [34,35]. Fortunately, we found that the use of an olefin as a hydrogen scavenger dramatically improved the efficiency of this silylation reaction. The reactivities of several olefins as hydrogen acceptors were also examined. Hence, the following olefins were screened:

*tert*-butylethylene (**4**) (93% yield), norbornene (**5**) (73% yield), styrene (68% yield), methyl acrylate (50% yield), 1-decene (44% yield), and octadecyl vinyl ether (9% yield). Among these olefins, **4** showed the highest reactivity.



(1)

The reaction of several aryloxazolines with **2** was examined under the same reaction conditions as were used in entry 2 in Eq. (1) (Table 1). In all cases, C–H/SiR<sub>3</sub> coupling took place at the position *ortho* to the functional group. The silylation described above is tolerant to both electron-withdrawing (CF<sub>3</sub> and F) and -donating (CH<sub>3</sub> and OCH<sub>3</sub>) groups (entries 1–6). When the reaction of 2-naphthyloxazoline was conducted using **4**, the product was obtained only in 69% yield (entry 7). Fortunately, when the hydrogen scavenger was simply changed from **4** to norbornene **5**, the silylation product was obtained in quantitative yield (entry 8). The reason of this high activity of **5** as the hydrogen acceptor is not clear at present. In all cases, the corresponding mono-silylation product was obtained as the sole reaction product.

The reaction of aromatic imines gave the *ortho* mono-silylation products exclusively (Table 2). The reaction of

Table 1

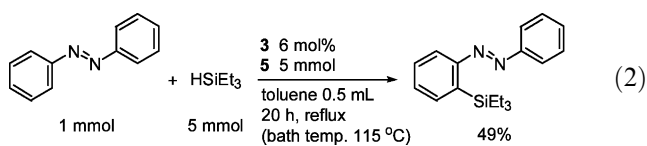
entry	substrate	time	product	yield
1		24 h		92%
2		24 h		94%
3		48 h		79%
4		20 h		49%
5		48 h		85%
6		48 h		26%
7		20 h		69%
8 <sup>b</sup>		20 h		quant

<sup>a</sup>Reaction conditions: aryloxazoline (**1**) (**2**) (5 mmol), 3,3-dimethyl-1-butene (**4**) (5 mmol), Ru<sub>3</sub>(CO)<sub>12</sub> (**3**) (0.06 mmol), toluene (0.5 ml), reflux (bath temperature, 115 °C), 20 h. <sup>b</sup>In place of **4**, norbornene **5** (5 mmol) was used.

Table 2


<sup>a</sup>Reaction conditions: imine (1 mmol) **2** (5 mmol) norbornene **5** (5 mmol), Ru<sub>3</sub>(CO)<sub>12</sub> (0.06 mmol), toluene (0.5 ml), reflux (bath temperature, 115 °C), 20 h.

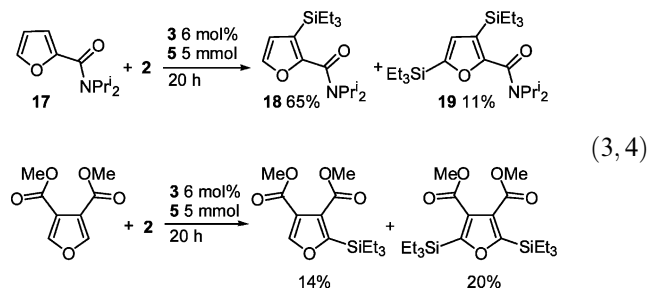
phenylimine with **2** in the presence of **5** gave the *ortho* silylation product in 98% yield. Several aromatic imines containing both electron-donating (Me and OMe) and -withdrawing (F) groups could be used in this C–H/SiR<sub>3</sub> coupling. In all cases, the corresponding 1:1 coupling products were obtained in good to excellent yields (63–98% yields). In the case of *m*-methoxyphenylimine, two different *ortho* C–H bonds are present, one of which is sterically congested (2-position), while the other is sterically less congested (6-position). The reaction took place only at the 6-position. This regioselectivity is different from that of the C–H/olefin coupling [6]. This observation suggests that a steric factor is more important than an electronic factor in the regioselectivity of this silylation reaction. An sp<sup>2</sup> nitrogen in azobenzene can also be used in this silylation reaction. In this case, the silylation product was obtained in 49% yield (Eq. (2)).



Nitrogen-containing heterocycles such as pyridine, pyrazole, imidazole, triazole, and tetrazole rings can also function as a directing group. Some selected results are listed in Table 3. The reaction of 2-phenylpyridine with **2** afforded a mixture of the 1:1 and the 1:2 silylation products in 61 and 32% yields, respectively (entry 1). The reaction of phenylpicoline **7** provided the corresponding 1:1 (**8**) and 1:2 coupling products (**9**) in 79 and 21% yields, respectively (entry 2). The formation of the 1:2 coupling product **9** is noteworthy. The results of our studies with respect to catalytic C–H/olefin coupling, the formation of a metalacycle is essential in achieving a successful catalytic reaction. In the 1:1 coupling product **8**, a steric repulsion between the methyl group on the pyridine ring and the triethylsilyl group would be predicted to inhibit the formation of the

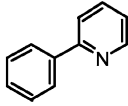
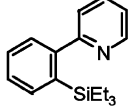
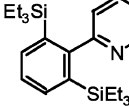
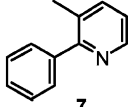
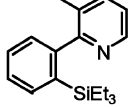
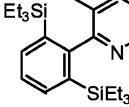
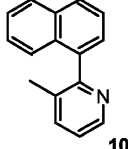
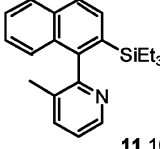
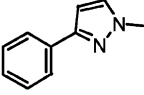
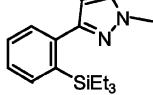
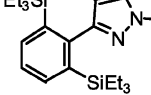
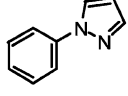
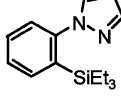
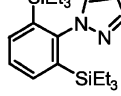
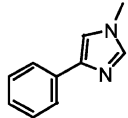
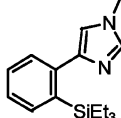
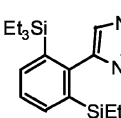
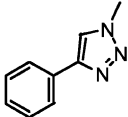
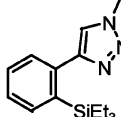
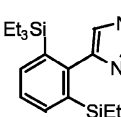
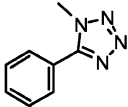
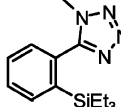
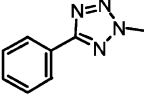
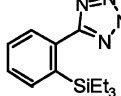
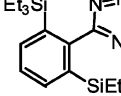
metalacycle intermediate. Interestingly, however, the corresponding 1:2 coupling product was obtained in 21% yield. A higher yield was observed in the case of 2-naphthyl-3-methylpyridine (entry 3). We thought that the severe steric repulsion between the methyl group and the peri-hydrogen would suppress the formation of the corresponding metalacycle. Interestingly, however, the silylation product was obtained in quantitative yield (entry 3). These results suggest that in the catalytic C–H/SiR<sub>3</sub> coupling with hydrosilanes the formation of a metalacycle is not essential in realizing the catalytic reaction. At present, we have no experimental evidence for explaining the reaction pathway. Further studies should be awaited for explaining the reason of the product selectivity. The reaction of 1-methyl-3-phenylpyrazole gave the 1:1 and the 1:2 coupling products in 56 and 37% yields, respectively (entry 4). This result indicates that steric congestion around the sp<sup>2</sup> nitrogen atom does not significantly affect the reactivity of the substrate. Two reaction sites are available in the case of *N*-phenylpyrazole; one is an *ortho* C–H bond and the other is at the 3-position of the pyrazole ring. The silylation took place predominantly at the *ortho* positions of the phenyl ring. Thus, the sp<sup>2</sup> nitrogen in a tetrazole ring can participate in the present silylation reaction. The position of the methyl group on the tetrazole moiety had an effect on product selectivity. In the reaction of 1-methyl-5-phenyl-1*H*-tetrazole (**12**), the 1:1 coupling product **13** was obtained in 70% yield as the sole product. On the other hand, the reaction of 2-methyl-5-phenyl-2*H*-tetrazole **14** afforded the 1:2 coupling product **16** (71%) as the major product.

The coordination of the carbonyl group of amides and esters can also assist the C–H/SiR<sub>3</sub> coupling. In the reaction of 2-*N,N*-diisopropylfuran **17**, the mono-silylation product **18** and the di-silylation product **19** were obtained in 65 and 11% yields, respectively (Eq. (3)). The formation of **19** indicates that the silylation can take place without chelation-assistance. This result may provide new opportunities for the catalytic use of C–H bonds. A furan derivative having an ester group at the 3- and 4-positions also reacted with **2** to give the corresponding 1:1 and 1:2 coupling products in 14 and 20% yields, respectively (Eq. (4)).



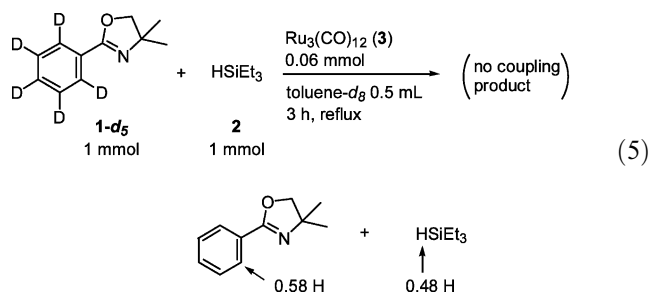
As described above, we elucidated the scope of the present C–H/SiR<sub>3</sub> coupling using hydrosilanes. The

Table 3

entry	substrate	products	
		1:1 coupling product	1:2 coupling product
1		 61%	 32%
2	 7	 8 79%	 9 21%
3	 10	 11 100%	
4		 56%	 37%
5		 36%	 25%
6		 13%	 56%
7		 14%	 46%
8	 12	 13 70%	
9	 14	 15 22%	 16 71%

<sup>a</sup>Reaction conditions: imine (1 mmol) **2** (5 mmol) norbornene **5** (5 mmol), Ru<sub>3</sub>(CO)<sub>12</sub> (0.06 mmol), toluene (0.5 ml), reflux (bath temperature, 115 °C), 20 h.

mechanism of this silylation reaction is our next interest. A deuterium-labeling experiment often affords useful information concerning the reaction mechanism. Thus, the reaction of phenyloxazoline- $d_5$  (**1- $d_5$** ) with **2** was carried out using  $\text{Ru}_3(\text{CO})_{12}$  as the catalyst. To avoid unfavorable complexities due to the H/D scrambling between **1- $d_5$**  and an olefin, the hydrogen scavenger, the reaction was conducted in the absence of olefin (Eq. (5)).

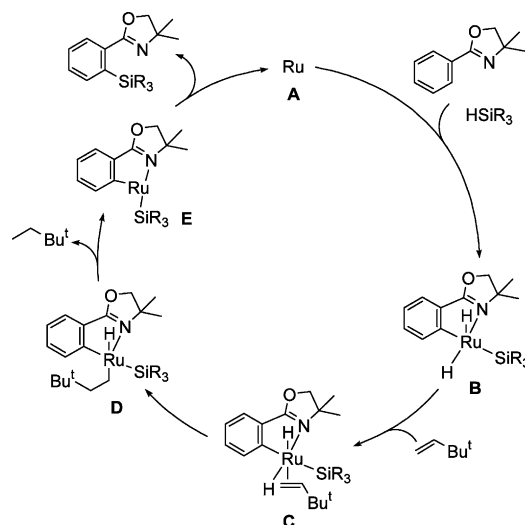


After heating for 3 h, the reaction was stopped, and the reaction mixture analyzed by GC and GC/MS. These analyses indicated that no coupling reaction took place.  $^1\text{H-NMR}$  spectra of the recovered starting materials showed that partial H/D exchange occurred between the *ortho* C–H bond of the phenyloxazoline and the Si–H bond in **2**. This suggests that C–H bond cleavage is not rate-determining and a rapid equilibrium is present prior to the C–Si bond formation step, i.e. reductive elimination.

One of the several possible reaction pathways that explain the present C–H/SiR<sub>3</sub> coupling reaction is shown in Scheme 1. An oxidative addition of the C–H bond of the phenyloxazoline to the ruthenium(0) complex **A** followed by an oxidative addition of triethylsilane (vice versa) leads to  $\text{Ru}(\text{Ar})(\text{SiEt}_3)(\text{H})_2$  intermediate **B** which is consistent with the deuterium-labeling results. The insertion of the olefin into the Ru–H bond in **C** yields intermediate **D**. After the reductive elimination of the corresponding alkane, the (aryl)(triethylsilyl)ruthenium(II) is formed [36]. From this intermediate, reductive elimination, producing a C–Si bond, leads to the corresponding silylation product and the regeneration of the active ruthenium(0) species. Investigations are currently underway to elucidate the mechanism of this reaction in more detail.

### 3. Conclusion

The  $\text{Ru}_3(\text{CO})_{12}$ -catalyzed silylation of aromatic and heteroaromatic C–H bonds with triethylsilane via C–H bond cleavage is described. A variety of aromatic and heteroaromatic compounds containing various directing groups can be used for this silylation protocol. In the cases of the reaction of aryloxazolines, arylimines, and azobenzene, the corresponding 1:1 coupling product was formed exclusively. On the other hand, the reactions of



Scheme 1. A plausible reaction pathway.

arylpiperidines and phenylazoles including phenylpyrazoles, -imidazoles, -triazoles, and -tetrazoles with **2** resulted in formation of the 1:1 and the 1:2 coupling products. Some carbonyl compounds such as *N,N*-diisopropylbenzamide, furan-2-carboxylic acid diisopropylamide, and furan-3,4-dicarboxylic acid dimethyl ester are also applicable to the C–H/SiR<sub>3</sub> coupling. The reaction of 2-naphthyl-3-methylpyridine with **2** gave the silylation product in quantitative yield. This finding suggests that the nitrogen atom may function bring the ruthenium closer to the *ortho* C–H bond, because the formation of the metalacycle would be expected to be inhibited by steric repulsion between the methyl group and the peri-hydrogen at the 8-position. A deuterium-labeling experiment using phenyloxazoline- $d_5$  indicates that the C–H bond cleavage step is not rate-determining and a rapid equilibrium occurs prior to the C–Si bond formation step.

## 4. Experimental

### 4.1. General information

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  were recorded on a JEOL JNM-EX270 spectrometer at 270 and 67.5 MHz, respectively. Chemical shifts of  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  signals are quoted relative to internal  $\text{CHCl}_3$  ( $\delta = 7.26$  and 77.0) or tetramethylsilane.  $^1\text{H-NMR}$  data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), relative intensity, and interpretation.  $^{13}\text{C-NMR}$  data are reported as follows: chemical shift in ppm ( $\delta$ ) and interpretation. IR spectra were obtained on a Hitachi 270-50 infrared spectrometer. GC/MS data

were collected on a Shimadzu GCMS QP-5000 gas chromatography interfaced with a mass spectrometer.

The conditions used for the GC analysis were as follows: Shimadzu GC-14A (equipped with CBP-10 25 m × 0.2 mm or CBP-20 25 m × 0.2 mm); initial temperature, 70–120 °C (0 min); final temperature, 230 °C (30 min); rate, 10 °C min<sup>-1</sup>; injection temperature, 270 °C; detector temperature, 270 °C.

Toluene was distilled over CaH<sub>2</sub> under nitrogen. Ru<sub>3</sub>(CO)<sub>12</sub> was prepared by literature methods [37].

#### 4.2. General procedure

The apparatus used in the reactions consisted of 10-ml two-necked flask equipped with a reflux condenser connected to a nitrogen line, a rubber septum, and a magnetic stirring bar. The flask was flame dried under a stream of nitrogen. The ruthenium complex (0.06 mmol), 0.5 ml of toluene, the phenyloxazoline (1 mmol), triethylsilane (5 mmol), and 3,3-dimethyl-1-butene (5 mmol) were then placed in the flask. The resulting solution was refluxed under a nitrogen atmosphere. The progress of the reaction was monitored by GC analysis and the product was isolated by silica gel column chromatography.

#### 4.3. Deuterium-labeling experiment

The apparatus used in this reaction consisted of 10-ml two-necked flask equipped with a reflux condenser connected to a nitrogen line, a rubber septum, and a magnetic stirring bar. The flask was flame dried under a stream of nitrogen. The ruthenium complex (0.06 mmol), 0.5 ml of toluene-*d*<sub>8</sub>, the phenyloxazoline-*d*<sub>5</sub> (1 mmol) and triethylsilane (1 mmol) were then placed in the flask. The resulting solution was refluxed under a nitrogen atmosphere. The progress of the reaction was monitored by GC analysis. After 3 h, the reaction was stopped. The reaction mixture was analyzed by <sup>1</sup>H-NMR spectroscopy.

#### 4.4. Spectral data

##### 4.4.1. 4,4-Dimethyl-2-(2-triethylsilylanyl-phenyl)-4,5-dihydro-oxazole

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) 0.86–0.96 (m, 15H, CH<sub>2</sub>CH<sub>3</sub>), 1.39 (s, 6H, CH<sub>3</sub>), 4.09 (s, 2H, CH<sub>2</sub>), 7.40 (m, 2H, ArH), 7.57 (dd, *J* = 6.6 Hz, 2.0 Hz, 1H, ArH), 7.83 (dd, *J* = 6.6 Hz, 2.6 Hz, 1H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 4.42 (SiCH<sub>2</sub>), 7.86 (CH<sub>2</sub>CH<sub>3</sub>), 28.53 (CH<sub>3</sub>), 67.74 (C(CH<sub>3</sub>)<sub>2</sub>), 79.07 (CH<sub>2</sub>), 128.39, 129.34, 129.69, 134.38, 136.02, 136.72 (Ar), 163.82 (C=N); IR (neat) 3058 w, 2960 s, 2876 s, 1656 s, 1464 m, 1435 m, 1420 m, 1364 m, 1349 m, 1306 s, 1279 m, 1248 m, 1235 m, 1210 m, 1187 m, 1128 m, 1091 s, 1055 m, 1039 s, 1002 s, 968 m, 779 m, 729 s, 692 s cm<sup>-1</sup>; MS *m/z* (% relative intensity) 261 (24), 260

([M<sup>+</sup> – Et], 100), 206 (10), 188 (11), 161 (10), 160 (40), 148 (16), 133 (13), 132 (62), 130 (10), 105 (21), 55 (28), 53 (11). Anal. Calc. for C<sub>17</sub>H<sub>27</sub>NOSi: C, 70.53; H, 9.40; N, 4.84. Found: C, 70.18; H, 9.58; N, 4.83%.

##### 4.4.2. 2-(4-Methoxy-2-triethylsilylanyl-phenyl)-4,4-dimethyl-4,5-dihydro-oxazole

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) 0.82–0.96 (m, 15H, CH<sub>2</sub>CH<sub>3</sub>), 1.37 (s, 6H, CH<sub>3</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 4.05 (s, 2H, CH<sub>2</sub>), 6.85 (dd, *J* = 8.6 Hz, 3.0 Hz, 1H, ArH), 7.11 (d, *J* = 3.0 Hz, 1H, ArH), 7.85 (d, *J* = 8.6 Hz, 1H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 4.52 (SiCH<sub>2</sub>), 7.92 (CH<sub>2</sub>CH<sub>3</sub>), 28.56 (CH<sub>3</sub>), 55.14 (OCH<sub>3</sub>), 67.58 (C(CH<sub>3</sub>)<sub>2</sub>), 78.93 (CH<sub>2</sub>), 112.42, 122.60, 126.60, 131.53, 139.04, 160.07 (Ar), 163.39 (C=N); IR (neat) 2960 s, 2876 m, 2838 w, 1655 s, 1592 s, 1566 s, 1465 m, 1442 w, 1420 w, 1384 w, 1364 w, 1349 m, 1309 s, 1288 s, 1242 s, 1226 s, 1181 m, 1141 w, 1085 s, 1050 m, 1031 s, 1002 m, 969 m, 923 w, 885 w, 822 m, 728 s, 692 m cm<sup>-1</sup>; MS *m/z* (% relative intensity) 319 ([M<sup>+</sup>], 1), 291 (24), 290 (100), 190 (20), 162 (45), 59 (19), 55 (19). Anal. Calc. for C<sub>18</sub>H<sub>29</sub>NO<sub>2</sub>Si: C, 67.66; H, 9.15; N, 4.38. Found: C, 67.62; H, 9.11; N, 4.38%.

##### 4.4.3. 4,4-Dimethyl-2-(4-methyl-2-triethylsilylanyl-phenyl)-4,5-dihydro-oxazole

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) 0.83–0.95 (m, 15H, CH<sub>2</sub>CH<sub>3</sub>), 1.38 (s, 6H, CH<sub>3</sub>), 2.37 (s, 3H, ArCH<sub>3</sub>), 4.07 (s, 2H, CH<sub>2</sub>), 7.17 (d, *J* = 7.6 Hz, 1H, ArH), 7.35 (brs, 1H, ArH), 7.74 (d, *J* = 7.6 Hz, 1H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 4.49 (SiCH<sub>2</sub>), 7.92 (CH<sub>2</sub>CH<sub>3</sub>), 21.71 (ArCH<sub>3</sub>), 28.56 (CH<sub>3</sub>), 67.65 (C(CH<sub>3</sub>)<sub>2</sub>), 78.98 (CH<sub>2</sub>), 129.09, 129.76, 131.52, 136.60, 136.86, 139.09 (Ar), 163.86 (C=N); IR (neat) 2960 m, 2876 m, 1656 s, 1598 w, 1565 w, 1463 m, 1420 w, 1382 w, 1364 w, 1348 m, 1305 m, 1279 w, 1235 w, 1207 w, 1188 w, 1149 w, 1095 s, 1041 s, 1002 m, 969 m, 923 w, 885 w, 848 w, 833 m, 728 s, 693 m, 668 w cm<sup>-1</sup>; MS *m/z* (% relative intensity) 303 ([M<sup>+</sup>], 1), 275 (22), 274 (100), 174 (29), 162 (11), 147 (11), 146 (50), 119 (14), 55 (18). Anal. Calc. for C<sub>18</sub>H<sub>29</sub>NOSi: C, 71.23; H, 9.63; N, 4.61. Found: C, 71.15; H, 9.62; N, 4.63%.

##### 4.4.4. 2-(4-Fluoro-2-triethylsilylanyl-phenyl)-4,4-dimethyl-4,5-dihydro-oxazole

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) 0.84–0.95 (m, 15H, CH<sub>2</sub>CH<sub>3</sub>), 1.38 (s, 6H, CH<sub>3</sub>), 4.08 (s, 2H, CH<sub>2</sub>), 7.03 (ddd, *J* = 8.3 Hz, 8.3 Hz, 2.6 Hz, 1H, ArH), 7.24 (dd, *J* = 9.9 Hz, 2.6 Hz, 1H, ArH), 7.86 (dd, *J* = 8.3 Hz, 5.6 Hz, 1H, ArH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 4.35 (SiCH<sub>2</sub>), 7.81 (CH<sub>2</sub>CH<sub>3</sub>), 28.52 (CH<sub>3</sub>), 67.84 (C(CH<sub>3</sub>)<sub>2</sub>), 79.14 (CH<sub>2</sub>), 115.18 (d, *J*<sub>C-F</sub> = 21.2 Hz, Ar), 122.73 (d, *J*<sub>C-F</sub> = 19.6 Hz, Ar), 130.32 (d, *J*<sub>C-F</sub> = 2.8 Hz, Ar), 131.98 (d, *J*<sub>C-F</sub> = 7.8 Hz, Ar), 140.86 (d, *J*<sub>C-F</sub> = 4.5 Hz, Ar), 162.81 (C=N), 163.29 (d, *J*<sub>C-F</sub> = 252.1 Hz, Ar); IR (neat) 2960 s, 2876 s, 1657 s, 1577 m, 1465 m, 1420 w, 1378 w, 1365 w, 1349 m, 1305 s, 1253 m, 1211 s, 1188 m, 1129 w, 1080 s, 1040 s, 1003 m, 968 m, 924 w, 884 w, 858

w, 833 m, 728 s, 705 m, 690 m  $\text{cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 307 ( $[\text{M}^+]$ , 4.4), 279 (23), 278 (100), 224 (14), 179 (11), 178 (43), 166 (18), 151 (14), 150 (65), 123 (16), 102 (11), 55 (54). Anal. Calc. for  $\text{C}_{17}\text{H}_{26}\text{FNOSi}$ : C, 66.41; H, 8.52; N, 4.56. Found: C, 66.14; H, 8.71; N, 4.48%.

#### 4.4.5. 4,4-Dimethyl-2-(2-methyl-6-triethylsilylanyl-phenyl)-4,5-dihydro-oxazole

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.81–0.97 (m, 15 H,  $\text{CH}_2\text{CH}_3$ ), 1.43 (s, 6 H,  $\text{CH}_3$ ), 2.35 (s, 3 H,  $\text{ArCH}_3$ ), 4.11 (s, 2 H,  $\text{CH}_2$ ), 7.19 (d,  $J = 7.16$  Hz, 1 H,  $\text{ArH}$ ), 7.26 (dd,  $J = 7.29$  Hz, 7.16 Hz, 1 H,  $\text{ArH}$ ), 7.35 (dd,  $J = 7.29$  Hz, 1.35 Hz, 1 H,  $\text{ArH}$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 3.86 ( $\text{SiCH}_2$ ), 7.55 ( $\text{CH}_2\text{CH}_3$ ), 19.92 ( $\text{ArCH}_3$ ), 28.68 ( $\text{CH}_3$ ), 68.20 ( $\text{C}(\text{CH}_3)_2$ ), 78.73 ( $\text{CH}_2$ ), 128.32, 130.66, 132.85, 134.82, 135.72, 136.74 (Ar), 163.07 ( $\text{C}=\text{N}$ ); IR (neat) 3056 w, 2960 s, 2878 m, 1664 s, 1580 w, 1464 m, 1420 w, 1381 w, 1364 w, 1343 w, 1287 w, 1240 w, 1209 w, 1190 w, 1148 w, 1093 w, 1038 s, 1004 m, 962 m, 918 w, 857 w, 776 w, 753 m, 730 s, 690  $\text{m cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 303 ( $[\text{M}^+]$ , 1.2), 275 (22), 274 (100), 202 (13), 175 (11), 174 (39), 162 (11), 147 (11), 146 (55), 119 (15), 55 (20). Anal. Calc. for  $\text{C}_{18}\text{H}_{29}\text{NOSi}$ : C, 71.23; H, 9.63; N, 4.61. Found: C, 71.22; H, 9.75; N, 4.66%.

#### 4.4.6. 2-(2-Fluoro-6-triethylsilylanyl-phenyl)-4,4-dimethyl-4,5-dihydro-oxazole

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.79–0.97 (m, 15H,  $\text{CH}_2\text{CH}_3$ ), 1.42 (s, 6H,  $\text{CH}_3$ ), 4.12 (s, 2H,  $\text{CH}_2$ ), 7.08 (ddd,  $J = 9.45$  Hz, 7.91 Hz, 1.7 Hz, 1H,  $\text{ArH}$ ), 7.29 (dd,  $J = 7.4$  Hz, 1.7 Hz, 1H,  $\text{ArH}$ ), 7.36 (ddd,  $J = 7.7$  Hz, 7.6 Hz, 5.3 Hz, 1H,  $\text{ArH}$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 3.83 ( $\text{SiCH}_2$ ), 7.50 ( $\text{CH}_2\text{CH}_3$ ), 28.51 ( $\text{CH}_3$ ), 68.39 ( $\text{C}(\text{CH}_3)_2$ ), 78.97 ( $\text{CH}_2$ ), 116.17 (d,  $J_{\text{C-F}} = 22.4$  Hz, Ar), 123.00 (d,  $J_{\text{C-F}} = 12.3$  Hz, Ar), 130.43 (d,  $J_{\text{C-F}} = 7.8$  Hz, Ar), 130.89 (d,  $J_{\text{C-F}} = 3.9$  Hz, Ar), 139.49 (d,  $J_{\text{C-F}} = 1.1$  Hz, Ar), 158.91 ( $\text{C}=\text{N}$ ), 160.78 (d,  $J_{\text{C-F}} = 249.8$  Hz, Ar); IR (neat) 2960 s, 2878 m, 1668 m, 1567 w, 1524 w, 1462 m, 1436 m, 1384 w, 1365 w, 1292 m, 1241 s, 1212 w, 1191 m, 1140 w, 1079 m, 1039 s, 1003 m, 963 m, 920 w, 866 w, 820 w, 788 w, 726 s, 688  $\text{w cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 307 ( $[\text{M}^+]$ , 6), 279 (23), 278 (100), 252 (13), 224 (32), 179 (12), 178 (48), 166 (17), 151 (16), 150 (66), 123 (13), 77 (10), 75 (12), 55 (49). Anal. Calc. for  $\text{C}_{17}\text{H}_{26}\text{FNOSi}$ : C, 66.41; H, 8.52; N, 4.56. Found: C, 66.07; H, 8.59; N, 4.58%.

#### 4.4.7. 4,4-Dimethyl-2-(2-triethylsilylanyl-6-trifluoromethyl-phenyl)-4,5-dihydro-oxazole

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.83–0.98 (m, 15H,  $\text{CH}_2\text{CH}_3$ ), 1.43 (s, 6H,  $\text{CH}_3$ ), 4.15 (s, 2H,  $\text{CH}_2$ ), 7.48 (t,  $J = 7.6$  Hz, 1H,  $\text{ArH}$ ), 7.69–7.73 (m, 2H,  $\text{ArH}$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 3.74 ( $\text{SiCH}_2$ ), 7.41 ( $\text{CH}_2\text{CH}_3$ ), 28.15 ( $\text{CH}_3$ ), 68.52 ( $\text{C}(\text{CH}_3)_2$ ), 79.37 ( $\text{CH}_2$ ), 123.85 (q,  $J_{\text{C-F}} = 273.9$  Hz, Ar), 126.63 (q,  $J_{\text{C-F}} = 5.0$  Hz, Ar), 128.34 (Ar),

129.51 (q,  $J_{\text{C-F}} = 30.7$  Hz, Ar), 133.65 (q,  $J_{\text{C-F}} = 1.7$  Hz, Ar), 138.63 (Ar), 138.70 (Ar), 160.50 ( $\text{C}=\text{N}$ ); IR (neat) 2962 m, 2880 m, 1668 m, 1577 w, 1466 w, 1435 w, 1384 w, 1366 w, 1346 w, 1312 s, 1292 m, 1238 w, 1211 w, 1170 m, 1137 s, 1105 s, 1073 s, 1040 m, 1003 m, 985 w, 962 m, 922 w, 869 w, 813 w, 801 w, 760 m, 734 m, 682  $\text{m cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 329 ( $[\text{M}^+]$ , 25), 328 (100), 274 (11), 254 (42), 228 (35), 226 (12), 216 (11), 201 (14), 200 (68), 132 (16), 126 (17), 115 (13), 107 (14), 89 (10), 87 (11), 77 (13), 75 (15), 63 (22), 59 (11), 57 (14), 56 (12), 55 (95). Anal. Calc. for  $\text{C}_{18}\text{H}_{26}\text{F}_3\text{NOSi}$ : C, 60.54; H, 7.42; N, 3.80. Found: C, 60.48; H, 7.33; N, 3.92%.

#### 4.4.8. 4,4-Dimethyl-2-(3-triethylsilylanyl-naphthalen-2-yl)-4,5-dihydro-oxazole

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.95 (s, 15H,  $\text{CH}_2\text{CH}_3$ ), 1.43 (s, 6H,  $\text{CH}_3$ ), 4.14 (s, 2H,  $\text{CH}_2$ ), 7.49–7.52 (m, 2 H,  $\text{ArH}$ ), 7.6–7.7 (m, 2H,  $\text{ArH}$ ), 8.04 (s, 1H,  $\text{ArH}$ ), 8.38 (s, 1H,  $\text{ArH}$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 4.73 ( $\text{CH}_2$ ), 7.97 ( $\text{CH}_2\text{CH}_3$ ), 28.53 ( $\text{CH}_3$ ), 67.85 ( $\text{C}(\text{CH}_3)_2$ ), 79.11 ( $\text{OCH}_2$ ), 126.74, 127.03, 127.76, 128.07, 129.54, 130.72, 132.53, 133.14, 133.32, 137.36 (Ar), 163.64 ( $\text{C}=\text{N}$ ); IR (neat) 3056 w, 2962 s, 2876 m, 1656 s, 1464 m, 1350 m, 1293 m, 1282 m, 1194 m, 1077 s, 1004 s, 900 m, 753 s, 728  $\text{s cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 311 (27), 310 ( $[\text{M}^+ - \text{Et}]$ , 100), 210 (21), 198 (12), 183 (13), 182 (54), 180 (11), 155 (22), 127 (11), 55 (24). Anal. Calc. for  $\text{C}_{21}\text{H}_{29}\text{NOSi}$ : C, 74.28; H, 8.61; N, 4.13. Found: C, 74.04; H, 8.89; N, 4.14%.

#### 4.4.9. tert-Butyl-(2-triethylsilylanyl-benzylidene)-amine

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.82–1.27 (m, 15H,  $\text{CH}_2\text{CH}_3$ ), 1.31 (s, 9H,  $\text{CH}_3$ ), 7.31–7.42 (m, 2H,  $\text{ArH}$ ), 7.50–7.53 (m, 1H,  $\text{ArH}$ ), 7.99–8.02 (m, 1H,  $\text{ArH}$ ), 8.59 (s, 1H,  $\text{CH}=\text{N}$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 5.01 ( $\text{CH}_2$ ), 7.67 ( $\text{CH}_2$ ), 29.82 ( $\text{CH}_3$ ), 57.59 ( $\text{C}(\text{CH}_3)_2$ ), 126.42, 128.81, 129.16, 135.28, 136.76, 142.90 (Ar), 156.05 ( $\text{C}=\text{N}$ ); IR (neat) 3056 w, 2964 s, 2916 m, 2884 m, 1642 m, 1590 w, 1564 w, 1464 m, 1422 w, 1378 w, 1360 w, 1286 w, 1226 m, 1202 m, 1118 w, 1072 w, 1004 w, 968 w, 908 w, 854 w, 758 m, 672  $\text{w cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 275 ( $[\text{M}^+]$ , 2), 261 (15), 260 (59), 246 (30), 219 (10), 218 (42), 203 (23), 202 (10), 191 (22), 190 (100), 175 (24), 173 (13), 162 (27), 147 (11), 134 (13), 133 (16), 132 (32), 105 (11), 87 (35), 58 (24), 57 (15). Anal. Calc. for  $\text{C}_{17}\text{H}_{29}\text{NSi}$ : C, 74.11; H, 10.61; N, 5.08. Found: C, 74.16; H, 10.78; N, 4.98%.

#### 4.4.10. tert-Butyl-(4-methyl-2-triethylsilylanyl-benzylidene)-amine

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ) 0.87–1.04 (m, 15H,  $\text{CH}_2\text{CH}_3$ ), 1.33 (s, 9H,  $\text{CH}_3$ ), 2.14 (s, 3 H,  $\text{CH}_3$ ), 7.07 (d,  $J = 7.9$  Hz, 1H,  $\text{ArH}$ ), 7.43 (s, 1H,  $\text{ArH}$ ), 8.38 (d,  $J = 7.9$  Hz, 1H,  $\text{ArH}$ ), 8.70 (s, 1H,  $\text{C}=\text{N}$ ); IR (neat) 2964 s, 2916 m, 2884 m, 1704 w, 1638 m, 1598 w, 1564 w, 1470 m, 1422 w, 1378 w, 1360 w, 1286 w, 1226 m, 1202 m, 1134 m, 1072 w, 972 w, 910 w, 884 w, 822 m, 730  $\text{s cm}^{-1}$ ; MS  $m/z$  (% relative

intensity) 274 (17), 260 (15), 233 (12), 232 (46), 217 (12), 205 (14), 204 (76), 189 (22), 187 (13), 176 (21), 174 (11), 161 (17), 159 (12), 148 (21), 147 (33), 146 (71), 145 (10), 119 (26), 105 (16), 95 (30), 93 (14), 91 (10), 87 (88), 81 (15), 74 (12), 73 (11), 59 (29), 58 (100), 57 (51). Anal. Calc. for  $C_{18}H_{31}NSi$ : C, 74.67; H, 10.79; N, 4.84. Found: C, 74.74; H, 10.50; N, 5.00%.

#### 4.4.11. *tert*-Butyl-(4-methoxy-2-triethylsilylanyl-benzylidene)-amine

$^1H$ -NMR ( $CDCl_3$ ) 0.82–0.98 (m, 15H,  $CH_2CH_3$ ), 1.30 (s, 9H,  $CH_3$ ), 3.83 (s, 3H,  $OCH_3$ ), 6.91 (dd,  $J = 8.3, 2.5$  Hz, 1H, ArH), 7.04 (d,  $J = 2.47$  Hz, 1H, ArH), 8.00 (d,  $J = 8.6$  Hz, 1H, ArH), 8.52 (s, 1H,  $CH=N$ );  $^{13}C$ -NMR ( $CDCl_3$ ) 4.98 ( $CH_2$ ), 7.67 ( $CH_3$ ), 29.93 ( $C(CH_3)$ ), 55.14 ( $OCH_3$ ), 57.25 ( $C(CH_3)$ ), 113.77, 121.17, 128.12, 135.65, 138.76, 155.29 (Ar), 159.84 ( $C=N$ ); IR (neat) 2960 s, 2884 s, 1640 m, 1592 s, 1566 m, 1468 m, 1420 w, 1380 w, 1360 w, 1276 m, 1242 s, 1220 s, 1180 m, 1132 w, 1062 m, 1042 m, 1006 m, 970 m, 912 w, 882 w, 820 m, 730  $m\ cm^{-1}$ ; MS  $m/z$  (% relative intensity) 248 ( $[M^+ - Bu]$ , 61), 233 (62), 232 (45), 220 (100), 205 (36), 190 (30), 177 (37), 163 (31), 162 (62), 148 (24), 115 (20), 103 (20), 87 (89), 74 (21), 59 (99), 58 (87), 57 (76), 55 (14). Anal. Calc. for  $C_{18}H_{31}NOSi$ : C, 70.76; H, 10.23; N, 4.58. Found: C, 70.60; H, 10.39; N, 4.59%.

#### 4.4.12. *tert*-Butyl-(4-fluoro-2-triethylsilylanyl-benzylidene)-amine

$^1H$ -NMR ( $CDCl_3$ ) 0.72–0.95 (m, 15H,  $CH_2CH_3$ ), 1.28 (s, 9H,  $CH_3$ ), 6.87 (td,  $J = 8.4$  Hz, 2.7 Hz, 1H, ArH), 7.30 (dd,  $J = 9.40$  Hz, 2.7 Hz, 1H, ArH), 8.26 (dd, 8.4 Hz, 5.9 Hz, 1H, ArH), 8.56 (s, 1H,  $CH=N$ );  $^{13}C$ -NMR ( $CDCl_3$ ) 5.27 ( $CH_2$ ), 7.84 ( $CH_3$ ), 30.02 ( $C(CH_3)$ ), 57.71 ( $C(CH_3)$ ), 116.49 (d,  $J_{H-F} = 21.2$  Hz), 122.21 (d,  $J_{H-F} = 19.6$  Hz), 129.95 (d,  $J_{H-F} = 7.8$  Hz), 139.57 (d,  $J_{H-F} = 3.4$  Hz), 140.34 (d,  $J_{H-F} = 3.9$  Hz) (Ar), 154.20 ( $C=N$ ), 163.87 (d,  $J_{H-F} = 251.0$  Hz); IR (neat) 2964 s, 2916 m, 2884 m, 1640 m, 1600 m, 1576 m, 1472 m, 1422 w, 1376 w, 1362 w, 1234 w, 1208 s, 1120 m, 1060 w, 1004 m, 970 w, 902 w, 880 w, 828 w, 732 s, 706  $m\ cm^{-1}$ ; MS  $m/z$  (% relative intensity) 278 ( $[M^+ - Me]$ , 16), 236 ( $[M^+ - Bu]$ , 20), 208 (45), 193 (15), 180 (16), 165 (13), 152 (17), 151 (25), 150 (43), 123 (14), 97 (23), 87 (52), 83 (16), 59 (17), 58 (100), 57 (72). Anal. Calc. for  $C_{17}H_{28}FNSi$ : C, 69.57; H, 9.62; N, 4.77. Found: C, 69.42; H, 9.74; N, 4.84%.

#### 4.4.13. *tert*-Butyl-(5-methoxy-2-triethylsilylanyl-benzylidene)-amine

$^1H$ -NMR ( $CDCl_3$ ) 0.58–0.96 (m, 15H,  $CH_2CH_3$ ), 1.38 (s,  $CH_3$ , 9H,  $CH_3$ ), 3.86 (s, 3H,  $OH_3$ ), 6.91 (dd,  $J = 8.2$  Hz, 2.6 Hz, 1H, ArH), 7.42 (d,  $J = 8.2$  Hz, 1H, ArH), 7.59 (d,  $J = 2.6$  Hz, 1H, ArH), 8.55 (s, 1H,  $CH=N$ );  $^{13}C$ -NMR ( $CDCl_3$ ) 5.15 ( $CH_2$ ), 7.68 ( $CH_3$ ), 29.83 ( $CH_3$ ), 55.15 ( $OCH_3$ ), 57.57 ( $C(CH_3)$ ), 110.73, 115.70,

128.01, 136.72, 144.67, 155.79 (Ar), 160.42 ( $C=N$ ); IR (neat) 3068 w, 2964 s, 2884 s, 1698 w, 1642 m, 1594 s, 1560 m, 1472 s, 1418 m, 1378 m, 1296 s, 1270 m, 1214 s, 1170 m, 1120 w, 1070 s, 1032 m, 1006 m, 960 m, 906 m, 876 w, 822 m, 790 m, 732  $s\ cm^{-1}$ ; MS  $m/z$  (% relative intensity) 290 ( $[M^+ - Me]$ , 12), 276 (32), 248 (38), 221 (22), 220 (100), 205 (16), 192 (29), 164 (18), 163 (16), 162 (56), 148 (10), 135 (11), 119 (10), 117 (10), 105 (10), 103 (14), 87 (58), 59 (58), 58 (69), 57 (67). Anal. Calc. for  $C_{18}H_{31}NOSi$ : C, 70.76; H, 10.23; N, 4.58. Found: C, 70.61; H, 10.40; N, 4.64%.

#### 4.4.14. Phenyl-(2-triethylsilylanyl-phenyl)-diazene

$^1H$ -NMR ( $C_6D_6$ ) 1.02 (brs, 15H,  $CH_2CH_3$ ), 7.09 (d, 7.29 Hz, 1H, ArH), 7.22 (m, 4H, ArH), 7.64 (m, 1H, ArH), 7.96 (m, 1H, ArH), 8.04 (dd,  $J = 8.0$  Hz, 2H, ArH);  $^{13}C$ -NMR (acetone- $d_6$ ) 5.27 ( $CH_2$ ), 7.90 ( $CH_3$ ), 115.24, 123.61, 130.08, 130.71, 130.95, 131.94, 136.56, 139.10, 153.16, 158.38 (Ar); IR (neat) 2960 s, 2916 m, 2888 m, 1586 w, 1566 w, 1466 m, 1420 m, 1236 m, 1116 m, 1070 m, 1004 m, 776 s, 724 s, 688  $s\ cm^{-1}$ ; MS  $m/z$  (% relative intensity) 296 ( $[M^+]$ , 4), 268 (24), 267 ( $[M^+ - Et]$ , 100), 211 (23), 210 (16), 204 (10), 161 (13), 149 (10), 134 (13), 120 (14), 119 (12), 107 (32), 106 (19), 105 (40), 77 (39), 59 (16), 53 (16), 51 (18). Anal. Calc. for  $C_{18}H_{24}N_2Si$ : C, 72.92; H, 8.16; N, 9.45. Found: C, 72.80; H, 8.30; N, 9.35%.

#### 4.4.15. 2-(2-Triethylsilylanyl-phenyl)-pyridine

$^1H$ -NMR ( $CDCl_3$ ) 0.55 (q,  $J = 7.7$  Hz, 6H,  $CH_2$ ), 0.83 (t,  $J = 7.7$  Hz, 9H,  $CH_3$ ), 7.26–7.80 (m, 6H, ArH), 8.62 (brs, 1H, ArH);  $^{13}C$ -NMR ( $CDCl_3$ ) 4.58 ( $CH_2$ ), 7.76 ( $CH_3$ ), 121.82, 123.10, 126.98, 128.40, 128.88, 135.75, 135.94, 136.18, 147.71, 148.34 (Ar), 161.67 ( $C=N$ ); IR (neat) 3078 m, 3054 m, 3002 m, 2956 s, 2910 s, 2876 s, 1587 s, 1570 m, 1559 m, 1481 m, 1468 s, 1426 s, 1235 m, 1123 m, 1098 m, 1003 s, 973 m, 798 m, 768 s, 752 s, 725 s, 674  $m\ cm^{-1}$ ; MS  $m/z$  (% relative intensity) 242 (6), 241 (22), 240 ( $[M^+ - Et]$ , 100), 183 (15), 182 (64), 106 (13), 91 (23). Anal. Calc. for  $C_{17}H_{23}NSi$ : C, 75.78; H, 8.60; N, 5.20. Found: C, 75.53; H, 8.82; N, 5.19%.

#### 4.4.16. 2-(2,6-bis-Triethylsilylanyl-phenyl)-pyridine

0.34 (q,  $J = 7.9$  Hz, 12H,  $CH_2$ ), 0.79 (t,  $J = 7.9$  Hz, 18H,  $CH_3$ ), 7.24 (d,  $J = 7.3$  Hz, 1H, ArH), 7.29–7.65 (m, 5H, ArH), 8.62 (d,  $J = 4.0$  Hz, 1H,  $CH=N$ );  $^{13}C$ -NMR ( $CDCl_3$ ) 4.02 ( $CH_2$ ), 7.72 ( $CH_3$ ), 122.38, 125.32, 125.59, 134.80, 134.94, 135.77, 148.17, 154.20, 162.57 (Ar); IR (neat) 3048 w, 2954 s, 2912 s, 2876 s, 1585 m, 1565 m, 1460 m, 1432 m, 1416 m, 1389 s, 1268 m, 1234 m, 1200 w, 1147 m, 1092 s, 1051 m, 1003 s, 970 m, 911 m, 803 s, 773 s, 719 s, 670 s, 620  $m\ cm^{-1}$ ; MS  $m/z$  (% relative intensity) 356 (12), 355 (35), 354 ( $[M^+ - Et]$ , 96), 324 (15), 266 (16), 208 (12), 182 (12), 149 (31), 135 (81), 134 (100), 120 (25), 106 (68), 105 (34), 59 (17). Anal. Calc.



for  $C_{23}H_{37}NSi$ : C, 71.99; H, 9.72; N, 3.65. Found: C, 72.09; H, 9.46; N, 3.61%.

#### 4.4.17. 3-Methyl-2-(2-triethylsilylanyl-phenyl)-pyridine

$^1H$ -NMR ( $CDCl_3$ ) 0.42 (q,  $J = 7.6$  Hz, 6H,  $CH_2$ ), 0.81 (t,  $J = 7.6$  Hz, 9H,  $CH_3$ ), 2.15 (s, 3H,  $CH_3$ ), 7.15–7.70 (m, 6H, ArH), 8.45 (brd, 3.5 Hz, 1H, ArH);  $^{13}C$ -NMR ( $CDCl_3$ ) 3.69 ( $CH_2$ ), 7.58 ( $CH_2CH_3$ ), 19.83 ( $CH_3$ ), 122.32, 126.52, 128.09, 128.63, 131.35, 135.70, 135.89, 137.51, 145.82, 147.08 (Ar), 161.15 (C=N); IR (neat) 2956 s, 2876 s, 1583 m, 1570 m, 1462 m, 1443 m, 1419 s, 1237 m, 1121 m, 1087 m, 1019 m, 1003 m, 792 m, 757 m, 740 s, 725 s  $cm^{-1}$ ; MS  $m/z$  (% relative intensity) 255 (23), 254 ( $[M^+ - Et]$ , 100), 197 (13), 196 (57), 99(30). Anal. Calc. for  $C_{18}H_{25}NSi$ : C, 76.26; H, 8.89; N, 4.94. Found: 76.15; H, 9.12; N, 5.01%.

#### 4.4.18. 2-(2,6-bis-Triethylsilylanyl-phenyl)-3-methylpyridine

$^1H$ -NMR ( $CDCl_3$ ) 0.31 (q,  $J = 7.8$  Hz, 12H,  $CH_2$ ), 0.78 (t,  $J = 7.8$  Hz, 18H,  $CH_3$ ), 1.96 (s, 3H,  $CH_3$ ), 7.20 (dd,  $J = 7.6$  Hz, 4.6 Hz, 1H, ArH), 7.33 (t, 7.6 Hz, 1H, ArH), 7.45 (d,  $J = 7.6$  Hz, 1H, ArH), 7.60 (d,  $J = 7.6$  Hz, 2H, ArH), 8.46 (d,  $J = 4.6$  Hz, ArH);  $^{13}C$ -NMR ( $CDCl_3$ ) 3.64 ( $CH_2$ ), 7.67 ( $CH_3$ ), 20.05 ( $CH_3$ ), 122.75, 125.20, 133.01, 134.86, 135.93, 136.88, 145.59, 153.31 (Ar), 161.81 (C=N); IR (KBr) 3048 m, 2956 s, 2916 s, 2880 s, 1724 m, 1588 m, 1574 m, 1462 s, 1422 s, 1384 s, 1280 m, 1236 s, 1190 m, 1146 m, 1130 m, 1086 m, 1000 s, 804 s, 776 s, 756 s, 724 s, 690 s, 672 s  $cm^{-1}$ ; MS  $m/z$  (% relative intensity) 368 ( $[M^+ - Et]$ , 68), 252 (29), 142 (18), 141 (100), 127 (19), 113 (35), 112 (36), 87 (35), 59 (36). Anal. Calc. for  $C_{24}H_{39}NSi_2$ : C, 72.47; H, 9.88; N, 3.52. Found: C, 72.22; H, 9.72; N, 3.41%.

#### 4.4.19. 3-Methyl-2-(2-triethylsilylanyl-naphthalen-1-yl)-pyridine

$^1H$ -NMR ( $CDCl_3$ ) 0.44 (q,  $J = 8.0$  Hz, 6H,  $CH_2$ ), 0.84 (t,  $J = 8.0$  Hz, 9H,  $CH_3$ ), 1.96 (s, 3H,  $CH_3$ ), 7.08 (d,  $J = 8.4$  Hz, 1H, ArH), 7.23–7.33 (m, 2H, ArH), 7.39–7.46 (m, 1H, ArH), 7.59 (brd,  $J = 7.6$  Hz, 1H, ArH), 7.70 (d,  $J = 8.4$  Hz, 1H, ArH), 7.83–7.87 (m, 2H, ArH), 8.57 (d,  $J = 3.5$  Hz, 1H, ArH);  $^{13}C$ -NMR ( $CDCl_3$ ) 3.45 ( $CH_2$ ), 7.63 ( $CH_3$ ), 19.14 ( $CH_3$ ), 122.69, 125.21, 125.92, 126.50, 127.81, 131.34, 131.39, 133.28, 133.44, 137.00, 145.21, 146.51 (Ar), 159.48 (C=N); IR (neat) 2956 s, 2912 m, 2878 s, 1463 m, 1446 m, 1236 m, 1111 m, 1095 m, 1002 s, 974 m, 865 m, 814 s, 787 m, 743 s, 730 s, 704 s  $cm^{-1}$ ; MS  $m/z$  (% relative intensity) 305 (28), 304 ( $[M^+ - Et]$ , 100), 246 (31), 152 (12), 124 (20), 123 (10), 122 (14). HRMS Calc. for  $C_{22}H_{27}NSi$ : 333.1913. Found: 333.1907%.

#### 4.4.20. 1-Methyl-3-(2-triethylsilylanyl-phenyl)-1H-pyrazole

$^1H$ -NMR ( $CDCl_3$ ) 0.64 (q,  $J = 7.8$  Hz, 6H,  $CH_2$ ), 0.85 (t, 7.8 Hz, 9H,  $CH_3$ ), 3.93 (s, 3H,  $NCH_3$ ), 6.29 (d,  $J =$

2.2 Hz, 1H, ArH), 7.28–7.42 (m, 3H, ArH), 7.38–7.39 (m, 1H, ArH), 7.57 (dd,  $J = 6.5$  Hz, 1.9 Hz, 1H, ArH);  $^{13}C$ -NMR ( $CDCl_3$ ) 4.38 ( $CH_2$ ), 7.75 ( $CH_3$ ), 38.82 ( $NCH_3$ ), 105.45, 126.49, 128.27, 129.44, 130.09, 135.88, 140.89, 153.99 (Ar); IR (neat) 2942 s, 2874 s, 1462 m, 1421 m, 1393 m, 1249 m, 1106 m, 1000 m, 950 m, 739 s, 720 s, 673 m  $cm^{-1}$ ; MS  $m/z$  (% relative intensity) 244 (22), 243 ( $[M^+ - Et]$ , 100), 185 (26), 107 (12), 93 (31). Anal. Calc. for  $C_{15}H_{22}N_2Si$ : C, 70.53; H, 8.88; N, 10.28. Found: C, 70.73; H, 9.11; N, 10.03%.

#### 4.4.21. 3-(2,6-bis-Triethylsilylanyl-phenyl)-1-methyl-1H-pyrazole

$^1H$ -NMR ( $CDCl_3$ ) 0.46 (q,  $J = 7.8$  Hz, 12H,  $SiCH_2$ ), 0.82 (t,  $J = 7.8$  Hz, 18 Hz,  $CH_3$ ), 3.93 (s, 3H,  $NCH_3$ ), 6.16 (d,  $J = 1.9$  Hz, 1H, ArH), 7.30 (t,  $J = 7.3$  Hz, 1H, ArH), 7.33 (d,  $J = 2.4$  Hz, 1H, ArH), 7.52 (d,  $J = 7.3$  Hz, 2H, ArH);  $^{13}C$ -NMR ( $CDCl_3$ ) 3.90 ( $SiCH_2$ ), 7.64 ( $CH_3$ ), 38.70 ( $NCH_3$ ), 108.34, 125.67, 129.07, 135.63, 137.07, 147.47, 153.67 (Ar); IR (neat) 3042 m, 2956 s, 2910 s, 2876 s, 1522 m, 1459 m, 1421 m, 1360 s, 1235 m, 1220 m, 1061 m, 1001 s, 780 m, 723 s, 677 s  $cm^{-1}$ ; MS  $m/z$  (% relative intensity) 359 (12), 358 (33), 357 ( $[M^+ - Et]$ , 100), 150 (31), 136 (44), 122 (38), 108 (84), 107 (30), 59 (12). Anal. Calc. for  $C_{22}H_{38}N_2Si_2$ : C, 68.33; H, 9.90; N, 7.24. Found: C, 68.35; H, 9.68; N, 7.07%.

#### 4.4.22. 1-(2-Triethylsilylanyl-phenyl)-1H-pyrazole

$^1H$ -NMR ( $CDCl_3$ ) 0.55 (q,  $J = 7.9$  Hz, 6H,  $CH_2$ ), 0.84 (t,  $J = 7.9$  Hz, 9H,  $CH_3$ ), 6.42 (t,  $J = 2.0$  Hz, 1H, ArH), 7.23–7.29 (m, 2H, ArH), 7.36–7.46 (m, 2H, ArH), 7.66 (d,  $J = 1.7$  Hz, 1H, ArH);  $^{13}C$ -NMR ( $CDCl_3$ ) 3.09 ( $CH_2$ ), 7.19 ( $CH_3$ ), 105.98, 125.50, 126.98, 128.96, 129.76, 133.15, 136.07, 139.19, 145.81 (Ar); IR (neat) 2956 s, 2912 m, 2880 s, 1594 m, 1518 m, 1486 m, 1464 m, 1442 m, 1420 m, 1396 m, 1238 m, 1118 m, 1078 m, 1046 m, 1006 m, 942 m, 916 w, 746 s, 728 s, 692 m  $cm^{-1}$ ; MS  $m/z$  (% relative intensity) 230 (21), 229 ( $[M^+ - Et]$ , 100), 171 (21), 117 (10). Anal. Calc. for  $C_{15}H_{22}N_2Si$ : C, 69.71; H, 8.58; N, 10.84. Found: C, 70.16; H, 8.86; N, 10.82%.

#### 4.4.23. 1-(2,6-bis-Triethylsilylanyl-phenyl)-1H-pyrazole

$^1H$ -NMR ( $CDCl_3$ ) 0.43 (q,  $J = 7.9$  Hz, 12H,  $CH_2$ ), 0.83 (t,  $J = 7.9$  Hz, 18 Hz,  $CH_3$ ), 6.39 (t,  $J = 2.0$  Hz, 1H, ArH), 7.37–7.43 (m, 2H, ArH), 7.57–7.63 (m, 3H, ArH);  $^{13}C$ -NMR ( $CDCl_3$ ) 3.13 ( $CH_2$ ), 7.56 ( $CH_2$ ), 105.82, 127.19, 132.08, 135.54, 137.11, 138.84, 151.54 (Ar); IR (neat) 3056 m, 2960 s, 2916 s, 2884 s, 2828 m, 1750 w, 1708 w, 1570 m, 1514 m, 1464 m, 1436 s, 1402 s, 1378 m, 1238 m, 1148 m, 1106 w, 1078 w, 1042 m, 1004 s, 976 m, 964 m, 940 m, 760 s, 726 s, 686 s  $cm^{-1}$ . Anal. Calc. for  $C_{21}H_{36}N_2Si_2$ : C, 67.68; H, 9.74; N, 7.52. Found: C, 67.79; H, 9.97; N, 7.37%.

4.4.24. *1-Methyl-4-(2-triethylsilylanyl-phenyl)-1H-imidazole*

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.64 (q,  $J = 7.5$  Hz, 6H,  $\text{SiCH}_2$ ), 0.86 (t,  $J = 7.5$  Hz, 9H,  $\text{CH}_3$ ), 3.74 (s, 3H,  $\text{NCH}_3$ ), 6.86 (s, 1H, ArH), 7.27–7.39 (m, 3H, ArH), 7.42 (s, 1H, ArH), 7.55 (dd,  $J = 6.2$  Hz, 1.2 Hz, 1H, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 4.43 ( $\text{SiCH}_2$ ), 7.77 ( $\text{CH}_3$ ), 33.41 ( $\text{NCH}_3$ ), 117.41, 126.07, 128.23, 129.62, 135.70, 135.76, 136.49, 141.53, 144.71 (Ar); IR (neat) 2954 s, 2910 s, 2876 s, 1506 m, 1456 s, 1431 m, 1419 m, 1376 m, 1234 m, 1224 m, 1213 m, 1180 m, 1117 m, 1086 m, 1049 m, 998 m, 956 m, 943 m, 833 m, 776 m, 737 s, 720 s, 677 m  $\text{cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 244 (22), 243 ( $[\text{M}^+ - \text{Et}]$ , 100), 185 (32), 107 (11), 93 (62). Anal. Calc. for  $\text{C}_{16}\text{H}_{24}\text{NSi}$ : C, 70.53; H, 8.88; N, 10.28. Found: C, 70.34; H, 8.60; N, 10.20%.

4.4.25. *4-(2,6-bis-Triethylsilylanyl-phenyl)-1-methyl-1H-imidazole*

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.47 (q,  $J = 7.8$  Hz, 12H,  $\text{SiCH}_2$ ), 0.83 (t,  $J = 7.8$  Hz, 18H,  $\text{CH}_3$ ), 3.74 (s, 3H,  $\text{NCH}_3$ ), 6.68 (d,  $J = 1.4$  Hz, 1H, ArH), 7.29 (t,  $J = 7.3$  Hz, 1H, ArH), 7.44 (d,  $J = 0.8$  Hz, 1H, ArH), 7.52 (d,  $J = 7.3$  Hz, 2H, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 3.95 ( $\text{SiCH}_2$ ), 7.68 ( $\text{CH}_3$ ), 33.31 ( $\text{NCH}_3$ ), 119.24, 125.57, 135.44, 135.66, 137.50, 144.05, 147.81 (Ar); IR (neat) 2952 s, 2910 s, 2874 s, 1502 m, 1458 m, 1421 s, 1373 m, 1342 m, 1273 m, 1233 m, 1212 m, 1183 m, 1001 s, 774 s, 715 s, 686 s, 666 s  $\text{cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 360 (11), 358 (35), 357 ( $[\text{M}^+ - \text{Et}]$ , 100), 150 (23), 136 (74), 108 (90), 107 (31). Anal. Calc. for  $\text{C}_{22}\text{H}_{38}\text{N}_2\text{Si}_2$ : C, 68.33; H, 9.90; N, 7.24. Found: C, 68.13; H, 9.69; N, 7.30%.

4.4.26. *1-Methyl-4-(2-triethylsilylanyl-phenyl)-1H-[1,2,3]triazole*

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.64 (q,  $J = 7.6$  Hz, 6H,  $\text{SiCH}_2$ ), 0.85 (t,  $J = 7.6$  Hz, 9H,  $\text{CH}_3$ ), 4.16 (s, 3H,  $\text{NCH}_3$ ), 7.30–7.40 (m, 3H, ArH), 7.60 (s, 1H, ArH), 7.61–7.63 (m, 1H, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 4.18 ( $\text{SiCH}_2$ ), 7.52 ( $\text{CH}_3$ ), 36.64 ( $\text{NCH}_3$ ), 122.40, 127.30, 128.53, 130.01, 136.14, 136.65, 137.11, 150.03 (Ar); IR (neat) 2940 s, 2906 s, 2872 s, 1724 w, 1590 w, 1564 w, 1458 s, 1427 s, 1377 m, 1340 w, 1278 m, 1247 m, 1233 m, 1214 m, 1179 m, 1119 m, 1089 m, 1058 m, 1000 s, 971m, 801 m, 762 s, 742 s, 720 s, 670 m  $\text{cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 245 (20), 244 ( $[\text{M}^+ - \text{Et}]$ , 100), 147 (10), 119 (19), 117 (10), 108 (12), 105 (10), 94 (16). Anal. Calc. for  $\text{C}_{15}\text{H}_{23}\text{N}_3\text{Si}$ : C, 65.88; H, 8.48; N, 15.37. Found: C, 66.00; H, 8.57; N, 15.50%.

4.4.27. *4-(2,6-bis-Triethylsilylanyl-phenyl)-1-methyl-1H-[1,2,3]triazole*

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.42 (q,  $J = 7.9$  Hz, 12H,  $\text{SiCH}_2$ ), 0.82 (t,  $J = 7.9$  Hz, 18H,  $\text{CH}_3$ ), 4.17 (s, 3H,  $\text{NCH}_3$ ), 7.36 (t,  $J = 7.4$  Hz, 1H, ArH), 7.37 (s, 1H, ArH), 7.57 (d,  $J = 7.4$  Hz, 2H, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 3.95 ( $\text{SiCH}_2$ ),

7.51 ( $\text{CH}_3$ ), 36.57 ( $\text{NCH}_3$ ), 124.25, 126.46, 135.85, 137.86, 143.06, 149.26 (Ar); IR (neat) 3124 m, 3048 m, 2952 s, 2910 s, 2874 s, 1716 w, 1556 w, 1457 m, 1419 m, 1377 m, 1320 m, 1234 m, 1209 m, 999 s, 970 m, 862 m, 773 s, 764 s, 741 m, 724 s, 669 s  $\text{cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 360 (12), 359 (30), 358 ( $[\text{M}^+ - \text{Et}]$ , 100), 151 (31), 136 (55), 109 (83), 87 (12), 59 (23). Anal. Calc. for  $\text{C}_{21}\text{H}_{37}\text{N}_3\text{Si}_2$ : C, 65.06; H, 9.62; N, 10.84. Found: C, 65.01; H, 9.35; N, 10.69%.

4.4.28. *1-Methyl-5-(2-triethylsilylanyl-phenyl)-1H-tetrazole*

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.54 (q,  $J = 7.8$  Hz, 6H,  $\text{CH}_2$ ), 0.84 (t,  $J = 7.8$  Hz, 9H,  $\text{CH}_3$ ), 3.92 (s, 1H,  $\text{CH}_3$ ), 7.25 (dd,  $J = 8.3$  Hz, 1.3 Hz, 1 H, ArH), 7.47–7.60 (m, 2H, ArH), 7.72 (dd,  $J = 6.9$  Hz, 1.7 Hz, 1H, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 3.41 ( $\text{CH}_2$ ), 7.39 ( $\text{CH}_3$ ), 34.11 ( $\text{CH}_3$ ), 128.79, 129.43, 129.54, 129.74, 136.42, 139.13 (Ar), 155.79 (C=N); IR (neat) 2958 s, 2912 s, 2878 s, 1463 s, 1446 s, 1421 s, 1289 m, 1242 m, 1164 w, 1127 m, 1110 m, 1079 m, 1047 m, 1002 s, 976 m, 775 s, 740 s, 728 s, 682 m  $\text{cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 248 (5), 246 (22), 245 ( $[\text{M}^+ - \text{Et}]$ , 100), 161 (42), 160 (17), 133 (13), 132 (27), 121 (11), 105 (21), 85 (23), 83 (28), 59 (10), 54 (11). HRMS Calc. for  $\text{C}_{14}\text{H}_{22}\text{N}_4\text{Si}$ : 275.1692. Found: 275.1686%.

4.4.29. *2-Methyl-5-(2-triethylsilylanyl-phenyl)-2H-tetrazole*

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.68 (q,  $J = 7.8$  Hz, 6H,  $\text{CH}_2$ ), 0.80 (t,  $J = 7.8$  Hz, 9H,  $\text{CH}_3$ ), 4.42 (s, 3H,  $\text{CH}_3$ ), 7.4–7.8 (m, 4H, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 4.26 ( $\text{CH}_2$ ), 7.63 ( $\text{CH}_3$ ), 39.40 ( $\text{CH}_3$ ), 128.72, 129.75, 133.41, 135.77, 136.24, 136.79 (Ar), 166.90 (C=N); MS  $m/z$  (% relative intensity) 246 (20), 245 ( $[\text{M}^+ - \text{Et}]$ , 100), 161 (19), 132 (35), 105 (16), 54 (10), 53 (12). Anal. Calc. for  $\text{C}_{14}\text{H}_{22}\text{N}_4\text{Si}$ : C, 61.27; H, 8.08; N, 20.42. Found: C, 61.25; H, 8.18; N, 20.25%.

4.4.30. *5-(2,6-bis-Triethylsilylanyl-phenyl)-2-methyl-2H-tetrazole*

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.41 (q,  $J = 7.8$  Hz, 12H,  $\text{CH}_2$ ), 0.82 (t,  $J = 7.8$  Hz, 18H,  $\text{CH}_3$ ), 4.42 (s, 3H,  $\text{CH}_3$ ), 7.43 (t,  $J = 7.4$  Hz, 1H, ArH), 7.61 (d,  $J = 7.4$  Hz, 2H, ArH),  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 3.83 ( $\text{CH}_2$ ), 7.52 ( $\text{CH}_3$ ), 39.34 ( $\text{CH}_3$ ), 127.32, 135.77, 137.90, 139.63 (Ar), 167.00 (C=N); IR (neat) 2960 s, 2884 s, 1520 w, 1462 w, 1422 w, 1378 w, 1342 w, 1236 w, 1110 w, 1074 w, 1002 m, 796 m, 774 m, 752 m, 722 s  $\text{cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 361 (14), 360 (30), 359 ( $[\text{M}^+ - \text{Et}]$ , 100), 151 (17), 137 (30), 123 (41), 110 (14), 109 (71), 59 (17). Anal. Calc. for  $\text{C}_{20}\text{H}_{36}\text{N}_4\text{Si}$ : C, 61.80; H, 9.34; N, 14.41. Found: C, 61.61; H, 8.96; N, 14.45%.

#### 4.4.31. 2-Triethylsilylanyl-furan-3-carboxylic acid diisopropylamide

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.77 (q,  $J = 7.6$  Hz, 6H,  $\text{CH}_2$ ), 0.93 (t,  $J = 7.6$  Hz, 9H,  $\text{CH}_3$ ), 1.32 (br, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 3.59 (br, 2H, CH), 6.37 (d,  $J = 1.6$  Hz, 1H, furyl), 7.36 (d,  $J = 1.6$  Hz, 1H, furyl);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 3.55 ( $\text{CH}_2$ ), 7.53 ( $\text{CH}_3$ ), 20.63 ( $\text{CH}_3$ ), 115.64, 116.78, 140.60, 154.21 (furyl), 162.21 (C=O); IR (neat) 3108 m, 2958 m, 2936 m, 2878 m, 1616 s, 1554 m, 1494 s, 1441 s, 1372 m, 1322 s, 1238 m, 1191 m, 1157 m, 1059 m, 1033 m, 1011 m, 1001 m, 893 m, 822 m, 779 m, 757 m, 732 s, 720 m, 706 s, 686  $\text{m cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 281 (22), 280 ( $[\text{M}^+ - \text{Et}]$ , 100), 238 (37), 197 (13), 196 (80), 178 (12), 153 (13), 150 (27), 138 (21), 125 (13), 122 (17), 95 (10), 75 (11), 59 (21). Anal. Calc. for  $\text{C}_{17}\text{H}_{31}\text{O}_2\text{NSi}$ : C, 65.97; H, 10.10; N, 4.53. Found: C, 65.84; H, 9.91; N, 4.38%.

#### 4.4.32. 3,5-bis-Triethylsilylanyl-furan-2-carboxylic acid diisopropylamide

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.78 (q,  $J = 7.3$  Hz, 12 H,  $\text{CH}_2$ ), 0.94 (t,  $J = 7.3$  Hz, 18 H,  $\text{CH}_3$ ), 1.20–1.50 (br, 12H,  $\text{CH}(\text{CH}_3)_2$ ), 3.50–3.67 (br, 2H, CH), 6.57 (s, 1H, furyl);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 3.33 ( $\text{CH}_2$ ), 3.67 ( $\text{CH}_2$ ), 7.41 ( $\text{CH}_3$ ), 7.64 ( $\text{CH}_3$ ), 20.51 ( $\text{CH}_2$ ), 21.03 ( $\text{CH}_2$ ), 116.39, 126.73, 156.20, 158.14 (furyl), 162.82 (C=O); IR (neat) 2960 s, 2884 m, 1636 s, 1434 m, 1328 s, 1006 m, 736  $\text{s cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 396 (15), 395 (34), 394 (100), 352 (18), 115 (11), 87 (64), 75 (16), 59 (93). HRMS Calc. for  $\text{C}_{23}\text{H}_{45}\text{NO}_2\text{Si}_2$ : 423.2989. Found: 423.2986%.

#### 4.4.33. 2,5-bis-Triethylsilylanyl-furan-3,4-dicarboxylic acid dimethyl ester

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 0.78–0.87 (m, 12 H,  $\text{CH}_2$ ), 0.92–0.99 (m, 18 H,  $\text{CH}_3$ ), 3.82 (s, 6H,  $\text{OCH}_3$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) 2.98 ( $\text{SiCH}_2$ ), 7.31 ( $\text{CH}_3$ ), 51.77 ( $\text{OCH}_3$ ), 127.65 (furyl), 164.66 (furyl), 167.42 (C=O); IR (neat) 2958 s, 2916 m, 2880 s, 1727 s, 1552 m, 1497 m, 1461 m, 1436 m, 1417 m, 1380 m, 1282 s, 1215 s, 1178 m, 1121 m, 1063 s, 1004 m, 976 m, 948 m, 823 m, 811 m, 782 m, 738 s, 705  $\text{s cm}^{-1}$ ; MS  $m/z$  (% relative intensity) 385 (13), 384 (30), 385 ( $[\text{M}^+ - \text{Et}]$ , 100), 177 (14), 149 (13), 148 (20), 134 (19), 117 (13), 89 (51), 87 (25), 61 (57), 59 (73). Anal. Calc. for  $\text{C}_{20}\text{H}_{36}\text{O}_5\text{Si}_2$ : C, 58.21; H, 8.79. Found: 58.20; H, 8.68%.

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