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Aromatic C–H silylation of arenes with 1-hydrosilatrane catalyzed by an iridium(I)/2,9-dimethylphenanthroline (dmphen) complex†

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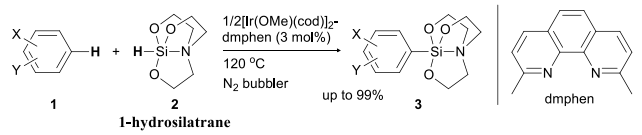
Aromatic C–H silylation of neat arenes with 1-hydrosilatrane was found to be efficiently catalyzed by iridium catalysts composed of 1/2[Ir(OMe)(cod)]$_2$ and 2,9-dimethyl-1,10-phenanthroline at 120˚C to afford the corresponding silylated products in high yields. The silylated products can be used to Hiyama cross-coupling reaction.

Silyl-substituted arenes are an important class of compounds that have been shown to be useful in synthetic organic chemistry,[1-3] material science,[4] and pharmaceutical sectors.[5] Traditional methods for their synthesis are based on alkylation of silicon electrophiles with aryl-lithium or -magnesium compounds.[6] Transition metal-catalyzed cross-coupling of aromatic halides with disilanes or hydrosilanes is a milder variant in which the preparation of magnesium or lithium reagents is avoided.[7] Alternatively, metal-catalyzed C–H silylation of arenes is highly attractive as a convenient, economical, and environmentally benign process. Thus, there have been several attempts at C–H functionalization of arenes with disilanes[8] or hydrosilanes.[8a,9]

Since tetraorganosilicon compounds reported in these precedents are inert to C–Si bond activation with F bases for metal-catalyzed bond-forming reactions, we reported the first access to aryldifluorosilanes via direct C–H silylation of arenes with [SiF$_2$(*t*-Bu)]$_2$ in the presence of iridium(I) catalysts.[10] Although the reaction achieved high yields for representative arenes, this protocol is limited due to the many tedious steps required for obtaining fluorodisilanes and the fact that only half of the silyl groups of the disilanes participate in the reaction. Such drawbacks prompted us to use easily available alkoxyhydrosilanes as silylation reagents. We disclose here a useful C–H silylation of arenes **1** with 1-hydro-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane[11] (1-hydrosilatrane) (**2**) catalyzed by a 1/2[Ir(OMe)(cod)]$_2$/2,9-dimethyl-1,10-phenanthroline (dmphen) complex at 120˚C to give the corresponding 1-arylsilatrane **3** in high yields (Scheme 1). The silylated products **3** can be used to Hiyama cross-coupling



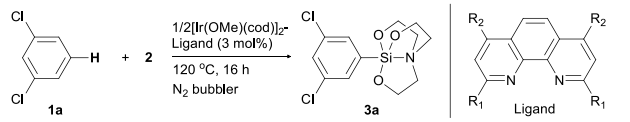
Scheme 1. C–H silylation of arenes with 1-hydrosilatrane.

procedure in high yield. Air- and moisture-stable 1-hydrosilatrane, obtained in one step by treatment of triethoxysilane with boratrane, is advantageous over fluorodisilanes for large-scale preparation from commercial materials.[11]

Ligands for catalysts of aromatic C–H silylation[10] such as modified 2,2'-bipyridines and unsubstituted 1,10-phenanthroline were not efficient for 1-hydrosilatrane **2**. Thus, the effects of steric and electronic properties of phenanthroline ligands (phen) were re-evaluated by using 1/2[Ir(OMe)(cod)]$_2$ as a catalyst precursor (Table 1). A phen possessing two methyl groups at the 2- and 9-positions (dmphen) displayed good reactivity (Entry 2), whereas its 2,9-di-*n*-butyl, 2,9-di-isopropyl and 2,9-di-*t*-butyl derivatives showed almost no activity (Entries 3–5). These results indicate the importance of an appropriately hindered coordination sphere around the iridium metal center. Electron-rich 2,9-dimethylphenanthroline ligands work better than electron-poor 2,9-dimethylphenanthroline ligands. Thus, the highest yield was obtained with 4,7-bis(dimethylamino) (Entry 6), whereas 4,7-dimethoxy, 4,7-dichloro and 4,7- bis(trifluoromethyl) derivatives displayed moderate or low activity (Entries 7–9). Metal-catalyzed C-H silylation with hydrosilanes is often retarded by hydrogen generated during coupling.[9] Thus, reactions were carried out in a flask fitted with a condenser and a nitrogen bubbler to remove hydrogen in place of a sealed Schlenk tube. As expected, 50% yield in a sealed Schlenk tube was improved to 74% in a flask fitted with a nitrogen bubbler (Entry 2). Use of hydrogen scavengers[9] such as 3,3-dimethyl-1-butene and 2-norbornene in a sealed Schlenk tube was not effective. Of the representative alkoxyhydrosilanes screened, small and thermally stable **2** provided the best yields, but ethoxydimethylsilane, diethoxymethylsilane, and triethoxysilane did not give any coupling products at all.

We evaluated the scope and limitations of the reaction using dmphen because of the commercial availability of this ligand. Reactions of **2** (1.0 mmol) in neat arenes (60 mmol) at 120˚C for 32 h in a flask fitted with a nitrogen bubbler are summarized in Table 2. In contrast to the control of regioselectivity of electrophilic and nucleophilic substitution of arenes by the electronic properties of substituents, the regiochemistry of the present C-H silylation is primarily controlled by the steric effect of substituents. Thus, reactions located *meta* or *para* to a

Table 1. Optimized phenanthroline ligands using 1,3-dichlorobenzene[a]

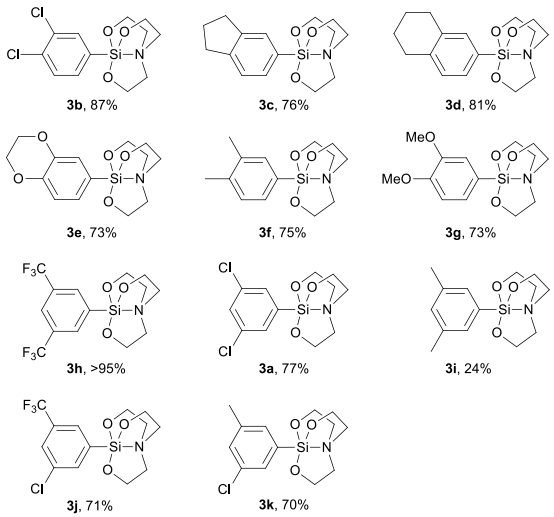


Entry	R_1	R_2	Yield of **3a** (%)[b]
1	H	H	<5
2	Me	H	74
3	*n*-Bu	H	<5
4	*i*-Pr	H	<5
5	*t*-Bu	H	0
6	Me	Me_2N	76
7	Me	MeO	59
8	Me	Cl	54
9	Me	CF_3	28

[a] The reactions were carried out by using 1,3-dichlorobenzene (60 mmol), **2** (1.0 mmol), $[Ir(OMe)(cod)]_2$ (0.015 mmol), and ligand (0.03 mmol) at 120°C for 16 h in a flask fitted with a condenser and a nitrogen bubbler. [b] ^{1}H NMR yeilds based on **2** by using mesitylene as an internal standard.

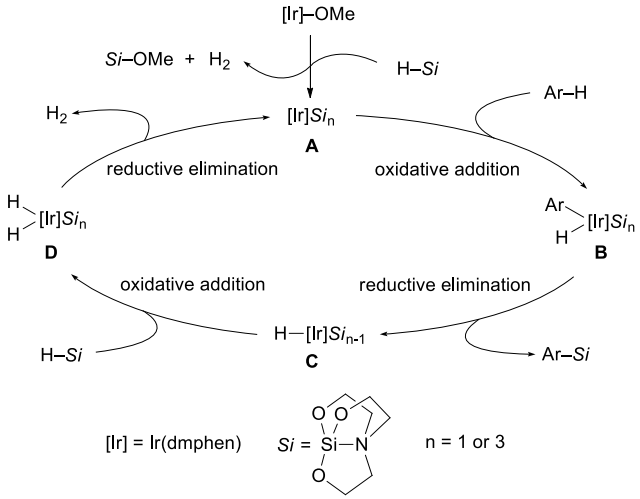
in preference of those located in the *ortho* position. 1,2- and 1,3-Dichlorobenzes gave a single coupling product at the *meta*-carbon (**3b**: 87%, **3a**: 77%). Bicyclic arenes such as indane, tetralin and 1,4-benzodioxane selectively yielded *β*-silylarenes (**3c**: 76%, **3d**: 81%, **3e**: 73%). Arenes in which the rings were electron-poor or electron-rich participated in the silylation reactions (**3b**: 87%, **3f**: 75%, **3g**: 73%), though *m*-xylene exceptionally resulted a low yield for an unknown reason (**3i**: 24%). The reaction of 1,3-disubstituted arenes selectively occurred only at the common *meta* position; therefore, isomerically pure silylarenes were obtained even with two distinct substitutes on the aromatic ring (**3j**: 71%, **3k**: 70%). It is notable that aromatic C–H bonds (112 kcal/mol) are selectively silylated in the presence of weaker benzylic C-H bonds (85 kcal/mol) or C–Cl bonds (95 kcal/mol).

Table 2. C–H silylation of various arenes with **2**[a,b]



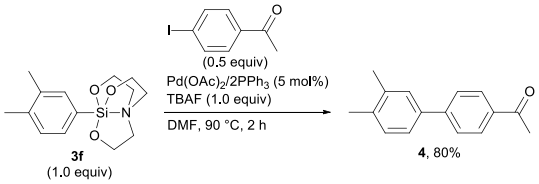
[a] The reactions were carried out by using arenes (60 mmol), **2** (1.0 mmol), $[Ir(OMe)(cod)]_2$ (0.015 mmol), and dmphen (0.03 mmol) at 120 °C for 32 h in a flask fitted with a condenser and a nitrogen bubbler. [b] Isomeric purities over 99% were determined by ^{1}H NMR. [c] ^{1}H NMR yeilds based on **2** by using mesitylene as an internal standard.

The reaction may proceed through a catalytic cycle analogous to that of aromatic C–H borylation:[12] (a) generation of a (silyl)iridium intermediate (**4**) from 1-hydrosilatrane **2** and the Ir(I)–OMe complex, (b) oxidative addition of an aromatic C–H bond to **4** followed by reductive elimination of an arylsilane **3** to give an iridium hydride complex (**5**), and (c) oxidative addition of **2** to **5** followed by reductive elimination of hydrogen to regenerate **4** (Scheme 2). A proposed catalytic cycle for C–H borylation involves oxidative addition of an aromatic C-H bond to a tris(boryl)iridium(III) intermediate.[12h, 13] Although there is no supporting information on whether the silyl intermediate is iridium(I) or iridium(III) complex (**4**, n=1 or 3), both complexes may allow C–H oxidative addition of arenes and reductive elimination of silylarenes.[12b]



Scheme 2. Plausible mechanism.

1-Arylsilatranes **3** thus obtained are useful reagents for carbon-carbon bond-forming reactions (Scheme 3). For example, silylarene **3** underwent Hiyama cross-coupling with aryl halides, thus suggesting that arylsilatranes are activated for transmetalation to transition metals in the presence of F bases.[14]



Scheme 3. Synthetic utility of **3**.

In summary, we provided the first access to arylsilatoranes via C–H silylation of arenes. Since organo(trialkoxy)silanes are versatile intermediates for metal-catalyzed bond-forming reactions, this procedure should be applicable for other silylated products as a useful method to obtain these potentially bioactive compounds. Further investigations to survey the scope and limitations as well as to elucidate the reaction mechanisms are in progress.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental procedures and spectral analyses. See DOI: 10.1039/b000000x/

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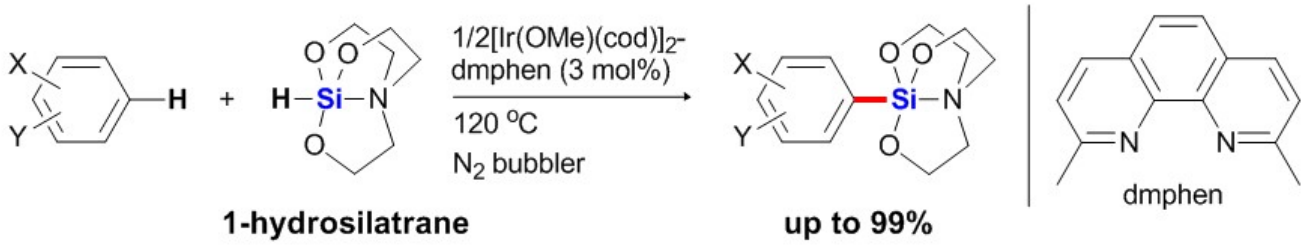
Grafical abstract



Aromatic C–H silylation of neat arenes with 1-hydrosilatrane was found to be efficiently catalyzed by iridium catalysts composed of 1/2[Ir(OMe)(cod)]$_2$ and 2,9-dimethyl-1,10-phenanthroline at 120˚C to afford the corresponding silylated products in high yields.

Supporting Information

Aromatic C–H silylation of arenes with 1-hydrosilatrane catalyzed by an iridium(I)/2,9-dimethylphenanthroline (dmphen) complex

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General. All the experiments were carried out under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using a JEOL JNM-A400II spectrometer (400 or 100 MHz) and Me_4Si or residual protiated solvent as an internal standard. Low- and high-resolution mass spectra were obtained on a JEOL JMS-DX303. GC analyses were conducted on a Hitachi G-3500 instrument equipped with a glass column (OV-101 on Uniport B, 2 m). $[Ir(OMe)(cod)]_2$,[1] 2,9-diisopropyl-1,10-phenanthroline,[2] 2,9-di-*tert*-butyl-1,10-phenanthroline,[2] 1-hydro-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane,[3] and 2,9-dimethyl-4,7-dichloro-1,10-phenanthroline[4] were synthesized by the reported procedure. 2,9-Dimethyl-4,7-bis(dimethylamino)-1,10-phenanthroline and 2,9-dimethyl-4,7-dimethoxy-1,10-phenanthroline were prepared by the methods similar to those for 4,7-bis(dimethylamino)-1,10-phenanthroline[5] and 4,7-dimethoxy-1,10-phenanthroline,[5] respectively. 2,9-Dimethyl-4,7-bis(trifluoromethyl)-1,10-phenanthroline was obtained by chlorine-iodine exchange[6] of 2,9-dimethyl-4,7-dichloro-1,10-phenanthroline and coupling[7] of the iodide with in situ generated (trifluoromethyl)copper. Arenes were purified by distillation from appropriate drying agents. All of other compounds were used as received.

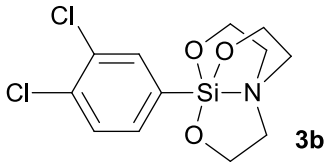
2,9-Dimethyl-4,7-bis(dimethylamino)-1,10-phenanthroline. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.84 (s, 6H), 3.03 (s, 12H), 6.88 (s, 2H), 7.89 (s, 2H); ^{13}C NMR (100 MHz) δ 26.32, 44.11, 109.93, 119.85, 120.64, 147.34, 157.72, 158.92; LRMS (EI) m/z 294 (M^+, 100), 279 (9.5), 263 (6.3), 250 (4.9), 236 (3.6), 147 (5.9), 139 (4.5); HRMS (EI) calcd for $C_{18}H_{22}N_4$ 294.1844, found 294.1833.

2,9-Dimethyl-4,7-dimethoxy-1,10-phenanthroline. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (s, 6H), 4.07 (s, 6H), 6.86 (s, 2H), 8.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.63, 55.66, 102.74, 117.95, 119.42, 145.97, 160.26, 162.28; LRMS (EI) m/z 268 (M^+, 100), 253 (14.1), 225 (22.8), 210 (4), 182 (7.5), 134 (4.9) ; HRMS (EI) calcd for $C_{16}H_{16}N_2O_2$ 268.1212, found 268.1207.

2,9-Dimethyl-4,7-bis(trifluoromethyl)-1,10-phenanthroline. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (s, 6H), 7.86 (s, 2H), 8.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.13, 120.81 (q, J = 5.2 Hz), 121.90 (q, J = 1.7 Hz), 122.78 (q, J = 1.7 Hz), 123.30 (q, J = 274.2 Hz), 134.74 (q, J = 319.4), 146.09, 159.94; LRMS (EI) m/z 344 (M^+, 100), 325 (4.7), 274 (6.7), 172 (5.5), 40 (9.3); HRMS (EI) calcd for $C_{16}H_{10}N_2F_6$ 344.0748, found 344.0750.

General procedure for the C–H silylation (Table 2). An oven-dried flask fitted with a condenser and a nitrogen bubbler was charged with 1-hydrosilatrane (1.0 mmol), $[\{Ir(OMe)(cod)\}_2]$ (0.015 mmol) and dmphen (0.03 mmol), and then flushed with nitrogen. Under a positive flow of nitrogen, an arene (60 mmol) was added. The reaction mixture was stirred at 120˚C for 32 h. The product was isolated by Kugelrohr distillation to give an analytically pure sample.

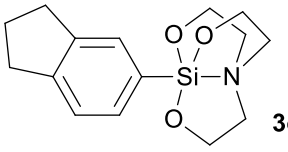
1-(3,4-Dichlorophenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3b).



3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92(t, J = 5.9 Hz, 6 H), 3.89 (t, J = 5.9 Hz, 6 H), 7.32 (d, J = 7.8 Hz, 1 H), 7.53 (dd, J = 1.5, 7.8 Hz, 1H), 7.79 (d, J = 1.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.95, 57.48, 129.22, 131.23, 131.28, 133.57, 136.19, 143.66; LRMS (EI) m/z 319 (M^+, 8), 174 (100); HRMS (EI) calcd for $C_{12}H_{15}NO_3SiCl_2$ 319.0198, found 319.0198.

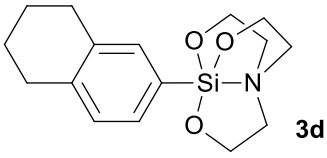
1-(5-Indanyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3c).



3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94-2.01 (m, 2 H), 2.81-2.90 (m, 7 H), 3.88 (t. *J* = 5.9 Hz, 6 H), 7.13 (d, *J* = 7.3 Hz, 1 H), 7.50 (d, *J* = 7.3 Hz, 1 H), 7.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.31, 32.76, 32.81, 51.08, 57.80, 123.33, 129.81, 131.82, 138.77, 142.82, 143.61; LRMS (EI) m/z 291 (M^+, 19.7), 174 (100); HRMS (EI) calcd for $C_{15}H_{21}NO_3Si$ 291.1291, found 291.1293.

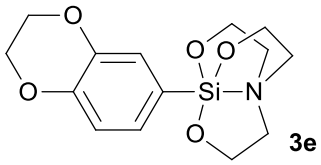
1-(6-Tetralinyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3d).



3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72-1.75 (m, 4 H), 2.69 (br s, 2 H), 2.75 (br s, 2 H), 2.89 (t, *J* = 5.9 Hz, 6 H), 3.88 (t, *J* = 5.9 Hz, 6 H), 6.96 (d, *J* = 7.3 Hz, 1 H), 7.41 (s, 1 H), 7.42 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.45, 23.56, 29.40, 29.49, 51.18, 57.86, 128.10, 131.14, 134.74, 135.65, 136.63, 137.98; LRMS (EI) m/z 305 (M^+, 18.5), 174 (100); HRMS (EI) calcd for $C_{16}H_{23}NO_3Si$ 305.1447, found 305.1449.

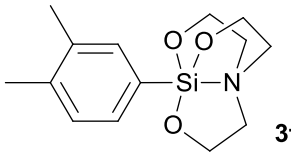
1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3e).



3e

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (t, *J* = 5.9 Hz, 6 H), 3.88 (t, *J* = 5.9 Hz, 6 H), 4.20 (s, 3 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 7.20 (dd, *J* = 1.5 and 8.0 Hz, 1 H), 7.25 (d, *J* = 1.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.06, 57.72, 64.26, 64.53, 116.28, 123.06, 127.38, 134.79, 142.78, 143.42; LRMS(EI) m/z 311 (M^+, 59.2), 174 (100); HRMS (EI) calcd for $C_{14}H_{21}NO_5Si$ 309.1032, found 309.1031.

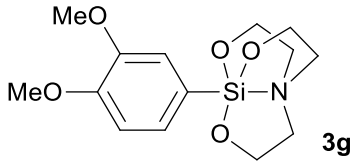
1-(3,4-Dimethylphenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3f).



3f

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.19 (s, 3 H), 2.29 (s, 3 H), 2.87 (t, *J* = 6.0 Hz, 6 H), 3.87 (t, *J* = 5.9 Hz, 6 H), 7.03 (d, *J* = 7.3 Hz, 1 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.47 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.68, 19.79, 51.11, 57.83, 128.66, 131.67, 134.96, 135.28, 135.85, 138.67; LRMS (EI) m/z 279 (M^+, 23), 236 (3.2), 206 (3.1), 174 (100), 119 (3); HRMS (EI) calcd for $C_{14}H_{21}O_3NSi$ 279.1291, found 279.1301.

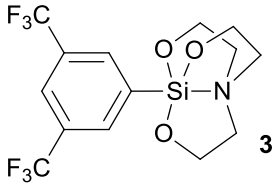
1-(3,4-Dimethoxyphenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3g).



3g

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (t, *J* = 6.1 Hz, 6 H), 3.84 (s, 3 H), 3.90 (t, *J* = 5.9 Hz, 6 H), 3.91 (s, 3 H), 6.83 (d, *J* = 7.8, 1 H), 7.28 (d, *J* = 1.5 Hz, 1 H), 7.30 (dd, *J* = 1.4 and 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.09, 55.59, 55.68, 57.81, 110.78, 116.65, 127.11, 133.67, 147.98, 148.88; LRMS(EI) m/z 311 (M^+, 59.2), 174 (100); HRMS (EI) calcd for $C_{14}H_{21}NO_5Si$ 311.1189, found 311.1194.

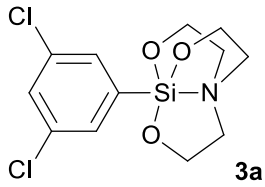
1-[3,5-Bis(trifluoromethyl)phenyl]-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3h).



3h

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 (t, *J* = 6.1 Hz, 6 H), 3.92 (t, *J* = 6.1 Hz, 6 H), 7.71 (s. 1 H), 8.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.97, 57.44, 121.09-121.25 (m), 124.18 (q, *J* = 272.3 Hz), 129.45 (q, *J* = 31.9 Hz), 134.25-134.50 (m), 146.26; LRMS (EI) m/z 387 (M^+, 3.2), 174 (100); HRMS (EI) calcd for $C_{14}H_{15}NO_3F_6Si$ 387.0725, found 387.0722.

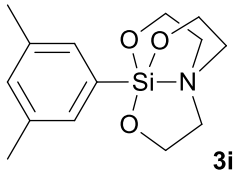
1-(3,5-Dichlorophenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3a).



3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (t, *J* = 6.1 Hz, 6 H), 3.91 (t, *J* = 6.1 Hz, 6 H), 7.21 (t, *J* = 2.0 Hz, 1 H), 7.58 (d, *J* = 2.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.01, 57.49, 127.42, 132.31, 133.93, 147.25; LEMS (EI) m/z 319 (M^+, 5.4), 174 (100), 130 (3); HRMS (EI) calcd for $C_{12}H_{15}NO_3SiCl_2$ 319.0198, found 319.0204.

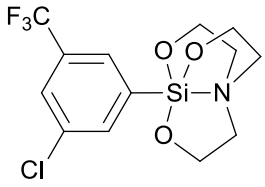
1-(3,5-Dimetylphenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3i).



3i

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 6 H), 2.90 (t, *J* = 5.9 Hz, 6 H), 3.90 (t, *J* = 5.9 Hz, 6 H), 6.88 (s, 1 H), 7.35 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.45, 51.09, 57.82, 129.58, 131.68, 136.26, 141.12; LRMS (EI) m/z 279 (M^+, 19), 174 (100), 148 (3.1), 119 (3.1), 105 (3.2); HRMS (EI) calcd for $C_{14}H_{21}O_3NSi$ 279.1291, found 279.1298.

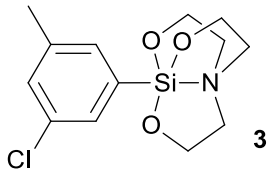
1-(3-Chloro-5-trifluoromethylphenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3j).



3j

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (t, *J* = 6.1 Hz, 6 H), 3.91 (t, *J* = 5.9 Hz, 6 H), 7.44 (s, 1 H), 7.87 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.94, 57.44, 124.01 (q, *J* = 272.3 Hz), 124.26 (q, *J* = 4.1 Hz), 128.97 (q, *J* = 3.9 Hz), 130.53 (q, *J* = 31.9 Hz), 133.59, 137.68, 147.12; LRMS (EI) m/z 353 (M^+, 4), 174 (100); HRMS (EI) calcd for $C_{13}H_{15}NO_3F_3SiCl$ 353.0462, found 353.0461.

1-(3-Chloro-5-methylphenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (3k).



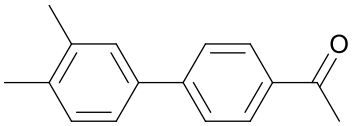
3k

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3 H), 2.92 (t, *J* = 5.9 Hz, 6 H), 3.90 (t, *J* = 5.9 Hz, 6 H), 7.02 (s, 1 H), 7.40 (s, 1 H), 7.51 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.20, 50.98, 57.60, 128.28, 131.04, 132.83, 133.20, 138.38, 144.61; LRMS (EI) m/z 299 (M^+, 10.3), 174 (100); HRMS (EI) calcd for $C_{13}H_{18}NClO_3Si$ 299.0744, found 299.0737.

Cross-coupling of 1-(3,4-dimethylphenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane with 4-iodoacetophenone (Scheme 3). A mixture of $Pd(OAc)_2$ (0.1 mmol), PPh_3 (0.2 mmol), 1-(3,4-dimethylphenyl)-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane (2.0 mmol), 4-

iodoacetophenone (1.0 mmol), and DMF (10 ml) was stirred at r.t. for 10 min. 1.0 M TBAF in THF (2.0 mmol) was added and the resulting mixture was stirred at 90 °C for 2 h. Isolation by column chromatography over silica gel gave an analytically pure sample.

4-(3,4-Dimethylphenyl)acetophenone 4.



4

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3 H), 2.35 (s, 3 H), 2.63 (s, 3 H), 7.24 (t, *J* = 6.6 Hz, 1 H), 7.38 (dd, *J* = 2.0 and 7.8 Hz, 1 H), 7.42 (d, *J* = 1.5 Hz, 1 H), 7.67 (dt, *J* = 2.0 and 8.3 Hz, 2 H), 8.02 (dt, *J* = 2.0 and 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.48, 19.90, 26.61, 124.59, 126.92, 128.43, 128.84, 130.22, 135.50, 136.89, 137.16, 137.38, 145.84, 197.74; HRMS (EI) calcd for $C_{16}H_{16}O$ 224.1201, found 224.1199.

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