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The Reaction of N-Phenylsulfonimidoyl Chloride with Trimethylsilylethene. A New Route to 2-Alkenylanilines

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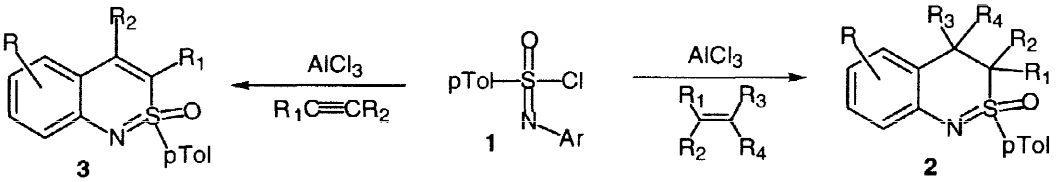
Summary: N-Phenylsulfonimidoyl chloride reacts with trimethylsilylethene in the presence of aluminum chloride to give two product benzothiazines, one of which has been desilylated. The silylated benzothiazine can be deprotonated and alkylated, sometimes with very high diastereocontrol. Upon treatment with fluoride, these silylated benzothiazines undergo desilylation with concomitant cleavage of the carbon-sulfur bond to give 2-alkenylsulfinanilides which can be hydrolyzed to the corresponding anilines. © 1998 Elsevier Science Ltd. All rights reserved.

Anilines which are substituted at the 2-position are valuable materials for the construction of a number of different classes of compounds. In particular, 2-alkenylanilines have been converted to indoles by means of a palladium-catalyzed cyclization process.[1] They have also served as precursors for the preparation of quinolines and cinnolines.[2] They have appeared as intermediates in a number of total syntheses of natural products.[3] The synthesis of 2-alkenylanilines is thus of great import. Several approaches have been introduced for their preparation but newer methods of increased generality are necessary to facilitate a wider range of substitution patterns and functionality on the target compounds.



Equation 1

We have been engaged in a study of the chemistry of benzothiazines (**2** and **3**) produced by the Lewis acid mediated reaction of sulfonimidoyl chlorides with alkenes or alkynes (equation 1). We have already demonstrated that such compounds can be converted to 2-alkylanilines through a reductive desulfurization procedure[4] and have developed two methods for the preparation of 2-alkenylanilines.[5] By virtue of the high regioselectivity associated with the formation of benzothiazines **2** and **3**, the anilines are produced cleanly as single regioisomers. Further, we recently introduced a new synthesis of 2-allylanilines[6] and have demonstrated the direct conversion of certain benzothiazines to indoles.[5a]

As part of a study involving steric effects in the synthesis of benzothiazines such as **2**, we treated **1a** with

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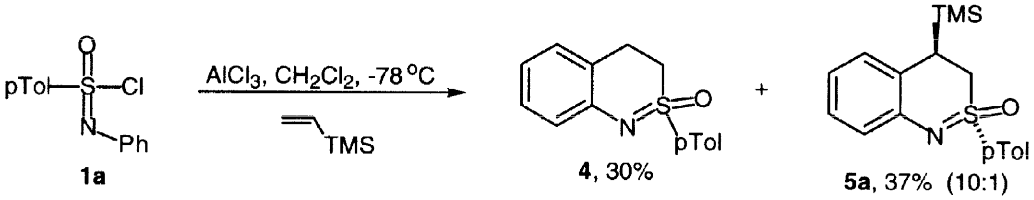
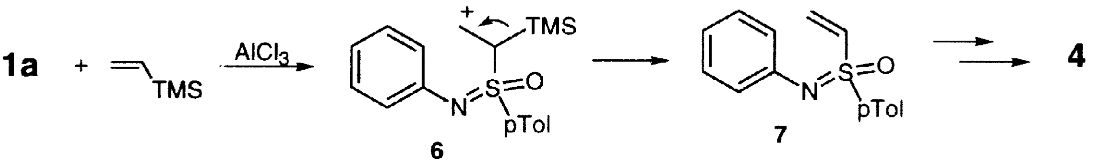
trimethylsilylethene in the presence of aluminum chloride (equation 2). Three products were obtained: the non-silylated benzothiazine **4** as well as the silylated product **5a** and its epimer **5b**. Attempts to convert **5a** into **4** were not successful[7] and it appears that **4** must be derived via a path independent of that leading to **5**. A plausible mechanism for the formation of **4** is shown in Scheme 1. In this case the regioselectivity of the process is guided by the carbocation-stabilizing ability of silicon (β-effect).[8] Thus, the reactive species derived from **1a** and Lewis acid leads to **6** upon reaction with trimethylsilylethene. Desilylation then leads to **7**, which closes under Lewis acid catalysis. This mechanism remains to be rigorously established. Presumably, steric effects are in opposition to electronic effects leading to the formation of a considerable amount of **4**. Interestingly, **5a** is formed highly diastereoselectively, for reasons which are still unclear. However, it is important to note that the reaction of t-butylethene with **1** affords t-butylated products analogous to **5a/b** but with a 4:1 ratio of diastereomers.[9]



Equation 2

The stereochemistry of the minor isomer **5b** was established by X-ray diffraction.[10] The major isomer **5a** is shown in equation 2. Optimization studies have led to increased yields of **5a** and **5b**. In the best case developed thus far, the reaction of **1a** with trimethylsilylethene in the presence of 1.2 equivalents of tin tetrachloride resulted in the formation of **5a**, **5b** and **4** in 55%, 6% and 18% yield, respectively.



Scheme 1

Even before having found a route to **5a** that proceeds in reasonable yield, we examined the alkylation of **5a**, in anticipation of the elimination process designed to lead to 2-alkenylanilines (Table 1). Treatment of **5a** with n-BuLi in THF at -78 °C followed by addition of an electrophile and slow warming led after work-up to the alkylation products **8**-**14** as mixtures of diastereomers in fair to good yields. When methyl iodide was the electrophile, the alkylation proceeded with very high stereoselectivity to give **8** as a 25:1 mixture of diastereomers as determined by ^1H NMR analysis of the crude reaction mixture. The structure of the major isomer was determined by X-ray analysis.[11] The other alkylation products were characterized as mixtures and the stereochemistry of the major isomer was assigned based on analogy to the methyl iodide case.

The desilylation step was essentially the same as that used for our allylaniline synthesis.[6] Thus, treatment of

5a and **8-14** with tetrabutylammonium fluoride in THF at room temperature resulted in an elimination reaction to produce 2-alkenylsulfinanilides in good yield. The results are collected in Table 2. If the elimination process were concerted and if the general stereochemical assignments associated with **8-14** are correct, one would expect a preponderance of the Z isomer of the sulfinanilide, as is observed. It is important to note, however, that the stereochemistry of the starting materials in this step is not generally reflected in the stereoisomer distribution of the products. It would thus appear that an intermediate intervenes which lacks stereochemical integrity. For

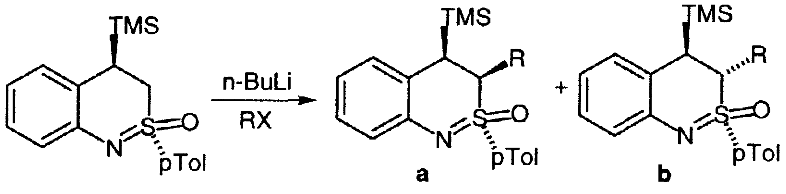


Table 1. Alkylation of Benzothiazine 5a

Entry	RX	Product	Yield (%)[a]	Ratio (a:b)[b]
1	MeI	**8**	88	25:1
2	EtBr	**9**	67	2:1
3	allyl bromide	**10**	89	4.6:1
4	benzyl bromide	**11**	87	4.9:1
5	MEM-Cl	**12**	63	3.7:1
6	4-bromobenzylbromide	**13**	55	2.5:1
7	4-[2-(5-Methylfuryl)]-4-methyliodopentane	**14**	87	1.5:1

[a]After chromatographic purification. [b]Based on ^1H NMR of the crude reaction mixture.

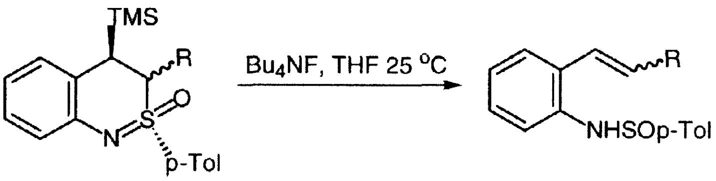


Table 2. Formation of 2-Alkenylsulfinanilides

Entry	Educt	R	Ratio[a]	Product	Yield (%)[b]	Ratio (E:Z)[c]
1	**5a**	H	NA	**5'**	95	NA
2	**8**	Me	99:1	**8'**	88	1:13.4
3	**9**	Et	1:1	**9'**	67	1:6.2
4	**10**	allyl	6.8:1	**10'**	74	1:11.5
5	**11**	benzyl	16.6:1	**11'**	82	only Z
6	**12**	MEM	2.6:1	**12'**	63	1:2.8
7	**13**	4-bromobenzyl	17:1	**13'**	55	only Z
8	**14**	4-[2-(5-methylfuryl)]-4-methylpentyl	2:1	**14'**	87	1:5.6

[a]Ratio of a/b isomers as depicted in Table 1. The tentative stereochemical assignment of these benzothiazines places the "R" group in the β orientation for the major "a" isomer. See the text. [b]After chromatographic purification. [c]Based on ^1H NMR of the crude reaction mixture.

example, formation of a benzylic carbanion which can eliminate via two stereochemically unique pathways would account for the loss in stereochemistry. It may be the case that two competing mechanisms produce product, or that the carbanion preferably eliminates to give the Z-isomer of the sulfinanilide. Our prior work lends some support to the latter idea.[5a] We found that treatment of **9a** with fluoride resulted in the formation of sulfinanilides **9'** as a 3:1 mixture of Z/E isomers in 73% yield. On the other hand, **9b** afforded an 18:1 mixture of the same Z/E isomers in 62% yield.

The stereochemistry of the sulfinanilides was established by ^{1}H NMR. For example, for (*Z*)-**8'** the coupling constant between the olefinic hydrogens for the major isomer was 11.2 Hz while that for the minor isomer was 15.6 Hz. Further, the chemical shift of the methyl groups for the major and minor isomers were 1.65 and 1.84 ppm, respectively. Earlier work in our group indicated that the upfield shift in the methyl group corresponds to a cis relationship to the aryl ring and thus overall Z stereochemistry.[5a] Other compounds were assigned analogously.

Basic hydrolysis of the sulfinanilides to give the corresponding anilines proceeded in reasonable yield as shown in Table 3. In some cases it appeared that the stereochemistry of the alkenylsulfinanilides was not retained during their basic hydrolysis to anilines. We have demonstrated that this is not due to loss of configuration during the hydrolysis process since careful, small scale hydrolysis reactions with both pure (*Z*)-**9'** and a 2:1 E/Z mixture of **9'** gave anilines with olefin configurations essentially the same as the corresponding sulfinanilides. We believe that either the loss of compound possessing a particular configuration or simply the inaccuracy associated with using intergration of NMR spectra to determine stereoisomer ratios may be responsible for the variance.

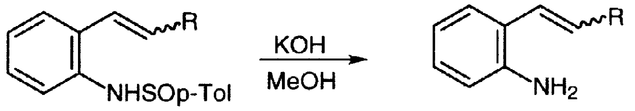


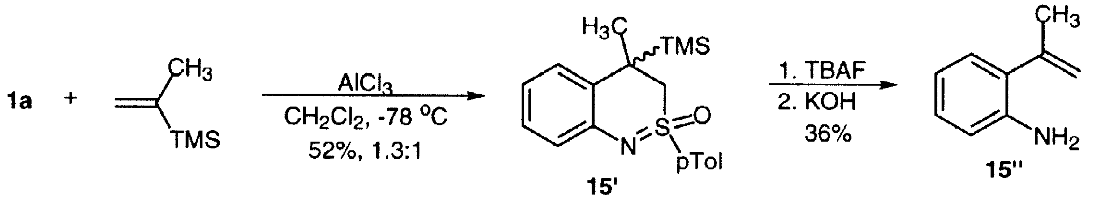
Table 3. Hydrolysis of 2-Alkenylsulfinanilides

Entry	Educt	R	Ratio (E:Z)[c]	Product	Yield (%)[b]	Ratio (E:Z)[c]
1	**5'**	H	NA	**5"**	71	NA
2	**8'**	Me	1:14.3	**8"**	63	1:11.4
3	**9'**	Et	1:6.2	**9"**	84	1:7.9
4	**10'**	allyl	1:6.2[d]	**10"**	55	d
5	**11'**	benzyl	only Z	**11"**	79	only Z
6	**12'**	MEM	1:3.1	**12"**	80	1:3.4
7	**13'**	4-bromobenzyl	only Z	**13"**	66	only Z
8	**14'**	4-[2-(5-methylfuryl)]-4-methylpentyl	1:5.6	**14"**	71	1:3.8

[a] Based on ^{1}H NMR analysis of the starting material. Ratio of a/b isomers as depicted in Table 1. The tentative stereochemical assignment of these benzothiazines places the "R" group in the β orientation for the major "a" isomer. See the text. [b] After chromatographic purification. [c] Based on ^{1}H NMR of the crude reaction mixture. [d] Not determined.

Finally, we have investigated in a preliminary fashion the reaction of 2-trimethylsilylpropene with **1a**. The Lewis acid mediated cyclization leads to benzothiazine **15'** in 52% yield. Treatment with fluoride and hydrolysis gives the aniline **15''** in 36% yield (Scheme 2). The optimization and scope of this process and reactions with more complex alkenylsilanes remain to be investigated.

In summary, we have demonstrated that benzothiazine **5a** is a useful starting material for a convenient synthesis of 2-alkenylanilines. The major problem with respect to this chemistry lies in the fair yield of **5a**, though its synthesis is fairly straightforward.



Scheme 2

Experimental Section

All air and moisture-sensitive reactions were carried out in flame-dried or oven-dried (at 120 °C) glassware under an inert atmosphere of nitrogen. All reactive liquid reagents were transferred by syringe or cannula and were added into the flask through a rubber septum. Methylene chloride was freshly distilled from CaH_2 prior to use. Tetrahydrofuran was distilled from sodium and benzophenone ketyl immediately prior to use. Methanol was distilled over magnesium methoxide prior to use. All other reagent grade solvents, hexanes, ethyl acetate etc., were distilled prior to use. Melting points were obtained on a Fisher-Johns Hot Stage melting point apparatus and are uncorrected. X-ray data were obtained on an Enraf-Nonius CAD-4 diffractometer. Elemental analysis for new compounds were performed by MHW labaratories, Phoenix, AZ. All analytical samples were either distilled, recrystallized or chromatographed using HPLC grade solvents before submitting them for elemental analysis.

Both ^1H and ^{13}C spectra were obtained on a Bruker AMX-500 and AMX-250 at 500, 250 MHz and 125, 62.9 MHz, respectively. All NMR spectra were obtained as a solution in $CDCl_3$ with TMS as the internal standard unless otherwise stated.

In the cases where mixtures of isomers were characterized, ^1H and ^{13}C spectra were reported as in the following sense. In the case of a major isomer in the presence of a small amount of a minor isomer, ^1H and ^{13}C NMR data were reported for only the major isomer. However, for the case of mixtures where the data were available for the both of the isomers, each signal and coupling constants for ^1H NMR spectra were located as accurately as possible, but ^{13}C spectra were reported for the mixture of isomers without any attempt to assign peaks.

Infrared spectra were obtained on a Nicolet 20DXB FTIR spectrometer either as a neat liquid with NaCl cells or in KBr pellets.

Analytical Thin Layer Chromatography (TLC) was performed on Merck silica gel plates (Merck Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Compounds were visualized under UV lamp or by developing in iodine, vanillin or phosphomolybdic acid followed by heating on a hot plate at 250-300 ^{o}C. Flash chromatography was performed on 230-400 mesh silica gel (Merck Kieselgel 60) with technical grade solvents that were distilled prior to use.

N-phenyl-sulfinamide was prepared as reported in the literature.[12] All other chemicals (trimethylsilylethene, $AlCl_3$, aniline, etc.) were obtained from commercial sources.

(±)-(2S*,4R*)-3,4-Dihydro-2-(4-methylphenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (5a), (±)-(2S*,4S*)-3,4-Dihydro-2-(4-methylphenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (5b) and (±)-3,4-Dihydro-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine-2-oxide (4). A flame-dried 100 mL recovery flask equipped with a magnetic stir bar, a septum and a nitrogen balloon was charged with 2.33 g (10 mmol, 1 eq.) of N-phenyl-p-toluenesulfinamide and 50 mL dry CH_2Cl_2 to give a 0.2 M solution. This solution was cooled down to -78 ^{o}C in an isopropanol/dry ice bath. *Tert*-butyl hypochlorite (1.25 ml, 10.5 mmol, 1.05 eq.) was added via a syringe over 5 min. A white precipitate formed and the solution turned yellow after 10 min. Upon completion, trimethylsilylethene (11 mmol, 1.1 eq.) was added into this solution via a syringe. The solution was allowed to stir for 5-10 min, followed by the addition of 2.09 g (20 mmol, 2 eq.) of powdered $AlCl_3$ in three portions over a 15 min. time period. The color of the solution turned to brown immediately. The mixture was allowed to stir at -78 ^{o}C for an hour. It was quenched with 10 mL of 1N HCl and diluted with 30 mL ethyl acetate in a separatory funnel. The organic layer was then washed with water (3x30 mL) and brine solution (1x30 mL), dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure on a rotary evaporator to give the product as light brown solid which was purified by flash chromatography (hexanes/ethyl acetate, 9:1) to give **5a**, **5b**, and **4** as white solids. Data for **5a**: yield: 37%. Recrystallization from hexane/ethyl acetate gave an analytical sample of **5a**. mp 132-133 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.86 (d, 2H, J = 8.2 Hz), 7.33 (d, 2H, J = 8.2 Hz), 7.17-7.06 (m, 2H), 6.97 (d, 1H, J = 6.7 Hz), 6.86 (dt, 1H, J = 1.2, 7.2 Hz), 3.56 (dd, 1H, J = 3.2, 12.6 Hz), 3.14 (dd, 1H, J = 6.6, 12.6 Hz), 2.78 (dd, 1H, J = 3.1, 6.5 Hz), 2.44 (s, 3H), 0.17 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz), 144.8, 144.8, 136.7, 129.8, 128.7, 127.6, 126.7, 123.7, 123.3, 120.1, 49.3, 28.4, 21.5, -1.8. IR(KBr) 3064 (s), 3054 (s), 1595 (m), 1305 (s), 1295 (s), 1277 (s), 1239 (s), 1210 (s), 1181 (s), 1120 (s), 1096 (s), 1082 (s), 1044 (s), 1010 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{23}NOSSi$: C, 65.61; H, 7.04. Found: C, 65.43; H, 6.94.

Compound **5b** (3.7%) was recrystallized from hexanes and ethyl acetate to give an analytical sample. mp 129-130 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.96 (d, 2H, J = 8.2 Hz), 7.38 (d, 2H, J = 8.2 Hz), 7.27-7.17 (m, 2H), 7.08 (dd, 1H, J = 1.4, 8.0 Hz), 6.86 (dt, 1H, J = 1.4, 7.5 Hz), 3.35 (dd, 1H, J = 4.0, 12.1 Hz), 3.06 (dd, 1H, J = 3.9, 15.0 Hz), 2.73 (dd, 1H, J=12.1 Hz, 15.0 Hz), 2.46 (s, 3H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.9, 144.8, 135.2, 129.9, 129.1, 128.2, 127.4, 124.4, 123.3, 120.0, 49.0, 22.3, 21.6, -1.2. IR (KBr) 1595 (s), 1499 (s), 1471 (s), 1442 (s), 1306 (s), 1270 (s), 1252 (s), 122 (s), 1011 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{23}NOSSi$: C, 65.61; H, 7.04. Found: C, 65.87; H, 6.80.

Compound **4** was obtained in 30% yield after chromatography and was recrystallized from hexanes and ethyl acetate to give an analytical sample. mp 94-95 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.93 (d, 2H, J = 8.2 Hz), 7.37 (d, 2H, J = 8.2 Hz), 7.21 (dt, 1H, J = 1.3, 7.6 Hz), 7.08 (dd, 1H, J = 1.1, 8.0 Hz), 7.06 (d, 1H, J = 7.5

Hz), 6.88 (dt, 1H, J = 1.3 Hz, J=7.4 Hz), 3.45-3.36 (m, 2H), 3.16 (ddd, 1H, J = 5.0, 5.9, 16.8 Hz), 3.05 (dt, 1H, J = 4.8, 12.7 Hz), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.2, 144.9, 135.5, 120.0, 129.0, 128.5, 128.3, 123.4, 120.9, 120.3, 46.2, 24.7, 21.6. IR (Neat) 1595 (m), 1477 (s), 1448 (s), 1305 (s), 1295 (s), 1239 (s), 1210 (s), 1120 (s), 1096 (s), 1082 (s), 1044 (s), 1023 (m), 1010 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; Found: C, 69.86; H, 5.97.

Optimized Procedure for the Preparation of 5a. A flame-dried 15 mL flask equipped with a magnetic stir bar, septum and a nitrogen balloon was charged with N-phenyl-p-toluenesulfinamide (0.30 g,1.30 mmol, 1 eq) and dry CH_2Cl_2 (6 mL) to give a ca. 0.20 M solution. The solution was cooled down to -78 °C in an isopropanol/dry ice bath. *Tert*-butyl hypochlorite (0.182 mL, 1.60 mmol, 1.25 eq) was added dropwise via a syringe. On addition of the hypochlorite the solution turned yellow in color. The reaction was monitored by TLC and upon completion (ca. 7 min.), the solution was concentrated on a rotary evaporator at 0 °C and dried on a vacuum line for about 10 min. to afford **1a** as a bright yellow solid. The sulfonimidoyl chloride was immediately treated as follows. The flask containing the sulfonimidoyl chloride was equipped with a septum and a nitrogen balloon and charged with CH_2Cl_2 (6 mL) to give an approximate 0.20 M solution. Trimethylsilylethene (1.5 mmol, 1.2 eq) was then added and the solution was cooled to -78 °C in an isopropanol/dry ice bath. $SnCl_4$ (1.5 mmol, 1.2eq) was added dropwise over 5 min. Upon addition of the Lewis acid the solution turned from bright yellow to a brown color. The reaction was allowed to stir at -78 °C and was monitored by TLC. Upon completion the reaction was quenched with 1N HCl solution (10 mL)and diluted with CH_2Cl_2 (20 mL) in a separatory funnel. The organic phase was washed with water (1x10 mL) and brine (1x10 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by flash chromatography to afford the product benzothiazines **5a**, **5b** and **4** in 55%, 6% and 18% yield, respectively.

General Procedure for Alkylation of Benzothiazine 5. Preparation of (±)-(2S*,3R*,4R*)-3,4-Dihydro-3-methyl-2-(4-methylphenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (8a) and (±)-(2S*,3S*,4R*)-3,4-Dihydro-3-methyl-2-(4-methylphenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (8b). A 5 mL flame-dried recovery flask equipped with a magnetic stir bar, an N_2 balloon and a septum was charged with 0.1 g of benzothiazine **5a** (0.3 mmol) with 1.5 mL of dry THF. The solution was cooled down to -78 °C in a dry ice/isopropanol bath and allowed to stir for 15-20 min. nBuLi (0.139 mL, 0.33 mmol, 2.4M solution in hexanes) was then added via a syringe slowly over 5 min. The resulting yellow solution was stirred for 15 minutes and iodomethane (0.33 mmol) was added. After stirring for 30 min. at -78 °C, the mixture was slowly warmed up to room temperature. The reaction was quenched by addition of brine. The mixture was rinsed into a separatory funnel and extracted with Et_2O (3x25 mL) and the combined organic layers were washed with water and brine, dried over Na_2SO_4. The solvent was removed on a rotary evaporator to give the crude product. The ratio of isomers was determined by ^{1}H NMR of the crude reaction mixture. Flash chromatographic purification with hexanes/ethyl acetate (4:1) gave **8a/b** as a solid, which recrystallized from hexane and ethyl acetate to afford an analytical sample. Yield: 88%. Data for **(8a):** mp 132-134 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, 2H, J = 8.3 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.17 (dt, 1H, J = 1.6, 7.8 Hz), 7.10 (dd, 1H, J = 1.2, 7.9 Hz), 6.95 (d, 1H, J = 6.6 Hz), 6.85 (dt, 1H, J = 1.3, 7.3 Hz), 3.33-3.31 (m, 1H), 2.62 (d, 1H, J = 4.7 Hz), 2.46 (s, 3H), 1.44 (d, 3H, J = 7.0 Hz), 0.19 (s, 9H). ^{13}C

NMR (125 MHz, $CDCl_3$) δ 145.9, 144.3, 135.4, 129.8, 129.3, 127.7, 126.9, 122.6, 119.6, 55.9, 35.3, 21.5, 12.7, 0.0. IR (KBr) 1596 (s), 1489 (s), 1448 (s), 1318 (s), 1282 (s), 1253 (s), 1206 (s), 1123 (s), 1093 (s), 1075 (s), 1040 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{25}NOSSi$: C, 66.42; H, 7.33. Found: C, 66.45; H, 7.26.

(±)-(2S*,3R*,4R*)-3,4-Dihydro-3-ethyl-2-(4-methylphenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (9a) and (±)-(2S*,3S*,4R*)-3,4-Dihydro-3-ethyl-2-(4-methylphenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (9b). Flash chromatographic purification with hexane/ethyl acetate (4:1) gave an inseparable mixture of **9a** and **9b** as an oil. Yield: 67%. **(9a, Major)** ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, 2H, J = 8.0 Hz), 7.37-7.26 (m, 2H), 7.15-7.04 (m, 2H), 6.95-6.81 (m, 2H), 3.14-3.08 (m, 2H), 2.83 (m, 1H), 2.44 (s, 3H), 2.02-1.92 (m, 1H), 1.84-1.76 (m, 1H), 0.87 (t, 3H, J = 7.4 Hz), 0.17 (s, 9H). **(9b, Minor)** ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, 2H, J = 8.0 Hz), 7.37-7.26 (m, 2H), 7.15-7.04 (m, 2H), 6.95-6.81 (m, 2H), 3.24 (d, 1H, J = 7.8 Hz), 2.78 (d, 1H, J = 4.8 Hz), 2.46 (s, 3H), 1.27-0.96 (m, 2H), 0.69 (t, 3H, J = 7.3Hz), 0.17 (s, 9H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 144.6, 143.5, 133.6 130.2, 129.8, 129.6, 129.6, 128.4, 127.7, 126.9, 126.5, 122.9, 122.5, 121.2, 120.1, 119.6, 62.4, 57.2, 32.1, 32.0, 22.4, 21.6, 21.6, 19.6, 11.3, 10.5, 0.0, -1.2. IR (Neat) 1596 (s), 1484 (s), 1448 (s), 1319 (s), 1272 (s), 1201 (s), 1107 (s), 1048 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{27}NOSSi$: C, 67.18; H, 7.61. Found: C, 67.20; H, 7.71.

(±)-(2S*,3R*,4R*)-3,4-Dihydro-2-(4-methylphenyl)-3-(2-propenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (10a) and (±)-(2S*,3S*,4R*)-3,4-Dihydro-2-(4-methylphenyl)-3-(2-propenyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (10b). Flash chromatographic purification with hexane/ethyl acetate (6:1) gave **10a/b** as an oil. Yield: 89%. **(10a, major)** ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, 2H, J = 8.3 Hz), 7.26 (d, 2H, J = 8.3 Hz), 7.05-7.01 (m, 2H), 6.79-6.76 (m, 2H), 5.37-5.20 (m, 1H), 4.92 (d, 1H, J = 10.2 Hz), 4.70 (d, 1H, J = 17.0 Hz), 3.33-3.27 (m, 1H), 2.80 (d, 1H, J = 1.4 Hz), 2.34 (s, 3H), 1.82-1.60 (m, 2H), 0.09 (s, 9H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 144.5, 143.2, 133.0, 132.0, 129.9, 129.5, 128.4, 126.2, 122.7, 120.7, 120.1, 119.0, 54.3, 33.6, 31.8, 21.3, -1.4. IR (Neat) 1596 (s), 1477 (s), 1459 (s), 1278 (s), 1243 (s), 1204 (s), 1016 (s) cm^{-1}. Anal. Calcd for $C_{21}H_{27}NOSSi$: C, 68.24; H, 7.36. Found: C, 68.50; H, 7.32.

(±)-(2S*,3R*,4R*)-3,4-Dihydro-2-(4-methylphenyl)-3-(phenylmethyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (11a) and (±)-(2S*,3S*,4R*)-3,4-Dihydro-2-(4-methylphenyl)-3-(phenylmethyl)-4-(trimethylsilyl)-2λ^4-2,1-benzothiazine-2-oxide (11b). Flash chromatographic purification with hexane/ethyl acetate (4:1) gave **11a/b** in 87% yield. Upon recrystallization from hexanes and ethyl acetate, **11a** was obtained as a single isomer. mp 116-118 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, 2H, J=8.3 Hz), 7.38 (d, 2H, J = 8.1 Hz), 7.25-7.09 (m, 5H), 6.88 (dt, 1H, J = 1.3, 7.5 Hz), 6.82-6.79 (m, 3H), 3.55 (ddd, 1H, J = 1.58 Hz, J = 5.7, 9.6 Hz), 2.54 (d, 1H, J = 1.4 Hz), 2.46 (s, 3H), 2.28-2.24 (m, 2H), 0.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 144.8, 143.4, 136.2, 133.4, 130.2, 129.8, 128.9, 128.8, 128.6, 126.9, 126.5, 123.0, 121.0, 120.5, 56.6, 35.5, 31.5, 21.6, -1.4. IR(KBr) 1603 (s), 1434 (s), 1447 (s), 1315 (s), 1279 (s), 1213 (s), 1128 (s), 1098 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{29}NOSSi$: C, 71.55; H, 6.97. Found: C, 71.79; H, 6.69.

(±)-(2S*,3R*,4R*)-3,4-Dihydro-3-(2-methoxyethoxymethyl)-2-(4-methylphenyl)-4-

(trimethylsilyl)-$2\lambda^4$-2,1-benzothiazine-2-oxide (12a) and (±)-(2S*,3S*,4R*)-3,4-Dihydro-3-(2-methoxyethoxymethyl)-2-(4-methylphenyl)-4-(trimethylsilyl)-$2\lambda^4$-2,1-benzothiazine-2-oxide (12b). Flash chromatographic purification with hexane/ethyl acetate (1:1) gave **12a/b** as an inseparable mixture of isomers in 63% yield. (**12a, major**) ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.76 (d, 2H, J = 8.0 Hz), 7.33-7.24 (m, 2H), 7.14-7.03 (m, 2H), 6.94-6.83 (m, 2H), 3.95-3.87 (m, 2H), 3.54-3.51 (m, 1H), 3.41-3.39 (m, 2H), 3.32-3.25 (m, 1H), 3.25 (s,3H), 3.05-2.95 (m, 1H), 2.86 (d, 1H, J = 4.9 Hz), 2.42 (s, 3H), 0.14 (s, 9H). ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 145.5, 144.2, 136.2, 129.6, 129.5, 127.8, 126.9, 126.5, 122.4, 119.8, 71.5, 70.3, 67.7, 60.5, 58.9, 31.6, 21.5, -0.2. IR (Neat) 1294 (s), 1248 (s), 1106 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{31}NO_3SSi$: C, 62.49; H, 7.24. Found: C, 62.62; H, 7.41.

(±)-(2S*,3R*,4R*)-3-(4-Bromophenylmethyl)-3,4-dihydro-2-(4-methylphenyl)-4-(trimethylsilyl)-$2\lambda^4$-2,1-benzothiazine-2-oxide (13a) and (±)-(2S*,3S*,4R*)-3-(4-Bromo phenylmethyl)-3,4-dihydro-2-(4-methylphenyl)-4-(trimethylsilyl)-$2\lambda^4$-2,1-benzothiazine-2-oxide (13b). Flash chromatographic purification with hexane/ethyl acetate (4:1) gave a inseparable mixture of **13a/b**. Yield 55%. (**13a, major**) ^{1}H NMR (250 MHz, CDCl$_3$) δ 8.00 (d, 2H, J = 8.1 Hz), 7.37 (m, 4H), 7.18-7.11 (m, 2H), 6.90-6.79 (m, 2H), 6.70 (d, 2H, J = 8.1 Hz), 3.51 (dd, 1H, J = 4.4, 6.4 Hz), 2.48 (s, 3H), 2.47 (d, 1H, J = 15.3 Hz), 2.27-2.20 (m, 2H), 0.08 (s, 9H). ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 145.0, 143.4, 135.3, 133.3, 131.8, 130.6, 130.2, 129.9, 128.7, 126.7, 123.1, 120.9, 120.8, 120.6, 56.3, 35.0, 31.6, 21.6, -1.3. IR (Neat) 1497 (s), 1474 (s), 1271 (s), 1249 (s), 1209 (s), 1108 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{27}BrNOSSi$: C, 60.23; H, 5.66. Found: C, 60.46; H, 5.64.

(±)-(2S*,3R*,4R*)-3,4-Dihydro-3-[4-methyl-4-[2-(5-methylfuryl)pentyl]-2-(4-methylphenyl)-4-(trimethylsilyl)-$2\lambda^4$-2,1-benzothiazine-2-oxide (14a) and (±)-(2S*,3S*,4R*)-3,4-Dihydro-3-[4-methyl-4-[2-(5-methylfuryl)pentyl]-2-(4-methylphenyl)-4-(trimethylsilyl)-$2\lambda^4$-2,1-benzothiazine-2-oxide (14b). Flash chromatographic purification with hexane/ethyl acetate (4:1) gave an inseparable mixture of **14a/b** in 87% yield. **(14a, major)** ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.89 (d, 2H, J = 8.3 Hz), 7.35-7.29 (m, 2H), 7.12-7.08 (m, 2H), 6.90-6.85 (m, 2H), 5.80-5.75 (m, 2H), 3.28 (ddd, 1H, J = 1.6, 4.1, 9.5 Hz), 2.68 (d, 1H, J = 4.9 Hz), 2.45 (s, 3H), 2.20 (s, 3H), 1.94-1.81 (m, 1H), 1.77-1.50 (m, 1H), 1.30-1.10 (m, 4H), 1.06 (s, 3H), 1.05 (s, 3H), 0.14 (s, 9H). **(14b, minor)** 7.76 (d, 2H, J = 8.3 Hz), 7.35-7.29 (m, 2H), 7.12-7.08 (m, 2H), 6.90-6.85 (m, 2H), 5.69-5.67 (m, 2H), 3.16-3.04 (m, 1H), 2.63 (d, 1H, J = 4.9 Hz), 2.43 (s, 3H), 2.20 (s, 3H), 1.43-1.35 (m, 1H), 1.32-1.30 (m, 1H), 1.0-0.6 (m, 4H), 1.13 (s, 3H), 1.11 (s, 3H), 0.10 (s, 9H). ^{13}C NMR (CDCl$_3$, 62.9 MHz) δ 160.5, 160.4, 150.1, 145.0, 144.6, 144.5, 143.6, 133.6, 130.2, 129.8, 129.6, 128.4, 127.6, 126.9, 126.4, 122.8, 122.5, 121.2, 120.1, 119.5, 105.4, 104.65, 103.8, 55.4, 41.3, 40.9, 35.4, 35.3, 33.1, 32.3, 29.7, 27.0, 26.8, 26.5, 26.4, 26.4, 21.6, 21.5, 21.0, 13.5, -0.1, -1.2. IR (Neat) 1592 (s). 1572 (s), 1484 (s), 1319 (s), 1272 (s), 1201 (s), 1107 (s), 1048 (s), 1007 (s), 854 (s) cm^{-1}. Anal. Calcd for $C_{29}H_{39}NO_2SSi$: C, 70.54; H, 7.96. Found: C, 70.38; H, 7.91.

(±)-(2S*,4R*)-3,4-Dihydro-4-methyl-2-(4-methylphenyl)-4-(trimethylsilyl)-$2\lambda^4$-2,1-benzothiazine-2-oxide (15a) and (±)-(2S*,4S*)-3,4-Dihydro-4-methyl-2-(4-methylphenyl)-4-(trimethylsilyl)-$2\lambda^4$-2,1-benzothiazine-2-oxide (15b). Flash chromatographic purification with hexane/ethyl acetate (4:1) gave **15** in 52% yield. Recrystallization from hexanes and ethyl acetate gave an analytical sample. mp 93-95 °C. **(15a, major)** ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.84 (d, 2H, J = 8.3 Hz), 7.31 (d, 2H, J = 8.3 Hz), 7.16-7.07 (m, 3H), 6.94 (m, 1H), 3.50 (d, 1H, J = 13.0 Hz), 2.82 (d,1H, J = 13.0 Hz), 2.42 (s, 3H), 1.46 (s, 3H), 0.14 (s, 9H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 145.0, 144.4, 137.4, 129.8,128.6, 128.5, 126.8, 124.6, 123.3, 120.4, 56.6, 28.4, 23.8, 21.5, -2.6. IR (KBr) 1596 (s), 1575 (s), 1489 (s), 1448 (s), 1318 (s), 1282 (s), 1253 (s), 1206 (s), 1123 (s), 1093 (s), 1075 (s), 1040 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{25}NOSSi$: C, 66.43; H, 7.33. Found: C, 66.58; H, 7.39.

General Procedure for the Desilylation of Benzothiazines. A 5 mL flame-dried recovery flask equipped with a magnetic stir bar, an N_2 balloon and a septum was charged with 50 mg of benzothiazine **8** (0.14 mmol) and dissolved in 0.73 mL of dry THF. To this solution, tetrabutylammonium fluoride (0.16 mmol, 0.159 mL, 1.0 M solution in THF was added via a syringe at room temperature. After stirring for 1 hour at room temperature, the solution turned yellow. The reaction was quenched by addition of water. The mixture was rinsed into a separatory funnel and extracted with Et_2O (3x25 mL) and the organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed on a rotary evaporator to give the crude product. The crude product was filtered through a small plug of silica gel and the conversion was confirmed by ^{1}H and ^{13}C NMR. These sulfinanilides were carried on to the next step without further characterization.

General Procedure for the Hydrolysis of Sulfinanilides. A 5 mL flame-dried recovery flask equipped with a magnetic stir bar, an N_2 balloon and a septum was charged with 80 mg of sulfinanilide **8'** (0.29 mmol) and 2.95 mL of dry MeOH. KOH (41 mg, 0.74 mmol) was added and the mixture was allowed to stir at room temperature for 12 to 24 hours. The reaction was quenched by addition of water. The mixture was rinsed into a separatory funnel and extracted with Et_2O (3x10 mL) and the combined organic layers were washed with water and brine, and dried over Na_2SO_4. The solvent was removed on a rotary evaporator to give the crude product. The crude product was purified by flash chromatography to afford the aniline.

(Z)-2-(prop-1-enyl)aniline (8''). Flash chromatographic purification with hexane/ethyl acetate (9:1) gave **8''**as an oil. An analytical sample was obtained after several flash chromatographies. Yield: 63%. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.05 (d, 2H, J = 7.5 Hz), 6.72 (dd, 2H, J = 1.0, 7.6 Hz), 6.30 (dd, 1h, J = 1.4, 11.2 Hz), 5.93-5.81 (m, 1H), 3.65 (s, 2H, br), 1.73 (dd, 3H, J=1.8, 6.9 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 143.9, 129.8, 128.8, 127.8, 125.9, 122.9, 118.0, 115.1, 14.4. IR (Neat) 2955 (s), 2938 (s), 2879 (s), 1611 (s), 1499 (s), 1458 (s) cm^{-1}. Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32. Found: C, 81.15; H, 8.16.

(Z)-2-(but-1-enyl)aniline (9''). Flash chromatographic purification with hexane/ethyl acetate (9:1) gave **9''** as an oil. An analytical sample was obtained after several flash chromatographies. Yield: 84%. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.11-7.04 (m, 2H), 6.77-6.69 (m, 2H), 6.26 (d, 1H, J = 11.3 Hz), 5.83-5.73 (m, 1H), 3.67 (s, 2H, br), 2.17 (dq, 2H, J = 1.6, 7.4 Hz), 1.01 (t, 3H, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 143.9, 136.5, 129.7, 127.9, 124.3, 123.3, 118.0, 115.1, 22.0, 14.3. IR (Neat) 2956 (s), 2938 (s), 2879 (s), 1611 (s), 1499 (s), 1458 (s) cm^{-1}. Anal. Calcd For $C_{10}H_{13}N$: C, 81.59; H, 8.90. Found: C, 81.50; H, 8.87.

(Z)-2-[(3-phenyl)prop-1-enyl] aniline (11''). Flash chromatographic purification with hexane/ethyl acetate (9:1) gave **11''**as an oil. An analytical sample was obtained after several flash chromatographies. Yield:

89%. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.31-7.06 (m, 7H), 6.77-6.64 (m, 2H), 6.43 (d, 1H, J = 11.0 Hz), 6.02-5.92 (m, 1H), 3.70 (s, 2H, br), 3.50 (d, 2H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 144.1, 140.6, 132.8, 129.6, 128.5, 128.3, 128.2, 127.6, 126.0, 122.7, 118.1, 115.2, 34.7. IR (Neat) 1623 (s), 1499 (s), 1460 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22. Found: C, 86.00; H, 7.07.

(Z)-2-(4,7-dioxaoct-1-enyl)aniline (12''). Flash chromatographic purification with hexane/ethyl acetate (1:1) gave **12''**as an oil. An analytical sample was obtained after several flash chromatographies. Yield: 80%. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.08 (dt, J = 1.4, 7.7 Hz), 6.96 (d, 1H, J = 7.4 Hz), 6.75-6.67 (m, 2H), 6.49 (d, 1H, J = 11.4 Hz), 6.01-5.91 (m, 1H), 4.15 (dd, 1H, J = 1.5, 6.5 Hz), 3.70 (s, 2H, br), 3.58-3.49 (m, 4H), 3.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 144.0, 130.3, 129.8, 128.6, 127.9, 122.1, 118.0, 115.2, 71.9, 69.6, 68.0, 59.0. IR (Neat) 3476 (w), 3370 (m), 2995 (w), 2925 (m), 2878 (s), 1625 (s), 1496 (s), 1455 (s), 1315 (w), 1145 (m), 1098 (s), 1045 (w), 764 (m). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 68.37; H, 7.82. Found: C, 68.50; H, 7.90.

(Z)-2-[3-(4-bromophenyl)prop-1-enyl]aniline (13''). Flash chromatographic purification with hexane/ethyl acetate (9:1) gave **13''**as an oil. An analytical sample was obtained after several flash chromatographies. Yield: 66%. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.39 (d, 2H, J = 8.3 Hz), 7.18-7.03 (m, 4H), 6.73 (t, 2H, J = 7.5 Hz), 6.43 (d, 1H, J = 11.0 Hz), 5.96-5.86 (m, 1H), 3.63 (s, 2H, br), 3.44 (d, 2H, J = 6.0 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 132.0, 131.6, 131.5, 130.1, 129.5, 128.4, 127.7, 126.5, 119.8, 118.1, 115.9, 115.2, 34.1. IR (Neat) 1625 (s), 1486 (s), 1456 (s), 1016 (s), cm^{-1}. Anal. Calcd for $C_{15}H_{14}BrN$: C, 62.52; H, 4.9. Found: 62.77; H, 4.88.

(Z)-2-[6-methyl-6-[2-(5-methylfuryl)]hept-1-enyl]aniline (14''). Flash chromatographic purification with hexane/ethyl acetate (6:1) gave **14''**as an oil. An analytical sample was obtained after several flash chromatographies. Yield: 71%. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.07-7.01 (m, 2H), 6.76-6.67 (m, 2H), 6.26 (d, 1H, J = 11.3 Hz), 5.83-5.80 (m, 2H), 5.79-5.69 (m, 1H), 3.65 (s, 2H, br), 2.76 (d, 3H, J = 0.6 Hz), 2.15-2.06 (m, 2H), 1.61-1.52 (m, 2H), 1.28-1.25 (m,2H), 1.21 (s, 6H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 161.2, 149.8, 143.9, 134.7, 129.7, 127.8, 127.9, 124.7, 117.9, 115.0, 105.3, 103.6, 41.5, 35.8, 28.9, 26.8, 24.8, 13.5. IR (Neat) 2979 (s), 2942 (s), 2860 (s), 1624 (s), 1498 (s), 1019 (m), cm^{-1}. Anal. Calcd for $C_{19}H_{25}NO$: C, 80.52; H, 8.89. Found: C, 80.36; H, 8.64.

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7. Conditions tried included: (a) 5 eq. $AlCl_3$, CH_2Cl_2, - 78 ^oC, 1 h, (b) 12 eq. TsOH, THF, Reflux, 24 h, (c) 5 eq. TsOH, CH_2Cl_2, Reflux, 24 h, (d) 5 eq. TsOH, CH_3CN, reflux, 24 h, (e) 2.6 eq HF, CH_3CN, reflux, 24 h.
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10. Data for **5** (minor isomer): Formula: $C_{18}H_{23}NOSSi$; MW = 329.53 Space Group: P21/n; a = 12.250(2)Å, b = 10.969(3)Å, c = 13.343(3)Å; V = 1792.9(7)$Å^3$; Z = 4; Dcalc = 1.221 $Mg.m^{-3}$; mu = 2.22 mm^{-1}; F(000)=704; Radiation=CuKα (λ=1.54056Å); Temperature = 23(1)^oC; Final R=0.043 for 1502 reflections with $I>2.5\sigma(I)$.
11. Data for **8**: Formula: $C_{19}H_{25}NOSSi$; MW = 343.55 Space Group: P21/c; a = 7.874(8)Å, b = 19.436(3)Å, c = 25.159(3)Å; V = 3850(4)$Å^3$; Z = 8; Dcalc = 1.185 $Mg.m^{-3}$; mu = 2.09 mm^{-1}; F(000)=1472; Radiation=CuKα (λ=1.54056Å); Temperature = 23(1)^oC; Final R=0.045 for 4975 reflections with $I>2.5\sigma(I)$.
12. Prepared by a modification of a procedure reported by Asefi, H.; Tillett, J. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1579-1582.