# Amelioration of the Leaving Group Ability of the Aryl Sulfone Moiety via Intramolecular Oxygen Silylation[1]

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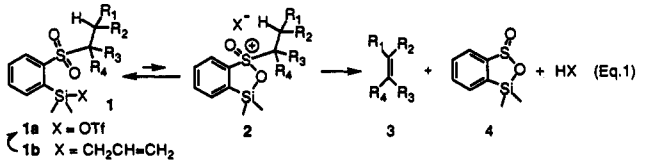
*Received December 13, 1993*®

**Abstract:** Phenyl sulfones bearing an ortho dimethylsilyl group capable of conversion to the aryldimethylsilyl triflate moiety display significantly enhanced leaving group ability relative to simple phenyl sulfones. Under mild acid catalyzed conditions, *ortho*-allyldimethylsilyl sulfone **1b** forms cyclic sultinium intermediate **2**, which readily eliminates to provide olefins and a previously unreported cyclic silyl sulfinate by-product, **4**. *ortho*-Allyldimethylsilyl aryl sulfones are easily prepared via *ortho*-allyldimethylsilyl mercaptide anion **5** and serve as the latent precursor of the activated silyltriflate intermediate. The sulfone elimination proceeds in high yield under mild conditions whether or not activated β-protons are present in the substrate. An attempt to effect intramolecular Friedel–Crafts alkylation via the interception of sultinium intermediate **17** resulted in formation of tricyclic olefin **22** as the major product.

## Introduction

Familiar synthetic applications which rely on the inductive effect of the aryl sulfone functional group include conjugate addition to vinyl sulfones and alkylation reactions of α-sulfonyl anions. Once having facilitated bond formation, the aryl sulfone moiety is often simply reductively removed.[2] More aggressive strategies which seek further functionalization can be seen to exploit the sulfone as a leaving group. Although olefin-forming reactions involving sulfinic acid elimination of aryl sulfones are known, these examples are all promoted by α-heteroatom substitution[3] or by allylic (π) activation of protons β to the sulfone.[4] To our knowledge, there are no examples of aryl sulfones lacking activated β-protons which eliminate in high yield under reasonable conditions.[5] This report describes an easily available aryl sulfonyl group capable of standard sulfone chemistry which undergoes elimination to olefin under mild acid catalyzed conditions.

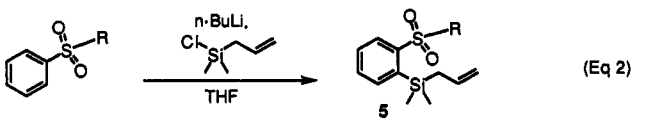
Trost and co-workers have demonstrated that Lewis acids can enhance the leaving group ability of certain phenyl sulfones and sulfoximines in intramolecular Friedel–Crafts reactions.[6] This led to the investigation of whether an electrophilic group placed *ortho* to the sulfone on the phenyl ring might act in a similar fashion, promoting sulfone ionization and subsequent elimination. We are pleased to report that certain silyl groups ortho to the sulfone undergo intramolecular oxygen silylation, forming a cyclic sultinium species **2** in equilibrium with the acyclic sulfone **1** (eq 1). Previous reports describing the intramolecular nucleophilic attack of sulfonyl oxygens have generally involved highly electrophilic carbon centers which were generated during electrophilic additions to carbon–carbon double bonds.[7] To our knowledge, this is the first example of a sulfonyl oxygen undergoing intramolecular nucleophilic attack on an electrophilic silicon center. The synthetic potential of silyl sultinium intermediates has never been explored.




## Results and Discussion

The sultinium intermediate **2** suffers bond cleavage under relatively mild conditions to give olefin products **3** in addition to the previously unknown cyclic silyl sulfinate by-product **4**. The elimination reaction has been examined with a variety of substituents on the silyl group (X = Cl, camphorsulfonate, triflate with relative rates of ~1:1:1500, respectively). Silyl triflates **1a** are easily generated from allylsilane precursors **1b** in the presence of triflic acid. Because of their relative stability, allylsilanes **1b** are employed as starting materials. The reaction only requires a catalytic amount of triflic acid since it is regenerated during the elimination step.

Ortho-silylation of phenyl sulfones bearing no acidic α-protons is accomplished by directed metalation followed by treatment with allyldimethylchlorosilane (eq 2) to give allylsilanes **5a–d** (Table 1). A more general method of silyl group introduction




employs mercaptide anion **6**, which can be prepared in one pot from thiophenol[8] (Scheme 1). *ortho*-Silyl phenyl sulfide deriva-

* Abstract published in *Advance ACS Abstracts*, June 1, 1994.

(1) Part 51 of the series Synthesis Via Vinyl Sulfones.

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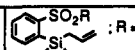
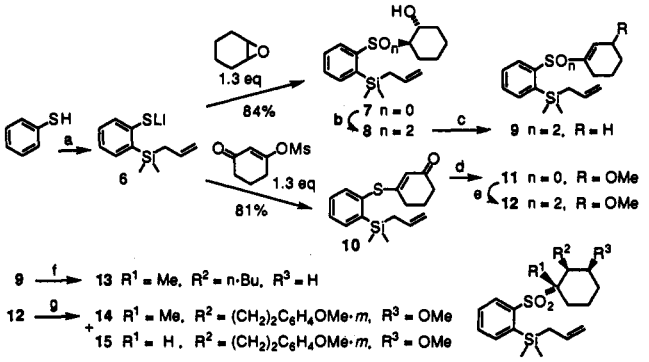
**Table 1.** Conditions and Yields for Silicon-Assisted Sulfone Elimination Reaction

| Entry # |  : R = | Solvent | mol% HOTf | Reaction Temp / Time | Major olefin Product [a] | NMR Yield [b] | Isolated Yield [b] |
|---|---|---|---|---|---|---|---|
| 1 | 5a | $CD_3CN$ | 30 | 25°C / 5 min |  | 98% | 78% |
| 2 | " | $CDCl_3$ | 30 | 25°C / 9 h | " | 97% | 96% |
| 3 | " | $CDCl_3$ | 20 | 62°C / 0.25 h | " | 99% | 98% |
| 4 | 5b | $CD_3CN$ | -5 | 25°C / 19 h |  | 87%[c] | 84% |
| 5 | " | $CDCl_3$ | 20 | 62°C / 24 h | " | 94% | 92% |
| 6 | 5c | $CD_3CN$ | 5 | 25°C / 55 h |  | 77% [d] | ... |
| 7 | " | $CDCl_3$ | 50 | 62°C / 18 h | " | 90% [e] | ... |
| 8 | 5d | $CDCl_3$ | 23 | 62°C / 13 h |  | 95% | 66% |
| 9 | 13 | $CDCl_3$ | 30 | 25°C / 16 h |  | 93% | 89% |
| 10 | " | $CDCl_3$ | 10 | 62°C / 0.75 h | " | 99% | 85% |

[a] The major olefin isomer comprised 90–98% of the olefin product mixture. [b] Yields include minor olein isomers. [c] A 12% yield of siloxane dimer (**16a**, R = $C(Me)_2(CH_2)_2C_6H_5$) was observed along with the olefin products. [d] The reaction was carried out in a sealed NMR tube so yield of isobutylene could be determined directly by $^1H$ NMR integration. Isobutylene yield was based on consumed starting material (the reaction had reached a 92% conversion of starting material). An 11% yield of siloxane dimer (**16b**, R = $C(Me)_3$) was also observed. [e] Yield based upon sultine **4** due to the volatility of the isobutylene.

**Scheme 1**



[a] Reagents and conditions: (a) TMEDA (2.2 equiv), *n*-BuLi (2.2 equiv), cyclohexane, –40 °C to 25 °C, 24 h, then $ClSi(Me)_2CH_2CH{=}CH_2$, 50/50 cyclohexane/THF, –78 °C to 25 °C; (b) $Na_2CO_3$, $H_2O_2$ (6 equiv), $CH_3CN$, reflux, 18 h (75%); (c) $Et_3N$, $MeSO_2Cl$, $CHCl_3$, 0 °C to 25 °C, DBU, reflux, 12 h (91%); (d) $CeCl_3$, $NaBH_4$ (1.0 equiv), 50/50 MeOH/$CH_2Cl_2$, 25 °C, 1 h, MeI (10.0 equiv), 25 °C, 12 h (93%); (e) $CH_3CN$ (10 equiv), $K_2CO_3$, $H_2O_2$ (6 equiv), MeOH, 25 °C, 1 h (69%); (f) *n*-BuLi (1.1 equiv), cyclohexane, 6 °C to 25 °C, 20 min, MeI (3 equiv), 25 °C, 24 h; (g) $Li(CH_2)_2C_6H_4OMe$-*m* (1.1 equiv), cyclohexane, 6 °C to 25 °C, 20 min, MeI (10 equiv), 25 °C, 72 h.

tives such as **7** and **10** are obtained in good yield by treating **6** in situ with the appropriate electrophile. Oxidation of sulfide **7** to sulfone **8**[9] followed by elimination of the β-hydroxy group provides vinyl sulfone **9** in 57% overall yield based on thiophenol. Reduction of ketone **10** followed by oxidation of sulfide **11**[9] provides sulfone **12** in 52% overall yield.

Vinyl sulfones **9** and **12** are open to a wide variety of transformations. For example, treatment of **8** with *n*-butyllithium in cyclohexane followed by a methyl iodide quench gives sulfone **13** (mixture of diastereomers) in 86% yield. Reaction of (*m*-methoxyphenethyl)lithium (prepared in situ by lithium halogen exchange with the corresponding iodide)[10] with **12** followed by a methyl iodide quench affords an easily separable mixture of **14**

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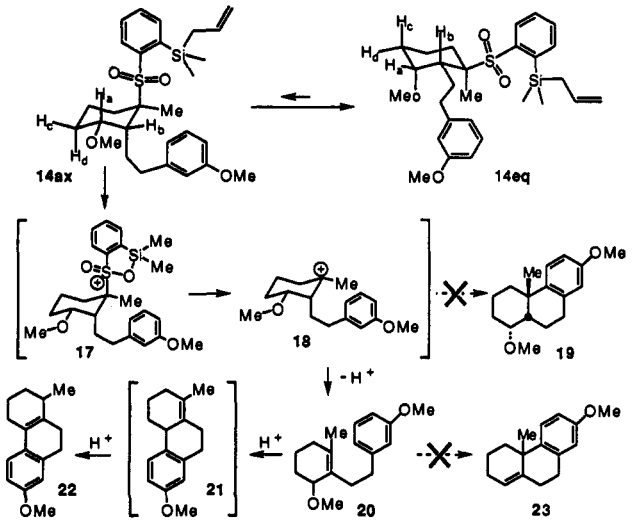
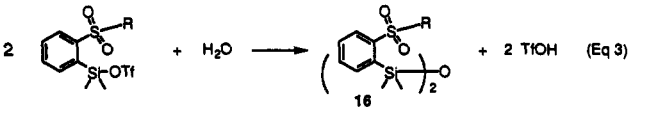
**Scheme 2**



(single diastereomer, stereochemistry verified by X-ray)[11] and **15** (single diastereomer) in 56% and 19% yields, respectively (Scheme 1).

Scheme 1 demonstrates that the silyl group can be introduced early in a reaction sequence, remains unaffected under a variety of reaction conditions, and does not inhibit the aryl sulfonyl moiety's ability to undergo standard sulfone chemistry. Activation of the sulfone for elimination is simply effected by exposure to a catalytic amount of triflic acid.

Table 1 shows relative rates and yields for silicon-assisted sulfone elimination of various substrates in chloroform and acetonitrile. The elimination reaction appears to be general for tertiary sulfones whether or not activated β-protons are present. Comparison of entries 1 and 2 shows that the elimination reaction proceeds at least 2 orders of magnitude faster in acetonitrile than in chloroform. Reasonable reaction times can be achieved at room temperature for most substrates in acetonitrile. Higher yields of olefin are generally obtained for a given substrate under a given set of reaction conditions when a smaller mol % of HOTf catalyst is used. The elimination favors a thermodynamic distribution of olefin products. NMR studies suggest that some olefin isomerization occurs during the reaction, especially at higher reaction temperatures. The presence of trace amounts of water during the elimination reaction is particularly damaging because each molecule of water consumes two molecules of silyl triflate to form oxygen-bridged siloxane dimer **16** (eq 3).



In all examples shown in Table 1, the cyclic silyl sulfinate by product **4** is formed quantitatively along with the olefin products. If desired, sultine **4** can also be isolated in excellent yield. Sultine **4** represents a new class of cyclic sulfinate derivatives where silicon is incorporated next to the oxygen on the sulfinate ring.

In an attempt to effect an intramolecular Friedel–Crafts alkylation via interception of the sultinium intermediate **17** (Scheme 2), tertiary sulfone **14** was treated with 5 mol % triflic acid in $CDCl_3$ at 62 °C. The targeted tricyclic ether **19** was not detected, but at short reaction times intermediate olefin **20** could be observed. Longer reaction times (2 h) served to further convert **20** in 67% isolated yield (based on **14**) to tricyclic olefin **22**, with

(11) Full X-ray data on compound **14** can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. Tel. 44-223-336408; Fax 44-223-336033.

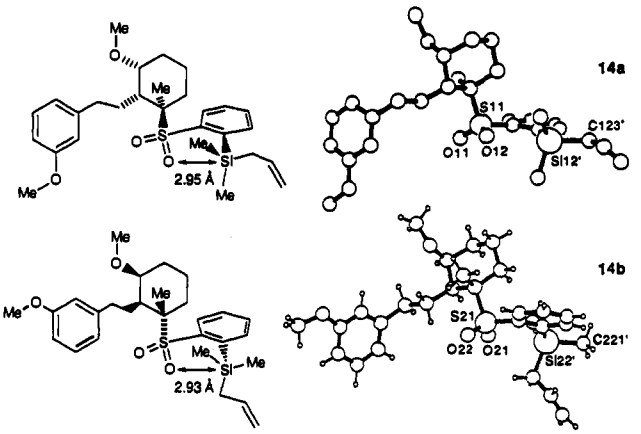



**Figure 1.** X-ray crystal structure of **14a** and **14b** (left) with a partial crystallographic numbering scheme along with schematic drawings (right).

no apparent concomitant production of olefin **23**, which would have occurred from arene alkylation at the more hindered site of the putative allylic cation.

As can be seen from Scheme 2, the intramolecular Friedel–Crafts reaction of the *m*-methoxyphenethyl group would seem to require the intermediacy of a conformer with an axial sulfonyl group for best overlap at the stage of sultinium ion **17** and/or carbonium ion **18**. However, the $^1$H NMR spectrum of **14** is consistent with the chair form having an equatorial sulfone moiety (**14eq**, Scheme 2) since $H_a$ has the appearance of a quartet with three ~3 Hz couplings to $H_{b,c,d}$, respectively, while the alternative conformation **14ax** would be expected to have one >10 Hz coupling for $J_{ad}$. Molecular mechanics calculations (Tektronix CAChe v 3.5) are consistent with the above structural information, favoring **14eq** over **14ax** by approximately 1.0 kcal/mol. Therefore, the failure of **14** to cyclize to tricyclic **19** may be partially attributable to unfavorable conformation factors.

The X-ray crystal structure of **14**[11] (Figure 1) revealed a surprisingly strong interaction between one of the sulfonyl oxygens and the allyldimethylsilyl group. The unit cell of racemic compound **14** crystallizes as a 1:1 mixture of conformational diastereomers **14a** and **14b** with respect to the ~180° sulfone oxygen–silicon–alkyl group vector. Form **14a** bears the allylsilane group (C123′) anti to the sulfone oxygen (O12), while form **14b** features a methyl group (C221′) on silicon anti to the oxygen (O21) of the sulfone moiety. The silicon–oxygen distances are 2.95 Å (O12–Si12′) and 2.93 Å (O21–Si22′), which is consistent with some partial SO–Si bond character (the sum of the van der Waals radii of Si and O is 3.6 Å[12]). A search of the Cambridge Crystallographic data base for structures with the connectivity O–S–C–C–Si found no sulfone oxygen–silicon distance closer than 3.7 Å. Given the significant sulfone oxygen–allylsilane interaction, it is not surprising that the silyl triflate moiety readily cyclizes to form sultinium intermediates (**2**) under mild conditions.

Extension of the intramolecular silylation strategy for activating secondary sulfones with respect to both inter- and intramolecular alkylation reactions is being investigated.

## Experimental Section

**General Methods.** Melting points were obtained on a MEL-TEMP apparatus and are uncorrected. Unless otherwise stated, reactions were carried out under argon in flame-dried glassware. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled from sodium benzophenone ketyl. Dichloromethane and benzene were distilled from calcium hydride. Cyclohexane was stored over sodium metal. Deuterated NMR solvents ($CDCl_3$ and $CD_3CN$) used in sulfone elimination reactions were stored over 4-Å molecular sieves for several days prior to use. Flash chromatography on silica gel was carried out as described by Still[13] (230–400-mesh silica gel was used). $^1$H and $^{13}$C NMR spectra were obtained using a GE QE-300 NMR spectrometer at 300 and 75 MHz, respectively. $^1$H NMR chemical shifts are reported in parts per million relative to the residual protonated solvent resonance: $CHCl_3$, $\delta$ 7.26; $C_6D_5H$, $\delta$ 7.15. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; br, broadened. Coupling constants ($J$) are reported in hertz. $^{13}$C NMR chemical shifts are reported in parts per million relative to solvent resonance: $CDCl_3$, $\delta$ 77.00; $C_6D_6$, $\delta$ 128.00. Peaks in $^{13}$C NMR spectra are denoted as "e" for carbons with zero or two attached protons or "o" for carbons with one or three attached protons, as determined from the APT pulse sequence. Mass spectral data were obtained on a Finnigan 4000 mass spectrometer (low resolution) and a CEC 21 110 B high-resolution mass spectrometer, with the molecular ion designated as M. Elemental analyses were performed by the Purdue Chemistry Department Microanalytical Laboratory.

**General Workup Procedure.** The reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate, and the aqueous phase was extracted three times with $CH_2Cl_2$. The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo, providing a crude product residue.

**Cyclic Sulfinate 4.** To a stirred solution of **5a** (147.1 mg, 0.388 mmol) in chloroform (5 mL) was added triflic acid (6.9 $\mu$L, 0.078 mmol) at 25 °C. The reaction mixture was then heated to reflux (62 °C) for 20 min, resulting in a clear, faint pink solution. Poly(4-vinylpyridine) (~20 mg) was then added, and after stirring at 25 °C for an additional 1 min, the reaction mixture was filtered through filter paper. The filtrate was concentrated in vacuo, leaving a clear, nearly colorless oil. Further purification was accomplished by distilling the residue under argon in a Kugelrohr distillation apparatus (70 °C, 0.2 Torr) to give 63.8 mg, 83% distilled yield, of **4**: colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.54 (s, 3H), 0.67 (s, 3H), 7.56–766 (m, 2H), 7.70 (br d, $J$ = 6.4, 1H), 7.76 (br d, $J$ = 6.6, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.22 (o), 1.90 (o), 124.60 (o), 131.49 (o, 3 carbons, not resolved), 133.10 (e), 157.08 (e); $^{13}$C NMR ($C_6D_6$) $\delta$ –0.73 (o), 1.61 (o), 124.86 (o), 131.17 (o), 131.46 (o), 131.52 (o), 133.46 (e), 158.47 (e); MS (CI, isobutane) $m/z$ 199 ($MH^+$); exact mass calculated for $C_8H_{11}O_2SSi$ ($MH^+$) 199.0249, found 199.0245.

**General Procedure for *ortho*-Silyl Aryl Sulfones 5a–d.** To a stirred 0.4 M solution of aryl sulfone in THF, cooled to –78 °C, was added *n*-butyllithium (1.05 equiv), resulting in a clear, yellow-orange solution. After stirring for 1.5 h at –78 °C, allyldimethylchlorosilane (1.2 equiv) was added, and the reaction mixture was allowed to warm to 25 °C. After stirring at 25 °C for 12 h, the clear, light yellow reaction mixture was worked up according to the general procedure, leaving a light yellow oil. The crude product was purified by flash chromatography on silica gel using 10% ethyl acetate in hexane as the eluent.

**5a** (1.12 g, 94% yield): white crystals, mp 63–64 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.42 (s, 6H), 0.86 (t, $J$ = 6.8, 3H), 1.00 (tq, $J$ = 3.8, 12.5, 1H), 1.19–1.42 (m, 6H), 1.47–1.70 (m, 5H), 1.81–1.92 (m, 4H), 1.97 (d, $J$ = 8.1, 2H), 4.80 (br d, $J$ = 10.0, 1H), 4.86 (br d, $J$ = 17.0, 1H), 5.74 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 7.50–7.61 (m, 2H), 7.82 (dd, $J$ = 2.0, 6.9, 1H), 7.90 (dd, $J$ = 2.0, 7.2, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.09 (o), 13.90 (o), 21.65 (e), 23.38 (e), 24.65 (e), 25.36 (e), 25.50 (e), 29.08 (e), 29.45 (e), 67.97 (e), 113.40 (e), 128.98 (o), 132.02 (o), 132.07 (o), 135.34 (o), 137.12 (o), 141.01 (e), 141.71 (e); MS (CI, $NH_3$) $m/z$ 396 ($MNH_4^+$). Anal. Calcd for $C_{21}H_{34}O_2SSi$: C, 66.61; H, 9.05; S, 8.47; Si, 7.42. Found: C, 66.87; H, 9.35; S, 8.22; Si, 7.29.

**5b** (2.68 g, 90% yield): colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.42 (s, 6H), 1.36 (s, 6H), 1.98 (d, $J$ = 8.1, 2H), 2.01–2.08 (m, 2H), 2.63–2.71 (m, 2H), 4.80 (br d, $J$ = 10.0, 1H), 4.86 (br d, $J$ = 17.0, 1H), 5.73 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 7.14–7.23 (m, 3H), 7.25–7.32 (m, 2H), 7.51–7.62 (m, 2H), 7.83 (dd, $J$ = 1.7, 7.1, 1H), 7.93 (dd, $J$ = 1.8, 7.3, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.20 (o), 21.55 (o), 25,23 (e), 30.39 (e), 37.30 (e), 64.36 (e), 113.47 (e), 126.06 (o), 128.23 (o), 128.43 (o), 129.11 (o), 131.87 (o), 132.29 (o), 135.17 (o), 137.15 (o), 140.91 (e), 141.12 (e), 141.22 (e); MS (CI, $NH_3$) $m/z$ 404 ($MNH_4^+$). Anal. Calcd for $C_{22}H_{30}O_2SSi$: C, 68.35; H, 7.82; S, 8.29; Si, 7.26. Found: C, 68.17; H, 7.78; S, 8.00; Si, 6.98.

**5c** (2.97 g, 93% yield): colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.42 (s, 6H), 1.32 (s, 9H), 1.98 (d, $J$ = 8.1, 2H), 4.80 (br d, $J$ = 10.0, 1H), 4.86 (br d, $J$ = 17.0, 1H), 5.74 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 7.51–7.62 (m, 2H), 7.82 (dd $J$ = 1.8, 7.1, 1H), 7.92 (dd, $J$ = 1.9, 7.3, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.22 (o), 24.26 (o), 25.24 (e), 61.18 (e), 113.48 (e), 129.03 (o), 131.87 (o), 132.26 (o), 135.25 (o), 137.09 (o), 140.72 (e), 141.21 (e); MS (CI, $NH_3$) $m/z$ 314 ($MNH_4^+$). Anal. Calcd for $C_{15}H_{24}O_2SSi$: C, 60.76; H, 8.16; S, 10.81; Si, 9.47. Found: C, 60.48; H, 7.90; S, 10.57; Si, 9.25.

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**5d** (0.142 g, 57% yield): colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.417 (s, 3H), 0.422 (s, 3H), 0.83 (t, $J$ = 6.9, 3H), 0.94–1.42 (m, 11H), 1.54–1.66 (m, 2H), 1.93–2.11 (m, 3H), 2.38–2.55 (m, 2H), 4.80 (br d, $J$ = 10.0, 1H), 4.86 (br d, $J$ = 17.0, 1H), 5.75 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 7.49–7.60 (m, 2H), 7.80 (dd, $J$ = 2.1, 6.9, 1H), 7.92 (dd, $J$ = 2.1, 7.1, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.26 (o), –0.21 (o), 14.02 (o), 18.51 (o), 22.73 (e), 22.87 (e), 25.31 (e), 30.52 (e), 31.02 (e), 31.61 (e), 37.21 (e), 43.38 (o), 71.76 (e), 113.43 (e), 129.19 (o), 131.31 (o), 132.08 (o), 135.31 (o), 136.99 (o), 140.77 (e), 142.46 (e); MS (CI, $NH_3$) $m/z$ 396 ($MNH_4^+$). Anal. Calcd for $C_{21}H_{34}O_2SSi$: C, 66.61; H, 9.05; S, 8.47; Si, 7.42. Found: C, 66.81; H, 9.39; S, 8.24; Si, 7.06.

***ortho*-Silyl Aryl Mercaptide 6.** To a stirred solution of *n*-butyllithium (44.0 mmol) and tetramethylethylenediamine (TMEDA) (6.64 mL, 44.0 mmol) in cyclohexane (30.0 mL), which had been immersed in a dry ice bath for 1 min, was added thiophenol (2.05 mL, 20.0 mmol), resulting in a clear, light yellow solution. The bath was removed, and the reaction mixture was stirred vigorously at 25 °C for 24 h, resulting in an opaque, fine off-white slurry.[8] THF (25 mL) was then added, causing the reaction mixture to turn clear, orange-yellow over 5 min. The reaction mixture was then immediately cooled to –78 °C, and allyldimethylchlorosilane (3.80 mL, 26.0 mmol) was added dropwise over 5 min. After stirring at –78 °C for 30 min, the reaction mixture was allowed to gradually warm to 25 °C over 2 h and was stirred for at least 1 h at 25 °C before quenching with an electrophile. The clear, orange-yellow solution of mercaptide **6** could be stored at 25 °C for at least 48 h without any noticeable decomposition.

***ortho*-Silyl Aryl Sulfide 7.** To a stirred solution of mercaptide **6** in situ (3.8 mmol) was added cyclohexene oxide (0.615 mL, 6.08 mmol) at 25 °C. After stirring at 25 °C for 24 h, the clear, orange-yellow reaction mixture was worked up according to the general procedure, leaving a slightly cloudy yellow oil. The crude product was purified by flash chromatography on silica gel using 25% hexane in $CH_2Cl_2$ as the eluent to afford 0.970 g (84% yield) of **7**: colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.38 (s, 6H), 1.20–1.55 (m, 4H), 1.67–1.81 (m, 2H), 1.96 (d, $J$ = 8.1, 2H), 2.07–2.21 (m, 2H), 2.71 (d, $J$ = 2.0, 1H), 3.08 (ddd, $J$ = 4.1, 9.9, 11.9, 1H), 3.53 (ddt, $J$ = 2.0, 4.3, 9.9, 1H), 4.81–4.93 (m, 2H), 5.78 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 7.18 (dt, $J$ = 0.9, 7.6, 1H), 7.32 (dt, $J$ = 1.6, 7.6, 1H), 7.43 (dd, $J$ = 1.6, 7.6, 1H), 7.52 (dd, $J$ = 0.9, 7.6, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –1.95 (o), –1.82 (o), 23.95 (e), 24.22 (e), 26.02 (e), 32.94 (e), 34.04 (e), 57.95 (o), 73.41 (o), 113.38 (e), 125.78 (o), 129.89 (o), 130.91 (o), 134.84 (o), 135.24 (o), 140.62 (e), 142.04 (e); MS (CI, isobutane) $m/z$ 307 ($MH^+$).

***ortho*-Silyl Aryl Sulfone 8.** To a stirred solution of **7** (0.419 g, 1.37 mmol) in acetonitrile (5 mL) was added $Na_2CO_3$ (0.10 g, 0.94 mmol) and 70% $H_2O_2$ (0.204 mL, 5.47 mmol) at 25 °C.[9] After heating to reflux (82 °C) for 5 h, an additional 0.10 mL (2.7 mmol) of 70% $H_2O_2$ was added, and the reaction mixture was heated to reflux for 13 h. By this point, the reaction mixture had become a light yellow slurry and tested negative for peroxides on potassium iodide–starch paper. The reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel using 20% ethyl acetate in hexane as the eluent to afford 0.349 g (75% yield) of **8**: colorless oil; $^1$H NMR ($C_6D_6$) $\delta$ 0.46 (s, 3H), 0.50 (s, 3H), 0.58 (tq, $J$ = 3.5, 12.8, 1H), 0.83 (tq, $J$ = 3.2, 12.8, 1H), 1.14–1.45 (m, 5H), 1.95–2.04 (m, 1H), 2.06 (d, $J$ = 8.1, 2H), 2.98 (ddd, $J$ = 4.6, 9.7, 11.7, 1H), 4.10 (s, 1H), 4.22 (dt, $J$ = 4.8, 9.7, 1H), 4.87 (br d, $J$ = 10.0, 1H), 4.95 (br d, $J$ = 16.9, 1H), 5.79 (ddt, $J$ = 10.0, 16.9, 8.1, 1H), 7.00–7.11 (m, 2H), 7.58 (dd, $J$ = 1.6, 7.3, 1H), 7.84 (dd, $J$ = 1.5, 7.6, 1H); $^{13}$C NMR ($C_6D_6$) $\delta$ –0.40 (o), –0.28 (o), 23.62 (e), 24.54 (e), 25.09 (e), 25.76 (e), 34.72 (e), 68.78 (o), 68.80 (o), 114.09 (e), 129.58 (o), 131.08 (o), 132.39 (o), 135.19 (o), 137.36 (o), 139.84 (e), 144.09 (e); MS (CI, $NH_3$) $m/z$ 356 ($MNH_4^+$).

**Vinyl Sulfone 9.** To a stirred solution of **8** (0.678 g, 2.00 mmol) in chloroform (HPLC grade, 7 mL) was added triethylamine (0.838 mL, 6.00 mmol) and methanesulfonyl chloride (0.466 mL, 6.00 mmol) at 0 °C. After 10 min, the ice bath was removed, and the reaction mixture was stirred at 25 °C for 2 h. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (1.8 mL, 12.0 mmol) was then added, and the reaction mixture was heated to reflux for 12 h, turning very dark over this time. The reaction mixture was worked up according to the general procedure, and the crude product (brown oil) was chromatographed on silica gel using 25% ethyl acetate in hexane as the eluent to afford 0.583 g (91% yield) of **9**: colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.41 (s, 6H), 1.55–1.71 (m, 4H), 2.00 (d, $J$ = 8.1, 2H), 2.14–2.21 (m, 2H), 2.23–2.30 (m, 2H), 4.82 (br d, $J$ = 10.0, 1H), 4.87 (br d, $J$ = 17.0, 1H), 5.76 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 6.81–6.85 (m, 1H), 7.47–7.57 (m, 2H), 7.76 (dd, $J$ = 2.1, 6.8, 1H), 7.81 (dd, $J$ = 2.1, 7.1, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.76 (o), 20.88 (e), 21.80 (e), 22.77 (e), 24.66 (e), 25.35 (e), 113.43 (e), 129.46 (o), 129.77 (o), 131.78 (o), 135.24 (o), 136.90 (o), 137.35 (o), 139.38 (e), 140.20 (e), 143.86 (e); MS (CI, isobutane) $m/z$ 321 ($MH^+$), 279 ($MH^+ - C_3H_6$).

**Vinylogous Thioester 10.** To a stirred solution of mercaptide **6** in situ (20 mmol) was added 1-oxo-2-cyclohexene-3-methanesulfonate (4.95 g, 26.0 mmol) at –20 °C. The reaction mixture was allowed to warm to 25 °C, and after 24 h, the cloudy, orange-yellow reaction mixture was worked up according to the general procedure, leaving a slightly cloudy yellow oil. The crude product was purified by flash chromatography on silica gel using 15% ethyl acetate in hexane as the eluent to afford 4.93 g (81% yield) of **10**: colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.28 (s, 6H), 1.82 (d, $J$ = 8.1, 2H), 2.01 (p, $J$ = 6.3, 2H), 2.34 (t, $J$ = 6.3, 2H), 2.50 (t, $J$ = 6.3, 2H), 4.78–4.85 (m, 2H), 5.32 (s, 1H), 5.68 (ddt, $J$ = 10.0, 16.7, 8.1, 1H), 7.35–7.45 (m, 3H), 7.54–7.57 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –2.37 (o), 22.81 (e), 23.59 (e), 30.17 (e), 37.08 (e), 113.63 (e), 121.05 (o), 129.22 (o), 130.41 (o), 133.97 (e), 134.18 (o), 136.30 (o), 137.30 (o), 144.83 (e), 167.42 (e), 195.72 (e); MS (CI, isobutane) $m/z$ 303 ($MH^+$).

**γ-Methoxy *ortho*-Silyl Aryl Sulfide 11.** To a stirred solution of **10** (4.87 g, 16.1 mmol) in 50/50 $CH_2Cl_2/CH_3OH$ (80 mL) was added $CeCl_3$ (4.04 g, 16.9 mmol) at 25 °C. After 15 min, the cloudy white reaction mixture was cooled to 0 °C, and $NaBH_4$ (0.609 g, 16.1 mmol) was added. After stirring at 25 °C for 20 min, MeI (10.0 mL, 161 mmol) was added, and the reaction mixture was stirred at 25 °C for 24 h. The reaction mixture was then worked up according to the general procedure, and the crude product residue was chromatographed on silica gel using 4% ethyl acetate in hexane as the eluent to afford 4.78 g (93% yield) of **11**: colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.34 (s, 3H), 0.35 (s, 3H), 1.55–1.86 (m, 4H), 1.92 (d, $J$ = 8.1, 2H), 2.00–2.22 (m, 2H), 3.31 (s, 3H), 3.75–3.81 (m, 1H), 4.79–4.91 (m, 2H), 5.62–5.66 (m, 1H), 5.76 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 7.26 (dt, $J$ = 1.2, 7.3, 1H), 7.33 (dt, $J$ = 1.7, 7.3, 1H), 7.43 (dd, $J$ = 1.2, 7.3, 1H), 7.49 (dd, $J$ = 1.7, 7.3, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –2.19 (o), –2.13 (o), 19.93 (e), 23.83 (e), 27.53 (e), 29.74 (e), 55.72 (o), 74.77 (o), 113.29 (e), 125.12 (o), 127.07 (o), 129.84 (o), 134.48 (o), 134.99 (o), 135.63 (o), 138.77 (e), 139.48 (e), 142.64 (e); MS (CI, isobutane) 319 ($MH^+$), 287 ($MH^+ - HOCH_3$), 277 ($MH^+ - C_3H_6$).

**γ-Methoxy Vinyl Sulfone 12.** To a stirred solution of **11** (4.77 g, 15.0 mmol) in $CH_3OH$ (60 mL) was added in order $CH_3CN$ (7.82 mL, 150 mmol), $K_2CO_3$ (1.5 g, 10.9 mmol), and 70% $H_2O_2$ (3.36 mL, 89.8 mmol) at 0 °C. After 5 min, the ice bath was removed, and the reaction mixture was stirred without cooling for 35 min[9] (some heat was evolved). Dimethyl sulfide (6.60 mL, 89.8 mmol) was then added to quench any residual peroxides. After stirring at 25 °C for 15 min, the reaction mixture was concentrated in vacuo and the residue chromatographed on silica gel using 25% ethyl acetate in hexane as the eluent to afford 3.61 g (69% yield) of **12**: colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.40 (s, 6H), 1.58 (p, $J$ = 6.4, 2H), 1.77–1.92 (m, 2H), 1.98 (d, $J$ = 8.1, 2H), 2.09–2.27 (m, 2H), 3.38 (s, 3H), 3.88–3.94 (m, 1H), 4.79 (br d, $J$ = 10.0, 1H), 4.86 (br d, $J$ = 17.0, 1H), 5.74 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 6.75–6.76 (m, 1H), 7.47–7.57 (m, 2H), 7.76 (dd, $J$ = 1.6, 7.2, 1H), 7.82 (dd, $J$ = 1.8, 7.2, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.86 (o, 2 carbons, not resolved), 19.11 (e), 22.86 (e), 24.57 (e), 27.00 (e), 56.40 (o), 73.98 (o), 113.46 (e), 129.57 (o), 129.96 (o), 132.05 (o), 134.93 (o), 135.02 (o), 136.90 (o), 139.54 (e), 143.07 (e, 2 carbons, not resolved); $^{13}$C NMR ($C_6D_6$) $\delta$ –0.46 (o, 2 carbons, not resolved), 19.16 (e), 23.30 (e), 25.06 (e), 27.19 (e), 56.11 (o), 73.95 (o), 113.81 (e), 129.70 (o), 130.19 (o), 131.94 (o), 135.49 (o, 2 carbons, not resolved), 137.18 (o), 139.69 (e), 143.40 (e), 144.50 (e); MS (CI, $NH_3$) $m/z$ 368 ($MNH_4^+$).

***ortho*-Silyl Aryl Sulfone 13.** To a stirred solution of **9** (0.367 g, 1.14 mmol) in cyclohexane (15 mL) was added *n*-butyllithium (1.43 mmol) at 6 °C. The resulting clear yellow reaction mixture was allowed to warm to 25 °C, and after stirring for 20 min, MeI (0.243 mL, 3.90 mmol) was added. The reaction mixture was stirred at 25 °C for 24 h, gradually decolorizing and turning cloudy over this time. The reaction mixture was then transferred directly to a column of silica gel and chromatographed, eluting with 100% hexane initially, followed by 5% ethyl acetate in hexane to afford 0.385 g (86% yield, mixture of diastereomers) of **13**: colorless oil; $^1$H NMR ($CDCl_3$) $\delta$ 0.42–0.45 (m, 6H), 0.84–2.36 (m, 23H), 4.80 (br d, $J$ = 10.0, 1H), 4.86 (br d, $J$ = 17.0, 1H), 5.74 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 7.49–7.58 (m, 2H), 7.78–7.81 (m, 1H), 7.85–7.89 (m, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ –0.11 (o), –0.03 (o), 0.00 (o), 14.19 (o), 14.28 (o), 20.29 (e), 21.52 (e), 21.99 (o), 22.08 (e), 22.73 (e), 22.94 (e), 24.80 (e), 25.29 (e), 25.35 (e), 25.38 (e), 27.65 (e), 28.04 (e), 29.64 (e), 29.83 (e), 30.40 (e), 30.99 (e), 34.49 (e), 39.48 (o), 41.22 (o), 68.22 (e), 69.36 (e), 113.37 (e), 129.14 (o), 129.18 (o), 131.01 (o), 131.26 (o), 131.83 (o), 131.87 (o), 135.40 (o), 136.95 (o), 140.38 (e), 140.56 (e),

142.65 (e), 143.55 (e); MS (CI, $NH_3$) $m/z$ 410 ($MNH_4^+$). Anal. Calcd for $C_{22}H_{36}O_2SSi$: C, 67.29; H, 9.24; S, 8.16; Si, 7.15. Found: C, 67.57; H, 9.54; S, 7.87; Si, 6.94.

**γ-Methoxy *ortho*-Silyl Aryl Sulfones 14 and 15.** To a stirred solution of *m*-methoxyphenethyl iodide (0.529 g, 2.02 mmol) in $Et_2O$ (3.6 mL) was added *tert*-butyllithium at −55 °C. The clear yellow reaction mixture was cooled to −78 °C for 35 min, causing some precipitation of light-colored solid. The reaction mixture was then allowed to warm to 25 °C over 20 min, turning back to clear yellow over this time.[10] This mixture was then transferred via cannula to a stirred solution of **12** (0.559 g, 1.60 mmol) in cyclohexane (20 mL) which had been cooled to 10 °C. The resulting slightly cloudy, yellow reaction mixture was allowed to warm to 25 °C, and after 20 min, MeI (0.685 mL, 11.0 mmol) was added. After stirring for 24 h at 25 °C, the yellow color had not completely faded, so additional MeI (0.50 mL, 8.0 mmol) was added. After stirring for an additional 48 h at 25 °C, the reaction mixture was transferred directly to a column of silica gel and chromatographed, eluting with 100% hexane initially, followed by 10% ethyl acetate in hexane to afford **14** (0.451 g, 56% yield, single diastereomer) and **15** (0.151 g, 19% yield, single diastereomer).

**14**: white crystals, mp 92–94.5 °C; $^1$H NMR ($CDCl_3$) δ 0.42 (s, 3H), 0.43 (s, 3H), 0.88–0.94 (m, 1H), 1.02–1.13 (m, 1H), 1.30–1.67 (m, 6H), 1.96–2.12 (m, 4H), 2.30 (dt, $J$ = 10.7, 2.8, 1H), 2.43 (dddd, $J$ = 2.8, 4.9, 8.8, 12.5, 1H), 2.60–2.81 (m, 2H), 3.27 (s, 3H), 3.62 (q, $J$ = 2.8, 1H), 3.82 (s, 3H), 4.79–4.91 (m, 2H), 5.75 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 6.75 (br d, $J$ = 7.9, 1H), 6.84–6.89 (m, 2H), 7.21 (t, $J$ = 7.9, 1H), 7.48 (dt, $J$ = 1.5, 7.4, 1H), 7.54 (dt, $J$ = 1.5, 7.4, 1H), 7.77–7.84 (m, 2H); $^{13}$C NMR ($CDCl_3$) δ −0.06 (o, 2 carbons, not resolved), 16.39 (e), 17.21 (o), 25.34 (e), 26.73 (e), 27.50 (e), 33.41 (e), 34.56 (e), 41.72 (o), 55.15 (o), 56.99 (o), 69.60 (e), 76.08 (o), 111.32 (o), 113.41 (e), 113.97 (o), 121.03 (o), 129.11 (o), 129.17 (o), 131.47 (o), 131.92 (o), 135.37 (o), 136.96 (o), 140.64 (e), 142.22 (e), 143.87 (e), 159.57 (e); MS (CI, $NH_3$) $m/z$ 518 ($MNH_4^+$); X-ray crystal structure.[11]

**15**: colorless oil; $^1$H NMR ($CDCl_3$) δ 0.43 (s, 3H), 0.45 (s, 3H), 1.40–1.60 (m, 3H), 1.63–1.78 (m, 3H), 1.95–2.07 (m, 4H), 2.29 (dq, $J$ = 3.6, 6.7, 1H), 2.53 (t, $J$ = 7.9, 2H), 3.27 (s, 3H), 3.34 (dt, $J$ = 4.5, 6.7, 1H), 3.78–3.83 (m, 4H), 4.83 (br d, $J$ = 10.0, 1H), 4.89 (br d, $J$ = 17.0, 1H), 5.75 (ddt, $J$ = 10.0, 17.0, 8.1, 1H), 6.64–6.73 (m, 3H), 7.14 (dt, $J$ = 1.4, 7.4, 1H), 7.49–7.60 (m, 2H), 7.79 (dd, $J$ = 1.8, 7.0, 1H), 7.93 (dd, $J$ = 1.8, 7.3, 1H); $^{13}$C NMR ($CDCl_3$) δ −0.69 (o), −0.58 (o), 19.44 (e), 24.16 (e), 24.75 (e), 26.38 (e), 28.68 (e), 33.46 (e), 38.69 (o), 55.10 (o), 56.04 (o), 63.43 (o), 76.00 (o), 111.21 (o), 113.69 (e), 113.91 (o), 120.75 (o), 129.17 (o), 129.36 (o), 130.66 (o), 132.06 (o), 134.94 (o), 137.19 (o), 139.15 (e), 143.35 (e), 144.02 (e), 159.55 (e); MS (CI, $NH_3$) $m/z$ 504 ($MNH_4^+$).

**Characterization of siloxane dimer 16b (R = C(Me)$_3$)**: white crystals, mp 154–155.5 °C; $^1$H NMR ($CDCl_3$) δ 0.58 (s, 12H), 1.35 (s, 18H), 7.52–7.62 (m, 4H), 7.90 (dd, $J$ = 1.8, 7.1, 2H), 8.20 (dd, $J$ = 2.0, 6.9, 2H); $^{13}$C NMR ($CDCl_3$) δ 3.78 (o, 4C), 24.21 (o, 6C), 61.08 (e, 2C), 129.08 (o, 2C), 131.27 (o, 2C), 132.40 (o, 2C), 137.12 (o, 2C), 140.42 (e, 2C), 142.54 (e, 2C); MS (CI, $NH_3$) $m/z$ 544 ($MNH_4^+$). Anal. Calcd for $C_{24}H_{38}O_5S_2Si_2$: C, 54.71; H, 7.27; S, 12.17; Si, 10.66. Found: C, 54.63; H, 7.48; S, 12.55; Si, 11.26.

**General Procedure for Sulfone Elimination.** *ortho*-Silyl sulfone starting materials were dried azeotropically by dissolving in benzene and concentrating in vacuo twice prior to setting up the elimination reaction. To a ~0.1 M solution of *ortho*-silyl sulfone starting material in chloroform or acetonitrile was added a catalytic amount of triflic acid, and if desired, the reaction mixture was heated for a period of time (see Table 1 for details on reaction temperatures, times, and mol % HOTf used). The reaction was monitored by TLC or NMR if a deuterated solvent was used. When the reaction was complete, the acid catalyst was quenched with poly(4-vinylpyridine). Reactions carried out in chloroform were then diluted by 50% with pentane and filtered through a ~12 cm plug of silica gel using pentane as the eluent. Because acetonitrile and pentane are immiscible, reactions carried out in acetonitrile were first concentrated in vacuo (0 °C, 18 Torr), then taken up in pentane, and filtered through silica gel (~12 cm plug) using pentane as the eluent. In all cases, the filtrate was concentrated in vacuo (0 °C, 18 Torr) to give olefin products. The structures of the olefin products listed in Table 1 were verified by $^1$H and $^{13}$C (APT) NMR and by mass spectral analysis.

**Tricyclic Olefin 22.** To a stirred solution of **14** (149 mg, 0.298 mmol) in $CDCl_3$ (5.0 mL) was added HOTf (1.3 μL, 0.015 mmol) at 25 °C. A 1.0-mL aliquot of the reaction mixture was then transferred to an NMR tube, and both the original reaction vessel and the NMR tube were placed in an oil bath heated to 65 °C, causing the reaction mixture in both vessels to reflux gently (bp of chloroform is 62 °C). The reaction was monitored periodically by NMR, and conversion to tricyclic olefin **22** appeared to be complete (71% NMR yield) after 130 min at 62 °C. At this point, the reaction mixture was allowed to cool, the NMR tube aliquot was transferred back to the original reaction vessel, and poly(4-vinylpyridine) (~50 mg) was added. After stirring for 5 min at 25 °C, the reaction mixture was filtered through a ~12 cm plug of silica gel using chloroform as the eluent. The filtrate was concentrated in vacuo, and the crude product residue was chromatographed on silica gel using 30% chloroform in hexane as the eluent to afford 45.6 mg (67% yield) of **22**: faint yellow oil; $^1$H NMR ($CDCl_3$) δ 1.11 (d, $J$ = 7.0, 3H), 1.40–1.52 (m, 1H), 1.65–1.92 (m, 3H), 2.06–2.18 (m, 1H), 2.19–2.47 (m, 4H), 2.65–2.82 (m, 2H), 3.82 (s, 3H), 6.70–6.77 (m, 2H), 7.15 (d, $J$ = 8.2, 1H); $^{13}$C NMR ($CDCl_3$) δ 19.47 (o), 20.18 (e), 25.98 (e), 27.07 (e), 29.00 (e), 31.24 (e), 33.88 (o), 55.17 (o), 110.71 (o), 113.16 (o), 122.68 (o), 126.20 (e), 130.01 (e), 136.13 (e), 137.06 (e), 157.69 (e); MS (CI, isobutane) $m/z$ 229 ($MH^+$).

**Acknowledgment.** Support of this work was provided by the NIH: GM-32693. We wish to express our gratitude to Arlene Rothwell for providing mass spectral data, Dr. Phillip Fanwick for providing X-ray data, and Dr. Hsiu-Pu Daniel Lee for providing elemental analyses.

**Supplementary Material Available**: $^1$H and $^{13}$C NMR spectra of all new compounds described in the text (41 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. X-ray structural information relating to compound **14** can be obtained from the Cambridge Crystallographic Data Centre.[11]