(Trimethylsilyl)methyl Allylic Sulfones in Intramolecular 4 + 3 Cycloadditions

Michael Harmata* and Barry F. Herron

Department of Chemistry, University of Missouri—Columbia, Columbia, Missouri 65211

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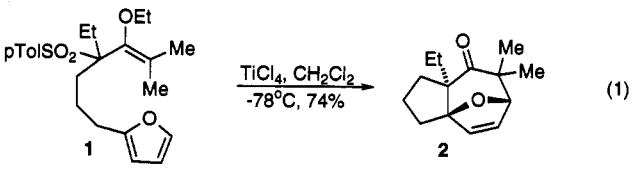
Treatment of (trimethylsilyl)methyl allylic sulfones tethered to a furan with trimethylaluminum results in the formation of products derived from the intramolecular 4 + 3 cycloaddition of the corresponding allylic cations. 2,5-Disubstitution on the furan precludes the formation of cycloadducts and results in two different classes of products which apparently result from ipso or ortho attack of the allylic cation on the furan ring followed by trapping of the resulting oxonium ions by trimethylaluminum.

The intramolecular 4 + 3 cycloaddition reaction represents a potentially powerful way to construct fused seven-membered and larger rings.[1,2] In spite of the great promise of this reaction, it has not received anywhere near the attention of the intramolecular Diels–Alder reaction.[3] As part of a program aimed at developing new methodology, gaining new mechanistic insight, and achieving various total syntheses associated with this reaction, we have been systematically investigating the process.[4] Some of our latest results are reported herein.

One of our early methodological achievements in this area involved the use of alkoxyallylic sulfones. As shown in eq 1, these easily prepared and stable compounds



(1)

underwent intramolecular 4 + 3 cycloaddition with great facility to give cycloadducts (e.g., **2**) in high yield. Nevertheless, occasional problems involving enol ether hydrolysis and other concerns led us to consider other terminators for this process. The (trimethylsilyl)methyl group was an obvious first choice.[5]

Cycloaddition substrates for this study were prepared by conjugate addition of a (trimethylsilyl)methyl cuprate to the appropriate allenic sulfone followed by a separate alkylation step as shown in Scheme I.[6] Direct alkylation of the cuprate adduct was not very successful. Interestingly, in all cases studied to date, a second alkylation has not been possible.[7]

Sulfone **5** was chosen for optimization studies. We were especially interested in finding an appropriate Lewis acid/solvent combination which would allow the cycloaddition to proceed under the mildest conditions possible. Table I summarizes some of the results. Strong Lewis acids were found to be not very effective, perhaps due to competitive decomposition of starting material and/or cycloadduct. Organoaluminums were anticipated to provide better results.[8] Indeed, upon treatment with trimethylaluminum in CH_2Cl_2, the reaction proceeded in over 70% yield. The changes in relative stereochemistry observed with different Lewis acids may correspond to mechanistic differences in the cycloaddition process, but this has not been firmly established. Optimal conditions for cycloaddition were determined to be treatment of **5** in CH_2Cl_2 with 1–2 equiv of trimethylaluminum at −78 °C followed by slow warming and stirring at room temperature for several hours. These conditions were applied to other allylic sulfones, and the results are shown in Table II.

Not surprisingly, the formation of 5,7 fused ring systems was more efficient than that of 6,7 fused ring systems (Table II, entries 1–4). Nevertheless, even in these latter cases, though yields are only fair, diastereocontrol is impressive and presumably kinetic in origin.[9] Relative stereochemistry in cycloadducts **6–12** was established by shift reagent studies[10] and corroborated by an X-ray crystal structure determination of **12b**.

Entries 5 and 6 of Table II demonstrate an interesting limitation associated with this methodology. 2,5-Disubstitution on the furan diene apparently precludes 4 + 3 cycloaddition but leads to two different classes of products which are of mechanistic interest and may be of synthetic

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(1) For reviews of the 4 + 3 cycloaddition reaction, see: (a) Hosomi, A.; Tominaga, Y. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, Chapter 5.1, pp 593–615. (b) Mann, J. *Tetrahedron* **1986**, *42*, 4611. (c) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 1. (d) Noyori, R.; Hayakawa, Y. *Org. React.* **1983**, *29*, 163. (e) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61.

(2) For intramolecular 4 + 3 cycloadditions, see: (a) Giguere, R. J.; Duncan, S. M.; Bean, J. M.; Puruis, L. *Tetrahedron Lett.* **1988**, 6071. (b) Giguere, R. J.; Tassely, S. M.; Rose, M. I. *Tetrahedron Lett.* **1990**, 4577. (c) Schultz, A. G.; Macielag, M.; Plummer, M. *J. Org. Chem.* **1988**, *53*, 391. (d) Föhlisch, B.; Gehrlach, E.; Herter, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 137. (e) Föhlisch, B.; Herter, R. *Chem. Ber.* **1984**, *117*, 2580. (f) Kaiser, R.; Föhlisch, B. *Helv. Chim. Acta* **1990**, *73*, 1504. (g) Hoffmann, H. M. R. Renning, R. *Helv. Chim. Acta* **1983**, *66*, 828. (h) Hoffmann, H.M.R.; Eggert, U.; Gibbels, U.; Giesel, K.; Koch, O.; Lies, R.; Rabe, J. *Tetrahedron* **1988**, *44*, 3899. (i) Noyori, R.; Nishizawa, M.; Shimizu, F.; Hayakawa, Y.; Maruoka, K.; Hashimoto, S.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 221.

(3) For a review of the intramolecular Diels–Alder reaction, see: Roush, W. R. In *Advances in Cycloaddition*; Curran, D.P., Ed.; JAI: Greenwich, 1990; Vol. 2, pp 91–146.

(4) (a) Harmata, M.; Gamlath, C. B. *J. Org. Chem.* **1988**, *53*, 6154. (b) Harmata, M.; Gamlath, C. B.; Barnes, C. L. *Tetrahedron Lett.* **1990**, 5981. (c) Harmata, M.; Fletcher, V. R.; Claassen, R. J., II. *J. Am. Chem. Soc.* **1991**, *113*, 9861. (d) Harmata, M.; Gamlath, C. B. *Tetrahedron Lett.* **1993**, 265. (e) Harmata, M.; Elahmad, S. *Tetrahedron Lett.* **1993**, 789. (f) Harmata, M.; Herron, B. F. *Tetrahedron Lett.* **1993**, 5381.

(5) For example see ref 2a,b.

(6) Harmata, M.; Herron, B. F. *Synthesis* **1993**, 202.

(7) Deuterium trapping experiments suggest that deprotonation of **5** is extremely slow. Harmata, M.; Herron, B. F. Unpublished results from these laboratories.

(8) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107.

(9) The cycloadducts maintain stereochemical integrity under the reaction conditions.

(10) For example, in the presence of 25 mol% of $Eu(fod)_3$, the angular proton of **6b** is shifted downfield by 1.69 ppm while that of **6a** is shifted downfield by only 0.15 ppm.

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Scheme I

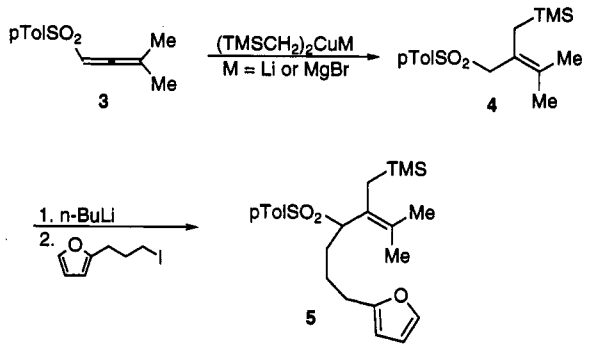
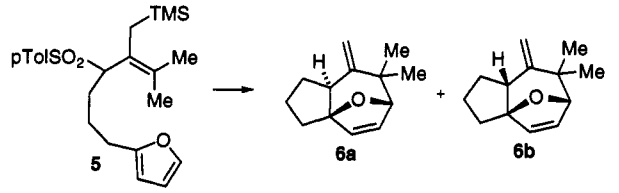


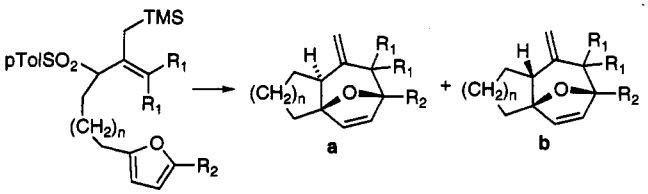
Table I. Optimization Studies for the Conversion of 5 to 6



entry[a]	Lewis acid[d]	time (h)	T (°C)	concn (M)	yield[e,f] (%)	(6a:6b)[g]
1	$TiCl_4$	0.3	−78	0.08	14	*d*
2	$ZnCl_2$	1	−78	0.05	41 (47)	1:3.9
3	$BF_3{\cdot}Et_2O$	4.6	−78 to −22	0.05	18 (19)	1:3.8
4	$SnCl_4$	4.5	−78 to −22	0.05	0	*h*
5	$AlCl_3$	0.8	−78	0.1	37 (49)	1.3:1
6	$AlClEt_2$	0.8	−78	0.05	40 (40)	1:2.3
7	$AlClEt_2$	4.5	−78 to +22	0.05	47	1.2:1
8	$AlClMe_2$	17.5	−78 to +22	0.01	62 (69)	1.1:1
9	$AlMe_3$	16.4	−78 to +22	0.01	71 (77)	1.7:1
10	$AlMe_3$	16.4	−78 to +22	0.005	63 (73)	1.4:1
11[b]	$AlMe_3$	17.3	−78 to +22	0.01	0	
12[c]	$AlMe_3$	9	−78 to +22	0.01	0	

[a] Unless otherwise stated, solvent was CH_2Cl_2. [b] Solvent was ether. [c] Solvent was $EtNO_2$. [d] 1.1–1.3 equiv used. [e] Yields in parentheses based on recovered starting material. [f] Yields based on isolated, chromatographically pure materials. [g] Ratios determined by capillary GC analysis of crude reaction mixtures. [h] Not determined.

Table II. Intramolecular 4 + 3 Cycloadditions of (Trimethylsilyl)methyl Allylic Sulfones

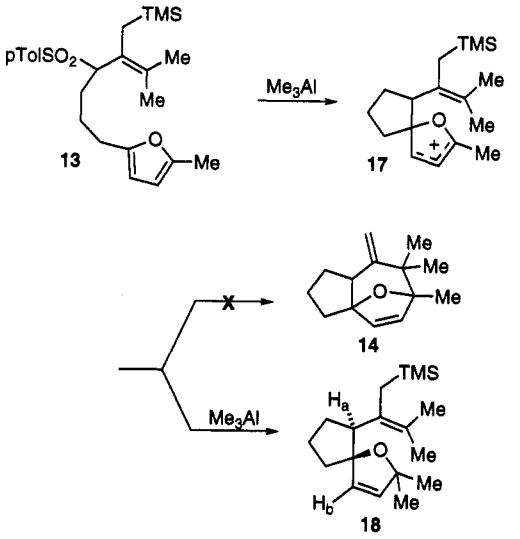


entry	substrate	R_1	R_2	*n*	cyclo-adduct	yield[a] (%)	ratio (a:b)[d]
1	**5**	Me	H	1	**6**	71 (77)	1.7:1
2	**7**	$-(CH_2)_5-$	H	1	**8**	71	1.7:1
3	**9**	Me	H	2	**10**	39 (46)[b]	1:93
4	**11**	$-(CH_2)_5-$	H	2	**12**	50[b]	1:13
5	**13**	Me	Me	1	**14**	0[c]	
6	**15**	Me	TMS	1	**16**	0[c]	

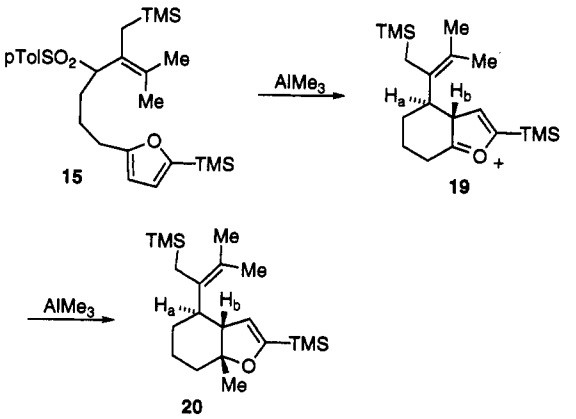
[a] Yields in parentheses are based on recovered starting materials. [b] Yield of major isomer only. [c] A side product was isolated. See text. [d] Ratios were determined by capillary GC analysis of crude reaction mixtures.

import. Sulfone **13** gave, under our standard reaction conditions, a 27% yield of spiroether **18**. That **18** was not a 4 + 3 cycloadduct was readily apparent upon inspection of its 500-MHz ^1H NMR spectrum. Apparently, cyclization occurred in a stepwise fashion to give oxonium ion **17** (Scheme II). Ring closure to 4 + 3 cycloadduct **14** was

Scheme II



Scheme III



impeded due to the presence of the methyl group on the furan ring. Delivery of a methyl group from trimethylaluminum resulted in the formation of **18**. No attempts have been made to optimize this reaction. The stereochemical assignment of **18** was based on a difference NOE experiment. Irradiation of H_a in **18** gave a 5.9% enhancement of the resonance assigned to H_b.

With sulfone **15** an even more pronounced steric effect was observed. Not only was no 4 + 3 cycloadduct produced, but cyclization occurred "ortho" to the tether-bearing carbon of the furan ring to produce oxonium ion **19**. This species was then trapped by trimethylaluminum to give **20** in 74% yield (Scheme III). A 10.6-Hz coupling constant between H_a and H_b in **20** suggested a trans relationship. The assignment of ring fusion stereochemistry is based on the presumed preference of attack on the convex face of **19** by trimethylaluminum.

The above results suggest that the mechanism of the 4 + 3 cycloaddition reaction may, in general, be a stepwise process. Further, they raise questions as to the nature of the reactive intermediate involved in the cycloaddition process, especially as a function of Lewis acid. Answers to these questions are currently being persued.

In summary, we have shown that (trimethylsilyl)methyl allylic sulfones are stable, useful precursors for intramolecular 4 + 3 cycloaddition reactions. A limitation with respect to furan substitution shed light on the mechanistic course of the cycloaddition process and may be of

independent synthetic utility. Further studies are in progress and will be reported in due course.[11]

Experimental Section

General. THF and ether were freshly distilled from sodium benzophenone ketyl. Reactions were performed in oven- (120 °C) or flame-dried glassware under an inert atmosphere of nitrogen. Flash chromatography was performed on 230–400-mesh silica gel. Visualization of compounds of silica gel plates was accomplished with UV light, iodine, and phosphomolybdic acid. NMR spectra were obtained as $CDCl_3$ solutions with TMS or dichloromethane (5.32 ppm) as the internal standard. IR spectra were obtained in CCl_4 solution. Low-resolution mass spectra were obtained on a capillary GC with a mass selective detector. Melting points are uncorrected. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

Preparation of Cyclization Substrates. General Procedure: 2-[6-Methyl-4-[(4-methylphenyl)sulfonyl]-5-[(trimethylsilyl)methyl]-5-heptenyl]furan (5). A solution of **4** (5.37 mmol, 1.66 g) in dry THF (54 mL) was cooled to −78 °C. *n*-BuLi (5.64 mmol, 5.1 mL of 2.26 M solution) was added followed after 15 min by 2-(3-iodopropyl)furan (5.9 mmol, 1.13 mL). The reaction mixture was allowed to slowly warm to 22 °C. Upon completion (TLC) the reaction was quenched with water and extracted with ether. The organic phase was washed with water and brine. The organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure. Flash chromatographic purification of the crude product (solvent system: hexane/ethyl acetate (10/1) gave **5** in 100% yield. An analytical sample was obtained by taking a center fraction of a flash chromatographic purification (solvent system: hexane/ethyl acetate (10/1)). Glassware used in this purification was washed with base (NH_4OH): ^1H NMR (500 MHz) δ 7.70 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 1.9 Hz, 1H), 6.27 (dd, J = 2.6, 1.9 Hz, 1H), 5.97 (d, J = 2.6 Hz, 1H), 4.10 (dd, J = 4.4, 8.7 Hz, 1H), 2.65 (d, septet, J = 13.0, 7.5 Hz, 2H), 2.45 (s, 3H), 2.22–2.15 (m, 1H), 1.87–1.79 (m, 1H), 1.79 (dd, J = 15.1, 142.7 Hz, 2H), 1.73–1.67 (m, 2H), 1.47 (s, 3H), 1.28 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (125.8 MHz,) δ 155.0, 144.0, 140.9, 135.9, 133.2, 129.1, 128.6, 122.7, 110.0, 105.1, 68.0, 27.6, 26.3, 21.5, 20.4, 18.0, 0.2; IR 1146 s, 1120 m, 1087 m cm^{-1}. Anal. Calcd for $C_{23}H_{24}SO_3Si$: C, 65.98; H, 8.19. Found: C, 66.32; H, 8.34.

2-[5-Cyclohexylidene-4-[(4-methylphenyl)sulfonyl]-5-[(trimethylsilyl)methyl]pentyl]furan (7). Purification of the crude product by MPLC (solvent system: 0%–100% ethyl acetate gradient in hexane) gave **7** in 94% yield. An analytical sample was obtained by taking a center fraction of an MPLC purification: mp 78–79 °C; ^1H NMR (500 MHz) δ 7.71 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 1.1 Hz, 1H), 6.27 (dd, J = 2.9, 1.0 Hz, 1H), 5.96 (d, J = 2.7 Hz, 1H), 4.20 (dd, J = 4.2, 8.9 Hz, 1H), 2.65 (d, septet, J = 12.3, 7.6 Hz, 2.45 (s, 3H), 2.23–2.16 (m, 1H), 1.95–1.90 (m, 2H), 1.83 (d septet, J = 9.5, 4.7 Hz, 1H), 1.81 (dd, J = 1 4.9, 158.6 Hz, 2H), 1.76–1.61 (m, 4H), 1.55–1.39 (m, 2H), 1.6–1.29 (m, 1H), 1.28–1.22 (m, 2H), 0.94–0.89 (m, 1H), 0.07 (s, 9H); ^{13}C NMR (125 MHz) δ 155.1, 144.0, 140.9, 136.0, 129.2, 128.8, 119.6, 110.04, 105.1, 67.2, 32.2, 30.5, 27.5, 27.3, 26.9, 26.3, 25.2, 21.5, 17.4, 0.3; IR 1314 m, 1302 m, 1249 m, 1145 s, 1087 m, 854 m, 841 m cm^{-1}. Anal. Calcd for $C_{26}H_{38}O_3SSi$: C, 68.90; H, 8.36. Found: C, 67.93; H, 8.33.

2-[7-Methyl-5-[(4-methylphenyl)sulfonyl]-6-[(trimethylsilyl)methyl]-6-octenyl]furan (9). Flash chromatographic purification of the crude product (solvent system: hexane/ethyl acetate (10/1)) gave **9** in 63% yield. An analytical sample was obtained by taking a center fraction of a MPLC purification (solvent system: 0%–100% ethyl acetate gradient in hexane): ^1H NMR (500 MHz) δ 7.70 (d, J = 8.1 Hz, 2H), 7.30–7.29 (m, 3H), 6.28 (dd, J = 1.9, 2.8 Hz, 1H), 5.97 (d, J = 2.5 Hz, 1H), 4.07 (dd, J = 3.8, 9.3 Hz, 1H), 2.62 (t, J = 7.4 Hz, 2H), 2.45 (s, 3H), 2.20–2.14 (m, 1H), 1.84–1.77 (m, 1H), 1.78 (dd, J 15.0, 149.7 Hz, 2H), 1.72–1.63 (m, 2H), 1.46 (s, 3H), 1.44–1.28 (m, 2H), 1.26 (s, 3H), 0.07 (s, 9H); ^{13}C NMR (125.8 MHz,) δ 155.7, 144.0, 140.8, 135.9, 133.3, 129.1, 128.6, 122.7, 110.0, 104.9, 68.2, 27.7, 27.7, 27.2, 25.3, 22.7, 21.6, 20.4, 18.0, 0.2; IR 1315 s, 1302 s, 1288 m, 1261 m, 1249 s, 1145 s, 1087 m, 1008 m, 856 s, 842 s cm^{-1}. Anal. Calcd for $C_{24}H_{36}SO_3Si$: C, 66.63; H, 8.39. Found: C, 66.48; H, 8.15.

2-[6-Cyclohexylidene-5-[(4-methylphenyl)sulfonyl]-7-[(trimethylsilyl)methyl]heptyl]furan (11). Flash chromatographic purification of the crude product (solvent system: hexane/ethyl acetate (10/1)) gave **11** in 67% yield. An analytical sample was obtained by recrystallization from ether: mp 49–50 °C; ^1H NMR (500 MHz) δ 7.72 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.30 (s, 1H), 6.29–6.28 (m), 5.97 (d, J = 2.7 Hz, 1H), 4.18 (dd, J = 3.7, 9.4 Hz, 1H), 2.62 (t, J = 7.4 Hz, 2H), 2.45 (s, 3H), 2.2–2.15 (m, 1H), 1.96–1.91 (m, 2H), 1.82 (dd, J = 15.0, 168.0 Hz, 2H), 1.81 (d, septet, J = 9.3, 4.8 Hz, 1H), 1.67–1.64 (m, 1H), 1.49–1.39 (m, 3H), 1. 36–1.31 (m, 2H), 1.29–1.23 (m, 2H), 0.91–0.88 (m, 1H), 0.08 (s, 9H); ^{13}C NMR (125.8 MHz) δ 155.6, 143.9, 140.8, 140.7, 136.0, 129.2, 128.7, 119.5, 110.0, 104.8, 67.3, 32.2, 30.4, 27.7, 27.63, 3.19, 27.1, 26.9, 26.3, 25.1, 21.5, 17.3, 0.3; IR 1314 m, 1248 m, 1145 s, 1087 m cm^{-1}. Anal. Calcd for $C_{27}H_{40}O_3SSi$: C, 68.61, H, 8.54. Found: C, 68.64; H, 8.58.

2-[7-Methyl-4-[(4-methylphenyl)sulfonyl]-5-[(trimethylsilyl)methyl]-5-heptenyl]-5-methylfuran (13). Flash chromatographic purification of the crude product (solvent system: hexane/ether (10/1)) gave **13** in 95% yield. An analytical sample was obtained by taking a center fraction of a MPLC purification (solvent system: 0%–100% ethyl acetate gradient in hexane). Glassware used in this purifiation was washed with base (NH_4-OH): ^1H NMR (500 MHz) δ 7.69 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 7.3 Hz, 2H), 5.82 (s, 2H), 4.09 (dd, J = 4.4, 8.9 Hz, 1H), 2.59 (d septet, J = 7.5, 14.1 Hz, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 2.17 (d septet, J = 9.7, 4.9 Hz, 1H), 1.83 (d septet, J = 9.7, 4.8 Hz, 1H), 1.77 (dd, J = 15.1, 142.9 Hz, 2H), 1.70–1.68 (m, 2H), 1.47 (s, 3H), 1.28 (s, 3H), 0.08 (s, 9H); ^{13}C N MR (125.8 MHz) δ 153.2, 150.3, 144.0, 136.0, 133.2, 129.1, 128.6, 122.7, 105.8, 105.8, 68.1, 27.7, 26.5, 25.3, 22.7, 21.6, 20.4, 18.1, 13.4, 0.22; IR 1598 m, 1456 m, 1419 m, 1314 s, 1302 s, 1288 s, 1261 s, 1249 s, 1145 s, 1119 s, 1087 s, 1020 s cm^{-1}. Anal. Calcd for $C_{24}H_{36}O_3SSi$: C, 66.63; H, 8.39. Found: C, 66.67; H, 8.46.

2-[7-Methyl-4-[(4-methylphenyl)sulfonyl]-5-[(trimethylsilyl)methyl]-2-heptenyl]-5-(trimethylsilyl)furan (15). Flash chromatographic purification of the crude product (solvent system: hexane/ether (10/1) gave **15** in 69% yield. An analytical sample was obtained by taking a center fraction of a MPLC purification (solvent system: 0%–100% ethyl acetate gradient in hexane): ^1H NMR (500 MHz) δ 7.70 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H), 6.51 (d, J = 3.0 Hz, 1H), 5.95 (d, J = 2.9 Hz, 1H), 4.11 (dd, J = 4.2, 9.1 Hz, 1H), 2.75–2.62 (m, 2H), 2.45 (s, 3H), 2.32–2.16 (m, 1H), 1.78 (dd, J = 146.2, 15.0 Hz, 2H), 1.47 (s, 3H), 1.28 (s, 3H), 0.25 (s, 9H), 0.08 (s, 9H); ^{13}C NMR (125.8 MHz) δ 159.4, 158.5, 144.0, 135.9, 133.2, 129.1, 128.6, 122.7, 120.3, 105.2, 68.1, 27.9, 26.3, 25.4, 22.7, 21.6, 20.48, 18.0, 0.2, −1.6; IR 1315 s, 1302 m, 1250 s, 1145 s, 1087 m cm^{-1}. Anal. Calcd for $C_{26}H_{42}O_3SSi_2$: C, 63.64; H, 8.63. Found: C, 63.90; H, 8.48.

Cyclization Products. General Procedure. Treatment of 5 with $AlMe_3$. Formation of 6a. A flask containing CH_2Cl_2 (47 mL) was charged with trimethylaluminum (0.517 mmol, 0.258 mL of a 2 M solution of toluene). The flask was placed in a dry ice/acetone bath and allowed to cool for 20 min. A solution of **5** (0.470 mmol, 0.197 g) in 1.5 mL of dichloromethane was added. The reaction mixture was allowed to stir at −78 °C for 20 min, and then the bath was removed. Upon completion (16.5 h) the reaction was quenched with water. The reaction mixture was filtered through Celite and then extracted with ether. The organic phase was washed with water and brine. The organic phase was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The ratio of **6a** and **6b** was 1.74:1 as determined by capillary GC analysis of the crude reaction mixture. The crude products were purified by flash chromatography (solvent system: 0%–20% ether gradient in hexane) to give **6a** and **6b** in 77% yield. An analytical sample was obtained by taking a center fraction of a MPLC purification (solvent system: 0%–5% ether gradient in hexane). **Data for 6a:** ^1H NMR (500 MHz) δ 6.21 (dd, J = 1.6, 5.9 Hz, 1H), 6.11 (d, J = 6.0 Hz, 1H), 5.00 (s, 1H), 4.87 (s, 1 H), 4.20 (s, 1H), 2.26 (dd, J = 8.0, 11.0 Hz, 1H), 2.04–1.84 (m, 5H), 1.75–1.65 (m, 1H), 1.35 (s, 3H), 1.01 (s, 3H); ^{13}C

(11) All new compounds exhibited acceptable ^1H and ^{13}C NMR and IR spectral data as well as satisfactory combustion analysis or exact mass data.

NMR (125.8 MHz) δ 154.1, 135.8, 132.7, 113.3, 93.6, 87.7, 49.9, 39.4, 32.4, 32.3, 31.4, 24.5, 22.6; IR 1653 w, 1635 w, 1631 w, 1462 m, 1241 m, 1080 s, 1049 m, 1036 m cm^{-1}; MS (70 eV) *m/z* 1 90 (M^+, 13), 175 (50), 147 (79), 94 (48), 91 (67), 81 (98), 79 (49), 77 (50), 67 (60), 53 (74), 41 (100), 39 (89). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.87; H, 9.58. **Data for 6b:** ^{1}H NMR (500 MHz) δ 6.31 (dd, *J* = 1.3, 5.9 Hz, 1H), 5.99 (d, *J* = 5.9 Hz, 1H), 4.79 (s, 1H), 4.60 (s, 1H), 4.24 (d, *J* = 1.4 Hz, 1H), 2.67–2.63 (m, 1H), 2.07–1.89 (m, 3H), 1.86–1.77 (m, 2H), 1.30 (s, 3H), 1.27–1.22 (m, 1H), 0.98 (s, 3H); ^{13}C NMR (125.8 MHz) δ 154.93, 133.90, 133.78, 107.01, 92.36, 88.95, 47.96, 38.40, 30.11, 26.83, 23.69, 23.23, 20.08; IR 1642 s, 1471 m, 1378 m, 1315 m, 1300 m, 1099 m, 1075 s, 1066 s, 1015 m, 996 s, 971 s, 892 s cm^{-1}; MS (70 eV) *m/z* 190 (M^+, 17), 175 (70), 147 (100), 119 (63), 94 (47), 91 (62), 81 (88), 67 (57), 53 (65), 41 (76), 39 (69). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found; C, 82.42; H, 9.73.

Treatment of 7 with $AlMe_3$. Formation of 8. Two equiv of $AlMe_3$ was used. The reaction was conducted on 0.198 g (0.432 mmol) of **7**. Reaction time: 7 h. The ratio of **8a** and **8b** was 1.7:1 as determined by capillary GC analysis of the crude reaction mixture. The crude products were purified by MPLC purification (solvent system: 0%–100% ether gradient in pentane) to give **8a** and **8b** in 71% yield. An analytical sample was obtained by taking a center fraction of a MPLC purification (solvent system: 0%–100% ether gradient in hexane). **Data for 8a:** mp 66–67 °C; ^{1}H NMR (500 MHz) δ 6.20 (dd, *J* = 1.7, 6.0 Hz, 1H), 6.08 (d, *J* = 6.0 Hz, 1H), 5.04 (s, 1H), 4.94 (s, 1H), 4.86 (s, 1H), 2.31–2.23 (m, 2H), 2.04–1.81 (m, 5H), 1.72–1.52 (m, 6H), 1.49–1.40 (m, 1H), 1.34–1.23 (m, 3H); ^{13}C NMR (125.8 MHz) δ 154.9, 135.8, 132.3, 113.7, 93.2, 80.8, 50.5, 42.7, 38.8, 33.2, 33.0, 32.4, 26.1, 22.6, 22.0, 21.9; IR 1653 w, 1626 m, 1467 m, 1453 s, 1436 m, 1341 m, 1326 m, 1189 m, 1083 s, 1057 m, 1047 s, 1035 s, 1009 m, 980 m, 959 m, 931 m, 959 m, 931 s, 908 m, 890 s cm^{-1}; MS (70 eV) *m/z* 231 (M + 1, 11), 230 (M^+, 73), 187 (84), 186 (59), 173 (51), 147 (58), 131 (56), 119 (53), 94 (59), 91 (97), 81 (100), 79 (66), 77 (56), 67 (50), 66 (51), 53 (46), 41 (69). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.27; H, 9.76. **Data for 8b:** mp 61.5–62.5 °C; ^{1}H NMR (500 MHz), δ 6.26 (dd, *J* = 1.5, 5.9 Hz, 1H), 5.95 (d, *J* = 5.9 Hz, 1H), 4.83 (s, 1H), 4.81 (s, 1H), 4.60 (s, 1H), 2.65–2.61 (m, 1H), 2.17–2.15 (m, 1H), 1.96–1.89 (m, 3H), 1.83–1.73 (m, 2H), 1.67–1.60 (m, 4H), 1.31–1.57 (m, 4H), 1.27–1.19 (m, 2H); ^{13}C NME (125.8 MHz) δ 155.1, 134.0, 133.2, 107.3, 92.4, 83.9, 47.9, 41.4, 34.5, 31.8, 30.0, 26.5, 23.9, 22.2, 21.8, 20.0; IR 1639 m, 1454 m, 1119 m, 1077 m, 998 m, 973 m, 908 m, 890 m cm^{-1}; MS (70 eV) *m/e* 230 (M^+, 45), 187 (87), 186 (74), 173 (45), 147 (52), 145 (44), 131 (51), 119 (51), 117 (62), 94 (52), 91 (85), 81 (100), 79 (64), 77 (47), 67 (44), 41 (66). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.40; H, 9.76.

Treatment of 9 with $AlMe_3$. Formation of 10. One and a half equiv of $AlMe_3$ was used. The reaction was conducted on 0.314 g (0.793 mmol) of **9**. Reaction time: 22.25 h. The ratio of **10a** and **10b** was 1:93 as determined by capillary GC analysis of the crude reaction mixture. The crude pructs were purified by flash chromatography (solvent system: pentane/ether (10/1) to give **10b** in 46% yield. An analytical sample was obtained by taking a center fraction of a MPLC purification (solvent system: pentane/ether, 0%–5% gradient of ether in pentane). **Data for 10b:** ^{1}H NMR (500 MHz) δ 6.27 (d, *J* = 5.6 Hz, 1H, br), 6.15 (d, *J* = 6.1 Hz, 1H), 4.82 (s, 1H), 4.73 (s, 1H), 4.18 (s, 1H), 2.47–2.35 (m, 1H), 1.94–1.85 (m, 4H), 1.74–1.68 (m, 1H), 1.47–1.33 (m, 2H), 130 (s, 3H), 0.98 (s, 3H), 1.00–0.92 (m, 1H); ^{13}C NMR (125.8 MHz) δ 155.3, 132.3, 132.6, 106.8, 87.5, 87.5, 44.8, 40.7, 34.1, 27.1, 27.0, 25.6, 24.2, 23.9; IR 1653 w, 1635 w, 1450 m, 1065 s, 973 m, 896 m cm^{-1}; MS (70 eV) *m/e* 204 (M^+, 36), 189 (100), 161 (89), 91 (57), 81 (53), 53 (54), 41 (61). Anal. Calcd for $C_{14}H_2O$: C, 82.30; H, 9.87. Found: C, 82.43; H, 9.76.

Treatment of 11 with $AlMe_3$. Formation of 12. Two equiv of $AlMe_3$ was used. Reaction time: 8 h. The ratio of **12a** and **12b** was 1:13.4 as determined by capillary GC analysis of the crude reaction mixture. The crude products were purified by flash chromatography (solvent system: hexane/ether, gradient) to give **12b** in 50% yield. An analytical sample was obtained by recrystallization in hexane. **Data on 12b:** mp 96.5–97.5 °C; ^{1}H NMR (500 MHz) δ 6.25 (d, *J* = 5.4 Hz, 1H), 6.13 (d, *J* = 6.1 Hz, 1H), 4.87 (d, *J* = 1.4 Hz, 1H), 4.80 (s, 1H), 4.74 (d, *J* = 1.5 Hz, 1H), 2.38–2.35 (m, 1H), 2.28–2.26 (m, 1H), 2.01–1.23 (m, 14H), 0.91–0.99 (m, 1H); ^{13}C NMR (125.8 MHz) δ 155.6, 132.7, 132.7, 119.0, 106.9, 87.7, 82.0, 44.6, 43.5, 34.8, 34.0, 32.2, 27.2, 26.6, 25.6, 24.3, 22.1, 21.7; IR 1451 m, 1073 w, 890 m cm^{-1}; MS (70 eV) *m/z* 245 (M + 1, 14), 244 (M^+ 71), 201 (100), 162 (50), 91 (65), 81 (63), 79 (47), 41 (55). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.91. Found: C, 83.67; H, 10.06.

Treatment of 13 with $AlMe_3$. Formation of 18. Two equiv of $AlMe_3$ was used. The reaction was conducted on 0.212 g (0.491 mmol) of **13**. Reaction time: 6.5 h. The crude products were purified by flash chromatography (solvent system: pentane/ether, 0%–100% gradient) to give **18** in 27.5% yield. An analytical sample was obtained by taking a center fraction of an MPLC purification (solvent: pentane): ^{1}H NMR (500 MHz) δ 5.57 (d, *J* = 5.8 Hz, 1H), 5.52 (d, *J* = 5.8 Hz, 1H), 2.85 (dd, *J* = 7.6 Hz, 1H), 1.95–1.87 (m, 3H), 1.78–1.54 (m, 5H), 1.64 (s, 3H), 1.60 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H), 0.02 (s, 9H); ^{13}C NMR (125.8 MHz) δ 133.8, 131.2, 129.6, 123.1, 101.4, 87.3, 50.9, 41.0, 30.1, 28.4, 23.2, 22.4, 22.2, 21.4, 0.2; IR 1247 s, 1164 m, 1000 w, 910 m, 839 s cm^{-1}; MS (70 eV) *m/e* 293 (M + 1, 1), 292 (M^+, 2), 136 (100), 73 (51). Anal. Calcd for $C_{18}H_{32}OSi$: C, 73.92; H, 11.04. Found: C, 73.88; H, 10.89.

Treatment of 15 with $AlMe_3$. Formation of 20. Two equiv of $AlMe_3$ was used. The reaction was conducted on 0.286 g (0.583 mmol) of **15**. Reaction time: 5 h. The crude products were purified by flash chromatography (solvent system: 0%–100% ether, gradient with pentane) to give **20** in 74% yield. An analytical sample was obtained by taking a center fraction of an MPLC purification (solvent system: 0%–100% ether, gradient with pentane): ^{1}H NMR (500 MHz) δ 5.20 (d, *J* = 2.6 Hz, 1H), 2.28 (ddd, *J* = 3.9, 12.5, 10.7 Hz, 1H), 2.14–2.09 (m, 1H), 2.04 (dd, *J* = 2.5, 10.5 Hz, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.59–1.42 (m, 5H), 1.37–1.34 (m, 1H), 1.15–1.12 (m, 1H), 1.16 (s, 3H), 0.14 (s, 9H), 0.06 (s, 9H); ^{13}C NMR (125.8 MHz) δ 16 0.0, 132.3, 122.1, 119.1, 85.5, 50.4, 45.9, 33.6, 27.8, 27.4, 22.5, 21.4, 20.7, 18.9, 0.3–2.44; IR 1258 m, 1249 s, 1102 m, 1093 m, 888 m cm^{-1}. Anal. Calcd for $C_{20}H_{38}OSi_2$: C, 68.52; H, 10.93. Found: C, 68.40; H, 10.72.

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