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Silicon-Promoted Carbon−Carbon Bond Formation between Ketones and Allyl- or Vinylsilanes Catalyzed by Manganese(IV) Dioxide

Jih Ru Hwu,*[,†,‡] Buh-Luen Chen,[†,§] and Shui-Sheng Shiao[‡]

Organosilicon and Synthesis Laboratory, Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan 11529, Republic of China, and Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

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The influence of silicon on the carbon−carbon bond formation was investigated by use of various silylalkenes to react with ketones. Treatment of an allylsilane ($CH_2{=}CHCH_2SiMe_mPh_n$; $m + n = 3$) with various ketones (20 equiv) in the presence of MnO_2 (2.0 equiv) and a drop of acetic acid at 140 °C in a sealed tube produced the corresponding hydrogen atom transfer adducts in 54−85% yields. Performance of the same reactions by replacement of the allylsilane with a vinylsilane (i.e., $CH_2{=}CHSiMe_3$ and $CH_2{=}CHSiMeEt_2$) afforded adducts in 59−75% yields. Furthermore, reaction of diallyldimethylsilane with acetone or 3-methyl-2-butanone under the same conditions afforded 4-(3,3-dimethyl-3-silacyclohexyl)butan-2-one (81%) and 4-(3,3-dimethyl-3-silacyclohexyl)-3,3-dimethylbutan-2-one (65%), respectively. The results indicate that the α- and the β-electronic effects of a silicon atom promoted the C−C bond formation, while the regioselectivity came from the steric effect of the silyl group.

Introduction

The electronic effect resulting from silicon can be used to control various types of organic reactions. Recent examples of silicon-promoted reactions include the Nef reaction[1] and ring contraction;[2,3] those of silicon-directed reactions include the aldol condensation,[4] alkylative cyclization,[5] Baeyer−Villiger oxidation,[6,7] Bamford−Stevens reaction,[8] Beckmann fragmentation,[9] carbon−carbon bond cleavage,[10,11] decarbonylations,[12,13] decarboxylation,[14] epoxide opening,[15] Mukaiyama−Michael tandem aldol condensation,[16] Nazarov reaction,[17,18] Norrish type I cleavage,[19] ring enlargement,[20] [2,3]-sigmatropic rearrangement,[21] Wittig rearrangement,[22] as well as formation of cyclopropylcarbinyls,[23] dienes,[24] α-hydroxyketones,[25] and tetrahydrofurans.[26] We attempted to utilize silyl groups to promote the carbon to carbon bond formation—one of the most important topics in chemistry.

Walsh, Auner, and their co-workers reported that a silicon atom stabilizes α- and β-carboradicals by 0.4[27] and 2.8 kcal/mol,[28] respectively. On the other hand, Barton et al.[29] reported that a Me_3Si group can stabilize an alkyl radical by 2.6 kcal/mol at either the α or the β position. These α- and β-stabilizing effects result from the silicon "σ−π hyperconjuation"[30−33] or "p−d homoconjugation" or both,[34,35] as depicted in Scheme 1.

Along the line of our systematic study on the use of silicon to control organic reactions, we explored the feasibility of silicon-promoted carbon−carbon bond for-

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[*] Recipient of the Federation of Asian Chemical Societies 1992 and 1993 Distinguished Young Chemist Award.

[†] Academia Sinica.

[‡] Department of Chemistry, National Tsing Hua University.

[§] B.-L.C. was a graduate student of The Johns Hopkins University.

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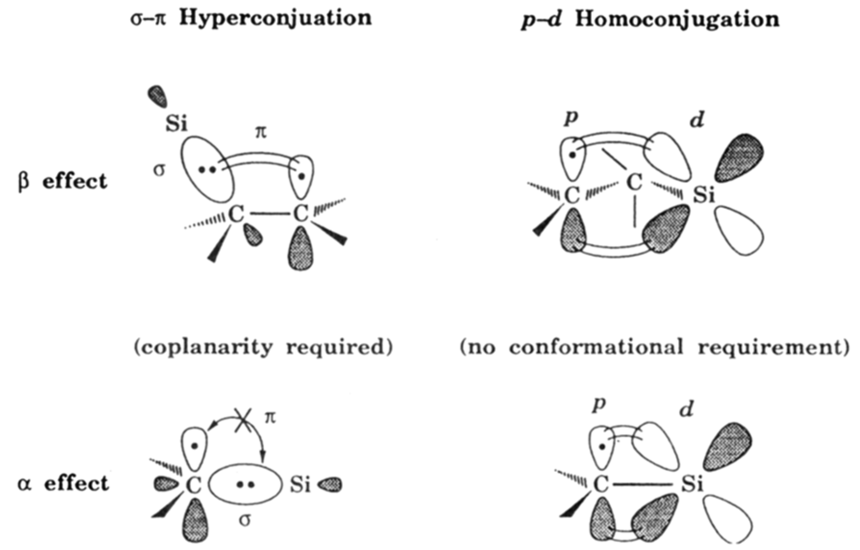
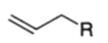
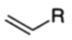
Scheme 1





1, R = SiMe$_3$
2, R = SiMe$_2$Ph
3, R = SiMePh$_2$
4, R = SiPh$_3$



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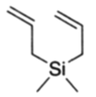

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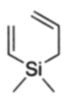

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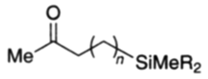
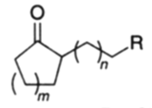
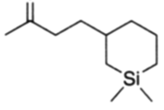


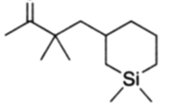
9, *n* = 3, R = Me
10, *n* = 2, R = Me
11, *n* = 2, R = Et



12, *m* = 1, *n* = 2, R = SiMe$_3$
13, *m* = 2, *n* = 2, R = SiMe$_3$
14, *m* = 3, *n* = 2, R = SiMe$_3$
15, *m* = 4, *n* = 2, R = SiMe$_3$
16, *m* = 8, *n* = 2, R = SiMe$_3$
17, *m* = 2, *n* = 2, R = SiMe$_2$Ph
18, *m* = 2, *n* = 2, R = SiMePh$_2$
19, *m* = 2, *n* = 2, R = SiPh$_3$
20, *m* = 1, *n* = 1, R = SiMe$_3$
21, *m* = 2, *n* = 1, R = SiMe$_3$
22, *m* = 3, *n* = 1, R = SiMe$_3$
23, *m* = 4, *n* = 1, R = SiMe$_3$
24, *m* = 8, *n* = 1, R = SiMe$_3$
25, *m* = 2, *n* = 1, R = SiMeEt$_2$
26, *m* = 2, *n* = 2, R = OH



27



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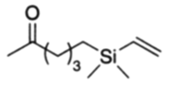

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Table 1. Reaction of Silylalkenes with Ketones in the Presence of MnO$_2$ and Acetic Acid to Give the Corresponding Hydrogen Atom Transfer Adducts at 140 °C

entry	silylalkene	ketone	product	% yield[a]
1	**1**	acetone	**9**	81
2	**1**	cyclopentanone	**12**	77
3	**1**	cyclohexanone	**13**	85
4	**1**	cycloheptanone	**14**	83
5	**1**	cyclooctanone	**15**	68
6	**1**	cyclododecanone	**16**	74
7	**2**	cyclohexanone	**17**	71
8	**3**	cyclohexanone	**18**	58
9	**4**	cyclohexanone	**19**	54
10	**5**	acetone	**10**	75
11	**5**	cyclopentanone	**20**	59
12	**5**	cyclohexanone	**21**	71
13	**5**	cycloheptanone	**22**	72
14	**5**	cyclooctanone	**23**	62
15	**5**	cyclododecanone	**24**	67
16	**6**	acetone	**11**	73
17	**6**	cyclohexanone	**25**	62
18	**7**	acetone	**27**	81
19	**7**	3-methyl-2-butanone	**28**	65
20	**8**	acetone	**29**	7

[a] On the basis of the silylalkenes.

mation. Addition of ketones to alkenes through radical intermediates can be accomplished by use of transition metal oxides.[36] The yields associated with those hydrogen atom transfer additions are generally not high enough to warrant their synthetic applicability.[37] Herein we reported the MnO$_2$-catalyzed addition of ketones (**30**) to allylsilanes or vinylsilanes (**32**) producing the corresponding hydrogen atom transfer adducts (**34**) in good yields (see Scheme 2).

Results

Addition of Ketones to Allylsilanes. To explore the feasibility of the silicon-controlled addition of a ketone to an allylsilane, we first heated an acetone (20 equiv) solution containing allyltrimethylsilane (1.0 equiv), MnO$_2$ (2.5 equiv), and a drop of acetic acid at 140 °C in a sealed tube for 14 h. The desired adduct 6-(trimethylsilyl)hexan-2-one (**9**) was obtained in 81% yield after purification by chromatography (Table 1, entry 1). By replacing acetone with five- to eight- and twelve-membered cycloalkanones to react with allyltrimethylsilane, we isolated the corresponding hydrogen atom transfer adducts **12**−**16** in 68−85% yields under similar reaction conditions (Table 1, entries 2−6). In all of these reactions, the C−C bond formation took place at the terminal sp^2 carbon in a highly regioselective manner.

We prepared phenyl-containing allylsilanes **2**−**4** from the corresponding silyllithium reagent and allyl bromide by following the procedure reported by Smith et al.[38] These compounds bear one to three phenyl groups with different size. Reaction of allylsilanes **2**−**4** with cyclohexanone in the presence of MnO$_2$ and acetic acid

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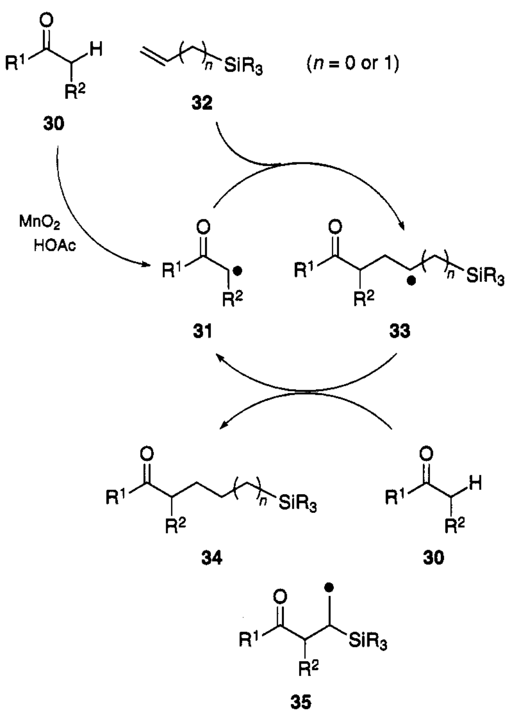
Scheme 2



afforded 54–71% yields of the corresponding adducts **17**–**19** (Table 1, entries 7–9).

Addition of Ketones to Vinylsilanes. Ketones may react with vinylsilanes in the presence of MnO_2 at the SiC= carbon to give a carboradical intermediate that is stabilized by a β-silyl group. It is also possible for the C–C bond formation taking place at the terminal sp^2 carbon of a vinylsilane to afford a carboradical that is stabilized by an α-silyl group. To realize the reaction pathway, we performed a series of experiments by treating vinylsilanes **5** and **6** with various ketones.

By mixing vinyltrimethylsilane (**5**) with MnO_2 (2.5 equiv) and a drop of acetic acid in acetone at 140 °C in a sealed tube, we obtained the adduct **10** in 75% yield after purification. Extension of this strategy to cycloalkanones produced the corresponding hydrogen atom transfer adducts (i.e., **20**–**24**) in 59–72% yields (Table 1, entries 11–15). Furthermore, use of vinyldiethylmethylsilane (**6**) to react with acetone and cyclohexanone also afforded the corresponding adducts (i.e., **11** and **25**) in good yields (Table 1, entries 16 and 17). Similar to the results obtained by use of allylsilanes was the C–C bond formation that occurred regioselectively at the terminal sp^2 carbon of the vinylsilanes.

Conversion of a δ-Silyl Ketone to a δ-Hydroxy Ketone. One-electron oxidants, such as ceric(IV) and manganese(III) acetates, can oxidize a radical intermediate to a carbocationic species.[39,40] In contrast, manganese dioxide does not oxidize radical intermediates.[36] On the other hand, the β-trimethylsilyl carbocation often fragments to give an alkene and Me_3Si^+,[41] but a β-trimethylsilyl carboradical normally does not eliminate to give an alkene and $Me_3Si^\bullet$.[42–44] Thus the β silyl group in carboradical **33** ($n = 1$) could be retained, which would lead to ketosilanes **34** upon a hydrogen atom transfer from ketones **30**.

Fleming et al.[45] reported that the dimethylphenylsilyl group can function as a masked form for the hydroxyl group. By combining the results from Fleming et al. and the newly developed method, we should be able to prepare δ-hydroxy ketones from a ketone and an allylsilane via a δ-silyl ketone intermediate. To test the feasibility of this strategy, we treated δ-(dimethylphenylsilyl) ketone **17**, the adduct of cyclohexanone and allylsilane **2**, with HBF_4 and then m-CPBA in triethylamine. The desired δ-hydroxy ketone **26** was obtained in 63% yield.

Intramolecular Cyclizations Involving Diallyl- and Allylvinylsilanes. A dicarbonyl compound could be produced when both allyl groups in a diallylsilane, such as **7**, react with ketones in the presence of MnO_2. On the other hand, after an α keto radical was added to the first allyl group, the second allyl group may be attacked by the carboradical center generated in situ to give an intramolecular cycloadduct.

To provide the answer for this puzzle, we carried out an experiment by treating diallyldimethylsilane (**7**) with MnO_2 and acetic acid in a large excess of acetone at 140 °C. Analysis of the crude reaction products by GC–mass spectroscopy showed that dicarbonyl compounds were not generated. After purification of the crude products by chromatography, the cycloadduct **27** was isolated in 81% yield. Under the same conditions, we treated **7** with 3-methyl-2-butanone, an unsymmetrical ketone. The C–C bond formation occurred regioselectively at the tertiary carbon of the ketone to give cycloadduct **28** in 65% yield. These results indicate that intermolecular addition of 2 equiv of ketones to diallyldimethylsilanes can not compete with the monoaddition followed by an intramolecular cycloaddition. The good yields associated with this newly developed cycloaddition method make it valuable for the synthesis of cyclosilanes. Its applicability, however, is limited to reactions involving allyldimethylvinylsilane. For example, by reacting **8** with acetone in the presence of MnO_2, we obtained a tar from which the monoketone **29** bearing an intact vinyl group was isolated in 7% yield only.

Discussion

Regioselectivity from Electronic and Steric Effects of Silyl Groups. The mechanism depicted in Scheme 2 illustrates the process for the MnO_2-initiated C–C bond formation between ketones **30** and silicon-containing reagents **32**.[37,46] Our results in entries 1–9 of Table 1 indicate the C–C bond formation occurred exclusively at the terminal sp^2 carbon of allylsilanes **1**–**4**. In addition to the steric effect resulting from the CH_2-SiR_3 moiety in the substrates, the electronic effect of the β silicon stabilizing carboradicals **33** ($n = 1$) could also contribute to the regioselective C–C bond formation.

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Table 2. Comparison of the Yields of Addition of Ketones to Allyltrimethylsilane (1) or Vinyltrimethylsilane (5) in the Presence of MnO_2 and Acetic Acid at 140 °C

	% yield of the adduct by isolation			
ketone	allyltrimethylsilane		vinyltrimethylsilane	% yield difference
acetone	81	>	75	6
cyclopentanone	77	>	59	18
cyclohexanone	85	>	71	14
cycloheptanone	83	>	72	11
cyclooctanone	68	>	62	6
cyclododecanone	74	>	67	7

Table 3. Comparison of the Yields Between 1-Octene and Allyltrimethylsilane in the Addition Reaction with Ketones in the Presence of MnO_2 and Acetic Acid at Elevated Temperature

	% yield of adduct by GC			% yield of adduct by isolation		
ketone	1-octene[a]		allyltrimethylsilane	1-octene[a]		allyltrimethylsilane
acetone	66	<	88	57	<	81
cyclopentanone	75	<	85	59	<	77
cyclohexanone	77	<	92	63	<	85

[a] Data are taken from ref 36.

For vinylsilanes **5** and **6**, the steric effect as well as the α stabilizing effect of a silyl group would direct the C−C bond formation occurring between α-keto radical **31** and the terminal sp^2 carbon of **32** ($n = 0$) to give secondary carboradical **33** ($n = 0$). In contrast, the β-stabilizing effect of a silyl group would lead the reaction to the primary carboradicals **35**. We found that, in all of our experiments involving vinylsilanes **5** and **6** (Table 1, entries 10−17), the hydrogen atom transfer adducts came from intermediates **33** ($n = 0$) exclusively.

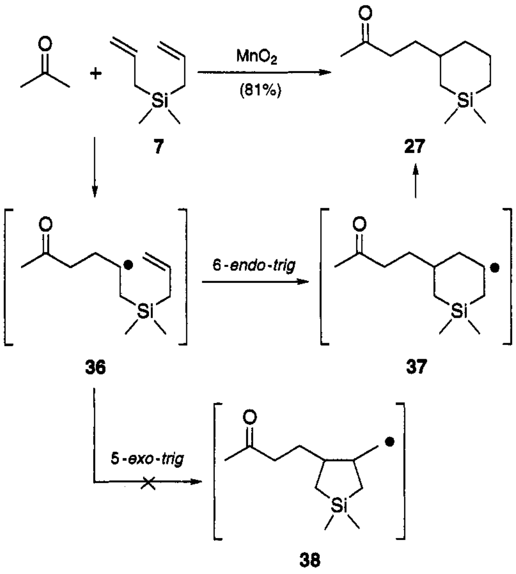
Allyltrimethylsilane versus Vinyltrimethylsilane in the Hydrogen Atom Transfer Additions. Under the same reaction conditions for performing hydrogen atom transfer additions, we always obtained a higher yield (i.e., 6−18% difference) by use of allyl- than vinylsilane (see Table 2). The substrates include acetone and cycloalkanones of different ring sizes (Table 1; entries 1−6 versus 10−15, respectively). Two factors could influence the efficiency of the C−C bond formation.

First, congestion created by the silyl groups in intermediates **33** would retard their capability to abstract a hydrogen atom from ketones **30**. We observed a clear trend for decreasing of the adduct yields by allowing cyclohexanone to react with allylsilanes **1**−**4** bearing a larger silyl group: 85% for **1** bearing $SiMe_3$, 71% for **2** bearing $SiMe_2Ph$, 58% for **3** bearing $SiMePh_2$, and 54% for **4** bearing $SiPh_3$. Consistent with these results were lower yields obtained by use of vinyldiethylmethylsilane (**6**) than vinyltrimethylsilane (**5**) in the reaction involving acetone and cyclohexanone (Table 1, entries 10 versus 16 and 12 versus 17). More importantly, a β silyl group in intermediates **33** with $n = 1$ creates a less steric congested environment than an α silyl group in **33** with $n = 0$. Thus, the hydrogen atom transfer would proceed easier from ketones **30** to the former species than the latter.

Second, the β electronic effect resulting from a silyl group can be attributed to the $\sigma-\pi$ hyperconjugation[30−33] and the p−d homoconjugation,[34,35] as shown in Scheme 1. For the α electronic effect, however, only the p−d homoconjugation exists. The σ bond is orthogonal to the p orbital of the carboradical; such an alignment would prohibit an effective $\sigma-\pi$ hyperconjugation. Consequently, the β effect exerts a greater influence than the α effect during the hydrogen atom transfer additions.

Silicon-Promoted Carbon−Carbon Bond Formation and Its Advantages. Hájek and Málek[36] reported their careful observations on the C−C bond formation between ketones and nonsilylated alkenes. In comparison with yields obtained by GC and by isolation shown in Table 3, use of allyltrimethylsilane always gave a higher yield than nonsilylated alkenes. These results indicate that silicon possesses a promoting effect on the C−C bond formation.

Scheme 3



Among various catalysts tested, we found that MnO_2 functioned more efficiently for the newly developed C−C bond formation than other commonly used metal oxides, including CuO, HgO, and PbO_2.[36] Manganese(IV) oxide is commercially available, cost effective, and adaptable to various ketones and silanes.

Intramolecular Cyclizations Involving Diallyl- and Allylvinylsilanes. In the MnO_2-initiated addition of acetone to diallyldimethylsilane (**7**) to afford cyclosilane **27**, the carboradical intermediate **36** underwent an intramolecular cyclization to give the six-membered ring species **37** (Scheme 3). According to the Baldwin's rules,[47] this reaction proceeded through a favorable 6-*endo-trig* mode. We did not observe any products resulting from the five-membered ring intermediate **38**, of which formation through a 5-*exo-trig* mode would be

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kinetically more favorable.[48] Our results are consistent with those from related reactions reported by Wilt,[49] Saigo,[50] Bertrand,[51] and co-workers, although their yields are relatively low (0.8–20%). Lengths of the C–Si and the C–C bonds,[49-51] conformation of the transition states,[49,52] and electronic effects of silicon[53] have been considered to be responsible for the generation of the six-membered cyclosilane **37**. To provide more information, we carried out AM1 calculations[54] on the heat of formation of carboradicals **37** ($\Delta H_f = -74.26$ kcal/mol) and **38** ($\Delta H_f = -67.62$ kcal/mol). Our computational results show that **37** was thermodynamically more stable than **38** by 6.64 kcal/mol.

Conclusions

A general and efficient method was developed for the hydrogen atom transfer addition of ketones to various allyl- and vinylsilanes by use of MnO_2 as the initiator. This new method is versatile, cost effective, and allows to produce γ- and δ-silyl ketones in high yields from readily available starting materials. In these reactions, the electronic effect resulting from the silicon atom provided a promoting effect for the C–C bond formation and its steric effect offered a regioselectivity.

Experimental Section

General Procedures. Ethyl acetate, acetic acid, and hexanes were purchased from Mallinckrodt Chemical Co. Ethyl acetate and hexanes were dried and distilled from CaH_2. Diethyl ether and THF from Mallinckrodt Chemicals Co. were dried by distillation from sodium and benzophenone under an atmosphere of nitrogen. Chlorodimethylvinylsilane, diallyldimethylsilane, and vinyldiethylmethylsilane were purchased from Hüls America. Tetrafluoroboric acid (solution in 54% in diethyl ether) was purchased from Merck, Inc. Allyldimethylvinylsilane was prepared according to Soderquist's procedure.[55] Unless stated otherwise, reagents were purchased from Aldrich or prepared as noted. An explosion-proof oven and the Pyrex combustion tubes (8 × 10 × 200 mm) were used to carry out experiments that required high temperature. Analytical TLC was performed on precoated plates (silica gel 60 F_{254}) purchased from Merck, Inc.; compounds were visualized by use of I_2 vapor or 2.5% phosphomolybdic acid in ethanol with heating. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument equipped with a 25-m cross-linked methyl silicone gum capillary column (0.32 mm i.d.). The flow rate was set at 14 mL/min for nitrogen as the carrier gas. The retention time t_R was measured under the following conditions: injector temperature 260 °C, the initial temperature for column 50 °C, duration 2.00 min, increment rate 10 °C/min, and the final temperature for column 250 °C. Medium-pressure liquid chromatography[56] (MPLC) separations were performed at a flow rate of 60 mL/h by use of a Waters Model M-45 metering pump or a JASCO Model 880-PU intelligent HPLC pump.

Standard Procedure for the Preparation of 2-Alkylated Ketones 9–29. A mixture of ketone (10–20 equiv), silylalkene (1.0 equiv), MnO_2 (2.1–3.0 equiv; from Aldrich without activation), and acetic acid (0.050 mL) were added into a Pyrex combustion tube, which was then sealed by torch. The sealed tube was heated at 140 °C for 12–18 h, during which time the tube was shaken thoroughly once for 10 min at 60 °C. The reaction mixture was cooled to room temperature, and the metal oxides were filtered off over Celite and washed with Et_2O (15 mL × 3). The combined filtrates were washed with water and saturated aqueous NaCl. The mixture was then dried over $MgSO_4(s)$, filtered, and concentrated under reduced pressure. The residue was purified by use of MPLC to provide the desired product.

6-(Trimethylsilyl)hexan-2-one (9). The standard procedure was followed by use of acetone (2.34 g, 40.3 mmol, 20 equiv), allyltrimethylsilane (0.227 g, 1.99 mmol, 1.0 equiv), MnO_2 (0.436 g, 5.02 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (1% EtOAc in hexanes as eluant) to give ketone **9** (0.279 g, 1.62 mmol) as a colorless liquid in 81% yield: TLC R_f 0.29 (5% EtOAc in hexanes); GC t_R 10.01 min; ^1H NMR ($CDCl_3$, 400 MHz) δ −0.05 (s, 9 H), 0.46–0.49 (m, 2 H), 1.24–1.30 (m, 2 H), 1.54–1.61 (m, 2 H), 2.12 (s, 3 H), 2.40 (t, $J = 7.4$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.74, 16.51, 23.61, 27.67, 29.77, 43.54, 209.19; IR (neat) 2935 (s), 1716 (s, C=O), 1413 (m), 1359 (m), 1247 (s, $SiCH_3$), 1169 (m), 944 (m), 860 (s), 837 (s, $SiCH_3$), 757 (m), 692 (m) cm^{-1}; MS m/z (relative intensity) 172 (M^+, 1), 157 (11), 143 (34), 130 (12), 115 (14), 114 (9), 75 (91), 74 (8), 73 (100); HRMS calcd for $C_9H_{20}OSi$ 172.1283, found (70 eV) 172.1283. Its spectroscopic characteristics are consistent with those of the same compound reported.[57]

5-(Trimethylsilyl)pentan-2-one (10). The standard procedure was followed by use of acetone (2.26 g, 38.9 mmol, 19 equiv), vinyltrimethylsilane (0.206 g, 2.06 mmol, 1.0 equiv), MnO_2 (0.363 g, 4.17 mmol, 2.1 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **10** (0.243 g, 1.54 mmol) as a colorless liquid in 75% yield: TLC R_f 0.27 (5% EtOAc in hexanes); GC t_R 8.16 min; ^1H NMR ($CDCl_3$, 400 MHz) δ −0.08 (s, 9 H), 0.41 (t, $J = 8.8$ Hz, 2 H), 1.20 (m, 2 H), 2.05 (s, 3 H), 2.37 (t, $J = 7.2$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.78, 16.39, 18.58, 29.85, 47.42, 209.35; IR (neat) 2933 (s), 1714 (s, C=O), 1412 (m), 1391 (m), 1248 (s, $SiCH_3$), 1176 (m), 1057 (m), 862 (s), 837 (s, $SiCH_3$), 755 (m), 692 (m) cm^{-1}; MS m/z (relative intensity) 158 (M^+, 1), 143 (11), 131 (4), 130 (33), 116 (11), 115 (100), 75 (41), 73 (38); HRMS calcd for $C_8H_{18}OSi$ 158.1127, found (70 eV) 158.1130. Its spectroscopic characteristics are consistent with those of the same compound reported.[57]

5-(Diethylmethylsilyl)pentan-2-one (11). The standard procedure was followed by use of acetone (2.36 g, 40.7 mmol, 20 equiv), vinyldiethylmethylsilane (0.266 g, 2.07 mmol, 1.0 equiv), MnO_2 (0.450 g, 5.17 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **11** (0.281 g, 1.51 mmol) as a colorless liquid in 73% yield: TLC R_f 0.42 (5% EtOAc in hexanes); GC t_R 11.96 min; ^1H NMR ($CDCl_3$, 400 MHz) δ −0.09 (s, 3 H), 0.39–0.48 (m, 2 H), 0.47 (q, $J = 8.1$ Hz, 6 H), 0.90 (t, $J = 8.1$ Hz, 4 H), 1.52–1.58 (m, 2 H), 2.10 (s, 3H), 2.42 (t, $J = 7.4$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −6.40, 4.78, 7.17, 12.69, 18.38, 29.66, 47.38, 208.71; IR (neat) 2950 (s), 2876 (s), 1716 (s, C=O), 1458 (m), 1360 (m), 1251 (m, $SiCH_3$), 1179 (m), 1012 (m), 795 (s), 833 (s), 750 (m), 706 (m) cm^{-1}; MS m/z (relative intensity) 171 ($M^+ - 15$, 2), 158 (7) 157 (52), 143 (12), 130 (12), 129 (100), 101 (31), 89 (10), 73 (21); HRMS calcd for $C_{10}H_{21}OSi$ ($M^+ - H$) 185.1362, found

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(70 eV) 185.1359. Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 64.70; H, 12.17.

2-[3-(Trimethylsilyl)propyl]cyclopentan-1-one (12). The standard procedure was followed by use of cyclopentanone (1.74 g, 20.7 mmol, 10 equiv), allyltrimethylsilane (0.233 g, 2.04 mmol, 1.0 equiv), MnO_2 (0.464 g, 5.33 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **12** (0.306 g, 1.54 mmol) as a colorless liquid in 77% yield: TLC R_f 0.28 (5% EtOAc in hexanes); GC t_R 13.78 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.05 (s, 9 H), 0.38−0.52 (m, 2 H), 1.20−2.40 (m, 11 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.69, 16.58, 20.75, 21.99, 29.55, 33.55, 38.10, 48.88, 221.39; IR (neat) 2927 (s), 1730 (s, C=O), 1452 (m), 1407 (m), 1247 (s, $SiCH_3$), 1154 (m), 1002 (m), 861 (s), 836 (s, $SiCH_3$), 752 (m), 693 (m) cm^{-1}; MS m/z (relative intensity) 198 (M$^+$, 2), 183 (33), 169 (100), 156 (51), 150 (34), 107 (3), 85 (20), 75 (47), 73 (71); HRMS calcd for $C_{11}H_{22}OSi$ 198.1440, found (70 eV) 198.1434. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.82; H, 11.02.

2-[3-(Trimethylsilyl)propyl]cyclohexan-1-one (13). The standard procedure was followed by use of cyclohexanone (2.44 g, 24.9 mmol, 12 equiv), allyltrimethylsilane (0.229 g, 2.01 mmol, 1.0 equiv), MnO_2 (0.427 g, 4.91 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **13** (0.363 g, 1.71 mmol) as a colorless liquid in 85% yield: TLC R_f 0.28 (5% EtOAc in hexanes); GC t_R 15.13 min; ^{1}H NMR ($CDCl_3$, 200 MHz) δ −0.06 (s, 9 H), 0.35−0.50 (m, 2 H), 1.10−2.40 (m, 13 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ −1.76, 16.69, 21.48, 24.68, 27.91, 33.24, 33.72, 41.84, 50.41, 213.47; IR (neat) 2932 (s), 2859 (s), 1707 (s, C=O), 1448 (m), 1245 (s, $SiCH_3$), 1175 (m), 1123 (m), 856 (s), 833 (s, $SiCH_3$), 756 (m), 691 (m) cm^{-1}; MS m/z (relative intensity) 212 (M$^+$, 2), 197 (20), 183 (22), 170 (31), 169 (22), 155 (7), 98 (96), 73 (100); HRMS calcd for $C_{12}H_{24}OSi$ 212.1596, found (70 eV) 212.1596. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.80; H, 11.49.

2-[3-(Trimethylsilyl)propyl]cycloheptan-1-one (14). The standard procedure was followed by use of cycloheptanone (0.219 g, 19.5 mmol, 10 equiv), allyltrimethylsilane (0.226 g, 1.98 mmol, 1.0 equiv), MnO_2 (0.424 g, 4.87 mmol, 2.4 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (1% EtOAc in hexanes as eluant) to give ketone **14** (0.377 g, 1.67 mmol) as a colorless liquid in 83% yield: TLC R_f 0.31 (5% EtOAc in hexanes); GC t_R 16.51 min; NMR ($CDCl_3$, 400 MHz) δ −0.06 (s, 9 H), 0.44 (t, J = 8.0 Hz, 2 H), 1.20−2.50 (m, 15 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.71, 16.71, 21.26, 24.63, 28.37, 29.57, 31.22, 36.25, 42.52, 52.12, 216.13; IR (neat) 2929 (s), 2856 (s), 1703 (s, C=O), 1451 (m), 1247 (s, $SiCH_3$), 1169 (m), 934 (m), 860 (s), 837 (s, $SiCH_3$), 754 (m), 694 (m) cm^{-1}; MS m/z (relative intensity) 226 (M$^+$, 0.5), 211 (11), 197 (13), 184 (20), 169 (15), 112 (100), 97 (15), 84 (18), 75 (38), 73 (65); HRMS calcd for $C_{13}H_{26}OSi$ 226.1752, found (70 eV) 226.1753. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.82; H, 11.59.

2-[3-(Trimethylsilyl)propyl]cyclooctan-1-one (15). The standard procedure was followed by use of cyclooctanone (2.43 g, 19.3 mmol, 10 equiv), allyltrimethylsilane (0.231 g, 2.02 mmol, 1.0 equiv), MnO_2 (0.432 g, 4.97 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (1% EtOAc in hexanes as eluant) to give ketone **15** (0.314 g, 1.31 mmol) as a colorless liquid in 65% yield: TLC R_f 0.35 (5% EtOAc in hexanes); GC t_R 17.83 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.05 (s, 9 H), 0.40−0.45 (m, 2 H), 1.10−2.60 (m, 17 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.72, 16.75, 21.82, 24.78, 25.63, 25.95, 27.29, 32.64, 36.54, 41.84, 50.57, 220.44; IR (neat) 2931 (s), 2855 (s), 1701 (s, C=O), 1446 (m), 1247 (s, $SiCH_3$), 1194 (m), 1166 (m), 860 (s), 837 (s, $SiCH_3$), 752 (m), 694 (m) cm^{-1}; MS m/z (relative intensity) 240 (M$^+$, 1), 225 (8), 143 (12), 126 (40), 98 (76), 84 (19), 75 (46), 73 (100); HRMS calcd for $C_{14}H_{28}OSi$ 240.1909, found (70 eV) 240.1904. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.95; H, 11.76.

2-[3-(Trimethylsilyl)propyl]cyclododecan-1-one (16). The standard procedure was followed by use of cyclododecanone (3.52 g, 19.3 mmol, 10 equiv), allyltrimethylsilane (0.234 g, 2.05 mmol, 1.0 equiv), MnO_2 (0.436 g, 5.01 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (1% EtOAc in hexanes as eluant) to give ketone **16** (0.434 g, 1.47 mmol) as a colorless liquid in 74% yield: TLC R_f 0.55 (5% EtOAc in hexanes); GC t_R 22.37 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.06 (s, 9 H), 0.46 (t, J = 8.4 Hz, 2 H), 1.10−2.60 (m, 25 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.67, 16.82, 21.95, 22.02, 22.24, 22.95, 23.62, 23.87, 24.09, 25.68, 26.12, 29.79, 35.50, 37.02, 52.04, 215.05; IR (neat) 2933 (s), 2861 (s), 1706 (s, C=O), 1443 (m), 1247 (s, $SiCH_3$), 1172 (m), 1001 (m), 860 (s), 836 (s, $SiCH_3$), 748 (m), 693 (m) cm^{-1}; MS m/z (relative intensity) 296 (M$^+$, 1), 281 (6), 182 (35), 171 (11), 169 (8), 98 (16), 75 (22), 73 (100); HRMS calcd for $C_{18}H_{36}OSi$ 296.2535, found (70 eV) 296.2536. Anal. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.24. Found: C, 72.71; H, 12.25.

2-[3-(Dimethylphenylsilyl)propyl]cyclohexan-1-one (17). The standard procedure was followed by use of cyclohexanone (2.52 g, 25.7 mmol, 20 equiv), allyldimethylphenylsilane (0.231 g, 1.31 mmol, 1.0 equiv), MnO_2 (0.234 g, 2.69 mmol, 2.0 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **17** (0.255 g, 0.930 mmol) as a yellow liquid in 71% yield: TLC R_f 0.22 (5% EtOAc in hexanes); GC t_R 19.47 min; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.24 (s, 6 H), 0.60−0.85 (m, 2 H), 1.10−2.40 (m, 13 H), 7.25−7.60 (m, 5H,); ^{13}C NMR ($CDCl_3$, 50 MHz) δ −3.21, 15.64, 21.36, 24.61, 27.82, 33.11, 33.65, 41.76, 50.22, 127.51, 128.57, 133.34, 139.31, 213.24; IR (neat) 3069 (m), 3048 (m), 2936 (s), 2862 (s), 1705 (s, C=O), 1446 (m), 1425 (m), 1246 (s, $SiCH_3$), 1111 (m), 1066 (w), 832 (s, $SiCH_3$), 817 (s), 785 (m), 729 (s), 700 (s) cm^{-1}; MS m/z (relative intensity) 274 (M$^+$, 2), 259 (31), 197 (23), 153 (11), 135 (100), 107 (10), 105 (15), 98 (30), 75 (36); HRMS calcd for $C_{17}H_{26}OSi$ 274.1753, found (70 eV) 274.1749. Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.30; H, 9.64.

2-[3-(Methyldiphenylsilyl)propyl]cyclohexan-1-one (18). The standard procedure was followed by use of cyclohexanone (1.515 g, 15.4 mmol, 10.4 equiv), allylmethyldiphenylsilane (0.354 g, 1.49 mmol, 1.0 equiv), MnO_2 (0.263 g, 3.02 mmol, 2.0 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 18 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **18** (0.291 g, 0.864 mmol) as a yellow solid in 58% yield: mp 32−35 °C (recrystallized from hexanes); TLC R_f 0.15 (5% EtOAc in hexanes); GC t_R 23.24 min; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.52 (s, 3 H), 0.95−1.15 (m, 2 H), 1.20−2.40 (m, 13 H), 7.25−7.60 (m, 10 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ −4.59, 14.19, 21.36, 24.68, 27.87, 33.20, 33.68, 41.83, 50.23, 127.66, 128.95, 134.31, 137.21, 213.26; IR (KBr) 3070 (m), 2959 (s), 2934 (s), 2869 (m), 1701 (s, C=O), 1425 (m), 1252 (m, $SiCH_3$), 1107 (s), 1068 (w), 1005 (w), 950 (w), 904 (w), 833 (w, $SiCH_3$), 784 (s), 736 (s), 699 (s) cm^{-1}; MS m/z (relative intensity) 336 (M$^+$, 2), 321 (1), 259 (55), 197 (100), 181 (11), 137 (30), 105 (13), 55 (6); HRMS calcd for $C_{22}H_{28}OSi$ 336.1909, found (70 eV) 336.1916. Anal. Calcd for $C_{22}H_{28}OSi$: C, 78.52; H, 8.39. Found: C, 78.45; H, 8.44.

2-[3-(Triphenylsilyl)propyl]cyclohexan-1-one (19). The standard procedure was followed by use of cyclohexanone (2.09 g, 21.3 mmol, 19 equiv), allyltriphenylsilane (0.336 g, 1.12 mmol, 1.0 equiv), MnO_2 (0.198 g, 2.27 mmol, 2.0 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 18 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **19** (0.243 g, 0.61 mmol) as a light yellow solid in 54% yield: mp 67−68 °C (recrystallized from hexanes); TLC R_f 0.15 (5% EtOAc in hexanes); GC t_R 34.22 min (column program: initial temperature 50 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 260 °C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.10−2.40 (m, 15 H), 7.25−7.60 (m, 15 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.27, 21.40, 24.59, 27.74, 33.28, 33.57, 41.71, 50.03, 127.63, 129.15, 135.00, 135.38, 212.86; IR (KBr) 3065 (m), 2936 (s), 2929 (s), 2860 (m), 1692 (m, C=O), 1421 (m), 1102 (s), 727 (s), 696 (s) cm^{-1}; MS *m/z* (relative intensity) 398 (M^+, 0.4), 322 (17), 321 (60), 260 (30), 259 (100), 199 (25), 181 (17), 155 (4), 105 (9); HRMS calcd for $C_{27}H_{30}OSi$ 398.2066, found (70 eV) 398.2071. Anal. Calcd for $C_{27}H_{30}OSi$: C, 81.35; H, 7.59. Found: C, 81.29; H, 7.63.

2-[2-(Trimethylsilyl)ethyl]cyclopentan-1-one (20). The standard procedure was followed by use of cyclopentanone (1.69 g, 20.1 mmol, 10 equiv), vinyltrimethylsilane (0.201 g, 2.01 mmol, 1.0 equiv), MnO_2 (0.441 g, 5.06 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **20** (0.215 g, 1.17 mmol) as a colorless liquid in 59% yield: TLC R_f 0.38 (5% EtOAc in hexanes); GC t_R 12.26 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.05 (s, 9 H), 0.48 (t, J = 8.8 Hz, 2 H), 1.20−2.30 (m, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.91, 14.16, 20.58, 23.95, 28.95, 38.43, 51.70, 221.41; IR (neat) 2940 (s), 2861 (s), 1711 (s, C=O), 1447 (m), 1248 (s, $SiCH_3$), 1125 (m), 1061 (m), 849 (s), 836 (s, $SiCH_3$), 762 (m), 690 (m) cm^{-1}; MS *m/z* (relative intensity) 184 (M^+, 1), 183 (33), 169 (100), 156 (51), 150 (34), 107 (3), 85 (20), 75 (47), 73 (71); HRMS calcd for $C_{10}H_{20}OSi$ 184.1283, found (70 eV) 184.1280. Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94. Found: C, 64.85; H, 10.74.

2-[2-(Trimethylsilyl)ethyl]cyclohexan-1-one (21).[58] The standard procedure was followed by use of cyclohexanone (2.01 g, 20.5 mmol, 10 equiv), vinyltrimethylsilane (0.199 g, 1.99 mmol, 1.0 equiv), MnO_2 (0.438 g, 5.03 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **21** (0.283 g, 1.43 mmol) as a colorless liquid in 71% yield: TLC R_f 0.43 (5% EtOAc in hexanes); GC t_R 13.69 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.04 (s, 9 H), 0.37−0.43 (m, 2 H), 1.10−2.40 (m, 11 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.88, 13.91, 23.56, 24.66, 27.99, 33.15, 41.88, 53.67, 213.62; IR (neat) 2938 (s), 2861 (s), 1709 (s, C=O), 1448 (m), 1248 (s, $SiCH_3$), 1179 (m), 1125 (m), 862 (s,), 836 (s $SiCH_3$), 758 (m), 694 (m) cm^{-1}; MS *m/z* (relative intensity) 183 (M^+ − 15, 31), 171 (15), 170 (100), 169 (29), 155 (75), 142 (14), 127 (20), 75 (97), 73 (72); HRMS calcd for $C_{11}H_{22}OSi$ 198.1439, found (70 eV) 198.1441.

2-[2-(Trimethylsilyl)ethyl]cycloheptan-1-one (22). The standard procedure was followed by use of cycloheptanone (2.25 g, 20.1 mmol, 10 equiv), vinyltrimethylsilane (0.201 g, 2.01 mmol, 1.0 equiv), MnO_2 (0.438 g; 5.02 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (1% EtOAc in hexanes as eluant) to give ketone **22** (0.303 g, 1.43 mmol) as a colorless liquid in 72% yield: TLC R_f 0.42 (5% EtOAc in hexanes); GC t_R 16.51 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.05 (s, 9 H), 0.38−0.44 (m, 2 H), 1.20−2.40 (m, 13 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.89, 14.07, 24.54, 26.59, 28.42, 29.54, 30.78, 42.76, 55.38, 216.47; IR (neat) 2932 (s), 2855 (s), 1702 (s, C=O), 1451 (m), 1247 (s, $SiCH_3$), 1168 (m), 1097 (m), 861 (s), 835 (s, $SiCH_3$), 757 (m), 692 (m) cm^{-1}; MS *m/z* (relative intensity) 212 (M^+, 0.2), 197 (47), 184 (70), 169 (87), 156 (31), 155 (32), 130 (25), 115 (25), 75 (92), 73 (100); HRMS calcd for $C_{12}H_{24}OSi$ 212.1596, found (70 eV) 212.1584. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.90; H, 11.23.

2-[2-(Trimethylsilyl)ethyl]cyclooctan-1-one (23). The standard procedure was followed by use of cyclooctanone (2.56 g, 20.3 mmol, 10 equiv), vinyltrimethylsilane (0.200 g, 2.00 mmol, 1.0 equiv), MnO_2 (0.433 g, 4.98 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (1% EtOAc in hexanes as eluant) to give ketone **23** (0.283 g, 1.25 mmol) as a colorless liquid in 62% yield: TLC R_f 0.43 (5% EtOAc in hexanes); GC t_R 16.57 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.05 (s, 9 H), 0.35−0.43 (m, 2 H), 1.20−2.50 (m, 15 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.98, 14.36, 24.74, 25.17, 25.73, 26.98, 27.32, 32.53, 42.29, 53.81, 220.32; IR (neat) 2931 (s), 2849 (s), 1697 (s, C=O), 1462 (m), 1246 (s, $SiCH_3$), 1167 (m), 859 (s), 835 (s, $SiCH_3$), 739 (m), 704 (m) cm^{-1}; MS *m/z* (relative intensity) 211 (M^+ − 15, 31), 198 (17), 183 (16), 170 (37), 169 (24), 143 (61), 130 (20), 115 (16), 75 (55), 73 (100); HRMS calcd for $C_{13}H_{26}OSi$ 226.1752, found (70 eV) 226.1751. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.79; H, 11.59.

2-[2-(Trimethylsilyl)ethyl]cyclododecan-1-one (24). The standard procedure was followed by use of cyclododecanone (3.54 g, 19.5 mmol, 10 equiv), vinyltrimethylsilane (0.202 g, 2.02 mmol, 1.0 equiv), MnO_2 (0.446 g, 5.13 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (1% EtOAc in hexanes as eluant) to give ketone **24** (0.378 g, 1.34 mmol) as a colorless liquid in 67% yield: TLC R_f 0.67 (5% EtOAc in hexanes); GC t_R 21.25 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.05 (s, 9 H), 0.35−0.42 (m, 2 H), 1.10−2.60 (m, 23 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.91, 14.58, 21.94, 22.24, 22.96, 23.60, 23.86, 24.13, 25.70, 25.97, 26.17, 29.47, 37.18, 55.56, 221.39; IR (neat) 2932 (s), 2861 (s), 1705 (s, C=O), 1468 (m), 1247 (s, $SiCH_3$), 1172 (m), 1017 (m), 861 (s), 836 (s, $SiCH_3$), 755 (m), 693 (m) cm^{-1}; MS *m/z* (relative intensity) 282 (M^+, 0.6), 267 (37), 254 (19), 183 (10), 143 (22), 130 (31), 75 (26), 73 (100); HRMS calcd for $C_{17}H_{34}OSi$ 282.2378, found (70 eV) 282.2375. Anal. Calcd for $C_{17}H_{34}OSi$: C, 72.27; H, 12.13. Found: C, 72.63; H, 12.10.

2-[2-(Diethylmethylsilyl)ethyl]cyclohexan-1-one (25). The standard procedure was followed by use of cyclohexanone (2.27 g, 23.2 mmol, 10 equiv), vinyldiethylmethylsilane (0.302 g, 2.35 mmol, 1.0 equiv), MnO_2 (0.474 g, 5.45 mmol, 2.3 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 14 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **25** (0.331 g, 1.46 mmol) as a colorless liquid in 62% yield: TLC R_f 0.42 (5% EtOAc in hexanes); GC t_R 16.92 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.09 (s, 3 H), 0.38−0.51 (m, 2 H), 0.47 (d, J = 8.1 Hz, 6 H), 0.90 (t, J = 8.1 Hz, 4 H), 1.10−2.40 (m, 11 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −6.35, 4.82, 7.29, 10.22, 23.50, 24.65, 27.99, 33.17, 41.88, 53.81, 213.65; IR (neat) 2938 (s), 2873 (s), 1710 (s, C=O), 1449 (m), 1250 (m, $SiCH_3$), 1179 (m), 1125 (m), 851 (w, $SiCH_3$), 791 (s), 751 (m) cm^{-1}; MS *m/z* (relative intensity) 211 (M^+ − 15, 3), 198 (18), 197 (83), 170 (14), 169 (100), 155 (8), 101 (8), 89 (48), 73 (34); HRMS calcd for $C_{13}H_{26}OSi$ 226.1752, found (70 eV) 226.1739. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.68; H, 11.66.

2-[3-(Hydroxy)propyl]cyclohexan-1-one (26).[59] A diethyl ether solution of HBF_4 (54%, 0.475 g, 2.92 mmol, 5.8 equiv) was added dropwise to a solution of ketosilane **17** (0.138 g, 0.501 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was stirred for 2 h, to which was added *m*-CPBA (50−60%, 0.536 g, ~1.71 mmol, ~3.5 equiv) and triethylamine (3.0 mL). After an additional 6 h, the reaction mixture was worked up, neutralized with 10% HCl, and extracted with Et_2O (15 mL × 2). The combined ethereal solutions were washed with water and saturated aqueous NaCl. The mixture was then dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was chromatographed through a column packed with silica gel to give **26** (49.2 mg, 0.315 mmol) as a colorless liquid in 63% yield: TLC R_f 0.46 (20% EtOAc in hexanes); GC t_R 9.96 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.82−2.45 (m, 13 H), 3.52−3.71 (m, 2 H), 3.93−4.06 (br, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.25, 25.01, 25.91, 26.46, 29.68, 39.06, 43.61, 60.98, 213.26; IR (neat) 3411 (b), 2933 (s), 2862(s), 1714 (s, C=O), 1448 (s), 1245 (m), 1185 (m), 1070 (m), 953 (m), 864 (m) cm^{-1}; MS *m/z* (relative intensity) 156 (M^+, 14), 138 (10), 113 (100), 110 (10), 109 (8), 98 (11), 95 (17), 68 (8), 67 (13), 55 (17).

4-(3,3-Dimethyl-3-silacyclohexyl)butan-2-one (27). The standard procedure was followed by use of acetone (2.41 g, 41.6 mmol, 20 equiv), diallyldimethylsilane (0.299 g, 2.13 mmol, 1.0 equiv), MnO_2 (0.467 g, 5.37 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 18 h and then worked up. The crude product was purified by MPLC

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(2% EtOAc in hexanes as eluant) to give ketone **27** (0.342 g, 1.73 mmol) as a colorless liquid in 81% yield: TLC R_f 0.26 (5% EtOAc in hexanes); GC t_R 13.74 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.03 (s, 3 H), −0.01 (s, 3 H), 0.15−0.96 (m, 4 H), 1.12−2.04 (m, 7 H), 2.10 (s, 3 H), 2.31−2.52 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.07, −1.60, 13.61, 20.76, 23.60, 29.77, 34.91, 35.99, 36.35, 41.27, 209.57; IR (neat) 2951 (s), 2909 (s), 2854 (s), 1706 (s, C=O), 1456 (m), 1354 (m), 1249 (s, $SiCH_3$), 1179 (m), 1148 (m), 984 (m), 851 (w), 841 (s, $SiCH_3$), 801 (s), 728 (m), cm^{-1}; MS m/z (relative intensity) 198 (M$^+$, 0.5), 183 (4), 169 (19), 155 (15), 140 (100), 128 (32), 127 (26), 112 (43), 99 (85), 75 (32); HRMS calcd for $C_{11}H_{22}OSi$ 198.1439, found (70 eV) 198.1441. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.85; H, 11.03.

4-(3,3-Dimethyl-3-silacyclohexyl)-3,3-dimethylbutan-2-one (28). The standard procedure was followed by use of 3-methyl-2-butanone (2.05 g, 23.8 mmol, 12 equiv), diallyldimethylsilane (0.283 g, 2.09 mmol, 1.0 equiv), MnO_2 (0.534 g, 6.14 mmol, 3.0 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 12 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **28** (0.307 g, 1.36 mmol) as a colorless liquid in 65% yield: TLC R_f 0.28 (5% EtOAc in hexanes); GC t_R 14.85 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.06 (s, 3 H), −0.02 (s, 3 H), 0.12−0.94 (m, 4 H), 1.05 (s, 3 H), 1.06 (s, 3 H), 1.13−1.94 (m, 7 H), 2.10 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.28, −1.70, 13.28, 22.62, 23.68, 24.50, 25.13, 25.55, 33.31, 37.68, 47.62, 51.39, 214.53; IR (neat) 2955 (s), 2909 (s), 2853 (s), 1705 (s, C=O), 1456 (m), 1354 (m), 1248 (s, $SiCH_3$), 1179 (m), 1148 (m), 984 (m), 851 (w), 839 (s, $SiCH_3$), 800 (s), 727 (m) cm^{-1}; MS m/z (relative intensity) 226 (M$^+$, 1), 211 (7), 183 (6), 141 (64), 127 (47), 113 (13), 99 (100), 86 (62), 75 (22), 59 (23); HRMS calcd for $C_{13}H_{26}OSi$ 226.1752, found (70 eV) 226.1743. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.75; H, 11.45.

6-(Dimethylvinylsilyl)hexan-2-one (29). The standard procedure was followed by use of acetone (2.56 g, 45.7 mmol, 20 equiv), allyldimethylvinylsilane (0.289 g, 2.29 mmol, 1.0 equiv), MnO_2 (0.285 g, 5.72 mmol, 2.5 equiv), and acetic acid (0.050 mL). The reaction mixture was heated for 16 h and then worked up. The crude product was purified by MPLC (2% EtOAc in hexanes as eluant) to give ketone **29** (29.0 mg, 0.158 mmol) as a colorless liquid in 7% yield: TLC R_f 0.27 (5% EtOAc in hexanes); GC t_R 11.46 min; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.04 (s, 6 H), 0.51−0.72 (m, 2 H), 1.20−1.60 (m, 4 H), 2.09 (s, 3 H), 2.41 (t, J = 7.2 Hz, 2 H), 4.76−4.88 (m, 2 H), 5.62−5.81 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −3.90, 14.57, 18.35, 28.05, 29.85, 47.35, 112.78, 134.89, 209.01; IR (neat) 3060 (w), 3020(w), 2917 (s), 1714 (s, C=O), 1598 (w, C=C), 1409 (m), 1360 (s), 1251 (s, $SiCH_3$), 1168 (m), 1006 (m), 829 (s, $SiCH_3$) cm^{-1}; MS m/z (relative intensity) 169 (M$^+$ − 15, 1), 143 (35), 127 (6), 115 (100), 99 (9), 87 (10), 85 (21), 75 (63), 61 (9), 59 (23); HRMS calcd for $C_{10}H_{20}OSi$ 184.1283, found (70 eV) 184.1286. Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94. Found: C, 64.93; H, 10.83.

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