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Silicon-controlled Carbon–Carbon Bond Formation and Cyclization between Carbonyl Compounds and Allyltrimethylsilane

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The effect of silicon on C–C bond formation between carbonyl compounds and allyltrimethylsilane was investigated. Treatment of 1,3-diketones, β-ketoesters or malonates with allyltrimethylsilane in the presence of ceric ammonium nitrate (CAN) in methanol produced the corresponding allylated products. Furthermore, introduction of $Mn(OAc)_3 \cdot 2H_2O$ into those reactions for replacement or assistance of CAN afforded silicon-containing cyclopentanes in 51–75% yields. A sequential process involving allylation, free-radical cyclization and elimination was also developed by use of CAN/$Mn(OAc)_3 \cdot 2H_2O$/$Cu(OAc)_2 \cdot H_2O$. Accordingly, β-ketoesters or malonates were allowed to react with allylsilanes in acetic acid to give silicon-containing cyclopentanes with an *exo* methylene unit in 52–71% yields. These reactions involved carbocationic and carboradical intermediates, of which formation and chemical activities were controlled by a β-silyl group.

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INTRODUCTION

Organosilyl groups have been used in the control of various types of reactions involving carbocationic, carbanionic and carboradical intermediates.[1] This is mainly due to the effect of stabilization or destabilization resulting from silicon.[2–6] We wish to use a silyl group for the promotion of C–C bond formation involving carbonyl compounds as the substrate–one of the most important topics in organic chemistry.

In the course of studying silicon-controlled organic reactions,[7–15] we investigated the synthetic applicability of addition of ketones to allylsilanes by use of ceric ammonium nitrate (CAN), manganese(III) acetate or a mixture of CAN and manganese(III) acetate along with cupric acetate. Manipulation of the reaction conditions would enable us to accomplish monoallylation, diallylation, allylation followed by ring formation, and allylation–cyclization–elimination of carbonyl compounds. Herein we report the full scope of these silicon-controlled reactions.

RESULTS AND DISCUSSION

Monoallylation of carbonyl compounds with allyltrimethylsilane by use of CAN

To explore the feasibility of the silicon-controlled addition of a ketone to an allylsilane, we treated cycloalkanones with five- to eight- and twelve-membered rings with allyltrimethylsilane (1.3 equiv) and CAN (2.1 equiv) in methanol at 25 °C for 4 h. The corresponding monoallylated products **1**–**5** were obtained in 21–75% yields (see Table 1). Under the same conditions,

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Table 1 Monoallylation of carbonyl compounds with allyltrimethylsilane (1.3 equiv) in the presence of CAN (2.1 equiv) in methanol at 25 °C

Carbonyl compound	Product	Yield (%)
Cyclopentanone	**1**	35
Cyclohexanone	**2**	39
Cycloheptanone	**3**	21
Cyclo-octanone	**4**	25
Cyclododecanone	**5**	75[a]
2,2,6,6-Tetramethyl-3,5-heptanedione	**6**	98[a]
Diethyl malonate	**7**	74[a]

[a] Ref. 9

2,2,6,6-tetramethyl-3,5-heptanedione and diethyl malonate were converted to monoallylated products **6** (98%) and **7** (74%), respectively. In all of these reactions, the C–C bond formation took place exclusively at the terminal sp^2 carbon of allyltrimethylsilane.

Diallylation of carbonyl compounds with allyltrimethylsilane by use of CAN (Scheme 1)

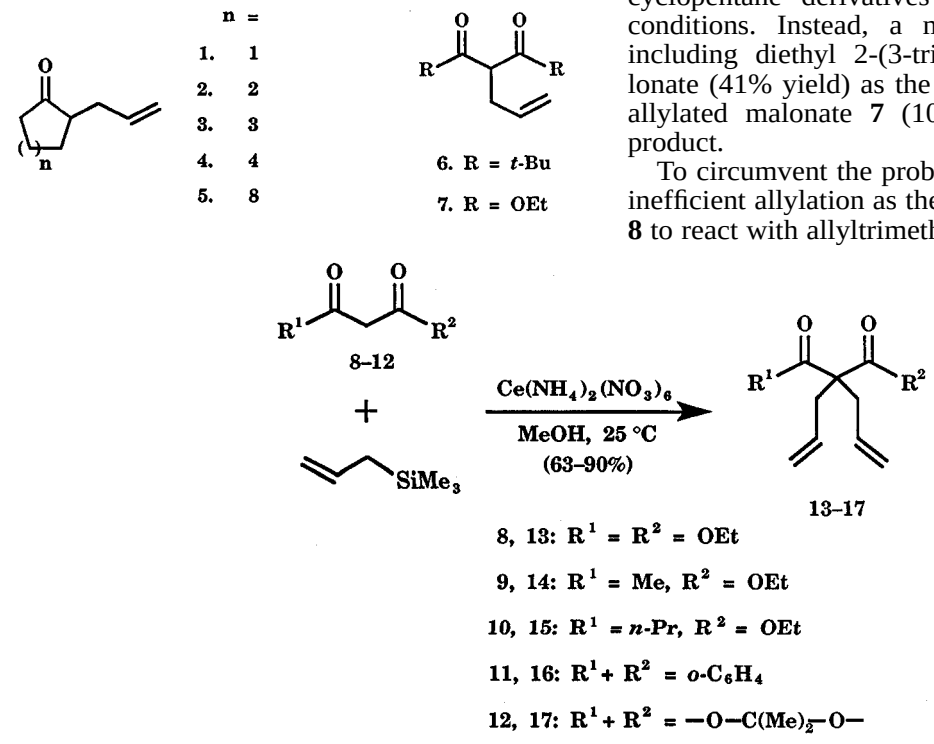
We found that addition of 1,3-dioxo compounds **8**–**12** to allyltrimethylsilane (2.6 equiv) produced good to excellent yields (63–90%) of diallylated products **13**–**17** by using 4.1 equiv of CAN in methanol at 25 °C. The results are summarized in Table 2.

Allylation followed by ring formation by use of $Mn(OAc)_3 \cdot 2H_2O$ (Scheme 2)

We planned to develop a new method for the synthesis of silicon-containing cyclopentanes by applying the allylation as the initial step. Thus we treated 1,3-indandione (**11**) with 2.6 equiv of allyltrimethylsilane in the presence of 4.2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ in acetic acid at 80 °C. After 1 h, the desired silicon-containing cyclopentanes **25** were obtained in 60% yield as a mixture of two diastereoisomers. Results from GC analysis indicate that the ratio was 5:1 for the *cis* to the *trans* isomers (see Table 3); the *cis* isomer was often obtained as the major product.[16, 17]

To broaden the scope of this method, we applied the same conditions to Meldrum's acid (**12**). The corresponding spiro compounds **26** were obtained in 51% yield. Nevertheless, diethylmalonate (**8**) was not converted to cyclopentane derivatives **27** under the same conditions. Instead, a mixture was obtained including diethyl 2-(3-trimethylsilylpropyl)malonate (41% yield) as the major component and allylated malonate **7** (10% yield) as the by-product.

To circumvent the problem resulting from the inefficient allylation as the first step, we allowed **8** to react with allyltrimethylsilane (1.3 equiv) in

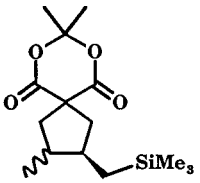


Scheme 1

Table 2 Diallylation of carbonyl compounds with allyltrimethylsilane (2.6 equiv) in the presence of CAN (4.1 equiv) in methanol at 25 °C

1,3-Dioxo Compound	Product	Yield (%)
8	**13**	63
9	**14**	81
10	**15**	76
11	**16**	90[a]
12	**17**	82[a]

[a] Ref. 9.



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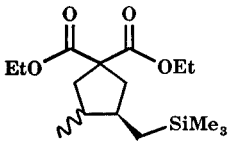

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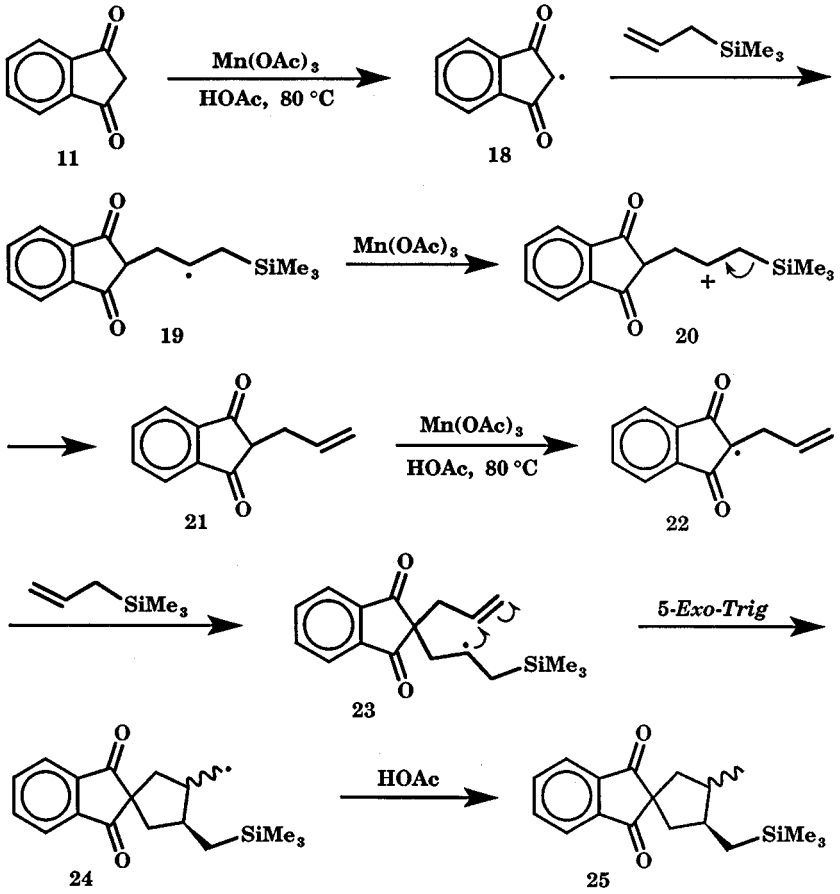
the presence of CAN (2.1 equiv) and acetic acid at 25 °C. After the orange color of the solution faded,[18] we added additional allyltrimethylsilane (1.3 equiv) and $Mn(OAc)_3 \cdot 2H_2O$ (2.1 equiv) into the reaction flask. Consequently, the desired cyclopentane derivatives **27** were obtained in 75% overall yield as a mixture of *cis* and *trans* isomers with a ratio of 5:1 (see Table 3).

The mechanism shown in Scheme 2 can account for the formation of the spiro products **25** from 1,3-indandione (**11**). Reaction of **11** with $Mn(OAc)_3 \cdot 2H_2O$ generated radical intermediate **18**.[19] Addition of **18** to allyltrimethylsilane produced intermediate **19**, in which the carboradical center is stabilized by a β-silyl group. Thus the possibility decreases for the reversion of **19** to **18** and allyltrimethylsilane. The intermediate **19** was then oxidized by $Mn(OAc)_3 \cdot 2H_2O$ *in situ*[20] to give the corresponding carbocation **20**. Elimination of the trimethylsilyl group in **20** afforded allylated species **21**. The driving force for the conversion of **21** to the stabilized radical **23** via



Scheme 2

Table 3 Syntheses of cyclopentane derivatives from 1,3-dioxo compounds with allyltrimetthylsilane (2.6 equiv) in the presence of oxidizing agents and acetic acid

1,3-Dioxo compound	Oxidizing agent	Temp. (°C)	Product	Yield (%)	Ratio of isomers, *cis*/*trans*[a]
11	$Mn(OAc)_3 \cdot 2H_2O$	80	**25**	60	5:1
12	$Mn(OAc)_3 \cdot 2H_2O$	80	**26**	51	6:1
8	$CAN + Mn(OAc)_3 \cdot 2H_2O$	25→80	**27**	75	5:1

[a] Determined by GC.

22 is the same as that in the conversion of **11** to **19** via **18**. Then intramolecular cyclization occurred in **23** through a favorable 5-*exo-trig* mode[16] to give the spiro intermediates **24**. Finally this primary carboradical species trapped a hydrogen radical from acetic acid[21] to give the silicon-containing spiro products **25**.

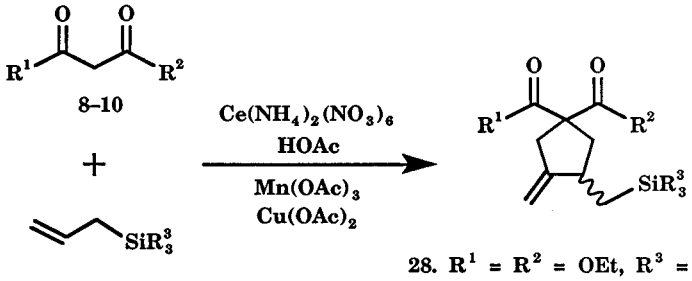
Intramolecular cyclization often takes place in 1,3-diketones and β-keto esters that bear a γ-carboradical moiety (such as **19**) to give dihydrofurans.[9, 19] Nevertheless, we did not obtain any dihydrofuran derivatives upon treatment of 1,3-indandione (**11**) with allyltrimethylsilane and $Mn(OAc)_3 \cdot 2H_2O$. We believe that the angle strain existing in the five-membered ring of the intermediate **19** may provide an unfavorable environment for the formation of an extra dihydrofuran ring fused to the indandione nucleus.

Sequential allylation, cyclization and elimination for the synthesis of silicon-containing cyclopentanes with an *exo* methylene unit

Our final goal was to establish a 'one-flask' method for the synthesis of new compounds **28**–**31**. Compounds of this class could become valuable synthons in organic synthesis.

Accordingly, we treated a malonate (i.e. **8**) or a β-keto ester (i.e. **9** and **10**) with allyltrimethylsilane (1.3 equiv) and CAN (2.1 equiv) in acetic acid at 25 °C for 4 h. To the mixture were added $Mn(OAc)_3 \cdot 2H_2O$ (1.1 equiv), $Cu(OAc)_2 \cdot H_2O$ (1.1 equiv) and the second portion of allyltrimethylsilane (1.3 equiv). After 1 h at 80 °C, the desired carbocycles possessing an *exo* methylene unit (i.e. **28**–**30**) were obtained in 61–71% yields (see Scheme 3 and Table 4). The mechanism for the conversion of **8**→**28** is depicted in Scheme 4, in which $Cu(OAc)_2 \cdot H_2O$ was applied to oxidize the primary carboradical **32** to the corresponding carbocation **33**.[21] Finally deprotonation occurred in **33** to give the desired product **28**.

Furthermore, we modified the procedure for the conversion of **8**→**28** by replacing the second portion of allyltrimethylsilane with allyltri-isopropylsilane (1.3 equiv). The tri-isopropylsilyl-containing product **31** was generated in 52% yield (see Table 4). These results indicate the possibility of introduction of different silyl groups into cyclopentane derivatives.



28. $R^1 = R^2 = OEt$, $R^3 = Me$

29. $R^1 = R^3 = Me$, $R^2 = OEt$

30. $R^1 = n$-Pr, $R^2 = OEt$, $R^3 = Me$

31. $R^1 = R^2 = OEt$, $R^3 = i$-Pr

Scheme 3

Table 4 Syntheses of cyclopentanes with an *exo* methylene from 1,3-dioxo compounds and allylsilanes in the presence of CAN, $Mn(OAc)_3 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$ and acetic acid

1,3-Dioxo compound	Allylsilane	Product	Yield (%)
8	Allyltrimethylsilane	**28**	61
9	Allyltrimethylsilane	**29**	71
10	Allyltrimethylsilane	**30**	67
8	Allyltrimethylsilane + allyltri-isopropylsilane	**31**	52

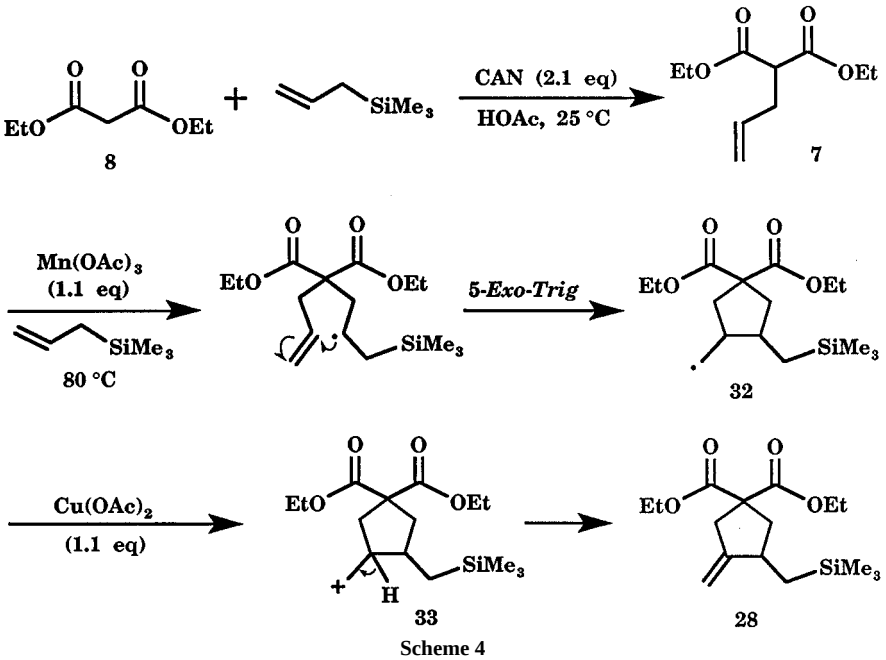
CONCLUSIONS

A new method was developed for the allylation of carbonyl compounds by use of allyltrimethylsilane in the presence of CAN and methanol. In these reactions, the electronic effect resulting from silicon provided a promoting effect for the C–C bond formation. Extension of this strategy by performance of the same reactions in the presence of acetic acid and $Mn(OAc)_3 \cdot 2H_2O$ or $CAN/Mn(OAc)_3 \cdot 2H_2O/Cu(OAc)_2 \cdot H_2O$ gave silicon-containing cyclopentane derivatives in good yields. These reactions went through an intramolecular radical cyclization pathway.

EXPERIMENTAL

General procedure

Ethyl acetate, glacial acetic acid, hexanes and methanol were purchased from Mallinckrodt Chemical Co. Ethyl acetate and hexanes were dried and distilled from CaH_2. Reagents purchased from Aldrich Chemical Co. included allyltriisopropylsilane, allyltrimethylsilane, cyclododecanone, cycloheptanone, cyclohexanone, cyclo-octanone, cyclopentanone, 2,2-dimethyl-1,3-dioxane-4,6-dione, ethyl buty-



Scheme 4

rylacetate, ethyl 2-methylacetoacetate, ethyl 2-oxocyclopentanecarboxylate, 1,3-indandione, 2,2,6,6-tetramethyl-3,5-heptanedione, ceric ammonium nitrate and cupric(II) acetate monohydrate. Diethyl malonate, ethyl acetoacetate and manganese (III) acetate dihydrate were purchased from Merck Inc. Analytical thin-layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254), purchased from Merck Inc. 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 methylsilicone gum capillary column (0.32 mm i.d.). Nitrogen was used as a carrier gas and the flow rate was kept constant at 14.0 ml min^{-1}. The retention time t_R was measured under the following conditions: injector temperature 260 °C; initial temperature of column 70 °C; duration 2.00 min; increment rate 10 °C min^{-1}; the final temperature of column 250 °C. Gas chromatography and low-resolution mass spectral analyses were performed on a Hewlett–Packard 5890 Series II instrument equipped with a Hewlett–Packard 5971A mass-selective detector and a capillary HP-1 column. Purification by gravity column chromatography was carried out by use of Merck Reagents silica gel 60 (particle size 0.063–0.200 mm, 70–230-mesh ASTM). Infrared (IR) spectra were measured on a Bomem Michelson Series FT-IR spectrometer. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Absorption intensities are indicated by the following abbreviations: s, strong; m, medium; w, weak. Proton NMR spectra were obtained on a Varian Unity-400 (400 MHz) spectrometer or a Varian Gemini-300 (300 MHz) spectrometer using chloroform-*d* as solvent and tetramethylsilane as internal standard. ^{13}C NMR spectra were obtained on a Varian Unity-400 (100 MHz) spectrometer or Varian Gemini-300 (75 MHz) spectrometer using chloroform-*d* as solvent. ^{13}C chemical shifts are referenced to the center of the $CDCl_3$ triplet (δ 77.0 ppm). Multiplicities are indicated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *J*, coupling constant (hertz). High-resolution mass spectra were obtained by means of a JEOL JMS-HX110 mass spectrometer. Elemental analyses were carried out on a Heraeus CHN-O RAPID element analyzer at the National Cheng-Kung University.

Standard procedure 1 for the syntheses of compounds 1–4

To a solution containing a carbonyl compound and allyltrimethylsilane in methanol (15 ml) was added CAN. The orange mixture was stirred at 25 °C for 4 h until the orange color faded. The reaction mixture was poured into cold water and then extracted with ether (4 × 25 ml). The combined organic extracts were dried over $MgSO_4$(s) and concentrated under reduced pressure. The residue was chromatographed with silica gel to provide the pure desired product.

2-Allylcyclopentanone (1)

The standard procedure 1 was followed, using cyclopentanone (42. 1mg, 0.501 mmol, 1.0 equiv), allyltrimethylsilane (74.2 mg, 0.651 mmol, 1.3 equiv), and CAN (576 mg, 1.05 mmol, 2.1 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 3% EtOAc in hexanes as eluant) to give pure **1** (21.7 mg, 0.175 mmol) as a colorless oil in 35% yield: GC t_R 5.61 min; TLC R_f 0.39 (20% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.21–2.65 (m, 9 H), 4.97–5.06 (m, 2 H, $=CH_2$), 5.67–5.78 (m, 1 H, =CH); IR (neat) 3076 (w, =C–H), 2955 (s, C–H), 2870 (s, C–H), 1736 (s, C=O), 1641 (w, C=C), 1442 (m), 1413 (m), 1156 (s), 995 (m), 842 (m) cm^{-1}; MS *m*/*z* (relative intensity) 124 (M^+, 38), 96 (68), 95 (43), 81 (30), 80 (29), 79 (28), 68 (62), 67 (100), 55 (48), 53 (36). Its spectroscopic characteristics are consistent with those of the same compound reported previously.[22]

2-Allylcyclohexanone (2)

The standard procedure 1 was followed using cyclohexanone (49.2 mg, 0.502 mmol, 1.0 equiv), allyltrimethylsilane (74.3 mg, 0.651 mmol, 1.3 equiv), and CAN (581 mg, 1.06 mmol, 2.1 equiv). The residue was purified by chromatography on silica (gel (1.5cm × 16cm column, 2% EtOAc in hexanes as eluant) to give pure **2** (26.9 mg, 0.195 mmol) as a colorless oil in 39% yield: GC t_R 7.23 min; TLC R_f 0.44 (20% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.15–2.58 (m, 11H), 5.01–5.07 (m, 2 H, $=CH_2$), 5.56–5.71 (m, 1H, =CH); IR (neat) 3074 (w, =C–H), 2932 (s, C–H), 2860 (s, C–H), 1710 (s, C=O), 1641 (w, C=C), 1442 (m), 1313 (m), 1126 (s), 986 (m), 913 (s) cm^{-1}; MS *m*/*z* (relative intensity) 138 (M^+, 72), 123 (30), 109 (62), 95 (67), 94 (100), 81 (58), 79 (86), 67 (91),

55 (45), 54 (42). Its spectroscopic characteristics are consistent with those of the same compound reported previously.[23]

2-Allylcycloheptanone (3)
The standard procedure 1 was followed using cycloheptanone (56.2 mg, 0.502 mmol, 1.0 equiv), allyltrimethylsilane (74.6 mg, 0.654 mmol, 1.3 equiv), and CAN (572 mg, 1.04 mmol, 2.1 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 2% EtOAc in hexanes as eluant) to give pure **3** (16.1 mg, 0.106 mmol) as a colorless oil in 21% yield: GC t_R 9.02 min; TLC R_f 0.52 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.14–2.69 (m, 13H), 5.03–5.12 (m, 2H, $=CH_2$), 5.64–5.77 (m, 1H, =CH); IR (neat) 3076 (w, =C–H), 2926 (s, C–H), 2858 (s, C–H), 1700 (s, C=O), 1641 (w, C=C), 1450 (s), 1339 (m), 1161 (w), 939 (m), 855 (m) cm^{-1}; MS *m*/*z* (relative intensity) 152 (M^+, 39), 109 (90), 98 (49), 95 (91), 84 (44), 81 (72), 79 (53), 67 (100), 55 (49), 54 (58). Its spectroscopic characteristics are consistent with those of the same compound reported previously.[23]

2-Allylcyclooctanone (4)
The standard procedure 1 was followed using cyclo-octanone (63.4 mg, 0.503 mmol, 1.0 equiv), allyltrimethylsilane (75.2 mg, 0.658 mmol, 1.3 equiv), and CAN (586 mg, 1.07 mmol, 2.1 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **4** (20.6 mg, 0.124 mmol) as a colorless oil in 25% yield: GC t_R 10.88 min; TLC R_f 0.57 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26–2.53 (m, 15 H), 4.99–5.05 (m, 2 H, $=CH_2$), 5.62–5.75 (m, 1 H, =CH); IR (neat) 3075 (w, =C–H), 2931 (s, C–H), 2856 (s, C–H), 1701 (s, C=O), 1640 (w, C=C), 1446 (m), 1192 (m), 861 (w), 837 (m) cm^{-1}; MS *m*/*z* (relative intensity) 166 (M^+, 12), 111 (54), 109 (59), 98 (88), 95 (59), 83 (35), 81 (67), 68 (40), 67 (88), 55 (100). Its spectroscopic characteristics are consistent with those of the same compound reported previously.[23]

Standard procedure 2 for the syntheses of compounds 13–15

To a solution containing a dioxo compound and allyltrimethylsilane in methanol (20 ml) was added CAN. The orange mixture was stirred at 25 °C for 4 h until the orange color faded. The reaction mixture was poured into cold water and then extracted with ether (4 × 25 ml). The combined organic extracts were dried over $MgSO_4$ (s) and concentrated under reduced pressure. The residue was chromatographed with silica gel to provide the desired product.

Diethyl diallylpropanedioate (13)

The standard procedure 2 was followed by use of diethyl malonate (**8**, 80.1 mg, 0.501 mmol, 1.0 equiv), allyltrimethylsilane (149 mg, 1.31 mmol, 2.6 equiv), and CAN (1.12 g, 2.04 mmol, 4.1 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 4%EtOAc in hexanes and eluant) to give pure **13** (75.7 mg, 0.315 mmol) as a colorless oil in 63% yield: GC t_R 11.59 min; TLC R_f 0.36 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, J=7.1 Hz, 6H, 2 × OCH_2CH_3), 2.60 (d, J=7.3 Hz, 4H, 2 × CH_2C=), 4.15 (q, J=7.1 Hz, 4H, 2 × OCH_2CH_3), 5.03–5.14 (m, 4H, 2 × $=CH_2$), 5.68–5.82 (m, 2 H, 2 × CH=); IR (neat) 3079 (w, =C–H), 2984 (m, C–H), 2957 (m, C–H), 1739 (s, C=O), 1641 (w, C=C), 1242 (m), 1144 (m), 1039 (m), 858 (m) cm^{-1}; MS *m*/*z* (relative intensity) 240 (M^+, 0.6), 199 (78), 166 (20), 153 (100), 148 (18), 125 (42), 121 (19), 93 (72), 79 (32), 77 (24). Its spectroscopic characteristics are consistent with those of the same compound reported previously.[24]

Ethyl 2,2-diallyl-4-pentenoate (14)
The standard procedure 2 was followed using ethyl acetoacetate (**9**, 65.4 mg, 0.503 mmol, 1.0 equiv), allyltrimethylsilane (151 mg, 1.32 mmol, 2.6 equiv) and CAN (1.13 g, 2.06 mmol, 4.1 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 4% EtOAc in hexanes as eluant) to give pure **14** (85.1 mg, 0.405 mmol) as a colorless oil in 81% yield: GC t_R 10.41 min; TLC R_f 0.53 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (t, J=7.1 Hz, 3H, OCH_2CH_3), 2.09 (s, 3H, $COCH_3$), 2.48–2.63 (m, 4H, 2 × CH_2C=), 4.15 (q, J=7.1 Hz, 2 H, OCH_2CH_3), 4.98–5.06 (m, 4H, 2 × $=CH_2$), 5.50–5.61 (m, 2H, 2 × CH=); IR (neat) 3079 (w, =C–H), 2983 (s, C–H), 2943 (m, C–H), 1725 (s, C=O), 1721 (s, C=O), 1641 (m, C=C), 1278 (m), 1208 (s), 1011 (m), 923 (m) cm^{-1}; MS *m*/*z* (relative intensity) 210 (M^+, 1), 169 (39), 168 (52), 123

(100), 95 (76), 93 (66), 81 (47), 79 (75), 77 (49), 67 (39). Its spectroscopic characteristics are consistent with those of the same compound reported previously.[25]

Ethyl 2,2-diallyl-3-oxohexanoate (15)
The standard procedure 2 was followed using ethyl butyrylacetate (**10**, 79.4 mg, 0.502 mmol, 1.0 equiv), allyltrimethylsilane (152 mg, 1.33 mmol, 2.6 equiv) and CAN (1.12 g, 2.05 mmol, 4.1 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 3% EtOAc in hexanes as eluant) to give pure **15** (90.4 mg, 0.380 mmol) as a colorless oil in 76% yield: GC t_R 12.84 min; TLC R_f 0.62 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86 (t, J=7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.23 (t, J=7.1 Hz, 3H, OCH_2CH_3), 1.53–1.66 (m, 2H, $CH_2CH_2CH_3$), 2.36 (t, J=7.2 Hz, 2H, $COCH_2CH_2$), 2.51–2.63 (m, 4H, 2×CH_2C=), 4.16 (q, J=7.1 Hz, 2H, OCH_2CH_3), 5.01–5.07 (m, 4H, 2×=CH_2), 5.42–5.61 (m, 2H, 2×CH=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.58, 14.01, 16.96, 35.76, 40.94, 61.20, 62.81, 118.95, 132.19, 171.51, 205.90; IR (neat) 3078 (w, =C–H), 2946 (s, C–H), 2933 (s, C–H), 2875 (m, C–H), 1724 (s, C=O), 1715 (s, C=O), 1641 (m, C=C), 1443 (m), 1209 (s), 1185 (s), 1034 (m), 921 (m), 821 (m) cm^{-1}; MS m/z (relative intensity) 238 (M^+, 0.5), 168 (31), 151 (9), 140 (8), 122 (9), 95 (19), 81 (10), 79 (18), 71 (100), 67 (9); exact mass calcd for $C_{14}H_{22}O_3$238.1569, found 238.1573. Analysis: calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.23; H, 8.98%.

Standard procedure 3 for the syntheses of compounds 25 and 26

To a sealable bottle containing a dioxo compound, allyltrimethylsilane and glacial acetic acid (20 ml), was added $Mn(OAc)_3 \cdot 2H_2O$. The bottle was sealed and the solution was stirred at 80 °C. The dark brown color faded after 1 h. Then the reaction mixture was cooled, diluted with water (20 ml), and neutralized with aqueous Na_2CO_3. The neutralized solution was extracted with ether (4×25 ml) and the combined organic solutions were washed with brine and dried over $MgSO_4$ (s). After the solvents were removed under reduced pressure, the residue was chromatographed through a silica-gel column to provide the desired product.

***cis*- and *trans*-2,3-Benzo-7- methyl-8-(trimethylsilyl)methylspiro[4.4]nonane-1,4-dione (25)**
The standard procedure 3 was followed using 1,3-indandione (**11**, 148 mg, 1.01 mmol, 1.0 equiv), allyltrimethylsilane (301 mg, 2.64 mmol, 2.6 equiv) and $Mn(OAc)_3 \cdot 2H_2O$ (1.14 g, 4.25 mmol, 4.2 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give **25** (181 mg, 0.603 mmol) as a pale yellow crystalline solid in 60% yield: GC t_R 20.14 and 20.55 min for the *trans* and the *cis* isomers, respectively; TLC R_f 0.57 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.29, −0.01 (2×s, 9H, *trans* and *cis* Si$(CH_3)_3$), 0.54–0.63 (m, 2H, $SiCH_2$–), 0.97–1.04 (m, 3H, CH_3), 1.53–2.51 (m, 6H), 7.74–7.89 (m, 4H, ArH); IR (neat) 3063 (w, =C–H), 2928 (s, C–H), 2862 (s, C–H), 1743 (m, C=O), 1703 (s), 1593 (m, Ph), 1332 (m), 1259 (s, Si–CH_3), 848 (s, Si–CH_3), 691 (m) cm^{-1}; MS m/z (relative intensity) 300 (M^+, 8), 285 (15), 231 (96), 195 (15), 168 (30), 142 (24), 128 (13), 115 (15), 104 (28), 73 (100). The *cis* isomer **25** was obtained pure as a white solid after recrystallization from hexanes: m.p. 77–79 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.01 (s, 9H, Si$(CH_3)_3$), 0.57–0.63 (m, 2H, $SiCH_2$), 1.00 (d, J=7.6 Hz, 3H, CH_3), 1.62–1.78 (m, 2H), 1.91 (dd, J=13.2, 7.2 Hz, 1H), 2.12 (dd, J=13.2, 7.6 Hz, 1H), 2.30–2.38 (m, 1H), 2.41–2.52 (m, 1H), 7.74–7.89 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.84, 14.69, 16.58; 39.25, 40.70, 41.51, 41.87, 59.57, 123.24, 123.32, 135.43, 135.46, 141.33, 141.78, 204.47, 205.19; exact mass calcd for $C_{18}H_{24}O_2Si$ 300.1545, found 300.1541. Analysis calcd for $C_{18}H_{24}O_2Si$; C, 71.95; H, 8.05. Found: C, 72.12; H, 8.31%.

***cis*- and *trans*-2,8,8-Trimethyl-3-(trimethylsilyl)methyl-7,9-dioxaspiro[4.5]decane-6,10-dione (26)**
The standard procedure 3 was followed using 2,2 - dimethyl - 1,3 - dioxane - 4,6 - dione (**12**, 146 mg, 1.01 mmol, 1.0 equiv), allyltrimethylsilane (306 mg, 2.68 mmol, 2.6 equiv), and $Mn(OAc)_3 \cdot 2H_2O$ (1.15 g, 4.28 mmol, 4.2 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give **26** (155 mg, 0.520 mmol) as a colorless oil in 51% yield: GC t_R 16.69 and 17.14 min for the *trans* and the *cis* isomers, respectively; TLC R_f 0.45

(5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.02, −0.01 (2×s, 9H, *trans* and *cis* $Si(CH_3)_3$), 0.53–0.64 (m, 2H, $SiCH_2$), 0.97 (d, J=5.4 Hz, 3H, CH_3), 1.71 (s, 6H, $C(CH_3)_2$), 2.02–2.53 (m, 6H); IR (neat) 2933 (s, C–H), 2865 (s, C–H), 1754 (s, C=O), 11291 (s, Si–CH_3), 1206 (m), 952 (m), 849 (s, Si–CH_3) cm^{-1}; MS m/z (relative intensity) 298 (M^+, 0.1), 212 (12), 181 (25), 131 (27), 122 (12), 108 (10), 74 (14), 75 (11), 73 (100), 59 (11); exact mass calcd for $C_{15}H_{26}O_4Si$ 298.1600, found 298.1598. Analysis: calcd for $C_{15}H_{26}O_4Si$: C, 60.37; H, 8.78. Found: C, 60.54; H, 8.69%.

cis- and *trans*-Diethyl 3-methyl-4-(trimethylsilyl)methylclopentane-1,1-dicarboxylate (27)

To a sealable bottle containing diethyl malonate (**8**, 315 mg, 1.97 mmol, 1.0 equiv), allyltrimethylsilane (304 mg, 2.67 mmol, 1.3 equiv) and glacial acetic acid (30 ml) was added CAN (2.27 g, 4.15 mmol, 2.1 equiv). The solution was stirred at 25 °C for 4 h and the orange color faded. To the reaction mixture were then added $Mn(OAc)_3 . 2H_2O$ (1.12 g, 4.15 mmol, 2.1 equiv) and the second portion of allyltrimethylsilane (289 mg, 2.54 mmol, 1.3 equiv). The bottle was sealed and the solution was stirred at 80 °C for 1 h. The dark brown color faded and the reaction mixture was cooled, diluted with water (20 ml) and neutralized with aqueous Na_2CO_3. The neutralized solution was extracted with ether (4×25 ml) and the combined organic solutions were washed with brine and dried over $MgSO_4$ (s). After the solvents were removed under reduced pressure, the residue was chromatographed through a silica-gel column (1.5 cm×16 cm column, 1% EtOAc in hexanes as eluant) to give pure **27** (464 mg, 1.48 mmol) as a colorless oil in 75% yield: GC t_R 15.77 and 16.21 min for the *trans* and the *cis* isomers respectively; TLC R_f 0.63 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.00 (s, 9 H, $Si(CH_3)_3$), 0.48–0.65 (m, 2H, $SiCH_2$), 0.83 (d, J=7.1 Hz, 3H, CH_3), 1.18–1.34 (m, 6H, 2×OCH_2CH_3), 1.82–2.53 (m, 6H), 4.12–4.27 (m, 4H, 2×OCH_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ–0.90, 14.00, 14.88, 16.64, 37.71, 38.97, 40.48, 41.07, 58.98, 61.23, 61.37, 172.98, 173.17; IR (neat) 2944 (m, C–H), 1733 (s, C=O), 1454 (m), 1366 (m), 1254 (s, Si–CH_3), 1178 (m), 850 (s, Si–CH_3), 705 (m), cm^{-1}; MS m/z (relative intensity) 314 (M^+, 0.2), 299 (3), 199 (7), 181 (13), 173 (100), 151 (11), 127 (14), 108 (13), 95 (9), 73 (49); exact mass calcd for $C_{16}H_{30}O_4Si$ 314.1913, found 314.1910. Analysis: calcd for $C_{16}H_{30}O_4Si$: C, 61.11; H, 9.61. Found: C, 61.38; H, 9.32%.

Standard procedure 4 for the syntheses of compounds 28–31

To a sealable bottle containing a dioxo compound, allyltrimethylsilane and glacial acetic acid (20 ml) was added CAN. The orange mixture was stirred at 25 °C until the color disappeared. To the reaction mixture were then added $MN(OAc)_3 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$ and the second portion of allyltrimethylsilane. The bottle was sealed and the solution was stirred at 80 °C. After 1 h, the reaction mixture was cooled, diluted with water (30 ml) and neutralized with aqueous Na_2CO_3. The neutralized solution was extracted with ether (4×30 ml) and the combined organic solutions were washed with brine and dried over $MgSO_4$ (s). After the solvents were removed under reduced pressure, the residue was chromatographed through a silica-gel column to provide the pure desired product.

Diethyl 3-Methylene-4-(trimethylsilyl)methylcyclopentane-1,1-dicarboxylate (28)

The standard procedure 4 was followed using diethyl malonate (**8**, 326 mg, 2.04 mmol, 1.0 equiv), allyltrimethylsilane (305 mg, 2.68 mmol, 1.3 equiv), CAN (2.29 g, 4.17 mmol, 2.1 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (598 mg, 2.23 mmol, 1.1 equiv), $Cu(OAc)_2 \cdot H_2O$ (439 mg, 2.19 mmol, 1.1 equiv) and the second portion of allyltrimethylsilane (296 mg, 2.60 mmol, 1.3 equiv). The residue was purified by chromatography on silica gel (1.5 cm×16 cm column, 1% EtOAc in hexanes as eluant) to give **28** (387 mg, 1.24 mmol) as a colorless oil in 61% yield: GC t_R 16.13 min; TLC R_f 0.38 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.15 (s, 9H, $Si(CH_3)_3$), 0.51 (dd, J=10.6, 14.5 Hz, 1H, SiCH), 1.01 (dd, J=3.6, 14.5 Hz, 1H, SiCH), 1.20–1.32 (m, 6H, 2×OCH_2CH_3), 1.77 (dd, J=11.6, 12.2 Hz, 1H), 2.42–2.58 (m, 2H), 2.83–3.08 (m, 2H), 4.13–4.28 (m, 4H, 2×OCH_2CH_3), 4.80–4.83 (m, 1H, CH=), 4.86–4.89 (m, 1H, CH=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.91, 13.91, 13.94, 20.50, 39.01, 39.84, 41.91, 58.04, 61.30, 61.31, 104.95, 154.64, 171.75, 171.85; IR (neat) 3069 (w, =C–H), 2960 (s), 1734 (s, C=O), 1632 (w, C=C),

1445 (m), 1367 (m), 1237 (s, Si–CH_3), 1096 (m), 1068 (m), 851 (m, Si–CH_3), 693 (m) cm^{-1}; MS *m*/*z* (relative intensity) 312 (M^+, 3), 166 (24), 165 (24), 149 (32), 121 (25), 120 (44), 119 (16), 93 (46), 92 (40), 73 (100). Its spectroscopic characteristics are consistent with those of the same compound reported previously.[26]

cis- and *trans*-Ethyl 1-acetyl-3-methylene-4-(trimethylsilyl)methylcyclopentane-1-carboxylate (29)

The standard procedure 4 was followed using ethyl acetoacetate (**9**, 261 mg, 2.01 mmol, 1.0 equiv), allyltrimethylsilane (304 mg, 2.67 mmol, 1.3 equiv), CAN (2.26 g, 4.12 mmol, 2.1 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (593 mg, 2.21 mmol, 1.1 equiv), $Cu(OAc)_2 \cdot H_2O$ (432 mg, 2.16 mmol, 1.1 equiv) and the second portion of allyltrimethylsilane (294 mg, 2.58 mmol, 1.3 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give **29** (403 mg, 1.43 mmol) as a colorless oil in 71% yield: GC t_R 15.26 min; TLC R_f 0.37 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.02, −0.01 (2×s, 9H, $Si(CH_3)_3$), 0.39–0.47 (m, 1H, SiCH), 0.81–0.99 (m, 1H, SiCH), 1.14–1.25 (m, 3H, OCH_2CH_3), 1.51–1.68 (m, 1H), 2.13, 2.15 (2×s, 3H, $COCH_3$), 2.44–2.57 (m, 2H), 2.83–2.98 (m, 2H), 4.14–4.24 (m, 2H, OCH_2CH_3), 4.81–4.83 (m, 1H, Ch=), 4.86–4.89 (m, 1H, CH=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −0.86, −0.85, 13.94, 13.96, 20.31, 20.63, 25.82, 26.40, 38.35, 38.46, 38.88, 39.24, 40.53, 40.90, 61.46, 61.50, 64.16, 64.85, 105.04, 105.05, 154.54, 154.63, 172.46, 172.49, 203.37, 203.41; IR (neat) 3063 (w, =C–H), 2933 (s, C–H), 2862 (m, C–H), 1718 (s, C=O), 1653 (w, C=C), 1360 (m), 1222 (m, Si–CH_3), 852 (m, Si–CH_3), 692 (m) cm^{-1}; MS *m*/*z* (relative intensity) 282 (M^+, 1), 239 (19), 209 (18), 193 (16), 165 (10), 119 (21), 93 (15), 75 (27), 73 (100), 59 (11); exact mass calcd for $C_{15}H_{26}O_3Si$ 282.1651, found 282.1648. Analysis: calcd for $C_{15}H_{26}O_3Si$: C, 63.79; H, 9.28. Found: C, 64.02; H, 9.34%.

cis- and *trans*-Ethyl 1-butyryl-3-methylene-4-(trimethylsilyl)methylcyclopentane-1-carboxylate (30)

The standard procedure 4 was followed using ethyl butyrylacetate (**10**, 319 mg, 2.02 mmol, 1.0 equiv), allyltrimethylsilane (302 mg, 2.65 mmol, 1.3 equiv), CAN (2.29 g, 4.18 mmol, 2.1 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (602 mg, 2.25 mmol, 1.1 equiv), $Cu(OAc)_2 \cdot H_2O$ (427 mg, 2.14 mmol, 1.1 equiv) and the second portion of allyltrimethylsilane (299 mg, 2.62 mmol, 1.3 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give **30** (419 mg, 1.35 mmol) as a colorless oil in 67% yield: GC t_R 17.01 min; TLC R_f 0.46 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.02, 0.03 (2×s, 9H, $Si(CH_3)_3$), 0.38–0.52 (m, 1H, SiCH), 0.81–0.92 (m, 3H, $CH_2CH_2CH_3$), 0.92–0.99 (m, 1H, SiCH), 1.19–1.26 (m, 3H, OCH_2CH_3), 1.52–1.69 (m, 3H), 2.38–2.47 (m, 2H, $COCH_2CH_2$), 2.48–2.57 (m, 2H), 2.83–2.98 (m, 2H), 4.14–4.24 (m, 2H, OCH_2CH_3), 4.77–4.79 (m, 1H, CH=), 4.81–4.85 (m, 1H, CH=); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −0.87, −0.86, 13.53, 13.58, 17.13, 17.46, 20.40, 20.71, 38.39, 38.46, 38.87, 39.18, 40.07, 40.50, 40.67, 40.92, 61.38, 61.42, 64.02, 64.76, 104.94, 104.99, 154.68, 154.82, 172.60, 172.84, 205.30, 205.33; IR (Neat) 3073 (w, =C–H), 2935 (s, C–H), 2859 (m, C–H), 1721 (s, C=O), 1647 (w, C=C), 1365 (m), 1231 (s, Si–CH_3), 1199 (m), 852 (s, Si–CH_3), 755 (m) cm^{-1}; MS *m*/*z* (relative intensity) 310 (M^+, 0.6), 239 (36), 221 (11), 193 (11), 165 (12), 121 (23), 93 (12), 89 (11), 73 (100), 59 (9); exact mass calcd for $C_{17}H_{30}O_3Si$ 310.1964, found 310.1962. Analysis: calcd for $C_{17}H_{30}O_3Si$: C, 65.76; H, 9.74. Found: C, 65.46; H, 9.97.

Diethyl 3-methylene-4-(triisopropylsilyl)methylcyclopentane-1,1-dicarboxylate (31)

The standard procedure 4 was followed using diethyl malonate (**8**, 318 mg, 1.99 mmol, 1.0 equiv), allyltrimethylsilane (298 mg, 2.61 mmol, 1.3 equiv), CAN (2.27 g, 4.14 mmol, 2.1 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (579 mg, 2.16 mmol, 1.1 equiv), $Cu(OAc)_2 \cdot H_2O$ (429 mg, 2.15 mmol, 1.1 equiv) and allyltriisopropylsilane (517 mg, 2.61 mmol, 1.3 equiv). The residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give **31** (411 mg, 1.04 mmol) as a colorless oil in 52% yield: GC t_R 22.30 min; TLC R_f 0.42 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.52 (dd, J = 14.2, 3.5 Hz, 1H, SiCH), 0.93–1.15 (m, 22H, $Si[CH(CH_3)_2]_3$ and SiCH), 1.23 (*t*, J = 7.1 Hz, 6H, 2×OCH_2CH_3), 1.74 (dd, J = 11.8, 11.8 Hz, 1H), 2.43–2.68 (m, 2H), 2.83–3.09 (m, 2H), 4.18 (m, J = 7.1 Hz, 4H, 2×OCH_2CH_3),

4.80–4.83 (m, 1H, CH=), 4.86–4.89 (m, 1H, CH=); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.45, 12.96, 13.99, 18.84, 38.84, 39.95, 42.52, 48.04, 61.42, 105.04, 155.02, 171.87, 171.92; IR (neat) 3067 (w, =C–H), 2944 (s, C–H), 2868 (s, C–H), 1734 (s, C=O), 1629 (m, C=C), 1462 (m), 1366 (m), 1253 (m, Si—CH_3), 1178 (m), 1068 (m), 881 (s, Si–CH_3), 739 (m), cm^{-1}; MS *m*/*z* (relative intensity) 396 (M^+, 0.1), 353 (74), 279 (36), 235 (100), 131 (25), 103 (24), 85 (26), 75 (28), 73 (37); exact mass calcd for $C_{22}H_{40}O_4Si$396.2696, found 396.2692. Analysis: calcd for $C_{22}H_{40}O_4Si$: C, 66.62; H, 10.16. Found: C, 66.80; H, 10.30.

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REFERENCES

1. A. R. Bassindale and P. G. Taylor, Activating and directive effects of silicon. In: *The Chemistry of Organic Silicon Compounds*, Patai, S. and Rappoport, Z. (eds), Wiley, New York, 1989, Part 2, Chapter 14.
2. S. Zhang, X.-M. Zhang and F. G. Bordwell, *J. Am. Chem. Soc.* **117**, 602 (1995).
3. E. A. Brinkman, S. Berger and J. I. Brauman, *J. Am. Chem. Soc.* **116**, 8304 (1994).
4. J. B. Lambert, R. W. Emblidge and S. Malany, *J. Am. Chem. Soc.* **115**, 1317 (1993).
5. M. A. Brook and A. Neuy, *J. Org. Chem.* **55**, 3609 (1990).
6. J. B. Lambert, *Tetrahedron* **46**, 2677 (1990).
7. J. R. Hwu and H. V. Patel, *Synlett* 989 (1995) and references cited therein.
8. J. R. Hwu, B.-L. Chen and S.-S. Shiao, *J. Org. Chem.* **60**, 2448 (1995).
9. J. R. Hwu, C. N. Chen and S.-Shiao, *J. Org. Chem.* **60**, 856 (1995).
10. L. C. Lin, L. L. Chueh, S.-C. Tsay and J. R. Hwu, *Tetrahedron Lett.* **36**, 4093 (1995).
11. J. R. Hwu, B.-L. Chen, L. W. Huang and T.-H. Yang, *J. Chem. Soc., Chem. Commun.* 299 (1995).
12. J. R. Hwu, K.-L. Chen, S. Ananthan and H. V. Patel, *Organometallics*, **15**, 499 (1996).
13. L. C. Lin, Y. C. Li, C. C. Lin and J. R. Hwu, *J. Chem. Soc., Chem. Commun.* 509 (1996).
14. J. R. Hwu, S.-C. Tsay, N. Wang and G. H. Hakimelahi, *Organometallics* **13**, 2461 (1994).
15. J. R. Hwu, K.-L. Chen and S. Ananthan, *J. Chem. Soc., Chem. Commun.* 1425 (1994).
16. A. L. Beckwith, *Tetrahedron* **37**, 3073 (1981).
17. I. Ryu, A. Kurihara, H. Muraoka, S. Tsunoi, N. Kambe and N. Sonoda, *J. Org. Chem.* **59**, 7570 (1994).
18. E. Baciocchi and R. Ruzziconi, *Synth. Commun.* **18**, 1841 (1988).
19. G. G. Melikyan, *Synthesis* 833 (1993).
20. G. Midgley and C. B. Thomas, *J. Chem. Soc. Perkin Trans. 2* 1103 (1987).
21. B. B. Snider and B. A. McCarthy, *J. Org. Chem.* **58**, 6217 (1993).
22. R. Noyori, I. Nishida and J. Sakata, *J. Am. Chem. Soc.* **105**, 1598 (1983).
23. H. C. Araújo and J. R. Mahajan, *Synthesis* 228 (1978).
24. B. C. Ranu and S. Bhar, *J. Chem. Soc., Perkin Trans. 1* 365 (1992).
25. S.-W. Zhang, T.-A. Mitsudo, T. Kondo and Y. Watanabe, *J. Organomet. Chem.* **450**, 197 (1993).
26. B. B. Snider and B. O. Buckman, *Tetrahedron* **45**, 6969 (1989).

