Silicon-Controlled Allylation of 1,3-Dioxo Compounds by Use of Allyltrimethylsilane and Ceric Ammonium Nitrate

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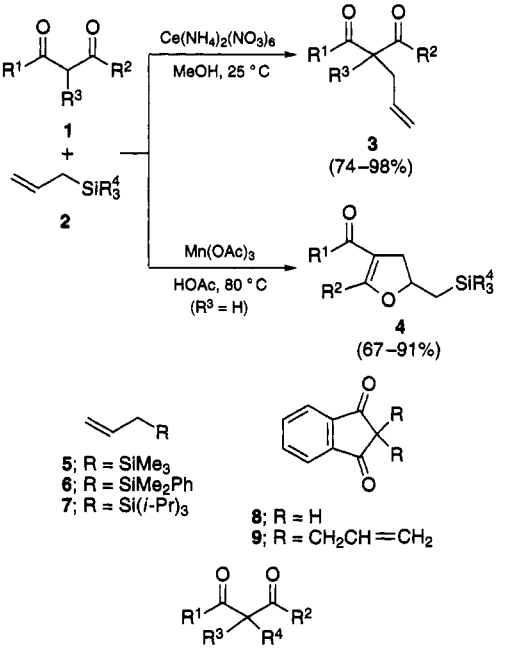
A new method was developed for allylation of 1,3-diketones, β-keto esters, and malonates. Treatment of those 1,3-dioxo compounds with allyltrimethylsilane (1.3 equiv) in the presence of ceric ammonium nitrate (2.1 equiv) in methanol at room temperature often gave the mono-*C*-allylated products in good to excellent yields (74–98%). These reactions, involving β-carboradical and β-carbocationic intermediates, were controlled by a silyl group. Replacement of ceric ammonium nitrate and methanol with manganese(III) acetate (2.4 equiv) and acetic acid afforded silicon-containing dihydrofurans in high yields at 80 °C.

Introduction

Oxidative additions of 1,3-dioxo compounds to alkenes can be initiated by use of one-electron oxidizing agents,[1] such as ceric ammonium nitrate[2] (CAN) and manganese(III) acetate.[3] These reactions often produce nitrate esters or dihydrofurans or both.[4,5] Results from mechanistic studies indicate that those reactions involve removal of a hydrogen atom from a 1,3-dioxo compound to give an electrophilic α-carboradical, its addition to an alkene, and termination of the reaction by trap of the carboradical adduct with a nitrate radical or by an intramolecular cyclization.[2,3] Along the line of studying silicon-controlled organic reactions,[6–11] we investigated the synthetic applicability of those oxidative additions to *C*-allylation of 1,3-dioxo compounds by using allylsilanes (i.e., **1** + **2** → **3** in Scheme 1).

Silicon can stabilize a β-carboradical by 2.6–2.8 kcal/mol[12,13] and a β-carbocation by 38 kcal/mol.[14,15] On the other hand, CAN and manganese(III) acetate possess different oxidizing capability toward carboradicals.[16]

Scheme 1



Utilizing these properties, we allylated 1,3-dioxo compounds in good to excellent yields by use of allyltrimethylsilane and CAN (Scheme 1). Performance of the same reactions by replacement of CAN with manganese(III) acetate produced silicon-containing dihydrofurans in high yields.

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(1) For a recent review and a book, see: (a) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, *94*, 519. (b) Giese, B. *Radical in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986; pp 89–94.
(2) Baciocchi, E.; Ruzziconi, R. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; NATO ASI Series; Kluwer Academic: Dordrecht, 1989; pp 155–185.
(3) Melikyan, G. G. *Synthesis* **1993**, 833.
(4) For representative works, see: (a) Baciocchi, E.; Ruzziconi, R. *J. Org. Chem.* **1986**, *51*, 1645. (b) Baciocchi, E.; Giese, B.; Farshchi, H.; Ruzziconi, R. *J. Org. Chem.* **1990**, *55*, 5688.
(5) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1974**, *39*, 3456.
(6) Furth, P. S.; Hwu, J. R. *J. Org. Chem.* **1989**, *54*, 3404.
(7) Hwu, J. R.; Furth, P. S. *J. Am. Chem. Soc.* **1989**, *111*, 8834.
(8) Furth, P. S.; Hwu, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 8842.
(9) Hwu, J. R.; Gilbert, B. A.; Lin, L. C.; Liaw, B. R. *J. Chem. Soc., Chem. Commun.* **1990**, 161.
(10) Hwu, J. R.; Gilbert, B. A. *J. Am. Chem. Soc.* **1991**, *113*, 5917.
(11) Hwu, J. R.; Wetzel, J. M. *J. Org. Chem.* **1992**, *57*, 922.
(12) Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207.
(13) Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Organometallics* **1987**, *6*, 644.
(14) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.
(15) Apeloig, Y. In *The Chemistry of Functional Groups: The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; Part 1, p 196.
(16) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1971**, *93*, 524.

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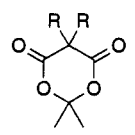
Results

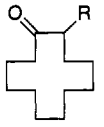
Allylation of 1,3-Dioxo Compounds by Use of Allyltrimethylsilane and CAN. We treated a methanol solution containing a 1,3-diketone (i.e., **10** and **12**) and allyltrimethylsilane (**5**, 1.3 equiv) in methanol with CAN (2.1 equiv). After ≤1 min at room temperature, the solution turned from dark brown to pale yellow or colorless. Change of the color indicated completion of the reactions. Workup followed by purification afforded the allylated product (i.e., **11** and **13**) in excellent yields (91–98%; entries 2 and 3 in Table 1). In these reactions involving aliphatic and aromatic 1,3-diketones, we obtained monoallylated products predominantly; only traces of diallylated products were detected by GC–mass spectroscopy. Application of the same conditions or an excess of **5** and CAN to indandione (**8**) afforded the diallylated product **9** (entry 1 in Table 1).

Monoallylation of carbonyl compounds plays a more important role than diallylation in organic synthesis. We thus explored the generality of monoallylation by using the combination of allyltrimethylsilane and CAN. Accordingly, β-keto esters **14** and **16**, which bear an α methylene unit, were converted smoothly to **15** (84% yield) and **17** (83% yield), respectively (entries 4 and 5 in Table 1). Furthermore, we successfully extend this newly developed method to allylation of an α-substituted and a cyclic β-keto ester, as shown in the conversions of **18** → **19** (76% yield) and **20** → **21** (81% yield, see entries 6 and 7).

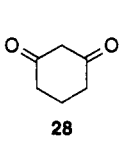
Application of the allylation method to diethyl malonate (**22**) gave the monoallyl product **23** in 74% yield (entry 8 in Table 1). Meldrum's acid (**24**), however,



24; R = H
25; R = $CH_2CH{=}CH_2$



26; R = H
27; R = $CH_2CH{=}CH_2$



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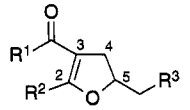


29; $R^1 = R^2$ = Ph, R^3 = $SiMe_3$
30; $R^1 + R^2 = (CH_2)_3$, R^3 = $SiMe_3$
31; R^1 = OEt, R^2 = Me, R^3 = $SiMe_3$
32; R^1 = OEt, R^2 = *n*-Pr, R^3 = $SiMe_3$
33; R^1 = OEt, R^2 = Me, R^3 = $SiMe_2Ph$
34; $R^1 = R^2$ = Ph, R^3 = $Si(i\text{-}Pr)_3$
35; R^1 = OEt, R^2 = Me, R^3 = $Si(i\text{-}Pr)_3$

reacted with 2.6 equiv of **5** and 4.1 equiv of CAN to afford diallylated product **25** in 82% yield (entry 9 in Table 1). Performance of this reaction involving lesser equiv of **5** and CAN did not lead to the monoallylated product in higher yields.[17]

Although combination of allyltrimethylsilane and CAN in methanol efficiently monoallylated most 1,3-dioxo compounds, we cannot apply this method widely to monoketones: five- to eight-membered cycloalkanones, 4-heptanone, 2,6-dimethyl-4-heptanone, and acetophenone led to the corresponding allylated products in a yield ≤40%. The only exception was the successful conversion of cyclododecanone (**26**) to **27** in 75% yield by use of 1.6 equiv of **5** and 3.0 equiv of CAN in methanol (0.25 M) at room temperature (entry 10 in Table 1). A decrease in concentration to 0.1 and 0.05 M gave a 41% yield or trace of **27**, respectively.

Table 1. Reaction of Dioxo Compounds with Allyltrimethylsilane (5) in the Presence of $Ce(NH_4)_2(NO_3)_6$ in Methanol at Room Temperature To Give the Corresponding *C*-Allylated Products

entry	dioxo compd	equiv of silane **5**	equiv of Ce(IV) salt	allylated product[a]	% yield by isolation
1	**8**	2.6	4.1	**9**	90
2	**10**	1.3	2.1	**11**	98
3	**12**	1.3	2.1	**13**	91
4	**14**	1.3	2.1	**15**	84
5	**16**	1.3	2.1	**17**	83
6	**18**	1.3	2.1	**19**	76
7	**20**	1.3	2.1	**21**	81
8	**22**	1.3	2.1	**23**	74
9	**24**	2.6	4.1	**25**	82
10	**26**[b]	1.6	3.0	**27**	75

[a] All are monoallylated products except that **9** and **25** are diallylated products. [b] Exception as a monoketone.

Table 2. Reaction of Dioxo Compounds with an Allylsilane in the Presence of $Mn(OAc)_3{\cdot}2\ H_2O$ (2.4 equiv) in Acetic Acid at 80 °C To Give Dihydrofurans

entry	dioxo compd	allyl-silane	equiv of allylsilane	dihydrofuran product	% yield by isolation
1	**12**	**5**	1.3	**29**	91
2	**28**	**5**	1.3	**30**	88
3	**14**	**5**	1.3	**31**	85
4	**16**	**5**	1.3	**32**	73
5	**14**	**6**	1.1	**33**	82
6	**12**	**7**	1.1	**34**	67
7	**14**	**7**	1.1	**35**	76

Table 3. Influence Resulting from the Size of the Silyl Group of Allylsilanes on the Product Ratio of the Allylated β-Keto Ester 15 to Dihydrofurans[a]

allyl-silane	equiv of allylsilane	possible products[a] keto ester (**15**) + dihydrofuran	product ratio **15**:dihydrofuran	overall yield (%)
5	1.3	**15** + **31**	100:0	84
6	1.1	**15** + **33**	16:1	80
7	1.1	**15** + **35**	0:100	76

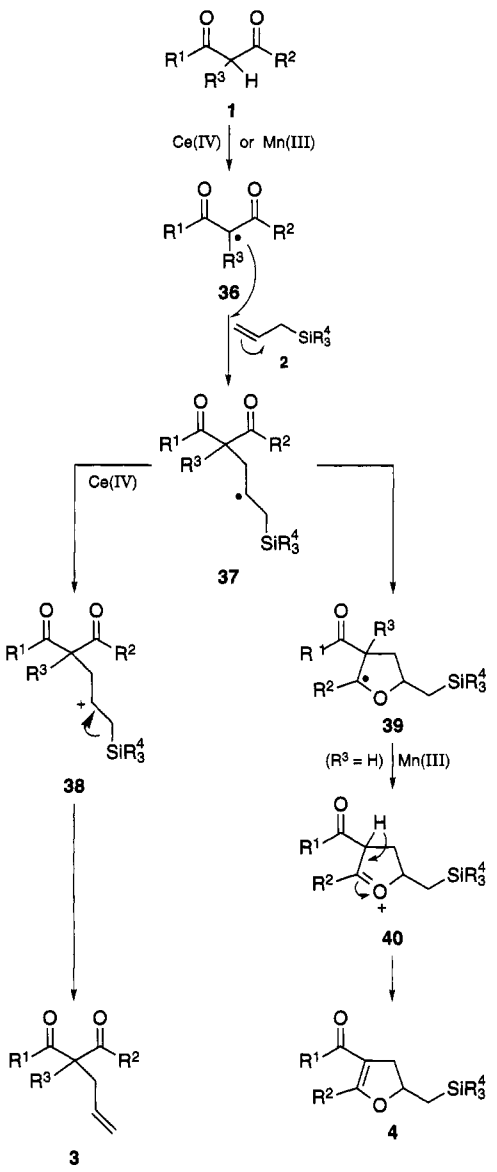
[a] Reactions between β-keto ester **14** and an allylsilane initiated by 2.1 equiv of CAN was carried out in methanol at room temperature.

Formation of Silicon-Containing Dihydrofurans Involving Manganese(III) Acetate. We found that use of $Mn(OAc)_3{\cdot}2H_2O$ and acetic acid to replace CAN and methanol for initiation of the reaction between allyltrimethylsilane (**5**) and a 1,3-diketone or a β-keto ester produced silicon-containing dihydrofurans in 73–91% yields (see Scheme 1 and entries 1–4 in Table 2). Furthermore, we treated diketone **12** and β-keto ester **14** with allyldimethylphenylsilane (**6**) or allyltriisopropylsilane (**7**), which contains a silyl group bulkier than Me_3Si. Dihydrofurans **33**–**35** were isolated in 67–82% yields (entries 5–7 in Table 2).

Allylation versus Dihydrofuran Formation. For understanding the influence of the size of a silyl group in allylsilanes on the allylation and dihydrofuran formation, we made a comparison with results obtained by using allylsilanes **5**–**7** (see Table 3). The size of the silyl groups follows the trend Me_3Si < $PhMe_2Si$ < $(i\text{-}Pr)_3Si$.[18]

(17) Diallylations often occur to the Meldrum's acid (**24**); see: (a) Lu, X.; Jiang, X.; Tao, X. *J. Organomet. Chem.* **1988**, *344*, 109. (b) Prat, M.; Moreno-Mañas, M.; Ribas, J. *Tetrahedron* **1988**, *44*, 7205.
(18) Hwu, J. R.; Wang, N. *Chem. Rev.* **1989**, *89*, 1599.

Scheme 2



By treating β-keto ester **14** with allyldimethylphenylsilane (**6**) and CAN in methanol at room temperature, we obtained a mixture of *C*-allylated product **15** and silicon-containing dihydrofuran **33** in a ratio of 16:1, as determined by NMR spectroscopy (Table 3). Under the same reaction conditions but replacement of **6** with allyltriisopropylsilane (**7**), dihydrofuran **35** was produced exclusively in 76% yield. In contrast, an experiment described previously involving allyltrimethylsilane (**5**) and **14** afforded *C*-allylated keto ester **15** as the only product (entry 4 in Table 1). These results indicate that the size of a silyl group in allylsilanes plays a prominent role in the determination of product ratios obtained from allylation and dihydrofuran formation.

Discussion

Silicon-Controlled Allylation. Often the addition of 1,3-dioxo compounds to alkenes in the presence of CAN goes through carboradical intermediates to give a mixture of nitrate esters and dihydrofurans.[2,4] We designed a way to control this reaction by using silicon and make it valuable for *C*-allylation of 1,3-dioxo compounds (Scheme 2).

Because a β-trimethylsilyl carbocation can easily undergo fragmentation to give an alkene,[19,20] the conversion of intermediates **38** (R^4 = Me) to *C*-allyl 1,3-dioxo products **3** would prevail over other competing pathways, such as an intramolecular cyclization. Furthermore, the capabilities of silicon stablizing a β-carboradical[12,13] and a β-carbocation[14,15] could also facilitate the following two processes: addition of **36** to allylsilanes **2** to give β-silyl carboradicals **37** and oxidation of **37** to β-silyl carbocations **38**. Our results shown in entries 2–8 in Table 1 with 74–98% yields indicate the efficiency of the new silicon-controlled allylation strategy.

It is more difficult to eliminate a larger than a smaller silyl group located at a β position in carbocationic intermediates to give alkenes.[21] Thus, intermediates **38** possessing a larger silyl group would have a greater chance to undergo intramolecular cyclization to form dihydrofurans **4** through oxonium species **40**. In addition, use of a bulky agent CAN[22] for the oxidation of carboradicals **37** bearing a large β-silyl group to give **38** could also be difficult; thus, intramolecular cyclization of such **37** to produce **39** would be more competitive than oxidation of **37** to afford **38**. We believe that these two factors play a role on the dramatic change of product ratios of **15**:dihydrofurans, among which **31**, **33**, and **35** possess a Me_3Si, $PhMe_2Si$, or $(i\text{-}Pr)_3Si$ group (see Table 3).

Dihydrofuran Formation Involving Manganese(III) Acetate versus Allylation Involving CAN. We obtained high yields of allylated products by using CAN and silicon-containing dihydrofurans by using manganese(III) acetate (cf. Tables 1 and 2). The diversity seems to come from the reactivity difference between CAN and manganese(III) acetate toward the oxidation of carboradicals **37**. Heiba and Dessau[16] reported the order to be 12:1 for the relative reactivity of Ce(IV) and Mn(III) in the oxidation of secondary alkyl radicals.

The radical center in **37** is stabilized by a β-silyl group; thus, the reactivity of manganese(III) acetate may not be high enough for oxidizing **37** to give carbocations **38**. Otherwise, allylated dioxo compounds **3** should be produced. On the other hand, after carboradicals **37** underwent an intramolecular cyclization, oxidation of the resultant radicals **39** by manganese(III) acetate would be relatively easy because stable oxonium species **40** are generated. Our explanation involving cyclization of radical intermediates is consistent with the mechanism proposed by Fristad and Peterson[23] for related reactions.

Advantages. Allylation of 1,3-dioxo compounds usually requires acidic[24] or basic conditions.[25] Our newly developed allylation method, however, proceeded under neutral conditions. More significant is that no *O*-allylation byproducts were observed in any examples shown in Table 1. Except for indandione and Meldrum's acid,

(19) Colvin, E. *Silicon in Organic Reactions*; Butterworths: London, 1981; pp 44–133.
(20) Fleming, I. *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, England, 1979; Vol. 3, pp 541–686.
(21) Fleming, I.; Langley, J. A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1421.
(22) Soucy, P.; Ho, T.-L.; Deslongchamps, P. *Can. J. Chem.* **1972**, *50*, 2047.
(23) Fristad, W. E.; Peterson, J. R. *J. Org. Chem.* **1985**, *50*, 10.
(24) Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1990**, *31*, 357.
(25) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*; VCH: New York, 1989; p 764 and references cited therein.

the new method provides an efficient way to prepare monoallylated dioxo compounds.

Allylation of 1,3-dioxo compounds by use of CAN in methanol involves simple manipulation. It can be performed under air and "wet" conditions. Completion of the reaction often requires a short period of time (≤4 h) and can be noted by the orange color faded from the solution. In addition, the allylating agent allyltrimethylsilane is commercially available and the *C*-allylated products were obtained in high yields.

Conclusions

A new and efficient method was developed for the allylation of 1,3-diketones, β-keto esters, and malonates by use of allyltrimethylsilane and CAN in methanol. The reaction pathway was controlled by a silyl group: a carbocationic intermediate with a β-trimethylsilyl group underwent elimination readily to give the desired allylated product. The advantages associated with the new method include neutral reaction conditions, tolerance of moisture and air during manipulation, a short period of reaction time, easy detection of the completion, commercial availability of the reagents, no competing *O*-allylation, and high yields of the allylated products. Performance of the same reactions in acetic acid and replacement of CAN with manganese(III) acetate, however, gave silicon-containing dihydrofurans in high yields.

Experimental Section

General Procedure.[7] 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. Allyl bromide from Merck was dried and distilled from CaH_2 and stored in serum-capped bottles under argon over molecular sieves 4A. Allyltriisopropylsilane, allyltrimethylsilane, chlorodimethylphenylsilane, cyclododecanone, 1,3-cyclohexanedione, 2,2-dimethyl-1,3-dioxane-4,6-dione, ethyl butyrylacetate, ethyl 2-methylacetoacetate, ethyl 2-oxocyclopentanecarboxylate, 1,3-indandione, 2,4-pentanedione, 2,2,6,6-tetramethyl-3,5-heptanedione, and ceric ammonium nitrate (CAN) were purchased from Aldrich Chemical Co. Allyl bromide, diethyl malonate, 1,3-diphenyl-1,3-propanedione, ethyl acetoacetate, and manganese(III) acetate dihydrate were purchased from Merck, Inc. Allyldimethylphenylsilane was prepared according to Kwart's procedure.[26] 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 methyl silicone gum capillary column (0.32 mm i.d.). Nitrogen gas was used as a carrier gas, and the flow rate was kept constant at 14.0 mL/min. The retention time t_R was measured under the following conditions: injector temperature 260 °C, the initial temperature for column 70 °C, duration 2.00 min, increment rate 10 °C/min, and the final temperature for column 250 °C.

Standard Procedure 1: Allylation of Carbonyl Compounds. To a methanol solution containing a dioxo compound and allylsilane was added CAN. The orange mixture was stirred at room temperature until the color disappeared. 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.

2,2-Diallylindandione (9).[27] The standard procedure 1 was followed by use of 1,3-indandione (**8**, 72.7 mg, 0.497 mmol, 1.0 equiv), allyltrimethylsilane (149 mg, 1.31 mmol, 2.6 equiv), CAN (1.13 g, 2.06 mmol, 4.1 equiv), and methanol (15 mL). After 20 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **9** (101 mg, 0.448 mmol) as a colorless oil in 90% yield: GC t_R 15.09 min; TLC R_f 0.38 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.52 (d, J = 7.6 Hz, 4 H), 4.84–4.87 (m, 2 H), 4.97–5.03 (m, 2 H), 5.39–5.49 (m, 2 H), 7.79–7.93 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.77, 58.25, 119.44, 122.89, 131.37, 135.68, 142.19, 203.29; IR (neat) 3078 (w, =CH), 2974 (w, CH), 2907 (w, CH), 1743 (m, C=O), 1707 (s), 1640 (w, C=C), 1595 (m, Ar), 1242 (m), 995 (m), 925 (m), 747 (m) cm^{-1}; MS *m/e* (relative intensity) 226 (M^+, 5), 198 (28), 184 (29), 157 (74), 129 (100), 128 (61), 127 (25), 115 (21), 104 (26), 77 (30), 76 (38); HRMS calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0999.

4-Allyl-2,2,6,6-tetramethyl-3,5-heptanedione (11).[28] The standard procedure 1 was followed by use of 2,2,6,6-tetramethyl-3,5-heptanedione (**10**, 92.5 mg, 0.502 mmol, 1.0 equiv), allyltrimethylsilane (75.2 mg, 0.658 mmol, 1.3 equiv), CAN (575 mg, 1.05 mmol, 2.1 equiv), and methanol (10 mL). After 15 s, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **11** (110 mg, 0.491 mmol) as a colorless oil in 98% yield: GC t_R 11.86 min; TLC R_f 0.55 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.13 (s, 18 H), 2.51 (dd, J = 6.8, 6.7 Hz, 2 H), 4.43 (t, J = 6.7 Hz, 1 H), 4.94–5.08 (m, 2 H), 5.52–5.66 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.22, 33.83, 44.43, 55.09, 117.11, 135.11, 209.66; IR (neat) 3081 (w, =CH), 2984 (s, CH), 2866 (m, CH), 1718 (s, C=O), 1693 (m), 1642 (w, C=C), 1475 (m), 1365 (m), 990 (m), 919 (m) cm^{-1}; MS *m/e* (relative intensity) 224 (M^+, 0.8), 168 (3), 140 (2), 86 (3), 85 (29), 83 (7), 58 (4), 57 (100), 55 (3); HRMS calcd for $C_{14}H_{24}O_2$ 224.1776, found 224.1787.

2-Allyl-1,3-diphenyl-1,3-propanedione (13).[29] The standard procedure 1 was followed by use of 1,3-diphenyl-1,3-propanedione (**12**, 110 mg, 0.491 mmol, 1.0 equiv), allyltrimethylsilane (73.5 mg, 0.643 mmol, 1.3 equiv), CAN (575 mg, 1.05 mmol, 2.1 equiv), and methanol (10 mL). After 1 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 2% EtOAc in hexanes as eluant) to give pure **13** (118 mg, 0.447 mmol) as a colorless oil in 91% yield: GC t_R 20.06 min; TLC R_f 0.31 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.82–2.86 (m, 2 H), 4.96–5.08 (m, 2 H), 5.32 (t, J = 7.0 Hz, 1 H), 5.78–5.91 (m, 1 H), 7.39 (t, J = 7.2 Hz, 4 H), 7.50 (t, J = 7.2 Hz, 2 H), 7.93 (d, J = 7.2 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 33.43, 56.44, 117.07, 128.41, 128.74, 133.40, 134.91, 135.86, 195.42; IR (neat) 3068 (w, =CH), 2980 (w, CH), 2931 (w, CH), 1694 (s, C=O), 1671 (s), 1640 (w, C=C), 1595 (m, Ph), 1447 (m), 998 (m), 919 (m), 754 (m), 689 (m) cm^{-1}; MS *m/e* (relative intensity) 264 (M^+, 0.3), 236 (4), 159 (7), 142(3), 106 (7), 105 (100), 78 (4), 77 (50), 51 (12); HRMS calcd for $C_{18}H_{16}O_2$ 264.1150, found 264.1152.

Ethyl 2-Acetyl-4-pentenoate (15). The standard procedure 1 was followed by use of ethyl acetoacetate (**14**, 65.3 mg, 0.502 mmol, 1.0 equiv), allyltrimethylsilane (74.1 mg, 0.648 mmol, 1.3 equiv), CAN (586 mg, 1.07 mmol, 2.1 equiv), and methanol (10 mL). After 20 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **15** (71.7 mg, 0.422 mmol) as a colorless oil in 84% yield: GC t_R 7.60 min; TLC R_f 0.37 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, J = 7.1 Hz, 3 H), 2.18 (s, 3 H), 2.51–2.56 (m, 2 H), 3.42–3.49 (m, 1 H), 4.15 (q, J = 7.1 Hz, 2 H), 4.98–5.07 (m, 2 H), 5.62–5.77 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.91, 28.96, 32.00, 59.20, 61.32, 117.22, 134.11, 169.16, 202.30; IR (neat) 3076 (w, =CH), 2977 (m, CH), 2948 (m, CH), 1726 (s, C=O), 1721 (s, C=O), 1643

(26) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.
(27) Bloch, R.; Orvane, P. *Synth. Commun.* **1981**, *11*, 913.
(28) Watanabe, S.; Fujita, T.; Suga, K.; Koiso, H. *Nippon Kagaku Kaishi* **1976**, 1251; *Chem. Abstr.* **1977**, *86*, 43151t.
(29) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D.; Balducci, R. *J. Org. Chem.* **1990**, *55*, 429.

(m, C=C), 1255 (m), 1196 (m), 1023 (m), 849 (m) cm^{-1}; MS m/e (relative intensity) 170 (M^+, 3), 128 (47), 127 (100), 100 (43), 99 (48), 97 (29), 83 (28), 82 (26), 81 (42), 55 (36), 54 (24), 53 (20); HRMS calcd for $C_9H_{14}O_3$ 170.0943, found 170.0950. Its spectroscopic characteristics are consistent with those of the same compound reported.[30]

Ethyl 2-Allyl-3-oxohexanoate (17). The standard procedure 1 was followed by use of ethyl butyrylacetate (**16**, 76.7 mg, 0.485 mmol, 1.0 equiv), allyltrimethylsilane (74.5 mg, 0.652 mmol, 1.3 equiv), CAN (572 mg, 1.04 mmol, 2.1 equiv), and methanol (10 mL). After 30 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **17** (79.7 mg, 0.40 mmol) as a colorless oil in 83% yield: GC t_R 10.31 min; TLC R_f 0.51 (20% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, J = 7.4 Hz, 3 H), 1.24 (t, J = 7.1 Hz, 3 H), 1.53–1.65 (m, 2 H), 2.38–2.59 (m, 4 H), 3.50 (t, J = 7.4 Hz, 1 H), 4.16 (q, J = 7.1 Hz, 2 H), 4.49–5.09 (m, 2 H), 5.64–5.78 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.47, 14.03, 16.77, 32.13, 43.97, 58.45, 61.27, 117.28, 134.33, 169.22, 204.52; IR (neat) 3078 (w, =CH), 2959 (s, CH), 2934 (s, CH), 2875 (m, CH), 1742 (s, C=O), 1715 (s, C=O), 1642 (m, C=C), 1454 (m), 1237 (m), 1185 (s), 1033 (m), 919 (m), 855 (m) cm^{-1}; MS m/e (relative intensity) 198 (M^+, 2), 128 (29), 127 (30), 109 (18), 100 (17), 99 (18), 82 (11), 81 (15), 71 (100), 55 (17); HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1260. Its spectroscopic characteristics are consistent with those of the same compound reported.[31]

Ethyl 2-Acetyl-2-methyl-4-pentenoate (19). The standard procedure 1 was followed by use of ethyl 2-methylacetoacetate (**18**, 69.3 mg, 0.481 mmol, 1.0 equiv), allyltrimethylsilane (73.8 mg, 0.646 mmol, 1.3 equiv), CAN (571 mg, 1.04 mmol, 2.1 equiv), and methanol (10 mL). After 2.5 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **19** (67.3 mg, 0.366 mmol) as a colorless oil in 76% yield: GC t_R 8.37 min; TLC R_f 0.42 (20% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, J = 7.1 Hz, 3 H), 1.31 (s, 3 H), 2.13 (s, 3 H), 2.48 (dd, J = 14.1, 7.6 Hz, 1 H), 2.62 (dd, J = 14.1, 7.1 Hz, 1 H), 4.17 (q, J = 7.1 Hz, 2 H), 5.03–5.10 (m, 2 H), 5.56–5.70 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.01, 18.83, 26.19, 39.27, 59.39, 61.31, 118.94, 132.60, 172.46, 205.06; IR (neat) 3063 (w, =CH), 2953 (m, CH), 2920 (m, CH), 2853 (m, CH), 1738 (s, C=O), 1717 (s, C=O), 1653 (m, C=C), 1456 (m), 1243 (s), 1022 (m), 852 (m) cm^{-1}; MS m/e (relative intensity) 184 (M^+, 0.7), 142 (99), 141 (32), 114 (100), 113 (29), 97 (38), 96 (24), 95 (28), 69 (71), 68 (27), 67 (37); HRMS calcd for $C_{10}H_{16}O_3$ 184.1100, found 184.1099. Its spectroscopic characteristics are consistent with those of the same compound reported.[32]

Ethyl 1-Allyl-2-oxocyclopentanecarboxylate (21). The standard procedure 1 was followed by use of ethyl 2-oxocyclopentanecarboxylate (**20**, 79.6 mg, 0.510 mmol, 1.0 equiv), allyltrimethylsilane (75.2 mg, 0.658 mmol, 1.3 equiv), CAN (576 mg, 1.05 mmol, 2.1 equiv), and methanol (10 mL). After 2.5 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **21** (80.9 mg, 0.413 mmol) as a colorless oil in 81% yield: GC t_R 11.04 min; TLC R_f 0.42 (20% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, J = 7.1 Hz, 3 H), 1.85–2.63 (m, 8 H), 4.12 (q, J = 7.1 Hz, 2 H), 5.02–5.09 (m, 2 H), 5.58–5.72 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.02, 19.44, 32.08, 37.77, 38.01, 59.86, 61.37, 118.98, 132.99, 170.85, 214.54; IR (neat) 3077 (w, =CH), 2977 (m, CH), 2906 (m, CH), 1750 (s, C=O), 1725 (s, C=O), 1639 (w, C=C), 1449 (w), 1225 (m), 1159 (m), 1023 (w), 922 (w), 858 (w) cm^{-1}; MS m/e (relative intensity) 196 (M^+, 4), 168 (68), 123 (50), 122 (50), 121 (35), 113 (36), 95 (100), 94 (78), 80 (63), 79 (53), 67 (75), 55 (30); HRMS calcd for $C_{11}H_{16}O_3$ 196.1100, found 196.1096. Its spectroscopic characteristics are consistent with those of the same compound reported.[33]

Diethyl Allylpropanedioate (23). The standard procedure 1 was followed by use of diethyl malonate (**22**, 78.6 mg, 0.491 mmol, 1.0 equiv), allyltrimethylsilane (75.1 mg, 0.657 mmol, 1.3 equiv), CAN (575 mg, 1.05 mmol, 2.1 equiv), and methanol (10 mL). After 4 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **23** (72.7 mg, 0.363 mmol) as a colorless oil in 74% yield: GC t_R 9.47 min; TLC R_f 0.70 (10% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, J = 7.1 Hz, 6 H), 2.62 (dd, J = 7.3, 7.0 Hz, 2 H), 3.39 (t, J = 7.3 Hz, 1 H), 4.17 (q, J = 7.1 Hz, 4 H), 5.03–5.14 (m, 2 H), 5.68–5.82 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.32, 32.69, 51.57, 61.25, 117.37, 134.05, 168.84; IR (neat) 3078 (w, =CH), 2984 (m, CH), 2957 (m, CH), 1739 (s, C=O), 1644 (w, C=C), 1242 (m), 1171 (m), 1032 (m), 853 (m) cm^{-1}; MS m/e (relative intensity) 200 (M^+, 0.6), 127 (78), 126 (36), 109 (86), 108 (39), 99 (45), 98 (100), 82 (35), 81 (72), 55 (36); HRMS calcd for $C_{10}H_{16}O_4$ 200.1049, found 200.1049. Its spectroscopic characteristics are consistent with those of the same compound reported.[30]

5,5-Diallyl-2,2-dimethyl-1,3-dioxane-4,6-dione (25). The standard procedure 1 was followed by use of 2,2-dimethyl-1,3-dioxane-4,6-dione (**24**, 75.4 mg, 0.523 mmol, 1.0 equiv), allyltrimethylsilane (154 mg, 1.35 mmol, 2.6 equiv), CAN (1.18 g, 2.15 mmol, 4.1 equiv), and methanol (15 mL). After 3 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 2% EtOAc in hexanes as eluant) to give pure **25** (96.1 mg, 0.429 mmol) as a colorless oil in 82% yield: GC t_R 11.60 min; TLC R_f 0.71 (10% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.63 (s, 6 H), 2.69 (d, J = 7.7 Hz, 4 H), 5.12–5.19 (m, 4 H), 5.58–5.72 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.11, 29.84, 42.73, 55.44, 105.75, 121.23, 130.85, 168.37; IR (neat) 3078 (w, =CH), 2994 (w, CH), 1774 (m, C=O), 1743 (s), 1640 (w, C=C), 1440 (w), 1349 (m), 1278 (m), 937 (m) cm^{-1}; MS m/e (relative intensity) 209 (0.01), 166 (27), 138 (26), 124 (30), 122 (28), 107 (23), 95 (38), 93 (46), 91 (22), 79 (100), 77 (30). Its spectroscopic characteristics are consistent with those of the same compound reported.[17a]

2-Allylcyclododecanone (27). The standard procedure 1 was followed by use of cyclododecanone (**26**, 90.9 mg, 0.499 mmol, 1.0 equiv), allyltrimethylsilane (91.4 mg, 0.800 mmol, 1.6 equiv), CAN (822 mg, 1.50 mmol, 3.0 equiv), and methanol (2.0 mL). After 4 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **27** (83.7 mg, 0.377 mmol) as a colorless oil in 75% yield: GC t_R 16.34 min; TLC R_f 0.62 (20% EtOAc in hexanes); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.16–2.67 (m, 23 H), 4.95–5.03 (m, 2 H), 5.62–5.75 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.88, 22.21, 22.52, 23.58, 23.84, 24.09, 25.68, 26.04, 29.22, 35.54, 37.56, 51.55, 116.43, 135.99, 214.11; IR (neat) 3076 (w, =CH), 2931 (s, CH), 2861 (s, CH), 1706 (s, C=O), 1641 (w, C=C), 1468 (m), 1441 (m), 992 (w), 913 (m), 729 (m) cm^{-1}; MS m/e (relative intensity) 222 (M^+, 14), 111 (35), 98 (64), 95 (41), 83 (39), 82 (31), 81 (61), 69 (36), 68 (33), 67 (70), 55 (100), 54 (30); HRMS calcd for $C_{15}H_{26}O$ 222.1984, found 222.1992. Its spectroscopic characteristics are consistent with those of the same compound reported.[34]

Standard Procedure 2: Cyclizations by Use of 1,3-Dioxo Compounds, Allylsilanes, and $Mn(OAc)_3 \cdot 2H_2O$. To a sealable bottle containing a dioxo compound, allylsilane, and glacial acetic acid was added $Mn(OAc)_3 \cdot 2H_2O$. The bottle was sealed, and the solution was stirred at 80 °C. After the color disappeared, the reaction mixture was cooled, diluted with water (20 mL), and neutralized with aqueous $NaHCO_3$. 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

(30) Ranu, B. C.; Bhar, S. *J. Chem. Soc., Perkin Trans. 1* **1992**, 365.
(31) Brown, E.; Lavoue, J.; Dhal, R. *Tetrahedron* **1973**, *29*, 455.
(32) Fráter, G.; Müller, U.; Günther, W. *Tetrahedron* **1984**, *40*, 1269.
(33) Gutsche, C. D.; Zandstra, H. R. *J. Org. Chem.* **1974**, *39*, 324.
(34) Araújo, H. C.; Mahajan, J. R. *Synthesis* **1978**, 228.

under reduced pressure, the residue was chromatographed through a silica gel column to provide the desired product.

3-Benzoyl-2-phenyl-5-[(trimethylsilyl)methyl]-4,5-dihydrofuran (29). The standard procedure 2 was followed by use of 1,3-diphenyl-1,3-propanedione (**12**, 224 mg, 1.00 mmol, 1.0 equiv), allyltrimethylsilane (150 mg, 1.31 mmol, 1.3 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (643 mg, 2.40 mmol, 2.4 equiv), and glacial acetic acid (10 mL). After 15 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 0.5% EtOAc in hexanes as eluant) to give pure **29** (306 mg, 0.910 mmol) as a colorless oil in 91% yield: GC t_R 25.03 min; TLC R_f 0.42 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.15 (s, 9 H), 1.24 (dd, J = 14.1, 8.7 Hz, 1 H), 1.43 (dd, J = 14.1, 6.0 Hz, 1 H), 2.97 (dd, J = 14.7, 9.5 Hz, 1 H), 3.38 (dd, J = 14.7, 9.3 Hz, 1 H), 4.96–5.09 (m, 1 H), 7.02–7.50 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −1.01, 24.94, 40.95, 81.83, 112.10, 127.39, 128.73, 129.20, 129.67, 130.25, 130.76, 139.14, 165.97, 193.43; IR (neat) 3059 (m, =CH), 2950 (m, CH), 2892 (m, CH), 1714 (s, C=O), 1683 (s, C=C), 1599 (m, Ph), 1492 (m, Ph), 1450 (m), 1272 (m), 1109 (m), 845 (m), 760 (m), 704 (m) cm^{-1}; MS m/e (relative intensity) 336 (M^+, 6), 245 (9), 231 (5), 141 (4), 115 (5), 106 (8), 105 (100), 77 (29), 75 (6), 73 (29); HRMS calcd for $C_{21}H_{24}O_2Si$ 336.1545, found 336.1547. Anal. Calcd for $C_{21}H_{24}O_2Si$: C, 74.96; H, 7.19. Found: C, 74.56; H, 7.33.

2-[(Trimethylsilyl)methyl]-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran (30). The standard procedure 2 was followed by use of 1,3-cyclohexanedione (**28**, 112 mg, 1.00 mmol, 1.0 equiv), allyltrimethylsilane (149 mg, 1.30 mmol, 1.3 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (644 mg, 2.40 mmol, 2.4 equiv), and glacial acetic acid (10 mL). After 15 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 4% EtOAc in hexanes as eluant) to give pure **30** (198 mg, 0.883 mmol) as a yellow oil in 88% yield: GC t_R 15.99 min; TLC R_f 0.29 (40% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.05 (s, 9 H), 1.06 (dd, J = 14.0, 9.3 Hz, 1 H), 1.24 (dd, J = 14.0, 5.7 Hz, 1 H), 1.95–2.04 (m, 2 H), 2.29–2.41 (m, 5 H), 2.88–2.97 (m, 1 H), 4.85–4.96 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −1.35, 21.29, 23.66, 25.26, 33.68, 35.97, 84.90, 112.54, 176.58, 194.74; IR (neat) 2948 (s, CH), 2893 (m, CH), 1729 (m, C=O), 1629 (m, C=C), 1454 (m), 1402 (m), 1247 (m, $SiCH_3$), 1180 (m), 1113 (m), 851 (s) cm^{-1}; MS m/e (relative intensity) 224 (M^+, 26), 223 (14), 210 (14), 209 (84), 195 (12), 181 (24), 153 (14), 75 (34), 73 (100); HRMS calcd for $C_{12}H_{20}O_2Si$ 224.1232, found 224.1229. Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98. Found: C, 64.07; H, 8.97.

Ethyl 2-Methyl-5-[(trimethylsilyl)methyl]-4,5-dihydrofuran-3-carboxylate (31). The standard procedure 2 was followed by use of ethyl acetoacetate (**14**, 130 mg, 1.00 mmol, 1.0 equiv), allyltrimethylsilane (150 mg, 1.31 mmol, 1.3 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (643 mg, 2.40 mmol, 2.4 equiv), and glacial acetic acid (10 mL). After 40 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 0.5% EtOAc in hexanes as eluant) to give pure **31** (206 mg, 0.851 mmol) as a colorless oil in 85% yield: GC t_R 13.69 min; TLC R_f 0.49 (5% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.00 (s, 9 H), 0.95 (dd, J = 14.1, 8.4 Hz, 1 H), 1.13 (dd, J = 14.1, 6.2 Hz, 1 H), 1.20 (t, J = 7.2 Hz, 3 H), 2.09 (s, 3 H), 2.40 (dd, J = 14.1, 8.2 Hz, 1 H), 2.91 (dd, J = 14.1, 9.6 Hz, 1 H), 4.09 (q, J = 7.2 Hz, 2 H), 4.63–4.71 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 1.05, 14.14, 14.39, 25.42, 37.90, 59.14, 81.39, 101.43, 166.27, 167.48; IR (neat) 2953 (s, CH), 2866 (m, CH), 1698 (s, C=O), 1645 (s, C=C), 1384 (m), 1250 (m, $SiCH_3$), 1227 (m), 1085 (m), 965 (m), 858 (s) cm^{-1}; MS m/e (relative intensity) 242 (M^+, 8), 227 (17), 199 (17), 181 (34), 124 (11), 123 (23), 109 (15), 97 (11), 81 (31), 75 (42), 73 (100); HRMS calcd for $C_{12}H_{22}O_3Si$ 242.1338, found 242.1343. Anal. Calcd for $C_{12}H_{22}O_3Si$: C, 59.46; H, 9.15. Found: C, 59.41; H, 9.06.

Ethyl 2-*n*-Propyl-5-[(trimethylsilyl)methyl]-4,5-dihydrofuran-3-carboxylate (32). The standard procedure 2 was followed by use of ethyl butyrylacetate (**16**, 159 mg, 1.01 mmol, 1.0 equiv), allyltrimethylsilane (149 mg, 1.30 mmol, 1.3 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (643 mg, 2.40 mmol, 2.4 equiv), and glacial acetic acid (10 mL). After 40 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **32** (198 mg, 0.733 mmol) as a colorless oil in 73% yield: GC t_R 15.16 min; TLC R_f 0.59 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.02 (s, 9 H), 0.90 (t, J = 7.6 Hz, 3 H), 0.98 (dd, J = 14.0, 8.8 Hz, 1 H), 1.15 (dd, J = 14.0, 6.4 Hz, 1 H), 1.23 (t, J = 7.2 Hz, 3 H), 1.50–1.58 (m, 2 H), 2.43 (dd, J = 14.0, 8.8 Hz, 1 H), 2.55 (t, J = 7.6 Hz, 2 H), 2.94 (dd, J = 14.0, 9.6 Hz, 1 H), 4.11 (q, J = 7.2 Hz, 2 H), 4.66–4.71 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 0.99, 13.76, 14.42, 20.18, 25.46, 29.73, 37.99, 59.18, 81.30, 101.16, 166.30, 171.16; IR (neat) 2957 (s, CH), 2872 (m, CH), 1697 (s, C=O), 1638 (s, C=C), 1459 (m), 1247 (m, $SiCH_3$), 1199 (m), 1099 (m), 1041 (m), 858 (s) cm^{-1}; MS m/e (relative intensity) 270 (M^+, 8), 255 (17), 227 (19), 209 (34), 181 (19), 151 (18), 109 (44), 81 (29), 75 (43), 73 (100), 71 (14); HRMS calcd for $C_{14}H_{26}O_3Si$ 270.1651, found 270.1657. Anal. Calcd for $C_{14}H_{26}O_3Si$: C, 62.18; H, 9.69. Found: C, 61.86; H, 9.62.

Ethyl 2-Methyl-5-[(dimethylphenylsilyl)methyl]-4,5-dihydrofuran-3-carboxylate (33). The standard procedure 2 was followed by use of ethyl acetoacetate (**14**, 130 mg, 1.00 mmol, 1.0 equiv), allyldimethylphenylsilane (192 mg, 1.09 mmol, 1.1 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (643 mg, 2.40 mmol, 2.4 equiv), and glacial acetic acid (10 mL). After 45 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **33** (250 mg, 0.822 mmol) as a colorless oil in 82% yield: GC t_R 19.86 min; TLC R_f 0.49 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.33 (s, 6 H), 1.24 (t, J = 7.1 Hz, 3 H), 1.17–1.26 (m, 1 H), 1.42 (dd, J = 14.2, 6.5 Hz, 1 H), 2.10 (s, 3 H), 2.42 (dd, J = 14.1, 8.1 Hz, 1 H), 2.91 (dd, J = 14.1, 9.9 Hz, 1 H), 4.13 (q, J = 7.1 Hz, 2 H), 4.63–4.75 (m, 1 H), 7.34–7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −2.34, 14.11, 14.38, 24.75, 37.84, 59.21, 81.04, 101.44, 127.78, 129.05, 133.41, 138.20, 166.31, 167.43; IR (neat) 3069 (w, =CH), 2952 (m, CH), 1696 (s, C=O), 1643 (s, C=C), 1427 (m, SiPh), 1253 (m, $SiCH_3$), 1117 (m), 832 (s), 730 (m), 701 (m) cm^{-1}; MS m/e (relative intensity) 304 (M^+, 2), 289 (6), 227 (26), 226 (16), 199 (14), 137 (17), 136 (14), 135 (100), 107 (10), 81 (9); HRMS calcd for $C_{17}H_{24}O_3Si$ 304.1495, found 304.1481. Anal. Calcd for $C_{17}H_{24}O_3Si$: C, 67.07; H, 7.95. Found: C, 67.09; H, 7.93.

3-Benzoyl-2-phenyl-5-[(triisopropylsilyl)methyl]-4,5-dihydrofuran (34). The standard procedure 2 was followed by use of 1,3-diphenyl-1,3-propanedione (**12**, 224 mg, 1.00 mmol, 1.0 equiv), allyltriisopropylsilane (216 mg, 1.09 mmol, 1.1 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (643 mg, 2.40 mmol, 2.4 equiv), and glacial acetic acid (10 mL). After 30 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **34** (281 mg, 0.672 mmol) as a yellow oil in 67% yield: GC t_R 29.25 min (the initial temperature for column 70 °C, duration 2.00 min, increment rate 10 °C/min, and the final temperature for column 300 °C); TLC R_f 0.51 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01–1.16 (m, 21 H), 1.25 (dd, J = 14.4, 8.1 Hz, 1 H), 1.45 (dd, J = 14.4, 6.6 Hz, 1 H), 2.99 (dd, J = 14.6, 9.8 Hz, 1 H), 3.36 (dd, J = 14.6, 9.1 Hz, 1 H), 5.02–5.14 (m, 1 H), 6.95–7.43 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.18, 17.84, 18.45, 41.70, 81.72, 112.10, 127.30, 127.35, 128.68, 129.17, 129.57, 130.22, 130.68, 139.14, 165.58, 193.12; IR (neat) 3061 (w, =CH), 2943 (s, CH), 2865 (s, CH), 1713 (s, C=O), 1688 (s, C=C), 1598 (m, Ph), 1454 (m), 1272 (m), 1107 (m), 744 (m), 712 (m) cm^{-1}; MS m/e (relative intensity) 420 (M^+, 0.3), 377 (30), 141 (6), 115 (22), 105 (100), 87 (12), 77 (44), 75 (11), 73 (17), 59 (23); HRMS calcd for $C_{27}H_{36}O_2Si$ 420.2484, found 420.2486. Anal. Calcd for $C_{27}H_{36}O_2Si$: C, 77.09; H, 8.63. Found: C, 76.75; H, 8.49.

Ethyl 2-Methyl-5-[(triisopropylsilyl)methyl]-4,5-dihydrofuran-3-carboxylate (35). Method 1. The standard procedure 1 was followed by use of ethyl acetoacetate (**14**, 65.2 mg, 0.500 mmol, 1.0 equiv), allyltriisopropylsilane (111 mg, 0.561 mmol, 1.1 equiv), CAN (576 mg, 1.05 mmol, 2.1 equiv), and methanol (10 mL). After 40 min, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **35** (124 mg, 0.380 mmol) as a

colorless oil in 76% yield: GC t_R 20.31 min; TLC R_f 0.65 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.98–1.05 (m, 22 H), 1.20–1.28 (m, 1 H), 1.25 (t, J = 7.1 Hz, 2 H), 2.14 (s, 3 H), 2.45–2.53 (m, 1 H), 2.97–3.05 (m, 1 H), 4.14 (q, J = 7.1 Hz, 2 H), 4.76–4.87 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.18, 14.12, 14.40, 18.37, 18.64, 38.64, 59.16, 81.19, 101.40, 166.28, 167.34; IR (neat) 2943 (s, CH), 2866 (s, CH), 1699 (s, C=O), 1645 (s, C=C), 1464 (m), 1382 (m), 1262 (m), 1228 (m), 1085 (m), 882 (m) cm^{-1}; MS m/e (relative intensity) 236 (M^+, 0.03), 284 (22), 283 (100), 255 (60), 237 (59), 131 (19), 125 (20), 115 (32), 103 (32), 87 (25), 77 (18), 75 (36), 73 (29), 59 (36); HRMS calcd for $C_{18}H_{34}O_3Si$ 326.2277, found 326.2275. Anal. Calcd for $C_{18}H_{34}O_3Si$: C, 66.21; H, 10.49. Found: C, 66.42; H, 10.74.

Method 2. The standard procedure 2 was followed by use of ethyl acetoacetate (**14**, 130 mg, 1.00 mmol, 1.0 equiv), allyltriisopropylsilane (215 mg, 1.09 mmol, 1.1 equiv), $Mn(OAc)_3 \cdot 2H_2O$ (642 mg, 2.40 mmol, 2.4 equiv), and glacial acetic acid (10 mL). After 1 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (1.5 cm × 16 cm column, 1% EtOAc in hexanes as eluant) to give pure **35** (248 mg, 0.760 mmol) as a colorless oil in 76% yield.

Reaction of Ethyl Acetoacetate with Allyldimethylphenylsilane Induced by CAN. The standard procedure 1 was followed by use of ethyl acetoacetate (**14**, 198 mg, 1.52 mmol, 1.0 equiv), allyldimethylphenylsilane (226 mg, 1.98 mmol, 1.3 equiv), CAN (1.75 g, 3.19 mmol, 2.1 equiv), and methanol (30 mL). After 30 min, the reaction mixture was worked up and purified to give a mixture of **15** and **33** in 80% overall yield. The ratio of **15** to **33** in the mixture was determined as 16:1 by ^{1}H NMR spectroscopy.

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