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Mn(III)-based C–C bond formation: regioselective α′-allylation of various α,β-unsaturated, α and β-alkoxy α,β-unsaturated ketones

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Abstract—The Manganese(III)-based regioselective α′-keto radical generation of unsaturated ketones is a versatile synthetic procedure with broad applicability. The generated α′-keto radical slowly creates a metal enolate in a solvent at reflux. The resultant metal enolate affords the corresponding α′-allylated α,β-unsaturated ketones in good yields. This method is the first example of the metal mediated regioselective α′-allylation of α,β-unsaturated ketones. The ketones that have α or β-alkoxy groups also work efficiently.

1. Introduction

The empirical endeavour on the synthesis of targets with wide complexity has resulted in the development of reactions that emphasize chemo-, regio-, and stereoselectivity. In defining the strategies and reactions to construct complex molecules, regioselectivity is required.[1] Metal-mediated allylation generally has a central position in the synthesis of various complex natural products. A wide variety of allylations are well known in the literature as useful methods for carbon–carbon bond formation, that is, metal-mediated allyl addition to carbonyl,[2,3] and the direct allylation on the α-position of ketones.[4,5] A considerable challenge is to affect a high regioselectivity between carbonyl carbons and the α and α′-positions of α,β-unsaturated ketones.

In the last decade, Mn(III)-based oxidative free-radical reactions have been developed into a versatile protocol for the formation of highly functionalized products from simple precursors.[6] In 1976, Williams and Hunter reported that the $Mn(OAc)_3 \cdot 2H_2O$ oxidation of enones in HOAc at reflux affords α′-acetoxy enones in low yields.[7] In connection with our synthetic studies with manganese(III) acetate,[8] we found that trapping of the α′-keto radicals that were obtained from β-alkoxy α,β-unsaturated ketones with benzene as solvent is much faster than acetoxylation, affording good yields of tandem oxidation products.[8d] These noteworthy results prompted us toward the development of a new method in the field of regioselective direct allylation of α,β-unsaturated ketones. Recently, we reported a complete regioselectivity related to the metal-mediated α′-allylation of enones.[8f] The allylation of enones mediated by Mn(III) shows exclusive selectivity toward the α′-position of α,β-unsaturated ketones. We describe here, the results of the $Mn(OAc)_3$ based allylation of various α,β-unsaturated ketones and α- or β-alkoxy α,β-unsaturated ketones.

2. Results and discussion

As a starting point, we have studied the use of manganese(III) acetate as a potentially useful mediator for the metal-promoted regioselective α′-allylation reaction of various enones. When 3-methyl-cyclopent-2-enone **1c** (entry 3) was stirred with 2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv of allyl bromide in benzene for 8 h at reflux, 81% of 5-allyl-3-methyl-cyclopent-2-enone **2c** was isolated. When 3 equiv of $Mn(OAc)_3 \cdot 2H_2O$ was used, the isolated yield of the allylation product substantially decreased to 53 and 25% of the α′-acetoxylation product[9] that was isolated. Changing the amount of $Mn(OAc)_3 \cdot 2H_2O$ to 1 equiv decreased the yield of the allylation product too (64%), and no α′-acetoxylation product was observed. The stoichiometric amount of manganese(III) acetate appears to be critical.

As a natural extension of this study, we have pursued a complementary investigation aimed at subjecting various α,β-unsaturated cyclic ketones to comparable scrutiny. Subsequently, a variety of cyclopentenones and cyclohexenones were tested with this allylation method (Scheme 1).

Keywords: Enones; Manganese and compounds; Allylation.
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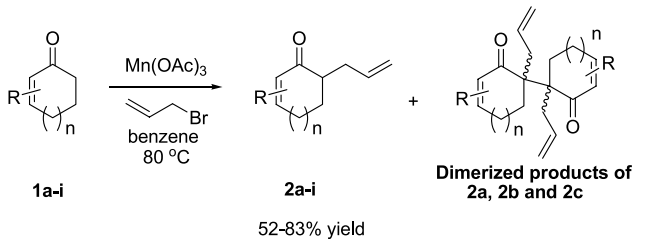


Scheme 1.

Selected examples are shown in Table 1. It was found that various cyclopentenones and cyclohexenones were efficiently allylated. In general, cyclopentenone derivatives afford higher chemical yields than cyclohexenone derivatives. We could not observe any substantial change in the chemical yields related to the substituents on the substrates. In entry 1, 2 and 3, the dimerized allylated products were isolated.[10] These results can strongly support the formation of a radical on the α′-position of enone systems. We attempted to replace benzene with a more innocuous solvent toluene in entries 1–3 and obtained a 5–7% decrease in the yields.[11] Regioselective allylation was also tested with an acyclic substrate mesityl oxide (entry 9) and the allylated acylic product **2i** was obtained in an acceptable yield.

We also examined the allylation reaction of β-alkoxy and α-alkoxy α,β-unsaturated ketones that play an important role in the synthesis of quassinoids and prostaglandines, respectively.

In the first part of that study, 3-ethoxy-5,5-dimethyl-2-cyclohexenone was chosen as a model compound. The reaction of **3e** in benzene with 2 equiv of Mn $(OAc)_3 \cdot 2H_2O$ and 1 equiv of allyl bromide for 8 h at reflux affords 75% of 6-allyl-3-ethoxy-5,5-dimethyl-2-cyclohexenone **4e** (entry 5). Selected examples are shown in Table 2 (Scheme 2).

In order to test the allylation reaction, whether it proceeds by a radical mechanism or by a nucleophilic substitution, 3-ethoxy-5,5-dimethyl-2-cyclohexenone **3e** and 3-methyl-2-cyclohexenone **2e** were reacted with crotyl bromide under the same conditions. Both afforded the nucleophilic substitution products **5a** and **5b** in 49 and 52% yields, respectively, (Scheme 3); the regioselectivity of the allylation implies that the reaction proceeds via an S_N2 mechanism and is not radical in nature.[12]

From these results in particular, with the results of the allylation where it was tested with different allyl side chains, we subsequently proposed a reaction mechanism as is shown in Scheme 4. The reaction presumably proceeds via the formation of Mn(III) enolate **6**, which by way of one electron oxidation, gives the α′-keto radical **7**.[13] The second equiv of $Mn(OAc)_3$ slowly forms the Mn(II) enolate **8**. Alkylation of this metal enolate with allyl bromide yields the α′-allyl α,β-unsaturated cyclic ketone **2**. Vinogradov et al. reported that α′-keto radicals generated by higher ketones would result in secondary radicals, which dimerize or lead to tertiary radicals, which are prone to further oxidation.[14] In accordance with this conclusion, in this current study the dimerization of product **2** was observed for entries 1, 2 and 3 as was mentioned above.

Table 1. α′-Allylation of α,β-unsaturated enones mediated by $Mn(OAc)_3$ in benzene

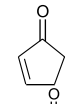
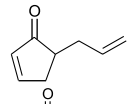
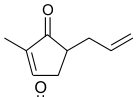
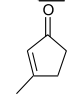
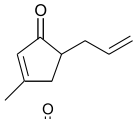
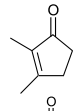
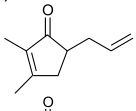
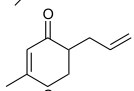
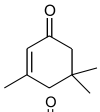
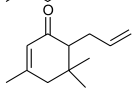
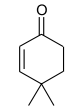
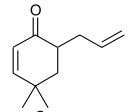
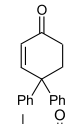
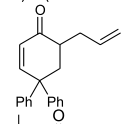
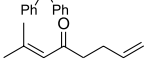
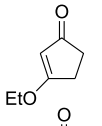
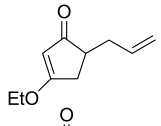
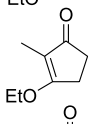
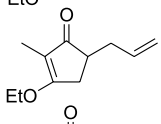
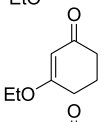
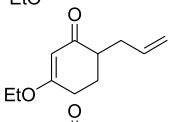
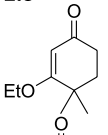
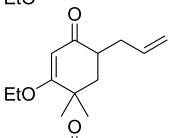
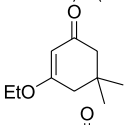
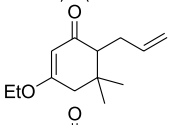
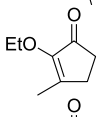
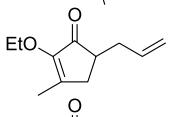
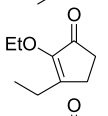
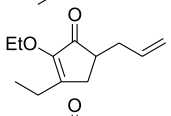
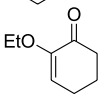
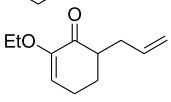
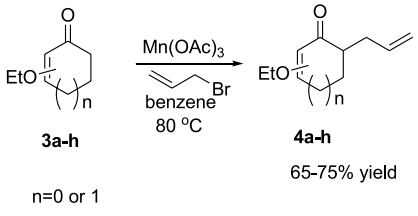
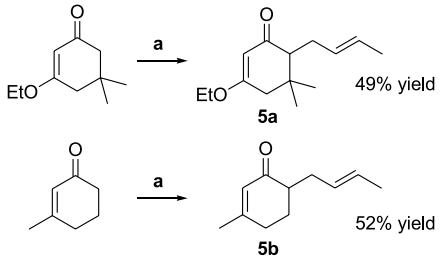
Entry	Reactant **1**	Product	**2**[11]	Yield (%)	Time (h)
1			**2a**	79	8
2			**2b**	80	8
3			**2c**	81	8
4			**2d**	83	10
5			**2e**	78	12
6			**2f**	68	12
7			**2g**	67	10
8			**2h**	72	12
9			**2i**	52	14

Table 2. α'-Allylation of α-alkoxy and β-alkoxy α,β-unsaturated enones mediated with $Mn(OAc)_3$

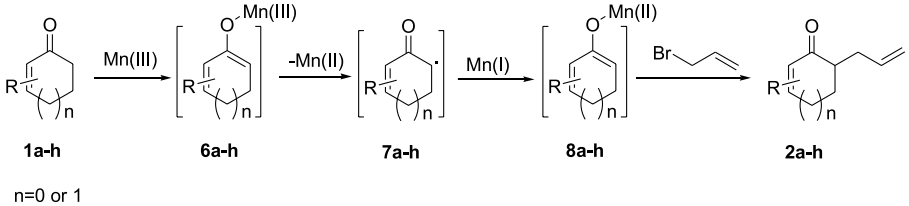
Entry	Reactant **3**	Product	**4**	Yield (%)	Time (h)
1			**4a**	69	7
2			**4b**	72	6
3			**4c**	67	7
4			**4d**	65	5
5			**4e**	75	8
6			**4f**	75	9
7			**4g**	72	12
8			**4h**	65	11



Scheme 2.



Scheme 3.



Scheme 4.

In conclusion, manganese(III) acetate is highly effective for mediating the α'-allylations of α,β-unsaturated cyclic ketones, α-alkoxy and β-alkoxy α,β-unsaturated cyclic ketones. This one-step reaction offers a complete regioselectivity towards the α'-allylation of cyclic enones and opens up a new class of $Mn(OAc)_3$ reactions.

3. Experimental

Nuclear magnetic resonance spectra were acquired on a Bruker Spectrospin Avance DPX 400 spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C, in $CDCl_3$. Chemical shifts are given in ppm from tetramethylsilane. IR spectra were obtained using a Perkin-Elmer Model 1600 series FT-IR spectrometer and are reported in cm^{-1}. Mass spectra were recorded with a Varian MAT 212. Flash chromatography: Merck silica gel 60 (230–400 mesh).

3.1. General procedure for the $Mn(OAc)_3$ based allylation of α,β-unsaturated ketones 1 and α and β-alkoxy α,β-unsaturated ketones 3

A mixture of $Mn(OAc)_3 \cdot 2H_2O$ (3.25 g, 14.0 mmol) in benzene (150 ml) was heated at reflux for 45 min using a Dean-Stark trap. The mixture was then cooled to room temperature and the α,β-unsaturated ketone (7.0 mmol) and allyl bromide (0.85 g, 7.0 mmol) were added. The mixture was heated to reflux until its dark brown colour disappeared. In addition, it was monitored by TLC. The reaction mixture was diluted with an equal amount of ethyl acetate, and the organic phase was washed with 1 M HCl followed by saturated $NaHCO_3$ and brine. The organic phase was dried over $MgSO_4$ and evaporated in vacuo. The crude product was separated by way of flash column chromatography using ethyl acetate/hexane as an eluent to afford the product.

3.1.1. 5-Allyl-cyclopent-2-enone 2a. (0.68 g, 79%) as a colourless oil; ν_{max} (neat) 2960, 2860, 1707, 1590 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.68–7.70 (1H, m, *H*C=CHCO), 6.19 (1H, dd, $J=2.1$, 7.6 Hz, HC=C*H*CO), 5.70–5.81 (1H, m, CH_2=C*H*CH_2), 5.08 (1H, d, $J=19.3$ Hz, C*H*$_a$H$_b$=CH), 5.04 (1H, d, $J=11.1$ Hz, CH_a*H*$_b$=CH), 2.80–2.86 (1H, m, CH_2C*H*CO), 2.52–2.57 (1H, m, C*H*$_a$H$_b$), 2.39–2.44 (2H, m, C*H*$_2$), 2.08–2.18 (1H, m, CH_a*H*$_b$); δ_C (100.6 MHz, $CDCl_3$) 212.0, 164.1, 135.6, 134.2, 117.2, 44.4, 35.6, 35.2; HRMS (EI): M^+, found 122.0737. $C_8H_{10}O$ requires 122.0732.

3.1.2. 5-Allyl-2-methyl-cyclopent-2-enone 2b. (0.76 g, 80%) as a colourless oil; ν_{max} (neat) 2910, 1682, 1615, 1431 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.28 (1H, d, $J=2.1$ Hz, *H*C=CMeCO), 5.70–5.80 (1H, m, CH_2C*H*=CH_2), 5.07 (1H, d, $J=17.1$ Hz, C*H*$_a$H$_b$=CH), 5.02 (1H, d, $J=10.7$ Hz, CH_a*H*$_b$=CH), 2.65–2.71 (1H, m, C*H*CO), 2.53–2.58 (1H, m, C*Ha* Hb), 2.42–2.45 (1H, m, CH_a*H*$_b$), 2.23–2.29 (1H, m, C*H*$_a$H$_b$), 2.10–2.15 (1H, m, CH_a*H*$_b$), 1.78 (3H, s, *Me*CCO); δ_C (100.6 MHz, $CDCl_3$) 211.7, 157.4, 141.6, 135.9, 117.0, 44.6, 35.9, 33.0, 10.6; HRMS (EI): M^+, found 136.0890. $C_9H_{12}O$ requires 136.0888.

3.1.3. 5-Allyl-3-methyl-cyclopent-2-enone 2c. (0.77 g, 81%) as a colourless oil; ν_{max} (neat) 3066, 2973, 1690, 1648 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.92 (1H, s, =C*H*CO), 5.70–5.79 (1H, m, CH_2C*H*=CH_2), 5.07 (1H, d, $J=17.3$ Hz, C*H*$_a$H$_b$=CH), 5.03 (1H, d, $J=10.5$ Hz, CH_a*H*$_b$=CH), 2.69 (1H, dd, $J=6.3$, 18.1 Hz, C*H*CO), 2.49–2.63 (2H, m, C*H*$_2$C=), 2.29 (1H, d, $J=18.1$ Hz, C*H*$_a$H$_b$CHCO), 2.13–2.14 (1H, m, CH_a*H*$_b$CHCO), 2.12 (3H, s); δ_C (100.6 MHz, $CDCl_3$) 211.4, 178.0, 135.7, 130.2, 117.0, 46.1, 39.2, 35.9, 19.7; HRMS (EI): M^+, found 136.0893. $C_9H_{12}O$ requires 136.0888.

3.1.4. 5-Allyl-2,3-dimethyl-cyclopent-2-enone 2d. (0.87 g, 83%) as a colourless oil; ν_{max} (neat) 3066, 2973, 2914, 1690, 1648 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.69–5.80 (1H, m, CH_2C*H*=CH_2), 5.06 (1H, d, $J=17.1$ Hz, C*H*$_a$H$_b$=CH), 5.01 (1H, d, $J=9.5$ Hz, CH_a*H*$_b$=CH), 2.64 (1H, dd, $J=5.8$, 19.3 Hz, C*H*CO), 2.52–2.62 (1H, m, C*H*$_a$H$_b$CH=CH_2), 2.42–2.44 (1H, m, CH_a*H*$_b$CH=CH_2), 2.05–2.10 (1H, m, C*H*$_a$H$_b$CHCO), 2.21 (1H, d, $J=19.3$ Hz, CH_a*H*$_b$CHCO), 2.04 (3H, s, *Me*CCO), 1.69 (3H, s, *Me*C=CMeCO); δ_C (100.6 MHz, $CDCl_3$) 211.1, 169.1, 136.0, 135.8, 116.8, 44.5, 38.1, 36.0, 17.4, 9.8; HRMS (EI): M^+, found 150.1040. $C_{10}H_{14}O$ requires 150.1045.

3.1.5. 6-Allyl-3-methyl-cyclohex-2-enone 2e. (0.82 g, 78%) as a colourless oil; ν_{max} (neat) 3024, 2923, 2855, 2357, 1659 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.78 (1H, s, =C*H*CO), 5.65–5.76 (1H, m, CH_2C*H*=CH_2), 5.09 (1H, d, $J=18.2$ Hz, C*H*$_a$H$_b$=CH), 4.96 (1H, d, $J=9.2$ Hz, CH_a*H*$_b$=CH), 2.53–2.56 (1H, m, C*H*CO), 2.15–2.23 (3H, m, C*H*$_2$CH=CH_2), 1.98–2.09 (2H, m, C*H*$_a$H$_b$CHCO), 1.87 (3H, s, *Me*), 1.58–1.70 (1H, m, CH_a*H*$_b$CHCO); δ_C (100.6 MHz, $CDCl_3$) 201.2, 162.3, 136.7, 126.7, 117.0, 45.4, 34.1, 30.7, 27.6, 24.6; HRMS (EI): M^+, found 150.1044. $C_{10}H_{14}O$ requires 150.1045.

3.1.6. 6-Allyl-3,5,5-trimethyl-cyclohex-2-enone 2f. (0.85 g, 68%) as a colourless oil; ν_{max} (neat) 2956, 1665, 1445, 1370 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.79–5.93 (2H, m, =C*H*CO and C*H*=CH_2), 5.04 (1H, d, $J=15.2$ Hz, C*H*$_a$H$_b$=CH), 4.96 (1H, d, $J=11.3$ Hz, CH_a*H*$_b$=CH), 2.15–2.31 (4H, m, C*H*$_2$CH and C*H*$_2$CMe_2), 2.08–2.12 (1H, m, C*H*CO), 1.91 (3H, s, *Me*C=), 1.05 (3H, s, *Me*$_2$C), 0.96 (3H, s, *Me*$_2$C); δ_C (100.6 MHz, $CDCl_3$) 202.1, 158.5, 138.0, 125.3, 115.7, 57.5, 45.1, 36.7, 30.7, 29.1, 24.6, 24.5; HRMS (EI): M^+, found 178.1355. $C_{12}H_{18}O$ requires 178.1358.

3.1.7. 6-Allyl-4,4-dimethyl-cyclohex-2-enone 2g. (0.77 g, 67%) as a colourless oil; ν_{max} (neat) 3211, 2892, 1715, 1665, 1515, 1289 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.40 (1H, d, $J=10.0$ Hz, C*H*=CHCO), 5.63 (1H, d, $J=10.0$ Hz, CH=C*H*CO), 5.59–5.62 (1H, m, C*H*=CH_2), 4.87 (1H, d, $J=17.1$ Hz, C*H*$_a$H$_b$=CH), 4.84 (1H, d, $J=9.1$ Hz, CH_a*H*$_b$=CH), 2.47–2.53 (1H, m, C*H*CO), 2.26–2.34 (1H, m, C*H*$_a$H$_b$CH=), 1.85–1.92 (1H, m, CH_a*H*$_b$CH=), 1.66 (1H, dd, $J=4.6$, 13.4 Hz, C*H*$_a$H$_b$CHCO), 1.41 (1H, t, $J=13.4$ Hz, CH_a*H*$_b$CHCO), 0.98 (3H, s, *Me*$_2$C), 0.95 (3H, s, *Me*$_2$C); δ_C (100.6 MHz, $CDCl_3$) 200.9, 159.2, 136.6, 127.0, 117.0, 57.3, 42.5, 42.0, 34.0, 30.9, 25.8; HRMS (EI): M^+, found 164.1207. $C_{11}H_{16}O$ requires 164.1202.

3.1.8. 6-Allyl-4,4-diphenyl-cyclohex-2-enone 2h. (1.45 g, 72%) as a colourless oil; ν_{max} (neat) 3024, 2931, 2885, 1665, 1589, 1437 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.20–7.47 (10H, m, *Ph*$_2$C), 7.15 (1H, d, $J=10.1$ Hz, C*H*=CHCO); 6.21 (1H, d, $J=10.1$ Hz, CH=*CH*CO), 5.67–5.77 (1H, m, C*H*=CH_2), 5.02–5.05 (2H, m, CH=C*H*$_2$), 2.67–2.75 (2H, m, C*H*$_2$CH=), 2.32–2.42 (2H, m, C*H*$_2$CHCO), 2.04–2.17 (1H, m, C*H*CO); δ_C (100.6 MHz, $CDCl_3$) 199.8, 155.2, 148.0, 143.1, 135.6, 129.1, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 127.8, 127.2, 127.0, 126.7, 117.1, 49.9, 42.7, 41.2, 33.2; HRMS (EI): M^+, found 288.1519. $C_{21}H_{20}O$ requires 288.1514.

3.1.9. 2-Methyl octa-2,7-dien-4-one 2i. (0.5 g, 52%) as a colourless oil; ν_{max} (neat) 3079, 1595, 1692, 981, 882 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.00 (1H, s, Me_2C=C*H*CO), 5.71–5.82 (1H, m, CH_2=C*H*), 4.96 (1H, d, $J=15.2$ Hz, C*H*$_a$H$_b$=CH), 4.90 (1H, d, $J=8.9$ Hz, CH_a*H*$_b$=CH), 2.43 (2H, t, $J=7.0$ Hz, COC*H*$_2$CH$_2$), 2.25–2.30 (2H, m, COCH$_2$C*H*$_2$), 2.08 (3H, s, *Me*$_2$C=), 1.82 (3H, s, *Me*$_2$C=); δ_C (100.6 MHz, $CDCl_3$) 200.5, 155.6, 137.9, 124.1, 115.3, 43.6, 28.5, 28.0,

21.1; HRMS (EI): MH^+, found 139.1116. $C_9H_{14}O$ requires 139.1123.

3.1.10. 5-Allyl-3-ethoxy-cyclopent-2-enone 4a. (0.72 g, 69%) as a colourless oil; ν_{max} (neat) 2950, 1125, 1700, 1560 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.65–5.74 (2H, m, =C*H*CO and C*H*=CH_2), 5.02 (1H, d, J=18.9 Hz, CH_a-H_b=CH), 4.98 (1H, d, J=11.0 Hz, CH_aH_b=CH), 3.97 (2H, q, J=7.1 Hz, MeCH_2O), 2.63 (1H, dd, J=6.8, 17.6 Hz, C*H*CO), 2.47–2.53 (2H, m, CH_2), 2.27 (1H, dd, J=1.7, 17.6 Hz, CH_aH_bCH=CH_2), 2.00–2.14 (1H, m, CH_aH_bCH=CH_2), 1.34 (3H, t, J=7.1 Hz, *Me*CH_2O); δ_C (100.6 MHz, $CDCl_3$) 207.8, 189.4, 135.7, 113.2, 104.3, 68.0, 44.7, 35.9, 34.5, 14.5; HRMS (EI): M^+, found 166.0991. $C_{10}H_{14}O_2$ requires 166.0994.

3.1.11. 5-Allyl-3-ethoxy-2-methyl-cyclopent-2-enone 4b. (0.9 g, 72%) as a colourless oil; ν_{max} (neat) 2900, 1675, 1400, 1120 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.64–5.74 (1H, m, C*H*=CH_2), 5.02 (1H, d, J=18.8 Hz, CH_aH_b=CH), 4.98 (1H, d, J=10.5 Hz, CH_aH_b=CH), 4.15–4.32 (2H, m, MeCH_2O), 3.07 (1H, dd, J=6.6, 18.9 Hz, CH_aH_bCHCO), 2.99 (1H, dd, J=6.7, 18.5 Hz, C*H*CO), 2.79 (1H, d, J=18.9 Hz, CH_aH_bCHCO), 1.47–2.56 (1H, m, CH_2=CHCH_aH_b), 1.98–2.11 (1H, m, CH_2=CHCH_aH_b), 1.71 (3H, s, *Me*C=), 1.37 (3H, t, J=7.0 Hz, *Me*CH_2O); δ_C (100.6 MHz, $CDCl_3$) 201.0, 178.8, 136.0, 119.1, 117.1, 66.2, 45.7, 45.2, 40.1, 15.7, 7.5; HRMS (EI): M^+, found 180.1156. $C_{11}H_{16}O_2$ requires 180.1150.

3.1.12. 6-Allyl-3-ethoxy-cyclohex-2-enone 4c. (0.74 g, 67%) as a colourless oil; ν_{max} (neat) 3020, 2915, 2852, 1650, 1110 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.75–5.86 (1H, m, C*H*=CH_2), 5.35 (1H, s, =C*H*CO), 5.08 (1H, d, J=15.2 Hz, CH_aH_b=CH), 5.05 (1H, d, J=5.1 Hz, CH_a-H_b=CH), 3.88–3.94 (2H, m, MeCH_2O), 2.64–2.68 (1H, m, C*H*CO), 2.43 (2H, t, J=5.3 Hz, CH_2CH=CH_2), 2.25–2.28 (1H, m, C$H_aH_b$$CH_2$CHCO), 2.05–2.19 (2H, m, CH_2CHO), 1.71–1.75 (1H, m, $CH_aH_b$$CH_2$CHCO), 1.38 (3H, t, J=7.0 Hz, *Me*CH_2); δ_C (100.6 MHz, $CDCl_3$) 200.5, 182.6, 137.0, 116.8, 101.3, 64.6, 41.8, 34.2, 27.4, 25.3, 14.4; HRMS (EI): M^+, found 180.1142. $C_{11}H_{16}O_2$ requires 180.1150.

3.1.13. 6-Allyl-3-ethoxy-4,4-dimethyl-cyclohex-2-enone 4d. (0.95 g, 65%) as a colourless oil; ν_{max} (neat) 3210, 2890, 1710, 1662, 1115 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.66–5.76 (1H, m, C*H*=CH_2), 5.16 (1H, s, =C*H*CO), 4.99 (1H, dd, J=15.1 Hz, CH_aH_b=CH), 4.96 (1H, d, J=7.7 Hz, CH_aH_b=CH), 3.72–3.89 (2H, m, MeCH_2O), 2.64–2.70 (1H, m, C*H*CO), 2.31–2.39 (1H, m, CH_aH_bCH=CH_2), 1.97–2.12 (1H, m, CH_aH_bCH=CH_2), 1.70 (1H, dd, J=4.8, 13.3 Hz, CH_aH_bCHCO), 1.54 (1H, t, J=13.5 Hz, CH_aH_bCHCO), 1.28 (3H, t, J=7.0 Hz, *Me*CH_2), 1.16 (3H, s, *Me*$_2$C), 1.09 (3H, s, *Me*$_2$C); δ_C (100.6 MHz, $CDCl_3$) 192.9, 174.8, 171.0, 100.8, 80.3, 77.9, 65.1, 43.7, 36.8, 27.5, 21.1, 20.5, 14.5; HRMS (EI): M^+, found 208.2967. $C_{13}H_{20}O_2$ requires 208.1464.

3.1.14. 6-Allyl-3-ethoxy-5,5-dimethyl-cyclohex-2-enone 4e. (1.24 g, 75%) as a colourless oil; ν_{max} (neat) 3019, 2960, 1740, 1640, 1598, 1456, 1372 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.76–5.87 (1H, m, C*H*=CH_2), 5.21 (1H, s, =C*H*CO), 4.94 (1H, d, J=17.2 Hz, CH_aH_b=CH), 4.90 (1H, d, J=10.3 Hz, CH_aH_b=CH), 3.82 (2H, q, J=7.1 Hz, MeCH_2O), 2.55 (1H, d, J=17.6 Hz, C*H*CO), 2.24–2.31 (2H, m, CH_aH_bCH=CH_2 and C$H_aH_b$$CMe_2$), 2.15 (1H, d, J=17.6 Hz, CH_aH_bCH=CH_2), 1.99–2.03 (1H, m, $CH_aH_b$$CMe_2$), 1.29 (3H, t, J=7.1 Hz, *Me*CH_2), 1.02 (3H, s, *Me*CH_2), 0.93 (3H, s, *Me*CH_2); δ_C (100.6 MHz, $CDCl_3$) 201.6, 174.6, 138.1, 115.5, 101.1, 64.4, 61.8, 57.3, 42.4, 35.5, 31.2, 14.5, 14.4; HRMS (EI): M^+, found 208.1463. $C_{13}H_{20}O_2$ requires 208.1464.

3.1.15. 5-Allyl-2-ethoxy-3-methyl-cyclopent-2-enone 4f. (0.95 g, 75%) as a colourless oil; ν_{max} (neat) 3060, 2970, 1680, 1645, 1115 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.63–5.77 (1H, m, C*H*=CH_2), 5.01 (1H, d, J=18.6 Hz, CH_aH_b=CH), 4.99 (1H, d, J=10.4 Hz, CH_aH_b=CH), 4.04–4.18 (2H, m, MeCH_2O), 2.49 (1H, dd, J=6.4, 16.8 Hz, C*H*CO), 2.48 (1H, dd, J=6.4, 17.9 Hz, CH_aH_bCH=CH_2), 2.32–2.35 (1H, m, CH_aH_bCH=CH_2), 2.02–2.10 (2H, m, CH_2CHCO), 1.90 (3H, s, *Me*C=), 1.19 (3H, t, J=7.0 Hz, *Me*CH_2); δ_C (100.6 MHz, $CDCl_3$) 205.2, 154.5, 151.6, 135.5, 117.2, 66.4, 43.0, 20.7, 33.9, 16.0, 15.2; HRMS (EI): M^+, found 180.1153. $C_{11}H_{16}O_2$ requires 180.1150.

3.1.16. 5-Allyl-2-ethoxy-3-ethyl-cyclopent-2-enone 4g. (0.9 g, 72%) as a colourless oil; ν_{max} (neat) 3055, 2842, 1674, 1145, 1209 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.58–5.78 (1H, m, C*H*=CH_2), 5.02 (1H, d, J=17.1 Hz, CH_aH_b=CH), 4.97 (1H, d, J=10.7 Hz, CH_aH_b=CH), 4.03–4.18 (2H, m, MeCH_2O), 2.50 (1H, dd, J=6.4, 18.1 Hz, C*H*CO), 2.44–2.49 (1H, m, CH_aH_bCH=CH_2), 2.34 (2H, q, J=7.6 Hz, MeCH_2C=), 1.96–2.10 (3H, m, CH_aH_bCH=CH_2 and CH_2CHCO), 1.18 (3H, t, J=7.0 Hz, *Me*CH_2O), 1.04 (3H, t, J=7.6 Hz, *Me*CH_2C=); δ_C (100.6 MHz, $CDCl_3$) 205.6, 160.0, 135.5, 117.2, 114.7, 66.5, 42.9, 36.0, 31.1, 22.3, 16.0, 11.9; HRMS (EI): M^+, found 194.1311. $C_{12}H_{18}O_2$ requires 194.1307.

3.1.17. 6-Allyl-2-ethoxy-cyclohex-2-enone 4h. (0.82 g, 65%) as a colourless oil; ν_{max} (neat) 3015, 2920, 2850, 1690, 1090 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.75 (1H, t, J=4.1 Hz, C*H*=COEt), 5.66–5.76 (1H, m, C*H*=CH_2), 5.00 (1H, d, J=14.9 Hz, CH_aH_b=CH), 4.97 (1H, d, J=8.3 Hz, CH_aH_b=CH), 3.68 (2H, q, J=7.0 Hz, MeCH_2O), 2.54–2.60 (1H, m, C*H*CO), 2.33–2.39 (3H, m, CH_2CH= and CH_aH_bCH=COEt), 2.10–2.14 (1H, m, CH_aH_bCH=COEt), 1.94–2.01 (1H, m, CH_aH_bCHCO), 1.61–1.69 (1H, m, CH_aH_bCHCO), 1.17 (3H, t, J=7.0 Hz, *Me*CH_2O); δ_C (100.6 MHz, $CDCl_3$) 196.2, 150.8, 136.4, 117.2, 116.7, 47.3, 35.4, 34.2, 27.8, 23.4, 14.8; HRMS (EI): M^+, found 180.1154. $C_{11}H_{16}O_2$ requires 180.1150.

3.1.18. 6-((*E*)-but-2-enyl)-3-ethoxy-5,5-dimethylcyclohex-2-enone 5a. (0.76 g, 49%) as a colourless oil; ν_{max} (neat) 3020, 2942, 1735, 1632, 1592, 1453, 1112 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.30–5.60 (2H, m, MeC*H*=C*H*), 5.19 (1H, s, =C*H*CO), 3.81 (2H, q, J=7.1 Hz, MeCH_2O), 2.29 (1H, dd, J=4.6, 17.6 Hz, C*H*CO), 2.14–2.17 (2H, m, =CHCH_2CHCO), 2.11 (1H, d, J=3.5 Hz, C$H_aH_b$$CMe_2$), 1.93–2.03 (1H, m, $CH_aH_b$$CMe_2$), 1.53–1.64 (3H, m, *Me*CH=), 1.29 (3H, t, J=7.0 Hz, *Me*CH_2O), 1.02 (3H, s, *Me*$_2$C), 0.91 (3H, s, *Me*$_2$C); δ_C (100.6 MHz, $CDCl_3$) 202.2, 174.6, 130.4, 126.2, 101.2, 64.4, 57.8, 42.3, 35.5, 30.1, 29.2,

24.9, 18.3, 14.5; HRMS (EI): MH^+, found 223.1703. $C_{14}H_{22}O_2$ requires 223.1698.

3.1.19. 6-((*E*)-but-2-enyl)-3-methyl-cyclohex-2-enone 5b. (0.59 g, 52%) as a colourless oil; ν_{max} (neat) 3022, 2913, 2852, 2255, 1654, 1525 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.78 (1H, s, =C*H*CO), 5.28–5.43 (2H, m, MeC*H*=C*H*), 2.44–2.52 (1H, m, C*H*CO), 2.21–2.22 (2H, m, CH_2CHCO), 2.11–2.16 (1H, m, CH_aH_bCH$_2$), 1.96–2.01 (2H, m, CH_2CHCO), 1.87 (3H, s, *Me*C=), 1.60–1.66 (1H, m, CH$_a$*H*$_b$CH$_2$), 1.59 (3H, d, J=6.0 Hz, *Me*CH=); δ_C (100.6 MHz, $CDCl_3$) 201.5, 161.9, 129.0, 127.6, 126.8, 45.8, 32.8, 30.7, 27.5, 24.6, 18.3; HRMS (EI): M^+, found 164.1205. $C_{11}H_{16}O$ requires 164.1202.

3.2. Byproducts of the reaction

3.2.1. Dimerized product of 2a 1,1′-diallyl-bicyclopentyl-3,3′-diene-2,2′-dione. As a colourless oil; ν_{max} (neat) 2990, 2973, 1707, 1690, 1589, 1437 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.62 (2H, ddd, J=6.7, 7.3, 10.2 Hz, 2×C*H*=CHCO), 6.27 (2H, d, J=10.2 Hz, 2×=C*H*CO), 5.67–5.77 (2H, m, 2×C*H*=CH$_2$), 5.20 (2H, d, J=17.2 Hz, 2×CH_aH$_b$=CH), 5.19 (2H, d, J=10.9 Hz, 2×CH$_a$*H*$_b$=CH), 3.19 (4H, t, J=2.4 Hz, 2×=CHCH_2), 2.82 (2H, dd, J=7.3, 14.2 Hz, 2×CH_aH$_b$CCO), 2.64 (2H, dd, J=6.7, 14.2 Hz, 2×CH$_a$*H*$_b$CCO); δ_C (100.6 MHz, $CDCl_3$) 203.7, 160.5, 132.5, 131.1, 120.5, 58.5, 45.5, 43.5; HRMS (EI): M^+, found 242.1318. $C_{16}H_{18}O_2$ requires 242.1307.

3.2.2. Dimerized product of 2b 1,1′-diallyl-3,3′-dimethyl-bicyclopentyl-3,3′-diene-2,2′-dione. As a colourless oil; ν_{max} (neat) 3066, 2914, 2873, 1707, 1640 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.21 (2H, dd, J=6.8, 7.3 Hz, 2×=C*H*CO), 5.66–5.76 (2H, m, 2×C*H*=CH$_2$), 5.19 (2H, d, J=16.6 Hz, 2×CH_aH$_b$=CH), 5.17 (2H, d, J=10.9 Hz, 2×CH$_a$*H*$_b$=CH), 3.05 (4H, t, J=2.2 Hz, 2×=CHCH_2), 2.82 (2H, dd, J=7.3, 14.2 Hz, 2×CH_aH$_b$CCO), 2.62 (2H, dd, J=6.8, 14.2 Hz, 2×CH$_a$*H*$_b$CCO), 1.86 (6H, s, 2×*Me*C=); δ_C (100.6 MHz, $CDCl_3$) 203.8, 153.8, 139.1, 132.7, 120.3, 59.3, 43.8, 43.6, 11.1; HRMS (EI): M^+, found 270.1611. $C_{18}H_{22}O_2$ requires 270.1620.

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References and notes

1. Trost, B. M. *Science* **1985**, *227*, 908.
2. (a) Li, C. J. *Tetrahedron* **1996**, *52*, 5643. (b) Chan, T. H.; Isaac, M. B. *Pure Appl. Chem.* **1996**, *68*, 919. (c) Lubineau, A.; Auge, J.; Queneau, Y. *Synthesis* **1994**, 741. (d) Li, C. J. *Chem. Rev.* **1993**, *93*, 2023. (e) Yamamato, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.
3. (a) Yanagisawa, A.; Habaue, S.; Yasue, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 6130. (b) Curran, D. P.; Hadida, S.; He, M. *J. Org. Chem.* **1997**, *62*, 6714. (c) Li, C. J.; Meng, Y.; Yi, X. H. *J. Org. Chem.* **1997**, *62*, 8632. (d) Paquette, L. A.; Bernardelli, P. *J. Org. Chem.* **1997**, *62*, 8284. (e) Zhou, J. Y.; Jia, Y.; Sun, G. F.; Wu, S. H. *Synth. Commun.* **1997**, *27*, 1899. (f) Paquette, L. A.; Lobben, P. C. *J. Org. Chem.* **1998**, *63*, 6990. (g) Li, C. J.; Meng, Y.; Yi, X. H.; Ma, J.; Chan, T. H. *J. Org. Chem.* **1998**, *63*, 7498. (h) Jacques, A.; Nadege, L. G.; Aurelie, T. W. *Tetrahedron Lett.* **1999**, *40*, 9245.
4. (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer: Berlin, 1981. (b) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. (c) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.
5. (a) Trost, B. M.; Schmuff, N. R.; Miller, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979. (b) Inoue, Y.; Toyofuku, M.; Hashimoto, H. *Chem. Lett.* **1984**, 1227. (c) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523. (d) Masuyama, Y.; Yamada, K.; Kurusu, Y. *Tetrahedron Lett.* **1985**, *28*, 443. (e) Cuvigny, T.; Julia, M. *J. Organomet. Chem.* **1986**, *317*, 383. (f) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107. (g) Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1990**, *31*, 357.
6. (a) Demir, A. S.; Jeganathan, A. *Synthesis* **1992**, 235. (b) Melikyan, G. G. *Synthesis* **1993**, 833. (c) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339. (d) Melikyan, G. G. In Paquette, L. A., Ed.; Organic Reactions; Wiley: New York, 1997; Vol. 49.
7. Williams, G. J.; Hunter, N. R. *Can. J. Chem.* **1976**, *54*, 3830.
8. (a) Tanyeli, C.; Demir, A. S.; Dikici, E. *Tetrahedron: Asymmetry* **1996**, *7*, 2399. (b) Demir, A. S.; Hamamci, H.; Tanyeli, C.; Akhmedov, I. M.; Doganel, F. *Tetrahedron: Asymmetry* **1998**, *9*, 1673. (c) Demir, A. S.; Tanyeli, C.; Altinel, E. *Tetrahedron Lett.* **1997**, *38*, 7267. (d) Tanyeli, C.; Sezen, B. *Tetrahedron Lett.* **2000**, *41*, 7973. (e) Tanyeli, C.; Sezen, B.; Iyigün, Ç.; Elmalı, O. *Tetrahedron Lett.* **2001**, *42*, 6397. (f) Tanyeli, C.; Özdemirhan, D. *Tetrahedron Lett.* **2002**, *43*, 3977. (g) Tanyeli, C.; Tosun, A.; Turkut, E.; Sezen, B. *Tetrahedron* **2003**, *59*, 1055.
9. For spectroscopic data of 5-acetoxy-3-methyl-2-cyclopentenone, see reference 8g.
10. The dimerized allylated products of **2a**, **2b** and **2c** were isolated in 7, 5 and 7% yields, respectively. For the dimerized product of **2c**, see Ref. 8f. The structure elucidation of dimerized products **2a** and **2b** is given in Section 3.
11. We repeated the experiments for entries 1–3 with toluene under the same conditions and obtained **2a**, **2b** and **2c** with 5, 7 and 5% decrease of the yield, respectively.
12. Chaiez, G.; Chau, F.; Blanchot, B. In Martin, S. F., Ed.; Organic Syntheses; Wiley: New York, 1999; Vol. 76, p 239.
13. Snider, B. B.; Kiselgof, E. Y. *Tetrahedron* **1996**, *52*, 6073.
14. Vinogradov, M. G.; Verenchikov, S. P.; Federova, T. M.; Nikishin, G. I. *Zh. Org. Khim.* **1975**, *11*, 947.