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Preparation of organomanganese reagents from organic halides with activated manganese

Hirotada Kakiya, Shinji Nishimae, Hiroshi Shinokubo and Koichiro Oshima*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

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Abstract—Reduction of Li_2MnCl_4 with magnesium metal provided activated manganese as a black suspension in THF. Treatment of organic halides such as allyl bromides, α-halo esters or aryl halides with activated manganese furnished various organomanganese reagents which reacted further with electrophiles to afford the corresponding adducts. The reaction of a ketone bearing an iodoaryl moiety with this active manganese induced cyclization to provide dihydroindene derivative.

1. Introduction

In 1936, H. Gillman and J. Bailie prepared diphenylmanganese and phenylmanganese iodide, which were the first organomanganese compounds synthesized. However, organomanganese chemistry had been mainly unexplored until J. F. Normant and G. Cahiez started studies on the preparation of organomanganese reagents and synthetic applications of these compounds.[1] Recently the studies of synthetic reactions using organomanganese reagents have been undertaken by several groups and ours.[2] Organomanganese compounds have proved to be useful reagents with high chemoselectivity for selective C–C bond formation. The organomanganese reagents are typically prepared via transmetalation of manganese salts with organolithiums or Grignard reagents. However, it is difficult to prepare the functionalized organomanganese reagents through the transmetalation protocol due to the difficulty in preparation of functionalized organolithiums or Grignard reagents. On the other hand, the direct preparation of the organomanganese reagents from organic halides with activated or non-activated manganese have been reported recently.[3,4] Among various methods, we have reported that the reduction of an ate-complex Li_2MnCl_4 with magnesium metal in THF afforded a black suspension of activated manganese[5] which initiated radical cyclization of allyl β-iodoacetals at room temperature.[6] In this paper, we wish to describe the reactivity of organomanganese reagents which were generated from activated manganese and organic halides such as allylic halides, α-halo esters, or aryl halides. The cyclization of a ketone bearing an iodoaryl moiety is also reported.

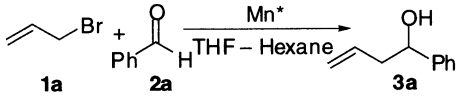
Keywords: manganese and compounds; alkyl halides; Reformatsky reactions/reagents; cyclization.

* Corresponding author. Tel.: +81-75753-5523; fax: +81-75753-4863; e-mail: oshima@fm1.kuic.kyoto-u.ac.jp

2. Results and discussion

2.1. Activated manganese-induced reaction of allylic bromides with carbonyl compounds

A pale yellow–green THF solution of Li_2MnCl_4, derived from 1.0 equiv. of $MnCl_2$ and 2.0 equiv. of LiCl, was added to the magnesium turnings activated by 1,2-dibromoethane. The resulting mixture was stirred for 24 h at room temperature to provide a black suspension of activated manganese. The suspension of activated manganese was introduced to a THF–hexane solution of allyl bromide (**1a**) and benzaldehyde (**2a**) at −42°C under argon atmosphere. Then, the mixture was warmed up to 25°C to provide 1-phenyl-3-buten-1-ol (**3a**) in 82% yield (Scheme 1).[7]



Scheme 1.

The results of the reaction of various allylic bromides with carbonyl compounds are shown in Table 1. Several comments are worth noting. (1) The reaction of aliphatic aldehydes such as decanal (**2b**) and cyclohexanecarbaldehyde (**2c**) afforded the corresponding allylated products as well as aromatic aldehyde (entries 2 and 3). (2) The use of ketones (acetophenone (**2d**) and cyclohexanone (**2e**)) in place of aldehydes also provided the corresponding homoallylic alcohols (entries 4 and 5). (3) The reaction of crotyl bromide (**1b**) afforded a regioisomeric mixture of α-adduct **3f** and γ-adduct **4f** in 32% and 14% yield, respectively. (4) In the case of cinnamyl bromide (**1c**), 3,4-diphenyl-1,5-hexadiene, 1,6-diphenyl-1,5-hexadiene, and 1,4-diphenyl-

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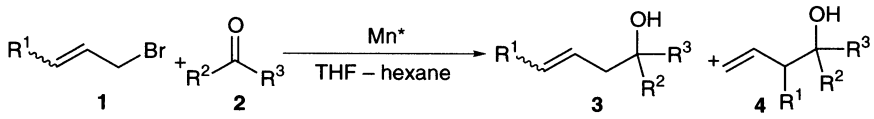
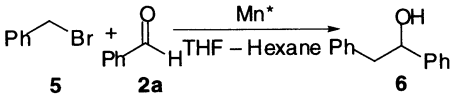
Table 1. Allylation of carbonyl compounds via the activated manganese



1 2 3 4

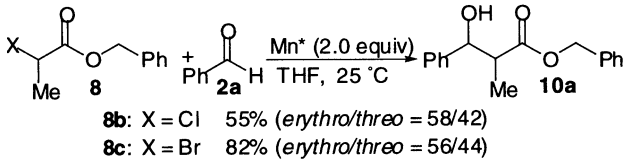
Entry	1	2		Yield (%)[a]	
	R^1	R^2	R^3	3	4
1	H (**1a**)	Ph	H (**2a**)	82 (**3a**)	
2	H (**1a**)	n-C_9H_{19}	H (**2b**)	47 (**3b**)	
3[b]	H (**1a**)	c-C_6H_{11}	H (**2c**)	52 (**3c**)	
4	H (**1a**)	Ph	Me (**2d**)	37 (**3d**)	
5	H (**1a**)	$-(CH_2)_5-$	(**2e**)	47 (**3e**)	
6[c]	Me (**1b**)	Ph	H (**2a**)	32 (**3f**)[d]	14 (**4f**)[e]
7[f]	Ph (**1c**)	Ph	H (**2a**)	30 (**3g**)[g]	9 (**4g**)[h]

The reactions were performed with **1** (1.0 mmol), **2** (2.0 mmol) and Mn* (3.0 mmol).
[a] Yields are based on **1**.
[b] c-C_6H_{11}=cyclohexyl.
[c] A mixture (88/12) of 1-bromo-2-butene (*E*/*Z*=84/16) and 3-bromo-1-butene was used.
[d] *E*/*Z*=75/25.
[e] *erythro*/*thero*=44/56.
[f] The coupling products of cinnamyl bromide, 3,4-diphenyl-1,5-hexadiene (7%), 1,6-diphenyl-1,5-hexadiene (21%), and 1,4-diphenyl-1,5-hexadiene (23%) were also obtained.
[g] *E* only.
[h] *erythro*/*threo*=50/50.



5 2a 6

Scheme 2.



8 2a 10a

Scheme 4.

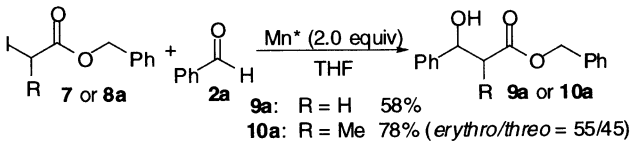
1,5-hexadiene were formed as by-products in addition to the desired allylated products **3g** and **4g**.

The reaction of benzyl bromide with benzaldehyde provided the corresponding benzylated product **6** in 41% yield (Scheme 2).

2.2. Activated manganese-mediated reaction of α-halo carbonyl compounds with aldehydes

We next picked up α-halo esters as reactive organic halides. Treatment of a mixture of benzyl 2-iodoacetate (**7**) and benzaldehyde (**2a**) with suspension of activated manganese at 25°C afforded a Reformatsky-type adduct, β-hydroxy ester **9a**, in 58% yield.[8] The reaction of benzyl 2-iodopropanoate (**8a**) in place of benzyl 2-iodoacetate (**7**) provided the corresponding adduct **10a** in 78% yield (Scheme 3).

The reaction of α-chloro ester **8b** or α-bromo ester **8c** instead of α-iodo ester was examined. In the case of **8b**, the starting material **8b** was recovered in 34% yield along



7 or 8a 2a 9a or 10a

Scheme 3.

with **10a** (55%). The treatment of α-bromo ester **8c** provided **10a** in good yield (Scheme 4).

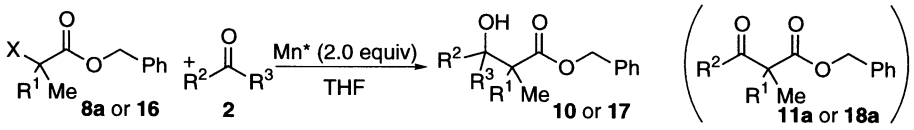
The results of the reaction of α-halo esters with various carbonyl compounds are summarized in Table 2. Several issues regarding the results in Table 2 merit comments. (1) The reactivity of benzyl 2-bromo-2-methylpropanoate (**16**) was similar to that of benzyl 2-iodopropanoate (**8a**). (2) The use of aliphatic aldehydes provided the corresponding adducts in good yields (entries 1–3, 8, 9). (3) Ketones were as reactive as aldehydes and afforded the Reformatsky-type products effectively (entries 4, 5, and 10). (4) α,β-Unsaturated carbonyl compounds reacted in a 1,2-manner exclusively. No 1,4-addition products were detected in the reaction mixture (entries 3, 5, and 9). (5) The reactions of acyl chloride proceeded effectively to afford the β-keto ester (entries 6 and 11).

To reveal the reaction mechanism, we carried out the reaction of **7** with activated manganese in the presence of methanol-*d* (Scheme 5).

The deuterium incorporation in **12-d** clearly suggested the generation of enolate **14** as an intermediate.[9,10] On the basis of this fact, we propose the following reaction mechanism (Scheme 6).

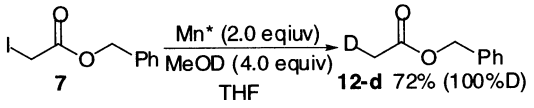
The reaction of α-halo lactones or α-halo amides instead of

Table 2. The reaction of α-iodo or α-bromo ester



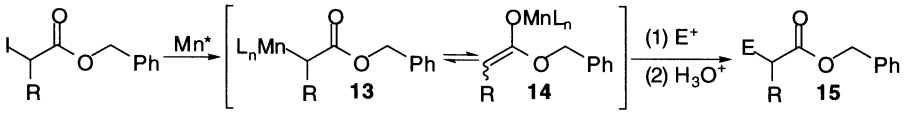
Entry	Ester		2		Time (h)	Yield (%)[a]	*erythro/threo*
	X	R^1	R^2	R^3			
1	I	H (**8a**)	*n*-C_6H_{13}	H (**2f**)	18.5	79 (**10b**)	52/48
2	I	H (**8a**)	*i*-Pr	H (**2g**)	15.5	78 (**10c**)	51/49
3[b]	I	H (**8a**)		H (**2h**)	17.5	94 (**10d**)	41/59
4	I	H (**8a**)	Me	Me (**2i**)	17.5	93 (**10e**)	
5[b]	I	H (**8a**)	2-cyclohexenone	(**2j**)	15	59 (**10f**)	55/45
6[c]	I	H (**8a**)	Ph	Cl (**2k**)	17	67 (**11a**)	
7	Br	Me (**16**)	Ph	H (**2a**)	18	84 (**17a**)	
8	Br	Me (**16**)	*i*-Pr	H (**2g**)	19.5	80 (**17b**)	
9[b]	Br	Me (**16**)		H (**2h**)	20.5	84 (**17c**)	
10	Br	Me (**16**)	Me	Me (**2i**)	17	91 (**17d**)	
11[d]	Br	Me (**16**)	Me	Cl (**2l**)	16.5	84 (**18a**)	

Reactions were performed with benzyl ester (0.5 mmol), **2** (0.6 mmol) and Mn* (1.0 mmol) in THF at 25°C.
[a] Yields are based on benzyl ester.
[b] Only 1,2-adduct was obtained and 1,4-adduct was not detected.
[c] The product was benzyl 2-methyl-3-oxo-3-phenylpropanoate (**11a**).
[d] The product was benzyl 2,2-dimethyl-3-oxobutanoate (**18a**).



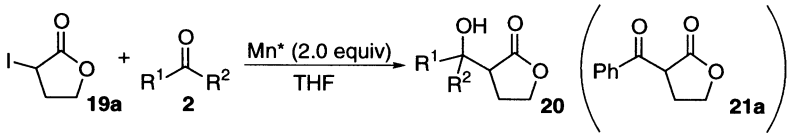
Scheme 5.

α-halo esters with various electrophiles proceeded efficiently to provide the corresponding adducts. Tables 3 and 4 show the results of the reaction of α-iodo lactones and α-iodo amides, respectively. In both reactions of α-iodo lactones and α-iodo amides, aldehydes or ketones were effective as electrophiles. In contrast, benzoyl chloride was less effective as an electrophile. The use of α-iodo ketone **25** as an α-halo carbonyl compound gave a



Scheme 6.

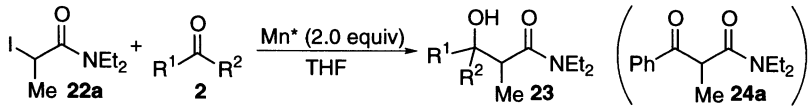
Table 3. The reaction of α-iodo lactone



Entry	2		Time (h)	Yield (%)[a]	*erythro/threo*
	R^1	R^2			
1	Ph	H (**2a**)	1	99 (**20a**)	50/40
2	*n*-C_6H_{13}	H (**2f**)	2.5	84 (**20b**)	60/40
3[b]		H (**2m**)	2.5	82 (**20c**)	55/45
4	Me	Me (**2i**)	2	97 (**20d**)	
5[c]	Ph	Cl (**2k**)	2	56 (**21a**)	

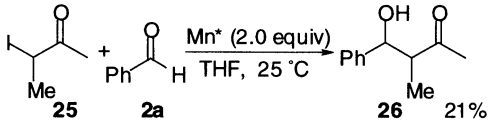
Reactions were performed with **19a** (0.5 mmol), **2** (0.6 mmol) and Mn* (1.0 mmol) in THF at 25°C.
[a] Yields are based on **19a**.
[b] Only 1,2-adduct was obtained and 1,4-adduct was not detected.
[c] The product was β-keto ester **21a**.

Table 4. The reaction of α-iodo amide



Entry	2		Time (h)	Yield (%)[a]	*erythro/threo*
	R^1	R^2			
1	Ph	H (**2a**)	23.5	99 (**23a**)	58/42
2	n-C_6H_{13}	H (**2f**)	21	88 (**23b**)	61/39
3	Me	Me (**2i**)	22	81 (**23c**)	
4[b]	Ph	Cl (**2k**)	24.5	trace (**24a**)	

Reactions were performed with **22a** (0.5 mmol), **2** (0.6 mmol) and Mn* (1.0 mmol) in THF at 25°C.
[a] Yields are based on **22a**.
[b] The product was β-keto amide **24a**.



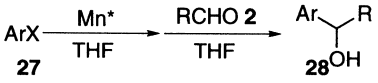
Scheme 7.

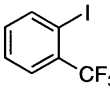
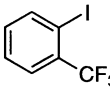
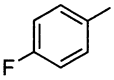
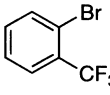
disappointing result. Treatment of 3-iodo-2-butanone (**25**) with activated manganese in the presence of benzaldehyde (**2a**) provided the corresponding β-hydroxy ketone **26** in only 21% yield (Scheme 7).

2.3. Activated manganese-mediated reaction of aryl halides with carbonyl compounds

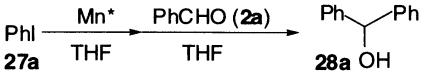
We next investigated the reaction of aryl halides. Treatment of a mixture of iodobenzene (**27a**) and benzaldehyde (**2a**) with activated manganese in THF provided a pinacol coupling adduct (hydrobenzoin) and none of the expected product was observed in the reaction mixture. This result indicates that the reduction of benzaldehyde proceeds much faster than that of iodobenzene. Then we treated iodobenzene (**27a**) with activated manganese in THF in the absence of benzaldehyde and found the formation of phenylmanganese iodide. Sequential addition of benzaldehyde (**2a**) provided diphenylmethanol (**28a**) in 21% yield (Scheme 8). The results of the reaction of various aryl halides are shown in Table 5.

Table 5. The reaction of aldehydes with arylmanganese derived from aryl halides and activated manganese



Entry	ArX	RCHO	Yield (%)[a]
1	 (**27b**)	PhCHO (**2a**)	72
2	 (**27b**)	n-C_6H_{13}CHO (**2f**)	80
3	 (**27c**)	PhCHO (**2a**)	59
4	 (**27d**)	PhCHO (**2a**)	31

Reactions were performed with aryl halide (1.0 mmol), aldehyde (2.0 mmol) and Mn* (4.0 mmol) in THF.
[a] Yield based on aldehyde.



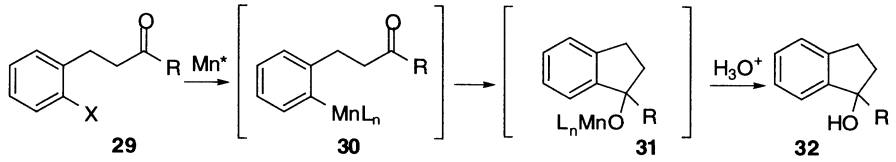
Scheme 8.

Several characteristics of this reaction are noteworthy. (1) Compared with iodobenzene (**27a**), the use of the substrate with electron-withdrawing group such as a trifluoromethyl moiety improved the yield of the desired product dramatically. (2) Aliphatic aldehyde **2f** is a good electrophile for the trapping of manganese species as well as aromatic aldehydes (entry 2). (3) Aryl bromide **27d** was less reactive than the corresponding aryl iodide **27b**, and the reaction with benzaldehyde afforded the benzylic alcohol **28** in only 31% yield.

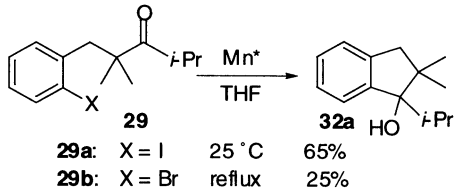
2.4. Reaction of ketones bearing an iodoaryl moiety with activated manganese

We found that activated manganese prepared by our procedure was less reactive toward ketones. It is hence expected that an addition of activated manganese to a iodobenzene, which has alkyl substituent bearing a ketone moiety on *ortho* position, would provide an arylmanganese species **30** without the reduction of the ketone moiety. This was indeed the case and treatment of 1-(2-iodophenyl)-2,2,4-trimethyl-3-pentanone (**29a**) with activated manganese afforded the cyclization product **32a** in 65% yield. The reaction would proceed as follows: (1) formation of arylmanganese species **30**, and (2) subsequent cyclization via an intramolecular addition to the carbonyl group (Scheme 9).[11]

The use of aryl bromide **29b** in place of **29a**, however, provided the desired product **32a** in only 25% yield even in refluxing THF, and a considerable amount of the starting material was recovered (Scheme 10).

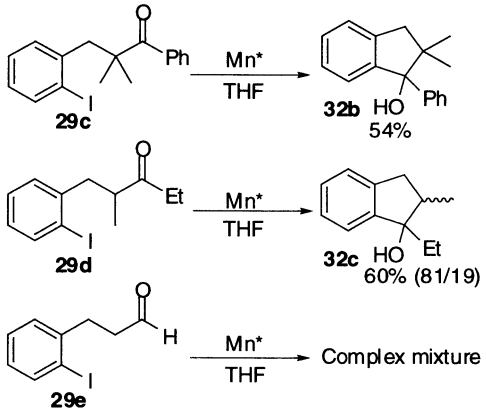


Scheme 9.



Scheme 10.

Other aryl iodides such as **29c** and **29d** also provided the corresponding products in moderate yields upon treatment with activated manganese. In contrast, aryl iodide **29e** having a formyl group gave a complex mixture along with none of desired cyclization product (Scheme 11).



Scheme 11.

3. Conclusions

We found that activated manganese, prepared by the reduction of Li_2MnCl_4 with magnesium metal, was effective for the direct preparation of various organic manganese reagents from organic halides. Various allylic halides could be converted into the corresponding allylic manganese upon treatment with activated manganese. Treatment of α-halo carbonyl compounds such as α-halo esters, α-halo lactones, α-halo amides, or α-halo ketones provided manganese enolates, which reacted with electrophiles to afford the corresponding products in good yield. One can also prepare arylmanganese compounds by the reduction of aryl iodides with activated manganese. Furthermore, activated manganese induced cyclization of aryl halides bearing a ketone moiety to provide the 2,3-dihydroinden-1-ol derivatives.

4. Experimental

4.1. General

NMR spectra (^1H and ^{13}C) were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Anhydrous manganese(II) chloride purchased from Aldrich was heated at 160°C for 2 h prior to use.

4.2. Starting materials

According to literature procedures, 1-(2-bromophenyl)-2,2,4-trimethyl-3-pentanone (**29b**)[11a] and 3-(2-iodophenyl)-propanal (**29e**)[12] were prepared. In a similar fashion,[11a] 1-(2-iodophenyl)-2,2,4-trimethyl-3-pentanone (**29a**), 3-(2-iodophenyl)-2,2-dimethyl-1-phenyl-1-propanone (**29c**), and 1-(2-iodophenyl)-2-methyl-3-pentanone (**29d**) were prepared.

4.3. Preparation of benzyl 2-iodopropanoate

To a solution of benzyl alcohol (1.08 g, 10 mmol) and pyridine (0.87 g, 11 mmol) in dichloromethane (15 mL) was added 2-chloropropanoyl chloride (1.40 g, 11 mmol) dropwise at 0°C, and the mixture was warmed to room temperature over a period of 4 h. The reaction was quenched with water and the reaction mixture was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to provide the benzyl 2-chloropropanoate. Sodium iodide (3.00 g, 20 mmol) was added to the crude product (1.97 g, 9.9 mmol) in acetone (10 mL) and the mixture was stirred for 12 h at 25°C. Usual workup followed by silica gel column chromatography afforded benzyl 2-iodopropanoate (2.81 g, 9.7 mmol) in 97% yield.

4.3.1. 1-(2-Iodophenyl)-2,2,4-trimethyl-3-pentanone (29a). Mp 51°C; IR (nujol) 2963, 1692, 1366, 1015, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (d, J=6.6 Hz, 6H), 1.20 (s, 6H), 3.11 (s, 2H), 3.20 (sept, J=6.6 Hz, 1H), 6.89 (dt, J=1.8, 7.8 Hz, 1H), 7.16 (dd, J=1.8, 7.8 Hz, 1H), 7.25 (dt, J=1.2, 7.8 Hz, 1H), 7.85 (dd, J=1.2, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.99, 23.71, 34.30, 46.43, 49.92, 103.41, 128.00, 128.18,

130.97, 140.03, 141.53, 219.81. Found: C, 50.64; H, 5.63%. Calcd for $C_{14}H_{19}IO$: C, 50.92; H, 5.80%.

4.3.2. 3-(2-Iodophenyl)-2,2-dimethyl-1-phenyl-1-propanone (29c). IR (neat) 3059, 2970, 2931, 1674, 1597, 1579, 1463, 1444, 1388, 1261, 1011, 959, 752, 729, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (s, 6H), 3.36 (s, 2H), 6.89 (dt, J=1.8, 7.5 Hz, 1H), 7.14 (dd, J=1.8, 7.5 Hz, 1H), 7.22 (dt, J=1.5, 7.5 Hz, 1H), 7.36–7.50 (m, 3H), 7.60–7.66 (m, 2H), 7.86 (dd, J=1.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.97, 48.41, 49.68, 103.31, 127.74, 128.10, 128.21, 128.28, 130.76, 130.89, 139.22, 140.09, 141.51, 209.56. HRMS Found: m/z 364.0342. Calcd for $C_{17}H_{17}IO$: M, 364.0324.

4.3.3. 1-(2-Iodophenyl)-2-methyl-3-pentanone (29d). IR (neat) 2972, 2936, 2876, 1713, 1562, 1462, 1375, 1010, 976, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (t, J=7.2 Hz, 3H), 1.10 (d, J=6.9 Hz, 3H), 2.30 (dq, J=18.0, 7.2 Hz, 1H), 2.47 (dq, J=18.0, 7.2 Hz, 1H), 2.74 (dd, J=6.9, 12.9 Hz, 1H), 3.00 (ddq, J=6.9, 6.9, 6.9 Hz, 1H), 3.09 (dd, J=6.9, 12.9 Hz, 1H), 6.90 (dt, J=2.1, 7.2 Hz, 1H), 7.14 (dd, J=2.1, 7.2 Hz, 1H), 7.24 (dt, J=1.2, 7.2 Hz, 1H), 7.82 (dd, J=1.2, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 7.52, 16.31, 35.29, 43.45, 45.52, 100.60, 128.17, 128.21, 130.80, 139.66, 142.38, 214.41. Found: C, 47.50; H, 4.89%. Calcd for $C_{12}H_{15}IO$: C, 47.70; H, 5.00%.

4.4. Preparation of the suspension of activated manganese

Magnesium turnings (1.22 g, 50 mmol) were activated by treatment with a solution of 1,2-dibromoethane (0.94 g, 5 mmol) in THF (10 mL) followed by washing with THF (4 mL×3). Then, a pale yellow–green solution of Li_2MnCl_4 (15 mmol), derived from $MnCl_2$ (1.89 g, 15 mmol) and LiCl (1.27 g, 30 mmol) in THF (40 mL), was added to magnesium turnings with vigorous stirring. The mixture was stirred for 24 h at room temperature.[13] The initial pale yellow–green color turned dark. This resulting black suspension of activated manganese in THF[14] was stable for at least one week at room temperature and was transferred in a reaction flask with a syringe.

4.5. General procedure for the preparation of allylic manganese

The reaction of benzaldehyde (**2a**) with allylmanganese bromide, generated from allyl bromide and activated manganese, is representative. The suspension of activated manganese (3.0 mmol) in THF was added to a solution of allyl bromide (121 mg, 1.0 mmol) and benzaldehyde (212 mg, 2.0 mmol) in THF/hexane (7/5 mL) at −42°C with a syringe. The mixture was stirred at −42°C for 1 h. The whole mixture was warmed up to room temperature over a period of 1.5 h. The resulting mixture was poured into sat. NH_4Cl and extracted with ethyl acetate (20 mL×3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate=3/1) to provide 1-phenyl-3-buten-1-ol (**3a**) in 82 % yield.

Spectroscopic data for 1-phenyl-3-buten-1-ol (**3a**),[15] 1-cyclohexyl-3-buten-1-ol (**3c**),[15] 2-phenyl-4-penten-2-ol (**3d**),[16] 1-allylcyclohexanol (**3e**),[15] 1-phenyl-3-penten-1-ol (**3f**),[17] 2-methyl-1-phenyl-3-buten-1-ol (**4f**),[18] 1,4-diphenyl-3-buten-1-ol (**3g**),[17] 1,2-diphenyl-3-buten-1-ol (**4g**),[19,20] 1,2-diphenylethanol (**6**),[21] 3,4-diphenyl-1,5-hexadiene,[22] 1,6-diphenyl-1,5-hexadiene,[23] and 1,4-diphenyl-1,5-hexadiene[24] were identical with those reported in literatures.

4.5.1. 1-Tridecen-4-ol (3b). IR (neat) 3348, 2925, 2856, 1712, 1466, 1441, 995, 912 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=6.6 Hz, 3H), 1.20–1.53 (m, 17H), 2.07–2.21 (m, 1H), 2.26–2.38 (m, 1H), 3.60–3.70 (m, 1H), 5.09–5.20 (m, 2H), 5.78–5.91 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 19.38, 22.57, 25.56, 29.22, 29.47, 29.52, 29.56, 31.81, 36.74, 41.85, 70.70, 118.10, 135.01. HRMS Found: m/z 198.1992. Calcd for $C_{13}H_{26}O$: M, 198.1984.

4.6. General procedure for the preparation of manganese enolate

The reaction of benzaldehyde with manganese enolate, derived from benzyl 2-iodopropanoate and activated manganese, is representative. The suspension of activated manganese (1 mmol) in THF was added to a solution of benzyl 2-iodopropanoate (145 mg, 0.5 mmol) and benzaldehyde (64 mg, 0.6 mmol) in THF (10 mL) at 25°C under argon. The resulting mixture was stirred for 15 h at 25°C. The mixture was poured into sat. NH_4Cl and extracted with ethyl acetate (20 mL×3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by silica gel column chromatography afforded benzyl 3-hydroxy-2-methyl-3-phenylpropanoate (**10a**) in 78% yield.

Spectroscopic data for benzyl 3-hydroxy-2-methyl-3-phenylpropanoate (**10a**),[25] benzyl 3-hydroxy-2,4-dimethylpentanoate (**10c**),[26] 3-[hydroxy(phenyl)methyl]-terahydrofuran-2-one (**20a**),[27] *N*,*N*-diethyl-3-hydroxy-2-methyl-3-phenylpropanamide (**23a**),[28] and 4-hydroxy-3-methyl-4-phenyl-2-butanone (**26**)[29,30] were identical with those reported in literatures.

4.6.1. Benzyl 3-hydroxy-2-methylnonanoate (10b, *erythro*/*threo*=52/48). IR (neat) 3445, 2930, 2858, 1715, 1456, 1381, 1170, 1030, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=6.0 Hz, 3H), 1.16–1.53 (m, 13H), 1.54–1.74 (m, 1H), 2.53–2.64 (m, 1H), 3.64–3.72 (m, 0.48H), 3.86–3.94 (m, 0.52H), 5.15 (s, 2H), 7.30–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 10.60, 14.01, 14.21, 22.54, 25.42, 25.87, 29.16, 31.71, 33.81, 34.68, 44.31, 45.26, 66.28, 66.35, 71.77, 73.37, 128.12, 128.15, 128.28, 128.31, 128.60, 135.78, 175.83, 175.98. HRMS Found: m/z 260.1761. Calcd for $C_{17}H_{24}O_2$: (M−H_2O), 260.1776.

4.6.2. Benzyl 3-hydroxy-2,4-dimethyl-4-heptenoate (10d, *erythro*/*threo*=41/59). IR (neat) 3447, 2964, 2937, 1732, 1456, 1256, 1169, 1024 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, J=7.8 Hz, 1.77H), 0.96 (t, J=7.8 Hz, 1.23H), 1.05 (d, J=7.2 Hz, 1.23H), 1.18 (d, J=7.2 Hz, 1.77H), 1.58 (s, 1.77H), 1.59 (s, 1.23H), 1.93–2.10 (m, 2H), 2.11–2.50 (bs, 1H), 2.65–2.80 (m, 1H), 4.11 (d, J=9.0 Hz, 0.41H), 4.27 (d, J=5.4 Hz, 0.59H), 5.11 (s, 1.18H), 5.15 (d, J=12.6 Hz, 0.41H), 5.18 (d, J=12.6 Hz, 0.41H),

5.39–5.50 (m, 1H), 7.29–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 10.56, 11.40, 12.28, 13.85, 13.93, 14.36, 20.73, 20.79, 40.10, 43.35, 66.30, 66.35, 79.90, 128.06, 128.12, 128.20, 128.23, 128.56, 129.04, 131.57, 133.26, 135.83, 135.88. HRMS Found: *m/z* 244.1470. Calcd for $C_{16}H_{20}O_2$: ($M-H_2O$), 244.1463.

4.6.3. Benzyl 3-hydroxy-2,3-dimethylbutanoate (10e). IR (neat) 3445, 2978, 1732, 1383, 1342, 1196, 1134, 784, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 3H), 1.23 (d, J=7.2 Hz, 3H), 1.24 (s, 3H), 2.55 (q, J=7.2 Hz, 1H), 2.62–3.04 (bs, 1H), 5.16 (s, 2H), 7.31–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 12.56, 25.87, 28.74, 49.16, 66.37, 71.05, 128.22, 128.37, 128.62, 135.61, 176.29. Found: C, 69.97; H, 8.31%. Calcd for $C_{13}H_{18}O_3$: C, 70.25; H, 8.16%.

4.6.4. Benzyl 2-(1-hydroxy-2-cyclohexen-1-yl)propanoate (10f, *erythro/threo*=55/45). IR (neat) 3501, 2939, 1728, 1456, 1337, 1161, 964, 739, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (d, J=7.2 Hz, 1.35H), 1.24 (d, J=7.5 Hz, 1.65H), 1.53–1.82 (m, 4H), 1.84–2.12 (m, 2H), 2.64 (q, J=7.2 Hz, 0.45H), 2.68 (q, J=7.2 Hz, 0.55H), 2.90–3.40 (bs, 1H), 5.15 (s, 1.1H), 5.17 (s, 0.9H), 5.53 (d, J=10.5 Hz, 0.45H), 5.78 (d, J=10.2 Hz, 0.55H), 5.82–5.91 (m, 1H), 7.28–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 12.12, 18.39, 18.64, 24.98, 31.70, 34.49, 48.32, 66.28, 66.42, 70.18, 70.31, 128.19, 128.28, 128.33, 128.57, 128.60, 129.00, 130.98, 131.03, 131.52, 135.65, 135.76, 175.84, 175.96. HRMS Found: *m/z* 242.1307. Calcd for $C_{16}H_{20}O_3$: ($M-H_2O$), 242.1315.

4.6.5. Benzyl 3-hydroxy-2,2-dimethyl-3-phenylpropanoate (17a). IR (neat) 3497, 2978, 1720, 1470, 1454, 1250, 1130, 1049, 745, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 3H), 1.18 (s, 3H), 2.64–3.36 (bs, 1H), 4.93 (s, 1H), 5.17 (s, 2H), 7.24–7.40 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 18.98, 22.93, 47.77, 66.51, 78.60, 127.64, 127.72, 127.75, 127.90, 128.17, 128.55, 135.87, 139.90, 177.45.

4.6.6. Benzyl 3-hydroxy-2,2,4-trimethylpentanoate (17b). IR (neat) 3420, 2970, 1715, 1456, 1387, 1261, 1138, 1028, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.79 (d, J=6.9 Hz, 3H), 0.94 (d, J=6.9 Hz, 3H), 1.21 (s, 3H), 1.29 (s, 3H), 1.77–1.90 (m, 1H), 2.66–2.99 (bs, 1H), 3.42 (d, J=3.9 Hz, 1H), 5.12 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 15.27, 21.64, 22.36, 23.49, 29.90, 46.05, 66.45, 81.46, 128.04, 128.24, 128.55, 135.60, 177.88. HRMS Found: *m/z* 250.1573. Calcd for $C_{15}H_{22}O_3$: M, 250.1569.

4.6.7. Benzyl 3-hydroxy-2,2,4-trimethyl-4-heptenoate (17c). IR (neat) 3483, 2966, 1720, 1458, 1254, 1132, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J=7.5 Hz, 3H), 1.17 (s, 3H), 1.23 (s, 3H), 1.55 (s, 3H), 1.93–2.10 (m, 2H), 2.96 (bs, 1H), 4.10 (s, 1H), 5.12 (d, J=12.3 Hz, 1H), 5.16 (d, J=12.3 Hz, 1H), 5.36 (t, J=6.9 Hz, 1H), 7.31–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 12.76, 13.79, 20.83, 20.89, 23.82, 46.65, 66.48, 82.60, 127.95, 128.20, 128.56, 131.86, 133.18, 135.78, 177.69. HRMS Found: *m/z* 258.1631. Calcd for $C_{17}H_{22}O_3$: ($M-H_2O$), 258.1620.

4.6.8. Benzyl 3-hydroxy-2,2,3-trimethylbutanoate (17d). IR (neat) 3493, 2980, 1713, 1468, 1377, 1269, 1117, 955, 737, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 6H), 1.26 (s, 6H), 3.00–3.80 (bs, 1H), 5.15 (s, 2H), 7.28–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.33, 25.12, 49.81, 66.58, 73.60, 128.01, 128.32, 128.60, 135.61, 178.27. HRMS Found: *m/z* 236.1422. Calcd for $C_{14}H_{20}O_3$: M, 236.1412.

4.6.9. 3-(1-Hydroxyheptyl)tetrahydrofuran-2-one (20b, *erythro/threo*=60/40). IR (neat) 3456, 2930, 2858, 1755, 1460, 1379, 1217, 1173, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.9 Hz, 3H), 1.20–1.60 (m, 10.6H), 1.95–2.12 (m, 0.4H), 2.13–2.26 (m, 0.6H), 2.27–2.46 (m, 1H), 2.52–2.72 (m, 1H), 3.00–3.60 (bs, 0.4H), 3.71–3.82 (m, 0.4H), 4.14–4.28 (m, 1.6H), 4.34–4.45 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.92, 21.61, 22.46, 24.91, 25.71, 28.99, 29.07, 31.64, 34.59, 34.82, 44.41, 45.40, 66.89, 67.12, 69.11, 71.71, 178.93, 179.71. HRMS Found: *m/z* 182.1311. Calcd for $C_{11}H_{18}O_2$: ($M-H_2O$), 182.1307.

4.6.10. 3-(1-Hydroxy-2-butenyl)tetrahydrofuran-2-one (20c, *erythro/threo*=55/45). IR (neat) 3450, 2918, 1760, 1452, 1380, 1178, 1024, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.73 (d, J=6.6 Hz, 3H), 1.96–2.13 (m, 0.45H), 2.16–2.41 (m, 2.10H), 2.64–2.81 (m, 1H), 3.52–3.85 (bs, 0.45H), 4.17–4.30 (m, 1.45H), 4.33–4.43 (m, 1H), 4.61 (dd, J=6.6, 3.0 Hz, 0.55H), 5.44–5.57 (m, 1H), 5.74–5.88 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 17.56, 17.65, 22.28, 25.49, 44.62, 45.36, 67.05, 67.28, 70.58, 73.19, 128.73, 129.69, 129.80, 130.22, 178.55, 178.13.

4.7. General procedure for the preparation of aryl manganese

The reaction of iodobenzene with activated manganese is representative. The suspension of manganese (4.0 mmol) in THF was added to a THF solution of iodobenzene (408 mg, 2.0 mmol) at 0°C. After stirring for 2 h at 0°C, benzaldehyde (106 mg, 1.0 mmol) was added and the whole mixture was stirred for 20 h at 25°C. The reaction was quenched with sat. NH_4Cl and extracted with ethyl acetate (20 mL×3). Purification by silica gel column chromatography afforded diphenylmethanol (**28a**) in 21% yield.

Spectroscopic data for (4-fluorophenyl)phenylmethanol were identical with those reported in the literatures.[31]

4.7.1. Phenyl[2-(trifluoromethyl)phenyl]methanol. IR (neat) 3344, 3066, 3034, 1609, 1585, 1454, 1313, 1161, 1124, 1038, 1020, 768, 737, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 1H), 6.32 (s, 1H), 7.24–7.44 (m, 6H), 7.55 (dd, J=7.2, 7.2 Hz, 1H), 7.64–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 70.83, 124.47 (q, J=273 Hz), 125.60 (q, J=5.7 Hz), 126.51, 127.63, 127.72 (q, J=29.9 Hz), 127.82, 128.46, 129.59, 132.40, 142.44, 142.83. Found: C, 66.71; H, 4.41%. Calcd for $C_{14}H_{11}F_3O$: C, 66.67; H, 4.40%.

4.7.2. 1-[2-(Trifluoromethyl)phenyl]-1-heptanol. IR (neat) 3363, 2928, 2860, 1609, 1585, 1456, 1313, 1163, 1122, 1059, 1036, 768 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=6.6 Hz, 3H), 1.01–1.40 (m, 7H), 1.45–1.60 (m, 1H), 1.62–1.80 (m, 2H), 1.94 (bs, 1H), 5.11 (t, J=6.6 Hz, 1H), 7.36 (t, J=7.2 Hz, 1H), 7.54–7.64 (m, 2H), 7.77 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.89, 22.44, 25.98, 28.92, 31.60, 39.13, 69.51, 124.52 (q, J=273 Hz), 125.47 (q, J=6.1 Hz), 126.92 (q, J=30 Hz), 127.42, 127.62,

132.36, 144.42. Found: C, 64.76; H, 7.46%. Calcd for $C_{14}H_{19}F_3O$: C, 64.60; H, 7.36%.

4.8. General procedure for the manganese-mediated cyclization reaction

The reaction of 1-(2-iodophenyl)-2,2,4-trimethyl-3-pentanone (**29a**) with activated manganese is representative. The suspension of manganese (1.5 mmol) in THF was added to a solution of 1-(2-iodophenyl)-2,2,4-trimethyl-3-pentanone (165 mg, 0.5 mmol) in THF (15 mL) at −42°C under argon atmosphere. The mixture was stirred for 1.5 h at −42°C and at 0°C for additional 1.5 h. The whole mixture was warmed up to room temperature over 30 min and stirred for another 17 h. Extractive workup (ethyl acetate/sat. NH_4Cl) followed by silica gel column purification provided 1-isopropyl-2,2-dimethyl-2,3-dihydroinden-1-ol (**32a**) in 65% yield.

Spectroscopic data for 1-isopropyl-2,2-dimethyl-2,3-dihydroinden-1-ol (**32a**)[11b] and 2,2-dimethyl-1-phenyl-2,3-dihydroinden-1-ol (**32b**)[11b] were identical with those reported in literatures.

4.8.1. 1-Ethyl-2-methyl-2,3-dihydroinden-1-ol (32c, 81/19). IR (neat) 3416, 2966, 2930, 1460, 756, 731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=7.5 Hz, 2.43H), 0.91 (t, J=7.2 Hz, 0.57H), 1.09 (d, J=6.9 Hz, 2.43H), 1.15 (d, J=6.6 Hz, 0.57H), 1.44–1.64 (m, 1.19H), 1.66–1.79 (m, 0.19H), 1.81–2.00 (m, 1.62H), 2.30–2.51 (m, 1.19H), 2.62 (dd, J=15.6, 6.9 Hz, 0.81H), 3.00 (dd, J=15.6, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 7.58, 9.03, 13.18, 13.77, 21.20, 30.79, 37.64, 37.99, 40.82, 48.61, 84.04, 84.29, 123.37, 123.93, 124.75, 125.08, 126.19, 126.61, 127.72, 128.23, 141.68, 142.80, 146.61, 147.83. HRMS Found: m/z 176.1198. Calcd for $C_{12}H_{16}O$: M, 176.1201.

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