



Manganese(III)-mediated oxidative annulation of vinylidenecyclopropanes with 1,3-dicarbonyl compounds

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ABSTRACT

Manganese(III)-mediated oxidative annulation of vinylidenecyclopropanes with 1,3-dicarbonyl compounds in acetonitrile/acetic acid produces the corresponding functionalized dihydrofuran derivatives in moderate to good yields under mild conditions. The substrate scope has been examined and a plausible reaction mechanism has been also proposed on the basis of experimental results and previous literature.

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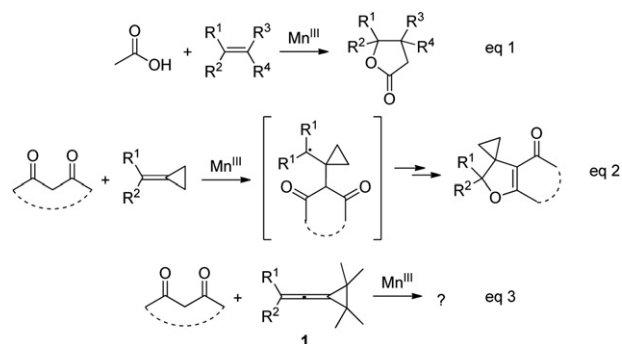
1. Introduction

Vinylidenecyclopropanes (VDCPs) **1**, which have highly strained cyclopropyl group connected with an allene moiety and yet are thermally stable and reactive substances in organic chemistry, are versatile intermediates in organic synthesis.¹ Thus far, many novel and useful transformations of these interesting highly strained small ring molecules have been disclosed by many organic chemists. For example, it has been demonstrated that VDCPs **1** are able to react with diverse nucleophiles, such as alcohols, amines or carboxylic acids, and other reactants, such as aldehydes or imines in the presence of Lewis acids/Brønsted acids/transition metals to produce a variety of interesting products.^{2–4} Many of these reactions are initiated by the electrophilic additions of the corresponding in situ generated active species to the electron-rich VDCPs. Moreover, several examples based on the radical species initiated reactions of VDCPs have been also explored recently.^{2d,5}

Mn(III)-mediated oxidative free-radical reactions have been extensively developed during the past two decades, which have been proven to be an extremely valuable method in numerous regio-, chemo-, and stereoselective carbon–carbon bond formations both in inter- and intramolecular reactions, and have been

also applied to the construction of complex natural and biologically active compounds.⁶ In this aspect, the oxidative addition of acetic acid to alkenes in the presence of 2.0 equiv of Mn(OAc)₃ in AcOH under reflux to give γ -lactones was first reported in 1968 by Heiba and Dessau^{7a,c} as well as Bush and Finkbeiner,^{7b} respectively (Scheme 1, Eq. 1). Over the past 40 years, the use of Mn(OAc)₃ to oxidatively initiate free-radical reactions of mono and 1,3-dicarbonyl compounds with other reactants has been widely reviewed with an emphasis on the synthetic applications.^{6e,8,9} In our previous work, we have also investigated the reactions between methylenecyclopropanes (MCPs) and 1,3-dicarbonyl compounds to produce the corresponding dihydrofuran derivatives through a mechanism of Mn(OAc)₃ induced free-radical oxidative process (Scheme 1, Eq. 2).¹⁰ However, among all these reports, there is no any example involving the reaction between 1,3-dicarbonyl compound and VDCP mediated by Mn(OAc)₃. We envisaged that VDCPs **1** having a highly strained cyclopropane ring connected with an allene moiety would be also suitable substrates in the reaction with 1,3-dicarbonyl compounds if using Mn(OAc)₃ as a promoter (Scheme 1, Eq. 3). In this paper, we wish to disclose that manganese(III)-mediated oxidative annulation of VDCPs with 1,3-dicarbonyl compounds can proceed smoothly in acetonitrile/acetic acid to produce the corresponding functionalized dihydrofuran derivatives in moderate to good yields under mild conditions, subsequently enriching the chemistry of Mn(III)-mediated oxidative free-radical reactions.

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Scheme 1. Mn(III)-mediated oxidative free-radical reactions.

Initial assays were carried out by using VDCP **1a** and cyclohexane-1,3-dione as the substrates. To our delight, the reaction of VDCP **1a** with cyclohexane-1,3-dione proceeded smoothly in HOAc within 12 h at room temperature (20 °C) to give the corresponding dihydrofuran derivative **2a** in 43% yield (Table 1, entry 1). Next, we attempted to optimize the reaction conditions and the results of these experiments are summarized in Table 1. Using acetonitrile (CH₃CN) as the solvent afforded **2a** in 45% yield upon extending the reaction time to 48 h (Table 1, entry 2) and moreover, using acetonitrile (CH₃CN) as the solvent combined with HOAc (2.0 equiv) produced **2a** in 54% yield within 12 h (Table 1, entry 3). Further increasing the employed amount of HOAc did not improve the yield of **2a** (Table 1, entries 4 and 5). The examination of solvent effects revealed that acetonitrile is the suitable solvent in this reaction compared with other solvents, such as *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF) and toluene (Table 1, entries 6–8). Upon raising the reaction temperature to 60 °C and reducing the reaction time to 6 h, we found that the corresponding dihydrofuran derivative **2a** could be obtained in 67% yield in the presence of 5.0 equiv of HOAc (Table 1, entry 10).

Under this optimized reaction conditions, we next set out to explore the substrate scope of this transformation and the results of these experiments are summarized in Table 2. As shown in Table 2, a variety of VDCPs **1** could react with cyclohexane-1,3-dione smoothly to give the corresponding dihydrofuran derivatives

Table 1
Optimization of the reaction conditions between VDCP **1a** and cyclohexane-1,3-dione in the presence of Mn(OAc)₃·2H₂O

Entry ^a	Solvent	x	y (h)	Temp (°C)	Yield(%) ^b
1	HOAc	—	12	rt	43
2	CH ₃ CN	—	48	rt	45
3	CH ₃ CN	2.0	12	rt	54
4	CH ₃ CN	5.0	12	rt	53
5	CH ₃ CN	10	12	rt	54
6	Toluene	5.0	12	rt	24
7	DMF	5.0	12	rt	30
8	THF	5.0	12	rt	23
9	CH ₃ CN	5.0	12	60	63
10	CH ₃ CN	5.0	6	60	67

^a VDCP **1**, cyclohexane-1,3-dione (3.0equiv) and Mn(OAc)₃·2H₂O (2.0equiv) were added into a flask under argon, and then, HOAc (x equiv) was injected into the flask under certain conditions. Reactions were carried out in the employed solvent at different temperature within y h under argon.

^b Isolated yields.

Table 2
Substrate scope of the reactions between VDCPs **1** and cyclohexane-1,3-dione in the presence of Mn(OAc)₃·2H₂O

Entry ^a	Ar ¹ /Ar ²	Yield (%) ^b
1	<i>p</i> -FC ₆ H ₄ / <i>p</i> -FC ₆ H ₄ , 1b	2b , 65
2	<i>p</i> -ClC ₆ H ₄ / <i>p</i> -ClC ₆ H ₄ , 1c	2c , 64
3	<i>p</i> -ClC ₆ H ₄ /C ₆ H ₅ , 1d	2d , 75
4	<i>p</i> -BrC ₆ H ₄ / <i>p</i> -BrC ₆ H ₄ , 1e	2e , 59
5	<i>o</i> -CH ₃ C ₆ H ₄ /C ₆ H ₅ , 1f	2f , 60
6	<i>p</i> -CH ₃ C ₆ H ₄ /C ₆ H ₅ , 1g	2g , 58
7	<i>p</i> -CH ₃ C ₆ H ₄ / <i>p</i> -CH ₃ C ₆ H ₄ , 1h	2h , 72
8	<i>p</i> -CH ₃ OC ₆ H ₄ / <i>p</i> -CH ₃ OC ₆ H ₄ , 1i	2i , 68

^a VDCP **1**, cyclohexane-1,3-dione (3.0 equiv) and Mn(OAc)₃·2H₂O (2.0 equiv) were added into a flask under argon, and then, HOAc (5.0 equiv) was injected into the flask. Reactions were carried out in CH₃CN at 60 °C within 6 h under argon.

^b Isolated yields.

2b–i in moderate to good yields under mild conditions. As for VDCPs **1b–e** bearing electron-withdrawing groups on their aromatic rings of Ar¹ and Ar², the corresponding products **2b–e** could be obtained in 59–75% yields (Table 2, entries 1–4). Meanwhile, introducing electron-donating groups onto aromatic rings of Ar¹ and Ar² could also afford the corresponding dihydrofuran derivatives **2f–i** in moderate to good yields, suggesting that the electronic property on the aromatic rings has little influence in this reaction (Table 2, entries 5–8).

Using dimedone as the 1,3-dicarbonyl compound to replace cyclohexane-1,3-dione, the reactions with VDCPs **1** also proceeded efficiently to afford the corresponding dihydrofuran derivatives **3** in good to high yields under the standard conditions. The results have been summarized in Table 3. As can be seen from Table 3, the corresponding dihydrofuran derivatives **3a–i** could be obtained in 64–92% yields whether they have electron-withdrawing or electron-donating groups on their aromatic rings of Ar¹ and Ar² (Table 3, entries 1–8). The structure of **3a** was unambiguously determined by X-ray diffraction. Its ORTEP drawing is shown in Fig. 1 and its CIF data are presented in the Supplementary data.¹¹

Table 3
Reactions of VDCPs **1** with dimedone in the presence of Mn(OAc)₃·2H₂O

Entry ^a	Ar ¹ /Ar ²	Yield (%) ^b
1	C ₆ H ₅ /C ₆ H ₅ , 1a	3a , 83
2	<i>p</i> -FC ₆ H ₄ / <i>p</i> -FC ₆ H ₄ , 1b	3b , 64
3	<i>p</i> -ClC ₆ H ₄ / <i>p</i> -ClC ₆ H ₄ , 1c	3c , 85
4	<i>p</i> -ClC ₆ H ₄ /C ₆ H ₅ , 1d	3d , 72
5	<i>p</i> -BrC ₆ H ₄ / <i>p</i> -BrC ₆ H ₄ , 1e	3e , 65
6	<i>p</i> -CH ₃ C ₆ H ₄ /C ₆ H ₅ , 1g	3g , 75
7	<i>p</i> -CH ₃ C ₆ H ₄ / <i>p</i> -CH ₃ C ₆ H ₄ , 1h	3h , 92
8	<i>p</i> -CH ₃ OC ₆ H ₄ / <i>p</i> -CH ₃ OC ₆ H ₄ , 1i	3i , 81

^a VDCP **1**, dimedone (3.0 equiv) and Mn(OAc)₃·2H₂O (2.0 equiv) were added into a flask under argon, and then, HOAc (5.0 equiv) was injected into the flask. Reactions were carried out in CH₃CN at 60 °C within 6 h under argon.

^b Isolated yields.

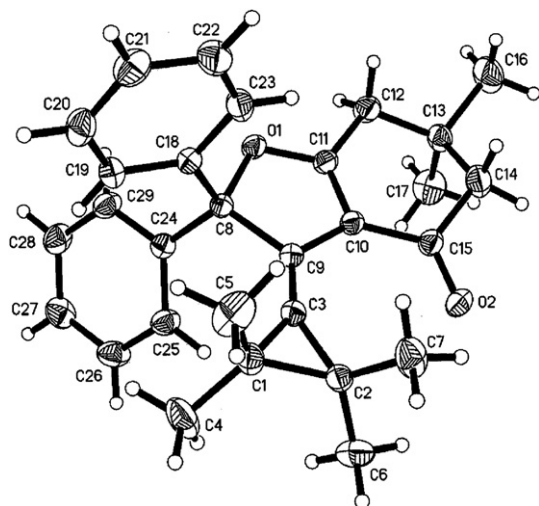
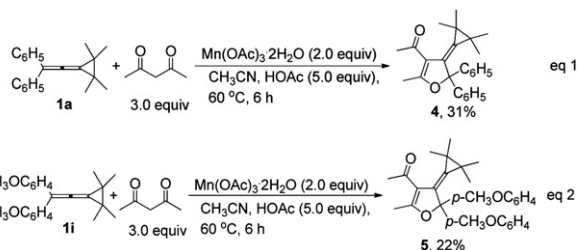
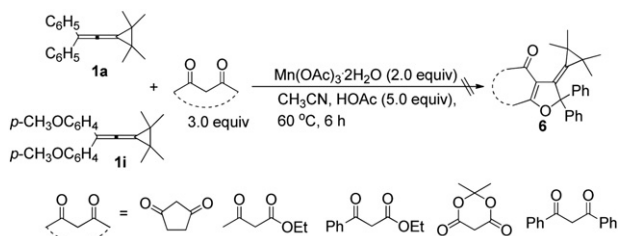


Fig. 1. ORTEP Drawing of 3a.

To further examine the substrate scope, we employed several other 1,3-dicarbonyl compounds in the reaction with VDCP **1a** under the standard conditions and the results of these experiments have been shown in Scheme 2. A brief screening of several 1,3-dicarbonyl compounds revealed that pentane-2,4-dione could also react with VDCP **1a** as well as VDCP **1i** to produce the corresponding dihydrofuran derivatives **4** and **5** in 31% and 22% yields, respectively (Scheme 2, Eq. 1 and Eq. 2). Using other 1,3-dicarbonyl compounds, such as cyclopentane-1,3-dione, ethyl 3-oxobutanoate, ethyl 3-oxo-3-phenylpropanoate, 2,2-dimethyl-1,3-dioxane-4,6-dione, and 1,3-diphenylpropane-1,3-dione as the reactants, either no reactions occurred or none of the corresponding dihydrofuran derivatives **6** was formed (Scheme 3). In addition, VDCP **1i** did not react with these 1,3-dicarbonyl compounds either. Moreover, as for VDCP substrates bearing aromatic substituent on their cyclopropanes, the reactions with cyclohexane-1,3-dione or dimedone gave complex product mixtures under the standard conditions.



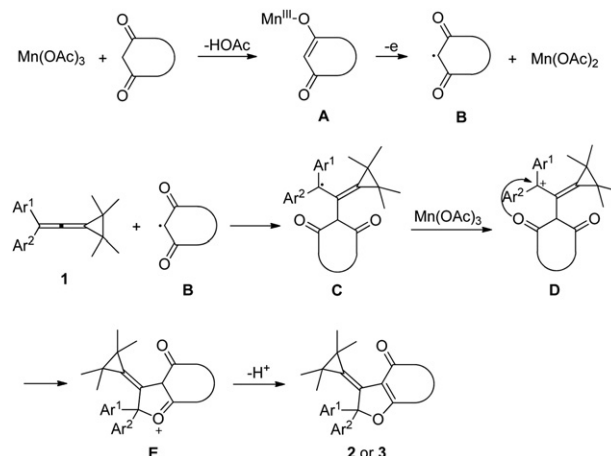
Scheme 2. Further screening of pentane-2,4-dione with VDCP's **1a** and **1i** in the presence of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$.



Scheme 3. Further screening of other 1,3-dicarbonyl compounds with VDCP's **1a** and **1i** in the presence of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$.

On the basis of above results and previous investigations on Mn(III)-mediated reactions,^{2d,5,10} a plausible mechanism for the

formation of dihydrofuran derivative **2** or **3** has been outlined in Scheme 4 using VDCP **1** as the reaction model. The reaction of 1,3-dicarbonyl compound with $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ affords a Mn(III)-enolate **A**, which rapidly undergoes electron loss to the oxo-centered Mn(III) metal complex to give the radical intermediate **B**. Then, the radical intermediate **B** adds to the double bond of VDCP **1** to furnish the corresponding radical intermediate **C**.^{6g} The oxidation of 1,3-dicarbonyl compound to give radical intermediate **C** has been considered as the rate determining step.^{6g} This radical intermediate is stabilized by two aromatic groups of VDCP **1**.¹² Therefore, it is further oxidized by another molecule of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ (2.0 equiv of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ in the reaction system) to produce the corresponding cationic intermediate **D**, which is also stabilized by the corresponding aromatic rings. At any sense, this cationic intermediate **D** is more stable than the radical intermediate **C** because it is exactly a long-lived cyclopropylcarbiny cation through the delocalization and resonance effects, providing a driving force for the transformation of intermediate **C** to intermediate **D**.¹³ The intramolecular attack of the oxygen atom at the carbonyl group gives the oxonium cation **E**, which undergoes deprotonation to produce the corresponding [3+2] annulation product **2** or **3**.



Scheme 4. A plausible reaction mechanism for the formation of **2** or **3**.

In conclusion, we have explored a novel transformation of VDCPs **1** with 1,3-dicarbonyl compounds in the presence of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ under mild conditions, affording the corresponding dihydrofuran derivatives in moderate to good yields and subsequently enriching the chemistry of Mn(III)-mediated oxidative free-radical reactions. Moreover, a plausible reaction mechanism has been proposed in this paper, that is, based on our experimental results and previous literature. Efforts are in progress to further elucidate the mechanistic details of this reaction and to determine its scope and limitations.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.06.109.

References and notes

- For the synthesis of diarylvinylicidencyclopropanes, please see: (a) Isagawa, K.; Mizuno, K.; Sugita, H.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2283–2285 and references therein; (b) Al-Dulayymi, J. R.; Baird, M. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1547–1548 For some other papers related to vinylidencyclopropanes: (c) Maeda, H.; Hirai, T.; Sugimoto, A.; Mizuno, K. *J. Org. Chem.* **2003**, 68, 7700–7706; (d) Pasto, D. J.; Brophy, J. E. *J. Org. Chem.* **1991**, 56, 4554–4556 For a recent review, see: (e) Maeda, H.; Mizuno, K. *J. Synth. Org. Chem. Jpn.* **2004**, 62, 1014–1025.
- (a) Xu, G.-C.; Liu, L.-P.; Lu, J.-M.; Shi, M. *J. Am. Chem. Soc.* **2005**, 127, 14552–14553; (b) Shi, M.; Lu, J.-M.; Xu, G.-C. *Tetrahedron Lett.* **2005**, 46, 4745–4748; (c) Li, Q.-J.; Shi, M.; Timmons, C.; Li, G.-G. *Org. Lett.* **2006**, 8, 625–628; (d) Shi, M.; Lu, J.-M. *Synlett* **2005**, 2352–2356; (e) Lu, J.-M.; Shi, M. *Org. Lett.* **2007**, 9, 1805–1808; (f) Lu, J.-M.; Shi, M. *Org. Lett.* **2006**, 8, 5317–5320; (g) Shi, M.; Li, W. *Tetrahedron* **2007**, 63, 6654–6660; (h) Lu, J.-M.; Zhu, Z.-B.; Shi, M. *Chem. Eur. J.* **2009**, 15, 963–971; (i) Zhu, Z.-B.; Shi, M. *Chem. Eur. J.* **2008**, 14, 10219–10222; (j) Shi, M.; Yao, L.-F. *Chem. Eur. J.* **2008**, 14, 8725–8731; (k) Lu, J.-M.; Shi, M. *J. Org. Chem.* **2007**, 73, 2206–2210; (l) Zhang, Y.-P.; Lu, J.-M.; Xu, G.-C.; Shi, M. *J. Org. Chem.* **2007**, 72, 509–516; (m) Lu, J.-M.; Shi, M. *Tetrahedron* **2007**, 63, 7545–7549.
- (a) Huang, X.; Su, C.-L.; Liu, Q.-Y.; Song, Y.-T. *Synlett* **2008**, 229–231; (b) Fall, Y.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2007**, 48, 3579–3581; (c) Poutsuma, M. L.; Ibarbia, P. A. *J. Am. Chem. Soc.* **1971**, 93, 440–450; (d) Smadja, W. *Chem. Rev.* **1983**, 83, 263–320; (e) Hendrick, M. E.; Hardie, J. A.; Jones, M. *J. Org. Chem.* **1971**, 36, 3061–3062; (f) Sugita, H.; Mizuno, K.; Saito, T.; Isagawa, K.; Otsuji, Y. *Tetrahedron Lett.* **1992**, 33, 2539–2542; (g) Mizuno, K.; Sugita, H.; Kamada, T.; Otsuji, Y. *Chem. Lett.* **1994**, 449–452 and references therein; (h) Sydnes, L. K. *Chem. Rev.* **2003**, 103, 1133–1150; (i) Akasaka, T.; Misawa, Y.; Ando, W. *Tetrahedron Lett.* **1990**, 31, 1173–1176; (j) Mizuno, K.; Sugita, H.; Isagawa, K.; Goto, M.; Otsuji, Y. *Tetrahedron Lett.* **1993**, 34, 5737–5738; (k) Mizuno, K.; Sugita, H.; Hirai, T.; Maeda, H. *Chem. Lett.* **2000**, 1144–1145; (l) Mizuno, K.; Nire, K.; Sugita, H.; Maeda, H. *Tetrahedron Lett.* **2001**, 42, 2689–2692.
- For some more recent papers related to VDCCs, please see: (a) Wu, L.; Shi, M. *Eur. J. Org. Chem.* **2011**, 1099–1105; (b) Lu, B.-L.; Shi, M. *Eur. J. Org. Chem.* **2011**, 243–248; (c) Wu, L.; Shi, M. *J. Org. Chem.* **2010**, 75, 2296–2301; (d) Shi, M.; Shao, L.-X.; Lu, J.-M.; Wei, Y.; Mizuno, K.; Maeda, H. *Chem. Rev.* **2010**, 110, 5883–5913; (e) Wu, L.; Shi, M. *Chem. Eur. J.* **2010**, 16, 1149–1152; (f) Lu, B.-L.; Wei, Y.; Shi, M. *Chem. Eur. J.* **2010**, 16, 10975–10979; (g) Yuan, W.; Shi, M. *Tetrahedron* **2010**, 66, 7104–7111; (h) Wu, L.; Shi, M.; Li, Y.-X. *Chem. Eur. J.* **2010**, 16, 5163–5172; (i) Yacoub, F.; Henri, D.; Maurice, S. *Tetrahedron* **2010**, 66, 2181–2188; (j) Li, W.; Yuan, W.; Surech, P.; Shi, M.; Li, G.-G. *Org. Lett.* **2010**, 10, 920–923; (k) Li, W.; Yuan, W.; Shi, M.; Erik, H.; Li, G.-G. *Org. Lett.* **2010**, 10, 64–67; (l) Lu, B.-L.; Lu, J.-M.; Shi, M. *Tetrahedron* **2009**, 65, 9328–9335; (m) Lu, B.-L.; Lu, J.-M.; Shi, M. *Tetrahedron Lett.* **2010**, 51, 321–324; (n) Su, C.-L.; Huang, X. *Adv. Synth. Catal.* **2009**, 351, 135–140; (o) Li, W.; Shi, M.; Li, Y.-X. *Chem. Eur. J.* **2009**, 15, 8852–8860; (p) Yao, L.-F.; Shi, M. *Eur. J. Org. Chem.* **2009**, 4036–4040; (q) Su, C.-L.; Huang, X.; Liu, Q.-Y.; Huang, X. *J. Org. Chem.* **2009**, 74, 8272–8279; (r) Yao, L.-F.; Shi, M. *Chem. Eur. J.* **2009**, 15, 3875–3881; (s) Li, W.; Shi, M. *Org. Biomol. Chem.* **2009**, 7, 1775–1777; (t) Li, W.; Shi, M. *Tetrahedron* **2009**, 65, 6815–6821; (u) Su, C.-L.; Liu, Q.-Y.; Ni, Y.; Huang, X. *Tetrahedron Lett.* **2009**, 50, 4381–4383; (v) Li, W.; Shi, M. *Eur. J. Org. Chem.* **2009**, 270–274; (w) Gu, X.-X.; Wang, F.-J.; Qi, M.-H.; Shao, L.-X.; Shi, M. *Organometallics* **2009**, 28, 1569–1574; (x) Li, W.; Shi, M. *J. Org. Chem.* **2009**, 74, 856–860; (y) Jiang, M.; Shi, M. *Tetrahedron* **2009**, 65, 5222–5227.
- Some examples are presented as followings: (a) Crombie, L.; Maddocks, P. J.; Pattenden, G. *Tetrahedron Lett.* **1978**, 19, 3483–3486; (b) Nair, V.; Balagopal, L.; Rajan, R.; Mathew, J. *Acc. Chem. Res.* **2004**, 37, 21–30.
- (a) de Klein, W. J. In *Organic Syntheses by Oxidation and Metal Compound*; Mijs, W. J., de Jonge, C. R. H. L., Eds.; Plenum: New York, NY, 1986, Chapter 4; (b) Snider, B. B. *Chemtracts: Org. Chem.* **1991**, 4, 403–419; (c) Demir, A. S.; Jegananathan, A. *Synthesis* **1992**, 235–247; (d) Melikyan, G. G. *Synthesis* **1993**, 833–850; (e) Melikyan, G. G. *Org. React.* **1997**, 49, 427–675; (f) Fristad, W. E.; Peterson, J. R.; Ernst, A. B. *Tetrahedron* **1986**, 42, 3429–3442; (g) Snider, B. B.; Patricia, J. J.; Kates, S. A. *J. Org. Chem.* **1988**, 53, 2137–2143; (h) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1985**, 26, 4291–4294; (i) Zhou, H.; Huang, X.; Chen, W. *J. Org. Chem.* **2004**, 69, 5471–5472.
- (a) Heiba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1968**, 90, 5905–5906; (b) Bush, J. B., Jr.; Finkbeiner, H. *J. Am. Chem. Soc.* **1968**, 90, 5903–5905; (c) Heiba, E. I.; Desau, R. M.; Rodewald, P. G. *J. Am. Chem. Soc.* **1975**, 97, 7977–7981.
- For reviews, please see: (a) Badanyan, S. O.; Melikyan, G. G.; Mkrtchyan, D. A. *Russ. Chem. Rev.* **1989**, 58, 286–296; (b) Badanyan, S. O.; Melikyan, G. G.; Mkrtchyan, D. A. *Usp. Khim.* **1989**, 58, 475–495; (c) Iqbal, J.; Bhatia, B.; Nayyar, N. K. *Chem. Rev.* **1994**, 94, 519–564; (d) Snider, B. B. *Chem. Rev.* **1996**, 96, 339–363; (e) Melikyan, G. G. *Aldrichimica Acta* **1998**, 31, 50–64; (f) Demir, A. S.; Emrullahoglu, M. *Curr. Org. Synth.* **2007**, 4, 321–350; (g) Snider, B. B. *Tetrahedron* **2009**, 65, 10738–10744.
- Some more recent papers related to Mn(III) promoted addition reactions of 1,3-dicarbonyl compounds, please see: (a) Yousuf, S. K.; Mukherjee, D. L. M.; Taneja, S. C. *Org. Lett.* **2011**, 13, 576–579; (b) Ng, E. P. J.; Wang, Y.-F.; Chiba, S. *Synlett* **2011**, 783–786; (c) Dickschat, A.; Studer, A. *Org. Lett.* **2010**, 12, 3972–3974; (d) Ito, Y.; Yoshinaga, T.; Nishino, H. *Tetrahedron* **2010**, 66, 2683–2694; (e) Mitasev, B.; Porco, J. A., Jr. *Org. Lett.* **2009**, 11, 2285–2288; (f) Tsubaki, T.; Nishono, H. *Tetrahedron* **2009**, 65, 9448–9459; (g) Wang, Y.-F.; Chiba, S. *J. Am. Chem. Soc.* **2009**, 131, 12570–12572; (h) Asahi, K.; Nishino, H. *Tetrahedron* **2008**, 64, 1620–1623; (i) Wang, Y.-F.; Toh, K. K.; Chiba, S.; Narasaka, K. *Org. Lett.* **2008**, 10, 5019–5022; (j) Asahi, K.; Nishino, H. *Tetrahedron* **2005**, 61, 11107–11124; (k) Kagayama, T.; Fuke, T.; Sakaguchi, S.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **2005**, 78, 1673–1676 and references therein.
- Huang, J.-W.; Shi, M. *J. Org. Chem.* **2005**, 70, 3859–3863.
- The crystal data of **3a** have been deposited in CCDC with number 814690. Empirical Formula: C₂₉H₃₂O₂; Formula Weight: 412.53; Crystal Color, Habit: colorless; Crystal System: monoclinic; Lattice Type: primitive; Crystal size: 0.30×0.20×0.15; Lattice Parameters: a=9.210(4) Å, b=13.927(6) Å, c=18.349(8) Å, α=90°, β=92.566(9)°, γ=90°, V=2351.2(18) Å³; Space group: P2(1)/c; Z=4; D_{calcd}=1.165 g/cm³; F₀₀₀=888; Final R indices [I>2σ(I)]: R1=0.0572; wR2=0.1850.
- (a) Kochi, J. K.; Krusic, P. J.; Eaton, D. R. *J. Am. Soc. Chem.* **1969**, 91, 877–1879; (b) Mathew, L.; Warkentin, J. *J. Am. Soc. Chem.* **1986**, 108, 7981–7984; (c) Bowry, V. W.; Lusztzyk, J.; Ingold, K. U. *J. Am. Soc. Chem.* **1991**, 113, 5687–5698; (d) Beckwith, A. L. J.; Bowry, V. W. *J. Am. Soc. Chem.* **1994**, 116, 2710–2716; (e) Masnovi, J.; Samsel, E. G.; Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1044–1045.
- Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, 92, 69–95.