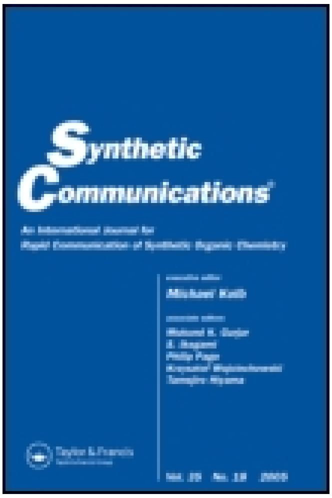

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

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To cite this article: Fei Li, Wei Zhou, Long-Sheng Zheng, Li Li, Zhan-Jiang Zheng & Li-Wen Xu (2014) Ar-BINMOL-Derived Salan-Cu(II) Complex-Catalyzed Silyl-Reformatsky Reaction of Aromatic Aldehydes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 44:19, 2861-2869, DOI: 10.1080/00397911.2014.920509

To link to this article: http://dx.doi.org/10.1080/00397911.2014.920509

Synthetic Communications®, 44: 2861–2869, 2014
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2014.920509

Ar-BINMOL–DERIVED SALAN–Cu(II) COMPLEX–CATALYZED SILYL-REFORMATSKY REACTION OF AROMATIC ALDEHYDES

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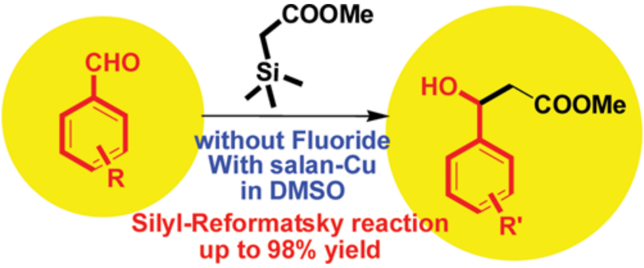
GRAPHICAL ABSTRACT



Abstract *In this work, we have developed a facile protocol with salan–Cu system for the facile and selective synthesis of β-hydroxyesters via silyl-Reformatsky reaction with α-silylester and aldehydes. The screening and optimization of reaction conditions led to the determination of a practical and efficient procedure in which the salan–Cu exhibited promising catalytic activity in dimethylsulfoxide, in which the silyl-Reformatsky reaction of aromatic aldehydes with α-trimethylsilylmethylacetate gave the corresponding β-hydroxyester derivatives in excellent yields (up to 98%) under fluoride-free reaction conditions.*

Keywords Ar-BINMOL; aromatic aldehydes; organosilicon chemistry; Reformatsky reaction; salan ligand

Received April 1, 2014.

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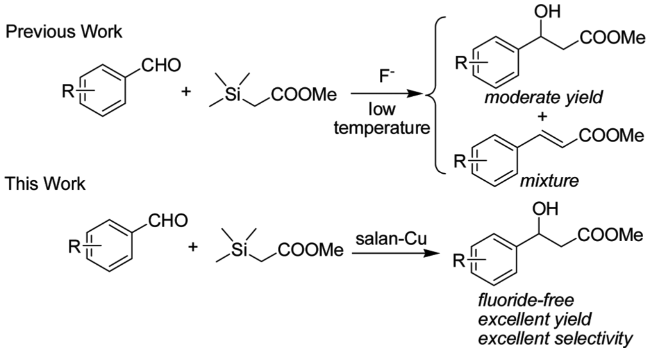
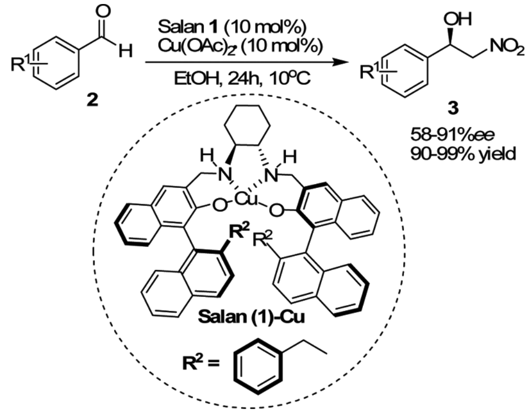
INTRODUCTION

The Reformatsky reaction is one of the most important fundamental carbon–carbon bond-forming reactions in organic chemistry because it affords synthetically and biologically important β-hydroxyesters.[1–7] The silyl-Reformatsky reaction with α-silylester and carbonyl compounds is an environmentally benign type of Reformatsky reaction that avoid the use of stoichiometric metal, such as zinc and other metal powder. Various fluoride reagents, such as tetrabutylammonium fluoride (TBAF) and CsF, have been employed as a fluoride ion for desilyl activating the α-silyl group to generate a naked carbanion, which then adds to the aldehydes. However, in previous work, the desired product yield was generally only poor to moderate (24–88% yield) and had poor selectivity under fluoride-promoted reaction conditions because of the unavoidable formation of both β-hydroxyester and α,β-unsaturated ester. Most of synthetic methods based on fluoride-promoted breaking of Si-C bond also were deficient in substrate scope, which always led to limited species of β-hydroxyesters.[3–7] Thus in this context, there is still a great need to develop a mild and efficient method, which can be valuable alternative for the silyl-Reformatsky reaction and facile synthesis of β-hydroxyester with good yields. Herein, we reported the development of salan–Cu–catalyzed silyl-Reformatsky reaction of aromatic aldehydes with α-trimethylsilylmethylacetate (Scheme 1).

Very recently, we have synthesized a sires of chiral Ar-BINMOL ligands that derived from chiral BINOL (1,1′-binaphthalene-2,2′-diol) through [1,2]-Wittig rearrangement.[8–10] The Ar-BINMOLs (1,1′-binaphthalene-2-α-arylmethanol-2′-ol) have rigid structures with C_2-axial and sp^3 carbon-central chirality, and could act as a supramolecular backbone due to the existence of hydrogen bonding and aromatic interactions of rotatable aromatic rings. Thus, we expected a high potential for the creation of a rotatable π wall in the designed salan ligand prepared from Ar-BINMOL via key [1,2]-Wittig rearrangement and subsequent six-step transformations.[11,12] Interestingly, the Ar-BINMOL-derived salan ligand exhibited unusual and unexpected catalytic efficiency in asymmetric Henry reaction of aldehydes in terms of enantioselectivities and conversions. As shown in Scheme 2, the salan (**1**)–copper complex exhibited good catalytic performance for nonsubstituted and halogen-substituted aromatic aldehydes in terms of conversion and enantioselectivity. On the



Scheme 1. Salan–copper–catalyzed silyl-Reformatsky reaction.



Scheme 2. Enantioselective salan–Cu–catalyzed Henry reaction.

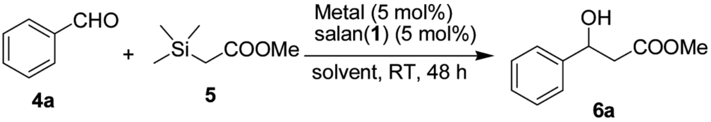
basis of our previous studies that the Ar-BINMOL-derived salan–copper–catalyzed Henry reaction of aromatic aldehydes was successful,[11] we postulated that the aromatic aldehydes could be also activated by salan (**1**)–copper complex in the silyl-Reformatsky reaction of aromatic aldehydes with α-silylester.

RESULTS AND DISCUSSION

The initial studies of the salan (**1**)–copper–catalyzed silyl-Reformatsky reaction of α-trimethylsilylmethylacetate (TMSMA, **5**) to benzaldehyde focused on the screening of different solvents and metal salts at room temperature. The results from these investigations are presented in Table 1. With salan (**1**)–Cu as catalyst, the solvent effect on the catalytic activity of salan (**1**)–copper was obvious and the dimethylsulfoxide (DMSO) was found to the best media to promote silyl-Reformatsky reaction with excellent yield (entry 6), whereas other solvents, such as methanol, 1,4-dioxane, dimethylformamide (DMF), N-methylpyrrolidone (NMP), and tetrahydrofuran (THF), resulted in no reaction or trace product (entries 1–5). Notably, only the salan ligand or $Cu(OAc)_2$ in the absence of another coordinator turned out to be poor catalyst in term of conversion (entries 7 and 8). Inspired by these findings, we continued to investigate various copper salts, such as CuF_2, $CuCl_2$, $Cu(OTf)_2$, CuCl, CuI, and CuCN, in the model silyl-Reformatsky reaction (entries 9–16). Surprisingly, only CuF_2 was found to be the best catalyst in this reaction (98% yield, entry 9), a result which is in accordance with the general observation from salan (**1**)–$Cu(OAc)_2$ system–catalyzed silyl-Reformatsky reaction. Interestingly, CuF_2 was also not effective for this addition in the absence of salan ligand (entry 10). Comparably, the use of other general metal fluorides (KF, ZnF_2) as catalyst gave poor conversion under the present reaction conditions (entries 17 and 18). Although AgOAc and HOAc were not successful in this reaction (entries 19 and 20), the importance of copper and acetic ion was confirmed on the basis of these results.

Therefore, beside the salan (**1**)–CuF_2 system, the fluoride-free salan (**1**)–$Cu(OAc)_2$ was observed to be a promising catalyst in the silyl-Reformatsky reaction

Table 1. Evaluation of salan (**1**)–copper complex as catalyst for the synthesis of β-hydroxyester in the silyl-Reformatsky reaction of benzaldehyde with α-trimethylsilylmethylacetate[a]

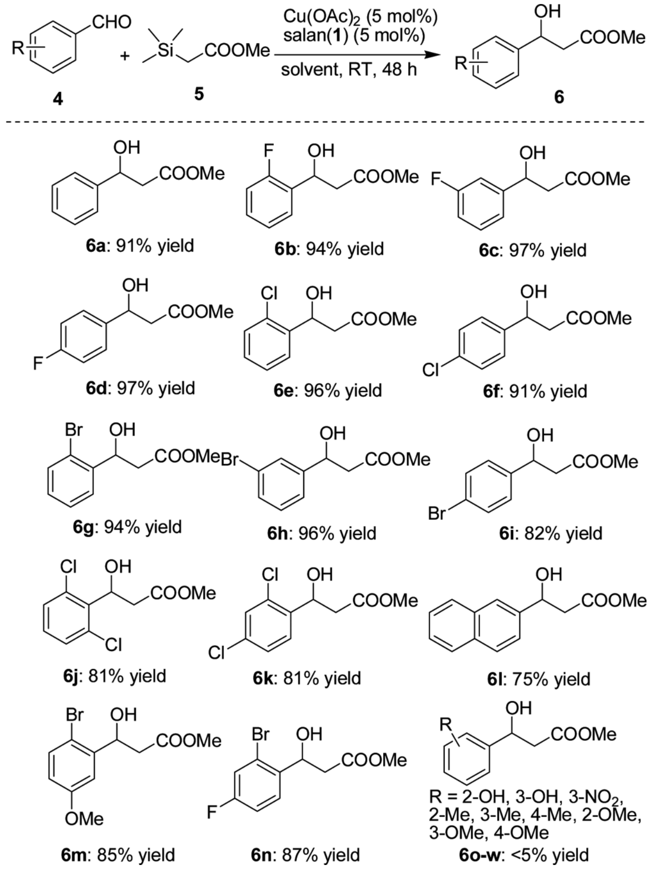


Entry	Metal salt	Ligand	Solvent	Yield (%)[b]
1	$Cu(OAc)_2$	Salan (**1**)	MeOH	Trace[c]
2	$Cu(OAc)_2$	Salan (**1**)	1,4-Dioxane	Trace
3	$Cu(OAc)_2$	Salan (**1**)	DMF	Trace
4	$Cu(OAc)_2$	Salan (**1**)	THF	Trace
5	$Cu(OAc)_2$	Salan (**1**)	NMP	Trace
6	$Cu(OAc)_2$	Salan (**1**)	DMSO	91
7	$Cu(OAc)_2$	—[d]	DMSO	Trace
8	—[e]	Salan (**1**)	DMSO	Trace
9	CuF_2	Salan (**1**)	DMSO	98
10	CuF_2	—[d]	DMSO	Trace
11	CuCl	Salan (**1**)	DMSO	Trace
12	CuI	Salan (**1**)	DMSO	Trace
13	CuCN	Salan (**1**)	DMSO	Trace
14	$CuCl_2$	Salan (**1**)	DMSO	Trace
15	$Cu(CH_3CN)_4PF_6$	Salan (**1**)	DMSO	Trace
16	$Cu(OTf)_2$	Salan (**1**)	DMSO	Trace
17	ZnF_2	Salan (**1**)	DMSO	25
18	KF	Salan (**1**)	DMSO	37
19	AgOAc	Salan (**1**)	DMSO	Trace
20	HOAc[f]	Salan (**1**)	DMSO	Trace

[a] All reactions were carried out with 5 mol% of catalyst and ligand at room temperature for 48 h.
[b] The yield was isolated by flash column.
[c] No reaction or only trace product was detected (<5% yield).
[d] No addition of salan (**1**) ligand.
[e] No addition of metal salt or other catalyst.
[f] The use of 10 mol% of acetic acid.

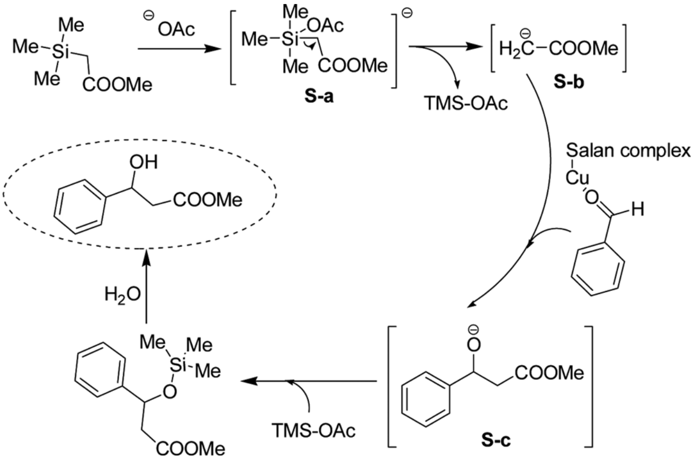
of α-trimethylsilylmethylacetate. Surprisingly, it is noteworthy that the reaction results in the desired methyl 3-hydroxy-3-phenylpropanoate (**6a**) without any side products, such as β-siloxylester {methyl 3-phenyl-3-(trimethylsilyloxy)propanoate} or α,β-unsaturated ester (methyl cinnamate), which is different from previous findings.[1–7] Although almost no enantioselectivity of the present silyl-Reformatsky reaction was determined by high-performance liquid chromatography (HPLC), it was concluded that the salan–copper was an efficient catalyst or promoter to accelerate the silyl-Reformatsky reaction for the clean and chemoselective synthesis of β-hydroxyesters under the reaction conditions.

With the optimized conditions in hand, the catalytic activity of salan (**1**)–copper generated in situ from salan (**1**) and $Cu(OAc)_2$ was then investigated in the silyl-Reformatsky reaction of various aromatic aldehydes. As shown in Scheme 3, the salan–copper catalyst was also applicable to the silyl-Reformatsky reaction of various aromatic aldehydes that were converted into corresponding β-hydroxyesters



Scheme 3. Salan (1)–Cu–catalyzed silyl-Reformatsky reaction of various aromatic aldehydes.

in good to excellent yields (75–97% yields for **6a–n**). Similar to the Henry reaction of aromatic aldehydes, a variety of aromatic aldehydes bearing halogen groups, such as fluoride, chloride, and bromide, at *p*-, *m*-, and *o*-positions afforded excellent yields (up to 97%). Sterically hindered aldehydes, such as 2-bromo-5-methoxybenzaldehyde, 2-bromo-4-fluorobenzaldehyde, and dichloro-benzaldehydes, were also resulted in good yields of the desired products (**6j, 6k, 6m**, and **6n**). 2-Naphthaldehyde also tolerated our reaction conditions to the formation of methyl 3-hydroxy-3-(naphthalen-2-yl)propanoate (**6l**) in 75% yield. As expectedly, the salan–copper catalyst was not effective in the silyl-Reformatsky reaction of aromatic aldehydes with hydroxyl, methyl, methoxy, and nitro-groups (**6o–w**) because almost no reaction occurred for these substrates. On the basis of these experimental results, the salan–copper catalyst still exhibited substrate-sensitive features in the silyl-Reformatsky reaction, which is different from previous reports on catalytic silyl-Reformatsky reaction of aromatic aldehydes that impacted by electronic and steric factors of substrates.[1b] It is worth noting that the selectivity to β-hydroxyesters is excellent because there are no by-products (β-siloxylester or α,β-unsaturated ester) in this reaction.[13] In addition, the synthetic method described in this reaction is also



Scheme 4. Proposed mechanism for salan–copper complex–catalyzed silyl-Reformatsky reaction.

a very mild and effective procedure for the high-yielding synthesis of various aldol products (β-hydroxyesters). Though no enantioselectivity of this silyl-Reformatsky reaction was observed, it is surprising that the catalytic role of the salan–copper complex was realized on the silyl-Reformatsky reaction for the first time. The present study seems to be the first and the best attempt to use fluoride-free metal complex as the catalyst for the desilylation and corresponding nucleophilic addition of α-trimethylsilylmethylacetate to aromatic aldehydes.

On the basis of these experimental results, a possible mechanistic procedure for the salan–copper-catalyzed silyl-Reformatsky reaction is shown in Scheme 4. As shown in Scheme 4, in the first step, reaction of acetic anion (OAc^-) and α-trimethylsilylmethylacetate afforded the anionic pentacoordinate intermediate (**S-a**) because the free acetic anion derived from salan ligand and $Cu(OAc)_2$ was an effective nucleophile to attack silicon center. The pentacoordinate intermediate was unstable in generally because of its high reactivity to form possible desilylated nucleophile **S-b**.[14–16] Simultaneously, the solvent effect of DMSO played an important role in the formation of key intermediates **S-b** and **S-c**, which accelerated the addition of intermediate **S-b** to aromatic aldehyde.[17] At the same time, similar to the previous report on Henry reaction,[11] the interaction of aromatic aldehyde and salan–copper catalyst activated the electrophile. Also inspired by previous findings on salan–copper–catalyzed Henry reactions, we can conclude that the presence of crowded phenyl groups in the salan ligand led to the activation of aldehydes is largely impacted by the salan–copper complex. Although cooperative effect of noncovalent interactions between aromatic aldehydes and salan–copper catalyst, such as hydrogen bonding, aromatic interactions, and metal coordination, on the catalytic activity of salan–copper cannot rationalized at present,[18,19] the enhanced activity of salan ligand with aromatic interactions can be identified in this reaction, consistent with previous reports on the aromatic interactions accelerating transformations.[20–28]

CONCLUSIONS

In summary, we have developed a novel protocol for the facile and selective synthesis of β-hydroxyesters via silyl-Reformatsky reaction with α-silylester and aldehydes. The screening and optimization of reaction conditions led to the determination of a practical and efficient procedure that the salan–Cu exhibited promising catalytic activity in DMSO, in which the silyl-Reformatsky reaction of aromatic aldehydes with α-trimethylsilylmethylacetate (TMSMA) gave the corresponding β-hydroxyester derivatives in excellent yields (up to 98%) under mild reaction conditions. In terms of the catalytic efficiency of salan–Cu system in DMSO, the silyl-Reformatsky reaction of α-trimethylsilylmethylacetate could occur in the absence of fluoride reagent. Although the detailed mechanism of salan–Cu–catalyzed silyl-Reformatsky reaction in DMSO is not clear at present, further efforts will be devoted to develop a chiral salan–copper asymmetric silyl-Reformatsky reaction.

EXPERIMENTAL

All reagents and solvents were used directly without purification. Flash column chromatography was performed over silica (200–300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on an Avance (Brucker) 400-MHz nuclear magnetic resonance spectrometer, and were referenced to the internal solvent signals. Thin-layer chromatography (TLC) was performed using silica gel F254 TLC plates and visualized with ultraviolet light. HPLC was carried out with a Waters 2695 Millennium system equipped with a photodiode array detector. Electron impact (EI) and chemical ionization (CI) mass spectra were performed on a Trace DSQ GC/MS spectrometer. Data are reported in the form of m/z. The electrospray ionization–mass spectrographic (ESI-MS) analysis of the samples was performed on an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4).

General Procedure for the Silyl-Reformatsky Reaction

A flame-dried flask under argon was charged with salan ligand **1** (47.8 mg, 0.05 mmol), $Cu(OAc)_2$ (10.0 mg, 0.05 mmol), and DMSO at room temperature. After the mixture was stirred for 1 h, methyl (trimethylsilyl)acetate (1.1 mmol) and aldehyde (1 mmol) were added successively to the solution, and the mixture was stirred at ambient temperature for 48 h. The reaction mixture was diluted with water and then extracted with dicholormethane (DCM). The organic layer were combined, washed with brine, dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The crude residue was purified by column chromatography. All the products are known[1–7,29–41] and confirmed by GC-MS, NMR, IR, and HRMS (see Supporting Information). For example, methyl 3-hydroxy-3-phenylpropanoate (**6a**): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.28$–7.35 (m, $J = 8.4$ Hz, 5H, and H_{Ar}), 5.12 (q, $J = 9.2$ Hz, H, and $C\underline{H}$-OH), 3.70 (s, 3H, and -$OC\underline{H}_3$), 2.72 (m, $J = 8.0$ Hz, 2H, and -$C\underline{H}_2COOMe$); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 172.3$ ($\underline{C}OOMe$), 142.6 (1-C_{Ar}), 128.6 (3-C_{Ar}), 127.8 (4-C_{Ar}), 125.7 (2-C_{Ar}), 70.3 ($\underline{C}HOH$), 60.9

(-$\underline{C}H_2COOMe$), 43.4 (-$O\underline{C}H_3$). IR (neat, cm^{-1}): 3461, 3063, 3031, 2953, 1732, 1454, 1438, 1361, 1269,1200, 1083, 1061, 1025, 988, 916,762, 701 cm^{-1}. Exact mass calcd. for $C_{10}H_{13}O_3[M+H]^+$, 181.0865. Found: 181.0850.

ACKNOWLEDGMENTS

X. L. W. thanks F. E. Zhu and C. Q. Sheng for their help.

FUNDING

This project was supported partially by the National Natural Science Founder of China (Nos. 21173064 and 51303043), Zhejiang Provincial Natural Science Foundation of China (LR14B030001 and LQ12B02004), and Program for Excellent Young Teachers in Hangzhou Normal University (HNUEYT, JTAS 2011-01-014).

SUPPORTING INFORMATION

Supplemental data for this article can be accessed on the publisher's website.

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13. We have found that the salan–Cu complex could be an efficient catalyst in the desilylation of β-siloxylester intermediate (methyl 3-phenyl-3-(trimethylsilyloxy)propanoate, **S-d** of Scheme 4) in DMSO.
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17. In the control experiment, we also found that NaOAc was a good catalyst in the silyl-Reformatsky reaction of benzaldehyde with α-trimethylsilylmethylacetate; however, the product is the mixture of methyl 3-phenyl-3-(trimethylsilyloxy)propanoate (**S-d**) and methyl 3-hydroxy-3-phenylpropanoate (**6a**). These results supported the theory that the acetic anion (OAc$^-$) could accelerate the 1,2-addition of nucleophile to aldehyde.
18. Although the catalytic system (mixture of this silyl-Reformatsky reaction) cannot in situ characterized by NMR spectroscopy because the salan–copper(II) complex was found to be a strong paramagnetic complex, we hypothesized that the catalyst–substrate interactions should be complicated, supported indirectly by the experimental results in this work. Representative examples of the enzyme-like cooperative catalysis via complicated substrate-catalyst interactions: Xu, H.; Zuend, S. J.; Woll, M. G.; Tao, Y.; Jacobsen, E. N. *Science* **2010**, *327*, 986.
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