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Manganese Salan Complexes As Catalysts For Hydrosilylation Of Aldehydes And Ketones

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Manganese Complexes as Catalysts in Hydrosilylation Reactions

by

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This thesis, submitted by Nora Almutairi in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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ABBREVATIONS

^{t}Bu	Tert-Butyl
$CDCl_3$	Deuterated Chloroform
CD_3CN	Trideuteroacetonitrile
C_6D_6	Hexadeuterobenzene
Cp	η^5-cyclopentadienyl
EtOAc	Ethyl acetate
equiv.	Equivalent
KIE	Kinetic isotope effect
LPO	Dilauroyl peroxide, $(n\text{-}C_{11}H_{23}COO)_2$
MeOH	Methanol
$Mn(OAc)_2 \cdot 4H_2O$	Manganese(II) acetate tetrahydrate
NHCs	N-Heterocyclic carbenes
NMR	Nuclear Magnetic Resonance Spectroscopy
$NaEt_3BH$	Sodium triethylborohydride
Ph	Phenyl

$PhSiH_3$	Phenylsilane
PhCHO	Benzaldehyde
PDI	Pyridine diamine
Ph_2PPr	Diphenylpropylphosphine
^{i}Pr	Isopropyl
Salan	N,N'-Dimethyl-N,N'-bis(hydroxybenzyl)-1,2-diaminoethane
THF	Tetrahydrofuran

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ABSTRACT

New types of manganese(III) complexes containing H_2salan ligand have been synthesized and examined as catalysts in the hydrosilylation of carbonyl compounds. Manganese(III) chloride complex (**4b**) exhibits minimal activity for the hydrosilylation of benzaldehyde at 120 ºC, but can be activated with silver perchlorate. Manganese(III) azide complex (**5b**) is characterized by the IR spectra, and the stretching frequency for the azide group is 2050 cm^{-1}. This complex shows good activity in the hydrosilylation of benzaldehyde at 120 ºC, generating the corresponding silyl ether in high conversion 99 % within 1 h. Under optimized reaction conditions, phenylsilane as the reductant in C_6D_6 under nitrogen, the substrate scope has been examined. Several types of aldehydes and ketones can be reduced with tolerance to a variety of functional groups.

Chapter 1. Manganese Complexes as Catalysts in Hydrosilylation Reactions

Introduction

Having environmentally friendly chemical processes in industry is essential; conversely, obtaining the final products with a large amount of byproducts and/or waste is less appealing. Efforts have been made to find alternative ways to carry out chemical reactions that are acceptable to the environment. In addition, another target is to have a system that could produce a large amount of the desired products with high conversion and less reaction times.

Homogenous catalysis remains an essential part of organometallic chemistry and catalytic systems with non-noble metals are of particular interest. Progress has been made to involve manganese in many catalytic applications for years (Fig. 1).[1] Manganese compounds have been extensively used in the epoxidation reaction for decades, but recent developments have shown that manganese catalysts could be utilized in reduction reactions, such as hydrosilylation, hydroboration, and hydrogenations, as well as in dehydrogenation reactions.

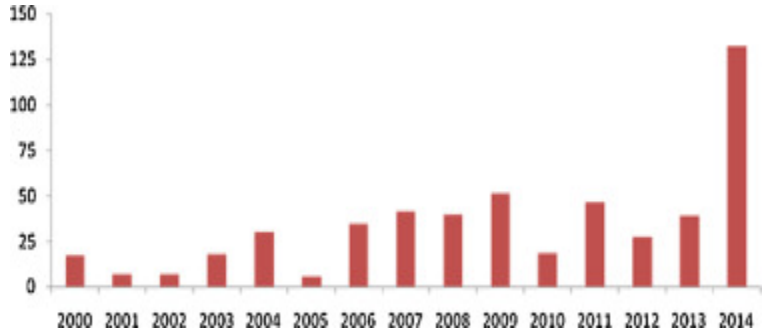


Figure 1. Number of applications of homogenous manganese complexes during years.[1]

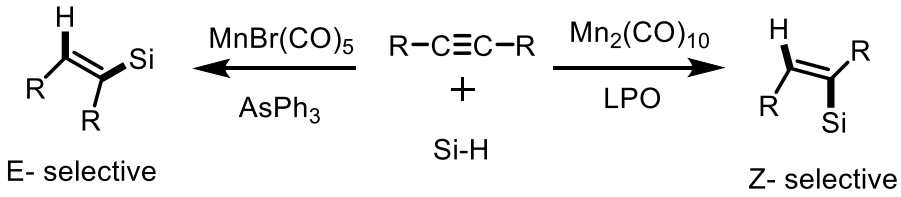
Organosilicon compounds have attracted a great deal of interest, since they can be utilized widely in organic syntheses and materials chemistry.[2] Many of the chemicals used in industry can be synthesized using organosilicon compounds, for instance alcohols.[3] One of the significant methods to generate organosilicon compounds in the laboratory is hydrosilylation.[4]

The aim of this chapter is to give a summary of recent research progress in manganese catalyzed hydrosilylation reactions. Several classes of supporting ligands such as carbonyl, pyridine, salen, and N-heterocyclic carbene (NHC), will be included in this chapter. I also will discuss the application of these complexes in the hydrosilylation reactions of several types of unsaturated organic compounds including aldehydes, ketones, esters, carbocyclic acid derivatives, alkenes, and alkynes.

Manganese carbonyl catalysts

Early studies by the Cutler group reported using manganese carbonyl as catalyst in the hydrosilylation of carbonyl compounds, especially for ketones.[5] Using 2.4 % of $(PPh_3)(CO)_4MnC(O)CH_3$ was efficient to reduce the carbonyl groups to silyl ethers. The yields were 90 % with $PhMe_2SiH$ in C_6D_6 with several ketone compounds such as acetone and cyclohexanone. Meanwhile, the reaction could proceed under solvent free conditions in a lower loading of the catalyst. This study suggested the reaction mechanism involved the coordination of the unsaturated manganese silyl as a reaction intermediate. Later, manganese carbonyl compounds were reported for the hydrosilylation of carboxylic acids to obtain aldehydes in excellent yields. In the presence of triethylsilane, 5 % of $Mn_2(CO)_{10}$ reduced 4-methylphenylacetic acid at room temperature to the corresponding aldehyde under UV irradiation.[6] More recently, researchers used the same catalyst in combination with the LPO (dilauroylperoxide) initiator was reduce alkynes to obtain *Z*-alkenes in a good regioselectivity (Scheme 1). The Mn catalyst, $Mn_2(CO)_{10}$ (10 mol%),

in an association with 20 mol% LPO, was able to hydrosilylate diphenylacetylene at 120 ºC in decalin as solvent. Meanwhile, mononuclear $MnBr(CO)_5$ with $AsPh_3$ ligand achieved *E*- products in high chemoselectivity (Scheme 1). Thus, 5% of this catalyst with 20% of $AsPh_3$ were used to convert diphenylacetylene to Z-alkene at 150 ºC in toluene in the presence of 1.5 equiv. of phenylsilane.[7] However, a major disadvantage is that the reaction required a higher temperature and the double amount of the additive ligands.



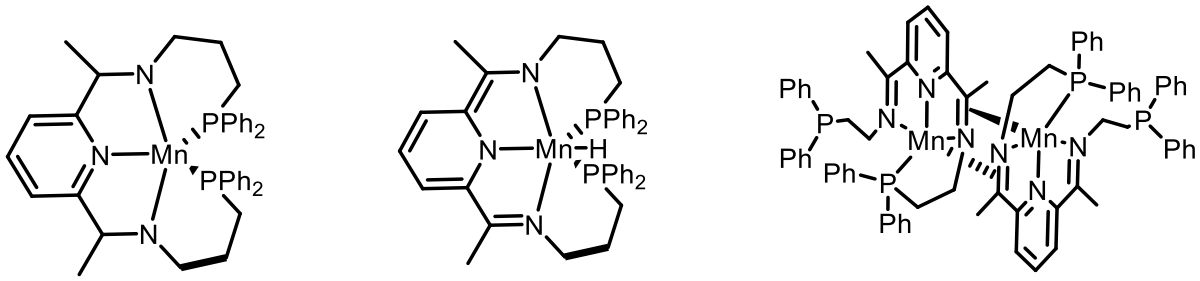
Scheme 1. Hydrosilylation of alkynes.

Manganese complexes with pyridine based ligands

The Trovitch group first reported the hydrosilylation of ketones and esters using manganese pyridine complexes.[8] Since then, the same group, Huang,[9] and Thomas[12] have extended their work to catalytic reduction of a variety of double bonds including carbonyls, carboxyls, and alkenes. In general, the activity and the selectivity of manganese pyridine complexes were excellent to intermediate.

Pyridine diamine manganese complex was an efficient catalyst for the reduction of ketones and esters through hydrosilylation reactions in the presence of 1 equiv. of $PhSiH_3$ with the catalyst loading of 0.01-1% (Scheme 2, **1**).[8] The reactions proceeded in the absence of a solvent with high turnover frequencies up to 1280 min^{-1}. Furthermore, using **1** with different hydrosilanes such as $(EtO)_3SiH$ and Ph_2SiH_2 reduced acetophenone. Notably, esters were also reduced in moderate yields under mild conditions, and the reaction proceeded by cleavage of the acyl C-O bond. It was

also shown that complex **1** was stabilized by phosphine groups. These studies demonstrated the high capability of manganese to catalyze the hydrosilylation transformation and achieved the highest turnover number for transition metals.



Scheme 2. Manganese pyridine complexes.

Manganese pyridine hydride complex was reported for the reduction of carboxylic acids (Scheme 2, **2**). The catalyst was prepared by the addition of $NaEt_3BH$ to manganese complex **1**.[9] It was found to catalyze the reduction of benzyl formate in similar conditions as the previous manganese complex **1**. When reactivity was compared, complex **2** was highly active for carboxylic acids reduction, while manganese complex **1** was active for carbonyls hydrosilylation. To gain additional insight, a large kinetic isotope effect (KIE = 4.2 ± 0.6) was found for diisopropyl ketone when it was catalyzed by complex **2**, indicating that the breaking of the Si-H bond was the rate determining step. This step was first order with respect to silanes and substrates. While the KIE was moderate (2.2 ± 0.1) for diisopropyl ketone with complex **1**, the kinetic analysis demonstrated that a first order mechanism relied on the concentration of substrate, manganese complex **1**, and silane. These observations can be explained on the basis that the catalysts undergo different mechanisms. The insertion mechanism was proposed for manganese complex **2**, while manganese complex **1** proceeded through the Ojima mechanism (Figures 2 & 3).

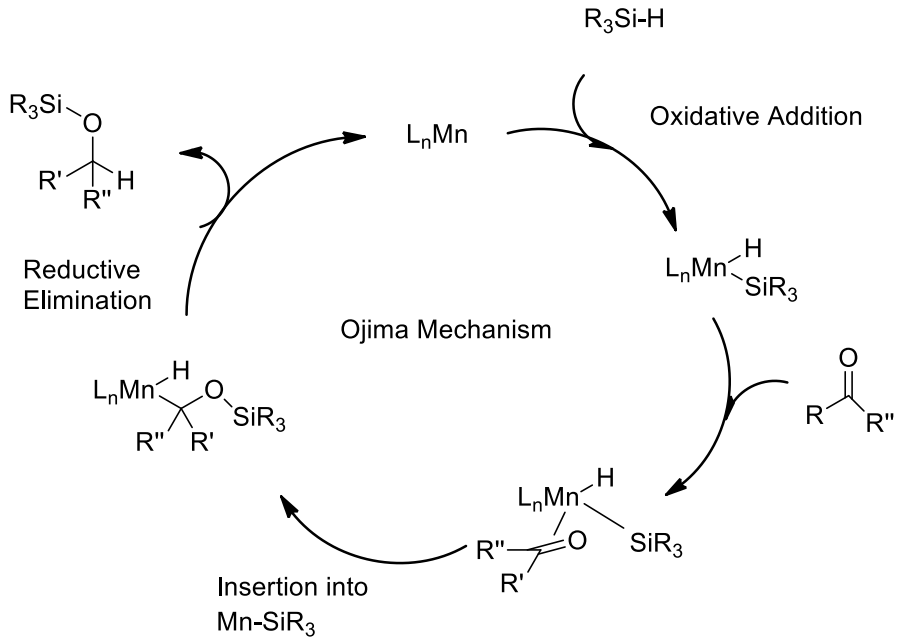


Figure 2. Ojima mechanism for hydrosilylation of carbonyl compounds.

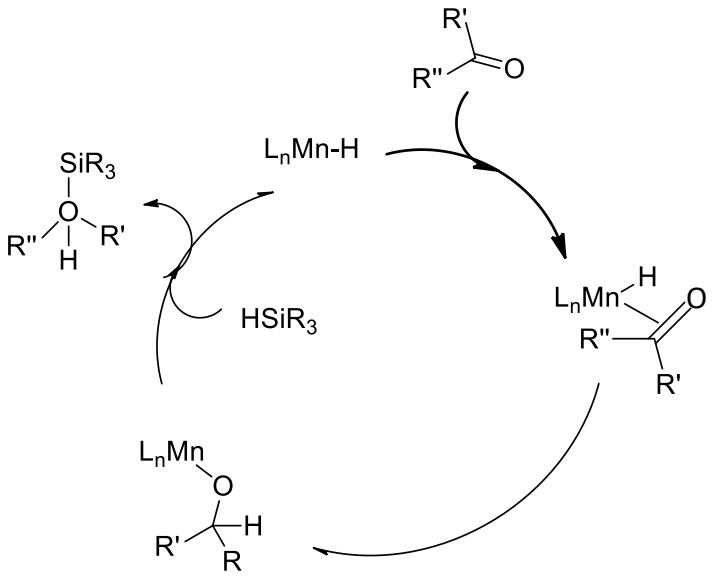
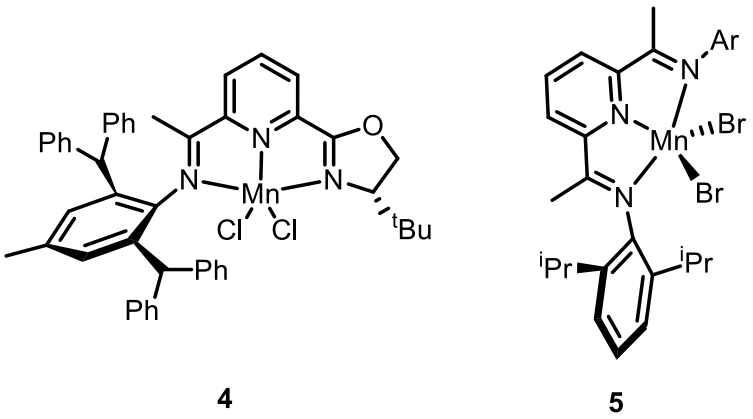


Figure 3. Insertion mechanism for hydrosilylation of carbonyl compounds.

Reduction of ($^{Ph}_2{}^{PEt}$PDI)$MnCl_2$ afforded dimer [(^{Ph2PEt}PDI)Mn]$_2$ (Scheme 2, **3**). Importantly, this new compound showed higher activity with lower loading at 0.001 mol% in the hydrosilylation of carbonyl compounds. Furthermore, the dihydrosilylation of carboxylic acids could be achieved using this catalyst, with turnover frequency up to 330 min^{-1}. The mechanistic study demonstrated that the catalyst system proceeded by the Ojima mechanism, involving the dissociation of phosphine and oxidative addition of Si-H bond to generate a five-coordinate silyl intermediate. The disadvantage of this compound is that its activity decreased with a donor function group such as alkenes. Similar observations were also reported with **2**.[10]

Iminopyridine oxazoline manganese dichloride complex was demonstrated by Huang's group for the asymmetrical reduction of aryl ketones for the first time (Scheme 3, **4**).[11] They found that 0.1 mol% of the catalyst was able to convert ketones to desired alcohols in high yields. The reaction proceeded by activation with $NaBEt_3H$. Primary silane achieved the highest enantioselectivity (up to 98%) compared to other silanes such as a tertiary and secondary silanes, which provided lower chemoselectivity. Increasing the steric bulk in a benzylic substituent in an acetophenone such as 1,2-diphenylethanone gave rise to lower enantioselectivity (69%).



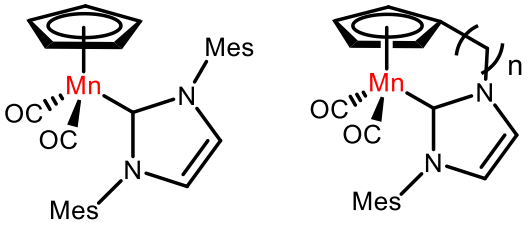
4 **5**

Scheme 3. Manganese pyridine complexes containing halogens.

Pyridine manganese dibromide complex has been developed for the catalytic hydrosilylation reaction (Scheme 3, **5**). Alkenes could be reduced in high regioselectivity in the presence of a base, NaO^{t}Bu. Several alkenes such as aliphatic alkenes and terminal alkenes were all converted with excellent yields to obtain corresponding linear hydrosilylation products at a low loading of the manganese compound (0.5%).[12] The detailed mechanism was not available, however, the base was essential to activate the catalyst, and the loading of the base should be triple of the manganese complex.

Manganese N-heterocyclic carbene complexes

Manganese complexes containing N-heterocyclic carbenes (NHC) and η5-cyclopentadienyl (Cp) ligands have been isolated and characterized (Scheme 4, **6**).[13] Compound **6** was obtained by treating [CpMn(CO)$_3$] with N-mesitylimidazole. It was an active catalyst to hydrosilylate ketones with 1 mol% loading under UV light. The reaction tolerated different functional groups such as methoxy and halogens. It was proposed that the catalyst was operative by the Ojima mechanism.[14] Linking the Cp ring with NHC afforded complex **7**, but it was found to be less active. Importantly, these complexes were not active without UV light.[14]

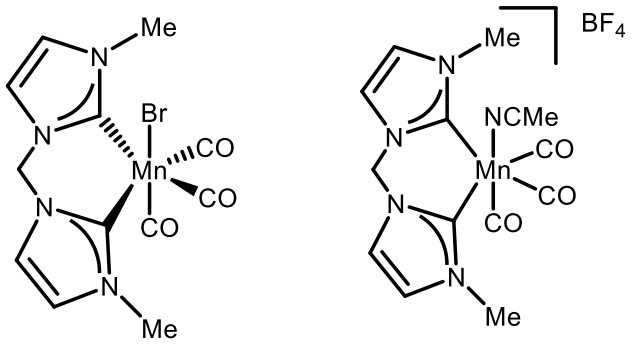


6 **7**

Scheme 4. Manganese NHC complexes.

Royo's group has redeveloped manganese compounds containing N- heterocyclic carbenes (NHCs) with tricarbonyl ligands in the hydrosilylation of ketones (Scheme 5, **8, 9**).[15] They revealed that the NHC ligand enhanced the reactivity by allowing flexibility of the coordination

environment. These complexes were easy to synthesize in one step by reacting $Mn(CO)_5Br$ with different imidazolium salts. They were stable at room temperature, and the catalytic reactions could be performed in the air. At 1 mol% loading, these complexes were active in the absence of UV light, but they required a temperature of 80 ºC. A variety of hydrosilanes such as polymethylhydrosiloxane, which was cheap and not harmful to the environment, were utilized to reduce the ketones and other unsaturated bonds. Functional groups such as nitro, methyl, methoxyl, and halogens exhibited mild yields. A radical mechanism was proposed for these transformations.



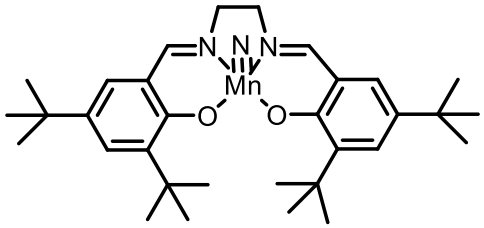
8 **9**

Scheme 5. Manganese NHCs complexes.

Manganese salen complex

Our group has developed a salen manganese complex, (3,5-t-Bu_2-salen)MnN, in hydrosilylation (Scheme 6, **10**). Catalyst loading as low as 0.1 mol% was capable of hydrosilylating carbonyl compounds.[16] Various aldehydes and ketones such as benzaldehyde, *p*-NO_2-benzaldehyde, and acetophenones were converted to alcohols in good yields under mild conditions. The turnover number was up to 196 min^{-1} with *p*-NO_2-benzaldehyde. Reactions could be performed at room temperature, for example, it took 22 hours for the complete conversion of benzaldehyde in $CDCl_3$ using 1 mol% of catalyst. Therefore, this system was typically heated at 80 ºC to operate, which resulted in a shorter reaction time of 2-3 h. The mechanism of this catalytic

transformation is still unclear, but it was suggested that Mn(V) underwent reduction first to give an active Mn(III) species followed by activation of hydrosilane and attack by the carbonyl groups.



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Scheme 6. Manganese salen complex.

Conclusions

Manganese complexes, based on an inexpensive metal, have proved to be viable alternative for precious metal based catalysts for reduction reactions of organic compounds. The ability to accommodate several types of ligands provides additional advantages in modifying the activity and selectivity in catalysis. Recently, manganese complexes have been shown to be effective catalysts in hydrosilylation of a number of unsaturated bonds, which also exhibit tolerance for other functional groups. In most cases, the Ojima mechanism was proposed for carbonyl groups. However, further progress is needed, for example, in finding convenient ways to synthesize ligands and catalysts, and dealing with more sterically bulky substrates. These results warrant further investigation in manganese catalysis.

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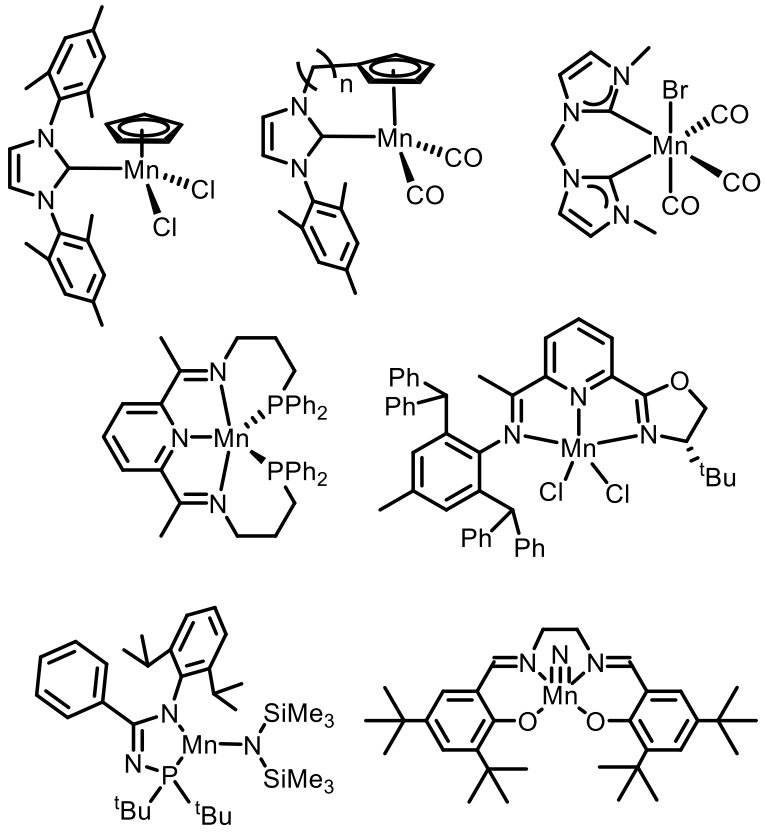
Chapter 2. Manganese Salan Complexes as Catalysts for Hydrosilylation of Aldehydes and Ketones

Introduction

There has been an emerging shift towards the first-row transition metals in catalysis.[1] Conventionally, the precious metals represented by palladium have dominated the field, particular in pharmaceutical industry. However, the toxicity and the increasing scarcity of these elements have raised health and sustainability concerns and stimulated the search for alternative catalytic systems. Because of their earth abundance and low toxicity, the first-row metals such as Fe, Co, Ni, Cu, and Zn[2] have attracted growing interest in various reactions. The distinct reactivity of first row metals may enable new transformations inaccessible by second and third row metals. As one of the most abundant transition metals, Mn has seen a recent resurgence of research beyond the traditional oxidation/oxygenation catalysis.[3] A wide variety of reactions, such as hydrogenation of CO_2, esters, ketones, and nitriles,[4] hydroboration of carbonyls and carboxylic acids,[5] electrochemical hydrogen production,[6] dehydrogenative olefination of alkyl-substituted heteroarenes and sulfones with alcohols,[7] alkylation of nitriles, esters and amides,[8] dehydrogenation of alcohols[9] and its application in synthesis of pyrroles and imides from amines and diols,[10] and dehydrogenative cross coupling of hydrosilanes and alcohols,[11] have been achieved with manganese catalysis.

Among these developments, hydrosilylation by manganese catalysts occupies a special place thanks to the early work by the Cutler group, showing simple manganese carbonyl complexes were effective catalysts for the hydrosilylation of various unsaturated substrates.[12] Hydrosilylation

of C=O containing compounds represents a mild and versatile approach for the reduction of these compounds and various metal and non-metal catalyzed reactions have been reported using commercial hydrosilane reagents. [13,14] Not surprisingly, recent research in manganese also provides a range of catalysts for the hydrosilylation of aldehydes, ketones, esters, amides, and carboxylic acids.[15,16] Efficient hydrosilylation of C=C double bonds by manganese catalysts have also been reported.[17] A few selected examples of manganese catalysts and precatalysts for hydrosilylation are shown in Scheme 7.



Scheme 7. Selected recent examples of Mn (Pre)Catalysts for hydrosilylation.

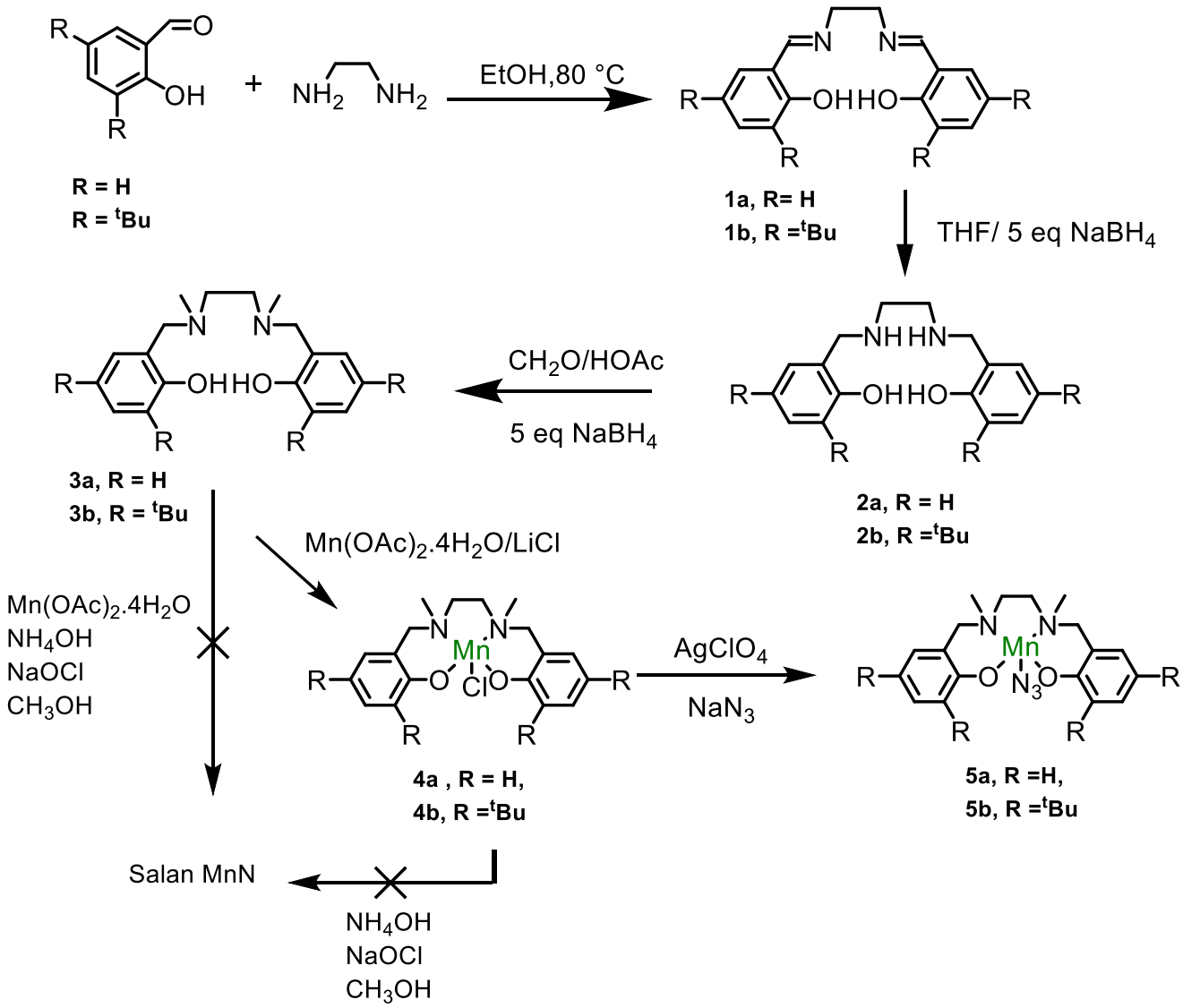
Metals supported by salen ligands have been widely reported as catalysts in different transformations. Previous work in our group has used a manganese salen complex to catalyze the hydrosilylation of carbonyl groups with low catalyst loading of 0.5 mol% and high yields, and

different function groups can be tolerated. On the other hand, salan ligands, which are derived from the hydrogenation of salen, have been less explored. Previous work has illustrated that salan could be a good ligand that bonds strongly to the transition metals, and provides catalytic reactivity as well as selectivity.[18] These results inspired us to characterize manganese salan complexes for the first time, where salan = N,N'-dimethyl-N,N'-bis(hydroxybenzyl)-1,2-diaminoethane. Salan ligand provides a flexible coordination site around the manganese center, so it helps the reaction to go. Therefore, to continue our interest in hydrosilylation reactions, we examined these complexes in reduction of different carbonyl compounds.

Results and Discussion

Synthesis and characterization of (salan)Mn complexes.

The salan ligands are synthesized by following the literature procedures.[19] Briefly, reaction of salicyaldehyde derivatives with diamine afforded the parent salen ligand, which was reduced with excess $NaBH_4$ to afford salan, which was subsequently methylated by reductive amination with $NaBH_4/CH_2O$. The metallation was carried out with $MnCl_2$ or $Mn(OAc)_2$ to first obtain the chloride compounds. The substitution with NaN_3 in the presence of $AgClO_4$ afforded the azido complex (Scheme 8).[23] The azido ligand in **5b** was confirmed by the peak at 2050 cm^{-1} in the FT-IR spectrum (Figure 4). Similarly, the parent (salan)$Mn(N_3)$ (**5a**) featured an azide stretching peak at 2037 cm^{-1}. The starting NaN_3 shows an IR peak at 2104 cm^{-1}. For comparison, the salen analogue, (salen-$^tBu_2$)$Mn(N_3)$, was also obtained in a similar procedure, and the IR peak for the azido ligand is observed at 2063 cm^{-1}. In the same context, Frantz et al. isolated (salen)MnN_3 derivatives, and the ν_{N3} vibrational mode appeared in the range 2046-2048 cm^{-1}.[20] The azide stretching frequencies for analogue (salan)CrN_3 of (**5a**) exhibits a peak at 2062.9 cm^{-1}, which is higher by 12 cm^{-1} approximately.[21]



Scheme 8. Synthesis of salan ligands and their Mn Complexes

Several attempts were made to prepare the manganese nitride complexes with salan ligands, because this would offer a direct comparison with the manganese nitride salen complex. However, these attempts were not successful (Scheme 8). The MnN(salen) complexes have been prepared using a procedure by Day et al, which employed bleach (NaOCl) as the oxidizing reagent in the presence of NH_4OH to furnish the Mn(V) nitride complexes. [22]We thought the salan ligands

were similar enough to the salen ligands, so this procedure was first attempted. However, our attempts under comparable conditions did not resulted in the desired diamagnetic products. Since the salan ligands could not dissolve completely in methanol in the reaction mixture in the first step, we changed the solvent to ethanol in this step but the product could not be dissolved in dichloromethane or water in the final stage. Other parameters such as reaction times and temperatures were also explored without any desirable results. A two-step process with separated reaction flasks, i.e. isolating the (salan)MnCl complex in the first step, and treating it with ammonia and bleach in the second step, seemed to lead to the isolation of the free ligand in the end. A different approach of photolysis of (salan)Mn(N_3) precursor under UV radiation was not successful either. Because of these results, we later focused on the (salan)Mn(N_3) complex which showed reasonable activity in hydrosilylation reaction.

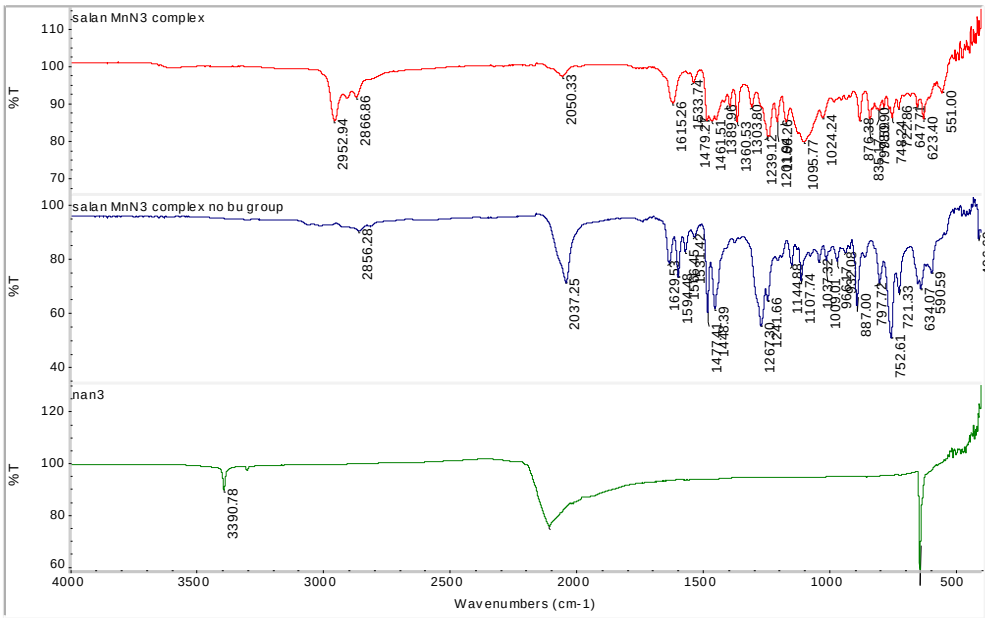


Figure 4. Comparison of FT-IR spectra of (salan-^{t}Bu$_2$)Mn(N_3) (**5b**) (top), (salan)Mn(N_3) (**5a**) (middle) and NaN_3 (bottom)

Catalytic Hydrosilylation

Having manganese(III) complexes in our hand, we first examined the efficacy of complex **5b** in the hydrosilylation under a variety of reaction conditions, with benzaldehyde as a model substrate with the results compiled in (Table 1). It can be seen that phenylsilane was chosen as a source of hydrogen. Screening different solvents in the reaction illustrated that benzene is an optimal solvent in this system, while the hydrosilylation in other common solvents such as CD_3CN and $CDCl_3$ are slower or with low conversions. To our delight, the reaction using benzene as solvent at elevated temperature exhibits high conversion of 100 % with 0.5 mol % loading of catalyst (entry 1, Table 1). When using 0.5 mol % of **5b** and $PhSiH_3$ in CD_3CN, a mixture of silyl ethers was observed by the NMR within 6.5 h with 94 % conversion (entry 5, Table 1). Unlike C_6D_6 and CD_3CN, $CDCl_3$ showed lower conversion after a long reaction time (entry 6, Table 1). Increasing the loading of the catalyst to 1 mol % did not enhance the activity and lowering the loading of the $PhSiH_3$ (0.5 equiv.) resulted in no reaction (entry 7&8, Table 1). The lower activity in $CDCl_3$ could be explained by the lower boiling point of chloroform compared to the other solvents. A tertiary silane, triethoxysilane, was also active for the hydrosilylation in CD_3CN and 54% conversion of PhCHO was observed after 8 h of reaction (entry 9, Table 1). At this point, the triethoxysilane was completely consumed, though the side reaction product was not identified. When the loading of the triethoxysilane was increased to two equivalents of PhCHO, the complete conversion of PhCHO could be achieved within 8 h (entry 10, Table 1). ^1H NMR spectra in Figure. 5 showed the conversion of PhCHO under this condition. Other reaction parameters were also explored. When the reaction was run at 80 ºC or at room temperature, the hydrosilylation reaction proceeded slowly (entry 2 & 3, Table 1), but the reaction could still reach 90% conversion after a

few days at 80 ºC. When the reaction was run under air, only minimal conversion was obtained within 5 h (entry 4, Table 1). So the rest of the reactions were carried out under N_2.

Table 1: Hydrosilylation of PhCHO under different conditions[a].

Entry	SalanMnN_3 (**5b**)	Silane(equiv.)	solvent	Temp (°C)	Time (h)	Conversion (%)
1	0.5%	$PhSiH_3$(1)	C_6D_6	120	40 min	100%
2	1 %	$PhSiH_3$(1)	C_6D_6	RT	67 h	20%
3	1%	$PhSiH_3$(1)	C_6D_6	80	13 h	90%
4[b]	1%	$PhSiH_3$(1)	C_6D_6	120	3 h	4.8%
5	0.5%	$PhSiH_3$(1)	CD_3CN	120	6.5	94%
6	0.5%	$PhSiH_3$(1)	$CDCl_3$	120	3 days	<1%
7	0.5%	$PhSiH_3$ (0.5)	$CDCl_3$	120	68 h	0 %
8	1%	$PhSiH_3$(1)	$CDCl_3$	120	4 days	10%
9	0.5%	$(EtO)_3SiH$(1)	CD_3CN	120	8 h	53.6 %
10	0.5%	$(EtO)_3SiH$(2)	CD_3CN	120	8 h	100 %
11[c]	0.5%	$PhSiH_3$(1)	C_6D_6	120	84 h	9 %
12[d]	0.5%	$PhSiH_3$(1)	C_6D_6	120	84 h	87%
13[f]	0.5%	$PhSiH_3$(1)	C_6D_6	120	2.3	>99
14[g]	0.5%	$PhSiH_3$(1)	C_6D_6	120	12 h	100

[a] Reaction conditions: PhCHO (1 equiv.). The temperature refers to the heating bath temperature. [b] the reaction run in the air. [c] Reaction with complex **4b**. [d] Combination of **4b** with $AgClO_4$. [f] Reaction with complex **5a**.[g] Reaction using (salen)MnN_3.

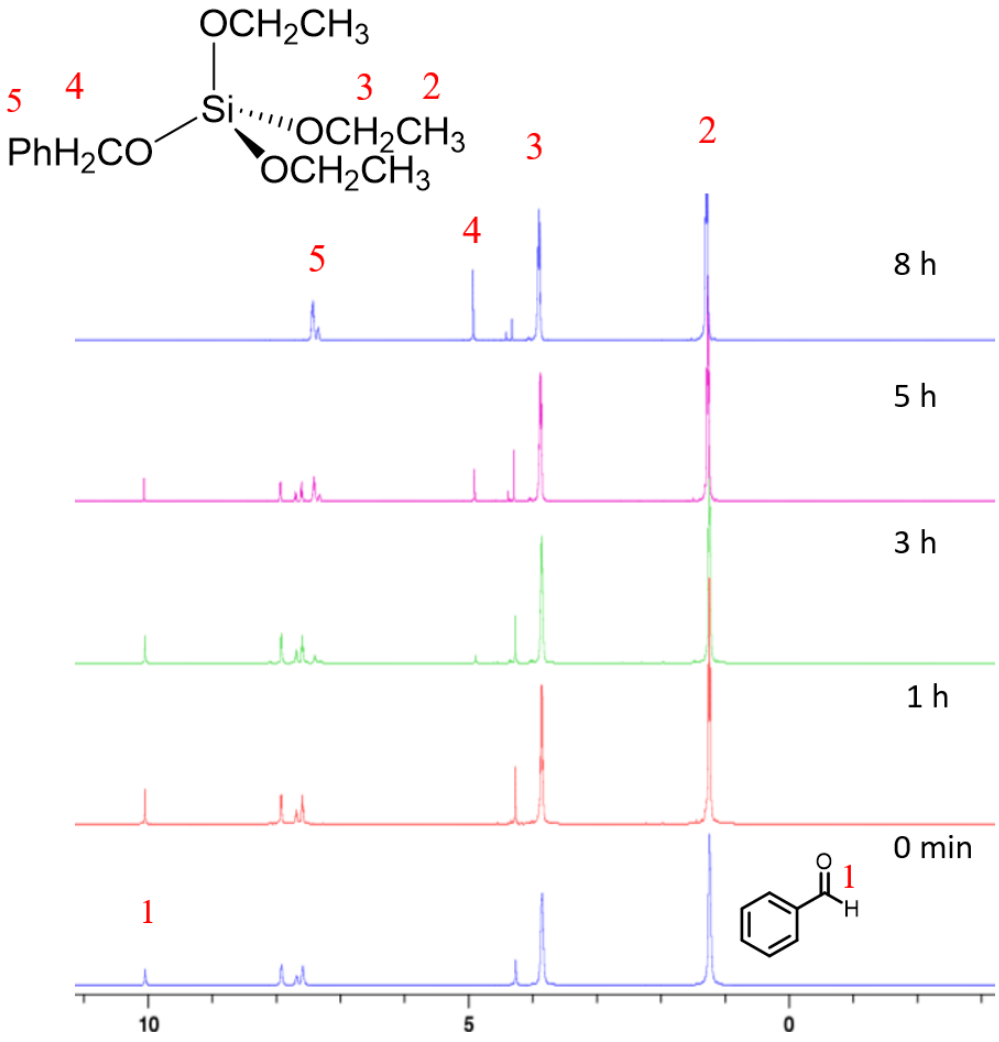


Figure 5. Reaction of benzaldehyde with triethoxysilane (Table 1, entry 10)

After we optimized the reaction condition, we examined the reaction with different types of salan Mn(III) complexes (entries 11-14, Table 1). The comparison of the reactivity of these catalytic systems were shown in (Figure 6). It is remarkable that the (3,5-^{t}Bu$_2$-salan)MnN$_3$ complex (**5b**) was the most active among these complexes. While the salan complex **5a** showed somewhat lower activity, the chloride complex (**4b)** alone showed little activity in hydrosilylation of PhCHO, but could be activated by treatment with $AgClO_4$. The hydrosilylation of PhCHO took place after an induction period and up to 90% conversion was achieved after 54 h.

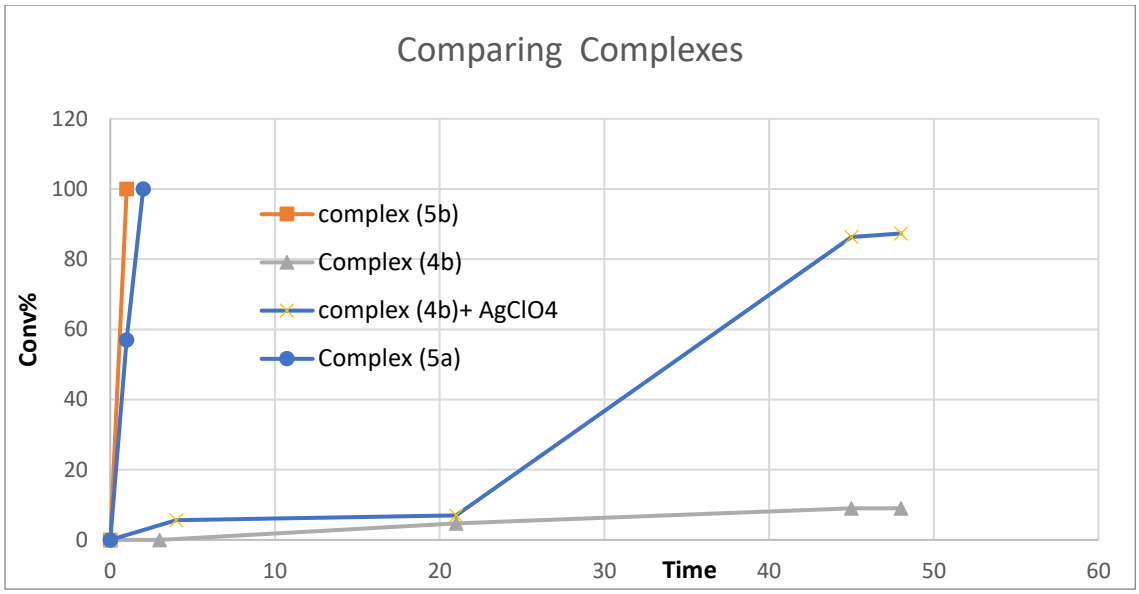
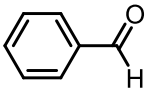
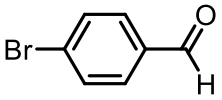
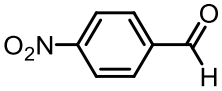
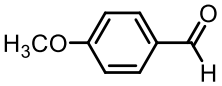
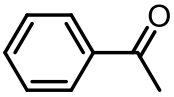
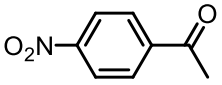
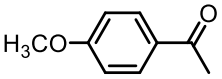
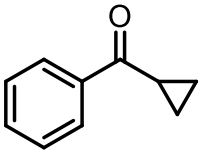
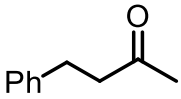
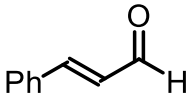
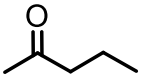


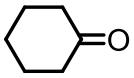
Figure 6. The conversion-time profile with different catalysts in hydrosilylation.

With the reaction condition established above, we carried out the hydrosilylation of a variety of carbonyl substrates in the presence of **5b**. Hydrosilylations of a variety of aldehydes and ketones occurred at 120 ºC with low loadings of the catalyst (0.5 mol %) in benzene-d_6 in presence of $PhSiH_3$ (Table 2). The corresponding alcohols were obtained after acidic workup. High conversions and good isolated yields were observed in these cases. The reaction proceeded faster with aldehydes when compared to ketones, as typically observed in hydrosilylation of carbonyl compounds.16[16] The aldehydes substrates bearing electron-withdrawing groups (Br, Cl, NO_2) were converted more rapidly than those with electron-donating groups (Me, OMe). Ketones with donating groups and withdrawing groups were tolerated (entry 5&6&7, Table 2). The progress of the reaction of ketone with methoxy group was shown in (Figure 7), and the methoxy group was shifted its place after 40 h (entry 7, Table 2). In addition, the reaction of the ketone bearing a nitro group in *para* position was peculiar under this condition in that no further conversion was observed at 40% after 12 h (entry 6, Table 2). The reaction was also selective toward carbonyl groups over

alkenes (entry 8, Table 2), since we couldn't see any reduction of unsaturated C=C double bond in cinnamaldehyde transformation (Figure 8). In addition to aromatic carbonyl compounds, aliphatic aldehydes and ketones also underwent hydrosilylation reactions under the same conditions (10&11&12, Table 2), and the conversions were generally high (>95%).

Table 1. Hydrosilylation of Aldehydes and Ketones Catalyzed by (salan)MnN_3[a].

Entry	Substrate	Time (h)	Conversion (%)	Yield (%)
1		40 min	100	-
2		5.3	100	60
3		2.3	100	70
4		61	100	95
5		41	93	73
6		12	40	-
7		40	100	62
8		15	100	-
9				
10		13	>99	85
11		36	>95	-

12		18	>96	-

[a] Reaction conditions: the reactions were performed with 1.0 equivalent of $PhSiH_3$, 0.5 mol% of catalyst **5b** in C_6D_6 at 120 °C in a J. Young NMR tube. The conversions were calculated from the ^1H NMR spectroscopy, and the yields were isolated yields of alcohols after acidic workup.

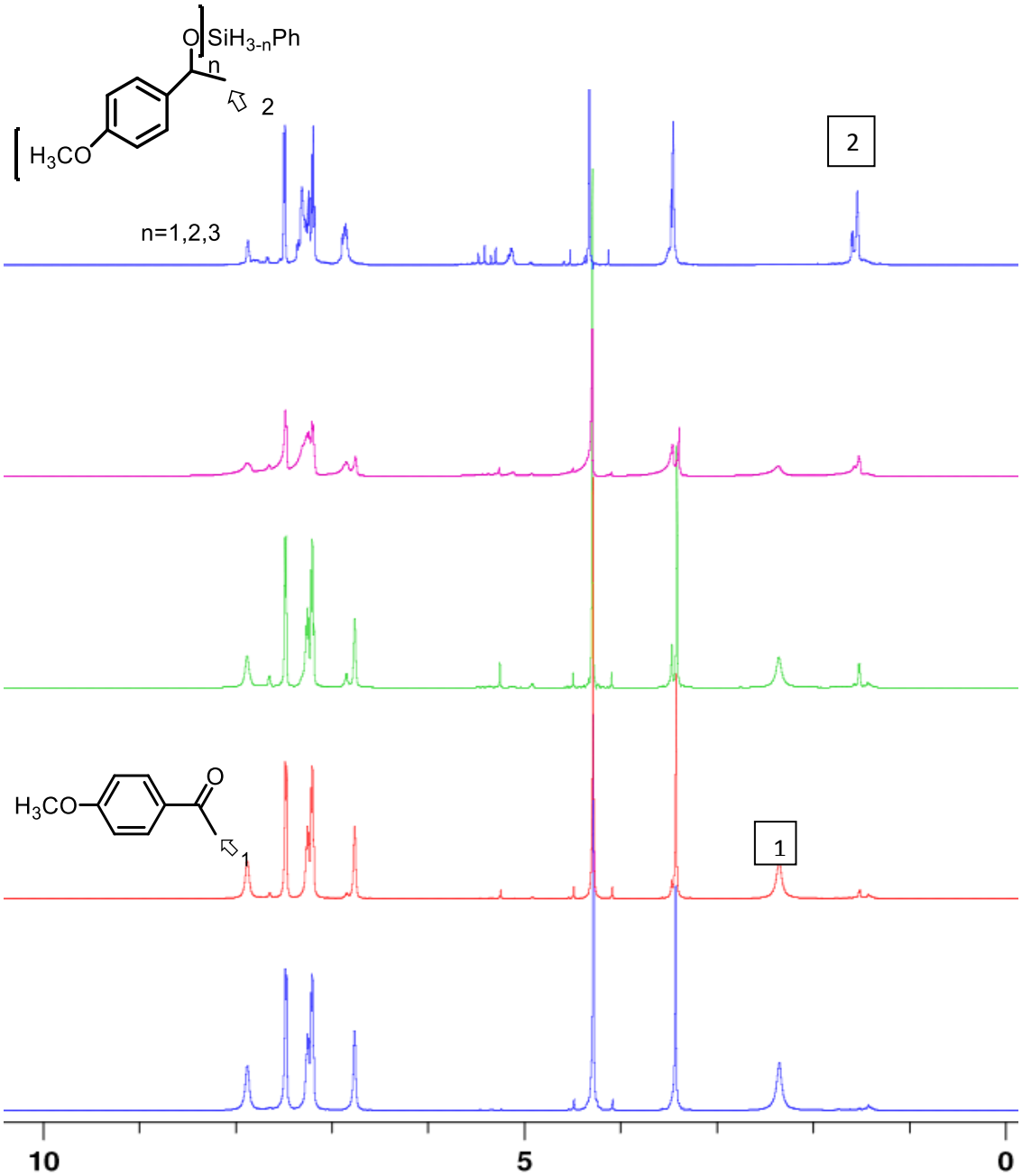


Figure 7. ^1H NMR of the Reaction of 4-methoxyacetophenone.

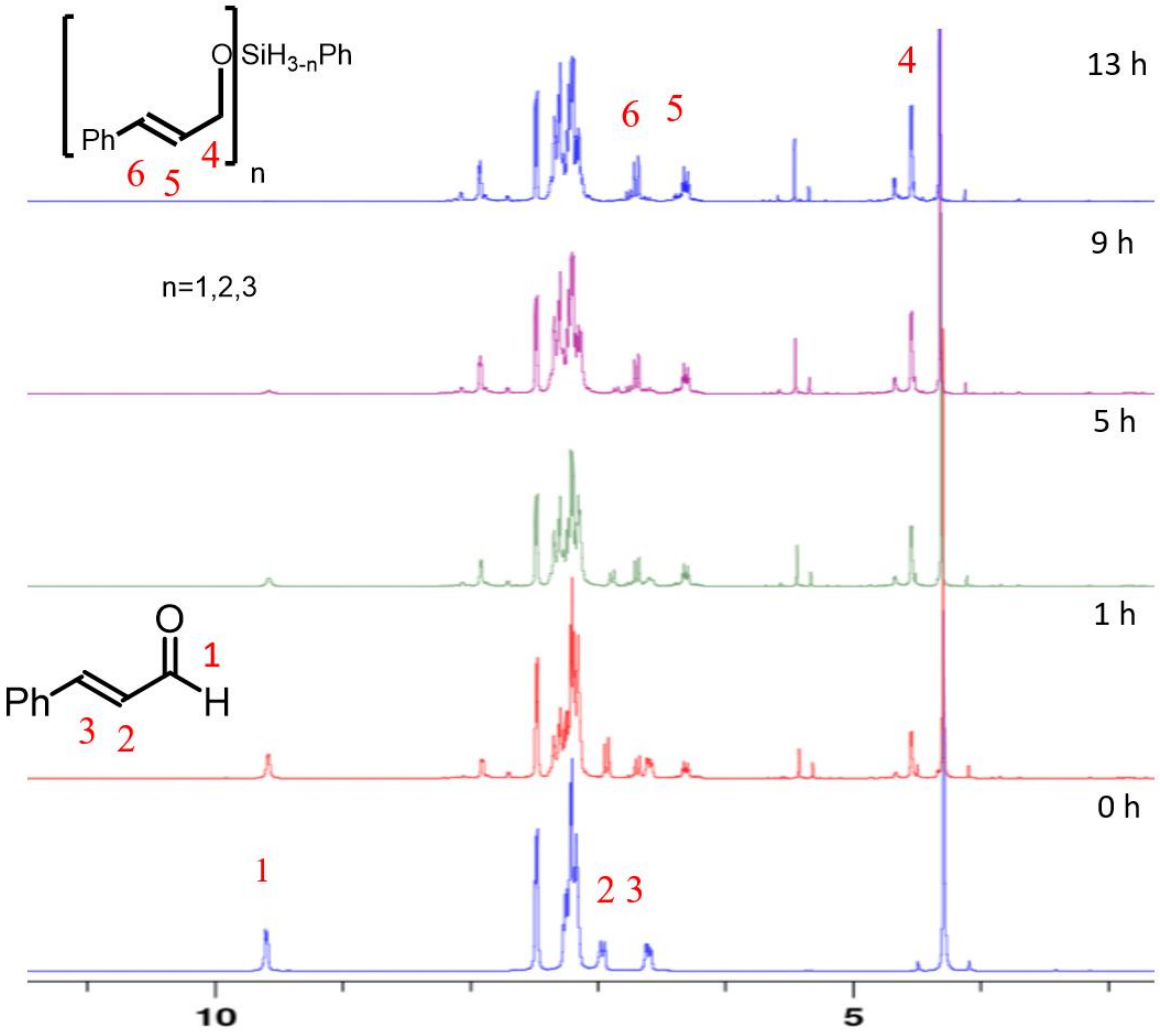


Figure 8. Hydrosilylation of cinnamaldehyde monitored by the NMR.

Mechanistic Aspects

In our previous study with (salen)MnN catalyst, it was observed that the reduction of MnN by hydrosilanes, as indicated by the color change and the NMR observations, was the first step of the activation of hydrosilanes. Though the exact nature of the reduced Mn species was not determined, it was thought to be a Mn(II) or Mn(III) species that could interact with hydrosilanes. In the current study we employed Mn(III) species as the (pre)catalyst so the reduction of Mn was not necessary. Different manganese(III) catalysts have shown in several hydrosilylation reactions, they could be efficient catalysts.[16] However, (salan)MnCl **4b** showed minimum catalytic activity

in the hydrosilylation of PhCHO, indicating that Mn(III) alone was probably not a determining factor. Activation of **4b** by $AgClO_4$ suggested that it was critical to open up the coordination site around the metal center for catalysis. The comparatively higher activity of **5b** (salan)MnN_3 *vs* **4b** (salan)MnCl could be attributed to the fact that azido is a better leaving group than chloride. Analogous (salan)CrN_3 complex was active in ring-opening reaction of epoxides, while (salan)CrCl complex was considered a precatalyst that required further activation.[23] By the same consideration, the reduction of MnN was presumably required to open up the coordination site in (salen)MnN catalysis. As to the further activation of the hydrosilanes, it is unclear at this stage, but the radical mechanistic is not expected, since no ring opening was observed with cyclopropyl phenyl ketone (Figure. 9).

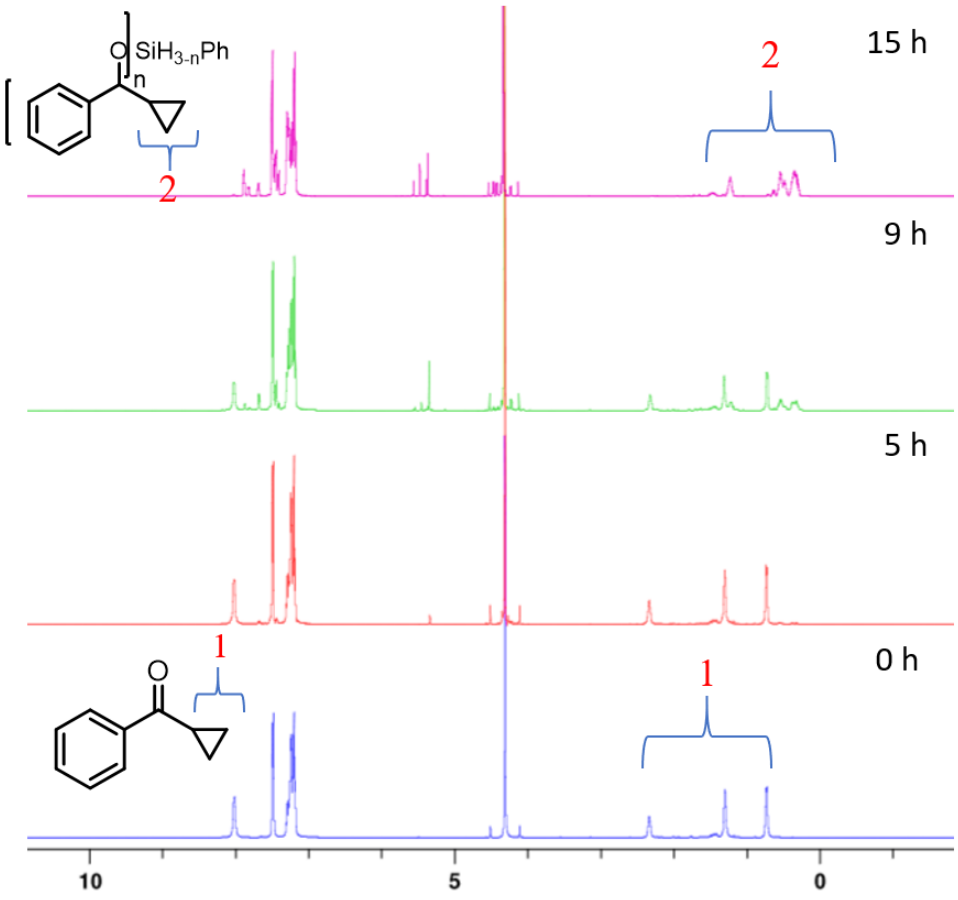


Figure 9. Hydrosilylation of cyclopropyl phenyl ketone monitored by the NMR.

Conclusions

A series of well-defined manganese salan complexes have been synthesized for the first time. These complexes exhibited catalytic activity in the hydrosilylation of various aldehydes and ketones. Decent to high yields of the corresponding alcohols were obtained after acidic workup, and a variety of functional groups in the carbonyl compounds such as methoxy, halides, and nitro groups were tolerated. The mechanistic study is under way. For future studies, different ligand systems may be used to improve the catalytic activity of manganese compounds.

Experimental Section

Method and Materials. All the substrates and reagents were obtained commercially, and the liquid substrates were degasified and dried over activated molecular sieves (4 Å) prior to the reaction. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-500 NMR spectrometer and referenced to the residue peaks in $CDCl_3$ (7.26), CD_3CN (1.94), or C_6D_6 (7.16).

Synthesis and Characterization of Ligand 2a. Ethylenediamine (55.1 mg, 0.917 mmol) in 30 mL of methanol was added dropwise to a stirred solution of salicylaldehyde (224 mg, 1.83 mmol) in 10 mL of methanol at RT. The reaction mixture was stirred for 5 min and sodium borohydride (693 mg, 1.83 mmol) was added portionwise within 10 min. After the mixture became colorless, was washed with distilled H_2O and extracted with dichloromethane. The organic phase was collected and dried over anhydrous Na_2SO_4, and the solvent was removed in a rotavapor. The ligand was obtained as white solid, and the yield was (244 mg, 98%). mp 117 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.77 (s, 4H), 3.93 (s, 4H), 6.72 (td, 2H), 6.77 (d, 2H), 6.91 (d, 2H), 7.11 (td, 2H); ^{13}C

NMR ($CDCl_3$, 125 MHz) δ 47.8 ($2CH_2$), 52.6 ($2CH_2$), 116.4 (2CH), 119.2 (2CH), 122.1 (2C), 128.4 (2CH), 128.9 (2CH), 157.9 (2C).

Synthesis and Characterization of Ligand 1b. To a stirred solution of salicylaldehyde (424 mg, 1.81 mmol) in 10 mL of methanol was slowly added a solution of ethylenediamine (54.3 mg, 0.904 mmol) in 30 mL of methanol. The mixture was refluxed for two hours and filtered through filter paper. A yellow solid was obtained as the product. The yield was 440 mg (99%), mp 174 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.28 (s, 18H), 1.43 (s, 20H), 3.92 (m, 2H), 7.06 (d, 2H), 7.36 (d, 2H), 8.38 (s, 2 H), 13.65 (s, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.4 ($6CH_3$), 29.5 ($6CH_3$), 33.3 (2C), 34.1 (2C), 35.0 ($2CH_2$), 117.9 (2C), 126.1 (2CH), 126.8 (2CH), 136.4 (2C), 139.9 (2C), 158.1 (2C), 165.9 (2CH).

Synthesis and Characterization of Ligand 2b. Ligand **1b** (541 mg, 1.09 mmol) was dissolved in 12 ml of THF then sodium borohydride (247 mg, 60 mmol) was added, and the reaction mixture was refluxed for three hours. When the mixture was colorless, it was washed with 100 mL of water and extracted with dichloromethane. The organic phases were dried over anhydrous Na_2SO_4, and the solvents were removed under the vacuum to obtain **2b** as a white solid. The yield was 528 mg (97%). mp 174 ºC ;^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.28 (s, 18H), 1.41 (s, 18H), 2.87 (s, 4H), 3.96 (s, 4H), 6.85 (d, 2H), 7.22 (d, 2H) 10.79 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.6 ($6CH_3$), 31.7 ($6CH_3$), 34.1 (2C), 34.9 (2C), 48.0 ($2CH_2$), 53.5 ($2CH_2$), 121.7 (2C), 123.1 (2CH), 123.2 (2CH), 136.0 (2C), 140.6 (2C), 154.4 (2C).

Preparation of Ligand 3a. Ligand **2a** (325 mg, 1.19 mmol) was dissolved in acetonitrile (27 mL) and acetic acid (4 mL) in a round bottom flask then formaldehyde (0.886 mL, 11.9 mmol, 37% in water) was added. After 20 min of stirring at room temperature, sodium borohydride (225 mg, 5.95 mmol) was added to the mixture and stirred for an additional 24 h at RT. Acetonitrile

was evaporated in a rotavapor, and the remaining residue was hydrolyzed with 2 N NaOH. The product was extracted using dichloromethane. The solvent was removed to obtain **3a** as a white powder. The yield was 510 mg (89%); mp 84 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.24 (s, 6H), 2.67 (s, 4H), 3.70 (s, 4H), 6.78 (td, 2H), 6.84 (dd, 2H), 6.96 (dd, 2H), 7.18, 10.75 (s, 2H) (td, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 41.7 ($2CH_3$), 54.1 ($2CH_2$), 61.8 ($2CH_2$), 116.2 (2CH), 119.1 (2CH), 121.6 (2C), 128.5 (2CH), 128.9 (2CH), 157.8 (2C).

Preparation of Ligand 3b. Ligand **3b** was prepared by the similar procedure as ligand **2a**. Ligand **2b** (541 mg, 1.09 mmol) was added to flask that containing acetonitrile (27 mL) and acetic acid (4 mL), after 5 min formaldehyde (0.812 mL,10.9 mmol) was added. The reaction was stirred at RT for 10 min, and sodium borohydride (206 mg, 5.45 mmol) was added. Then, the reaction was stirred at RT for 24 h. Acetonitrile was removed under vacuum, and the mixture was hydrolyzed with 2N NaOH and the product was extracted with dichloromethane. The yield was 542 mg (95%). mp 142-147 ºC;^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.27 (s, 18H), 1.39 (s, 18H), 2.26 (s, 6H), 2.63 (s, 4H), 3.66 (s, 4H), 6.80 (d, 2H), 7.20 (d, 2H), 10.68 (b, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 29.6 ($6CH_3$), 31.7 ($6CH_3$), 34.1 (2C), 34.8 (2C), 41.6 ($2CH_3$), 53.8 ($2CH_2$), 62.7 ($2CH_2$), 121.0 (2C), 123.0 (2CH), 123.3 (2CH), 135.6 (2C), 140.5 (2C), 154.2 (2C).

Preparation of Manganese Complex 4a. Ligand **3a** (121mg, 10 mmol) was dissolved in ethanol (70 mL), and then $Mn(OAc)_2 \cdot 4H_2O$ (182 mg, 20 mmol) was added to the reaction mixture. The resulting mixture was refluxed for 3 hours, and LiCl (47.4 mg, 30 mmol) was added. This solution was refluxed for an additional two hours. The solvent was removed under the vacuum, and dichloromethane was added. The mixture was washed with brine and H_2O solutions, then dried with an anhydrous Na_2SO_4. The solvent was removed under the vacuum to obtain **4a** as a brown solid. The yield was 115 mg (80 %); mp 178 -185 ºC; FT-IR 3362, 1554, 1353, 1263, 1184, 1034,

943, 756, 671,756 cm^{-1}. UV-vis in CH_3CN [nm, ε (M^{-1} cm^{-1})]: 325 ($1.70*10^4$), 275 ($7.84*10^4$), 220 ($1.70*10^5$).

Preparation of Manganese Complex 4b. Manganese complex **4b** was prepared by the similar procedure as manganese complex **4a**. Ligand **3b** (231 mg, 0.440 mmol) was dissolved in ethanol (100 mL) with constant stirring at RT, then $Mn(OAc)_2 \cdot 4H_2O$ (215 mg, 0.880 mmol) was added to the mixture. The reaction mixture was refluxed for three hours, and LiCl (55.9 mg, 1.32 mmol) was added. The mixture was then refluxed for an additional two hours. Ethanol was removed, and dichloromethane was added. The mixture was washed with brine and H_2O. The organic phase was isolated, and the solvent was removed. The yield was 231 mg (86 %); mp 184 ºC; IR 2953, 2904, 2867, 1605, 1463, 1443, 1390, 1304, 1236, 1203, 1166, 1172, 1104, 1019, 979 cm^{-1}. UV-vis in CH_3CN [nm, ε (M^{-1} cm^{-1})]: 325 ($5.83*10^4$), 285 ($1.16*10^5$), 225 ($2.04*10^5$).

Preparation of Manganese Complex 5a. In flask 1, ligand **4a** (221 mg, 0.568 mmol) was dissolved in in 10 mL of CH_3CN. In flask 2, $AgClO_4$ (117 mg, 0.568 mmol) was dissolved in 2 mL of CH_3CN. The mixture of flask 1 was added to flask 2 during 5 min of intervals. The precipitation of AgCl was observed immediately, and the mixture was stirred at RT for 16 hours. The mixture was then washed with CH_3CN through a silica, and NaN_3 (111 mg, 1.71 mmol) was added to the filtrate. The filtrate was stirred at RT for 24 hours. Then, ethyl ether was added, and the solution mixture was washed with H_2O three times. The organic phase was isolated and dried, and the solvent was evaporated under the vacuum to obtain **5a** as a brown solid. The yield was 135 mg (60%); mp 169- 173 ºC; IR 2855, 2036, 1629, 1594, 1566, 1531, 1477,1448, 1370, 1267, 1242, 1145,1107, 1037, 1009, 966. UV-vis in CH_3CN [nm, ε (M^{-1} cm^{-1})]: 460 ($2.27*10^4$), 375 ($5.45*10^4$), 340 ($5.91*10^4$), 310 ($9.09*10^4$), 260 ($1.09*10^5$), 240 ($1.45*10^5$).

Preparation of Manganese Complex 5b. It was prepared by a procedure similar to complex **5a**. (343 mg, 0.561 mmol) of **4a** in acetonitrile was added to the solution of (116 mg, 0.561 mmol) $AgClO_4$ in acetonitrile over 5 min. The mixture was stirred for 16 hours and filtered through silica using 20 mL of CN_3CN two times. After that, NaN_3 (109 mg, 1.63 mmol) was added, and the mixture was stirred at RT for 24 h. The mixture then diluted with ethyl ether (15 mL) and washed with H_2O. The organic phase was isolated and dried, and the solvent was removed under the vacuum. The yield was 242 mg (70%); mp 183 ºC; IR 2956, 2904, 2866, 2049, 1612, 1534, 1474, 1467, 1443, 1390, 1360, 1303, 1234, 1202, 1165, 1103, 1018, 979 cm^{-1}. UV-vis in CH_3CN [nm, ε (M^{-1} cm^{-1})]: 475 (30864), 285 (73170), 240 ($8.53*10^4$), 215($3.41*10^5$), 225 ($2.43*10^4$).

General Procedures for Hydrosilylation. In a J Young NMR tube catalyst (0.5 mol %), substrate (1 equiv.), C_6D_6 (0.35 mL), and $PhSiH_3$ (1 equiv.) were added in order under nitrogen. The mixture was heated at 120 ºC and monitored by the NMR. When the reaction was completed, it was transferred to a vial by 2 mL of diethyl ether. The mixture was then hydrolyzed using HCl (2 mL, 1M) and extracted with diethyl ether. The organic phase was combined and dried over Na_2SO_4. After removal of solvent, the alcohol product was isolated by column chromatography using silica with hexane-EtOAc as eluent. The final products were confirmed by ^1H NMR.

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