Leibniz-Institut für Katalyse e.V.

an der Universität Rostock

Isomerization of Allylic Alcohols to the Ketones Catalyzed by First-Row Transition Metal Pincer Complexes

Dissertation

zur Erlangung des akademischen Grades

Doctor rerum naturalium (Dr. rer. nat.)

der Mathematisch-Naturwissenschaftlichen Fakultät

der Universität Rostock

vorgelegt von

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geb. am 19. 06. 1987 in P. R. China

Rostock, 24.05.2018

urn:nbn:de:gbv:28-diss2018-0103-8

Die vorliegende Arbeit entstand in der Zeit von September 2014 bis April 2018 am Leibniz-Institut für Katalyse e.V. an der Universität Rostock.

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Tag der Einreichung: 24.05.2018

Tag der Verteidigung: 03.07.2018

After endless mountains and rivers that leave doubt whether there is a path out, suddenly one encounters the shade of a willow, bright flowers and a lovely village.

山穷水尽疑无路，柳暗花明又一村。 [宋] 陆游

Acknowledgement

For more than 3 years learning chemistry and doing chemical research in such a wonderful institute, I have got countless help from many nice people. Without the assistance of them, I could not imagine that this thesis could have been finished. Therefore, I want to express my sincere appreciations to all of these lovely people who gave me so much support during my researching period in Rostock.

Foremost, I would like to extend my deeply gratitude to my supervisor Prof. Dr. Johannes Gerardus de Vries, who gave me an invaluable opportunity to join such a perfect international group. To be as a distinguished homogeneous chemistry scientist, his ingenious insight and artistic idea towards research, also his consistent patient supervision and kind inspiration throughout my scientific research showed me how to grow into a qualified, upright and responsible researcher.

High tribute shall be paid to my group leader Dr. Sandra Hinze for her advanced experiment skills and fruitful knowledge about chemistry. I would like to express my gratitude to her for the patient discussion and careful correction of my papers and this dissertation.

I want to thank my group leader Dr. Sergey Tin for his patient help in this thesis.

My profound appreciation will go to Prof. Dr. Haijun Jiao who shows so much consideration to my research and this thesis. At the same time, I am very indebted to Zhihong Wei for her detailed careful computational work and useful discussion about the mechanism.

Thanks should be given to Brian Speigelberg for his big contributions to the cobalt and iron projects.

It is very generous of Delong Han for sharing his catalyst and also showing me the synthesis of the catalyst at the very beginning. I would like to I warmly appreciate the vehement assistance from him that made me feel hopeful about my research and also saved lots of time.

I am so grateful for the aid from Prof. Dr. Angelika Brückner, Dr. Jabor Rabeah, Dr. Ursula Bentrup and Sven Adomeit for their in-situ measurement and also their professional discussion about the results.

It’s my honor to be a colleague with Dr. Yuting Fan, Dr. Arianna Savini, Dr. Sergey Tin, Brian Spiegelberg, Richard van Heck, Pim Puylaert, Bartosz Wozniak, Fatima El Ouahabi, Ronald A. Farrar Tobar, Christoph Prichatz, Bernhard Stadler, I would like to give thanks to all of them for their assistances to me in both lab and life.

I would like to appreciate all my friends: Prof. Dr. Shuping Luo, Prof. Dr. Qiang Liu, Prof. Dr Yuehui Li, Prof.Dr. Xiaofeng Wu, Prof. Dr. Lin He, Prof. Dr. Xianjie Fang, Prof. Dr. Kaiwu Dong, Dr. Dengxu Wang, Dr. Junhui Wang, Dr. Wu Li, Dr. Xinjiang Cui, Dr. Feng Chen, Dr. Haoquan Li, Dr. Conghui Tang, Dr. Jianbin Chen, Dr. Jiawang Liu, Dr. Jianbo Feng, Dr. Lin Wang, Dr. Weiping Liu, Dr. Tao Wang, Dr. Shaoli Liu, Dr. Yun Shi, Dr. Xinxin Tian, Dr. Jie Liu, Dr. Jiawang Liu, Dr. Yun Zhao, Yahui Li, Xin Liu, Rui Sang, Yuya Hu, Shaoke Zhang, Zechao Wang, Zhiping Yin, Teng Li, Bin Xing, Yaoyuan Zhang, Jiadong Xiao, Yanjun Sun, Wei Zhou, Shanlei Han, Fengxiang Zhu, Jianxing Xu, for giving me such a nice time in LIKAT.

Acknowledgement

I wish to give my sincere appreciation to all my friends in Rostock.

I am truly grateful to the analytical department of LIKAT for their efficient and constructive analysis of my chemistry.

It is really a nice time to play together with all the LIKAT football players. I really enjoy every match with them, thanks a lot, Prost!

I deeply appreciate the China Scholarship Council (CSC) for the 3 years financial support.

Last but not the least, special thanks should be given to my parents and my sister, of course, also my lovely nephew, for their consistent encouragement and support which are very important for me, I love you all forever.

Abstract

Isomerization of Allylic Alcohols to the Ketones Catalyzed by First-Row Transition Metal Pincer Complexes

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This thesis mainly describes the isomerization of allylic and homo-allylic alcohols to the corresponding carbonyl compounds in the presence of inexpensive transition metal complexes. [Fe(PNP)(CO)HCl] (PNP=di-(2-diisopropylphosphanyl-ethyl)amine), activated in situ with KO^{t}Bu, is a highly active catalyst for the isomerization of allylic and homo-allylic alcohols to ketones without an external hydrogen supply. High reaction rates were obtained at 80 ^{o}C, but the catalyst is also sufficiently active at room temperature with most substrates. Isomerization of allylic alcohols to the desired ketones could be performed in the presence of 0.1 mol% of [Mn(PNP)(CO)$_2$Br] (PNP=di-(2-diphenylphosphanyl-ethyl)amine) and KO^{t}Bu. An additive free [Co(PNP)Cl$_2$] (PNP=di-(2-diphenylphosphanyl-ethyl)amine) catalyzed isomerization reactions of allyl alcohols to the corresponding ketones is described. Both aliphatic and aromatic allylic alcohols are suitable substrates. The aromatic substrates may possess electron-withdrawing or electron-donating substituents, in all possible positions of the phenyl ring. In addition the proposed reaction mechanism was verified by DFT computation.

Isomerisierung von Allylalkoholen zu Ketonen katalysiert durch Übergangsmetallkomplexe der ersten Reihe mit Pinzettenliganden

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Diese Arbeit beschreibt die Isomerisierung von Allyl- und Homoallylalkoholen zu den entsprechenden Carbonylverbindungen in Gegenwart von kostengünstigen Übergangsmetallkomplexen. [Fe (PNP) (CO) HCl] (PNP = Di- (2-Diisopropylphosphanyl-ethyl) amin), in situ mit KOtBu aktiviert, ist ein hochaktiver Katalysator für die Isomerisierung von Allyl- und Homoallylalkoholen zu Ketonen ohne externe Wasserstoffversorgung mit hohen Reaktionsgeschwindigkeiten bei 80°C. Daneben zeigt der Katalysator auch bei Raumtemperatur mit den meisten Substraten ausreichend Aktivität. Weiterhing wird gezeigt, dass die Isomerisierung von Allylalkoholen zu den gewünschten Ketonen ebenfalls in Gegenwart von 0,1 Mol-% [Mn (PNP) (CO) 2Br] (PNP = Di- (2-diphenylphosphanyl-ethyl) amin) und KOtBu durchgeführt werden kann. Eine additivfreie [Co (PNP) Cl2] (PNP = Di- (2-diphenylphosphanylethyl) amin) -katalysierte Isomerisierung von Allylalkoholen zu den entsprechenden Ketonen wird ebenfalls beschrieben. Sowohl aliphatische als auch aromatische Allylalkohole sind hierbei geeignete Substrate. Die aromatischen Substrate können elektronenziehende oder elektronenschiebende Substituenten in allen möglichen Positionen des Phenylrings besitzen. Zusätzlich wurde der postulierte Reaktionsmechanismus mittels Dichtefunktionaltheorie(DFT) untersucht und verifiziert.

List of abbreviations

Ad	Adamantyl
atm	Atmospheric pressure
$BAr^{F}_{4}^{-}$	Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion
binap	(±)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene
BMIM	1-butyl-3-methylimidazolium
Cat.	Catalyst
COD	1,5-Cyclooctadiene
con.	Conversion
cot	Cyclooctatetraene
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cpr	Cyclopropyl
Cy	Cyclohexyl
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCE	Dichloroethane
DCM	Dichloromethane
DFT	Density functional theory
dipb	1,2-Bis(diisopropylphosphino)butane
DMF	Dimethylformamide
DPPB	1,4-Bis(diphenylphosphino)butane
DPPE	1,1-Bis(diphenylphosphino)methane
DPPM	1,2-Bis(diphenylphosphino)ethane
DPPP	1,3-Bis(diphenylphosphino)propane
DPPPS	Sulfonated 1,3-bis(-diphenylphosphino)propane
GC	Gas chromatography
GC-MS	Gas chromatography–mass spectrometry
h	Hour
HFIP	Hexafluoro-2-propanol
HMDSO	Hexamethyldisiloxane
HSS	Sulfonated tetrahydrosalen
Imes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IPA	Isopropanol
iPr	Isopropyl
L	Ligand
Me	Methyl
nbd	Norbornadiene

List of abbreviations

NHC	N-heterocyclic carbene
PBO	4-phenylbut-3-en-2-one
Ph	Phenyl
PMHS	Polymethylhydrosiloxane
psig	Pound per square inch
PTA	1,3,5-triaza-7-phosphaadamantane
RT	Room temperature
S	Solvent
^{t}Bu	tert-butyl
TEA	Triethylamine
TFA	Trifluoroacetic acid
TFE	Trifluoroethanol
THF	Tetrahydrofuran
TOF	Turnover Frequency
TON	Turnover number
TPAP	Tetrapropylammonium perruthenate
TPPTS	3,3’,3”-Phosphanetriyltris(benzenesulfonic acid) trisodium salt

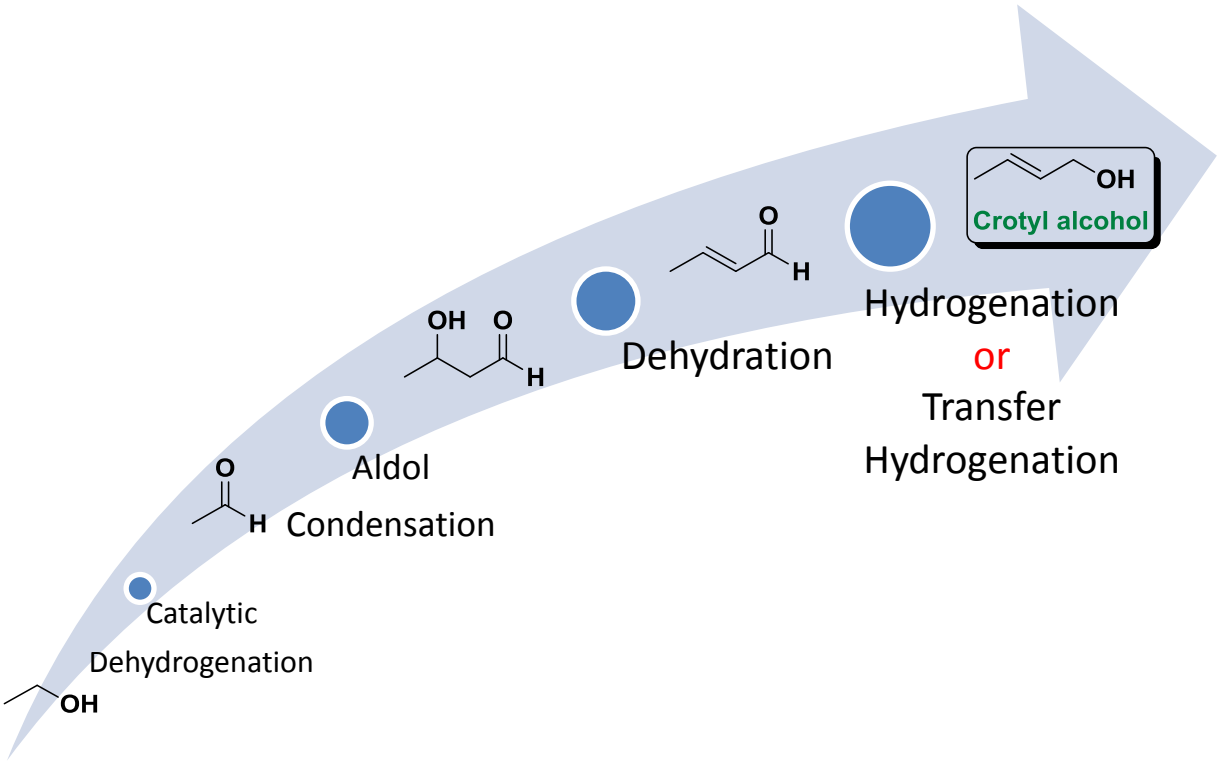
Contents

1 Introduction

Catalysis is the art of enhancing the efficiency of a chemical reaction otherwise establishing a new reaction in the presence of a tiny amount of a compound named catalyst, which is generally not consumed and could be recycled. [1] A catalytic reaction is accelerated with respect to the uncatalyzed reaction due to the reduction of activation energy. Catalysis can be classified into the following main types: 1) Homogeneous catalysis; 2) Heterogeneous catalysis; 3) Enzyme/bio- catalysis; 4) Electrocatalysis; 5) Photocatalysis; 6) Acid/base catalysis; 7) Phase-Transfer Catalysis; 8) Nanocatalysis; 9) Autocatalysis. In this thesis, I will mainly describe the use of homogeneous catalysis.

In the past century, fossil fuels have been the preferred resource for most of our chemical and energy needs.[2] However, use of fossil fuels is depleting energy that took millions of years to generate, and the rate of consumption far exceeds the rate of generation. The growing demand for energy and chemicals (especially in China) and the imminent shortage of fossil fuels have forced people to find or replace raw materials for fuels and chemicals. [3] One obvious renewable raw material for the production of fuels and chemicals is biomass. Biomass is either living or dead organic matter, which has been formed through photosynthesis; this includes all plants and animals and microorganisms. It has always been one of the significant sources of energy for human survival and it is the fourth largest energy source after coal, oil, and natural gas and thus occupies an important position in the entire energy system.

Bioethanol is a biofuel which is produced through microbial fermentation of various types of biomass, such as starches and sugars. Interestingly, crotyl alcohols can be generated from bioethanol through several steps (Scheme1). [4] Crotyl alcohol is an interesting C4 building block, which can be used as raw material for a range of chemicals.



Scheme 1 Production of crotyl alcohol from bioethanol

Butyraldehyde is a bulk chemical which is used primarily as a raw material for plasticizers. It is currently made via hydroformylation of fossil-derived propene. However, it could also be obtained via isomerization of crotyl alcohol.

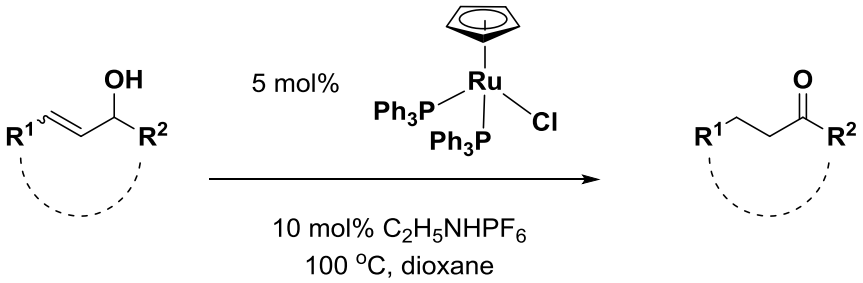
Atom efficiency has been widely used in both homogeneous and heterogeneous chemistry as an important metric, since Trost proposed this concept in 1995.[5] Isomerization reactions can be considered as one of the most proper examples in atom economy and green chemistry because all the atoms from the substrate are totally retained in the products without generation of any waste.[6] One of the most interesting and widely investigated isomerization reactions is the transformation of readily available allylic alcohols into ketones and aldehydes which are the basic components of many chemicals in both laboratory and industry.[7] Herein, I will introduce different transition metal catalyzed isomerization of allylic alcohols to the corresponding carbonyl compounds.

1.1 Ruthenium catalyzed isomerization

1.1.1 Half sandwich ruthenium catalysts

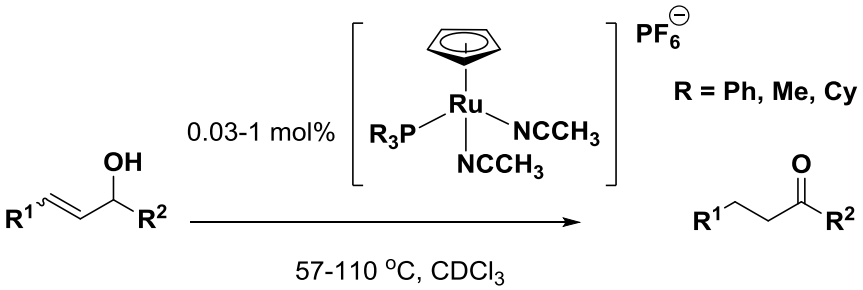
Half-sandwich complexes are the compounds that consist of two parts coordinating with the central metals. The “bread” part is generally an aromatic polyhapto ligand, *e.g.* cyclopentadienyl or phenyl. The other part could be either one or more monodentate ligands or a bidentate ligand. [8] The first half-sandwich ruthenium complex catalyzed isomerization of allylic alcohols to saturated ketones and aldehydes was reported by Trost and Kulawiec in 1991 (Scheme 2). [9] The ruthenium compound ($Cp(PPh_3)_2RuCl$) is built up by one

cyclohexadienyl with two triphenylphosphine and one chloride, which is a typical 18-electron coordination compound. [10] The benchmark reaction conditions are 5 mol% of $Cp(PPh_3)_2RuCl$, 10 mol% of triethylammonium hexafluorophosphate in dioxane at 100 °C. Moderate to excellent yields were realized under those standard conditions with both primary and secondary allylic alcohols in 1 to 8 hours. Notably, the yields declined obviously in the absence of the acid (triethylammonium hexafluorophosphate). Conversion of cyclic allylic alcohols was poor, even though a longer reaction time (24 hours) was used. Additionally, when the number of substituents was more than 3 (Include 3), poor reactivity was observed.



Scheme 2 $Cp(PPh_3)_2RuCl$ catalyzed isomerization of allylic alcohols to ketones and aldehydes

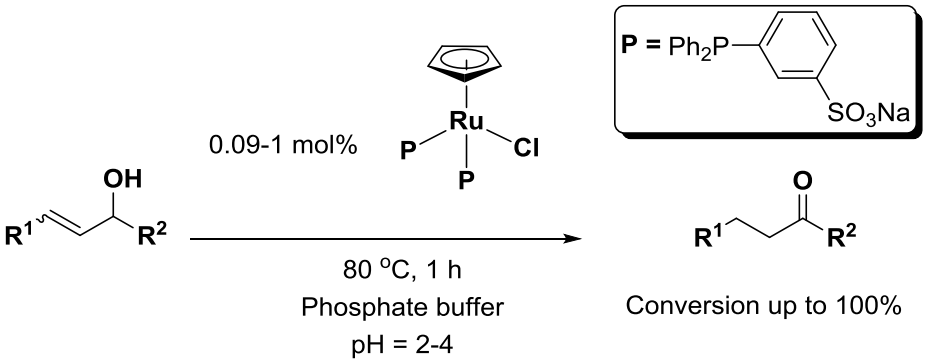
In 1999, Kirchner and co-workers reported a series of $[RuCp(PR_3)(CH_3CN)_2]PF_6$ complexes, where Cp is cyclopentadienyl and R could be Ph, Me and Cy (Scheme 3). These complexes were shown to be highly active for the isomerization of allylic alcohols to ketones and aldehydes. [11] High turnover number (TON) and turnover frequency (TOF) could be reached (up to 2570 and 30800/h respectively). Compared with the half-sandwich compound introduced by Trost, this cationic catalyst showed higher activity and the ability to perform the reaction at lower catalyst loadings. However, the compatibility of this catalyst is poor since it was compatible with a very limited number of functional groups in the allylic substrates. Interestingly, the half-sandwich cationic complex $CpRuPMe_3(CH_3CN)_2$ could be protected from decomposition through incorporating into a water-soluble supramolecular assembly that was designed by Raymond and co-workers in 2011. [12] Although a minor decrease in rate was observed in the transformations of allylic alcohols to the corresponding carbonyl compounds, this novel methodology showed a potential applicability in "green" chemistry.



Scheme 3 $CpRuPR_3(CH_3CN)_2$ catalyzed isomerization of allylic alcohols to carbonyl compounds

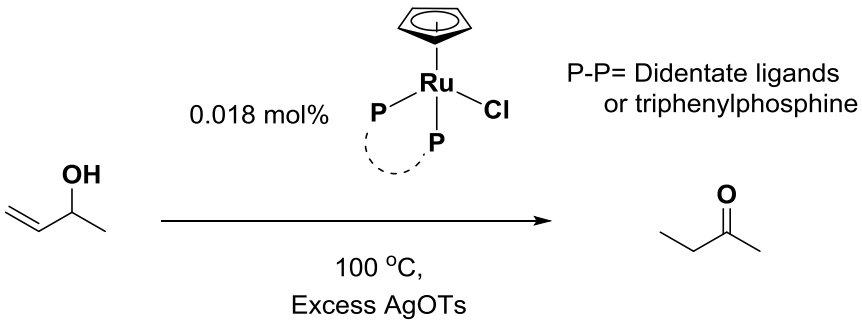
Water is green, readily available and cheap in comparison to other organic solvents that are utilized in the isomerization of allylic alcohols to the corresponding carbonyl compounds. In 2007, Romerosa and co-workers reported a water-soluble half-sandwich complex, in which the solubility was achieved by utilizing a water-soluble monosulfonated triphenylphosphine ligand (Scheme 4). [13] However, the limitations of this catalyst are

the requirement of a narrow acidic pH range as well as a limited substrate scope.



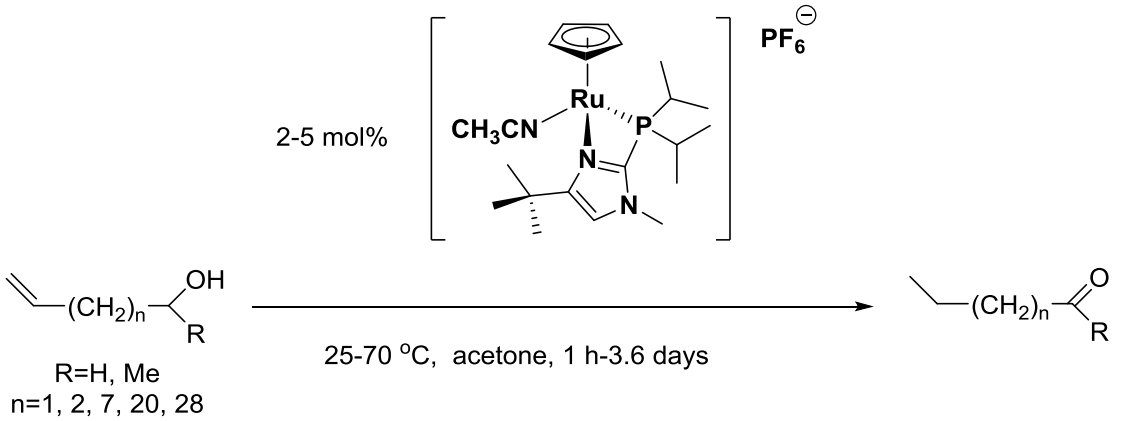
Scheme 4 $CpRuP_2Cl$ catalyzed isomerization of allylic alcohols to ketones

A variety of Cp(bidentate phosphine)Ru(II) complexes, which could efficiently catalyze the isomerization of 3-buten-2-ol to butanone, were reported by Bouwman and co-workers in 2000 (Scheme 5). [14] The chain length between two phosphines plays a significant role in the catalytic activity of this isomerization reaction with a trend: dppm< dppe< dppp< dppb. Further, no reactivity was observed by using rigid bidentate phosphine ligands (*e.g*. *cis*-dppv and dppph) coordinated ruthenium half-sandwich complexes. However, triphenyl phosphine showed much higher reactivity than other bidentate ligands in the isomerization of 3-buten-2-ol to butanone with a turnover frequency as high as 200000/h. There are 3 possible reasons to explain this high activity: 1) the substrate used in this paper is relatively small compared to the allylic alcohols utilized before; 2) the silver salt leads to formation of the cationic complex which apparently is more active than the hydride complex used in Trost's paper [5]; 3) the use of solvents (water or organic solvents) in other papers inhibits the transformation of allylic alcohols to the corresponding carbonyl compounds.



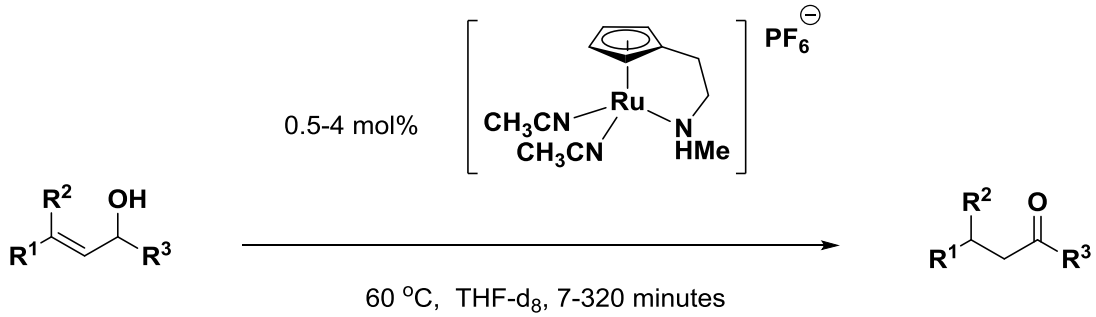
Scheme 5 BidentateCpRuCl catalyzed isomerization of 3-buten-2-ol to butanone

In 2007, Grotjahn and co-workers reported a novel ionic ruthenium complex, which contains a cyclopentadienyl ligand, a PN-bidentate ligand with a short bite-angle and acetonitrile as ligands and PF_6^- as a counter-ion. [15] Despite that rather long reaction times (1 hour to 3.6 days) were required, this catalyst showed the ability to isomerize substrates with a larger number of methylene groups between the alcohol and vinyl groups(Scheme 6).



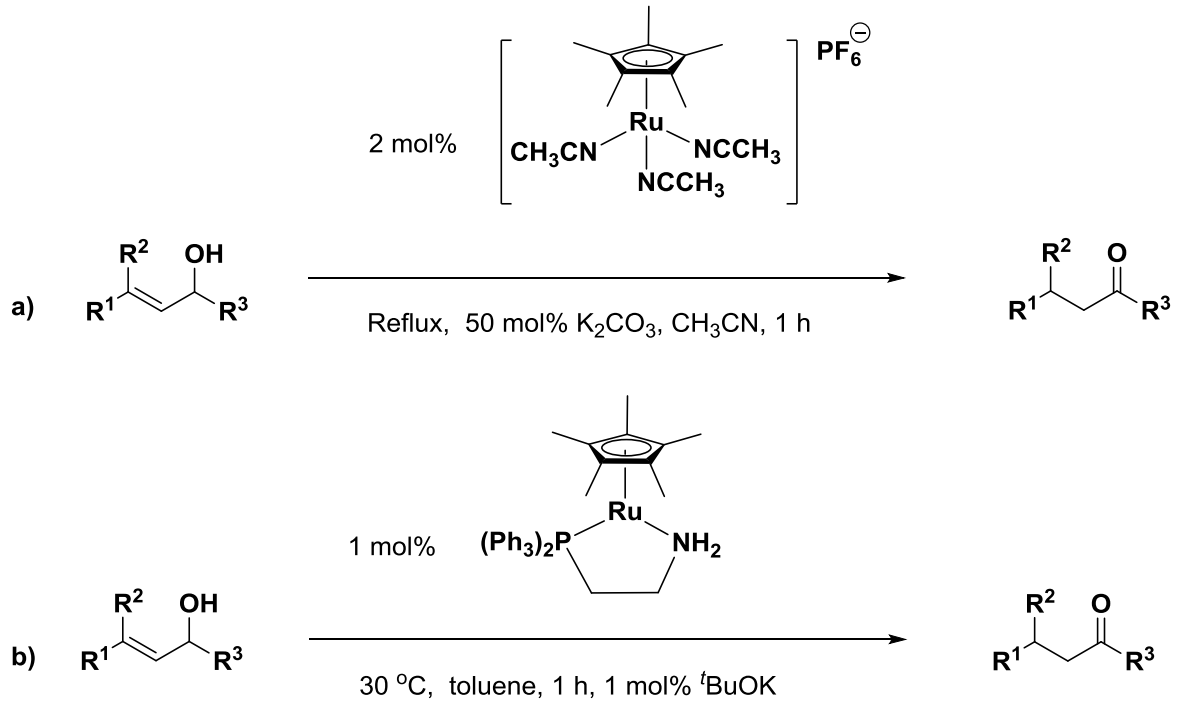
Scheme 6 PNCpRuCl catalyzed isomerization of alkenes

The preparation of a novel series of half-sandwich ruthenium complexes (as shown in Scheme 7), were reported by Esteruelas and co-workers in 2010. [16] Highly catalytic activities were observed in the isomerization of secondary allylic alcohols to the desired ketones. However, the selectivity in the isomerization of primary allylic alcohols to aldehydes is rather low with large amounts of by-product formation (aldol reaction product) and overall poor conversion for some substrates.



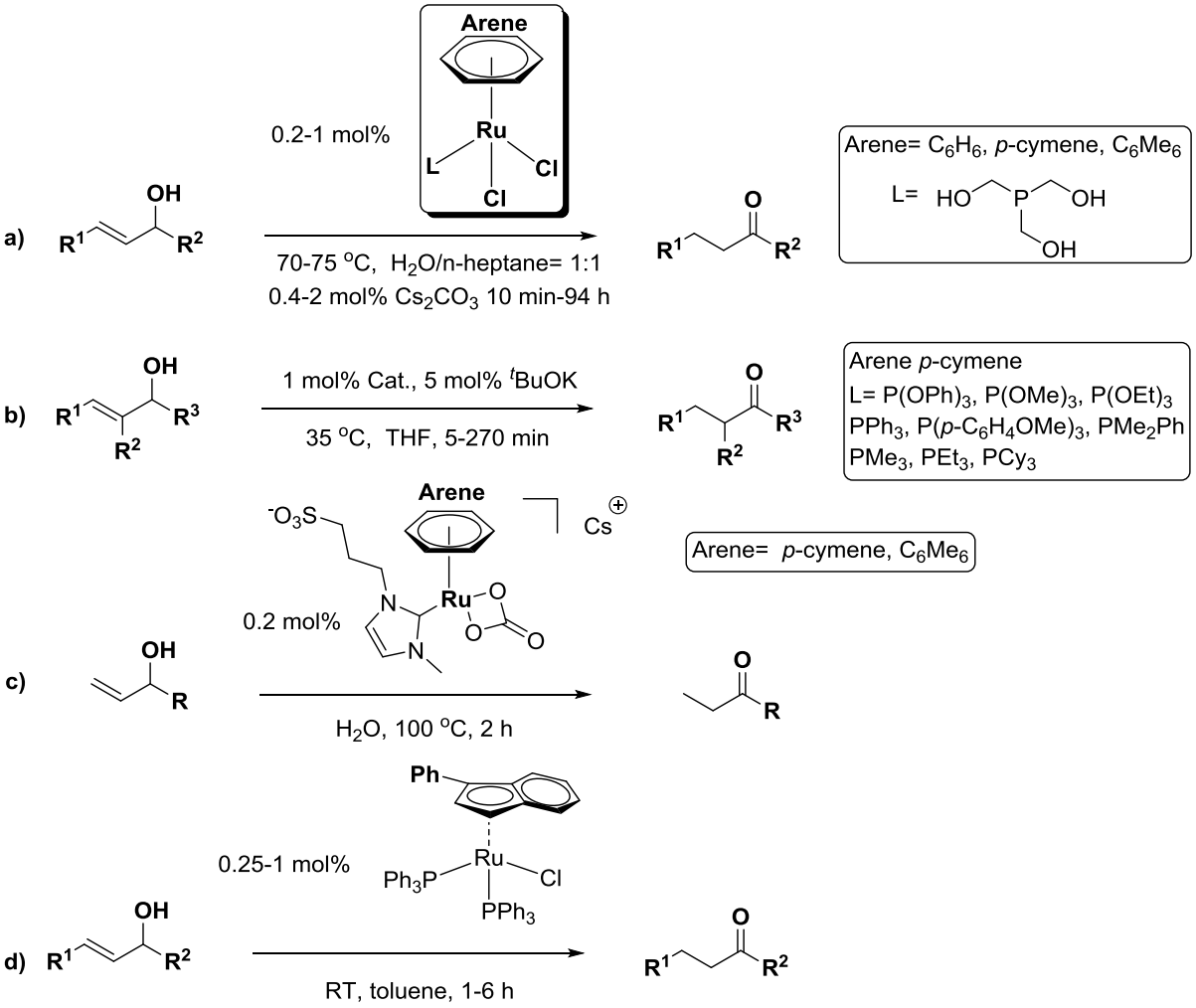
Scheme 7 PNCpRuCl catalyzed isomerization of allylic alcohols

In comparison with cyclopentadienyl, pentamethylcyclopentadienyl (Cp*) is a more electron-donating ligand and more difficult to be replaced from metal. Renaud and co-workers reported pentamethylcyclopentadienyl and monodentate ligand coordinated ruthenium complexes as catalysts for the isomerization of functionalized allylic alcohols to the corresponding carbonyl compounds in 2008 (Scheme 8, a)). [17] However, high temperatures, high catalyst loadings and large amount of base were needed for the reaction to proceed. In 2006, Ikariya and co-workers reported a series of Cp* ruthenium phosphine-primary amine (PN) bidentate complexes which could isomerize allylic alcohols to the corresponding carbonyl compounds (Scheme 8, b)). These half-sandwich ruthenium compounds were proven to be bifunctional catalysts where the ligand is non-innocent; where the hydride was delivered to the carbonyl carbon atom and the proton from the ligand to the oxygen atom. [18]



Scheme 8 Cp* ruthenium half-sandwich catalyzed isomerization of allylic alcohols to carbonyls

The replacements of the "bread" part in half-sandwich complexes are well developed, where the cyclic compounds can be changed from cyclopentadienyl to benzene, *p*-cymene (1-Methyl-4-(propan-2-yl)benzene) and others. In 2004, Cadierno and co-workers reported a list of arene dichloride phosphine ruthenium complexes, in which the phosphine ligand enables these complexes to be water-soluble (Scheme 9, a)). [19] A biphasic solvent system is necessary for these reactions (a mixture of water and n-heptane 1:1 was typically used). Interestingly, although catalytic efficiency decreased, this catalytic system could be reused for several times (up to 8 cycles) in the isomerization of allylic alcohols to the corresponding carbonyl compounds. In coordination chemistry, phosphite $(RO)_3P$ is a good replacement of the phosphine ligand. In 2006, Crochet and co-workers reported phosphines and phosphites coordinated (arene)$Ru(P)Cl_2$ complexes in the isomerization of allylic alcohols to the corresponding ketones, where (*p*-cymene)$Ru(P(OEt)_3)Cl_2$ showed the best catalytic activity (Scheme 9, b)). [20] Trisubstituted allylic alcohols could be smoothly isomerized to the desired ketones under mild reaction conditions. Additionally, an N-heterocyclic carbene (NHC) water soluble half-sandwich ruthenium complex catalyzed the isomerization of secondary allylic alcohols to the corresponding ketones as reported by Peris in 2010 (Scheme 9, c)). [21] Further modification of the arene part was investigated by Nolan and co-workers in 2014 (Scheme 9, d)). [22] High activity was achieved in both primary and secondary allylic alcohols in the presence of 0.25-1 mol% of the half-sandwich ruthenium complex containing an indenyl ligand at room temperature.

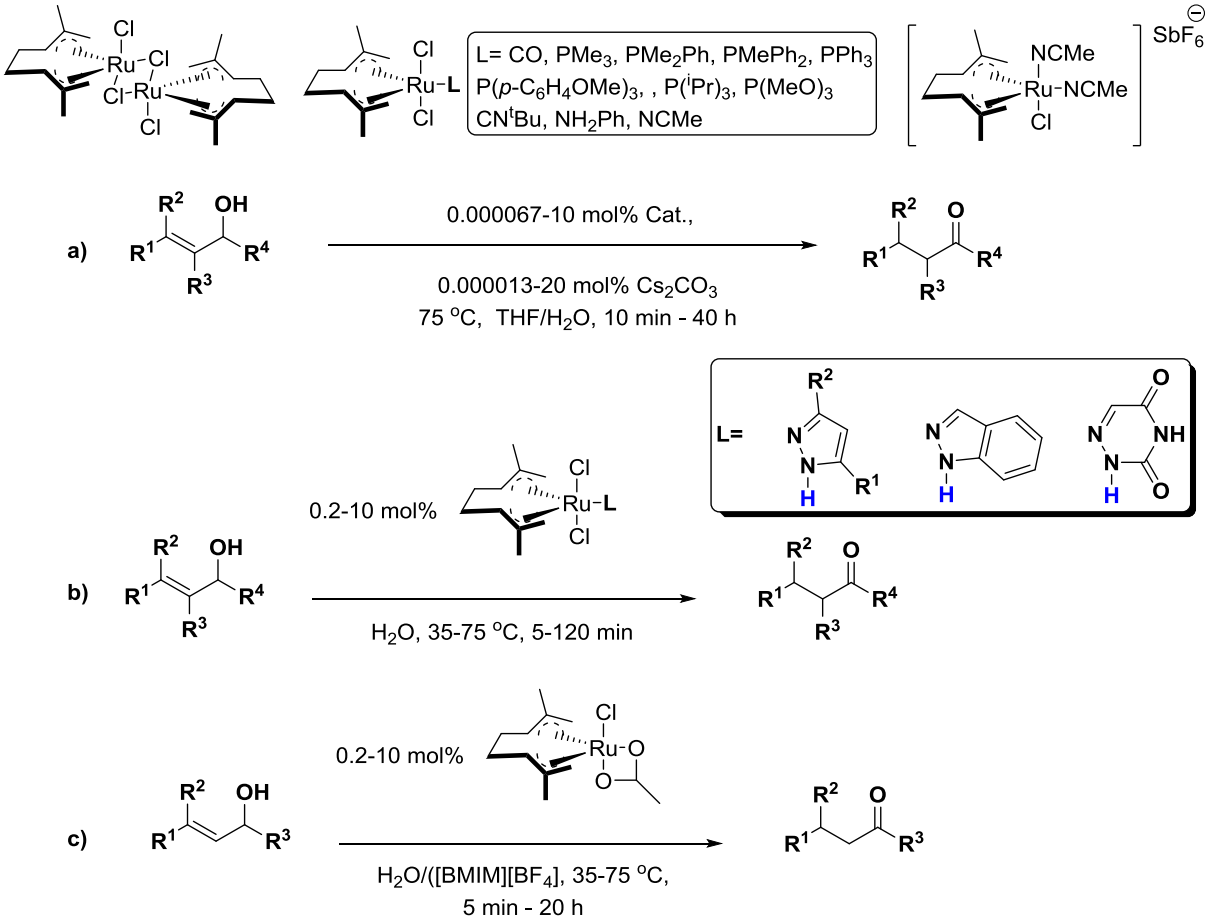


Scheme 9 Arene ruthenium half-sandwich catalyzed isomerization of allylic alcohols to carbonyl compounds

1.1.2 Bis(allyl) ruthenium catalysts

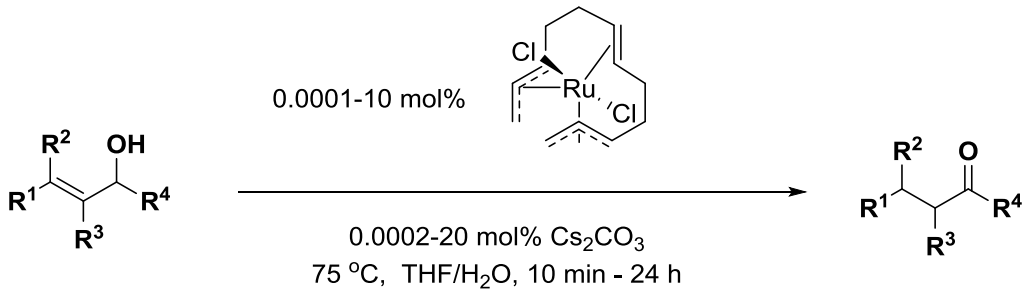
A range of bis(allyl) ruthenium complexes (more than 10) were reported by Cadierno and co-workers in 2006 (Scheme 10, a)). [23] There are 3 main types of complexes used in the isomerization reactions: 1) dinuclear ruthenium complexes 2) mononuclear ruthenium compounds 3) mononuclear cationic ruthenium complexes. The dimer ruthenium complexes were proven to be the most efficient catalysts in this paper for the isomerization of allylic alcohols to the corresponding ketones in the presence of Cs_2CO_3 in THF or H_2O, where the highest TOF and TON reached were 62 500/h and 1 500 000 respectively. High yields were obtained for both primary and secondary allylic alcohols. Conjugated dienes were regarded to be poisonous to the ruthenium catalysts due to coordination to the metal center leading to their deactivation. Furthermore, a range of bifunctional imidazole coordinated ruthenium complexes were reported by Gimeno in 2012 for the efficient isomerization of allylic alcohols to the corresponding carbonyl compounds in water (Scheme 10, b)). [24] High activities were observed in the isomerization of both primary and secondary allylic alcohols to the desired aldehydes and ketones. An extremely high turnover frequency of 60 000 h^{-1} was achieved. The bis(allyl) ruthenium complex was further modified by changing the ligand that was tested in the isomerization of allylic alcohols from the same group (Scheme 10, c)). [25] The solvent could be either water or 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]). Interestingly, the catalyst used in this catalytic system

could be recycled.



Scheme 10 Bis(allyl) ruthenium complexes catalyzed isomerization of allylic alcohols to carbonyl compounds

Another type, bis(allyl) ruthenium complex, that was reported by Cadierno to be an efficient catalyst for the isomerization of allylic alcohols to the corresponding carbonyl compounds in both organic and aqueous media is shown in Scheme 11. [26] High activity in the isomerization of secondary allylic alcohols to the desired ketones was observed. In comparison, longer reaction times and large amounts of catalyst were necessary for the isomerization of primary and cyclic allylic alcohols to the corresponding aldehydes and cyclic ketones.

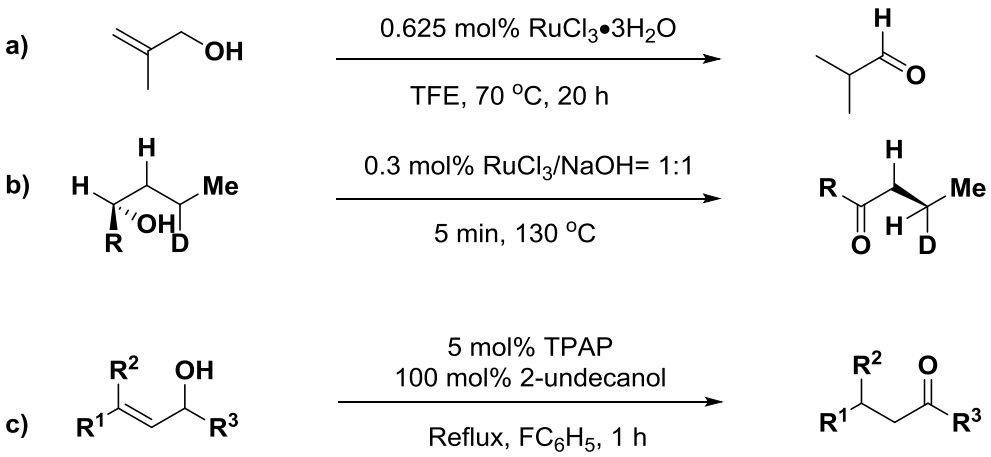


Scheme 11 C12 bis(allyl) ruthenium complexes catalyzed isomerization of allylic alcohols to carbonyl compounds

1.1.3 Other ruthenium complexes

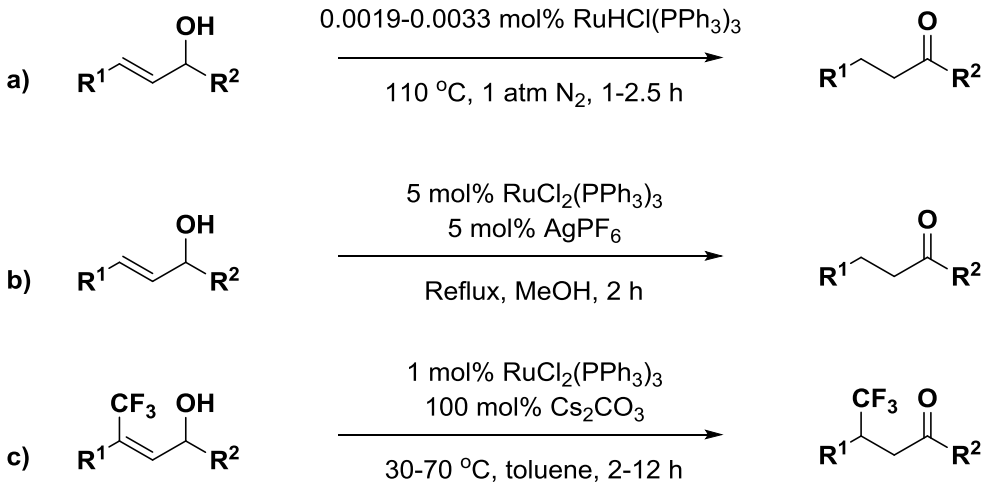
Widely available $RuCl_3$ as its hydrate can isomerize allylic alcohols to the corresponding carbonyl compounds.

Initial studies were carried out in the presence of 0.625 mol% of $RuCl_3 \cdot 3H_2O$ in trifluoroethanol (TFE) at 70 °C (Scheme 12, a)). [27] After 20 hours, 82% of the desired isobutanal was obtained from isobutenol. Further investigations were reported by Georgoulis and co-workers using equimolar amounts of $RuCl_3$ (0.3 mol%) and NaOH (0.3 mol%) at 130 °C that could smoothly isomerize deuterated allylic alcohols to the corresponding ketones with a moderate yield (Scheme 12, b)). [28] The isomerization of allylic alcohols to the corresponding carbonyls could also be catalyzed by tetrapropylammonium perruthenate (TPAP) (Scheme 12, c)). [29] Both primary and secondary allylic alcohols were isomerized to the desired aldehydes and ketones smoothly. Nevertheless, the requirement of 5 mol% of TPAP and 100 mol% of 2-decanol as additives still limited applicability of this reaction.



Scheme 12 Ruthenium salts catalyzed isomerization of allylic alcohols to carbonyl compounds

Triphenylphosphine coordinated ruthenium complexes have been well investigated for the isomerization of allylic alcohols to the corresponding ketones. Early experiments were performed in neat 0.5 mL of substrate in the presence of 10 mg hydridochlorotris(triphenylphosphine)ruthenium without any additives (Scheme 13, a)). [30] High yields were obtained with most of the primary and secondary allylic alcohols as substrates. Interestingly, the yield of the desired ketone could reach up to 79% when homo-allylic alcohol was selected as a substrate. However, no isomerized product was observed when 2-buten-1-ol was used as a starting material. In addition, dichlorotris(triphenylphosphine)ruthenium could be used as the catalyst for the rearrangement of allyl alcohols to the corresponding carbonyl compounds in the presence of the equimolar amounts of additives at reflux temperatures (Scheme 13, b)). [31] Furthermore, β-CF_3-substituted ketones could be obtained from the isomerization of CF_3- substituted allylic alcohols in the presence of dichlorotris(triphenylphosphine)ruthenium and stoichiometric amount of cesium carbonate in toluene as a solvent (Scheme 13, c)). [32]

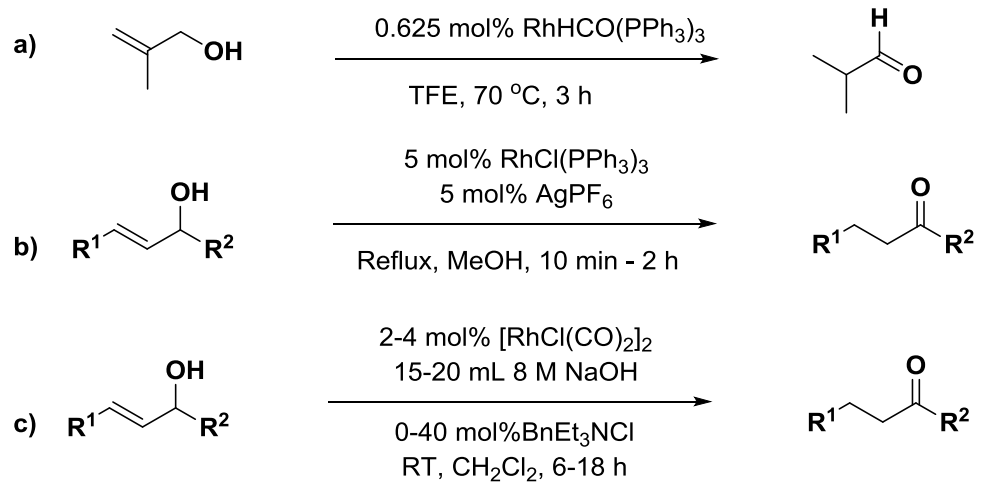


Scheme 13 Triphenylphosphine ruthenium catalyzed isomerization of allylic alcohols to carbonyl compounds

1.2 Rhodium

1.2.1 Monodentate ligand coordinated rhodium catalysts

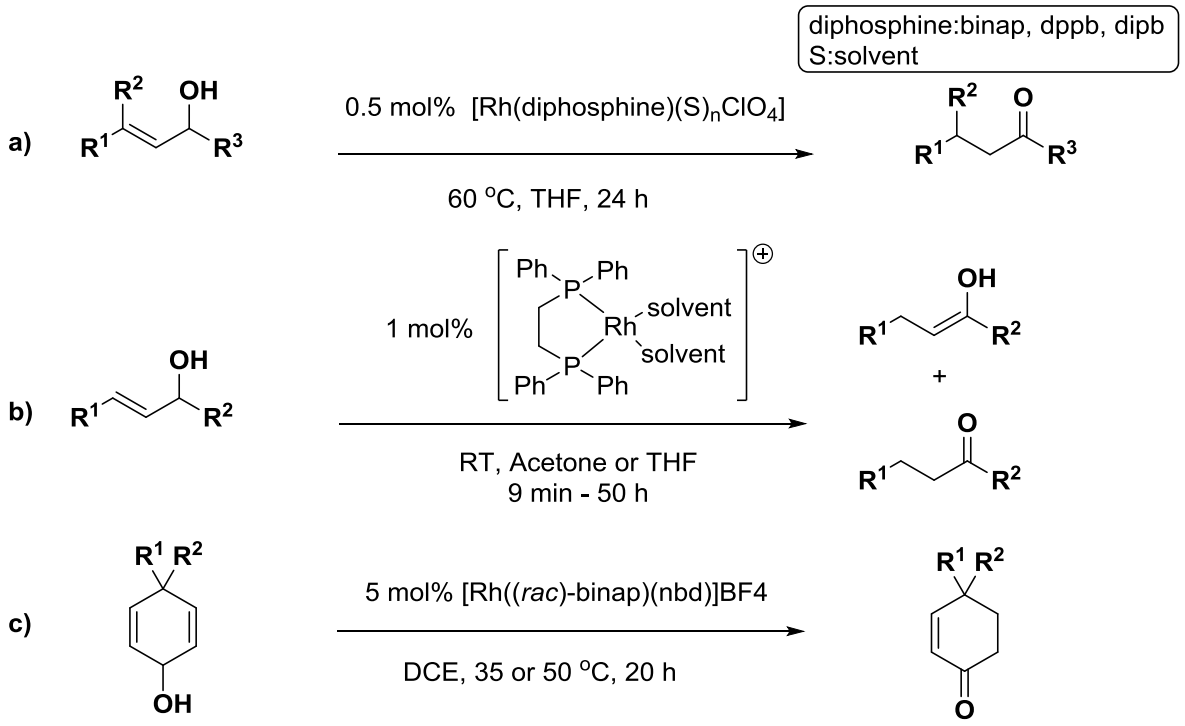
Rhodium complexes have been well investigated for the isomerization of allylic alcohols to the corresponding carbonyl compounds, where the catalytic system either consisted of rhodium complexes or inorganic rhodium salts with organic ligands. In 1975, Weigelt and Strohmeier reported the rearrangement of isobutenol to isobutanal in quantitative yield in the presence of a catalytic amount (0.625 mol%) of $RhHCO(PPh_3)_3$ in trifluoroethanol at 70 °C (Scheme 14, a)). [27] Further investigations on triphenylphosphine coordinated rhodium complexes were reported by Grée and co-workers in 2001 (Scheme 14, b)). [31] High yields were obtained in the presence of 5 mol% of catalyst and additives in methanol after 10 minutes to 2 hours. Additionally, a ruthenium dimer complex $[Rh(CO)_2Cl]_2$ could also be used as the isomerization catalyst of secondary allylic alcohols to the corresponding ketones (Scheme 14, c)). [33] The experiments were carried out at room temperature using 2-4 mol% of catalyst in 6-18 hours that resulted in quantitative yields. However, extremely basic conditions are necessary for this reaction and some of the substrates require 40% of additives ($BnEt_3NCl$).



Scheme 14 Monodentate ligands in ruthenium catalyzed isomerization of allylic alcohols

1.2.2 Bidentate ligand coordinated rhodium catalysts

Bidentate phosphine ligands coordinated rhodium complexes could also be used in the isomerization of allylic alcohols to the corresponding carbonyl compounds. In 1985, Tani reported a range of rhodium complexes, ligated with bidentate phosphines as catalysts in the isomerization of both primary and secondary allylic alcohols to the desired saturated carbonyl compound, where the biphosphine could be 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap), 1,4-bis(diphenylphosphino)butane (dppb) and 1,2-Bis(diisopropylphosphino) butane (dipb) (Scheme 15, a)). [34] High conversions were obtained for the substrates though with poor selectivities in some cases. Further investigation of these rhodium catalyzed isomerization reactions were reported by Bosnich and Bergens in 1991 (Scheme 15, b)). [35] In 2015, Lautens and co-workers reported a rhodium catalyzed redox isomerisation of cyclohexa-2,5-dienols for the synthesis of γ,γ-disubstituted cyclohexenones (Scheme 15, c)). [36] The catalyst utilized in this reaction is built up by (±)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthalene (BINAP), norbornadiene (nbd) and BF_4^- anion. Many substituents on the allylic alcohols were tolerated. Good to excellent yields were achieved by using 5 mol% [Rh((*rac*)-BINAP)(nbd)]BF_4 at 35 or 50 °C and 20 hours reaction times.

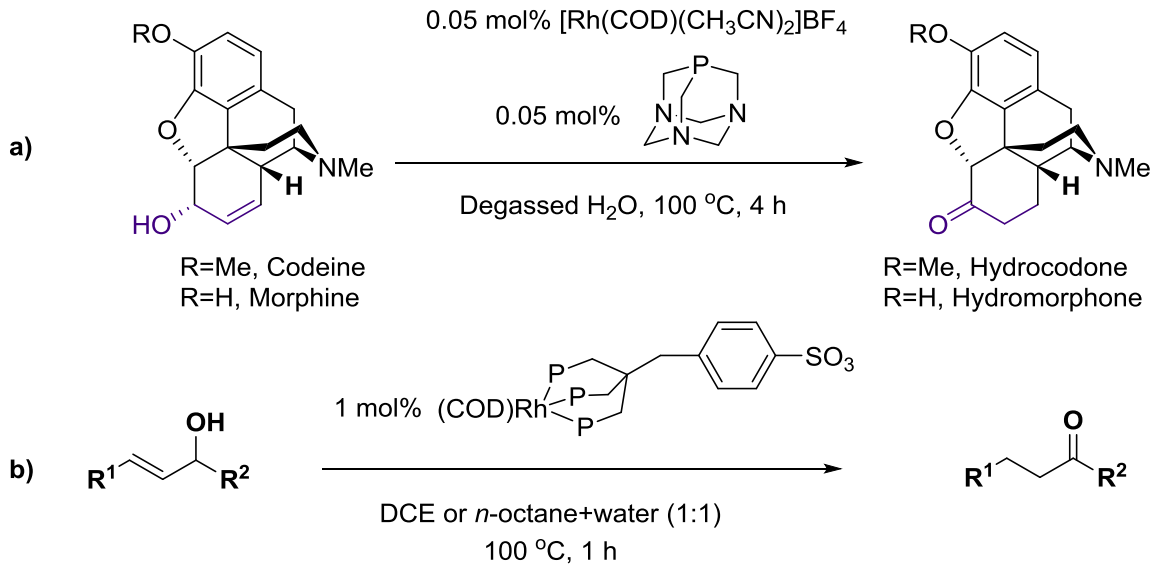


Scheme 15 Rh(diphosphine)L catalyzed isomerization of allylic alcohols to carbonyl compounds

1.2.3 Other rhodium complexes

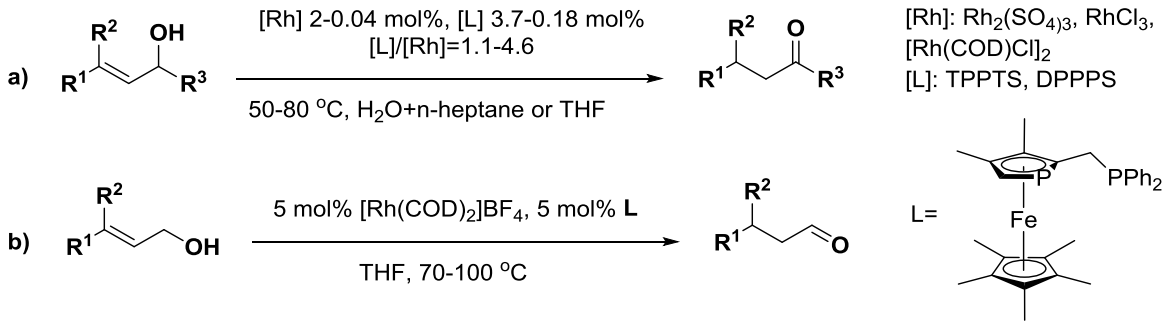
Hydrocodone and hydromorphone are important semi-synthetic opioids that are used as analgesics, antitussives and sedatives. A convenient method for the synthesis of these compounds is the isomerization of codeine and morphine to the corresponding hydrocodone and hydromorphone. In 2014, Martín-Matute and co-workers reported the synthesis of these compounds in the presence of 0.05 mol% of $[Rh(COD)(CH_3CN)_2]BF_4$ and 1,3,5-triaza-7-phosphaadamantane (PTA) in water at 100 °C for 4 hours (Scheme 16, a)). [37] Notably,

quantitative yields could be achieved under these reaction conditions and the scale of these reactions could reach up to 100g. In addition, Bianchini and co-workers reported COD and tridentate phosphine ligands coordinated rhodium catalyzed isomerization of allylic alcohols to the corresponding carbonyl compounds hours (Scheme 16, a)). [38] However, the compatibility of this catalyst to the functional groups in the substrates was poor in both organic and biphasic aqueous-organic solvent systems.



Scheme 16 Rh(COD)L catalyzed isomerization of allylic alcohols to carbonyl compounds

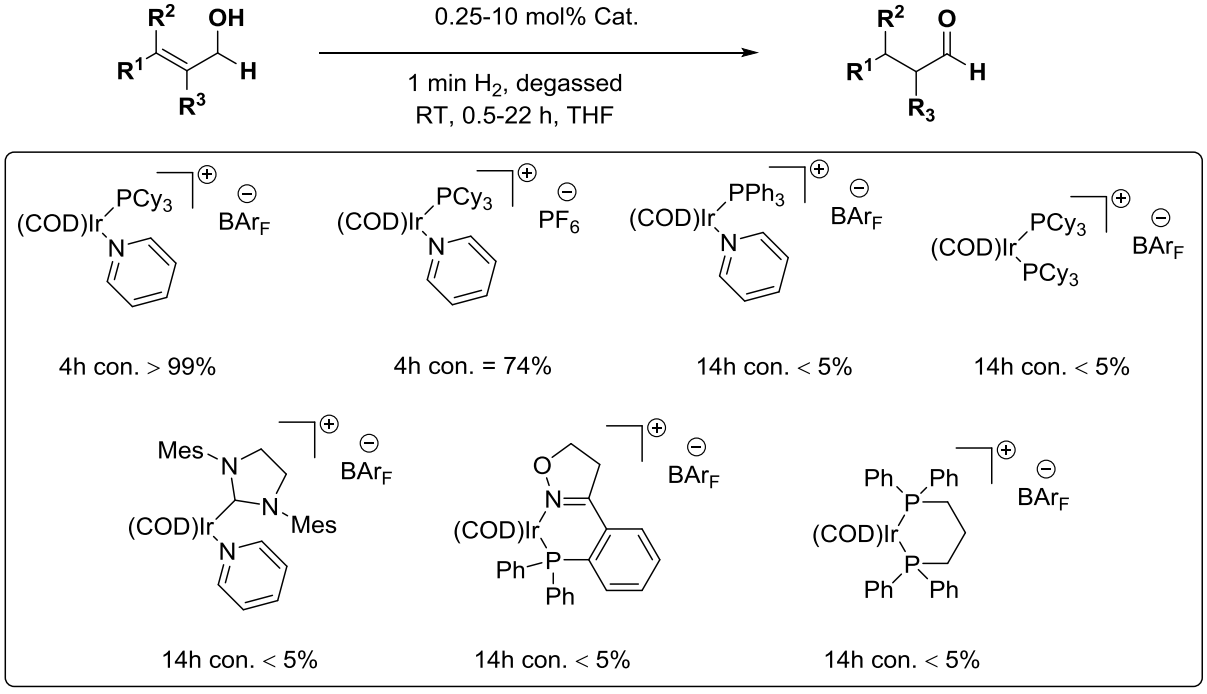
The combination of rhodiumsalts or other rhodium precursors with ligands leads to the formation of a good catalytic system for the isomerization of allylic alcohols to the corresponding carbonyl compounds. Early experiments were carried out using inorganic rhodium salts like $Rh_2(SO_4)_3$ and $RhCl_3$ as well as the organometallic rhodium precursor $[Rh(COD)Cl]_2$ as metal sources (Scheme 17, a)). [39] The ligands could be either 3,3',3"-Phosphanetriyltris(benzenesulfonic acid) trisodium salt (TPPTS) or sulfonated 1,3-bis(-diphenylphosphino)propane (DPPPS), where the sodium sulfonate substituent enable this catalytic system to be water soluble. A biphasic solvent mixture like n-heptane with water or pure organic solvent like THF could be utilized as suitable solvents for these isomerization reactions. The same group has also reported that multiphasic catalysis could be performed in microreactors that could reduce the amount of chemicals in the optimization reactions (to µg levels) (Scheme 17, b)). [40] Furthermore, Fu and co-workers reported isomerization of the relatively hard to isomerize substrates (primary allylic alcohols) to the corresponding carbonyl compounds catalyzed by 5 mol% of $[Rh(COD)_2]BF_4$ and phosphaferrocene ligand in THF. Moderate to excellent yields could be achieved with different primary allylic alcohols as substrates.



Scheme 17 Combination of Rh salts and ligands catalyzed isomerization of allylic alcohols to carbonyl compounds

1.3 Iridium

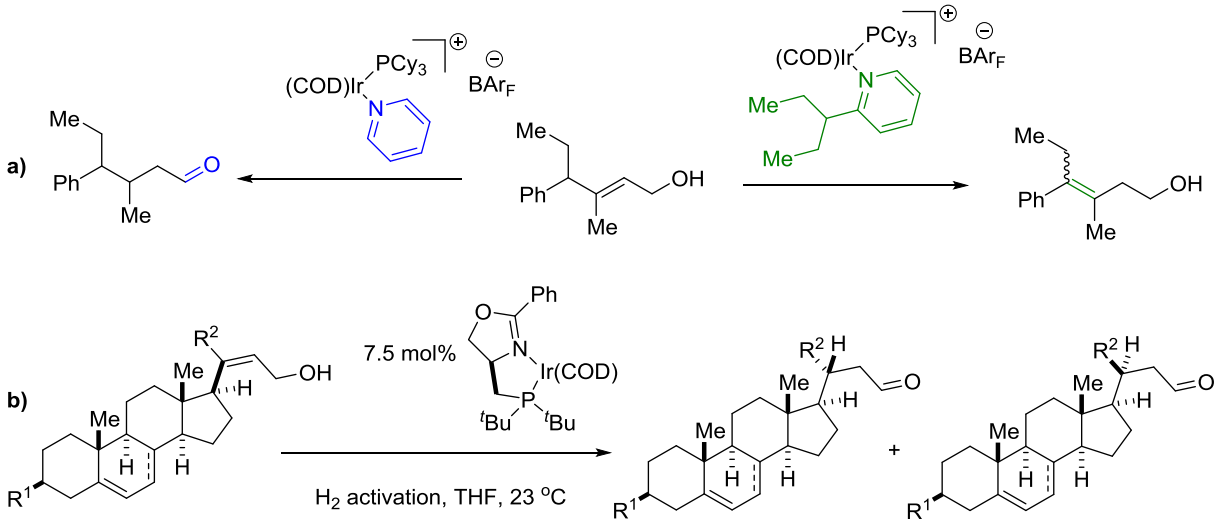
In comparison to secondary allylic alcohols, the required conditions for the isomerization of primary allylic alcohols are more rigorous and generally needed longer reaction times and higher catalyst loadings. Therefore, it is a big challenge to isomerize primary allylic alcohols to the corresponding aldehydes under mild reaction condition. In the last decade, Mazet and co-workers reported various 1,5-cyclooctadiene (COD) coordinated iridium complexes with additional P and N ligands which could be in situ activated by H_2 gas to catalyze the isomerization of allylic and homo-allylic alcohols to the corresponding aldehydes and ketones. [7h] In 2009, Mazet and Mantilli reported a range of iridium catalysts for the transformation of primary allylic alcohols to the desired aldehydes. [41] The ligands in these iridium complexes play a significant role in the catalytic activity, where the combination of PCy_3 and pyridine was proven to be the best ligand system for this rearrangement reaction.



Scheme 18 $(COD)IrL_2$ catalyzed isomerization of primary allylic alcohols to aldehydes

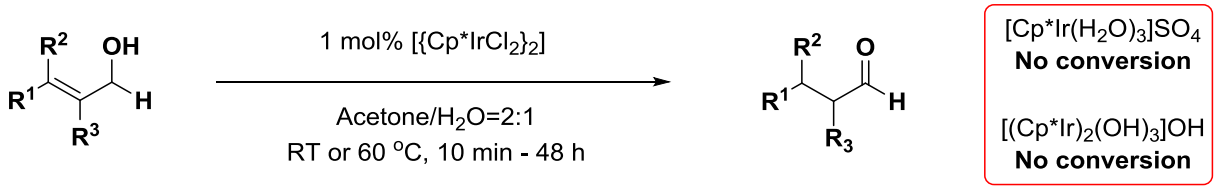
Furthermore, Mazet and co-workers reported the influence of the substituent on the pyridine of the COD

iridium tricyclohexylphosphine pyridine complexes, where the reactions could result in different products (Scheme 19, a)). [42] In contrast, when a substituted pyridine was selected as the ligand coordinated to iridium, the products formed were homo-allylic alcohols instead of aldehydes. In addition, Mazet and co-workers designed various C-20 steroidal derivatives that could be potentially utilized in pharmaceutical applications, where the C-20 aldehyde compounds could be synthesized via the isomerization of primary allylic alcohols (Scheme 19, b)). [43]



Scheme 19 COD iridium catalyst catalyzed isomerization of primary allylic alcohols to aldehydes

Additionally, Martín-Matute and co-workers reported the influence of the counter-ion of the iridium complex in the isomerization of primary allylic alcohols to the corresponding aldehydes (Scheme 20). [44] The iridium compounds with a non-halogen counter-ion like $[Cp^*Ir(H_2O)_3]SO_4$ and $[(Cp^*Ir)_2(OH)_3]OH$ are totally inactive for this isomerization reaction. Furthermore, it was discovered that for the chlorinated Ir catalyst no ligand or additives are needed in this catalytic reaction and moderate to high yields were obtained.

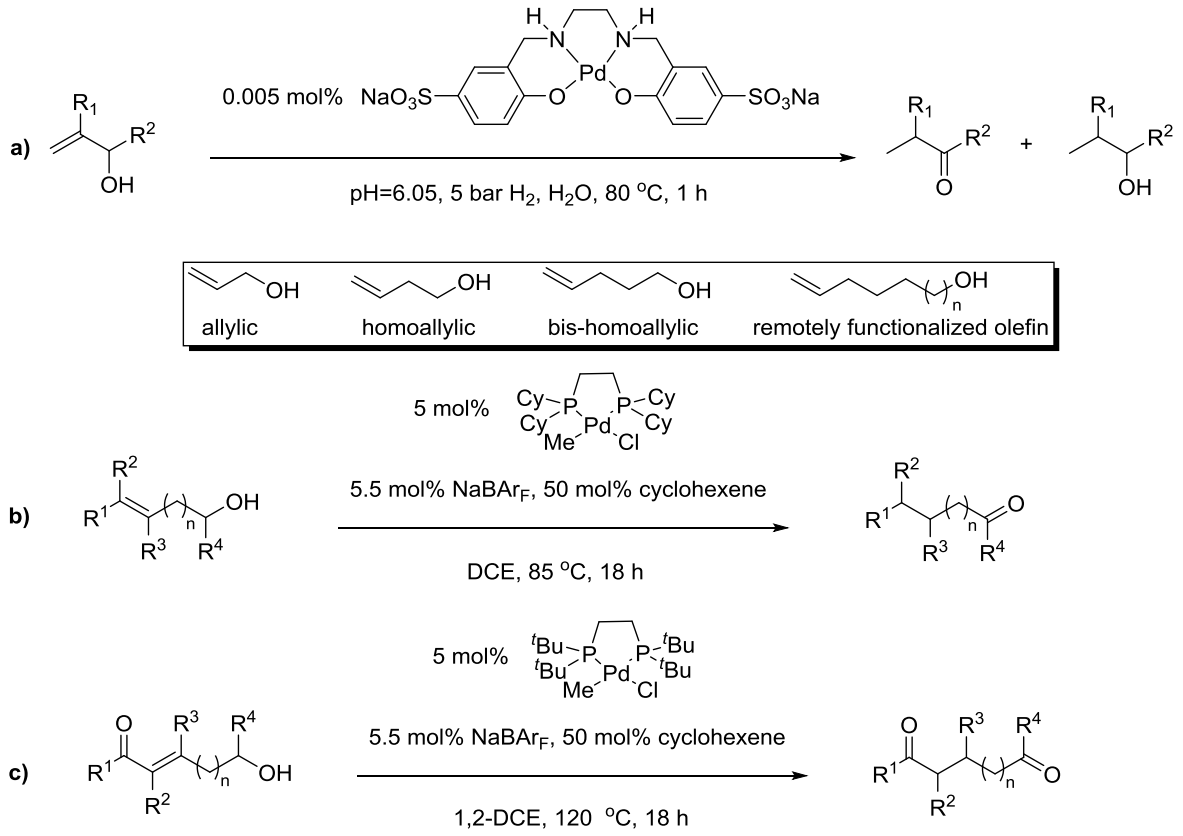


Scheme 20 $(Cp^*IrCl_2)_2$ catalyzed isomerization of primary allylic alcohols to aldehydes

1.4 Palladium

There are only a limited number of articles about palladium catalyzed isomerization of allylic alcohols to the corresponding carbonyl compounds. In 2013, Voronova and co-workers reported a sulfonated tetrahydrosalen (sulfosalan, HHS) palladium complex, which could be used as a catalyst for the isomerization reactions of allylic alcohols to the corresponding ketones in a phosphate buffer solution. [45] The catalytic system could be either built up by a catalytic amount of water-soluble salen palladium complex or the *in situ* formation from the reaction of the salen ligand and $(NH_4)_2[PdCl_4]$ in water at 60 °C. However, because of the use of H_2 (H_2 is used for the activation of the catalyst), this catalytic system has a big issue with the selectivity between isomerization

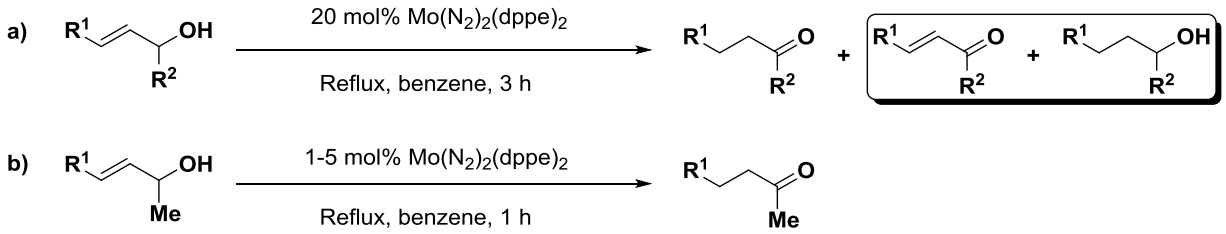
and hydrogenation. Furthermore, Mazet and co-workers reported a range of isomerizations of allylic, homo-allylic, bis-homoallylic and remotely hydroxyl functionalized olefin to the corresponding ketones and aldehydes catalyzed by a catalyst based on palladium and a bidentate phosphine ligand. [46] More than 40 substrates could be converted using this catalytic system with moderate to high yields in the presence of 5 mol% palladium catalyst, 5.5 mol% of $NaBAr_F$ and 50 mol% of cyclohexene at 80 °C. In 2016, Mazet and co-workers reported deconjugative isomerization reactions catalyzed by a palladium complex based on another bidentate ligands to produce the corresponding carbonyl compounds with the similar catalytic system used in 2014. [47] Interestingly, the carbon number between the C=C and hydroxyl group could reach as high as 30under the standard reaction conditions.



Scheme 21 Palladium complexes catalyzed isomerization of primary allylic alcohols to aldehydes

1.5 Molybdenum

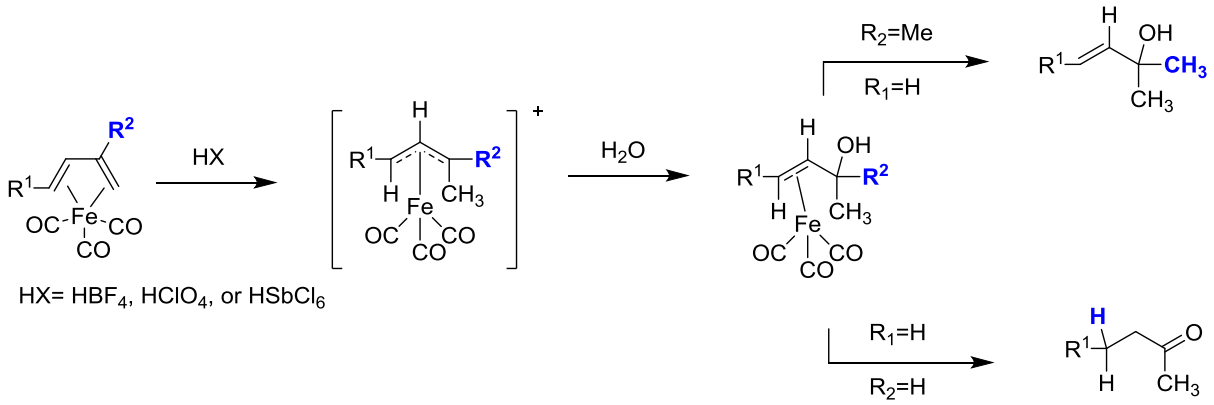
Isomerization of allylic alcohols, ethers and amines could be catalyzed by a *trans*-$Mo(N_2)_2(dppe)_2$ complex, as was reported by different groups (Lu and Tominaga) in 1983 (Scheme 22). [48] Lu reports that high conversions and good selectivities were achieved after 3 hours by using 20 mol% of a molybdenum complex based on dppe in the isomerization of secondary allylic alcohols to the desired ketones (Scheme 22, a)). [48a] Although high conversions could be achieved in the case of the rearrangement of primary and cyclic allylic alcohols, the selectivity of these reactions were poor as large amounts of by-products like conjugated carbonyls and alcohols were formed. Tominaga showed that the catalyst loading could be reduced to 1-5 mol% under the same reaction conditions which resulted in high yields of the desired product (Scheme 22, a)). [48b] However, only 2 secondary allylic alcohols were tested in this catalytic system.



Scheme 22 Molybdenum compound catalyzed isomerization of allyl alcohols to carbonyl compounds

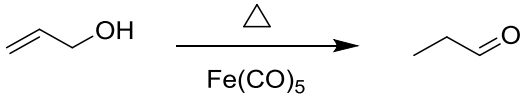
1.6 Iron

The first isomerization of an allylic alcohol to a carbonyl compound catalyzed by iron was discovered in 1962 by Emerson and Pettit (Scheme 23).[49] This reaction was observed during the investigation of the hydrolysis of π –allyl–iron tricarbonyl cation salts which came from the reaction between butadiene-iron tricarbonyl and an acid (like HBF_4, $HClO_4$, or $HSbCl_6$). The catalysts that were tested are either butadiene-iron tricarbonyl, isoprene-iron tricarbonyl, trans-piperylene-iron tricarbonyl or phenylbutadiene-iron tricarbonyl. The purpose of this reaction was to produce the π –allyl–iron tricarbonyl complex but the final product of the reaction was the organic carbonyl compound.



Scheme 23 First isomerization of an allylic alcohol to a ketone

Moreover, to support this mechanism allyl alcohol was heated together with $Fe(CO)_5$ and propionaldehyde was detected (Scheme 24).



Scheme 24 Isomerization of an allyl alcohol to an aldehyde

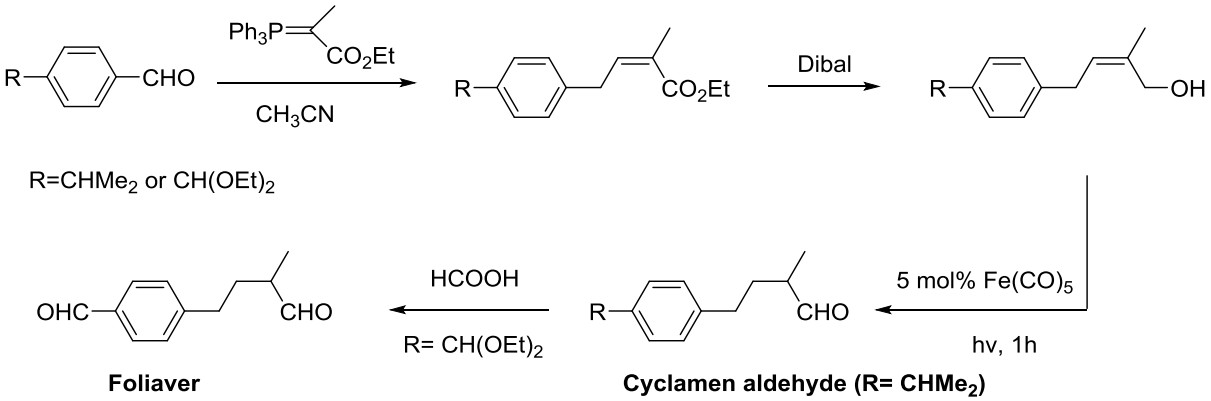
The paper of Emerson and Pettit reported no experimental details or analytic data. Consequently, after 5 years of the discovery of this reaction, Damico and Logan[50] extended the substrate scope and reported the experimental details and analytic data. Good yields could be achieved by using secondary allylic alcohols and homoallylic alcohol as the substrates. Although 20 mol% of catalyst were used for the isomerization of the cyclic substrate at 124 °C, the isolated yield was only 20%. Furthermore, if the high temperature was changed to an irradiation from a 200-w high-pressure mercury lamp at 20 °C, the yield of ketone was 40% even using only 3 mol% of $Fe(CO)_5$ as the catalyst in 4 hours. When irradiation is used, the reaction time must be reduced as

dimerization of the product (ketone or aldehyde) was observed. Isomerisation of primary allylic alcohols was also reported in this article, but not enough data was provided to support the results.

In spite of being applicable for a wide range of double bonds migrations, $Fe(CO)_5$ still has many drawbacks such as low activity, rather low yields of products, the requirement of high temperature, and it's toxicity as a liquid. Iranpoor and Mottaghinejad[51] further improved the isomerization of unsaturated alcohols by using $Fe_3(CO)_{12}$ as a catalyst and irradiation at wavelengths > 560nm in heptane or pentane as a solvent at 25-30 ^oC. The advantages of this new system are higher efficiency, reduced reaction temperatures and higher yields of the products. Homoallyl alcohols and alcohols with even more remote double bonds were also isomerized to the aldehydes and ketones

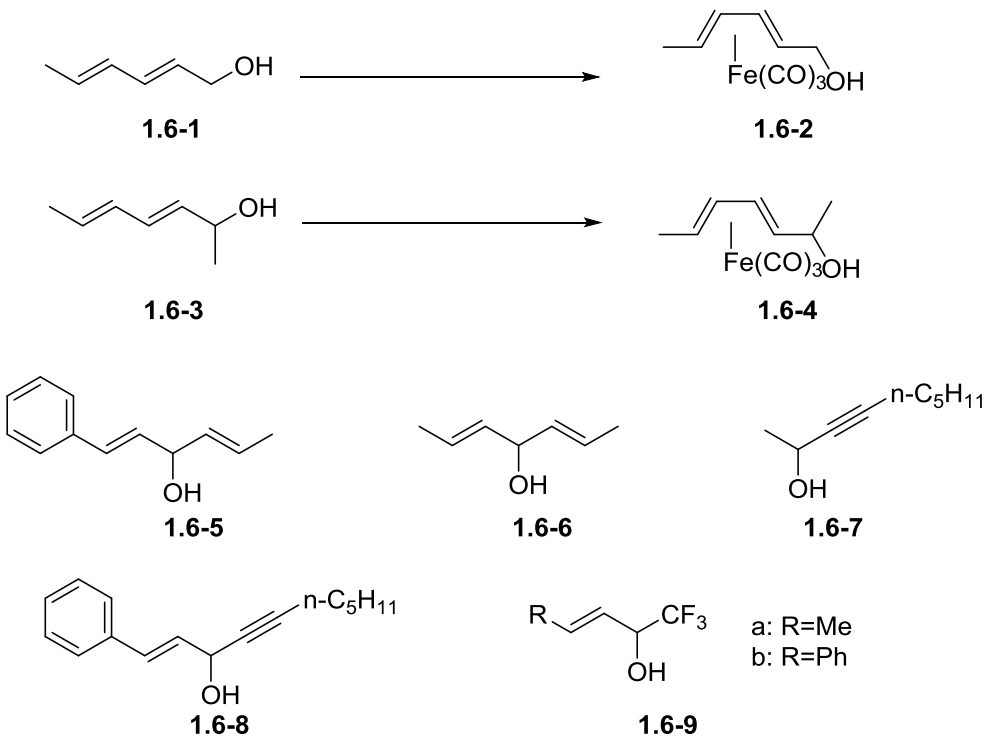
In 2001, Grée *et al.*[52] extended the substrate scope by increasing the number of substituents on the double bond to two and three (Scheme 25). These substituents bear different steric hindrance and electronic properties. Typically moderate to good yields were achieved.

This isomerization process was also applied in the synthesis of cyclamen aldehyde and foliaver which are the components of some perfumes (Scheme 25).[52] The allylic alcohol was easily prepared from a commercially available aldehyde through a two step-reaction with a good overall yield.



Scheme 25 Synthesis of foliaver and cyclamen aldehyde

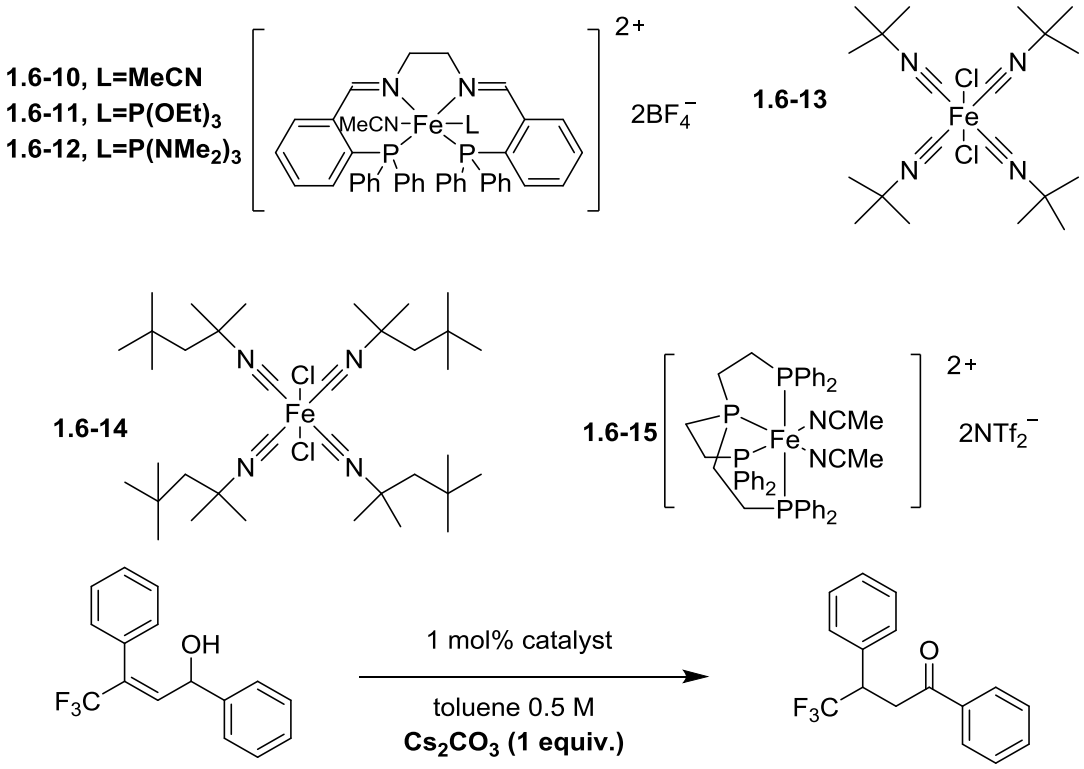
The $Fe(CO)_5$-catalyzed isomerization of allylic alcohols fails with a number of substrate types (Scheme 26). Naturally, the isomerization of compounds **1.6-1** and **1.6-3** were very hard because the complexation of the conjugated C=C bond with iron tricarbonyl complexes leads to stable diene-ligated complexes that do not produce the π-allyl-iron tricarbonyl complexes (Scheme 26, **1.6-2** and **1.6-4**). Some other multi unsaturated substrates like compounds **1.6-5**, **1.6-6** and **1.6-8** also failed to undergo the isomerization reaction under standard condition. If the amount of catalyst was increased to 25 mol%, only a small amount of undetermined decomposed product was observed. Furthermore, propargylic alcohols, for example complexes **1.6-7** and **1.6-8**, also failed to give the isomerized product. It is well known that electronic property is an important factor in chemistry. The reason seems to be obvious in the case of the trifluoromethyl group (Scheme 26, **1.6-9**) that the electron-withdrawing substituent prevents the formation of the π-allyl-iron tricarbonyl complex.



Scheme 26 Allylic alcohols which do not rearrange in the presence of $Fe(CO)_5$ catalyst

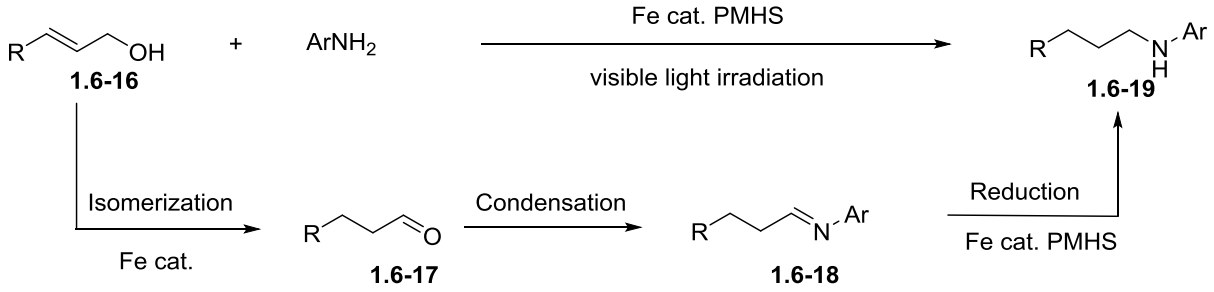
Nevertheless, there is one report on iron(II) complexes which are suitable catalysts for the isomerization of trifluoromethylated allylic alcohols and the synthesis of trifluoromethylated dihydrochalcones (Scheme 27).[53] This is also the only paper about the isomerization of allylic alcohols to ketones catalyzed by iron(II) complexes containing ligands other than CO. Among these complexes, **1.6-13** and **1.6-14** are the most efficient catalysts. Initially, compounds **1.6-10**, **1.6-11** and **1.6-12**, which are good catalysts for transfer hydrogenation, were used in this reaction to afford moderate to good conversions and yields but a rather long reaction time (18-22 hours) was required as well as the use of 1 equivalent of base. In comparison with complex **1.6-10**, catalysts **1.6-13** and **1.6-14** resulted in 100% conversion of the substrate and similar yields were obtained. The isolated yield dropped appreciably if the reaction time was shortened from 22 hours to 7 hours. No conversion was observed using compound **1.6-15** as a catalyst.

Notably, I have attempted the synthesis of the iron-catalysts **1.6-13** and **1.6.14** by using different isocyanides. The compounds I assumed to be **1.6-13** and **1.6.14** could be isolated as solids. In spite of the fact that I was using the same method as mentioned in the article I did not obtain the expected products. Mass spectral analysis revealed that what I have isolated are penta- isocyanide coordinated complexes. This means that 5 ligands reacted with one molecule of $FeCl_2$. We have obtained an X-ray for one of the structures in which we found that the counterion was $FeCl_4$. Presumably this is $FeCl_4^-$. This would mean that the complex is a monocationic Fe(II) complex. More analysis is needed to determine this with certainty. In the meantime, I have tested these complexes in the isomerization of crotyl alcohol to butyraldehyde under different conditions. Different bases, solvents, catalysts, reaction time and additives were used in this reaction. Unfortunately, in none of these reactions did we find any isomerization.



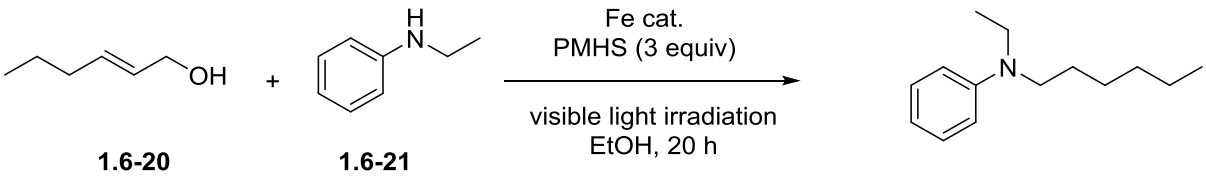
Scheme 27 Iron(II) complexes catalyzed isomerization of trifluoromethyl substituted allylic alcohols

Iron catalyzed isomerization may be part of a tandem reaction. In 2014, Li *et al*. reported the reaction of an allylic alcohol and aniline to produce an alkylated aniline with iron carbonyl as catalyst and PMHS (polymethylhydrosiloxane) as a hydrogen source under the exposure of visible light irradiation in ethanol (Scheme 28).[54] In reality, this process is a tandem reaction which consists of 3 reactions: the first reaction is the iron catalyzed isomerization of allylic alcohol to produce aldehyde followed by condensation of the aldehyde with anilines. The final step is the iron catalyzed reduction reaction (Scheme 28).



Scheme 28 Iron catalyzed tandem reaction

First of all, the catalysts that were performing the isomerization of allylic alcohols to carbonyl compounds were tested. It was found that iron carbonyl compounds were good catalysts for the isomerization reaction of the allylic alcohol. In the meantime, some other iron(0) complexes, for example $Fe(PBO)(CO)_3$ (PBO = 4-phenylbut-3-en-2-one), $Fe(cot)(CO)_3$ (cot = cyclooctatetraene) and $Fe(IMes)(CO)_3$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) were also tested in this tandem reaction. After comparing different conditions, 5 mol% of catalyst (**1.6-20**/**1.6-21** = 1.5) at 50 °C afforded the best conversion (95%) after 20 hours under activation with visible light. More than 30 different combinations of **1.6-20** and **1.6-21** were used here and moderate to good yields (31-95%) were achieved.

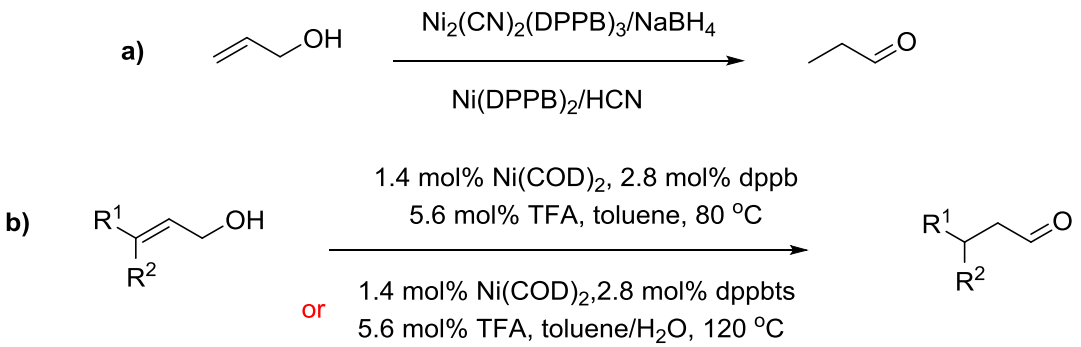


1.6-20 **1.6-21**

Scheme 29 Optimization of Iron catalyzed tandem reaction

1.7 Nickel

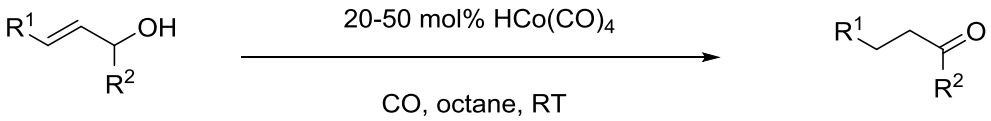
Corain and co-workers reported the first example of the isomerization reaction of allylic alcohol catalyzed by a combination of $Ni_2(CN)_2(DPPB)_3/NaBH_4$ or $Ni(DPPB)_2$/HX (HX= HCN, CF_3COOH, CCl_3COOH, and H_2SO_4) (Scheme 30, a)). [55] The combination of $Ni(DPPB)_2$/HCN is a bad choice from the application point of view due to extremely high toxicity of HCN. And then similar systems of nickel compounds after activation with acids were also reported. Iron carbonyl compounds have been used as catalysts in the isomerization delivering high yields and turnover frequencies (Scheme 30, b)). [56] Further investigation was reported by Monflier and co-workers in 1998 (Scheme 30, b)). [57] The catalytic system consisted of nickel (0), a bidentate ligand and acid. Interestingly, it is a good choice to use a biphasic solvent system for the isomerization of geraniol but it is not suitable for prenol as substrate. However, only low to moderate conversion could be obtained in the isomerization of geraniol to the corresponding aldehydes.



Scheme 30 Nickel catalyzed isomerization of allyl alcohols to aldehydes

1.8 Cobalt

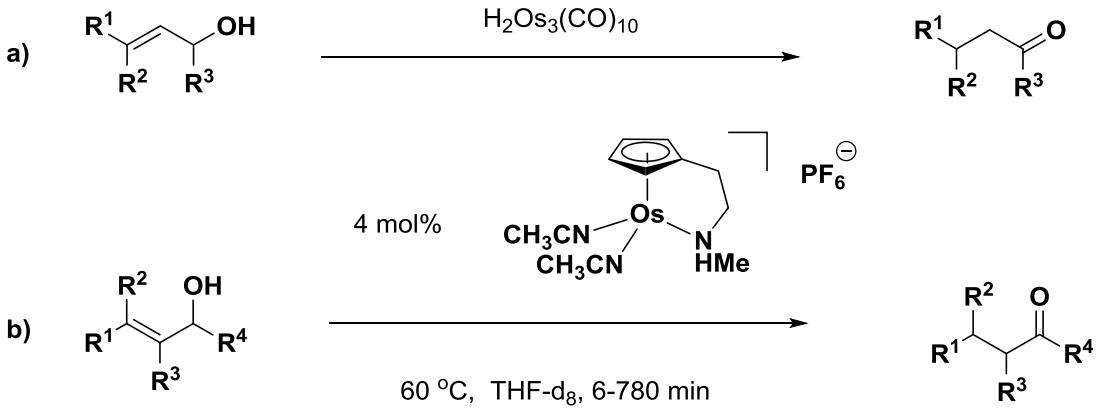
Cobalt catalyzed isomerization of allylic alcohols to the corresponding carbonyls was discovered in 1963 by Goetz and Orchin (Scheme 31). [58] To the best of our knowledge, this is the only cobalt compound ($Co(CO)_4H$) which was reported to promote the isomerization of allylic alcohols to aldehydes or ketones. It is worth mentioning that extremely high catalyst loadings (from 20% to 50%) were required and only low selectivities (some unidentified products) and yields (up to 21%) were achieved



Scheme 31 Cobalt catalyzed isomerization of allyl alcohols to carbonyl compounds

1.9 Osmium

The osmium complex $H_2Os_3(CO)_{10}$ catalyzes the isomerization of allylic alcohols to the corresponding carbonyl compounds as reported by Hasso and Deeming in 1976 (Scheme 32, a)). [59] However, no information about the catalyst loadings and yields of the desired products were reported. In 2010, Esteruelas and co-workers reported a half-sandwich osmium complex catalyzed isomerization of allylic alcohols to the corresponding carbonyl compounds (Scheme 32, a)). [16] High conversion and good selectivity could be obtained in the presence of 4 mol% osmium catalyst at 60 °C in the isomerization of secondary allylic alcohols to the corresponding ketones. For the primary allylic alcohols, the activities and selectivities (above 69%) are both good except with 2-methyl-2-propen-1-ol as substrate where a large amount of by-product (aldol reaction product) was formed.

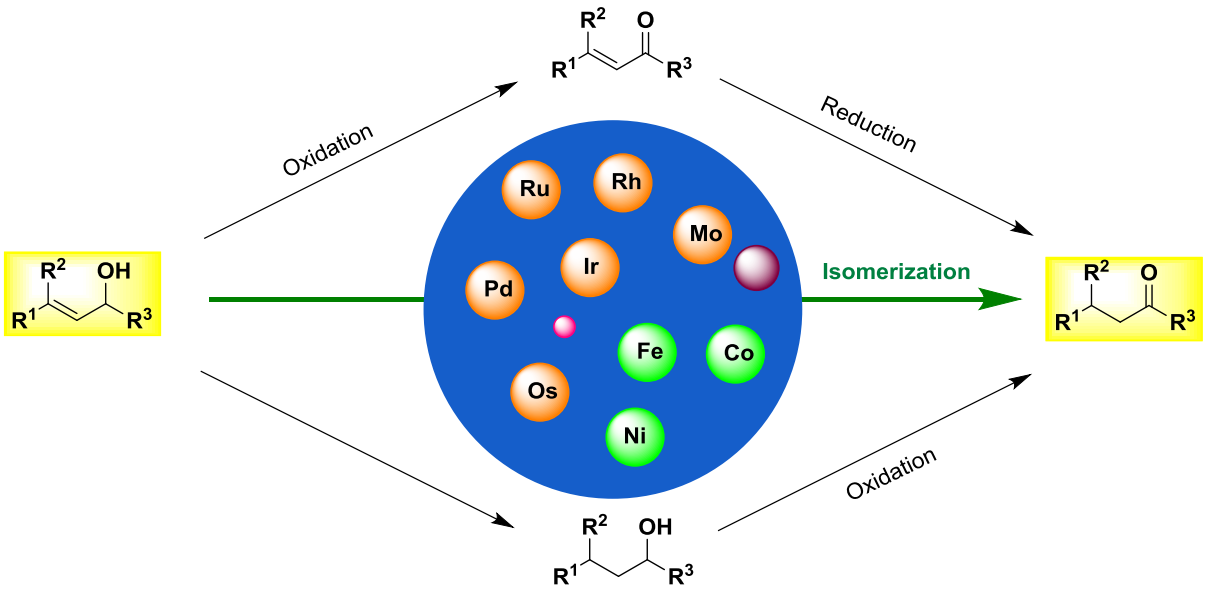


Scheme 32 Osmium compounds catalyzed isomerization of allyl alcohols to carbonyl compounds

1.10 The goals of this research

As described above in the introduction, the isomerization reaction is considered as a green, environmentally friendly, very atomically economical method widely used in academia and this method has great potential for application in industry. Compared with the traditional two-step method, the allyl alcohol isomerization reaction can avoid the use of expensive/highly toxic oxidation and/or reduction reagents (Scheme 33). In the past half century, this method has been extensively studied and has achieved rich results.

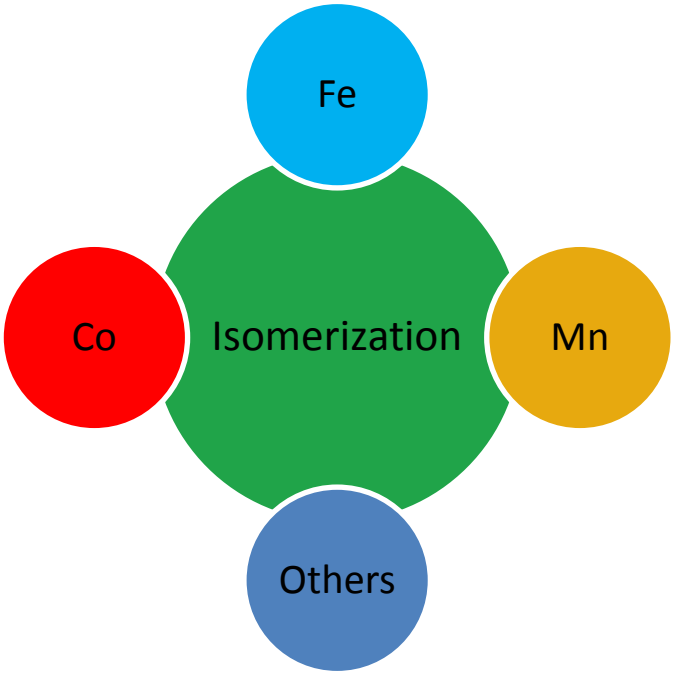
The noble transition metal complexes are the most important catalysts for the isomerization of allylic alcohols to form carbonyl compounds (Scheme 33). However, we know that noble transition metals are expensive and have poor compatibility with the environment. In the process of producing additives or drugs, the residue standards for such metals are very strict, and they are very harmful to the human body. There are three main types of inexpensive transition metals (iron, nickel and cobalt) that can be used for the reaction of allyl alcohols to form carbonyl compounds. Although a very limited number of inexpensive metal complexes can be used to catalyze the isomerization of allyl alcohols to generate carbonyl compounds, this has played a pioneering role in the future development.



Scheme 33 Ways to generate carbonyl compounds from allylic alcohols and metals used in isomerization

Carbonyl iron complexes are the most widely used catalysts for iron-catalyzed reactions for the isomerization of allyl alcohols to carbonyl compounds. From a practical point of view, the production of carbon monoxide is a major cause of the limited use of this compound. The best solution to this problem is to use other iron complexes instead of iron (0) compounds. To the best of our knowledge, only one article has reported that ferrous iron can catalyze the isomerization of allyl alcohols to carbonyl compounds. Although the amount of catalyst is only 1 mol%, the substrate must have a trifluoromethyl substituent on C=C bond and one 100 mol% of cesium carbonate should be used. Therefore, the development of a new type of iron-catalyzed isomerization of allyl alcohols to carbonyl compounds is very urgent. Our goal is to develop new and inexpensive first-row transition metals catalyzed the isomerization of allyl alcohols into carbonyl compounds. Simultaneously, this

type of catalytic system requires a low catalyst amount and mild conditions and can achieve high reaction activity and selectivity (Scheme 34).



Scheme 34 Goals of our research

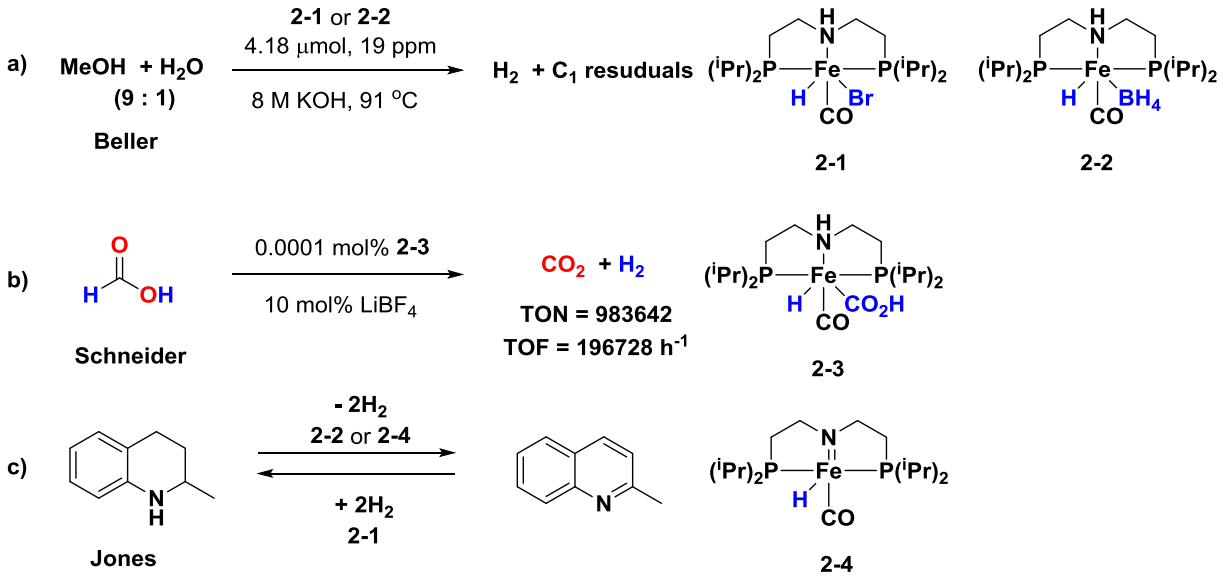
2 Results and discussion

2.1 Iron catalyzed isomerization of allylic alcohols

(This part of work has already been published in 2018. [60] would like to appreciate Zhihong Wei and Haijun Jiao for their contributions to the proposed mechanism, and Brian Spiegelberg for his contributions to the deuterium labeling experiments and development of the substrates scope of the reaction)

Iron is the most abundant transition metal in Earth's crust and the 4th most common of all elements after oxygen, silicon and aluminium. [2] Compared to noble transition metals like iridium, rhodium or ruthenium, iron is cheap, green and much more environmentally friendly. Therefore, it is desirable to prepare catalysts which are based on iron.

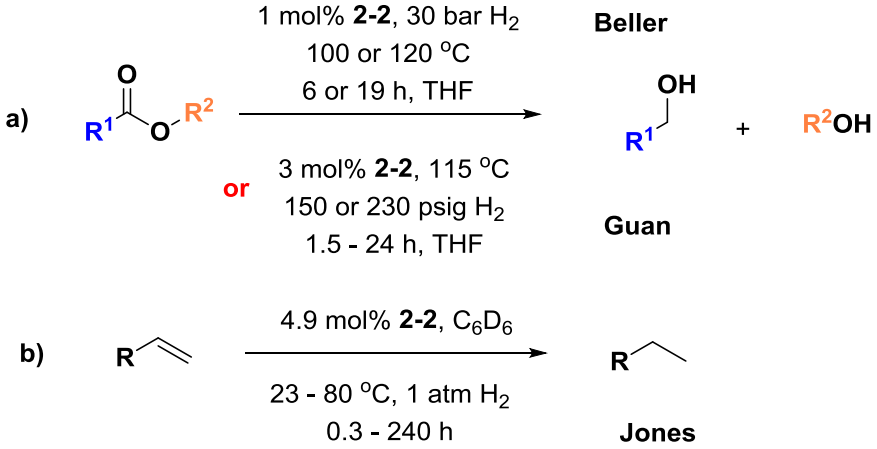
In recent years, pincer-ligated iron complexes have been widely developed for catalytic applications.[3] In 2013, Beller and co-workers were the first to report the synthesis of aliphatic PNP pincer iron complexes, which could be applied for an efficient hydrogen generation from methanol in a basic solution (Scheme 35). [4] Shortly afterwards, Schneider and co-workers reported a highly efficient iron catalyst for the dehydrogenation of formic acid, where the TON (Turnover number) could reach a TON of almost up to a million with a TOF (Turnover frequency) of 196728 per hour. [5] Simultaneously, Jones and co-workers reported dehydrogenation of N-heterocycles catalyzed by a PNP iron complex. [6] Interestingly, the dehydrogenated products could also be utilized as substrates to perform hydrogenation reactions with different iron compound.



Scheme 35 PNP iron catalyzed dehydrogenation

In 2014, Beller's [7] and Guan's [8] group independently reported an iron catalyzed hydrogenation of esters to alcohols (Scheme 36). These are the first base-free iron catalyzed hydrogenations under relatively mild reaction conditions. Furthermore, selectively of the hydrogenation of C=C bond in alkenes to alkanes catalyzed by a PNP iron complex was reported by Jones, where the substrates could bear various unsaturated substituents, like -CO_2Me and –CN. However, hydrogenation of α,β-unsaturated ketones were not selective, which resulted in

saturated alcohols as the main products.

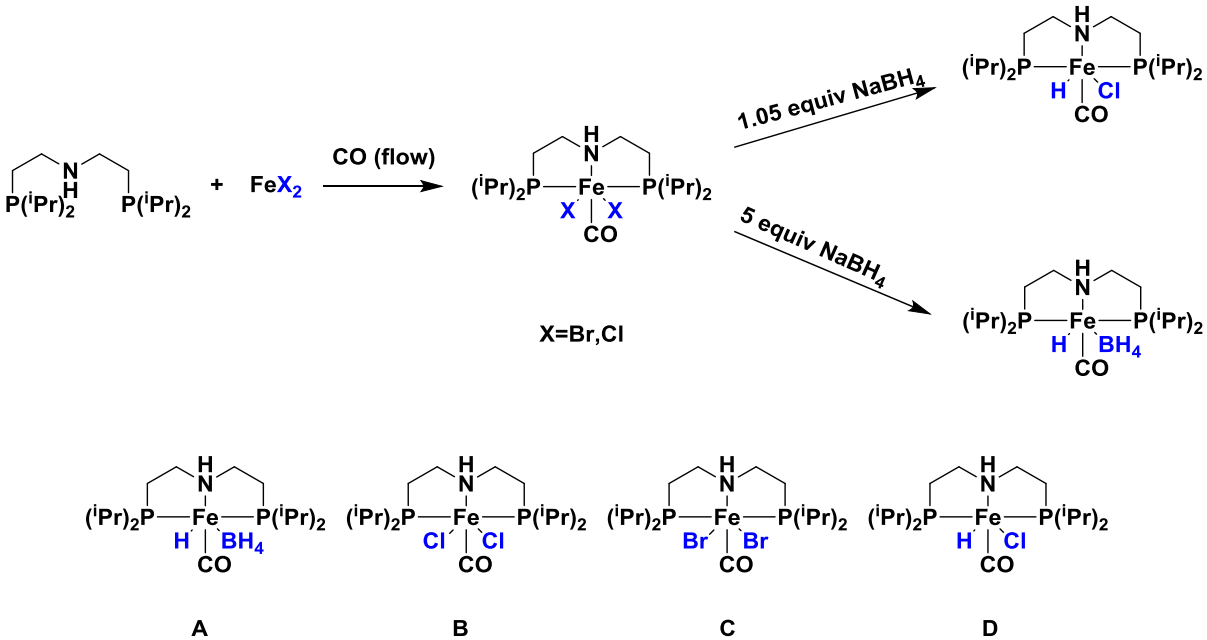


Scheme 36 PNP iron catalyzed hydrogenation

Intrigued by iron catalyzed hydrogenation and dehydrogenation reactions, we assumed that these PNP pincer iron compounds might also be suitable for isomerization reactions and tested them in the isomerization of oct-1-en-3-ol to 3-octanone.

2.1.1 Synthesis of iron compounds

The synthesis of pincer iron complexes was reported by Beller's, Guan's and Schneider's groups. The *trans*-dihalogen iron complexes (**B** and **C**) were synthesized by mixing a PNP ligand and FeX_2 (X = Cl, Br) under an atmosphere of carbon monoxide. By using different amounts of $NaBH_4$, compounds **A** and **D** can be prepared from complex **B** respectively. Compound **A** could also be produced from complex **C** by using 5-10 equivalents of $NaBH_4$ (Scheme 37).

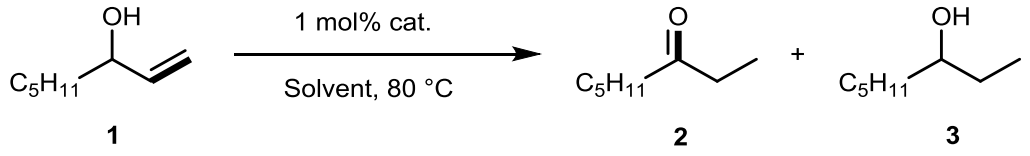


Scheme 37 PNP-Iron compounds (**A**-**D**) applied to the isomerization of non-activated allylic alcohols in this work

2.1.2 Optimization reactions

We started the tests for the isomerization of oct-1-en-3-ol to 3-octanone in the presence of different pincer iron complexes in different solvents at 80 °C. Various solvents (Toluene, IPA, ^{t}BuOH and EtOH) were used in the isomerization of oct-1-en-3-ol with catalyst A that resulted in traces of 3-octanone (Table 1, entries 1-4). No conversion was observed by using neat reaction condition (Entry 5). Bases are known additives in the activation of the catalysts. In fact, the addition of 2 mol% of ^{t}BuOK leads to a 90% conversion despite low selectivity to the desired product (Entry 6). In comparison, when using THF instead of isopropanol as a solvent, the conversion and yield of the reaction both decreased significantly (Table 1, entry 7). None of the compounds B and C exhibited any catalytic activity under the same conditions (Table 1, entries 8 and 9). When Compound D is used as a catalyst, 100% conversion could be obtained, yet again with poor selectivity towards the desired product **2** (Table 1, entry 10). The reaction still maintains higher activity under conditions of reduced reaction time and catalyst loading (Table 1, entries 11 and 12). These tests show that catalyst D is much more reactive than other compounds in the activity of the reaction.

Table 1 Optimization of Catalysts (This table is from the published article [60])[a]



1 **2** **3**

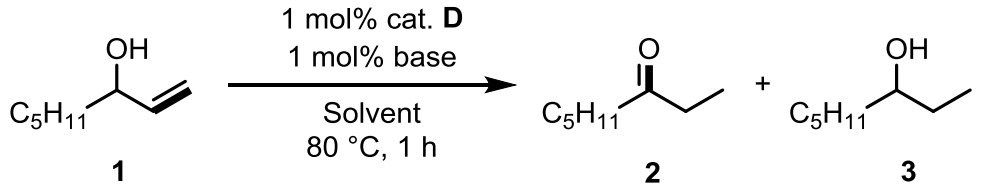
Entry	Cat.	Solvent	Time	Conv. 1 [b]	2 Yield [b]	3 Yield [b]
1	**A**	Toluene	15 H	Trace	trace	trace
2	**A**	^{i}PrOH	15 H	Trace	trace	trace
3	**A**	^{t}BuOH	15 H	Trace	trace	trace
4	**A**	Ethanol	15 H	Trace	trace	trace
5	**A**	neat	15 H	No	no	no
6[c]	**A**	^{i}PrOH	15 H	90%	28%	60%
7[c]	**A**	THF	15 H	15%	15%	no
8[d]	**B**	^{i}PrOH	24 H	No	no	no
9[d]	**C**	^{i}PrOH	24 H	No	no	no
10[d]	**D**	^{i}PrOH	24 H	99%	9%	90%
11[c]	**D**	^{i}PrOH	24 H	99%	11%	88%
12[e]	**D**	^{i}PrOH	3 H	100	15%	84%

[a] 1 mmol of substrate. [b] Determined by GC and GC-MS, dodecane as an internal standard. [c] 2 mol% ^{t}BuOK w.r.t. substrate. [d] 2 mol% catalyst and 4 mol% ^{t}BuOK w.r.t. substrate. [e] 1 mol% ^{t}BuOK w.r.t. substrate.

Subsequently, we tested the influence of solvents and bases on the selectivity of the reaction. The use of other protic solvents (EtOH and MeOH) can lead to reduced yields (Table 2, entries 1-3). When this isomerization reaction was carried out in THF, very high yields and conversions could be achieved. (Table 2, entry 4). For the

isomerization of allyl alcohol, the use of toluene and benzene as the solvent can produce 100% conversion (Table 2, entries 5-7, respectively). Only low conversions were obtained when using acetonitrile and heptane as solvents (Entry 9-10). At the same time, we also tested many other bases. If sodium/lithium tert-butoxide were used instead of potassium tert-butoxide as the base, there would be a significant reduction in both yield and selectivity (Table 2, entries 11 and 12). Using a weak base instead of a strong base, the yields of the isomerization reactions were reduced or even unreactive (Table 2, entry 13-17).

Table 2 Solvent and base screening (This table is from the published article [60]) [a]



Entry	Base	Solvent	Conv. **1** [%][b]	Yield **2** [%][b]	Yield **3** [%][b]
1[c]	^{t}BuOK	*i*PrOH	100	15	84
2[c]	^{t}BuOK	EtOH	60	31	29
3[c]	^{t}BuOK	MeOH	3	3	trace
4[c]	^{t}BuOK	THF	98	96	2
5[c]	**^{t}BuOK**	**Toluene**	**100**	**99**	**1**
6	**^{t}BuOK**	**Toluene**	**100**	**98**	**2**
7	^{t}BuOK	Benzene	100	99	trace
8	^{t}BuOK	DMF	97	93	4
9	^{t}BuOK	Heptane	3	3	0
10	^{t}BuOK	CH_3CN	33	33	0
11[d]	^{t}BuONa	THF	85	79	5
12[d]	^{t}BuOLi	THF	43	39	3
13	K_3PO_4	Toluene	25	25	0
14	K_2CO_3	Toluene	trace	Trace	0
16	$KHCO_3$	Toluene	trace	Trace	0
16	Na_2CO_3	Toluene	0	0	0
17	$NaHCO_3$	Toluene	0	0	0

[a] 1 mmol of substrate. [b] Determined by GC with dodecane as an internal standard. [c] Reaction time 3 h. [d] Reaction time 1.5 h.

In further experiments, either toluene or THF can be utilized as a solvent from the efficiency, toxicity and price

point of view. Having the optimized conditions in hand (Table 2, entry 5), we then monitored the isomerization reaction of the allyl alcohol to the corresponding ketone every 2 minutes (Figure 1).Full conversion could be achieved in 20 minutes at room temperature (Figure 1, red curve). In comparison, it only took 6 minutes to get a full conversion at 80 °C (Figure 1, black curve).

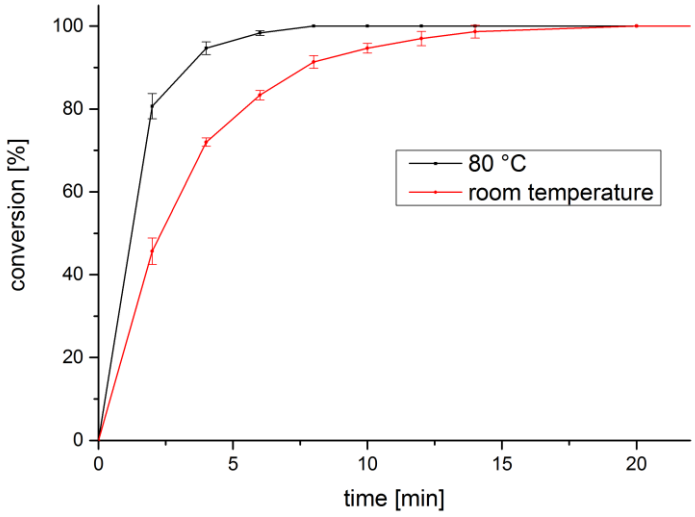
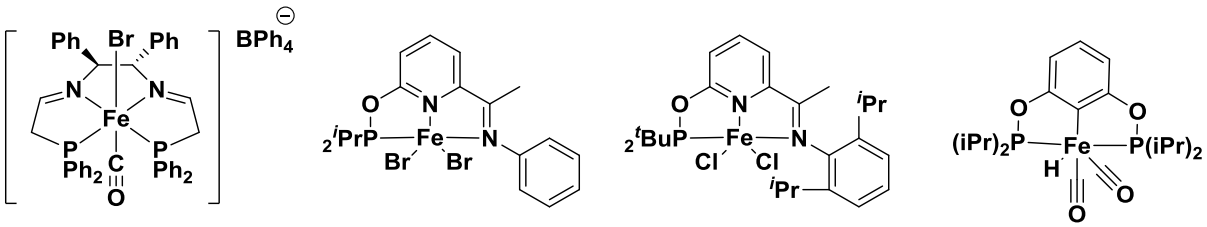


Figure 1 Monitoring the isomerization reaction over time: 1 mmol oct-1-en-3-ol, 1 mol% catalyst **D**, 1 mol% of ^{t}BuOK, 1 mL D-toluene, monitored by ^{1}H-NMR. Data given are averaged conversions of three reactions. (This figure is from the published article [60])

Simultaneously, some other iron compounds were also tested in the isomerization of oct-1-en-3-ol to 3-octanone (Scheme 38). A PNNP type iron complex **2.3-1** was introduced by Morris, which is an efficient catalyst for asymmetric (transfer) hydrogenation of ketones and imines. [68] This compound could be active after being activated with 2-8 equivalents of ^{t}BuOK at room temperature. The resulted catalyst has the ability to accept 2 H atoms both from hydrogen gas (hydrogenation) and ^{i}PrOH (transfer hydrogenation). We presumed that these compounds may catalyse the isomerization of allylic alcohols to ketones.



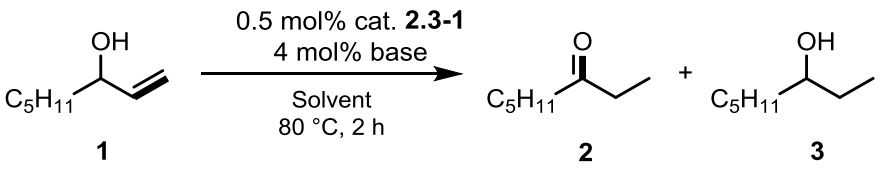
2.3-1 **2.3-2** **2.3-3** **2.3-4**

Scheme 38 Other iron compounds used in isomerization of allylic alcohols to ketones

Initially, we carried out the experiments in different solvents as well as under neat conditions with catalytic amount (0.5 mol%) of catalyst **2.3-1** and 8 equivalents of ^{t}BuOK at 80 ^{o}C (Table 3). Interestingly, the conversion is low when the experiment was performed in IPA (isopropanol), which is the best solvent in hydrogenation of ketone (Entry 7). Another protic solvent (ethanol) was also tested in this isomerization reaction with similar

conversion (Entry 6). Nevertheless, high conversions were achieved by utilizing aprotic solvents like heptane and diethyl ether (Entries 1-2). Notably, when the isomerization reaction was carried out under neat conditions, high conversion was observed (Entry 9). Suitable solvents for PNP iron catalyzed isomerization like THF, toluene and DCM are not good choices for these reactions (Entries 3, 5 and 8). In all cases, there are no satisfactory results obtained in isomerization reaction with some transfer hydrogenation products. Unfortunately, all of the pincer complexes **2.3-2** to **2.3-4** were not active for this isomerization reaction under the same conditions. In conclusion, PNNP iron compound is a promising catalyst for isomerization of allylic alcohols to ketones while further optimizations in order to get good selectivities are required.

Table 3 Solvent screening of the catalyst **2.3-1**. [a]



1 **2** **3**

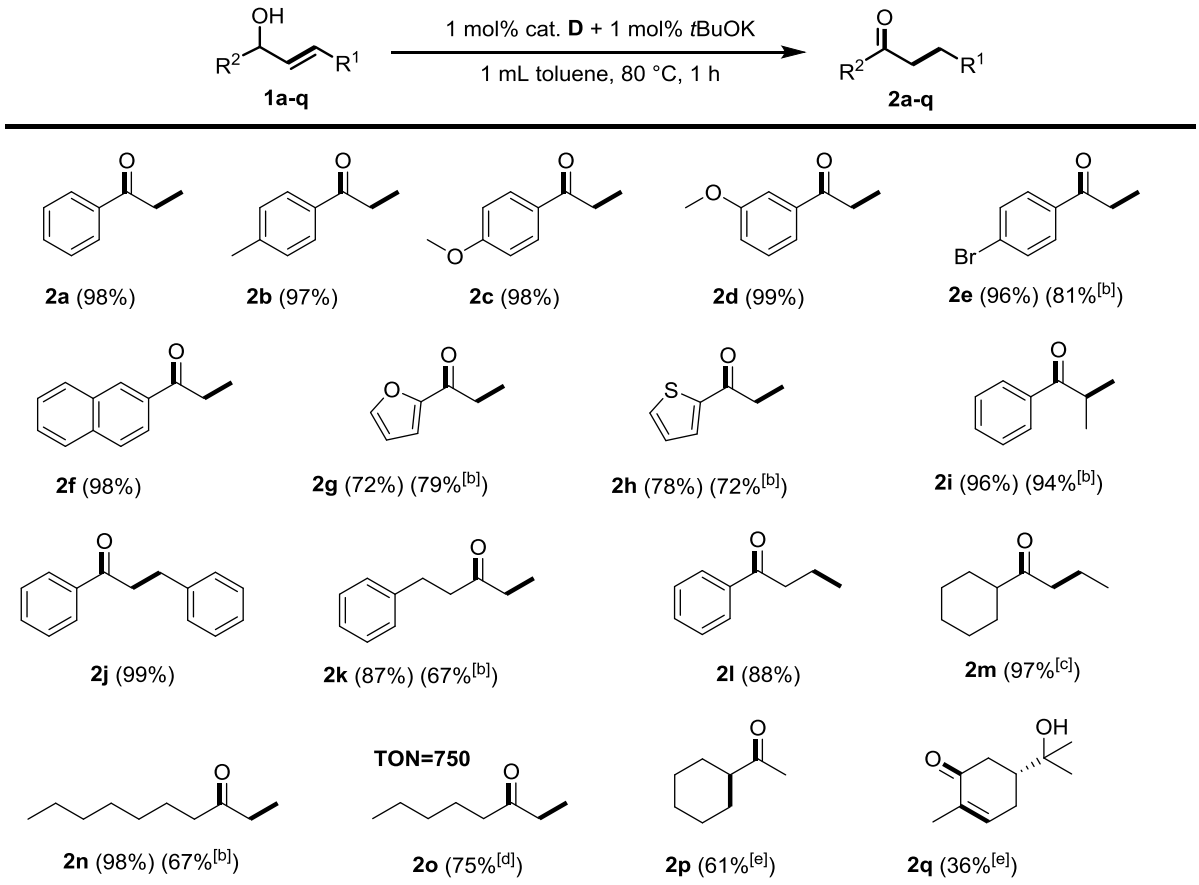
Entry	Base	Solvent	Conv. 1 [%][b]	Yield 2 [%][b]	Yield 3 [%][b]
1	^{t}BuOK	Heptane	87	67	20
2	^{t}BuOK	Et_2O	99	78	21
3	^{t}BuOK	THF	36	20	16
4	^{t}BuOK	MeCN	47	14	33
5	^{t}BuOK	DCM	15	15	0
6	^{t}BuOK	EtOH	28	23	5
7	^{t}BuOK	IPA	21	13	8
8	^{t}BuOK	Toluene	50	40	10
9	^{t}BuOK	neat	96	72	24

[a] 1 mmol substrate. [b] Determined by GC with n-dodecane as internal standard.

2.1.3 Substrates scope

Having the optimized reaction conditions in hand, we tested the scope and limitations of this catalytic system on a range of substrates, which included both aromatic and aliphatic allylic alcohols (Scheme 39). Aromatic substrates containing both electron-donating groups and electron-withdrawing groups can achieve excellent yields (Scheme 39, **2a** to **2e**). A high isolated yield (98%) can be achieved with the substrate containing a naphthyl group (Scheme 39, **2f**). Satisfactory yields can be obtained by using heterocyclic furyl or thienyl substituted substrates (Scheme 39, **2g** and **2f**). The additional substituents on the C=C bond have no adverse effect on the conversion of allyl alcohol to the corresponding ketone (**2j**). The smooth conversion from 1k to 2k indicates that not only benzyl alcohol compounds are suitable for this reaction. It is worth mentioning that the isomerized ketone can also be obtained by using homo-allylic alcohol as a substrate. Good to excellent yield can

achieved using aliphatic allylic alcohols as substrates (Scheme 39**, 2m** to **2o**). Notably, high yields can be obtained in the isomerization reactions at room temperature (Scheme 39, **2e**, **2g**, **2h**, **2i**, **2k**, **2n**). The saturated ketone 2p can be obtained from cyclic substrate 1p in good isolated yield (61%). When *trans*-sobrerol was selected as a substrate, only the dehydrogenation product (**2q**) was discovered. This is probably caused by the steric hindrance of the extra methyl group, which hinders the hydrogenation of olefins.

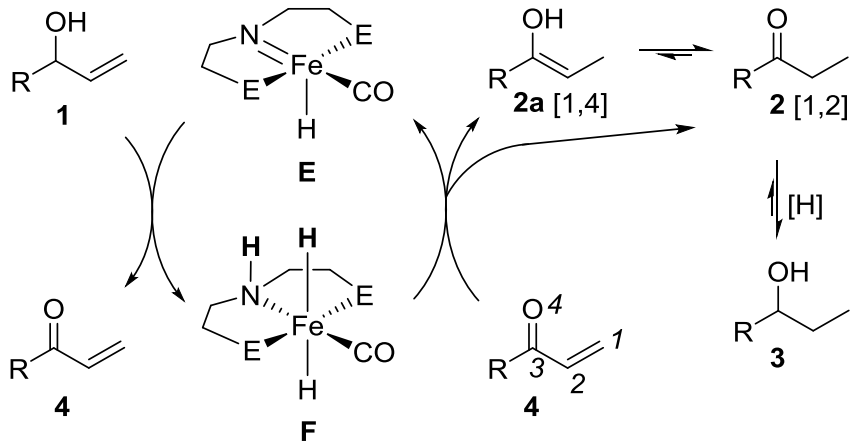


[a] 1 mmol of substrate, isolated yields, the blue bond is the position of the original C=C bond in the substrates. [b] Room temperature was used, reaction time was 2 hours [c] The substrate is a mixture of cis- and trans-isomers. [d] Neat conditions on 10 mmol scale and catalyst is 0.1 mol% for 2 hours. [e] Reaction time was 16 hours, 5 mol% catalyst **D** and 5 mol% ^{t}BuOK.

Scheme 39 Substrate scope of iron-catalyzed allylic alcohol isomerization (This scheme is from the published article [60]) [a]

2.1.4 Proposed mechanism

First of all, precatalyst **D** produces a truly active catalyst **E** in the presence of a base (^{t}BuOK). Catalyst D can dehydrogenate allylic alcohol (**1**) to conjugated carbonyl compound (**4**) that results in complex **F** (Scheme 40). The following step is the hydrogenation of C=C bond by compound **F** via two possible pathways: 1) 1,2 addition of compound **4** directly produce saturated ketone **2**; 2) 1,4 addition of conjugated ketone **4** to form enol first and then tautomerizes to saturated ketone. If there is enough hydrogen in the reaction system, the saturated ketone will be further hydrogenated to produce a saturated alcohol.

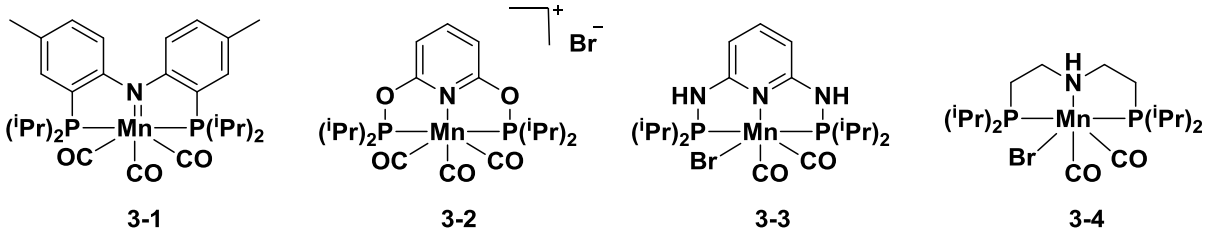


Scheme 40 Proposed mechanism (R = C_5H_{11}, E = $P(^iPr)_2$) (This scheme is from the published article [60])

Figure 2 ^1H and ^{13}C NMR spectra of products

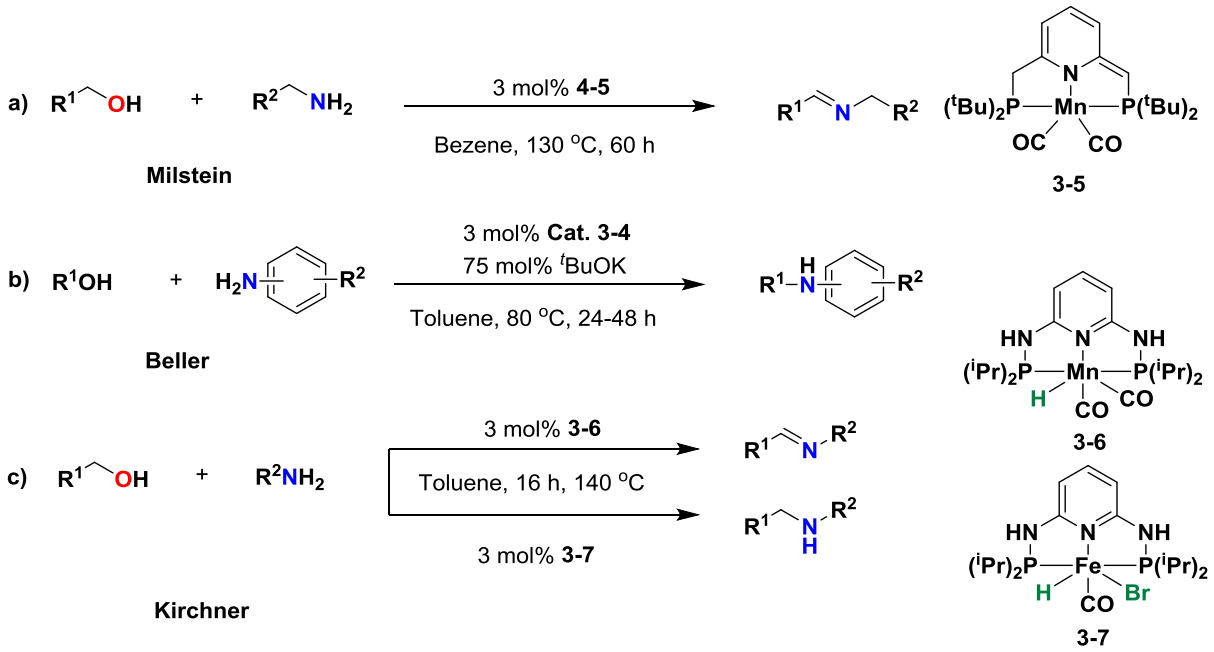
2.2 Manganese catalyzed isomerization of allylic alcohols

Manganese is the 3rd most abundant transition metal in Earth's crust after iron and titanium. It is mainly utilized in the manufacture of steel. [1] Compared to noble transition metals, manganese is ubiquitous, inexpensive, non-toxic and hence environmentally friendly. Recently, tridentate PNP manganese compounds have attracted significant interest from chemical researchers not only focused on replacing expensive metal catalyzed reactions, but also for new catalytic transformations. [2] The first PNP pincer ligated manganese complex was reported by Nocera and Ozerov in 2009. This complex was prepared by a reaction of the ligand with $Mn_2(CO)_{10}$ or $Mn(CO)_5Br$ to afford $PNPMn(CO)_3$ (Scheme 41, compound **3-1**). [3] This method has been utilized as a model reaction in the syntheses of many other PNP manganese complexes. Subsequently, Boncella and co-worker synthesized and characterized a range of PNP pincer manganese complexes (Scheme 41, compounds **3-2** to **3-4**). [4] However, no catalytic activity of these pincer type compounds was reported by these authors.



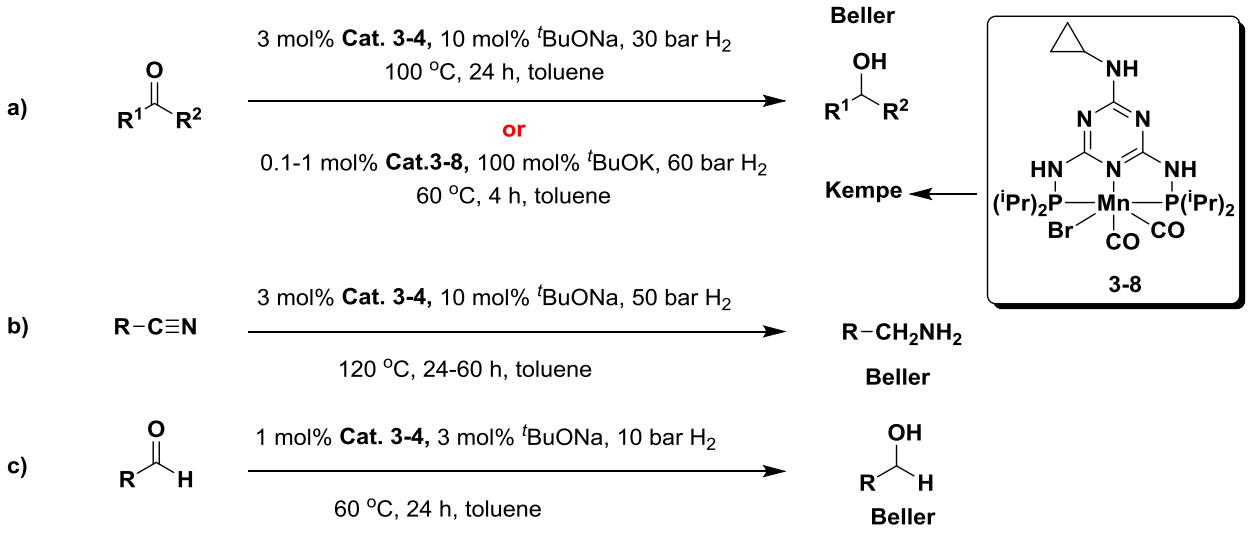
Scheme 41 Examples of known PNP pincer manganese compounds

In 2016 Milstein and co-workers reported the first reaction catalyzed by a PNP pincer-ligated manganese compound. [5] A dehydrogenative coupling of alcohols and amines to produce aldimines and hydrogen gas in the presence of catalyst **3-5** was described (Scheme 41, a). In comparison, Beller and co-workers reported reactions between alcohols and amines with pre-catalyst **3-4** and base, which resulted in the formation of amines rather than secondary aldimines (Scheme 41, b). [6] Interestingly, Kirchner and co-workers carried out experiments under the same reaction conditions with manganese and iron catalysts that produced aldimines and amines respectively (Scheme 41, c). [7]



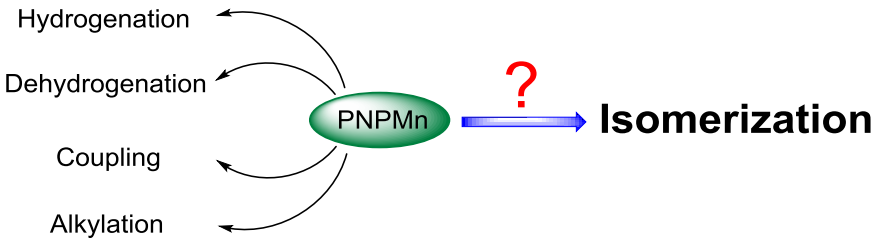
Scheme 42 Mn-catalyzed C-N bond formation

Beller's group was the first one to report an aliphatic PNP-ligated manganese pincer compound, which is a good catalyst for the hydrogenations of ketones, nitriles and aldehydes. [8] In the same year, a more efficient catalyst with an aromatic PNP ligand was developed for the hydrogenation of ketone with 1 equivalent base was reported by Kempe and co-workers. [9]



Scheme 43 Mn-catalyzed Hydrogenation

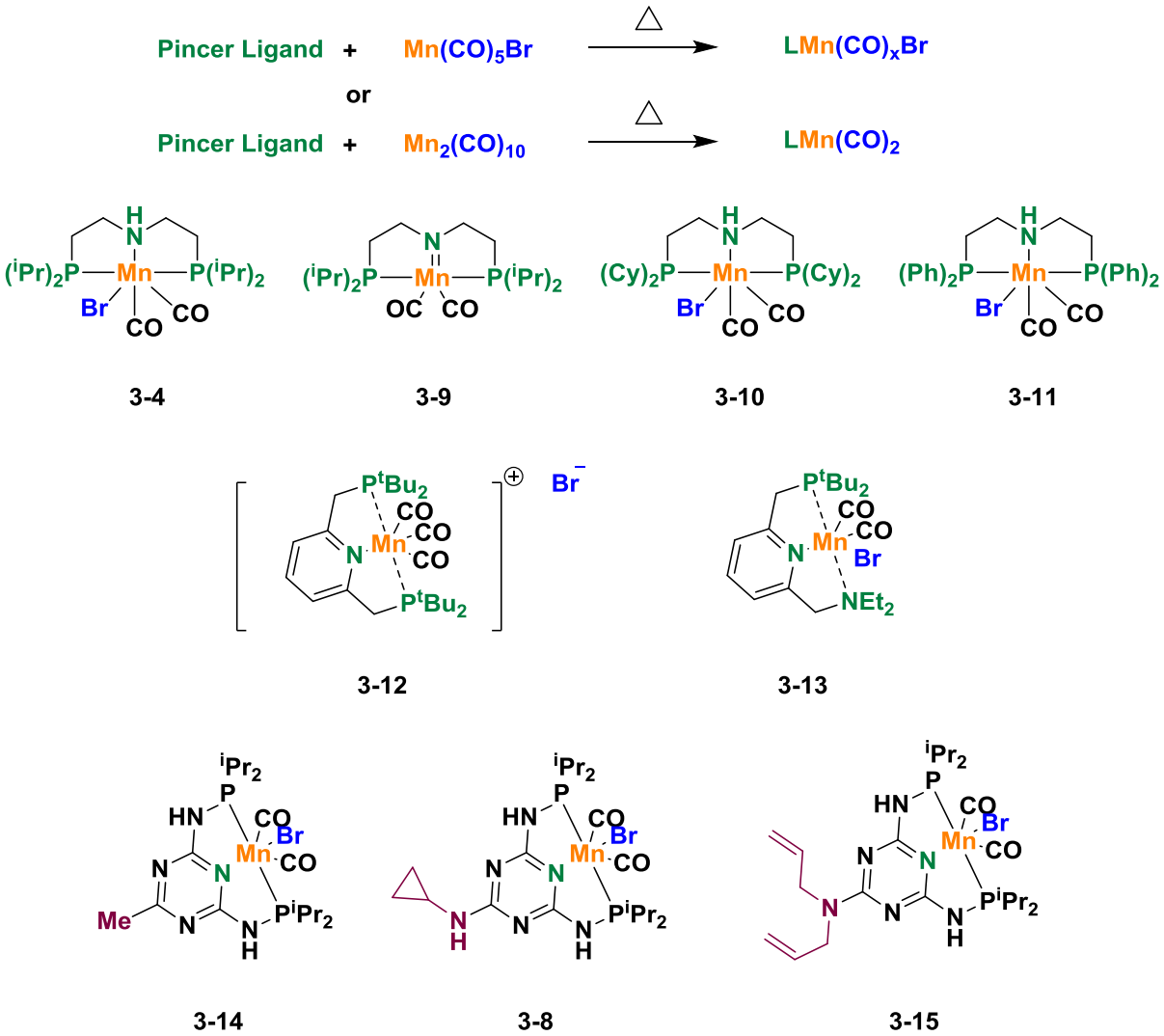
Intrigued by previously successful application of PNP-pincer manganese complexes in a range of catalytic reactions, especially in hydrogenation, we presumed that the isomerization of allylic alcohols to form the corresponding ketones could also be catalyzed by these manganese complexes.



Scheme 44 Ideas for manganese catalyzed isomerization

2.2.1 Synthesis of manganese compounds

Since Beller and co-workers discovered that the aliphatic PNP-pincer manganese compounds were good choices for hydrogenation reactions, this type of catalysts were broadly exploited in catalytic reactions related to hydrogen transfer. As the PNP ligands in these complexes are considered to be non-innocent, which indicate that the ligand also actively participates in the catalytic reaction. These organometallics are synthesized from a PNP ligand and $Mn(CO)_5Br$ (Scheme 45). [72, 75-76] Alternatively, compound **3-9** may be prepared by mixing a PNP ligand, HMDSO (hexamethyldisiloxane) and $Mn_2(CO)_{10}$ (the details are shown in the experimental part).



Scheme 45 Synthesis of manganese complexes

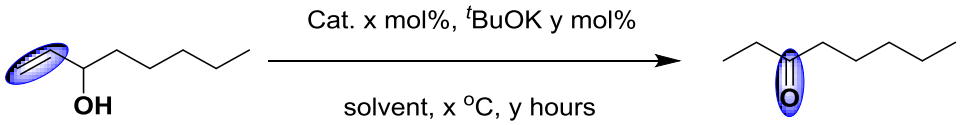
2.2.2 Optimization reactions

Our initial experiments were performed at 80 or 120°C in different solvents by using oct-1-en-3-ol as a substrate in the presence of a catalytic amount of pincer manganese compounds **3-4**, **3-9** or **3-10** (Table 4). These reaction conditions were the best choice for the iron-catalysed isomerization reaction system described in the previous chapter. We began our isomerization reaction of oct-1-en-3-ol by using 1 mol% of typical Beller's catalyst **3-4** in combination with 1 mol% of base (^{t}BuOK) in toluene at 80 ^{o}C and 20 hours reaction time (Table 4, entry 1). Although only 3% of product was observed, this meant that the manganese compound could also be used as a catalyst in the isomerization of an allylic alcohol to a ketone. Further, the isomerization of oct-1-en-3-ol was carried out by using different polar protic solvents (MeOH, EtOH and iPrOH) under the same conditions. iPrOH performed better than MeOH or EtOH but the conversion was only 18% (Table 4, entries 2-4). Similarly, THF was selected as a solvent because the iron catalysed isomerization performed well in it. Only a low conversion and yield (17%) was obtained (entry 5).

Penta-coordinated manganese compound **3-9**, which was synthesized by the reaction of PNP ligand (Bis[(2-di-i-propylphosphino)ethyl]amine) with $Mn_2(CO)_{10}$ and HMDSO (hexamethyldisiloxane) by heating under reflux, was assumed to be the active intermediate in this reaction. We then wanted to see if the use of "active" catalyst **3-9** was a better strategy than the combination of catalyst **3-4** with ^{t}BuOK. The isomerization of oct-1-en-3-ol to 3-octanone was performed in different solvents at 80 ^{o}C for 16 hours by using 1 mol% of complex **3-9** (Table 4, entries 6-14). Similar conversions were obtained when protic solvents (MeOH, EtOH and iPrOH) were used, where the reaction in isopropanol performed better (Table 4, entries 6-8). Additionally, when the isomerization reactions of oct-1-en-3-ol were carried out in THF and acetonitrile, no formation of the desired product occurred (Table 4, entries 10 and 14). Compound **3-9** showed the same low activity in both DCM and benzene as solvents in the catalytic isomerization reaction (Table 4, entries 11 and 13). Furthermore, when toluene was selected as a solvent for this isomerization reaction, low conversion and yield were obtained (Table 4, entry 9). In comparison, utilization of heptane as a solvent resulted in higher yield of the product, but still only 24% yield was achieved using **3-9** as catalyst (Table 4, entry 12). We then decided to increase the temperature and catalyst loading since no high conversion was achieved. In fact, an obvious increase of conversion and yield were achieved by using 5 mol% of catalyst **3-9** at 120 ^{o}C in different solvents or neat conditions (Table 4, entries 15-19). Heptane was proven to be a better solvent than toluene or benzene (Table 4, entries 15-17). When ^{i}PrOH was selected as a solvent in the presence of 5 mol% of catalyst **3-9**, quantitative conversion was achieved albeit with moderate selectivity in favor of the desired ketone product (Table 4, entry 18). It is interesting to note that when the reaction was performed under neat conditions, 69 % of the desired product was obtained after 9 hours (Table 4, entry 19).

Meanwhile, we also performed this isomerization reaction in the presence of compound **3-10** which is an efficient catalyst for the hydrogenation of benzonitrile. Different reaction solvents were tested in the presence of 5 mol% of catalyst and base in 2 and 16 hours at 120 ^{o}C. Similarly, isopropanol performed as the best solvent where good selectivity towards the desired ketone was achieved. High conversions and yields were obtained by using heptane, toluene and benzene as solvents (entries 20 – 22). Similar conversion and yield was also observed by running the reaction under neat conditions. To sum up, although high conversions and yields could be achieved, the drawbacks are long reaction times and high catalyst loadings.

Table 4 Optimization of the isomerization of oct-1-en-3-ol with PNP pincer catalysts 3-4, 3-9 or 3-10 [a]



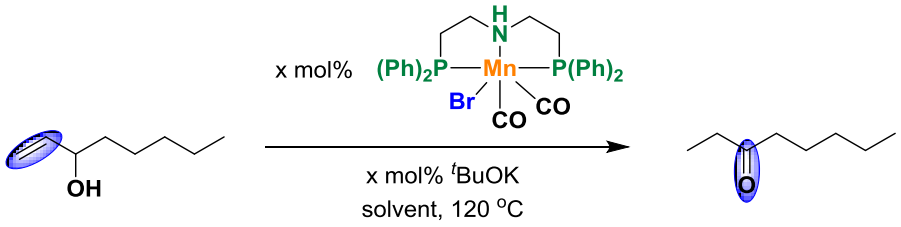
Entry	Cat. (%)	^{t}BuOK (%)	Solvent	Reaction Time (hour)	Temperature (^{o}C)	Conversion (%) [b]	Yield (%)[b]
1	**3-4** (1)	1	Toluene	20	80	3	3
2	**3-4** (1)	1	MeOH	20	80	trace	trace
3	**3-4** (1)	1	EtOH	20	80	2	2
4	**3-4** (1)	1	^{i}PrOH	20	80	18	15
5	**3-4** (1)	1	THF	20	80	17	17
6	**3-9** (1)	0	MeOH	16	80	0	0
7	**3-9** (1)	0	EtOH	16	80	trace	trace
8	**3-9** (1)	0	^{i}PrOH	16	80	14	14
9	**3-9** (1)	0	Toluene	16	80	8	8
10	**3-9** (1)	0	THF	16	80	0	0
11	**3-9** (1)	0	Benzene	16	80	10	10
12	**3-9** (1)	0	Heptane	16	80	24	24
13	**3-9** (1)	0	DCM	16	80	10	10
14	**3-9** (1)	0	MeCN	16	80	0	0
15	**3-9** (5)	0	Toluene	1 and 9	120	19 and 82	19 and 82
16	**3-9** (5)	0	Benzene	1 and 9	120	14 and 65	14 and 63
17	**3-9** (5)	0	Heptane	1 and 9	120	30 and 90	30 and 88
18	**3-9** (5)	0	iPrOH	1 and 9	120	25 and 99	24 and 82
19 [c]	**3-9** (0.5)	0	Neat	1 and 9	120	19 and 70	19 and 69
20	**3-10** (5)	5	Toluene	2 and 16	120	33 and 97	33 and 94
21	**3-10** (5)	5	Benzene	2 and 16	120	22 and 91	22 and 91
22	**3-10** (5)	5	Heptane	2 and 16	120	45 and 98	44 and 88
23	**3-10** (5)	5	iPrOH	2 and 16	120	61 and 100	53 and 81
24 [c]	**3-10** (0.5)	0.5	Neat	2 and 16	120	52 and 92	51 and 90

[a] General conditions: 1 mmol of substrate, catalyst, base (if used), 1 mL of solvent (if used). [b] Determined by GC with dodecane as an internal standard. [c] 10 mmol of substrate.

Next, we focused on compound **3-11** which was previously reported as an efficient catalyst for the alkylation of ketones with primary alcohols which proceeds via a borrowing hydrogen mechanism. [77] To our delight, complete conversion was obtained in the presence of 5 mol% of compound **3-11** and ^{t}BuOK after only 2 hours in different solvents at 120 ^{o}C (Table 5, entries 1-4). Use of 1,4-Dioxane, which is a good solvent for ester

hydrogenation with compound **3-11**, resulted in the highest amount (98%) of the corresponding product (Table 5, entry 2). [78] This catalyst showed the same selectivity in both toluene and cyclohexane (Table 5, entries 1 and 3). Compared to other solvents, the reaction in heptane resulted in poor selectivity under the same reaction conditions (Table 5, entry 4). In the case of neat conditions, full conversion of the substrate was observed with 97% yield of the desired product (Table 5, entry 5). Decreasing catalyst and base loading to 1 mol% resulted in quantitative conversion and yield of the desired product at 80 °C after 1 hour (Table 5, entry 6). Notably, this catalytic reaction also showed good conversion and yield even at room temperature after both 1 hour and 16 hours (Table 5, entry 7). Furthermore, the conversion and yield dropped when the catalyst and ^{t}BuOK loadings were decreased to 0.1 mol% in 1,4-dioxane (Table 5, entry 8). Catalyst **3-11** showed high activities in both cyclohexane and toluene (Table 5, entries 9-10). It is worth mentioning that the isomerization reaction proceeds in neat oct-1-en-3-ol and yields 94% of the desired 3-octanone (Table 5, entry 11). Meanwhile, the catalytic activity of compound **3-11** was also tested under the same reaction condition at room temperature. However, this led to a dramatic decline of its activity (6% yield after 16 hours). Unfortunately, when the loading of the catalyst was reduced to 0.01 mol%, merely 3% of the desired products had formed after 16 hours at 120 °C.

Table 5 Optimization of the isomerization reaction catalyzed by PNP pincer catalyst 3-11 [a]

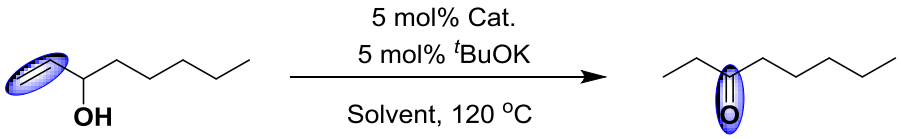


Entry	x (mol%)	Solvent	Time (hours)	Conversion (%) [b]	Yield (%) [b]
1	5	Toluene	2	100	93
2	5	1,4-Dioxane	2	100	98
3	5	Cyclohexane	2	100	93
4	5	Heptane	2	100	87
5	0.5	Neat	2	100	97
6	1	1,4-Dioxane	1	100	100
7 [c]	1	1,4-Dioxane	1; 16	88; 100	76; 83
8 [d]	0.1	1,4-Dioxane	1	70	68
9 [d]	0.1	Cyclohexane	1	97	95
10 [d]	**0.1**	**Toluene**	**1**	**100**	**99**
11 [d]	**0.1**	**Neat**	**1**	**94**	**94**
12 [c]	0.1	Neat	16	6	6
13 [e]	0.01	Neat	16	3	3

[a] General conditions: 1 mmol of substrate, catalyst and base (the same loadings), 1 mL of solvent (if used). [b] Determined by GC with dodecane as an internal standard. [c] Room temperature. [d] 10 mmol of substrate.

Additionally, some other compounds, like the Milstein catalyst (Complex **3-12**) and the Kempe catalysts (**3-8** and **3-15**) were also tested in the isomerization reactions of allylic alcohols to ketones (Table 6). All of the experiments were carried out at 120 ^{o}C for 2 or 6 hours. The Milstein catalyst (Complex **3-12**) showed low to average activities in different solvents (entries 1–5). The activity of complex **3-12** in cyclohexane was much better than in other solvents albeit still low (Table 6, entries 1-4). The catalyst was shown to be inactive if a solvent-free system was used (Table 6, entry 5). In comparison, the Kempe catalyst **3-8** was not as good as the Milstein catalyst in all the solvents (Table 6, entries 6-9). Interestingly, catalyst **3-8** favoured solvent-free conditions (entry 10). The same trend was also true for the Kempe catalyst **3-15** which appeared to be a much better catalyst than compounds **3-12** and **3-8** in the isomerization of allylic alcohols to ketones (Table 6, entry 15). Use of catalyst **3-15** also resulted in moderate to excellent conversions of the corresponding substrate to the desired product in different solvents (Table 6, entries 11-14).

Table 6 Optimization of the isomerization process with other pincer catalyst [a]



Entry	Cat.	Solvent	Reaction Time (hours)	Conversion (%) [b]	Yield (%) [b]
1	**3-12**	Toluene	2; 6	13; 16	11; 12
2	**3-12**	1,4-Dioxane	2; 6	8; 9	7; 7
3	**3-12**	Cyclohexane	2; 6	27; 43	24; 39
4	**3-12**	Heptane	2; 6	17; 22	15; 18
5	**3-12**	Neat	2; 6	1; 1	1; 1
6	**3-8**	Toluene	2; 6	4; 11	2; 4
7	**3-8**	1,4-Dioxane	2; 6	5; 10	4; 6
8	**3-8**	Cyclohexane	2; 6	1; 7	0; 3
9	**3-8**	Heptane	2; 6	3; 9	2; 3
10	**3-8**	Neat	2; 6	22; 27	18; 21
11	**3-15**	Toluene	2; 6	75; 91	73; 82
12	**3-15**	1,4-Dioxane	2; 6	36; 56	35; 48
13	**3-15**	Cyclohexane	2; 6	65; 88	61; 71
14	**3-15**	Heptane	2; 6	52; 62	51; 61
15	**3-15**	Neat	2; 6	79; 96	77; 86

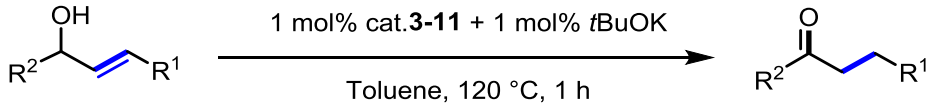
[a] General conditions: 1 mmol of substrate, 5 mol% catalyst, 5 mol% base, 1 mL of solvent (if used), 120 ^{o}C. [b] Determined by GC with dodecane as an internal standard.

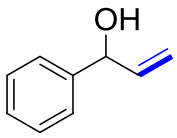
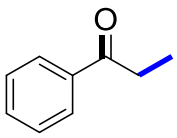
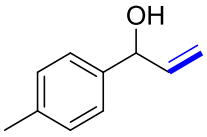
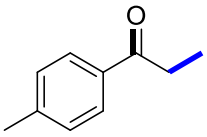
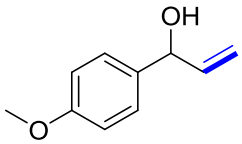
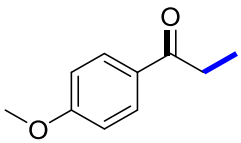
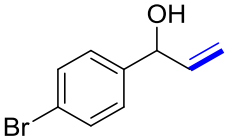
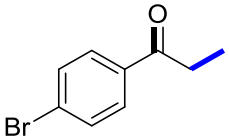
2.2.3 Substrates scope

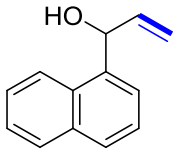
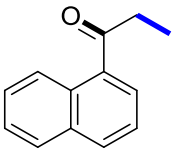
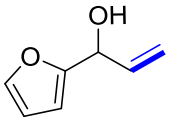
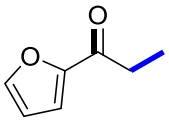
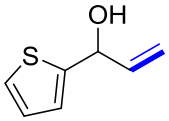
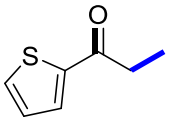
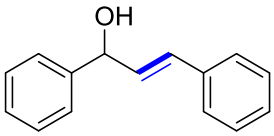
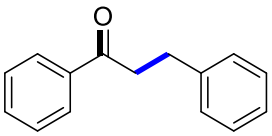
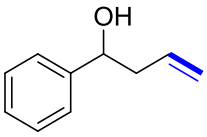
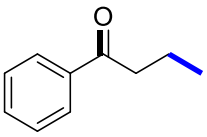
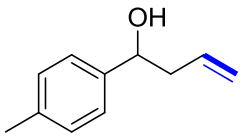
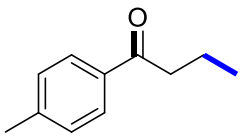
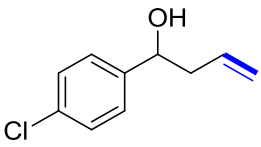
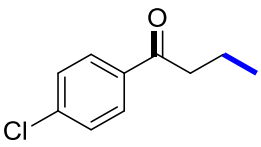
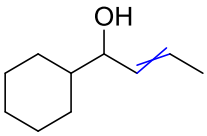
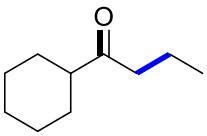
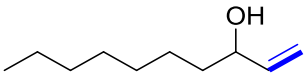
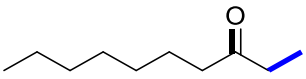
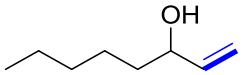
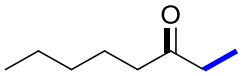
With the optimized reaction conditions in hand, we subsequently tested the scope and limitations of this catalytic system which included various aromatic and aliphatic allylic alcohols (Table 7). Exceptional yields of the

ketones were achieved in the isomerization of aromatic allylic alcohols and homo-allylic alcohols. Both electron-rich and electron-poor substituents were well-tolerated (Table 7, entries 1-11). Isomerization of 1-phenylprop-2-en-1-ol which was selected as the parent substrate resulted in a high yield of the corresponding ketone (Table 7, entry 1). A methyl substituent on the *para*-position of the aromatic ring had no influence on the yield of the desired product (Table 7, entry 2). A slight decrease of the catalytic activity was observed when the methyl substituent was replaced by a methoxy group in the *para* position of the aromatic ring (Table 7, entry 3). This catalytic system also showed good compatibility with the presence of a bromine atom and isomerization of the *para*-bromo compound led to a good yield of 87% (Table 7, entry 4). An excellent yield (89%) was obtained when the reaction was carried out on the naphthyl derivative (entry 5). Substrates with heteroaromatic rings, e.g. furanyl- and thienyl-, showed high isomerization activity in terms of the yield of the desired ketones (Table 7, entries 6 and 7). The substrate with an internal double bond was also converted into the corresponding carbonyl compound affording 95% yield (Table 7, entry 8). Good to excellent yields of the corresponding carbonyl derivatives were also obtained by using homo-allylic alcohols (Table 7, entries 9-11). Apart from starting materials with aromatic groups, aliphatic ones were also tested. 1-Cyclohexyl-but-2-en-1-ol (entry 12), which was used as a mixture of *cis*- and *trans*- isomers, was converted to 1-cyclohexylbutan-1-one in a high isolated yield. Linear allylic alcohols were isomerized to the saturated ketones with excellent yields using this catalytic system (Table 7, entries 13 and 14). Notably, when we used 10 mmol (1.5 grams scale) of oct-1-en-3-ol as substrate in 10 mL of toluene, the purification procedure of 3-octanone required only filtering off the catalyst and salts and removal of the solvent.

Table 7 Substrate scope of manganese-catalysed allylic alcohol isomerization [a]



Entry	Allylic alcohol	Ketone	Yield (%)[b]
1			91
2			90
3			74
4			87

5			89
6			91
7			96
8			95
9			93
10			93
11			73
12			93
13			94
14[c]			91

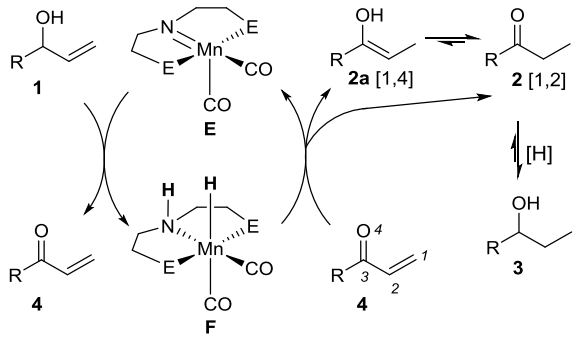
[a] General conditions: 1 mmol of substrate, 1 mol% catalyst, 1 mol% base, 1 mL of toluene, 120 °C, 1 hour. [b] Isolated yield. [c] 10 mmol substrate in 10 mL toluene.

2.2.4 Proposed mechanism

To understand these mechanistic insights, density functional theory computation on the isopropyl as well as phenyl substituted PNP amine and amido Mn catalysts by using the Gaussian 09 program was carried out.[79] All structures were optimized at the B3PW91[80] level with the TZVP[81] basis set (LANL2DZ[82] for Mn). The applicability of the B3PW91 functional was validated intensively and extensively.[83] Intensive and extensive testing and benchmarking of different methods with and without solvation effect and dispersion as well as intensive comparisons with the available experimental data and computational data for different transition metal PNP type complexes (M = Fe, Ru, Os, Ir, Mn, Mo and W) were carried out.[84] All optimized structures were characterized as either energy minimums without imaginary frequencies or transition states with only one imaginary mode by frequency calculations; and the imaginary model connects the initial and the final states.

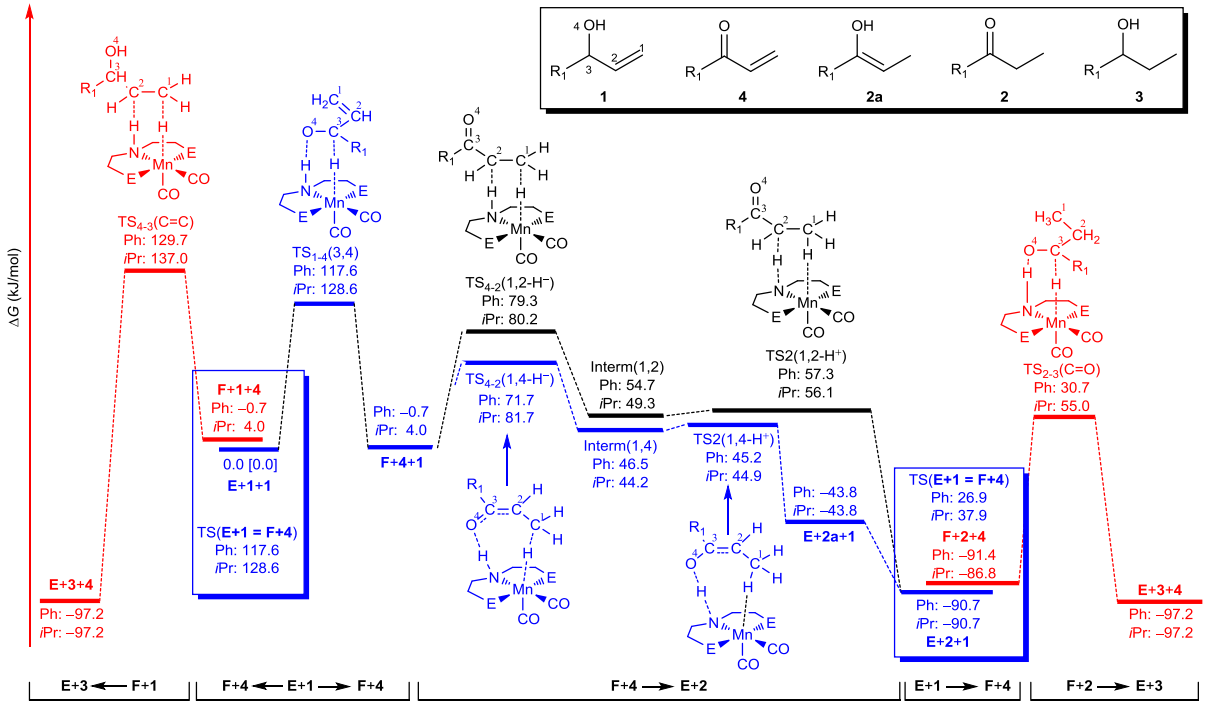
The thermal correction to Gibbs free energy at 298 K from the frequency analysis was added to the total electronic energy.

The available experimental and computational studies show that the pre-catalyst bromide-amino complex (Mn-Br, cat.3-4: Mn-Br-*i*Pr and cat.3-11: Mn-Br-Ph) needs to be activated by base to the active amido catalyst (E-*i*Pr/Ph). Starting from amido complex E-*i*Pr/Ph (shown in Scheme 46), the self-transfer hydrogenation isomerization from 1 to 2 by outer-sphere mechanism without external out hydrogen source was computed. The full potential energy surface is shown in Scheme 47.



Scheme 46 Proposed Mechanism (R = C_5H_{11}, E = $P(^iPr)_2$ or $P(Ph)_2$)

Without external hydrogen supply, the first step is the dehydrogenation of **1** to **4** by using complex **E-*i*Pr/Ph**. Although great efforts have been made, the transition state corresponding to proton transfer as well as PN^HP-Mn^+–$RCH(O^-)CH{=}CH_2$ intermediate for both isopropyl and phenyl substituted complexes could not be located and all attempts to optimize such structures resulted in reactant or transition state of hydride transfer. As hydride transfer is proved to be the rate-determining step for C=O bond hydrogenation on Fe as well as on Mn and d^5-, d^6- metal PNP pincer complexes,[84c, 85] we assume that the energy barrier of dehydrogenation of **1** to **4** is determined by hydride transfer. It is found that the transition state corresponding to hydride transfer has Gibbs free energy barrier of 128.6 and 117.6 kJ/mol for **E-*i*Pr** and **E-Ph**, respectively. And the reaction is endergonic by 4.0 kJ/mol for **E-*i*Pr** and and exergonic by -0.7 kJ/mol for **E-Ph**.



Scheme 47 Proposed Mechanism (R = C_5H_{11}, E = $P(^iPr)_2$ or $P(Ph)_2$)

The next step is the hydrogenation of the C=C bond from the newly formed **4** to **2** by complex **F-*i*Pr/Ph** *via* either 1,2-addition directly to **2** or *via* 1,4-addition to form the enol **2a**, which can tautomerize into **2**. For the 1,2-addition, we found a stepwise mechanism; i.e.; the first step passes through the transition state for Mn−H transfer to C_1, for breaking the Mn−H bond and forming the C-H bond, leading to an intermediate. The second step passes through the transition state of N−H transfer to C_2 for breaking the N−H bond and forming the terminal C_1−H bond. For 1,2-addition, the free energy barrier of the Mn−H hydride transfer is 76.2 and 80.0 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. The intermediate is endergonic by 45.3 and 55.4 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. The N−H proton transfer has a free energy barrier of 52.1 and 58.0 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. This hydrogenation step is exergonic by 94.7 and 90.0 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively.

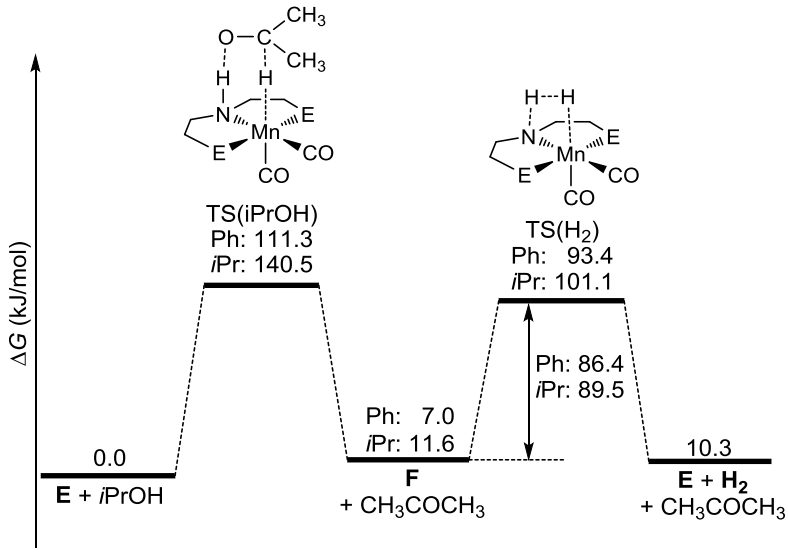
For the 1,4-addition, we also found a stepwise mechanism; i.e.; the first step passes through the transition state for Mn−H transfer to the C_1 for breaking the Mn−H bond and forming the C−H bond, leading to an intermediate. The second step passes through the transition state of N−H transfer to the O_4 for breaking the N−H bond and forming the terminal O−H bond. From the starting point for 1,4-addition, the free energy barrier of the Mn−H hydride transfer is 77.7 and 72.4 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively., the intermediate is endergonic by 40.2 and 47.2 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. The N−H proton transfer has a free energy barrier of 40.9 and 45.9 kJ/mol for **F-*i*Pr** and **F-Ph,** respectively. This hydrogenation step is exergonic by 47.8 and 43.1 kJ/mol for **F-*i*Pr** and **F-Ph,** respectively. The tautomerization from **2a** to **2** is exergonic by 46.9 kJ/mol. For **F-Ph**, 1,4-addition is slightly more favored kinetically than 1,2-addition by 7.6 kJ/mol, while both 1,2-addition (76.2 kJ/mol) and 1,4-addition (77.7 kJ/mol) have close barriers and are competitive for **F-*i*Pr**. Compared with dehydrogenation of **1** to **4**, the hydrogenation of **4** to product **2** is kinetically more favored by 52.4 (128.6 vs. 76.2 kJ/mol) and 45.2 kJ/mol (117.6 vs. 72.4 kJ/mol) for **E/F-*i*Pr** and **E/F-Ph**, and thermodynamically more favored by 94.7 (-90.7 vs. 4.0 kJ/mol) and 90.0 kJ/mol (-90.7 vs. -0.7 kJ/mol) for **E/F-*i*Pr** and **E/F-Ph** (-95.7 vs. 5.0 kJ/mol). Therefore, **4,**

once formed, can be easily converted to **2**. Taking rate-determining step of **1** to **4** into consideration, the energy barrier of phenyl substituted catalyst **E/F-Ph** is lower than isopropyl substituted catalyst **E/F-*i*Pr** by 11.0 kJ/mol.

In addition, we computed the competitive hydrogenation of **1** to **3** by using complex **F-*i*Pr/Ph** after the dehydrogenation of one equivalent **1** into **4**. For **1** hydrogenation to **3**, this reaction proceeds *via* a one-step mechanism mainly corresponding to the hydride transfer and is exergonic by 101.2 and 96.5 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. And the barrier is 133.0 and 133.4 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. This indicating that the isolated C=C double bond hydrogenation of **1** is less competitive kinetically than the conjugated C=C double bond hydrogenation of **4** by 56.8 (133.0 vs.76.2 kJ/mol) and 61.0 kJ/mol (133.4 vs. 72.4 kJ/mol) for **F-*i*Pr** and **F-Ph**, respectively. Furthermore, we also computed the consecutive hydrogenation of **2** to **3** by using complex **F-*i*Pr/Ph** after the dehydrogenation of another one equivalent **1** into **4**. The hydrogenation of **2** to **3** by using complex **F-*i*Pr/Ph** is also found a one-step process. The computed barrier is 141.8 and 122.1 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. And the reaction is exergonic by 10.4 and 5.8 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively.

All these reveal that **2** is the principal and preferred product. Without external hydrogen supply, the hydrogenation of **1** to **3** as well as **2** to **3** by using complex **F-*i*Pr/Ph** are not competitive kinetically. This agrees perfectly with the results that ketone is the major product. For investigating the stability of the catalysts, we computed the dehydrogenation or hydrogen elimination from complex **F-*i*Pr/Ph** to complex **E-*i*Pr/Ph** (F = E + H_2), which has Gibbs free energy barrier of 89.5 and 86.4 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively; is slightly exergonic by 1.3 kJ/mol for **F-*i*Pr**, while slightly endergonic by 3.3 kJ/mol (Scheme 48). Compared with the barrier of **4** to **2**, the H_2 elimination from complex **F** to **E** is less favorable than hydrogenation of **4** to **2** by 13.3 and 14.0 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. Therefore, once **F** formed, **4** will easily hydrogenated to **2** rather than H_2 elimination from **F**.

Our computations show that without external hydrogen supply, the reaction of allyl alcohol **1** takes place *via* the self-transfer hydrogenation isomerization mechanism *via* the α,β-unsaturated ketone **4** as intermediate; and the principal produce should be the ketone **2**. The calculated result is in perfect agreement with experimental result that phenyl substituted catalyst **E/F-Ph** shows higher activity than isopropyl substituted catalyst **E/F-*i*Pr**.



Scheme 48 Potential energy surface of H_2 elimination from F. (E = $P(^{i}Pr)_2$ or $P(Ph)_2$)

Next we considered the transfer hydrogenation of ketone **2** to alcohol **3** using isopropanol as solvent and hydrogen source [**E** + isopropanol + **2** = **E** + acetone + **3**]. On the basis of the potential energy surfaces (Scheme 47) and isopropanol as hydrogen source (Scheme 48), the effective barrier of the hydrogenation of ketone **2** to alcohol **3** is 141.8 and 122.1 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. And the barrier of the isopropanol dehydrogenation is 140.5 and 111.3 kJ/mol for **F-*i*Pr** and **F-Ph**, respectively. Therefore, the hydrogenation of ketone **2** to alcohol **3** is the rate determining step of the transfer hydrogenation of [isopropanol + **1** = acetone + **3**]. Compared with the rate determining step of isomerization of allylic alcohol **1** to ketone **2** (128.6 kJ/mol for **E-*i*Pr** and 117.6 kJ/mol for **E-Ph**), the isomerization of allylic alcohol **1** to ketone **2** is more favorable than transfer hydrogenation to alcohol **3** by 13.2 and 4.5 kJ/mol for **E/F-*i*Pr** and **E/F-Ph**, respectively. This indicating isomerization is slightly more favorable than transfer hydrogenation by using **E/F-Ph** as catalyst, and isomerization can be accelerated by using isopropanol as solvent as well as increasing temperature.

Our computations show that without external hydrogen supply, the reaction of allyl alcohol **1** takes place *via* the self-transfer hydrogenation isomerization mechanism *via* the α,β-unsaturated ketone **4** as intermediate; and the principal produce should be the ketone **2**. This is indeed observed for the reaction in benzene or toluene. Using isopropanol as external hydrogen source, the same reaction mechanism can be proposed, however, the formed ketone **2** can be partially hydrogenated into the saturated alcohol on the basis of their thermodynamic properties.

In order to get insight into the steric effect of the substitution of ligand, we dissected the electronic activation energy of the transition states of rate-determining step (**$TS_{1\text{-}4}$(3,4)**, $\Delta E^{\ddagger}$) into the geometrical strain energy (ΔE_{strain}) and interaction energy (ΔE_{int}) by using the proposed activation strain model (ASM, **Figure 3**) [86], where the electronic activation energy $\Delta E^{\ddagger}$ is defined as the electronic energy difference between the optimized TS and the sum of substrate and catalyst in their optimized structures; and the geometrical strain energy $\Delta E_{strain}^{\ddagger}$ is defined as the electronic energy difference between the sum of the structurally deformed substrate and catalyst individually taken from the optimized TS and the sum of reactant and catalyst in their optimized TS structures. Accordingly, the difference between $\Delta E_{strain}^{\ddagger}$ and $\Delta E^{\ddagger}$ is the interaction energy between substrate and

catalyst in the TS. In addition, $\Delta E_{strain}^{\ddagger}$ can be divided into the strain energy of substrate ($\Delta E_{strain/sub}^{\ddagger}$) and catalyst ($\Delta E_{strain/cat}^{\ddagger}$) accordingly and $\Delta E_{strain}^{\ddagger} = \Delta E_{strain/sub}^{\ddagger} + \Delta E_{strain/cat}^{\ddagger}$. All these data based on reactions [**E** + **1** = **F** + **4**] are shown in **Table 8**.

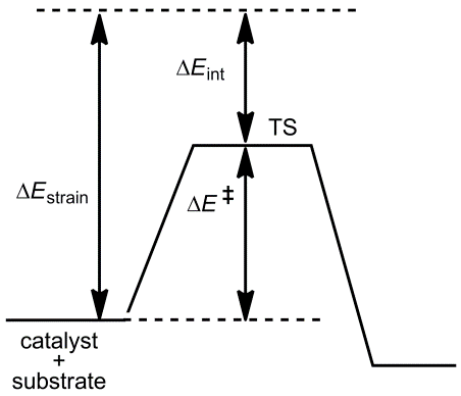


Figure 3. Activation strain model

Table 8. ASM analysis of $TS_{1\text{-}4}$(3,4) of reaction [**E** + **1** = **F** + **4**]

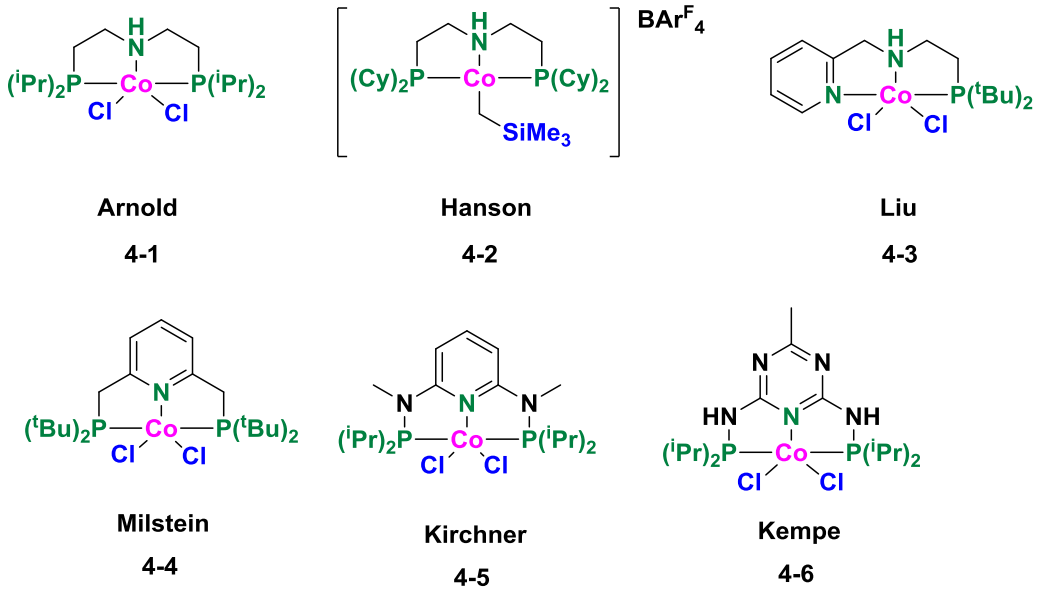
$\Delta E^{\ddagger}$	$TS_{1\text{-}4}$(3,4) [**E** + **1** = **F** + **4**]		
kJ/mol	*i*Pr	Ph	$\Delta\Delta E^{\ddagger}$(*i*Pr - Ph)
$\Delta E^{\ddagger}$	71.7	57.9	13.8
$\Delta E_{strain}^{\ddagger}$	670.8	590.0	80.8
$\Delta E_{strain/sub}^{\ddagger}$	584.8	518.6	66.2
$\Delta E_{strain/cat}^{\ddagger}$	86.0	71.4	14.6
$\Delta E_{int}^{\ddagger}$	559.1	532.1	67.0

As shown in **Table 8**, for the hydrogenation of **1** to **4**, the energy barrier of **$TS_{1\text{-}4}$(3,4)-Ph** is lower in energy than that of the **$TS_{1\text{-}4}$(3,4)-*i*Pr** ($\Delta\Delta E^{\ddagger}$) by 13.8 kJ/mol. Further analyses into difference of geometrical strain energy ($\Delta\Delta E^{\ddagger}_{strain}$) and interaction energy ($\Delta\Delta E^{\ddagger}_{int}$) reveal that the $\Delta\Delta E^{\ddagger}$ is dominated by $\Delta\Delta E^{\ddagger}_{strain}$. In addition, the $\Delta\Delta E^{\ddagger}_{strain/sub}$ contributes much stronger than the $\Delta E^{\ddagger}_{strain/cat}$ to $\Delta E^{\ddagger}_{strain}$; and also dominates the $\Delta E^{\ddagger}_{strain}$. These results demonstrated that the isopropyl substituted Mn PNP catalyst causes larger geometrical distortion than phenyl substituted Mn PNP catalyst, and this is the reason why **E/F-Ph** shows higher activity than isopropyl substituted catalyst **E/F-*i*Pr**.

2.3 Cobalt catalyzed isomerizations of allylic alcohols

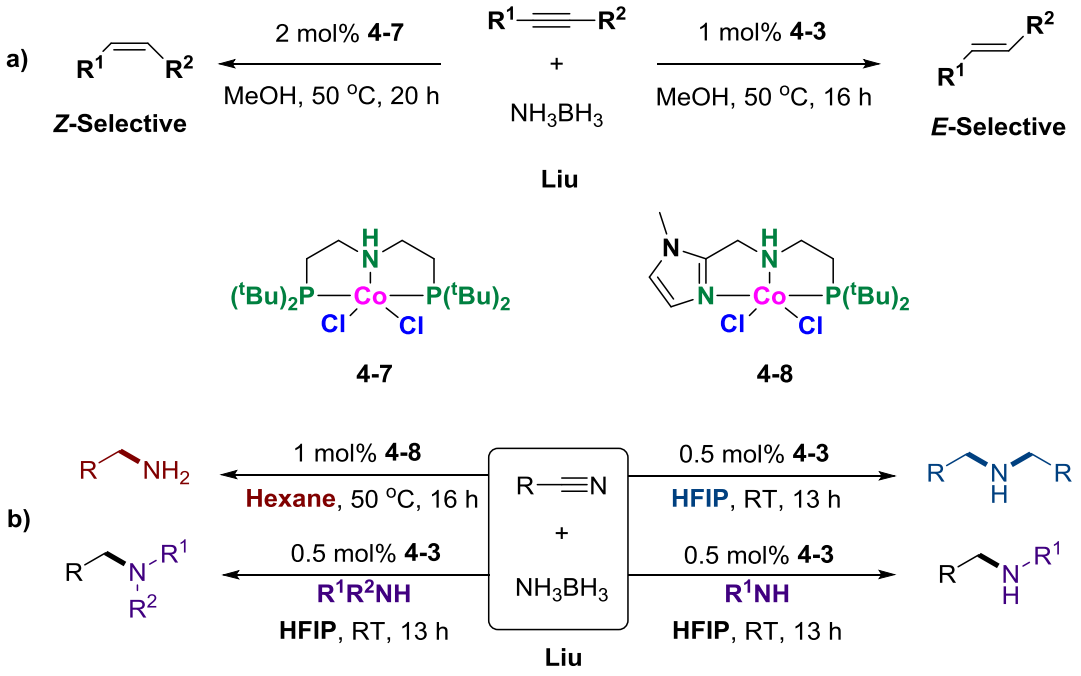
(I would like to thank Brian Spiegelberg for his contributions to this part of work)

Recently, many reports have appeared on the use of first-row transition metals in catalysis since these metals are cheap, sustainable and abundantly available. As cobalt is one of the most significant first-row transition metals, recently, PNP pincer complexes of it were widely investigated for a range of catalytic reactions. [90] In 2011, Arnold and co-workers were the first to report the synthesis of aliphatic PNP pincer cobalt complex **4-1,** although no tests of catalytic properties were performed. [91] Similarly, Hanson and co-workers synthesized ionic PNP cobalt complex **4-2**, which is an efficient catalyst for the hydrogenation of C=C, C=N and C=O bonds. [90a] Some other PNP coordinated pincer complexes were reported for various homogeneous catalytic reactions during the last several years. [90b-d, 92]



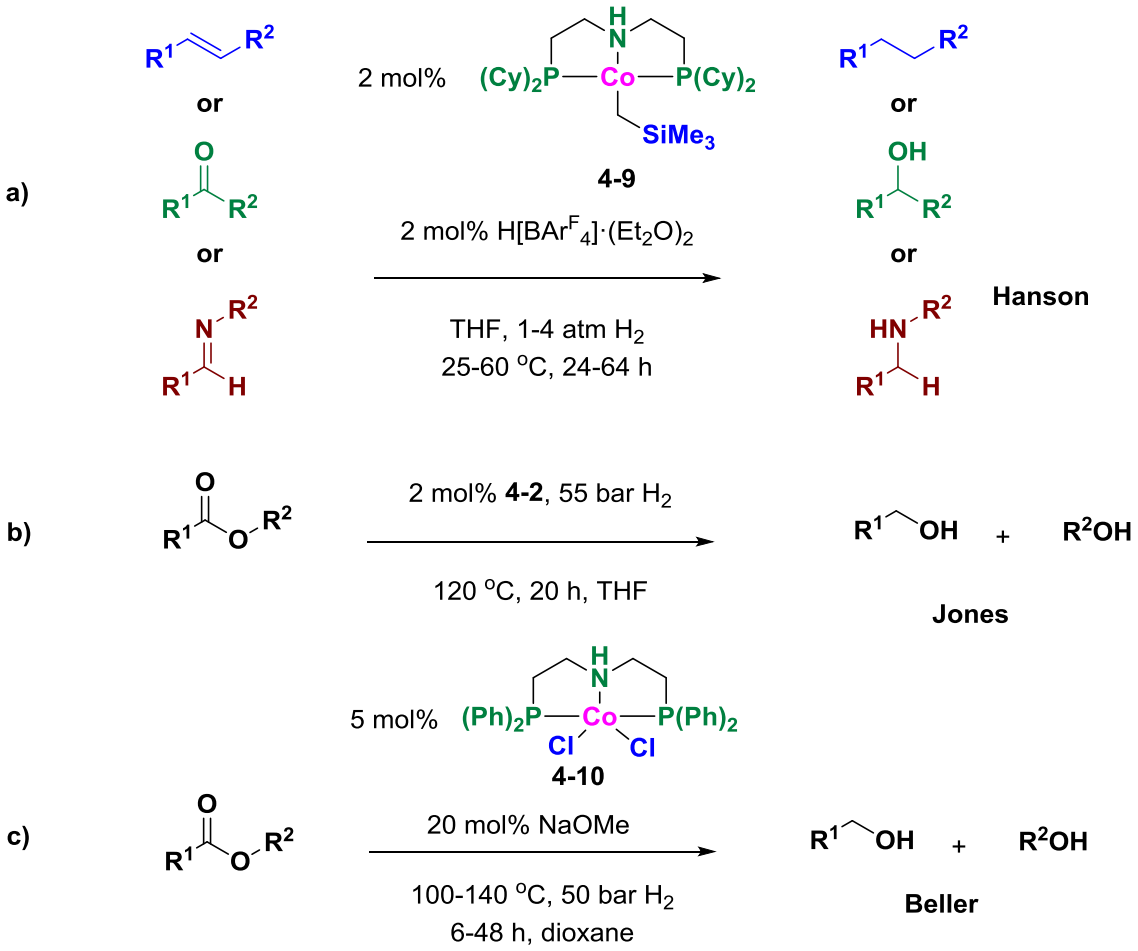
Scheme 49 Examples of PNP pincer cobalt complexes

In 2016, Liu and co-workers reported transfer hydrogenation of alkynes utilizing ammonia borane as the hydrogen source to produce *Z*- or *E*-alkenes, where the selectivity could be controlled by using different pincer cobalt catalysts (Scheme 50). [92] A range of substrates were converted to the alkenes (more than 50 examples) using this method with good to excellent stereoselectivities. In the same year, Liu and co-workers reported the first cobalt catalyzed transfer hydrogenation of nitriles to give primary, secondary and tertiary amines. [93] Both the catalyst and the solvent play significant roles in rate and chemoselectivity of these transfer hydrogenation reactions. Exceptional applicability was shown by utilizing more than 70 substrates with a range of functional groups in this reaction.



Scheme 50 Cobalt-catalyzed transfer hydrogenation of triple bonds

In 2012, Hanson and co-workers reported the first hydrogenation of alkenes, aldehydes, ketones and imines catalyzed by aliphatic-PNP Co complexes under mild reaction conditions. [90a] The utilization of an equimolar amount of acid ($H[BAr^F_4]\cdot(Et_2O)_2$) relative to the cobalt catalyst is essential for the generation of an ionic pincer cobalt compound. This cobalt compound displays exceptional compatibility with substrates bearing a wide range of substituents. The cobalt catalyst can selectively hydrogenate the C=C bond of unsaturated carboxylic acids or esters. In 2017, Jones and co-workers reported an additive-free cobalt **4-2** catalyzed hydrogenation of esters to alcohols. [94] Notably, methyl esters showed lower reactivity than the corresponding ethyl esters, and the authors propose that cleavage of the O-CH_3 bond renders the cobalt catalyst inactive. In 2018, Beller and co-workers reported PNP pincer cobalt **4-10** catalyzed hydrogenation of esters to alcohols. [95] Various substrates bearing both aromatic and aliphatic esters were tested to produce the corresponding alcohols and most of them were converted in moderate to good conversions and yields. Furthermore, high conversions and yields could be achieved in the hydrogenation of methyl esters to the corresponding alcohols with Beller's catalyst although a high amount of base was required.

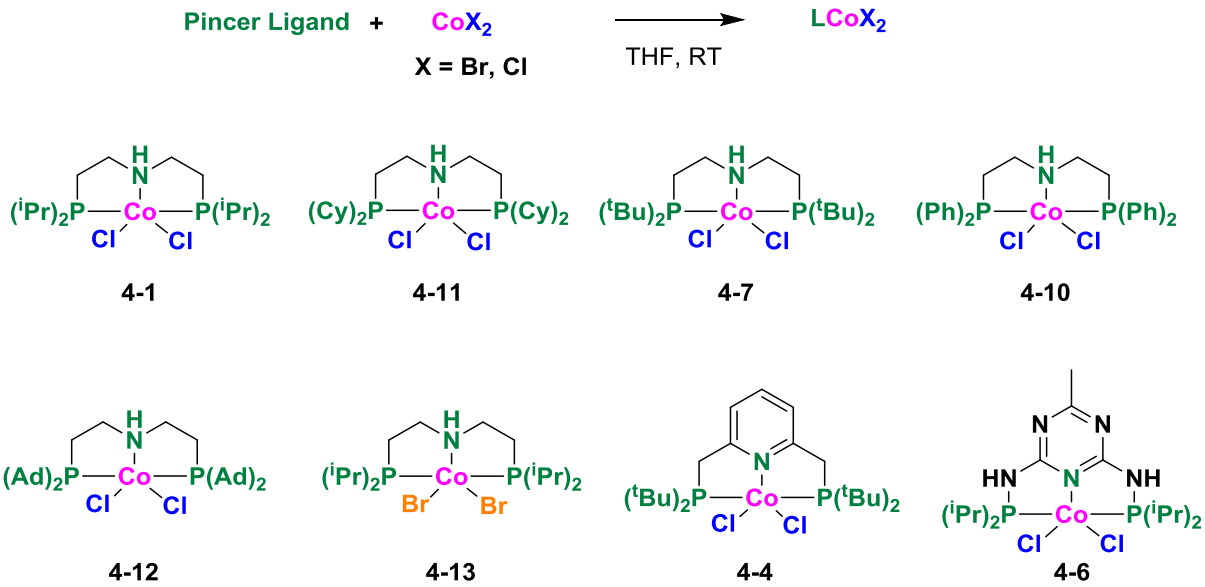


Scheme 51 Examples of cobalt-catalyzed hydrogenation reactions

Inspired by the current achievements utilizing homogeneous PNP cobalt catalyzed transfer hydrogenation and hydrogenation reactions with the proposed mechanism implying that these cobalt compounds were able to transfer hydrogen, we then presumed that these pincer cobalt compounds could isomerize allylic alcohols to the corresponding ketones or aldehydes via a hydrogen transfer mechanism.

2.3.1 Synthesis of cobalt compounds

Since Arnold first synthesized the aliphatic PNP pincer cobalt compound **4-1**, Liu and Beller independently reported similar synthetic processes to produce this type of cobalt complexes. The synthesis of this cobalt compound is very simple as it only requires a single step to produce the desired cobalt product. We prepared 5 aliphatic PNP cobalt compounds with different substituents (**4-1**, **4-7**, **4-10**, **4-11** and **4-12**) on the phosphorus atoms and replacing chloride with bromide (**4-13**) in the isopropyl PNP cobalt compounds. Simultaneously, the Milstein catalyst (**4-4**) and the Kempe catalyst (**4-6**) were also prepared using a similar method (the details are in the experimental part).



Scheme 52 Synthesis of pincer cobalt complexes

2.3.2 Optimization reactions

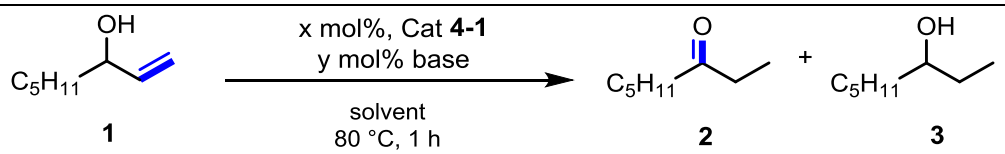
Having these PNP-ligated cobalt complexes in hand, we started the tests for the isomerization of oct-1-en-3-ol to 3-octanone in the presence of complex **4-1**, which consist of the isopropyl PNP ligand and cobalt(II) chloride (Table 9). Initially, we carried out the experiments in different protic solvents with 1 mol% catalyst at 80 ^{o}C for 1 hour (Entries 1-3). We found that methanol, which is an exceptional solvent in transfer hydrogenation of alkynes, was a much better choice than other protic solvents (IPA and ethanol). Solvents which performed well in the iron catalyzed isomerization of allylic alcohols (See Chapter 2) such as toluene, benzene, DCM and THF were shown to be non-suitable for the cobalt-catalyzed isomerization (Entries 5-7 and 10). Also no conversion of substrate was observed in hexane and MeCN (Entries 4 and 9). When the experiment was performed under aerobic conditions, this catalytic reaction was entirely inactive (Entry 11). Furthermore, the extension of the reaction time from 1 hour to 3 and 16 hours resulted in a slight increase of yields and conversions (Entries 13 and 14).

Base is significant in view of the activation of the catalyst for the isomerization reactions. Therefore, addition of an equimolar amount of ^{t}BuOK w.r.t. the cobalt complex increased the activity of the catalyst (entries 3 and 15). Furthermore, in order to improve the conversion, both the amount of catalyst and base was increased from 1 mol% to 3 mol% (Entry 16). Increasing the catalyst and base loadings further (3 mol% to 5 mol%), resulted in full conversion under otherwise identical reaction conditions (Entry 17).

Additionally, different bases were tested in these isomerization reactions (Entries 18-26). First, the reaction was performed in the presence of ^{t}BuONa; this led to an evident decrease in both conversion and yield (Entry 18). The similar base ^{t}BuOLi was also utilized and a slight decrease of the activity was observed (Entry 26). TEA (Triethylamine) was proven to be a favorable base the use of which resulted in 85 % conversion (Entry 19). DBU is known to be a very strong organic base and was also used in this reaction. Presence of DBU led to an obvious drop of both conversion and yield (Entry 24). The use of an inorganic weak base like K_3PO_4 resulted in a

moderate conversion of oct-1-en-3-ol (Entry 20). Another inorganic base (Cs_2CO_3) was also tested for this reaction, but this led to a decrease in the conversion of the substrate (Entry 21). Moderate reactivity was obtained when KOH was used as base under the same reaction condition (Entry 22). In comparison, high conversion and yield were achieved by using a weak inorganic base (Na_2CO_3) (Entry 23). Interestingly, a low yield was observed with K_2CO_3 as base compared to Na_2CO_3.

Table 9 Optimization of the reaction catalyzed by PNP pincer cobalt catalyst 4-1 [a]



1 **2** **3**

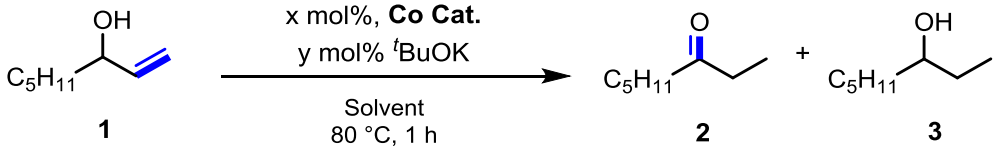
Entry	Cat. (mol %)	Base (mol%)	Solvent	Conversion 1 (%)	Yield 2 (%) [b]	Yield 3 (%)[b]
1	1	0	^{i}PrOH	0	0	0
2	1	0	EtOH	3	2	1
3	1	0	MeOH	37	31	6
4	1	0	MeCN	0	0	0
5	1	0	Toluene	0	0	0
6	1	0	DCM	0	0	0
7	1	0	Benzene	0	0	0
8	1	0	DMF	0	0	0
9	1	0	Hexane	0	0	0
10	1	0	THF	0	0	0
11	1	0	MeOH(air)	0	0	0
12 [c]	1	0	neat	0	0	0
13 [d]	1	0	MeOH	42	42	0
14 [e]	1	0	MeOH	59	58	0
15	1	^{t}BuOK(1)	MeOH	47	47	0
16	**3**	**^{t}BuOK (3)**	**MeOH**	**98**	**94**	**4**
17	**5**	**^{t}BuOK (5)**	**MeOH**	**100**	**97**	**3**
18	3	^{t}BuONa (3)	MeOH	54	52	2
19	3	TEA (3)	MeOH	85	80	5
20	3	K_3PO_4 (3)	MeOH	74	70	4
21	3	Cs_2CO_3(3)	MeOH	13	11	2
22	3	KOH(3)	MeOH	61	59	2
23	3	Na_2CO_3(3)	MeOH	90	85	5

24	3	DBU(3)	MeOH	16	16	0
25	3	K_2CO_3(3)	MeOH	53	51	2
26	3	^{t}BuOLi(3)	MeOH	83	79	4

[a] 1 mmol of substrate. [b] Determined by GC with dodecane as an internal standard. [c] 10 mmol of substrate. [d] Reaction time is 3 hours. [d] Reaction time is 16 hours.

Next, other PNP pincer cobalt complexes were tested as catalyst in the isomerization of oct-1-en-3-ol to 3-octanone in the presence of base (Table 10). The first experiments were performed with the *tert*-butyl PNP cobalt pincer complex **4-7**, which is a competent catalyst for the transfer hydrogenation of nitriles to amines. [92] However, this catalyst was not active for the desired reaction in both protic and aprotic solvents (entries 2-8). Then the tests were continued with the cyclohexyl PNP cobalt complex **4-8** for the conversion of oct-1-en-3-ol to 3-octanone (Table 10, entries 9-15). Use of methanol and ethanol led to the formation of more product than use of other solvents, but conversion and yield remained low. In addition, the effect of the halogen counterion in the isopropyl PNP cobalt complex was tested. Similar reactivity was observed with the chloro (**4-1**) and brom (**4-13**) complexes under the same reaction conditions (entries 16 and 17, compared with table 1, entry 16). When the amount of catalyst and base were reduced to 1 mol%, at 120 °C only a slight decrease in conversion was found (Entry 18). If the reaction was carried out without base at 120 °C, an obvious decline of the activity was detected (Entry 19). Interestingly, full conversion was obtained in the presence of phenyl PNP cobalt complex and equimolar amount of base (Entry 20). In view of the exceptional performance of compound **4-10**, more bulky adamantyl PNP cobalt complex was also examined in this isomerization reaction. However, no reactivity was detected in both THF and ethanol in the presence of compound **4-12** (Entries 21 and 22).

Table 10 Testing different PNP pincer catalysts for the isomerization of 1 to 2 [a]



Entry	Cat. (mol %)	^{t}BuOK (mol%)	Solvent	Conversion 1 (%)	Yield 2 (%) [b]	Yield 3 (%)[b]
1	**4-1** (3)	3	MeOH	98	94	4
2	**4-7** (3)	3	Heptane	0	0	0
3	**4-7** (3)	3	MeCN	0	0	0
4	**4-7** (3)	3	MeOH	0	0	0
5	**4-7** (3)	3	EtOH	0	0	0
6	**4-7** (3)	3	THF	0	0	0
7	**4-7** (3)	3	Toluene	0	0	0
8	**4-7** (3)	3	Dioxane	0	0	0
9	**4-11** (3)	3	MeOH	49	45	4

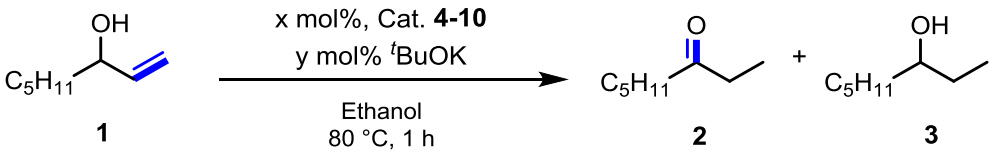
10	**4-11** (3)	3	Toluene	0	0	0
11	**4-11** (3)	3	Heptane	0	0	0
12	**4-11** (3)	3	MeCN	16	16	0
13	**4-11** (3)	3	Dioxan	0	0	0
14	**4-11** (3)	3	THF	0	0	0
15	**4-11** (3)	3	EtOH	46	42	4
16	**4-13** (3)	3	EtOH	100	94	6
17	**4-13** (3)	3	MeOH	96	93	3
18 [c]	**4-13** (1)	1	EtOH	96	91	5
19 [c]	**4-13** (1)	-	EtOH	54	50	4
20	**4-10** (3)	3	MeOH	100	100	0
21	**4-12** (3)	3	THF	0	0	0
22	**4-12** (3)	3	EtOH	0	0	0

[a] 1 mmol of substrate. [b] Determined by GC with dodecane as an internal standard. [c] Reaction temperature at 120 °C.

In order to gain a better understanding of the performance of compound **4-10**, more optimization reactions were carried out in the presence of this catalyst in different solvents (Table 11, entries 1-4). Thus, ethanol was selected as the first solvent with 3 mol% of base and compound **4-10** at 80 ^{o}C, which exhibited remarkable reactivity toward the formation of 3-octanone (Entry 1). The results in MeCN as a solvent were similar to those in ethanol (Entry 2). A decrease of conversion was obtained when toluene was selected as a solvent (Entry 3). Interestingly, while THF was not a good solvent for other cobalt catalysts described in this chapter, it turned out to be a very suitable one for **4-10** as a catalyst (Entry 4). However, an evident declination of the activity was detected when the experiment was carried out in the absence of any solvent (Entry 5).

The amount of base could be reduced to 1 mol% from 3 mol% without any influence on the conversion towards the desired product (Entry 6). Nevertheless, the conversion decreased from 100% to 86% in the absence of base (Entry 7). Full conversion could be achieved by reducing the catalyst and base loadings to 1 mol% (Entry 8). Still, a slight decrease of activity was observed under base-free conditions (Entry 9). Notably, high reactivity was achieved by increasing the temperature from 80 ^{o}C to 120 ^{o}C in the absence of base (Entry 11). Dropping the catalyst loading to 0.5 mol% results in only half of substrate converted. Full conversion with lower catalyst loading could be achieved by extending the reaction time from 1 hour to 5 hours (Entry 13). Finally, 0.1 mol% of catalyst was also feasible for achieving full conversion by prolonging the reaction time to 8 hours (Entries 14-16).

Table 11 Optimization of the isomerization reaction catalyzed by cobalt catalyst 4-10 [a]

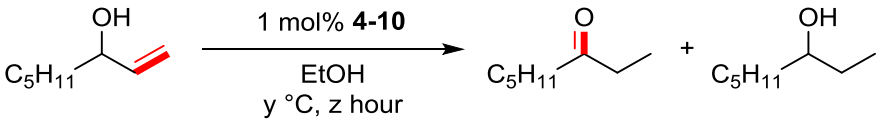


1 2 3

Entry	Cat. (mol %)	Base (mol%)	Solvent	Conversion 1 (%)	Yield 2 (%) [b]	Yield 3 (%)[b]
1	3	3	EtOH	100	100	0
2	3	3	MeCN	96	96	0
3	3	3	Toluene	30	30	0
4	3	3	THF	100	100	0
5	3	3	neat	15	15	0
6	3	1	EtOH	100	100	0
7	3	0	EtOH	86	86	0
8	1	1	EtOH	100	100	0
9	1	0	EtOH	82	82	0
10 [c]	1	1	EtOH	100	100	0
11 [c]	**1**	**0**	**EtOH**	**100**	**100**	**0**
12	0.5	0	EtOH	53	53	0
13 [c] [d]	**0.5**	**0**	**EtOH**	**100**	**100**	**0**
14 [c]	0.1	0	EtOH	10	10	0
15 [c] [d]	0.1	0	EtOH	87	87	0
16 [c] [e]	**0.1**	**0**	**EtOH**	**100**	**100**	**0**

[a] 1 mmol of substrate. [b] Determined by GC with dodecane as an internal standard. [c] Reaction temperature is 120 °C. [d] Reaction time is 5 hours. [e] Reaction time is 8 hours.

Additionally, we tested the influence of temperature on this isomerization with different reaction times. As we can see from Figure 4, temperature plays a critical role in the activity. This chemical reaction is entirely inactive when the experiments were performed below 60 °C. Moderate yields were observed with the reaction temperature of 70 °C in 1 hour. At least 120 °C is needed to achieve a quantitative yield in 1 hour. Nevertheless, 80 °C suffices for a full yield after 3 hours.



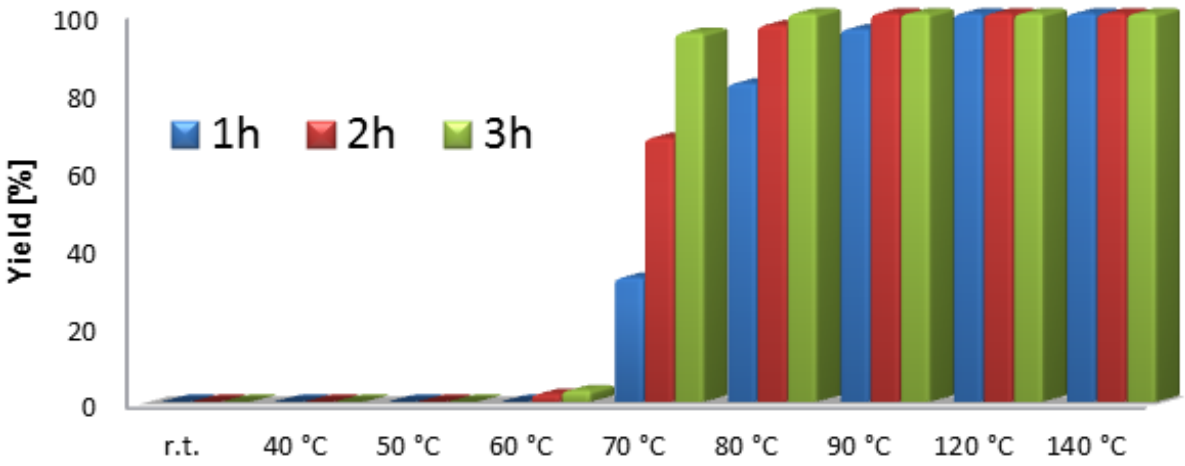
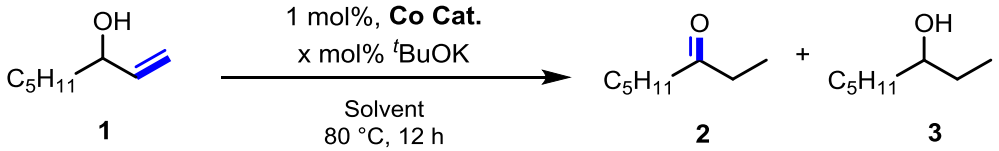


Figure 4 Effect of the temperature on the isomerization reactions of oct-1-en-3-ol catalyzed by compound **4-10**

The Milstein and Kempe catalysts were also evaluated in our catalytic system with 1 mol% pincer compound in different solvents at 80 °C (Table 4.3.4). It was found that the Milstein catalyst was entirely inactive at 1 mol% loading in different solvents (Entries 1-3). Furthermore, the addition of the same amount of base under identical reaction conditions did not activate this catalyst for the desired reaction (Entries 4-6). The Kempe catalyst was likewise inactive under similar reaction conditions in different solvents (Entries 12-17). It was shown that $NaBHEt_3$ is an essential additive for the pincer cobalt catalyzed hydrogenation of nitriles to primary amines; [90b] presumably the Co(II)-complex is the active catalyst in this case. Thus, the effect of this reductant on the isomerization of the allylic alcohol to the ketone was also tested (Entries 7-11). However, only low conversion was obtained after 12 hours in the presence of 1 mol% $NaBHEt_3$.

Table 4.3.4 Isomerization of 1 in the presence of the Milstein and Kempe catalysts [a]



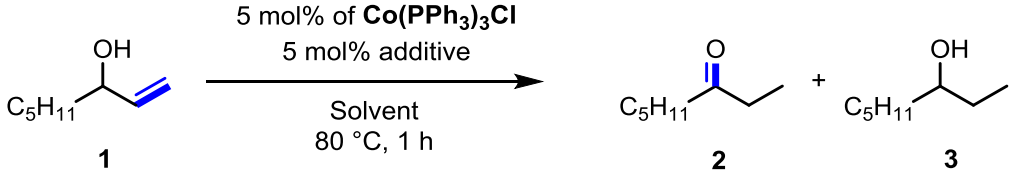
Entry	Cat. (mol %)	Base (mol%)	Solvent	Conversion 1 (%)	Yield 2 (%) [b]	Yield 3 (%)[b]
1	**4-4** (1)	0	IPA	0	0	0
2	**4-4** (1)	0	MeOH	0	0	0
3	**4-4** (1)	0	Toluene	0	0	0
4	**4-4** (1)	1	IPA	0	0	0
5	**4-4** (1)	1	MeOH	0	0	0
6	**4-4** (1)	1	Toluene	0	0	0
7 [c]	**4-4** (1)	1	MeOH	7	6	1

8 [c]	**4-4** (1)	1	IPA	24	21	3
9 [c]	**4-4** (1)	1	EtOH	12	12	0
10 [c]	**4-4** (1)	1	THF	25	24	1
11 [c]	**4-4** (1)	1	Toluene	14	14	0
12	**4-6** (1)	1	IPA	0	0	0
13	**4-6** (1)	1	MeOH	0	0	0
14	**4-6** (1)	1	Toluene	0	0	0
15	**4-6** (1)	0	IPA	0	0	0
16	**4-6** (1)	0	MeOH	0	0	0
17	**4-6** (1)	0	Toluene	0	0	0

[a] 1 mmol of substrate. [b] Determined by GC with dodecane as an internal standard. [c] 1 mol% of $NaBHEt_3$ was added.

In addition, the feasibility of that a triphenylphosphine coordinated cobalt compound, [96] was utilized together with $NaBHEt_3$ (to get cobalt-hydride complex)to isomerize oct-1-en-3-ol to 3-octanone in different solvents was verified (Table 12). Initially, the experiment was carried out in the presence of 5 mol% of $Co(PPh_3)_3Cl$ and $NaBHEt_3$ at 80 ^{o}C in 1 hour in heptane resulting in a moderate yield (Entry 1). Methanol, which is one of the best solvents for the phenyl PNP pincer cobalt catalyzed isomerization of oct-1-en-3-ol to 3-octanone, was totally inactive in this catalytic reaction (Entry 2). A moderate yield was detected when THF was used as a solvent (Entry 3). The highest conversion and yield was achieved by using toluene as a solvent (Entry 5). Notably, when the reaction was carried out under neat conditions, 49 % conversion of substrate was observed (Entry 6). However, the catalytic reaction was totally halted by changing the additive from $NaBHEt_3$ to ^{t}BuOK under otherwise identical reaction conditions (Entry 7). Both the catalyst and the additive play significant roles in this isomerization. In the absence of catalyst or base, no reactivity was observed in this isomerization of oct-1-en-3-ol (Entry 8-11). Nevertheless, further optimization of catalyst and additive would be needed to further improve the isomerization of oct-1-en-3-ol to 3-octanone with this catalyst.

Table 12 Other non-pincer catalysts in the isomerization of 1 [a]



1 **2** **3**

Entry	Additive	Solvent	Conversion 1 (%)	Yield 2 (%) [b]	Yield 3 (%) [b]
1	$NaBHEt_3$	Heptane	69	62	7
2	$NaBHEt_3$	MeOH	0	0	0
3	$NaBHEt_3$	THF	58	53	5
4	$NaBHEt_3$	MeCN	0	0	0
5	$NaBHEt_3$	Toluene	81	75	6

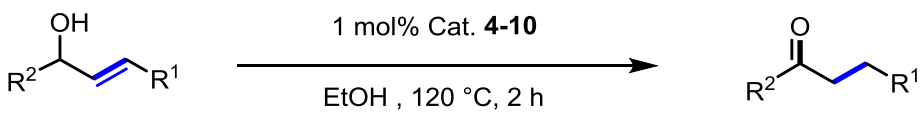
6	$NaBHEt_3$	neat	49	47	2
7	^tBuOK	Toluene	0	0	0
8	-	MeOH	0	0	0
9	-	Toluene	0	0	0
10	-	Heptane	0	0	0
11 [c]	$NaBHEt_3$	Toluene	0	0	0

[a] 1 mmol of substrate. [b] Determined by GC with dodecane as an internal standard. [c] Without catalyst.

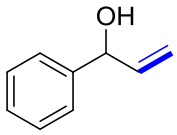
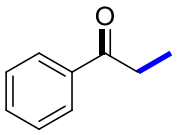
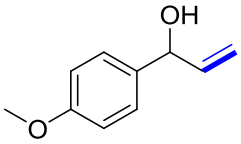
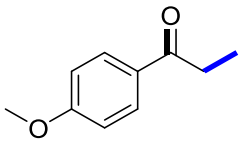
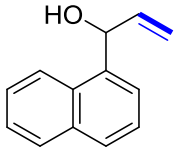
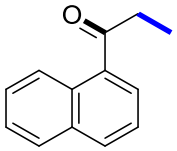
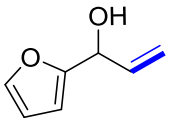
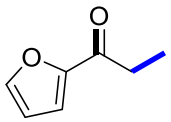
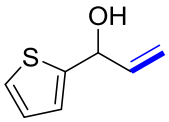
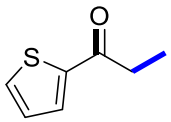
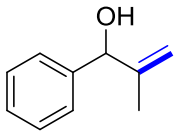
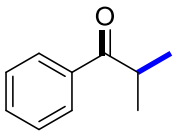
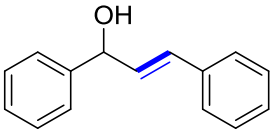
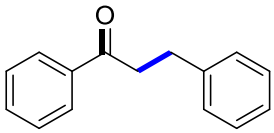
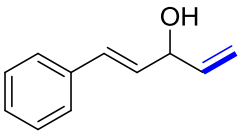
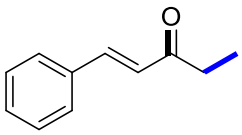
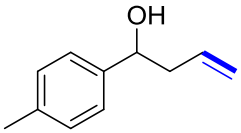
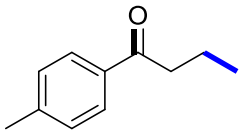
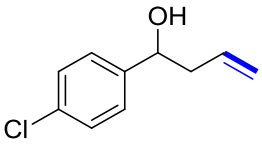
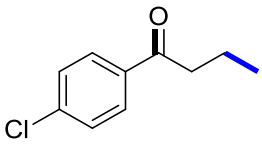
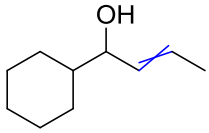
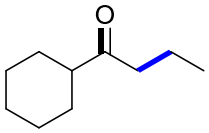
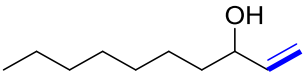
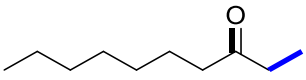
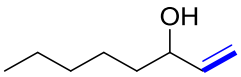
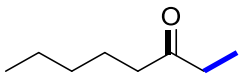
2.3.3 Substrate scope

With the optimized reaction conditions in hand, we tested the scope and limitations of this catalytic system on a range of substrates, which included various aromatic and aliphatic allylic alcohols (Table 13). Exceptional yields of isomerization of aromatic allylic/homo-allylic alcohols to ketones with a range of electron-rich and electron-poor substituents were achieved (Table 13, entries 1-11). 1-Phenylprop-2-en-1-ol was selected as a substrate which resulted in a high yield of the corresponding carbonyl derivative (Table 13, entry 1). A methyl substituent in the para position of the aromatic ring had no influence on the yield of the desired product (Table 13, entry 2). A slight decrease in yield was observed when the methyl substituent was replaced by a methoxy group in the para position of the aromatic substrate (Table 13, entry 3). This catalytic system also showed good compatibility with an aromatic bromide substituent, which was retained leading to a good yield of the ketone of 87% (Table 13, entry 4). An excellent yield (89%) was obtained when the reaction was carried out on 1-naphthyl-propenol. Heteroaromatic substrates, e.g. the furanyl- and thienyl- substituted allylic alcohols, gave good yields of the desired ketones (Table 13, entries 6 and 7). 1-Phenylpenta-1,4-dien-3-ol containing two alkene groups was also converted by selective isomerization of the vinyl alcohol into the carbonyl compound with 95% yield (Table 13, entry 8). Good to excellent yields of the corresponding carbonyl derivatives were obtained from the homo-allylic alcohols (Table 13, entries 9-10). Interestingly, 1-cyclohexyl-but-2-en-1-ol (entry 11), which was a mixture of the *cis* and *trans* isomers, was also converted to 1-cyclohexylbutan-1-one in high isolated yield. Aliphatic allylic alcohols were isomerized to the saturated ketones with excellent yields with this catalytic system (Table 13, entries 13 and 14). Notably, when 10 mmol (Gram scale) of oct-1-en-3-ol was used and 10 mL of toluene as the solvent, the purification of 3-octanone only required filtration of the catalyst and the salts and subsequent removal of the solvent to obtain the pure product.

Table 13 Substrate scope of the PNP cobalt-catalysed allylic alcohol isomerization [a]



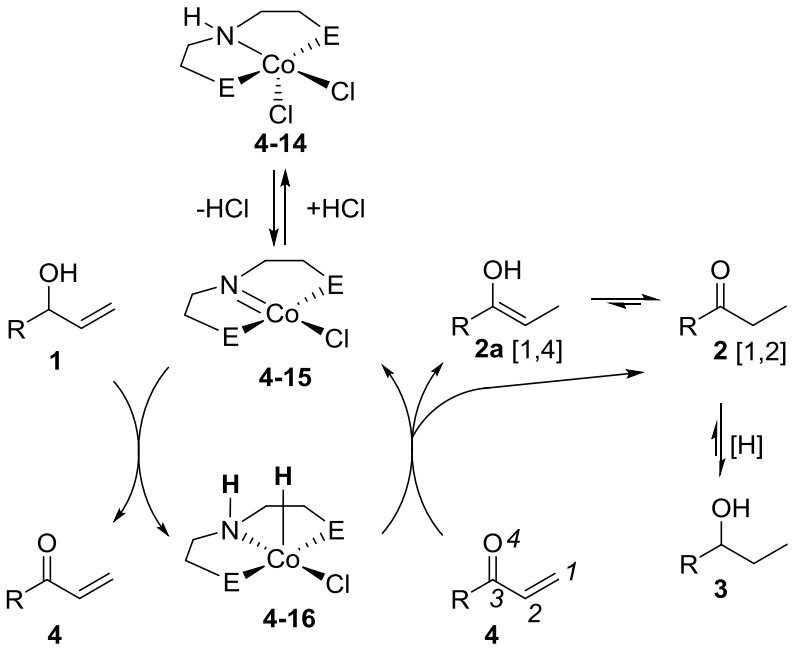
Entry	Allylic alcohol	Ketone	Yield (%)[b]

1			97; 69 [c]
2			95
3			95
4			82
5			80
6			0; 72 [d]
7			20; 90 [d]
8			92; 21 [d]
9			49 [e]
10			57 [e]
11			11; 91 [d]
12			97 [c]
13			97; 94 [c]

[a] 1 mmol of substrate. [b] Isolated yield. [c] 0.1 mol% of catalyst, reaction time is 8 hours. [d] Solvent is trifluoroethanol (TFE). [e] Reaction time is 4 hours.

2.3.4 Proposed mechanism

Based on the reaction mechanism in the isomerization of allylic alcohols to the corresponding ketones previously catalyzed by iron (chapter 2.1) and manganese (chapter 2.2) pincer complexes, we proposed a dehydrogenation-hydrogenation two-step reaction mechanism. There is a balance between compounds 4-14 and 4-15. When ^{t}BuOK was added as a base in the catalytic system, compound 4-14 smoothly converted to compound 4-15. In the absence of an external hydrogen supply, the first step was to dehydrogenate compound 1 to compound 4 by using complex 4-15. Then it is the catalytic addition reaction of compound 4. The target compound 2 can be either directly obtained through the 1,2 addition or the tautomerization after the 1,4 addition from compound 4.



Scheme 53 Proposed mechanism (R = C_5H_{11}, E = P(^{i}Pr)$_2$ or P(Ph)$_2$)

3 Summary

We have discovered a catalyst for the isomerization of allyl/ homo-allylic to carbonyls based on inexpensive, non-toxic iron and PNP pincer ligands. Good to excellent yields can be achieved with various substrates at 80 ^{o}C in the presence of 1 mol% catalyst and base. Monitoring the reaction shows that the isomerization reaction can be completed at room temperature for 20 minutes, and it takes only 6 minutes to complete the reaction at 80 ^{o}C. Compared with weak bases, strong bases show better results in both conversion and yield. Room temperature can be used in some selected substrates with good isolated yields. In the case of using isopropanol as a solvent, the major product of this reaction is a saturated alcohol. We propose a two-step reaction mechanism consisting of dehydrogenation and hydrogenation. There is a selectivity of a 1,2-addition and 1,4-addition reaction in the catalytic hydrogenation of conjugated ketones.

We have shown for the first time that manganese PNP pincer complexes are efficient catalysts for the isomerization of allylic alcohols to the corresponding ketones with catalyst amounts as low as 0.1 mol% in the presence of base. Notably, the efficiency of the catalysts could be evidently increased by changing the substituent on the phosphorus atom from isopropyl group to phenyl. Good to excellent yields could be achieved in both aromatic and aliphatic allylic or homo-allylic alcohols. Neat reaction can be used in this system with a high conversion and yield. A two-step mechanism with a dehydrogenation and hydrogenation process is proposed.

We have shown for the first time that cobalt (II) compounds are efficient catalysts for the isomerization of allylic alcohols to ketones in in the presence of base. Notably, the efficiency of catalyst could be increased by changing the substituents on the phosphorus atoms of the PNP pincer ligand from isopropyl to phenyl. Good to excellent yields could be achieved in the isomerization of both aromatic and aliphaticl allylic or homo-allylic alcohols.

4. Experimental work and data analysis

All experiments were performed under inert argon atmosphere by using standard Schlenk technic or glove box, if not stated otherwise. $PNP^{(iPr)}$ and $PNP^{(tBu)}$ ligands were purchased from Strem as a solution in THF and $PNP^{(Cy)}$ were purchased from Strem as a solid, $PNP^{(Ph)}$ was purchased from Abcr as a solid and all of these ligands were used directly. THF, toluene, ethanol, acetonitrile, DMF, dichloromethane and heptane and hexane were used as taken from the solvents purification system without further purification. Isopropanol, methanol, chloroform, benzene, all the deuterated solvents and liquid substrates were degassed and stored in Schlenk flasks over 3Å molecular sieves. Solid starting materials were added to a Schlenk tube and stored under an Ar atmosphere before use. Commercially available chemicals were purchased from Sigma, Alfa, Strem, Abcr, Acros and TCI. The synthesis complexes L1[87], L2[76], 3-4[75], 3-10[75], 3-9[88], 3-12[72], 3-13[89], 3-8[76], 3-14[76] were reported in literature. The use of complex 3-11 was reported in literature, but no analytical data was reported. [77]

4.1 Synthesis of catalysts and ligands

(PNP)Fe(CO)Cl_2. A suspension of $FeCl_2$ (378 mg, 3 mmol) in THF (100 mL) was stirred for 1 hour at room temperature under argon atmosphere and a THF solution of PNP ligand (Bis[(2-di-i-propylphosphino)ethyl]amine, wt 10%, 9.5 g, 3.1 mmol,) was added. CO flow was introduced via bubbling through the resulting gray suspension and a purple solution was produced immediately. The carbon monoxide flow was kept for 1 hour, and then stopped. The resulting solution was stirred overnight under CO atmosphere, filtered through celite and THF was removed *in vacuo*. The solid residue was washed with heptane (3 x 20 mL) to afford the desired product as a purple solid (950 mg, 69%).**^{1}H NMR** (300 MHz, Chloroform-*d*) δ 5.24 (t, *J* = 12.4 Hz, 1H), 3.69 – 3.51 (m, 2H), 3.36 (q, *J* = 12.8 Hz, 2H), 2.53 (ddt, *J* = 21.7, 14.5, 6.6 Hz, 6H), 2.07 (ddd, *J* = 14.9, 9.0, 5.7 Hz, 2H), 1.55 – 1.33 (m, 25H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 49.8, 26.6, 23.6, 21.6, 20.2, 19.8, 19.00, 18.8.**^{31}P NMR** (121 MHz, $CDCl_3$) δ 67.2

(PNP)Fe(CO)HCl. A solution of (PNP)$FeCl_2$(CO) (460 mg, 1 equiv) and $NaBH_4$ (40mg, 1.05 equiv) in 0 °C ethanol (100 mL) was stirred gradually to room temperature and overnight under argon atmosphere . Ethanol was removed by pump under low pressure to produce a yellow solid. 20 mL toluene was added to dissolve iron compound and transfer to another Schlenk tube by cannula filtration. After the solution was concentrated to 10 mL, 20 mL heptane was carefully added to the Schlenk tube. Crystal product was produced by keeping the solution in the fridge after 24 hours (375 mg, 84%). **^{1}H NMR** (300 MHz, CD_2Cl_2, δ in ppm): 3.30 (br, 1H), 2.75 – 2.60 (m, 2H), 2.45 – 2.11 (m, 6H), 1.84 – 1.64 (m, 2H), 1.60 – 1.43 (m, 6H), 1.39 – 0.80 (m, 20H), −19.3 (t, J_{P-H} = 52.8 Hz, 1H). **^{31}P NMR** (121 MHz, CD_2Cl_2, δ in ppm): 94.00.

(3-4) $^{(iPr)}$(PNHP)$Mn(CO)_2Br$. A solution of $PNP^{(iPr)}$ ligand (5 mL, 1.6 mmol, 10% wt in THF) was added to a suspension of $Mn(CO)_5Br$ (427mg, 1.5 mmol) in toluene (50 mL) by syringe (very strong CO evolution was observed during this stage). After half an hour, the mixture was heated to 100 °C and stirred for 24 hours. A precipitate was formed during the heating process. The mixture was cooled down to room temperature after another half hour and the solution was removed by filtration. The resulting solid was washed with heptane (3 x 20 mL) and dried *in vacuo* to afford the title compound (415mg, 56%). ^{1}H NMR (400 MHz, Benzene-d_6) δ 3.40 –

3.17 (m, 2H), 2.78 (s, 1H), 2.40 (s, 2H), 2.21 (qd, *J* = 7.0, 2.5 Hz, 2H), 1.94 (d, *J* = 13.2 Hz, 2H), 1.64 (d, *J* = 14.1 Hz, 2H), 1.60 – 1.39 (m, 6H), 1.39 – 1.11 (m, 15H), 1.05 (td, *J* = 7.1, 4.1 Hz, 7H), 0.90 (d, *J* = 20.4 Hz, 6H).^{31}P NMR (121 MHz, C_6D6) δ 81.79. ESI-HRMS: Calculated for [$C_{18}H_{37}MnNO_2P_2$] [M^+]: 416.16745; found: 416.16785. Elemental analysis: Calculated for [$C_{18}H_{37}MnNO_2P_2$]: C, 43.56; H, 7.51; N, 2.82; found: C, 42.68; H, 7.07; N, 2.79.

(3-10) $^{(Cy)}$(PNHP)Mn(CO)$_2$Br. A solution of PNP$^{(Cy)}$ ligand (500mg, 1.07 mmol) in 10 mL toluene was added to a suspension of $Mn(CO)_5Br$ (280mg, 1.02 mmol) in toluene (40 mL) by syringe. (Be careful about this step, CO evolution was very strong). After an hour, the mixture was heated to 100 ^{o}C and stirred for 24 hours. A precipitate was formed during the heating process. The mixture was cooled down to room temperature after another half hour and the solution was removed by filtration. The resulting solid was washed with heptane (3 x 20 mL) and dried *in vacuo* to afford the title compound (515mg, 79%). ^{1}H NMR (300 MHz, Benzene-d_6) δ 3.03 (d, *J* = 11.1 Hz, 3H), 2.76 (d, *J* = 11.2 Hz, 2H), 2.65 (d, *J* = 15.5 Hz, 2H), 2.25 – 2.06 (m, 3H), 2.01 (d, *J* = 12.6 Hz, 4H), 1.95 – 1.42 (m, 30H), 1.26 (dt, *J* = 27.7, 10.9 Hz, 18H). ^{31}P NMR (121 MHz, C_6D_6) δ 73.11.

(3-11) $^{(Ph)}$(PNHP)Mn(CO)$_2$Br. A suspension of PNP$^{(Ph)}$ ligand (600mg, 1.26 mmol) and NEt_3 (0.2 mL, 1.45 mmol) in 20mL THF was stirred for 15 minutes at room temperature. The liquid part of this suspension was dropwise added through cannula filtration to another suspension of $Mn(CO)_5Br$ (275mg, 1 mmol) in 40 mL THF (Be careful about this step, CO evolution was very strong). After an hour, the mixture was heated to 100 ^{o}C and stirred for 24 hours. A precipitate was formed during the heating process. The mixture was cooled down to room temperature after another half hour and the solution was removed by filtration. The resulting solid was washed with heptane (3 x 20 mL) and dried *in vacuo* to afford the title compound (388mg, 61%). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 8.16 – 6.76 (m, 20H), 3.39 (d, *J* = 155.2 Hz, 4H), 2.51 (d, *J* = 136.0 Hz, 4H). ^{31}P NMR (162 MHz, CD_2Cl2) δ 69.67. IR: 3190, 3033, 2932, 2870, 1911, 1830, 1574, 1482, 1462, 1434, 1406, 1330, 1304, 1206, 1167, 1097, 1068, 1021, 959, 830, 737, 695, 624, 579, 523, 473, 442. Elemental analysis: Calculated for [$C_{30}H_{29}BrMnNO_2P_2$]: C, 56.98; H, 3.62; N, 2.22; found: C, 56.26; H, 3.46; N, 2.23. Single crystal suitable for X-ray diffraction measurement was obtained from slow diffusion of heptane into the solution of the title compound in toluene.

(3-9) $^{(iPr)}$(PNP)Mn(CO)$_2$. A solution of PNP$^{(iPr)}$ ligand (9.4 g, 3.08 mmol, 10% wt in THF) and 7 mL dry HMDSO (hexamethyldisiloxane) was added to a suspension of $Mn_2(CO)_{10}$ (600mg, 1.54 mmol) in toluene (15 mL) by syringe. Then the mixture was heated to reflux over 48 hours. A dark red solution was obtained and the solvent was removed by pump under low pressure. The red sticky mixture was washed by heptane (15mL x 3) and cannula filtration was used to transfer the solution to another Schlenk tube. After keeping the solution in the freezer (-30 ^{o}C) 24 hours, the liquid was removed by syringe and a dark red solid was obtained (720mg, 56%). ^{31}P NMR (121 MHz, C_6D6) δ 113.49.

(3-12) $^{(tBu)}$(PN(pyridine)P)Mn(CO)$_3$Br. A solution of PN(pyridine)P$^{(tBu)}$ ligand (537 mg, 1.36 mmol) in benzene (9 mL) was added to a suspension of $Mn(CO)_5Br$ (380 mg, 1.36 mmol) in benzene (9 mL) by syringe. The mixture was stirred at room temperature for 30 hours. A precipitate was formed during this process. Cannula filtration was used to separate the solid and liquid. The resulting solid was washed with heptane (3 x 20 mL) and dried *in vacuo* to afford the title compound (678mg, 81%). ^{31}P NMR (121 MHz, $CDCl_3$) δ 109.97. ESI-HRMS: Calculated

for $[C_{26}H_{43}MnNO_3P_2]$ $[M^+]$: 534.20932; found: 534.20900.

(3-13) $^{(tBu)}$PN(pyridine)N$^{(Et)}$Mn(CO)$_2$Br. A solution of a $^{(tBu)}$PN(pyridine)N$^{(Et)}$ ligand (644 mg, 2 mmol) in THF (10 mL) was added to a suspension of $Mn(CO)_5Br$ (550 mg, 2 mmol) in THF (10 mL) by syringe. The mixture was stirred at room temperature for 60 hours. Half of the THF was removed by pump under vacuum and then 20 mL of heptane was added resulting in a suspension. The liquid was removed and the solid was dried in *vacuo* (769mg, 75%). ^{31}P NMR (122 MHz, $CDCl_3$) δ 120.19. ESI-HRMS: Calculated for $[C_{21}H_{35}MnN_2O_2P]$ $[M^+]$: 433.18112; found: 433.18131.

(3-14) (4-Me)Triaz(NHP*i*Pr$_2$)$_2$Mn(CO)$_2$Br.A suspension of (4-Me)Triaz(NHP*i*Pr$_2$)$_2$ (1.07 g, 3 mmol) and $Mn(CO)_5Br$ (0.82 g, 3 mmol) in 40 mL toluene was refluxed overnight. A precipitate was formed during the heating process. The mixture was cooled down to room temperature after another half hour and the solution was removed by filtration. The resulting solid was washed with heptane (3 x 20 mL) and dried *in vacuo* to afford the title compound (1280mg, 74%). ^{31}P NMR (121 MHz, $CDCl_3$) δ 136.42.

(3-8) (4- NHCpr)Triaz(NHP*i*Pr$_2$)$_2$Mn(CO)$_2$Br. A suspension of (4- NHCpr)Triaz(NHP*i*Pr$_2$)$_2$ (1.2 g, 3 mmol) and $Mn(CO)_5Br$ (0.82 g, 3 mmol) in 40 mL toluene was refluxed overnight. A precipitate was formed during the heating process. The mixture was cooled down to room temperature after another half hour and the solution was removed by filtration. The resulting solid was washed with heptane (3 x 20 mL) and dried *in vacuo* to afford the title compound (500mg, 28%). ^{31}P NMR (121 MHz, $CDCl_3$) δ 132.93.

(3-15) (4- N(allyl)$_2$)Triaz(NHP*i*Pr$_2$)$_2$Mn(CO)$_2$Br. A suspension of (4- N(allyl)$_2$)Triaz(NHP*i*Pr$_2$)$_2$ (1.32 g, 3 mmol) and $Mn(CO)_5Br$ (0.82 g, 3 mmol) in 40 mL toluene was refluxed overnight. A precipitate was formed during the heating process. The mixture was cooled down to room temperature after another half hour and the solution was removed by filtration. The resulting solid was washed with heptane (3 x 20 mL) and dried *in vacuo* to afford the title compound (1530mg, 81%). ^{31}P NMR (162 MHz, $CDCl_3$) δ 133.10.

$^{(iPr)}$(PNHP)CoCl$_2$. A solution of bis[2-(di-*iso*-propylphosphino)ethyl]amine (125 mg, 0.410 mmol) in THF (10 mL) was added to a suspension of $CoCl_2$ (50 mg, 0.390 mmol) in THF (20 mL). The reaction mixture was stirred overnight at room temperature. The color of the suspension changed from blue to pink during the course of the reaction. The solvent was then removed under vacuum. The obtained pink solid was washed with heptane (2 x 15 mL). To obtain the pure product, the solid was dried for 4 hours under reduced pressure. Yield: 132 mg (78%). HRMS-ESI (M+) calculated for $C_{16}H_{37}Cl_2CoNP_2$: 434.11048 found: 434.11076. EA calculated for $C_{16}H_{37}Cl_2CoNP_2$: C, 44.15; H, 8.57; N, 3.22; P, 14.23 found: C, 44.08; H, 8.43; N, 2.89; P, 13.80. ATR-IR (solid): ν(N-H): 3246 cm^{-1}; ν(C-H): 2953 cm^{-1}, 2922 cm^{-1}, 2868 cm^{-1}.

$^{(tBu)}$(PNHP)CoCl$_2$. A solution of bis[2-(di-*tert*-butylphosphino)ethyl]amine (148 mg, 0.410 mmol) in THF (10 mL) was added to a suspension of $CoCl_2$ (50 mg, 0.390 mmol) in THF (20 mL). The reaction mixture was stirred overnight at room temperature. The color of the suspension changed from bright blue to dark blue during the course of the reaction. The solvent was then removed under vacuum. The obtained pink solid was washed with heptane (2 x 15 mL) through cannula filtration. To obtain the pure product, the solid was dried 4 hours under reduced pressure. Yield: 138 mg (72%). HRMS-ESI (M+) calculated for $C_{20}H_{45}ClCoNP_2$: 455.20423 found:

455.20398. EA calculated for $C_{20}H_{45}Cl_2CoNP_2$: C, 48.89; H, 9.23; N, 2.85; P, 12.61 found: C, 48.76; H, 8.99; N, 2.65; P, 11.97. ATR-IR (solid): ν(N-H): 3214 cm^{-1}; ν(C-H): 2940 cm^{-1}, 2899 cm^{-1}, 2867 cm^{-1}.

$^{(Cy)}$(PNHP)CoCl$_2$. A solution of bis[2-(di-cyclohexylphosphino)ethyl]amine (191 mg, 0.410 mmol) in THF (10 mL) was added to a suspension of $CoCl_2$ (50 mg, 0.390 mmol) in THF (20 mL). The reaction mixture was stirred overnight at room temperature. The color of the suspension changed from blue to pink during the course of the reaction. The solvent was then removed under vacuum. The obtained pink solid was washed with heptane (2 x 15 mL) through cannula filtration. To obtain the pure product, the solid was dried 4 hours under reduced pressure. Yield: 179 mg (77%). HRMS-ESI (M+) calculated for $C_{28}H_{53}Cl_2CoNP_2$: 594.23568 found: 594.23552. EA calculated for $C_{28}H_{53}Cl_2CoNP_2$: C, 56.47; H, 8.97; N, 2.35; P, 10.40 found: C, 57.07; H, 8.91; N, 2.12; P, 10.24. ATR-IR (solid): ν(N-H): 3250 cm^{-1}; ν(C-H): 2923 cm^{-1}, 2852 cm^{-1}.

$^{(Ph)}$(PNHP)CoCl$_2$. To a white suspension of bis[(2-di-phenylphosphino)ethyl]ammonium chloride (2 g, 4.18 mmol) in THF (25 mL), triethylamine (0.44 g, 0.61 ml, 4.39 mmol) was added and allowed to stir for 15 min at room temperature. The resulting free ligand was transferred *via* cannula filtration to a solution of $CoCl_2$ (0.65 g, 5.02 mmol) in ethanol (60 mL). During the dropwise addition, a purple precipitate was formed. After completed addition, the suspension was allowed to stir overnight at room temperature. The solvent was then removed under vacuum. The pink powder was washed with 2 x 10 mL of ethanol and 1 x 10 ml heptane through cannula filtration. To obtain the pure product, the solid was dried 4 hours under reduced pressure. Crystals suitable for a single-crystal X-ray diffraction study were grown from a concentrated solution of CH_2Cl_2 layered with diethylether. Yield: 2290 mg (96%). HRMS-ESI (M+) calculated for $C_{28}H_{29}Cl_2CoNP_2$: 570.05132 found: 570.05113. EA calculated for $C_{28}H_{29}Cl_2CoNP_2$: C, 58.86; H, 5.12; N, 2.45; P, 10.84 found: C, 58.76; H, 5.11; N, 2.53; P, 10.70. ATR-IR (solid): ν(N-H): 3298 cm^{-1}; ν(C-H): 2856 cm^{-1}, 1483 cm^{-1}, 1433 cm^{-1}, 1407 cm^{-1}, 1358 cm^{-1}.

$^{(Ad)}$(PNHP)CoCl$_2$. A solution of bis[2-(di-adamantylphosphino)ethyl]amine (539 mg, 0.80 mmol) in THF (15 mL) was added to a suspension of $CoCl_2$ (100 mg, 0.77 mmol) in THF (25 mL). The reaction mixture was stirred overnight at room temperature. The color of the suspension changed from bright blue to dark blue during the course of the reaction. The solvent was then removed under vacuum. The obtained blue solid was washed with heptane (2 x 20 mL) through cannula filtration. To obtain the pure product, the solid was dried 4 hours under reduced pressure. Yield: 558 mg (90%). HRMS-ESI (M+H)+ calculated for $C_{44}H_{69}Cl_2CoNP_2$: 803.36871 found: 803.36905. EA calculated for $C_{44}H_{69}Cl_2CoNP_2$: C, 65.75; H, 8.65; N, 1.74; P, 7.71 found: C, 65.88; H, 8.43; N, 1.82; P, 7.45. ATR-IR (solid): ν(N-H): 3170 cm^{-1}, ν(C-H): 2902 cm^{-1}, 2880 cm^{-1}, 2847 cm^{-1}.

$^{(iPr)}$(PNHP)CoBr$_2$. A solution of bis[2-(di-*iso*-propylphosphino)ethyl]amine (122 mg, 0.400 mmol) in THF (10 mL) was added to a suspension of $CoBr_2$ (85 mg, 0.390 mmol) in THF (20 mL). The reaction mixture was stirred overnight at room temperature. The color of the suspension changed from blue to pink during the course of the reaction. The solvent was then removed under vacuum. The obtained pink solid was washed with heptane (2 x 15 mL) through cannula filtration. To obtain the pure product Co-6, the solid was dried 4 hours under reduced pressure. Yield: 182 mg (89%). HRMS-ESI (M+) calculated for $C_{16}H_{36}BrCoNP_2$: 442.08329 found: 442.08201. EA calculated for $C_{16}H_{37}Br_2CoNP_2$: C, 36.66; H, 7.12; N, 2.67; P, 11.82 found: C, 36.44; H, 7.13; N, 2.45; P, 11.61. ATR-IR (solid): ν(N-H): 3098 cm^{-1}; ν(C-H): 2951 cm^{-1}, 2923 cm^{-1}, 2867 cm^{-1}.

(L1) [(4-Me)Triaz(NHP*i*Pr$_2$)$_2$] *N^2,N^4-bis(diisopropylphosphanyl)-6-methyl-1,3,5-triazine-2,4-diamine*. P(^{i}Pr)$_2$Cl (8 mL, 50 mmol) was added dropwise through a dropping funnel to a solution of 6-methyl-1,3,5-triazine-2,4-diamine (3g, 24 mmol) , NEt$_3$ (8.5 mL, 60 mmol) and 35 mL THF. The mixture were stirred at room temperature for 30 minutes and then refluxed overnight. A suspension appeared when the mixture was cooled to room temperature. Cannula filtration was used to separate the solid and liquid. The solvent in the liquid part was removed by pump under vacuum. The resulting solid was washed with heptane (3 x 5 mL) and dried *in vacuo* to afford the title compound (7966mg, 93%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.04 (s, 2H), 2.36 (s, 3H), 1.95 – 1.74 (m, 4H), 1.22 – 1.00 (m, 25H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 169.4, 169.2, 26.2, 26.0, 18.7, 18.5, 17.5, 17.4. ^{31}P NMR (121 MHz, CDCl$_3$) δ 50.33, 47.50.

(L2) [(4- NHCpr)Triaz(NHP*i*Pr$_2$)$_2$]. *N^2-cyclopropyl-N^4,N^6-bis(diisopropylphosphanyl)-1,3,5-triazine-2,4,6-triamine*. P(^{i}Pr)$_2$Cl (8 mL, 50 mmol) was added dropwise through a dropping funnel to a solution of N^2-cyclopropyl-1,3,5-triazine-2,4,6-triamine (3.9 g, 24 mmol) , NEt$_3$ (8.5 mL, 60 mmol) and 35 mL THF. The mixture were stirred at room temperature for 30 minutes and then refluxed overnight. A suspension appeared when the mixture was cooled to room temperature. Cannula filtration was used to separate the solid and liquid. The solvent in the liquid was removed by pump under reduced pressure. The resulting solid was washed with heptane (3 x 5 mL) and dried *in vacuo* to afford the title compound (8763mg, 92%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.98 (s, 2H), 2.79 (tq, *J* = 7.0, 3.5 Hz, 1H), 1.86 (tdd, *J* = 8.7, 3.4, 2.0 Hz, 4H), 1.08 (ddd, *J* = 13.2, 7.1, 2.5 Hz, 24H), 0.80 – 0.64 (m, 2H), 0.50 (dt, *J* = 3.6, 1.5 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 169.3, 167.5, 26.1, 26.0, 23.4, 18.6, 17.8, 7.1.^{31}P NMR (162 MHz, CDCl$_3$) δ 56.37. ESI-HRMS: Calculated for [$C_{18}H_{36}N_6P_2$] [M+H]$^+$: 399.25494; found: 399.25481.

(L3) [(4- N(allyl)$_2$)Triaz(NHP*i*Pr$_2$)$_2$] *N^2,N^2-diallyl-N^4,N^6-bis(diisopropylphosphanyl)-1,3,5-triazine-2,4,6-triamine*. P(^{i}Pr)$_2$Cl (8 mL, 50 mmol) was added dropwise through a dropping funnel to a solution of N^2,N^2-diallyl-1,3,5-triazine-2,4,6-triamine (5 g, 24 mmol) , NEt$_3$ (8.5 mL, 60 mmol) and 35 mL THF. The mixture were stirred at room temperature for 30 minutes and then refluxed overnight. A suspension appeared when the mixture was cooled to room temperature. Cannula filtration was used to separate the solid and liquid. The solvent in the liquid part was removed by pump under low pressure. The resulting solid was washed with heptane (3 x 5 mL) and dried *in vacuo* to afford the title compound (8264mg, 79%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.86 (ddt, *J* = 16.9, 10.0, 5.9 Hz, 2H), 5.27 – 5.11 (m, 4H), 3.76 (d, *J* = 8.3 Hz, 2H), 3.30 – 4.14 (m, 4H), 1.85 (pd, *J* = 7.0, 1.9 Hz, 4H), 1.23 – 1.04 (m, 26H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 232.3, 133.3, 116.7, 47.9, 26.3, 26.1, 19.0, 18.7, 17.8, 17.6. ^{31}P NMR (121 MHz, CDCl$_3$) δ 50.19. ESI-HRMS: Calculated for [$C_{21}H_{40}N_6P_2$] [M+H]$^+$: 439.28624; found: 439.28602.

4.2 General procedure for the isomerization of allylic alcohols

An oven dried 4 mL pressure tube (or 10 mL schlenk tube) with a stirring bar was charged with PNP pincer metal complex and 1 mL solvent was added sequentially. Then 1 mmol of substrate was added immediately to the pressure tube (or 10 mL schlenk tube). The solution was stirred for the mentioned time and temperature. GC yields were determined with dodecane as internal standard. Isolated yields were obtained by using silica gel

chromatography after rotary evaporation.

4.3 Monitoring reactions

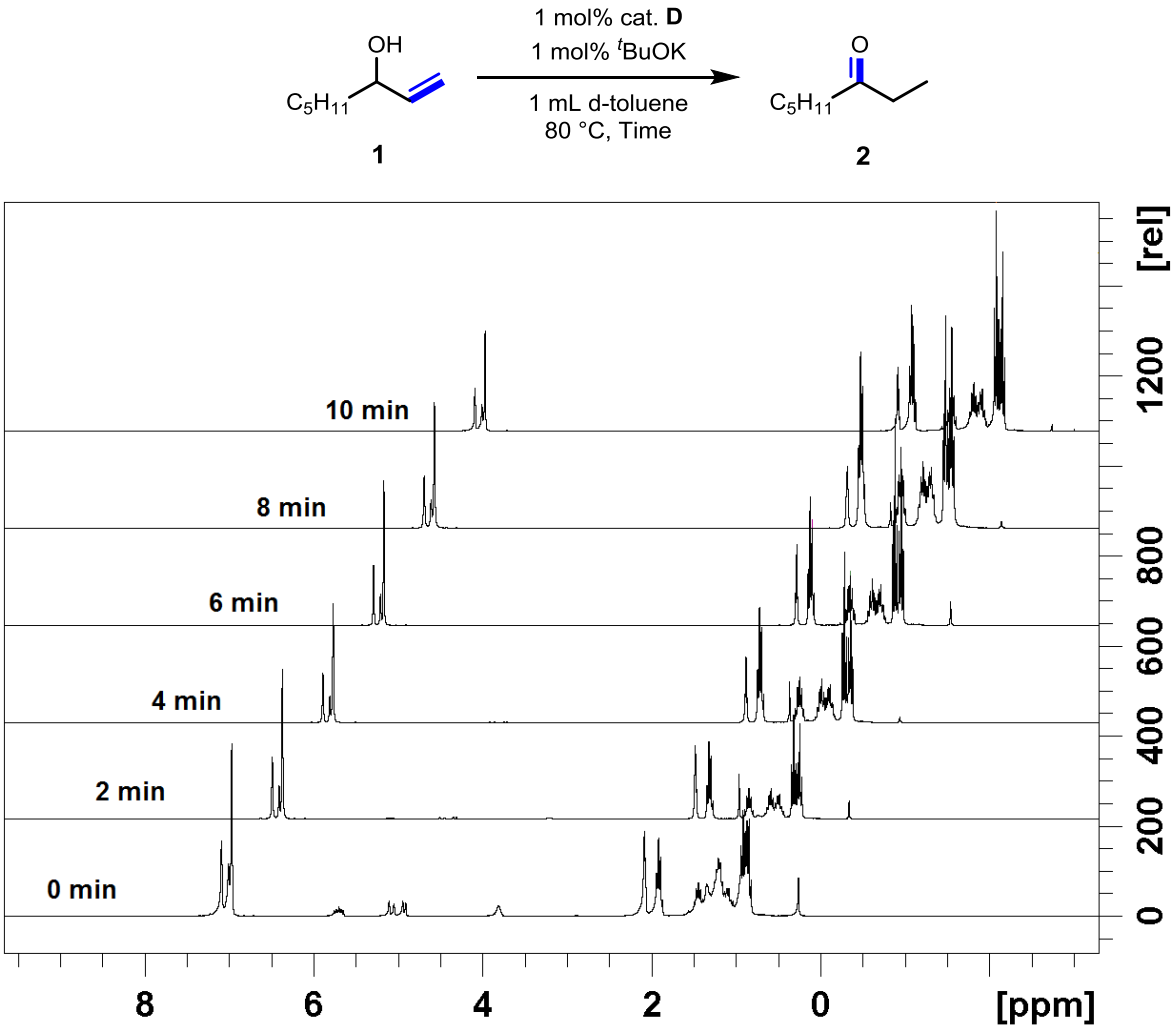
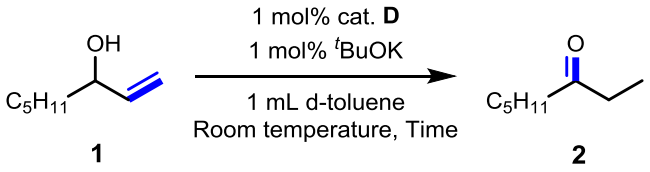


Figure 5 ^{1}H-NMR monitoring at 80 °C (This figure is from the published article [60])



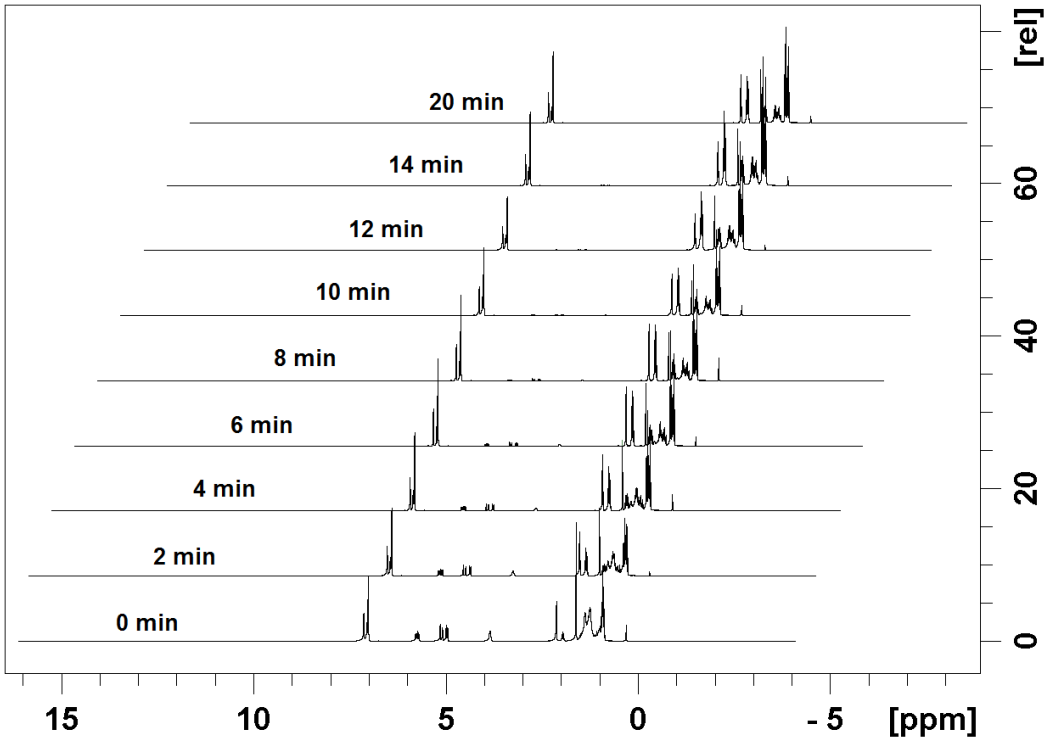
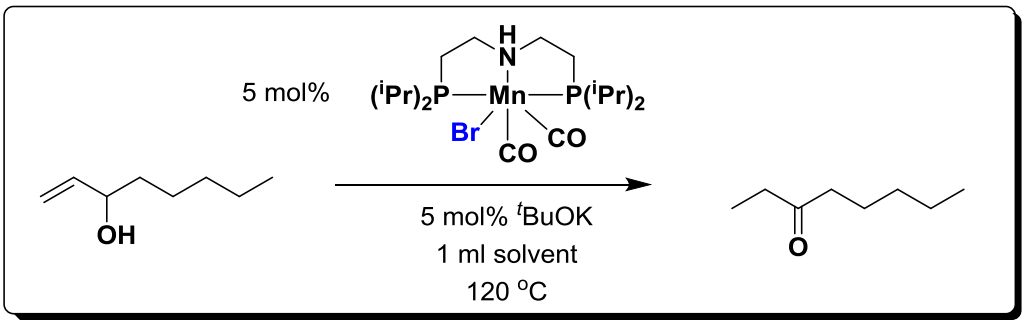
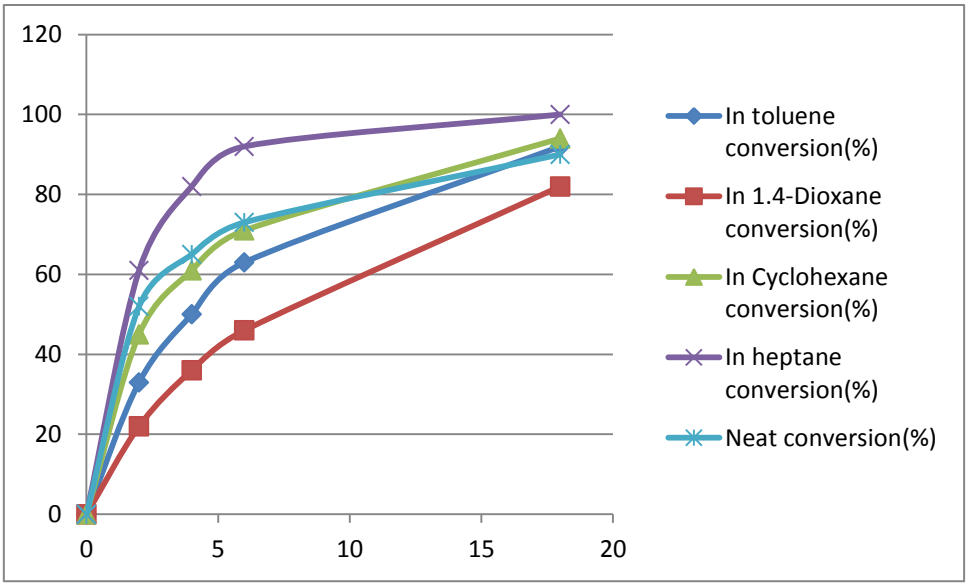
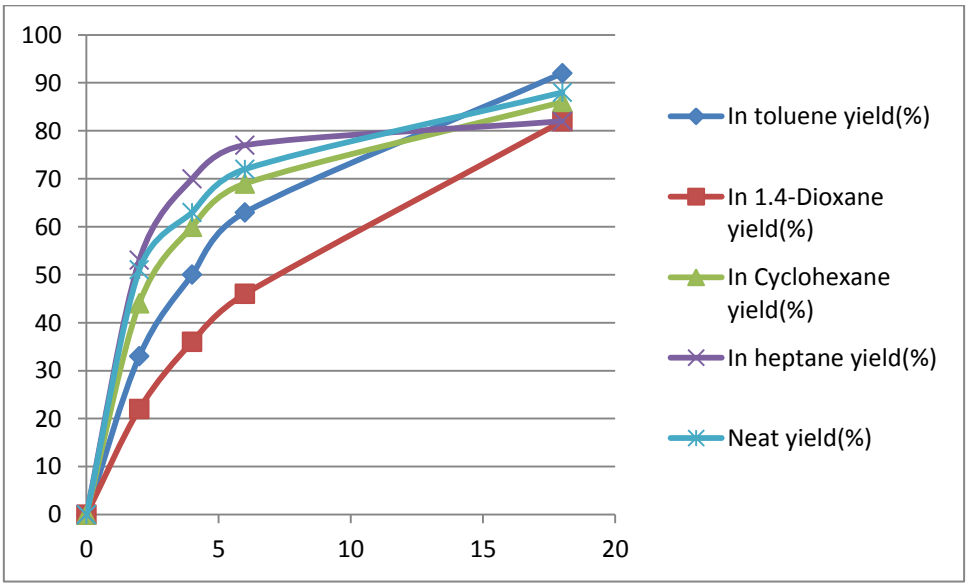


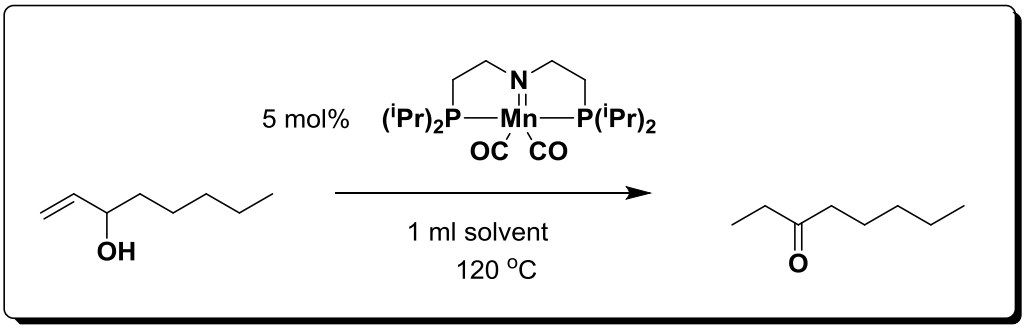
Figure 6 ^{1}**H-NMR** monitoring at room temperature (This figure is from the published article [60])

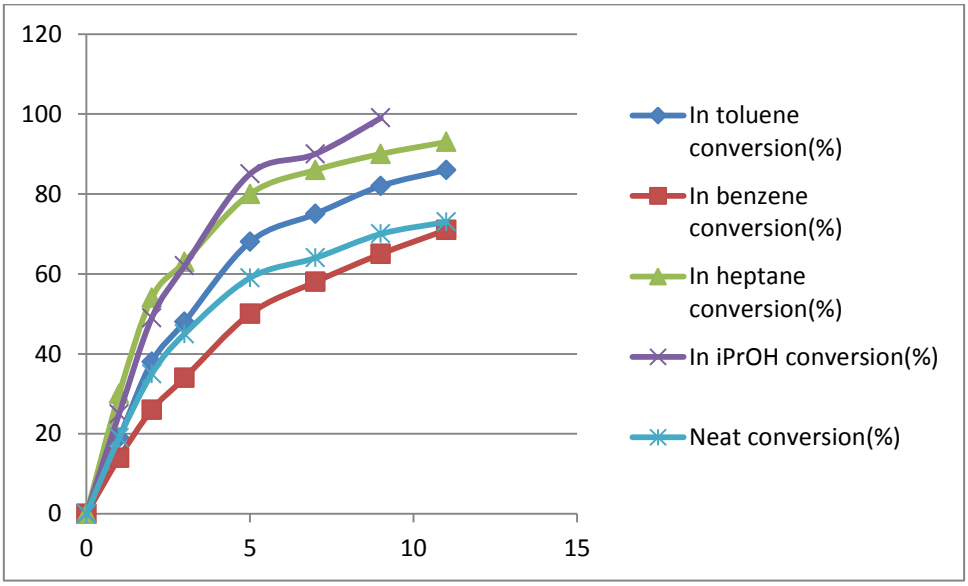
An oven dried 10 ml Schlenk tube with a stirring bar was charged with PNPFeXY(CO) (4.5 mg, 0.01 mmol, 1 mol%) and potassium tert-butoxide (1.2 mg, 0.01 mmol, 1 mol%) was added sequentially. After the addition of 1 ml of d-toluene, 1-octen-3-ol was added immediately to the catalytic system. According to that, the solution stirred at room temperature, at 80 °C, respectively. To follow the reaction progress over the time, every two minutes up to 14 minutes, including also at 20 min and 30 min, the samples were taken by syringe under continuously argon flow. The conversion was determined by the integration of the appropriate signals based on the difference with respect to the signals at 0 min. The monitoring was carried out three times for both temperatures. The average of each point is shown in the graph; additionally the standard deviation is given.

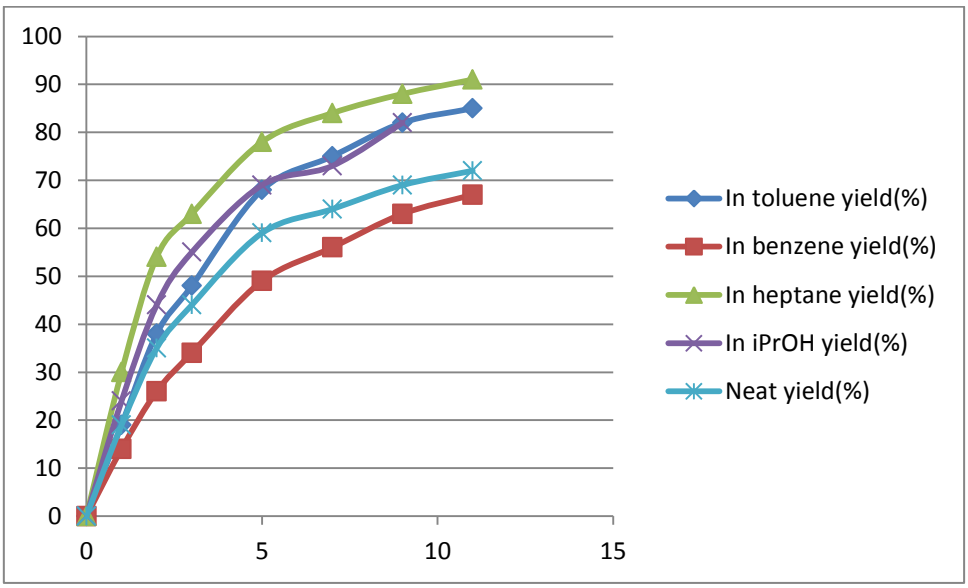


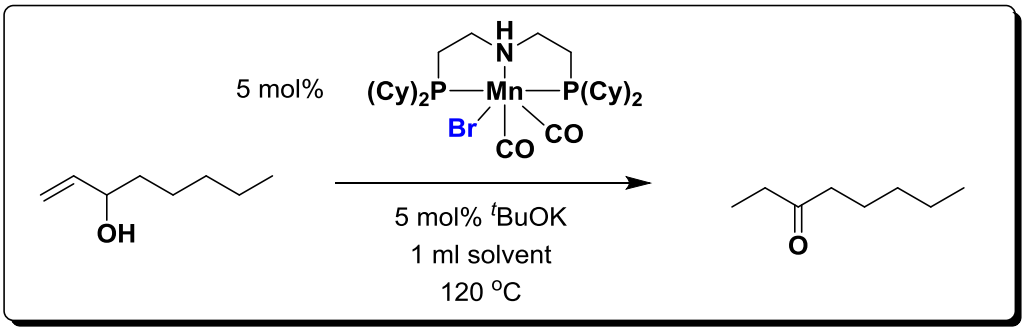

120
100
80
60
40
20
0
0
5
10
15
20
In toluene conversion(%)
In 1.4-Dioxane conversion(%)
In Cyclohexane conversion(%)
In heptane conversion(%)
Neat conversion(%)

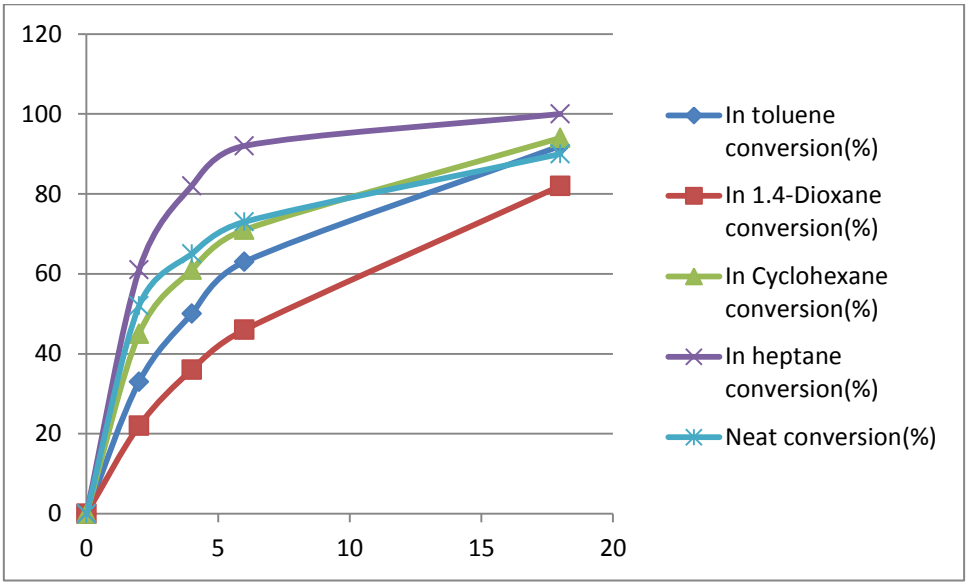

100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
In toluene yield(%)
In 1.4-Dioxane yield(%)
In Cyclohexane yield(%)
In heptane yield(%)
Neat yield(%)

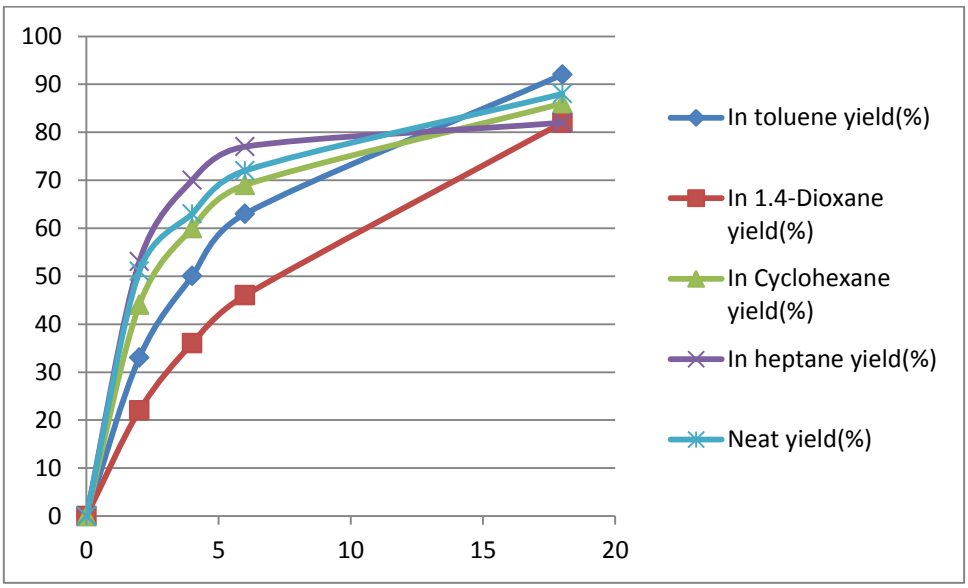

5 mol%
N
(iPr)2P
Mn
P(iPr)2
OC
CO
OH
1 ml solvent
120 °C
O

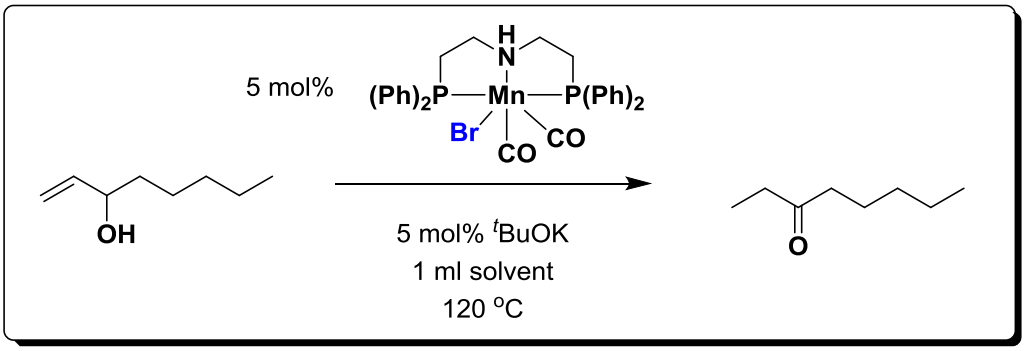

120
100
80
60
40
20
0
0
5
10
15
In toluene conversion(%)
In benzene conversion(%)
In heptane conversion(%)
In iPrOH conversion(%)
Neat conversion(%)

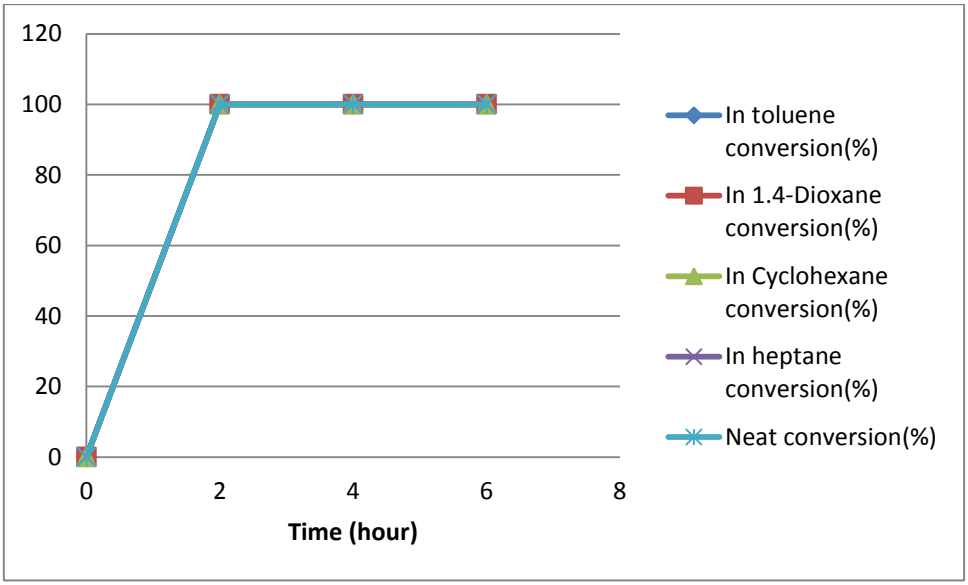

100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
In toluene yield(%)
In benzene yield(%)
In heptane yield(%)
In iPrOH yield(%)
Neat yield(%)

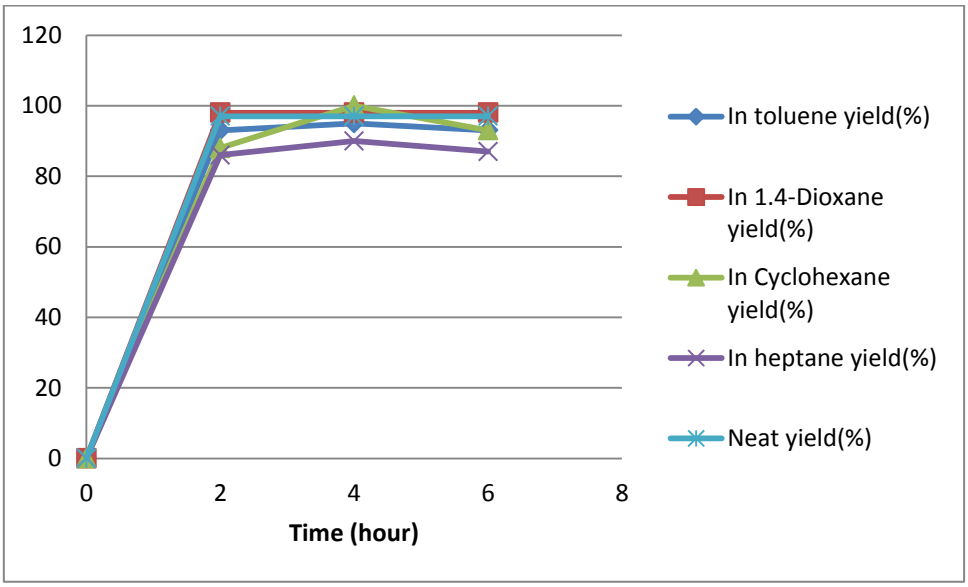

5 mol%
H
N
(Cy)2P
Mn
P(Cy)2
Br
CO
CO
OH
5 mol% tBuOK
1 ml solvent
120 °C
O

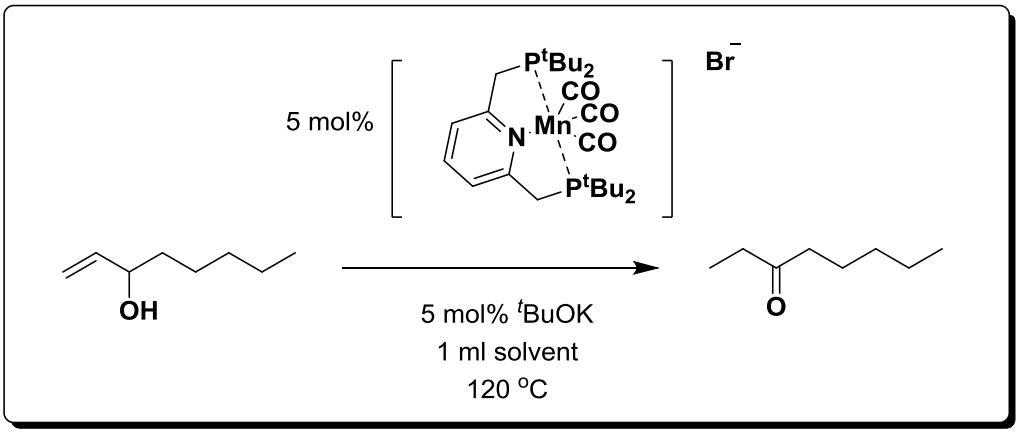

120
100
80
60
40
20
0
0
5
10
15
20
In toluene conversion(%)
In 1.4-Dioxane conversion(%)
In Cyclohexane conversion(%)
In heptane conversion(%)
Neat conversion(%)

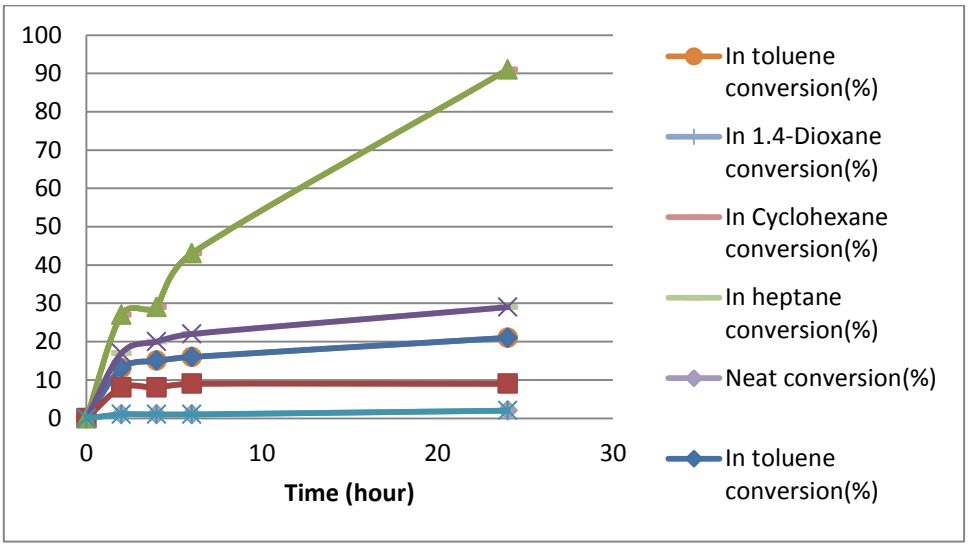

100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
In toluene yield(%)
In 1.4-Dioxane yield(%)
In Cyclohexane yield(%)
In heptane yield(%)
Neat yield(%)

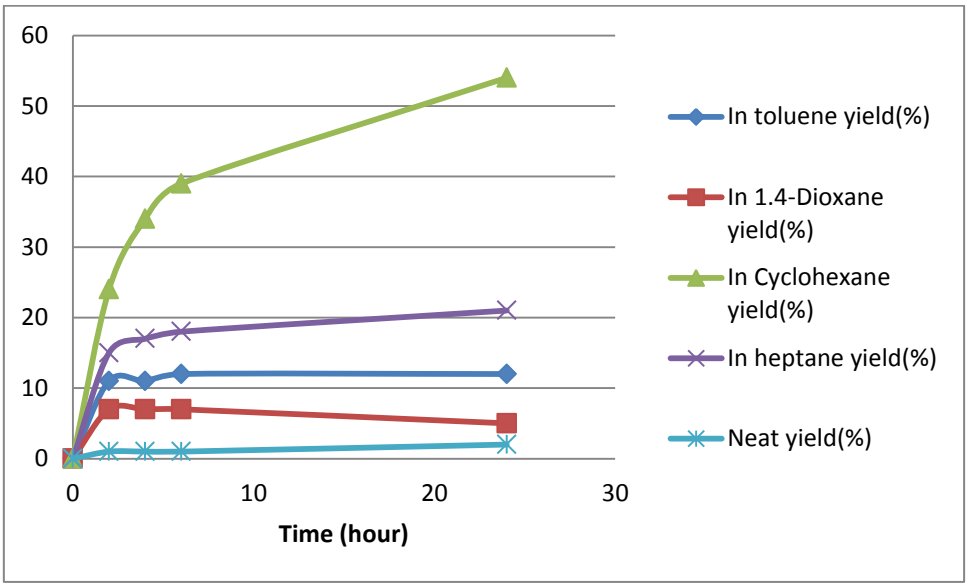

5 mol%
H
N
(Ph)2P
Mn
P(Ph)2
Br
CO
CO
OH
5 mol% tBuOK
1 ml solvent
120 °C
O

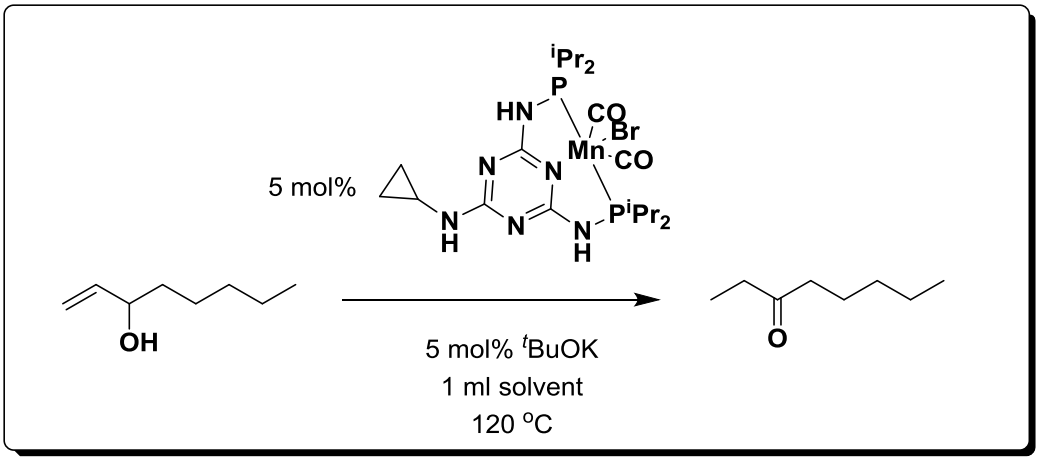

120
100
80
60
40
20
0
0
2
4
6
8
Time (hour)
In toluene conversion(%)
In 1.4-Dioxane conversion(%)
In Cyclohexane conversion(%)
In heptane conversion(%)
Neat conversion(%)

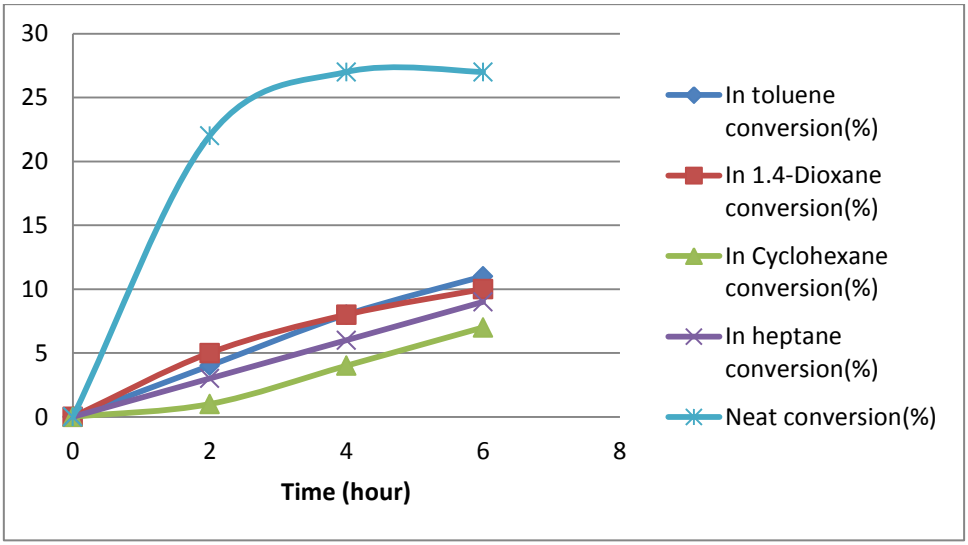

120
100
80
60
40
20
0
0
2
4
6
8
Time (hour)
In toluene yield(%)
In 1.4-Dioxane yield(%)
In Cyclohexane yield(%)
In heptane yield(%)
Neat yield(%)

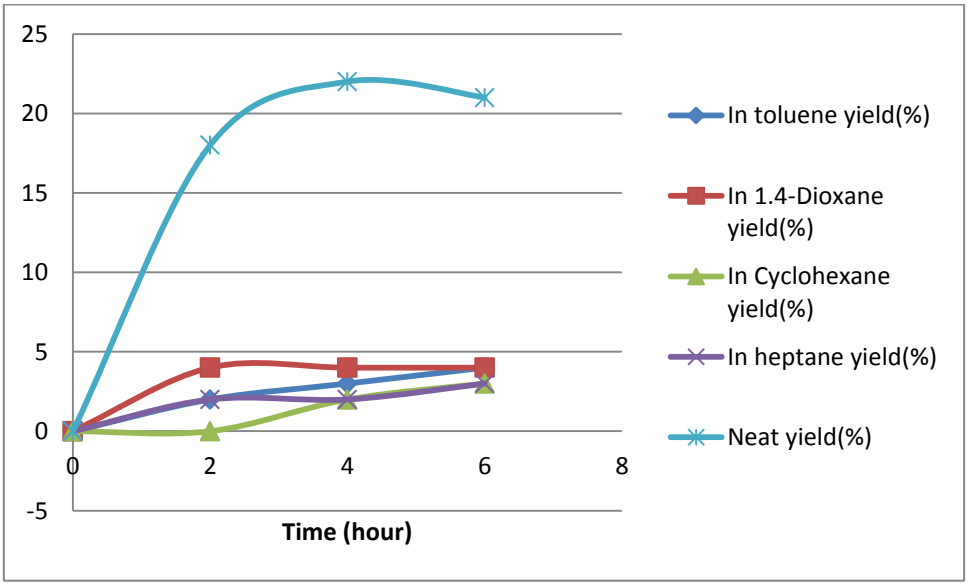

5 mol%
P^{t}Bu$_2$
CO
CO
N
Mn
CO
P^{t}Bu$_2$
Br$^-$
OH
O
5 mol% ^{t}BuOK
1 ml solvent
120 °C

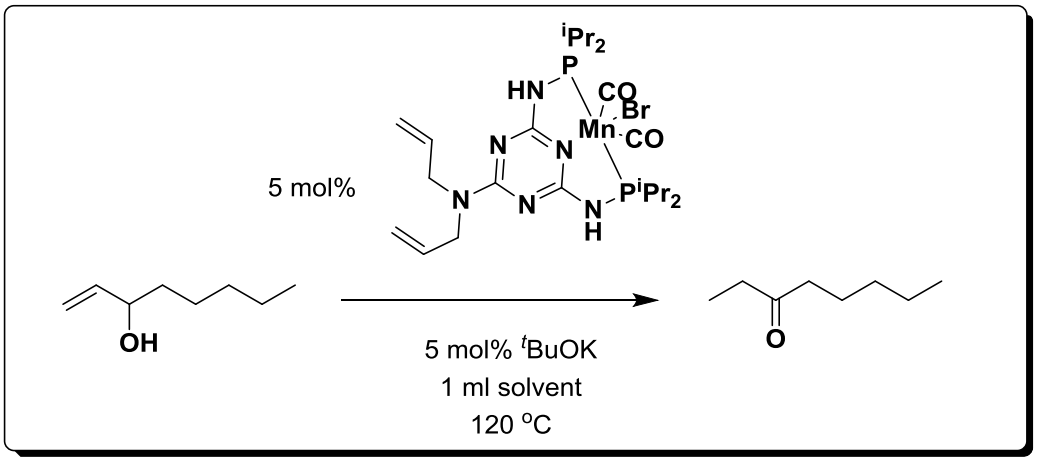

100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
Time (hour)
In toluene conversion(%)
In 1.4-Dioxane conversion(%)
In Cyclohexane conversion(%)
In heptane conversion(%)
Neat conversion(%)
In toluene conversion(%)

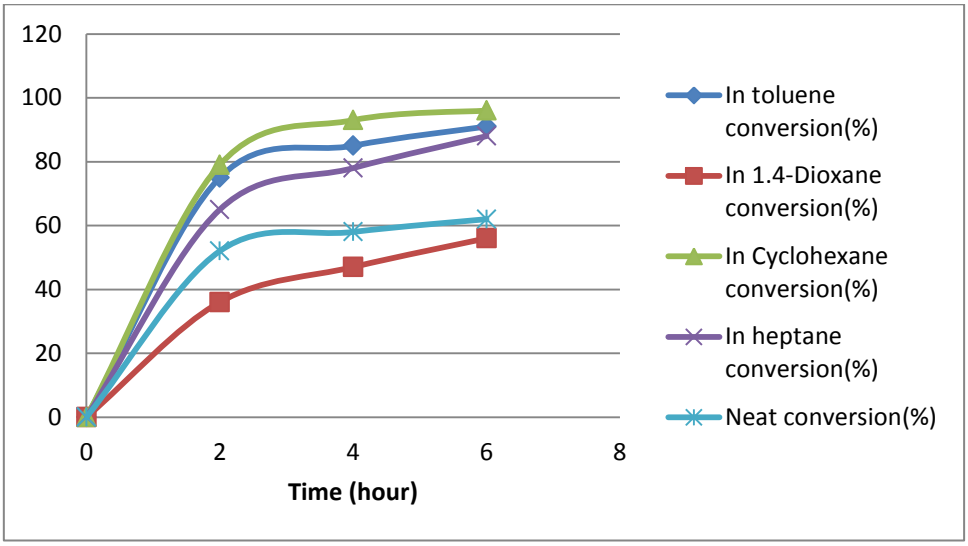

60
50
40
30
20
10
0
0
10
20
30
Time (hour)
In toluene yield(%)
In 1.4-Dioxane yield(%)
In Cyclohexane yield(%)
In heptane yield(%)
Neat yield(%)

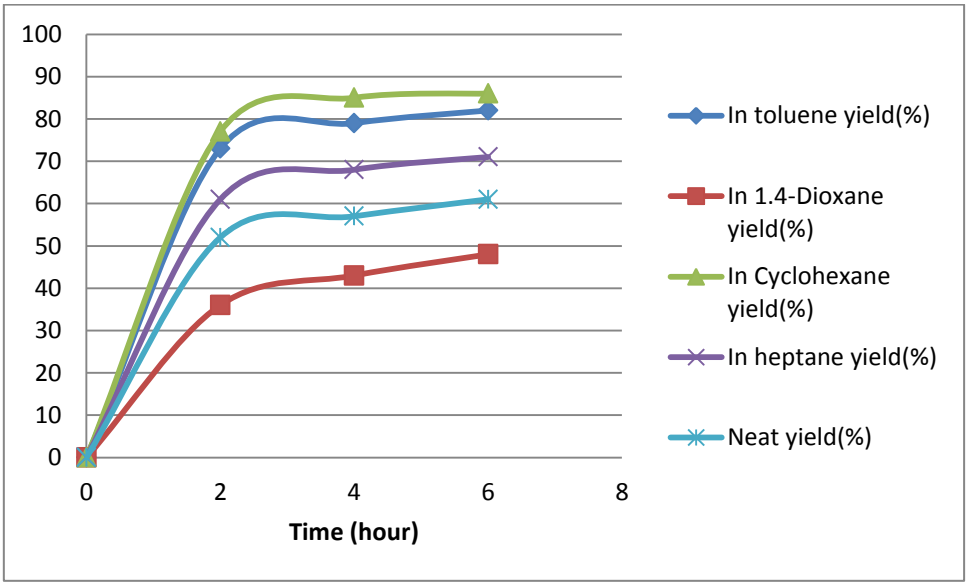

5 mol%
OH
5 mol% tBuOK
1 ml solvent
120 °C
O


30
25
20
15
10
5
0
0
2
4
6
8
Time (hour)
In toluene conversion(%)
In 1.4-Dioxane conversion(%)
In Cyclohexane conversion(%)
In heptane conversion(%)
Neat conversion(%)

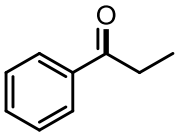
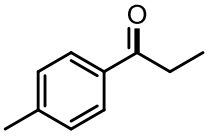
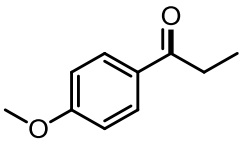
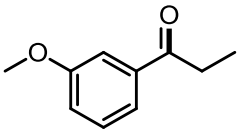
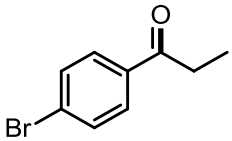
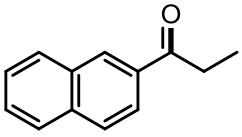

25
20
15
10
5
0
-5
0
2
4
6
8
Time (hour)
In toluene yield(%)
In 1.4-Dioxane yield(%)
In Cyclohexane yield(%)
In heptane yield(%)
Neat yield(%)

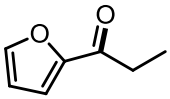
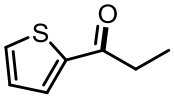
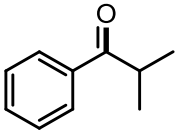
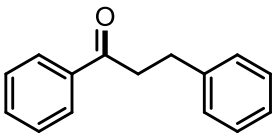
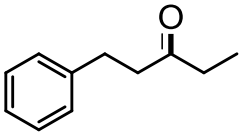
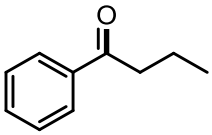

5 mol%
OH
5 mol% tBuOK
1 ml solvent
120 °C
O

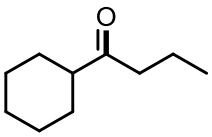
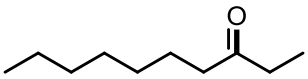
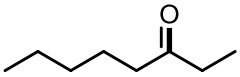
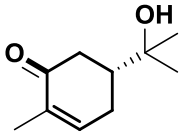
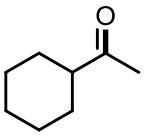
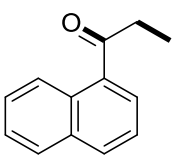

120
100
80
60
40
20
0
0
2
4
6
8
Time (hour)
In toluene conversion(%)
In 1.4-Dioxane conversion(%)
In Cyclohexane conversion(%)
In heptane conversion(%)
Neat conversion(%)

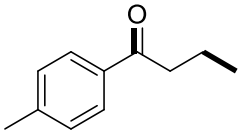
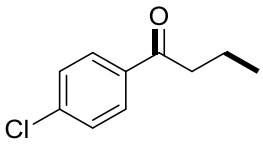

100
90
80
70
60
50
40
30
20
10
0
0
2
4
6
8
Time (hour)
In toluene yield(%)
In 1.4-Dioxane yield(%)
In Cyclohexane yield(%)
In heptane yield(%)
Neat yield(%)

4.4 Analysis data

	^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00 – 7.80 (m, 2H), 7.55 – 7.26 (m, 3H), 2.92 (q, *J*=7.2, 2H), 1.15 (t, *J*=7.2, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 200.9, 137.0, 132.9, 128.6, 128.0, 31.8, 8.3. HRMS-ESI (M + H) calcd. for $C_9H_{11}O$ 135.08099, found 135.08040.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.82 – 7.72 (m, 2H), 7.16 (d, *J*=8.1, 2H), 2.88 (q, *J*=7.3, 2H), 2.31 (s, 3H), 1.13 (t, *J*=7.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 200.5, 143.6, 134.5, 129.2, 128.1, 31.7, 21.6, 8.4. HRMS-ESI (M + H) calcd. for $C_{10}H_{13}O$ 149.09609, found 149.09596.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.84 (d, *J*=8.9, 2H), 6.82 (d, *J*=8.9, 2H), 3.76 (s, 3H), 2.84 (q, *J*=7.3, 2H), 1.11 (t, *J*=7.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.5, 163.3, 130.2, 130.0, 113.7, 55.4, 31.4, 8.4. HRMS-ESI (M + H) calcd. for $C_{10}H_{13}O_2$ 165.09101, found 165.09195.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.54 – 7.37 (m, 2H), 7.28 (t, *J*=7.9, 1H), 7.01 (ddd, *J*=8.2, 2.7, 1.0, 1H), 3.77 (s, 3H), 2.91 (q, *J*=7.2, 2H), 1.14 (t, *J*=7.2, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 200.7, 159.8, 138.3, 129.6, 120.6, 119.3, 112.3, 55.4, 31.9, 8.3. HRMS-ESI (M + H) calcd. for $C_{10}H_{13}O_2$ 165.09101, found 165.09102.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.86 (d, *J*=8.5, 2H), 7.63 (d, *J*=8.5, 2H), 3.00 (q, *J*=7.2, 2H), 1.25 (t, *J*=7.2, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.7, 135.6, 131.9, 129.5, 128.0, 31.8, 8.2. HRMS-ESI (M + H) calcd. for $C_9H_{10}BrO$ 212.99090, found 212.99052.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.43 – 8.30 (m, 1H), 7.95 (dd, *J*=8.6, 1.8, 1H), 7.91 – 7.84 (m, 1H), 7.84 – 7.72 (m, 2H), 7.55 – 7.39 (m, 2H), 3.04 (q, *J*=7.2, 2H), 1.20 (t, *J*=7.2, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 200.8, 135.6, 134.3, 132.6, 129.6,129.5, 128.42,

	128.35, 127.8, 126.7, 124.0, 31.9, 8.5. HRMS-ESI (M + H) calcd. for $C_{13}H_{13}O$ 185.09609, found 185.09632.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.50 (dt, *J*=1.3, 0.6, 1H), 7.15 – 7.05 (m, 1H), 6.45 (ddd, *J*=3.5, 1.8, 0.5, 1H), 2.78 (q, *J*=7.4, 2H), 1.13 (t, *J*=7.6, 7.1, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 190.2, 152.7, 146.1, 116.7, 112.1, 31.7, 8.1. HRMS-EI (M) calcd. for $C_7H_8O_2$ 124.05188, found 124.05211.
	^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.62 (dd, *J*=3.8, 1.2, 1H), 7.54 (dd, *J*=4.9, 1.2, 1H), 7.05 (dd, *J*=5.0, 3.8, 1H), 2.84 (q, *J*=7.3, 2H), 1.10 (t, *J*=7.3, 3H). ^{13}C NMR (75 MHz, CD_2Cl2) δ = 194.02, 144.69, 133.46, 131.96, 128.49. HRMS-ESI (M + Na) calcd. for C_7H_8NaOS 163.01881, found 163.01841.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 – 7.78 (m, 2H), 7.50 – 7.35 (m, 3H), 3.56 – 3.36 (m, 1 H), 1.14 (d, *J*=6.8, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 204.6, 136.3, 132.8, 128.6, 128.4, 35.4, 19.2. HRMS-ESI (M + H) calcd. for $C_{10}H_{13}O$ 149.09664, found 149.09586.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.95 – 7.80 (m, 2H), 7.53 – 7.31 (m, 3H), 7.25 – 7.09 (m, 5H), 3.29 – 3.16 (m, 2H), 3.00 (dd, *J*=8.5, 6.8, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.26, 141.33, 136.89, 133.10, 128.64, 128.57, 128.46, 128.08, 126.17, 40.49, 30.16. HRMS-ESI (M + H) calcd. for $C_{15}H_{15}O$ 211.11229, found 211.11198.
	^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.22 – 7.07 (m, 5H), 2.85 – 2.71 (m, 2H), 2.69 – 2.55 (m, 2H), 2.31 (q, *J*=7.3, 2H), 0.92 (t, *J*=7.3, 2H). ^{13}C NMR (75 MHz, CD_2Cl2) δ = 210.18, 141.46, 128.35, 128.25, 125.91, 43.68, 35.89, 29.71, 7.51. HRMS-EI (M) calcd. for $C_{11}H_{14}O$ 162.10391, found 162.10371.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94 – 7.79 (m, 2H), 7.54 – 7.30 (m, 3H), 2.86 (t, J=7.3, 2H), 1.69 (q, J=7.4, 2H), 0.92 (t, J=7.4, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 200.5, 137.1, 132.9, 128.6, 128.1, 40.5, 17.8,

	13.9. HRMS-ESI (M + H) calcd. for $C_{10}H_{13}O$ 149.09609, found 149.09599
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.43 (t, *J*=7.3, 2H), 1.91 – 1.54 (m, 8H), 1.42 – 1.20 (m, 5H), 0.93 (t, *J*=7.4, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 214.3, 50.8, 42.6, 28.5, 25.9, 25.7, 17.2, 13.8. HRMS-ESI (M + H) calcd. for $C_{10}H_{19}O$ 155.14359, found 155.14303.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.40 – 2.28 (m, 4H), 1.56 – 1.43 (m, 2H), 1.26 – 1.14 (m, 8H), 0.98 (t, *J*=7.3, 3H), 0.85 – 0.76 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 211.9, 42.4, 35.8, 31.7, 29.2, 29.1, 23.9, 22.6, 14.0, 7.8. HRMS-ESI (M + H) calcd. for $C_{10}H_{20}O$ 157.15869, found 157.15873.
	^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.42 – 2.23 (m, 4H), 1.60 – 1.40 (m, 2H), 1.32 – 1.07 (m, 4H), 0.98 (td, *J*=7.3, 0.9, 3H), 0.82 (t, *J*=6.8, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 212.0, 42.4, 35.9, 31.5, 23.7, 22.5, 13.9, 7.9. HRMS-ESI (M + H) calcd. for $C_8H_{17}O$ 129.127, found 129.127.
	^{1}H NMR (300 MHz, $CDCl_3$) δ 6.70 (dp, J = 5.1, 1.3 Hz, 1H), 2.54 (ddd, J = 15.7, 3.3, 1.6 Hz, 1H), 2.46 – 2.31 (m, 1H), 2.24 – 1.90 (m, 4H), 1.70 (dq, J = 3.0, 1.4 Hz, 4H), 1.16 (d, J = 2.5 Hz, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.39, 145.22, 135.17, 71.47, 46.08, 39.63, 27.28, 27.23, 27.02, 15.59.
	^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (ddd, J = 11.2, 7.6, 3.5 Hz, 1H), 2.06 (s, 3H), 1.83 – 1.77 (m, 2H), 1.74 – 1.67 (m, 2H), 1.64 – 1.54 (m, 2H), 1.26 – 1.17 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.55, 46.73, 23.69, 23.11, 21.12, 20.89.
	**^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.50 – 8.44 (m, 1H), 7.87 – 7.81 (m, 1H), 7.77 – 7.68 (m, 2H), 7.50 – 7.32 (m, 3H), 2.95 (q, *J* = 7.3 Hz, 2H), 1.17 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 205.30, 136.23, 133.99, 132.33, 130.18, 128.43, 127.81, 127.17, 126.42, 125.85, 123.43, 35.38, 8.70.

	**^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 2H), 7.20 – 7.14 (m, 2H), 2.84 (dd, *J* = 7.6, 7.0 Hz, 2H), 2.33 (p, *J* = 0.4 Hz, 3H), 1.76 – 1.59 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 200.13, 143.59, 133.67, 129.23, 128.18, 40.44, 21.62, 17.90, 13.93.
	**^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.83 – 7.78 (m, 1H), 7.35 – 7.30 (m, 1H), 2.82 (dd, *J* = 7.5, 7.0 Hz, 1H), 1.74 – 1.60 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.06, 139.25, 135.39, 129.46, 128.84, 40.46, 17.67, 13.84.

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6 Curriculum Vitae

Tian Xia

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Education

- 09/2014 – present Ph.D. candidate, Leibniz Institute for Catalysis at the University of Rostock, Germany

  Research Supervisor: Prof. Johannes G. de Vries

  Research topic: Isomerization of Allylic Alcohols to the Ketones Catalyzed by First-Row Transition Metal Pincer Complexes

- 09/2011 – 07/2014 Master., Dalian University of Technology, State Key Laboratory of Fine Chemicals, China

  Research Supervisor: Prof. Xiao-Bing Lu and Dr. Wen-Zhen Zhang.

  Thesis Topic: Transition-metal-free Transformation of CO_2 into Oxazolidine-2,4-diones.

- 09/2006 – 07/2010 Bachelor, Shenyang Agricultural University, China

Skills

ChemDraw (Proficient), Mnova (Proficient), Power Point (Proficient), Word (Proficient), Excel (Proficient), Origin (Proficient), Sci-Finder (Proficient), GC (Proficient), GC-MS (Proficient), NMR (Proficient), Shelx (Basic), Photoshop (Basic)

Scholarships and Awards

- China Scholarship Council (CSC) Scholarship (2014-2017)
- 2017 CGCA Annual Conference "Best Poster" (Only One)

Publications

- "Isomerization of Allylic Alcohols to Ketones Catalyzed by Well-Defined Iron PNP Pincer Catalysts"**.T. Xia**, Z. Wei, B. Spiegelberg, H. Jiao, S. Hinze, J. G. de Vries, *Chem. Eur. J.* **2018**, *24*, 4043-4049.(Cover picture)
- "Synthesis of oxazolidine-2,4-diones by a tandem phosphorus-mediated carboxylative condensation–cyclizationreaction using atmospheric carbon dioxide". W.-Z. Zhang, **T. Xia**, X.-T. Yang, X.-B. Lu, Chem. Commun. 2015, 51 ,6175-6178.

7 Statements

Universität Rostock
Dezernat 1
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Doktorandinnen/Doktoranden-Erklärung gemäß § 4 Absatz 1 Buchstaben g und h der Promotionsordnung der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock

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Ich habe eine Dissertation zum Thema

Isomerization of Allylic Alcohols to the Ketones Catalyzed by First-Row Transition Metal Pincer Complexes

an der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Rostock angefertigt. Dabei wurde ich von Frau/Herrn

Prof. Dr. Johannes G. de Vries

betreut.

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