Iron-Catalyzed Carbon-Carbon Bond Activation

Von der Fakultät Chemie der Universität Stuttgart
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vorgelegt von
Che-Hung Lin
aus Taipei, Taiwan

Hauptberichter:	Prof. Dr. Bernd Plietker
Mitberichterin:	Prof. Dr. Sabine Laschat
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Die vorliegende Arbeit entstand auf Anregung und unter Anleitung von Herrn Prof. Dr. Bernd Plietker am Institut für Organische Chemie der Universität Stuttgart im Zeitraum von Januar 2014 bis Januar 2018.

Parts of this thesis have been published:

1. "*The evolution of Fe-catalyzed nucleophilic activation of acceptor-substituted vinyl- and arylcyclopropanes*" C.-H. Lin, B. Plietker, *Isr. J. Chem.* **2016**, *56*, 409-416.

2. "*Non-decarbonylative photochemical versus thermal activation of $Bu_4N[Fe(CO)_3(NO)]$ - the Fe-catalyzed Cloke-Wilson rearrangement of vinyl and arylcyclopropanes*" C.-H. Lin, D. Pursley, J. Klein, J. Teske, J. Allen, F. Rami, A. Köhn, B. Plietker, *Chem. Sci.* **2015**, *6*, 7034-7043.

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Erklärung über die Eigenständigkeit der Dissertation

Hiermit erkläre ich, dass ich die vorliegende Dissertation „Iron-Catalyzed Carbon-Carbon Bond Activation“ selbstständig verfasst und keine anderen als die genannten Quellen und Hilfsmittel verwendet habe. Die aus fremden Quellen entnommenen Passagen und Gedanken sind als solche kenntlich gemacht.

Stuttgart, den 31.01.2018 Che-Hung Lin

“We can only see a short distance ahead,
but we can see plenty there that needs to be done.”

— Alan Turing, Computing machinery and intelligence

Table of Contents

List of Abbreviations

Ac	Acetyl
Ar	Aryl
ATR	Attenuated Total Reflection
BIAP	bis-(imidazolonyl)pyridine
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
Bn	Benzyl
Boc	*tert*-Butyloxycarbonyl
t-Bu	*tert*-Butyl
CASSCF	Complete Active Space Self-Consistent Field
COD	1,5-Cyclooctadiene
Conv.	Conversion
Conc.	Concentration
dba	bis(dibenzylideneacetone)
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
1,2-DCE	1,2-Dichloroethene
DCM	Dichloromethane
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
DMAP	4-Dimethylaminopyridine
dmb	5,5′-dimethyl-2,2′-bipyridyl
DMF	Dimethylformamide
DMP	Dess–Martin Periodinane
DMSO	Dimethyl Sulfoxide
EA	Ethyl Acetate
EI	Electron Ionization
equiv.	equivalent
ESI	Electrospray Ionization
Et	Ethyl
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
h	hour
Hz	Hertz
i	*iso*
IBO	Intrinsic Bond-Orbital Analysis and Orbital localization
IR	Infrared Spectroscopy

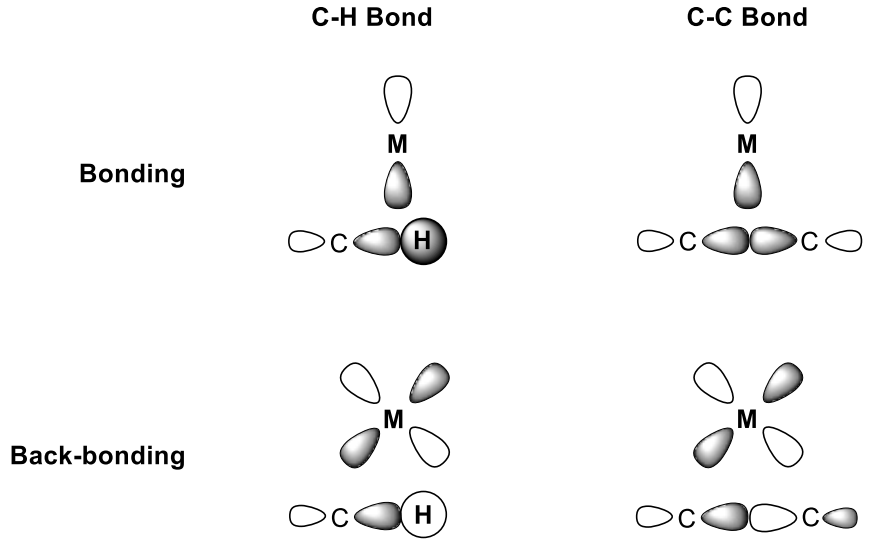
J	Coupling Constant
Cat.	Catalyst
LAH	Lithium Aluminium Hydride
M	Molarity
Me	Methyl
min	minute
MRCI	Multireference Configuration Interaction
4 Å MS	4 Å Molecular Sieves
m.p.	melting point
MS	Mass Spectrometry
MTBE	Methyl *tert*-Butyl Ether
N.R.	No Reaction
NMR	Nuclear Magnetic Resonance
PE	Petroleum Ether
Ph	Phenyl
ppm	Parts Per Million
i-Pr	*iso*-Propyl
R_f	Retardation factor
rt	room temperature
sat.	saturated
t	*tert*
TBAF	Tetra-*n*-butylammonium fluoride
TBA[Fe]	Tetra-*n*-butylammonium ferrate $Bu_4N[Fe(CO)_3NO]$
TFAA	Trifluoroacetic Anhydride
THF	Tetrahydrofuran
Ts	Tosyl
Vol.	Volume

I. Theoretical Section

1. Introduction

1.1 Transition-Metal-Catalyzed C-C Bond Activations

Since the mid-20th century, scientists have intensively studied transition-metal-catalyzed reactions.[1] Carbon-carbon (C-C) bond activation and carbon-hydrogen (C-H) bond activation are the main fields in transition-metal-catalyzed reactions because of their economic and ecological advantages in organic synthesis.[2] However, research in selective C-H bond activation is much more advanced than C-C σ-bond activation. There are two major factors behind this difference. First, the higher inertness of C-C bonds, which are less abundant and more hindered than C-H bonds. Second, the C-C bonds are highly directed, which have a less favorable orbital directionality for transition-metals compared to C-H bonds (Scheme 1). Therefore, it has been a challenging issue in the field of organometallic chemistry to cleave C-C bonds by the insertion of transition-metal complexes.

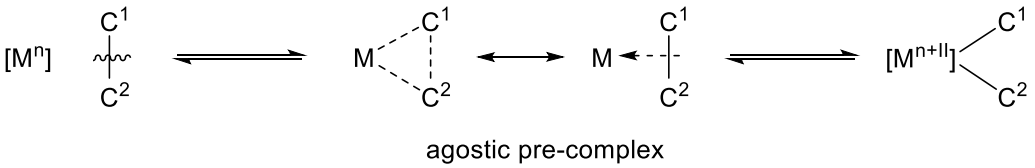


Scheme 1: A comparison of the interactions of metal orbitals with C-H bond and non-polarized C-C bond.

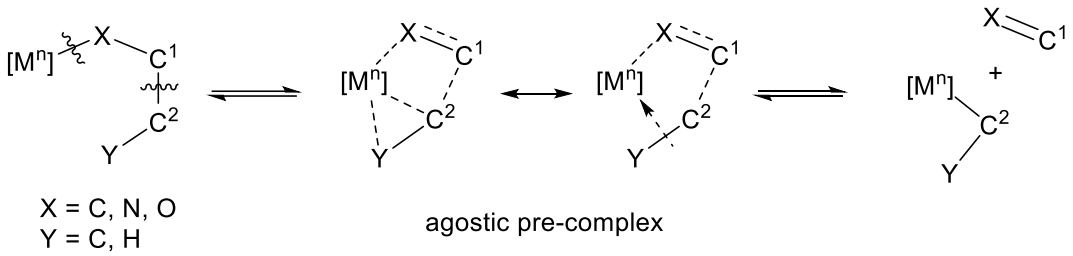
The mechanisms of transition-metal-catalyzed C-C bond activation can be divided into three types (Scheme 2). First, direct C-C bond cleavage via oxidative addition to a transition-metal (Scheme 2, Path A). The difficulty of this pathway is that it is

thermodynamically not favored as the dissociation energy of C-C bond is around 85 kcal/mol compared with 30 kcal/mol for the two newly formed C-M bonds. Therefore, additional thermodynamic driving forces are needed, which are normally ring strain, accompanying aromatization or allylation, and subsequent energy-releasing reactions.

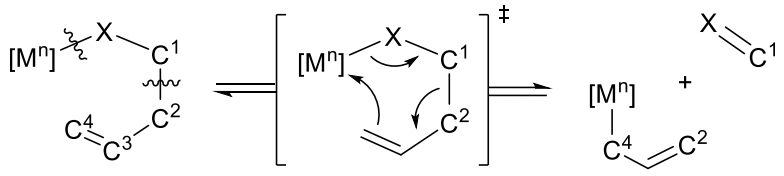
Path A: Oxidative Addition



Path B: β-Carbon Elimination



Path C: Retro-Allylation



Scheme 2: Mechanisms of transition-metal-catalyzed C-C bond activation reactions.

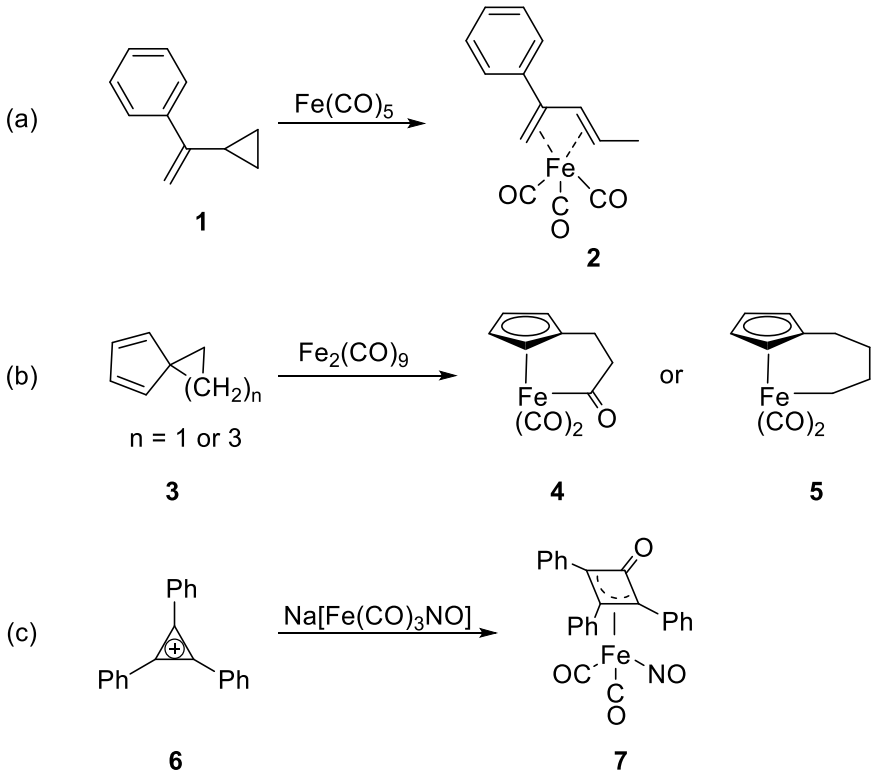
Another possible pathway is the *σ*-carbon elimination (Scheme 2, Path B). Until now, its mechanism has been assumed to be common *β*-H elimination, which has a *β*-agostic interaction between the metal center and hydrogen preceding the elimination. In many of the cases, the driving force of this pathway comes from the formation of a strong C=X bond. Unlike oxidative addition, *β*-carbon elimination does not require low oxidation state or electron-rich metals. It is also possible to use electron-poor early transition-metals in their high oxidation states. In this scenario, the X is normally an sp^3-carbon, because heteroatoms such as N or O are too electronegative, which makes the X-M bond hard to

break. N and O atoms are mainly used in late transition-metal catalyzed reactions which have a much weaker bond between the transition-metal center and the heteroatom.

The third pathway is the retro-allylation (Scheme 2, Path C), which generates an allyl metal species and a C=X bond, consisted with the *β*-carbon elimination pathway, where the *β*-carbon is also eliminated in retro-allylation. However, it proceeds via a six-membered cyclic transition state. The retro-allylation can be differentiated from *β*-carbon elimination by observing the changing substituents of C^2 and the chirality transfers from the 1-position (C^1) to 4-position (C^4).

1.2 Iron-Catalyzed C-C Bond Activations

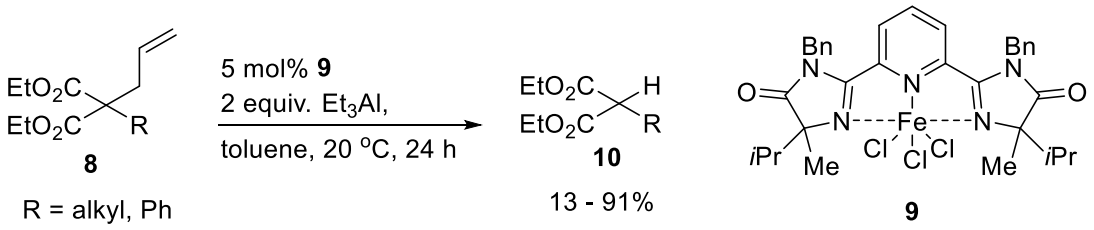
Transition-metals such as Pd, Rh, Ir, Ru, Ni, Au, and Co have been widely studied for the C-C bond activation reactions.[3] However, those transition-metals are normally toxic and very expensive. Therefore, in recent years, scientists are devising catalytic reactions that use more sustainable metals, such as iron, which is cheap, abundant, and environmentally friendly.[4]



Scheme 3: Stoichiometric iron-mediated C-C bond breaking reactions.

Iron complexes have been known to break C-C bonds stoichiometrically from the primal results. In 1965, Sarel and his coworkers showed that $Fe(CO)_5$ can first coordinate to the vinyl group of cyclopropane **1**, then followed by a ring-opening, and a hydrogen shift forming a *trans*-dienic *π*-complex **2** (Scheme 3 (a)).[5] In 1980, Eilbracht reported the C-C bond of cyclopentadiene derivatives **3** can be broken by $Fe_2(CO)_9$ giving *σ*-alkyl- or *σ*-acyl-*π*-cyclopentadienyl iron complexes **4** or **5** (Scheme 3 (b)).[6] In 1982, Hughes demonstrated that the anionic iron complex $Na[Fe(CO)_3NO]$ was able to carbonylate cyclopropenium cation **6** to yield the ring-expansion product η^3-oxocyclobutenyl complex **7** (Scheme 3 (c)).[7]

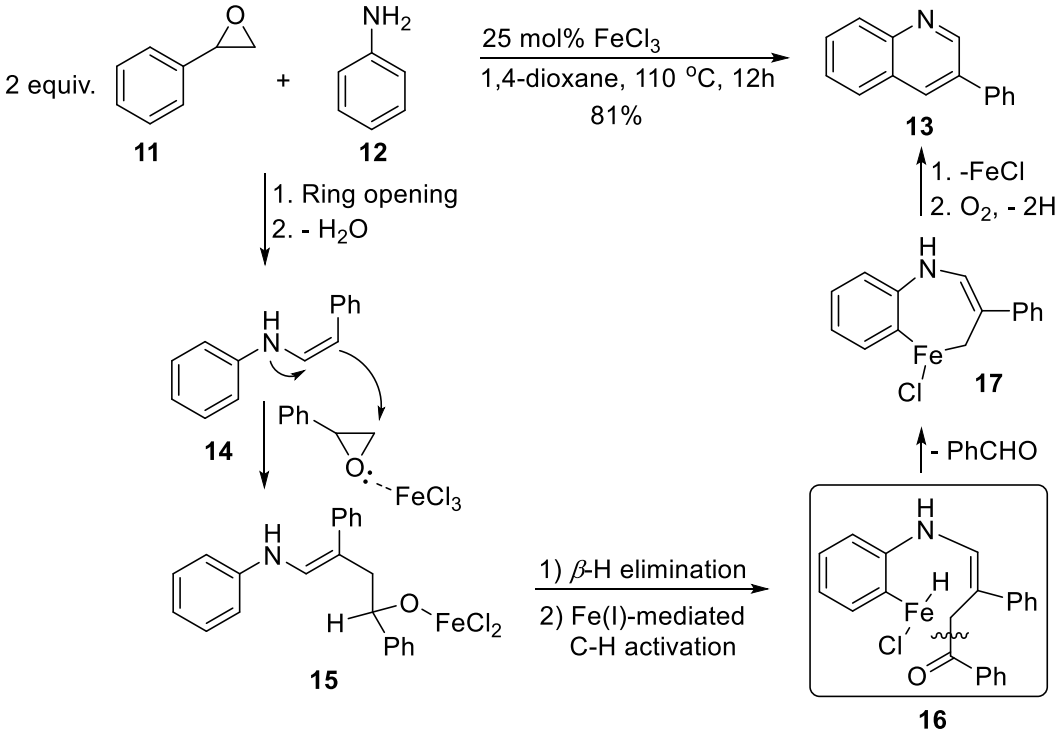
Using catalytic amounts of iron catalysts for C-C bond activations were published more recently. The allylic position is known to be activated in organic molecules, therefore it is not surprising that several C-C bond cleavage reactions have been documented. One of the examples was shown by Kotora, in which allylmalonates **8** proceeded deallylation by treating them with an Fe(III)(BIAP)Cl_3 complex **9** in the presence of triethylaluminum (Scheme **4**).[8]



Scheme 4: Deallylation of allylmalonates.

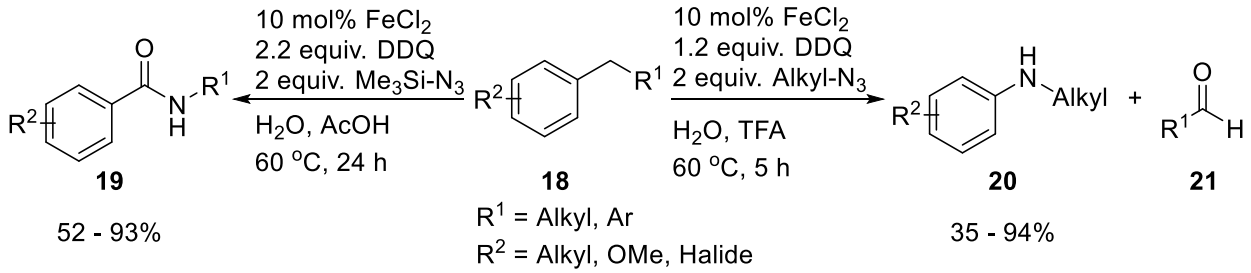
Wang reported $FeCl_3$-catalyzed 3-phenylquionline synthesis from two equivalents of styrene oxide **11** and aniline **12** which involved a C-C bond activation mechanism (Scheme 5).[9] First, aniline **12** attacked the styrene oxide **11** forming a *β*-amino alcohol in presence of $FeCl_3$ as a Lewis acid catalyst, then, followed by a dehydration, the enamine **14** was formed. Enamine **14** reacted with another styrene oxide to generate intermediate **15**. Intermediate **15** underwent subsequently a *β*-H elimination and Fe(I)-mediated directed C-H bond activation at the *ortho*-position of aniline moiety resulting in the formation of intermediate **16**. The intermediate **16** then underwent chelation-assisted C-C bond activation to form the 7-membered cycloferrate **17** under elimination of benzaldehyde. In the end, followed by reductive elimination and dehydrogenative

oxidation, the desired quinoline **14** was obtained.



Scheme 5: Iron-catalyzed synthesis of quinolines.

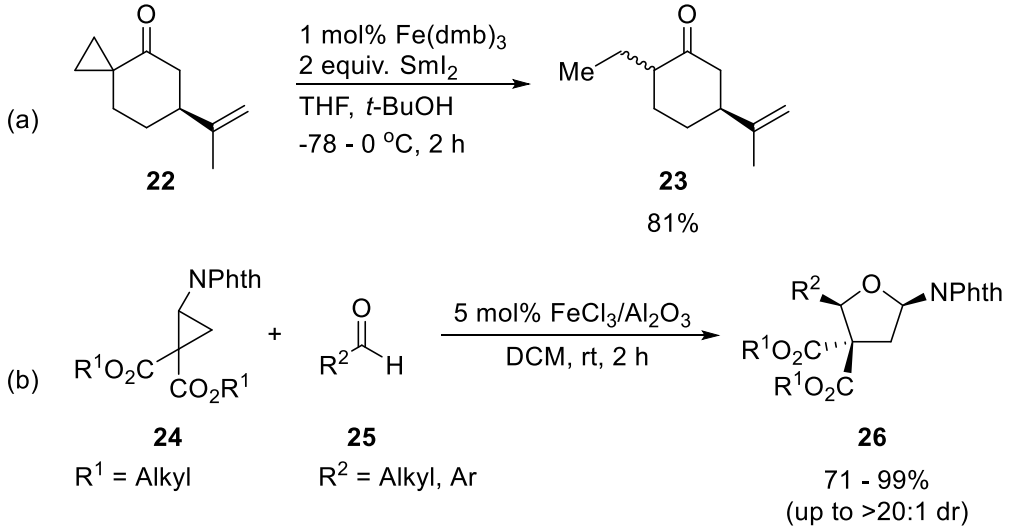
Jiao and coworkers developed $FeCl_2$-promoted oxidative C-C bond activation reactions (Scheme 6).[10] They successfully broke the aromatic C(sp^2)-C(sp^3) bond of benzyl hydrocarbon **18** by using $FeCl_2$ with azides and DDQ. Different azide sources would yield diverse products. The amides **19** were formed by using TMS-N_3 and the use of aliphatic azide resulted in the formation of anilines **20** and aldehydes **21**.



Scheme 6: Oxidative C-C bond activation.

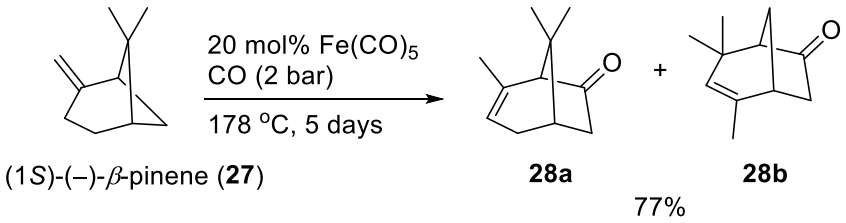
Another type of C-C bond activation is to activate the C-C bonds on strained rings, such as cyclopropanes. Molander published an Fe(dmb)$_2$-catalyzed indirect ring-opening of

cyclopropane **22** in presence of SmI_2 as a reductive agent (Scheme 7(a)). Waser also demonstrated the [3+2] annulation of donor-acceptor aminocylopropanes **24** with aldehydes **25** (Scheme 7(b)).[11] The reaction is catalyzed by $FeCl_3$ supported on Al_2O_3 to result tetrahydorfurans **26** with excellent yields and good *cis* selectivities (up to >20:1). This method is an atom-economic and stereoselective way to access 2-aminotetrahydrofurans, which are building blocks of DNA and RNA.[12]



Scheme 7: Iron-catalyzed C-C bond activation of cyclopropanes.

Blechert reported the ketone intermediates **28a** and **28b** were obtained as a 1:1 mixture from (1*S*)-(-)-*β*-pinene **27** by $Fe(CO)_5$-catalyzed CO-insertion at elevated temperature (Scheme 8) in the synthesis of Taxodic A/B-ring fragments.[13] In addition, the same reaction also had been reported by using stoichiometric amounts of iron pentacarbonyl, but without presence of CO gas.[14]



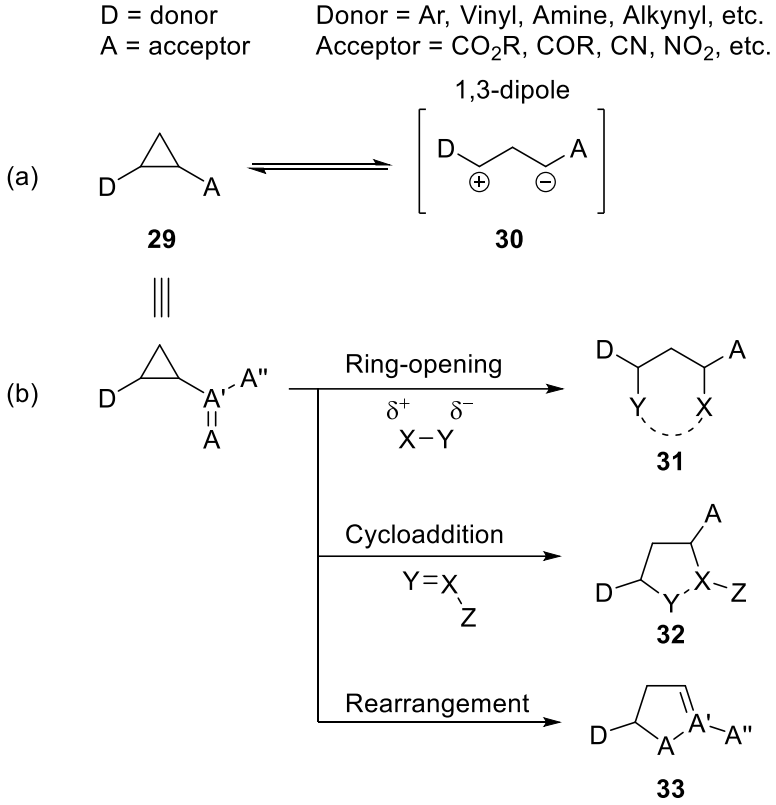
Scheme 8: Catalytic carbonylation involving C-C bond activation.

1.3 Synthetic Applications of Three- and Four-Membered Rings

Cyclopropanes and cyclobutanes are known to have high ring-strain because of their very small sp^3-bond angles.[15] The strain energy is associated with increased reactivity. Therefore, these compounds have been widely used in organic chemistry.[16]

1.3.1 Donor-Acceptor Cyclopropanes

Cyclopropanes which have one or more electron-donating groups and electron-withdrawing groups on adjacent carbons are so-called donor-acceptor cyclopropanes. In the 1960s and 1970s, the studies on activated cyclopropanes, which were only bearing acceptor groups.[17] Since 1980 the research groups of Wenkert and Reissig started the investigation on now a day donor-acceptor cyclopropanes.[18] The term donor-acceptor cyclopropane was first introduced by Reissig.

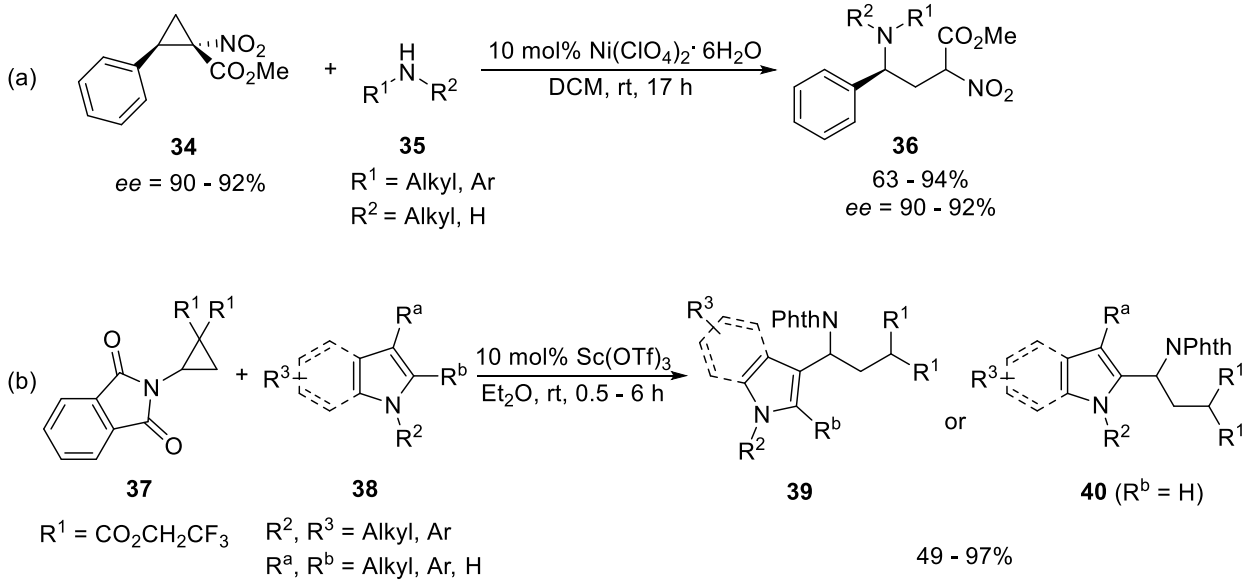


Scheme 9: (a) Zwitterionic relationship of D-A cyclopropanes. (b) Different types of reactions of D-A cyclopropanes.

Donor-acceptor cyclopropanes **29** are even much easier to be cleaved than non-functionalized cyclopropanes because the charged intermediates **30** can be stabilized by the vicinal groups (Scheme 9 (a)).[19] This 1,3-dipole intermediate **30** is generally quite versatile which allows for a multitude of different reactions such as ring-opening, cycloaddition, and rearrangement (Scheme 9 (b)).

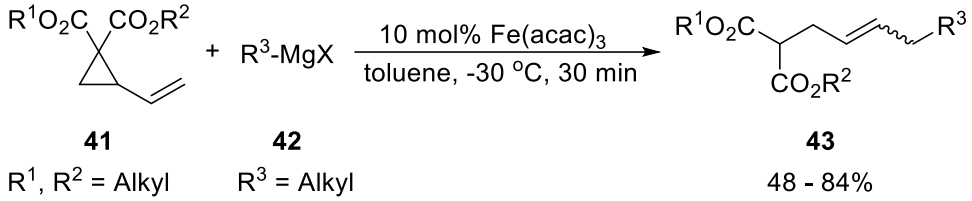
1.3.1.1 Ring-Opening reactions

The ring-opening reaction is the most basic transformation of donor-acceptor cyclopropanes. The reactions are often carried out in presence of a Lewis acid catalyst and the positive charge is captured by hetero-containing nucleophiles, which led to 1,3-bifunctional derivatives. Chartte reported a 1-nitrocyclopropanecarboxylate **34** ring-opening reaction with primary or secondary amines **35** by using $Ni(ClO_4)_2$ as a Lewis acid catalyst (Scheme 10 (a)).[20] The enantiomeric purity in the electrophilic center of the cyclopropanes was preserved to the acyclic product **36**. Waser published a $Sc(OTf)_3$-catalyzed ring-opening reaction of aminocyclopropanes **37** with indoles **38** (Scheme 10 (b)).[21] The indole alkylated either at the C^2 or C^3 position, which gave quick access to many bioactive *γ*-aminobutyric acid (GABA) derivatives.



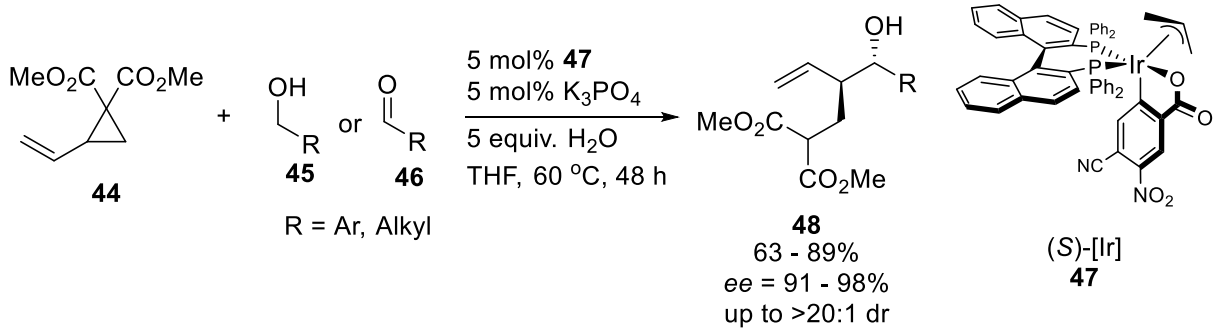
Scheme 10: Lewis acid-catalyzed ring-opening reactions of donor-acceptor cyclopropanes with nucleophiles.

Fürstner showed a $Fe(acac)_3$-catalyzed conjugated addition of Grignard reagent **42** to acceptor-substituted vinylcyclopropanes **41** with concomitant C-C bond cleavage in the formation of major product **43** (Scheme 11).[22] This is the first example of the use of hard organometallic nucleophiles in ring-opening reaction of donor-acceptor cyclopropanes.



Scheme 11: Iron-catalyzed nucleophilic ring-opening of donor-acceptor cyclopropanes.

Similar to the analogous reactions employing nucleophiles, the electrophilic trapping at the donor site of cyclopropanes were also described by Johnson and Krische (Scheme 12).[23] The diastereo- and enantioselective homoallylic alcohols **48** were formed from vinylcyclopropane **44** and alcohols **45** or aldehydes **46** with a (*S*)-BINAP modified cyclometalated iridium catalyst **47**.

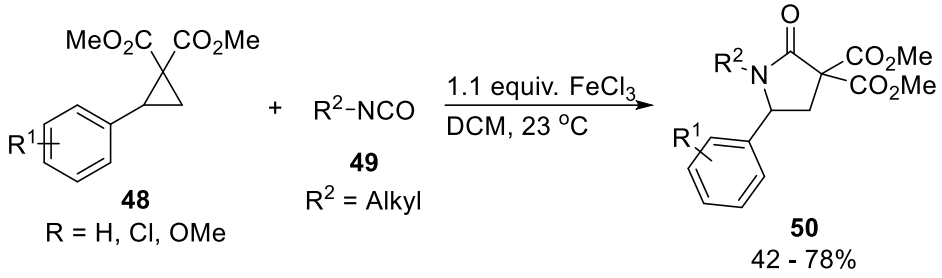


Scheme 12: Iridium-catalyzed ring-opening with electrophiles.

1.3.1.2 Cycloaddition reactions

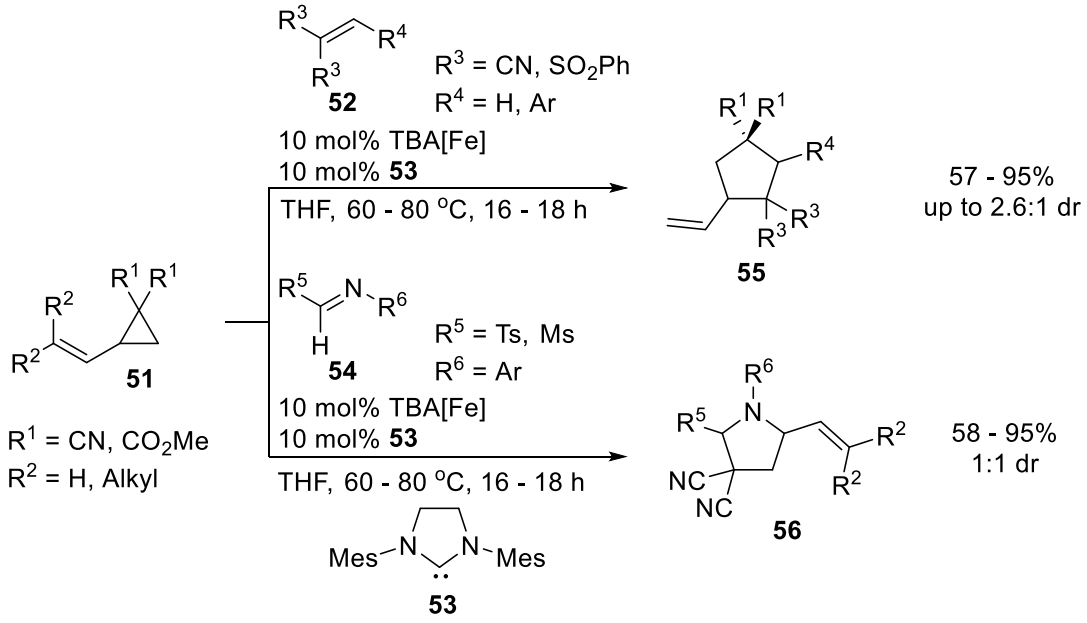
The cycloaddition reaction of donor-acceptor cyclopropanes is a powerful way to access highly functionalized five, six, or seven-membered rings. These reactions usually occur with very high regioselectivity. Diastereo- and enantioselectivity are also possible when chiral substrates, ligands or catalysts are used. An $FeCl_3$-mediated [3+2] cycloaddition of arylcyclopropanes **48** with isocyanates **49** was reported by Stoltz (Scheme 13).[24] A variety of *N*-alkyl substituted lactams **50** could be synthesized by this

method.



Scheme 13: [3+2] cycloaddition of arylcyclopropanes with isocyanates.

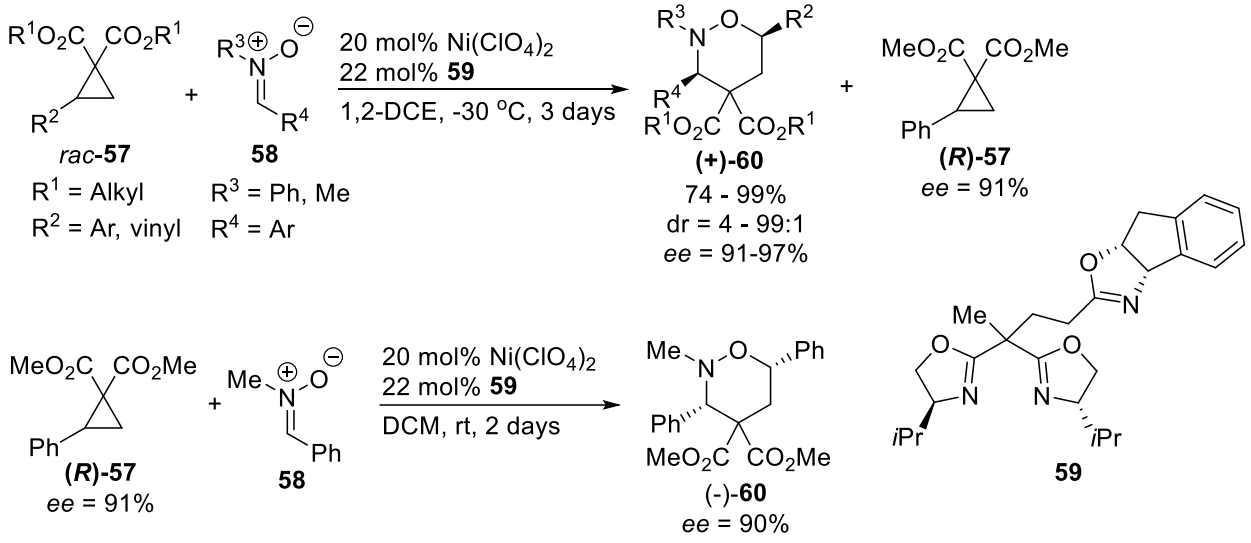
Plietker's group published the $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) catalyzed [3+2] cycloaddition of vinylcyclopropanes **51** with various Michael acceptors (Scheme 14). Dieskau and Holzwarth from the group performed the reaction by using 1,1-bis(phenylsulphonyl)-ethylene **52** as a Michael acceptor with NHC ligand **53** to provide vinylcyclopentane **55**.[25] Pursley and Dieskau showed that substituted pyrrolidines **56** were formed when the Michael was acceptor changed to aldimines **54** under the same reaction conditions.[26]



Scheme 14: Iron-catalyzed [3+2] cycloaddition of vinylcyclopropanes.

Tang developed a highly diastereoselective and enantioselective Ni(II)-catalyzed [3+3] cycloaddition of donor-acceptor cyclopropanes **57** with nitrones **58** in presence of an

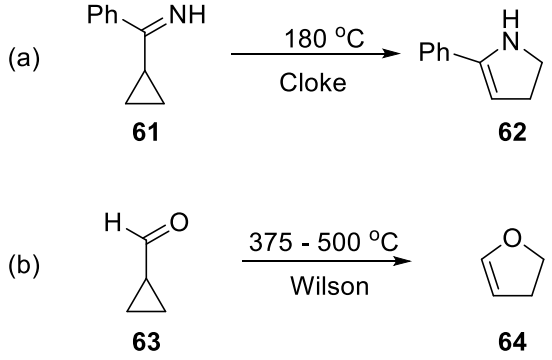
asymmetric trisoxazoline ligand **59** (Scheme 15). Interestingly, only one enantiomer of racemic cyclopropane **57** reacted to form **(+)-60**.[27] The remaining cyclopropane **(*R*)-57** could be recovered with good *ee* values, which could transform to the same level of enantiomeric purity of tetrahydro-1,2-oxazine **(-)-60** under a similar reaction condition but without ligand **59**. Therefore, starting from racemic cyclopropane **57** both enantiomers of tetrahydro-1,2-oxazine **60** could be prepared.



Scheme 15: Asymmetric [3+3] cycloaddition of cyclopropanes with nitrones.

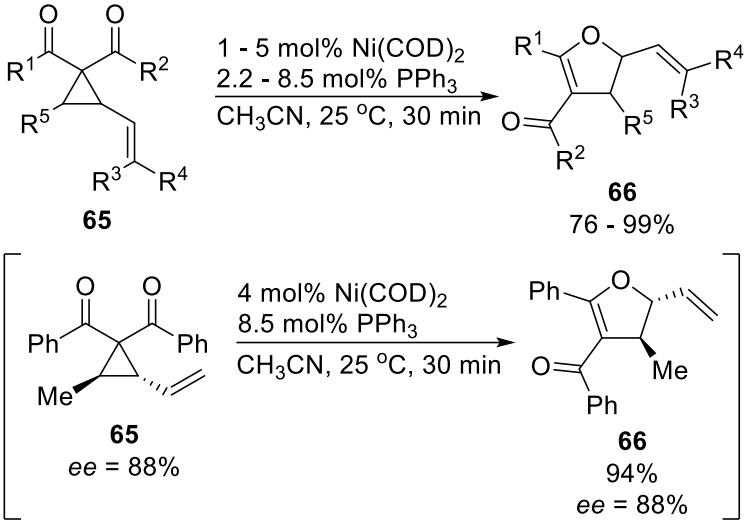
1.3.1.3 Rearrangements

Rearrangements of functionalized cyclopropanes are very common ring-expansion reactions to form heterocyclopentenes. The first two examples were described by Cloke in 1929[28] and Wilson in 1947[29] at elevated temperatures (Scheme 16).



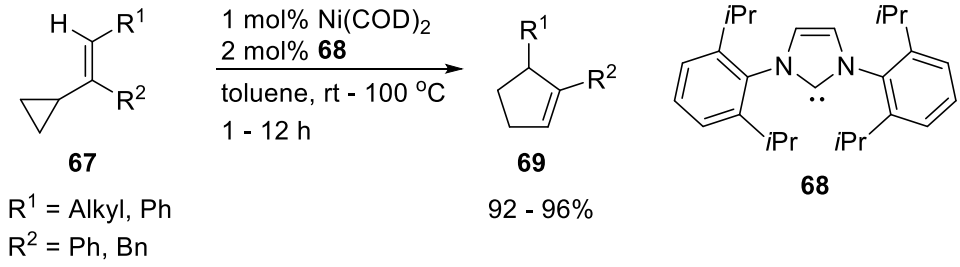
Scheme 16: (a) Cyclopropylimine-pyrroline rearrangement.
(b) Cyclopropylcarbaldehyde-dihydrofuran rearrangement.

Cu(I)[30] and Ru(I)-catalyzed[31] Cloke-Wilson rearrangements of donor-acceptor cyclopropanes have been published. However, these two reactions also proceeded under harsh conditions. In 2006, Johnson reported a nickel-catalyzed Cloke-Wilson rearrangement of vinylcyclopropanes **65** to dihydrofurans **66** under mild reaction conditions (Scheme 17).[32] The stereocenter was persistent, which implies a double-inversion mechanism in the reactions.



Scheme 17: Rearrangement of vinylcyclopropanes to dihydrofurans.

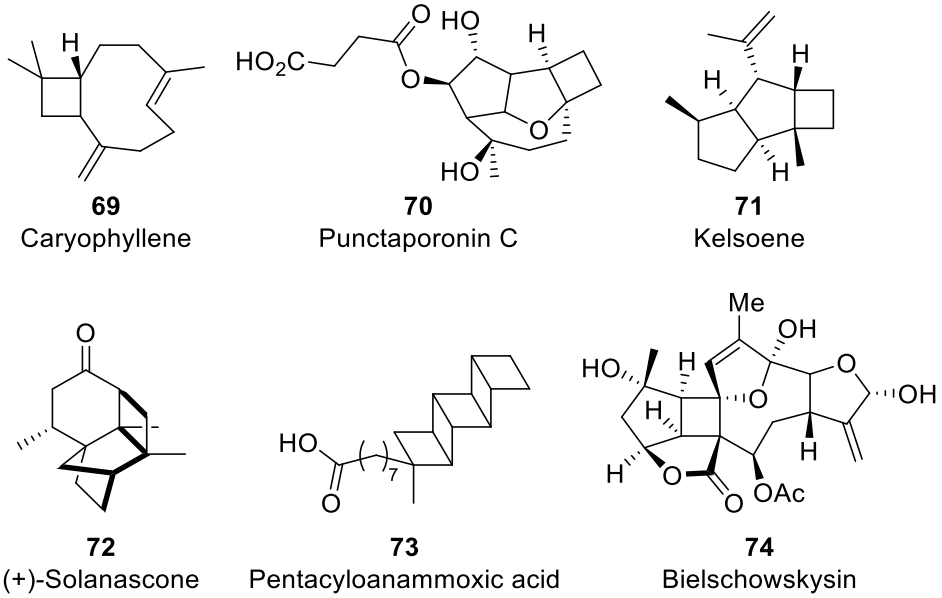
The same nickel catalyst has been previously reported to catalyze a rearrangement reaction of unactivated vinylcyclopropanes **67** to substituted cyclopentane **69** in presence of NHC ligand **68** by Louie (Scheme 18).[33]



Scheme 18: Nickel-catalyzed rearrangement of unactivated vinylcyclopropanes.

1.3.2 Cyclobutanes

The ring strain energy of cyclobutane (26.7 kcal/mol) is similar to that of cyclopropane (27.5 kcal/mol). However, unlike cyclopropanes which have drawn most of the interest, cyclobutanes are still underutilized due to the difficult synthetic access of these compounds.[34] Natural products which contain four-membered rings are not uncommon and most of them were synthesized using [2+2] cycloaddition of olefins (Scheme 19).[35] They have shown various biological activities and may serve as potential drug leads.[36]



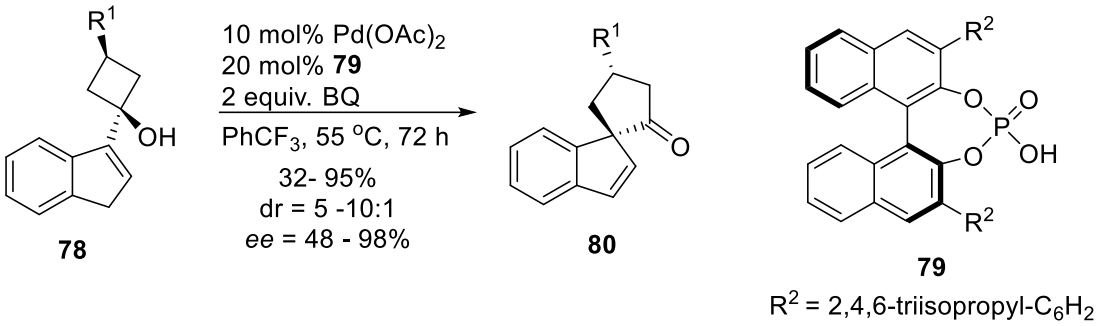
Scheme 19: Four-membered rings containing natural products

Similar with cyclopropanes which are shown in **Chapter 1.2.1.1**, cyclobutanes also proceed in ring-opening reactions to release the strain energy. In addition, they can also undergo many ring-contraction reactions and ring-expansion reactions (from four to five-, six-, seven-, eight-, nine-membered rings).[34c] This flexibility makes cyclobutanes became valuable intermediates in natural product synthesis.

Johnson has developed a Lewis acid-catalyzed [4+2] cycloaddition of donor-acceptor cyclobutanes **75** with aldehydes **76** (Scheme 20).[37] The highly diastereoselective 2,6-*cis*-disubstituted tetrahydropyrans **77** were formed in presence of $Sc(OTf)_3$ as a catalyst. The reaction proceeded under mild conditions and a broad scope of aldehydes are competent in this system.

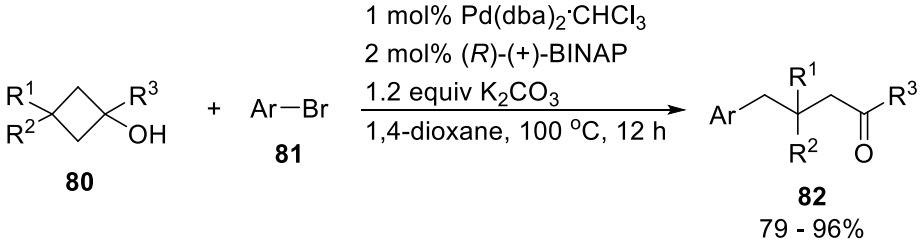
Scheme 20: $Sc(OTf)_3$-catalyzed [4+2] cycloaddition of donor-acceptor cyclobutanes.

A Pd(II)/Brønsted acid-catalyzed ring-expansion of cyclobutanes **78** for the synthesis of spirocyclic indenes **80** in presence of 1,4-benzoquinone (BQ) as an oxidant was described by Rainey (Scheme 21).[38] It is believed that a direct enantioselective allylic C-H activation was involved in the reaction mechanism.



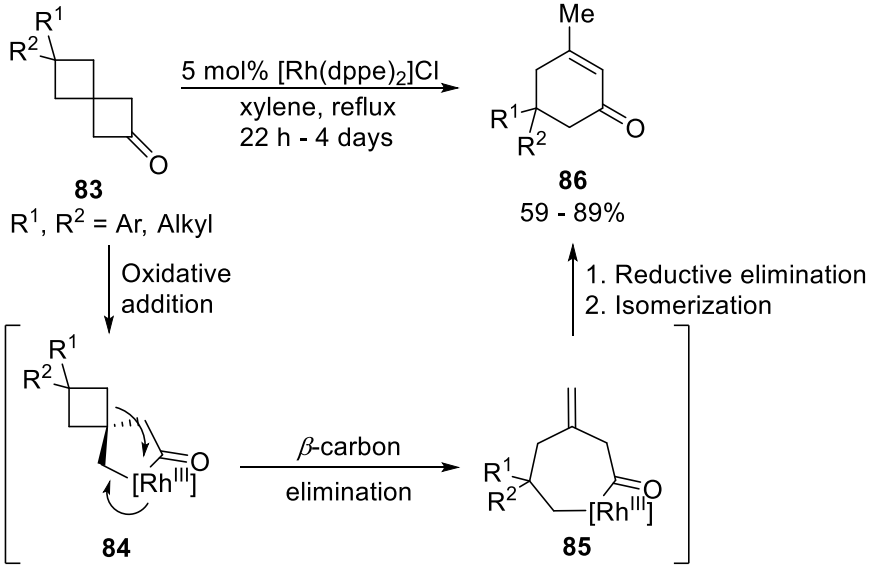
Scheme 21: Four- to five-membered ring expansion reaction of cyclobutanes.

Transition-metal-catalyzed C-C bond activation of cyclobutanes has also been published. Uemura showed a palladium-catalyzed arylation of cyclobutanols **80** with aryl bromides **81** via C-C bond cleavage (Scheme 22).[39] First, Pd(II) species were generated via oxidative addition of an aryl bromide and followed by a *β*-carbon elimination to form the alkyl palladium intermediate. Then, reductive elimination led to the arylated ketones **82**.



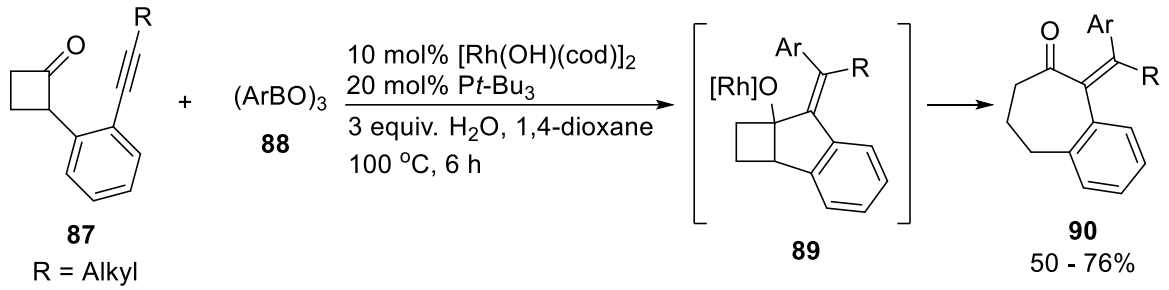
Scheme 22: Palladium-catalyzed ring-opening reaction of cyclobutanols.

A rhodium-catalyzed two consecutive C-C bond activation of spiro cyclobutanes was reported by Murakami and Ito (Scheme 23).[40] Initially, an oxidative addition of the acyl-carbon bond of spirocyclobutanone **83** to rhodium(I), and five-membered cyclic acylrhodium **84** was formed. Subsequently, the rhodacycle underwent *β*-carbon elimination leading to a ring-opening of adjacent cyclobutane which gave seven-membered cyclic acylrhodium **85**. Cyclohexanone **86** was formed after reductive elimination, and isomerization from acylrhodium **85**.



Scheme 23: Rhodium(I)-catalyzed successive double cleavage of C-C bonds of spiro cyclobutanones.

Murakami developed another rhodium-catalyzed C-C bond activation of alkyne-substituted cyclobutanones **87** with triarylboroxines **88** via a different reaction pathway (Scheme 24).[41] Rhodium *tert*-cyclobutanolates **89** were first formed through a 1,2-addition of an adjacent carbonyl group from the vinyl rhodium species. Subsequent regioselective *β*-carbon elimination occurred which lead to ring-expansion. Seven-membered-ring ketones **90** were formed after successive *β*-hydride elimination/readdition processes and protonolysis.



Scheme 24: Rhodium-catalyzed ring-expansion of alkyne-substituted cyclobutanones.

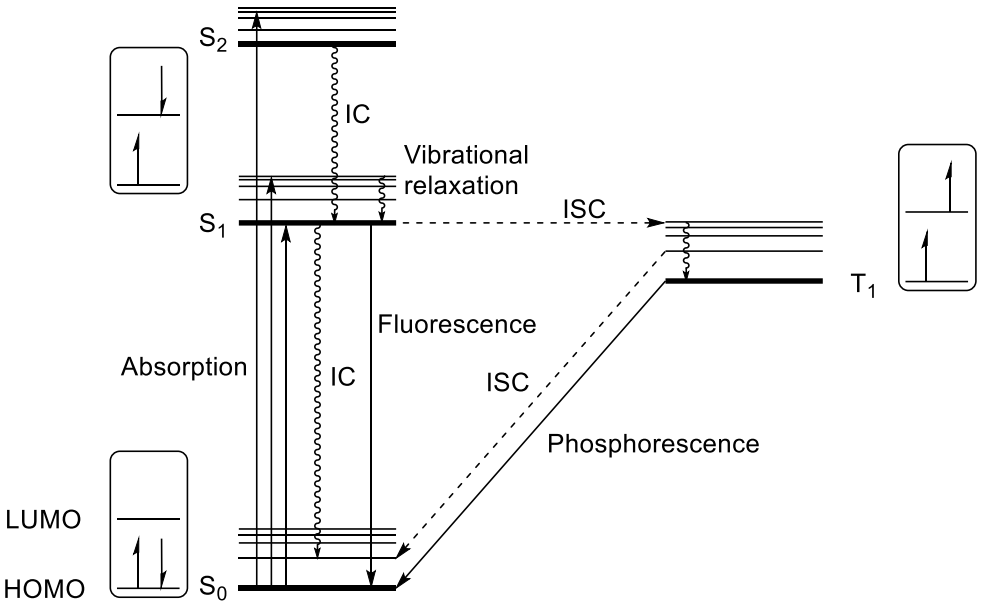
1.4 Photochemistry

1.4.1 Introduction

Photochemistry, a division of chemistry, is the study of chemical processes related to light (or electromagnetic radiation). This term generally represents that a chemical reaction is caused by absorption of infrared radiation (IR) (wavelength from 2500 to 750 nm), visible light (750 - 400 nm), or ultraviolet light (UV) (400 - 100 nm). Differing to thermally induced reactions, the absorption of photons in photochemical reactions not only provides necessary activation energy for the molecules but also changes the symmetry of the molecules' electronic configurations, permitting an otherwise inaccessible reaction path.

The first step in a photochemical process is photoexcitation, in which a molecule elevates to a higher energy state (or excited state) by absorbing light. The photochemical transformation follows two fundamental principles: 1. The first law of photochemistry, known as the Grotthuss-Draper law, is a statement that light must be absorbed by a molecule in order for a photochemical reaction to take place. 2. The second law of photochemistry, known as the Stark-Einstein law, states that every photon that is absorbed will cause a (primary) chemical or physical reaction.

The Jablonski diagram shows the electronic states of a molecule and the transitions between them (Scheme 25). When a molecule absorbs light in its ground state (denoted S_0, assuming a singlet state), one electron is excited to a higher singlet orbital level. According to the spin selection rule, this electron must maintain its spin. The singlet excitation states can be the lowest excited state S_1, or other higher excited states S_2, S_3…, depending on the absorption wavelength.



Scheme 25: Jablonski diagram illustrates electron transition between different electron states. IC: Internal conversion; ISC: Intersystem crossing.

Once an electron is excited, it can quickly relax to lower singlet orbital levels by non-radiative processes such as vibrational relaxation or internal conversion (IC). Another possible pathway to deal with the absorbed energy for the molecule is to emit a photon. This process is called fluorescence. According to Kasha's rule, fluorescence is usually, though not always, observed between the first excited electron state (S_1) and the ground state (S_0).

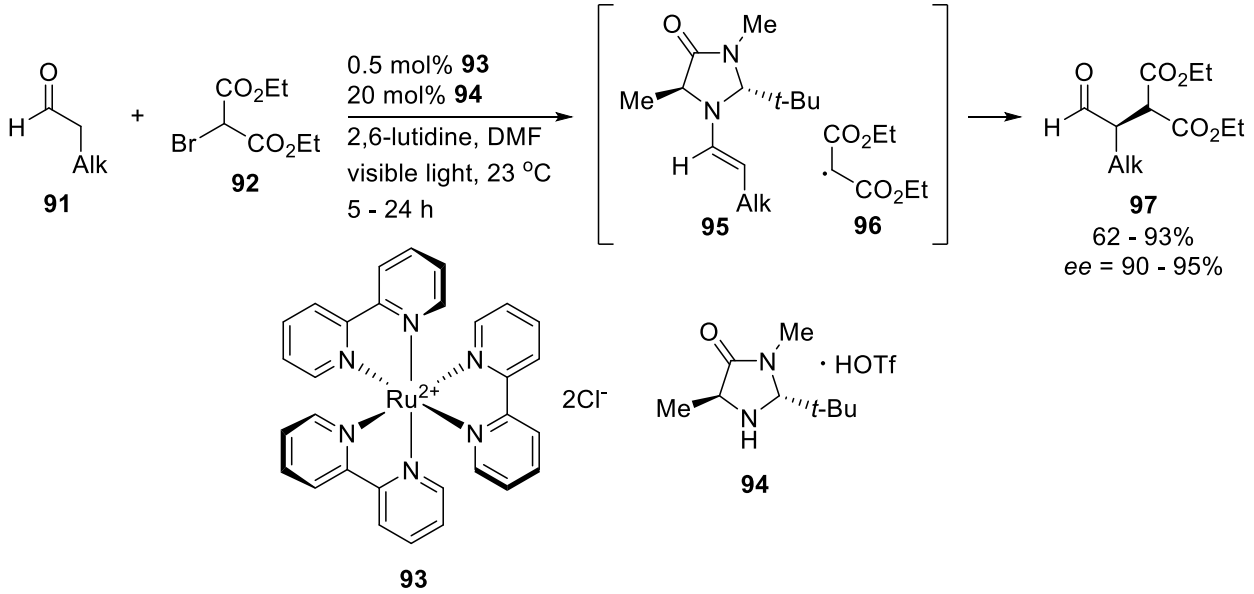
Alternatively, the excited state (S_1) may undergo a spin inversion generating a triplet excited state (T_1) which has two unpaired electrons with the same spin. This radiationless process is called intersystem crossing (ISC). The T_1 state can also relax to the ground state (S_0) via an intersystem crossing or a radiative decay called phosphorescence. Phosphorescence is much slower than fluorescence because this transition involves a change of electronic spin, which is forbidden by spin selection rules.

The photoexcited molecule can also act as a photosensitizer which transfers energy to an adjacent molecule. The opposite process is called quenching where an excited molecule is deactivated by a chemical reagent. Naturally, a reaction can actually occur on the molecule after photoexcitation. It may undergo an intramolecular (or internal) rearrangement, a photodissociation or react with other molecules. The excited states

such as S_1 and T_1, have an electron in a high energy orbital, which is consequently more reducing than the ground state (S_0). However, at the same time, they have a half empty low-energy orbital and are more oxidizing as well.

1.4.2 Photoredox Catalysis

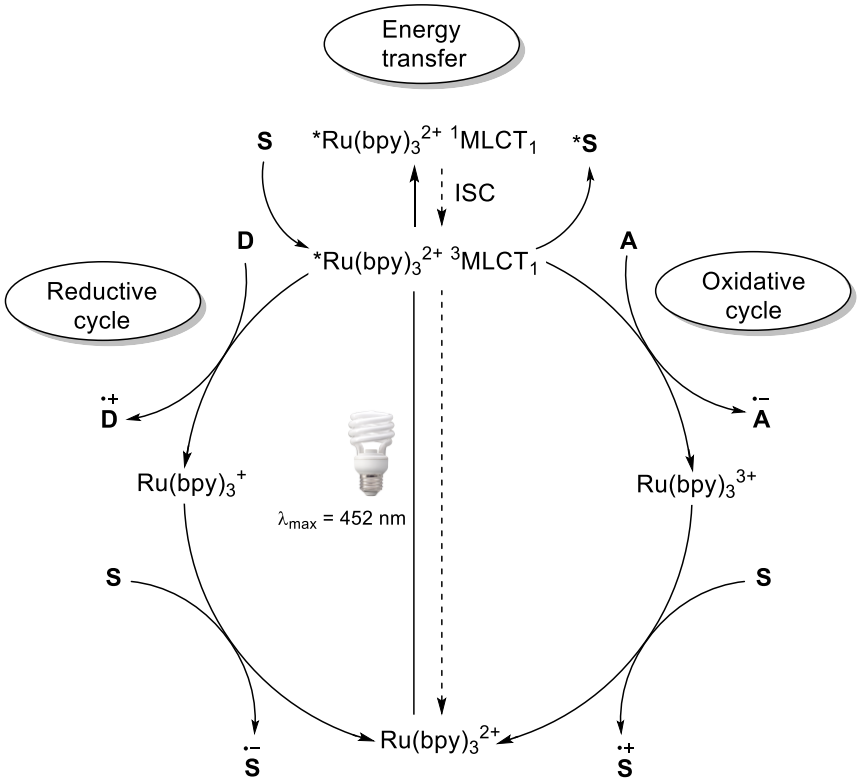
Recently, visible light photoredox catalysis, a new branch of photochemistry has attracted lots of attention by synthetic chemists.[42] Visible light is a very simple light source compared to UV light, that is the most used in organic chemistry. In addition, it allows better use of solar energy, since the solar radiation that penetrates the atmosphere is abundant in the visible light region and with its highest intensity. More importantly, using visible light avoids side reactions or unproductive decompositions that are normally caused by UV photons.



Scheme 26: Asymmetric *α*-alkylation of aldehydes through the merging of photoredox catalysis and organocatalysis.

In 2008, MacMillan published an enantioselective *α*-alkylation of aldehydes **91** by combining photoredox catalyst **93** and organocatalyst **94** (Scheme 26).[43] After this pioneering work, there have been many publications in the field of photoredox catalysis.[42a, 42e, 44] He used the most common photoredox catalyst, $Ru(bpy)_3Cl_2$ (**93**), which absorbs light at a wavelength of 452 nm (Scheme 27). After the photoexcitation

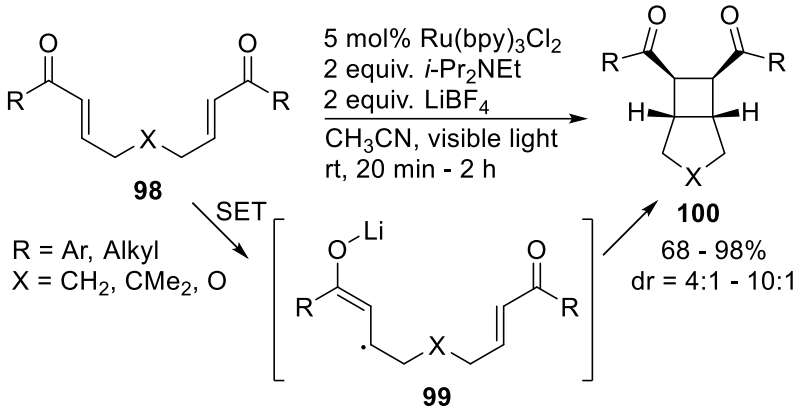
and intersystem crossing, the catalyst would reach a triplet excited state *Ru(bpy)$_3^{2+}$. This excited species can then either receive one electron from an electron donor (D) or give away one electron to an electron acceptor (A) to from a strong reducing-catalyst Ru(bpy)$_3^{+}$ or a strong oxidizing-catalyst Ru(bpy)$_3^{3+}$. They can then individually oxidize or reduce the organic substrate (S), and return to the ground state Ru(bpy)$_3^{2+}$. Alternatively, the triplet excited state of *Ru(bpy)$_3^{2+}$ can also start a process termed triplet-triplet energy transfer (TTET), which *Ru(bpy)$_3^{2+}$ directly transfers energy to the organic substrate to promote the molecule from its ground state (S_0) to its lowest-energy triplet state (T_1).



Scheme 27: Three different catalytic pathways of Ru(bpy)$_3^{2+}$.

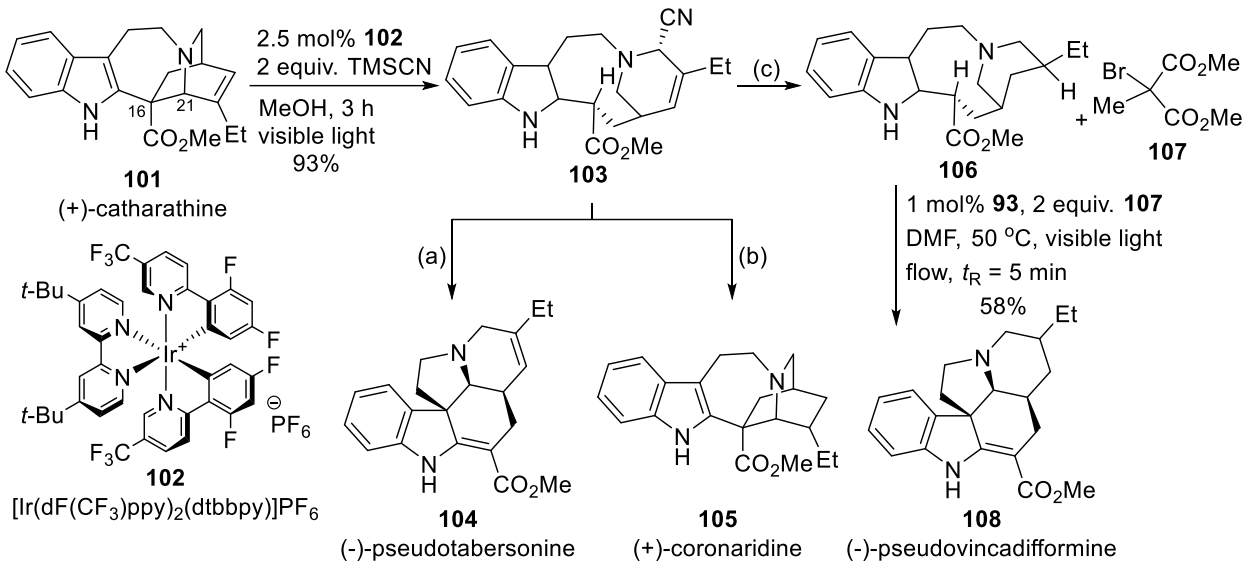
In the same year, 2008, Yoon's group also used the same photocatalyst for [2+2] enone cycloadditions (Scheme 28).[45] Bis(enones) **98** cyclized upon visible light irradiation in presence of Ru(bpy)$_3$Cl$_2$, *N*,*N*-diisopropylethylamine (DIPEA), and LiBF$_4$. DIPEA acted as an electron donor for photoexcited catalyst *Ru(bpy)$_3^{2+}$ in the catalytic cycle to form the reductive catalyst Ru(bpy)$_3^{+}$. Ru(bpy)$_3^{+}$ then transferred one electron to a lithium-activated enone **99**, undergoing the [2+2] cycloaddition to a cyclobutane-containing

adduct **100** and regenerating the ground state catalyst $Ru(bpy)_3^{2+}$ (**93**).



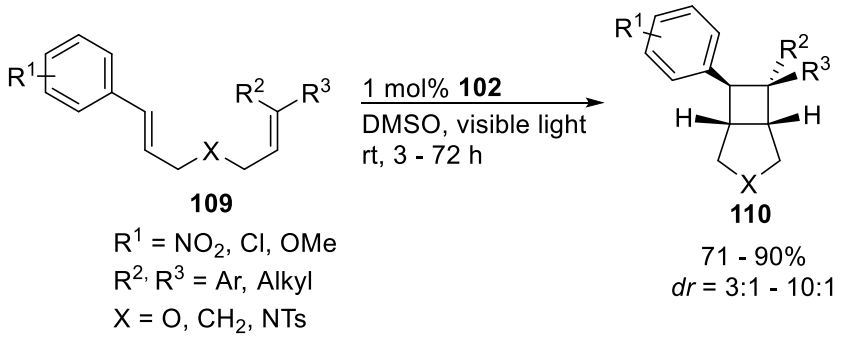
Scheme 28: Visible light photocatalysis of [2+2] enone cycloadditions. SET: single electron transfer.

Stephenson demonstrated that photoredox catalysis is a powerful tool for natural product synthesis as well.[46] Starting from commercially available (+)-catharathine **101**, the structurally related natural products can be rapidly accessed (Scheme 29). (+)-Catharathine **101** underwent a C^{16}-C^{21} bond fragmentation under visible light irradiation by using the photocatalyst $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ **102** with trimethylsilyl cyanide (TMSCN) to provide a cyanated intermediate **103**. The common intermediate **103** can then transform to (-)-pseudotabersonine **104** and (+)-coronaridine **105** in 1-2 step(s). (-)-pseudovincadifformine **108** can be synthesized from amine **106** under another photoredox condition employing photocatalyst **93** and malonate **107** as a terminal oxidant. The amine **106** was formed from intermediate **103** after hydrogenation with Pd/C and followed by $NaBH_4$ reduction.



Scheme 29: Synthesis of alkaloid natural products enabled by photoredox catalysis. (a) 1 equiv. TFA, toluene, reflux, 3 h, 90%. (b) (1) 10 mol% Pd/C, H_2 (1 atm), MeOH, rt, 25 min. (2) 1 equiv. TFA, toluene, reflux, 3 h, 48% (over 2 steps). (c) (1) 20 mol% Pd/C, H_2 (1 atm), MeOH, rt, 25 min. (2) 4 equiv. $NaBH_4$, 0 °C, 10 min, 98% (over 2 steps).

Yoon exploited the photocatalyst **102** to perform a [2+2] styrene cycloaddition via energy transfer (Scheme 30).[47] Since the styrenes **109** were activated by energy transfer rather than electron transfer, the substrate scope is considerably broader. Even electron-deficient 4-nitrostyrene could undergo cycloaddition to cyclobutane **110**.

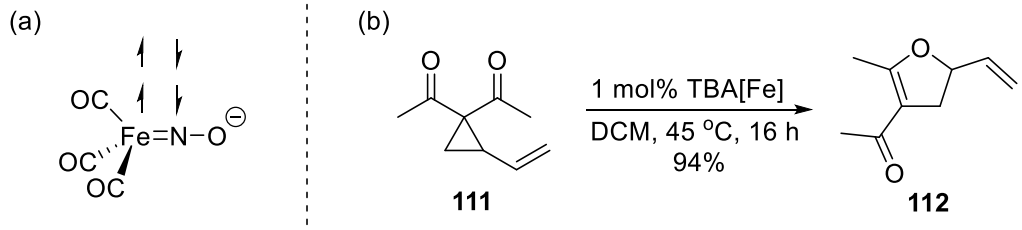


Scheme 30: Visible light photocatalysis of [2+2] styrene cycloadditions by energy transfer.

2. Photoactive $Bu_4N[Fe(CO)_3NO]$-Catalyzed Cloke-Wilson Rearrangement of Vinyl- and Arylcyclopropanes

2.1 Purpose of this Research

Catalytic activities of the shelf-stable, electron rich, and readily accessible iron complex: $Bu_4N[Fe(CO)_3NO]$ (TBA[Fe]) has been a topic of interest in our group for a number of years.[48] A variety of TBA[Fe]-catalyzed reactions have been reported, such as allylic substitutions,[25] hydrosilylations,[49] transesterifications,[50] carbene-transfer reactions,[51] [3+2] cycloadditions,[25-26] and C(sp^2)-H aminations.[52] In order to further understand the reactivity of the complex, its electron configuration has been studied by our group.[53] A combined in-depth spectroscopic and experimental study showed that the ground state metal center of TBA[Fe] should be described as zero-valent and the negative charge being located at the NO-ligand (Scheme 31 (a)). In addition, based on the analysis of CASSCF and IBO, the Fe-NO-moiety should be considered as a singlet ground state complex with a triplet Fe^0, which is antiferromagnetically bound by two nonpolar covalent π-bonds to a triplet NO-anion.



Scheme 31: (a) electronic ground state structure of TBA[Fe]. (b) TBA[Fe]-catalyzed Cloke-Wilson rearrangement of vinylcyclopropane **111**.

The TBA[Fe]-catalyzed Cloke-Wilson rearrangement of vinylcyclopropanes (VCPs) under thermal conditions were observed while studying the Fe-catalyzed C-C bond activation of vinylcyclopropanes (Scheme 31 (b)).[25] The mechanism of this reaction was investigated by theoretical calculations, which showed that the metal-centered atom orbitals are not involved in the reaction, but instead, with one of the two Fe-N π-bonds that reacts with the incoming VCP.[54] The NO-ligand is oxidized while the metal does not change its oxidation state throughout the reaction. Both the S_N2'-*anti* and the S_N2-*anti* mechanisms are energetically accessible.

With regards to the unusual electronic ground state of the ferrate complex, we were eager to know whether the activation for catalytic transformations upon irradiation of light was possible. Because the addition of phosphine or *N*-heterocyclic carbene (NHC) ligands is not required for the TBA[Fe]-catalyzed Cloke-Wilson rearrangement of vinylcyclopropanes under thermal conditions, we believe that it is an ideal reaction for examining the photochemical activation of TBA[Fe].

However, iron-carbonyl complexes are known to easily undergo decarbonylation upon UV-light irradiation. Recently, Beller[55] and Darcel[56] reported that $Fe(CO)_5^-$ or $(NHC)Fe(CO)_4^-$ are activated after photochemical decarbonylation. Although the exact mechanism of the photochemical activation-decarbonylation is not well understood, important perceptions were benefited through combined flash photolysis-ultrafast IR spectroscopy,[57] ultrafast electron diffraction,[58] and femtosecond X-ray spectroscopy.[59] Therefore, under the photochemical conditions, it is important to know whether TBA[Fe] remains intact or undergoes decarbonylation during the reaction. Furthermore, comparing with many examples of metal-carbonyl complexes activation through photodecarbonylation, a nondecarbonylative photochemical activation of a metal-carbonyl catalyst is not known in the literature.

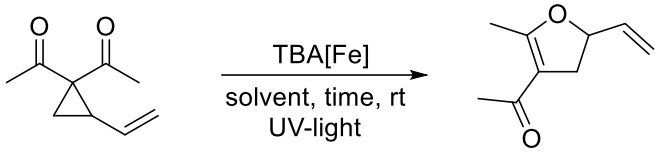
2.2 Results and Discussion

2.2.1 Fe-Catalyzed Cloke-Wilson Rearrangement of Vinylcyclopropanes

2.2.1.1 Optimization of the Cloke-Wilson Rearrangement of Vinylcyclopropanes

Inspired by the thermal reaction of the Cloke-Wilson rearrangement of vinylcyclopropane **111** to dihydrofuran **112**, we used the same vinylcyclopropane **111** to optimize the reaction conditions of photochemical reactions (Table 1).

Table 1. Optimization of the Cloke-Wilson rearrangement of vinylcyclopropanes.



111 **112**

Entry[a]	Cat. [mol%]	Solvent	Time	T. [°C]	Conversion[b] [%]
1	5	DCM	70 min	20	95
2	5	DMF	70 min	20	80
3	5	CH_3CN	70 min	20	full conversion
4	5	acetone	70 min	20	82
5	5	CH_3CN	60 min	20	95
6	5	MTBE	60 min	20	74
7	5	toluene	60 min	20	71
8	5	THF	60 min	20	75
9	2.5	CH_3CN	3 h	20	full conversion
10	1	CH_3CN	14 h	20	16
11	-	CH_3CN	3 h	20	-
12[c]	2.5	CH_3CN	3 h	28	-

[a] All reactions were performed with the substrate (0.4 mmol), and catalyst in solvent (1 mL) under UV-light irradiation (180 W Hg lamp). [b] Determined through ^{1}H-NMR-integration by using mesitylene as internal standard. [c] No UV-light irradiation.

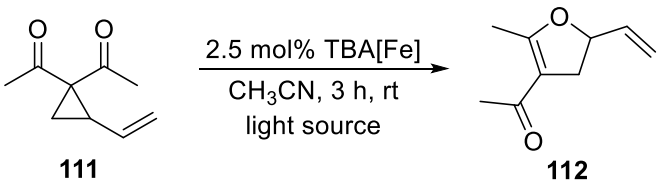
A variety of solvents with 5 mol% of TBA[Fe] were tested in the beginning at room temperature upon UV light irradiation (180 W Hg lamp). We were surprised that the reaction occurred quickly. Full conversion was observed with acetonitrile as a solvent within 70 min (Entry 1-4, Table 1). It is slightly better than DCM that is used as a solvent in the standard thermal reaction. The reaction time was then reduced to 60 min to compare with other solvents, and we found that acetonitrile was the optimal solvent for the reaction (Entry 5-8, Table 1). The catalyst loading was decreased to 2.5 mol% and the reaction was completed after 3 hours (Entry 9, Table 1). However, if the catalyst loading was decreased to 1 mol%, only 16% of conversion was observed, even after 14 hours irradiated by light (Entry 10, Table 1).

The high-pressure mercury lamp is known to emit heat while operating. In order to exclude this effect, a temperature-time correlation of the reaction mixture was measured using *in-operando* IR spectroscopy/thermometry. An increase of temperature from 20 °C (room temperature) to 28 °C was recorded. We believe that was attributed to the exothermicity of the reaction, because no temperature increased without the presence of TBA[Fe], and of course, no reaction occurred without catalyst (Entry 11, Table 1). Importantly, the Cloke-Wilson rearrangement did not take place at 28 °C without UV-light irradiation (Entry 12, Table 1).

2.2.1.2 Scope of the Cloke-Wilson Rearrangement of Vinylcyclopropanes

After optimization of the reaction conditions, we knew that the rearrangement proceeds under photochemical conditions using a 180 W Hg lamp (Entry 1, Table 2). We were then wondering whether less-intense UV light or even visible light irradiation could activate the iron complex. We were pleased to find that using a 75 W Xe-UV lamp and even a commercial 23 W household lamp (compact fluorescent lamp (CFL)) led to the formation of dihydrofuran **112** with excellent isolated yields (Entry 2-3, Table 2).

Table 2. The effect of different light sources for the Cloke-Wilson rearrangement of vinylcyclopropanes.



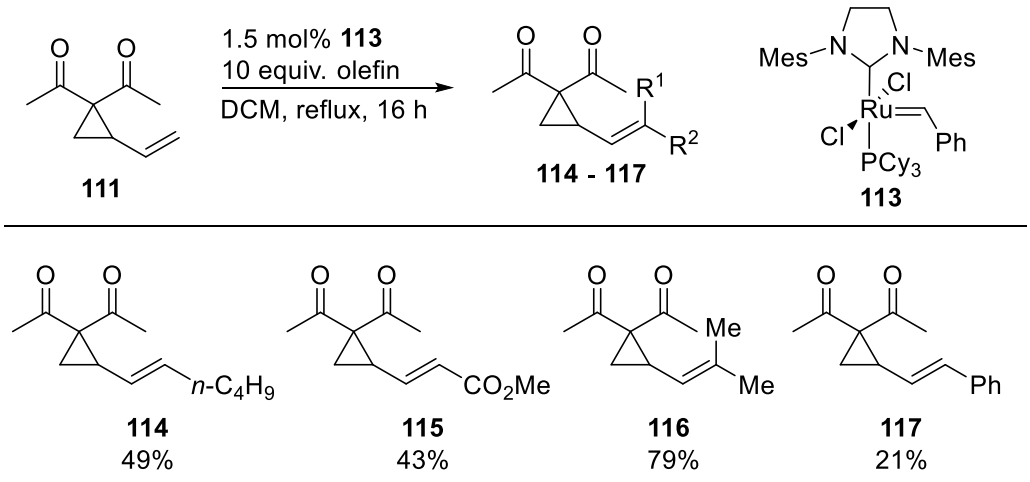
111 **112**

Entry[a]	Light source	Yield[b] [%]
1	180 W Hg lamp	96
2	75 W Xe lamp	93
3	23 W CFL	92

[a] All reactions were performed with the substrate (0.4 mmol), and 2.5 mol% TBA[Fe] in solvent (1 mL) under UV-light irradiation at room temperature. [b] Isolated yield.

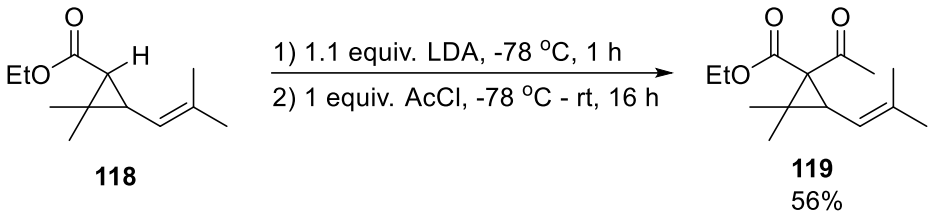
With the optimized conditions in hand, we turned our attention towards an exploration of the scope of the Cloke-Wilson rearrangement. In order to compare the activity and activation mode of TBA[Fe], the Fe-catalyzed Cloke-Wilson rearrangement of vinylcyclopropanes under the thermal conditions are also discussed in this chapter. They were done in collaboration with Pursley[60] and the optimization of thermal conditions was done by Teske.[61] Parts of the vinylcyclopropanes were synthesized by Pursley[60] and Teske.[61]

A series of functionalized vinylcyclopropanes were prepared before exploring the substrate scope of the Fe-catalyzed Cloke-Wilson rearrangement of vinylcyclopropanes. Vinylcyclopropanes bearing a terminal olefin were synthesized according to literature procedures. The double bond functionalized vinylcyclopropanes were synthesized by olefin cross metathesis utilizing a Grubbs 2nd generation catalyst and the corresponding alkenes (Scheme 32).



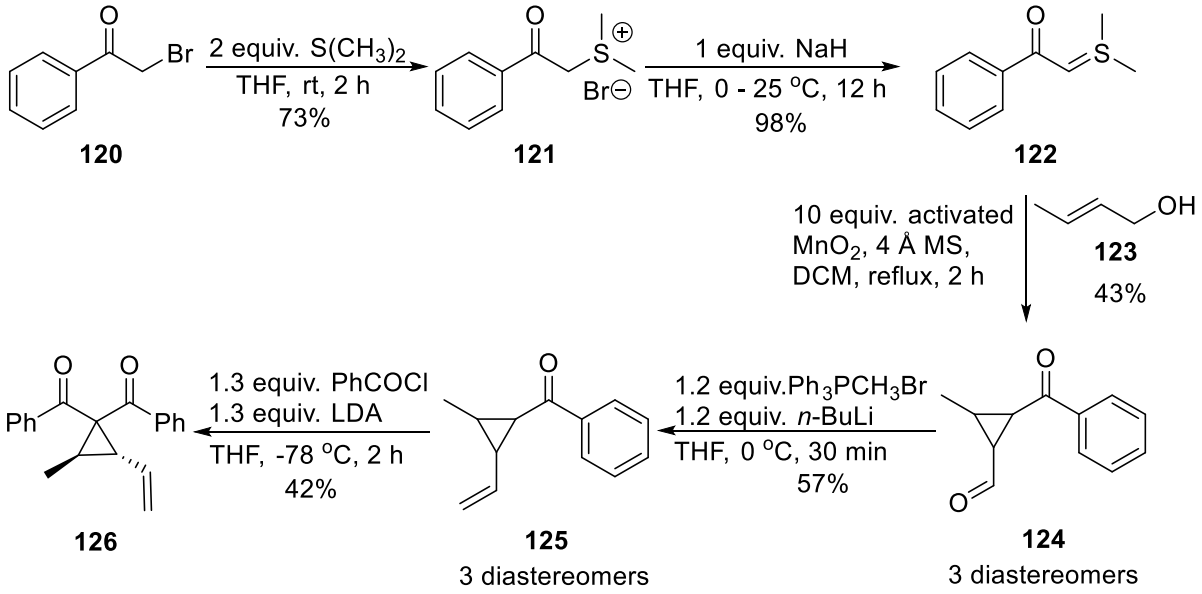
Scheme 32: Synthesis of double bond substituted vinylcyclopropanes.

Highly substituted vinylcyclopropane **119** was synthesized from ethyl chrysanthemate **118**, which was deprotonated by lithium diisopropylamide (LDA), and followed by acetylation with acetyl chloride (Scheme 33).



Scheme 33: Synthesis of highly substituted vinylcyclopropane **119**.

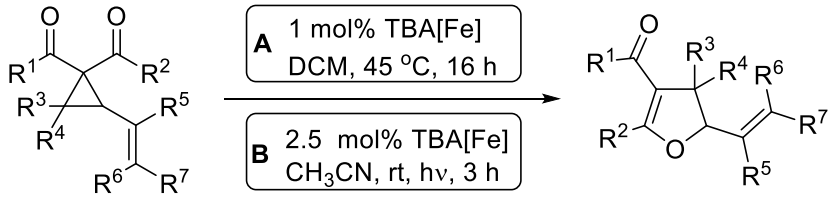
Methyl substituted vinylcyclopropane **126** was also synthesized (Scheme 34), which was obtained five steps from 2-bromoacetophenone **120** according to a modified literature procedure.[32]

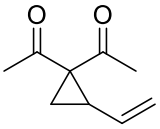
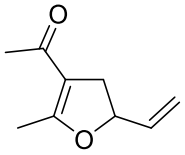
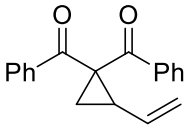
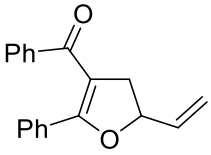
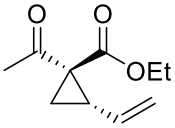
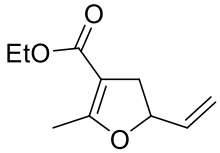
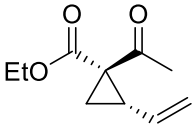
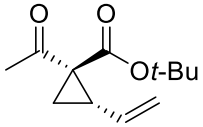
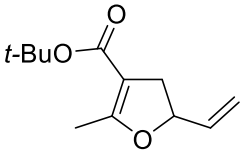
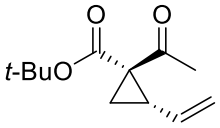


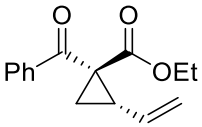
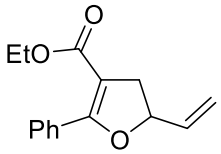
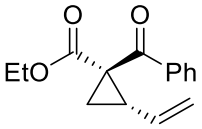
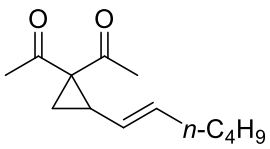
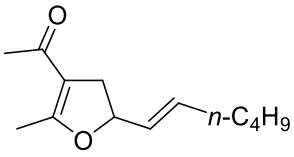
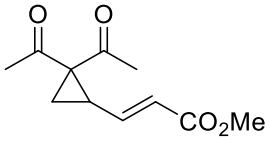
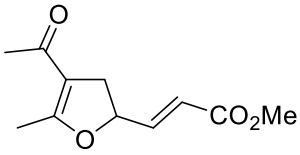
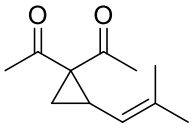
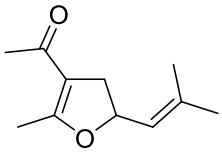
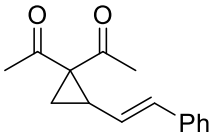
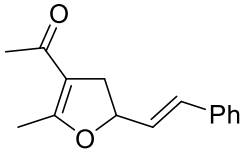
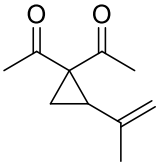
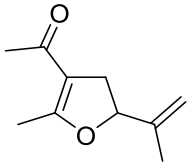
Scheme 34: Synthesis of vinylcyclopropane **126**.

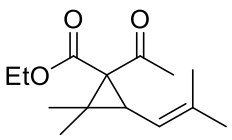
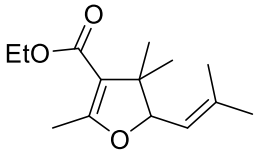
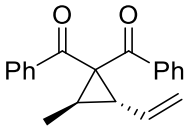
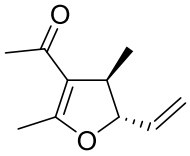
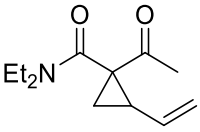
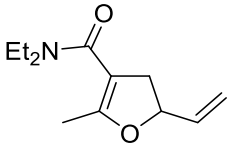
The scope of thermal and photochemical Fe-catalyzed Cloke-Wilson rearrangement of vinylcyclopropanes were summarized in Table 3.

Table 3. The scope of the thermal and photochemical Fe-catalyzed Cloke-Wilson rearrangement of vinylcyclopropanes.



Entry	Substrate	Product	Condition[a]	Yield[b] [%]
1	 **111**	 **112**	A	94
2			B	96, 93[c], 92[d]
3	 **127**	 **128**	A	92
4			B	93
5	 **129a**	 **130**	A	93
6			B	94, 93[d]
7	 **129b**		A	92
8			B	92, 92[d]
9	 **131a**	 **132**	A	94
10			B	85
11	 **131b**		A	60
12			B	91

13[e]			A	87
14	**133a**		B	91
		134		
15			A	86
16	**133b**		B	92
17[e]			A	87
18[e], [f]	**114**	**135**	B	87
19[e]			A	86
20[e], [f]	**115**	**136**	B	89
21[e]			A	54
22[e], [f]	**116**	**137**	B	75, 76[d]
23[e]			A	98
24[e], [f]	**117**	**138**	B	98
25[e]			A	96
26	**139**	**140**	B	97

23[e]			A	–
24[g]	**119**	**141**	B	98, 96[c], 19[d]
23			A	72
24	**126**	**142**	B	92
25[h]			B	-
	143	**144**		

[a] Condition A: 0.5 mmol of substrate, 1 mol% of TBA[Fe] in DCM (1 mL), 45 °C, 16 h; condition B: 0.4 mmol of substrate, 2.5 mol% of TBA[Fe] in CH_3CN (1 mL), 180 W Hg lamp, 20 °C, 3 h. [b] Isolated yield. [c] 75 W Xe lamp. [d] 23 W compact fluorescence lamp. [e] 5 mol% of TBA[Fe]. [f] 6 h. [g] 10 mol% of TBA[Fe] in THF (1 mL), 24 h. [h] 10 mol% of TBA[Fe] in CH_3CN (1 mL), 24 h.

Both thermal and photochemical conditions proved to be broadly applicable to the formation of dihydrofurans. Very high isolated yields were obtained for most of the substrates under both reaction conditions. However, there are still some differences between these two methods, which implies they have different activation modes. Stereocenters within the substrates play an important role in the thermal condition. The overall yield of the *cis*-oriented (*tert*-butyl ester and the vinyl group) VCP **131b** is significantly lower than the *trans*-oriented VCP **131a** (Entry 9 and 11, Table 3). This indicated that the sterically demanding *tert*-butyl ester blocked the S_N2'- (or S_N2-) *anti* trajectory of the incoming nucleophilic catalyst. The same effect can be observed from VCP **133a** and **133b**. *cis*-oriented VCP **133a** needs five times more catalyst loading than VCP **133b** to have a comparable overall yield (Entry 13 and 15, Table 3). In contrast, the activity of both diastereomers is almost identical under photochemical conditions (Entry 5-16, Table 3). Furthermore, the highly substituted sterically hindered VCP **119** was thermally unreactive, but the desired dihydrofuran **141** could be obtained under

photochemical conditions (Entry 23 and 24, Table 3). These results might imply the change of complex configuration upon irradiation. Therefore, quantum chemical studies of the photoactivation process and the structure of the activated iron complex will be discussed in Chapter 2.2.3. In addition, we observed that the yield can be correlated with the power of the light source. Using a 180 W Hg lamp and a 75 W Xe lamp to activate TBA[Fe] at room temperature can both transform the VCP **119** to dihydrofuran **141** with full conversion as well as the isolated yields by 98% and 96%, respectively (Entry 24, Table 3). While using a 23 W compact fluorescence lamp, the desired product was obtained in 19% isolated yield (Entry 24, Table 3). Amide functionalized vinylcyclopropane **143** stayed nonreacted even when 10 mol% of TBA[Fe] was employed for 24 hours (Entry 25, Table 3). It could be due to the electron withdrawing ability of amides being not as good as ketones or esters to stabilize the negative charge during the reaction.

2.2.2 Fe-Catalyzed Cloke-Wilson Rearrangement of Arylcyclopropanes

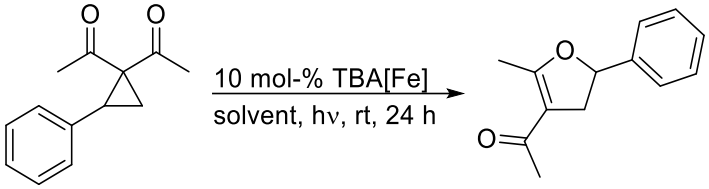
2.2.2.1 Optimization of the Cloke-Wilson Rearrangement of Arylcyclopropanes

After successfully developing a protocol of photochemical activation of TBA[Fe] for the Cloke-Wilson rearrangement of vinylcyclopropanes, we subsequently focused on the Cloke-Wilson rearrangement of arylcyclopropanes (ACPs). Arylcyclopropanes are known to be less reactive than vinylcyclopropanes. Most of the ring-enlargement reactions of arylcyclopropanes require strong Lewis/Brønsted acids[62] or noble metal catalysts[63] under harsh conditions.[64] Therefore, a metal-catalyzed C-C bond activation of arylcyclopropanes under mild conditions is desired.

Using 10 mol% of TBA[Fe] with arylcyclopropane **145** in acetonitrile (the best solvent for VCP Cloke-Wilson rearrangement in photochemical conditions) under 180 W UV-lamp irradiation at room temperature for 24 hours only led to trace amount of rearrangement product **146** (Entry 1, Table 4). Due to the inertness of arylcyclopropanes, using various solvents such as methanol, THF, DCM, and *n*-pentane could not provide any conversion (Entry 3-6, Table 4). The reaction did not work in the absence of light or without catalyst (Entry 7-8, Table 4). In the end, we found that DMF as a more polar solvent is the best and only solvent for the Fe-catalyzed Cloke-Wilson rearrangement of arylcyclopropanes under photochemical conditions (Entry 2, Table 4). In DMF, TBA[Fe] might exist as a

solvent-separated ion pair which significantly increases the nucleophilicity of the metal center.

Table 4. Optimization of the Cloke-Wilson rearrangement of arylcyclopropanes.



145 **146**

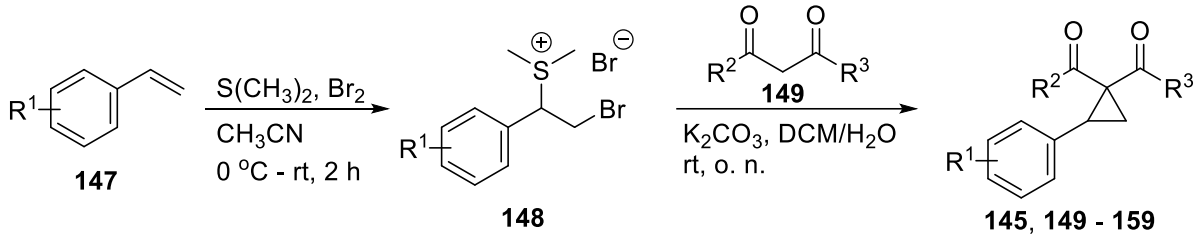
Entry[a]	Solvent	Yield[b] [%]
1	CH_3CN	<5
2	DMF	82[c]
3	DCM	-
4	THF	-
5	CH_3OH	-
6	*n*-pentane	-
7[d]	DMF	-
8[e]	DMF	-

[a] All reactions were performed with the substrate (0.4 mmol), and 10 mol% of TBA[Fe] in solvent (1 mL) under UV-light irradiation (180 W Hg lamp). [b] Determined through ^{1}H-NMR-integration by using mesitylene as internal standard. [c] Isolated yield. [d] No TBA[Fe]. [e] In the dark.

2.2.2.2 Scope of the Cloke-Wilson Rearrangement of Arylcyclopropanes

A series of functionalized arylcyclopropanes were prepared before exploring the substrate scope of the Fe-catalyzed Cloke-Wilson rearrangement of arylcyclopropanes (Table 5). The synthetic route was modified from a known procedure.[65] Parts of the arylcyclopropanes were synthesized by Pursley[60] and Klein[66]. The functionalized aryl bromosulfonium bromides **148** were formed from the corresponding styrene derivatives **147** with dimethyl sulfide and bromine. Then the bromosulfonium bromides **148** were converted to desired arylcyclopropanes **158** or **159** with 1,3-diketones or *β*-keto esters **149** via cyclopropanation.

Table 5. Synthesis of functionalized arylcyclopropanes.

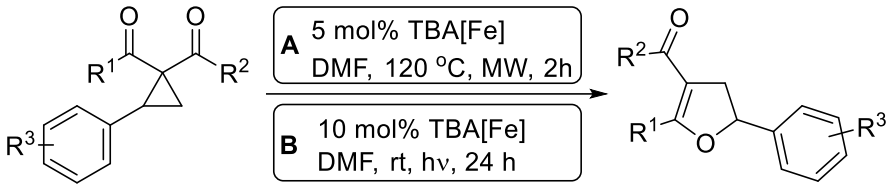


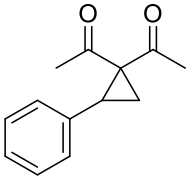
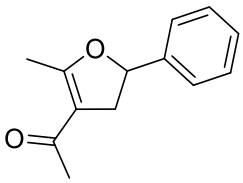
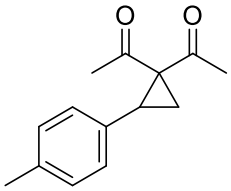
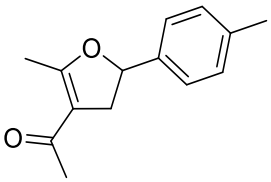
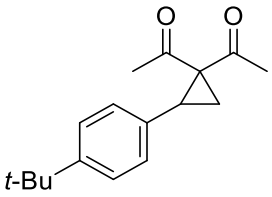
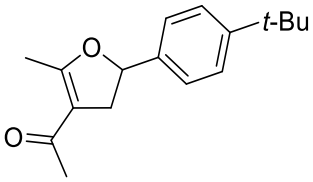
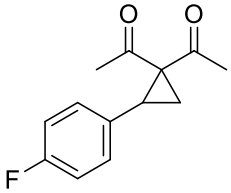
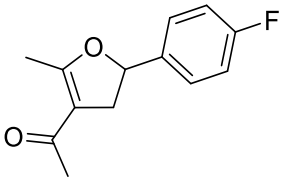
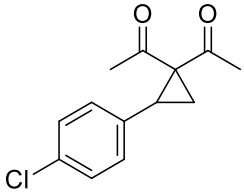
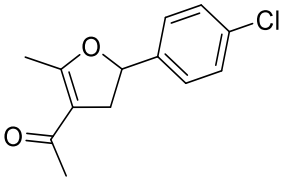
ACP	R^1	R^2	R^3	Yield[a] [%]
145	H	Me	Me	22
149	*p*-Me	Me	Me	23
150	*p*-*t*-Bu	Me	Me	8
151	*p*-F	Me	Me	37
152	*p*-Cl	Me	Me	38
153	*p*-Br	Me	Me	19
154	*m*-OMe	Me	Me	35
155	*m*-Cl	Me	Me	17
156	*m*-Br	Me	Me	13
157	*o*-OMe	Me	Me	43
158	H	Me	OMe	24
159	H	Ph	Ph	23

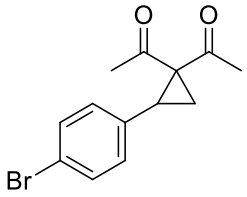
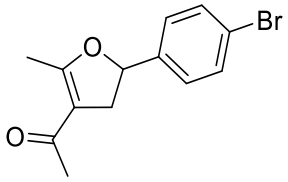
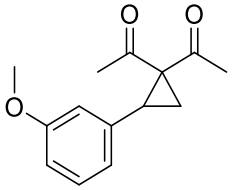
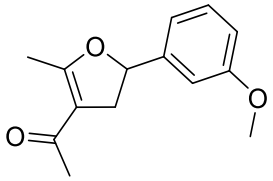
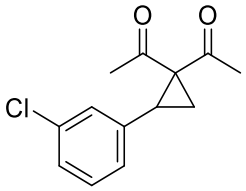
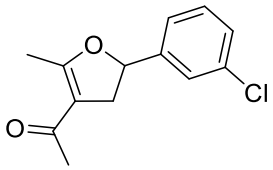
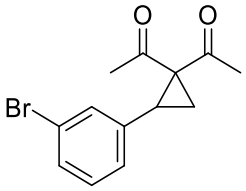
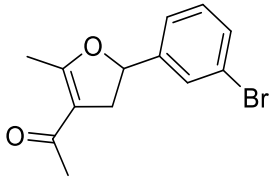
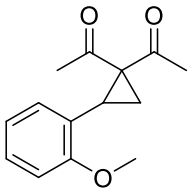
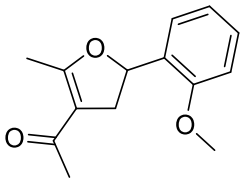
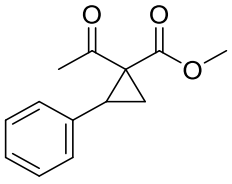
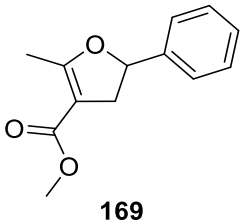
[a] Isolated yield over two steps.

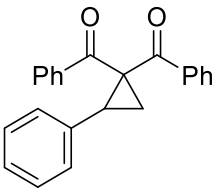
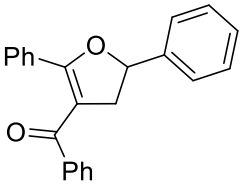
The Fe-catalyzed Cloke-Wilson rearrangement of arylcyclopropanes under thermal conditions is also discussed in this chapter, which was done in collaboration with Pursley[60] and the optimization of thermal conditions was done by Klein[66] and Pursley[60]. The scope of the thermal and photochemical Fe-catalyzed Cloke-Wilson rearrangement of vinylcyclopropanes are summarized in Table 6.

Table 6. Substrate scope of the thermal and photochemical Fe-catalyzed Cloke-Wilson rearrangement of arylcyclopropanes.



Entry	Substrate	Product	Condition[a]	Yield[b] [%]
1	 **145**	 **146**	A	99
2			B	82, 57[c], 5[d]
3	 **149**	 **160**	A	99
4			B	85
5	 **150**	 **161**	A	75
6			B	77
7	 **151**	 **162**	A	76
8			B	62
9	 **152**	 **163**	A	92
10			B	75

11	 **153**	 **164**	A	97
12			B	-
13	 **154**	 **165**	A	85
14			B	93
15	 **155**	 **166**	A	90
16			B	72
17	 **156**	 **167**	A	92
18			B	-
19	 **157**	 **168**	A	92
20			B	75
21	 **158**	 **169**	A	92
22			B	75

23			A	93
24			B	40
	159	**170**		

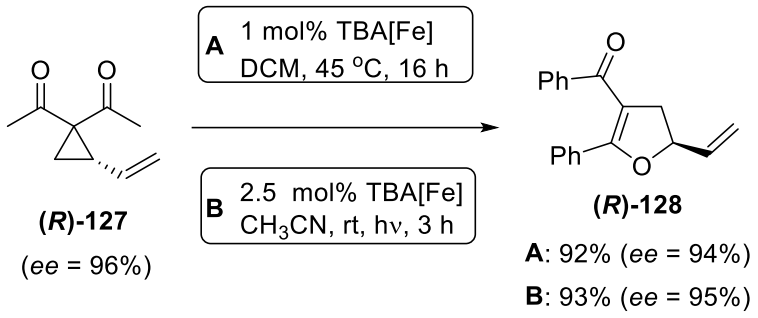
[a] Conditions A: 0.25 mmol of substrate, 5 mol% of TBA[Fe] in DMF (1 mL), 120 °C, microwave (200 W), 2 h; conditions B: 0.4 mmol of substrate, 10 mol% of TBA[Fe] in DMF (1 mL), 180 W Hg lamp, 20 °C, 24 h. [b] Isolated yield. [c] 75 W Xe lamp. [d] 23 W compact fluorescence lamp.

The TBA[Fe]-catalyzed Clock-Wilson rearrangement of arylcyclopropanes was able to proceed under both thermal and photochemical conditions. Although the thermal conditions are rather harsh, the arylcyclopropanes had to be treated with 5 mol% of TBA[Fe] under microwave irradiation at 120 °C for 2 hours in DMF, but the reaction times were shorter and the catalyst loadings were lower as compared to the photochemical conditions. However, we are still surprised that rather unreactive arylcyclopropanes can rearrange at room temperature with 10 mol% of TBA[Fe] under UV-light irradiation for 24 hours. The power of light source plays an important role in the rearrangement of ACPs, since using a 180 W Hg lamp for the standard ACP **145** resulted in a smooth rearrangement with 82% isolated yield of dihydrofuran **146**. However, using a 75 W Xe lamp and a 23 W compact fluorescence lamp resulted in a dramatic decrease of the yield to 57% and 5% respectively (Entry 2, Table 6). Functional group effects were observed under photochemical conditions, particularly in ACPs with *para*-substitution of the aromatic unit. ACPs with an electron donating methyl group **149** were transformed better than non-substituted **145** and halide-substituted ACPs (Entry 2, 4, 8, and 10, Table 6). In addition, the yield of *para*-chloro substituted ACP **151** (75%) is higher than *para*-fluoro substituted ACP **152** (62%) (Entry 8 and 10, Table 6). The same effect was also found for the corresponding *meta*-substituted ACPs **154** and **155** (Entry 14 and 16, Table 6). No conversions were observed for *para*-bromo and *meta*-bromo substituted ACPs (Entry 12 and 18, Table 6). Although we did not observe the product of photodehalogenation, we cannot exclude this side-reaction being present and leading to catalyst decomposition. The rearrangement of 1,3-diketone ACPs with diphenyl substituted **159** or *β*-keto esters

158 is also possible in both thermal and photochemical conditions (Entry 21-24, Table 6).

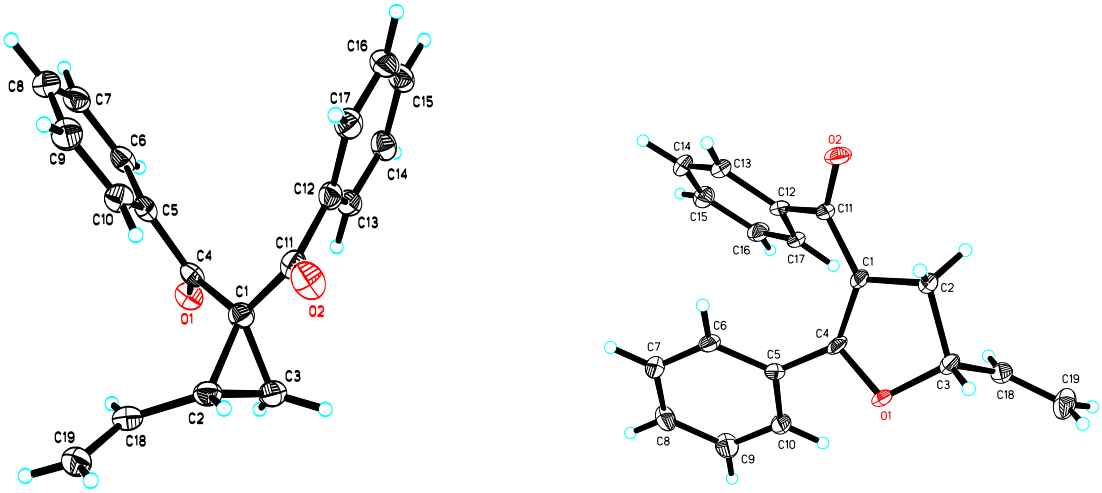
2.2.3 Investigation of the Reaction Mechanism

The mechanism of the TBA[Fe]-catalyzed Cloke-Wilson rearrangement under thermal condition via an S_N2'-*anti* or S_N2-*anti* pathway was studied by Klein via the IBO analysis.[54] In order to understand the reaction mechanism under photochemical conditions and to compare it to the previous results, we first used the enantiomerically enriched (*ee* = 95%) vinylcyclopropane **(*R*)-127** for the study. VCP **(*R*)-127** and **(*S*)-127** were obtained from racemic VCP **127** by chiral HPLC separation. Under standard photochemical conditions, the VCP **(*R*)-127** rearranged to the corresponding enantiomerically enriched (*ee* = 95%) dihydrofuran **(*R*)-128** with 92% isolated yield (Scheme 35, B).



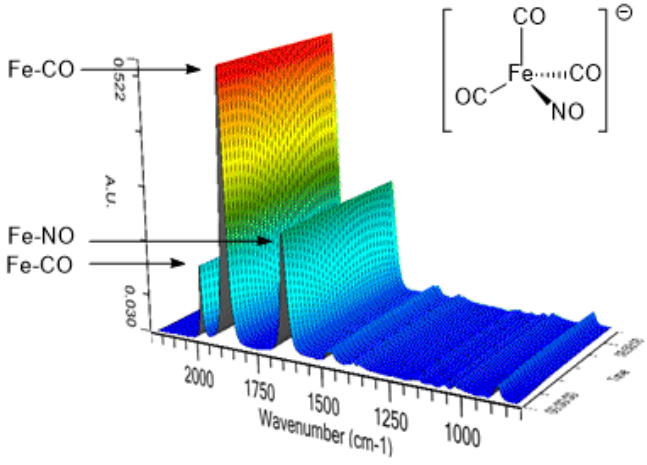
Scheme 35: Stereoselectivity of the Fe-catalyzed Cloke-Wilson rearrangement.

The configuration of the newly formed C-O bond retained and the enantiopurity was almost completely transferred. This result indicates that a double S_N2'-*anti* or S_N2-*anti* mechanism is present. The same result was observed under thermal conditions. It is also in agreement with the previously proposed mechanism (Scheme 35, A). Enantiomerically enriched VCP **(*S*)-127** was also tested under photochemical and thermal conditions, and the isolated yield and *ee* of the corresponding dihydrofuran **(*S*)-128** were identical with the experiment of VCP **(*R*)-127** (see experimental part). In addition, the absolute configuration of **(*R*)-127**, **(*R*)-128** (Scheme 36), **(*S*)-127**, and **(*S*)-128** (see experimental part) were assigned using X-ray diffractometry.



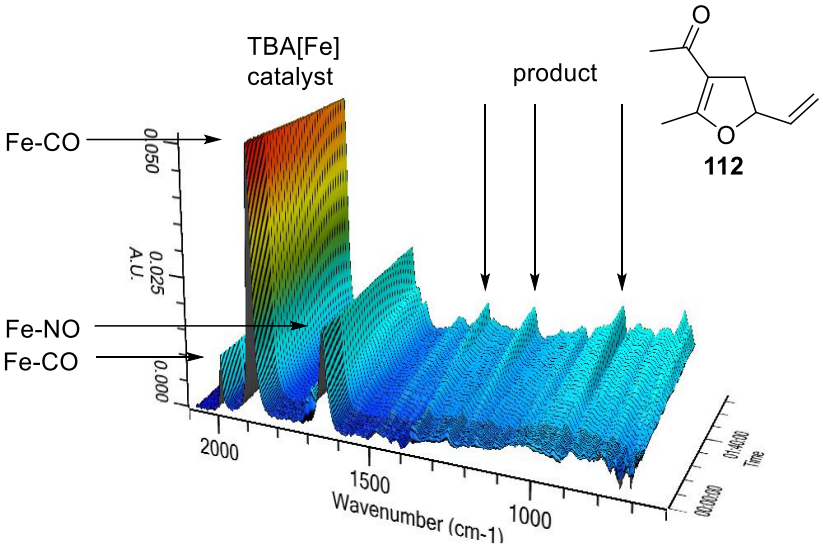
Scheme 36: X-ray structure of **(*R*)-127** and **(*R*)-128**.

To elucidate the probable activation mode of TBA[Fe] under photochemical conditions, TBA[Fe] was dissolved in acetonitrile and irradiated with a 180 W Hg lamp at room temperature. The carbonyl and nitrosyl peaks were tracked upon irradiation by using *in situ* IR-ATR spectroscopy. Scheme 37 shows that even after an extended irradiation time, no significant change in the IR-spectrum was observed.



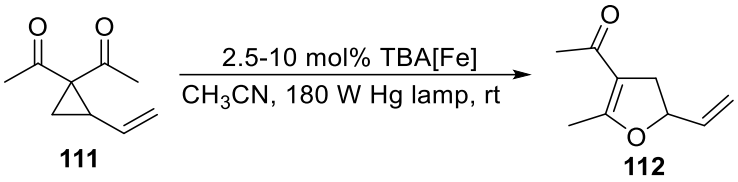
Scheme 37: *In situ* IR spectroscopic analysis of TBA[Fe] under UV-irradiation.

In addition, the same experiment was repeated with addition of 5 equiv. of triphenylphosphine as a suitable ligand. No ligand exchange could be observed even after four hours of irradiation (see experimental part). Furthermore, 1 equiv. of VCP **111** was added to the TBA[Fe] reaction mixture upon irradiation, and was again monitored by *in situ* IR spectroscopy (Scheme 38). The IR peaks of TBA[Fe] showed no change even after full conversion of dihydrofuran **112** was detected. To summarize the observations so far, we can confidently say that a photochemically induced decarbonylation of TBA[Fe] is not the activating step.



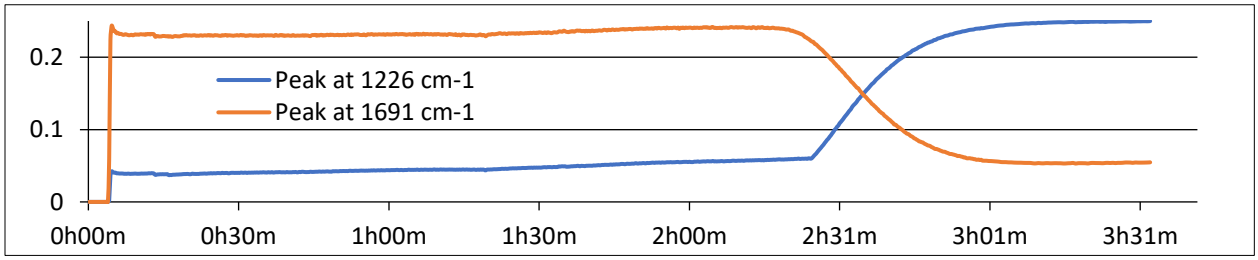
Scheme 38: *In situ* IR spectroscopic analysis of the photochemical TBA[Fe]-catalyzed Cloke-Wilson rearrangement of VCP **111**.

A kinetic study was done by using different concentrations (2.5, 5, 7, and 10 mol%) of catalyst in the reaction mixture. The consumption of VCP **111** and the formation of dihydrofuran **112** were monitored by *in situ* IR spectroscopy (Scheme 39). After exposure to UV-light, the reactions did not start immediately. Instead, no reaction was observed for a certain induction period, then rapid transformations occurred. Higher concentrations of catalyst caused an earlier reaction and a faster reaction rate. These results indicate that the reaction will not start until a sufficient amount of the photoactivated catalyst was formed.

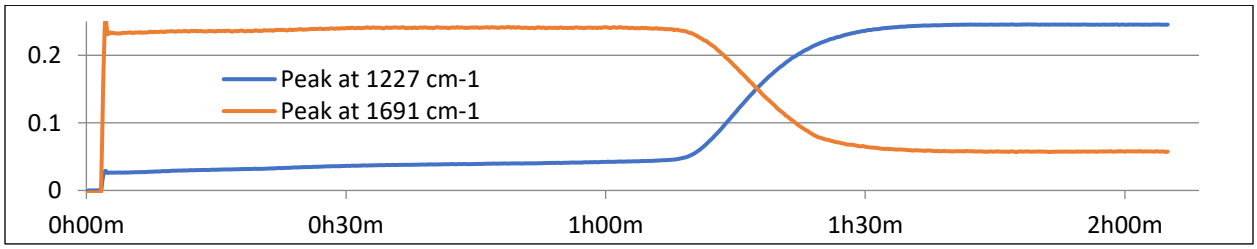


111 **112**

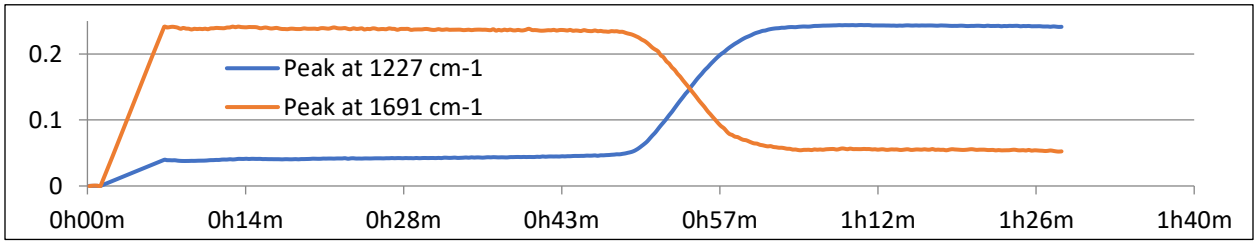
(a) 2.5 mol% TBA[Fe]:



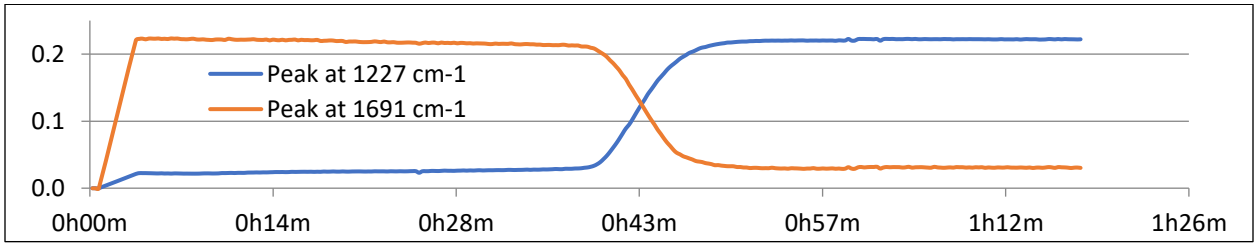
(b) 5 mol% TBA[Fe]:



(c) 7 mol% TBA[Fe]:

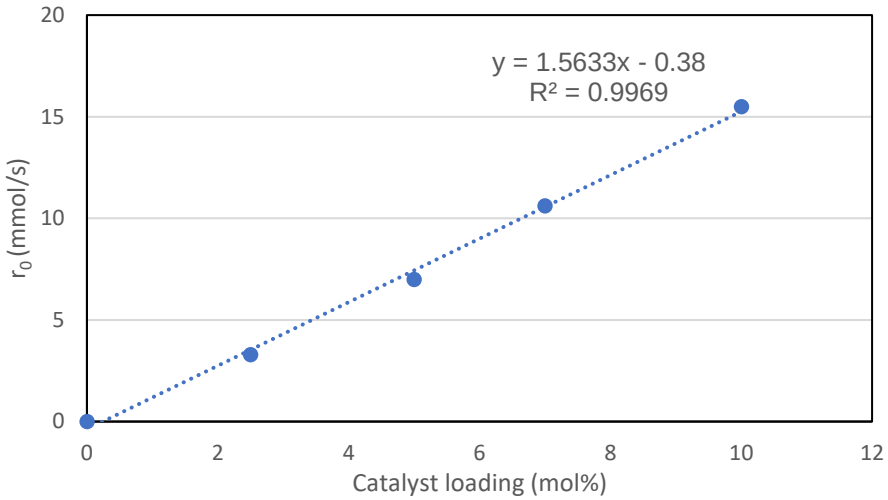


(d) 10 mol% TBA[Fe]:



Scheme 39: Peak height vs time plot of different catalyst concentrations. The peak at 1226 cm^{-1} belongs to VCP **111**. The peak at 1691 cm^{-1} belongs to dihydrofuran **112**.

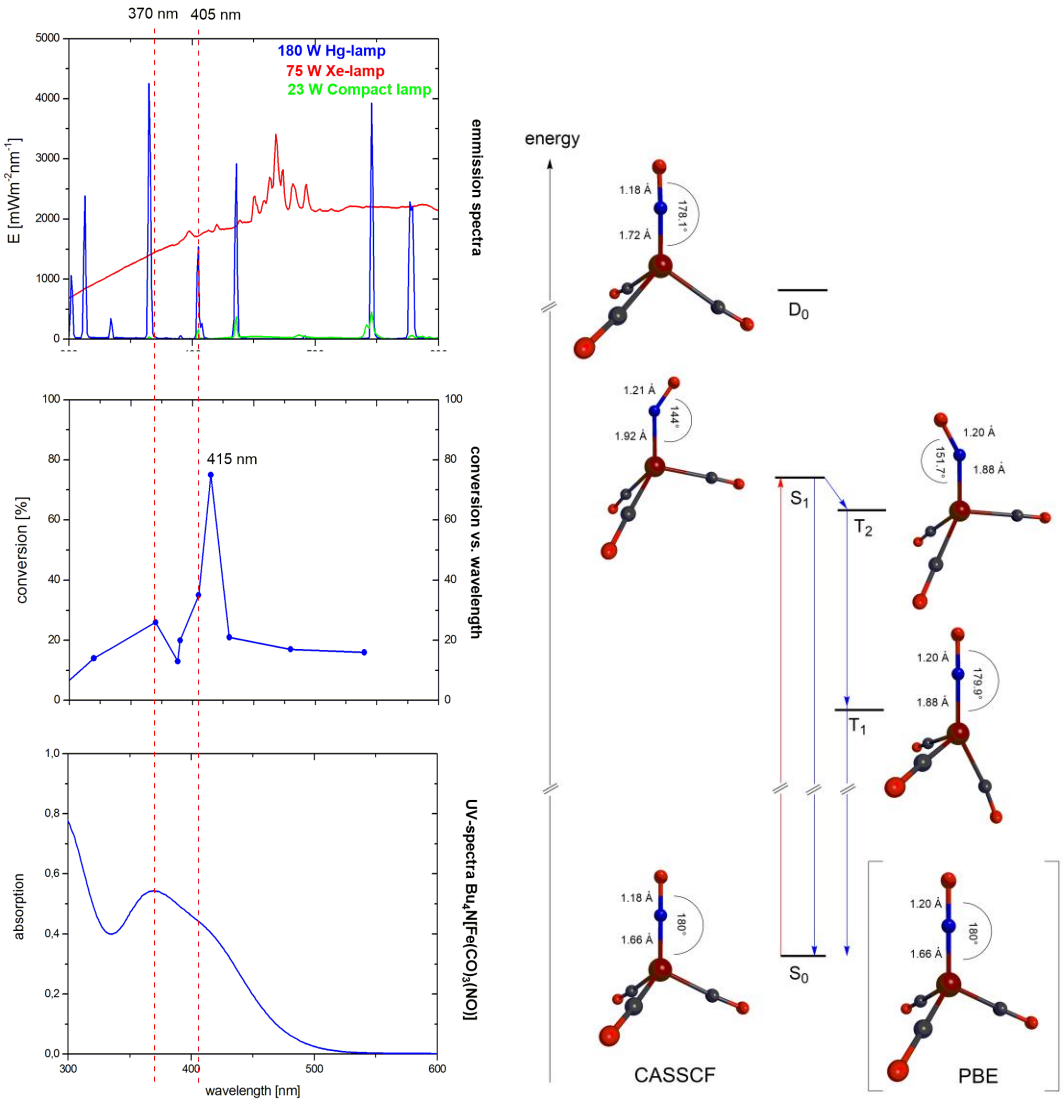
The effect of the catalyst loading on the initial rate (r_0) of dihydrofuran **112** formation is shown in Scheme 40. The initial rates were determined from the tangent slope at the point of reaction initiated in the peak height vs time plots. The rate of formation was found to increase linearly with the increase in catalyst loading. This linear dependency may indicate an individual interaction between the catalyst and substrate **111**. Because there is only one reactant in the reaction, the rate law would be: $r_0 = {}^{d[P]}/_{dt} = k[cat.]^x$ (P: product, t: time). Since the plot of [cat.] vs r_0 is linear, we know that x = 1. Therefore, we can confirm that this is a first-order reaction.



Scheme 40: The effect of catalyst loading on the initial rate.

We wanted to find out the exact wavelength for the activation of the catalyst. First, the emission spectra of three light sources (180 W Hg lamp, 75 W Xe lamp, and 23 W household lamp) were measured (Scheme 41 (a)). Both of the Hg lamp and Xe lamp have strong emissions in the UV and visible light region. The emission spectrum of a Xe lamp is continuous, but the Hg and household lamps are discrete. As we expect, the higher power of light represents a higher intensity of light emission, which means a higher photon flux was produced. The UV-Vis absorption spectrum shows that TBA[Fe] has absorption maxima at 242, 263, 292, and 370 nm and, interestingly, there is a saddle point at 410 nm (Scheme 41 (a)). A conversion-wavelength correlation of the TBA[Fe]-catalyzed rearrangement of **111** showed that the complex has the highest activity at 415 nm, which

is close to the saddle point within the absorption curve of the ferrate. It is notable that a significant drop in conversion was observed at wavelengths between 405 nm and 370 nm (Scheme 41 (a)).



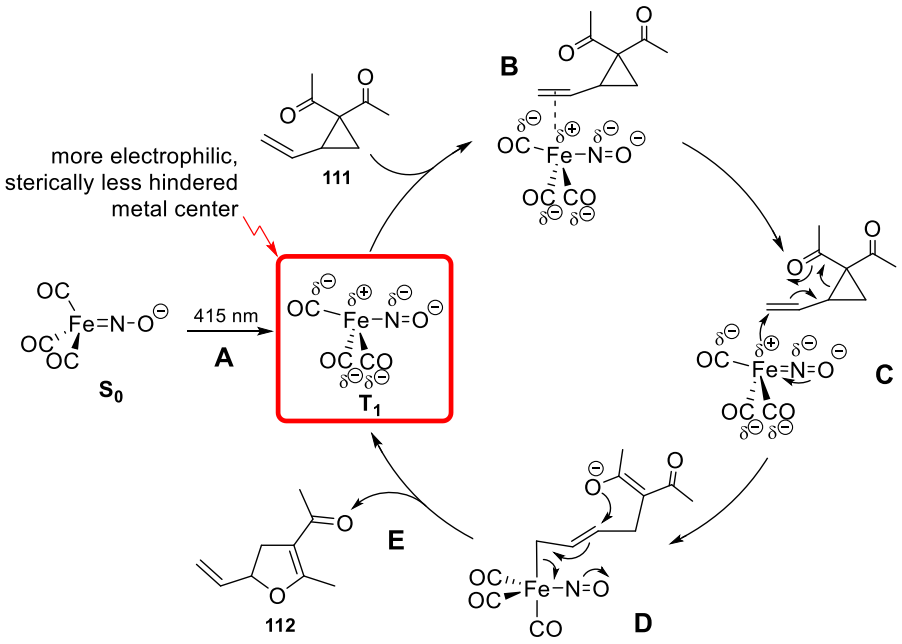
(a) (b)

Scheme 41: (a) Overlay of emission and absorption spectra with the conversion-wavelength correlation of the rearrangement of VCP **111**. (b) Schematic energy level diagram along with CASSCF/def2-TZVPP equilibrium structures of $[Fe(CO)_3(NO)]$. Anionic ground state S_0, anionic lowest singlet excited state S_1, anionic lowest triplet excited state T_1, anionic triplet state T_2, and neutral doublet ground state D_0. The DFT (PBE/def2-TZVPP) derived S_0 equilibrium structures of the anionic ferrate is shown in square brackets.

At the current stage of the research, we believe that this higher photon flux accounts for the increase in reactivity, *e.g.* in the rearrangement of ACPs. Based on our assumption that TBA[Fe] is the active catalyst and in order to get a deeper insight into the electronic structure of the potential activated species, quantum chemical investigations were carried out.

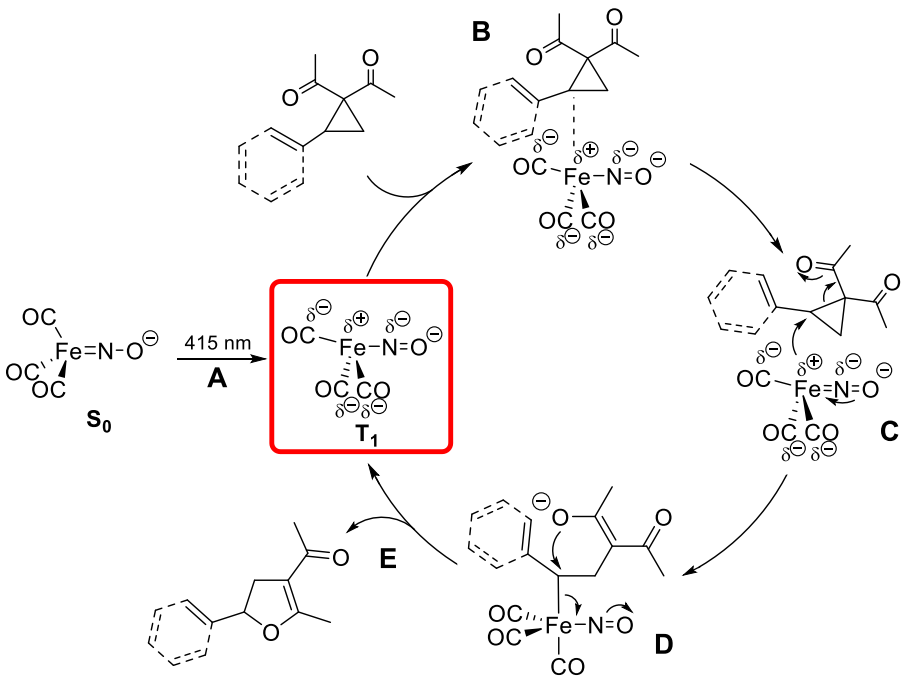
The theoretical studies were done in collaboration with Prof. Dr. Köhn's group and Fabian Rami from our group.[67] The excited state structures calculated using CASSCF are shown in Scheme 41 (b), along with a schematic energy level scheme derived from MRCI+Q and CASSCF calculations. The calculation result showed that the energy levels of the S_1 and the T_2 state are close, especially at the relaxed S_1 structure where the S_1 energy is even 0.03 eV below the T_2 energy at the CASSCF level. This is in agreement with the S_1 structure, which has an Fe-N-O bond angle of 144°, indicating the loss of *π*-bond character and the reduction of the NO ligand (the electron density is shifted from the metal center to the NO ligand). The near-degeneracy close to the S_1 equilibrium structure will cause efficient intersystem crossing to T_2, followed by swift internal conversion to T_1. Therefore, we assume that the T_1 state is the active $[Fe(CO)_3(NO)]^-$ species, which shows an almost trigonal-bipyramidal configuration with an Fe-N-O angle of close to 180°. In this state, the metal center features an open (and sterically accessible) binding site. This could explain the inapparent of the steric effect in the Cloke-Wilson rearrangement of VCPs under the photochemical conditions.

Based on all the experimental, spectroscopic, and theoretical results, we proposed an S_N2'-*anti* mechanism for the photochemical TBA[Fe]-catalyzed Cloke-Wilson rearrangement of VCPs (Scheme 42).



Scheme 42: Mechanistic proposal for the photochemical Fe-catalyzed Cloke-Wilson rearrangement of VCPs following an S_N2'-*anti* mechanism.

The catalyst at the ground state S_0 absorbs light at 415 nm and then is excited to the T_1 state through intersystem crossing and internal crossing (stage A). At the T_1 state, the more electrophilic and wide opened metal center can easily approach to the double bond of the VCP (stage B). At this stage, the more electron-deficient Fe can coordinate the electron-rich alkene more easily. The nitrogen and the carbon atoms of the CO ligand act as electron-donating centers that transfer electrons into the antibonding $\pi^*_{C=C}$-orbital of the C=C bond within the substrate (stage C). The allyl-Fe complex, which is formed upon electron transfer reacts with the O-nucleophile in an S_N2'-*anti* fashion (stage D), forming the dihydrofuran product and regenerating the Fe complex in the T_1 state (stage E).



Scheme 43: Mechanistic proposal for the photochemical Fe-catalyzed Cloke-Wilson rearrangement of VCPs/ACPs following an S_N2-*anti* mechanism.

On the other hand, an S_N2-*anti* mechanism was proposed for the ACPs in the TBA[Fe]-catalyzed Cloke-Wilson rearrangement (Scheme 43). In addition, this mechanism is also possible for VCPs. In the first step, the trigonal-bipyramidal configurated T_1 state is formed after irradiation of light (stage A). Then the electron-rich, formally unsaturated and sterically less hindered Fe complex could access the $\sigma^*_{c\text{-}c}$-orbital of the tertiary benzylic (or allylic) carbon atom in aryl- or vinylcyclopropanes (stage B). The electrons are transferred from the NO ligand to the cyclopropane with concomitant C-C bond activation (stage C). The reaction with the formed O-nucleophile in an S_N2-fashion closes the catalytic cycle (stage D) with the formation of the respective dihydrofuran product and the regeneration of the Fe complex in the T_1 state (stage E).

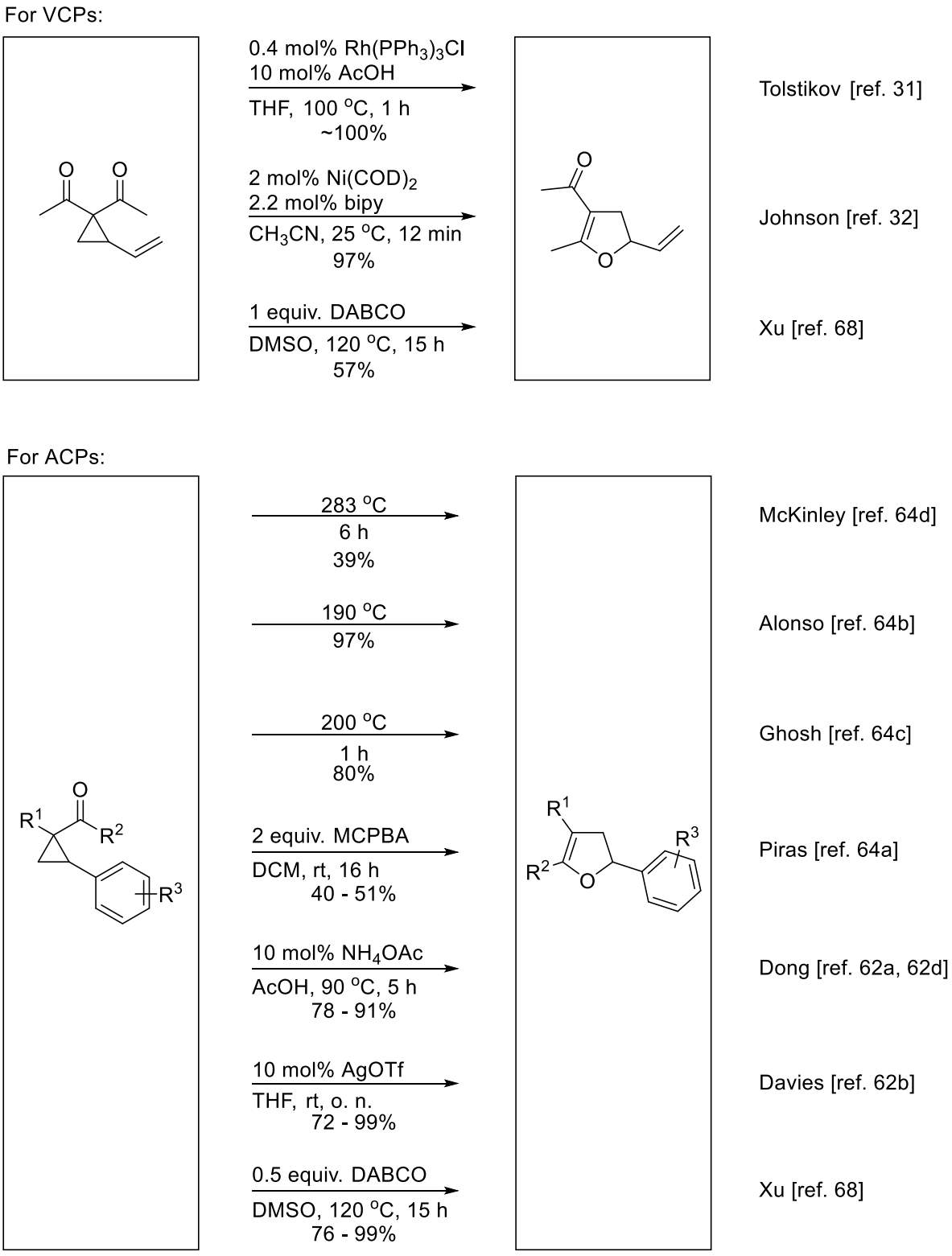
2.3 Conclusion and Outlook

Herein we disclose a study of the Cloke-Wilson rearrangement of vinyl- and arylcyclopropanes by using photoactivated $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) as well as comparing these results with thermal activations of TBA[Fe]. The catalyst shows good reactivity under both conditions. As compared with known procedures in the literature, our methods provide a convenient, economic, and environmentally friendly way to prepare a variety of substituted dihydrofurans under mild conditions (Scheme 44).[31-32, 68]

In addition, *in-operando* spectroscopic investigations suggest that the Fe-carbonyl catalyst does not undergo decarbonylation under photochemical conditions. This is the first example of nondecarbonylative photochemical activation of a metal-carbonyl catalyst.

Furthermore, the wavelength *versus* conversion study showed that the iron carbonyl was best activated by light at 415 nm. The following quantum chemical investigation suggested that the ferrate has an S_1-state, from which the activated species can undergo intersystem crossing into the nearly isoenergetic triplet state, T_2, from which the energetically favorable T_1 state is accessible via internal conversion. The catalytically active state T_1 has a nearly 180° of Fe-N-O bond angle, which provides a wide-opened binding site of the metal center. The quick transformation of the substrate to the product starts after enough activated T_1 state was formed.

These results open up a new research direction using $Bu_4N[Fe(CO)_3(NO)]$ as a stable catalyst that is selectively activated at 415 nm, a region in which common (non-catalytic) photochemical organic (side) reactions are not operative. Studies aiming to use this concept for the activation of less reactive C-H and C-C bonds are currently being carried out in our laboratories.

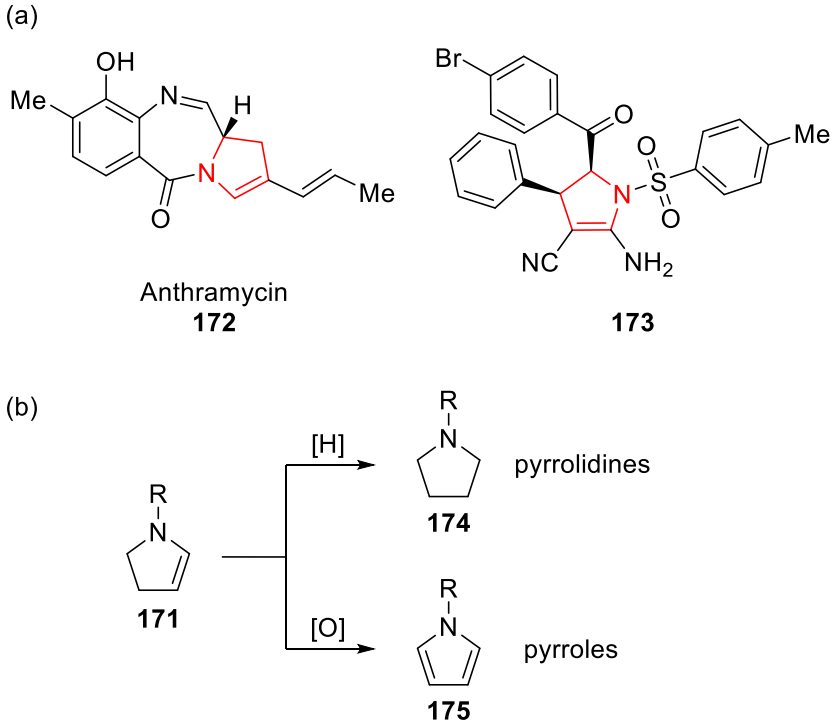


Scheme 44: Cloke-Wilson rearrangements of VCPs and ACPs.

3. TBA[Fe]-catalyzed Cyclopropylimine Rearrangement

3.1 Purpose of this Research

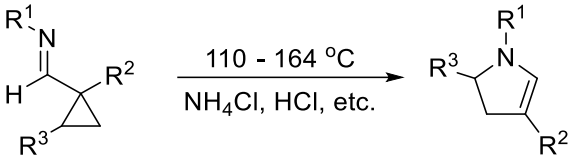
2,3-Dihydropyrroles **171** have gained significant attention among nitrogen-containing five-membered heterocycles because they are important skeletons of various natural products and pharmaceutically relevant compounds.[69] For example, anthramycin **172** and *cis*-2-pyrroline **173**, which are potential antitumor drugs (Scheme 45 (a)).[70] In addition, 2,3-dihydropyrroles can be used as versatile synthetic intermediates in the preparation of functionalized pyrrolidines **174** (their fully reduced counterparts), pyrroles **175** (their fully oxidized counterparts), and other more complex systems (Scheme 45 (b)).



Scheme 45: (a) Representative examples of biologically active products. (b) Reactivity of 2,3-dihydropyrroles **171**.

A variety of synthetic methods to prepare 2,3-dihydropyrroles have been reported such as [3+2] cycloaddition,[71] nucleophilic amine ring-opening cyclization,[72] and iodocyclization of alkenyl-substituted *β*-enamino esters.[73] Metal-mediated reactions and other approaches are also reported.[74] Among all of them, one of the common ways to

obtain 2,3-dihydropyrroles is via cyclopropylimine rearrangement. However, the reactions usually require very high temperature[75] and normally combine with strong Lewis acid[76] or Brønsted acid[77] (Scheme 46). Therefore, an efficient and practical way for performing the cyclopropylimine rearrangement is eagerly awaited.



176 **177**

R^1, R^2, R^3 = Alkyl, Aryl

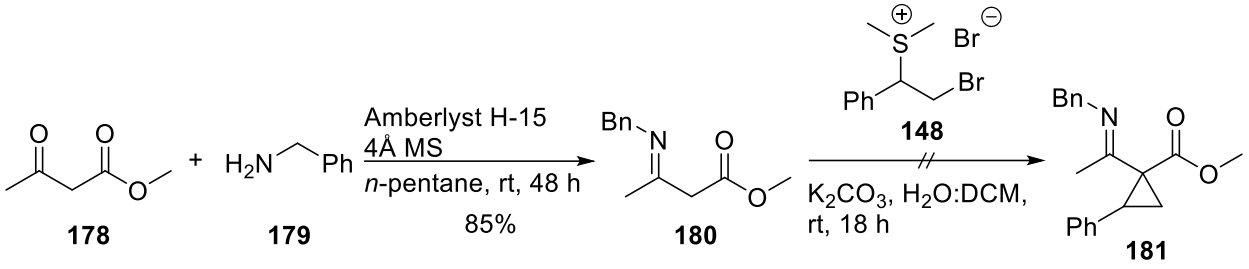
Scheme 46: 2,3-Dihydropyrrole formation via cyclopropylimine rearrangement.

Since we have successfully developed the TBA[Fe]-catalyzed Cloke-Wilson rearrangement of vinyl- and arylcyclopropanes, we believe that the cyclopropylimines might undergo a similar pathway to rearrange to the desired 2,3-dihydropyrroles. Furthermore, to the best of our knowledge a transition-metal-catalyzed cyclopropylimine rearrangement has not yet been described. The aim of this project is to develop a convenient, rapid, and economical method for cyclopropylimine rearrangement by our ferrate catalyst.

3.2 Results and Discussion

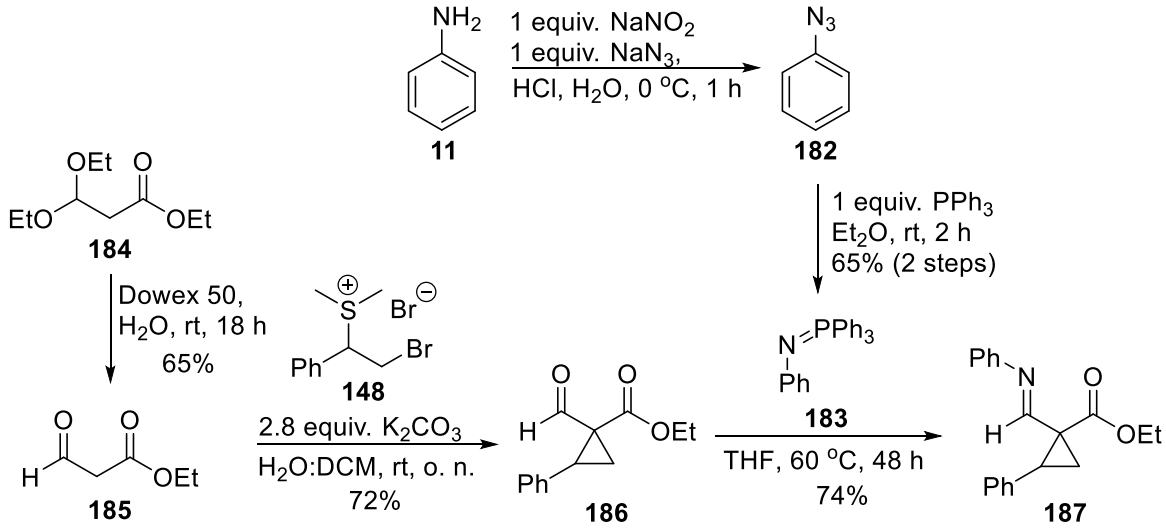
3.2.1 Cyclopropylimine Synthesis

In order to prepare the suitable cyclopropylimines for the optimization reactions, we proposed different synthetic routes. In the beginning, we examined the cyclopropanation method that has been used for the preparation of arylcyclopropanes in Chapter 2 (Scheme 47). Methyl 3-benzyliminobutanoate **180** was easily obtained by the condensation of methyl acetoacetate **178** and benzylamine **179**. However, the desired cyclopropylimine was not formed via the cyclopropanation of methyl 3-benzyliminobutanoate **180** and bromosulfonium bromide **148**. Both of the starting materials remained nonreacted.



Scheme 47: Preparation of cyclopropylimine via bromosulfonium bromide **148** cyclopropanation with methyl 3-benzyliminobutanoate **180**.

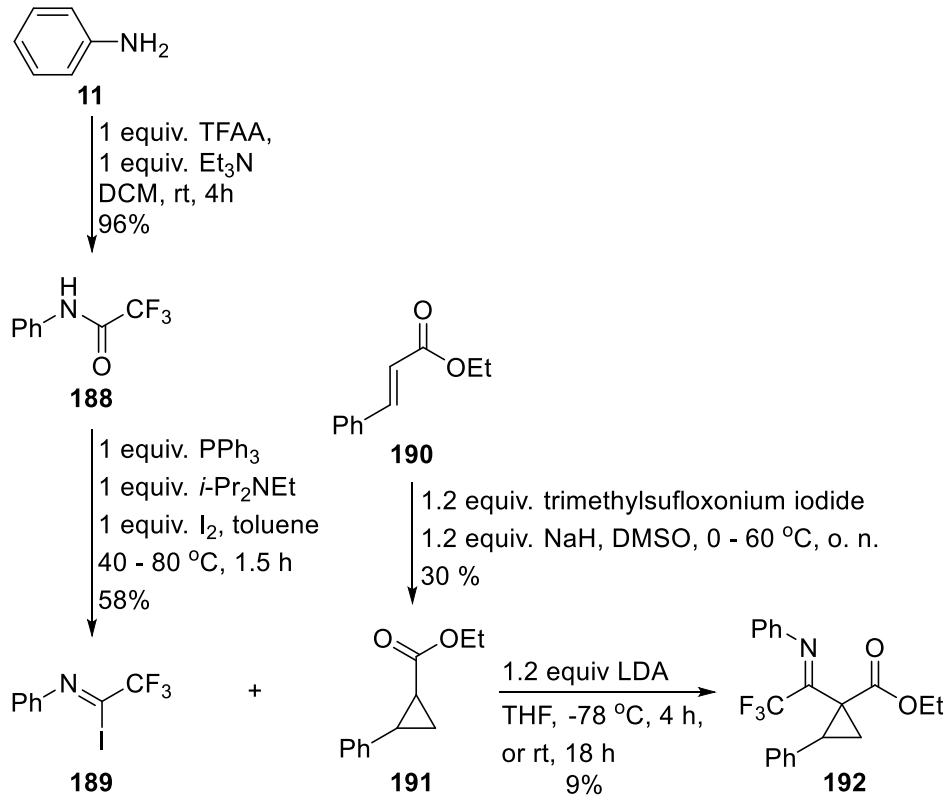
We successfully synthesized the desired cyclopropylimine **187** by using the aza-Wittig reaction to construct the carbon-nitrogen double bond (Scheme 48). The aza-Wittig reagent **183** was prepared from aniline **11** via Sandmeyer reaction and subsequent treatment of the intermediate azide **182** with triphenylphosphine. In order to have better yield for the aza-Wittig reaction, formylcyclopropane **186** was chosen, which was synthesized via cyclopropanation from ethyl formylacetate **185**. Formylacetic esters are known to be unstable. They polymerize readily even at room temperature. Therefore, ethyl formylacetate **185** had to be prepared from the corresponding acetal **184** and used immediately after preparation.



Scheme 48: Synthetic route towards cyclopropylimine **187**.

Another way to synthesize cyclopropylimines was also be discovered (Scheme 49). The arylcyclopropane **195** was prepared from ethyl cinnamate **190** via the Corey-

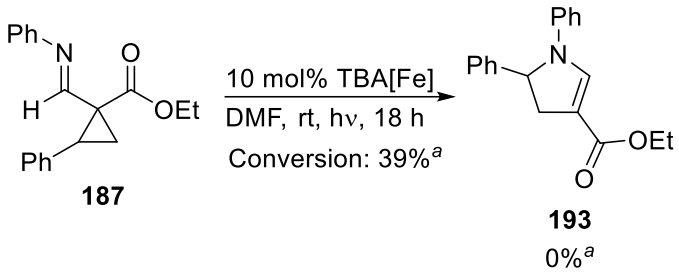
Chaykovsky reaction. Trifluoroacetimidoyl iodide **189** was react with deprotonated arylcyclopropane **191** to form the cyclopropylimine **192**. The trifluoroacetimidoyl iodide **189** could be quickly accessed from aniline **11** in two steps. However, due to the substrate limitations and the low overall yields, we do not use this route any further.



Scheme 49: Synthetic route towards cyclopropylimine **192**.

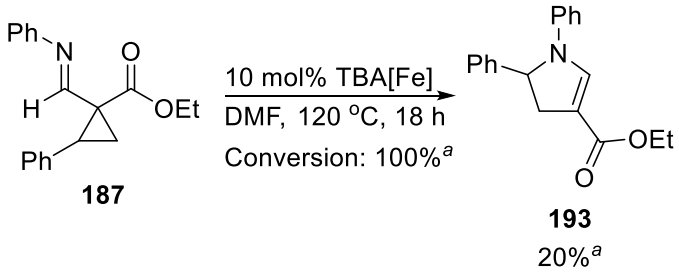
3.2.2 Optimization of the TBA[Fe]-catalyzed Cyclopropylimine Rearrangement

With the cyclopropylimine **187** in hand, we started to optimize the reaction conditions of the rearrangement reaction by using our iron complex. Frist, we tried the standard photochemical conditions of the ACP rearrangement for the cyclopropylimine rearrangement (Scheme 50). However, 61% of the starting material **187** stayed nonreactive, and the desired rearrangement product **193** was not observed.



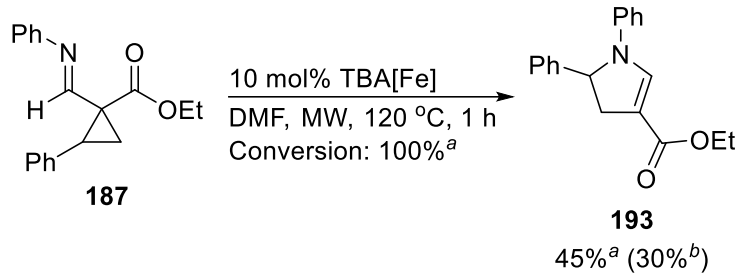
Scheme 50: TBA[Fe]-catalyzed cyclopropylimine rearrangement under photochemical condition. [a]Conversion or yield was determined through ^{1}H-NMR-integration by using mesitylene as internal standard.

Thermal conditions were also tested, carrying out the reaction at 120 °C in an oil bath for 18 hours (Scheme 51). Here we observed full conversion of starting material, but only 20% of 2,3-dihydropyrrole **193** was formed. We assume most of the cyclopropylimine **187** was decomposed, due to the very messy crude ^{1}H-NMR spectrum was seen.



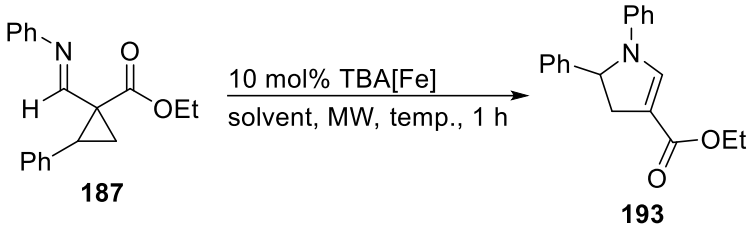
Scheme 51: TBA[Fe]-catalyzed cyclopropylimine rearrangement under thermal condition. [a]Conversion or yield was determined through ^{1}H-NMR-integration by using mesitylene as internal standard.

Fortunately, when the reaction was carried out under microwave irradiation at 120 °C for one hour, we could observe 45% of ^{1}H-NMR yield and 30% of isolated yield of desired rearrangement product **193** (Scheme 52). Similar with the thermal conditions, the decomposition of starting material was observed from the crude ^{1}H-NMR spectrum. Although the isolated yield is not ideal, it gave us a starting point to optimize the reaction conditions.



Scheme 52: TBA[Fe]-catalyzed cyclopropylimine rearrangement under microwave irradiation (200 W). [a]Conversion or yield was determined through ^{1}H-NMR-integration by using mesitylene as internal standard. [b]Isolated yield.

Table 7. Optimization of the cyclopropylimine rearrangement under microwave condition.



Entry[a]	Solvent	T. [°C]	**193**[b] [%]	**187**[b] [%]
1	DMF	80	6	22
2	DMF	100	20	-
3	DMF	120	45(30[c])	-
4	1,2-DCE	120	13	-
5	toluene	120	5	18
6[d]	DMF	120	13	20
7	DMF	135	76(69[c])	-
8[e]	DMF	135	45	-
9[d]	DMF	135	13	5

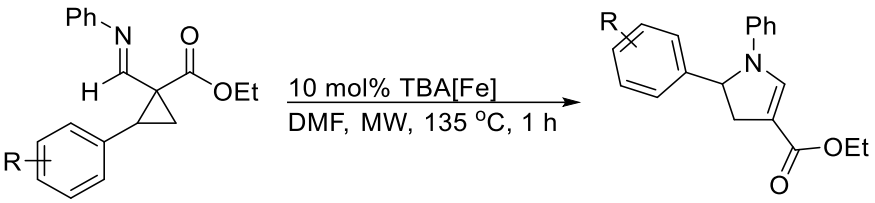
[a] All reactions were performed with the substrate (0.4 mmol), and 10 mol% of TBA[Fe] in solvent (1 mL) under microwave irradiation (200 W) at indicated temperature for 1 h. [b] Yield was determined through ^{1}H-NMR-integration by using mesitylene as internal standard. [c] Isolated yield. [d] No TBA[Fe]. [e] 30 min.

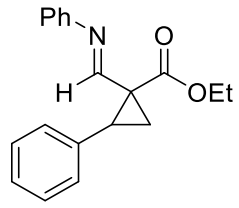
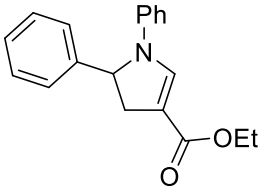
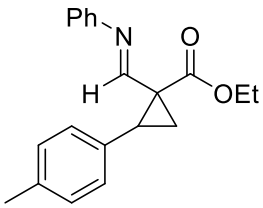
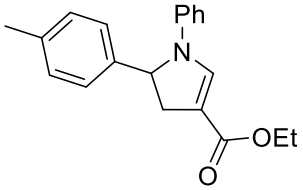
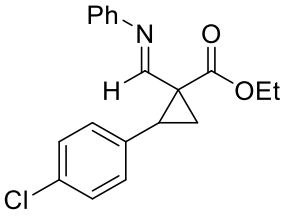
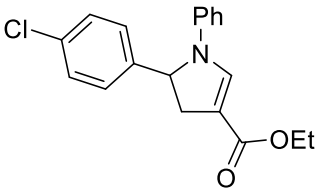
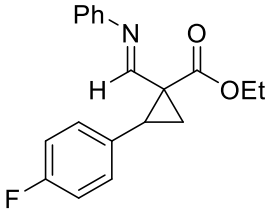
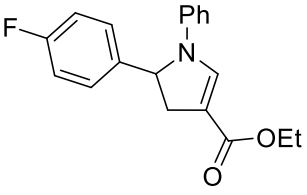
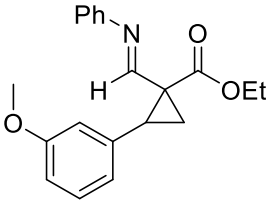
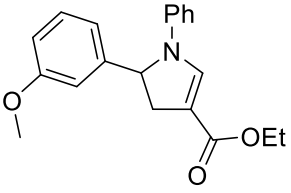
The optimization of the cyclopropylimine rearrangement of cyclopropylimine **187** under microwave conditions is summarized in Table 7. We first changed the solvent from DMF to 1,2-DCE, but the yield of 2,3-dihydropyrrole **193** dropped to 13% (Entry 4, Table 7). When toluene was used, the yield of 2,3-dihydropyrrole **193** is even lowered to 5% (Entry 5, Table 7). DMF remained the best solvent for the reaction throughout the optimizations. (Entry 3, Table 7). Without using TBA[Fe] in the reaction, only 13% yield of 2,3-dihydropyrrole **193** was found (Entry 6, Table 7). In order to reduce decomposition of the starting materials, we considered to decrease the reaction temperature. Unfortunately, 78% conversion was observed when the reaction was carried out at 80 ^{o}C, but the yield of 2,3-dihydropyrrole **193** dropped to 6%. When the reaction temperature was reduced to 100 ^{o}C, only 20% of 2,3-dihydropyrrole **193** was observed, even though there was no starting material left after 1 hour microwave irradiation. (Entry 1 -2, Table 7). It implies that cyclopropylimine **187** underwent decomposition under microwave conditions during the reaction time. Therefore, we changed our strategy to increase the reaction temperature, in order to force a faster transformation to the cyclopropylimine before its thermal decomposition. Luckily, when the reaction temperature was increased to 135 ^{o}C, the yield of 2,3-dihydropyrrole **193** increased to 76% (Entry 7, Table 7). Without TBA[Fe] at 135 ^{o}C, the yield of 2,3-dihydropyrrole **193** was only 13% (Entry 9, Table 7). When the reaction time was reduced to 30 minutes, the yield decreased to 45% (Entry 8, Table 7).

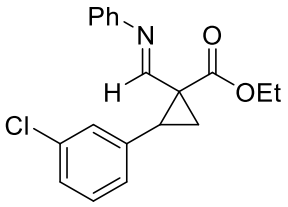
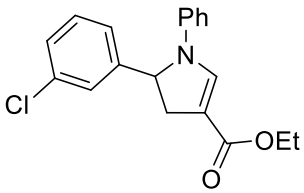
3.2.3 Substrate Scope of the TBA[Fe]-Catalyzed Cyclopropylimine Rearrangement

With the optimized conditions found, we turned our attention towards an exploration of the scope of the TBA[Fe]-catalyzed cyclopropylimine rearrangement under microwave conditions. The functionalized cyclopropylimines were synthesized from the corresponding bromosulfonium bromides by following the procedure that has been described in Chapter 3.2.1. All the functionalized cyclopropylimines are easyly hydrolyzed to the initial amines under acid condition, so 3% of triethylamine must be added to the eluent of the column chromatography. The cyclopropylimines quickly have to be subjected to the TBA[Fe]-catalyzed reaction quickly after purification. The substrate scope of the TBA[Fe]-catalyzed cyclopropylimine rearrangement is summarized in Table 8.

Table 8. Substrate scope of the TBA[Fe]-catalyzed cyclopropylimine rearrangement.



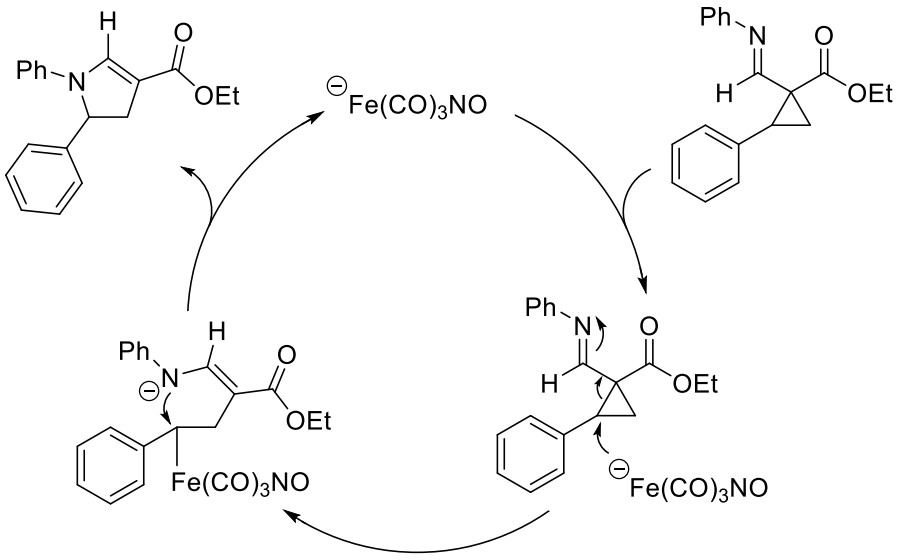
Entry[a]	Substrate	Product	Yield[b] [%]
1	 **187**	 **193**	69
2	 **194**	 **195**	90
3	 **196**	 **197**	44
4	 **198**	 **199**	48
5	 **200**	 **201**	71

6  **202**  **203** 63

[a] All reactions were performed with the substrate (0.5 mmol), and 10 mol% of TBA[Fe] in DMF (1 mL) under microwave irradiation (200 W) at 135 °C for 1 h. [b] Isolated yield.

All the cyclopropylimines **187** - **203** successfully underwent the rearrangement to form the 2,3-dihydropyrroles. The yield (90%) of the cyclopropylimine **194** with an electron-donating methyl group at *para*-position of the aromatic unit is much higher than the yield (69%) for the non-substituted phenyl cyclopropylimine **187** (Entry 1-2, Table 8). In addition, yields of the cyclopropylimines (**196** and **198**) with electron-withdrawing groups such as Cl and F atom at *para*-position of the aromatic units are only 44% and 48% respectively (Entry 3-4, Table 8). The same effect was also seen for the cyclopropylimine with *meta*-substitution at the aromatic unit. The yield of methoxy-substituted cyclopropylimine **200** is 71% and chloro-substituted cyclopropylimine **202** is 63% (Entry 1-2, Table 8).

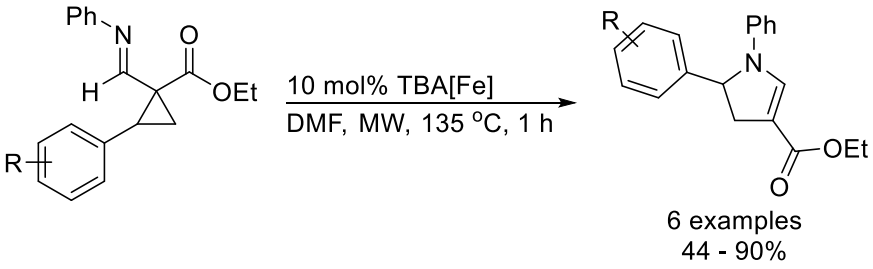
Although the reaction mechanism is not yet clear, we assumed the reaction pathway might be similar to the TBA[Fe]-catalyzed Cloke-Wilson rearrangement of arylcyclopropanes. The proposed mechanism is shown in Scheme 53. First, the electron rich iron complex $Fe(CO)_3(NO)^-$ attacks the phenyl carbon on the cyclopropane. The cyclopropane ring is opened to form an ene-amide. Then, the nucleophilic nitrogen atom attacks back to the iron-coordinated carbon in an S_N2-fashion, yielding the 2,3-dihydropyrrole and releasing the iron complex (TBA[Fe]).



Scheme 53: Proposed mechanism for the TBA[Fe]-catalyzed cyclopropylimine rearrangement.

3.3 Conclusion and Outlook

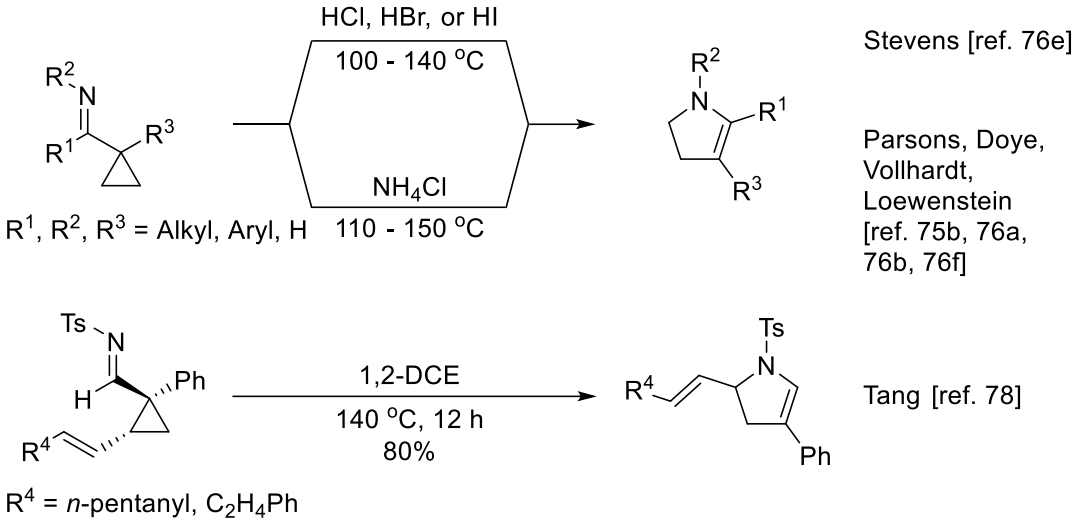
Herein we showed a study of the TBA[Fe]-catalyzed cyclopropylimine rearrangement. A series of functionalized cyclopropylimines were applicable in this method (Scheme 54).



Scheme 54: TBA[Fe]-catalyzed cyclopropylimine rearrangement.

Comparing with the procedures in the literature, it provides an efficient, simple, and inexpensive way to transform cyclopropylimines to 2,3-dihydropyrroles (Scheme 55).[75b, 76a, 76b, 76e, 76f, 78] We anticipate that this approach could be useful in synthesis, drug discovery, and various fields in which 2,3-dihydropyrroles are important. Furthermore, these results demonstrated that the cyclopropylimine rearrangement can successfully proceed in transition-metal-catalyzed reactions.

A further investigation of the reaction mechanism is still ongoing. A greater variety of functionalized cyclopropylimines and vinylcyclopropylimines are going to be synthesized and tested in future work.

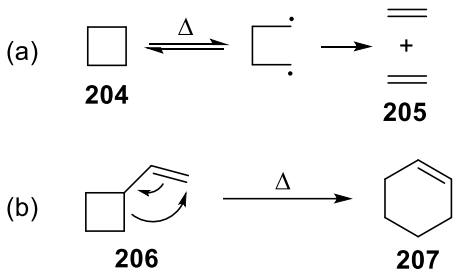


Scheme 55: Cyclopropylimine rearrangement under thermal or (Lewis) acid-catalyzed conditions.

4. TBA[Fe]-Catalyzed Cyclobutane Rearrangement

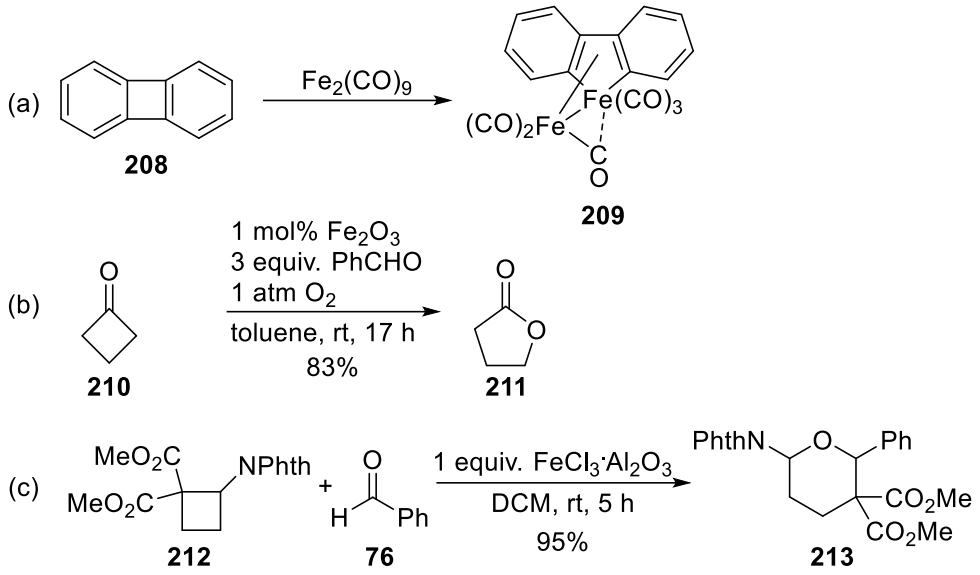
4.1 Purpose of this Research

Reactions of cyclobutane-containing systems normally include ring-opening or ring-expansion in the mechanistic steps because of the ring strain.[34b] For example, thermolysis of cyclobutane **204** leads to a fragmentation to yield olefins **205** (Scheme 56 (a)). A thermally-induced vinylcyclobutane rearrangement transforms vinylcyclobutane **206** to cyclohexene **207** via a 1,3-alkyl shift (Scheme 56 (b)).



Scheme 56: Ring-opening and ring-expansion reaction of cyclobutanes

Due to the relatively weaker C-C bond of cyclobutanes than the normal C-C bond of alkanes, it is able to undergo all kinds of metal-catalyzed C-C bond activation reactions which have been described in Chapter 1.3.2. However, among all these examples, iron-catalyzed C-C bond activation of cyclobutanes are still in development. There are only a few iron-involved cyclobutane activation reactions have been reported in the literature. Yeh showed that $Fe_2(CO)_9$ can activate the bridging bonds of biphenylene **208** to generate the iron complex $Fe_2(CO)_5(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^4\text{-}(C_6H_4)_2)$ **209** (Scheme 57 (a)).[79] Murahashi developed an iron-catalyzed Baeyer-Villiger oxidation of ketones, in which Fe_2O_3 assists the formation of *γ*-butyrolactone **211** under aerobic conditions.[80] One has to note that iron does not directly cleave the C-C bond of ketone **210**, it plays only a minor role in the actual scission (Scheme 57 (b)). Waser used $FeCl_3{\cdot}Al_2O_3$ to catalyze [4+2]-annulations between aldehyde **76** and aminocyclobutane **212** (Scheme 57 (c)).[81] The iron complex is employed as a Lewis acid, so it is not participating in the C-C bond scission as well. Nevertheless, a direct iron-catalyzed C-C bond activation of saturated cyclobutanes has not been reported yet.



Scheme 57: cyclobutane reactions which involved iron catalysts.

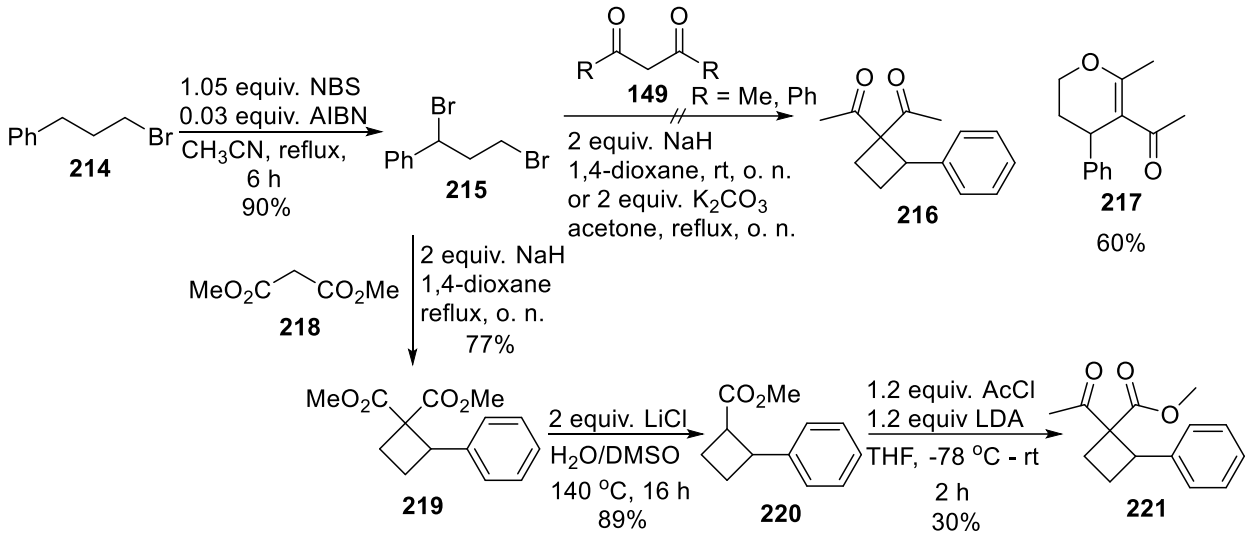
The low-valent iron complex TBA[Fe] is known to activate the C-C bond of vinylcyclopropanes, which has been shown in Chapter 1.3.1.2. In addition, we also described the TBA[Fe]-catalyzed Cloke-Wilson rearrangement of vinyl- and arylcyclopropanes and cyclopropylimine rearrangement in this dissertation. Therefore, we believe that TBA[Fe] is the best choice for developing an iron-catalyzed C-C bond activation of cyclobutanes.

4.2 Results and Discussion

4.2.1 Arylcyclobutane Synthesis

Similar to vinylcyclopropane synthesis, we were thinking to use a cyclization of 1,3-diketones **149** with 1,3-dibromo-1-phenylpropane **215** yielding the corresponding arylcyclobutane **216** (Scheme 58). 1,3-dibromo-1-phenylpropane **215** was easily synthesized from 1-bromo-3-phenylpropane **214** with 90% isolated yield. However, we did not obtain the desired arylcyclobutane **216** from 1,3-dibromo-1-phenylpropane **215** by using different deprotonation conditions. Instead, 3,4-dihydropyran **217** was formed as the second substitution was done by *O*-nucleophilic attack. Unfortunately, when the reaction temperature was reduced to room temperature or 0 °C, only the yield of 3,4-dihydropyran **217** was decreased or there was no conversion, but no desired

arylcyclobutane **216** was observed.

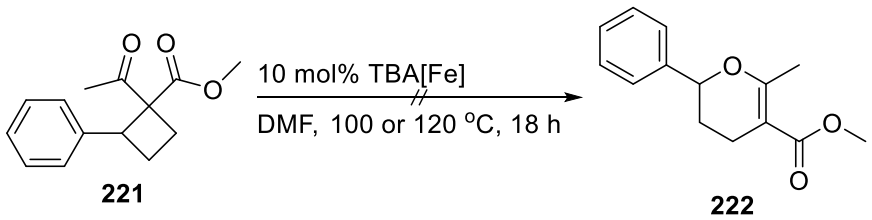


Scheme 58: Synthesis route towards arylcyclopropane **221**.

We then modified the synthetic route to use dimethyl malonate **218** with 1,3-dibromo-1-phenylpropane **215** forming cyclobutane **219**. The diester-substituted cyclobutane **219** can be smoothly converted to a monoester-substituted cyclobutane **220** by Krapcho decarboxylation. The final desired arylcyclobutane **221** was obtained by acetylation of cyclobutane **220** with acetyl chloride.

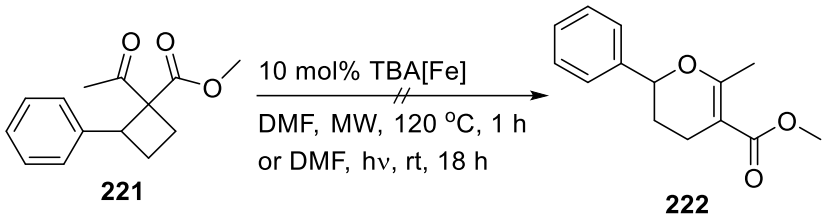
4.2.2 TBA[Fe]-catalyzed Arylcyclobutane Rearrangement

After successfully synthesizing the arylcyclobutane **221**, we tried to activate its C-C bond by using TBA[Fe] under different reaction conditions. In the beginning, the general thermal conditions were tested (Scheme 59). Unfortunately, no conversion was observed either when the reaction was heated to 100 °C or 120 °C with 10 mol% of iron catalyst in DMF for 18 hours.



Scheme 59: TBA[Fe]-catalyzed arylcyclobutane rearrangement under thermal conditions.

We also tried to use the reaction conditions of the TBA[Fe]-catalyzed Cloke-Wilson rearrangement of arylcyclopropanes (Scheme 60). However, both photochemical and microwave conditions could not transform arylcyclopropane **221** to 3,4-dihydropyran **222**, even in the case of increased catalyst loading to 10 mol%.

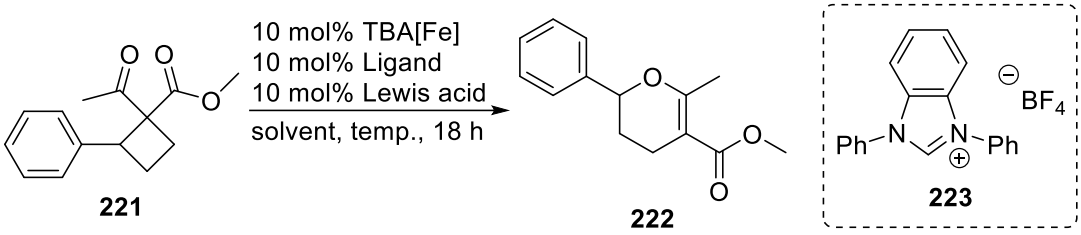


221 **222**

Scheme 60: TBA[Fe]-catalyzed arylcyclobutane rearrangement under photochemical and microwave (200 W) conditions.

Reactions with additional ligands or Lewis acids were investigated as well. The results are summarized in Table 9. Adding triphenylphosphine or NHC ligand **223** to the reaction mixture did not help to improve the yield (Entry 1 and 2, Table 9). Since Lewis acids are known to assist ring opening reactions, we then tried to added a variety of them in the reaction. Unfortunately, we could not observe any conversion even when adding additional $ZnCl_2$ or $SnCl_2$ and combing with NHC ligand **223** at 100 °C or 130 °C as well (Entry 3, 4 and 6, Table 9). It seems like $AlCl_3$ is a too strong Lewis acid for arylcyclobutane **221** because no starting material was left after 18 hours, but no desired 3,4-dihydropyran **222** could be detected (Entry 5, Table 9), hence we assumed that arylcyclobutane **221** was completely decomposed. In the end, the catalyst loading, ligand **223**, and Lewis acid ($Y(OTf)_3$, $Yb(OTf)_3$, and $Sn(OTf)_3$) were increased to 1 equivalent, but regrettably no 3,4-dihydropyran **222** was formed (Entry 7-9, Table 9). No conversion was observed when $Y(OTf)_3$ or $Yb(OTf)_3$ was used (Entry 7 and 8, Table 9). The starting materials were decomposed when $Sn(OTf)_3$ was used (Entry 9, Table 9).

Table 9. TBA[Fe]-catalyzed arylcyclobutane rearrangement.

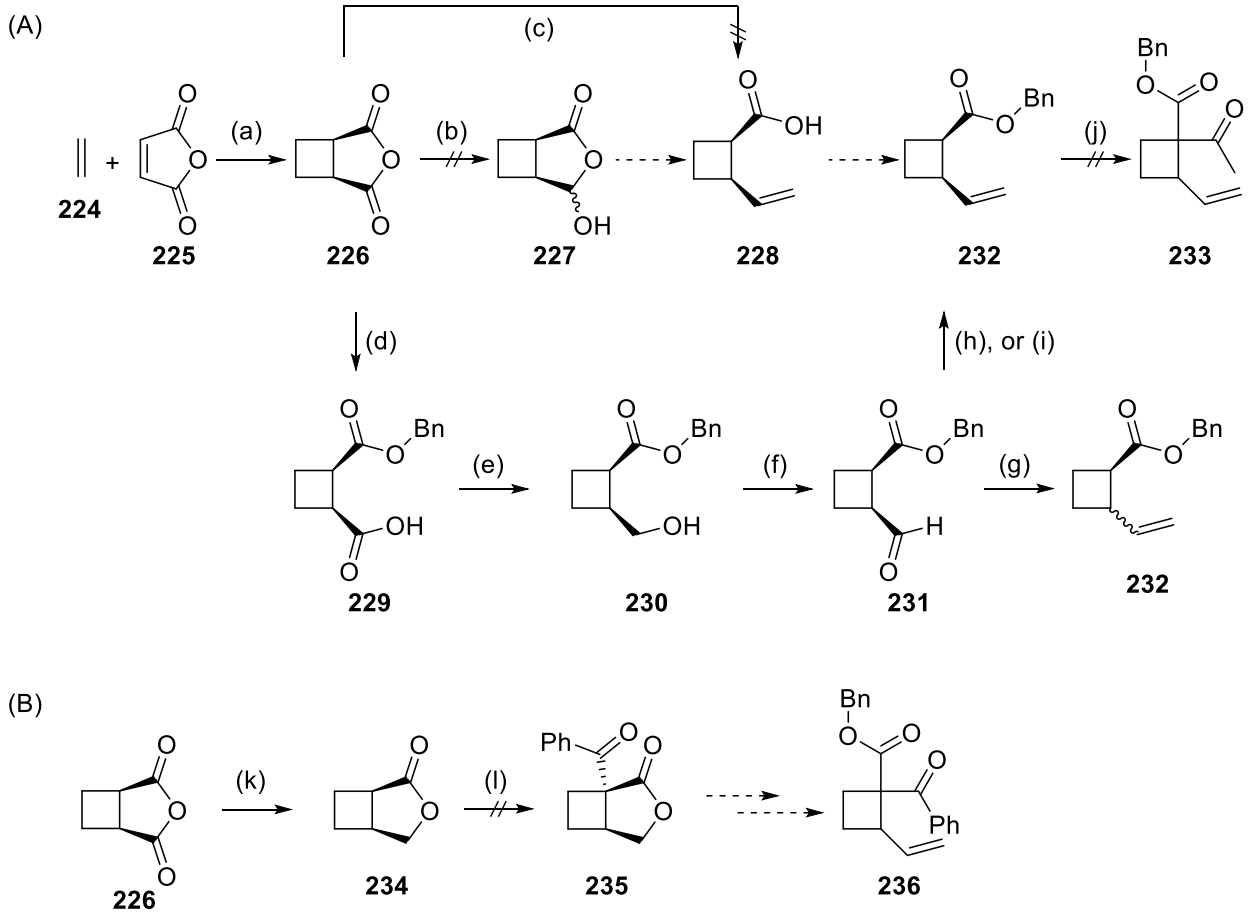


Entry[a]	Ligand	Lewis acid	T. [°C]	Solvent	Yield[b] [%]
1	PPh_3	-	120	DMF	-
2[c]	**223**	-	100	THF	-
3[c]	**223**	$ZnCl_2$	100	THF	-
4	**223**	$ZnCl_2$	130	THF	-
5	**223**	$AlCl_3$	130	THF	-
6	**223**	$SnCl_2$	130	THF	-
7[d]	**223**	$Y(OTf)_3$	130	THF	-
8[d]	**223**	$Yb(OTf)_3$	130	THF	-
9[d]	**223**	$Sn(OTf)_3$	130	THF	-

[a] All reactions were performed with the substrate (0.1 mmol), 10 mol% of TBA[Fe], and 10 mol% of ligand in solvent (1 mL) for 18 h. The NHC ligand was deprotonated by $NaNH_2$ (0.06 mmol). [b] Determined through ^{1}H-NMR-integration by using mesitylene as internal standard. [c] 24 h. [d] 1 equiv. of TBA[Fe], ligand, and Lewis acid, 6 equiv. of $NaNH_2$.

4.2.3 Vinylcyclobutane and Vinylcyclobutanone Synthesis

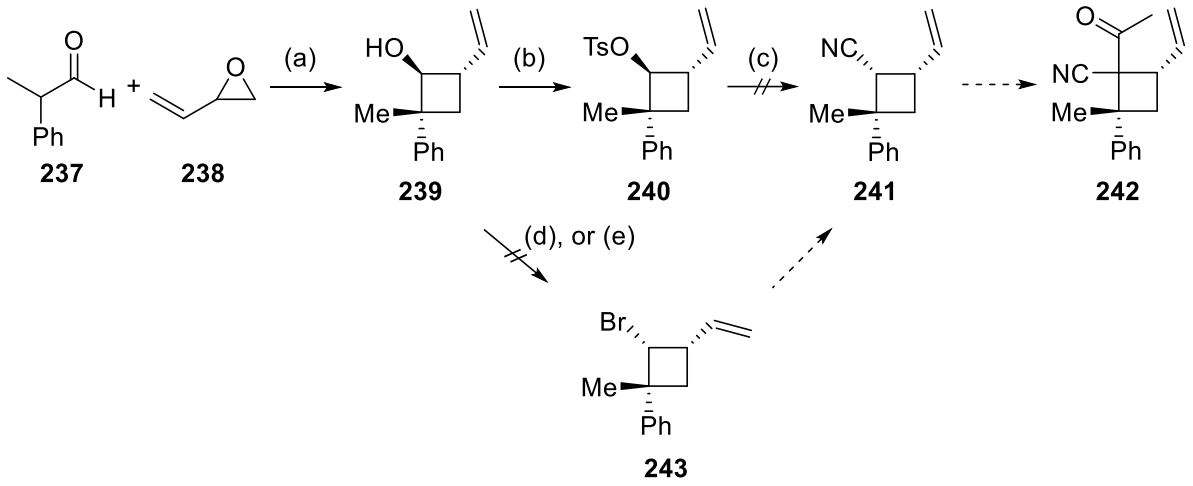
Since we were not able to activate the C-C bond of arylcyclobutane **221** by TBA[Fe], we considered another type of cyclobutane: vinylcyclobutane. In order to obtain vinylcyclobutanes for the initial investigations, we started to search for a synthetic procedure in the literature. However, there is no concise route to reach this type of products. Therefore, we planned a multi-step route to get the desired vinylcyclobutanes (Scheme 61).



Scheme 61: Synthetic route of vinylcyclobutane. (a) Acetophenone, CH_3CN, hν, rt, 5 h, 65%. (b) 1 equiv. $LiAlH(Ot\text{-}Bu)_3$, THF, -78 °C to -25°C, 5 h. (c) 1) 1 equiv. $LiAlH(Ot\text{-}Bu)_3$, THF, -78 °C to -20 °C. 2) 1.15 equiv. Ph_3PCH_3Br, 1.12 equiv. *n*-BuLi, THF, 0 °C to rt, o. n. (d) 0.83 equiv. Benzyl alcohol, 0.83 equiv. DMAP, DCM, rt, 18 h, 81%. (e) 2.2 equiv. BH_3·THF, THF, -10 °C to rt, overnight, 56%. (f) 1.5 equiv. DMP, DCM, rt, o. n., 85%. (g) Wittig reaction: 1.15 equiv. Ph_3PCH_3Br, 1.12 equiv. *n*-BuLi, THF, 0 °C to 40 °C, o. n., 13% (h) Takai-Lombardo methylenation: 1.2 equiv. $Zn\text{-}CH_2Br\text{-}TiCl_4$, THF, DCM, 5 °C, 3 days then rt, 4 h, 23%. (i) Tebbe methylenation: 1.1 equiv. Cp_2TiCl_2, 2.2 equiv. $AlMe_3$, toluene, THF, rt, 3 days then rt, 6 h, 22%. (j) 2.6 equiv. Benzoyl chloride, 1.3 equiv. LDA, THF, -78 °C to rt, o. n. (k) 1.03 equiv. $NaBH_4$, THF, -65 °C, 2 h, 34%. (l) 1.5 equiv. Benzoyl chloride, 1.3 equiv. LDA or *t*-BuLi, THF, -78 °C, 2 h - o. n.

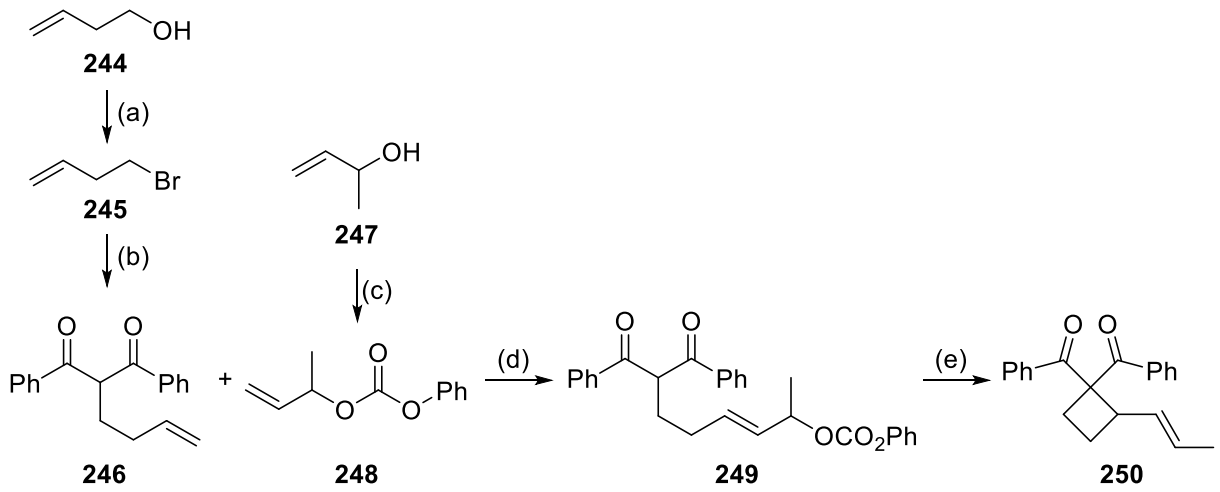
The cyclobutane ring was formed in the first instance via a [2+2] cycloaddition between ethene **224** and maleic anhydride **225** (Scheme 61 (A)). We then wanted to selectively reduce *cis*-cyclobutane dicarboxylic acid anhydride **226** to a hydroxybutyrolactone **227**, which can then be quickly constructed to form a vinyl group in the next step. However, after trying many reducing reagents and reaction conditions for the reduction of **226**, we could only isolate the over-reductive product *γ*-butyrolactone **234**, but not the desired hydroxybutyrolactone **227**. We also tried to combine the reduction and Wittig reaction in one pot to prevent the over reduction which might form during workup of the reaction mixture, but still, no vinylcyclobutane **228** was observed. The synthesis route was modified again. The acid anhydride **226** was transformed to a benzyl ester **229**. The carboxyl group of **229** could be reduced to an alcohol **230**, which then was oxidized to aldehyde **231**. The subsequent olefination was not as simple as we expected. Using the Wittig reagent for the olefination, we could only obtain 13% of the desired product, and the stereocenter of vinylcyclobutane **232** was lost. To avoid using strong bases in the reaction, the Takai-Lombardo and Tebbe methylenation have been investigated as well. By using these two methods, the yields were slightly increased to 22-23% without losing the absolute configuration at the stereocenter. Although the yields were not satisfactory, we could move on to the last step to reach the final vinylcyclobutane **233**. Unfortunately, the acetylation of vinylcyclobutane **232** was not successful, even after different reaction conditions were employed. It seemed like the vinylcyclobutane **232** was decomposed under all reaction conditions. Because of the failure of the acetylation in the last step, we changed the route to make the acetylation in the beginning of the synthesis. c*is*-Cyclobutane dicarboxylic acid anhydride **226** was reduced to the *γ*-butyrolactone **234**, followed the key acetylation (Scheme 61 (B)). Regrettably, the acetylation was not successful, only decomposition of *γ*-butyrolactone **234** was observed under all reaction conditions.

Tamaru's group reported a Pd-catalyzed amphiphilic allylation of aldehydes with vinyl epoxides to form vinylcyclobutanols (Scheme 62).[82] Following their procedure, we could obtain vinylcyclobutanol **239** in two steps. The alcohol group of vinylcyclobutanol **239** was then tosylated to form vinylcyclobutane **240** for the substitution reaction. Sadly, no conversion was observed in the cyanide substitution, even after crown ether was added and after prolonged reaction times. We tried to transform the hydroxyl group of **239** to a bromine group. However, the functional groups (phenyl-, methyl-, or vinyl-) on the cyclobutane migrated when the carbocation was formed during the bromination, therefore, we could not obtain the expected bromocyclobutane **243**.



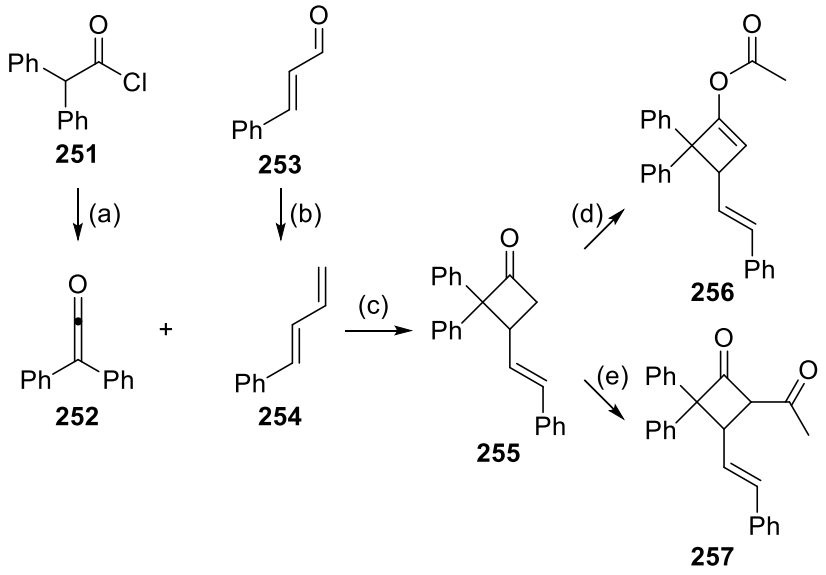
Scheme 62: Synthetic route of vinylcyclobutane **242**. (a) 1) 5 mol% $Pd(PPh_3)_4$, DMSO, rt, 1 h, 64%. 2) 10 mol% $Pd(acac)_2$, 20 mol% *n*-Bu_3P, 3 equiv. Et_3B, THF, 50 °C, 20 h, 51%. (b) 1.3 equiv. *p*-Toluenesulfonyl chloride, 2.5 equiv. Et_3N, 0.5 equiv. DMAP, DCM, rt, 18 h, 70%. (c) 2 equiv. NaCN, DMSO, 50 °C, 18 h, or 2 equiv. NaCN, 2 equiv. 15-crown-5 ether, rt, 48 h. (d) 1.1 equiv. CBr_4, 1.1 equiv. PPh_3, THF, 0 °C, o. n. (e) 1.2 equiv. Ph_3PBr_2, 1.2 equiv. imidazole, solvent: DCM, THF, or *n*-pentane, 0 °C to rt, o. n.

Based on these results we came to the conclusion of doing a late stage cyclization (Scheme 63). Target intermediate **249** was synthesized from two olefins **246** and **248** via cross metathesis. Olefin **246** was obtained from 3-buten-1-ol **244** via a bromination and substitution in two steps. Olefin **248** was formed by esterification of 3-buten-2-ol **247** with phenyl chloroformate. Fortunately, we could obtain the desired vinylcyclobutane **250** from olefin **249** via cyclization with 14% yield.



Scheme 63: Synthetic route of vinylcyclobutane **250**. (a) 0.5 equiv. PBr_3, 0.3 equiv. pyridine, 0 °C, 30 min, 56 %. (b) 1.1 equiv. 1,3-Diphenylpropanedione, 1.12 equiv. NaH, 0.6 equiv. NaI, DMF, THF, reflux, overnight, 56%. (c) 1 equiv. Phenyl chloroformate, 1.2 equiv. pyridine, 0.1 equiv. DMAP, DCM, rt, overnight, 89%. (d) 1.5 mol% Grubbs 2nd generation catalyst, DCM, reflux, 20 h, 37%. (e) 2 equiv. NaH, toluene, rt to 55 °C, 16 h, 14%.

After having obtained vinylcyclobutane **250**, the vinylcyclobutanone **257** was also prepared (Scheme 64). Starting from diphenyl ketene **252** and butadiene **254** to form the vinylcyclobutanone **255** via [2+2] cycloaddition. In case of acetyl chloride as acetylation reagent of vinylcyclobutanone **255**, the unwanted *O*-acetylation product **256** was formed. Luckily, when pyruvonitrile was used in the acetylation reaction, the desired vinylcyclobutanone **257** could be obtained.

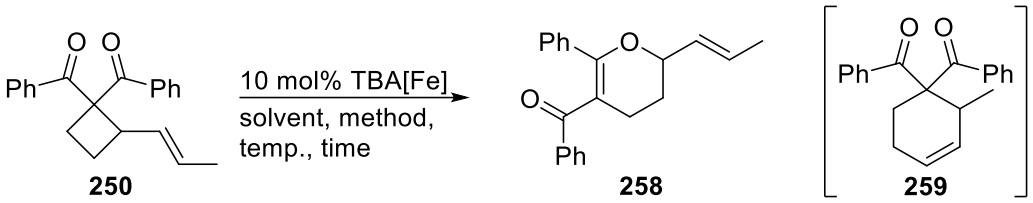


Scheme 64: Synthesis route of vinylcyclobutanone **257**. (a) 1.05 equiv. Et_3N, Et_2O, 0 °C, o. n. (b) 1.2 equiv. CH_3PPh_3Br, 1.2 equiv. *n*-BuLi, 0 °C to rt, 2 h, 75%. (c) rt, 7 days, 85%. (d) 1.5 equiv. Acetyl chloride, 1.3 equiv. LDA, -78 °C to rt, o. n. (e) 1.8 equiv. Pyruvonitrile, 1.3 equiv. LDA, -78 °C to rt, 2 h, 26%.

4.2.4 TBA[Fe]-catalyzed Vinylcyclobutane Rearrangement

Analogous to previous attempts, we used thermal, photochemical, and microwave conditions to investigate if we are able to activate the C-C bond of vinylcyclobutane **250** (Table 10). Under UV-light irradiation at room temperature or thermal condition at 120 °C for 24 hours, no conversion was observed in both cases (Entry 1 and 2, Table 10). Only the starting material **250** was observed. Under microwave condition in DMF at 120 °C for two hours, we could not detect any of the 3,4-dihydropyran **258** either (Entry 3, Table 10). Instead, we could isolate the thermal rearrangement product: cyclohexene **259** in 91% yield.

Table 10. TBA[Fe]-catalyzed vinylcyclobutane rearrangement.

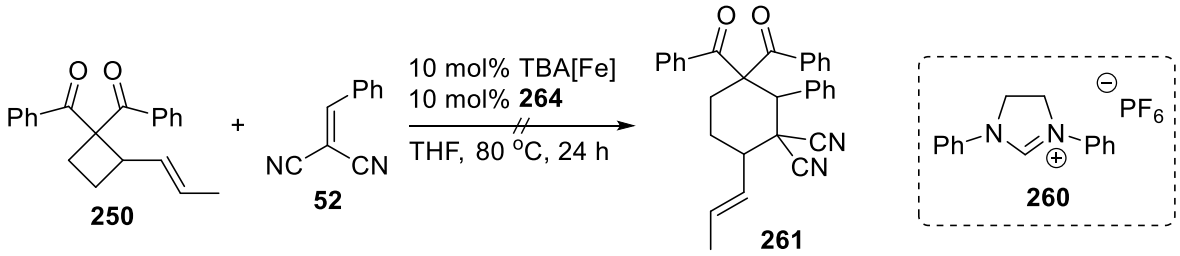


250 **258** **259**

Entry[a]	Solvent	Method	T. [°C]	Time [h]	**258**[b] [%]
1	CH_3CN	UV-light (Hg lamp)	rt	24	-
2	DCM	thermal (oil bath)	60	24	-
3	DMF	microwave (200W)	120	2	-

[a] All reactions were performed with the substrate (0.1 mmol), 10 mol% of TBA[Fe] in solvent (1 mL). [b] Yield in % was determined through ^{1}H-NMR-integration by using mesitylene as internal standard.

Inspired by Dieskau's work of Fe-catalyzed allylic C-C bond activation of vinylcyclopropanes, we tried to use similar reaction conditions for the C-C bond activation of vinylcyclobutane **250**. However, no conversion was observed for the [4+2] cycloaddition reaction of vinylcyclobutane **250** with benzylidenemalononitrile **54**, even when the catalyst loading was increased to 10 mol% for 24 hours (Scheme 65).

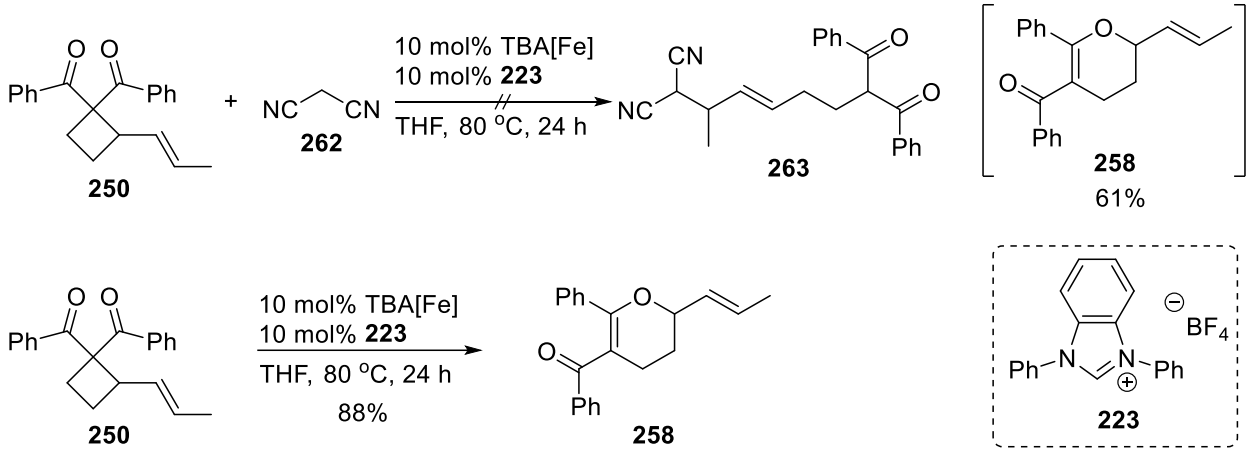


250 **52** **261** **260**

Scheme 65: TBA[Fe]-catalyzed [4+2] cycloaddition of vinylcyclobutane **250**.

By using the traceless allylic substitution conditions with 10 mol% TBA[Fe] for the activation of vinylcyclobutane **250**, no expected ring opening product **263** was formed (Scheme 66). However, surprisingly, we isolated 61% of the 3,4-dihydropyran **258**, which we could not obtain from the previous attempts. We then quickly repeated the reaction, without the presence of malononitrile **262**. We found that the isolated yield of 3,4-dihydropyran **258** was increased to 88%. Therefore, we could exclude that malononitrile

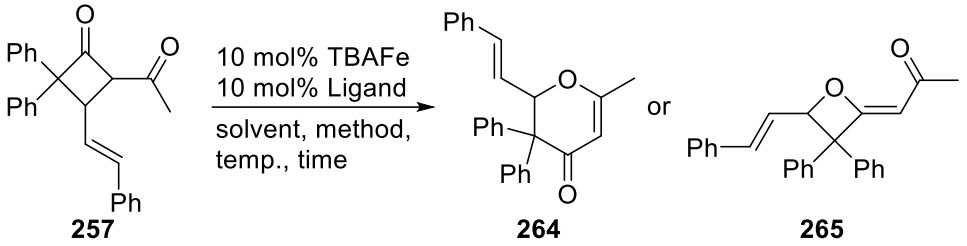
262 was assisting the C-C bond activation in the reaction. NHC ligands are the most widely used ligands in transition-metal catalysis due to their *σ*-donor character. We assumed NHC ligand **223** was coordinated to the iron catalyst, resulting in a much higher nucleophilic iron complex. This could be the reason that the newly formed iron complex was able to attack the double bond of the vinylcyclobutane **250**, which caused the activation of the C-C bond of the butane ring. In addition, no conversion was observed without presence of TBA[Fe] and NHC ligand **223**. When only NHC ligand **223** was employed in reaction without presence of TBA[Fe], no conversion was observed as well.



Scheme 66: TBA[Fe]-catalyzed traceless allylic substitution and rearrangement of vinylcyclobutane **250**.

We then hoped that vinylcyclobutanone **257** could also be activated by TBA[Fe] to yield the rearrangement products **264** or **265**. Several reaction conditions have been tested and the results are summarized in Table 11. No conversion was observed under photochemical condition and thermal conditions at 120 °C (Entry 1 and 2, Table 11). When the temperature increased to 140 °C under thermal conditions, only decomposition of the starting material **257** was observed (Entry 3, Table 11). Using microwave condition at 120 °C for 2 hours also led to starting material decomposition as well (Entry 4, Table 11). When the reaction condition which was applied in TBA[Fe]-catalyzed vinylcyclobutane rearrangement was used, however, no conversion could be detected (Entry 5, Table 11).

Table 11. TBA[Fe]-catalyzed vinylcyclobutanone rearrangement.



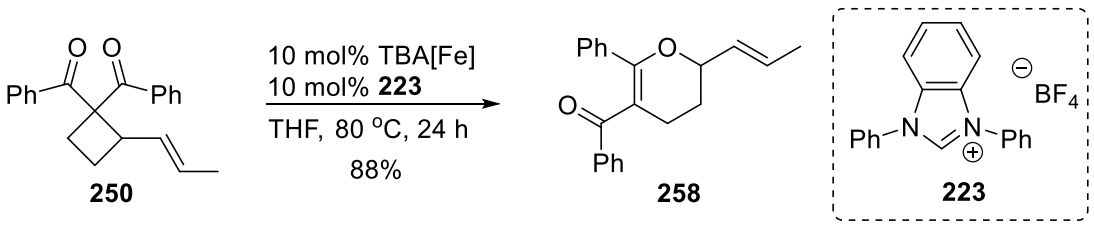
257 **264** **265**

Entry[a]	Ligand	Solvent	Method	T. [°C]	Time [h]	**264**/**265**[b] [%]
1	-	CH_3CN	UV-light (Hg lamp)	rt	18	-
2	-	DMF	thermal (oil bath)	120	18	-
3	-	DMF	thermal (oil bath)	140	18	-
4	-	DMF	microwave (200 W)	120	2	-
5	**223**	THF	thermal (oil bath)	80	18	-

[a] All reactions were performed with the substrate (0.1 mmol), 10 mol% of TBA[Fe] in solvent (1 mL). [b] Yield iwas determined through ^{1}H-NMR-integration by using mesitylene as internal standard.

4.3 Conclusion and Outlook

Herein we reported novel ways to prepare vinylcyclobutane **250** and vinylcyclobutanone **257**. Arylcyclobutane **221** and vinylcyclobutanone **257** were not able to rearrange in all kinds of reaction conditions (Scheme 67). We also showed primary results of TBA[Fe]-catalyzed cyclobutane rearrangement. Vinylcyclobutane **250** could undergo rearrangement forming the 3,4-dihydropyran **258** with 88% of isolated yield by using 10 mol% of TBA[Fe] and NHC ligand **223** in THF at 80 °C for 18 hours. Presumably NHC ligand **223** significantly enhanced the nucleophilicity of the iron complex after the coordination. More importantly, we believe this is the first example of Fe-catalyzed C-C bond activation of cyclobutanes.



250 **258** **223**

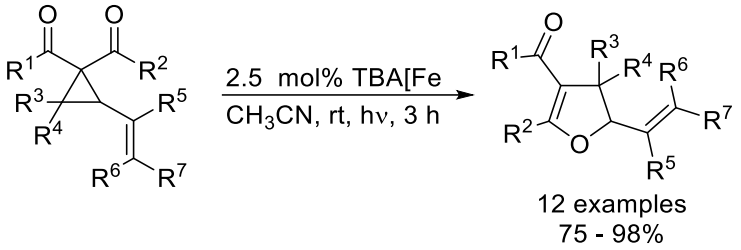
Scheme 67: TBA[Fe]-catalyzed vinylcyclobutane rearrangement.

Currently, there are still a few challenges in this project. First, the optimization of the reaction is being investigated in our group, with the aim to reduce the catalyst loading and the reaction time. Second, in order to explore the substrate scope of the reaction, a concise route to prepare functionalized cyclobutanes is highly required. Third, the reaction mechanism is still unclear, further investigations such as quantum chemical calculations and spectroscopic experiments are awaiting.

5. Summary and Future Work

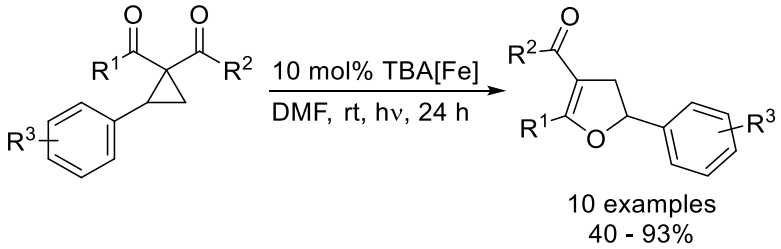
In this thesis, we described a variety of iron-catalyzed C-C bond activation reactions of strained ring systems.

First, the TBA[Fe]-catalyzed Cloke-Wilson rearrangement of vinyl- and arylcyclopropanes was shown. A broad range of dihydrofurans could be accessed under mild conditions. Under photochemical conditions, the vinylcyclopropanes were able to rearrange to the dihydrofurans by using 2.5 mol% of TBA[Fe] at room temperature within 3 hours only (Scheme 68).



Scheme 68: TBA[Fe]-catalyzed Cloke-Wilson rearrangement of vinylcyclopropanes.

In addition, arylcyclopropanes could be rearranged by using 10 mol% of TBA[Fe] at room temperature for 24 hours (Scheme 69). These mild reaction conditions have to be highly emphasized since arylcyclopropanes display a low reactivity.

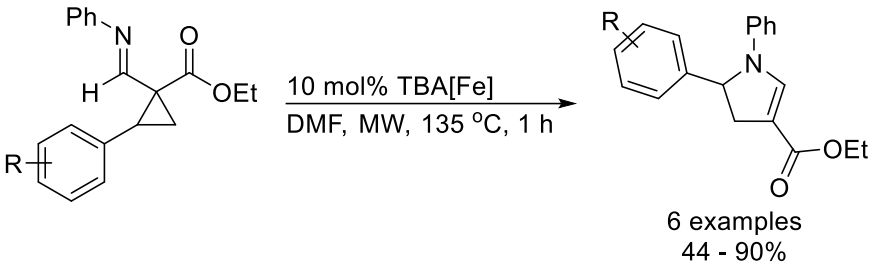


Scheme 69: TBA[Fe]-catalyzed Cloke-Wilson rearrangement of arylcyclopropanes.

Furthermore, the spectroscopic and theoretical studies showed that the complex was best activated by light at 415 nm via a nondecarbonylative photochemical process and the active $[Fe(CO)_3(NO)]^-$ species shows an almost trigonal-bipyramidal configuration with an Fe-N-O angle of close to 180° which provides a wide-opened binding site of the metal center. This opens a new door for discovering the activation of less reactive C-H and C-C bonds under the photochemical condition and avoiding most of the organic side

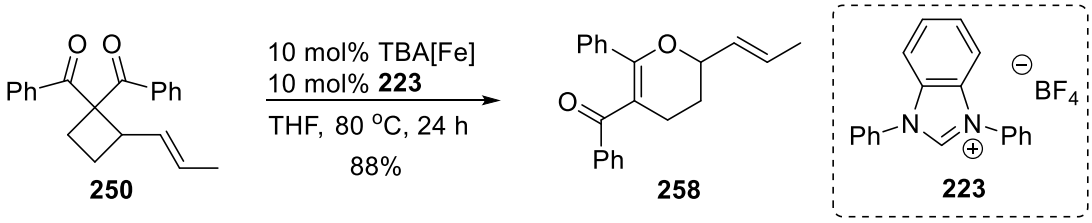
reactions upon irradiation.

Second, a TBA[Fe]-catalyzed cyclopropylimine rearrangement was reported (Scheme 70). A series of 2,3-dihydropyrroles were successfully transformed starting from cyclopropylimine by using this simple and economical method. Moreover, this is the first example of a transition-metal-catalyzed cyclopropylimine rearrangement.



Scheme 70: TBA[Fe]-catalyzed cyclopropylimine rearrangement.

Third, and last but not least, an iron-catalyzed C-C bond activation of cyclobutanes was demonstrated (Scheme 71). Vinylcyclobutane **250** rearranged to 3,4-dihydropyran **258** by using 10 mol% of TBA[Fe] with NHC ligand **223** in THF at 80 °C for 24 hours. To the best of our knowledge, an Fe-catalyzed C-C bond activation of cyclobutanes has not been described yet.



Scheme 71: TBA[Fe]-catalyzed vinylcyclobutane rearrangement.

In the end, we can confidently say that $Bu_4N[Fe(CO)_3NO]$ (TBA[Fe]) is a powerful catalyst for the activation of C-C bonds of cyclopropanes and cyclobutanes. In the future, non-strained C-C bonds will also be examined. In addition, exploring a better synthetic route of functionalized cyclobutanes as well as the substrate scope of cyclopropylimine and vinylcyclobutane are currently being carried out in our laboratories.

6. Abstract (English)

The stable and readily accessible electron rich complex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) has been a matter of interest in our group for a number of years. Our previous spectroscopic and experimental studies indicated that the metal center should be regarded as being zero-valent, while the negative charge is located at the NO-ligand, which implies that the ferrate complex could be activated for catalytic transformations upon irradiation of light.

The TBA[Fe]-catalyzed Cloke-Wilson rearrangement of vinyl- and arylcyclopropanes under both photochemical and thermal conditions are shown in this dissertation. The *in situ* IR spectroscopy experiments showed that there was no detectable decarbonylation of TBA[Fe] upon irradiation with UV-light during the reactions. In addition, according to quantum chemical calculations and conversion-wavelength experiments, TBA[Fe] can be selectively activated at 415 nm.

In addition, similar to the Cloke-Wilson rearrangement of cyclopropanes, cyclopropylimines could also undergo rearrangement to give the corresponding 2,3-dihydropyrroles, by using TBA[Fe] under microwave conditions. A series of functionalized cyclopropylimines were prepared and show moderate to good yields in the rearrangement reaction.

Moreover, a synthetic route for functionalized vinylcyclobutane was successfully developed. Furthermore, TBA[Fe] was able to activate the C-C bond of a vinylcyclobutane after coordinated with a NHC ligand. The σ-donor character of the NHC ligand significantly increased the nucleophilicity of the iron complex.

To sum up, TBA[Fe], again, revealed its power in the field of C-C bond activation of strained rings. Further investigations on activating less reactive (non-strained) C-C bonds and C-H bonds by using TBA[Fe] under photochemical, microwave, or thermal conditions are currently being carried out in our laboratories.

7. Abstract (Deutsch)

Seit vielen Jahren ist der stabile und leicht zugängliche, elektronenreiche Komplex $Bu_4N[Fe(CO)_3(NO)]$ (TBA[Fe]) für unsere Gruppe von großem Interesse. Basierend auf unseren bisherigen spektroskopischen und experimentellen Studien zeigte sich, dass das Metallzentrum als neutral geladen angesehen werden sollte, während sich die negative Ladung am NO-Liganden befindet, was bedeutet, dass der Ferratkomplex für katalytische Transformationen durch die Bestrahlung von Licht aktiviert werden könnte.

Die TBA[Fe]-katalysierte Cloke-Wilson-Umlagerung von Vinyl- und Arylcyclopropanen unter photochemischen und thermischen Bedingungen wird in dieser Dissertation gezeigt. Das in-situ-IR-Spektroskopie-Experiment zeigte, dass bei der Bestrahlung mit UV-Licht während der Reaktionen keine Decarbonylierung von TBA[Fe] erfolgte. Zusätzlich kann nach quantenchemischen Berechnungen und Umsatz-Wellenlängen-Korrelationen TBA[Fe] selektiv bei 415 nm aktiviert werden.

Zusätzlich können, ähnlich zu der Cloke-Wilson-Umlagerung von Cyclopropanen, Cyclopropylimine einer Umlagerung unterzogen werden, um die entsprechenden 2,3-Dihydropyrrole unter Verwendung von TBA[Fe] und Mikrowellenbedingungen zu bilden. Eine Reihe von funktionalisierten Cyclopropyliminen wurde hergestellt und in moderaten bis guten Ausbeuten zu den 2,3-Dihydropyrrolen umgesetzt.

Darüber hinaus wurde ein Syntheseweg für ein funktionalisiertes Vinylcyclobutan erfolgreich entwickelt. Außerdem war TBA[Fe] in der Lage, die C-C-Bindung von diesem Vinylcyclobutan nach Koordination eines NHC-Liganden zu aktivieren. Der σ-Donor-Charakter des NHC-Liganden erhöhte die Nucleophilie des Eisenkomplexes signifikant.

Zusammenfassend lässt sich sagen, dass TBA[Fe] wieder seine Aktivität auf dem Gebiet der C-C-Bindungsaktivierung von gespannten Ringen offenbarte. Weitere Untersuchungen zur Aktivierung von weniger reaktiven (nicht gespannten) C-C- und C-H-Bindungen unter Verwendung von TBA[Fe] unter photochemischen, mikrowellen- oder thermischen Bedingungen werden derzeit in unseren Laboratorien durchgeführt.

II. Experimental Section

8. General Remarks

All reactions sensitive to moisture and/or air were carried out under an atmosphere of dry nitrogen (N_2) using anhydrous solvents. Solvents were either dried by passing them through commercially available columns (*n*-pentane, DCM) or distilling them from CaH_2 (CCl_4, $C_2H_2Cl_4$, $C_2H_4Cl_2$, toluene, DMF). THF was freshly distilled from Na/benzophenone (ketyl radical). IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer equipped with a Specac Golden Gate ATR unit. Intensities are specified as br (broad), s (strong), m (medium) and w (weak). The unit of IR measurement is wavenumber, abbreviated as cm^{-1}. High resolution mass spectra (HRMS) were recorded using a Finnigan MAT 95 spectrometer (EI) or a Bruker micrOTOF-Q spectrometer (ESI). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 250 MHz, 300 MHz, 400 MHz, 500 MHz, or 700 MHz spectrometer and calibrated using the residual non-deuterated solvent signal or tetramethylsilane (TMS) as an internal standard. Signals are indicated as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sex (sextet), sep (septet), m (multiplet) and br (broad). Column chromatography (CC) was carried out using silica gel (60 Dm, 0.040-0.063 mm) and thin layer chromatography (TLC) was carried out using silica gel plated aluminum sheets (silica gel 60, F254). High performance liquid chromatography (HPLC) was carried out using a K-501 pump and a K 2400 RI-detector in combination with a Eurospher-100 Si column by KNAUER. The photochemical reactions were carried out using a Heraeus Hg lamp (180 W), a ORIEL Xenon Lamp (75 W), or a MEGAMAN Compact Fluorescent Lamp (23 W, 1395 Lumen).

9. IR spectra of TBA[Fe]

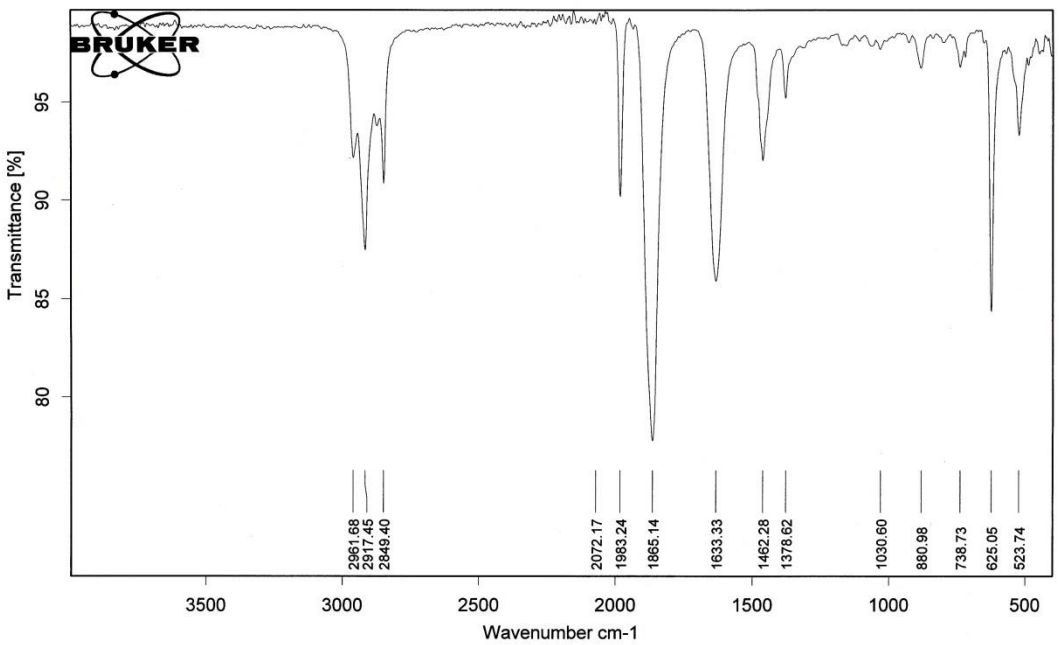


Figure S1: TBA[Fe] in CH_3CN - no irradiation.

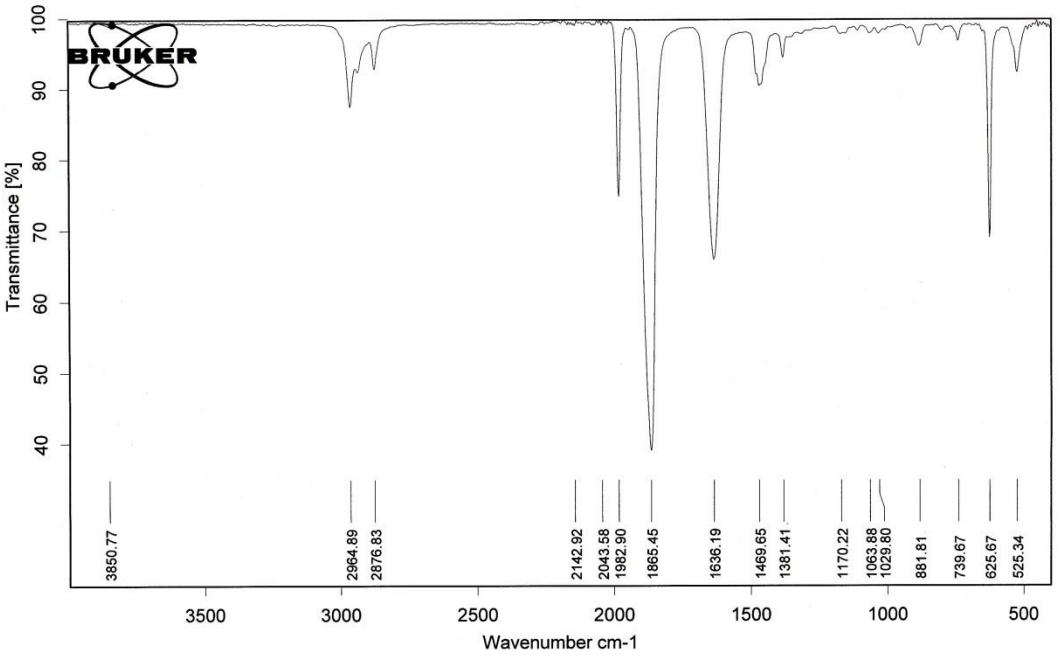


Figure S2: TBA[Fe] in CH_3CN - after 6 h irradiation (180 W, Hg lamp).

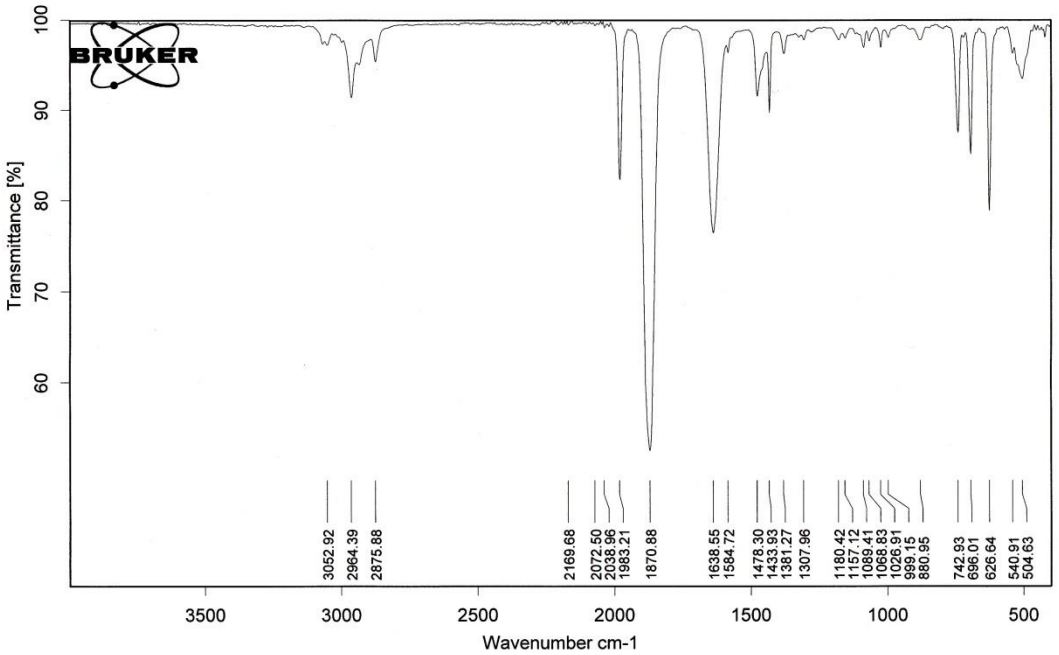


Figure S3: TBA[Fe] + PPh_3 (1.5 equiv.) in CH_3CN - after 4 h irradiation (180 W, Hg lamp).

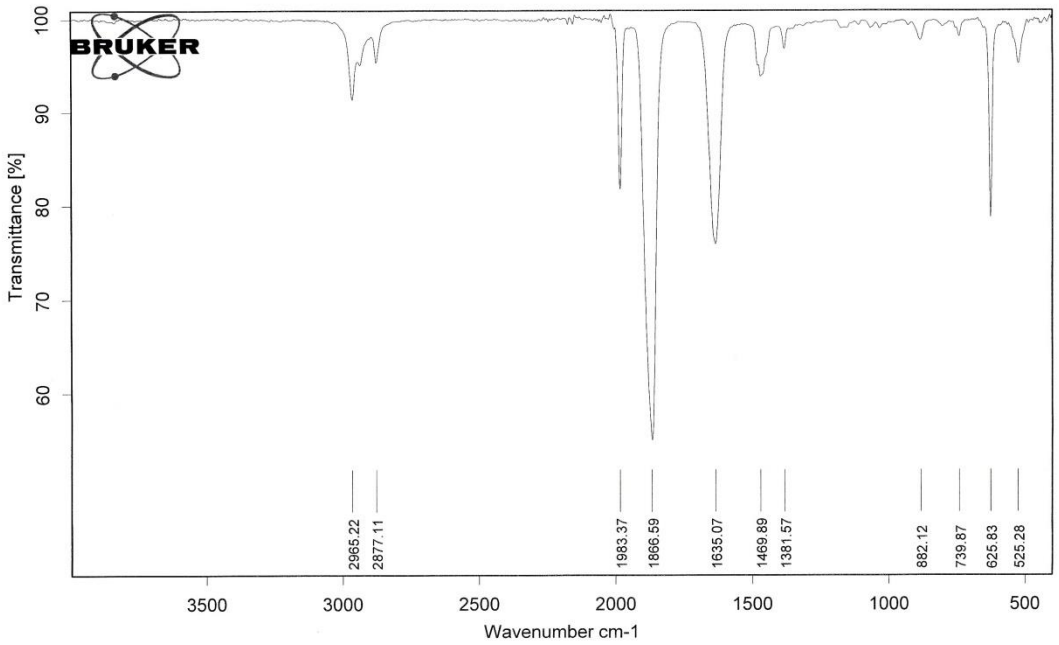


Figure S4: TBA[Fe] in DCM - no heating.

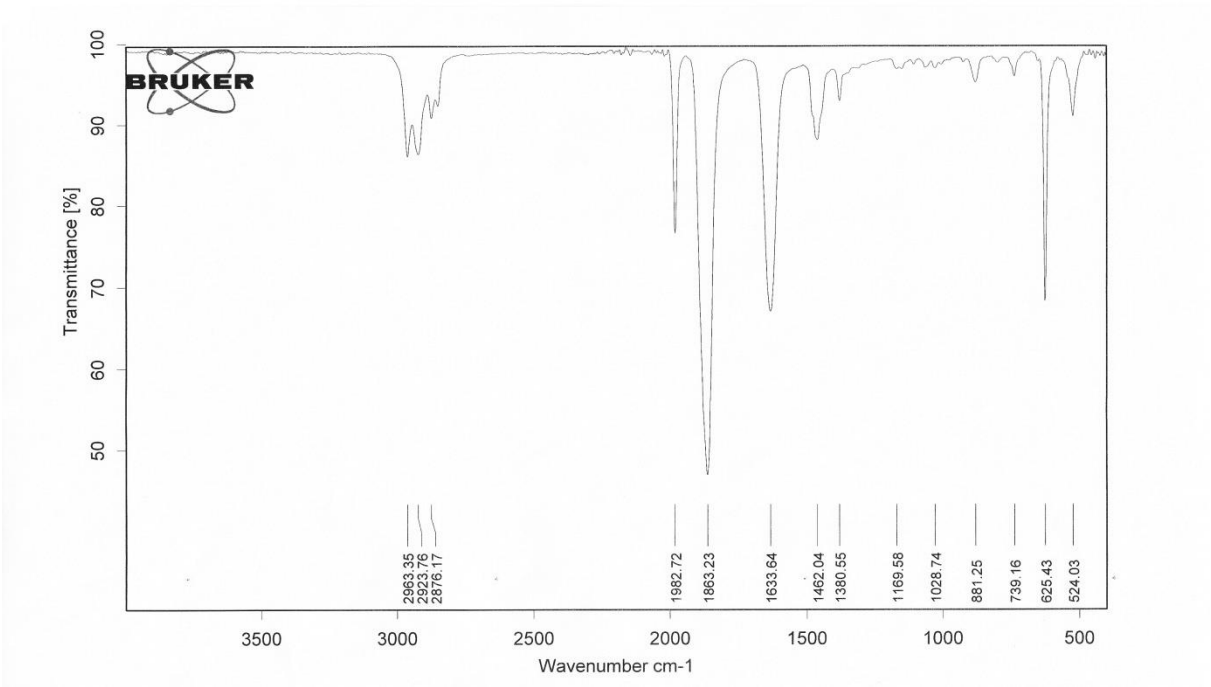


Figure S5: TBA[Fe] in DCM - after 6 h at 45 ºC.

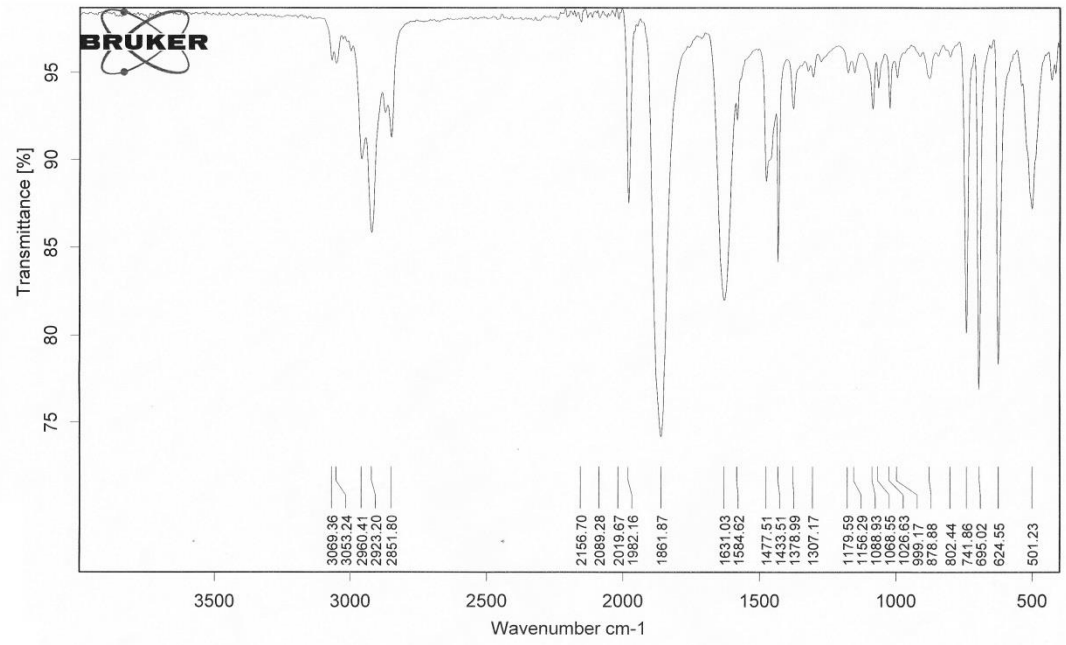


Figure S6: TBA[Fe] + PPh_3 (2 equiv.) in DCM - after 4 h at 45 ºC.

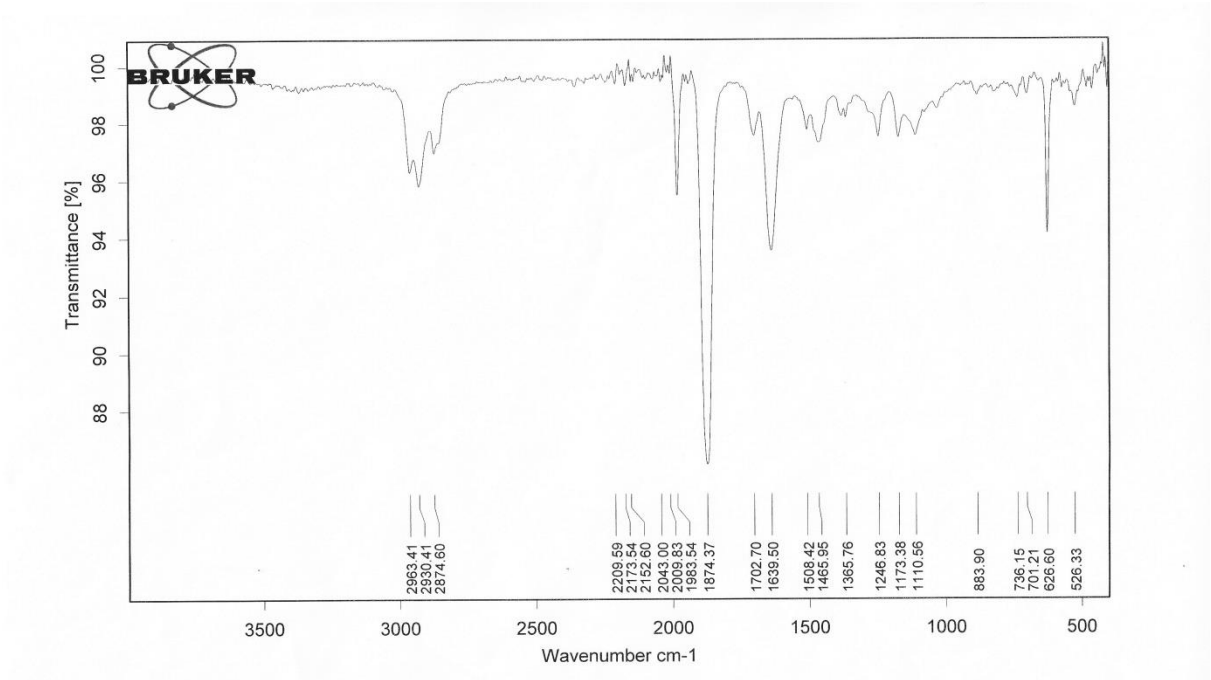


Figure S7: TBA[Fe] in Toluene - no MW.

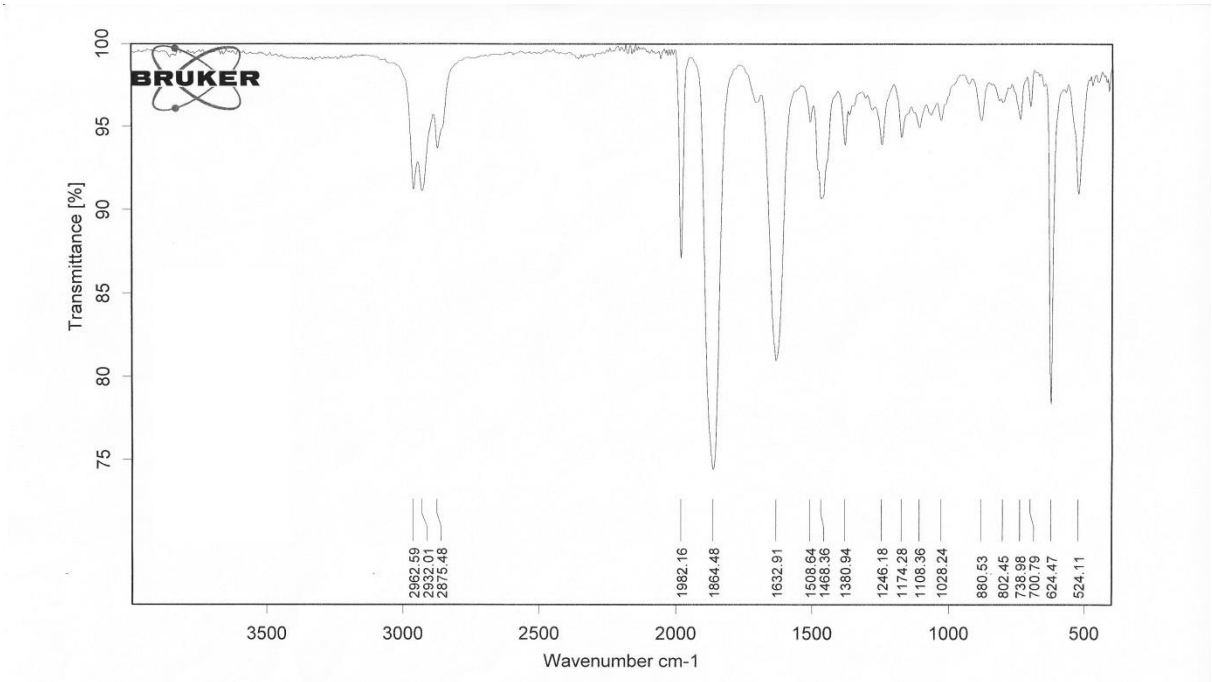


Figure S8: TBA[Fe] in Toluene - after 2 h MW at 120 ºC.

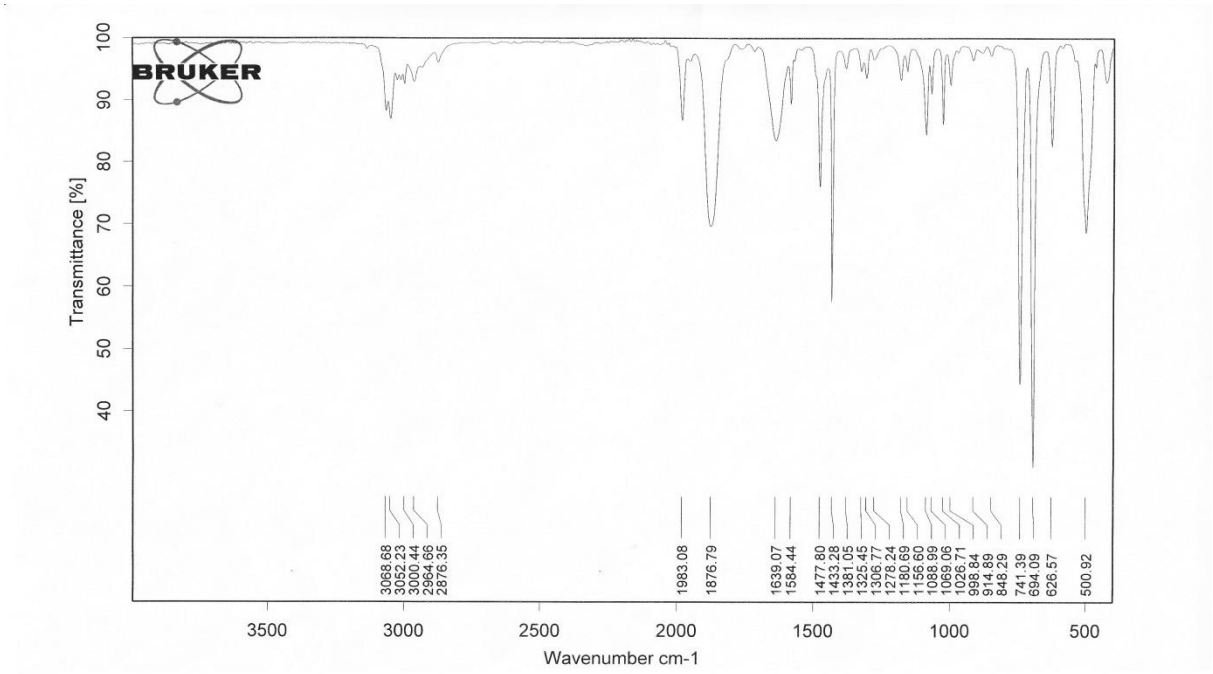


Figure S9: TBA[Fe] + PPh_3 (2 equiv.) in Toluene - after 2 h MW at 120 ^oC.

10. UV spectrum of TBA[Fe]

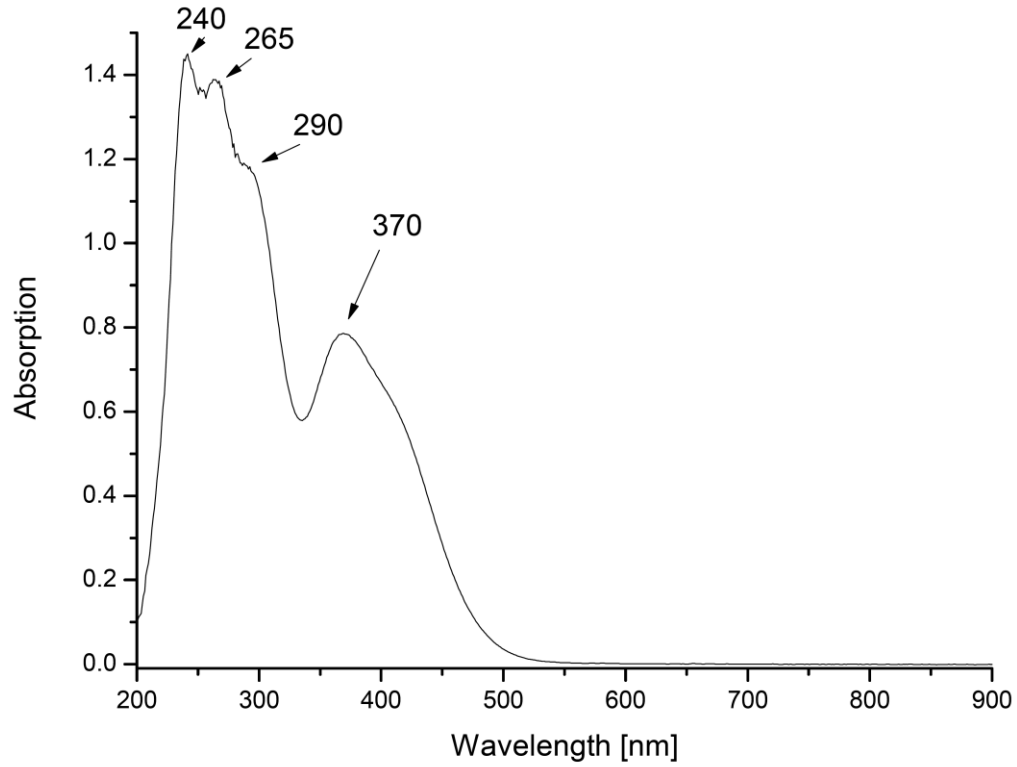


Figure S10: UV spectrum of TBA[Fe] in CH_3CN.

11. Fluorescence spectrum of TBA[Fe]

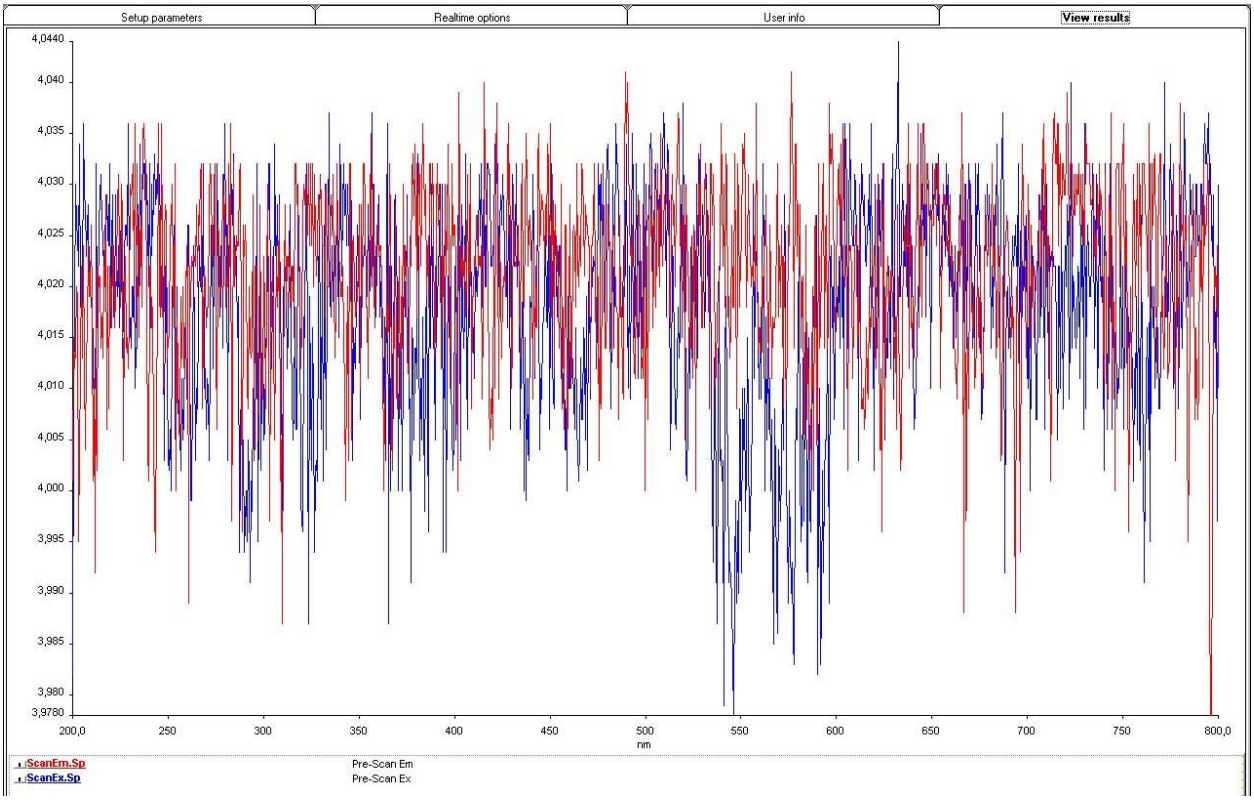


Figure S11: Fluorescence spectrum of TBA[Fe] in CH_3CN. The excitation scan (blue) and emission scan (red).

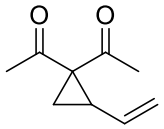
12. TBA[Fe]-Catalyzed Cloke-Wilson Rearrangement of Vinyl- and Arylcyclopropanes

12.1 Preparation of Vinylcyclopropanes

General Procedure I: Preparation of Olefin-Substituted VCPs (GP-I)

The appropriate vinylcyclopropane (1 equiv.) and Grubbs 2nd generation catalyst (0.015 equiv.) was weighed into a dried Schlenk tube under an atmosphere of dry nitrogen. DCM (0.6 M) was added followed by the appropriate alkene (10 equiv.). The Schlenk tube was sealed under an atmosphere of dry nitrogen and the mixture stirred at 45 °C for 16 h. The solvent was removed under reduced pressure and the residue subjected to column chromatography on silica gel.

12.1.1 1,1'-(2-Vinylcyclopropane-1,1-diyl)diethanone (111)

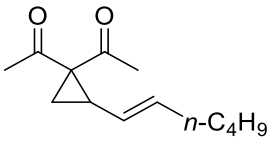


111

(*trans*)-1,4-Dibrombut-2-ene (4.278 g, 20 mmol, 1 equiv.) and K_2CO_3 (8.154 g, 59 mmol, 2.95 equiv.) were suspended in acetone (35 mL). 2,4-Pentanedione (2.0 mL, 20 mmol, 1.0 equiv.) was added drop wise and the mixture was heated to reflux for 14.75 h. The reaction mixture was cooled to room temperature and Et_2O (35 mL) was added. The resulting precipitate was removed via filtration and washed with Et_2O (2 x 25 mL). The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) yielding 1.547 g (51%) of the desired product **111** as a colorless oil.

***R*$_f$** = 0.29 (*n*-pentane/Et_2O, 4:1 (v/v)); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 5.33-5.28 (m, 2H), 5.17-5.13 (m, 1H), 2.67-2.58 (m, 1H), 2.27 (s, 3H), 2.17 (s, 3H), 1.84 (dd, *J* = 7.1, 5.3 Hz, 1H), 1.49 (dd, *J* = 8.8, 5.1 Hz, 1H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 202.7, 202.4, 132.8, 118.9, 51.2, 32.4, 30.9, 26.9, 20.2 ppm; **IR** (ATR, neat) 3088, 3010, 1684, 1638 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) 152 (M^+, 5), 137 (40), 109 (100), 95 (22), 91 (33), 67 (44).

12.1.2 (*E*)-1,1'-(2-(Hex-1-en-1-yl)cyclopropane-1,1-diyl)diethanone (114)

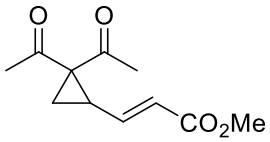


114

The reaction was carried out on a 5 mmol scale based on vinylcyclopropane **111**. The *title compound* was obtained according to GP-I after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) to afford 511 mg (49%) of **114** as a tan oil.

R_f = 0.39 (*n*-pentane/Et_2O, 4:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.80-5.66 (m, 1H), 4.93 (dd, *J* = 15.3, 8.5 Hz, 1H), 2.57 (q, *J* = 8.3 Hz, 1H), 2.26 (s, 3H), 2.15 (s, 3H), 1.98 (m, 2H), 1.80 (dd, *J* = 7.4, 5.1 Hz, 1H), 1.47 (dd, *J* = 8.8, 5.1 Hz, 1H), 1.34-1.25 (m, 4H), 0.88 (m, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 203.1, 136.0, 124.1, 51.2, 32.3, 32.1, 31.3, 30.9, 26.8, 22.1, 20.4, 13.8 ppm; **IR** (ATR) 2958, 2928, 2873, 2855, 1681, 1422, 1357, 1310, 1250, 1163, 1100, 968, 936 cm^{-1}; **GC/MS** (ESI) m/z (%) = 209.15 (M + H^+, 28), 191 (15), 167 (16), 149 (20), 135 (13), 123 (23), 113 (100); **HRMS** (ESI) calc. for [$C_{12}H_{20}O_2$ + Na^+]: 231.1356, found: 231.1346.

12.1.3 Methyl (*E*)-3-(2,2-diacetylcyclopropyl)acrylate (115)

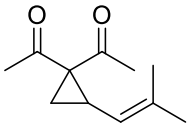


115

The reaction was carried out on a 5 mmol scale based on vinylcyclopropane **111**. The *title compound* was obtained according to GP-I after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 450 mg (43%) of **115** as a tan oil.

R_f = 0.19 (*n*-pentane/Et_2O, 2:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 6.34 (dd, *J* = 15.5, 9.9 Hz, 1H), 6.05 (d, *J* = 15.5 Hz, 1H), 3.72 (s, 3H), 2.77-2.64 (m, 1H), 2.29 (s, 3H), 2.22 (s, 3H), 1.91 (dd, *J* = 7.0, 5.1 Hz, 1H), 1.59 (dd, *J* = 8.6, 5.1 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 201.6, 201.4, 165.9, 143.2, 124.0, 51.7, 51.7, 30.7, 30.5, 27.5, 21.4 ppm; **IR** (ATR) 2954, 2919, 2849, 1722, 1686, 1651, 1435, 1358, 1308, 1273, 1252,1204, 1148 cm^{-1}; **GC/MS** (ESI) m/z (%) = 211 (M + H^+, 6), 137 (100), 119 (18), 111 (45); **HRMS** (ESI) calc. for [$C_{11}H_{14}O_4$ + Na^+]: 233.0784, found: 233.0786.

12.1.4 1,1'-(2-(2-Methylprop-1-en-1-yl)cyclopropane-1,1-diyl)diethanone (116)

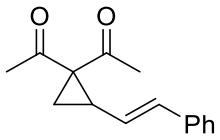


116

The reaction was carried out on 6 mmol scale based on vinylcyclopropane **111**. The *title compound* was obtained according to GP-I after purification via column chromatography on aluminium oxide (neutral) eluting with *n*-pentane/Et_2O 4:1 (v/v) to afford 854 mg (79%) of **116** as a pale-yellow oil.

***R*f** = 0.34 (*n*-pentane/Et_2O, 4:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 4.66-4.59 (m, 1H), 2.67 (dd, *J* = 16.4, 8.6 Hz, 1H), 2.22 (s, 3H), 2.18 (s, 3H), 1.78-1.72 (m, 4H), 1.69 (s, 3H), 1.52 (dd, *J* = 8.9, 4.8 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 203.3, 203.2, 138.5, 119.2, 51.0, 30.5, 29.2, 27.2, 25.6, 21.7, 18.4 ppm; **IR** (ATR) 2916, 1681, 1620, 1451, 1357, 1303, 1252, 1171, 1103, 933, 855, 823 cm^{-1}; **GC/MS** (ESI) m/z (%) = 181 ($M + H^+$, 15), 163 (18), 145 (35), 121 (100), 113 (17), 105 (23); **HRMS** (ESI) calc. for [$C_{11}H_{16}O_2 + Na^+$]: 203.1043, found: 203.1046.

12.1.5 1,1'-(2-Styrylcyclopropane-1,1-diyl)bis(ethan-1-one) (117)

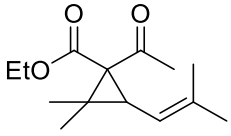


117

The reaction was carried out on a 7 mmol scale based on vinylcyclopropane **111**. The *title compound* was obtained according to GP-I after purification via column chromatography on silica gel eluting PE/EA 5:1 (v/v) followed by semi-prep. HPLC eluting with PE/EA 5:1 (v/v) to afford 340 mg (21%) of **117** as a tan oil.

***R*f** = 0.25 (PE/EA, 5:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.31 - 7.19 (m, 5H), 6.65 (d, *J* = 15.8 Hz, 1H), 5.66 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.78 (dd, *J* = 16.3, 8.7 Hz, 1H), 2.28 (s, 3H), 2.21 (s, 3H), 1.96 (dd, *J* = 7.3, 5.1 Hz, 1H), 1.59 (dd, *J* = 8.7, 5.1 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.68, 202.65, 136.38, 134.06, 128.64, 127.80, 126.14, 124.30, 51.62, 32.72, 30.98, 27.12, 21.07 ppm; **IR** (ATR) 3026, 1682, 1598, 1492, 1448, 1358 cm^{-1}; **GC/MS** (ESI) m/z (%) = 251 (100) [M^+ + Na]; **HRMS** (ESI) calc. for [$C_{15}H_{16}O_2 + Na^+$]: 251.1043, found: 251.1030.

12.1.6 Ethyl 1-acetyl-2,2-dimethyl-3-(2-methylprop-1-en-1-yl)cyclopropane-1-carboxylate (119)



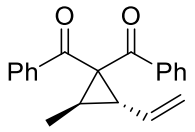
119

A solution of diisopropylamine (1.55 mL, 11 mmol, 1.1 equiv.) in THF (20 mL) was cooled to -78 °C and 1.6 M *n*-BuLi (6.87 mL, 11 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was warmed to room temperature for 15 min, then re-cool to -78 °C. Ethyl chrysanthemate (2.17 mL, 10 mmol, 1 equiv.) was added dropwise in to the reaction mixture and stirred for 30 min at -78 °C then 1 h at room temperature. The reaction mixture was re-cooled to -78 °C again and acetyl chloride (0.71 mL, 10 mmol, 1 equiv.) was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched by sat. NH_4Cl, diluted with water, and extract with three time of diethyl ether. The combined organic layers were dried over $MgSO_4$, filtered and then

concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with *n*-pentane/EA 40:1 (v/v) to afford 1.3345 g (56%) of **119** as a colorless oil.

***R*$_f$** = 0.37 (*n*-pentane /EA, 40:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.03-5.00 (m , 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.58 (d, *J* = 8.0 Hz, 1H), 2.27 (s, 3H), 1.73 (s, 3H), 1.71 (s, 3H), 1.33 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.11 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 201.3, 168.6, 137.1, 117.1, 60.8, 51.2, 34.8, 33.4, 30.2, 25.7, 22.0, 18.7, 18.0, 14.1 ppm; **IR** (ATR) 2980, 2929, 1733, 1700, 1446, 1377, 1355, 1304, 1274, 1178, 1095, 852 cm^{-1}; **HRMS** (ESI) calc. for [$C_{14}H_{22}O_3$ + Na^+]: 261.1461, found: 261.1452.

12.1.7 (2-Methyl-3-vinylcyclopropane-1,1-diyl)bis(phenylmethanone) (126)

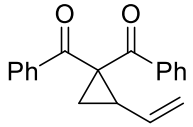


126

The *title compound* was synthesized according to literature (also has been described in Chapter 2.2.1.2) and was purified via column chromatography on silica gel eluting with PE/EA 40:1 (v/v) to afford **126** as a white solid.

***R*$_f$** = 0.34 (PE/EA 40:1 (v/v)); **mp** 108-111°C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.73-7.66 (m, 1H), 7.66-7.59 (m, 1H), 7.42-7.30 (m, 2H), 7.30-7.18 (m, 4H) 5.42-5.32 (m, 2H), 5.06-4.98 (m, 1H) 3.12-3.03 (m, 1H) 2.84-2.73 (m, 1H), 1.12 (d, *J* = 6.4 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 196.5, 196.1, 138.6, 138.5, 133.3, 132.9, 132.8, 128.55, 128.53, 128.49, 128.42, 118.1, 53.6, 37.4, 27.3, 11.9 ppm; **IR** (ATR) 3062, 3027, 1720, 1656, 1490, 1346, 1310, 1125, 848, 761 cm^{-1}.

12.1.8 (2-Vinylcyclopropane-1,1-diyl)bis(phenylmethanone) (127)



127

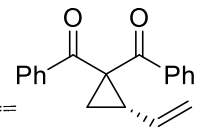
1,3-Diphenyl-1,3-propanedione (3.364 g, 15 mmol, 1 equiv.) was dissolved in anhydrous THF (20 mL) under an atmosphere of dry nitrogen. NaH (1.200 g, 60% in mineral oil, 30 mmol) was added as a solid and the suspension stirred for 15 min at room temperature. (*trans*)-1,4-Dibrombut-2-ene (3.158 g, 15 mmol, 1 equiv.) was added and the reaction mixture stirred for 66 h at room temperature. The resulting suspension was diluted with Et2O and the precipitate removed via filtration and washed with Et_2O. A saturated solution of NH_4Cl (100 mL) was added. The mixture was extracted with Et_2O (2 x 150 mL) and EA (100 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified via column chromatography on silica gel eluting with PE/EA 20:1 to 10:1 (v/v) to yield a mixture of product and unreacted starting materials. Pure product was obtained via additional purification using HPLC eluting with PE/EA 20:1 giving 758 mg (18%) of **127** as a colorless solid.

R_f = 0.33 (PE/EA, 20:1(v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.72-7.64 (m, 4H), 7.39-7.32 (m, 2H), 7.26-7.21 (m, 4H), 5.42-5.38 (m, 2H), 3.37-3.29 (m, 1H), 2.34 (dd, *J* = 7.2, 4.4 Hz, 1H), 1.58 (dd, *J* = 8.6, 4.4 Hz, 1H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) 196.7, 196.0, 138.1, 137.7, 133.0, 132.9, 132.85, 128.6, 128.43, 128.4, 118.7, 47.7, 31.2, 21.3 ppm; **IR** (ATR, neat) 3061, 2986, 1680, 1660, 1633, 1594, 1575, 1446 cm^{-1}; **HRMS** (ESI) calc. for [$C_{19}H_{16}O_2$ + Na^+]: 299.1043, found 299.1036.

(*R*)-127: $[\alpha]_D^{20}$: +305.6 (c = 5.33, $CHCl_3$); **(*S*)-127**: $[\alpha]_D^{20}$: -305.6 (c = 5.33, $CHCl_3$).

Data File C:\HPCHEM\1\DATA\DP\DP65H200.D Sample Name: DP65h2

Chiralcel OD-H; Heptan/Isopropanol 95:5, 0.5 mL/min; 3µ
l



(*R*)-127

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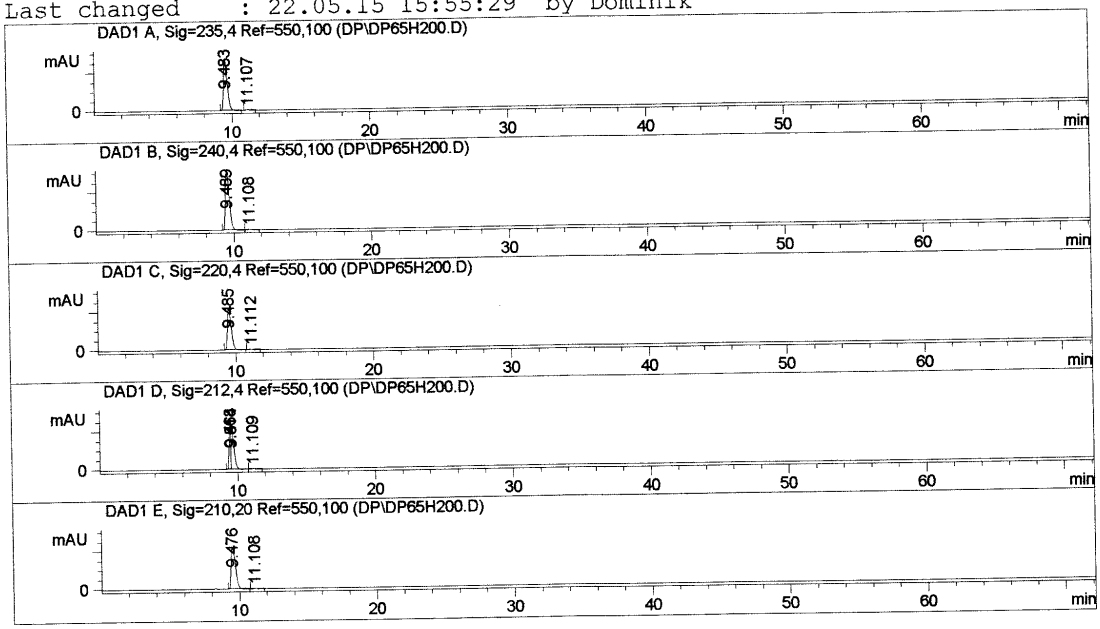
Injection Date : 27.05.15 14:26:59
Sample Name : DP65h2
Acq. Operator : Dominik

Vial : 12

Inj Volume : 3 µl

Method : C:\HPCHEM\1\METHODS\BPOD9_1.M
Last changed : 22.05.15 15:55:29 by Dominik



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Area Percent Report

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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

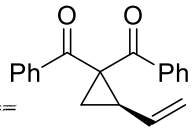
Signal 1: DAD1 A, Sig=235,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.483	PB	0.2796	4.96877e4	2640.18140	99.4388
2	11.107	BP	0.2726	280.42484	14.31167	0.5612
Totals :				4.99682e4	2654.49306	

Results obtained with enhanced integrator!

Data File C:\HPCHEM\1\DATA\DP\DP65H300.D Sample Name: DP65H3

Chiralcel OD-H; Heptan/Isopropanol 95:5, 0.5 mL/min; 3µ
1



(*S*)-127

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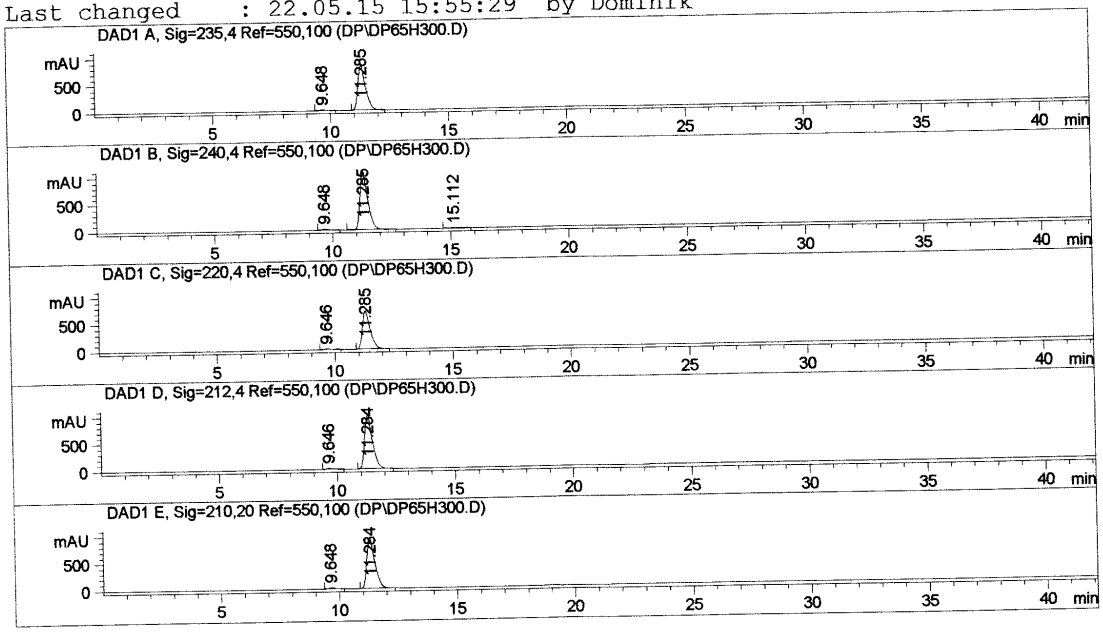
Injection Date : 20.05.15 15:59:54
Sample Name : DP65H3
Acq. Operator : Dominik

Vial : 12

Inj Volume : 3 µl

Acq. Method : C:\HPCHEM\1\METHODS\BPOD9_1.M
Last changed : 20.05.15 15:58:17 by Isabel
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\BPOD9_1.M
Last changed : 22.05.15 15:55:29 by Dominik



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Area Percent Report

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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 A, Sig=235,4 Ref=550,100

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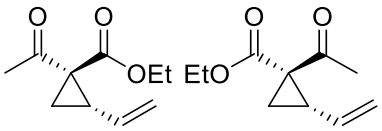
2	11.285	BB	0.3328	1.87413e4	825.64966	98.3250
Totals :				1.90606e4	842.30539	

Results obtained with enhanced integrator!

12.1.9 (anti) and (syn) Ethyl 1-acetyl-2-vinylcyclopropanecarboxylate (129a and 129b)



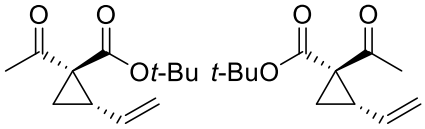
129a **129b**

(*trans*)-1,4-Dibrombut-2-ene (1.390 g, 6.5 mmol) and K_2CO_3 (2.695 g, 19.5 mmol) were added to a dried flask under an atmosphere of dry nitrogen. Anhydrous ethanol (14 mL) was added followed by the drop wise addition of ethyl acetoacetate (0.8 mL, 6.5 mmol). The reaction mixture was heated to reflux for 15 h then cooled to room temperature and diluted with Et_2O (15 mL). The precipitate was removed via filtration and washed with Et_2O (2 x 10 mL). The solvent was removed under reduced pressure. The reaction gave rise to three major products: Diastereoisomer **129a** and **129b** alongside some dihydrofurane **130**. Diastereoisomer **129b** could be separated by regular column chromatography on silica gel eluting with PE/EA 20:1 (v/v) to give 0.457 g (39%) as a colorless oil. Diastereoisomer **129a** was purified via HPLC eluting again with PE/EA 20:1 (v/v) giving 0.231 g (20%) as a colorless oil. The yield of dihydrofurane **130** was not determined.

129a:
R_f = 0.29 (PE/EA, 20:1 (v/v)); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 5.35-5.26 (m, 2H), 5.15-5.11 (m, 1H), 4.33-4.13 (m, 2H), 2.67-2.57 (m, 1H), 2.33 (s, 3H), 1.85 (dd, *J* = 7.5, 4.6 Hz, 1H), 1.53 (dd, *J* = 8.8, 4.6 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 201.1, 170.4, 132.8, 118.9, 61.5, 42.7, 33.5, 30.5, 20.1, 14.1 ppm; **IR** (ATR, neat) 3088, 2984, 2929, 1702, 1637 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) 182 (M^+, found), 139 (54), 136 (45), 135 (48), 121 (100), 94 (65), 93 (56), 67 (55), 66 (98), 65 (43).

129b:
R_f = 0.23 (PE/EA, 20:1 (v/v)); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 5.58-5.44 (m, 1H), 5.29 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.14 (dd, *J* = 10.1, 1.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.61 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 2.40 (s, 3H), 1.76 (dd, *J* = 7.7, 4.4 Hz, 1H), 1.58 (dd, *J* = 8.9, 4.4 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 202.0, 168.8, 133.1, 118.8, 61.4, 43.2, 34.3, 29.5, 23.1, 14.2 ppm; **IR** (ATR, neat) v 3088 , 2984 , 2938 , 1724 , 1695 , 1638 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) 182 (M^+, found), 139 (61), 136 (43), 135 (50), 121 (100), 94 (64), 93 (56), 67 (54), 66 (97), 65 (44).

12.1.10 (anti) and (syn) *tert*-Butyl 1-acetyl-2-vinylcyclopropane-1-carboxylate (131a and 131b)



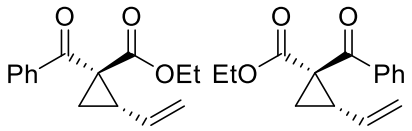
131a **131b**

NaH (0.800 g, 60% in mineral oil, 20 mmol) was suspended in anhydrous THF (16 mL) under an atmosphere of dry nitrogen. The reaction mixture was cooled to 0 °C (cryostat). *tert*-Butyl acetoacetate (1.6 mL, 9.51 mmol) was added drop wise and the reaction mixture stirred at 0 °C for 1 h. (*trans*)-1,4-Dibrombut-2-ene (2.034 g, 9.51 mmol) was added drop wise as a solution in anhydrous THF (6 mL). Upon completion of the addition the cooling bath was removed and the reaction mixture stirred for 40 h. The resulting suspension was diluted with Et_2O (20 mL) and the precipitate removed via filtration and washed with Et_2O (2 x 10 mL). The solvent was removed under reduced pressure. Diastereoisomer **131a** and **131b** alongside some dihydrofurane **132**. Diastereoisomer **131b** could be isolated via regular column chromatography on silica gel elution with PE/EA 20:1 (v/v) giving 0.267 g (13%) as a colorless oil. Diastereoisomer **131a** was isolated via HPLC eluting with PE/EA 20:1 (v/v) yielding 0.409 g (21%) as a colorless oil. The yield of dihydrofurane **132** was not determined.

131a:
***R*$_f$** = 0.37 (PE/EA, 20:1 (v/v)), **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 5.30-5.25 (m, 2H), 5.14-5.09 (m, 1H), 2.59-2.49 (m, 1H), 2.29 (s, 3H), 1.76 (dd, *J* = 7.5, 4.5 Hz, 1H), 1.49 (s, 9H), 1.45 (dd, *J* = 8.8, 4.6 Hz, 1H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 201.4, 169.4, 133.1, 118.6, 82.3, 43.7, 32.8, 30.4, 28.0, 19.8 ppm; **IR** (ATR, neat) 2978, 2932, 1701, 1637 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) 210 (M^+, found), 154 (50), 135 (32), 121 (58), 111 (45), 94 (60), 66 (37), 57 (100).

131b:
***R*$_f$** = 0.29 (PE/EA, 20:1 (v/v)); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 5.59-5.45 (m, 1H), 5.29 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.14 (dd, *J* = 10.1, 1.6 Hz, 1H), 2.58 (ddd, *J* = 8.3, 8.3, 8.3 Hz, 1H), 2.40 (s, 3H), 1.69-1.62 (m, 1H), 1.51-1.46 (m, 1H), 1.49 (s, 9H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 202.4, 167.8, 133.3, 118.4, 82.2, 44.2, 33.6, 29.5, 28.1, 22.9 ppm; **IR** (ATR, neat) 3087, 2978, 2934, 1719, 1696, 1638 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) 210 (M^+, found), 154 (47), 135 (32), 121 (57), 111 (48), 94 (57), 93 (29), 66 (37), 57 (100).

12.1.11 (anti) and (syn) Ethyl 1-benzoyl-2-vinylcyclopropane-1-carboxylate (133a and 133b)



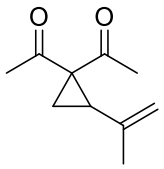
133a **133b**

Ethyl benzoylacetate (2.883 g, 15 mmol, 1 equiv.) was dissolved in anhydrous EtOH (20 mL) under an atmosphere of dry nitrogen. K_2CO_3 (4.146 g, 30 mmol, 2 equiv.) was added and the suspension stirred at room temperature for 15 min. Additional anhydrous EtOH (10 mL) was added prior to the addition of (*trans*)-1,4-dibrombut-2-ene (3.158 g, 15 mmol, 1 equiv.). The reaction mixture was stirred for 95 h at room temperature. The reaction mixture was diluted with Et_2O and the precipitate removed via filtration and washed with additional Et_2O. The solvent was removed under reduced pressure. The residue was portioned between H_2O (30 mL) and Et_2O (40 mL). The aqueous layer was extracted with Et_2O (3 x 40 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 20:1 (v/v) followed by HPLC eluting with PE/EA 20:1 (v/v) giving 1.374 g (37%) of diastereoisomer **133b** as a colorless oil and 936 mg (26%) of diastereoisomer **133a** as a colorless oil. The assignment of the diastereoisomers is based on the assignment of the ethyl and *tert*-butyl esters above.

133a:
***R*$_f$** = 0.33 (*n*-pentane/Et_2O, 20:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.84-7.80 (m, 2H), 7.55-7.750 (m, 1H), 7.45-7.40 (m, 1H), 5.33 (dd, *J* = 16.9, 2.0 Hz, 1H), 5.25-5.13 (m, 1H), 5.01 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.14-3.90 (m, 2H), 2.96-2.88 (m, 1H), 1.95 (dd, J = 7.4, 4.6 Hz, 1H), 1.62 (dd, *J* = 8.7, 4.6 Hz, 1H), 0.92 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 193.7, 171.0, 137.7, 133.2, 132.8, 128.5, 128.4, 118.6, 61.5, 39.8, 32.9, 19.6, 13.6 ppm; **IR** (ATR, neat) 2982, 1722, 1677, 1638, 1598, 1580, 1449 cm^{-1}; **HRMS** (ESI) calc. for [$C_{15}H_{16}O_3$ + Na^+]: 267.0992, found 267.0977.

133b:
***R*$_f$** = 0.33 (*n*-pentane/Et_2O, 20:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2H), 7.57-7.52 (m, 1H), 7.46-7.41 (m, 2H), 5.83-5.71 (m, 1H), 5.43-5.37 (m, 1H), 5.23-5.19 (m, 1H), 4.00 (q, *J* = 7.4 Hz, 2H), 2.79-2.71 (m, 1H), 1.94 (dd, *J* = 7.7, 4.8 Hz, 1H), 1.66 (dd, 9.0, 4.8 Hz, 1H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.5, 169.3, 137.3, 133.1, 132.8, 128.5, 128.2, 118.8, 61.3, 40.6, 30.4, 21.6, 13.7 ppm; **IR** (ATR, neat) 3086, 2982, 1727, 1678, 1637, 1598, 1581, 1448 cm^{-1}; **HRMS** (ESI) calc. for [$C_{15}H_{16}O_3$ + Na^+]: 267.0992, found 267.0980.

12.1.12 1,1'-(2-(Prop-1-en-2-yl)cyclopropane-1,1-diyl)bis(ethan-1-one) (139)



139

1,4-Dibromo-2-methylbut-2-ene (1,59 g, 7 mmol, 1 equiv.) and K_2CO_3 (2,90 g, 21 mmol, 3 equiv.) were suspended in acetone (20 mL). 2,4-Pentanedione (0,7 mL, 7 mmol, 1.0 equiv.) was added drop wise and the mixture was heated to reflux for 18 h. The reaction mixture was cooled to room temperature and Et_2O (35 mL) was added. The resulting precipitate was removed via filtration and washed with Et_2O (2 x 25 mL). The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) yielding 378 mg (32%) of the desired product **139** as a yellow oil.

***R*$_f$** = 0.38 (*n*-pentane/Et_2O, 4:1 (v/v)); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 4.94 (d, *J* = 0.8 Hz, 1H), 4.75 (s, 1H), 2.57 (t, *J* = 8.4 Hz, 1H), 2.23 (d, *J* = 1.2 Hz, 3H), 2.20 (d, *J* = 1.2 Hz, 3H), 1.94 (ddd, *J* = 8.0, 5.1, 1.0 Hz, 1H), 1.76 (d, *J* = 0.5 Hz, 3H), 1.50-1.41 (m, 1H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 203.2, 202.5, 138.6, 113.9, 51.2, 35.9, 30.7, 27.8, 23.0, 19.2 ppm; **IR** (ATR) 2973, 2918, 1688, 1423, 1357, 1309, 1256 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%)166 (M^+, found), 151 (14), 123 (67), 43 (100); **HRMS** (EI) calc. for [$C_{10}H_{14}O_2$]: 166.0994, found: 166.0991.

12.2 TBA[Fe]-Catalyzed Cloke-Wilson Rearrangement of Vinylcyclopropanes

General Procedure II: Thermal conditions for the C.-W. R. of VCPs (GP-II)

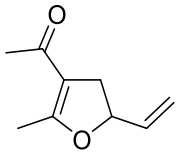
TBA[Fe] (10.3 mg, 0.025 mmol) was weighed into a dried Schlenk tube. Anhydrous DCM (5 mL) was added and the mixture stirred until homogenous. 1 mL (0.005 mmol TBA[Fe]) of this solution was transferred to a separate dried Schlenk tube which was subsequently charged with the appropriate vinylcyclopropane (0.5 mmol). The Schlenk tube was sealed under an atmosphere of dry nitrogen and heated to 45 °C for 14 h. The solvent was removed under reduced pressure and the residue subjected to column chromatography on silica gel.

General Procedure III: Photochemical conditions for the C.-W. R. of VCPs (GP-III)

A 10-mL Schlenk tube was charged with vinylcyclopropane (0.40 mmol, 1 equiv.), TBA[Fe] (0.001 mmol, 0.025 equiv.), and CH_3CN (1 mL) under N_2. The reactions were carried out at room temperature under irradiation of UV light (180 W, Hg lamp or 75 W, Xenon lamp

at distance of 15 cm) or visible light (23 W, Compact Fluorescent Lamp at distance of 15 cm) for 3 h. The reaction was quenched with diethyl ether and concentrated *in vacuo*. Purification by silica column chromatography afforded the desired dihydrofuran product.

12.2.1 1-(2-Methyl-5-vinyl-4,5-dihydrofuran-3-yl)ethenone (112)



112

Thermal condition:
The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 71.3 mg (94%) of **112** as a colorless oil.

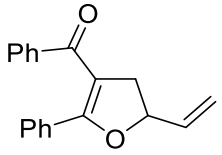
UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 58.4 mg (96%) of **112** as a colorless oil.

UV-Light (75 W, Xenon Lamp) condition:
The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 56.6 mg (93%) of **112** as a colorless oil.

Visible-Light (23 W, Compact Fluorescent Lamp) condition:
The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 56.0 mg (92%) of **112** as a colorless oil.

***R*$_f$** = 0.16 (*n*-pentane/Et_2O, 2:1 (v/v)); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 5.93 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.31 (dt, *J* = 17.1, 1.1 Hz, 1H), 5.22 (dt, *J* = 10.4, 1.1 Hz, 1H), 5.09-4.99 (m, 1H), 3.18-3.08 (m, 1H), 2.78-2.69 (m, 1H), 2.24 (t, *J* = 1.4 Hz, 3H), 2.20 (s, 3H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 194.4, 167.3, 136.7, 116.9, 111.9, 82.6, 36.3, 29.4, 15.0 ppm; **IR** (ATR, neat) 3409, 3086, 2989, 2923, 2864, 1670, 1593 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) 152 (M^+, 100), 137 (36), 109 (72), 95 (26), 91 (40), 67 (45).

12.2.2 Phenyl(2-phenyl-5-vinyl-4,5-dihydrofuran-3-yl)methanone (128)



128

Thermal condition:
The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 10:1 (v/v) to afford 126.5 mg (92%) of **128** as a colorless solid.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 10:1 (v/v) to afford 102.8 mg (93%) of **128** as a colorless solid.

***R*$_f$** = 0.13 (*n*-pentane/Et_2O, 10:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.24-7.15 (m, 4H), 7.10-7.03 (m, 4H), 6.10 (ddd, *J* = 17.0, 10.2, 6.5 Hz, 1H), 5.46 (dt, *J* = 17.1, 1.1 Hz, 1H), 5.23-5.33 (m, 2H), 3.45 (dd, *J* = 14.7, 9.9 Hz, 1H), 3.14 (dd, *J* = 14.9, 8.3 Hz, 1H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 193.4, 165.5, 139.0, 136.6, 131.1, 130.0, 129.9, 129.4, 128.9, 127.6, 127.58, 117.2, 111.7, 82.5, 38.7 ppm; **IR** (ATR, neat) 3081, 3027, 2985, 2848, 1615, 1600, 1587, 1565, 1487 cm^{-1}; **HRMS** (ESI) calc. for [$C_{19}H_{16}O_2$ + Na^+]: 299.1043, found 299.1054.

(*R*)-128: $[\alpha]_D^{20}$: -22.5 (c = 5.33, $CHCl_3$); **(*S*)-128**: $[\alpha]_D^{20}$: +22.5 (c = 5.33, $CHCl_3$).

Data File C:\HPCHEM\1\DATA\DP\CL-24A00.D Sample Name: CL-24A

Chiralcel OD-H; Heptan/Isopropanol 95:5, 0.5 mL/min; 3µ
l

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Injection Date : 22.05.15 14:34:47
Sample Name : CL-24A
Acq. Operator : Dominik

Vial : 11
Inj Volume : 3 µl

Acq. Method : C:\HPCHEM\1\METHODS\BPOD9_1.M
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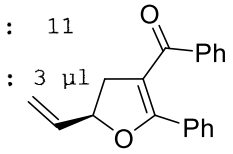
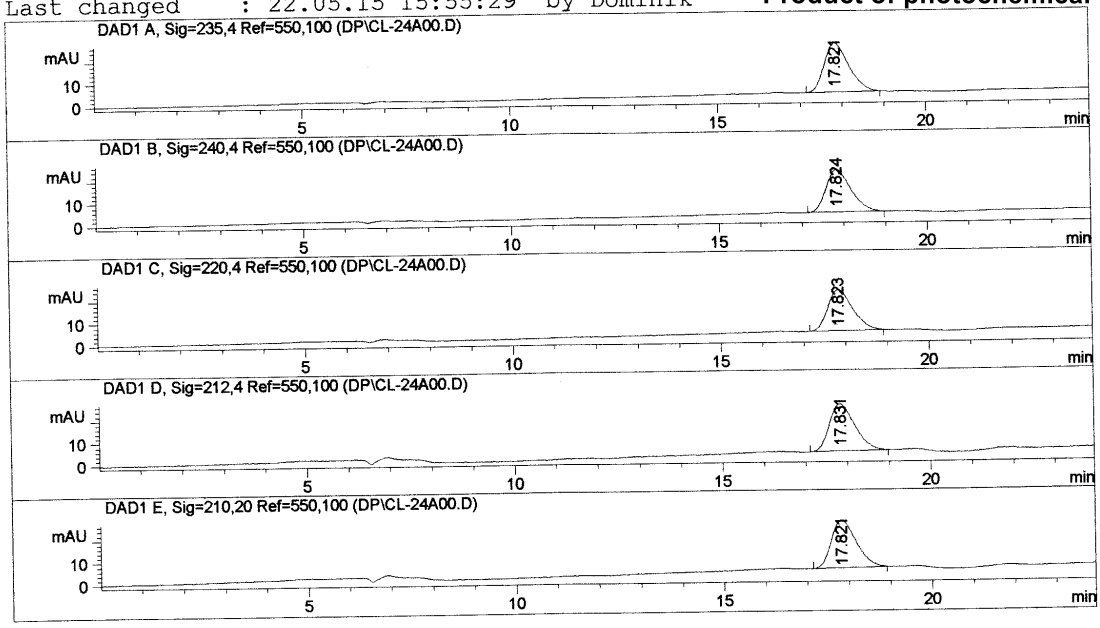
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\BPOD9_1.M
Last changed : 22.05.15 15:55:29 by Dominik



(*R*)-128
Product of photochemical condition



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Area Percent Report

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Dilution : 1.0000

Signal 1: DAD1 A, Sig=235,4 Ref=550,100

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Totals :				908.40143	21.97522	

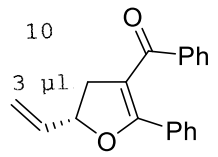
Results obtained with enhanced integrator!

Data File C:\HPCHEM\1\DATA\DP\CL-24B00.D Sample Name: CL-24B

Chiralcel OD-H; Heptan/Isopropanol 95:5, 0.5 mL/min; 3µ
l

Injection Date : 22.05.15 14:59:51
Sample Name : CL-24B
Acq. Operator : Dominik

Vial : 10
Inj Volume : 3 µl



(*S*)-128
Product of photochemical condition

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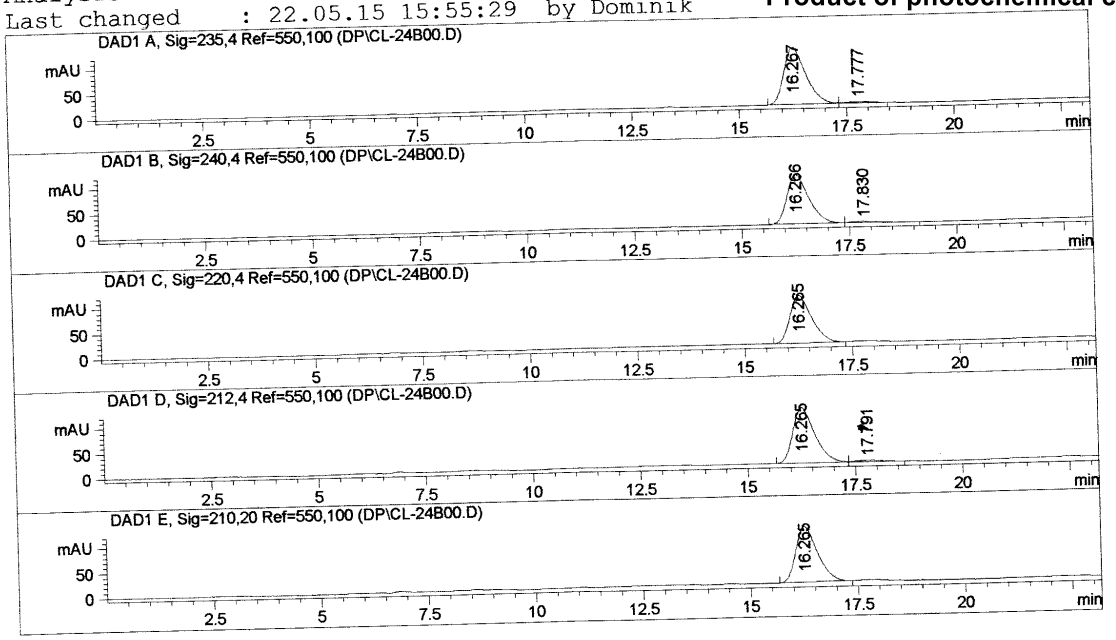
Last changed : 22.05.15 14:33:48 by Dominik
(modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\BPOD9_1.M
Last changed : 22.05.15 15:55:29 by Dominik



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 A, Sig=235,4 Ref=550,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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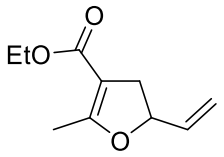
Totals :				4162.68339	116.52580	

Results obtained with enhanced integrator!

Instrument 1 26.05.15 10:58:12 Dominik

12.2.3 Ethyl 2-methyl-5-vinyl-4,5-dihydrofuran-3-carboxylate (130)



130

Thermal condition:
Starting from diastereoisomer **129a**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 84.6 mg (93%) of **130** as a colorless oil.

UV-Light (180 W, Hg lamp) condition:
Starting from diastereoisomer **129a**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 68.5 mg (94%) of **130** as a colorless oil.

Visible-Light (23 W, Compact Fluorescent Lamp) condition:
Starting from diastereoisomer **129a**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 67.8 mg (93%) of **130** as a colorless oil.

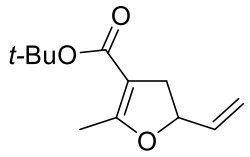
Thermal condition:
Starting from diastereoisomer **129b**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 83.9 mg (92%) of **130** as a colorless oil.

UV-Light (180 W, Hg lamp) condition:
Starting from diastereoisomer **129b**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 67.1 mg (92%) of **130** as a colorless oil.

Visible-Light (23 W, Compact Fluorescent Lamp) condition:
Starting from diastereoisomer **129b**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 67.1 mg (92%) of **130** as a colorless oil.

R_f = 0.26 (*n*-pentane/Et_2O, 15:1 (v/v)); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 5.93 (ddd, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.29 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.20 (dt, *J* = 10.3, 1.1 Hz, 1H), 5.08-4.98 (m, 1H), 4.17 (q, *J* = 7 Hz, 2H), 3.12-3.01 (m, 1H), 2.72-2.62 (m, 1H), 2.21 (t, *J* = 1.5 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 167.5, 166.1, 136.9, 116.6, 101.7, 82.5, 59.5, 35.6, 14.4, 14.1 ppm; **IR** (ATR, neat) 2981, 2928, 2870, 1695, 1642 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) 182 (M^+, 54), 139 (53), 137 (55), 135 (46), 121 (100), 94 (64), 93 (54), 67 (50), 66 (83), 65 (30), 55 (25).

12.2.4 *tert*-Butyl 2-methyl-5-vinyl-4,5-dihydrofuran-3-carboxylate (132)



132

Thermal condition:
Starting from diastereoisomer **131a**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 98.7 mg (94%) of **132** as a colorless oil.

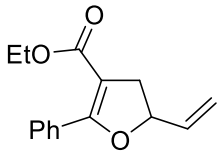
UV-Light (180 W, Hg lamp) condition:
Starting from diastereoisomer **131a**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 71.5 mg (85%) of **132** as a colorless oil.

Thermal condition:
Starting from diastereoisomer **131b**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 62.9 mg (60%) of **132** as a colorless oil.

UV-Light (180 W, Hg lamp) condition:
Starting from diastereoisomer **131b**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 15:1 (v/v) to afford 76.5 mg (91%) of **132** as a colorless oil.

***R_f* =** 0.37 (*n*-pentane/Et_2O, 15:1 (v/v)); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 5.93 (ddd, *J* = 17.0, 10.3, 6.7 Hz 1H), 5.29 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.19 (dt, *J* = 10.4, 1.1 Hz, 1H), 5.04-4.94 (m, 1H), 3.07-2.97 (m, 1H), 2.68-2.58 (m, 1H), 2.17 (t, *J* = 1.6 Hz, 3H), 1.48 (s, 9H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 166.2, 165.6, 137.1, 116.5, 103.1, 82.2, 79.5, 35.9, 28.4, 14.1 ppm; **IR** (ATR, neat) 2975, 2928, 2869, 1687, 1645 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) 210 (M^+, 32), 154 (63), 137 (63), 135 (55), 121 (91), 111 (88), 94 (100), 93 (47), 66 (56), 57 (46).

12.2.5 Ethyl 2-phenyl-5-vinyl-4,5-dihydrofuran-3-carboxylate (134)



134

Thermal condition:
Starting from diastereoisomer **133a**: 5 mol% TBA[Fe] were used. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 10:1 (v/v) to afford 106.4 (87%) of **134** as a colorless oil.

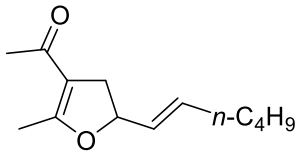
UV-Light (180 W, Hg lamp) condition:
Starting from diastereoisomer **133a**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 10:1 (v/v) to afford 88.9 (91%) of **134** as a colorless oil.

Thermal condition:
Starting from diastereoisomer **133b**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 10:1 (v/v) to afford 104.9 mg (86%) of **134** as a colorless oil.

UV-Light (180 W, Hg lamp) condition:
Starting from diastereoisomer **133b**: The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 10:1 (v/v) to afford 89.9 mg (92%) of **134** as a colorless oil.

R_f = 0.27 (*n*-pentane/Et_2O, 10:1 (v/v)); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 7.81-7.77 (m, 2H), 7.42-7.33 (m, 3H), 6.03 (ddd, *J* = 17.1, 10.3, 6.5 Hz, 1H), 5.41-5.12 (m, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.30 (dd, *J* = 5.1, 10.6 Hz, 1H), 2.92 (dd, *J* = 15.1, 8.3 Hz, 1H), 1.20 (t, *J* = 7.2, 3H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ 165.2, 164.6, 136.8, 130.3, 129.9, 129.3, 127.6, 116.8, 102.1, 82.0, 59.7, 37.3, 14.2 ppm; **IR** (ATR) 2980, 2867, 1703, 1680, 1623, 1597, 1574, 1493, 1446 cm^{-1}; **HRMS (ESI)** calc. for [$C_{15}H_{16}O_3$ + Na^+] 267.0992, found 267.0994.

12.2.6 (*E*)-1-(5-(Hex-1-en-1-yl)-2-methyl-4,5-dihydrofuran-3-yl)ethan-1-one (135)



135

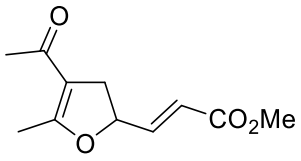
Thermal condition:
This reaction was performed using 5 mol% TBA[Fe]. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) to afford 90 mg (87%) of **135** as a brown oil.

UV-Light (180 W, Hg lamp) condition:
This reaction was performed by using 5 mol% TBA[Fe] for 6 hours. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) to afford 72.5 mg (87%) of **135** as a yellow oil.

R_f = 0.22 (*n*-pentane/Et_2O, 4:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.76 (m, 1H), 5.61-5.51 (m, 1H), 5.00 (dd, *J* = 18.0, 8.0 Hz, 1H), 3.09 (m, 1H), 2.71 (m, 1H), 2.22 (t, *J* = 1.3 Hz, 3H), 2.19 (s, 3H), 2.07 (dd, *J* = 13.6, 6.8 Hz, 2H), 1.44-1.27 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.6, 167.4, 135.1, 128.5, 112.1, 83.2, 36.7, 31.8, 30.9, 29.4, 22.2, 15.0, 13.9 ppm; **IR** (ATR) 2957, 2927, 2857, 1671, 1591, 1381, 1216, 1132, 1061, 967, 926, 625 cm^{-1}; **GC/MS** (ESI) m/z (%)209 (M + H^+, 25), 167 (16), 149 (18), 123 (25), 113 (100); **HRMS** (ESI) calc. for [$C_{13}H_{20}O_2$ + Na^+] 231.1356, found:

231.1358.

12.2.7 Methyl (*E*)-3-(4-acetyl-5-methyl-2,3-dihydrofuran-2-yl)acrylate (136)



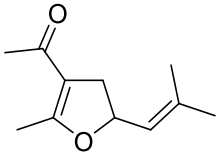
136

Thermal condition:
This reaction was performed using 5 mol% TBA[Fe]. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) to afford 101 mg (96%) of **136** as a red oil.

UV-Light (180 W, Hg lamp) condition:
This reaction was performed by using 5 mol% TBA[Fe] for 6 hours. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) to afford 74.8 mg (89%) of **136** as a yellow oil.

***R*f** = 0.19 (*n*-pentane /Et_2O, 2:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 6.93 (dd, *J* = 15.6, 4.8 Hz, 1H), 6.02 (d, *J* = 15.6 Hz, 1H), 5.28-5.16 (m, 1H), 3.76 (s, 3H), 3.30-3.15 (m, 1H), 2.77 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.26 (s, 3H), 2.21 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.0, 166.8, 166.2, 145.2, 120.8, 111.6, 79.5, 51.7, 36.0, 29.4, 14.7 ppm; **IR** (ATR) 2953, 2923, 1722, 1673, 1597,1435, 1389, 1362, 1305, 1272, 1219, 1172, 987, 928, 732, 625 cm^{-1}; **GC/MS** (ESI) m/z (%) 211 (M + H^+, 17), 137 (100), 119 (12); **HRMS** (ESI) calc. for [$C_{11}H_{14}O_4$ + H^+]: 211.0965, found: 211.0961.

12.2.8 1-(2-Methyl-5-(2-methylprop-1-en-1-yl)-4,5-dihydrofuran-3-yl)ethan-1-one (137)



137

Thermal condition:
The reaction was performed on a 0.275 mmol scale using 5 mol-% TBA[Fe]. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) to afford 27 mg (54%) of **137** as a purple oil.

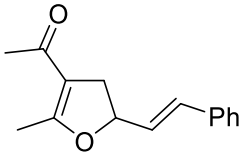
UV-Light (180 W, Hg lamp) condition:
This reaction was performed by using 5 mol-% TBA[Fe] for 6 hours. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) to afford 54.1 mg (75%) of **137** as a colorless oil.

Visible-Light (23 W, Compact Fluorescent Lamp) condition:
This reaction was performed by using 5 mol-% TBA[Fe] for 6 hours. The *title compound*

was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 4:1 (v/v) to afford 54.8 mg (76%) of **137** as a colorless oil.

***R*$_f$** = 0.25 (*n*-pentane/Et_2O, 4:1(v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.39-5.23 (m, 2H), 3.17-3.02 (m, 1H), 2.73-2.58 (m, 1H), 2.21 (t, *J* = 1.4 Hz, 3H), 2.19 (s, 3H), 1.78 (s, 3H), 1.74 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.7, 167.9, 138.5, 124.2, 112.1, 79.3, 37.1, 29.4, 25.8, 18.3, 15.2 ppm; **IR** (ATR) v 2972, 2916, 2859, 1714, 1669, 1589, 1451, 1380, 1216, 1132, 928, 865, 625 cm^{-1}; **GC/MS** (ESI) m/z (%) 181 (M^+, 21), 163 (18), 145 (25),123 (100), 113 (24),105 (25); **HRMS** (ESI) calc. for [$C_{11}H_{16}O_2$ + Na^+]: 203.1043, found: 203.1039.

12.2.9 (*E*)-1-(2-Methyl-5-styryl-4,5-dihydrofuran-3-yl)ethan-1-one (138)



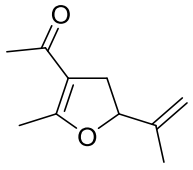
138

Thermal condition:
This reaction was performed on a 0.25 mmol scale using 5 mol% TBA[Fe]. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 56 mg (98%) of **138** as a brown oil.

UV-Light (180 W, Hg lamp) condition:
This reaction was performed by using 5 mol% TBA[Fe] for 6 hours. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 89.5 mg (98%) of **138** as a brown oil.

***R*$_f$** = 0.25 (*n*-pentane/Et_2O, 4:1(v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.43-7.23 (m, 5H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.26 (dd, *J* = 15.8, 7.3 Hz, 1H), 5.26-5.15 (m, 1H), 3.19 (m, 1H), 2.83 (m, 1H), 2.26 (t, *J* = 1.4 Hz, 3H), 2.21 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.46, 167.39, 135.97, 132.57, 128.66, 128.22, 127.63, 126.71, 112.09, 82.74, 36.76, 29.48, 15.08 ppm; **IR** (Film) 2922, 2863, 1669, 1592, 1494, 1449, 1423, 1219 cm^{-1}; **HRMS** (ESI) calc. for [$C_{15}H_{16}O_2$ + Na^+] 251.1043, found: 251.1040.

12.2.10 1-(2-Methyl-5-(prop-1-en-2-yl)-4,5-dihydrofuran-3-yl)ethan-1-one (140)



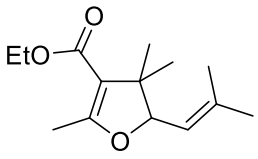
140

Thermal condition:
This reaction was performed using 5 mol% TBA[Fe]. The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 80 mg (96%) of **140** as a yellow oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 64.5 mg (97%) of **140** as a yellow oil.

***R*$_f$** = 0.46 (*n*-pentane/Et_2O 2:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.05-4.97 (m, 2H), 4.91-4.88 (m, 1H), 3.09 (ddq, *J* = 13.5, 10.6, 1.4 Hz, 1H), 2.76 (ddq, *J* = 14.1, 8.4, 1.5 Hz, 1H), 2.25 (t, *J* = 1.5 Hz, 3H), 2.21 (s, 3H), 1.74 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.4, 167.6, 143.3, 112.1, 112.0, 84.8, 35.3, 29.4, 17.0, 14.9 ppm; **IR** (Film) 2918, 2865, 1672, 1598, 1389, 1219 cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 166 (30) [M^+], 123 (37), 43 (100) **HRMS** (EI) calc. for [$C_{10}H_{14}O_2$]: 166.0994, found: 166.0995.

12.2.11 Ethyl 2,4,4-trimethyl-5-(2-methylprop-1-en-1-yl)-4,5-dihydrofuran-3-carboxylate (141)



141

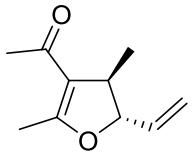
UV-Light (180 W, Hg lamp) condition:
This reaction was performed by using 10 mol% TBA[Fe] in THF (1 mL) for 24 hours. The *title compound* was purified via column chromatography on silica gel eluting with PE/EA 20:1 (v/v) to afford 93.3 mg (98%) of **141** as a colorless oil.

UV-Light (75 W, Xenon Lamp) condition:
This reaction was performed by using 10 mol% TBA[Fe] in THF (1 mL) for 24 hours. The *title compound* was purified via column chromatography on silica gel eluting with PE/EA 20:1 (v/v) to afford 91.5 mg (96%) of **141** as a colorless oil.

Visible-Light (23 W, Compact Fluorescent Lamp) condition:
This reaction was performed by using 10 mol% TBA[Fe] in THF (1 mL) for 24 hours. The *title compound* was purified via column chromatography on silica gel eluting with PE/EA 20:1 (v/v) to afford 18.1 mg (19%) of **141** as a colorless oil.

***R*$_f$** = 0.35 (PE/EA 20:1(v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 5.32 (dq, *J* = 9.8, 1.3 Hz, 1H), 4.78 (d, *J* = 9.8 Hz, 1H), 4.18 (dq, *J* = 7.1, 1.7 Hz, 2H), 2.17 (s, 3H), 1.82 (d, *J* = 1.2 Hz, 3H), 1.74 (d, *J* = 1.3 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.23 (s, 3H), 1.05 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 167.7, 166.1, 139.7, 119.2, 119.9, 88.5, 59.0, 46.2, 26.2, 25.6, 21.8, 18.4, 14.9, 14.3 ppm; **IR** (ATR) 1693, 1628, 1334, 1308, 1253, 1078, 1061, 976, 951, 776 cm^{-1}; **HRMS** (ESI) calc. for [$C_{14}H_{22}O_3$ + Na^+]: 261.1461, found: 261.1460.

12.2.12 (4-Methyl-2-phenyl-5-vinyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (142)



142

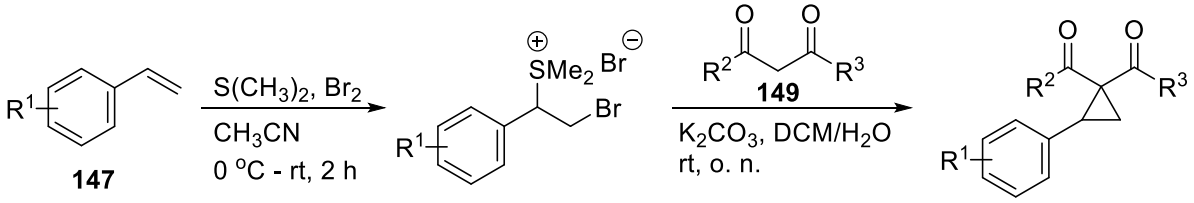
Thermal condition:
The *title compound* was purified via column chromatography on silica gel eluting with PE/EA 20:1 (v/v) to afford 52 mg (72%) of **142** as a colorless oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified via column chromatography on silica gel eluting with PE/EA 20:1 (v/v) to afford 106.7 mg (92%) of **142** as a colorless oil.

***R*$_f$** = 0.33 (PE/EA, 20:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.56-7.47 (m, 2H), 7.27-7.19 (m, 3H), 7.19-7.12 (m, 1H), 7.12-7.00 (m, 4H), 6.07 (ddd, *J* = 17.1, 10.4, 6.8 Hz, 1H), 5.44 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.30 (dt, *J* = 10.4, 1.0 Hz, 1H), 4.77- 4.69 (m, 1H), 3.58-3.46 (m, 1H), 1.36 (d, *J* = 6.6 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 193.8, 164.3, 139.2, 135.9, 131.4, 130.03, 129.97, 129.4, 129.0, 127.7, 127.6, 117.5, 116.8, 90.2, 46.5, 17.9 ppm; **IR** (ATR) 3061, 2958, 1721, 1613, 1593, 1572, 1490, 1447, 1158, 889, 729, 692 cm^{-1}; **HRMS** (ESI) calc. for [$C_{20}H_{18}O_2$ + Na^+]: 313.1199, found: 313.1193.

12.3 Preparation of Arylcyclopropanes

General Procedure IV: Preparation of ACPs (GP-IV)

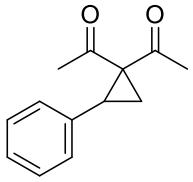


The procedure was modified from the literature. A solution of bromine (1.02 mL, 20 mmol) in DCM (5 mL) was added in a solution of dimethyl sulfide (7.34 mL, 100 mmol) in CH_3CN (20 mL) at 0 °C to give a yellow precipitate. The corresponding styrene derivative **147** (20 mmol) was then added at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred for 2 hours. Diethyl ether (30 mL) was added to give a precipitate, which was then filtered and washed with diethyl ether to give the corresponding bromosulfonium bromide **148** without further purification.

The bromosulfonium bromide **148** (10 mmol) and potassium carbonate (4.15 g, 30 mmol) were dissolved in DCM:H_2O (1:1) mixture (200 mL). Pentane-2,4-dione (2.05 mL, 20 mmol), 1,3-diphenyl-1,3-propanedione (4.49 g, 20 mmol) or methyl acetoacetate (2.15 mL, 20 mmol) was added and stirred at room temperature overnight. The DCM layer was separated and the aqueous layer was extracted with 3 portions of DCM. The combined

organic layers were dried over $MgSO_4$, filtered and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O (5:1 to 2:1) to give the desired arylcyclopropane.

12.3.1 1,1'-(2-Phenylcyclopropane-1,1-diyl)bis(ethan-1-one) (145)

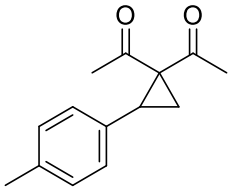


145

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 5:1 (v/v) to afford 656 mg (22% two steps overall yield) of **145** as a colorless solid.

***R*$_f$** = 0.23 (*n*-pentane/Et_2O, 5:1 (v/v)); **m.p.** 61-62 °C [lit. 58 °C]; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.31-7.21 (m, 3H), 7.15-7.12 (m, 2H), 3.29 (bt, *J* = 8.5 Hz, 1H), 2.28 (s, 3H), 2.26 (dd, *J* = 7.9, 5.3 Hz, 1H), 1.81 (s, 3H), 1.65 (dd, *J* = 9.0, 5.3 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.7, 202.2, 134.1, 128.5, 128.4 , 127.5, 52.7, 33.6, 30.4, 27.7, 19.1 ppm; **IR** (ATR) 3098, 3065, 3020, 1702, 1681, 1453 cm^{-1}; **HRMS** (ESI): calc. for [$C_{13}H_{14}O_2$ + Na^+]: 225.0886, found: 225.0871.

12.3.2 1,1'-(2-(*p*-Tolyl)cyclopropane-1,1-diyl)bis(ethan-1-one)) (149)

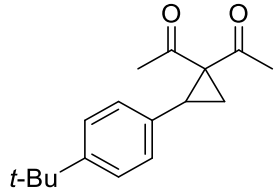


149

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 1000 mg (23% two steps overall yield) of **149** as a yellow solid.

***R*$_f$** = 0.38 (*n*-pentane /Et_2O, 3:1 (v/v)); **m.p.** 52-54 °C [lit.57.6-59 °C]; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.10 (m, 2H), 7.06-7.01 (m, 2H), 3.27 (t, *J* = 8.5 Hz, 1H), 2.32 (s, 3H), 2.30-2.23 (m, 4H), 1.84 (s, 3H), 1.67 (dd, *J* = 8.0, 4.3 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ (ppm) 202.9, 202.4, 137.3, 130.9, 129.2, 128.3, 52.7, 33.6, 30.5, 27.6, 21.1, 19.1 ppm; **IR** (ATR) 3013, 2923, 1681, 1517, 1425, 1356 cm^{-1}; **HRMS** (ESI): calc. for [$C_{14}H_{16}O_2$ + Na^+]: 239.1043, found: 239.1033.

12.3.3 1,1'-(2-(4-(*tert*-Butyl)phenyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (150)

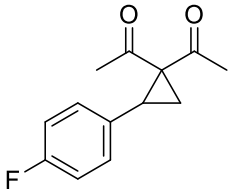


150

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 504 mg (8% two steps overall yield) of **150** as a colorless solid.

***R*f** = 0.35 (*n*-pentane /Et_2O, 3:1 (v/v)); **m.p.** 51-53 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.08-7.03 (m, 2H), 3.25 (t, *J* = 8.5 Hz, 1H), 2.27 (s, 3H), 2.24 (dd, *J* = 8.0, 5.3 Hz, 1H), 1.82 (s, 3H), 1.65 (dd, *J* = 9.1, 5.3 Hz, 1H), 1.28 (s, 9H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.9, 202.6, 150.6, 130.9, 128.0, 125.5, 52.7, 34.4, 33.5, 31.3, 30.5, 27.7, 19.2 ppm; **IR** (ATR) 2962, 2869, 1684, 1518, 1425, 1359 cm^{-1}; **HRMS** (ESI): calc. for [$C_{17}H_{22}O + Na^+$]: 281.1512, found: 281.1494.

12.3.4 1,1'-(2-(4-Fluorophenyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (151)

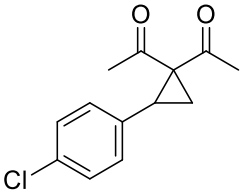


151

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 815 mg (37% two steps overall yield) of **151** as a colorless oil.

***R*f** = 0.17 (*n*-pentane/Et_2O, 3:1 (v/v));**^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.15-7.07 (m, 2H), 7.02-6.93 (m, 2H), 3.27 (t, *J* = 8.5 Hz, 1H), 2.28 (s, 3H), 2.22 (dd, *J* = 7.9, 5.4 Hz, 1H), 1.84 (s, 3H), 1.64 (dd, *J* = 9.1, 5.4 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.6, 201.9, 162.1 (d, *J* = 245.2 Hz), 130.0 (d, *J* = 8.1 Hz), 129.9 (d, *J* = 3.24 Hz), 115.5 (d, *J* = 21.5 Hz), 52.6, 32.8, 30.5, 27.8, 19.3 ppm; **IR** (ATR) 3010, 1684, 1605, 1512, 1430, 1359, 1224, 842 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{13}FO_2 + Na^+$]: 243.0792, found: 243.0802.

12.3.5 1,1'-(2-(4-Chlorophenyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (152)



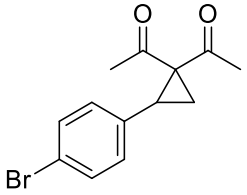
152

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 899 mg (38%

two steps overall yield) of **152** as a colorless solid.

R_f = 0.28 (*n*-pentane/Et_2O, 2:1 (v/v)); **m.p.** 77-78 °C [lit. 76.6-77.5 °C]; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.29-7.22 (m, 2H), 7.10-7.04 (m, 2H), 3.26 (t, *J* = 8.5 Hz, 1H), 2.28 (s, 3H), 2.22 (dd, *J* = 7.8, 5.3 Hz, 1H), 1.86 (s, 3H), 1.64 (dd, *J* = 9.1, 5.4 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.4, 201.7, 133.4, 132.7, 129.7, 128.7, 52.7, 32.8, 30.5, 27.8, 19.1 ppm; **IR** (ATR) 3087, 3053, 1705, 1670, 1593, 1494, 1404, 1373, 1104, 851, 592, 560 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{13}ClO_2$ + Na^+]: 259.0496, found: 259.0485.

12.3.6 1,1'-(2-(4-Bromophenyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (153)

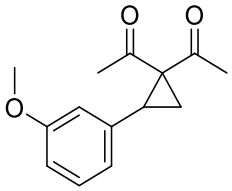


153

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 534 mg (19% two steps overall yield) of **153** as a colorless solid.

R_f = 0.3 (*n*-pentane/Et_2O, 3:1 (v/v)); **m.p.** 75-76 °C [lit. 72.2-73.2 °C]; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.45-7.37 (m, 2H), 7.06-6.97 (m, 2H), 3.24 (t, *J* = 8.5, 1H), 2,28 (s, 3H), 2,22 (dd, *J* = 7.8, 5.4 Hz, 1H), 1.86 (s, 3H), 1.63 (dd, *J* = 9.0, 5.4 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.4, 201.7, 133.3, 131.7, 130.1, 121.6, 52.7, 32.8, 30.5, 27.8, 19.1 ppm; **IR** (ATR) 3008, 1681, 1491, 1357, 1027, 822 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{13}BrO_2$ + Na^+]: 280.0099, found: 280.0103.

12.3.7 1,1'-(2-(3-Methoxyphenyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (154)

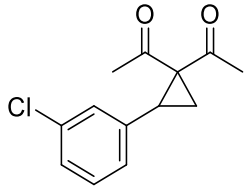


154

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 813 mg (35% two steps overall yield) of **154** as a colorless oil.

R_f = 0.21 (*n*-pentane/Et_2O, 2:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.92 Hz, 1H), 6.81-6.75 (m, 1H), 6.74-6.65 (m, 2H), 3.78 (s, 3H) 3.26 (t, *J* = 8.5 Hz, 1H), 2.28 (s, 3H), 2.22 (dd, *J* = 7.9, 5.3 Hz, 1H), 1.84 (s, 3H), 1.64 (dd, *J* = 9.0, 5.3 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.7, 202.3, 159.6, 135.8, 129.5, 120.6, 114.1, 113.0, 55.2, 52.6, 33.5, 30.4, 27.7, 19.3 ppm; **IR** (ATR) 3006, 2926, 2838, 1683, 1601, 1584, 1492, 1358, 1256, 783, 721 cm^{-1}; **HRMS** (ESI) calc. for [$C_{14}H_{16}O_3$ + Na^+]: 255.0992, found: 255.0981.

12.3.8 1,1'-(2-(3-Chlorophenyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (155)

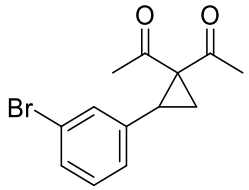


155

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 402 mg (17% two steps overall yield) of **155** as a colorless oil.

R_f = 0.24 (*n*-pentane/Et_2O, 3:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.24-7.19 (m, 2H), 7.18-7.14 (m, 1H), 7.04-6.96 (m, 1H), 3.26 (t, *J* = 8.5 Hz, 1H), 2.29 (s, 3H), 2.22 (dd, *J* = 7.9, 5.3 Hz, 1H), 1.88 (s, 3H), 1.64 (dd, *J* = 9.1, 5.4 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.3, 201.6, 136.4, 134.4, 129.7, 128.7, 127.8, 126.5, 52.6, 32.7, 30.5, 27.8, 19.1 ppm; **IR** (ATR) 3009, 2927, 1687, 1598, 1421, 1309, 781, 699 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{13}ClO_2$ + Na^+]: 259.0496, found: 259.0483.

12.3.9 1,1'-(2-(3-Bromophenyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (156)

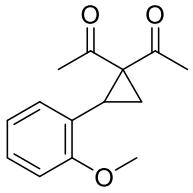


156

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 712 mg (13% two steps overall yield) of **156** as a colorless oil.

R_f = 0.33 (*n*-pentane /Et_2O, 3:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.40-7.35 (m, 1H), 7.32 (t, *J* = 1.8 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 3.25 (t, *J* = 8.4 Hz, 1H), 2.29 (s, 3H), 2.22 (dd, *J* = 7.9, 5.4 Hz, 1H), 1.88 (s, 3H), 1.63 (dd, *J* = 9.0, 5.4 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.3, 201.6, 136.7, 131.7, 130.7, 130.0, 126.9, 122.6, 52.6, 32.7, 30.5, 27.9, 19.1 ppm; **IR** (ATR)□3059, 3010, 2923, 1683, 1594, 1564, 1478, 1421, 1357 cm^{-1}; **HRMS** (ESI): calc. for [$C_{13}H_{13}BrO_2$ + Na^+]: 304.9972, found: 304.9974.

12.3.10 1,1'-(2-(2-Methoxyphenyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (157)



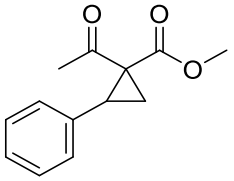
157

The *title compound* was obtained according to GP-IV after purification via column

chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 760 mg (43% two steps overall yield) of **157** as a colorless solid.

***R*$_f$** = 0.24 (*n*-pentane /Et_2O, 3:1 (v/v)); **m.p.** 60-63 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.22 (m, 1H), 6.98 (m, 1H), 6.87 (m, 2H), 3.84 (s, 3H), 3.24 (t, *J* = 8.7 Hz, 1H), 2.30-2.25 (m, 4H), 1.82 (s, 3H), 1.69 (dd, *J* = 9.0, 5.3 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 203.9, 202.2, 158.6, 128.9, 128.6, 122.6, 120.4, 109.8, 55.3, 51.6, 30.2, 29.4, 27.1, 17.5 ppm; **IR** (ATR) 3006, 2939, 2838, 1682, 1601, 1495 cm^{-1}; **HRMS** (ESI): calc. for [$C_{14}H_{16}O_3$ + Na^+]: 255.0992, found: 255.0982.

12.3.11 Methyl 1-acetyl-2-phenylcyclopropane-1-carboxylate (158)

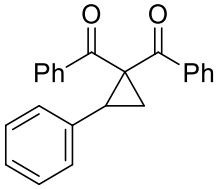


158

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 5:1 (v/v) to afford 806 mg (24% two steps overall yield) of **158** as a colorless oil as a 3:1 mixture of *cis*- and *trans*-isomers.

***R*$_f$** = 0.45 (*n*-pentane/Et_2O, 5:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.30-7.11 (m, 5H *cis*, 5H *trans*), 3.81 (s, 3H *trans*); 3.35 (s, 3H *cis*), 3.28 (bt, *J* = 8.7 Hz, 1H *cis*), 3.27 (bt, *J* = 8.7 Hz, 1H *trans*), 2.45 (s, 3H *cis*), 2.31 (dd, *J* = 8.1, 5.0 Hz, 1H *trans*), 2.24 (dd, *J* = 8.1, 4.6 Hz, 1H *cis*), 1.93 (s, 3H *trans*), 1.74 (dd, *J* = 9.2, 4.7 Hz, 1H *cis*), 1.71 (dd, *J* = 9.1, 5.1 Hz, 1H *trans*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 202.2 (*cis*), 199.9 (*trans*), 171.0 (*trans*), 168.7 (*cis*), 134.8 (*cis*), 133.7 (*trans*), 128.7 (*cis*), 128.4 (*trans*), 128.3 (*trans*), 128.1 (*cis*), 127.5 (*trans*), 127.4 (*cis*), 52.6 (*trans*), 51.9 (*cis*), 44.6 (*cis*), 44.2 (*trans*), 35.5 (*cis*), 34.5 (*trans*), 30.2 (*trans*), 29.6 (*cis*), 21.6 (*cis*), 17.8 (*trans*) ppm; **IR** (ATR) 3031, 3005, 2952, 1733, 1690, 1604, 1499, 1454, 1435 cm^{-1}; **HRMS** (EI): calc. for [$C_{13}H_{14}O_3$]: 218.0943, found: 218.0947.

12.3.12 (2-Phenylcyclopropane-1,1-diyl)bis(phenylmethanone) (159)



159

The *title compound* was obtained according to GP-IV after purification via column chromatography on silica gel eluting with *n*-pentane/Et_2O 10:1 (v/v) to afford 1.16 g (23% two steps overall yield) of **159** as a colorless solid.

***R*$_f$** = 0.37 (*n*-pentane/Et_2O, 10:1 (v/v)); **m.p.** 130-131 °C; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.78-7.73 (m, 2H), 7.59-7.56 (m, 2H); 7.39-7.34 (m, 1H), 7.28-7.22 (m, 5H), 7.18- 7.05 (m, 5H), 3.99 (bt, *J* = 8.5 Hz, 1H), 2.84 (dd, *J* = 8.2, 4.8 Hz, 1H), 1.73 (dd, *J* = 9.1, 5.0 Hz,

1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 197.0, 194.4, 137.8, 137.7, 134.1, 132.9, 132.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.1, 49.8, 32.4, 19.7; **IR** (ATR) 3085, 3064, 3004, 1656, 1595, 1576, 1499, 1447 cm^{-1}; **HRMS** (ESI): calc. for [($C_{23}H_{18}O_2$ + Na^+]: 349.1199, found: 349.1195.

12.4 TBA[Fe]-Catalyzed Cloke-Wilson Rearrangement of Arylcyclopropanes

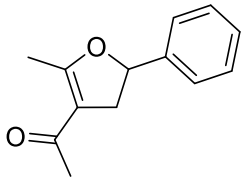
General Procedure V: Thermal conditions for the C.-W. R. of ACPs (GP-V)

TBA[Fe] (5.2 mg, 0.0125 mmol, 0.05 equiv.) and the corresponding ACP (0.25 mmol, 1 equiv.) were weighed into a dried 10 mL microwave tube. Anhydrous DMF (1 mL) was added and the tube was sealed under an atmosphere of dry nitrogen. The reaction mixture was stirred for 2 h at 120 °C under microwave conditions. The product was obtained via chromatography on silica gel.

General Procedure VI: Photochemical conditions for the C.-W. R. of ACPs (GP-VI)

A 10-mL Schlenk tube was charged with Arylcyclopropane (0.40 mmol, 1 equiv.), TBA[Fe] (0.04 mmol, 0.1 equiv.), and DMF (1 mL) under N_2. The reactions were carried out at room temperature under irradiation of UV light (180 W, Hg lamp or 75 W, Xe lamp at distance of 15 cm) or visible light (23 W, Compact Fluorescent Lamp at distance of 15 cm) for 24 h. The reaction was quenched with diethyl ether and concentrated *in vacuo*. Purification by silica column chromatography afforded the desired dihydrofuran product.

12.4.1 1-(2-Methyl-5-phenyl-4,5-dihydrofuran-3-yl)ethan-1-one (146)



146

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 50 mg (99%) of **146** as a colorless oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 66.3 mg (82%) of **146** as a colorless oil.

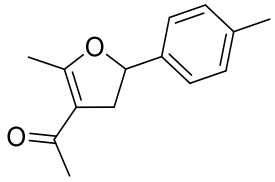
UV-Light (75 W, Xenon Lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-

pentane/Et_2O 2:1 (v/v) to afford 46.1 mg (57%) of **146** as a colorless oil.

Visible-Light (23 W, Compact Fluorescent Lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 4.0 mg (5%) of **146** as a colorless oil.

***R*$_f$** = 0.46 (*n*-Pentane/Et_2O, 2:1 (v/v)); **^{1}H-NMR** (300 MHz, CDCl3) δ 7.41-7.29 (m, 5H), 5.60 (dd, *J* = 10.6, 8.4 Hz, 1H), 3.40 (ddq, *J* = 14.3, 10.7, 1.5 Hz, 1H), 2.97 (ddq, *J* = 14.2, 8.4, 1.5 Hz, 1H), 2.31 (t, *J* = 1.5 Hz, 3H), 2.22 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, CDCl3) δ 194.4, 167.4, 141.2, 128.7, 128.2, 125.6, 111.8, 83.1, 38.7, 29.4, 15.0 ppm; **IR** (ATR) 3063, 3032, 3002, 2954, 2919, 2865, 1670, 1595, 1495, 1452, 1423 cm^{-1}; **HRMS** (ESI): calc. for [$C_{13}H_{14}O_2$ + Na^+]: 225.0886, found: 225.0892.

12.4.2 1-(2-Methyl-5-(*p*-tolyl)-4,5-dihydrofuran-3-yl)ethan-1-one (160)



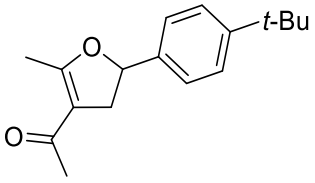
160

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 54 mg (99%) of **160** as a yellow oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 73.5 mg (85%) of **160** as a colorless oil.

R_f = 0.21 (*n*-pentane/Et_2O, 3:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.25-7.15 (m, 4H), 5.56 (dd, *J* = 10.6, 8.4 Hz, 1H), 3.36 (m, 1H), 2.96 (m, 1H), 2.35 (s, 3H), 2.30 (t, *J* = 1.5 Hz, 3H), 2.21 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.5, 167.5, 138.3, 138.1, 129.4, 125.7, 111.9, 83.3, 38.7, 29.5, 21.2, 15.0 ppm; **IR** (Film) 2921 (w), 2864 (w), 1670 (m), 1592 (s), 1516 (m), 1423 (m), 1381 (m),1359 (m) cm^{-1}; **GC/MS** (ESI) m/z (%) = 239 (100) [M^+ + Na]; **HRMS** (ESI) calc. for [$C_{14}H_{16}O_2$ + Na^+]: 239.1043, found: 239.1033.

12.4.3 1-(5-(4-(*tert*-Butyl)phenyl)-2-methyl-4,5-dihydrofuran-3-yl)ethan-1-one (161)



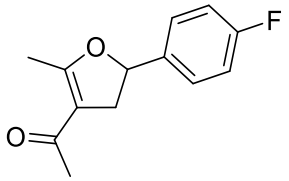
161

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 48 mg (75%) of **161** as a yellow oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 79.6 mg (77%) of **161** as a yellow oil.

R_f = 0.31 (*n*-pentane/Et_2O, 3:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.43-7.38 (m, 2H), 7.27 (dt, *J* = 2.0, 1.2 Hz, 2H), 5.57 (dd, *J* = 10.6, 8.4 Hz, 1H), 3.37 (m, 1H), 3.00 (m, 1H), 2.30 (t, *J* = 1.5 Hz, 3H), 2.21 (s, 3H), 1.32 (s, 9H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.5, 167.5, 151.4, 138.2, 125.7, 125.6, 111.9, 83.2, 38.5, 34.6, 31.3, 29.5, 15.0 ppm; **IR** (Film) 2959 (m), 2867 (w), 1671 (m), 1595 (s), 1512 (w), 1382 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 258 (100) [M^+], 243 (69), 169 (25), 57 (25), 43 (57); **HRMS** (EI) calc. for [$C_{17}H_{22}O_2$]: 258.1620, found: 258.1622.

12.4.4 1-(5-(4-Fluorophenyl)-2-methyl-4,5-dihydrofuran-3-yl)ethan-1-one (162)



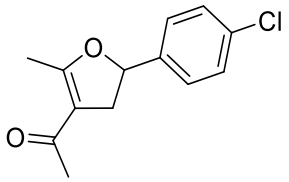
162

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 42 mg (76%) of **162** as a yellow oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 54.6 mg (62%) of **162** as a yellow oil.

R_f = 0.21 (*n*-pentane/Et_2O, 3:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.36-7.26 (m, 2H), 7.12-7.01 (m, 2H), 5.57 (dd, *J* = 10.4, 8.4 Hz, 1H), 3.46-3.32 (m, 1H), 3.00-2.88 (m, 1H), 2.30 (t, *J* = 1.4 Hz, 3H), 2.22 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.3, 167.2, 162.5 (d, *J* = 245.5 Hz), 137.1 (d, *J* = 3.2 Hz), 127.5 (d, *J* = 8.2 Hz), 115.6 (d, *J* = 21.2 Hz), 111.9, 82.5, 38.8, 29.5, 15.0 ppm; **IR** (ATR) 2924, 1671, 1593, 1510, 1424, 1216, 929, 833, 624. 611 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{13}FO_2$ + Na^+]: 243.0792, found: 243.0785.

12.4.5 1-(5-(4-Chlorophenyl)-2-methyl-4,5-dihydrofuran-3-yl)ethan-1-one (163)



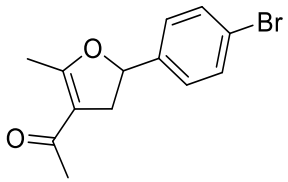
163

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 54 mg (92%) of **163** as a yellow oil.
UV-Light (180 W, Hg lamp) condition:

The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 71.3 mg (75%) of **163** as a yellow oil.

***R*f** = 0.18 (*n*-pentane/Et_2O, 3:1 (v/v)); **^{1}H-NMR** (300 MHz, CDCl3) δ 7.39-7.32 (m, 2H), 7.30-7.22 (m, 2H), 5.56 (dd, *J* = 10.7, 8.3 Hz, 1H), 3.48-3.33 (m, 1H), 2.97-2.86 (m, 1H), 2.30 (t, *J* = 1.5 Hz, 3H), 2.21 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.3, 167.2, 139.8, 134.0, 128.9, 127.0, 111.9, 82.3, 38.8, 29.5, 15.0 ppm; **IR** (ATR) 2921, 1672, 1592, 1492, 1381, 1215, 1134, 930, 624 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{13}ClO_2$ + Na^+]: 259.0496, found: 259.0484.

12.4.6 1-(5-(4-Bromophenyl)-2-methyl-4,5-dihydrofuran-3-yl)ethan-1-one (164)

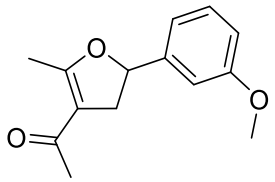


164

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 3:1 (v/v) to afford 68 mg (97%) of **164** as a yellow oil.

***R*f** = 0.22 (*n*-pentane/Et_2O, 3:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.54 - 7.48 (m, 2H), 7.24 - 7.17 (m, 2H), 5.55 (dd, *J* = 10.7, 8.3 Hz, 1H), 3.39 (m, 1H), 2.91 (m, 1H), 2.31 (t, *J* = 1.5 Hz, 3H), 2.22 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.3, 167.2, 140.4, 131.9, 127.3, 122.1, 111.9, 82.4, 38.7, 29.5, 15.0 ppm; **IR** (Film) 2922 (w), 2866 (w), 1671 (m), 1601 (s), 1488 (m), 1382 (m) cm^{-1}; **GC/MS** (EI, 70 eV) m/z (%) = 280 (63) [M^+], 186 (28), 115 (23), 14,5 (100); **HRMS** (EI) calc. for [$C_{13}H_{13}BrO_2$]: 280.0099, found: 280.0097.

12.4.7 1-(5-(3-Methoxyphenyl)-2-methyl-4,5-dihydrofuran-3-yl)ethan-1-one (165)



165

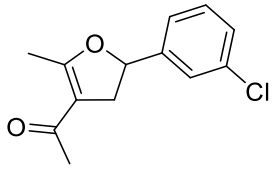
Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 49 mg (85%) of **165** as a yellow oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 86.4 mg (93%) of **165** as a yellow oil.

***R*f** = 0.27 (*n*-pentane/Et_2O, 2:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.34-7.26 (m, 3H), 6.94-6.82 (m, 1H), 5.56 (dd, *J* = 10.7, 8.4 Hz, 1H), 3.82 (s, 3H), 3.45-3.32 (m, 1H), 3.03-2.90 (m, 1H), 2.31 (t, *J* = 1.5 Hz, 3H), 2.21 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ

194.4, 167.4, 159.9, 142.9, 129.9, 117.8, 113.4, 111.9, 111.3, 83.0, 55.3, 38.8, 29.5, 15.0 ppm; **IR** (ATR) 2938, 2837, 1670, 1586, 1489, 1383, 1259, 1216, 926, 782, 697, 625 cm^{-1}; **HRMS** (ESI) calc. for [$C_{14}H_{16}O_3$ + Na^+]: 255.0992, found: 255.0974.

12.4.8 1-(5-(3-Chlorophenyl)-2-methyl-4,5-dihydrofuran-3-yl)ethan-1-one (166)



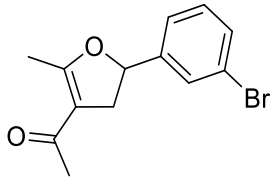
166

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 53 mg (90%) of **166** as a yellow oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 68.1 mg (72%) of **166** as a yellow oil.

R_f = 0.32 (*n*-pentane/Et_2O, 2:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.35-7.27 (m, 3H), 7.24-7.15 (m, 1H), 5.56 (dd, *J* = 10.7, 8.3 Hz, 1H), 3.47-3.35 (m, 1H), 2.99-2.87 (m, 1H), 2.32 (t, *J* = 1.5 Hz, 3H), 2.22 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.3, 167.2, 143.4, 134.7, 130.1, 128.3, 125.7, 123.7, 111.9, 82.2, 38.8, 29.5, 15.0 ppm; **IR** (ATR) 2998, 2922, 1672, 1593, 1383, 1360, 1215, 923, 785, 693, 624 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{13}ClO_2$ + Na^+]: 259.0496, found: 259.0492.

12.4.9 1-(5-(3-Bromophenyl)-2-methyl-4,5-dihydrofuran-3-yl)ethan-1-one (167)

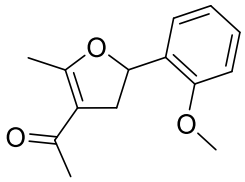


167

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 59 mg (84%) of **167** as a yellow oil.

R_f = 0.29 (*n*-pentane/Et_2O, 2:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.26-7.23 (m, 2H), 5.55 (dd, *J* = 10.7, 8.3 Hz, 1H), 3.40 (m, 1H), 2.93 (m, 1H), 2.32 (t, *J* = 1.5 Hz, 3H), 2.22 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.3, 167.2, 143.7, 131.3, 130.4, 128.6, 124.2, 122.8, 111.9, 82.1, 38.8, 29.5, 14.9 ppm; **IR** (Film) 2922 (w), 2865 (w),1672 (m), 1595 (s), 1475 (w), 1424 (m), 1385 (m) cm^{-1}; **GC/MS** (ESI) m/z (%) = 303 (100) [M^+ + Na]; **HRMS** (ESI) calc. for [$C_{13}H_{13}BrO_2$ + Na^+]: 302.9991, found: 302.9969.

12.4.10 1-(5-(2-Methoxyphenyl)-2-methyl-4,5-dihydrofuran-3-yl)ethan-1-one (168)



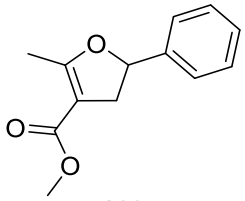
168

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 48 mg (83%) of **168** as a yellow oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 38.1 mg (41%) of **168** as a yellow oil.

***R*$_f$** = 0.44 (*n*-pentane/Et_2O, 2:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.32-7.25 (m, 2H), 6.97 (m, 1H), 6.90 (m, 1H), 5.87 (dd, *J* = 10.7, 8.0 Hz, 1H), 3.84 (s, 3H), 3.42 (m, 1H), 2.79 (m, 1H), 2.34 (t, *J* = 1.5 Hz, 3H), 2.18 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 194.8, 167.5, 155.9, 129.9, 128.9, 125.3, 120.6, 111.9, 110.4, 78.8, 55.4, 38.2, 29.5, 15.0 ppm; **IR** (Film) 2938 (w), 2838 (w), 1670 (m), 1588 (s), 1492 (m), 1462 (m), 1437 (m) cm^{-1}; **GC/MS** (ESI) m/z (%) = 255 (100) [M^+ + Na]; **HRMS** (ESI) calc. for [$C_{14}H_{16}O_3$ + Na^+]: 255.0992, found: 255.0978.

12.4.11 Methyl 2-methyl-5-phenyl-4,5-dihydrofuran-3-carboxylate (169)



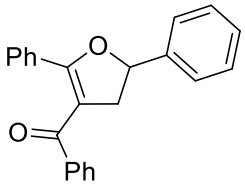
169

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 40 mg (74%) of **169** as a colorless oil.

UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 2:1 (v/v) to afford 70.7 mg (81%) of **169** as a colorless oil.

***R*$_f$** = 0.27 (*n*-pentane/Et_2O, 10:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.41-7.27 (m, 5H), 5.59 (dd, *J* = 10.7, 8.3 Hz, 1H), 3.71 (s, 3H), 3.33 (ddq, *J* = 14.5, 10.8, 1.6 Hz, 1H), 2.91 (ddq, *J* = 14.5, 8.3, 1.6 Hz, 1H), 2.29 (t, *J* = 1.6 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 168.0, 166.4, 141.5, 128.7, 128.2, 125.7, 101.4, 83.2, 50.9, 37.9, 14.1 ppm; **IR** (ATR) 3032, 2949, 1690, 1647, 1495, 1435 cm^{-1}; **HRMS** (ESI): calc. for [$C_{13}H_{14}O_3$ + Na^+]: 241.0835, found: 241.0832.

12.4.12 (2,5-Diphenyl-4,5-dihydrofuran-3-yl)(phenyl)methanone (170)



170

Thermal condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 5:1 (v/v) to afford 76 mg (93%) of **170** as a colorless solid.

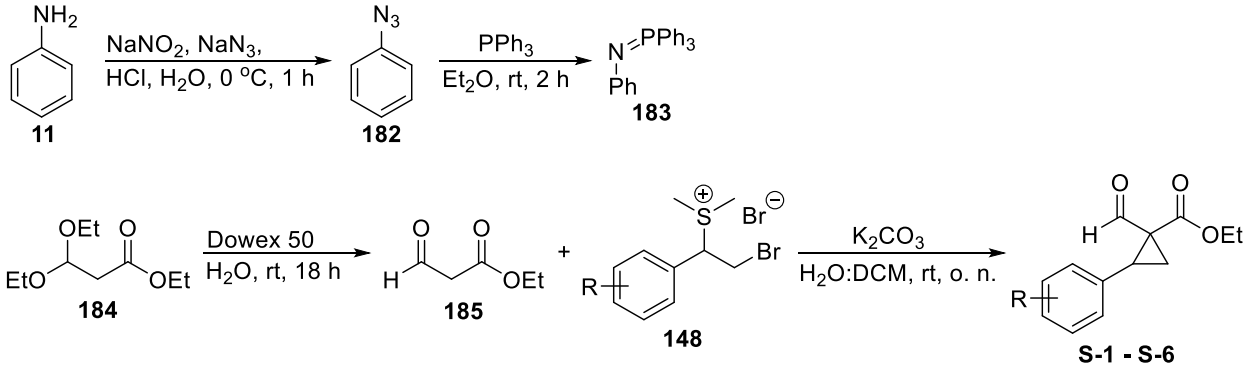
UV-Light (180 W, Hg lamp) condition:
The *title compound* was purified by column chromatography on silica gel eluting with *n*-pentane/Et_2O 5:1 (v/v) to afford 52.2 mg (40%) of **170** as a colorless solid.

***R**f* = 0.33 (*n*-pentane/Et_2O, 5:1 (v/v)); **m.p.** 111-112 °C; **^{1}H-NMR** (250 MHz, $CDCl_3$) δ 7.51-7.05 (m, 15H), 5.85 (bt, *J* = 9.5 Hz, 1H), 3.71 (dd, *J* = 15.1, 10.3 Hz, 1H), 3.39 (dd, *J* = 15.1, 9.0 Hz, 1H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) 193.4, 165.5, 141.1, 139.0, 131.2 , 130.1, 129.9, 129.5, 128.9, 128.8, 128.3, 127.7, 127.6, 125.9, 111.8, 83.2, 41.1 ppm; **IR** (ATR) 3061, 3030, 1611, 1592, 1573, 1492, 1446 cm^{-1}; **HRMS** (ESI): calc. for [$C_{23}H_{18}O_2$ + Na^+]: 349.1199, found: 349.1215.

13. TBA[Fe]-catalyzed Cyclopropylimine Rearrangement

13.1 Preparation of Cyclopropylimines

General Procedure VII: Preparation of formylcyclopropane (GP-VII)



Aniline **11** (1.82 mL, 20 mmol) was dissolved in HCl (6M, 12.6 mL), and the solution was cooled at 0 °C. An aqueous solution of sodium nitrite [1.40 g, 20.3 mmol, in H_2O (7 mL)] was slowly added. The reaction temperature was not allowed to rise above 5 °C. In the same way, an aqueous solution of NaN_3 [1.30 g, 20.1 mmol, in H_2O (7 mL)] was added, and stirring was continued for 15 min at room temperature. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$, and the product was extracted with diethyl ether (6*50 mL). The combined organic layers were dried with Na_2SO_4, filtered, and

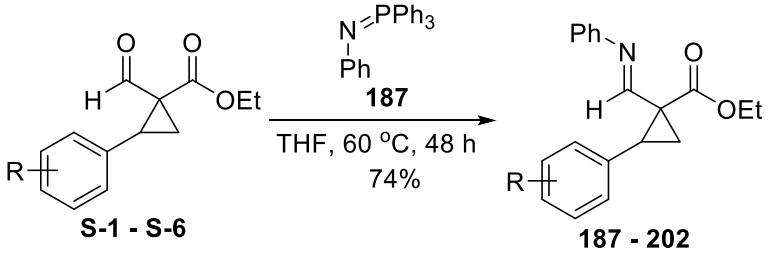
concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (PE:EA, 5:2) to give phenyl azide **182** as a yellow oil. The crude phenyl azide **182** was used in the next step without further purification.

To a stirring solution of phenyl azide **182** (1.90 g, 16 mmol) in ether (24 mL) was slowly added a solution of triphenylphosphine (4.20 g, 16 mmol) in ether (24 mL). The reaction mixture was stirred for 2 h at room temperature. The volatiles were removed in vacuo. The crude material was purified by recrystallization from n-pentane/EA (1:1) to yield triphenylphosphine phenylimide **183** as a pale-yellow solid.

Ethyl 3,3-diethoxypropionate **184** (0.97 mL) was dissolved in degassed water (25 mL) under N_2, and then Dowex 50W (2 g) was added into the solution. The reaction mixture was stirred at room temperature for 18 hours. The reaction mixture was filtered and the aqueous phase was extracted with DCM for several times. The organic phases were combined washed with brine, dried over $MgSO_4$, concentrated under reduced pressure to give the ethyl formylacetate **185**. The crude ethyl formylacetate **185** was used in the next step without further purification.

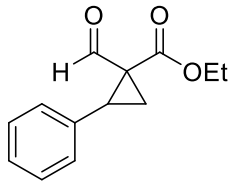
The bromosulfonium bromide **148** (10 mmol) and potassium carbonate (3.87 g, 28 mmol) were dissolved in DCM:H_2O (1:1) mixture (200 mL). ethyl formylacetate **185** (1.86 g, 16 mmol) was added and stirred at room temperature overnight. The DCM layer was separated and the aqueous layer was extracted with 3 portions of DCM. The combined organic layers were dried over $MgSO_4$, filtered and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with PE/EA (20:1 to 10:1) to give the desired formylcyclopropane **S1** - **S6.**

General Procedure VIII: Preparation of formylcyclopropane (GP-VIII)



To a solution of triphenylphosphine phenylimide (5.98 g, 16.9 mmol) in THF (42 mL) was added formylcyclopropane **S1** - **S6** (2.37 g, 9.4 mmol) under N_2. The reaction mixture was stirred at 55 °C for overnight. then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with PE/EA (20:1 to 10:1) to give the desired cyclopropylimine **187** - **202**.

13.1.1 Ethyl 1-formyl-2-phenylcyclopropane-1-carboxylate (S1)

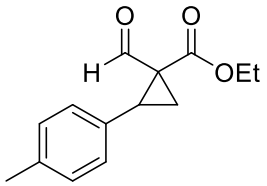


S-1

The *title compound* was obtained according to GP-VII after purification via column chromatography on silica gel eluting with PE/EA 20:1 (v/v) to afford **S1** as a colorless oil.

***R*f** = 0.33 (PE/EA, 20:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.34 (s, 1H *trans*), 9.95 (s, 1H *cis*), 7.32-7.19 (m, 5H *trans*, 5H *cis*), 4.34 (q, *J* = 7.1 Hz, 2H *cis*), 3.97-3.83 (m, 2H *trans*), 3.44 (t, *J* = 9.0 Hz, 1H *cis*), 3.20 (t, *J* = 8.9 Hz, 1H, *trans*), 2.36 (dq, *J* = 7.1, 4.4 Hz, 2H *cis*), 2.06 (q, *J* = 4.5, 2H *trans*), 1.36 (t, *J* = 7.1 Hz, 3H *cis*), 0.89 (t, *J* = 7.1 Hz, 3H *trans*) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 198.0 (*trans*), 194.8 (*cis*), 170.6 (*cis*), 168.1 (*trans*), 134.1 (*trans*), 132.9 (*cis*), 129.7 (*cis*), 129.4 (trans), 128.2 (*trans*), 127.8 (*cis*), 61.7 (*cis*), 61.1 (*trans*), 41.7 (*cis*), 41.7 (*trans*), 41.3 (*cis*), 41.2 (*trans*), 21.8 (*trans*), 20.2 (*cis*), 14.2 (*cis*), 13.7 (*trans*); **IR** (ATR) 3465, 2982, 1706, 1313, 1149, 1027, 698 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{14}O_3$ + Na^+]: 241.0835, found: 241.0833.

13.1.2 Ethyl 1-formyl-2-(*p*-tolyl)cyclopropane-1-carboxylate (S2)

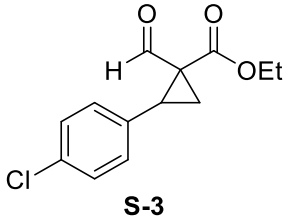


S-2

The *title compound* was obtained according to GP-VII after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **S2** as a colorless oil.

***R*f** = 0.43 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.33 (s, 1H *trans*), 9.94 (s, 1H *cis*), 7.14-7.06 (m, 4H *trans*, 4H *cis*), 4.34 (q, *J* = 7.1 Hz, 2H *cis*), 3.92 (dq, *J* = 7.1, 3.0 Hz, 2H *trans*), 3.41 (t, *J* = 9.0 Hz, 1H *cis*), 3.16 (t, *J* = 8.9 Hz, 1H, *trans*), 2.36 (dt, *J* = 8.5, 4.4 Hz, 2H *cis*), 2.31 (s, 3H *trans*), 2.30 (s, 3H *cis*), 2.08-2.00 (m, 2H *trans*), 1.36 (t, *J* = 7.1 Hz, 3H *cis*), 0.93 (t, *J* = 7.1 Hz, 3H *trans*) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 198.0 (*trans*), 194.9 (*cis*), 170.7 (*cis*), 168.1 (*trans*), 137.54 (*cis*), 137.52 (*trans*), 131.0 (*trans*), 129.7 (*cis*), 129.5 (cis), 129.2 (*trans*), 128.9 (*cis*), 128.8 (*trans*), 61.6 (*cis*), 61.1 (*trans*), 42.9 (*cis*, *trans*), 41.8 (*cis*), 41.4 (*trans*), 21.9 (*trans*), 21.1 (*cis*, *trans*), 20.2 (*cis*), 14.2 (*cis*), 13.8 (*trans*) ppm; **IR** (ATR) 2981, 2926, 2865, 1704, 1311, 1277, 1148, 819 cm^{-1}; **HRMS** (ESI) calc. for [$C_{14}H_{16}O_3$ + Na^+]: 255.0992, found: 255.0981.

13.1.3 Ethyl 2-(4-chlorophenyl)-1-formylcyclopropane-1-carboxylate (S3)

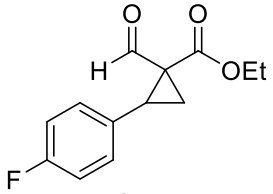


S-3

The *title compound* was obtained according to GP-VII after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **S3** as a colorless oil.

***R*f** = 0.25 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 10.33 (s, 1H *trans*), 9.98 (s, 1H *cis*), 7.29-7.22 (m, 2H *trans*, 2H *cis*), 7.20-7.12 (m, 2H *trans*, 2H *cis*), 4.34 (q, *J* = 7.1 Hz, 2H *cis*), 3.96 (dq, *J* = 7.3, 0.8 Hz, 2H *trans*), 3.39 (t, *J* = 9.0 Hz, 1H *cis*), 3.15 (t, *J* = 8.9 Hz, 1H, *trans*), 2.33 (dt, *J* = 8.7, 4.8 Hz, 2H *cis*), 2.06 (dd, *J* = 9.3, 4.3 Hz, 2H *trans*), 1.36 (t, *J* = 7.2 Hz, 3H *cis*), 0.96 (t, *J* = 7.1 Hz, 3H *trans*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 197.7 (*trans*), 194.8 (*cis*), 170.4 (*trans*), 167.8 (*cis*), 133.7 (*cis*), 132.7 (*trans*), 131.0 (*trans*), 130.7 (*cis*), 128.3 (*cis*, *trans*), 61.8 (*cis*), 61.3 (*trans*), 42.5 (*cis*), 41.2 (*trans*), 40.8 (*cis*), 40.1 (*trans*), 22.0 (*trans*), 20.5 (*cis*), 14.2 (*cis*), 13.9 (*trans*) ppm; **IR** (ATR) 2982, 2869, 1701, 1311, 1279, 1145, 1091, 1015, 828, 521 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{13}ClO_3$ + Na^+]: 275.0445, found: 275.0423.

13.1.4 Ethyl 2-(4-fluorophenyl)-1-formylcyclopropane-1-carboxylate (S4)

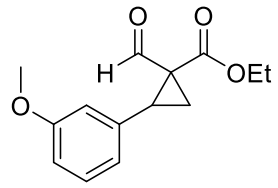


S-4

The *title compound* was obtained according to GP-VII after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **S4** as a colorless oil.

***R*f** = 0.29 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 10.34 (s, 1H *trans*), 9.98 (s, 1H *cis*), 7.25-7.15 (m, 2H *trans*, 2H *cis*), 7.03-6.92 (m, 2H *trans*, 2H *cis*), 4.34 (q, *J* = 7.1 Hz, 2H *cis*), 3.94 (dq, *J* = 7.1, 2.1 Hz, 2H *trans*), 3.40 (t, *J* = 8.9 Hz, 1H *cis*), 3.16 (t, *J* = 8.9 Hz, 1H, *trans*), 2.38-2.29 (m, 2H *cis*), 2.06 (dd, *J* = 9.2, 4.4 Hz, 2H *trans*), 1.36 (t, *J* = 7.1 Hz, 3H *cis*), 0.95 (t, *J* = 7.1 Hz, 3H *trans*) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 197.8 (*trans*), 194.90 (*cis*), 170.5 (*trans*), 163.9 (*cis*), 131.3 (d, *J* = 8.2 Hz *cis*), 131.0 (d, *J* = 8.2 Hz *trans*), 115.2 (*cis*), 115.0 (*trans*), 61.8 (*cis*), 61.2 (*trans*), 42.6 (*cis*), 41.3 (*trans*), 41.0 (*cis*), 40.3 (*trans*), 22.1 (*trans*), 20.6 (*cis*), 14.2 (*trans*), 13.8 (*cis*) ppm; **IR** (ATR) 2983, 2867, 1706, 1514, 1312, 1230, 1150, 841 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{13}FO_3$ + Na^+]: 259.0741, found: 259.0732.

13.1.5 Ethyl 1-formyl-2-(3-methoxyphenyl)cyclopropane-1-carboxylate (S5)

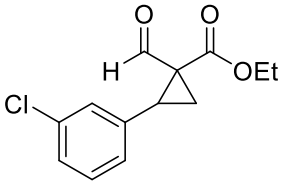


S-5

The *title compound* was obtained according to GP-VII after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **S5** as a colorless oil.

***R*f** = 0.29 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.34 (s, 1H *trans*), 9.95 (s, 1H *cis*), 7.18 (t, *J* = 7.8 Hz, 1H *trans*, 1H *cis*), 6.85-6.73 (m, 3H *trans*, 3H *cis*) 4.34 (q, *J* = 7.1 Hz, 2H *cis*), 3.94 (dq, *J* = 7.1, 1.1 Hz, 2H *trans*), 3.78 (s, 3H *trans*, 3H *cis*) 3.40 (t, *J* = 8.9 Hz, 1H *cis*), 3.17 (t, *J* = 8.9 Hz, 1H, *trans*), 2.35 (dq, *J* = 6.9, 4.3 Hz, 2H *cis*), 2.03 (dq, *J* = 6.1, 4.5 Hz, 2H *trans*), 1.36 (t, *J* = 7.1 Hz, 3H *cis*), 0.92 (t, *J* = 7.1 Hz, 3H *trans*) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 198.0 (*trans*), 194.7 (*cis*), 170.6 (*cis*), 168.1 (*trans*), 160.4 (*cis*), 159.4 (*trans*), 135.7 (*trans*), 134.4 (*cis*), 129.1 (*cis*, *trans*), 122.0 (*cis*), 121.7 (*trans*), 115.5 (*cis*), 115.0 (*trans*), 113.4 (*trans*), 113.2 (*cis*), 61.7 (*cis*), 61.1 (*trans*), 55.3 (*trans*), 55.2 (*cis*), 42.6 (*trans*), 41.4 (*cis*), 41.2 (*cis*), 41.1 (*trans*), 22.0 (*trans*), 20.1 (*cis*), 14.2 (*cis*), 13.8 (*trans*) ppm; **IR** (ATR) 2980, 2939, 1708, 1313, 1281, 1148, 700 cm^{-1}; **HRMS** (ESI) calc. for [$C_{14}H_{16}O_3$ + Na^+]: 271.0941, found: 271.0933.

13.1.6 Ethyl 2-(3-chlorophenyl)-1-formylcyclopropane-1-carboxylate (S6)

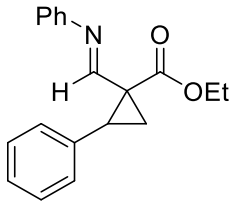


S-6

The *title compound* was obtained according to GP-VII after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **S6** as a colorless oil.

***R*f** = 0.38 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 10.34 (s, 1H *trans*), 9.99 (s, 1H *cis*), 7.25-7.18 (m, 3H *trans*, 3H *cis*), 7.14-7.06 (m, 1H *trans*, 1H *cis*) 4.35 (q, *J* = 7.2 Hz, 2H *cis*), 3.96 (dq, *J* = 7.1, 1.2 Hz, 2H *trans*), 3.39 (t, *J* = 8.9 Hz, 1H *cis*), 3.15 (t, *J* = 8.9 Hz, 1H, *trans*), 2.34 (dt, *J* = 8.9, 4.6 Hz, 1H *cis*), 2.03 (dd, *J* = 9.3, 4.4 Hz, 1H *trans*), 1.38 (t, *J* = 7.1 Hz, 3H *cis*), 0.95 (t, *J* = 7.1 Hz, 3H *trans*) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 197.7 (*trans*), 194.6 (*cis*), 170.3 (*trans*), 167.8 (*cis*), 136.3 (*trans*), 135.0 (*cis*), 134.11 (*cis*), 134.06 (*trans*), 129.9 (*cis*), 129.44 (*trans*), 129.42 (*cis*) 129.4 (*trans*), 127.99 (*cis*), 127.95 (*trans*), 127.8 (*cis*), 127.7 (*trans*), 61.6 (*cis*), 61.3 (*trans*), 42.3 (*trans*), 41.0 (*cis*), 40.6 (*cis*), 39.9 (*trans*), 21.9 (*trans*), 20.4 (*cis*), 14.2 (*cis*), 13.8 (*trans*) ppm.

13.1.7 Ethyl (*E*)-2-phenyl-1-((phenylimino)methyl)cyclopropane-1-carboxylate (187)

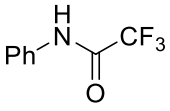


187

The *title compound* was obtained according to GP-VIII after purification via column chromatography on silica gel eluting with PE/EA 5:1 (v/v) with 3% of Et_3N to afford **187** as a colorless oil.

***R*f** = 0.2 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.39-7.15 (m, 8H), 7.11-7.05 (m, 2H), 3.93-3.77 (m, 2H), 3.30 (t, *J* = 8.7 Hz, 1H), 2.24 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.22 (dd, *J* = 9.1, 4.2 Hz, 1H), 0.86 (t, *J* = 7.12 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 169.6, 163.4, 151.6, 135.6, 129.4, 129.0, 128.0, 127,2, 125.6, 120.8, 60.8, 40.8, 37.1, 21.8, 13.7 ppm; **IR** (ATR) 2980, 1713, 1637, 1594, 1304, 1208, 1143, 757, 696 cm^{-1}; **HRMS** (EI) calc. for [$C_{19}H_{19}NO_2$]: 293.1416, found: 293.1415.

13.1.8 2,2,2-trifluoro-*N*-phenylacetamide (188)

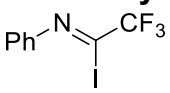


188

To a 100 mL round-bottom flask, was added aniline (1.82 mL, 20 mmol), triethylamine (2.82 mL, 20 mmol) in DCM (40 mL). Trifluoroacetic anhydride (2.8 mL, 20 mmol) was added dropwise to the mixture over 30 min at ice bath. Then reaction mixture was warmed to room temperature and stirred for about 4 hours. The mixture was washed by water and extracted with DCM, the solvent was removed under reduced pressure. Then the crude product was purified by column chromatography (PE:EA = 5:1 to 1:1) to afford 3.6458 g (96%) of **188** as a white solid.

***R*f** = 0.41 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.60-7.53 (m, 2H), 7.44-7.35 (m, 2H), 7.28-7.24 (m, 1H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.8 (d, *J* = 37.1 Hz), 135.1, 129.4, 126.4, 120.5, 115.7 (q, *J* = 288.6 Hz) ppm; **IR** (ATR) 3317, 1703, 1548, 1285, 1151, 755, 732, 691 cm^{-1}.

13.1.9 (*Z*)-2,2,2-trifluoro-*N*-phenylacetimidoyl iodide (189)



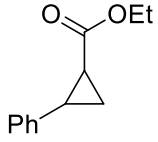
189

To a stirred solution of triphenylphosphine (2.6229 g, 10 mmol) in toluene (40 mL) was added iodine (2.5381 g, 10 mmol) at 20 °C under N_2 within 10 min. The mixture was stirred at 40 °C for 30 min until complete dissolution of iodine. Subsequently, 2,2,2-trifluoro-*N*-phenylacetamine **188** (1.8913 g, 10 mmol) and *N*,*N*-diisopropylethylamine

(1.74 mL, 10 mmol) were added, the resulting mixture was stirred at 80 °C for 1 h and cooled to 20 °C. *n*-Pentane (40 mL) was added and the mixture was filtered through a 1 cm silica gel plug. The filtrate was concentrated and purified by flash chromatography (PE:EA = 10:1) to afford 1.5848 g (53%) of **189** as a dark red oil.

***R*f** = 0.40 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.49-7.41 (m, 2H), 7.37-7.30 (m, 1H), 6.93-6.87 (m, 2H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 149.5, 129.4, 129.0 (d, *J* = 81.47 Hz), 127.1, 118.3, 115.3 (q, *J* = 278.6 Hz) ppm; **IR** (ATR) 2925, 2853, 1687, 1271, 1161, 912, 888, 690 cm^{-1}; **HRMS** (EI) calc. for [$C_8H_5F_3I$]: 298.9419, found: 298.9411.

13.1.10 Ethyl 2-phenylcyclopropane-1-carboxylate (191)

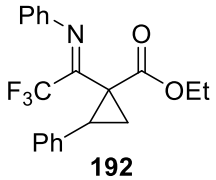


191

To a suspension of trimethyl sulfoxonium iodide (3.9616 g, 18 mmol) in DMSO (40 mL) with vigorous stirring was added sodium hydride (0.72 g, 18 mmol) under N_2 atmosphere. After 30 min, the reaction mixture was cooled to 0 °C and ethyl cinnamate (2.52 mL, 15 mmol) was then added to the reaction mixture. The mixture was stirred at room temperature for overnight. The reaction mixture was quenched with water (60 mL) and extracted with diethyl ether (3*50 mL), the combined organic layer washed with brine (50 mL), dried over $MgSO_4$, filtered, and evaporated. Then the crude product was purified by column chromatography (PE:EA = 10:1) to afford 0.8561 g (30%) of **191** as a colorless oil.

***R*f** = 0.55 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), 7.23-7.16 (m, 1H), 7.13-7.05 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.52 (ddd, *J* = 9.3, 6.4, 4.1 Hz, 1H), 1.90 (dq, *J* = 5.2, 4.2 Hz, 1H), 1.63-1.56 (m, 1H), 1.33-1.29 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 173.4, 140.1, 128.5, 126.5, 126.2, 60.7, 26.2, 24.2, 17.0, 14.3 ppm.

13.1.11 Ethyl (*Z*)-2-phenyl-1-(2,2,2-trifluoro-1-(phenylimino)ethyl)cyclopropane-1-carboxylate (192)



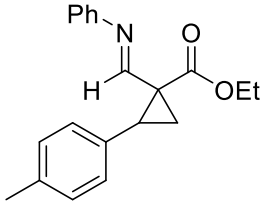
192

Mixed diisopropylamine (0.63 mL, 4.5 mmol) with THF (7 mL) at -78 °C, then dropped *n*-BuLi (2.81 mL, 4.5 mmol) slowly into the solution under N_2 condition. Then the solution was warmed up to room temperature for 30 min. Then the solution was cooled to at -78 °C, then slowly dropped in ethyl 2-phenylcyclopropane-1-carboxylate **191** (0.5707 g, 3.0 mmol) in THF (2 mL). The solution was stirred at -78 °C for 1 hour, then at room temperature for 10 min. The solution was cooled back to -78 °C again, and dropped in (*Z*)-2,2,2-trifluoro-N-phenylacetimidoyl iodide **189** (0.9569 g, 3.2 mmol) in THF (2 mL)

slowly into the solution. The reaction mixture was stirred at the same temperature for 4 hours or at room temperature for overnight. The reaction was quenched with saturated NH_4Cl solution, the water phase was extracted with diethyl ether, the combined organic phase was dried over $MgSO_4$, the solvent was removed under reduced pressure and purified by column chromatography (PE:EA = 20:1) to afford 0.0976 g (9%) of **192** as a pale-yellow oil.

***R*f** = 0.59 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.43-7.37 (m, 2H), 7.27-7.22 (m, 1H), 7.30-7.14 (m, 3H), 7.00-6.94 (m, 2H), 6.89-6.81 (m, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 8.9 Hz, 1H), 2.05 (dd, *J* = 8.8, 5.8 Hz, 1H), 1.37 (dd, *J* = 9.0, 5.6 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 167.4, 155.7 (q, *J* = 32.8 Hz), 146.8, 133.6, 129.4, 129.2, 127.8, 127.3, 125.8, 119.5 (d, *J* = 281.5 Hz), 119.2, 61.8, 33.9, 32.3, 19.5, 13.8 ppm; **IR** (ATR) 2982, 2923, 2852, 1738, 1713, 1175, 1153, 1026, 1014, 774, 693 cm^{-1}; **HRMS** (EI) calc. for [$C_{20}H_{18}F_3NO_2$]: 361.1290, found: 361.1281.

13.1.12 Ethyl (*E*)-1-((phenylimino)methyl)-2-(*p*-tolyl)cyclopropane-1-carboxylate (194)

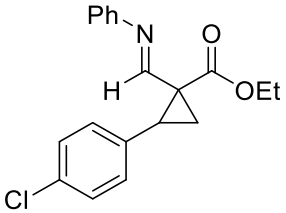


194

The *title compound* was obtained according to GP-VIII after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) with 3% of Et_3N to afford **194** as a colorless oil.

***R*f** = 0.54 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.39-7.31 (m, 2H), 7.23-7.15 (m, 3H), 7.12-7.04 (m, 4H), 3.96-3.81 (m, 2H), 3.25 (t, *J* = 8.7 Hz, 1H), 2.38 (dd, *J* = 8.4, 4.2 Hz, 1H), 2.32 (s, 3H), 2.21 (dd, *J* = 9.1, 4.2 Hz, 1H), 0.91 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 169.6, 163.5, 151.7, 136.9, 132.4, 129.3, 129.0, 128.7, 125.6, 120.8, 60.8, 40.9, 37.2, 21.9, 21.1,13.8 ppm; **IR** (ATR) 2979, 1715, 1637, 1305, 1209, 1143, 1027, 758, 697 cm^{-1}; **HRMS** (ESI) calc. for [$C_{20}H_{21}NO_2$ + Na^+]: 330.1464, found: 330.1453.

13.1.13 Ethyl (*E*)-2-(4-chlorophenyl)-1-((phenylimino)methyl)cyclopropane-1-carboxylate (196)



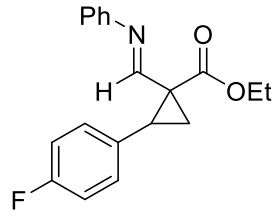
196

The *title compound* was obtained according to GP-VIII after purification via column

chromatography on silica gel eluting with PE/EA 10:1 (v/v) with 3% of Et_3N to afford **196** as a colorless oil.

***R*f** = 0.53 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.70 (s, 2H), 7.39-7.31 (m, 2H), 7.29-7.16 (m, 5H), 7.11-7.04 (m, 2H), 4.00-3.82 (m, 2H), 3.26 (t, *J* = 8.7 Hz, 1H), 2.35 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.20 (dd, *J* = 9.1, 4.3 Hz, 1H), 0.94 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 169.3, 162.9, 151.4, 134.2, 133.1, 130.8, 129.1, 128.2, 125.7, 120.8, 61.0, 39.7, 37.1, 22.1, 13.9 ppm; **IR** (ATR) 3059, 2981, 2904, 1712, 1636, 1593, 1487, 1301, 1204, 1140, 1093, 1016, 832, 758, 696 cm^{-1}; **HRMS** (ESI) calc. for [$C_{19}H_{18}ClNO_2$ + Na^+]: 350.0918, found: 350.0911.

13.1.14 Ethyl (*E*)-2-(4-fluorophenyl)-1-((phenylimino)methyl)cyclopropane-1-carboxylate (198)

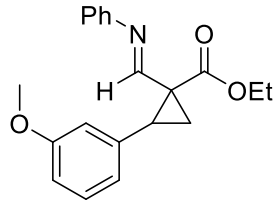


198

The *title compound* was obtained according to GP-VIII after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) with 3% of Et_3N to afford **198** as a colorless oil.

***R*f** = 0.55 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.70 (s, 2H), 7.39-7.31 (m, 2H), 7.29-7.16 (m, 5H), 7.11-7.04 (m, 2H), 4.00-3.82 (m, 2H), 3.26 (t, *J* = 8.7 Hz, 1H), 2.35 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.20 (dd, *J* = 9.1, 4.3 Hz, 1H), 0.94 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 169.4 (*trans*), 163.7 (*cis*), 163.1 (*trans*), 159.2 (*cis*), 151.9 (*cis*), 151.5 (*trans*), 131.4 (d, *J* = 9.1 Hz *cis*), 131.3 (*trans*), 131.0 (d, *J* = 8.1 *trans*), 129.1 (*trans*), 128.8 (*cis*), 125.7 (*trans*), 125.3 (*cis*), 120.8 (*trans*), 120.2 (*cis*), 114.9 (d, *J* = 21.5 Hz *trans*), 114.8 (d, *J* = 21.8 Hz *cis*), 61.53 (*cis*), 61.9 (*trans*), 39.9 (*trans*), 38.4 (*cis*), 37.1 (*trans*), 36.4 (*cis*), 22.1 (*trans*), 18.1 (*cis*), 15.6 (*cis*), 13.9 (*trans*) ppm. **HRMS** (ESI) calc. for [$C_{19}H_{18}FNO_2$ + Na^+]: 334.1214, found: 334.1234.

13.1.15 Ethyl (*E*)-2-(3-methoxyphenyl)-1-((phenylimino)methyl)cyclopropane-1-carboxylate (200)

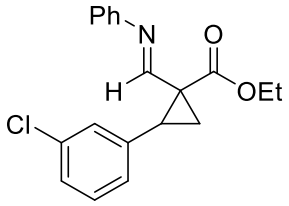


200

The *title compound* was obtained according to GP-VIII after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) with 3% of Et_3N to afford **200** as a colorless oil.

***R*f** = 0.45 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.38-7.32 (m, 2H), 7.23-7.16 (m, 2H), 7.12-7.06 (m, 2H), 6.92-6.75 (m, 3H), 3.98-3.82 (m, 2H), 3.80 (s, 3H), 3.27 (t, *J* = 8.7 Hz, 1H), 2.38 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.20 (dd, *J* = 9.1, 4.2 Hz, 1H), 0.93 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 169.6, 163.4, 159.4, 151.6, 137.2, 129.1, 129.0, 125.6, 121.8, 120.8, 115.0, 112.9, 60.8, 55.2, 40.7, 37.0, 22.0,13.8 ppm; **IR** (ATR) 2981, 2958, 2936, 1714, 1637, 1594, 1487, 1306, 1171, 759, 696 cm^{-1}; **HRMS** (ESI) calc. for [$C_{20}H_{21}NO_3$ + Na^+]: 346.1414, found: 346.1419.

13.1.16 Ethyl (*E*)-2-(3-chlorophenyl)-1-((phenylimino)methyl)cyclopropane-1-carboxylate (202)



202

The *title compound* was obtained according to GP-VIII after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) with 3% of Et_3N to afford **202** as a colorless oil.

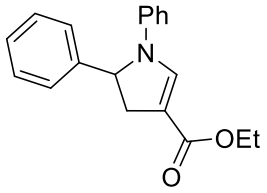
***R*f** = 0.38 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.39-7.32 (m, 2H), 7.32-7.28 (m, 1H), 7.24-7.16 (m, 4H), 7.11-7.05 (m, 2H), 4.00-3.84 (m, 2H), 3.28 (t, *J* = 8.7 Hz, 1H), 2.37 (dd, *J* = 8.3, 4.3 Hz, 1H), 2.20 (dd, *J* = 9.1, 4.3 Hz, 1H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 169.4, 162.9, 151.4, 137.8, 133.9, 129.5, 129.3, 129.1, 127.7, 127.4, 125.8, 120.8, 61.0, 55.2, 39.6, 36.9, 22.0,13.8 ppm; **IR** (ATR) 2981, 1716, 1638, 1594, 1305, 1209, 1143, 1026, 759, 694 cm^{-1}; **HRMS** (ESI) calc. for [$C_{19}H_{18}ClNO_2$ + Na^+]: 350.0918, found: 350.0922.

13.2 Substrate Scope of the TBA[Fe]-Catalyzed Cyclopropylimine Rearrangement

General Procedure IX: Microwave conditions for the Cyclopropylimine Rearrangement (GP-IX)

TBA[Fe] (20.8 mg, 0.05 mmol, 0.1 equiv.) and the corresponding cyclopropylimine (0.5 mmol, 1 equiv.) were weighed into a dried 10 mL microwave tube. Anhydrous DMF (1 mL) was added and the tube was sealed under an atmosphere of dry nitrogen. The reaction mixture was stirred for 1 h at 135 °C under microwave irradiation. The product was obtained via chromatography on silica gel.

13.2.1 Ethyl 1,5-diphenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (193)

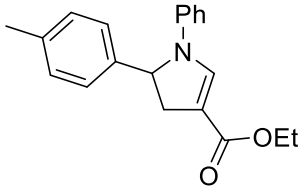


193

The *title compound* was obtained according to GP-IX after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **193** as a colorless oil.

***R*f** = 0.30 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.40-7.27 (m, 3H), 7.25-7.12 (m, 4H), 6.90-6.80 (m, 3H), 5.34 (dd, *J* = 11.9, 5.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.53 (ddd, *J* = 15.5, 12.0, 1.6 Hz, 1H), 2.77 (ddd, *J* = 15.5, 5.6, 0.9 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 166.1, 142.5, 142.4, 141.1, 129.3, 129.1, 127.5, 125.5, 121.1, 115.0, 105.0, 65.3, 59.5, 38.8, 14.6 ppm; **IR** (ATR) 2979, 2928, 1686, 1593, 1579, 1235, 1101, 750, 699 cm^{-1}; **HRMS** (ESI) calc. for [$C_{19}H_{19}NO_2$ + Na^+]: 316.1308, found: 316.1292.

13.2.2 Ethyl 1-phenyl-5-(*p*-tolyl)-4,5-dihydro-1H-pyrrole-3-carboxylate (195)

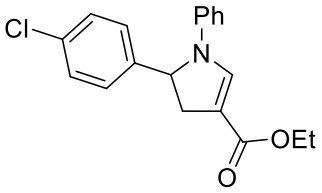


195

The *title compound* was obtained according to GP-IX after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **195** as a light red solid.

***R*f** = 0.28 (PE/EA, 10:1 (v/v)); **m.p.** 115 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.20-7.07 (m, 6H), 6.88-6.80 (m, 3H), 5.30 (dd, *J* = 11.8, 5.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.50 (ddd, *J* = 15.4, 11.9, 1.6 Hz, 1H), 2.75 (ddd, *J* = 15.5, 5.5, 1.0 Hz, 1H), 2.29 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 166.1, 142.6, 141.1, 139.5, 137.2, 129.7, 129.3, 125.4, 121.1, 115.0, 105.0, 65.1, 59.5, 38.9, 21.1, 14.6 ppm; **IR** (ATR) 2978, 2926, 1679, 1590, 1578, 1501, 1231, 1210, 1095, 750, 728, 687 cm^{-1}; **HRMS** (ESI) calc. for [$C_{20}H_{21}NO_2$ + Na^+]: 330.1464, found: 330.1457.

13.2.3 Ethyl 5-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (197)

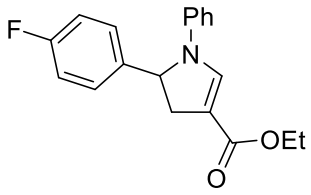


197

The *title compound* was obtained according to GP-IX after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **197** as a pale-yellow solid.

***R*f** = 0.23 (PE/EA, 10:1 (v/v)); **m.p.** 119 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.31-7.24 (m, 2H), 7.22-7.14 (m, 4H), 6.91-6.84 (m, 1H), 6.84-6.77 (m, 2H), 5.32 (dd, *J* = 12.0, 5.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.52 (ddd, *J* = 15.5, 12.0, 1.6 Hz, 1H), 2.73 (ddd, *J* = 15.6, 5.5, 0.8 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.9, 142.4, 140.9, 140.8, 133.3, 129.4, 129.3, 127.0, 121.4, 115.0, 105.0, 64.6, 59.6, 38.7, 14.6 ppm; **IR** (ATR) 2982, 1714, 1636, 1302, 1224, 1207, 1157, 1141, 1024, 839, 758, 669 cm^{-1}; **HRMS** (ESI) calc. for [$C_{19}H_{18}ClNO_2$ + Na^+]: 350.0918, found: 350.0906.

13.2.4 Ethyl 5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (199)

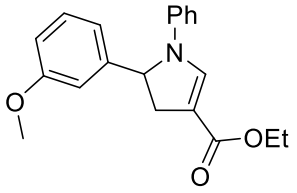


199

The *title compound* was obtained according to GP-IX after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **199** as a light yellow solid.

***R*f** = 0.20 (PE/EA, 10:1 (v/v)); **m.p.** 100 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.27-7.13 (m, 4H), 7.03-6.95 (m, 2H), 6.90-6.84 (m, 1H), 6.84-6.78 (m, 2H), 5.33 (dd, *J* = 11.9, 5.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.51 (ddd, *J* = 15.5, 11.9, 1.6 Hz, 1H), 2.74 (ddd, *J* = 15.5, 5.5, 0.8 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 166.0, 162.1 (d, *J* = 245.9 Hz), 142.5, 140.9, 138.2 (d, *J* = 3.3 Hz), 129.4, 127.2 (d, *J* = 8.1 Hz), 121.3, 116.0 (d, *J* = 21.6 Hz), 115.0, 105.0, 64.6, 59.6, 38.8, 14.6 ppm; **IR** (ATR) 2968, 1685, 1594, 1505, 1236, 1102, 754 cm^{-1}; **HRMS** (EI) calc. for [$C_{19}H_{18}FNO_2$]: 311.1322, found: 311.1315.

13.2.5 Ethyl 5-(3-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (201)



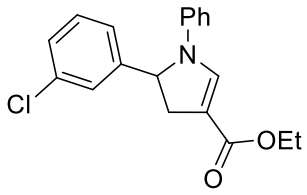
201

The *title compound* was obtained according to GP-IX after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **201** as a colorless oil.

***R*f** = 0.21 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.27-7.12 (m,

3H), 6.90-6.72 (m, 6H), 5.30 (dd, *J* = 11.9, 5.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.51 (ddd, *J* = 15.5, 12.0, 1.7 Hz, 1H), 2.77 (ddd, *J* = 15.5, 5.6, 1.1 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.1, 160.2, 144.1 142.5, 141.1, 130.2, 129.3, 121.1, 117.8, 114.9, 112.6, 111.3, 105.1, 65.2, 59.5, 55.2, 38.7, 14.6 ppm; **IR** (ATR) 2934, 1678, 1590, 1577, 1502, 1230, 1207, 1095, 750, 728, 687 cm^{-1}; **HRMS** (ESI) calc. for [$C_{20}H_{21}NO_3$ + Na^+]: 346.1414, found: 346.1413.

13.2.6 Ethyl 5-(3-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrrole-3-carboxylate (203)



203

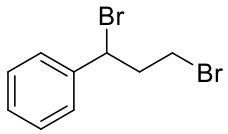
The *title compound* was obtained according to GP-IX after purification via column chromatography on silica gel eluting with PE/EA 10:1 (v/v) to afford **203** as a colorless oil.

***R*$_f$** = 0.23 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.29-7.11 (m, 6H), 6.92-6.85 (m, 1H), 6.85-6.78 (m, 2H), 5.30 (dd, *J* = 11.9, 5.4 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.52 (ddd, *J* = 15.6, 12.0, 1.7 Hz, 1H), 2.74 (ddd, *J* = 15.6, 5.4, 1.2 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 165.9, 144.5, 142.4, 140.8, 135.0, 130.4, 129.5, 127.9, 125.7, 123.7, 121.4, 114.9, 105.1, 64.7, 59.6, 38.7, 14.6 ppm; **IR** (ATR) 2978, 2931, 1680, 1613, 1592, 1579, 1233, 1197, 1100, 751, 689 cm^{-1}; **HRMS** (ESI) calc. for [$C_{19}H_{18}ClNO_2$ + Na^+]: 350.0918, found: 350.0902.

14. TBA[Fe]-Catalyzed Cyclobutane Rearrangement

14.1 Preparation of Arylcyclobutanes

14.1.1 1,3-Dibromo-1-phenylpropane (215)



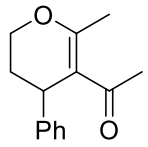
215

In a two-necked flask fitted with a reflux condenser are placed 1-bromo-3-phenylpropane **214** (3.04 mL, 20 mmol), *N*-bromosuccinimide (3.7376 g, 21 mmol), azobisisobutyronitrile (0.0776 g), DCM (20 mL), and CH_3CN (10 mL). The mixture was heated cautiously with to reflux until a spontaneous reaction starts. Ice-bath cooling was then applied if necessary. If more than a negligible amount of *N*-bromosuccinimide remained in the bottom of the flask (succinimide rose to the surface of the solvent), heating and stirring were continued until an evolution of hydrogen bromide was noted. The mixture was cooled, and the solids were removed by suction filtration and washed with DCM. The

washings were combined with the original filtrate, and the bulk of the solvent was removed under reduced pressure to afford 5.4275 g (98%) of **215** as an orange-yellow oil. The crude **215** was used without further purification in the next step.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.44-7.27 (m, 5H), 5.30 (dd, *J* = 11.9, 5.4 Hz, 1H), 5.19 (dd, *J* = 8.8, 5.8 Hz, 1H), 4.00-3.51 (m, 1H), 3.48-3.37 (m, 1H), 2.84-2.71 (m, 1H), 2.62-2.50 (m, 1H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 140.8, 128.9, 128.7, 127.4, 52.5, 42.2, 31.0 ppm.

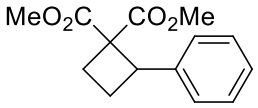
14.1.2 1-(6-Methyl-4-phenyl-3,4-dihydro-2H-pyran-5-yl)ethan-1-one (217)



217

***R*$_f$** = 0.23 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 2H), 7.25-7.16 (m, 3H), 4.10-4.03 (m, 1H), 4.02-3.95 (m, 1H), 3.84-3.73 (m, 1H), 2.33 (s, 3H), 2.27-2.18 (m, 1H), 1.98 (s, 3H), 1.90 - 1.82 (m, 1H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 199.6, 165.5, 145.2, 128.6, 128.1, 126.6, 111.5, 62.3, 37.9, 30.3, 29.2, 21.2 ppm; **IR** (ATR) 2957, 2924, 1667, 1565, 1264, 1087, 1602, 1027, 935, 755, 702, 641, 602 cm^{-1}; **MS** (ESI) [M + Na$^+$] 239.

14.1.3 Dimethyl 2-phenylcyclobutane-1,1-dicarboxylate (219)

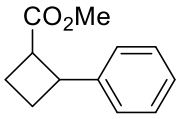


219

Under N_2, a flame dried 250 mL 2-necked round-bottomed flask containing a magnetic stir bar was charged with 1,3-dibromo-1-phenylpropane **215** (5.4275 g, 19.6 mmol), dimethyl malonate **218** (2.8483 mL, 21.56 mmol), and anhydrous 1,4-dioxane (63 mL). The flask was affixed with a reflux condenser and the solution was heated to reflux. Sodium hydride (0.8075 g, 40.376 mmol) was added in small portions over approximately 10 minutes. The reaction was allowed to reflux for 1 hour, at which point additional sodium hydride (0.8075 g) was added in an analogous manner. The reaction was heated at reflux for an additional 12 hours, at which point it was slowly cooled to room temperature. The resulting heterogeneous mixture was filtered through celite. The filter cake was washed with copious Et_2O and the filtrate was concentrated. Run flash chromatography (2.5-3.3-5.0% EA/PE) to provide 3.7532 g (77%) of **219** as a slightly yellow clear oil.

***R*$_f$** = 0.23 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 4H), 7.24-7.17 (m, 1H), 4.37 (t, *J* = 9.5 Hz, 1H), 3.78 (s, 3H), 3.24 (s, 3H), 2.77-2.56 (m, 2H), 2.33-2.23 (m, 1H), 2.23-2.13 (m, 1H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 172.2, 169.8, 139.1, 128.0, 127.6, 126.9, 59.7, 52.5, 51.9, 45.1, 25.7, 20.7 ppm; **IR** (ATR) 2949, 1728, 1242, 1195, 1166, 753, 698 cm^{-1}.

14.1.4 Methyl 2-phenylcyclobutane-1-carboxylate (220)

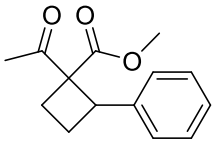


220

A stirred mixture of dimethyl 2-phenylcyclobutane-1,1-dicarboxylate **219** (3.4986 g, 14.09 mmol), LiCl (1.2724 g, 30.02 mmol), and water (0.28 mL) in DMSO (19.31 mL) was heated to 140 °C and stirred for 16 hours. After cooling to room temperature, the mixture was diluted with diethyl ether (100 mL) then was washed sequentially with water (3 times) and brine. The organic phase was dried and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with *n*-pentane:Et_2O = 20:1) to give 2.3859 g (89%) of **220** as a colorless oil.

***R*f** = 0.39 (*n*-pentane/ Et_2O, 20:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.37-7.14 (m, 5H *trans*, 5H *cis*), 4.04-3.90 (m, 1H *cis*), 3.88-3.73 (m, 1H *trans*), 3.70 (s, 3H *trans*), 3.26 (s, 3H *cis*), 3.23-3.15 (m, 1H *trans*), 2.68-2.55 (m, 1H *cis*), 2.45-2.03 (m, 4H *trans*, 4H *cis*) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 174.8 (*trans*), 173,8 (*cis*), 143.6 (*trans*), 140.9 (*cis*), 128.4 (*trans*), 128.1 (*cis*), 127.2 (*trans*), 126.5 (*cis*), 126.4 (*trans*, *cis*), 51.7 (*trans*), 51.0 (*cis*), 45.2 (*trans*), 45.1 (*cis*), 43.2 (*trans*), 42.7 (*cis*), 25.4 (*trans*), 24.5 (*cis*), 21.7 (*trans*), 20.2 (*cis*) ppm; **IR** (ATR) 2988, 2950, 1732, 1435, 1243, 1196, 1168, 699 cm^{-1}; **HRMS** (ESI) calc. for [$C_{12}H_{14}O_2$ + Na^+]: 213.0886, found: 213.0886.

14.1.5 Methyl 1-acetyl-2-phenylcyclobutane-1-carboxylate (221)



221

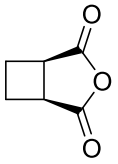
To a solution of diisopropylamine (0.34 mL, 2.4 mmol) in THF (6 mL) was added *n*-BuLi (1.5 mL, 2.44 mmol) at -78 °C and stirred for 30 min, and then warmed to room temperature for 30 min. The solution of LDA was cooled to -78 °C and methyl 2-phenylcyclobutane-1-carboxylate **220** (0.3805 g, 2.0 mmol) in THF (2 mL) was added and stirred for 30 min. The reaction was warmed to 0°C and stirred for a further 30 min. The reaction was cooled to -78 °C and acetyl chloride (0.18 mL, 2.6 mmol) in THF (2 mL) was added dropwise. The reaction was stirred at -78°C for 2 hours. The reaction was quenched by adding sat. NH_4Cl (10 mL). The aqueous phase was extracted with Et_2O (10*3 mL). The organic phase was dried ($MgSO_4$) and concentrated on a rotary evaporator and the was purified by column chromatography (PE:EA = 10:1) to afford 0.1394 g (30%) of **221** as a colorless oil.

***R*f** = 0.43 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 4H), 7.22-7.15 (m, 1H), 4.28 (t, *J* = 8.6 Hz, 1H), 3.23 (s, 3H), 2.76-2.66 (m, 1H), 2.66-2.53 (m, 1H), 2.18-2.05 (m, 2H), 2.11 (s, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 203.1, 170.2, 139.4, 128.0, 127.7, 126.8, 66.4, 51.8, 43.1, 25.7, 25.1, 20.1 ppm; **IR** (ATR) 2951, 1739, 1708, 1433,

1282, 1243, 1178, 1118, 740, 698 cm^{-1}; **HRMS** (ESI) calc. for [$C_{14}H_{16}O_3$ + Na^+]: 255.0992, found: 255.1017.

14.2 Preparation of Vinylcyclobutanes

14.2.1 3-Oxabicyclo[3.2.0]heptane-2,4-dione (226)

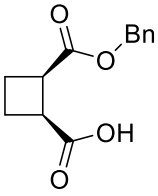


226

Maleic anhydride **225** (5.8836 g, 60 mmol) was introduced into a cylindrical reactor containing CH_3CN (1 L) with acetophenone (0.7 mL, 6 mmol). The reaction was stirred at room temperature, degassed with argon for 30 min, and then saturated with ethylene **224** for 30 min. While ethylene **224** bubbling continued, the mixture was irradiated with a 400 W medium-pressure mercury lamp fitted with a Pyrex filter for 5 h. The solvent was evaporated and the solid residue was recrystallized from a *n*-pentane solution to afford 4.7670 g (65%) of **226** as a white solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.60-3.45 (m, 2H), 2.89-2.66 (m, 2H), 2.53-2.32 (m, 2H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 173.4, 38.7, 23.1 ppm; **IR** (ATR) 2969, 1780, 1299, 1257, 1171, 912 cm^{-1}; **HRMS** (EI) calc. for [$C_6H_6O_3$]: 126.0317, found: 126.0319.

14.2.2 2-((Benzyloxy)carbonyl)cyclobutane-1-carboxylic acid (229)

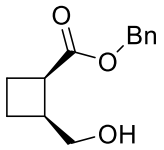


229

A mixture of 3-oxabicyclo[3.2.0]heptane-2,4-dione **226** (2.5222g, 20 mmol), benzyl alcohol (1.7 mL, 16.6 mmol), and DMAP (2.0280 g, 16.6 mmol) in DCM (60 mL) was stirred at room temperature for 18 hours. After this time, a solution of 5% Na_2CO_3 was poured into the reaction mixture and the layers separated. The acid layer was acidified with 1 M HCl and extracted with EA. The EA layer was washed with brine, dried over Na_2SO_4, and evaporated to give 3.7949 g (81%) of crude **229**, which was used without further purification in the next step.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5H), 5.11 (dd, *J* = 21.1, 12.3 Hz, 2H), 3.53-3.37 (m, 2H), 2.50-2.31 (m, 2H), 2.31-2.15 (m, 2H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 179.1, 173.0, 135.7, 128.5, 128.3, 128.2, 66.6, 40.5, 40.4, 22.2, 22.0 ppm; **IR** (ATR) 2956 (bs), 1731, 1704, 1345, 1169, 750, 698 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{14}O_4$ + Na^+]: 257.0784, found: 257.0785.

14.2.3 Benzyl 2-(hydroxymethyl)cyclobutane-1-carboxylate (230)

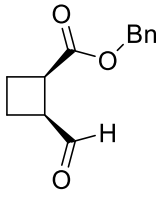


230

To the solution of 2-((benzyloxy)carbonyl)cyclobutane-1-carboxylic acid **229** (1.6398 g, 7 mmol) in THF (13 mL) was added 1 M BH_3-THF complex (15.4 mL, 15.4 mmol) at -10 °C under N_2, and the reaction mixture was allowed to warm to room temperature with stirring for overnight. 5% $NaHCO_3$ aqueous solution (13 mL) was added to the reaction and then the reduced alcohol was extracted with EA (3*13 mL). The ethyl acetate solution was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (eluting with PE:EA = 5:1) to give 0.8572 g (56%) of **230** as a colorless oil.

***R*f** = 0.22 (PE/EA, 5:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 5.12 (s, 2H), 3.71 (dd, *J* = 11.5, 8.3 Hz 1H), 3.59 (dd, *J* = 11.5, 5.3 Hz 1H), 3.34 (q, *J* = 8.2 Hz 1H), 2.87-2.75 (m, 1H), 2.70 (bs, 1H), 2.42-2.27 (m, 1H), 2.19-1.99 (m, 2H), 1.77-1.69 (m, 1H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 174.7, 135.8, 128.6, 128.40, 123.37, 66.5, 63.5, 39.74, 39.70, 21.8, 21.0 ppm; **IR** (ATR) 3419 (bs), 2974, 2859, 1726, 1164, 1038, 980, 737, 698 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{16}O_3$ + Na^+]: 243.0992, found: 243.0989.

14.2.4 Benzyl 2-formylcyclobutane-1-carboxylate (231)

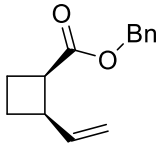


231

Benzyl 2-(hydroxymethyl)cyclobutane-1-carboxylate **230** (0.2202 g, 1 mmol) and DMP (0.8483 g, 1.5 mmol) was added in DCM (3 mL) and then stirred at room temperature for overnight. The reaction mixture was passed through a short pot of silica gel by using EA as solvent and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with PE:EA = 5:1) to give 0.1768 g (81%) of **231** as a colorless oil.

***R*f** = 0.37 (PE/EA, 5:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.80 (d, *J* = 1.8 Hz, 1H), 7.42-7.28 (m, 5H), 5.12 (s, 2H), 3.59-3.45 (m, 1H), 3.45-3.32 (m, 1H), 2.46-2.06 (m, 4H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 200.9, 172.8, 135.6, 128.6, 128.42, 128.36, 66.7, 47.0, 40.3, 22.5, 19.4 ppm; **IR** (ATR) 2953, 1728, 1243, 1172, 751, 699 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{14}O_3$ + Na^+]: 241.0835, found: 241.0838.

14.2.5 Benzyl 2-vinylcyclobutane-1-carboxylate (232)



232

Wittig reaction: *n*-BuLi (08375 mL, 1.34 mmol) was added dropwise to a solution of methyltriphenylphosphonium bromide (0.4930 g, 1.38 mmol) in THF (5 mL) at 0 °C. The yellow solution was allowed to stir for 30 min. The benzyl 2-formylcyclobutane-1-carboxylate **231** (0.2619 g, 1.2 mmol) in THF (1 mL) was added into the reaction mixture at 0 °C. The reaction mixture was stirred at room temperature for 1 h and then heated to 40 °C for overnight. The saturated ammonium chloride was added and the mixture was extracted with DCM. The organic layers were dried by $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluting with PE:EA = 40:1) to give 0.0337 g (13%) of **232** as a colorless oil.

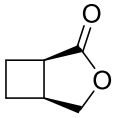
Takai-Lombardo methylenation: A 10 ml two-necked round bottom flask was added activated Zn powder (0.2877 g, 4.4 mmol) (activated with 0.1 N HCl) in THF (2 mL), dibromomethane (0.1 mL, 1.4 mmol) was stirred at -40 °C. To the stirred reaction mixture was added dropwise titanium tetrachloride (0.12 mL, 1.1 mmol) over 15 min. The cooling bath is removed and the mixture is stirred at 5 °C for 3 days under a N_2 condition. The dark-gray slurry was cooled with an ice-water bath and 2-formylcyclobutane-1-carboxylate **231** (0.2183 g, 1 mmol) in DCM (2 mL) was added over a period of 10 min. The cooling bath was removed and the mixture was stirred at room temperature for 4 hours. The reaction mixture was diluted with diethyl ether (4 mL) and a saturated $NaHCO_3$ solution (2 mL) was added cautiously over 1 hour. The clear organic solution was washed 3 times of diethyl ether (10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo to provide the crude product, which was purified by column chromatography on silica gel (eluting with PE:EA = 40:1) to give 0.0497 g (23%) of **232** as a colorless oil.

Tebbe methylenation: A Schlank tube was added titanocene dichloride (0.5477 g, 1.1 mmol) and trimethylaluminum (2 M) in toluene (1.1 mL, 2.2 mmol). Methane gas evolved by the reaction is allowed to vent as the resulting red solution is stirred room temperature for 3 days. The Tebbe thus formed and was used in situ by cooling the mixture in an ice-water bath, then added 2-formylcyclobutane-1-carboxylate **231** (0.2183 g, 1 mmol) in THF (1 mL) over 5 -10 min. The solution was allowed to warm to room temperature and stirred for 3 days and then 6 hours at the same temperature. The reaction mixture was diluted with ether (2.5 ml) and 1 M NaOH solution (2.5 drops) was added over 10 - 20 min. Stirring was continued until gas evolution essentially ceases. The resulting organic slurry was dried over sodium sulfate to remove excess water. The mixture was filtered through a Celite pad with ether. Concentrated the filtrate to provide the crude product, which was purified by column chromatography on silica gel (eluting with PE:EA = 40:1) to give 0.0476 g (22%) of **232** as a colorless oil.

R_f = 0.25 (PE/EA, 40:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 5.90 (ddd,

J = 17.2, 10.1, 7.3 Hz, 1H), 5.09 (s, 2H), 5.06-4.95 (m, 2H), 3.42-3.23 (m, 2H), 2.43-2.26 (m, 1H), 2.22-1.99 (m, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 173.4, 137.9,136.1, 128.5, 128.4, 128.2, 115.4, 66.1, 43.1, 41.4, 24.2, 20.4 ppm; **HRMS** (EI) calc. for [$C_{14}H_{16}O_2$]: 216.1150, found: 216.1150.

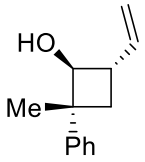
14.2.6 3-Oxabicyclo[3.2.0]heptan-2-one (234)



234

Into a 50 mL round-bottomed flask were placed of sodium borohydride (0.9155 g, 24.2 mmol) and THF (10 mL) under N_2 atmosphere. The flask was cooled in a dry ice/acetone bath at -65 °C. Under nitrogen atmosphere and with stirring, a solution of 3-oxabicyclo[3.2.0]heptane-2,4-dione **226** (2.9640 g, 23.5 mmol) in THF (10 mL) was added over a period of 30 min. The cooling bath was removed, and the mixture was continuously stirred for a further 2 h at room temperature. The reaction was treated by slow addition of 1.0 M HCl until all the solid had dissolved. The mixture was extracted three times with diethyl ether (3*25 mL). The combined organic layers were washed with saturated aqueous NaCl, dried with anhydrous $NaSO_4$, and concentrated to afford 0.8959 g (34%) of **234**. The crude product was used without further purification in the next step.

14.2.7 2-Methyl-2-phenyl-4-vinylcyclobutan-1-ol (239)

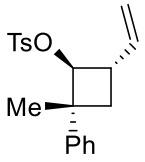


239

The *title compound* was synthesized according to literature and was purified via column chromatography on silica gel (eluting with PE:EA = 10:1) to afford **239** as a colorless oil.

***R*$_f$** = 0.24 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.24-7.14 (m, 3H), 5.90 (ddd, *J* = 17.2, 10.3, 7.0 Hz, 1H), 5.12 (dt, *J* = 17.2, 1.4 Hz, 1H), 4.99 (dt, *J* = 10.3, 1.3 Hz, 1H), 4.16-4.04 (m, 1H), 2.93-2.80 (m, 1H), 2.29 (bs, 1H), 2.10 (t, *J* = 9.9 Hz, 1H), 1.75 (t, *J* = 10.3 Hz, 1H), 1.42 (s, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.8, 139.5, 128.4, 125.7, 124.9, 114.5, 78.4, 46.3, 45.5, 31.8, 22.9 ppm.

14.2.8 2-Methyl-2-phenyl-4-vinylcyclobutyl 4-methylbenzenesulfonate (240)



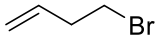
240

Into a 10 mL Schlenk tube, was placed 2-methyl-2-phenyl-4-vinylcyclobutan-1-ol **239** (0.0483 g, 0.257 mmol), DCM (1 mL), triethylamine (0.09 mL, 0.643 mmol), then cooled

to 0 °C. This was followed by the addition of DMAP (0.0157 g, 0.129 mmol), then a solution of *p*-toluenesulfonyl chloride (0.0636 g, 0.334 mmol) in DCM (1 mL) by dropwise with stirring over 30 min. The resulting solution was stirred at room temperature for overnight. The resulting solution was diluted with DCM. The resulting mixture was washed with sat. tbrine (3*30 mL). The mixture was dried over anhydrous sodium sulfate and concentrated under vacuum to provide the crude product. The residue was purified by column chromatography on silica gel (eluting with PE:EA = 10:1) to give 0.0616 g (70%) of **240** as a colorless oil.

***R*f** = 0.20 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.26-7.18 (m, 2H), 7.18-7.12 (m, 1H), 7.04-6.98 (m, 2H), 5.69 (ddd, *J* = 17.0, 10.4, 6.7 Hz, 1H), 4.89 (dt, *J* = 7.8, 1.4 Hz, 1H), 4.86 (d, *J* = 1.2 Hz, 1H), 4.73 (d, *J* = 7.9 Hz, 1H), 3.21-3.08 (m, 1H), 2.44 (s, 3H), 2.17 (t, *J* = 10.2 Hz, 1H), 1.80 (t, *J* = 10.4 Hz, 1H), 1.46 (s, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 148.6, 144.7, 137.2, 134.0, 129.7, 128.4, 128.1, 126.1, 124.7, 115.2, 84.1, 45.8, 42.8, 32.1, 24.2, 21.6 ppm; **IR** (ATR) 2971, 1367, 1189, 1176, 986, 860, 827, 813, 701, 670, 554 cm^{-1}; **HRMS** (EI) calc. for [$C_{20}H_{22}O_3S$]: 342.1290, found: 342.1288.

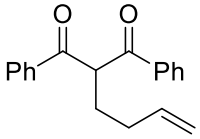
14.2.9 4-Bromobut-1-ene (245)



245

A solution of 3-buten-1-ol **244** (0.86 mL, 10 mmol) in Pyridine (0.24 mL, 3 mmol) was cooled to 0 °C, and PBr_3 (0.47 mL, 5 mmol) was added. The solution was stirred at 0 °C for 30 min. After allowing the reaction mixture to warm to room temperature, the product was distilled off into a cooled (-78 °C) receiving flask to provide 0.7560 g of **245** (56%). The compound was used in the next step without further purification.

14.2.10 2-(But-3-en-1-yl)-1,3-diphenylpropane-1,3-dione (246)



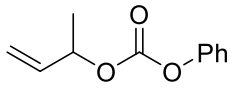
246

To a 250 mL around-bottom flask, NaH (1.2042g, 60% in mineral oil 30.11 mmol) was added in dry THF (60 mL) and then 1,3-diphenyl-1,3-propanedione (6.6602 g, 29.7 mmol) in dry DMF (60 mL) was added into the suspension soultion at 0 °C under a N_2 atmosphere. The reaction was stirred for 30 min. 4-bromobut-1-ene **245** (2.74 mL, 27 mmol) and anhydrous NaI (2.4282 g, 16.2 mmol) were added at room temperature. The mixture was heated to reflux for overnight. The mixture was quenched with a saturated NH_4Cl solution. The aqueous layer was extracted three times with diethyl ether. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluting with PE:EA = 20:1) to afford 4.2087 g (56%) of **246** as a colorless oil.

***R*f** = 0.43 (PE/EA, 9:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.00 - 7.91 (m, 4H), 7.61-7.52 (m, 2H), 7.50-7.40 (m, 4H), 5.96-5.74 (m, 1H), 5.30-5.21 (m, 1H), 5.09-4.97 (m, 2H), 2.30-

2.14 (m, 4H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 153.0, 151.1, 136.6, 129.4, 125.9, 121.1, 117.2, 20.0 ppm; **IR** (ATR) 3064, 2931, 1693, 1669, 1447, 1232, 1197, 1180, 999, 915, 741, 689, 596 cm^{-1}; **HRMS** (ESI) calc. for [$C_{13}H_{14}O_3$ + H^+]: 278.1380, found: 279.1394.

14.2.11 But-3-en-2-yl phenyl carbonate (248)

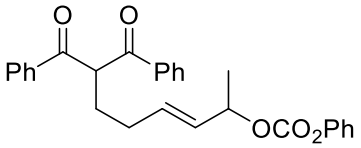


248

A solution of 3-buten-2-ol **247** (7.58 mL, 87.5 mmol), and phenyl chloroformate (8.78 mL, 70 mmol) in DCM (100 mL) was stirred in a 250 mL round-bottom flask for 30 min under N_2 condition. A catalytic amount of DMAP (0.8552 g, 7 mmol) and pyridine (6.79 mL, 84 mmol) were added to the reaction mixture and stirred at room temperature overnight. The reaction mixture was washed with 1N HCl (3*60 mL) and the organic layer was dried over $MgSO_4$. After evaporation of the solvent, the remaining yellow oil was purified by flash column chromatography on silica gel (eluting with PE:EA = 20:1) to afford 11.9747 g (89%) of **248** as a colorless oil.

***R*$_f$** = 0.65 (PE/EA, 9:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.43-7.33 (m, 2H), 7.28-7.15 (m, 3H), 5.93 (ddd, *J* = 17.2, 10.6, 6.5 Hz, 1H), 5.36 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.29 (tt, *J* = 6.4, 1.2 Hz, 1H), 5.23 (dt, *J* = 10.6, 1.1 Hz, 1H), 1.46 (d, *J* = 6.5 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 153.0, 151.1, 136.6, 129.4, 125.9, 121.1, 117.2, 20.0 ppm; **IR** (ATR) 2953, 1728, 1243, 1172, 751, 699 cm^{-1}; **HRMS** (EI) calc. for [$C_{11}H_{12}O_3$]: 192.0786, found: 192.0787.

14.2.12 (*E*)-7-Benzoyl-8-oxo-8-phenyloct-3-en-2-yl phenyl carbonate (249)

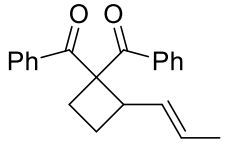


249

To a 50 mL round-bottom flask was added in Grubbs 2nd generation catalyst (0.2094 g, 0.2466 mmol) and DCM (53 mL) under an atmosphere of dry nitrogen. 2-(But-3-en-1-yl)-1,3-diphenylpropane-1,3-dione **246** (4.5756 g, 16.44 mmol) and but-3-en-2-yl phenyl carbonate **248** (5.5970 g, 29.12 mmol) were added into the upper flask, then filled with DCM. The reaction mixture was stirred at 45 ^oC (reflux) for overnight. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluting with PE:EA = 15:1) to afford 2.6916 g (37%) of **249** as a dark oil.

***R*$_f$** = 0.23 (PE/EA, 15:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 8.03-7.88 (m, 4H), 7.60-7.49 (m, 2H), 7.48-7.29 (m, 6H), 7.27-7.11 (m, 3H), 5.93-5.76 (m, 1H), 5.54 (dd, *J* = 15.4, 7.1 Hz, 1H), 5.34-5.18 (m, 2H), 2.34-2.12 (m, 4H), 1.40 (d, *J* = 6.5 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 196.0, 195.9, 153.0, 151.1, 136.1, 136.0, 133.57, 133.55, 133.2, 130.4, 129.4, 128.9, 128.6, 128.5, 125.9, 121.1, 76.3, 55.5, 30.4, 28.4, 20.3 ppm.

14.2.13 (*E*)-(2-(Prop-1-en-1-yl)cyclobutane-1,1-diyl)bis(phenylmethanone) (250)

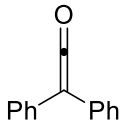


250

A 25 ml two-necked round-bottom flask was charged with (*E*)-7-Benzoyl-8-oxo-8-phenyloct-3-en-2-yl phenyl carbonate **249** (0.8850 g, 2 mmol) and toluene (5.6 mL) and cooled to 0 °C. NaH (0.16 g, 4 mmol) was washed with *n*-pentane to remove the oil and was suspended in toluene (3.9 mL). To this suspension was added to the reaction mixture over 20 min followed by a toluene wash (2.2 mL). The reaction was stirred at room temperature for 30 min and then warmed to 55 °C for an addition 16 h. The reaction was cooled to room temperature and poured into water (2.8 ml). The organic layer was separated and the aqueous layer extracted with diethyl ether (3*14 mL). The combined organic layers were washed with 2 M aq. NaOH (2*14 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (eluting with PE:EA = 15:1) to afford 0.0852 g (14%) of **250** as a colorless oil.

***R*f** = 0.48 (PE/EA, 15:1 (v/v)); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.74-7.62 (m, 4H), 7.44-7.18 (m, 6H), 5.58 (ddq, *J* = 15.1, 6.4, 0.9 Hz, 1H), 5.36 (ddq, *J* = 15.0, 9.4, 1.5 Hz, 1H), 4.35-4.22 (m, 1H), 3.43-3.29 (m, 1H), 2.35-2.12 (m, 2H), 2.07-1.93 (m, 1H), 1.41 (dd, *J* = 6.4, 1.6 Hz, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 197.8, 197.1,136.9, 135.2, 133.0, 132.8, 130.3, 129.3, 128.9, 128.5, 128.3, 128.1, 68.6, 43.6, 27.1, 23.0 17.6 ppm; **IR** (ATR) 2941, 2916, 1656, 1447, 1376, 1253, 1180, 952, 695, 666 cm^{-1}; **HRMS** (ESI) calc. for [$C_{21}H_{20}O_2$ + Na^+]: 327.1356, found: 327.1354.

14.2.14 Diphenylketene (252)

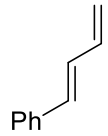


252

To a 25 mL two-necked round-bottom flask was charged with a solution of diphenylcaetyl chloride (1.3841g, 6 mmol) in diethyl ether (9 mL) under a N_2 atmosphere. The flask was cooled in an ice-bath and triethylamine (0.88 mL, 6.3 mmol) was added fropwise over 30 min to the reaction mixture. Triethylamine hydrochloride precipitates as a colorless solid, and the ether becomes bright yellow in color. When addition of the triethylamine was complete, the reaction mixture was stirred at room temperature for overnight. The triethylamine hydrochloride was separated by filtration (under N_2 atmosphere) and was washed with anhydrous diethyl ether until the washings were colorless. The ether was removed under reduced pressure and the residual red oil was used for the next step without further purification.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.13 (m, 10H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 201.1, 130.8, 129.2, 127.7, 126.2, 46.9 ppm.

14.2.15 (*E*)-Buta-1,3-dien-1-ylbenzene (254)

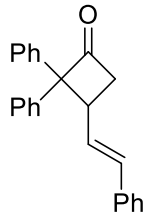


254

To a suspension of methyltriphenylphosphonium bromide (11.4310 g, 32 mmol) in THF (100 mL) at 0 °C was added dropwise *n*-butyllithium (20 mL, 32 mmol). The reaction mixture was stirred for 15 min. The cinnamaldehyde (3.36 mL, 26.67 mmol) was added in to the reaction mixture. After 1 h the solution was warmed to room temperature and stirred for additional 1 h. A saturated solution of NH_4Cl (100 mL) was added and the mixture was extracted with Et_2O (3*100 mL). The combined organic phases were washed with brine (100 mL), dried over $MgSO_4$, and the solvents were removed under reduced pressure (300 mbar, 40 °C). The residue was purified by flash column chromatography in pure PE as eluent to give the title compound as a colorless liquid.

***R*f** = 0.68 (PE); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.44-7.37 (m, 2H), 7.35-7.28 (m, 2H), 7.26-7.18 (m, 1H), 6.79 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.60-6.44 (m, 2H), 5.33 (d, *J* = 16.9 Hz, 1H), 5.17 (d, *J* = 10.0 Hz, 1H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 137.2, 137.1, 132.9, 129.6, 128.6, 127.6, 126.4, 117.6 ppm.

14.2.16 (*E*)-2,2-Diphenyl-3-styrylcyclobutan-1-one (255)

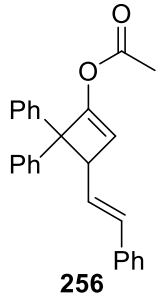


255

To a Schlenk tube was added in diphenylketene **252** (0.5827 g, 3 mmol) and (*E*)-buta-1,3-dien-1-ylbenzene **254** (1.1717 g, 9 mmol) under N_2 at room temperature. Stirred the reaction mixture at room temperature for 4 days. Removed the excess of **254**, and purified by column chromatography on silica gel (eluting with PE:EA = 40:1) to afford 1.6482 (85%) of **255** as a colorless oil.

***R*f** = 0.22 (PE/EA, 20:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.52-7.46 (m, 2H), 7.38-7.30 (m, 2H), 7.30-7.24 (m, 5H), 7.24-7.16 (m, 6H), 6.66 (d, *J* = 15.7 Hz, 1H), 5.86 (dd, *J* = 15.7, 9.3 Hz, 1H), 4.01 (q, *J* = 8.9 Hz, 1H), 3.35 (dd, *J* = 17.6, 9.0 Hz, 1H), 3.19 (dd, *J* = 17.6, 8.4 Hz, 1H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 207.6, 141.9, 139.4, 136.9, 131.6, 130.6, 128.63, 128.61, 128.5, 127.9, 127.5, 127.1, 127.0, 126.6, 126.3, 79.5, 49.9, 39.5 ppm; **IR** (ATR) 3027, 1776, 1493, 1557, 746, 696 cm^{-1}; **HRMS** (EI) calc. for [$C_{24}H_{20}O$]: 324.1514, found: 324.1511.

14.2.17 (*E*)-4,4-Diphenyl-3-styrylcyclobut-1-en-1-yl acetate (256)

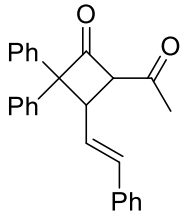


256

Diisopropylamine (0.36 mL, 2.6 mmol) was mixed with THF (4 mL) at -78 °C, then *n*-BuLi (1.63 mL, 2.6 mmol) was dropped slowly into the solution under N_2 atmosphere. Then the reaction mixture was warmed to room temperature for 30 min. The solution was cooled to -78 °C, then (*E*)-2,2-Diphenyl-3-styrylcyclobutan-1-one **255** (0.6488 g, 2.0 mmol) in THF (1 mL) was slowly dropped into the reaction mixture. The solution was stirred at -78 °C for 1 h, then was stirred at room temperature for 30 min. The solution was cooled back to -78 °C again, and acetyl chloride (0.21 mL, 3.0 mmol) was slowly dropped into the solution. Then the reaction mixture was stirred at room temperature for overnight. The reaction was quenched with sat. NH_4Cl solution, the water phase was extracted with diethyl ether, the combined organic phase was dried over $MgSO_4$, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluting with PE:EA = 10:1) to afford **256** as a colorless oil.

***R*f** = 0.48 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.40-7.15 (m, 15H), 6.78 (ddd, *J* = 15.6, 7.2, 2.7 Hz, 1H), 6.61 (d, *J* = 15.5 Hz, 1H), 6.48-6.44 (m, 2H), 2.06 (s, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 168.7, 143.5, 139.4, 139.3, 137.2, 134.2, 133.7, 130.9, 130.4, 129.5, 128.7, 128.6, 128.3, 128.0, 127.83, 127.79, 127.5, 126.5, 125.7, 20.8 ppm; **IR** (ATR) 3024, 1768, 1493, 1446, 1190, 1369, 748, 699 cm^{-1}; **HRMS** (EI) calc. for [$C_{26}H_{22}O_2$]: 366.1620, found: 366.1623.

14.2.17 (*E*)-4-Acetyl-2,2-diphenyl-3-styrylcyclobutan-1-one (257)



257

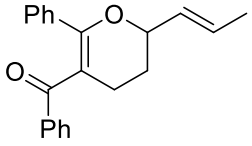
Diisopropylamine (0.36 mL, 2.6 mmol) was mixed with THF (5 mL) at -78 °C, then *n*-BuLi (1.63 mL, 2.6 mmol) was slowly dropped into the solution under N_2 condition. Then the solution was warmed up to room temperature for 30 min. The solution was cooled to -78 °C, then (*E*)-2,2-Diphenyl-3-styrylcyclobutan-1-one **255** (0.6488 g, 2 mmol) in THF (2 mL) was slowly dropped in to the mixture. The solution was stirred at -78 °C for 1 h, then was stirred at room temperature for 10 min. The solution was cooled back to -78 °C again, and pyruvonitrile (0.26 mL, 3.6 mmol) was slowly dropped into the solution, and the reaction mixture was stirred it at the same temperature for 2 hours. The reaction was quenched with sat. NH_4Cl solution, the water phase was extracted with diethyl ether, the combined

organic phase was dried over $MgSO_4$, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluting with PE:EA = 10:1) to afford 0.1906 g (26%) of **257** as a colorless oil.

***R*f** = 0.38 (PE/EA, 10:1 (v/v)); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.48-7.41 (m, 2H), 7.39-7.30 (m, 8H), 7.30-7.20 (m, 6H), 7.09-6.94 (m, 2H), 5.72 (s, 1H), 2.23 (s, 3H) ppm; **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 203.0, 196.7, 145.4, 142.6, 140.7, 138.4, 135.4, 130.0, 129.2, 128.9, 128.8, 127.8, 127.3, 123.2, 59.3, 31.5 ppm; **IR** (ATR) 3060, 3026, 1653, 1607, 1578, 1279, 1201, 1150, 971, 748, 730, 689, 614 cm^{-1}; **HRMS** (EI) calc. for [$C_{26}H_{22}O_2$]: 366.1620, found: 366.1617.

14.3 TBA[Fe]-Catalyzed Vinylcyclobutane

14.3.1 (*E*)-Phenyl(6-phenyl-2-(prop-1-en-1-yl)-3,4-dihydro-2H-pyran-5-yl)methanone (258)

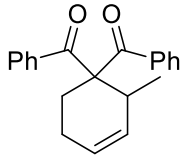


258

A 10 ml Schlenk tube was charged at r.t. with NHC ligand **223** (0.0034 g, 0.008 mmol). Dry THF (0.7 mL) was added followed by solid $NaNH_2$ (0.0019 g, 0.0096 mmol). The Schlenk tube was heated to 55 °C for 2 h, and the mixture was heated to 80 °C for another 1 h. The solution (0.7 mL) was added to a 10 ml Schlenk tube contained with TBA[Fe] (0.0033 g. 0.08 mmol). The Schlenk tube was heated to 60 °C for 1 h. After cooling to room temperature (*E*)-(2-(prop-1-en-1-yl)cyclobutane-1,1-diyl)bis(phenylmethanone) **250** (0.0243 g, 0.08 mmol) were added. The reaction was stirred at 80 °C for 24 h. The reaction was quenched with diethyl ether and concentrated in reduced pressure. The residue was purified by silica column chromatography (eluting with PE:EA = 35:1) to afford 0.0214 g (88%) of **258** as a colorless oil.

***R*f** = 0.13 (PE/EA, 35:1 (v/v)); **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 7.55-7.48 (m, 2H), 7.25-7.20 (m, 2H), 7.20-7.15 (m, 1H), 7.10-6.98 (m, 5H), 5.97-5.87 (m, 1H), 5.74-5.67 (m, 1H), 4.63 (t, *J* = 7.7 Hz, 1H), 2.90-2.80 (m, 1H), 2.51 (ddd, *J* = 17.0, 10.2, 6.8 Hz, 1H), 2.16-2.07 (m, 1H), 1.90-1.81 (m, 1H), 1.79 (d, *J* = 6.4 Hz, 3H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 198.9, 161.1, 139.3, 135.7, 131.2, 129.8, 129.5, 129.3, 129.2, 128.9, 127.63, 127.57, 112.0, 77.6, 27.5, 23.4, 17.9 ppm; **IR** (ATR) 2879, 2852, 1613, 1595, 1492, 1335, 1212, 1158, 967, 717, 696 cm^{-1}; **HRMS** (ESI) calc. for [$C_{21}H_{20}O_2$ + Na^+]: 327.1356, found: 327.1354.

14.3.1 (2-Methylcyclohex-3-ene-1,1-diyl)bis(phenylmethanone) (259)



259

TBA[Fe] (0.0104 g, 0.025 mmol) and (*E*)-(2-(prop-1-en-1-yl)cyclobutane-1,1-diyl)bis(phenylmethanone) **250** (0.0753 g, 0.25 mmol)) were weighed into a dried 10 mL microwave tube. Anhydrous DMF (1 mL) was added and the tube was sealed under an atmosphere of dry nitrogen. The reaction mixture was stirred for 2 h at 120 °C under microwave irradiation. The reaction was quenched with diethyl ether and concentrated in reduced pressure. The residue was purified by silica column chromatography (eluting with PE:EA = 30:1) to afford 0.0692 g (91%) of **259** as a colorless oil.

R_f = 0.30 (PE/EA, 30:1 (v/v)); **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 8.00-7.95 (m, 2H), 7.85-7.79 (m, 2H), 7.48-7.38 (m, 2H), 7.38-7.24 (m, 4H), 5.83-5.75 (m, 1H), 5.61-5.52 (m, 1H), 3.54-3.43 (m, 1H), 2.45-2.30 (m, 2H), 2.06-1.95 (m, 1H), 1.63-1.53 (m, 1H), 0.82 (d, *J* = 7.1 Hz, 3H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 199.1, 198.6, 137.1, 136.1, 133.3, 132.8, 131.9, 128.84, 128.78, 128.5, 123.3, 66.7, 34.9, 25.7, 21.9, 16.8 ppm; **IR** (ATR) 2916, 1682, 1124, 1205, 1175, 973, 732, 688, 648, 559 cm^{-1}; **HRMS** (ESI) calc. for [$C_{21}H_{20}O_2$ + Na^+]: 327.1356, found: 327.1350.

15. X-Ray Diffraction Analysis

15.1 (*R*)-(2-Vinylcyclopropane-1,1-diyl)bis(phenylmethanone) (*R*)-127

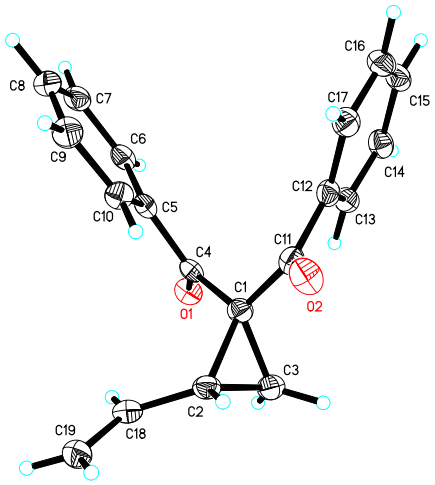


Table S1. Crystal data and structure refinement for **(*R*)-127**.

Identification code	s2179lc (compound h2)
Empirical formula	C19 H16 O2
Formula weight	276.32
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, C 2
Unit cell dimensions	a = 14.3210(8) A alpha = 90 deg. b = 8.9769(5) A beta = 91.660(2) c = 11.7100(7) A gamma = 90 deg.
Volume	1504.78(15) A^3
Z, Calculated density	4, 1.220 Mg/m^3
Absorption coefficient	0.618 mm^{-1}
F(000)	584
Crystal size	0.59 x 0.40 x 0.23 mm
Theta range for data collection	3.78 to 65.82 deg.
Limiting indices	-16<=h<=16, -9<=k<=10, -13<=l<=13

Reflections collected / unique	8918 / 2432 [R(int) = 0.0386]
Completeness to theta = 65.82	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6481
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2432 / 1 / 191
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR2 = 0.0611
R indices (all data)	R1 = 0.0232, wR2 = 0.0612
Absolute structure parameter	0.04(16)
Extinction coefficient	0.0046(3)
Largest diff. peak and hole	0.152 and -0.117 e.A^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **(*R*)-127**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	8220(1)	9840(1)	1002(1)	24(1)
C(1)	6872(1)	11133(1)	1633(1)	20(1)
O(2)	5476(1)	11548(1)	2652(1)	30(1)
C(2)	7035(1)	12823(1)	1512(1)	22(1)
C(3)	6736(1)	11912(2)	491(1)	25(1)
C(4)	7733(1)	10182(1)	1798(1)	19(1)
C(5)	7995(1)	9741(1)	2991(1)	19(1)
C(6)	8571(1)	8501(1)	3169(1)	22(1)
C(7)	8859(1)	8112(2)	4265(1)	26(1)
C(8)	8596(1)	8970(2)	5191(1)	28(1)
C(9)	8031(1)	10208(2)	5016(1)	28(1)
C(10)	7723(1)	10585(1)	3923(1)	23(1)
C(11)	6006(1)	10654(1)	2228(1)	21(1)
C(12)	5796(1)	9026(1)	2243(1)	21(1)
C(13)	6034(1)	8118(1)	1328(1)	22(1)
C(14)	5790(1)	6619(1)	1320(1)	25(1)
C(15)	5331(1)	6018(2)	2237(1)	26(1)
C(16)	5107(1)	6911(2)	3162(1)	27(1)

C(17)	5330(1)	8410(2)	3161(1)	25(1)
C(18)	7985(1)	13444(1)	1643(1)	23(1)
C(19)	8159(1)	14773(2)	2084(1)	26(1)

Table S3. Bond lengths [A] and angles [deg] for **(*R*)-127.**

O(1)-C(4)	1.2193(14)
C(1)-C(11)	1.5030(16)
C(1)-C(4)	1.5080(17)
C(1)-C(3)	1.5170(16)
C(1)-C(2)	1.5418(17)
O(2)-C(11)	1.2202(15)
C(2)-C(18)	1.4742(17)
C(2)-C(3)	1.5007(17)
C(2)-H(2)	1.0000
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.4898(17)
C(5)-C(10)	1.3926(17)
C(5)-C(6)	1.3972(17)
C(6)-C(7)	1.3818(18)
C(6)-H(6)	0.9500
C(7)-C(8)	1.3898(19)
C(7)-H(7)	0.9500
C(8)-C(9)	1.3863(19)
C(8)-H(8)	0.9500
C(9)-C(10)	1.3838(18)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-C(12)	1.4921(17)
C(12)-C(17)	1.3964(17)
C(12)-C(13)	1.3969(17)
C(13)-C(14)	1.3903(19)
C(13)-H(13)	0.9500
C(14)-C(15)	1.3841(18)
C(14)-H(14)	0.9500
C(15)-C(16)	1.3933(19)
C(15)-H(15)	0.9500
C(16)-C(17)	1.382(2)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(19)	1.321(2)
C(18)-H(18)	0.9500
C(19)-H(19A)	0.9500
C(19)-H(19B)	0.9500
C(11)-C(1)-C(4)	117.47(10)
C(11)-C(1)-C(3)	117.00(10)
C(4)-C(1)-C(3)	117.27(10)
C(11)-C(1)-C(2)	116.97(10)
C(4)-C(1)-C(2)	116.31(10)

C(3)-C(1)-C(2)	58.75(8)
C(18)-C(2)-C(3)	122.09(10)
C(18)-C(2)-C(1)	120.30(10)
C(3)-C(2)-C(1)	59.80(8)
C(18)-C(2)-H(2)	114.6
C(3)-C(2)-H(2)	114.6
C(1)-C(2)-H(2)	114.6
C(2)-C(3)-C(1)	61.45(7)
C(2)-C(3)-H(3A)	117.6
C(1)-C(3)-H(3A)	117.6
C(2)-C(3)-H(3B)	117.6
C(1)-C(3)-H(3B)	117.6
H(3A)-C(3)-H(3B)	114.7
O(1)-C(4)-C(5)	121.11(10)
O(1)-C(4)-C(1)	121.88(10)
C(5)-C(4)-C(1)	116.93(10)
C(10)-C(5)-C(6)	119.57(11)
C(10)-C(5)-C(4)	121.48(10)
C(6)-C(5)-C(4)	118.84(10)
C(7)-C(6)-C(5)	119.92(11)
C(7)-C(6)-H(6)	120.0
C(5)-C(6)-H(6)	120.0
C(6)-C(7)-C(8)	120.27(12)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(9)-C(8)-C(7)	119.93(12)
C(9)-C(8)-H(8)	120.0
C(7)-C(8)-H(8)	120.0
C(10)-C(9)-C(8)	120.10(12)
C(10)-C(9)-H(9)	120.0
C(8)-C(9)-H(9)	120.0
C(9)-C(10)-C(5)	120.19(11)
C(9)-C(10)-H(10)	119.9
C(5)-C(10)-H(10)	119.9
O(2)-C(11)-C(12)	120.76(11)
O(2)-C(11)-C(1)	122.12(11)
C(12)-C(11)-C(1)	117.08(10)
C(17)-C(12)-C(13)	119.48(11)
C(17)-C(12)-C(11)	119.90(11)
C(13)-C(12)-C(11)	120.58(11)
C(14)-C(13)-C(12)	120.20(11)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(15)-C(14)-C(13)	119.82(12)
C(15)-C(14)-H(14)	120.1
C(13)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	120.27(12)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(17)-C(16)-C(15)	120.07(11)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(12)	120.12(11)
C(16)-C(17)-H(17)	119.9

C(12)-C(17)-H(17)	119.9
C(19)-C(18)-C(2)	123.10(11)
C(19)-C(18)-H(18)	118.5
C(2)-C(18)-H(18)	118.5
C(18)-C(19)-H(19A)	120.0
C(18)-C(19)-H(19B)	120.0
H(19A)-C(19)-H(19B)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for **(*R*)-127**.
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12]$

	U11	U22	U33	U23	U13	U12
O(1)	26(1)	22(1)	25(1)	-4(1)	6(1)	0(1)
C(1)	24(1)	16(1)	21(1)	-1(1)	-1(1)	0(1)
O(2)	26(1)	24(1)	41(1)	-7(1)	7(1)	1(1)
C(2)	26(1)	16(1)	23(1)	2(1)	-1(1)	1(1)
C(3)	30(1)	22(1)	23(1)	3(1)	-3(1)	-1(1)
C(4)	21(1)	13(1)	23(1)	-2(1)	3(1)	-4(1)
C(5)	16(1)	16(1)	25(1)	-1(1)	2(1)	-3(1)
C(6)	20(1)	16(1)	30(1)	-1(1)	3(1)	-2(1)
C(7)	24(1)	18(1)	36(1)	6(1)	-3(1)	-1(1)
C(8)	27(1)	31(1)	26(1)	9(1)	-3(1)	-6(1)
C(9)	28(1)	31(1)	24(1)	-2(1)	4(1)	-1(1)
C(10)	22(1)	21(1)	25(1)	0(1)	2(1)	3(1)
C(11)	20(1)	22(1)	22(1)	-1(1)	-2(1)	2(1)
C(12)	16(1)	22(1)	24(1)	0(1)	-1(1)	1(1)
C(13)	22(1)	22(1)	24(1)	1(1)	1(1)	-1(1)
C(14)	22(1)	22(1)	31(1)	-4(1)	1(1)	0(1)
C(15)	21(1)	19(1)	40(1)	3(1)	0(1)	-1(1)
C(16)	21(1)	29(1)	31(1)	7(1)	4(1)	-3(1)
C(17)	21(1)	28(1)	25(1)	0(1)	2(1)	1(1)
C(18)	27(1)	19(1)	22(1)	4(1)	2(1)	3(1)
C(19)	26(1)	22(1)	31(1)	1(1)	-1(1)	-1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **(*R*)-127**.

	x	y	z	U(eq)
H(2)	6532	13460	1830	26
H(3A)	7204	11725	-99	30
H(3B)	6087	12041	189	30
H(6)	8764	7926	2537	27
H(7)	9238	7255	4387	31
H(8)	8804	8708	5942	34
H(9)	7855	10798	5648	33
H(10)	7325	11421	3808	27
H(13)	6364	8525	709	27
H(14)	5937	6009	688	30
H(15)	5169	4992	2235	32
H(16)	4800	6491	3795	32
H(17)	5165	9021	3786	30
H(18)	8496	12862	1399	27
H(19A)	7660	15377	2334	32
H(19B)	8784	15126	2152	32

Table S6. Torsion angles [deg] for **(*R*)-127**.

C(11)-C(1)-C(2)-C(18)	141.50(11)
C(4)-C(1)-C(2)-C(18)	-4.50(16)
C(3)-C(1)-C(2)-C(18)	-111.82(13)
C(11)-C(1)-C(2)-C(3)	-106.68(11)
C(4)-C(1)-C(2)-C(3)	107.33(11)
C(18)-C(2)-C(3)-C(1)	108.91(12)
C(11)-C(1)-C(3)-C(2)	106.63(11)
C(4)-C(1)-C(3)-C(2)	-105.70(11)
C(11)-C(1)-C(4)-O(1)	135.43(11)
C(3)-C(1)-C(4)-O(1)	-12.09(16)
C(2)-C(1)-C(4)-O(1)	-78.75(14)
C(11)-C(1)-C(4)-C(5)	-47.73(14)
C(3)-C(1)-C(4)-C(5)	164.75(10)
C(2)-C(1)-C(4)-C(5)	98.09(12)
O(1)-C(4)-C(5)-C(10)	151.98(11)
C(1)-C(4)-C(5)-C(10)	-24.89(16)
O(1)-C(4)-C(5)-C(6)	-24.20(17)
C(1)-C(4)-C(5)-C(6)	158.93(10)
C(10)-C(5)-C(6)-C(7)	0.65(17)
C(4)-C(5)-C(6)-C(7)	176.91(10)
C(5)-C(6)-C(7)-C(8)	-1.54(17)
C(6)-C(7)-C(8)-C(9)	1.02(18)
C(7)-C(8)-C(9)-C(10)	0.41(18)
C(8)-C(9)-C(10)-C(5)	-1.30(18)
C(6)-C(5)-C(10)-C(9)	0.77(17)
C(4)-C(5)-C(10)-C(9)	-175.39(11)
C(4)-C(1)-C(11)-O(2)	141.85(12)
C(3)-C(1)-C(11)-O(2)	-70.54(15)
C(2)-C(1)-C(11)-O(2)	-3.75(16)

C(4)-C(1)-C(11)-C(12)	-40.41(14)
C(3)-C(1)-C(11)-C(12)	107.20(12)
C(2)-C(1)-C(11)-C(12)	173.99(10)
O(2)-C(11)-C(12)-C(17)	-33.00(17)
C(1)-C(11)-C(12)-C(17)	149.23(11)
O(2)-C(11)-C(12)-C(13)	144.85(11)
C(1)-C(11)-C(12)-C(13)	-32.92(16)
C(17)-C(12)-C(13)-C(14)	1.42(17)
C(11)-C(12)-C(13)-C(14)	-176.44(11)
C(12)-C(13)-C(14)-C(15)	-1.71(18)
C(13)-C(14)-C(15)-C(16)	0.54(18)
C(14)-C(15)-C(16)-C(17)	0.93(18)
C(15)-C(16)-C(17)-C(12)	-1.22(18)
C(13)-C(12)-C(17)-C(16)	0.05(17)
C(11)-C(12)-C(17)-C(16)	177.93(11)
C(3)-C(2)-C(18)-C(19)	142.07(12)
C(1)-C(2)-C(18)-C(19)	-146.68(12)

Symmetry transformations used to generate equivalent atoms:

15.2 (*S*)-(2-Vinylcyclopropane-1,1-diyl)bis(phenylmethanone) (*S*)-127

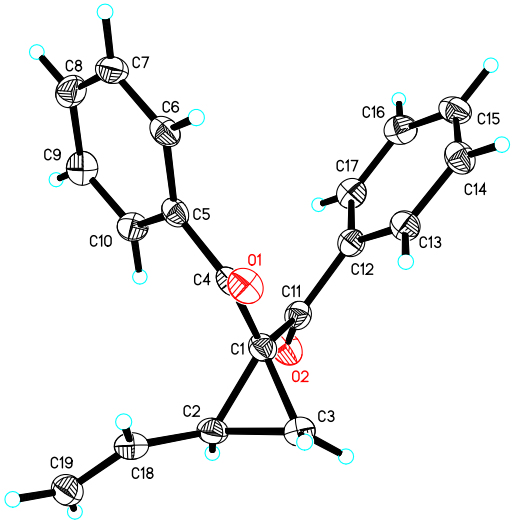


Table S7. Crystal data and structure refinement for **(*S*)-127**.

Identification code	s2181lc (compound h3)
Empirical formula	C19 H16 O2
Formula weight	276.32

Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, C 2
Unit cell dimensions	a = 14.3185(10) A alpha = 90 deg. b = 8.9738(6) A beta = 91.675(3) c = 11.7148(8) A gamma = 90 deg.
Volume	1504.61(18) A^3
Z, Calculated density	4, 1.220 Mg/m^3
Absorption coefficient	0.619 mm^-1
F(000)	584
Crystal size	0.53 x 0.49 x 0.27 mm
Theta range for data collection	3.77 to 65.86 deg.
Limiting indices	-16<=h<=16, -9<=k<=10, -13<=l<=13
Reflections collected / unique	8708 / 2353 [R(int) = 0.0340]
Completeness to theta = 65.86	96.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6797
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2353 / 1 / 191
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0233, wR2 = 0.0593
R indices (all data)	R1 = 0.0233, wR2 = 0.0594
Absolute structure parameter	0.00(16)
Extinction coefficient	0.0041(2)
Largest diff. peak and hole	0.137 and -0.101 $e.A^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **(*S*)-127**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	1780(1)	159(1)	8999(1)	25(1)
C(1)	3128(1)	-1133(1)	8367(1)	21(1)
O(2)	4524(1)	-1548(1)	7348(1)	31(1)
C(2)	2965(1)	-2823(1)	8489(1)	23(1)
C(3)	3264(1)	-1913(2)	9509(1)	26(1)
C(4)	2267(1)	-183(1)	8201(1)	20(1)
C(5)	2006(1)	258(1)	7010(1)	20(1)
C(6)	1431(1)	1499(1)	6832(1)	23(1)
C(7)	1142(1)	1889(2)	5737(1)	27(1)
C(8)	1404(1)	1031(2)	4810(1)	29(1)
C(9)	1968(1)	-206(2)	4985(1)	28(1)
C(10)	2276(1)	-584(1)	6078(1)	23(1)
C(11)	3994(1)	-654(1)	7773(1)	22(1)
C(12)	4204(1)	975(1)	7759(1)	22(1)
C(13)	3967(1)	1883(2)	8671(1)	23(1)
C(14)	4210(1)	3380(2)	8681(1)	26(1)
C(15)	4669(1)	3982(2)	7762(1)	27(1)
C(16)	4893(1)	3089(2)	6839(1)	28(1)
C(17)	4670(1)	1591(2)	6839(1)	26(1)
C(18)	2016(1)	-3445(1)	8357(1)	23(1)
C(19)	1841(1)	-4772(2)	7916(1)	27(1)

Table S9. Bond lengths [A] and angles [deg] for **(*S*)-127**.

O(1)-C(4)	1.2221(14)
C(1)-C(11)	1.5026(16)
C(1)-C(4)	1.5064(17)
C(1)-C(3)	1.5167(17)
C(1)-C(2)	1.5423(18)
O(2)-C(11)	1.2198(15)
C(2)-C(18)	1.4722(17)
C(2)-C(3)	1.4992(18)
C(2)-H(2)	1.0000
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.4877(17)
C(5)-C(10)	1.3923(17)
C(5)-C(6)	1.3972(18)
C(6)-C(7)	1.3809(18)
C(6)-H(6)	0.9500
C(7)-C(8)	1.392(2)
C(7)-H(7)	0.9500
C(8)-C(9)	1.384(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.3839(18)
C(9)-H(9)	0.9500

C(10)-H(10)	0.9500
C(11)-C(12)	1.4931(18)
C(12)-C(13)	1.3940(18)
C(12)-C(17)	1.3972(17)
C(13)-C(14)	1.388(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.3870(19)
C(14)-H(14)	0.9500
C(15)-C(16)	1.391(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.381(2)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(19)	1.320(2)
C(18)-H(18)	0.9500
C(19)-H(19A)	0.9500
C(19)-H(19B)	0.9500

C(11)-C(1)-C(4)	117.52(10)
C(11)-C(1)-C(3)	117.00(10)
C(4)-C(1)-C(3)	117.29(10)
C(11)-C(1)-C(2)	116.97(10)
C(4)-C(1)-C(2)	116.24(10)
C(3)-C(1)-C(2)	58.69(8)
C(18)-C(2)-C(3)	122.11(11)
C(18)-C(2)-C(1)	120.34(11)
C(3)-C(2)-C(1)	59.80(8)
C(18)-C(2)-H(2)	114.6
C(3)-C(2)-H(2)	114.6
C(1)-C(2)-H(2)	114.6
C(2)-C(3)-C(1)	61.51(8)
C(2)-C(3)-H(3A)	117.6
C(1)-C(3)-H(3A)	117.6
C(2)-C(3)-H(3B)	117.6
C(1)-C(3)-H(3B)	117.6
H(3A)-C(3)-H(3B)	114.7
O(1)-C(4)-C(5)	121.09(11)
O(1)-C(4)-C(1)	121.81(11)
C(5)-C(4)-C(1)	117.03(10)
C(10)-C(5)-C(6)	119.41(11)
C(10)-C(5)-C(4)	121.56(11)
C(6)-C(5)-C(4)	118.93(10)
C(7)-C(6)-C(5)	120.03(11)
C(7)-C(6)-H(6)	120.0
C(5)-C(6)-H(6)	120.0
C(6)-C(7)-C(8)	120.25(12)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(9)-C(8)-C(7)	119.87(12)
C(9)-C(8)-H(8)	120.1
C(7)-C(8)-H(8)	120.1
C(10)-C(9)-C(8)	120.12(12)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9

C(9)-C(10)-C(5)	120.31(12)
C(9)-C(10)-H(10)	119.8
C(5)-C(10)-H(10)	119.8
O(2)-C(11)-C(12)	120.79(11)
O(2)-C(11)-C(1)	122.18(12)
C(12)-C(11)-C(1)	116.99(10)
C(13)-C(12)-C(17)	119.51(11)
C(13)-C(12)-C(11)	120.69(11)
C(17)-C(12)-C(11)	119.76(11)
C(14)-C(13)-C(12)	120.34(11)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(15)-C(14)-C(13)	119.71(12)
C(15)-C(14)-H(14)	120.1
C(13)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	120.23(13)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(17)-C(16)-C(15)	120.18(11)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(12)	120.00(12)
C(16)-C(17)-H(17)	120.0
C(12)-C(17)-H(17)	120.0
C(19)-C(18)-C(2)	123.14(11)
C(19)-C(18)-H(18)	118.4
C(2)-C(18)-H(18)	118.4
C(18)-C(19)-H(19A)	120.0
C(18)-C(19)-H(19B)	120.0
H(19A)-C(19)-H(19B)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters (A^2 x 10^3) for **(*S*)-127**.
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12]$

	U11	U22	U33	U23	U13	U12
O(1)	27(1)	24(1)	25(1)	-3(1)	7(1)	0(1)
C(1)	24(1)	18(1)	22(1)	-2(1)	1(1)	0(1)
O(2)	25(1)	27(1)	41(1)	-7(1)	7(1)	2(1)
C(2)	27(1)	17(1)	24(1)	2(1)	1(1)	2(1)
C(3)	30(1)	24(1)	24(1)	3(1)	-2(1)	-1(1)
C(4)	21(1)	15(1)	23(1)	-3(1)	4(1)	-4(1)
C(5)	16(1)	18(1)	25(1)	-1(1)	3(1)	-3(1)

C(6)	21(1)	18(1)	31(1)	-1(1)	3(1)	-3(1)
C(7)	24(1)	20(1)	36(1)	6(1)	-1(1)	-1(1)
C(8)	27(1)	34(1)	26(1)	8(1)	-3(1)	-6(1)
C(9)	27(1)	33(1)	25(1)	-2(1)	4(1)	-1(1)
C(10)	23(1)	22(1)	25(1)	0(1)	3(1)	2(1)
C(11)	20(1)	24(1)	22(1)	-1(1)	-1(1)	2(1)
C(12)	17(1)	23(1)	25(1)	0(1)	-1(1)	1(1)
C(13)	22(1)	24(1)	25(1)	1(1)	2(1)	-2(1)
C(14)	22(1)	23(1)	32(1)	-4(1)	2(1)	-1(1)
C(15)	22(1)	20(1)	40(1)	4(1)	0(1)	-1(1)
C(16)	22(1)	31(1)	31(1)	8(1)	5(1)	-2(1)
C(17)	21(1)	30(1)	26(1)	0(1)	3(1)	1(1)
C(18)	27(1)	21(1)	22(1)	4(1)	3(1)	3(1)
C(19)	26(1)	23(1)	32(1)	1(1)	0(1)	-1(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **(*S*)-127.**

	x	y	z	U(eq)
H(2)	3467	-3461	8171	27
H(3A)	3912	-2043	9810	31
H(3B)	2796	-1726	10097	31
H(6)	1239	2076	7463	27
H(7)	762	2746	5616	32
H(8)	1196	1293	4059	35
H(9)	2144	-797	4353	34
H(10)	2673	-1422	6192	28
H(13)	3637	1475	9290	28
H(14)	4063	3990	9313	31
H(15)	4832	5009	7763	33
H(16)	5199	3509	6207	33
H(17)	4834	979	6214	31
H(18)	1505	-2862	8602	28
H(19A)	2340	-5376	7666	32
H(19B)	1216	-5124	7849	32

Table S12. Torsion angles [deg] for **(*S*)-217.**

C(11)-C(1)-C(2)-C(18)	-141.50(11)
C(4)-C(1)-C(2)-C(18)	4.48(16)
C(3)-C(1)-C(2)-C(18)	111.84(13)
C(11)-C(1)-C(2)-C(3)	106.65(12)
C(4)-C(1)-C(2)-C(3)	-107.36(11)
C(18)-C(2)-C(3)-C(1)	-108.95(13)

C(11)-C(1)-C(3)-C(2)	-106.61(12)
C(4)-C(1)-C(3)-C(2)	105.58(12)
C(11)-C(1)-C(4)-O(1)	-135.45(12)
C(3)-C(1)-C(4)-O(1)	12.19(17)
C(2)-C(1)-C(4)-O(1)	78.76(15)
C(11)-C(1)-C(4)-C(5)	47.69(15)
C(3)-C(1)-C(4)-C(5)	-164.67(10)
C(2)-C(1)-C(4)-C(5)	-98.10(12)
O(1)-C(4)-C(5)-C(10)	-151.97(12)
C(1)-C(4)-C(5)-C(10)	24.92(16)
O(1)-C(4)-C(5)-C(6)	24.36(17)
C(1)-C(4)-C(5)-C(6)	-158.75(10)
C(10)-C(5)-C(6)-C(7)	-0.49(17)
C(4)-C(5)-C(6)-C(7)	-176.90(11)
C(5)-C(6)-C(7)-C(8)	1.36(18)
C(6)-C(7)-C(8)-C(9)	-0.91(18)
C(7)-C(8)-C(9)-C(10)	-0.41(19)
C(8)-C(9)-C(10)-C(5)	1.28(19)
C(6)-C(5)-C(10)-C(9)	-0.83(18)
C(4)-C(5)-C(10)-C(9)	175.49(11)
C(4)-C(1)-C(11)-O(2)	-141.75(12)
C(3)-C(1)-C(11)-O(2)	70.52(15)
C(2)-C(1)-C(11)-O(2)	3.80(17)
C(4)-C(1)-C(11)-C(12)	40.50(15)
C(3)-C(1)-C(11)-C(12)	-107.24(13)
C(2)-C(1)-C(11)-C(12)	-173.96(11)
O(2)-C(11)-C(12)-C(13)	-144.85(12)
C(1)-C(11)-C(12)-C(13)	32.94(16)
O(2)-C(11)-C(12)-C(17)	33.06(18)
C(1)-C(11)-C(12)-C(17)	-149.15(11)
C(17)-C(12)-C(13)-C(14)	-1.49(18)
C(11)-C(12)-C(13)-C(14)	176.43(11)
C(12)-C(13)-C(14)-C(15)	1.75(18)
C(13)-C(14)-C(15)-C(16)	-0.56(18)
C(14)-C(15)-C(16)-C(17)	-0.91(18)
C(15)-C(16)-C(17)-C(12)	1.17(18)
C(13)-C(12)-C(17)-C(16)	0.02(18)
C(11)-C(12)-C(17)-C(16)	-177.92(11)
C(3)-C(2)-C(18)-C(19)	-142.11(13)
C(1)-C(2)-C(18)-C(19)	146.59(12)

Symmetry transformations used to generate equivalent atoms:

15.3 (*R*)-(Phenyl(2-phenyl-5-vinyl-4,5-dihydrofuran-3-yl)methanone (*R*)-128

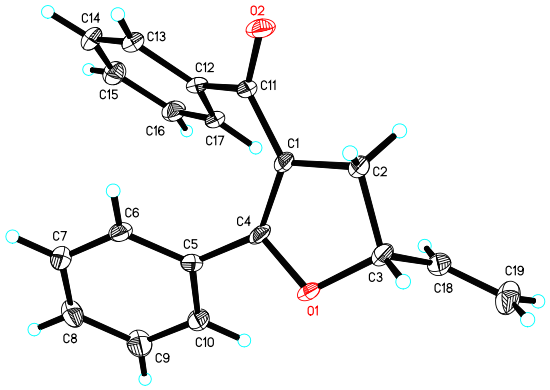


Table S13. Crystal data and structure refinement for **(*R*)-128**.

Identification code	s2180lc (compound 24A)
Empirical formula	C19 H16 O2
Formula weight	276.32
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 6.3155(3) A alpha = 90 deg. b = 7.7433(4) A beta = 100.579(3) c = 15.0935(9) A gamma = 90 deg.
Volume	725.57(7) A^3
Z, Calculated density	2, 1.265 Mg/m^3
Absorption coefficient	0.641 mm^{-1}
F(000)	292
Crystal size	0.54 x 0.20 x 0.08 mm
Theta range for data collection	2.98 to 65.87 deg.
Limiting indices	-6<=h<=7, -8<=k<=9, -17<=l<=17
Reflections collected / unique	8588 / 2439 [R(int) = 0.0583]
Completeness to theta = 65.87	98.7 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.5323
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2439 / 1 / 191
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0971
R indices (all data)	R1 = 0.0386, wR2 = 0.0976
Absolute structure parameter	0.2(2)
Extinction coefficient	0.0060(16)
Largest diff. peak and hole	0.198 and -0.246 e.A^{-3}

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **(*R*)-128**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	5947(2)	3292(2)	4181(1)	18(1)
C(1)	3155(3)	4361(2)	3164(1)	15(1)
O(2)	-162(2)	5438(2)	2431(1)	22(1)
C(2)	3397(3)	5597(2)	3948(1)	18(1)
C(3)	5585(3)	5046(2)	4509(1)	18(1)
C(4)	4597(2)	3063(2)	3371(1)	16(1)
C(5)	4920(3)	1410(2)	2937(1)	16(1)
C(6)	3169(3)	413(2)	2536(1)	19(1)
C(7)	3479(3)	-1129(2)	2117(1)	21(1)
C(8)	5556(3)	-1704(2)	2108(1)	24(1)
C(9)	7312(3)	-743(3)	2520(1)	26(1)
C(10)	7004(3)	808(2)	2930(1)	21(1)
C(11)	1423(3)	4550(2)	2379(1)	16(1)
C(12)	1598(3)	3720(2)	1498(1)	17(1)
C(13)	-243(3)	2969(2)	994(1)	19(1)
C(14)	-154(3)	2200(2)	172(1)	23(1)
C(15)	1751(3)	2234(3)	-167(1)	23(1)
C(16)	3570(3)	3008(3)	322(1)	21(1)
C(17)	3514(3)	3723(2)	1161(1)	18(1)
C(18)	7429(3)	6141(2)	4363(1)	21(1)
C(19)	8672(3)	7004(3)	5014(2)	30(1)

Table S15. Bond lengths [A] and angles [deg] for **(*R*)-128.**

O(1)-C(4)	1.367(2)
O(1)-C(3)	1.478(2)
C(1)-C(4)	1.354(2)
C(1)-C(11)	1.465(2)
C(1)-C(2)	1.507(2)
O(2)-C(11)	1.229(2)
C(2)-C(3)	1.542(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(18)	1.489(2)
C(3)-H(3)	1.0000
C(4)-C(5)	1.469(2)
C(5)-C(6)	1.392(2)
C(5)-C(10)	1.398(2)
C(6)-C(7)	1.383(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.387(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.385(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.381(3)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-C(12)	1.499(2)
C(12)-C(13)	1.394(2)
C(12)-C(17)	1.396(2)
C(13)-C(14)	1.386(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.392(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.383(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.389(3)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(19)	1.321(3)
C(18)-H(18)	0.9500
C(19)-H(19A)	0.9500
C(19)-H(19B)	0.9500
C(4)-O(1)-C(3)	108.01(12)
C(4)-C(1)-C(11)	129.13(15)
C(4)-C(1)-C(2)	108.89(14)
C(11)-C(1)-C(2)	121.64(14)
C(1)-C(2)-C(3)	101.91(13)
C(1)-C(2)-H(2A)	111.4
C(3)-C(2)-H(2A)	111.4
C(1)-C(2)-H(2B)	111.4
C(3)-C(2)-H(2B)	111.4
H(2A)-C(2)-H(2B)	109.3
O(1)-C(3)-C(18)	107.50(13)

O(1)-C(3)-C(2)	104.38(13)
C(18)-C(3)-C(2)	114.07(15)
O(1)-C(3)-H(3)	110.2
C(18)-C(3)-H(3)	110.2
C(2)-C(3)-H(3)	110.2
C(1)-C(4)-O(1)	113.11(15)
C(1)-C(4)-C(5)	133.39(15)
O(1)-C(4)-C(5)	113.35(14)
C(6)-C(5)-C(10)	119.05(16)
C(6)-C(5)-C(4)	120.82(15)
C(10)-C(5)-C(4)	120.13(15)
C(7)-C(6)-C(5)	120.64(15)
C(7)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
C(6)-C(7)-C(8)	119.71(16)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1
C(9)-C(8)-C(7)	120.23(17)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(10)-C(9)-C(8)	120.11(16)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(9)-C(10)-C(5)	120.24(17)
C(9)-C(10)-H(10)	119.9
C(5)-C(10)-H(10)	119.9
O(2)-C(11)-C(1)	120.00(15)
O(2)-C(11)-C(12)	119.35(14)
C(1)-C(11)-C(12)	120.62(14)
C(13)-C(12)-C(17)	119.60(15)
C(13)-C(12)-C(11)	118.23(14)
C(17)-C(12)-C(11)	122.15(14)
C(14)-C(13)-C(12)	120.04(16)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(13)-C(14)-C(15)	120.04(16)
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-H(14)	120.0
C(16)-C(15)-C(14)	120.12(16)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(15)-C(16)-C(17)	120.10(15)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-H(16)	120.0
C(16)-C(17)-C(12)	120.03(15)
C(16)-C(17)-H(17)	120.0
C(12)-C(17)-H(17)	120.0
C(19)-C(18)-C(3)	123.55(18)
C(19)-C(18)-H(18)	118.2
C(3)-C(18)-H(18)	118.2
C(18)-C(19)-H(19A)	120.0
C(18)-C(19)-H(19B)	120.0
H(19A)-C(19)-H(19B)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters (A^2 x 10^3) for **(*R*)-128**.
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12]$

	U11	U22	U33	U23	U13	U12
O(1)	13(1)	19(1)	18(1)	-2(1)	-7(1)	3(1)
C(1)	10(1)	16(1)	18(1)	-3(1)	-1(1)	-1(1)
O(2)	14(1)	26(1)	25(1)	-2(1)	-3(1)	7(1)
C(2)	14(1)	17(1)	20(1)	-4(1)	-2(1)	1(1)
C(3)	15(1)	20(1)	17(1)	-4(1)	-4(1)	0(1)
C(4)	8(1)	20(1)	17(1)	1(1)	-3(1)	-3(1)
C(5)	14(1)	15(1)	17(1)	3(1)	-1(1)	2(1)
C(6)	12(1)	20(1)	22(1)	5(1)	-2(1)	-1(1)
C(7)	20(1)	18(1)	23(1)	1(1)	-1(1)	-4(1)
C(8)	28(1)	15(1)	30(1)	-2(1)	7(1)	0(1)
C(9)	16(1)	22(1)	42(1)	-3(1)	8(1)	3(1)
C(10)	12(1)	19(1)	31(1)	-1(1)	-1(1)	0(1)
C(11)	10(1)	13(1)	21(1)	1(1)	-3(1)	0(1)
C(12)	12(1)	16(1)	19(1)	1(1)	-4(1)	3(1)
C(13)	12(1)	19(1)	23(1)	0(1)	-2(1)	0(1)
C(14)	18(1)	23(1)	23(1)	-4(1)	-6(1)	-3(1)
C(15)	23(1)	25(1)	20(1)	-3(1)	-1(1)	-1(1)
C(16)	15(1)	24(1)	24(1)	-1(1)	2(1)	2(1)
C(17)	12(1)	16(1)	22(1)	1(1)	-4(1)	0(1)
C(18)	14(1)	19(1)	27(1)	-3(1)	-1(1)	2(1)
C(19)	13(1)	32(1)	43(1)	-16(1)	2(1)	-2(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **(*R*)-128**.

	x	y	z	U(eq)
H(2A)	2218	5453	4294	21
H(2B)	3429	6811	3745	21
H(3)	5502	5011	5164	22
H(6)	1748	798	2551	22
H(7)	2276	-1793	1837	25

H(8)	5774	-2761	1818	29
H(9)	8731	-1151	2521	31
H(10)	8212	1468	3208	25
H(13)	-1559	2984	1214	22
H(14)	-1395	1649	-160	27
H(15)	1802	1725	-735	28
H(16)	4861	3051	83	25
H(17)	4781	4214	1506	21
H(18)	7727	6224	3770	25
H(19A)	8411	6945	5613	36
H(19B)	9828	7684	4883	36

Table S18. Torsion angles [deg] for **(*R*)-128**.

C(4)-C(1)-C(2)-C(3)	14.66(17)
C(11)-C(1)-C(2)-C(3)	-171.48(15)
C(4)-O(1)-C(3)-C(18)	-104.38(15)
C(4)-O(1)-C(3)-C(2)	17.11(16)
C(1)-C(2)-C(3)-O(1)	-18.63(16)
C(1)-C(2)-C(3)-C(18)	98.41(16)
C(11)-C(1)-C(4)-O(1)	-177.88(16)
C(2)-C(1)-C(4)-O(1)	-4.62(18)
C(11)-C(1)-C(4)-C(5)	-2.7(3)
C(2)-C(1)-C(4)-C(5)	170.54(17)
C(3)-O(1)-C(4)-C(1)	-8.32(18)
C(3)-O(1)-C(4)-C(5)	175.51(12)
C(1)-C(4)-C(5)-C(6)	-38.6(3)
O(1)-C(4)-C(5)-C(6)	136.56(15)
C(1)-C(4)-C(5)-C(10)	141.99(19)
O(1)-C(4)-C(5)-C(10)	-42.9(2)
C(10)-C(5)-C(6)-C(7)	-1.5(2)
C(4)-C(5)-C(6)-C(7)	179.04(15)
C(5)-C(6)-C(7)-C(8)	1.0(3)
C(6)-C(7)-C(8)-C(9)	0.3(3)
C(7)-C(8)-C(9)-C(10)	-1.1(3)
C(8)-C(9)-C(10)-C(5)	0.5(3)
C(6)-C(5)-C(10)-C(9)	0.8(3)
C(4)-C(5)-C(10)-C(9)	-179.78(16)
C(4)-C(1)-C(11)-O(2)	154.56(17)
C(2)-C(1)-C(11)-O(2)	-17.9(3)
C(4)-C(1)-C(11)-C(12)	-27.6(3)
C(2)-C(1)-C(11)-C(12)	159.87(15)
O(2)-C(11)-C(12)-C(13)	-42.0(2)
C(1)-C(11)-C(12)-C(13)	140.22(16)
O(2)-C(11)-C(12)-C(17)	136.18(17)
C(1)-C(11)-C(12)-C(17)	-41.6(2)
C(17)-C(12)-C(13)-C(14)	1.3(3)
C(11)-C(12)-C(13)-C(14)	179.49(16)
C(12)-C(13)-C(14)-C(15)	-2.4(3)
C(13)-C(14)-C(15)-C(16)	1.2(3)
C(14)-C(15)-C(16)-C(17)	1.3(3)

C(15)-C(16)-C(17)-C(12)	-2.4(3)
C(13)-C(12)-C(17)-C(16)	1.1(2)
C(11)-C(12)-C(17)-C(16)	-176.98(16)
O(1)-C(3)-C(18)-C(19)	-123.66(19)
C(2)-C(3)-C(18)-C(19)	121.1(2)

Symmetry transformations used to generate equivalent atoms:

15.3 (*S*)-(Phenyl(2-phenyl-5-vinyl-4,5-dihydrofuran-3-yl)methanone (*S*)-128

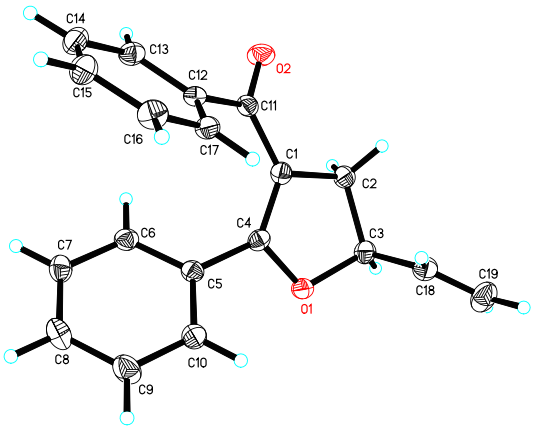


Table S19. Crystal data and structure refinement for **(*S*)-128**.

Identification code	s2182lc (compound 24B)
Empirical formula	C19 H16 O2
Formula weight	276.32
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 6.309(2) A alpha = 90 deg. b = 7.753(2) A beta = 100.736(14) c = 15.117(5) A gamma = 90 deg.
Volume	726.5(4) A^3
Z, Calculated density	2, 1.263 Mg/m^3
Absorption coefficient	0.640 mm^{-1}

F(000)	292
Crystal size	0.41 x 0.37 x 0.31 mm
Theta range for data collection	2.98 to 65.60 deg.
Limiting indices	-4<=h<=7, -9<=k<=9, -17<=l<=16
Reflections collected / unique	8149 / 2402 [R(int) = 0.0335]
Completeness to theta = 65.60	96.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6318
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2402 / 1 / 191
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.0234, wR2 = 0.0573
R indices (all data)	R1 = 0.0237, wR2 = 0.0576
Absolute structure parameter	-0.03(16)
Extinction coefficient	0.0085(7)
Largest diff. peak and hole	0.112 and -0.133 e.A^{-3}

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **(*S*)-128**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	4054(1)	6709(1)	5822(1)	20(1)
C(1)	6846(2)	5641(2)	6839(1)	18(1)
O(2)	10165(1)	4563(1)	7568(1)	25(1)
C(2)	6601(2)	4406(2)	6050(1)	20(1)
C(3)	4420(2)	4950(2)	5495(1)	20(1)
C(4)	5397(2)	6933(2)	6627(1)	17(1)
C(5)	5073(2)	8589(2)	7065(1)	18(1)
C(6)	6831(2)	9587(2)	7464(1)	20(1)
C(7)	6520(2)	11131(2)	7884(1)	22(1)
C(8)	4446(2)	11706(2)	7893(1)	26(1)

C(9)	2685(2)	10747(2)	7483(1)	28(1)
C(10)	2996(2)	9190(2)	7068(1)	23(1)
C(11)	8566(2)	5453(2)	7621(1)	18(1)
C(12)	8397(2)	6281(2)	8502(1)	17(1)
C(13)	10238(2)	7028(2)	9007(1)	21(1)
C(14)	10150(2)	7799(2)	9827(1)	24(1)
C(15)	8252(2)	7763(2)	10168(1)	25(1)
C(16)	6428(2)	6988(2)	9678(1)	23(1)
C(17)	6487(2)	6274(2)	8840(1)	19(1)
C(18)	2567(2)	3859(2)	5633(1)	23(1)
C(19)	1331(2)	3001(2)	4986(1)	32(1)

Table S21. Bond lengths [A] and angles [deg] for **(*S*)-128**.

O(1)-C(4)	1.3586(15)
O(1)-C(3)	1.4835(15)
C(1)-C(4)	1.3540(18)
C(1)-C(11)	1.4553(18)
C(1)-C(2)	1.5143(17)
O(2)-C(11)	1.2373(16)
C(2)-C(3)	1.5312(18)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(18)	1.4894(19)
C(3)-H(3)	1.0000
C(4)-C(5)	1.4758(18)
C(5)-C(10)	1.3921(19)
C(5)-C(6)	1.3942(18)
C(6)-C(7)	1.386(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.385(2)
C(7)-H(7)	0.9500
C(8)-C(9)	1.384(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.391(2)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-C(12)	1.4999(17)
C(12)-C(13)	1.3922(18)
C(12)-C(17)	1.3936(18)
C(13)-C(14)	1.3861(19)
C(13)-H(13)	0.9500
C(14)-C(15)	1.390(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.385(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.3888(19)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(19)	1.313(2)
C(18)-H(18)	0.9500

C(19)-H(19A)	0.9500
C(19)-H(19B)	0.9500
C(4)-O(1)-C(3)	107.83(9)
C(4)-C(1)-C(11)	129.35(11)
C(4)-C(1)-C(2)	108.43(11)
C(11)-C(1)-C(2)	121.88(11)
C(1)-C(2)-C(3)	101.96(10)
C(1)-C(2)-H(2A)	111.4
C(3)-C(2)-H(2A)	111.4
C(1)-C(2)-H(2B)	111.4
C(3)-C(2)-H(2B)	111.4
H(2A)-C(2)-H(2B)	109.2
O(1)-C(3)-C(18)	107.46(10)
O(1)-C(3)-C(2)	104.49(10)
C(18)-C(3)-C(2)	114.54(11)
O(1)-C(3)-H(3)	110.0
C(18)-C(3)-H(3)	110.0
C(2)-C(3)-H(3)	110.0
C(1)-C(4)-O(1)	113.46(11)
C(1)-C(4)-C(5)	132.97(11)
O(1)-C(4)-C(5)	113.42(10)
C(10)-C(5)-C(6)	119.09(12)
C(10)-C(5)-C(4)	120.13(11)
C(6)-C(5)-C(4)	120.76(11)
C(7)-C(6)-C(5)	120.56(12)
C(7)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
C(8)-C(7)-C(6)	119.81(12)
C(8)-C(7)-H(7)	120.1
C(6)-C(7)-H(7)	120.1
C(9)-C(8)-C(7)	120.26(13)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(8)-C(9)-C(10)	119.96(13)
C(8)-C(9)-H(9)	120.0
C(10)-C(9)-H(9)	120.0
C(9)-C(10)-C(5)	120.28(12)
C(9)-C(10)-H(10)	119.9
C(5)-C(10)-H(10)	119.9
O(2)-C(11)-C(1)	119.80(11)
O(2)-C(11)-C(12)	119.29(11)
C(1)-C(11)-C(12)	120.89(11)
C(13)-C(12)-C(17)	119.35(11)
C(13)-C(12)-C(11)	118.38(11)
C(17)-C(12)-C(11)	122.23(11)
C(14)-C(13)-C(12)	120.12(12)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(13)-C(14)-C(15)	120.26(12)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	119.83(12)
C(16)-C(15)-H(15)	120.1

C(14)-C(15)-H(15)	120.1
C(15)-C(16)-C(17)	120.03(12)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-H(16)	120.0
C(16)-C(17)-C(12)	120.33(12)
C(16)-C(17)-H(17)	119.8
C(12)-C(17)-H(17)	119.8
C(19)-C(18)-C(3)	123.75(13)
C(19)-C(18)-H(18)	118.1
C(3)-C(18)-H(18)	118.1
C(18)-C(19)-H(19A)	120.0
C(18)-C(19)-H(19B)	120.0
H(19A)-C(19)-H(19B)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S22. Anisotropic displacement parameters (A^2 x 10^3) for **(*S*)-128**.
The anisotropic displacement factor exponent takes the form:
$-2\ pi^2\ [h^2\ a^{*2}\ U11 + ... + 2\ h\ k\ a^*\ b^*\ U12]$

	U11	U22	U33	U23	U13	U12
O(1)	20(1)	19(1)	20(1)	-2(1)	0(1)	3(1)
C(1)	17(1)	18(1)	19(1)	-2(1)	5(1)	0(1)
O(2)	19(1)	28(1)	26(1)	-2(1)	3(1)	8(1)
C(2)	20(1)	19(1)	21(1)	-3(1)	4(1)	2(1)
C(3)	22(1)	21(1)	17(1)	-4(1)	2(1)	0(1)
C(4)	14(1)	20(1)	18(1)	1(1)	4(1)	-2(1)
C(5)	19(1)	17(1)	17(1)	1(1)	3(1)	1(1)
C(6)	18(1)	20(1)	22(1)	4(1)	3(1)	0(1)
C(7)	25(1)	18(1)	24(1)	0(1)	5(1)	-4(1)
C(8)	32(1)	17(1)	31(1)	-2(1)	13(1)	-1(1)
C(9)	23(1)	23(1)	42(1)	-4(1)	13(1)	2(1)
C(10)	18(1)	21(1)	31(1)	-2(1)	4(1)	0(1)
C(11)	17(1)	15(1)	22(1)	1(1)	4(1)	0(1)
C(12)	17(1)	17(1)	17(1)	2(1)	1(1)	2(1)
C(13)	17(1)	23(1)	22(1)	2(1)	3(1)	1(1)
C(14)	22(1)	26(1)	22(1)	-2(1)	0(1)	-3(1)
C(15)	29(1)	27(1)	18(1)	-3(1)	3(1)	0(1)
C(16)	20(1)	27(1)	24(1)	0(1)	8(1)	1(1)
C(17)	17(1)	19(1)	20(1)	2(1)	1(1)	0(1)
C(18)	19(1)	24(1)	27(1)	-3(1)	5(1)	2(1)
C(19)	20(1)	36(1)	41(1)	-15(1)	7(1)	-2(1)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **(*S*)-128.**

	x	y	z	U(eq)
H(2A)	6573	3192	6250	24
H(2B)	7777	4555	5705	24
H(3)	4503	4987	4841	24
H(6)	8254	9206	7447	24
H(7)	7726	11793	8165	27
H(8)	4231	12762	8182	31
H(9)	1265	11152	7484	34
H(10)	1785	8534	6786	28
H(13)	11557	7009	8790	25
H(14)	11392	8354	10157	29
H(15)	8206	8268	10737	30
H(16)	5136	6944	9914	28
H(17)	5220	5779	8496	23
H(18)	2261	3780	6224	28
H(19A)	1598	3056	4389	39
H(19B)	170	2325	5115	39

Table S24. Torsion angles [deg] for **(*S*)-128.**

C(4)-C(1)-C(2)-C(3)	-14.87(13)
C(11)-C(1)-C(2)-C(3)	171.19(12)
C(4)-O(1)-C(3)-C(18)	104.62(11)
C(4)-O(1)-C(3)-C(2)	-17.45(12)
C(1)-C(2)-C(3)-O(1)	18.92(12)
C(1)-C(2)-C(3)-C(18)	-98.37(12)
C(11)-C(1)-C(4)-O(1)	177.93(12)
C(2)-C(1)-C(4)-O(1)	4.59(14)
C(11)-C(1)-C(4)-C(5)	2.7(2)
C(2)-C(1)-C(4)-C(5)	-170.64(12)
C(3)-O(1)-C(4)-C(1)	8.45(13)
C(3)-O(1)-C(4)-C(5)	-175.36(10)
C(1)-C(4)-C(5)-C(10)	-142.14(14)
O(1)-C(4)-C(5)-C(10)	42.64(16)
C(1)-C(4)-C(5)-C(6)	39.1(2)
O(1)-C(4)-C(5)-C(6)	-136.11(11)
C(10)-C(5)-C(6)-C(7)	2.06(18)
C(4)-C(5)-C(6)-C(7)	-179.19(11)
C(5)-C(6)-C(7)-C(8)	-1.27(19)
C(6)-C(7)-C(8)-C(9)	-0.2(2)
C(7)-C(8)-C(9)-C(10)	0.8(2)
C(8)-C(9)-C(10)-C(5)	0.1(2)
C(6)-C(5)-C(10)-C(9)	-1.45(19)
C(4)-C(5)-C(10)-C(9)	179.79(12)

C(4)-C(1)-C(11)-O(2)	-154.48(13)
C(2)-C(1)-C(11)-O(2)	18.08(19)
C(4)-C(1)-C(11)-C(12)	27.5(2)
C(2)-C(1)-C(11)-C(12)	-159.98(11)
O(2)-C(11)-C(12)-C(13)	41.75(17)
C(1)-C(11)-C(12)-C(13)	-140.18(12)
O(2)-C(11)-C(12)-C(17)	-136.11(13)
C(1)-C(11)-C(12)-C(17)	41.96(18)
C(17)-C(12)-C(13)-C(14)	-1.81(18)
C(11)-C(12)-C(13)-C(14)	-179.73(12)
C(12)-C(13)-C(14)-C(15)	2.9(2)
C(13)-C(14)-C(15)-C(16)	-1.5(2)
C(14)-C(15)-C(16)-C(17)	-1.1(2)
C(15)-C(16)-C(17)-C(12)	2.2(2)
C(13)-C(12)-C(17)-C(16)	-0.76(18)
C(11)-C(12)-C(17)-C(16)	177.08(12)
O(1)-C(3)-C(18)-C(19)	123.69(14)
C(2)-C(3)-C(18)-C(19)	-120.72(15)

Symmetry transformations used to generate equivalent atoms:

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