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# A Versatile Route to Acyl (MIDA)Boronates and Acyl silanes

Hui Qiao

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NNT : 2023IPPAX121

Thèse de doctorat



# A Versatile Route to Acylsilanes and Acyl(MIDA)boronates

Thèse de doctorat de l'Institut Polytechnique de Paris  
préparée à l'École Polytechnique

École doctorale n°626 de l'Institut Polytechnique de Paris  
(ED IP Paris)  
Spécialité de doctorat: Chimie

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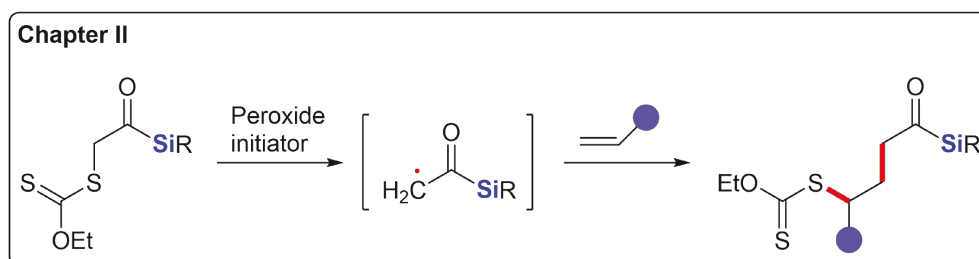
Sincere gratitude should also go to all my learned Professors and warm-hearted teachers who have greatly helped me in my study as well as in my life. And my warm gratitude also goes to my friends and family who gave me much encouragement and financial support respectively. Moreover, I wish to extend my thanks to the library and the electronic reading room for their providing much useful information for my thesis. Finally, I want to thank the China Science Council (CSC) for a scholarship to my PhD.

## Résumé

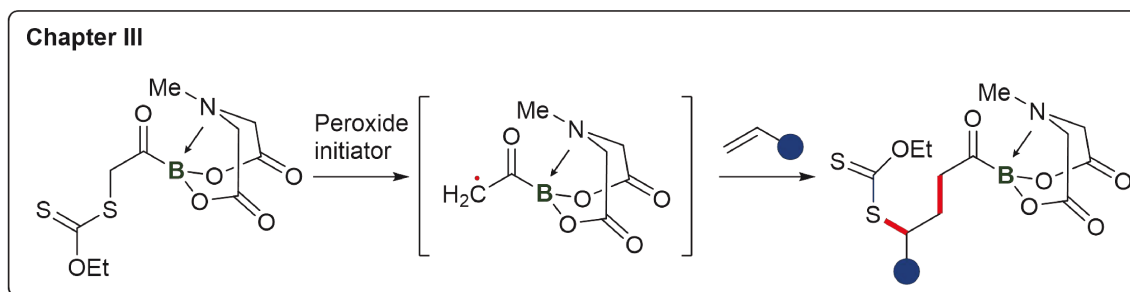
Ce travail de recherche se concentre sur la synthèse et les applications des acylsilanes et des acyl(MIDA)boronates en utilisant la chimie radicalaire des dithiocarbonates (xanthates), dans laquelle les xanthates agissent en tant que source de radicaux. Le transfert dégénérateur réversible du xanthate apparaît comme l'un des outils les plus efficaces pour la génération de liaisons C-C au cours des dernières années, permettant la formation de nombreuses molécules complexes. L'objectif de ce travail est de développer des nouveaux radicaux dérivés des xanthates et liés aux acylsilanes et aux acyl(MIDA)boronates. En outre, l'objectif est également de comprendre en profondeur leur réactivité et de les utiliser dans diverses transformations utiles.

Cette thèse se compose de trois chapitres et contient deux projets principaux. Dans le chapitre I, les informations de base sur les radicaux et les réactions radicalaires sont résumées et la génération de radicaux à partir de xanthates, et en particulier le processus d'addition-transfert de xanthate, est principalement introduite.

Le chapitre II décrit une approche modulaire, directe et flexible des acylsilanes fonctionnels. L'utilisation des acylsilanes en synthèse organique a augmenté de manière significative au cours des dernières années en raison de leurs propriétés uniques et de la découverte de nouvelles réactions intéressantes. Dans ce travail, une grande variété d'acylsilanes fonctionnels a été synthétisée efficacement, grâce à la caractéristique électrophile du radical acylsilane intermédiaire dérivé du xanthate et à la nature nucléophile de l'oléfine partenaire. En outre, les acylsilanes formés ont été engagés dans la formation de 2-pyrrolylsilanes, ainsi que des pyrrolylsilanes multi-substitués qui sont difficiles d'accès par d'autres moyens.



Les acylboranes et les acylboronates constituent une classe intrigante de composés, dont les propriétés remarquables et la réactivité pour la synthèse n'ont été reconnues que récemment. Le chapitre III présente un xanthate nouveau et réactif comme réactif de transfert d'acylboronates pour synthétiser divers acyl(MIDA)boronates. Notre synthèse repose sur l'addition de radicaux dérivés du xanthate correspondant et d'alcènes fonctionnels, ce qui conduit à la formation de précieux acyl(MIDA)boronates. La douceur des conditions de réaction et la grande tolérance pour une variété de groupes fonctionnels permettent la construction d'échafaudages plus complexes, y compris, mais sans s'y limiter, les (MIDA)boronates de 2-pyrrolyle et les (MIDA)boronates de fureyle.

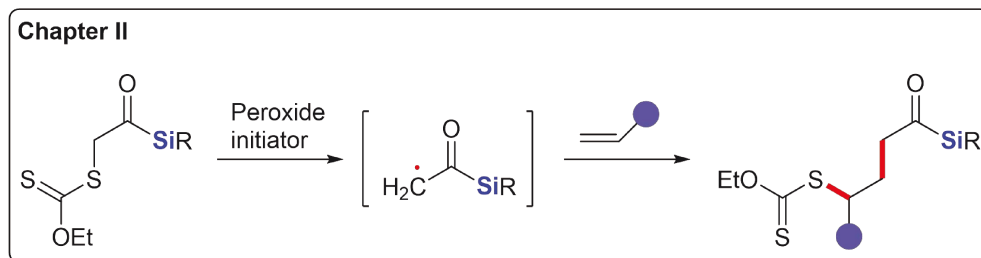


## Abstract

This research work focuses on the synthesis and applications of acylsilanes and acyl(MIDA)boronates by utilizing the radical chemistry of dithiocarbonates (xanthates) in which xanthates act as the radical source. The degenerative reversible transfer of xanthate is emerging as one of the most effective tools for the generation of C-C bonds in recent years, allowing the formation of numerous complex molecules. The purpose of this work is to develop new-fashioned radicals derived from xanthates and related to acylsilanes and acyl(MIDA)boronates. Moreover, the aim is also to deeply understand their reactivity, and to employ them in various useful transformations.

This thesis consists of three chapters and contains two main projects. In **Chapter I**, the basic information on radicals and radical reactions is summarized and the generation of radicals from xanthates, and particularly the xanthate addition-transfer process, is mainly introduced.

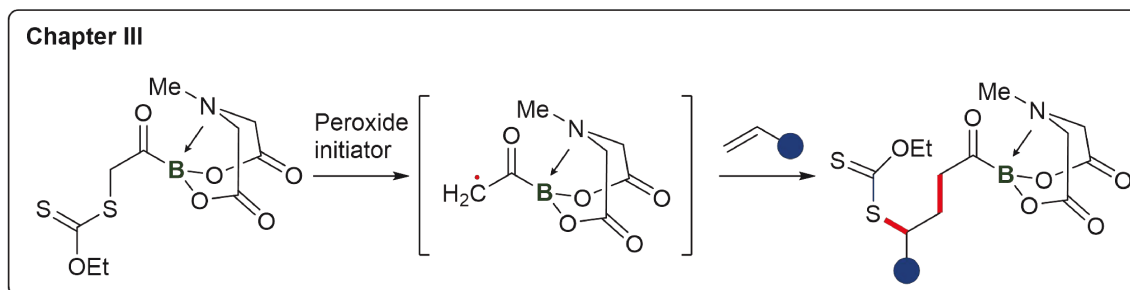
In **Chapter II**, a modular, straightforward, and flexible approach to functional acylsilanes is described. The use of acylsilanes in organic synthesis has increased significantly over the last few years due to their unique properties and the discovery of valuable new reactions. In this work, a wide variety of functional acylsilanes were efficiently synthesized, implemented by the electrophilic feature of the intermediate acylsilane radical derived from the xanthate and the nucleophilic nature of the olefin partner. In addition, the formed acylsilanes were engaged in the formation of 2-pyrrolyl silanes, even the multi-substituted pyrrolyl silanes that are difficult to access by other means.



Acylboranes and acylboronates are an intriguing class of compounds, and their remarkable properties and reactivities for synthesis have only recently been recognized. In **Chapter III**, a novel and reactive xanthate as an acylboron transfer reagent for



synthesizing various acyl(MIDA)boronates is presented. Our synthesis relies on the addition of radical derived from the corresponding xanthate and functional alkenes, leading to the formation of valuable acyl(MIDA)boronates. The mildness of the reaction conditions and broad tolerance for a variety of functional groups allow the construction of more complex scaffolds, including but not limited to 2-pyrrolyl (MIDA)boronates and furyl (MIDA)boronates.



## Contents

Chapter I. General introduction .....	1
1.1 Discovery and development of radical reactions .....	1
1.2 Typical radical reactions .....	5
1.2.1 Chain reactions .....	5
1.2.2 Chain reaction based on organotin hydrides .....	7
1.3 The xanthate addition-transfer process .....	10
1.3.1 Discovery of xanthate in radical synthesis .....	10
1.3.2 Mechanism of xanthate addition-transfer process .....	13
1.4 Synthetic utilities of xanthate .....	15
1.4.1 Convergent xanthate route to pyrroles .....	15
1.4.2 Convergent xanthate route to other 1,4-dicarbonyl derivatives .....	20
1.5 Conclusion .....	22
1.6 References .....	23
Chapter II. The xanthate route to acylsilanes .....	26
2.1 Introduction .....	26
2.2 Methods for the synthesis of acylsilanes .....	28
2.2.1 From $\alpha$ -silylalcohols .....	29
2.2.2 From Aldehydes .....	31
2.2.3 From carboxylic acids and carboxylic acid derivatives .....	33
2.2.4 From other organic functionalities .....	35
2.3 Experimental design and initial attempts .....	36
2.4 Results and Discussion .....	43
2.4.1 Scope of alkenes .....	43
2.4.2 The Brook rearrangement of the synthesized acylsilanes .....	45
2.4.3 The thiol group from xanthate and its subsequent transformations .....	48
2.4.4 Synthesis of 2-pyrrolyl silanes .....	49

2.4.5 Carbene generation of acylsilanes and subsequent synthetic applications .....	53
2.5 Conclusion .....	55
2.6 References .....	56
Chapter III. The xanthate chemistry of acyl (MIDA)boronates .....	59
3.1 Introduction .....	59
3.2 Main routes to acylboranes .....	60
3.2.1 Synthesis of NHC-stabilized acylboranes .....	60
3.2.2 Synthesis of potassium acyltrifluoroborates .....	62
3.2.3 Synthesis of acyl(MIDA)boronates .....	66
3.3 Experimental design of this project .....	69
3.4 Results and Discussion .....	71
3.4.1 Initial attempts in the synthesis of xanthate III-9 .....	71
3.4.2 Scope of alkenes .....	71
3.4.4 Subsequent transformations of adduct III-11 .....	76
3.4.4.1 Preliminary attempts .....	76
3.4.4.2 Synthesis of 2-pyrrolyl (MIDA)boronates .....	78
3.4.4.3 Synthesis of furyl (MIDA)boronates .....	80
3.4.5 Reactivity of radical III-10 derived from xanthate III-9 .....	82
3.5 Conclusion .....	83
3.6 References .....	84
General Conclusion .....	86
General Experimental Methods .....	87
Experimental Procedures .....	88
Reference .....	180

## Abbreviations

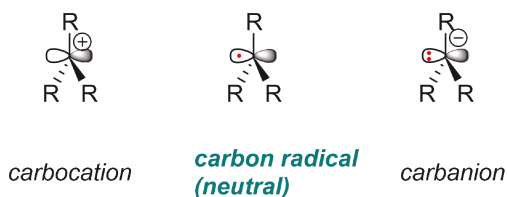
Ac	Acetyl
AIBN	2,2'-azo-bis-isobutyronitrile
Ar	Aryl
Boc	tert-butoxycarbonyl
t-Bu	tert-butyl
Bz	Benzoyl
Bn	Benzyl
Cat.	catalytic quantity
m-CPBA	meta-chloroperoxybenzoic acid
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DIPEA	<i>N,N</i> -Diisopropylethylamine
DCE	1,2-dichloroethane
DCM	dichloromethane
DLP	dilauroyl peroxide
dipp	2,6-diisopropylphenyl
Et	Ethyl
Equiv.	Equivalent
FTIR	Fourier-transform infrared spectroscopy
HPLC	High performance liquid chromatography
h	Hour
ICy	1,3-Dicyclohexylimidazolium
LDBB	Lithium 4,4'-di(tert-butyl)biphenyl
MIDA	<i>N</i> -methyliminodiacetic acid
MeCN	Acetonitrile
Me	Methyl
M	mole per litre
NMR	nuclear magnetic resonance
Nu	nucleophile
Npht	Phthalimide

NBS	<i>N</i> -bromosuccinimide
NHC	<i>N</i> -heterocyclic carbene
OAc	Acetoxy
Ph	Phenyl
PE	Petroleum ether
PhCl	Chlorobenzene
Piv	Pivalate
pin	Pinacol
<i>i</i> -Pr	isopropyl
ppm	parts per million
r.t.	Room temperature
S <sub>N</sub> 2	Bimolecular nucleophilic substitution
S <sub>H</sub> 2	Bimolecular homolytic substitution
Stoich.	stoichiometric
TEA	triethylamine
THF	tetrahydrofuran
TMS	trimethylsilyl
TTMSS	Tris(trimethylsilyl)silane
TBS	tert-butyldimethylsilyl
TEMEDA	Tetramethylethyl enediamine
TLC	thin layer chromatography
°C	degree Celsius
Xa	<i>O</i> -ethyl xanthate

## Chapter I. General introduction

### 1.1 Discovery and development of radical reactions

In a chemical reaction, or under an external influence (light, heat, radiation, etc.), the covalent bond of the molecules is cleaved, leading to a shared electron pair becoming exclusive to one party<sup>[1]</sup>. An ion is then formed, this is called covalent heterolysis. If the split result is that the shared electron pair belongs to two parties, atoms or groups, radicals are then formed. In this case, the cleavage of the covalent bond is homolytic<sup>[2]</sup>. For instance, carbon radicals, where the odd electron occupies an essentially pure *p*-orbital are highly chemically reactive yet can be harnessed into highly useful intermediates in organic synthesis<sup>[3]</sup> (Scheme 1-1).

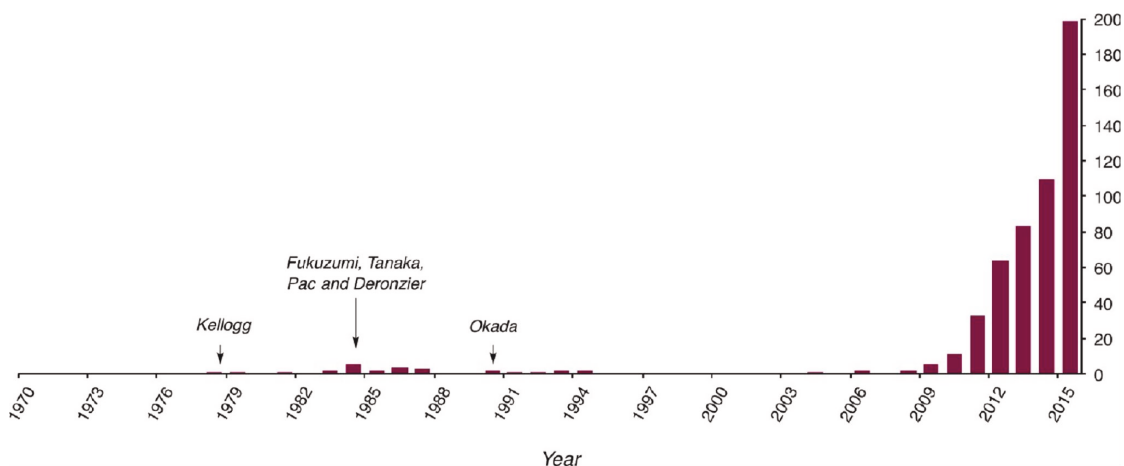


Scheme 1-1. Carbon radicals

Compared to traditional polar/ionic reactions and more emerging transition metal catalytic reactions, radical reactions were once considered chaotic, mysterious, and difficult to control, and could not be used for delicate synthesis<sup>[4]</sup>. In fact, the mystery of radical reactions is being unraveled little by little, and the development is extremely fast. Since the 1970's, many powerful (high yield, high chemoselectivity/region selectivity, and, in some cases, even high enantioselectivity) and elegant (concise, greatly shortened as compared to previous synthetic route) radical methodologies have been devised. They have largely solved many problems that were difficult to tackle using traditional polar-type reactions and even transition metal catalytic reactions<sup>[5]</sup>.

A radical reaction has unique advantages such as solvent effects, which are much smaller than for polar reaction. As a result, the sensitivity to steric hindrance is reduced. Furthermore, the reaction energy barriers are generally lower, yet the tolerance for many functional groups, especially polar entities (-OH, amides, acids), is remarkable. Radicals

can also be used to activate certain inert chemical bonds (mainly C-H), which are hard accomplished with traditional reactions<sup>[6]</sup>. Indeed, according to statistics published by David W.C. MacMillan in 2016<sup>[7]</sup>, photoredox catalysis, just one field of radical chemistry, has grown explosively since 2000 and many reactions have already been applied well (Scheme 1-2).



**Note:** Image referenced from MacMilla, D.W.C. *J. Org. Chem.* **2016**, *81*, 6898.

Scheme 1-2. Papers published per year in the field of organic photoredox catalysis

The emergence of the first radical processes can be traced back to the Kolbe electrolytic decarboxylation reaction in 1848<sup>[8]</sup>, the pinacol coupling reaction in 1851<sup>[9]</sup>, and the Borodin-Hunsdiecker decarboxylative halogenation reaction in 1861<sup>[10]</sup>. Later, a powerful intramolecular C-H activation reaction, the Hofmann–Löffler–Freitag (HLF) reaction, was discovered in 1883<sup>[11]</sup> and has been in use ever since. At that time, people had no experience and means to speculate about the nature of these reactions, even if they were used in practice. It was not until 1900 that Gomberg<sup>[12]</sup> stumbled on the first visually observable carbon radical. Reacted triphenylchloromethane with Ag and obtained a yellow solution, which deepened upon heating. He boldly speculated that this yellow substance was a trivalent carbon, namely a triphenylmethyl radical, that reversibly dimerized into hexaphenylethane. As he wrote in his published article: “*It might be said that, perhaps, it does polymerize to hexaphenylethane, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>C-C(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, but this hydrocarbon is so unstable that mere exposure to air is sufficient to break it down*”.

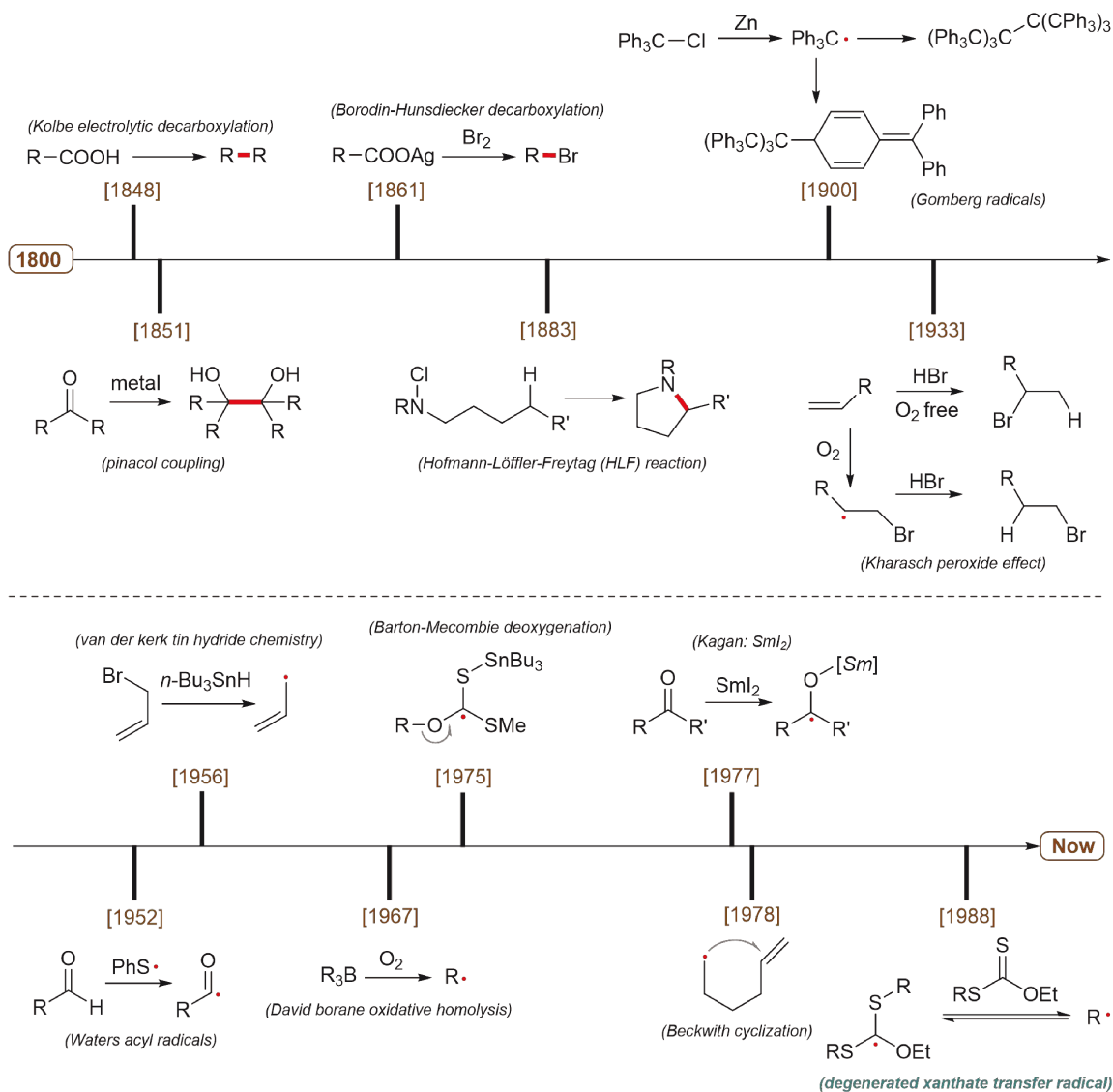
In fact, due to the huge steric congestion of hexaphenylethane and the stability of the homolysis product, this compound has not been prepared so far. The dimer that Gomberg speculated actually contained a quinonemethide-like structure in which the aromatic structure of one benzene ring is destroyed. Although Gomberg's structural predictions for the triphenylmethyl radical dimer were incorrect, his courageous and correct guess about triphenylmethyl radicals became one of the greatest achievements in the history of organic chemistry. Triphenylmethyl radicals, hence, are called Gomberg radicals.

Afterwards, in 1933, Kharasch<sup>[13]</sup> discovered that oxygen can alter the regioselectivity in the addition of HBr to olefins, the well-known peroxide effect often mentioned in textbooks, which did not seem to obey the Markovnikov selectivity. Although the mechanism of the reaction was uncertain at the time, Kharasch realized that free radicals were involved in this transformation, which represents the earliest radical chain process.

In the 50s, there were many exciting discoveries in the field of radical reaction: Waters<sup>[14]</sup> discovered that sulfur radicals can be used to abstract hydrogen atom from aldehyde groups to access acyl radicals. This discovery subsequently led to Walling's<sup>[15]</sup> research on the polarity effect in free radicals and led to the entire field of radical polarity reversal catalysis. Almost at the same time, van der Kerk<sup>[16]</sup> began developing the use of stannanes in synthesis. The dissociation energy of Sn-H bonds in stannane is low, allowing the generation of stannyl radicals which in turn can be used to produce carbon radicals selectively and under very mild conditions.

In 1967, Davies<sup>[17]</sup> discovered that trialkyl boron can form alkyl radicals in the presence of oxygen. This reaction can also be carried out at low temperatures down to -78 °C, which is currently commonly used as a low temperature radical initiation system. Around the 70s, the development of radical reactions and the study of their mechanisms showed an accelerated and deepening trend. In 1975, the powerful Barton-Mecombie deoxygenation<sup>[26]</sup> of alcohols was reported and found immediately widespread applications, especially in the carbohydrate field, where deoxygenations by classical methods are particularly difficult.





Scheme 1-3. A brief timeline of radical chemistry

In 1977, Kagan<sup>[18]</sup> discovered that the single-electron reductant samarium diiodide ( $SmI_2$ ) can reduce carbonyl groups to generate carbon radicals. In 1978, Beckwith<sup>[19]</sup> studied the significant kinetic selectivity in radical cyclization (5-exo-trig cyclization is faster than 6-endo-cyclization), which provided theoretical guidance for many subsequent five-membered radical cyclization reactions.

Radical reactions began to spring up after the 80s, their characteristics became more and more close to modern efficient methodologies and the scope of radical precursors was appreciably expanded. Importantly, in 1988, Zard<sup>[20]</sup> reported an alternative radical

source, from xanthates, and the xanthate transfer chemistry found numerous applications in both polymerization and organic synthesis which is also related to this work and will be discussed further (Scheme 1-3).

Radical reactions have thus become one of the backbones of organic chemistry. These spectacular discoveries will continue to be milestones and it has been proven that radicals can be utilized in unique and exciting ways to provide useful structures in an efficient fashion and in some cases, in a more concise manner.

## **1.2 Typical radical reactions**

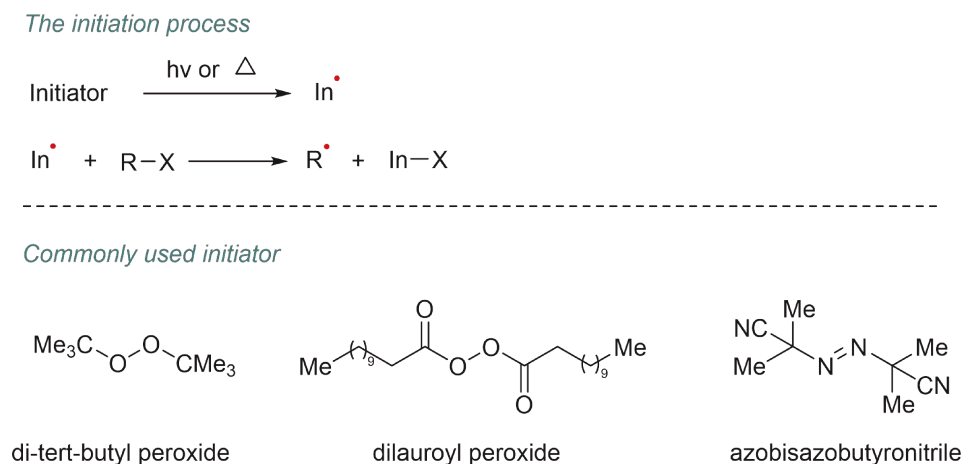
### **1.2.1 Chain reactions**

Radical reaction, as the name implies, refers to the reaction in which radical transfer dominates the cleavage of old bonds and the formation of new ones. However, the radical transfer process is quite different from the traditional ionic reactions and usually the former is faster. In the case of radical chain reactions, a sequence consisting of elementary steps starting with chain initiation, then chain propagation, and finally chain termination is involved<sup>[21]</sup>.

During the initiation step, the radicals are generated from some specific species (initiator) which generally require heat or light to be applied, or a redox process involving an electron transfer to generate in turn a radical from the reactant. The initiator is like the starter of an engine, and the generated radicals can participate in the subsequent transformations. Basically, the initiation process can be accomplished in various ways depending on the type of the initiator used. While the core feature of all initiators is that they all have low bond dissociation energy (BDE, around 30-39 kcal/mol), the lower the bond dissociation energy, the easier the homolysis of initiators to produce active radicals.

There are many kinds of initiators, and the most important classes are organic peroxides (for instance, dilauroyl peroxide generates radicals upon heating through homolysis of the oxygen-oxygen bond) and azo-compounds (for instance, azobisisobutyronitrile AIBN generates radicals upon heating through homolysis of carbon-nitrogen bond and liberation of molecular nitrogen). It is worth noting that the characteristic parameters of

initiators are important for radical reactions, such as the decomposition rate, half-life period, and activation energy. At a certain temperature, the decomposition rate of the initiator greatly affects the rate of radical reactions. The activation energy determines how hard it is for the initiator to decompose into radicals. These parameters can be used as a basis when selecting radical initiator for radical reactions. Once an initial radical is generated, it will rapidly react with a non-radical entity in the medium, leading to the formation of a new radical, therefore starting the chain propagation process (Scheme 1-4).

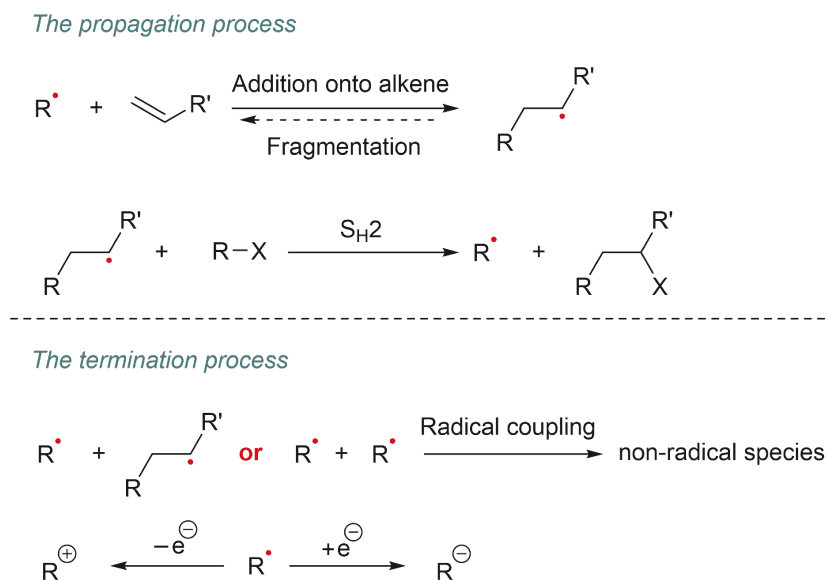


Scheme 1-4. Initiation step and radical initiators

Generally, the propagation process takes place according to the following pattern. In this step, the new radical can undergo a series of typical elementary radical reactions, such as the addition to an unsaturated reactant (the reverse step is a fragmentation or  $\beta$ -scission). In the case of carbon-centered radicals, the addition reaction results in the formation of a new carbon-carbon bond. Besides, it can also undergo the homolytic substitution ( $S_H2$ ) by analogy with the classical ionic  $S_N2$  process and gives rise to a main product. The regenerated starting radical can continue the propagation process.

The chain propagation process is driven by the continuous production of new radicals. Since the concentration of radicals is extremely low compared to the concentration of reactant at any given time, the chance of collisions between radicals and molecules is much greater than the collision of two radicals. Therefore, the propagation reaction, if

sufficiently fast, already proceeds to a significant extent before the more rare collision of two radicals happens. However, when the reactants in the system are completely consumed or in very low concentrations, the chance of collisions between two radicals increases, which leads to chain termination, essentially the reverse of the initiation process. The termination step takes place by a recombination or disproportionation of radicals, or a redox process that converts the radicals into an anionic or cationic species. That is, as the radical transforms into non-radical products, when the radical reaction stops (Scheme 1-5).



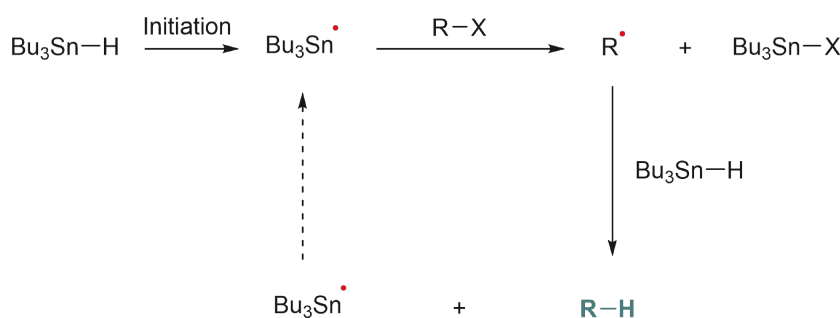
Scheme 1-5. The propagation and termination process

### 1.2.2 Chain reaction based on organotin hydrides

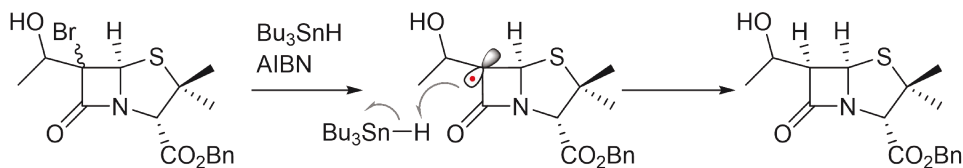
Radical chain reactions related to organotin hydrides are by far the most commonly employed in organic synthesis. A wide variety of carbon- and heteroatom-centered radicals can thus be generated and captured by numerous molecules. As described earlier, van der Kerk developed the use of the simplest tributyltin-hydrides-mediated reaction, the replacement of a halogen with hydrogen. The radical reaction process could be described in a more general form whereby a number of functional groups, represented by **R-X**, can in fact be reduced by a similar mechanism. In addition, tributyltin hydride and

triphenyltin hydride, the latter used in van der Kerk's initial works, are the most common reagents, but the same can apply for other organotin hydrides.

Due to the low BDE of the Sn-H bond<sup>[22]</sup>, a stannyl radical can be easily generated from the organotin hydrides in the presence of an initiator (AIBN is by far the most employed) which then starts the propagation process. The first propagation step relies on the reaction of the stannyl radical with the substrate **R-X** (it can be a halide, a sulfide, an isocyanide, or a chalcogenide), resulting in the ensuing radical **R** and the stannane *n*-**Bu<sub>3</sub>SnX**. The radical **R** then participates in the second propagation step, such as cyclization. In the end, the resulting radical abstracts a hydrogen from the organotin hydrides, leading to the main product **R-H** and a new stannyl radical that can propagate the chain reaction (Scheme 1-6).



**Example - Aimetti 1979**

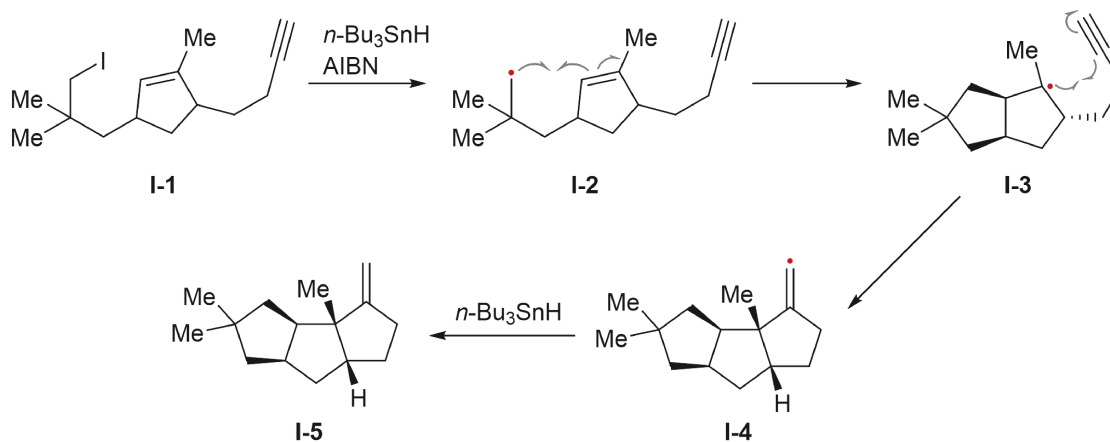


Scheme 1-6. Radical chain reduction using organotin hydride

Reduction of organic hydrides can be performed on substrates that are more complex than the original allyl bromide. A classic example is the efficient reduction of the bromo penicillinate, accomplished by Aimetti<sup>[23]</sup> and co-workers in 1979 (Scheme 1-6). The use of organotin hydrides as a selective reducing agent toward halogen has been proven to be effective. In this strategy, the stereoselectivity of the product is determined by the intermediate radical in the hydrogen abstraction step where the bulky Bu<sub>3</sub>SnH traps the

intermediate radical at the unencumbered convex face of the cup-shaped penicillin molecule.

Moreover, radical **R** generated from the first propagation step of the organotin-hydrides-mediated reaction can also undergo a series of intramolecular reactions such as cyclization before the hydrogen abstraction. One such instance was described by Curran<sup>[24]</sup> and co-workers in 1985 which features a tandem radical cyclization to produce a triquinane. Treatment of iodide **I-1** with tri-*n*-butyltin hydride in the presence of AIBN as initiator generates radical **I-2**. Radical **I-2** is in turn trapped by the double bond in a *5-exo-trig* fashion, resulting in the first five-membered ring and a new carbon-centered radical. Intermediate radical **I-3** is then trapped by the alkyne and gives rise to the construction of the second five-membered ring. Finally, a hydrogen abstraction furnishes the final product **I-5** (Scheme 1-7).



Scheme 1-7. Synthesis of hirsutene

However, despite the widespread use of organotin reagents in radical processes, the toxicity of tin-based compounds remains a great challenge to their extensive applications. In addition, organotin-hydrides-mediated reactions usually end up with a hydrogen abstraction which means that the additional transformations of radical **R**, if it occurs, must be faster than the hydrogen abstraction. In the case of intramolecular reactions, it usually goes well as in the sequence in scheme 1-7. While in the case of intermolecular reactions, the results are unpredictable.

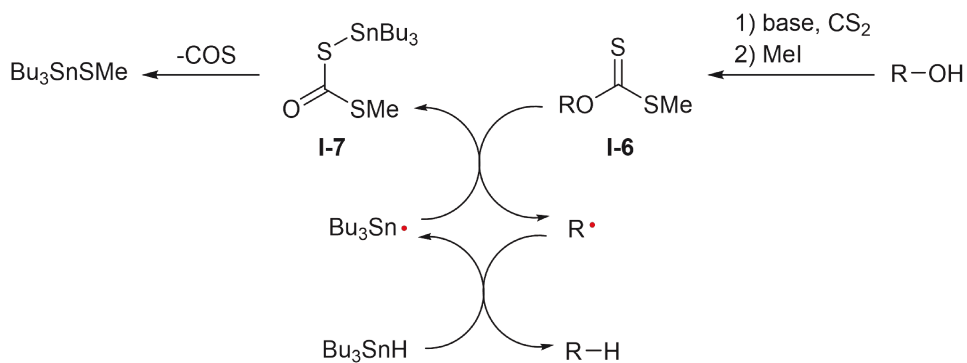
Alternatively, a new radical source, xanthate, was developed, allowing the generation of a variety of radicals in a mild and metal-free environment. The unique xanthate addition-transfer process presents tremendous synthetic potential both for intra- and intermolecular reactions and provides plenty of opportunities for the formation of structures not readily available through the traditional routes.

### 1.3 The xanthate addition-transfer process

#### 1.3.1 Discovery of xanthate in radical synthesis

Since the discovery of xanthates (dithiocarbonates) by Zeise<sup>[25]</sup> in 1822, they were barely used in organic synthesis, and were not considered as radical precursors. It was not until 1975 that the Barton-McCombie<sup>[26]</sup> reaction for deoxygenating secondary alcohols (primary and tertiary alcohols present specific problems) was conceived and thus opened the door for the use of xanthate in radical chemistry.

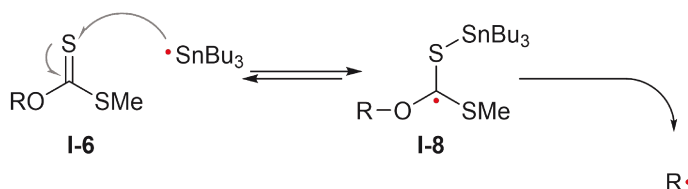
Normally, the deoxygenation of alcohols can not take place by direct reaction of alcohols with an organotin hydride. A more applicable approach, developed by Barton and McCombie, takes advantage of the affinity of tin for sulfur, and involves the first conversion of the alcohol into a reactive carbonothioyl intermediate such as a xanthate. Treatment of the thiocarbonyl group of xanthate **I-6** with a stannyl radical results in the formation of a co-product **I-7** and radicals **R**. In this process, carbon-centered radical intermediates are first generated and then undergo  $\beta$ -scission of the carbon-oxygen bond. Co-product **I-7** is unstable and prone to elimination of carbon oxysulfide. Radicals **R** then abstract a hydrogen from the organotin hydride and give rise to the deoxygenated product (Scheme 1-8).



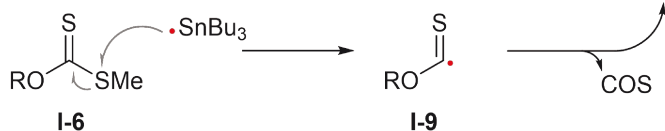
Scheme 1-8. Barton-McCombie deoxygenation

The mechanism of the Barton-McCombie deoxygenation later provoked some discussion. Almost a decade after its publication, the proposed mechanism by Barton and McCombie was questioned by Beckwith and Barker, who observed a different radical transfer process related to the formation of an unknown alkoxy thiocarbonyl radical **I-9**. This observation raised the critical question of the regioselective addition of tributyltin radical onto the xanthate group. Different from the Barton-McCombie mechanism where the radical attack occurs at the thiocarbonyl sulfur, Beckwith and Barker<sup>[27]</sup> propose the attack of tributyltin radical at the sulfide sulfur atom to generate radical **I-9** evidenced by electron spin resonance spectroscopy. This radical was assumed to extrude carbon oxysulfide by analogy with its oxygen counterpart (Scheme 1-9).

*The Barton-McCombie mechanism*



*The Beckwith-Barker mechanism*

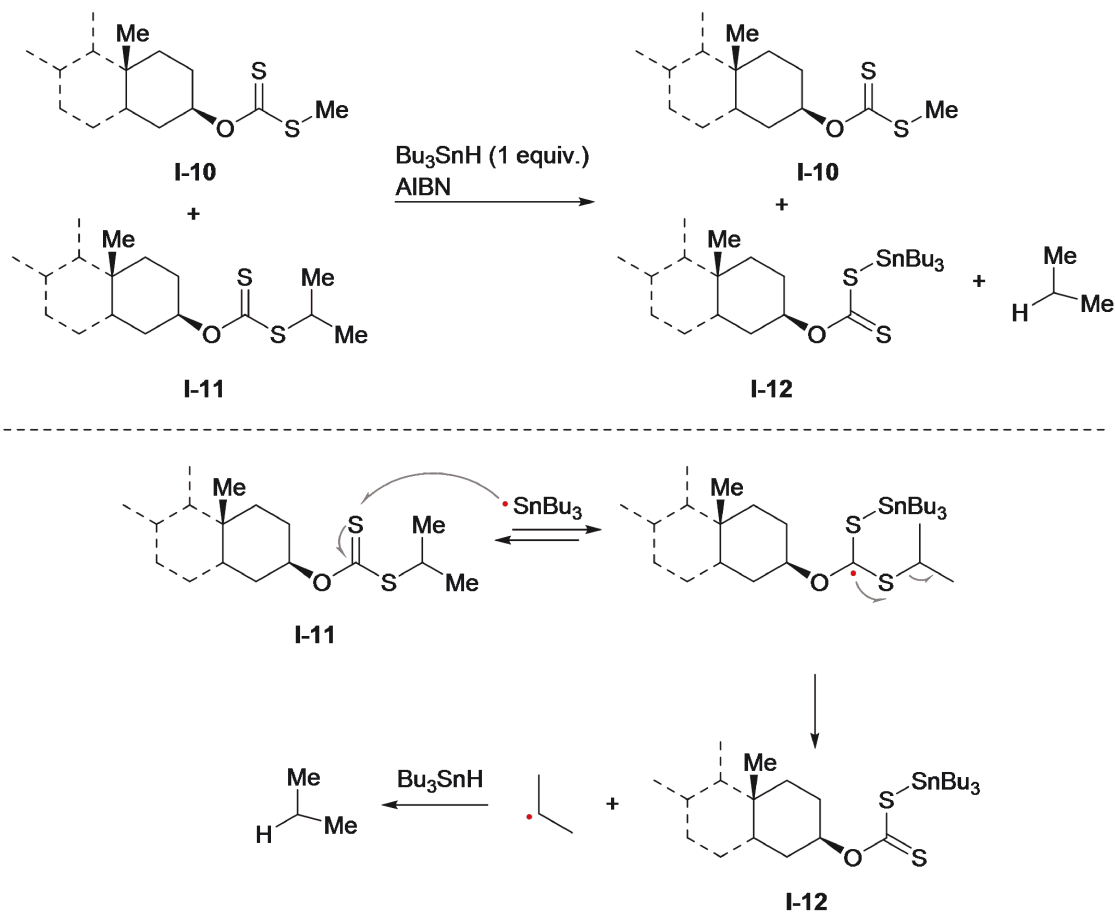


Scheme 1-9. Two possible mechanisms for the deoxygenation reaction

To identify the actual mechanism, more systematic studies were undertaken by Barton and co-workers. A competition experiment was performed to get a clear picture of the deoxygenation whereby an equimolar mixture of each of *S*-methyl and *S*-2-propyl



cholestannyl xanthates were mixed with one equivalent of stannane (Scheme 1-10)<sup>[28]</sup>. Theoretically, if the first attack of organotin radical occurs at the sulfide sulfur atom, its reaction with *S*-2-propyl xanthate **I-11** should be slowed down due to the steric hindrance of the isopropyl group and the *S*-methyl xanthate **I-10** should be consumed faster. In contrast, if the reaction center is at the thiocarbonyl sulfur atom, there should be no significant difference (Scheme 1-10).



Scheme 1-10. Competition reaction

Unexpectedly, the result of this competition reaction was neither of these two possibilities. As it turned out only the *S*-2-propyl xanthate **I-11** was consumed completely, and most *S*-methyl xanthate **I-10** remained intact. Besides, instead of deoxygenation product, *S*-tributylstannyl dithiocarbonate **I-12** and propane were obtained. These results indicated two facts: a) the addition of organotin radical is more likely to occur on the thiocarbonyl group which is fast and reversible (if it is not reversible, the *S*-methyl

xanthate **I-10** would not have been recovered largely unchanged); b) the obtained propane illustrates that the  $\beta$ -scission of carbon-sulfur bond is more preferable than carbon-oxygen bond in cases when radicals of similar stability are produced (here, both the isopropyl radical and 3-cholestanyl are secondary)<sup>[29, 21b]</sup>.

These exciting findings indicated that the cleavage of the weaker carbon-sulfur bond of xanthates may be implicated in a much more general radical-chain process not involving stannane. The reversible addition of carbon radicals on the thiocarbonyl group of xanthates was thus developed in our group. Since then, the use of xanthates as direct radical precursors has really been explored in organic synthesis.

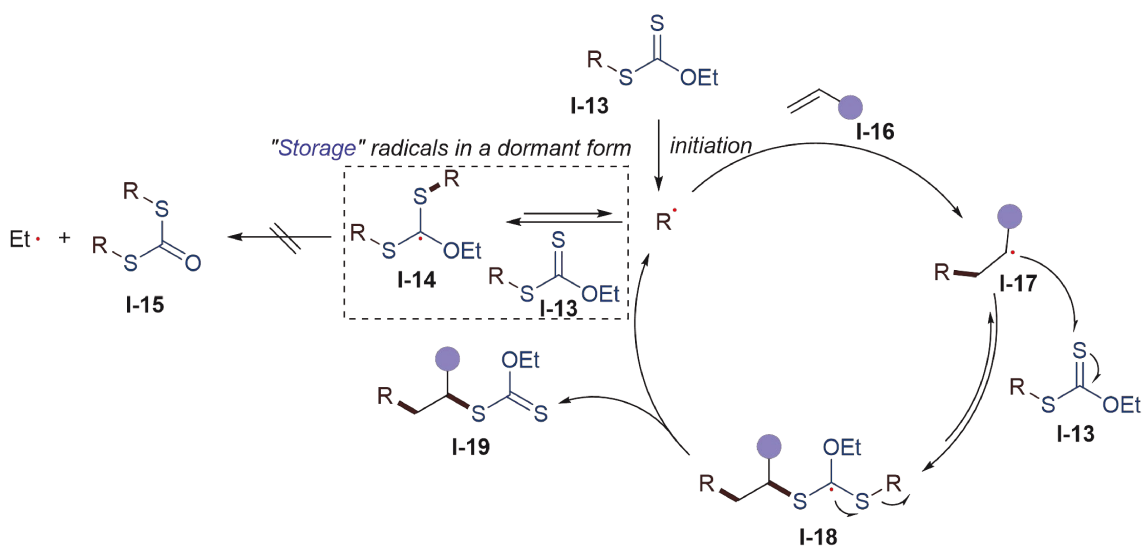
### 1.3.2 Mechanism of xanthate addition-transfer process

Instead of relying on the addition of stannyl radicals to the thiocarbonyl group of xanthates, an alternative form of xanthates is designed which can generate carbon-centered radicals under a chemical or photochemical initiation step. It actually represents the behavior of xanthates such as **I-13** where the  $\beta$ -scission process for generating radical **R** occurs by rupturing the carbon-sulfur bond rather than the carbon-oxygen bond<sup>[30]</sup>.

A simplified mechanism of the xanthate transfer process is shown in Scheme I-11. Radical **R** is formed by the initiation process from its precursor, xanthate **I-13**. It has the choice of either attacking the thiocarbonyl sulfur atom of xanthate **I-13** to form carbon-centered radical **I-14** (the xanthate here serves as a radical trap) or reacting with a given trap such as an olefin. The former transformation results in the adduct radical **I-14** which is bulky and stabilized by three heteroatoms and thus rather persistent. However, the  $\beta$ -scission of carbon-oxygen bond of radical **I-14** is unfavorable since it will extrude an ethyl radical which is thermodynamically less stable than radical **R**. Therefore, it can essentially only fragment back to radical **R**, via  $\beta$ -scission of the carbon-sulfur bond, and the starting xanthate **I-13**. The same fragmentation scheme will apply to each case where the ethyl group attached to the oxygen atom is replaced by another group, as long as the stability of the corresponding radical is lower than that of radical **R**. Since the reaction of radical **R** with xanthate **I-14** is fast but reversible, this process does not consume radical

**R**, which therefore considerably increases its lifetime in the medium, allowing it to be captured by relatively unreactive traps that cannot generally be employed with other radical-generating systems. The degenerate process between radical **R** and xanthate **I-13** is the key point of this reaction system. Thus, this equilibrium could be considered as a storage mechanism for radical **R** by keeping it in a dormant form. As a result, radical **R** is now sufficiently long-lived to react with non-activated alkenes.

Subsequently, radical **R** reacts with alkene **I-16** and gives rise to a new adduct radical **I-17**, which in turn is reversibly captured by xanthate **I-13** to give intermediate **I-18** in the same manner as for radical **I-14**. Importantly, if radical **R** is more stable than radical **I-17**, the formed intermediate **I-18** fragments preferentially toward radical **R** and leads to the target adduct **I-19**. In turn, the new radical **R** can further propagate the radical chain reaction, starting an addition to another alkene molecule until the total consumption of xanthate **I-13**. It is worth noting that the desired adduct **I-19** also bears a xanthate group, therefore in some cases it can also be a radical precursor and proceed by the same xanthate addition-transfer process or undergo numerous radical and non-radical transformations such as cyclization and reduction.



Scheme 1-11. Simplified mechanism for the Xanthate Addition-Transfer process

The feasibility of the xanthate addition-transfer process for generating and capturing radicals was widely verified by the addition of a variety of xanthates to intra- and

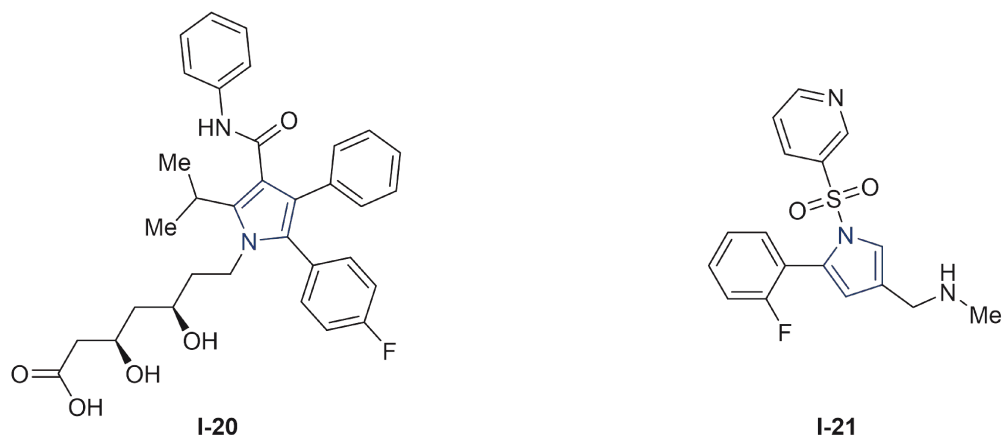
intermolecular olefinic traps. No toxic metals are involved in such a process, and the mild reaction conditions are noteworthy: mere heating of the xanthate and olefinic trap in an inert solvent under an inert atmosphere and in the presence of a small amount of an initiator. The initiation process can be accomplished by using different initiators, depending on the reaction temperature. One of the most used and simplest is the dilauroyl peroxide (DLP) which decomposes upon mild heating. Moreover, most of the olefinic traps in the xanthate addition-transfer process are non-activated and therefore can not be implemented in many other radical methods. Notably, the desired compounds **I-19** are obtained by creating a new C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bond, demonstrating the powerful synthetic utilities of the degenerative reversible transfer process of xanthates in organic chemistry.

## **1.4 Synthetic utilities of xanthate**

### **1.4.1 Convergent xanthate route to pyrroles**

Pyrrole and its derivatives belong to one of the most fundamental heteroaromatic families in organic chemistry, they consist of a five-membered ring containing four carbon atoms and one nitrogen atom. They have a characteristic smell and are found in various natural sources such as coal tar, bone oil, and crude oil. In addition, they are a component of certain biological molecules, including some amino acids (such as pyrrolysine) and porphyrins, which are essential for various biological processes. Furthermore, pyrrole is widely used in organic synthesis and serves as a building block for the production of various compounds. It is particularly important in the synthesis of pharmaceuticals, agrochemicals, and dyes. Pyrrole derivatives exhibit a range of properties and can be tailored to possess specific characteristics depending on the desired application.

The pyrrole ring exists in various alkaloids and biologically active molecules<sup>[31]</sup>, such as Lipitor **I-20**, drug used to lower cholesterol levels in the blood. Another more recent example, compound **I-21**, also known by its generic name vonoprazan (TAK-438), is a medication used for the treatment of gastric acid-related conditions (Scheme 1-12).

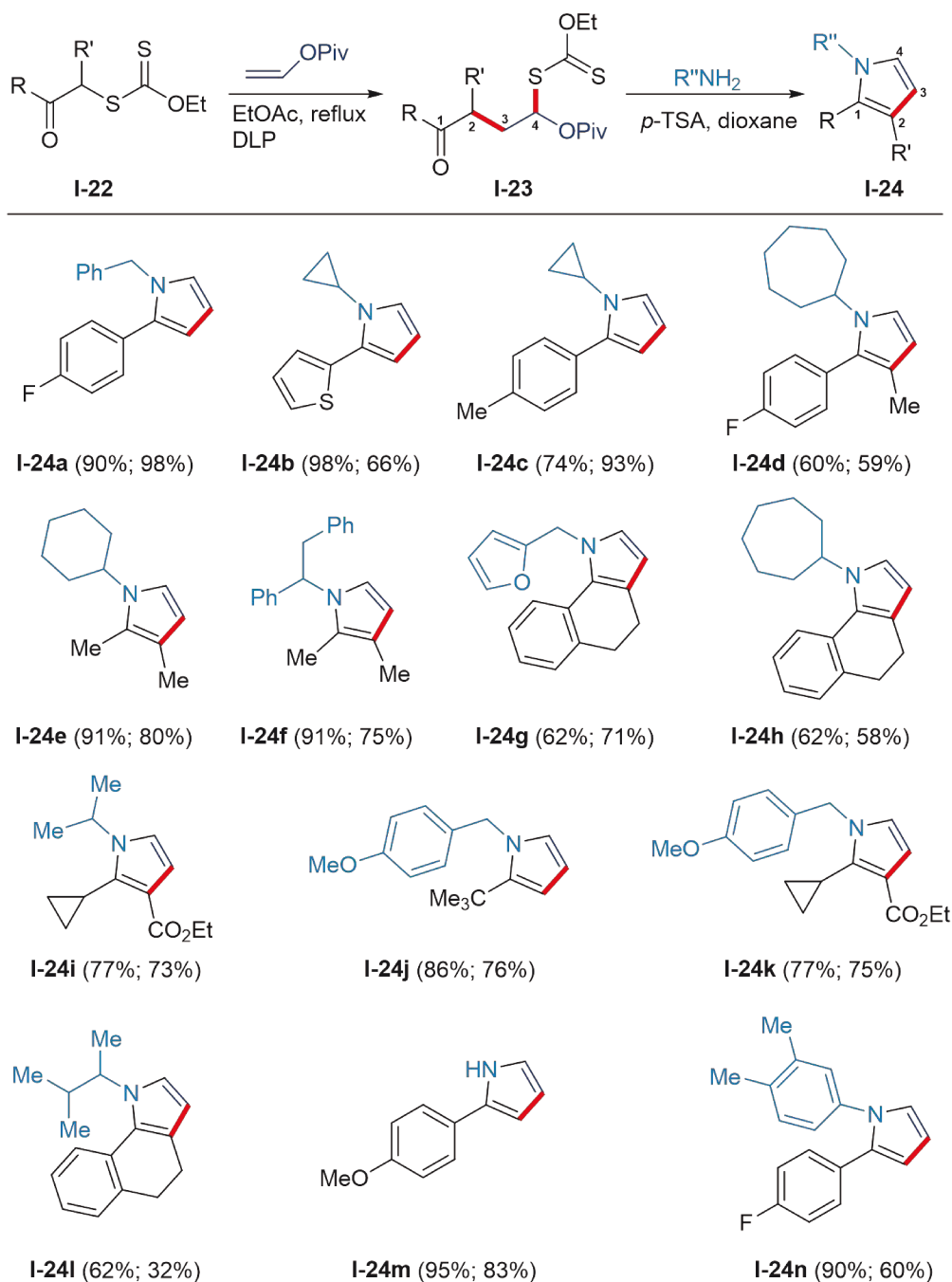


Scheme 1-12. Examples of biologically active pyrroles

A large number of synthetic approaches to pyrroles have been described over the years, while the synthesis of pyrrole derivatives with specific molecular structures can still present difficulties. Radical-based strategies have rarely been used. Our group has a longstanding interest in the synthesis of pyrrole derivatives by taking advantage of the powerful degenerative xanthate transfer process and numerous substituted pyrroles have been synthesized in a flexible, convergent manner.

Through the addition ability of xanthates with wide variety of non-activated alkenes in the xanthate addition-transfer process, the obtained adducts can be designed to a latent form of 1,4-dicarbonyl derivatives, which can then react with ammonia or a primary amine to furnish the corresponding pyrroles by analogy with the well-known Paal-Knorr reaction<sup>[32]</sup>. Thus, the crucial step of this strategy is the formation of latent 1,4-dicarbonyl derivatives, which can not only be used for the synthesis of pyrroles, but also for another fundamental heteroaromatic family, namely furans. Indeed, the design for the formation of 1,4-dicarbonyl derivatives or precursors can be readily reduced to practice.

The addition of various  $\alpha$ -ketonyl xanthates **I-22** to vinyl pivalate (or vinyl acetate) gives adducts **I-23** in which the terminal carbon (C-4) bearing both the xanthate group and the ester has the oxidation level of an aldehyde and can be viewed as a masked form of 1,4-diketoaldehyde. The condensation of adducts **I-23** with amines will then furnish the desired substituted pyrroles **I-24**. Numerous combinations of xanthates and amines can be employed in this strategy, some examples are presented in Scheme 1-13.



Scheme 1-13. Pyrroles from radical addition to vinyl pivalate

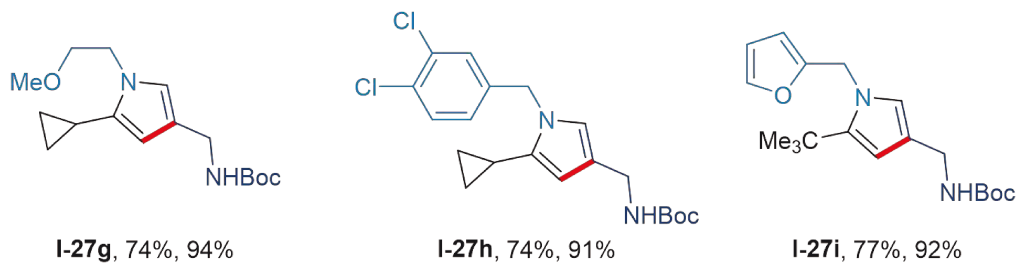
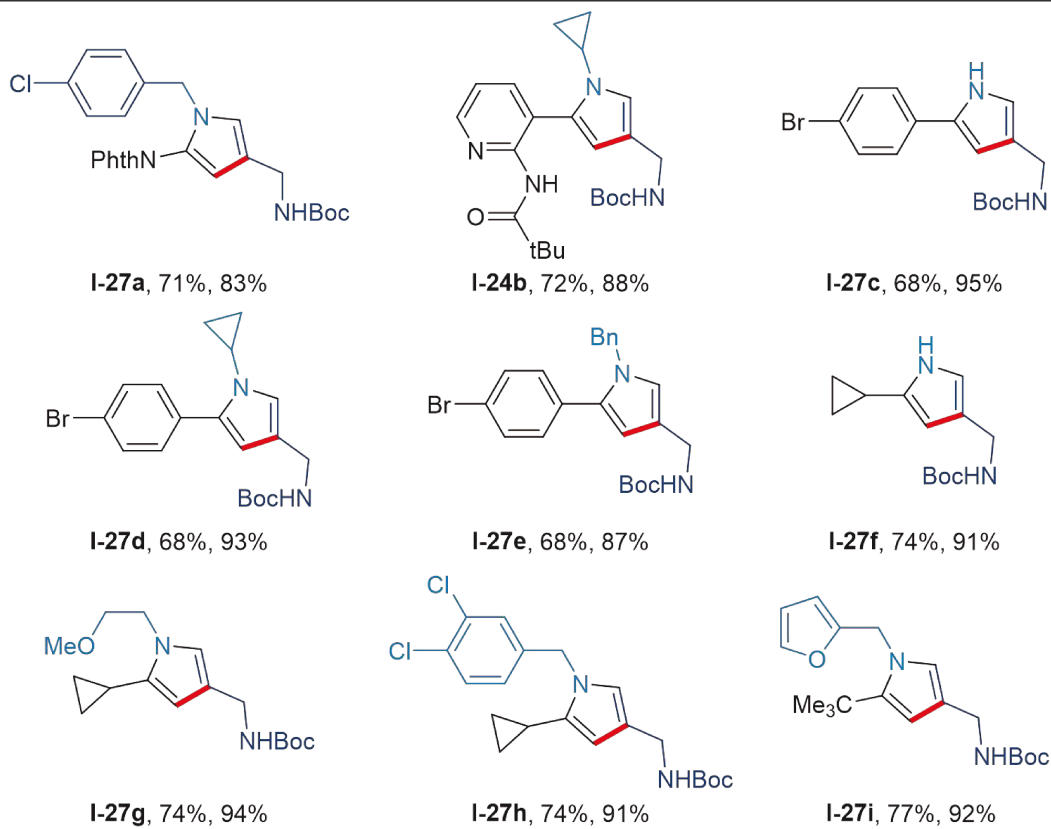
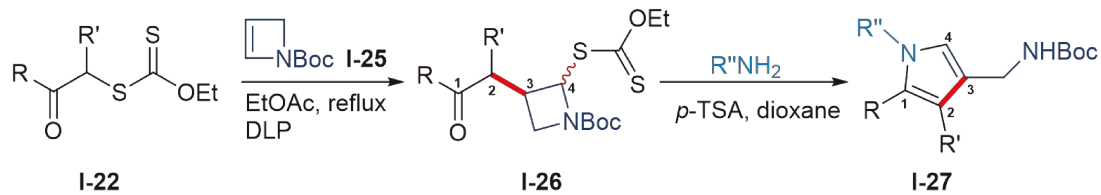
The two yields displayed represent the yield of the first addition step to adducts **I-23** and the yield of the second condensation to pyrroles **I-24**, respectively. The latter is accomplished by merely heating adduct **I-23** with the amine and a catalytic amount of *p*-toluenesulfonic in dioxane. As a result, a series of 1- or 1,2-substituted pyrroles were

synthesized in generally high yields. Thus, the mild reaction conditions and the high yields of this approach provide a general and powerful tool for the synthesis pyrrole derivatives.

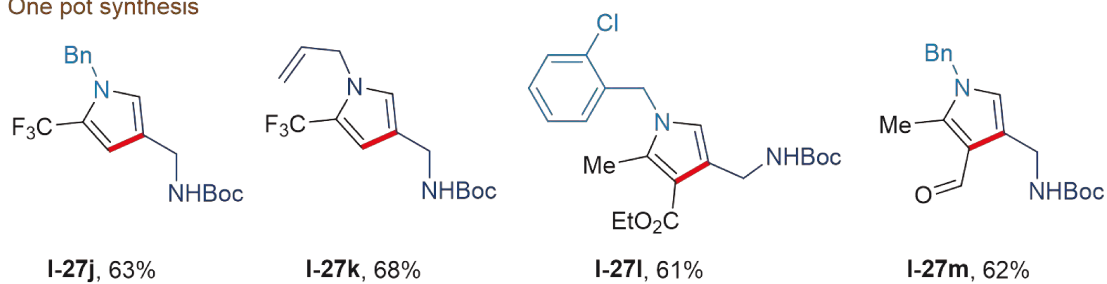
The pyrroles presented above are all substituted on C-1 or C-2 atom, and C-3 and C-4 positions remain free. Therefore, another xanthate precursor with a 1,4-dicarbonyl form can be further designed for the synthesis of 1,3-substituted pyrroles. Pyrroles with a different substitution pattern can be accessed by the addition of  $\alpha$ -ketonyl xanthates **I-22** onto azetine **I-25** as the olefinic partner. Importantly, the corresponding adduct **I-26** also acts as a masked 1,4-diketoaldehyde, lurking in the guise of a geminal xanthyl carbamate moiety. Therefore, its condensation with amines will result in the formation of pyrroles **I-27** in a similar manner to adduct **I-23**. Both largely similar reaction mechanisms will be described later in Chapter II. This conception was also easily reduced to practice, as presented in Scheme 1-14. It is worth noting that this strategy can also be performed in a one pot synthesis, directly obtaining the desired 1,3-substituted, and even 1,2,3-substituted pyrroles **I-27** (such as compound **I-271**) in good yields from the starting xanthate **I-22**<sup>[33]</sup>.

Numerous amines can be employed in this synthetic strategy, in particular primary amines, aniline, and even ammonia. Notably, the structure of pyrroles **I-27** is related to TAK-438, **I-21**, which also bears an aminomethyl substituent on the same carbon. In this respect, it is the fact that by simply changing the substituents on pyrrole **I-27**, we can obtain a wide range of pyrrolic building blocks.

The use of radical addition of xanthates has created diverse compound libraries for substituted pyrroles and as an efficient approach, has gained more and more momentum. Xanthates offer plenty of outstanding synthetic advantages in terms of cheapness, variety functional group tolerance, and mild experimental procedures. Thus, it's worth exploring more broadly the synthetic potential of this uniquely powerful chemistry, such as in the synthesis of valuable silane-substituted and boron-substituted pyrroles which is normally difficult to achieve by other means.



One pot synthesis



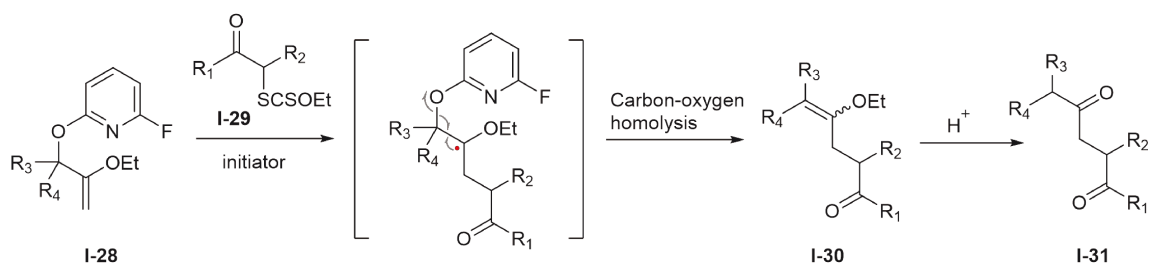
Scheme 1-14. Pyrroles from radical addition to azetine



### 1.4.2 Convergent xanthate route to other 1,4-dicarbonyl derivatives

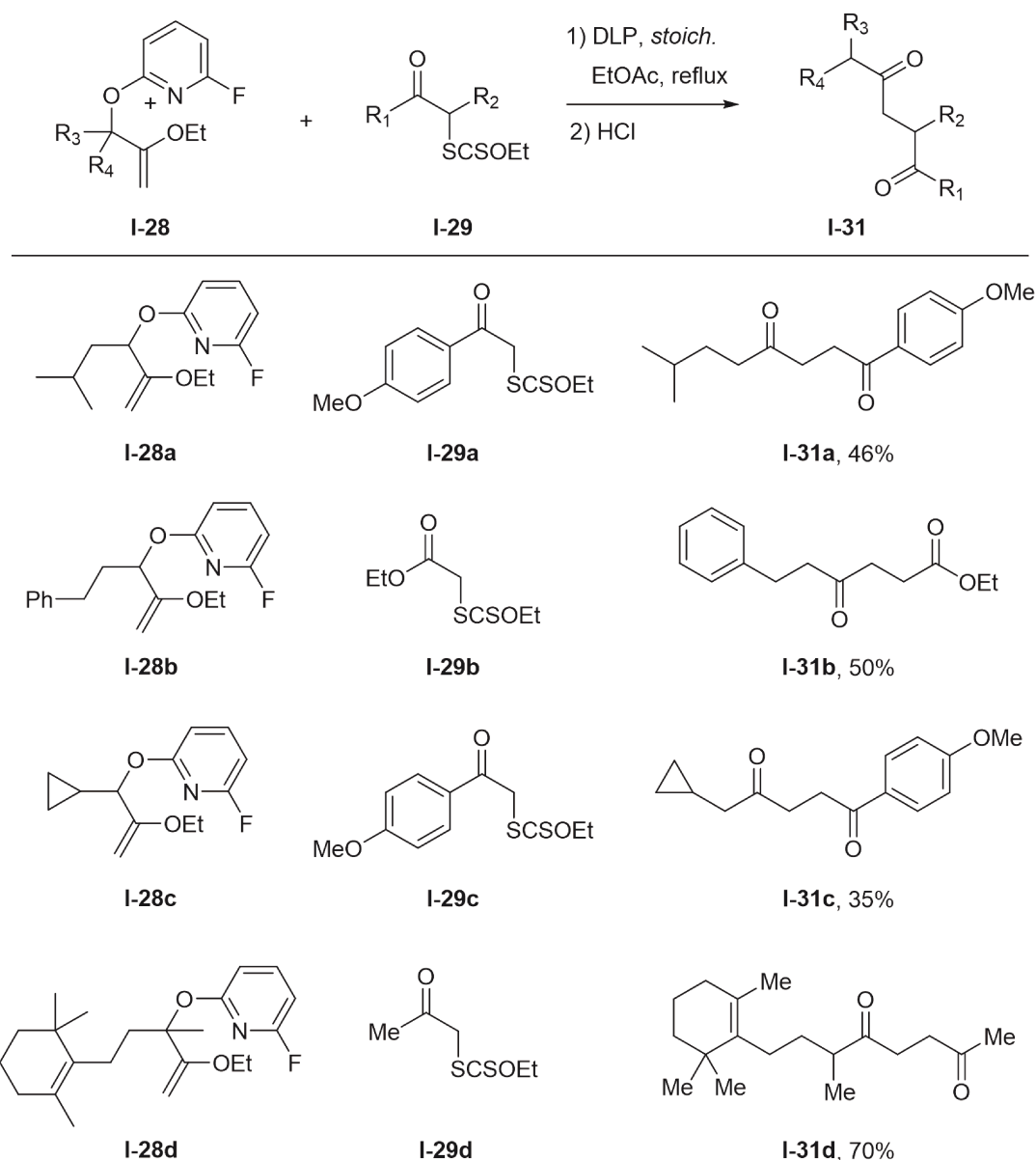
Encouraged by the success in the synthesis of substituted pyrroles, our group turned to develop other routes to functionalized 1,4-diketones and engage them into the synthesis of not only substituted pyrroles, but also substituted furans. Furan has both industrial and laboratory applications. It serves as a starting material for the synthesis of other organic compounds and is used in the production of pharmaceuticals, agricultural chemicals, and flavorings. Furan derivatives are found in some drugs used for treating cardiovascular diseases and fungal infections.

In the previous research of our group, our colleagues discovered that when a 6-fluoro-pyridin-2-ol moiety is located vicinal to a radical center, it can undergo  $\beta$ -elimination, essentially converting an alcohol into a leaving group in a radical sense. In this process, the strong carbon-oxygen bond is homolytically cleaved which is rare in radical chemistry and thus is poorly exploited in synthesis<sup>[34]</sup>. In this respect, xanthate **I-29**, as an excellent radical precursor, reacts with the 6-fluoro-6-pyridinyloxy derivative **I-28** by an addition-fragmentation pathway to furnish highly functionalized 1,4-diketones after acid hydrolysis. The relative transformation is depicted in Scheme 1-15.



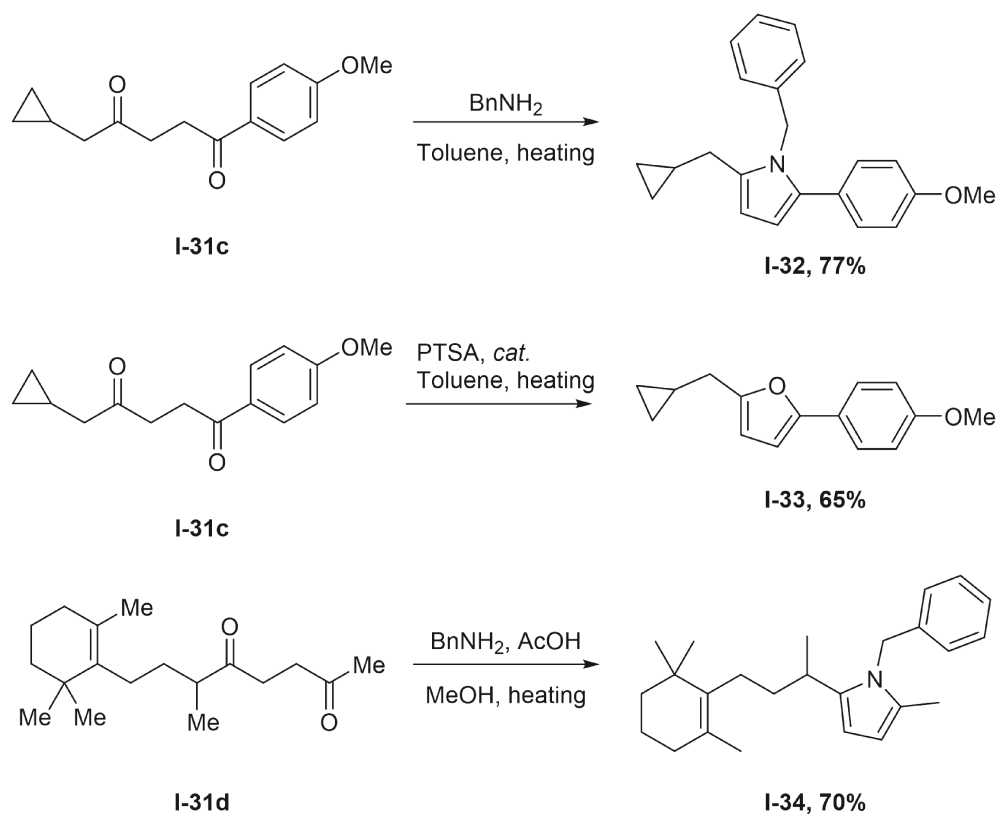
Scheme 1-15. Synthesis of 1,4-diketones

Structures containing the 1,4-dicarbonyl group are readily obtained in this strategy and numerous combinations can be envisaged either by modifying the xanthate or the starting enol ether **I-28** (Scheme 1-16). The ability of compound **I-28** to undergo homolytic cleavage of the carbon-oxygen bond under mild reaction conditions offers tremendous synthetic possibilities. It is worth noting that 1,4-diketones are the most standard reactant in the Paal-Knorr pyrrole and furan synthesis.



Scheme 1-16. Examples of synthesized 1,4-diketones

Having successfully accomplished the synthesis of 1,4-diketone compounds, their synthetic utilities in the synthesis of substituted pyrroles and furans were also explored. As a result, pyrroles **I-32** and **I-34**, furan **I-33**, were swiftly prepared in good yield (Scheme 1-17). The mildness of the experimental conditions and broad tolerance for most of the common functional groups open up numerous synthetic opportunities for the synthesis of more complex scaffolds, which were eventually achieved in this work.



Scheme 1-17. Transformation of 1,4-diketones to pyrrole and furan

## 1.5 Conclusion

The formation of C-C bonds is again the backbone of organic synthesis. Certainly, radical reactions have proven to be powerful for C-C bond formation. The degenerative reversible transfer of xanthate is emerging as one of the most effective tools for the generation of C-C bonds in recent years. It has a unique ability to store reactive radicals through a series of reversible processes and then remarkably extend the effective lifetime of the formed radicals. It allows intermolecular radical additions, especially to non-activated olefins, to construct  $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$  bonds. By taking advantage of the xanthate addition-transfer process, numerous functionalized compounds can be synthesized under mild reaction conditions and convergent synthetic routes. Moreover, the xanthate radical reaction has been proven to be extremely effective for the synthesis of substituted pyrroles and furans. Much more synthetic potential of xanthate chemistry remains untapped and deserves further development.

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## Chapter II. The xanthate route to acylsilanes

### 2.1 Introduction

Acylsilanes ( $R'CO\text{SiR}_3$ ) are a class of compounds that are of wide interest and have been investigated as important synthetic intermediates and products with useful chemical and physical properties<sup>[1]</sup>. The bulky trisubstituted silyl group in acyl silanes endows them with unique steric and electronic features, which have proven to be pivotal for gaining excellent regio- and diastereo-selectivities in several of their synthetic applications.

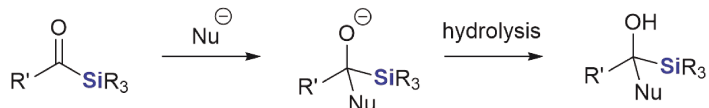
The use of acylsilanes in organic synthesis has improved significantly over the past few decades due to the disclosure of powerful new reactions and the development of synthetic methods for accessing acylsilanes and for their subsequent transformations<sup>[2-3]</sup>. In principle, acylsilanes can be viewed as carbonyl compounds. Therefore, one of their long-standing uses in organic synthesis is as an aldehyde equivalent, whereby the nucleophilic addition reaction of acylsilanes with nucleophiles to afford silyl alkoxides, which are further hydrolysed to furnish  $\alpha$ -silyl alcohols (Entry 1, Scheme 2-1)<sup>[4]</sup>. In addition, the Brook rearrangement, after carbonyl addition with nucleophiles, is a commonly observed transformation, in which the silyl group migrates from the carbon atom to the oxygen atom. The silyloxalkenes are then formed when an anion stabilizing group is attached to the carbonyl group (Entry 2, Scheme 2-1)<sup>[5]</sup>.

The unique reactivity of acylsilanes as an acyl anion equivalent has attracted significant attention. Treatment of acylsilanes with a nucleophile, such as fluoride anions, would provide the desilylated acyl anion, which can be readily converted into ketones in the presence of electrophiles (Entry 3, Scheme 2-1)<sup>[6]</sup>. Particularly, the cyclization of *1,4*-dicarbonyl acylsilanes under acid condition would afford the substituted 2-silylfurans (Entry 4, Scheme 2-1)<sup>[7]</sup>. The intramolecular cyclization of acylsilanes with alkyl or aryl radicals could be facilitated by trialkyltin radicals, followed by Brook rearrangement, and furnishes the cyclic silyl enol ether (Entry 5, Scheme 2-1)<sup>[8]</sup>.

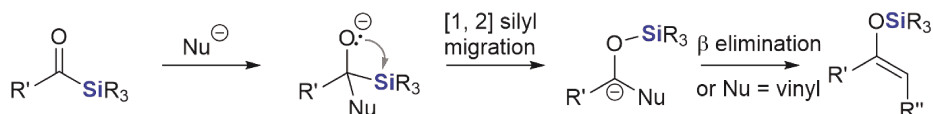
In light of their remarkable synthetic utility, the synthesis of acylsilanes is extraordinarily important, especially for the modular assembly of complex scaffolds. Many efforts have

been devoted to developing synthetic routes for substituted acylsilanes and a number of efficient methods have been reported during these years.

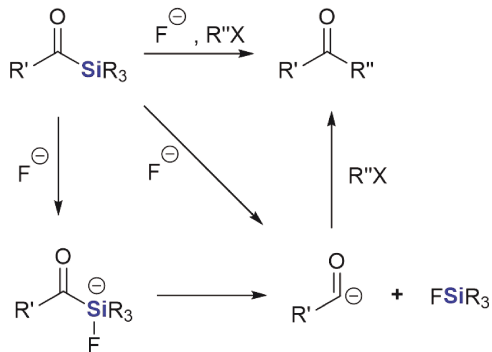
**Entry 1.** As aldehyde equivalent for nucleophilic addition



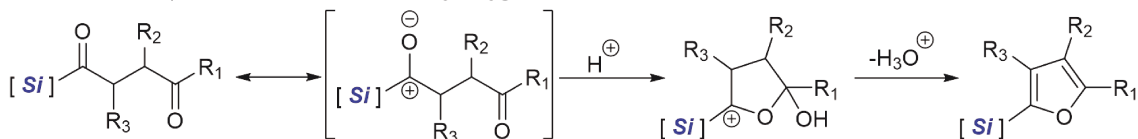
**Entry 2.** Brook rearrangement



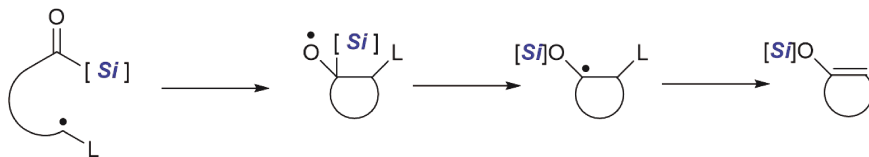
**Entry 3.** As acyl anions with electrophiles



**Entry 4.** Nucleophilic reaction of the carbonyl oxygen



**Entry 5.** Radical reactions of acylsilanes



L = Radical leaving group

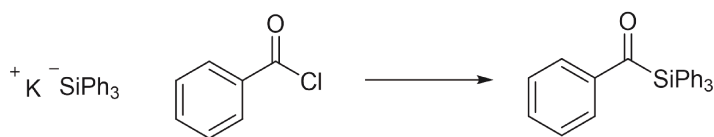
Scheme 2-1. The reactions of acylsilanes



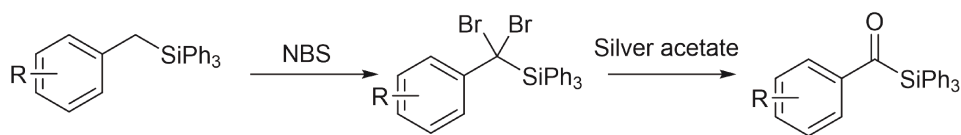
## 2.2 Methods for the synthesis of acylsilanes

In 1957, Brook first reported the synthesis of an acylsilane, benzoyltriphenylsilane, in two ways. The first approach was accomplished by the reaction of triphenylsilyl potassium with benzoyl chloride in only 6% yield (Entry 1, Scheme 2-2). The same compound was synthesized in much better yield by hydrolysis of the triphenyl- $\alpha$ ,  $\alpha$ -dibromobenzylsilane (Entry 2, Scheme 2-2)<sup>[9]</sup>.

### Entry 1

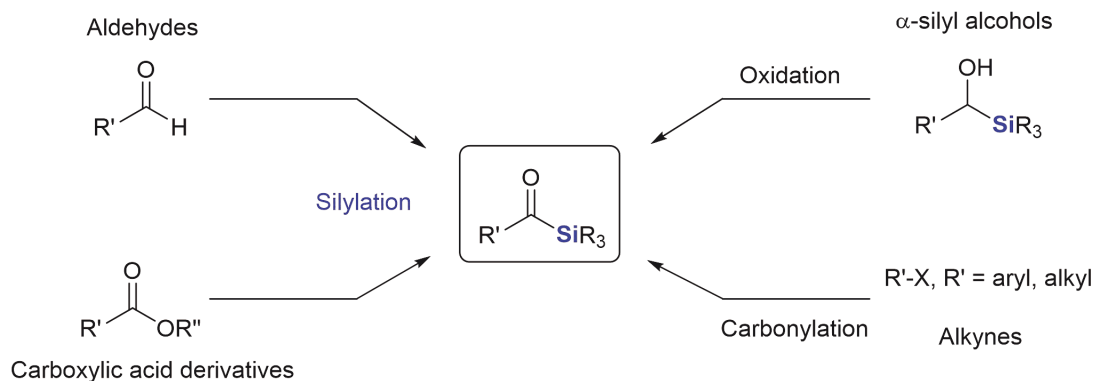


### Entry 2



Scheme 2-2. The first synthesis of benzoyltriphenylsilane

Despite the inefficiency of these methods and the instability of the acylsilanes under the conditions used, leading to C-Si cleavage, this early work does play a pioneering role for the development of acylsilane chemistry. It demonstrated that acylsilanes exhibit great potential for synthesis due to the abnormal behavior of the “ $\alpha$ -silicon effect”, such as treatment with phenyl magnesium reagent or phenyl lithium reagent. After a long gestation period, efficient paths for synthesizing acylsilanes have mostly been concentrated in a few methods (Scheme 2-3).

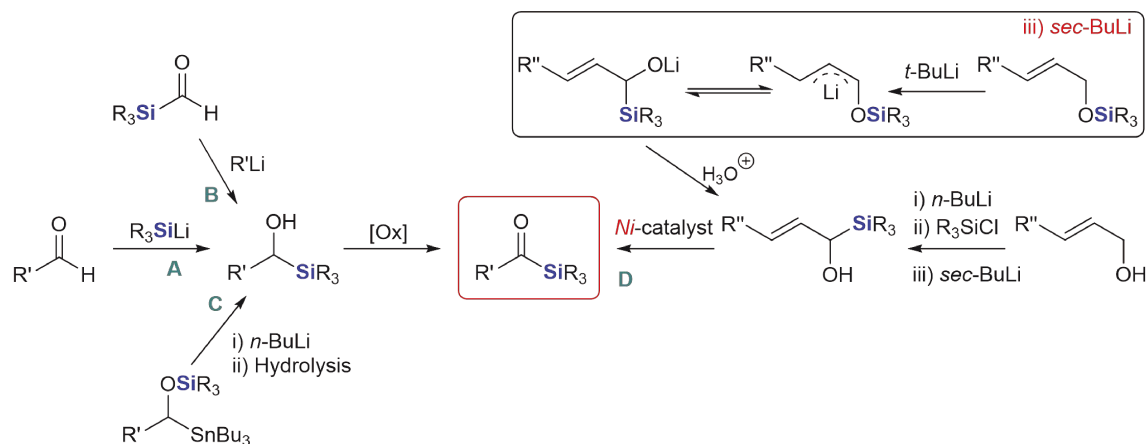


Scheme 2-3. Main methods to substituted acylsilanes

### 2.2.1 From $\alpha$ -silyl alcohols

The most general method to access acylsilanes relies on the direct oxidation of  $\alpha$ -silyl alcohols in which the alcohol precursors can be synthesized in many ways (Scheme 2-4). One of the most effective methods to  $\alpha$ -silyl alcohols involves the condensation of silyl anion equivalents with aldehydes, which are then readily oxidized to acylsilanes (Path A)<sup>[10]</sup>. Apparently, the direct addition of nucleophiles to formylsilanes also gives a straightforward pathway to substituted acylsilanes (Path B)<sup>[11]</sup>.

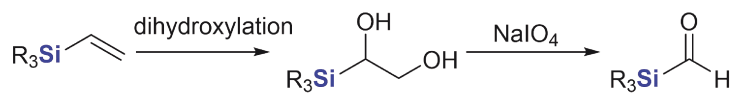
However, these routes are relatively limited in some cases which may lead to C-Si bond cleavage and the formed acylsilanes may be over-oxidized to carboxylic acids. The reverse Brook rearrangement is considered to be a safe and effective method to access  $\alpha$ -silyl alcohols. For instance, in 1990, Ghannam and co-workers reported the transmetalation and rearrangement of  $\alpha$ -[(trialkylsilyl)-oxy]alkyl]stannanes, followed by mild oxidation, such as Swern oxidation, to furnish the corresponding acylsilanes (Path C)<sup>[12]</sup>. Besides, Gree and co-workers disclosed a new method to  $\alpha,\beta$ -unsaturated acylsilanes in 2013, involving the retro Brook rearrangement of silylated allylic alcohols to  $\alpha$ -hydroxyallylsilanes. Then, transition-metal-mediated isomerization in the presence of nickel-catalyst provided acylsilanes in good yields (Path D)<sup>[13]</sup>. Therefore the large use of organolithium reagent and cumbersome reaction process makes it difficult to be used effectively in the synthesis of complex molecules.



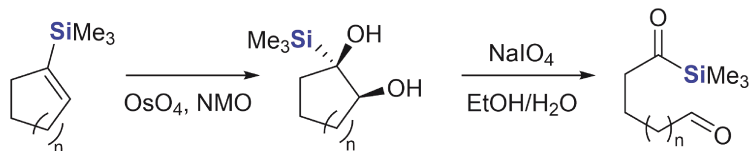
Scheme 2-4. Acylsilanes derived from  $\alpha$ -silylalcohols

Noteworthy, the simplest acylsilanes, formylsilanes, as significant precursors give much more opportunities for the synthesis of substituted acylsilanes. In 2013, Strand and co-workers disclosed an easy-to-operate way to formylsilanes from  $\alpha$ -silyl diol in the presence of  $\text{NaIO}_4$  as oxidant (Entry 1, Scheme 2-5)<sup>[14]</sup>. The successful cleavage of diol with  $\text{NaIO}_4$  prompted the related investigations for the preparation of acylsilanes. Inspired by this work, in 2019, Metz and co-workers reported another approach relying on the diol cleavage of cyclic 1,2-dihydroxysilanes with  $\text{NaIO}_4$ . The desired bifunctional acylsilanes were obtained in good yields under mild reaction conditions (Entry 2, Scheme 2-5)<sup>[15]</sup>. However, the scope of the structures in this method is limited, and the use of  $\text{OsO}_4$  for preparing the diol limited its subsequent application for synthesis.

**Entry 1.** The oxidative cleavage of  $\alpha$ -silyl diol



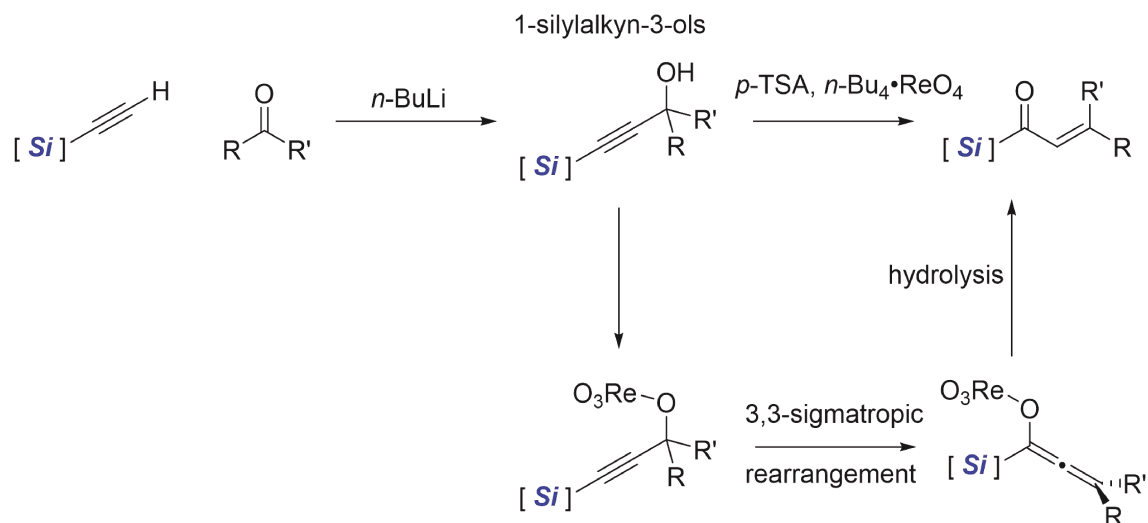
**Entry 2.** The diol cleavage of cyclic 1,2-dihydroxysilanes



Scheme 2-5. Acylsilanes from the diol cleavage

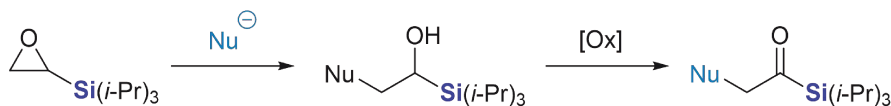
With regard to the  $\alpha,\beta$ -unsaturated acylsilanes, in 2015, Orellana and co-workers reported a more direct approach via the perrhenate-catalyzed Meyer–Schuster rearrangement of

1-silylalkyn-3-ols. The propargylic alcohols obtained in one step were readily converted into the desired acylsilanes using a combination of *p*-TSA and *n*-Bu<sub>4</sub>N·ReO<sub>4</sub> (Scheme 2-6)<sup>[16]</sup>. However, some substrates can not be employed in this method and the secondary propargylic alcohols with aliphatic substituent were unreactive in this transformation.



Scheme 2-6. Meyer-Schuster rearrangement of 1-silylalkyn-3-ols.

Especially, in 1994, Lipshutz described a unique method to access  $\alpha$ -silylalcohols involving the nucleophilic ring-opening of epoxide, followed by a mild oxidation to furnish acylsilanes in good to excellent yields (Scheme 2-7)<sup>[17]</sup>. Nevertheless, the diversity of the functional structures of the prepared acylsilanes comes from organolithium reagents, which leads to much less adaptability of this method in some cases.



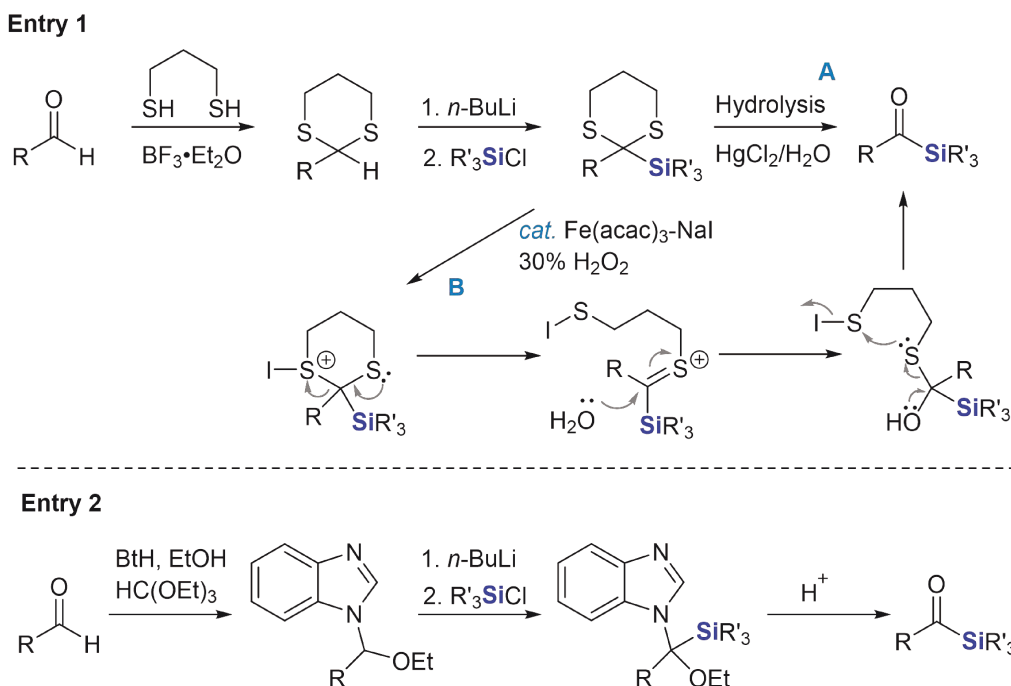
Scheme 2-7. Acylsilanes from epoxide

### 2.2.2 From Aldehydes

In general, the addition of silyllithium reagents to aldehydes gives  $\alpha$ -silylalcohols, which were further converted into acylsilanes as described above. However, the earliest and most widely used method for the formation of acylsilanes from aldehydes is the

Brook-Corey strategy in which aldehydes are more commonly converted into 1,3-dithiane, followed by lithiation and silylation to 2-silyl-1,3-dithiane. The hydrolysis of 2-silyl-1,3-dithiane was first investigated in this strategy, and give successful access to acylsilanes (Entry 1A, Scheme 2-8)<sup>[18]</sup>. But this hydrolysis process is problematic due to the use of highly toxic mercury salts, thus greatly limiting their synthetic value.

Other methods for the hydrolysis process have been developed, such as treatment with *N*-bromosuccinimide (NBS) and I<sub>2</sub>/CaCO<sub>3</sub>. More recently, in 2017, Kirihara and co-workers reported an environmentally benign method for the hydrolysis of 2-silyl-1,3-dithiane by using 30% aqueous hydrogen peroxide catalyzed by Fe(III)-NaI. In the presence of a catalyst, a so-called “I<sup>+</sup> equivalent” is generated *in situ*, which then reacts with 2-silyl-1,3-dithiane and finally transformed into the corresponding acylsilanes (Entry 1B, Scheme 2-8)<sup>[19]</sup>.



Scheme 2-8. Acylsilanes from 1,3-dithiane and *N,O*-acetals

Apart from the silyl 1,3-dithiane, other  $\alpha$ -silyl acylation equivalents were also engaged for the synthesis of acylsilanes. For instance, the benzotriazole derivatives formed from aldehydes also display a similar characteristic to the 1,3-dithiane, offering advantage in the hydrolysis process after the common silylation. Under mild conditions, various

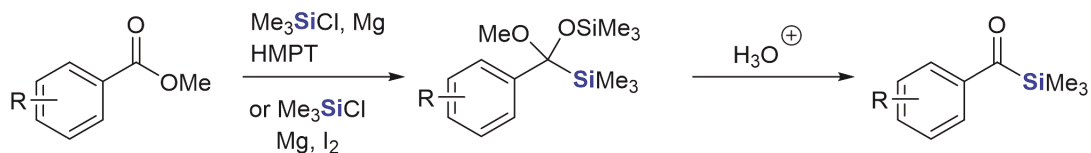
acylsilanes were obtained in good yields, even  $\alpha,\beta$ -unsaturated alkenoyl and alkynoylsilanes (Entry 2, Scheme 2-8)<sup>[20]</sup>. However, it appears that now these strategies are indirect and require verbose protection-deprotection steps.

### 2.2.3 From carboxylic acids and carboxylic acid derivatives

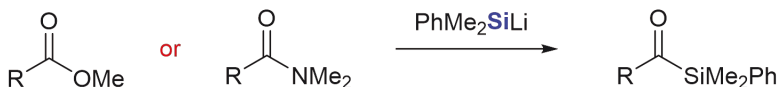
Nucleophilic silylation of carboxylic acid derivatives to access acylsilanes was also extensively studied and viewed as an effective protocol over the years. One of the early first approaches proceeded by the reductive silylation of esters or acyl chlorides with silyl-Grignard derivatives to furnish acylsilanes (Entry 1, Scheme 2-9)<sup>[21]</sup>. This method generally gives poor yields and therefore has seldom been employed.

Moreover, the direct silylation of carboxylic acid derivatives in the presence of silyllithium reagents is apparently an extremely important method for the synthesis of acylsilanes (Entry 2a, Scheme 2-9)<sup>[22]</sup>. However, the reaction of silyllithium reagents with esters generally affords disilylalcohols as undesired by-products and requires an extra one-step oxidation (Entry 2b, Scheme 2-9)<sup>[23]</sup>. In the case of acid chloride, this procedure usually provides complex reaction mixtures.

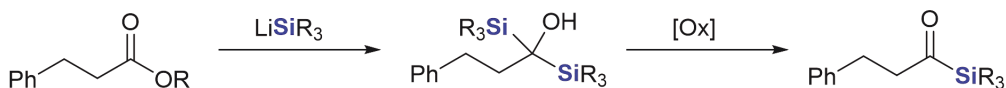
#### Entry 1



#### Entry 2a

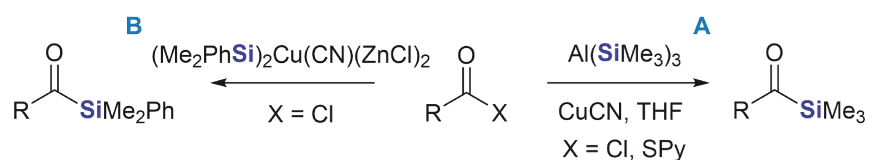


#### Entry 2b Double nucleophilic attack



Scheme 2-9. General methods to acylsilanes from carboxylic acid derivatives

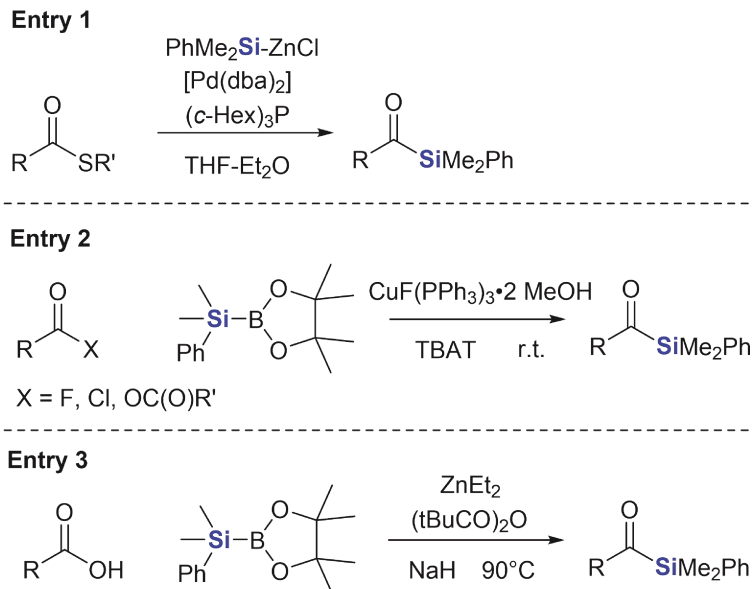
Afterwards, in 1991, Ohno and co-workers reported a new method relying on the reaction of the readily available Al-Si reagents,  $\text{Al}(\text{SiMe}_3)_3$  with acid chlorides and *S*-2-pyridyl esters in the presence of CuCN to afford acylsilanes (Path A, Scheme 2-10)<sup>[24]</sup>. A much more readily applicable metal-silicon reagent was developed by Ricci and co-workers in 1995<sup>[25]</sup>, whereby a silyl-zinc cyanocuprate  $(\text{Me}_2\text{PhSi})_2\text{Cu}(\text{CN})(\text{ZnCl})_2$  reacts with acyl chlorides to directly give acylsilanes (Path B, Scheme 2-10). These types of Al-Si reagents have been applied to the synthesis of acylsilanes containing cyano, halo and other common groups. However, a limitation of this methodology is that the highly activated cuprates may undesirably react with other polar functional groups in the substrate.



Scheme 2-10. The use of Al-Si reagents in the synthesis of acylsilanes

In contrast to the classical synthetic methods described above, transition metal-catalyzed preparation of acylsilanes under mild reaction conditions are reliable. More recently, in 2011, Tokuyama and co-workers<sup>[26]</sup> reported an efficient method to access acylsilanes via palladium-catalyzed cross-coupling reaction of thiol esters with silylzinc chloride, which was carried out at room temperature (Entry 1, Scheme 2-11).

Furthermore, in 2013, Riant and co-workers disclosed a new synthetic strategy towards acylsilanes through the Copper(I)-catalyzed addition of silicon nucleophiles to carboxylic anhydrides. In the presence of copper catalyst, Suginome's reagent produces the active Cu-Si species, and then reacts with carboxylic anhydrides to furnish acylsilanes in good yields (Entry 2, Scheme 2-11)<sup>[27]</sup>. Similarly, in 2019, Fujihara and co-workers<sup>[28]</sup> reported the Zn-catalyzed reaction of carboxylic acids with Suginome's reagent in the presence of pivalic anhydride to yield the corresponding acylsilanes (Entry 3, Scheme 2-11). However, most of the reported approaches concerning the transition metal-catalysis required high catalyst loading, and also complex ligands on the catalysts in many cases, which may lead to decreased chemoselectivity.



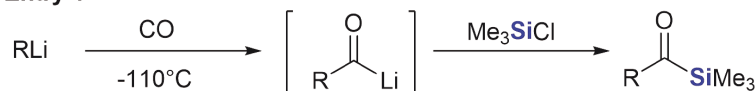
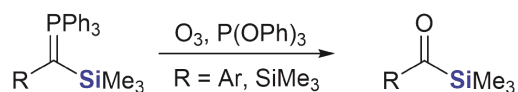
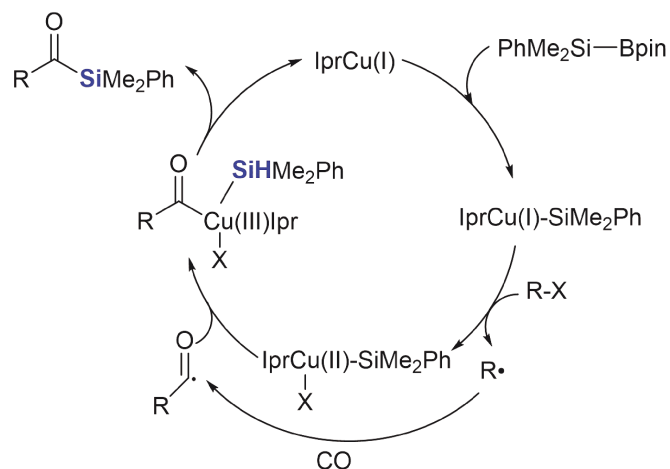
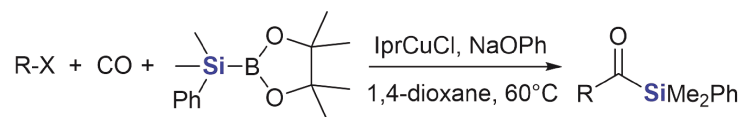
Scheme 2-11. Transition metal-catalyzed preparation of acylsilanes

## 2.2.4 From other organic functionalities

The carbonylation of silyl-substituted compounds also constitutes an efficient pathway to access substituted acylsilanes. The most common available route relies on the carbonylation of organolithium reagents to produce acyllithium intermediates, followed by the reaction with chlorosilane to give acylsilanes (Entry 1, Scheme 2-12)<sup>[29]</sup>. It is worth noting that the direct oxidation of phosphonium ylides in the presence of ozone gives acylsilanes in useful yields (Entry 2, Scheme 2-12)<sup>[30]</sup>. However, the relatively harsh reaction conditions in both of these methods constrains their adaptability for the synthesis of complex molecules, and the use of gas as a starting material requires more complex experimental equipment and leads to difficulties in large scale preparation.

More recently, in 2020, Mankad and co-workers<sup>[31]</sup> reported the Cu-catalyzed carbonylative silylation of alkyl halides for the synthesis of alkyl-substituted acylsilanes. This strategy involves the formation of an acyl radical and then converts into the corresponding acylsilanes within a Cu-catalyzed transfer process (Entry 3, Scheme 2-12). Although the transformation of acyl radicals gives this method a great potential in the synthesis of acylsilanes, it can only be applied to alkyl acylsilanes and its generality has not been developed. Additionally, the use of CO for acylation is also challenging.



**Entry 1****Entry 2****Entry 3**

Scheme 2-12. Carbonylation of silyl-substituted compounds

**2.3 Experimental design and initial attempts**

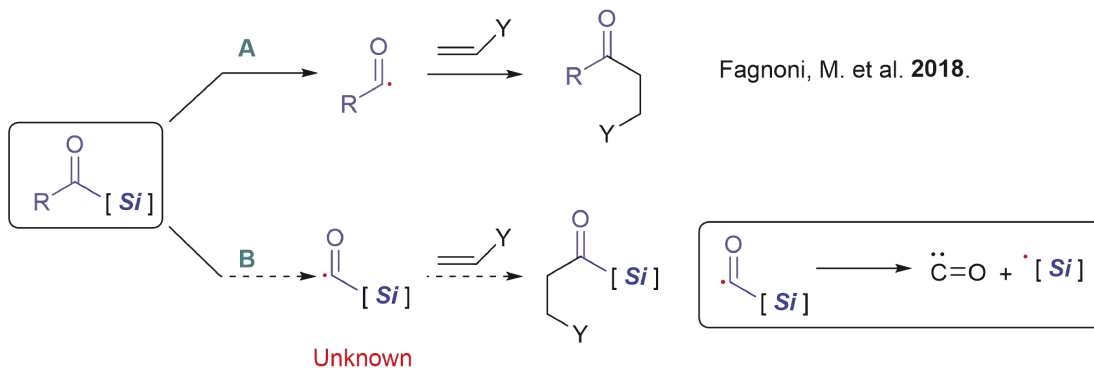
The preceding summary underscores the fact that the efficient synthesis of acylsilanes remains a challenging project. Most of the reported examples require the use of harsh reaction conditions, are less general, require precursors that are not readily available. In this case, it would be more advantageous to develop a mild and convenient method to access acylsilanes, allowing to start from a common precursor and apply it to the synthesis of a wide variety of compounds that are not easily accessible by other methods. In fact, radical reactions have proven to be very useful in organic synthesis and allow access to valuable otherwise unreachable structures, but their applications in the synthesis

of acylsilanes were still rare. Developing a general and modular radical synthesis route to acylsilanes could enrich their structural diversity and subsequent transformations.

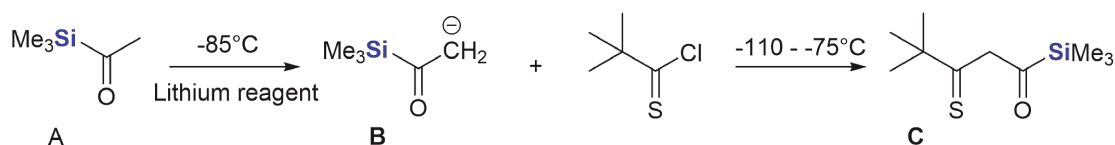
At the same time, it is well known that acylsilanes could undergo a series of radical transformations, such as acyl radicals generation under photoredox-catalyzed conditions with the loss of the silane moiety, which was developed by Fagnoni and co-workers<sup>[32]</sup> in 2018 (Path A, Scheme 2-13a). The formed acyl radicals were used for the acylation of Michael acceptors to give ketones, despite the process of producing acyl radicals being more complicated.

Complementary to these results, one can consider whether it is feasible that the silyl acyl radicals could also be generated and further added onto Michael acceptors. This would associate the acylsilanes with functional groups from alkenes while retaining the acylsilane moiety to furnish more useful acylsilane compounds (Path B, Scheme 2-13a). However, the generation and applications of silyl acyl radicals has not been reported so far. It is likely that C-Si bond can cleave to furnish carbon monoxide and a silyl radical. The stability of silyl acyl radicals is thus questionable.

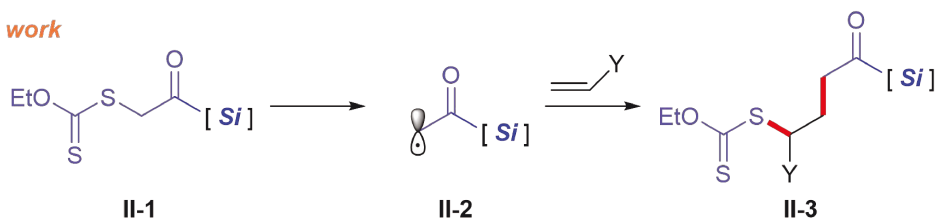
Moreover, in 2000, Kaloyeros and co-workers<sup>[33]</sup> reported an interesting acylsilane anion equivalent **B**, generated from the corresponding acylsilane **A** by deprotonation in the presence of lithium reagent. Its capture with an electrophile provided the desired acylsilane **C**. This approach opens a new pathway for the synthesis of this family of compounds. However, the harsh reaction conditions for the generation of the anion equivalent limit its synthetic applications, thus there were no more follow-up research (Scheme 2-13a).



Kaloyeros, A. E. et al. 2000.

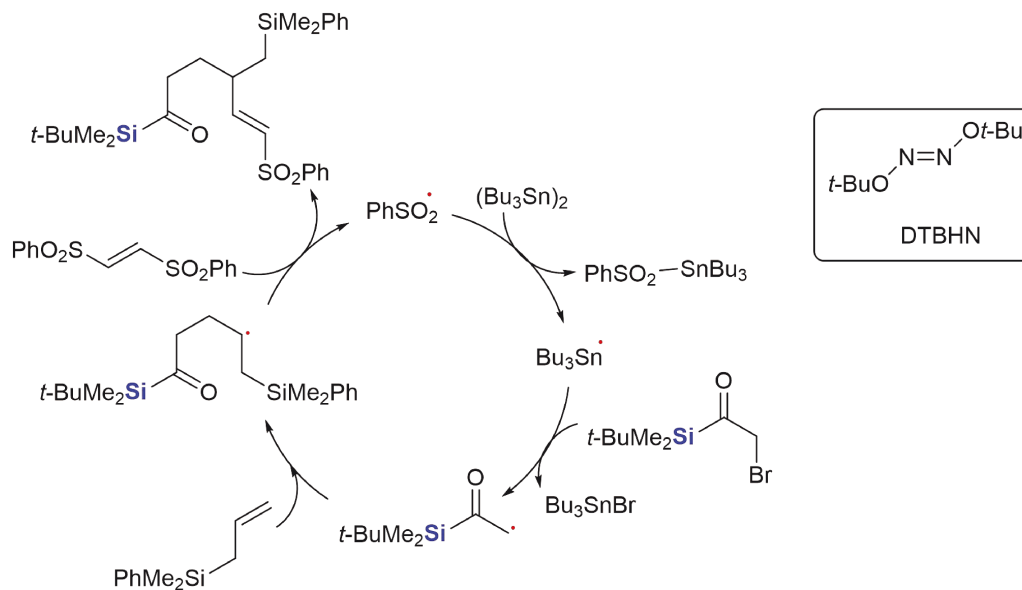
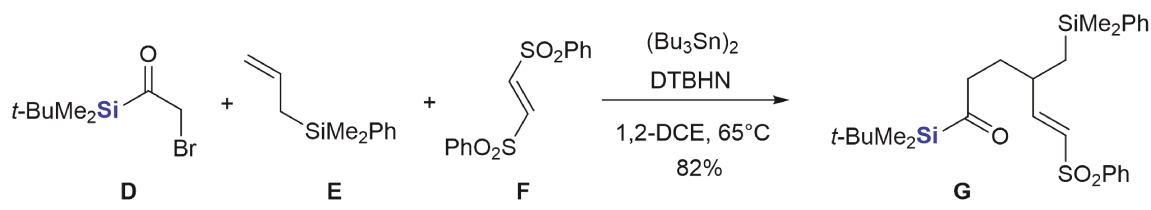


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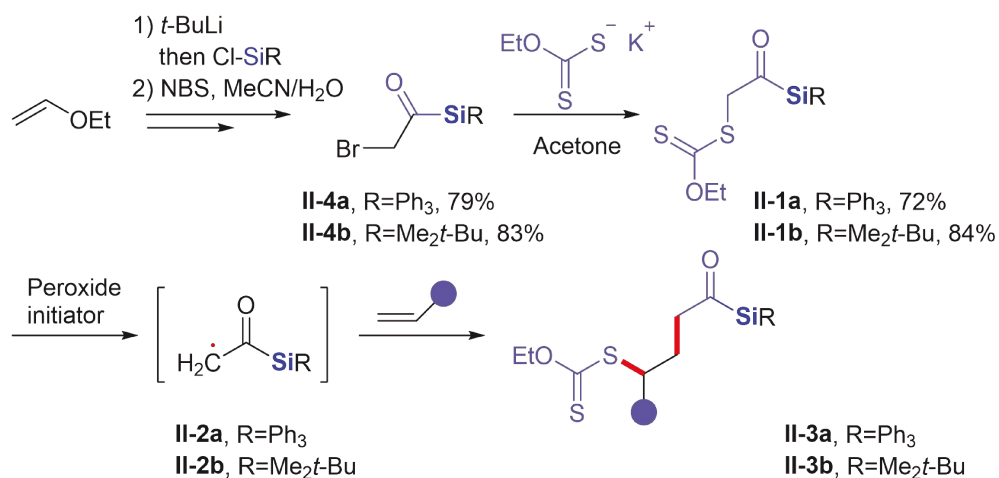
Scheme 2-13a. Radicals derived from acylsilanes

Keeping in mind these considerations, we focus on another more reasonable radical **II-2**, which in principle can be generated from its convenient precursor xanthate **II-1**. Then, addition with alkenes by taking advantage of the xanthate addition-transfer process to afford large libraries of acylsilane compounds **II-3** (Scheme 2-13a). It is noteworthy that radical **II-2** is structurally stable due to the unique stabilization of  $\alpha$ -ketonyl group<sup>[34]</sup>. In 2011, Landais and co-workers<sup>[35]</sup> reported a three-component carboalkenylation of olefins to provide acylsilane **G**, involving the addition of radical generated from the corresponding bromomethyl acylsilane **D** in the presence of organotin reagent with an alkene **E**, followed by the coupling of the resulting electron-rich radical with an unsaturated sulfonyl acceptor **F**. This strategy involves an  $\alpha$ -acylsilyl radical but requires starting with an organotin reagent, which limits its use in synthesis (Scheme 2-13b). Thus, we shift our attention to explore the synthetic feasibility of xanthate **II-1**.



Scheme 2-13b. Three-Component Carboalkenylation with Acylsilanes

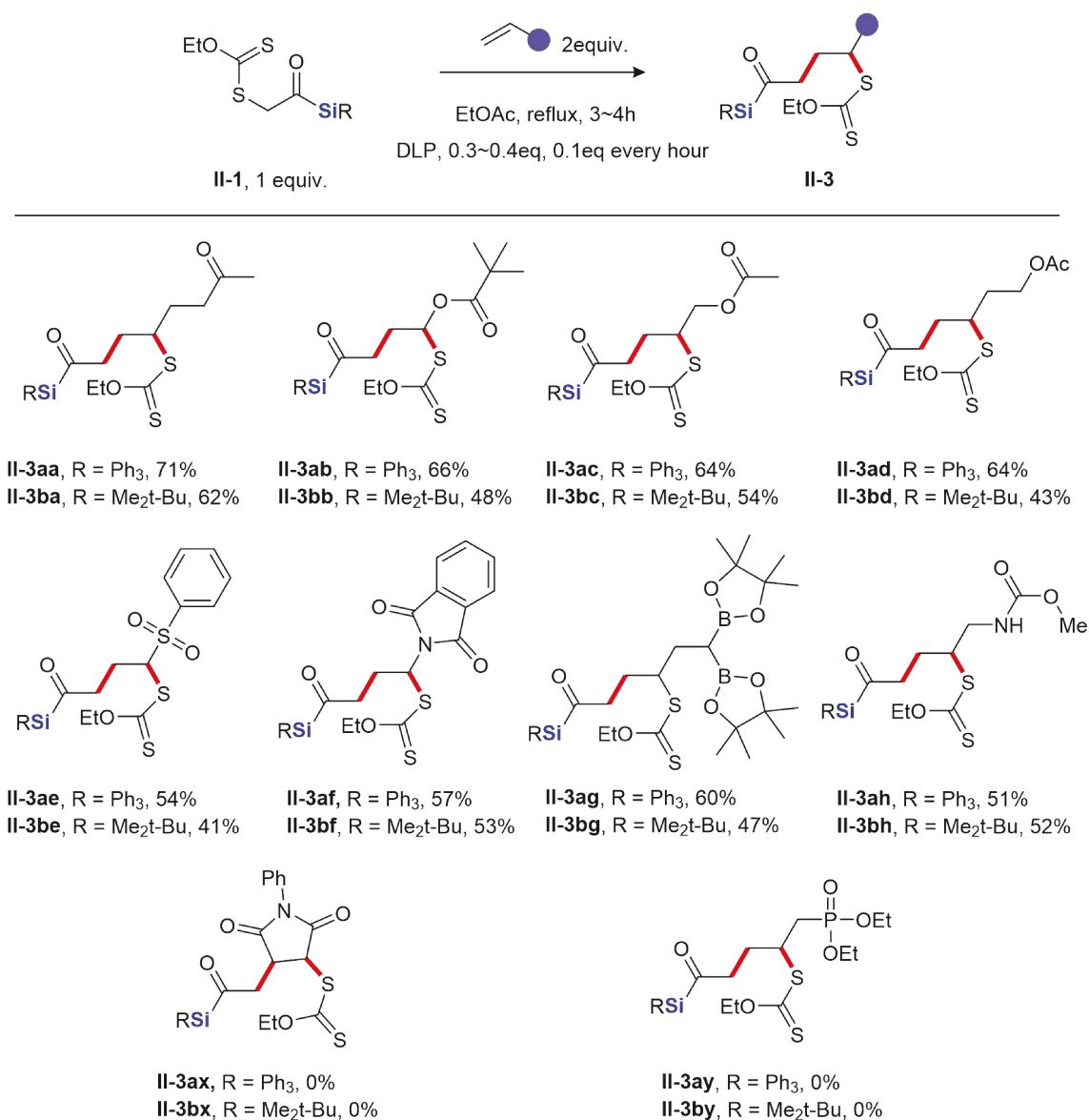
To construct the xanthate **II-1**, we examined the following route whereby the bromomethyl acylsilanes **II-4** were synthesized from ethyl vinyl ether in two steps without purification, involving lithiation, silylation, and electrophilic addition<sup>[36]</sup>. The formed bromomethyl acylsilanes **II-4** was then made to react with commercially available xanthate salts to directly give the desired xanthates **II-1** in excellent yields. Xanthate **II-1** can then be involved in the radical addition reaction with various alkenes, promoted by heating with peroxide as the initiator. The xanthate transfer process results in the formation of the more complex acylsilanes **II-3**, which would be suitable for many other useful transformations (Scheme 2-14).



Scheme 2-14. Proposed route to xanthate **II-1**

As displayed in this strategy, the substituents on the silicon atom should, in principle, have a significant effect on the addition step. We therefore compared the reactivity of these two radicals so as to choose the one with the better reactivity with alkenes before continuing the subsequent applications.

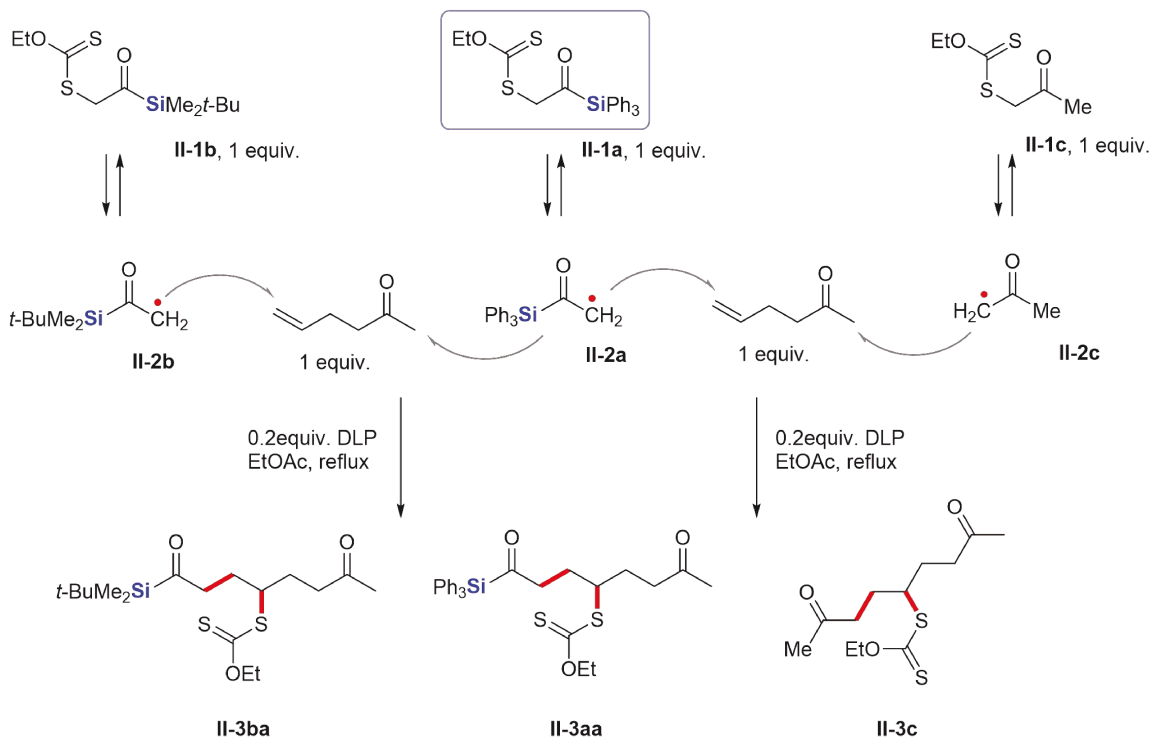
This attempt commenced with the radical addition of xanthate **II-1** with selected non-activated alkenes. The mixture was heated to reflux in the presence of dilauroyl peroxide (DLP) as an initiator. Gratifyingly, the target adducts **II-3** were obtained and isolated in good yields. However, the addition failed in the case of *N*-phenylmaleimide, probably due to self-polymerization, and no adducts **II-3ax** or **II-3bx** were found. A similar problem was observed in the case when diethyl allylphosphonate was used and there was no reaction with either of the two starting xanthates (Scheme 2-15). The reason for the failure in this case is not clean, as this olefin was previously successfully used with other xanthates.



Scheme 2-15. Addition of xanthate **II-1** with alkenes

The difference in yield of adducts **II-3a** and **II-3b** is however not significant, even if it generally favored xanthate **II-1a**. For clarifying the reactivity of xanthate **II-1**, we further performed the competition reaction depicted in Scheme 2-16, where one equivalent each of xanthate **II-1a** and **II-1b** and 5-hexen-2-one were mixed and heated in refluxing ethyl acetate in the presence of 20 mol% DLP as an initiator. In this case, radicals **II-2a** and **II-2b**, derived respectively from xanthate **II-1a** and **II-1b**, would add onto the alkene at the same time. As mentioned before, the formed radicals are in equilibrium through the fast-reversible exchange with the xanthate group. This process is much faster than the

addition to the alkene which occurred at the same time to give rise to adducts **II-3**. The yield of adduct **II-3a** and **II-3b** visually reflects the reactivity of these radicals, if the reaction is stopped early to limit concentration effects.



Scheme 2-16. Competition experiment

In this event, the molar ratio of adducts **II-3aa** over **II-3ba** was 4. We also evaluated the reactivity of radical **II-2a** as compared to the more common acetyl radical **II-2c** in the same manner and the molar ratio of adducts **II-3aa** over **II-3c** was 3. These satisfying results indicate that the reactivity of radical **II-2a** is better than radical **II-2b**, and even radical **II-2c**. Thus, xanthate **II-1a** was chosen for the subsequent studies.

These initial successful attempts provide us with information that the reactivity of xanthate **II-1** is as good as expected. The successful synthesis of the desired acylsilane compounds **II-3** bearing a series of functional groups encouraged us to explore further the functional group tolerance of this addition-transfer process and engage them to subsequent transformations. The purpose of this work is to gain a deeper understanding of the reactivity of acetylsilane radicals and to apply it for the synthesis of structures that are unreachable by other means.

## 2.4 Results and Discussion

### 2.4.1 Scope of alkenes

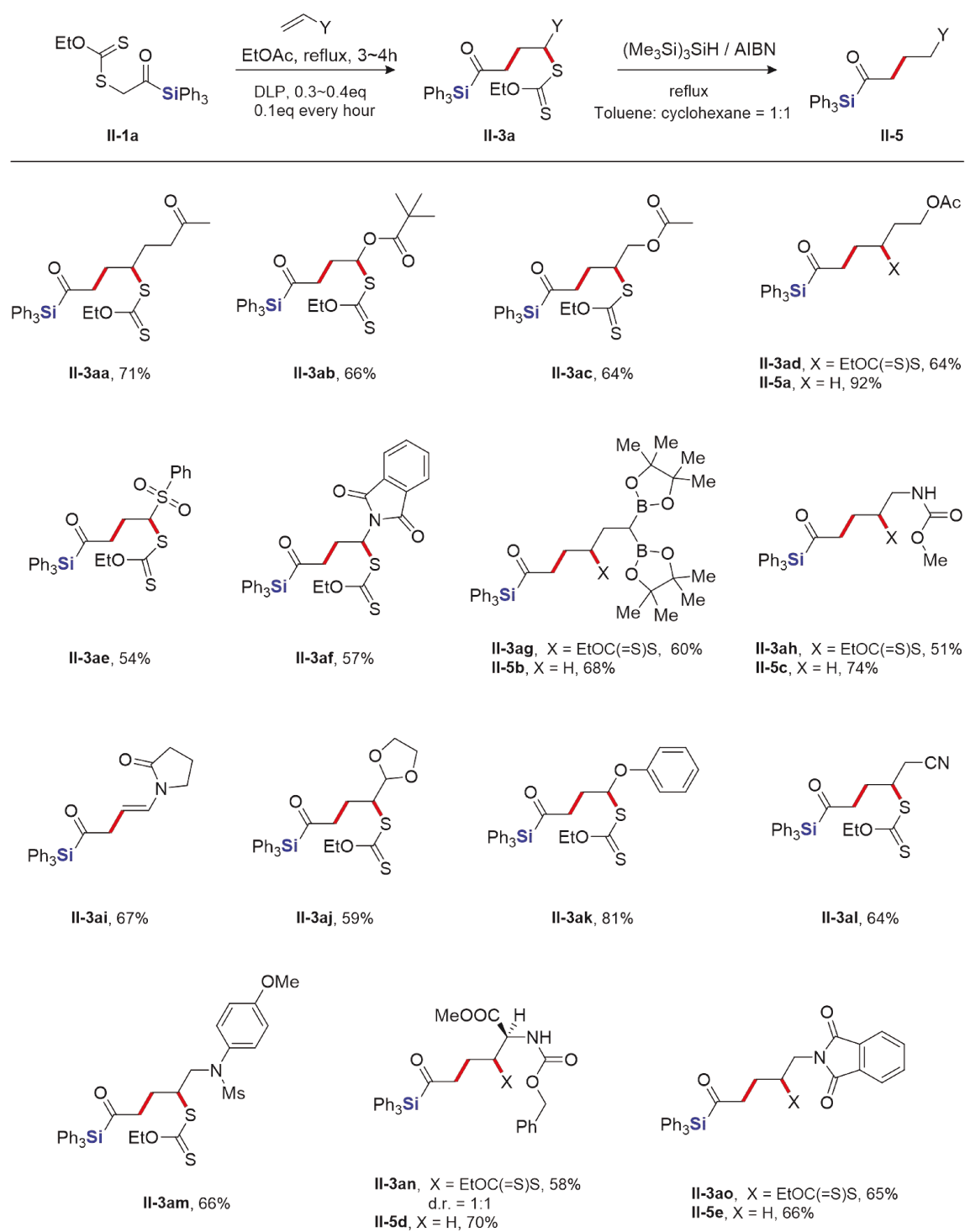
We thus turned our attention to examining the scope as far as the olefinic partners are concerned. A series of olefins bearing different functional groups were tested in the xanthate addition-transfer process with xanthate **II-1a**. The addition reactions were accomplished in refluxing ethyl acetate (0.2M) in the presence of DLP as initiator. All the products of the radical addition reaction were isolated by column chromatography and were stable in air, water and their structures were characterized by NMR, IR and HPLC-MS.

To our delight, the reaction was satisfactory, and a wide variety of corresponding adducts **II-3aa-3ax** were obtained in good yields regardless of the nature of the alkene. Some valuable compounds, such as pinacolato derivatives **II-3as** and **II-3at**, caffeine derivative **II-3au** and glucose derivative **II-3av**, were readily obtained. Sulfones, nitriles and heterocycles are tolerated, and the protected amino acid **II-3an** and **II-3ao** are noteworthy. In the case of compound **II-3ai**, the xanthate group was eliminated directly upon heating to form an enamide. Further notable products are **II-3aq** and **II-3ar** which contain a four-membered heterocyclic ring, and thus confirming the excellent reactivity of radical **II-2a** derived from the xanthate **II-1a**. For compounds **II-3ab** and **II-3ar**, the addition reaction could be easily scaled up to 5 mmol and 3.5 mmol scale respectively, and the isolated yields were comparable. In most cases, the isolated yields were synthetically useful. In particular, the yields of compound **II-3ak** and **II-3ar** are higher than 80%.

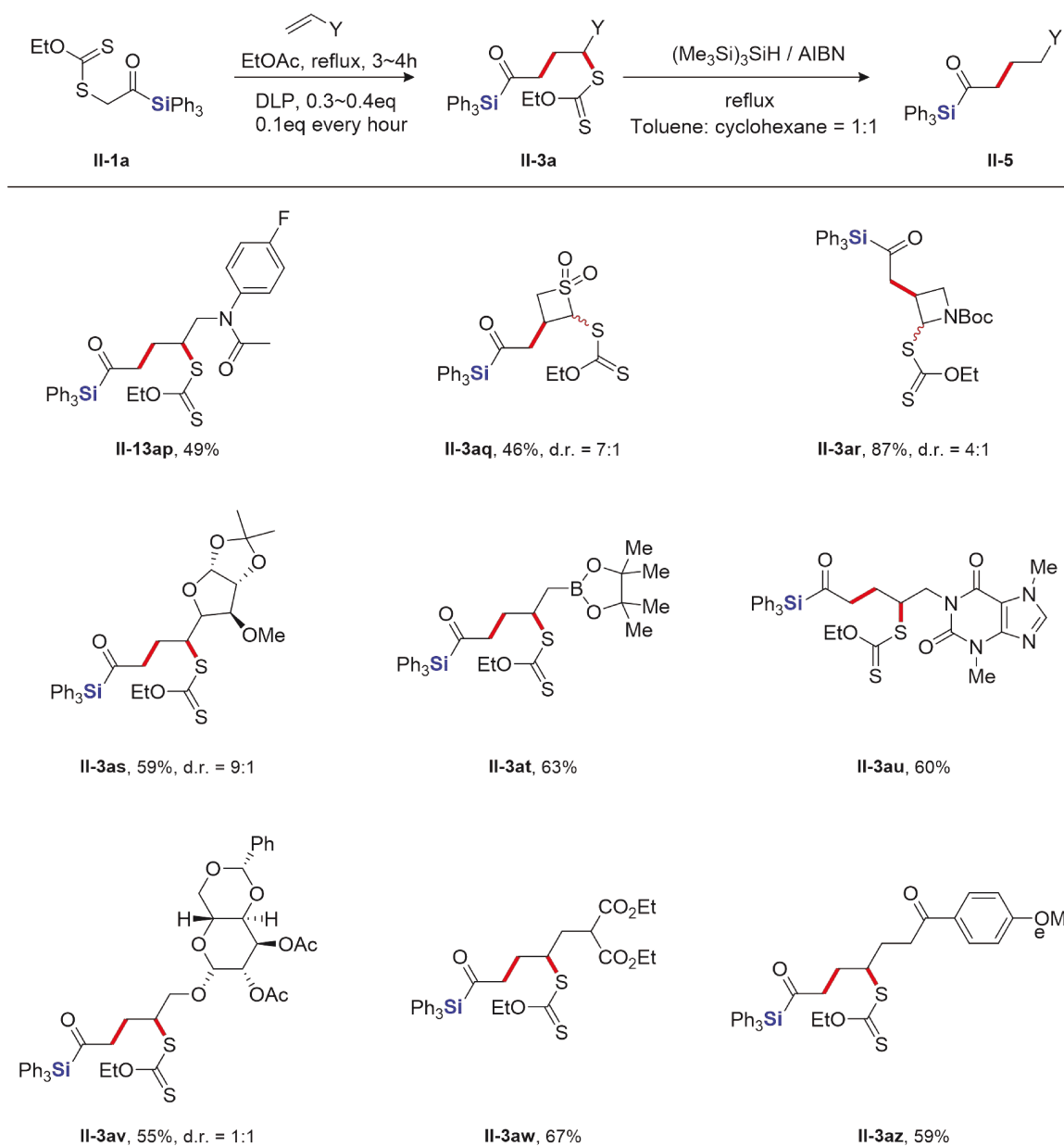
The wide functional group tolerance opens access to structures that are not available by the existing methods summarized in this chapter. Nevertheless, due to the rich chemistry of xanthate, the presence of xanthate group in the adducts provides an entry into all manner of sulfur-containing compounds by further creating new carbon-carbon bonds. It can also be reductively removed with tris(trimethylsilyl)silane and AIBN to provide simpler acylsilane compounds **II-5** in a high yield, in which a new C-C bond was created



efficiently between the acylsilane motif derived from the xanthate **II-1a** and the functional groups derived from the olefin partners.



Scheme 2-17a. Scope of olefin for the addition reaction



Scheme 2-17b. Scope of olefin for the addition reaction

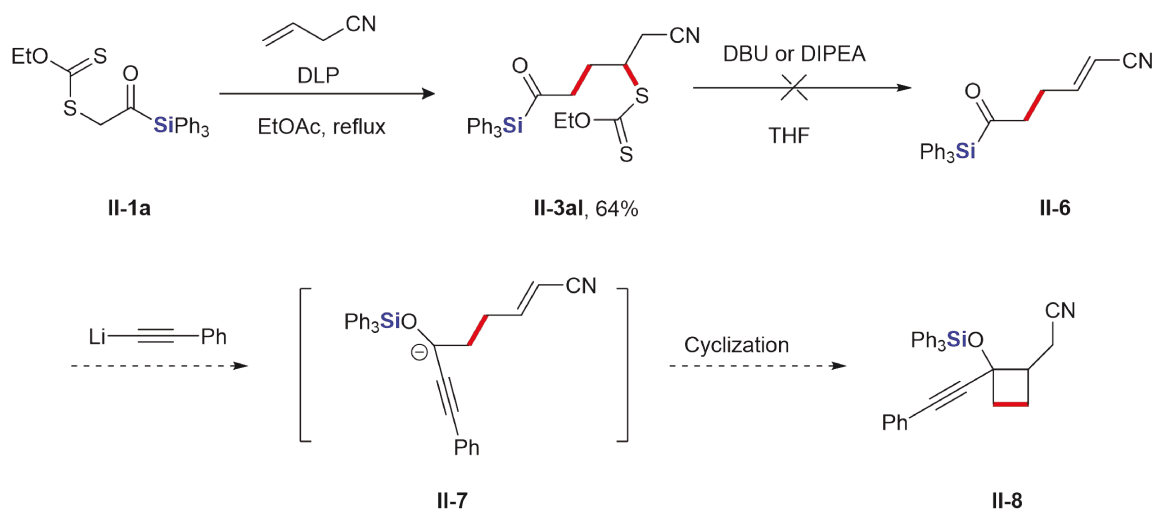
## 2.4.2 The Brook rearrangement of the synthesized acylsilanes

After extending the olefin scope, we turned to developing the functionalization of xanthate **II-1a** and its applications. It is well known that the Brook rearrangement of acylsilanes has been established as an important strategy to build complex architectures in synthesis through the controllable disconnection and reconstruction of carbon-carbon

bond which was shown in Scheme 2-1. Thus, we tested the potential rearrangement ability of adducts **II-3a** and then applied it to more useful transformations.

In the proposed strategy, adduct **II-3al** was first prepared through the addition of xanthate **II-1a** and allyl cyanide. We expected that the xanthate group could act as a leaving group and be eliminated in the presence of base such as diazabicycloundecene (DBU) or *N,N*-Diisopropylethylamine (DIPEA) to afford the  $\alpha,\beta$ -unsaturated acylsilane **II-6**, which allows bis-functionalization of the original carbonyl carbon. The subsequent nucleophilic attack of a lithium reagent would facilitate the carbon to oxygen silyl migration and would result in the formation of intermediate **II-7**. In principle, the resultant carbanion should participate in an intramolecular Michael addition with the tethered unsaturated nitrite, providing a one-pot tandem sequence for the synthesis of four-membered ring carbocyclic product **II-8** <sup>[37]</sup>. The main challenge of this strategy is whether the  $\alpha,\beta$ -unsaturated acylsilane **II-6** and the corresponding carbanion could be generated in situ and what role the xanthate group plays.

However, the elimination of adduct **II-3al** didn't give the desired compound **II-6**. In the case where DBU was used as a base, adduct **II-3al** decomposed rapidly, even when slowing the reaction rate by decreasing the reaction temperature and adding CH<sub>3</sub>I to irreversibly capture the eliminated xanthate. In the case of when DIPEA was used as a base, the conversion rate of the elimination reaction was less than 5%, and no target compound **II-6** was found. Possibly this is because the DIPEA was not strong enough to deprotonate hydrogen from adduct **II-3al** (Scheme 2-18 and Table 2-1).



Scheme 2-18. The Brook rearrangement of adduct II-3al

Table 2-1. Conditions of the elimination of adduct II-3al

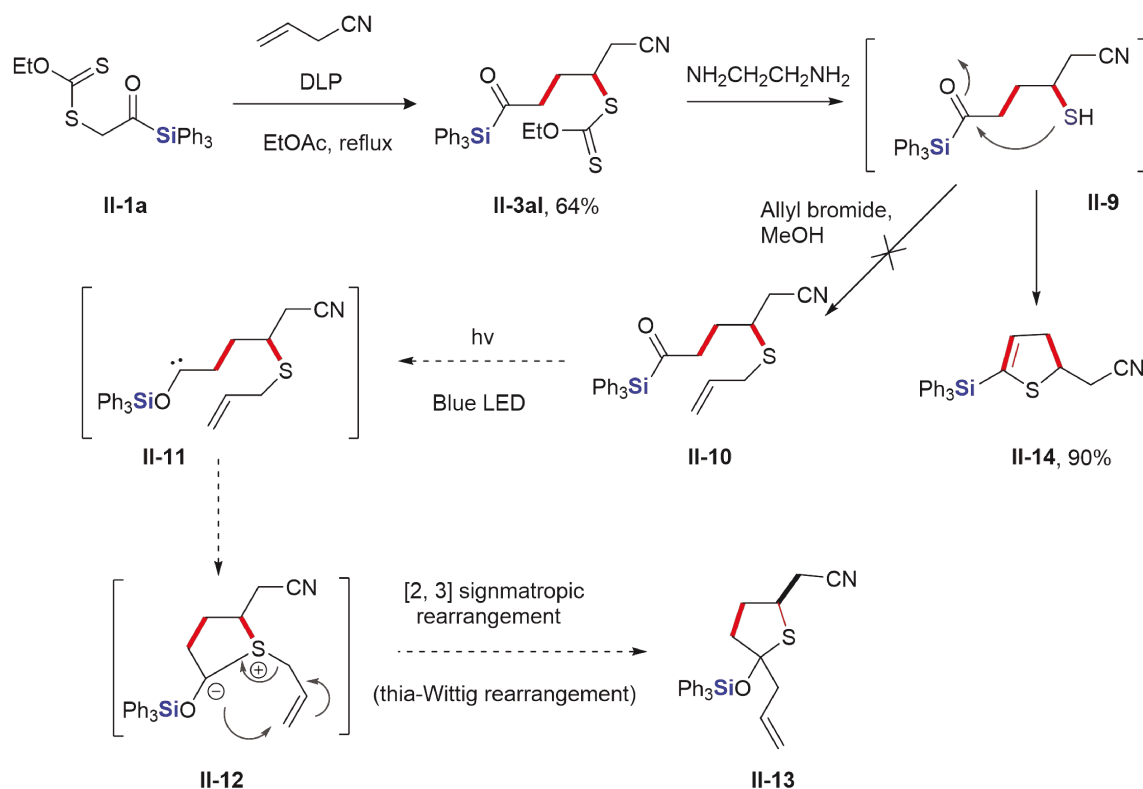
Entry	Base	CH <sub>3</sub> l	Time	II-3al consumption	Temperature	Solvent	Yield
1	DBU(1.2eq)	0	25min	100%	r.t.	MeCN	n.d.
2	DBU(1.2eq)	0	2h	100%	-5°C	MeCN	n.d.
3	DBU(1.2eq)	0	4h	100%	-78°C~0°C~r.t.	CH <sub>2</sub> Cl <sub>2</sub>	n.d.
4	DBU(1.2eq)	1.5eq	15h	100%	-78°C~0°C~r.t.	CH <sub>2</sub> Cl <sub>2</sub>	n.d.
5	DBU(1.2eq)	1.5eq	15h	100%	-35°C	CH <sub>2</sub> Cl <sub>2</sub>	n.d.
6	DBU(1.2eq)	1.5eq	6h	≈70%	-35°C	THF/ <i>t</i> BuOH	n.d.
7	DIPEA(1.2eq)	1.5eq	Over night	<5%	-78°C~0°C~r.t.	THF/ <i>t</i> BuOH	n.r.
8	DIPEA(1.2eq)	1.5eq	Over night	<5%	40~60°C	THF/ <i>t</i> BuOH	n.r.

Although unsatisfactory, these attempts still provided us with information that the elimination of the xanthate is difficult without harm to the acylsilane motif. Thus, we looked for an alternative use for the xanthate group, in particular its conversion into a thiol. This could in principle be accomplished in many ways. Also in some cases, the xanthate could further react directly with suitable functional groups to furnish heterocyclic compounds.

### 2.4.3 The thiol group from xanthate and its subsequent transformations

Sulfur-containing heterocyclic compounds widely exist in numerous natural products and biologically active molecules which are important building blocks used in the production of pharmaceuticals, agrochemicals, and dyes<sup>[38]</sup>. The existence of C=S bond in xanthate group as an analogue of C=O bond gives plenty of opportunities for many transformations, such as nucleophilic addition with amines leading to the formation of a thiol. In light of this consideration, we proposed a conceivable synthesis route depicted in Scheme 2-19 in which adduct **II-3al** was synthesized as the starting precursor for this strategy. Not only because its simple structure could simplify the spectral analysis, but also because the stable nitrile group will not interfere with the subsequent transformations.

In principle, the nucleophilic addition of compound **II-3al** with ethylenediamine would generate the thiol intermediate **II-9** which was then engaged in the allylation with allyl bromide or allyl chloride to access compound **II-10**<sup>[39]</sup>. To construct the sulfur-containing heterocyclic compounds, we hoped to take advantage of the carbene-formation ability of acylsilanes upon irradiation with blue light whereby the corresponding silyl group undergo 1,2-shift to generate  $\alpha$ -silyloxycarbenes **II-11**. Indeed, these are highly versatile synthetic intermediates that contain a divalent carbon atom with two unshared electrons<sup>[40]</sup>. In this case, the sulfur atom can act as a nucleophile and attack the carbon atom of the carbene in an intramolecular fashion, forming a new C-S bond to furnish sulfur ylide **II-12**. This would be followed by a 2,3-wittig to give the desired sulfur-containing allyl heterocycles **II-13**.



Scheme 2-19. The thiol group from xanthate and its subsequent transformations

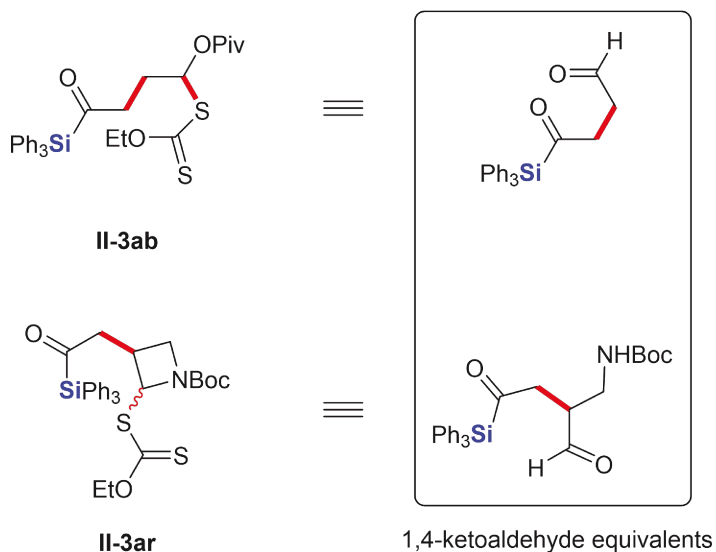
However, the cleavage of xanthate adduct **II-3aI** with ethylenediamine successfully gave the thiol intermediate **II-9**, but it rapidly ring-closed on the carbonyl group to furnish substituted dihydrothiophene **II-14** in 90% yield with loss of a molecule of water. Indeed, the formation of compound **II-14** is predictable due to the fact that the nucleophilic addition of thiol group with carbonyl group is a common reaction, and in the present case, it proved to be constructing such building blocks in organic chemistry faster than the desired allylation.

#### 2.4.4 Synthesis of 2-pyrrolyl silanes

To explore the applicability of the developed strategy for acylsilanes in more transformations, we also examined the possibility to access basic heteroaromatic derivatives such as silane-substituted pyrroles. 2-Pyrrolyl silanes are a class of organic compounds that consist of a pyrrole ring attached to a silicon atom through a carbon-silicon (C-Si) bond, which are versatile building blocks in organic synthesis<sup>[41]</sup>. They possess both the reactivity of the pyrrole ring and the silicon functionality, allowing

for diverse synthetic applications. Benefiting greatly from the broad functional group tolerance, a wide variety of adducts **II-3a** have been obtained and each has its own unique synthetic potential, two (**II-3ab** and **II-3ar**) of which proved to be very efficient in 2-pyrrolyl silane synthesis.

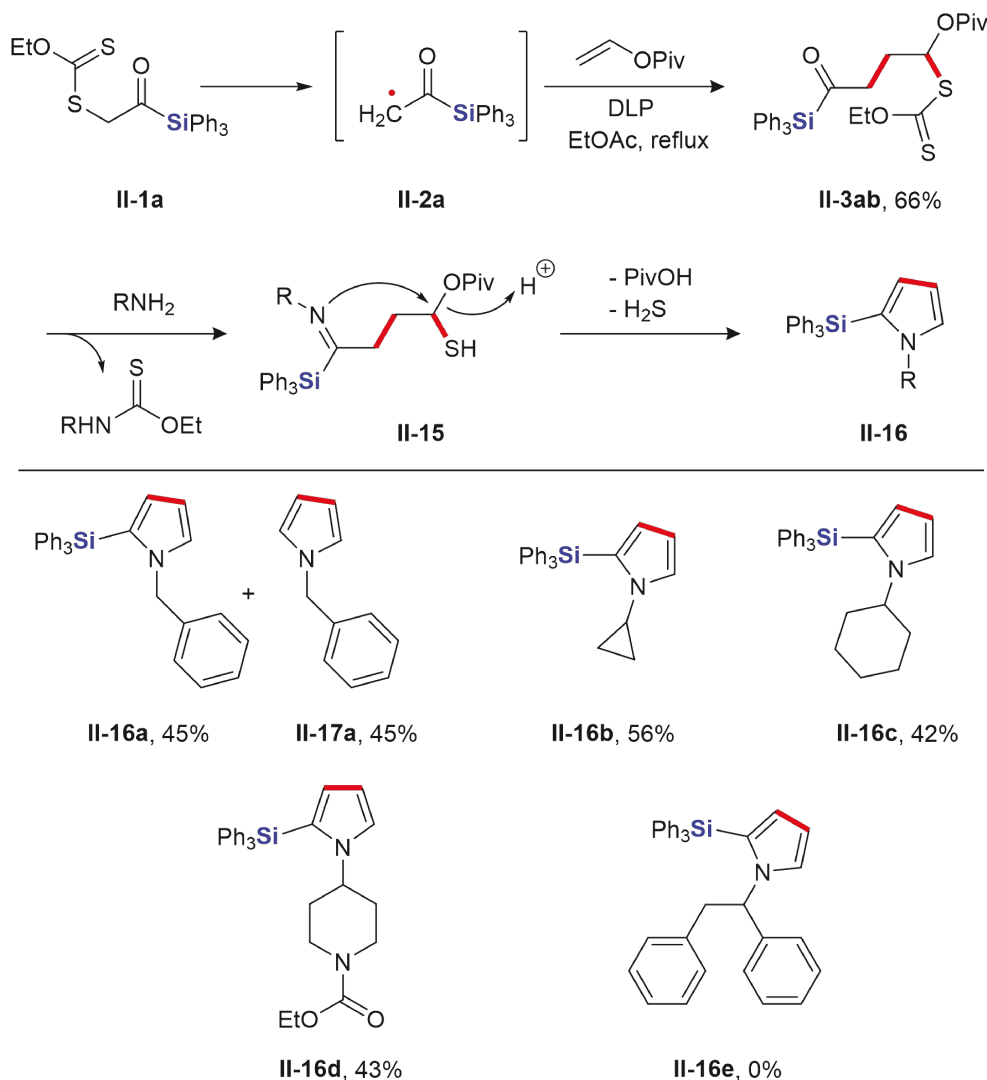
Adducts **II-3ab** and **II-3ar** were smoothly obtained from the radical addition step, favored in part by the electrophilic character of the intermediate acylsilane radical derived from the xanthate **II-1a** and the nucleophilic nature of the olefin partner. In both cases, the carbon atom attached to both the pivaloxy group or N-Boc group and the xanthate has the oxidative level of an aldehyde and adducts **II-3ab** and **II-3ar** can be viewed as 1,4-ketoaldehyde equivalents<sup>[42, 43]</sup>. Such derivatives would be extremely difficult to access (Scheme 2-20). It is well known that the Paal-Knorr reaction is a simple and robust route to pyrroles whereby an amine is condensed with a 1,4-dicarbonyl derivative<sup>[44]</sup>. The main challenge of the Paal-Knorr synthesis is to access the desired diketone precursors or 1,4-diketone equivalents. Therefore, the chemical performance of adducts **II-3ab** and **II-3ar** related to their synthetic potential in the Paal-Knorr reaction indeed could provide a new access to 2-pyrrolyl silanes.



Scheme 2-20. 1,4-ketoaldehyde equivalents for Paal-Knorr synthesis

In the case of adduct **II-3ab**, exposing it to an amine would generate the imine intermediate **II-15** by condensation. While the xanthate group is converted into a thiol at

the same time, giving rise to a geminal pivaloxy-thiol unit or thioaldehyde. The subsequent nucleophilic attack of the nitrogen with loss of pivalic acid and hydrogen sulfide furnishes the desired 2-pyrrolyl silanes **II-16** by analogy with the Paal-Knorr synthesis (Scheme 2-21).

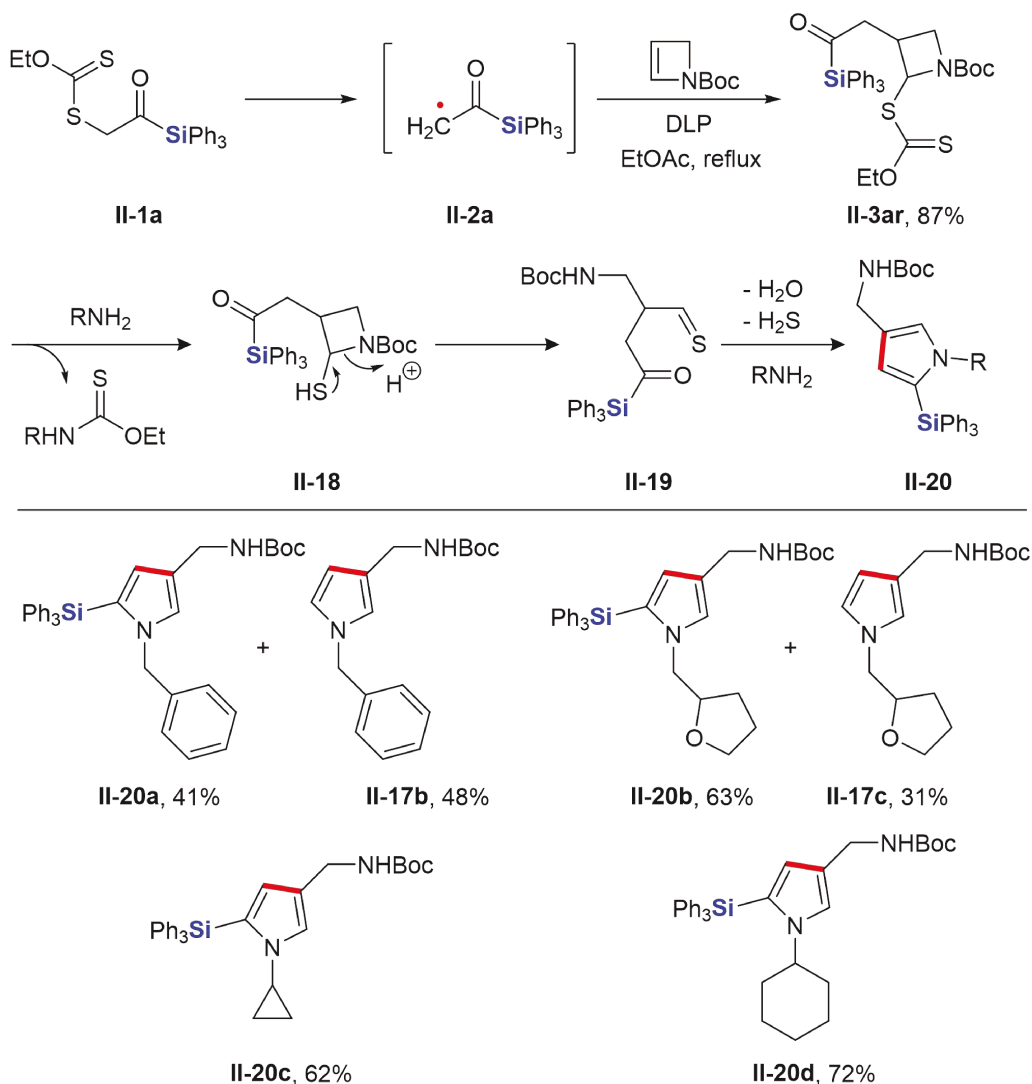


Scheme 2-21. Synthesis of 2-pyrrolyl silanes from II-3ab

We then expanded the scope of the amines that can be introduced to synthesize a variety of 2-pyrrolyl silanes by this strategy. Amines bearing different functional groups such as benzyl-, cyclopropyl-, cyclohexyl-, and protected amino- all gave the desired pyrrole compounds in moderate yields. Both primary and secondary amines exhibited good



selectivity in the formation of 2-pyrrolyl silanes. However, the sterically hindered diphenylethylamine did not afford the desired product **II-16e**.



Scheme 2-22. Synthesis of 2-pyrrolyl silanes from **II-3ar**

In the case of adduct **II-3ar**, similarly, aminolysis of the xanthate group would result in the formation of thiol intermediate **II-18**, which spontaneously undergoes ring-opening into thioaldehyde **II-19** to relieve the strain of the azetidine ring. The final condensation of the amine with both of the reactive thioaldehyde and the ketone provides the desired 2-pyrrolyl silanes **II-20**. The scope of the amines for this synthetic strategy was also expanded and products **II-20** bearing a series of functional groups were obtained in good yields (Scheme 2-22). However, in the case of unbranched amines, the pyrrole synthesis

of adduct **II-3ab** and **II-3ar** gave byproducts **II-17** with loss of silyl group. The causes of this behavior are not obvious at this moment and more work is needed to clarify the matter.

Finally, it is worth noting that in the related approach involving addition to vinyl pivalate, 2-substituted pyrroles **II-16** are readily available, but not 2,4-disubstituted pyrroles. While the double condensation of amine with adduct **II-3ar** successfully provides various 2,4-disubstituted pyrroles as a complement and opens numerous pathways to multi-substituted pyrrolyl silanes.

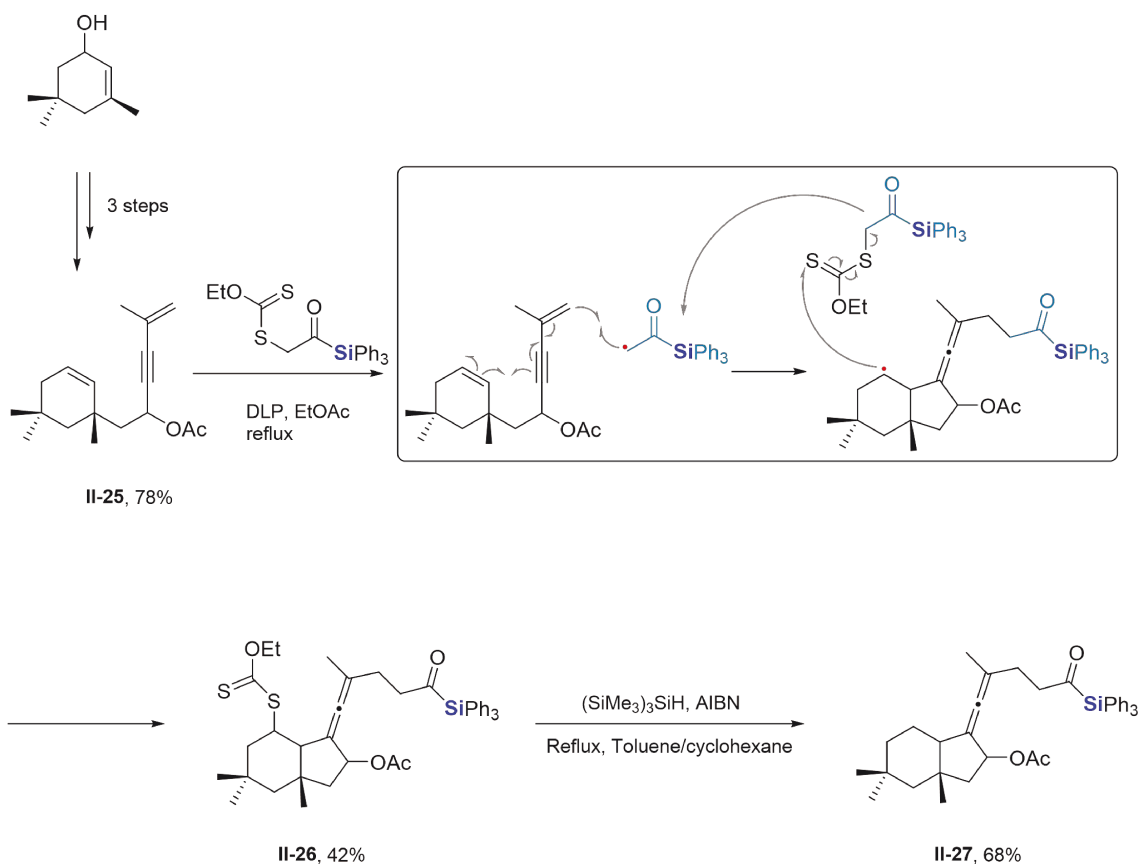
#### **2.4.5 Carbene generation of acylsilanes and subsequent synthetic applications**

Photochemistry has recently gained great attention in synthetic chemistry, since light is cheap, allows for spatiotemporal control and can be turned in terms of its wavelength and intensity, without producing any waste. These features render photochemistry highly valuable in synthesis and light-mediated processes have also found applications in biological chemistry<sup>[45]</sup>.

Particularly, acylsilanes feature an elongated bond between the carbonyl group and the silyl moiety which is cleaved upon visible light irradiation (for acylsilanes with a  $\pi$ -system on conjugation to the carbonyl group)<sup>[46]</sup>. Thereby, siloxycarbene is generated, a reactive intermediate whose utility in organic synthesis has so far remained limited. Thus, the ability to generate reactive carbenes which can undergo fast insertion reactions with high selectivity by visible light irradiation, along with their ready access render acylsilanes promising candidates as reactive functionalities in organic chemistry<sup>[47]</sup>.

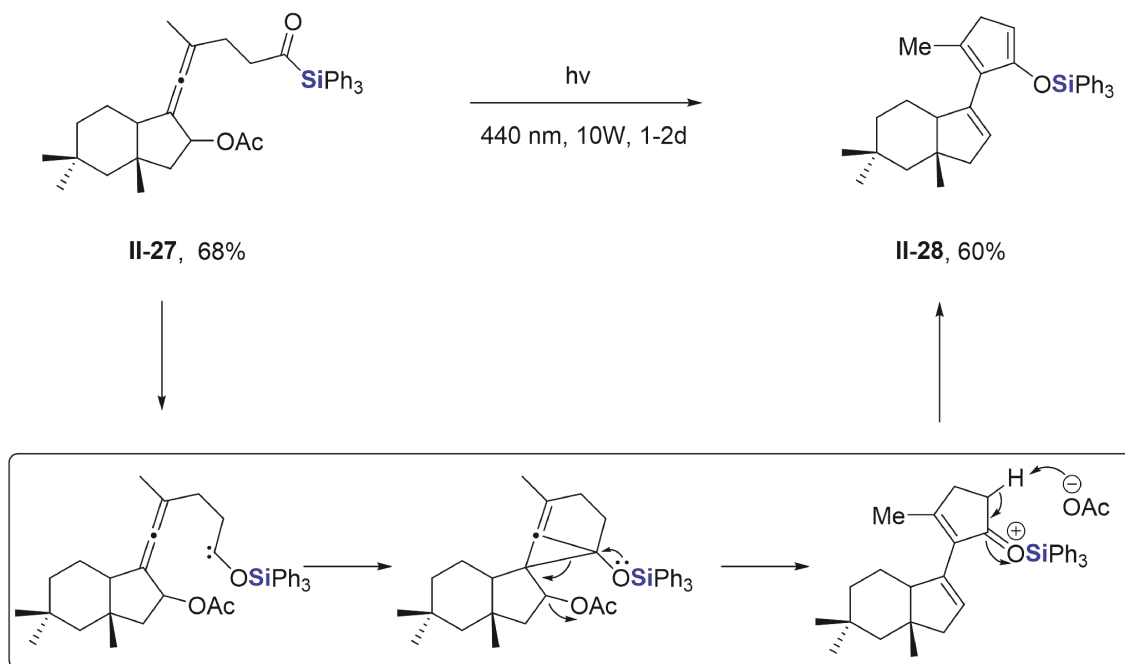
Taking into account these facts, we therefore remain highly interested in the photocatalytic production of carbenes from acylsilanes, since the former strategy didn't reach this step. Moreover, we expected the formed carbene intermediate can be involved in the reaction with functional groups brought about by the xanthate radical-addition transfer process and in an intramolecular manner. On the basis of this assumption, we proposed the following strategy to synthesize the target product **II-27** which can theoretically be cyclized upon irradiation to furnish a polycyclic compound with a wide range of applications in synthesis.

Specifically, compound **II-25** was synthesized in three steps by following the strategy reported by our group<sup>[48]</sup> and as an addition partner with xanthate **II-1a**. Its addition with radicals derived from xanthate **II-1a** will generate a propargyl radical, which was then captured by the alkyne group to form an allenyl radical. Subsequent cyclization of the allenyl radical provides the allene **II-26**, which was then reduced to give the notable compound **II-27** in good yields.



Scheme 2-23. Route to allene **II-27**

In this case, compound **II-27**, bearing an acylsilane motif and an allene, was engaged in the irradiation with blue light. Surprisingly, the carbene intermediate was successfully obtained and the generated carbene spontaneously inserted into the allenyl group, followed by the nucleophilic attack of oxygen atom and deprotonation to furnish cyclic compound **II-28** in good yield and in an intramolecular manner. Thus, an interesting and useful polycyclic compound was effectively constructed by combining the xanthate radical-addition transfer process and the rich chemical properties of acylsilanes.



Scheme 2-24. Carbene generation from compound **II-27**

## 2.5 Conclusion

In conclusion, a modular, straightforward, and flexible approach to functional acylsilanes was developed in this chapter, proceeding by radical addition of xanthate **II-1** onto a wide range of non-activated alkenes. In contrast to the reported methods, the mild reaction conditions and tolerance to various functional group provide a new manner for synthesizing diverse acylsilanes, allowing the construction of more complex scaffolds not readily available through more traditional routes. The synthesized acylsilanes were then engaged in the synthesis of 2-substituted and even 2,4-disubstituted pyrroles, and perhaps substituted dihydrothiophenes. Particularly, the carbene-generating ability of acylsilanes was successfully validated which can be introduced into more powerful synthetic applications. It is worth emphasizing the fact that the synthetic potential of the acylsilanes **II-3** obtained in this work open up numerous opportunities for many other transformations.

## 2.6 References

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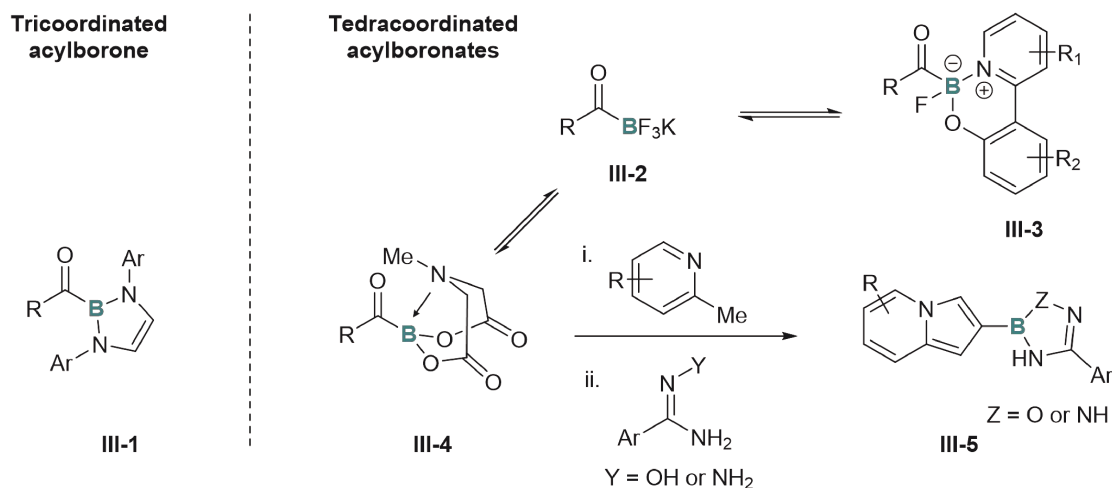
## Chapter III. The xanthate chemistry of acyl (MIDA)boronates

### 3.1 Introduction

Acylboranes and acylboronates are an intriguing class of compounds that are promising for various fields of chemistry, ranging from organic synthesis to pharmaceuticals<sup>[1]</sup>. The unique carbonyl compounds with  $sp^2$  hybrid carbon atoms on the carbonyl group directly attached to the boron atom and oxygen atom have attracted widespread attention<sup>[2, 3]</sup>. Acylborons have been proposed as reactive intermediates in many transformations<sup>[4]</sup>, but their remarkable properties and reactivities for synthesis have only recently been recognized due to that the assumed instability of acylborons hampered both isolation and characterization of these molecules. Indeed, in 2005, Stevenson stated that “no verified examples of acylborons derivatives had ever been prepared and theoretical calculations indicated that acylboranes are highly active species and apt to rearrangement”<sup>[5]</sup>.

In the past decades, much effort has been devoted to investigating both their preparation and synthetic utility in organic chemistry. The four most common acylboranes subclasses, such as compounds **III-1** to **III-4**, have recently emerged as highly promising organoboron compounds profiting from their remarkable stability and high reactivities (Scheme 3-1). Those are NHC-stabilized acylboranes **III-1**, potassium acyltrifluoroborates **III-2**, monofluoroacylboronates **III-3**<sup>[6]</sup> and acyl(MIDA)boronates **III-4**. For instance, acyl(MIDA)boronates **III-4** react with 2-methylpyridines and then hydrazonamides to furnish the novel heterocyclic compound **III-5** by condensation-driven reactions<sup>[7]</sup>. Many other interesting possibilities for their use were developed, while the number of routes to access acylboranes are relatively limited.





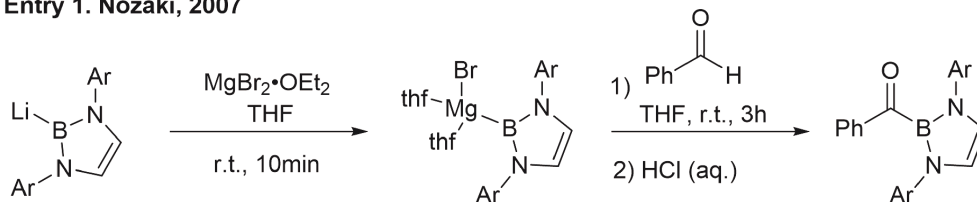
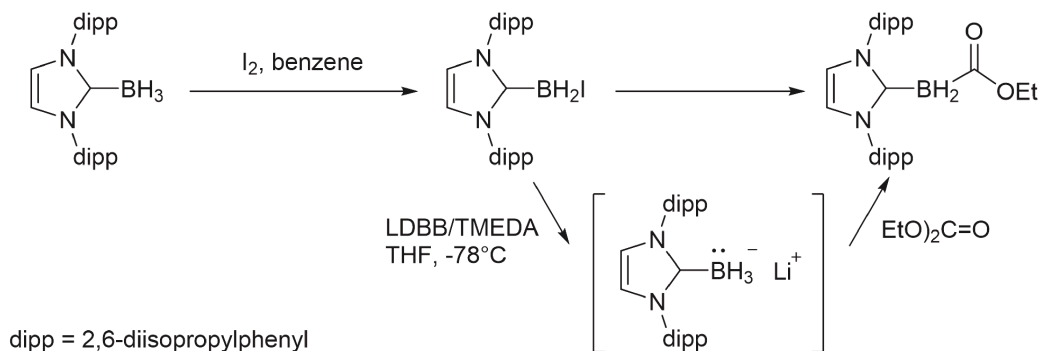
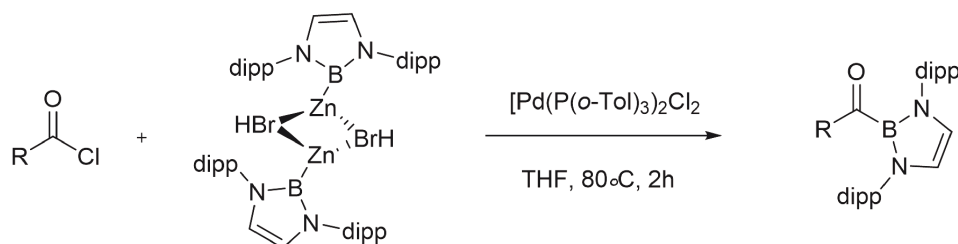
Scheme 3-1. The most common acylboranes subclasses.

## 3.2 Main routes to acylboranes

### 3.2.1 Synthesis of NHC-stabilized acylboranes

The potential chemical properties of acylboranes were postulated as early as the 1960s<sup>[8]</sup>. However, it was not until 2007 that Nozaki and co-workers<sup>[9]</sup> first isolated and fully characterized an acylborane compound, involving the formation of a boryl anion, which reacts with Grignard reagent to access the corresponding boryl magnesium compound. By further reacting with benzaldehyde in the presence of aqueous HCl, the amino-stabilized acylborane (N-heterocyclic carbene acylborane, NHC acylborane) was afforded in a moderate yield (Entry 1, Scheme 3-2).

After three years, in 2010, Curran and co-workers<sup>[10]</sup> proposed a new method to NHC acylboranes, starting from the iodization of unsubstituted NHC borane to access the NHC-boryl iodide, which was then reduced by a strong reductant LDBB in the presence of TMEDA to the corresponding highly reactive boryl lithium intermediate. The formed lithiated boryl anion was finally trapped with electrophiles, such as diethyl carbonate, to furnish a series of NHC-stabilized acylboranes (Entry 2, Scheme 3-2).

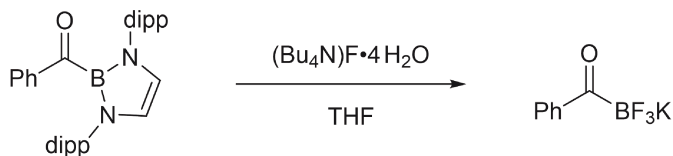
**Entry 1. Nozaki, 2007****Entry 2. Curran, 2010****Entry 3. Aldridge, 2015**

Scheme 3-2. Synthesis of NHC-stabilized acylboranes

In 2015, based on Nozaki's work, Aldridge and co-workers<sup>[11]</sup> reported firstly a catalytic method to prepare NHC-stabilized acylboranes. In their practice, palladium-catalyzed borylation chemistry proved to be feasible for constituting a practical methodology for C-B bond formation. A stable bis(boryl)zinc reagent was synthesized and introduced to react with acyl chlorides by palladium-catalyzed cross-coupling reaction. A wide variety of acylboranes were obtained in high yields (Entry 3, Scheme 3-2).

The successful synthesis and isolation of NHC-stabilized acylboranes became the first verified example. Unfortunately, these acylboranes were found to be chemically inert, perhaps due to the bulky heterocyclic structure on boron atom, which limited their subsequent applications for synthesis. Only one representative example relies on the

reaction of benzoylborane with  $(\text{Bu}_4\text{N})\text{F}\cdot 4\text{H}_2\text{O}$  in THF to the corresponding acyltrifluoroborate, which was more useful for many transformations in organoboron chemistry (Scheme 3-3).

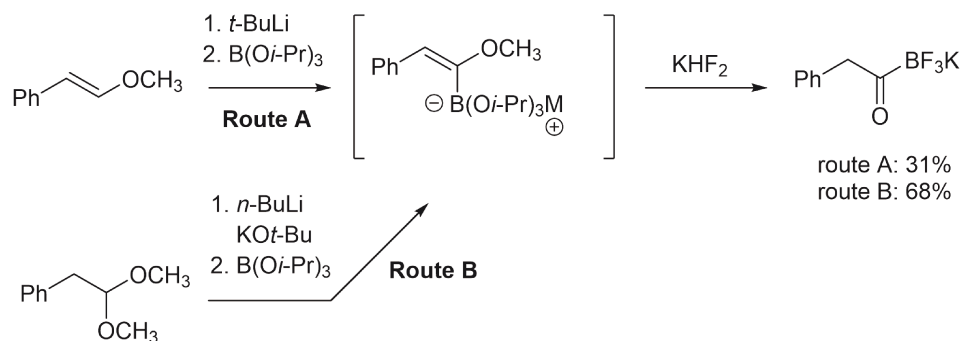


Scheme 3-3. Conversion of NHC-stabilized acylboranes

### 3.2.2 Synthesis of potassium acyltrifluoroborates

The synthesis of the first stable potassium acyltrifluoroborate (KAT) was reported by Molander and co-workers in 2010<sup>[12]</sup>. They are air- and moisture-stable and remarkably tolerant of strong oxidative conditions. To avoid destructive rearrangement, this strategy relies on the carbonyl formation simultaneously with that of the trifluoroborate through the deprotonation of (E)-(2-methoxyvinyl)benzene with organolithium reagent, followed by quenching with triisopropyl borate and treatment with  $\text{KHF}_2$  (Route A, Scheme 3-4). The intermediate enol ether “ate” complex can also be accessed by metalation of dimethoxy acetal with organolithium reagent in the presence of potassium *t*-butoxide as base (Route B, Scheme 3-4).

Molander, 2010



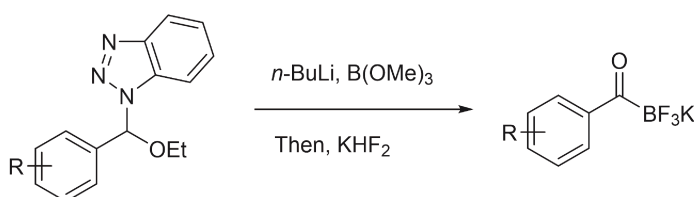
Scheme 3-4. First synthesis of potassium acyltrifluoroborates

Shortly afterwards, in 2012, Bode and co-workers exploited a more general method to furnish KATs from benzotriazole-ethoxy *N,O*-acetals, based on the consideration that an

ideal starting material for acyltrifluoroborate would be an acyl anion equivalent which is readily deprotonated<sup>[13]</sup>. The generated anion from *N,O*-acetals is quenched with  $B(OMe)_3$  followed by the addition of aqueous  $KHF_2$  to access the target molecules. A broadened substrate scope for KATs was developed following this strategy (Entry 1, Scheme 3-5).

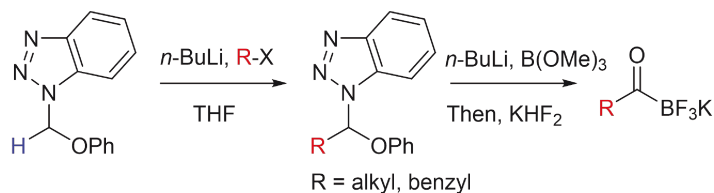
**Bode, 2012**

Entry 1 Benzoyltrifluoroborates



Benzotriazole-ethoxy  
*N,O*-acetals

Entry 2 Non-benzoyl acyltrifluoroborates



R = alkyl, benzyl

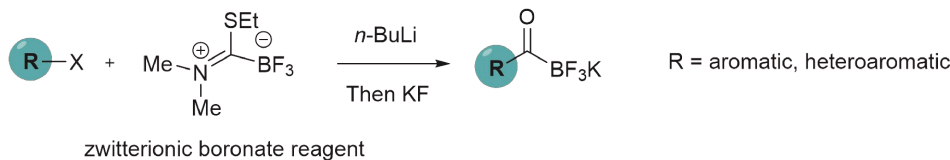
Scheme 3-5. Potassium acyltrifluoroborates from *N,O*-acetals

Having demonstrated that *N,O*-acetals could be used as acyl anion equivalents leading to acyltrifluoroborates, non-benzoyl products were prepared by replacing ethoxy with phenoxy<sup>[14]</sup>, which allowed the lithiation of alkyl-substituted *N,O*-acetals, and further fluorination/hydrolysis (Entry 2, Scheme 3-5). However, the reaction conditions and the use of  $KHF_2$  restricted the structure of the prepared KATs to a small class and many substrates, such as molecules containing basic nitrogen atom or esters were excluded.

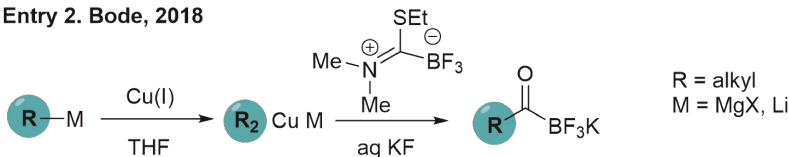
In addition to this procedure, in 2014, Bode and co-workers<sup>[15]</sup> revealed a novel synthetic strategy relying on introducing a new zwitterionic boronate reagent, which was prepared by *S*-alkylation of thioformamide trifluoroborate as an internal salt of the trifluoroborate anion and dimethyliminium cation. This method starts from the lithiation of aryl- and heteroaryl-halides followed by reacting with the acylboron transfer reagent to

furnish a range of KATs with different functional groups, such as aromatic nitro compounds, nitriles and pyridine-derived acyltrifluoroborates (Entry 1, Scheme 3-6).

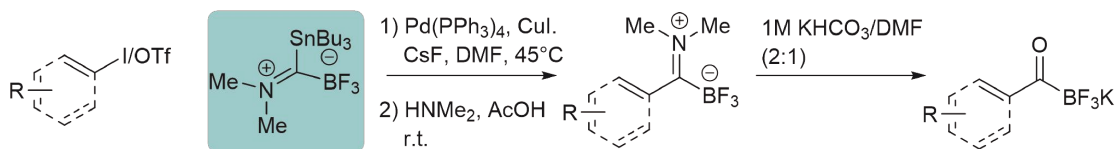
**Entry 1. Bode, 2014**



**Entry 2. Bode, 2018**



**Entry 3. Bode, 2019**

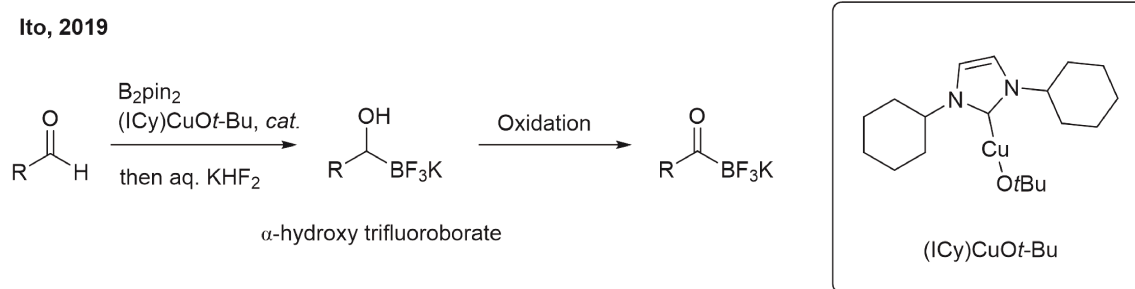


Scheme 3-6. Synthesis of new KATs

In 2018, the scope of this strategy was extended to allow the synthesis of alkyl substituted KATs<sup>[16]</sup>. Inspired by the selective monoalkylation of thioiminium moieties with organocuprates, the addition of organocuprates, generated by the transmetalation of *n*-butylmagnesium chloride or *n*-butyllithium onto Copper(I) salts, to the same zwitterionic boronate reagent was attempted and successfully obtained an array of aliphatic KATs in good yields (Entry 2, Scheme 3-6).

Furthermore, in 2019, Bode and co-workers<sup>[17]</sup> embellished the zwitterionic boronate reagent by modifying the EtS- leaving group to the tributylstannane moiety, allowing this new acylboron transfer reagent to undergo palladium-catalyzed Stille coupling with aryl halides and vinyl triflates and a subsequent hydrolysis to afford the desired KATs. This procedure gives rise to the first catalytic method to prepare KATs that does not require the use of organolithium reagents (Entry 3, Scheme 3-6).

In the same year, Ito and co-workers<sup>[18]</sup> disclosed a more concise method to afford KATs in two steps from widely available aldehydes. This strategy began with the Cu(I)-catalyzed borylation of aldehydes, followed by treatment with  $\text{KHF}_2$  to access  $\alpha$ -hydroxy trifluoroborates, which was reported by Sadighi and co-workers<sup>[19]</sup>. The oxidation of  $\alpha$ -hydroxy trifluoroborates furnished the corresponding potassium acyltrifluoroborate, which was discovered and reported firstly by the Ito's group (Scheme 3-7).

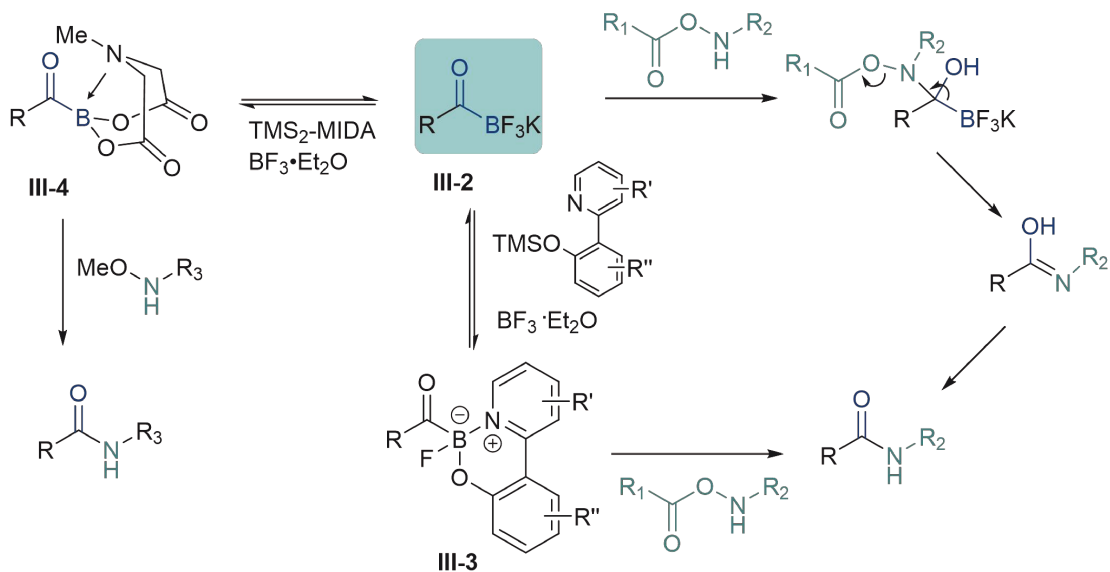


Scheme 3-7. Oxidation of potassium  $\alpha$ -hydroxy trifluoroborate

In summary, the emergence of KATs gave organic chemists more inspiration both for its applications in organoboron chemistry and synthesis of other new acylboranes. The amide-forming ligations of KATs with hydroxylamines was the most studied synthetic route in the last years<sup>[14a]</sup>. Acyltrifluoroborates were found to serve as surrogates for  $\alpha$ -ketoacids in amide-formation by reaction with hydroxylamines<sup>[14b]</sup>. This transformation was developed by the Bode's group that the chemoselective acylation of primary amines and primary amides with KATs under acidic conditions could also furnish amides and imides, respectively<sup>[14c]</sup>.

However, the variety of KATs was still limited and their applications in synthesis has remained limited. With the efforts of Bode and co-workers, KATs could be easily convert into monofluoro acylboronates **III-3**<sup>[6]</sup> and acyl(MIDA)boronates **III-4**<sup>[20]</sup> both in one step and found to possess even higher reactivity with hydroxylamines to give amides than KATs, especially the unique acyl(MIDA)boronates **III-4** (Scheme 3-8). Remarkably, acyl(MIDA)boronates are stable in air even after silica gel chromatography without the cleavage of C-B bond. Easier isolation means that it is better able to participate in more transformations. Therefore, tetracoordinated acyl(MID)boronates attracted a greater

interest in recent years both in their synthesis and applications to access other useful compounds.

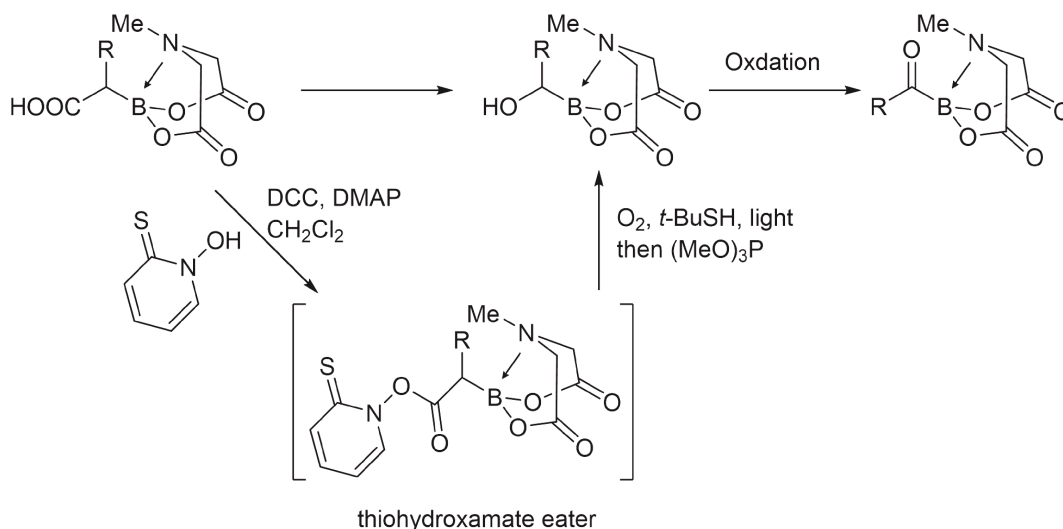


Scheme 3-8. Applications of KATs

### 3.2.3 Synthesis of acyl(MIDA)boronates

In 2012, Yudin and co-workers<sup>[21]</sup> reported a synthetic route to acyl(MIDA)boronates, starting first from the coupling of MIDA  $\alpha$ -borylcarboxylic acid with  $N$ -hydroxypyridine-2-thione to the corresponding thiohydroxamate ester, followed by taking advantage of Barton radical decarboxylative hydroxylation to afford the desired MIDA  $\alpha$ -hydroxyboronates. The resulting  $\alpha$ -hydroxyboronates were subsequently converted to acylboronates by oxidizing the alcohol function (Scheme 3-9).

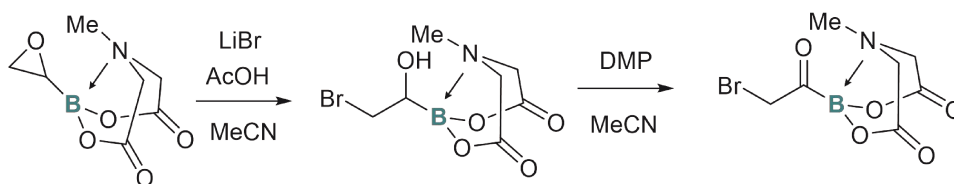
Yudin, 2012



Scheme 3-9. First synthesis of acyl(MIDA)boronates

Later, another significant acyl(MIDA)boronate synthesis was disclosed by Yudin and co-workers in 2020<sup>[22]</sup>. It involves bromoacetyl (MIDA)boronate. The presence of a bromo-substituent and an acyl group endows it with tremendous potential for subsequent transformations. The synthesis of bromoacetyl (MIDA)boronate starts from the ring-opening reaction of 2-MIDA (*N*-methyliminodiacetic acid) boryl oxirane with lithium bromide in the presence of acetic acid to  $\alpha$ -bromomethyl alcohol, followed by Dess-martin oxidation of the alcohol to provide the corresponding bromoacetyl (MIDA)boronate in a good yield (Scheme 3-10).

Yudin, 2020



Scheme 3-10. Synthesis of bromomethyl acyl(MIDA)boronate

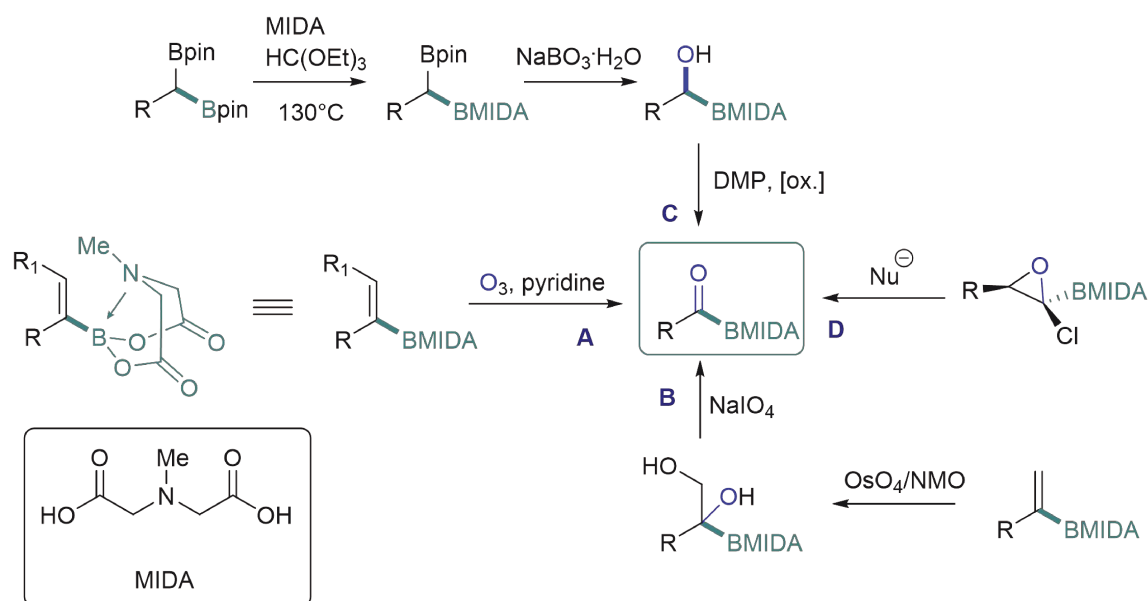
In 2017, Bode, Ito, and co-workers<sup>[23]</sup> reported a concise acylboron synthesis by the ozonolysis of alkenyl (MIDA)boronates in the presence of pyridine under mild reaction conditions (Route A, Scheme 3-11). In the same year, Perrin and co-workers<sup>[24]</sup> described



a two-step pathway in which the reactivity of olefins played a crucial role, whereby an alkenyl-2-boronateMIDAester undergoes dihydroxylation to the corresponding diol compound under standard conditions of the well-known Upjohn process, followed by the oxidative diol cleavage with NaIO<sub>4</sub> to furnish the desired acyl(MIDA)boronates (Route B, Scheme 3-11).

In 2019, Sharma and co-workers<sup>[25]</sup> disclosed a modular approach to acyl(MIDA)boronates, starting from regioselective dihydroborylation of terminal alkynes or alkenes to a symmetrical geminal diborylalkanes, followed by conversion of one of the pinacol boronic ester (Bpin) groups to B(MIDA) by heating with MIDA and (EtO)<sub>3</sub>CH. Subsequent chemoselective oxidation of the remaining Bpin group in the presence of NaBO<sub>3</sub>·H<sub>2</sub>O into hydroxy group gives the corresponding α-hydroxy (MIDA)boronates, which were then oxidized by DMP to the desired acyl(MIDA)boronates (Route C, Scheme 3-11).

The newest approach for synthesizing acyl(MIDA)boronates was reported by Wang and co-workers in 2019<sup>[26]</sup>, through the nucleophilic ring-opening reaction of α-chloroepoxyboronates (Route D, Scheme 3-11).



Scheme 3-11. Synthesis of acyl(MIDA)boronate

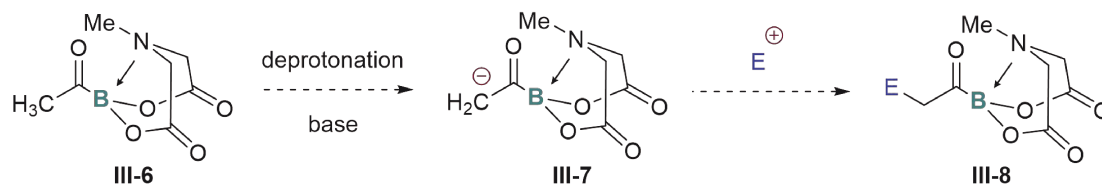
Overall, after ten years of efforts, acyl(MIDA)boronates have become one of the most attractive acylboron derivatives due to both their remarkable reactivity and wide applications. Besides, the mild reaction conditions in most applications are also noteworthy. However, the molecular structures of acyl(MIDA)boronates accessible by the reported methods are generally relatively simple and devoid of complex functional substituents. Radical reactions have proven to be powerful tools in organic synthesis in general, but still rare in the case of acyl(MIDA)boronates, with the notable exception of the Barton decarboxylation exploited by Yudin as detailed above.

### 3.3 Experimental design of this project

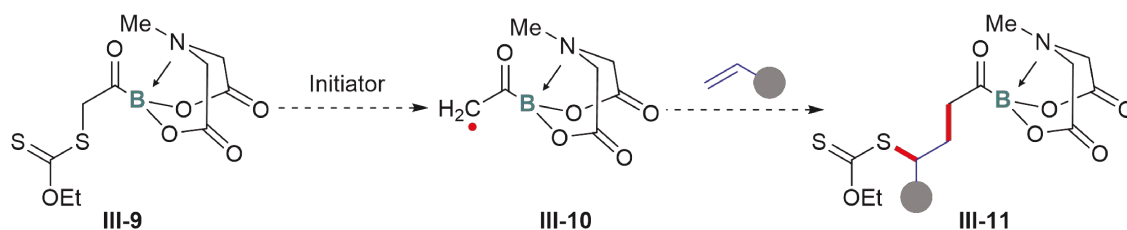
Of all the reported approaches, only the strategy developed by Bode and co-workers involves an acylboron anion equivalent<sup>[16]</sup>, but for the same reason, the requirement of organolithium reagent limited its applications in some cases. In support of this line of thinking, the formation of an acylboron enolate such as compound **III-7** and its capture with an electrophile would seem to be an optimal path to access various acyl(MIDA)boronates. However, in fact, this hypothesis has not yet been reported, probably due to the incompatibility of acylboronates **III-6** with strong basic conditions, which is indispensable for generating the corresponding enolates **III-7** (Scheme 3-12a).

In terms of radical chemistry, the initial radical **III-10** spontaneously comes into our view in that it could be easily generated by the xanthate method and implicated in synthetically widespread transformations. In our group's previous work, xanthates proved to be quite effective for producing a number of acetyl radicals. If so, the active radical **III-10** could thus undergo many reactions, especially radical additions to non-activated alkenes to furnish a series of adduct **III-11**. In this way, the focus of this project switched to the synthesis of  $\alpha$ -xanthyl acetyl(MIDA)boronate **III-9** and its behavior in subsequent transformations (Scheme 3-12b).

a) Alkylation of the enolate of acyl (MIDA) boronate - **So far unreported**

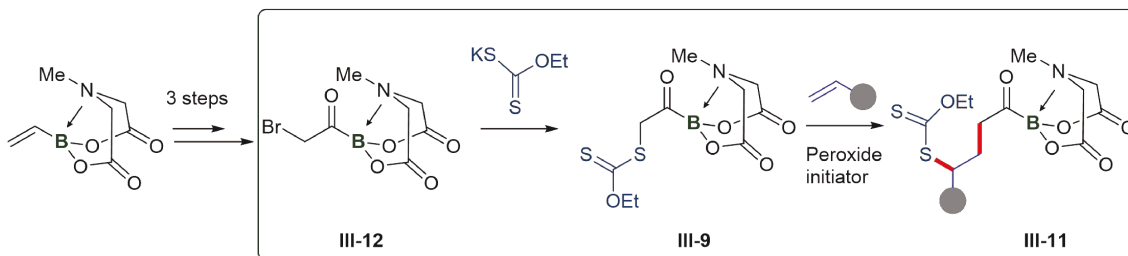


b) Generation and capture of the acyl (MIDA) boronate radical - **This work**



Scheme 3-12. Anion and radical derived from acetyl (MIDA)boronate

Our synthesis starts from the bromoacetyl (MIDA)boronate **III-12**, reported by Yudin and co-workers<sup>[22]</sup>, and its reaction with potassium *O*-ethyl xanthate to furnish the corresponding xanthate **III-9**. We are then pleased to take advantage of the xanthate radical addition-transfer process, through the radical addition of xanthate **III-9** with alkenes bearing different functional groups in the presence of an initiator to produce a broad range of acyl(MIDA)boronates **III-11**. Besides, it's worth noting that adducts **III-11** also bear a xanthate group, which could be exploited in many ways, such as reduction and numerous non-radical reactions associated with sulfur (Scheme 3-13).

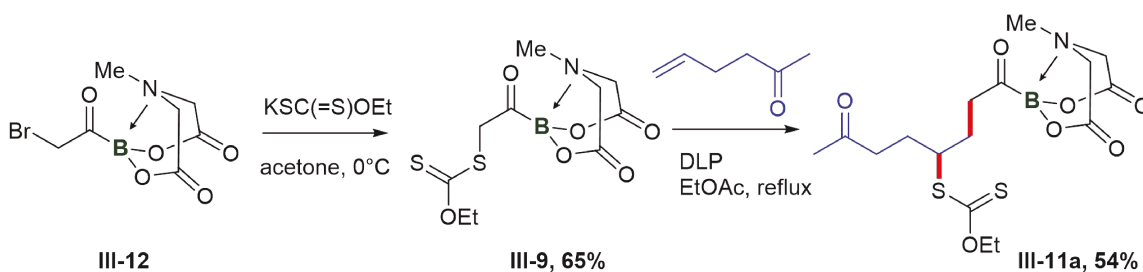


Scheme 3-13. Synthetic route of  $\alpha$ -xanthyl acyl(MIDA)boronate III-9

## 3.4 Results and Discussion

### 3.4.1 Initial attempts in the synthesis of xanthate III-9

The reaction of bromoacetyl (MIDA)boronate **III-12** with potassium *O*-ethyl xanthate was carried out at 0°C in acetone for 2.5h under nitrogen atmosphere and succeeded in obtaining the corresponding xanthate **III-9** in 65% yield. This fact encouraged us to investigate its reactivity with alkenes. The radical addition of xanthate **III-9** with the 5-hexen-2-one was then carried out at reflux in ethyl acetate, in the presence of dilauroyl peroxide (DLP) as initiator. Surprisingly, the reaction went smoothly and afforded the corresponding adduct **III-11a** in 55% yield (Scheme 3-14). Compound **III-11a** was purified by silica gel chromatography and its structure was characterized by NMR, FTIR and HPLC-MS.



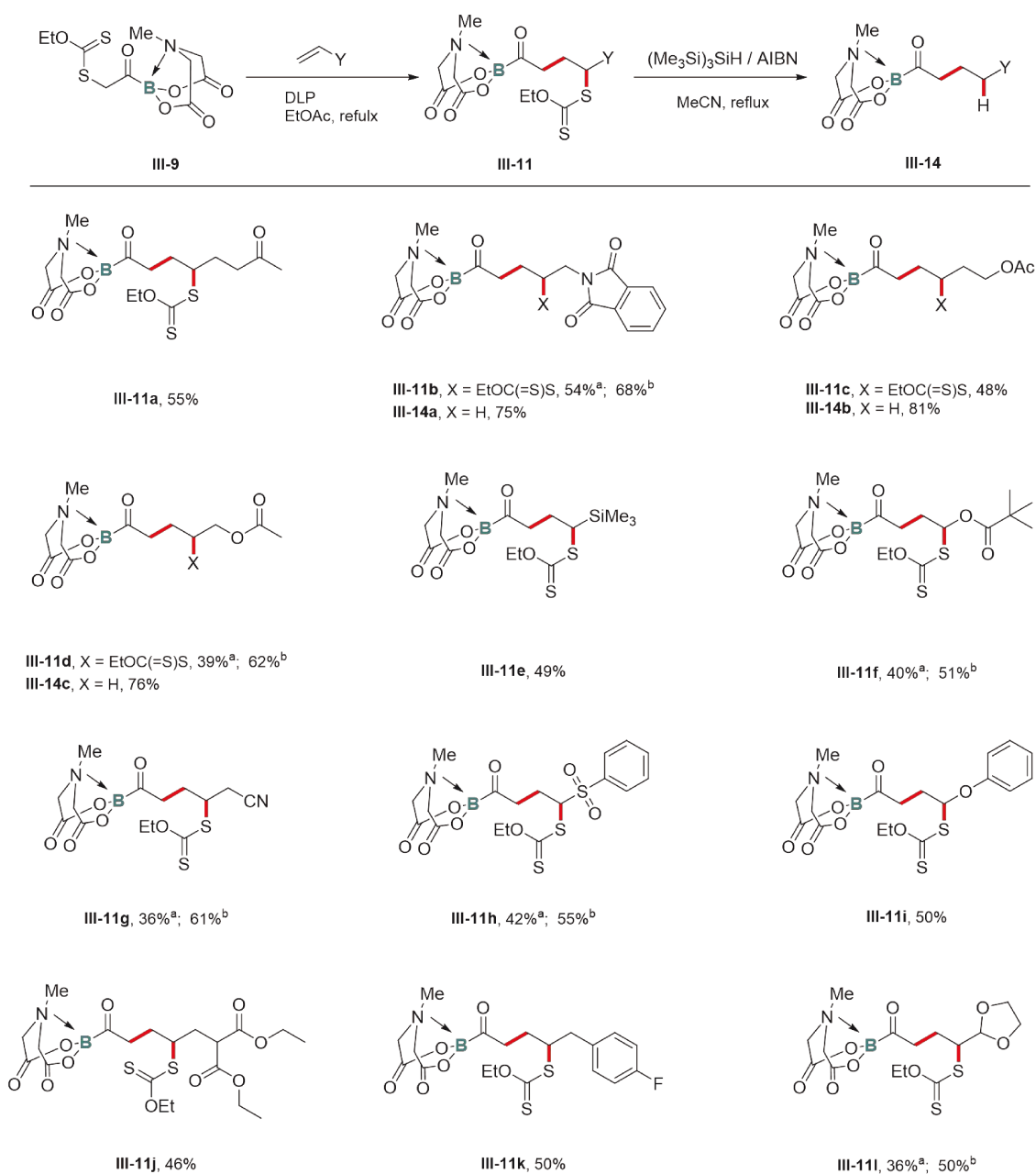
Scheme 3-14. Initial attempts in synthesis of xanthate III-9 and adduct III-11

Thus, a versatile route to access numerous acyl(MIDA)boronates by xanthate radical addition-transfer process appeared feasible. The mild reaction conditions, concise synthetic path and configurational stability constitute a novel convenient route for the synthesis of organoboron compounds. These preliminary results also encouraged us to explore further the functional group tolerance for this reaction.

### 3.4.2 Scope of alkenes

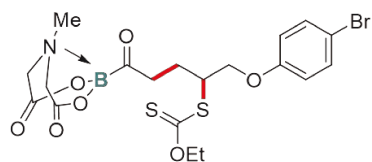
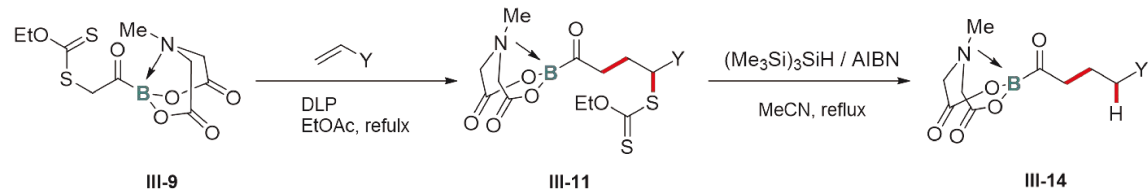
We next investigated the scope of the addition reaction with respect to the alkenes. Various olefin partners bearing different functional groups were introduced in additions with xanthate **III-9** to furnish an array of adducts **III-11**, which were purified by column chromatography. All the synthesized acylboronate compounds **III-11** are stable at room

temperature, air, and the mild acidity of the silica gel. However, we observed that adducts **III-11** rapidly decomposed in alcoholic solvents such as methanol.

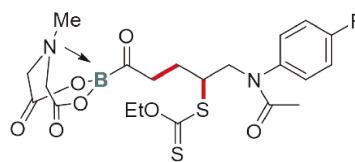


Condition **a**) 0.2 equiv DLP added every 2h(0.4-0.6 equiv in total); reaction time ca 4-6h.  
Condition **b**) 0.05 equiv DLP added every hour(0.4 equiv in total); reaction time ca 9-12h.

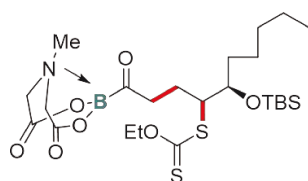
Scheme 3-15a. Scope of olefin for the addition reaction



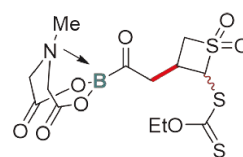
**III-11m**, 46%



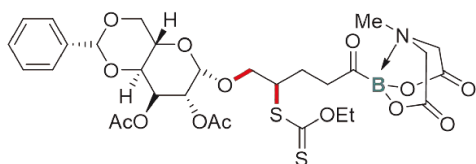
**III-11n**, 46%



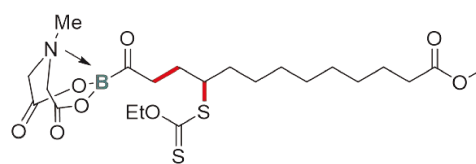
**III-11o**, 49%; d.r. = 1:0.5



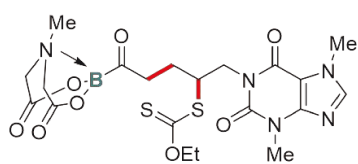
**III-11p**, 45%; d.r. = 1:0.3



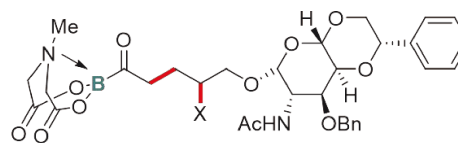
**III-11q**, 37%; d.r. = 1:1



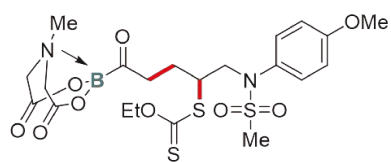
**III-11r**, 47%



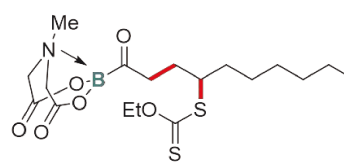
**III-11s**, 51%



**III-11t**, X = EtOC(=S)S, 46%; d.r. = 1:0.3  
**III-14d**, X = H, 69%



**III-11u**, 52%



**III-11v**, 58%

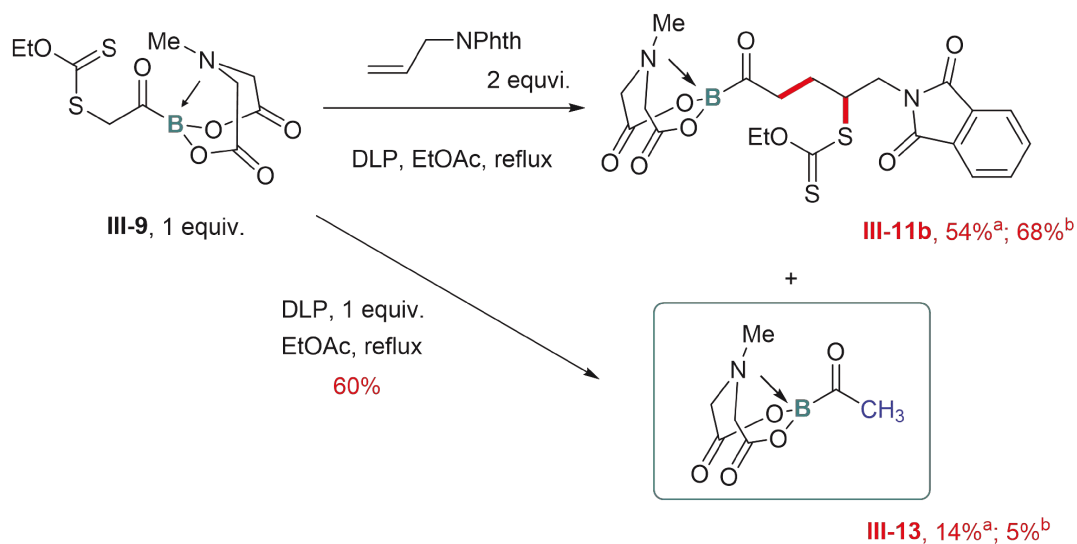
Condition a) 0.2 equiv DLP added every 2h(0.4-0.6 equiv in total); reaction time ca 4-6h.  
 Condition b) 0.05 equiv DLP added every hour(0.4 equiv in total); reaction time ca 9-12h.

Scheme 3-15b. Scope of olefin for the addition reaction

The results were satisfactory, acylboronates bearing different substituents were synthesized in good yields. Alkyl, esters, sulfones, and heterocycles are tolerated. More complex scaffold, for instance, compound **III-11e**, contains a borane moiety and a silane moiety. Glucose derivatives **III-11q** and **III-11t**, caffeine derivative **III-11s** are readily synthesized. Note that compound **III-11p** constitutes an interesting rigid building block. For compound **III-11f**, the isolated yield was comparable when performed on a gram scale (5mmol scale), demonstrating the stable reactivity of the xanthate **III-9** (Scheme 3-15). In the case of adducts (**III-11o**, **III-11p**, **III-11q**, and **III-11t**), the diastereoselectivity is as expected low. The low diastereoselectivity is due to the high rate of the xanthate transfer and its low sensitivity to steric effects.

In order to characterize the molecular structure of the adducts more easily and to eliminate the presence of diastereoisomers due to the xanthate without harm to the other functional groups, several of adducts **III-11** were reductively dexanthylated with tris(trimethylsilyl)silane and AIBN to give compounds **III-14** in a very high yield. Thus, the acylMIDA boronate moiety was efficiently attached to the functional alkenes by creating a new C-C bond.

After extending the olefin scope, we noticed that the isolated yield of adducts **III-11** was unexpectedly low under the usual conditions (Scheme 3-15, condition **a**) in a few cases. For instance, the radical addition of xanthate **III-9** to allyl acetate and allyl cyanide produced adducts **III-11d** and **III-11g** in 39% and 36% yield, respectively. In order to improve the yield and get more information from this reaction, we reinspected the addition reaction carefully by using *N*-allyl phthalimide as an example, not only because of its excellent reactivity, but we hope that the bulky phthalimide group would simplify the tracking of the side products and allowing the obtention of a better mass balance for this reaction.



- a) 0.2 equiv DLP added every 2h (0.4-0.6 equiv in total); reaction time ca 4-6h.  
 b) 0.05 equiv DLP added every hour (0.4 equiv in total); reaction time ca 9-12h.

Scheme 3-16 By-product derived from starting xanthate

The main side product was ultimately isolated in 14% yield. It did not contain any phthalimide group and turned out to be compound **III-13**. The intermediate radical **III-10** had in fact captured a hydrogen presumably from solvent (Scheme 3-16, condition **a**). This compound is obviously generated from the starting xanthate **III-9** and its formation indicates perhaps an excessively high flux of radical **III-10** during the addition process, which gives more opportunity for unwanted radical reaction, such as the formation of compound **III-13**. Indeed, mixing xanthate **III-9** with a stoichiometric amount of DLP resulted compound **III-13** in 60% yield. In the light of these observations, we then reduced the flux of radicals in the reaction process by adding the peroxide initiator in smaller amounts over a longer period of time (Scheme 3-16, condition **b**). Under the modified conditions, the isolated yield of adduct **III-11a** increased to 68% while the isolated yield of side product **III-13** decreased to 5%. We also reexamined the addition of xanthate **9** onto several alkenes under condition **b**, and all noted a similar increase. The yield of **III-11d**, **III-11f**, **III-11g**, **III-11h** and **III-11i** increased significantly from 39%, 40%, 36%, 42%, and 36% to 62%, 51%, 61%, 55%, and 50%, respectively. Thus, a broad range of acyl(MIDA)boronates were obtained in useful yields in this way. Furthermore, by taking advantage of the rich xanthate chemistry, a variety of useful transformations of those adducts could be explored to furnish a large array of valuable compounds.

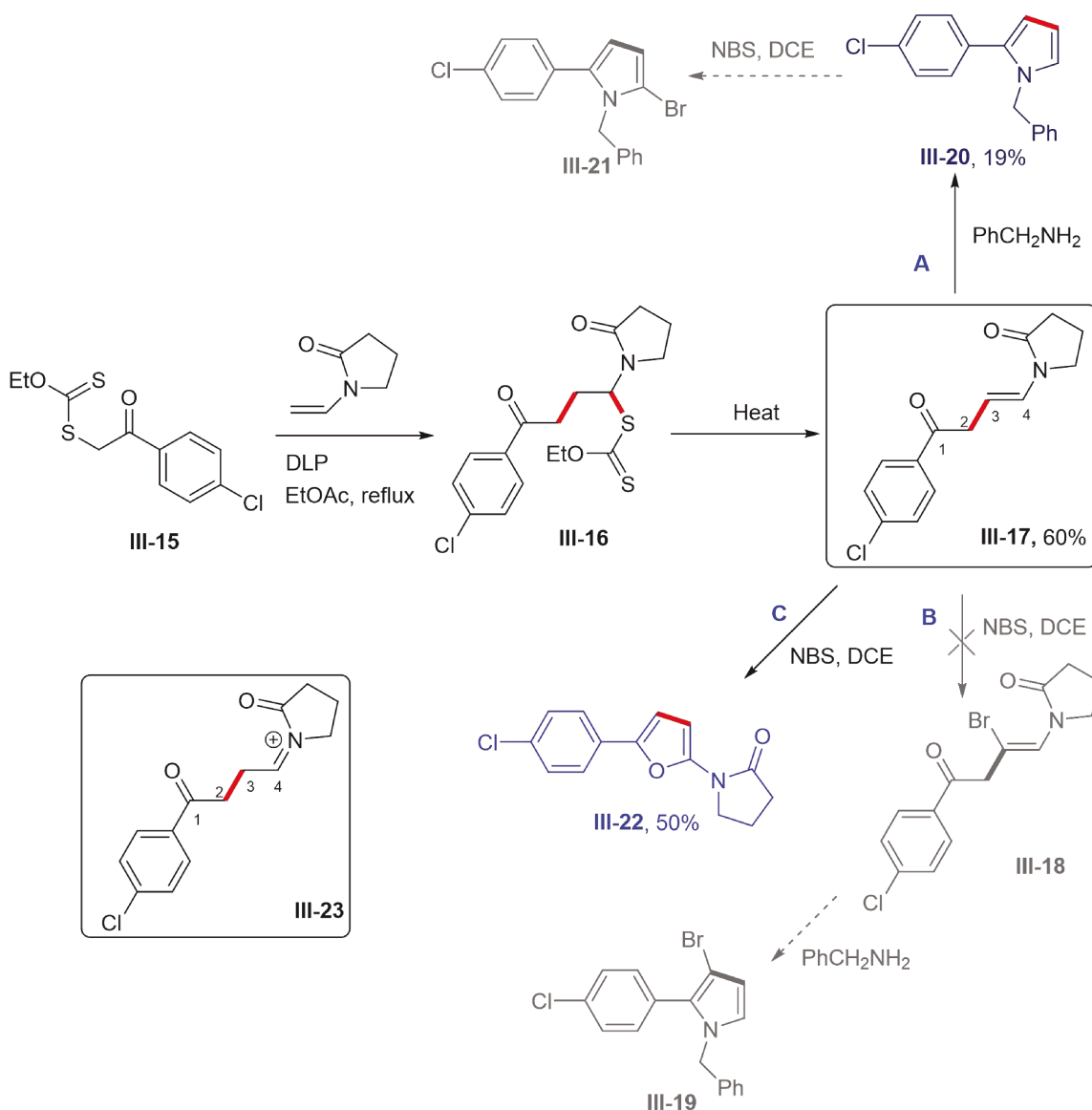


### 3.4.4 Subsequent transformations of adduct **III-11**

#### 3.4.4.1 Preliminary attempts

With a series of acyl(MIDA)boronates in hand, we then turned our attention to probe their synthetic utility. The broad functional group tolerance translates into the ability of combining the acyl(MIDA)boronate motif with various other groups, thus offering a number of possibilities for subsequent transformations. For instance, pyrroles are important compounds found in many biologically active and valuable natural and pharmaceutical products<sup>[27]</sup>. By taking advantage of the Paal-Knorr pyrrole synthesis, 1,4-diketones and, more generally, 1,4-dicarbonyls are ideal substrates for the synthesis of valuable five-membered carbo- and heterocycles such as pyrroles or furans by condensation with amines or catalysis under acid condition, respectively<sup>[28]</sup>.

The feasibility of the synthetic strategy to access pyrrole compounds was evaluated by using a common xanthate **III-15**. First, xanthate **III-15** was subjected to addition with *N*-vinyl pyrrolidone to afford adduct **III-16**, which spontaneously eliminates xanthic acid to give enamide **III-17** upon heating in 60% yield<sup>[29]</sup>. Similarly, enol-keto tautomerism enamide **III-17** could also tautomerize with acyliminium **III-23**. The latter could be viewed as a 1,4-dicarbonyl analogue and in principle engage in a similar condensation with primary amines by analogy with the Paal-Knorr reaction<sup>[30]</sup>. To our delight, pyrrole compound **III-20** was obtained smoothly although the isolated yield was unexpectedly low in 19% yield (Route A, Scheme 3-18).



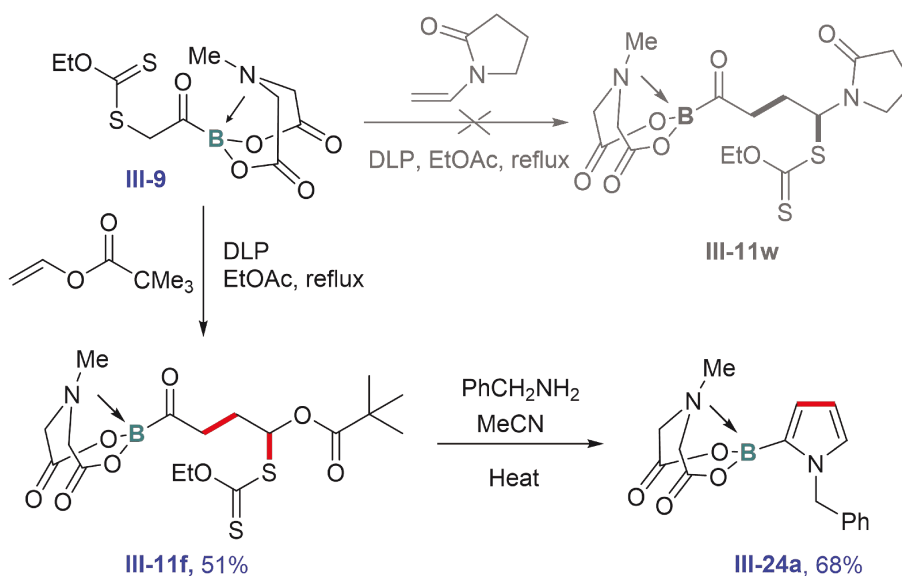
Scheme 3-18. Pyrrrole synthesis of xanthate **III-15**

On the other hand, the chemo-selective bromination of compound **III-17** with NBS (*N*-Bromosuccinimide) should theoretically furnish the corresponding bromoenamide **III-18**, which could be condensed with benzylamine to access pyrrole **III-19** (Route B, Scheme 3-18). However, the reaction of compound **III-17** with NBS directly gave furan **III-22** in 50% yield bearing a pyrrolidine and a chlorophenyl on C-1 and C-4, respectively (Route C, Scheme 3-18). Since we have gotten enough information from these initial attempts that pyrrole or furan compounds could be synthesized by following

this strategy, we then focused on the behavior of adducts from xanthate **III-9** to see if pyrroles maintaining a (MIDA)boronate motif could be prepared in this way.

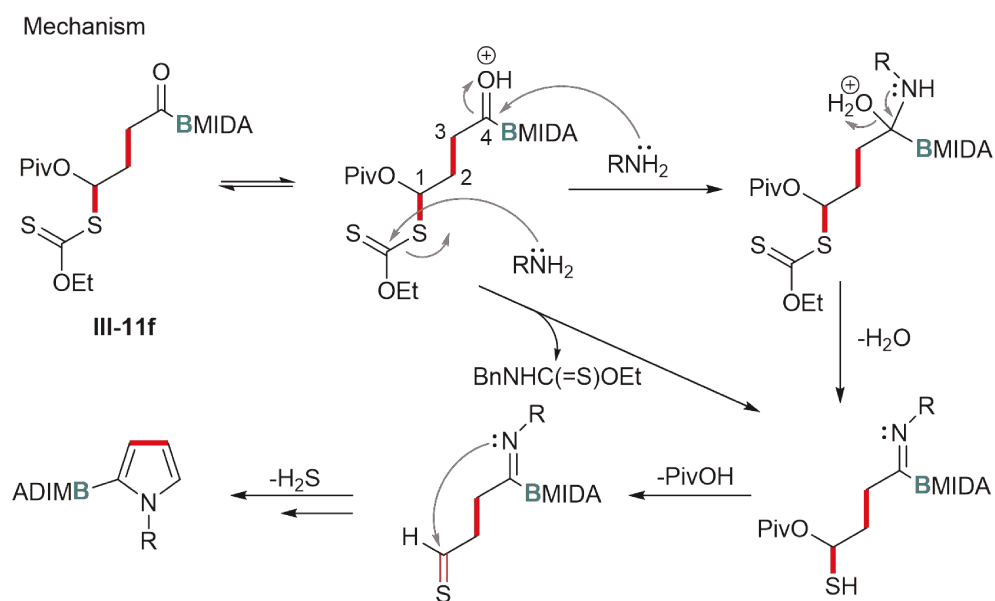
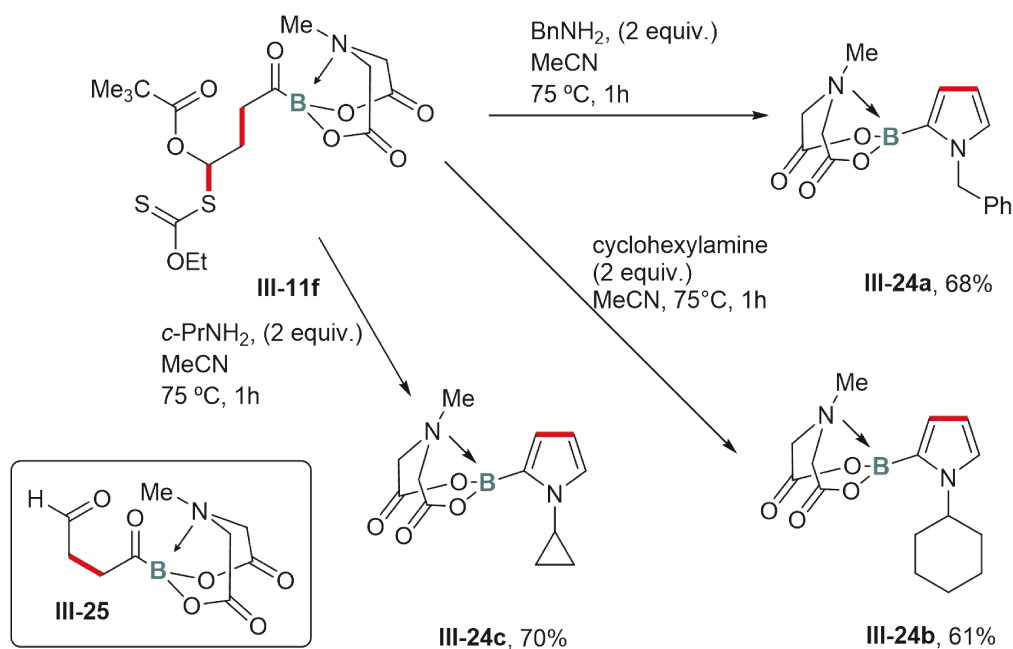
#### 3.4.4.2 Synthesis of 2-pyrrolyl (MIDA)boronates

In the same manner, xanthate **III-9** was reacted with *N*-vinyl pyrrolidone. But, to our disappointment, this addition reaction gave a complex mixture and no desired adduct **III-11w** was found. Thankfully, the addition of xanthate **III-9** onto vinyl private successfully gave adduct **III-11f**, as a synthetic equivalent to adduct **III-11w**. In principle, adduct **III-11f** can also be viewed as a latent form of 1,4-ketoaldehyde **III-25** and therefore subject to the condensation with primary amines by analogy with the Paal-Knorr pyrrole synthesis<sup>[30]</sup>. The result was satisfactory, pyrrole **III-24a** bearing a B(MIDA) group on C-2 was obtained in 68% yield (Scheme 3-19A).



Scheme 3-19A. Synthesis of 2-pyrrolyl (MIDA)boronates

Encouraged by these results, we then expanded the scope of amines that can be engaged to synthesize the corresponding pyrrole compounds. Therefore, pyrroles **III-24a-c** were prepared all in good yield by this strategy (Scheme 3-19B). Pyrrole **III-24c**, an intriguing and rare pyrrole, contains a cyclopropane ring attached to the nitrogen atom and a B(MIDA) sidechain.



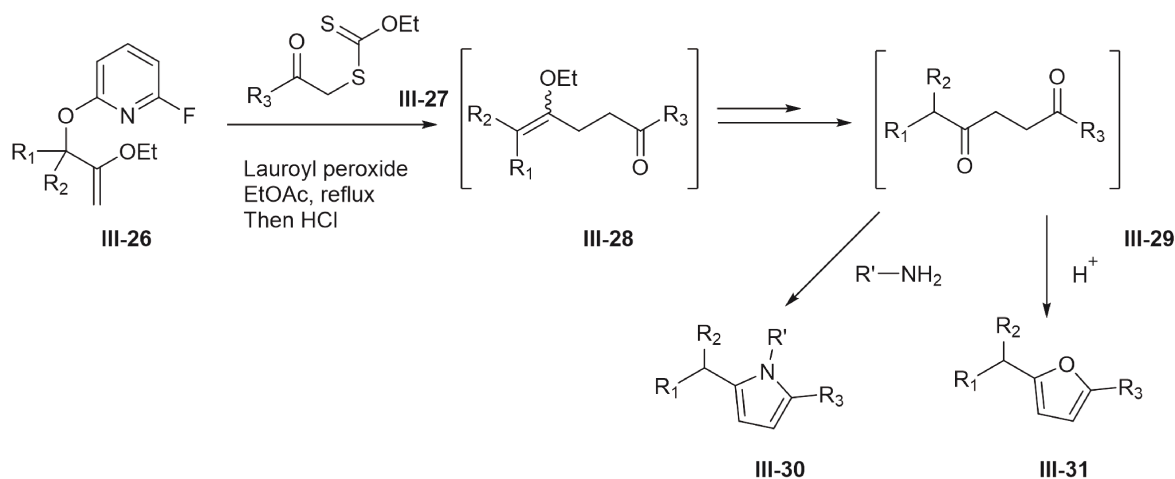
Scheme 3-19B. Scope of amine in the synthesis of 2-pyrrolyl (MIDA)boronates

A plausible mechanism for the pyrrole formation is outlined in Scheme 3-19B. The C-1 of compound **III-11f** which bears both the pivaloxy and xanthate group is at the oxidation level of an aldehyde. Based on this, exposing compound **III-11f** to an amine results the formation of imine intermediate by a condensation process. At the same time, aminolysis of the xanthate group gives the corresponding thiol group, which therefore converts into

the reactive thioaldehyde with loss of pivalic acid. The subsequent nucleophilic attack of the nitrogen furnishes the desired pyrroles **III-24** with loss of H<sub>2</sub>S.

### 3.4.4.3 Synthesis of furyl (MIDA)boronates

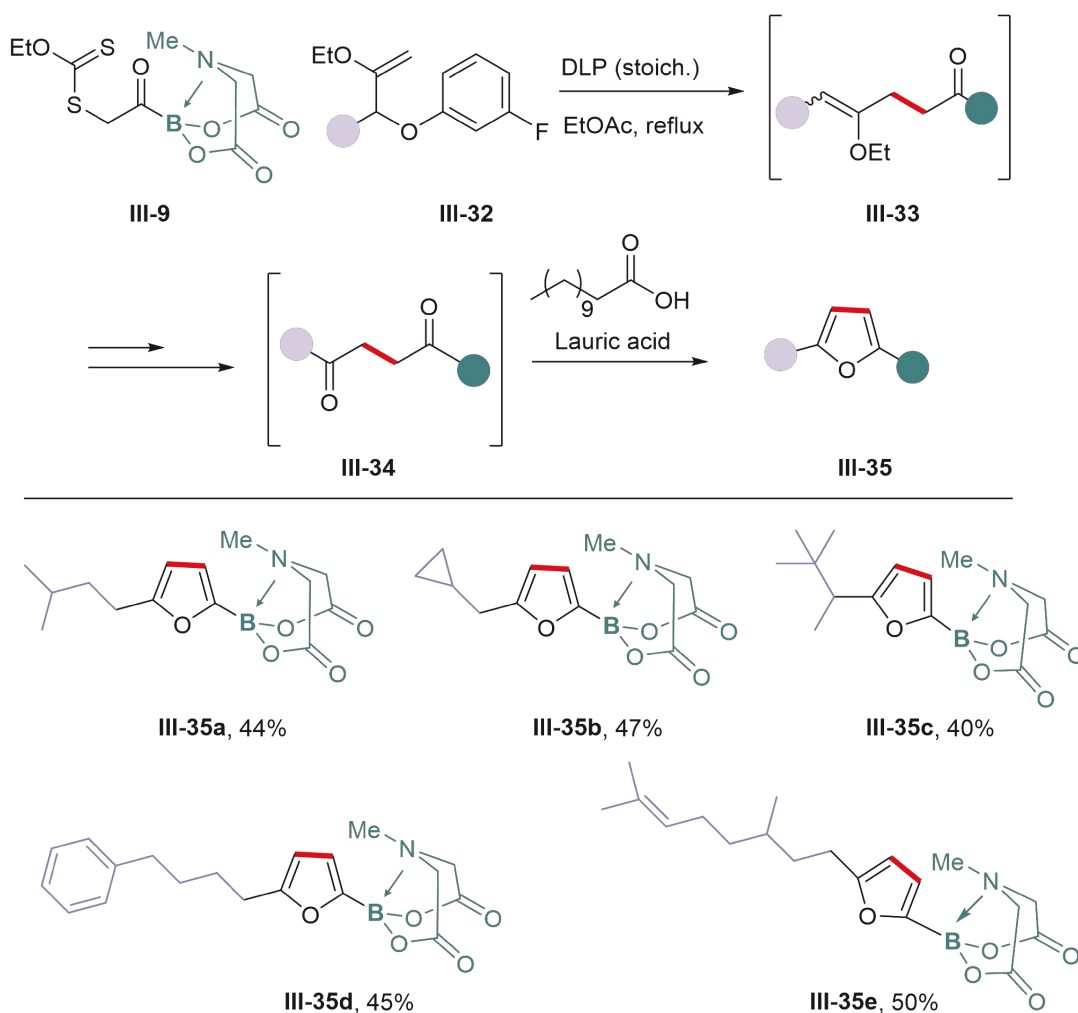
Having demonstrated the feasibility of a Paal-Knorr type synthesis of pyrrolyl (MIDA)boronates, we then tried to prepare another 1,4-dicarbonyl derivate equivalent. Based on previous work of our group<sup>[31]</sup>, compound **III-26**, containing a 6-fluoro-pyridine-2-oxy-moiety, reacts with radicals derived from xanthates **III-27** by an addition-fragmentation pathway to give a highly functionalized diketones **III-29** via intermediates **III-28**, which are regarded as a most standard 1,4-diketone substrate for the Paal-Knorr reaction to access pyrroles **III-30** or furans **III-31** (Scheme 3-20).



Scheme 3-20. Synthetic approach to functionalized diketones

Inspired by these results, we tested the addition-fragmentation reaction of xanthate **III-9** and enol ether partner **III-32** under the same conditions. The addition step is followed by  $\beta$ -scission of the fluoropyridinoxy group to give enol ether intermediates **III-33**. Interestingly, this reaction required the use of stoichiometric amounts of peroxide (DLP), which would co-produce lauric acid in the process of producing radicals. Surprisingly, we found that the lauric acid catalyzed *in situ* the ring-closure directly into furans **III-35** with loss of ethanol and the MIDA boronate moiety remaining intact (Scheme 3-21).

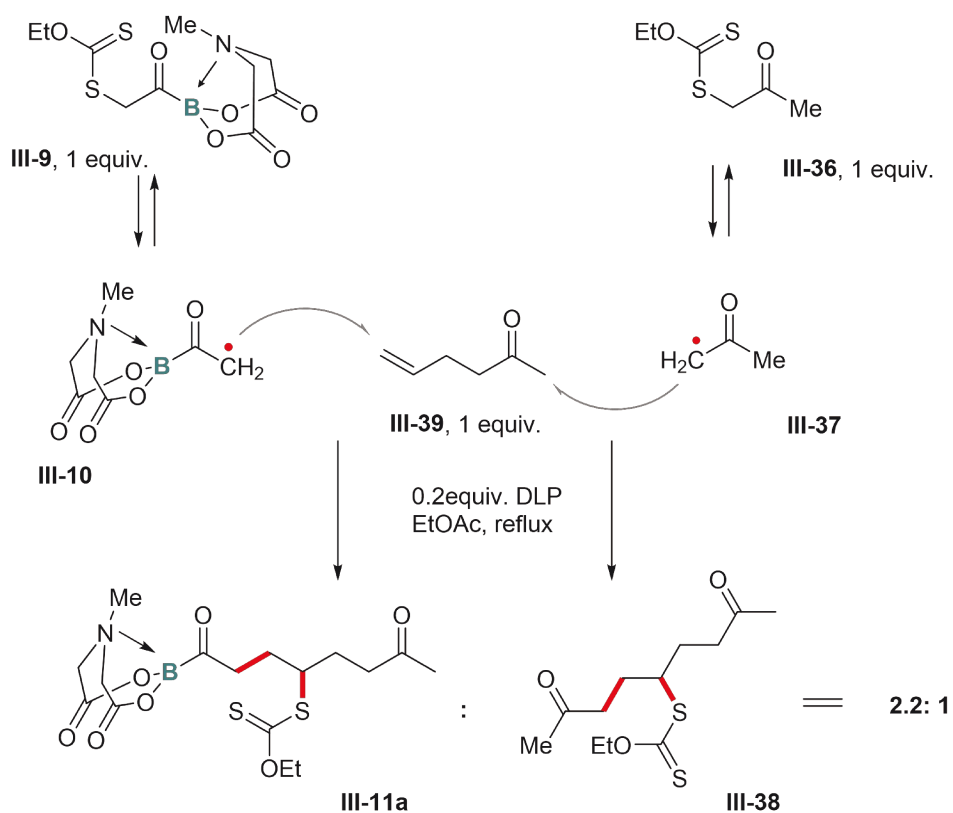
An array of furyl (MIDA)boronates were then swiftly prepared in useful yields by following this unique strategy. The side chains in these substrates **III-32** were readily extended through the addition-fragmentation procedure to the corresponding enol ether **III-35**. In summary, the addition of xanthate **III-9** to allylic fluoropyridinyloxy derivatives represents a highly versatile approach to access not only 1,4-dicarbonyls, but also in principle alkenyl sulfides, sulfones and alkenyl pinacolato- and MIDA boronates as shown with other xanthates<sup>[32]</sup>. Thus, the special radical addition-transfer process of xanthate **III-9** provides a number of strategies to furnish diverse useful compounds that are not readily accessible otherwise.



Scheme 3-21. Synthesis of furyl (MIDA)boronates

### 3.4.5 Reactivity of radical **III-10** derived from xanthate **III-9**

Finally, we evaluated the reactivity of radical **III-10** derived from xanthate **III-9** that was hitherto never studied by comparing it with the more common acetyl radical **III-37**. To clarify this topic, we performed the competition reaction depicted in Scheme 3-22 whereby one equivalent each of xanthate **III-9** and **III-36** and hexenone **III-39** were heated to reflux for 2h in the presence of 10% DLP as initiator. This reaction was not allowed to proceed to completion but stopped at around 50% conversion in order to limit the effect of the concentration on the result. In the event, radicals **III-10** and **III-37**, derived from xanthate **III-9** and **III-36** respectively, are all prone to irreversible addition to alkene **III-39** and then give rise to adducts **III-11a** and **III-38** in a molar ratio of 2.2: 1.



Scheme 3-22 Reactivity of radical **III-10**

This fact illustrated that either the addition of acylboron radical **III-10** with alkene **III-39** is faster than that of acetyl radical **III-37** or that the production rate of radical **III-10** is higher in the equilibrium through the fast exchange of the xanthate group than radical

**III-37**, and the amount of adduct **III-11a** produced reflects in turn the higher real-time concentration of radical **III-10**. The difference is, however, too small to allow attributing it to one factor or the other, or even both.

### **3.5 Conclusion**

In conclusion, this work developed a novel and reactive xanthate **III-9** as an acylboron transfer reagent for synthesizing various acyl(MIDA)boronates. Its remarkable reactivity and synthetic utility were underlined comprehensively. By taking advantage of xanthate addition-transfer processes, a series of acyl(MIDA)boronates were synthesized in good yields that could then be further transformed in certain cases into pyrroles and furans. Importantly, the mildness of the reaction conditions and broad tolerance for a variety of functional groups provide an array of new synthetic strategies for multifarious and rare acyl(MIDA)boronate compounds that are not readily accessible by other routes and confirm further the remarkable synthetic potential of xanthates.



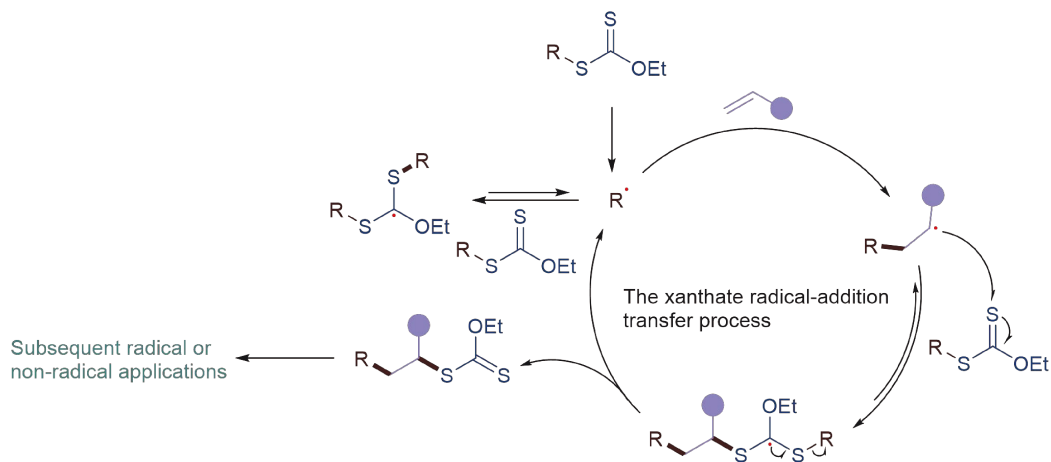
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## General Conclusion

In summary, a versatile route to acylsilanes and acyl(MIDA)boronates was developed in this work, involving the addition of radicals, derived from the corresponding xanthates, with non-activated alkenes. A series of functionalized acylsilanes and acyl(MIDA)boronates were synthesized by taking advantage of the xanthate radical-addition transfer process which are not readily available by other routes. The mild reaction conditions and broad tolerance for diverse functional groups allow the construction of more complex scaffolds. Furthermore, the obtained structurally enriched acylsilanes and acyl(MIDA)boronates can be engaged in large-scale radical or non-radical synthetic transformations.



Thus, this work demonstrates the remarkable reactivity of the xanthate transfer process, whereby structurally complex radicals can be produced from this process and maintained in the equilibrium through the fast exchange of the xanthate group. Importantly, these radicals are also remarkably reactive, and addition to diverse alkenes yields a wide variety of functionalized adducts in one step by creating a new C-C bond.

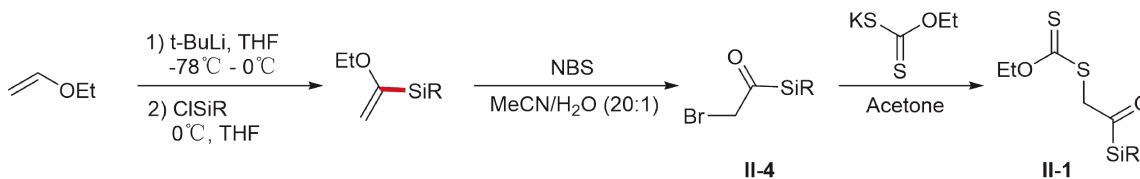
## General Experimental Methods

All reactions were carried out under an inert atmosphere of nitrogen or argon. Thin Layer Chromatography (TLC) was performed on alumina plates precoated with silica gel (Merck silica gel, 60 F254). Products spots were visualized by the quenching of UV fluorescence when applicable (max = 254 nm and/or 366 nm) and/or by staining with vanillin in ethanol and/or  $\text{KMnO}_4$  in ethanol followed by heating. Most products were purified by flash chromatography on Kieselgel 60 (40-63  $\mu\text{m}$ ). Preparative TLC was performed on glass plates coated with silica gel (Merck PLC silica gel, 60 F254). Infrared spectra were recorded on a Perkin-Elmer Spectrum Two. Absorption maxima ( $\nu_{\text{max}}$ ) are reported in wavenumbers ( $\text{cm}^{-1}$ ). Nuclear magnetic resonance spectra were recorded at ambient temperature on a Bruker Avance DPX 400 instrument. Proton magnetic resonance spectra ( $^1\text{H}$  NMR) were recorded at 400 MHz and coupling constants (J) are reported to  $\pm 0.5$  Hz. The following abbreviations were utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Carbon magnetic resonance spectra ( $^{13}\text{C}$  NMR) were recorded at 101 MHz. Chemical shifts (H, C) are quoted in parts per million (ppm) and are referenced to the residual solvent peak ( $(\text{CD}_3)_2\text{CO}$ :  $\delta\text{H}= 2.05$  and  $\delta\text{C}= 29.84, 206.26$  and  $\text{CD}_3\text{CN}$ :  $\delta\text{H}= 1.94$  and  $\delta\text{C}= 1.32, 118.26$ ). Carbons exhibiting significant line broadening brought about by boron substituents were not reported (quadrupolar relaxation). The  $\text{CH}_2$  carbon neighboring the acylboron functionality (usually around 44 ppm) gave a weak signal most of the time. High-resolution mass spectra were recorded by electrospray ionization in positive mode (ESI+) on a timsTOF mass spectrometer (Bruker, France). The quoted masses are accurate to  $\pm 5$  ppm.

## Experimental Procedures

### Chapter II. The xanthate chemistry of acylsilanes

#### *General procedure A: Synthesis of xanthate II-1*



To a solution of ethyl ether (1.6n mmol, 1.6 equiv.) in THF (n mL) was added *t*-BuLi (1.6M in THF, 1.3 mmol, 1.3 equiv.) at -78 °C and stirred for 1 h. The reaction mixture was allowed to warm to 0 °C for 2 h and then transferred to a solution of chlorosilane (n mmol, 1 equiv.) in THF (2n mL) at 0 °C<sup>[1]</sup>. The resulting mixture was then stirred for 48 h. The crude residue was dissolved in Et<sub>2</sub>O (10n mL), and deionized water (10n mL) then separated. The aqueous layer was extracted with Et<sub>2</sub>O (5n mL) for three times. The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo to afford 2-silyl-2-ethoxyethene.

To a solution of N-bromosuccinimide (n mmol, 1 equiv.) in CH<sub>3</sub>CN (5n mL) and H<sub>2</sub>O (2.5n mL) at -40 °C was added 2-silyl-2-ethoxyethene (n mmol, 1 equiv.) dropwise over 15 min. The mixture was maintained at -40 °C for 2 h, followed warm to -10 °C for 1 h. Then the crude residue was partitioned between H<sub>2</sub>O (5n mL) and pentane (3n mL) and then separated. The organic phase was washed with H<sub>2</sub>O (5n mL) and pentane (3n mL) and then separated. The combined aqueous layers were extracted with pentane (3n mL) for two times. The combined organic phases were dried over MgSO<sub>4</sub>. Filtered and concentrated under reduced pressure to afforded bromomethyl acylsilane **II-4**.

To a solution of bromomethyl acylsilane **II-4** (n mmol, 1 equiv.) in acetone (3n mL) at 0 °C with N<sub>2</sub> was added potassium O-ethylxanthate salt (1.1n mmol, 1.1 equiv.) portionwise over 5 min<sup>[2]</sup>. The mixture was stirred for 2 h. Then, ice water was added to the suspension and the resulting aqueous solution was extracted twice with dichloromethane. The combined organic layers were washed by brine and dried over anhydrous MgSO<sub>4</sub>. Filtered and concentrated under reduced pressure. Flash

chromatography on silica gel (petroleum ether/dichloromethane = 9/1 to 7/3) afforded the desired product **II-1**.

***General procedure B: Radical addition with non-activated alkenes***

Xanthate (1.0 equiv.), olefin (1.5-3.0 equiv.) and dilauroyl peroxide (DLP) (0.1 equiv., according to xanthate) were mixed in a vial and dissolved in EtOAc (2n mL), then air in the vial was excluded by argon. The vial was sealed and heated at 83 °C. Additional dilauroyl peroxide (DLP) was added portion-wise (0.1 equiv.) every hour until total consumption of the starting xanthate (typically 3-5 portions of DLP)<sup>[3]</sup>. The reaction mixture was then cooled down to room temperature and purified by flash chromatography on silica gel.

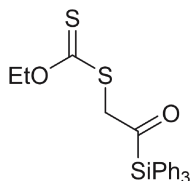
***General procedure C: Reduction of the xanthate group***

A solution of xanthate (1.0 equiv.) and tris(trimethylsilyl)silane (TTMSS, 1.1 equiv.) in Toluene/cyclohexane (1:1, 0.1M according to xanthate) was refluxed under nitrogen for 10 min. Then AIBN was added portionwise (20 mol% according to xanthate) every hour until total consumption of the starting xanthate (2 h total reaction time)<sup>[4]</sup>. The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation (CAUTION: manipulate under well-ventilated fumehoods due to the strong smell!). Flash chromatography on silica gel of the crude material gave the desired product.

***General procedure D: Synthesis of 2-pyrrole silanes***

To a solution of adduct **II-3ab** or **II-3ar** (n mmol, 1 equiv.) in Toluene (10n mL) was added amines (2.5n mmol, 2.5 equiv.)<sup>[5]</sup>. The flask was equipped with a condenser and the suspension was stirred at 40 °C with a heating block until completion of the reaction (followed by TLC, usually 1 h). The reaction mixture was then cooled down to room temperature, purified by flash chromatography on silica gel.

O-ethyl S-(2-oxo-2-(triphenylsilyl)ethyl) carbonodithioate (**II-1a**)



C<sub>23</sub>H<sub>22</sub>O<sub>2</sub>S<sub>2</sub>Si  
M = 422.0830

According to general procedure A, to a solution of bromomethyl acylsilane **II-4a** (9.5 g, 25 mmol, 1 equiv.) in acetone (75 mL) at 0 °C with N<sub>2</sub> was added potassium O-ethylxanthate salt (4.4 g, 27.5 mmol, 1.1 equiv.) portionwise over 5 min. The mixture was stirred for 2 h. Then, ice water was added to the suspension and the resulting aqueous solution was extracted twice with dichloromethane. The combined organic layers were washed by brine and dried over anhydrous MgSO<sub>4</sub>. Filtered and concentrated under reduced pressure. Flash chromatography on silica gel (petroleum ether/dichloromethane = 9/1 to 7/3) afforded desired product **II-1a** as a colorless solid (7.6 g, 18 mmol, 72%).

**<sup>1</sup>H NMR** δ (ppm) = 7.76 – 7.66 (m, 6H), 7.55 – 7.49 (m, 3H), 7.48 (m, 6H), 4.56 (q, J = 7.1, 1.0 Hz, 2H), 4.36 (s, 2H), 1.34 (t, J = 7.1 Hz, 3H).  
(400 MHz, CDCl<sub>3</sub>)

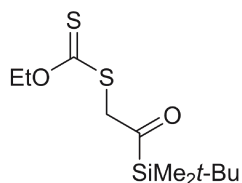
**<sup>13</sup>C NMR** δ (ppm) = 213.1, 136.2 (6C), 130.6 (3C), 130.4 (3C), 128.3 (6C), 70.6, 52.3, 13.6. (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3045, 1654, 1485, 1429, 1363, 1223, 1146, 1111, 1046, 998, 904, 724.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>23</sub>H<sub>23</sub>O<sub>2</sub>S<sub>2</sub>Si]<sup>+</sup>: 423.0903; Found 423.0898

**mp:** 89 - 95°C

O-ethyl S-(2-oxo-2-silylethyl) carbonodithioate (**II-1b**)



C<sub>11</sub>H<sub>22</sub>O<sub>2</sub>S<sub>2</sub>Si  
M = 278.0830

According to general procedure A, to a solution of bromomethyl acylsilane **II-4b** (10 g, 42.2 mmol, 1 equiv.) in acetone (125 mL) at 0 °C with N<sub>2</sub> was added potassium O-ethylxanthate salt (7.4 g, 46.4 mmol, 1.1 equiv.) portionwise over 5 min. The mixture was stirred for 2 h. Then, ice water was added to the suspension and the resulting aqueous solution was extracted twice with dichloromethane. The combined organic layers were washed by brine and dried over anhydrous MgSO<sub>4</sub>. Filtered and concentrated under reduced pressure. Flash chromatography on silica gel (petroleum ether/dichloromethane = 9/1 to 7/3) afforded desired product **II-1a** as a light-yellow oil (9.8 g, 35.3 mmol, 84%).

**<sup>1</sup>H NMR** δ (ppm) = 4.58 (q, J = 7.1 Hz, 2H), 4.23 (s, 2H), 1.38 (t, J = 7.1 Hz, 3H), 0.95 (s, 9H), 0.27 (s, 6H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 213.9, 70.7, 52.2, 26.4 (3C), 16.8, 13.8, -6.6 (2C).  
(101 MHz, CDCl<sub>3</sub>)  
(Si-C=O not observed).

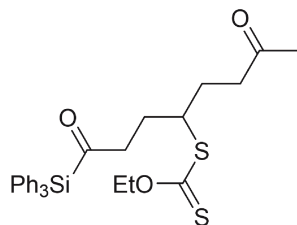
**IR** (neat) ν (cm<sup>-1</sup>) = 2953, 2929, 2858, 1654, 1463, 1364, 1250, 1216, 1145, 1112, 1048, 1006, 824, 780.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>11</sub>H<sub>23</sub>O<sub>2</sub>S<sub>2</sub>Si<sup>+</sup>]: 279.0903; Found 279.0911



## Substrate Scope

### S-(1,7-dioxo-1-(triphenylsilyl)octan-4-yl) O-ethyl carbonodithioate (**II-3aa**)



C<sub>29</sub>H<sub>32</sub>O<sub>3</sub>S<sub>2</sub>Si  
M = 520.1562

According to general procedure B, xanthate **II-1a** (211 mg, 0.5 mmol, 1 equiv.), 5-Hexen-2-one (73.6 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 96/4) afforded compound **II-3aa** as a colorless oil (184 mg, 0.36 mmol, 71% yield).

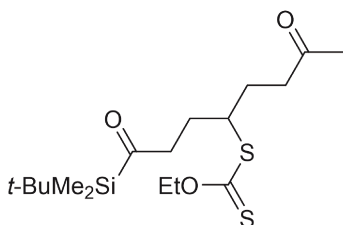
**<sup>1</sup>H NMR** δ (ppm) = 7.60 – 7.55 (m, 6H), 7.50 – 7.44 (m, 3H), 7.43 – 7.37 (m, 6H), 4.61 – 4.50 (m, 2H), 3.63 (m, 1H), 2.99 – 2.80 (m, 2H), 2.54 (t, J = 7.5 Hz, 2H), 2.11 (s, 3H), 2.04 – 1.88 (m, 2H), 1.82 – 1.70 (m, 2H), 1.38 – 1.33 (m, 3H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 213.9, 207.7, 136.2 (6C), 131.1 (3C), 130.4 (3C), 128.3 (6C), 70.0, 50.5, 47.6, 40.7, 30.0, 28.5, 26.8, 13.7.  
(101 MHz, CDCl<sub>3</sub>) (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2982, 2922, 1720, 1642, 1584, 1467, 1428, 1366, 1291, 1215, 1143, 1044, 990, 855, 697.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>29</sub>H<sub>32</sub>NaO<sub>3</sub>S<sub>2</sub>Si]<sup>+</sup>: 543.1454; Found 543.1441

S-(1-(tert-butyl(dimethyl)silyl)-1,7-dioxooctan-4-yl) O-ethyl carbonodithioate (**II-3ba**)



C<sub>17</sub>H<sub>32</sub>O<sub>3</sub>S<sub>2</sub>Si  
M = 376.1562

According to general procedure B, xanthate **II-1b** (139 mg, 0.5 mmol, 1 equiv.), 5-Hexen-2-one (73.6 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 95/5) afforded compound **II-3ba** as a colorless oil (117 mg, 0.31 mmol, 62% yield).

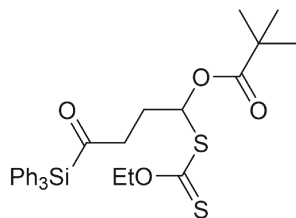
**<sup>1</sup>H NMR** δ (ppm) = 4.66 – 4.58 (m, 2H), 3.67 (m, 1H), 2.83 – 2.66 (m, 2H), 2.63 – 2.57 (m, 2H), 2.13 (s, 3H), 1.99 (m, 2H), 1.89 – 1.69 (m, 2H), 1.44 – 1.38 (t, J = 7.1Hz, 3H), 0.92 – 0.89 (s, 9H), 0.17 (s, 6H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 214.2, 207.8, 70.1, 50.7, 47.2, 40.7, 30.1, 28.5, 26.5 (3C), 26.3, 16.5, 13.8, -6.9 (2C). (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 2955, 2932, 1720, 1640, 1552, 1447, 1410, 1365, 1287, 1209, 1124, 1047, 990, 758.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>17</sub>H<sub>32</sub>NaO<sub>3</sub>S<sub>2</sub>Si]<sup>+</sup>: 399.1454; Found 399.1458

1-((ethoxycarbonothioyl)thio)-4-oxo-4-(triphenylsilyl)butyl pivalate (**II-3ab**)



C<sub>30</sub>H<sub>34</sub>O<sub>4</sub>S<sub>2</sub>Si

M = 550.1668

According to general procedure B, xanthate **II-1a** (844 mg, 2 mmol, 1 equiv.), vinyl pivalate (515 mg, 4 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (4 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 97/3) afforded compound **II-3ab** as a colorless oil (726 mg, 1.3 mmol, 66% yield).

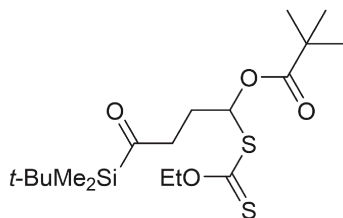
**<sup>1</sup>H NMR** δ (ppm) = 7.60 – 7.56 (m, 6H), 7.50 – 7.45 (m, 3H), 7.43 – 7.38 (m, 6H), 6.52 (t, J = 6.4 Hz, 1H), 4.58 (q, J = 7.2 Hz, 2H), 2.85 (m, 2H), 2.28 – 2.07 (m, 2H), 1.37 (t, J = 7.1 Hz, 3H), 1.09 (s, 9H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 210.1, 176.6, 136.1 (6C), 130.9 (3C), 130.5 (3C), 128.3 (6C), 79.9, 70.1, 45.9, 38.8, 26.9 (3C), 26.6, 13.7.  
(101 MHz, CDCl<sub>3</sub>) (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3069, 2975, 2930, 1737, 1646, 1479, 1428, 1396, 1365, 1273, 1228, 1132, 1110, 1048, 1030, 997, 709.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>30</sub>H<sub>34</sub>NaO<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 573.1560; Found 573.1550

4-(tert-butyldimethylsilyl)-1-((ethoxycarbonothioyl)thio)-4-oxobutyl pivalate (**II-3bb**)



C<sub>18</sub>H<sub>34</sub>O<sub>4</sub>S<sub>2</sub>Si

M = 406.1668

According to general procedure B, xanthate **II-1b** (139 mg, 0.5 mmol, 1 equiv.), vinyl pivalate (77.2 mg, 1.6 mmol, 1.2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 97/3) afforded compound **II-3bb** as a colorless oil (97.5 mg, 0.24 mmol, 48% yield).

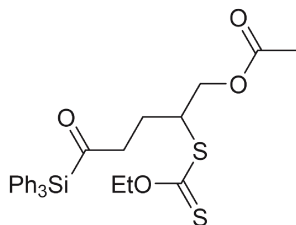
**<sup>1</sup>H NMR** δ (ppm) = 6.57 (t, J = 6.6 Hz, 1H), 4.62 (m, 2H), 2.71 (m, 2H), (400 MHz, CDCl<sub>3</sub>) 2.24 – 2.05 (m, 2H), 1.41 (t, J = 7.1 Hz, 3H), 1.18 (s, 9H), 0.91 (s, 9H), 0.18 (d, J = 0.4 Hz, 6H).

**<sup>13</sup>C NMR** δ (ppm) = 210.3, 176.7, 80.2, 70.2, 45.4, 38.9, 27.1 (3C), 26.5 (3C), 26.4, 16.5, 13.7, -6.9 (2C). (Si-C=O not observed). (101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3054, 2945, 2921, 1740, 1646, 1428, 1367, 1342, 1266, 1210, 1132, 1110, 1047, 1026, 958, 790.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>18</sub>H<sub>34</sub>NaO<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 429.1560; Found 429.1555

2-((ethoxycarbonothioyl)thio)-5-oxo-5-(triphenylsilyl)pentyl acetate (**II-3ac**)



C<sub>28</sub>H<sub>30</sub>O<sub>4</sub>S<sub>2</sub>Si  
M = 522.1355

According to general procedure B, xanthate **II-1a** (211 mg, 0.5 mmol, 1 equiv.), allyl acetate (75 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 97/3) afforded compound **II-3ac** as a colorless oil (167 mg, 0.32 mmol, 64% yield).

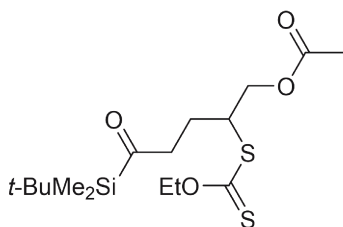
**<sup>1</sup>H NMR** δ (ppm) = 7.61 – 7.56 (m, 6H), 7.47 (m, 3H), 7.44 – 7.37 (m, 6H), 4.58 (m, 2H), 4.18 (m, 2H), 3.92 – 3.83 (m, 1H), 2.92 (m, 2H), 2.18 – 2.06 (m, 1H), 2.02 (s, 3H), 1.85 – 1.73 (m, 1H) 1.37 (t, J = 0.4 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 212.8, 170.7, 136.2 (6C), 131.0 (3C), 130.4 (3C), 128.3 (6C), 70.2, 65.8, 48.8, 47.4, 23.2, 20.8, 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3069, 2924, 1743, 1644, 1485, 1428, 1381, 1363, 1223, 1111, 1047, 998, 857, 709.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>28</sub>H<sub>31</sub>O<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 523.1428; Found 523.1408

5-(tert-butyldimethylsilyl)-2-((ethoxycarbonothioyl)thio)-5-oxopentyl acetate (**II-3bc**)



C<sub>16</sub>H<sub>30</sub>O<sub>4</sub>S<sub>2</sub>Si  
M = 378.1355

According to general procedure B, xanthate **II-1b** (139 mg, 0.5 mmol, 1 equiv.), allyl acetate (75 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 97/3) afforded compound **II-3bc** as a colorless oil (102 mg, 0.27 mmol, 54% yield).

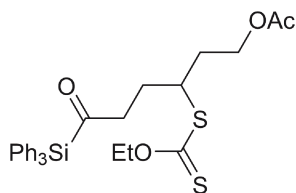
**<sup>1</sup>H NMR** δ (ppm) = 4.63 (m, 2H), 4.34 – 4.16 (m, 2H), 3.97 – 3.86 (m, 1H), 2.77 (m, 2H), 2.06 (m, 4H), 1.82 – 1.71 (m, 1H), 1.41 (t, J = 7.1 Hz, 3H), 0.91 (s, 9H), 0.17 (s, 6H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 213.1, 170.7, 70.3, 65.8, 49.1, 47.0, 26.4 (3C), 22.7, 20.8, 16.5, 13.8, -6.9 (2C). (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 2958, 2930, 1740, 1648, 1417, 1367, 1342, 1270, 1210, 1132, 1110, 1048, 1026, 969, 698.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>16</sub>H<sub>31</sub>O<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 379.1428; Found 379.1425

3-((ethoxycarbonothioyl)thio)-6-oxo-6-(triphenylsilyl)hexyl acetate (**II-3ad**)



C<sub>29</sub>H<sub>32</sub>O<sub>4</sub>S<sub>2</sub>Si  
M = 536.1511

According to general procedure B, xanthate **II-1a** (211 mg, 0.5 mmol, 1 equiv.), 3-butenyl acetate (86 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 97/3) afforded compound **II-3ad** as a colorless oil (172 mg, 0.32 mmol, 64% yield).

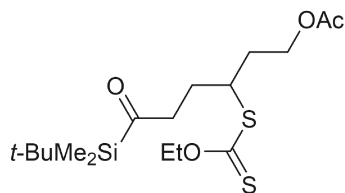
**<sup>1</sup>H NMR** δ (ppm) = 7.60 – 7.56 (m, 6H), 7.49 – 7.44 (m, 3H), 7.41 – 7.36 (m, 6H), 4.54 (m, 2H), 4.12 (t, J = 6.5 Hz, 2H), 3.80 – 3.70 (m, 1H), 2.98 – 2.75 (m, 2H), 2.10 – 2.03 (m, 1H), 2.02 (s, 3H), 1.97 – 1.87 (m, 2H), 1.83 – 1.70 (m, 1H), 1.35 (t, J = 7.1 Hz, 3H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 213.6, 170.9, 136.2 (6C), 131.0 (3C), 130.4 (3C), 128.3 (6C), 70.0, 61.8, 47.8, 47.5, 33.7, 26.7, 21.0, 13.7.  
(101 MHz, CDCl<sub>3</sub>) (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3050, 2982, 1736, 1642, 1588, 1485, 1428, 1385, 1365, 1264, 1217, 1146, 1109, 1044, 909, 734.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>29</sub>H<sub>33</sub>O<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 537.1584; Found 537.1585

6-(tert-butyldimethylsilyl)-3-((ethoxycarbonothioyl)thio)-6-oxohexyl acetate (**II-3bd**)



C<sub>17</sub>H<sub>32</sub>O<sub>4</sub>S<sub>2</sub>Si  
M = 392.1511

According to general procedure B, xanthate **II-1b** (139 mg, 0.5 mmol, 1 equiv.), 3-butenyl acetate (86 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 97/3) afforded compound **II-3bd** as a colorless oil (84 mg, 0.22 mmol, 43% yield).

**<sup>1</sup>H NMR** δ (ppm) = 4.62 (m, 2H), 4.17 (t, J = 1.6 Hz, 2H), 3.83 – 3.72 (m, 1H), 2.84 – 2.66 (m, 2H), 2.10 – 1.93 (m, 6H), 1.77 (m, 1H), 1.43 – 1.36 (t, J = 7.1 Hz, 3H), 0.92 – 0.86 (s, 9H), 0.16 (s, 6H). (400 MHz, CDCl<sub>3</sub>)

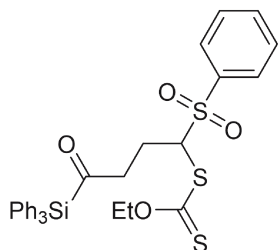
**<sup>13</sup>C NMR** δ (ppm) = 213.1, 170.7, 70.4, 65.8, 49.1, 47.1, 34.7, 26.5 (3C), 22.8, 20.8, 16.5, 13.8, -6.9 (2C). (Si-C=O not observed). (101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 2954, 2850, 1736, 1643, 1438, 1426, 1380, 1355, 1248, 1217, 1110, 1047, 998, 909, 856, 697.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>17</sub>H<sub>33</sub>O<sub>4</sub>S<sub>2</sub>Si<sup>+</sup>]: 393.1584; Found 393.1580



O-ethyl S-(4-oxo-1-(phenylsulfonyl)-4-(triphenylsilyl)butyl) carbonodithioate (**II-3ae**)



C<sub>31</sub>H<sub>30</sub>O<sub>4</sub>S<sub>3</sub>Si  
M = 590.1075

According to general procedure B, xanthate **II-1a** (211 mg, 0.5 mmol, 1 equiv.), phenyl vinyl sulfone (101 mg, 0.6 mmol, 1.2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1 to 8/2) afforded compound **II-3ae** as a colorless oil (159 mg, 0.27 mmol, 54% yield).

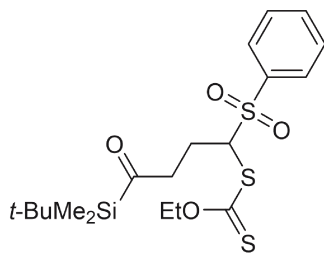
**<sup>1</sup>H NMR** δ (ppm) = 7.95 – 7.90 (m, 2H), 7.67 – 7.61 (m, 1H), 7.56 – 7.51 (m, 7H), 7.48 – 7.44 (m, 4H), 7.41 – 7.36 (m, 6H), 5.26 (m, 1H), 4.36 (m, 2H), 2.98 (m, 2H), 2.71 – 2.58 (m, 1H), 2.01 – 1.90 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 208.9, 136.5, 136.1 (6C), 134.1, 130.6 (2C), 130.5 (3C), 129.8 (3C), 128.9 (2C), 128.3 (6C), 71.3, 70.8, 46.2, 20.3, 13.5. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3068, 2924, 1643, 1586, 1484, 1446, 1428, 1391, 1365, 1318, 1290, 1230, 1147, 1109, 1038, 969, 734.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>31</sub>H<sub>30</sub>NaO<sub>4</sub>S<sub>3</sub>Si]<sup>+</sup>: 613.0968; Found 613.0938

S-(4-(tert-butyldimethylsilyl)-4-oxo-1-(phenylsulfonyl)butyl) O-ethyl carbonodithioate  
**(II-3be)**



C<sub>19</sub>H<sub>30</sub>O<sub>4</sub>S<sub>3</sub>Si  
M = 446.1075

According to general procedure B, xanthate **II-1b** (139 mg, 0.5 mmol, 1 equiv.), phenyl vinyl sulfone (101 mg, 0.6 mmol, 1.2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 96/4) afforded compound **II-3be** as a colorless oil (109 mg, 0.24 mmol, 49% yield).

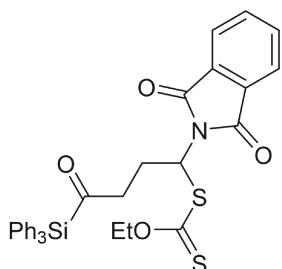
**<sup>1</sup>H NMR** δ (ppm) = 7.99 – 7.92 (m, 2H), 7.66 – 7.51 (m, 3H), 5.32 – 5.22 (m, 1H), 4.45 (m, 2H), 2.89 – 2.79 (m, 2H), 2.60 (m, 1H), 2.03 (m, 1H), 1.32 (t, J = 7.1 Hz, 3H), 0.88 (s, 9H), 0.14 (s, 6H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 209.2, 136.6, 134.1, 129.8 (2C), 128.9 (2C), 71.4, 71.0, 45.8, 26.3 (3C), 20.0, 16.5, 13.6, -6.9 (2C). (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3046, 2950, 1644, 1586, 1484, 1446, 1428, 1365, 1308, 1290, 1189, 1147, 1109, 1084, 1047, 997, 850.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>19</sub>H<sub>30</sub>NaO<sub>4</sub>S<sub>3</sub>Si]<sup>+</sup>: 469.0968; Found 469.0957

S-(1-(1,3-dioxoisindolin-2-yl)-4-oxo-4-(triphenylsilyl)butyl) O-ethyl carbonodithioate  
**(II-3af)**



C<sub>33</sub>H<sub>29</sub>NO<sub>4</sub>S<sub>2</sub>Si  
M = 595.1307

According to general procedure B, xanthate **II-1a** (844 mg, 2 mmol, 2 equiv.), *N*-vinyl phthalimide (173 mg, 1 mmol, 1 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (4 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 94/6) afforded compound **II-3af** as a colorless oil (339 mg, 0.57 mmol, 57% yield).

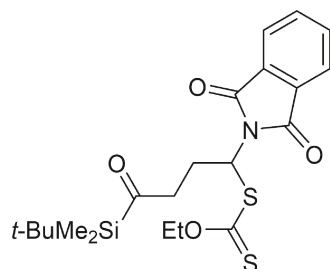
**<sup>1</sup>H NMR** δ (ppm) = 7.84 – 7.76 (m, 2H), 7.76 – 7.70 (m, 2H), 7.57 – 7.52 (m, 6H), 7.45 – 7.40 (m, 3H), 7.39 – 7.33 (m, 6H), 6.19 (m, 1H), 4.56 (m, 2H), 2.86 (m, 2H), 2.48 – 2.32 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 210.8, 166.6 (2C), 136.1 (6C), 134.3 (3C), 131.5 (2C), 130.8 (2C), 130.4 (3C), 128.3 (6C), 123.6 (2C), 70.4, 57.1, 46.8, 25.9, 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3068, 2924, 1777, 1715, 1643, 1612, 1588, 1485, 1468, 1428, 1377, 1356, 1332, 1289, 1224, 1189, 1149, 1109, 1042, 997, 880, 696.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>33</sub>H<sub>29</sub>NaO<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 618.1199; Found 618.1190

S-(4-(tert-butyldimethylsilyl)-1-(1,3-dioxisoindolin-2-yl)-4-oxobutyl)-O-ethyl-carbonodithioate (**II-3bf**)



C<sub>21</sub>H<sub>29</sub>NO<sub>4</sub>S<sub>2</sub>Si  
M = 451.1307

According to general procedure B, xanthate **II-1b** (278 mg, 1 mmol, 1 equiv.), *N*-vinyl phthalimide (346 mg, 2 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 95/5) afforded compound **II-3bf** as a colorless oil (239 mg, 0.53 mmol, 53% yield).

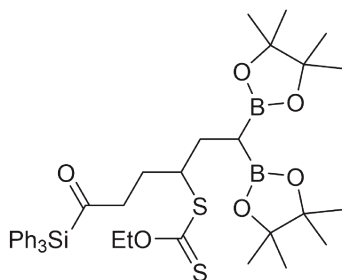
**<sup>1</sup>H NMR** δ (ppm) = 7.84 (m, 2H), 7.73 (m, 2H), 6.26 – 6.15 (m, 1H), 4.66 – 4.51 (m, 2H), 2.73 (m, 2H), 2.51 – 2.32 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H), 0.86 (s, 9H), 0.12 (m, 6H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 211.1, 166.7 (2C), 134.3 (2C), 131.6 (2C), 123.6 (2C), 70.4, 57.5, 46.5, 26.3 (3C), 25.7, 16.4, 13.7, -6.9 (2C).  
(101 MHz, CDCl<sub>3</sub>) (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2928, 2856, 1779, 1717, 1640, 1468, 1378, 1334, 1110, 1045, 1006, 837, 776.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>21</sub>H<sub>29</sub>NNaO<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 474.1199; Found 474.1199

O-ethylS-(6-oxo-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(triphenylsilyl)hexan-3-yl) carbonodithioate (**II-3ag**)



$C_{39}H_{52}B_2O_6S_2Si$   
M = 730.3161

According to general procedure B, xanthate **II-1a** (695 mg, 1.6 mmol, 1 equiv.), 2,2'-(but-3-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (739 mg, 2.4 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (4 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 94/6) afforded compound **II-3ag** as a colorless oil (701 mg, 0.96 mmol, 60% yield).

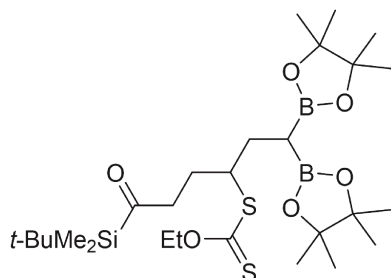
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 7.60 – 7.56 (m, 6H), 7.48 – 7.43 (m, 3H), 7.42 – 7.37 (m, 6H), 4.51 (q, J = 7.1Hz, 2H), 3.61 (m, 1H), 2.90 (m, 2H), 2.08 – 1.96 (m, 1H), 1.90 (m, 1H), 1.83 – 1.68 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.20 (m, 24H), 0.89 (t, J = 1.7 Hz, 1H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 214.4, 136.2 (6C), 131.3 (3C), 130.2 (3C), 128.2 (6C), 83.1 (4C), 69.5, 53.5, 47.9, 30.1, 27.5, 25.0 (2C), 24.9 (2C), 24.7 (2C), 24.6 (2C), 24.5, 13.7. (Si-C=O not observed).

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 3051, 2978, 2930, 1736, 1643, 1428, 1379, 1370, 1312, 1264, 1213, 1136, 1110, 1048, 968, 848.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>39</sub>H<sub>53</sub>B<sub>2</sub>O<sub>6</sub>S<sub>2</sub>Si]<sup>+</sup>: 731.3233; Found 731.3231

O-ethylS-(6-oxo-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(triphenylsilyl)hexan-3-yl) carbonodithioate (**II-3bg**)



C<sub>27</sub>H<sub>52</sub>B<sub>2</sub>O<sub>6</sub>S<sub>2</sub>Si  
M = 586.3161

According to general procedure B, xanthate **II-1b** (600 mg, 2.2 mmol, 1 equiv.), 2,2'-(but-3-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1g, 3.3 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (4 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 94/6) afforded compound **II-3bg** as a colorless oil (606 mg, 1 mmol, 47% yield).

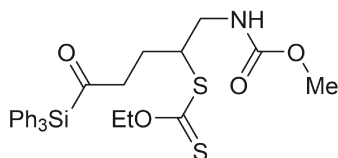
**<sup>1</sup>H NMR** δ (ppm) = 4.65 – 4.55 (m, 2H), 3.72 – 3.58 (m, 1H), 2.82 – 2.62 (m, 2H), 1.96 (m, 2H), 1.85 – 1.72 (m, 2H), 1.41 – 1.36 (t, J = 7.1 Hz, 3H), 1.22 (m, 25H), 0.90 (s, 9H), 0.16 (s, 6H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 214.8, 83.2 (4C), 69.6, 53.8, 47.4, 30.0, 27.0, 26.5 (3C), 25.0 (2C), 24.9 (2C), 24.7 (2C), 24.6 (2C), 24.5, 16.5, 13.8, -6.9 (2C). (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 2978, 2952, 1640, 1370, 1315, 1215, 1139, 1052, 970, 849.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>27</sub>H<sub>53</sub>B<sub>2</sub>O<sub>6</sub>S<sub>2</sub>Si]<sup>+</sup>: 587.3233; Found 587.3244

methyl (2-((ethoxycarbonothioyl)thio)-5-oxo-5-(triphenylsilyl)pentyl)carbamate (**II-3ah**)



$C_{28}H_{31}NO_4S_2Si$   
M = 537.1464

According to general procedure B, xanthate **II-1a** (211 mg, 0.5 mmol, 1 equiv.), methyl allylcarbamate (115 mg, 1 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1 to 85/15) afforded compound **II-3ah** as a colorless oil (136 mg, 0.26 mmol, 51% yield).

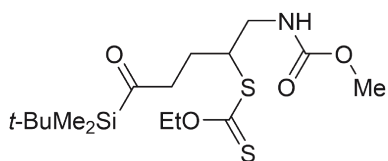
**$^1H$  NMR**  $\delta$  (ppm) = 7.59 – 7.54 (m, 6H), 7.50 – 7.45 (m, 3H), 7.43 – 7.37 (m, 6H), 5.02 (s, 1H), 4.56 (q, J = 7.1Hz, 2H), 3.74 (m, 1H), 3.64 (s, 3H), 3.49 – 3.27 (m, 2H), 3.05 – 2.81 (m, 2H), 2.11 – 1.98 (m, 1H), 1.80 – 1.67 (m, 1H), 1.37 (t, J = 7.1 Hz, 3H).  
(400 MHz,  $CDCl_3$ )

**$^{13}C$  NMR**  $\delta$  (ppm) = 213.2, 157.0, 136.1 (6C), 130.9 (3C), 130.4 (3C), 128.3 (6C), 70.2, 52.3, 50.8, 47.4, 44.4, 23.4, 13.7. (Si-C=O not observed).  
(101 MHz,  $CDCl_3$ )

**IR** (neat)  $\nu$  ( $cm^{-1}$ ) = 3354, 3069, 2939, 1724, 1642, 1519, 1428, 1219, 1110, 1047, 740, 698.

**HRMS** (EI<sup>+</sup>) m/z:  $[M+H]^+$ , Calcd for  $[C_{28}H_{32}NO_4S_2Si]^+$ : 538.1537; Found 538.1543

methyl (5-(tert-butyldimethylsilyl)-2-((ethoxycarbonothioyl)thio)-5-oxopentyl)carbamate  
**(II-3bh)**



C<sub>16</sub>H<sub>31</sub>NO<sub>4</sub>S<sub>2</sub>Si  
M = 393.1464

According to general procedure B, xanthate **II-1b** (556 mg, 2 mmol, 1 equiv.), methyl allylcarbamate (460 mg, 4 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (4 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1) afforded compound **II-3bh** as a colorless oil (408 mg, 1.1 mmol, 52% yield)

**<sup>1</sup>H NMR** δ (ppm) = 5.10 (s, 1H), 4.68 – 4.56 (q, J = 7.1Hz, 2H), 3.78 (m, 1H), 3.65 (s, 3H), 3.51 – 3.35 (m, 2H), 2.91 – 2.72 (m, 2H), 2.01 (m, 1H), 1.82 – 1.68 (m, 1H), 1.41 (t, J = 7.1 Hz, 3H), 0.90 (s, 9H), 0.17 (s, 6H).  
(400 MHz, CDCl<sub>3</sub>)

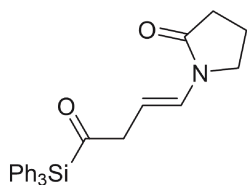
**<sup>13</sup>C NMR** δ (ppm) = 213.4, 157.1, 70.3, 51.0, 47.0, 44.5, 29.6, 26.4 (3C), 23.0, 16.5, 13.8, -6.9 (2C). (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3350, 2953, 2928, 2857, 1711, 1643, 1521, 1443, 1382, 1220, 1112, 1049, 1006, 824.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>16</sub>H<sub>32</sub>NO<sub>4</sub>S<sub>2</sub>Si<sup>+</sup>]: 394.1537; Found 394.1543



(E)-1-(4-oxo-4-(triphenylsilyl)but-1-en-1-yl)pyrrolidin-2-one (**II-3ai**)



C<sub>26</sub>H<sub>25</sub>NO<sub>2</sub>Si  
M = 411.1655

According to general procedure B, xanthate **II-1a** (126 mg, 0.3 mmol, 1 equiv.), vinyl pyrrolidin (50 mg, 0.45 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1 to 5/5) afforded compound **II-3ai** as a colorless oil (83 mg, 0.2 mmol, 67% yield)

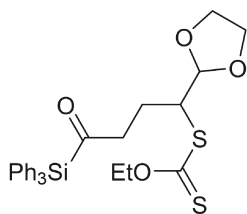
**<sup>1</sup>H NMR** δ (ppm) = 7.62 – 7.57 (m, 6H), 7.48 – 7.41 (m, 3H), 7.40 – 7.33 (m, 6H), 6.59 (m, 1H), 5.29 (t, J = 2.5 Hz, 1H), 3.16 (m, 2H), 2.94 (m, 1H), 2.43 (m, 1H), 2.35 (m, 2H), 1.98 – 1.85 (m, 2H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 175.1, 136.1 (6C), 132.5 (3C), 130.0 (3C), 127.9 (6C), 115.3, 83.7, 41.4, 33.4, 31.3, 18.0. (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3069, 2924, 2853, 1702, 1485, 1461, 1428, 1368, 1243, 1112, 1044, 1022, 997, 742.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>26</sub>H<sub>26</sub>NO<sub>2</sub>Si]<sup>+</sup>: 412.1727; Found 412.1720

S-(1-(1,3-dioxolan-2-yl)-4-oxo-4-(triphenylsilyl)butyl) O-ethyl carbonodithioate (**II-3aj**)



C<sub>28</sub>H<sub>30</sub>O<sub>4</sub>S<sub>2</sub>Si  
M = 522.1355

According to general procedure B, xanthate **II-1a** (126 mg, 0.3 mmol, 1 equiv.), 2-vinyl-1,3-dioxolane (60 mg, 0.6 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 92/8) afforded compound **II-3aj** as a colorless oil (92 mg, 0.18 mmol, 59% yield)

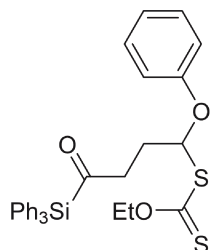
**<sup>1</sup>H NMR** δ (ppm) = 7.58 (m, 6H), 7.49 – 7.44 (m, 3H), 7.42 – 7.37 (m, 6H), 5.03 (d, J = 2.5 Hz, 1H), 4.53 (m, 2H), 3.82 (m, 1H), 2.96 (m, 4H), 2.96, (m, 2H), 2.24 – 2.11 (m, 1H), 1.80 (m, 1H), 1.33 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 213.8, 136.2 (6C), 131.2 (3C), 130.3 (3C), 128.3 (6C), 104.3 (2C), 70.2, 65.6, 53.2, 47.6, 21.5, 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3068, 2884, 1643, 1484, 1428, 1386, 1215, 1141, 1110, 1047, 998, 708, 698.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>28</sub>H<sub>30</sub>NaO<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 545.1266; Found 545.1257

O-ethyl S-(4-oxo-1-phenoxy-4-(triphenylsilyl)butyl) carbonodithioate (**II-3ak**)



C<sub>31</sub>H<sub>30</sub>O<sub>3</sub>S<sub>2</sub>Si  
M = 542.1406

According to general procedure B, xanthate **II-1a** (126 mg, 0.3 mmol, 1 equiv.), (vinylxy)benzene (72 mg, 0.45 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 99/1) afforded compound **II-3ak** as a colorless oil (132 mg, 0.24 mmol, 81% yield)

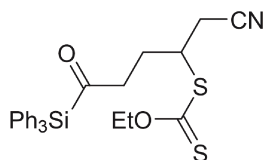
**<sup>1</sup>H NMR** δ (ppm) = 7.61 – 7.58 (m, 6H), 7.50 – 7.46 (m, 3H), 7.42 – 7.37 (m, 6H), 7.28 – 7.24 (m, 2H), 7.01 (m, 1H), 6.93 – 6.90 (m, 2H), 6.14 (t, J = 6.8Hz, 1H), 4.54 (m, 2H), 3.08 – 3.02 (m, 2H), 2.46 – 2.34 (m, 2H), 1.33 – 1.29 (t, J = 7.1 Hz, 3H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 211.8, 156.5, 136.2 (6C), 130.4 (3C), 129.5 (3C), 128.3 (6C), 127.9 (2C), 122.5, 116.7 (2C), 87.5, 69.9, 46.1, 28.9, 13.6. (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3068, 3048, 2922, 1642, 1484, 1428, 1357, 1211, 1108, 1043, 997, 740, 697.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>31</sub>H<sub>30</sub>NaO<sub>3</sub>S<sub>2</sub>Si<sup>+</sup>]: 565.1298; Found 565.1290

S-(1-cyano-5-oxo-5-(triphenylsilyl)pentan-2-yl) O-ethyl carbonodithioate (**II-3al**)



C<sub>27</sub>H<sub>27</sub>NO<sub>2</sub>S<sub>2</sub>Si  
M = 489.1252

According to general procedure B, xanthate **II-1a** (1 g, 2.37 mmol, 1 equiv.), but-3-enenitrile (509 mg, 7.58 mmol, 3.2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (4.5 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 92/8) afforded compound **II-3al** as a colorless oil (742 mg, 1.52 mmol, 64% yield)

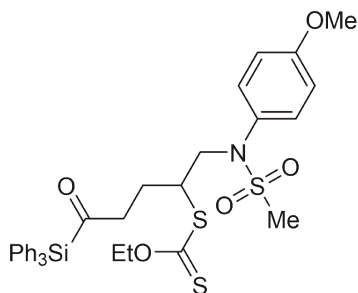
**<sup>1</sup>H NMR** δ (ppm) = 7.59 – 7.55 (m, 6H), 7.51 – 7.45 (m, 3H), 7.43 – 7.38 (m, 6H), 4.59 (q, J = 7.1, 2H), 3.86 – 3.76 (m, 1H), 3.05 – 2.71 (m, 4H), 2.23 – 2.12 (m, 1H), 1.89 (m, 1H), 1.39 (t, J = 7.1 Hz, 3H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 212.0, 136.1 (6C), 130.7 (3C), 130.5 (3C), 128.4 (6C), 117.0, 70.5, 46.9, 45.9, 24.8, 24.3, 13.8. (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3038, 2932, 1643, 1428, 1224, 1148, 1111, 1050, 854, 742, 698.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>27</sub>H<sub>27</sub>NNaO<sub>2</sub>S<sub>2</sub>Si]<sup>+</sup>: 512.1145; Found 512.1146

O-ethylS-(1-(N-(4-methoxyphenyl)methylsulfonamido)-5-oxo-5-(triphenylsilyl)pentan-2-yl) carbonodithioate (**II-3am**)



C<sub>34</sub>H<sub>37</sub>NO<sub>5</sub>S<sub>3</sub>Si  
M = 663.1603

According to general procedure B, xanthate **II-1a** (633 mg, 1.5 mmol, 1 equiv.), N-allyl-N-(4-methoxyphenyl)methanesulfonamide (724 mg, 3 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (3 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1 to 5/5) afforded compound **II-3am** as a colorless oil (657 mg, 0.99 mmol, 66% yield)

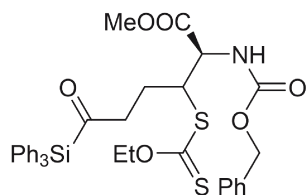
**<sup>1</sup>H NMR** δ (ppm) = 7.60 – 7.53 (m, 6H), 7.46 (m, 3H), 7.42 – 7.37 (m, 6H), 7.28 (d, J = 2.1 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.48 (m, 2H), 3.80 (m, 5H), 3.59 (m, 1H), 2.87 (m, 5H), 2.30 (m, 1H), 1.78 – 1.66 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 212.5, 159.5, 136.1 (6C), 131.1, 131.0 (3C), 130.3 (3C), 130.3 (2C), 128.3 (6C), 114.7 (2C), 70.0, 55.5, 53.9, 48.7, 47.2, 37.4, 23.0, 13.6. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2926, 2853, 1642, 1606, 1508, 1428, 1338, 1299, 1248, 1216, 1150, 1109, 1044, 997, 908, 758.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>34</sub>H<sub>38</sub>NO<sub>5</sub>S<sub>3</sub>Si]<sup>+</sup>: 664.1676; Found 664.1675

methyl(2R)-2-(((benzyloxy)carbonyl)amino)-3-((ethoxycarbonothioyl)thio)-6-oxo-6-(triphenylsilyl)hexanoate (**II-3an**)



C<sub>36</sub>H<sub>37</sub>NO<sub>6</sub>S<sub>2</sub>Si  
M = 671.1832

According to general procedure B, xanthate **II-1a** (211g, 0.5 mmol, 1 equiv.), methyl 2-(((benzyloxy)carbonyl)amino)but-3-enoate (186 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1 to 5/5) afforded compound **II-3an** as a colorless oil (194 mg, 0.29 mmol, 58% yield, d.r. = 1:1)

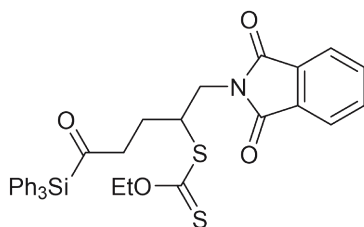
**<sup>1</sup>H NMR** δ (ppm) = 7.62 – 7.54 (m, 6H), 7.50 – 7.44 (m, 3H), 7.43 – 7.37 (m, 6H), 7.35 (m, 5H), 5.48 (m, 1H), 5.10 (m, 2H), 4.82 – 4.67 (m, 1H), 4.60 – 4.44 (m, 2H), 4.35 – 4.12 (m, 1H), 3.72 (s, 3H), 2.93 (m, 2H), 2.22 – 1.97 (m, 1H), 1.88 – 1.69 (m, 1H), 1.33 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 212.5, 170.3, 156.1, 136.2 (6C), 131.0, 130.9 (2C), 130.4 (3C), 128.6 (3C), 128.3 (6C), 128.1 (2C), 70.4, 67.3, 57.3, 52.8, 47.4, 24.6, 22.6, 13.6. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3344, 2925, 1722, 1643, 1504, 1428, 1335, 1264, 1213, 1110, 1043, 997, 734, 696.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>36</sub>H<sub>38</sub>NO<sub>6</sub>S<sub>2</sub>Si]<sup>+</sup>: 672.1904; Found 672.1901

S-(1-(1,3-dioxoisindolin-2-yl)-5-oxo-5-(triphenylsilyl)pentan-2-yl)-O-ethyl-carbonodithioate (**II-3ao**)



C<sub>34</sub>H<sub>31</sub>NO<sub>4</sub>S<sub>2</sub>Si  
M = 609.1464

According to general procedure B, xanthate **II-1a** (211g, 0.5 mmol, 1 equiv.), 2-allylisindoline-1,3-dione (140 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1) afforded compound **II-3ao** as a colorless oil (198 mg, 0.33 mmol, 65% yield)

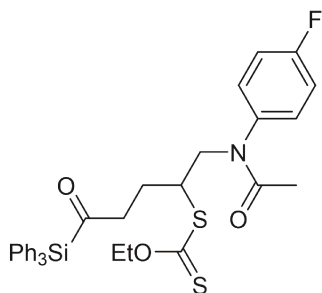
**<sup>1</sup>H NMR** δ (ppm) = 7.86 – 7.80 (m, 2H), 7.74 – 7.69 (m, 2H), 7.61 – 7.52 (m, 6H), 7.48 – 7.42 (m, 3H), 7.42 – 7.35 (m, 6H), 4.51 (q, J = 7.1 Hz, 2H), 4.10 – 3.99 (m, 1H), 3.95 – 3.78 (m, 2H), 2.95 (t, J = 7.4, 2H), 2.14 – 2.01 (m, 1H), 1.77 (m, 1H), 1.35 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 212.2, 168.0 (2C), 136.1 (6C), 134.1 (3C), 131.9 (2C), 130.9 (2C), 130.4 (3C), 128.3 (6C), 123.5 (2C), 70.2, 48.8, 47.4, 41.1, 24.0, 13.6. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3049, 2924, 2853, 1773, 1714, 1642, 1467, 1428, 1392, 1360, 1216, 1189, 1109, 1044, 997, 736, 696.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>34</sub>H<sub>32</sub>NO<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 610.1537; Found 610.1538

O-ethylS-(1-(N-(4-fluorophenyl)acetamido)-5-oxo-5-(triphenylsilyl)pentan-2-yl)-carbono  
dithioate (**II-3ap**)



C<sub>34</sub>H<sub>34</sub>FNO<sub>3</sub>S<sub>2</sub>Si  
M = 615.1733

According to general procedure B, xanthate **II-1a** (126g, 0.3 mmol, 1 equiv.), N-allyl-N-(4-fluorophenyl)acetamide (116 mg, 0.6 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1) afforded compound **II-3ap** as a colorless oil (91 mg, 0.15 mmol, 49% yield)

**<sup>1</sup>H NMR** δ (ppm) = 7.59 – 7.53 (m, 6H), 7.50 – 7.44 (m, 3H), 7.42 – 7.36 (m, 6H), 7.29 – 7.26 (m, 2H), 7.13 – 7.07 (m, 2H), 4.43 (m, 2H), 4.12 (m, 1H), 3.73 – 3.59 (m, 2H), 3.07 – 2.95 (m, 1H), 2.86 – 2.72 (m, 1H), 2.27, (m, 1H), 1.83 (s, 3H), 1.65 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H).

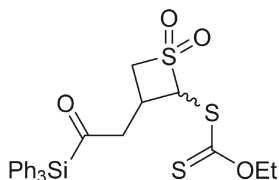
**<sup>13</sup>C NMR** δ (ppm) = 213.0, 170.9, 163.2 (d = 988 Hz), 138.5, 136.1 (6C), 131.0 (3C), 130.4 (3C), 130.3 (d = 36 HZ) (2C), 128.3 (6C), 116.8 (d = 92 Hz) (2C), 69.9, 51.6, 48.6, 47.3, 23.4, 22.8, 13.6. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3069, 2983, 2926, 1662, 1643, 1506, 1485, 1428, 1390, 1364, 1289, 1212, 1153, 1109, 1153, 1046, 997, 844.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>34</sub>H<sub>35</sub>FNO<sub>3</sub>S<sub>2</sub>Si]<sup>+</sup>: 616.1806; Found 610.1790



S-(1,1-dioxido-3-(2-oxo-2-(triphenylsilyl)ethyl)thietan-2-yl) O-ethyl carbonodithioate  
**(II-3aq)**



C<sub>26</sub>H<sub>26</sub>O<sub>4</sub>S<sub>3</sub>Si  
M = 526.0762

According to general procedure B, xanthate **II-1a** (126g, 0.3 mmol, 1 equiv.), 2*H*-thiete 1,1-dioxide (63 mg, 0.6 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 85/15) afforded compound **II-3aq** as a colorless solid (73 mg, 0.14 mmol, 46% yield, d.r. = 7:1)

**<sup>1</sup>H NMR** δ (ppm) = 7.58 – 7.55 (m, 6H), 7.51 – 7.47 (m, 3H), 7.45 – 7.41 (m, 6H), 5.56 (m, 1H), 4.65 – 4.57 (m, 2H), 4.31 (m, 1H), 3.66 – 3.57 (m, 1H), 3.32 (m, 1H), 3.18 – 3.09 (m, 1H), 2.72 (m, 1H), 1.41 (t, J = 7.1 Hz, 3H).

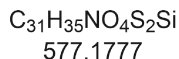
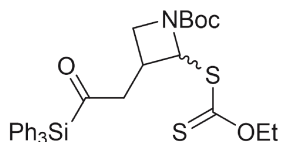
**<sup>13</sup>C NMR** δ (ppm) = 208.2, 136.1 (6C), 130.8 (3C), 130.6 (3C), 128.6 (6C), 83.2, 71.4, 68.3, 53.2, 22.6, 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3069, 2924, 2854, 1704, 1643, 1485, 1428, 1329, 1241, 1196, 1140, 1110, 1044, 998, 741.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>26</sub>H<sub>27</sub>O<sub>4</sub>S<sub>3</sub>Si]<sup>+</sup>: 527.0835; Found 527.0831

**mp:** 167 - 170°C

tert-butyl 2-((ethoxycarbonothioyl)thio)-3-(2-oxo-2-(triphenylsilyl)ethyl)azetidine-1-carboxylate (**II-3ar**)



According to general procedure B, xanthate **II-1a** (1.27g, 3 mmol, 1 equiv.), *tert*-butyl azete-1(2*H*)-carboxylate (900 mg, 6 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (6 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 20 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 96/4) afforded compound **II-3ar** as a colorless oil (1.5g, 2.61 mmol, 87% yield, d.r. = 4:1)

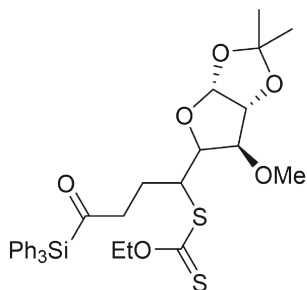
**<sup>1</sup>H NMR** δ (ppm) = 7.58 – 7.55 (m, 6H), 7.50 – 7.45 (m, 3H), 7.43 – 7.38 (m, 6H), 6.10 (d, J = 7.6 Hz, 1H), 4.51 (m, 2H), 4.04 (t, J = 8.3 Hz, 1H), 3.56 – 3.46 (m, 1H), 3.38 (m, 1H), 3.24 (m, 1H), 3.01 (m, 1H), 1.39 (s, 9H), 1.34 (t, J = 7.1 Hz, 3H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 211.4, 154.7, 136.1 (6C), 130.7 (3C), 130.5 (3C), 128.4 (6C), 80.7, 77.3, 69.6, 51.4, 29.6, 28.3 (4C), 13.7.  
(101 MHz, CDCl<sub>3</sub>)  
(Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3069, 2978, 2930, 1704, 1642, 1484, 1428, 1388, 1366, 1220, 1146, 1110, 1048, 998, 739.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>31</sub>H<sub>36</sub>NO<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 578.1850; Found 578.1844

O-ethylS-(1-((3aR,6R,6aR)-6-methoxy-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)-4-oxo-4-(triphenylsilyl)butyl) carbonodithioate (**II-3as**)



C<sub>33</sub>H<sub>38</sub>O<sub>6</sub>S<sub>2</sub>Si  
M = 622.1879

According to general procedure B, xanthate **II-1a** (211g, 0.5 mmol, 1 equiv.), (3aR,6S,6aR)-6-methoxy-2,2-dimethyl-5-vinyltetrahydrofuro[2,3-d][1,3]dioxole (150 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 85/15) afforded compound **II-3as** as a colorless oil (184 mg, 0.30 mmol, 59% yield, d.r. = 9:1)

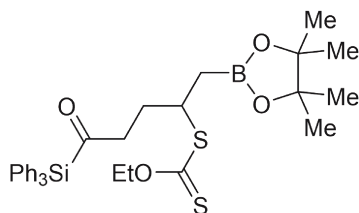
**<sup>1</sup>H NMR** δ (ppm) = 7.59 – 7.56 (m, 6H), 7.48 – 7.43 (m, 3H), 7.41 – 7.36 (m, 6H), 5.85 (d, J = 3.8 Hz, 1H), 4.52 – 4.47 (m, 3H), 4.20 (m, 1H), 4.00 (m, 1H), 3.70 (d, J = 3.2 Hz, 1H), 3.30 (s, 3H), 2.95 (t, J = 7.4 Hz, 2H), 2.31 – 2.21 (m, 1H), 1.88 (m, 1H), 1.44 (s, 3H), 1.31 (m, 6H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 212.9, 136.2 (6C), 131.2 (3C), 130.3 (3C), 128.2 (6C), 111.7, 105.2, 84.0 (2C), 81.2, 70.0, 57.8, 48.1, 26.9 (2C), 26.3, 24.8, 13.7. (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3069, 2985, 2930, 1735, 1643, 1428, 1373, 1213, 1163, 1109, 1077, 1044, 1015, 852, 697.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>33</sub>H<sub>38</sub>NaO<sub>6</sub>S<sub>2</sub>Si]<sup>+</sup>: 645.1771; Found 645.1768

O-ethylS-(5-oxo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(triphenylsilyl)pentan-2-yl) carbonodithioate (**II-3at**)



C<sub>32</sub>H<sub>39</sub>BO<sub>4</sub>S<sub>2</sub>Si  
M = 590.2152

According to general procedure B, xanthate **II-1a** (211g, 0.5 mmol, 1 equiv.), 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (168 mg, 1 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1) afforded compound **II-3at** as a colorless oil (186 mg, 0.32 mmol, 63% yield)

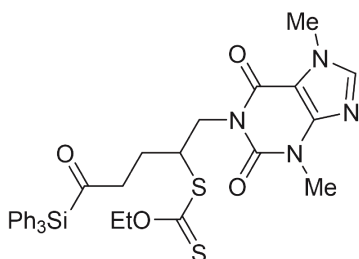
**<sup>1</sup>H NMR** δ (ppm) = 7.60 – 7.56 (m, 6H), 7.49 – 7.44 (m, 3H), 7.42 – 7.37 (m, 6H), 4.61 – 4.47 (m, 2H), 3.89 – 3.77 (m, 1H), 2.88 (m, 2H), 2.06 – 1.96 (m, 1H), 1.90 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.25 – 1.13 (m, 14H).

**<sup>13</sup>C NMR** δ (ppm) = 214.1, 136.2 (6C), 131.2 (3C), 130.3 (3C), 128.3 (6C), 83.5 (2C), 69.5, 47.9, 47.1, 28.7, 24.8 (5C), 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3049, 2976, 2926, 1643, 1428, 1363, 1328, 1265, 1211, 1141, 1108, 1046, 997, 966, 845, 735.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>32</sub>H<sub>40</sub>BO<sub>4</sub>S<sub>2</sub>Si<sup>+</sup>]: 591.2225; Found 591.2223

S-(1-(3,7-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-1-yl)-5-oxo-5-(triphenylsilyl)pentan-2-yl) O-ethyl carbonodithioate (**II-3au**)



C<sub>33</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>Si  
M = 642.1791

According to general procedure B, xanthate **II-1a** (211g, 0.5 mmol, 1 equiv.), 1-allyl-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione (165 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1) afforded compound **II-3au** as a white solid (193 mg, 0.3 mmol, 60% yield)

**<sup>1</sup>H NMR** δ (ppm) = 7.58 – 7.55 (m, 6H), 7.48 – 7.43 (m, 3H), 7.41 – 7.35 (m, 6H), 6.98 (d, J = 0.7 Hz, 1H), 4.50 (q, J = 7.1 Hz, 2H), 4.28 (m, 1H), 4.21 – 4.13 (m, 1H), 4.08 (m, 1H), 3.94 (s, 3H), 3.54 (s, 3H), 2.97 (m, 2H), 2.09 – 1.99 (m, 1H), 1.90 – 1.82 (m, 1H), 1.33 (t, J = 7.1 Hz, 3H).

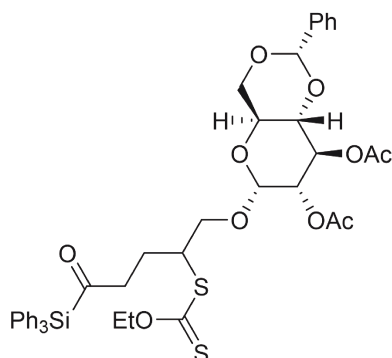
**<sup>13</sup>C NMR** δ (ppm) = 213.2, 155.1, 151.4, 141.6, 136.2 (6C), 131.1 (3C), 130.3 (3C), 128.3 (6C), 125.6, 107.5, 70.0, 47.7, 43.5, 33.6, 30.3, 29.8, 24.4, 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3052, 2951, 1703, 1656, 1603, 1548, 1485, 1455, 1428, 1392, 1364, 1318, 1286, 1265, 1233, 1188, 1110, 1046, 996, 731.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>33</sub>H<sub>35</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 643.1864; Found 643.1861

**mp:** 140 - 142°C

(2S,4aS,6R,7S,8R,8aS)-6-((2-((ethoxycarbonothioyl)thio)-5-oxo-5-(triphenylsilyl)pentyl)oxy)-2-phenylhexahydropyrano[3,2-d][1,3]dioxine-7,8-diyl diacetate (**II-3av**)



C<sub>43</sub>H<sub>46</sub>O<sub>10</sub>S<sub>2</sub>Si  
M = 814.2302

According to general procedure B, xanthate **II-1a** (211g, 0.5 mmol, 1 equiv.), (2S,4aS,6R,7S,8R,8aS)-6-(allyloxy)-2-phenylhexahydropyrano[3,2-d][1,3]dioxine-7,8-diyl diacetate (294 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1) afforded compound **II-3av** as a colorless oil (224 mg, 0.28 mmol, 55% yield, d.r. = 1:1)

**<sup>1</sup>H NMR** δ (ppm) = 7.57 (m, 6H), 7.47 – 7.33 (m, 14H), 5.56 – 5.47 (m, 2H), 5.05 (m, 1H), 4.85 (m, 1H), 4.61 – 4.47 (m, 2H), 4.25 (m, 1H), 3.95 – 3.69 (m, 4H), 3.64 – 3.58 (m, 1H), 3.55 (m, 1H), 2.98 – 2.86 (m, 2H), 2.21 – 2.12 (m, 1H), 2.06 – 2.04 (m, 6H), 1.87 – 1.72 (m, 1H), 1.35 (t, J = 7.1, 4.6 Hz, 3H).

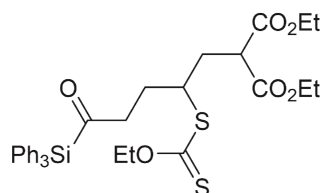
**<sup>13</sup>C NMR** δ (ppm) = 213.4, 170.6, 169.8, 137.0, 136.2 (6C), 131.0 (3C), 130.4 (3C), 129.1 (6C), 128.3, 128.2 (2C), 126.2 (2C), 101.5, 97.2, 96.5, 79.2, 71.5, 70.2, 69.0, 68.8, 62.6, 49.8, 49.5, 47.5, 23.0, 20.9, 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2924, 2850, 1746, 1643, 1485, 1428, 1368, 1220, 1150, 1110, 1031, 997, 910, 739, 698.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>43</sub>H<sub>47</sub>BO<sub>10</sub>S<sub>2</sub>Si]<sup>+</sup>: 815.2374; Found 815.2574

Diethyl2-(2-((ethoxycarbonothioyl)thio)-5-oxo-5-(triphenylsilyl)pentyl)malonate

**(II-3aw)**



C<sub>33</sub>H<sub>38</sub>O<sub>6</sub>S<sub>2</sub>Si  
M = 622.1879

According to general procedure B, xanthate **II-1a** (126g, 0.3 mmol, 1 equiv.), diethyl 2-allylmalonate (120 mg, 0.6 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 30 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 9/1) afforded compound **II-3aw** as a colorless oil (125 mg, 0.2 mmol, 67% yield)

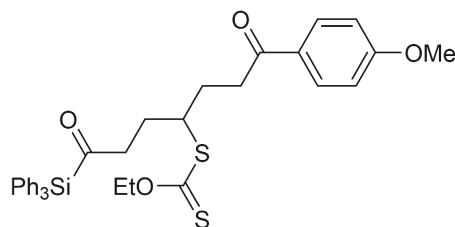
**<sup>1</sup>H NMR** δ (ppm) = 7.59 – 7.56 (m, 6H), 7.49 – 7.44 (m, 3H), 7.42 – 7.37 (m, 6H), 4.60 – 4.49 (q, J = 7.1 Hz, 2H), 4.23 – 4.12 (m, 4H), 3.69 (m, 1H), 3.55 (m, 1H), 2.90 (m, 2H), 2.28 (m, 1H), 2.11 – 1.99 (m, 2H), 1.88 – 1.76 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.24 (m, 6H).

**<sup>13</sup>C NMR** δ (ppm) = 213.2, 169.0, 168.8, 136.1 (6C), 131.0 (3C), 130.3 (3C), 128.3 (6C), 70.1, 61.7, 49.7 (2C), 49.1, 47.6, 33.5, 27.3, 14.1 (2C), 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3069, 2980, 2934, 1746, 1729, 1643, 1428, 1368, 1334, 1213, 1147, 1109, 1045, 998, 856, 741, 698.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>33</sub>H<sub>38</sub>NaO<sub>6</sub>S<sub>2</sub>Si]<sup>+</sup>: 645.1771; Found 645.1808

O-ethylS-(1-(4-methoxyphenyl)-1,7-dioxo-7-(triphenylsilyl)heptan-4-yl)carbonodithioate  
**(II-3az)**



C<sub>35</sub>H<sub>36</sub>O<sub>4</sub>S<sub>2</sub>Si  
M = 612.1824

According to general procedure B, xanthate **II-1a** (422g, 1 mmol, 1 equiv.), diethyl 2-allylmalonate (380 mg, 2 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 95/5) afforded compound **II-3az** as a colorless oil (361 mg, 0.59 mmol, 59% yield)

**<sup>1</sup>H NMR** δ (ppm) = 7.92 – 7.88 (m, 2H), 7.60 – 7.55 (m, 6H), 7.49 – 7.43 (m, 3H), 7.42 – 7.37 (m, 6H), 6.94 – 6.90 (m, 2H), 4.51 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 3.77 – 3.69 (m, 1H), 3.08 – 2.98 (m, 2H), 2.98 – 2.84 (m, 2H), 2.15 – 2.01 (m, 2H), 1.97 – 1.77 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H).

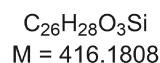
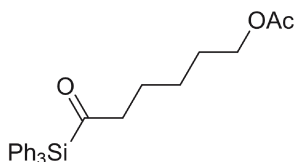
**<sup>13</sup>C NMR** δ (ppm) = 213.8, 197.7, 163.5, 136.2 (6C), 131.0 (3C), 130.4 (3C), 130.3 (2C), 129.9, 128.3 (6C), 113.7 (2C), 70.0, 55.5, 50.6, 47.7, 35.4, 29.1, 26.9, 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2951, 2929, 2857, 1704, 1637, 1472, 1462, 1361, 1251, 1190, 1142, 1099, 1031, 1002, 832, 776.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>35</sub>H<sub>37</sub>O<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 613.1897; Found 613.1899



6-oxo-6-(triphenylsilyl)hexyl acetate (**II-5a**)



According to general procedure C, a solution of **II-3ad** (90 mg, 0.17 mmol, 1 equiv.) and tris(trimethylsilyl)silane (TTMSS, 50 mg, 1.1 equiv.) in Toluene/cyclohexane (1:1, 1.7 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portion wise (20 mol% according to xanthate) every hour until total consumption of the starting xanthate (2h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 95/5) afforded compound **II-5a** as a colorless oil (35 mg, 0.09 mmol, 92% yield).

**$^1H$  NMR**  $\delta$  (ppm) = 7.62 – 7.58 (m, 6H), 7.50 – 7.45 (m, 3H), 7.44 – 7.38 (m, 6H), 3.98 (t, J = 7.1 Hz, 2H), 2.75 (t, J = 7.2 Hz, 2H), 2.02 (s, 3H), 1.55 (m, 4H), 1.24 (m, 2H).  
(400 MHz,  $CDCl_3$ )

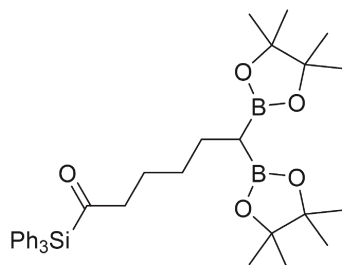
**$^{13}C$  NMR**  $\delta$  (ppm) = 171.2, 136.1 (6C), 131.3 (3C), 130.3 (3C), 128.2 (6C), 64.3, 50.4, 28.5, 25.5, 21.8, 21.0. (Si-C=O not observed).  
(101 MHz,  $CDCl_3$ )

**IR** (neat)  $\nu$  ( $cm^{-1}$ ) = 3069, 2937, 2861, 1733, 1642, 1428, 1364, 1235, 1189, 1109, 1042, 997, 739, 697.

**HRMS** (EI<sup>+</sup>) m/z:  $[M+Na]^+$ , Calcd for  $[C_{26}H_{28}NaO_3Si]^+$ : 439.17; Found 439.17

6,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triphenylsilyl)hexan-1-one

**(II-5b)**



C<sub>36</sub>H<sub>48</sub>B<sub>2</sub>O<sub>5</sub>Si  
M = 610.3457

According to general procedure C, a solution of **II-3ag** (330 mg, 0.45 mmol, 1 equiv.) and tris(trimethylsilyl)silane (TTMSS, 121 mg, 1.1 equiv.) in Toluene/cyclohexane (1:1, 4.5 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portion wise (20 mol% according to xanthate) every hour until total consumption of the starting xanthate (2h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 94/6) afforded compound **II-5b** as a colorless oil (187 mg, 0.31 mmol, 68% yield).

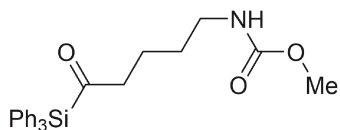
**<sup>1</sup>H NMR** δ (ppm) = 7.61 – 7.56 (m, 6H), 7.48 – 7.43 (m, 3H), 7.41 – 7.36 (m, 6H), 2.71 (t, J = 7.3 Hz, 2H), 1.53 – 1.42 (m, 4H), 1.20 (m, 26H), 0.64 (t, J = 7.8 Hz, 1H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 136.1 (6C), 131.5 (3C), 130.2 (3C), 128.2 (6C), 82.9 (5C), 50.7, 32.1, 25.4, 24.9 (4C), 24.5 (4C), 22.3. (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 2976, 2929, 2859, 1643, 1428, 1378, 1358, 1310, 1264, 1214, 1137, 1109, 968, 909, 849, 736, 708, 697.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>36</sub>H<sub>49</sub>B<sub>2</sub>O<sub>5</sub>Si<sup>+</sup>]: 611.3530; Found 611.3531

methyl (5-oxo-5-(triphenylsilyl)pentyl)carbamate (**II-5c**)



C<sub>25</sub>H<sub>27</sub>NO<sub>3</sub>Si  
417.1760

According to general procedure C, a solution of **II-3ah** (57 mg, 0.11 mmol, 1 equiv.) and tris(trimethylsilyl)silane (TTMSS, 30 mg, 1.1 equiv.) in Toluene/cyclohexane (1:1, 1 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portion wise (20 mol% according to xanthate) every hour until total consumption of the starting xanthate (2h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 85/15) afforded compound **II-5c** as a colorless oil (34 mg, 0.08 mmol, 74% yield).

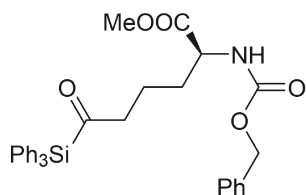
**<sup>1</sup>H NMR** δ (ppm) = 7.60 – 7.55 (m, 6H), 7.50 – 7.45 (m, 3H), 7.43 – 7.38 (m, 6H), 4.67 (s, 1H), 3.64 (m, 3H), 3.11 – 3.02 (m, 2H), 2.74 (t, J = 6.9 Hz, 2H), 1.57 – 1.48 (m, 2H), 1.37 (t, J = 7.6 Hz, 2H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 157.1, 136.1 (6C), 131.2 (3C), 130.4 (3C), 128.3 (6C), 52.0, 50.1, 40.7, 29.4, 19.1. (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3349, 3069, 2933, 1702, 1642, 1525, 1446, 1428, 1384, 1261, 1190, 1111, 845, 742, 699.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>25</sub>H<sub>28</sub>NO<sub>3</sub>Si]<sup>+</sup>: 418.1833; Found 418.1832

methyl (S)-2-(((benzyloxy)carbonyl)amino)-6-oxo-6-(triphenylsilyl)hexanoate (**II-5d**)



C<sub>33</sub>H<sub>33</sub>NO<sub>5</sub>Si  
M = 551.2128

According to general procedure C, a solution of **II-3an** (120 mg, 0.18 mmol, 1 equiv.) and tris(trimethylsilyl)silane (TTMSS, 50 mg, 1.1 equiv.) in Toluene/cyclohexane (1:1, 2 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portion wise (20 mol% according to xanthate) every hour until total consumption of the starting xanthate (2h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 9/1 to 83/17) afforded compound **II-5d** as a colorless oil (69 mg, 0.13 mmol, 70% yield).

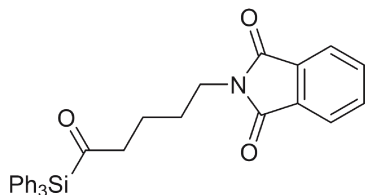
**<sup>1</sup>H NMR** δ (ppm) = 7.61 – 7.56 (m, 6H), 7.51 – 7.45 (m, 3H), 7.44 – 7.38 (m, 6H), 7.36 (m, 5H), 5.30 (m, 1H), 5.09 (s, 2H), 4.30 (m, 1H), 3.69 (s, 3H), 2.76 (t, J = 6.5 Hz, 2H), 1.72 (s, 1H), 1.56 (q, J = 6.2 Hz, 3H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 172.7, 155.9, 136.1 (6C), 135.0, 131.1 (3C), 130.4 (3C), 128.5 (2C), 128.3 (6C), 128.2 (2C), 128.1, 67.0, 53.7, 52.3, 49.8, 31.8, 17.8. (Si-C=O not observed).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3346, 3068, 2951, 1714, 1641, 1514, 1485, 1454, 1428, 1335, 1209, 1110, 1051, 1028, 997, 910, 736.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>33</sub>H<sub>34</sub>NO<sub>5</sub>Si]<sup>+</sup>: 552.2201; Found 552.2198

2-(5-oxo-5-(triphenylsilyl)pentyl)isoindoline-1,3-dione (**II-5e**)



C<sub>31</sub>H<sub>27</sub>NO<sub>3</sub>Si  
M = 489.1760

According to general procedure C, a solution of **II-3ao** (140 mg, 0.24 mmol, 1 equiv.) and tris(trimethylsilyl)silane (TTMSS, 67 mg, 1.1 equiv.) in Toluene/cyclohexane (1:1, 2 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portion wise (20 mol% according to xanthate) every hour until total consumption of the starting xanthate (2h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 9/1 to 85/15) afforded compound **II-5e** as a colorless solid (78 mg, 0.16 mmol, 66% yield).

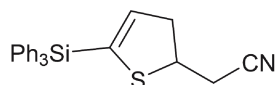
**<sup>1</sup>H NMR**            δ (ppm) = 7.81 (m, 2H), 7.70 – 7.67 (m, 2H), 7.60 – 7.56 (m, 6H), 7.48 – 7.43 (m, 3H), 7.42 – 7.36 (m, 6H), 3.64 – 3.56 (m, 2H), 2.82 – 2.74 (m, 2H), 1.61 – 1.50 (m, 4H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR**            δ (ppm) = 168.3 (2C), 136.1 (6C), 133.8 (3C), 132.1 (2C), 131.2 (2C), 130.3 (3C), 128.2 (6C), 123.2 (2C), 49.9, 37.7, 28.0, 19.4.  
(101 MHz, CDCl<sub>3</sub>) (Si-C=O not observed).

**IR (neat)**            ν (cm<sup>-1</sup>) = 3069, 2939, 1770, 1706, 1641, 1484, 1467, 1428, 1395, 1370, 1188, 1109, 1028, 997, 907, 719.

**HRMS (EI<sup>+</sup>) m/z:** [M+Na]<sup>+</sup>, Calcd for [C<sub>31</sub>H<sub>27</sub>NNaO<sub>3</sub>Si<sup>+</sup>]: 512.1652; Found 512.1648

2-(5-(triphenylsilyl)-2,3-dihydrothiophen-2-yl)acetonitrile (**II-14**)



C<sub>24</sub>H<sub>21</sub>NSSi  
M = 383.1164

According to the reported method<sup>[6]</sup>, to a solution of compound **II-3a1** (245 mg, 0.5 mmol, 1 equiv.) in dichloromethane at r.t. was added ethane diamine (90 mg, 1.5 mmol, 3 equiv.), the resulting mixture was stirred at r.t. for 1h. Then, deionized water, hydrochloric acid, and brine were added to the suspension and the resulting aqueous solution was extracted twice with dichloromethane. The combined organic layers were dried over anhydrous MgSO<sub>4</sub>. Filtered and concentrated under reduced pressure. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 9/1) afforded compound **II-14** as a colorless solid (172 mg, 0.45 mmol, 90%).

**<sup>1</sup>H NMR** δ (ppm) = 7.59 – 7.55 (m, 6H), 7.49 – 7.43 (m, 3H), 7.42 – 7.37 (m, 6H), 5.83 (m, 1H), 3.97 (m, 1H), 3.11 (m, 1H), 2.90 – 2.81 (m, 1H), 2.64 – 2.58 (m, 2H).  
(400 MHz, CDCl<sub>3</sub>)

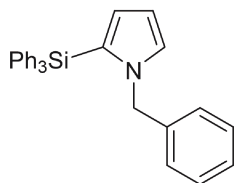
**<sup>13</sup>C NMR** δ (ppm) = 136.0 (6C), 135.0, 134.9, 132.7 (3C), 130.1 (3C), 128.0 (6C), 117.8, 45.4, 43.4, 24.8.  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3068, 3048, 1564, 1484, 1428, 1299, 1158, 1110, 1029, 997, 912, 838, 708.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>24</sub>H<sub>22</sub>NSSi<sup>+</sup>]: 384.1237; Found 384.1233

**mp:** 132 - 135°C

1-benzyl-2-(triphenylsilyl)-1H-pyrrole (**II-16a**)



C<sub>29</sub>H<sub>25</sub>NSi  
M = 415.1756

According to general procedure D, to a solution of compound **II-3ab** (86 mg, 0.16 mmol, 1 equiv.) in toluene (1.6 mL) was added benzylamine (43 mg, 0.4 mmol, 2.5 equiv.). The flask was equipped with a condenser and the suspension was stirred at 40 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (petroleum ether/ethyl acetate = 98/2) afforded compound **II-16a** as a colorless oil (30 mg, 0.072 mmol, 45% yield).

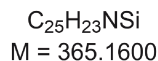
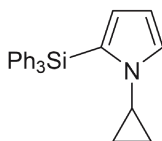
**<sup>1</sup>H NMR** δ (ppm) = 7.65 – 7.61 (m, 6H), 7.43 – 7.38 (m, 3H), 7.37 – 7.32 (m, 6H), 7.18 – 7.12 (m, 5H), 6.89 (m, 1H), 6.43 (m, 1H), 6.31 (m, 1H), 4.90 (s, 2H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 137.8, 136.2 (6C), 134.4 (3C), 129.6 (3C), 128.7, 128.3 (2C), 127.9 (6C), 127.3 (2C), 124.4, 121.2, 109.2, 108.5, 53.8.  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3066, 2919, 1496, 1454, 1428, 1355, 1286, 1079, 1029, 998, 968, 722, 699.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>29</sub>H<sub>26</sub>NSi]<sup>+</sup>: 416.1829; Found 416.1819

1-cyclopropyl-2-(triphenylsilyl)-1H-pyrrole (**II-16b**)



According to general procedure D, to a solution of compound **II-3ab** (80 mg, 0.15 mmol, 1 equiv.) in toluene (1.6 mL) was added cyclopropylamine (17 mg, 0.3 mmol, 2 equiv.). The flask was equipped with a condenser and the suspension was stirred at 40 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (petroleum ether/ethyl acetate = 98/2) afforded compound **II-16b** as a colorless oil (31 mg, 0.08 mmol, 56% yield).

**<sup>1</sup>H NMR**  $\delta$  (ppm) = 7.70 – 7.64 (m, 6H), 7.44 – 7.34 (m, 9H), 6.93 (m, 1H), 6.36 (m, 1H), 6.17 (m, 1H), 2.98 – 2.89 (m, 1H), 0.72 – 0.63 (m, 2H), 0.39 – 0.30 (m, 2H).  
(400 MHz, CDCl<sub>3</sub>)

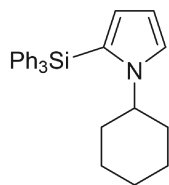
**<sup>13</sup>C NMR**  $\delta$  (ppm) = 136.3 (6C), 134.9 (3C), 129.5 (3C), 127.8 (6C), 127.7, 125.7, 125.3, 107.7, 32.2, 7.9 (2C).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 3067, 3012, 2924, 1547, 1510, 1484, 1428, 1370, 1263, 1188, 1108, 1052, 1028, 998, 742, 700.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>25</sub>H<sub>24</sub>NSi]<sup>+</sup>: 366.5585; Found 366.5579



1-cyclohexyl-2-(triphenylsilyl)-1H-pyrrole (**II-16c**)



C<sub>28</sub>H<sub>29</sub>NSi  
M = 407.2069

According to general procedure D, to a solution of compound **II-3ab** (150 mg, 0.27 mmol, 1 equiv.) in toluene (2.7 mL) was added cyclohexylamine (66 mg, 0.67 mmol, 2.5 equiv.). The flask was equipped with a condenser and the suspension was stirred at 40 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (petroleum ether/ethyl acetate = 98/2) afforded compound **II-16c** as a colorless oil (46 mg, 0.11 mmol, 42% yield).

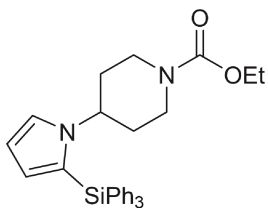
**<sup>1</sup>H NMR** δ (ppm) = 7.70 – 7.64 (m, 6H), 7.46 – 7.36 (m, 9H), 7.05 (m, 1H), 6.31 – 6.25 (m, 2H), 3.67 (m, 1H), 1.64 – 1.50 (m, 4H), 1.48 – 1.37 (m, 4H), 0.75 – 0.60 (m, 2H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 136.2 (6C), 134.7 (3C), 129.5 (3C), 127.8 (6C), 126.2, 122.5, 108.8, 107.4, 59.0, 35.0 (2C), 25.7 (2C), 25.2.  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3067, 2931, 2854, 1428, 1278, 1108, 1053, 997, 854, 700.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>28</sub>H<sub>30</sub>NSi]<sup>+</sup>: 408.2142; Found 408.2146

ethyl 4-(2-(triphenylsilyl)-1H-pyrrol-1-yl)piperidine-1-carboxylate (**II-16d**)



C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>Si  
M = 480.2233

According to general procedure D, to a solution of compound **II-3ab** (130 mg, 0.23 mmol, 1 equiv.) in toluene (2.3 mL) was added ethyl-4-aminopiperidine-1-carboxylate (80 mg, 0.46 mmol, 2 equiv.). The flask was equipped with a condenser and the suspension was stirred at 40 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (petroleum ether/ethyl acetate = 95/5) afforded compound **II-16d** as a colorless oil (47 mg, 0.10 mmol, 43% yield).

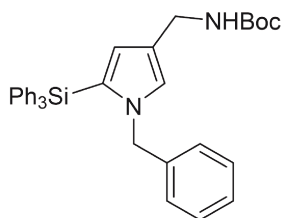
**<sup>1</sup>H NMR** δ (ppm) = 7.66 (m, 6H), 7.43 – 7.35 (m, 9H), 6.99 (m, 1H), 6.37 – 6.29 (m, 2H), 4.08 (q, J = 7.1Hz, 2H), 3.84 – 3.77 (m, 1H), 2.15 – 2.02 (m, 2H), 1.64 – 1.42 (m, 6H), 1.25 – 1.18 (t, J = 7.1Hz, 3H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 155.4, 136.0 (6C), 135.0 (3C), 129.2 (3C), 127.7 (6C), 120.0, 118.4, 115.5, 108.0, 61.6, 56.7 (2C), 43.2 (2C), 33.5, 14.7.  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3067, 2928, 2854, 1696, 1480, 1428, 1379, 1279, 1255, 1224, 1127, 1109, 1028, 984, 940, 878, 701.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>30</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub>Si<sup>+</sup>]: 481.2306; Found 481.2307

tert-butyl ((1-benzyl-5-(triphenylsilyl)-1H-pyrrol-3-yl)methyl)carbamate (**II-20a**)



C<sub>35</sub>H<sub>36</sub>N<sub>2</sub>O<sub>2</sub>Si  
M = 544.2546

According to general procedure D, to a solution of compound **II-3ar** (161 mg, 0.28 mmol, 1 equiv.) in toluene (2.8 mL) was added benzylamine (75 mg, 0.7 mmol, 2 equiv.). The flask was equipped with a condenser and the suspension was stirred at 40 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (petroleum ether/ethyl acetate = 95/5) afforded compound **II-20a** as a colorless oil (62 mg, 0.12 mmol, 41% yield).

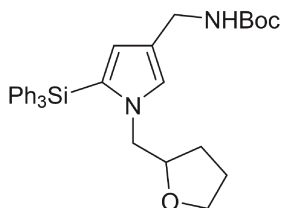
**<sup>1</sup>H NMR** δ (ppm) = 7.63 – 7.59 (m, 6H), 7.43 – 7.38 (m, 3H), 7.36 – 7.33 (m, 6H), 7.18 – 7.11 (m, 5H), 6.28 (d, J = 1.7 Hz, 1H), 6.12 (t, J = 2.2 Hz, 1H), 5.01 (s, 2H), 4.61 (s, 1H), 4.19 – 4.15 (m, 2H), 1.46 (s, 9H).

**<sup>13</sup>C NMR** δ (ppm) = 155.8, 137.5, 136.1 (6C), 134.1 (3C), 129.7 (3C), 128.8 (2C), 128.3 (2C), 127.9 (6C), 127.7, 123.6, 121.6, 119.5, 108.3, 79.1, 53.9, 53.4, 28.5 (3C).

**IR** (neat) ν (cm<sup>-1</sup>) = 3374, 2956, 2928, 1712, 1534, 1436, 1324, 1247, 1159, 1110, 989, 767, 698.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>35</sub>H<sub>37</sub>N<sub>2</sub>O<sub>2</sub>Si]<sup>+</sup>: 545.2619; Found 545.2618

tert-butyl((1-((tetrahydrofuran-2-yl)methyl)-5-(triphenylsilyl)-1H-pyrrol-3-yl)methyl)carbamate (**II-20b**)



C<sub>33</sub>H<sub>38</sub>N<sub>2</sub>O<sub>3</sub>Si  
M = 538.2652

According to general procedure D, to a solution of compound **II-3ar** (174 mg, 0.3 mmol, 1 equiv.) in toluene (3 mL) was added (tetrahydrofuran-2-yl)methylamine (76 mg, 0.75 mmol, 2.5 equiv.). The flask was equipped with a condenser and the suspension was stirred at 40 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (petroleum ether/ethyl acetate = 88/12) afforded compound **II-20b** as a colorless oil (102 mg, 0.19 mmol, 63% yield).

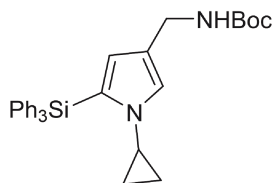
**<sup>1</sup>H NMR** δ (ppm) = 7.63 – 7.60 (m, 6H), 7.44 – 7.36 (m, 9H), 7.10 (d, J = 1.7 Hz, 1H), 6.22 (d, J = 1.7 Hz, 1H), 4.63 (s, 1H), 4.14 (m, 2H), 3.76 – 3.57 (m, 4H), 3.54 – 3.46 (m, 1H), 1.59 (m, 3H), 1.43 (s, 9H), 1.42 (m, 1H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 155.8, 136.2 (6C), 134.4 (3C), 129.7 (3C), 128.0 (6C), 127.2, 126.1, 123.4, 121.4, 79.0, 78.6, 67.9, 54.1, 37.8, 28.7, 28.5 (3C), 25.4.  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3353, 2974, 2928, 2871, 1711, 1500, 1454, 1428, 1390, 1365, 1247, 1169, 1108, 1068, 969, 742.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>33</sub>H<sub>39</sub>N<sub>2</sub>O<sub>3</sub>Si]<sup>+</sup>: 539.2724; Found 539.2718

tert-butyl ((1-cyclopropyl-5-(triphenylsilyl)-1H-pyrrol-3-yl)methyl)carbamate (**II-20c**)



C<sub>31</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>Si  
M = 494.2390

According to general procedure D, to a solution of compound **II-3ar** (161 mg, 0.28 mmol, 1 equiv.) in toluene (2.8 mL) was added cyclopropylamine (40 mg, 0.7 mmol, 2.5 equiv.). The flask was equipped with a condenser and the suspension was stirred at 40 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (petroleum ether/ethyl acetate = 95/5) afforded compound **II-20c** as a colorless oil (86 mg, 0.17 mmol, 62% yield).

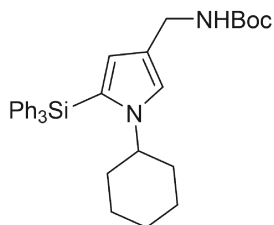
**<sup>1</sup>H NMR** δ (ppm) = 7.69 – 7.63 (m, 6H), 7.44 – 7.37 (m, 9H), 6.88 – 6.78 (m, 1H), 6.25 (d, J = 1.8 Hz, 1H), 4.64 (s, 1H), 4.17 – 4.07 (m, 2H), 2.88 (m, 1H), 1.44 (s, 9H), 0.65 (m, 2H), 0.33 (m, 2H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 155.8, 136.2 (6C), 134.7 (3C), 129.5 (3C), 127.8 (6C), 124.5, 124.4, 121.7, 120.3, 79.1, 37.6, 32.2, 28.5 (3C), 7.9 (2C).  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3376, 2952, 2924, 2856, 1724, 1550, 1438, 1364, 1228, 1148, 1110, 1064, 998, 767.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>31</sub>H<sub>34</sub>N<sub>2</sub>NaO<sub>2</sub>Si]<sup>+</sup>: 517,2282; Found 517.2274

tert-butyl ((1-cyclohexyl-5-(triphenylsilyl)-1H-pyrrol-3-yl)methyl)carbamate (**II-20d**)



C<sub>34</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>Si  
M = 536.2859

According to general procedure D, to a solution of compound **II-3ar** (174 mg, 0.3 mmol, 1 equiv.) in toluene (3 mL) was added cyclohexylamine (74 mg, 0.75 mmol, 2.5 equiv.). The flask was equipped with a condenser and the suspension was stirred at 40 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (petroleum ether/ethyl acetate = 96/4) afforded compound **II-20d** as a colorless oil (116 mg, 0.22 mmol, 72% yield).

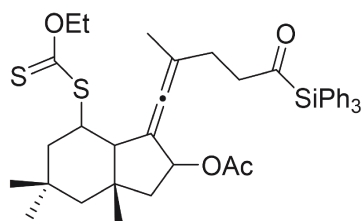
**<sup>1</sup>H NMR** δ (ppm) = 7.68 – 7.58 (m, 6H), 7.45 – 7.31 (m, 9H), 6.92 (m, 1H), 6.15 (d, J = 1.6 Hz, 1H), 4.63 (s, 1H), 4.15 (m, 2H), 3.79 – 3.65 (m, 1H), 2.12 – 1.99 (m, 2H), 1.87 (m, 2H), 1.72 (m, 2H), 1.64 – 1.52 (m, 4H), 1.45 (s, 9H).  
(400 MHz, CDCl<sub>3</sub>)

**<sup>13</sup>C NMR** δ (ppm) = 155.8, 136.1 (6C), 134.5 (3C), 129.6 (3C), 127.9 (6C), 121.9, 118.8, 117.0, 107.2, 79.1, 58.7, 38.0, 34.7 (2C), 28.5 (3C), 25.7 (2C), 25.2.  
(101 MHz, CDCl<sub>3</sub>)

**IR** (neat) ν (cm<sup>-1</sup>) = 3375, 2930, 2855, 1704, 1495, 1451, 1428, 1390, 1365, 1316, 1246, 1163, 1110, 1046, 866, 701.

**HRMS** (EI<sup>+</sup>) m/z: [M+Na]<sup>+</sup>, Calcd for [C<sub>34</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub>Si]<sup>+</sup>: 537.2932; Found 537.2927

(3aS)-7-((ethoxycarbonylthio)thio)-3a,5,5-trimethyl-1-(2-methyl-5-oxo-5-(triphenylsilyl)pent-1-en-1-ylidene)octahydro-1H-inden-2-yl acetate (**II-26**)



C<sub>41</sub>H<sub>48</sub>O<sub>4</sub>S<sub>2</sub>Si  
M = 696.2763

According to general procedure B, xanthate **II-1a** (1.3 g, 3 mmol, 1 equiv.), compound **II-25** (1.2 mg, 4.5 mmol, 1.5 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (15 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (petroleum ether / ethyl acetate = 96/4) afforded compound **II-26** as a colorless oil (877 mg, 1.26 mmol, 42% yield)

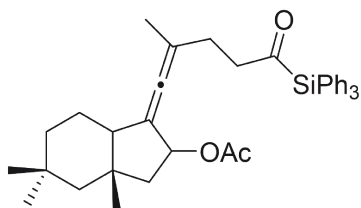
**<sup>1</sup>H NMR** δ (ppm) = 7.66 – 7.56 (m, 6H), 7.45 (m, 3H), 7.41 (m, 6H), 5.56 (m, 1H), 4.51 – 4.38 (m, 2H), 3.77 (m, 1H), 3.00 – 2.80 (m, 2H), 2.40 – 2.31 (m, 1H), 2.06 (m, 3H), 1.95 (s, 3H), 1.69 (s, 1H), 1.58 (m, 3H), 1.46 – 1.32 (m, 4H), 1.27 (m, 3H), 1.13 (s, 3H), 1.04 (s, 3H), 0.96 (s, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 214.3, 199.0, 170.5, 136.2 (6C), 135.0 (3C), 130.2 (3C), 128.2 (6C), 105.8, 102.9, 74.6, 69.7, 53.3, 52.3, 49.6, 47.3, 42.4, 34.4, 33.6, 31.7 (2C), 28.6, 27.3, 26.4, 21.3, 19.1, 13.7. (Si-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3069, 2952, 1736, 1642, 1428, 1369, 1232, 1144, 1110, 1049, 998, 859, 739. 709, 698.

**HRMS** (EI<sup>+</sup>) m/z: [M+H]<sup>+</sup>, Calcd for [C<sub>41</sub>H<sub>49</sub>O<sub>4</sub>S<sub>2</sub>Si]<sup>+</sup>: 697.2836; Found 697.2843

(3a*S*)-3a,5,5-trimethyl-1-(2-methyl-5-oxo-5-(triphenylsilyl)pent-1-en-1-ylidene)octahydro-1*H*-inden-2-yl acetate (**II-27**)



$C_{38}H_{44}O_3Si$   
M = 576.3060

According to general procedure C, a solution of **II-26** (791 mg, 1.14 mmol, 1 equiv.) and tris(trimethylsilyl)silane (TTMSS, 313 mg, 1.1 equiv.) in Toluene/cyclohexane (1:1, 10 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portion wise (10 mol% according to xanthate) every hour until total consumption of the starting xanthate (1h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 95/5) afforded compound **II-27** as a colorless oil (447 mg, 0.77 mmol, 68% yield).

**$^1H$  NMR**  $\delta$  (ppm) = 7.60 – 7.56 (m, 6H), 7.49 – 7.43 (m, 3H), 7.42 – 7.36 (m, 6H), 5.59 – 5.47 (m, 1H), 2.95 – 2.84 (m, 2H), 2.17 (s, 3H), 2.12 – 2.03 (m, 2H), 1.82 – 1.76 (m, 1H), 1.70 (s, 3H), 1.67 – 1.64 (m, 2H), 1.63 – 1.59 (m, 2H), 1.47 – 1.37 (m, 2H), 1.23 – 1.18 (m, 2H), 1.08 (s, 3H), 0.94 – 0.90 (m, 6H).  
(400 MHz,  $CDCl_3$ )

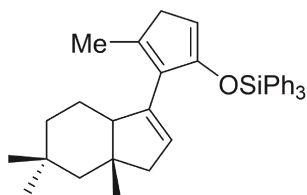
**$^{13}C$  NMR**  $\delta$  (ppm) = 196.8, 170.7, 136.2 (6C), 131.4 (3C), 130.3 (3C), 128.2 (6C), 108.2, 104.1, 75.2, 49.2, 48.8, 47.1, 46.7, 40.0, 34.5, 33.0, 30.4 (2C), 27.7, 27.3, 25.9, 21.1, 19.0. (Si-C=O not observed).  
(101 MHz,  $CDCl_3$ )

**IR** (neat)  $\nu$  ( $cm^{-1}$ ) = 3069, 2925, 2852, 1735, 1644, 1428, 1370, 1237, 1111, 998, 740, 699.

**HRMS** (EI<sup>+</sup>) m/z:  $[M+H]^+$ , Calcd for  $[C_{38}H_{45}O_3Si]^+$ : 577.3132; Found 577.3132



((4-methyl-5-((7aR)-6,6,7a-trimethyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl)cyclopenta-1,4-dien-1-yl)oxy)triphenylsilane (**II-28**)



$C_{36}H_{40}OSi$   
M = 516.2848

To an over dried screwcap 5 mL reaction tube was charged compound II-27 (255 mg, 0.44 mmol). The tube was then evacuated and backfilled with nitrogen for 3 times. Subsequently, cyclohexane (2 mL) was added into the tube under nitrogen. Once added, the tube was closed, and the reaction mixture was stirred and irradiated in a photo box with blue LEDs ( $\lambda_{max} = 440$  nm) for 1-2 days. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 98/2) afforded compound **II-28** as a colorless oil (136 mg, 0.26 mmol, 60% yield).

**$^1H$  NMR**  $\delta$  (ppm) = 7.63 (m, 6H), 7.45 – 7.41 (m, 3H), 7.40 – 7.36 (m, 6H), 5.82 – 5.76 (m, 1H), 5.43 (m, 1H), 2.70 – 2.60 (m, 2H), 2.56 – 2.48 (m, 1H), 2.23 – 2.12 (m, 1H), 1.78 (m, 1H), 1.55 – 1.41 (m, 2H), 1.34 – 1.23 (m, 4H), 1.20 (s, 3H), 1.03 (s, 3H), 0.93 – 0.89 (m, 6H).  
(400 MHz,  $CDCl_3$ )

**$^{13}C$  NMR**  $\delta$  (ppm) = 161.6, 159.2, 140.5, 136.2 (6C), 133.0 (3C), 129.9 (3C), 128.0 (6C), 123.7, 118.2, 92.7, 53.3, 47.1, 45.1, 36.0, 33.6, 30.3 (2C), 28.2, 27.0, 25.9, 24.9, 20.0.  
(101 MHz,  $CDCl_3$ )

**IR** (neat)  $\nu$  ( $cm^{-1}$ ) = 3069, 2948, 2924, 2868, 1643, 1456, 1428, 1376, 1306, 1213, 1188, 1110, 1030, 987, 962, 739, 698.

**HRMS** (EI<sup>+</sup>) m/z:  $[M+H]^+$ , Calcd for  $[C_{36}H_{41}OSi]^+$ : 517.2921; Found 517.2927

### Chapter III. The xanthate chemistry of acyl(MIDA)boronates

#### ***General procedure A: Radical addition with non-activated alkenes***

Xanthate (1.0 equiv.), olefin (1.5-3.0 equiv.) and dilauroyl peroxide (DLP) (0.05 equiv., according to xanthate) were mixed in a vial and dissolved in EtOAc, then air in the vial was excluded by argon (*note: the air was excluded by using a balloon filled with argon and a long needle, which goes deep into the reaction mixture and slowly bubbles for 1 min and repeats 2-3 times*). The vial was sealed and heated at 83 °C. Additional dilauroyl peroxide (DLP) was added portion-wise (0.05 equiv.) every hour until total consumption of the starting xanthate (typically 8-10 portions of DLP)<sup>[3]</sup>. The reaction mixture was then cooled down to room temperature and purified by flash chromatography on silica gel.

#### ***General procedure B: Reduction of the xanthate group***

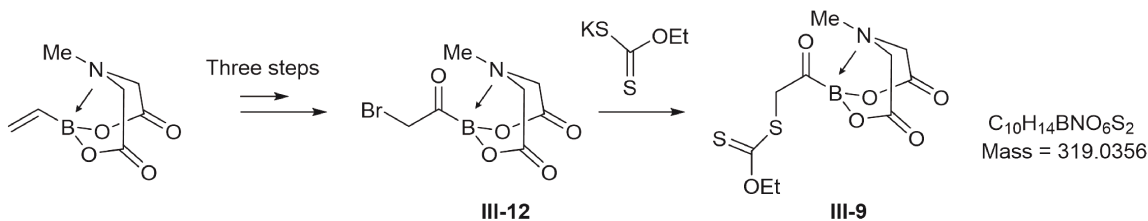
A solution of xanthate (1.0 equiv.) and tris(trimethylsilyl)silane (TTMSS, 1.1 equiv.) in MeCN (0.2M according to xanthate) was refluxed under nitrogen for 10 min. Then AIBN was added portionwise (20 mol% according to xanthate) every hour until total consumption of the starting xanthate (2 h total reaction time)<sup>[4]</sup>. The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation (CAUTION: manipulate under well ventilated fumehoods due to the strong smell!). Flash chromatography on silica gel of the crude material gave the desired product.

#### ***General procedure C: Synthesis of 2-pyrrole(MIDA) boronates***

To a solution of adduct **III-11f** (n mmol, 1 equiv.) in MeCN (8n mL) was added primary amines (2n mmol, 2 equiv.)<sup>[5a, 5b, 5c]</sup>. The flask was equipped with a condenser and the suspension was stirred at 75 °C with a heating block until completion of the reaction (followed by TLC, usually 1 h). The reaction mixture was then cooled down to room temperature, purified by flash chromatography on silica gel.

### Preparation of Xanthate III-9

O-ethylS-(2-(6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)-2-oxoethyl)carbonyl dithioate (**III-9**)



According to the reported method<sup>[7]</sup>, to a solution of vinyl MIDA boronate (9.5 g, 52.0 mmol, 1 equiv.) in MeCN (500 mL) under ambient atmosphere was added 3-chloroperbenzoic acid (mCPBA, 25.5 g, 114.2 mmol, 2.2 equiv.) in one portion. The resulting mixture was stirred at 35 °C for 26 h. The resulting mixture was cooled to room temperature. The volatiles were removed in vacuo (30 °C, 20 mmHg). Diethyl ether (945 mL) was then added to the reaction mixture and the resulting suspension was stirred at room temperature for 16 h. The suspension was filtered through a medium fritted funnel where the filter cake was broken up and washed further with diethyl ether (280 mL). The solids were collected via vacuum filtration to afford the desired product, oxiran-2-yl MIDA boronate as a white solid (9.53 g, 98% yield).

To a solution of oxiran-2-yl MIDA boronate (9.0 g, 45.2 mmol, 1 equiv.) in MeCN (450 mL) under ambient atmosphere was added LiBr (19.6 g, 226 mmol, 5 equiv.) and glacial acetic acid (38.8 mL, 678 mmol, 15 equiv.) at room temperature. The resulting mixture was allowed to stir at room temperature for 3 h. The solvent was removed in vacuo (30 °C, 20 mmHg) and the crude residue was dissolved in EtOAc (600 mL) and acetone (180 mL). The mixture was washed with deionized water (300 mL), then separated. The aqueous layer was extracted with EtOAc/acetone (3 x 400 mL, 3:1 EtOAc/acetone ratio). The combined organic phase is dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo (30 °C, 20 mmHg) to afford (2-bromo-1-hydroxyethyl) MIDA boronate (11.3 g, 93% yield).

(2-bromo-1-hydroxyethyl) MIDA boronate (11.3 g, 40.4 mmol, 1 equiv.) was dissolved in MeCN (200 mL) and EtOAc (200 mL) and stirred at room temperature for 20 min in order to completely dissolve in solution. Upon solvation, the resulting mixture was

cooled to 0 °C and stirred for 10 min. To the solution was added Dess–Martin periodinane DMP (20.6 g, 48.5 mmol, 1.2 equiv.) in one portion and then allowed to stir at 0 °C for 1 h. The resulting mixture was followed diluted with a 1:1 mixture of EtOAc and MeCN (400 mL), whereby the liquid phase was slowly decanted through a funnel by vacuum filtration and the volatiles of the filtrate were removed in vacuo to afford a yellow residue. The resulting residue was suspended with EtOAc (300 mL) and stirred at room temperature for 0.5 h under ambient atmosphere. The mixture was filtered through a pad of Celite via vacuum filtration and the volatiles of the filtrate were removed in vacuo and to the resulting residue was added a 1:1 mixture of EtOAc/acetone (30 mL) which was sonicated and stirred to afford a thick suspension. Diethyl ether (300 mL) was added slowly and then stirred at room temperature for an additional 10min. The suspension was filtered via vacuum filtration where the filter cake was allowed to dry under vacuum. The filter cake was collected and then added EtOAc (150 mL) and DCM (250 mL). The suspension was stirred at room temperature for 0.5 h. Toluene (1 L) was then added to the stirred suspension over 5 min and stirred at room temperature for 16 h. The suspension was filtered through a medium fritted funnel by vacuum filtration, then the filter cake was collected and dried under vacuo. Acetone (250 mL) was then added to the resulting filter cake and stirred at 0 °C for 1 h. After 1h, the suspension was filtered through a pad of Celite by vacuum filtration and the volatiles filtrate were removed in vacuo (20 °C, 10 mmHg) to obtain the desired product (2-Bromoacetyl) MIDA boronate **III-12** as a colorless solid (7.6 g, 67% yield).

To a solution of (2-Bromoacetyl) MIDA boronate **III-12** (4.3 g, 15.5 mmol, 1 equiv.) in acetone (75 mL) at 0 °C under N<sub>2</sub> was added potassium O-ethylxanthate salt (2.8 g, 17.0 mmol, 1.1 equiv.) portionwise over 5 min<sup>[2]</sup>. The mixture was stirred for 2 h. Then, water at 0 °C and CH<sub>2</sub>Cl<sub>2</sub> was added to the suspension and the resulting aqueous solution was extracted twice with dichloromethane. The combined organic layer was washed by brine, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. Flash chromatography on silica gel (Dichloromethane /acetonitrile = 9/1 to 8/2) afforded desired product **III-9** as a colorless solid (3.3 g, 10.2 mmol, 68% yield).

**<sup>1</sup>H NMR**  $\delta$  (ppm) = 4.62 (q, J = 7.1 Hz, 2H), 4.46 (s, 2H), 4.42 (d, J = 17.0 Hz, 2H), 4.19 (d, J = 16.9 Hz, 2H), 3.13 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H).  
(400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO)

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 214.8, 168.5 (2C), 71.1, 63.2 (2C), 47.5, 30.1, 13.9.  
(101 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) (B-C=O not observed).

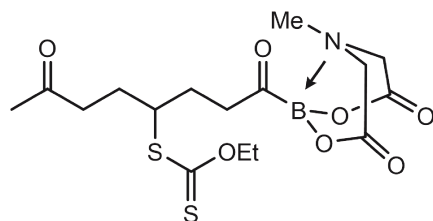
**IR (neat)**  $\nu$  (cm<sup>-1</sup>) = 2976, 1769, 1677, 1458, 1336, 1278, 1226, 1139, 1113, 1051, 991, 961, 891, 819, 691.

**HRMS (EI<sup>+</sup>) m/z:** [M + H]<sup>+</sup>, Calcd for [C<sub>10</sub>H<sub>15</sub>BNO<sub>6</sub>S<sub>2</sub><sup>+</sup>]: 320.0428; Found 320.0429

**mp:** 117-120°C

## Substrate Scope

O-ethylS-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1,7-dioxooctan-4-yl)-carbonyl dithioate (**III-11a**)



$C_{16}H_{24}BNO_7S_2$   
M = 417.1087

According to general procedure A, xanthate **III-9** (153 mg, 0.5 mmol, 1 equiv.), 5-Hexen-2-one (98 mg, 1 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11a** as a colorless amorphous solid (115 mg, 0.27 mmol, 55% yield).

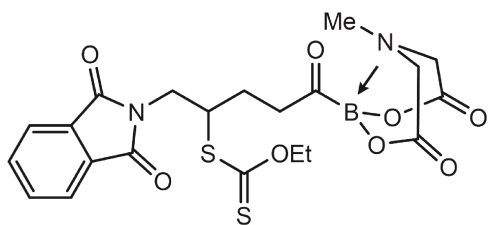
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 4.66 (q, J = 7.1 Hz, 2H), 4.35 (d, J = 16.9 Hz, 2H),  
(400 MHz,  $(CD_3)_2CO$ ) 4.12 (d, J = 16.9, 2.0 Hz, 2H), 3.75 (m, 1H), 3.08 (s, 3H), 2.84  
(t, J = 8.0, 6.7 Hz, 2H), 2.65 (t, J = 7.5 Hz, 2H), 2.10 (s, 3H),  
2.00 (m, 2H), 1.91 – 1.79 (m, 2H), 1.41 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 215.1, 207.2, 168.7 (2C), 70.8, 63.0 (2C), 51.3, 47.1,  
(101 MHz,  $(CD_3)_2CO$ ) 44.4, 40.8, 30.1, 28.9, 27.0, 13.9. (B-C=O not observed).

**IR** (neat)  $\nu$  ( $cm^{-1}$ ) = 2951, 1769, 1711, 1662, 1452, 1363, 1337, 1280,  
1221, 1148, 1111, 1052, 992, 898, 860, 712.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>16</sub>H<sub>25</sub>BNO<sub>7</sub>S<sub>2</sub><sup>+</sup>]: 418.116; Found 418.115

S-(1-(1,3-dioxisoindolin-2-yl)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)-5-oxopentane-2-yl) O-ethyl carbonodithioate (**III-11b**)



C<sub>21</sub>H<sub>23</sub>BN<sub>2</sub>O<sub>8</sub>S<sub>2</sub>  
M = 506.0989

According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), 2-allylisoindoline-1,3-dione (187 mg, 1.0 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11b** as a colorless amorphous solid (172 mg, 0.34 mmol, 68% yield).

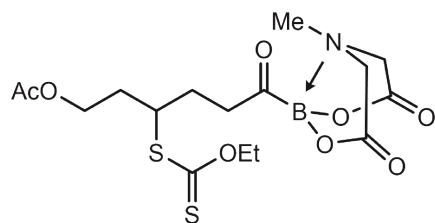
**<sup>1</sup>H NMR** δ (ppm) = 8.00 – 7.78 (m, 4H), 4.65 – 4.49 (m, 2H), 4.35 (d, J = 17.0, 0.8 Hz, 2H), 4.22 – 4.16 (m, 1H), 4.13 (d, J = 16.9, 3.0 Hz, 2H), 4.04 – 3.91 (m, 2H), 3.08 (s, 3H), 2.95 (t, J = 7.2 Hz, 2H), 2.17 – 2.08 (m, 1H), 1.93 – 1.80 (m, 1H), 1.39 (t, J = 7.1 Hz, 3H).  
(CD<sub>3</sub>)<sub>2</sub>CO

**<sup>13</sup>C NMR** δ (ppm) = 213.6, 168.6 (4C), 135.22 (2C), 132.91 (2C), 123.94 (2C), 71.10, 63.08 (2C), 50.07, 47.24, 44.41, 41.78, 24.50, 13.85. (B-C=O not observed).  
(CD<sub>3</sub>)<sub>2</sub>CO

**IR** (neat) ν (cm<sup>-1</sup>) = 3495, 2957, 2926, 1767, 1710, 1662, 1614, 1467, 1430, 1361, 1334, 1277, 1248, 1220, 1192, 1172, 1148, 1110, 1088, 1042, 989, 962, 897, 861, 797, 721.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>21</sub>H<sub>24</sub>BN<sub>2</sub>O<sub>8</sub>S<sub>2</sub><sup>+</sup>]: 507.1062; Found 507.1047

3-((ethoxycarbonothioyl)thio)-6-(6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)-6-oxo  
hexyl acetate (**III-11c**)



C<sub>16</sub>H<sub>24</sub>BNO<sub>8</sub>S<sub>2</sub>  
M = 433.1036

According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), ethylene-vinyl acetate (86 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated in at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11c** as a colorless amorphous solid (104 mg, 0.24 mmol, 48% yield).

**<sup>1</sup>H NMR** δ (ppm) = 4.66 – 4.63 (q, 2H), 4.35 (d, J = 16.9 Hz, 2H), 4.18 (t, (400 MHz, J = 6.6 Hz, 2H), 4.16 – 4.08 (d, J = 16.9, 0.6 Hz, 2H), 3.87 (m, (CD<sub>3</sub>)<sub>2</sub>CO) 1H), 3.08 (s, 3H), 2.86 (t, J = 7.3 Hz, 2H), 2.14 – 2.07 (m, 2H), 2.04 – 2.01 (m, 1H), 2.01 (s, J = 0.5 Hz, 3H), 1.87 (m, 1H), 1.42 (t, J = 7.1, 0.5 Hz, 3H).

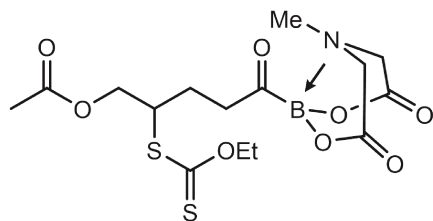
**<sup>13</sup>C NMR** δ (ppm) = 214.7, 170.9, 168.7 (2C), 70.9, 63.1 (2C), 62.2, 48.6, (101 MHz, 47.1, 44.5, 34.2, 26.9, 20.8, 13.9. (B-C=O not observed). (CD<sub>3</sub>)<sub>2</sub>CO)

**IR** (neat) ν (cm<sup>-1</sup>) = 2946, 1766, 1732, 1662, 1456, 1388, 1365, 1336, 1274, 1232, 1147, 1111, 1046, 990, 962, 896, 872, 820, 722.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>16</sub>H<sub>25</sub>BNO<sub>8</sub>S<sub>2</sub><sup>+</sup>]: 434.1109; Found 434.1121



2-((ethoxycarbonothioyl)thio)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-oxo  
pentyl acetate (**III-11d**)



C<sub>15</sub>H<sub>22</sub>BNO<sub>8</sub>S<sub>2</sub>  
M = 419.0880

According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), allyl acetate (75 mg, 0.75 mmol, 1.5 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 50 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11d** as a colorless amorphous solid (130 mg, 0.31 mmol, 62% yield).

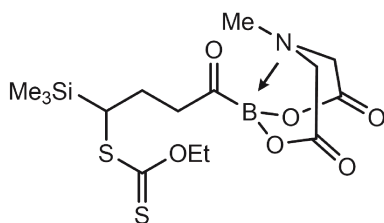
**<sup>1</sup>H NMR** δ (ppm) = 4.72 – 4.64 (q, J = 7.1 Hz, 2H), 4.35 (d, J = 16.9 Hz, 2H), 4.29 (t, J = 5.7 Hz, 2H), 4.13 (d, J = 16.9, 1.2 Hz, 2H), 4.01 (d, J = 9.1, 5.5 Hz, 1H), 3.08 (s, 3H), 2.89 (d, J = 7.9, 6.7 Hz, 2H), 2.14 – 2.08 (m, 1H), 2.04 (s, J = 0.3 Hz, 3H), 1.92 – 1.80 (m, 1H), 1.42 (t, J = 7.1, 0.4 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 214.2, 170.7, 168.7 (2C), 71.1, 65.9, 63.0 (2C), 49.9, 47.1, 44.4, 23.6, 20.6, 13.9. (B-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2923, 1768, 1710, 1362, 1268, 1212, 1146, 1110, 1089, 1043, 988, 961, 895, 857, 732.

**HRMS** (EI<sup>+</sup>) m/z:[M + Na]<sup>+</sup>, Calcd for [C<sub>15</sub>H<sub>22</sub>BNNaO<sub>8</sub>S<sub>2</sub><sup>+</sup>]: 442.0772; Found 442.0759

O-ethyl S-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-oxo-1-(trimethylsilyl)butyl) carbonodithioate (**III-11e**)



$C_{15}H_{26}BNO_6S_2Si$   
M = 419.1064

According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), vinyltrimethyl silane (300 mg, 3.0 mmol, 6 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11e** as a colorless amorphous solid (102 mg, 0.24 mmol, 49% yield).

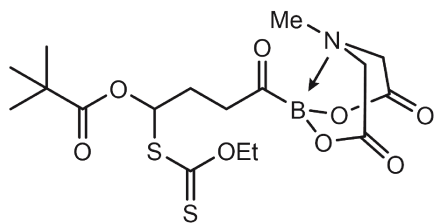
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 4.67 – 4.64 (q, 2H), 4.34 (d, J = 16.9 Hz, 2H), 4.14 – 4.07 (d, J = 17.0, 2.4 Hz, 2H), 3.21 – 3.19 (m, 1H), 3.07 (s, 3H), (CD<sub>3</sub>)<sub>2</sub>CO 2.84 (m, 2H), 2.21 – 2.11 (m, 1H), 1.78 – 1.63 (m, 1H), 1.42 (t, J = 7.1, 0.4 Hz, 3H), 0.17 – 0.11 (m, 9H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 217.1, 168.7 (2C), 71.2, 63.1 (2C), 47.2, 45.8, 37.2, 23.5, 14.1, -2.4 (3C). (B-C=O not observed). (CD<sub>3</sub>)<sub>2</sub>CO

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 2954, 2924, 1740, 1710, 1445, 1366, 1290, 1249, 1213, 1146, 1110, 1045, 838, 753.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>15</sub>H<sub>27</sub>BNO<sub>6</sub>S<sub>2</sub>Si]<sup>+</sup>: 420.1137; Found 420.1142

1-((ethoxycarbonothioyl)thio)-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)-4-oxo  
butylpivalate (**III-11f**)



C<sub>17</sub>H<sub>26</sub>BNO<sub>8</sub>S<sub>2</sub>  
M = 447.1193

According to general procedure A, xanthate **III-9** (1.6 g, 5 mmol, 1 equiv.), vinyl pivalate (1.28 g, 10 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (20 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11f** as a colorless amorphous solid (1.14 g, 2.5 mmol, 51% yield).

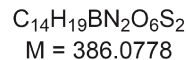
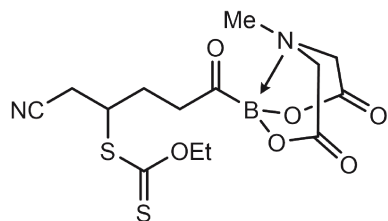
**<sup>1</sup>H NMR** δ (ppm) = 6.63 (t, J = 7.0, 6.0, 0.7 Hz, 1H), 4.66 (m, 2H), 4.36 (400 MHz, (d, J = 17.0, 0.9 Hz, 2H), 4.14 (d, J = 17.0, 0.9 Hz, 2H), 3.11 (s, (CD<sub>3</sub>)<sub>2</sub>CO) 3H), 2.95 – 2.72 (m, 2H), 2.33 – 2.18 (m, 1H), 2.17 – 2.08 (m, 1H), 1.42 (t, J = 7.1, 0.7 Hz, 3H), 1.20 (d, J = 0.7 Hz, 9H).

**<sup>13</sup>C NMR** δ (ppm) = 211.3, 177.0, 168.7 (2C), 80.7, 71.2, 63.1 (2C), 47.3, (101 MHz, (CD<sub>3</sub>)<sub>2</sub>CO) 42.4, 39.4, 27.5, 27.2 (3C), 13.9. (B-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2953, 2924, 1763, 1662, 1452, 1366, 1231, 1139, 1046, 897, 766

**HRMS** (EI<sup>+</sup>) m/z: [M - PivO]<sup>+</sup>, Calcd for [C<sub>12</sub>H<sub>17</sub>BNO<sub>6</sub>S<sub>2</sub><sup>+</sup>]: 346.0585; Found 346.0580

S-(1-cyano-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-oxopentan-2-yl)O-ethylcarbonodithioate (**III-11g**)



According to general procedure A, xanthate **III-9** (128 mg, 0.4 mmol, 1 equiv.), allyl cyanide (110 mg, 1.6 mmol, 4 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (1.6 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11g** as a colorless amorphous solid (94 mg, 0.24 mmol, 61% yield).

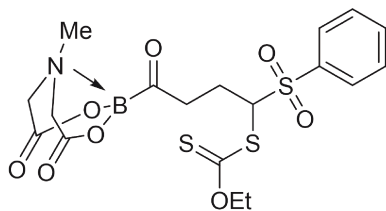
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 4.72 – 4.66 (q, 2H), 4.35 (d, J = 16.9 Hz, 2H), 4.17 – 4.09 (d, J = 17.0 Hz, 2H), 4.00 – 3.95 (m, 1H), 3.15 – 3.08 (m, 2H), 3.08 (s, 3H), 2.94 (t, J = 7.7, 6.6 Hz, 2H), 2.18 – 2.10 (m, 1H), 1.96 (m, 1H), 1.44 (t, J = 7.1, 0.5 Hz, 3H).  
( $CD_3)_2CO$ )

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 213.2, 168.6 (2C), 118.1, 71.3, 63.0 (2C), 47.1, 46.9, 44.2, 25.6, 24.1, 13.8. (B-C=O not observed).  
( $CD_3)_2CO$ )

**IR** (neat)  $\nu$  ( $cm^{-1}$ ) = 2926, 2854, 2249, 1765, 1699, 1664, 1456, 1421, 1364, 1336, 1277, 1226, 1147, 1111, 1045, 989, 962, 896, 856, 708.

**HRMS** (EI<sup>+</sup>) m/z: [M + Na]<sup>+</sup>, Calcd for [ $C_{14}H_{19}BN_2NaO_6S_2^+$ ]: 409.0670; Found 409.0682

O-ethylS-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)-4-oxo-1(phenylsulfonyl)butyl)carbonodithioate (**III-11h**)



$C_{18}H_{22}BNO_8S_3$   
M = 487.0601

According to general procedure A, xanthate **III-9** (100 mg, 0.3 mmol, 1 equiv.), phenyl vinyl sulfone (104 mg, 0.4 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (1.2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11h** as a colorless amorphous solid (80 mg, 0.16 mmol, 55% yield).

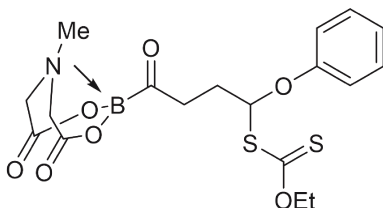
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 8.03 – 7.93 (m, 2H), 7.81 – 7.74 (m, 1H), 7.72 – 7.65 (m, 2H), 5.34 (d, J = 11.3, 3.9 Hz, 1H), 4.61 – 4.40 (m, 2H), 4.35 (d, J = 16.9 Hz, 2H), 4.12 (d, J = 16.9, 3.3 Hz, 2H), 3.07 (s, 3H), 3.01 – 2.91 (m, 2H), 2.63 – 2.59 (m, 1H), 2.02 – 1.87 (m, 1H), 1.33 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 209.7, 168.6 (2C), 137.9, 135.1, 130.4 (2C), 130.0 (2C), 72.2, 71.2, 63.1 (2C), 47.2, 43.3, 20.5, 13.7. (B-C=O not observed).

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 3484, 2957, 2927, 2855, 1770, 1701, 1666, 1584, 1447, 1391, 1366, 1286, 1247, 1147, 1112, 1083, 1040, 997, 897, 752.

**HRMS** (EI<sup>+</sup>) m/z: [M + Na]<sup>+</sup>, Calcd for [C<sub>18</sub>H<sub>22</sub>BNNaO<sub>8</sub>S<sub>3</sub><sup>+</sup>]: 510.0493; Found 510.0489

O-ethylS-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-oxo-1-phenoxybutyl)-c  
arbo-dithioate (**III-11i**)



C<sub>18</sub>H<sub>22</sub>BNO<sub>7</sub>S<sub>2</sub>  
M = 439.0931

According to general procedure A, xanthate **III-9** (319 mg, 1 mmol, 1 equiv.), allyl phenyl ether (260 mg, 2 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (4 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11i** as a colorless amorphous solid (219 mg, 0.49 mmol, 50% yield).

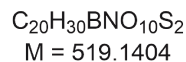
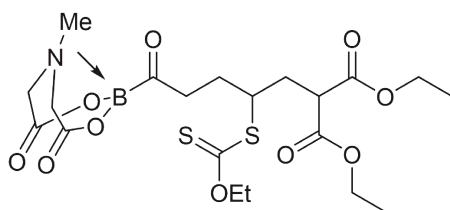
**<sup>1</sup>H NMR** δ (ppm) = 7.37 – 7.30 (m, 2H), 7.07 – 7.01 (m, 3H), 6.23 (t, J = 6.4 Hz, 1H), 4.67 – 4.54 (m, 2H), 4.07 (d, J = 16.8 Hz, 2H), 3.92 (CD<sub>3</sub>CN) (dd, J = 17.0, 1.7 Hz, 2H), 2.97 (t, J = 7.1 Hz, 2H), 2.84 (s, 3H), 2.44 – 2.28 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 212.8, 168.9 (2C), 157.5, 130.5 (2C), 123.6, 117.9 (2C), 88.4, 71.4, 63.0 (2C), 47.4, 42.9, 29.1, 13.7. (B-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3092, 2989, 2909, 2261, 1775, 1632, 1491, 1281, 1225, 1194, 1101, 1036, 832, 760.

**HRMS** (EI <sup>+</sup>) m/z: [M-S(C=S)OEt]<sup>+</sup>, Calcd for [C<sub>15</sub>H<sub>17</sub>BNO<sub>6</sub><sup>+</sup>]: 318.1143; Found 318.1124

Ethyl-4-((ethoxycarbothioyl)thio)-2-(2-methoxyacetyl)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxaza borocan-2-yl)-7-oxoheptanoate (**III-11j**)



According to general procedure A, xanthate **III-9** (64 mg, 0.2 mmol, 1 equiv.), diethyl allyl malonate (80 mg, 0.4 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (0.8 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11j** as a colorless amorphous solid (48 mg, 0.092 mmol, 46% yield).

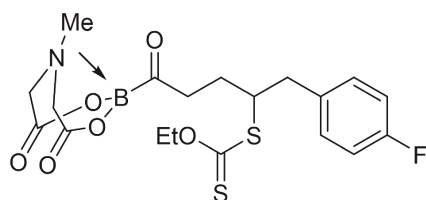
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 4.69 – 4.61 (q, J = 7.1, 3.4, 0.8 Hz, 2H), 4.27 – 4.11 (m, 4H), 4.05 (d, J = 17.0 Hz, 2H), 3.91 (d, J = 17.0 Hz, 2H), (CD<sub>3</sub>CN) 3.73 (m, 1H), 3.59 – 3.53 (m, 1H), 2.83 (s, 3H), 2.83 – 2.79 (t, 2H), 2.39 – 2.29 (m, 1H), 2.17 – 2.07 (m, 1H), 2.05 – 1.99 (m, 1H), 1.90 – 1.78 (m, 1H), 1.40 (t, J = 7.1, 0.8 Hz, 3H), 1.24 (t, J = 7.8, 7.1, 0.8 Hz, 6H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 214.7, 169.8 (2C), 168.9 (2C), 71.4, 62.9 (2C), 62.5, (101 MHz, CD<sub>3</sub>CN) 62.4, 50.6, 49.9, 47.4, 44.3, 34.0, 27.3, 14.3, 14.2, 13.8. (B-C=O not observed).

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 2981, 2936, 1767, 1743, 1726, 1662, 1464, 1447, 1390, 1368, 1336, 1272, 1215, 1147, 1111, 1091, 1044, 989, 896, 856.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>20</sub>H<sub>31</sub>BNO<sub>10</sub>S<sub>2</sub><sup>+</sup>]: 520.1477; Found 520.1492

O-ethylS-(1-(4-fluorophenyl)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-oxo  
pentan-2-yl) carbonodithioate (**III-11k**)



C<sub>19</sub>H<sub>23</sub>BFNO<sub>6</sub>S<sub>2</sub>  
M = 455.1044

According to general procedure A, xanthate **III-9** (64 mg, 0.2 mmol, 1 equiv.), 1-Allyl-4-fluorobenzene (55 mg, 0.4 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (0.8 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11k** as a colorless amorphous solid (46 mg, 0.10 mmol, 50% yield).

**<sup>1</sup>H NMR** δ (ppm) = 7.44 – 7.31 (m, 2H), 7.16 – 6.98 (m, 2H), 4.62 (q, J = (400 MHz, 7.1, 3.7 Hz, 2H), 4.34 (q, J = 16.9 Hz, 2H), 4.16 – 4.06 (m, 2H), (CD<sub>3</sub>)<sub>2</sub>CO) 3.98 (m, 1H), 3.13 – 2.96 (m, 5H), 2.92 – 2.84 (m, 2H), 2.05 – 1.97 (m, 1H), 1.79 (m, 1H), 1.44 – 1.37 (t, J = 7.1 Hz, 3H).

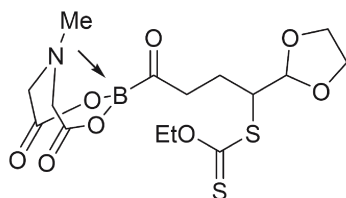
**<sup>13</sup>C NMR** δ (ppm) = 214.8, 168.7 (2C), 163.8, 161.4 (d = 242.2 Hz), 135.7 (101 MHz, (d = 3.0 Hz), 132.1 (d = 8.1 Hz) (2C), 115.9 (d = 20.2 Hz) (2C), (CD<sub>3</sub>)<sub>2</sub>CO) 70.8, 63.1 (2C), 52.9, 47.2, 44.6, 40.7, 25.8, 14.0. (B-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2957, 2927, 1770, 1661, 1601, 1509, 1449, 1362, 1336, 1280, 1220, 1168, 1111, 1050, 991, 897, 858, 729.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>19</sub>H<sub>24</sub>BFNO<sub>6</sub>S<sub>2</sub><sup>+</sup>]: 456.1117; Found 456.1114



S-(1-(1,3-dioxolan-2-yl)-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-4-oxobutyl)  
O-ethyl carbonodithioate (**III-111**)



C<sub>15</sub>H<sub>22</sub>BNO<sub>8</sub>S<sub>2</sub>  
M = 419.0880

According to general procedure A, xanthate **III-9** (96 mg, 0.3 mmol, 1 equiv.), 2-Vinyl-1,3-dioxolane (60 mg, 0.6 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (1.2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-111** as a colorless amorphous solid (63 mg, 0.15 mmol, 50% yield).

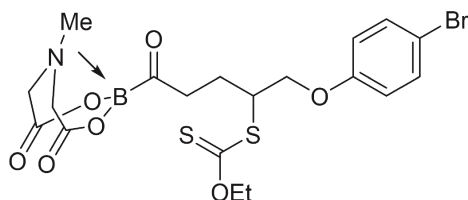
**<sup>1</sup>H NMR** δ (ppm) = 5.08 (d, J = 2.5 Hz, 1H), 4.67 (q, J = 7.1 Hz, 2H), 4.34 (400 MHz, (d, J = 16.7 Hz, 2H), 4.16 – 4.06 (m, 3H), 4.01 – 3.96 (m, 2H), (CD<sub>3</sub>)<sub>2</sub>CO) 3.91 – 3.86 (m, 2H), 3.08 (s, 3H), 2.95 – 2.89 (m, 2H), 2.18 – 2.10 (m, 1H), 1.82 (m, 1H), 1.42 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 215.1, 168.7 (2C), 104.9, 71.1, 66.3 (2C), 63.1 (2C), (101 MHz, 54.1, 49.6, 47.1, 22.3, 13.9. (B-C=O not observed). (CD<sub>3</sub>)<sub>2</sub>CO)

**IR** (neat) ν (cm<sup>-1</sup>) = 2957, 2925, 1766, 1662, 1453, 1416, 1338, 1281, 1228, 1148, 1056, 992, 960, 897, 857, 710.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>15</sub>H<sub>23</sub>BNO<sub>8</sub>S<sub>2</sub><sup>+</sup>]: 420.0953; Found 420.0939

S-(1-(4-bromophenoxy)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-oxopentane-2-yl)- O-ethyl carbonodithioate (**III-11m**)



C<sub>19</sub>H<sub>23</sub>BBrNO<sub>7</sub>S<sub>2</sub>  
M = 531.0192

According to general procedure A, xanthate **III-9** (64 mg, 0.2 mmol, 1 equiv.), 4-(allyloxy)bromobenzene (85 mg, 0.4 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (0.8 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11m** as a colorless amorphous solid (49 mg, 0.10 mmol, 46% yield).

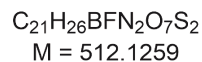
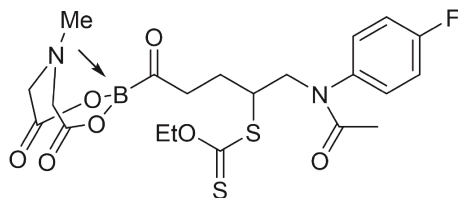
**<sup>1</sup>H NMR** δ (ppm) = 7.59 – 7.52 (m, 2H), 6.93 – 6.90 (m, 2H), 4.67 (q, J = (400 MHz, 7.1 Hz, 2H), 4.35 – 4.33 (d, J = 16.9 Hz, 2H), 4.31 – 4.22 (m, (CD<sub>3</sub>)<sub>2</sub>CO) 1H), 4.19 – 4.16 (m, 2H), 4.13 (d, J = 16.9, 1.3 Hz, 2H), 3.07 (s, 3H), 2.93 (t, J = 7.9, 6.4, 2.4 Hz, 2H), 2.27 – 2.18 (m, 1H), 2.00 – 1.89 (m, 1H), 1.41 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 214.6, 168.7 (2C), 155.4, 134.3, 121.4 (2C), 115.6 (101 MHz, 2C), 71.1, 70.7, 63.0 (2C), 50.5, 47.1, 44.5, 24.1, 13.9. (B-C=O (CD<sub>3</sub>)<sub>2</sub>CO) not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2926, 2854, 1768, 1696, 1663, 1604, 1542, 1510, 1463, 1410, 1337, 1280, 1233, 1148, 1111, 1052, 992, 896, 832.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>19</sub>H<sub>24</sub>BBrNO<sub>7</sub>S<sub>2</sub><sup>+</sup>]: 532.0265; Found 532.0267

O-ethylS-(1-(N-(4-fluorophenyl)acetamido)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)-5-oxopentan-2-yl) carbonodithioate (**III-11n**)



According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), N-allyl-N-(4-fluoro-phenyl)acetamide (193.2 mg, 1.0 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11n** as a colorless amorphous solid (117 mg, 0.23 mmol, 46% yield).

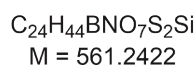
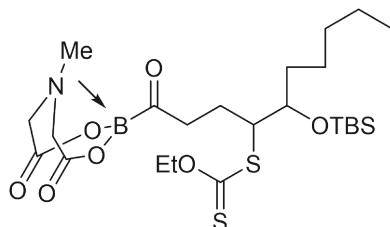
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 7.60 – 7.40 (m, 2H), 7.28 (t, J = 8.4 Hz, 2H), 4.58 – 4.50 (400 MHz, q, 2H), 4.36 (d, J = 17.0, 1.1 Hz, 2H), 4.29 – 4.19 (m, 1H), (CD<sub>3</sub>)<sub>2</sub>CO) 4.18 – 4.09 (m, 2H), 3.79 (m, 1H), 3.69 (m, 1H), 3.10 – 3.03 (s, 3H), 2.91 – 2.82 (m, 2H), 2.20 – 2.12 (m, 1H), 1.79 (s, 3H), 1.76 (m, 1H), 1.27 (t, J = 7.1, 1.0 Hz, 3H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 213.9, 170.5, 168.7 (2C), 163.8, 161.4 (J = 264.4 Hz), (101 MHz, 139.8 (J = 3.0 Hz), 131.45 (J = 8.1 Hz) (2C), 117.0 (J = 22.2 Hz) (CD<sub>3</sub>)<sub>2</sub>CO) (2C), 70.7, 62.9 (2C), 51.6, 49.3, 47.1, 44.2, 23.8, 22.7, 13.6. (B-C=O not observed).

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 3010, 2958, 2925, 1766, 1698, 1656, 1507, 1448, 1396, 1365, 1336, 1276, 1246, 1217, 1152, 1111, 1044, 986, 896, 847.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>21</sub>H<sub>27</sub>BFN<sub>2</sub>O<sub>7</sub>S<sub>2</sub><sup>+</sup>]: 513.1331; Found 513.1338

S-(5-((tert-butyl-dimethylsilyl)-oxy)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-oxodecan-4-yl) O-ethyl carbonodithioate (**III-11o**)



According to general procedure A, xanthate **III-9** (319 mg, 1 mmol, 1 equiv.), tert-butyl-dimethyl-(1-vinyl-hexyloxy)-silane (485 mg, 2 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (4 mL), air in the vial was excluded by argon, then the vial was sealed and at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11o** as a colorless amorphous solid (275 mg, 0.49 mmol, 49% yield, d.r. = 2:1).

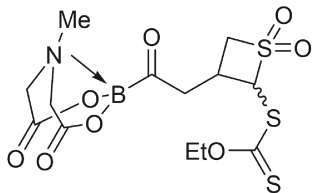
**<sup>1</sup>H NMR** δ (ppm) = 4.60 – 4.50 (m, 2H), 4.25 – 4.18 (m, 2H), 4.02 – 3.95 (m, 2H), 3.88 (m, 1H), 3.86 – 3.80 (m, 1H), 2.95 (s, 3H), 2.76 – 2.71 (m, 2H), 2.10 – 1.97 (m, 1H), 1.79 – 1.67 (m, 1H), 1.58 – 1.38 (m, 4H), 1.29 (t, J = 7.1, 2.6 Hz, 3H), 1.26 – 1.18 (m, 5H), 0.82 – 0.78 (m, 12H), 0.06 – -0.03 (m, 6H).

**<sup>13</sup>C NMR** δ (ppm)(major isomer) = 216.1, 168.6 (2C), 75.1, 71.1, 63.1 (2C), 56.9, 47.1, 45.2, 35.8, 35.3, 32.5, 26.2 (3C), 24.6, 23.2, 20.9, 18.6, 14.3, -3.9 (2C). (B-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2954, 2927, 2855, 1767, 1660, 1462, 1361, 1337, 1278, 1252, 1211, 1145, 1110, 1049, 1004, 963, 895, 836, 775.

**HRMS** (EI<sup>+</sup>) m/z:[M + Na]<sup>+</sup>, Calcd for [C<sub>24</sub>H<sub>44</sub>BNNaO<sub>7</sub>S<sub>2</sub>Si]<sup>+</sup>: 584.2314; Found 584.2318

O-ethyl-S-((2S)-3-(2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-oxoethyl)-1,1-dioxidothietan-2-yl) carbonodithioate (**III-11p**)



$C_{13}H_{18}BNO_8S_3$   
M = 423.0288

According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), thiete 1,1-dioxide (104 mg, 1.0 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11p** as a light-yellow amorphous solid. (97 mg, 0.23 mmol, 46% yield, d.r. = 3.3:1).

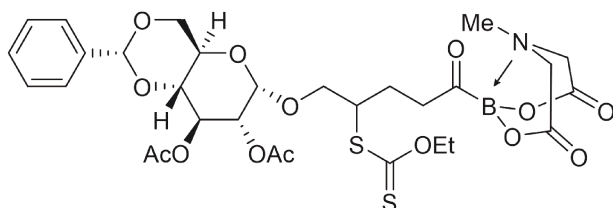
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 5.84 (d, J = 8.5 Hz, 1H), 4.74 – 4.63 (m, 2H), 4.40 (d, (400 MHz, J = 16.9 Hz, 2H), 4.35 – 4.29 (m, 1H), 4.15 (m, 2H), 3.96 (m, (CD<sub>3</sub>)<sub>2</sub>CO) 1H), 3.49 – 3.28 (m, 2H), 3.10 (s, 3H), 2.76 – 2.67 (m, 1H), 1.44 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 210.2, 168.6 (2C), 82.6, 72.1, 68.4, 63.1 (2C), 48.0, (101 MHz, 47.4, 23.3, 13.8. (B-C=O not observed). (CD<sub>3</sub>)<sub>2</sub>CO)

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 3014, 2958, 2854, 1771, 1666, 1465, 1365, 1322, 1278, 1250, 1198, 1139, 1112, 1046, 995, 961, 897, 769.

**HRMS** (EI<sup>+</sup>) m/z: [M + Na]<sup>+</sup>, Calcd for [C<sub>13</sub>H<sub>18</sub>BNNaO<sub>8</sub>S<sub>3</sub><sup>+</sup>]: 446.0180; Found 446.0177

6-((2-((ethoxycarbonothioyl)thio)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)-5-oxopentyl)oxy)-2-phenylhexahydropyrano[3,2-d][1,3]dioxine-7,8-diyl diacetate (**III-11q**)



$C_{30}H_{38}BNO_{14}S_2$   
M = 711.1827

According to general procedure A, xanthate **III-9** (128 mg, 0.4 mmol, 1 equiv.), allyl-2,3-di-Oacetyl-4,6-O-benzylidene- $\alpha$ -D-glycopyranoside (235 mg, 0.6 mmol, 1.5 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (1.6 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11q** as a colorless amorphous solid (105 mg, 0.15 mmol, 37% yield, d.r. = 1:1).

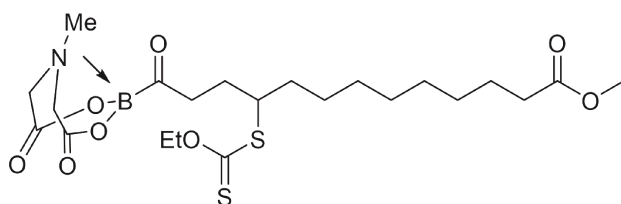
**$^1H$  NMR**  $\delta$  (ppm) = 7.52 – 7.42 (m, 2H), 7.42 – 7.32 (m, 3H), 5.64 (d, J = 12.5 Hz, 1H), 5.59 – 5.47 (t, 1H), 5.19 (d, J = 19.8, 3.8 Hz, 1H), (CD<sub>3</sub>)<sub>2</sub>CO, 4.97 – 4.83 (m, 1H), 4.69 (q, J = 7.1, 6.3, 2.5 Hz, 2H), 4.39 – 4.30 (d, J = 17.0, 4.4, 1.7 Hz, 2H), 4.30 – 4.24 (m, 1H), 4.16 – 4.06 (m, 3H), 4.06 – 3.92 (d, J = 1.5 Hz, 2H), 3.89 – 3.80 (m, 2H), 3.80 – 3.64 (m, 1H), 3.09 – 3.03 (m, 3H), 2.93 (t, J = 7.5 Hz, 2H), 2.27 – 2.15 (m, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 1.96 – 1.84 (m, 1H), 1.42 (t, J = 7.1, 1.2 Hz, 3H).

**$^{13}C$  NMR**  $\delta$  (ppm) = 214.3, 170.7, 170.1, 168.7 (2C), 138.6, 129.6, 128.8 (2C), 127.1 (2C), 102.1, 97.9, 97.3, 79.6, 72.1, 71.0, 70.2, 69.6, (CD<sub>3</sub>)<sub>2</sub>CO, 69.1, 63.8, 63.0 (2C), 50.4, 47.1, 44.4, 23.6, 20.6, 13.9. (B-C=O not observed).

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 2936, 1769, 1747, 1698, 1663, 1456, 1369, 1335, 1277, 1225, 1150, 1097, 1046, 1030, 989, 900, 757.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>30</sub>H<sub>39</sub>BNO<sub>14</sub>S<sub>2</sub><sup>+</sup>]: 712.1900; Found 712.1889

Methyl-10-((ethoxycarbonothioyl)thio)-13-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-13-oxotridecanoate (**III-11r**)



C<sub>22</sub>H<sub>36</sub>BNO<sub>8</sub>S<sub>2</sub>  
M = 517.1975

According to general procedure A, xanthate **III-9** (96 mg, 0.3 mmol, 1 equiv.), Methyl-10-undecenoate (120 mg, 0.6 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (1.2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11r** as a colorless amorphous solid (73 mg, 0.14 mmol, 47% yield).

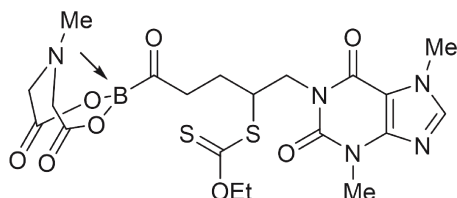
**<sup>1</sup>H NMR** δ (ppm) = 4.66 (q, J = 7.1, 1.5 Hz, 2H), 4.34 (d, J = 16.9, 1.5 Hz, 2H), 4.12 (d, J = 16.8, 1.3 Hz, 2H), 3.77 (m, J = 6.3 Hz, 1H), (CD<sub>3</sub>)<sub>2</sub>CO 3.62 (s, J = 1.5 Hz, 3H), 3.07 (s, J = 1.5 Hz, 3H), 2.88 – 2.80 (t, 2H), 2.30 (t, J = 7.5, 1.4 Hz, 2H), 2.06 – 1.99 (m, 1H), 1.83 (m, 1H), 1.71 (m, 2H), 1.59 (t, J = 7.3 Hz, 2H), 1.48 (d, J = 14.2, 7.8 Hz, 2H), 1.45 – 1.39 (m, 3H), 1.39 – 1.28 (m, 8H).

**<sup>13</sup>C NMR** δ (ppm) = 215.4, 174.1, 168.7 (2C), 70.6, 63.1 (2C), 51.8, 51.4, (101 MHz, 47.1, 44.5, 35.1, 34.3, 30.1, 30.0, 29.9, 29.7, 27.5, 26.9, 25.6, (CD<sub>3</sub>)<sub>2</sub>CO) 14.0. (B-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2926, 2854, 1768, 1736, 1661, 1451, 1362, 1336, 1275, 1210, 1172, 1146, 1110, 1045, 988, 895, 860, 779.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>22</sub>H<sub>37</sub>BNO<sub>8</sub>S<sub>2</sub><sup>+</sup>]: 518.2048; Found 518.2058

S-(1-(3,7-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-1-yl)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)-5-oxopentan-2-yl) O-ethyl carbonodithioate (**III-11s**)



$C_{20}H_{26}BN_5O_8S_2$   
M = 539.1316

According to general procedure A, xanthate **III-9** (120 mg, 0.35 mmol, 1 equiv.), 3,7dimethyl-1-prop-2-enyl-4,5-dihydropurine-2,6-dione (154 mg, 0.7 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (1.4 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11s** as a colorless amorphous solid. (96 mg, 0.18 mmol, 51% yield).

**<sup>1</sup>H NMR**  $\delta$  (ppm) = 7.83 (d, J = 1.2, 0.6 Hz, 1H), 4.61 – 4.53 (m, 2H), (400 MHz,  $(CD_3)_2CO$ ) 4.39 – 4.33 (m, 2H), 4.32 – 4.28 (m, 1H), 4.25 – 4.20 (m, 1H), 4.18 – 4.11 (m, 3H), 3.98 – 3.96 (m, 3H), 3.48 (s, 3H), 3.10 (s, 3H), 2.95 – 2.92 (m, 2H), 2.04 – 1.99 (m, 1H), 1.95 – 1.88 (m, 1H), 1.38 – 1.35 (t, J = 7.1 Hz, 3H).

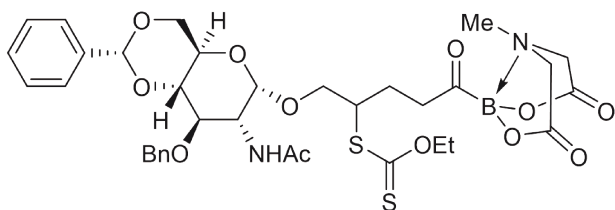
**<sup>13</sup>C NMR**  $\delta$  (ppm) = 214.3, 168.7 (2C), 155.6, 152.1, 149.7, 143.5, 117.6, (101 MHz,  $(CD_3)_2CO$ ) 107.8, 70.7, 63.0 (2C), 49.5, 47.2, 44.4, 43.7, 33.6, 24.9, 13.8. (B-C=O not observed).

**IR** (neat)  $\nu$  ( $cm^{-1}$ ) = 2955, 1768, 1697, 1657, 1604, 1549, 1452, 1356, 1325, 1280, 1245, 1146, 1113, 1042, 990, 959, 896, 874, 763.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [ $C_{20}H_{27}BN_5O_8S_2^+$ ]: 540.1389; Found 540.1398



S-(1-(((2R,4aR,6S,7R,8R,8aS)-7-acetamido-8-(benzyloxy)-phenylhexahydropyrano[3,2-d][1,3]dioxin-6-yl)oxy)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5oxopentan-2-yl) O-ethyl carbonodithioate (**III-11t**)



$C_{35}H_{43}BN_2O_{12}S_2$   
M = 758.2350

According to general procedure A, xanthate **III-9** (83 mg, 0.26 mmol, 1 equiv.), N-((2R,4aR,6S,7R,8R,8aS)-6-Allyloxy-8-benzyloxy-2-phenyl-hexahydro-pyrano[3,2,d][1,3] dioxin-7-yl)-acetamide (210 mg, 0.52 mmol, 1.5 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (1 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11t** as a colorless amorphous solid (91 mg, 0.12 mmol, 46% yield, d.r. = 3.3:1).

**<sup>1</sup>H NMR**  $\delta$  (ppm) = 7.53 – 7.42 (m, 4H), 7.40 – 7.34 (m, 5H), 7.31 – 7.25 (400 MHz, (m, 1H), 6.75 (d, J = 9.1 Hz, 1H), 5.68 (s, 1H), 5.00 (d, J = 12.1, (CD<sub>3</sub>)<sub>2</sub>CO) 2.9 Hz, 1H), 4.81 (d, J = 4.4 Hz, 1H), 4.71 – 4.64 (m, 2H), 4.61 (d, J = 12.1 Hz, 1H), 4.40 – 4.36 (m, 2H), 4.36 – 4.30 (m, 2H), 4.28 – 4.23 (m, 1H), 4.10 – 3.96 (m, 5H), 3.90 (dt, J = 9.5, 2.3 Hz, 1H), 3.83 – 3.71 (m, 1H), 3.60 (q, J = 10.0, 5.8 Hz, 1H), 2.99 (s, 3H), 2.89 (t, J = 7.3 Hz, 2H), 2.29 (m, 1H), 2.00 – 1.89 (m, 1H), 1.86 (s, 3H), 1.42 (t, J = 7.1, 0.9 Hz, 3H).

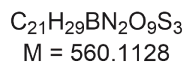
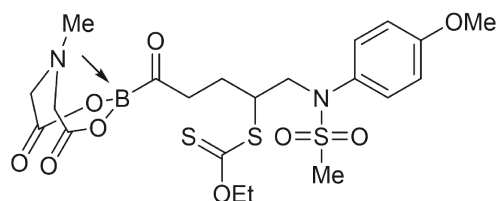
**<sup>13</sup>C NMR**  $\delta$  (ppm) = 214.7, 169.41 (2C), 168.5, 140.2, 139.0, 129.4, 128.9 (101 MHz, (2C), 128.7 (2C), 127.9 (2C), 127.8, 127.0 (2C), 102.3, 98.6, (CD<sub>3</sub>)<sub>2</sub>CO) 80.3, 75.6, 74.8, 70.9 (2C), 70.3, 69.5, 62.9, 59.1, 51.2, 50.2, 46.9, 44.4, 23.8, 22.8, 13.8. (B-C=O not observed).

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 3433, 2936, 2854, 1766, 1698, 1662, 1512, 1454,

1376, 1334, 1277, 1249, 1148, 1124, 1101, 1055, 1027, 960,  
902, 700, 594.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>35</sub>H<sub>44</sub>BN<sub>2</sub>O<sub>12</sub>S<sub>2</sub><sup>+</sup>]: 759.2423; Found 759.2396

O-ethylS-(1-(N-(4-methoxyphenyl)methylsulfonamido)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxaza borocan-2-yl)-5-oxopentan-2-yl) carbonodithioate (**III-11u**)



According to general procedure A, xanthate **III-9** (100 mg, 0.3 mmol, 1 equiv.), N-(4-methoxyphenyl)-N-(prop-2-en-1-yl) methanesulfonamide (150 mg, 1.0 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (1.2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11u** as a colorless amorphous solid (87 mg, 0.16 mmol, 52% yield).

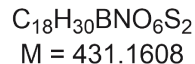
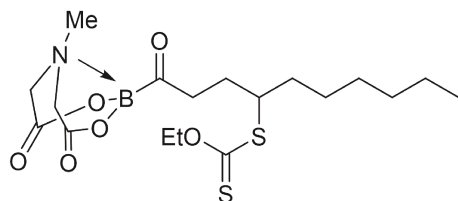
**<sup>1</sup>H NMR** δ (ppm) = 7.49 – 7.37 (m, 2H), 7.05 – 6.96 (m, 2H), 4.57 (q, J = 11.1, 6.9, 4.3 Hz, 2H), 4.34 (d, J = 16.9, 2.0 Hz, 2H), 4.12 (d, J = 16.9, 2.2 Hz, 2H), 3.98 – 3.89 (m, 2H), 3.84 (s, 3H), 3.73 – 3.60 (m, 1H), 3.04 (s, 3H), 2.96 (s, J = 1.4 Hz, 3H), 2.90 – 2.78 (m, 2H), 2.36 – 2.23 (m, 1H), 1.89 – 1.72 (m, 1H), 1.31 (t, J = 6.8, 1.5 Hz, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 213.7, 168.8 (2C), 160.3, 132.7, 131.3 (2C), 115.2 (2C), 70.9, 63.1 (2C), 55.8, 54.5, 49.5, 47.2, 44.1, 37.1, 23.4, 13.8. (B-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 2954, 2931, 1767, 1698, 1662, 1606, 1508, 1463, 1333, 1278, 1247, 1220, 1148, 1110, 1089, 1042, 990, 960, 895, 851, 759.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>21</sub>H<sub>30</sub>BN<sub>2</sub>O<sub>9</sub>S<sub>3</sub><sup>+</sup>]: 561.1201; Found 561.1199

O-ethyl-S-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-oxodecan-4-yl)carbonodithioae (**III-11v**)



According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), oct-1-ene (112.2 mg, 1.0 mmol, 2 equiv.) and dilauroyl peroxide (5 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and at 83 °C. The reaction required 40 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-11v** as a colorless amorphous solid (125 mg, 0.29 mmol, 58% yield).

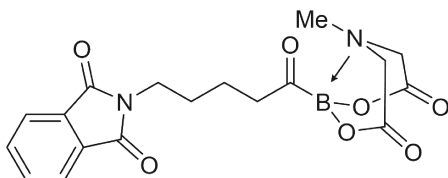
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 4.65 (q, J = 7.2, 5.4, 2.1 Hz, 2H), 4.34 (d, J = 16.9, 2.3 Hz, 2H), 4.12 (d, J = 16.9, 3.1 Hz, 2H), 3.75 (m, 1H), 3.10 – 3.04 (s, 3H), 2.84 (t, J = 5.8, 1.7 Hz, 2H), 2.09 – 1.98 (m, 2H), 1.82 (m, 1H), 1.75 – 1.65 (m, 1H), 1.41 (t, J = 7.1, 3.1, 1.2 Hz, 3H), 1.37 – 1.23 (m, 8H), 0.90 (t, J = 7.9, 3.9 Hz, 3H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 215.4, 168.7 (2C), 70.6, 63.1 (2C), 51.8, 47.1, 44.6, 35.2, 32.4, 29.8, 27.5, 26.9, 23.2, 14.3, 14.1. (B-C=O not observed).

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 2954, 2925, 2855, 1768, 1453, 1378, 1338, 1285, 1210, 1146, 1110, 1048, 1006, 963, 814.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>18</sub>H<sub>31</sub>BNO<sub>6</sub>S<sub>2</sub><sup>+</sup>]: 432.1680; Found 432.1687

2-(5-(1,3-dioxoisindolin-2-yl)pentanoyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione  
**(III-14a)**



$C_{18}H_{19}BN_2O_7$   
M = 386.1285

According to general procedure B, a solution of **III-11b** (61 mg, 0.12 mmol, 1.0 equiv.) and tris(trimethylsilyl)silane (TTMSS, 33 mg, 1.1 equiv.) in MeCN (1 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portionwise (20 mol % according to xanthate) every hour until total consumption of the starting xanthate (2 h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **21a** as a colorless amorphous solid (35 mg, 0.09 mmol, 75% yield).

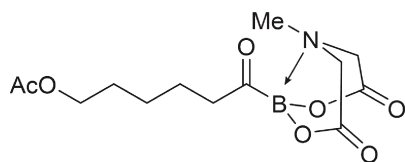
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 7.87 – 7.83 (m, 4H), 4.33 (d, J = 16.8 Hz, 2H), 4.11 (400 MHz, (d, J = 16.8 Hz, 2H), 3.66 (t, J = 6.9 Hz, 2H), 3.05 (s, 3H), 2.74 (CD<sub>3</sub>)<sub>2</sub>CO) (t, J = 7.0 Hz, 2H), 1.69 – 1.64 (m, 2H), 1.60 – 1.52 (m, 2H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 168.9 (2C), 168.8 (2C), 135. (2C), 133.2(2C), 123.7 (101 MHz, (2C), 63.0 (2C), 47.1, 46.6, 38.3, 28.8, 19.9. (B-C=O not (CD<sub>3</sub>)<sub>2</sub>CO) observed).

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 2955, 2854, 1766, 1704, 1664, 1614, 1512, 1466, 1397, 1370, 1336, 1278, 1249, 1188, 1057, 988, 868, 720.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>18</sub>H<sub>20</sub>BN<sub>2</sub>O<sub>7</sub><sup>+</sup>]: 387.1358; Found 387.1363

6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-6-oxohexyl acetate (**III-14b**)



C<sub>13</sub>H<sub>20</sub>BNO<sub>7</sub>  
M = 313.1333

According to general procedure B, a solution of **III-11c** (50 mg, 0.12 mmol, 1.0 equiv.) and tris(trimethylsilyl)silane (TTMSS, 33 mg, 1.1 equiv.) in MeCN (1 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portionwise (20 mol % according to xanthate) every hour until total consumption of the starting xanthate (2 h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-14b** as a colorless amorphous solid (30 mg, 0.1 mmol, 81% yield).

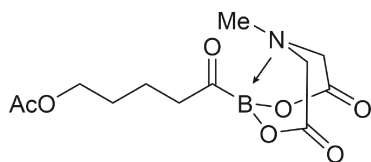
**<sup>1</sup>H NMR** δ (ppm) = 4.34 (d, J = 16.8 Hz, 2H), 4.12 (d, J = 16.8 Hz, 2H),  
(400 MHz, 4.02 (t, J = 6.7 Hz, 2H), 3.06 (s, 3H), 2.67 (t, J = 7.2 Hz, 2H),  
(CD<sub>3</sub>)<sub>2</sub>CO) 1.98 (s, 3H), 1.69 – 1.53 (m, 4H), 1.36 – 1.29 (m, 2H).

**<sup>13</sup>C NMR** δ (ppm) = 171.0, 168.8 (2C), 64.6, 63.0 (2C), 47.0, 30.1, 29.2,  
(101 MHz, 6.3, 22.3, 20.8. (B-C=O not observed).  
(CD<sub>3</sub>)<sub>2</sub>CO)

**IR** (neat) ν (cm<sup>-1</sup>) = 2955, 1763, 1726, 1659, 1453, 1366, 1337, 1241,  
1196, 1149, 1054, 989, 962, 896, 864, 709.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>13</sub>H<sub>21</sub>BNO<sub>7</sub><sup>+</sup>]: 314.1406; Found 314.1398

5-(6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)-5-oxopentyl acetate (**III-14c**)



$C_{12}H_{18}BNO_7$   
M = 299.1176

According to general procedure B, a solution of **III-11d** (42 mg, 0.1 mmol, 1.0 equiv.) and tris(trimethylsilyl)silane (TTMSS, 28 mg, 1.1 equiv.) in MeCN (1 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portionwise (20 mol % according to xanthate) every hour until total consumption of the starting xanthate (2 h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-14c** as a colorless amorphous solid (23 mg, 0.08 mmol, 76% yield).

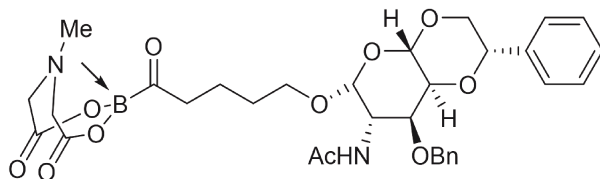
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 4.34 (d, J = 16.8 Hz, 2H), 4.12 (d, J = 16.8 Hz, 2H), (400 MHz,  $(CD_3)_2CO$ ) 4.07 – 3.98 (m, 2H), 3.07 (s, 3H), 2.72 – 2.63 (m, 2H), 1.99 (s, 3H), 1.60 – 1.54 (m, 4H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 171.1, 168.8 (2C), 64.7, 63.1 (2C), 47.1, 46.7, 29.1, (101 MHz,  $(CD_3)_2CO$ ) 20.9, 19.2. (B-C=O not observed).

**IR** (neat)  $\nu$  ( $cm^{-1}$ ) = 2956, 1767, 1726, 1659, 1453, 1366, 1337, 1241, 1196, 1149, 1054, 989, 962, 896, 864.

**HRMS** (EI<sup>+</sup>) m/z: [M + Na]<sup>+</sup>, Calcd for [C<sub>12</sub>H<sub>18</sub>BNNaO<sub>7</sub><sup>+</sup>]: 322.1069; Found 322.1076

N-((2S,4aS,6R,7S,8S,8aS)-8-(benzyloxy)-6-((5-(6-methyl-4,8-dioxo-1,3,6,2dioxazaboro can-2-yl)-5-oxopentyl)oxy)-2-phenylhexahydro-6H-pyrano[2,3-b][1,4]dioxin-7-yl)acet amide (**III-14d**)



C<sub>32</sub>H<sub>39</sub>BN<sub>2</sub>O<sub>11</sub>  
M = 638.2647

According to general procedure B, a solution of **III-11t** (60 mg, 0.08 mmol, 1.0 equiv.) and tris(trimethylsilyl)silane (TTMSS, 23 mg, 1.1 equiv.) in MeCN (1 mL) was refluxed under nitrogen for 10 min. Then AIBN was added portionwise (20 mol % according to xanthate) every hour until total consumption of the starting xanthate (2 h total reaction time). The reaction mixture was then cooled down to room temperature and volatiles were removed by rotary evaporation. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-14d** as a colorless amorphous solid (35 mg, 0.05 mmol, 69% yield).

**<sup>1</sup>H NMR** δ (ppm) = 7.36 – 7.21 (m, 4H), 7.21 – 7.12 (m, 5H), 7.11 – 7.05 (400 MHz, (m, 1H), 6.67 (d, J = 9.1 Hz, 1H), 5.48 (s, 1H), 4.80 – 4.73 (m, (CD<sub>3</sub>)<sub>2</sub>CO) 1H), 4.55 (d, J = 4.4 Hz, 1H), 4.41 (d, J = 12.1 Hz, 1H), 4.20 – 4.11 (m, 2H), 4.11 – 4.02 (m, 4H), 3.92 – 3.88 (m, 2H), 3.88 (m, 1H), 3.69 (m, 1H), 3.63 – 3.52 (m, 2H), 3.21 (m, 1H), 2.83 (s, 3H), 2.53 (t, J = 6.8, 2.5 Hz, 1H), 1.70 – 1.67 (s, 3H), 1.56 – 1.36 (m, 4H).

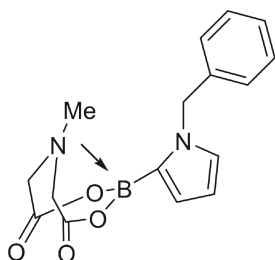
**<sup>13</sup>C NMR** δ (ppm) = 168.4 (2C), 167.6, 139.3, 138.2, 128.4, 127.8 (2C), (101 MHz, 127.7 (2C), 127.0 (2C), 126.8, 126.0 (2C), 101.3, 97.1, 79.5, (CD<sub>3</sub>)<sub>2</sub>CO) 74.6, 73.7, 68.6, 67.7, 61.9 (2C), 57.8, 49.3, 45.9, 28.9, 28.7, 21.7, 18.3. (B-C=O not observed).

**IR** (neat) ν (cm<sup>-1</sup>) = 3433, 2936, 2854, 1768, 1698, 1662, 1512, 1454, 1376, 1334, 1277, 1249, 1148, 1124, 1101, 1055, 1027, 960, 902, 700.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>32</sub>H<sub>40</sub>BN<sub>2</sub>O<sub>11</sub>]<sup>+</sup>: 639.2720; Found 639.2713



2-(1-benzyl-1H-pyrrol-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**III-24a**)



C<sub>16</sub>H<sub>17</sub>BN<sub>2</sub>O<sub>4</sub>  
M = 312.1281

According to general procedure C, to a solution of adduct **III-11f** (134 mg, 0.3 mmol, 1 equiv.) in MeCN (2.4 mL) was added benzylamine (64 mg, 0.6 mmol, 2 equiv.). The flask was equipped with a condenser and the suspension was stirred at 75 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (Dichloromethane / acetonitrile = 95/5 to 90/10) afforded compound **III-24a** as a colorless amorphous solid (57 mg, 0.18 mmol, 61% yield).

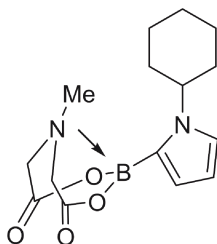
**<sup>1</sup>H NMR** δ (ppm) = 7.36 – 7.25 (m, 3H), 7.19 – 7.14 (m, 2H), 6.96 (d, J = 2.5, 1.7 Hz, 1H), 6.32 (m, 1H), 6.14 (d, J = 3.5, 2.5 Hz, 1H), (CD<sub>3</sub>)<sub>2</sub>CO 5.31 (s, 2H), 4.20 – 4.14 (d, J = 17.0 Hz, 2H), 3.85 – 3.79 (d, J = 16.8 Hz, 2H), 2.47 (s, 3H).

**<sup>13</sup>C NMR** δ (ppm) = 168.9 (2C), 140.8, 129.2 (2C), 128.1, 127.9 (2C), (101 MHz, CD<sub>3</sub>)<sub>2</sub>CO 127.4, 118.8, 109.0, 62.1 (2C), 53.0, 47.3, 27.4.

**IR** (neat) ν (cm<sup>-1</sup>) = 2924, 2825, 1766, 1527, 1496, 1336, 1285, 1248, 1223, 1159, 1040, 987, 890, 840, 727.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>16</sub>H<sub>18</sub>BN<sub>2</sub>O<sub>4</sub><sup>+</sup>]: 313.1354; Found 313.1337

2-(1-cyclohexyl-1H-pyrrol-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**III-24b**)



C<sub>15</sub>H<sub>21</sub>BN<sub>2</sub>O<sub>4</sub>  
M = 304.1594

According to general procedure C, to a solution of adduct **III-11f** (116 mg, 0.26 mmol, 1 equiv.) in MeCN (2 mL) was added cyclohexylamine (51 mg, 0.52 mmol, 2 equiv.). The flask was equipped with a condenser and the suspension was stirred at 75 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (Dichloromethane / acetonitrile = 95/5 to 90/10) afforded compound **III-24b** as a colorless amorphous solid (54 mg, 0.18 mmol, 68% yield).

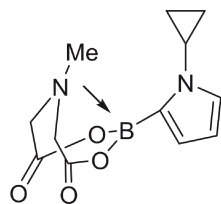
**<sup>1</sup>H NMR** δ (ppm) = 7.03 (m, 1H), 6.20 (d, J = 3.5, 1.7 Hz, 1H), 6.08 (t, J = 3.5, 2.6 Hz, 1H), 4.27 (d, J = 17.0 Hz, 2H), 4.07 – 3.99 (m, 3H), (CD<sub>3</sub>)<sub>2</sub>CO 2.78 (s, 3H), 2.05 – 2.00 (m, 2H), 1.85 – 1.81 (m, 2H), 1.71 – 1.64 (m, 4H), 1.53 – 1.36 (m, 2H).

**<sup>13</sup>C NMR** δ (ppm) = 169.1 (2C), 135.5, 122.0, 117.5, 108.7, 62.1 (2C), (101 MHz, 58.4, 47.4, 35.9 (2C), 26.7 (2C), 26.1. (CD<sub>3</sub>)<sub>2</sub>CO)

**IR** (neat) ν (cm<sup>-1</sup>) = 2960, 2854, 1764, 1724, 1525, 1480, 1450, 1417, 1397, 1369, 1336, 1283, 1247, 1156, 1111, 1026, 985, 873, 729.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>15</sub>H<sub>22</sub>BN<sub>2</sub>O<sub>4</sub><sup>+</sup>]: 305.1667; Found 305.1677

2-(1-cyclopropyl-1H-pyrrol-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**III-24c**)



C<sub>12</sub>H<sub>15</sub>BN<sub>2</sub>O<sub>4</sub>  
M = 262.1125

According to general procedure C, to a solution of adduct **III-11f** (201 mg, 0.45 mmol, 1 equiv.) in MeCN (3.6 mL) was added cyclopropylamine (51 mg, 0.9 mmol, 2 equiv.). The flask was equipped with a condenser and the suspension was stirred at 75 °C with a heating block until completion of the reaction. The reaction mixture was then cooled down to room temperature, Flash chromatography on silica gel (Dichloromethane / acetonitrile = 95/5 to 90/10) afforded compound **III-24c** as a colorless amorphous solid (83 mg, 0.32 mmol, 70% yield).

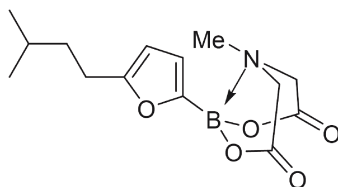
**<sup>1</sup>H NMR** δ (ppm) = 6.86 – 6.81, (m, 1H), 6.32 (q, J = 3.5, 1.7 Hz, 1H),  
(400 MHz, 5.99 (q, J = 3.5, 2.6 Hz, 1H), 4.31 (d, J = 17.0 Hz, 2H), 4.16 –  
(CD<sub>3</sub>)<sub>2</sub>CO) 4.09 (q, J = 16.8 Hz, 2H), 3.54 – 3.46, (m, 1H), 2.81 (s, 3H),  
1.01 – 0.99 (m, 4H).

**<sup>13</sup>C NMR** δ (ppm) = 169.2 (2C), 124.5, 119.5, 107.8, 62.7 (2C), 48.1, 31.4,  
(101 MHz, 27.2, 7.9 (2C).  
(CD<sub>3</sub>)<sub>2</sub>CO)

**IR** (neat) ν (cm<sup>-1</sup>) = 2931, 2856, 1765, 1699, 1522, 1453, 1336, 1282,  
1248, 1219, 1170, 1041, 980, 893, 838, 725.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>12</sub>H<sub>16</sub>BN<sub>2</sub>O<sub>4</sub><sup>+</sup>]: 263.1198; Found 263.1195

2-(5-isopentylfuran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (**III-35a**)



C<sub>14</sub>H<sub>20</sub>BNO<sub>5</sub>  
M = 293.1435

According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), 2-((2-Ethoxy-5-methylhex-1-en-3-yl)oxy)-6-fluoropyridine<sup>[8]</sup> (253 mg, 1 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 100 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-35a** as a colorless amorphous solid (64 mg, 0.17 mmol, 44% yield).

**<sup>1</sup>H NMR** δ (ppm) = 6.57 (d, J = 3.1, 0.5 Hz, 1H), 6.04 (m, 1H), 4.33 (d, J = 16.9 Hz, 2H), 4.10 (d, J = 16.9 Hz, 2H), 2.85 (s, 3H), 2.68 – 2.60 (m, 2H), 1.64 – 1.57 (m, 1H), 1.56 – 1.50 (m, 2H), 0.93 – 0.89 (d, J = 6.3 Hz, 6H).

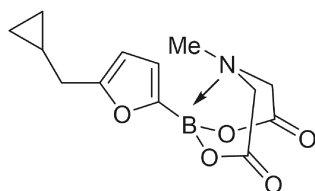
**<sup>13</sup>C NMR** δ (ppm) = 174.6, 168.9 (2C), 160.6, 119.5, 105.9, 62.3 (2C), 47.6, 37.9, 28.2, 26.6, 22.6 (2C).

**IR** (neat) ν (cm<sup>-1</sup>) = 2955, 2924, 2854, 1768, 1713, 1595, 1534, 1453, 1394, 1366, 1336, 1280, 1231, 1192, 1149, 1046, 1022, 1007, 961, 895, 836, 790.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>14</sub>H<sub>21</sub>BNO<sub>5</sub><sup>+</sup>]: 294.1507; Found 294.1503

2-(5-(cyclopropylmethyl)furan-2-yl)6methyl-1,3,6,2-dioxazaborocane-4,8-dione

**(III-35b)**



C<sub>13</sub>H<sub>16</sub>BNO<sub>5</sub>  
M = 277.1122

According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), 2-((1-Cyclopropyl-2-ethoxyallyl)oxy)-6-fluoropyridine<sup>[8]</sup> (237 mg, 1 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 100 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-35b** as a colorless amorphous solid (66 mg, 0.20 mmol, 47% yield).

**<sup>1</sup>H NMR** δ (ppm) = 6.59 (d, J = 3.1, 0.5 Hz, 1H), 6.11 (m, 1H), 4.04 (d, J = 17.0 Hz, 2H), 3.87 (d, J = 17.0 Hz, 2H), 2.62 (s, 3H), 2.55 (d, J = 7.0, 0.8 Hz, 2H), 1.07 – 0.96 (m, 1H), 0.54 – 0.44 (m, 2H), 0.21 – 0.09 (dd, J = 4.9, 1.5 Hz, 2H).

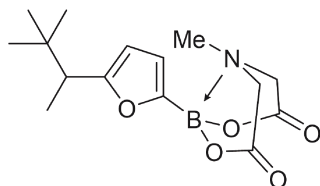
**<sup>13</sup>C NMR** δ (ppm) = 169.2 (2C), 160.5, 119.9, 106.2 (2C), 62.2 (2C), 47.8, 33.1, 10.3, 4.7 (2C).  
(101 MHz, CD<sub>3</sub>CN)

**IR** (neat) ν (cm<sup>-1</sup>) = 3006, 2924, 2853, 1754, 1595, 1534, 1453, 1335, 1280, 1252, 1226, 1193, 1150, 1046, 1007, 965, 894, 835, 789.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>13</sub>H<sub>17</sub>BNO<sub>5</sub><sup>+</sup>]: 278.1194; Found 278.1195

2-(5-(3,3-dimethylbutyl)furan-2-yl)-6methyl-1,3,6,2-dioxazaborocane-4,8-dione

**(III-35c)**



$C_{15}H_{22}BNO_5$   
M = 307.1591

According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), 2-((2-Ethoxy-3,4,4-trimethylpent-1-en-3-yl)oxy)-6-fluoropyridine<sup>[8]</sup> (268 mg, 1 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 100 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-35c** as a colorless amorphous solid (61 mg, 0.20 mmol, 40% yield).

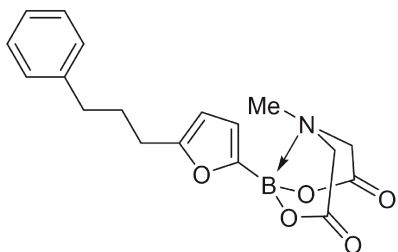
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 6.62 (d, J = 3.2, 0.5 Hz, 1H), 6.06 (d, J = 3.1, 0.4 Hz, 1H), 4.06 (d, J = 17.1, 2.6 Hz, 2H), 3.90 (d, J = 3.0 Hz, 2H), (CD<sub>3</sub>CN) 2.74 – 2.68 (m, 1H), 2.65 (s, 3H), 1.24 – 1.19 (m, 3H), 0.90 (s, 9H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 169.1 (2C), 164.0, 119.7, 106.7 (2C), 62.2 (2C), 47.9, (101 MHz, CD<sub>3</sub>CN) 44.3, 34.3, 28.0 (3C), 14.8.

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 2957, 2924, 2854, 1770, 1711, 1672, 1588, 1532, 1458, 1396, 1376, 1364, 1336, 1282, 1253, 1194, 1155, 1051, 1008, 955, 894, 836, 792.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>15</sub>H<sub>23</sub>BNO<sub>5</sub><sup>+</sup>]: 308.1664; Found 308.1656

6-methyl-2-(5-(3-phenylpropyl)furan-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (**III-35d**)



$C_{18}H_{20}BNO_5$   
M = 341.1435

According to general procedure A, xanthate **III-9** (319 mg, 1 mmol, 1 equiv.), 2-((2-Ethoxy-5-phenylpent-1-en-3-yl)oxy)-6- fluoropyridine<sup>[8]</sup> (452 mg, 1.5 mmol, 1.5 equiv.) and dilauroyl peroxide (20 mol%) were mixed in a vial and dissolved in EtOAc (4 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 100 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-35d** as a colorless amorphous solid (154 mg, 0.39 mmol, 45% yield).

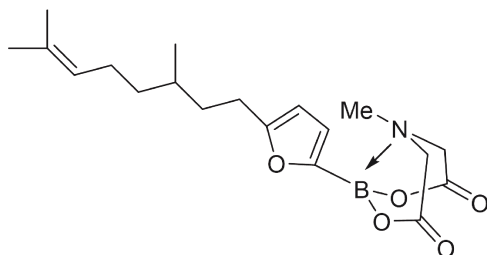
**<sup>1</sup>H NMR**  $\delta$  (ppm) = 7.37 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H), 6.67 – 6.58 (m, 1H), 6.09 (d, J = 3.1 Hz, 1H), 4.06 (d, J = 17.0 Hz, 2H), 3.89 (CD<sub>3</sub>CN) (d, J = 17.0 Hz, 2H), 2.68 (m, 4H), 2.64 (s, 3H). 1.94 (m, 2H).

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 169.1 (2C), 160.5, 143.1, 129.3 (2C), 129.2 (2C), (101 MHz, CD<sub>3</sub>CN) 126.7 (2C), 120.0, 106.4, 62.3 (2C), 47.9, 35.7, 30.7, 28.1.

**IR** (neat)  $\nu$  (cm<sup>-1</sup>) = 2924, 2852, 1770, 1602, 1534, 1496, 1453, 1336, 1284, 1231, 1193, 1150, 10522, 1010, 962, 894, 836, 792, 748.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [C<sub>18</sub>H<sub>21</sub>BNO<sub>5</sub><sup>+</sup>]: 342.1507; Found 342.1494

2-(5-(3,7-dimethyloct-6-en-1-yl)furan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione  
**(III-35e)**



$C_{19}H_{28}BNO_5$   
M = 361.2061

According to general procedure A, xanthate **III-9** (160 mg, 0.5 mmol, 1 equiv.), 2-((2-Ethoxy-5,9-dimethyldeca-1,8-dien-3-yl)oxy)-6-fluoropyridine<sup>[8]</sup> (321 mg, 1 mmol, 2 equiv.) and dilauroyl peroxide (10 mol%) were mixed in a vial and dissolved in EtOAc (2 mL), air in the vial was excluded by argon, then the vial was sealed and heated at 83 °C. The reaction required 100 mol% DLP for the xanthate to be consumed. Flash chromatography on silica gel (Dichloromethane / acetonitrile = 9/1 to 8/2) afforded compound **III-35e** as a colorless amorphous solid (90 mg, 0.25 mmol, 50% yield).

**<sup>1</sup>H NMR**  $\delta$  (ppm) = 6.57 (d, J = 3.1, 0.4 Hz, 1H), 6.03 (m, 1H), 5.10 (m, 1H), 4.04 (d, J = 16.9 Hz, 2H), 3.86 (d, J = 16.0 Hz, 2H), 2.68 – 2.64 (m, 2H). 2.60 (s, 3H), 2.02 – 1.97 (m, 2H), 1.67 – 1.59 (m, 3H), 1.46 – 1.40 (m, 3H), 1.29 – 1.26 (m, 4H), 1.20 – 1.13 (m, 1H), 0.91 – 0.88 (d, 3H).  
(400 MHz,  $CD_3CN$ )

**<sup>13</sup>C NMR**  $\delta$  (ppm) = 169.1 (2C), 161.1, 131.9, 125.6 (2C), 119.9, 106.1, 62.3 (2C), 47.8, 37.5, 35.8, 32.7, 26.2, 26.1, 25.7, 19.5, 17.6.  
(101 MHz,  $CD_3CN$ )

**IR** (neat)  $\nu$  ( $cm^{-1}$ ) = 2956, 2922, 2853, 1756, 1649, 1614, 1533, 1450, 1376, 1335, 1278, 1230, 1149, 1049, 1007, 963, 894, 874, 789.

**HRMS** (EI<sup>+</sup>) m/z: [M + H]<sup>+</sup>, Calcd for [ $C_{19}H_{29}BNO_5^+$ ]: 362.2133; Found 362.2128



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**Titre :** Une voie polyvalente vers les acylsilanes et les acyl(MIDA)boronates

**Mots clés :** Réactions radicalaires; xanthate; acylsilanes; acyl(MIDA)boronates

**Résumé :** Le transfert dégénératif réversible du xanthate apparaît comme l'un des outils les plus efficaces pour la génération de liaisons C-C au cours des dernières années. Il possède une capacité unique à stocker des radicaux réactifs par le biais d'une série de processus réversibles et donc à prolonger remarquablement la durée de vie effective des radicaux formés. Il permet des additions intermoléculaires de radicaux, en particulier à des oléfines non activées, pour construire des liaisons C(sp<sup>3</sup>)-C(sp<sup>3</sup>). Les acylsilanes (RCOSiR'<sub>3</sub>) et les acylboronates sont des classes de composés intrigants qui suscitent un grand intérêt. Leurs propriétés et leurs réactivités remarquables n'ont été reconnues que récemment. Le processus d'addition-transfert du xanthate a été exploité comme une méthode pratique pour la synthèse d'acylsilanes et d'acylboronates fonctionnalisés.

Ici, la première synthèse de deux xanthates nouveaux et réactifs, portant respectivement un groupement acylsilane et un groupement boronate acylMIDA, a été mise au point. Une série d'adduits a été préparée avec un rendement élevé en utilisant le processus d'addition-transfert de xanthate et a pu être transformée en dérivés de pyrrole et de furane. Notamment, la douceur des conditions de réaction et la large tolérance pour divers groupes fonctionnels fournissent une nouvelle méthode de synthèse pour divers composés de cette classe qui ne sont pas facilement accessibles par d'autres voies.

**Title :** A Versatile Route to Acyl (MIDA)Boronates and Acyl silanes

**Keywords :** Radical reactions; xanthate; acylsilanes; acyl(MIDA)boronates

**Abstract :** The degenerative reversible transfer of xanthate is emerging as one of the most effective tools for the generation of C-C bonds in recent years. It has a unique ability to store reactive radicals through a series of reversible processes and thus remarkably extend the effective lifetime of the formed radicals. It allows intermolecular radical additions, especially to non-activated olefins, to construct C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bonds. Acylsilanes (RCOSiR'<sub>3</sub>) and acylboronates are intriguing classes of compounds that are of wide interest. Their remarkable properties and reactivities have only recently been recognized. The xanthate addition-transfer process has been exploited as a convenient method for the synthesis of functionalized acylsilanes and acylboronates.

Herein, the first synthesis of two novel and reactive xanthates, bearing an acylsilane moiety and an acyl(MIDA) boronate moiety, respectively, was developed. A series of adducts were prepared in a high yield using the xanthate addition-transfer process and could be further transformed to pyrrole and furan derivatives. Notably, the mildness of the reaction conditions and broad tolerance for diverse functional groups provide a new synthesis method for various compounds of this class that are not readily accessible by other routes.