

Synthesis and functionalization of organogermanes in the three-dimensional chemical space

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vorgelegt von

Eric Ahrweiler, M. Sc.

aus

Erkelenz, Deutschland

Berichter: *Prof. Dr. Franziska Schoenebeck*
Prof. Dr. Frédéric Patureau

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Datum

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Diese Arbeit widme ich meiner liebevollen Familie.

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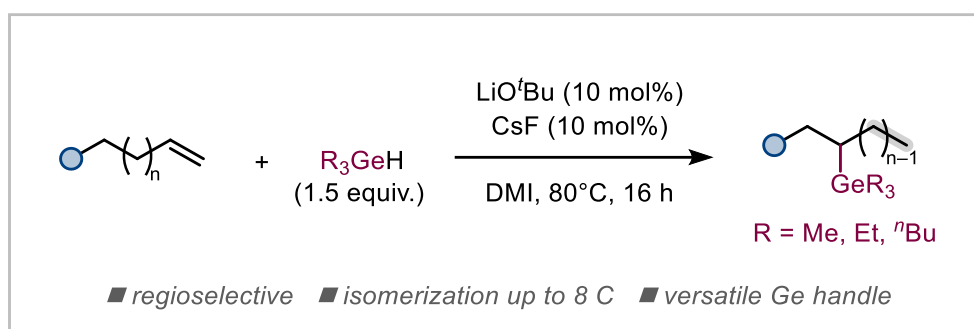
Abstract

Due to the ever-increasing demand for novel synthetic transformations of organic compounds, operationally simple and bench stable alternatives to literature known examples are especially sought after. The introduction of a non-toxic and robust functional group, like the alkylgermanium handle, would open new possibilities to navigate the chemical landscape. In the two-dimensional space, transition metal catalyzed approaches have enabled a multitude of decoration possibilities in the last decades; however, the three-dimensional area lacks diverse and efficient transformation possibilities.

In the first chapter, the C-GeEt₃ handle is introduced *via* a rare base catalyzed remote hydrogermylation reaction of alkenes (Scheme 1). The straightforward reaction conditions, combined with commercially available starting materials, underscore the operational simplicity of the novel method. Under optimized conditions, it was shown that catalytic amounts of LiO^tBu and CsF isomerize alkene carbon chains of up to eight carbons and subsequently hydrogermylate the internal double bond to the corresponding product in a one-pot reaction. This methodology proved effective for a range of substrates, including aromatic systems bearing electron-donating and electron-withdrawing substituents, as well as heteroaryl and non-aromatic compounds such as allyl phosphine, silane, and Bpin derivatives. Interestingly, different germanium sources are viable for the herein reported remote hydrofunctionalization, whereas analogous hydroborylation or hydrosilylation reagents failed to achieve productive results, highlighting the unique reactivity of the germanium group.

Further mechanistic investigations have revealed that upon salt metathesis, the strong base CsO^tBu might be formed and responsible for the unexpected reactivity. DFT calculations of the relevant pK_a values are in line with the proposed anionic reaction mechanism, which was also supported by deuterium labeling studies. Additionally, ICP-MS analysis and control reactions with various transition metals were conducted to exclude the observed reactivity origins from metal contamination.

Scheme 1 | Base catalyzed remote hydrogermylation. Scheme adapted from reference.^[1]

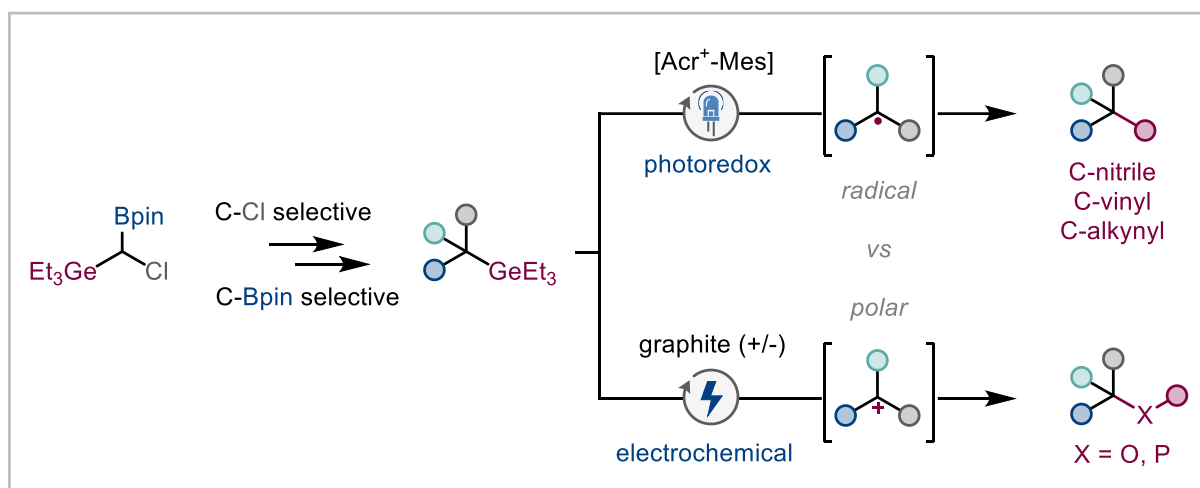


The second chapter focuses on the full functionalization of the established building block containing three different handles on one carbon, namely the C-Cl, C-Bpin and C-GeEt₃ group (Scheme 2). In this context, several fully decorated compounds were synthesized to demonstrate rapid access to complex structures. To achieve this full functionalization various reported transformations of the C-Cl and C-Bpin units were applied. During these transformations the alkylgermanium group repeatedly proved its robustness under harsh conditions, e.g. organometallic reagents and peroxides, making it an ideal handle within the building

block. In these cases, the C-Bpin group was successfully oxidized, (hetero)arylated and vinyated following the reported procedures. Beyond known transformations, such as Giese addition and dual photoredox catalysis with nickel, additional investigations were carried out to functionalize the C-GeEt₃ moiety. The photochemically generated alkyl radical was efficiently trapped by sulfonyl reagents, incorporating nitrile, vinyl and alkynyl groups. Furthermore, vinyl sulfonium salts were utilized to unlock a novel Giese type addition reaction, where formally an electron rich double bond ends up in the final product, which was previously not possible. Notably, when an alcohol in the α -position to the alkylgermanium group was present under dual photoredox conditions, the cross-coupled product featured selective oxidation of the alcohol to an α -aryl ketone.

In addition to photochemical transformations, an electrochemical approach was utilized to further expand the scope of possible functionalizations, particularly for C-heteroatom bond formations. This method provided rapid access to three additional complex structures.

Scheme 2 | Full functionalization sequence of the building block using photo- and electrochemical approaches.



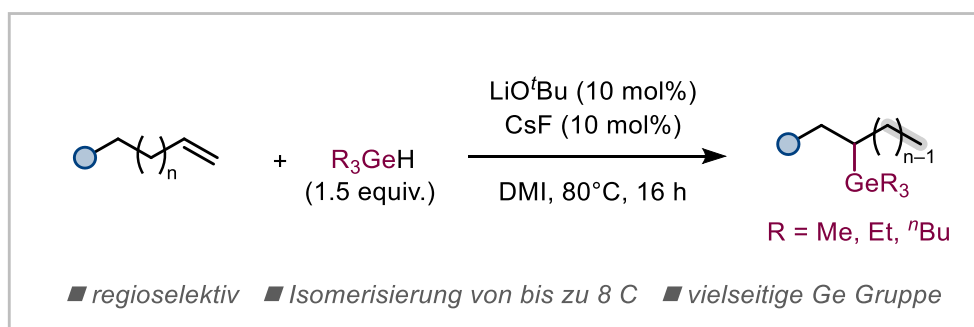
Zusammenfassung

Aufgrund der stetig wachsenden Nachfrage nach neuen Synthese- und Transformationsmethoden für organische Verbindungen werden insbesondere operationell einfache und robuste Alternativen zu den in der Literatur bekannten Methoden gesucht. Die Einführung einer ungiftigen und robusten funktionellen Gruppe, wie der Alkylgermaniumgruppe, könnte neue Möglichkeiten zur Erschließung des chemischen Raums eröffnen. Während für zweidimensionale Strukturen in den letzten Jahrzehnten zahlreiche Funktionalisierungsmethoden durch Übergangsmetallkatalyse entwickelt wurden, mangelt es im dreidimensionalen Bereich an vielfältigen und effizienten Transformationsmöglichkeiten.

Im ersten Kapitel wird die C-GeEt₃ Gruppe durch eine ungewöhnliche basenkatalysierte, remote Hydrogermylierung von Alkenen eingeführt (Scheme 3). Die unkomplizierten Reaktionsbedingungen in Kombination mit kommerziell erhältlichen Ausgangsmaterialien verdeutlichen die operationelle Einfachheit dieser neuartigen Methode. Unter optimierten Bedingungen konnte gezeigt werden, dass katalytische Mengen von LiO^tBu und CsF in der Lage sind, Alkenketten von bis zu acht Kohlenstoffatomen zu isomerisieren und anschließend die interne Doppelbindung in einer One-Pot Reaktion zu hydrogermylieren. Diese Methode erwies sich als effektiv für viele verschiedene Substrate, darunter aromatische Systeme mit elektronenziehenden und elektronenschiebenden Substituenten sowie heteroaromatische und nicht-aromatische Verbindungen wie Allylphosphine, -silane und -Bpin. Interessanterweise sind verschiedene Germaniumquellen für diese remote Hydrofunktionalisierung geeignet, während analoge Hydroborylierungs- oder Hydrosilylierungsreagenzien keine produktiven Ergebnisse erzielten, was die einzigartige Reaktivität der Alkylgermaniumgruppe noch einmal unterstreicht.

Weitere Untersuchungen des Mechanismus zeigten, dass durch Salzmetathese die starke Base CsO^tBu gebildet wird, die potentiell für die unerwartete Reaktivität verantwortlich ist. DFT-Berechnungen der entsprechenden pK_a Werte unterstützen den vorgeschlagenen anionischen Reaktionsmechanismus, der zusätzlich durch Deuterium Reaktionen bestätigt wurde. Darüber hinaus wurden ICP-MS Analysen sowie Kontrollreaktionen mit verschiedenen Übergangsmetallen durchgeführt, um auszuschließen, dass die beobachtete Reaktivität auf Metallverunreinigungen zurückzuführen ist.

Scheme 3 | Basenkatalysierte remote Hydrogermylierung. Das Scheme ist angelehnt an die original Quelle.^[1]



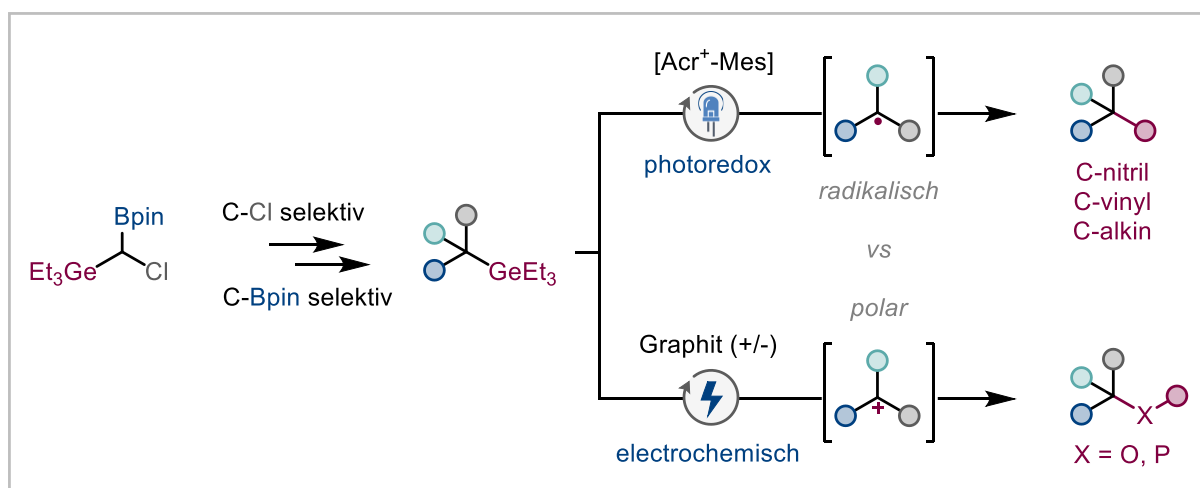
Das zweite Kapitel konzentriert sich auf die vollständige Funktionalisierung einer etablierten Plattform, die drei verschiedene funktionelle Gruppen enthält und zwar C-Cl, C-Bpin und C-GeEt₃ (Scheme 4). Um die

Vielseitigkeit dieser Plattform zu demonstrieren, wurden mehrere vollständig funktionalisierte Verbindungen synthetisiert. Hierbei kamen verschiedene etablierte Methoden zur Funktionalisierung der C-Cl und C-Bpin Gruppen zum Einsatz. Während dieser Transformationen erwies sich die Alkylgermaniumgruppe wiederholt als äußerst stabil unter harschen Bedingungen, einschließlich der Anwendung von metallorganischen Reagenzien und Peroxiden, wodurch sie sich als ideale funktionelle Gruppe innerhalb der Plattform auszeichnet. Die C-Bpin Gruppe wurde erfolgreich oxidiert, (hetero)aryliert und vinyliert, wie es in der Literatur beschrieben wurde.

Über bekannte Transformationen wie die Giese Addition und die duale Photoredoxkatalyse mit Nickel hinaus, wurden zusätzliche Forschungen zur Funktionalisierung der C-GeEt₃ Gruppe durchgeführt. Das photochemisch generierte Alkylradikal wurde effizient durch Sulfonylreagenzien eingefangen, wodurch Nitril-, Vinyl- und Alkynylgruppen eingeführt wurden. Zudem konnten mit Vinylsulfoniumsalzen neue Giese ähnliche Additionsreaktionen realisiert werden, bei denen formal eine elektronreiche Doppelbindung in das Endprodukt überführt wurde, was vorher nicht möglich war. Besonders bemerkenswert ist, dass bei Vorhandensein einer Hydroxygruppe in α -Position zum Alkylgermanium, unter dualen Photoredoxbedingungen, das mit Arylen gekuppelte Produkt eine selektive Oxidation des Alkohols zur α -Aryl Ketogruppe zeigte.

Neben den photochemischen Transformationen wurde auch ein elektrochemischer Ansatz benutzt, um die Auswahl möglicher Funktionalisierungen weiterzuentwickeln, insbesondere für C-Heteroatom Bindungen. Diese Methode ermöglichte den schnellen Zugang zu drei weiteren komplexen Strukturen.

Scheme 4 | Vollständige Funktionalisierungssequenz der Plattform mittels Photo- und Elektrochemie.



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Parts of the work described in this thesis have already been published in the following publications:

Eric Ahrweiler[†], Dr. Aymane Selmani[†], Prof. Dr. Franziska Schoenebeck, *Angew. Chem. Int. Ed.* **2025**, e202503573. († These authors contributed equally to this work)

Eric Ahrweiler[†], Markus D. Schoetz[†], Dr. Gurdeep Singh, Quentin P. Bindschaedler, Alba Sorroche, Prof. Dr. Franziska Schoenebeck, *Angew. Chem. Int. Ed.* **2024**, 63, e202401545. († These authors contributed equally to this work)

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Parts of the work described in this thesis have been presented in poster presentations during conferences:

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Abbreviations

4CzIPN	1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene
Å	Ångström (1 Å = 0.1 nm)
ACN	acetonitrile
Acr	acridinium
Alk	alkyl
Ar	aryl
B3LYP	DFT method (hybrid GGA using Becke's 3-parameter exchange functional and Lee-Yang-Parr correlation functional)
BF ₃ K	Potassium trifluoroborate
Bpin	Boronic acid pinacol ester
CN	cyanide
CPCM	conductor polarizable continuum model (solvation model)
Cy	cyclohexyl
dba	dibenzylideneacetone (<i>trans,trans</i> -1,5-diphenyl-1,4-pentadien-3-one)
DC	Direct current
DCE	1,2-dichloroethane
DCM	dichloromethane
def2-TZVP	Ahlrichs basis set; split-valence triple-zeta
DFT	density functional theory
DMAc	dimethylacetamide
DME	dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMI	1,3-Dimethyl-2-imidazolidinone
DMSO	dimethylsulfoxide
Et	ethyl
GC-MS	Gas chromatography mass spectrometry
h	hour
HF	Hartree-Fock
HPLC	High performance liquid chromatography
ICP	Inductively coupled plasma
<i>i</i> Pr	<i>iso</i> -propyl (2-propyl)
L	ligand
LDA	Lithium diisopropylamide
LED	Light emitting diode
Li	Lithium
LiTMP	lithium 2,2,6,6-tetramethylpiperidide
M06L	DFT method (metaGGA, Minnesota suite)
MA	Michael acceptor
Me	methyl
MeOH	methanol
Mes	mesityl (2,4,6-trimethylphenyl)
min	minute
<i>n</i> Bu	<i>n</i> -butyl (1-butyl)
NMP	<i>N</i> -methyl-2-pyrrolidone
NMR	nuclear magnetic resonance spectroscopy
OAc	acetate
OTf	triflate (trifluoromethanesulfonate)
Ph	phenyl
phen	phenanthroline
rt	Room temperature
SET	Single electron transfer
<i>t</i> Bu	<i>tert</i> -butyl
TBS	<i>Tert</i> -butyldimethylsilyl
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl radical
TFA	Trifluoroacetic acid
THF	tetrahydrofuran
TM	Transition metal
TMS	trimethylsilyl

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1

Base catalyzed remote hydrogermylation of olefins

The results described in this chapter were published in Angewandte Chemie.^[1] Experimental work was carried out in collaboration with Dr. Aymane Selmani (method development), whose contributions are highlighted for the corresponding results.

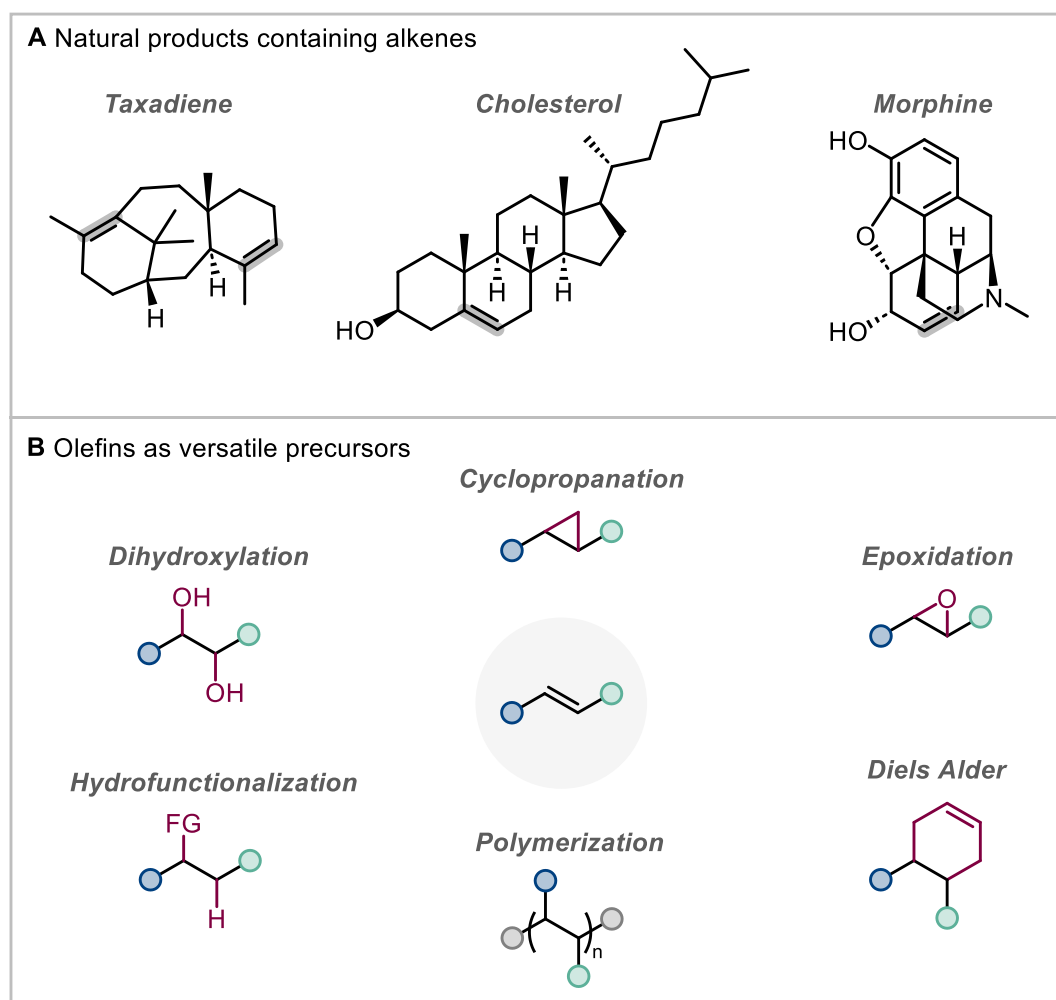
1 Base catalyzed remote hydrogermylation of olefins

1.1 Introduction

1.1.1 General introduction of olefins

An olefin, also called an alkene, describes an organic compound containing one or more double bonds between two carbon atoms. Molecules containing double bonds are commonly found in natural products (Figure 1A) and are used in a broad range of applications, especially in pharmaceutical, agrochemical and food industries.^[2] Due to the significant importance of alkene containing compounds in human life,^[3] the literature presents a vast body of knowledge on olefin synthesis and functionalizations. In view of the importance of alkenes, many name reactions for the synthesis of those became well known, e.g. the Cope elimination,^[4] the Wittig reaction,^[5] olefin metathesis^[6] or the Heck reaction,^[7] just to name a few. Besides their application as final products in the above-mentioned fields, olefins act as versatile precursors for numerous functionalization reactions (Figure 1B). Well-known examples include Sharpless dihydroxylation,^[8] cyclopropanation,^[9] epoxidation,^[10] Diels-Alder cycloaddition,^[11] polymerization^[12] and hydrofunctionalizations,^[13] which will be discussed in detail later in the chapter.

Figure 1 | Overview of natural products containing alkenes and transformation possibilities of olefins.



1.1.2 Transition metal catalyzed and metal free isomerization of olefins

Another impactful transformation of olefins is the isomerization of the double bond. In comparison to the previously mentioned functionalization methods (Chapter 1.1.1), the double bond isomerization does not introduce a new functional group, it simply describes the relocation of the olefin or the change from *E*- to *Z*-isomer or *vice versa*. Given the high demand industrially for alkene containing compounds,^[2] the isomerization reaction is an atom-efficient tool to create new compounds within one step. An illustrative example of the importance of different isomers is the drug tamoxifen, which is used in breast cancer treatments to selectively block estrogen receptors (Figure 2A).^[14] In this specific case, the *Z*-isomer of tamoxifen is 100 times more biologically active than the *E*-isomer,^[14] underscoring the importance of efficient and selective isomerization methods for olefins. In this regard, it is crucial that the formation of a new double bond is both regioselective and stereoselective, as the separation of the different isomers remains difficult.^[2]

To achieve selective isomerization of olefins, numerous transition metal catalyzed approaches have been published, demonstrating double bond migration over one or more carbon atoms.^[15] In this context, isomerization over multiple carbon bonds is also referred to as a “chain-walk”, which is mostly shown with transition metal catalysts and a few examples of Lewis acidic boranes for longer carbon chains.^[16, 17] Transition metal catalyzed chain walking can go through different possible mechanisms or even combinations of them (Figure 2B).^[18] The work reported in the literature primarily focuses on the 1,2- or the 1,3-hydride shifts, while our group recently reported a novel approach utilizing a metalloradical 1,3-H atom relocation.^[2, 19, 20]

In the 1,2-hydride shift mechanism, the transition metal provides a metal hydride and contains a vacant coordination site. The transition metal first coordinates to the π -electrons of the double bond and subsequently migrates into the olefin to generate a defined alkyl-metal species. After subsequent β -hydride elimination, either the *E*- or *Z*-isomer is formed and the process can repeat, allowing the double bond to move along the carbon chain.^[19, 20]

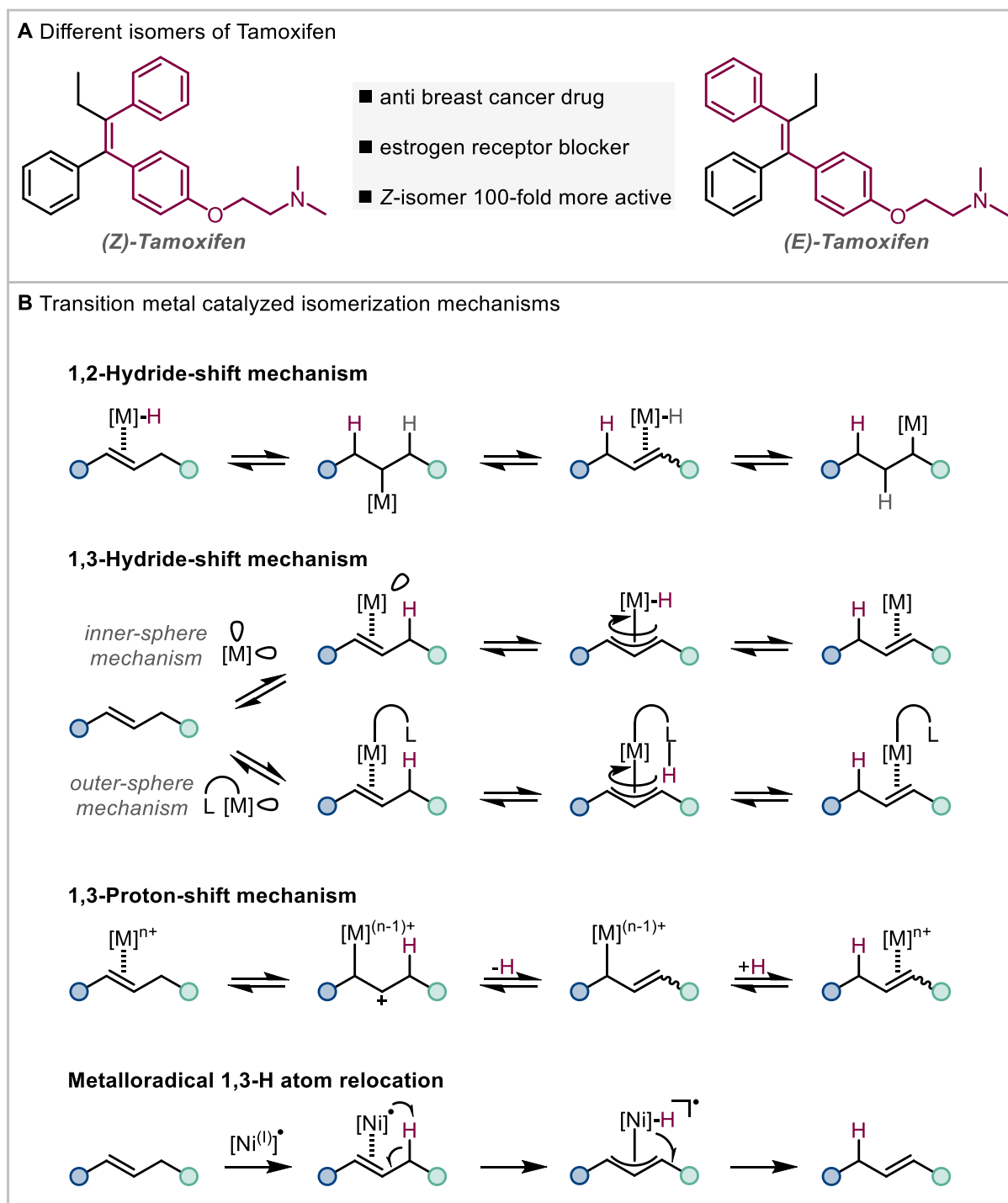
In contrast to that, the 1,3-hydride shift inner-sphere mechanism requires two free coordination sites and no metal hydride. First, one of the free sites of the metal coordinates to the π -electrons of the double bond, followed by allylic C-H activation and oxidative addition to form an η^3 -allyl metal-hydride complex. This complex can collapse either to generate the starting material or the rearranged new product. The outer-sphere mechanism utilizes a base at one of the free coordination sites of the catalyst, to abstract the allylic proton after coordination of the metal to the double bond. This will again form the η^3 -allyl metal-hydride complex, which forms the isomerized product after reductive elimination.^[19, 20]

Additionally, a cationic 1,3-proton shift mechanism has been described for electrophilic transition metal complexes, such as Pd^(II) complexes.^[21] After coordination of the metal to the olefin, a carbonium ion is formed which generates a cationic allyl intermediate upon loss of H⁺. This proton will cleave the metal carbon bond to release the catalyst and the isomerized product. All of the described mechanistic steps are in equilibrium and the final product is dependent on the metal, ligand and solvent employed.^[18]

Moreover, the Schoenebeck group recently published a novel metalloradical 1,3-H atom relocation using a nickel dimer.^[2] Computational studies support a homolytic cleavage of the dimer by the solvent or substrate to form a Ni^(I)-substrate monomer complex, generating a metal-substrate complex with radical character.

The H-atom transfer to the nickel center generates an intermediate, which rapidly relocates the hydrogen atom, to form the more stable nickel complex. Further experimental and computational data support the observed formation of the more stable *E*-isomer.^[2]

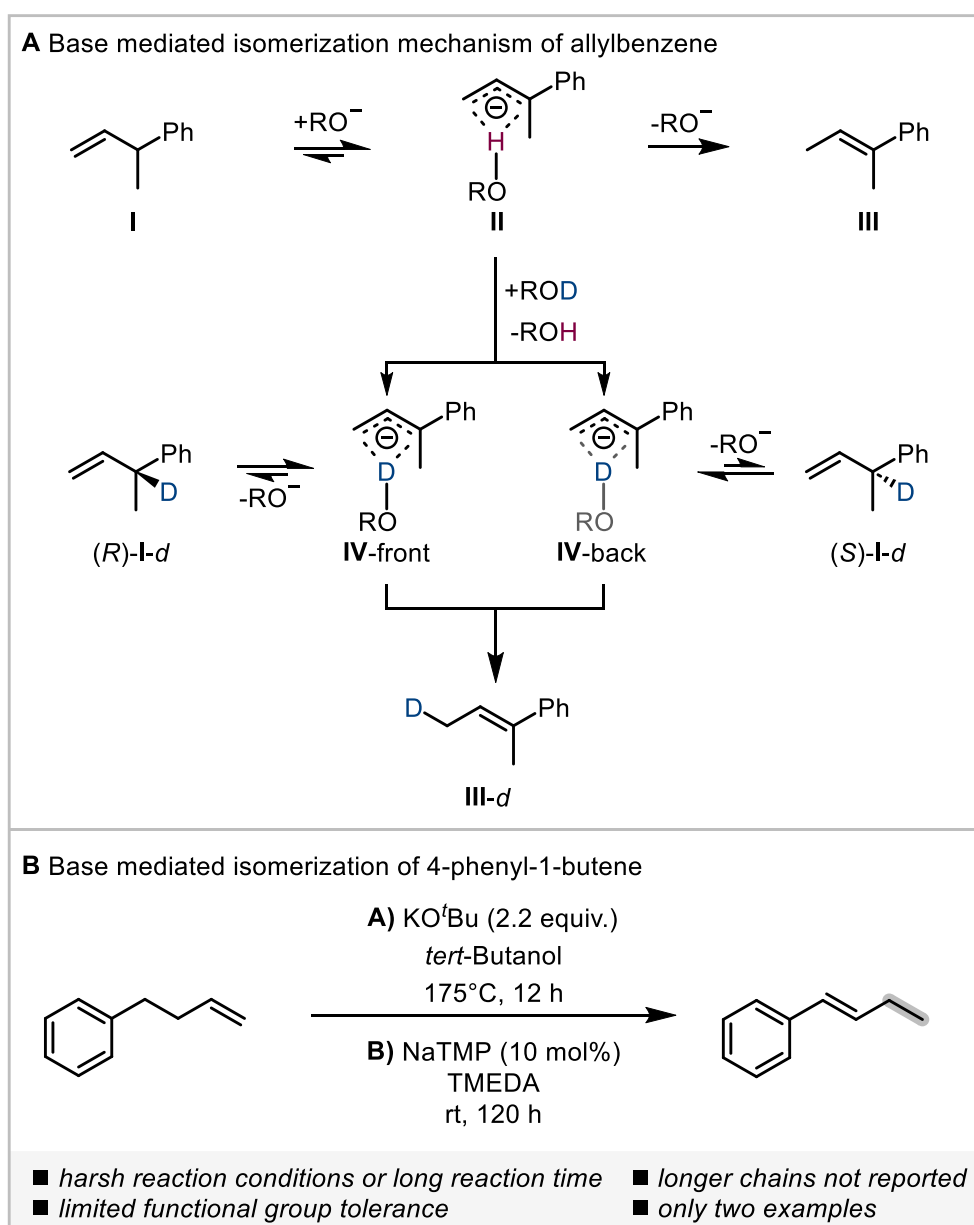
Figure 2 | Overview of different transition metal catalyzed isomerization mechanisms. Figure adapted from references.^[2, 18, 20]



Another alternative method to isomerize double bonds is *via* a base mediated pathway.^[19] In particular, the base induced isomerization of allylbenzene was extensively studied by Cram and Uyeda in the early 1960s.^[22] Based on their findings, they proposed a mechanism that can proceed *via* either an intramolecular

or intermolecular pathway, depending on the solvent and base used (Scheme 5A). They suggested that the model substrate 3-phenyl-1-butene (**I**) undergoes deprotonation at the benzylic position by the alkoxide base to form intermediate **II**, which represents a coplanar allylic anion system. The abstracted hydrogen from the newly formed alcohol (**ROH**) is hydrogen bonded to the two terminal carbons of the allylic anion. Upon collapse of this system, either the starting material can be regenerated, since the abstraction is in equilibrium, or the intramolecularly isomerized product (**III**) can be obtained. Another possibility is that an additional molecule of the formed alcohol exchanges with the one in intermediate **II** and when deuterium labeled compounds (**ROD**) were applied, they could also prove the incorporation of those. If the exchange occurs from the front site of **II**, the same intermediate (**IV-front**) is generated, whereas exchange from the back side results in the enantiomer (**IV-back**). Both of these allylic anions can then collapse to form either the deuterated starting material ((*R*) or (*S*) **I-d**) or the deuterated isomerized product (**III-d**).^[22]

Scheme 5 | Base mediated isomerization of allylbenzene mechanism.^[19, 22]



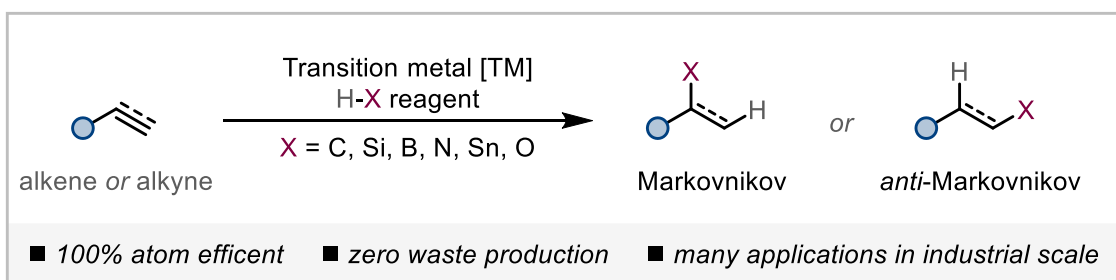
Due to the ever-increasing interest in metal free approaches, a few alternative strategies have been explored in the literature.^[19, 23] Beyond alkoxide bases, a sodium-amide superbase has recently been shown to selectively isomerize olefins to their thermodynamically most stable position.^[24] In comparison with transition metal catalyzed approaches,^[15] the longest chain length that has been successfully isomerized is 4-phenyl-1-butene, with a four carbon chain.^[24, 25] Since the only two literature known examples of base catalyzed isomerization of 4-phenyl-1-butene require either 175°C or a sodium-amide superbase,^[24, 25] there remains a need for milder reaction conditions and the ability to isomerize extended carbon chains (Scheme 5B).

One possible alternative are the previously mentioned Lewis acidic boranes, specifically tris(pentafluorophenyl)borane $B(C_6F_5)_3$.^[17] Catalytic amounts of this borane were sufficient to efficiently isomerize phenyl alkenes from the terminal to the thermodynamically more stable internal isomer. Based on these results by Morrill and co-workers, the group of Gellrich demonstrated the utilization of the comparable catalyst bis(pentafluorophenyl)borane $HB(C_6F_5)_2$ as tool for efficient isomerization of olefin chains up to 12 carbons.^[16] However, a significant drawback of these reactions is the requirement for high reaction temperatures, specifically 150°C and 120°C, respectively.

1.1.3 Hydrofunctionalization of olefins

In Chapter 1.1.2, it was mentioned that there are a variety of methods to functionalize olefins, including hydrofunctionalization. Generally, hydrofunctionalization describes a powerful way of adding a reagent H-X (X = C, Si, B, N, Sn, O) across an unsaturated multiple bond of an organic structure (Scheme 6).^[26-28] The obvious benefits of these types of reactions are the complete incorporation of the reagent, leading to high atom economy and consequently the production of minimal amounts of waste. On an industrial scale, transition metal catalyzed approaches are primarily used for hydroformylation, -silylation, -boration, -amination, -stannation and others of olefins.^[26-28] The generated products are further applied in the production of pharmaceuticals, flavors, materials and fine chemicals, emphasizing the importance and impact of hydrofunctionalization.^[28] During these processes, the employed catalyst, ligands and solvent system are crucial for the chemo-, regio- and stereoselectivity of the formed products. In this context, the hydrofunctionalization of terminal olefins can result in the formation of two different constitutional isomer, the Markovnikov and the *anti*-Markovnikov products.^[29]

Scheme 6 | Hydrofunctionalization of alkenes and alkynes.



One of the most prominent hydrofunctionalizations is the hydrosilylation of multiple bonds to form industrially relevant silicon coupling reagents or silicon polymers, which are further used as oils, resins and rubbers.^[30] In these cases, the terminal hydrosilylated, or *anti*-Markovnikov, product is preferred due to the high demand in silicon industries.^[28] Interestingly, the first transition metal catalyzed hydrosilylation was performed with a platinum catalyst by Speier which was reported in the late 1950s.^[31] In 1973, Karstedt published a new Platinum catalyst, which outcompeted the previously reported catalysts in activity and selectivity.^[32] Over the last few decades, research efforts have focused to successfully improve the reactivity and selectivity of the transition metal catalyzed hydrosilylation reaction.^[28] In consideration of the low abundance and high cost of precious metals, first row transition metals like iron, nickel or titanium were found to be effective alternatives, even showing improved reactivity or selectivity for specific examples.^[30] Furthermore, transition metal free approaches were reported to enable the hydrosilylation of olefins, e.g. using Lewis acidic B(C₆F₅)₃ or alkali metal fluorides.^[33, 34]

Another industrially relevant hydrofunctionalization reaction is the hydroboration of alkenes and alkynes. In these processes, alkyl or vinyl boranes/boronic esters are synthesized for further functionalization in Suzuki-Miyaura cross-coupling or other important transformations, such as oxidation to an alcohol or amination.^[35] The first hydroboration of carbon-carbon multiple bonds was reported by H. C. Brown in 1956,^[36] for which he was awarded the Nobel Prize in 1979. Over the last decades, various transition metal catalyzed protocols have been published that control the regio- and enantioselectivity of the formed boronic

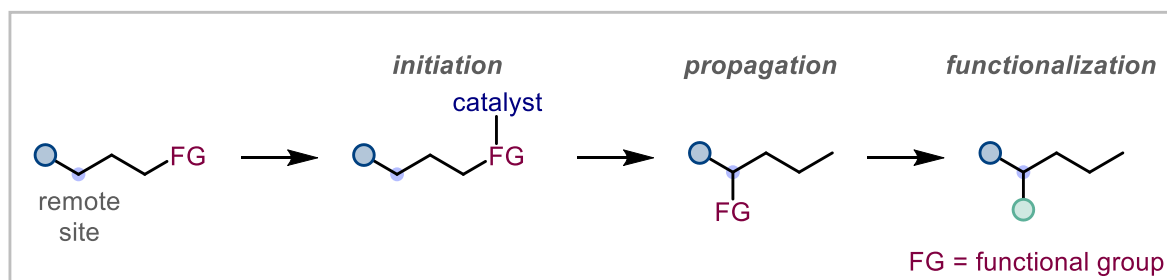
ester products, which are air- and bench-stable in comparison to their borane counterparts.^[28, 35] As mentioned previously, efforts have been made to reduce the use of precious transition metals or metal catalysts in general and therefore, elegant methods for hydroboration have been published, using Lewis acids or base catalyzed approaches.^[37-39]

Comparable attention has also been paid to the hydrostannalation reaction of alkenes and alkynes, due to the broad application of organostannanes in further functionalization as Stille cross-coupling reagents.^[40] In this regard, the synthesis of vinyl stannanes is of more interest than alkyl stannanes. Synthetic methods are mostly based on transition metal catalyzed hydrostannalation of carbon-carbon multiple bonds, but free-radical methods are also well established.^[41] Transition metal free approaches have been described with the Lewis acidic $\text{B}(\text{C}_6\text{F}_5)_3$.^[42] In comparison to the already mentioned hydrofunctionalization reagents, organotin compounds are very toxic and because of this, novel functionalization methods aim to avoid the use of this moiety.

1.1.4 Remote hydrofunctionalization of olefins

The rapid construction of complexity within an undecorated and abundant starting material remains a primary goal of synthetic chemistry. In general, catalytic strategies that combine the advantages of practicality, atom-efficiency and broad applicability are particularly sought after, especially in the C_{sp^3} landscape.^[43, 44] Within this context, the remote functionalization of alkenes represents a transformative approach, enabling the introduction of different functional groups at unactivated C_{sp^3} -H positions distal to the original reactive site.^[18, 20, 45-48] Unlike conventional alkene functionalization methods, the reactive site is efficiently traversed along the hydrocarbon chain, allowing chemical modification at a distant position and unlocking novel pathways for diverse modifications. In general, a functional group interacts with a catalyst, which then facilitates the chain walking on the carbon chain, leading to the remote site and subsequently functionalizing this group (Scheme 7). This strategy combines the previously described chain walking along the carbon chain with the hydrofunctionalization of the carbon-carbon double bond. Such reactions are not only synthetically challenging but also offer versatile platforms for molecular diversification, as shown for C-C,^[49] C-Si,^[50, 51] and C-B^[52, 53] bond formations.

Scheme 7 | General overview of a remote functionalization reaction.^[18]



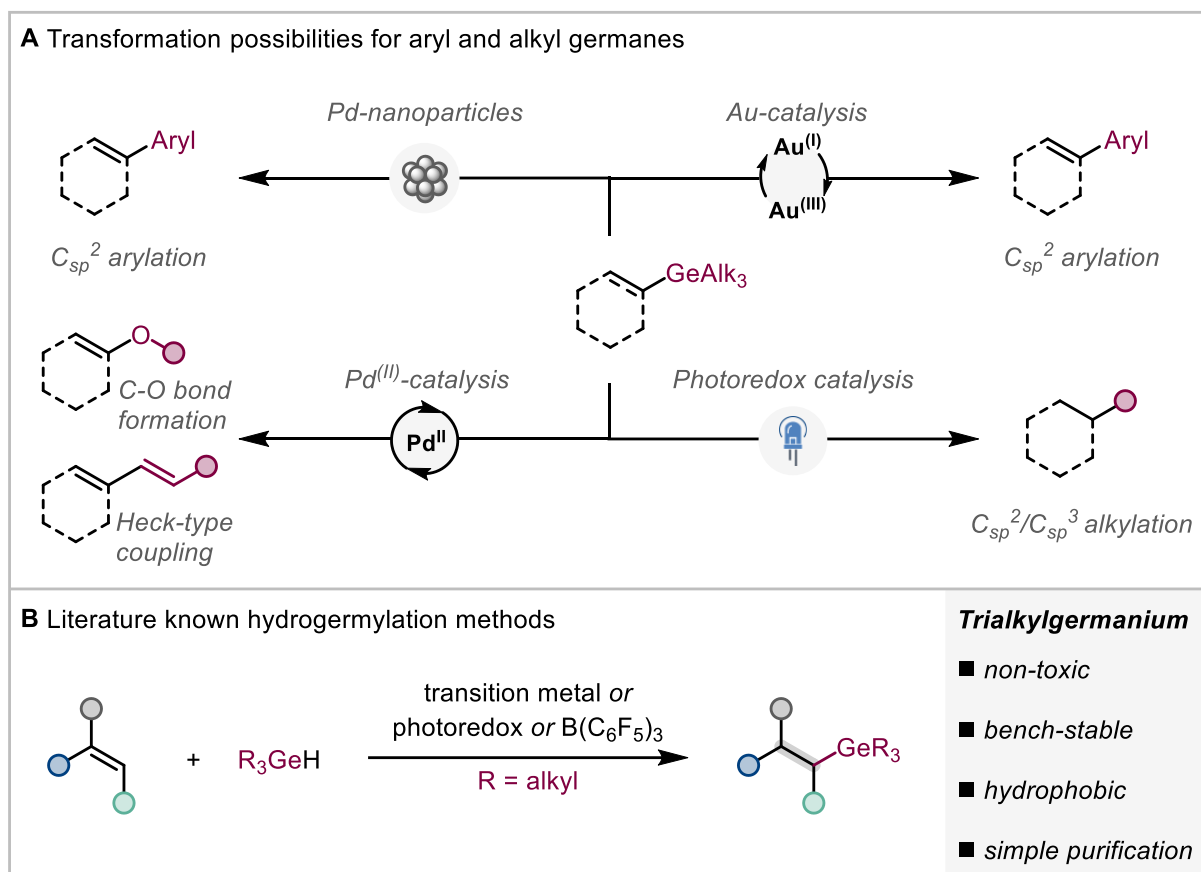
Literature reported remote hydrofunctionalization reactions mostly rely on the addition of transition metal catalysts to perform the isomerization and subsequent hydrofunctionalization steps.^[18, 20] Transition metal catalysts are therefore instrumental in controlling the efficiency and selectivity of this process, with performance highly dependent on metal species, oxidation state and ligand environment. Achieving selective olefin isomerization over functionalization is challenging and often requires tailored catalytic systems for specific functional groups. Furthermore, the high cost, scarcity and functional group incompatibility of certain transition metals, in conjunction with concerns over metal residues in pharmaceuticals, highlight the need for metal-free alternatives.^[54] One recently published example is the borenium catalyzed chain walking with a terminating hydroboration on the thermodynamically most stable internal isomer.^[54] The resulting borane product has been shown to undergo well-established transformations, such as oxidation to an alcohol, opening a broad range of possible functionalizations. Due to the previously mentioned benefits of a transition metal free remote hydrofunctionalization approaches, further investigations are required to introduce different functional groups.

1.1.5 Trialkylgermanium as a versatile moiety

The trialkylgermanium group would be a suitable candidate for the remote hydrofunctionalization reaction, due to the attractive properties of organogermanium compounds; these compounds benefit from being non-toxic, hydrophobic and bench-stable, in addition to being easy to handle and purify.^[55] Historically, germanium was discovered by Clemens Winkler in Germany in 1886, which was the reason for the name of the new element.^[56] In the periodic table of elements, germanium is part of the carbon group together with carbon, silicon, tin and lead.^[57] Intensive investigations in the last decades have clearly shown that organogermanium compounds have unambiguously different properties in chemical and pharmaceutical applications, in comparison to their analogues.^[58-60] Notable examples of this are the utilization in organic light-emitting diodes or the significant increase in biological activity, when a carbon atom was exchanged with germanium.^[58, 59]

In the 1970s and 1980s, global breakthroughs were made in the palladium catalyzed cross-couplings of aryl halides with aryl stannanes or silanes.^[61, 62] At the time, organogermanium compounds did not show any productive reactivity under usual $\text{Pd}^{(0)}/\text{Pd}^{(\text{II})}$ conditions, unless they were exposed to harsh reaction conditions.^[63] Limited to the underdeveloped reaction conditions for organogermenes, the aryl germane was overlooked and outperformed by the aforementioned aryl stannane and silane equivalents.^[64]

In recent years, the reactivity and activation mechanisms of organogermanium compounds have been thoroughly investigated by our group.^[60] These studies revealed that the trialkylgermanium species are prone to electrophilic C–Ge bond activation strategies, utilizing palladium nanoparticles, $\text{Pd}^{(\text{II})}$ or $\text{Au}^{(\text{I})}/\text{Au}^{(\text{III})}$ catalysts (Scheme 8A).^[65-70] In these findings it was reported that the organogermanium moiety chemoselectively reacted in the presence of other well-known cross-coupling partners, such as aryl silane or aryl boronic acids and esters, demonstrating orthogonal selectivity. In this context, the trialkylgermanium group remains intact under standard cross-coupling conditions, enabling new possibilities as shown in the sequential coupling of aryl germanes to rapidly access polyarenes.^[71] Besides trialkylgermanium aryl functionalizations, recent advances in photochemical transformations of C_{sp^3} –trialkylgermanium compounds have been shown (discussed in detail in Chapter 2).^[72, 73]

Scheme 8 | Trialkylgermanium functionalization strategies and literature known hydrogermylation approaches.^[60]

Due to the increasing numbers of different functionalization possibilities, the synthesis of trialkylgermanium compounds has led to new methodologies. Accessing the desired trialkylgermanes is frequently done by nucleophilic substitution of either the germanium-based nucleophile (e.g. R_3GeMgX or R_3GeZnX) and an alkyl halide, or equivalently organometallic reagents in combination with a germanium electrophile (e.g. Et_3GeCl).^[74-77] To overcome the limitations associated with organometallic reagents, further protocols have been reported such as nickel catalyzed reductive coupling of trialkylgermanium chlorides with alkyl bromides or photoinduced germyl radical formation, which allows addition to olefins.^[78-81] Another viable and atom-efficient method is the hydrogermylation of alkenes, which has been applied in numerous publications (Scheme 8B).^[82-86] In addition to transition metal catalyzed examples, Lewis acid catalyzed reactions have been shown to be highly efficient and selective.^[87, 88]

1.2 Base catalyzed remote hydrogermylation of olefins: results and discussion

1.2.1 Optimization studies

Expanding on prior findings of the hydrogermylation of terminal olefins with $B(C_6F_5)_3$,^[88] Dr. Aymane Selmani from our group discovered a novel base mediated approach. These first results were achieved using stoichiometric amounts of LiO^tBu and CsF (3.0 equiv. each) in DMI at 80°C for 16 h, with the olefin as limiting reagent and 2.5 equivalents of triethylgermanium hydride (Et_3GeH). During these studies, Dr. Aymane Selmani found that the hydrogermylation selectively takes place at the homobenzylic position of styrenes and their derivatives. Interestingly, when the carbon chain of terminal olefins was extended, the isomer underwent chain walking to the styrene position, followed by subsequent hydrogermylation. With this newly discovered remote hydrofunctionalization in hand, this work focuses on the optimization of reaction conditions towards a catalytic approach, scope and the elucidation of the reaction mechanism. The model substrate for the optimization studies was 1-(but-3-en-1-yl)-4-fluorobenzene, which furnished organogermane **1**; this compound must undergo the isomerization to the styrene position before the hydrogermylation can take place and the yield could be determined by quantitative ^{19}F NMR analysis. In the first optimization sequence, different bases were screened with various alkali metal fluorides (Table 1).

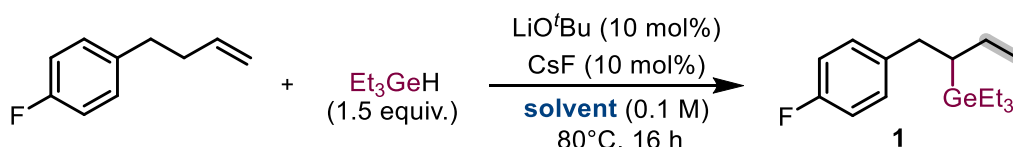
Table 1 | Optimization of bases and alkali fluorides.

Entry	Base	Alkali fluoride	Base loading	^{19}F NMR yield (%) ^a
1	LiO^tBu	CsF	2.0 equiv.	91
2	NaO^tBu	CsF	2.0 equiv.	18
3	KO^tBu	CsF	2.0 equiv.	56
4	$LiOMe$	CsF	2.0 equiv.	2
5	LiO^tBu	LiF	2.0 equiv.	0
6	LiO^tBu	NaF	2.0 equiv.	0
7	LiO^tBu	KF	2.0 equiv.	14
8	LiO^tBu	RbF	2.0 equiv.	12
9	KO^tBu	KF	2.0 equiv.	81
10	LiO^tBu	CsF	10 mol%	91
11	LiO^tBu	-	10 mol%	0
12	NaO^tBu	-	10 mol%	0
13	KO^tBu	-	10 mol%	87

Reaction conditions: in an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with base (10 mol% - 2.0 equiv.) and alkali fluoride (10 mol% - 2.0 equiv.) and dissolved in anhydrous DMI (1.0 mL, 0.1 M). To the mixture were added 1-(but-3-en-1-yl)-4-fluorobenzene (15.0 mg, 0.1 mmol, 1.0 equiv.) and Et_3GeH (24.3 μ L, 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. a) After cooling down to room temperature 1,4-difluorobenzene was added as internal standard for ^{19}F NMR yield determination. Additionally, a small aliquot was taken and analyzed by GC-MS measurement.

Entries 1-3 show that lithium, sodium and potassium *tert*-butoxide bases with CsF generate in all three cases the desired product, while the highest yield of 91% was obtained using LiO^{*t*}Bu (Table 1). Exchanging LiO^{*t*}Bu with LiOMe under similar conditions resulted in only traces of product (entry 4), which leads to the assumption that a *tert*-butoxide base is required for this reaction. Since LiO^{*t*}Bu achieved the highest yield, the remaining alkali metal fluorides were screened with this base. As shown in entries 5-8, no product was formed with LiF and NaF, while KF and RbF generated the product in low yields. In comparison, KO^{*t*}Bu with KF achieved an increased yield of 81%, indicating that the nature of the *tert*-butoxide base plays a pivotal role in this reaction. The dependence of the counter cation of the *tert*-butoxide base was further probed when different bases were used without any alkali metal fluoride and only KO^{*t*}Bu showed product formation in 87% yield (entries 11-13). Interestingly, it was found that low base loadings of 10 mol% LiO^{*t*}Bu and CsF were sufficient to achieve a selective and high yielding reaction of 91%, culminating in the highest yield obtained in this optimization study. These observations lead to the conclusion that an *in-situ* salt metathesis between LiO^{*t*}Bu and CsF may take place to form CsO^{*t*}Bu, resulting in increased reactivity.^[89] An in-depth discussion on the dependency of the *tert*-butoxide base and a proposed catalytic cycle will be further evaluated in the mechanistic discussion part (Chapter 1.2.5).

Table 2 | Optimization of solvents.



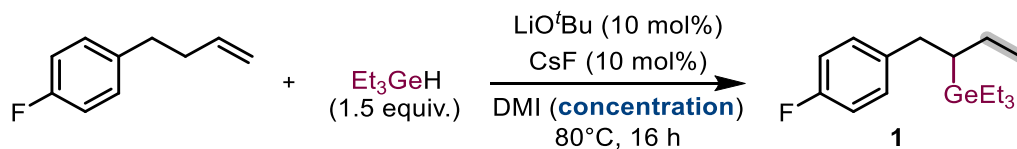
Entry	Solvent	¹⁹ F NMR yield (%) ^a
1	DMI	91
2	DMF	45
3	DMAc	13
4	NMP	0
5	DMSO	66
6	ACN	0
7	THF	0
8	benzene	0
9	cyclohexane	0

Reaction conditions: in an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^{*t*}Bu (0.8 mg, 0.1 equiv.) and CsF (1.5 mg, 0.1 equiv.) and dissolved in anhydrous solvent (1.0 mL, 0.1 M). To the mixture were added 1-(but-3-en-1-yl)-4-fluorobenzene (15.0 mg, 0.1 mmol, 1.0 equiv.) and Et₃GeH (24.3 μL, 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature 1,4-difluorobenzene was added as internal standard for ¹⁹F NMR yield determination. Additionally, a small aliquot was taken and analyzed by GC-MS measurement.

Next, solvent screening (as shown in Table 2) was carried out. In this study amide-based solvents (entries 1-4), polar aprotic solvents (entries 5-7) as well as aromatic and aliphatic solvents (entries 8 and 9), were tested. The initially used DMI once again achieved the highest yield, while other amide-containing solvents like DMF and DMAc showed decreased yields ranging from 13-45%. When other polar aprotic solvents like

DMSO, ACN and THF were tested, only DMSO achieved product formation with a 66% yield. This finding aligns with the literature reported reactions with KO^tBu in DMSO.^[90] Aromatic and aliphatic solvents like benzene and cyclohexane were unproductive and did not show any desired product formation.

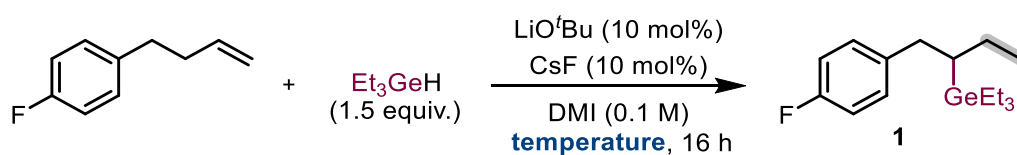
Table 3 | Optimization of the solvent concentration.



Entry	Concentration (M)	^{19}F NMR yield (%) ^a
1	0.4	67
2	0.2	84
3	0.1	91
4	0.05	80

Reaction conditions: in an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (0.8 mg, 0.1 equiv.) and CsF (1.5 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.05-0.4 M). To the mixture were added 1-(but-3-en-1-yl)-4-fluorobenzene (15.0 mg, 0.1 mmol, 1.0 equiv.) and Et_3GeH (24.3 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature 1,4-difluorobenzene was added as internal standard for ^{19}F NMR yield determination. Additionally, a small aliquot was taken and analyzed by GC-MS measurement.

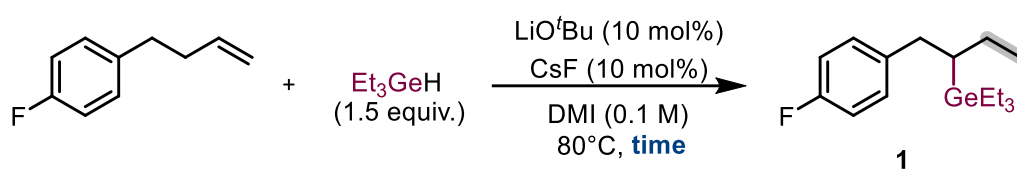
Following this, investigations were made for the optimal reaction concentration with DMI for high yielding product formation (Table 3). Besides the initially used concentration of 0.1 M, more concentrated reaction mixtures (entries 1 and 2) and a more diluted condition (entry 4) were compared. Interestingly, both increasing and decreasing the reaction concentration by half resulted in similar yields of 80-84%, while the standard condition still obtained the highest yield. Further reduction in solvent volume led to a decreased yield of 67%, emphasizing the necessity of an ideal concentration for optimal yield. A possible reason for the decreased yield in a more concentrated reaction could be the lower solubility of the base.

Table 4 | Optimization of reaction temperature.

Entry	Temperature (°C)	^{19}F NMR yield (%)
1	room temperature	0
2	40	0
3	60	6
4	80	91
5	100	89
6	120	86

Reaction conditions: in an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (0.8 mg, 0.1 equiv.) and CsF (1.5 mg, 0.1 equiv.) and dissolved in anhydrous solvent (1.0 mL, 0.1 M). To the mixture were added 1-(but-3-en-1-yl)-4-fluorobenzene (15.0 mg, 0.1 mmol, 1.0 equiv.) and Et_3GeH (24.3 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at the temperature shown overnight. After cooling down to room temperature 1,4-difluorobenzene was added as internal standard for ^{19}F NMR yield determination. Additionally, a small aliquot was taken and analyzed by GC-MS measurement.

After screening the bases, solvents and concentrations it was proceeded with the comparison of different temperatures in a range from room temperature to 120°C (Table 4). While at room temperature and 40°C no product formation was observed at all, traces of the desired product were obtained at a reaction temperature of 60°C. Using a reaction temperature of 80°C, as shown in the initial reaction conditions, the highest ^{19}F NMR yield of 91% was obtained. Interestingly, when the reaction temperature was increased to 100°C and 120°C, a slightly lower yield of 86–89% was achieved, respectively. The elevated temperatures might have caused partial deactivation of the catalyst or undesired side reactions involving the olefin. Moreover, the obtained ^{19}F NMR yields are very comparable, leading to the conclusion that a reaction temperature above 80°C is neither necessary nor beneficial for further yield improvement.

Table 5 | Optimization of reaction time.

Entry	Time (h)	^{19}F NMR yield (%)
1	2	0
2	4	19
3	6	29
4	8	56
5	16	91

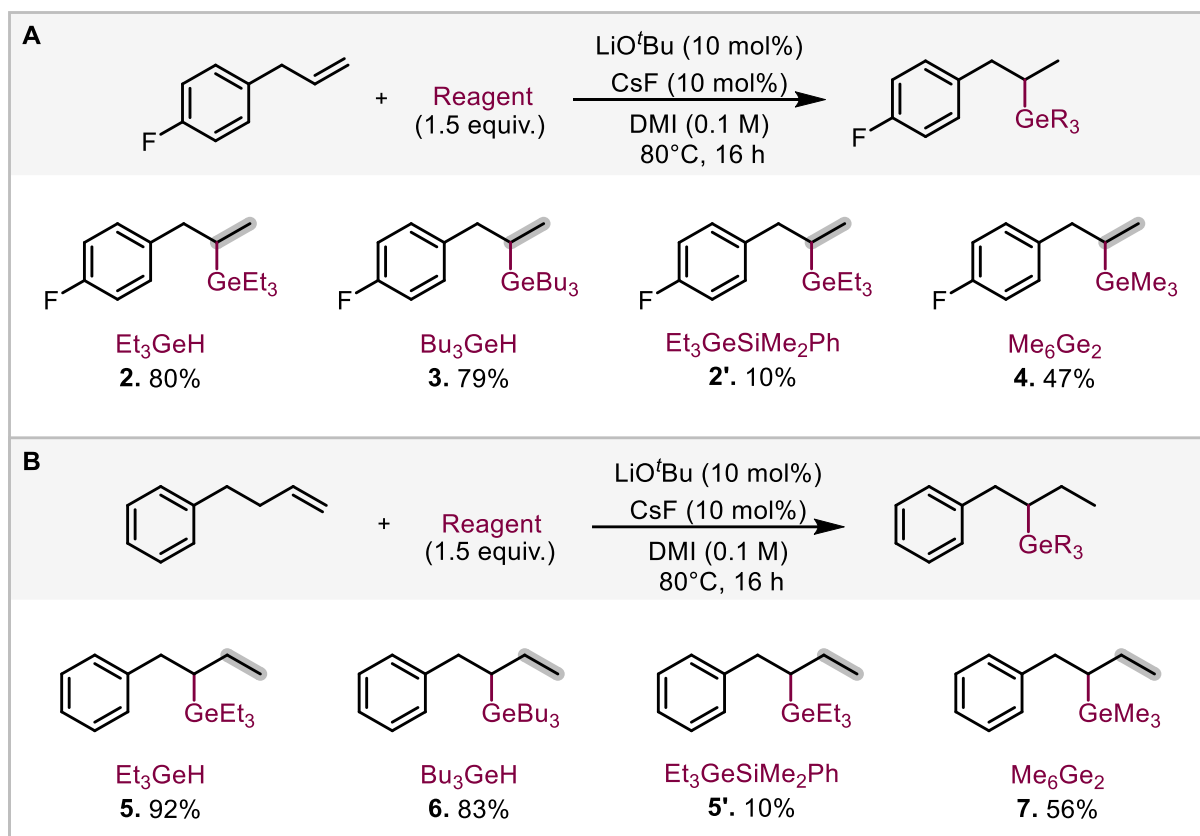
Reaction conditions: in an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous solvent (3.0 mL, 0.1 M). To the mixture were added 1-(but-3-en-1-yl)-4-fluorobenzene (45.0 mg, 0.3 mmol, 1.0 equiv.), Et_3GeH (72.9 μL , 1.5 equiv.) and 4,4'-difluoro-1,1'-biphenyl was added as internal standard for ^{19}F NMR yield determination. The vial was sealed and stirred in a heating block at 80°C and samples were taken at every shown time. Additionally, a small aliquot was taken and analyzed by GC-MS measurement.

As a final parameter, the reaction time of the remote hydrogermylation reaction was evaluated over a range from 2 to 16 h (Table 5). To provide consistent results, one reaction vial was set up with 4,4'-difluoro-1,1'-biphenyl as an internal standard, stirred inside the glovebox and samples were taken at the specified times. After 2 h of reaction time, no desired product formation was observed by ^{19}F NMR or GC-MS, with most of the starting material remaining and only traces of isomerized olefin. After additional 2 h (entry 2), the starting material was fully isomerized and a desired product signal was observed by GC-MS analysis. With increasing reaction time, the yield also increased to 29% after 6 h (entry 3) and 56% after 8 h (entry 4) of stirring. After 16 h (entry 5), the previously mentioned yield of 91% was obtained. Since a longer reaction time did not increase the product yield, the standard condition of 16 h was used for all further experiments.

1.2.2 Different Germanium sources

The next reaction parameter to be investigated was the employment of various germanium sources for the remote hydrogermylation reaction. First, 1-allyl-4-fluorobenzene was used as a model substrate with Et_3GeH , Bu_3GeH , $\text{Et}_3\text{GeSiMe}_2\text{Ph}$ and Me_6Ge_2 as reagents (Scheme 9A). Dr. Aymane Selmani from our group previously evaluated these germanium sources and demonstrated their efficacy in generating the desired products under non-optimized reaction conditions. Following with the optimized conditions, all reactions obtained the desired products, while the best yields were achieved with Et_3GeH as the germanium source, furnishing 80% (**2**) with catalytic amounts of base. Bu_3GeH demonstrated another germanium hydride that can undergo the hydrogermylation reaction selectively at the homobenzylic position, resulting in a high yield of 79% (**3**) with a catalytic amount of base. Besides germanium hydrides, a germanium silane reagent ($\text{Et}_3\text{GeSiMe}_2\text{Ph}$) was also tested under standard conditions, displaying different reactivity compared to the previously mentioned reagents. Dr. Aymane Selmani showed that using 2.0 equivalents of base with this reagent led to the desired product in a high yield of 93%, but with only 10% of base, just 10% of the desired product (**2'**) was isolated. Based on these results, it can be concluded that the germanium silane reagent requires at least one equivalent of base to be activated and achieve full conversion to the product. Another non-hydride species tested was the germanium dimer hexamethyldigermane (Me_6Ge_2), obtaining a 47% (**4**) yield with catalytic amounts of base. In comparison to the germanium silane reagent, the germanium dimer does not require stoichiometric amounts of base for sufficient product formation. This can potentially be explained by the literature known formation of a silane *tert*-butoxide, which was also observed by GC-MS analysis and is believed to inhibit further product formation after catalyst removal from the reaction.^[91]

To demonstrate that the shown hydrogermylation reagents are also feasible for longer alkene chains, 4-phenyl-1-butene was used as another model substrate (Scheme 9B). First, it was confirmed that the hydrogermylation with Et_3GeH once again obtained the highest yield among these reagents, yielding 92% (**5**). A slightly lower yield of 83% (**6**) was achieved with Bu_3GeH , while the germanium silane reagent obtained the expected 10% (**5'**) yield under catalytic conditions. Applying the germanium dimer Me_6Ge_2 as hydrogermylation reagent resulted in 56% of the desired product (**7**), following the same trend observed with the previous model substrate. Based on the obtained results, Et_3GeH remains the most promising hydrogermylation reagent and thus was further utilized under standard conditions for the substrate scope and mechanistic investigations. The germanium silane and the germanium dimer possibly react *via* a different mechanism and consequently, were not further investigated.

Scheme 9 | Evaluation of different germanium sources for the hydrogermylation of alkenes.

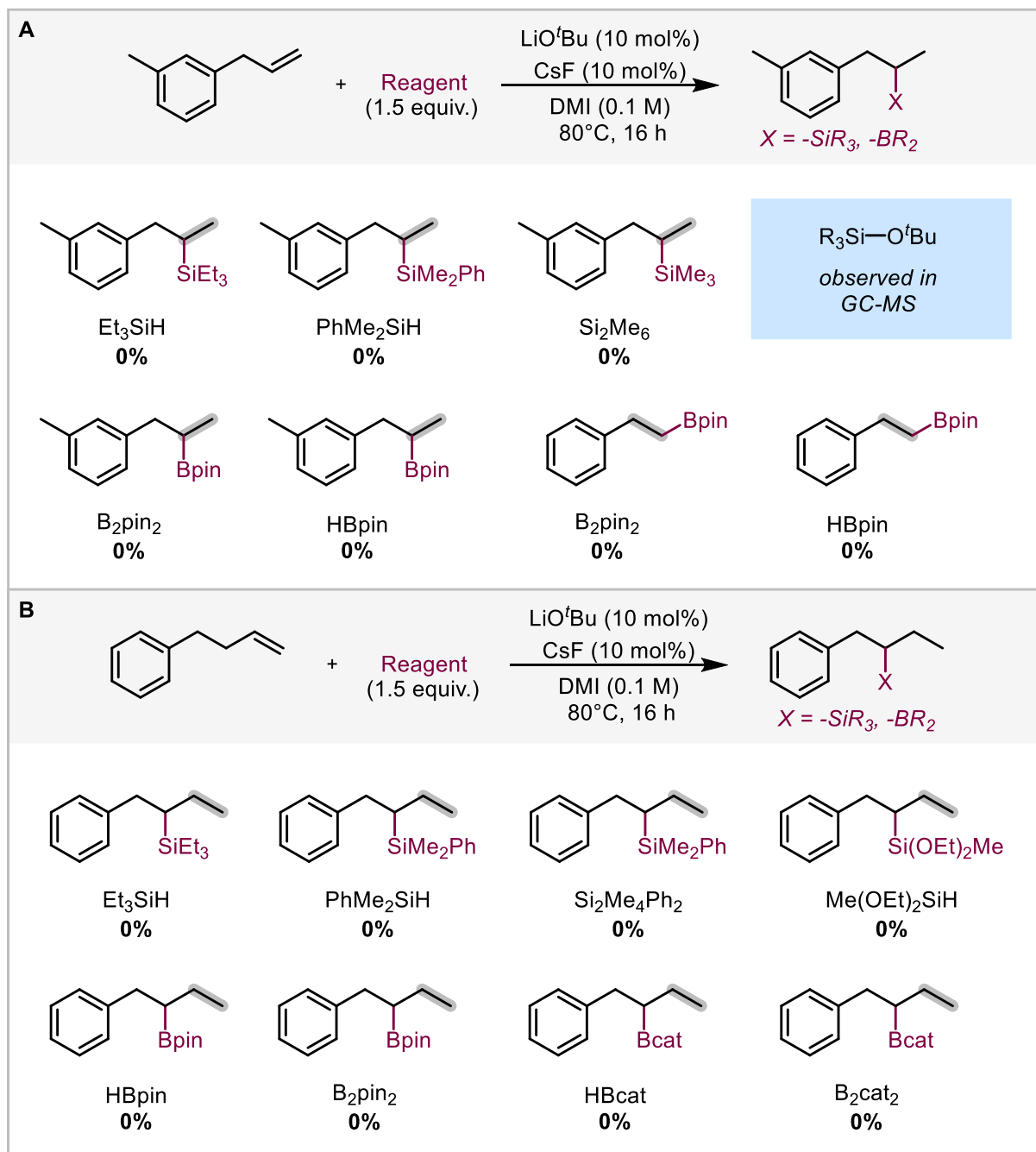
Reaction conditions for A and B: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added alkene (0.3 mmol, 1.0 equiv.) and the hydrogermylation reagent (1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

Besides the germanium sources previously discussed, it was also tested whether different hydrofunctionalization agents were compatible under the applied reaction conditions. First, several hydrosilylation reagents, such as Et_3SiH , PhMe_2SiH and Me_6Si_2 were tested with the model substrate 1-allyl-3-methylbenzene (Scheme 10A). Although these silanes are structurally similar to the previously tested germanes, no desired product formation was observed. In all cases, the formation of a silane *tert*-butoxide species was detected by GC-MS analysis, as previously reported in the literature.^[91] The formation of this undesired byproduct leads to deactivation of the base catalyst, inhibiting further isomerization of the double bond and subsequent hydrofunctionalization. Additionally, 4-phenyl-1-butene was used as starting material with the same silanes, as well as $\text{PhMe}_2\text{Si-SiMe}_2\text{Ph}$ and $\text{Me}(\text{EtO})_2\text{SiH}$, which led to the same unproductive results (Scheme 10B). Even the use of stoichiometric amount of base did not help to achieve the desired product formation.

Similar to hydrosilylation, hydroborylation reagents were tested under standard conditions (Scheme 10). For this reason, literature reported hydroborylation reagents such as HBpin and B_2pin_2 were applied to the previously used model substrate, as well as simple styrene. Unfortunately, in all cases the desired product did not form under catalytic conditions. Switching to the second model substrate, 4-phenyl-1-butene, also resulted in no desired product formation, even when using other borylation reagents such as HBcat and

B₂cat₂. Unlike the silane reagents, the hydroborylation reagents did not show any *tert*-butoxide based side-product formation. Consistent with the hydrosilylation results, increasing the amount of base did not facilitate the expected product formation. In conclusion, the germanium reagents were shown to demonstrate unique reactivity in these transformations, highlighting their potential for future applications.

Scheme 10 | Test reactions for further suitable reagents for the remote hydrofunctionalization.



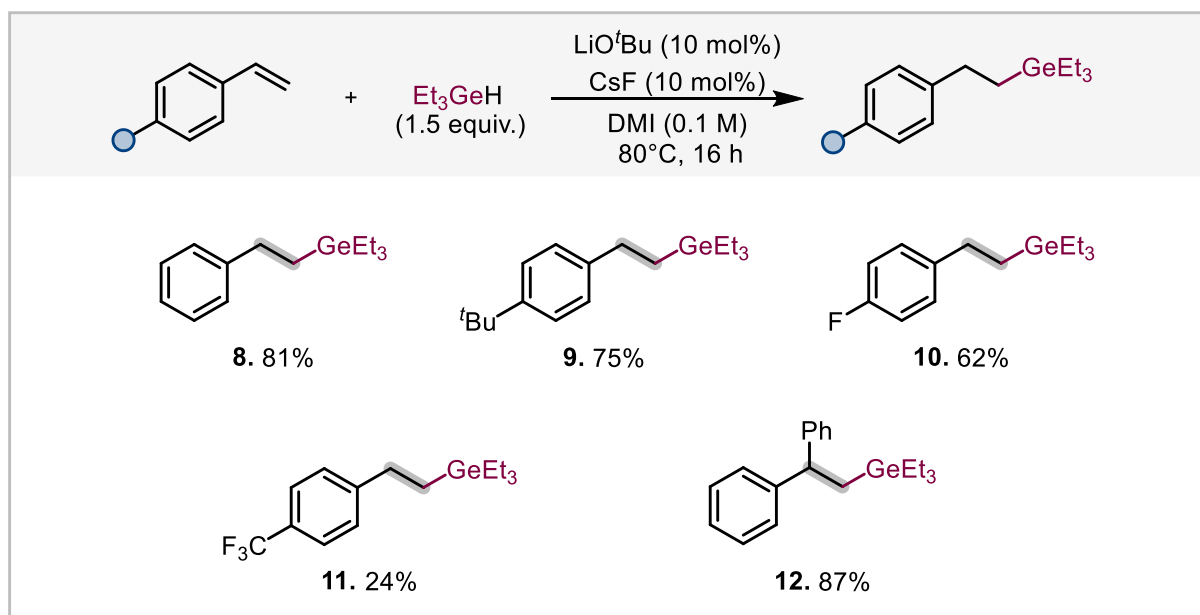
Reaction conditions for A and B: in an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (0.8 mg, 0.1 equiv.) and CsF (1.5 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added the alkene (0.1 mmol, 1.0 equiv.) and the hydrofunctionalization reagent (1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was analyzed by GC-MS analysis.

After an extensive screening process, it was concluded that the optimal reaction conditions for the desired product formation were catalytic amounts of LiO^tBu and CsF in DMI at 80°C for 16 h, with the olefin as the limiting reagent and Et_3GeH as germanium source. In the following scope and mechanistic discussions, it will always be specified whether catalytic or stoichiometric amounts of base were used in the reaction conditions.

1.2.3 Scope for the base catalyzed remote hydrogermylation

First, simple styrene derivatives were tested for the hydrogermylation reaction, as no isomerization can occur with these substrates. Fortunately, the *anti*-Markovnikov products from styrene and its derivatives were selectively obtained in high yields ranging from 62–87% (Scheme 11), demonstrating the tolerance towards electron donating groups as well as fluorine and steric hindrance at the benzylic position. Only 4-(trifluoromethyl)styrene stood out as an outlier with a low yield of 25%, which might be due to the incompatibility of this functional group under the applied reaction conditions, because of its strong electron withdrawing effect.

Scheme 11 | Hydrogermylation of styrene and styrene derivatives.

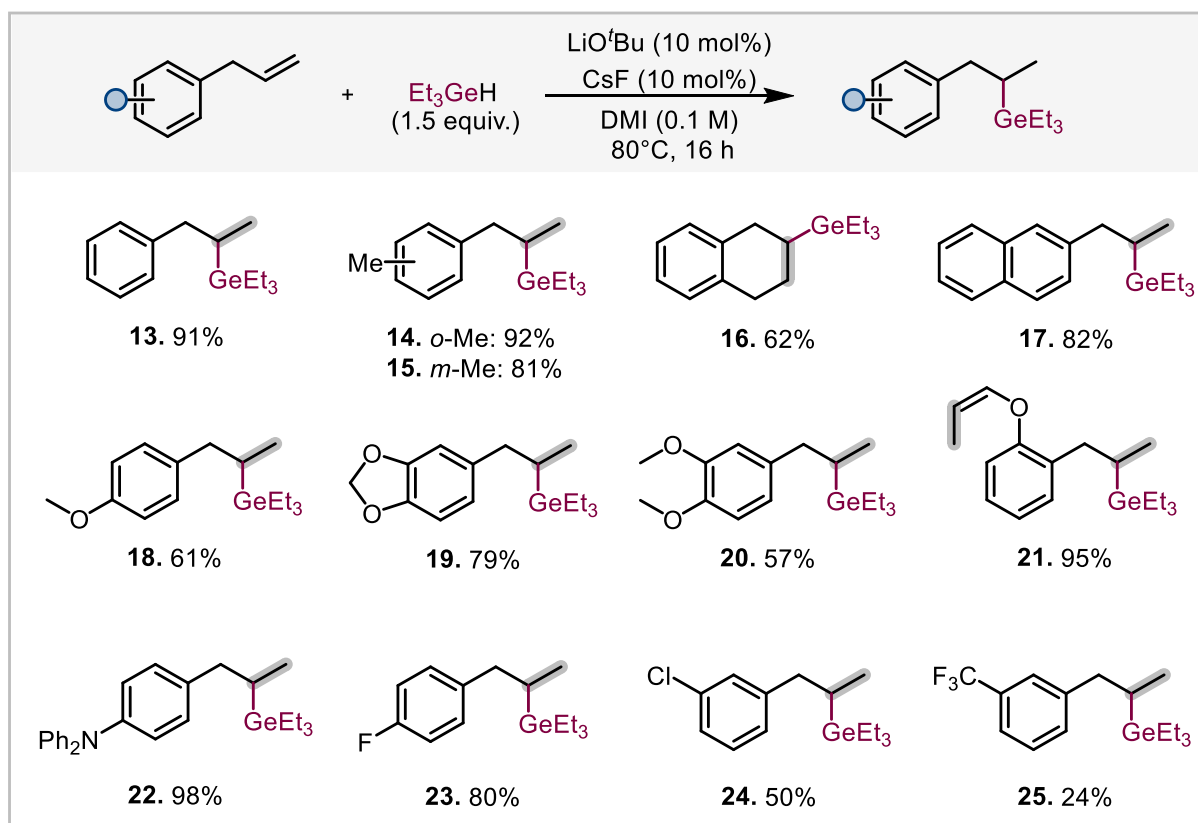


Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added styrene (0.3 mmol, 1.0 equiv.) and Et_3GeH (72.9 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

Expanding the olefin chain to allyl compounds enabled the isomerization of the double bond to the thermodynamically more stable position which successfully underwent hydrogermylation at the homobenzylic position. By using commercially available allylic compounds, it was possible to demonstrate the tolerance of substituents at any position on the aromatic system, as well as several functional groups like ethers (**18–20**), vinyl ethers (**21**), tertiary amines (**22**) and halides (**23–25**) in high yields up to 98% (Scheme 12). Specifically, aromatic substitutions with methyl groups at the *ortho*- and *meta*- positions achieved high yields of 81–92% under catalytic conditions. Additionally, a cyclic alkene example was demonstrated with 1,4-dihydronaphthalene, resulting in the desired hydrogermylated product (**16**). Furthermore, important natural products like estragole, safrole and methyl eugenol could be used as starting materials for the successful synthesis of the hydrogermylated products (**18–20**) at the homobenzylic position with high yields up to 79% under catalytic conditions. Interestingly, when an allyl ether was present in the compound, the expected isomerization to the thermodynamic stable *cis* alkene was

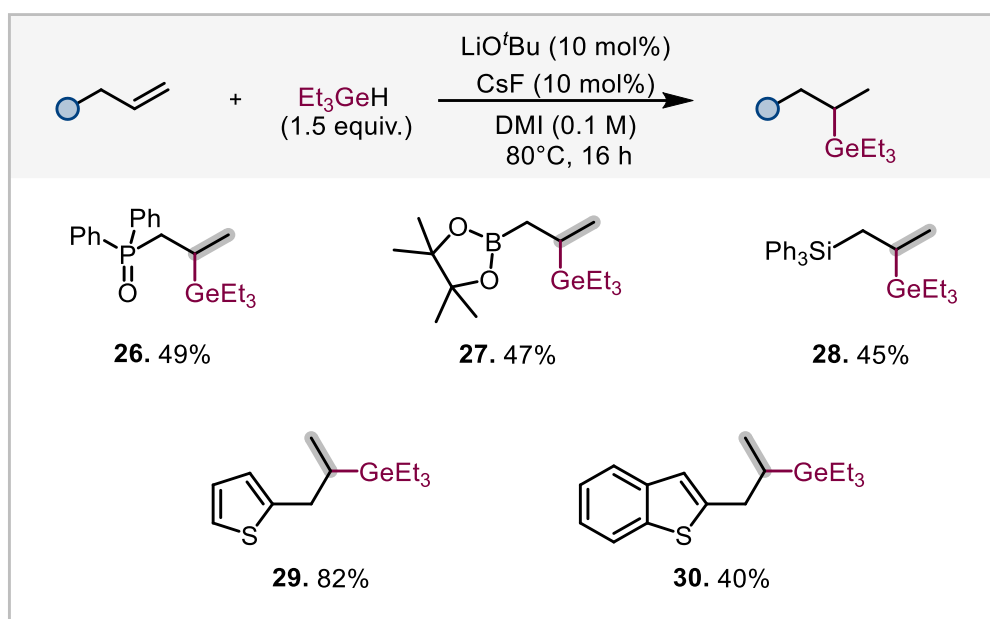
observed,^[92] but no hydrogermylation took place on this moiety. Instead, hydrogermylation occurred exclusively on the alkene functionality in a high yield of 95% (**21**). Besides this, tertiary amines were demonstrated as functional group in a high yield of 98% under catalytic conditions. As already mentioned in the styrene scope, it was showcased that halides, such as fluorides and chlorides, are tolerated under catalytic conditions, with isolated yields ranging from 24% to 80% (**23-25**).

Scheme 12 | Hydrogermylation of allylbenzenes.



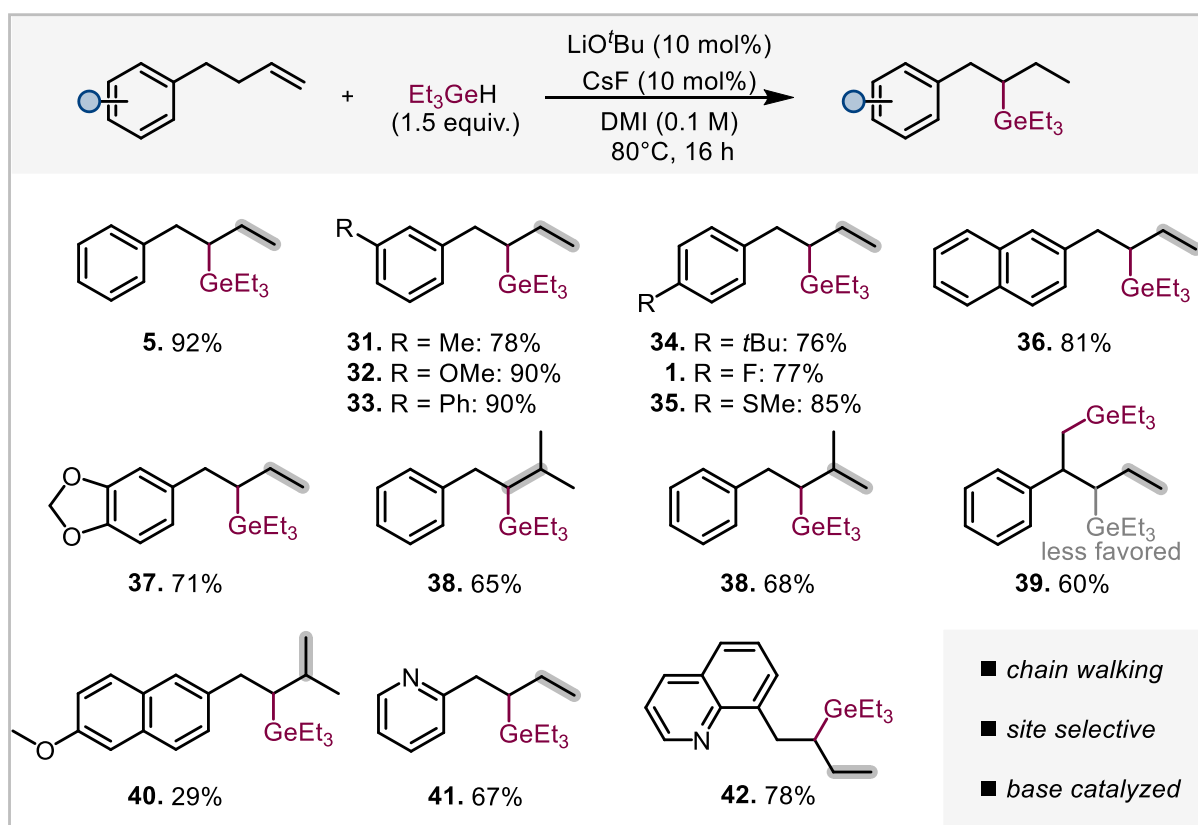
Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiOtBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added allylbenzene (0.3 mmol, 1.0 equiv.) and Et_3GeH (72.9 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

To further enhance the scope, non-aromatic and heteroaryl-allyl systems were demonstrated as potential starting material candidates, yielding the desired products in moderate to high yields under catalytic conditions (Scheme 13). For compound **26**, allyldiphenylphosphine was used as the starting material, which was directly oxidized to the phosphine oxide after the hydrogermylation due to its air sensitivity, resulting in the desired product in 49% yield. Moreover, allyl-Bpin and allyltriphenylsilane were utilized to generate the corresponding hydrogermylated products (**27-28**) in moderate yields of 45–47%. Remarkably, in comparison to the previous examples, these compounds do not contain an aromatic system. Additionally, heteroaromatic allylic compounds, such as thiophene (**29**) and benzothiophene (**30**), showed moderate to high yields of 40–82% under catalytic conditions.

Scheme 13 | Hetero- and non-aryl allyl systems for the hydrogermylation reaction.

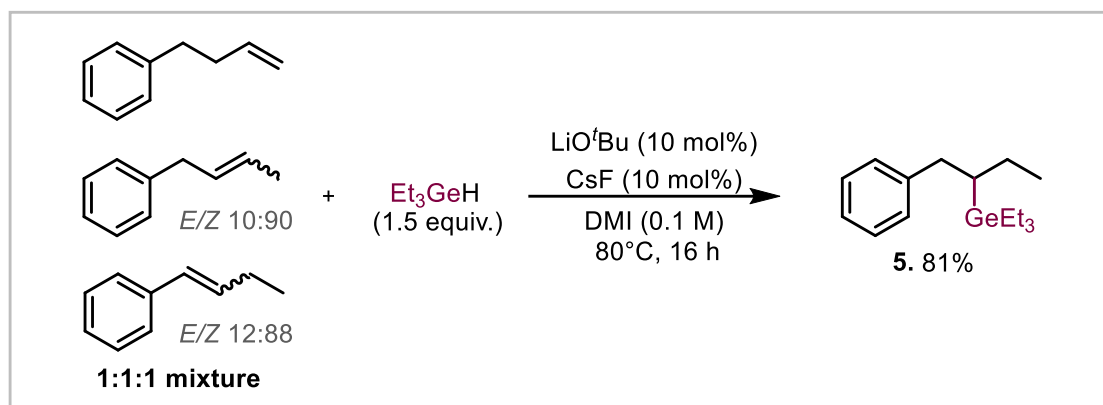
Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiOtBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added the allyl substrate (0.3 mmol, 1.0 equiv.) and Et_3GeH (72.9 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

Attention was then focused on phenylbutene compounds with an extended carbon chain, which demonstrated the occurrence of a remote hydrofunctionalization, since first the isomerization to the internal position must occur and then a subsequent hydrogermylation can take place (for more mechanistic details, see Chapter 1.2.5). In comparison to the two reported literature procedures on (super)base catalyzed isomerization,^[24, 25] it was shown that this method is capable of isomerizing phenylbutenes faster and under much milder conditions. As shown in the allylbenzene scope, it was demonstrated that several functional groups including electron donating alkyl (**31,34**), ether (**32,40**), phenyl (**33**), fluoride (**1**) and sulfide (**35**) are well tolerated at different positions on the aromatic system, achieving high yields of up to 90% (Scheme 14). Additionally, this methodology enabled the synthesis of a safrole derivative (**37**), bearing a germanium moiety at the homobenzylic position in 71% yield. Compound **38** yielded in the same product with the same yield but were synthesized from two different isomers of a starting material (the previous position of the double bond is highlighted in gray), which emphasizes that steric hindrance next to the double bond does not prevent the isomerization. Interestingly, when compound **39** was synthesized with a starting material containing two possible homobenzylic positions for the hydrogermylation, the primary, less hindered position was favored to form the product in 60% yield, while the secondary, more hindered position showed only traces of product. Besides the presented phenylbutene substrates, pharmaceutically relevant pyridine (**41**) and quinoline (**42**) derivatives showed the desired product formation in high yields of up to 78%.

Scheme 14 | Remote hydrogermylation scope of phenylbutene substrates.

Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiOtBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added the allyl substrate (0.3 mmol, 1.0 equiv.) and Et_3GeH (72.9 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

To further demonstrate the versatility of this novel method, experiments were conducted in which a 1:1:1 mixture of three different isomers of one olefin was reacted under standard catalytic conditions (Scheme 15). The model substrate for this reaction was 4-phenyl-1-butene with its two isomers (*E/Z*)-but-2-en-1-ylbenzene (*E/Z* 10:90) and (*E/Z*)-but-1-en-1-ylbenzene (*E/Z* 12:88), as *E/Z* mixtures. With this mixture of olefins, it was possible to evaluate the efficiency of the method with both constitutional and stereoisomers present in the same reaction. Fortunately, only the desired product (**5**) was observed and isolated in a high yield of 81%, underlining the power and versatility of the new method. This selective reactivity is especially interesting for industrial applications, where a broad range of different isomers from feedstock could be transformed into a single product without the need for cost intensive separation prior to the reaction.

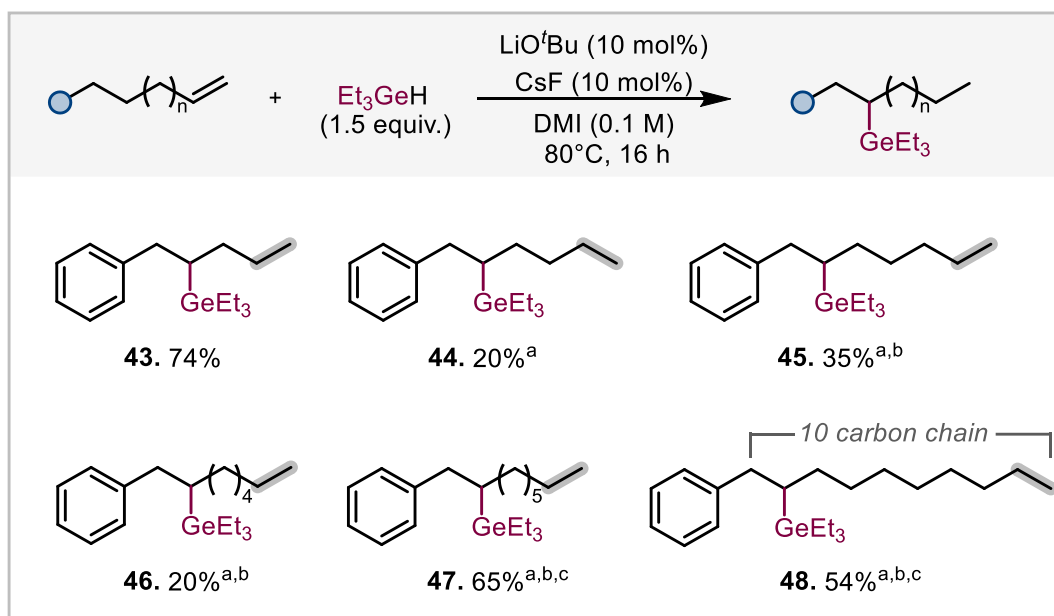
Scheme 15 | Selective hydrogermylation of an olefin mixture resulting in one desired product.

Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added the 1:1:1 olefin mixture (0.3 mmol, 1.0 equiv.) and Et_3GeH (72.9 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

Since metal catalysts or Lewis acids are necessary in previous literature examples for the isomerization of olefin chains longer than four carbons,^[24, 25] the chain length limitation of the new method was investigated (Scheme 16). In addition to simple isomerization, this approach not only enhances the product value but also introduces a functional group at the remote position using the base catalyst. Starting with 5-phenyl-1-pentene a yield of 74% (**43**) was achieved with catalytic amounts of base, while stoichiometric amounts yielded 81% of the isolated product (as shown by Dr. Aymane Selmani). When 6-phenyl-1-hexene was used as the starting material, no product formation was observed with catalytic base loadings, as GC-MS analysis indicated that most of the starting material remained unreacted, showing only traces of its isomerized form. To enhance reactivity, the same reaction was repeated with 2.0 equivalents of base, resulting in an isolated yield of 20% (**44**). To overcome low conversion issues with increasing chain length, the reaction time was extended from 16 h to 72 h for 7-phenyl-1-heptene and 8-phenyl-1-octene with stoichiometric amounts of base, obtaining the desired products in 35% (**45**) and 20% (**46**) isolated yield, respectively. To demonstrate the full potential of this novel protocol, even longer carbon chains, such as 9-phenyl-1-nonene and 10-phenyl-1-decene, were tested for the remote hydrogermylation. Since previous experiments indicated that longer reaction times and stoichiometric amounts of base might be necessary, these two substrates were stirred for seven days at 80°C . After this period, the desired products were isolated in low yields of 5–17% (compound **47** and **48**) and GC-MS analysis of the crude reaction mixture revealed that the major product remained the isomerized starting material, which had not yet undergone hydrogermylation. The reaction temperature was increased to 120°C and indeed, after just 16 h of reaction time, the desired products (**47**–**48**) were isolated in significantly increased yields of 45% each. Interestingly, in both reactions, a mixture of isomerized starting material was isolated in 35–45% yield, suggesting that further isomerization and subsequent hydrogermylation might occur with extended reaction time. Notably, when the reaction was stirred at 120°C for 72 h, yields further increased to 65% (**47**) and 54% (**48**). To the best of our knowledge, a base catalyzed remote hydrofunctionalization over such extended carbon chain lengths has not been reported before. Comparable transition metal or borenium catalyzed hydroboration methodologies have

been published recently, achieving remote functionalization over similar carbon chain lengths. However, in the first case they always obtained a mixture of different product isomers, which has never been observed during the remote hydrogermylation.^[53, 54]

Scheme 16 | Remote hydrogermylation scope of extended olefin chains.

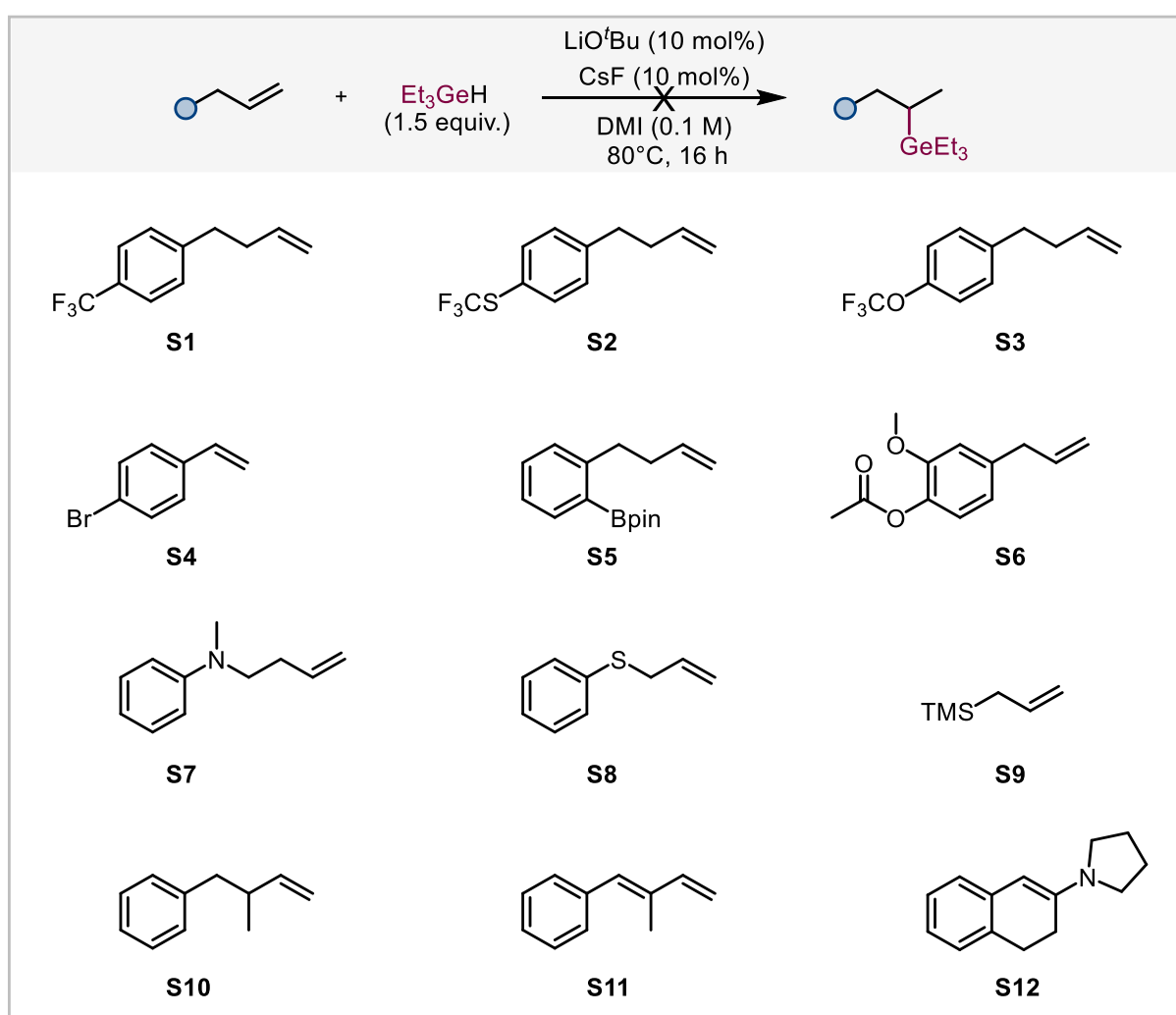


Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiOtBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added the alkene (0.3 mmol, 1.0 equiv.) and Et_3GeH (72.9 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product. a) The reaction was conducted with 2.0 equivalents of LiOtBu and CsF . b) Reaction time of 72 h. c) Reaction temperature of 120°C .

As previously discussed, styrenes, allylbenzenes, phenylbutenes and further extended carbon chains were shown to react successfully under the applied reaction conditions. In Scheme 17, selected examples of incompatible substrates are displayed, which either showed only traces of product (based on GC-MS) or no product formation at all. First, trifluoromethyl derivatives in *para*-positions such as compounds **S1-S3** did not show any product formation at all and appeared either to decompose or polymerize, as no starting material was recovered after the reaction. The incompatibility of the trifluoromethyl group under the applied conditions has already been observed with shorter carbon chain compounds **11** and **25**. More labile aryl halides (e.g. compound **S4**) than the previously shown fluoride and chloride compounds were not tolerated under the standard reaction conditions, which is also reported in literature for aryl bromides.^[93] GC-MS analysis detected only unreacted starting material and styrene, indicating that cleavage of the carbon bromine bond had occurred. In addition to aryl bromides, aryl Bpin derivatives (**S5**) were also unreactive under the usual reaction conditions, leading to no product formation and partial decomposition of the starting material. Surprisingly, in compound **27**, the alkyl Bpin moiety was well tolerated, yielding in the desired product. Other naturally derived products, such as eugenyl acetate (**S6**), did not form the desired products, which might be caused by the incompatibility of the carbonyl group. As described in the following mechanistic discussion, the applied base is sufficiently strong to deprotonate the solvent, making it

reasonable that it also deprotonates the α -carbonyl position and thus preventing the desired reactivity. In Scheme 13, allyl compounds containing heteroatoms in the walking chain were feasible starting materials, but if an amine (**S7**) or sulfide (**S8**) was present on the olefin chain, no desired products were observed. The specific case of allyl-trimethylsilane (**S9**) showed that it is dependent on the substituents on the silane, if the product can be successfully formed or not, since allyltriphenylsilane (**28**) showed the desired product, while the first one decomposed. Furthermore, compounds bearing a substituent at the homobenzylic position (**S10-S12**) were unsuccessful in forming the desired products, possibly due to steric hindrance or electronic effects. Beyond the compounds shown, simple linear olefins, such as 1-octene or various Michael acceptors failed to yield any products under these conditions.

Scheme 17 | Scope of unsuccessful substrates for the remote hydrogermylation reaction.



Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiOtBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added the alkene (0.3 mmol, 1.0 equiv.) and Et_3GeH (72.9 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was analyzed by GC-MS.

1.2.4 ICP-MS analysis evaluation

After successful demonstration of a broad scope of various functional groups and chain lengths up to ten carbons, it was proceeded with a detailed investigation of the mechanism underlying the remote hydrogermylation reaction. Similar to literature known base catalyzed reactions,^[94] the used reagents were submitted to an ICP-MS (inductively coupled plasma mass spectroscopy) analysis at the Uniklinik Aachen, to verify that the reaction is not catalyzed by trace amounts of transition metals. In Table 6 the tested reagents are listed with the detected amounts of transition metals in nanograms per gram (ng/g), which is equivalent to parts per billion (ppb).

Table 6 | ICP-MS analysis of the used reagents for the remote hydrogermylation reaction.

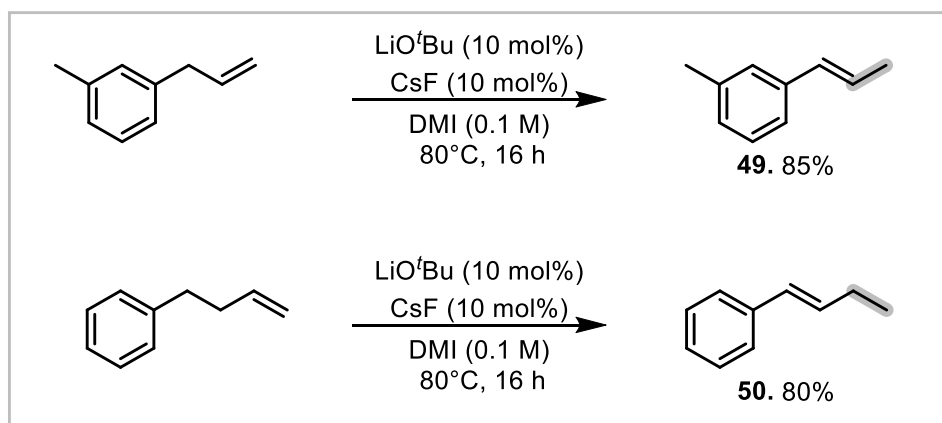
Element	LiO ^t Bu (Alfa Aesar)	CsF (chemPUR)	DMI (Sigma)	4- phenyl- 1-butene (Sigma)	Et ₃ GeH (Alfa Aesar)	Et ₃ GeH (self- made)	<i>n</i> Bu ₃ GeH (Sigma)
Silver	< 2	< 2	< 2	< 2	< 20	< 100	< 20
Cobalt	< 2	< 2	< 2	< 2	< 20	< 20	< 20
Copper	< 2	< 2	< 2	< 2	< 20	< 20	< 20
Iron	< 8	< 8	< 8	< 8	< 80	< 400	< 80
Iridium	< 2	< 2	< 2	< 2	< 20	56	< 20
Manganese	< 2	< 2	< 2	< 2	< 20	< 20	< 20
Molybdenum	< 2	203	< 2	< 2	< 20	94	< 20
Nickel	< 2	360	< 2	< 2	< 20	< 20	< 20
Palladium	< 2	< 2	< 2	< 2	147	98	< 20
Platinum	< 2	< 2	< 2	< 2	< 20	229	< 20
Ruthenium	< 2	< 2	< 2	< 2	< 20	< 20	< 20
Titanium	< 2	< 2	< 2	9890	< 20	221	< 20
Zirconium	1360	39300	< 5	< 5	< 20	683	< 20

Values are given in ng/g which equals parts per billion (ppb).

For this analysis LiO^tBu (99.99% trace metal basis) from Alfa Aesar, CsF (99.9%) from chempur, DMI (absolute, over molecular sieve, H₂O ≤ 0.04%, ≥ 99.5%) from Sigma Aldrich, 4-phenyl-1-butene and *n*Bu₃GeH from Sigma Aldrich, Et₃GeH from Alfa Aesar as well as self-made Et₃GeH were tested. The ICP-MS analysis revealed that the used base catalysts LiO^tBu and CsF contained 0.2 ppm molybdenum, 0.3 ppm nickel as well as 1.4-39.3 ppm of zirconium, while all other tested transition metals were at the lowest limit of detection. The used solvent DMI had no detectable amount of transition metals and our alkene model substrate 4-phenyl-1-butene contained around 9.9 ppm of titanium. Interestingly, the comparison of the commercially available Et₃GeH and the self-made one showed that the latter one contains different traces of transition metals, while the commercial material contained around 0.1 ppm of palladium. Furthermore, the self-made Et₃GeH or the bought one from Sigma Aldrich had no significant change in yield or selectivity. Due to the literature reported examples of palladium catalyzed hydrogermylations,^[84] *n*Bu₃GeH was also

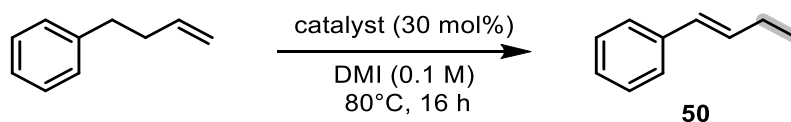
tested and as shown in Table 6, only the lowest limit of detection was measured for every transition metal. Since in Chapter 1.2.2. it was shown that $n\text{Bu}_3\text{GeH}$ leads to the desired product in high yield, these results strongly indicate that the reaction is not palladium catalyzed. However, to further prove that the traces of transition metals in the bases and germanium hydrides are not responsible for the observed reactivity in the remote hydrogermylation reaction, it was decided to conduct several control experiments.

Scheme 18 | Base catalyzed isomerization of terminal to internal olefins.



Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiOtBu (2.4 mg, 0.1 equiv.) and CsF (4.6 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture was added the alkene (0.3 mmol, 1.0 equiv.) and the vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature, the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

Table 7 | Control reactions with different catalysts for the isomerization of terminal to internal olefins.



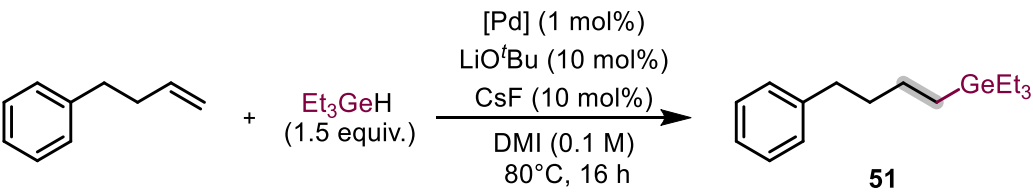
Entry	Catalyst	GC-MS analysis
1	NiF_2	only starting material
2	NiI_2	only starting material
3	$\text{Ti}(\text{O}^i\text{Pr})_4$	only starting material
4	ZrCl_4	only starting material
5	$\text{Zr}(\text{O}^t\text{Bu})_4$	only starting material

Reaction conditions: in an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with the catalyst (0.03 mmol, 0.3 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture was added the alkene (0.1 mmol, 1.0 equiv.) and the vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was analyzed by GC-MS.

First, exclusively the isomerization of the alkene was tested without any source of germanium (Scheme 18). The control experiments showed that compounds **49** and **50** were isomerized to the expected internal olefin products under catalytic conditions, achieving high yields of 80–85%, respectively. The isomerization of compound **50** has previously been demonstrated in the literature only with two (super)base catalyzed

examples,^[24, 25] in which the compound was heated to 175°C and yielded in a mixture of isomers, or by using a superbases, emphasizing the efficiency of a novel and much milder method. Applying the same reaction conditions with 30% of the observed transition metals nickel, titanium or zirconium instead of LiO^tBu and CsF, did not isomerize the alkene to the internal product. Because it was also shown in Table 1 that various *tert*-butoxide sources from different suppliers are feasible for the desired product formation, it can be postulated that the isomerization reaction is base catalyzed without any contribution from transition metals. Since the ICP-MS analysis can only detect transition metals without any information about coordinating ligands, the simplest structures were used of the corresponding metals.

Table 8 | Control reactions with different palladium catalysts for the hydrogermylation of alkenes.



Reaction scheme: 1-phenyl-1,3-butadiene + Et₃GeH (1.5 equiv.) $\xrightarrow[\text{DMI (0.1 M), 80}^\circ\text{C, 16 h}]{[\text{Pd}] (1 \text{ mol\%}), \text{LiO}^t\text{Bu (10 mol\%)}, \text{CsF (10 mol\%)}}$ Product **51** (1-phenyl-3-(triethylgermyl)-1,3-butadiene).

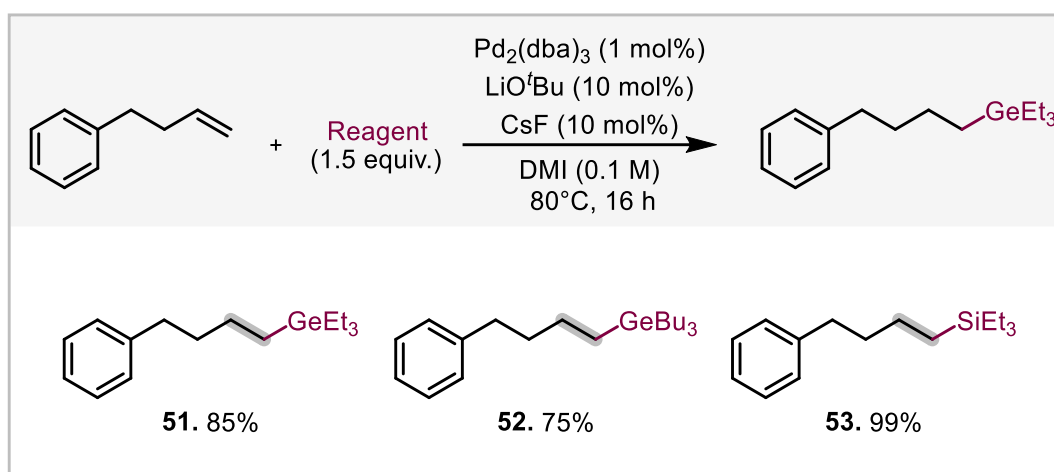
Entry	Pd catalyst	GC-MS analysis
1	Pd(dba) ₂	product observed
2	Pd(dba) ₂ , no bases	no product
3	Pd ₂ (dba) ₃	product observed
4	[Pd ^I (μ-I)P(^t Bu) ₃] ₂	product observed
5	PdCl ₂	product observed
6	PdCl ₂ , no bases	no product
7	XantPhos Pd G3	product observed

Reaction conditions: in an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with [Pd] catalyst (0.01 equiv.) LiO^tBu (0.8 mg, 0.1 equiv.) and CsF (1.5 mg, 0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added the alkene (0.1 mmol, 1.0 equiv.) and Et₃GeH (24.3 μL, 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was analyzed by GC-MS.

Since the commercially available Et₃GeH contained approximately 0.1 ppm of palladium, several palladium catalysts were screened to demonstrate that the observed hydrogermylated product is not generated by the trace amounts of transition metal impurities. In this screening, 1 mol% of palladium catalysts with different oxidation states (Pd⁽⁰⁾ to Pd^(II)) and ligand systems were added to the usual reaction conditions, as shown in Table 8. Entries 1-3 show Pd⁽⁰⁾ catalysts, which resulted in the formation of a product with a significantly different retention time in GC-MS compared to **5**. Remarkably, when LiO^tBu and CsF were omitted from the reaction mixture, only starting material was recovered and no product formation was observed. Next, the established Pd^(I) dimer^[95] from our group was added to the reaction, resulting in full conversion to the newly discovered product **51**. Similar results were obtained with the Pd^(II) catalysts in entries 5-7, which showed formation of the new product and in absence of bases, there was again no product formation. Based on GC-MS analysis, all reactions generated the same product, which exhibited a different retention time than the hydrogermylated compound **5**. Indeed, after isolating the detected product using Pd₂dba₃ as Pd⁽⁰⁾ catalyst the *anti*-Markovnikov product on the terminal position was obtained in a high yield of 85% (Scheme 19).

For a better comparison, $n\text{Bu}_3\text{GeH}$ with no detected trace metal impurities, led to the same terminal product (**52**) in a similar isolated yield of 75%. Interestingly, under these conditions the hydrosilylation with Et_3SiH was also successful and formed the corresponding product **53** in quantitative yield. The addition of palladium might change the reactivity of the silane reagent crucially, as no product formation was observed using Et_3SiH under the optimized standard conditions. In summary, even if trace amounts of active palladium species were present in the Et_3GeH , it will lead to the terminal product instead, as shown with the base catalyzed conditions.

Scheme 19 | Pd-catalyzed *anti*-Markovnikov hydrofunctionalization with germanium hydride and silane reagents.

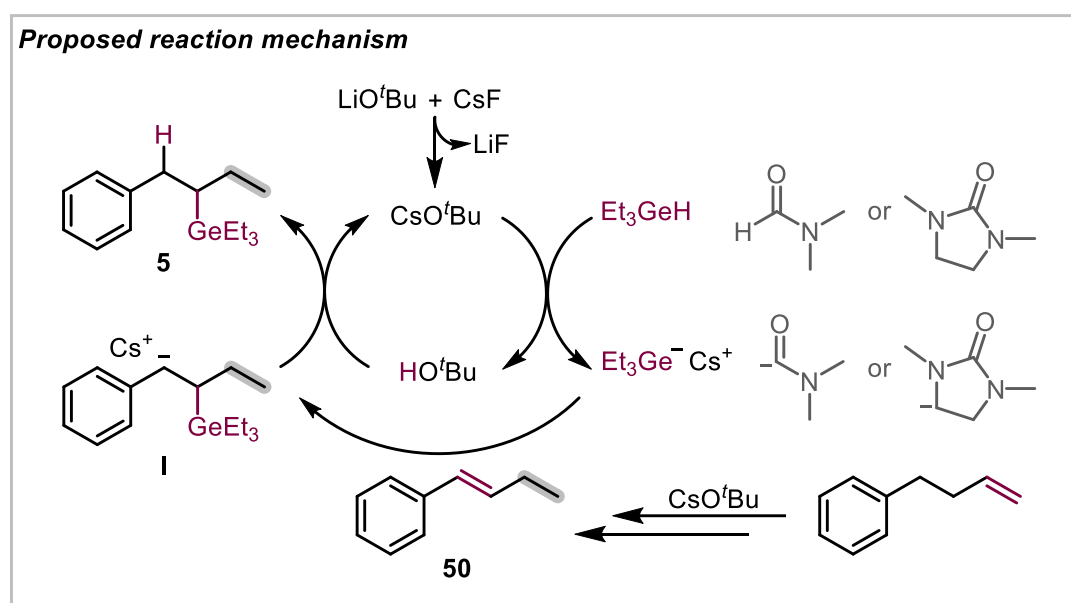


Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with $\text{Pd}_2(\text{dba})_3$ (0.01 equiv.), LiO^tBu (0.1 equiv.) and CsF (0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added the alkene (0.1-0.3 mmol, 1.0 equiv.) and the hydride (1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

1.2.5 Mechanistic investigations

After excluding that the remote hydrogermylation is catalyzed by trace metal impurities, a detailed investigation on the potential mechanism was conducted (Scheme 20). The general reaction mechanism can be divided into four steps which will be further elucidated in the following: i) Formation of CsO^tBu from LiO^tBu and CsF in DMI. ii) Deprotonation of Et_3GeH by this *in-situ* formed base to form a cesium stabilized triethylgermanium anion and *tert*-butanol. iii) Simultaneously, the terminal alkene is isomerized by CsO^tBu to the thermodynamically favored conjugated position and then attacked by the triethylgermanium anion on the β -position to form intermediate **I**. iv) After protonation by *tert*-butanol or Et_3GeH , the desired product is obtained and the base catalyst is recovered to close the catalytic cycle.

Scheme 20 | Proposed reaction mechanism for the base-catalyzed remote hydrogermylation. Adapted from reference.[1]



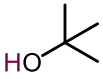
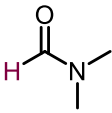
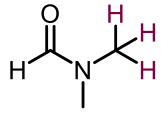
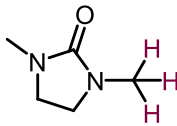
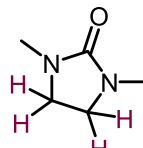
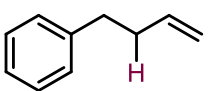
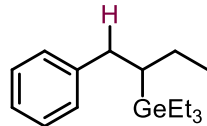
The first step of the proposed catalytic cycle is the *in-situ* formation of CsO^tBu , a strong base, from commercially available reagents LiO^tBu and CsF . This observation was already reported by the group of Kondo who showed by ^{133}Cs -NMR that the combination of LiO^tBu and CsF in DMI at 80°C forms CsO^tBu .^[89, 96] This explanation aligns with the previously demonstrated optimization screening where several *tert*-butoxide bases with CsF showed the desired product formation, most probably forming CsO^tBu *in-situ*. Additionally, KO^tBu without CsF showed productive results as well, emphasizing that the *tert*-butoxide base is responsible for the catalytic reactivity. In comparison, sodium and lithium *tert*-butoxide did not show any product formation without CsF , demonstrating that there is a salt metathesis occurring under these conditions. This dependence was computationally investigated by the Taillefer group in 2015, who showed that the strength of an alkali metal *tert*-butoxide base is related to stability.^[97] In their calculated energy diagram, the stability of lithium and potassium *tert*-butoxide was compared with the free anion in DMF at the M06-2X/6-311+G(d,p) level of theory. These calculations were done to prove that KO^tBu can deprotonate DMF under their applied reaction conditions and why LiO^tBu does not show any productive results. Based on their explanation LiO^tBu might be too stable and thus create a high reaction barrier for

the deprotonation, in contrast to KO^tBu. After analyzing the trend shown of alkali metal *tert*-butoxide stability and the corresponding ability to deprotonate DMF, the *in-situ* generated CsO^tBu should be even more reactive. Since it was demonstrated in the optimization part that DMF is also a suitable solvent for the remote hydrogermylation reaction (Chapter 1.2.1.), these findings can be combined for the discussion of the potential mechanism (Scheme 20).

In the following, a series of pK_a calculations were conducted and the obtained values were compared using two different approaches (Figure 3, see SI for details). The first method was a geometry optimization of the neutral and anionic molecule at the B3LYP^[98]/6-31+G(d)^[99] level of theory in DMSO, using Gaussian 16.^[100] The optimized structure was used to generate an input file for COSMOTherm using Turbomole and then the obtained files of the neutral and anionic molecule were used to calculate the corresponding pK_a value in DMSO.^[101] The second method considered the presence of different conformers, using the CREST package^[102] in xTB^[103, 104] to explore the conformational space. The obtained conformers were optimized at the M06-2X^[105]/def2-TZVPP^[106] level of theory and the minimum energy conformer was used for further calculations as already described.

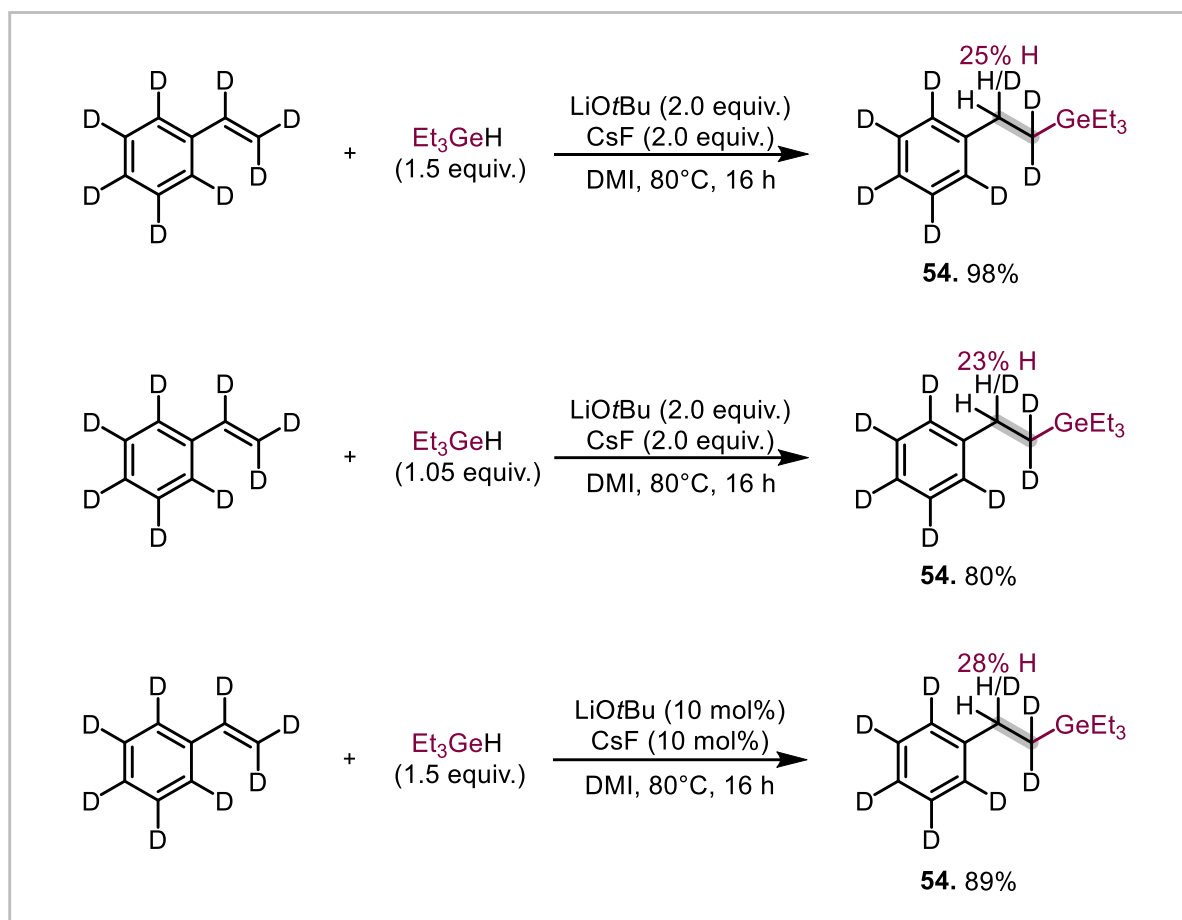
However, the lowest pK_a values were obtained for triethylgermanium hydride and *tert*-butanol with values of 29.7 and 29.6, showing no obvious difference in both methods for these molecules (Figure 3). The comparison of these two values indicates that the employed CsO^tBu should be able to deprotonate either the Et₃GeH or *tert*-butanol, at least to a certain degree. While the experimental pK_a value of *tert*-butanol is 32.2,^[107] these calculations should not be interpreted in absolute terms but rather give information of the relative pK_a values to serve as a means for comparison. To further distinguish, if the utilized solvents can be deprotonated on the highlighted positions, the corresponding pK_a values were calculated accordingly. For either of the methods used, the proton next to the carbonyl group of DMF is the most acidic position resulting in the lowest value of 39.5, which is in line with the previously mentioned report.^[97] In comparison to this, the protons on the *N*-methyl groups are obviously much less acidic with values around 45.0. In direct contrast, the pK_a of the *N*-methyl groups in the standard solvent DMI have a surprisingly lower calculated value of 43.3, even though they have a similar scaffold compared to DMF. However, the most acidic position in DMI is calculated to be the methylene protons, with a pK_a value of 41.9, for both used methods. Since it was shown that KO^tBu can deprotonate DMF, it is proposed that the theoretically stronger base, or less stable CsO^tBu, should be able to deprotonate DMI in these reaction conditions too. Combining the calculated pK_a values with the computational data from the literature, leads to the conclusion, that the *in-situ* formed CsO^tBu could deprotonate Et₃GeH or the solvent DMI/DMF, to form a triethylgermanium anion or a deprotonated solvent and thus form *tert*-butanol as result (Scheme 20).

Figure 3 | Calculated pK_a values of the substrates shown in the proposed reaction mechanism.

Calculated pK_a values				
	Triethylgermanium hydride 	<i>tert</i> -Butanol 	DMF 	DMF 
B3LYP/6-31+G(d)	29.7	29.6	39.7	45.0
M06-2X/def2-TZVPP	29.6	29.6	39.5	44.9
	DMI 	DMI 	4-Phenyl-1-butene 	Compound 5 
B3LYP/6-31+G(d)	43.9	41.9	35.8	32.9
M06-2X/def2-TZVPP	43.3	41.9	34.8	34.6

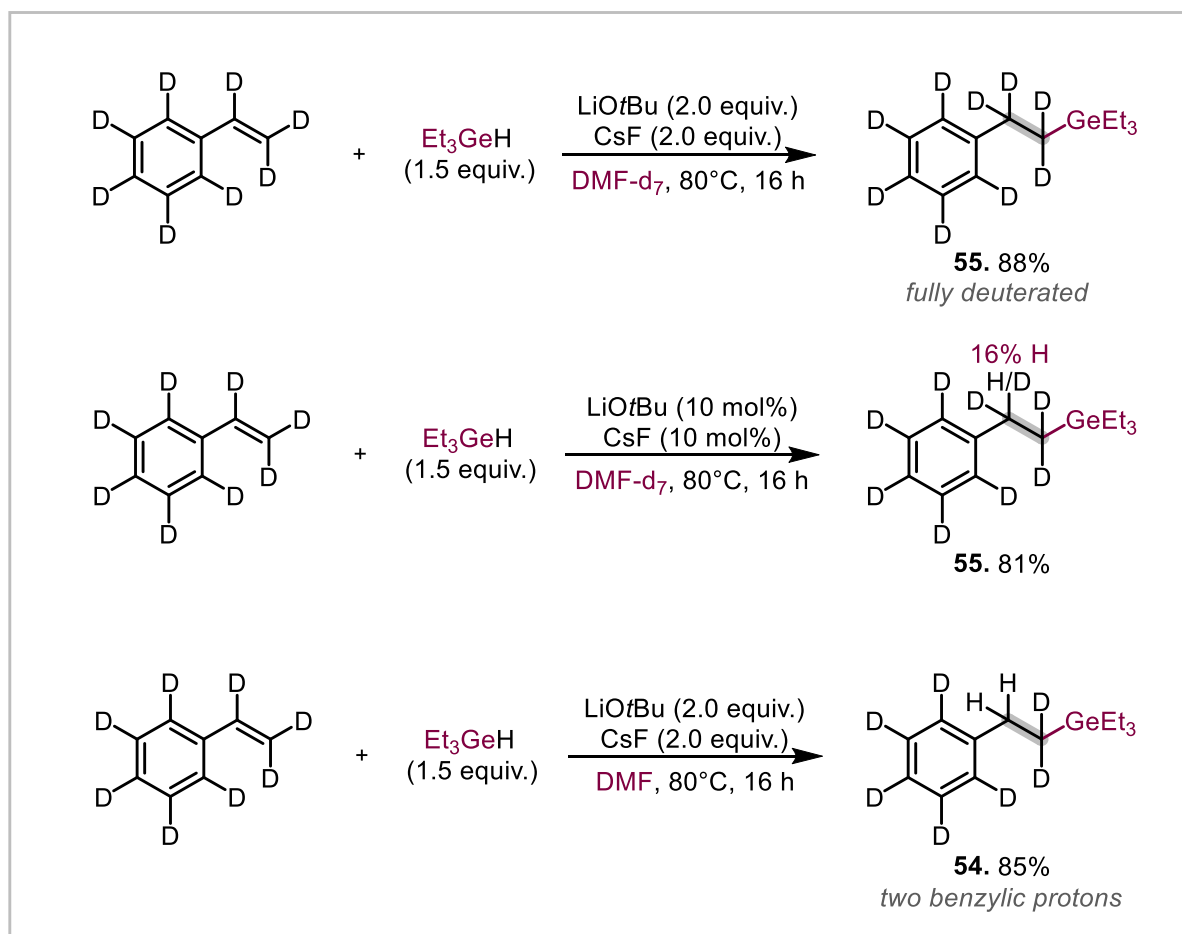
Furthermore, the allylic proton of the model substrate 4-phenyl-1-butene has a calculated pK_a value of 34.8 (or 35.8), which is still lower than the values obtained for the solvents DMF or DMI. With this information in hand, it is postulated that the employed base system is capable of deprotonating the allylic proton, forming a π -allyl-complex which then either reverts back to the starting material or leads to the migrated double bond (Scheme 5). This equilibrium process is repeated until the most thermodynamically stable product, in this case the conjugated styrene derivative, is formed. This base catalyzed isomerization mechanism was previously proposed by Cram and Uyeda.^[22]

After successful isomerization of the alkene to the thermodynamically favored position, the cesium stabilized triethylgermanium anion attacks at the β -position of the styrene derivative to form intermediate **I**, where the negative charge is stabilized by the conjugated system and the cesium counterion. The calculated pK_a values of 32.9 and 34.6 for the intermediate are, based on the previous results, in line with the proposal that the protonation can occur either by the generated *tert*-butanol and thus recovery the active base catalyst or by Et_3GeH , to form the desired product (**5**) and close the catalytic cycle.

Scheme 21 | Deuterium labeling studies in DMI with styrene-d₈.

Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiOtBu (0.1-2.0 equiv.) and CsF (0.1-2.0 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added styrene-d₈ (0.3 mmol, 1.0 equiv.) and triethylgermanium hydride (1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

To further validate the proposed reaction mechanism, several deuterium labeling reactions were performed (Scheme 21). When styrene-d₈ was used as starting material under standard conditions, but with 2.0 equivalents of base, an isolated yield of 98% (**54**) was achieved. Interestingly, it was expected that one benzylic proton and one benzylic deuterium would appear in the final product, but contrary to this expectation, the benzylic deuterium signal consisted of 25% ¹H and 75% ²H, based on ¹H NMR. The most plausible explanation for this observation is that the excess amount of Et₃GeH causes the deuterium proton exchange at the benzylic position. Due to this, another experiment with similar conditions was conducted, but in this case the equivalents of germanium hydride were reduced to 1.05 and interestingly, the yield reduced to 80%, but the ratio of proton and deuterium remained the same. Additionally, the standard conditions with catalytic amounts of base were used to observe the similar proton incorporation of 28%, at one of the benzylic positions. The combination of these three experiments leads to the conclusion that the equivalents of germanium hydride and base are not relevant for the proton/deuterium ratio. The only other proton source could be the solvent in this case.

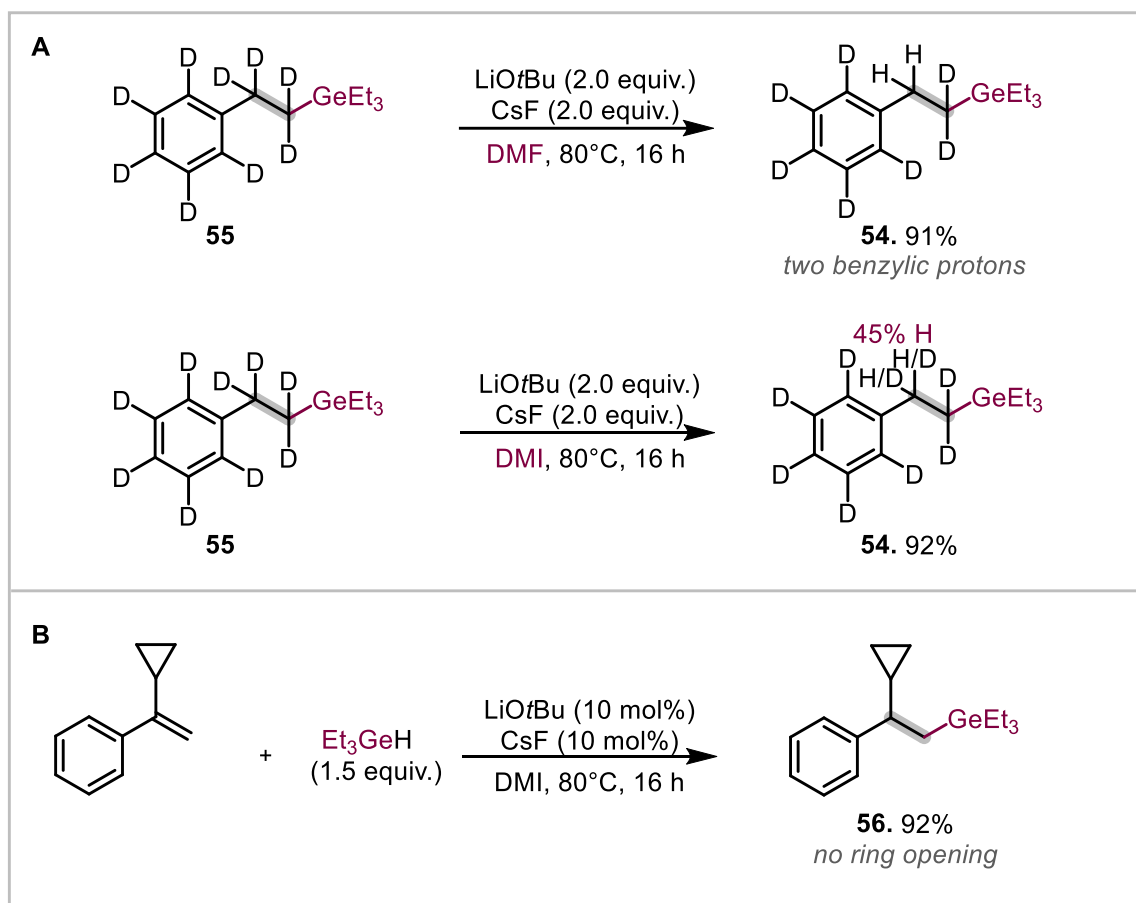
Scheme 22 | Deuterium labeling experiments in DMF-d₇ with styrene-d₈.

Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiOtBu (0.1-2.0 equiv.) and CsF (0.1-2.0 equiv.) and dissolved in anhydrous DMF (0.1 M). To the mixture were added styrene-d₈ (0.3 mmol, 1.0 equiv.) and triethylgermanium hydride (1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

Due to this, the same reactions with catalytic and stoichiometric amounts of base were repeated in perdeuterated DMF-d₇ (Scheme 22). Since it was established in the optimization studies that DMF is a suitable solvent, the commercially available deuterated version DMF-d₇ was used in some examples (deuterated DMI is not commercially available). Indeed, when 2.0 equivalents of bases were used a fully deuterated product (**55**) was obtained in 88% isolated yield, which emphasizes that the solvent in this case is also the donor for deuterium. Reducing the amount of base to 10 mol% leads to a product where 16% of ¹H remains at one benzylic position and thus underlines the hypothesis that the solvent is responsible for the proton/deuterium exchange, because less *tert*-butoxide is available to deprotonate the solvent and protonate the resulting product. To further prove the proton/deuterium exchange with the solvent, the same reaction conditions were used, but with non-deuterated DMF (Scheme 22 bottom). As expected, the desired product (**54**) was obtained with two protons on the benzylic position supporting the hypothesis of proton/deuterium exchange with the solvent. The higher percentage of proton/deuterium exchange in DMF than in DMI is also in line with the calculated pK_a values, which revealed that DMF is much more acidic (39.5 vs 41.9, for DMF and DMI, respectively).

Further examples are shown in Scheme 23A, where the fully deuterated germanium compound **55** was applied as starting material, using stoichiometric amount of base in non-deuterated solvents. In DMF, the benzylic position was fully protonated (**54**), while in DMI only 45% of the two benzylic protons were exchanged. The observed results are in line with the previously calculated pK_a values which indicated that DMF is more acidic than DMI and thus easier to deprotonate. The base catalyzed proton/deuterium exchange at benzylic positions from solvents is a literature known reactivity,^[108] which helped to prove that the applied base system is able to deprotonate the used solvents DMI and DMF.

Scheme 23 | Deuterium labeling experiments with deuterated organogermane and radical clock experiment.

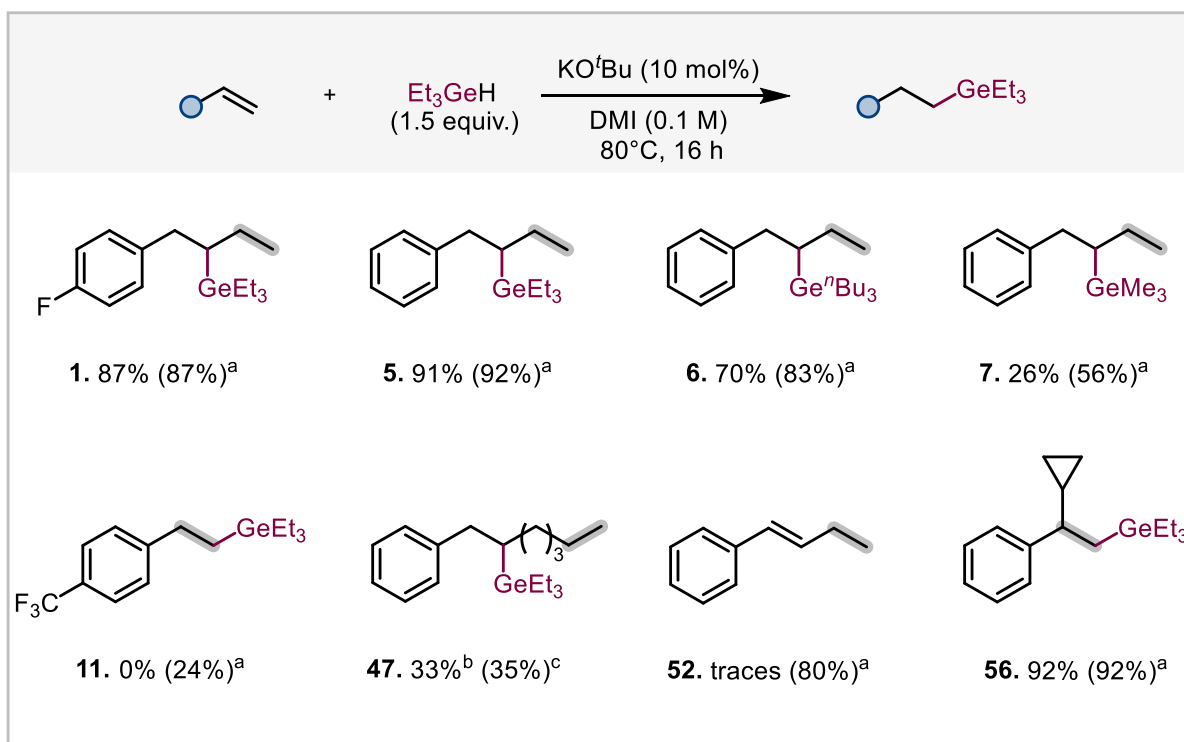


Reaction conditions: in an argon-filled glovebox, a 4- or 8-mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiOtBu (0.1-2.0 equiv.) and CsF (0.1-2.0 equiv.) and dissolved in anhydrous DMI (0.1 M). a) To the mixture was added the starting material (0.1-0.3 mmol, 1.0 equiv.). b) To the mixture were added the alkene (0.3 mmol, 1.0 equiv.) and triethylgermanium hydride (1.5 equiv.). The vials were sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

To further prove that the proposed mechanism is going through an anionic instead of a radical pathway, a radical clock experiment was conducted as shown in Scheme 23B. The generation of a germyl radical with the base used should be considered possible, since it has been shown that Et_3SiH and KO^tBu can react in this way.^[109] To probe this experimentally, a styrene derivative bearing cyclopropane was chosen, because a radical based mechanism would result in ring opening and double bond formation. This experiment

supports an anionic pathway due to the fact that the hydrogermylation took place as expected, without any ring opening and achieving a high yield of 92% (compound **56**).

In Chapter 1.2.1., it was shown that KO^tBu is a suitable base for the remote hydrogermylation reaction. This observation was further investigated by repeating relevant reactions with catalytic amounts of potassium *tert*-butoxide, instead of the *in-situ* formed cesium *tert*-butoxide under the standard conditions (Scheme 24). Initially, it was investigated whether the model substrate 1-(but-3-en-1-yl)-4-fluorobenzene would yield the desired product (**1**) when using stoichiometric amounts of base. Indeed, the desired product was achieved in 81% NMR yield while the same reaction with LiO^tBu and CsF furnished an NMR yield of 91%. Surprisingly, when the catalytic standard conditions were applied, an isolated yield of 87% was achieved, which was the same outcome as was previously observed with LiO^tBu and CsF. When different germanium sources were utilized for the remote hydrogermylation, a significant difference in yields could be observed. While Et₃GeH resulted in the same isolated yield of 91% (**5**), *n*Bu₃GeH and Me₆Ge₂ obtained remarkably lower yields of 70% (**6**) and 26% (**7**), respectively. Interestingly, when 4-trifluoromethyl-styrene was used as the starting material, neither catalytic nor stoichiometric amounts of base were successful in achieving the desired product (**11**), which was shown to be successful before with the LiO^tBu/CsF combination. In contrast, the extended carbon chain of seven carbons units could be isolated in a similar yield of 33% (**47**). Furthermore, the simple isomerization of 4-phenyl-1-butene with catalytic amounts of KO^tBu showed only traces of the desired internal isomer (**52**) by ¹H NMR, while the major products were undefined side products. In contrast, with LiO^tBu/CsF a clean reaction with an isolated yield of 80% was achieved. To further prove that the reaction with KO^tBu proceeds *via* the same mechanism, the radical clock experiment was repeated, resulting in the same product (**56**) with the same yield, excluding radical formation. In general, the reaction works comparably to the standard conditions with most of the shown substrates, but different germanium sources as well as selected examples demonstrate that the combination of LiO^tBu and CsF has clearly increased yields and versatility.

Scheme 24 | Comparison of isolated yields with KO^tBu as base using previously demonstrated substrates.

Reaction conditions: in an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with KO^tBu (0.1 equiv.) and dissolved in anhydrous DMI (0.1 M). To the mixture were added the alkene (0.3 mmol, 1.0 equiv.) and triethylgermanium hydride (1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product. a) Yield when catalytic amounts of LiO^tBu and CsF were used. b) KO^tBu (2.0 equiv.) was used and stirred for 72 h. c) LiO^tBu (2.0 equiv.) and CsF (2.0 equiv.) were used and stirred for 72 h.

1.2.6 Summary

In summary, an operationally simple base-catalyzed remote hydrogermylation reaction of alkenes with a broad scope was demonstrated. The detailed optimization studies revealed that the best reaction conditions for alkenes are 10 mol% of LiO^tBu and CsF in DMI (0.1 M) with 1.5 equivalents of Et₃GeH at 80°C for 16 hours. Under these conditions, terminal alkenes were selectively isomerized to the internal, conjugated position and subsequently hydrogermylated at the β -position. If no germanium source was added, the final product was the thermodynamically more stable *E*-isomer with an outstanding selectivity. Interestingly, other literature known hydrofunctionalization reagents such as Et₃SiH and HBpin did not yield any desired product, highlighting the unique reactivity of organogermanium compounds under these conditions due to the compatibility of the calculated pK_a values.

The demonstrated substrate scope consists of different carbon chain lengths starting from styrene, allylbenzene and phenylbutene up to a maximum chain length of ten carbons, which successfully underwent remote hydrogermylation. In this context, a broad range of substrates were well tolerated, containing substitutions including methyl, *tert*-butyl, methoxide, sulfide, tertiary amine, allyl ether, aryl fluoride and chloride, *para*-CF₃, as well as heterocycles like thiophene, benzothiophene, pyridine and quinoline. Interestingly, functional groups like diphenylphosphineoxide, triphenylsilane and alkyl-Bpin stayed untouched. Remarkably, when an olefin mixture of different isomers was applied to the catalytic standard conditions, only one product was obtained, which emphasizes the powerful synthetic utility of the remote hydrogermylation.

Besides the broad scope, extensive mechanistic investigations have been conducted. After excluding reactivity mediated by transition metal impurities and a radical pathway, an anionic mechanism was proposed. In line with literature known reports, the combination of LiO^tBu and CsF *in-situ* generates CsO^tBu which undergoes the isomerization of the terminal olefin to the internal, more thermodynamically stable one. Following this, the base deprotonates the germanium hydride, forming a germanium anion which attacks at the β -position, resulting in an intermediate. Followed by the protonation of this intermediate by the formed *tert*-butanol or excess of Et₃GeH, the desired product is generated and the catalytic cycle closed, regenerating the *tert*-butoxide again. The proposed mechanism was further supported by pK_a calculations and deuterium labeling studies, providing strong evidence for the underlying reaction pathway.

2

Orthogonal functionalization in three-dimensional chemical space

The results described in this chapter were published in Angewandte Chemie International Edition and Journal of the American Chemical Society.^[110, 111] Experimental work was carried out in collaboration with Markus Schoetz and Dr. Gurdeep Singh from the Schoenebeck Group (both assisted with method development and scope), whose contributions are highlighted for the corresponding results.

2 Orthogonal functionalization in three-dimensional chemical space

2.1 Introduction

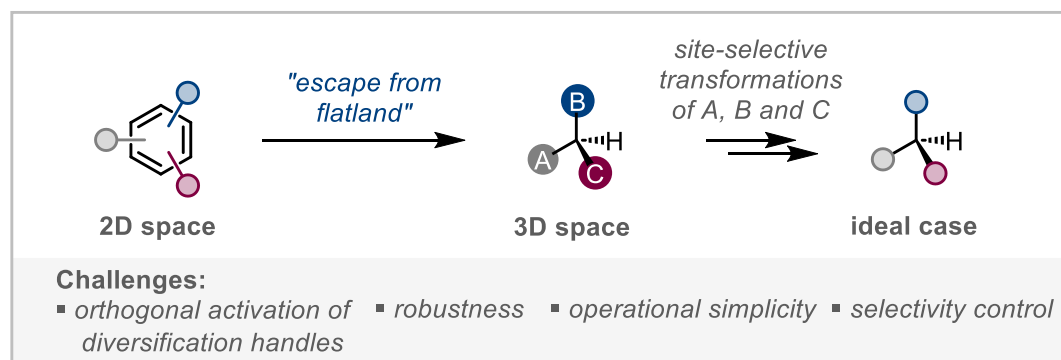
2.1.1 The escape from flatland

The development of novel therapeutics in pharmaceutical research necessitates a paradigm shift towards three-dimensional molecular architectures.^[43] The term “escape from flatland” captures the prevailing reliance on sp^2 -rich frameworks in drug discovery and highlights the growing interest in leveraging the unexplored structural space of sp^3 -rich molecules to identify innovative drugs and bioactive compounds.^[43] This transition is crucial, as the immense diversity of chemical space (estimated at 10^{60} potential candidates)^[43] drives the demand for synthetic methodologies that facilitate the efficient construction of C_{-sp^3} molecules, while simultaneously enabling the optimization of structure-activity relationships through access to diverse analogues.^[43]

The increasing importance of sp^3 -rich molecules in drug discovery is driven by the objective of enhancing the physicochemical characteristics of drug candidates. Medicinal chemistry research has demonstrated that a high fraction of sp^3 carbons (F_{sp^3}), defined as the ratio of sp^3 -hybridized carbon atoms to the total carbon count, alongside the presence of chiral centers, positively correlates with successful drug development.^[43] These attributes are associated with improved physicochemical properties, such as greater solubility and increased molecular complexity, which are advantageous for biological activity.^[43]

In recent decades, the widespread adoption of high-throughput synthesis has often led to a focus on achiral, aromatic compounds, which frequently underperform in clinical settings.^[43] In contrast, more structurally complex molecules with elevated F_{sp^3} content and significant chirality have demonstrated not only increased success rates in clinical phases but also reduced promiscuity and diminished toxicity risks.^[44] Addressing toxicity is particularly vital, as it remains one of the leading causes of drug candidate attrition in clinical trials.^[44]

Figure 4 | The escape from flatland. Adapted with permission from *Angew. Chem. Int. Ed.* **2024**, 63, e202401545.



Consequently, developing synthetic strategies that enable the assembly of complex, sp^3 -rich molecules is essential. The aim is to create robust, efficient and modular synthetic approaches that facilitate selective functionalization under mild conditions, thereby promoting the development of new drug libraries (Figure 4).

Palladium catalyzed cross-coupling reactions, recognized with the Nobel Prize in Chemistry in 2010, revolutionized organic synthesis by enabling efficient C–C bond formation, particularly between sp^2 -hybridized carbons.^[112] These reactions, including the widely used Suzuki–Miyaura^[113], Heck^[7] and Sonogashira^[114] couplings, have significantly impacted both academic and industrial chemistry by offering robust and versatile methods for constructing complex molecules. Therefore, it is of utmost importance to discover similar approaches for the C_{sp^3} -space.

Developing synthetic strategies to construct complex, three-dimensional molecules remains a fundamental challenge in modern organic chemistry. An efficient approach to achieving high molecular complexity involves employing modular building blocks equipped with multiple reactive handles. Ideally, these handles should exhibit orthogonal reactivity, enabling selective functionalization without cross-reactivity. Despite recent advances in photochemically catalyzed formation of C_{sp^3} -X bonds,^[115] existing methods are often limited to single substitution reactions, primarily using simple starting materials to demonstrate feasibility. Moreover, the presence of multiple functional handles on a single carbon atom is rarely achieved, as they often share similar oxidation windows, leading to competing reactions and compromising selectivity.^[115]

To overcome these challenges, modular approaches that facilitate sequential functionalizations are essential. Building blocks bearing multiple, well-defined reactive handles offer a promising solution, especially when these handles differ significantly in reactivity and stability. The ideal scenario involves orthogonal activation modes, allowing selective transformation without interference from adjacent functional groups.^[116] Alkylboron derivatives have shown considerable potential in this context, often combined with halides or low-reactivity silanes.^[117-123] However, despite their utility, the majority of current dual functional building blocks incorporate only two reactive sites, limiting structural diversity and functional complexity (Figure 5A).^[122, 124-126]

Recent developments have introduced novel platforms that expand modularity beyond dual handle systems.^[72, 127] For instance, Dr. Aymane Selmani from our group designed one such multifunctional handle **A**,^[72] providing a basis for potential full functionalizations. Particularly, a single carbon unit that contains C_{sp^3} -Ge, C_{sp^3} -Bpin and C_{sp^3} -halogen to introduce a third dimension of reactivity, enabling more diverse functionalization pathways (Figure 5B). During the design of this modular platform, the selection of functional groups amenable to orthogonal functionalization was of central importance. Each group has to be chosen to enable selective transformation without interfering with other functionalities. These robust and non-ionic handles not only enhance stability and operational simplicity but also facilitate the synthesis of highly complex, multifunctional molecules. By enabling selective transformations under mild conditions, such modular strategies represent a significant advancement toward the rapid construction of intricate molecular architectures and the exploration of three-dimensional chemical space.^[72]

The synthesis of such a versatile building block was demonstrated by Dr. Aymane Selmani in the already mentioned publication,^[72] following an operationally simple two step synthetic pathway to obtain the desired building block **A** in good yields (Figure 5B). In the aforementioned report, a third step to modify the C–Cl site to a C–I motif was proposed, however, as part of this work our recent publication demonstrated that this modification is not necessary for further downstream functionalizations.^[111]

modular scaffold was not demonstrated and will therefore be the central focus of the present work, as well as new methods for the functionalization of the C_{sp^3} -Ge moiety.

With regard to accessing molecular complexity, photochemical transformations enable the successful decoration of a variety of different functional groups and hence, the following chapter (Chapter 2.1.2) introduces photoredox chemistry as a suitable approach for obtaining numerous transformations of established functional groups, including the trialkylgermanium moiety.

2.1.2 Photochemical C_{sp}³ functionalizations

Photochemistry is the study of chemical reactions initiated by light and has significantly contributed to the advancement of synthetic methodologies over the past decades. Despite the transformative potential offered by photochemistry, the widespread application of light driven chemical processes remained limited for many decades.^[128] This was primarily due to the challenges associated with employing high energy light and the diverse absorption characteristics of organic molecules. Early photochemical transformations, such as the [2+2] cycloaddition reactions of natural products under sunlight,^[129] highlighted the potential of converting photonic energy into chemical energy, attracting the interest of synthetic chemists since their discovery.

The development of efficient photoredox catalysts in recent decades has revolutionized the field,^[130] allowing for light mediated transformations across a broad spectrum of substrates. Photoredox catalysis, which leverages single electron transfer (SET) and energy transfer mechanisms, has emerged as a key strategy for driving challenging organic reactions. This innovation has been greatly facilitated by the discovery of organometallic and organic catalysts capable of efficiently absorbing visible light, thereby bypassing the limitations posed by traditional high energy photochemistry.^[131, 132]

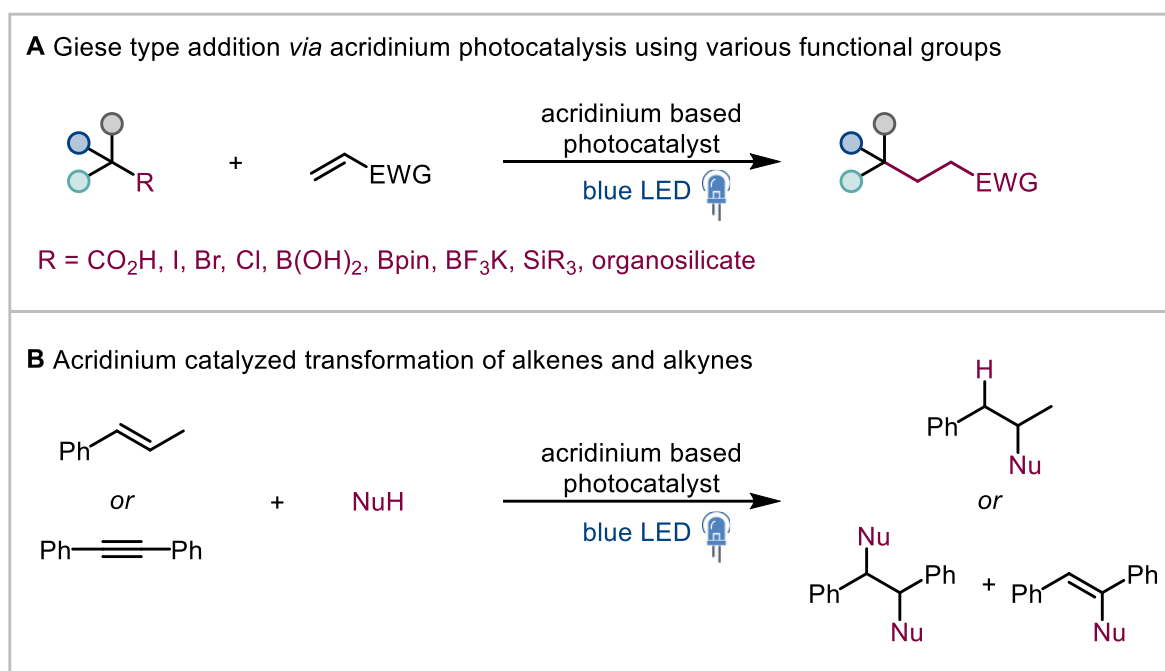
When a molecule absorbs light, it transitions from the ground state (S_0) to an electronically excited state, typically the singlet excited state (S_1).^[133] Depending on the energy of the absorbed photon, various vibrational levels within the excited state can be populated, but rapid relaxation usually leads to the lowest vibrational level of S_1 . From here, the molecule might return to the ground state *via* radiative processes, such as fluorescence or through nonradiative pathways, like internal conversion. Alternatively, a spin-forbidden intersystem crossing might occur, converting S_1 to a triplet excited state (T_1), which is typically longer lived and might decay *via* phosphorescence or nonradiative mechanisms.^[133] The ability of both S_1 and T_1 to participate in bimolecular reactions, including energy transfer and electron transfer, forms the foundation of photoredox catalysis.

Building on the fundamental principles of photoexcitation, photoredox catalysts can be broadly categorized into inorganic/organometallic and organic systems. Inorganic and organometallic photoredox catalysts, particularly those based on ruthenium and iridium complexes, exhibit strong absorption of visible light,^[131] efficiently transitioning to long lived triplet states through intersystem crossing. These long lived triplet states facilitate single electron transfer *via* metal to ligand charge transfer processes, rendering them highly effective as redox mediators.^[128] Despite their excellent performance, the practical application of these catalysts is often constrained by high costs and their smaller window of excited state redox potentials compared to organic systems.^[130]

In contrast, organic photoredox catalysts offer distinct advantages, primarily due to their wider redox windows.^[130] Operating predominantly *via* singlet excited states rather than triplets, these catalysts typically exhibit shorter lifetimes, but their cost-effectiveness and tunable properties make them highly attractive. Among the most widely used organic photocatalysts are acridinium salts and cyanoarenes (e.g. 4CzIPN),^[130] each providing unique reactivity profiles that make them suitable for a variety of synthetic transformations.

In recent years, the popularity of these organic photoredox catalysts has led to an increased number of publications in this area.^[133] Notable, the acridinium based catalysts have been extensively applied in various transformations^[133], which was pioneered and developed by Fukuzumi *et. al*^[134, 135], while first applications have been demonstrated by Nicewicz and his co-workers.^[136-138] Motivated by this, the acridinium based catalysts have been utilized to transform different functional groups like carboxylic acids,^[139, 140] alkyl and aryl halides,^[141, 142] alkenes,^[143] alkynes,^[144] alkyl boronic acids,^[145] alkyl boronic esters^[146] and their boron trifluoroborates^[139] as well as silanes^[147, 148] and silicates (Scheme 25).^[149] Carboxylic acids suffer from the notable drawback of requiring activation with an added base,^[150] while alkyl silanes can only be functionalized when they are in the benzylic position or in α -position to a heteroatom.^[147, 148] A well-developed reaction in this context is the Giese addition under photoredox conditions.^[151] This reaction is a radical based carbon-carbon bond forming reaction, in which a carbon centered radical adds to an electron deficient alkene, typically an acrylate or related Michael acceptor. Furthermore, the photoredox Giese reaction is valuable as it enables the construction of C-C bonds under mild and redox-neutral conditions, avoiding potential side reactions like hydrostannylation and radical quenching, when the radical initiator Bu₃SnH is used.^[152]

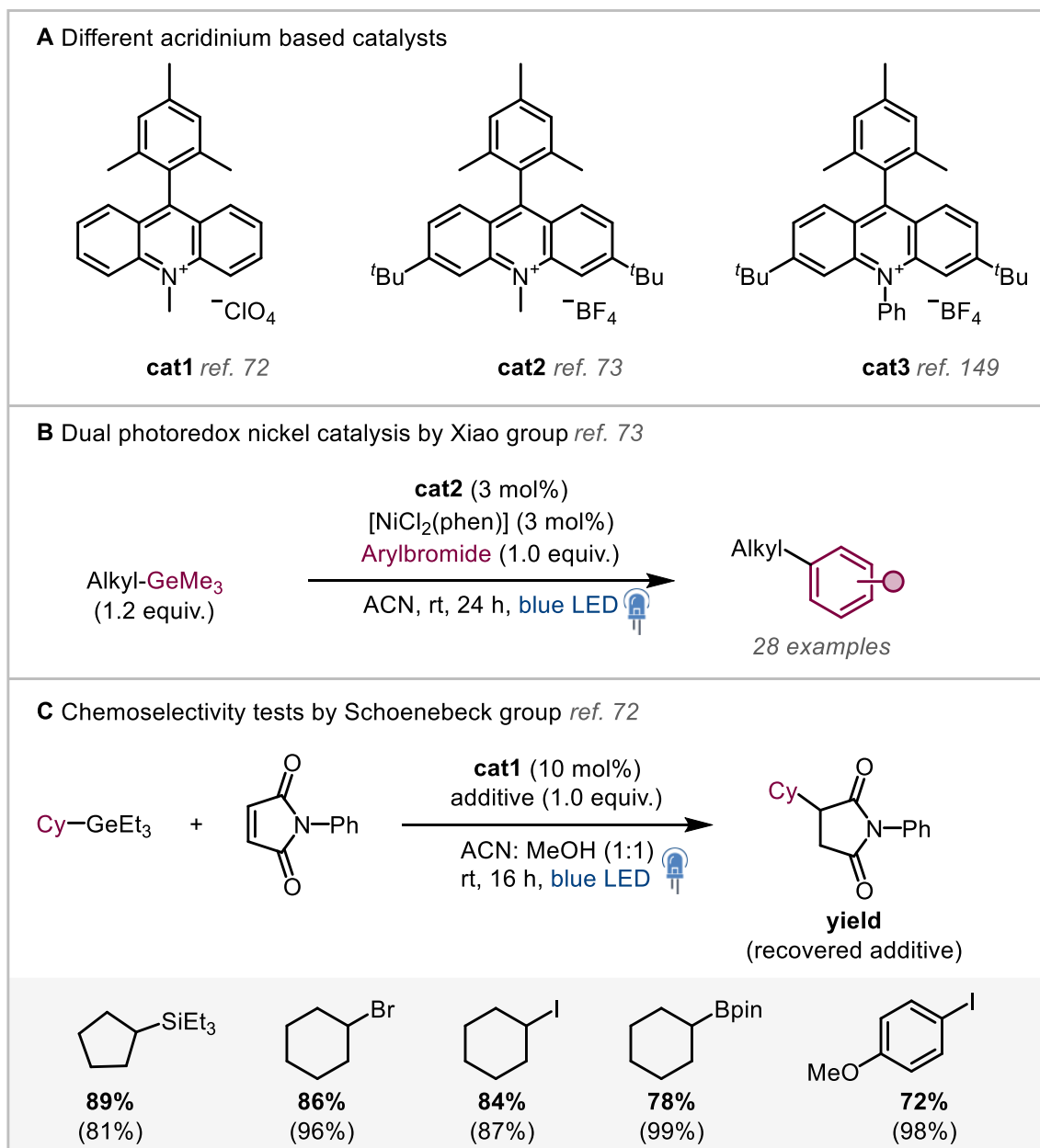
Scheme 25 | Literature reported examples of various functional group transformations using acridinium based photocatalysts.



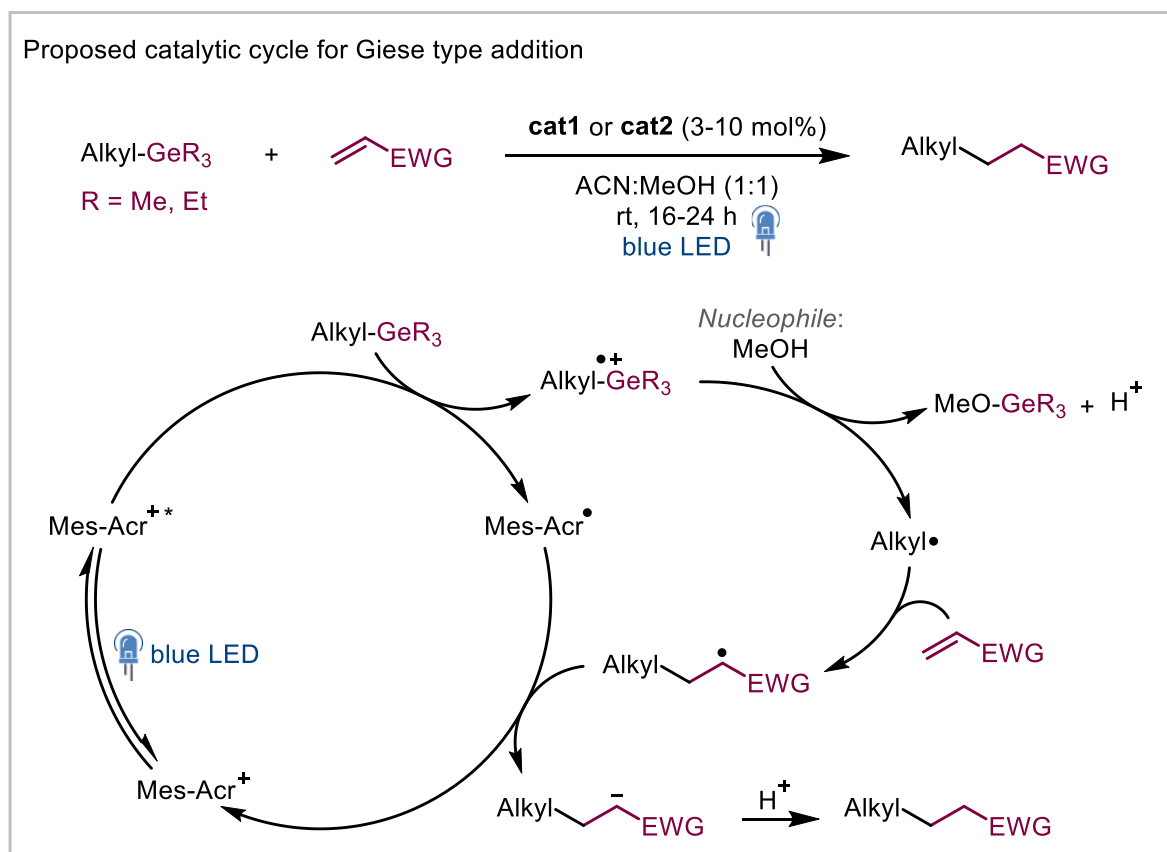
In the context of acridinium catalyzed transformations, the groups of Schoenebeck^[72] and Xiao^[73] simultaneously developed a Giese type addition reaction using different alkylgermanium species under photochemical conditions, to form the desired alkyl radical. These two publications presented similar reaction conditions, both employing an acridinium based photoredox catalyst. Our group used **cat1**, while the Xiao group used **cat2** for their successful transformation of the alkylgermanium motif (Scheme 26A), highlighting that different acridinium based catalysts are feasible for the oxidation of the C-Ge bond. Based on a previous study by the Nicewicz group,^[153] the structures of both acridinium catalysts used are not

optimal for their desired utilization as photocatalyst. Research indicates that **cat1** is vulnerable to demethylation and nucleophilic attack, which contribute to its degradation and the loss of its chromophore's color.^[153] Therefore, the modified **cat3** was chosen as standard photoredox catalysts for the work described in this thesis, with a high excited state potential of +2.08 V and a nearly doubled excited state lifetime of 14.4 ns, relative to **cat1**.^[153]

Besides the Giese type addition of alkyl radicals, the Xiao group demonstrated the successful combination of the organogermanium based alkyl radical with metallaphotoredox chemistry using a dual catalyst system consisting of the acridinium and a nickel catalyst (Scheme 26B).^[73] Under these conditions they were able to showcase the C_{sp^3} - C_{sp^2} cross-coupling with aryl bromides in high yields. Our group on the other hand established building block **A** and demonstrated the modularity of this platform as described in the previous chapter 2.1.1.^[72] Furthermore, selective oxidation of cyclohexyl-GeEt₃ was demonstrated in the presence of various functional groups, including C-SiEt₃, C-Br, C-I, and C-Bpin, affording the desired product while leaving the functionalized additives untouched (Scheme 26C).^[72] Additionally, it was shown that electron-rich aromatic additives did not significantly lower the yield of the Giese type reaction. These chemoselectivity tests emphasize the powerful potential of the C-Ge group as modular handle on the building block **A**.

Scheme 26 | Acridinium catalysts, dual photoredox catalyzed cross-coupling of alkylgermanes and chemoselectivity tests of the C–Ge Giese addition.^[72, 73]

The mechanism for the acridinium catalyzed Giese type addition is shown in Figure 6. Upon photoexcitation, the photocatalyst undergoes SET, oxidizing the alkylgermane to generate a radical cation intermediate. This species undergoes homolytic cleavage of the C–Ge bond, facilitated by a nucleophile (MeOH as solvent), leading to the formation of germanium byproduct Et₃GeOMe (observed in GC-MS) and a carbon-centered radical.^[72] The latter engages in a radical addition to the electron-deficient alkene, forming a new C–C bond. The intermediate radical species is subsequently reduced by the reduced form of the photocatalyst, regenerating the active catalytic cycle. The resulting carbanion undergoes protonation, yielding the desired product.^[72, 73]

Figure 6 | Proposed mechanism for the photoredox Giese addition.^[72, 73]

2.1.3 Electrochemical transformations in the C_{sp}³ regime

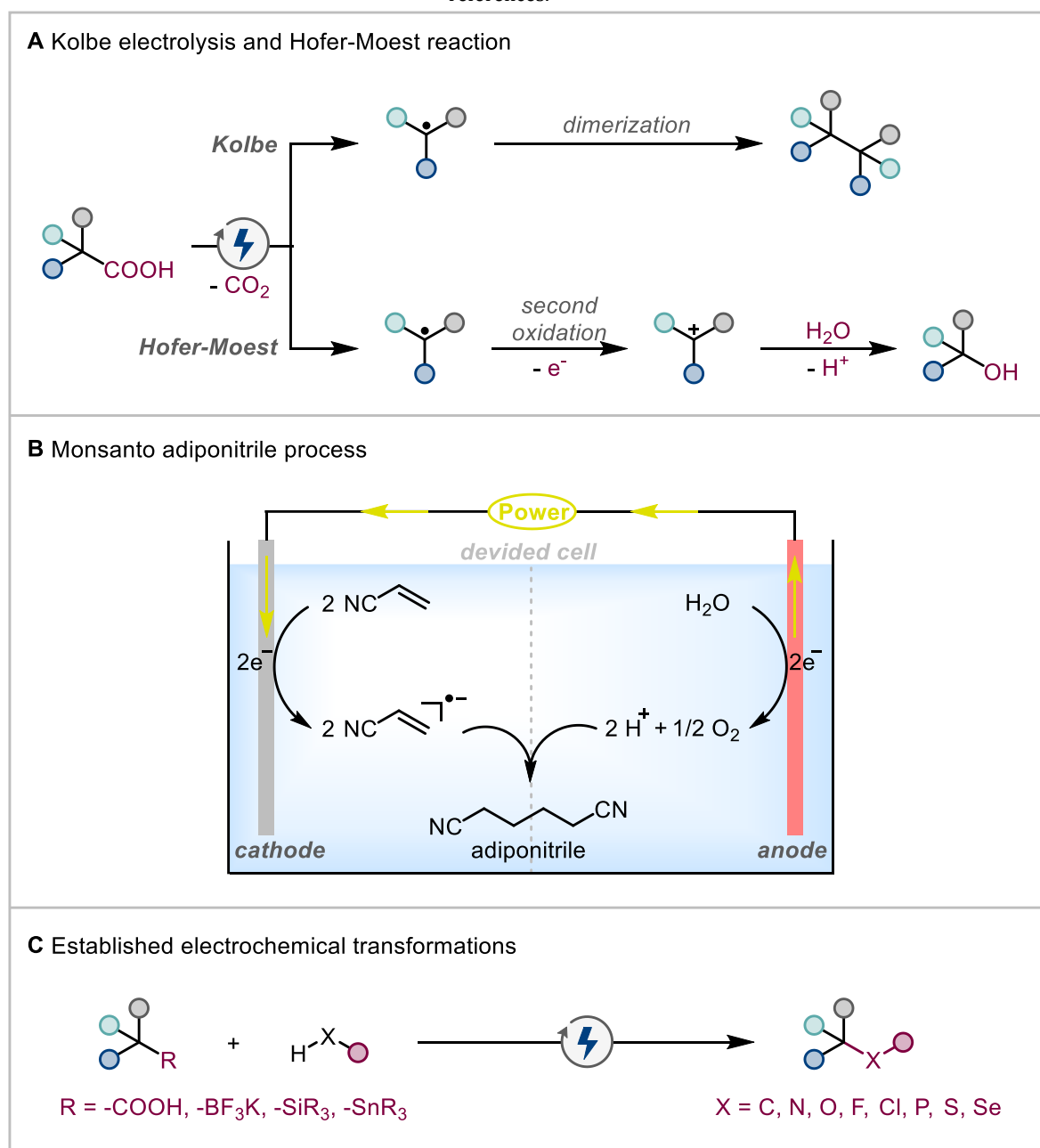
The transition from photochemistry to electrochemistry in organic synthesis is driven by the fundamental processes that generate reactive intermediates. While photochemistry utilizes light energy to excite electrons and produce radical species, electrochemistry involves the direct application of an electrical potential to induce redox transformations. Both methods offer unique pathways for the formation of reactive species and have found significant applications in synthetic chemistry.^[154-156]

Electrochemistry has a history dating back to the early 19th century. Although the invention of the Volta Pile in 1800 provided the first continuous source of electric current, it was Michael Faraday's work in the 1830s that laid the foundation for electrochemistry as a scientific discipline.^[155] Faraday's systematic studies led to the discovery of key principles such as electrolysis and the introduction of terminology like anode, cathode and ion migration. His electrolysis of acetic acid paved the way for one of the earliest and most influential electroorganic reactions, namely the Kolbe electrolysis, discovered by Hermann Kolbe in 1847 (Figure 7A).^[157] This reaction demonstrated that the anodic oxidation of carboxylates could generate alkyl radicals, leading to the formation of alkanes through radical dimerization.

One notable extension of Kolbe electrolysis is the Hofer-Moest reaction^[158], also known as the interrupted Kolbe reaction (Figure 7A). In this process, anodic oxidation of a carboxylic acid generates an alkyl radical, analogous to radical formation under photochemical conditions. However, when carbon electrodes are employed, the radical undergoes further oxidation to yield a carbocation.^[159] This carbocation is then attacked by a nucleophile, enabling a broader range of functionalization compared to radical pathways alone.

The industrial relevance of electrochemistry became evident with the development of large scale processes such as the Monsanto process for adiponitrile synthesis (Figure 7B).^[155] This electrochemical method replaced conventional cyanation techniques, offering a more sustainable and efficient approach to producing adiponitrile, a key precursor for nylon-6,6.^[160] The success of this process underscored the advantages of electrochemical transformations, including operational simplicity, selectivity, and scalability. Electrochemical setups can generally be categorized into divided and undivided cells.^[155] In an undivided cell, both the anode and cathode are in the same reaction chamber, allowing for direct electron transfer between reaction intermediates. However, in cases where undesired side reactions occur, a divided cell is employed, separating the electrodes using a membrane or salt bridge to prevent cross reactions.^[154] The choice of electrodes and electrolytes further influences reaction efficiency. Common electrode materials include carbon-based electrodes,^[161] noble metals (e.g. platinum),^[162] and transition metals (e.g. nickel).^[163, 164] Electrolytes, typically ionic salts, enhance conductivity and stabilize reactive intermediates.

Figure 7 | History and current advances in modern electrochemistry. The divided cell figure was combined from references.^[155, 165]



Recent advances in electrochemical methodologies have expanded the scope of alkyl functional groups amenable to the Hofer-Moest, or interrupted Kolbe reaction, enabling selective C-heteroatom bond formation (Figure 7C). While alkyl carboxylic acids are widely accessible and have been extensively used in electrochemical functionalization, their direct oxidation requires activation. Baran and co-workers have developed several methodologies to incorporate carboxylic acids into the interrupted Kolbe reaction, demonstrating their utility for C-O, C-N, and C-F bond formations.^[166, 167] However, their approach necessitates the addition of a base to form a carboxylate with a lower oxidation potential. Alternatively, the lower redox potentials of alkyl trifluoroborates enable more efficient oxidation, but their ionic nature reduces their modular utility in multistep functionalizations.^[110, 161, 168, 169] Although organosilanes and organostannanes are viable precursors, they are often hindered by their high oxidation potential or toxicity,

respectively.^[170-172] In contrast, alkyl germanes offer a promising alternative as their non-ionic and non-toxic nature ensures improved practical utility.

2.2 Orthogonal functionalization in three-dimensional space: results and discussion

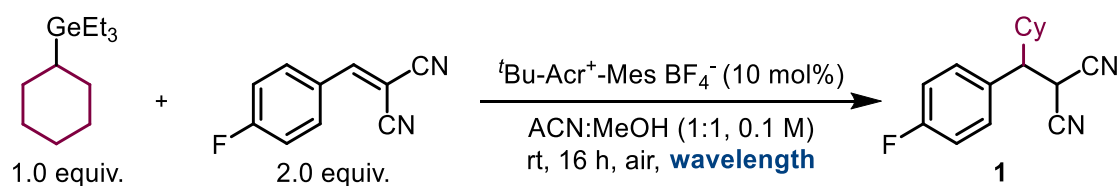
2.2.1 Optimization of reaction conditions for alkyl radical formation

To expand the diversification possibilities, the work in this thesis demonstrates the full functionalization of the already established building block with the aid of photo- and electrochemically catalyzed carbon-germanium bond functionalizations.^[110, 111] In this chapter, the robustness and ease of handling of organogermanium compounds is demonstrated by sequential functionalization of the carbon-halogen and carbon-Bpin moiety, followed by various novel transformation of the trialkyl germanium motif.

Initially, an optimization screening was conducted of the photoredox catalyzed carbon-germanium bond oxidation, as in the previous publications different acridinium photocatalysts as well as slightly different reaction conditions were shown.^[72, 73] The previously reported acridinium catalysts **cat1** and **cat2** were not further screened in this study for the reasons discussed above. Besides these two catalysts, there is another acridinium based photocatalyst **cat3**, with a slight modification of **cat2**. The difference between these catalysts is that **cat3** contains a phenyl group instead of the methyl group on the nitrogen of the acridinium scaffold. According to a report from Nicewicz and co-workers,^[153] this modification leads to a longer lifetime of the excited state and thus lead to more efficient oxidation of the carbon-germanium bond than the previously shown ones.

For this optimization study, cyclohexyltriethylgermane (1.0 equiv.) was used as an alkyl radical source, 2-(4-fluorobenzylidene)malononitrile (2.0 equiv.) as a Michael acceptor and **cat3** (10 mol%) as the photocatalyst, resulting in the formation of product **1**. These reactions were carried out in a 1:1 mixture of acetonitrile and methanol (0.1 M). In the following schemes, **cat3** is referred to as [^tBu-Acr⁺-Mes BF₄⁻].

Table 9 | Optimization screening of different wavelengths.



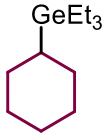
Entry	Wavelength (nm)	¹⁹ F NMR yield (%) ^a
1	405	64
2	425	67
3	450	75
4	475	74
5	Blue LED strip	78

Reaction conditions: Cyclohexyltriethylgermane (1.0 equiv.), [^tBu-Acr⁺-Mes BF₄⁻] (0.1 equiv.), 2-(4-fluorobenzylidene)malononitrile (2.0 equiv.), ACN:MeOH (1:1, 0.1 M), rt, 16 h, different wavelength. For detailed description see SI. a) 1,4-difluorobenzene was used as an internal standard.

Different wavelengths of light were evaluated as the first parameter to be investigated in this optimization run (Table 9). The λ_{max} value of **cat3** has been reported to be $\lambda = 420$ nm.^[153] Therefore, a wavelength range

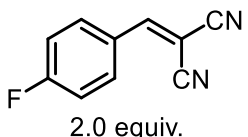
of 405 nm to 475 nm was selected. The lowest wavelength of 405 nm resulted in a ^{19}F NMR yield of 64% (entry 1), which is similar to the 67% (entry 2) achieved with a lamp emitting 425 nm light. Increasing the wavelength to 450 nm significantly increased the yield to 75% (entry 3), and 74% (entry 4) with 475 nm, respectively. Interestingly, when a commercially available blue LED strip was used, an increased NMR yield of 78% (entry 5) was observed. Due to the minor margin of error associated with the quantification of yields using ^{19}F NMR spectroscopy, the first two and last three entries in this screening can be considered to have analogous yields. Thus, 450 nm was used for further screening, because it is the closest to the λ_{max} value.

Table 10 | Optimization screening of the reaction concentration.



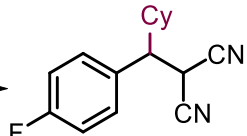
1.0 equiv.

+



2.0 equiv.

→



1

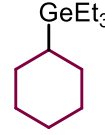
${}^t\text{Bu-Acr}^+-\text{Mes BF}_4^-$ (10 mol%)
 ACN:MeOH (1:1, **conc.**)
 rt, 16 h, air, 450 nm

Entry	Concentration (M)	^{19}F NMR yield (%) ^a
1	0.05	69
2	0.1	75
3	0.2	85

Reaction conditions: Cyclohexyltriethylgermane (1.0 equiv.), ${}^t\text{Bu-Acr}^+-\text{Mes BF}_4^-$ (0.1 equiv.), 2-(4-fluorobenzylidene)malononitrile (2.0 equiv.), ACN:MeOH (1:1), rt, 16 h, 450 nm. For detailed description see SI. a) 1,4-difluorobenzene was used as an internal standard.

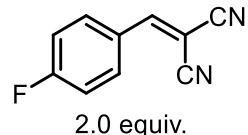
Secondly, the reaction concentration of the 1:1 acetonitrile and methanol mixture was screened within a range of 0.05–0.2 M (Table 10). Entry 1 represents the most diluted reaction, with a doubled volume of solvent resulting in a 0.05 M mixture and yielded 69% of the desired product. This represents a decrease in yield, relative to the previous standard conditions. Furthermore, when the reaction concentration was increased to 0.2 M, an improved NMR yield of 85% (entry 3) was observed. Due to these observations, the following optimization studies were conducted under 0.2 M reaction conditions.

Table 11 | Optimization screening of the photocatalyst loading.



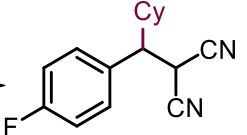
1.0 equiv.

+



2.0 equiv.

→



1

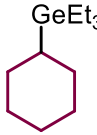
${}^t\text{Bu-Acr}^+-\text{Mes BF}_4^-$ (**loading**)
 ACN:MeOH (1:1, 0.2 M)
 rt, 16 h, air, 450 nm

Entry	Catalyst loading (mol%)	^{19}F NMR yield (%) ^a
1	1	69
2	2	73
3	5	85
4	10	85

Reaction conditions: Cyclohexyltriethylgermane (1.0 equiv.), ${}^t\text{Bu-Acr}^+-\text{Mes BF}_4^-$ (mol%), 2-(4-fluorobenzylidene)malononitrile (2.0 equiv.), ACN:MeOH (1:1, 0.2 M), rt, 16 h, 450 nm. For detailed description see SI. a) 1,4-difluorobenzene was used as an internal standard.

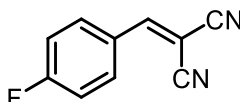
Thirdly, the photocatalyst loading was evaluated within a range of 1–10 mol% of **cat3** (Table 11). Interestingly, when the photocatalyst loading was lowered from 10 mol% to 5 mol%, the same ^{19}F NMR yield of 85% (entry 3) was obtained as under the previous conditions. A further lowering to 2 mol% resulted in a decrease in yield to 73% (entry 2), while lowering it even further led to a yield drop to 69% (entry 1). Based on these results, 5 mol% of photocatalyst was used for further optimization screening.

Table 12 | Optimization screening of used equivalents for the Michael acceptor (MA).



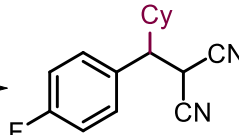
1.0 equiv.

+



equivalents

→



1

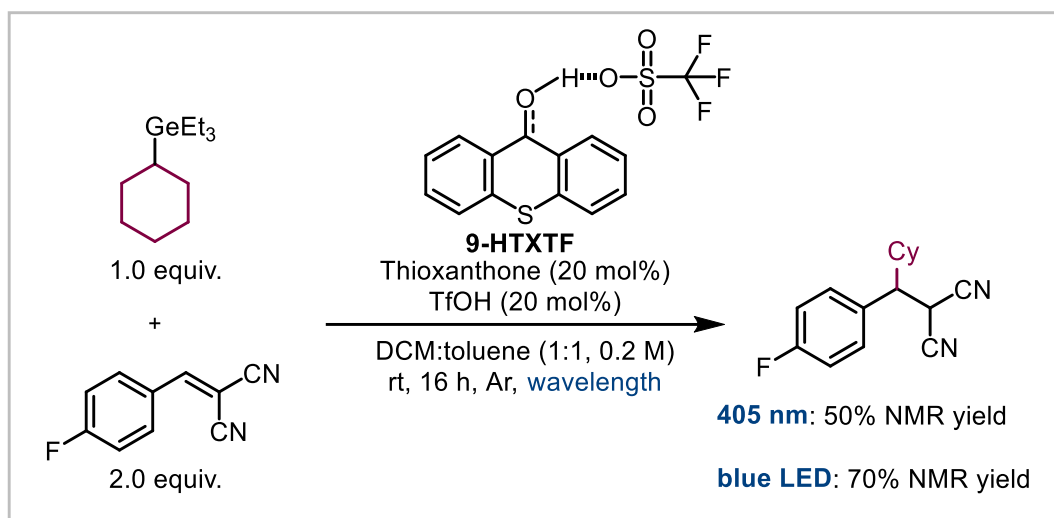
${}^t\text{Bu-Acr}^+-\text{Mes BF}_4^-$ (5 mol%)
 ACN:MeOH (1:1, 0.2 M)
 rt, 16 h, air, 450 nm

Entry	Equivalents of MA (%)	^{19}F NMR yield (%) ^a
1	1.1	68
2	1.5	75
3	2.0	85
4 ^b	2.0	85

Reaction conditions: Cyclohexyltriethylgermane (1.0 equiv.), ${}^t\text{Bu-Acr}^+-\text{Mes BF}_4^-$ (0.05 equiv.), 2-(4-fluorobenzylidene)malononitrile (equiv.), ACN:MeOH (1:1, 0.2 M), rt, 16 h, 450 nm. For detailed description see SI. a) 1,4-difluorobenzene was used as an internal standard. b) blue LED strips were used as light source,

Finally, the applied equivalents of the Michael acceptor (MA) were screened within a range of 1.1 to 2.0 equivalents (Table 12). In entry 1, only 1.1 equivalents of the Michael acceptor were used, resulting in a decreased ^{19}F NMR yield of 68%. Increasing the loading to 1.5 equivalents resulted in an increase in yield to 75% (entry 2), but the highest yield of 85% (entry 3) was obtained under the previous conditions using 2.0 equivalents of the Michael acceptor. Further increases in equivalents did not further increase the yield under these conditions. When the optimized conditions were conducted under blue LED strip light, the same high yield of 85% was achieved (entry 4).

Besides the acridinium based photocatalyst, also a recently published photocatalyst called “9-HTXTF” was also tested in the literature known Giese addition (Scheme 27).^[173] This catalyst is formed *in-situ* by a 1:1 combination of thioxanthone (TX) and triflic acid (TfOH), resulting in a strongly oxidizing photocatalyst with a potential of +2.53 V. Adapting the conditions from the original publication, this novel catalyst was successful in generating the desired product in a lower yield of 50% at 405 nm and 70% using the blue LED strip. The results obtained prove that the new catalyst is feasible for the demonstrated reaction, but due to the strong acidity of the triflic acid, the handling and functional group tolerance under these conditions are not ideal.

Scheme 27 | Photocatalyst “9-HTXTF” used in the standard Giese addition.

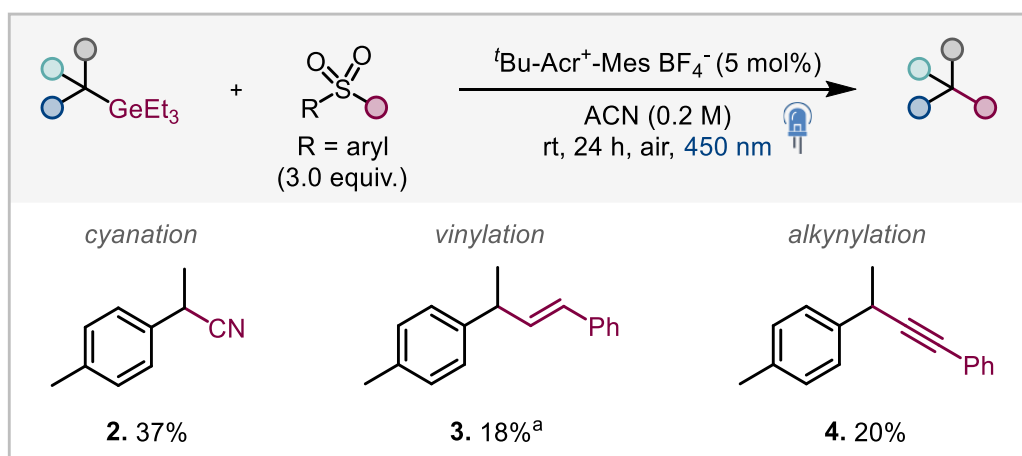
Reaction conditions: Cyclohexyltriethylgermane (1.0 equiv.), thioxanthone (0.2 equiv.), triflic acid (2.0 equiv.) 2-(4-fluorobenzylidene)malononitrile (2.0 equiv.), DCM:toluene (1:1, 0.2 M), rt, 16 h. For detailed description see SI. 1,4-difluorobenzene was used as an internal standard.

In summary, this optimization study resulted in the identification of conditions that formed the target compound in a high ^{19}F NMR yield of 85%; this was achieved by employing 5 mol% photocatalyst, 2.0 equivalents of Michael Acceptor, 0.2 M reaction concentration and either a 450 nm lamp or blue LED strips as light source, as both resulted in comparable yields. In the following sub-chapters, the optimized conditions were applied whenever possible, but due to the complexity of the compounds shown, the reaction conditions vary in small details.

2.2.2 Novel Germanium transformations

Besides the optimization of conditions for the literature known Giese addition of trialkyl germane reagents, the work described in this thesis also focuses on novel transformation possibilities of the C–Ge bond. Markus Schoetz^[111, 174] demonstrated that sulfonyl trapping reagents were discovered as a means of functionalizing the generated alkyl radical. These compounds and their reactivity were shown before in published reports and adapted well to the standard conditions of our protocol.^[175, 176] Following the optimized conditions, different sulfonyl trapping reagents were used to demonstrate the successful cyanation, vinylation and alkylation of the C–Ge bond (Scheme 28). The cyanation reaction furnished the nitrile containing product in a moderate yield of 37% (**2**), while the vinylation (**3**) and alkylation (**4**) products were formed in lower yields of 20% and 18%, respectively. The low yields of these compounds might be because of the organogermanium starting material employed, since in the publication cyclohexyl- and adamantyl triethylgermane were converted in high yields up to 88%, e.g. for the azidation.^[111] Furthermore, the styrene motif in compound **3** is prone to oxidation by photocatalysts, which has been previously reported and might also explain the observed low yield.^[177] In addition to the compounds which were described as part of this thesis, we published also the heteroarylation, thiolation, azidation and chlorination of the carbon-germanium bond in high yields (synthesized by Markus Schoetz),^[174] highlighting the novel diversification possibilities of the organogermane.^[111]

Scheme 28 | Novel C–Ge transformations using sulfonyl radical trapping reagents.

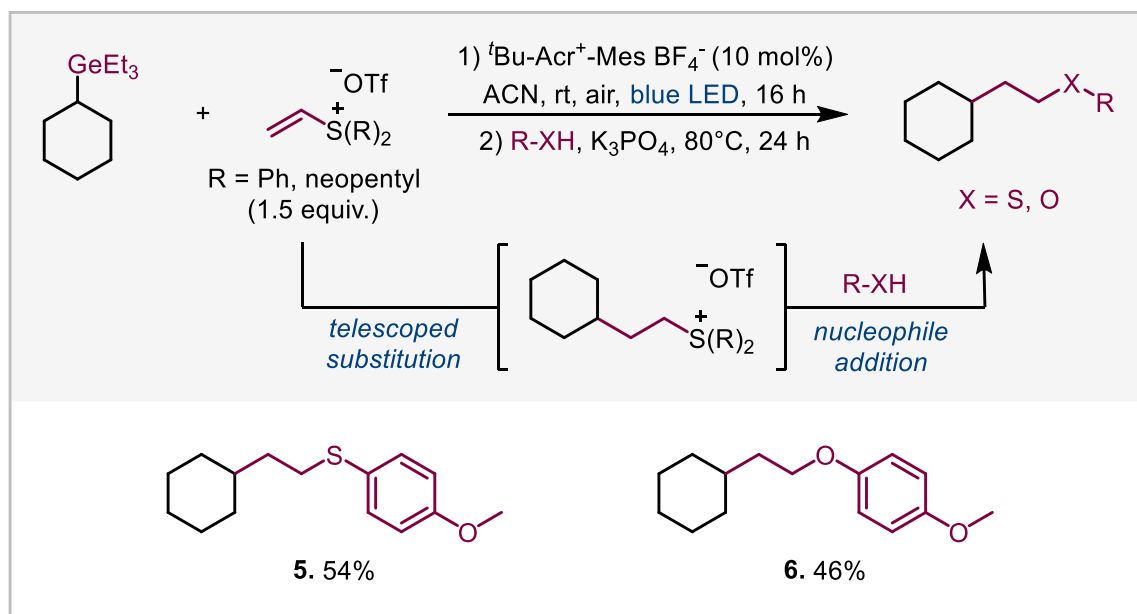


Reaction conditions: alkylgermane (1.0 equiv.), tBu-Acr⁺-Mes BF₄[−] (0.05 equiv.), sulfonyl trapping reagent (3.0 equiv.), ACN (0.2 M), rt, 24 h. For detailed description see SI. a) DCE (0.2 M) was used as solvent.

To further expand the repertoire of potential C–Ge bond transformations, investigations were made about the compatibility of Silvi and co-workers polarity transduction strategy, to formally introduce electron-rich double bonds *via* Giese addition (Scheme 29).^[178] In this recently published method, a system was developed which overcomes the limitations of electron-rich double bonds as Michael acceptors by utilizing sulfonium salts as electron-poor alkenes and a subsequent substitution with an incoming nucleophile results in the formal addition of an electron-rich alkene to the final product. In this publication 4CzIPN was used as photocatalyst to generate organoalkyl radicals from carboxylic acids and fortunately similar conditions with **cat3** [tBu-Acr⁺-Mes BF₄[−]] and cyclohexyltriethylgermane revealed a comparable reactivity,

resulting in the desired products. Initial results could be successfully shown with 4-methoxybenzenethiol (**5**) and 4-methoxyphenol (**6**) as nucleophiles to generate the desired, formally electron-rich double bond in the final products in good yields. Interestingly, it was observed that the diphenyl sulfonium salt was able to generate the desired products with different nucleophiles ($-\text{SH}$, $-\text{OH}$) when **cat3** is used, but in the original publication 4CzIPN only formed low amounts of the desired product by employing a thiol nucleophile. Silvi and co-workers rationalized this outcome by noting that diphenyl sulfonium salts tend to cleave under reductive conditions. They therefore replaced the sulfonium ligand with a branched neopentyl group, thereby enabling the use of a broader range of nucleophiles for a successful reaction outcome. Since the acridinium based photocatalyst (**cat3**) in this protocol has a lower ground state reduction potential of $-0.59\text{ V}^{[153]}$ (-1.21 V for 4CzIPN) $^{[179]}$, this undesired reactivity was not observed and the wanted products were obtained using either the diphenyl or dineopentyl sulfonium salts, without a significant change in yields.

Scheme 29 | Polarity transduction with alkyl germane and various nucleophiles.



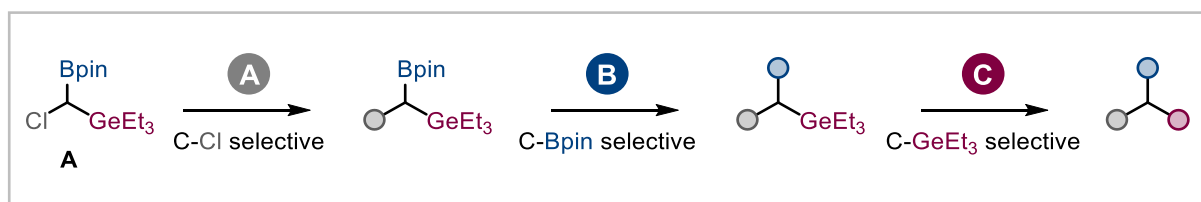
Reaction conditions: 1) alkylgermane (1.0 equiv.), $t\text{Bu-Acr}^+\text{-Mes BF}_4^-$ (0.1 equiv.), vinyl sulfonium salt (1.5 equiv.), ACN (0.2 M), rt, 16 h. 2) nucleophile (2.5 equiv.), K_3PO_4 (1.5 equiv.), 80°C , 24 h. For detailed description see SI.

2.2.3 Full functionalization sequence of the building block

In the introduction (Chapter 2.1.1), it was mentioned that our working group established a modular building block **A**, consisting of a C–halogen, C–Bpin and C–Ge group on the same carbon center.^[72] This recently published paper demonstrated that after functionalization of the C–halide bond with a benzylic group, the C–Bpin and C–Ge moieties could subsequently be transformed in an sequential manner.^[72] However, the full functionalization of this modular platform was not shown. The next logical goal was to explore the true potential of this developed platform and investigate which possible decorations of the different functional groups can be incorporated to access this remaining goal. In general, rapid access to a broad range of complex molecules is highly sought after in organic chemistry, highlighting the endless possibilities of a selectively functionalizable building block.^[43, 44, 116]

After a series of test reactions in collaboration with Markus Schoetz,^[174] it was determined that the C–halide bond must be functionalized in the first place due to its high reactivity and incompatibility with the reaction conditions of the other functional groups. The applied derivatization of this handle was mainly focused on Grignard reactions, achieving substitution of the C_{sp}³–Cl bond with an alkyl or aryl group. Following this step, the C–Bpin unit had to be transformed next, since functionalization of the C–Ge group under photoredox conditions is limited to homobenzylic germanium groups.^[72] A possible explanation for this observation can be the hyperconjugation of the borane group,^[180, 181] which leads to a weak α -boron nucleophile. In this step, the C–Bpin group was oxidized to the corresponding secondary alcohols or underwent (hetero)arylation using Aggarwals method.^[182] Fortunately, the trialkylgermanium moiety is very robust and stable, which has been shown in previous work and thus remained intact under the conditions required to functionalize the other two groups.^[81] In the final step of the full functionalization sequence, the C–Ge bond was decorated with the established Giese addition and nickel catalyzed arylation as well as the novel transformations using vinyl sulfonium salts and sulfonyl trapping reagents. The following chapters cover the sequential full functionalization as shown in Scheme 30 and will discuss the results obtained in more detail.

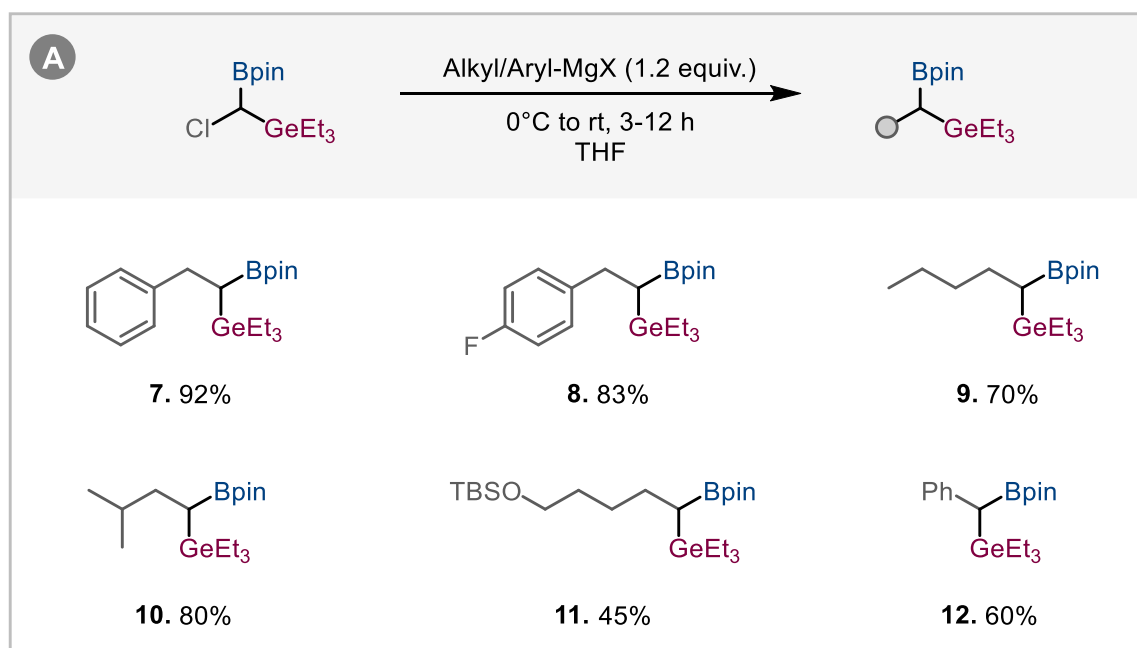
Scheme 30 | Sequential full functionalization route of the established building block. Adapted from reference with permission. *Angew. Chem. Int. Ed.* **2024**, 63, e202401545.



2.2.4 C-Halide functionalization

Based on Dr. Aymane Selmani's previous studies and the observations discussed above, the first step of the full functionalization sequence has to start with the alkylation of the carbon halide bond using various Grignard reagents.^[72] In Scheme 31, the successful alkylation with different Grignard reagents is demonstrated, resulting in the desired products in high yields. Compound **7** contains a benzylic structure, which was already shown by Dr. Aymane Selmani in the previously mentioned publication,^[72] but by changing the reaction conditions it was possible to obtain a significantly higher yield of 92% (see SI for details). A slightly different compound was synthesized using a *para*-fluorobenzene Grignard, obtaining the desired product **8** in a high yield of 83%. Besides the known compound, additionally new alkylated building blocks were synthesized, utilizing a linear (**9**) and a branched (**10**) butane Grignard reagent achieving the desired products in high yields of 70% and 80%, respectively. Additionally, a protected alcohol with a tert-butyl-silyl group (**11**, previously synthesized by Markus Schoetz with the same method)^[111, 174] and a simple phenyl (**12**) were successfully used as Grignard reagents to generate the desired products in moderate yields. This extended scope demonstrated again that the choice of functionalities on the building block is crucial for rapid access to diverse structures, since the C-Bpin and C-Ge groups remained untouched and stable under the applied nucleophilic conditions.

Scheme 31 | C_{sp}³-Cl functionalization of the established building block with Grignard reagents.

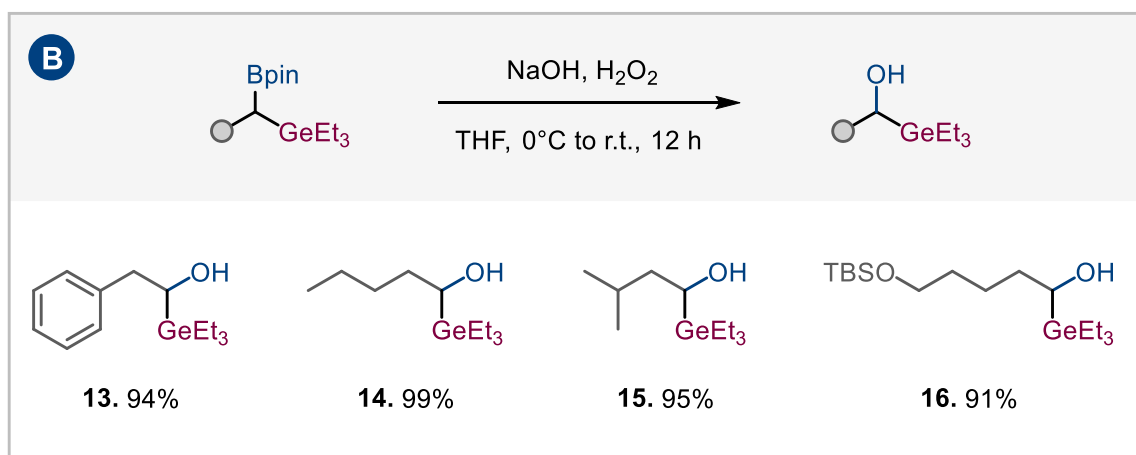


Reaction conditions: building block **A** (1.0 equiv.), RMgX (1.2 equiv.), THF (0.2-1.1 M), 0°C to rt, 3-12 h. For detailed description see SI. Compound **7** was already synthesized as shown by Dr. Aymane Selmani.^[72] Compound **11** was already synthesized as shown by Markus Schoetz.^[111, 174]

2.2.5 C-Bpin functionalizations

The second step of the functionalization sequence was focused on the C-Bpin moiety. Literature reported transformations^[182-188] were applied building up on Dr. Aymane Selmani's findings.^[72] A frequently employed functionalization of an alkyl C-Bpin handle in synthetic chemistry is the peroxide-promoted oxidation to an alcohol,^[184] to introduce a heteroatom on the alkyl carbon. As shown in Scheme 32, NaOH and H₂O₂ are added at 0°C to the alkylated building block and after stirring for 12 h, the desired oxidized products are obtained in nearly quantitative isolated yields. First, the alkylated compound **7** was oxidized to obtain the desired alcohol (**13**) in high yield of 94%. Following, it was also shown that compounds **9** and **10** were successfully oxidized, achieving the expected products in excellent yields of 99% for **14** and 95% for **15**, respectively. Fortunately, compound **11**, bearing a protected alcohol, was also selectively oxidized resulting in the desired product **16** in 91% yield. These examples further illustrate the robust nature of the C-Ge handle, due its stability under strongly oxidizing conditions, underlining its potential power for late stage functionalizations.

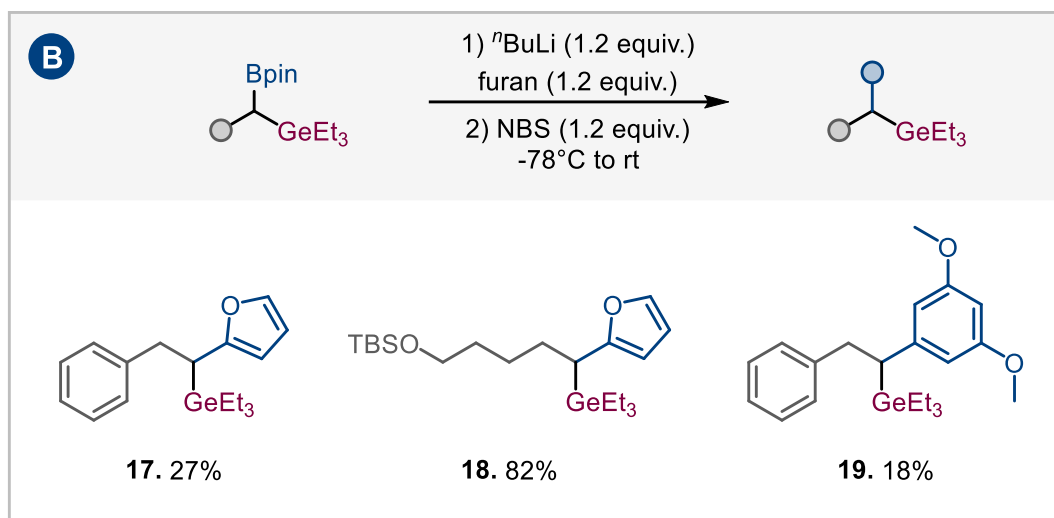
Scheme 32 | C_{sp}³-Bpin oxidation to alcohols.



Reaction conditions: alkyl-Bpin (1.0 equiv.), slow addition of aq. NaOH (3 M, 3.0 equiv.) and H₂O₂ (30 wt% in H₂O, 9.0 equiv.), THF, 0°C to room temperature, 12 h. For detailed description see SI.

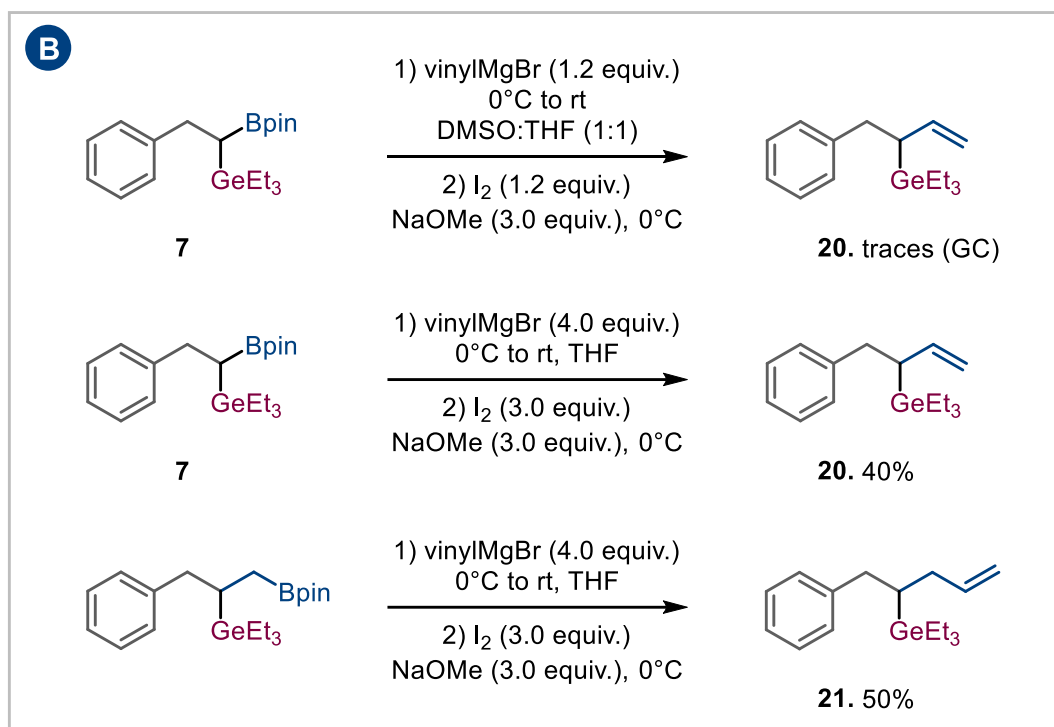
Another powerful transformation is the (hetero)arylation of C-Bpin, which was published by the group of Aggarwal (Scheme 33).^[182, 186] Dr. Aymane Selmani already demonstrated the compatibility of these conditions with the building block in the previous publication,^[72] using compound **7** and furan for the heteroarylation. This reaction was repeated and obtained the desired product **17** in moderate yield. In addition to this, compound **11** was used for another heteroarylation with furan achieving a high yield of 82%, resulting in the desired product **18**. Furthermore, compound **19** was synthesized according to the reported procedure but in significantly lower yield. By showcasing the obtained products, it is again demonstrated that the C-Ge group is a suitable functional group to enable orthogonal functionalizations, since the reaction conditions include strong organometallic nucleophiles and *N*-bromo succinimide (NBS), which has been earlier shown to brominate aryl germanium species.^[189] This methodology can be extended to further incorporate heteroaryl or aryl systems into the building block, as shown by Markus Schoetz.^{[111,}

174]

Scheme 33 | C_{sp}³-Bpin heteroarylation.

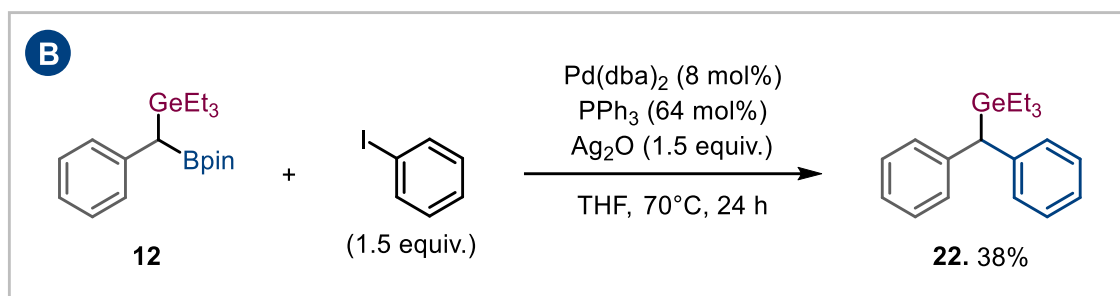
Reaction conditions: alkyl-Bpin (1.0 equiv.), ⁿBuLi (1.2 equiv.), furan (1.2 equiv.), NBS (1.2 equiv.), THF, -78°C to room temperature. For detailed description see SI. Compounds 17 and 19 were synthesized according to Dr. Aymane Selmani's publication.^[72]

Besides the oxidation and (hetero)arylation of C_{sp}³-Bpin moieties, another versatile method that converts alkyl Bpin to olefins is called the Zweifel olefination.^[183] In this functionalization, a new carbon-carbon bond is generated to exchange an olefin from a Grignard or organolithium reagent with the Bpin unit.^[188] One of the commonly used variations is the introduction of an unsubstituted vinyl group, as first described by the group of Aggarwal.^[185] In this case, a C_{sp}³-Bpin is treated with excess (4.0 equivalents) of vinyl Grignard to form a trivinyl boronate complex. Subsequent addition of I₂ and NaOMe leads to a 1,2-metallate rearrangement and releases the desired vinylated product.^[188] In further studies, they found out that the applied vinyl Grignard could be reduced to 1.2 equivalents by switching to a solvent system of DMSO:THF in a 1:1 ratio.^[190] In this particular example, the formation of a boronate complex with only one vinyl group was detected. With this information in hand, investigations were made into possible applications of compound **7** (Scheme 34). Conducting the experiment with similar conditions, as shown in the previously mentioned publication, resulted only in product traces, based on GC-MS and mostly remaining starting material. After a few optimization reactions, it was found that the initial conditions with excess of vinyl Grignard, as reported by Aggarwal, achieved the best product formation conditions. Additionally, it was necessary to increase the reaction time of the first step to an overnight reaction and in the second step 3.0 equivalents of iodine instead of 1.2 equivalents were needed. These amended conditions enabled the preparation of the olefinated product **20** in 40% yield, when compound **7** was used as starting material. In Scheme 34, it was demonstrated that the same reaction with a similar compound resulted in the desired product **21**, in a slightly higher yield of 50%. The starting material for this product was synthesized by Markus Schoetz^[174] *via* the well-known homologation reaction, which was initially found by Matteson and further developed by the group of Aggarwal.^[191, 192] This reaction describes another possibility to functionalize the C-Bpin bond, since a CH₂ group is inserted between the carbon and the boron atom, extending the chain length of the compound.

Scheme 34 | Zweifel Olefination of the alkyl-Bpin group.

Reaction conditions: alkyl-Bpin (1.0 equiv.), vinylMgBr (4.0 equiv.), 0°C to room temperature, THF, overnight. Then I_2 (3.0 equiv.), NaOMe (3.0 equiv.), THF, 0°C , 30 min. For detailed description see SI.

Finally, the transition metal catalyzed cross-coupling of the C_{sp}^3 -Bpin unit with an aryl halide was demonstrated (Scheme 35). The palladium catalyzed Suzuki-Miyaura^[113] coupling of organoboranes and aryl halides is of utmost importance in academia and industry, to easily access a variety of biaryls. These biaryl systems are highly sought after in pharmaceutical and material industries, underlining the importance of this cross-coupling reaction.^[187] The group of Crudden developed a variation, where they could couple benzylic Bpin compounds with aryl iodides, using the commercially available $\text{Pd}(\text{dba})_2$ catalyst.^[187] Since synthesized compound **12** contains a benzylic C_{sp}^3 -Bpin group, investigations were made to prove the compatibility with the neighboring C_{sp}^3 -GeEt₃ group. Fortunately, the reported standard conditions showed product formation in GC-MS, but also a lot of remaining starting material as well as homocoupling of the aryl iodide. Interestingly, when solvents were switched from dimethoxyethane (DME) to THF the observed peak of homocoupled side product significantly decreased. Applying these slightly changed reaction conditions to compound **12** resulted in the desired product (**22**) formation in 38% yield. There were no further optimizations made to increase the yield, since the aim was to prove that the functionalization of the Bpin handle is possible in presence of the triethylgermanium group, leaving it untouched for a potential follow up transformation of the C_{sp}^3 -GeEt₃ moiety.

Scheme 35 | Palladium catalyzed cross-coupling of C_{sp}³-Bpin.

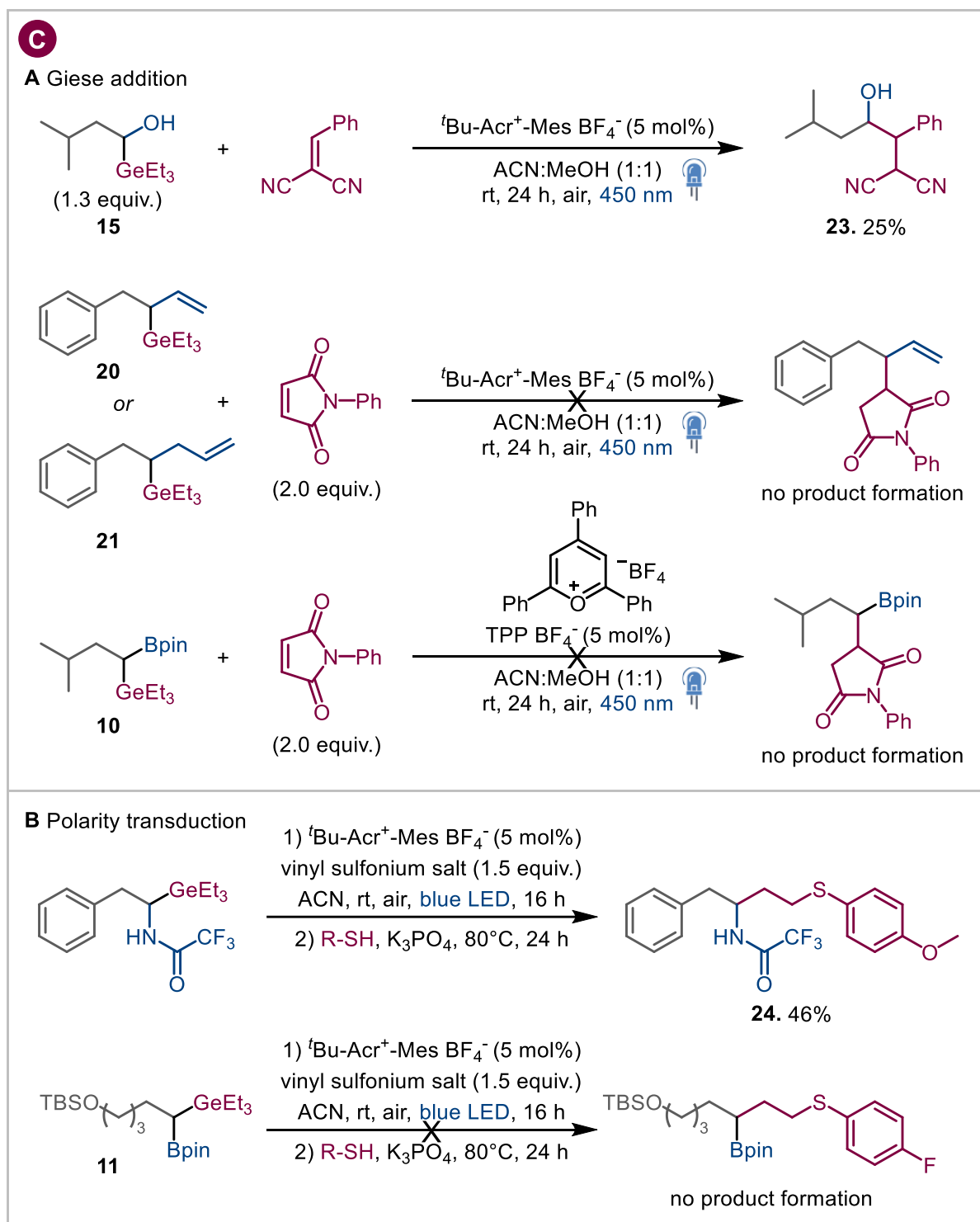
Reaction conditions: alkyl-Bpin (1.0 equiv.), iodobenzene (1.5 equiv.), $\text{Pd}(\text{dba})_2$ (8 mol%), PPh_3 (64 mol%), Ag_2O (1.5 equiv.), THF, 70°C, 24 h. For detailed description see SI.

2.2.6 C-GeEt₃ functionalizations

Based upon the previous work of Dr. Aymane Selmani,^[72] the work described in this thesis focused on the functionalization of the C_{sp}³-GeEt₃ handle under photochemical conditions. In this chapter, the desired full functionalization of building block **A** will be demonstrated, with transformations of the germanium group in the final sequence. In the previous chapters it was shown that the alkylgermanium group persists through harsh reaction conditions and remains untouched during the transformation of the C_{sp}³-Cl and C_{sp}³-Bpin handles. Thus, specifically tailored reaction conditions for the C_{sp}³-GeEt₃ moiety are needed to selectively decorate the desired position of the building block.

Starting with the well-known Giese addition of alkyl radicals to electron-poor Michael acceptors,^[72] the successful sequential functionalization to the desired product **23** was shown (Scheme 36A). In this case, the applied starting material **15** contains a branched butyl on the C_{sp}³-Cl site and an alcohol on the C_{sp}³-Bpin site after oxidation. In comparison to the report mentioned above, it was necessary to switch the Michael acceptor as the limiting reagent, due to isolation challenges. Using the Michael acceptor 2-benzylidenemalononitrile as limiting reagent and compound **15** in slight excess, a yield of 25% of the desired product (**23**) was obtained. The rather low yield is in line with the reported Giese addition of the same Michael acceptor using compound **7** as starting material, obtaining the same 25% of yield.^[72] Even though excess of the germanium containing starting material was used, there was still unreacted Michael acceptor left after the reaction. Significantly higher yields could be achieved, when the C-Bpin group underwent amination prior to the Michael addition as shown in our publication.^[111] Furthermore, compounds **20** and **21** were used as starting materials for the photocatalyzed Giese addition. However, the desired products were not obtained, leaving the starting materials untouched. As already mentioned in the previous chapters, the direct oxidation of the carbon-germanium bond was limited to one specific substrate if the C-Bpin handle was not functionalized before. To overcome this limitation, different photocatalysts were investigated with higher oxidation potential than the used **cat3**. In a demonstration example, compound **10** was applied under the standard reaction conditions, but in this case the photocatalyst 2,4,6-triphenylpyrylium tetrafluoroborate (TPP BF₄⁻) with an oxidation potential of +2.55 V was used.^[130] The switch to a photocatalyst with higher oxidation potential was also not successful in the desired product formation, since only starting material was observed in GC-MS.

Besides the Giese addition, the comparable polarity transduction was shown to be feasible in the full functionalization sequence (Scheme 36B). Based on the initial result studies with vinyl sulfonium salts and different nucleophiles described in this thesis (Scheme 28), Dr. Gurdeep Singh used these findings to successfully demonstrate the addition to a formally electron-rich double bond. For this reaction, compound **7** was aminated at the Bpin handle to obtain the starting material 2,2,2-trifluoro-N-(2-phenyl-1-(triethylgermyl)ethyl)acetamide, which was then used to achieve the desired product **24** in 46% yield.^[111] In addition to the shown thiol nucleophile, it should also be possible to use different alcohols as nucleophiles as shown in the initial results.

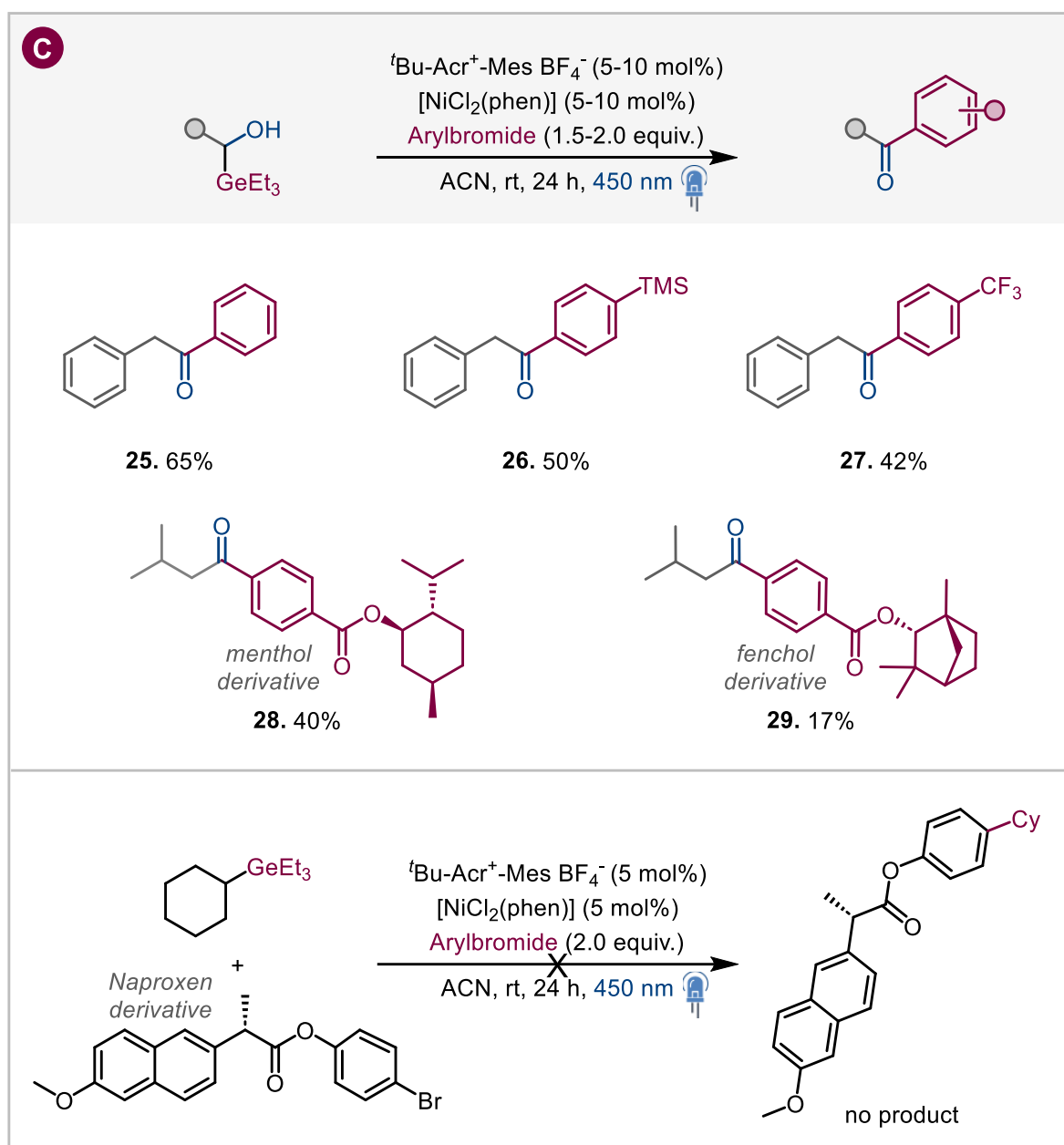
Scheme 36 | Alkyl radical addition to electron-poor and -rich Michael acceptors *via* Giese type reactions.

Reaction conditions: A) Alkylgermane (1.3 equiv.), 2-benzylidenemalononitrile (1.0 equiv.), $t\text{Bu-Acr}^+-\text{Mes BF}_4^-$ (0.05 equiv.), ACN:MeOH (1:1, 0.2 M), rt, 16 h, 450 nm. B) alkylgermane (1.0 equiv.), $t\text{Bu-Acr}^+-\text{Mes BF}_4^-$ (5 mol%), vinyl sulfonium salt (1.5 equiv.), ACN (0.2 M), rt, 16 h. Then nucleophile (2.5 equiv.), K_3PO_4 (2.0 equiv.), 80°C, 24 h. For detailed description see SI. Compound **24** was synthesized by Dr. Gurdeep Singh.

Furthermore, the established dual photoredox nickel catalysis was applied for the demonstration of the full functionalization of the building block. In this context, the group of Xiao presented the cross-coupling compatibility of alkyl germanium species with aryl bromides under photoredox conditions.^[73] Since the

publication only showed simple alkyl germanium compounds, a first test reaction was done to determine the reactivity of the building block, when another functional group was present next to the alkylgermane. Specifically, compound **13** was used as limiting reagent and bromobenzene in excess as the aryl halide coupling partner (Scheme 37). The reaction conditions were slightly adjusted to the previously optimized reaction conditions in the first chapter (Chapter 2.2.1.), using **cat3** in 5–10 mol% as well as 5–10 mol% of the nickel catalyst. Surprisingly, the crude GC-MS analysis did not show the desired product mass, but a significant peak with a mass of minus two of the expected product. After isolation of the detected compound, further analysis revealed that compound **25** was generated in 65% yield. The formation of this α -aryl-ketone led to the conclusion that the hydroxy group was oxidized to the corresponding ketone. To further investigate this observation, aryl bromides with different functional groups on the aromatic ring were used. Indeed, the aryl-TMS and the aryl-CF₃ compounds were successfully cross-coupled obtaining the corresponding α -aryl-ketones in 50% (**26**) and 42% (**27**) yield, respectively.

After the successful demonstration of the compatibility with simple aryl halides, the methodology was applied in the synthesis of more complex substrates, using both natural products and drug derivatives for the cross-coupling (Scheme 37). In these cases, the natural product or drug was subjected to an esterification to generate the corresponding aryl bromide derivative (see SI for further details). The best result was obtained when compound **15** and a menthol derivative (synthesized by Dr. Gurdeep Singh) were used as starting materials, achieving a yield of 40% (**28**). Another natural product derivative (**29**) was synthesized, when a fenchol derivative was applied as aryl bromide starting material. However, the yield of this product was rather low and the majority of the starting material remained untouched. An unsuccessful substrate was identified when the drug derivative of Naproxen was used, which resulted in no desired product formation (Scheme 37 bottom). A possible explanation for this lack of reactivity is the structural difference of the compounds. While the natural product derivatives were synthesized from alcohol and thus the ester group is connected *via* a carbon-carbon bond with the aryl bromide, the Naproxen drug derivative originates from an acid and the ester group linked *via* a carbon-oxygen bond with the aromatic ring. In recent publications, it was demonstrated that aryl methoxy groups can be oxidized and transformed in nucleophilic aromatic substitution reactions under photoredox conditions with acridinium based catalysts.^[193] Based on these observations, it might be hypothesized that the drug derivative follows the same mechanism and thus consuming the photocatalyst without regenerating it, resulting in no efficient product formation.

Scheme 37 | Dual photoredox nickel catalysis.

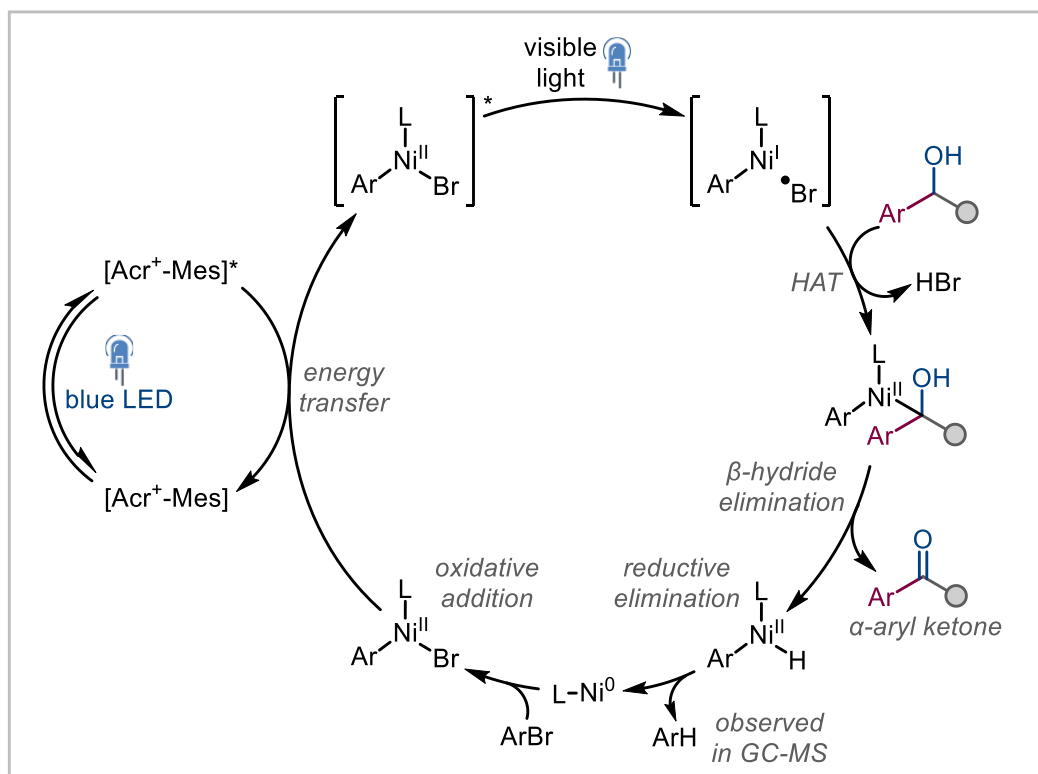
Reaction conditions: Alkylgermane (1.0 equiv.), arylbromide (1.5-2.0 equiv.), $t\text{Bu-Acr}^+\text{-Mes BF}_4^-$ (0.05-0.1 equiv.), $[\text{NiCl}_2(\text{phen})]$ (0.05-0.1 equiv.), ACN, rt, 24 h, 450 nm.

In Scheme 38, a proposed mechanism is presented for the dual photoredox catalyzed oxidation of benzylic alcohols to α -aryl-ketones. The proposed mechanism is based on previously reported findings from Rueping and co-workers,^[194] in which a similar acridinium photocatalyst (**cat1**) and a comparable nickel catalyst were employed under blue LED light. The shown mechanism for the oxidation of benzylic alcohols is based on experimental observations made during the reaction, however, no detailed mechanistic studies, either experimental or computational, have been performed to confirm the pathway.

The proposed catalytic cycle starts with the oxidative addition of the aryl bromide to the nickel complex and undergoes energy transfer from the excited state acridinium photocatalyst.^[194] Upon visible light induced homolytic cleavage, a bromine radical is generated,^[195] which undergoes HAT and abstracts a

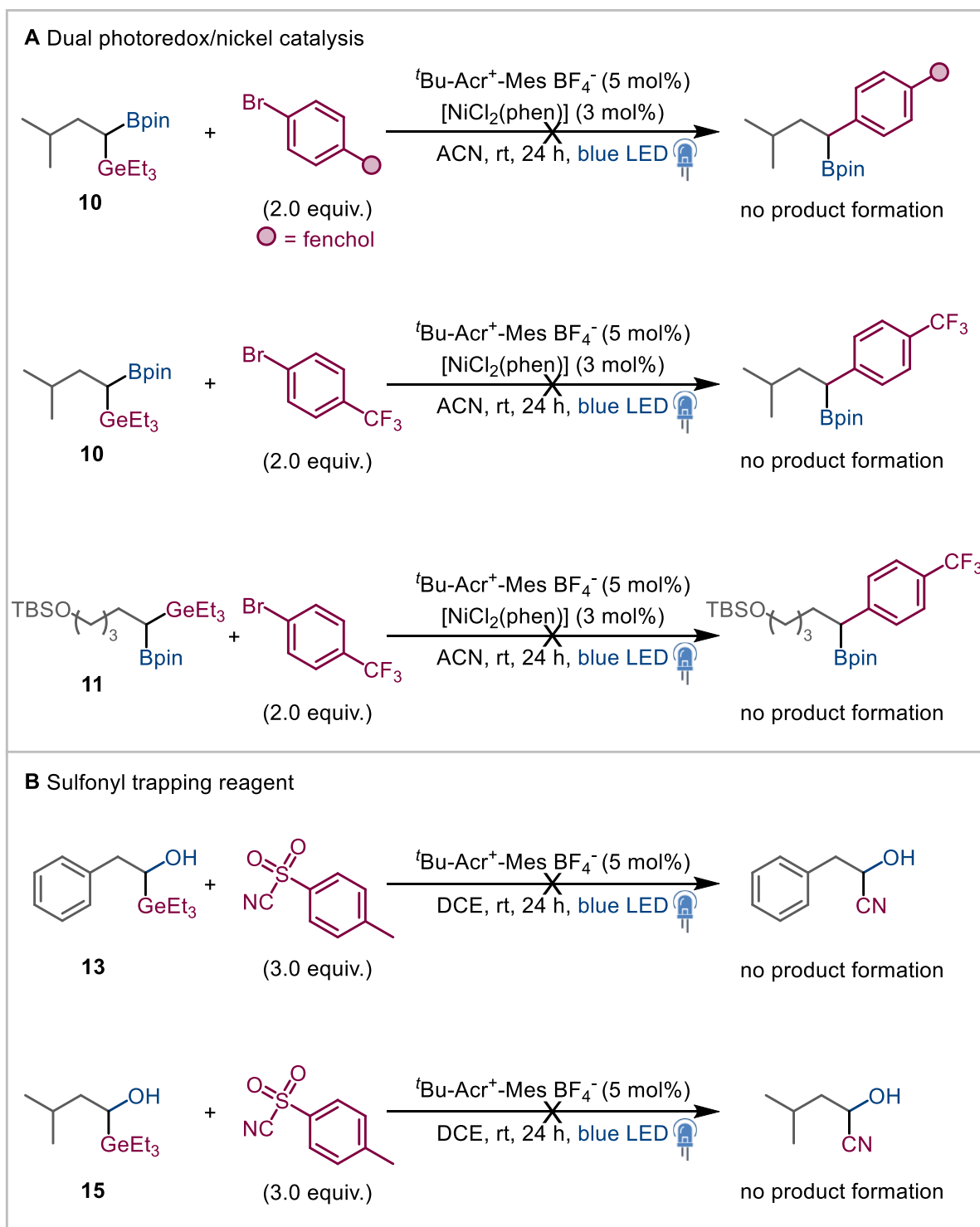
hydrogen atom radical from the benzylic alcohol. The generated benzylic radical combines with the nickel complex, which subsequently undergoes β -hydride elimination, to yield the observed α -aryl-ketone product. Reductive elimination from the nickel complex produces the corresponding aryl-H, as detected by GC-MS, thereby closing the catalytic cycle.^[194] It should be noted that, in the absence of supporting mechanistic investigations, the exact pathway remains speculative, especially the β -hydride elimination^[196] step and might differ from the proposed mechanism.

Scheme 38 | Proposed mechanism for the oxidation of benzylic alcohols under oxygen free conditions. Adapted from a previously reported mechanism by the Rueping group.^[194]



Further unproductive reactions are shown in Scheme 39, using different building blocks that still contain an unfunctionalized C-Bpin handle. The first reaction employs compound **10** as starting material in conjunction with a fenchol derivative for the known cross-coupling reaction (Scheme 39A). Previously, it was demonstrated that the fenchol derivative is a suitable candidate for the desired cross-coupling reaction. However, in this case, no product formation was observed and the starting material remained untouched. To lower the complexity of the starting materials used, the aryl bromide was switched to a simpler one, which was also shown to be productive in the previous scheme (Scheme 37). However, even the *para*-CF₃ substituted aryl bromide showed no desired product formation and the starting material could be recovered. Additionally, compound **11** was used as starting material with the same aryl bromide. Similar to the previous results, this reaction also led to no desired product formation, without any reaction of the starting material. In addition to the results obtained with the usual Giese addition (Chapter 2.2.6.), it can be concluded that the unfunctionalized C-Bpin site is also in this case the reason for an unsuccessful oxidation of the trialkylgermanium handle.

In Scheme 39B the two compounds **13** and **15** have been used to demonstrate the limitations of the sulfonyl trapping reagent reaction. The successful cyanation of the C-GeEt₃ handle was already showcased in the publication,^[111] but when the same conditions were applied to the compounds bearing the oxidized C-Bpin group, again no desired product formation could be observed. The alkylgermanium starting materials were consumed, based on GC-MS, but no product generation could be detected. In comparison to that, under dual photoredox nickel cross-coupling conditions these starting materials yielded in the wanted products (**25** and **28**).

Scheme 39 | Unsuccessful results with the dual photoredox nickel catalysis (A) and sulfonyl trapping reagent (B).

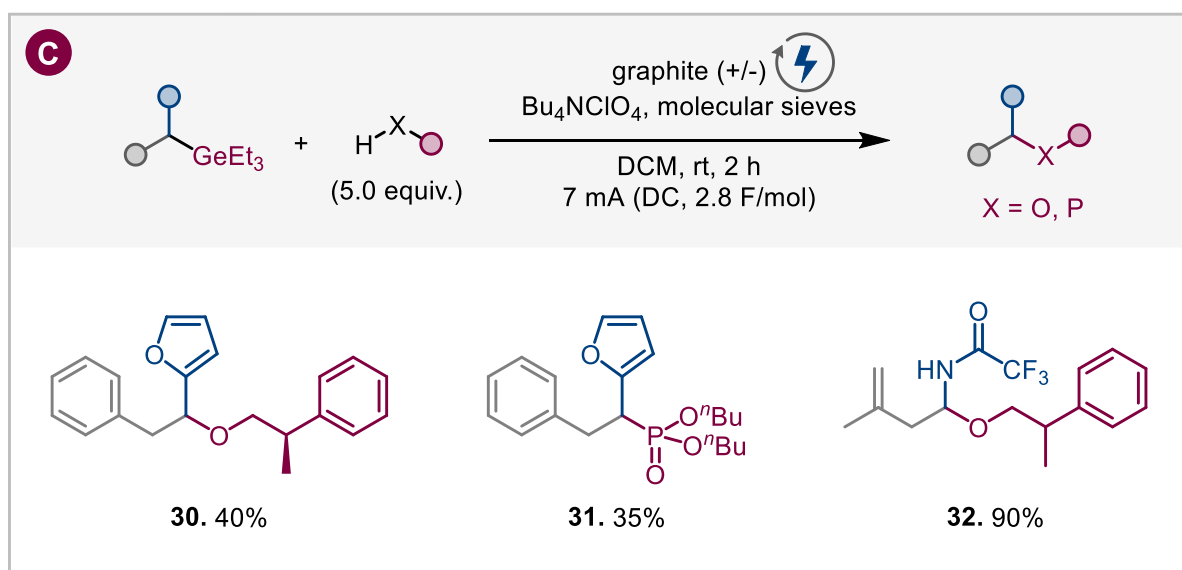
Reaction conditions: A) Alkylgermane (1.0 equiv.), aryl bromide (2.0 equiv.), $\text{'Bu-Acr}^+\text{-Mes BF}_4^-$ (0.05 equiv.), $[\text{NiCl}_2(\text{phen})]$ (0.03 equiv.), ACN, rt, 24 h, blue LED. B) Alkylgermane (1.0 equiv.), sulfonyl trapping reagent (3.0 equiv.), $\text{'Bu-Acr}^+\text{-Mes BF}_4^-$ (0.05 equiv.), DCE, rt, 24 h, blue LED.

In parallel to this work, a novel electrochemical methodology for alkylgermane functionalization has been developed by Markus Schoetz,^[110, 174] offering a versatile platform for the formation of diverse carbon-heteroatom bonds, particularly C–O and C–N bonds, which are highly relevant in the pharmaceutical and agrochemical industries.^[197, 198] In contrast, photochemical approaches predominantly yield new C–C

bonds, with only a few exceptions reported, such as chlorination, azidation, and C–S bond formation.^[111] While the photochemical methods rely on the formation of an alkyl radical, the electrochemical approach further oxidizes the radical to a carbocation, which can be utilized for reactions with numerous nucleophiles.

At the outset of this project, Markus Schoetz and Kristina Deckers (technician from our group) carried out the optimization of reaction conditions for the successful electrochemical transformation of the alkylgermane group with different nucleophiles, generating a broad portfolio of several new carbon bond formations. They found that an undivided cell with graphite electrodes, Bu₄NClO₄ as electrolyte and molecular sieves in DCM resulted in the best yields. Building on the successful full functionalization of the established building block **A**, subsequent efforts focused on enabling heteroatom-carbon bond formation (particularly C–O and C–P), which was previously unachievable under radical conditions (Scheme 40). Following the same sequence as shown before in the photochemical approach, the C_{sp}³–Cl site must be functionalized in the first step, with a subsequent transformation of the C_{sp}³–Bpin site. In the examples shown compound **17** was utilized, which was previously functionalized with a benzyl Grignard and furan as heterocycle. The first example was demonstrated with the alcohol (*R*)-2-phenyl-1-propanol, resulting in the desired product **30** with a yield of 40%. Secondly, the same alkylgermane starting material was used for the C–P bond formation using tributyl phosphite and resulted in product **31** in 35% yield. The third alkylgermane starting material was synthesized by Annika Hoeppner under the supervision of Markus Schoetz, following the reported procedures,^[72] which contains a double bond on the alkyl chain as well as a protected amine on the C_{sp}³–Bpin site. With this starting material the racemic 2-phenyl-1-propanol was used as nucleophile to generate the desired product **32** in an excellent yield of 90%. The furan containing starting material resulted in a significantly lower yield than the amine protecting group compound, which was not only observed during my studies but as well as for my other colleagues as reported in our publications.^[110, 111]

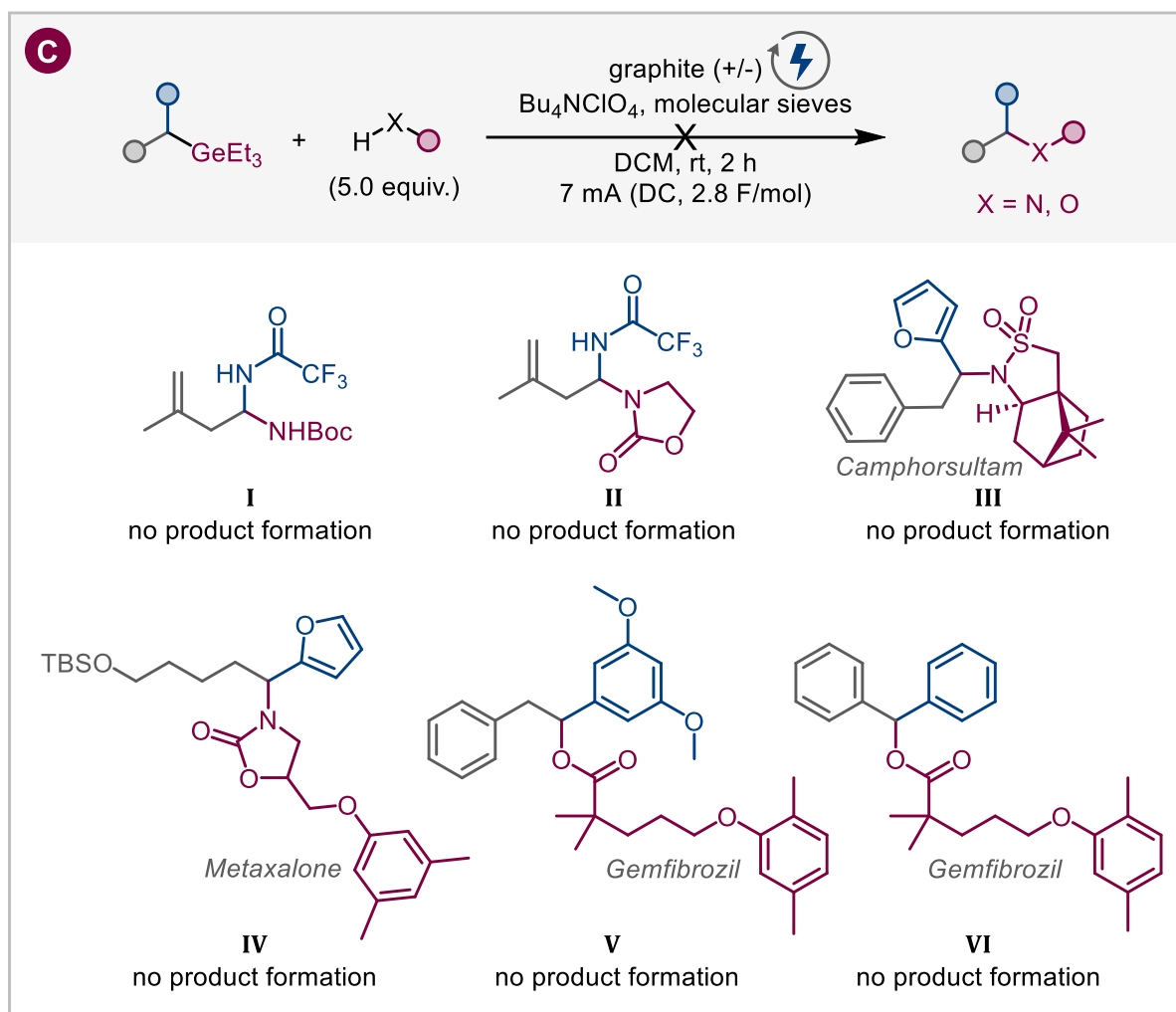
Scheme 40 | Electrochemical full functionalization of the building block.



Reaction conditions: Alkylgermane (1.0 equiv.), nucleophile (5.0 equiv.), ⁿBu₄ClO₄ (0.3 mmol), DCM (3 mL), 4 Å molecular sieve (150 mg), rt, 7 mA, 2.8 F/mol.

Besides the successfully synthesized substrates, different nucleophiles were identified which were not productive in building up a complex molecule structure. Most of the nucleophiles which are unproductive showed product formation in moderate to high yields with simpler organogermanium compounds in the publication.^[110] The generation of either no product, or only trace quantities in the GC-MS analysis, is likely due to the increased complexity of the building block bearing various functionalities. Selected examples of unproductive nucleophiles and alkylgermanium species are shown in Scheme 41.

Scheme 41 | Unproductive nucleophiles in the electrochemical functionalization of C-GeEt₃.



Reaction conditions: Alkylgermane (1.0 equiv.), nucleophile (5.0 equiv.), Bu_4NClO_4 (0.3 mmol), DCM (3 mL), 4 Å molecular sieve (150 mg), rt, 7 mA, 2.8 F/mol.

The same alkylgermane that gave an excellent yield in the previous reaction with an alcohol as nucleophile, was unsuccessful with different carbamates or oxazolidinones (**I** and **II**). Also, the sulfonamide camphorsultam and **17** did not generate the desired product (**III**) under standard conditions as demonstrated in the publication.^[110] In this particular case, the sulfonamide could be used as productive nucleophile, when the C_{sp^3} -Bpin site was functionalized with an amide group in advance.^[110] Another oxazolidinone containing nucleophile was tested with the drug Metaxalone, a drug prescribed for muscle relaxation and pain relief,^[199] and the alkylgermane **18** as starting materials. However, compound **18** was not suitable for this nucleophile and resulted in no desired product (**IV**) formation. Interestingly, the

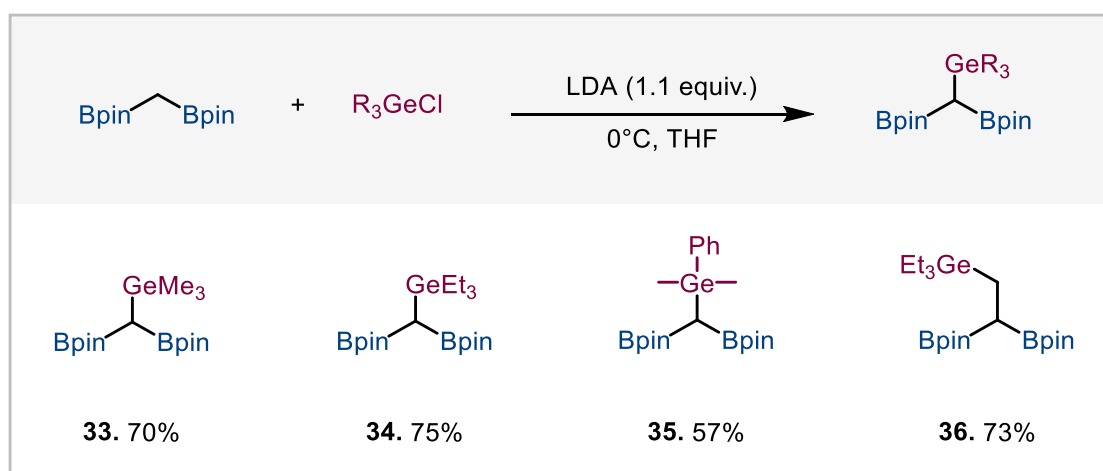
compounds obtained after heteroarylation with furan at the C_{sp}³-Bpin site were generating the desired products, when alcohol (**30**) or phosphite (**31**) were used as nucleophiles (Scheme 40). Another interesting nucleophile for the electrochemical transformation of the C_{sp}³-GeEt₃ site is the drug Gemfibrozil, which is used to treat abnormally high or low blood lipid levels.^[200] In this specific case the nucleophile is an acid, which showed successful product formation in our publication.^[110] Nonetheless, neither building block **19** nor **22** were suitable candidates for the desired product formation of **V** and **VI**, respectively.

2.2.7 Alternative approach for a building block achieving full functionalization

The established building block **A** represents a compound that contains three different functional groups on the same carbon atom. These three handles were shown to be transformed under their own specific conditions, allowing rapid access to a variety of complex structures as shown in the previous chapters. Although each functional group had to be decorated in a sequential way, building block **A** was successfully demonstrated as versatile linchpin for a diverse substrate scope. Besides this building block, also other potential starting platforms were considered as efficient molecules to build up high complexity within a few steps. The investigations described in this chapter were conducted in parallel with the preceding studies, which led to the examination of photocatalytic oxidation of the C–Ge motif in the presence of the C–Bpin group.

One promising alternative candidate is a building block containing two C–Bpin groups (bis-Bpin) on the same carbon as the C–GeEt₃ moiety. Similar building blocks like this have been reported in the literature, which implemented a silane, stannane or halide instead of the alkylgermane group as described in the introduction part (Chapter 2.1.1.).^[118, 122, 201–205] Since these functionalities have rather limited possibilities to be efficiently transformed, an alternative platform containing a trialkylgermane group might overcome their known limitations. This building block was synthesized in a straightforward pathway *via* one simple step, using bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane and R₃GeCl as starting materials. The reaction procedure obtaining the desired products in high yields is based on a publication from Matteson in the early 1980s.^[206] He described the deprotonation of 1,1-diboronic esters and a subsequent reaction of the formed carbanion with an alkyl halide using LiTMP in THF. Based on this publication, initial results using LDA, instead of LiTMP, showed desired product formation in GC-MS analysis and were used for the synthesis in large scales (Scheme 42). The 1,1-diboronic ester bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane was in every case the starting material for the shown syntheses. By selecting different trialkylgermanium chloride species it was possible to synthesize a variety of new building blocks.

Scheme 42 | Synthesis of the alternative bis-Bpin building blocks.

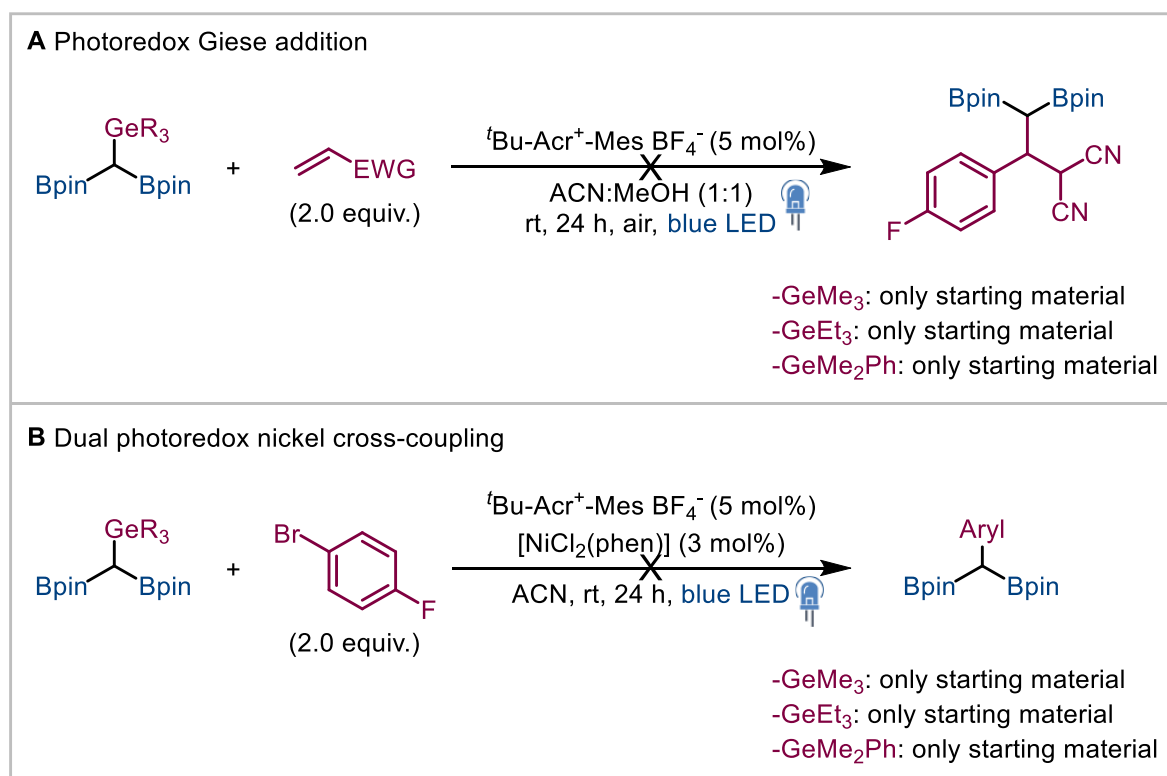


Reaction conditions: bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (1.0 equiv.), R₃GeCl (1.0 equiv.), LDA (1.1 equiv.), THF (0.3 M), 0°C, overnight.

First, Me_3GeCl and Et_3GeCl were used to synthesize the corresponding compounds in satisfying yields of 70% (**33**) and 75% (**34**), respectively. A different alkylgermanium chloride, Me_2PhGeCl , was also employed in the reaction which furnished the desired product **35** in 57% yield. The last building block was prepared from (chloromethyl)triethylgermane, which is also synthesized in the first step of the established building block **A**.^[72] Following the same procedure, the wanted compound **36** was synthesized in 73% yield.

The synthesized building blocks were further applied in the established reaction conditions known to decorate the $\text{C}_{\text{sp}^3}\text{-Ge}$ site (Scheme 43). Even though it was shown in Dr. Aymane Selmani's publication^[72] that the trialkylgermanium group could be photochemically oxidized in presence of the unfunctionalized Bpin group, it was not possible to use any other alkyl group than the benzylic Grignard (**7**) for a successful transformation. It was investigated to further explore the reactivity of the $\text{C}_{\text{sp}^3}\text{-Ge}$ unit when attached to a bis-Bpin on the same carbon. In Scheme 43A, investigations were made about the reaction outcome under the established photocatalytic Giese addition conditions. Building blocks **33-35** were not productive under the applied conditions, resulting in untouched starting materials. To further prove that the $\text{C}_{\text{sp}^3}\text{-Ge}$ moiety cannot be oxidized when located on the same carbon atom as two Bpin groups, the reactivity under the dual photoredox cross-coupling conditions with the nickel catalyst was evaluated (Scheme 43B). Again, the building blocks did not show any desired product formation, leaving the starting materials untouched. A candidate for a potentially successful reaction would be building block **36**, since in the previously mentioned publication it was shown that also primary alkylgermanium groups could be utilized in the Giese addition.^[72]

Scheme 43 | Photocatalyzed oxidation of the C-Ge bond of the new building blocks.

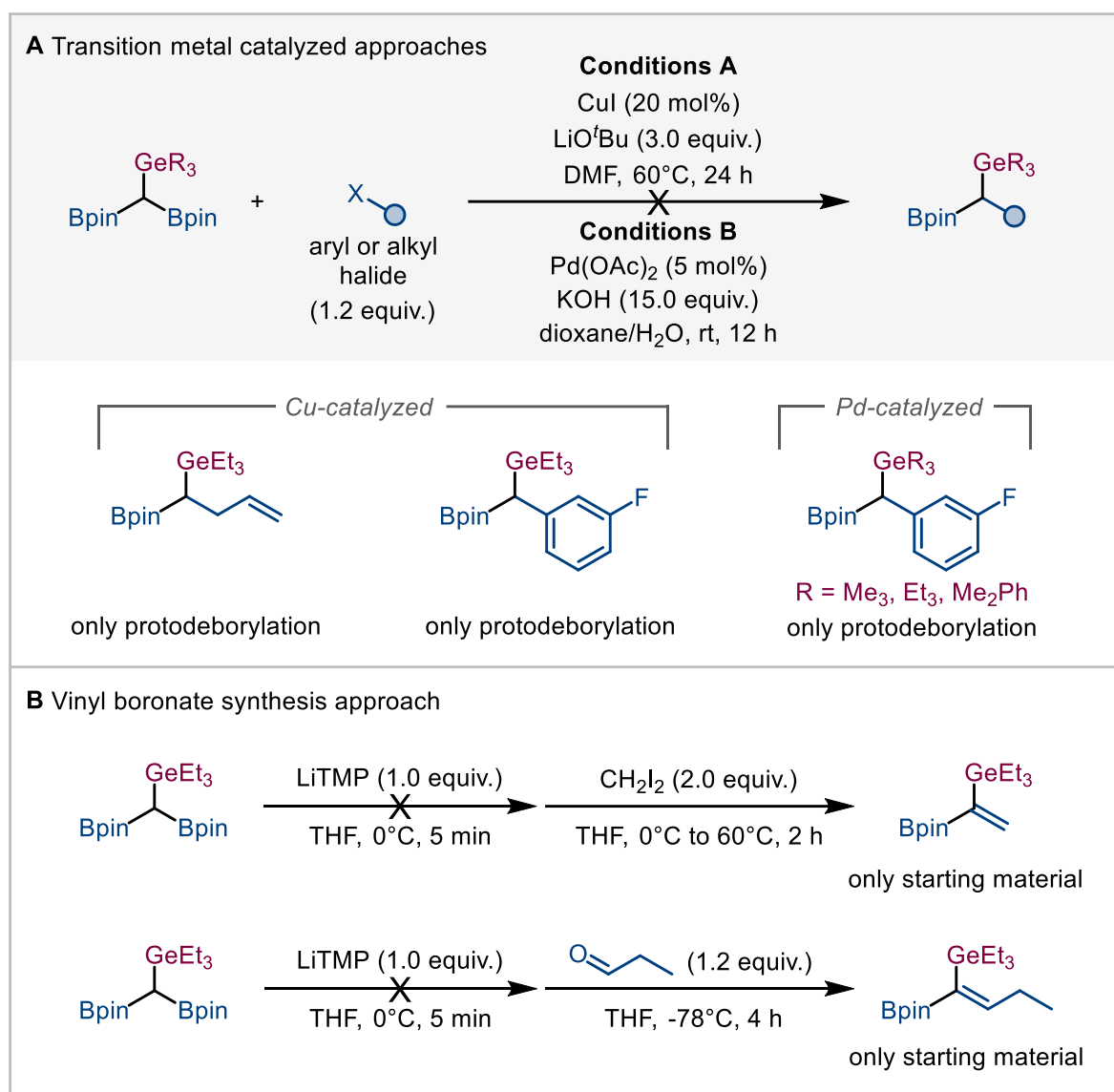


Reaction conditions: A) Building block (1.0 equiv.), Michael acceptor (2.0 equiv.), $t\text{Bu-Acr}^+\text{-Mes BF}_4^-$ (0.05 equiv.), ACN:MeOH (1:1, 0.2 M), rt, 24 h, blue LED. B) Building block (1.0 equiv.), aryl bromide (2.0 equiv.), $t\text{Bu-Acr}^+\text{-Mes BF}_4^-$ (0.05-0.1 equiv.), $[\text{NiCl}_2(\text{phen})]$ (0.03 equiv.), ACN, rt, 24 h, blue LED.

These results are in line with the previous observations that were made, that the C-Bpin handle has to be functionalized as a first step. Based on that, it was further continued with different literature reported approaches for the functionalization of bis-Bpin groups (Scheme 44).^[201, 203] In recent years, various methods have been developed to transform one of these groups predominantly into a new carbon-carbon bond. Following this pathway, it would be similar to the previously shown building block **A**, which also had to be functionalized first on the C-Cl site with alkyl or aryl Grignard species.

Several well-known transition metal catalyzed functionalization of bis-Bpin groups are depicted in Scheme 44A, showing the utilization of a copper and palladium catalyzed approach.^[207, 208] In conditions A, CuI is used in catalytic amounts with a stoichiometric amount of LiO^tBu as base in DMF at elevated temperatures.^[207] In their publication it was shown, that even substituted 1,1-diborylalkanes were efficiently reacted with corresponding alkyl halides to form the product in high yields. When the reaction was repeated under the same conditions with building block **34**, only protodeborylation of one Bpin group was observed in GC-MS analysis. Since the alkyl bromide did not form any of the desired product, it was also tested if an aryl bromide would furnish the desired product, but again only protodeborylation of the starting material was observed. Switching to the palladium catalyzed Suzuki cross-coupling reaction with aryl halides, the literature reported conditions from the Morken group were used (conditions B).^[208] In these examples building blocks **33-35** were used with an aryl iodide, but no desired product was formed and only protodeborylation of one Bpin group was observed in GC-MS.

Besides these transition metal catalyzed approaches, there are also various other transformations shown in literature.^[203] For example, the synthesis of vinyl boronates *via* a boron-Wittig type reaction from a bis-C-Bpin handle was demonstrated by the group of Morken, based on initial results from Matteson.^[209] In this example, LiTMP was used to deprotonate the central carbon of the bis-Bpin compound which then reacts with an aldehyde to form the desired vinyl boron compound. Following both of their shown reaction conditions with building block **34**, no desired products could be observed, with the starting material remaining untouched (Scheme 44B). The observed lack of product formation could be rationalized by the fact that in their publication only linear alkyl substituents were shown and that one example with a *tert*-butyl group had only 30% of conversion without a given yield. Based on their results it can be postulated that the bulky GeEt₃ group might not be suitable under these conditions.

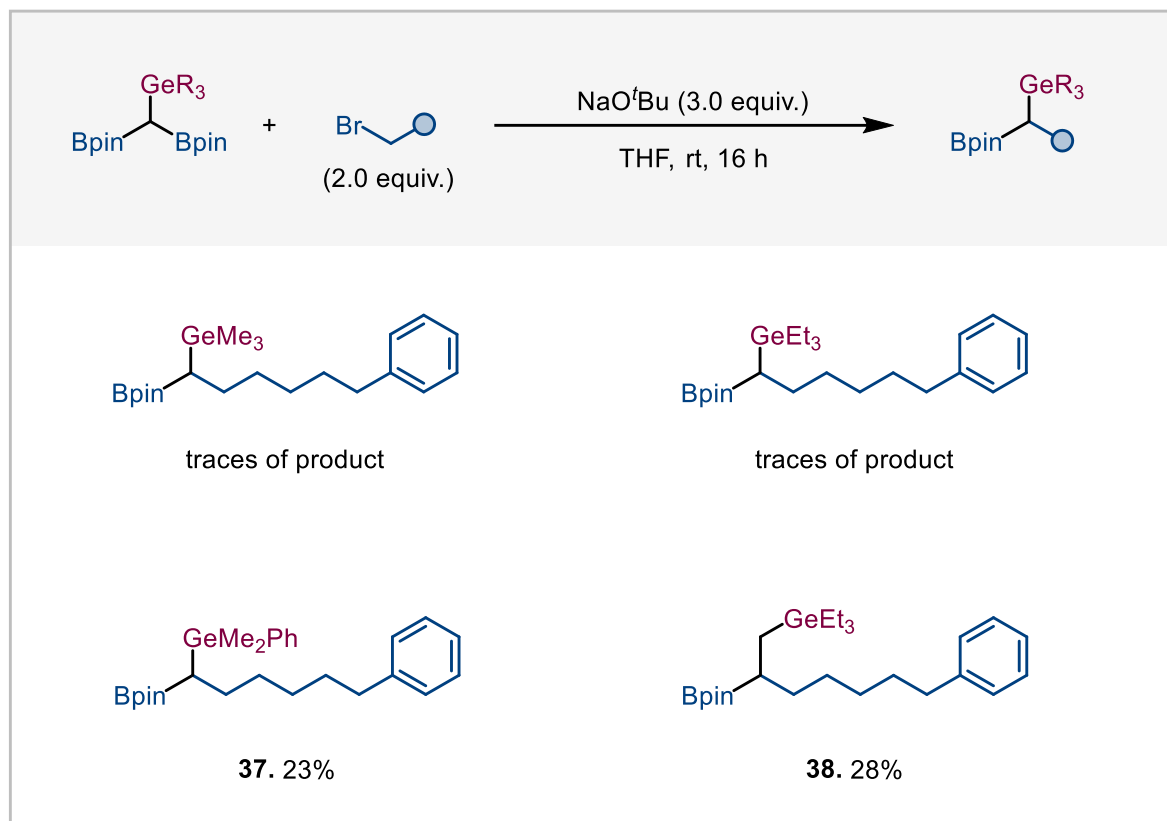
Scheme 44 | Different attempts to functionalize the bis-Bpin group.

Reaction conditions: A) Conditions A: Building block (1.0 equiv.), alkyl or aryl halide (1.2 equiv.), Cul (0.2 equiv.), DMF (0.2 M), 60°C, 24 h. Conditions B: Building block (1.0 equiv.), aryl halide (1.2 equiv.), Pd(OAc)₂ (0.05 equiv.), KOH (15.0 equiv.), dioxane/H₂O, rt, 12 h. B) top: building block (1.0 equiv.), LiTMP (1.0 equiv.), THF, 0°C, 5 min, then CH₂I₂ (2.0 equiv.), THF, 0°C to 60°C, 2 h. bottom: building block (1.0 equiv.), LiTMP (1.0 equiv.), THF, 0°C, 5 min, then aldehyde (1.2 equiv.), THF, -78°C, 4 h.

Another transition metal free approach was published by the group of Morken on the base mediated alkylation of bis-Bpin groups.^[210] In these conditions they explored the utilization of stoichiometric amounts of NaO^tBu in THF at room temperature, to obtain the desired alkylated products in high yields. Besides simple bis-Bpin compounds, fully substituted examples were shown to efficiently generate the wanted products. In Scheme 45, all synthesized building blocks were used for the previously described reaction conditions, applying (5-bromopentyl)benzene as alkylating reagent. Analogous to the already shown transformation attempts, building blocks **33** and **34** did not result in the desired products and only showed traces of formed products in GC-MS analysis. Once again it was postulated that the bulkiness of the substituents might interfere with the alkyl halide and thus inhibit the product formation. Interestingly, when building block **35** was used, the desired product **37** was generated in a yield of 23%. The difference

between building block **33** and **35** is that one methyl group on the C–Ge moiety was exchanged with a phenyl group, which might impact both the steric hindrance and electronic properties of the substrate sufficiently, that the desired product formation in moderate yield took place. Fortunately, building block **36** also formed the desired product **38** in 28% yield, demonstrating two successful examples for the base mediated alkylation of the bis-Bpin unit, when a germanium handle is located on the same carbon atom or on the neighboring one.

Scheme 45 | The partially successful alkylation of the bis-Bpin unit.



Reaction conditions: Building block (1.0 equiv.), alkyl halide (2.0 equiv.), NaO^tBu (3.0 equiv.), THF (0.15 M), rt, 16 h.

Based on the results obtained with the bis-Bpin building blocks **33–36** it was decided not to continue using these alternative platforms for the sequential full functionalization. As demonstrated with compound **37** and **38**, the yields were relatively low and the same structures could be synthesized with significantly higher yields from building block **A**, with an alkyl Grignard reagent. Because of this, no further functionalization attempts were conducted on **37** and **38**, leaving the bis-Bpin unit as potential alternative to the already established building block.

2.2.8 Summary

In summary, the work in this chapter started with the optimization studies of the Giese addition using **cat3**, where various reaction parameters were evaluated, including wavelength, solvent concentration, catalyst loading and Michael acceptor equivalents. In addition to this, it was found out that the photocatalyst "9-HTXTF" is also feasible for the activation of the carbon-germanium bond to form the desired product. However, the yield was lower than that achieved with the acridinium based photocatalyst and not further investigated.

A scope was shown that the C-GeEt₃ unit could be efficiently transformed under photoredox conditions by trapping the generated alkyl radical (found by Markus Schoetz) with various sulfonyl compounds to introduce nitrile, vinyl or alkyne groups. Furthermore, the polarity transduction approach was applied, developed by Silvi and co-workers for alkyl carboxylic acids,^[178] to demonstrate that the alkylgermanium motif is also a feasible functional group for the Giese addition of formally electron rich double bonds. With this new functionalization in hand, it is now possible to use electron deficient Michael acceptors for the established Giese addition or formally electron rich double bonds for the telescopic approach utilizing vinyl sulfonium salts.

Since the full functionalization of building block **A** was the primary objective of this chapter, it was demonstrated that the alkylgermanium handle had to be functionalized after the C-Bpin, due to low or no reactivity in the presence of this functional group. Therefore, a sequential functionalization of the established building block had to be followed to achieve rapid access to a variety of complex molecule structures. Based on reactivities reported in the literature, the C-Cl handle was functionalized with alkyl Grignard reagents to obtain the desired products in high yields. Following on from this, various reported functionalizations of the C-Bpin group were applied, such as the quantitative oxidation to alcohols, Aggarwal (hetero)arylation, Zweifel olefination as well as the palladium catalyzed Suzuki cross-coupling with aryl halides. In the last step, the C-GeEt₃ unit was decorated with the established Giese addition^[72] and the dual photoredox catalysis with nickel,^[73] to achieve the full functionalization of the building block. In the latter one, it was investigated that compounds in which the C-Bpin group had been previously oxidized to an alcohol underwent photoredox catalyzed oxidation under standard conditions, generating the corresponding α -aryl ketone. In this context, natural product derivatives like menthol and fenchol were shown to be productive under the applied conditions, generating the desired compounds.

In parallel to that, it was also applied that the C-GeEt₃ handle can be oxidized under electrochemical conditions (developed by Markus Schoetz) to form a carbocation and react with incoming nucleophiles. Following the aim to show the full functionalization of the building block, three different fully decorated structures with moderate to high yields were synthesized.

Finally, an alternative set of building blocks with a bis-Bpin group were synthesized and tested under the demonstrated transformation conditions. However, only the base mediated alkylation showed successful product formation in rather low yield. The same products could have been synthesized with the established building block **A** under Grignard conditions, with most likely significantly higher yields and therefore no further investigations with these building blocks were carried out.

3

Supporting Information

3 Supporting Information

3.1 General experimental details

Techniques

All reactions were performed utilizing standard Schlenk techniques under an Argon atmosphere or inside a glovebox unless otherwise stated. Glassware and magnetic stir bars were dried in an oven (110 °C) for at least 24 hours prior to use. Unless otherwise stated, experiments were carried out at room temperature (25 ± 2 °C). The removal of solvents in vacuo was achieved using a rotary evaporator (bath temperatures up to 40 °C) at a pressure of 20 mmHg (diaphragm pump), or at 0.1 mmHg (oil pump) on a vacuum line at room temperature.

Solvents, reagents and starting materials

Unless otherwise stated, all anhydrous solvents were purchased from Sigma Aldrich. Anhydrous 1,3-dimethyl-2-imidazolidinone (DMI, absolute, over molecular sieve (H₂O ≤0.04%), ≥99.5% (GC)) was purchased from Sigma Aldrich. *Note: DMI with lower purity than 90% and higher contamination of H₂O leads to low conversion.* LiO^tBu (99.99% trace metal basis) was purchased from Alfa Aesar and CsF (99.9%) was purchased from chemPUR. THF and Et₂O were dried using a PS-MD-5 solvent purification system from Innovative Technology. Technical grade solvents were distilled prior to use for chromatography and extraction.

Unless otherwise stated, all reagents and starting materials were commercially available and used as received.

Purification

Thin layer chromatography (TLC) was performed on Macherey Nagel ALUGRAM Xtra SIL G UV254 aluminium plates with unmodified silica and visualized either under UV light or stained with iodine or KMnO₄. Flash silica gel column chromatography was performed with silica gel (0.04 – 0.063 mm particle size) purchased from Macherey Nagel. Preparative HPLC was performed on a Knauer Azura HPLC (employing UV detector 2600, at 254 and 230 nm) using a LiChrosorb Si60 column (Merck, 250 x 25 mm, 7 µm silica porosity).

Characterization

All ¹H, ¹³C and ¹⁹F NMR spectra were recorded on Bruker Avance Neo 600, Varian VNMRs 600 or Varian VNMRs 400 or Bruker Avance Neo 400 spectrometers at ambient temperature (unless otherwise specified). Chemical shifts (δ) are reported in parts per million (ppm) and were referenced either to residual solvent peak (for ¹H and ¹³C spectra) or internally by the instrument after locking and shimming to the deuterated solvent (for ¹⁹F). Coupling constants (*J*) are given in Hertz (Hz). Multiplicities of signals in ¹H, ¹⁹F, and ¹³C NMR were designated as s (singlet), d (doublet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublets of doublets), t (triplet), td (triplet of doublets), q (quartet), p (quintet), h (sextet), hept (septet), and m (multiplet).

Gas chromatography coupled with mass spectrometry (GC-MS) was performed on an Agilent Technologies 5975 series MSD mass spectrometer under electrospray ionization (EI) mode coupled with an Agilent

Technologies 7820A gas chromatograph employing an Agilent 19091s-433 HP-5MS column (30 m x 0.250 μm x 0.250 μm). High-resolution mass spectrometry (HRMS) was performed using a Thermo Scientific LTQ Orbitrap XL spectrometer (ESI), Finnigan MAT 95 (EI) or Bruker Maxis II LC-MS-System (APCI). Low-resolution masses of known compounds were extracted from their GC-MS chromatograms. IR spectra were recorded on a Spectrum 100 spectrometer with a UATR Diamond/KRS-5 crystal with attenuated total reflectance (ATR).

ICP-MS analysis was conducted on an Agilent 8900 Triple Quadrupole (ICP QQQ) at the RWTH Uniklinik Aachen.

Photo- and electrochemistry setup

All the photochemical reactions were carried out in an EvoluChem™ PhotoRedOxBox (see photo below, left) equipped with one EvoluChem 450PF LED lamp ($\lambda_{\text{max}} = 450 \text{ nm}$, 30 W) or in a setup made of a foiled vessel (135 mm) equipped with a blue LED stripe (1 m, 18.6 W, 465 – 470 nm, $\lambda_{\text{max}} = 467 \text{ nm}$), a stirring plate, and two cooling fans providing ambient temperature (see photo below, middle). The blue LED stripe was purchased from Ledxon® GmbH.^[111]

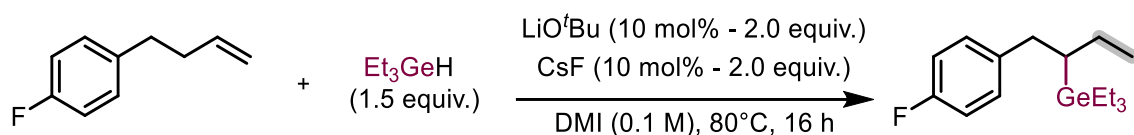
All electrochemical reactions were performed using an IKA ElectraSyn2.0 instrument equipped with two graphite electrodes and a 5mL vial with magnetic stir bar (see photo below, right).^[110]



3.2 Supporting information for chapter 1

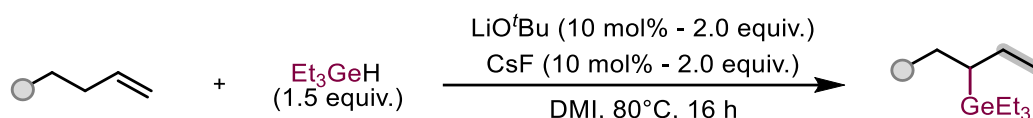
3.2.1 Optimization of reaction conditions

All reaction optimization and screening reactions were carried out using the following general procedure:



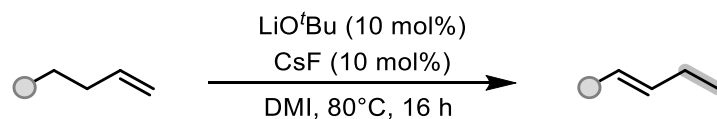
In an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (0.1-2.0 equiv.) and CsF (0.1-2.0 equiv.) and dissolved in anhydrous DMI (1.0 mL, 0.1 M). To the mixture were added 1-(but-3-en-1-yl)-4-fluorobenzene (15.0 mg, 0.1 mmol, 1.0 equiv.) and Et_3GeH (24.3 μL , 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature 1,4-difluorobenzene was added as internal standard for ^{19}F NMR yield determination. Additionally, a small aliquot was taken and analyzed by GC-MS.

3.2.2 General procedure A



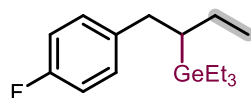
In an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (10 mol% - 2.0 equiv.) and CsF (10 mol% - 2.0 equiv.) and dissolved in anhydrous DMI (1.0 mL, 0.1 M). To the mixture were added the alkene (0.10 - 0.30 mmol, 1.0 equiv.) and Et_3GeH (0.15 - 0.45 mmol, 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

3.2.3 General procedure B



In an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (10 mol%) and CsF (10 mol%) and dissolved in anhydrous DMI (1.0 mL, 0.1 M) and to the mixture was added the alkene (0.10 - 0.30 mmol, 1.0 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel to obtain the desired product.

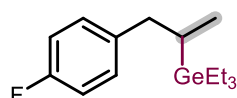
3.2.4 Characterization data of products

Triethyl(1-(4-fluorophenyl)butan-2-yl)germane (1)

Prepared, following the general procedure A from 1-(but-3-en-1-yl)-4-fluorobenzene (45.1 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (81.2 mg, 0.26 mmol, 87%).

Prepared, following the general procedure A from 1-(but-3-en-1-yl)-4-fluorobenzene (45.1 mg, 0.30 mmol) with KO^tBu (3.4 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (81.4 mg, 0.26 mmol, 87%).

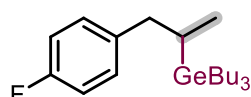
R_f = 0.84 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.14 – 7.09 (m, 2H), 6.97 – 6.92 (m, 2H), 2.75 (dd, J = 14.0, 5.4 Hz, 1H), 2.59 (dd, J = 14.1, 10.3 Hz, 1H), 1.49 – 1.38 (m, 2H), 1.37 – 1.32 (m, 1H), 1.03 (t, J = 7.9 Hz, 9H), 0.86 (t, J = 7.4 Hz, 3H), 0.77 – 0.71 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 161.3 (d, J = 242.9 Hz), 138.7 (d, J = 3.1 Hz), 130.2 (d, J = 7.5 Hz), 114.9 (d, J = 21.1 Hz) 36.3, 29.5, 23.2, 13.7, 9.3, 3.9. **¹⁹F NMR** (564 MHz, CDCl₃) δ /ppm = -118.18 (s, 1F). **HRMS** (APCI) calculated for C₁₄H₂₂GeF: 283.0912 [M-CH₂CH₃]⁺, found: 283.0904. **IR** (neat): ν /cm⁻¹ = 2951, 2871, 1878, 1601, 1507.

Triethyl(1-(4-fluorophenyl)propan-2-yl)germane (2)

Prepared, following the general procedure A from 1-allyl-4-fluorobenzene (40.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (71.3 mg, 0.24 mmol, 80%).

Prepared, following the general procedure A from 1-allyl-4-fluorobenzene (40.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.) but Et₃GeSiMe₂Ph (132.8 mg, 0.45 mmol, 1.5 equiv.) as Germanium source. The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (8.9 mg, 0.03 mmol, 10%).

R_f = 0.91 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.12 – 7.07 (m, 2H), 6.98 – 6.92 (m, 2H), 2.86 (dd, J = 13.7, 4.1 Hz, 1H), 2.40 – 2.33 (m, 1H), 1.38 – 1.30 (m, 1H), 1.05 (t, J = 7.9 Hz, 9H), 0.92 (d, J = 7.3 Hz, 3H), 0.76 (q, J = 7.8 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 161.34 (d, J = 242.9 Hz), 138.38 (d, J = 3.3 Hz), 130.16 (d, J = 7.8 Hz), 114.9 (d, J = 21.1 Hz) 39.0, 21.5, 15.4, 9.3, 2.9. **¹⁹F NMR** (564 MHz, CDCl₃) δ /ppm = -118.23 (s, 1F). **HRMS** (APCI) calculated for C₁₃H₂₀GeF: 269.0755 [M-CH₂CH₃]⁺, found: 269.0755. **IR** (neat): ν /cm⁻¹ = 2947, 2870, 2323, 1881, 1507, 1222.

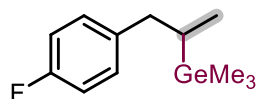
Tributyl(1-(4-fluorophenyl)propan-2-yl)germane (3)

Prepared, following the general procedure B from 1-allyl-4-fluorobenzene (40.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.), CsF (4.6 mg, 0.03 mmol, 0.1 equiv.) and tributylgermanium hydride (110.2 mg, 0.45 mmol, 1.5 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (90.4 mg, 0.24 mmol, 79%).

R_f = 0.74 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.12 – 7.07 (m, 2H), 6.98 – 6.93 (m, 2H), 2.85 (dd, J = 13.8, 4.3 Hz, 1H), 2.34 (dd, J = 13.8, 11.5 Hz, 1H), 1.38 – 1.30 (m, 13H), 0.93 – 0.88 (m, 12H), 0.77 – 0.71

(m, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 161.33 (d, J = 242.8 Hz), 138.43 (d, J = 3.1 Hz), 130.17 (d, J = 7.7 Hz), 114.91 (d, J = 20.9 Hz), 39.0, 27.8, 26.9, 22.1, 15.4, 13.9, 11.4. **¹⁹F NMR** (564 MHz, CDCl₃) δ /ppm = -118.3. **HRMS** (ESI) calculated for C₁₇H₂₈FGe: 325.1381 [M-(CH₂)₃CH₃]⁺, found: 325.1380. **IR** (neat): ν /cm⁻¹ = 2955, 2860, 1507, 1233, 1080.

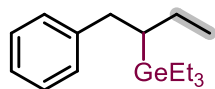
(1-(4-Fluorophenyl)propan-2-yl)trimethylgermane (4)



Prepared, following the general procedure B from 1-allyl-4-fluorobenzene (40.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.), CsF (4.6 mg, 0.03 mmol, 0.1 equiv.) and hexamethyldigermane (106.0 mg, 0.45 mmol, 1.5 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (36.1 mg, 0.14 mmol, 47%).

R_f = 0.56 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.13 – 7.07 (m, 2H), 6.99 – 6.92 (m, 2H), 2.80 (dd, J = 13.8, 5.3 Hz, 1H), 2.37 (dd, J = 13.8, 10.7 Hz, 1H), 1.20 (dq, J = 13.6, 6.9 Hz, 1H), 0.92 (d, J = 7.3 Hz, 3H), 0.08 (s, 9H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 161.4 (d, J = 242.9 Hz), 138.2 (d, J = 3.2 Hz), 130.2 (d, J = 7.7 Hz), 114.6 (d, J = 20.9 Hz), 38.7, 23.9, 15.1, -3.9. **¹⁹F NMR** (564 MHz, CDCl₃) δ /ppm = -118.2. **HRMS** (ESI) calculated for C₁₁H₁₆FGe: 241.0442 [M-CH₃]⁺, found: 241.0442. **IR** (neat): ν /cm⁻¹ = 2956, 2862, 1507, 1224, 819.

Triethyl(1-phenylbutan-2-yl)germane (5)



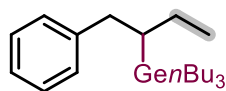
Prepared, following the general procedure A from but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (80.0 mg, 0.27 mmol, 92%).

Prepared, following the general procedure A from but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.) but Et₃GeSiMe₂Ph (132.8 mg, 0.45 mmol, 1.5 equiv.) as Germanium source. The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (8.8 mg, 0.03 mmol, 10%).

Prepared, following general procedure A from a mixture of olefins in a 1:1:1 ratio (39.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (71.3 mg, 0.24 mmol, 81%).

Prepared, following the general procedure A from but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) with KO^tBu (3.4 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (79.7 mg, 0.27 mmol, 91%).

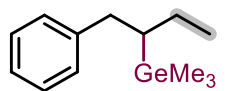
R_f = 0. (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.30 – 7.25 (m, 2H), 7.21 – 7.15 (m, 3H), 2.80 (dd, J = 13.9, 4.9 Hz, 1H), 2.63 (dd, J = 13.6, 10.3 Hz, 1H), 1.51 – 1.38 (m, 3H), 1.05 (t, J = 7.9 Hz, 9H), 0.88 (t, J = 7.3 Hz, 3H), 0.76 (q, J = 7.8 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 143.2, 129.0, 128.2, 125.7, 37.1, 29.3, 23.3, 13.7, 9.4, 3.9. **HRMS** (ESI) calculated for C₁₄H₂₃Ge: 265.1006 [M-CH₂CH₃]⁺, found: 265.0999. **IR** (neat): ν /cm⁻¹ = 3026, 2951, 2871, 1456, 1428.

Tributyl(1-phenylbutan-2-yl)germane (6)

Prepared, following the general procedure A from but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.), CsF (4.6 mg, 0.03 mmol, 0.1 equiv.) and tributylgermanium hydride (110.2 mg, 0.45 mmol, 1.5 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (94.1 mg, 0.25 mmol, 83%).

Prepared, following the general procedure A from but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) with KO^tBu (3.4 mg, 0.03 mmol, 0.1 equiv.) and tributylgermanium hydride (110.2 mg, 0.45 mmol, 1.5 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (79.2 mg, 0.21 mmol, 70%).

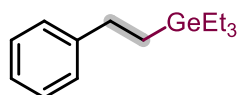
$R_f = 0.81$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.29 - 7.24$ (m, 2H), 7.20 - 7.15 (m, 3H), 2.79 (dd, $J = 13.9, 5.3$ Hz, 1H), 2.62 (dd, $J = 13.9, 10.2$ Hz, 1H), 1.51 - 1.40 (m, 2H), 1.40 - 1.28 (m, 13H), 0.90 (t, $J = 7.0$ Hz, 9H), 0.87 (t, $J = 7.4$ Hz, 3H), 0.76 - 0.69 (m, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta/\text{ppm} = 143.2, 129.0, 128.2, 125.7, 37.1, 29.9, 27.8, 27.0, 23.4, 13.9, 13.7, 12.4$. **HRMS** (EI) calculated for $\text{C}_{18}\text{H}_{31}\text{Ge}$: 321.1632 [$\text{M} - (\text{CH}_2)_3\text{CH}_3$] $^+$, found: 321.1631. **IR** (neat): $\nu/\text{cm}^{-1} = 2956, 2858, 1457, 1079$.

Trimethyl(1-phenylbutan-2-yl)germane (7)

Prepared, following the general procedure A from but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.), CsF (4.6 mg, 0.03 mmol, 0.1 equiv.) and hexamethyldigermane (106.0 mg, 0.45 mmol, 1.5 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (42.3 mg, 0.17 mmol, 56%).

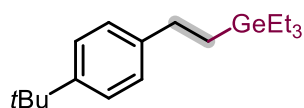
Prepared, following the general procedure A from but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) with KO^tBu (3.4 mg, 0.03 mmol, 0.1 equiv.) and hexamethyldigermane (106.0 mg, 0.45 mmol, 1.5 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (19.6 mg, 0.08 mmol, 26%).

$R_f = 0.71$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.28 - 7.24$ (m, 2H), 7.19 - 7.14 (m, 3H), 2.75 (dd, $J = 13.9, 6.2$ Hz, 1H), 2.62 (dd, $J = 13.9, 9.7$ Hz, 1H), 1.48 - 1.42 (m, 2H), 1.28 - 1.22 (m, 1H), 0.88 (t, $J = 7.4$ Hz, 3H), 0.08 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta/\text{ppm} = 142.9, 129.0, 128.3, 125.7, 36.8, 31.9, 23.3, 13.3, -2.5$. **HRMS** (ESI) calculated for $\text{C}_{12}\text{H}_{19}\text{FGe}$: 237.0693 [$\text{M} - \text{CH}_3$] $^+$, found: 237.0691. **IR** (neat): $\nu/\text{cm}^{-1} = 2963, 2859, 1454, 1234, 819$.

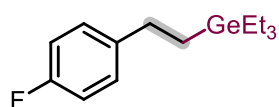
Triethyl(phenethyl)germane (8)

Prepared, following the general procedure A from styrene (31.2 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (60.2 mg, 0.24 mmol, 81%).

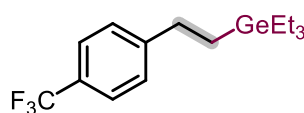
$R_f = 0.70$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.30 - 7.26$ (m, 2H), 7.21 (d, $J = 7.5$ Hz, 2H), 7.18 - 7.15 (m, 1H), 2.69 - 2.65 (m, 2H), 1.09 - 0.99 (m, 11H), 0.74 (q, $J = 7.9$ Hz, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta/\text{ppm} = 145.6, 128.4, 127.9, 125.7, 31.5, 13.7, 9.1, 4.0$. **MS** (EI) m/z (%): 237 (100) [$\text{M} - \text{CH}_2\text{CH}_3$] $^+$, 133 (86), 105 (80). These data are in agreement with those reported previously in the literature.^[87]

(4-(*tert*-Butyl)phenethyl)triethylgermane (9)

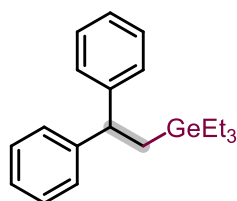
Prepared, following the general procedure A from 4-*tert*-butylstyrene (48.1 mg, 0.30 mmol) with LiO^{*t*}Bu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (72.0 mg, 0.22 mmol, 75%). *R*_f = 0.76 (*n*-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.31 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 2.66 – 2.62 (m, 2H), 1.31 (s, 9H), 1.08 – 1.04 (m, 2H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.74 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 148.5, 142.6, 127.5, 125.3, 34.5, 31.6, 30.8, 13.6, 9.1, 4.0. HRMS (ESI) calculated for C₁₃H₂₁Ge: 293.1319 [M-CH₂CH₃]⁺, found: 293.1320. IR (neat): ν/cm⁻¹ = 2955, 2873, 1683, 1300, 1016.

Triethyl(4-fluorophenethyl)germane (10)

Prepared, following the general procedure A from 4-fluorostyrene (36.6 mg, 0.30 mmol) with LiO^{*t*}Bu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (52.6 mg, 0.19 mmol, 62%). *R*_f = 0.83 (*n*-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.17 – 7.12 (m, 2H), 6.98 – 6.92 (m, 2H), 2.67 – 2.61 (m, 2H), 1.06 – 0.99 (m, 11H), 0.73 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 161.2 (d, *J* = 242.8 Hz), 141.2 (d, *J* = 3.2 Hz), 129.2 (d, *J* = 7.7 Hz), 115.1 (d, *J* = 21.0 Hz), 30.7, 13.8, 9.1, 4.0. ¹⁹F NMR (564 MHz, CDCl₃) δ/ppm = -118.4 (s, 1F). HRMS (ESI) calculated for C₁₂H₁₈FGe: 255.0599 [M-CH₂CH₃]⁺, found: 255.0598. IR (neat): ν/cm⁻¹ = 2948, 2872, 1507, 1223, 1015.

Triethyl(4-(trifluoromethyl)phenethyl)germane (11)

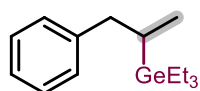
Prepared, following the general procedure A from 4-(trifluoromethyl)styrene (51.6 mg, 0.30 mmol) with LiO^{*t*}Bu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (24.3 mg, 0.07 mmol, 24%). *R*_f = 0.74 (*n*-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.52 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.74 – 2.68 (m, 2H), 1.08 – 1.00 (m, 11H), 0.75 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 149.7, 128.2, 128.0 (q, *J* = 32.3 Hz), 125.4 (q, *J* = 3.9 Hz), 124.6 (q, *J* = 272.0 Hz), 31.4, 13.5, 9.1, 4.0. ¹⁹F NMR (564 MHz, CDCl₃) δ/ppm = -62.2. MS (EI) *m/z* (%): 305 (21) [M-CH₂CH₃]⁺, 153 (100), 133 (10). These data are in agreement with those reported previously in the literature.^[80]

(2,2-Diphenylethyl)triethylgermane (12)

Prepared, following the general procedure A from 1,1-diphenylethylene (54.1 mg, 0.30 mmol) with LiO^{*t*}Bu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (88.7 mg, 0.26 mmol, 87%). *R*_f = 0.82 (*n*-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.29 (dd, *J* = 8.1, 1.5 Hz, 4H), 7.27 – 7.23 (m, 4H), 7.17 – 7.12 (m, 2H), 4.09 (t, *J* = 8.1 Hz, 1H), 1.56 (d, *J* = 8.1 Hz, 2H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.53 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 147.4, 128.5, 127.6, 126.1, 48.2, 19.6, 9.0, 4.3. MS (EI) *m/z* (%):

313 (100) $[M-CH_2CH_3]^+$, 209 (49), 133 (40). These data are in agreement with those reported previously in the literature.^[87]

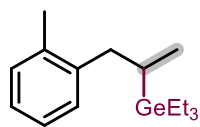
Triethyl(1-phenylpropan-2-yl)germane (13)



Prepared, following the general procedure A from allylbenzene (35.5 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (75.9 mg, 0.27 mmol, 91%).

R_f = 0.87 (*n*-pentane). 1H NMR (600 MHz, $CDCl_3$) δ /ppm = 7.29 – 7.26 (m, 2H), 7.19 – 7.14 (m, 3H), 2.90 (dd, J = 13.7, 4.2 Hz, 1H), 2.43 – 2.36 (m, 1H), 1.44 – 1.36 (m, 1H), 1.06 (t, J = 7.9 Hz, 9H), 0.94 (d, J = 7.4 Hz, 3H), 0.77 (q, J = 8.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ /ppm = 142.8, 129.0, 128.2, 125.7, 39.8, 21.4, 15.5, 9.3, 2.9. HRMS (ESI) calculated for $C_{13}H_{21}Ge$: 251.0850 $[M-CH_2CH_3]^+$, found: 251.0852. IR (neat): ν/cm^{-1} = 2947, 2870, 1456, 1015.

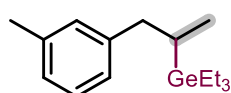
Triethyl(1-(2-tolyl)propan-2-yl)germane (14)



Prepared, following the general procedure A from 1-allyl-2-methylbenzene (39.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (80.9 mg, 0.28 mmol, 92%).

R_f = 0.91 (*n*-pentane). 1H NMR (600 MHz, $CDCl_3$) δ /ppm = 7.14 – 7.07 (m, 4H), 2.90 (dd, J = 13.8, 3.7 Hz, 1H), 2.44 – 2.38 (m, 1H), 2.30 (s, 3H), 1.38 (dq, J = 11.3, 7.3, 3.8 Hz, 1H), 1.07 (t, J = 7.9 Hz, 9H), 0.94 (d, J = 7.3 Hz, 3H), 0.80 (q, J = 8.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ /ppm = 140.7, 136.1, 130.4, 129.9, 125.8, 125.6, 36.7, 19.9, 19.6, 15.4, 9.4, 2.9. HRMS (APCI) calculated for $C_{14}H_{23}Ge$: 265.1006 $[M-CH_2CH_3]^+$, found: 265.1005. IR (neat): ν/cm^{-1} = 3016, 2947, 1458, 1015.

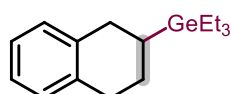
Triethyl(1-(3-tolyl)propan-2-yl)germane (15)



Prepared, following the general procedure A from 1-allyl-3-methylbenzene (39.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (70.3 mg, 0.24 mmol, 81%).

R_f = 0.90 (*n*-pentane). 1H NMR (600 MHz, $CDCl_3$) δ /ppm = 7.18 – 7.13 (m, 1H), 7.00 – 6.94 (m, 3H), 2.86 (dd, J = 13.6, 4.1 Hz, 1H), 2.39 – 2.32 (m, 4H), 1.42 – 1.34 (m, 1H), 1.08 – 1.04 (m, 9H), 0.94 (d, J = 7.4 Hz, 3H), 0.77 (q, J = 8.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ /ppm = 142.8, 137.7, 129.7, 128.1, 126.4, 126.0, 39.7, 21.6, 21.3, 15.5, 9.4, 2.9. HRMS (APCI) calculated for $C_{14}H_{23}Ge$: 265.1006 $[M-CH_2CH_3]^+$, found: 265.1005. IR (neat): ν/cm^{-1} = 3052, 2947, 2870, 1601, 1458, 1232.

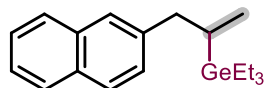
Triethyl(1,2,3,4-tetrahydronaphthalen-2-yl)germane (16)



Prepared, following the general procedure A from 1,4-dihydronaphthalene (39.1 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (54.1 mg, 0.19 mmol, 62%).

$R_f = 0.72$ (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.10 – 7.02 (m, 4H), 2.85 – 2.72 (m, 4H), 2.03 – 1.96 (m, 1H), 1.70 – 1.61 (m, 1H), 1.43 (tdd, $J = 12.5, 5.6, 2.7$ Hz, 1H), 1.06 (t, $J = 7.9$ Hz, 9H), 0.80 (q, $J = 7.9$ Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 138.1, 137.3, 129.4, 128.9, 125.5, 125.5, 32.2, 30.6, 26.0, 21.6, 9.4, 2.7. **HRMS** (APCI) calculated for C₁₄H₂₁Ge: 263.0850 [M-CH₂CH₃]⁺, found: 263.0849. **IR** (neat): ν /cm⁻¹ = 2910, 2872, 2324, 1796, 1454, 1014.

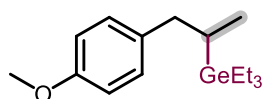
Triethyl(1-(naphthalen-2-yl)propan-2-yl)germane (17)



Prepared, following the general procedure A from 2-allylnaphthalene (50.5 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (80.8 mg, 0.25 mmol, 82%).

$R_f = 0.89$ (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.82 – 7.74 (m, 3H), 7.58 (d, $J = 1.6$ Hz, 1H), 7.44 (ddd, $J = 8.2, 6.8, 1.5$ Hz, 1H), 7.41 (ddd, $J = 8.1, 6.8, 1.4$ Hz, 1H), 7.32 (dd, $J = 8.3, 1.8$ Hz, 1H), 3.07 (dd, $J = 13.7, 4.1$ Hz, 1H), 2.58 – 2.50 (m, 1H), 1.54 – 1.46 (m, 1H), 1.08 (t, $J = 7.9$ Hz, 9H), 0.96 (d, $J = 7.4$ Hz, 3H), 0.80 (q, $J = 7.9$ Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 140.3, 133.7, 132.1, 127.8, 127.8, 127.7, 127.6, 127.0, 125.9, 125.1, 39.9, 21.2, 15.4, 9.4, 2.9. **HRMS** (APCI) calculated for C₁₇H₂₃Ge: 301.1006 [M-CH₂CH₃]⁺, found: 301.1002. **IR** (neat): ν /cm⁻¹ = 3052, 2947, 2869, 1906, 1599, 1458.

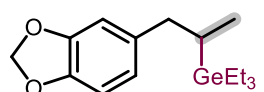
Triethyl(1-(4-methoxyphenyl)propan-2-yl)germane (18)



Prepared, following the general procedure A from 4-allylanisole (44.5 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane/Et₂O 98:2) as a colorless oil (56.5 mg, 0.18 mmol, 61%).

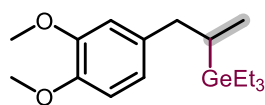
$R_f = 0.68$ (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.07 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 3.79 (s, 3H), 2.84 (dd, $J = 13.8, 4.3$ Hz, 1H), 2.36 – 2.30 (m, 1H), 1.38 – 1.30 (m, 1H), 1.05 (t, $J = 7.9$ Hz, 9H), 0.93 (d, $J = 7.4$ Hz, 3H), 0.76 (q, $J = 8.0$ Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 157.8, 134.9, 129.8, 113.7, 55.4, 38.9, 21.5, 15.5, 9.4, 2.9. **HRMS** (APCI) calculated for C₁₄H₂₃GeO: 281.0955 [M-CH₂CH₃]⁺, found: 281.0951. **IR** (neat): ν /cm⁻¹ = 2946, 2906, 2870, 1610, 1509, 1245.

(1-(Benzo[d][1,3]dioxol-5-yl)propan-2-yl)triethylgermane (19)



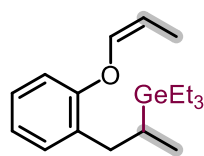
Prepared, following the general procedure A from safrole (48.6 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane/Et₂O 94:6) as a colorless oil (76.1 mg, 0.24 mmol, 79%).

$R_f = 0.34$ (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 6.72 (d, $J = 7.9$ Hz, 1H), 6.65 (s, 1H), 6.60 (d, $J = 7.8$ Hz, 1H), 5.92 (s, 2H), 2.82 (dd, $J = 13.7, 4.3$ Hz, 1H), 2.34 – 2.28 (m, 1H), 1.37 – 1.29 (m, 1H), 1.05 (t, $J = 7.9$ Hz, 9H), 0.93 (d, $J = 7.4$ Hz, 3H), 0.76 (q, $J = 7.9$ Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 147.6, 145.6, 136.8, 121.7, 109.2, 108.0, 100.8, 39.6, 21.6, 15.4, 9.3, 2.9. **HRMS** (APCI) calculated for C₁₄H₂₁GeO₂: 295.0748 [M-CH₂CH₃]⁺, found: 295.0744. **IR** (neat): ν /cm⁻¹ = 2947, 2871, 1608, 1244, 1039.

(1-(3,4-Dimethoxyphenyl)propan-2-yl)triethylgermane (20)

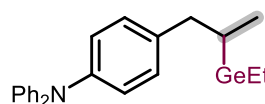
Prepared, following the general procedure A from methyl eugenol (53.5 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane/ Et_2O 94:6) as a colorless oil (57.6 mg, 0.17 mmol, 57%).

R_f = 0.22 (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 6.79 (d, J = 8.0 Hz, 1H), 6.71 – 6.66 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 2.84 (dd, J = 13.8, 4.5 Hz, 1H), 2.38 – 2.32 (m, 1H), 1.40 – 1.32 (m, 1H), 1.05 (t, J = 7.9 Hz, 9H), 0.95 (d, J = 7.4 Hz, 3H), 0.76 (q, J = 7.6 Hz, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 148.8, 147.2, 135.5, 120.8, 112.2, 111.2, 56.1, 56.0, 39.5, 21.5, 15.6, 9.4, 2.9. **HRMS** (ESI) calculated for $\text{C}_{17}\text{H}_{30}\text{O}_2\text{GeNa}$: 363.1350 $[\text{M}+\text{Na}]^+$, found: 363.1346. **IR** (neat): ν/cm^{-1} = 2945, 2870, 1590, 1458, 1261, 1026.

(Z)-triethyl(1-(2-(prop-1-en-1-yloxy)phenyl)propan-2-yl)germane (21)

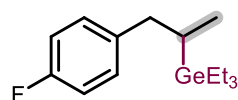
Prepared, following the general procedure A from 1-allyl-2-(allyloxy)benzene (52.3 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane/ Et_2O 98:2) as a colorless oil (95.4 mg, 0.28 mmol, 95%).

R_f = 0.84 (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.18 – 7.10 (m, 2H), 6.99 – 6.94 (m, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.34 (d, J = 5.8 Hz, 1H), 4.86 – 4.80 (m, 1H), 2.99 (dd, J = 13.3, 3.5 Hz, 1H), 2.50 – 2.41 (m, 1H), 1.72 (d, J = 6.7 Hz, 3H), 1.50 – 1.41 (m, 1H), 1.07 (t, J = 7.9 Hz, 9H), 0.94 (d, J = 7.4 Hz, 3H), 0.79 (q, J = 7.9 Hz, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 155.83, 141.66, 132.03, 131.08, 126.98, 122.13, 114.95, 106.45, 33.90, 20.09, 15.46, 9.57, 9.33, 2.87. **HRMS** (APCI) calculated for $\text{C}_{16}\text{H}_{25}\text{GeO}$: 307.1112 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 307.1110. **IR** (neat): ν/cm^{-1} = 3044, 2946, 2870, 1668, 1487, 1247.

***N,N*-Diphenyl-4-(2-(triethylgermyl)propyl)aniline (22)**

Prepared, following the general procedure A from 4-allyl-*N,N*-diphenylaniline (85.6 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane/ Et_2O 98:2) as a clear yellowish oil (130.6 mg, 0.29 mmol, 98%).

R_f = 0.80 (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.24 – 7.20 (m, 4H), 7.08 – 7.04 (m, 6H), 7.02 – 7.00 (m, 2H), 6.99 – 6.94 (m, 2H), 2.82 (dd, J = 13.7, 5.0 Hz, 1H), 2.44 – 2.38 (m, 1H), 1.39 (ddd, J = 11.8, 7.7, 5.0 Hz, 1H), 1.04 (t, J = 7.9 Hz, 9H), 0.99 (d, J = 7.3 Hz, 3H), 0.75 (q, J = 7.9 Hz, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 148.2, 145.6, 137.8, 129.8, 129.2, 124.9, 123.8, 122.3, 39.4, 21.6, 15.9, 9.4, 3.0. **HRMS** (ESI) calculated for $\text{C}_{25}\text{H}_{30}\text{GeN}$: 418.1585 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 418.1581. **IR** (neat): ν/cm^{-1} = 2939, 2866, 1689, 1589, 1501, 1281.

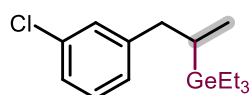
Triethyl(1-(4-fluorophenyl)propan-2-yl)germane (23)

Prepared, following the general procedure A from 1-allyl-4-fluorobenzene (40.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol,

0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (71.3 mg, 0.24 mmol, 80%).

R_f = 0.91 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.12 – 7.07 (m, 2H), 6.98 – 6.92 (m, 2H), 2.86 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.40 – 2.33 (m, 1H), 1.38 – 1.30 (m, 1H), 1.05 (t, *J* = 7.9 Hz, 9H), 0.92 (d, *J* = 7.3 Hz, 3H), 0.76 (q, *J* = 7.8 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 161.34 (d, *J* = 242.9 Hz), 138.38 (d, *J* = 3.3 Hz), 130.16 (d, *J* = 7.8 Hz), 114.9 (d, *J* = 21.1 Hz), 39.0, 21.5, 15.4, 9.3, 2.9. **¹⁹F NMR** (564 MHz, CDCl₃) δ/ppm = -118.23 (s, 1F). **HRMS** (APCI) calculated for C₁₃H₂₀GeF: 269.0755 [M-CH₂CH₃]⁺, found: 269.0755. **IR** (neat): ν/cm⁻¹ = 2947, 2870, 2323, 1881, 1507, 1222.

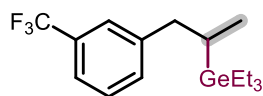
(1-(3-Chlorophenyl)propan-2-yl)triethylgermane (24)



Prepared, following the general procedure A from 1-allyl-3-chlorobenzene (45.8 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (46.6 mg, 0.15 mmol, 50%).

R_f = 0.90 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.21 – 7.17 (m, 1H), 7.17 – 7.13 (m, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 2.87 (dd, *J* = 13.9, 4.2 Hz, 1H), 2.36 (ddd, *J* = 13.6, 11.5, 1.7 Hz, 1H), 1.41 – 1.32 (m, 1H), 1.06 (t, *J* = 7.9 Hz, 9H), 0.93 (d, *J* = 7.3 Hz, 3H), 0.77 (q, *J* = 7.7 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 145.0, 134.1, 129.5, 129.0, 127.2, 125.9, 39.5, 21.2, 15.4, 9.3, 2.9. **HRMS** (APCI) calculated for C₁₃H₂₀GeCl: 285.0460 [M-CH₂CH₃]⁺, found: 285.0457. **IR** (neat): ν/cm⁻¹ = 2947, 2870, 2325, 2090, 1864, 1595, 1461.

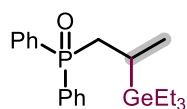
Triethyl(1-(3-(trifluoromethyl)phenyl)propan-2-yl)germane (25)



Prepared, following the general procedure A from 1-allyl-3-(trifluoromethyl)benzene (55.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (25.1 mg, 0.07 mmol, 24%).

R_f = 0.91 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.44 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.33 (d, *J* = 7.7 Hz, 1H), 2.94 (dd, *J* = 13.8, 4.4 Hz, 1H), 2.46 (dd, *J* = 13.7, 11.7 Hz, 1H), 1.43 – 1.35 (m, 1H), 1.06 (t, *J* = 7.9 Hz, 9H), 0.93 (d, *J* = 7.3 Hz, 3H), 0.78 (q, *J* = 7.9 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 143.7, 132.3, 130.6 (q, *J* = 31.9 Hz), 128.6, 125.5 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 272.3 Hz), 122.7 (q, *J* = 3.8 Hz), 39.7, 21.2, 15.4, 9.3, 2.9. **¹⁹F NMR** (564 MHz, CDCl₃) δ/ppm = 62.52 (s, 3F). **HRMS** (APCI) calculated for C₁₄H₂₀GeF₃: 319.0723 [M-CH₂CH₃]⁺, found: 319.0720. **IR** (neat): ν/cm⁻¹ = 2950, 2872, 1452, 1327, 1125, 699.

Diphenyl(2-(triethylgermyl)propyl)phosphine oxide (26)



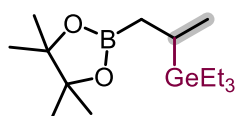
Prepared, following the general procedure A from allyldiphenylphosphine (67.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by preparative HPLC (ethylacetate, 20 mL/min) as white solid (59.4 mg, 0.15 mmol, 49%).

R_f = 0. (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.79 – 7.71 (m, 4H), 7.52 – 7.42 (m, 6H), 2.42 – 2.32 (m, 1H), 2.28 – 2.18 (m, 1H), 1.67 – 1.56 (m, 1H), 1.14 (d, *J* = 7.3 Hz, 3H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.78 – 0.71

(m, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 131.6 (d, J = 7.1 Hz), 131.0 (d, J = 8.1 Hz), 130.8 (d, J = 8.8 Hz), 128.7 (d, J = 10.6 Hz), 33.1 (d, J = 66.6 Hz), 17.4, 12.9 (d, J = 7.0 Hz), 9.2, 2.6. **³¹P NMR** (243 MHz, CDCl₃) δ /ppm = 32.18 (s, 1P). **HRMS** (ESI) calculated for C₂₁H₃₁GePO: 427.1217 [M+Na]⁺, found: 427.1234. **IR** (neat): ν /cm⁻¹ = 2950, 2873, 1459, 1435, 1176.

Note: The phosphine oxidizes quickly to the phosphine oxide. Only the oxide could be isolated.

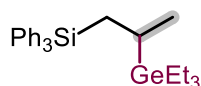
Triethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)germane (27)



Prepared, following the general procedure A from 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50.4 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification

by flash chromatography on silica gel (*n*-pentane/Et₂O 94:6) as a colorless oil (46.4 mg, 0.14 mmol, 47%). **R_f** = 0.90 (*n*-pentane/Et₂O 94:6). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 1.35 – 1.27 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.07 (d, J = 7.4 Hz, 3H), 1.02 (t, J = 8.0 Hz, 9H), 1.05 – 0.96 (m, 1H), 0.80 – 0.74 (m, 1H), 0.72 (q, J = 7.7 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 83.1, 25.2, 24.9, 19.0, 14.8, 9.4, 2.7. **HRMS** (ESI) calculated for C₁₃H₂₈GeBO₂: 301.1389 [M-CH₂CH₃]⁺, found: 301.1382. **IR** (neat): ν /cm⁻¹ = 2946, 2871, 1800, 1355, 1233.

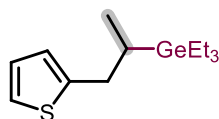
Triphenyl(2-(triethylgermyl)propyl)silane (28)



Prepared, following the general procedure A from allyltriphenylsilane (90.1 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a milky viscous oil (62.3 mg, 0.14 mmol, 45%).

R_f = 0.38 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.57 – 7.54 (m, 6H), 7.42 – 7.34 (m, 9H), 1.65 (d, J = 13.9 Hz, 1H), 1.44 – 1.33 (m, 2H), 1.01 (t, J = 7.9 Hz, 9H), 0.89 (d, J = 6.9 Hz, 3H), 0.74 (q, J = 7.9 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 136.1, 135.9, 129.4, 127.9, 19.1, 16.7, 14.2, 9.4, 2.6. **HRMS** (ESI) calculated for C₂₅H₃₁GeSi: 433.1401 [M-CH₂CH₃]⁺, found: 433.1408. **IR** (neat): ν /cm⁻¹ = 3066, 2926, 2326, 1763, 1426, 1107.

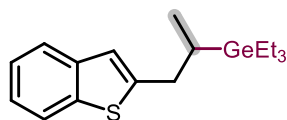
Triethyl(1-(thiophen-2-yl)propan-2-yl)germane (29)



Prepared, following the general procedure A from 2-allylthiophene (37.3 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography

on silica gel (*n*-pentane) as colorless oil (69.9 mg, 0.25 mmol, 82%).

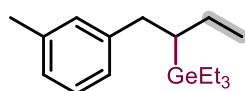
R_f = 0.80 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.11 (dd, J = 5.1, 1.2 Hz, 1H), 6.91 (dd, J = 5.1, 3.4 Hz, 1H), 6.78 – 6.75 (m, 1H), 3.06 (dd, J = 14.8, 5.0 Hz, 1H), 2.68 (dd, J = 14.8, 11.2 Hz, 1H), 1.43 – 1.35 (m, 1H), 1.06 – 1.02 (m, 12H), 0.76 (q, J = 8.0 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 146.2, 126.7, 124.6, 123.0, 34.0, 22.4, 15.8, 9.3, 2.9. **HRMS** (ESI) calculated for C₁₁H₁₉GeS: 257.0414 [M-CH₂CH₃]⁺, found: 257.0410. **IR** (neat): ν /cm⁻¹ = 2947, 2906, 2870, 1458, 1015.

(1-(Benzo[*b*]thiophen-2-yl)propan-2-yl)triethylgermane (30)

Prepared, following the general procedure A from 2-allylbenzo[*b*]thiophene (52.3 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification

by flash chromatography on silica gel (*n*-pentane) as colorless oil (40.2 mg, 0.12 mmol, 40%).

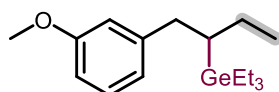
*R*_f = 0.81 (*n*-pentane/Et₂O 94:6). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.76 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.26 – 7.22 (m, 1H), 6.99 (s, 1H), 3.14 (dd, *J* = 14.8, 3.9 Hz, 1H), 2.77 – 2.71 (m, 1H), 1.52 – 1.44 (m, 1H), 1.11 – 1.04 (m, 12H), 0.80 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 147.4, 140.4, 139.6, 124.1, 123.4, 122.8, 122.3, 121.1, 34.9, 21.7, 15.7, 9.3, 2.9. HRMS (ESI) calculated for C₁₅H₂₁GeS: 307.0570 [M-CH₂CH₃]⁺, found: 307.0567. IR (neat): ν/cm⁻¹ = 2947, 2870, 1677, 1457, 1014.

Triethyl(1-(3-tolyl)butan-2-yl)germane (31)

Prepared, following the general procedure A from 1-(but-3-en-1-yl)-3-methylbenzene (43.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after

purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (72.3 mg, 0.24 mmol, 78%).

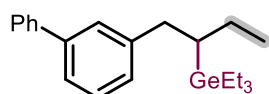
*R*_f = 0.86 (*n*-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.17 – 7.12 (m, 1H), 7.01 – 6.94 (m, 3H), 2.75 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.57 (dd, *J* = 13.9, 10.3 Hz, 1H), 2.33 (s, 3H), 1.49 – 1.42 (m, 2H), 1.42 – 1.37 (m, 1H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.86 (t, *J* = 7.3 Hz, 3H), 0.75 (q, *J* = 8.1 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 143.1, 137.7, 129.7, 128.1, 126.4, 126.0, 37.0, 29.3, 23.3, 21.6, 13.7, 9.4, 3.9. HRMS (ESI) calculated for C₁₅H₂₅Ge: 279.1163 [M-CH₂CH₃]⁺, found: 279.1164. IR (neat): ν/cm⁻¹ = 3016, 2950, 1457, 1014.

Triethyl(1-(3-methoxyphenyl)butan-2-yl)germane (32)

Prepared, following the general procedure A from 1-(but-3-en-1-yl)-3-methoxybenzene (48.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was

obtained after purification by flash chromatography on silica gel (*n*-pentane/Et₂O 98:2) as colorless oil (87.2 mg, 0.27 mmol, 90%).

*R*_f = 0.85 (*n*-pentane/Et₂O 98:2). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.21 – 7.14 (m, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.73 – 6.70 (m, 2H), 3.80 (s, 3H), 2.76 (dd, *J* = 13.9, 5.1 Hz, 1H), 2.59 (dd, *J* = 13.9, 10.2 Hz, 1H), 1.50 – 1.37 (m, 3H), 1.04 (t, *J* = 7.9 Hz, 9H), 0.86 (t, *J* = 7.3 Hz, 3H), 0.75 (q, *J* = 8.0 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 159.6, 144.9, 129.1, 121.5, 114.8, 110.9, 55.3, 37.1, 29.2, 23.4, 13.7, 9.4, 3.9. HRMS (ESI) calculated for C₁₅H₂₅GeO: 295.1112 [M-CH₂CH₃]⁺, found: 295.1122. IR (neat): ν/cm⁻¹ = 2949, 2871, 2090, 1763, 1596, 1259, 1153.

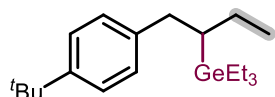
(1-([1,1'-Biphenyl]-3-yl)butan-2-yl)triethylgermane (33)

Prepared, following the general procedure A from 3-(but-3-en-1-yl)-1,1'-biphenyl (62.4 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after

purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (100.0 mg, 0.27 mmol, 90%).

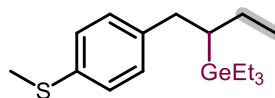
$R_f = 0.55$ (*n*-pentane). **^1H NMR** (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.61 - 7.57$ (m, 2H), 7.46 – 7.42 (m, 2H), 7.40 (d, $J = 8.9$ Hz, 2H), 7.36 – 7.32 (m, 2H), 7.17 (d, $J = 7.5$ Hz, 1H), 2.86 (dd, $J = 13.9, 4.9$ Hz, 1H), 2.69 (dd, $J = 13.8, 10.1$ Hz, 1H), 1.54 – 1.42 (m, 3H), 1.05 (t, $J = 7.9$ Hz, 9H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.77 (q, $J = 8.0$ Hz, 6H). **^{13}C NMR** (151 MHz, CDCl_3) $\delta/\text{ppm} = 143.6, 141.7, 141.2, 128.8, 128.6, 127.9, 127.8, 127.3, 127.3, 124.7, 37.2, 29.4, 23.4, 13.7, 9.4, 4.0$. **HRMS** (APCI) calculated for $\text{C}_{20}\text{H}_{27}\text{Ge}$: 341.1319 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 341.1315. **IR** (neat): $\nu/\text{cm}^{-1} = 3059, 2950, 2870, 2324, 2111, 1598, 1457$.

(1-(4-(*tert*-Butyl)phenyl)butan-2-yl)triethylgermane (34)



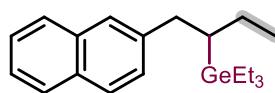
Prepared, following the general procedure A from 1-(but-3-en-1-yl)-4-(*tert*-butyl)benzene (56.5 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (79.6 mg, 0.23 mmol, 76%). $R_f = 0.83$ (*n*-pentane). **^1H NMR** (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.28$ (d, $J = 8.1$ Hz, 2H), 7.10 (d, $J = 8.1$ Hz, 2H), 2.75 (dd, $J = 14.0, 5.1$ Hz, 1H), 2.59 (dd, $J = 14.0, 10.4$ Hz, 1H), 1.49 – 1.43 (m, 2H), 1.43 – 1.36 (m, 1H), 1.31 (s, 9H), 1.03 (t, $J = 7.9$ Hz, 9H), 0.87 (t, $J = 7.4$ Hz, 3H), 0.74 (q, $J = 8.0$ Hz, 6H). **^{13}C NMR** (151 MHz, CDCl_3) $\delta/\text{ppm} = 148.5, 134.0, 128.5, 125.1, 36.4, 34.5, 31.6, 29.3, 23.3, 13.6, 9.4, 3.9$. **HRMS** (APCI) calculated for $\text{C}_{18}\text{H}_{31}\text{Ge}$: 321.1632 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 321.1634. **IR** (neat): $\nu/\text{cm}^{-1} = 2955, 2870, 2090, 1897, 1459, 1016$.

Triethyl(1-(4-(methylthio)phenyl)butan-2-yl)germane (35)



Prepared, following the general procedure A from (4-(but-3-en-1-yl)phenyl)(methyl)sulfane (53.5 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (86.6 mg, 0.26 mmol, 85%). $R_f = 0.68$ (*n*-pentane). **^1H NMR** (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.19$ (d, $J = 8.2$ Hz, 2H), 7.10 (d, $J = 8.2$ Hz, 2H), 2.75 (dd, $J = 14.0, 5.2$ Hz, 1H), 2.57 (dd, $J = 14.0, 10.4$ Hz, 1H), 2.47 (s, 3H), 1.48 – 1.40 (m, 2H), 1.40 – 1.34 (m, 1H), 1.04 (t, $J = 7.9$ Hz, 9H), 0.86 (t, $J = 7.4$ Hz, 3H), 0.75 (q, $J = 7.8$ Hz, 6H). **^{13}C NMR** (151 MHz, CDCl_3) $\delta/\text{ppm} = 140.4, 135.0, 129.5, 127.2, 36.5, 29.3, 23.2, 16.6, 13.7, 9.4, 3.9$. **HRMS** (APCI) calculated for $\text{C}_{15}\text{H}_{25}\text{GeS}$: 311.0883 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 311.0886. **IR** (neat): $\nu/\text{cm}^{-1} = 2937, 2864, 1687, 1503, 1397, 1284$.

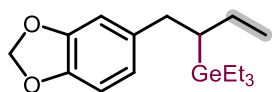
Triethyl(1-(naphthalen-2-yl)butan-2-yl)germane (36)



Prepared, following the general procedure A from 2-(but-3-en-1-yl)naphthalene (54.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (83.0 mg, 0.24 mmol, 81%). $R_f = 0.79$ (*n*-pentane). **^1H NMR** (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.82 - 7.74$ (m, 3H), 7.60 (s, 1H), 7.47 – 7.39 (m, 2H), 7.34 (dd, $J = 8.3, 1.8$ Hz, 1H), 2.97 (dd, $J = 14.0, 4.7$ Hz, 1H), 2.77 (dd, $J = 13.8, 10.5$ Hz, 1H), 1.55 – 1.45 (m, 3H), 1.06 (t, $J = 7.9$ Hz, 9H), 0.87 (t, $J = 7.3$ Hz, 3H), 0.79 (q, $J = 8.0$ Hz, 6H). **^{13}C NMR** (151 MHz, CDCl_3) $\delta/\text{ppm} = 140.7, 133.7, 132.1, 127.8, 127.7$ (2C), 127.5, 127.0, 125.9, 125.1, 37.3, 29.1, 23.3, 13.7, 9.4, 4.0.

HRMS (APCI) calculated for $C_{18}H_{25}Ge$: 315.1163 $[M-CH_2CH_3]^+$, found: 315.1169. **IR** (neat): ν/cm^{-1} = 3052, 2950, 2327, 1796, 1457.

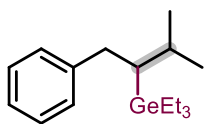
(1-(Benzo[d][1,3]dioxol-5-yl)butan-2-yl)triethylgermane (37)



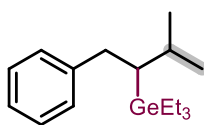
Prepared, following the general procedure A from 5-(but-3-en-1-yl)benzo[d][1,3]dioxole (52.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane/ Et_2O 98:2) as colorless oil (71.7 mg, 0.21 mmol, 71%).

R_f = 0.85 (*n*-pentane/ Et_2O 98:2). **1H NMR** (600 MHz, $CDCl_3$) δ/ppm = 6.71 (d, J = 7.8 Hz, 1H), 6.69 – 6.65 (m, 1H), 6.63 – 6.60 (m, 1H), 5.92 (s, 2H), 2.71 (dd, J = 14.0, 5.2 Hz, 1H), 2.53 (dd, J = 14.0, 10.5 Hz, 1H), 1.49 – 1.41 (m, 2H), 1.36 – 1.30 (m, 1H), 1.04 (t, J = 7.9 Hz, 9H), 0.86 (t, J = 7.4 Hz, 3H), 0.75 (q, J = 7.9 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ/ppm = 147.6, 145.5, 137.1, 121.6, 109.2, 108.0, 100.8, 36.8, 29.5, 23.2, 13.7, 9.4, 3.9. **HRMS** (ESI) calculated for $C_{15}H_{23}GeO_2$: 309.0904 $[M-CH_2CH_3]^+$, found: 309.0901. **IR** (neat): ν/cm^{-1} = 2954, 2872, 1442, 1243.

Triethyl(3-methyl-1-phenylbutan-2-yl)germane (38)



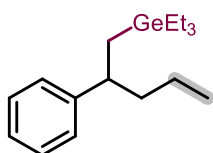
Prepared, following the general procedure A from (3-methylbut-2-en-1-yl)benzene (43.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (59.9 mg, 0.20 mmol, 65%).



Prepared, following the general procedure A from (3-methylbut-3-en-1-yl)benzene (43.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (62.1 mg, 0.20 mmol, 68%).

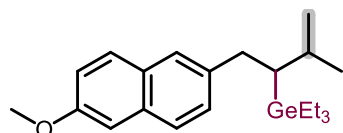
R_f = 0.68 (*n*-pentane). **1H NMR** (600 MHz, $CDCl_3$) δ/ppm = 7.30 – 7.25 (m, 2H), 7.22 – 7.17 (m, 3H), 2.81 – 2.70 (m, 2H), 1.95 – 1.87 (m, 1H), 1.56 – 1.51 (m, 1H), 1.04 (t, J = 7.9 Hz, 9H), 0.97 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 7.0 Hz, 3H), 0.82 – 0.70 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ/ppm = 143.5, 129.0, 128.2, 125.7, 36.1, 34.2, 28.8, 22.1, 21.8, 9.4, 4.9. **HRMS** (APCI) calculated for $C_{15}H_{25}Ge$: 279.1163 $[M-CH_2CH_3]^+$, found: 279.1157. **IR** (neat): ν/cm^{-1} = 2944, 2868, 2325, 1696, 1502, 1397.

Triethyl(2-phenylpentyl)germane (39)



Prepared, following the general procedure A from pent-4-en-2-ylbenzene (43.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (55.3 mg, 0.18 mmol, 60%).

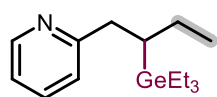
R_f = 0.75 (*n*-pentane). **1H NMR** (600 MHz, $CDCl_3$) δ/ppm = 7.27 – 7.23 (m, 2H), 7.18 – 7.13 (m, 3H), 2.69 – 2.61 (m, 1H), 1.59 – 1.51 (m, 2H), 1.19 – 1.05 (m, 4H), 0.91 (t, J = 7.9 Hz, 9H), 0.83 (t, J = 7.3 Hz, 3H), 0.60 – 0.46 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ/ppm = 148.1, 128.3, 127.5, 125.9, 43.1, 42.6, 21.0, 20.4, 14.2, 9.0, 4.5. **HRMS** (APCI) calculated for $C_{15}H_{25}Ge$: 279.1163 $[M-CH_2CH_3]^+$, found: 279.1158. **IR** (neat): ν/cm^{-1} = 3062, 3026, 2951, 2871, 1800, 1455, 1014.

Triethyl(1-(6-methoxynaphthalen-2-yl)-3-methylbutan-2-yl)germane (40)

Prepared, following the general procedure A from 2-methoxy-6-(3-methylbut-3-en-1-yl)naphthalene (67.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.).

The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane/Et₂O 98:2) as colorless oil (33.7 mg, 0.09 mmol, 29%).

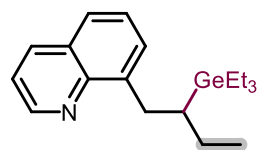
*R*_f = 0.34 (*n*-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.69 – 7.63 (m, 2H), 7.52 (s, 1H), 7.32 – 7.28 (m, 1H), 7.14 – 7.08 (m, 2H), 3.91 (s, 3H), 2.90 – 2.81 (m, 2H), 1.95 – 1.85 (m, 1H), 1.63 – 1.57 (m, 1H), 1.02 (t, *J* = 7.9 Hz, 9H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.81 – 0.71 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 157.2, 138.7, 133.0, 129.1, 129.0, 128.2, 126.9, 126.7, 118.7, 105.8, 55.4, 36.0, 34.3, 28.8, 22.2, 21.8, 9.4, 5.0. HRMS (ESI) calculated for C₂₀H₂₉GeO: 359.1425 [M-CH₂CH₃]⁺, found: 359.1423. IR (neat): ν/cm⁻¹ = 2951, 2870, 1903, 1604, 1459, 1264.

2-(2-(Triethylgermyl)butyl)pyridine (41)

Prepared, following the general procedure A from 2-(but-3-en-1-yl)pyridine (40.0 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography

on silica gel (*n*-pentane/Et₂O 9:1) as colorless oil (58.9 mg, 0.20 mmol, 67%).

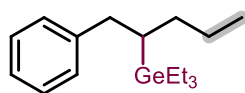
*R*_f = 0.23 (*n*-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 8.54 – 8.50 (m, 1H), 7.58 – 7.53 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 7.5, 4.9 Hz, 1H), 2.93 (dd, *J* = 13.9, 5.8 Hz, 1H), 2.84 (dd, *J* = 13.9, 10.1 Hz, 1H), 1.68 – 1.62 (m, 1H), 1.54 – 1.40 (m, 2H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.74 (q, *J* = 8.2 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 163.1, 149.3, 136.1, 123.3, 121.0, 39.8, 28.0, 23.8, 13.8, 9.4, 3.8. HRMS (ESI) calculated for C₁₅H₂₈GeN: 296.1428 [M-CH₂CH₃]⁺, found: 296.1423. IR (neat): ν/cm⁻¹ = 3068, 3006, 2950, 2871, 2321, 1900, 1588, 1464.

8-(2-(Triethylgermyl)butyl)quinoline (42)

Prepared, following the general procedure A from 8-(but-3-en-1-yl)quinoline (55.0 mg, 0.30 mmol) with (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane /Et₂O 98:2) as a clear yellow oil (80.5 mg,

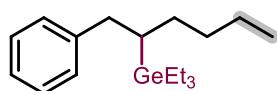
0.23 mmol, 78%).

*R*_f = 0.39 (*n*-pentane/Et₂O 98:2). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 8.91 (dd, *J* = 4.1, 1.9 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.65 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.56 (d, *J* = 7.0 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.36 (dd, *J* = 8.2, 4.1 Hz, 1H), 3.52 (dd, *J* = 13.7, 5.2 Hz, 1H), 3.29 (dd, *J* = 13.7, 10.4 Hz, 1H), 1.78 – 1.70 (m, 1H), 1.54 – 1.40 (m, 2H), 1.05 (t, *J* = 7.9 Hz, 9H), 0.86 (t, *J* = 7.4 Hz, 3H), 0.79 (q, *J* = 7.8 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 149.2, 147.4, 142.1, 136.2, 129.2, 128.5, 126.1, 125.8, 120.8, 32.1, 28.6, 23.8, 13.8, 9.4, 4.0. HRMS (ESI) calculated for C₁₉H₃₀GeN: 346.1585 [M+H]⁺, found: 346.1581. IR (neat): ν/cm⁻¹ = 3042, 2949, 2870, 2326, 1718, 1459.

Triethyl(1-phenylpentan-2-yl)germane (43)

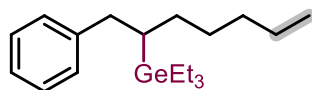
Prepared, following the general procedure A from pent-4-en-1-ylbenzene (43.9 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (68.2 mg, 0.22 mmol, 74%).

$R_f = 0.86$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.28 – 7.24 (m, 2H), 7.19 – 7.15 (m, 3H), 2.79 (dd, $J = 14.0, 5.5$ Hz, 1H), 2.61 (dd, $J = 13.9, 9.9$ Hz, 1H), 1.48 – 1.41 (m, 1H), 1.42 – 1.26 (m, 3H), 1.25 – 1.17 (m, 1H), 1.03 (t, $J = 7.9$ Hz, 9H), 0.81 (t, $J = 7.1$ Hz, 3H), 0.73 (q, $J = 7.8$ Hz, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 143.2, 128.9, 128.2, 125.7, 37.6, 33.3, 27.4, 22.3, 14.6, 9.4, 3.8. **HRMS** (ESI) calculated for $\text{C}_{15}\text{H}_{25}\text{Ge}$: 279.1163 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 279.1164. **IR** (neat): $\nu/\text{cm}^{-1} = 3063, 3025, 2950, 2109, 1602, 1454, 1014$.

Triethyl(1-phenylhexan-2-yl)germane (44)

Prepared, following the general procedure A from hex-5-en-1-ylbenzene (48.1 mg, 0.30 mmol) with LiO^tBu (48.0 mg, 0.60 mmol, 2.0 equiv.) and CsF (91.1 mg, 0.60 mmol, 2.0 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (19.3 mg, 0.06 mmol, 20%).

$R_f = 0.89$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.28 – 7.24 (m, 2H), 7.18 – 7.15 (m, 3H), 2.79 (dd, $J = 13.9, 4.6$ Hz, 1H), 2.62 (dd, $J = 13.6, 9.6$ Hz, 1H), 1.47 – 1.36 (m, 3H), 1.30 – 1.24 (m, 1H), 1.23 – 1.13 (m, 3H), 1.03 (t, $J = 7.9$ Hz, 9H), 0.83 (t, $J = 6.9$ Hz, 3H), 0.74 (q, $J = 7.8$ Hz, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 143.2, 128.9, 128.2, 125.7, 37.6, 31.4, 30.5, 27.5, 23.1, 14.2, 9.4, 3.8. **HRMS** (APCI) calculated for $\text{C}_{16}\text{H}_{27}\text{Ge}$: 293.1319 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 293.1326. **IR** (neat): $\nu/\text{cm}^{-1} = 3026, 2924, 2870, 1602, 1494, 1456$.

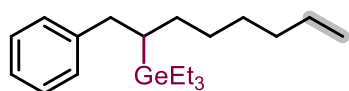
Triethyl(1-phenylheptan-2-yl)germane (45)

Prepared, following the general procedure A, but stirring for 72 h, from hept-6-en-1-ylbenzene (52.3 mg, 0.30 mmol) with LiO^tBu (48.0 mg, 0.60 mmol, 2.0 equiv.) and CsF (91.1 mg, 0.60 mmol, 2.0 equiv.). The title product was

obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (35.7 mg, 0.11 mmol, 35%).

Prepared, following the general procedure A, but stirring for 72 h, from hept-6-en-1-ylbenzene (52.3 mg, 0.30 mmol) with KO^tBu (67.3 mg, 0.60 mmol, 2.0 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (33.2 mg, 0.10 mmol, 33%).

$R_f = 0.85$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.28 – 7.24 (m, 2H), 7.19 – 7.15 (m, 3H), 2.79 (dd, $J = 13.9, 5.1$ Hz, 1H), 2.62 (dd, $J = 13.9, 9.7$ Hz, 1H), 1.46 – 1.35 (m, 3H), 1.32 – 1.22 (m, 3H), 1.21 – 1.14 (m, 3H), 1.03 (t, $J = 7.9$ Hz, 9H), 0.84 (t, $J = 7.2$ Hz, 3H), 0.73 (q, $J = 7.8$ Hz, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 143.2, 128.9, 128.2, 125.7, 37.6, 32.4, 30.8, 28.8, 27.6, 22.7, 14.2, 9.4, 3.8. **HRMS** (APCI) calculated for $\text{C}_{17}\text{H}_{29}\text{Ge}$: 307.1476 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 307.1474. **IR** (neat): $\nu/\text{cm}^{-1} = 2924, 2869, 1455, 1376, 1014$.

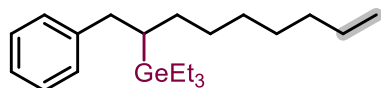
Triethyl(1-phenyloctan-2-yl)germane (46)

Prepared, following the general procedure A, but stirring for 72 h, from oct-7-en-1-ylbenzene (56.5 mg, 0.30 mmol) with LiO^tBu (48.0 mg, 0.60 mmol, 2.0 equiv.) and CsF (91.1 mg, 0.60 mmol, 2.0 equiv.). The title

product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (20.9 mg, 0.06 mmol, 20%).

$R_f = 0.77$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.28 - 7.24$ (m, 2H), 7.19 – 7.14 (m, 3H), 2.78 (dd, $J = 13.9, 5.2$ Hz, 1H), 2.61 (dd, $J = 14.0, 9.6$ Hz, 1H), 1.46 – 1.34 (m, 3H), 1.30 – 1.22 (m, 3H), 1.21 – 1.14 (m, 5H), 1.03 (t, $J = 7.9$ Hz, 9H), 0.86 (t, $J = 7.2$ Hz, 3H), 0.76 – 0.70 (m, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta/\text{ppm} = 143.2, 128.9, 128.2, 125.7, 37.6, 31.9, 30.8, 29.8, 29.1, 27.6, 22.8, 14.2, 9.4, 3.8$. **HRMS** (APCI) calculated for $\text{C}_{18}\text{H}_{31}\text{Ge}$: 321.1632 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 321.1630. **IR** (neat): $\nu/\text{cm}^{-1} = 2923, 2868, 1456, 1377, 1014$.

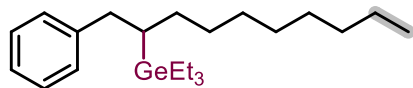
Triethyl(1-phenylnonan-2-yl)germane (47)



Prepared, following the general procedure A, but stirring for 72 h and heating at 120°C , from non-8-en-1-ylbenzene (60.7 mg, 0.30 mmol) with LiO^tBu (48.0 mg, 0.60 mmol, 2.0 equiv.) and CsF (91.1 mg, 0.60 mmol, 2.0 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (70.8 mg, 0.20 mmol, 65%).

$R_f = 0.81$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.28 - 7.23$ (m, 2H), 7.19 – 7.14 (m, 3H), 2.78 (dd, $J = 13.9, 5.1$ Hz, 1H), 2.61 (dd, $J = 14.0, 9.6$ Hz, 1H), 1.46 – 1.35 (m, 3H), 1.29 – 1.24 (m, 3H), 1.22 – 1.14 (m, 7H), 1.02 (t, $J = 7.9$ Hz, 9H), 0.87 (t, $J = 7.2$ Hz, 3H), 0.73 (q, $J = 7.9$ Hz, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta/\text{ppm} = 143.2, 128.9, 128.2, 125.7, 37.6, 32.0, 30.8, 30.1, 29.4, 29.1, 27.6, 22.8, 14.2, 9.4, 3.8$. **HRMS** (ESI) calculated for $\text{C}_{19}\text{H}_{33}\text{Ge}$: 335.1789 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 335.1788. **IR** (neat): $\nu/\text{cm}^{-1} = 2923, 2865, 1457, 1257, 1020$.

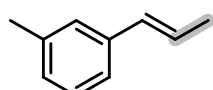
Triethyl(1-phenyldecan-2-yl)germane (48)



Prepared, following the general procedure A, but stirring for 72 h and heating at 120°C , from non-8-en-1-ylbenzene (60.7 mg, 0.30 mmol) with LiO^tBu (48.0 mg, 0.60 mmol, 2.0 equiv.) and CsF (91.1 mg, 0.60 mmol, 2.0 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (61.1 mg, 0.16 mmol, 54%).

$R_f = 0.78$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.29 - 7.25$ (m, 2H), 7.20 – 7.16 (m, 3H), 2.80 (dd, $J = 13.9, 5.1$ Hz, 1H), 2.63 (dd, $J = 13.9, 9.6$ Hz, 1H), 1.48 – 1.35 (m, 3H), 1.32 – 1.27 (m, 3H), 1.25 – 1.16 (m, 9H), 1.04 (t, $J = 7.9$ Hz, 9H), 0.89 (t, $J = 7.1$ Hz, 3H), 0.75 (q, $J = 7.9$ Hz, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta/\text{ppm} = 143.2, 128.9, 128.2, 125.7, 37.6, 32.0, 30.8, 30.1, 29.7, 29.4, 29.1, 27.6, 22.8, 14.3, 9.4, 3.8$. **HRMS** (ESI) calculated for $\text{C}_{20}\text{H}_{35}\text{Ge}$: 349.1945 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 349.1943. **IR** (neat): $\nu/\text{cm}^{-1} = 2923, 2858, 1494, 1457, 1014$.

(E)-1-methyl-3-(prop-1-en-1-yl)benzene (49)

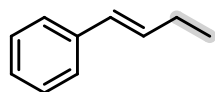


Prepared, following the general procedure B from 1-allyl-3-methylbenzene (39.7 mg, 0.3 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after column chromatography (*n*-pentane) as a colorless oil (33.6 mg, 0.25 mmol, 85%).

$R_f = 0.82$ (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) $\delta/\text{ppm} = 7.18$ (t, $J = 7.6$ Hz, 1H), 7.16 – 7.11 (m, 2H), 7.01 (d, $J = 7.4$ Hz, 1H), 6.39 – 6.35 (m, 1H), 6.26 – 6.19 (m, 1H), 2.33 (s, 3H), 1.87 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta/\text{ppm} = 138.1, 138.0, 131.2, 128.5, 127.7, 126.7, 125.6, 123.1, 21.6, 18.6$. **MS** (EI) m/z

(%): 132 (85), 117 (100), 91 (20). These data are in agreement with those reported previously in the literature.^[211]

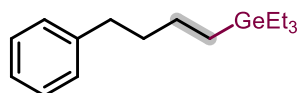
(*E*)-but-1-en-1-ylbenzene (50)



Prepared, following the general procedure B from but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.), CsF (4.6 mg, 0.03 mmol, 0.1 equiv.). The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (31.7 mg, 0.27 mmol, 80%).

R_f = 0.82 (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.35 (d, J = 7.5 Hz, 2H), 7.29 (dd, J = 7.6 Hz, 2H), 7.19 (dd, J = 7.3 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.27 (dt, J = 15.8, 6.4 Hz, 1H), 2.28 – 2.20 (m, 2H), 1.10 (t, J = 7.5 Hz, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 138.1, 132.8, 128.9, 128.6, 126.9, 126.0, 26.2, 13.8. **MS** (EI) m/z (%): 132 (55) $[\text{M}]^+$, 117 (100), 91 (20). These data are in agreement with those reported previously in the literature.^[212]

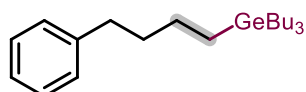
Triethyl(4-phenylbutyl)germane (51)



In an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.) and Pd_2dba_3 (6.9 mg, 0.008 mmol, 0.025 equiv.) and dissolved in anhydrous DMI (3.0 mL, 0.1 M). To the mixture were added but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) and Et_3GeH (72.8 μL , 0.45 mmol, 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel (*n*-pentane) to obtain the desired product as a colorless oil (74.3 mg, 0.25 mmol, 85%).

R_f = 0.91 (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.30 – 7.26 (m, 2H), 7.20 – 7.14 (m, 3H), 2.61 (t, J = 7.8 Hz, 2H), 1.63 (p, J = 7.6 Hz, 2H), 1.42 (p, J = 7.7 Hz, 2H), 1.00 (t, J = 7.9 Hz, 9H), 0.77 – 0.66 (m, 8H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 143.1, 128.5, 128.4, 125.7, 35.8, 35.6, 25.1, 11.5, 9.1, 4.1. **HRMS** (EI) calculated for $\text{C}_{14}\text{H}_{23}\text{Ge}$: 265.1006 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 265.1007. **IR** (neat): ν/cm^{-1} = 2925, 1495, 1456, 1015, 696. These data are in agreement with those reported previously in the literature.^[213]

Tributyl(4-phenylbutyl)germane (52)

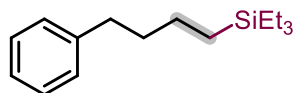


In an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (0.8 mg, 0.01 mmol, 0.1 equiv.) and CsF (1.5 mg, 0.01 mmol, 0.1 equiv.) and Pd_2dba_3 (2.3 mg, 0.003 mmol, 0.025 equiv.) and dissolved in anhydrous DMI (1.0 mL, 0.1 M). To the mixture were added but-3-en-1-ylbenzene (13.2 mg, 0.10 mmol) and $n\text{-Bu}_3\text{GeH}$ (116.2 μL , 0.45 mmol, 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel (*n*-pentane) to obtain the desired product as a colorless oil (28.2 mg, 0.07 mmol, 75%).

R_f = 0.89 (*n*-pentane). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.29 – 7.26 (m, 2H), 7.19 – 7.15 (m, 3H), 2.62 (t, J = 7.8 Hz, 2H), 1.63 (p, J = 7.4 Hz, 2H), 1.43 – 1.36 (m, 2H), 1.32 – 1.29 (m, 12H), 0.88 (t, J = 7.0 Hz, 9H), 0.75 – 0.65 (m, 8H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 143.1, 128.6, 128.4, 125.7, 35.7, 35.6, 27.7, 26.8, 25.1,

13.9, 12.7, 12.6. **HRMS** (EI) calculated for $C_{18}H_{31}Ge$: 321.1632 $[M-CH_2CH_3]^+$, found: 321.1631. **IR** (neat): ν/cm^{-1} = 3027, 2870, 1456, 1015, 743.

Triethyl(4-phenylbutyl)silane (53)



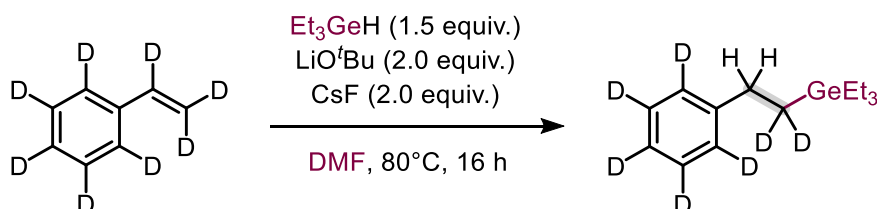
In an argon-filled glovebox, an 8 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (2.4 mg, 0.03 mmol, 0.1 equiv.) and CsF (4.6 mg, 0.03 mmol, 0.1 equiv.) and Pd_2dba_3 (6.9 mg, 0.008 mmol, 0.025 equiv.) and dissolved in anhydrous DMI (3.0 mL, 0.1 M). To the mixture were added but-3-en-1-ylbenzene (39.7 mg, 0.30 mmol) and Et_3SiH (71.9 μL , 0.45 mmol, 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel (*n*-pentane) to obtain the desired product as a colorless oil (73.8 mg, 0.3 mmol, 99%).

R_f = 0.35 (*n*-pentane). **1H NMR** (600 MHz, $CDCl_3$) δ/ppm = 7.29 – 7.25 (m, 2H), 7.20 – 7.14 (m, 3H), 2.65 – 2.57 (m, 2H), 1.69 – 1.58 (m, 2H), 1.39 – 1.32 (m, 2H), 0.92 (t, J = 7.9 Hz, 9H), 0.57 – 0.53 (m, 2H), 0.50 (q, J = 7.9 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ/ppm = 143.09, 128.53, 128.36, 125.66, 35.84, 35.81, 32.23, 23.77, 11.36, 7.62, 3.48. **MS** (EI) m/z (%): 219 (100) $[M-CH_2CH_3]^+$, 191 (15), 115 (17), 87 (50).

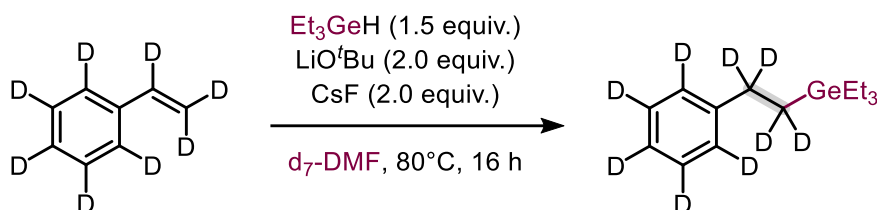
These data are in agreement with those reported previously in the literature.^[214]

3.2.5 Deuterium labeling studies

Triethyl(2-(phenyl- d_5)ethyl-1,1- d_2)germane (54)

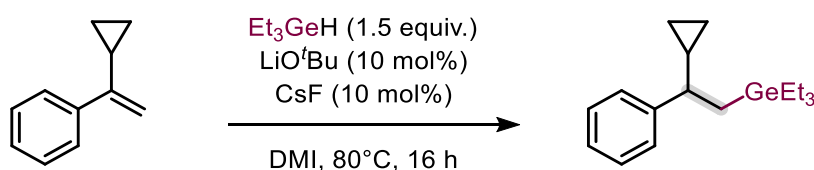


Prepared, following the general procedure A from styrene- d_8 (33.7 mg, 0.30 mmol) with LiO^tBu (48.0 mg, 0.60 mmol, 2.0 equiv.) and CsF (91.1 mg, 0.60 mmol, 2.0 equiv.) in DMF. The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (71.8 mg, 0.26 mmol, 85%). Prepared, following general procedure B from 55 (82.2 mg, 0.3 mmol, 1.0 equiv.) with LiO^tBu (48.0 mg, 0.60 mmol, 2.0 equiv.) and CsF (91.1 mg, 0.60 mmol, 2.0 equiv.) in DMF. The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (74.3 mg, 0.27 mmol, 91%). R_f = 0.87 (*n*-pentane). **1H NMR** (600 MHz, $CDCl_3$) δ/ppm = 2.67 (s, 2H), 1.04 (t, J = 7.9 Hz, 9H), 0.75 (q, J = 7.9 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ/ppm = 145.4, 127.9 (t, J = 23.6 Hz), 127.5 (t, J = 23.6 Hz), 125.1 (t, J = 24.3, 23.5 Hz), 31.2, 12.9 (p, J = 20.0, 19.3, 11.2 Hz), 9.1, 4.0. **HRMS** (EI) calculated for $C_{12}H_{12}^2H_7Ge$: 244.1132 $[M-CH_2CH_3]^+$, found: 244.1137. **IR** (neat): ν/cm^{-1} = 2948, 2870, 1457, 1379, 1014.

Triethyl(2-(phenyl-*d*₅)ethyl-1,1,2,2-*d*₄)germane (55)

Prepared, following the general procedure A from styrene-*d*₈ (33.7 mg, 0.30 mmol) with LiO^tBu (48.0 mg, 0.60 mmol, 2.0 equiv.) and CsF (91.1 mg, 0.60 mmol, 2.0 equiv.) in DMF-*d*₇. The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless oil (72.4 mg, 0.27 mmol, 88%).

*R*_f = 0.85 (*n*-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 1.03 (t, *J* = 7.9 Hz, 9H), 0.74 (q, *J* = 7.9 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 145.4, 127.9 (t, *J* = 24.2 Hz), 127.5 (t, *J* = 23.7 Hz), 125.1 (t, *J* = 24.2 Hz), 30.5 (p, *J* = 19.7, 19.1, 15.9 Hz), 12.7 (p, *J* = 19.2, 18.8 Hz), 9.1, 4.0. HRMS (APCI) calculated for C₁₂H₁₀²H₉Ge: 246.1258 [M-CH₂CH₃]⁺, found: 246.1258. IR (neat): ν/cm⁻¹ = 2948, 2906, 1458, 1379, 1015.

3.2.6 Radical clock experiment**(2-Cyclopropyl-2-phenylethyl)triethylgermane (56)**

In an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with LiO^tBu (0.8 mg, 0.01 mmol, 0.1 equiv.) and CsF (1.5 mg, 0.01 mmol, 0.1 equiv.) and dissolved in anhydrous DMI (1.0 mL, 0.1 M). To the mixture were added (1-cyclopropylvinyl)benzene (14.4 mg, 0.10 mmol) and Et₃GeH (24.3 μL, 0.15 mmol, 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel (*n*-pentane) to obtain the desired product as a colorless oil (28.0 mg, 0.09 mmol, 92%).

In an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with KO^tBu (1.1 mg, 0.01 mmol, 0.1 equiv.) and dissolved in anhydrous DMI (1.0 mL, 0.1 M). To the mixture were added (1-cyclopropylvinyl)benzene (14.4 mg, 0.10 mmol) and Et₃GeH (24.3 μL, 0.15 mmol, 1.5 equiv.). The vial was sealed and brought out of glovebox and stirred in a heating block at 80°C overnight. After cooling down to room temperature the crude reaction mixture was directly subjected to flash column chromatography on silica gel (*n*-pentane) to obtain the desired product as a colorless oil (28.1 mg, 0.09 mmol, 92%).

*R*_f = 0.90 (*n*-pentane). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.28 – 7.25 (m, 2H), 7.20 – 7.16 (m, 3H), 1.93 (td, *J* = 9.4, 5.4 Hz, 1H), 1.30 – 1.21 (m, 2H), 1.01 – 0.95 (m, 1H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.58 – 0.45 (m, 7H), 0.37 – 0.31 (m, 1H), 0.22 – 0.15 (m, 1H), 0.11 – 0.05 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 147.7, 128.3,

127.5, 126.1, 48.0, 21.3, 19.4, 9.0, 5.9, 4.5, 4.5. **HRMS** (EI) calculated for $C_{15}H_{23}Ge$: 277.1006 $[M-CH_2CH_3]^+$, found: 277.1004. **IR** (neat): ν/cm^{-1} = 2947, 2871, 2326, 1455, 1014.

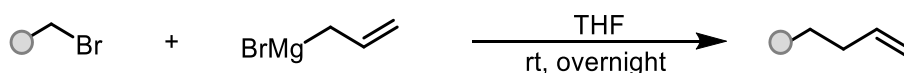
3.2.7 Starting material synthesis

Note: The following compounds were synthesized as previously reported:

1-allyl-2-(allyloxy)benzene^[215], 1-(but-3-en-1-yl)-3-methylbenzene^[216], 1-(but-3-en-1-yl)-4-(tert-butyl)benzene^[216], 2-(but-3-en-1-yl)naphthalene^[217], 1-(but-3-en-1-yl)-4-fluorobenzene^[216], 1-(but-3-en-1-yl)-3-methoxybenzene^[218], (3-methylbut-2-en-1-yl)benzene^[219], pent-4-en-2-ylbenzene^[220], pent-4-en-1-ylbenzene^[217], hex-5-en-1-ylbenzene^[217], hept-6-en-1-ylbenzene^[221], oct-7-en-1-ylbenzene^[221], non-8-en-1-ylbenzene^[222], dec-9-en-1-ylbenzene^[221], 1-(but-3-en-1-yl)-4-(trifluoromethyl)benzene^[223], 1-(but-3-en-1-yl)-4-(trifluoromethoxy)benzene^[224], N-(but-3-en-1-yl)-N-methylaniline^[225], (2-methylbut-3-en-1-yl)benzene^[226], (*E*)-(2-methylbuta-1,3-dien-1-yl)benzene^[227], (1-cyclopropylvinyl)benzene (synthesized by our lab technician Daniela Dreßler).

Following compounds were synthesized by Dr. Aymane Selmani: 2-methoxy-6-(3-methylbut-3-en-1-yl)naphthalene^[88], 2-(but-3-en-1-yl)pyridine^[228], 5-(but-3-en-1-yl)benzo[d][1,3]dioxole, (4-(but-3-en-1-yl)phenyl)(methyl)sulfane.

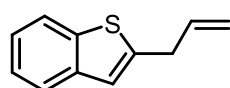
3.2.8 General procedure C



Benzylbromide (2.0-5.0 mmol, 1.0 equiv.) and THF (0.5 M) were added to an oven dried flask under argon atmosphere. Then, allylmagnesiumbromide (1.0 M in 2-Me-THF or Et₂O, 7.5-10.0 mmol, 1.5-2.0 equiv.) was added slowly to the stirring mixture at ambient temperature and left stirring overnight. The reaction mixture was quenched by the addition of aqueous NH₄Cl, the organic layer was separated and the aqueous layer extracted three times with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The product was obtained after column chromatography on silica gel.

3.2.9 Characterization data of alkene starting material

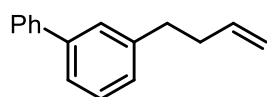
2-allylbenzo[b]thiophene



Prepared, following the general procedure C from 2-bromobenzo[b]thiophene (1.00 g, 4.70 mmol, 1.0 equiv.) and allylmagnesiumbromide (7.05 mL, 7.05 mmol, 1.5 equiv.). The title compound was obtained after purification by preparative HPLC

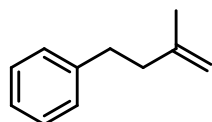
(*n*-hexane, 20 mL/min) as colorless oil (696.0 mg, 4.00 mmol, 85%).

R_f = 0.78 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.77 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.28 – 7.24 (m, 1H), 7.04 (s, 1H), 6.05 (ddtd, J = 16.8, 10.0, 6.7, 1.3 Hz, 1H), 5.23 (dt, J = 17.0, 1.5 Hz, 1H), 5.17 (dt, J = 10.0, 1.4 Hz, 1H), 3.66 (dt, J = 6.6, 1.3 Hz, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 144.1, 140.3, 139.8, 135.9, 124.3, 123.7, 123.0, 122.3, 121.2, 117.0, 35.2. **MS** (EI) m/z (%): 174 (100), 147 (66), 129 (14). These data are in agreement with those reported previously in the literature.^[229]

3-(But-3-en-1-yl)-1,1'-biphenyl

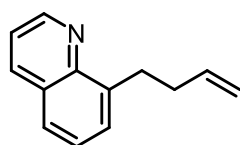
Prepared, following the general procedure C from 3-(bromomethyl)-1,1'-biphenyl (1.235 g, 5.0 mmol, 1.0 equiv.) and allylmagnesiumbromide (7.5 mL, 7.5 mmol, 1.5 equiv.). The title compound was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (344.2 mg, 1.65 mmol, 33%).

R_f = 0.75 (*n*-pentane). **^1H NMR** (600 MHz, CDCl_3) δ /ppm = 7.61 – 7.58 (m, 2H), 7.46 – 7.41 (m, 4H), 7.38 – 7.32 (m, 2H), 7.19 (d, J = 7.5 Hz, 1H), 5.94 – 5.85 (m, 1H), 5.08 (dd, J = 17.1, 1.7 Hz, 1H), 5.00 (dd, J = 10.2, 1.7 Hz, 1H), 2.79 (t, J = 7.9 Hz, 2H), 2.47 – 2.40 (m, 2H). **^{13}C NMR** (151 MHz, CDCl_3) δ /ppm = 142.5, 141.5, 141.4, 138.2, 128.8, 127.5, 127.5, 127.3, 127.3, 127.3, 124.9, 115.2, 35.7, 35.6. **MS** (EI) m/z (%): 208 (86) $[\text{M}]^+$, 178 (10), 167 (100), 152 (45). These data are in agreement with those reported previously in the literature.^[230]

(3-Methylbut-3-en-1-yl)benzene

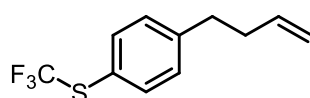
Prepared, following the general procedure C from (bromomethyl)benzene (855.2 mg, 5.0 mmol, 1.0 equiv.) and 2-methylallylmagnesium bromide (0.5 M in THF, 15.0 mL, 7.5 mmol, 1.5 equiv.). The title compound was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (662.7 mg, 4.53 mmol, 91%).

R_f = 0.50 (*n*-pentane). **^1H NMR** (600 MHz, CDCl_3) δ /ppm = 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 4.74 (s, 1H), 4.72 (s, 1H), 2.78 – 2.73 (m, 2H), 2.33 (dd, J = 9.5, 6.9 Hz, 2H), 1.78 (s, 3H). **^{13}C NMR** (151 MHz, CDCl_3) δ /ppm = 145.6, 142.4, 128.5, 128.4, 125.9, 110.3, 39.8, 34.4, 22.8. **HRMS** (APCI) calculated for $\text{C}_{11}\text{H}_{15}$: 147.1168 $[\text{M}+\text{H}]^+$, found: 147.1176. These data are in agreement with those reported previously in the literature.^[231]

8-(But-3-en-1-yl)quinoline

Prepared, following the general procedure C from 8-(bromomethyl)quinoline (1.0 g, 4.5 mmol, 1.0 equiv.) and allylmagnesiumbromide (6.75 mL, 6.75 mmol, 1.5 equiv.). The title compound was obtained after purification by preparative HPLC (*n*-hexane/EtOAc 7:3, 18 mL/min) as colorless oil (305.3 mg, 1.67 mmol, 37%).

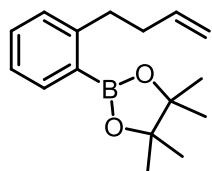
R_f = 0.52 (*n*-pentane/Et₂O 9:1). **^1H NMR** (600 MHz, CDCl_3) δ /ppm = 8.95 (dd, J = 4.2, 1.8 Hz, 1H), 8.13 (dd, J = 8.2, 1.8 Hz, 1H), 7.67 (dd, J = 8.2, 1.5 Hz, 1H), 7.56 (dd, J = 7.0, 1.5 Hz, 1H), 7.47 (dd, J = 8.1, 7.0 Hz, 1H), 7.39 (dd, J = 8.2, 4.1 Hz, 1H), 5.97 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.07 (dd, J = 17.1, 1.8 Hz, 1H), 4.99 (dd, J = 10.2, 1.7 Hz, 1H), 3.41 – 3.37 (m, 2H), 2.61 – 2.56 (m, 2H). **^{13}C NMR** (151 MHz, CDCl_3) δ /ppm = 149.4, 147.0, 140.7, 138.8, 136.5, 129.0, 128.6, 126.4, 126.2, 120.9, 114.8, 34.8, 31.1. **HRMS** (ESI) calculated for $\text{C}_{13}\text{H}_{14}\text{N}$: 184.1121 $[\text{M}+\text{H}]^+$, found: 184.1119. **IR** (neat): ν/cm^{-1} = 3070, 2975, 2920, 1639, 1595, 1497.

(4-(But-3-en-1-yl)phenyl)(trifluoromethyl)sulfane

Prepared, following the general procedure C from (4-(bromomethyl)phenyl)(trifluoromethyl)sulfane (1.0 g, 3.68 mmol, 1.0 equiv.) and allylmagnesiumbromide (5.5 mL, 5.50 mmol, 1.5 equiv.). The title compound was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (562.1 mg, 2.40 mmol, 66%).

$R_f = 0.83$ (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.56 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.88 – 5.79 (m, 1H), 5.08 – 4.98 (m, 2H), 2.77 – 2.72 (m, 2H), 2.42 – 2.36 (m, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 145.3, 137.6, 136.6, 129.8, 129.8 (q, *J* = 308.2 Hz), 121.5, 115.6, 35.21 (d, *J* = 2.9 Hz). **¹⁹F NMR** (564 MHz, CDCl₃) δ /ppm = -43.1. **HRMS** (EI) calculated for C₁₁H₁₁F₃S: 232.0528 [M]⁺, found: 232.0533. **IR** (neat): ν /cm⁻¹ = 3079, 2982, 2932, 1641, 1115.

2-(2-(but-3-en-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



Prepared, following the general procedure C from 2-(2-(bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 g, 3.36 mmol, 1.0 equiv.) and allylmagnesiumbromide (5.1 mL, 5.05 mmol, 1.5 equiv.). The title compound was obtained after purification by flash chromatography on silica gel (*n*-pentane) as colorless oil (746.0 mg, 2.89 mmol, 86%).

$R_f = 0.25$ (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.78 (d, *J* = 7.5 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.20 – 7.15 (m, 2H), 5.94 – 5.85 (m, 1H), 5.03 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.97 – 4.93 (m, 1H), 2.99 – 2.95 (m, 2H), 2.34 – 2.28 (m, 2H), 1.35 (s, 13H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 149.2, 139.0, 136.2, 131.0, 129.4, 125.2, 114.4, 83.6, 37.6, 35.6, 25.0. **MS** (EI) *m/z* (%): 258 (6), 217 (71), 130 (100). These data are in agreement with those reported previously in the literature.^[232]

3.2.10 Computational data

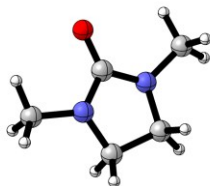
The pK_a values were computed at two levels of theory, B3LYP/6-31+G(d) and M06-2X/def2-TZVPP, as described below. The calculated values obtained with B3LYP/6-31+G(d) were done without any exploration of the conformational space.

I) First, the CREST package^[102] in xTB^[103, 104] was used to explore conformational space for both the neutral molecules as well as their anions (after deprotonation). If more than 10 conformers were obtained the clustering option of CREST was utilized to select the most representative conformers. The number of representatives (i.e. clusters) was initially not specified, but set to 10 in those cases where more than 10 clusters/representatives were formed.

II) The selected conformers were then further optimized at the DFT level using the Gaussian 16 program package (revision A.03).^[100] Geometry optimizations were carried out using M06-2X and def2-TZVPP basis set on all atoms and accounting for solvation using the SMD model for DMSO. The minimum energy conformer of each structure was then used to calculate the pK_a using COSMOtherm.^[101] Input structures for COSMOtherm were generated from single-point energy calculations at the BP86^[233, 234]/def2-TZVPD^[235] level of theory using Turbomole 7.5.1.^[236] Figures were created using CYLView.^[237]

3.2.11 XYZ coordinates and energies of optimized structures

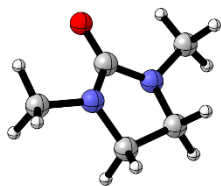
DMI neutral (B3LYP)



C	0.76160	1.49746	-0.09878
C	-0.00008	-0.70050	0.00011
C	-0.76156	1.49742	0.09872
H	1.28049	2.18977	0.56951
H	1.03178	1.73893	-1.13888
H	-1.28067	2.18952	-0.56960
H	-1.03168	1.73893	1.13884
N	1.10046	0.10793	0.20636
N	-1.10049	0.10780	-0.20622
C	2.44821	-0.38041	-0.01925
H	2.49290	-1.43692	0.25224
H	2.74540	-0.26813	-1.07347
H	3.15014	0.18032	0.60559
C	-2.44826	-0.38039	0.01914
H	-3.14995	0.17943	-0.60673
H	-2.49256	-1.43730	-0.25100
H	-2.74621	-0.26694	1.07306
O	0.00014	-1.93990	-0.00003

Zero-point correction = 0.156228 (Hartree/Particle)
 Thermal correction to Energy = 0.164472
 Thermal correction to Enthalpy = 0.165417
 Thermal correction to Gibbs Free Energy = 0.123661
 Sum of electronic and zero-point Energies = -381.176805
 Sum of electronic and thermal Energies = -381.168560
 Sum of electronic and thermal Enthalpies = -381.167616
 Sum of electronic and thermal Free Energies = -381.209372

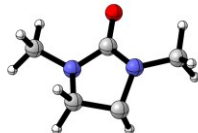
DMI neutral (M06-2X)



C	0.75668	1.48722	-0.09968
C	-0.00000	-0.70039	-0.00001
C	-0.75668	1.48722	0.09968
H	1.27224	2.17914	0.56323
H	1.02121	1.72287	-1.13656
H	-1.27223	2.17915	-0.56323
H	-1.02120	1.72287	1.13656
N	1.09193	0.10699	0.20731
N	-1.09193	0.10699	-0.20730
C	2.43048	-0.37802	-0.01922
H	3.13200	0.17576	0.60395
H	2.47563	-1.43117	0.24700
H	2.72718	-0.26193	-1.06730
C	-2.43048	-0.37802	0.01922
H	-3.13201	0.17586	-0.60385
H	-2.47567	-1.43113	-0.24713
H	-2.72714	-0.26206	1.06733
O	-0.00001	-1.92192	0.00000

Zero-point correction = 0.156473 (Hartree/Particle)
 Thermal correction to Energy = 0.164804
 Thermal correction to Enthalpy = 0.165748
 Thermal correction to Gibbs Free Energy = 0.123708
 Sum of electronic and zero-point Energies = -381.142907
 Sum of electronic and thermal Energies = -381.134576
 Sum of electronic and thermal Enthalpies = -381.133631
 Sum of electronic and thermal Free Energies = -381.175672

DMI anion C (B3LYP)

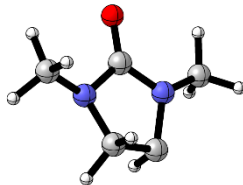


C	0.74508	1.61580	0.07189
C	0.04859	-0.65755	0.04780
C	-0.76121	1.50290	-0.14716
H	0.89398	1.77514	1.16621
H	-1.05728	1.61352	-1.21113
H	-1.34130	2.22588	0.43894
N	1.10055	0.18400	-0.16127
N	-1.09173	0.11332	0.26045
C	2.46310	-0.27629	-0.06422
C	2.51502	-1.34635	-0.28446
H	3.08880	0.27463	-0.77614
H	2.87306	-0.10726	0.94686
C	-2.39451	-0.43355	-0.06268
H	-2.61073	-0.35904	-1.14350
H	-2.43503	-1.48628	0.22895

H	-3.17056	0.11644	0.48055
O	0.07201	-1.91197	0.04820

Zero-point correction = 0.140602 (Hartree/Particle)
 Thermal correction to Energy = 0.148746
 Thermal correction to Enthalpy = 0.149690
 Thermal correction to Gibbs Free Energy = 0.108221
 Sum of electronic and zero-point Energies = -380.629126
 Sum of electronic and thermal Energies = -380.620982
 Sum of electronic and thermal Enthalpies = -380.620038
 Sum of electronic and thermal Free Energies = -380.661507

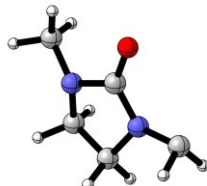
DMI anion C (M06-2X)



C	-0.73832	1.60627	-0.07962
C	-0.04982	-0.65695	-0.05086
C	0.76233	1.48962	0.15002
H	-0.85821	1.75061	-1.17467
H	1.04314	1.59688	1.21182
H	1.34230	2.21299	-0.42535
N	-1.09253	0.18466	0.15990
N	1.08338	0.11439	-0.25995
C	-2.44814	-0.27250	0.06846
H	-2.49227	-1.34130	0.27086
H	-3.06890	0.25733	0.79332
H	-2.86827	-0.09046	-0.92944
C	2.37430	-0.43621	0.06583
H	2.58373	-0.37103	1.14194
H	2.40990	-1.48221	-0.23188
H	3.15467	0.10850	-0.46638
O	-0.07302	-1.88949	-0.05160

Zero-point correction = 0.141552 (Hartree/Particle)
 Thermal correction to Energy = 0.149690
 Thermal correction to Enthalpy = 0.150635
 Thermal correction to Gibbs Free Energy = 0.109129
 Sum of electronic and zero-point Energies = -380.597378
 Sum of electronic and thermal Energies = -380.589240
 Sum of electronic and thermal Enthalpies = -380.588296
 Sum of electronic and thermal Free Energies = -380.629801

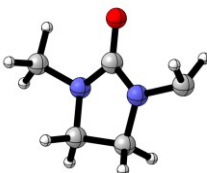
DMI anion N (B3LYP)



C	0.89286	1.40220	-0.10382
C	-0.00108	-0.72995	-0.03766
C	-0.62200	1.51357	0.10105
H	1.46883	2.01156	0.59911
H	1.18979	1.68396	-1.12777
H	-1.09792	2.27460	-0.52543
H	-0.86617	1.72662	1.15652
N	1.15697	-0.02597	0.11648
N	-1.05985	0.16839	-0.26393
C	2.51770	-0.57432	0.07342
H	2.94787	-0.30231	-0.91397
H	3.10172	-0.00682	0.82007
C	-2.41511	-0.22515	0.07328
H	-3.12336	0.43618	-0.43671
H	-2.58636	-1.25201	-0.25583
H	-2.60262	-0.16577	1.15945
O	-0.16823	-1.96513	-0.01012

Zero-point correction = 0.140586 (Hartree/Particle)
 Thermal correction to Energy = 0.148649
 Thermal correction to Enthalpy = 0.149594
 Thermal correction to Gibbs Free Energy = 0.108403
 Sum of electronic and zero-point Energies = -380.627180
 Sum of electronic and thermal Energies = -380.619117
 Sum of electronic and thermal Enthalpies = -380.618173
 Sum of electronic and thermal Free Energies = -380.659364

DMI anion N (M06-2X)

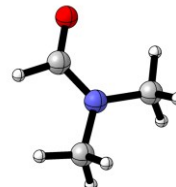


C	-0.75750	1.50865	-0.11263
C	-0.07293	-0.68521	-0.03942
C	0.75006	1.46892	0.11202
H	-1.00072	1.81058	-1.13864
H	-1.26933	2.18156	0.57301

H	0.99492	1.63956	1.16867
H	1.29845	2.18804	-0.49457
N	-1.14873	0.12660	0.11558
N	1.06009	0.10014	-0.26432
C	-2.54740	-0.29198	0.02493
H	-2.60853	-1.08018	-0.74018
H	-2.81873	-0.79093	0.96793
C	2.35853	-0.42562	0.07712
H	2.42103	-1.46266	-0.24366
H	3.13210	0.14905	-0.43250
H	2.54775	-0.37834	1.15720
O	-0.05763	-1.91155	-0.01852

Zero-point correction = 0.141385 (Hartree/Particle)
 Thermal correction to Energy = 0.149586
 Thermal correction to Enthalpy = 0.150530
 Thermal correction to Gibbs Free Energy = 0.108914
 Sum of electronic and zero-point Energies = -380.596606
 Sum of electronic and thermal Energies = -380.588405
 Sum of electronic and thermal Enthalpies = -380.587461
 Sum of electronic and thermal Free Energies = -380.629077

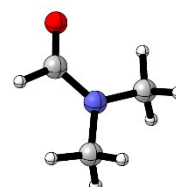
DMF neutral (B3LYP)



O	1.96849	0.08337	-0.00004
N	-0.33643	0.02332	0.00003
C	-0.44563	-1.43085	0.00002
H	-0.99100	-1.76540	0.89050
H	-0.99005	-1.76548	-0.89102
H	0.55376	-1.86681	0.00052
C	-1.58622	0.77521	-0.00003
H	-1.37725	1.84789	0.00009
H	-2.17586	0.52938	-0.89111
H	-2.17610	0.52921	0.89085
C	0.86286	0.64221	0.00003
H	0.77753	1.74160	0.00014

Zero-point correction = 0.102829 (Hartree/Particle)
 Thermal correction to Energy = 0.108951
 Thermal correction to Enthalpy = 0.109895
 Thermal correction to Gibbs Free Energy = 0.073525
 Sum of electronic and zero-point Energies = -248.433839
 Sum of electronic and thermal Energies = -248.427717
 Sum of electronic and thermal Enthalpies = -248.426773
 Sum of electronic and thermal Free Energies = -248.463143

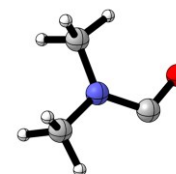
DMF neutral (M06-2X)



O	1.94811	-0.08192	-0.00003
N	-0.33320	-0.02324	0.00016
C	-1.57146	-0.76964	-0.00005
H	-1.35816	-1.83657	0.00046
H	-2.16123	-0.52526	0.88559
H	-2.16053	-0.52581	-0.88628
C	-0.44188	1.41899	-0.00002
H	0.55383	1.85179	-0.00005
H	-0.98489	1.75341	-0.88611
H	-0.98490	1.75366	0.88597
C	0.85939	-0.63622	-0.00000
H	0.76711	-1.73201	-0.00005

Zero-point correction = 0.103250 (Hartree/Particle)
 Thermal correction to Energy = 0.109323
 Thermal correction to Enthalpy = 0.110267
 Thermal correction to Gibbs Free Energy = 0.074095
 Sum of electronic and zero-point Energies = -248.406191
 Sum of electronic and thermal Energies = -248.400119
 Sum of electronic and thermal Enthalpies = -248.399174
 Sum of electronic and thermal Free Energies = -248.435346

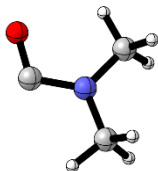
DMF anion C (B3LYP)



O	1.95430	0.15303	-0.00006
N	-0.30980	0.06475	0.00051
C	-0.36172	-1.39303	-0.00007
H	-0.88845	-1.77321	0.88891
H	-0.89015	-1.77217	-0.88848
H	0.66201	-1.77680	-0.00119

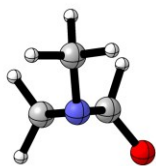
C	-1.59781	0.72540	-0.00011
H	-1.43463	1.80825	-0.00056
H	-2.19185	0.45540	-0.88856
H	-2.19226	0.45634	0.88836
C	0.87111	0.82174	-0.00008

Zero-point correction = 0.087903 (Hartree/Particle)
Thermal correction to Energy = 0.094009
Thermal correction to Enthalpy = 0.094954
Thermal correction to Gibbs Free Energy = 0.058635
Sum of electronic and zero-point Energies = -247.903401
Sum of electronic and thermal Energies = -247.897295
Sum of electronic and thermal Enthalpies = -247.896350
Sum of electronic and thermal Free Energies = -247.932669

DMF anion C (M06-2X)

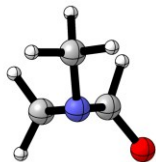
O	1.92747	-0.16129	-0.00001
N	-0.31271	-0.06504	0.00006
C	-0.33531	1.37866	-0.00001
H	-0.85055	1.77308	0.88333
H	0.69409	1.73171	0.00004
H	-0.85042	1.77301	-0.88346
C	-1.59882	-0.70304	-0.00001
H	-2.18998	-0.43075	-0.88305
H	-1.45611	-1.78395	0.00008
H	-2.19013	-0.43062	0.88287
C	0.86952	-0.82342	-0.00001

Zero-point correction = 0.088450 (Hartree/Particle)
Thermal correction to Energy = 0.094513
Thermal correction to Enthalpy = 0.095457
Thermal correction to Gibbs Free Energy = 0.059308
Sum of electronic and zero-point Energies = -247.870571
Sum of electronic and thermal Energies = -247.864508
Sum of electronic and thermal Enthalpies = -247.863564
Sum of electronic and thermal Free Energies = -247.899712

DMF anion N (B3LYP)

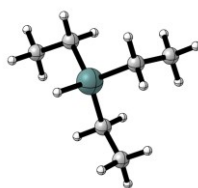
O	-1.89745	0.54282	-0.13289
N	0.49528	0.04992	-0.53224
C	1.76801	0.47058	0.04504
H	1.82539	0.32967	1.14091
H	2.59268	-0.10143	-0.40392
H	1.93360	1.53507	-0.16689
C	-0.07078	-1.18779	0.05457
H	-0.54373	-1.86229	-0.66097
H	0.52121	-1.69311	0.82446
C	-0.72622	0.14438	0.35141
H	-0.44262	0.53702	1.34905

Zero-point correction = 0.088449 (Hartree/Particle)
Thermal correction to Energy = 0.093601
Thermal correction to Enthalpy = 0.094545
Thermal correction to Gibbs Free Energy = 0.060598
Sum of electronic and zero-point Energies = -247.889762
Sum of electronic and thermal Energies = -247.884611
Sum of electronic and thermal Enthalpies = -247.883667
Sum of electronic and thermal Free Energies = -247.917614

DMF anion N (M06-2X)

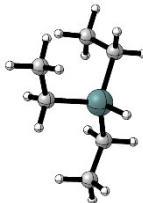
O	1.88386	-0.51834	-0.12474
N	-0.48649	-0.05036	-0.54217
C	-1.74371	-0.46584	0.04530
H	-1.93310	-1.51814	-0.18106
H	-1.76660	-0.34541	1.13846
H	-2.57062	0.12299	-0.36420
C	0.05476	1.17272	0.06431
H	0.53897	1.85396	-0.62809
H	-0.56225	1.65460	0.81988
C	0.72586	-0.15782	0.33862
H	0.40666	-0.56315	1.31871

Zero-point correction = 0.089098 (Hartree/Particle)
Thermal correction to Energy = 0.094161
Thermal correction to Enthalpy = 0.095105
Thermal correction to Gibbs Free Energy = 0.061370
Sum of electronic and zero-point Energies = -247.854880
Sum of electronic and thermal Energies = -247.849818
Sum of electronic and thermal Enthalpies = -247.848873
Sum of electronic and thermal Free Energies = -247.882609

Et₃GeH neutral (B3LYP)

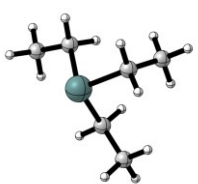
Ge	-0.14464	-0.00777	-0.46587
C	-1.82418	-0.72003	0.30356
H	-2.13563	-1.57852	-0.30575
H	-1.58717	-1.11314	1.30128
C	-2.95940	0.31241	0.39637
H	-3.22377	0.70971	-0.59222
H	-3.86937	-0.12647	0.82772
H	-2.67677	1.16506	1.02666
C	0.49832	1.53360	0.59977
H	-0.27208	2.31464	0.57439
H	0.57029	1.19908	1.64351
C	1.84845	2.09599	0.12727
H	2.17309	2.94237	0.74773
H	2.63802	1.33513	0.17230
H	1.79564	2.45095	-0.91018
C	1.25446	-1.40976	-0.51447
H	2.10649	-1.01703	-1.08410
H	0.86128	-2.26200	-1.08373
C	1.71190	-1.86281	0.88224
H	2.48832	-2.63727	0.82051
H	2.12860	-1.02727	1.45911
H	0.88008	-2.27925	1.46466
H	-0.42573	0.47606	-1.92250

Zero-point correction = 0.204038 (Hartree/Particle)
Thermal correction to Energy = 0.215940
Thermal correction to Enthalpy = 0.216884
Thermal correction to Gibbs Free Energy = 0.165335
Sum of electronic and zero-point Energies = -2312.846687
Sum of electronic and thermal Energies = -2312.834785
Sum of electronic and thermal Enthalpies = -2312.833841
Sum of electronic and thermal Free Energies = -2312.885391

Et₃GeH neutral (M06-2X)

Ge	-0.15435	0.01785	-0.47342
C	0.47289	-1.52908	0.57819
H	0.50159	-1.23464	1.63045
H	-0.26557	-2.32938	0.49812
C	1.84571	-2.02094	0.12210
H	2.60309	-1.24163	0.23047
H	2.18045	-2.88503	0.69988
H	1.83184	-2.31571	-0.92954
C	-1.82261	0.73822	0.29040
H	-1.58924	1.16865	1.26721
H	-2.16405	1.56098	-0.34141
C	-2.91264	-0.32392	0.42584
H	-3.83659	0.09299	0.83204
H	-3.15268	-0.77275	-0.54041
H	-2.59834	-1.13092	1.09052
C	1.26475	1.38692	-0.50251
H	0.89165	2.26339	-1.03657
C	2.10748	1.00303	-1.08138
C	1.71492	1.76829	0.90734
H	0.88646	2.16852	1.49546
H	2.10791	0.90331	1.44626
H	2.50006	2.52702	0.89040
H	-0.44297	-0.46617	-1.93018

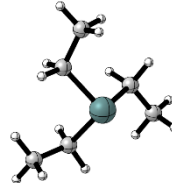
Zero-point correction = 0.203756 (Hartree/Particle)
Thermal correction to Energy = 0.215678
Thermal correction to Enthalpy = 0.216622
Thermal correction to Gibbs Free Energy = 0.165277
Sum of electronic and zero-point Energies = -2315.047985
Sum of electronic and thermal Energies = -2315.036064
Sum of electronic and thermal Enthalpies = -2315.035120
Sum of electronic and thermal Free Energies = -2315.086464

Et₃GeH anion (B3LYP)

Ge	-0.18540	0.07523	-0.72742
C	-1.72775	-0.61111	0.43755
H	-2.09002	-1.56051	0.01246
H	-1.32864	-0.84576	1.43713
C	-2.89710	0.37592	0.57547
H	-3.33004	0.62388	-0.40486
H	-3.71616	-0.00907	1.20400
H	-2.56566	1.32315	1.02446

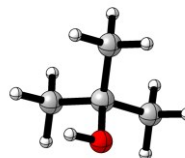
C	0.59108	1.40193	0.63311
H	-0.08667	2.26683	0.69471
H	0.57383	0.92235	1.62512
C	2.01412	1.87875	0.30991
H	2.40803	2.59872	1.04516
H	2.71634	1.03404	0.27695
H	2.05800	2.36668	-0.67524
C	1.14328	-1.47477	-0.45876
H	2.06247	-1.21406	-1.00589
H	0.72197	-2.34933	-0.97986
C	1.49913	-1.85540	0.98655
H	2.21508	-2.69198	1.04442
H	1.94975	-1.00940	1.52309
H	0.60813	-2.15487	1.55397

Zero-point correction = 0.193592 (Hartree/Particle)
Thermal correction to Energy = 0.205184
Thermal correction to Enthalpy = 0.206128
Thermal correction to Gibbs Free Energy = 0.156006
Sum of electronic and zero-point Energies = -2312.332462
Sum of electronic and thermal Energies = -2312.320870
Sum of electronic and thermal Enthalpies = -2312.319926
Sum of electronic and thermal Free Energies = -2312.370048

Et₃GeH anion (M06-2X)

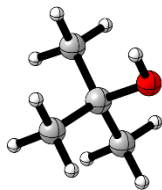
Ge	-0.00013	-0.00091	-0.59230
C	-1.75198	-0.25512	0.43170
H	-1.57163	-0.06000	1.49645
H	-2.48403	0.48817	0.10104
C	-2.33451	-1.65630	0.25483
H	-1.65220	-2.41945	0.63797
H	-3.29064	-1.79451	0.76917
H	-2.50150	-1.88372	-0.80228
C	0.65579	1.64555	0.42836
H	0.73957	1.39211	1.49283
H	1.66352	1.91057	0.09390
C	-0.26967	2.84884	0.25580
H	-0.38817	3.10712	-0.80077
H	-1.26956	2.63734	0.64341
H	0.08948	3.74647	0.76877
C	1.09817	-1.38890	0.43182
H	0.82260	-2.39545	0.10197
H	0.83911	-1.33035	1.49656
C	2.60260	-1.19082	0.25535
H	3.20068	-1.94994	0.76907
H	2.88338	-1.22034	-0.80175
H	2.92118	-0.21854	0.63987

Zero-point correction = 0.193518 (Hartree/Particle)
Thermal correction to Energy = 0.205255
Thermal correction to Enthalpy = 0.206200
Thermal correction to Gibbs Free Energy = 0.155627
Sum of electronic and zero-point Energies = -2314.535289
Sum of electronic and thermal Energies = -2314.523552
Sum of electronic and thermal Enthalpies = -2314.522607
Sum of electronic and thermal Free Energies = -2314.573180

tert-Butanol neutral (B3LYP)

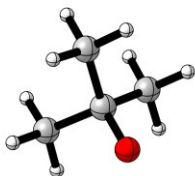
C	-0.00608	0.00000	0.01039
C	0.67765	-1.26443	-0.52736
H	0.61290	-1.30748	-1.62097
H	1.74003	-1.27968	-0.25175
H	2.00058	-2.16071	-0.11497
C	0.67752	1.26449	-0.52739
H	0.61270	1.30754	-1.62100
H	0.20041	2.16073	-0.11496
H	1.73991	1.27980	-0.25184
C	-1.49832	-0.00008	-0.32477
H	-1.98456	-0.88966	0.09184
H	-1.98470	0.88936	0.09197
H	-1.64713	-0.00002	-1.41007
O	0.05241	0.00003	1.46056
H	0.98594	0.00001	1.73206

Zero-point correction = 0.135950 (Hartree/Particle)
Thermal correction to Energy = 0.142534
Thermal correction to Enthalpy = 0.143478
Thermal correction to Gibbs Free Energy = 0.107106
Sum of electronic and zero-point Energies = -233.560572
Sum of electronic and thermal Energies = -233.553988
Sum of electronic and thermal Enthalpies = -233.553043
Sum of electronic and thermal Free Energies = -233.589415

tert-Butanol neutral (M06-2X)

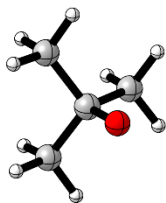
C	0.00780	-0.00000	0.01668
C	1.49372	-0.00059	-0.29502
H	1.96953	-0.88676	0.12758
H	1.65580	-0.00057	-1.37333
H	1.97023	0.88515	0.12770
C	-0.65969	1.25279	-0.53574
H	-0.57991	1.28845	-1.62330
H	-1.72020	1.26737	-0.27269
H	-0.18839	2.14578	-0.12263
C	-0.66072	-1.25218	-0.53588
H	-1.72125	-1.26591	-0.27282
H	-0.58098	-1.28779	-1.62344
H	-0.19016	-2.14561	-0.12288
O	-0.08520	-0.00005	1.44681
H	-1.01971	0.00020	1.68101

Zero-point correction = 0.135980 (Hartree/Particle)
Thermal correction to Energy = 0.142652
Thermal correction to Enthalpy = 0.143596
Thermal correction to Gibbs Free Energy = 0.107057
Sum of electronic and zero-point Energies = -233.527544
Sum of electronic and thermal Energies = -233.520872
Sum of electronic and thermal Enthalpies = -233.519928
Sum of electronic and thermal Free Energies = -233.556467

tert-Butanol anion (B3LYP)

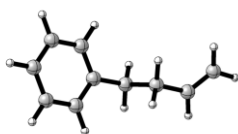
C	0.00002	-0.00001	0.12880
C	-0.81214	1.20152	-0.43395
H	-0.83088	1.23142	-1.53443
H	-1.84951	1.14873	-0.07539
H	-0.37793	2.14437	-0.07333
C	-0.63456	-1.30397	-0.43401
H	-0.65051	-1.33534	-1.53448
H	-0.07091	-2.17630	-0.07499
H	-1.66838	-1.39890	-0.07395
C	1.44669	0.10251	-0.43397
H	1.92010	1.02693	-0.07528
H	2.04579	-0.74533	-0.07416
H	1.48166	0.10437	-1.53447
O	0.00006	-0.00003	1.51115

Zero-point correction = 0.122086 (Hartree/Particle)
Thermal correction to Energy = 0.128221
Thermal correction to Enthalpy = 0.129165
Thermal correction to Gibbs Free Energy = 0.093613
Sum of electronic and zero-point Energies = -233.065621
Sum of electronic and thermal Energies = -233.059486
Sum of electronic and thermal Enthalpies = -233.058542
Sum of electronic and thermal Free Energies = -233.094094

tert-Butanol anion (M06-2X)

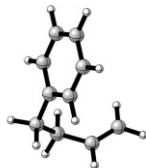
C	0.00025	-0.00026	0.14088
C	-1.14243	-0.87640	-0.43075
H	-1.02609	-1.90190	-0.06892
H	-2.10175	-0.50033	-0.06416
H	-1.17739	-0.89976	-1.52581
C	1.32947	-0.54947	-0.43457
H	1.36670	-0.56305	-1.52969
H	2.15896	0.06301	-0.06991
H	1.48387	-1.56986	-0.07253
C	-0.18975	1.42711	-0.43061
H	0.61590	2.07081	-0.06627
H	-0.19562	1.46904	-1.52560
H	-1.13545	1.83808	-0.06586
O	0.00320	-0.00149	1.48988

Zero-point correction = 0.121510 (Hartree/Particle)
Thermal correction to Energy = 0.127779
Thermal correction to Enthalpy = 0.128724
Thermal correction to Gibbs Free Energy = 0.092926
Sum of electronic and zero-point Energies = -233.009417
Sum of electronic and thermal Energies = -233.003148
Sum of electronic and thermal Enthalpies = -233.002204
Sum of electronic and thermal Free Energies = -233.038001

but-3-en-1-ylbenzene (B3LYP)

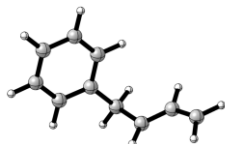
C	2.49553	1.30334	-0.07927
C	1.15783	1.18535	0.31411
C	0.54420	-0.07310	0.41868
C	1.30628	-1.21385	0.11833
C	2.64399	-1.10242	-0.27556
C	3.24399	0.15845	-0.37609
H	2.95288	2.28724	-0.15042
H	0.58287	2.08007	0.54510
H	0.84745	-2.19770	0.19668
H	3.21772	-1.99846	-0.49971
H	4.28414	0.24736	-0.67910
C	-0.91609	-0.19563	0.79539
C	-1.84072	-0.20617	-0.44829
H	-1.20876	0.63853	1.44513
H	-1.07862	-1.11915	1.36641
H	-1.70003	0.72373	-1.01444
H	-1.52535	-1.03239	-1.10241
C	-3.28925	-0.37921	-0.08065
C	-4.26045	0.50727	-0.33156
H	-3.53693	-1.30489	0.44361
H	-5.29088	0.32709	-0.03325
H	-4.05633	1.44446	-0.84816

Zero-point correction = 0.190433 (Hartree/Particle)
Thermal correction to Energy = 0.199917
Thermal correction to Enthalpy = 0.200861
Thermal correction to Gibbs Free Energy = 0.154271
Sum of electronic and zero-point Energies = -388.107847
Sum of electronic and thermal Energies = -388.098363
Sum of electronic and thermal Enthalpies = -388.097419
Sum of electronic and thermal Free Energies = -388.144009

but-3-en-1-ylbenzene (M06-2X)

C	-1.95412	1.06618	0.78062
C	-0.75896	0.45716	1.14538
C	-0.26789	-0.63705	0.43686
C	-1.00205	-1.10648	-0.65230
C	-2.19612	-0.50187	-1.02127
C	-2.67649	0.58847	-0.30474
H	-2.32041	1.91430	1.34501
H	-0.19862	0.83406	1.99325
H	-0.63299	-1.95804	-1.21299
H	-2.75446	-0.88340	-1.86670
H	-3.60796	1.05995	-0.58994
C	1.04916	-1.26997	0.79590
H	1.30630	-1.02481	1.82822
H	0.96646	-2.35574	0.72630
C	2.18810	-0.80719	-0.13130
H	3.08599	-1.37543	0.12485
C	2.46945	0.65568	0.00535
C	2.30578	1.55214	-0.95836
H	2.51300	2.60314	-0.79824
H	1.96009	1.25971	-1.94453
H	2.80916	0.98482	0.98500
H	1.93234	-1.04098	-1.16713

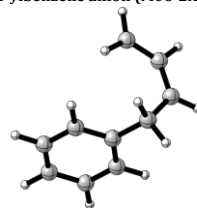
Zero-point correction = 0.191318 (Hartree/Particle)
Thermal correction to Energy = 0.200614
Thermal correction to Enthalpy = 0.201558
Thermal correction to Gibbs Free Energy = 0.155631
Sum of electronic and zero-point Energies = -388.050560
Sum of electronic and thermal Energies = -388.041264
Sum of electronic and thermal Enthalpies = -388.040320
Sum of electronic and thermal Free Energies = -388.086247

but-3-en-1-ylbenzene anion (B3LYP)

C	0.74868	0.87167	0.71047
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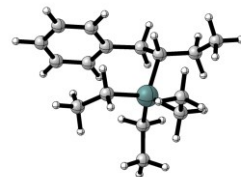
C	0.48069	-0.48414	0.44483
C	1.44922	-1.21760	-0.26150
C	2.63582	-0.61836	-0.70340
C	2.88483	0.73227	-0.43460
C	1.93392	1.47468	0.28108
H	0.01128	1.45747	1.25659
H	1.26929	-2.27147	-0.46963
H	3.36796	-1.20830	-1.25100
H	3.80678	1.19976	-0.77169
H	2.12008	2.52285	0.50587
C	-0.84363	-1.11376	0.86045
C	-1.97099	-0.81432	-0.10710
H	-1.11171	-0.73378	1.85872
H	-0.68171	-2.19854	0.97429
H	-1.88984	-1.28304	-1.09361
C	-2.84092	0.26190	0.06170
C	-3.75862	0.86346	-0.81770
H	-2.80063	0.72049	1.06086
H	-4.48346	1.58929	-0.45236
H	-3.92203	0.47056	-1.82344

Zero-point correction = 0.173743 (Hartree/Particle)
Thermal correction to Energy = 0.183509
Thermal correction to Enthalpy = 0.184453
Thermal correction to Gibbs Free Energy = 0.137699
Sum of electronic and zero-point Energies = -387.578461
Sum of electronic and thermal Energies = -387.568695
Sum of electronic and thermal Enthalpies = -387.567751
Sum of electronic and thermal Free Energies = -387.614505

but-3-en-1-ylbenzene anion (M06-2X)

C	-2.02955	1.29885	0.21197
C	-0.78324	0.95114	0.72737
C	-0.26002	-0.32644	0.54531
C	-1.02517	-1.25357	-0.16638
C	-2.27097	-0.91796	-0.67445
C	-2.77828	0.36584	-0.49001
H	-2.41276	2.30074	0.36062
H	-0.20930	1.68225	1.28597
H	-0.63176	-2.25264	-0.32033
H	-2.85042	-1.65650	-1.21444
H	-3.74825	0.63192	-0.88985
C	1.10682	-0.71577	1.08106
H	1.44213	0.09551	1.74319
H	0.97946	-1.60054	1.71112
C	2.13652	-0.99044	0.01940
C	2.74844	0.03378	-0.67801
C	2.57316	1.41401	-0.57708
H	3.17766	2.08886	-1.16960
H	1.86684	1.85839	0.11432
H	3.48489	-0.28557	-1.41793
H	2.39527	-2.01908	-0.19817

Zero-point correction = 0.175856 (Hartree/Particle)
Thermal correction to Energy = 0.185173
Thermal correction to Enthalpy = 0.186117
Thermal correction to Gibbs Free Energy = 0.141111
Sum of electronic and zero-point Energies = -387.529385
Sum of electronic and thermal Energies = -387.520068
Sum of electronic and thermal Enthalpies = -387.519124
Sum of electronic and thermal Free Energies = -387.564130

Triethyl(1-phenylbutan-2-yl)germane neutral (B3LYP)

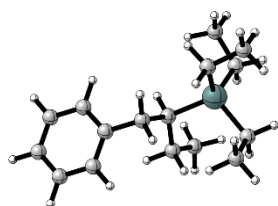
C	3.54728	0.71358	-1.42465
C	2.37086	1.26804	-0.91344
C	1.98740	1.05046	0.42027
C	2.82370	0.26452	1.22805
C	4.00760	-0.28768	0.72534
C	4.37294	-0.06720	-0.60625
H	3.82040	0.89097	-2.46212
H	1.74350	1.87635	-1.56038
H	2.54486	0.08202	2.26377
H	4.63743	-0.89434	1.37153
H	5.28796	-0.49913	-1.00348
C	0.73986	1.69307	0.99342
H	0.59713	1.33484	2.02120
H	0.92895	2.77556	1.08079
C	-0.58097	1.50851	0.20458
H	-0.44402	1.93059	-0.80080
C	-1.70395	2.30676	0.91427
H	-2.17447	1.69606	1.69929
H	-1.24945	3.15872	1.44353
C	-2.78474	2.86339	-0.02115
H	-3.31912	2.07163	-0.55285
H	-3.52599	3.44542	0.54065
H	-2.33832	3.52591	-0.77426
C	-0.03161	-1.30980	-1.50195
H	-0.75565	-1.90542	-2.07294
H	0.32302	-0.52036	-2.17634
C	1.14336	-2.19923	-1.06924
H	0.81080	-3.01704	-0.41803
H	1.63968	-2.65463	-1.93782

Supporting Information

H	1.89864	-1.62959	-0.52142
C	-2.98145	-0.67959	-0.44172
H	-3.21830	-1.72511	-0.20382
H	-3.57298	-0.06699	0.25050
C	-3.37564	-0.38765	-1.89953
H	-2.86181	-1.06259	-2.59466
H	-4.45507	-0.51698	-2.05910
H	-3.12191	0.63615	-2.20063
C	-0.66092	-1.32414	1.71264
H	-0.98571	-0.64799	2.51502
H	0.42983	-1.40424	1.79999
C	-1.31039	-2.70517	1.89546
H	-1.01619	-3.16671	2.84837
H	-2.40516	-2.63897	1.88977
H	-1.02355	-3.39942	1.09524
Ge	-1.04920	-0.43506	-0.02427

Zero-point correction = 0.401724 (Hartree/Particle)
Thermal correction to Energy = 0.423437
Thermal correction to Enthalpy = 0.424381
Thermal correction to Gibbs Free Energy = 0.351095
Sum of electronic and zero-point Energies = -2700.987937
Sum of electronic and thermal Energies = -2700.966223
Sum of electronic and thermal Enthalpies = -2700.965279
Sum of electronic and thermal Free Energies = -2701.038566

Triethyl(1-phenylbutan-2-yl)germane neutral (M06-2X)

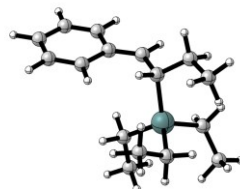


C	-4.47067	-1.47937	-0.37467
C	-3.11199	-1.27629	-0.57239
C	-2.57798	0.01202	-0.63083
C	-3.44344	1.09220	-0.46480
C	-4.80551	0.89515	-0.26591
C	-5.32377	-0.39205	-0.21960
H	-4.86636	-2.48673	-0.34494
H	-2.45223	-2.12811	-0.69549
H	-3.04405	2.09949	-0.49939
H	-5.46128	1.74838	-0.14705
H	-6.38363	-0.54849	-0.06634
C	-1.09428	0.21141	-0.80279
H	-0.75877	-0.41076	-1.63563
H	-0.90500	1.25086	-1.08566
C	-0.27358	-0.13748	0.45431
H	-0.47023	-1.18774	0.70165
C	-0.67616	0.71930	1.65722
H	-0.46526	1.77239	1.43944
H	-1.75846	0.65213	1.80606
C	0.01593	0.31653	2.95370
H	-0.36965	0.88867	3.79875
H	-0.14709	-0.74297	3.16510
H	1.09369	0.48307	2.91049
C	2.33553	1.81870	0.46428
H	2.08801	2.06381	1.49973
H	3.42693	1.80138	0.40490
C	1.77189	2.87875	-0.48196
H	2.15864	3.87451	-0.25360
H	2.02685	2.66050	-1.52136
H	0.68268	2.92969	-0.41941
C	1.99875	-0.35505	-1.86131
H	1.57412	-1.32928	-2.11694
H	1.45410	0.38436	-2.45304
C	3.48824	-0.31574	-2.20154
H	4.04591	-1.06534	-1.63518
H	3.67134	-0.50554	-3.26149
H	3.92337	0.65819	-1.96482

C	2.71162	-1.35614	1.07271
H	2.48216	-1.26178	2.13580
H	3.77389	-1.12277	0.96216
C	2.43043	-2.77899	0.59093
H	1.37017	-3.02754	0.67877
H	2.70675	-2.90434	-0.45826
H	2.98764	-3.52182	1.16597
Ge	1.68018	-0.00444	0.06017

Zero-point correction = 0.400931 (Hartree/Particle)
Thermal correction to Energy = 0.422943
Thermal correction to Enthalpy = 0.423887
Thermal correction to Gibbs Free Energy = 0.348378
Sum of electronic and zero-point Energies = -2703.138742
Sum of electronic and thermal Energies = -2703.116731
Sum of electronic and thermal Enthalpies = -2703.115787
Sum of electronic and thermal Free Energies = -2703.191296

Triethyl(1-phenylbutan-2-yl)germane anion (B3LYP)

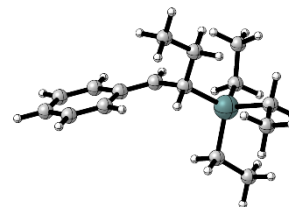


C	3.85694	-0.36373	-1.34859
C	2.63373	0.15460	-0.93531
C	2.38806	0.57004	0.43782
C	3.51871	0.34486	1.32632
C	4.72523	-0.17820	0.89100
C	4.93912	-0.54278	-0.46211
H	3.97162	-0.65191	-2.39527
H	1.82967	0.23705	-1.66324
H	3.40303	0.61361	2.37788
H	5.53034	-0.31214	1.61544
H	5.88780	-0.95546	-0.79636
C	1.19276	1.13119	0.88493
H	1.09404	1.34045	1.95357
C	-0.03018	1.39048	0.04367
H	0.25705	1.54773	-1.00793
C	-0.76627	2.66711	0.50609
H	-1.01387	2.57772	1.57469
C	-0.05655	3.50723	0.43761
H	-2.03872	3.02817	-0.27341
H	-2.85279	2.31969	-0.08170
H	-2.40068	4.02575	0.00658
H	-1.85074	3.30342	-1.35516
C	-2.52685	-0.29381	-1.50118
H	-2.97947	-1.29561	-1.50455
H	-3.34346	0.41563	-1.32007
C	-1.86872	-0.01005	-2.86124
H	-1.04442	-0.70718	-3.06310
H	-2.58227	-0.10047	-3.69275
H	-1.44983	1.00359	-2.89841
C	-2.25183	-0.30756	1.73983
H	-1.60011	-0.76766	2.49501
H	-2.42959	0.72350	2.07277
C	-3.58825	-1.06428	1.65989
H	-3.44622	-2.10752	1.35261
H	-4.11028	-1.07566	2.62766
H	-4.26469	-0.60252	0.92959
C	-0.13481	-1.88182	-0.14749
H	0.76265	-1.74095	0.46534
H	0.21014	-1.94456	-1.18764
C	-0.86986	-3.17302	0.24483
H	-0.23530	-4.06138	0.11226
H	-1.18371	-3.15249	1.29642
H	-1.77373	-3.32841	-0.35945
Ge	-1.23134	-0.23017	0.02431

Zero-point correction = 0.384718 (Hartree/Particle)

Thermal correction to Energy = 0.406921
Thermal correction to Enthalpy = 0.407865
Thermal correction to Gibbs Free Energy = 0.332487
Sum of electronic and zero-point Energies = -2700.459194
Sum of electronic and thermal Energies = -2700.436992
Sum of electronic and thermal Enthalpies = -2700.436048
Sum of electronic and thermal Free Energies = -2700.511425

Triethyl(1-phenylbutan-2-yl)germane anion (M06-2X)

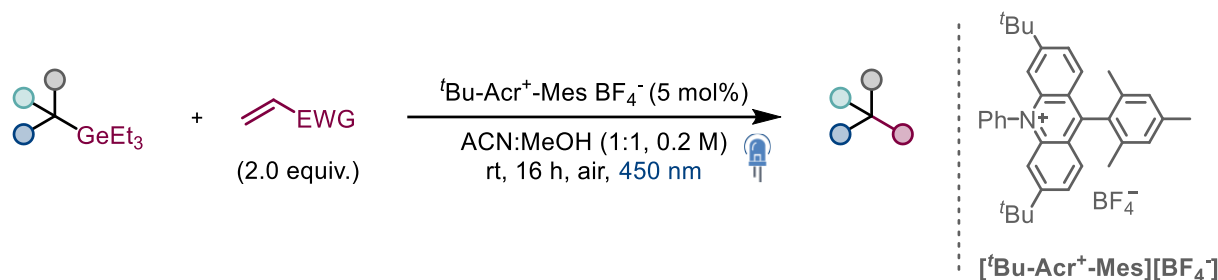


C	1.13849	0.10511	0.69757
H	0.87008	-0.24630	1.69267
C	0.06423	0.79097	-0.10458
H	0.30717	0.72212	-1.17322
C	-0.14859	2.28710	0.20524
H	-1.02287	2.66038	-0.34003
H	-0.37706	2.40547	1.26913
C	1.05711	3.15077	-0.14922
H	0.89776	4.19647	0.12209
H	1.95205	2.80186	0.37021
H	1.25705	3.11125	-1.22269
C	-1.99352	-0.74254	1.94731
H	-2.98106	-1.21174	1.96944
H	-1.28071	-1.51068	2.25747
C	-1.95304	0.43928	2.91605
H	-2.63080	1.23716	2.60317
H	-2.24059	0.14647	3.92874
H	-0.95122	0.86905	2.97268
C	-1.46068	-1.91517	-0.99787
H	-1.11699	-1.65504	-2.00251
H	-0.67534	-2.53148	-0.55276
C	-2.77238	-2.69571	-1.07181
H	-3.55819	-2.10593	-1.54951
H	-2.66838	-3.62165	-1.64231
H	-3.13129	-2.96619	-0.07610
C	-3.16658	0.76536	-0.64492
H	-3.27896	1.69089	-0.07474
H	-4.07493	0.18230	-0.47041
C	-3.00996	1.07272	-2.13388
H	-2.93624	0.15413	-2.72103
H	-3.85188	1.64563	-2.52954
H	-2.10285	1.65115	-2.32696
H	-2.10285	-0.25129	0.06523
Ge	-1.61734	-0.25129	0.06523
C	2.43364	-0.15298	0.27427
C	3.38187	-0.86359	1.10715
C	2.97577	0.23830	-1.00802
C	4.66728	-1.13899	0.70783
H	3.05060	-1.19023	2.08837
C	4.27172	-0.05802	-1.38462
H	2.35024	0.79010	-1.69885
C	5.15642	-0.75004	-0.55186
H	5.31945	-1.67568	1.39019
H	4.60984	0.26734	-2.36408
H	6.16935	-0.97105	-0.85861

Zero-point correction = 0.384841 (Hartree/Particle)
Thermal correction to Energy = 0.407222
Thermal correction to Enthalpy = 0.408166
Thermal correction to Gibbs Free Energy = 0.331706
Sum of electronic and zero-point Energies = -2702.613415
Sum of electronic and thermal Energies = -2702.591035
Sum of electronic and thermal Enthalpies = -2702.590090
Sum of electronic and thermal Free Energies = -2702.666550

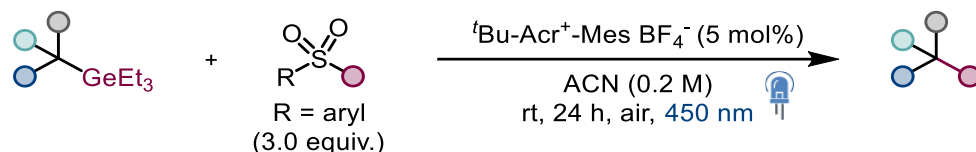
3.3 Supporting information for chapter 2

3.3.1 General procedure A: Giese-type addition



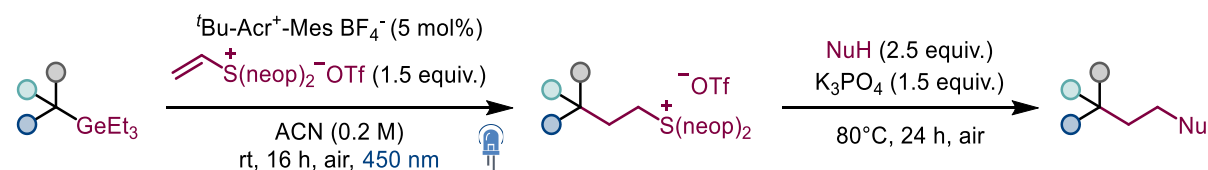
In an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with the alkyl germane Alkyl-GeEt₃ (1.0 equiv.) and [tBu-Acr⁺-Mes][BF₄⁻] (5 mol%) in ACN/MeOH (1:1, 0.2 M). The vial was sealed and brought out of glovebox. Then, the vial was opened under air for five minutes and the corresponding alkene (2.0 equiv.) was added. The vial was re-sealed, placed under blue LEDs or inside EvoluChem™ PhotoRedOxBox (450 nm) and irradiated for 24 h. The resulting solution was concentrated under reduced pressure and the obtained crude residue was purified by flash chromatography or preparative TLC on silica gel.

3.3.2 General procedure B: Sulfonyl trapping reagents



In an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with the alkyl germane Alkyl-GeEt₃ (1.0 equiv.) and [tBu-Acr⁺-Mes][BF₄⁻] (5 mol%) in ACN or DCE (0.2 M). The vial was sealed and brought out of glovebox. Then, the vial was opened to air for five minutes and the corresponding electrophile (3.0 equiv.) was added. The vial was re-sealed, placed under blue LEDs or inside EvoluChem™ PhotoRedOxBox (450 nm) and irradiated for 24 h. The resulting solution was concentrated under reduced pressure and the obtained crude residue was purified by flash chromatography or preparative TLC on silica gel.

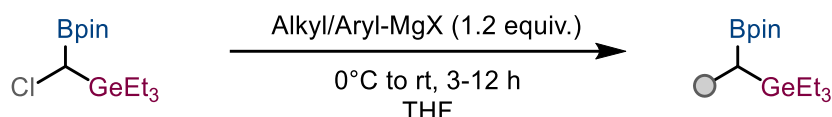
3.3.3 General procedure C: Giese-type addition with polarity transduction



In an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with the alkyl germane Alkyl-GeEt₃ (1.0 equiv.), dineopentyl(vinyl)sulfonium trifluoromethanesulfonate (1.5 equiv.) and [tBu-Acr⁺-Mes][BF₄⁻] (10 mol%) in ACN (0.2 M). The vial was sealed, brought out of

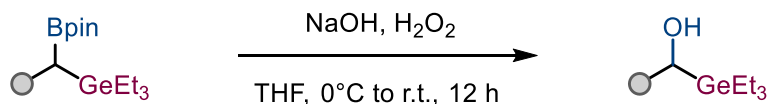
glovebox, placed under blue LEDs and irradiated for 16 h. Then, the nucleophile (2.5 equiv.) and K_3PO_4 (1.5 equiv.) were added and the reaction mixture was stirred at 80 °C for another 24 h. The resulting mixture was concentrated under reduced pressure and the obtained crude residue was purified by flash chromatography on silica gel.

3.3.4 General procedure D: alkylation and arylation via nucleophilic substitution



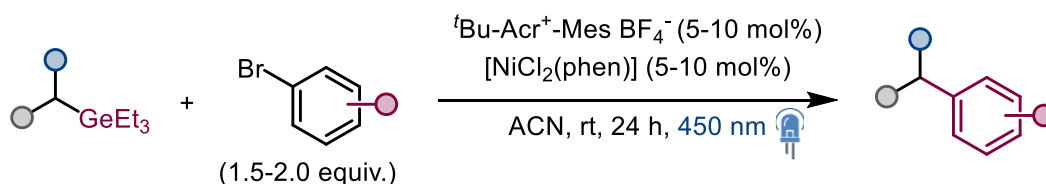
Under Argon, a schlenk-tube was charged with organomagnesium (1.2 equiv.), deluted in anhydrous THF (0.3 – 0.5 M) and cooled to 0 °C. Then triethyl(chloro(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)germane (1.0 equiv.) in THF (0.2 – 1.1 M) or neat was added dropwise. After addition, the reaction was slowly allowed to warm to room temperature. After the reaction was complete (as checked by GC-MS or TLC, usually 3-12 h), anhydrous ammonium chloride solution was added to quench remaining Grignard reagent. The layers were separated and the aqueous phase was extracted three times with Et_2O . The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The obtained crude was purified by flash chromatography on silica gel.

3.3.5 General procedure E: C-Bpin oxidation



Under argon atmosphere, the alkyl-Bpin starting material (1.0 equiv.) was dissolved in anhydrous THF (0.1 M) and the solution cooled to 0 °C. A degassed aqueous NaOH solution (3.0 M, 3.0 equiv.) was added dropwise to the reaction solution, followed by the same volume of 30 wt% hydrogen peroxide solution in water. After dropwise addition the mixture was allowed to warm up to room temperature and stirred for 12 h. The reaction was diluted with Et_2O and water. The layers were separated and the aqueous phase was extracted three times with Et_2O . The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel.

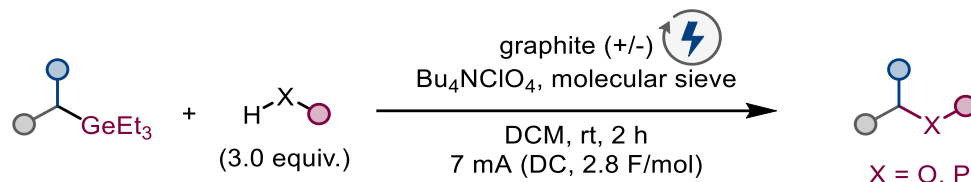
3.3.6 General procedure F: Nickel catalyzed arylation



In an argon-filled glovebox, a 4 mL screw-capped glass vial equipped with a magnetic stir bar was charged with the alkyl germane Alkyl- $GeEt_3$ (1.0 equiv.), aryl halide (1.5 – 2.0 equiv.), $Ni(phen)Cl_2$ (5 – 10 mol%) and $[^tBu-Acr^+-Mes][BF_4^-]$ (5 – 10 mol%) in ACN (0.1 M). The vial was sealed, brought out of the glovebox, placed

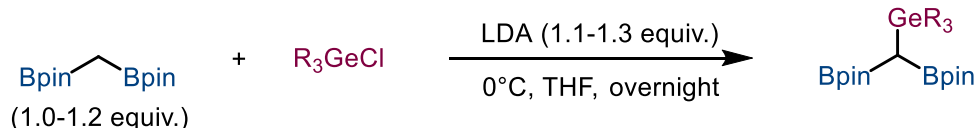
under blue LEDs or inside EvoluChem™ PhotoRedOxBox (450 nm) and irradiated for 24 h. The resulting mixture was filtered through a short silica pipette column eluting with Et₂O, concentrated under reduced pressure and the obtained crude residue was purified by flash chromatography or preparative TLC on silica gel.

3.3.7 General procedure G: Electrochemical transformation of alkylgermanes



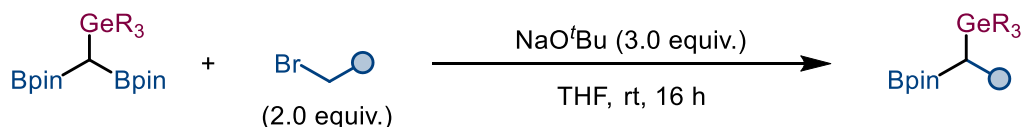
Under air, an oven dried Electrasyn vial (5 mL) equipped with a magnetic stir bar was charged with the alkyl germane Alkyl-GeEt₃ (1.0 equiv.), nucleophile (5.0 equiv.), ⁿBu₄NClO₄ (0.3 mmol, 0.1 M, 102.6 mg, 3.0 equiv.), 4 Å molecular sieve powder (150 mg) and DCM (3.0 mL). The Electrasyn cap equipped with graphite anode and cathode was screwed on the vial. The mixture was pre-stirred for 10 min before electrolyzing at a constant current of 7 mA for 2.8 F/mol at 1000 rpm if not stated otherwise. For some reactions, a polarity switch every 2 min was applied. The resulting mixture was filtered over a plug of cotton (to remove molecular sieves), concentrated under reduced pressure and the obtained crude residue was purified by flash column chromatography or preparative TLC on silica gel.

3.3.8 General procedure H: Synthesis of bis-Bpin building block



Under argon, bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (1.0-1.2 equiv.) was dissolved in anhydrous THF (0.3 M) and cooled down to 0°C. LDA (1.1-1.3 equiv.) was added slowly and the reaction was stirred at the same temperature for 10 min, before the germanium source (1.0 equiv.) was added slowly. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. After the reaction was complete (as checked by GC-MS), anhydrous ammonium chloride solution was added to quench remaining organolithium reagent. The layers were separated and the aqueous phase was extracted three times with Et₂O. The combined organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The obtained crude was purified by flash chromatography on silica gel.

3.3.9 General procedure I: Alkylation of bis-Bpin compounds



In an argon filled glovebox, the bis-Bpin building block (1.0 equiv.) and alkyl bromide (2.0 equiv.) were dissolved in anhydrous THF (0.15 M). NaOtBu (3.0 equiv.) was added to the reaction mixture and the vial

was sealed and brought out of glovebox. It was stirred at room temperature for 16 h and afterwards filtered through a pad of silica. The solvents were removed and the obtained crude was purified by preparative TLC.

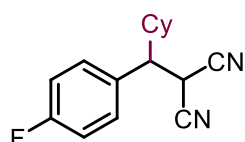
3.3.10 Characterization data of products

The following starting materials were synthesized by Markus Schoetz^[174]: triethyl(1-(*p*-tolyl)ethyl)germane, dineopentyl(vinyl)sulfonium trifluoromethanesulfonate, triethyl(1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)germane, 2,2,2-trifluoro-*N*-(3-methyl-1-(triethylgermyl)but-3-en-1-yl)acetamide (by Annika Hoepfner under Markus Schoetz supervision).

The following starting materials were synthesized by Dr. Gurdeep Singh: (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromobenzoate.

The following compound was synthesized according to Dr. Aymane Selmani's procedure, who recently made the same compound: triethyl(1-(furan-2-yl)-2-phenylethyl)germane (**17**), (1-(3,5-dimethoxyphenyl)-2-phenylethyl)triethylgermane (**19**).^[72]

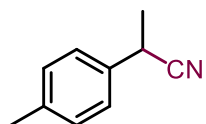
2-(Cyclohexyl(4-fluorophenyl)methyl)malononitrile (**1**)



Prepared, following general procedure A from cyclohexyltriethylgermane (48.6 mg, 0.2 mmol, 1.0 equiv.), 2-(4-fluorobenzylidene)malononitrile (68.7 mg, 0.4 mmol, 2.0 equiv.) and [^tBu-Acr⁺-Mes][BF₄⁻] (5.7 mg, 0.01 mmol, 5.0 mol%) in ACN:MeOH (1:1, 1.0 mL). The title product was obtained after purification by preparative HPLC (*n*-hexane:ethylacetate 7:3, 20 mL/min) as viscous yellowish oil (39.3 mg, 0.15 mmol, 77%).

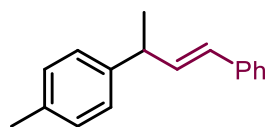
*R*_f = 0.54 (*n*-pentane/EtOAc 4:1). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.33 – 7.28 (m, 2H), 7.13 – 7.07 (m, 2H), 4.18 (d, *J* = 5.4 Hz, 1H), 2.87 (dd, *J* = 9.9, 5.3 Hz, 1H), 2.01 – 1.81 (m, 3H), 1.72 – 1.63 (m, 2H), 1.48 – 1.42 (m, 1H), 1.42 – 1.33 (m, 1H), 1.24 – 1.01 (m, 3H), 0.84 – 0.76 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 163.0 (d, *J* = 248.1 Hz), 132.5 (d, *J* = 3.3 Hz), 130.1 (d, *J* = 8.2 Hz), 116.3 (d, *J* = 21.6 Hz), 112.2, 111.8, 51.8, 39.4, 31.2, 30.8, 27.3, 25.9, 25.8. ¹⁹F NMR (564 MHz, CDCl₃) δ/ppm = -112.9. HRMS (EI) calculated for C₁₃H₁₆F: 191.1236 [M-C₃HN₂]⁺, found: 191.1230. IR (neat): ν/cm⁻¹ = 2928, 2855, 1604, 1510 1230. MS (EI) *m/z* (%): 256 (4) [M]⁺, 229 (1), 191 (52), 147 (45), 109 (100).

2-(*p*-Tolyl)propanenitrile (**2**)



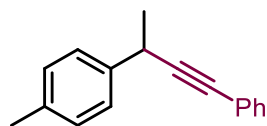
Prepared, following the general procedure A from triethyl(1-(*p*-tolyl)ethyl)germane (31.1 mg, 0.10 mmol, 1.0 equiv.), 4-methylbenzenesulfonyl cyanide (54.4 mg, 0.3 mmol, 3.0 equiv.) and [^tBu-Acr⁺-Mes][BF₄⁻] (2.9 mg, 0.005 mmol, 5.0 mol%) in ACN (1.0 mL). The title product was obtained after purification by preparative TLC (*n*-pentane/EtOAc 9:1) as a colorless oil (5.9 mg, 0.1 mmol, 37%).

*R*_f = 0.76 (*n*-pentane/EtOAc 9:1). ¹H NMR (600 MHz, CDCl₃) δ/ppm = 7.24 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 3.86 (q, *J* = 7.3 Hz, 1H), 2.35 (s, 3H), 1.63 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ/ppm = 138.0, 134.3, 129.9, 126.7, 121.9, 31.0, 21.7, 21.2. MS (EI) *m/z* (%): 145 (37) [M]⁺, 130 (100), 117 (5), 103 (15), 91 (7). These data are in agreement with those reported previously in the literature.^[238]

(E)-1-Methyl-4-(4-phenylbut-3-en-2-yl)benzene (3)

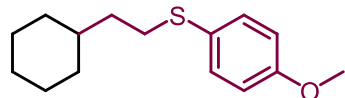
Prepared, following the general procedure A from triethyl(1-(*p*-tolyl)ethyl)germane (56.9 mg, 0.20 mmol, 1.0 equiv.), (*E*)-(2-(phenylsulfonyl)vinyl)benzene (146.6 mg, 0.6 mmol, 3.0 equiv.) and [^tBu-Acr⁺-Mes][BF₄⁻] (5.7 mg, 0.01 mmol, 5.0 mol%) in dichloroethane (1.0 mL). The title product was obtained after purification by preparative HPLC (*n*-hexane/EtOAc 97:3, 18 mL/min) as a colorless oil (8.1 mg, 0.04 mmol, 18%).

R_f = 0.25 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.37 – 7.33 (m, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.21 – 7.11 (m, 5H), 6.43 – 6.34 (m, 2H), 3.64 – 3.58 (m, 1H), 2.33 (s, 3H), 1.45 (d, *J* = 7.0 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 142.8, 137.8, 135.9, 135.6, 129.3, 128.6, 128.5, 127.3, 127.1, 126.3, 42.3, 21.4, 21.1. **MS** (EI) *m/z* (%): 222 (58) [M]⁺, 207 (100), 192 (17), 129 (44), 115 (38). These data are in agreement with those reported previously in the literature.^[239]

1-Methyl-4-(4-phenylbut-3-yn-2-yl)benzene (4)

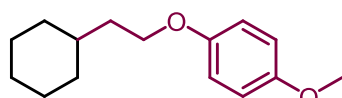
Prepared, following the general procedure A from triethyl(1-(*p*-tolyl)ethyl)germane (30.1 mg, 0.1 mmol, 1.0 equiv.), ((phenylethynyl)sulfonyl)benzene (72.8 mg, 0.3 mmol, 3.0 equiv.) and [^tBu-Acr⁺-Mes][BF₄⁻] (2.9 mg, 0.005 mmol, 5.0 mol%) in ACN (1.0 mL). The title product was obtained after purification by preparative TLC (pentane/Et₂O 98:2) as a colorless oil (4.8 mg, 0.1 mmol, 20%).

R_f = 0.71 (*n*-pentane/Et₂O 98:2). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.46 – 7.41 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 5.6, 1.8 Hz, 3H), 7.16 (d, *J* = 7.7 Hz, 2H), 3.95 (q, *J* = 7.1 Hz, 1H), 2.34 (s, 3H), 1.56 (d, *J* = 7.1 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 140.5, 136.4, 131.8, 129.4, 128.3, 127.8, 127.0, 124.0, 93.0, 82.4, 32.2, 24.7, 21.2. **MS** (EI) *m/z* (%): 220 (58) [M]⁺, 205 (100), 190 (6), 178 (5), 165 (4). These data are in agreement with those reported previously in the literature.^[240]

(2-Cyclohexylethyl)(4-methoxyphenyl)sulfane (5)

Prepared, following the general procedure B, cyclohexyltriethylgermane (49.7 mg, 0.2 mmol, 1.0 equiv.), dineopentyl(vinyl)sulfonium trifluoromethanesulfonate (105.0 mg, 0.3 mmol, 1.5 equiv.), and [^tBu-Acr⁺-Mes][BF₄⁻] (11.5 mg, 0.02 mmol, 10 mol%) followed by 4-methoxybenzenethiol (61.5 μL, 0.5 mmol, 2.5 equiv.) and K₃PO₄ (63.7 mg, 0.3 mmol, 1.5 equiv.) were used to obtain the title product after purification by flash chromatography on silica gel (pentane/Et₂O 95:5) as colorless oil (27.6 mg, 0.2 mmol, 54%).

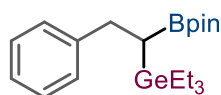
R_f = 0.70 (*n*-pentane/Et₂O 95:5). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.32 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.87 – 2.81 (m, 2H), 1.76 – 1.59 (m, 5H), 1.51 – 1.44 (m, 2H), 1.41 – 1.33 (m, 1H), 1.27 – 1.11 (m, 3H), 0.92 – 0.83 (m, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 158.7, 132.7, 127.1, 114.5, 55.3, 36.9, 36.9, 33.4, 33.0, 26.6, 26.2. **HRMS** (EI) calculated for C₁₅H₂₂OS: 250.1386 [M]⁺, found: 250.1385. **IR** (neat): ν/cm⁻¹ = 2920, 2848, 1592, 1491, 1241.

1-(2-Cyclohexylethoxy)-4-methoxybenzene (6)

Prepared, following the general procedure B, cyclohexyltriethylgermane (48.6 mg, 0.2 mmol, 1.0 equiv.), dineopentyl(vinyl)sulfonium trifluoromethanesulfonate (105.0 mg, 0.3 mmol, 1.5 equiv.), and [^tBu-Acr⁺-

Mes][BF₄⁻] (11.5 mg, 0.02 mmol, 10 mol%) followed by 4-methoxyphenol (62.1 mg, 0.5 mmol, 2.5 equiv.) and K₃PO₄ (63.7 mg, 0.3 mmol, 1.5 equiv.) were used to obtain the title product after purification by flash chromatography on silica gel (pentane/EtOAc 95:5) as colorless oil (21.4 mg, 0. mmol, 46%).

R_f = 0.54 (*n*-pentane/EtOAc 95:5). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 6.86 – 6.80 (m, 4H), 3.94 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 3H), 1.79 – 1.73 (m, 2H), 1.71 (dt, *J* = 12.6, 3.3 Hz, 2H), 1.68 – 1.63 (m, 2H), 1.54 – 1.46 (m, 1H), 1.30 – 1.13 (m, 4H), 1.01 – 0.92 (m, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 153.8, 153.5, 115.6, 114.8, 66.8, 55.9, 36.9, 34.7, 33.5, 26.7, 26.4. **HRMS** (EI) calculated for C₁₅H₂₂O₂: 234.1614[M]⁺, found: 234.1614. **IR** (neat): ν/ cm⁻¹ = 2921, 2851, 1507, 1224, 1036.

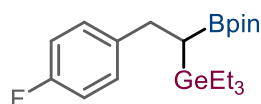
Triethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)germane (7)

Prepared, following the general procedure D from *n*-benzylmagnesium chloride solution (1.4 M in THF, 2.47 mL, 3.46 mmol, 1.2 equiv.) in additional anhydrous THF (10 mL) and (chloro(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)

triethylgermane **A** (966 mg, 2.88 mmol, 1.0 equiv.). The reaction was stirred for 3 h before quenching. The title product was obtained after purification by flash chromatography on silica gel (pentane/DCM 4:1) as a colorless liquid (1039.9 mg, 2.66 mmol, 92%).

R_f = 0.88 (*n*-pentane/Et₂O 9:1). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.23 – 7.20 (m, 4H), 7.11 – 7.09 (m, 1H), 2.85 (dd, *J* = 13.9, 12.6 Hz, 1H), 2.73 (dd, *J* = 13.9, 3.8 Hz, 1H), 1.12 – 1.07 (m, 21H), 1.02 (dd, *J* = 12.6, 3.8 Hz, 1H), 0.86 (q, *J* = 7.8 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 145.4, 128.4, 128.1, 125.4, 82.8, 32.5, 25.2, 24.9, 9.2, 4.4. **MS** (EI) *m/z* (%): 377 (2) [M-Me]⁺, 363 (100), 279 (50), 263 (67), 235 (90), 133 (45), 104 (35).

Note: The carbon attached to boron was not observed in ¹³C NMR.^[241] These data are in agreement with those reported previously in the literature.^[72] This compound was synthesized before by Markus Schoetz using the same procedure.^[174]

Triethyl(2-(4-fluorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)germane (8)

Grignard formation: In an argon filled glovebox, an oven dried 4 mL vial equipped with magnetic stirring bar was charged with 1-(bromomethyl)-4-fluorobenzene (15.0 μL, 0.12 mmol, 1.2 equiv.). To this vial was added Mg-turnings (2.9 mg,

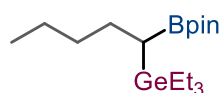
0.12 mmol, 1.2 equiv.) and THF (0.5 mL). One grain of iodine was added and the reaction was heated at 65 °C for 2 h.

Alkylation: Prepared, following the general procedure D from the freshly prepared Grignard in THF and (chloro(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)triethylgermane **A** (33.5 mg, 0.10 mmol, 1.0 equiv.) in anhydrous THF (0.5 mL). The reaction was stirred for 12 h before quenching. The title product was obtained after purification by flash chromatography on preparative TLC (pentane/DCM 4:1) as a colorless liquid (33.9 mg, 0.08 mmol, 83%).

R_f = 0.88 (*n*-pentane/DCM 4:1). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.17 (dd, *J* = 8.5, 5.7 Hz, 2H), 6.92 – 6.87 (m, 2H), 2.81 (t, *J* = 13.4 Hz, 1H), 2.69 (dd, *J* = 14.0, 3.9 Hz, 1H), 1.12 – 1.06 (m, 21H), 1.00 – 0.95 (m, 1H),

0.85 (q, $J = 7.8$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) $\delta/\text{ppm} = 141.1, 129.66$ (d, $J = 7.7$ Hz), 114.8, 114.6, 82.8, 31.8, 25.2, 24.9, 9.2, 4.4. ^{19}F NMR (564 MHz, CDCl_3) $\delta/\text{ppm} = -118.7$. HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{34}\text{O}_2\text{B}^{74}\text{GeFNa}$: 433.1740 $[\text{M}+\text{Na}]^+$, found: 433.1746. IR (neat): $\nu/\text{cm}^{-1} = 2947, 2873, 1508, 1354, 1142$. Note: The carbon attached to boron was not observed in ^{13}C NMR.^[241]

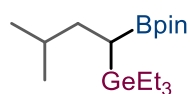
Triethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)germane (9)



Prepared, following the general procedure D from *n*-butylmagnesium chloride solution (2.0 M in THF, 1.1 mL, 2.3 mmol, 1.2 equiv.) in anhydrous THF (5 mL) and (chloro(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl) triethylgermane **A** (622.6 mg, 1.9 mmol, 1.0 equiv.). The reaction was stirred for 12 h before quenching. The title product was obtained after purification by flash chromatography on silica gel (pentane/DCM 4:1) as a colorless liquid (473.5 mg, 1.3 mmol, 70%).

$R_f = 0.37$ (*n*-pentane/DCM 4:1). ^1H NMR (600 MHz, CDCl_3) $\delta/\text{ppm} = 1.63 - 1.55$ (m, 1H), 1.38 – 1.24 (m, 5H), 1.23 (s, 6H), 1.22 (s, 6H), 1.03 (t, $J = 7.9$ Hz, 9H), 0.86 (t, $J = 7.0$ Hz, 3H), 0.78 (q, $J = 7.7$ Hz, 6H), 0.62 (dd, $J = 12.3, 2.9$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) $\delta/\text{ppm} = 82.6, 35.8, 31.0, 25.3, 25.0, 23.5, 21.6, 9.2, 4.3$. Note: The carbon attached to boron was not observed in ^{13}C NMR.^[241] HRMS (EI) calculated for $\text{C}_{15}\text{H}_{32}\text{O}_2\text{B}^{74}\text{Ge}$: 329.1702 $[\text{M}-\text{Et}]^+$, found: 329.1697. IR (neat): $\nu/\text{cm}^{-1} = 2925, 2872, 1356, 1144, 1013$.

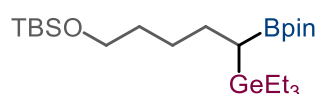
Triethyl(3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)germane (10)



Prepared, following the general procedure D from isobutylmagnesium bromide solution (2.0 M in Et_2O , 2.7 mL, 5.4 mmol, 1.2 equiv.) in anhydrous THF (10 mL) and (chloro(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)triethylgermane **A** (1496.3 mg, 4.5 mmol, 1.0 equiv.). The reaction was stirred for 4 h before quenching. The title product was obtained after purification by flash chromatography on silica gel (pentane/DCM 4:1) as a colorless liquid (1270.4 mg, 3.6 mmol, 80%).

$R_f = 0.86$ (*n*-pentane/DCM 4:1). ^1H NMR (600 MHz, CDCl_3) $\delta/\text{ppm} = 1.64 - 1.58$ (m, 1H), 1.52 – 1.42 (m, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.15 – 1.09 (m, 1H), 1.03 (t, $J = 7.9$ Hz, 9H), 0.87 (d, $J = 6.6$ Hz, 3H), 0.83 (d, $J = 6.6$ Hz, 3H), 0.81 – 0.76 (m, 6H), 0.71 (dd, $J = 12.5, 3.1$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) $\delta/\text{ppm} = 82.6, 35.8, 31.0, 25.3, 25.0, 23.5, 21.6, 9.2, 4.3$. Note: The carbon attached to boron was not observed in ^{13}C NMR.^[241] MS (EI) m/z (%): 459 (100) $[\text{M}-\text{Et}]^+$, 359 (86), 331 (41), 211 (26), 169 (58), 133 (37), 101 (18), 73 (17). HRMS (EI) calculated for $\text{C}_{15}\text{H}_{32}\text{O}_2\text{B}^{74}\text{Ge}$: 329.1702 $[\text{M}-\text{Et}]^+$, found: 329.1698. IR (neat): $\nu/\text{cm}^{-1} = 2951, 2872, 1360, 1144, 1009$.

Tert-butyldimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(triethylgermyl)pentyl)oxy)silane (11)

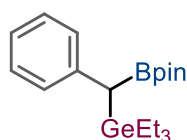


Grignard formation: In an argon filled glovebox, an oven dried 20 mL vial equipped with magnetic stirring bar was charged with (4-bromobutoxy)(*tert*-butyl)dimethylsilane (917.7 mg, 3.43 mmol, 1.2 equiv.). To this vial was added Mg-turnings (96.0 mg, 4.0 mmol, 1.4 equiv.) and THF (8 mL). One grain of iodine was added and the reaction was heated at 65 °C for 2 h.

Alkylation: Prepared, following the general procedure F from the freshly prepared Grignard in THF and (chloro(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)triethylgermane **A** (958.8 mg, 2.86 mmol, 1.0 equiv.) in anhydrous THF (10.0 mL). The reaction was stirred for 12 h before quenching. The title product was obtained after purification by flash chromatography on silica gel (pentane/DCM 4:1) as a colorless liquid (733.8 mg, 1.51 mmol, 53%).

R_f = 0.45 (*n*-pentane/EtOAc 20:1). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 3.58 (t, J = 6.6 Hz, 2H), 1.64 – 1.56 (m, 1H), 1.54 – 1.45 (m, 2H), 1.45 – 1.30 (m, 2H), 1.22 (d, J = 5.8 Hz, 12H), 1.03 (t, J = 7.9 Hz, 9H), 0.88 (s, 9H), 0.78 (q, J = 7.9 Hz, 6H), 0.63 (dd, J = 12.3, 3.3 Hz, 1H), 0.03 (s, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 82.6, 63.5, 33.0, 29.8, 26.7, 26.1, 25.4, 24.9, 18.5, 9.2, 4.3, -5.1. *Note:* The carbon attached to boron was not observed in $^{13}\text{C NMR}$.^[241] **MS** (EI) m/z (%): 459 (75) $[\text{M-Et}]^+$, 359 (100), 331 (38), 211 (37), 169 (83), 133 (50). These data are in agreement with those reported previously in the literature.^[111] This compound was synthesized before by Markus Schoetz^[174] using the same procedure.

Triethyl(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)germane (**12**)

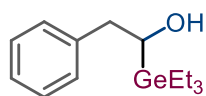


Prepared, following the general procedure D from phenylmagnesium bromide solution (1.0 M in THF, 0.12 mL, 0.12 mmol, 1.2 equiv.) in anhydrous THF (0.5 mL) and (chloro(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl) triethylgermane **A** (33.5 mg, 0.1 mmol, 1.0 equiv.). The reaction was stirred for 12 h before quenching. The

title product was obtained after purification on preparative TLC (pentane/DCM 4:1) as a colorless liquid (22.8 mg, 0.06 mmol, 60%).

R_f = 0.84 (*n*-pentane/DCM 4:1). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.20 – 7.15 (m, 4H), 7.02 – 6.99 (m, 1H), 2.17 (s, 1H), 1.25 (d, J = 15.5 Hz, 12H), 0.98 (t, J = 7.9 Hz, 9H), 0.79 – 0.73 (m, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 142.1, 128.6, 127.9, 123.3, 83.1, 25.4, 25.1, 9.0, 4.6. *Note:* The carbon attached to boron was not observed in $^{13}\text{C NMR}$.^[241] **HRMS** (ESI) calculated for $\text{C}_{19}\text{H}_{33}\text{O}_2\text{B}^{74}\text{GeNa}$: 401.1678 $[\text{M}+\text{Na}]^+$, found: 401.1686. **IR** (neat): ν/cm^{-1} = 2948, 2873, 1456, 1351, 1141.

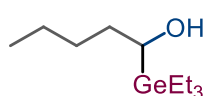
2-Phenyl-1-(triethylgermyl)ethan-1-ol (**13**)



Prepared, following the general procedure E from triethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)germane **7** (1039.9 mg, 2.7 mmol, 1.0 equiv.). The title product was obtained after purification by flash chromatography

on silica gel (*n*-pentane/ Et_2O 4:1) as a colorless liquid (699.1 mg, 2.5 mmol, 94%).

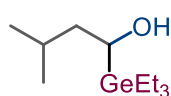
R_f = 0.58 (*n*-pentane/ Et_2O 4:1). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ /ppm = 7.34 – 7.30 (m, 2H), 7.25 – 7.21 (m, 3H), 3.96 – 3.89 (m, 1H), 2.95 – 2.81 (m, 2H), 1.28 (s, 1H), 1.10 (t, J = 7.9 Hz, 9H), 0.93 – 0.80 (m, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ /ppm = 139.9, 129.2, 128.8, 126.6, 67.2, 42.0, 9.3, 2.9. **HRMS** (ESI) calculated for $\text{C}_{14}\text{H}_{24}\text{O}^{74}\text{GeNa}$: 305.0931 $[\text{M}+\text{Na}]^+$, found: 305.0923. **IR** (neat): ν/cm^{-1} = 3529, 3442, 2947, 2871, 1456, 1017.

1-(Triethylgermyl)pentan-1-ol (14)

Prepared, following the general procedure E from **9** (236.2 mg, 0.66 mmol, 1.0 equiv.).

The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane/Et₂O 95:5) as a colorless liquid (164.5 mg, 0.66 mmol, 99%).

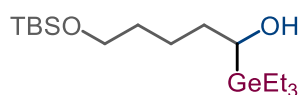
R_f = 0.13 (*n*-pentane/Et₂O 95:5). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 3.76 (dd, *J* = 10.2, 3.8 Hz, 1H), 1.72 – 1.64 (m, 1H), 1.62 – 1.55 (m, 1H), 1.55 – 1.47 (m, 1H), 1.41 – 1.25 (m, 3H), 1.07 (t, *J* = 7.9 Hz, 9H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.87 – 0.75 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 66.9, 35.5, 29.2, 22.7, 14.2, 9.3, 2.8. **HRMS** (EI) calculated for C₉H₂₁O⁷⁴Ge: 219.0799 [M-Et]⁺, found: 219.0798. **IR** (neat): ν/cm⁻¹ = 3388, 2951, 2871, 2121, 1460, 1014.

3-Methyl-1-(triethylgermyl)butan-1-ol (15)

Prepared, following the general procedure E from triethyl(3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)germane **10** (500.0 mg, 1.4 mmol, 1.0 equiv.).

The title product was obtained after purification by flash chromatography on silica gel (pentane/Et₂O 95:5) as a colorless liquid (328.5 mg, 1.3 mmol, 95%).

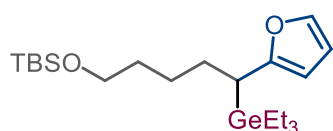
R_f = 0.21 (*n*-pentane/Et₂O 95:5). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 3.90 (dd, *J* = 11.7, 2.9 Hz, 1H), 1.88 – 1.80 (m, 1H), 1.70 (ddd, *J* = 14.1, 11.6, 4.2 Hz, 1H), 1.24 (ddd, *J* = 14.1, 9.6, 3.0 Hz, 1H), 1.07 (t, *J* = 8.0 Hz, 9H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.85 – 0.73 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 64.4, 44.8, 24.6, 24.0, 21.3, 9.3, 2.7. **HRMS** (EI) calculated for C₉H₂₂O⁷⁴Ge: 220.0877 [M-Et+H]⁺, found: 220.0879. **IR** (neat): ν/cm⁻¹ = 3396, 2951, 2872, 1461, 1015.

5-((Tert-butyldimethylsilyl)oxy)-1-(triethylgermyl)pentan-1-ol (16)

Prepared, following the general procedure E from *tert*-butyldimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(triethylgermyl)pentyl)oxy)silane **11** (472.0 mg, 0.97 mmol, 1.0 equiv.).

The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane/Et₂O 9:1) as a colorless liquid (331.9 mg, 0.9 mmol, 91%).

R_f = 0.23 (*n*-pentane/Et₂O 9:1). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 3.80 – 3.74 (m, 1H), 3.67 – 3.58 (m, 2H), 1.74 – 1.64 (m, 1H), 1.64 – 1.49 (m, 4H), 1.42 – 1.32 (m, 1H), 1.16 – 1.12 (m, 1H), 1.06 (t, *J* = 8.0 Hz, 9H), 0.89 (s, 9H), 0.87 – 0.75 (m, 6H), 0.05 (s, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 66.8, 63.3, 35.6, 32.8, 26.1, 23.2, 18.5, 9.3, 2.8, -5.1. **HRMS** (APCI) calculated for C₁₇H₄₁O₂ ⁷⁴GeSi: 379.2082 [M+H]⁺, found: 379.2083. **IR** (neat): ν/cm⁻¹ = 3435, 2932, 2864, 1463, 1099.

***Tert*-Butyl((5-(furan-2-yl)-5-(triethylgermyl)pentyl)oxy)dimethylsilane (18)**

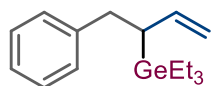
Under argon, a 5 mL Schlenk tube was charged with furan (17.5 μL, 0.24 mmol, 1.2 eq.) in THF (0.6 mL). The solution was cooled to -78°C and

ⁿBuLi (0.24 mmol, 1.6 M in hexane, 0.15 mL, 1.2 equiv.) was added dropwise. The reaction was stirred for 1 h at this temperature before *tert*-butyldimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(triethylgermyl)pentyl)oxy)silane **11** (97.4 mg, 0.20 mmol, 1.0 equiv.) in THF (0.4 mL) was added dropwise. After 1 h of stirring at -78°C, NBS (43 mg, 0.24 mmol, 1.2 equiv.) in THF (0.6 mL) was added dropwise. The reaction mixture was again stirred for 1 h before

saturated $\text{Na}_2\text{S}_2\text{O}_3$ (2.0 mL) was added to quench the reaction. The obtained mixture was diluted with Et_2O , the organic layer separated and the aqueous layer extracted three times with Et_2O . The combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel (pentane/ Et_2O 98:2) to give the product as a colorless liquid (69.9 mg, 0.16 mmol, 82%).

R_f = 0.59 (*n*-pentane/ Et_2O 98:2). **^1H NMR** (600 MHz, CDCl_3) δ /ppm = 7.22 (dd, J = 1.8, 0.9 Hz, 1H), 6.24 (dd, J = 3.1, 1.8 Hz, 1H), 5.79 (d, J = 3.1 Hz, 1H), 3.59 – 3.52 (m, 2H), 2.43 (dd, J = 11.7, 4.0 Hz, 1H), 1.87 – 1.78 (m, 1H), 1.66 – 1.58 (m, 1H), 1.57 – 1.49 (m, 1H), 1.48 – 1.41 (m, 1H), 1.40 – 1.31 (m, 1H), 1.27 – 1.18 (m, 1H), 0.98 (t, J = 7.9 Hz, 9H), 0.88 (s, 9H), 0.73 (q, J = 7.8 Hz, 6H), 0.02 (s, 6H). **^{13}C NMR** (151 MHz, CDCl_3) δ /ppm = 159.26, 139.69, 110.23, 103.12, 63.28, 32.80, 29.56, 27.45, 26.12, 25.91, 18.50, 9.00, 3.72, -5.13. **MS** (EI) m/z (%): 428 (8) $[\text{M}]^+$, 267 (8), 250 (10), 209 (16), 161 (100), 133 (69), 131 (51), 105 (15), 73 (15). **HRMS** (ESI) calculated for $\text{C}_{21}\text{H}_{42}\text{O}_2^{74}\text{GeNaSi}$: 451.2058 $[\text{M}+\text{Na}]^+$, found: 451.2044. **IR** (neat): ν/cm^{-1} = 2932, 2863, 2735, 2327, 2107, 1914, 1580, 1503, 1463, 1429, 1384, 1252, 1100, 1009, 972, 835, 775, 713.

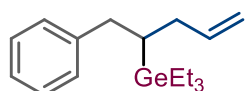
Triethyl(1-phenylbut-3-en-2-yl)germane (20)



Under Argon, compound **7** (117.3 mg, 0.3 mmol, 1.0 equiv.) was dissolved in THF (1.5 mL) and cooled down to 0°C. The vinylMgBr (1.0 M, 1.2 mL, 1.2 mmol, 4.0 equiv.) was added dropwise to the reaction and the mixture was allowed to warm up to room temperature and was stirred overnight. The mixture was cooled down to 0°C and a solution of I_2 (3.0 M in MeOH, 0.9 mmol, 3.0 equiv.) as well as a suspension of NaOMe (3.0 M in MeOH, 0.9 mmol, 3.0 equiv.) were added in one portion and stirred for 30 minutes. The reaction was quenched with aqueous saturated $\text{Na}_2\text{S}_2\text{O}_3$ (5.0 mL) and diluted with Et_2O . The organic layer was separated and the aqueous layer extracted three times with Et_2O . The combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated under reduced pressure. The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless liquid (35.0 mg, 0.12 mmol, 40%).

R_f = 0.75 (*n*-pentane). **^1H NMR** (600 MHz, CDCl_3) δ /ppm = 7.27 – 7.23 (m, 2H), 7.18 – 7.14 (m, 3H), 5.81 – 5.73 (m, 1H), 4.78 – 4.69 (m, 2H), 2.88 (dd, J = 14.3, 4.2 Hz, 1H), 2.79 (dd, J = 14.2, 11.2 Hz, 1H), 2.29 (td, J = 10.2, 4.1 Hz, 1H), 1.06 (t, J = 7.9, 1.3 Hz, 9H), 0.83 – 0.77 (m, 6H). **^{13}C NMR** (151 MHz, CDCl_3) δ /ppm = 142.4, 140.5, 128.6, 128.1, 125.6, 111.2, 36.1, 34.5, 9.1, 3.1. **HRMS** (EI) calculated for $\text{C}_{14}\text{H}_{21}^{74}\text{Ge}$: 263.0850 $[\text{M}-\text{CH}_2\text{CH}_3]^+$, found: 263.0848. **IR** (neat): ν/cm^{-1} = 3330, 2923, 1741, 1369, 1218.

Triethyl(1-phenylpent-4-en-2-yl)germane (21)

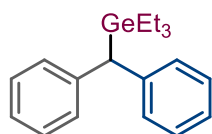


Under Argon, triethyl(1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)germane (121.5 mg, 0.3 mmol, 1.0 equiv.) was dissolved in THF (1.5 mL) and cooled down to 0°C. The vinylMgBr (1.0 M, 1.2 mL, 1.2 mmol, 4.0 equiv.) was added dropwise to the reaction and the mixture was allowed to warm up to room temperature and was stirred overnight. The mixture was cooled down to 0°C and a solution of I_2 (3.0 M in MeOH, 0.9 mmol, 3.0 equiv.) as well as a suspension of NaOMe (3.0 M in MeOH, 0.9 mmol, 3.0 equiv.) were added in one portion and stirred for 30 minutes. The reaction was quenched with aqueous saturated $\text{Na}_2\text{S}_2\text{O}_3$ (5.0 mL) and diluted with Et_2O . The organic layer was separated and the aqueous layer extracted three times with Et_2O . The combined organic layers were washed with brine, dried over MgSO_4 , filtered and

concentrated under reduced pressure. The title product was obtained after purification by flash chromatography on silica gel (*n*-pentane) as a colorless liquid (45.8 mg, 0.15 mmol, 50%).

R_f = 0.78 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.29 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 5.78 – 5.69 (m, 1H), 5.01 – 4.92 (m, 2H), 2.76 (dd, J = 14.0, 5.7 Hz, 1H), 2.66 (dd, J = 13.9, 10.0 Hz, 1H), 2.24 – 2.12 (m, 2H), 1.56 – 1.49 (m, 1H), 1.02 (t, J = 7.9 Hz, 9H), 0.74 (q, J = 8.1 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 142.8, 138.9, 129.1, 128.3, 125.8, 115.5, 37.0, 35.2, 27.3, 9.3, 3.9. **HRMS** (EI) calculated for C₁₅H₂₃⁷⁴Ge: 277.1006 [M-CH₂CH₃]⁺, found: 277.1005. **IR** (neat): ν /cm⁻¹ = 3068, 2907, 1802, 1453, 1012.

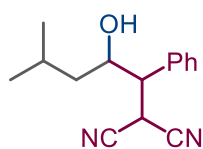
Benzhydryltriethylgermane (22)



Prepared, following modified literature known procedure:^[187] In glovebox, three 4 mL vials were charged with a total amount of triethyl(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)germane **12** (90. mg, 0.24 mmol, 1.0 equiv.), iodobenzene (73.4 mg, 0.36 mmol, 1.5 equiv.), Pd(dba)₂ (11.5 mg, 0.02 mmol, 0.08 equiv.), triphenylphosphine (40.3 mg, 0.15 mmol, 0.64 equiv.), silver oxide (Ag₂O, 83.4 mg, 0.36 mmol, 1.5 equiv.) and dissolved in THF (2.4 mL, 0.1 M). The vials were taken out of glovebox and stirred in a heating block at 70°C for 24 h. The vials were collected and filtered through a small silica pad and solvents were removed under reduced pressure. The title product was obtained after purification by preparative TLC (*n*-pentane) as a colorless oil (30.2 mg, 0.09 mmol, 38%).

R_f = 0.87 (*n*-pentane). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.30 – 7.24 (m, 8H), 7.17 – 7.13 (m, 2H), 3.88 (s, 1H), 0.96 (t, J = 7.9 Hz, 9H), 0.82 (q, J = 8.5, 7.9 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 143.6, 128.5, 128.4, 125.0, 43.2, 9.0, 4.7. **HRMS** (EI) calculated for C₁₇H₂₁⁷⁴Ge: 299.0845 [M-CH₂CH₃]⁺, found: 299.0848. **IR** (neat): ν /cm⁻¹ = 3059, 2948, 1596, 1491, 1014.

2-(2-Hydroxy-4-methyl-1-phenylpentyl)malononitrile (23)

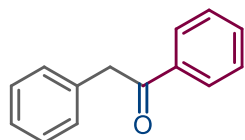


Prepared, following the general procedure A from **15** (88.9 mg, 0.4 mmol, 1.3 equiv.), 2-benzylidenemalononitrile (45.9 mg, 0.3 mmol, 1.0 equiv.) and [^tBu-Acr⁺-Mes][BF₄⁻] (11.5 mg, 0.02 mmol, 5.0 mol%) in ACN:MeOH (1:1, 4.0 mL). The title product was obtained after purification by column chromatography (pentane/Et₂O 7:3) as a white solid (12.2 mg, 0.1 mmol, 25%).

R_f = 0.33 (*n*-pentane/Et₂O 7:3). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.42 – 7.38 (m, 3H), 7.33 – 7.29 (m, 2H), 4.43 (d, J = 10.9 Hz, 1H), 4.36 – 4.28 (m, 1H), 3.21 (dd, J = 10.9, 3.1 Hz, 1H), 1.74 – 1.65 (m, 1H), 1.56 (d, J = 6.1 Hz, 1H), 1.17 – 1.05 (m, 2H), 0.93 – 0.89 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 133.7, 129.3, 129.3, 129.2, 112.6, 112.4, 69.0, 51.9, 44.7, 26.7, 24.8, 23.2, 22.2. **HRMS** (ESI) calculated for C₁₅H₁₈ON₂Na: 265.1311 [M+Na]⁺, found: 265.1312. **IR** (neat): ν /cm⁻¹ = 3497, 2953, 2175, 1454, 1079.

These data are in agreement with those reported previously in the literature.^[242]

1,2-Diphenylethan-1-one (25)

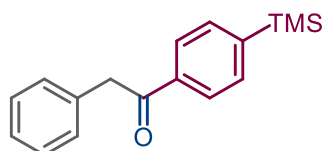


Prepared, following the general procedure F from 2-Phenyl-1-(triethylgermyl)ethan-1-ol **7** (33.5 mg, 0.12 mmol, 1.0 equiv.), bromobenzene (37.7 mg, 0.24 mmol, 2.0 equiv.), Ni(phen)Cl₂ (1.9 mg, 0.01 mmol, 0.05 equiv.) and [^tBu-Acr⁺-Mes][BF₄⁻] (3.4 mg, 0.01 mmol, 0.05 equiv.) in ACN (1.0 mL). The title product

was obtained after purification by preparative TLC (pentane/EtOAc 9:1) as a white solid (15.2 mg, 0.08 mmol, 65%).

R_f = 0.38 (*n*-pentane/EtOAc 9:1). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 8.04 – 8.00 (m, 2H), 7.58 – 7.54 (m, 1H), 7.49 – 7.44 (m, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.25 (m, 3H), 4.29 (s, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 197.7, 136.8, 134.7, 133.3, 129.6, 128.8, 128.8, 128.8, 127.0, 45.7. **MS** (EI) *m/z* (%): 196 (4) [M]⁺, 105 (100), 77 (25). These data are in agreement with those reported previously in the literature.^[243]

2-Phenyl-1-(4-(trimethylsilyl)phenyl)ethan-1-one (26)

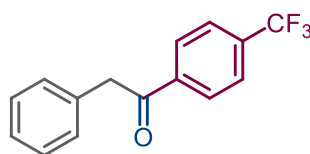


Prepared, following the general procedure F from 2-Phenyl-1-(triethylgermyl)ethan-1-ol **7** (61.7 mg, 0.22 mmol, 1.0 equiv.), (4-bromophenyl)trimethylsilane (100.8 mg, 0.44 mmol, 2.0 equiv.), Ni(phen)Cl₂ (6.8 mg, 0.02 mmol, 0.1 equiv.) and [^tBu-Acr⁺-Mes][BF₄⁻] (12.6

mg, 0.02 mmol, 0.1 equiv.) in ACN (2.0 mL). The title product was obtained after purification by column chromatography (pentane/Et₂O 95:5) as a viscous yellow oil (29.5 mg, 0.11 mmol, 50%).

R_f = 0.27 (*n*-pentane/Et₂O 95:5). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.97 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.26 (m, 3H), 4.28 (s, 2H), 0.28 (s, 9H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 198.0, 147.5, 136.8, 134.8, 133.7, 129.6, 128.8, 127.7, 127.0, 45.7, -1.2. **MS** (EI) *m/z* (%): 253 (18) [M-CH₃]⁺, 177 (100), 149 (16). These data are in agreement with those reported previously in the literature.^[244]

2-Phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (27)

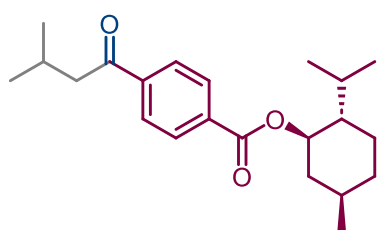


Prepared, following the general procedure F from 2-Phenyl-1-(triethylgermyl)ethan-1-ol **7** (58.8 mg, 0.21 mmol, 1.0 equiv.), 1-bromo-4-(trifluoromethyl)benzene (94.5 mg, 0.42 mmol, 2.0 equiv.), Ni(phen)Cl₂ (6.5 mg, 0.02 mmol, 0.1 equiv.) and [^tBu-Acr⁺-Mes][BF₄⁻] (12.0 mg, 0.02

mmol, 0.1 equiv.) in ACN (2.0 mL). The title product was obtained after purification by column chromatography (pentane/Et₂O 95:5) as a yellowish solid (23.3 mg, 0.09 mmol, 42%).

R_f = 0.40 (*n*-pentane/Et₂O 95:5). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 8.10 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.29 – 7.24 (m, 3H), 4.31 (s, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 196.7, 139.4, 134.5, 133.9, 129.5, 129.1, 129.0, 127.3, 125.9 (q, *J* = 3.9 Hz), 46.0. *Note: Due to low resolution one quartet and one carbon signal are not visible.* **¹⁹F NMR** (564 MHz, CDCl₃) δ /ppm = -63.2. **MS** (EI) *m/z* (%): 264 (5) [M]⁺, 173 (100), 145 (30). These data are in agreement with those reported previously in the literature.^[245]

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(3-methylbutanoyl)benzoate (28)

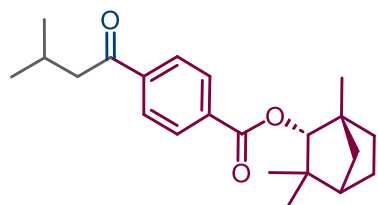


Prepared, following the general procedure F from 3-Methyl-1-(triethylgermyl)butan-1-ol **15** (49.4 mg, 0.2 mmol, 1.0 equiv.), (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromobenzoate (101.8 mg, 0.3 mmol, 1.5 equiv.), Ni(phen)Cl₂ (6.2 mg, 0.02 mmol, 0.1 equiv.) and [^tBu-Acr⁺-Mes][BF₄⁻] (11.5 mg, 0.02 mmol, 0.1 equiv.) in ACN (2.0 mL). The title product was obtained after purification by column

chromatography (pentane/Et₂O 19:1) as a colorless oil (26.8 mg, 0.1 mmol, 40%).

R_f = 0.32 (*n*-pentane/Et₂O 95:5). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 8.13 – 8.09 (m, 2H), 8.00 – 7.97 (m, 2H), 4.98 – 4.92 (m, 1H), 2.85 (d, J = 6.9 Hz, 2H), 2.34 – 2.25 (m, 1H), 2.16 – 2.10 (m, 1H), 1.97 – 1.90 (m, 1H), 1.77 – 1.71 (m, 2H), 1.61 – 1.53 (m, 2H), 1.18 – 1.08 (m, 2H), 1.00 (d, J = 6.7 Hz, 6H), 0.95 – 0.90 (m, 7H), 0.80 (d, J = 7.0 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 199.9, 165.4, 140.6, 134.6, 129.9, 128.1, 75.6, 48.0, 47.4, 41.1, 34.4, 31.6, 26.7, 25.3, 23.8, 22.9, 22.2, 20.9, 16.7. **HRMS** (EI) calculated for C₂₁H₂₉O₃: 329.2111 [M-Me]⁺, found: 329.2111. **IR** (neat): ν /cm⁻¹ = 2955, 2870, 1715, 1270, 1107.

(1*R*,2*R*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(3-methylbutanoyl)benzoate (29)

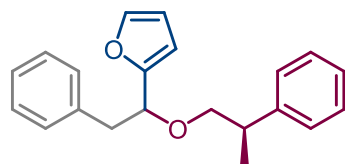


Prepared, following the general procedure F from 3-Methyl-1-(triethylgermyl)butan-1-ol **15** (24.7 mg, 0.1 mmol, 1.0 equiv.), (1*R*,2*R*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-bromobenzoate (50.6 mg, 0.15 mmol, 1.5 equiv.), Ni(phen)Cl₂ (1.5 mg, 0.01 mmol, 0.05 equiv.) and [tBu-Acr⁺-Mes][BF₄⁻] (2.9 mg, 0.01 mmol, 0.05 equiv.) in ACN (1.0 mL)

and a small amount of DCE (0.1 mL) to dissolve the bromobenzoate. The title product was obtained after purification by column chromatography (pentane/Et₂O 95:5) as a viscous colorless oil (5.8 mg, 0.02 mmol, 17%).

R_f = 0.30 (*n*-pentane/Et₂O 95:5). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 8.15 – 8.12 (m, 2H), 8.02 – 7.99 (m, 2H), 4.64 (d, J = 1.9 Hz, 1H), 2.86 (d, J = 6.9 Hz, 2H), 2.33 – 2.27 (m, 1H), 1.92 (dddd, J = 12.3, 8.3, 5.7, 2.1 Hz, 1H), 1.82 – 1.78 (m, 2H), 1.70 – 1.65 (m, 1H), 1.53 (ddd, J = 12.6, 6.3, 2.2 Hz, 1H), 1.28 – 1.25 (m, 1H), 1.24 – 1.21 (m, 1H), 1.19 (s, 3H), 1.12 (s, 3H), 1.00 (d, J = 6.7 Hz, 6H), 0.84 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 199.9, 166.2, 140.7, 134.4, 129.9, 128.2, 87.4, 48.8, 48.6, 48.0, 41.6, 40.0, 29.9, 27.0, 26.1, 25.3, 22.9, 20.4, 19.6. **HRMS** (APCI) calculated for C₂₂H₃₁O₃: 343.2268 [M+H]⁺, found: 343.2272. **IR** (neat): ν /cm⁻¹ = 2956, 2874, 1719, 1689, 1272.

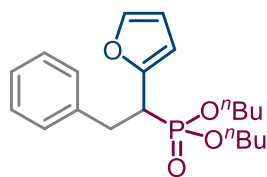
2-(2-Phenyl-1-((*R*)-2-phenylpropoxy)ethyl)furan (30)



Prepared, following the general procedure G from triethyl(1-(furan-2-yl)-2-phenylethyl)germane **17** (25.3 mg, 0.08 mmol, 1.0 equiv.) and (*R*)-2-phenyl-1-propanol (54.4 mg, 0.4 mmol, 5.0 equiv.). The title product was obtained as a mixture of diastereomers (d.r. of 1:1 according to ¹H NMR)

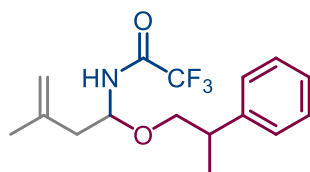
after purification by HPLC (*n*-hexane/EtOAc 9:1) as a colorless liquid (9.3 mg, 0.03 mmol, 40%).

R_f = 0.20 (pentane/EtOAc 9:1). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.40 (dd, J = 1.8, 0.8 Hz, 1H), 7.38 (dd, J = 1.8, 0.8 Hz, 1H), 7.26 – 7.22 (m, 6H), 7.21 – 7.10 (m, 12H), 7.07 – 7.04 (m, 2H), 6.29 (dd, J = 3.2, 1.8 Hz, 1H), 6.28 (dd, J = 3.2, 1.8 Hz, 1H), 6.13 (dd, J = 3.2, 0.9 Hz, 1H), 6.10 (dd, J = 3.2, 0.9 Hz, 1H), 4.43 (dd, J = 7.8, 6.1 Hz, 1H), 4.39 (dd, J = 7.6, 6.2 Hz, 1H), 3.53 (dd, J = 9.2, 5.6 Hz, 1H), 3.43 – 3.36 (m, 2H), 3.25 (dd, J = 9.2, 8.0 Hz, 1H), 3.18 – 3.02 (m, 4H), 2.96 – 2.88 (m, 2H), 1.19 (d, J = 6.9 Hz, 3H), 1.18 (d, J = 7.0 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 154.4, 144.6, 144.5, 142.2, 138.3, 138.3, 129.6, 129.5, 128.4, 128.2, 128.2, 127.5, 126.4, 126.3, 126.3, 110.1, 108.1, 108.0, 76.8, 76.5, 75.0, 74.9, 41.2, 41.1, 40.2, 40.0, 18.5, 18.3. **HRMS** (ESI) calculated for C₂₁H₂₂O₂Na: 329.1512 [M+Na]⁺, found: 329.1510. **IR** (neat): ν /cm⁻¹ = 3061, 2959, 2920, 1602, 1495, 1452, 1333, 1077.

Dibutyl (1-(furan-2-yl)-2-phenylethyl)phosphonate (31)

Prepared, following the general procedure G from triethyl(1-(furan-2-yl)-2-phenylethyl)germane **17** (43.0 mg, 0.13 mmol, 1.0 equiv.) and tributyl phosphite (162.7 mg, 0.65 mmol, 5.0 equiv.). The title product was obtained after purification by column chromatography (pentane/EtOAc 8:2) as a colorless liquid (16.6 mg, 0.05 mmol, 35%).

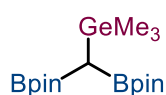
R_f = 0.30 (pentane/EtOAc 8:2). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.32 (s, 1H), 7.21 – 7.18 (m, 2H), 7.17 – 7.13 (m, 1H), 7.03 (d, *J* = 7.0 Hz, 2H), 6.27 (s, 1H), 6.16 – 6.13 (m, 1H), 4.04 – 3.94 (m, 3H), 3.88 – 3.81 (m, 1H), 3.48 (ddd, *J* = 22.6, 11.5, 3.9 Hz, 1H), 3.35 (ddd, *J* = 13.0, 8.7, 3.8 Hz, 1H), 3.21 (ddd, *J* = 13.9, 11.5, 8.1 Hz, 1H), 1.64 – 1.58 (m, 2H), 1.58 – 1.52 (m, 2H), 1.36 (dp, *J* = 22.7, 7.5 Hz, 4H), 0.91 (dt, *J* = 15.0, 7.4 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 149.4 (d, *J*_{C-P} = 8.6 Hz), 141.9 (d, *J*_{C-P} = 3.3 Hz), 139.1 (d, *J*_{C-P} = 15.6 Hz), 128.8, 128.4, 126.5, 110.8 (d, *J*_{C-P} = 3.0 Hz), 108.9 (d, *J*_{C-P} = 7.4 Hz), 66.5 (d, *J*_{C-P} = 6.9 Hz), 66.1 (d, *J*_{C-P} = 7.2 Hz), 40.7 (d, *J*_{C-P} = 140.9 Hz), 34.9 (d, *J*_{C-P} = 1.9 Hz), 32.7 (d, *J*_{C-P} = 6.0 Hz), 32.7 (d, *J*_{C-P} = 5.8 Hz), 18.9, 18.8, 13.8, 13.8. **³¹P NMR** (243 MHz, CDCl₃) δ /ppm = 24.8 (s, 1P). (*Note: The product contains traces of tributyl phosphite starting material (based on ³¹P NMR) due to purification challenges.*) **MS** (EI) *m/z* (%): 364 (5) [M]⁺, 273 (7), 217 (12), 207 (14), 170 (100), 163 (16), 91 (10), 81 (12). **HRMS** (ESI) calculated for C₂₀H₂₉O₄NaP: 387.1696 [M+Na]⁺, found: 387.1685. **IR** (neat): ν /cm⁻¹ = 2959, 2874, 1462, 1263, 1022, 907.

2,2,2-Trifluoro-*N*-(3-methyl-1-(2-phenylpropoxy)but-3-en-1-yl)acetamide (32)

Prepared, following the general procedure G from 2,2,2-trifluoro-*N*-(3-methyl-1-(triethylgermyl)but-3-en-1-yl)acetamide (69.0 mg, 0.2 mmol, 1.0 equiv.) and 2-phenylpropan-1-ol (136.2 mg, 1.0 mmol, 5.0 equiv.). The title product was obtained as a mixture of diastereomers (d.r. of 1:1.5

according to ¹H and ¹⁹F NMR) after purification by HPLC (*n*-hexane/EtOAc 7:3) as a colorless liquid (57.7 mg, 0.18 mmol, 90%).

R_f = 0.55 (pentane/EtOAc 95:5). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 3H), 6.37 (d, *J* = 8.2 Hz, 1H major), 6.25 (d, *J* = 8.6 Hz, 1H minor), 5.35 (dt, *J* = 9.4, 5.8 Hz, 1H minor), 5.30 (dt, *J* = 9.4, 5.8 Hz, 1H major), 4.89 – 4.87 (m, 1H minor), 4.87 – 4.84 (m, 1H major), 4.74 – 4.73 (m, 1H minor), 4.73 – 4.70 (m, 1H major), 3.70 – 3.56 (m, 2H), 3.04 – 2.94 (m, 1H), 2.42 – 2.28 (m, 2H), 1.73 (t, *J* = 1.1 Hz, 3H minor), 1.69 (t, *J* = 1.1 Hz, 3H major), 1.27 (d, *J* = 7.0 Hz, 3H major), 1.27 (d, *J* = 7.0 Hz, 3H minor). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 157.2 (d, *J* = 37.4 Hz), 157.2 (d, *J* = 37.2 Hz), 144.0, 143.8, 140.1, 140.1, 128.5, 128.5, 127.5, 127.4, 126.7, 115.8 (d, *J* = 288.5 Hz), 114.9, 114.9, 79.6, 79.5, 75.1, 75.0, 43.4, 43.3, 40.1, 40.0, 23.2, 23.1, 18.4, 18.1. *Note:* Due to insufficient resolution only the middle “doublets” of the expected quartets of the C=O and CF₃ moiety could be observed in ¹³C NMR. **¹⁹F NMR** (564 MHz, CDCl₃) δ /ppm = -76.11 (s, 3F, minor), -76.12 (s, 3F, major). **HRMS** (EI) calculated for C₇H₉ONF₃: 180.0631 [M-C₉H₁₁O]⁺, found: 180.0631. **IR** (neat): ν /cm⁻¹ = 2967, 2920, 1710, 1542, 1163, 698.

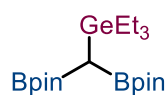
(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylgermane (33)

Prepared, following the general procedure H from bis[(pinacolato)boryl]methane (2090.2 mg, 7.8 mmol, 1.2 equiv.) and trimethylchlorogermane (0.81 mL, 6.5 mmol,

1.0 equiv.). The title product was obtained after purification by column chromatography (pentane/Et₂O 9:1) as colorless oil (1750.7 mg, 4.55 mmol, 70%).

R_f = 0.25 (*n*-pentane/Et₂O 9:1). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 1.22 (s, 12H), 1.21 (s, 12H), 0.26 (s, 1H), 0.25 (s, 9H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 82.7, 25.2, 24.7, 0.3. **HRMS** (EI) calculated for C₁₅H₃₁O₄B₂⁷⁴Ge: 371.1615 [M-CH₃]⁺, found: 371.1610. **IR** (neat): ν /cm⁻¹ = 2978, 2930, 1320, 1143, 1069.

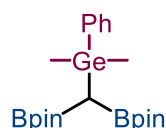
(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)triethylgermane (34)



Prepared, following the general procedure H from bis[(pinacolato)boryl]methane (3386.0 mg, 12.6 mmol, 1.0 equiv.) and triethylchlorogermane (2.09 mL, 12.6 mmol, 1.0 equiv.). The title product was obtained after purification by column chromatography (pentane/Et₂O 95:5) as colorless oil (4016.6 mg, 9.14 mmol, 75%).

R_f = 0.45 (*n*-pentane/Et₂O 95:5). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 1.21 (s, 12H), 1.19 (s, 12H), 1.04 (t, *J* = 7.9 Hz, 9H), 0.85 (q, *J* = 7.9 Hz, 6H), 0.30 (s, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 82.6, 25.2, 24.7, 9.1, 6.3. **HRMS** (ESI) calculated for C₁₉H₄₀O₄B₂⁷⁴GeNa: 451.2217 [M+Na]⁺, found: 451.2211. **IR** (neat): ν /cm⁻¹ = 2976, 2944, 1461, 1318, 1143.

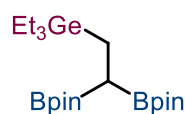
(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)dimethyl(phenyl)germane (35)



Prepared, following the general procedure H from bis[(pinacolato)boryl]methane (2411.7 mg, 9.0 mmol, 1.2 equiv.) and chlorodimethyl(phenyl)germane (1.06 mL, 7.5 mmol, 1.0 equiv.). The title product was obtained after purification by column chromatography (pentane/Et₂O 9:1) as white solid (1900.9 mg, 4.25 mmol, 57%).

R_f = 0.28 (*n*-pentane/Et₂O 9:1). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.54 – 7.51 (m, 2H), 7.32 – 7.27 (m, 3H), 1.15 (s, 12H), 1.11 (s, 12H), 0.55 (s, 1H), 0.52 (s, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 142.3, 133.5, 128.3, 127.8, 82.8, 25.1, 24.6, -1.2. **HRMS** (EI) calculated for C₂₀H₃₃O₄B₂⁷⁴Ge: 433.1771 [M-CH₃]⁺, found: 433.1775. **IR** (neat): ν /cm⁻¹ = 2978, 2927, 1303, 1139, 1074.

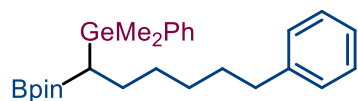
(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)triethylgermane (36)



Prepared, following the general procedure H from bis[(pinacolato)boryl]methane (3215.6 mg, 12.0 mmol, 1.2 equiv.) and (chloromethyl)triethylgermane (2092.9 mg, 10.0 mmol, 1.0 equiv.). The title product was obtained after purification by column chromatography (pentane/Et₂O 9:1) as white solid (3224.9 mg, 7.32 mmol, 73%).

R_f = 0.30 (*n*-pentane/Et₂O 9:1). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 1.22 (s, 24H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.94 (d, *J* = 6.9 Hz, 2H), 0.75 (t, *J* = 6.8 Hz, 1H), 0.69 (q, *J* = 7.9 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 83.1, 24.9, 24.9, 9.1, 5.6, 4.0. **HRMS** (EI) calculated for C₁₈H₃₇O₄B₂⁷⁴Ge: 413.2084 [M-CH₂CH₃]⁺, found: 413.2083. **IR** (neat): ν /cm⁻¹ = 2977, 2946, 1462, 1352, 1139.

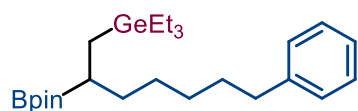
Dimethyl(phenyl)(6-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)germane (37)



Prepared, following the general procedure I from (Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)dimethyl(phenyl)germane (134.0 mg, 0.30 mmol, 1.0 equiv.) and (5-bromopentyl)benzene (110.8 μ L, 0.6 mmol, 2.0 equiv.). The title product was obtained after purification by preparative TLC (pentane/Et₂O 96:4) as colorless oil (33.3 mg, 0.07 mmol, 23%).

$R_f = 0.78$ (*n*-pentane/Et₂O 96:4). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.49 – 7.46 (m, 2H), 7.35 – 7.28 (m, 3H), 7.28 – 7.23 (m, 2H), 7.19 – 7.12 (m, 3H), 2.55 (t, $J = 7.7$ Hz, 2H), 1.63 – 1.50 (m, 3H), 1.41 – 1.32 (m, 2H), 1.32 – 1.23 (m, 3H), 1.17 (d, $J = 21.3$ Hz, 12H), 0.79 (dd, $J = 12.1, 3.2$ Hz, 1H), 0.44 – 0.39 (m, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 143.1, 141.4, 133.6, 128.5, 128.4, 128.3, 127.9, 125.7, 82.8, 36.1, 33.1, 31.6, 29.2, 26.6, 25.3, 24.9, -2.9, -3.7. **HRMS** (EI) calculated for C₂₅H₃₆O₂B⁷⁴Ge: 453.2015 [M-CH₃]⁺, found: 453.2018. **IR** (neat): ν /cm⁻¹ = 3063, 2977, 2924, 1456, 1143.

Triethyl(7-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)germane (38)

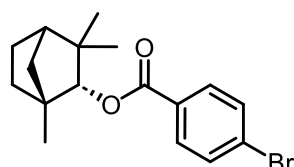


Prepared, following the general procedure I from (2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)triethylgermane (132.2 mg, 0.30 mmol, 1.0 equiv.) and (5-bromopentyl)benzene (110.8 μ L, 0.6 mmol, 2.0 equiv.). The title product was obtained after purification by preparative TLC (pentane/Et₂O 96:4) as colorless oil (38.3 mg, 0.08 mmol, 28%).

$R_f = 0.70$ (*n*-pentane/Et₂O 96:4). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.29 – 7.24 (m, 2H), 7.17 (d, $J = 7.4$ Hz, 3H), 2.62 – 2.56 (m, 2H), 1.64 – 1.57 (m, 2H), 1.45 – 1.28 (m, 6H), 1.24 (d, $J = 3.6$ Hz, 12H), 1.07 – 1.02 (m, 1H), 1.00 (t, $J = 7.9$ Hz, 9H), 0.88 (dd, $J = 13.7, 7.5$ Hz, 1H), 0.74 – 0.66 (m, 7H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 143.1, 128.5, 128.4, 125.7, 82.9, 36.1, 34.8, 31.6, 29.8, 29.1, 25.1, 24.9, 12.9, 9.2, 4.6. **HRMS** (EI) calculated for C₂₃H₄₀O₂B⁷⁴Ge: 433.2328 [M-CH₂CH₃]⁺, found: 433.2328. **IR** (neat): ν /cm⁻¹ = 3026, 2925, 1457, 1374, 1143.

3.3.11 Starting material synthesis

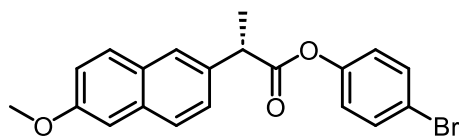
(1*R*,2*R*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl 4-bromobenzoate



In a round bottom flask, 4-bromobenzoic acid (1005.1 mg, 5.00 mmol, 1.0 equiv.), (1*R*)-endo-(+)-fenchyl alcohol (771.3 mg, 5.00 mmol, 1.0 equiv.), *N,N'*-dicyclohexylcarbodiimide (1134.8 mg, 5.50 mmol, 1.1 equiv.) and 4-dimethylaminopyridine (30.5 mg, 0.25 mmol, 0.05 equiv.) were dissolved in

anhydrous DCM (40 mL) and stirred at room temperature overnight. The precipitate was filtered off and the filtrate was added to a saturated aqueous solution of NaHCO₃. After three extractions with DCM, the organic phases were combined, washed with brine and dried over MgSO₄, before the solvents were removed under reduced pressure. The title product was obtained after purification by column chromatography (pentane/Et₂O 95:5) as a white solid (1061.7 mg, 3.15 mmol, 63%).

$R_f = 0.73$ (*n*-pentane/Et₂O 95:5). **¹H NMR** (600 MHz, CDCl₃) δ /ppm = 7.92 (d, $J = 8.1$ Hz, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 4.61 (s, 1H), 1.93 – 1.86 (m, 1H), 1.81 – 1.74 (m, 2H), 1.66 (d, $J = 10.4$ Hz, 1H), 1.56 – 1.48 (m, 1H), 1.26 (d, $J = 10.4$ Hz, 1H), 1.21 (d, $J = 12.9$ Hz, 1H), 1.18 (s, 3H), 1.10 (s, 3H), 0.83 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ /ppm = 166.3, 131.9, 131.2, 129.8, 128.0, 87.2, 48.8, 48.5, 41.6, 40.0, 29.9, 27.0, 26.0, 20.4, 19.6. **HRMS** (ESI) calculated for C₁₇H₂₁O₂BrNa: 359.0617 [M+Na]⁺, found: 359.0619. **IR** (neat): ν /cm⁻¹ = 2956, 2871, 1712, 1587, 1268.

4-Bromophenyl-(S)-2-(6-methoxynaphthalen-2-yl)propanoate

In a round bottom flask, 4-bromophenol (415.2 mg, 2.40 mmol, 1.0 equiv.) and (S)-2-(6-methoxynaphthalen-2-yl)propanoic acid (555.3 mg, 2.40 mmol, 1.0 equiv.), *N,N'*-dicyclohexylcarbodiimide (544.7 mg, 2.64 mmol, 1.1 equiv.) and 4-dimethylaminopyridine (14.6 mg, 0.12 mmol, 0.05 equiv.) were dissolved in anhydrous DCM (30 mL) and stirred at room temperature overnight. The precipitate was filtered off and the filtrate was added to a saturated aqueous solution of NaHCO₃. After three extractions with DCM, the organic phases were combined, washed with brine and dried over MgSO₄, before the solvents were removed under reduced pressure. The title product was obtained after purification by column chromatography (pentane/Et₂O 9:1) as a white solid (809.1 mg, 2.10 mmol, 88%).

R_f = 0.52 (*n*-pentane/Et₂O 9:1). **¹H NMR** (600 MHz, CDCl₃) δ/ppm = 7.77 – 7.72 (m, 3H), 7.48 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 2H), 7.20 – 7.12 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ/ppm = 173.0, 158.0, 150.0, 135.0, 134.0, 132.5, 129.5, 129.1, 127.6, 126.3, 126.1, 123.4, 119.3, 119.0, 105.8, 55.5, 45.7, 18.6. **HRMS** (ESI) calculated for C₂₀H₁₇O₃BrNa: 407.0253 [M+Na]⁺, found: 407.0252. **IR** (neat): ν/cm⁻¹ = 2980, 2938, 1760, 1602, 1481.

4

Literature

4 Literature

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