Department of Chemistry
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C- AND N- CARBOXYLATIONS IN FINE CHEMICAL SYNTHESIS USING CARBON DIOXIDE

Aleksi Mikael Sahari

DOCTORAL DISSERTATION

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ABSTRACT

Organic chemistry is essentially chemistry of the element carbon, which has the unique property of forming stable bonds with itself and many of the other elements. From this property can be derived a vast variety of highly complex molecules that are needed to support life. Much of the complexity of the chemicals we use can be traced back to the biological processes that fix carbon dioxide, which act as the fundamental building block of organic chemistry. Anthropogenic efforts have historically focused on moving in the other direction, releasing carbon dioxide from chemicals, but in the recent decades, we have also started to study the utilization of carbon dioxide in complex molecule synthesis.

This thesis covers a literature overview of the challenges of utilizing carbon dioxide and the many methods that have been developed to carboxylate carbon and nitrogen centers. Carbon dioxide is a thermodynamically stable and natively nonpolar but highly polarizable molecule due to its electrophilicity. Polarization of carbon dioxide corresponds with a change in geometry from linear to planar, which induces a negative charge on oxygen atoms, which can be stabilized with a Lewis acid, which is important for kinetic reactivity. In carboxylations of carbon atoms, the challenge is generating a negatively charged, highly polarizing carbon atom. Organometallic chemistry has been traditionally utilized due to the electronegativity differences between metals and carbon, and catalytic methods have been developed for all saturation states of carbon. In contrast, amines are highly nucleophilic by themselves and can easily polarize carbon dioxide to form carbamate anions. However, these salts decompose quickly in the presence of water and are not very useful compounds by themselves. They need to be stabilized by further reactions to form carbamate, and there we need to consider the weak nucleophilicity of the polarized carbon dioxide.

The experimental section presents the original work in the thesis. The first publication presents a multicomponent method to produce butyrolactones in a C-carboxylation reaction with carbon dioxide, benzaldehyde, and a Grignard reagent or alkene. In the second publication, O-aryl carbamates are synthesized by N-carboxylation from amines, carbon dioxide, and aryl iodides or bromides. The reaction utilized photochemical activation to avoid using highly energetic starting materials or reagents. The third publication studies different methods to form oxazolidinones by N-carboxylation to create a method with high selectivity and without undesired inversion of stereochemistry.

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CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications:

I **Aleksi Sahari**, Cuong Dat Do, Jere K. Mannisto, Emanuele Antico, Angelo Amaratunga, Kathrin H. Hopmann, Timo Repo, Titanium isopropoxide-mediated cis-selective synthesis of 3,4-substituted butyrolactones from CO_2, *Chem. Commun.,* **2022**, 58, 3027–3030

II **Aleksi Sahari**, Jukka Puumi, Jere K. Mannisto, and Timo Repo, Dual Nickel Photocatalysis for O-Aryl Carbamate Synthesis from Carbon Dioxide, *J. Org. Chem.* **2023**, 88, 3822–3829

III **Aleksi Sahari**, Jukka Puumi, Andrea Záková, Jere K. Mannistom, Timo Repo, Evaluation of electrophilic oxygen abstracting reagents in carbon dioxide based oxazolidinone synthesis, *Manuscript in preparation.*

The publications are referred to in the text by their roman numerals.

AUTHOR’S CONTRIBUTION

I The author conceived the project and conducted most of the experimental work and analysis. Cuong Dat Do and Kathrin H. Hopman conducted the computational studies. Jere K. Mannisto, Emanuele Antico and Angelo Amaratunga performed experimental work and contributed to the optimisation process of the study. The work was supervised by Timo Repo. The author wrote the manuscript with input from all the co-authors.

II The author conceived the project and conducted the initial studies, most of the analysis and the experimental work in mechanistic studies and substrate scope. Jukka Puumi conducted most of the experimental work in optimization and photocatalyst characterisation. Jere K. Mannisto contributed to the analysis of the work. The work was supervised by Timo Repo. The author wrote the manuscript with input from all the co-authors

III The author conceived the project and conducted most of the experimental work and analysis. Jukka Puumi and Andrea Záková synthesized and analysed some of the substrates and products. Jere K. Mannisto contributed to the analysis and provided part of the substrates. The work was supervised by Timo Repo. The author drafted the manuscript.

OTHER PUBLICATIONS RELATING TO CO_2

IV Jere K. Mannisto, **Aleksi Sahari**, Kalle Lagerblom, Teemu Niemi, Martin Nieger, Gábor Sztanó, Timo Repo, One-Step Synthesis of 3,4-Disubstituted 2-Oxazolidinones by Base-Catalyzed CO2 Fixation and Aza-Michael Addition *Chem. Eur. J.* 2019, 25, 10284-10289

V Jere K. Mannisto, Ljiljana Pavlovic, Tony Tiainen, Martin Nieger, **Aleksi Sahari**, Kathrin H. Hopmann Timo Repo, Mechanistic insights into carbamate formation from CO2 and amines: the role of guanidine–CO2 adducts, *Catal. Sci. Technol.,* **2021**, 11, 6877–6886

VI Jere K. Mannisto, Ljiljana Pavlovic, Tony Tiainen, Martin Nieger, **Aleksi Sahari**, Norbert Maier, Kathrin H. Hopmann Timo Repo, Timo, N-Heteroaryl Carbamates from Carbon Dioxide via Chemoselective Superbase–Catalysis: Substrate Scope and Mechanistic Investigation, *Submitted*

ABBREVIATIONS

acac	Acetylacetone
Alk	Alkyl
Ar	Aryl
9-BBN	9-Borabicyclo[3.3.1]nonane
BEMP	2-tert-Butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine
BenzP*	(R,R)-(+)-1,2-Bis(t-butylmethylphosphino)benzene
bpy	2,2’-bipyridine
cod	1,5-cyclooctadiene
4CzIPN	2,4,5,6-tetracarbazole-isophtalonitrile
DBU	1,8-Diazabicyclo(5.4.0)undec-7-ene
DBAD	Di-tert-butyl azodicarboxylate
DCC	N,N'-Dicyclohexylcarbodiimide
DCPE	1,2-Bis(dicyclohexylphosphino)ethane
DBAD	Di-tert-butyl azodicarboxylate
DEAD	Diethylazodicarboxylate
DG	Directing group
DMAc	Dimethylacetamide
DMEDA	Dimethylethylenediamine
DMF	Dimethylformamide
DMI	1,3-Dimethyl-2-imidazolidinone
DMSO	Dimethylsulfoxide
dtbbpy	4,4′-Di-tert-butyl-2,2′-dipyridyl
DPPA	Diphenylphosphoryl azide
DPPCl	Diphenyl chlorophosphite
dppf	Diphenylphosphineferrocene
dppp	1,2-Bis(diphenylphosphino)propane
EWG	Electron withdrawing group
IMes	1,3-bis(1,3,5-trimethyl)-imidazol-2-ylidene
IPr	1,3-bis-(2,6-diisopropylphenyl)-imidazol2-ylidene
PCp_3	Tricyclopentylphosphine
PCy_3	Tricyclohexylphosphine
phen	Phenantroline
ppy	2-phenylpyridine
SPhos	Dicyclohexyl(2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphane
TBD	Triazabicyclodecene
THF	Tetrahydrofuran
TMP	Tetramethylpiperidine
TMS	Trimethylsilyl
Ts	p-Toluenesulfonyl

1 SCOPE OF THE THESIS

This thesis focuses on CO_2 carboxylation reactions of carbon and nitrogen to form carboxylic acids and carbamates. First, the literature review covers methods to form carboxylic acids bound to sp, sp^2 and sp^3 hybridized carbons and carbamates generated directly from CO_2. The results and discussion chapter describes the findings in the original publications.

Publication I presents a method for 1,2-difunctionalization of Grignard reagents or alkenes with carbon dioxide and benzaldehydes to yield *cis*-butyrolactones. Difunctionalization of saturated compounds is especially difficult with carbon dioxide and the described method provides quick access to increased complexity.

Publication II describes a method for O-aryl carbamate synthesis using aryl iodides and bromides with dual visible-light photo- and nickel-catalysis. Compared to previous CO_2 based methods, this method uses commercial substrates in mild conditions without stoichiometric activating reagents.

Publication III is a study of mild activating reagents in oxazolidinone synthesis. This study shows that stereochemical inversion and other side reactions can be minimized with an activating reagent that matches the carbamate reactivity.

2 INTRODUCTION

The element carbon is at the center of organic chemistry. It has multiple stable oxidation states, and it can form stable bonds with itself and other elements. This allows building carbon backbones and connecting them to other elements to create a virtually infinite variety of structures. This variety has made it possible for life to evolve and to create even more emerging complexity. Nowadays, we utilize carbon to create polymers, pharmaceuticals, fuels, agrochemicals etc.

Carbon dioxide is the highest oxidation state of carbon. It is abundant in the atmosphere, and it is constantly being created through natural and industrial combustion processes. The abundancy and renewability have generated interest in the possibility that carbon dioxide could be utilized as a building block in organic synthesis, where it might replace other C1-reagents.[1] These include carbon monoxide, phosgene and methyl iodide. These are much more toxic and expensive than carbon dioxide. However, since carbon dioxide is the combustion product, it is very thermodynamically stable.[2] In this thesis, we look at the properties of carbon dioxide and some of the methods to overcome this thermodynamic barrier.

While thermodynamically stable, carbon dioxide is a good electrophile. When a nucleophile reacts with it, the carbon adopts a planar trigonal shape from its initial linear shape, and negative charge is distributed to the oxygens. Binding of a gaseous molecule and loss of symmetry axis are entropically unfavorable, and in combination with unstabilized negative charges, they lead to very unfavorable thermodynamics. Therefore, while many nucleophiles can react with carbon dioxide, the products are often unstable. To promote the reaction, the charge can be stabilized by Lewis adduct or hydrogen bond formation, or higher pressure can be used to reduce the loss of entropy.

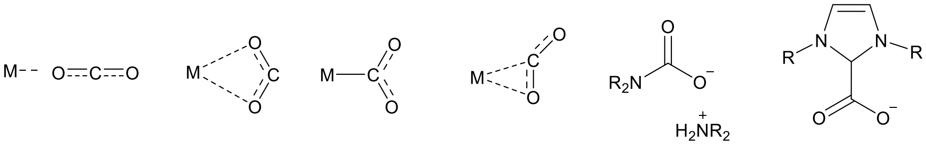
Carbon dioxide utilization is also of interest, as carbon dioxide is a greenhouse gas and contributes to climate change. However, carbon dioxide utilisation cannot greatly reduce the amount of CO_2 as the utilized CO_2 is not removed from the carbon cycle. Rather the increased utilization of CO_2 may reduce the dependence on fossil fuels. To remove carbon dioxide from carbon cycle, it would need to be converted into a form that can’t be utilized by microbes or stored somewhere, like deep underground.[3] However, studies in to the properties of CO_2 may also induce breakthroughs in the field of carbon storage

Other important reactions in CO_2 utilization that will not be covered are formation of carbonates and ureas, the reduction to formic acid, carbon monoxide and methanol, and the subsequent utilization of these materials. [4] Currently, commercial utilization of CO_2 is limited to the production of urea from ammonia, methanol from reduction, salicylic acids from phenols, and inorganic and organic carbonates.[3] CO_2 is also used as foaming gas and for carbonation of soft drinks. The expected utilisation of CO_2 is expected to reach 10^3 Mt scale, compared to the 10^{10} Mt scale of total anthropogenic emissions.

3 REVIEW OF THE LITERATURE

Carbon dioxide (CO_2) is a comparably stable molecule owing to its high bond dissociation energy of the C=O bond, linear geometry, and net zero dipole moment.[2] Therefore, the processes utilizing CO_2 often require high temperatures and pressure. Since CO_2 is a gaseous molecule and the linear geometry is broken in chemical transformations, the reaction with CO_2 generally has a negative entropy term. Therefore, increasing temperature is generally detrimental to CO_2 reactivity. This can be counteracted by extreme pressure or using high energy reagents.

Kinetically, CO_2 is quite reactive.A comparison in Mayr parameters places CO_2 to be about as reactive as benzaldehyde (-16 to -11 for CO_2, 12.9 to benzaldehyde).[5] However, this requires that the reactant be polarizing enough to break the linear geometry and induce a dipole to CO_2. If the reactant is unable to do this by itself, a catalyst can be used. The reagent or the catalyst can coordinate with CO_2 in multiple ways due to its amphiphilic character, as shown in Scheme 1.[6] The oxygen atoms in CO_2 have Lewis basic character and can coordinate in η^1-O or η^2-O,O type. The carbon atom is connected to two more electronegative oxygen atoms and therefore exhibits Lewis acidic behavior, as is shown by η^1-C and η^2-C,O type binding and reactions with organic nucleophiles. All of these binding modes induce a dipole moment to CO_2 and all except η^1-O also disrupt the linear geometry.



Scheme 1: Examples oif carbon dioxide modes of binding[7] η^1-O, η^2-O,O, η^1-C, η^2-C,O, carbamate, N-heterocyclic carbene, where M is a (transition) metal or Lewis acid.

The difficulty in using a metal catalytic approach stems from the product carboxylates coordinate strongly to the catalyst and can inhibit further catalytic cycles. Forming a covalent carboxylate derivative or transmetallation can be used to decrease the coordination of the product.

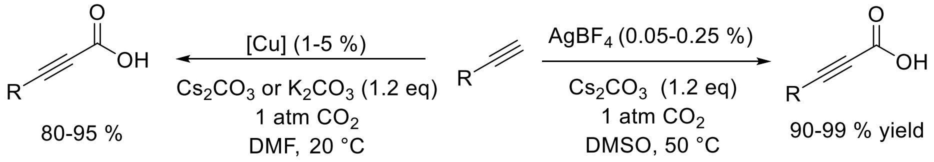
3.1 C-CARBOXYLATIONS

Carboxylic acids and their derivatives are very common chemical moieties found in solvents, dyes, pharmaceuticals, agrochemicals, and polymers or used in their production. The global market value of carboxylic acids is expected to reach 16 billion euros by 2024.[8] Many methods exist to synthesize carboxylic acids, for example, hydrolysis of nitriles, oxidation of primary alcohols or aldehydes, or oxidative cleavage of alkenes. Utilization of CO_2 in carboxylic acid synthesis offers an alternative route to chemical manufacturing. In bulk chemical manufacturing, this could lower the carbon footprint, increase sustainability, and reduce costs due to the low cost of CO_2. In fine chemical synthesis, CO_2-utilization may afford new synthetic strategies as an electrophilic C1 synthon. In the following chapters, methods are discussed to synthesize carboxylic acid from CO_2 connected to either sp, sp^2 or sp^3 carbon. The general strategy in CO_2-based carboxylation is the generation of a δ^- carbon nucleophile and using a Lewis acid catalyst to mediate polarization and delinearization of the CO_2.

Carboxylic acids can also be generated indirectly from CO_2 by *in situ* reduction to CO followed by formylation of an alkene.[9] Since formylation chemistry is an expansive area of study on its own, it will not be covered in detail here.[10] Challenges with this approach are that CO_2 requires high pressure and temperature and that the formylation regioselectivity is not very high.

3.1.1 PROPARGYLIC ACIDS

Terminal alkynes are mildly acidic (pKa≈25) and they can be deprotonated with a strong base to form a nucleophilic carbon that can react with the electrophilic CO_2. Transition metal catalysts can coordinate with the terminal end of the alkyne, which facilitates the deprotonation and also the insertion of CO_2. Copper and silver catalysts have been shown to be very effective catalysts with broad functional group tolerance (Scheme 2).[11] With $AgBF_4$, only 500 ppm was enough to give excellent yields in 1 atm CO_2.

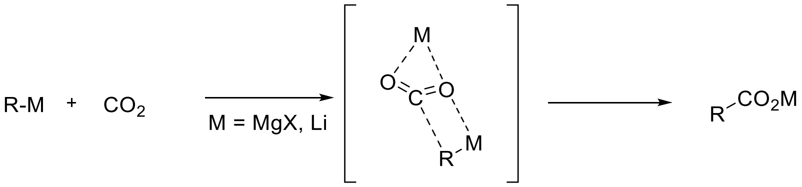


Scheme 2: Terminal alkyne carboxylation.

Transition metal free carboxylations have also been reported for terminal alkynes.[12] However, these results have some variance between them, which could be explained by trace transition metal impurities, since only very low amounts of silver was required for efficient catalysis.

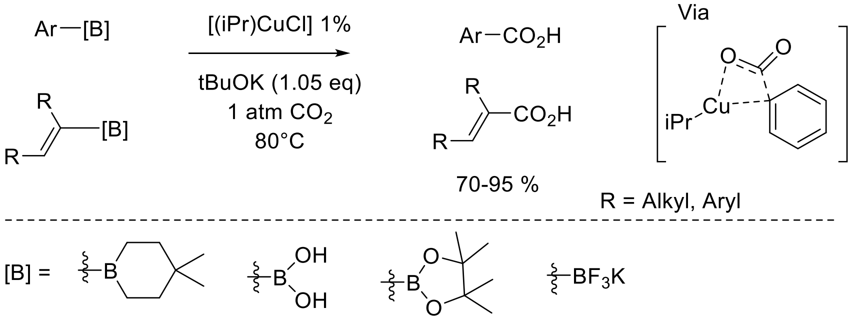
3.1.2 ACRYLIC AND ARYL ACIDS

The first reported carboxylation was made with highly nucleophilic Grignard or organolithium reagents, and it remains a viable method for sp^2 and sp^3 carboxylations.[13] The CO_2 inserts very quickly into the very polar metal-carbon bond, even at very low temperatures (< -78°C). However, due to the high reactivity of these reagents, they are often poorly selective and therefore cannot be applied in the later stages of synthesis when the substrate already has other reactive functionalities. To remedy the problems with the chemoselectivity, transition metals can be used instead of Mg or Li, as they produce a less polar carbon-metal bond. Many transition metals are known to insert CO_2 (Rh[14], Ni[15], Cu[16]) These could be further developed into catalytic systems by transmetallating with organoboronates, -stannates and -zinc reagents, inspired by the progress made in cross-coupling chemistry. [17]



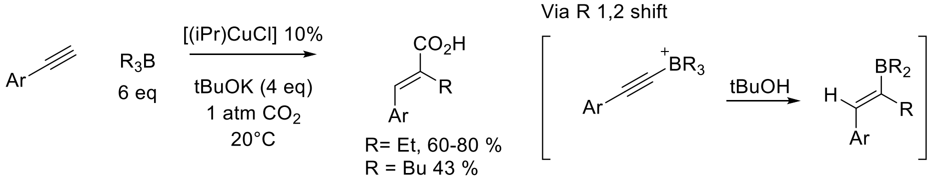
Scheme 3: Carboxylations with organomagnesium or organolithium reagent.

For example, Cu(IPr) has been shown to be a very general catalyst for sp^2-boron carboxylation reactions (Scheme 4).[18] The reactions have a high functional group tolerance, and boranes, borane esters, boric acids and trifluoroboranes could be used as substrates. The CO_2-insertion is the rate-determining step, and it proceeds through the inner-sphere mechanism, where the CO_2 -molecule coordinates directly to the metal, as opposed to outer sphere mechanism. where there would be no direct interaction with the metal and CO_2.[19] By adding a fluoride source, aryl silanes could also be carboxylated in similar conditions.[20] Similar systems were also developed for ruthenium, silver and nickel, but they provided limited utility compared to the copper catalyst.[21] [22]



Scheme 4: Cu-N-heterocyclic carbene complex catalysed carboxylation of aryl boranes.

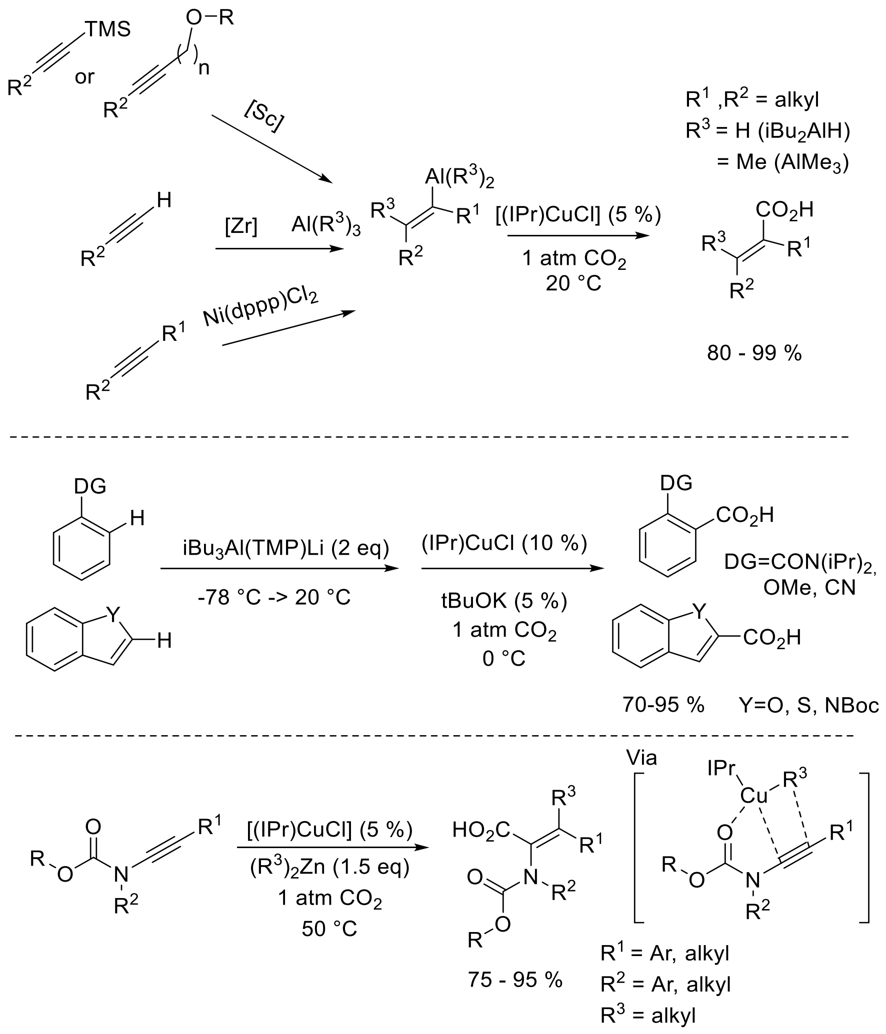
The copper catalyzed system could be further adapted to multicomponent reactions with alkyne, trialkylborane and CO_2 yielding α,β-substituted acrylic acids, where the sp^2 borane is generated *in situ*. (Scheme 5).[23] The reaction was limited to terminal aryl alkynes and hindered by large stoichiometry and a limited scope of organoboranes.



Scheme 5: Copper catalysed synthesis of acrylic acids. IPr= 1,3-bis-(2,6-diisopropylphenyl)-imidazol2-ylidene

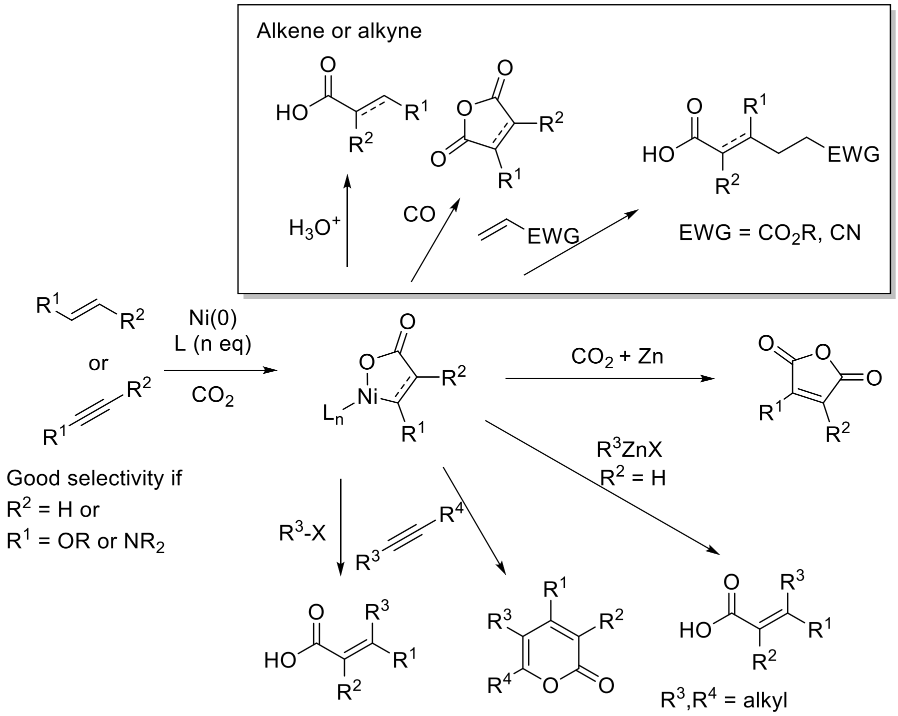
Using alkyl aluminum or zinc reagents, the alkyl could be added across the alkyne (Scheme 6).[24] With aluminum reagents, higher yields were achieved than with borane, but the vinyl aluminium reagent had to be prepared before adding CO_2 to avoid CO_2 reacting directly with the alkyl aluminium (Scheme 6, top). Aluminium aryl compounds could also be carboxylated in the same conditions (Scheme 6, middle).[25] Dialkyl zinc reagents were stable under CO_2, but the addition of Cu-alkyl to the alkyne only provided good results with polarized ynamides (Scheme 6, bottom).

Another common reaction between unsaturated compounds, transition metals and CO_2 is the formation of metallalactones. Nickellactone was one of the first well studied metallalactones (Scheme 7).[26] While nickelalactone is quite stable, various reagents can be inserted to it, to yield difunctionalized compounds. Analogous reactivity is known for Zr[27] Co[28], Fe[29], Ti[30]. Metallalactones can be formed from alkenes, allenes and alkynes, but the alkyne variant is generally the most susceptible to insertion reactions.



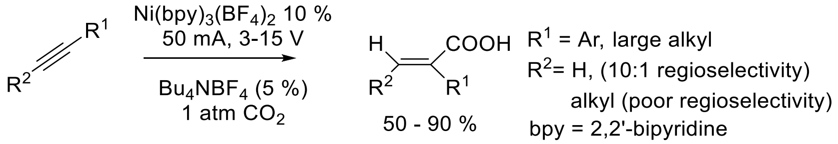
Scheme 6: Copper catalysed carboxylation of vinyl metalates derived from alkynes. dppp=1,2-Bis(diphenylphosphino)propane, TMP = tetramethylpiperidine, IPr= 1,3-bis-(2,6-diisopropylphenyl)-imidazol2-ylidene

In these reactions, the metal ends up in a stable complex that is unable to go through reductive elimination, which would regenerate the active species, and therefore these reactions are stoichiometric. To overcome this, an additional reductant can be used to reduce the metal and achieve catalytic activity. The first example of catalysis was made by using electrochemical reduction (Scheme 8).[31] Good to moderate yields could be obtained, and with terminal alkynes high regioselectivity towards branched carboxylation was obtained. The problems with electrochemical approaches are poor functional group tolerance, low regioselectivity without a polarized substrate, and the small details in reaction set-up causing high variance in results.

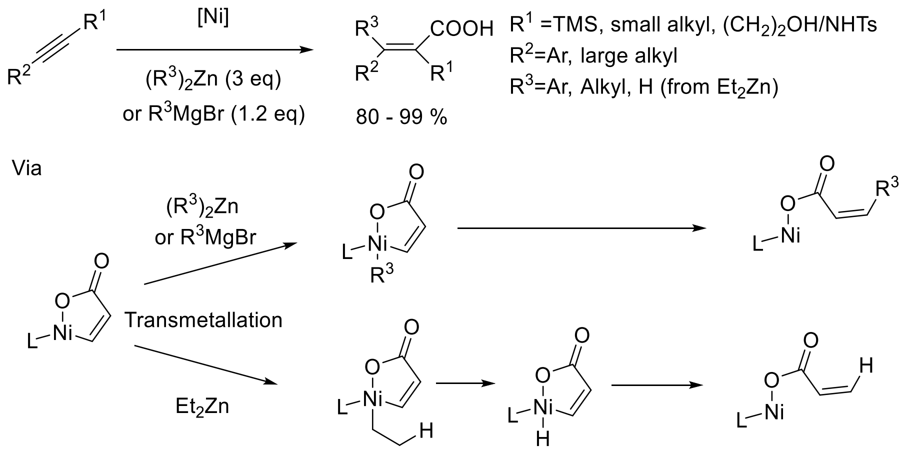


Scheme 7: Reactions of nickelactone derived from either alkene or alkyne.

Thermal catalysis could first be achieved with an organozinc or an aryl Grignard reagent and a nickel catalyst. High yield and selectivity could be obtained to form highly substituted acrylic acids. The carboxylation took place selectively at the less hindered carbon or it could be directed by TMS, pendant OH, or NHTs group (Scheme 9). [26d, 32] The organometal reagent inserted on the same side as the carboxylic acid via reductive elimination. Complete stereoselectivity is achieved due to the nickelalactone intermediate. Interestingly, when diethyl zinc was used, a β-hydride elimination occurred instead of direct reductive elimination, and the hydride was added to the product.[32c] Dienes and allenes also react analogously.[33]

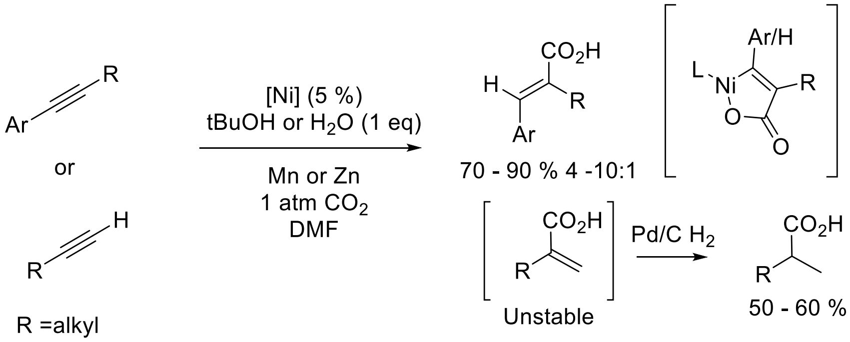


Scheme 8: Electroreductive carboxylation of alkynes.



Scheme 9: Catalytic alkyne carboxylation. L= ligand, TMS = trimethylsilyl, Ts = p-toluenesulfonyl

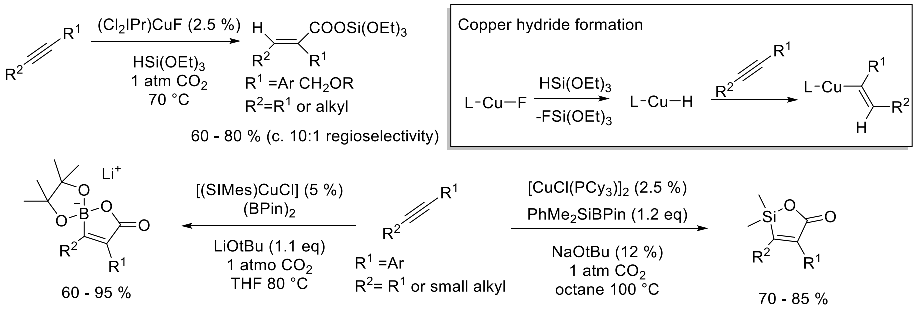
Instead of Et_2Zn, different hydride sources could be used. Nickel catalyst with Mn or Zn reductant with alcohol or water as proton source could form substituted acrylic acids from alkynes and ynamides, with the same regioselectivity as Et_2Zn (Scheme 10).[34] Terminal alkynes, again, provided branched carboxylic acids.[35]



Scheme 10: Alkyne carboxylation with metallic reductant. Terminal alkyne or internal with R=Ar or alk [Ni] = $NiCl_2$bathocuproine. Internal with R= NR(EWG) [Ni] = $Ni(cod)_2$ + bipy.

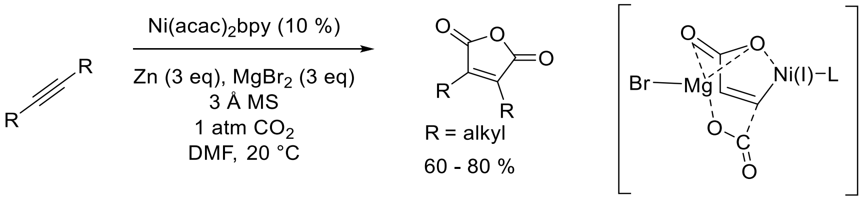
Other approaches to same transformation include Fe-catalyst with EtMgBr reductant and hydride source.[29] A cobalt catalyst could be reduced by metallic zinc, after forming the metallacycle with alkyne and CO2, to generate β-acrylic acid zinc reagents. [28] They could further react with strong electrophiles like H^+ or I_2, or be used *in situ* in Negishi type couplings.

Hydride addition could also be accomplished by using hydrosilanes as a hydride source instead of an air-sensitive Et_2Zn with nickel or copper catalyst (Scheme 11 top).[36] The copper catalyzed version was more regioselective when internal aryl alkynes were used, where carboxylation takes place next to the aryl group. This had the opposite regioselectivity to the nickel catalyzed carboxylation since the Cu catalyst did not form a metallalactone. With terminal alkynes, the Cu catalyst yielded linear products and the Ni-catalysed carboxylation yielded branched products. Alternatively, when (BPin)$_2$ (pin =pinacol) or PhMe$_2$SiBPin was used instead of a hydride, the β-carbon could be borylated or silylated (Scheme 11, bottom).[37] These reactions proceeded through formation of Cu-BPin or CuSiPhMe$_2$ species.



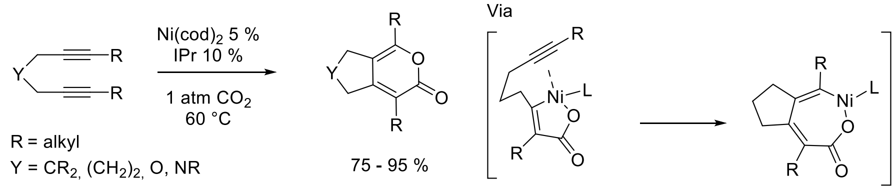
Scheme 11: Copper catalysed carboxylation of internal alkynes with hydrosilanes. Cl2IPr =4,5-dichloro, 1,3-bis-(2,6-diisopropylphenyl)-imidazol2-ylidene SIMes = 1,3-Bis(2,4,6-trimethylphenyl) imidazoline-2-ylidene PCy3 = tricyclohexylphosphine, (BPin)$_2$ = bispinacolatodiboron

Doublecarboxylation of an alkyne could also be made catalytic with a simple Ni(acac)2bpy catalyst with a Zn reductant and MgBr$_2$ additive (Scheme 12).[38] DFT studies showed that MgBr$_2$ facilitated the reduction to Ni(I) and greatly reduced the energy barrier of the second carboxylation from 21.9 kcal/mol to just 5 kcal/mol. TMS allenes could also be catalytically doubly carboxylated.[39]



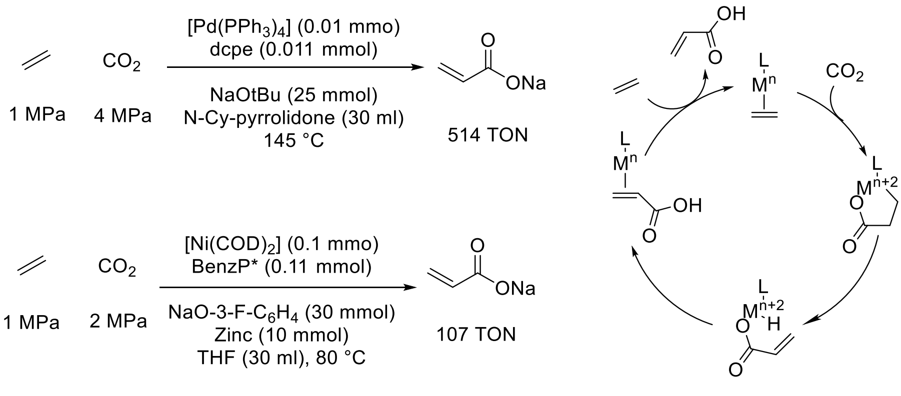
Scheme 12: Double carboxylation of alkynes. acac = acetylacetone, bpy = bipyridine, L=ligand

A catalytic variant was also developed for the addition of another alkyne to the nickelalactone for internal cycloaddition of dialkynes to form pyrones (Scheme 13). [40] Bulky substituents on both of R^3 stopped the reaction, but if only one substituent was sterically hindered, the carboxylation preferred the less hindered alkyne. Some intermolecular reactions could also be catalytic but provided very low yields. [41]



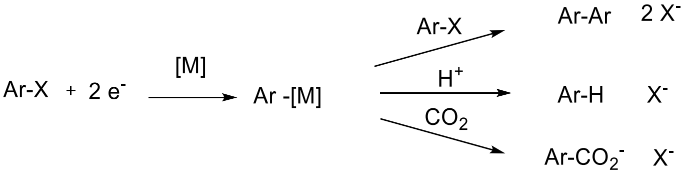
Scheme 13: Nickel catalysed [2+2+2]-cycloaddition of internal diyne and carbon dioxide. cod = cyclooctadiene, IPr = 1,3-bis-(2,6-diisopropylphenyl)-imidazol2-ylidene

Acrylic acids could also be generated directly from alkenes and CO_2 in a redox neutral process (Scheme 14).[42] The reaction has three difficult steps to overcome: metallalactone formation, β-hydride elimination, and reductive elimination. DFT study with Ni(DBU)-complex calculated energy barriers to be 121.8 KJ/mol, 147.4 KJ/mol, and 104.1 KJ/mol, respectively, identifying the β-hydride elimination as the most difficult step.[43] Moreover, the reaction has positive enthalpy and, in standard conditions, a negative entropy term.[44] Extreme pressure or energetic additives are therefore needed to drive the reaction. The β-hydride elimination could be stoichiometrically induced by adding methylating reagent or strong Lewis acid $B(PhF_5)_3$.[45] Catalytic activity could be achieved by adding sodium alkoxide or phenoxide bases, or LiI with Et_3N.[46] These facilitated the β-hydride elimination by Na^+ or Li^+ coordinating to the carboxylate, which reduced the Ni-O bond strength and enabled the complex to adopt suitable conformation for β-hydride elimination. These also improved the enthalpy of the reaction by forming a more stable product, sodium ester and protonated alcohol or amine. Optimization has led to catalytic systems with Pd (up to 514 TON)[47], Ni (up to 107 TON)[48] and Rh (up to 16 TON)[49]. However, much better catalytic process would be needed for industrial implementation, preferably one that yields directly acrylic acid or an ester instead of a salt. Catalytic activity could also be obtained for primary alkenes and dienes with a turnover number of 10-100.[47-48, 50] In chemical yield, this translated to around 5-30%. These reactions did not reach full conversion since replacing the acrylate, with M-O coordination by an alkene is difficult.



Scheme 14: Catalytic cycle for acrylic acid formation from CO_2. dcpe= 1,2-Bis(dicyclohexylphosphino)ethane BenzP* = (R,R)-(+)-1,2-Bis(t-butylmethylphosphino)benzene

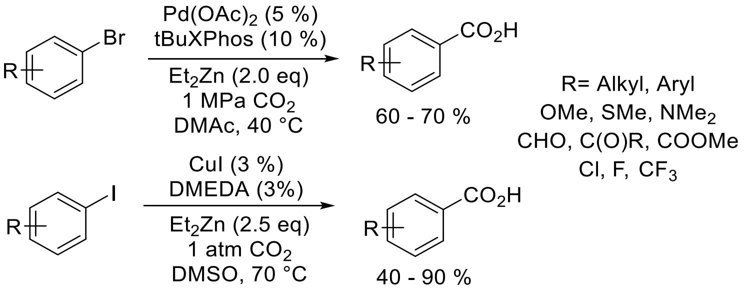
The aryl and vinyl organometallic that can be readily used in carboxylations, are often made from the corresponding (pseudo)halides. Therefore it would be attractive to directly carboxylate the (pseudo)halide, as they are readily available and can be stored for extended periods.[51] The electronegative halide induces a positive partial charge on carbon and since the CO_2 carbon is electrophilic, this would be a cross electrophile coupling and it would require a reducing agent to proceed.[52] Appropriate choice of reductant and catalyst is essential to avoid direct reduction of the (pseudo)halide or reductive homocoupling (Scheme 15).



Scheme 15: Cross electrophile coupling and side reactions. X = (Pseudo)halide, [M] = transition metal catalyst

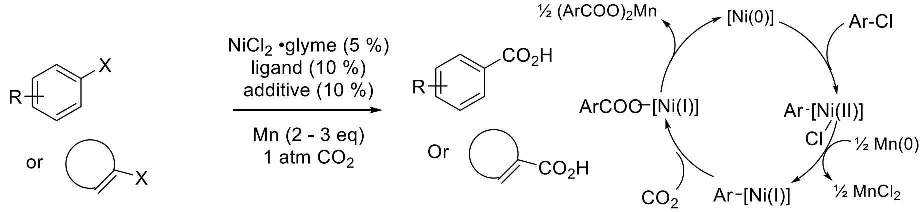
The first examples utilized electrochemistry to carboxylate aryl and vinyl bromides and iodides, with $NiCl_2$dppe (bis(diphenylphosphine)ethane) or $PdCl_2(PPh_3)_2$ or without a catalyst. [53] However, significant amounts of homocoupling and dehalogenation was observed.

Thermal carboxylation could be first achieved with a $Pd(OAc)_2$tBuXPhos catalyst and Et_2Zn reductant (Scheme 16).[54] Moderate yields could be obtained for electron-rich and -poor aryl bromides, but the reaction was hindered by 10 atm CO_2 pressure and use of pyrophoric reductant. Similar reactivity was also observed with CuI/DMEDA (dimethylethylenediamine) catalyst with aryl iodides, but this time 1 atm of CO_2 was enough for the conversion.[55]



Scheme 16: Early aryl halide carboxylations with diethyl zinc reductant. tBuXPhos = ditert-butyl (2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphane, DMAc = dimethylacetamide, DMEDA = dimethylethylenediamine

The reactivity was extended to aryl and vinyl chlorides, triflates, tosylates, fluorosulfates, esters, and sulfonium salts by nickel catalysts with phosphine or phenantroline ligands. (Scheme 17).[56] Additionally, pyrophoric Et_2Zn could be replaced by air-stable metallic Mn powder, which, as a milder reductant, also increases functional group tolerance. The Et_4NI additive was sometimes essential for any reactivity and was thought to assist the electron transfer from Mn to nickel complex. Mechanistic analysis showed that CO_2 can only insert in to $(PPh_3)_2Ni(I)$-Ar complex instead of $(PPh_3)_2Ni(II)$-ArX. However, with a bipyridine ligand, CO_2 insertion into Ni(II)-ArX has also been demonstrated.[15] The same reactivity was observed with CoI_2neocuproine catalyst with aryl triflates, but the cobalt catalyzed mechanism has been less studied.[57] Using a copper catalyst and Et_2Zn reductant, arylthianthrenes could also be carboxylated. [58]

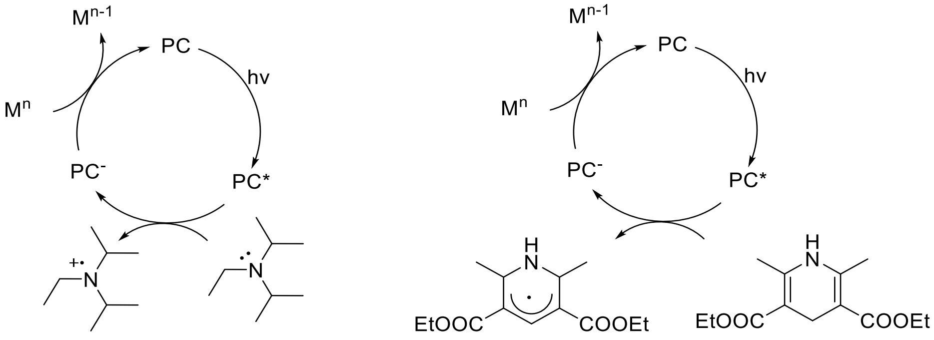


Ligand and additive for X

	X=Cl,Br,OTf	X = OTs	X = O_2CR	X=OSO_2F	X = SMe_2^+ OTf^-
Ligand	PPh_3	bpy	dppf	neocuproine	neocuproine
Other changes	Et_4NI additive	None	None	None	Zn instead of Mn
Typical yield	60 - 90 %	40 - 60 %	50 - 70 %	80 - 95 %	60 - 90 %

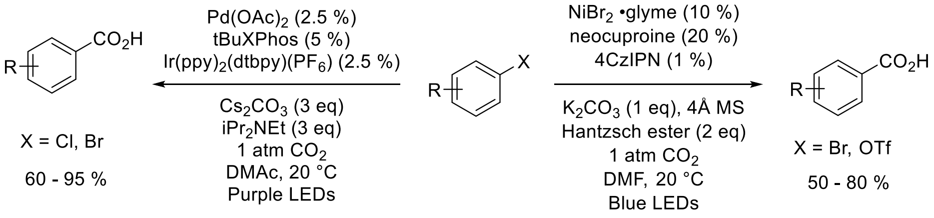
Scheme 17: Nickel catalysed carboxylation of aryl (pseudo)halides. bpy = 2,2'-bipyridine, dppf=bis(diphenylphosphine)ferrocene, neocuproine = 2,9-Dimethyl-1,10-phenanthroline

Alternatively, visible-light photoredox catalysis has become a powerful method to facilitate reduction in mild conditions using organic, soluble reductants (Scheme 18). [59] Commonly used reductants are tertiary amines and Hantzsch esters. Large variety of photocatalysts have been developed that span a wide range of reduction potentials.



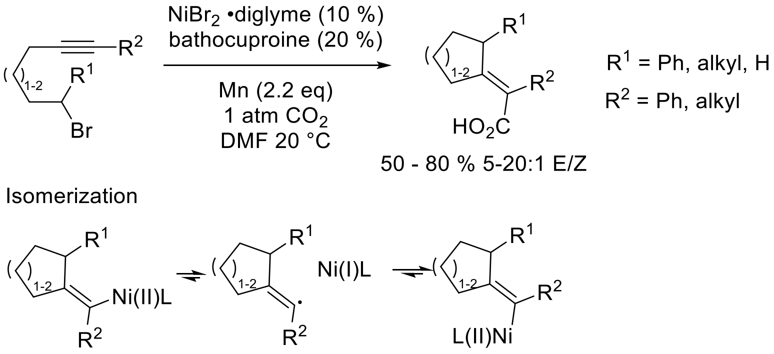
Scheme 18: Generic photoredox cycle for tertiary amine and Hanzstch ester.

Methods have been developed to combine photoredox catalysis with Pd and Ni catalyzed carboxylations (Scheme 19).[60] Pd-catalyzed carboxylation utilized iridium photocatalyst and tertiary amine reductant, whereas the Ni-catalyzed used organic photocatalyst 4CzIPN (1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-Tetrakis(9H-carbazol-9-yl) isophthalonitrile) and Hantzsch ester as reductant.



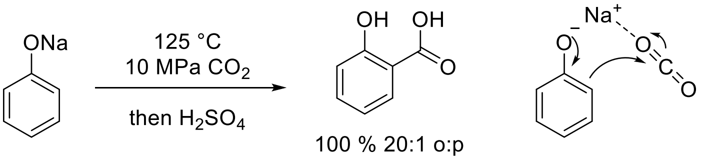
Scheme 19: Aryl halide carboxylation by photoredox catalysis merged with transition metal catalysis. tBuXPhos = ditert-butyl (2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphane, ppy = 2-phenylpyridine, dtbpy =4,4'-ditertbutyl-2,2'-bibyridine DMAc = dimethylacetamide

Cross electrophile coupling could also be adapted to the type of reaction where organometallic reagents are added across an internal alkynes. Intramolecular coupling of alkyl bromide to alkyne in reductive conditions , followed by carboxylation, yielded tetrasubstituted acrylic acids (Scheme 20).[61] Reaction stereochemistry was controlled by the steric bulk as the vinyl-nickel intermediate isomerized to the equilibrium product via reversible homolytic M-C dissociation.



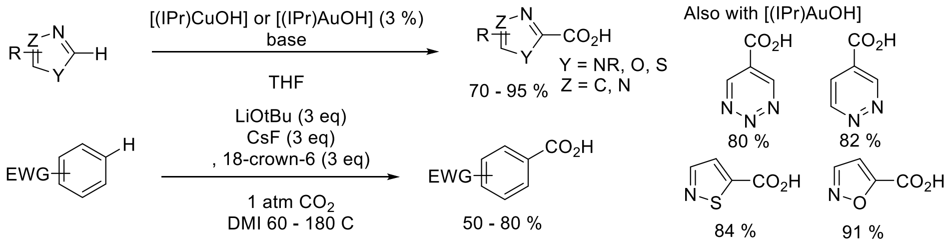
Scheme 20: Nickel catalysed alkyl bromide alkyne cascade carboxylation.

Even better than using (pseudo)halides, would be to directly activate the C-H bond in a redox neutral way. Well-known sp^2 C-H activation is the Kolbe-Smith reaction, which is used commercially to produce o-salicylic acid and other ortho and para amino and hydroxy acids.[62] The reaction is facilitated by the phenolate behaving like an enol, making the ortho and para carbons more nucleophilic. Sodium ion directed the carboxylation to ortho, whereas potassium or other metal salts produced a mixture of ortho and para carboxylation. Electron withdrawing substituents decreased the reactivity.



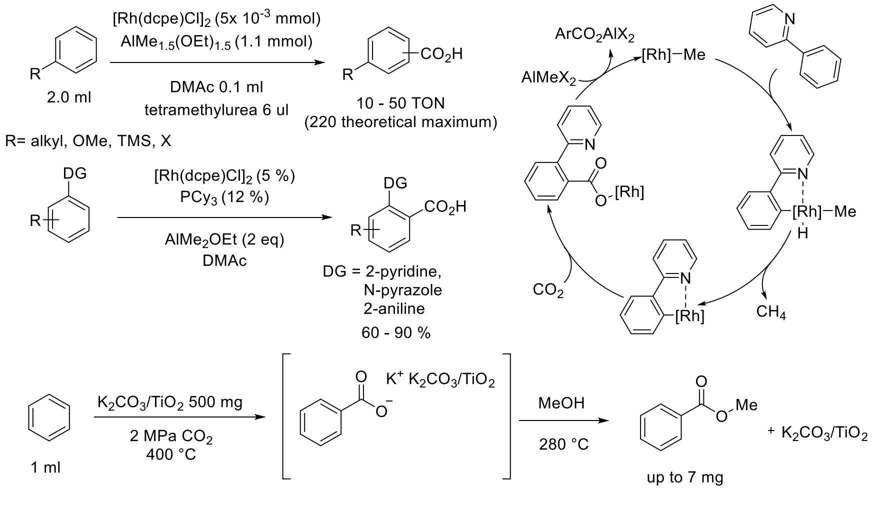
Scheme 21: Kolbe-Schmitt reaction.

Electron poor (hetero)aromatic compounds are mildly acidic (pKa≈25) and therefore moderately strong bases could be used to generate a suitable carbon nucleophile for carboxylation (Scheme 22).[63] 1,3 azoles are especially suitable for C2 carboxylation as the deprotonated intermediate is stabilised by the carbene tautomer. For more general reactivity with any electron poor aromatic, a mixture of LiOtBu, CsF and 18-crown-6 was found to be good combination of bases to enable deprotonation and carboxylation, though for very electron poor phenyls, weaker bases could be used.[64]



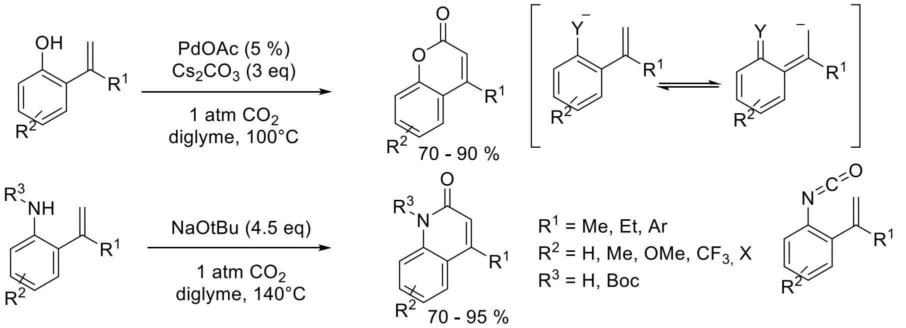
Scheme 22: Electron poor heteroaromatic C-H carboxylation. IPr =1,3-bis-(2,6-diisopropylphenyl)-imidazol2-ylidene, THF = tetrahydrofuran, DMI = 1,3-Dimethyl-2-imidazolidinone, EWG = electrom withdrawing group

Without electron withdrawing groups, the direct insertion of CO_2 into sp^2 C-H bond is thermodynamically uphill, like with the formation of acrylic acid.[65] For the reaction to work, a more stable product than a free acid needs to be formed.[66] With Rh catalyst, $AlMe_2(OEt)$ was used to propagate the reaction, where the activated C-H proton is released as methane and the aluminum salt binds strongly with the formed carbamate to release the Rh catalyst (Scheme 23).[67] The reaction could be performed with low yields and regioselectivity with simple substituted benzenes, but results were greatly improved if there was a directing group, that was able to coordinate to the catalyst, present in the structure (Scheme 23, middle).[68] Carboxylation of benzene could also be mediated by K_2CO_3/TiO_2 at 400 °C and 2 MPa CO_2 pressure, but it provided a very low yield (Scheme 23).[69] The reagent could be recycled by releasing the acid through esterification with methanol and high pressure distillation of all volatiles.



Scheme 23: Aromatic sp2 carboxylation. dcpe = 1,2-Bis(dicyclohexylphosphino)ethane, DMAc = dimethylacetamide,

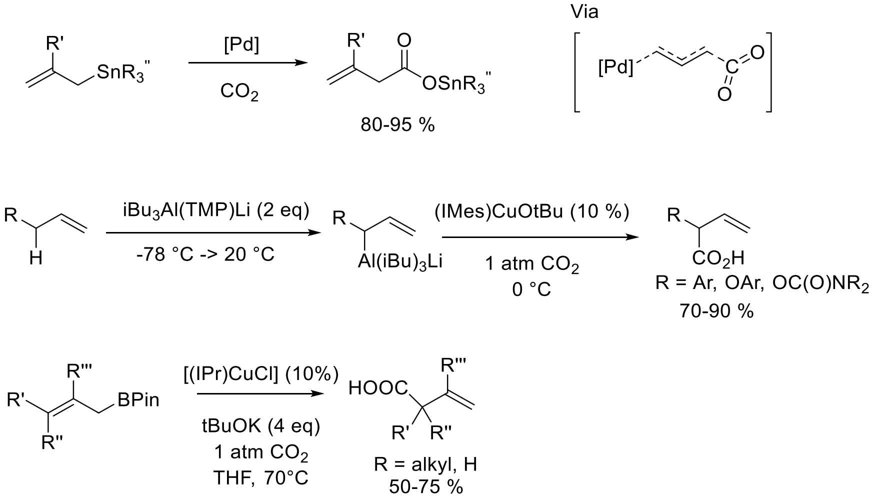
A special case of alkene sp^2 C-H activation was shown with o-hydroxy or amino styrenes to yield coumarins and quinolones (Scheme 24).[70] Like the Kolbe-Smith reaction, this reaction also takes advantage of tautomerization which increases the nucleophilicity of the terminal vinyl carbon. The coumarin synthesis required a $Pd(OAc)_2$ catalyst, but the quinolone only needed a base as the reaction proceeds through the formation of an isocyanate. For quinolone synthesis, the alkene could also be a part of another aromatic ring.



Scheme 24: Coumarin and quinolone synthesis with carbon dioxide.

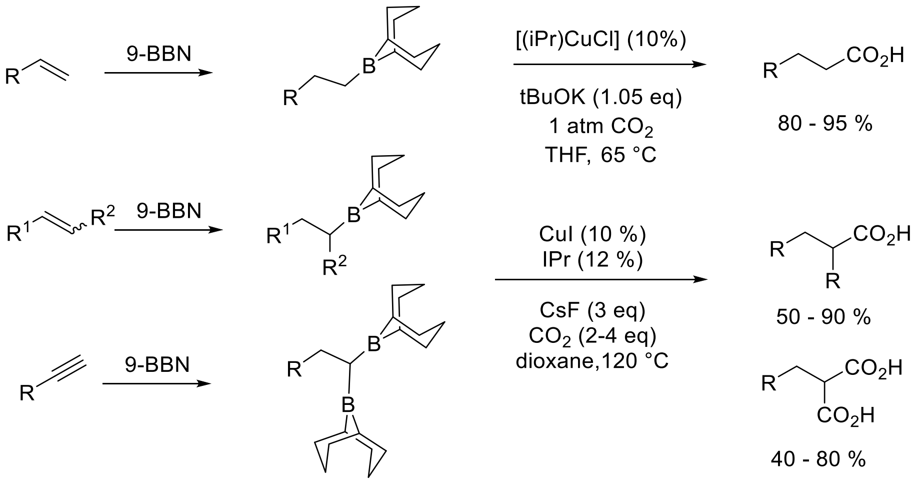
3.1.3 SATURATED CARBOXYLIX ACIDS

As with sp^2, sp^3 carbons can be carboxylated directly by forming an organolithium or magnesium reagent or catalytically by using organostannate, -aluminium, -boronate, and zinc reagents, but β-hydride elimination was initially a major difficulty. Allylic stannate, boronate and aluminum substrates form a stabilized η^3-allyl complex with the transition metal catalyst, and β-hydride elimination cannot happen. Therefore, these initial studies were made with these substrates (Scheme 25). [71] The carboxylation proceeds through a η^1-allyl intermediate via an outer-sphere mechanism where the metal coordinates to the less hindered carbon and carboxylation takes place on the more hindered side. [71e, f, 72]



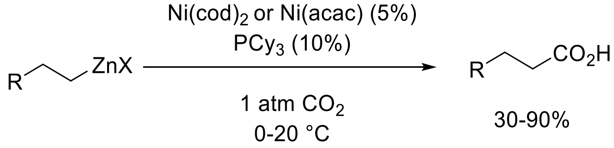
Scheme 25: Allylic carboxylation. IMes = 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium ylidine, IPr = 1,3-Bis-(2,6-diisopropylphenyl)imidazolinium ylidine

When organoborane 9-BBN (9-Borabicyclo[3.3.1]nonane) and a Cu/NHC (N-heterocyclic carbene) catalyst were used, the reaction could be extended to non-allylic compounds without significant β-hydride elimination (Scheme 26).[73] The 9-BBN substrate could be conveniently produced by hydroboration of alkenes without intermediate purification. By changing the alkoxy base to CsF, the procedure could be further extended to the carboxylation of secondary alkyls and the double carboxylation of 1,1 di-9-BBN, derived from alkynes.[74] CsF is thought to aid in removing the carboxylic acid from the copper by transmetallation, and the generated Cu-F facilitates the transmetallation with the alkyl borane.



Scheme 26: Copper catalysed carboxylations of unactivated alkanes. 9-BBN = 9-borabicyclo[3.3.1]nonane, IPr = 1,3-Bis-(2,6-diisopropylphenyl)imidazolinium ylidine, THF = tetrahydrofuran

Nickel catalysed method for alkyl zincs was also developed, but the β-hydride elimination caused significant issues with many substrates (Scheme 27).[75]

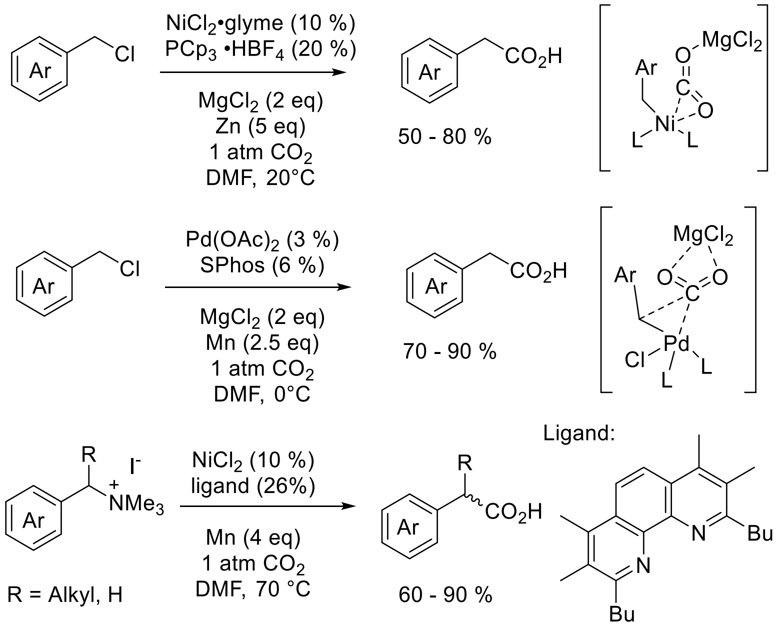


Scheme 27: Nickel catalysed carboxylation of alkyl zincs. cod = 1,5-cyclooctadiene, acac = acetylacetone, PCy_3 = tricyclohexylphosphine

Like with sp^2 carbons, cross electrophile carboxylation would be of interest since (pseudo)halides are better available and are more convenient to store and use. However, sp^3 cross electrophile coupling is especially difficult.[76] Both oxidative addition and reductive elimination is slower with sp^3 than with sp^2 since partial charges in transition states are not stabilized by the π-bonds. Additionally, β-Hydride elimination, hydride shifts, and single electron transfer reactions result in unproductive reactions or deactivation of the catalyst. To achieve good catalysis, the CO_2 must insert faster into the *in situ* formed metal-carbon bond, than these side reactions. The use of bulky ligands has generally been a good strategy for limiting common side reactions. Additionally, with sp^3 carbons it is often important that the chirality is not lost on the metalation step.

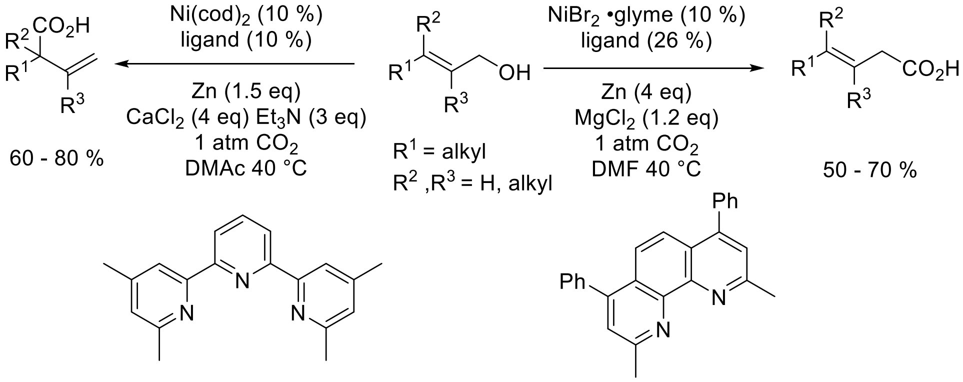
Many electrochemical methods have been developed for carboxylation of allylic and benzylic halides, esters, carbonates, and triflates since the reduction of the allyl anion can take place without a catalyst. [53e, 77] Even simple unactivated halides could be carboxylated.[78] However, the generated carbanions tend to be very reactive, and the scope and selectivity of the reaction has been limited. Catalysts have been developed to improve reactions, but the regioselectivity of allyls is still very poor with most substrates.[79]

Initially, alkyl halide carboxylation was developed for benzylic halides with Ni and Pd catalysts using zinc and manganese reductants (Scheme 28).[80] The use of electron-rich phosphines and $MgCl_2$-additive was found to be important. DFT studies identified that the $MgCl_2$ can facilitate the single electron reduction of the Ni(II)-complex and also the insertion of CO_2 into Ni(I)-Ar bond.[81] With secondary benzyl amines, racemization occurred, and when applicable, β-hydride elimination was also a significant problem. Using benzylic tertiary alkyl ammonium salt instead of halide, greatly reduced the β-hydride elimination and increased the substrate scope to alkyl substituted benzylic compounds.[82] Benzylic carboxylation could also be extended to comparably unreactive benzylic esters.[56c]



Scheme 28:Benzylic (pseudo)halide carboxylation with nickel or palladium catalyst. Electron poor and rich aryls were tolerated. PCp_3 = tricyclopentylphosphine, SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl, DMF = dimethylformamide

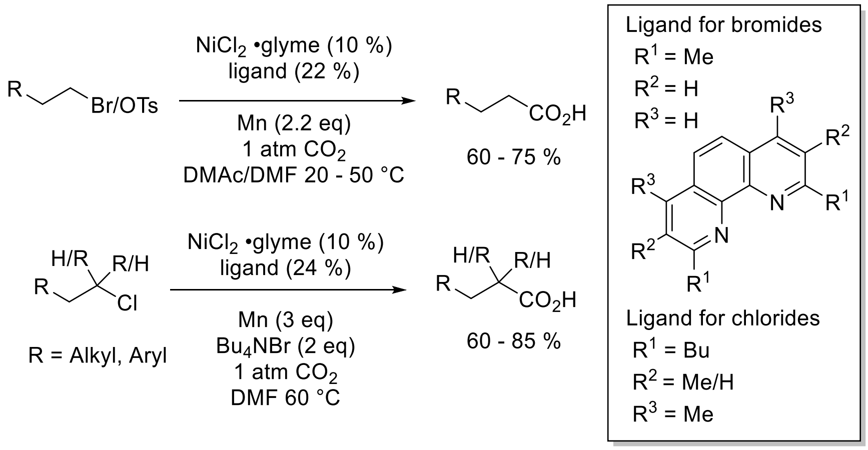
The reaction could be further developed to allylic esters[83] and even to alcohols (Scheme 29).[84]When the allyl contained a terminal carbon, divergent regioselectivity could be obtained with different ligands, neocuproines preferred a linear product, while terpyridines preferred a branched product. Propargylic alcohols were reduced under these conditions to yield allylic carboxylates. However, with a CoI_2Phenenatroline catalyst, this overreduction could be managed. [85] Mechanistic studies showed that the alcohol formed a carbonate intermediate in presence of water, which weakened the C-O bond of the alcohol.[86] This effect could be utilized more generally in allylic alcohol substitution reactions.[87] A photoredox-nickel catalyzed variant has also been developed for allylic and benzylic esters and alcohols, which provided slightly lower yields.[88]



Scheme 29: Regiodivergent carboxylation of allyl alcohols. cod = 1,5-cyclooctadiene, DMAc = dimethylacetamide, DMF = dimethylformamide

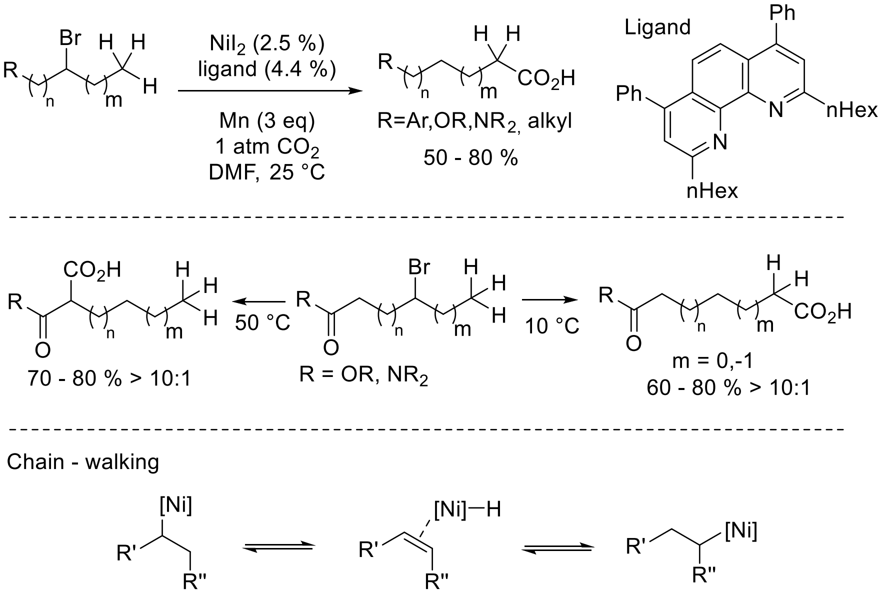
Direct benzyl alcohol activation is more difficult with a metal catalyst than with allyl alcohol activation, as the formed η^3- complex is less stable due to reduced aromaticity. The use of a photoredox catalyst and $NaBPh_4$ as an oxygen abstractor, enabled the carboxylation of benzylic alcohols by forming benzylic radicals, which were converted to benzyl anions by the photoredox catalyst.[89]

To generalize alkyl halide carboxylation to unactivated and β-hydrogen containing alkyls, a 2,9 dialkyl substituted 1,10 phenantroline ligand with Ni was developed (Scheme 30).[90] The increased bulk near the catalytic site was thought to slow β-hydride elimination enough for CO_2 insertion to become the main reaction path. First, the reaction was developed for primary bromides and tosylates, and was later adapted to primary, secondary and tertiary chlorides.[61b] Interestingly, though the systems are very similar, the chloride variant did not work with bromides and iodides but leads to almost exclusively β-hydride elimination.



Scheme 30: Nickel catalysed unactivated alkyl halide carboxylation. DMAc = dimethylacetamide, DMF = dimethylformamide

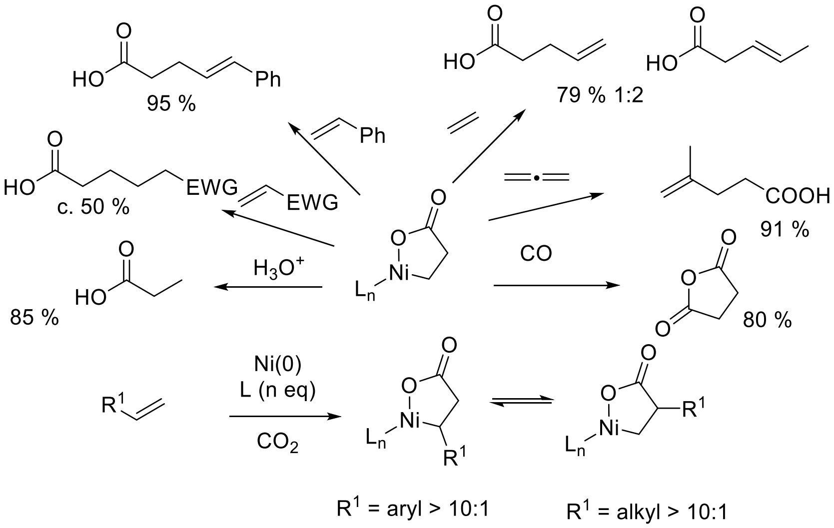
An adaptation of alkyl bromide carboxylation takes advantage of β-hydride elimination to convert secondary alkyl bromides to distal carboxylic acids through a chain-walking process (Scheme 31).[91] There, the nickel inserts into the alkyl bromide, β-hydride elimination forms an olefin and a nickel hydride, which can reinsert into the neighboring carbon. If these steps are much faster than the carboxylation, then the Ni-C equilibriates to the most stable position. Either a primary carbon because of steric effects or next to a stabilizing group due to an electronic or coordinating effect. If there were multiple stabilized sites, kinetic or thermodynamic selectivity could be obtained if the bromide was on or next to the less stable site. Remarkably, chiral stereocenters are often retained during chain walking if the metal olefin is not broken.[92] This type of reactivity can be especially useful in convergent synthesis with different regioisomeric substrates.[93]



Scheme 31: Nickel catalysed remote carboxylation of alkyl bromides. DMF = dimethylformamide

Alkenes react similarly to alkynes in carboxylation reactions but are less reactive. Initial investigations on alkene carboxylations were based on nickelalactone intermediates. H^+, CO, allenes, and alkenes could be inserted into the nickelalactone made from ethylene and CO_2 (Scheme 32 top).[26a, 94] With primary olefins, the regioselectivity was controlled by the substrates (Scheme 32, bottom).[42b, 95] Styrenes were carboxylated from terminal carbon, whereas alkyl olefins were carboxylated from the internal carbon.

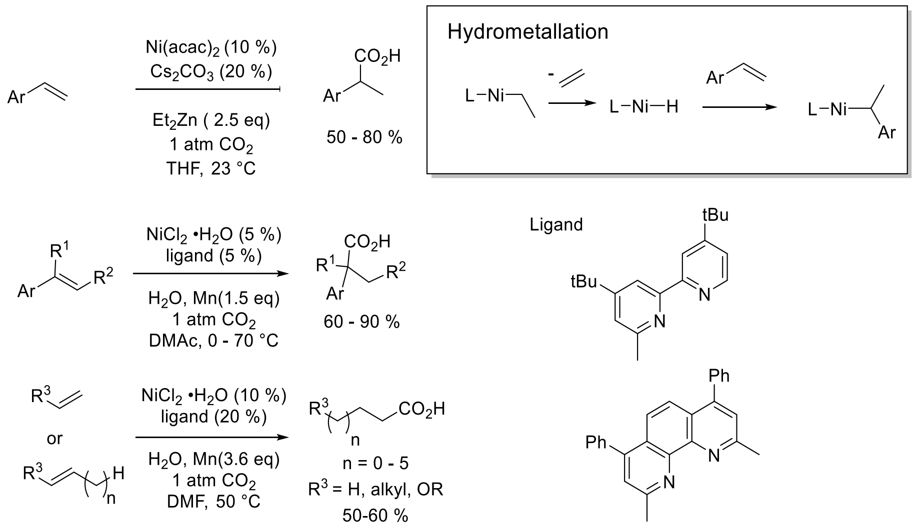
Zr(II), Ti(II) and Fe(0) have been also known to form metallalactones with alkenes and CO_2.[96] These tended to be more reactive towards various insertions but also formed more stable products after insertion, which has limited their catalytic applications compared to nickel. For example, $Fe(0)(PEt_3)_2(C_2H_4)$ complex was able to doubly carboxylate ethylene stoichiometrically.[96c] In publication I, we showed a method to generate titanium metallalactones from CO_2 and alkenes or Grignard reagents and inserted a benzaldehyde into the Ti-C bond.[97] Reaction that did not proceed with analogous nickel.



Scheme 32: Alkene generated nickelalactone reactivity.

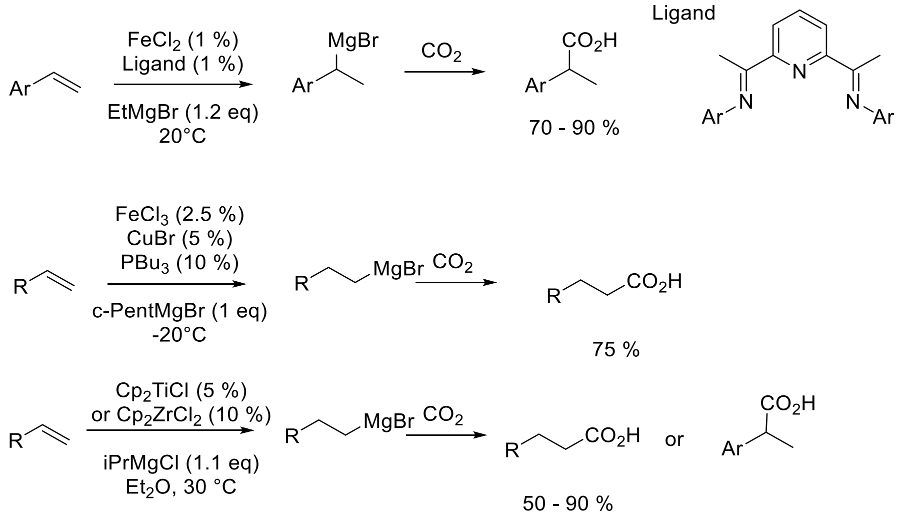
Like with alkynes, a catalytic system could be developed by using a reductant. For example, nickel could catalytically carboxylate styrenes to yield branched carboxylic acids (Scheme 33, top). [98] However, since the formation of the metallacycle is much slower with alkene than with alkyne, these reactions tended to go through a metal hydride intermediate instead of the metallalactone. This system could be adapted to alkyl alkenes and chain walking, using Mn as a reductant (Scheme 33, bottom).[35] Good regioselectivity was observed, where styrenes were carboxylated at the benzylic site and terminal alkenes were carboxylated on the terminal carbon. With chain walking, mixtures of alkene isomers could be used to yield only terminal product.

1,3-dienes and allenes could be analogously hydrocarboxylated or dihydrocarboxylated, and similar substrate- or ligand-dependent regioselectivities could be observed.[33a, 39, 99] They are more reactive substrates than alkenes, and there are many early examples of their reactivity with CO_2 .[100] Early examples had problems with dimerization (specifically telomerization) of dienes and allenes and with regioselectivity (1,4 vs 1,2 and which side reacts), but with suitable ligands, high selectivity could be obtained.



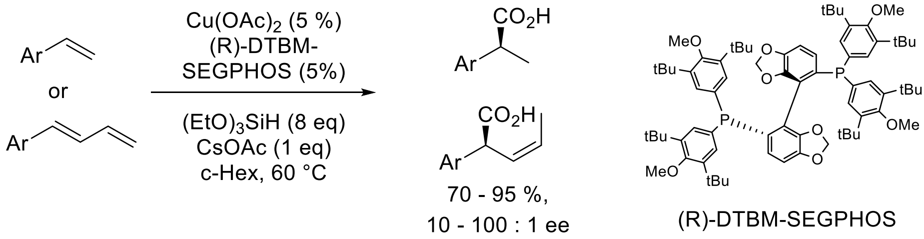
Scheme 33: Carboxylation of alkenes with in-situ generate nickel hydride. acac = acetylacetone, DMAc = dimethylacetamide, DMF = dimethylformamide

Other metalhydrides than Ni-H could also be used. Fe-H could be generated from an iron catalyst and an ethyl or secondary Grignard reagent, which could be used to make Grignard reagents from alkenes (Scheme 34, top).[101] Electron rich styrenes and primary alkyl alkenes could be used, which formed either benzylic or primary Grignard reagents. Since the hydride-forming Grignard reagent also reacted with CO_2, CO_2 must be added after the reaction. Additionally, the same selectivity and scope limitations exist as did for the direct use of Grignard reagents. Similar reactivity was also observed for Ti and Zr (Scheme 34, bottom).[30b, 102]



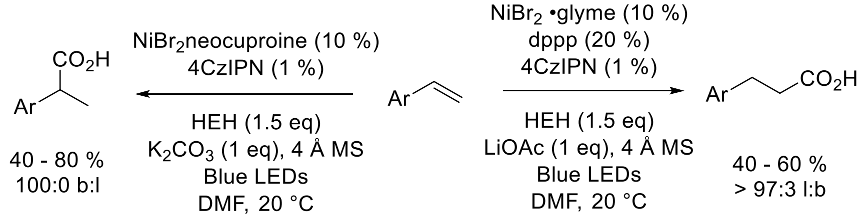
Scheme 34: Carboxylation of styrenes via Grignard reagent made by hydrometallation

Cu-H could be generated using silanes. With a chiral ligand, styrenes and dienes could be enantioselectively carboxylated and further reduced to the corresponding alcohol, to yield hydroxymethylated products (Scheme 35).[103]High regioselectivity to benzylic carboxylation was observed, dienes provided almost exclusively the Z-isomer and the enantioselectivity ranged from good to excellent (90:10 to 99.5:0.5 er).



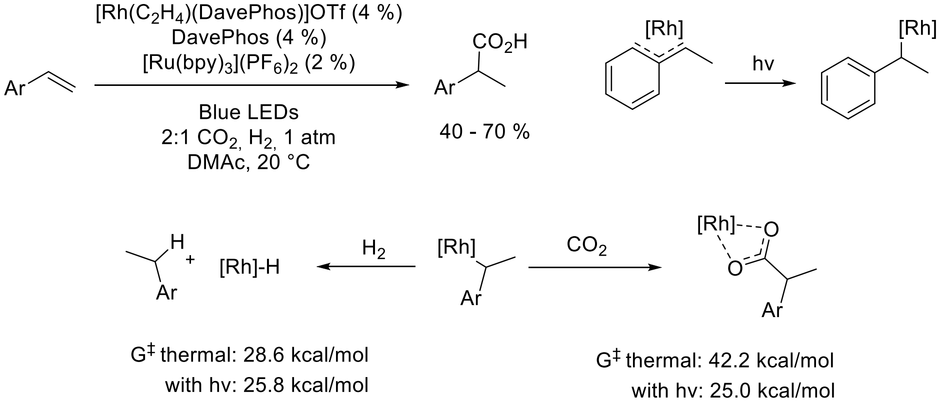
Scheme 35: Enantioselective copper catalysed hydroxymethylation with CO_2.

Photoredox catalysis could also be used to generate the metal hydride. Photocatalyzed variant was developed for nickel catalyst with Hanzsch ester reductant, where regioselectivity could be managed by a ligand (Scheme 36).[104] With the neocuproine ligand, a standard selectivity to benzylic carbon was observed, whereas with the phosphine ligand dppp, selectivity to the terminal carbon was observed.



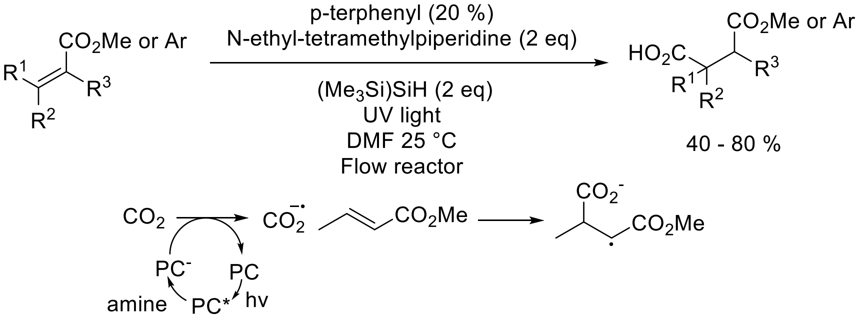
Scheme 36: Ligand controlled carboxylation of styrenes. 4CzIPN = 2,4,5,6-tetracarbazole-isophtalonitrile , HEH = Hanzscht ester, dppp = 1,2-Bis(diphenylphosphino)propane

With photocatalysis, rhodium catalyzed styrene carboxylations could also be developed.[105] While this provided lower yields than the Ni catalyzed reaction, it could use H_2 as a hydrogen source in addition to the commonly used organic reductants (Scheme 37).[106] The reaction also did not use any bases; therefore, the acid was generated directly. This eliminated the generation of salt waste on work-up, which is very important to industrial implementation. The challenge for this reaction was how to selectively carboxylate over direct hydrogenation, since Rh has been known to be a very active hydrogenation catalyst for alkenes. The photocatalyst could excite the Rh-η^3-benzylic complex to a destabilized η^1-complex. The excited state complex was more reactive to both carboxylation and hydrogenation, but the effect on carboxylation was much larger, leading to selectivity (Scheme 37, bottom).



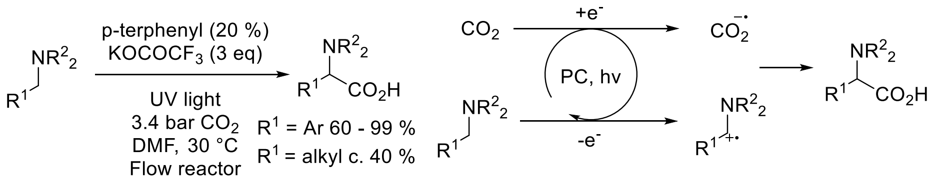
Scheme 37: Rhodium catalysed carboxylation of styrenes using hydrogen. DMAc = dimethylacetamide

With photocatalysis using uv-light, single electron reduction of CO_2 could be achieved. The CO_2^- radical could react with radical acceptors such as styrene or α,β-unsaturated esters in flow reactor (Scheme 38).[107] While tertiary amine radicals can usually act as hydrogen atom donors, the addition of water or silane as additional donors, greatly improved the yield, through faster quenching of the radical intermediate avoiding side reactions.



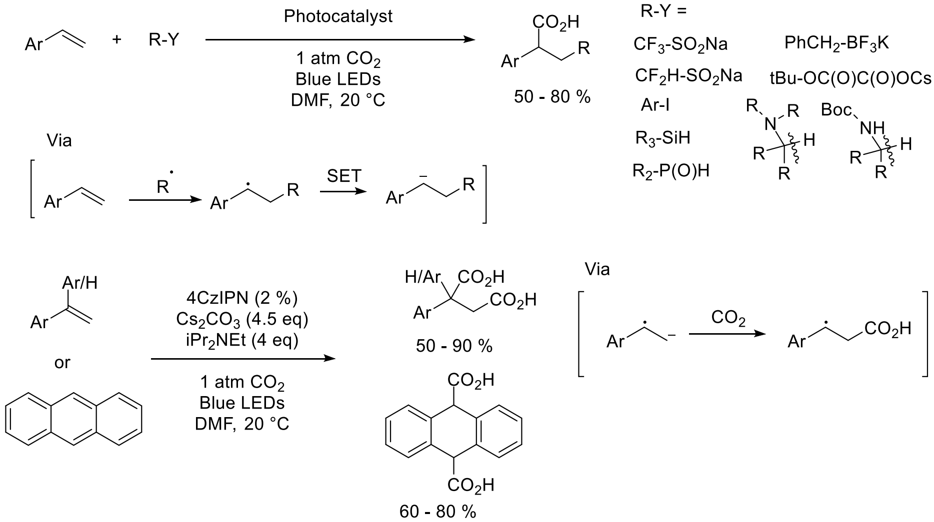
Scheme 38: CO_2 radical generation and reaction with α,β-unsaturated esters and styrenes. DMF = dimethylformamide.

The CO_2^- radical could also react directly with another radical generated from an amine to yield amino acids (Scheme 39).[108] The main challenge was generating the α-amino radical regioselectively, which was achieved by filtering out the highest energy light of <280 nm. α-Aryl substituted products could be generated with excellent yields, since the benzylic carbon is more susceptible to oxidation, while only alkyl substituted substrates lead to mixtures of products.



Scheme 39: Photocatalysed formation of amino acids from CO_2 and tertiary amines. DMF = dimethylformamide

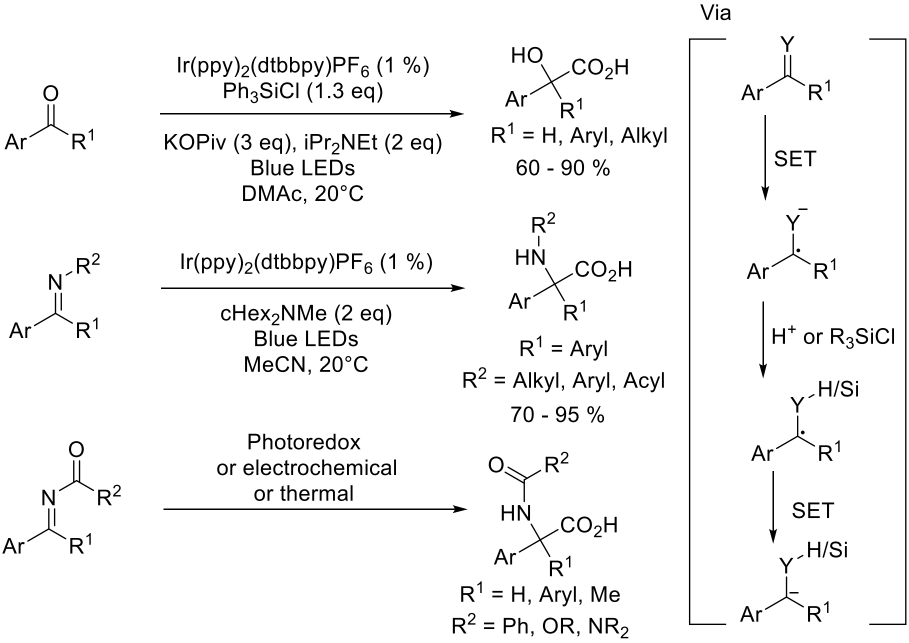
Variety of sources exist for photochemical radical generation and these could react with alkenes, resulting in an alkyl radical (Scheme 40, top).[109] The alkyl radical could be further reduced to a nucleophilic anion that could react with CO_2. With these methods difunctionalised compounds could be made from alkenes. Radical sources included sulfinates, trifluoroboraniums, carbamate anhydrides, aryl iodides, silanes, phosphinates and α-amines. Since CO_2 radical is not generated, the conditions are more chemoselective, which enabled a wider scope. With a strongly reducing photocatalyst 4CzIPN, styrenes, allenes and anthracenes could be reduced directly to radical anions which would react twice with CO_2 (Scheme 40, bottom).[110]



Scheme 40: Photocatalysed carbocarboxylation with various radical sources. 4CzIPN = 2,4,5,6-tetracarbazole-isophtalonitrile

Only limited examples of thermal alkene difunctionalization exist. Cu-catalyst using $(BPin)_2$, could form a Cu-BPin intermediate which could borocarboxylate styrenes under CO_2 analogously to the alkyne variant (Scheme 11).[111] Intramolecular cyclisation reactions could facilitate difunctionalisation, where alkene is inserted to the R-[M] bond and is subsequently carboxylated. [112] 5 and 6 membered rings could be created with Pd and Ni catalysts.

Imines, ketones, and aldehydes have δ^+ polarity on carbon and cannot react with CO_2 directly to form C-C bonds. However, several umpolung methods have emerged for the synthesis of hydroxy and amino acids. Aldehyde umpolung could be achieved by traditional cyanide- and base-mediated mechanisms by using $Ti(OiPr)_4$ as Lewis acidic additive.[113] Imines and ketones could be carboxylated in reductive conditions.[114] Two single electron transfers generate an anion on the carbon, which reacts with CO_2. Benzyl hydrazones could also be carboxylated with a ruthenium catalyst yielding phenyl acetic acids, where the hydrazine acts as a reductant by forming nitrogen gas.[115]



Scheme 41: Reductive carboxylation of carbonyls and imines. ppy = 2-2phenylpyridine, dtbbpy = 4,4′-Di-tert-butyl-2,2′-dipyridyl, DMac = dimethylformamide

Direct C-H activation of alkane would be very desirable, however Sp^3 C-H activation is very challenging since they lack p orbitals that would interact with a metal. General strategies for activation include use of directing groups, targeting C-H bonds polarized by nearby functional groups or homolytic cleave of C-H bond for example by energetic light, but so far, these only work with very specific substrates.

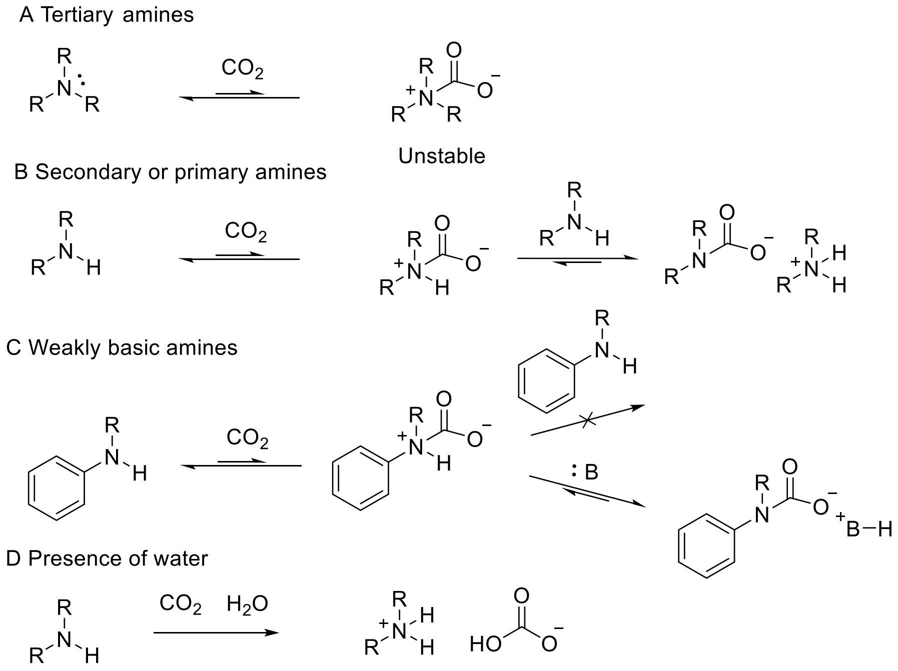
Base promoted approach to benzylic C-H carboxylation was achieved using combination of bases LiOtBu/CsF/18-crown-6.[116] The method required an electron withdrawing or π conjugated para substituent to stabilise the negative charge of deprotonation. Yields were between 60 and 90 %, depending on the degree of substituent stabilisation.

Benzylic and allylic bonds are especially susceptible to hydrogen atom transfer reactions. UV light mediated method catalysed by a ketone hydrogen atom transfer mediator and a visible light method with thiol catalyst were developed for carboxylation.[117] [118] The UV light methods also carboxylated unactivated sp^3 C-H bonds, but without selectivity.

Thermally, allylic C-H bonds could be activated also by [CoXantphos] catalyst using $AlMe_3$ to drive the reaction by release of methane.[119] Reaction proceeds through a η^3 intermediate and the terminal carbon is carboxylated. The allylic C-H had to be further activated by a benzyl or another allyl group to form a conjugated π-system. 50-90 % yields could be achieved for variety of allyl arenes.

3.2 N-CARBOXYLATIONS

Carbon dioxide, as a Lewis acid, interacts readily with nucleophilic nitrogen compounds to form transient zwitterionic carbamate species, whose stability depends on the basicity of the nitrogen compound and other stabilizing interactions like hydrogen bonding (Scheme 42A). Secondary and primary amines have an N-H proton, which after carboxylation becomes more acidic. Deprotonation forms a carbamate anion, which greatly stabilizes the compound (Scheme 42B). Primary and secondary amines are basic enough that another equivalent can deprotonate the zwitterion; therefore, these compounds easily absorb CO_2, and the reaction is often very exothermic. With an additional non-nucleophilic base, all of the amine can be converted to a carbamate anion instead of using the additional equivalent for deprotonation. With a stronger base, less basic amines, like anilines and pyrroles, can also be converted to carbamate anions (Scheme 42C). If water is present, then the amine, as a stronger base, deprotonates the water and carbonates form instead (Scheme 42D). Also, the carbamate anions convert to carbonates in presence of water. Therefore, carbamate anions are not suitable chemical products by themselves, but they must be further converted to, for example, carbamates.



Scheme 42: Carbon dioxide reactivity with amines. Tertiary amines form unstable zwitterion. Secondary and primary amines can further react with another equivalent to form carbamate anion. Anilines are too weakly basic to deprotonate themselves and another strong base is needed. In presence of water ammonium carbonates form.

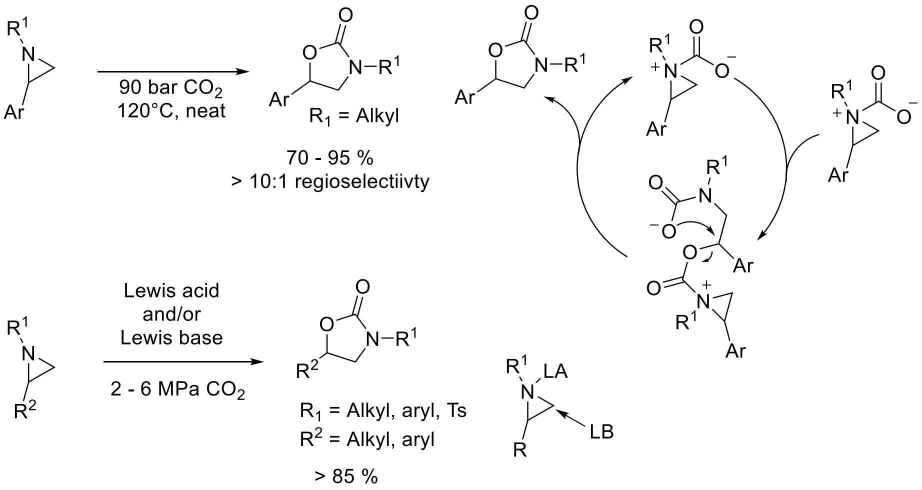
Carbamates are often found in pharmaceuticals and in agrochemicals.[120] Organic carbamates are usually produced using phosgene derivatives (eg. triphosgene, CDI), chloroformates or isocyanates. These are toxic reagents, therefore their replacement with non-toxic and abundant CO_2 desirable. CO_2 based carbamate synthesis can use two strategies, either utilize the nucleophilicity of the O-anion or the electrophilicity of the C-atom.

3.2.1 CYCLIC CARBAMATES

Ring formation of size less than 7 improves the kinetics of the reaction, and 5- and 6-membered rings are also thermodynamically more stable. Compared to linear carbamates, there are more methods for their synthesis, so they are covered first.

5-membered cyclic carbamates (oxazolidinones) can be synthesised using aziridines without any additives at 120°C and 90 bar CO_2 pressure.[121] The reaction is thought to be self-catalyzed by formation of zwitterion, which stabilizes the ring opening done by another equivalent of the zwitterion (Scheme 43). The reaction only works for 2-aryl aziridines with a more reactive benzylic carbon and the zwitterion generation requires very high pressures.

Catalytic methods use similar approaches, with a Lewis acid instead of CO_2 coordinating to the aziridine and a Lewis base that opens the aziridine ring but is also a good leaving group (Scheme 43, bottom). Metal complexes and organic hydrogen bonding catalysts have been used as Lewis acids.[122] Halides, N-heterocyclic carbenes, and carboxylic acids have been used as Lewis bases.[123] Without N-substitution, a bromide ion catalyst is enough for reaction to proceed in 1 atm CO_2 pressure.[123a] With N-substituents, high pressure is needed for ring activation by CO_2. With N-alkyl-2-aryl aziridines, using bromide ion source catalyst will yield >85% product with >20:1 regioselectivity at 60 bar CO_2 pressure and 100 °C, a modest improvement to the method without a catalyst.[124] Use of an additional Lewis acid catalyst has enabled dropping the pressure to 20 bars with identical results, and increased the scope to N-aryl and N-tosyl substrates.[122, 123c, 125] Metal salen, porphyrin, and aminoalkyldiphosphonate complexes have been successful here.

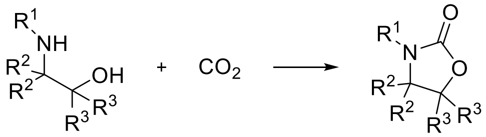


Scheme 43: Catalyst and additive free oxazolidinone synthesis with aziridines.

Amino alcohols are more attractive substrates than aziridines as they are less toxic, better available, and can be stored for longer. In the cyclic carbamate formation, water is removed. This can be done catalytically or by using a stoichiometric dehydrating reagent. Wider substrate scope and milder conditions have been achieved with a dehydrating reagent, while the catalytic methods avoid the stoichiometric waste of dehydrating reagent.

The catalytic methods were limited to simple amino alcohols. Very simple ethanolamine and 1,2 propanolamine can even be carboxylated without a catalyst (Table 1). The mechanism proceeded through acyl substitution, and one of the CO_2 oxygens is removed as water. A catalyst assisted removal of water by bonding to the leaving OH group and by hydrogen bonding the alcohol O-H to increase O nucleophilicity. [126] With catalytic methods, less CO_2 pressure and temperature were needed, and more substituents are tolerated on the amino carbon. However, nitrogen and alcohol carbon substituents are limited to small groups like linear alkyls chains.

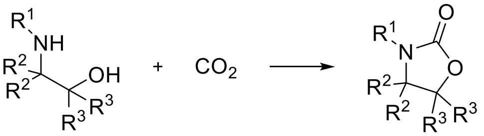
Table 1: Catalytic methods for oxazolidine synthesis from amino alcohols.



#	R^1	R^2	R^3	Catalyst	P (MPa)	T (°C)	Yield (%)	Ref
1	H	Me,H	H	none	6	150	97	127
2	Me	H,H	H	Cs_2CO_3 (15%)	0.3	160	70	128
3	H	Alk,H	H	Cs_2CO_3 (10%)	0.1	150	40-90	129
4	Alk	H,H	H,	np-CeO_2	0.7	160	60-70	130
5	H; Alk	1° Alk,H	1°Alk,H	np-CeO_2	5	150	>95	126
6	H	Alk/Ph,H	H	Ph_3SIF (10 %)	0.1	150	60-90	131
7	H/Alk	Alk/Ph,H	H	$(SnOBu_2Cl)_n$	1.7	150	50-60	132

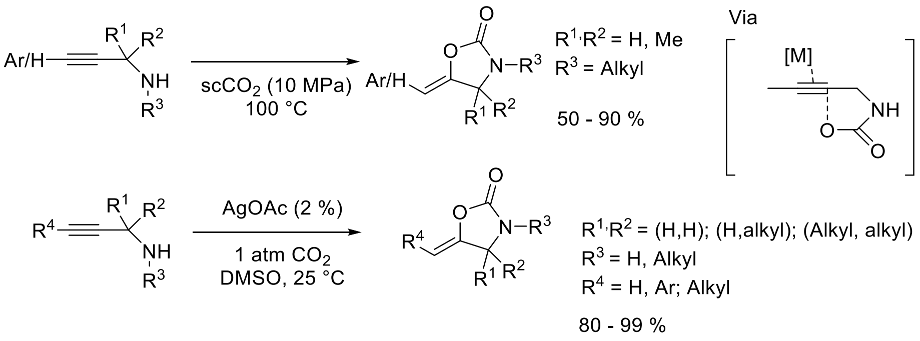
With dehydrating reagents, atmospheric pressure, a lower temperature and a wider range of substrates could be used. Many of these methods also worked for larger cycles and linear carbamates and ureas. Either the alcohol or CO_2 oxygen may be dehydrated, depending on the substrate and reagent used. If the alcohol was chiral, then either a retention or inversion could take place, but in many cases a mixture of both happened.[133] Mitsunobu conditions could be used to produce cyclic carbamates (Table 2, entries 1-3), where a phosphine reagent is converted to a pentavalent electrophilic phosphorus derivative. It could react with either the alcohol or the carbamate anion to convert the oxygen to a good leaving group. Inversion/retention could be modulated by a choice of phosphine and the activating reagent.[134] Inversion was heavily favoured by N-substituents. Use of aromatic phosphine with carbodiimide reagent DEAD (diethylazodicarboxylate) also favoured inversion. Using pyridine dithione reagent or azide reagent favoured retention. More straightforward generation of the leaving group could be done with eg., AcCl, p-TsCl or $SOCl_2$. From these, atleast $SOCl_2$ and TsCl caused inversion. In publication III, we studied weaker activating reagents to see if we could achieve CO_2 oxygen activation only and therefore retain stereochemistry. Of the studied reagents, BuCl provided the best results and only provided the retention product, but high temperatures had to be used. Overall, Mitsunobu conditions work well for non-N and N-alkyl substituted amino alcohols, and N-aryls can be done with TsCl. Some limitations still exist for bulky alcohol carbon substituents and the stereoselectivity of the alcohol carbon.

Table 2: Oxazolidine synthesis with dehydrating reagents Alk = alkyl, Ar = Aryl. DPPA = Diphenylphosphoryl azide, DPPCl = diphenylphosphinic chloride, DBAD = di-tert-butyl azodicarboxylate, DBU = 1,8-Diazabicyclo(5.4.0)undec-7-ene, TsCl = para-toluenesulfonic chloride



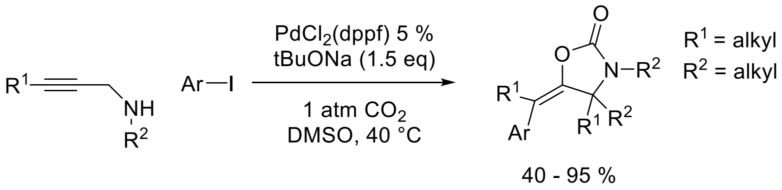
#	R1	R2	R3	Reagent	P (MPa)	T (°C)	Yield (%)	Ref
1	H or Alk	Alk	1° Alk or Ph	DPPA/DPPCl + Et_3N	0.1	-40	>75	135
2	H	Alk	1° Alk or Ph	AcCl + Et_3N	0.1	-40	>90	135a
3	H or Alk	Any	1° Alk or Ph	nBu_3P+DBAD + DBU	0.1	0	>80	133
4	H	Alk/ Ph, H	H	DCC	8.6	40	70- 95	136
5	Alk	H or Alk	H	$SOCl_2$	0.1	0	60	137, 135a
6	Ar	H	Alk	TsCl+ Cs_2CO_3	0.5	20	50-85	138
7	H	Alk or Ph	H or Ph	TsCl + Base	0.4	20	70- 90	139
8	Alk /Ar	Any	1° Alk or Ph	BuCl + Base	0.1	140	70-99	140

Cyclization can also proceed by the carbamate anion reacting with a carbon electrophile. Of this type, propargylic amines have been the most studied. This reaction could be done without a catalyst in supercritical CO_2 (Scheme 44 top). With a catalyst, the reaction proceeded at ambient pressure and temperature, with wider scope and higher yield. Metal catalysts such as Ag[141],Au,[142] Cd-MOF[143], Cu[144], Ni[145], Ru,[146] Pd[147], Zn[148] could polarize the triple bond, making it more susceptible to cyclization by the nucleophilic carbamate anion. For example, using 2 mol-% AgOAc in DMSO at room temperature at 1 atm pressure yields near quantitative yields of a wide variety of substrates (Scheme 44, bottom). The only limitation of this method was aryl amines, but for them a binuclear copper catalyst was successful (though with limited examples).[144b] With the Pd catalyzed methods larger rings can also be formed.[141a] Metal free catalysts consist of nBu_4F,[149] organic bases,[150] ionic liquids,[151] NHCs,[152] which work as Lewis bases and make the CO_2 more nucleophilic. These methods have been more limited in scope or have harsher conditions than the metal catalyzed methods.



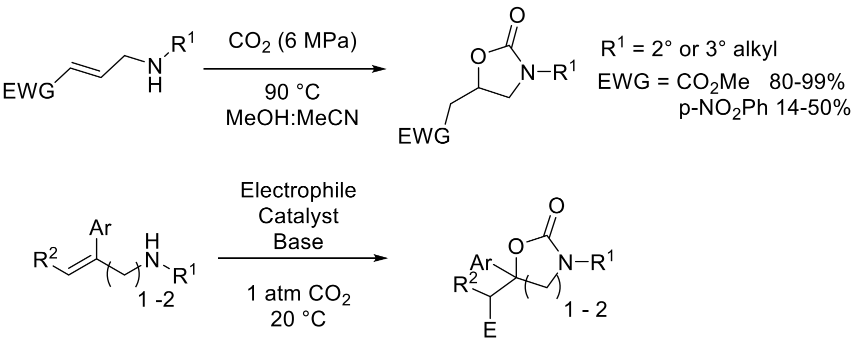
Scheme 44: Cyclication of propargyluic amines and CO_2.

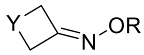
With a Pd catalyst, the reaction could also be accompanied by a cross-coupling to arylate the alkyne (Scheme 45).[153] Better results were obtained with electron poor arenes. Additionally, with terminal alkynes and the addition of CuI, a Sonogashira coupling could be done in one-pot to yield diarylated product. Analogous reactivity has been used for iodation and phosphonylation.[154]



Scheme 45: Propargyl amine carboxylation and arylation.

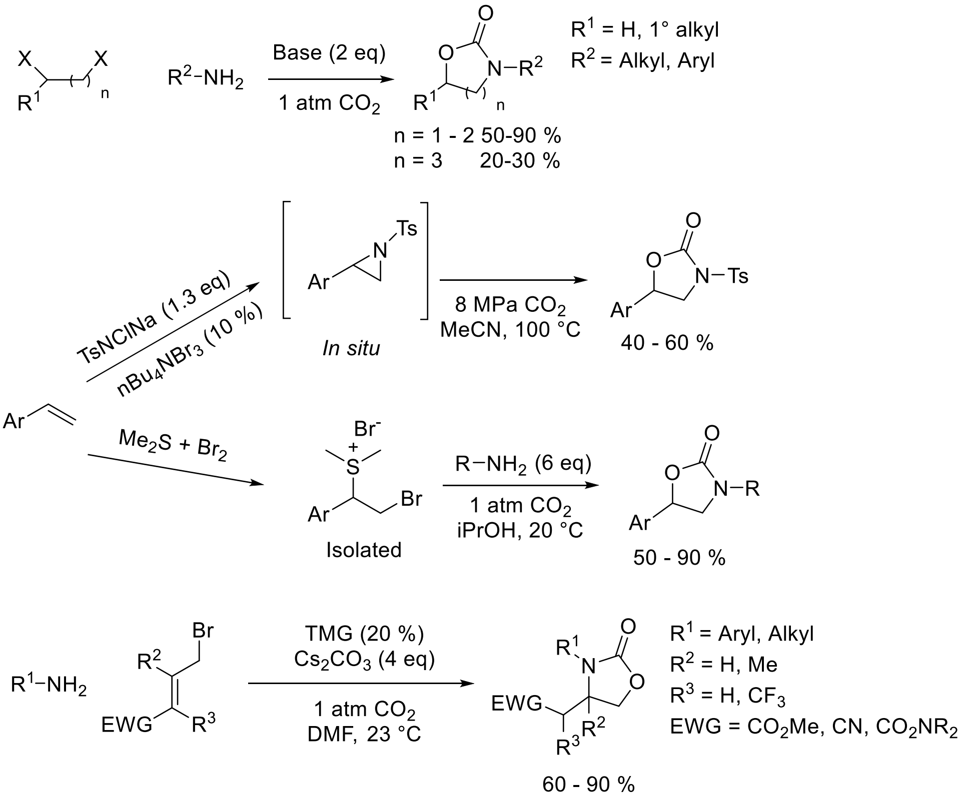
The analogous allylic amines were much less reactive. The alkene had to be activated by an electron withdrawing group (Michael addition) (Scheme 46, top)[155] or the reaction could be mediated by the addition of a strong electrophile. Iodine could be used in the presence of a base, at 1 atm of CO_2 and room temperature (Scheme 46, middle).[156] This reaction could also be used to make 6-membered cyclic carbamates with 3-butylamines. With 4-pentenamines, the N-reactivity formed a 5-membered ring, where the fused oxazolidinone is formed by S_N2 reaction with the iodide.[157] Electrophilic radical reagents could be used in place of iodine (Scheme 46, bottom).[158] [159] The aromatic group on the alkene helped to stabilize the intermediate radical and was important to achieve high yield.



Electrophile	Catalyst	E	Yield
I_2	TMG (20 %)	I	50 - 80 %
Togni reagent II	$[Cu(MeCN)_4]PF_6$ (10%)	CF_3	60 - 90 %
Alkyl - Br	$Pd(PPH_3)_4$ (10 %), Blue LEDs	Alkyl	50 - 90 %
$CF_3(CF_2)_nI$	White light	$CF_3(CF_2)_n$	80 - 95 %
$BrCF_2CO_2Et$	$Ru(bpy)_3Cl_2$, Blue LEDs	$-CF_2COOEt$	60 - 80 %
 Y= O, CR_2, NBoc	$[Cu(MeCN)_4]PF_6$ (10%)	$-CH_2YCH_2CN$	60 - 80 %

Scheme 46: Allylic amine carboxylation.

These methods had the amine already incorporated into the substrate, but with dielectrophilic compounds, the primary carbamate anion could react both from its oxygen and nitrogen in a three-component reaction. Here, the oxygen was much more nucleophilic, and it reacted first. Reaction with the amide like nitrogen closed the ring. Alkyl dihalides could be used with alkyl or aryl amine to yield 5- and 6-membered rings in good yields at atmospheric pressure (Scheme 47 top).[160] 7-membered rings could also be made, but in poor yield. Styrenes could be oxidized with different methods to create 1,2 dielectrophiles (Scheme 47, middle). Tosyl chloroamines in the presence of bromide was used to generate in situ tosyl aziridines from alkenes, which could form carbamates under CO_2.[161] Aziridines are commonly made by reacting styrenes with bromine, dimethylthioether, and amine via the bromothionium intermediate. This intermediate could be isolated and it reacts with carbamate anions to form oxazolidinones.[162] The intermediate was more reactive than the aziridine and therefore the reaction could proceed at ambient pressure. Allylic bromides with an electron withdrawing group could also react with the carbamate anion, where the oxygen first reacted with the bromide and then the nitrogen cyclized with the Michael acceptor (Scheme 47, bottom).[163] This reaction proceeded in ambient conditions with both aryl and alkyl amines.



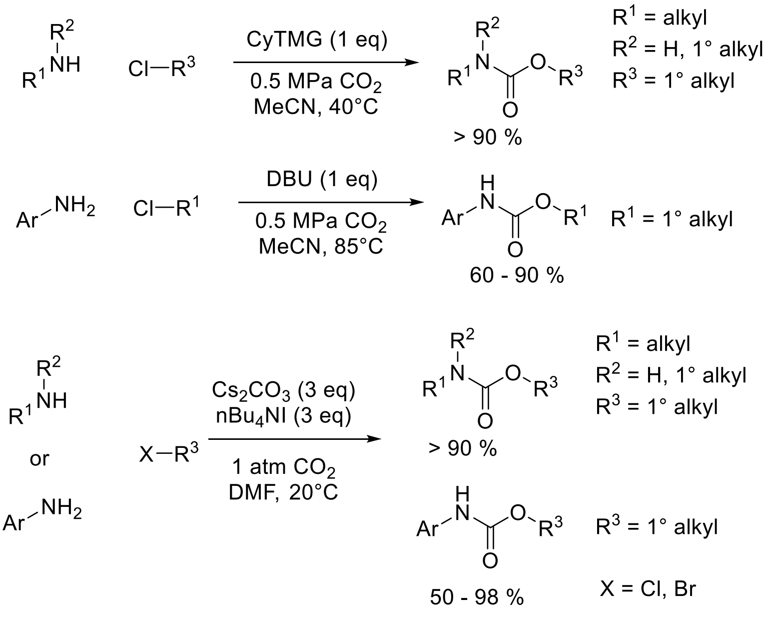
Scheme 47: Multicomponent cyclic carbamate synthesis

3.2.2 LINEAR CARBAMATES

Like cyclic carbamates, linear carbamate synthesis takes advantage of carbamate anion nucleophilicity, but direct acyl substitution is too unfavorable and can only proceed through an isocyanate intermediate. For example, Mitsunobu conditions could activate the carbamate anion to form an isocyanate with primary amines.[164] With secondary amines isocyanate formation was unfavored, and the alcohol was activated instead and caused a stereoinversion. Overall, Mitsunobu is a very general method for aliphatic carbamate synthesis with good to moderate yields.

The base-mediated reaction of amine, CO_2 and alkyl halide formed linear carbamates (Scheme 48).[165] The choice of base was highly important to get high selectivity between O-alkylation and N-alkylation.[166] A strong base drived the free amine-carbamate anion equilibrium towards the carbamate anion formation. Sterically hindered organic amidine and guanidine bases were especially well suited for this reaction. Out of the inorganic bases, Cs_2CO_3 has been commonly employed due to its high basicity and solubility in organic solvents.[167] The addition of nBu_4NI to the Cs_2CO_3 improved the selectivity, especially with anilines.[168] This reactivity could be extended to hydrazines, which react preferentially from their terminal nitrogen.[169] The general trend in alkyl halide reactivity was that primary and benzylic halides react very well. Secondary halides were less reactive; therefore, the use of bromides over chlorides was advantageous. Tertiary halides did not react. Primary and less bulky secondary amines reacted very well. Anilines required a strong base, and their selectivity drops when they are heated due to the instability of the carbamate anion. A chiral version has been developed for allylic chlorides using iridium catalyst with a chiral ligand, with moderate yield and enantioselectivity.[170] Alkyl halides could also be generated in-situ with by α-iodation of ketones, a formal C-H activation. Iodine could be sourced from I_2 or iodide anion with an oxidant.[171]

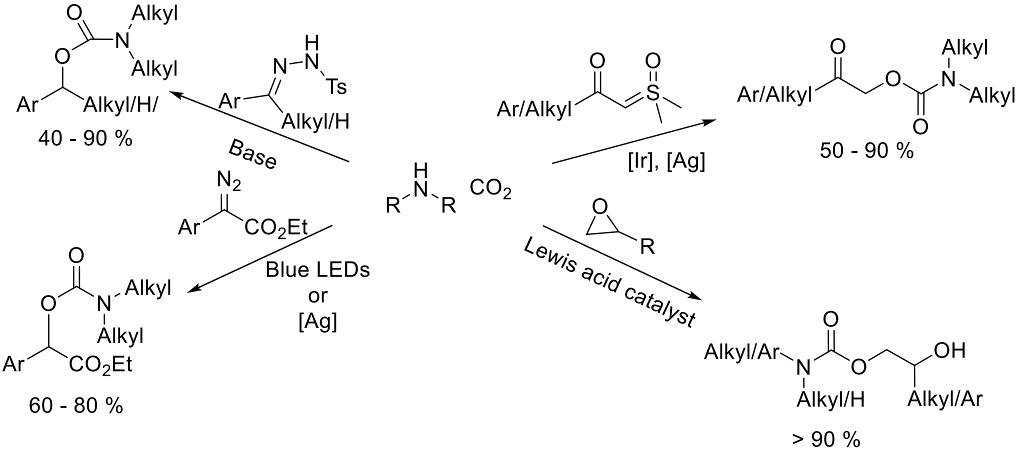
Heterocyles with pyrrole like nitrogen could also react with CO_2 and with an addition of methyl iodide a carbamate could be formed.[63c] Unlike amines, pyrrole lone-pair electron is delocalized to the aromatic ring and it cannot interact directly with CO_2. A copper catalyst and CsOH base were needed to facilitate the deprotonation of the heterocycle followed by the insertion of CO_2.



Scheme 48: Linear carbamates by reaction with alkyl halides

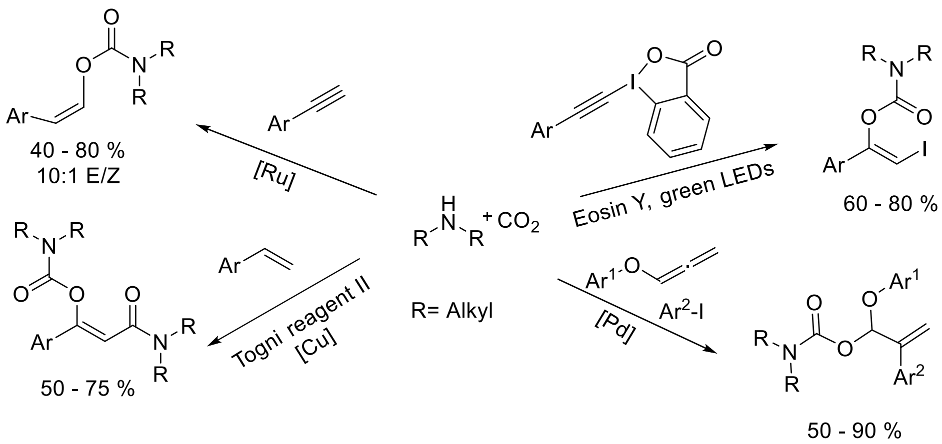
Without an added base poor yields (<30%) were obtained, since hydrohalic acid was formed in the process that protonated the amine, making it unable to absorb CO_2.[172] However, with a zeolite/nEt_4N based catalyst high yields could be obtained for primary amines with butyl bromide, without an added base.[173]

Besides alkyl halides, other alkyl electrophiles could also be utilised. These included epoxides,[174] hydrazones,[175], diazoniums[176] and sulfoxonium ylides (Scheme 49).[177] Other than epoxides, these approaches were limited to secondary alkyl amines, while epoxide was suitable for primary, secondary and aryl amines.



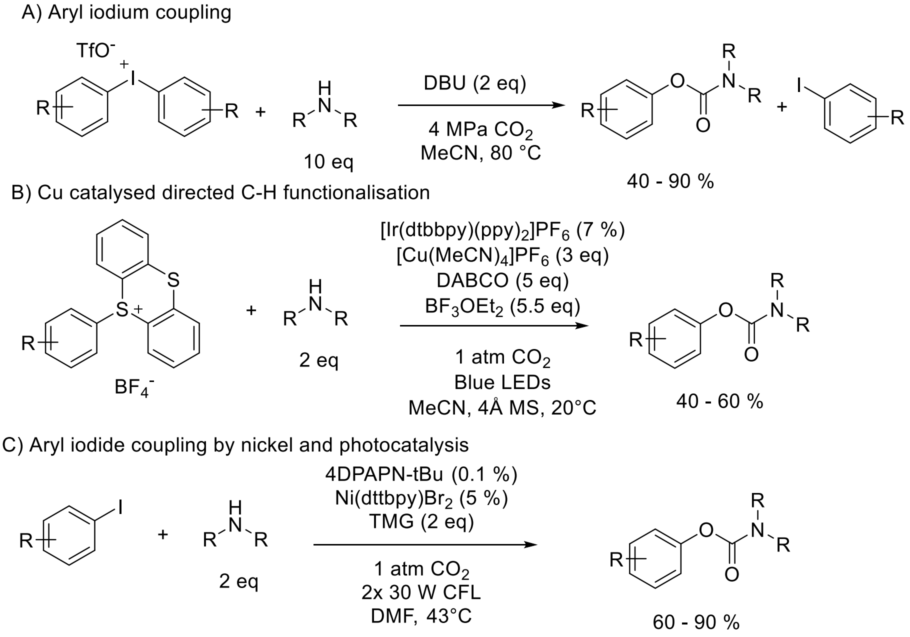
Scheme 49: Non-halide alkyl electrophiles for linear carbamate synthesis.

Analogously to cyclic carbamate synthesis, alkynes, alkenes, and allenes could act as electrophiles in linear carbamate synthesis when polarized by a transition metal catalyst or the substituents in the substrate. However, the reactions were more limited as they were not assisted by the formation of a 5- or 6-membered ring (Scheme 50). Terminal aryl alkynes could react with secondary amine carbamate anions with a ruthenium catalyst with moderate yields and good stereoselectivity.[178] Iodium salts generated from terminal aryl alkynes could also react with carbamates, but their regioselectivity was different than with the ruthenium catalyst.[179] E/Z stereoisomerism could be controlled by the photocatalyst. Aryl oxyallenes could also react in the presence of a transition metal catalyst, and with palladium, this reaction could be coupled with aryl iodides. [180] Carbamate anion could also be added also to styrenes, using copper catalyst and Togni reagent, but the added CF_3 was defluorinated in the reaction conditions to form an amide.[181]



Scheme 50: Linear carbamate synthesis with unsaturated compounds.

O-aryl carbamate synthesis is more difficult than O-alkyl carbamate since the phenolic carboxylate bond is weaker and aryl halides are too stable to directly go through substitution. The generation of diaryliodium salt made the aryl halide reactive enough to react with the carbamate anion in the absence of a catalyst (Scheme 51A).[182] The carbamate anion could coordinate to the iodium salt and the O-aryl carbamate forms by reductive elimination. Electron poor and ortho-substituted aryls worked well with this method, but 10 equivalents of amine and 4 MPa of CO_2 were required. Aryl thianthenes could also act as activated groups (Scheme 51B).[183] They formed aryl radicals under photocatalysis and could be coupled with carbamate anion in copper mediated reaction. The reported reaction required excess of Cu(I), DABCO and BF_3, but this type of reaction could potentially proceed catalytically in terms of copper. The thianthrenes could be generated from arenes by electrophilic aromatic substitution. In publication II, we described a method to directly use commercial aryl iodides and bromides to form O-aryl carbamates by utilising dual-nickel-photocatalysis (Scheme 51C). The photocatalysis allows access to highly active Ni(I-III) catalytic cycle, which eliminates the need of BF_3 type additives as seen with copper. The reaction was limited to electron poor aryls, due to sluggish oxidative addition.

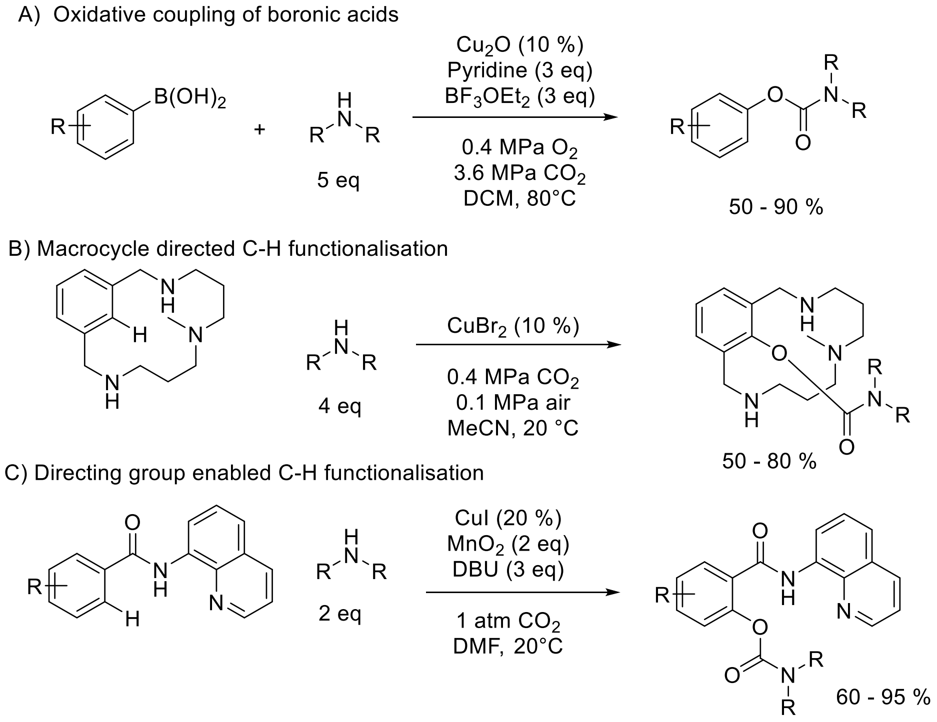

A) Aryl iodium coupling

B) Cu catalysed directed C-H functionalisation

C) Aryl iodide coupling by nickel and photocatalysis

Scheme 51: O-aryl carbamate synthesis from aryl electrophiles.

Another approach was to use oxidative conditions with copper catalysis. Aryl boronic acids yielded O-aryl carbamates in moderate yields with broad functional group tolerance (Scheme 52A).[184] However, the reaction required high pressure, excess amine, and a stoichiometric BF_3 additive, which limited the advantages of CO_2-based synthesis. With a macrocyclic copper binding directing group, aryl C-H activation could be achieved with oxidative copper catalysis (Scheme 52B).[185] Good yields could be obtained with secondary amines, but the utility of the reaction is limited by the nature of the directing group. A more general amide bound directing group was developed, and a very large variety of (hetero)aromatics could be used in ambient conditions, with MnO_2 or Ag_2CO_3 as oxidant (Scheme 52C).[186]



Scheme 52: Oxidative couplings to form O-aryl carbamates.

4 RESULTS AND DISCUSSION

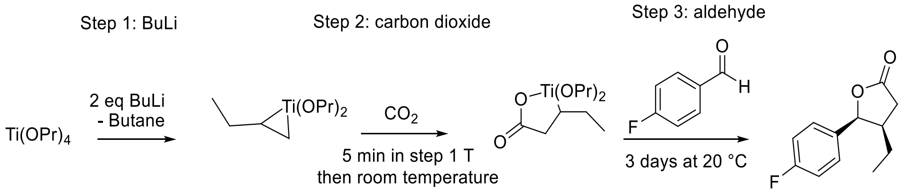
4.1 PUBLICATION 1

In this publication, we developed a 1,2 dicarbofunctionalization method that utilizes CO_2 to generate *cis*-3,4-substituted butyrolactones. This type of functionalization is difficult for unsaturated compounds, and the reactions are usually substrate dependant. In Scheme 32 there are examples of using ethylene generated nickelalactone reactivity, but these tend to provide poor results with substituted alkenes. Photocatalytic methods in Scheme 40 have provided a major improvement in difunctionalization, but they require a styrene substrate to stabilize the radical intermediate. Major improvements are therefore still possible in this area.

We decided to study titanium to further expand 1,2-dicarbofunctionalization with carbon dioxide. Titanium is famously known to catalyze the 1,2-difunctionalization of alkenes in the Kulinkovich reaction to form cyclopropanols. The reaction proceeds through a titanacyclopropane intermediate, which is a 1,2 dinucleophile. In the Kulinkovich reaction, this intermediate reacts twice with an ester, but many other electrophiles have also been studied. Among these, it has been previously shown that CO_2 will very easily insert into the titanacycle only once and create a titanalactone. In previous work, it was shown that strong inorganic electrophiles like I_2, O_2 and H_3O^+ could insert into the remaining Ti-C bond. In this study, we wanted to explore the reactivity with carbon electrophiles.

We initially optimized the reaction with n-BuLi, $Ti(OiPr)_4$ and p-fluorobenzaldehyde and up to 77% of cis-butyrolactone was formed, with 11% of the trans diastereomer and only traces of other chemoselective products (Table 3). Conducting the reaction at 0°C or -20°C was important, but at -40°C reaction failed due to precipitation after adding BuLi (entries 1-4). Very important was also the reaction time of step 1; too long a time reduced the yield, likely due to decomposition of the titanacycle intermediate; with too short a time, the reaction was too sensitive to internal temperature to receive repeatable results (entries 18-21). While the reaction with CO_2 was fast, extending the step 2 reaction time turned out to be beneficial (entries 14-17). We believed that this delay allowed decomposition of reduced titanium species into less active forms which were less likely to react with the aldehyde to form McMurry and pinacol coupling products. We also studied other titanium sources, but of the studied reagents, only $TiCl(OiPr)_3$ had good solubility, but it too provided slightly inferior results to $Ti(OiPr)_4$.

Table 3: Optimization with BuLi. 3 ml THF, 1 mmol p-benzaldehyde, Ti(OiPr)$_4$ and BuLi according to stoichiometry a) Stoichimetry as BuLi : Ti(OiPr)$_4$:p-fluorobenzaldehyde b) cis-isomer yield measured by GC-MS c) Added 2.6 mmol LiCl

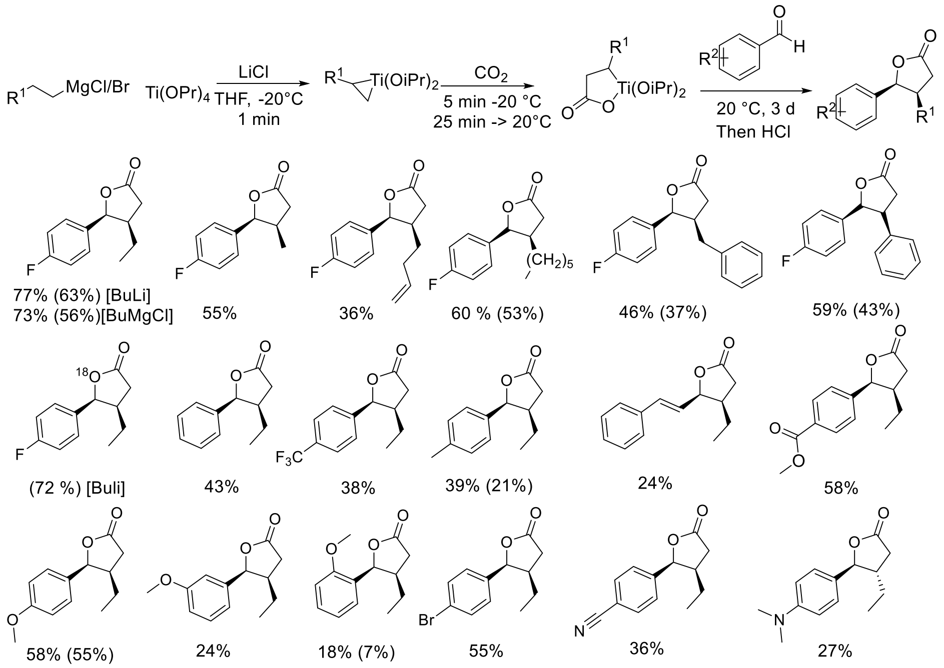


	Step 1 T (°C)	Solvent	Stoichiometry^a	Step 1	Step 2	Ti	Yield (%)^b
1	20	THF	2.1:1.05:1	5 min	2h	Ti(OiPr)$_4$	Trace
2	0	THF	2.1:1.05:1	5 min	2h	Ti(OiPr)$_4$	26
3	-20	THF	2.1:1.05:1	5 min	2h	Ti(OiPr)$_4$	26
4	-40	THF	2.1:1.05:1	5 min	2h	Ti(OiPr)$_4$	2
5	0	Et$_2$O	2.1:1.05:1	5 min	2h	Ti(OiPr)$_4$	27
6	0	Toluene	2.1:1.05:1	5 min	2h	Ti(OiPr)$_4$	0
7	0	Hexane	2.1:1.05:1	5 min	2h	Ti(OiPr)$_4$	0
8	0	THF	2.0:1.2:1	5 min	2h	Ti(OiPr)$_4$	27
9	0	Et$_2$O	2.0:1.2:1	5 min	2h	Ti(OiPr)$_4$	20
10	0	THF	2.6:1.3:1	5 min	2h	Ti(OiPr)$_4$	39
11	0	Et$_2$O	2.6:1.3:2	5 min	2h	Ti(OiPr)$_4$	19
12	0	THF	3.0:1.5:1	5 min	2h	Ti(OiPr)$_4$	36
13	0	Et$_2$O	3.0:1.5:2	5 min	2h	Ti(OiPr)$_4$	Trace
14	0	THF	2.6:1.3:1	5 min	5 min	Ti(OiPr)$_4$	41
15	0	THF	2.6:1.3:1	5 min	15 min	Ti(OiPr)$_4$	44
16	0	THF	2.6:1.3:1	5 min	30 min	Ti(OiPr)$_4$	53
17	0	THF	2.6:1.3:1	5 min	1h	Ti(OiPr)$_4$	34
18	0	THF	2.6:1.3:1	15 min	30 min	Ti(OiPr)$_4$	22
19	0	THF	2.6:1.3:1	2 min	30 min	Ti(OiPr)$_4$	63
20	0	THF	2.6:1.3:1	1 min	30 min	Ti(OiPr)$_4$	77
21	0	THF	2.6:1.3:1	30 sec	30 min	Ti(OiPr)$_4$	Variable
22	0	THF	2.6:1.3:1	1 min	30 min	Ti(OiPr)$_4$	71^c
23	0	THF	2.6:1.3:1	1 min	30 min	TiCl(OiPr)$_3$	56
24	0	THF	2.6:1.3:1	1 min	30 min	Ti(OMe)$_4$	< 5
25	0	THF	2.6:1.3:1	1 min	30 min	Ti(OBu)$_4$	25
26	0	THF	2.6:1.3:1	1 min	30 min	TiCp$_2$Cl$_2$	0
27	0	THF	2.6:1.3:1	1 min	30 min	TiCl$_4$	0

We expanded our study to Grignard reagents as they are better available and more convenient to prepare. This required reducing the temperature to -20°C and saturating the solution with LiCl. LiCl was thought to break up the aggregated Grignard reagents, which would form the titanacycle faster, which was important since the titanacycle was unstable. The optimized condition for BuMgCl provided slightly poorer results than with BuLi (73% instead of 77%), but with these conditions in hand, we could explore the substrate scope.

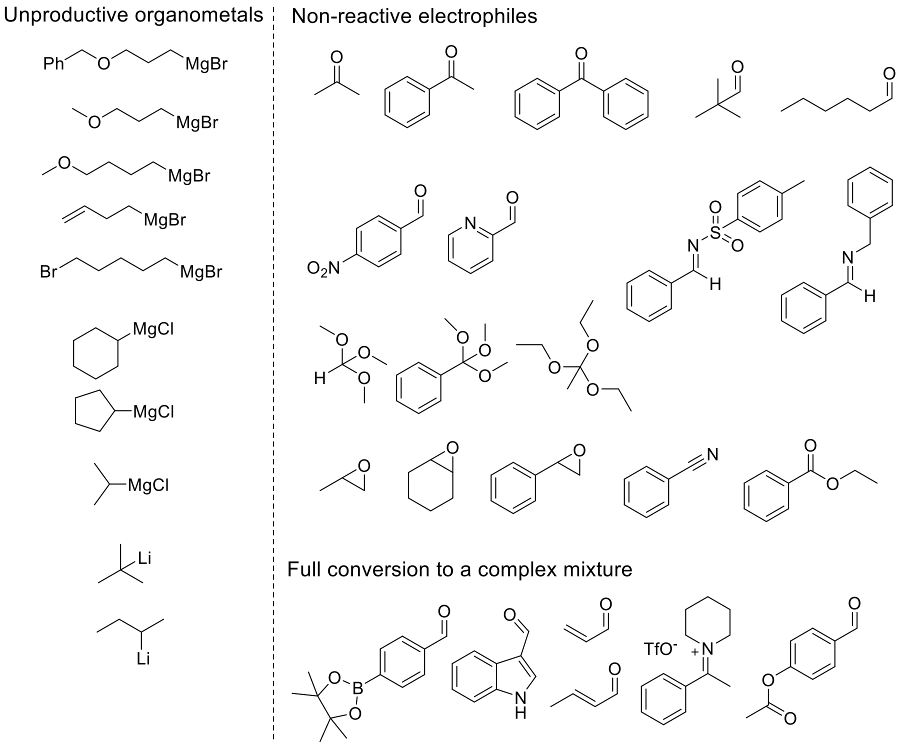
Different primary Grignard reagents with monosubstituted β-carbon worked well in the reaction and provided the cis-3,4-butyrolactones with near exclusive chemoselectivity and 5-7:1 diastereomeric selectivity (Scheme 53). Secondary Grignard or alkyl lithium reagents yielded no product. Reagents with ether groups are eliminated in the reaction conditions. Various benzaldehydes and cinnamic acid could be used as substrates. The reaction did not show preference for the electronic effect of the substituents, and both electron withdrawing and donating groups provided moderate yields. We also studied ^{18}O-labeled p-fluorobenzaldehyde and observed that the endocyclic oxygen comes from the aldehyde, which suggested that the ester was formed by a standard acid catalysed esterification. Surprisingly, 4-dimethylaminobenzaldehyde yielded only *trans*-isomer, but it turned out that the *cis*-isomer isomerizes to *trans* quickly in acidic workup or on silica.

We also studied other carbon electrophiles but could not observe any product (Scheme 54). Ketones, aliphatic aldehydes, imines, orthoesters, epoxides, and esters were non-reactive in the reaction conditions, while more electrophilic acrolein and iminiums reacted fully, but resulted in a tarry mixture.

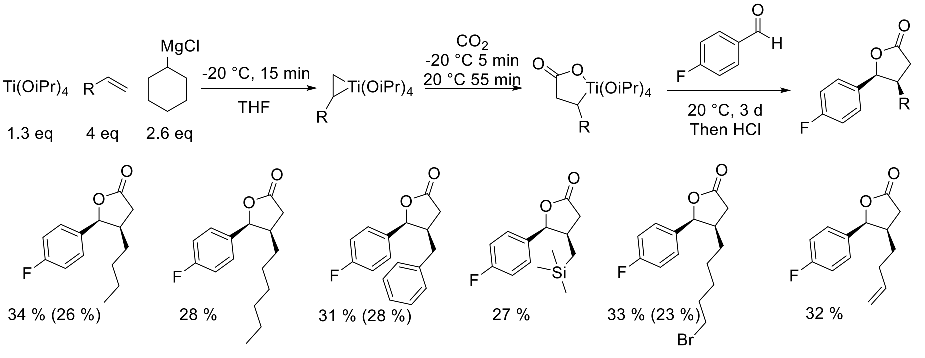


Scheme 53: Substrate scope for the titanium mediated butyrolactone formation. Yield is the NMR-yield of shown isomer, isolated yield is in brackets.

The titanacycle intermediate could also exchange the alkyl with a primary alkene, which further expanded the substrate scope. Adding the primary alkene to the reaction mixture with BuMgCl or BuLi provided mixture of the exchanged and non-exchanged lactone. Using c-HexMgCl instead, provided exclusively the exchanged product (Scheme 55). The formation of the titanacycle seemed to be slower, and therefore the step 1 time was increased from 1 minute to 15 minutes. Unfortunately, since the intermediate is unstable this leads to only ca. 30% yield. However, TMS and bromo substituted alkenes could be used which would be unavailable using the Grignard reagent pathway.



Scheme 54: Unproductive substrates in the reaction conditions described in Scheme 52.



Scheme 55: Cis-butyrolactone synthesis by using primary alkenes.

We studied the mechanism using DFT calculations (Figure 1). The initial formation of the titanacycle was already well studied by Bertrus and therefore we focused on the insertion of CO_2 and the aldehyde into the metallacycle. The CO_2 inserted via the inner-sphere mechanism, where the CO_2 directly coordinates to the titanium during the transition state, specifically in η^2-C,O type. The inner-sphere insertion mechanism had only a 2.2 kcal/mol energy barrier compared to 24.8 kcal/mol of the outer-sphere mechanism, where the titanium polarizes the butyl substrate, which then reacts with the CO_2, without

CO_2 coordinating to the metal. This demonstrated the strong effect of the metal on CO_2 activation. The aldehyde readily coordinated with the titanalactone, but the insertion to Ti-C bond had a disfavored geometry, which resulted in an energy barrier of 16.8 kcal/mol and the long reaction time. The energy barriers for acetophenone and phenylmethanimine were 20.9 and 28.6 kcal/mol. This would suggest that with minor improvements, ketones could also be an accessible substrate.

We also studied the mechanism of the alkene exchange, where the energetically preferred route proceeds through a generation of a titanacycle with the c-HexMgCl, then coordination of the primary alkene (6.8 kcal/mol with 1-hexene) followed by decoordination of cyclohexene (2.3 kcal/mol). The direct decoordination of the cyclohexene was very unfavorable (28.4 kcal/mol).

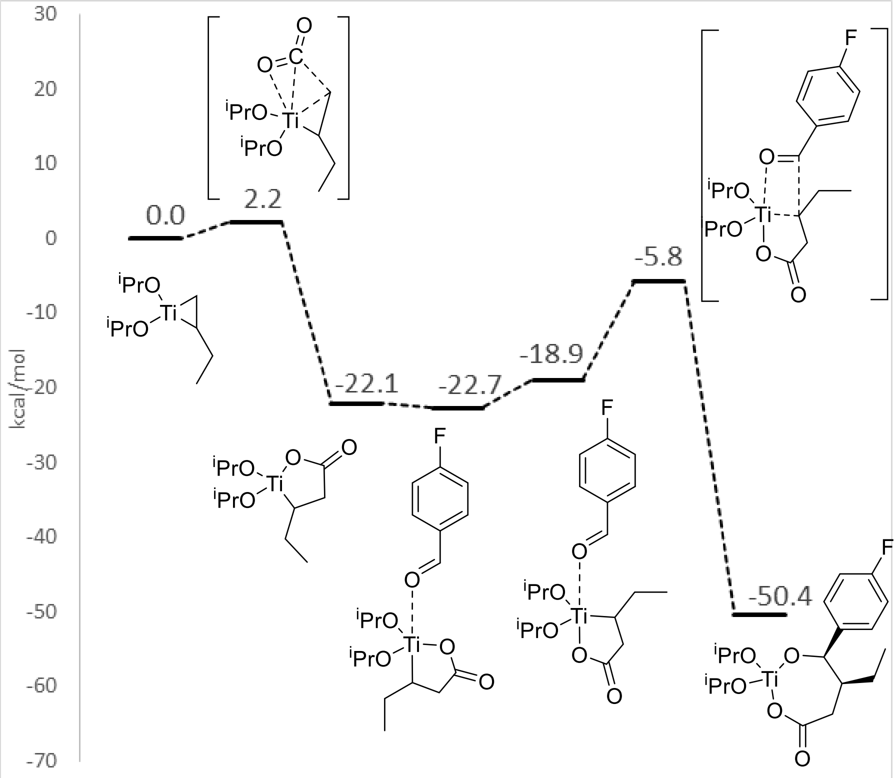


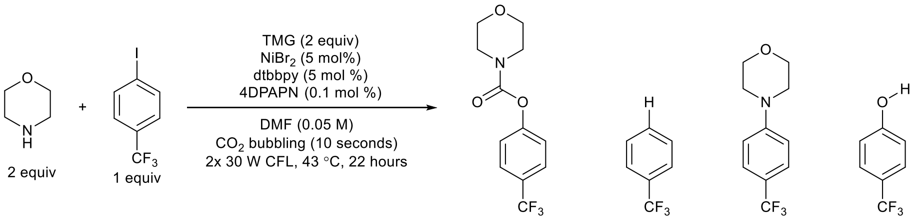
Figure 1: Gibbs free energy profile for titanium mediated butyrolactone synthesis. B3LYP-D3/def2-TZVP,CPCM[THF]//B3LYP-D3/6-31+G(d,p),CPCM[THF]).

4.2 PUBLICATION II

In this study, we presented a CO_2-based method for O-aryl carbamate synthesis that avoids toxic reagents and stoichiometric activators, but rather uses commercially available substrates at ambient pressure and low temperature, with visible light photocatalysis. O-aryl carbamates are found in pharmaceuticals and pesticides, and they are usually synthesized via a toxic phosgene-derived methods. [1878] CO_2-based methods have been published, but they use high pressures and stoichiometric activating reagents to facilitate the poor reactivity of the carbamate anion. [126, 129, 131, 167b, 184, 188]

We decided to study if a photocatalytic method would facilitate the reaction between a carbamate anion and an aryl halide. Previously, dual nickel photocatalysis has provided great results in nucleophile – aryl halide coupling reactions with, for example, amines, amides and carboxylic acids. [189] Based on these results, we proceeded with an initial screening of conditions to yield up to 78 % product.

Table 4: Effect of selected deviations to reaction conditions in the dual nickel-photocatalysed O-aryl carbamate synthesis.



#	Deviation from above	Unreacted	Carbamate	Dehalogenated	Aniline	Phenol
1	None	0 %	78 %	16 %	3 %	3 %
2	No nickel	37 %	0 %	62 %	0 %	0 %
3	No photocatalyst	99 %	<1 %	< 1 %	0 %	0 %
4	Dark	100 %	0 %	0 %	0 %	0 %
5	Blue led	0 %	66 %	8 %	6 %	20 %
6	bipy instead of dtbbpy	15 %	28 %	5 %	35 %	18 %
7	iPr_2NH as a base	22 %	44 %	21 %	8 %	5 %
8	Et_2iPrN as a base	81 %	9 %	3 %	5 %	2 %
9	Cs_2CO_3 as a base	2 %	77 %	16 %	3 %	3 %
10	DBU as a base	0 %	69 %	20 %	4 %	7 %
11	1.1 eq morpholine	7 %	72 %	13 %	3 %	5 %
12	1.1 eq morpholine and TMG	23 %	62 %	4 %	3 %	6 %
13	Added 1 eq H_2O	0 %	65 %	19 %	4 %	11 %
14	Added 1 eq O_2	0 %	68 %	18 %	4 %	9 %
15	Added 1 eq stilbene	8 %	76 %	6 %	3 %	6 %
16	$Ir(ppy)_3$ instead of DPAPN	6 %	71 %	18 %	2 %	2 %
17	4CzIPN instead of 4DPAPN	24 %	62 %	6 %	3 %	5 %

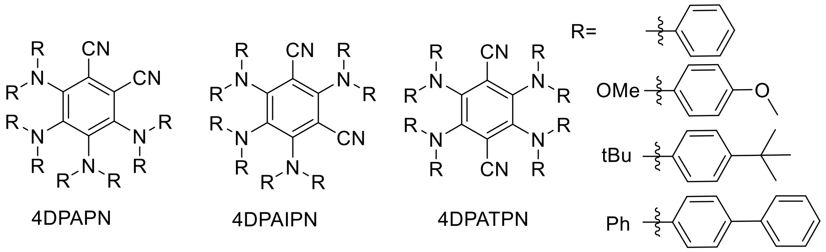
The optimal conditions were in-line with previous studies in to dual nickel photocatalysis; the reaction used a visible light, a photocatalyst, a nickel salt with a ditertbutylbipyridine (dtbbpy) ligand and a base (Table 4, entries 1-6).[190] The reaction differed from the previous studies due to the low reactivity of the carbamate anion, which caused challenges due to competing side reactions. The significant side reactions were protodehalogenation, phenol formation, and direct N-arylation.

Generally, tertiary amine bases have been used as a reductant for photoredox catalysis, but here they provided lower reactivity and selectivity by forming more dehalogenated product (Table 4, entries 7-8). To push the amine-carbamate equilibrium more towards carbamate, a stronger base was used. Either DBU, TMG or Cs_2CO_3 could be used, with TMG yielding the best results (Table 4, entries 9-10). DBU and TMG can be reducing agents by themselves, but the good result with Cs_2CO_3 suggest that the morpholine/morpholine carbamate is the major reducing agent, which is in-line with the relative reduction potentials (DBU 1.26 V, TMG 1.24 V vs. secondary amines 0.9-1.1 V).[191] Since the desired reaction is redox neutral and the dehalogenation is reductive, having less reductive agents could be beneficial. This is seen especially when using only 1.1 eq of morpholine and TMG, which produced very little dehalogenated product (Table 4, entry 12).

After optimizing the base, the major side reaction was protodehalogenation, which is a known photocatalytic reaction. Using blue LEDs instead of a compact fluorescent lamp slightly increased it, as did using $Ir(Ppy)_3$ instead of the organic photocatalyst 4DPAPN (Table 4, entries 5, 16). Since the properties of the photocatalyst seemed to affect this sidereaction, we synthesised several variants of the 4DPAPN structure to study the effect of electron withdrawing substituents on the catalyst properties and the reaction. We found that larger $E(PC/PC^-)$ correlates with increased activity, while smaller $E^*(PC/PC^-)$ correlates loosely with selectivity, but with too low potential the reaction stops completely as was seen with MeO substituted 4DPAPNs (Table 5). Of the studied photocatalysts, 4DPAPN-tBu turned out to be the best and was used for further studies.

The reaction worked well with a variety of amines with p-iodobenzotrifluoride (Scheme 56). We also studied p-bromobenzotrifluoride, and it provided slightly poorer results than the iodo compound and had a very poor result with a select few compounds. These had in common an extra carbonyl functionality in their structure, which may have increased their coordination to the metal, which could inhibit the oxidative addition of the less reactive bromo compound.

Table 5: Photocatalyst optimization.

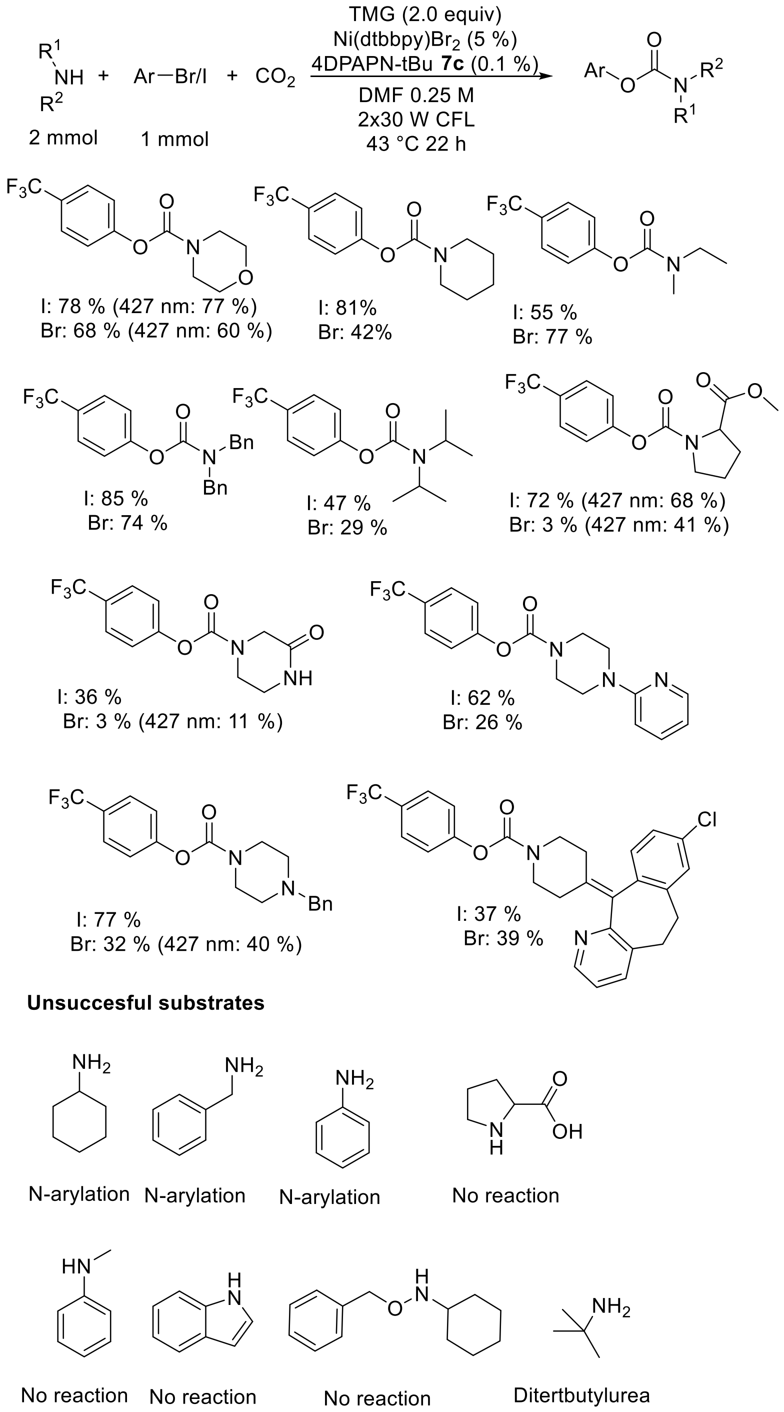


Acronym	E[a]	E*	Unreacted[b]	Carbamate	Dehalogenated	Aniline	Phenol
4DPAPN	-1.54[c]	0.90	0 %	78 %	16 %	3 %	3 %
4DPAIPN	-1.66[c]	0.84	0 %	72 %	19 %	3 %	5 %
4DPATPN	- 1.45	0.82	0 %	59 %	30 %	4 %	7 %
4DPAPN-OMe	-1.64	0.73	100 %	0 %	0 %	0 %	0 %
4DPAIPN-OMe	-1.80[c]	0.51	80 %	16 %	2 %	1 %	2 %
4DPATPN-OMe	-1.54	0.54	89 %	8 %	2 %	1 %	1 %
4DPAPN-^{t}Bu	-1.60[c]	0.74	0 %	87 %	5 %	5 %	4 %
4DPAIPN-^{t}Bu	-1.67[c]	0.71	0 %	79 %	14 %	43 %	2 %
4DPATPN-^{t}Bu	-1.36	0.80	41 %	50 %	3 %	2 %	3 %
4DPAPN-Ph	-1.44[c]	0.87	30 %	41 %	25 %	3 %	1 %
4DPAIPN-Ph	-1.56[c]	0.83	0 %	72 %	25 %	4 %	1 %
4DPATPN-Ph	-1.49	0.69	72 %	19 %	7 %	<1%	<1%

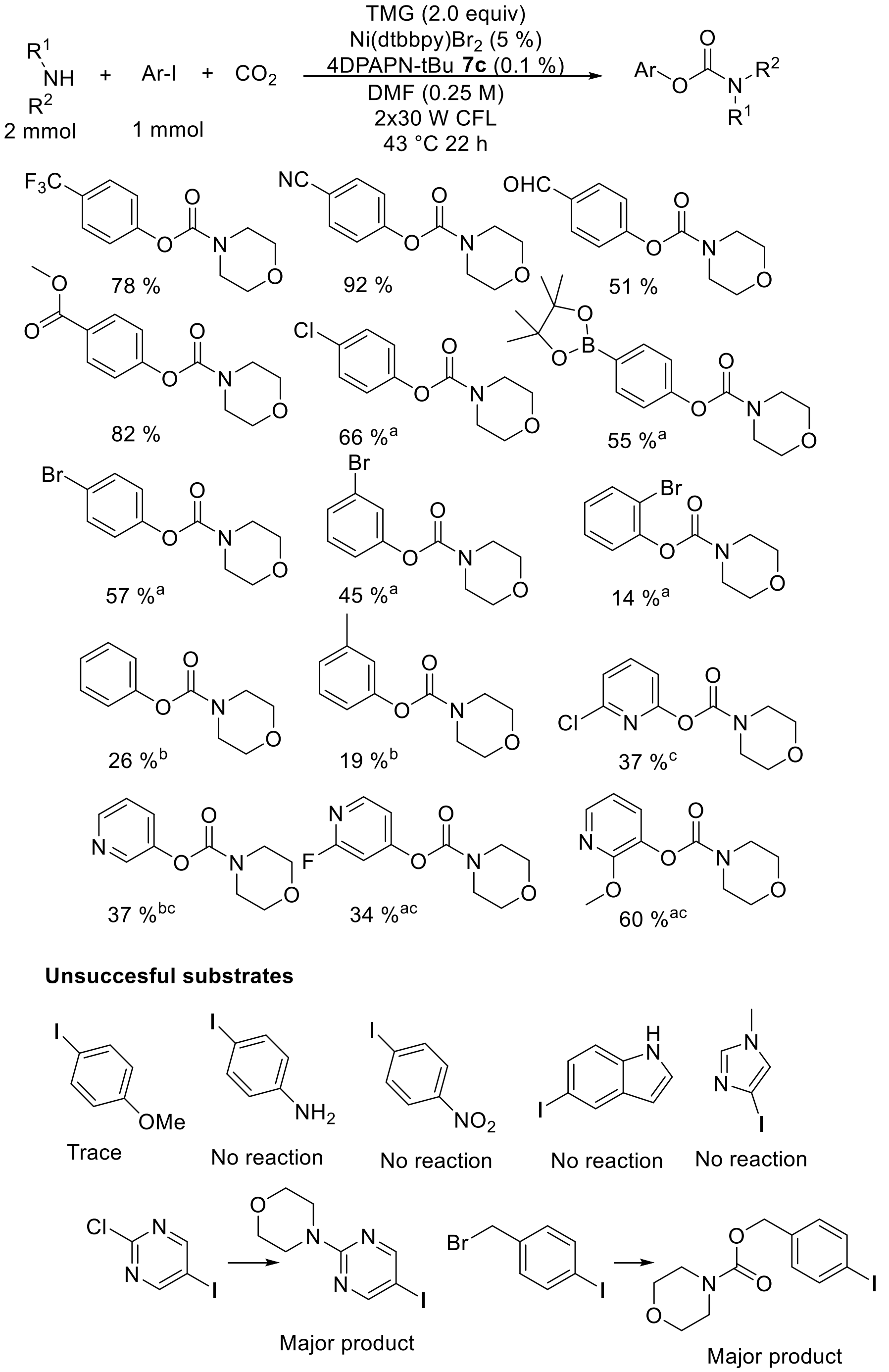
a) E is the reduction potential of the photocatalyst and the E* is the excited state reduction potential. b) Reaction conditions; 0.4 mmol 4-iodobenzotrifluoride, 0.8 mmol TMG, 0.8 mmol morpholine, 0.02 mmol $NiBr_2$dtbbpy, 0.004 mmol photocatalyst in DMF(0.1M). Flushed with CO_2. 2x30W CFL, 22 hours, 43 °C., Yield measured by NMR with hexafluorobenzene as internal standard c) Measured in acetonitrile instead of DMF due to low solubility.

Primary amines only formed N-arylated products. This was likely because in the monocarbamate anion, the nitrogen was more reactive that the the oxygen. This was supported by bare oxazolidinone also forming N-arylated product in the reaction conditions. Using BuLi to make the dicarbamate anion completely stopped the reaction. Anilines also only provided N-arylated products.

The aryl iodides were very sensitive to the electronic effect of the aryl substituent, where electron-poor arenes provided high yields while electron-rich arenes reacted very slowly or not at all (Scheme 57). Compared to phenol and phosgene-based synthesis, electron poor phenols are often the more difficult substrates as the phenol nucleophilicity becomes weaker. Another difficult substrates for phenol based synthesis are hydroxypyridines due to tautomerization and N,O selectivity. With this method, we were able to synthesize pyridine carbamates with moderate yields. The yield was limited by the product reacting further to form urea, which could be reduced by using only 1 equivalent of the amine. Of the studied pyridines, OMe substituted yielded the best result, because of lower urea formation due to the stabilizing effect of OMe.

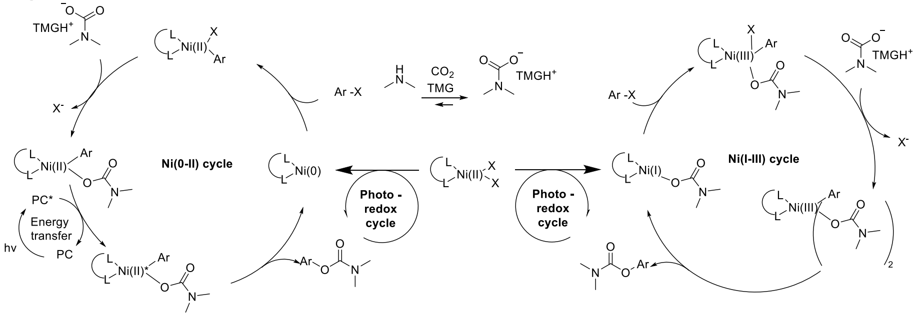


Scheme 56: Amine substrates. 427 nm = Blue LEDs instead of CFL



Scheme 57: Aryliodide scope. a) 44h reaction, b) 66h reaction, c) 1.1 mmol morpholine instead of 2 mmol

We also studied the mechanism of the reaction, as previous studies into dual nickel-photocatalytic aryl heteroatom coupling reactions have shown that different mechanisms are possible, and that the major route depends on the fine details of the reaction. The two main suggested mechanisms are the Ni(I-III) cycle and energy transfer (Scheme 58). In the Ni(I-III) cycle, the photocatalyst reduces the initial Ni(II) complex to Ni(I), which reacts with aryl iodide via oxidative addition to give the Ni(III) complex. The iodide is replaced by the carbamate, and reductive elimination yields the product and regenerates the Ni(I)-complex. Since Ni(III) and Ni(I) are unstable, they can comproportionate or react with other redox active species in the reaction to form Ni(II), which is then reactivated by the photocatalyst. In energy transfer mechanism the Ni(II) is initially activated by reduction to Ni(O), which reacts with aryl iodide to form Ni(II) complex. This complex is exited either directly by the light or by triplet energy transfer by the photocatalyst, and the exited state complex goes through a reductive elimination to yield product and regenerate Ni(O).



Scheme 58: Two plausible mechanisms, energy transfer mechanism on the left proceeds through Ni(0-II) cycle. The experimentally validated mechanism on the right proceeds through a Ni(I-III) cycle.

To differentiate between these mechanisms, we synthesized a dtbbpyNi(o-tolyl)Br complex. Treating this complex with the carbamate anion and light, with or without photocatalyst, only yielded toluene and bromotoluene. Adding $FeCp_2BF_4$, a strong oxidant, yielded the product carbamate in 32 %. This strongly suggest, that Ni(III) is needed to form the product. Additional evidence against energy transfer mechanism is that triplet quenchers O_2 or stilbene had a very little impact on the reaction, while in studies with energy transfer mechanism, additional O_2 stopped the reaction almost completely. However, when we used other reductants instead of a photoredoxcatalyst, we observed distinct difference between reactions with and without irradiation. This could suggest the formation of excited state nickel species, but Doyle et al. has also reported that Ni(I) and Ni(III) species can form via disproportionation under visible light irradiation.

We also studied the reaction kinetics. The reaction profile is sigmoidal, due to the initial photoredox-catalyzed nickel reduction being a slow reaction. Adding more photocatalyst reduced the activation period (Figure 2), but at 5%

nickel, the maximum reaction rate was saturated at 0.5 % of 4DPAPN-tBu. The reaction rate was zeroth order in terms of the carbamate anion and first order in terms of the arylhalide, which suggested that the oxidative addition was the rate-limiting step. The 4DPAPN-tBu had a 0.5-0.6 rate order and the dtbbpyNiBr$_2$ had a 0.3 rate order, which indicated that their concentrations affected both the activating and deactivating pathways of the active nickel species concentration. The photocatalyst itself and oxidized amines could react with Ni(I) and (III) in single electron transfer to deactivate it. The nickel rate order could be explained by deactivation via comproportionation.

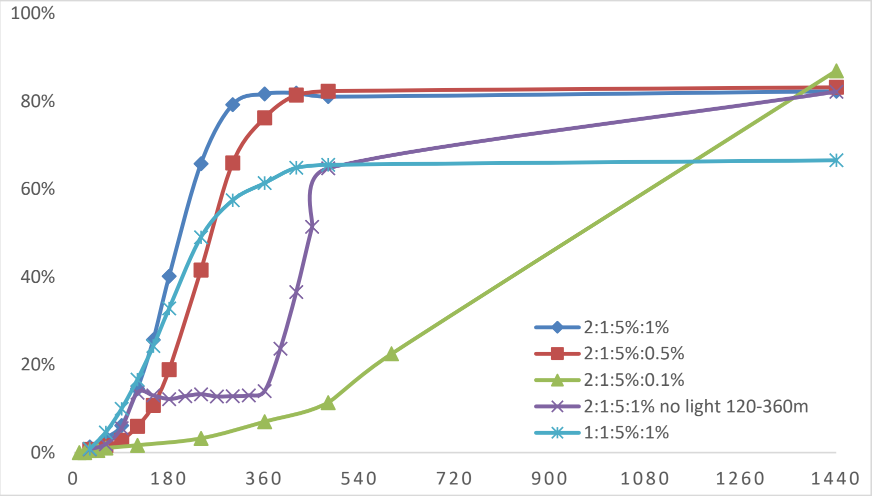


Figure 2: Reaction profile, stoichiometry in legend is morpholine, p-iodobenzotrifluoride, Ni(dtbppy)Cl$_2$, 4DPAPN-tBu.

4.3 PUBLICATION III

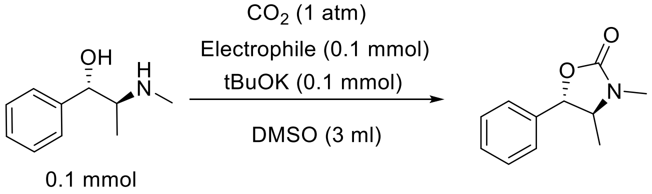
In publication III, we studied different electrophilic activating reagents in oxazolidinone formation as previous studies into the area had shown significant issues with either selectivity or scope (covered in section 3.2.1).

First, we screened various electrophiles by mixing (+)-pseudoephedrine, CO_2, and tBuOK in DMSO followed by adding an electrophile, then slowly increasing the temperature of the reaction by 10°C/30 min up to 150°C and then heating for 16 hours (Table 6). Initial studies had shown that the product was very stable in these conditionts, and slow heating to a high temperature would avoid biasing the results towards either very reactive or poorly reactive reagents. (+)-pseudoephedrine with two chiral carbons would enable the detection of inversion or retention of the product. N-alkyl chlorides and bromides provided high yields, with the exception of benzyl chloride, from which BuCl was considered the most atom economical while being convenient to use (entries 1-5). BuI however, tended to provide a lot of N-butylated oxazolidinone. With secondary and tertiary alkyl chlorides, the reaction did not reach completion, potentially due to competing elimination reactivity (entries 6-8). Of the tested electrophiles, only propylene oxide provided moderately good results (entry 9). Even strong Michael acceptors were not very reactive in the reaction conditions (entries 12-16), but also no significant side reactions were detected either. The minor reactivity shown here, might be of further interest, as the Michael acceptor could potentially act as a catalytic H_2O shuttle if its properties could be further tuned. Esters provided a mixture of inversion and retention products (entires 16-19), while anhydrides consumed the aminoalcohol but did not generate any oxazolidinone. AcCl, TsCl, NsCl could react with DMSO in these conditions and therefore did not provide any product. Therefore, they were also studied in ACN and starting from 0°C, however their major product was the direct reaction with the nitrogen, even when CO_2 was flushed for 15 minutes prior to electrophile addition (entries 22-24). Even though they provided good results with primary amines in previous studies. [135a]

We further studied the reaction conditions with BuCl. Heating the reaction overnight at 80 °C provided mainly the linear butyl carbamate, which completely converted to the oxazolidinone when heated for 2 hours at 140°C. Increasing the stoichiometry from 1 equivalent of all reagents to 1 equivalent aminoalcohol, 1.1 equivalent base, and 1.2 equivalent BuCl increased the conversion to quantitative and provided ca. 10% higher yield (

Table 7). A solvent screen showed that DMSO as solvent is vital for the reaction, while DMF also provided some product. Other solvents that provided only traces product were sulfolane, toluene, EtOAc, trifluorotoluene. In these solvents, the carbamate anion was mostly insoluable.

Table 6: Electrophile screen



Entry[a]	Base	Electrophile	Yield (%)[b]
1	tBuOK	n-BuCl	87
2	tBuOK	n-BuBr	85
3	tBuOK	n-BuI	10
4	tBuOK	BnCl	30
5	tBuOK	n-OctDecCl	79
6	tBuOK	sec-BuCl	37
7	tBuOK	t-BuCl	5
8	tBuOK	c-hexCl	11
9	tBuOK	propylene oxide	57
10	tBuOK	$(EtO)_3Et$	5
11	tBuOK	TMSCl	0
12	tBuOK	Acrolein	6
13	tBuOK	2-benzylidenemalononitrile	8
14	tBuOK	Nitrostyrene	11
15	tBuOK	Methyl methacrylate	13
16	tBuOK	Methyl Cinnamate	12 (11)[c]
17	tBuOK	Methyl Benzoate	5 (23)[c]
18	tBuOK	Benzyl benzoate	9 (25)[c]
19	tBuOK	Diethylsuccinate	9 (6)[c]
20	tBuOK	Succinic anhydride	0
21	tBuOK	Maleric anhydride	0
22[d]	DBU	AcCl	0
23[d]	DBU	TsCl	45
24[d]	DBU	NsCl	31
25[d]	DBU	TMSCl	0
26[d]	DBU	I_2	0

a) Conditions 0.1 mmol of (+)-pseudoephedrine in 4 ml of DMSO, added CO_2, Base (0.1 mmol), electrophile (0.1 mmol)
b) Calibrated GC/MS yield with 0.1 mmol mesitylene as internal standard
c) Inversion product yield in brackets
d) In ACN, started ramping from 0 °C, until 120°C

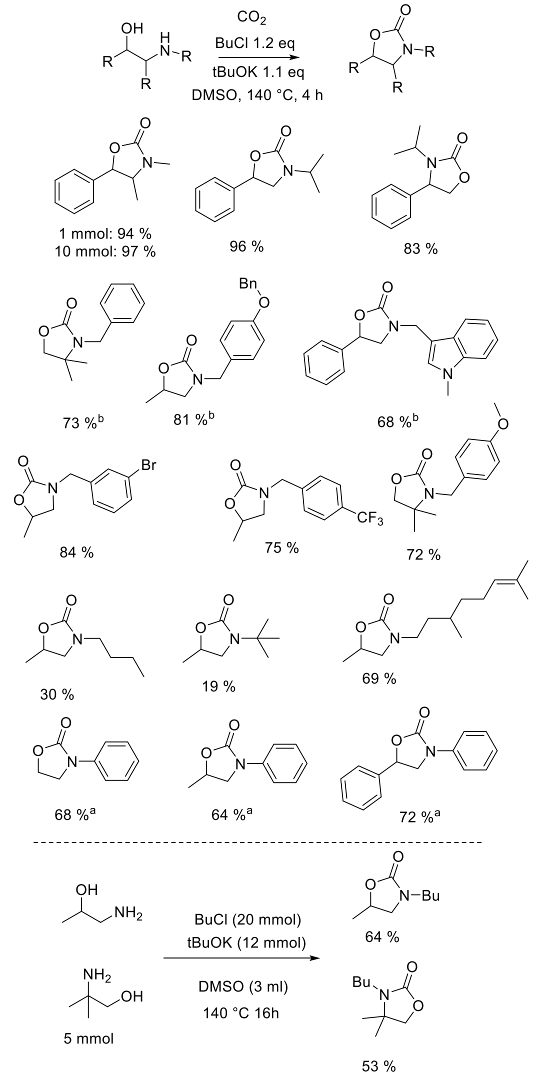
Table 7: Base and solvent screen

Entry[a]	Base	Solvent	Ratios (Base : BuCl)	Yield (%)[b]
1	K_2CO_3	DMSO	1:1	74
2	tBuOK	DMSO	1:1	87
3	K_3PO_4	DMSO	1:1	54
4	Cs_2CO_3	DMSO	1:1	64
5	K_2CO_3	DMSO	1.1 : 1.2	96
6	tBuOK	DMSO	1.1 : 1.2	91
7	K_3PO_4	DMSO	1.1 : 1.2	47
8	Cs_2CO_3	DMSO	1.1 : 1.2	87
9	tBuONa	DMSO	1.1 : 1.2	15
10	Na_2CO_3	DMSO	1.1 : 1.2	0
11	Li_2CO_3	DMSO	1.1 : 1.2	0
12	DBU	DMSO	1.1 : 1.2	18
13	K_2CO_3	DMF	1.1 : 1.2	14
14	tBuOK	DMF	1.1 : 1.2	46
15	Cs_2CO_3	DMF	1.1 : 1.2	57
16	K_2CO_3	ACN	1.1 : 1.2	0
17	tBuOK	ACN	1.1 : 1.2	< 5
18	Cs_2CO_3	ACN	1.1 : 1.2	0
19	K_2CO_3	Diglyme	1.1 : 1.2	10
20	tBuOK	Diglyme	1.1 : 1.2	0
21	Cs_2CO_3	Diglyme	1.1 : 1.2	12

a) Conditions 0.1 mmol of (+)-pseudoephedrine in 4 ml of DMSO, added CO_2, Base (0.1 mmol), electrophile (0.1 mmol). 150°C 4 hours.
b) Calibrated GC/MS yield with 0.1 mmol mesitylene as internal standard

The base could be substituted for K_2CO_3 or Cs_2CO_3, but when the reaction was scaled up to 10 mmol, K_2CO_3 only provided 40% conversion after an overnight reaction, while Cs_2CO_3 and tBuOK provided quantitative conversion in 4 hours. This indicates issues caused by the solubility and comparably inferior stirring on a larger scale. The addition order of reagents could be any without any impact on the yield, whereas most previous studies require 15 min CO_2 purge before adding the more reactive activating reagent. In most cases, only extraction and filtration through a small silica plug were needed to receive a pure product.

Next, we studied the scope of the reaction with different amino alcohols. The reaction provided high yields of alkyl oxazolidinones in less than 4 hours and scaled up well to the gram scale (Scheme 59). Aryl amines also worked well in the reaction, but they require an overnight reaction. With benzyl amines, when CO_2 was added after tBuOK, a minor reactant decomposition was observed, but this could be avoided by flushing with CO_2 first for 10 seconds or by using Cs_2CO_3 as a base. Unfortunately, larger cyclic carbamates only provided linear butyl carbamates and did not cyclize. With primary amines, N-butylated oxazolidinone was the favored product and by using excess BuCl this product could be obtained in high yield. However, only minor quantities of N-H oxazolidinone were observed with any stoichiometry.



Scheme 59: Substrate scope of amino alcohols a) reaction time 24h, b) reaction time 24h, base Cs_2CO_3

5 CONCLUSIONS

The past few decades have greatly expanded the methodologies that utilise CO_2 fine chemical synthesis. In both C and N-carboxylations all of the large product classes have atleast some examples CO_2 based synthesis. C-carboxylations with sp, sp2 and aromatic carbons have been extensively developed and recently there has been quick progress also in sp3 carboxylations. For N-carboxylations there are variety of activating reagents that can be used to generate almost any N-carboxylation product. However, there has been comparably little adoption of these methods in either laboratory scale synthesis or in industrial use.

For laboratory scale preparitive synthesis, CO_2, as a gas, can be somewhat cumbersome to work with, compared to solid or liquid C_1 sources. For CO_2 chemistry to be adopted in laboratories that do not otherwise use CO_2, the methods would need to provide acces to products that are hard to achieve by other means. This might mean focusing on multicomponent reactions to skip longer synthesis paths or focusing on selective C-H functionalisation reactions. For the latter, single electron chemistry, either electro- or photochemistry, could provide novel reactivity as well as aid with the thermodynamic issues often faced in CO_2 chemistry. In N-carboxylations, CO_2 could have some selectivity advantages with compounds that have multiple nucleophiles, as the carbamate anion formation is very favorable kinetically and thermodynamically and this could be further explored.

For industrial utilization, the main drawback of CO_2 chemistry is that most methods produce by-products due to utilization of activating reagents or bases. And without these, the reactions are usually thermodynamically very unfavorable to the point that even using extreme pressure is not enough to overcome it. To overcome this challenge, the reaction would need to be coupled to another high energy reaction, such as reduction with hydrogen, or via the use of energy-transfer photocatalysis or electrochemistry. Some initial progress in this area has been already reported.

This thesis aimed to further study the chemistry of carbon dioxide by developing new reactions that utilize carbon dioxide in synthesis. In publication I, the thermodynamic stability of CO_2 is utilized in combination with a highly reactive organotitanium species to generate moderately reactive intermediate that is unable to react with CO_2, but that does react with benzaldehydes. This was utilized to make cis-δ-lactones, that would otherwise require multiple steps to synthesize.

Publication II used photochemistry to avoid activating reagents, and therefore byproducts, to provide thermodynamically fairly unstable O-aryl carbamates. While base could not be eliminated in this case, similar redox neutral photochemical strategies could be used in the future to develope completely byproduct free reactions.

In publication III, selectivity of carbamate formation and further cyclisation in to oxazolidinones was studied. Highly chemoselective and enantioretaining reaction could be developed, by using a fairly poorly reactive activating reagent. This is in comparison to reported methods using more reactive reagents that often are accompanied to various sidereactions. The insights from this manuscript indicate that high selectivities can be achieved with CO_2 chemistry if reactivities of CO_2 and the reagents are matched.

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