Novel Electrosynthetic methods: Focus on Carbon Dioxide Utilisation

A Doctoral Thesis

By

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Acknowledgments

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Abbreviations

CCS	Carbon Capture Storage
CDU	Carbon Dioxide Utilisation
SO_x	Sulphur Oxides
NO_x	Nitrogen Oxides
MEA	Monoethanolamine
DEA	Diethanolamine
EOR	Enhanced Oil Recovery
MEK	2-Butanone
THF	Tetrahydrofuran
TON	Turnover number
TOF	Turnover frequency
KH	Potassium Hydroxide
GHG	Greenhouse gases
$scCO_2$	Supercritical Carbon Dioxide
MPa	Megapascal
DMA	Dimethylacetamide
DMF	Dimethylformamide
NMP	1-Methyl-2-pyrrolidone
DMSO	Dimethyl sulfoxide
$(TPPTS)_3$	3,3',3''-Phosphanetriyltris(benzenesulfonic acid) trisodium salt
$TMSCHN_2$	Trimethylsilyldiazomethane
PCy_3	Tricyclohexylphosphine
Et_2Zn	Diethyl zinc
$AlEt_3$	Triethylaluminium
rac-Me-DuPhos	Bis[(2S,5S)-2,5-dimethylpholano]benzene
MOF	Metal organic framework
NSAIDs	Nonsteroidal anti-inflammatory drugs
MMP	3-Methylmercaptopropionaldehyde

MHA	2-Hydroxy-4-methylmercaptobutyric acid
CEM	Cation exchange membrane
Bu$_4$NI	TetraButylammonium iodide
Bu$_4$NBr	TetraButylammonium bromide
Et$_4$NI	TetraEthylammonium iodide
TEOA	Triethanolamine
TEA	Triethylamine
NEC	Novel electrochemical cell
DCC	Dicyclohexylcarbodiimide
MeCN	Acetonitrile
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxidanyl
n-BuLi	n-Butyllithium
NMR	Nuclear Magnetic Resonance
TLC	Thin Layer Chromatography
IR	Infra-red
Ppm	Parts per million
rt	Room temperature
lit.	Literature
s	Singlet
d	Doublet
dd	Doublet of doublets
t	Triplet
q	Quartet
m	Multiplet
h	Hour

Abstract

The release of CO_2 into the earth's atmosphere has been increasing exponentially since the dawn of the industrial age. Mainly due to the burning of fossil fuels; needed for power generation this increased amount of CO_2 has been a direct cause to the increased greenhouse effect which in turn brings about severe consequences. Various ways of limiting the release CO_2 have been developed over the years, with varying degrees of efficiency and success. Carbon Dioxide utilisation (CDU) is a relatively new technique which utilises CO_2 rather than storing it. The main challenges associated with this technique stem from a sustainability aspect, therefore research is placed into developing methods which are environmentally friendly as well as energy and cost efficient.

Many research groups from around the world have developed various techniques and approaches to incorporate CO_2 into a variety of organics ranging from haloalkanes to alkynes. These techniques have ranged from using standard chemical reactions, intricate photocatalysts to using electrochemical processes, all with the main goal of forming a stable C-C bond, however all these methods possess some form of shortcomings. This project addresses the shortcomings in electrochemical methods associated with CO_2. The discovery of a novel electrochemical process using non-sacrificial carbon electrodes in the hydrocarboxylation of styrenes was achieved under mild conditions, (10 Volts, 1 atm CO_2 pressure, room temperature, non-sacrificial electrodes) was achieved producing the corresponding mono-carboxylic acids in a highly regioselective manner in good to excellent yields (50-85%). The novel method also proved successful in incorporating CO_2 in alkynes, dienes, and acrylates as well as the reducing of internal double bonds. Furthermore, mechanistic analysis was undertaken to deduce the mode of action, this included the use of deuterium labelled reagents, cyclopropyl traps as well as common radical traps. This work has shown the potential of non-sacrificial electrochemical cells, by-passing the environmental and efficiency issues attributed with common electrochemical cells. The bonus of high regioselectivity, robustness towards various functional groups and potential to apply to various starting materials further enhances the potential of this method in become a valuable tool in organic synthesis.

Contents

1.0 Introduction

Carbon Dioxide has been ever present in the earth's atmosphere since the formation of the planet 4.6 billion years ago. Early volcanic activity on the earth's surface produced an early prehistoric atmosphere mainly consisting of H_2O, CO_2, N_2, CH_4 and NH_3 in particular CO_2 was at a level 200 times higher than today's norms.[1] Its general abundance in the atmosphere and prehistoric oceans was crucial in the development of photosynthesis in early cyanobacteria [2] , which in turn was instrumental in a prehistoric event called the great oxygenation event causing the evolution of eukaryotic species; (human beings earliest pre-historic ancestors)

In the present-day, CO_2 is once again playing a major role in the earth's development. Through the continuous consumption of fossil fuels due to a variety of anthropologic activities CO_2 concentration has been steadily since the industrial revolution. The Mauna Loa Observatory in Hawaii has collected an unbroken record of CO_2 concentration in the air since 1957, with the data unequivocally showing a steady rise in CO_2 [3] (Figure 1) with the most recent measurement for May 2018 showing 411.25ppm of CO_2 ,up from 409.65ppm for the same time last year.
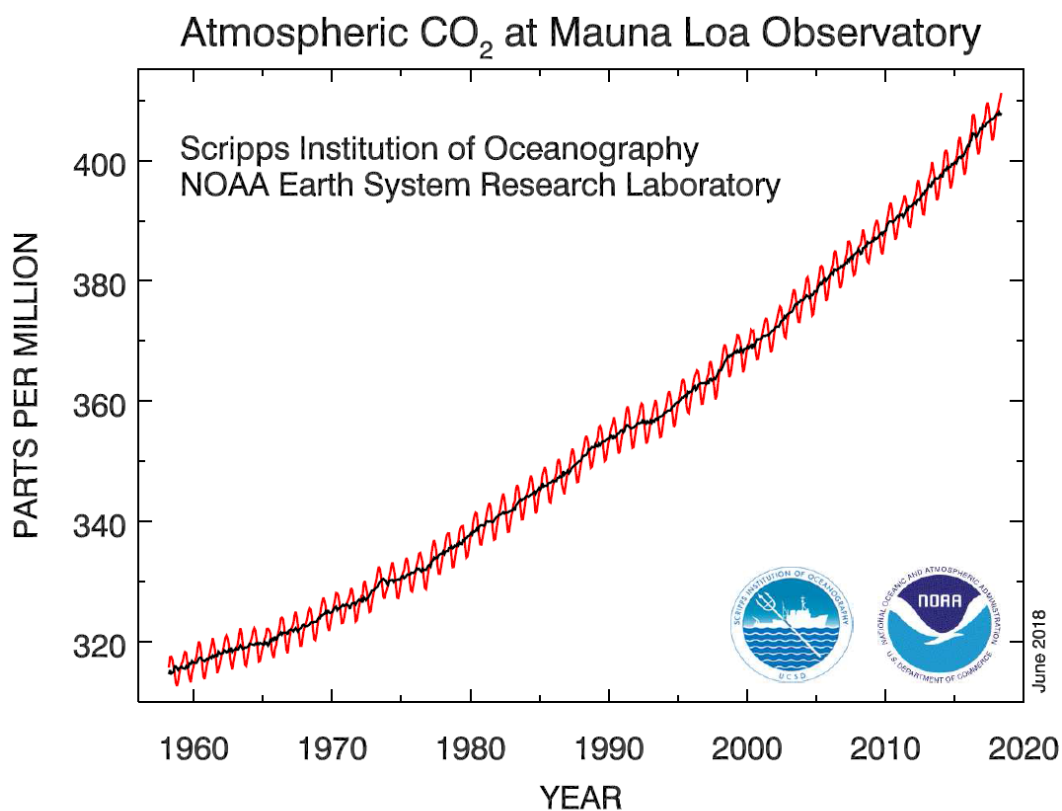
Figure 1: Atmospheric CO_2 measurements at the Mauna Loa Observatory in Hawaii[3]

To put this increase into further perspective ice core data, taken from multiple locations have indicated that atmospheric carbon dioxide had not reached levels above 300ppm for approximately 650,000 years, at which point human life was yet to exist (Figure 2). A paper published in Science goes even further estimating the last time CO_2 levels where as high as they are today was in the middle Miocene 20 million years ago[4].
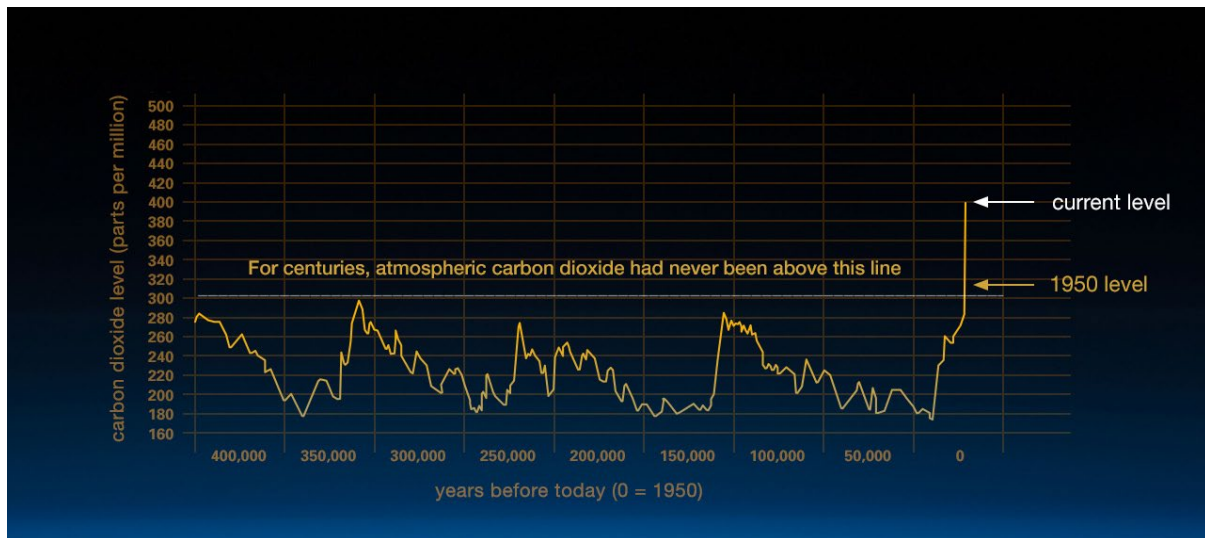
Figure 2: Vostok Ice core data in conjunction with Mauna Loa Observatory[5],[6]

CO_2 (as well as CH_4 and H_2O) is widely known to be one of the major greenhouse gases contributing to the well-known Global warming phenomenon. The greenhouse effect refers to a process in which solar radiation is absorbed and refracted by the surface of the earth. This outgoing radiation usually takes the forms of infra-red radiation of a longer wavelength than the incoming solar radiation. Due to this the outgoing radiation is absorbed by the greenhouse gases in the troposphere. These greenhouse gas increase their thermal energy which is re-emit and produces a warming effect. It therefore stands to reason that an increased amount of CO_2 would increase the effect of the greenhouse effect.

With an increased greenhouse effect, global warming is becoming more apparent as well as all the risks that come with it such as rising sea levels, desertification and destructive climate change. With impending danger greater efforts have been placed on the research and development on strategies which can reduce the amount of CO_2 emissions from anthropological sources.

1.1 Carbon Capture and Storage (CCS)

One strategy used to achieve the desired effect is carbon capture and storage (CCS).[7] CCS is a multi-step process in which carbon dioxide is produced in large amounts at point sources such as electricity generating plants, steel-works and cement plants is captured, compressed and transported via pipeline or a dedicated container ship and finally stored in a geological formation or stored in mineral form (mineral carbonation). Although effective at offsetting the amount of carbon dioxide released into atmosphere, there are little additional benefits after the carbon dioxide is stored.

1.1.1 Current CCS techniques

The success of CCS techniques is centres around 2 important processes which demand a high level of sophistication; the processes in question are CO_2 capture and CO_2 separation. Significant amounts of resources and time have been placed into developing suitable techniques which can prove to be cost effective on an industrial scale.

1.1.1.1 CO₂ Capture Techniques

Detailed studies have shown that initial capture of CO_2 can account for approximately 70-80% of the cost of a complete CCS system including transport and storage [8], therefore significant attempts have been made to optimise this process. The 3 main techniques for CO_2 capture revolve mainly around power generation plants namely the processes are post combustion, pre-combustion and oxyfuel combustion.

1.1.1.1.1 Post combustion

As the name suggests, this technique focuses on capturing CO_2 from the flue gas produced from point sources, mostly coal and gas fired power stations. This is a proven technology which is able to capture 800 tonnes of CO_2 per day.[9] However there are several drawbacks to this technique, the concentration of CO_2 in flue gas is relatively small (4%- 17%) making this method quite inefficient and the parasitic effect of other compounds in flue gases (SO_x and NO_x) can hinder the capture of CO_2. These negative effect have an overall effect of increasing the price of electricity produced at power stations by 32% to 65% with this type of capture technology installed.[10]

1.1.1.1.2 Pre-combustion

The pre-combustion capture of CO_2 involves the pre-treatment of the fuels used in electricity generation such as coal and gas (Scheme 1) . Coal is presented to the process of gasification affording a syngas mixture of carbon monoxide and hydrogen, a further reaction with steam will convert any carbon monoxide to carbon dioxide and hydrogen gas. This method allows for a higher percentage of CO_2 in the final product (>20%) allowing for easier extraction.[11]

$$Coal \xrightarrow{\text{Gasification}} CO + H_2$$

$$CO + H_2O \xrightarrow{\text{water gas shift}} H_2 + CO_2$$

$$CH_4 + H_2O \xrightarrow{\text{reform}} CO + H_2$$
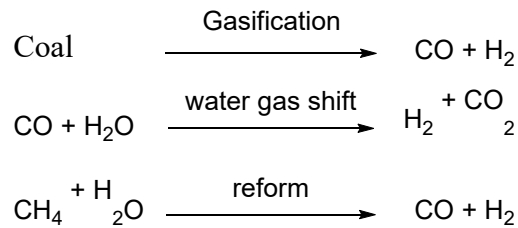
Scheme 1: Pre-treatment of coal and natural gas

A similar process of reform is taken with natural gas to produce the syngas mixture. This process is involves several addition process however it has been proven to be effective in capturing CO_2 as well as being relatively economical by Hoffmann *et al*. [12]

1.1.1.1.3 Oxyfuel Combustion

This final process revolves around the fact that burning fuel in an oxygen high atmosphere produces a higher concentration of CO_2. It is well known that perfect combustion produces only water and CO_2, in the case of fuels a certain amount of SO_x and particulates are produced with a markable reduction in the production of NO_x. The resulting SO_x and particulates can easily be removed with well-developed techniques such as electrostatic precipitators as well as flue gas desulphurisation. As of 2014 only small scale pilot projects have been developed [13] , mainly due to the added financial cost associated with using increased amounts of O_2 causing a higher cost for subsequent electricity.[14]

CO$_2$ separation is a key step in the CCS process, ultimately all the CO$_2$ captured from various sources is not pure. The main source; flue gas from power stations contains a variety of impurities such as N$_2$, O$_2$, NO$_x$, SO$_x$, H$_2$O and CO as well as particulates, which requires purification if a pure stream of CO$_2$ is required. There are several ways to achieve these goals, here we will discuss the three most popular options:

1. Absorption
2. Adsorption
3. Cryogenic Distillation

1.1.1.2.1 Absorption

Perhaps the most viable and well researched separation is CO$_2$ absorption through the use of amine-based solvents. Of these alkanolamine solvents monoethanolamine (MEA) and diethanolamine (DEA); and MEA has been shown to be significantly effective. The basic principle behind the action of this solvent, is that chemical affinity for CO$_2$ is higher than all the other compounds in flue gas allowing for easy absorption. The ideal conditions for absorption are low temperatures and high pressures whilst desorption is quite the opposite with high temperatures and low pressures allowing for successful desorption. The mode of action of MEA based solvents has been widely studied with Jing *et al*.[15] showing in 2015 that the CO$_2$ made a huge difference with carbamate formation being favoured at low CO $_2$ concentrations and CO$_2$ hydration preferring a higher concentration of CO$_2$ (Scheme 2).
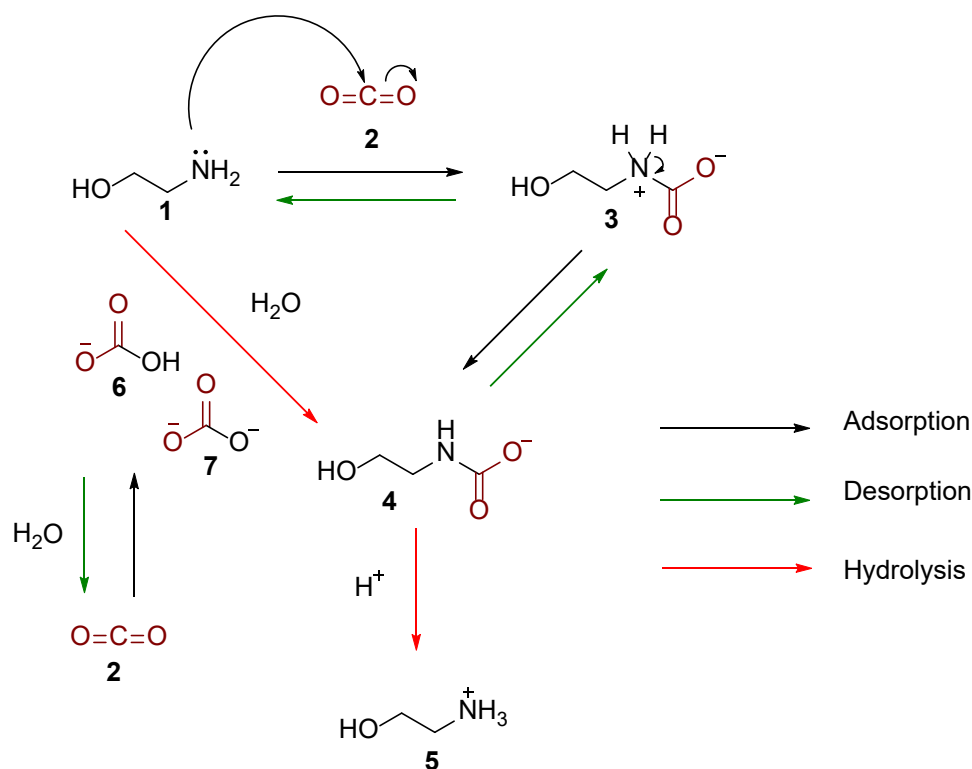
Scheme 2: Potential mode of action of MEA.

Perhaps the most successful application of absorption technology has been undertaken by Mitsubishi Heavy Industries (MHI), as of 2014 they have received an order for a fully-fledged post combustion capture and separation unit to be retrofitted to an existing coal fired power station in Texas, with the potential capture a total of 4776 metric ton per day. This is partly down to KS-1 solvent used which was shown to have a higher potential loading of CO_2 as well as a lower energy requirement for regeneration.[16] However all absorption systems are held back by some major drawbacks such high energy cost of regenerating the solvent, high levels of corrosiveness and large volumes of absorber material needed, this has led to research into a viable alternative.

1.1.1.2.2 Adsorption

Adsorption is quite similar to the previous method of CO_2, the main difference being that whilst, absorption is based on the solvation of CO_2 in a solvent, adsorption is a process whereby CO_2 molecules are trapped on a solid surface to be recovered at a later time. Adsorption can be achieved by a variety of materials. Physical carbonaceous sorbents such as activated carbon[17] and graphene[18] have been shown to be a low cost option with high thermal stability, however they are hindered by a lack of selectivity towards CO_2 as well as a lowered activity as higher temperatures. The Fauth group explored the idea of using binary and ternary eutectic salt-modified Li_2ZrO_3 as possible sorbents.[19] The groups premise was based on the reaction of Li_2ZrO_3 and CO_2 to form Li_2CO_3 (Scheme 3), by doping the

simple Li_2ZrO_3 with alkali metal carbonates they found that the amount CO_2 and speed of adoption can be significantly increased. These types of metallic based sorbents are highly sensitive to water, showing a marked reduction in activity with water present.

$$Li_2ZrO_3 \cdot CO_2 \longrightarrow Li_2CO_3 \cdot ZrO_2$$
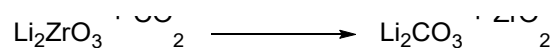
Scheme 3: Formation of Lithium carbonate from CO_2

Recently the Yang group has been able to use amine grafted silica to show good CO_2 adsorption at relevant conditions (0.15 bar and 25°C).[20] The group found that by increasing the porosity of SBA-15 silica via ethanol extraction or high temperature calcination followed by effective grafting of 3-aminopropyl they were able to increasing the volume of grafted amine. This translated into a rise of CO_2 adsorption capacity from 1.05 mmol/g to 1.6 mmol/g, an overall increase of about 52%. Coupled with the increased selectivity towards CO_2 as well as the overall robustness of the compound produced, this method has proven that doping simple silica-based sorbents can prove to be an effective means of separating CO_2.

1.1.1.2.3 Cryogenic Distillation

One thing that both the previous technologies have is their lack of purity, any CO_2 produced after separation will still have impurities present ranging from 2%-5%. If the CO_2 is needed for storage in geological formation or EOR then this would not pose a problem; however, this CO_2 would be considered too impure to use in a chemical setting. Cryogenic distillation was pioneered by Carl von Linde in the 19th century, with the purpose of producing high purity gases. It carries this out in a similar way to fractional distillation of liquids albeit under increased pressures and reduced temperatures. This concept was taken further by the Liu group who conducted simulation and techno-economic studies showing that producing CO_2 with 99.99% purity at 0.425MJ/kg was theoretically possible.[21] If these numbers where to be achieved they would prove to be about 50% cheaper than the current MEA based absorption methods. One significant drawback that hinders this particular study is the fact that the group was using atmospheric air, flue gas from a point source may prove to impure and require added purification before undergoing cryogenic distillation, thereby increasing the energy and economic cost.

1.2 Carbon Dioxide Utilisation (CDU)

An alternative to CCS is carbon dioxide utilisation (CDU); the utilisation of CO_2 to form value added products. The various techniques employed to achieve this are described and are the main focus of this literature review.

Carbon dioxide (CO_2) is an abundant, economical and non-toxic gas. It can also be deemed environmentally friendly as it can be used as a substitute for phosgene which is widely used as a C1 building block in industry and research laboratories alike. These properties should in practise make CO_2 the perfect reagent, however being the most oxidised form of carbon has its downfalls, the main being the low energy level of CO2. In other words, for CO_2 to react a large input of energy is necessary, this can be achieved by:

1. Using high energy reagents, such as unsaturated compounds and organometallics (chemical).
2. Aim for low energy oxidised target products, such as carbonates (chemical).
3. Supply physical energy to the reaction, through electricity or light (electrochemical, photochemical).

These methods can be further enhanced by the use of catalysts. As well as chemical, electrochemical and photochemical pathways, biological and inorganic methods of carbon dioxide transformation is possible through the use of bacteria and mineralisation; this literature review will mainly focus on the various chemical, electrochemical and photochemical state of the art methods currently being researched and utilised. Scheme 4 shows the current transformations of carbon dioxide which are at the forefront of research.
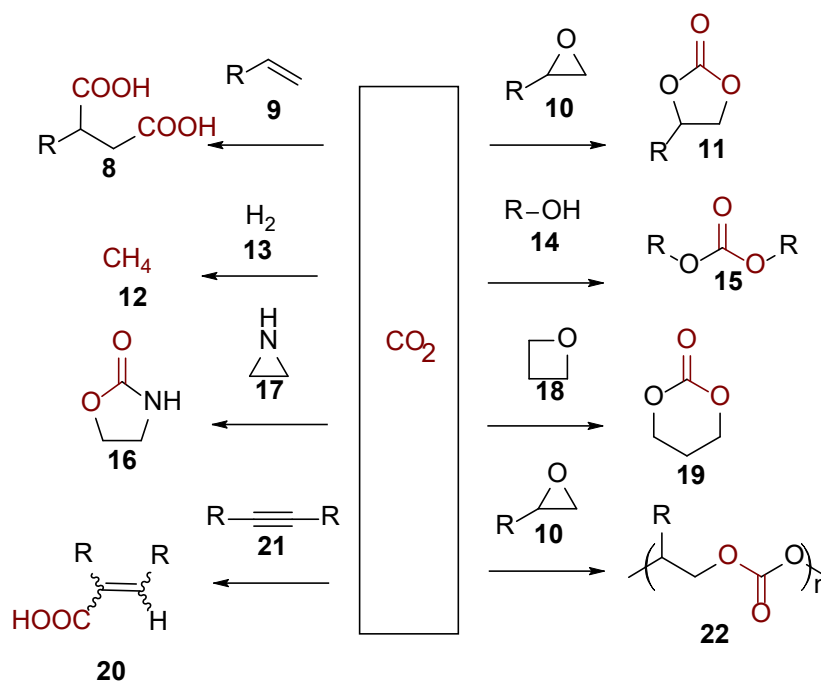
Scheme 4: Transformations of carbon dioxide currently being researched

1.3 Chemical transformations of CO_2

Carbon dioxide is effectively the most oxidised form of carbon making it extremely low-energy, this being said a high energy input must be applied to initiate a reaction. In many circumstances high temperatures and high pressures can be applied. Whilst this is not particularly efficient, an alternative to this would be to use high energy reactants such as epoxides, aziridines and organometallics coupled with catalysts.

1.3.1 Catalytic reactions with epoxides

Epoxides are a type of cyclic ether with a highly strained ring system making them highly reactive, therefore being used extensively in reactions with carbon dioxides utilisation reactions particularly in the synthesis of various cyclic carbonates and polycarbonates. (Scheme 5)
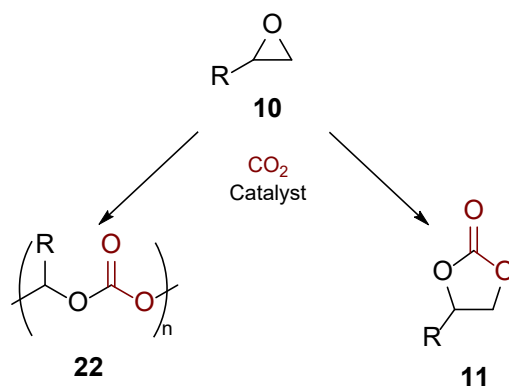
Scheme 5: Potential routes for the reaction of epoxides with CO_2

1.3.1.1 Synthesis of Cyclic Carbonates

Cyclic carbonates have been used as intermediates for polycarbonates, electrolytes in Li-ion batteries, and green solvents. The main route for synthesis of these useful compounds is the cycloaddition of CO_2 to epoxides and oxetanes to give 5 and 6 membered rings.[22] (Scheme 6)
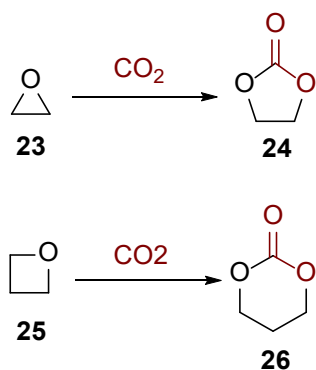
Scheme 6: Reaction of epoxide and oxetane with CO_2

As stated previously the formation of cyclic carbonates with relation to CO_2 is not a particularly new with certain processes focused around the production of ethylene carbonate and propylene carbonate being effectively commercialised since the 1950s.[23,24] Various literature has been posted since then involving many catalysts but the underlying high energy conditions persisted.

Recently research carried out by Kleij and co-workers reported a Zn(salphen) catalyst (Figure 3) which proved to be a very efficient catalyst in the production of cyclic carbonates from terminal epoxides, the notable exception being that all these reactions were carried out under very mild conditions.[25]
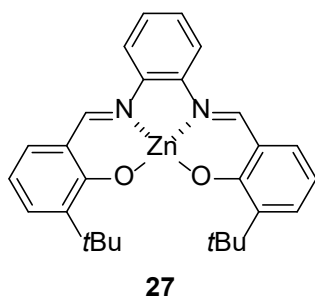
Figure 3: Zn(salphen) catalyst developed by Kleij group
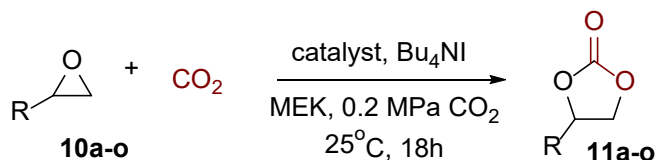
Scheme 7: General reaction conditions for the cycloaddition of CO2 as developed by Kleij and co-workers.

Features of note in this catalytic system centre around the catalysts ease of synthesis, non-toxicity and abundance. With regards to the reaction conditions, after a trail of potential solvents MEK was shown to be most effective owing to the fact it has a higher affinity for CO_2 allowing for easier dissolution of the gas. The physical conditions of the protocol were very mild with the reaction progressing under room temperature and a slightly increased pressure of CO_2. All these properties make this protocol quite an attractive option for potential integration into industrial application.

Although very promising a lack of scope hinders this reaction as good to excellent yields was only achieved for 9 epoxides with a limited variation in functionality, as it shown nearly all products have aliphatic groups adjacent to the carbonate system. The only variation being the aromatic product which carries a very low yield. (Figure 4)

86%
11a

83%
11b

80%
11c

55%
11d

15%
11e

89%
11f

73%
11g

34%
11h

79%
11i
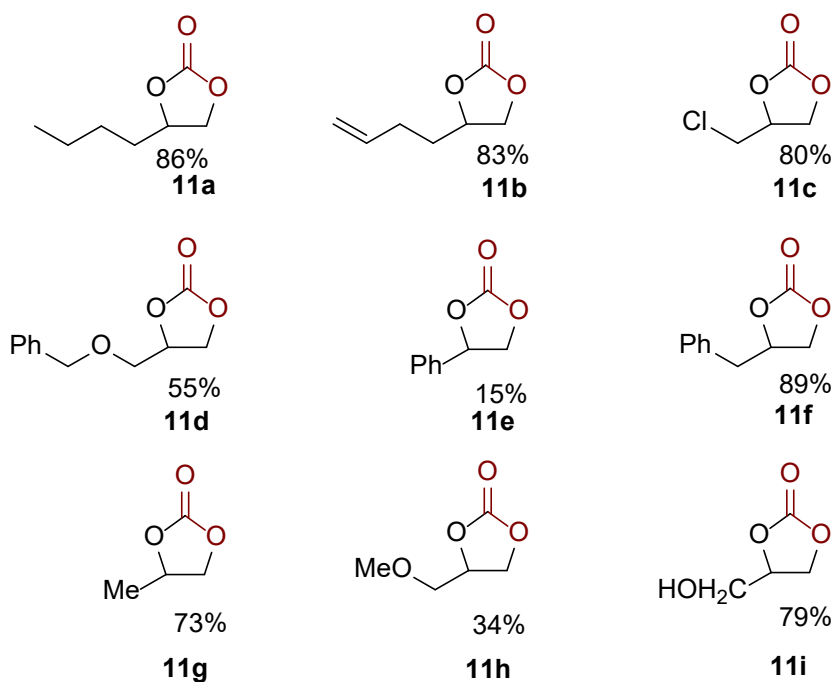
Figure 4: Brief representation of the scope of the Kleij catalytic system.

To try and remedy this lack of scope, Kleij and co-workers developed an aluminium based complex with an amino triphenolate ligand. [26] The facile synthesis of this ligand was carried out by reacting AlMe₃ and the necessary ligand in the THF, afford the Al complex in high yield (80%) (Scheme 8)
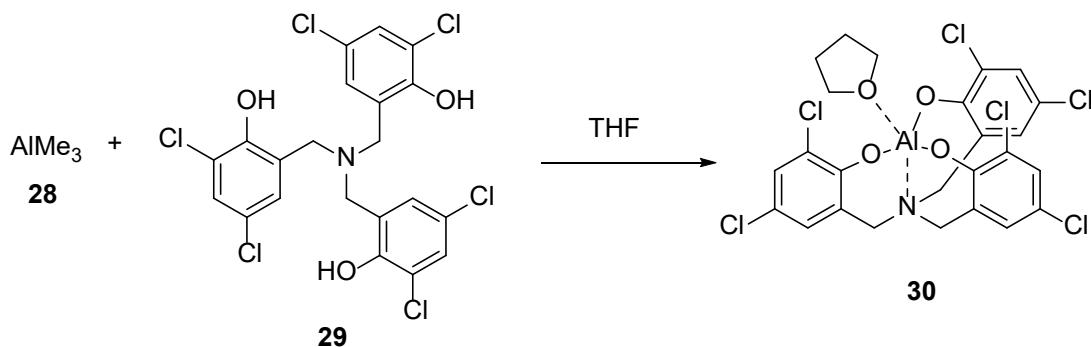
Scheme 8: Synthesis of Al complex

This Al complex coupled with a Bu₄NI cocatalyst was shown to be effective in converting severally highly functionalised terminal epoxides, with yields ranging from excellent to adequate (98%-40%). Many of these highly functionalised epoxides contained O and N atoms which could potentially coordinate with the metal centre, thereby hindering the reaction, however no such coordination observed allowing for conversion to the cyclic carbonates to proceed.
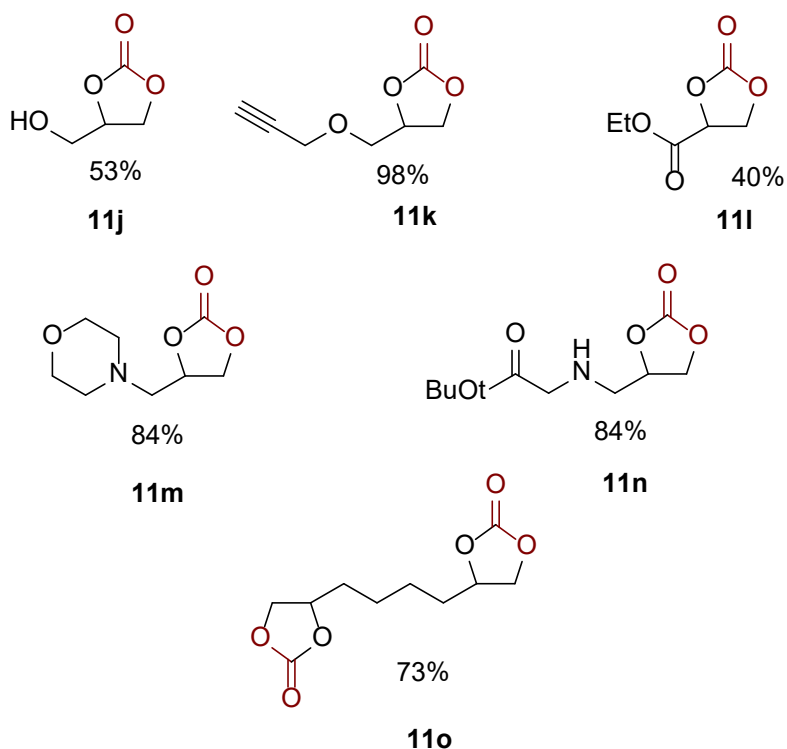
Figure 5: Scope of the Al complex

This method was also successful in converting internal epoxides and oxetanes into their corresponding cyclic carbonates, although in these cases the added stability of the epoxides and oxetanes meant alterations to the reaction conditions such as a change in cocatalyst or an increase in reaction temperature. A defining quality of this catalytic system is the high turnover of frequencies (TOF) going as high as 36 000 h^{-1} in some cases, currently these kinds of numbers are the highest reported in any cycloaddition of CO_2 to epoxides.

North and co-workers hypothesised that bimetallic salen complex would yield further improvements in the synthesis of cyclic carbonates from epoxides. [27] The group chose to use aluminium as the base for their new catalyst. Catalyst **32** was prepared by the reacting salen ligand **31** with triethoxyaluminium.
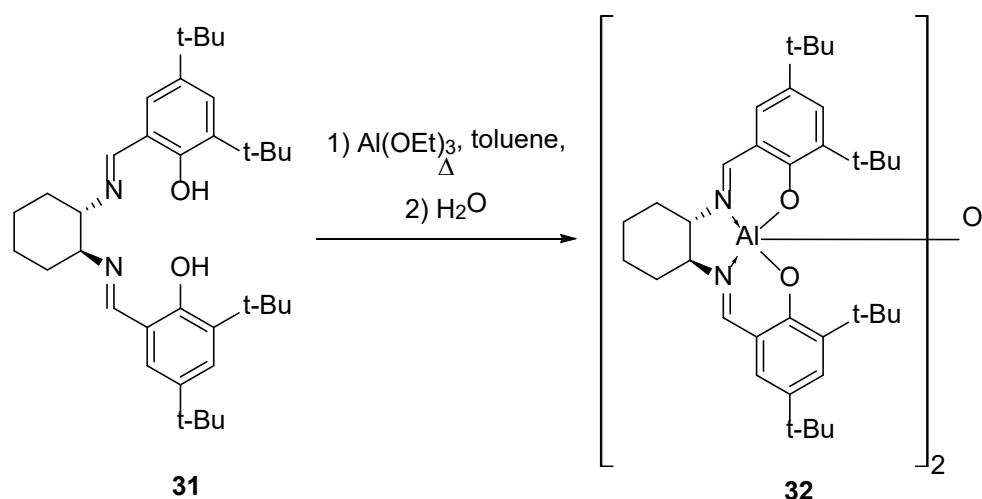
*Scheme 9: Synthesis of catalyst **32***

The catalyst was shown to be catalytically inactive when introduced without the tetrabutylammonium bromide cocatalyst, and at optimal conditions (catalyst loading of 2.5 mol%, cocatalyst loading 2.5 mol%, pressure, 1 atm, temperature, 25°C, time, 24 hours) the reaction in scheme 11 had a conversion of 98%. Further study on this catalytic system showed that it can work on a variety of epoxides, (table 2) as well as being quite robust, as after 60 uses there was minimal loss of activity.

Kinetic studies showed that the reaction exhibited first order kinetics for all the reaction components except for TBABr which exhibited second order kinetics. This prompted the group to propose a potential catalytic cycle (Scheme 10).
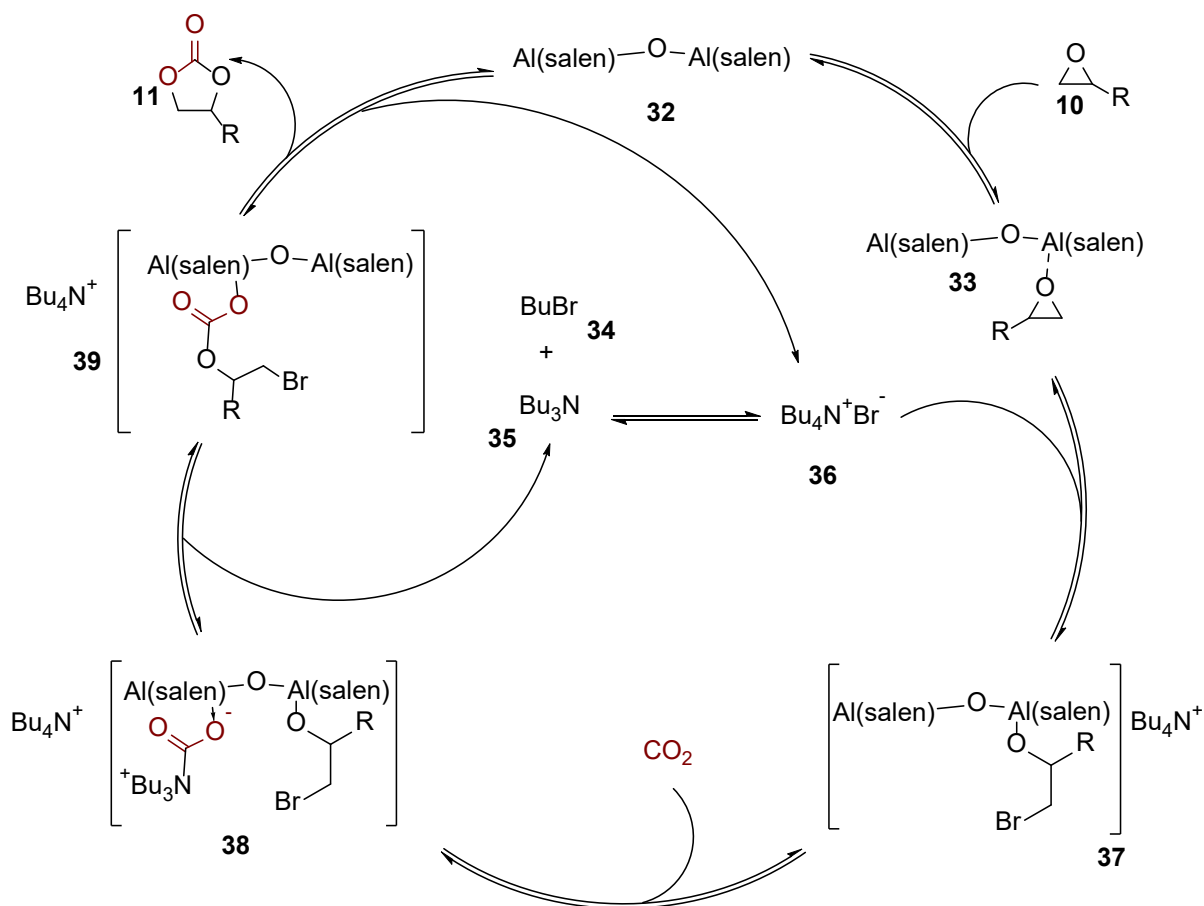
Scheme 10: Proposed catalytic cycle of catalyst 32

North and co-workers had a goal of utilising waste carbon dioxide in flue gas as a carbon dioxide source. This posed a variety of problems; firstly, the composition of the flue gas is so varied. The main component of flue gas is N_2, just like in air it accounts for around 70%, the next major components tend to be O_2, CO_2 and H_2O with concentration of about 10%, 10% and 5%. The last 5% has various species in it most notably SO_2, SO_3, CO and oxides of nitrogen. In prior studies the source of CO_2 for the experiments was acquired from either dry ice pellets or pure CO_2 cylinders, both of these are mostly pure CO_2, so no study was carried out to see how the catalyst would react to these various reactive species and if they would kill the catalytic action. Another problem faced was that if the reaction with flue gas was to be implemented it would have to be part of a continuous flow reactor, which would mean the reaction would have to take place in the gas phase with an immobilised catalyst. To be immobilised the catalyst would have to be modified do it can function as a one component catalyst with the TBABr or similar molecule incorporated into its structure[28].

The catalyst **40** (Figure 6) was based heavily on catalyst **32** although it was synthesised through a completely different route due to the presence of tetraalkylammonium groups.

15
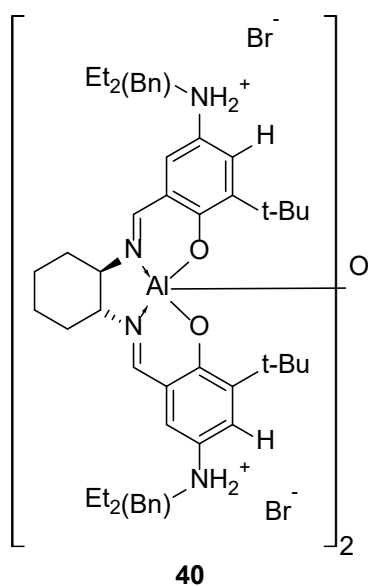
Figure 6: North salen catalyst

The catalyst was shown to be reactive with a variety of epoxides as shown in table 1.
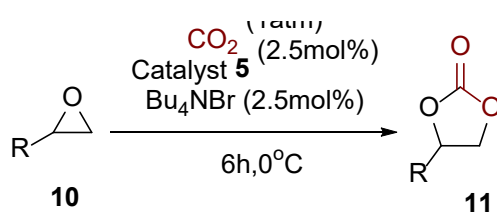
Scheme 11: General reaction conditions for cycloaddition of epoxides

Table 1: Cycloaddition of epoxides with North catalyst

Entry	Epoxide	Conversion	Yield %
1	R= Ph	97%	89%
2	R= Oct^n	81%	68%
3	R= CH_2Cl	100%	81%
4	R= CH_2OH	79%	65%
5	R= Me	50%	62%
6	R= $4\text{-}BrC_6H_4$	93%	85%

The group then went on to successfully immobilise the catalyst on a variety of mediums such as polystyrene, amorphous silica and aluminium pillared clay. Of these the catalyst immobilised on silica proved to be the most successful. A gas-phase flow reactor was created, and experiments were run with ethylene oxide as the control substrate (Figure 7).
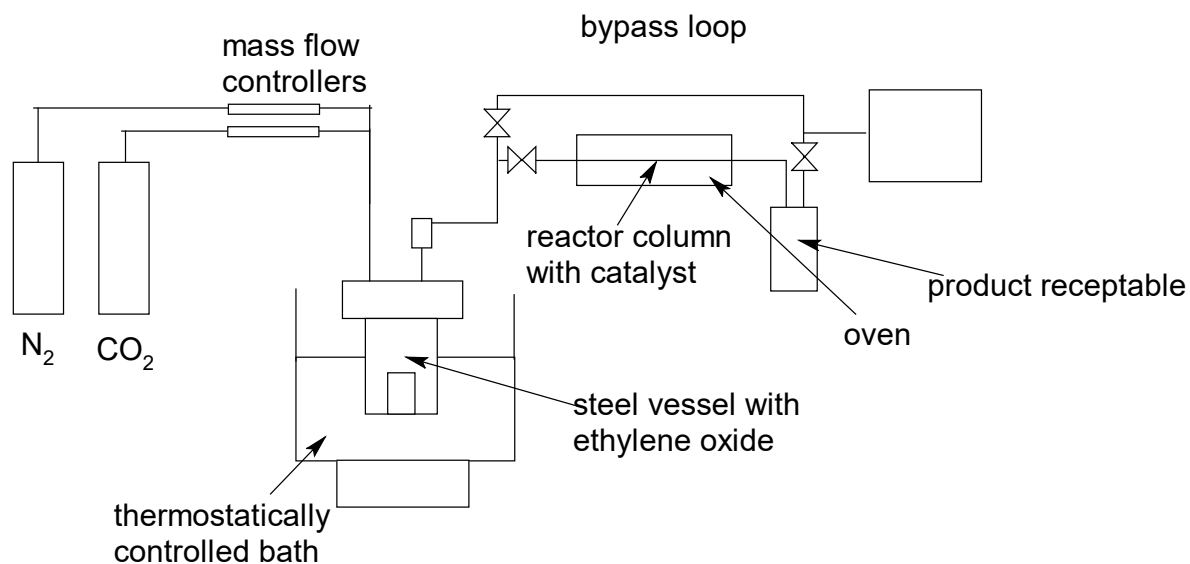
Figure 7: Gas-phase flow reactor created by North and co-workers

Results had shown that high conversion could be achieved on several occasions. Future work in this area will focus on making the catalyst more robust due to the fact that prolonged exposure slowly deactivates the catalyst, sometimes irreversibly.

1.3.1.2 Synthesis of Polycarbonates and Polyurethanes

1.3.1.2.1 Polycarbonates

Cyclic carbonates have found many uses in today's world in the form of valuable precursors for medical applications, polar aprotic solvents and useful intermediates in organic syntheses. They are also extensively used as the raw ingredients in the formation of polycarbonates. Polycarbonates have found many uses due to their outstanding physical properties; polycarbonates are highly impact resistant and can withstand high amounts of strain. These properties can be attributed to the fact that most polycarbonates are amorphous and contain long polymer chains which can distribute impact force throughout the structure rather than have it focused on a single point. Coupled with a relatively low glass transition temperature making them ideal for use in various objects ranging from water-bottles and plastic sheeting to fighter jet canopies and car roofs.

Currently many examples of polycarbonate formation can be found in the literature, nearly all iterations of this reaction employ a Zn catalyst, of these catalytic systems, the one reported by the Williams group has been shown to be highly active under pressures as low as a single atmosphere of CO_2.[29] The catalyst shown is easily prepared in a three-step process with and overall satisfactory yield (60%) (Scheme 12).

1: KH, THF, -78°C,1h
2: Zn(OAc)$_2$, THF, rt, 16h

X = OAc

41   **42**
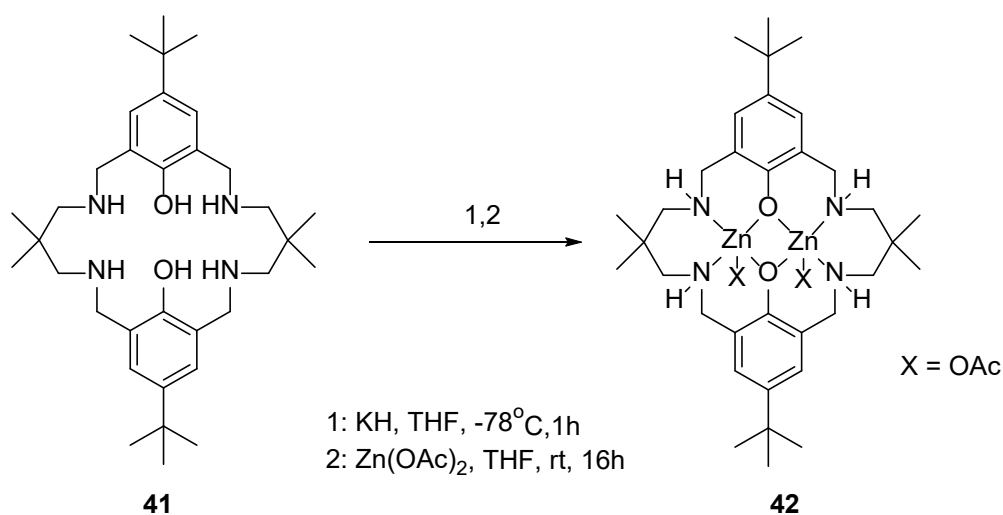
Scheme 12: Synthesis of Williams catalyst

The Williams group catalyst showed excellent levels of activity and robustness comparable with several other catalysts described in the literature, the defining quality of this catalyst was the fact that activity was not compromised when the pressure of CO_2 was dropped to that of one atmosphere.[30,31] The group believe that it is the macrocyclic nature of the ligand coupled with the bimetallic core which

instils the catalysts attributes. The only mark against this research is the extremely limited scope presented with only cyclohexene oxide being polymerised.
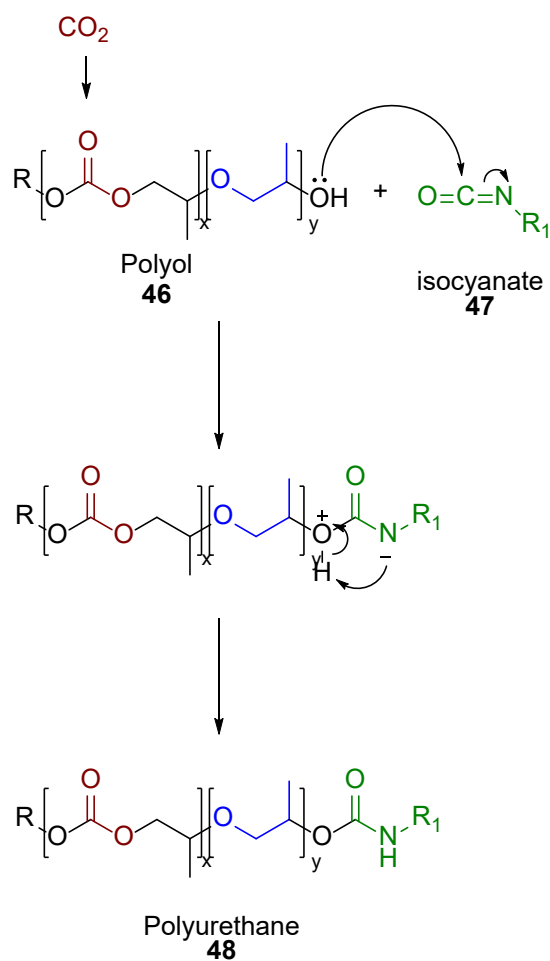
1.3.1.2.2 Polyurethanes

Polyurethanes are an important class of polymer, which has found multiple uses in the modern world, from foam in mattresses, corrosion resistant coatings and thermal insulations. These varied application stem from the highly changeable chemical and morphological nature of polyurethanes. Traditionally polyurethane was formed from the polycondensation of diisocyntaes and diols (Scheme 13) , this type of formation presents problems in terms of health risks and the environmental impact. [32,33] Recently innovative protocols have been reported in the literature discussing the use of CO_2 as a substrate in the direct or indirect formation of polyurethanes.

$$HO-R-OH \quad + \quad OCN-R_1-NCO \longrightarrow$$

43   **44**

45
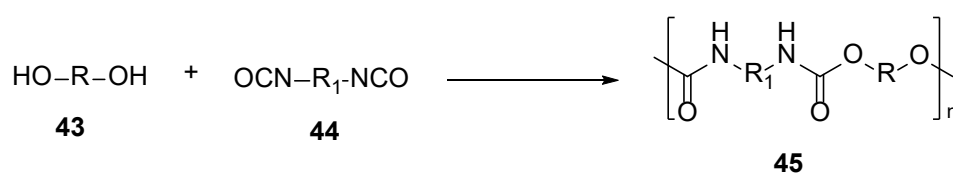
Scheme 13: Tradioanal polyurethane synthesis

Indirectly CO_2 can be used to synthesis polycarbonate polyols which when used in a copolymerisation reaction with isocyanate to produce various polyurethanes. The synthesis of polyols has received a lot of attention with various groups reporting new protocols in the formation of highly specialised polyols, coupling this wide the vast array of potential isocyanates allows for the formation of polyurethanes, which due to their varying physical and chemical properties can be used as foams, elastomers, fire retardant and insulating coatings, adhesives, sealants and membranes. [34-36] This type of reaction has been elevated to a high standing recently by Covestro (formerly Bayer MaterialScience) who have developed an innovative industrial process which produces cardyon™, this new polyol has CO_2 incorporated directly in its structure accounting for 20%. The polyol showed comparable properties to that of Arcol® Polyol 1108 and Desmophen® 1159, these two polyols are already established reactants in the production of PU foam used in mattresses. With a production capacity of 5000 metric tons per year cardyon™ is a viable alternative which can take a significant step in reducing CO_2 in the atmosphere. [37] Life cycle assessment produced by Bardow and Assen on the use of CO_2 in a polyol production in pilot plants state that although this technique does not act as an overall greenhouse gas sink, however it does allow for an overall reduction between 11-19% in GHG produced from comparable processes. [38] This drop on GHG will have a positive effect on reducing and hopefully reversing environmental damage such as terrestrial acidification and ozone depletion.

Scheme 14 shows the general reaction of CO_2 based polyols with isocyanate forming polyurethanes.

Scheme 14: Synthesis of polyurethanes from polyols and isocyante

As we have seen previously epoxides can be used in conjunction with CO_2 to form various cyclic and poly carbonates, aziridines are another type of cyclic compound which has the potential to react with CO_2 to form cyclic urethanes and polyurethanes. [39] (Scheme 15)
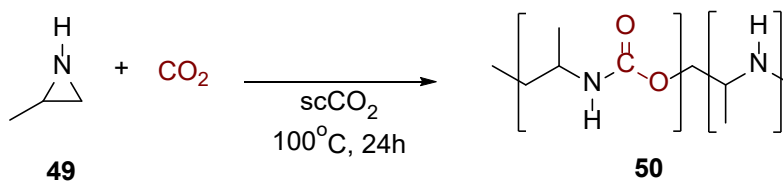
Scheme 15: Synthesis of polyurethanes from aziridines

The Ikeda group reported a simple protocol to form 2-oxazolindes from 2-methylazirines in 1976. This is an interesting reaction however the research carried out was minimal, with very investigation into the effect of the variables and no scope presented. [40] (Scheme 16)
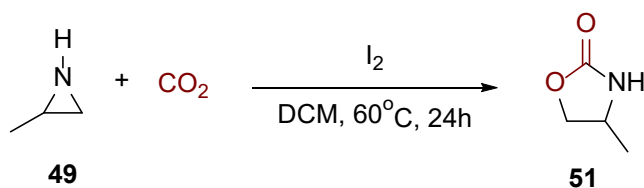
Scheme 16: Synthesis of 2-oxazolindes

The first reported incident of CO_2 being used in the formation of polyurethanes was reported by the same group 2 years prior. Ikeda and co-workers investigated the copolymerisation of propyleneimine with carbon dioxide.[41] Initial results showed a meagre CO_2 concentration of 10mol% in the subsequent polymer, however an increase in polymerisation temperature pushed the CO_2 composition of the polyurethane to 35%.

To date research in this area has been very limited, one significant paper put forward by Kayaki and Ikariya further investigated the reaction in Scheme 14 and the effects of supercritical CO_2 on the urethane content of the subsequent polymer.[39] Their research showed that an increase of carbon dioxide pressure from 3.0 MPa to 22.0MPa increased the urethane content from 32% to 62%, urethane content could be further increased through the addition of N,N-dimethylacetamide.

These protocols are hindered greatly by the fact that high amounts of energy are necessary for them to proceed reducing their economic impact and majorly offsetting any gain in environmental impact.

1.4 Heterogenous catalysis with CO_2

Carbon dioxide as a C1 building block has seen utilisation in an industrial setting since the invention of the Kolbe-Schmitt synthesis. Hermann Kolbe reported in 1860 the successful synthesis of salicylic acid (2-hydroxy-benzoic acid) (Scheme 17) through the heating of sodium phenoxide under a carbon dioxide atmosphere followed by an acid workup.
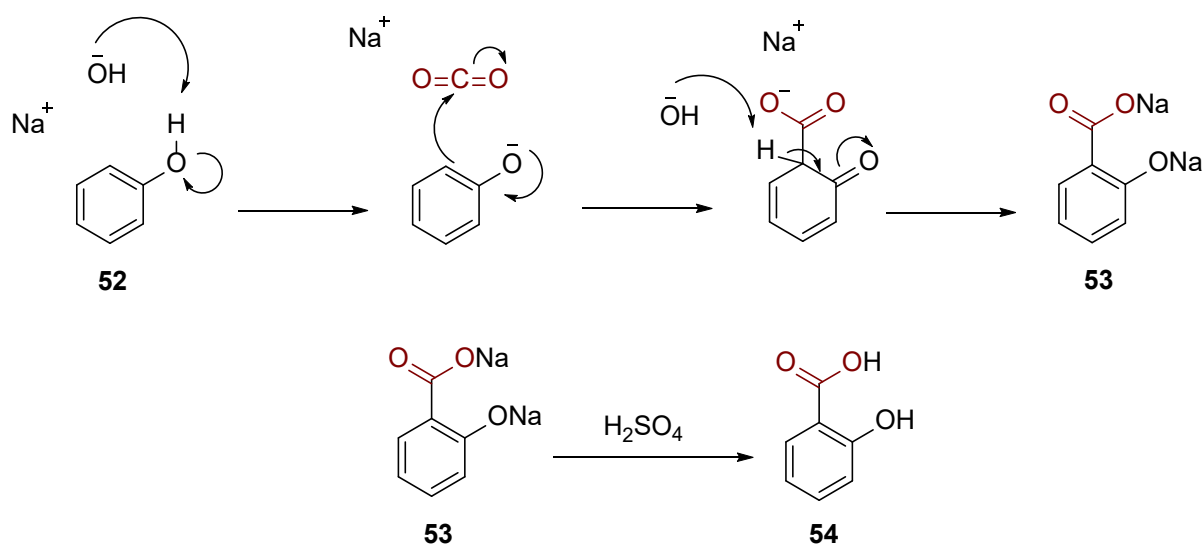
Scheme 17: Kolbe synthesis of Salicylic acid

This reaction has proven to be extremely successful with subsequent modification improving the yield and allowing it to still see use today as an important step in the synthesis of Aspirin. [42] Another early approach used to incorporate CO_2 into organic molecules is by the use of so called "Grignard Reagents "and other organometallic species. Grignard reagents act as strong nucleophiles attacking the electrophilic centre of carbon dioxide affording the corresponding carboxylic acid after acid workup (Scheme 18). The nature of Grignard reagents accounts for this method's main drawbacks, this method cannot be readily applied to form highly functionalised carboxylic acids, as well as the production of harmful by products. [43]
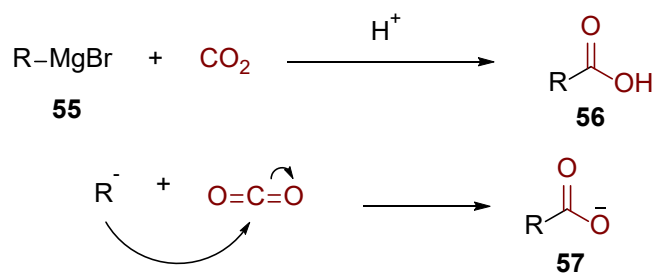
Scheme 18: Grignard reaction with CO_2

It was therefore necessary to develop new methods to achieve effective carboxylation of various substrates, one method that has been adopted by several groups recently utilises bi-metallic catalytic systems which can be easily tuned to afford a desired product.

Several catalysts with varying metallic cores have been reported, with Pd, Rh, Cu, Ni, and Zn proving to be some of the most effective.

1.4.1 Palladium

Initial attempts to for a catalytic system to perform carboxylation with CO_2 was undertaken by the Shi group, the group reported a palladium catalysed carboxylation of allyl stannanes (Scheme 19), [44] initial reactions of the carboxylation where carried out in the absence of any catalyst, and even under a pressure of 33 atm and 70°C no reaction of allylstannane and CO_2 was observed, investigation into catalysis was undertaken. The catalyst employed was the highly popular and well used palladium tetrakis; which has previously been used in many named coupling reactions.
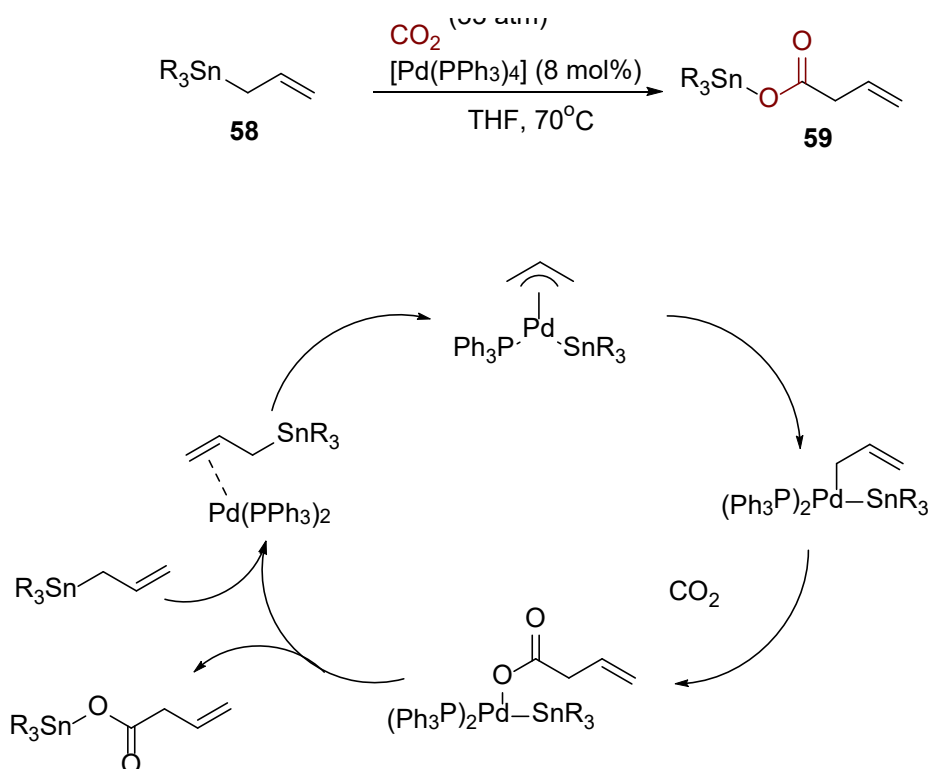
Scheme 19: Palladium catalysed carboxylation of allyl stannanes and propsed catalytic cycle

Under the same conditions and in the presence of 8 mol % Pd(PPh$_3$)$_4$ compound **58** was converted to the corresponding carboxylates. Although highly novel and significant the application of this process was severely limited by the substrate scope, and harsh reaction conditions.

Another significant drawback with the Shi catalytic system is the relative difficulty associated with acquiring the starting substrates, with allylstannanes not being readily available. Research was undertaken by several groups to uncover carboxylation reactions which used more readily available starting materials. One such discovery was reported by the Martin group in 2009.

The group's research focused on the synthesis of benzoic acids through the direct carboxylation of aryl bromides. (Scheme 20) In the past this type of transformation was carried out with the use Carbon monoxide (CO), this carbonylation has proven to be successful in synthesising compounds such as carboxylic acids, esters, amides as well as anhydrides, ketones and aldehydes.[45] Although highly adaptable, one serious drawback of such a reaction is the heavy usage of CO which is extremely toxic. This drove the Martin group to explore avenues whereby CO_2 can form a direct substitute to CO.

The groups initial investigation focused around a Pd(OAc)$_2$ as this proved to be the most viable catalyst. To render the system catalytic Et$_2$Zn was added in stochiometric amounts to act as a reducing agent thereby by completing the catalytic cycle and recovering the Pd^0 active species. This technique has been widely used by many other groups. [46] [47]
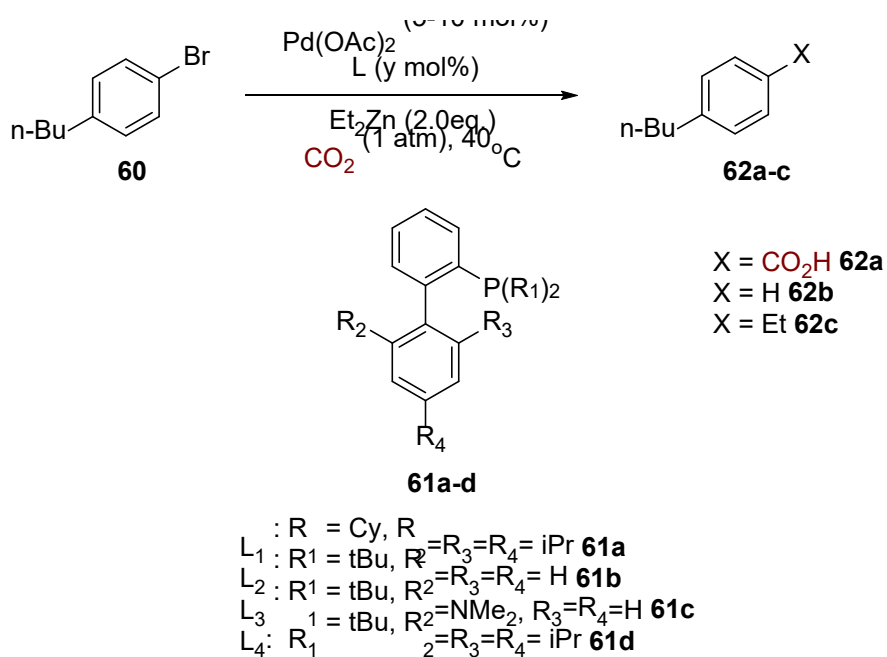
Scheme 20: Palladium catalysed carboxyaltion of aryl bromides

Table 2 : Optimisation towards synthesis *62a*

Entry	L (y mol%)	Solvent	62a (%)	62b (%)	62c (%)
1	**61a** (20)	DMA	0	0	99
2	**61b** (20)	DMA	0	0	99
3	**61c** (20)	DMA	0	0	99
4	**61d** (10)	DMA	56	24	0
5	**61d** (10)	DMF	19	28	27
6	**61d** (10)	NMP	0	99	0
7	**61d** (10)	DMSO	0	31	69
8	**61d** (10)	DEA	0	19	81
9	**61d** (10)	DMA	64	17	0

It was shown that temperature, ligand structure and even solvent had a distinctive impact on the yield of the target compound. In nearly all cases dehalogenation occurred forming Neigishi type by products such as **62b** and **62c**. This can be partly explained by the theorised transmetallation with the Et_2Zn. With optimised conditions keeping by products at a minimum the group was allowed to show that this type of catalytic system was quite robust and showed a good tolerance to various functionalities with a few examples shown in Figure 8.
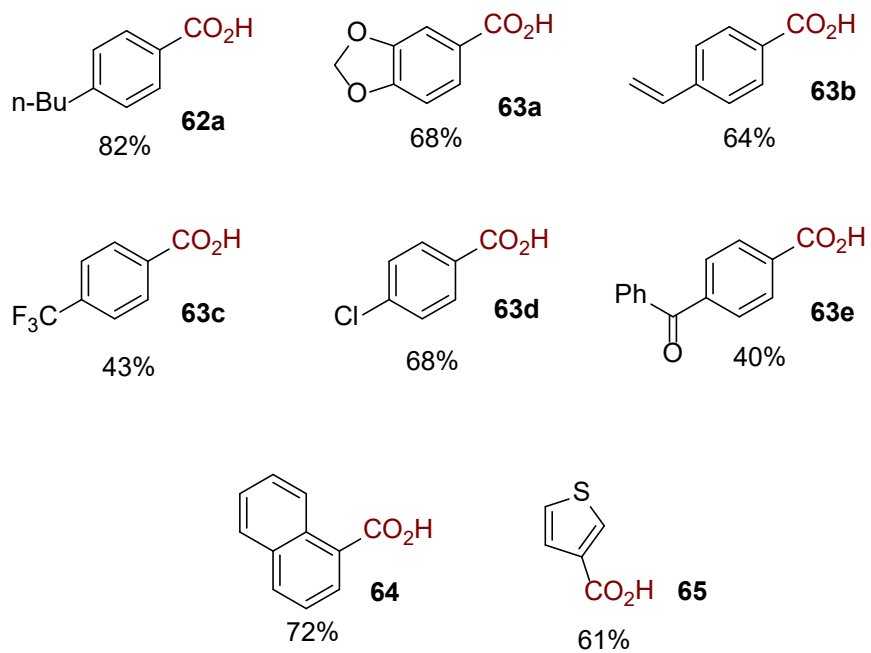
Figure 8: Scope of Martin carboxyaltion of aryl bromides

1.4.2 Rhodium

Formic acid is used extensively in various industrial sectors finding its main use as a preservative, the main mechanism for its formation is the reaction of methanol with carbon monoxide producing methyl formate, which subsequently undergoes hydrolysis to form formic acid. This method is highly energy intensive and uses toxic reagents and forms undesirable by products. (Scheme 21)
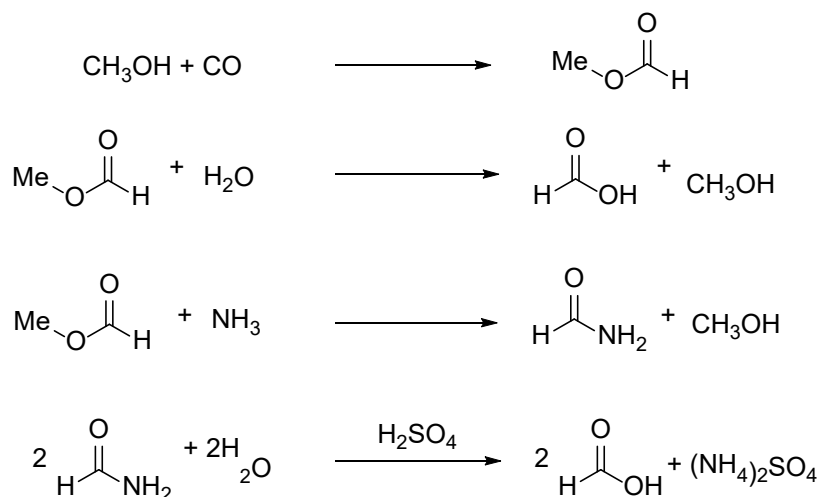
Scheme 21: Traditional synthesis of formic acid

Various new methods for the formation of formic acid have been trailed, one showing significant promise is the direct hydrogenation of carbon dioxide. In the early 90s it was shown by Nicholas *et al*. that catalyst ([Rh(NBD) (PMe$_2$Ph)$_3$]- BF$_4$) could effectively reduce CO$_2$ into formic acid in the presence of H$_2$, with H$_2$O as an additional additive. (Scheme 22) [48]
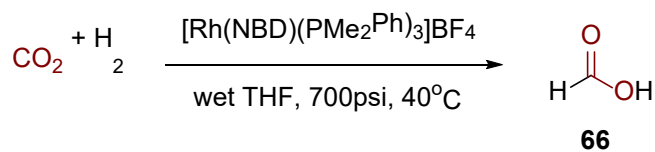
Scheme 22: Rhodium catalysed reduction of CO$_2$

This initial method proved successful although it was severely hindered by a lack of catalytic activity as well high amounts of pressure needed to drive the reaction. Following on from this, a catalytic system developed by Walter Leitner's group improved the catalytic function massively. By employing (TPPTS)$_3$ as a ligand the catalytic system was made to be homogenous improving both turnover number and frequency.[49] Again, the process has hindered by the need to use high pressures.

Recently, a method for the direct carboxylation of arenes through the activation of C—H bonds under atmospheric CO_2 was reported by the Iwasawa group (Scheme 22). [50] C—H Bond activation is an increasing important area of research with significant advances being made in the field utilising new and existing methods to promote new mays to functionalise the usually stable and inert C—H bond. Rhodium complexes have long been used in the sphere of C—H bond activation[51], therefore the Iwasawa group used this as their basis. After much work the group where successful in promoting the carboxylation of various phenylpyridines (Figure 9) and phenylpyrazoles (Figure 23) in good to excellent yields.
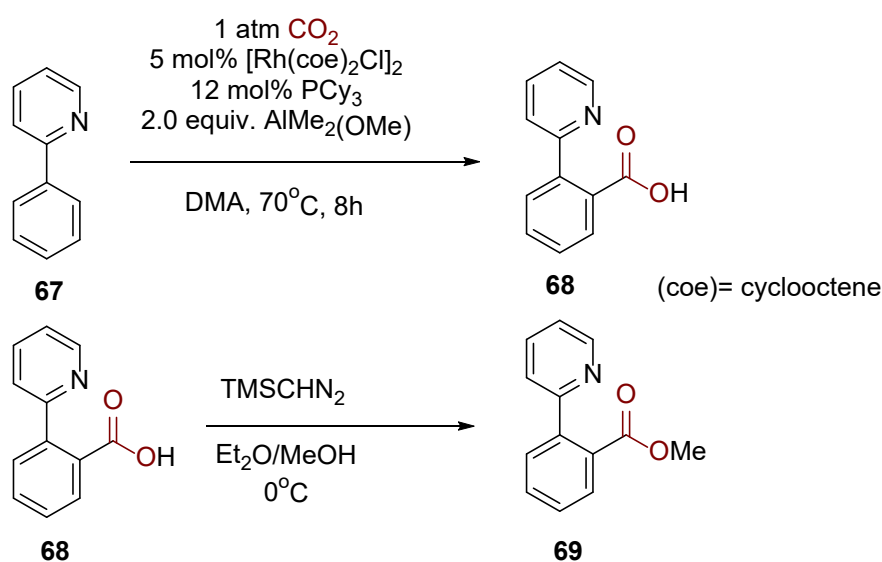
Scheme 23: Rhodium catalysed carboxyaltion of arenes through activation of C-H bond
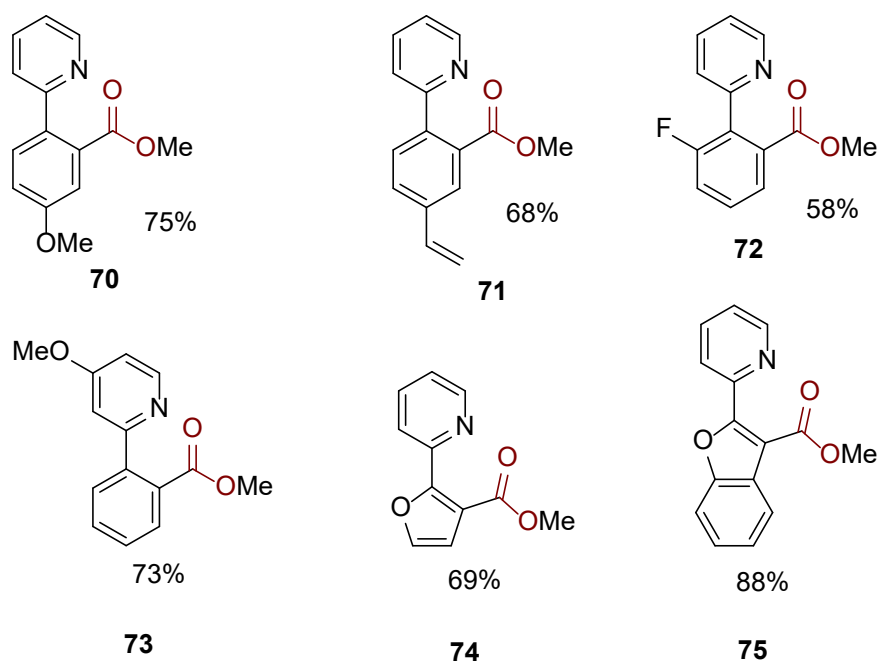
Figure 9: Iwasawa carboxylation of phenylpyridines
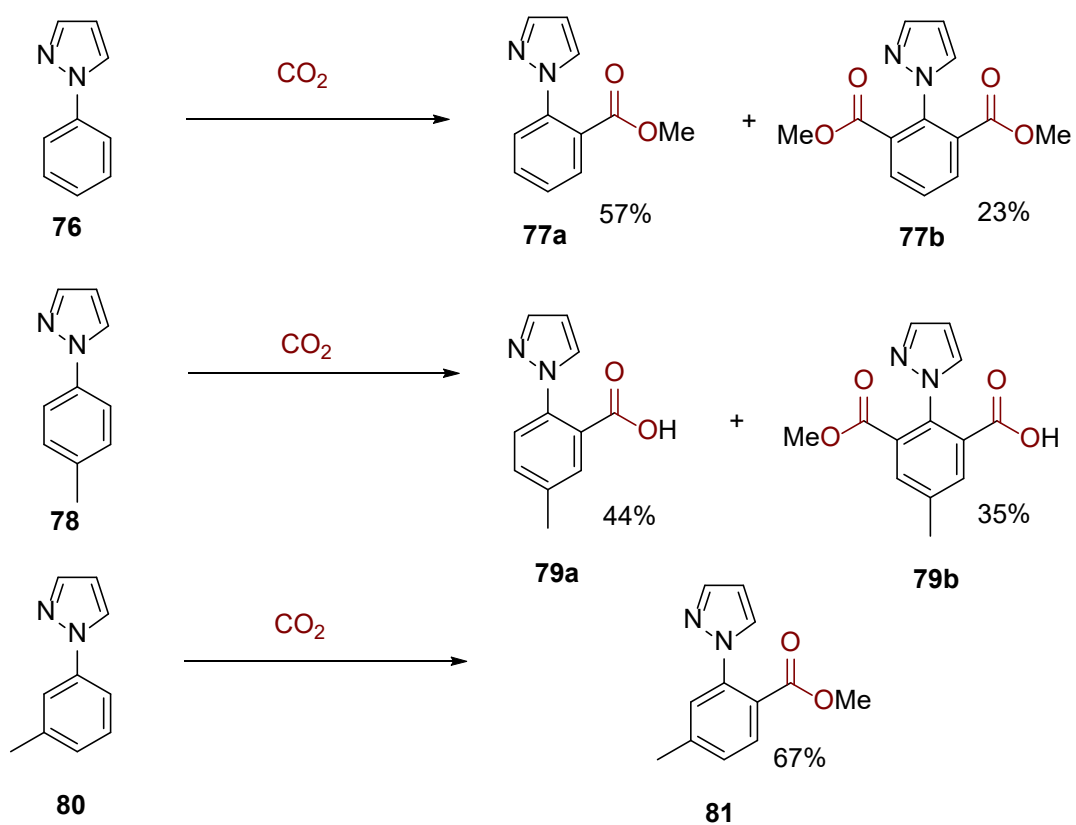
Scheme 24: Iwasawa carboxylation of phenylpyrazoles

In the case of the phenylpyridines especially the catalytic system showed that the synthesis of highly functionalised pyridylarene carboxylic acid was possible, with functional moieties such as vinyl groups, as well as heteroaromatic derivatives such as furans surviving the catalytic sequence. Although not fully understood the group believed that the reaction proceeded through a methylrhodium(I) species, which inserted into the C—H bond closest to the nitrogen of the pyridine, followed by subsequent nucleophilic addition of CO_2 dioxide. The catalyst is then recovered via transmetallation. (Scheme 25)
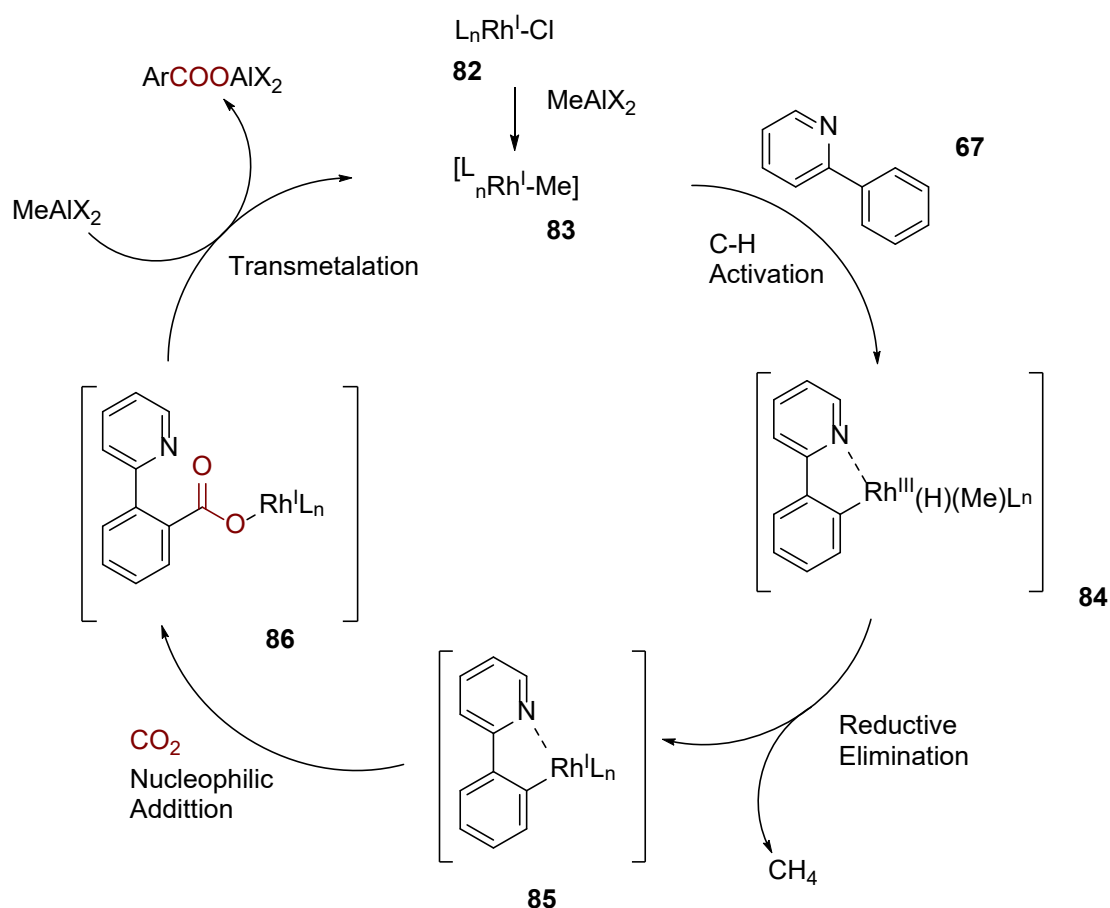
Scheme 25: Proposed catalytic cycle by Iwasawa group

Whilst being novel and to some degree sustainable with no need for extremely high temperatures or pressures, the concept is held back by the need of a very specific substrate, even when the pyridine is substituted with pyrazoles; the amount of by products produced increases and it can be deduced that without a nitrogen containing ring system present coordination with the Rh complex will prove unlikely causing the reaction to cease.

1.4.3 Copper

With the basic principles of utilising CO_2 as a reagent requiring a large amount of energy input it is wise to investigate using already high energy reagents thereby lowering the amount of energy needed to form a reaction with CO_2. Compounds containing C—C multiple bonds have proven to be very reactive in the presence of certain metal catalysts allowing for relatively easy Incorparation of CO_2.

The C—C triple bond present in alkynes is extremely useful and has be shown to react in several different ways to produce various transformations. This is mainly due to the high electron density present in the bond accompanied with the δ+ environment, providing a unique environment which can accommodate addition reactions, electrophilic attack as well as complexation reactions with metallic complexes. Terminal alkynes especially, react well with metal cations to form metal acetylides due to the relatively high pKa of the terminal alkynes, when compared with other hydrocarbons

This type of reactivity was exploited by the Tsuji group in 2011 to achieve the hydrocarboxylation of alkynes under atmospheric CO_2 conditions.[52] The group employed a copper complex with hydrosilane being employed as a reducing agent, thereby forming what is hypothesised to be a copper hydride species. The catalytic cycle is then followed by the insertion of the alkyne and CO_2, the hydrosilane is then used to regenerate the active catalyst. (Scheme 26)
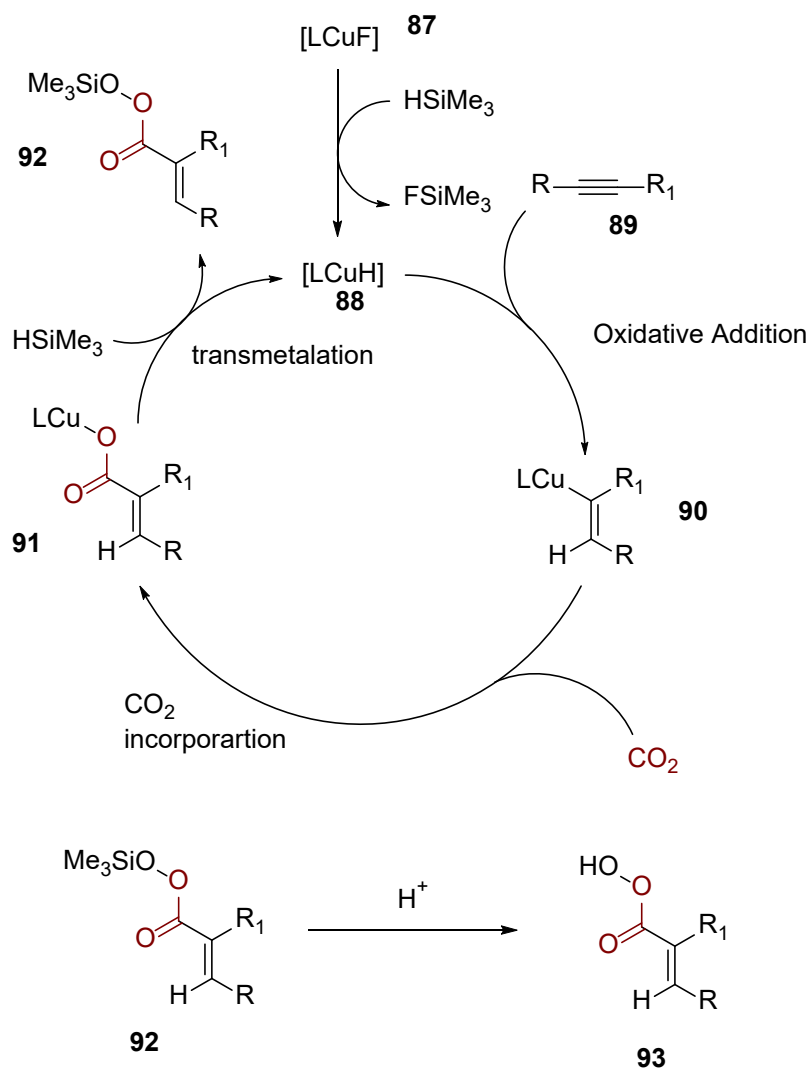
Scheme 26: Proposed catalytic cycle by Tsuji group for the hydrocarboxylation of alkynes

Similar catalytic systems which focus on the insertion of CO_2 into C—C multiple bonds require the presence of a organometallic reducing agent such as $ZnEt_2$ or $AlEt_3$. [47,50] These types of reagents are extremely air sensitive and difficult to handle. The Tsuji catalytic system bypasses this problem by using a milder hydrosilane as their reducing agents as well as being able to proceed under a single atmosphere of CO_2 (balloon) Through the use of this copper catalytic system the group reports the efficient hydrocarboxylation of various alkynes to produce α-β unsaturated carboxylic acids. By varying the ligand complexed with the copper the group was able achieve good to average yields for a number of different alkynes with both electron withdrawing and donating groups. Although this shows quite an extensive scope for this catalytic system one underlying similarity with the substrates is visible; the presence of an aryl system or an oxygens atoms lone pair is crucial as no hydrocarboxylation of aliphatic alkynes is reported, this leads us to hypothesis that conjugation is necessary for the reaction to proceed.

Organosilanes have long been deemed as useful intermediates and building blocks due to the versatility of the C—Si allowing for a multitude of transformations, [53] a specific focus should be placed on the formation of allyl and vinlysilanes, from the reaction of alkynes and allenes. Silylcuparartion has been shown to promote this type of reaction, in the case of allenes even directing the stereochemistry of the product. After the introduction of the C—Cu bond further reaction with electrophiles opens up the possibility for interesting synthesis products.

The Tsuji group used this knowledge and early research into catalytic hydrosilylation carried out by Loh group[54] in China, to achieve a copper catalysed method for the regiodivergent silacarboxalation of allenes (Scheme 27). The discoveries reported by the group show that regioselectivity can be achieved by controlling the nature of the ligand and varying certain important factors such as solvent, primarily to achieve a higher proportion of the allyl silane rac-Me-DuPhos was used as the ligand, while PCy$_3$ was used as the ligand to achieve vinyl silanes as the major product.
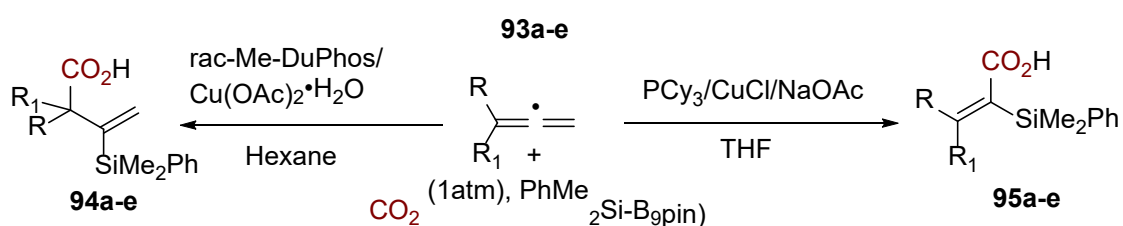
Scheme 27: Regiodivergent silacarboxylaation of allenes

33
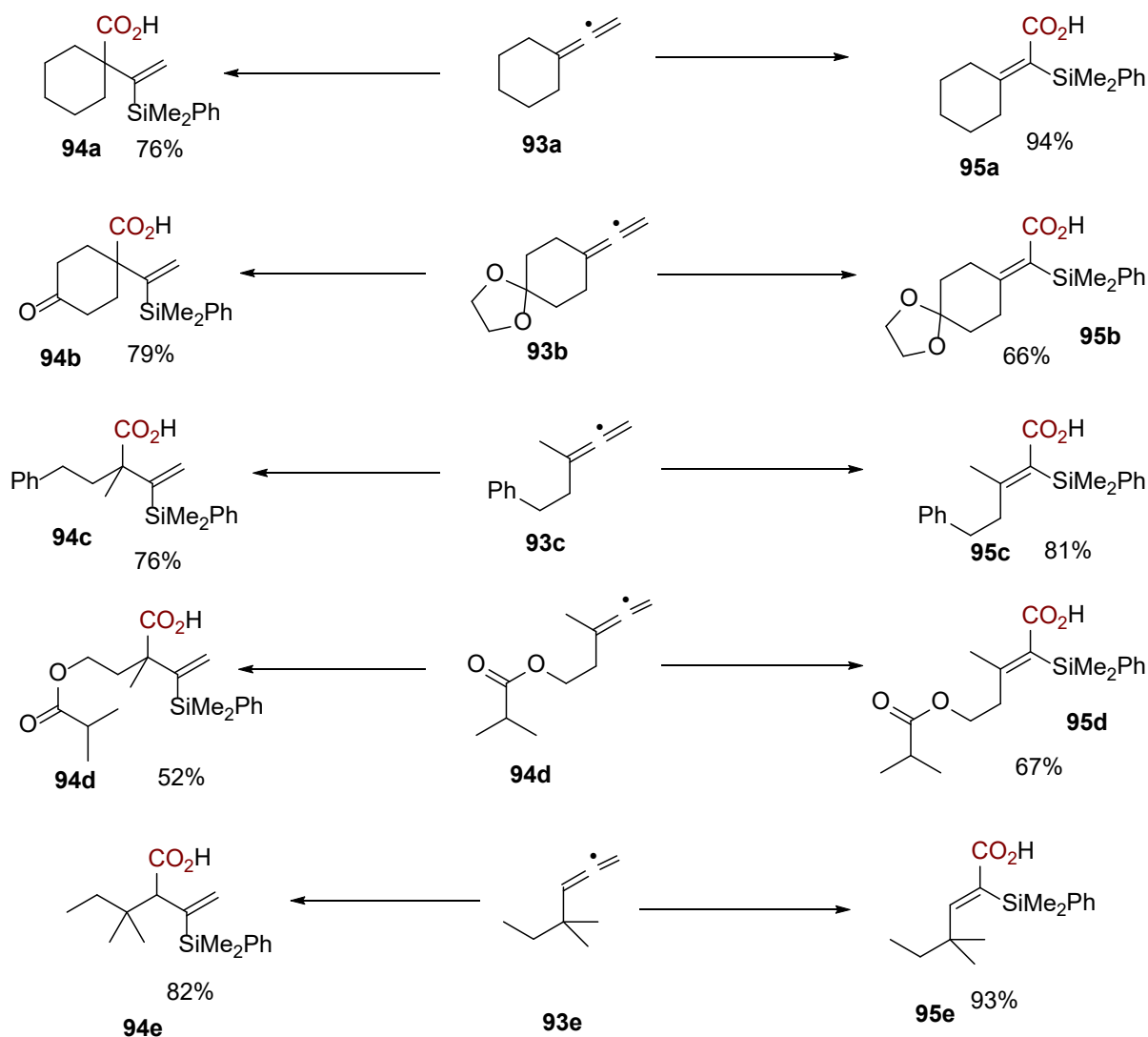
Scheme 28: Scope of silacarboxylaation of allenes

As well as showing the versatility of the catalytic system, the group showed a considerable scope for this system (Scheme 28), with ketal, alkenyl, bromo and ester groups tolerating the catalytic reaction. All products where produced in good yields, although in most cases a mixture of both the *E* and *Z* isomers where produced. This is an area which is being investigated by the group as well as research into the mechanism of the catalytic cycle.

1.4.4 Conclusions

As we have seen over the years many groups have turned to traditional methods such as heterogenous metal catalysis to achieve the transformations of carbon dioxide. Many of these techniques produce very useful and interesting molecules, however, are held back by the usual restrictions associated with metal catalysis, such as expensive catalysts, the need for additional reducing agents as well as harsh experimental conditions. For these specific carbon dioxide transformations to become economically, but more importantly environmentally viable a shift needs to be made with less focus on traditional catalytic methods.

1.5 Photochemical fixation of CO_2

During the last decade emphasis has been put on the sustainability of CDU techniques. Catalytic systems usually require high pressures and temperature, the solvents used in many of these reactions is DMF which is not an environmentally friendly solvent. Electrocarboxylation also has problems such as the use of sacrificial electrodes, which get used up as well as electricity itself. The logical step has been to research photocatalytic systems. Inspired by nature these catalysts work by using sunlight as the driving factor for the reduction of CO_2, much like the chlorophyll in plants which transforms CO_2 into carbohydrates and O_2.

The first real success in this area of research was achieved by Inoue co-workers. [55] They discovered that several semiconductors but especially TiO_2, SiC and GaP allowed for the photoreduction of CO_2 in water. The products formed were mainly were formaldehyde, methanol and formic acid. Although this was a massive step in the right direction major issues still persisted. The fundamental problem with these types of photocatalytic reductions of CO_2 is that the photocatalytic reduction of H_2O takes place simultaneously. This proves a challenge as the reduction of water to H_2 is mechanistically and kinetically more favourable then the reduction of CO_2. For example, the formation of methanol requires six electrons and six protons going through various intermediate states. This problem can be rectified by removing H_2O as a source of protons. This has been implemented recently by Sastre and co-workers [56] in Valencia.

1.5.1 Photocatalytic reduction of CO_2 under H_2

Sastre *et al*. developed a nickel supported on silica-alumina photocatalyst. According to X-ray power diffraction (XRD) the photocatalyst had a mixture of Ni and NiO nanoparticles. It is believed that the Ni compounds are the active species while the silica-alumina provides a stable support which increases the surface area of the photocatalyst. The group designed the catalytic system to take CO_2 and convert it to CH_4 in the gas phase in the presence of an excess of H_2 (Scheme 29) . It was shown the under the right conditions,

$$CO_2 \;+\; H_2 \xrightarrow[\substack{\text{excess } H_2, \\ \text{mass of catalyst 250 mg,} \\ 1h}]{Ni/SiO.Al_2O_3} CH_4$$
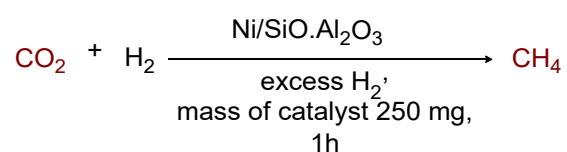
Scheme 29: Conversion of CO_2 to CH_4

A conversion of 95% and selectivity of 97% can be achieved, in a very short space of time (1hr). The supported catalyst was also shown to be highly robust and reusable showing no drop-in activity and selectivity even after 6 cycles. The groups finding also pointed to the fact the NiO was also a potent catalyst however it was shown that after 3 cycles conversion would drop to below 14%.

1.5.2 Photocatalytic reduction of CO_2 to formic acid.

Another potential product formed from the reduction of CO_2 is formic acid. Formic acid is widely used in industry as a preservative and antibacterial pesticide in both crops and animal feedstock [57] as well as being integral in the tanning of leather. Vast amounts of catalytic systems utilising noble metals such as Rh, Ru and Pd as their basis have been reported recently in high quality publications.[58-60] A special emphasis has also been put on the catalytic hydrogenation of CO_2 to afford formic acid. Although useful these systems suffer from the various drawbacks of catalytic chemistry.

Maeda and co-workers have recently developed a visible light driven CO_2 reduction in conjunction with carbon nitride and ruthenium catalysts. [61] The group has identified graphitic carbon nitiride (g-C_3N_4) as a suitable basis to construct a potential catalytic system. Carbon nitiride has been shown to be an effective photocatalyst in the reduction/oxidation of water, organic transformations as well as hydrogen peroxide formation (Figure 10). A defining feature of this carbon nitride system is its ability to perform under ambient pressures as well as room temperature, unlike conventional heterogenous catalytic systems which require high temperatures and elevated pressures.

96
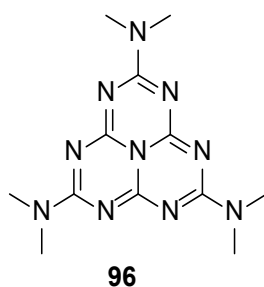
Figure 10: Structure of carbon nitride

The group theorised that coupling carbon nitride with a Ru complex may form a superior catalytic system which can perform under these more facile and environmentally friendly conditions.
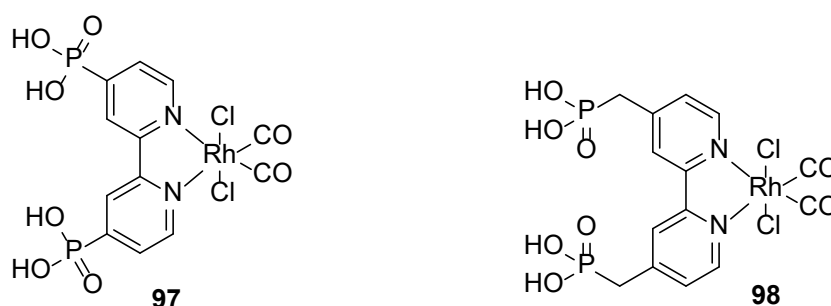
*Figure 11: RuP **97** and RuCP **98***

RuP and RuCP (Figure 11) were selected as suitable complexes due to their phosphate groups providing a suitable "anchor" to the carbon nitride. Subsequent testing was implemented to deduce the favoured solvent as well as which catalytic system performed better. Final results showed that the RuP/C$_3$N$_4$ photocatalyst was able to achieve TON over a 1000 and an apparent quantum yield (AQY) of 5.7% towards formic acid under visible light irradiation at a wavelength of 400nm. These values are currently superior to all other heterogenous photocatalysts. This type of system has a large scope for improvement, with current criticism based around the fact that the system also produces H$_2$ as well as CO showing a certain lack of selectivity towards HCOOH production.

1.5.3 Photocatalytic reductive carboxylation of alkyl halides

Nomoto and co-workers developed a process for the reductive carboxylation of alkyl halides by using a SmI_2/Sm suspension under atmospheric CO_2 through a radical pathway.[62] The first reaction attempted was the carboxylation of n-dodecylchloride under a Xe lamp, with 3/6 mmol of SmI_2/Sm. (Scheme 30)
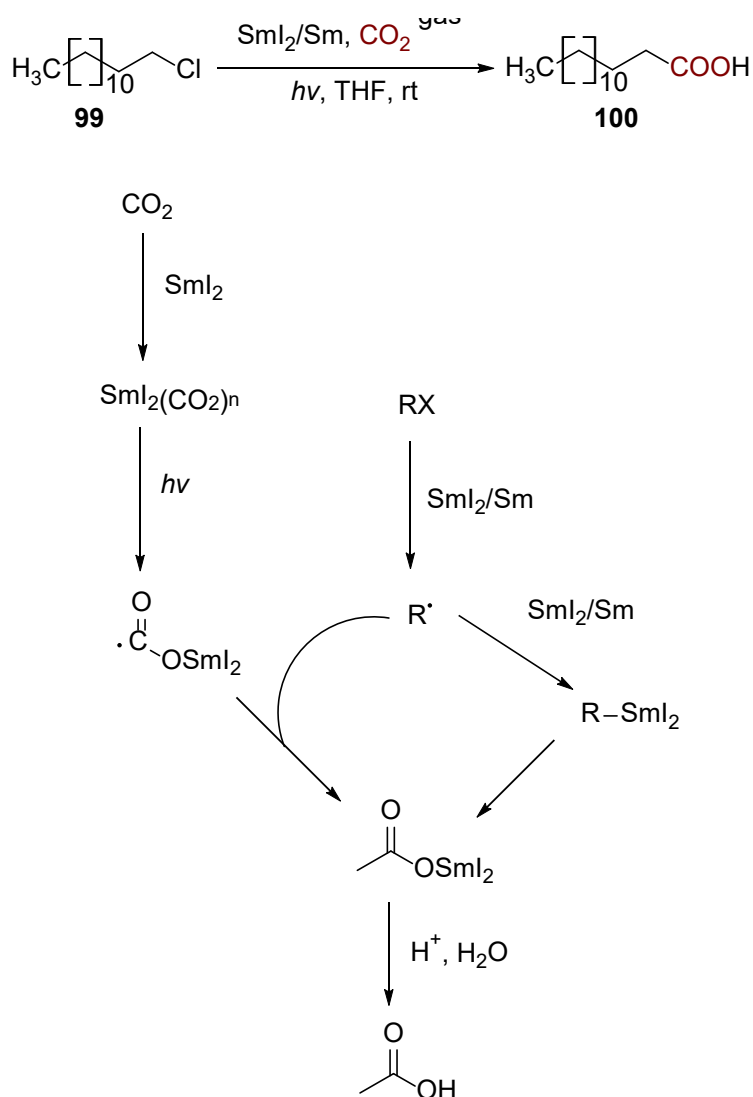
Scheme 30: Reductive carboxylation of alkyl halides and prospective mechanistic pathways

This produced a yield of 68% after 6 hours, although not particularly good optimisation of the reaction proved key as yield of 89% was achieved after reducing the amount of SmI_2/Sm to 1.5/0.5 mmol respectively and swapping the lamp for a tungsten lamp. This reaction was also shown to have some limited scope with secondary alkyl halides although tertiary alkyl halides proved unreactive. This led the group to believe that the reaction proceeds through the product of an aryl halide.

1.5.4 Photocatalytic reduction of Carbon Dioxide in conjunction with semi-conductor MOF systems.

Metal organic frameworks (MOFs) (Figure 13) are a relatively new species of material, comprising of metal-based nodes bridged by organic linking groups, these highly porous and adaptable compounds have shown to be highly useful in several applications. The extremely high surface area and especially the tuneable pore size allow have allowed MOFs to find many uses, such as drug delivery [63], gas separation[64], chemical sensors[65] and the adsorption of gases. In particular a significant amount of focus has been placed on MOFs ability to successfully adsorb CO_2 allowing for further reaction of this CO_2.[66]
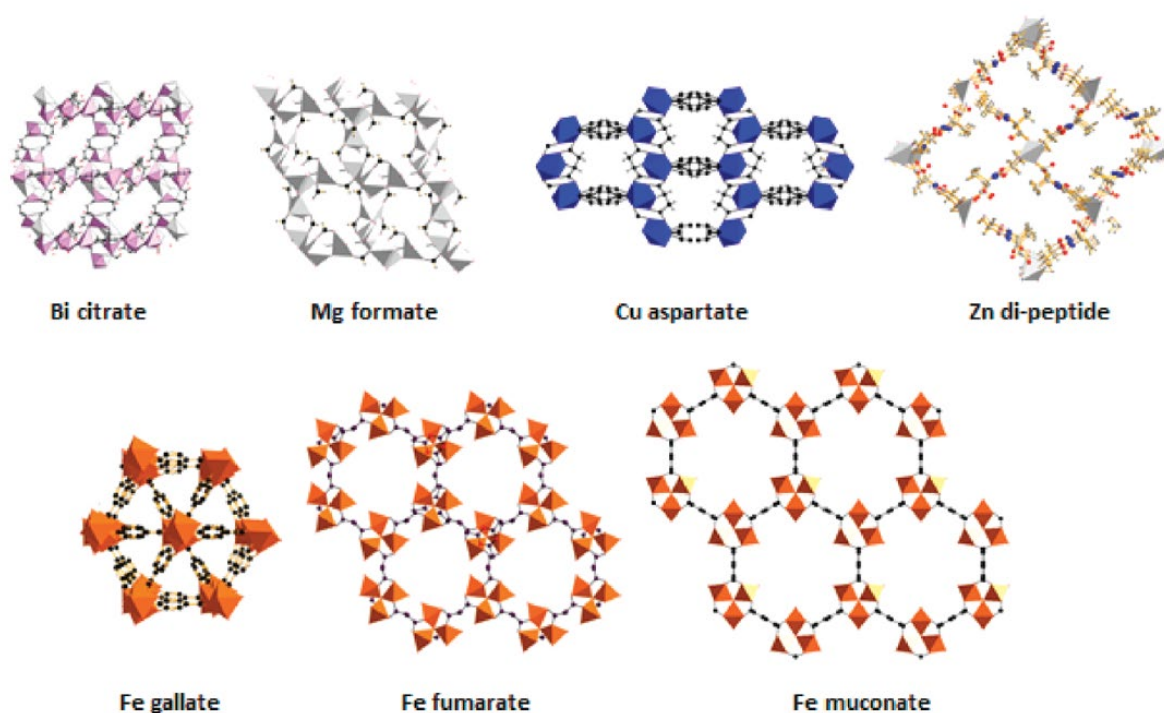
Figure 12 Selection of MOFs [67]

Titanium has been utilised as a photocatalyst for the reduction carbon dioxide for a number of years with the first report being published by Anpo and co workers in 1994. [68] The Xiong group hypothesised that combining the properties of both MOFs and TiO_2 could allude to a hybrid material capable of high levels of carbon dioxide reduction (Figure 13). [69] The MOF used as a basis was the $Cu_3(BTC)_2$ (BTC = benzene-1,3,5-tricarboxylate), it has been proven in previous that this particular MOF performs highly in terms of CO_2 adsorption.[70] Once combined the group found that TiO_2 nanocrystals formed as definitive shells engulfing the MOF.
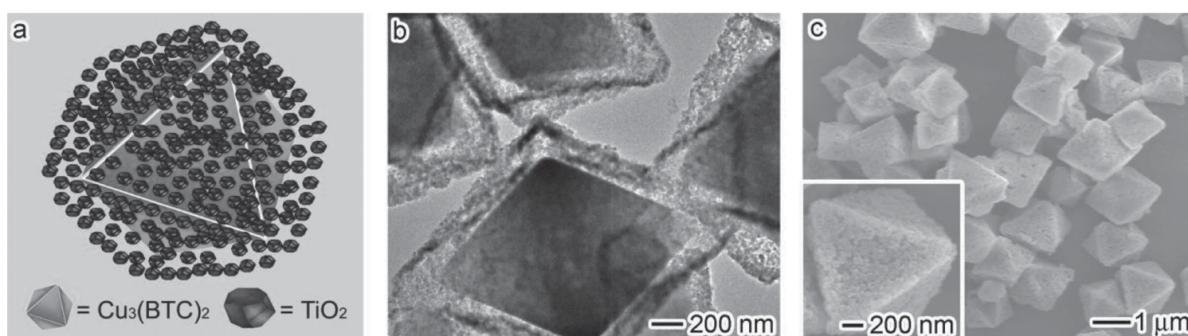
Figure 13: Structure of Xiong group TiO_2-MOF hybrid material [69]

Whilst the TiO_2 doped MOF has a lower adsorption than virgin $Cu_3(BTC)_2$ it is still a reasonably high level. What the hybrid material loses in adsorption it gains in chemical activity. As opposed to bare TiO_2 the hybrid material shows increased selectivity and activity towards CH_4 production with no significant production of H_2, it was also shown that the hybrid material has significant reusability with no noticeable drop in activity after 3 subsequent runs. (Figure 15)
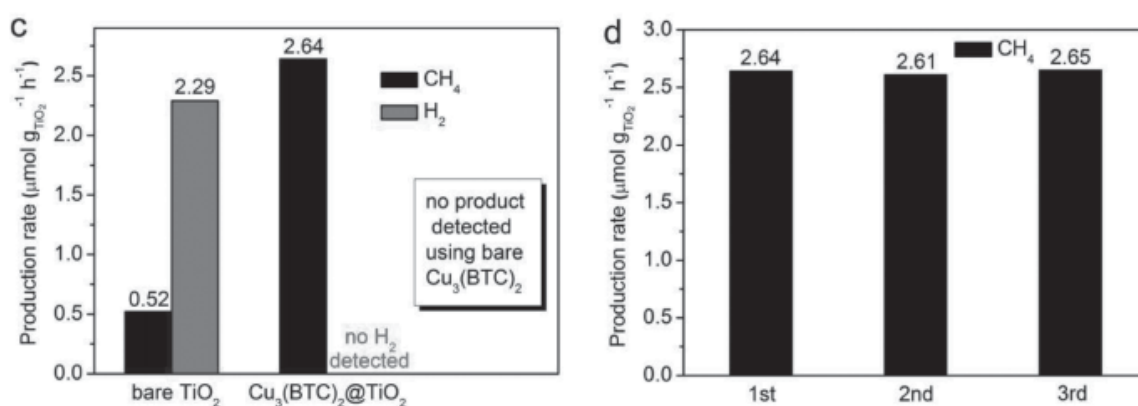
Figure 14: Chemical activity of hybrid material [69]

1.6 Electrosynthesis

1.6.1 Introduction

Electrochemistry has seen use in various spheres of chemistry since the early discoveries and inventions of Volta, Galvani and Faraday, these famous names forever being immortalised in the units of measurements commonly used in dealing with electrical terms. Throughout the 19th and 20th century inventions such as the electroplating of metals, electrolytic recovery of metals from their ores, sacrificial protection of metals, electrolytic production of chlorine and hydrogen and finally fuel cells showed the benefits of a greater understanding of electrochemistry, with a lot of these processes proving indispensable in our current society.

The application of electricity in synthetic chemistry has seen limited use due to perceived flaws in reproducibility and an apparent cumbersome nature. However, electrosynthesis provides a new avenue for organic synthesis as the transfer of electrons; (crucial to organic transformations) is driven by the electronic nature of the electrodes and electrical conditions as opposed to the usual metal centric catalysts, strong acids/bases and reducing and oxidising agents. These type of electrosynthetic reactions also carry the bonus of limiting the amount of toxic waste being produced usually associated with metal catalysed synthetic processes.

Electrosynthesis has seen a significant resurgence in its fortunes, with several new synthetic applications being published in leading journals. The Waldvogel[71] (Scheme 31) and Yoshida[72] (Scheme 32) groups have both recently reported novel metal and chemical free cross-coupling of benzylic and aromatic moieties through the activation of C—H bonds.
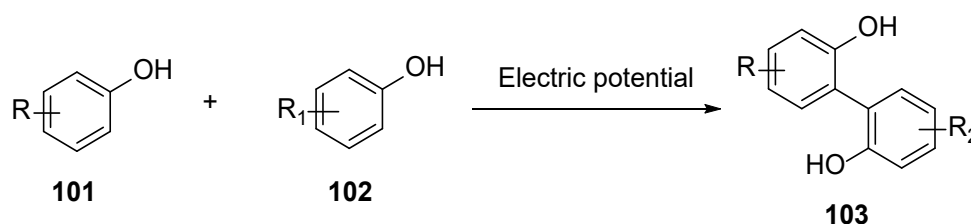
Scheme 31: Waldvogel Cross-coupling
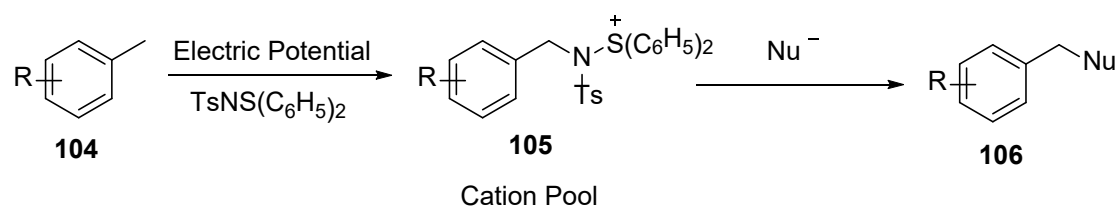
Scheme 32: Yoshida Cross-Coupling

Both these groups showed that these types of reactions can be influenced and directed by employing steric and protecting groups. In the case of Yoshida it was shown that their method was viable in the synthesise of **110** a key inhibitor of PTPases [73]. (Scheme 33)
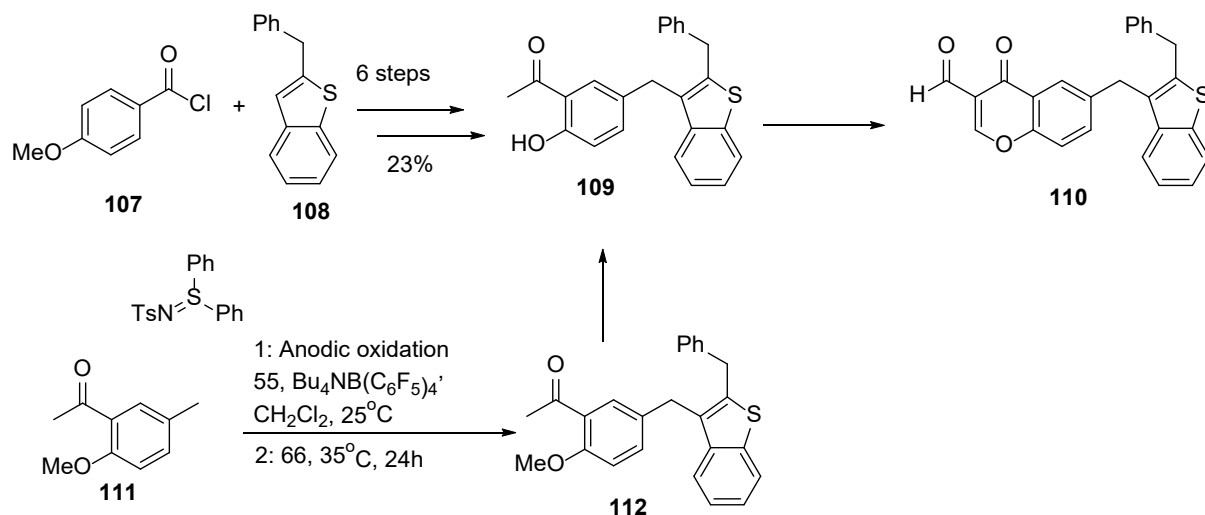
Scheme 33: Various syntheses of **110**

Baran and co-workers have been at the forefront of new electrosynthetic techniques, in 2016 they reported a sustainable electrochemical C—H oxidation[74] (Scheme 35). An important transformation considered to be vital in the total synthesis of drug scaffolds is Riley oxidation and all the subsequent variations, the usual reagent employed is selenium dioxide. (Scheme 34)

111
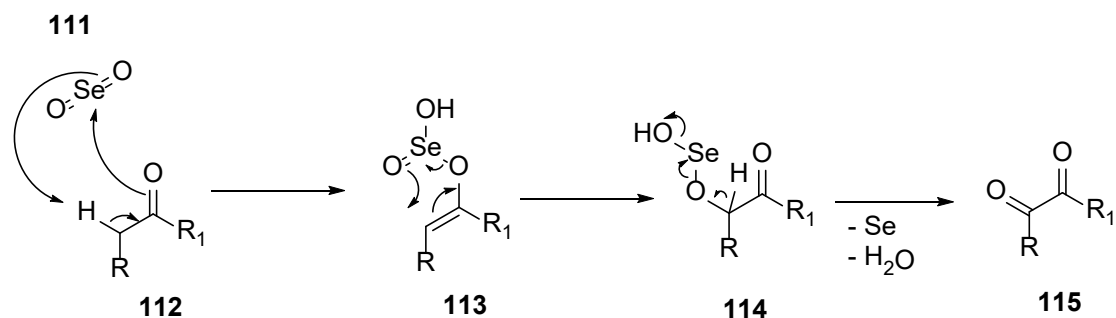
Scheme 34: Riley oxidation

A consequence of the use of this reagent is the production of toxic waste, the stated reactions also have limited applicability in large scale industrial process. The Baran groups electrosynthetic method completely bypasses the need for selenium dioxide; in contrast only requiring sustainable and readily available reagents. The was able to show that this type of oxidation was effective in accruing various drug scaffolds such as steroids, sesquiterpene, triterpene in good to modest yields. (Figure 15)
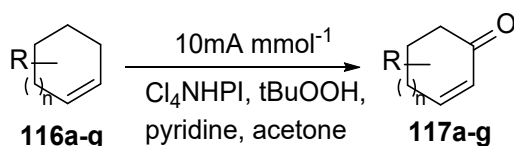
Scheme 35: Baran electrochemical C-H Oxidation
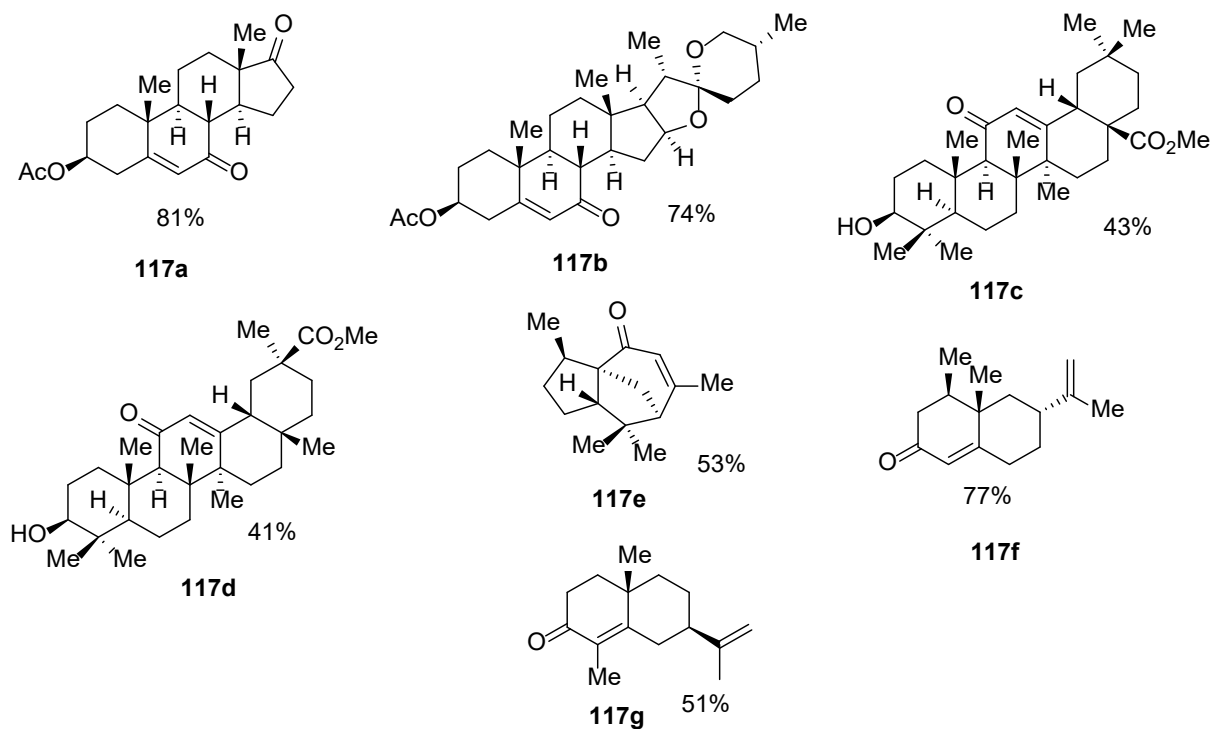
Figure 15: Scope of Baran electrochemical oxidation

43

Furthermore, the group showed that the reaction can be effective scalable up to a 100g scale, comparable reactions with conventional means would need large amounts of metal reagent, showing the feasibility and possible further application of this method in an industrial setting.

1.6.2 Electrocatalytic transformations of CO_2

As shown in the previous section most of the catalytic reactions with CO_2 took place under increased pressures and temperatures as well as dangerous chemicals. The use of electrochemistry can help alleviate these problems. CO_2 exhibits a high thermodynamic and kinetic stability which is the main reason for the relatively harsh reaction conditions used in transformations of CO_2. To bypass this electrochemistry can be used to reduce CO_2 into more reactive intermediates. This type of reduction can usually take place under standard conditions as the reaction is governed by the voltage applied and not so much by thermodynamics. Thereafter, the reactive species formed can easily react with a variety of substrates to produce value added products. A typical set up for the electrochemical reduction of CO_2 is displayed in figure 16
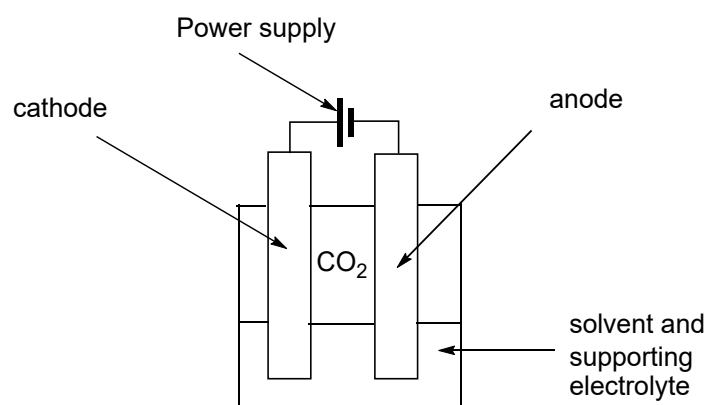
Figure 16: Typical Electrochemical cell setup

Electrochemical reduction of either CO_2 or the substrate takes place at the cathode surface, so a corresponding oxidation must take place at the anode. This can be either a metal which is usually present in sacrificial electrodes or an organic reducing agent. This type of technology has a lot of potential in the sphere of environmental science, because if implemented with well enough it can provide value added products such as methane, formic acid, formate, carboxylic acids, carbonates and diols, all while using renewable electricity, CO_2 present in the atmosphere and minimum waste products.

1.6.3 Electrocarboxylation

Electrocarboxylation is the term given to electrochemical reactions which incorporate carbon dioxide into organic molecules to form carboxylic acids. This has been achieved with a variety of molecules with varying success to achieve a variety of products. Carboxylate anions are usually produced during the reaction, these can complex with the metal ions yielded by the sacrificial anode or any other anodic reactant. One of the earliest reports on electrocarboxylation dates back to the 1960s. Loveland patented the electrolytic production of acyclic carboxylic acids from olefins in 1962. [75] This process was quite a revolutionary step although hard to reproduce and prompted further research and development in this area (Scheme 36).
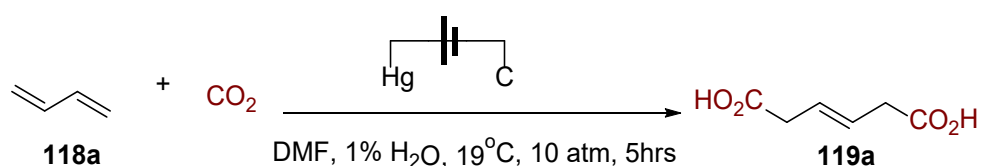
Scheme 36: System for electrocarboxylation of 1,4-butadiene, patented by Loveland

1.6.4 Electrochemical synthesis of dionic acids from dienes.

In 2010 Li and co-workers reported a method to achieve highly regioselective dionic acids from dienes. Their experiments were based around the reaction of 1,3-butadiene with CO_2 which produced 3-hexene-1,6-dionic acid.[76] (Scheme 37)
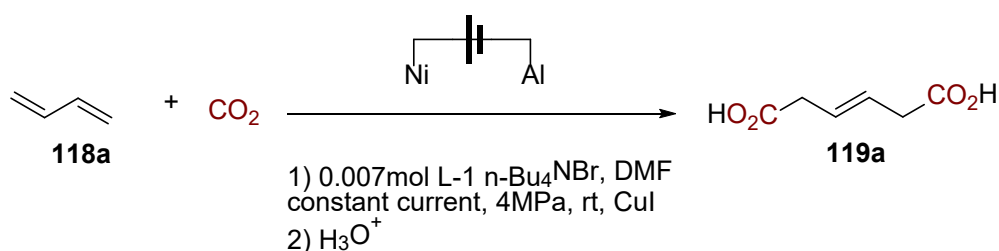
Scheme 37: Carboxylation of 1,3-butadiene

The group used an electrochemical cell with aluminium anode; as the sacrificial electrode, Ni cathode and Bu_4NBr as the electrolyte. The reaction was carried out under room temperature and at a CO_2 pressure of 30atm. The group carried out the same experiment on a variety of 1,3-dienes. (Table 3)

The reaction scheme shows substrate **118a-e** with R groups and CO₂ reacting under Ni/Al electrodes to give product **119a-e**.

$$\textbf{118a-e} + CO_2 \xrightarrow{\text{Ni} \quad \text{Al}} \textbf{119a-e}$$
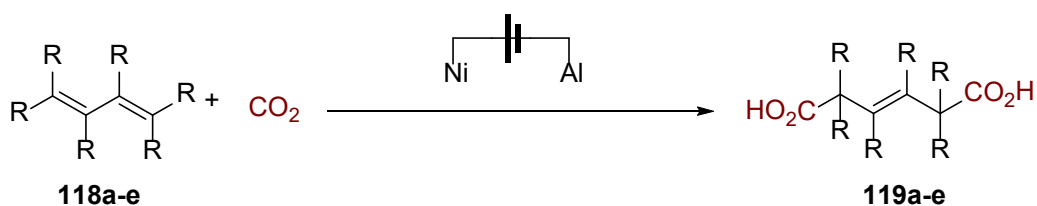
Table 3: Screening of potential substrates

Entry	Substrate	Product	Yield (%)
1	118a	119a	84
2	118b	119b	80
3	118c	119c	87
4	118d	119d	90
5	118e	119e	70

Substrate (6.9mmol), DMF (35 mL), CO_2 (30 atm), rt, Bu$_4$NBr (2.5 mmol), current (10 mAcm^{-1}), Ni cathode, Al anode

The products of entries 2-4 were 100% *trans* thus making the reaction stereoselective. The group investigated the effect of all the variables on the reaction. They report that an increase in CO_2 pressure allows for a higher yield, this can be attributed to the solubility of CO_2 in DMF which increases at higher pressures. An increase of electricity also achieves an increased yield. This method is a dramatic improvement on the first techniques used by Loveland, however it can still be improved further as in this method aluminium is used as a sacrificial electrode, this increases the environmental impact, coupled with the increased pressures used dramatically lowers this technique's green credentials.

1.6.5 Electrocaboxylation of alkynes and alkenes

Alkenes and alkynes react according to similar mechanism and pathways when exposed to CO_2. There have been many studies undertaken and reports published exhibiting the electrocarboxylation of both of these species. [52,77-79] A few interesting results have been achieved, such as the formation of a maleic anhydride derivative from the reaction of alkynes and CO_2.

1.6.6 Electrocarboxylation of alkyne in the presence of metal salts.

A method for achieving tricarboxylic and dicarboxylic acids from the carboxylation of alkynes in the presence of metal salts was report by the Li and co-workers in 2010.[80] The set up used is very similar to the groups' previous work shown above with dienes. Scheme 38 shows a typical reaction. Both the dicarboxylic and tricarboxylic acid products produced in various yields. The yields changed according to the cathode material and the effect of substituted groups on the benzene ring.
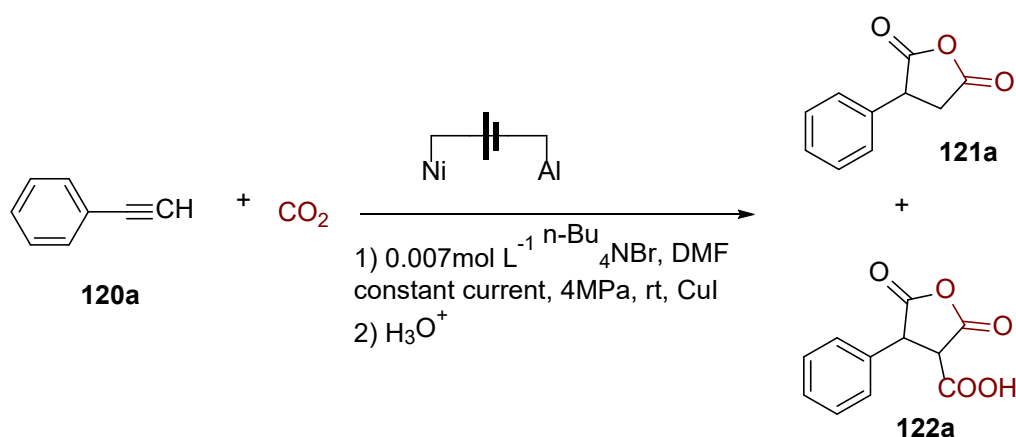
Scheme 38: Electrocarboxylation of Phenylacetylene

The group tested many different alkynes with entries 2 and 4 producing higher yield of the tricarboxylic acid due to the electron withdrawing groups present. (Table 4)
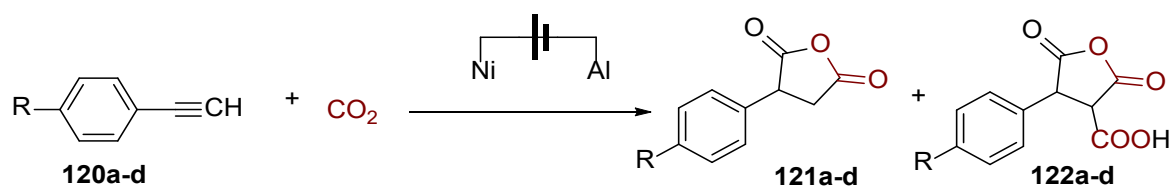
Table 4: Substrate Screening

Entry	Substrate	Products	Current efficiency (η/%)
1	**120a**	**121a** **122a** 27%: 70%	73%
2	**120b**	**121b** **122b** 15% :83%	74%
3	**120c**	**121c** **122c** 12% :68%	60%
4	N_2O **120d**	**121d** **122d** 7%: 68%	53%

Alkyne (2 mmol), DMF (35 mL), CO_2 (40 atm), rt, Bu$_4$NBr (2.5 mmol), current (10 mAcm^{-1}) CuI (1 mmol)

Current efficiency η= Q_1/Q_2 (Q_1: quantity of electricity consumed in forming product, Q_2: Total electricity quantity in the electrolysis.

The group also investigated the effect of different metal salt catalysts (Table 5)

Table 5: Catalyst Screening

Entry	Catalyst	Yield of **121a (%)**	Yield of **122b(%)**
1	CuI	27	70
2	$FeCl_3$	30	61
3	$CuCl_2$	26	52
4	$FeCl_2$	27	50
5	$Pd(OAc)_2$	5	31

Phenylacetylene (2 mmol), DMF (35 ml), CO_2 (40 atm), rt, Bu_4NBr (2.5 mmol), current (10 mAcm^{-1}), catalyst (1 mmol)

CuI produced the highest yield, although the mechanism is not fully understood it is theorised that the presence of iodine allows for easier coordination of the metal salt with CO_2 which allows it to be easily reduced into a radical ion.

1.6.7 Electrocarboxylation of substituted alkenes.

We have seen in the previous section the electrocarboxylation of dienes, in this section a method described by Senboku and co-workers for the electrocarboxylation of phenyl-substituted alkenes.[81] Scheme 39 shows the general reaction which was developed.
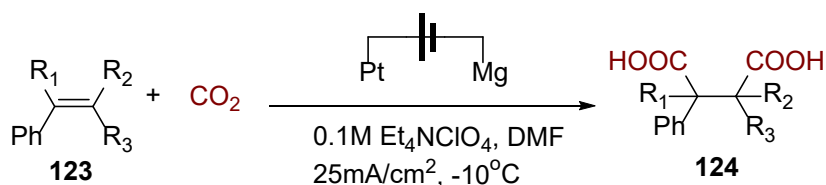
Scheme 39: Electrocarboxylation of olefin

The reaction conditions of this reaction are also very mild as the reaction proceeds under room temperature and atmospheric pressure CO_2 although the use of a sacrificial electrode is not ideal. The group also demonstrated that this setup can be used for various substituted alkenes, all achieving a high conversion (73%-98%) and high overall yields (69%-99%). The reaction pathway is similar to that of the electrocarboxylation of alkynes. The oxidation of the Mg anode allows for the reduction of CO_2 or the alkene depending on which one is easier to reduce. (Scheme 40)
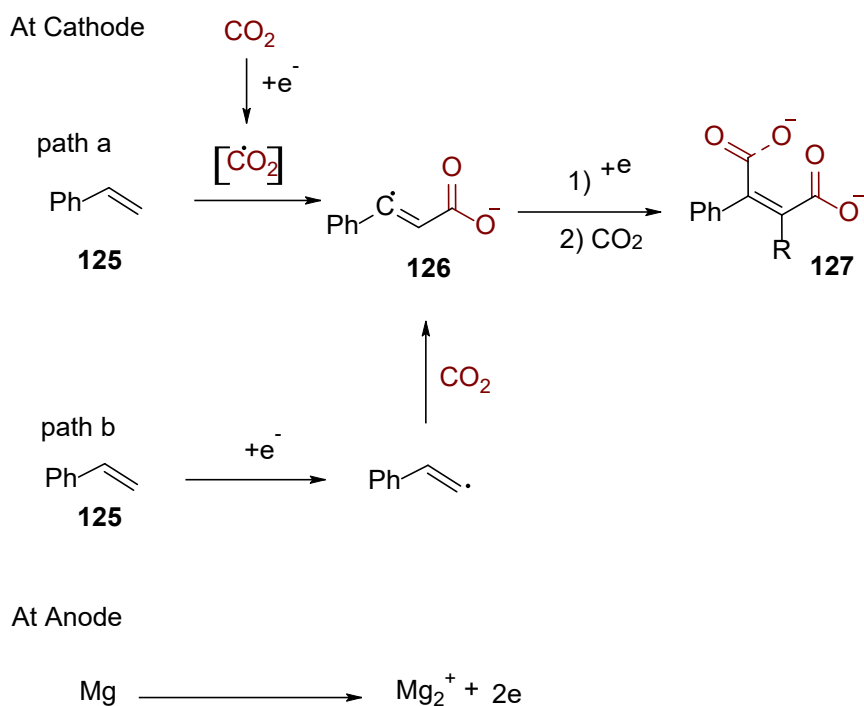
Scheme 40: Mechanism for the electrocarboxylation of olefins

The only major drawback of this reaction would be the presence of the sacrificial electrode which is made of magnesium; this element is not produced using a green process which in turn lowers the sustainability of this reaction.

1.6.8 Electrocarboxylation of ketones, aldehydes and imines

As seen in the previous section electrocarboxylation applies for a variety of substrates, this is also the case for ketones, aldehydes and imines. The scope of the reactions that these substrates have with CO_2 is large with a few even going as far as being applied in semi-industrial processes to produce value added products such as drug precursors, and precursors for further chemical reactions.

1.6.8.1 Electrocarboxylation of aromatic ketones: Providing an alternative pathway for the synthesis of non-steroidal anti-inflammatory drugs (NSAIDs)

In the 1960s the first example of electrocarboxylation of ketones was described by Wawzonek and Gundersen.[82] This technique provides a unique way to synthesis α-aryl propionic acid, which are the basis of many of the NSAIDs. NSAIDS are now widely used due to their anti-inflammatory and analgesic attributes. These drugs include ibuprofen, naproxen and aspirin. These drugs are produced in great numbers annually, so it is in the best interests of both the general public and chemical companies alike to achieve a method of synthesising these drugs in a way which is both economical and environmentally friendly.

In 1994 a research group headed by Chan reported a novel synthesis of hydroxyl-naproxen (HN) from 2-acetyl-6-methoxynaphthalene (AMN). [83] (Scheme 41)
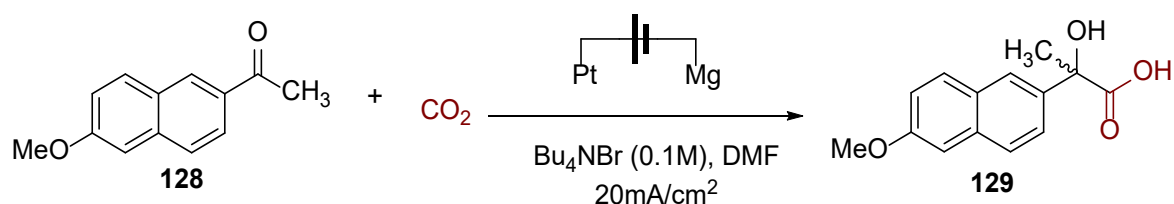
Scheme 41: Synthesis of HN from AMN

The group achieved a good conversion of 84% and a high yield (92%). This was all done under atmospheric pressure CO_2 which is a huge step in making this reaction sustainable. The groups' investigations also showed that the same reaction conditions and set up worked for *p*-isobutylacetophenone in even higher yields. This research was applied in a flow cell reactor set up by Datta, Marron, King and Wagenknect.[84] The group began on a 0.2 L scale cell, various variables were changed to see if they brought about a change in yield.

Various changes were implemented the most effective proved to be an increase pressure from 138kPa to 690kPa which improved both converision and selectivity, as did the change in electrolyte to Et_4NCl;

H_2O. These changes were applied and a 1L reactor cell was constructed. At ideal condtions this reactor cell produced conversions of 92.5% with 96% selectivity. This shows that there is scope for this process to be fully indutrialised, however problems may arise as the groups atempts to increase the cell size to 75L was met with a real big loss in yield down to 58%.

1.6.8.2 Electrocarboxylation of Aldehydes: Synthesis of 2-hydroxy-4-methylmercaptobutyric acid (MHA)

MHA has been used as an industrial feedstock for some time. The conventional way of synthesising this molecule has been through the use of hydrogen cyanide, which have various health risk as well as an extremely high toxicity and substantial pollution attached to it. Recently a patent has been accepted in the US and Europe for the electrocarboxylation of 3-methylmercaptopropionaldehyde (MMP) to form MHA,[85] In this process an electrochemical cell which is separated by a cation exchange membrane (CEM) with a boron doped permeable diamond cathode and a platinum coated non-sacrificial anode. A detailed representation is shown in Scheme 42.
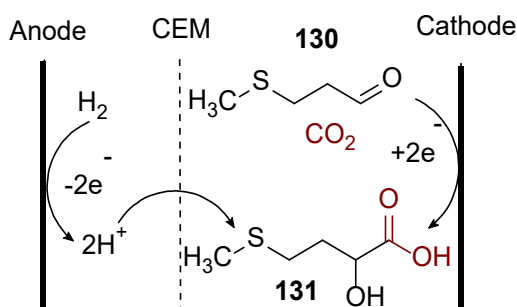
Scheme 42: Electrocarboxylation of MMP to MHA

Due to the fact that the anode is non-sacrificial, the electrons necessary for the reaction to proceed must be provided from a different source, in this case hydrogen is bubbled into the anodic compartment. The hydrogen is oxidised this provides the electrons needed for the reduction of MMP to MHA. This process is much safer than the conventional use of hydrogen cyanide, however at the moment the maximum yields that were obtained by this reaction is only 30% so more development must be done on this reaction before it replaces the current industrial process.

In the 1980s Silvestri and co-workers conducted extensive research into electrocarboxylation of various substrates. The group was widely successful with a wide variety of substrates; one of which was the electrocarboxylation of benzalaniline to the corresponding α-amino acid. [86] This reaction was so successful that the group implemented into a semi continuous reaction vessel. The cell was shown to be very efficient achieving a conversion of 92% and a yield of 85% for the desired product.

1.6.9 Conclusion

This review has only covered a few examples of the various catalytic, electrocatalytic and photocatalytic systems that can utilise CO_2 and transform it into useful molecules. A lot of this research is promising however it is not at the stage where it can be implemented on an industrial scale. That being said companies have been set up which are starting to look at implementing CDU techniques on a larger scale. One such company is Air Fuel Development Ltd (AFD).

AFD was created in 2011 to further research and apply the air fuel synthesis (AFS) Process. [87] This process uses CO_2 captured from the air and H_2 produced by the electrolyses of water to produce hydrocarbon fuels.

$$nCO_2 + 3nH_2 = C_nH_{2n} + 2nH_2O$$
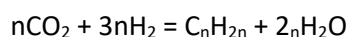
AFSs fuels have many advantages, their availability and price of the raw materials needed is unrestricted, transport of the raw materials is unnecessary, and it is unaffected by issues of land use or food availability that trouble existing biofuels. AFD has funded the production of a demonstration unit which can produce 5 litres of air fuel per day at the Centre for Process Innovation (CPI) in the north of England. This unit showed that the complete process requires 21.38 KWh for every litre of fuel produced. For this process to be fully beneficial it requires the energy input to be from renewable energy, this would make the complete process carbon neutral. The AFD believes that if this technology can be made more efficient and scaled up in size it may provide remote communities which don't have access to traditional fuel sources a with an alternative liquid fuel source.

Although photochemical fixation of CO_2 has shown immense growth and innovation in the area, drawbacks still exist. One of the most prominent is the use of rare metals in the processes, it is inevitable that rare noble metals are used as they are usually the photoactive component of the catalytic systems, a lot of these systems also require high pressures, further putting a strain on its environmental impact.

Focusing more on the electrosynthetic techniques shown here and broader afield, one defining factor is present; the use of sacrificial electrodes. This has been easily visualised by the Baran group in their recent review. [88] In Figure 17 it is clear that in most cases of electrocarboxylation the sacrificial anodes are aluminium or magnesium. This use of metals is rather inefficient; with the potential for various by products being formed and has a significant effect on the environment, this presents a rather unique niche into developing electrochemical techniques which can bypass the use of sacrificial metal electrodes.
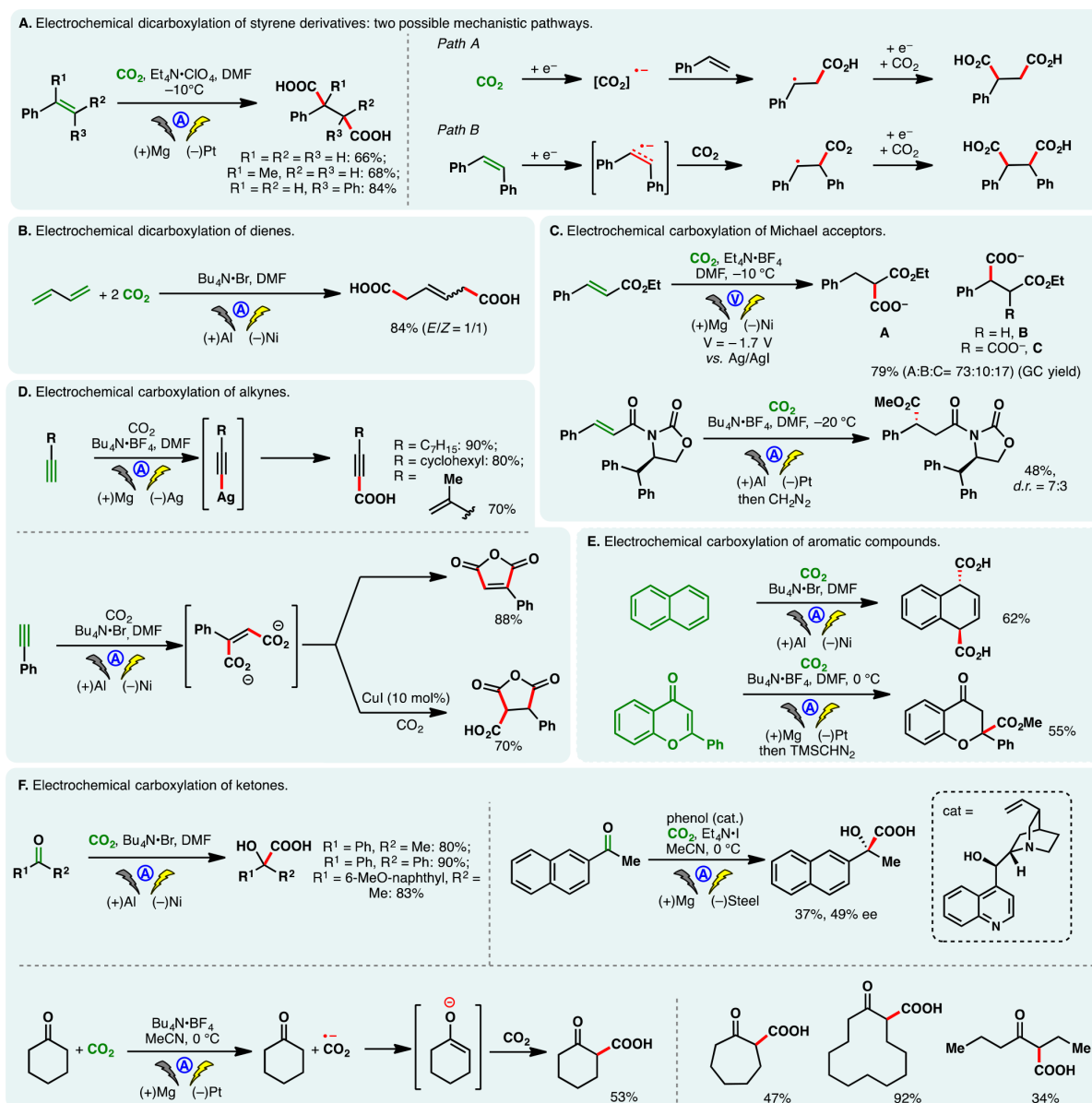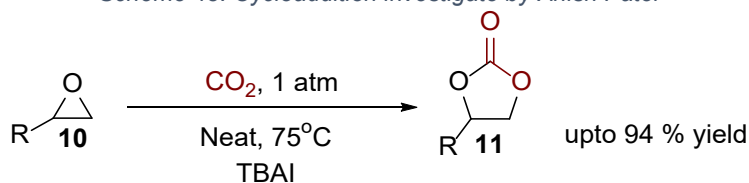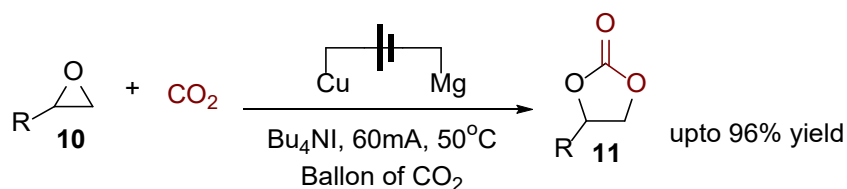

Figure 17: Various Sacrificial Electrode carboxylations [88] (taken from Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance Baran et al.).

2.0 Results and Discussion

2.1 Aims and Objectives

The main aim of this project was to develop novel methods of utilising carbon dioxide as a feedstock with a variety of reactants in electrochemical reactions to produce value added products. [89] A certain emphasis was placed on finding sustainable "green" processes, which limited the harmful effects to the environment as well as minimising the chemical and process costs.

Previous work carried out by the Buckley group provided a good basis to start from as significant advances have been made by both Anish Patel and Vanessa Silvestre in the field of electrochemistry and the incorporation of carbon dioxide (Scheme 43 and 44).

Scheme 43: Cycloaddition investigate by Anish Patel

Scheme 44: Cycloaddition investigate by Vanessa Silvestre

Research conducted by Anish Patel was focused around addressing the shortcomings of previous procedures focussed around CO_2 incorporation in epoxides. As reported by Patel previous incorporations of CO_2 into epoxides utilised catalytic systems such zinc and cobalt. [29,90] Patel's research was focused on circumventing this need for metal catalysts and developing an electrochemical method for the incorporation of CO_2. It was found that by using a magnesium anode and copper cathode and Bu$_4$NBr as a supporting electrolyte under mild conditions, the electrocarboxylation of mono-substituted epoxides was possible achieving good to excellent yields. It was shown that the scope of this setup extended to analogous mono-substituted aziridines.

Following on from this research, Vanessa Silvestre looked to further increase the cost efficiency and minimise the energy needed to carry out CO_2 utilisation reactions. A major drawback of CDU reactions is the fact that high amounts of energy are needed to overcome the activation energy of CO_2, be it chemical, electrical or photochemical energy. Taking the electrocarboxylation of mono-substituted

epoxides previously reported by Patel, Silvestre conducted extensive background research into all of the possible variables that dictated the rate of the experiment. It was found that the most prevalent variables were the concentrations of supporting electrolyte and epoxides, this prompted investigation into a system which removed the need for electricity as its driving factor. It was found that at high concentrations of both epoxide and supporting electrolyte (Bu_4NI) carboxylation of epoxides was achieved in average to excellent yield (50%- 100%).

Both these systems show a limited scope as a certain degree of focus is placed on the formation of cyclic carbonates from epoxides, which is already a well-researched reaction. [27 91-93]

The main drawback with the system proposed in Scheme 43 is the use of a sacrificial electrode. This has a serious impact on the sustainability of the reaction. To improve these systems research into potential substitutes for the sacrificial electrodes; with an emphasis placed on novel non-sacrificial electrode systems. Due to this novel approach extensive research and testing must be carried out into the effects of the variables on the reaction.

2.2 Initial exploratory experiments

Initial exploratory experiments where focussed on garnering a wider knowledge of electrochemistry with a certain emphasis on the utilisation of carbon dioxide in a gas delivery system. Initial experiments from the work carried out by previous members of the Buckley group; Anish Patel[94] and Vanessa Silvestre. [95]

2.2.1 Oxalate Formation

The electrocarboxylation of simple styrene oxide under the conditions reported by Anish Patel was chosen as the starting point. (Scheme 45)
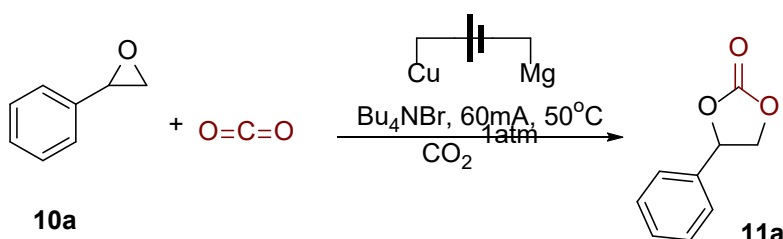
Scheme 45: Electrochemical Cycloaddtion of styrene oxide

General reaction conditions: epoxide (2 mmol), copper cathode, magnesium ribbon anode, ACN (50 mL), Bu₄NBr (4 mmol), CO_2 (bubbled 1 atm), current density (60 mAcm^{-1}), 50°C, 12h.

The experiment proceeded as expected and the corresponding carbonate was produced in good to excellent yields (75%- 90% evaluated from ^{1}H NMR).

It was observed that during the reaction a white precipitate was being formed on the magnesium anode. It is well known that under electrochemical conditions magnesium is easily oxidised in the presence of oxygen or water to form the corresponding magnesium oxide or magnesium hydroxide, because of this magnesium is commonly used as a sacrificial anode to protect more desirable metals. It was believed that the white precipitate being formed is in fact magnesium carbonate or magnesium oxalate.

Although the mechanism to produce this by product is not known, it is fair to assume that carbon dioxide in solution is chelating with the free metal ions; in this instance Mg^{2+}. Allowing for the formation of a di-radical intermediate, which in turn allows for a coupling to produce magnesium oxalate (Scheme 46).
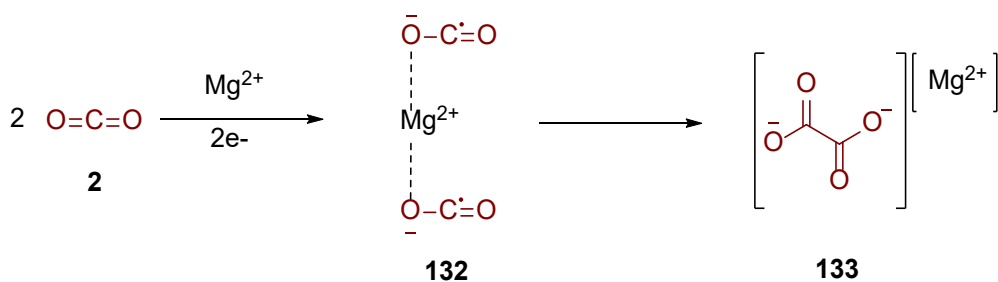
Scheme 46: Formation of Magnesium oxalate

It was decided that additional research should be undertaken to try and ascertain the true nature of the reaction which produces this interesting by-product.

Oxalic acid is the simplest dicarboxylic acid and it occurs naturally in many foods and plants. Oxalic acid and its corresponding anion oxalate have found many real-world applications. Oxalate itself is a strong chelating agent and ligand for metal ions most notably in anti-cancer drugs such as oxaliplatin. The main manufacturing technique used to produce oxalic acid is through the oxidation of carbohydrates; primarily sucrose using nitric acid in the presence of a vanadium pentoxide catalyst.[96] The Bouwman group developed an electrocatalytic method for the production of oxalic acid in good quantities with the help of a copper complex (Figure 18), although the system lacks in efficiency and still requires a catalyst. [97]
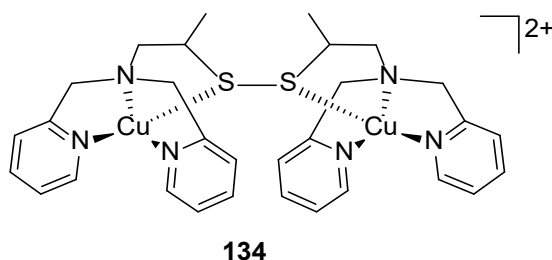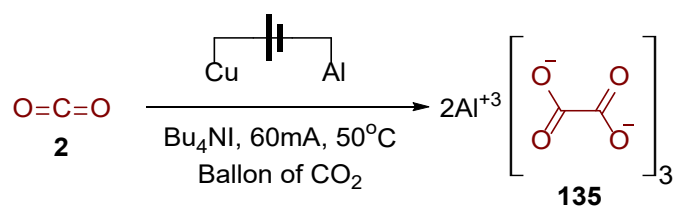

Figure 18: Copper complex developed by Bouwman et al.

Minor changes were made to the original electrochemical setup of Anish Patel, replacing the magnesium electrode with aluminium was necessary due to fragility of the magnesium ribbon under the electrochemical conditions. (Scheme 47)

Scheme 47: Electrochamical synthesis of aluminium oxalte

The first of this iteration of this experiment was a success with a white solid (0.292g, 68%) formed with recovery of Bu$_4$NI at 78%. Immediate attempts were made to make this reaction more sustainable as the use of a sacrificial aluminium anode is not sustainable. It was thought that a different source of Al, in conjunction with a non-sacrificial electrode could achieve similar results.

2.2.2 Aluminium isopropoxide

The Meerwein-Ponndorf-Verley reduction[98] is a reaction which exhibits the reduction of ketones and aldehydes to their corresponding alcohols, aluminium alkoxides catalyse this reaction in the presence of a sacrificial alcohol. This seemed like the first logical step towards a sustainable process. Two experiments were setup; both experiments had aluminium isopropoxide present, with variation being in the anode; copper and carbon, respectively (Scheme 48). These experiments were unsuccessful, showing no reaction whatsoever, further attempts in this direction of research were halted.
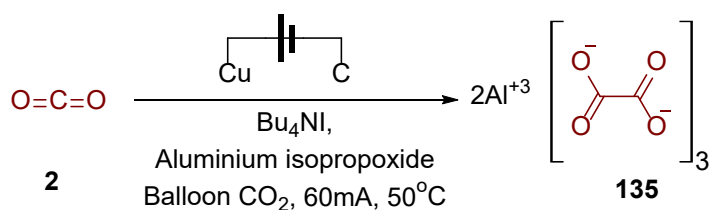
Scheme 48: Attempted synthesis of aluminium oxalate

2.2.3 Two compartment cell

Reverting to the original setup an investigation designed to see how the reaction would proceed in a two-compartment cell. This was carried out to see if limited migration between the two electrodes would influence the reaction. The limited migration of the charged species through the glass-sinter had the effect of impeding the electrochemical reaction, (Figure 19) in effect showing that migration of electronic species between the electrodes is necessary.
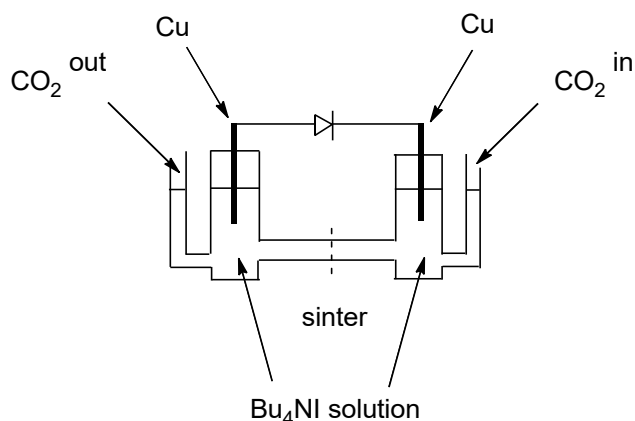
Figure 19: Setup of 2-compartment cell

2.3 Electrocarboxylation of olefins (using old setup)

It is believed that oxalate formation proceeds through a radical reaction involving CO_2 radical anions. These anions are produced through the reduction of carbon dioxide under electrochemical conditions, this concept has been verified by many groups. It was hypothesised by the Vasliev group that this reactive radical anion can react with so called acceptor molecules, for instance ethylene.[99] This type of reaction would "trap" the radical anion and prevent it from dimerising to form the oxalic acid, consequently forming a dicarboxylic acid and in the case of ethylene this would form succinic acid and longer chained dicarboxylic acids. (Scheme 49)
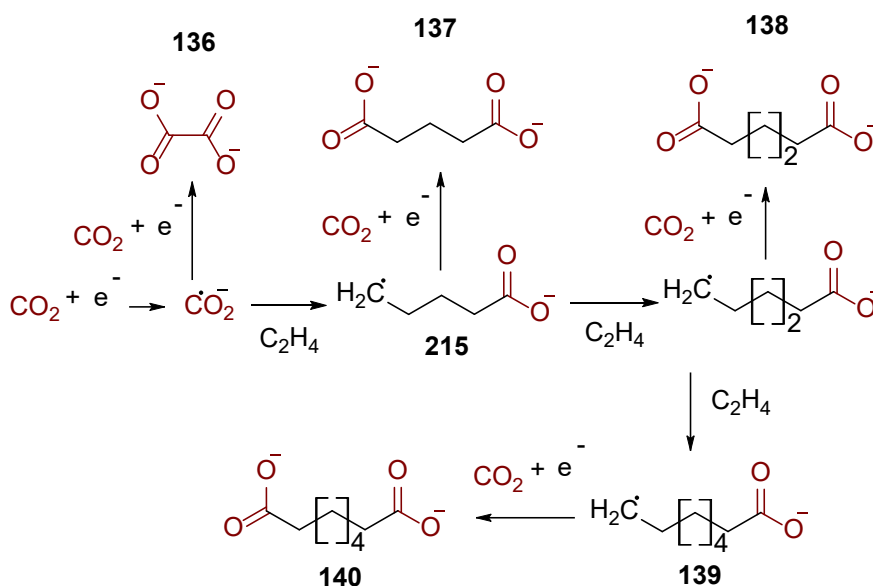
Scheme 49: Vasliev synthesis of dicarboxylaic acids

Styrene was selected as a test substrate because it was similar to ethylene in terms of functionality as well as being readily available, it was also hypothesised that with the presence of the benzene ring any radical intermediates would be stabilised. The same electrochemical setup that was used in the previous oxalate experiments was employed. (Scheme 50)
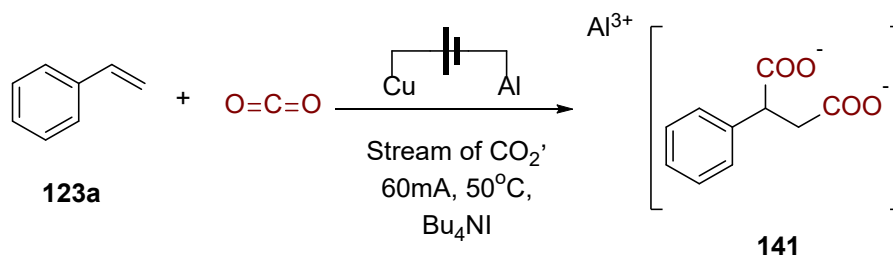
Scheme 50: Electrochemical carboxylation of styrene

General reaction conditions: substrate (2mmol), copper cathode, Aluminium anode, MeCN (50mL), Bu_4NI (1mmol), CO_2 (bubbled 1atm), current density (60mAcm^{-1}), 50°C, 12hs.

The production of a white precipitate was observed, similar to previous reaction. It was theorised that this is the corresponding aluminium adduct in this case **141.** However, after an acidic work up peaks at 2.63, 3.10 and 4.03 ppm, respectively were observed in the ^{1}H NMR spectrum. These peaks match the literature values for compound **124a**. Compound **124a** was produced in average to good yield (68%-80% evaluated form ^{1}H NMR). (Scheme 51).
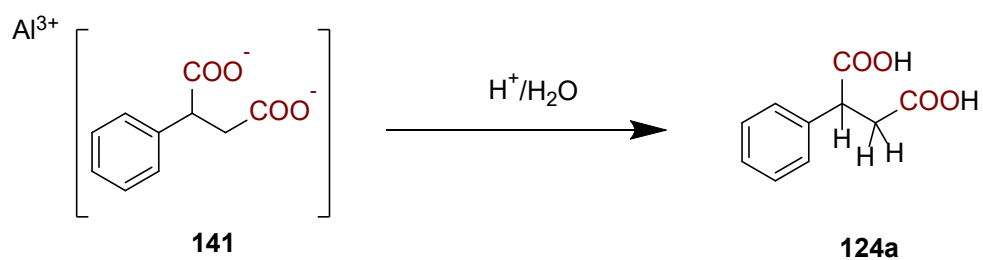
*Scheme 51: Acidic workup to yield **124a***

Additionally, conversion of the starting material was as high 99 % with no noticeable by products. Similar processes have been reported in a variety of journals and papers although nearly all instances use CO_2 at an increased pressure, this technique bypasses that need. [100,101]

2.3.1 Substrate screening

Following the promising performance of the test substrate a variety of compounds containing the olefin moiety where tested. The purpose of this screen was to identify the potential scope of this particular experiment, all substrates contained the olefin moiety in varying compounds ranging from aliphatic and cyclical olefins to heterocycles. Special consideration was also taken to use "bulky" substrates (Entry 5 and 7), the reasoning behind this decision was that, due to the constant flow of CO_2 it would be beneficial to have compounds with a relatively low volatility. (Table 6)

123a-g + O=C=O → **124a-g**
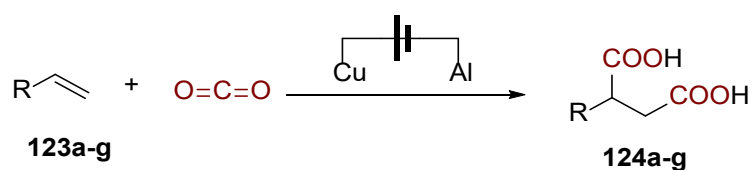
Table 6: Substrate screening

Entry	Substrate	Isolated Yield
1	**123a**	75%
2	**123b**	88%
3	**123c**	N/A
4	**123d**	N/A
5	**123e**	N/A
6	**123f**	N/A
7	**123g**	N/A

General reaction conditions: substrate (2 mmol), copper cathode, aluminium anode, MeCN (50 mL), Bu$_4$NI (1 mmol), CO_2 (bubbled 1atm), current density (60 mAcm^{-1}), 50°C, 12h.

It was evident that only entry 1 and 2 achieved any sort of conversion, with yields varying slightly. Just from this basic screen we can determine that the presence of an aromatic system directly attached to the double bond is crucial. Entry 6 has the necessary aromatic system but exhibits very limited conversion; it is believed that the presence of the nitrogen and its extra lone pair of electrons might interfere with the electronics of the system and potentially react with the CO_2 radical creating an undesirable mixture of by-products.

As stated, prior, it is believed that the reaction proceeds through a radical pathway. If this is the case the presence of an aromatic system can prove beneficial as it can provide delocalisation for the radical charge which translates to a marked difference in stability. This added stability may act as a driving force in the reaction. (Scheme 52)
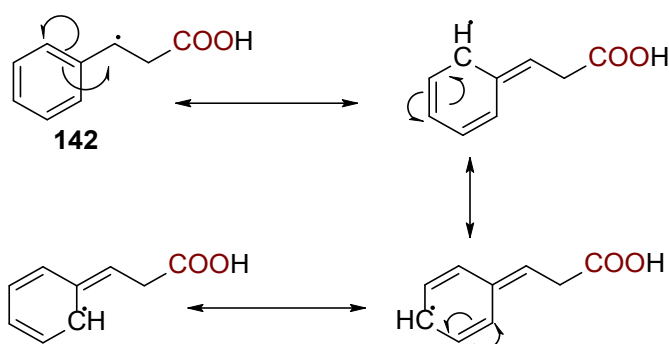
Scheme 52: Delocalisation of radical charge across benzene ring

Although this experiment was quite successful it does not prove to be highly novel as similar dicarboxylations in the presence of CO_2 have been carried out by various groups. [100-102] This type of reaction showed a large amount of promise, mainly due to the fact that the conditions where quite mild compared to other electrocatalytic reactions. However, one major drawback is the sacrificial nature of the aluminium anode as the reaction requires stoichiometric amounts of Al^{3+} to proceed. To alleviate this significant drawback a novel electrochemical system employing the use of non-sacrificial electrodes was envisaged.

2.4 Development of a non-sacrificial electrode method

As previously stated, the main aim of this was to create novel methods to use carbon dioxide as a chemical feedstock, an important facet to this objective was to create sustainable and green methods. These methods would ideally use cheap renewable sources of energy a prime example of this would be the use of electricity garnered from a solar cell. As well as renewable sources of electricity sustainable reactants and feedstocks are necessary, if this is to be achieved fundamental changes need to be made to the previous electrochemical setup. The first step would be to remove the sacrificial electrode and replace it with a sustainable alternative. As shown in the literature the use of sacrificial electrodes is widespread, [76,103,104] the main drive behind this is the high yields, high conversion and regioselectivity achieved through the use of these electrodes. In this electrochemical setup the anode is the driving force as it provides electrons to the system, this can be clearly illustrated in the following scheme (scheme 53).
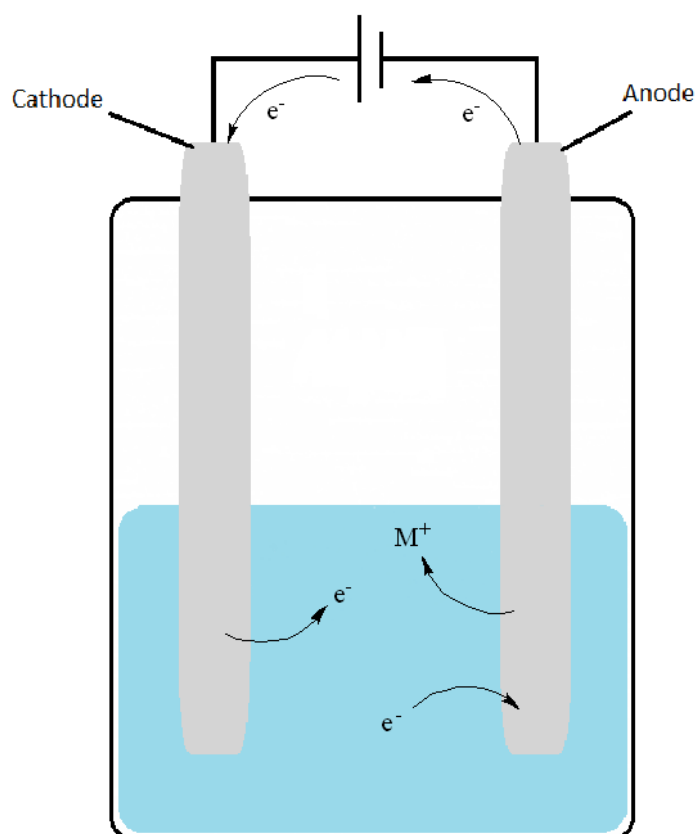
Scheme 53: Electron movement through electrochemical cell

As shown in this system the anode donates electrons to the system as well as producing metal cations which can complex with potential products as was the case in the formation of various oxalates and dicarboxylic adducts in the previous experiments.

Of all the possible non-sacrificial electrodes carbon or graphite was decided upon as a good starting base as carbon electrodes are stable cheap and readily available. An initial exploratory experiment was carried out with similar conditions to previous experiments with the anode being replaced with a carbon anode. It was predicted that this change in itself would not prove successful and additional alterations to the system would have to be made. This hypothesis was proven to be correct as there was no conversion of styrene with nearly all of it being recovered (90%), further investigation into a non-sacrificial electrode setup was needed. (Scheme 54)
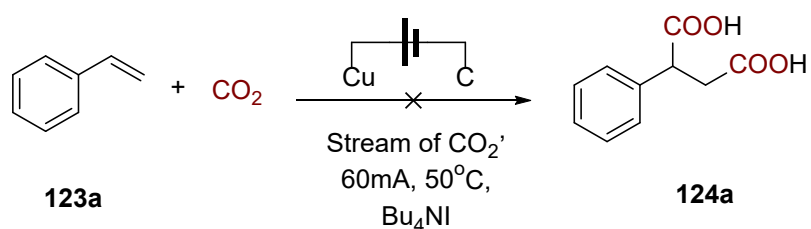
Scheme 54: Attempted carboxlation of styrene with non sacrificial electrode

2.4.1 Additional Electron donor investigation.

In the original sacrificial electrochemical cell as the target molecule was being reduced at the cathode, a complimentary oxidation was happening at the anode. In the case of the original cell it involved the oxidation of the anode itself to form free metal ions, in effect the anode is acting as a source of electrons. The replacement of the metal anode with carbon means this no longer becomes viable due to the carbon electrodes stability. Therefore, a suitable electron donor must be found to provide an effective substitute. The use of electron donors is extremely prevalent in photochemical redox systems. Various molecules can be used as electron donors; after consulting the literature triethanolamine (TEOA) was chosen as the electron donor.[105-107]
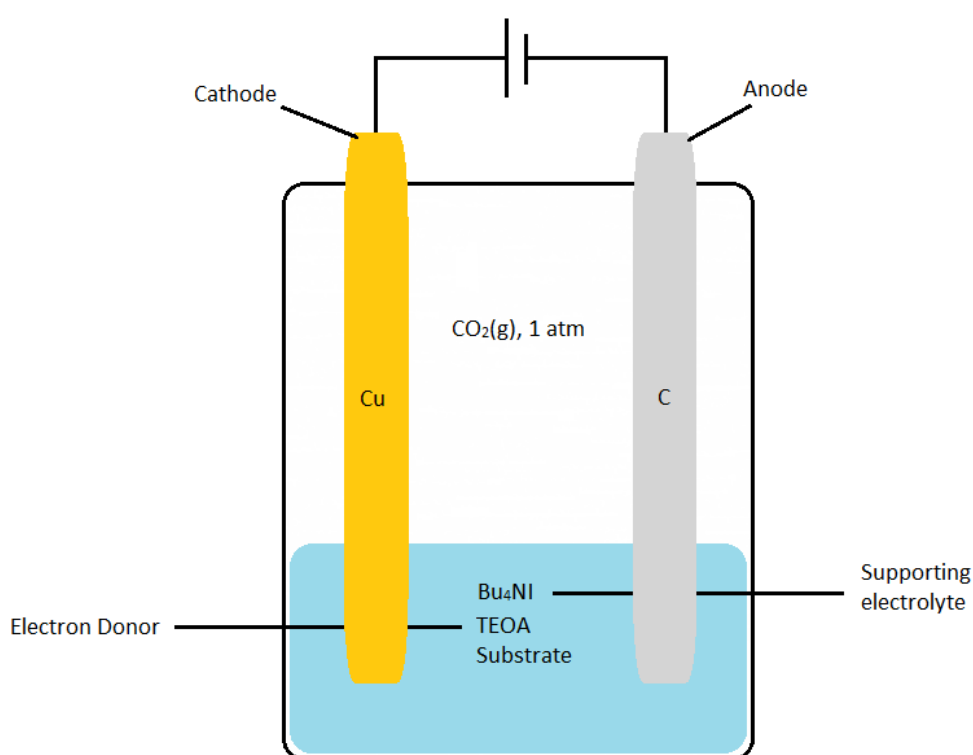
Figure 20: Initial novel electrochemical cell

After the addition of the electron donor the experiment proceeded albeit with unexpected results. The production of the di-carboxylic acid seen previously in the sacrificial electrode system was not present this time. Instead β mono carboxylic acid was synthesised as well as the corresponding cyclic carbonate in a 3:1 ratio, with >99% conversion of styrene (Scheme 55).
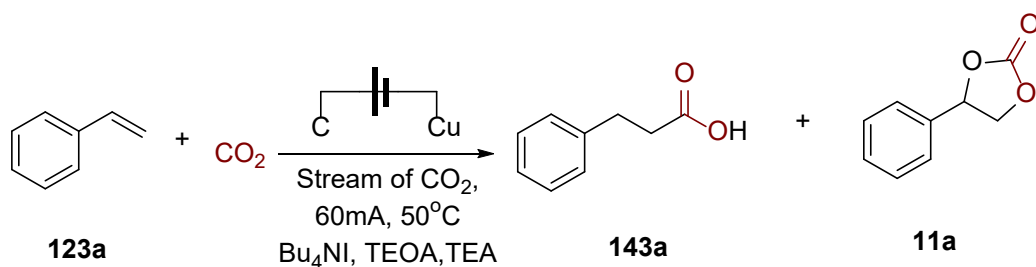
Scheme 55: Electrocarboxyaltion of styrene with novel electrochemical cell
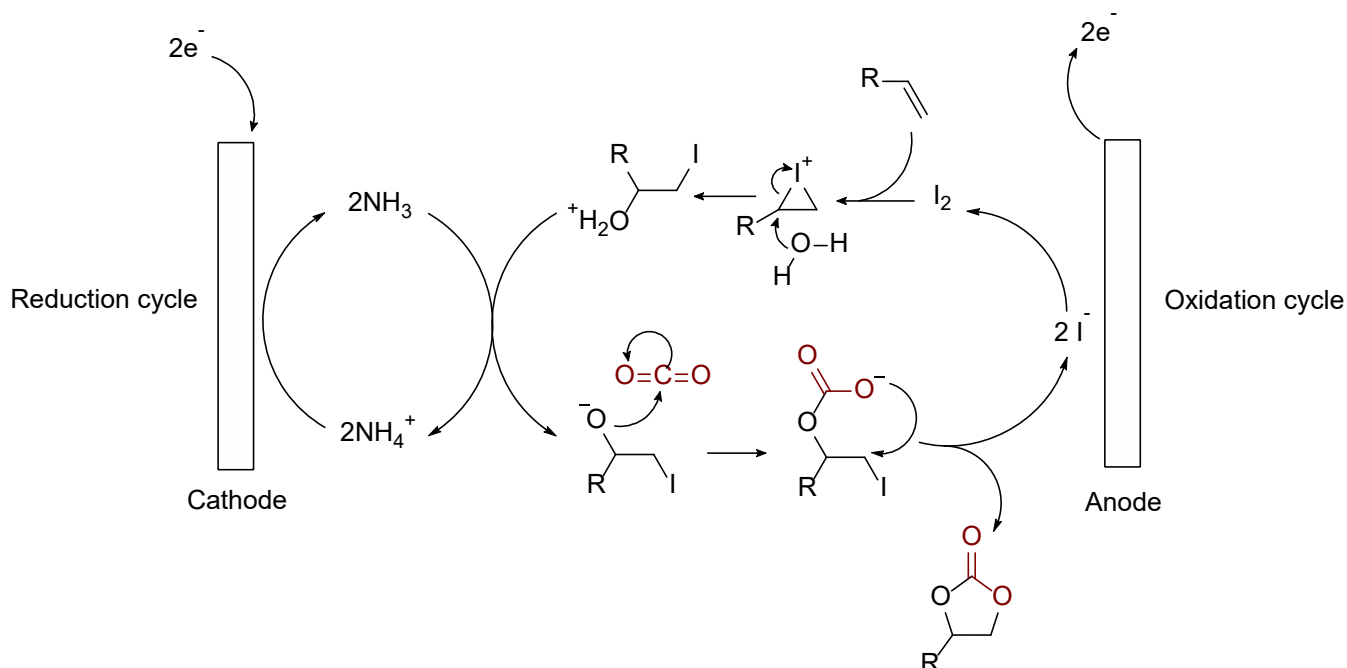
Scheme 56: Formation of cyclic carbonates predicted by Gao et al.

Although unexpected the synthesis of the monoacid is quite interesting as it is a very versatile molecule which can be used further in synthetic pathways, coupled with the fact that carboxylation was achieved regioselectively at the terminal β carbon and the potential of this novel electrical chemical cell is evident. Further optimisations had to be undertaken as separating and isolating the acid and cyclic carbonate without loss of either is challenging, it would also be preferable if the selectivity of the reaction can be tuned to afford a single product (preferably the acid) and not a mixture.

2.5 Optimisation of Novel Electrochemical cell.

The presence of two major products was not an initially favourable result, it was believed that manipulation of the wide range of reaction conditions and variables would help to optimise the novel electrochemical cell (NEC) towards a single product.

2.5.1 Functionalisation of Carboxylic Acid

To achieve accurate measurements and employ the use of gas chromatography to track certain reactions the carboxylic acid product must be functionalised. The most facile transformation of a carboxylic acid would be alkylation, more specifically methylation to form the corresponding methyl ester. Methylation of a carboxylic acid can be achieved through a variety of procedures. The most common methylation procedures would be the Fischer-Speier Esterification[108] and Steglich Esterification [109].

A relatively new and efficient way of producing methyl esters from their corresponding carboxylic acids was developed in 1981 by the Hashimoto group, [110] they showed that carboxylic acids, even complex fatty acid types would almost always react quantitatively to give the corresponding methyl ester. (Scheme 57)

A test was carried out to see if this type of protocol would be applicable to our experiment and the general carboxylic acid substrate.
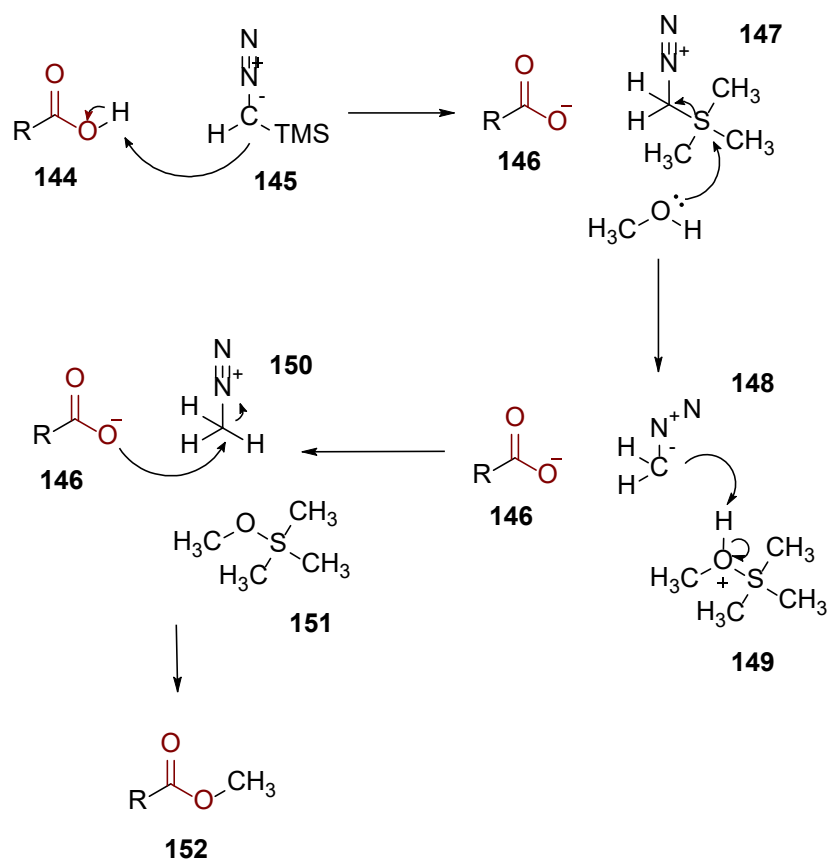
Scheme 57: Methylation of carboxylic acids developed Hashimoto group

The methylation was extremely successful providing a quantitative yield of the methyl ester, it was therefore adopted into the standard protocol when analysis through gas chromatography was required. The functionalisation of the carboxylic acid to afford the methyl ester also allowed for easier purification as the methyl ester is easily columned unlike the carboxylic acid.

2.5.2 Removal of Triethylamine (TEA)

TEA was first used in the reaction as an H+ scrub, several groups have used this mild base to pick up unwanted H+ ions which could hinder the reaction. It was theorised that the additional H+ ions would increase the number of by-products exhibited. Removal of this co-reactant showed no signs of hindering the reaction, so a decision was taken to omit it from any further experiments in the interest of sustainability.

2.5.3 Altering the electrodes

Another key area of optimisation was directed towards the electrodes themselves, it was assumed that certain materials might perform better leading to an increase in the conversion and yield. The initial system comprised of a copper cathode and a graphite (carbon) anode. Although it is not fully understood the assumption was made that the copper anode was an important part of the system because background research produced various papers which showed that copper complexes have been used extensively in the reduction of CO_2.[97,111,112] There has also been significant research into the use of Nickel complexes in the reduction of CO_2.[101,113] An investigation of various metal cathodes was undertaken to see which proved to be the optimum for the electrocarboxylation reaction.

The copper anode was replaced with nickel while all the other reaction conditions remained constant. This proved fruitless as there was a marked drop in conversion while the yield and ratio of by-products did not change markedly. Various combinations of anodes and cathodes where trailed.

It was observed that if two metal electrodes are present the current density of the electrochemical cell increased dramatically, this is to be expected as metals are very good conductors with very low resistances. As a consequence of this the rate of reaction was particularly high, this does however come with a few drawbacks. The stability of the electrodes is questionable as it was observed that degradation was present on all metal electrodes. This was most prevalent in the case of copper electrodes with a green precipitate coating the electrodes over time most likely cooper carbonate. This precipitate inhibited electronic efficiency of the cell, minimising the conversion of the substrate as well as producing a wide range of by-products making purification unlikely. The changing of the electrodes also did not have a visible effect on the final products formed as the cyclic carbonate by-product was still ever present.
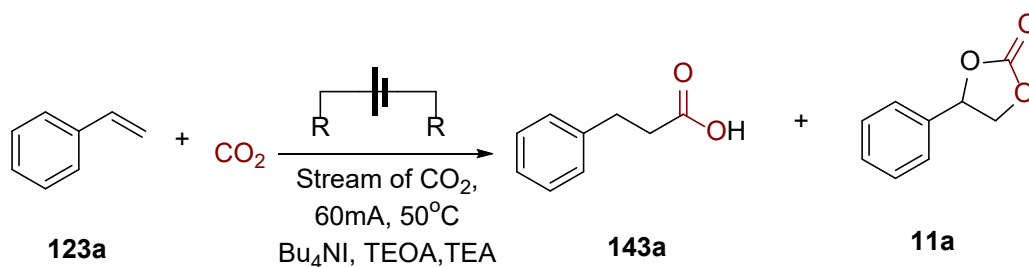
123a + CO₂ → 143a + 11a

Stream of CO₂,
60mA, 50°C
Bu₄NI, TEOA,TEA

Table 7: Screening of Electrode materials

Entry	Anode	Cathode	Conversion	Ratio
1	Copper	Copper	99%	3:1
2	Carbon	Copper	99%	3:1
3	Carbon	Nickel	40%	1:1
4*	Steel	Steel	99%	1:0

General reaction conditions: substrate (2 mmol), varying cathode, varying anode, MeCN (50 mL), Bu₄NI (1 mmol), TEOA (2 mmoL), CO_2 (bubbled 1atm), current density (60 mAcm⁻¹), 50°C, 12 h.

*: substrate (1mmol), varying cathode, varying anode, DMF (10 mL), Et₄NI (1 mmol), TEOA (2 mmol), CO_2 (bubbled 1 atm), volts (10 V), 25°C, 12h.

During the initial experimentation (entries 1-3) the voltage was not controlled. This manifested during the reactions as it observed that the voltage would gradually rise as the power supply compensated for the increase in resistance, trying to keep the current constant. Although not fully understood it can be fair to assume that the varying voltage might have a distinct influence on the final composition of crude mixture as an increase in overpotential may promote various side reactions, thereby lowering the overall amount of monoacid produced.

Although under fully optimised conditions, entry 4 presented the potency of stainless-steel electrodes. The electrodes did show slight signs of degradation after completion of the reaction, however visible signs of carbonate or oxalate formation was not present. This could be attributed to the robustness of the electrodes or perhaps, under the optimised conditions the production of carbonate and oxalate cannot proceed due to a higher overpotential, thereby effectively stopping the formation of carbonates and oxalates proceeding. The only real benefit attributed to using these electrodes was the increased rate of reaction as they are superior conductors when compared to their carbon analogues.

As stated previously it is important to make the reaction and cell as sustainable as possible, therefore it was only natural to try and replace the anode with a carbon material analogous to that of the cathode, this would also improve the purity of the final products formed as well as remove any production of metal carbonates.

Initially, a graphite anode analogous to the cathode was used. After running the experiment, it was evident that the graphite electrodes where superior. Again, the yields and the conversion did not dramatically change, however after work up the resulting reaction mixture was shown to be less contaminated by minor by-products. This aids us in further reactions or purification of the reaction mixture.

Further, investigation was done into different carbon materials in particular carbon fibre, the hypothesises behind this decision was that an increased surface area would allow the reaction to proceed faster and maybe influence the final ratio of the mixture. In truth after various experiments it was shown, however, that again there was no marked distinction between the graphite carbon initially used and the new carbon fibre.

It was decided that due to the carbon fibres economical properties and the fact that it was easier to manipulate that it would be brought forward for any future experiments.
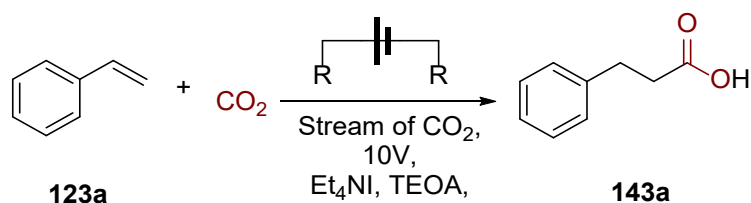
Table 8: Screening of carbon electrodes

Entry	Anode	Cathode	Yield
1	Graphite	Graphite	65%
2	Carbon fibre	Carbon fibre	67%

General Conditions: substrate (1mmol), varying cathode, varying anode, DMF (10 mL), Et_4NI (1 mmol), TEOA (2 mmol), CO_2 (bubbled 1 atm), volts (10 V), 25°C, 12 h.

2.5.4 Solvent Screening

It is well known that the solvent system can have a vast impact a reaction, with the various properties that a solvent has playing major contributing factors. Initial experiments were carried out in acetonitrile. Acetonitrile has many favourable properties such as its low boiling point, high dielectric constant, polar nature and electronic stability which allow it to perform well in an electrochemical setting. Attempts were made to substitute the solvent to try and improve yield, conversion and by product production.

The dielectric constant **ε** of a solvent is a measure of a substances ability to insulate charges from each other. A higher dielectric constant usually corresponds to a higher polarity, which in turn accounts for a substances ability to stabilise charge. The dielectric constant of acetonitrile is 37.5 ε, [114] this value is quite high allowing acetonitrile to work well in the electrochemical cell. With this information a wide selection of solvents where tested to determine their applicability and effects on the novel electrochemical cell. The conversion of styrene as well as the ratio of main product to by-product was focussed on as the defining results.
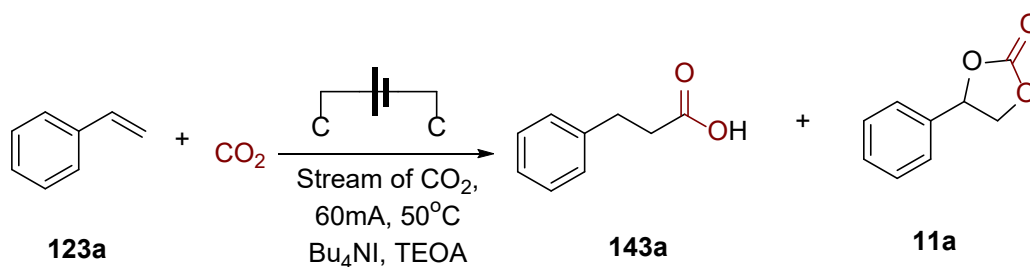
123a + CO_2 → Stream of CO_2, 60mA, 50°C, Bu$_4$NI, TEOA → **143a** + **11a**

Table 9: Sovent Screening

Solvent	Dielectric Constant ε	Conversion	Ratio	Yield
Acetonitrile	37.50	99%	3:1	66%
DMF	36.70	99%	3:1	70%
THF	7.60	0%	N/A	N/a
Acetone	20.7	0%	N/A	N/A
MeOH	32.6	0%	N/A	N/A

General reaction conditions: styrene (2 mmol), carbon cathode, carbon anode, solvent (25 mL), Bu$_4$NI (1 mmol), TEOA (2 mmol) CO_2 (bubbled 1 atm), current density (60 mAcm^{-1}), 50°C, 12h.

As shown in the table generally solvents with a higher di-electric constant performed better, with both higher conversions and preferable ratio of product to by-products. Both acetonitrile and DMF have similar di-electric constants but it was observed that DMF faired marginally better in terms of increased yield, with a higher purity after workup.

As well as needing a high di-electric constant, prospective solvents must also be able to effectively solvate CO_2. The solubility of CO_2 in various organic solvents has been disputed over the years, with various groups quoting different experimental and theoretical values.[115] Consensus has be reached is the idea that "like dissolves like" if this is implemented with CO_2 in mind organic solvents which contain C=O groups are ideal. DMF best fits this description.

Furthermore, an investigation was carried out on the actual volume of DMF needed in the reaction. Reducing the amount of DMF would be beneficial from an economic, safety and "green" standpoint.

Table 10: DMF volume screening

Entry	Volume	Isolated Yield
1[a]	25	57.59%
2	10	68.6 %
3	5	60 %

General reaction conditions: substrate (2mmol), carbon cathode, carbon anode, DMF, Bu_4NI (1 mmol), TEOA (2 mmol) CO_2 (bubbled 1 atm), current density (60 mAcm^{-1}), Voltage (10 V), 50°C, 12hs.

a = 13V

It was pretty evident that a lower volume of DMF contributed to a higher yield, this could be down to the fact that with a lower volume the concentration of all the substrates in solution is drastically increased. An increase in concentration being a commonly used method of increasing yield and rate of reaction in many well-known reactions. It was decided that 10 mL of DMF would be used in all further reactions.

2.5.5 Screening of the Electronic conditions

The voltage and current of the electrochemical system are key variables which have a major influence on yield, conversion and by-product formation. The voltage dictates what electronically active species are formed as compounds are reduced and oxidised at specific potentials. Common in many electrochemical cells is the phenomenon called overpotential. Overpotential refers to the difference between a half-reaction thermodynamically determined reduction potential and the potential at which the redox occurs. The reduction of CO_2 has multiple half-reactions, here we see the most common one's vs a standard hydrogen electrode at a pH of 7. (Table 11)

Table 11: Half-reactions for potenial reductions of CO_2

Possible half-reactions of electrochemical CO_2 reduction	Electrode potentials (V vs SHE) at pH 7
CO_2 (g) + e$^-$ → *COO$^-$	-1.90
CO_2 (g) + 2H$^+$ + 2e$^-$ → HCOOH (l)	-0.61
CO_2 (g) + H$_2$O (l) + 2e$^-$ → HCOO$^-$ (aq) + OH$^-$	-0.43
CO_2 (g) +2H$^+$ + 2e$^-$ → CO (g) + H$_2$O (l)	-0.53
CO_2 (g) + H$_2$O (l) + 2e$^-$ → CO (g) + 2OH$^-$	-0.52
CO_2 (g) + 4H$^+$ + 2e$^-$ → HCHO(l) + H$_2$O (l)	-0.48
CO_2 (g) + 3H$_2$O (l) + 4e$^-$ → HCHO (l) + 4OH$^-$	-0.89
CO_2 (g) + 6H$^+$ (l) + 6e$^-$ → CH$_3$OH (l) + H$_2$O (l)	-0.38
CO_2 (g) + 5H$_2$O (l) + 6e$^-$ → CH$_3$OH (l) + 6OH$^-$	-0.81
CO_2 (g) + 8H$^+$ + 8e$^-$ → CH$_4$ (g) + 2H$_2$O (l)	-0.24
CO_2 (g) + 6H$_2$O (l) + 8e$^-$ → CH$_4$ (g) + 8OH$^-$	-0.25
2CO$_2$ (g) + 12H$^+$ + 12e$^-$ → C$_2$H$_4$ (g) + 4H$_2$O (l)	0.06
2CO$_2$ (g) + 8H$_2$O (l) + 12e$^-$ → C$_2$H$_4$ (g) + 12OH$^-$	-0.34
2CO$_2$ (g) + 12H$^+$ + 12e$^-$ → CH$_3$CH$_2$OH (l) + 3H$_2$O (l)	0.08
2CO$_2$ (g) + 9H$_2$O (l) + 12e$^-$ → CH$_3$CH$_2$OH (l) + 12OH$^-$ (l)	-0.33

The 1st half reaction showing the reduction of a CO_2 molecule to its radical form is the hypothesised half reaction taking place in the novel electrochemical cell. As shown in table the reduction potential of that half reaction is -1.90V, this value is quite high when compared to all the other various half-cell reductions. This value for the reduction potential is thermodynamically, in experimental cases this value would not be enough to allow for reaction to proceed. In electrolytic and electrochemical cells, a higher potential is usually needed for the reactions to proceed, this is given the name overpotential.

The overpotential can be divided into various categories such as activation overpotential, resistance overpotential and concentration overpotential although it is hard to measure how much each specific category contributes to the overall overpotential. The setup of the novel electrochemical cell has quite a few components which can contribute to this overpotential especially the resistance produced by the carbon electrodes. The overpotential of initial experiments was as high as 60V, this amount of overpotential is very poor Faradaic efficiency as the current density of the electrochemical is extremely low and a lot of the potential is lost through heat which can be deemed a hazard as the reactions are done in a flammable liquid. Many groups have investigated the possibility of lowering overpotential of electrochemical cells[116-119] as it would increase the Faradaic efficiency and economical legitimacy of the experiment.

The current electrical conditions focussed on keeping the current constant at 60ma, with this being the case the voltage is allowed to fluctuate significantly especially if any precipitate is formed on the electrodes. The formation of the precipitate reduces the working area of the electrode increasing the resistance and lowering the current, to compensate for the electrical power supply increasing the voltage to try and keep the current constant. As the voltage provides the driving force of the reaction it was deemed important to keep it constant. An effective range of 5-20V was investigated to see which would provide the best results on the yield and ratio of products to by-products. Analysis of the nmr spectra achieved showed that as the voltage is increased form 5V to 15V (through 10V) the ratio of acid to by product increases from 3:1 to 8:1.
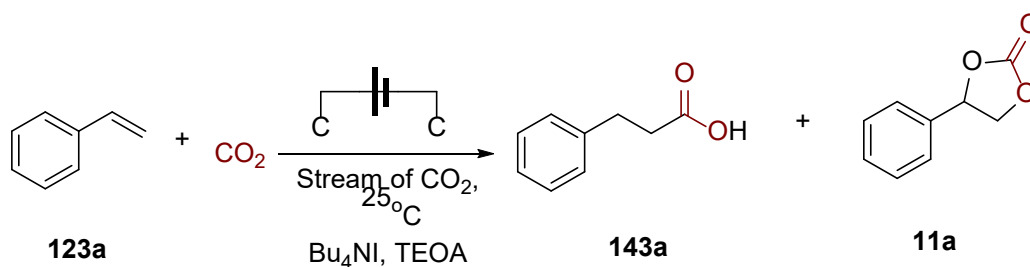
123a   +   CO₂   →   143a   +   11a

Stream of CO₂,
25°C
Bu₄NI, TEOA

Table 12: Volatge Screening

Experiment	Voltage	Ratio	Conversion
1	5V	3:1	99%
2	10V	3.5:1	99%
3	15V	8:1	99%
4	20V	N/A	N/A

General reaction conditions: styrene (2 mmol), carbon cathode, carbon anode, DMF (25 mL), Bu₄NI (1 mmol), TEOA (2mmol) CO_2 (bubbled 1atm), 25°C, 12 h.

Coupled with higher conversions it is evident that a higher voltage has a beneficial effect on the electrochemical system, this can be credited to the fact that a higher overpotential is needed to drive the reaction forward, as well a higher voltage the current achieved is higher. It has been observed at various times during this investigation that a higher current correlates with a higher rate of reaction. At 20V the NMR analysis showed a lack of acid product being produced, this could be due to the fact that the higher voltage is destroying the acid product as its being formed although this is just a hypothesis.

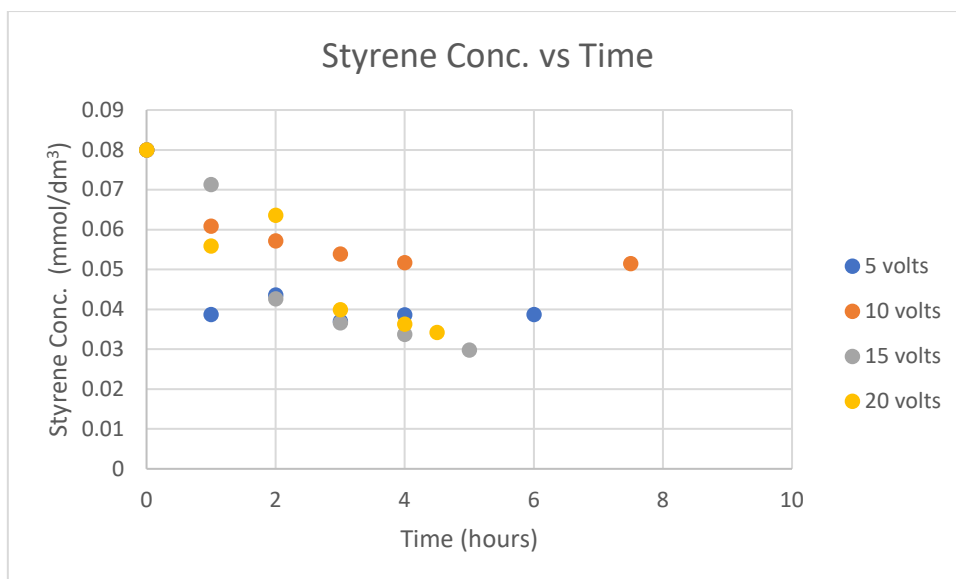Gas chromatography analysis was carried so a better understanding of the rate of reaction can be achieved.

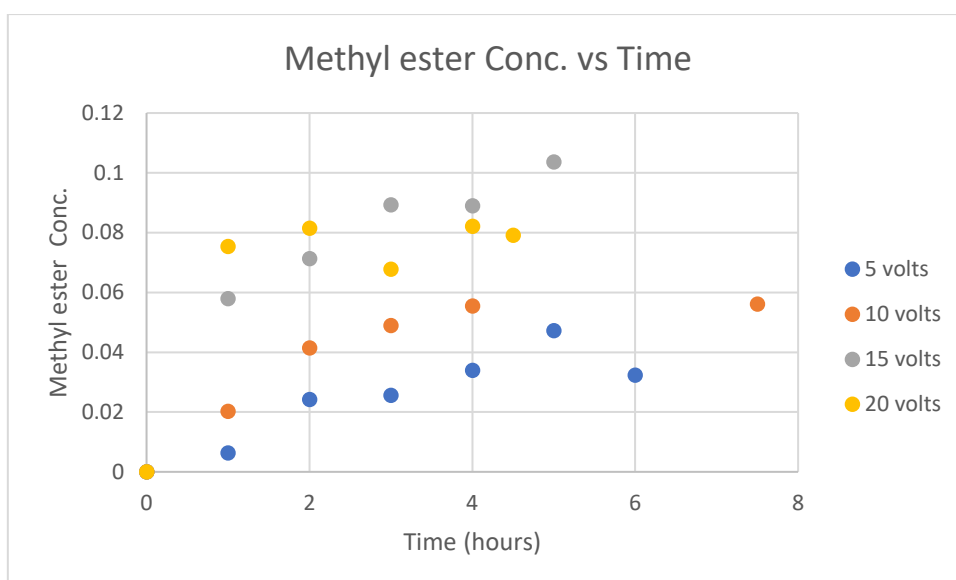Figure 21: Styrene conc. vs Time

Figure 22: Methyl ester conc. vs Time

Aliquots of the reaction mixture were taken at 1-hour intervals via a syringe, these aliquots were then methylated using TMS-diazomethane. Each aliquot was then analysed with a GC equipped with an FID detector, naphthalene was used as the internal standard mainly looking at the decreasing concentration of styrene as well as the increase in concentration of Methyl 3-phenylpropanoate. Analysis showed that as the voltage was increased the rate of reaction and final yield also increased. The clearest representation of this can be found in Figure 22. Initial production of the acid (analogous to methyl ester) varies greatly with greater amounts produced at higher voltages. Although not measured accurately it was observed that the current was higher at higher voltages. It would stand to reason that at higher currents the rate of reaction is higher due to the increased flow of electrons

through the system. The production starts to plateau after 3 to 4 hours, this occurs at all voltages. This maybe be down to a build-up of deposits on the electrodes inhibiting the electrochemical reaction. After taking into consideration both the GC and NMR data as well looking to make the process as efficient as possible, it was decided to limit the voltage for all future experiments to between 10 and 15 volts.

2.5.6 Sacrificial Electron donor screening

For the reduction of CO_2 to its active species to occur a transfer of electrons must occur, as the CO_2 is being reduced a subsequent oxidation must occur to balance the reaction. In the case of the sacrificial electrode system it is the metal anode which provides the electrons necessary for the reduction of CO_2. As the metal anodes oxidise and degrade CO_2 is reduced to its reactive radical form. Since the novel electrochemical cell has non-sacrificial electrodes, the electrons required for the reduction of CO_2 must come from a suitable electron donor. (Scheme 58)

$$Al \longrightarrow Al^{3+} + 3e^-$$

$$Mg \longrightarrow Mg^{2+} + 2e^-$$
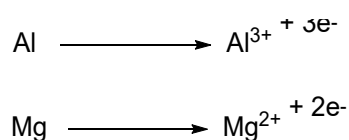
Scheme 58: Oxidation of non sacrificial electrodes (Al and Mg)

As previously stated the sacrificial electron donor is a key component of the novel system as with it the reaction does not proceed. It has been shown by many groups especially in the sphere of photochemistry and photochemical reduction of CO_2 that Tertiary aliphatic amines are perfect sacrificial electron donors. [120,121,122]

The Carpenter Group in particular has been able to create a viable sacrificial electron donor in the reduction of CO_2 which carries highly sought after renewable qualities.[123] The group identified the potential of a conformationally restricted tricyclic amine **153**, (Scheme 59) the group's decision was based on extensive research carried out on the reduction of CO_2 by amines such as TEA [124] and arylamines. [125] Using computational models which take into account reaction enthalpies of various gas phase reactions, electronic structures, harmonic vibration frequencies and density functional theory, the group predicted that this type of particular amine would restrict the formation undesirable by products.
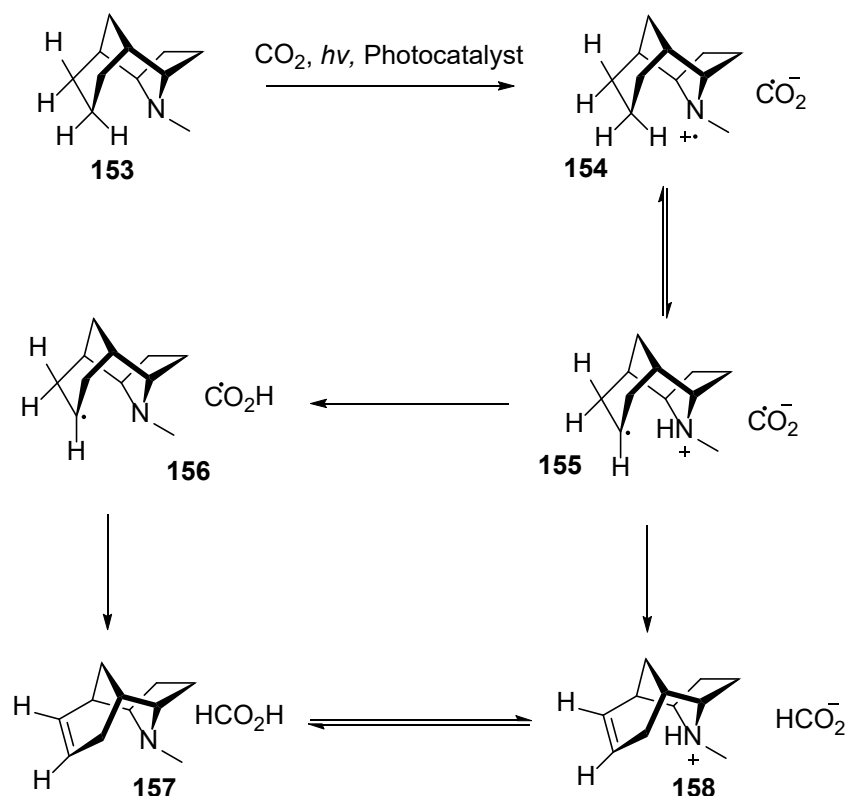
Scheme 59: Photochemical reduction of CO_2 by amine **153**

Scheme 59 illustrates the calculated mechanism for the photochemical reduction of CO_2 by amine **153**. The photoexcitation of both amine **153** and CO_2 produces 2 radical species, following 1,5 hydrogen atom shift within the amine. This is followed by the abstraction of a hydrogen atom to form a reactive formate species. The group showed that with a similar amine **159** it was possible to reduce CO_2 to the formate ion, amine **159** is subsequently oxidised to amine **160**. It was then possible to hydrogenate and regenerate amine **159** with the use of palladium-on-carbon (Pd/C). This showed that a sustainable amine can be used in the photochemical reduction of CO_2.
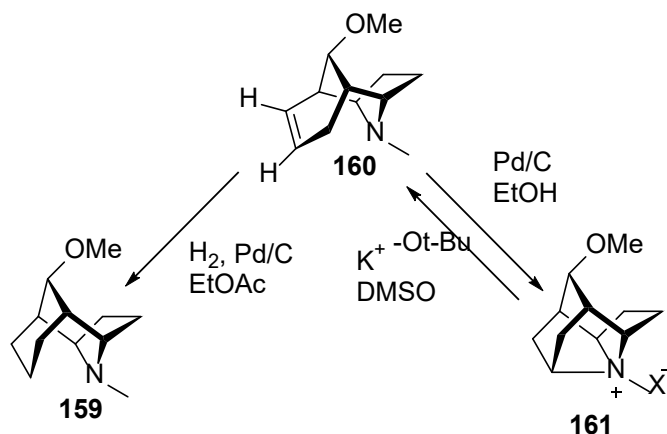
Scheme 60: Regenration of **159**
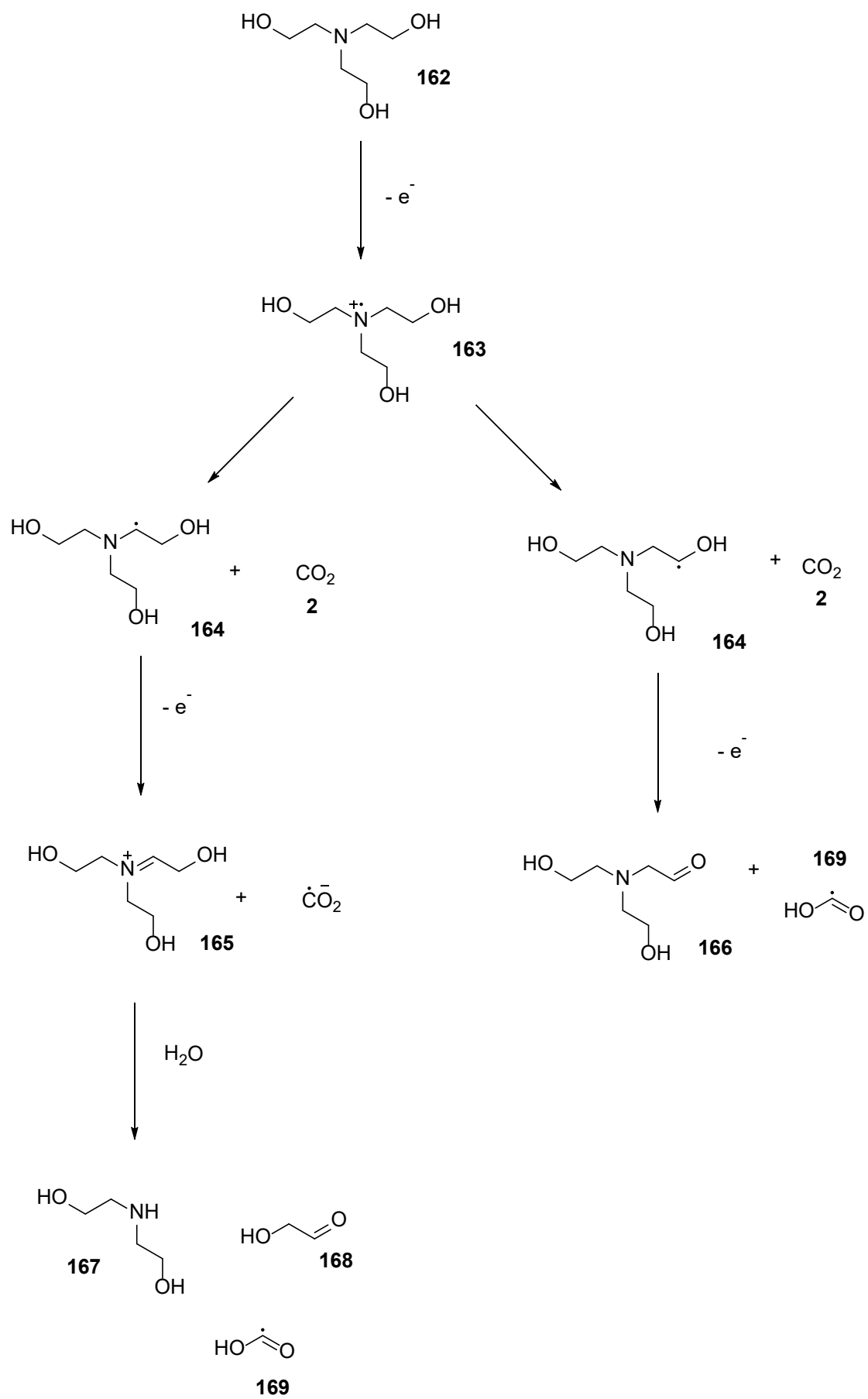
Scheme 61: Prospective mechanism of TEOA as reductant

Tertiary amines such as triethanolamine (TEOA) are ideal sacrificial electron donors (SED) as they are irreversibly oxidised at around 0.7V vs SCE, this allows the activated SED to partake in electron transfer and facilitate the reduction of CO_2. Another important feature of TEOA is that it is irreversibly oxidised into inert molecules, which do not interfere in the main reaction. As shown in the charge a radical charge may form in two positions, the alpha position favouring the formation of a double bond with the nitrogen, whilst the beta position favours the formation of a double bond with the oxygen. It was hypothesised that TEOA may be replaced by a simple alcohol which may be able to perform the same task. The first four simple alcohols where screened, as well as screening TEA in the absence of TEOA.

Initial results from ^{1}H NMR spectroscopy confirm that all the simple alcohols serve the job of TEOA, however, further investigation and analysis show that some perform better than others. As well NMR analysis the reactions where tracked by gas chromatography using the same standards and methods used in previous analyses.
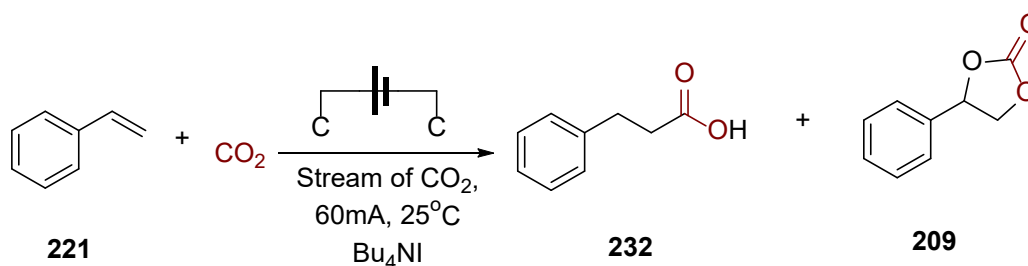

Table 13: Screening reductant

Entry	Reductant	Conversion	Ratio (acid to carbonate
1	TEOA	>99%	1:0
2	MeOH	80%	1:0
3	EtOH	80%	1:0.6
4	IPA	55%	2:1
5	t-BuOH[a]	N/A	1:0.2
6*	TEA	0%	N/A

General reaction conditions: substrate (2 mmol), ACN (25 mL), Bu$_4$NI (1 mmol), Reductant (2 mmol) CO$_2$ (bubbled 1 atm), current density (60 mAcm^{-1}), rt, 6 h. a: Samples for t-BuOH degraded before accurate GC spectroscopy could be run. * Solvent: DMF 25mL
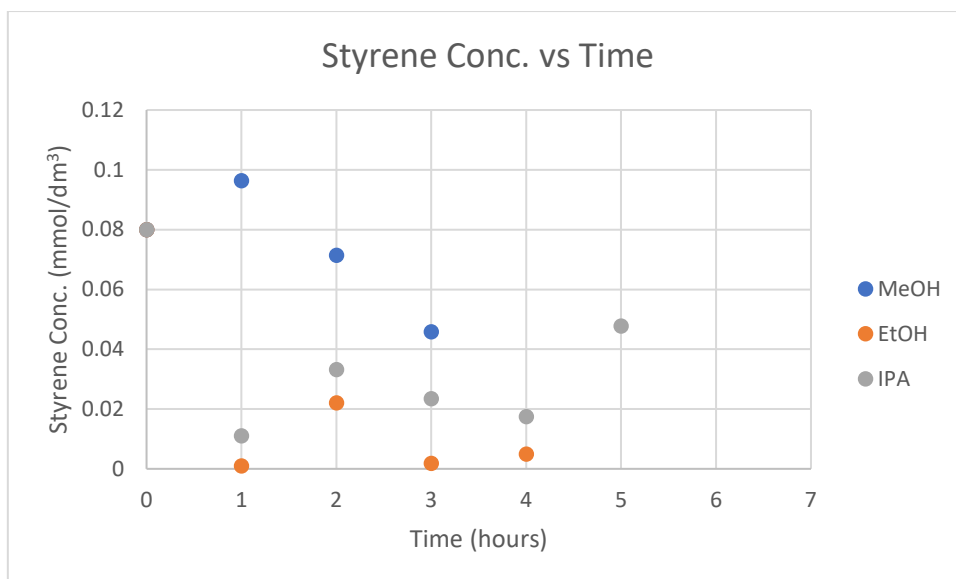
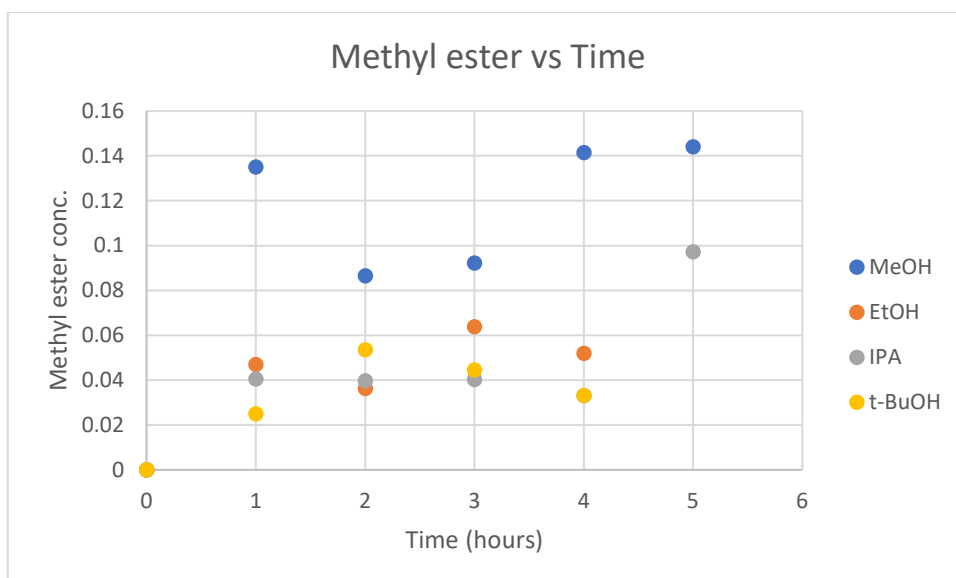Figure 23: Styrene conc. vs Time

Figure 24: Methyl ester conc. vs time

Data collected from GC analysis did not elude to any definitive impact on the rate of reaction for the electrocarboxylation reaction but affirmed previous results. TEOA was chosen as the designated electron donor due to its better conversion of the substrate.

2.5.7 Supporting Electrolyte

Supporting electrolytes are crucial components of an electrochemical setup. They are usually ionic salts with quaternary ammonium salts being used extensively by many groups in a host of different electrochemical cells.[113,126] Their primary use is to increase the conductivity of a non-aqueous electrochemical system. It is also believed that the supporting electrolyte can play an important role in directing and influencing electrochemical reactions, thus investigation and screening of different supporting electrolytes with varying concentrations was undertaken to better understand how the supporting electrolyte influences the yield of our novel electrochemical reaction. It was decided that as starting basis half an equivalent of the supporting electrolyte would be used as stated in previous work carried out by the Buckley group (Table 14).
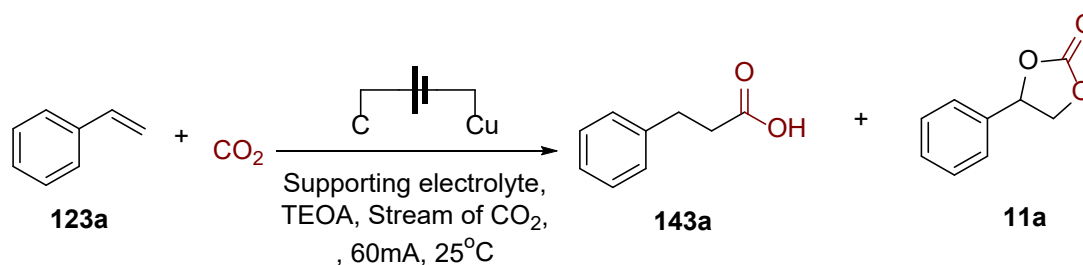

Table 14: Screening supporting electrolytes

Entry	Electrolyte	Conversion	Ratio: Acid to carbonate
1	Bu_4NI	>99%	3:1
2	Bu_4NBr	>99%	1:1
3	Bu_4NCl	>99%	1:1
4	Bu_4NPF_6	<5%	N/A
5	Bu_4NHSO_4	<5%	N/A
6	KI	<5%	N/A

General reaction conditions: substrate (2 mmol), ACN (50 mL), Supporting electrolyte (1mmol), TEOA (2 mmol)

CO_2 (bubbled 1 atm), current density (60 mAcm^{-1}), rt, 18 h.

Initial screening revolved around testing supporting electrolytes which are similar to Bu₄NI, these include the bromine and chlorine adducts. As shown all the halide containing tetrabutylammonium salts performed extremely well, so much so it was hard to distinguish the which was superior just from the interpretation of the NMR data. It is evident that the presence of a halide ion is essential as well as the presence of the tetrabutylammonium ion. Further testing was carried out on the loading of the supporting electrolyte. (Table 15)
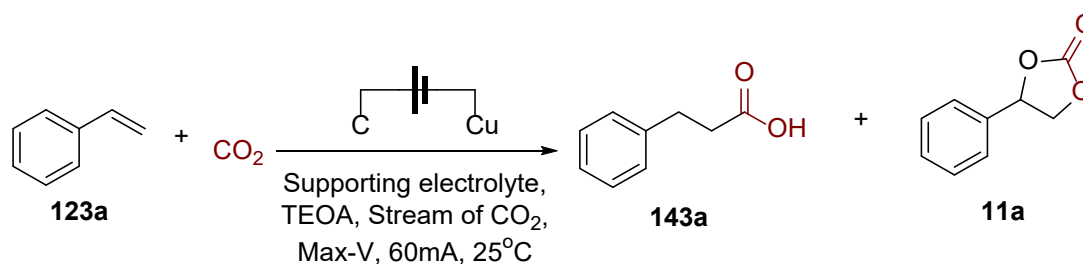

Table 15: Screening loading of supporting electrolyte

Entry	Electrolyte	Conversion	Ratio
1	BuN₄I (0.5mmol)[a]	N/A	14:1
2	BuN₄I (1mmol)	60%	100:4
3	BuN₄I (2mmol)	>99%	7:1

General reaction conditions: substrate (2 mmol), ACN (25 mL), Supporting electrolyte (1 mmol), TEOA (2 mmol) CO_2 (bubbled 1 atm), current density (60 mAcm^{-1}), rt, 18 h.

a: Samples degraded before accurate GC spectroscopy could be achieved.

An initial screening test was carried out varying the concentration from 0.25 equivalents, 0.5 equivalents and 1 equivalent of the tetrabutylammonium salt with regards to the starting material. Although quantitative data was not achieved enough analysis was done through other methods to get a clear picture of how the concentrations influenced the reaction.
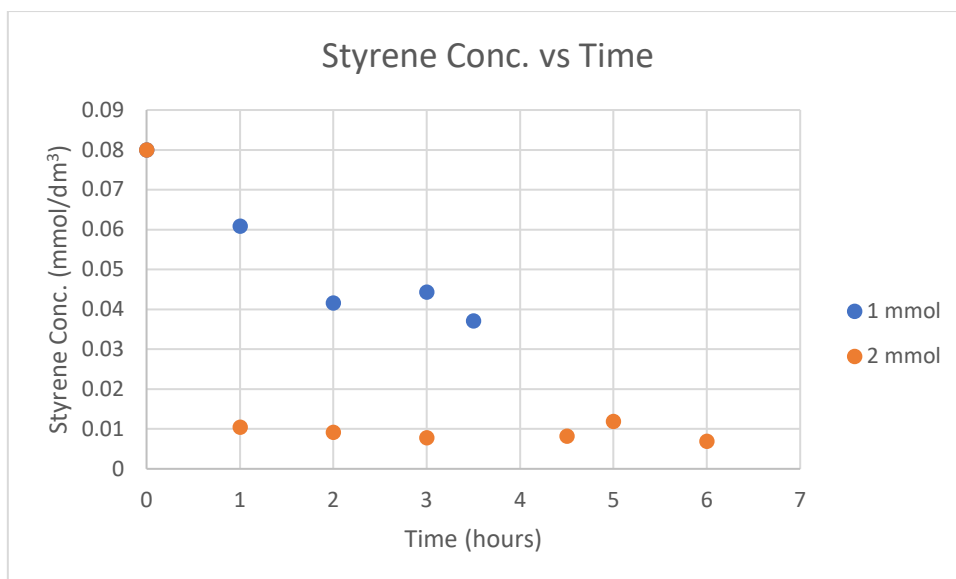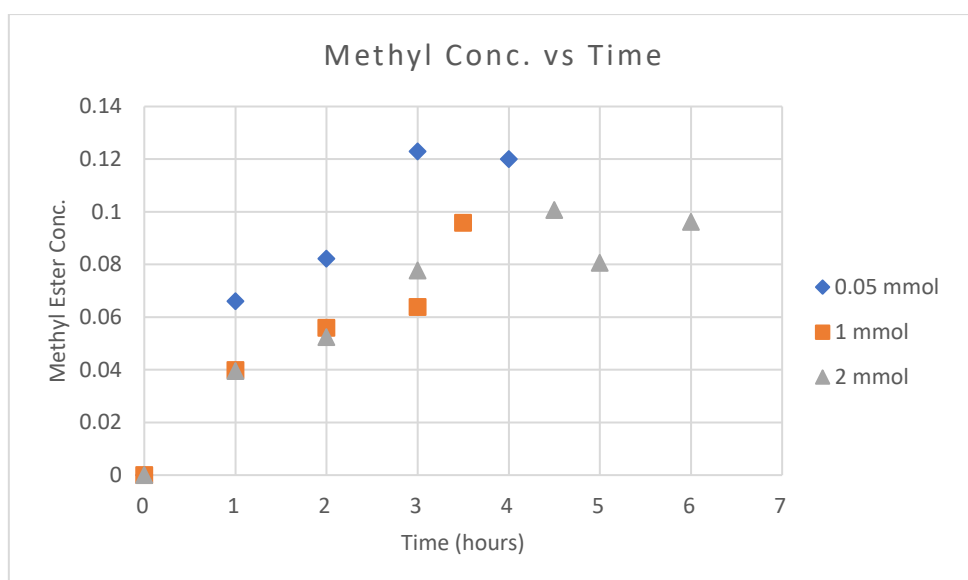
Figure 25: Styrene conc. vs time

Figure 26: Methyl ester conc. vs time

Through the interpretation of GC and NMR spectra we can see the concentrations of Bu_4NI has a direct influence on the amount of by-product produced and on the conversion of the starting material. At higher concentrations of supporting electrolyte there is a higher conversion of the styrene, this is shown clearly in both the NMR spectra and GC data analysis. Due to the higher concentration of electrolyte more current can be passed through the cell equalling higher levels of conversion and quicker rates of reaction. Although these results are positive, they come with a certain drawback, it seems that increased concentration of supporting electrolyte allows for more of the cyclic carbonate to be produced.

Although a definitive mechanism for the production of the cyclic carbonate is not known, a possible route might have been suggested by Gao *et al*. in Scheme 56

As shown in the proposed mechanism an active iodonium species is formed, this species then undergoes further reaction with water and carbon dioxide to from a cyclic carbonate. Therefore, it is fair to assume that if there is more I^- present in the cell there would be a higher chance of this reaction pathway taking place, this is backed up by previous results also showing that the reaction does not proceed without a halide present. Therefore, the concentration of the supporting electrolyte was kept at 1 mmol to minimise these effects.

From an experimental point of view the use of Bu_4NI as the supporting electrolyte is justified as it produced the highest conversion and yield. As well as being an excellent supporting electrolyte Bu_4NI is also a very power phase transfer catalyst. [127]

Phase transfer catalysts are an important class of compound as they provide an avenue for reactive species to migrate between aqueous and organic phases allowing for faster reactions, higher conversions and eliminating the need for dangerous solvents which dissolve all reactants in phase. However, when it comes to the work up and purification of the reaction mixture this compound proves very tricky to remove.

After favourable reaction conditions were achieved the type of supporting electrolyte was revisited, with the hypothesis that reducing the size of the alkyl chains in the ammonium salt would stunt the electrolytes phase transfer capabilities and therefore allow for a smoother workup and purification process.

Tetraethylammonium iodide was trailed as well as all the other conventional ammonium salts, due to the fact optimised condition where reached.
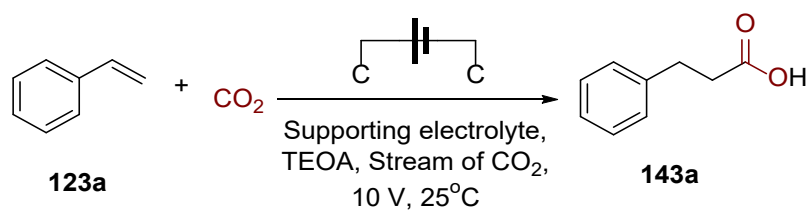
Table 16: Screening of supporting electrolytes

Entry	Electrolyte	Yield
1	Bu$_4$NI	70%
2	Bu$_4$NBr	61%
3	Bu$_4$NCl	47%
4	Et$_4$NI	70%
5	Bu$_4$NHSO$_4$	45%

General reaction conditions: substrate (2 mmol), DMF (10 mL), Supporting electrolyte (1 mmol), TEOA (2 mmol) CO$_2$ (bubbled 1atm), Voltage (10V), rt, 18 h.

The results show us that both entry 1 and entry 4 achieved similar results. Whilst a black powder solid was observed in both phases during extraction this was not present when Et$_4$NI was used. The interpretation of the subsequent NMR spectra showed clearly that less ammonium salt was present in the final reaction mixture. With this information the standard electrolyte was changed to Et$_4$NI.

Another interesting result was entry 5 which showed achieved a poor yield but nonetheless a drastic improvement on previous experiments with the corresponding salt which yielded no conversion whatsoever. The fully optimised conditions seem to have a drastic effect on this.

2.5.8 Additives and their effects

2.5.8.1 Benzonitrile

The use of additives in electrochemical and photochemical experiments has been investigated extensively, one of the main uses of additives is to facilitate the transport of electrons as homogenous electron transfer agents (Scheme 62).
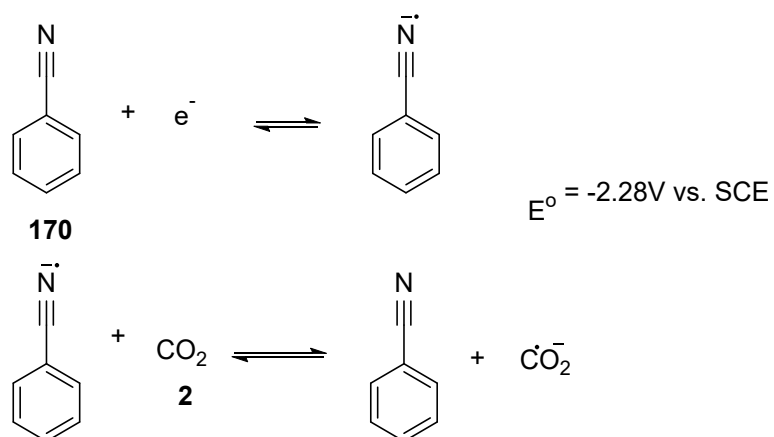
Scheme 62: Reduction of benzonitrile

Common electron transfer agents such benzonitrile and its derivatives are used in a variety of instances form photochemical to supercapacitors[128-130] the electron affinity of these compounds proving to be a major fact as they can easily accept electrons from a system. As shown in the figure in some cases it is easier to reduce benzonitrile than the target molecule due to benzonitriles low reduction potential. After the reduction of benzonitrile occurs electron transfer is facile allowing for easy production of the reduced carbon dioxide species.
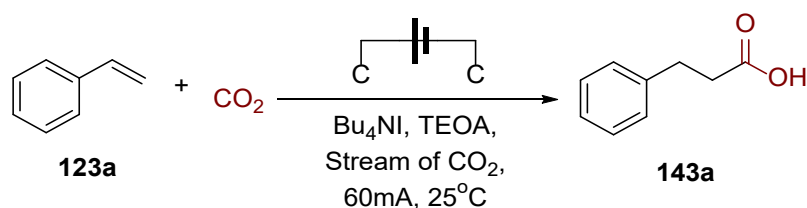
Table 17: Screening of Benzonitrile

Entry	Benzonitrile	Yield
1	-	50%
2	2 mmol	54%

General reaction conditions: substrate (2 mmol), ACN (25 mL), Bu₄NI (1 mmol), TEOA (2 mmol), CO₂ (bubbled 1 atm), current density (60 mAcm⁻¹), rt, 18 h.

Only preliminary exploratory experiments were carried out with this additive. Initial results where clear in showing a slight increase in yield and conversion at lower voltages. Although promising it was decided that the benefits of this additive are minimal and in the interest of keeping the process "green" it was omitted from further experiments

2.5.8.2 Metal Catalysts

Metal catalysts are commonly used as additives to increase yield, influence selectivity and speed up the rate of various reactions. Metal catalysts can be loosely categorised into 3 main groups depending on the influence they have on CO_2. SN and Pb based catalysts mainly produce $HCOO^-$ active species leading to the formation of formic acid [131] whilst noble metal catalysts focus more on the production of CO.[132] Copper based catalysts have proved to be highly effective at generating various active species of CO_2 leading to the production of various carbonaceous compounds.[111,133] Due to the adaptability of copper catalysts and the fact that it can produce carbon-carbon bonds an investigation was initiated to see how they could influence the novel electrochemical cell. Copper triflate was used as a test molecule to see how a metal catalyst would affect our system. The following experiment was setup (Scheme 63).
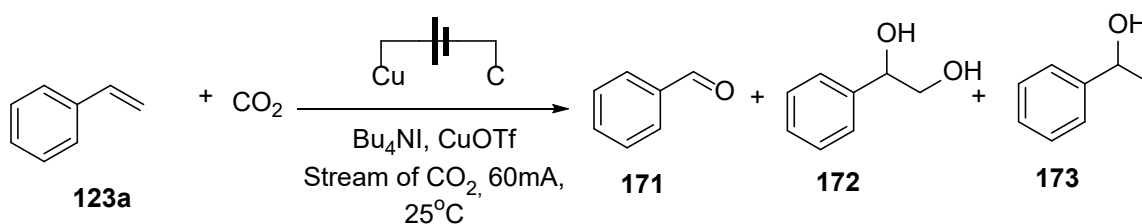
Scheme 63: Electrocarboxyaltion of styrene in the presence of copper triflate

Production of the monoacid and cyclic carbonate ceased, with various other potential products such as benzaldehyde, mono-alcohol and diols being formed (confirmed by comparing NMR and MS data with literature values). In terms of reactions pathways for these products it is apparent that the production of the mono alcohol stems from the addition of water across the double bond. The diol product produced is akin to the reaction of olefins with osmium tetroxide although it is not known which isomer is produced in a higher frequency.
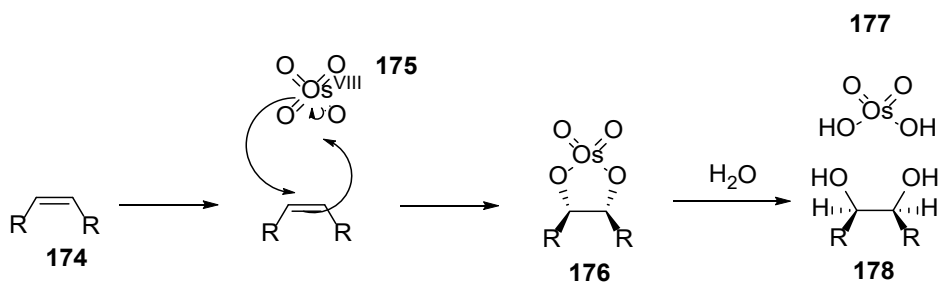
Scheme 64: Synthesis of diols with osmium tetroxide

2.5.8.3 Drying agents: Molecular sieves and desiccant.

Optimisation of all the potential variables did not achieve the desired of removing the cyclic carbonate by-product, as stated previously H_2O is a key reactant in the formation of the cyclic carbonate. It stands to reason that the removal of water from the reaction cell would eliminate formation of the cyclic carbonate.

Drying of all potential solvents and reactants significantly alleviated the production of the by-product although not eliminating it entirely, it was theorised that the addition of a desiccant in the form of activate 4Å molecular sieves to the reaction mixture would further eliminate the presence of water.

Addition of the activated molecular sieves did not prove to alter the mixture of main product to by-product, it was believed that due to the current conditions of the electrochemical cell the absorbing performance of the molecular sieves was compromised leading to the release of water. Therefore, further reactions did not include the sieves.
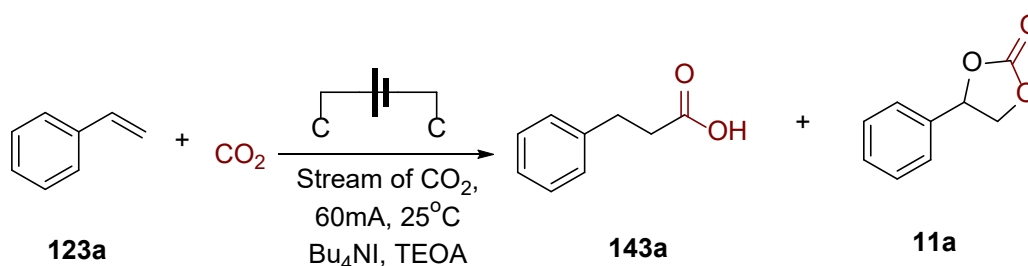

Table 18: Screening of desiccants and molecular sieves

Entry	Desiccant	Molecular Sieves	Ratio
1	-	-	3:1
2	-	Present	3:1
3	Present	-	1:0

General reaction conditions: substrate (2 mmol), ACN (25 mL), Bu$_4$NI (1 mmol), TEOA (2 mmol) CO$_2$ (bubbled 1 atm), current density (60 mAcm^{-1}), rt, 18 h.

Assuming that all reactants and solvents are dry the last possible source of H_2O would be from the carbon dioxide feedstock. This is most likely the case as the CO_2 used specified that there would be a percentage of water present. Silica gel desiccant was added to the CO_2 delivery system before and after the flow rate controller. The results achieved where very positive as there was complete elimination of the cyclic carbonate by-product with loss in yield and conversion.

Final working conditions for the novel electrochemical cell after all optimisations where implemented was as follows:
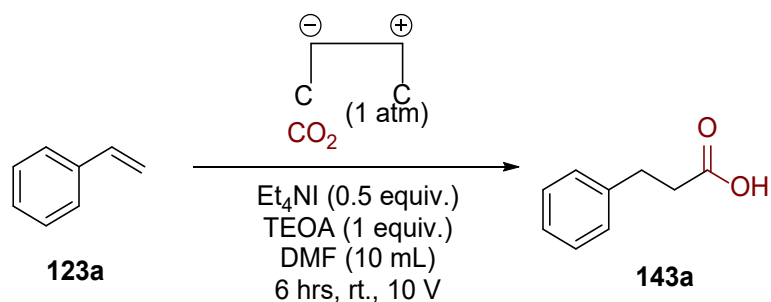
Scheme 65: Optimised conditions for novel electrochemical cell

2.6 Electrocarboxylation of Olefins

2.6.1 Electrocarboxylation of substituted styrenes.

2.6.1.1 Substituents on the benzene ring

Optimisation of the electrocarboxylation reaction with the control substrate (styrene) achieved a final yield of 70%, this was deemed to be sufficient, so substrate screening was carried out to deduce the scope and robustness of this new carboxylation technique.

Initial screening was focused on seeing how the addition of various functional groups on the benzene ring would affect the reaction. The different functional groups also provide a platform to observe how EDG and EWG groups affect yield and rate. (Table 19)
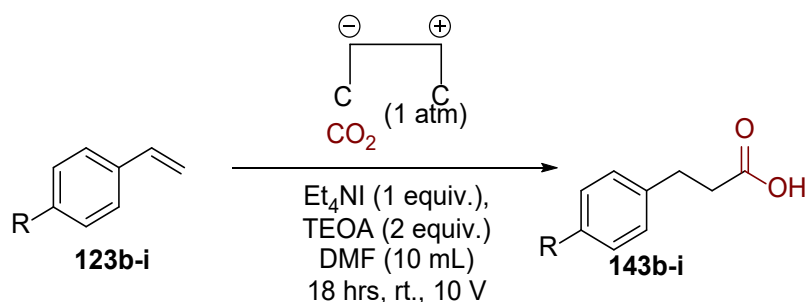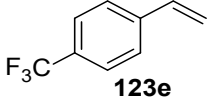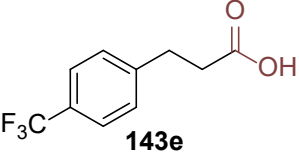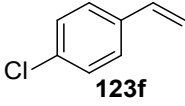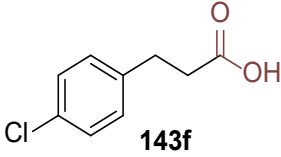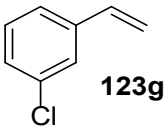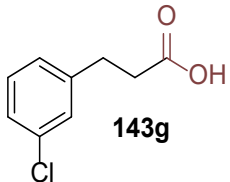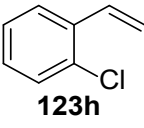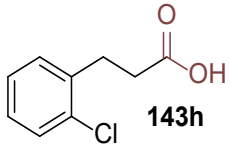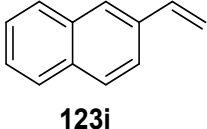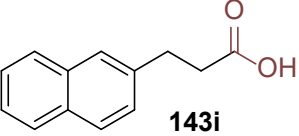

Table 19: Screening of EWG amd EDG groups

Entry	Substrate	Product	Yield
1	123b	143b	80%
2	123c	143c	96%
3	123d	143d	67%

4	 **123e**	 **143e**	66%
5	 **123f**	 **143f**	50%
6	 **123g**	 **143g**	33%
7	 **123h**	 **143h**	33%
8	 **123i**	 **143i**	50%

General reaction conditions: substrate (1 mmol), DMF (10 mL), Et$_4$NI (1 mmol), TEOA (2 mmol) CO$_2$ (bubbled 1atm), Voltage (10 V), rt, 18h.

If the hypothesis of the electrocarboxylation proceeding through a radical pathway is to be believed, electronically active groups substituted on the benzene ring could greatly impact the electrocarboxylation through addition or subtraction of electron density in the benzene ring which in turn would impact the stabilisation it has on any potential radicals formed on the alpha carbon.

It is well known that a benzyl radical is quite stable due to the multiple resonance forms it can adopt with the assistance of the pi system in the benzene ring, the effect of EDGs and EWGs on the stability of the benzyl radical has also been investigated multiple time throughout the years. [134] Multiple groups conducting said research, have concluded that both EDGs and EWGs located in the ortho and para positions have an overall stabilising effect on a benzyl radical, whilst meta orientated groups have a destabilising. The stabilisation effect is attributed to the substituents ability to provide spin delocalisation to the radical charge.

The only groups that have been shown to have a destabilisation effect are; CF$_3$ and F substituents, although in the case of CF$_3$ it hasn't been universally accepted as having a destabilising substituent due to the very small effect it has, meaning it is more neutral.

By consulting the data achieved from the screening of substrates it is evident that there is no direct correlation between the various electronic groups and their effect on the overall yield achieved, with reference to their stabilisation effect.

If the stabilisation effect of substituents is not a driving factor, then the effect the electronic groups have on the reductional potential of the substrates is key. Although it is highly likely that CO_2 is being reduced to form an active species it is not unlikely that the substrate may be reduced. Cyclic voltammetry must be carried out on the substrates to achieve a greater understanding of this.

2.6.1.2 Substitutions along the double bond (di-tri Substituted alkenes)

As demonstrated the electrocarboxylation of the benzyl-substituted styrenes was successful in showing that the reaction is quite robust and proceeds even in the presence of various electronically active groups which also bring a certain degree of functionality.

The next area of investigation would be di- and tri-substituted alkenes. As this is the area in the molecule where the reaction takes place it is imperative, we observe how the addition of various groups alter or obstruct this reaction as well as potentially directing the stereochemistry of the reaction (Table 20).

R_1 / R_3 / R_2 (182a-i)

CO_2 (1 atm)

Et$_4$NI (1 equiv.)
TEOA (2 equiv.)
DMF (10 mL)
18hrs, rt., 10 V

R_1 R_3 / R_2 COOH (183a-i)
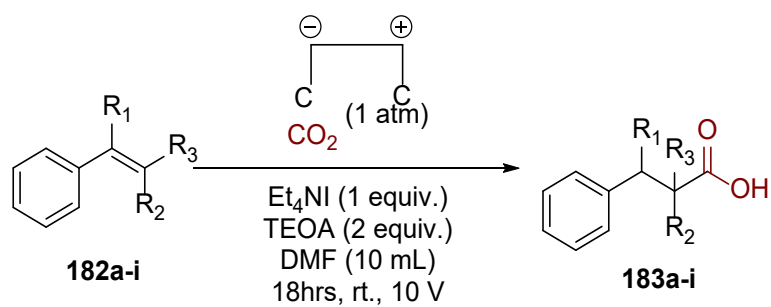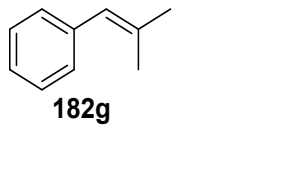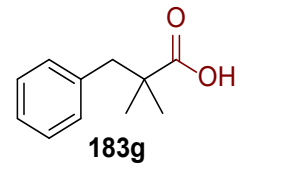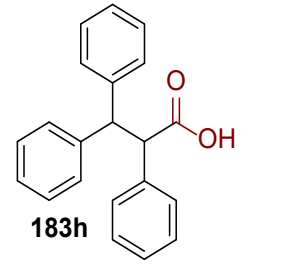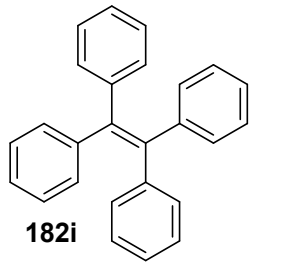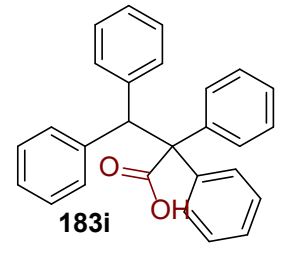
Table 20: Screening of substitutions along the double bond

Entry	Substrate	Product	Yield
1	182a	183a	85%
2	182b	183b	86%
3	182c	183c	84%
4	182d	183d	70%
5	182e	183e	70%
6	182f	183f	80%

99

7	**182g**	**183g**	75%
8	**182h**	**183h**	53%
9	**182i**	**183i**	<5%

General reaction conditions: substrate (1 mmol), DMF (10 mL), Et_4NI (1 mmol), TEOA (2 mmol) CO_2 (bubbled 1atm), Voltage (10 V), rt, 18h.

It is quite evident that the addition of methyl and benzyl groups either at the alpha or beta positions of the double bond greatly increase the yield. The positive inductive effect exhibited by both the methyl and phenyl results in added electron density being concentrated near the double bond. The added electron density and bulk given by the extra groups could stabilise t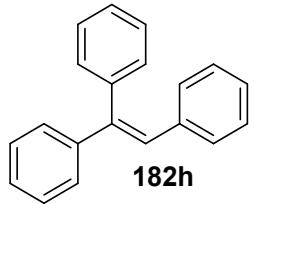he radical species formed in the reaction, similar to how a tertiary carbocation is more stable than a primary carbocation, this may enhance the yield achieved by the electrocarboxylation.

Another objective of the addition of groups around the double bond was to see if this could influence the stereochemistry of the product formed. As stated previously this electrocarboxylation exclusively forms the monoacid, but more importantly it only forms the terminal isomer with no evidence of the branched isomer. This is intriguing because even after the addition of two methyl groups to the terminal carbon it did not provide sufficient steric hinderance to impede electrocarboxylation.

100

2.6.2 4-Chlorostyrene

The electrocarboxylation chlorosytrene proved be a special case, as it did not completely afford the corresponding mono acid product. On closer inspection it was shown that there was significant production of the corresponding β-iodohydrin as well an β-iodoformate. (Figure 27)
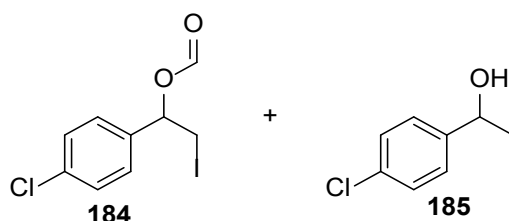
Figure 27: By products formed during carboxylation of 4-chlorostyrene

This was mostly prevalent in the electrocarboxylation of 4-chlorostyrene. Although chlorine is only a slightly electron withdrawing group it is shown to have quite a profound effect. Recently similar results have been achieved by 2 groups, in particular Narender *et al*. report a protocol where it is possible to achieve both products in high yields. [135] The method reported uses NH_4I as an iodine source and Oxone® as an oxidant, varying the solvent system of the experiment between CH_3CN/H_2O (1:1) and DMF/DMA has the effect of changing the final end product. (Scheme 66)
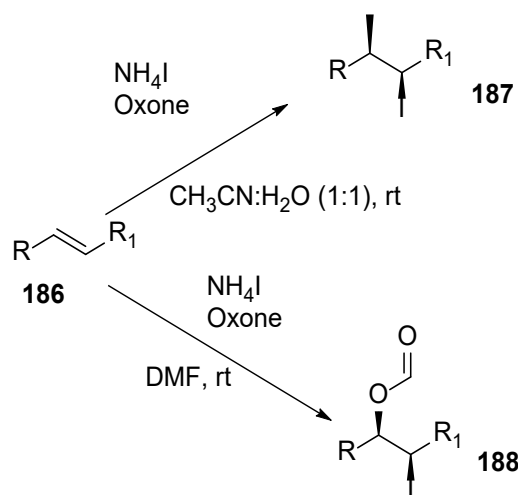
Scheme 66: Narender group's synthesis of 187 and 188

In terms of the mechanism the group speculate that Oxone® effectively oxidises I^- (NH_4I) to I^+ which reacts through electrophilic addition to form a cyclic iodonium species. This highly reactive species then undergoes nucleophilic attack from the O atoms in DMF to form **188** subsequent hydrolysis forms **192**.

189
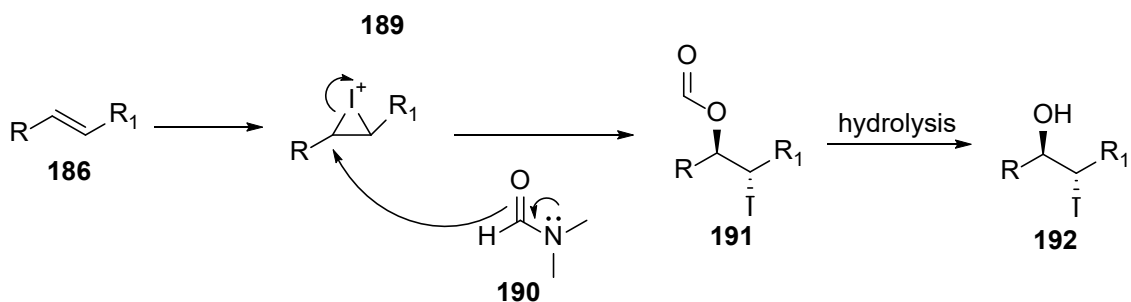
Scheme 67: Propsed formation of by products **191** and **192** in novel electrochemical cell.

Following on from his we hypothesised that without the presence of I⁻ ions the formation of the cyclic iodonium species. This hypothesis was tested by replacing the supporting electrolyte salt with one which has a lack of halides present, Bu_4NHSO_4 was chosen as the supporting electrolyte.
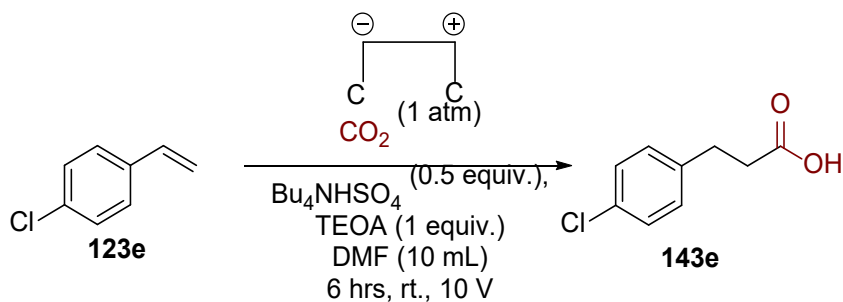
Scheme 68: " Clean " electrocarboxylation of 4-chlorostyrene

The hypothesis proved correct as removal of the halide source eliminated all forms of by-product from the reaction. This detail is helpful with further determination of mechanism behind this reaction. (Scheme 69)

2.6.2 Electrocarboxylation of miscellaneous substrates

The overarching focus of this project was to find novel methods to utilise carbon dioxide as a feedstock, once it was identified that reaction with olefins was possible and produced favourable results a greater amount of time and energy was placed into developing this process further. Whilst this was undertaken several exploratory experiments were carried out to explore the potential reaction of CO_2 with different substrates.

2.6.2.1 Electrocarboxylation of triple bonds.

An immediate concern was to investigate the potential of molecules with triple bonds, triple bonds are structurally and electronically similar to double bonds therefore it was theorised that they might prove reactive in the novel electrochemical cell. Phenylacetylene was selected as the substrate since it is very similar to styrene. (Scheme 70)
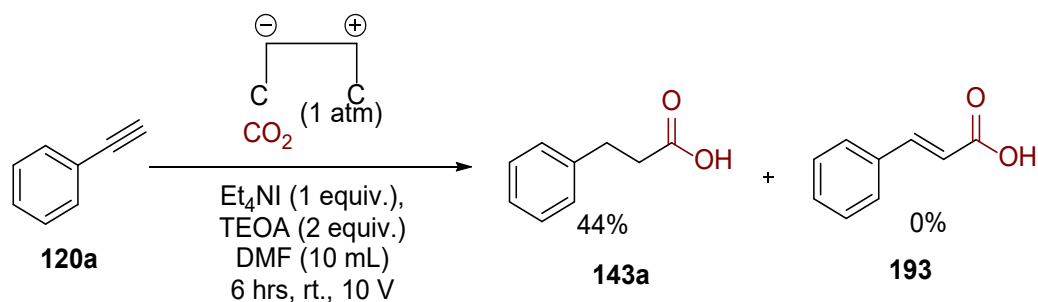
Scheme 69: Electrocarboxylation of phenylacetylene

As with the reaction with styrene the corresponding acid was afforded in a poor yield (44%). Although this yield is substantially lower than previous yields achieved by the double bond containing compounds, it does open some interesting avenues for investigation. Through NMR analysis it was identified that there was no alkene **193** present. With this experiment showing that electrocarboxylation of triple bonds is possible it was decided that this system could be optimised after the electrocarboxylation of double bonds was perfected.

This is an interesting detail as it alludes to that reduction of any potential double bond formed proceeds after carboxylation. It was hypothesised that due to the carboxylation at the β position further carboxylation is not possible, to further test this hypothesis **194** was subjected to the electrochemical cell.
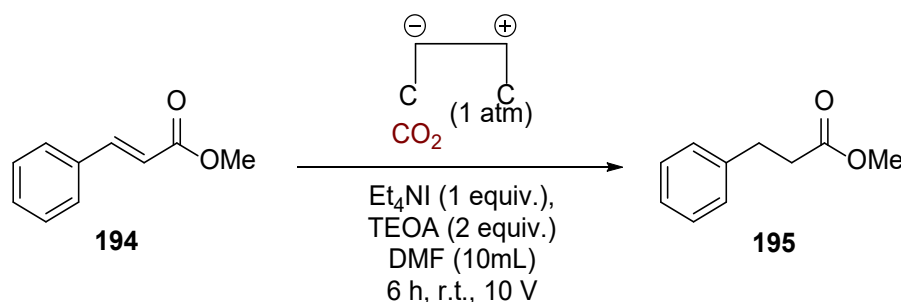
Scheme 70: Reduction of **194**

Via NMR analysis it was identified that the main product of the experiment was the reduced product **195** with only a small amount of dicarboxylic acid formed (1%). Although the exact mechanism for this process is unknown, we can clearly see that the double bond is being reduced to the alkane. The reduction of alkenes to alkanes has historically been undertaken in a process called hydrogenation which requires H_2 gas as well as Pd/C as a catalyst. This type of reaction is highly unlikely in this case; however, we can hypothesise that if a radical species is formed on the double bond it could react with the TEOA to gain a hydrogen atom thereby reducing the alkene. This result provides a valuable insight showing that further carboxylation is not favoured with reduction of the double bond proving more favourable.

2.6.2.3 Electrocarboxylation of aliphatic alkenes (allylbenzene and oct-1-ene)

As it has been shown carboxylation of aryl olefins is highly successful, with both styrene derivatives and triple bond molecules affording good yields and high selectivity towards beta directed carboxylated. The presence of a benzylic system adjacent to the multiple C—C was shown to be essential. Undeterred experiments were carried out to observe if any carboxylation could be achieved in aliphatic olefins. Allylbenzene was deemed to be an ideal test compound due to the similar structure with regards to styrene, oct-1-ene was also chosen as it is a bulkier olefin, with superior physical properties allowing it to remain present in the highly energetic electrochemical cell. (Scheme 71)
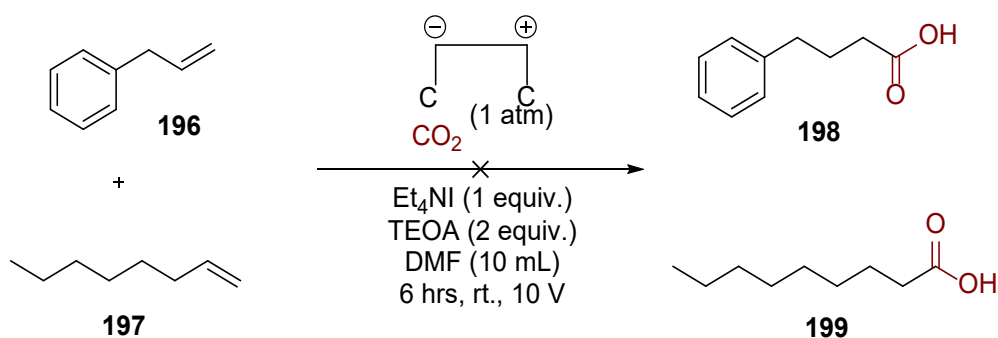
Scheme 71: Attempted electrocarboxyaltion of aliphatic alkenes

In the case of oct-1-ene there was no production of the acid as deduced by NMR analysis, with nearly all the starting material being recovered. In the case of allylbenzene, some limited conversion to the acid was exhibited in some iterations of the experiment. Although through GC-MS and NMR analysis this was shown to be below 1%, thereby further solidifying the assumption that an aromatic system adjacent to the reactive centre is critical in allowing the reaction to proceed.

2.6.2.4 Electrocarboxylation of methyl methacrylate

As well as providing a stabilising effect for any potential radicals formed during the electrocarboxylation of substrates the benzene ring can provide a place for delocalisation of charge. This is crucial to the fulfilment of the reaction. It was hypothesised that groups that provide this similar effect may also facilitate electrocarboxylation. Methyl methacrylate was chosen as the target substrate, it was hypothesised that the ester group would provide a perfect location for the delocalisation of any radical formed. (Scheme 72 and 74)
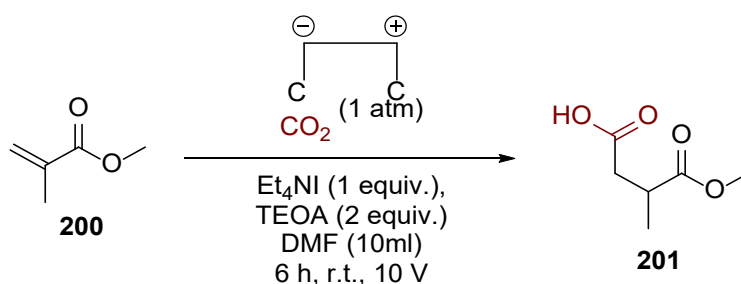
Scheme 72: Electrocarboxylation of methyl methacrylate:

105
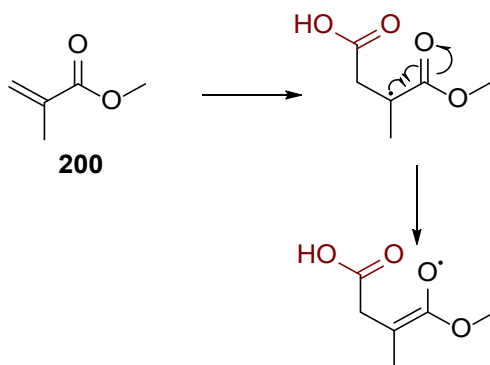
Scheme 73: Hypothesised delocalisation of radical charge

Potential tautomerization may also help stabilise any product formed. (Scheme 75)
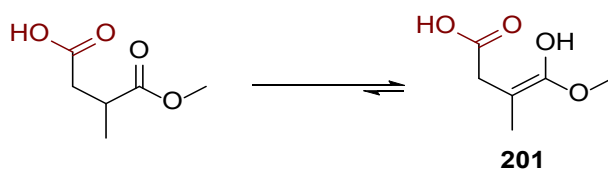
*Scheme 74: Tautomerization of **201***

Through NMR analysis it was shown that the experiment was success with **201** being formed with a high level of conversion (yield was not noted). This breakthrough opens the prospect of further research being carried out into this area. Although this type of moiety is not extremely common in natural products there is potential to optimise this reaction to work in the presence of a ketone or aldehyde.

2.7 Mechanistic Analyses

Due to the novel nature of the electrochemical cell, there is no past literature which can help elude what the potential mechanism could be in regard to carbon dioxides relationship to the non-sacrificial electrodes. It was deemed essential to implement a variety of tests to help deduce mechanistic pathways of the reaction.

2.7.1 TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl

TEMPO is a chemical compound which finds uses in many areas of chemistry and biology as a popular reagent, catalyst, and structural probe for biological systems. TEMPO's primary use in chemistry is that of a radical trap, it is uniquely suited to this role as it exists as a stable radical. (Figure 28)

202
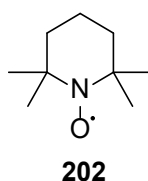
Figure 28: Structure of TEMPO

It was theorised that if a radical formed on the α carbon it would rapidly react to form the monoacid product with tempo incorporated into the structure. (Scheme 75)
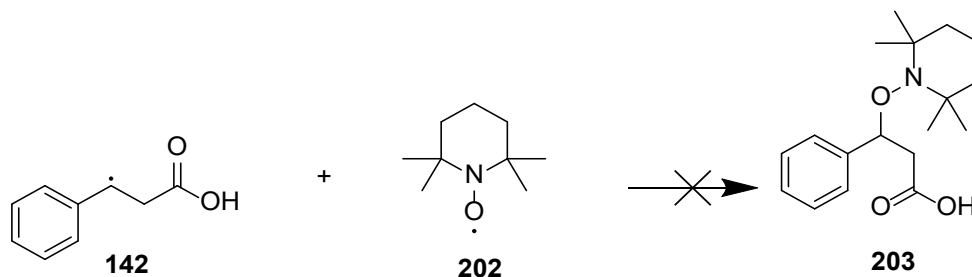
Scheme 75: Failed incorparation of TEMPO

However, after analysis of the NMR spectra of the final mixture it became evident that this did not occur, the reasons for this are unknown, it is possible that TEMPO underwent a termination reaction therefore becoming inactive or the rate of reaction of TEMPO with the radical formed is much slower than competing reactions.

2.7.2 Cyclo-propyl investigation

A classic experiment which is used to measure and study the kinetics of radical reactions is that of a clock reaction.[136] Radical clock reactions focus on the rearrangements of key cyclic species and how they are effected by a separate radical reaction acting as a radical trap. The two most popular radical rearrangements are that of the cyclisation of 5-hexenyl and the ring opening of cyclopropyl methyl (Scheme 76).

204   **205**

206   **207**
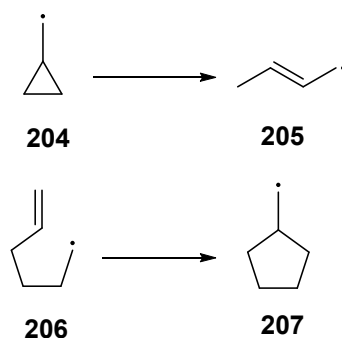
Scheme 76: Radical rearrangemtns of 334 and 336

As is shown in the case of the reaction of **204**, if a radical is formed adjacent to the cyclopropyl ring it quickly ring opens to form the corresponding molecule, thereby relieving the massive amounts of ring strain present. The rate constant for this rearrangement is extremely high standing at 8.6×10^7 s^{-1} at 298 K. These defining features of this rearrangement allowed us to test the theory of radical formation across the double bond. If a radical is formed on the double bond with a cyclopropyl ring substituted on to it, ring opening should occur (Scheme 77).

208   **209**   **210**
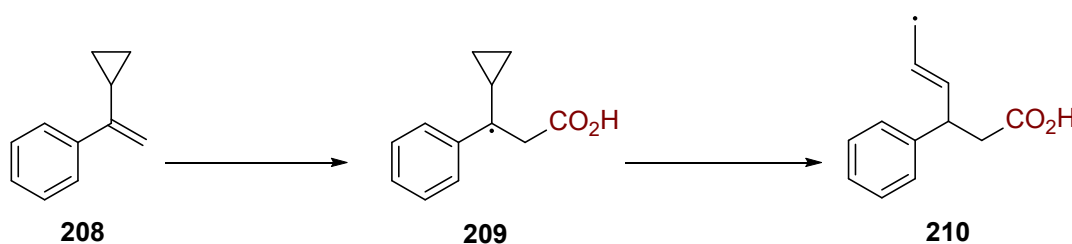
Scheme 77: Propsed radical ring opening of 209

2.7.2.1 Synthesis of cyclopropyl substituted styrenes

To begin the testing, it was decided that 2 simple styrene derivatives will be used with cyclopropyl groups substituted at both the α and β positions of the double bond, thereby removing any uncertainty of which position a radical is formed. (Figure 29)

208   **211**
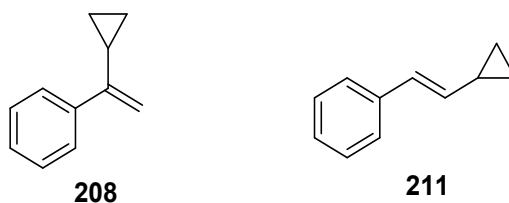
Figure 29: Cyclopropyl styrene derivatives

A quick and facile method for producing these cyclopropyl-substituted styrenes was needed, preferably one which required the least number of steps thereby increasing the yield. It is known that Wittig reactions are highly efficient and quick, thereby offering a perfect platform to synthesise the necessary products.

208 was formed through a simple Wittig reaction with the corresponding cyclopropyl phenyl ketone, achieving good to excellent yield (75%-85%) (Scheme 78).

212   **208**
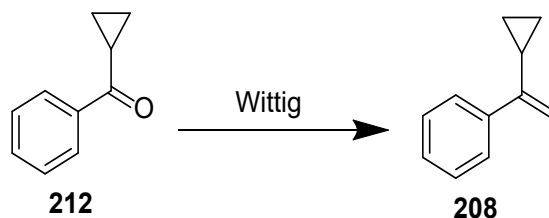
*Scheme 78: Synthesis of **208***

General reaction conditions: cyclopropylphenyl ketone (5 mmol), THF (50 mL), methyltriphenylphosphonium bromide (5.5mmol), n-BuLi (5.1 mmol), rt, 6h.

211 was formed in a similar way to **208**, firstly the corresponding phenylphosphnium salt was synthesised using traditional techniques first used in the 1970s by Bestmann *et al*. [137]
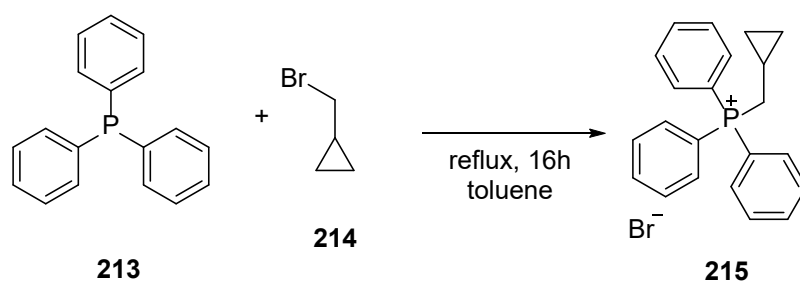
Scheme 79: Synthesis of 215

Cyclopropyltriphenylphosphonium bromide was afforded as a white crystalline solid in high yield (90-95%). The salt was then used in a standard Wittig type reaction to afford **211** in good to high yields (75%- 85%).
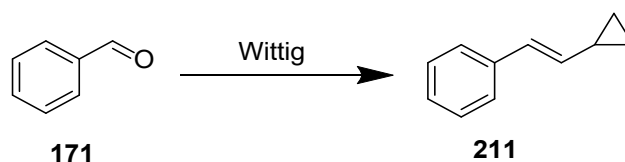
Scheme 80

General reaction conditions: benzaldehyde(5 mmol), THF (50 mL), cyclopropyltriphenylphosphonium bromide (5.5 mmol), n-BuLi (5.1mmol), rt, 6h.

2.7.2.2 Reaction of Compounds 11 and 12

Compounds **208** and **211** were exposed to the standard electrochemical conditions, results achieved where not as expected. As expected, carboxylic acids where achieved as the final products, however the cyclopropyl rings in both cases did not open as confirmed with NMR data.
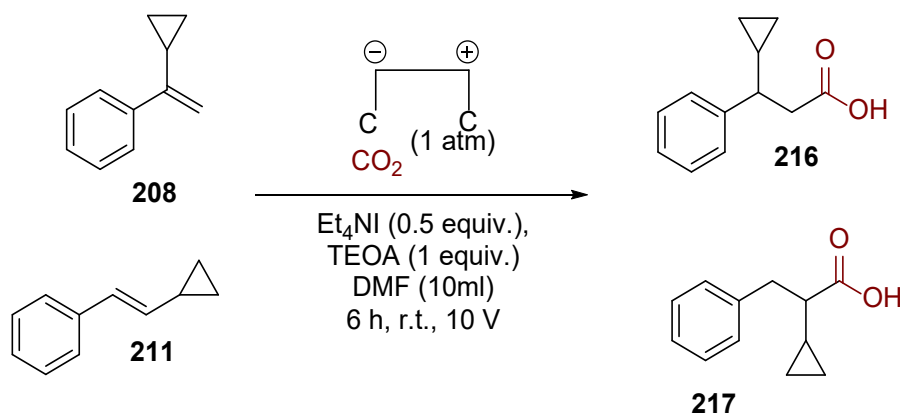
Scheme 81

This is quite unusual especially in the case of **208** as it is hypothesised that a radical is formed on the carbon directly adjacent to the cyclopropyl ring this should in theory open the cyclopropyl ring to afford an alkyl chain. It can be assumed that because this does not take place the cyclopropyl ring is still relatively stable and is not susceptible to radical attack, or perhaps the reaction of is concerted and the radical is too short lived to influence the cyclopropyl ring.

2.7.3 d^4-Methanol and d^3-acetonitrile deuterium labelling

Deuterium labelling is a commonly used technique in chemistry which provides an insight into a compounds structure as well as allowing the research into mechanistic pathways. The hydrogen atoms of a reagent or solvent can be replaced by deuterium (deuterated) and as a reaction takes place the subsequent position of these atoms can be monitored since deuterium is not "seen" during normal NMR spectroscopy.

In the electrocarboxylation exhibited the net gain of the substrate is CO_2H_2, with the CO_2 coming from the carbon dioxide present, it is not known where the hydrogens are acquired from. The hydrogen of the carboxylic acid group is thought to be taken from trace amounts of water in the system. It is less clear where the hydrogen which attached on to the alpha carbon comes from, it was theorised that as carbon dioxide is reduced, the electron source is subsequently oxidised, it is possible that a hydrogen is abstracted from this compound and incorporated into the product. Another possibility that a hydrogen is taken from a solvent molecule.

To shed some light on this process deuterated electron sources and solvents where used. Firstly, a deuterated electron source was trailed, because of the difficulty and financial constraints of acquiring deuterated TEOA it was decided that due to the fact that methanol proved to be an effective electron source d_4 methanol would be used.
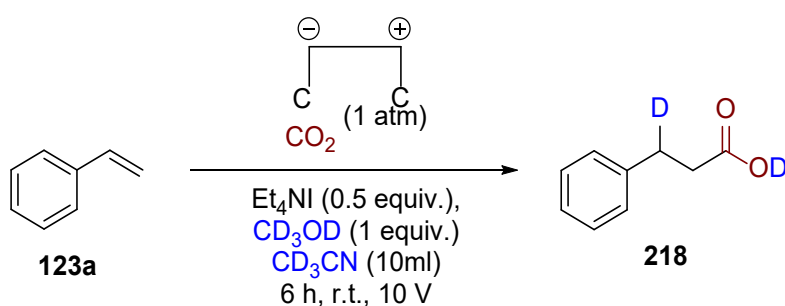
Scheme 82: Hypothesised incorparartion of deutirium

Although the reaction proceeded with a high conversion and yield as expected, there was no evidence of deuterium incorporation at either position. This proved to be the case when testing the theory by using deuterated solvent (d^3-acetonitrile) as well as both electron source and solvent in tandem. (Scheme 82)

After multiple attempts as well as changing the substrate to a more substituted version deuterium incorporation was never observed. Possible explanations for this phenomenon stem from the fact that both the deuterated compounds aren't taking part in the reaction mechanism, therefore the final potential source of hydrogen atoms is the supporting electrolyte salt. The deuterated form of this compound is very expensive so an investigation into its effects was not possible. Trace amounts of water may also be a viable hydrogen source.

2.7.4 (2-Iodoethyl)benzene

Experimentation with the halogen substituted styrenes opened up an interesting discovery with iodine incorporated species.

While it is known that a cyclic iodonium species can be formed during electrocarboxylation it was hypothesised that iodoehthy-benzene could be a potential intermediate in the mechanistic pathway of the electrocarboxylation. To test this theory the styrene substrate was replaced with (2-iodoethyl)benzene in an attempt to gain further insight into the potential mechanism.
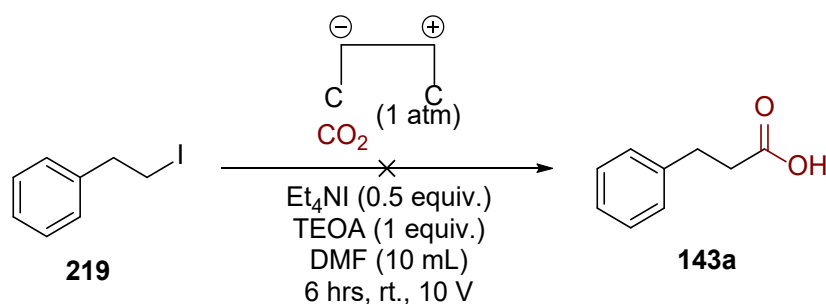
Scheme 83: Attempted electrocarboxylation of **218**

The experiment showed no reaction of the substrate. (Scheme 83)

These setbacks leave a large gap in the mechanistic analysis as not much information has been gathered from these multiple failures, attributed to this it is hard to build a definitive and reliable picture of the mechanism.

2.8 Electrocaboxylation of further conjugated systems.

During the investigation of potential substrates during the screening phase it become distinctly evident that the presence of conjugation between the double bond and the pi system of the benzene ring was imperative. Even in the case of allylbenzene which is structurally extremely similar to styrene no reaction was observed. (Scheme 84)
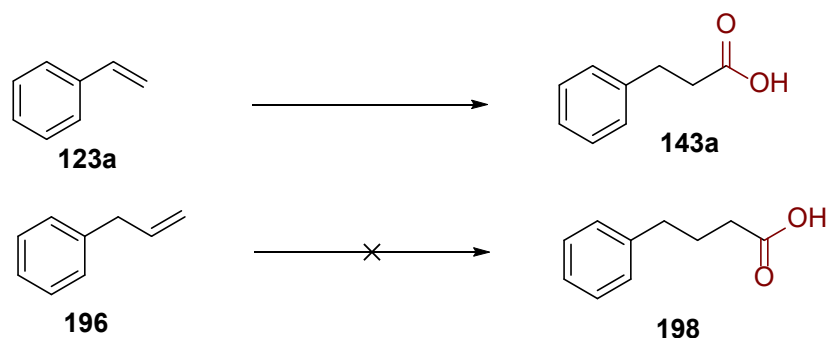
Scheme 84: Necessity of conjugation

From this information we can speculate that further conjugated and pi systems may also allow for the electrocarboxylation to proceed. Initial experimentation was focussed on diene and furan systems.

It is well known that adjacent pi bonds form a conjugated system, due to this extra conjugation it was hypothesised that certain dienes such as **220** would allow for electrocarboxylation.

220
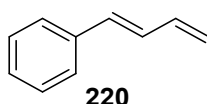
Figure 30: Structure of **220**

The conjugation would allow any radical formed to move along the alkyl chain toward the benzene ring where it can use the pi system to stabilise itself. As we believe this stabilisation is key for the progress of the electrocarboxylation it is justified to think that dienes would prove a successful substrate.

2.8.1 Synthesis of dienes

Synthesis of the diene was carried out by a simple Wittig of the corresponding aldehydes.
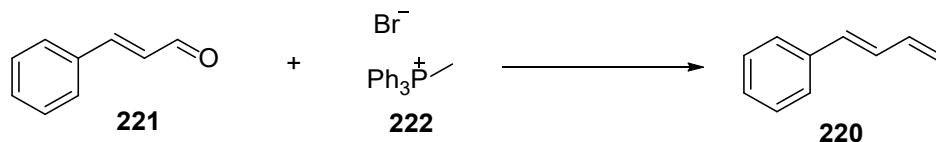
Scheme 85: Synthesis of 220

General conditions: substrate (5.5mmol), methytriphenylphosphnium bromide (5 mmol), n-BuLi (5.5 mmol), THF 50 mL

By using to readily accessible phosphonium salts, diene **220** was produced in excellent yield (90%). (Figure 31)
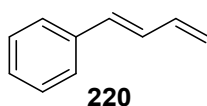
Figure 31: Structures of 220

2.8.2 Electrocarboxylation of Dienes

Diene **220** where tested in the standard electrochemical cell under the optimised conditions.
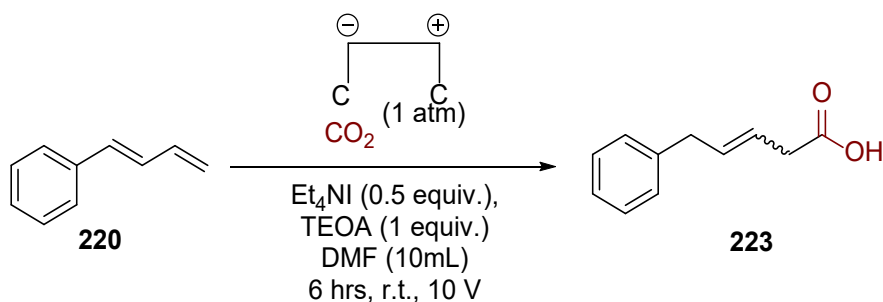
Scheme 86: Electrocarboxyaltion of 220

It was shown that the reaction did proceed and that **223** was produced in a racemic mixture in good yield. This proves that dienes react in a similar fashion to olefins if they can conjugate with a benzene ring (Scheme 86).

114
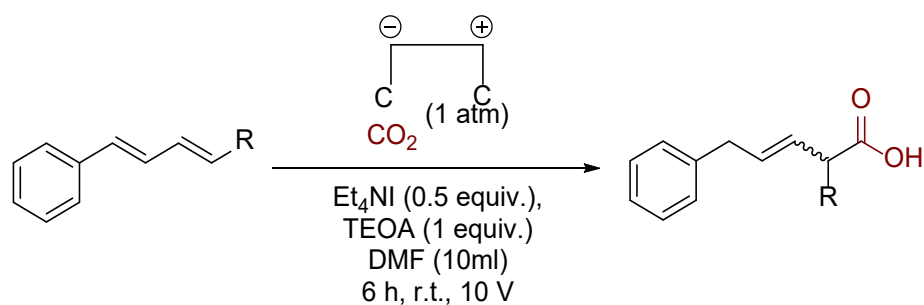
Table 21: Screening of Dienes

Entry	Diene	Product	Yield
1	**220**	**223**	58%
			Ratio E/Z : 1:1

The formation of a racemic internal double bond may shed some light on the potential reaction mechanism. With a potential mechanism displayed. Formation of compound **225** is not exhibited whatsoever, this observation further reinforces the theory that the resulting radical is stabilised within the benzene ring. (Scheme 87)
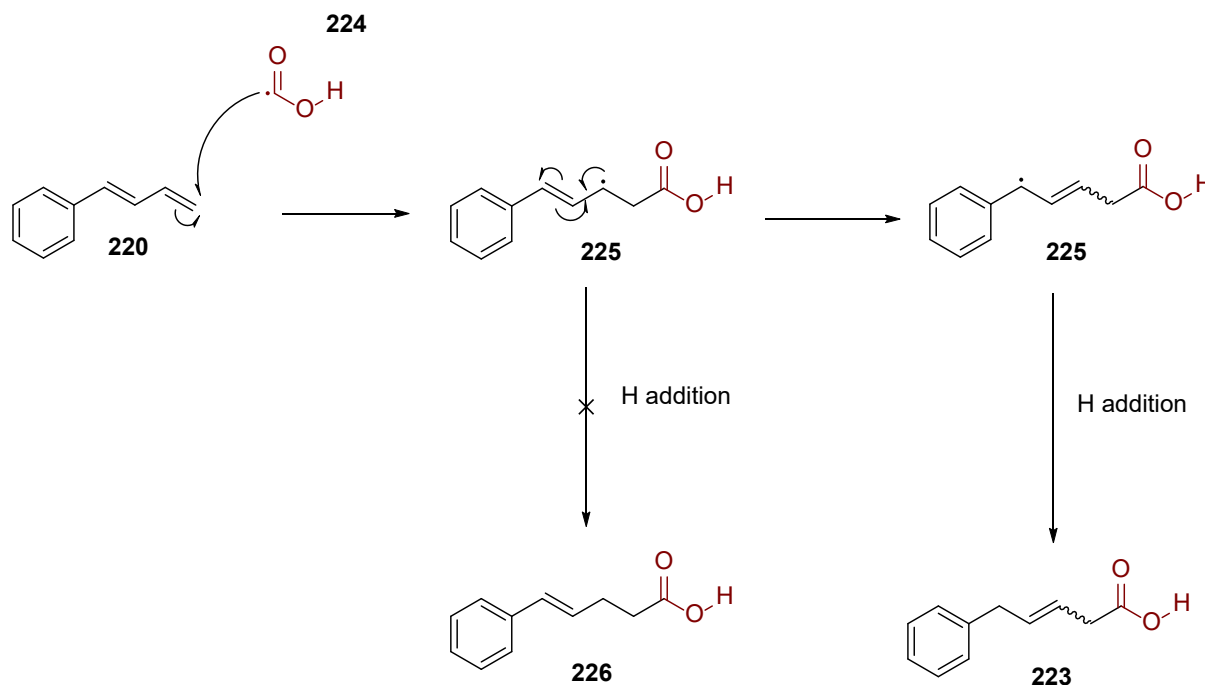
Scheme 87: Potential mechanism for the electrocarboxyaltion of **220**

115

As with the electrocarboxylation of olefins, carboxylation is only exhibited at the terminal double bond of the diene, allowing for no branched isomers, this type of specificity is highly sort after. This type of reaction opens the door for further synthesis as a double bond is very facile and reactive, allowing for the formation of more complex molecules.

As the test reactants have shown that dienes are viable substrates for electrocarboxylation, further work into the scope for dienes wasn't initiated due to time constraints although this should be immediately investigated in further work.

2.9 IKA experiments

One of the many challenges faced over the course of this project was a lack of accurate reproducibility and a lack of accurately measuring the amount of charge being passed through every iteration of the experiment. Build up on the electrodes also servery impaired the reaction over prolonged periods of time. The ElectraSyn 2.0 developed by IKA in collaboration with Professor Phil Baran removed a great many of these problems allowing for accurate and quick experiments to be carried.

Although only a limited amount of experimentation was carried out on this new setup the initial results are comparable if not superior to that of the original non-sacrificial electrochemical cell.
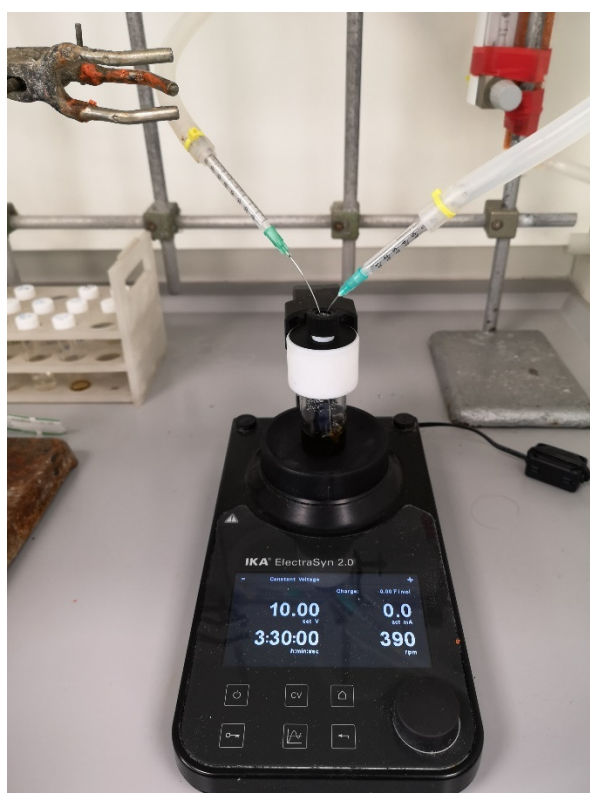
Figure 32: ElectraSyn 2.0 Setup

Firstly, it was noted that the rate of reaction was greatly increased; whilst in previous iterations full conversion of the substrate took a minimum of 4 hour, the IKA equipment allowed for full conversion within 1 hour. This observation could be attributed to many factors which where effected by the change in equipment.

Primarily, due to the small reaction vessel the amount of substrate and reagent had to be halved, therefore it would be right to assume that this would reduce the reaction time, however the concentrations of substrate to reagents was kept equal therefore it follows that the reaction time shouldn't be altered. We believed that the reasons for this drastic drop in reaction time is inherently linked to the properties of the equipment. An important function on the IKA was the ability to change the polarity of the electrodes every 30 seconds, this function reduces the amount of build-up on any one electrode, allowing for a steady current to be provided to the reaction mixture. Another important feature of the IKA equipment was the presence of graphite electrodes purpose built for electrochemistry. Previous electrodes where just simple carbon fibre rods, although they are cheap and readily available they are not built for electrochemistry, in terms of current allowed to pass thorough the solution the carbon fibre allowed for a maximum of 30mAh at a voltage of 10V, whilst the IKA setup achieved values of 100mAh. As the current is hypothesised to be the driving factor of the reaction it is satisfactory to think that a nearly 3-fold increase in the current would allow for a faster rate of reaction.

2.9.1 TEOA concentration screening

Due to the speed of the experiment the IKA setup was used to investigate the effect TEOA concentration would have on the yields produced. Three readings were taken varying the concentration of TEAO in relation to the remaining reagents. 4-methylstyrene was used as the substrate due to the ease of purification. (Table 22)
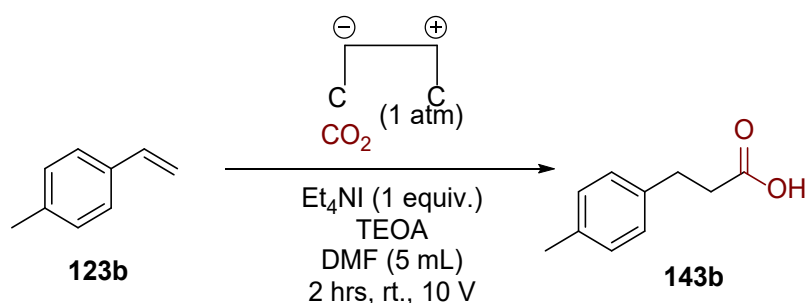
Table 22: Screening of TEOA concentration.

Entry	TEOA conc.	Conversion	Yield
1	0.25 mmol	>99%	73%
2	0.5 mmol	>99%	77%
3	1 mmol	>99%	77%
4	2 mmol	>99%	72%

General reaction conditions: substrate (0.5mmol), DMF (5 mL), Et$_4$NI (0.5 mmol), TEOA (x mmol), CO$_2$ (bubbled 1 atm), Voltage (10V), rt, 2h.

As it was stated in previous sections of this report, the electron donor is crucial to the progression of the reaction. It would compute that varying the concentration of TEOA would influence the results of the reaction, this however does not prove to be the case. The screening tests showed that varying the concentration of TEOA from a base of 0.5 equivalents to 4 equivalents made no substantial difference. Interestingly if half of an equivalent of TEOA was used you would still see full conversion, this leads us to believe that each TEOA molecule provides electrons to 2 equivalents of CO$_2$. Perhaps, due to the structure of TEOA it could provide electrons to 3 equivalents of CO$_2$, or potentially using the final oxidised products of TEOA as electron donors might provide further insight. The fact that this investigation was carried out on the new IKA equipment may have played an important role as in

118

general reaction seemed to be produce less by products, so it would be beneficial to optimise conditions for the IKA setup.

2.10 Conclusions and Future Work

2.10.1 Conclusions from Optimisation of Novel Electrochemical Cell

To conclude, in this work we have developed a novel non-sacrificial electrochemical cell which has proven to be effective in the stereospecific carboxylation of styrene derivatives to their monoacid products under mild and environmentally friendly conditions: 10V, atmospheric conditions of CO_2 in a solution of DMF using carbon fibre electrodes, Et_4NI as a supporting electrolyte and TEOA as an electron donor. (Figure 33)
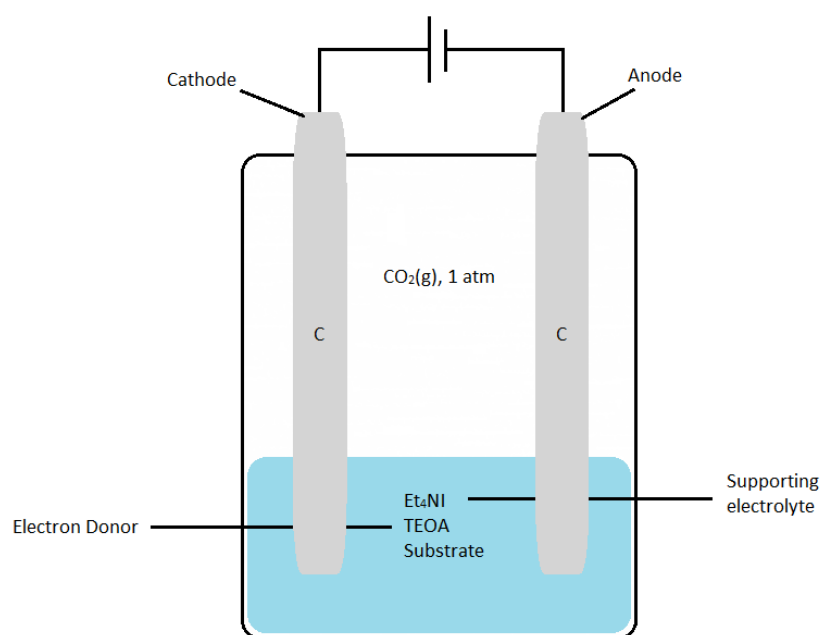
Figure 33: Final optimised novel electrochemical cell

The main focus of the investigation into the variables was to deduce the effect that the variables had on the final products produced, with a particular focus on the elimination of the cyclic carbonate by-product. It was evident after various tests and experiments the source of the cyclic carbonate was rooted in the presence of trace amounts of water. With the introduction of drying agents into the CO_2 stream we saw the elimination of the cyclic carbonate.

The key variables which exhibited a direct impact on the yield as well as the rate of reaction were the concentrations of both the starting electrolyte (Et_4NI) and the electron donor (TEOA). Increased amounts of electrolyte allowed for an increased current, impacting directly on the rate of reaction. While the electron donor was proven to be the key reagent, no reaction was observed in its absence.

Various screening reactions were carried out on the potential electrocarboxylation of different compounds such as; alkynes, dienes, acrylates, and aliphatic alkenes. The process was successful to some degree for all the compounds, except electrocarboxylation of aliphatic alkenes which was unsuccessful.

2.10.2 Conclusions and Future work attributed to Mechanistic Studies

Mechanistic analysis employing the use of various methods such as TEMPO, cyclopropyl groups, and the deuterium labelling of key components was carried out to try to deduce the method of action of the novel electrocarboxylation. These attempts were mainly met with failure as no experiment gave a positive result in proving that a radical pathway is the mode of action or to the nature of the hydrogens introduced in to the final product. Reasons for this failure can be attributed to many factors, in the case of the radical experiments the stability of the radical. If the radical produced is extremely stable, then potential attempts to trap it or utilise it may prove ineffective. In addition to this if the radical produced is very short lived and reacts immediately with other species present, attempts to monitor or trap it would be futile.

In the case of the deuterated experiments, the last area to investigated is the supporting electrolyte salt. This could prove useful insight, however if this results in a negative outcome the hydrogens need to fulfil the requirements for the experiment would probably be acquired from trace amounts of water present.

One avenue which hasn't been explored is cyclic voltammetry. An investigation can be initiated into how each species reacts under varying electronic conditions. This could provide extremely useful information in general, but more specifically it can answer the question as to whether it is the olefin or CO_2 that gets reduced into the activated species. Furthermore, we could see if any part of this process is reversible. The use of cyclic voltammetry can deduce specific voltages at which reduction and oxidation takes place allowing for a greater understanding of the mechanism.

2.10.3 Future Work

Overall future work should be focussed on the testing of various other functional groups such as ketones, aldehydes, alcohols as well as the nitrogen containing groups, as these not have been fully investigated. This could unlock the full potential of the electrochemical cell.

In terms of the triple bonded compound it has been shown that they perform in a similar way to olefins. The triple bonded compounds appear to go through full reduction to the alkyl product, future work in this area may be able to elude to a protocol which could suspend the reduction of a double bond formed. This would add significant amounts of versatility for further functionalisation, potentially finding a use in total synthesis of organic molecules. (Scheme 89)
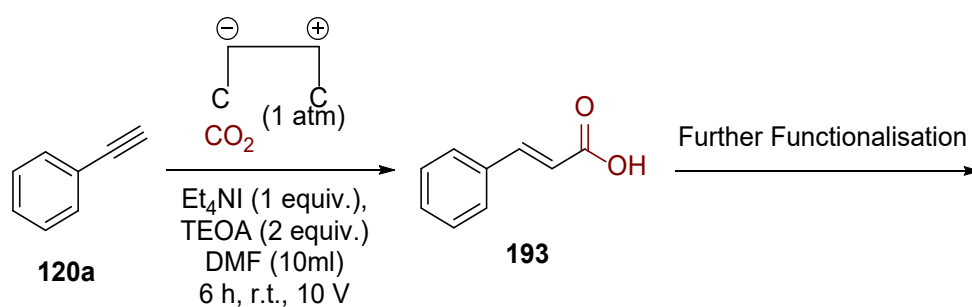
*Scheme 88: Potential utility of the electrocarboxyaltion of **120a***

The reduction of double bonds itself is an important reaction with significant research being carried out in this area. Currently nearly all methods involve the use of palladium as a catalyst as well as H_2 gas. If a robust method for the reduction of double can be produced bypassing these expensive and dangerous reagents it would prove to be worthwhile research.[138,139] (Scheme 89)
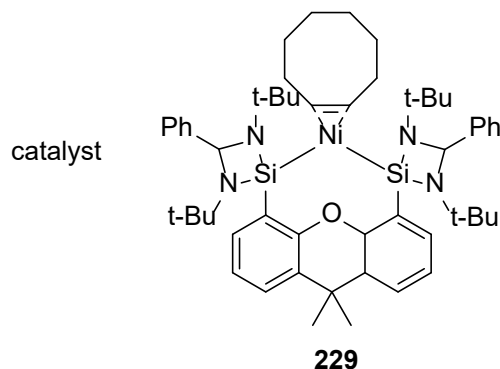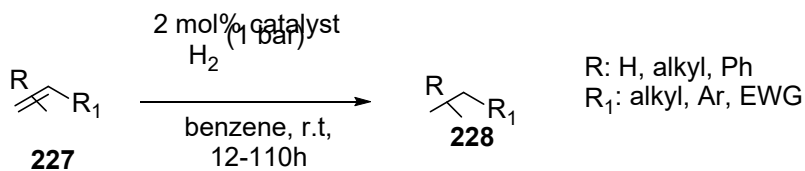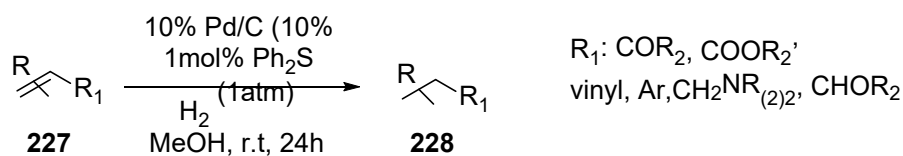
Scheme 89: Current methods for the hydrogentation of double bonds

Investigation needs to be carried out on the scope of this reduction and make sure it's not limited to methyl ester containing compounds.

In the case of the alkyl-based substrates it seems electrocarboxylation with the current setup proves ineffective. This corroborates the view that for the electrocarboxylation to proceed the presence of aromaticity is required. Although not a positive result it helps to reinforce the hypothesis regarding the preferred mode of action. Perhaps changing the conditions of the experiment or introducing certain additives may allow for the electrocarboxylation of alkyl olefins, so further work is necessary.

It has already been shown that electrocarboxylation can occur in unconventional systems, as has been exhibited with the case of 2 vinyl-naphthalene. It was deemed necessary to investigate how unconventional aromatic systems would react to electrocarboxylation. Other than conjugated benzene ring systems, certain 5 membered ring species exhibit aromaticity. This is true for systems such as furan, pyrrole and thiophene. (Figure 34)
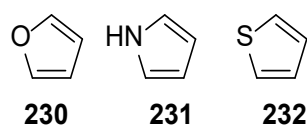
Figure 34: Aromoatic 5 memebered ring systems

Due to the aromaticity of these systems they should allow for the delocalisation of a radical species formed during electrocarboxylation. It is therefore necessary for future work to test these aromatic systems.

Perhaps the most interesting result from these various screening tests is attributed to the electrocarboxylation of methyl methacrylate. The success of this experiment shows that the presence of aromaticity is not essential. This opens up the potential scope of the novel electrochemical cell allowing for investigation of different substrates. Considerable research should be invested into this area. Firstly, deducing which element of methyl methacrylate molecules promotes the electrocarboxylation, whether it is the carbonyl group or the ester moiety as a whole. In the case that it is the presence of carbonyl group providing the stabilising factor, for the reaction to proceed this could be manipulated in such a way that may allow for the electrocarboxylation of alkyl olefins, one possible example maybe compound **233**. (Figure 35)
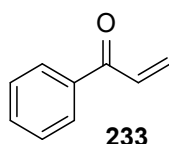
Figure 35: Potential substrate for electrocarboxylation

This type of structural formation may bridge the gap between the double bond and benzene ring potentially allowing for electrocarboxylation to occur. Again further research needs to be carried out, but it seems that these exploratory experiments have opened up various avenues to further develop the novel electrochemical cell into a tool that can be used for many transformations, even maybe deviating from the original tenant and removing carbon dioxide as the primary reagent and substituting it with similar reagents such as isocyanate and CO or using nitrogen and sulphur containing compounds, such as NO_2 and SO_2, which have previously been deemed to be waste gases.

To fully realise the environmentally friendly aspect of the process, research must be carried out on the elements of the electrochemical cell which still carry on environmental penalty. The solvent system is one such element; DMF although an excellent solvent carries many health risks with it especially in the area of reproductive health as well as being slightly harder to work with on a laboratory scale due to its high boiling point. A rapidly growing area in solvent chemistry has been focussed on bio derived solvents. One such example, Dihydrolevoglucosenone (Cyrene)(Figure 36) has been identified as a potential substitute for common dipolar aprotic solvents such as NMP and DMF. [140] Cyrene carries similar properties of traditional solvents but carries the benefit of being produced from cellulose.
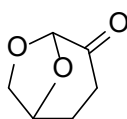
234

Figure 36: Cyrene

3.0 Experimental

3.1 General Experimental

Reaction solvents were obtained anhydrous or non-anhydrous from commercial suppliers or in the case of DMF distilled.

Reactions that required anhydrous conditions were carried out using flame dried glassware under inert atmosphere

Reactions that required electrolysis were carried out using a Thutlby Thander EX355 bench power supply.

Reactions were monitored by thin layer chromatography (TLC) using aluminium backed plates with a Merck Kiesel 60 F254 silica gel stationary phase, with visualisation carried out by UV irradiation at a wavelength of 254nm, or after staining with ethanoic solution of vanillin, potassium permanganate and bromocresol green.

^{1}H and ^{13}C NMR spectra were measured at 400 and 100 MHz, respectively using a Bruker DPX 400 MHz spectrometer or a JEOL ECS 400MHz Spectrometer. Tetramethylsilane (TMS) was used as the internal standard. Chemical shifts are given in parts per million(ppm) and *J* values are given in Hertz (Hz)

^{1}H NMR yield achieved through the use of trichloroethylene as a standard. Due to the distinctive response given by trichloroethylene it was possible to correlate with the desired product to achieve an NMR yield.

3.2 General setup of electrochemical cell

3.2.1 Preparation and regeneration of electrodes.

All metal electrodes cut, the oxide layer was removed with sandpaper and manipulated in such a way to afford maximum surface area contact with the reaction mixture. For instance, copper wire is twisted into a coil as shown, whilst less malleable metals are turned into loops. Graphite and carbon fibre rods where divided into 8cm sections. Post experiment all electrodes cleaned with traditional methods; detergent wash, acetone wash then dried and stored in a desiccator. In the case of the carbonaceous the electrodes are placed in a 1M solution of HCl and allowed to soak for 2 hours.

3.3 Electrocarboxylation of epoxides
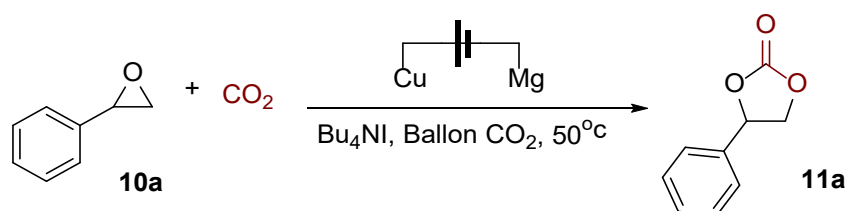
Styrene oxide **10a** (0.21 g, 1.7 mmol) was added to a solution of Bu_4NI (0.64 g, 2.6 mmol) in acetonitrile (150 mL). The resulting mixture was flushed with CO_2 for 1h (at a flow rate of 463 mL min^{-1}). The mixture was heated to 50°C and electrolysed at a current of 60mA with stirring for 5h in a single compartment cell containing a copper cathode and magnesium anode with a constant CO_2 flow (flow rate 463 ml min^{-1}). The crude mixture was filtered under suction and evaporated under reduced pressure to afford a light-yellow oil. Ethyl acetate (20 mL) was added and Bu_4NI allowed to precipitate for 15 mins, (0.39g, 74% recovered). The precipitate was removed by gravity filtration and solvent evaporated to afford amber oil. The amber oil was then subjected to column chromatography eluting with light petroleum:ethyl acetate (3:1) to yield the product 4-phenyl-1,3-dioxolan-2-one **11a** as a colourless solid (0.22g, 79% yield). [141]

11a
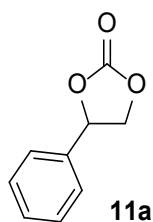
4-Phenyl-1,3-dioxolan-2-one (11a)[27]

^{1}H NMR (400MHz, CDCl$_3$) δ 7.34-7.56 (m,5 H), 5.69 (t, *J* = 8.0 Hz, 1 H), 4.79 (t, *J* = 8.4 Hz, 1 H), 4.34 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100MHz, CDCl$_3$) δ 71.19, 78.01, 125.88, 129.27, 129.77, 135.80, 154.83.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 1162 (C-O), 1779 (C=O).

3.4 Synthesis of Metal Oxalates

3.4.1 Representative procedure
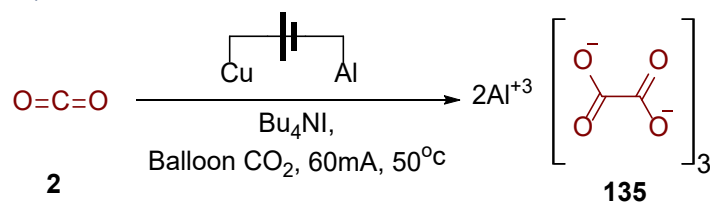
Bu$_4$NI (1.1 g, 3.0 mmol) was added to acetonitrile (150 mL). The resulting mixture was flushed with CO$_2$ for 1hs (at a flow rate of 463 mL min^{-1}.) The mixture was heated to 50°C and electrolysed at a current of 60mA with stirring for 24h in a single compartment cell containing a copper cathode and aluminium anode with a constant CO$_2$ flow (flow rate 463 mL min^{-1}). The crude mixture was filtered under suction, precipitate removed. Solution evaporated under reduced pressure to afford Bu$_4$NI (78%). Followed by recrystallisation aluminium oxalate **135** recrystallised (0.29 g, yield 63%).

127

3.4.2 Attempted Procedure
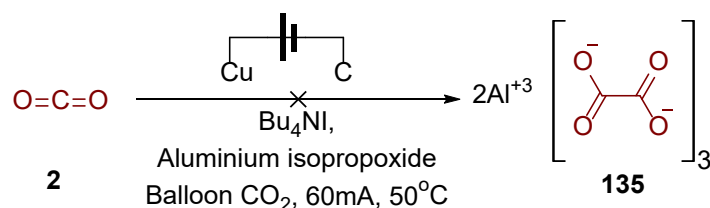
Bu$_4$NI (1.1 g, 3.0 mmol) and aluminium isopropoxide (0.62 g, 3.0 mmol) was added to acetonitrile (150mL). The resulting mixture was flushed with CO_2 for 16h (at a flow rate of 463 mL min^{-1}). The mixture was heated to 50°C and electrolysed at a current of 60mA with stirring for 24h in a single compartment cell containing a copper cathode and carbon anode with a constant CO_2 flow (flow rate 463 mL min^{-1}). The crude mixture was filtered under suction, to yield crude orange oil. NMR analysis showed no reaction.

3.5 Acidification and Functionalisation of Aluminium oxalate
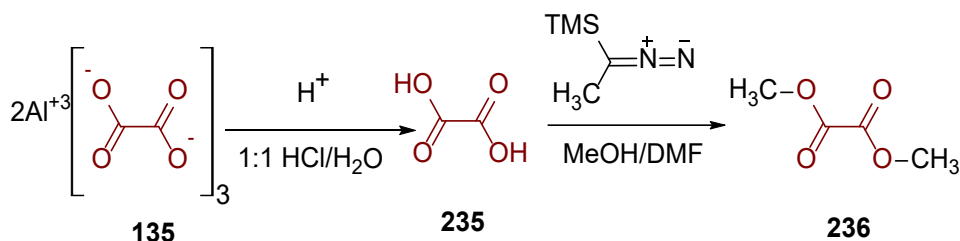
Aluminium oxalate **135** (0.38 g, 1.2 mmol) dissolved in minimum amount of 1:1 HCl/H$_2$O, solution and allowed to stir for 30 mins. The solvent was evaporated under reduced pressure to afford oxalic acid **235** as white solid (0.98 g, 1.08 mmol). TMS-diazomethane (80 µL) added to a solution of oxalic acid (0.0017 g, 0.08 mmol) in DMF-MeOH (9:1, 10 mL) and allowed to stir for 30mins. The reaction mixture was quenched with acetic acid (1 mL) and stirred for 30mins. The resulting mixture was extracted with ethyl acetate (2 x 5mL) and washed with brine (3 x 10 mL). The solvent was removed under reduced pressure to afford an amber oil.

3.6 Sacrificial carboxylation of olefins

3.6.1 General procedure
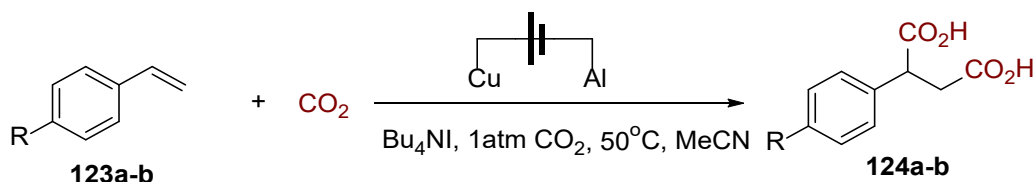
Substrate (2 mmol) was added to a solution of Bu$_4$NI (0.55 g, 1.5 mmol) in acetonitrile (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was heated to 50°C and electrolysed at a current of 60mA in a single compartment cell containing a copper cathode and aluminium anode with a constant CO_2 flow (flow rate 463 mL min^{-1}) with stirring for 24h. Crude reaction mixture filtered under suction to afford off white solid (2.64 g). Off White solid (0.508 g) acidified by addition of HCl/H$_2$O (1:1, 20 mL) and extracted with ethyl acetate (3x20 mL) to afford a white solid.

4-Bromostyrene **123b** (0.47 g, 2 mmol) afforded 2-(4-bromophenyl)butanedioic acid (**124b**) (0.096 g, 88% yield) as colourless solid.
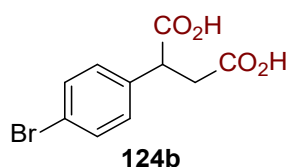
2-(4-bromophenyl)butanedioic acid (124b)[142]

^{1}H NMR (400MHz, CDCl$_3$) δ 7.29 -7.18 (m, 5H), 3.96 (dd, J= 5.2, 15.2 Hz, 1H), 3.05 (dd, J = 10.0, 19.2 Hz, 1H), 2.65 (dd, J= 5.2, 17.2 Hz, 1H).

^{13}C NMR (100MHz, CDCl$_3$) δ 27.26, 41.27, 131.04, 131.41, 132.32, 142.40, 177.68, 179.11.

V$_{max}$(ATR: diamond)/cm^{-1} 1203 (C-O) 1689 (C=O).

m.p. 188-208°C (Lit. 210-211°C).

Styrene **123a** (0.21 g, 2mmol) afforded 2-phenylbutanedioic acid (**124a**) (0.057 g, 68% yield) as colourless solid.
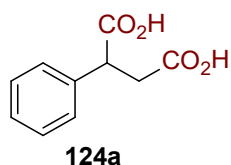
124a

2-phenylbutanedioic acid (124a)[100]

¹H NMR (400MHz, CDCl₃) δ 7.24 -7.36 (m, 5H), 3.95 (dd, *J* = 5.2, 15.6 Hz, 1H), 3.05 (dd, *J*= 10.0, 14.8 Hz, 1H), 2.63 (dd, *J*= 5.2, 17.2 Hz, 1H).

¹³C NMR (100MHz, CDCl₃) δ 25.2, 41.2, 131.0, 131.4, 132.3, 142.4, 177.6, 179.1.

V$_{max}$(ATR: diamond)/cm^{-1} 1203 (C-O) 1689 (C=O).

m.p. 162-166°C (Lit. 166-168°C).

3.6.2 Attempted Procedures

124c
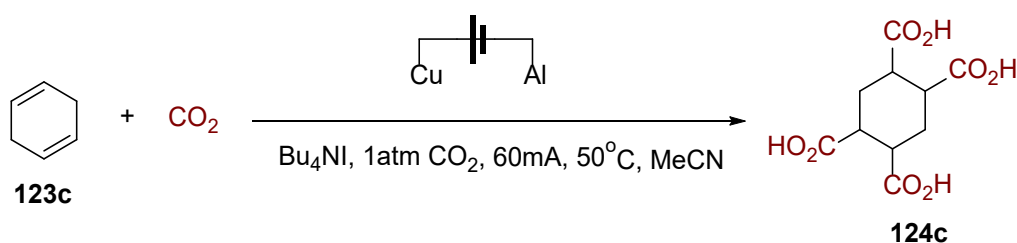
123c

Cyclohexadiene **123c** (0.80 g, 10 mmol) was added to a solution of Bu₄NI (0.96g, 3 mmol) in acetonitrile (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was heated to 50°C and electrolysed at a current of 60mA in a single compartment cell containing a copper cathode and aluminium anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude precipitate (2.0 g) was afforded. Crude precipitate (0.56 g) was acidified with HCl/H₂O (1:1, 10 mL) and extracted with ethyl acetate (3x10 mL). NMR analysis showed that no reaction took place.
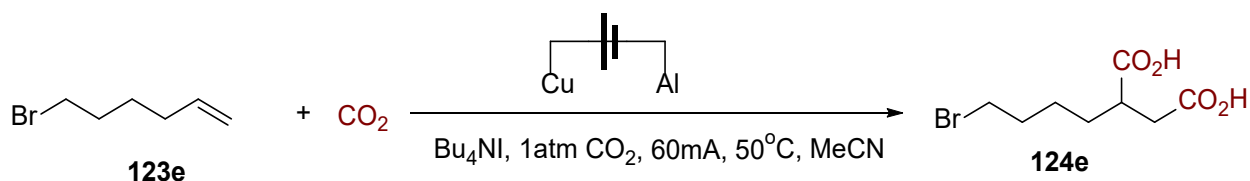
6-Bromo-1-hexene **123e** (0.33 g, 2 mmol) was added to a solution of Bu$_4$NI (0.37 g, 1mmol) in acetonitrile (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was heated to 50°C and electrolysed at a current of 60 mA in a single compartment cell containing a copper cathode and aluminium anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture filtered under suction to afford crude solid (1.82g). Crude solid (0.60 g) acidified by addition of HCl/H$_2$O (1:1, 20 mL) and extracted with ethyl acetate (3x20 mL), no end product was afforded.

Cyclopentene **123d** (0.14 g, 2 mmol) was added to a solution of Bu$_4$NI (0.37 g, 1 mmol) in acetonitrile (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was heated to 50°c and electrolysed at a current of 60mA in a single compartment cell containing a copper cathode and aluminium anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture filtered under suction to afford crude solid (1.82 g). Crude solid (0.60 g) acidified by addition of HCl/H$_2$O (1:1, 20 mL) and extracted with ethyl acetate (3x20 mL), no end product was afforded.

123g + CO₂ → **124g**

Cis-Cyclooctene **123g** (0.22 g, 2 mmol) was added to a solution of Bu₄NI (0.37 g, 1 mmol) in acetonitrile (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min⁻¹) for 1h. The mixture was heated to 50°c and electrolysed at a current of 60 mA in a single compartment cell containing a copper cathode and aluminium anode with a constant CO_2 flow (flow rate 463 ml min⁻¹) with stirring for 24h. Crude reaction mixture filtered under suction to afford crude solid (1.82 g). Crude solid (0.60g) acidified by addition of HCl/H₂O (1:1, 20 mL) and extracted with ethyl acetate (3x20 mL), no end product was afforded.

123f + CO₂ → **124f**
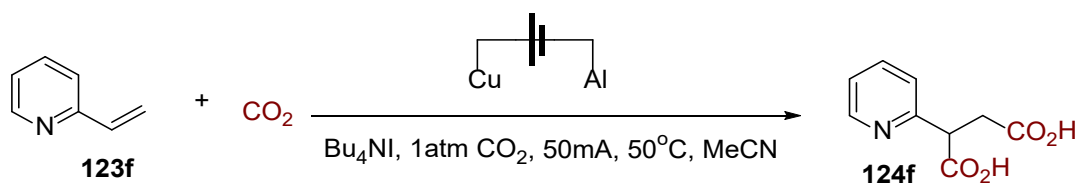
2-Vinylpyridine **123f** (0.21 g, 2 mmol) was added to a solution of Bu₄NI (0.38g, 1mmol) in acetonitrile (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min⁻¹) for 1h. The mixture was heated to 50°c and electrolysed at a current of 60mA in a single compartment cell containing a copper cathode and aluminium anode with a constant CO_2 flow (flow rate 463 mL min⁻¹) with stirring for 24h. Crude sticky amorphous polymer (0.44 g) obtained, unable to purify.

3.7 Electrocarboxylation of olefins using Non-sacrificial electrochemical cell

3.7.1 General Procedure
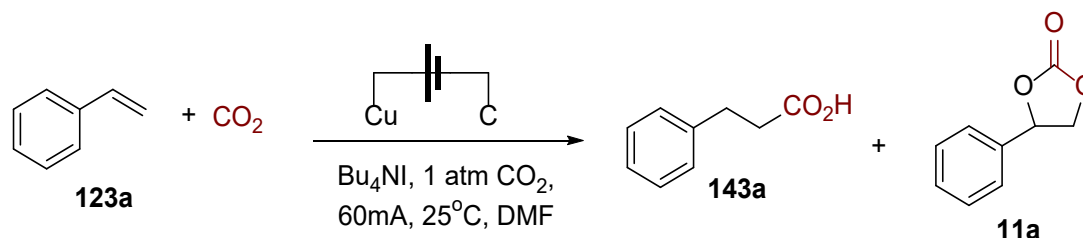
Styrene **123a** (0.2079 g, 2 mmol) was added to a solution of Bu$_4$NI (0.760 g, 2 mmol), TEA (2 mmol) and TEOA (2 mmol) in DMF (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a current of 60mA in a single compartment cell containing a copper cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 20 mL) and extracted with diethylether (3x20 mL) to afford amber oil. NMR analysis shows presence of two compounds **143a** and **11a** in a ratio of 3:1.
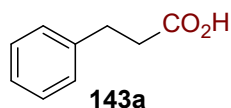
Benzenepropanoic acid (143a)[143]

^{1}H NMR (400MHz, CDCl$_3$) δ = 7.19- 7.40 (m, 5H), 2.89 (t, *J* = 8 Hz, 2H), 2.62 (t, *J* = 8 Hz, 2H).

^{13}C NMR (100MHz, CDCl$_3$) δ 30.5, 35.5, 126.4, 128.2, 128.5, 140.1, 178.7.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 3030, 2934, 2642 (0-H), 1700 (C=O), 1157 (C-O) 910 (O-H).

3.7.2 Optimisation Procedures

Styrene **123a** (0.208 g, 2 mmol) was added to a solution of Bu$_4$NI (0.760 g, 2 mmol), and TEOA (2 mmol) in DMF (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a current of 60 mA in a single compartment cell containing a copper cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 20 mL) and extracted with diethylether (3x20 mL) to afford amber oil. TEA removed (99% conv. Conversion not affected).

Styrene **123a** (0.208 g, 2 mmol) was added to a solution of Bu$_4$NI (0.760 g, 2 mmol), and TEOA (2 mmol) in DMF (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a current of 60 mA in a single compartment cell containing a cathode and anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 20 mL) and extracted with diethylether (3x20 mL) to afford amber oil. Cu/Cu (99%, 3:1), Cu/C (99%, 3:1), Ni/C (40%, 1:1), C/C (99%, 6:1).

Styrene **123a** (0.208 g, 2 mmol) was added to a solution of Bu$_4$NI (0.760 g, 1 mmol), and TEOA (2 mmol) in solvent. The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a current of 60 mA in a single compartment cell containing a copper cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. MeCN, 25 mL (99%, 3:1), DMF, 25 mL (99%, 3:1), THF,25 mL (0%), Acetone, 25 mL (0%).

Styrene **123a** (0.208 g, 2 mmol) was added to a solution of Bu$_4$NI (0.760 g, 1 mmol), and TEOA (2 mmol) in solvent. The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a voltage of 10V in a single compartment cell containing a copper cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. DMF, 25 mL (isolated yield, 57.59%), 10 mL (isolated yield, 68.6 %), 5 mL (isolated yield, 60%).

Styrene **123a** (0.2079 g, 2 mmol) was added to a solution of Bu$_4$NI (0.760 g, 1 mmol), and TEOA (2 mmol) in DMF (25 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed under voltage in a single compartment cell containing a copper cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether

(3x20 mL) to afford amber oil. 5 volts (99%, 3:1), 10 volts (99%, 3.5:1), 15 volts (99%, 8:1), 20 volts (N/A, N/A).

Styrene **123a** (0.208 g, 2 mmol) was added to a solution of Bu$_4$NI (0.760g, 1 mmol), and electron donor (2 mmol) in MeCN (25 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a current of 60 mA in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. TEOA (99%, 1:0), MeOH (80%, 1:0), EtOH (80%, 1:0.6), IPA(55%, 2:1), tBuOH (N/A, 1:0.2), TEA(0%, N/A).

Styrene **123a** (0.208 g, 2 mmol) was added to a solution of supporting electrolyte, and TEOA (2mmol) in MeCN (25 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a current of 60 mA in a single compartment cell containing a copper cathode and carbon anode with a constant CO_2 flow (flow rate 463 mL min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. Bu$_4$NI 0.5 mmol (N/A, 14:1), Bu$_4$NI 1 mmol (60%, 100:4), Bu$_4$NI 2 mmol (99%, 7:1), Bu$_4$NBr 1 mmol (99%, 1:1), Bu$_4$NCl 1 mmol (99%, 1:1), Bu$_4$NPF$_6$ 1 mmol (<5%, N/A), Bu$_4$NHSO$_4$ 1 mmol (<5%, N/A), KI 1 mmol (<5 %, N/A).

Styrene **123a** (0.208 g, 2 mmol) was added to a solution of supporting electrolyte (1 mmol,) and TEOA (2 mmol) in DMF (10 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. Bu$_4$NI (70% yield), Bu$_4$NBr (61%), Bu$_4$NCl (47%), Et$_4$NI (70%), Bu$_4$NHSO$_4$ (45%).

3.7.3 Optimised Procedure

Substrate (1 mmol) was added to a solution of Et$_4$NI (1 mmol) and TEOA (2 mmol) in DMF (10 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1hr. The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1: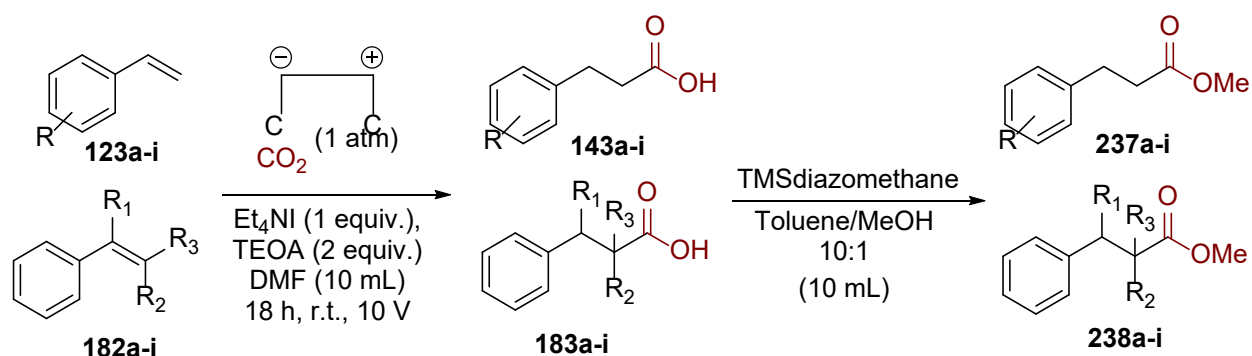1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. The resulting mixture was suspended in 10:1 toluene/MeOH solution (10 mL) and stirred for 10 mins. TMS-diazomethane to resulting mixture until pale yellow colour persists followed by additional stirring for 30 mins. Reaction mixture concentrated in vacuo. to afford pale yellow oil followed by purification by column chromatography on silica to final methyl ester product.

237a

Methyl 3-phenylpropanoate (237a)[144] Following the general procedure to give **237a** (0.105 g, 70% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 - 7.17 (m, 5H), 3.66 (s, 3H), 2.94 (t, *J* = 7.6 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 1H)

¹³C NMR (100 MHz, Chloroform-*d*) δ 31.0, 35.8, 51.7, 126.3, 128.6, 128.3, 140.5, 173.4.
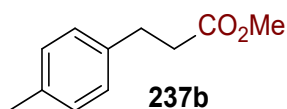
237b

Methyl 3-(*p*-tolyl)propanoate (237b)[145] Following the general procedure to give **237b** (0.129 g, 80% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 -7.06 (m, 4H), 3.66 (s, 3H), 2.90 (t, *J* = 8.4 Hz, 1H), 2.60 (t, *J* = 8.4 Hz)

¹³C NMR (100 MHz, Chloroform-*d*) δ 21.1, 30.6, 35.9, 51.7, 128.2, 129.2, 135.8, 137.5, 173.5.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 1720, 1677(C=O), 1348, 1318 (C-O), 728 (C-H).

237c

3-(4-*tert*-Butyl-phenyl)-propionate (237c)[145] Following the general procedure to give **237c** (0.196g, 96% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.66 (s, 3H), 2.91 (t, *J* = 16.0 Hz, 2H), 2.61 (t, *J* = 16.0 Hz, 2H), 1.29 (s, 9H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 30.0, 31.4, 34.4, 35.6, 50.7, 125.5, 128.0, 137.1, 149.2, 179.4.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 1738 (C=O), 1358, 1328 (C-O), 824 (C-H).
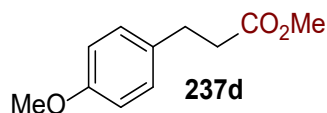
237d

Methyl 3-(4-methoxyphenyl)propanoate (237d)[146] Following the general procedure to give **237d** (0.119 g, 67% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 3.77 (s, 3H), 3.65 (s, 3H), 2.88 (t, *J* = 8.0 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H)

¹³C NMR (100 MHz, Chloroform-*d*) δ 31.0, 36.1, 51.6, 55.3, 113.9, 129.3, 132.6, 158.1.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 1702, 1613 (C=O), 1512, 1328, 1205 (C-O), 823 (C-H).
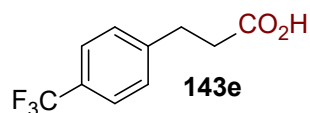
3-[4-(trifluoromethyl)phenyl]propanoic acid (143e)[147] Following the general procedure to give **143e** (0.143 g, 66% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8Hz, 2H), 7.34 (d, *J* = 8Hz, 2H) 3.02 (t, *J* = 7.6, 2H), 2.73 (t, *J* = 7.6, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 30.2, 34.9, 125.4, 126.1, 128.1, 129,2, 144.1, 177.7.

V_{max} (CH₂Cl₂)/cm⁻¹ 2935 (O-H), 1654 (C=O), 1255 (C-F), 1103 (C-O).
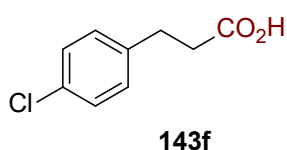
Methyl 3-(4-chlorophenyl)propanoic acid (143f)[148] Following the general procedure to give **143f** (0.093 g, 50% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 -7.18 (m, 4H), 2.95 (t, *J* = 8.4Hz, 2H), 2.67 (t, *J* = 8.4Hz, 2H)

¹³C NMR (100 MHz, Chloroform-*d*) δ 30.6, 35.5, 126.4, 128.3, 128.6, 140.2, 178.0

V_{max} (CH₂Cl₂)/cm⁻¹ 2968 (O-H), 1643 (C=O), 1118 (C-O), 738 (C-Cl)
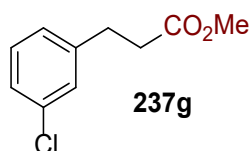
Methyl 3-(3-chlorophenyl)propionate (237g)[149] Following the general procedure to give **237g** (0.061 g, 33% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 -7.06 (m, 4H), 3.66 (s, 3H), 2.96-2.89 (m, 2H), 2.64-2.59 (m, 2H)

¹³C NMR (100 MHz, Chloroform-*d*) δ 30.6, 35.4, 51.7, 126.3, 128.3, 128.5, 140.5, 173.4.

V_{max} (CH₂Cl₂)/cm⁻¹ 1723, 1609 (C=O), 1331, 1225 (C-O), 756 (C-Cl).
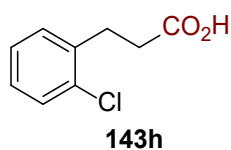
143h

Methyl 3-(2-chlorophenyl)propanoic acid (143h)[148] Following the general procedure to give **143h** (0.062 g, 33% yield). Amber oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 -7.14 (m, 4H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 30.6, 35.4, 51.7, 126.3, 128.3, 128.5, 140.5, 173.4.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 2953 (O-H), 1701 (C=O), 1332 (C-O), 752 (C-Cl).
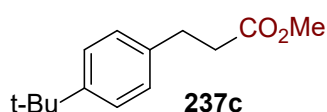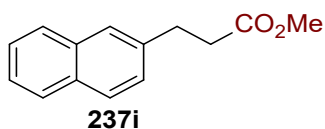

237i

Methyl 3-(2-naphthyl)propanoate (237i)[150] Following the general procedure to give **237i** (0.101 g, 50% yield). Amber oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (t, *J* = 10.0 Hz, 3H), 7.63 (s, 1H), 7.46 -7.40 (m, 2H), 7.32 (dd, *J* = 8.8, 1.6 Hz, 1H), 3.66 (s, 3h), 3.10 (t, *J* = 8.0 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 31.1, 35.7, 51.7, 125.4, 126.1, 126.5, 127.0, 127.5, 128.2, 132.2, 133.6, 138.0, 173.4.
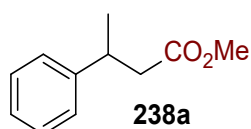
238a

Methyl 3-phenylbutanoate (238a)[151] Following the general procedure to give **238a** (0.139 g, 85% yield). Amber oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 -7.14 (m, 5H), 3.62 (s, 3H), 3.01 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.72 (m, 1H), 2.65 (dd, *J* = 13.2, 7.6 Hz, 1H), 1.14 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 16.8, 39.7, 41.5, 51.6, 126.4, 128.4, 128.5, 129.0, 139.4, 176,6.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 1746 (C=O), 1231, 1155 (C-O), 705 (C-H).
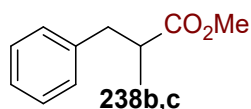
238b,c

Methyl 2-methyl-3-phenylpropanoate (238b,c)[152] Following the general procedure to give **238b,c** (0.141 g, 86% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-d) δ 7.19 -7.04 (m, 5H), 3.53 (s, 3H), 2.92 (dd, J = 13.2, 6.4 Hz, 1H), 2.63 (m, 1H), 2.55 (dd, J = 13.2, 7.6 Hz, 1H), 1.04 (d, J = 6.4 Hz, 3H)

¹³C NMR (100 MHz, Chloroform-d) δ 16.7, 39.6, 41.4, 51.5, 126.3, 128.3, 128.9, 139.3, 176.5.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 1739, (C=O), 1228, 1136 (C-O), 711 (C-H.)
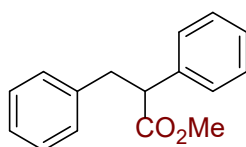
238d,e

Methyl 2,3-diphenylpropanoate (238d,e)[153] Following the general procedure to give **237d,e** (0.158 g, 50% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-d) δ 7.30 -7.10 (m, 10H), 3.84 (dd, J = 8.4, 6.4Hz, 1H), 3.59 (s, 3H), 3.41 (dd, J = 13.6, 8.8Hz, 1H), 3.01 (dd, J = 14.0, 7.2Hz, 1H).

¹³C NMR (100 MHz, Chloroform-d) δ 39.9, 52.0, 53.6, 126.4, 127.4, 128.0, 128.4, 128.7, 129.0, 138.7, 139.1, 173.9.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 1706, 1627 (C=O), 1431, 1255 (C-O).
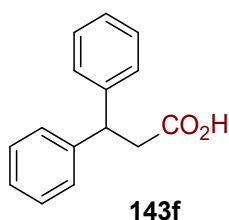
143f

Methyl 2,2,3-triphenylpropanoic acid (143f)[154] Following the general procedure to give **143f** (0.181 g, 80% yield). Amber oil.

¹H NMR (400 MHz, Chloroform-d) δ 7.29 -7.18 (m, 10H), 4.51 (t, J = 8.0 Hz, 1H), 3.08 (d, J = 7.6 Hz, 2H).

¹³C NMR (100MHz, Chloroform-d) δ 40.3, 46.7, 126.7, 127.6, 128.7, 143.3, 177.3.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 3003 (O-H) 1706, 1598 (C=O), 1521, 1455, 1218 (C-O), 701 (C-H).
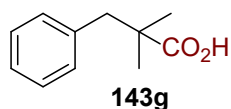
143g

Methyl 2,2-dimethyl-3-phenylpropanoic acid (143g)[155] Following the general procedure to give **143g** (0.133 g, 75% yield). Amber oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 -7.19 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 2H), 3.64 (s, 3H), 2.83 (s, 2H), 1.66 (s, 6H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 24.7, 43.4, 45.9, 126.6, 128.1, 130.3, 137.5, 183.5.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 3073 (O-H) 1715, 1598 (C=O), 1268 (C-O), 771 (C-H)
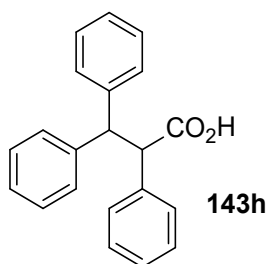

143h

Methyl 2,2,3-triphenylpropanoic acid (143h) Following the general procedure to give **143h** (0.160 g, 53% yield). Amber oil.

^{1}H NMR (400 Mhz, Chloroform-*d*) δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.30 -6.97 (m, 13H), 4.69 (d, *J* = 12.4 Hz, 1H), 4.43 (d, *J* = 12.4 Hz, 1H), 3.46 (s, 3H).

^{13}C NMR (100Mhz, Chloroform-*d*) δ 52.0, 54.8, 56.7, 126.2, 126.7, 127.4, 127.7, 128.2, 128.3, 128.4, 128.6, 137.0, 141.6, 142.9, 173.3.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 3155, 1706, 1644, 1560, 1382, 733.

3.7.4 Attempted Procedures
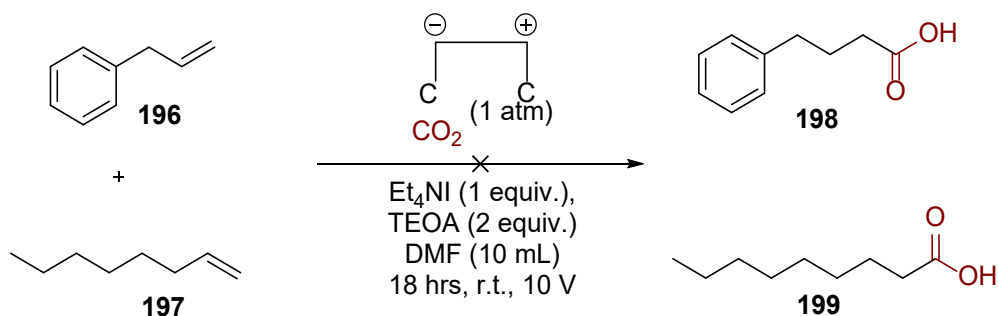
Substrate (1 mmol) was added to a solution of Et$_4$NI (0.257g, 1 mmol) and TEOA (2 mmol) in DMF (10 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a constant voltage of 10V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. NMR analysis shows that no reaction occurred.

3.8 Electrocarboxylation of styrene in the presence of Cu(II)triflate

3.8.1 General Procedure
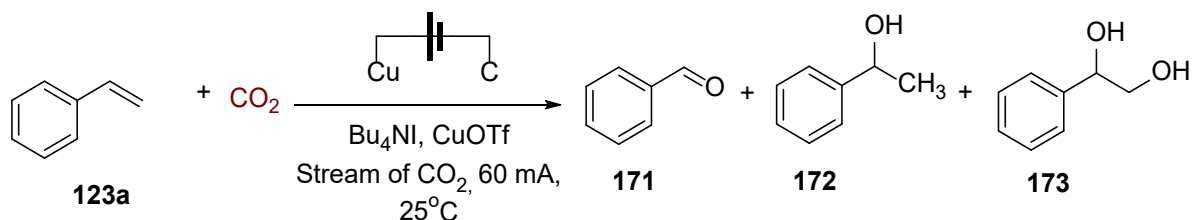
Styrene **123a** (0.212 g, 2 mmol) was added to a solution of Bu$_4$NI (0.355 g, 1 mmol) and CuOTf (0.253 g, 0.7 mmol) in DMF (50 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a current of 60 mA in a single compartment cell containing a copper cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 24h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 20 mL) and extracted with diethylether (3x20 mL) to afford amber oil. NMR analysis and GCMS analysis showed three compounds.

171
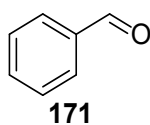
Benzaldehyde (171)

¹H NMR (400MHz, Chloroform-*d*) δ 9.93 (s, 1H), 7.97 -7.63 (m, 5H).

¹³C NMR (100MHz, Chloroform-*d*) δ 128.7, 129.2, 134.5, 136.2, 192.6.

172
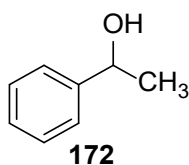
1-Phenylethanol (172)

¹H NMR (400MHz, Chloroform-*d*) δ 7.41 -7.15 (m, 5H), 5.01 -4.80 (m, 1H), 1.49 (d, *J*= 6.4 Hz, 3H).

¹³C NMR (100MHz, Chloroform-*d*) δ 25.2, 70.5, 127.0, 127.7, 128.9, 145.8.

173
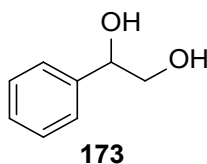
1-Phenyl-1,2-ethanediol (173)

¹H NMR (400MHz, Chloroform-*d*) δ 7.45 -7.14 (m, 5H), 4.88 (t, *J*= 6.8 Hz, 1H), 3.74 (dd *J*= 3.6, 11.2Hz, 1H), 3.64 (dd, *J*= 8.0, 11.2Hz, 1H).

¹³C NMR (100MHz, Chloroform-*d*) δ 65.4, 74.7, 127.0, 127.7, 128.8, 140.5.

3.9 Electrocarboxylation of 4-chlorostyrene

3.9.1 General Procedure
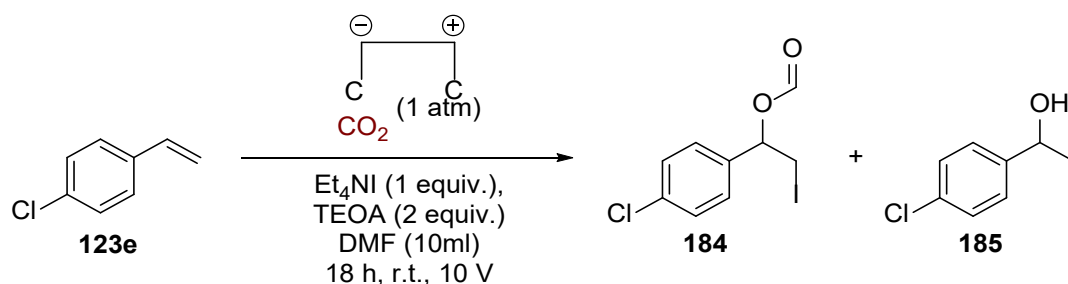
4-Chlorostyrene **123e** (1 mmol) was added to a solution of Et_4NI (1 mmol) and TEOA (2 mmol) in DMF (10 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. Followed by purification by column chromatography on silica to afford 2-iodo-1-(4-chlorophenyl)ethyl formate **184** and 1-(4-Chloro-phenyl)-2-iodo-ethanol **185** in varying ratios.
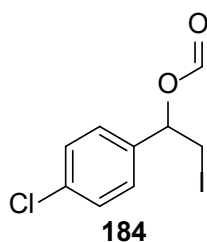
2-Iodo-1-(4-chlorophenyl)ethyl formate (184)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.93 (t, *J* = 6 Hz, 1H), 3.44 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 6.5, 74.4, 127.9, 129,1, 135.0, 136.3, 159.5.

185
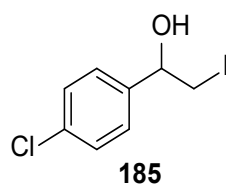
1-(4-Chloro-phenyl)-2-iodo-ethanol (185)

¹H NMR (400 MHz, Chloroform-*d*) δ ppm 7.35- 7.29 (m, 4H), 4.79 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.46 (dd, *J* = 10.4, 3.6 Hz, 1H), 3.35 (dd, *J* = 10.4, 8.8 Hz, 1H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 15.2, 73.3, 127.2, 128.9, 134.1, 139.5.

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3.10 Synthesis of Dienes

3.10.1 General Procedure
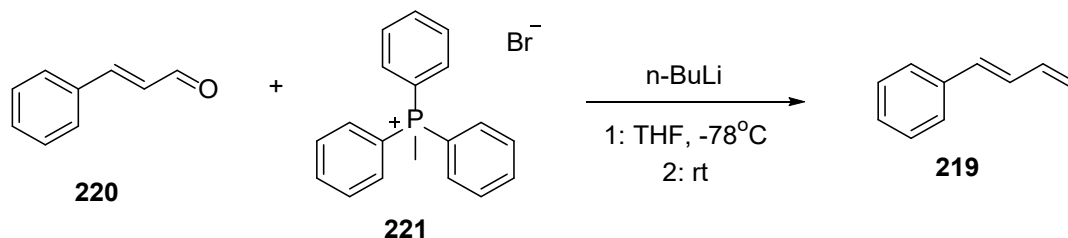
N-BuLi (5.5 mmol) added slowly to a solution of methyltriphenylphosphonium bromide **221** (1.78g, 5 mmol) in THF (50 mL) under nitrogen atmosphere at -78°C. Solution allowed to stir for 30mins. Trans- cinnamaldehyde **220** (0.73 g, 5.5 mmol) added dropwise to reaction mixture and stirred for further 4 h. Reaction mixture quenched with MeOH (5 mL) and solvent evaporated under vacuum to afford crude off white solid. Followed by purification by column chromatography to afford 1-phenyl-1,3-butadiene **219** (0.61 g, 95%).
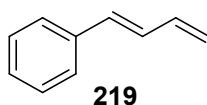
1-Phenyl-1,3-butadiene (219)[156]

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.82 (dd, *J* = 10.8, 15.6 Hz, 1H), 6.61-6.49 (m, 2H), 5.37 (d, *J* = 16.8 Hz, 1H), 5.21 (d, *J* = 10.4 Hz, 1H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 117.7, 126.5, 127.7, 128.7, 129.7, 132.9, 137.3.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 3030, 1633, 1602, 1449.

3.11 Electrocarboxylation of dienes

### 3.11.1 General Procedure
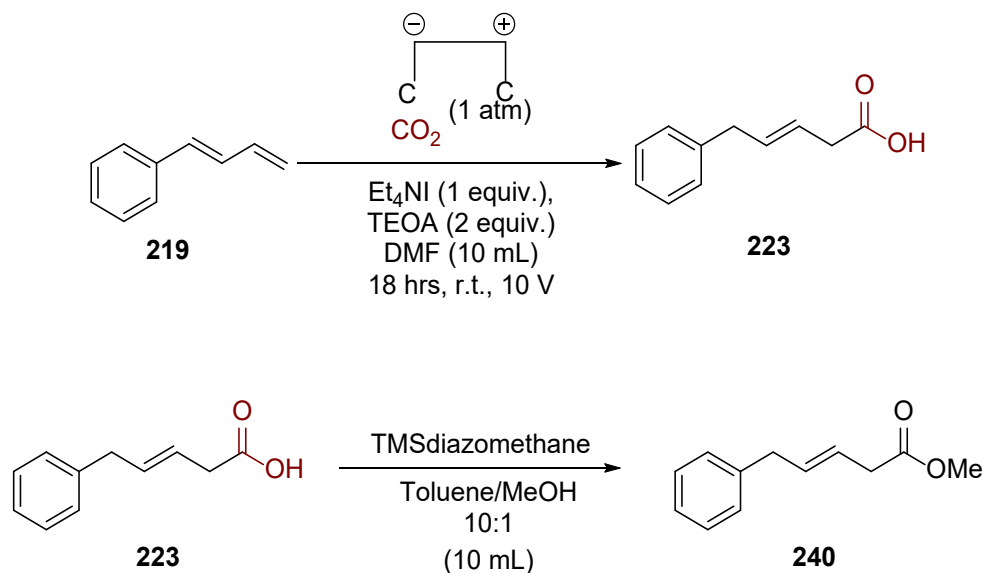
1-Phenyl-1,3-butadiene **219** (1 mmol, 0.130 g) was added to a solution of Et_4NI (0.257g, 1 mmol) and TEOA (2 mmol) in DMF (10 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1h. The mixture was electrolysed at a constant voltage of 10V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H_2O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. The resulting mixture was suspended in 10:1 toluene/MeOH solution (10 mL) and stirred for 10 mins. TMS-diazomethane to resulting mixture until pale yellow colour persists followed by additional stirring for 30 mins. Reaction mixture concentrated in vacuo. to afford pale yellow oil followed by purification by column chromatography on silica to afford Methyl 5-phenyl-3-pentenoate **240** (0.110 g, 58%).

240
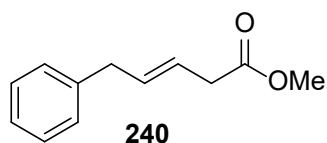
Methyl 5-phenyl-3-pentenoate (240)[157]

¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 -7.16 (m, 5H), 5.74 -5.58 (m, 2H), 3.67 (s, 3H), 3.37 (d, *J* = 6.8 Hz, 2H), 3.07 (d, *J* = 6.8 Hz, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 37.8, 38.9, 51.9, 123.1, 126.2, 128.6, 133.3, 140.1, 172.5.

V_{max} (CH₂Cl₂)/cm⁻¹ 3030, 2252, 1602, 1449, 1004, 694.

3.12 Electrocarboxylation of Alkynes

3.12.1 General Procedure
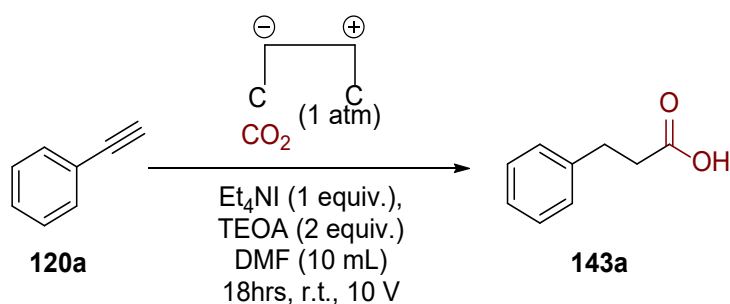
Phenylacetylene **120a** (0.101 g, 1 mmol) was added to a solution of Et₄NI (0.257g, 1 mmol) and TEOA (2 mmol) in DMF (10 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min⁻¹) for 1 hr. The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min⁻¹) with stirring for 18 h. Crude reaction mixture acidified by addition of HCl/H₂O (1:1, 5 ml) and extracted with diethylether (3x20 mL) to afford amber oil (0.054 g, 44%).

3.13 Electrocarboxylation of methyl methacrylate

### 3.13.1 Representative Procedure
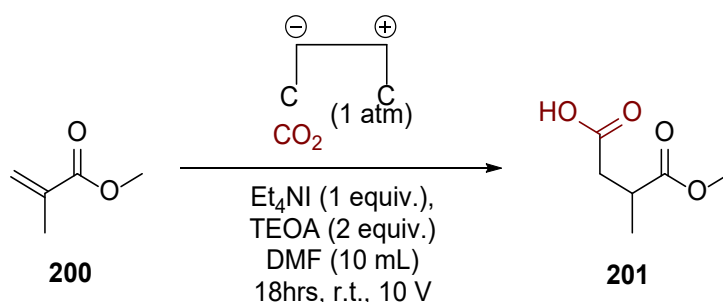
Methyl methacrylate **200** (0.100g, 1 mmol) was added to a solution of Et_4NI (0.257g, 1 mmol) and TEOA (2 mmol) in DMF (10 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1hr. The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H_2O (1:1, 5 mL and extracted with diethylether (3x20 mL) to afford 1-methyl 2-methylsuccinate **201** (0.073 g, 50%) as an amber oil.

201
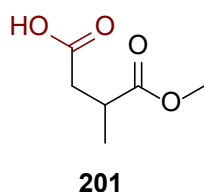
1-Methyl 2-methylsuccinate (201)[158]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.67 (s, 3H), 2.93-2.84 (m, 1H), 2.77 (dd, *J* = 8.2, 16.8 Hz, 1H), 2.43 (dd, *J* = 8.2, 16.8 Hz, 1H), 1.21 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 17.0, 35.5, 37.3, 51.1, 175.7, 177.6.

V_{max} (CH_2Cl_2)/cm^{-1} 2254, 1713, 908, 733.

3.14 Mechanistic Analysis: Electrocarboxylation of styrene in the presence of TEMPO

3.14.1 Attempted Procedure
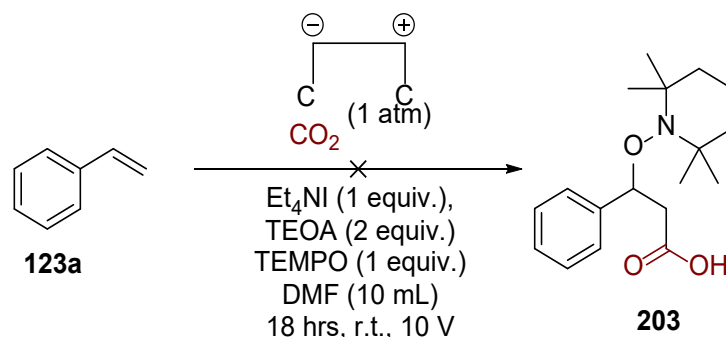
Styrene **123a** (0.103 g, 1 mmol) was added to a solution of Et$_4$NI (0.257g, 1 mmol), TEOA (2 mmol) and TEMPO (1 mmol) in DMF (10mL). The resulting mixture was flushed with CO$_2$ (at a flow rate of 463 mL min^{-1}) for 1hr. The mixture was electrolysed at a constant voltage of 10V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO$_2$ flow (flow rate 463 ml min^{-1}) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. NMR analysis showed no incorporation of TEMPO.

3.15 Mechanistic Analysis: Electrocarboxylation of styrene in the presence of deuterated reagents

3.15.1 Attempted Procedure
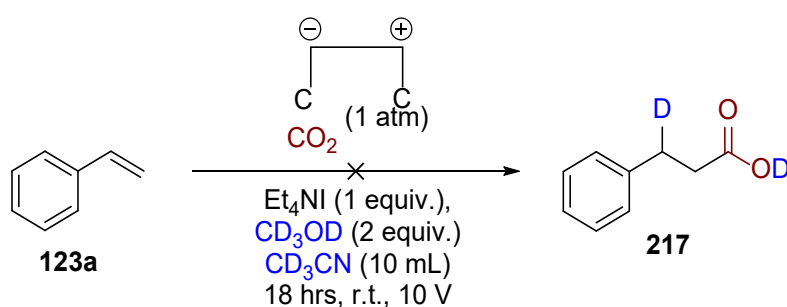
Styrene **123a** (0.103 g, 1 mmol) was added to a solution of Et$_4$NI (0.257g ,1 mmol) and CD$_3$OD (2 mmol) in CD$_3$CN (10 mL). The resulting mixture was flushed with CO$_2$ (at a flow rate of 463 mL min^{-1}) for 1hr. The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO$_2$ flow (flow rate 463 ml min^{-1}) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. NMR analysis showed no incorporation of deuterium.

3.16 Mechanistic Analysis: Synthesis of cyclo-propyl containing derivatives

3.16.1 Representative Procedure
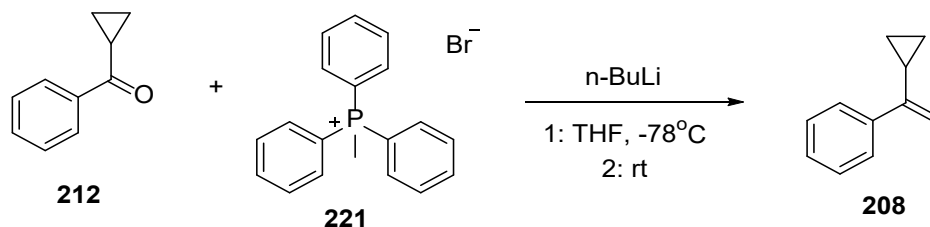
N-BuLi (5.5 mmol) added slowly to a solution of methyltriphenylphosphonium **221** bromide (1.78 g, 5 mmol) in THF (50 mL) under nitrogen atmosphere at -78°C. Solution allowed to stir for 30 mins. Cyclopropyl phenyl ketone **212** (0.80 g 5.5 mmol) added dropwise to reaction mixture and stirred for further 4 h. Reaction mixture quenched with MeOH (5 mL) and solvent evaporated under vacuum to afford (1-cyclopropylethenyl)benzene **208**. (0.59 g, 82%)

208
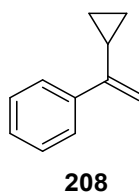
(1-Cyclopropylethenyl)benzene (208)[79]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 6.8Hz, 2H) 7.40 -7.30 (m, 3H), 5.32 (s, 1H), 4.98 (s, 1H), 1.73- 1.69 (m, 1H), 0.90- 0.84 (m, 2H), 0.67- 0.62 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 6.8, 15.7, 109.1, 126.2, 127.5, 128.2, 141.7, 149.4.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 3085 (C=CH), 1624 (C=C), 1600 (CH=CH$_2$), 1494 (C-C), 650 (C-H).

3.16.2 Representative Procedure
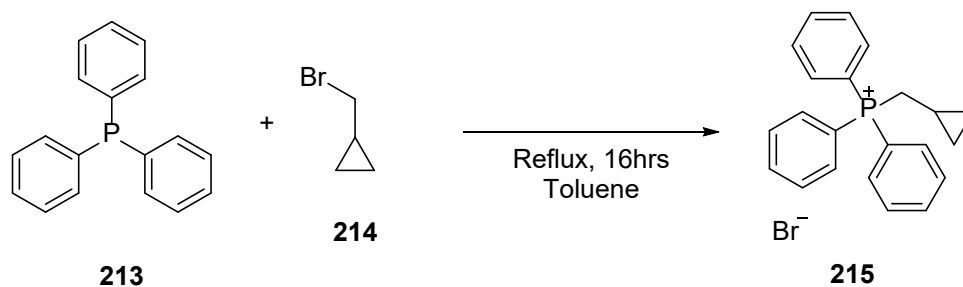
Solution of triphenylphosphine **213** (0.464 g 1 mmol) and (bromomethyl)cyclopropane **214** (0.1 mL, 1 mmol) in toluene (5 mL) was refluxed for 16 h. Resulting solution concentrated in vacuo followed by addition of diethylether to initiate precipitation. Resulting precipitate was filtered to afford (cyclopropylmethyl)triphenylphosphonium bromide **215** as white solid (0.65 g, 88%).

3.16.3 Representative Procedure
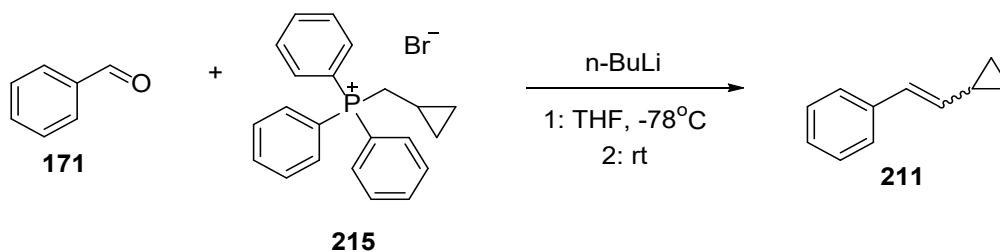
N-BuLi (5.5 mmol) added slowly to a solution of (cyclopropylmethyl)triphenylphosphonium **215** bromide (1.78 g, 5 mmol) in THF (50 mL) under nitrogen atmosphere at -78°C. Solution allowed to stir for 30 mins. Cinnamaldehyde **171** (0.73 g, 5.5 mmol) added dropwise to reaction mixture and stirred for further 4 h. Reaction mixture quenched with MeOH (5 mL) and solvent evaporated under vacuum to afford crude off white solid **211** (0.56 g, 78%).

211

β-Cyclopropylstyrene (211)[159]

¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 6.8 Hz, 2H), 7.40 -7.30 (m, 3H), 5.32 (s, 1H), 4.98 (s, 1H), 1.72 -1.66 (m, 1H), 0.90 -0.86 (m, 2H), 0.66 -0.62 (m, 2H).

¹³C NMR (100 MHz, Chloroform) δ 6.8, 15.7, 109.1, 126.2, 127.5, 128.2, 141.7, 149.4

V_{max} (CH₂Cl₂)/cm⁻¹ 3009 (C=CH), 1638 (C=C), 1600 (CH=CH₂), 1448 (C-C), 650 (C-H)

3.16.4 General Procedure

Substrate (1 mmol) was added to a solution of Et₄NI (1 mmol) and TEOA (2 mmol) in DMF (10 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min⁻¹) for 1hr. The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min⁻¹) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H₂O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. The resulting mixture was suspended in 10:1 toluene/MeOH solution (10 mL) and stirred for 10 mins. TMSdiazomethane to resulting mixture until pale yellow colour persists followed by additional stirring for 30 mins. Reaction mixture concentrated *in vacuo.* to afford pale yellow oil followed by purification by column chromatography on silica to final methyl ester product.

239a

(1-Phenylvinyl)cyclopropane 208 affords **β-cyclopropylbenzenepropanoic acid 239a**[160] (0.155g, 76%)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 -7.18 (m, 5H), 3.58 (s, 3H), 2.79 -2.68 (m, 2H), 2.34 (q, *J* = 7.6 Hz, 1H), 1.05 -0.99 (m, 1H), 0.59 -0.53 (m, 1H), 0.43 -0.36 (m, 1H), 0.27 -0.20 (m, 1H), 0.15 -0.09 (m, 1H).

¹³C NMR (100 MHz, Chloroform) δ 4.1, 5.3, 17.2, 41.2, 47.2, 51.5, 126.5, 127.3, 128.4, 144.1, 172.9.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 3155, 2253, 1470, 1382, 911, 650.
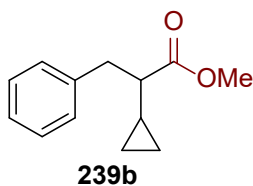
239b

β-Cyclopropylstyrene 211 affords **α-cyclopropylbenzenepropanoic acid 239b** (0.146g, 72%)

¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 -7.13 (m, 5H), 3.58 (s, 3H), 3.03 -2.92 (m, 2H), 1.90 -1.84 (m, 1H), 0.98 -0.94 (m, 1H), 0.53 -0.43 (m, 2H), 0.30 -0.24 (m, 1H), 0.06 -0.01 (m, 1H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 3.6, 4.8, 13.8, 38.7, 51.5, 52.8, 126.3, 128.3, 128.9, 139.4, 175.5.

V_{max} (CH$_2$Cl$_2$)/cm^{-1} 3155, 2253, 1469, 1381, 907, 650.

3.17 Mechanistic analysis: Electrocarboxylation of (2-Iodoethyl)benzene

3.17.1 Attempted Procedure
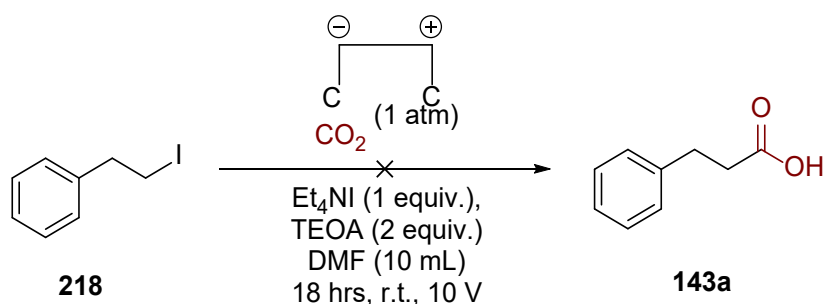
(2-Iodoethyl)benzene **218** (1 mmol) was added to a solution of Et_4NI (1 mmol) and TEOA (2 mmol) in DMF (10 mL). The resulting mixture was flushed with CO_2 (at a flow rate of 463 mL min^{-1}) for 1hr. The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO_2 flow (flow rate 463 ml min^{-1}) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H_2O (1:1, 5 mL) and extracted with diethylether (3x20 mL) to afford amber oil. NMR analysis shows that no reaction occurred.

3.18 Electrocarboxylation of olefins with the IKA Electrosyn

3.18.1 General Procedure
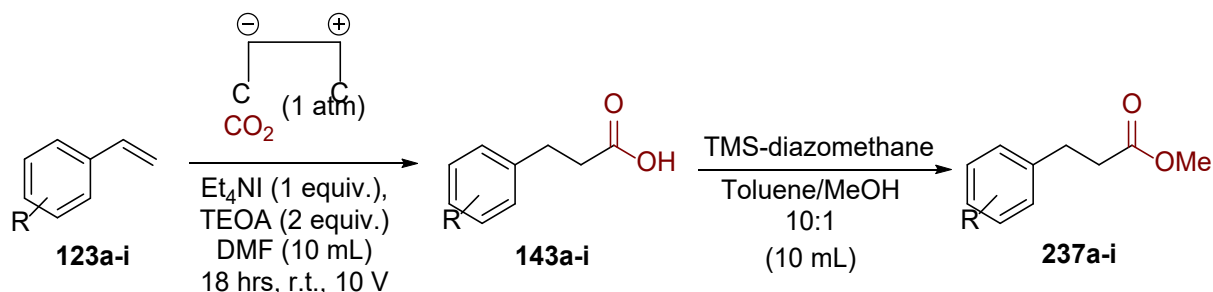
Substrate (0.5 mmol) was added to a solution of Et$_4$NI (0.5 mmol) and TEOA (1 mmol) in DMF (5 mL). The resulting mixture was flushed with CO$_2$ (at a flow rate of 463 mL min^{-1}) for 1hr. The mixture was electrolysed at a constant voltage of 10 V in a single compartment cell containing a carbon cathode and carbon anode with a constant CO$_2$ flow (flow rate 463 ml min^{-1}) with stirring for 18h. Crude reaction mixture acidified by addition of HCl/H$_2$O (1:1, 2 mL) and extracted with diethylether (3x10 mL) to afford amber oil. The resulting mixture was suspended in 10:1 toluene/MeOH solution (10 mL) and stirred for 10 mins. TMS-diazomethane to resulting mixture until pale yellow colour persists followed by additional stirring for 30 mins. Reaction mixture concentrated *in vacuo.* to afford pale yellow oil followed by purification by column chromatography on silica to final methyl ester product.

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