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Synthesis of acrylic acid derivatives from carbon dioxide and ethylene mediated by molecular nickel complexes

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Contents

Abbreviations

ATR	attentuated total reflection
Bz	benzyl
Bpy	2,2'-bipyridine
Bupy	4-tert-butylpyridine
*n*Bu, *t*Bu	n-butyl, tert-butyl
η^6-cdt	trans, trans-1,5,9-cyclododecatriene
η^4-cod	cis,cis-1,5-cyclooctadiene
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
Cy	cyclohexyl
dbu	diazabicyclo-undec-7-ene
*m*dbu	abbreviated-diazabicyclo-undec-7-ene
diars	1,2-bis(diphenylarsino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
dcpe	1,2-bis(dicyclophosphino)ethane
dppm	1,1-bis(diphenylphosphino)methane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
dppb	1,4-bis(diphenylphosphino)butane
dtbpe	1,2-bis(di-tertbutylphosphino)ethane
dtbpm	1,2-bis(di-tertbutylphosphino)methane
Et	ethyl
HSQC	heteronuclear single quantum correlation

kt	kilo ton (10^3)
IR	infrared-red
L	ligand
Me	methyl
MeOTf	methyl triflate
MeI	methyl iodide
mol. equiv.	mole equivalent
Mt	mega ton (10^6)
$Ni(cod)_2$	bis(cyclooctadiene)nickel(0)
NMR	nuclear magnetic resonance
Ph	phenyl
PPh_3	triphenylphosphine
*i*Pr, *n*Pr	iso-propyl, n-propyl
Py	pyridine
Ph_3As	triphenyl arsine
THF	tetrahydrofuran
tmeda	N, N, N', N'-tetramethylethylenediamine
TOF	turnover frequency
TON	turnover number

1. Introduction

The use of carbon dioxide as chemical feedstock for the synthesis of chemicals, additives and technological fluids in a sustainable way using efficient energy (e.g. solar, wind) for the chemical processing is a promising route. CO_2 is exploited for the production of many organic chemicals because it has the advantages of being non-toxic, ubiquitous and economical.[1] Hence, CO_2 can potentially substitute basic reagents (e.g. phosgene, carbon monoxide) that are currently used as raw materials in the synthesis of tens of millions of tons of chemical products in the industries. Despite its wide availability, there are only four important large-scale industrial processes in which CO_2 is used for organic synthesis: the synthesis of urea (70 Mt CO_2 / year), salicylic acid (20 kt CO_2 / year), cyclic carbonates (and polycarbonates) (~ kt CO_2 / year), and the use as an additive to CO for the synthesis of methanol (6 Mt CO_2 / year).[2]

Several new possibilities for the reduction of industrially and technologically-based CO_2 emissions and to capture and store CO_2 have been developed but these concepts are either still in their early stage of development, or they consume considerable amount of energy, and is therefore far from industrial applicability.[3] In order to exploit the utilization of the relatively chemical inert CO_2, the high thermodynamic energy barriers of CO_2 can be lowered through the assistance of catalysts. The transformation of CO_2, a carbon source available from the carbon cycle, is therefore an important goal of homogeneous catalysis, and an overview of the current organometallic concepts for the catalytic activation of CO_2 is presented.

1.1 Coordination of CO_2 to transition-metal complexes

The coordination chemistry of carbon dioxide to metal complexes is well studied.[1] CO_2 molecule is a 16-electron, linear tri-atomic molecule, with point group $D_{\infty h}$. CO_2 is a molecule with several potentially reactive sites: the carbon atom is a Lewis acid (electrophilic center) and the oxygen atoms are Lewis bases (nucleophilic centers). A metal center can therefore react with a CO_2 molecule in four general modes of coordination: (i) $\eta^1(\sigma$-C) side-on coordination, (ii) $\eta^2(\sigma$-C,O) side-on coordination, (iii) $\eta^1(\sigma$-O) end-on coordination, and (iv) π-coordination (Figure 1), amongst them, (i) – (iii) are the most commonly reported modes of electrophilic CO_2 binding to Lewis basic transition-metal center(s), unlike the σ-O coordination mode (iii) in which the CO_2 ligand does not have to orientate to be "forced" to coordinate end-on at the metal center (Figure 1.1).[4]

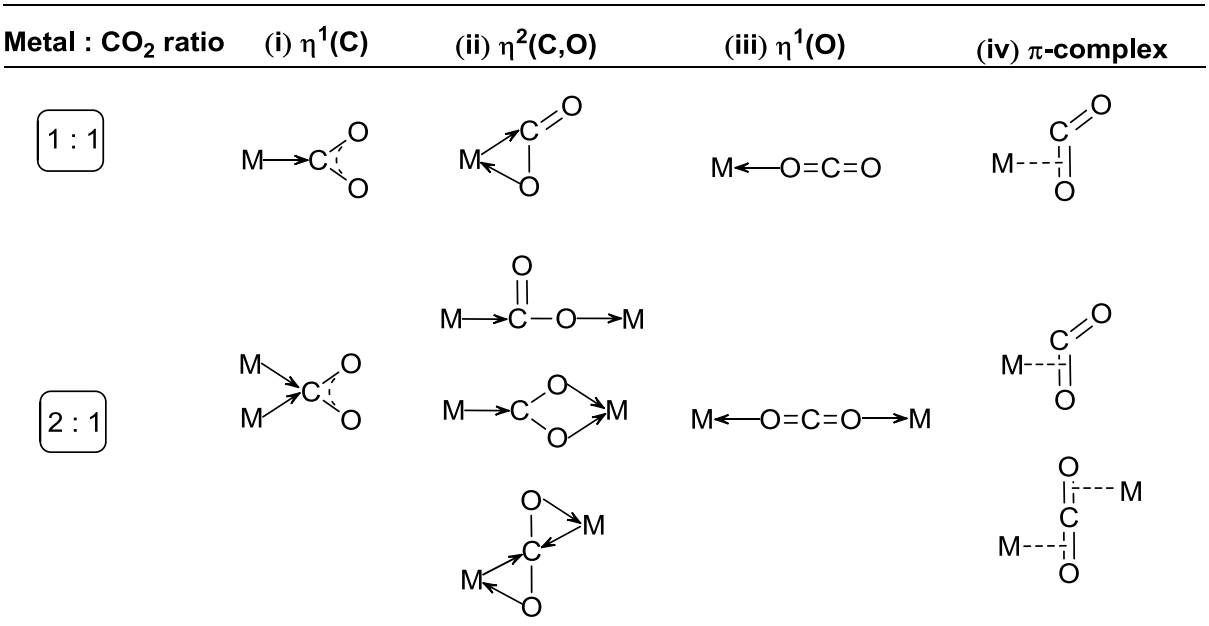


Figure 1.1. Potential coordination modes of CO_2 to one or two transition metal centers (M).

Metal-CO_2 complexes are usually generated by direct reaction of a metal complex with CO_2 as a ligand. Most of these metal centers have either a coordination vacancy or an easily displaced ligand, and are typically highly nucleophilic.[1c, 1f, 1h] The $\eta^1(CO_2)$ metal complexes are usually air and moisture sensitive, and many of these complexes dissociate the CO_2 ligand readily. The first rhodium and iridium $\eta^1(CO_2)$ complexes (Table 1.1) were reported by Herskovitz et al.[5] Other examples of side-on complexes of CO_2 ($\eta^2(C,O)$) with transition metals such as $[Ni(PCy_3)_2(CO_2)]$ and $[(Cp')_2Nb(CO_2)(CH_2SiMe_3)]$ were synthesized by Aresta and Nobile[6] and Lappert et al.[7] respectively. These are some of the early examples in which oxophilic transition metals coordinate to CO_2 to form stable complexes. $\eta^1(O)$ end-on coordination mode is much less known, mainly because of difficulty for a metal to bind to CO_2 *via* a linear oxygen-bound η^1-OCO mode. An example would be the uranium complex $[(({}^{ad}ArO)_3tacn)U^{IV}(\eta^1\text{-}OCO)]$, $(({}^{ad}ArO)_3tacn)$ = 1,4,7-tris(3-adamantyl-5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane).[8]

Table 1.1 summarizes the structurally characterized η^1- and η^2-(CO_2) metal complexes prepared by direct carbonylation with CO_2. In addition, CO_2 can also function as a bridging ligand to two metal centers *via* the coordination of the carbon atom to one metal center and one of the oxygen atoms to other metal to form a μ_2-η^2 CO_2-bridged bimetallic complex. The earliest reports of μ_2-η^2 bimetallacyclic complexes with a CO_2 bridged between iridium and osmium were made by Collins et al.[9] The first structurally characterized complex of this type was reported by Bennett.[10] Other more complicated coordination modes of CO_2 are also known in which more than two metal centers are available for bonding to CO_2. One example is

Table 1.1. Summary of CO_2 – Metal complexes prepared by direct reaction with CO_2.

Compound	$\nu_{c=o}$(cm^{-1})	δCO_2 (ppm)	Ref
η^1 -complexes			
$Ir(diars)_2(Cl)(CO_2)$	1550	n.a.	[5a]
$Ir(dmpe)_2(Cl)(CO_2)$	1550	n.a.	[5a]
$Rh(diars)_2(Cl)(CO_2)$	1610	n.a.	[5b]
$(({}^{ad}ArO)_3tacn)U^{IV}(\eta^1\text{-}OCO)$	2187	n.a.	[8]
η^2 -complexes			
$Ni(PCy_3)_2(CO_2)$	1740	159.28	[6, 11]
$Ni(PR_3)(CO_2)$, R = *n*-Bu, Et	1660, 1635	n.a.	[12]
$Rh(P(n\text{-}Bu)_3)_2(Cl)(CO_2)$	1668, 1630	n.a.	[13]
$Fe(PMe_3)_4(CO_2)$	1620	n.a.	[14]
$Fe(depe)_2(CO_2)$	1630	n.a.	[15]
$Pd(PMePh_2)_2(CO_2)$	1658, 1634	166.2	[16]
$(Cp')_2Nb(CH_2SiMe_3)(CO_2)$, Cp' = $\eta\text{-}C_5H_4Me$	1695	200.5	[7]
$(Cp')_2Nb(R)(CO_2)$, R = CH_2CMe_3, CH_2Ph, CH_3	1698-1738	200.6	[17]
$(Cp)_2Mo(CO_2)$	1705	n.a.	[18]
$(Cp)_2Ti(PMe_3)(CO_2)$	1673	212.3	[19]
trans-$W(dppe)_{2(}CO)(CO_2)$	1677	n.a.	[20]
trans-$Mo(PMe_3)_4(CO_2)_2$	1670	206.1	[21]
trans-$Mo(PMe_3)_3(CNR)(CO_2)_2$, R = Me, *i*-Pr, *t*-Bu, Cy, CH_2Ph	1660-1680	201-202	[22]
trans-Mo $(PMe_3)_2$(P-P) $(CO_2)_2$, P-P = dmpe, depe, dmpm, dppe	1660-1680	n.a.	[23]
trans-Mo $(P\text{-}P)_2(CO_2)_2$, P-P = dmpe, depe	1650-1660	n.a.	[23]
trans-$Mo(depe)(PMe_3)(CNR)(CO_2)_2$, R = *t*-Bu, Cy	1710, 1680-1690	n.a.	[23]
μ_2-η^2-complexes			
$(PPh_3)_2(Cl)$(*t*-Bupy)Ir(μ-O)$(CO_2)Os(O)_2$(*t*-Bupy)$_2$	1593	187.2	[9]
$(PPh_3)_2$(*t*-BuNC)(*t*-Bupy)Ir(μ-O)$(CO_2)Os(O)_2$(*t*-Bupy)$_2{}^+Cl^-$	1583	207.5	[9]
$[Pt(PEt_3)_2(Ph)]_2(CO_2)$	1495	201.0	[10]
μ_n-η^m-complex			
$[PPN^+HOs_3(CO)_{10}(CO_2)Os_6(CO)_{17}^-]$	n.a.	n.a.	[24]
Other η^2 -complex			
$Ir(Cl)(PMe_3)_3(C_2O_4)$	1725, 1680	n.a.	[25]

the osmium cluster [$PPN^{+}HOs_3(CO)_{10}(CO_2)Os_6(CO)_{17}^{-}$] prepared by Lewis et al.[24] In the case where two or more CO_2 molecules are bound to the same metal center, only a few of such complexes have been prepared. An example is the iridium complex [$Ir(Cl)(PMe_3)_3(C_2O_4)$] synthesized by Herskovitz et al.[25]

Infrared-red (IR) and nuclear magnetic resonance (NMR) spectroscopic techniques are commonly used as diagnostic tools for the state of the CO_2 molecule and/or for quantitative determination. Although the *C=O* symmetric stretching is IR inactive, the asymmetric stretch of free CO_2 is at ν_{asym} 2349 cm^{-1}.[26] The IR asymmetrical stretching vibration for coordinated CO_2 is summarized in Table 1.1. The utilization of labeled $^{13}CO_2$ and $C^{18}O_2$ in NMR spectroscopy aids in determining the bonding mode of CO_2 in metal-CO_2 species. In ^{13}C-NMR spectrum of CO_2, CO_2 dissolved in non-polar solvents (e.g. benzene) shows a resonance at 126 ppm. CO_2-complexes such as metallocarboxylates exhibit low-field resonances for the carbonyl carbon in ^{13}C NMR. The ^{13}C chemical shifts of the CO_2 ligand for some η^1 and η^2-CO_2 metal complexes are shown in Table 1.1.

1.2 Transformation of CO_2 into organic products

The coordination chemistry of carbon dioxide and its relevance for catalysis is very important in the conversion of CO_2 into useful organic products, and the most significant reaction is the oxidative coupling of CO_2 and a substrate (e.g. oxygen, aldehydes, amines, imines, alkenes, dienes) at transition metal centers. The

combination of CO_2 and a substrate (RX) to form the product RCO_2X at a transition metal center can occur through three possible routes (Figure 1.2).[1h]

(1) Coordination of CO_2 to the metal center to form a metal-CO_2 complex **I**, followed by reaction of the metal-CO_2 complex with substrate to form **III**, subsequently a reductive elimination releases RCO_2X and reforms the starting metal complex

(2) Simultaneous coordination of CO_2 and substrate at the metal center to form **III**, followed by a reductive elimination to release RCO_2X and reform the starting metal complex.

(3) Coordination of substrate to the metal center to form a metal-substrate complex **II**, followed by reaction of the metal-substrate complex with CO_2 to form **III**, and a reductive elimination releases RCO_2X and reforms the starting metal complex.

These three routes of coordination show that the binding of CO_2 molecule and substrate molecule at the same transition-metal center is a crucial step in designing both stoichiometric and catalytic transformations of CO_2 into useful organic products.

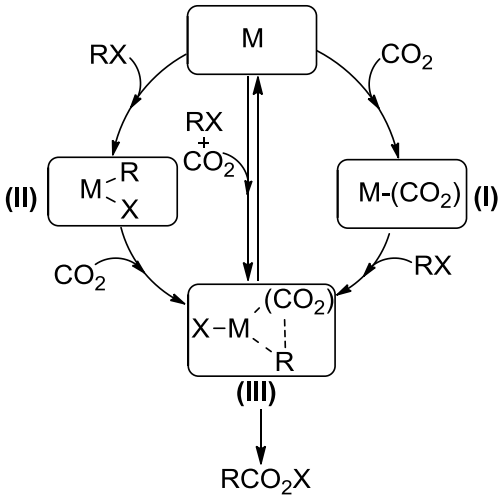


Figure 1.2. Three possible routes in the reaction of CO_2 with substrate (RX) at transition metal center (M).

1.2.1 Reaction of metal-CO_2 complexes

There are numerous reports on the reactivity of metal-CO_2 complexes (Figure 1.2, I), of which the most common reactions are (1) insertion of a second CO_2 into the M-CO_2 bond to form CO and CO_3^{-}[27] and (2) electrophilic attack on the oxygen atom of η^1- and η^2-CO_2 metal complexes to form hydroxycarbonyl or carbonyl species.[15, 28] Much of the research on CO_2 reactions are channeled towards the formal insertion of CO_2 into M-X (X = C, H, N, O, P, Si) bonds to form new C-X bond and new organic products.

1.2.2 Insertion of CO_2 into metal-element bonds

The formal insertion of CO_2 into M-C, M-H, M-O and M-N bonds has been widely described in literature. Figure 1.3 shows some of the possible CO_2- adducts obtained from these insertion reactions.

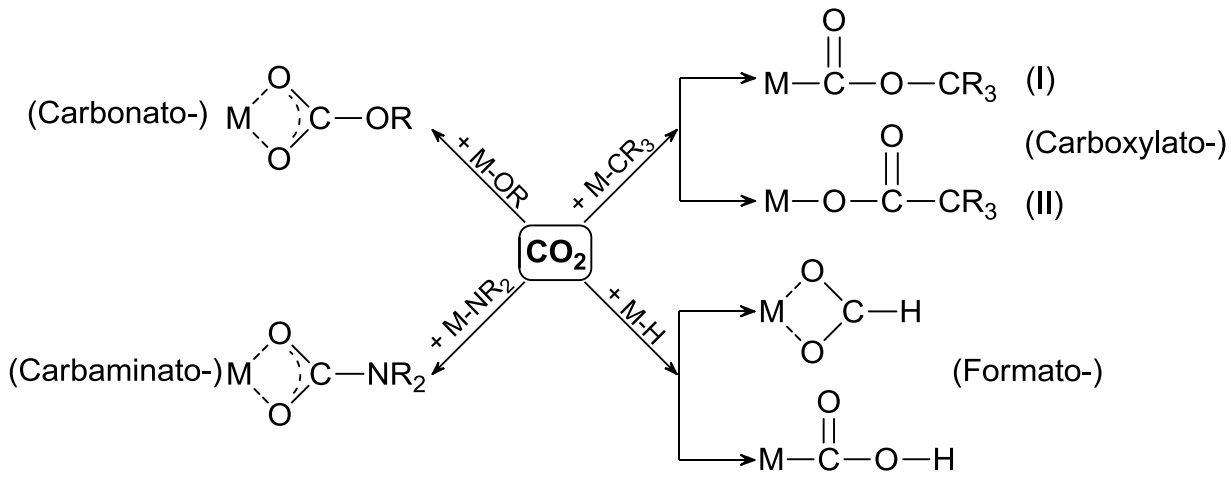


Figure 1.3. CO_2 insertion into M-X bonds (X = C, H, O, N) to form carboxylato, formato, carbonato and carbaminato complexes.

1.2.2.1 Insertion of CO_2 into the M – H bond

The insertion of CO_2 to M-H bond either through η^1 or η^2 coordination mode leads to metal-formato complexes or O-bonded formates. Some examples of CO_2 insertion into metal-hydrido complexes of cobalt,[29] rhodium[30] and platinum[31] are shown in Table 1.2. CO_2 can also insert into η^2-dihydrogen metal complexes such as Rh-η^2-(H_2) complexes[32] to form hydrio-formate complexes. The insertion of CO_2 into M-H bond is however not limited to the formation of formato complexes. For instance, $Zr(Cp)_2ClH$ reacts with CO_2 to form $(Zr(Cp)_2Cl)_2O$ and formaldehyde (CH_2O).[33]

1.2.2.2 Insertion of CO_2 into the M – O bond

Transition metal alkoxides complexes (M-OR) can undergo CO_2 insertion into the M-O bond to form carbonato complexes (R = alkyl, aryl) or hydrogen carbonato complexes (R = H). Some examples of carbonato complexes for zirconium,[34] vanadium,[35] molybdenum[36] and tungsten[37] are shown in Table 1.2. Hydrogen carbonato complexes for rhodium[38],[39] and iridium[38] can also be prepared. Dimeric carbonato complexes of platinum with CO_2 bridged-ligand have also been synthesized.[40]. In addition, CO_2 can also insert into di-oxygen complexes of Pt[41] and Rh[42] to form peroxocarbonates such as $[(PPh_3)_2Pt(OCO_3)]$, which then converts to the carbonato complex $[(PPh_3)_2Pt(CO_3)]$ and phosphine oxide with excess phosphine.

1.2.2.3 Insertion of CO_2 into the M – N bond

The insertion of CO_2 into M-N bonds of early (e.g. Ti, Zr, V)[43] and late transition metals (e.g. Ru,[44] Pd,[45] Cu[46]) have been investigated. Mechanistic studies show a nucleophilic attack of CO_2 on nitrogen of the amide moiety as a key step in the insertion of CO_2 into M-N bonds, postulating that the amine first reacts with CO_2 to form a carbamic acid (HO_2CNRR'), which then reacts with the metal-amide to form a metal-carbaminato complex.[44-45, 47] On the other hand, a direct nucleophilic attack by CO_2 on the nitrogen of the amine-bounded metal to form C-N bond is also reported. An example is the insertion of CO_2 into Pt-N bond of platinum amide complex, which subsequently undergoes re-arrangement to form an oxygen bonded platinum carbamate.[48]

1.2.2.4 Insertion of CO_2 into the M – C bond

From the point of view of “atom efficiency”, the formation of new C-C bonds between the reactions of CO_2 with saturated/unsaturated hydrocarbons to form organic products with COO moiety is an application of “green chemistry”. There are two major modes of CO_2 insertion: (I) normal insertion to form a carboxylate complex and (II) inverse insertion to form an alkoxycarbonyl complex (Figure 1.3). The insertion of CO_2 into metal-alkyl/aryl/cycloalkyl bonds, metal-allyl bonds, metal-alkyne bonds and metal-olefin bonds have been extensively investigated, because of the keen interests in the areas of C-C bond formations.

1.2.2.4.1 Insertion of CO_2 into metal-alkyl/aryl/cycloalkyl bonds

The insertion of CO_2 into diphenyltitanocene forms a five-membered cyclic carboxylate which can then be isolated as methyl benzoate after esterification with methanol/BF_3; a second insertion of CO_2 leads to the formation of dimethyl phathalate after a similar esterification reaction work-up.[49] Phenylnickel complexes can also undergo CO_2 insertion to form nickel benzoate complexes, which are then esterified with methanol/BF_3 to release methyl benzoate.[50] Apart from CO_2 insertion, these phenylnickel complexes can also undergo ethylene insertion to form (2-phenylethyl)nickel complexes.[50] In addition, Behr et al. also reported a tandem insertion (CO_2 and C_2H_4) into Ni-C bond using phenylnickel complexes, which hydrolyzes (methanol/BF_3) to form methyl phenyl propionate.[50] On the other hand, metallacycloalkanes (e.g. nickelalacyclobutane[51], manganaphosphacyclobutane[52]) undergo CO_2 insertion to form 6-membered metal-carboxylato rings. The insertion of CO_2 into anionic complexes of tungsten to form stable 7-membered rings was also reported by Darensbourg et. al.[53]

1.2.2.4.2 Reactions of CO_2 with unsaturated hydrocarbons at metal centers

The oxidative coupling of CO_2 with unsaturated hydrocarbons (e.g. olefins, alkynes) mediated by metal catalysts such as Ti, Zr, Mo, W, Fe, Rh, Ni and Pd complexes at low temperature homogeneous reactions to produce lactones, carboxylic acids, and acrylate derivatives have been extensively studied.[2, 54]

1.2.2.4.2.1 Insertion of CO_2 into metal-allyl bonds

The insertion of CO_2 into η^3-allyl complexes of Ti, Ni, and Pd have been extensively investigated. Sato et al. reported that a (η^3-butadiene)titanium complex reacts with CO_2 to form a crotonato Ti-complex, which was then hydrolyzed by HCl to form 2-methyl-3-butenoic acid and reforms the starting $TiCp_2Cl_2$ complex.[55] The reactions of other similar (η^3-allyl)Ti complexes with CO_2 to give insertion products were also published by Klei et. al.[56] Bis(η^3-allyl)nickel complexes also react with CO_2 to form η^3-allyl(vinylacetato)nickel to release δ-butyrolactone and δ-crotonolactone upon heat treatment at 140 °C.[57] Jolly et al. isloated a similar CO_2-coordinated bis(η^3-methylally)nickel complex [$(PCy_3)Ni(\eta^3\text{-}C_4H_7)(O_2CC_4H_7)$].[58] Later, Hoberg et al. synthesized five-membered nickelalactone complexes from the oxidative coupling of dienes (allene, 3-methyl-allene, 3-methyl-1,2-butadiene) and CO_2 on Ni^0 center.[59] These nickelalactones were either esterified or hydrolyzed to form acids, esters and lactones.[59] Similarly, butadiene and CO_2 oxidative coupling reactions were also performed with Pd^0 catalysts.[60]

1.2.2.4.2.2 Insertion of CO_2 into metal-alkyne bonds

The carboxylation reactions of CO_2 with alkynes and electro donating ligands (e.g. amines, phosphines) to produce pyrones (double insertion of alkyne) on Ni^0 was first developed by the groups of Inoue[61], Hoberg[62] and Walther[63]. Figure 1.4 shows the mechanism of pyrone formation from hexyne and CO_2 on Ni centers.[63]

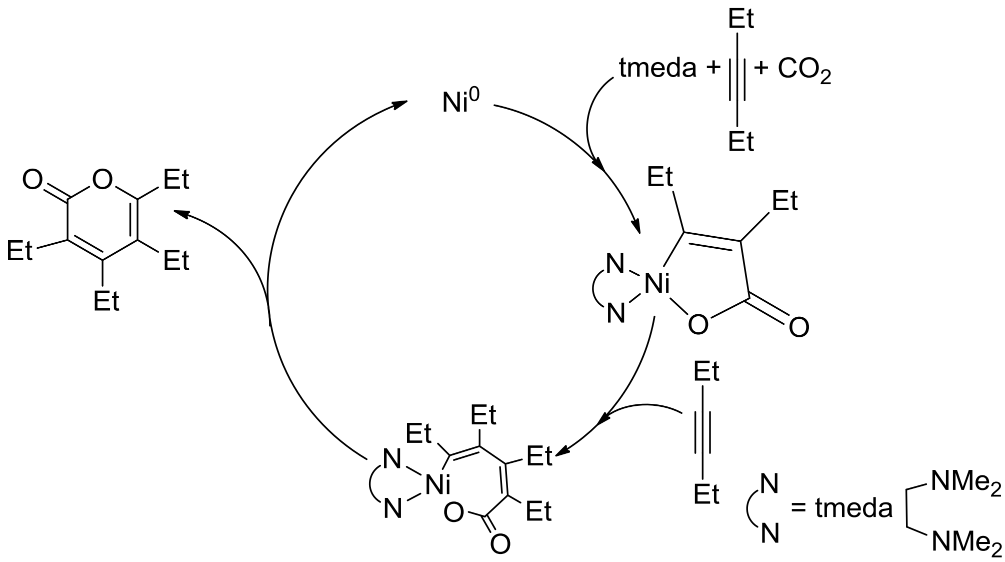


Figure 1.4. Catalytic cycle of pyrone synthesis from 3-hexyne and CO_2 with Ni catalysts.

The mechanism of oxidative coupling reaction of acetylene and CO_2 on nickel centers was investigated with computation studies by Buntine et al.[64], and they published that CO_2 inserts into the η^2-alkyne-Ni complex to form an unsaturated nickelacycle (both α- and β-substitution are possible when asymmetric alkynes precursors are used, in this case, the β-substitution is shown) which then release α, β-unsaturated acids by reductive elimination (Figure 1.5).

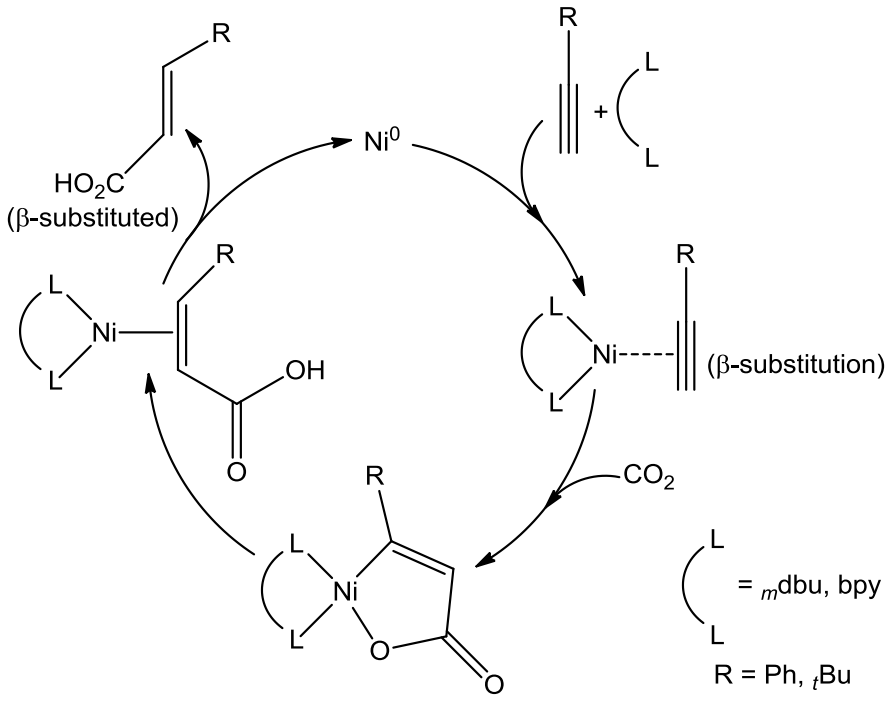


Figure 1.5. Reaction mechanism for the nickel-catalyzed oxidative coupling reaction of alkyne and CO_2 (Buntine et al.).

Five-membered titanacycles[65] and zirconacycles[66] and can also be synthesized from complexes of Zr- and Ti-alkyne with CO_2.

1.2.2.4.2.3 Insertion of CO_2 into metal-olefin bonds

It is well known that late transition metal complexes (e.g. electron-rich d^{8-10} metals such as Fe^0, Rh^I, Ni^0, Pd^0, Pt^0, and Ni^0) mediate CO_2 coupling with olefins because they are very basic and CO_2 ligands can easily be activated by back-bonding to the metal center.[4] However, there are also many examples where early transition metals can also aid in CO_2 insertion into metal-olefin bonds. For instance, CO_2 reacts with bis(ethylene)molybdenum complexes $[Mo(C_2H_4)_2(PR_3)_4]$ to form a bi-nuclear molybdenum complexes with two bridged acrylic acid ligands.[67] Upon hydrogenation with hydrogen, a hydrido-propionate molybdenum complex is formed,

which releases lithium propionate and reforms the starting complex when n-butyllithium and ethylene was added (Figure 1.6).[67b] Similarly, $[W(C_2H_4)(depe)(PMe_3)_2]$ also forms W-hydride-acrylate complexes with CO_2.[67a] Other examples such as $[(\eta^5\text{-}Cp^*)_2Ti(\eta\text{-}C_2H_4)]$[65b], $[(Cp^*)Ta(\eta^4\text{-}C_4H_6)(\eta^2\text{-}C_6H_4)]$[68] and $[Rh(bpy)(\eta\text{-}C_2H_4)Cl]$[69] are also known to undergo CO_2 insertion into the metal-olefin bond to form five-membered metallacycle complexes. Double insertion of CO_2 into metal complexes was also feasible. Hoberg et al.[70] reported that iron complex $[Fe(PEt_3)_2(C_2H_4)_2]$ forms a five-membered Fe-carboxylate complex which can undergo a second insertion of CO_2 to form dicarboxylic acids (isolated as dicarboxylates) when hydrolyzed with methanol/HCl.

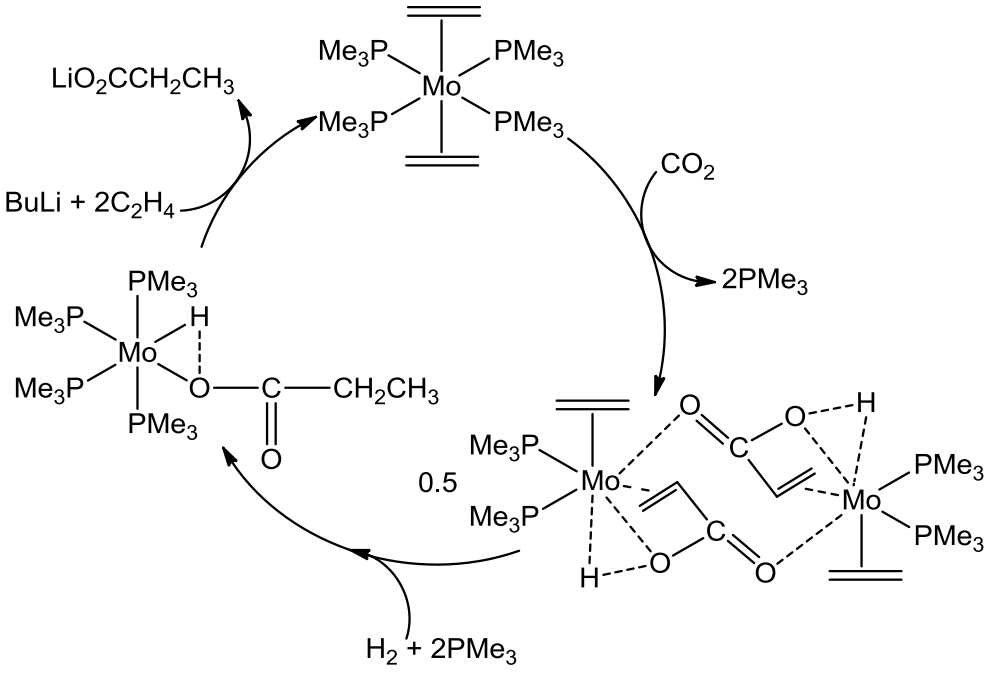


Figure 1.6. Insertion of CO_2 into Mo-ethylene bond to form acrylates.

1.2.2.4.2.3.1 Insertion of CO_2 into Nickel-olefin bond

The first isolation of the side-on η^2-(CO_2) nickel complex [Ni(dcpe)(CO_2)] by Aresta et al.[12] sparked great interest towards the activation of nickel – coordinated CO_2 ligands and its activities towards olefins and alkynes addition to transform into useful organic products, as illustrated by the groups of Hoberg, Inoue and Walther.[4] Oxidative coupling of CO_2 and other olefins such as ethylene[71], styrene,[72] allenes,[59] 1,3-butadiene,[73] norbornene[74] and dicyclopentadiene[75] on Ni^0 centers to form cyclic nickelalactone systems have also been studied by the groups of Hoberg and Walter.

Typically, Ni^0 starting complexes (e.g. $[Ni(cod)_2]$[76], [Ni(cdt)][77]) first undergo ligand exchange with bulky σ-donating ligands (e.g. bpy, dcpe, dbu) to form highly nucleophilic 14-electron Ni^0 species in-*situ* which behaves as strong nucleophiles that binds to olefins (e.g. ethylene). In the second step, CO_2 inserts into the M-η^2-olefin bond to form a metallacycle (nickelalactone). This reaction is reversible and a treatment of the nickelalactone with a different olefin results in ligand substitution to form new nickelalactones. Acid hydrolysis of nickelalactones leads to ligand protonation to form carboxylic acids, together with ligand dissociation and decomposition of the nickel complex (Figure 1.7).

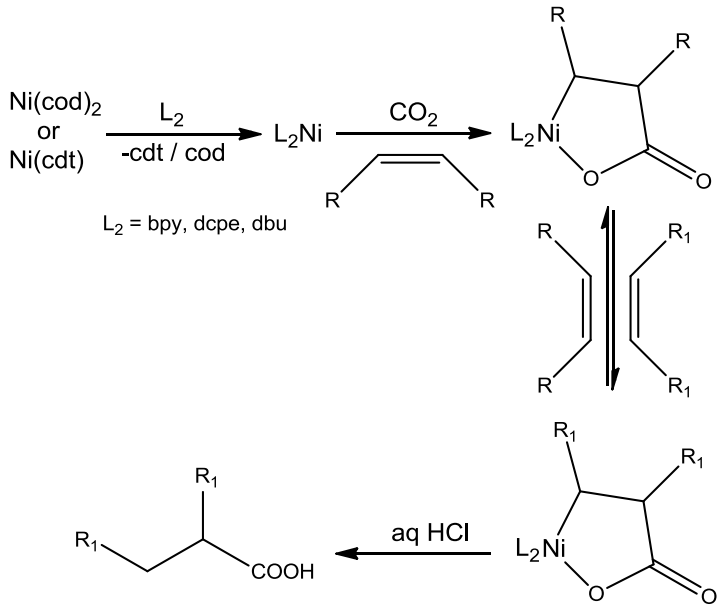


Figure 1.7. Synthesis of nickelalactones and protonation into carboxylic acids.

However, according to Bernskoetter and Tyler, the oxidative coupling reaction of CO_2 and olefin on the metal center can also be a concerted reaction, where both the CO_2 and ethylene are π-bounded to the molybdenum center prior to conversion into acrylates (Figure 1.8, I).[78] To date, all reports on the oxidative coupling of CO_2 and olefin at nickel centers remain non-catalytic and leads to either the formation of carboxylic acid (from acid hydrolysis) or methyl carboxylate esters (from methanolysis with methanol/HCl).

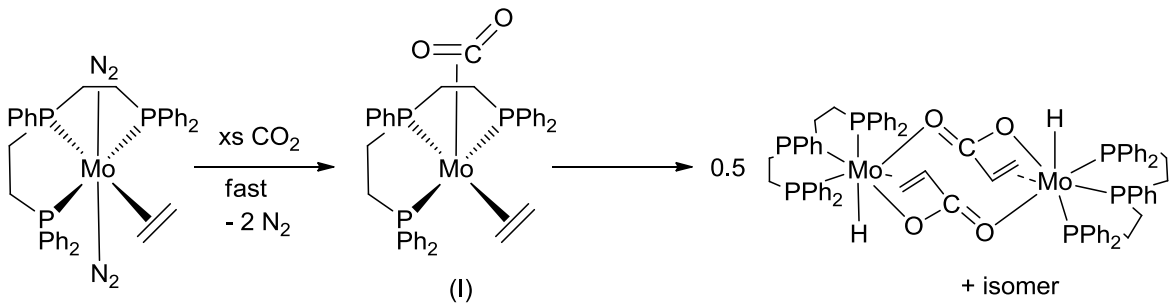


Figure 1.8. Oxidative coupling of ethylene and CO_2 to form Mo(II) acrylate hydride complex.

Table 1.2. Summary of insertion of CO_2 into M-X bonds (X = H, O, N, C).

Compound	$\nu_{C=O}$(cm^{-1})	δCO(ppm)	Ref
Metal-formato complexes			
$Co(HCOO)(PPh_3)_3$	1620	n.a.	[29]
$[Rh_2(\mu\text{-}O_2CH)(CO)_2(dppm)_2]^+PF_6^-$	1548	n.a.	[30]
trans-$Pt(H)(O_2CH)(PCy_3)_2$	1620	n.a.	[31]
$Rh(HC(CH_2CH_2P(tBu)_2))(O_2CH)$	1581	170.74	[32]
Metal-carbonato complexes			
$Zr(O\text{-}nBu)_3(OCO_2\text{-}nBu)$	1600	n.a.	[34]
$V(O\text{-}tBu)_2(OCO_2\text{-}tBu)$	1600	n.a.	[35]
$Mo_2(OR)_4(\mu\text{-}O_2COR)_2$, R = iPr, tBu, Me_3C, Me_2CH, Me_3CCH_2, Me_3Si	1540-1562	173-174	[36]
$W(O\text{-}tBu)_4(O_2CO\text{-}tBu)_2$	n.a.	n.a.	[37]
$Rh(PPh_3)_2(CO)(OCO_2H)$	1655	n.a.	[38]
$Ir(PPh_3)_2(CO)(OCO_2H)$	1655	n.a.	[38]
$Rh(H)_2(PR_3)_2(O_2COH)$, R = iPr, tBu, Cy	1583-1587	n.a.	[39]
$Pt_2(PPh_3)_4(Ph)_2(\mu\text{-}CO_3)$	1625	n.a.	[40]
$Pt(PPh_3)_2(OCO_3)$	1678	n.a.	[41]
$Rh(S_2CNMe_2)(PPh_3)_2(OCO_3)$	1665	n.a.	[42]
Metal-carbaminato complexes			
$M(O_2CNMe_2)$, M= Ti, Zr, V	1560 - 1685	n.a.	[43]
$[Ru(PMe_2Ph)_4(O_2CNMe_2)]^+[PF_6]^-$	1565	n.a.	[44]
$Pd(L)_2Me(O_2CNRR')$, L = PEt_3, $PMeEt_2$, PPh_3, R = H, Et, R' = H, Et, $_n$Bu, Ph, CH_2Ph	1263 - 1635	n.a.	[45]
$Cu(PPh_3)_2(O_2CNHPh)$	1600, 1580	n.a.	[46b]
trans-$Pt(Ph)(PCy_3)_2(NHCO_2H)$	1602	162.5	[48]
Metal-carboxylato complexes			
$(Cp)_2Ti(O2CC_6H_4CO_2)$	1620, 1660	n.a.	[49]
$L_nNi(C_6H_5COO)$, L_n = Ref.[50]	n.a.	n.a.	[50]
$Mn(CO)_4(PPh_2C_2H_4COO)$	1591	223	[52]
$[W(CO)_4(PPh_2C_3H_6COO)]^-[PPh_4]^+$	1612.4	n.a.	[53]
$Ti(Cp)_2(O_2CC_4H_6)$	n.a.	n.a.	[55]
$Ni(PCy_3)(\eta^3\text{-}C_4H_7)(O_2CC_4H_7)$	1610	175.09	[58]
$Ni(dcpe)(O_2CC(CH_2)CH_2)$	1645	n.a.	[59]
$(Cp^*)_2Ti(O_2CC_2H_4)$	1653	171.5	[65b]
$[Mo(PMe_3)_2(C_2H_4)(CH_2CHCO_2H)]_2$	1500	175-180	[67b]
$[Mo(H)(PMe_2Ph)_2(C_2H_4)(OOCCH{=}CH_2)]_2$	1540	n.a.	[67a]
$W(H)(PMe_3)(depe)(OOCCH{=}CH_2)$	1630	179.9	[67a]
$Ta(Cp^*)(\eta^4\text{-}C_4H_6)(O_2CC_6H_4)$	1670	176.2	[68]
$Rh(bpy)(Cl)(O_2CC_2H_4)$	1650	174.01	[69]
$Fe(PMe_3)_2(O_2CC_2H_4)$	1580	n.a.	[70]

1.3 Synthesis of acrylic acid and its derivatives

Acrylic acid is an important bulk chemical for the synthesis of polyacrylates and superabsorbants, therefore, the oxidative coupling of ethylene and CO_2 to form high-demand acrylic acid is an excellent example of tapping on the cheap and abundant C1 feedstock CO_2 to produce value-added industrially important products. The current industrially production of acrylic acid (3 million tons / year) is based on the SOHIO process by the oxidation of acrolein over molybdenum / bismuth mixed oxides catalysts at 300 - 400 °C.[79] The need for high operating temperatures and multiple distillations to remove aldehyde impurities render it necessary to develop a cost-effective and energy-saving method to synthesize acrylic acid, and this makes the synthesis of acrylic acid from cheap CO_2 and ethylene very attractive. In addition, the direct synthesis of acrylates from CO_2 and alkenes is also very economically attractive.

Around 30 years ago, Hoberg et al. postulated: Ni^0 mediated oxidative coupling of ethylene and CO_2 form nickelalactones, which can eliminate the carboxylate moiety from the nickel center by β-hydride elimination reaction to form a nickel acrylate complex which then releases acrylic acid and regenerates the nickel complex to repeat the catalytic cycle (Figure 1.9).[71, 74] However, most of the nickelalactones formed are stable and the cleavage of either the Ni-C or Ni-O bond by acid hydrolysis to release acrylic acid decompose the nickel complex and render it catalytically inactive. The β-hydride elimination reaction is believed to be unfavored due to steric factors: the five-membered ring of the nickelalactone is flat and rigid, therefore it does not allow the β-hydrogen to come close to the nickel center for an agnostic interaction to form an acrylate.[4, 80]

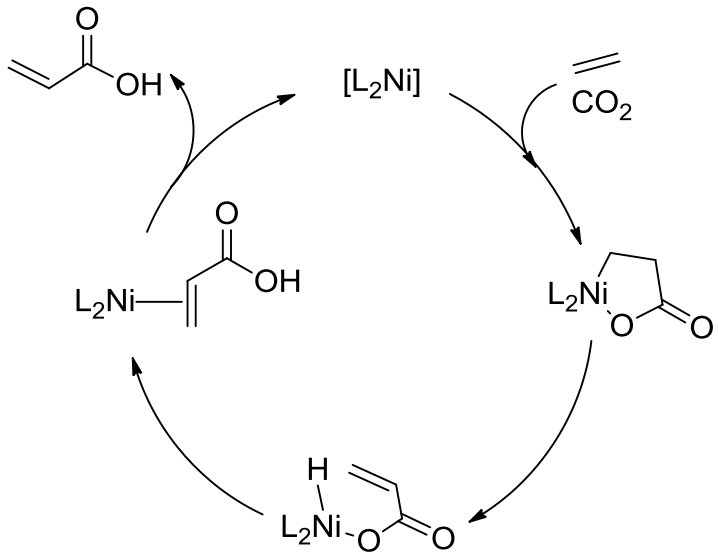


Figure 1.9. Proposed catalytic cycle of acrylic acid synthesis from ethylene and CO_2 with Ni catalysts (Hoberg et al.).

1.3.1 Theoretical studies on the synthesis of acrylic acid

Computational chemistry carried out to elucidate the mechanism of metal-assisted catalytic synthesis of acrylic acid have been based mainly on molybdenum[80] and nickel[54, 81] mediated catalytic systems. Pápai et al.[81a] found that that the C-C bond formation occurs in a single elementary step from the reaction of NiL_2-ethylene complex with a CO_2 molecule. Additionally, the square-planar nickelalactone is found at the lowest potential energy surface, and the C_2H_4-CO_2 coupling has a higher barrier than the simple dissociation of CO_2 before the reaction can occur, therefore proving that nickelalactone are indeed thermodynamic sinks in this reaction. Later, Buntine et al.[54] studied the full catalytic cycle and they identified the NiL_2-ethylene complex as the catalytic active species (Figure 1.10, I), in which the CO_2 has to be coordinated to the Ni center (or a ligand) at least in a transition

state before reacting with neighboring ligands and finally, the reaction product is released an the catalytic resting state is restored.

In both cases, although the CO_2 activation is relatively easy, nickelalactone is a thermodynamic sink (overall free energy of the whole process is +79 kJ/mol, Buntine et al.[54]), therefore, a catalytic process is not easily achieved. This also means that a although CO_2 can be captured, it is difficult to be transformed into acrylic acid.[54, 81a, 82] In the theoretically study for the ring opening of nickelalactones with electrophilic methyl iodide to form methyl acrylate, DFT results predict that the rate determining step of the β-hydride elimination reaction is the concerted attack of CH_3I on the Ni-O bond.[83]

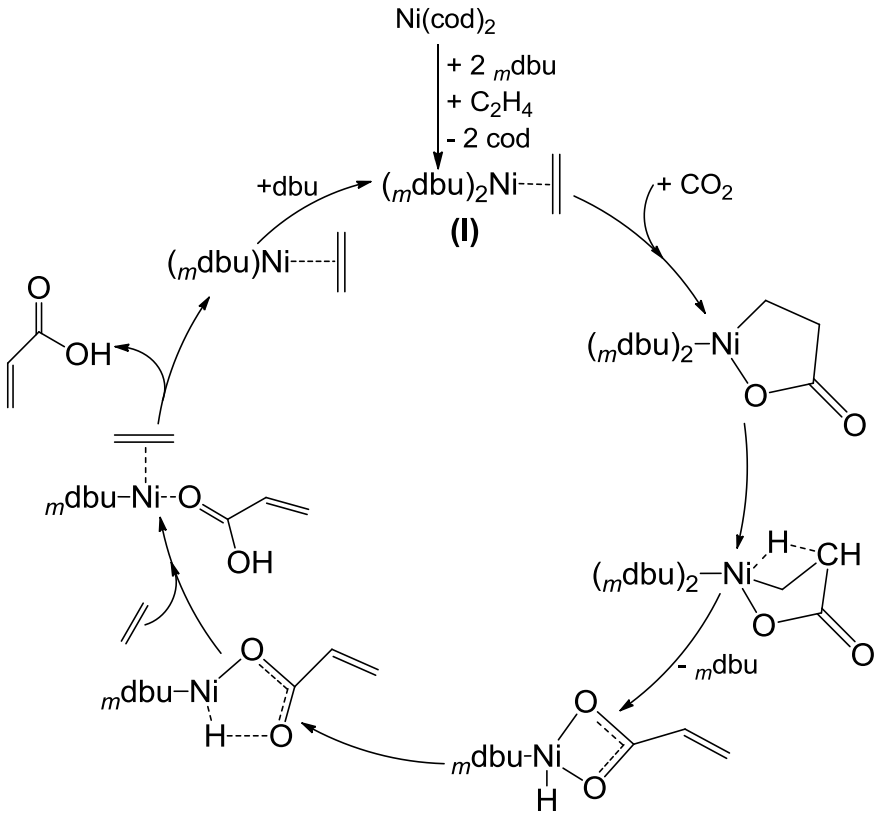


Figure 1.10. Reaction mechanism for the nickel-catalyzed oxidative coupling reaction of ethylene and CO_2 to acrylic acid (Buntine et al.).

2. Motivation and Objectives

Carbon dioxide is an ideal C_1-synthon for organic synthesis, and the development of organometallic catalysts to activate the relatively thermodynamically stable CO_2, with the resultant formation of new C-C bonds, is a challenge for both the academia and industry.

The main objective of this work was the catalytic synthesis of acrylic acid derivatives from the oxidative coupling of CO_2 with ethylene using nickel complexes at mild operating conditions. This work was focused on firstly, a synthetic protocol for the catalytic synthesis of acrylic acid and its acrylate derivatives from CO_2 and ethylene with nickel complexes, and secondly, an optimization of the conditions for the ring- opening and β-hydride elimination reaction of pre-formed nickelalactones to release the acrylate moiety as methyl acrylate. Theoretical studies were also performed to better under the reaction mechanisms of the β-hydride elimination reaction and the catalytic synthesis of acrylic acid derivatives.

3. Results and Discussion

3.1 Synthesis of acrylic acid through Ni^0 mediated oxidative coupling of CO_2 and ethylene

3.1.1 Abstract

C-C bond formation from the oxidative coupling of CO_2 and ethylene to form acrylic acid (isolated as methyl acrylate) was carried out with nickel catalysts. The formation of nickelalactones was successful with dtbpe ligand, however, the yield of dtbpe-nickelalactone was low (5.4 %), with little success to reduce the Ni^{II} hydride complex (after β-hydride elimination of methyl acrylate with methyl iodide and methyl triflate) into the active Ni^0 starting complex to close the catalytic cycle.

3.1.2 Introduction

The reaction of carbon dioxide with η^2- unsaturated hydrocarbons (e.g. olefins, alkynes) and η^3- allyls (e.g. butadiene) on nickel center is well studied.[71, 72b, 74, 84] Particularly, the reaction of CO_2 with ethylene is highly attractive, because the synthesis of acrylic acid (bulk chemical commodity) is highly relevant in the chemical industries. The groups of Hoberg[62, 71, 74] and Walther[75] have been studying the feasibility of this catalytic reaction for the past thirty years. In 2000s, DFT calculations on the mechanistic studies of the formation of lactone and acrylic acid formation were carried out by the groups of Pápai[80-81] and Buntine[54] independently. Figure 3.1a shows the full catalytic cycle of the synthesis of acrylic acid from CO_2

and ethylene mediated by nickel catalysts. Under thermodynamic conditions, the overall ΔG for the synthesis of acrylic acid is + 42.7 kJ mol^{-1}.[54]

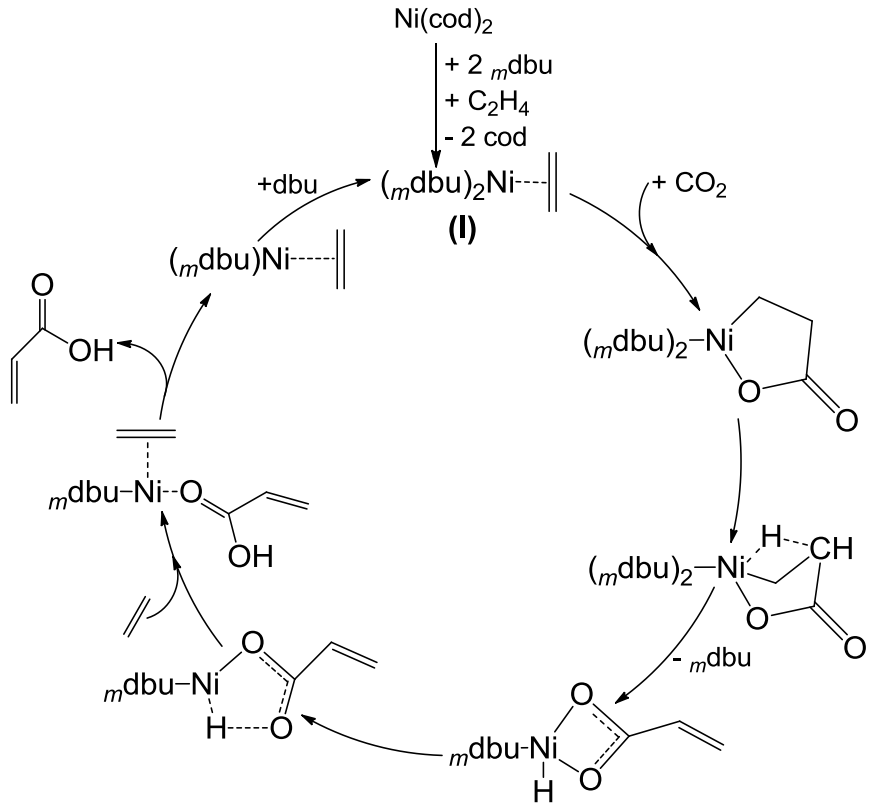


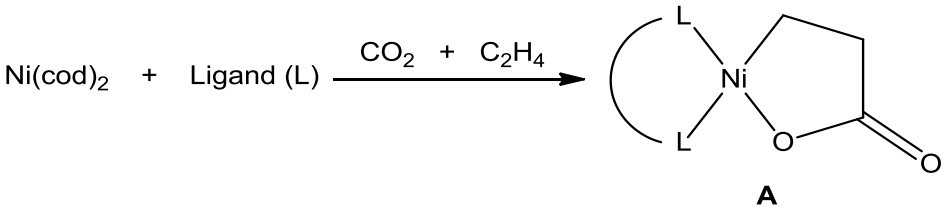
Figure 3.1a. Hypothetic catalytic cycle for the oxidative coupling reaction of CO_2 and ethylene to acrylic acid (Buntine et al.).[54]

In order to develop a basic understanding of the relevance of ligands on the synthesis of nickelalactones, as well as to investigate the possibility for the release of acrylate moiety from the Ni center and the regeneration of Ni^0 complex for a catalytic synthesis of acrylic acid to approach the final goal of using CO_2 as starting molecule for organic synthesis.

3.1.3 Results and discussion

The synthesis of nickelalactones from the oxidative coupling of carbon dioxide and ethylene with Ni^0 were conducted in 100 mL high-pressure stainless steel autoclaves. The influence of the ligand in the oxidative coupling reaction at mild working conditions was studied and the outcomes are presented in Table 3.1a. Despite several attempts, the synthesis of nickelalactone from CO_2 and ethylene was largely unsuccessful. These outcomes were consistent with reports by Limbach et al.[85] and Nobile et al.[86] that Ni^0 forms stable 14-electron tetra-coordinated complexes with chelating diphosphines. Only phosphines with high steric bulk (e.g. dtbpe, dtbpm) were suitable for the oxidative coupling of from ethylene and CO_2 to form nickelalactones.[85] The yield of nickelalactones was also temperature and pressure dependent, an increase of reaction temperature from 25 °C to 50 °C at higher pressures increases the yield of nickelalactones by eight times (Table 3.1a, entries 9-11).[85]

Table 3.1a. Oxidative coupling of CO_2 and ethylene to form nickelalactones.



A

Entry	Ligand (L)	ρCO_2 (bar)	ρC_2H_4 (bar)	Temp (°C)	Time (h)	Yield (%)	Ref.
1	dbu	10	10	25	24	-	
2	dbu	15	30	40	90	60	[71b]
3	tmeda	6	2	25	24	-	
4	py	6	2	25	48	-	
5	bpy	1	1	25	168	20.5	[71a]
6	dcpe	1	1	25	168	11.2	[71a]
7	dtbpm	6	2	25	19	60 [a]	[85]
8	dtbpe	6	2	50	72	5.4	
9	dtbpe	6	2	50	72	35[a]	[85]
10	dtbpe	5	35	25	6	9	[85]
11	dtbpe	40	20	45	16	73	[85]
12	PPh_3	1	1	25	24	-	

Reaction conditions: 8 mL toluene was added to $Ni(cod)_2$ (0.135 g, 0.0005 mol) into an autoclave and the suspension was stirred at r.t. for 30 min before ligand (L, 0.0005 mol) was added. The autoclave was then pressurized with C_2H_4 at r.t., thereafter with CO_2 at r.t.. The autoclave was then heated to the appropriate temperature. (a) NMR scale experiment.

In addition, one-pot reaction of $Ni(cod)_2$, ethylene, CO_2, dtbpe and methyl triflate was added in a potable autoclave (100 mL) filled with toluene (8 mL), and the reaction was stirred at 50 °C for 72 h. Only $Ni(dtbpe)_2$ was identified as the major species in the reaction mixture, and neither dtbpe-nickelalactone nor methyl acrylate was obtained.

3.1.4 Conclusion

The oxidative coupling of carbon dioxide and CO_2 mediated by $Ni(cod)_2$ to form nickelalactone is difficult because of high thermodynamic and kinetic barriers. Under mild reaction conditions, the yield of dtbpe-nickelalactone was low at 5.4%. Also, one-pot reaction synthesis using methyl triflate as additive to isolate the cyclic lactone as methyl acrylate was unsuccessful.

3.2 Transformation of nickelalactones to methyl acrylate with methyl iodide

3.2.1 Abstract

The CH_3I-mediated ring opening of nickelalactones, which can be formed by oxidative coupling of CO_2 and ethylene at Ni^0 complexes, induces a β-hydride elimination to produce methyl acrylate in yields up to 56 %. This reaction was found to be very sensitive with respect to the ligands coordinated to Ni.

3.2.2 Introduction

Carbon dioxide is, besides natural gas and biomass, the most ubiquitous carbon source. [1] The utilization of the abundant CO_2 is very attractive to chemical industry for the production of value-added products.[2] However, (industrial) conversion of CO_2 is still scarce, particularly when compared to its abundance. So far, transformation with transition metal complexes in solution is often constrained to stoichiometric reactions. To date, there are only few molecular catalysts which enable the utilization of CO_2 in homogeneous phase on a large scale.[5] From an industrial point of view, the synthesis of acrylic acid – which is widely used in polymer chemistry – from ethylene and CO_2 is a particular challenge.

The reaction of ethylene and CO_2 at Ni^0 centers forming nickelalactones is reported by the groups of Hoberg[71a, 74] and Walther[87] in some detail. However, the nickelalactones are quite stable compounds, which do not allow β-hydride elimination to yield acrylic acid according to Figure 3.2a, left, due to the ring strain and the resulting long distance of Ni to β-H atoms, so that transformation to an

acrylate is not possible, since step (2) in Figure 3.2a does not take place via a Ni-C bond scission spontaneously. Experimental findings[67, 87a] and theoretical calculations[54] showed that such a conversion is possible, albeit thermodynamically unfavorable. Buntine et al.[54] performed DFT calculations for nickel-mediated oxidative coupling of CO_2 and ethylene using $_m$dbu as ligand. The calculations suggest an exothermic formation of nickelalactone with an energy sink at the nickelalactone (ΔG = -17.2 kJ mol^{-1} relative to ethylene and CO_2) in step (1), with steps (2)-(4) leading to an overall thermodynamically unfavored (79.2 kJ mol^{-1}) reaction relative to L_2Ni, ethylene and CO_2 (Figure 3.2a, steps (1)-(4)). The crucial step, namely the β-H elimination, involves a transition step which is very high in energy (ΔG = 145.2 (*via* three-center-three-ligand) or 82.8 (*via* five-center-three-ligand) kJ mol^{-1}), due to the strain of the five-membered ring. Buntine et al.[54] also reported that the reaction from lactone to acrylate (Figure 3.2a, steps (2)-(3)) proceed *via* elongation and results in scission of the Ni-O bond before allowing the β-H atom to approach the Ni center to form a nickel-hydrido-acrylate species in which the acrylate is bounded through two oxygen atoms for a β-H elimination to form acrylic acid.

Based on that finding, Rieger et al.[88] synthesized a model complex, [(dppp)Ni(cyclo-($C_2H_4CO_2$)], which was treated with methyl iodide (Figure 3.2a, step (i)), leading to Ni-O bond cleavage. The resulting formation of an alkyl ester ligand leads to β-H elimination (Figure 3.2a, step (ii)), releasing methyl acrylate (Figure 3.2a, step (iii)). However, this reaction is, albeit being the first successful attempt to synthesize acrylates from Ni-lactones, so far not catalytic and the yields are rather low (max. 33 %).

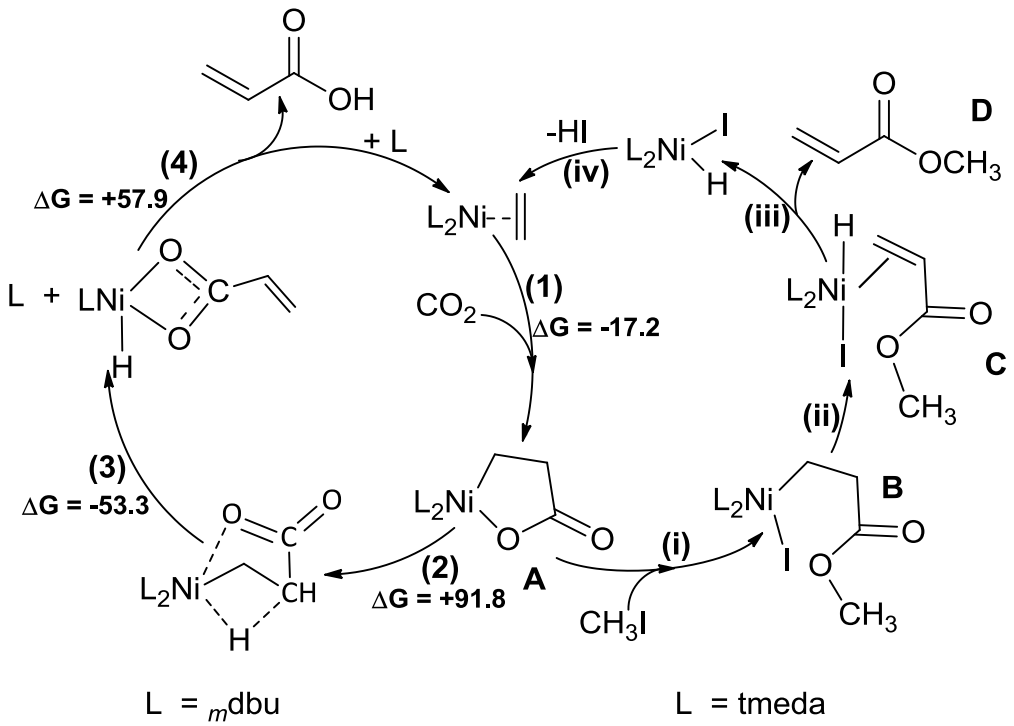


Figure 3.2a. Left: hypothetical cycle of Ni-catalyzed synthesis of acrylic acid from ethylene and CO_2. Right: Synthesis of methyl acrylate via Ni-O bond cleavage of a nickelalactone. Solvent (THF)- corrected Gibbs free energy (ΔG) of the left cycle are given in kJ mol^{-1} and taken from Buntine et al. [54]

This led us to examine the influence of different ligands at Ni and the applied reaction conditions on the methyl acrylate yield. Additionally, we want to present useful insights in the reaction mechanism of this new reaction type.

3.2.3 Results and discussion

In addition to previous investigations,[88] literature-known nickelalactones bearing different ligands, such as tmeda, dppe, dppb and pyridine (Figure 3.2b, Complexes A1-5) were treated with methyl iodide and the methyl acrylate yield was determined by means of advanced in *situ*-IR techniques and ^{1}H NMR spectroscopy ($CHCl_3$ as internal standard).

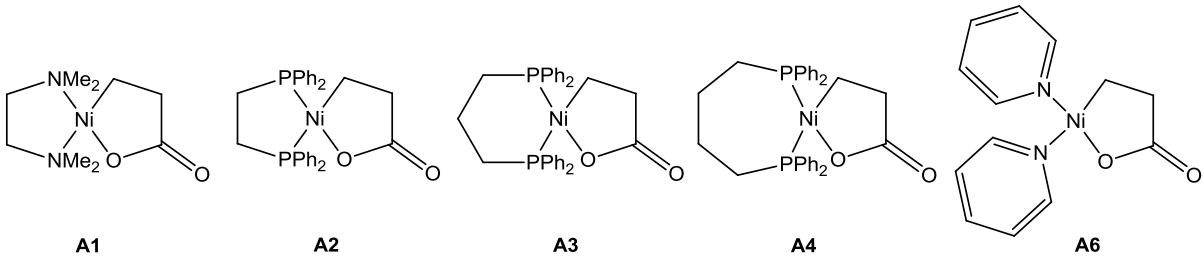


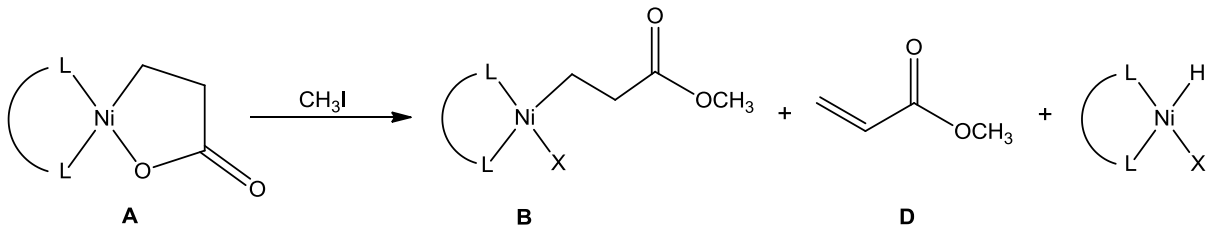
Figure 3.2b. Nickelalactone complexes treated with methyl iodide to form methyl acrylate.

The tmeda-nickelalactone (Figure 3.2b, *A1*) (crystal structure, see appendix 1) was treated with 10 mol. equiv. CH_3I and the yield of methyl acrylate was found to be only 2 % after 3 h (Table 3.2a, entry 1). When the amount of CH_3I was increased to 100 mol. equiv., a maximum yield of 56 % was reached in 3 h. It was noted that the conversion of complex *A1* was quantitative (no NMR and IR signals of complex *A1* was observed after the reaction, vide infra). The by-products, however, could not be unambiguously identified. NMR experiments indicate the formation of methyl 3-iodopropanoate, which might be produced by reductive elimination of the iodide and acrylate ligands of species *B* (Figure 3.2a, *B*) from the Ni center, prior to the β-H elimination reaction.

Subsequently, the reactivity of the nickelalactones *A1-5* (Figure 3.2b) and the following β-H transfer (Figure 3.2a, steps (i)-(iii)) were investigated by ATR-FTIR spectroscopy, and the yields of methyl acrylate were also independently quantified by FTIR. The reaction of *A1* and CH_3I was monitored *via* time-resolved FTIR spectroscopy by a decrease of the typical IR bands of the nickelalactone carbonyl groups ($\nu_{C=O}$) at 1580-1625 cm^{-1} and the simultaneous formation of a new vibration band of methyl acrylate at around 1730 cm^{-1} (Figure 3.2c). The small deviations of the wave numbers of $\nu_{C=O}$ were attributed to minor temperature fluctuations during the experiments.

After addition of 10 mol. equiv. CH_3I to a solution of tmeda-nickelalactone in CH_2Cl_2, methyl acrylate was formed in 21 % yield after 3 h (Table 3.2a, entry 1). When the amount of CH_3I was increased to 100 mol. equiv., the yield reached 40 % in 45 min (Table 3.2a, entry 2) and remained constant with further reaction time (3 h). In comparison, when the ligand was changed to dppe, the yield of methyl acrylate reached 14 % and 37 % in 24 h when 10 and 100 mol. equiv. CH_3I was added respectively. For dppp-nickelalactone *(A3)*, the yield of methyl acrylate was only 29 % after 48 h (Table 3.2a, entry 6). This finding prompted us to investigate the influence of other ancillary ligands (see Figure 3.2b) on the efficiency of the Ni-O bond splitting and β-hydride elimination with different amounts of CH_3I.

Table 3.2a. Yield of methyl acrylate obtained from methylation of nickelalactones with various ligands.



Entry	Complex	Equiv. CH_3I	Time (h)	Yield (%)
1	A1	10	3	21* (2 **)
2	A1	100	3	40* (56 **)
3	A2	10	24	14* (18**)
4	A2	100	24	37* (48**)
5	A3	10	48	14**[88]
6	A3	100	48	29**[88]
7	A4	10	24	0
8	A4	100	24	0
9	A6	10	24	0

*yield determined by ATR-FTIR, **yield determined by ^{1}H NMR.

Reaction conditions: ^{1}H NMR samples: 0.0002 mol of nickelalactone was dissolved in 0.6 mL CD_2Cl_2 and $CHCl_3$ (16 µL, 0.0002 mol) as internal standard. CH_3I (10 or 100 mol. equiv.) was added and the spectrums were recorded at 25 °C.

For a comparison of the nickelalactone complex reactivity in dependence of the ligand, complexes *A2-6* (Figure 3.2b) were examined as well. However, all these complexes show an inferior reactivity to that of complex *A1* (Table 3.2a, entries 3-9). The kinetics of the reaction could most clearly be investigated when the tmeda-nickelalactone *A1* was applied. Figure 3.2c shows the pattern change of the $\nu_{(C=O)}$ bond stretch of nickelalactone *A2* upon addition of 100 equivalent CH_3I in CH_2Cl_2 solution which was monitored by ATR-FTIR.

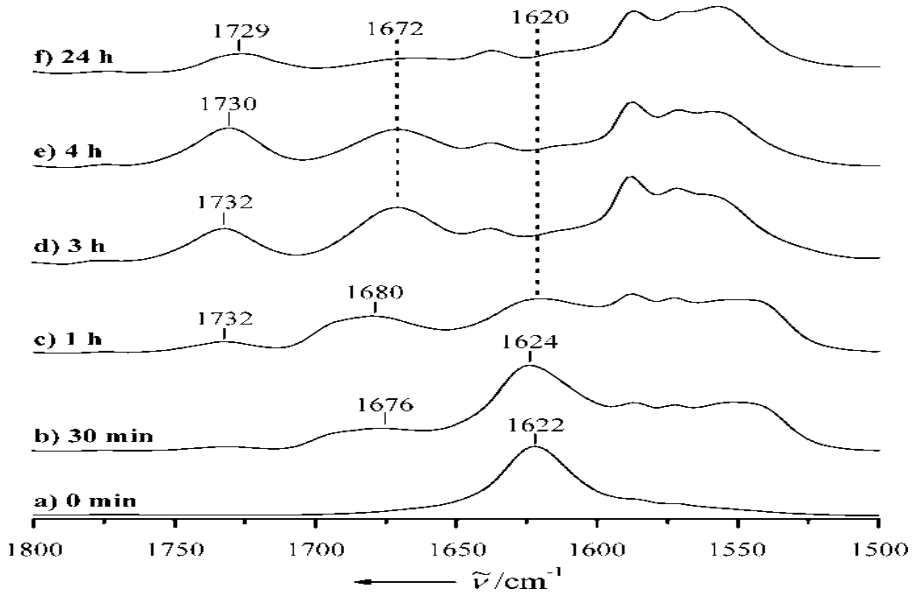


Figure 3.2c. Time-resolved IR spectrums of the reaction of nickel complex *A2* with 100 mol. equiv. CH_3I in CH_2Cl_2.

From time 0 to 30 min, a new band was observed at around 1680 cm^{-1}, which was attributed to the intermediate complex (species *B*, Figure 3.2a), whereby the Ni–O bond dissociates and increases the bond stretching frequency of the carbonyl bond. The calculated wavenumber ($\nu_{(C=O)}$) of the *C=O* stretching bond in species B is 1720 ± 30 cm^{-1}. Similar compounds such as the complex [(PNP)Ni(CH(CH$_3$)C(O)OCH$_3$)] (PNP = [N(o-C$_6$H$_4$PR$_2$)$_2$]$^-$, R=Ph, *i*Pr, Cy)[89] and [Ni(dppe)(CH(C(O)OCH$_3$)CH$_2$C(O)N(C$_6$H$_5$))][90] exhibit *C=O* bands at around 1690-

1700 cm^{-1},[89-90] which lie in the range of the *C=O* band of the proposed species *B*. Literature known parent diphosphine-[91] tmeda-[92] and bipyridine[93] Ni^0 complexes with π-bonded η^2-methyl acrylate (species *C*, Figure 3.2a) show *C=O* bands at slightly lower wavenumbers (1670–1680 cm^{-1}). As the reaction progressed from 30 min to 1 h, the band arising from the *C=O* bond stretching of methyl acrylate was observed, and this band continued to intensify up to 3 h. After 24 h, a mixture of intermediate B (species *B*, Figure 3.2a) and methyl acrylate were found by IR. The low intensities of the bands were attributed to decomposition of the complexes with time. Accordingly, in the ^1H NMR of the reactions of complexes *A1-3*, resonances attributed to a species, which would correspond to intermediate *B* could be found, pointing to an incomplete conversion i.e. β-H elimination. However, a quantification of the amount of this species was not possible due to a superposition of signals. Despite numerous attempts, the intermediate *B* with the tmeda ligand could not be isolated from the reaction mixture. Separation has shown to be very intricate, since the complex is not stable as such, reacting to methyl acrylate as main product. It was also not possible to quantify the amount of methyl acrylate by means of gas chromatography, since the organic product(s) and the organometallic species are very difficult to separate. When nickelalactones *A4* and *A6* (Figure 3.2b) were used, methyl acrylate could not be found by NMR or IR; hence, nickelalactones *A4* and *A6* seemed not to react with methyl iodide to form methyl acrylate. Generally, with the exception of Entry 1, Table 3.2a, the yields obtained by ATR-FT-IR were in accordance with the NMR results.

The different reactivity of the investigated nickelalactones is rather surprising. It appears that ligands with a sp^2-donor atom negatively influence the reaction of the

nickelalactone with methyl iodide, whereas chelating amino- or phosphine ligands are more suitable. On the other hand, nickelalactone with the dppb ligand (Figure 3.2b, *A4*) does not show any reactivity with CH_3I. According to the X-ray single crystal structures of nickelalactones *A1-6*,[87a, 87c] the Ni–O bond lengths are all in a quite narrow range between 1.85 and 1.89 Å. Hence, it appears that the *trans*-effect of the ligand does not seem to play a significant role on the feasibility of the Ni–O bond cleavage. From DFT calculations performed previously,[54] steric bulkiness of the ligand hinders the approach of other molecules towards the Ni center, hence this effect was taken into account in our studies. Nickelalactone *A6* expectedly has the shortest Ni-ligand bond length because of significant π-back bonding from the aromatic pyridine ligands. It has to be noted that despite close similarities of the crystal structures of the nickelalactones bearing diphosphine ligands, there were irregularities in their performance of β-H elimination with CH_3I. We rationalize that the different bridging lengths of the bidentate ligands, which affects the chelating bond angle (P-Ni-P) during the reaction, is the decisive factor for the inactivity of nickelalactone *A4*. Liang et al.[89] have shown that Ni fragments bearing sterically encumbering PNP pincer ligands form stable bonds with alkyl esters, which are inert towards β-H elimination. The pincer ligands prevent the rotation of the alkyl group, i.e. the β-H atoms towards the Ni center. Hence, if the ligand at Ni is too bulky, the Ni-O bond of a nickelalactone may well be cleaved, but the acrylate conversion will still be hindered.

In order to elucidate the reaction mechanism of the reaction of a nickelalactone with methyl iodide and to show the validity of the reaction shown on the right side of Figure 3.1a, we performed DFT calculations on the possible

transition states and the reaction energies. The DFT calculations (B3LYP/6-31+G**) were carried out with our most active nickelalctone *A1* (Figure 3.2d).

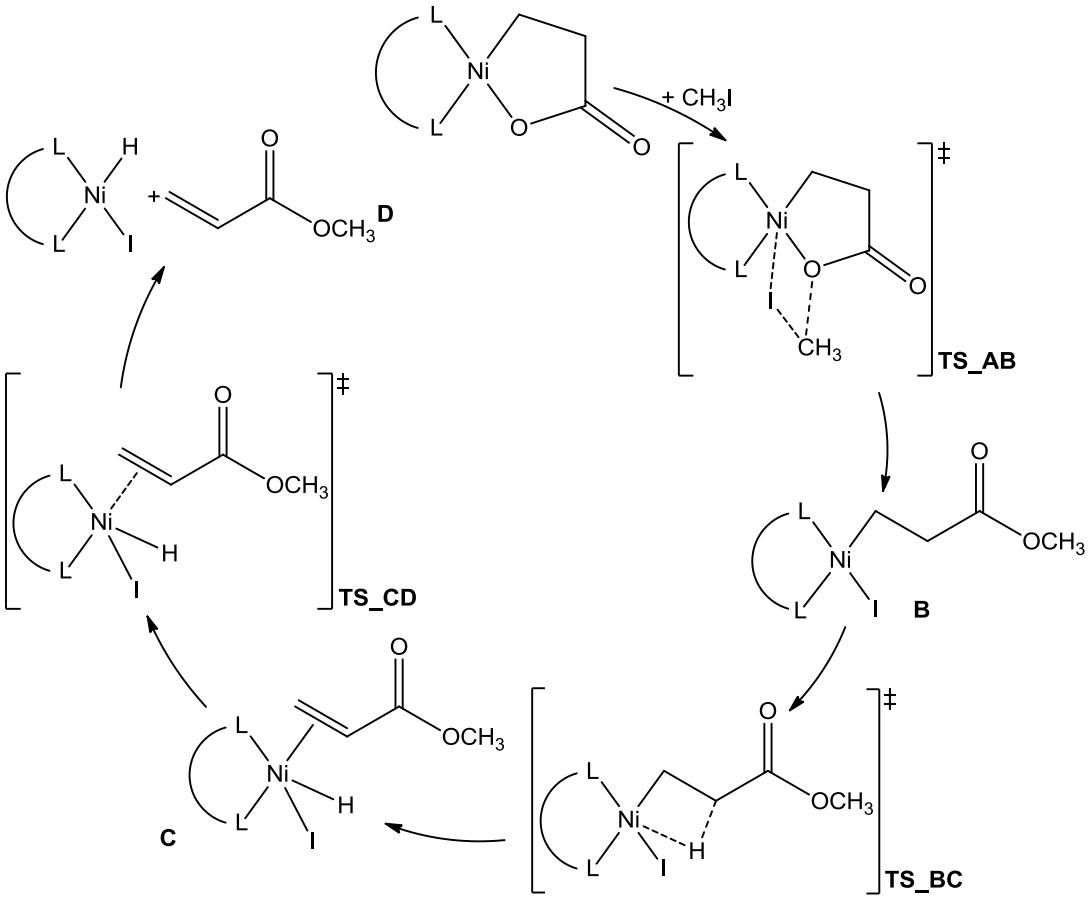


Figure 3.2d. Pathway from the nickelalactone *A1* to the free methyl acrylate *D*.

The most crucial and most energy demanding step in the formation of methyl acrylate is certainly the reaction of methyl iodide with the nickelalactone (see Figures 3.2d and 3.2e). Assuming that the reaction is concerted, a possible transition state would involve a penta-coordinated Ni species, which most presumably represents a rather high thermodynamic barrier. This is also most likely the reason why such a high excess of CH_3I is required to open the ring. We set out to investigate with computational methods, whether ligand dissociation enables a faster reaction rate of

Ni-lactones with CH_3I. In this investigation, the energy profiles for the lactone-to-acrylic ester conversion were examined (Figure 3.2a, steps (i)-(iii)). Figure 3.2d gives an overview of the ΔG energies of the pathway from the nickelalactone complex to the free methyl acrylate. From the calculations, it can be seen that the rate-determining step of the reaction is the addition of CH_3I (*TS_AB*) to cleave the Ni–O bond for ring opening of the Ni-lactone into the Ni-bound methyl acrylate, with a thermodynamic barrier of 245.3 kJ mol^{-1}. The ring-opened Ni-acrylate (*B*) can now undergo a β-H elimination from *B* to *C*, requiring a barrier of 106.8 kJ mol^{-1} and leading to the endergonic formation of *C* (78.3 kJ mol^{-1}) with respect to *B*) that includes a η^2-coordination of the acrylic ester to the Ni center. Finally, the acrylic ester is eliminated from *C via* a moderate barrier of 57.7 kJ mol^{-1} in an exergonic reaction (-77.5 kJ mol^{-1} with respect to *C*). The full energy plot is presented in Figure 3.2e.

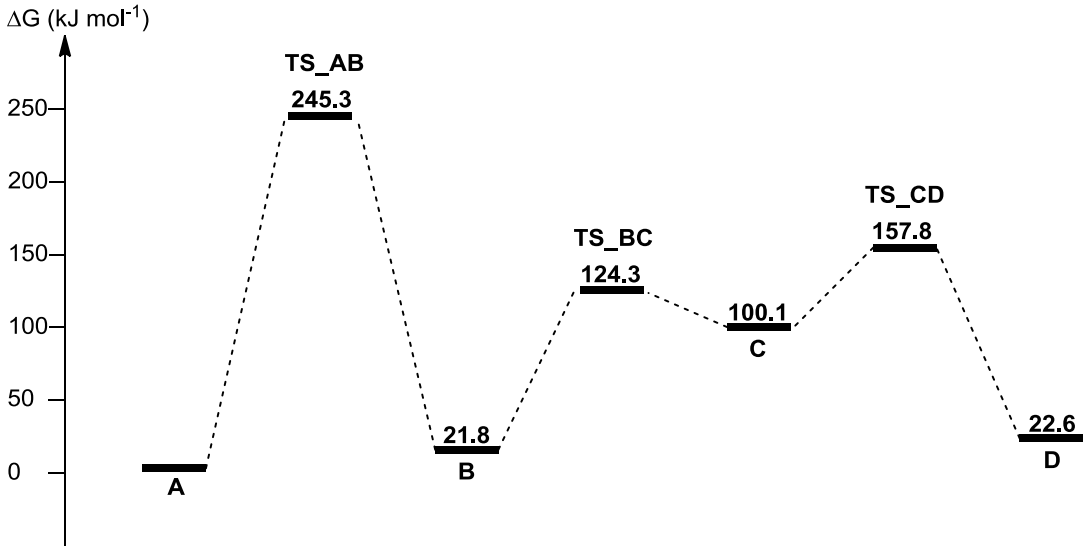


Figure 3.2e. DFT calculated ΔG profile of the investigated reaction sequence relative to the starting complex *A1* and CH_3I.

A detailed computational result (including discussions on the geometry of the transition states) can be found in Appendix 1. In comparison to the left cycle in Figure 3.2a, the mechanism involving CH_3I for cleaving the cyclic lactone has some thermodynamic advantages, but also some higher barriers. Therefore investigations of different bidentate ligands with varying steric demand, as well as other cleaving reagents are in progress both experimentally and theoretically. Preliminary calculations employing diphosphine ligands show that there is no large difference between diamines and diphosphines.

3.2.4 Conclusion

Ligand variation at nickelalactones has a significant influence on the yield of methyl acrylate. High excess of methyl iodide is also necessary to overcome the high thermodynamic barriers in the β-H elimination reaction to release methyl acrylate. Additionally, the identification of an intermediate Ni-acrylate species (Figure 3.2b, species *B*) is a first step in establishing the mechanism of the β-H elimination reaction. The results presented here demonstrate that nickelalactones bearing chelating diamines or diphosphines, respectively, undergo successfully β-H elimination to produce methyl acrylate. Similarly, the strength of the Ni-ligand bond can also affect the β-hydride elimination reaction. A loosely bound ligand improves the flexibility of the steric environment because one arm can easily dissociate and reduce the steric hindrance for the approach of the β-H atom towards the Ni center. Based on these results, it may be concluded that the efficiency of the reductive elimination of methyl acrylate from nickelalactones is dependent on the ligand

employed due to their electronic and steric effects on the nickel atom. Further investigations on finding an appropriate Ni-O bond cleaving agent, the closure of the catalytic cycle, i.e. the production of methyl acrylate under more realistic conditions (ethylene and CO_2 pressure), and detailed DFT investigations on the ligand effect on the thermodynamic barriers of the key steps are currently under way.

3.3 Transformation of nickelalactones to methyl acrylate with methyl triflate

3.3.1 Abstract

The cleavage of Ni-O bond of nickelalactone and the β-hydride elimination reaction to form methyl acrylate was examined with various electrophiles. Only strong methylating agents such as methyl iodide and methyl triflate form the ring-opened nickel-acrylate intermediate *B* and methyl acrylate when reacted with nickelalctones. Here, we report of the observation and isolation of intermediate *B* when tmeda-nickelalactone was reacted with methyl triflate. The best result of β-H elimination reaction with methyl triflate was obtained for dppe-nickelalactone with a yield of 43.5 % methyl acrylate.

3.3.2 Introduction

Carbon dioxide is a cheap and abundantly available C_1 source which can be exploited for the production of organic chemicals in the industries. The direct production of acrylic acid and its derivatives from CO_2 and ethylene is economically attractive. Its catalytic synthesis is greatly discussed in computational chemistry,[54, 81] but the experimental details are still broadly discussed. The nickel-catalyzed oxidative coupling of CO_2 and alkenes and alkynes have been studied over the past thirty years, and the key steps of the catalytic cycle detailed were (1) oxidative coupling of CO_2 and ethylene mediated by Ni centers to form nickelalactones, (2) β-hydride elimination to release acrylic acid, and (3) reductive elimination to recycle the Ni^0 active species. To date, the entire catalytic synthesis has not been realized with a profitable TOF, because of high thermodynamic barriers in the dissociation of the

Ni-O bonds in nickelalactones, and the relatively high energies barriers to the elimination of acrylic acid, and the reduction from Ni^{II} to Ni^{0} to close the catalytic cycle. In addition, the overall thermodynamics for the synthesis of acrylic acid from the oxidative coupling of CO_2 and ethylene is endothermic and therefore unfavorable ($\Delta G = + 42.7$ kJ mol^{-1}).[54]

The first step (i.e. oxidative coupling of CO_2 and ethylene on Ni^{0}) to form nickelalactones has been well described experimentally,[71a, 74, 87] as well as in DFT calculations for this reaction.[54, 81] The nickelalactones isolated were found to be stable intermediates in the reaction. Later investigations showed the first proof of β-H transfer in a nickelalactone to form a nickel acrylate complex (Walter et al.).[87a] In their example, the ligand activation of β-H transfer of nickelalactones with excess dppm forms a stable binuclear Ni^{I} complex with an acrylate as a bridging ligand.[87a] Later, Rieger et al.[88] reported on the cleavage of the Ni-O bond of nickelalactones with methyl iodide, and with a β-H elimination reaction, releases methyl acrylate (33%). This was in accordance with DFT calculations[54] which showed that an elongation of Ni-O bond promotes β-H elimination. In addition, Kühn et al.[83] supported this reaction and improved the yields of methyl acrylate (56%) by using nickelalactones with tmeda instead of dppp as the ligand. Mechanistic studies on the reaction mechanism of nickelalactones with methyl iodide was conducted, and the highest thermodynamic barrier was the first step, i.e. the addition of methyl iodide to nickelalactone (Figure 3.3a).[83]

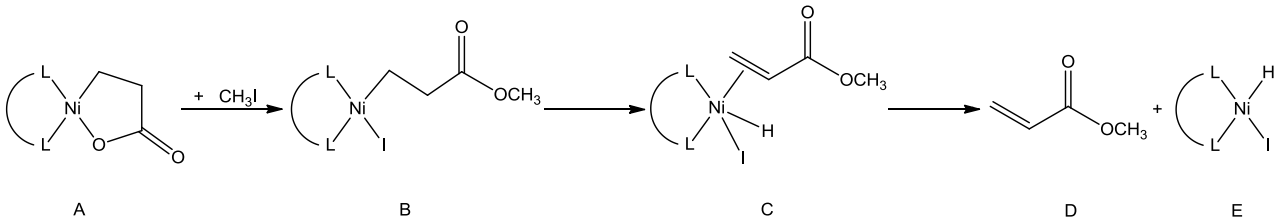


Figure 3.3a. β-H elimination reaction of nickelalactone *A* to methyl acrylate *D* with CH_3I.

Despite a number of experimental and computational reports on the β-H elimination of the nickelalactones, the reaction of nickelalactones with methyl iodide has a high thermodynamic barrier and is limited to a small set of ligands, therefore, more investigations is required to study other possible routes for the β-H elimination reaction.

3.3.3 Results and discussion

The cleavage of the Ni-O bond of nickelalactones (Figure 3.3b, A1-6) to form Ni-acrylate complexes and methyl acrylate were investigated with methyl triflate.

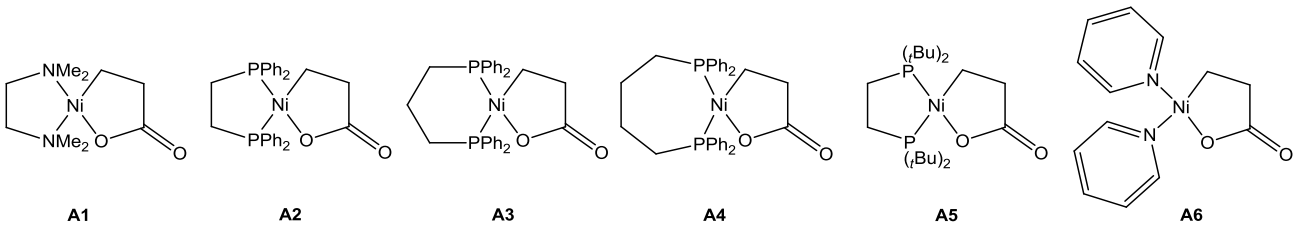


Figure 3.3b. Nickelalactones investigated in the β-H elimination reaction.

When methyl triflate was added to nickelalactone *A1-6*, the influence of ligands on the β-H elimination reaction was compared. When one mol. equiv. of

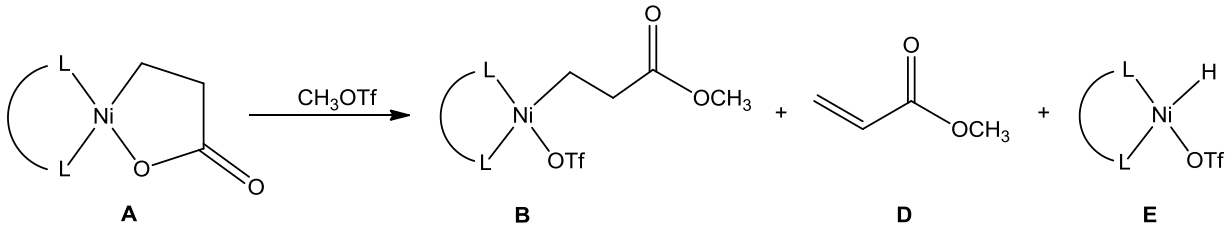
methyl triflate was added to a solution of tmeda-nickelalactone (Figure 3.3b, *A1*) in CD_2Cl_2, all the nickelalactone was converted into intermediate *B1* (see Appendix 2). This was the first time that intermediate *B1* could be isolated. The ^{1}H and ^{13}C NMR characteristic peaks correspond to similar Ni-acrylate complexes reported in literature.[89-90] No olefinic protons (sp_2 carbon) were observed as intermediate *B1* was unable to undergo β-H transfer to form complex *C* and subsequently release methyl acrylate. Unfortunately, it was not possible to grow single crystals of suitable quality for X-ray diffraction. The carbonyl (*C=O*) resonance of intermediate *B* formed from the addition of methyl triflate to nickelalactones (*A1-5*) was observed as doublets at 194 - 197 ppm in the ^{13}C NMR (see Appendix 2). The addition of methyl triflate to py_2-nickelalactone (Figure 3.3b, *A6*) led to immediate decomposition of *A6* (Table 3.3a, entries 15-16).

A separate experiment with five mol. equiv. of methyl triflate resulted only in a low yields of methyl acrylate (6 %, Table 3.3a, entry 2), together with intermediate *B1*. However, complex *C* was also not observed in this case.

Dppe-nickelalactone (Figure 3.3b, *A2*) was reacted with 0.5 mol. equiv of methyl triflate to give a yield of methyl acrylate of 43.2 % (Table 3.3a, entry 3). When the amount of methyl triflate was increased to one and five mol. equiv., the yield of methyl acrylate decreased dramatically to only 4 % and 1 % respectively (Table 3.3a, entries 4-5). It seemed that high amount of methyl triflate reduces the reactivity of the β-H elimination reaction of the nickelalactone into methyl acrylate. This observation was also similarly observed with the other phosphine-nickelalactones (Table 3.3a, entries 6-14). Dppe-nickelalactone (Figure 3.3b, *A2*) gives the highest yield of methyl acrylate (43.2 %) with 0.5 mol. equiv. methyl triflate (Table 3.3a, entry

3). The IR spectrums (see Appendix 2) of the nickelalactone solutions were also measured before and after addition of methyl triflate, and in all except nickelalactone *A6*, a new carbonxy stretching band at 1730-1733 cm^{-1} was observed, which was identified as the $v_{(C=O)}$ of methyl acrylate.

Table 3.3a. β-H elimination reaction of nickelalactone with methyl triflate to form methyl acrylate.



A B D E

Entry	Ligand	mol. equiv. MeOTf	Yield of D (%)[a]
1	tmeda	1	0
2	tmeda	5	6.0
3	dppe	0.5	43.2
4	dppe	1	4.0
5	dppe	5	1.0
6	dppp	0.5	26.6
7	dppp	1	24.3
8	dppp	5	9.0
9	dppb	0.5	38.8
10	dppb	1	24.2
11	dppb	5	4.0
12	dtbpe	0.5	22.2
13	dtbpe	1	25.8
14	dtbpe	5	6.0
15	2 py	1	-
16	2 py	5	-

Reaction conditions: ^{1}H NMR samples: 0.0001 mol of nickelalactone was dissolved in 0.5 mL CD_2Cl_2 and $CHCl_3$ (8.05 µL, 0.0001 mol) as internal standard. CH_3OTf was added and the spectrums were recorded at 25 °C.

[(a)]Yields of D determined by ^{1}H NMR using $CHCl_3$ as standard.

Table 3.3b shows the chemical shifts of the Ni-H proton of [LNiHOTf] complex (Table 3.2a, *E*) after successful β-H elimination to release methyl acrylate. The ^{1}H NMR spectrums of [Ni(H)(OTf)] clearly establish the presence of a Ni-hydride, and the hydride signals were observed as a singlet/triplet at δ -3.76 to -4.74 ppm (see Appendix 2), with a more upfield chemical shift as compared to literature known Ni-H complexes (e.g. $[(PCy_3)_2Ni(H)(OTf)]$, δ -28.0 ppm[94], PNPNiH, δ -18.5 ppm[95] PCPNIH, δ -10.0 ppm[96] or $[LNi(\mu\text{-}H)_2]$, δ < -9 ppm[97]). Instead, our Ni-hydrides formed have chemical shifts that are in agreement with pincer-supported Ni-H complexes of the type [PSiPNiH[98]], δ -3.5 ppm.[98]

In all previous discussions on the product formed after β-hydride elimination, the Ni-H species is expected to be reduced back into Ni^0. I[54, 81a, 82-83, 88] Molar equivalent amount of triethylamine was then added into NMR mixtures (containing the nickel-hydride complex ([LNiHOTf]) in an attempt to remove the triflic acid from the Ni-hydride complex *E* and regenerate the active Ni^0. However, neither triethylammonium triflate nor Ni^0 was observed in all cases.

Table 3.3b. NMR chemical shift (δ) of nickel hydride, *E* produced from the β-H elimination of nickelalactones.

Nickelalactone	**Ligand**	**δ ^{1}H**
A1	tmeda	-1.65 (broad singlet)
A2	dppe	-3.76 (triplet)
A3	dppp	-4.22 (triplet)
A4	dppb	-4.74 (triplet)
A5	dtbpe	-4.53 (triplet)

Other methylating agents were also screened for suitability in β-H elimination reaction of nickelalactone to form methyl acrylate. Weak methylating agents such as dimethyl carbonate, trimethyl phosphate, 2,2-dimethoxypropane and trimethyloxonium tetraborate were ineffective in cleaving the Ni-O bond and β-H elimination reaction. Other strong methylating agents such as dimethyl sulfate and methyl methanesulfonate tested positive but only produce low yields of methyl acrylate (< 10%). No further investigation was carried out because these two methyl sulfonates are highly toxic.

3.3.3.1 Comparison of selectivity: methyl triflate *vs* methyl iodide

The reactivities of methyl iodide and methyl triflate in the β-hydride elimination reaction of nickelalactones was compared. From previous experiments, the β-H elimination reaction is known to be highly sensitive to ligands, and the methylating agents also have high selectivity. The best combination for highest yield of methyl acrylate was tmeda-nickelalctone with methyl iodide (Table 3.3c, entry 1). However, a very high amount (100 mol. equiv.) of methyl iodide was required. On the other hand, low amount of methyl triflate was required for β-H elimination reaction, but the maximum yield was 25% lower than using methyl iodide. However, methyl triflate has a lower selectivity for ligands; nickelalactones with diphosphine ligands undergo β-H elimination reaction with relatively similar kinetics to produce methyl acrylate (Table 3.3c, entries 8, 10). The kinetics of nickelalactone with methyl triflate for the β-H elimination reaction was also faster than with methyl iodide (15 min *vs* 3 - 48 h).

Table 3.3c. Comparison of selectivity of methyl iodide and methyl triflate.

Entry	Nickelalactone	CH_3X	mol. equiv.	Yield (%)[a]
1	*A1*	methyl iodide	100	56.0[b]
2	*A1*	methyl triflate	5	6.0[c]
3	*A2*	methyl iodide	100	48.0[d]
4	*A2*	methyl triflate	0.5	43.5[c]
5	*A3*	methyl iodide	100	29.0[e]
6	*A3*	methyl triflate	0.5	26.6[c]
7	*A4*	methyl iodide	100	0
8	*A4*	methyl triflate	0.5	38.8[c]
9	*A5*	methyl iodide	100	0
10	*A5*	methyl triflate	0.5	22.2[c]
11	*A6*	methyl iodide	100	0
12	*A6*	methyl triflate	1	0

[(a)] Yields of methyl acrylate determined by ^{1}H NMR using $CHCl_3$ as standard. [(b)] 3h, 25 °C, [(c)] 15 min, 25 °C. [(d)] 24 h, 25 °C, [(e)] 48 h, 40 °C.

3.3.4 Conclusion

The β-H elimination reaction of nickelalactones was investigated with methyl triflate to form methyl acrylate. Ligand variation at nickelalactones has some influence on the yield of methyl acrylate. As compared to methyl iodide, only 0.5 mol. equiv. of methyl triflate is required for the nickelalactone to undergo β-hydride elimination to form methyl acrylate, with the best result obtained for dppe-nickelalactone to give a yield of 43.5 % methyl acrylate. A clean isolation of Ni-acrylate (intermediate *B1*) was isolated when tmeda-nickelalactone was reacted with one mol. equiv. methyl triflate. This intermediate *B1* was unable to undergo β-H elimination to release methyl acrylate even when more methyl triflate was added. The results presented here demonstrate that nickelalactones bearing chelating diphosphines undergo β-H elimination to produce methyl acrylate. The efficiency of the reductive elimination of methyl acrylate from nickelalactones is dependent on the amount of methyl triflate added. Experimental identification of key intermediates *B* and Ni-hydride *E* of the β-hydride elimination reaction is complementary to theoretical calculations, and is important for future design of experimental conditions or additive selection for possible breakthrough in catalytic synthetic routes.

4. Summary

The oxidative coupling of ethylene and CO_2 on Ni^0 to form nickelalactones at mild working conditions was carried out with various ligands. Despite repeated attempts, very low yields (5.4 %) of dtbpe-Nickelalactone was obtained at mild operating conditions (6 bars CO_2, 2 bars ethylene, 50 °C, 72 h). Other ligands such as dbu, tmeda, dppe, dppp ligands were ineffective at these experimental conditions. In-*situ* IR experiments were also conducted to monitor both the formation of nickelalactone, as well as the β-H elimination reaction with methyl triflate. From the real-time kinetic monitoring of the asymmetric stretching frequency of the carbonyl band band, the oxidative coupling step was slow, but the ring-opening reaction was fast. However, the Ni^{II} species remained in the reaction mixture and triflic acid was not released and therefore, Ni^0 could not be recovered. Despite multiple attempts, it was impossible to overcome the non- catalytic nature of the oxidative coupling reaction to form acrylic acid from CO_2 and ethylene by addition of an electrophile to induce β-H elimination because the active nickel species (Ni^0) could not be regenerated (Figure 4.3).

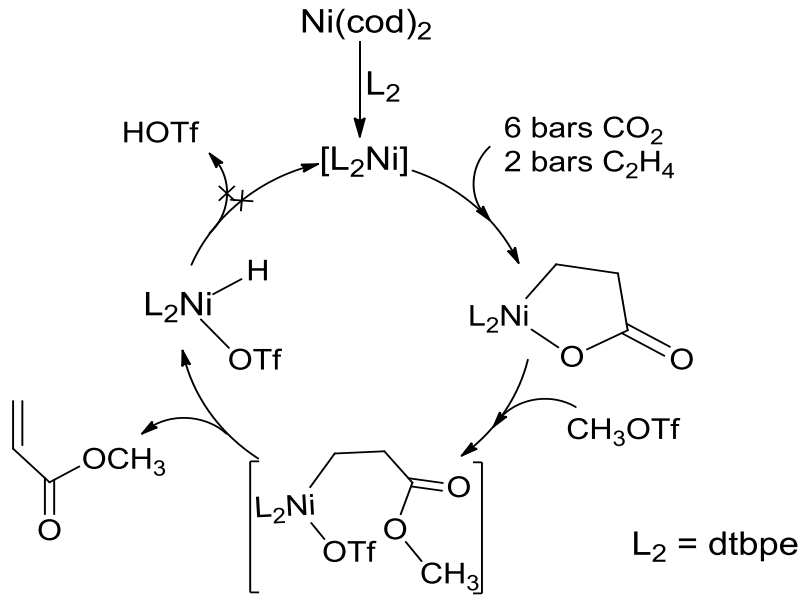


Figure 4.3. Oxidative coupling of CO_2, ethylene and methyl triflate to form methyl acrylate mediated by Ni^0.

A series of nickelalactones bearing different bidentate ligands were investigated in the β-hydride elimination reaction to release methyl acrylate with various methylating agents. The main focus was in the optimization of reaction conditions to obtain high yields of methyl acrylate with the most effective electrophile. The β-hydride elimination reaction with methyl iodide was found to be highly ligand selective, when the ligand is too bulky, or has a large bite angle, the ring-opened intermediate (Figure 4.1, *B*), cannot undergo β-H elimination to release methyl acrylate with CH_3I. The highest yield of methyl acrylate (56 %) was obtained with the tmeda ligand. Theorical calculations revealed that the rate determining step was the concerted attack of CH_3I on the Ni-O bond (Figure 4.2, *TS_ AB*).

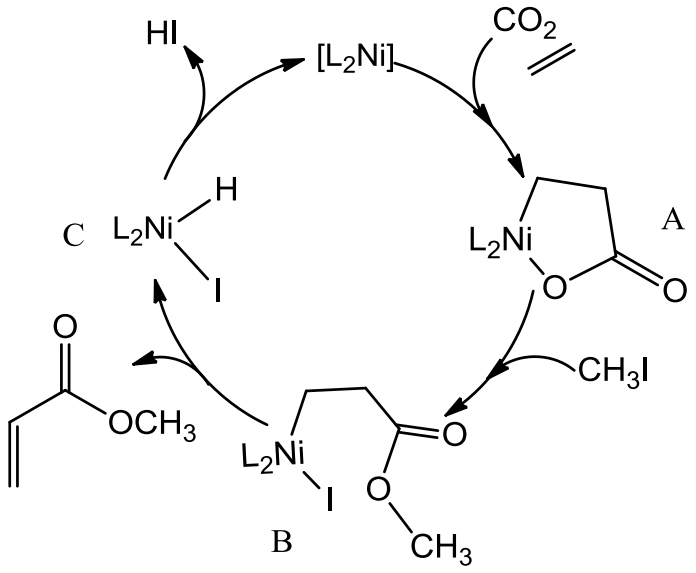


Figure 4.1. Synthesis of methyl acrylate from CO_2, ethylene and methyl iodide mediated by Ni catalyst.

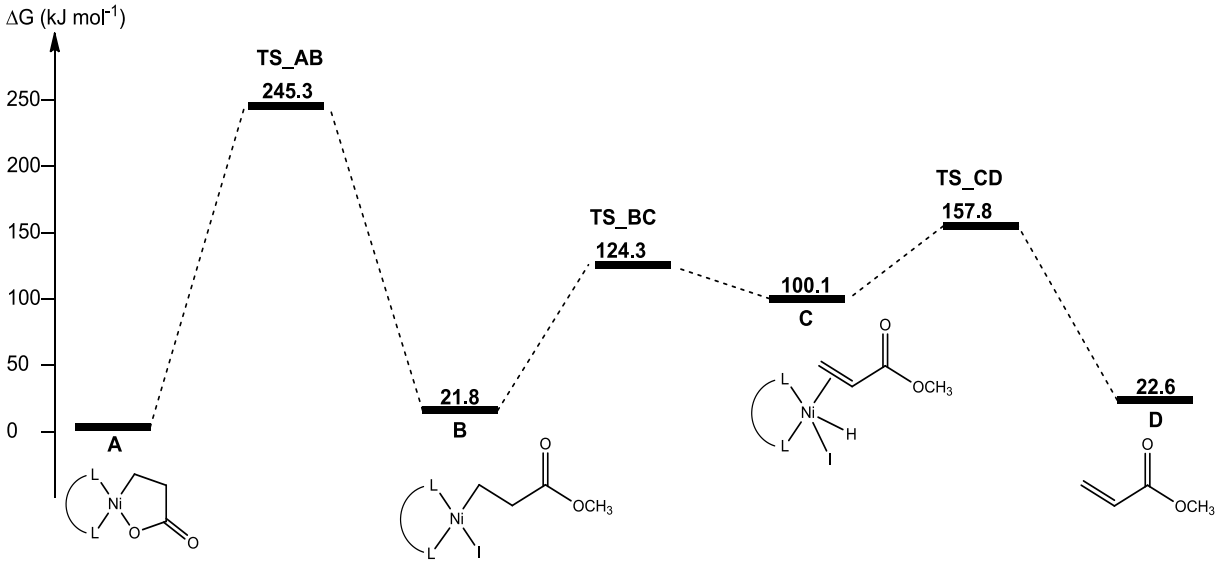


Figure 4.2. Theorical calculations for the oxidative addition of CH_3I to (tmeda)Nickelalactone to form methyl acrylate, ΔG = kJ mol^{-1}.

Oxidative addition of methyl triflate to nickelalactones was then carried out to investigate if stronger electrophiles can attack Ni-O bond more readily for β-H elimination to proceed. However, MeOTf was ineffective in the case of tmeda-Nickelalactone as its intermediate complex *B1* was stable in dichloromethane and was unable to undergo β-H elimination to release methyl acrylate unless excess MeOTf was added (5 mol. equiv., 6% methyl acrylate). The advantage of using MeOTf over CH_3I was that only molar equivalent amount of methylating agent was required for the conversion of the cyclic lactone into methyl acrylate, a significant improvement from using 100 mol. equiv. of CH_3I in the previous study. The highest yield (43.5 %) was obtained with the dppe ligand in 15 minutes at room temperature. The β-hydride elimination reaction with methyl triflate was also highly ligand selective, bidentate phosphine ligands were more superior than tmeda ligand in this case, as the tmeda ligand was not bulky enough for the ring-opened acrylate intermediate to undergo β-H elimination to release methyl acrylate. Weaker methylating electrophiles such as trimethyloxonium tetraborate, dimethyl carbonate and dimethoxypropane tested negative for the β-H elimination reaction.

In conclusion, it is difficult to liberate acrylic acid from nickelalactones, and this has been proven both in theorical calculations and in experiments, unless the ring opening is induced by strong electrophiles to facilitate the approach of β-hydrogen atom to the nickel center for β-H elimination. Moreover, more investigation has to be carried out to locate a suitable electrophile which on one hand can induce ring opening and β-H elimination, and on the other hand, its nucleophilic counterion can be discharged from the Ni-H center to regenerate the active Ni^0 species for a catalytic synthesis to be possible.

5. Experimental

General procedures: All manipulations were performed under a purified argon atmosphere under standard air-free techniques in a glove-box or on a dual-manifold schlenk line. Tetrahydrofuran was vacuum-transferred from Na / benzophenone ketyl and stored under argon before use. Chloroform, dichloromethane, diethyl ether, hexane and toluene were purified over activated alumina and dried over 3Å molecular sieves. Nuclear magnetic resonance (NMR) measurements were performed using Bruker AVANCE 400 MHz spectrometers. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent resonances. The spectra were processed using the MestReNova software package.

ATR-FTIR spectroscopy: Fourier transform infrared-red (FTIR) spectroscopic measurements conducted on either a Varian 670-IR spectrometer fitted with a KRS-5 Thallium bromoiodide optical crystal or a Thermo Scientific Nicolet 6700 FT-IR spectrometer with a ATR diamond probe head. The transmittance spectrums were processed using the accompanied Varian Resolutions-Pro software or OMNIC software package.

In-*situ* IR spectroscopy: Reactions were conducted in 50 mL vessels equipped with Mettler-Toledo ReactIR 45m / MultiMax RB04-50 instrument for in-*situ* ATR-FTIR measurements.

General oxidative coupling reaction procedure: Reactions were conducted in 50 mL stainless-steel autoclaves vessels equipped with Mettler-Toledo ReactIR 45m

/ MultiMax RB04-50 instrument for in-*situ* ATR-FTIR measurements under high-pressure conditions. For the preparation of the reaction, $Ni(cod)_2$ (0.135 g, 0.0005 mol) was suspended in 8 mL THF. 0.0005 mol ligand was added and the mixture was stirred at 25 °C for 30 min. the autoclave was then pressurized with 2 bars ethylene and and the mixture was stirred for at 25 °C for 30 min. CO_2 (6 bars) was added and the autoclave was heated at the stated temperature and time. The autoclave was then depressurized the reaction mixture transferred to a schlenk. The solvent was removed and the nickelalactone was precipitated from diethyl ether or hexane.

Preparation of ligands: 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), pyridine and N,N,N',N'-tetramethane-1,2-diamine (tmeda) were purchased from Sigma-Aldrich and used without further purification. Bis-(di-tert-butylphosphino)ethane (dtbpe) was prepared according to literature procedures.[99]

Preparation of Ni^0 precursor: Bis(1,5-cyclooctadiene)nickel(0) was prepared as previously reported.[100] 400-MHz ^1H NMR (C_6D_6): δ 2.08 (8H, singlet), 4.30 (4H, singlet). 100.6-MHz ^{13}C NMR (C_6D_6): δ 30.72, 89.93.[100]

Synthesis of (tmeda)-Nickelalactone (***A1***): Bis(1,5-cyclooctadiene)nickel(0) (9.5 g, 0.0345 mol), succinic anhydride (2.3 g, 0.023 mol) were suspended in tmeda (30 mL). The mixture was stirred at room temperature for 10 h. The light green complex was filtered, washed with diethyl ether and dried in vacuum to give a light green powder (ca. 55% yield).[101] 400-MHz ^1H NMR (CD_2Cl_2): δ 0.58 (2H, triplet), 1.63 (2H, triplet), 2.27 (4H, singlet), 2.31 (6H, singlet), 2.51 (6H, singlet). 100.6-MHz

^{13}C NMR (CD_2Cl_2): δ 47.34, 49.27, 56.61, 61.49, 163.00. ATR-FTIR: $\nu_{(C=O)}$ = 1579 cm^{-1}.

Synthesis of (dppe)-Nickelalactone (***A2***)**:** Dppe (1.01 g, 0.00253 mol) was added to a suspension of tmeda-Nickelalactone (0.62 g, 0.0025 mol) in tetrahydrofuran (30 mL). The mixture was stirred for 1 h at room temperature, and the yellow product was filtered, washed with diethyl ether and dried in vacuum to give a yellow powder (80 % yield).[87a, 102] 400-MHz ^{1}H NMR (CD_2Cl_2): δ 0.84 (2H, multiplet), 2.09 (2H, multiplet), 2.29 (4H, multiplet), 7.47 (12H, multiplet), 7.71 (4H, multiplet), 7.86 (4H, multiplet). 162-MHz ^{31}P NMR (CD_2Cl_2): δ 35.54 (singlet), 59.14 (singlet). 100.6-MHz ^{13}C NMR (CD_2Cl_2): δ 15.60, 17.99, 22.48, 29.66, 37.80, 66.13, 129.3, 131.16, 131.56, 133.16, 133.48, 191.51. ATR-FTIR: $\nu_{(C=O)}$ = 1622 cm^{-1}.

Synthesis of (dppp)-Nickelalactone (***A3***)**:** Dppp (1.04 g, 0.00253 mol) was added to a suspension of tmeda-Nickelalactone (0.62 g, 0.0025 mol) in tetrahydrofuran (30 mL). The mixture was stirred for 1 h at room temperature, and the yellow product was filtered, washed with diethyl ether and dried in vacuum to give a yellow powder (82 % yield).[87a] 400-MHz ^{1}H NMR (CD_2Cl_2): δ 0.61 (2H, multiplet), 1.77 (2H, multiplet), 2.18 (2H, multiplet), 2.24 (2H, multiplet), 7.42 (12H, multiplet, 7.74 (8H, multiplet). 162-MHz ^{31}P NMR (CD_2Cl_2): δ -1.33 (doublet, $^3J_{PP}$ = 29.17), 30.34 (doublet, $^3J_{PP}$ = 29.17). 100.6-MHz ^{13}C NMR (CD_2Cl_2): δ 19.26, 21.63, 26.73, 28.39, 28.64, 37.85, 128.97, 130.60, 131.04, 133.43, 189.87. ATR-FTIR: $\nu_{(C=O)}$ = 1622 cm^{-1}.

Synthesis of (dppb)-Nickelalactone (***A4***)**:** Dppb (1.08 g, 0.00253 mol) was added to a suspension of tmeda-Nickelalactone (0.62 g, 0.0025 mol) in

tetrahydrofuran (30 mL). The mixture was stirred for 1 h at room temperature, and the yellow product was filtered, washed with diethyl ether and dried in vacuum to give a yellow powder (80 % yield).[87a] 400-MHz ^{1}H NMR (CD_2Cl_2): δ 0.64 (2H, multiplet), 1.68 (4H, multiplet), 2.05 (2H, multiplet), 2.15 (2H, multiplet), 2.27 (2H, multiplet), 7.47 (12H, multiplet), 7.72 – 7.78 (8H, multiplet). 162-MHz ^{31}P NMR (CD_2Cl_2): δ 15.12 (doublet, $^{3}J_{PP}$ = 12.97), 38.22 (doublet, $^{3}J_{PP}$ = 12.97). 100.6-MHz ^{13}C NMR (CD_2Cl_2): δ 189.15. ATR-FTIR: $\nu_{(C=O)}$ = 1626 cm^{-1}.

Synthesis of nickelalactone ***(A5)*** (method 1): A suspension of dtbpe (0.16 g, 0.0005 mol) and Ni(cod)$_2$ (0.135 g, 0.00005 mol) was suspended in 8 mL THF and stirred for 30 min in a 100 mL potable steel autoclave. The autoclave was pressurized with 2 bars ethylene, and the mixture was stirred for at 25 °C for 30 min. CO_2 (6 bars) was added and the autoclave was heated at 50 °C for 3 days. The autoclave was depressurized and THF was removed in vacuum. The crude solid was redissolved in thf and precipitate from diethyl ether to obtain a yield of 0.45 g dtbpe-nickelalactone (5.4 %).

Synthesis of (dtbpe)-Nickelalactone (***A5***) (method 2). dtbpe (0.64 g, 0.002 mol) was added to a suspension of tmeda-Nickelalactone (0.12 g, 0.0005 mol) in tetrahydrofuran (10 mL). The mixture was stirred for 1 h at room temperature, and the yellow product was filtered, washed with diethyl ether and dried in vacuum to give a orange powder (80 % yield). 400-mHz ^{1}H NMR (CD_2Cl_2): δ 1.18 (2H, triplet), 1.35-1.39 (36H, multiplet), 1.48 (2H, multiplet), 1.78 (2H, multiplet) & 2.06 (2H, multiplet). 162-mHz ^{31}P NMR (CD_2Cl_2): 77.7 (d, $J_{P,P}$ 8.1) & 80.5 (d, $J_{P,P}$ 8.1). 100.6-mHz ^{13}C NMR (CD_2Cl_2): -1.27, 9.77, 18.85, 30.47, 30.82, 35.08, 37.14, 189.89. ATR-FTIR: $\nu_{(C=O)}$= 1615 cm^{-1}.

Synthesis of (py_2)-Nickelalactone (***A6***): Excess pyridine (10 mL) was added to tmeda-Nickelalactone (0.32 g, 0.0013 mol), and the resulting solution was stirred for 1 h at room temperature. The solvent was removed in vacuum, and the product was isolated as a green powder (90% yield).[87c] 400-MHz ^{1}H NMR (CD_2Cl_2): δ 0.83 (2H, triplet), 1.96 (2H, triplet), 7.22 (4H, singlet), 7.69 (2H, singlet), 8.19 (2H, singlet), 8.83 (2H, singlet). FTIR: $\nu_{(C=O)}$ = 1587 cm^{-1}.

In-situ IR reactions of β-hydride elimination reaction with methyl iodide: 0.4 mmol nickelalactone complex was dissolved in 4 mL CH_2Cl_2 transferred to the IR vessel. CH_3I was introduced using a syringe. IR measurements were measured at 1 min intervals at 25 °C for 3-24 h.

General procedure for the preparation of ^{1}H NMR samples (methyl iodide): 0.0002 mol of nickelalactone was dissolved in 0.6 mL CD_2Cl_2 and $CHCl_3$ (16 µL, 0.0002 mol) as internal standard. CH_3I (10 or 100 mol. equiv.) was added and the NMR spectrums were recorded at 25 °C.

General procedure for the preparation of NMR samples (methyl triflate): 0.0001 mol of nickelalactone was dissolved in 0.5 mL CD_2Cl_2 and $CHCl_3$ (8.05 µL, 0.0001 mol) as internal standard. CH_3OTf (11.3 µL, 0.0001 mol) was added and the NMR spectrums were recorded at 25 °C.

Reaction of tmeda-Nickelalactone with methyl triflate to form intermediate (***B1***). Tmeda-nickelalactone (0.0247g, 0.0001 mol) was dissolved in 0.5 mL CD_2Cl_2, and methyl triflate (11.3 µL, 0.0001 mol) was added. The product was identified with 1D and 2D NMR. 400-mHz ^{1}H NMR (CD_2Cl_2): δ 0.61 (2H, triplet), 2.20 (2H, triplet),

2.39 (10H, singlet), 2.56 (6H, singlet), 3.72 (3H, singlet). 100.6-mHz ^{13}C NMR (CD_2Cl_2): -0.35, 36.63, 47.28, 50.07, 56.05, 56.51, 62.28, 194.11.

Theoretical computation details: All calculations were performed with GAUSSIAN-03[103] using the density functional/Hartree-Fock hybrid model Becke3LYP[104] and the split valence double-ζ (DZ) basis set 6-31+G**.[105] No symmetry or internal coordinate constraints were applied during optimizations. All reported intermediates were verified as being true minima by the absence of negative eigenvalues in the vibrational frequency analysis. Transition-state structures (indicated by TS) were located using the Berny algorithm[106] until the Hessian matrix had only one imaginary eigenvalue. The identities of all transition states were confirmed by IRC calculations, and by animating the negative eigenvector coordinate with MOLDEN[107] and GaussView.[108] Approximate free energies (ΔG) and enthalpies (ΔH) were obtained through thermochemical analysis of frequency calculations, using the thermal correction to Gibbs free energy as reported by GAUSSIAN-03. This takes into account zero-point effects, thermal enthalpy corrections, and entropy. All energies reported in this paper, unless otherwise noted, are free energies or enthalpies at 298 K, using unscaled frequencies. All transition states are maxima on the electronic potential energy surface (PES), which may not correspond to maxima on the free energy surface.

X-ray single crystal structure: The X-ray diffraction measurement was performed on a single crystal of A1 coated with Paratone oil and mounted on a Kaptan loop. The crystal was frozen under a stream of dinitrogen while data were collected on an X-ray diffractometer equipped with a CCD detector (APEX II, κ-CCD), a rotating anode (Bruker AXS, FR591) with MoK_α radiation (λ = 0.71073 Å),

and a graphite monochromator by using the SMART software package.[109] A matrix scan using at least 20 centered reflections was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT 4.15.[110] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[111] Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps, and was refined against all data using WinGX[112] based on Sir-92.[113] All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas all hydrogen atoms were refined with isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with SHELXL-97[114] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[115] Images of the crystal structures were generated by Diamond 3.1.[116] Crystallographic data (excluding structure factors) of *A1* have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-822360.

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7. Appendix

7.1 Appendix 1

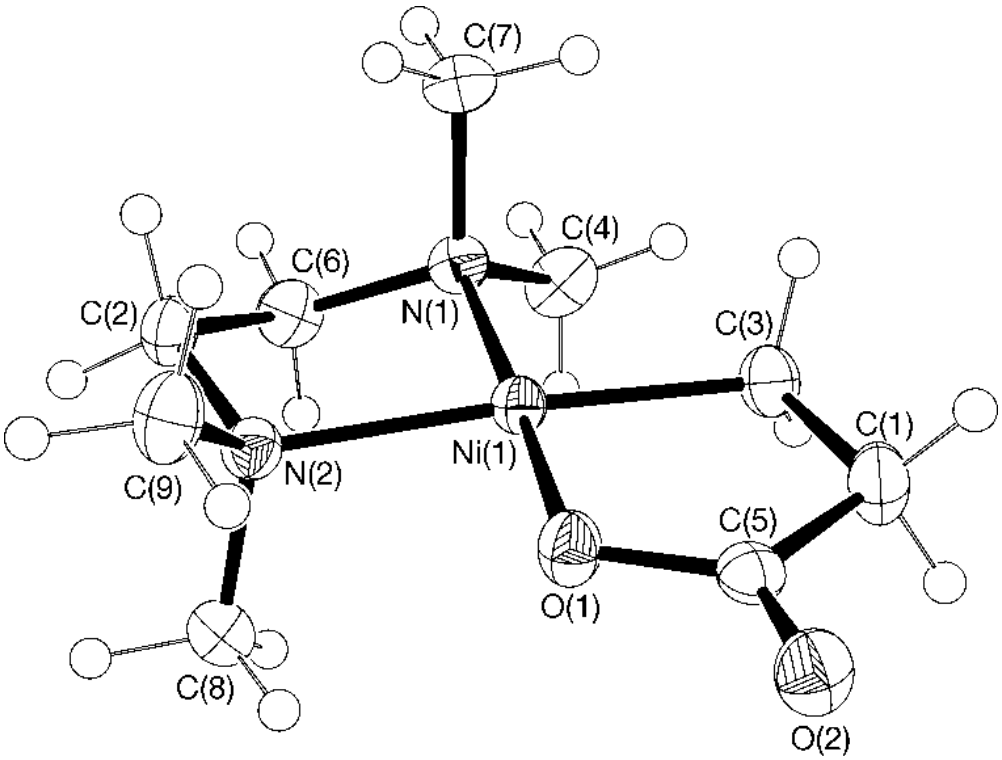


Figure 1a. ORTEP view of the structure of tmeda-nickelactone (complex *A1*).

Selected bond lengths (Å) and angles (°): Ni(1)–O(1) 1.854(2), Ni(1)–C(3) 1.925(2), Ni(1)–N(1) 1.960(2), Ni(1)–N(2) 2.032(2), N(1)–Ni(1)–O(1) 175.67(8), N(2)–Ni(1)–C(3) 175.9(1), N(1)–Ni(1)–N(2) 87.38(8), O(1)–Ni(1)–C(3) 87.22(9), N(1)–Ni(1)–C(3) 95.9(1), N(2)–Ni(1)–O(1) 89.64(8), N(1)–N(2)–O(1)–C(3) 4.2.

Table 1a. X-ray single crystal structure data for nickelalactone *A1*.

Compound Name	**(tmeda)Nickelalactone**
formula	$C_9H_{20}N_2O_2Ni$
M_r (g/mol)	246.96
Crstal description	green fragment
Crystal dimensions (mm^3)	0.05 x 0.13 x 0.15
Temperature (K)	173(2)
crystal system, space group	monoclinic, $P2_1/c$
a(Å)	8.9316(9)
b(Å)	7.8422(8)
c(Å)	16.1611(16)
a(°)	90
b(°)	91.946(5)
g(°)	90
V($Å^3$)	1131.3(2)
Z	4
d_{calc} (g/cm^3)	1.45
F_{000}	528
m (mm^{-1})	1.694
Index ranges (±h, ±k, ±l)	11/-11, 9/-8, 19/-19
q ranges (°)	2.28 - 26.17
Collected reflections	15499
Unique reflections [all data]	2236
R_{int} / R_s	0.0604 / 0.0346
Unique reflections [t_0>2 s(t_0)]	1950
Data/Restraints/Parameter	2236/0/207
GoF (on F^2)	1.043
R_1/*w*R_2 [t_0>2 s(t_0)]	0.0324/0.0846
R_1/*w*R_2 [all data]	0.0407/0.0928
Max./Min. residual electron density	0.624/-0.563

FTIR spectrums of the β-hydride elimination reaction of Nickelalactones with 100 mol.equiv. CH_3I to form methyl acrylate (figure 1b-f).

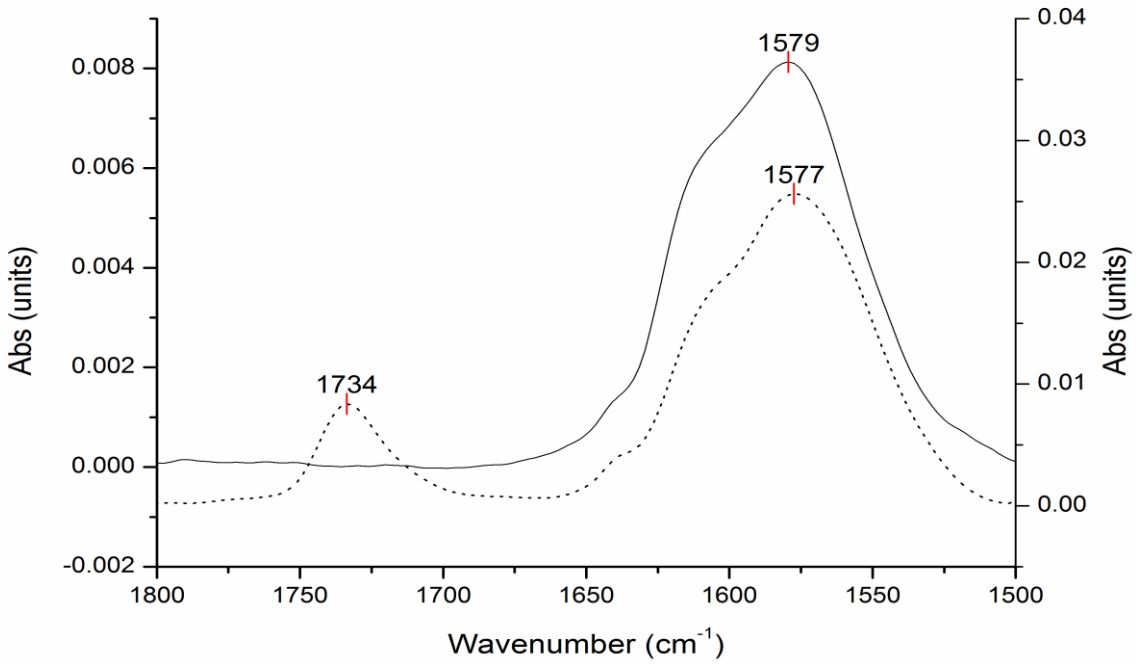


Figure 1b. IR spectra before and after 24 h of reaction (solid line: IR of nickelalactone *A1* in CH_2Cl_2, dotted line: IR of reaction mixture after 24 h).

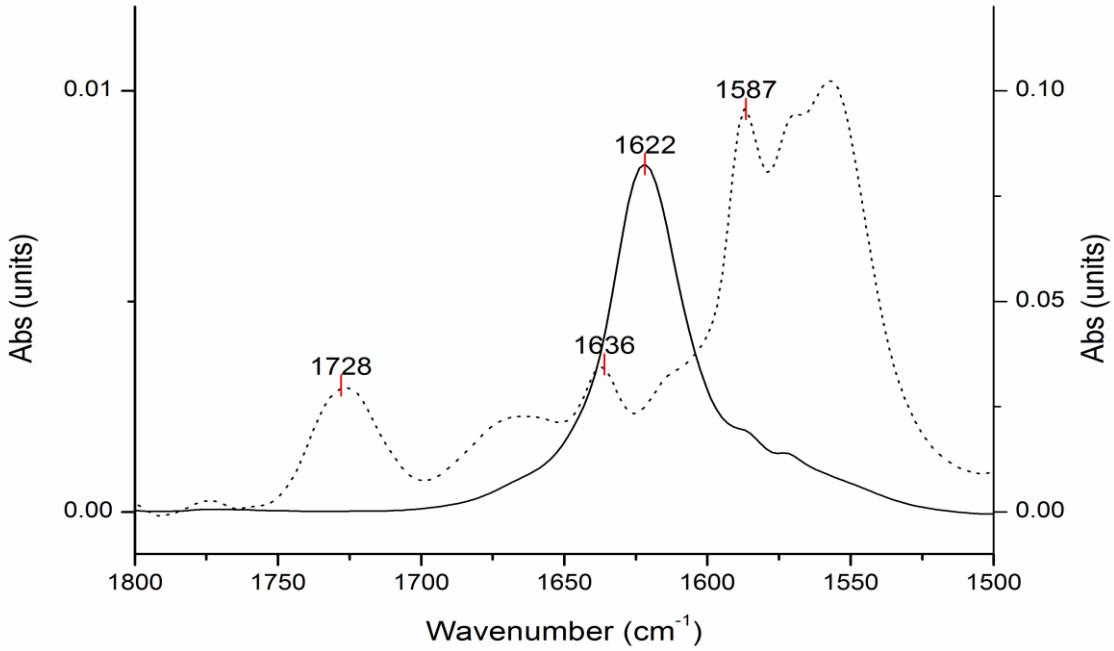


Figure 1c. IR spectra before and after 24 h of reaction (solid line: IR of nickelalactone *A2* in CH_2Cl_2, dotted line: IR of the reaction mixture after 24 h).

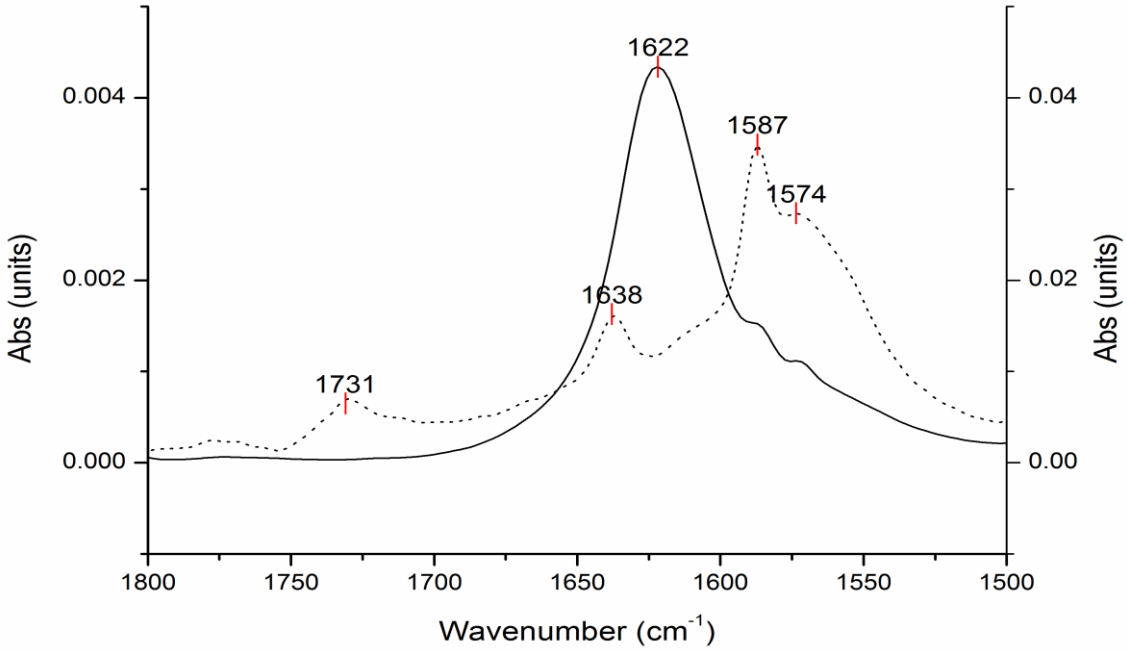


Figure 1d. IR spectra before and after 24 h of reaction (solid line: IR of nickelalactone *A3* in CH_2Cl_2, dotted line: IR of the reaction mixture after 24 h).

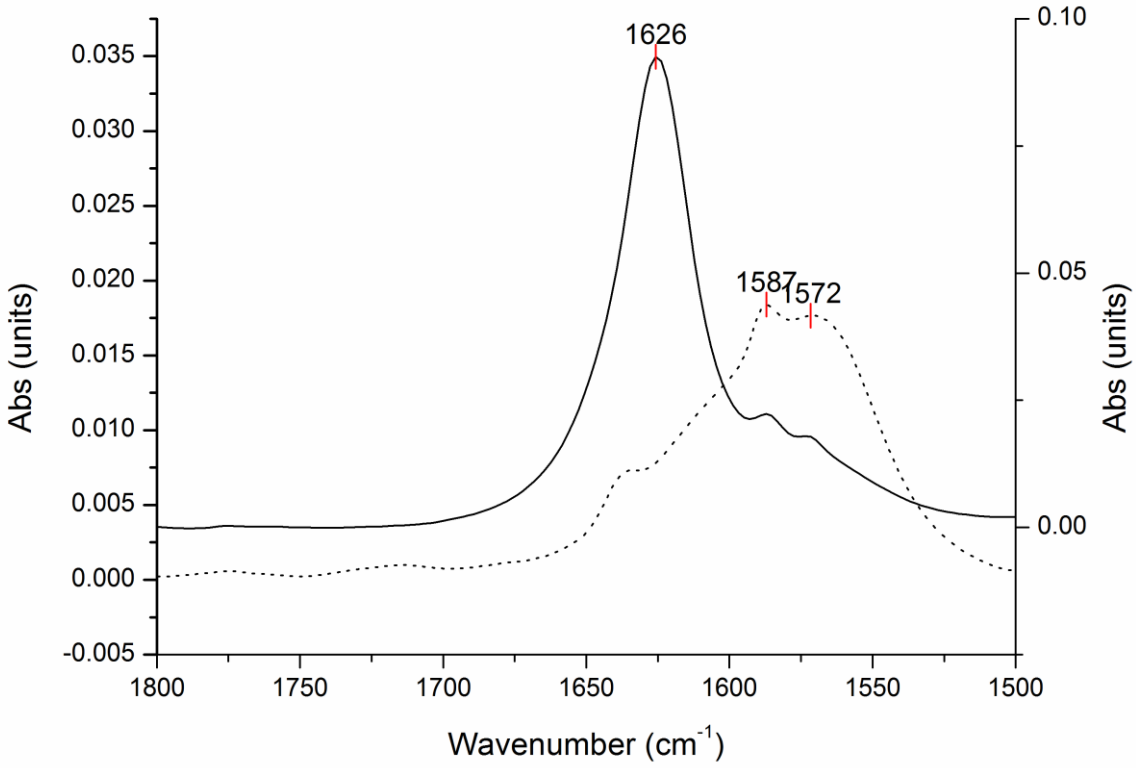


Figure 1e. IR spectra before and after 24 h of reaction (solid line: IR of nickelalactone *A4* in CH_2Cl_2, broken line: IR of the reaction mixture after 24 h).

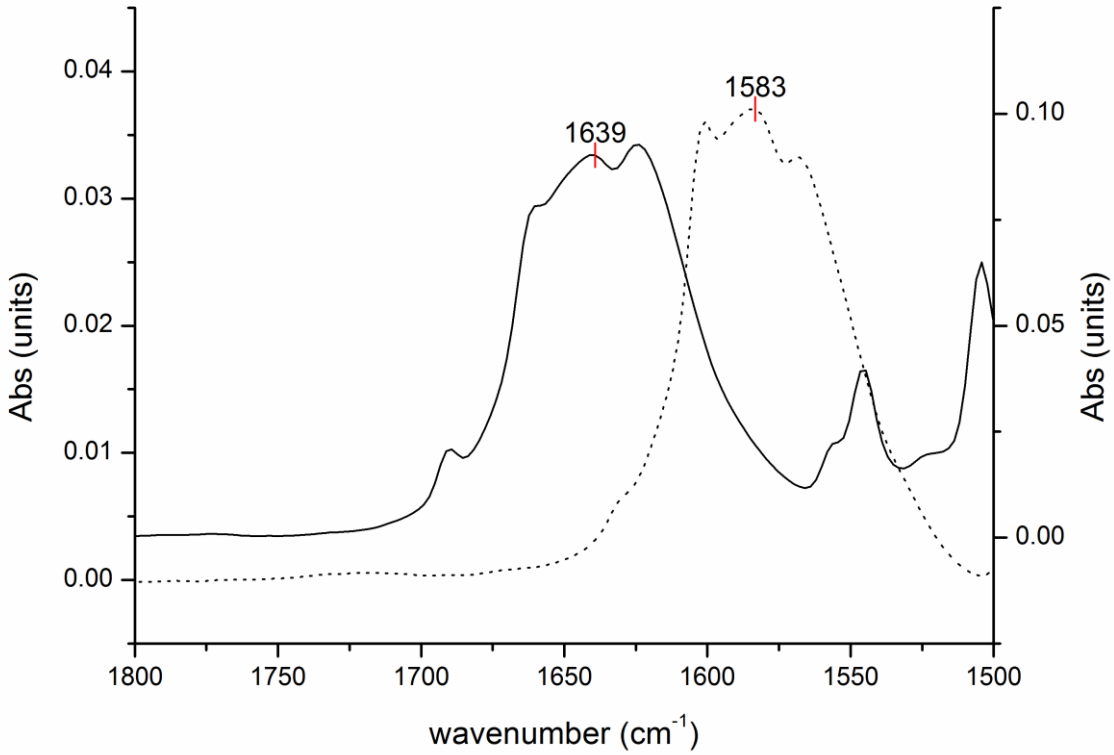


Figure 1f. IR spectra before and after 24 h of reaction (solid line: IR of nickelalactone *A5* in CH_2Cl_2, broken line: IR of the reaction mixture after 24 h).

DFT calculations: With DFT calculations, it was attempted to quantify the mechanism for the lactone-to-acrylic ester conversion. The choice of bidentate ligands is to use the best ligand of the experimental study, therefore tmeda was chosen. From the results, it can be concluded that the rate-determining step is the addition of the methyl iodide to open the lactone. tmeda and bipy show equal barriers of 245.3 kJ mol^{-1} (free energy). Figure 1g shows the optimized geometry for all three transition states for occurring in this mechanism. The geometry of *TS_AB* shows that the methyl iodide is already separated and the carbon atom of the methyl group shows significantly sp^2 hybridization character (partly cationic). Although no solvent effects have yet been included, DCM is less polar and therefore also this higher barrier is expected even with respect of such effects.

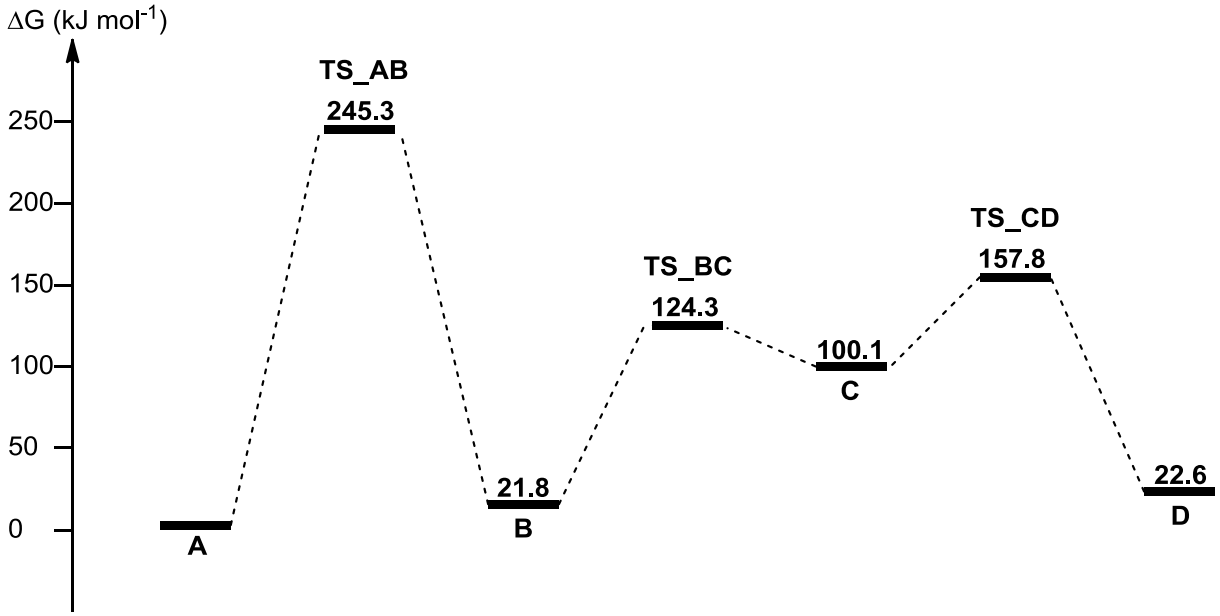
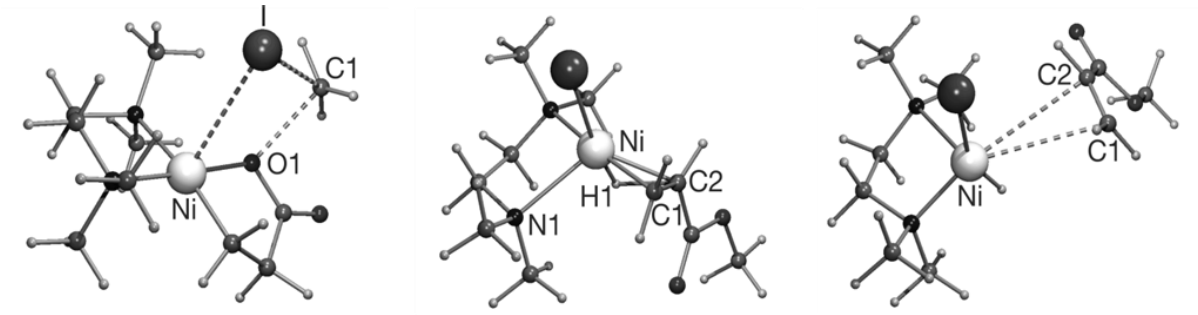


Figure 1g. DFT calculated ΔG profile of the investigated reaction sequence relative to the starting complex *A1* and CH_3I.



TS_AB **TS_BC** **TS_CD**

Selected bond lengths (Å):

I–Ni	3.39	C1–C2	1.41	C1–C2	1.34
I–C1	3.13	C1–Ni	2.00	C1–Ni	3.36
Ni–O1	1.89	C2–Ni	2.08	C2–Ni	3.43
C1–O1	2.30	C2–H1	1.77		
		Ni–H1	1.44		
		Ni–N1	2.43		

Figure 1h. Structures of all calculated transition states with selected bond lengths.

Intermediate *B* can be regarded as the Ni bound methyl arylate. The formation is endergonic compared to the starting compounds. This result might lead to an explanation why this reaction can only proceed with a hundred-fold excess of methyl iodide. The second step is the β-H shift from intermediate *B* to create the η^2-coordinated olefin in order to transform into the “free” methyl acrylate. The corresponding transition state *TS_BC* shows a barrier of 102.5 kJ mol^{-1} on the ΔG scale. In case of tmeda, the bidentate ligand loses almost one of its nitrogen-nickel contacts according to the elongation from 2.12 to 2.43 Å (Figure 1h). *TS_BC* is a late transition state with the hydrogen already transferred to the nickel and the η^2-coordination of the olefin already established. The resulting bidentate Ni-hydrido-iodo complex *C* is even more endothermic and endergonic than *A* and *B*. The reaction sequence is finally completed by the dissociation of methyl acrylate *D*. The barrier

height in this *TS_CD* is 57.7 kJ mol^{-1} for tmeda. This is also a late transition state while the C-Ni distances have already been elongated to around 3.4 Å (Figure 1h).

7.2 Appendix 2

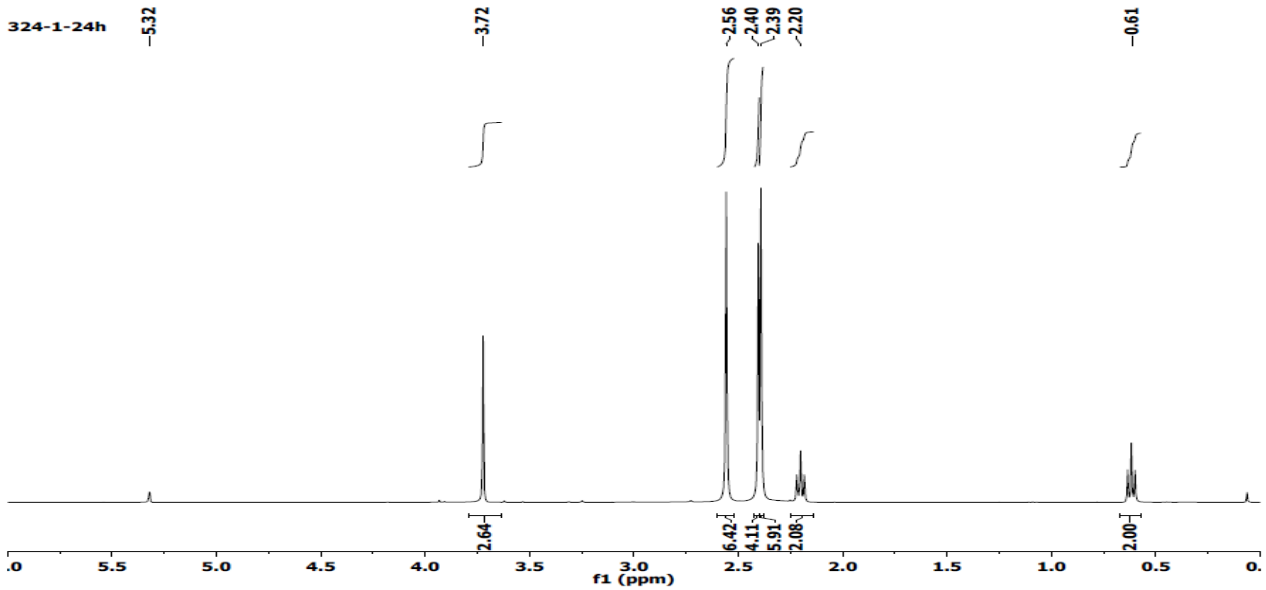


Figure 2a. ^{1}H NMR spectrum of intermediate ***B1*** (CD_2Cl_2, r.t.).

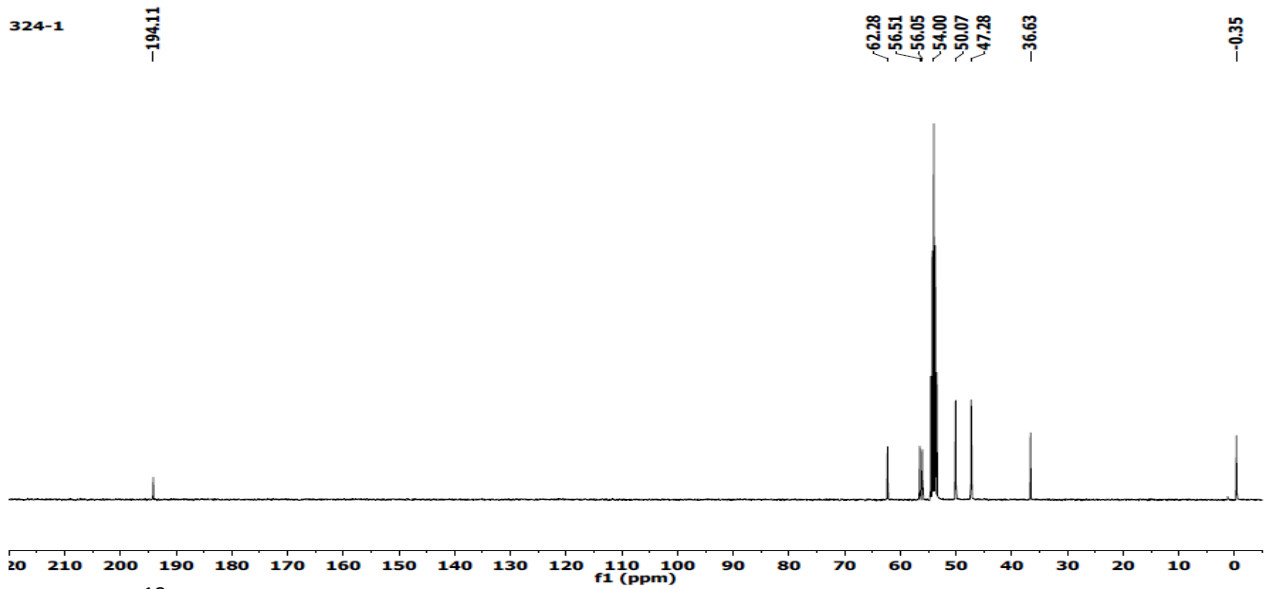


Figure 2b. ^{13}C NMR spectrum of intermediate ***B1*** (CD_2Cl_2, r.t.).

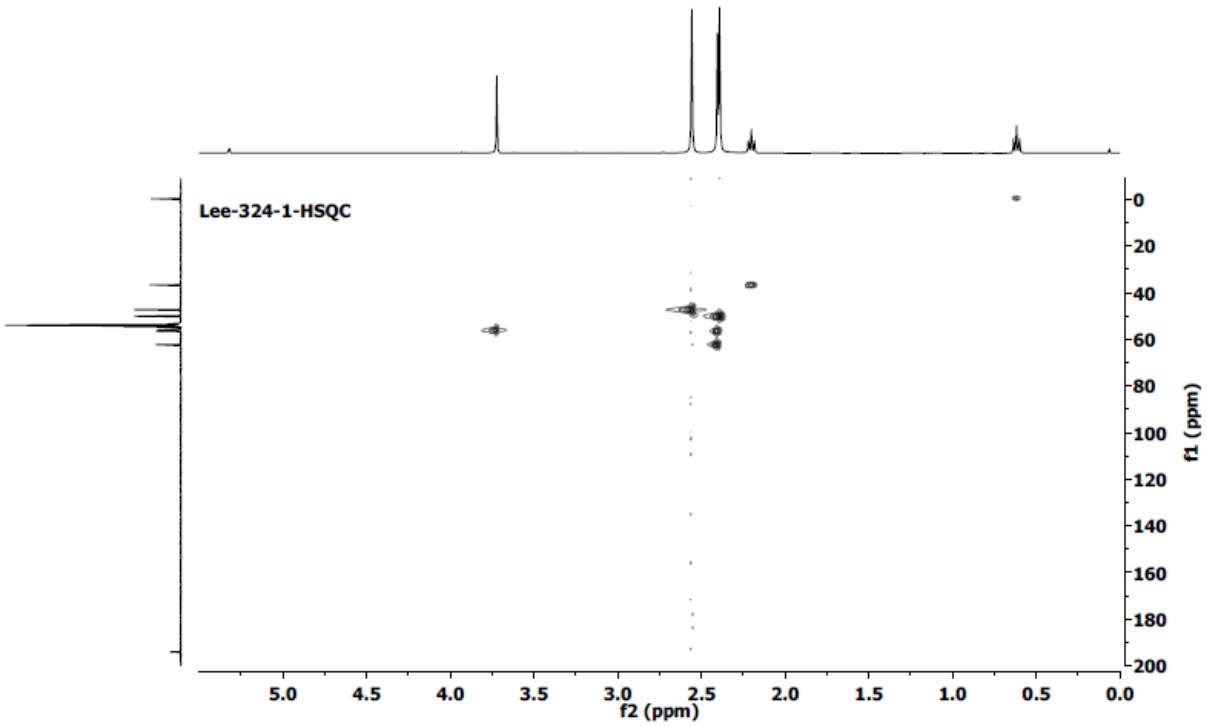


Figure 2c. ^{1}H-^{13}C-HSQC NMR spectrum of intermediate ***B1*** (CD_2Cl_2, r.t.).

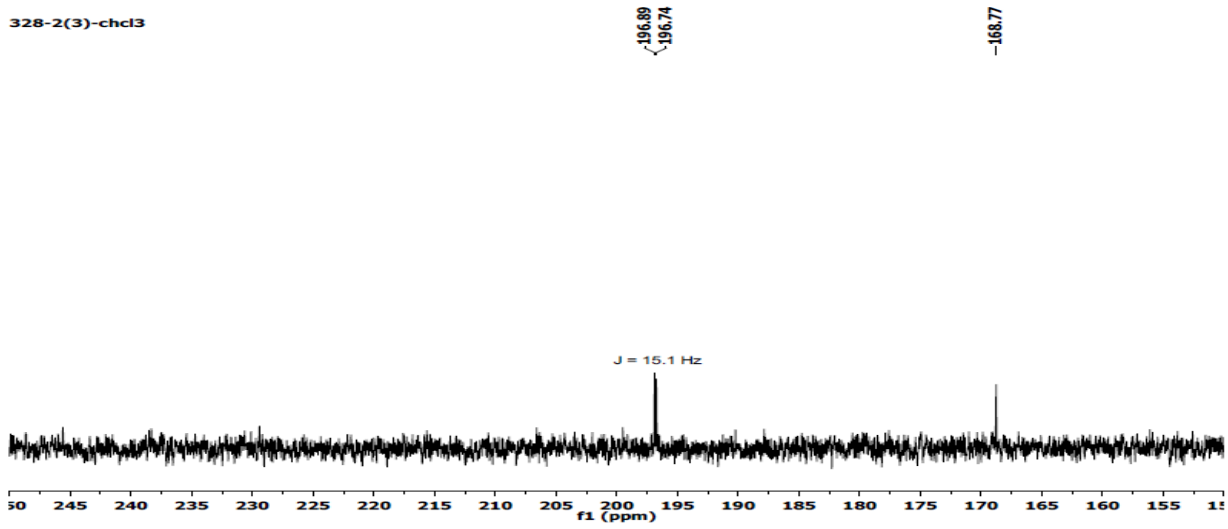


Figure 2d. ^{13}C NMR of carbonyl (*C*=*O*) resonance of [dppe-Ni($CH_2CH_2COOCH_3$)(OTf)] and methyl acrylate (CD_2Cl_2, r.t.).

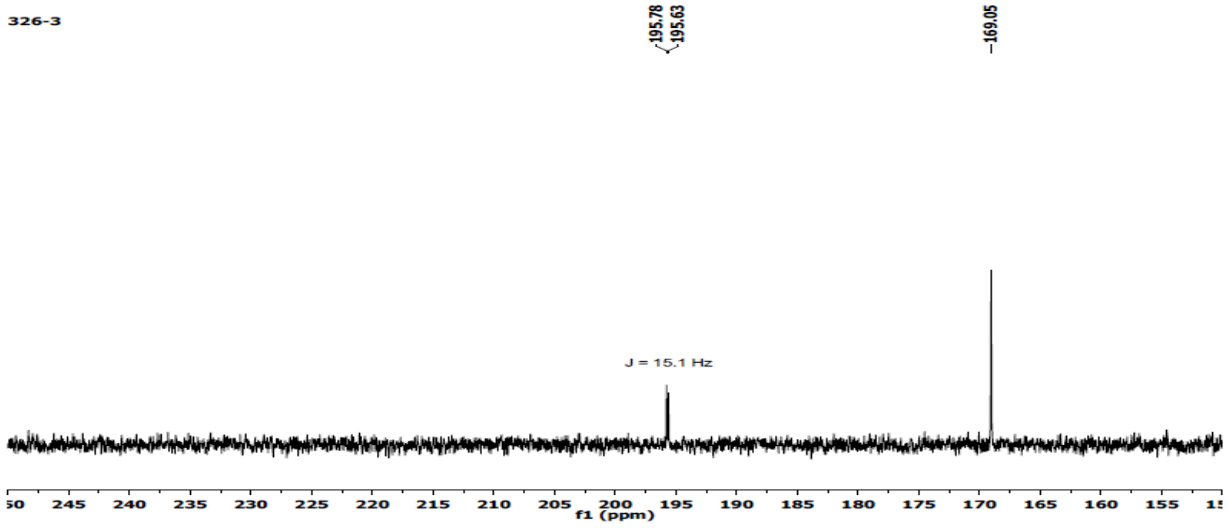


Figure 2e. ^{13}C NMR of carbonyl (*C*=*O*) resonance of [dppp-Ni($CH_2CH_2COOCH_3$)(OTf)] and methyl acrylate (CD_2Cl_2, r.t.).

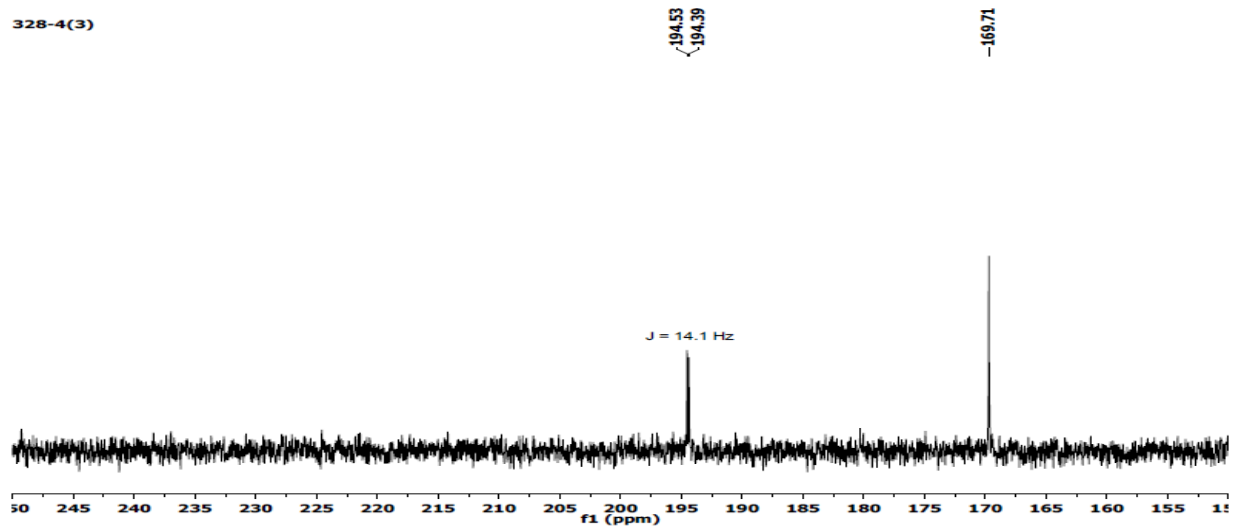


Figure 2f. ^{13}C NMR of carbonyl (*C*=*O*) resonance of [dppb-Ni($CH_2CH_2COOCH_3$)(OTf)] and methyl acrylate (CD_2Cl_2, r.t.).

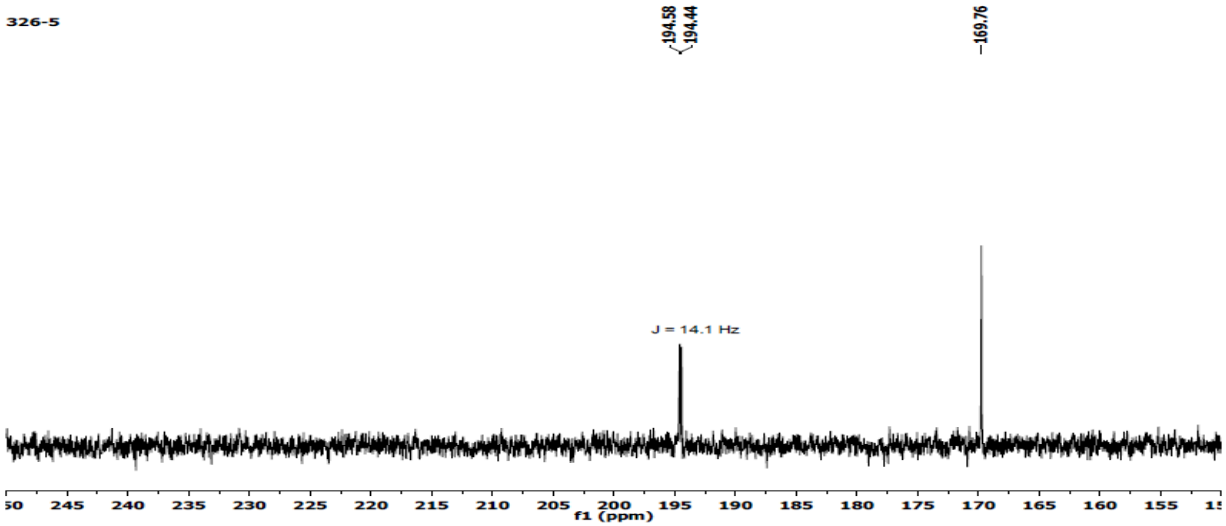


Figure 2g. ^{13}C NMR of carbonyl (*C*=*O*) of [dtbpe-Ni($CH_2CH_2COOCH_3$)(OTf)] and methyl acrylate (CD_2Cl_2, r.t.).

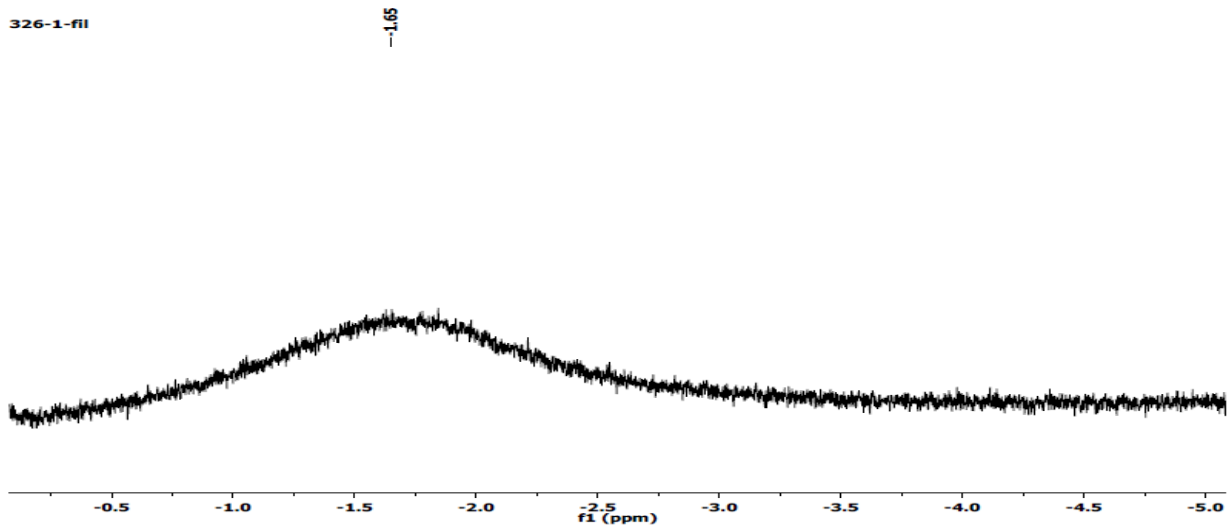


Figure 2h. ^{1}H NMR of Ni-H resonance of [tmeda-Ni(H)(OTf)] (CD_2Cl_2, r.t.).

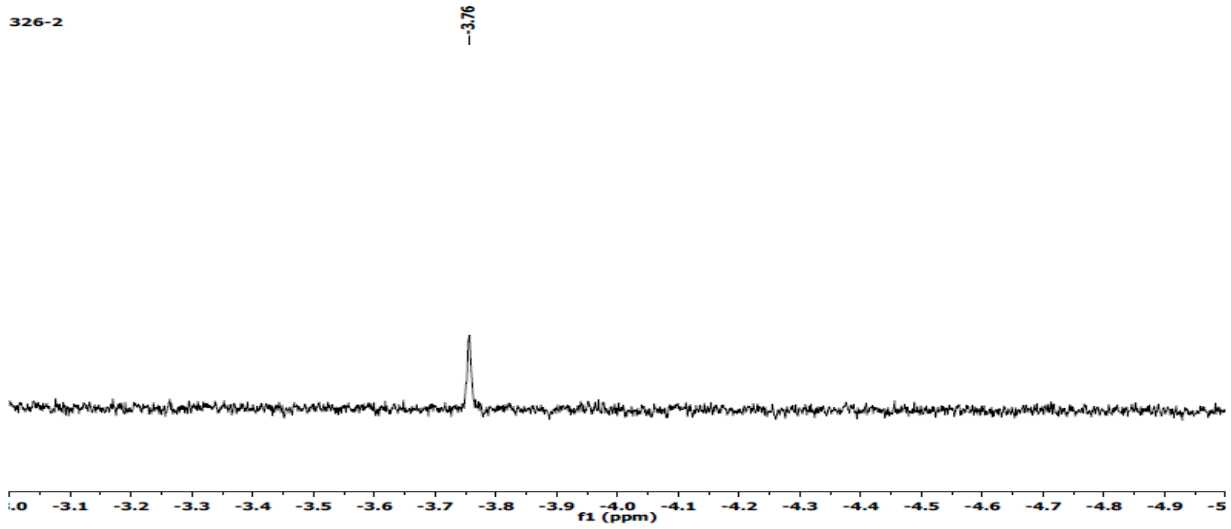


Figure 2i. ^{1}H NMR of Ni-H resonance of [dppe-Ni(H)(OTf)] (CD_2Cl_2, r.t.).

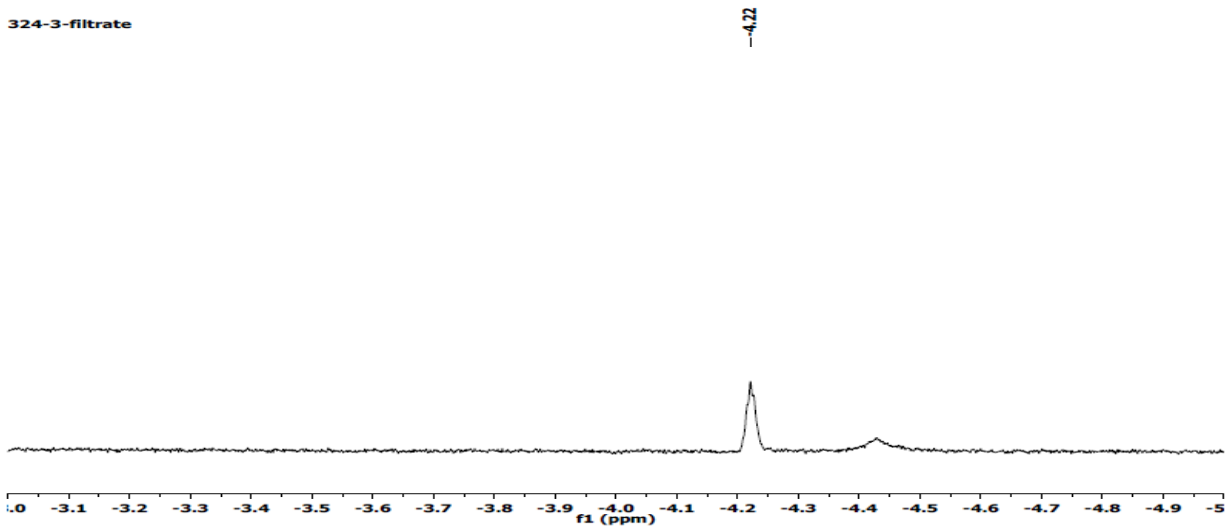


Figure 2j. ^{1}H NMR of Ni-H resonance of [dppp-Ni(H)(OTf)] (CD_2Cl_2, r.t.).

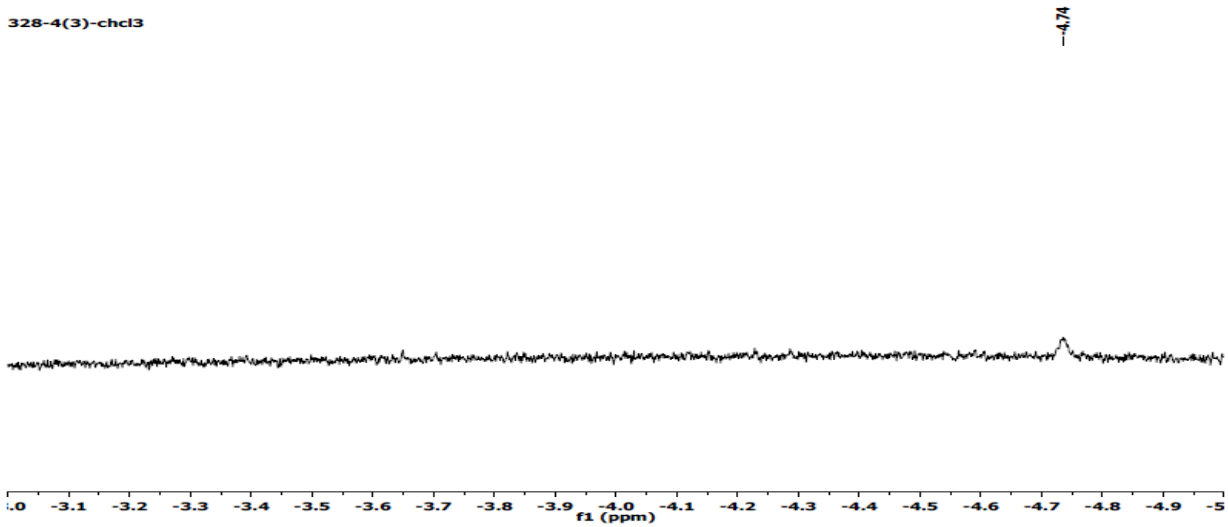


Figure 2k. ^{1}H NMR of Ni-H resonance of [dppb-Ni(H)(OTf)] (CD_2Cl_2, r.t.).

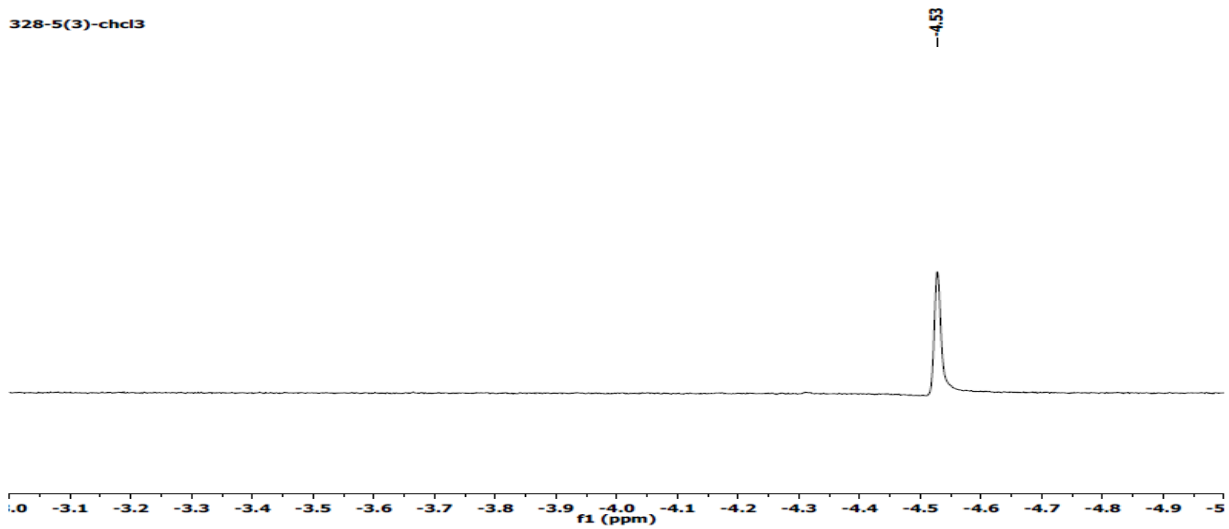


Figure 2l. ^{1}H NMR of Ni-H resonance of [dtbpe-Ni(H)(OTf)] (CD_2Cl_2, r.t.).

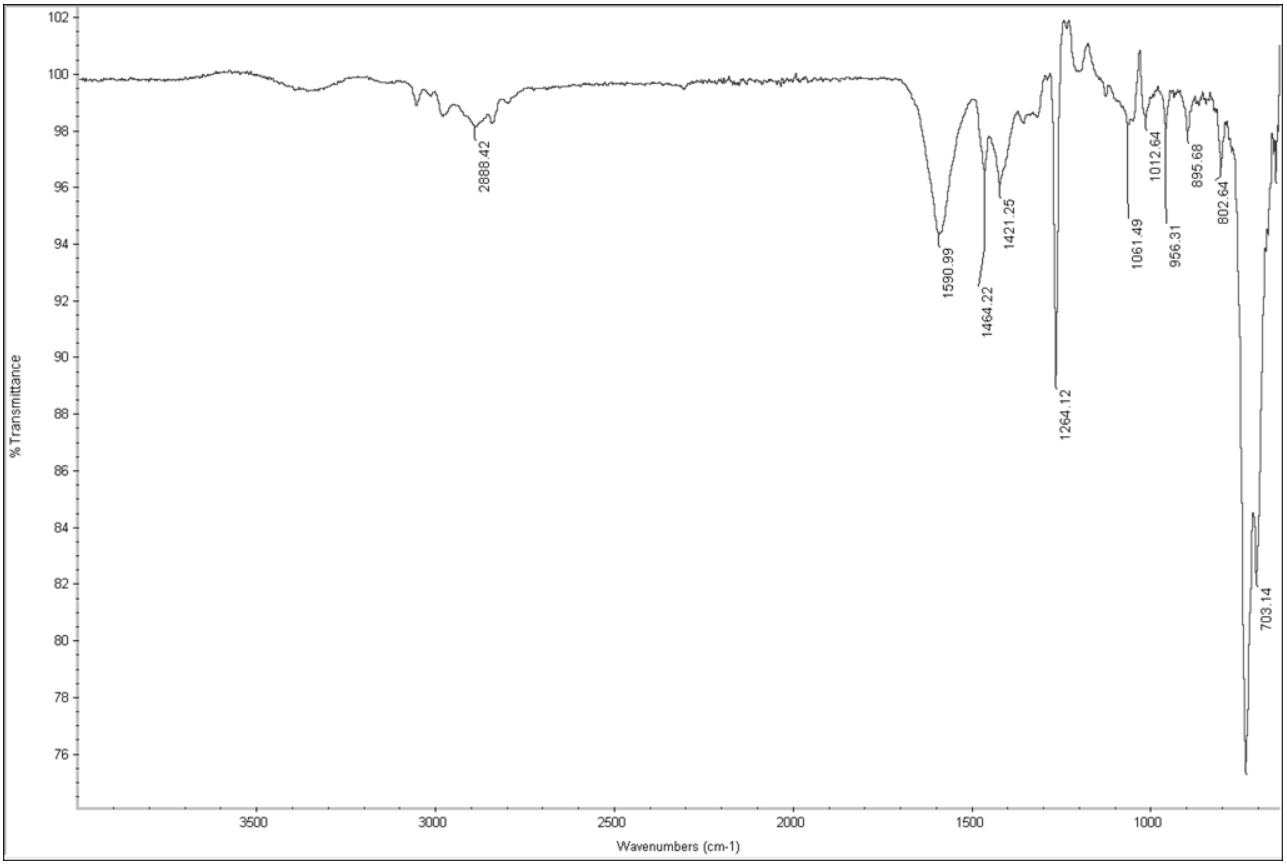


Figure 2m. ATR-FTIR spectrum of nickelalactone ***A1*** in dichloromethane, $\nu_{(C=O)}$ = 1591 cm^{-1}.

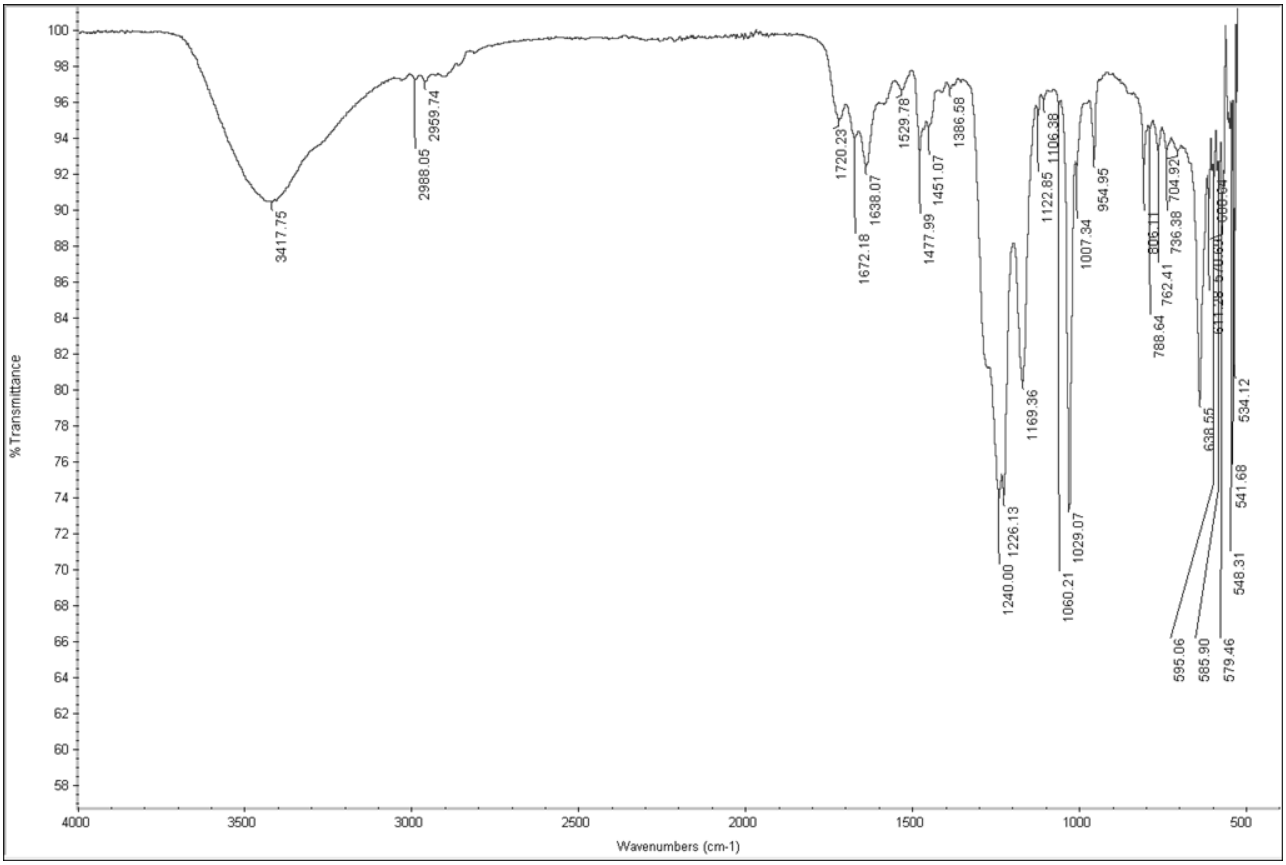


Figure 2n. ATR-FTIR spectrum of reaction mixure after addition of 4 mol. equiv. methyl triflate into ***A1*** in dichloromethane, $\nu_{(C=O)}$ of methyl acrylate = 1720 cm^{-1}, $\nu_{(C=O)}$ of intermediate = 1638, 1672 cm^{-1}.

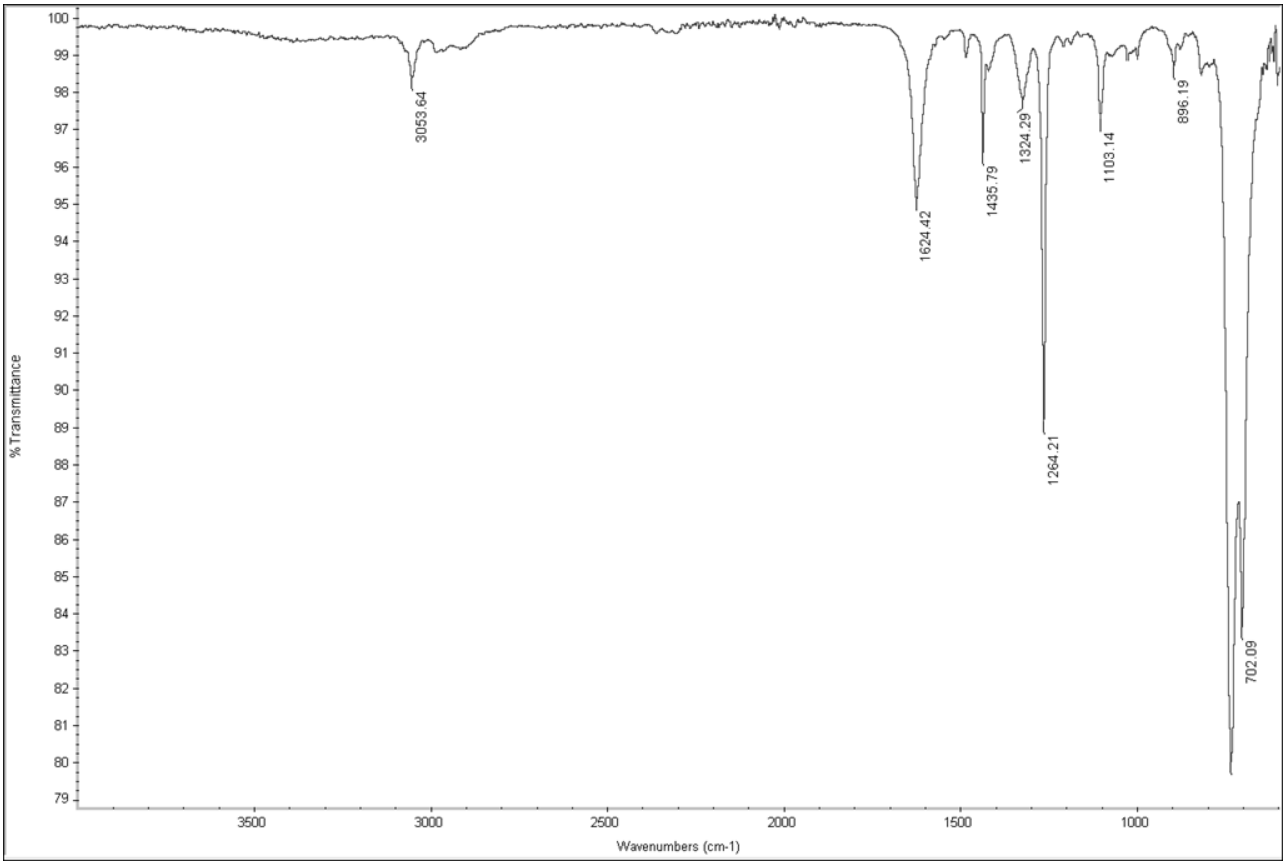


Figure 2o. ATR-FTIR spectrum of nickelalactone ***A2*** in dichloromethane, $\nu_{(C=O)}$ = 1624 cm^{-1}.

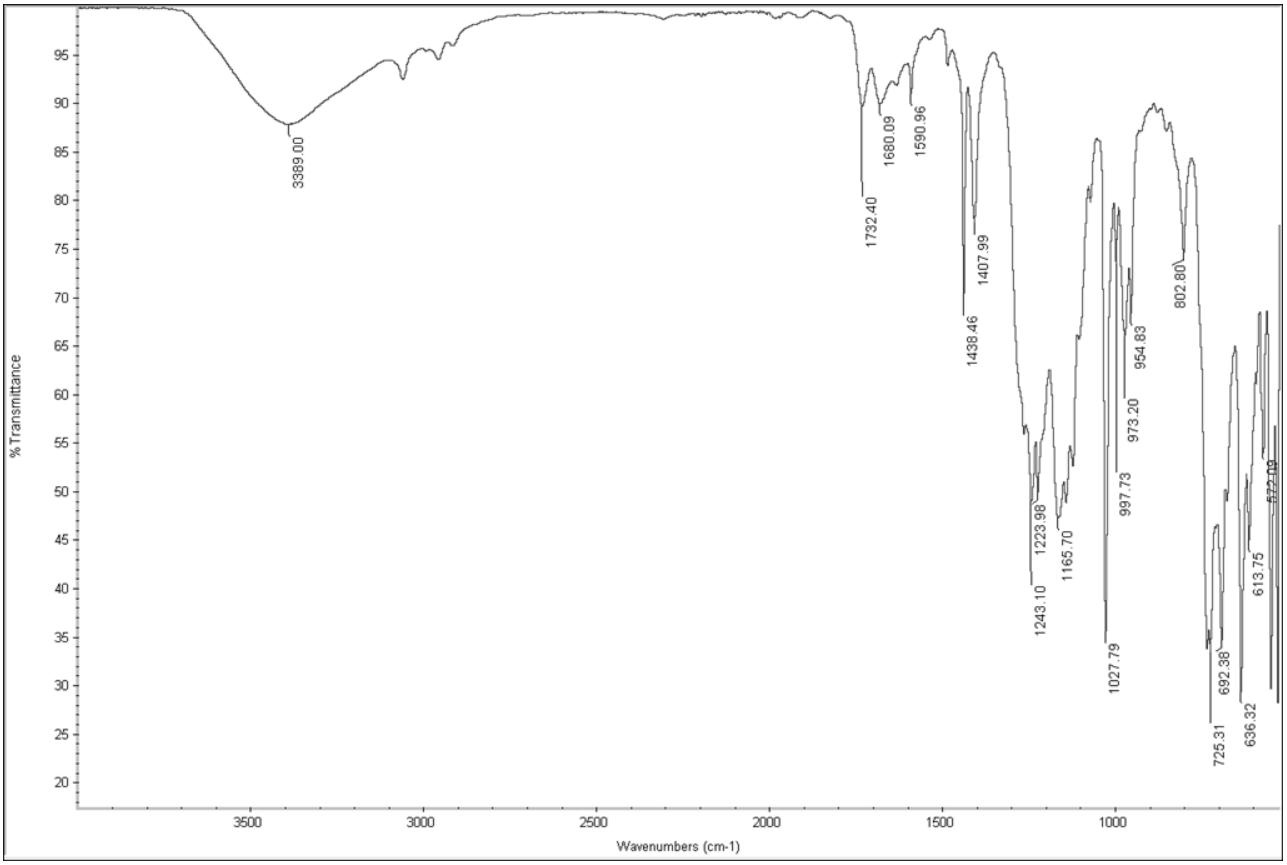


Figure 2p. ATR-FTIR spectrum of reaction mixure after addition of 4 mol. equiv. methyl triflate into ***A2*** in dichloromethane, $\nu_{(C=O)}$ of methyl acrylate = 1732 cm^{-1}, $\nu_{(C=O)}$ of intermediate = 1680 cm^{-1}.

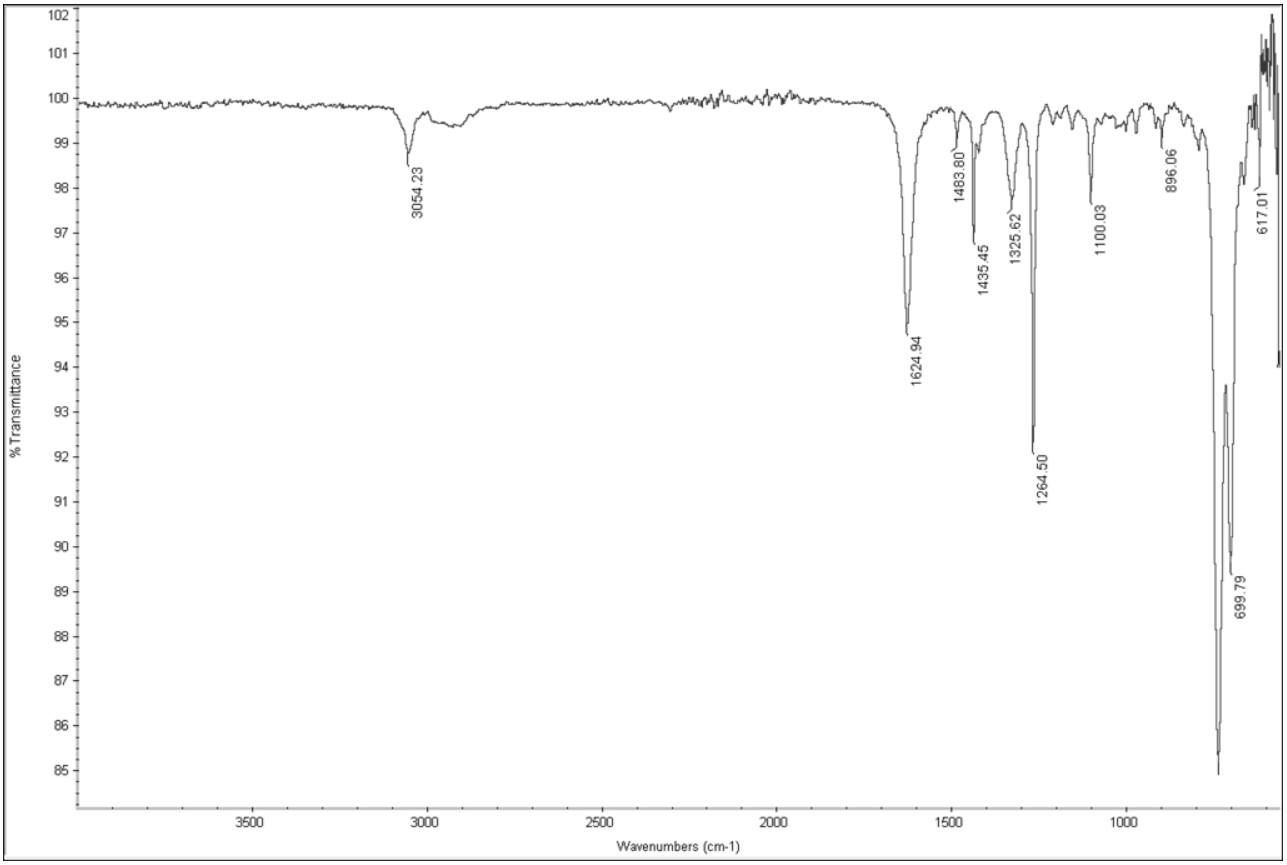


Figure 2q. ATR-FTIR spectrum of nickelalactone ***A3*** in dichloromethane, $\nu_{(C=O)}$ = 1625 cm^{-1}.

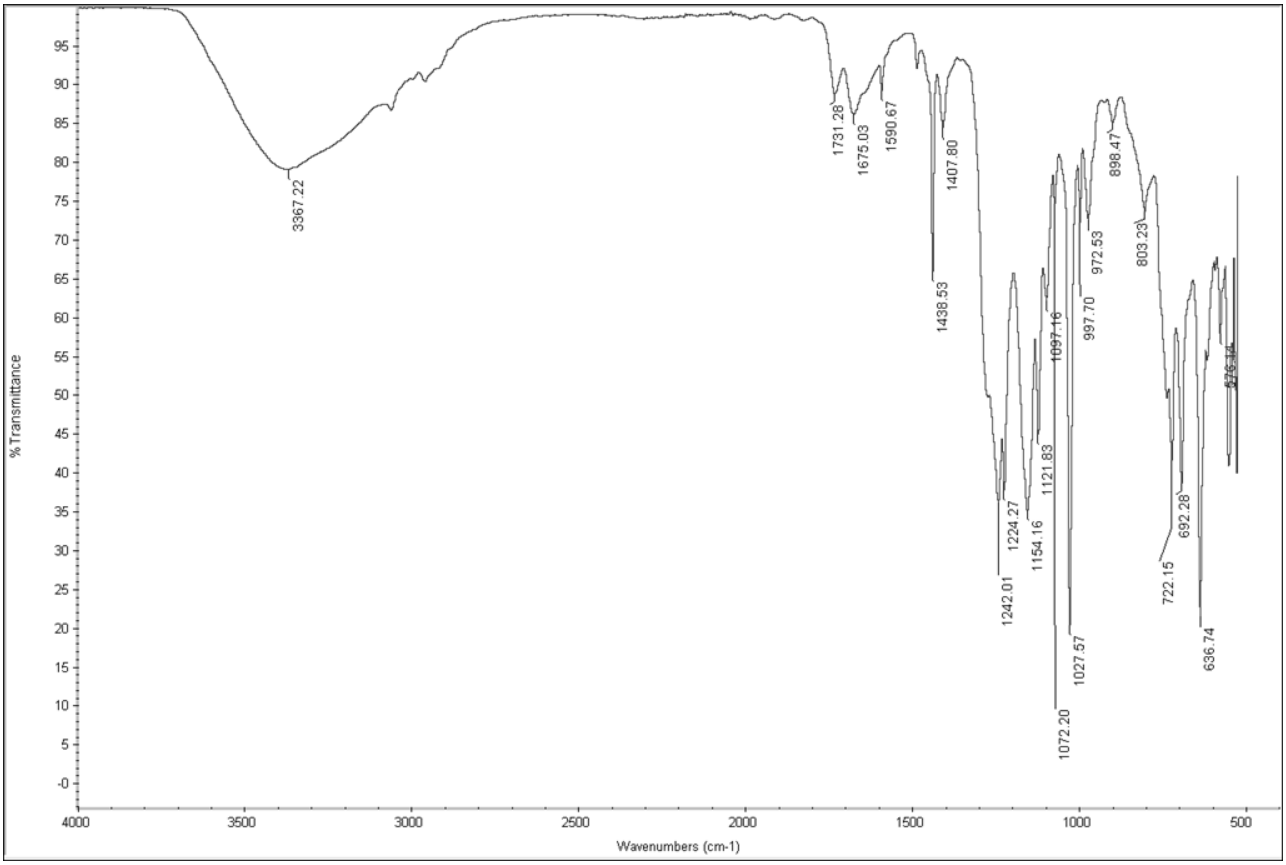


Figure 2r. ATR-FTIR spectrum of reaction mixure after addition of 4 mol. equiv. methyl triflate into ***A3*** in dichloromethane, $\nu_{(C=O)}$ of methyl acrylate = 1731 cm^{-1}, $\nu_{(C=O)}$ of intermediate = 1675 cm^{-1}.

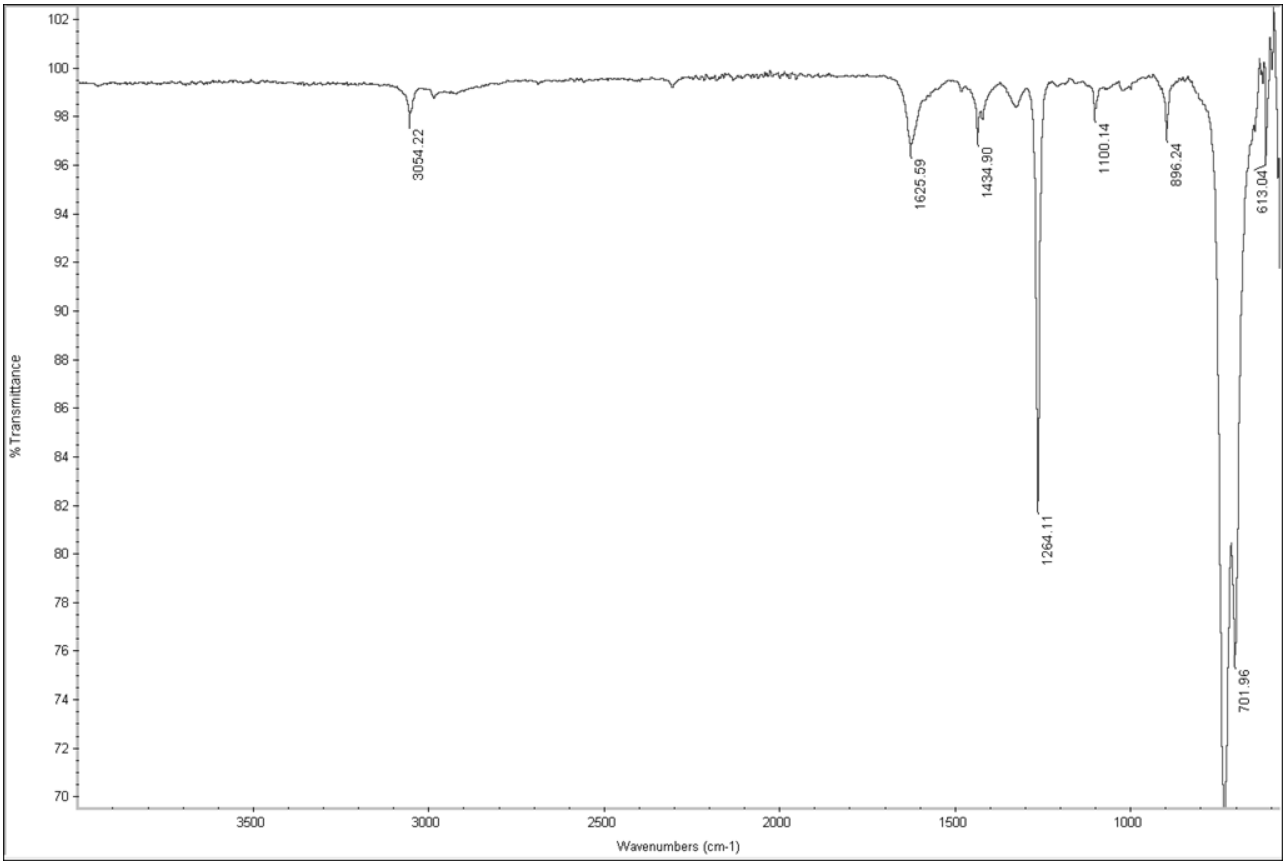


Figure 2s. ATR-FTIR spectrum of nickelalactone ***A4*** in dichloromethane, $\nu_{(C=O)}$ = 1626 cm^{-1}.

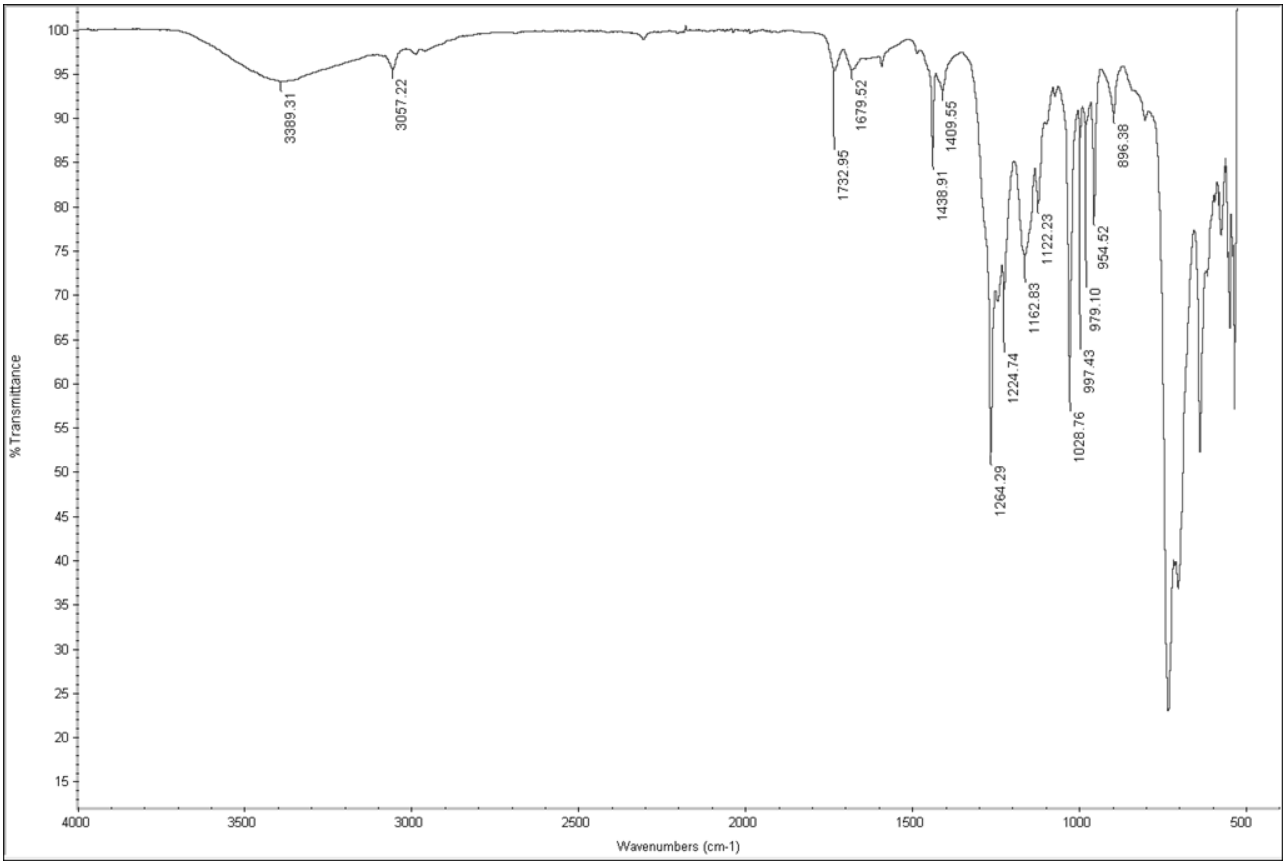


Figure 2t. ATR-FTIR spectrum of reaction mixure after addition of 4 mol. equiv. methyl triflate into ***A4*** in dichloromethane, $\nu_{(C=O)}$ of methyl acrylate = 1733 cm^{-1}, $\nu_{(C=O)}$ of intermediate = 1680 cm^{-1}.

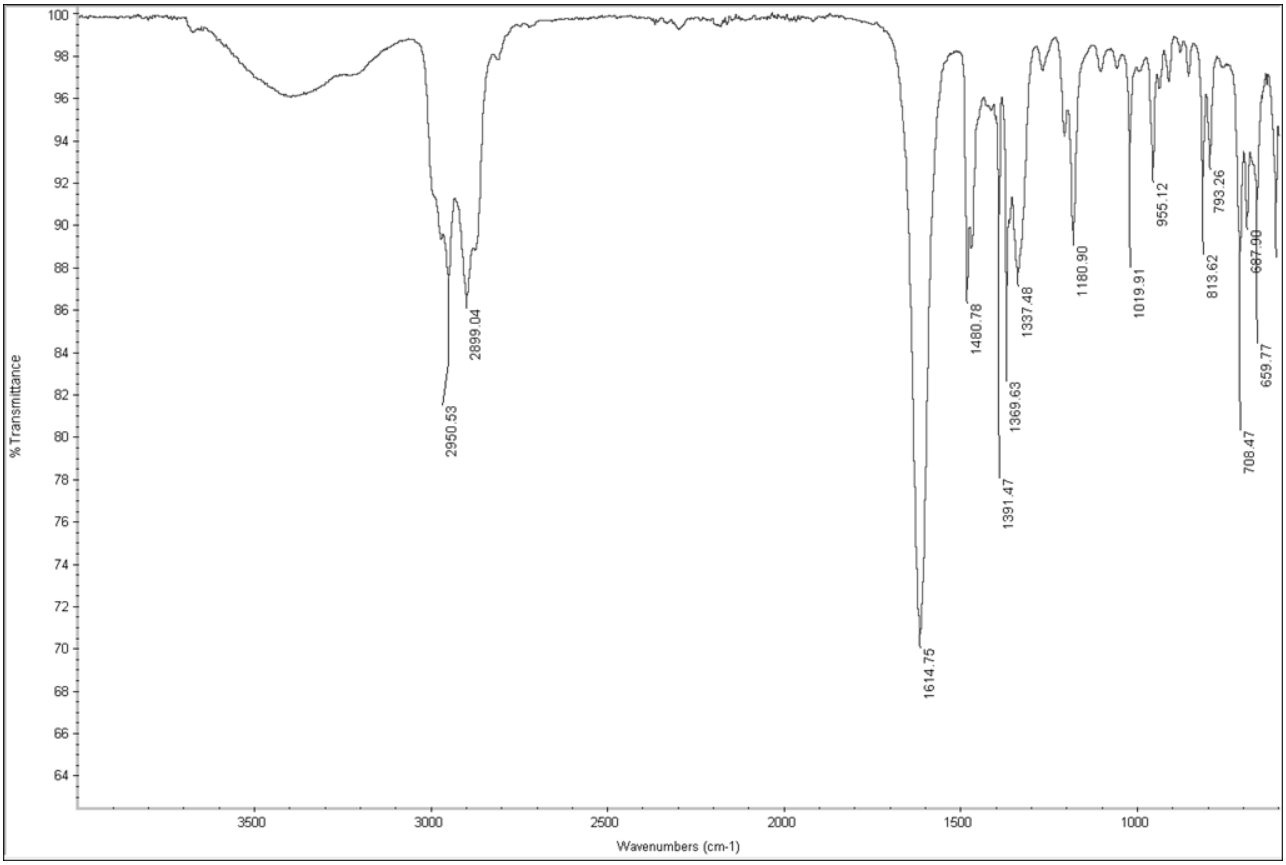


Figure 2u. ATR-FTIR spectrum of nickelalactone ***A5*** in dichloromethane, $\nu_{(C=O)}$ = 1615 cm^{-1}.

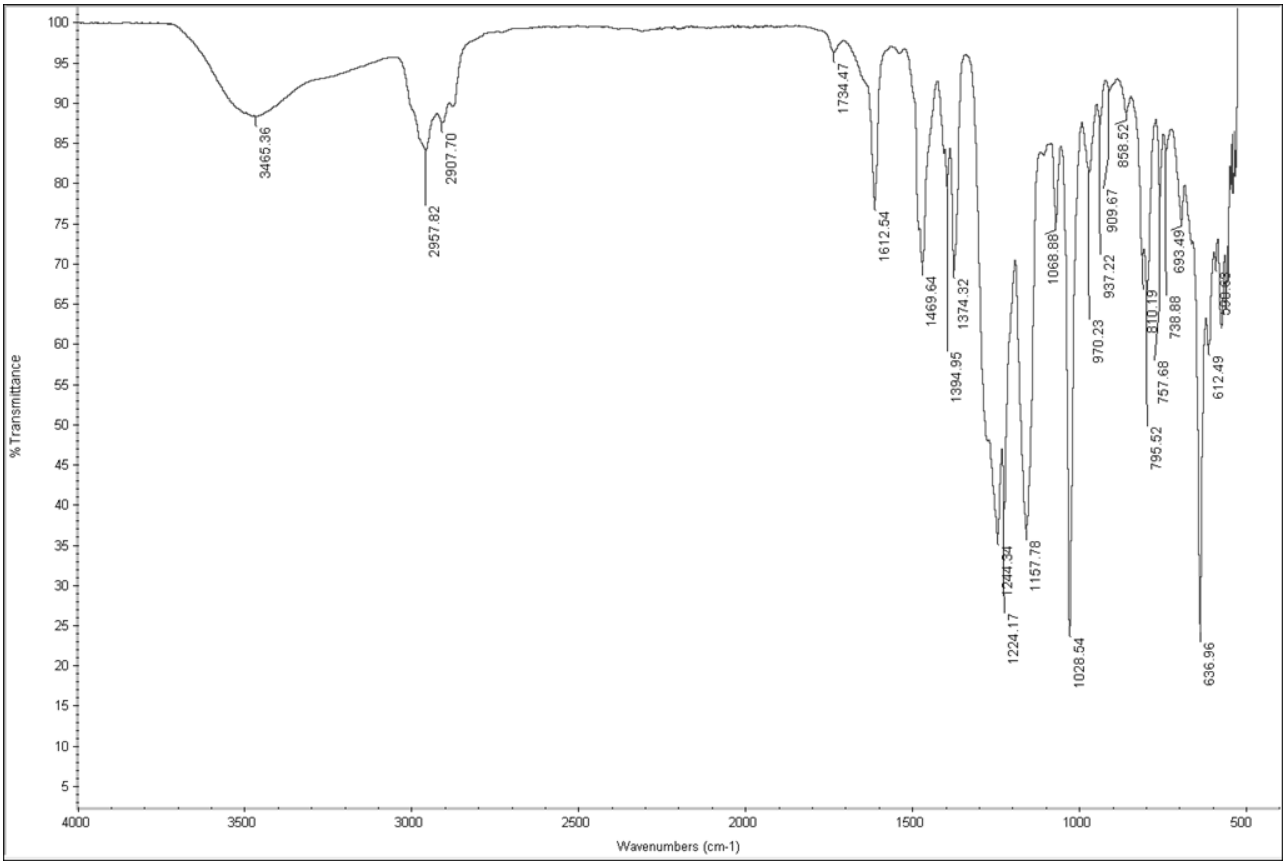


Figure 2v. ATR-FTIR spectrum of reaction mixure after addition of 4 mol. equiv. methyl triflate into ***A5*** in dichloromethane, $\nu_{(C=O)}$ of methyl acrylate = 1735 cm^{-1}.

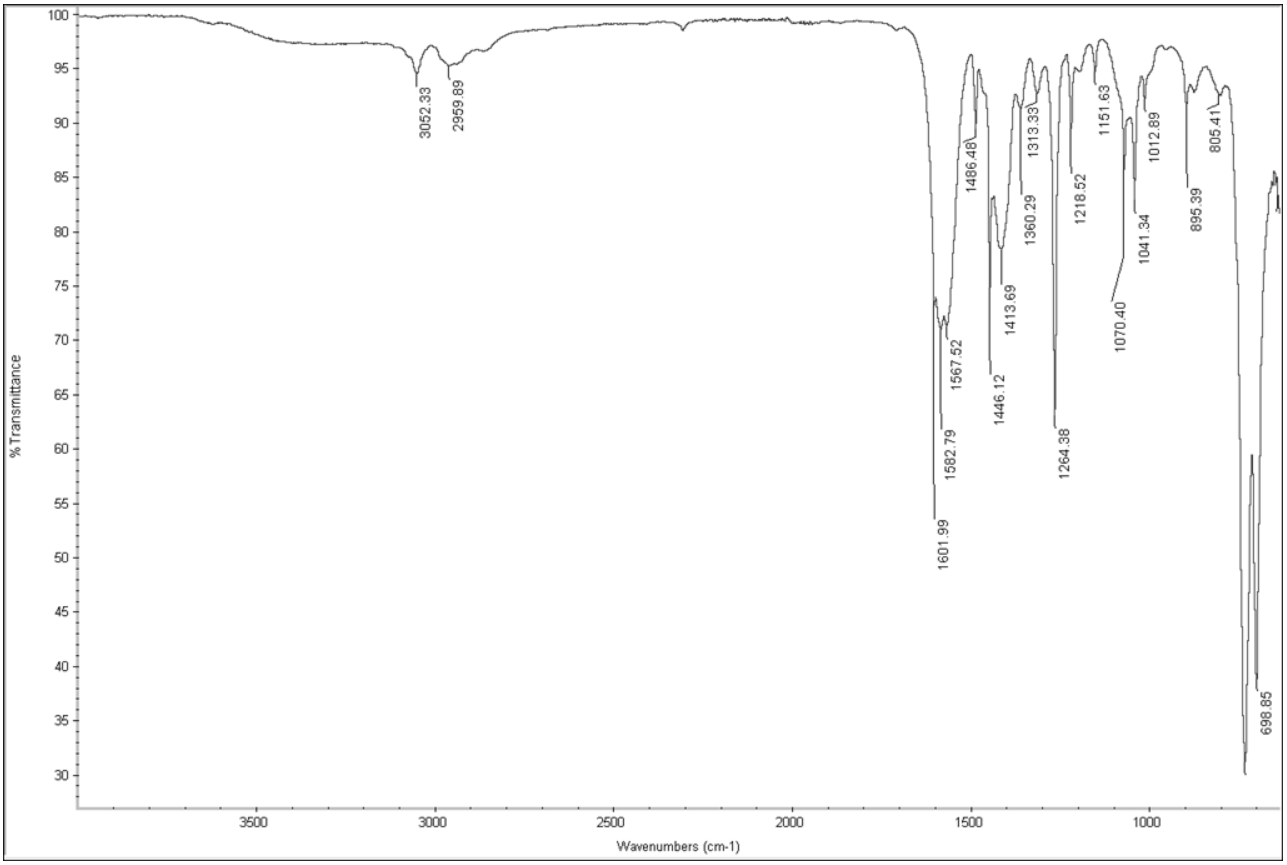


Figure 2w. ATR-FTIR spectrum of nickelalactone ***A6*** in dichloromethane, $\nu_{(C=O)}$ = 1602 cm^{-1}.

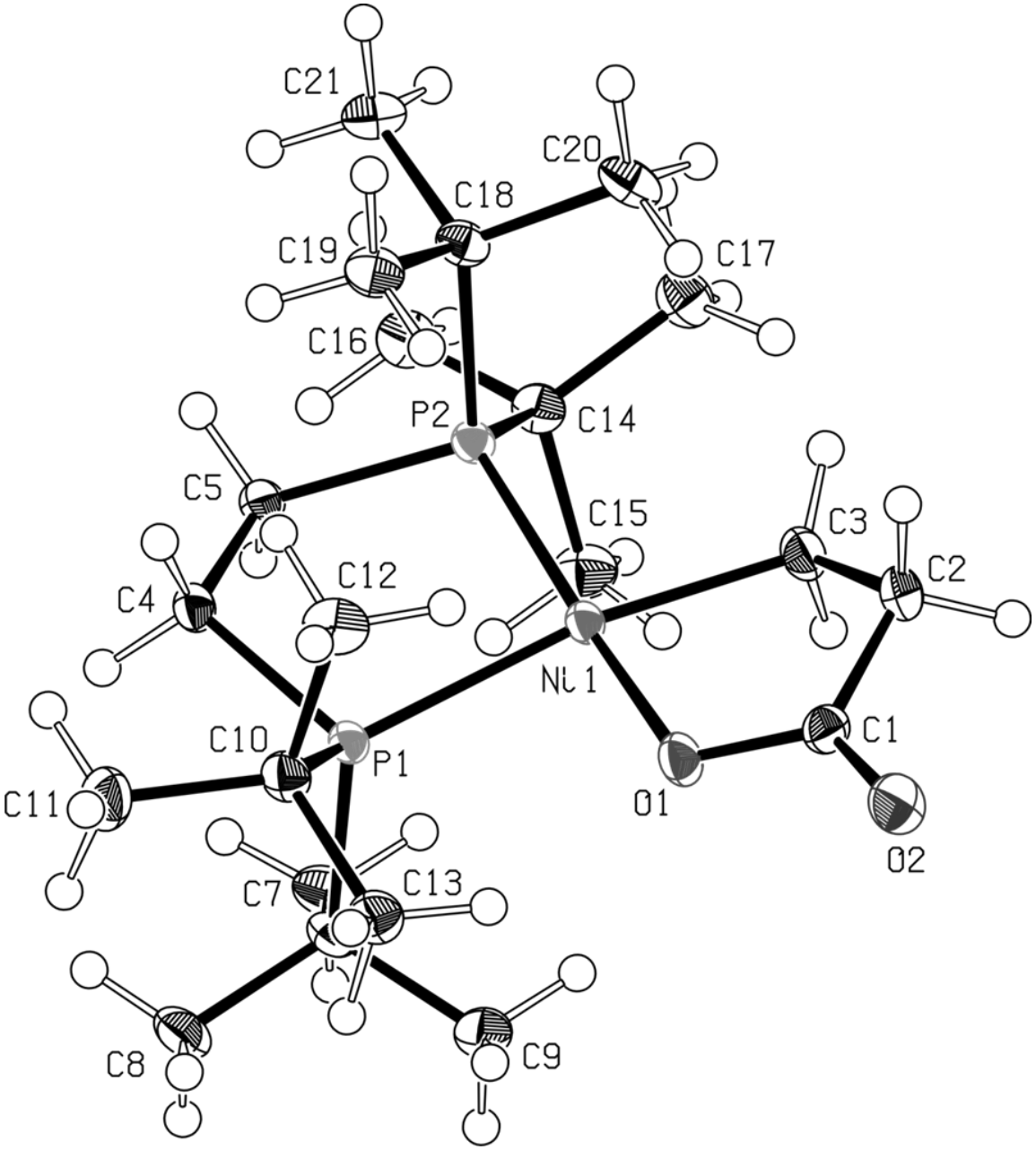


Figure 2x. ORTEP view of the structure of dtbpe-nickelactone ***A5***.

Selected bond lengths (Å) and angles (°): Ni(1)–O(1) 1.8931(14), Ni(1)–C(3) 1.958(2), Ni(1)–P(1) 2.2493(5), Ni(1)–P(2) 2.1617(5)), P(1)–Ni(1)–O(1) 90.18(4)), P(2)–Ni(1)–C(3) 95.13(6)), P(1)–Ni(1)–P(2) 90.80(2)), O(1)–Ni(1)–C(3) 85.04(7)), P(1)–Ni(1)–C(3) 170.33), P(2)–Ni(1)–O(1) 171.86).

Table 2a. X-ray single crystal structure data for nickelalactone *A5*.

Compound Name	**(dtbpe)Nickelalactone**
formula	$C_{21}H_{44}P_2O_2Ni$
M_r (g/mol)	534.12
Crstal description	orange fragment
Crystal dimensions (mm^3)	0.23 x 0.43 x 0.50
Temperature (K)	123
crystal system, space group	triclinic, P-1
a(Å)	9.4567(3)
b(Å)	10.9552(3)
c(Å)	12.9491(4)
a(°)	95.1504(14)
b(°)	96.6068(15)
g(°)	90.1289(14)
V($Å^3$)	1327.13(7)
Z	2
d_{calc} (g/cm^3)	1.337
F_{000}	572
m (mm^{-1})	1.069
Index ranges (±h, ±k, ±l)	-11/11, -13/13, -15/15
q ranges (°)	1.6 – 25.4
Collected reflections	52388
Unique reflections [all data]	4898
R_{int} / R_s	0.0352 / 0.0191
Unique reflections [t_0>2 s(t_0)]	3920
Data/Restraints/Parameter	4897/0/446
GoF (on F^2)	1.09
R_1/*w*R_2 [t_0>2 s(t_0)]	0.0280/0.0674
R_1/*w*R_2 [all data]	0.7934/-0.6170
Max./Min. residual electron density	0.98/-0.55

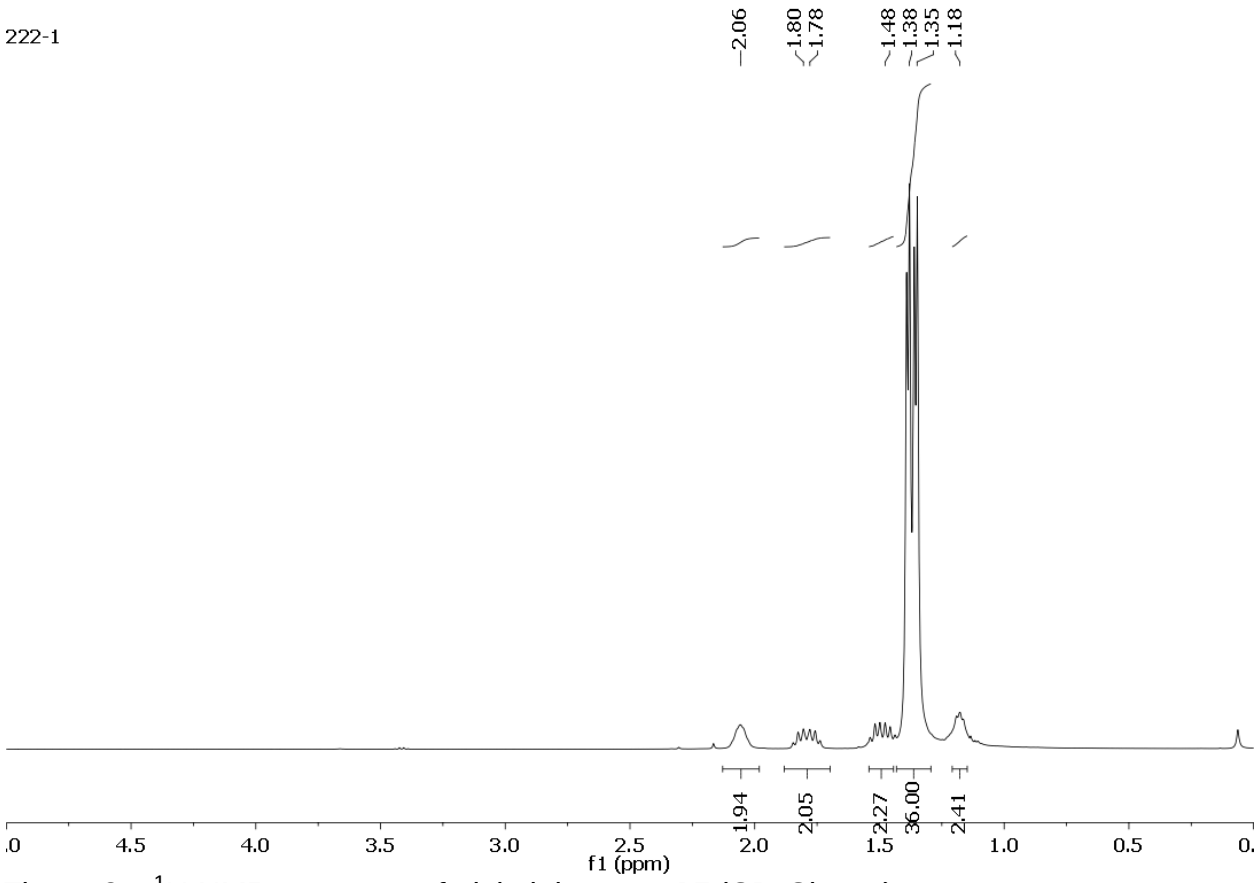


Figure 2y. ^{1}H NMR spectrum of nickelalactone ***A5*** (CD_2Cl_2, r.t.).

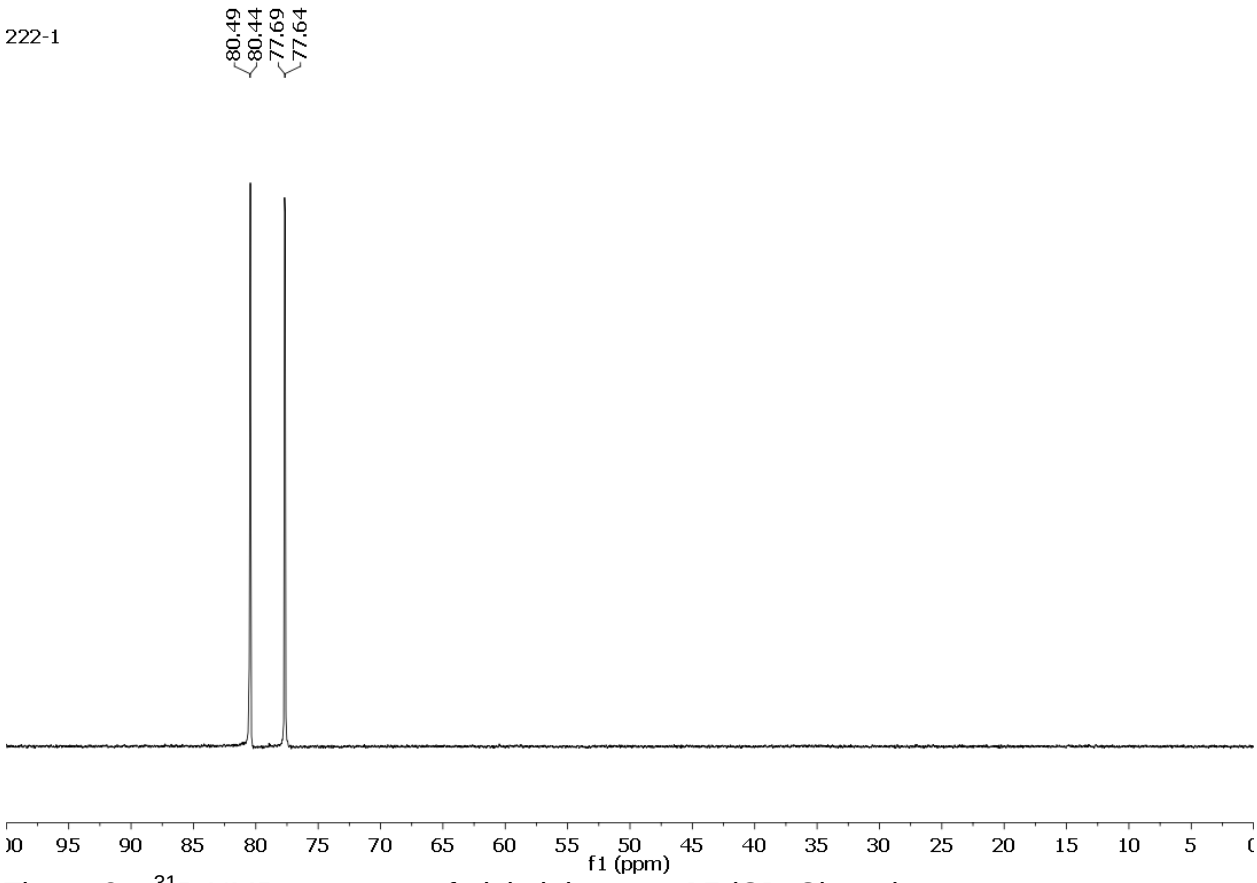


Figure 2z. ^{31}P NMR spectrum of nickelalactone ***A5*** (CD_2Cl_2, r.t.).

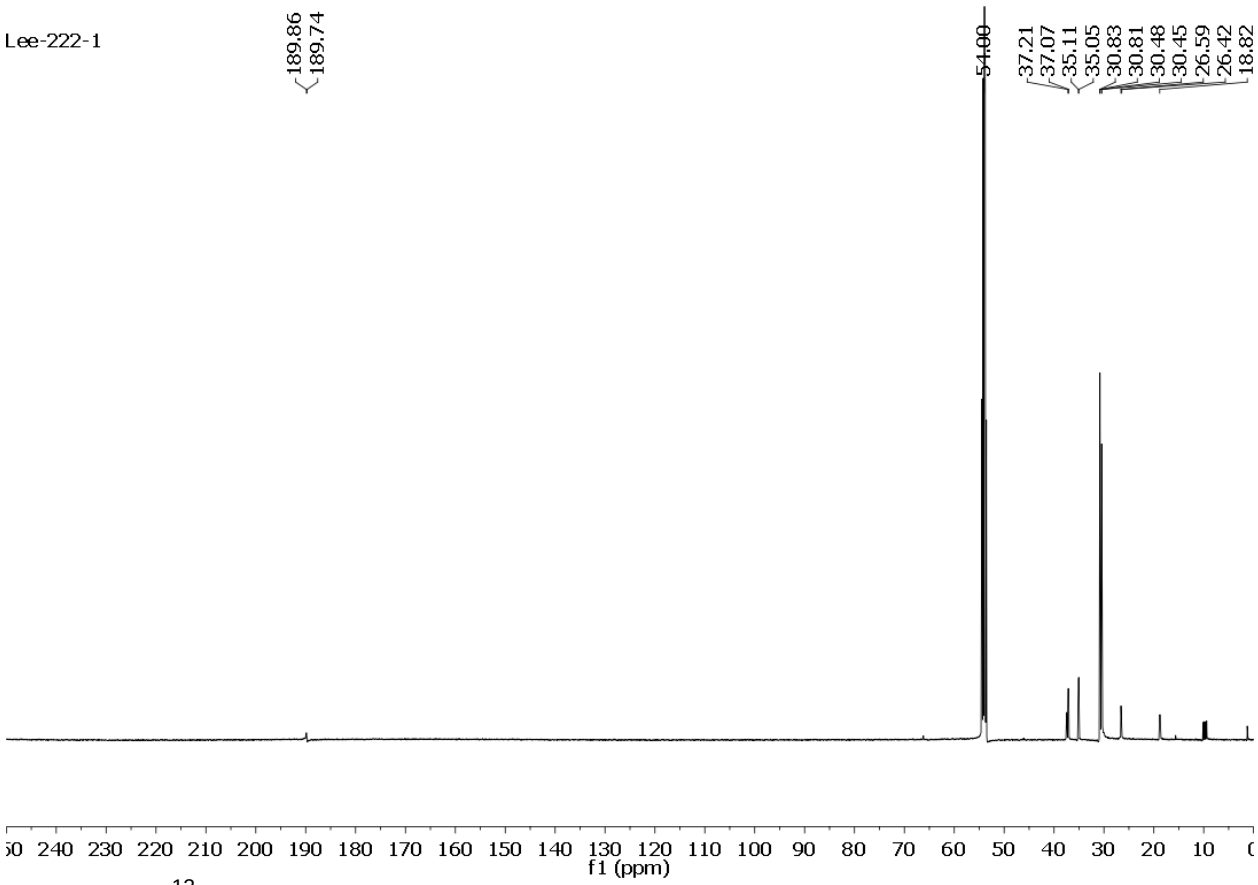


Figure 2za. ^{13}C NMR spectrum of nickelalactone ***A5*** (CD_2Cl_2, r.t.).

8. Curriculum Vitae

Personal Information	
Name:	Sin Ying Tina Lee
Date of Birth:	05-Sep-1984
Place of Birth:	Singapore
Education	
01/1990 – 12/1996	Red Swastika School, Singapore
01/1997 – 12/2000	Ngee Ann Secondary School, Singapore
01/2001 – 12/2002	Temasek Junior College, Singapore
University	
08/2003 – 06/2007	National University Singapore Bachelor of Science (Honors) Major: Chemistry, Minor: Management
08/2007 – 04/2009	German Institute of Science & Technology Master of Science in Industrial Chemistry
08/2009 – 12/2012	PhD in organometallic chemistry at the Technical University Munich, supervised by Prof. Dr. Kühn, Department of Molecular Catalysis.
Internship & Research Exchange	
06/2008 – 02/2009	Internship at BASF SE, Ludwigshafen, "Synthesis of Biopolymers"
11/2011 – 10/2012	Research Exchange at KAUST, Saudi Arabia
Publication	

1. Lee, S. Y. T.; Cokoja, M.; Drees, M.; Li, Y.; Mink, J.; Herrmann, W. A.; Kühn, F. E., "Transformation of Nickelalactones to Methyl Acrylate: On the Way to a Catalytic Conversion of Carbon Dioxide" *ChemSusChem* **2011**, *4* (9), 1275-1279.