

Synthesis and Characterization of NCN Pincer Nickel Complexes

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Abstract

In this work, a series of nickel NCN complexes and ligands have been synthesized with the goal of determining whether they can perform so-called CO₂-insertion reactions into Ni-C bonds. So far, only the synthesis of the Ni-Br precursor complexes to the previously mentioned Ni-C complexes have been synthesized. Attempts to synthesize the target complexes have been made and are described herein. Some ideas for future research are also presented.

Acknowledgements

Thank you, Professor Ola Wendt, for giving me the opportunity to do my thesis work in your group. I've had a lot of fun and I've learned a ton!

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Populärvetenskaplig sammanfattning

Koldioxid är ett kemiskt ämne som får mycket uppmärksamhet på grund av dess roll som växthusgas. *Carbon Capture* är ett koncept som går ut på att fånga koldioxid från atmosfären i fast form för att på så sätt avlägsna det och mildra de skadliga effekter som det har på klimatet. Koldioxid är på grund av sina starka dubbelbindningar mellan kol och syre synnerligen inert och det krävs ofta hårda reaktionsbetingelser för att gasen ska reagera med någonting. Tidigare forskning har resulterat i upptäckten att så kallade *pincer*-komplex, eller kniptångskomplex - en sorts metallkomplex där en metall och en organisk molekyl binder till varandra, kan agera som en katalysator och få koldioxid att enklare reagera med andra molekyler och bilda nya ämnen. De komplexen innehåller framför allt dyra och sällsynta ädelmetaller.

Det här arbetet har försökt undersöka huruvida kniptångskomplex som koordinerar till nickel med kväve, kol och kväve, NCN, har förmågan att få koldioxid att reagera med andra ämnen.

1. Introduction to Pincer Complexes and CO₂ Insertion

1.1 Pincer Complexes and Background

Chemistry involving pincer-type complexes is a field within organometallic chemistry that attracts more and more interest. Such complexes are part of research in a wide array of areas such as activation of strong bonds, homogenous catalysis, enantioselective organic transformations and supported materials.^{1,2} Their synthesis can be achieved in many ways, including C-H activation, oxidative addition and transmetalation³. The very first synthesis of what would later be referred to as a pincer complex was published in 1976 by Bernard Shaw⁴ and described the synthesis of complexes using so called PCP pincer ligands chelated with nickel, palladium, platinum, rhodium and iridium. The background to the discovery was an attempt to generate bulky tridentate *trans*-phosphine ligands that would bind to metals where bulky phosphine monodentate ligands would not. Since the coining of the phrase “pincer ligands” in 1989 by van Koten, Pincer complexes have gained an increasing amount of interest due to their great thermal stability and the numerous options that exist when choosing among different substituents, which is very useful in homogenous catalysis where harsh conditions can be required.⁵

In this diploma work, pincer ligand nomenclature will be used frequently, hence a short guide follows with a visual representation in *Figure 1*.

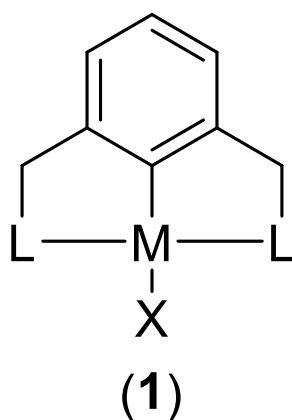


Figure 1. General example of a pincer complex.

The above example would be named LCL since the binding atoms are denoted, in order from right-to-left or left-to-right L, C, and L. However, not all ligands include an aromatic moiety with a binding sp² carbon atom, and not all ligands are symmetrical. In *Figure 2* below, a few examples of different types of pincer complexes are given with a short explanation.

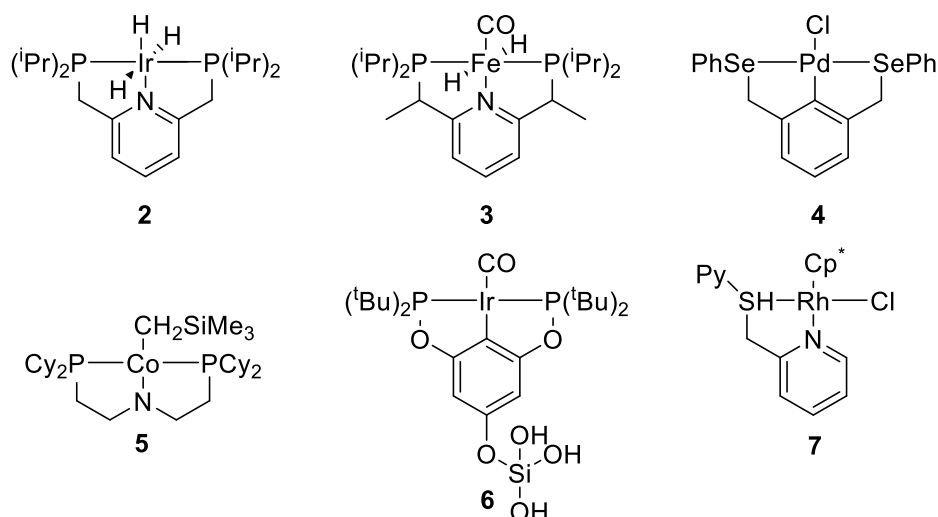


Figure 2. Different types of pincer complexes used in research since the discovery of pincer complexes.

Compound **2** is a PNP Ir complex used for catalytic reduction of CO_2 ⁶; **3** is a PNP Fe complex for selective hydrogenation of aldehydes⁷; **4** is a SeCSe Pd complex for direct boronation of allylic alcohols⁸; **5** is a PNP Co complex for hydrogenation alkenes, imines and ketones⁹; **6** is a POCOP Ir complex immobilized on silica used for LOHC hydrogen generation¹⁰; and **7** is a SNCp* half-pincer complex for transfer hydrogenation/oxidation of ketones/alcohols.¹¹

These are just some examples of various pincer complexes. Practically all *d* block metals can be used, with a variety of symmetric and asymmetric ligands. Complexes **2-6** above are symmetric, but if one were to change one of the phosphorous atoms in complex **2** for a nitrogen atom, the complex would be asymmetrical. Complex **7** is a so-called half-pincer complex since it only has one “side-arm”. Recently, pincer ligands have found use outside of the *d*-block chemistry, being employed in actinoid chemistry. Actinoids have similar size as lanthanoids but have access to a higher number of oxidation states, like *d*-block metals.² They are still scarcely used in catalysis but to mention a few uses, some ligands have served as selective extraction from nuclear waste and others in ring-opening polymerizations. The 5f orbitals of actinoids make their reactivity unique, however research is slow due to geopolitical constraints.¹²

1.2 Pincer Ligands and Reactivity

The special arrangement of the tridentate pincer ligands makes fine-tuning of the chemical properties possible by simple alterations on the ligand motif, such as exchanging *tert*-butyl groups for *iso*-propyl groups, or exchanging aromatic groups. One such example is presented above in *Figure 2* where **7** is reported to produce acetophenone in 85% yield, but exchanging the pyridine moiety for a phenyl raises the yield in the same process to 95%. After Shaw's synthesis of the first published pincer compounds in the 1970's, van Koten coined the term *pincer* in 1989⁵. Since then, the definition of a pincer complex have seen some development. They now state that the ligand must be *meridional* rather than *facial* (see *Figure 3* below). A definition in *Organometallic Chemistry* by Spessard and Miessler defines meridional as “three ligands arranged to define a plane through an octahedral complex” and facial as “three ligands occupy the same face of an octahedral complex”.

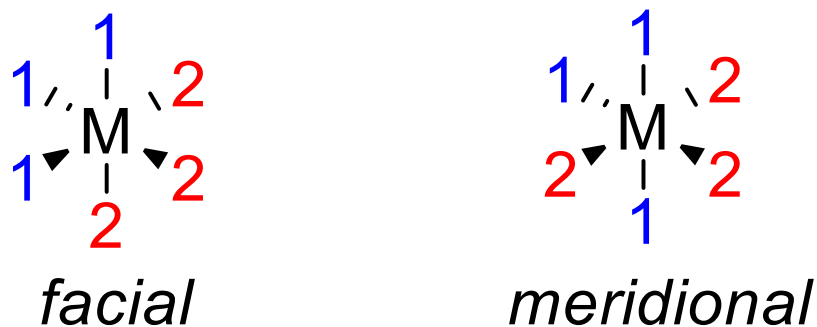


Figure 3. An illustration of the two possible isomers in an octahedral metal complex.

A great example of a ligands that allow for fine-tuning of properties, not only for pincer metal complexes but for all types of complexes, are phosphines. An introduction is given in Chapter 7 of *Organometallic Chemistry* by Spessard and Miessler¹³. The phosphine ligands, PR_3 , with a lone pair on the phosphorous atom, are known as so called σ donors and π acceptors.

To give a brief explanation to different kinds of donors in organometallic chemistry, σ type of bonds are characterized by orbitals interacting while pointing toward each other, much like covalent single bonds in organic chemistry. The simplest type of σ bond is one formed between two s orbitals, but other types of σ bonds are also possible, for example between sp^2 or sp^3 orbitals on carbon or nitrogen atoms and the d orbitals on a metal. σ donor ligands have an electron pair capable of binding to an empty or partly empty metal orbital.

In contrast to this, π bonds or in more general terms π interactions, are formed between parallel orbitals that interact off to the side. In organic chemistry, typical π bonds are formed by interactions of two p orbitals like in N_2 , CO_2 , or in ethene, C_2H_4 . In organometallics, the bond between a ligand and a metal typically occurs between p orbitals on the ligand and a d orbital on the metal. This type of interaction can occur in two different ways; there are π acceptor ligands and π donating ligands. In the case of π donating ligands, they donate electrons to the metal in a π fashion much like between σ donors and metals. In the case of π accepting ligands however, some ligands that act in a σ donating way also have the property of accepting electrons from the metal using suitable orbitals. Usually this is an empty p orbital on the ligand and a filled d orbital on the metal.

In other words, the substituents determine the electronic properties of the ligand, and this makes phosphines highly versatile as ligands, not only in the case of pincer complexes. In addition, the general size or bulkiness of the R groups determine much of the reactivity. In 1977 Tolman introduced the concept of *cone angles*¹⁴ to simplify selection of substituents on phosphine ligands. Bulky ligands with a large cone angle lead to a faster ligand dissociation rate than ligands with a smaller cone angle.

Phosphines are a common motif in pincer ligands¹⁵ but are not studied in this diploma work. However, phosphines are worth mentioning when discussing the so-called *trans effect*. This phenomenon is noted in substitution reactions involving metal complexes where ligands that exhibit a strong trans effect cause the ligands situated trans to themselves to have a weaker bond to the metal. In general, ligands that are strong σ donors and strong π acceptors have a high trans effect. Since phosphines have great variability in their steric and electronic properties, one can alter the size of the trans effect by exchanging the substituents¹³.

1.3 Properties and Applications

Exploration of pincer ligands did not really gain traction until the late 1990's, but since then the field has exploded and now the topic has seen a clear increase in the number of books² and articles¹⁵. One key characteristic of pincer complexes is that they are very robust. The most common application is within catalysis¹⁵ and here robustness is an important feature. When the area of interest is breaking or activating inert bonds, such as in CO₂ or N₂, harsh conditions are sometimes needed and the catalyst must be able to withstand such conditions without degradation.

When it comes to pincer complexes, due to their rigid nature they can be employed as catalysts in reactions that require harsh conditions. One example is from 2006 by Brookhart and Goldman¹⁶ where they developed a tandem catalytic system for metathesis of *n*-alkanes. In short, the PCP Iridium complex used in this catalysis withstood 175 °C for a period of nine days. Since the ligands are tridentate, they are well anchored to the metal and though the side-arms can dissociate from the metal the rest of the ligand is still attached, allowing subsequent re-association.

At the time of writing this thesis, a recently published Nature article¹⁷ describes a catalytic method employing a PCP N-heterocyclic Molybdenum complex, see *Figure 4* below, for reducing N₂ gas to NH₃, ammonia. This is an industrial process performed on a huge scale today, mainly through the Haber-Bosch process developed in the early 20th century. It is one of the most important chemical processes ever developed and supplies more than 50% of the planet's food production with fertilizer¹⁸. Unfortunately, this process is highly energy demanding and in 2010 released ca. 1% of all emitted CO₂ and consumed the same percentage of the world's total energy production. The hydrogen used in the process mostly stems from fossil sources, which poses a challenge from a climate point of view.

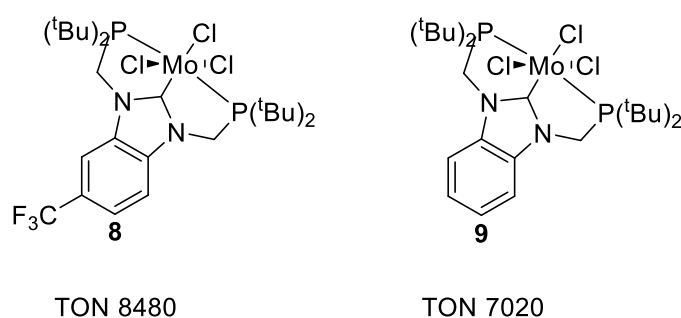


Figure 4. Two versions of a PCP NHC pincer catalyst developed for reduction of nitrogen to ammonia,

The research group had previously developed a similar catalyst¹⁹ but now managed to improve the yield, due to fine-tuning the properties of the pincer ligand by adding an electron-withdrawing CF₃ group to the central aromatic moiety of the ligand (**8** and **9**). A great example of the possibilities that exist when using pincer complexes for catalysis. This led to an increase in the *turn over number* (TON) with ca. 20%, and an increase in *turn over frequency* with over 30%. In addition, the source of hydrogen in this process is not H₂ from fossil sources, but water and SmI₂, samarium diiodide¹⁷. Additionally, the process runs at ambient temperature rather than 500°C like the Haber-Bosch process¹⁸.

Looking back at **7** in Figure 2, that iridium complex is one of the most successful catalysts in performing catalytic hydrogenation of CO₂. The authors report that two different complexes were made with different side-arms on the phosphorous atoms, iso-propyl and tert-butyl. The iso-propyl variant showed higher activity, probably due to better solubility⁶. This is yet another example of how pincer ligands can be fine-tuned to achieve higher activity, and another factor to take in consideration when designing them.

1.4 CO₂

Carbon dioxide is a very inert molecule with bonds that are tough to break. The energy required to break the bonds of this molecule is a great challenge that this diploma work strives to explore. It is a gas used for many industrial purposes, but it also poses a threat due to its effect on the climate²⁰. More and more research focus on different ways of cutting CO₂ emissions, but also using it in more efficient ways, as well as storing or chemically converting it to other materials. The following two sections will discuss CO₂ in different aspects. From a chemical point of view, CO₂ is an interesting 1C source as it is abundant, cheap and relatively non-toxic.⁶

1.4.1 CO₂ in industry and climate change

According to the Intergovernmental Panel on Climate Change, IPCC, greenhouse gas emissions are mainly consisting of methane and CO₂²⁰. To reduce emissions and reach net zero emissions, carbon dioxide removal will be necessary. There are different ways to remove carbon dioxide from the atmosphere, but two general concepts that have gained much attention lately is *Carbon Capture & Storage* (CCS) as well as *Carbon Capture, Usage & Storage* (CCUS). The first technique is done by separating CO₂ from other gases in industrial plants, such as steel mills or refineries, then compressing it and transporting it to a suitable geological site for geological storage. CCUS on the other hand is a technique that captures the CO₂ from industrial facilities or power stations that generate CO₂ from fossil or biomass-based fuels. The gas is then used in products or services and finally transported to a storage, just like in CCS described above²¹.

The IPCC's Sixth Assessment Report summarises the current knowledge regarding climate change, mitigation and adaptation, among other things. According to the report, deep reduction in greenhouse gas emissions is required, even net-negative emissions. To achieve this, some kind of removal of greenhouse gases is required. One such technique could be to convert CO₂ into other chemicals, such as methanol, formic acid and formaldehyde, simply by using it as a chemical feedstock in industrial processes that make carbon containing products.²² According to the IEA however²³, the potential for negative emissions stemming from CO₂ use is very limited and CCS has a much higher capacity for emission reductions. Further research, development and demonstration (RD&D) are needed, especially in technologies that can contribute to a net-zero CO₂ emission economy. Those include chemicals and fuels derived from CO₂. When looking at what products that can be derived from CO₂, it is important to consider the life-cycle of these products. Depending on the life-cycle, the carbon is stored for varying amounts of time and can only be said to reduce emissions if certain criteria are met.²²

Besides being a green-house gas that leads to heating of the planet, carbon dioxide has a wide range of uses and applications in industry. To mention a few, CO₂ is used for carbonating beverages and as a propellant in aerosol cans. In its solid form, known as "dry ice" (because it

sublimates to a gas rather than melt to a liquid at atmospheric pressure), it is used as a coolant for transportation of food or even storage. In terms of chemical industry, it can be used to produce methanol and urea, and is used for that purpose to some extent. There is also widespread use in welding to improve the quality of the weld, as well as the rate²⁴. In terms of size, the largest users are the fertilizer industry (130 Mt per year) and the oil/gas industry (70-80 Mt per year).²³

1.4.2 Pincer complexes in CO₂ Insertion reactions

Chapter 4 in *Pincer Compounds: Chemistry and Applications* gives a great overview of the current progress in CO₂ insertion performed by pincer complexes. Interestingly, pincer complexes containing Ni as the metal mostly utilize PCP ligands, with a few exceptions². The work in this thesis has the aim of investigating the reactivity of NCN nickel(II) complexes towards CO₂ which is a relatively unexplored area. The most efficient catalysts reported in the literature utilize noble metals such as Pd, Pt, Ir, Re and Rh. However, using more earth-abundant metals is of course preferred if possible, and some reports of first-row elements utilized in pincer complexes exist, mainly Fe, Co and Ni. However, the TON and TOF for these catalysts have a long way to go compared to more efficient Ir systems⁶. The first CO₂-insertion into a nickel-hydride was reported in 1987²⁵. The complex *trans*-(PCy₃)₂Ni(Ph)(H) was reacted with CO₂ to form the complex (PCy₃)₂Ni(Ph)O₂CH. Since then, research has come a long way but there are still a limited number of examples of catalytic insertions described.

Related research in this field has focused on PCP and PCN Pd and Ni pincer complexes, however no reports of NCN nickel complexes performing CO₂-insertion reactions exist. In fact, there are no reports on catalytic CO₂ insertion using Ni pincer hydride complexes to date. The closest example²⁶ is the reduction of sodium bicarbonate to formate by a PCP Ni complex that utilizes CO₂ as a form of hydrogen storage by reducing it with hydrogen gas to form formate catalytically. A computational study from 2012²⁷ suggests that in the case of insertion into Ni-H bonds, the *trans* influence of the ligand opposite to the hydride is important for insertion to take place. In chapter 4 of *Pincer Compounds*², it is argued that compounds that have a carbon on the “central” donor atom of the ligand all can perform CO₂ insertion easily, while ligands with a weaker *trans* effect require harsher conditions.

Recently published articles from the Ola Wendt group concludes that certain types of PCN pincer nickel complexes can undergo CO₂ insertion reactions, see *Figure 5* below.

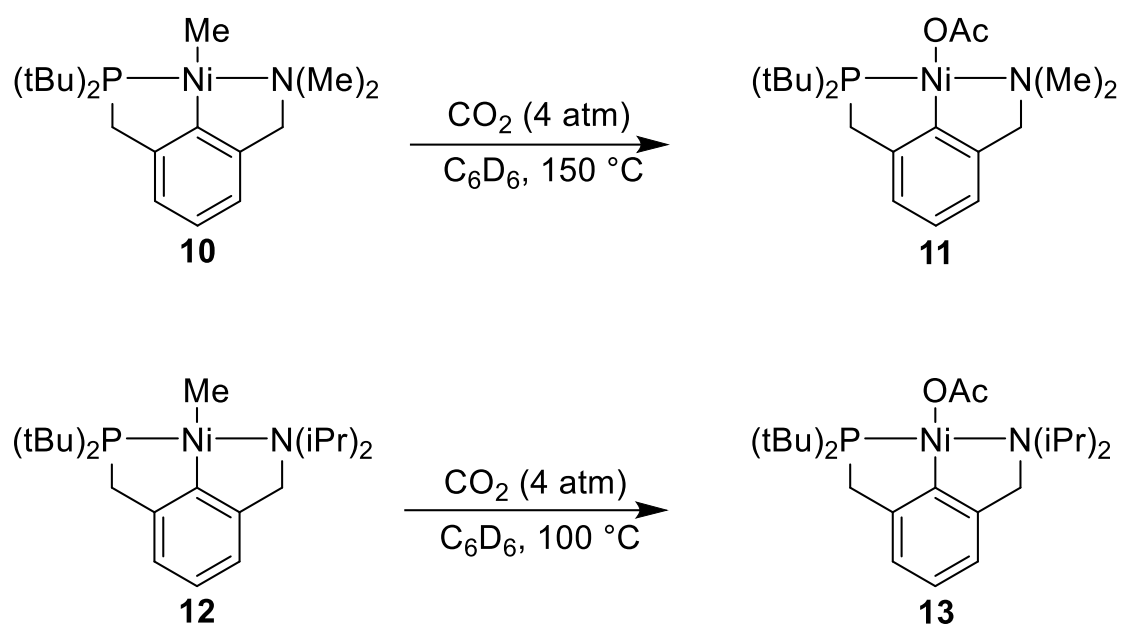


Figure 5. Known CO₂ insertion reaction from recent publications^{28,29}

Interestingly, exchanging the substituents on the amine side arms to isopropyl allows the complex to undergo the insertion reaction at a lower temperature. One explanation could be the increased steric hindrance causing higher stability and decreased decomposition in the reaction. The study of these complexes in the Wendt group has led to curiosity to see if NCN Pincer complexes show the same kind of reactivity toward CO₂, and a comparison to previously studied PCP nickel complexes would be interesting. A 2005 paper³⁰ from this research group showed the first ever CO₂ insertion into a Pd-C bond and since then, work has been put into finding a similar type of reactivity in Ni and other more abundant metals.

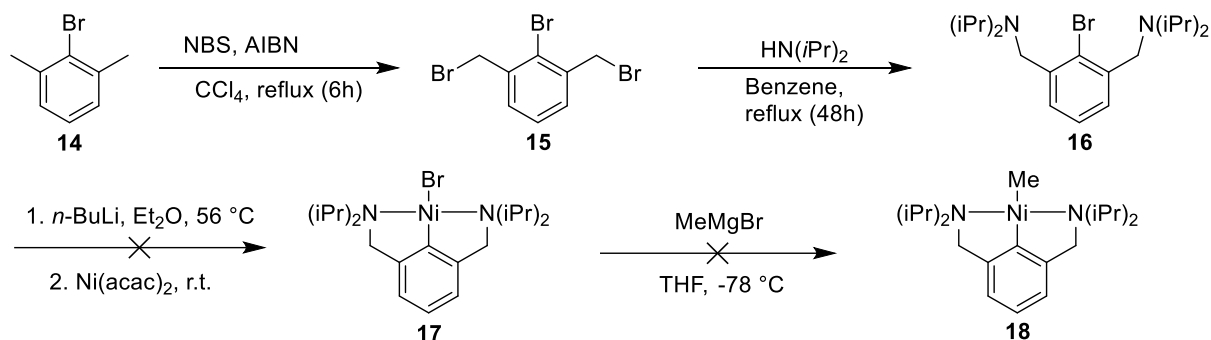
Stoichiometric reactions of CO₂-reactions have been known for some time, however many of the formed M-O bonds are too strong to undergo further reactions. It has been shown that insertion into group 9 or 10 metals results in relatively weak M-O bonds that are promising for developing catalytic processes.³¹ So far, only a few systems with practical applications have been developed. The issue can be summarized as CO₂ being a very stable molecule yet once it is inserted into a bond, the formed bond must be weak enough to dissociate from the metal.

2 Aim

The aim in this diploma work was to synthesize different NCN pincer complexes and test their ability to perform CO₂ insertion. Originally, two different complexes were envisioned with varying side-arms but along the way a complex with pyridine side-arms was added to the project. The three different syntheses are described in the following subsections, where the two first describe very similar routes.

2.1 The *iso*-Propyl Route

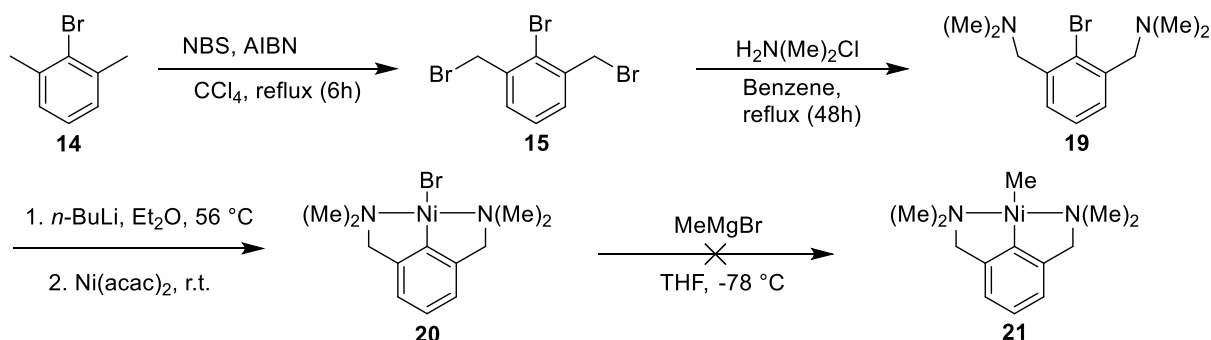
The planned synthetic route is presented below in *Scheme 1*. Starting from 2-bromo-1,3-dimethylbenzene (**14**), NBS and AIBN are used to perform a radical bromination to generate Compound **15**, which can be used in both this route and the route described in the next section. Next, an S_N2 reaction using diisopropylamine as a nucleophile, is performed to give the desired ligand **16**. Through a transmetalation reaction using *n*-BuLi, the ligand is then added to a nickel reagent yielding **17**. Lastly, the methyl complex **18** desired for testing CO₂ insertion is synthesized through a ligand exchange.



Scheme 1. Conversion of a xylene starting material to a ^{iPr}NCNi^{iPr}NiMe complex.

2.2 The Methyl Route

This route is identical to the one in the previous section, except where the second reaction where dimethylamine hydrochloride is used instead of diisopropylamine. Thus, radical bromination of **14** gives Compound **15**, which is then converted to ligand **19**. Then, the steps making the bromide pincer complex **20** and the following ligand exchange resulting in **21** are just like in the previous subsection.



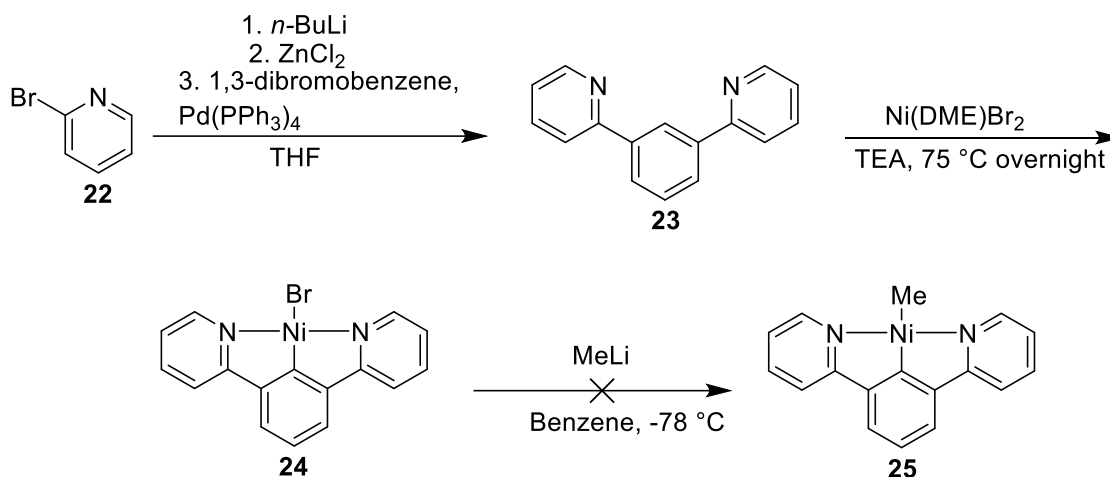
Scheme 2. Conversion of xylene starting material to ^{Me}NCNi^{Me}NiMe complex.

2.3 The PyPhPy route

A paper³² published in 2020 describes the synthesis of precursor compound **24** and the corresponding Cl and I complexes. During the crystallization of the chloride complex the acetate complex was obtained as well, and it was characterized by X-Ray Diffraction, XRD. It was not synthesized by CO₂ insertion, which is the aim in this work, but it allows for

comparison. In a previous paper³³ by the same research group, an analogous CNN [(Phbpy)NiBr] complex was synthesized and the XRD results showed that the increased *trans*-donor effect of the phenide group weakens the Ni-Br bond significantly, by 10 pm. This bond weakening could be promising for catalytic purposes.

In **18** and **21**, the nitrogen side arms can be said to be sp³ hybridized, while the pyridine moieties of **24** (Scheme 3) are sp² hybridized, giving an interesting comparison. In the synthesis, 2 equivalents of **22** are used in a Negishi coupling reaction to give ligand **23**. Subsequently, C-H activation gives the bromide complex **24** and finally ligand exchange should result in the final complex **25**.



Scheme 3. Conversion of pyridine starting material to ^{P,N}CPy^eNiMe complex.

3 Results and Discussion

3.1 The iso-Propyl Route

The first two steps in the synthesis were carried out as planned, and ligand **16** was acquired in good yields. However, several attempts at synthesizing **17** were unsuccessful and the NCNNiMe complex was never completed, so CO₂ insertion could never be tried. Trying a different type of nickel reagent could be attempted, or perhaps starting from a different ligand without the bromine, to instead try a C-H activation route.

3.2 The Methyl Route

Initially, **15** was synthesized by using 2-bromoxylene performing a radical bromination in CCl₄ using 2 equivalents of NBS and 0.03 equivalents of AIBN. After purification through recrystallization in hexane, the product was obtained with typical yields of 35-40%. This reaction was performed several times with good results.

The next step is an S_N2 reaction with **15** and dimethylamine hydrochloride in Et₃N and DCM to produce the desired NCN ligand, **19**.

An oxidative addition was carried out with Ni(COD)₂ in dry, distilled THF to obtain **20**, the first NCN pincer complex in the synthesis. The purification step included a filtration through celite and washing with cold hexane before the material was recrystallized from MeOH. The

low yield could possibly be explained by the presence of water in any of the reagents or solvent used, but also by the fact that Ni(COD)₂ is extremely moisture and air sensitive.

Several attempts were made to synthesize **21**, the compound to be used for CO₂ insertion, but unfortunately they were all unsuccessful. A grignard reagent (MeMgBr) was used in dry THF but the expected signal from the methyl protons were not identified in the ¹H-NMR. The complex is presumed to have decomposed during or after the synthesis, or it was never formed. An alternative to using a Grignard reagent is to use MeLi. If methylation of **20** is not feasible, then perhaps another similar type of complex can be made, and CO₂ insertion attempted using this complex instead.

3.3 PyPhPy Route

The synthesis of **24** was successfully performed starting from **22**. Decent amounts of this bromide complex were obtained, closer to 1 g of material. However, no methylation attempts were successful and hence no CO₂ insertion could be attempted. Compound **24** was stable in air and not moisture sensitive, so the starting material could not have been decomposed due to any moisture in solvents or reagents, but the methyl reagent could have been decomposed, partly decomposed or the conditions simply not suitable for this type of reagent.

The space group was determined to be $P2_1/n$, which matches what Kletsch Hörner and Klein determined in a recent paper³². The structure as determined by Single Crystal X-ray Diffraction (SXRD) can be seen in Figure 6 below.

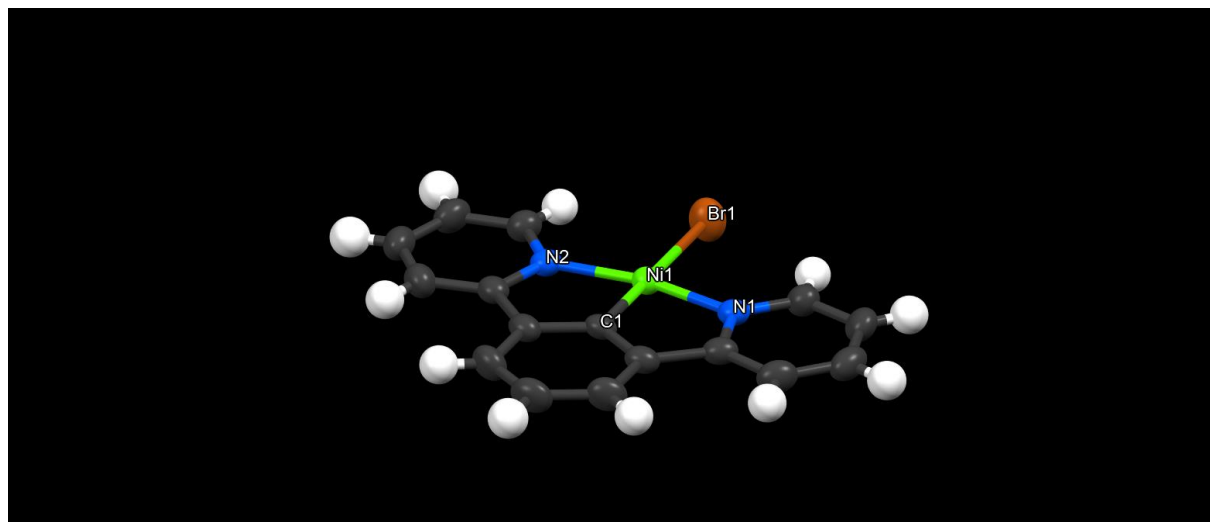


Figure 6. SXRD of Compound **24**. Select bond distances (Å): Ni1 – Br1 = 2.3822, Ni1 – C1 = 1.824(3), Ni1 – N1 = 1.946(4), Ni1 – N2 = 1.948(4). Select bond angles (°): Br1 – Ni1 – N1 = 97.6, Br1 – Ni1 – N2 = 98.6, Br1 – Ni1 – C1 = 179.5, N1 – Ni1 – N2 = 163.8.

The data from the SXRD is presented in the Appendix.

4 Conclusions and Future Outlook

Three different routes for synthesizing NCN nickel pincer complexes have been investigated. In two cases, with pyridine and dimethylamine sidearms respectively, the ligands were successfully added to nickel, yielding the desired bromide precursors to the methyl complexes. Several attempts were made to make the methyl complexes from the two synthesized bromide nickel complexes, but no product was observed. In the third case with diisopropyl sidearms, cyclometallation was attempted but was not found to be successful.

Further work should aim to investigate whether using methyl lithium in benzene for methylation of the bromide complexes is more successful. As an alternative to cyclometallation of the diisopropyl ligands, Ni(COD)₂ could be used just like in the case with the dimethyl amine ligands, which in that case worked. In conclusion, the synthetic routes should be completed and CO₂ insertion investigated.

An interesting prospect for future investigations is insertion into Ni-C bonds of other hybridisations (sp, sp²). Especially since the CO₂-insertion into Ni-H bonds was never studied in this diploma work. The effect of the s-character in the ligand active in the insertion ligand could therefore be studied using several different complexes.

5 Experimental Procedure

5.1 General experimental methods

All complexes were characterized by ¹H-NMR and/or ¹³C-NMR spectroscopy. Furthermore, the N^{Py}C^{Py}N complex **X** was characterized by Single Crystal X-ray diffraction (SXRD).

All manipulations of organometallic character were carried out using standard Schleck techniques or glove box work. All solvents used in the synthesis of organometallic compounds were distilled before use.

The NMR experiments were carried out using a Bruker 400 MHz machine. Shifts were recorded with respect to TMS and the solvent peaks of CDCl₃, CD₃OD and C₆D₆ (¹H-NMR shifts of 7.26, 3.31 and 7.26 respectively) were used as reference.

Single crystal X-ray diffraction was done using an Oxford Diffraction Xcalibur 3 system, using ω-scans and Mo Kα (λ = 0.71073 Å) radiation. The data were extracted and integrated using CrysAlis RED.

TLC analysis in association with flash column chromatography was done using Merck silica gel 60 F₂₅₄ coated on aluminium plates and visualized under a UV-lamp. The silica gel used for column chromatography had a pore size of 60 Å and mesh 40-60 μm.

HRMS of compounds **20** was **24** was performed by personnel at the department using a Waters Xevo-G2 QTOF with ESI+.

5.2 Iso-Propyl Route

2-bromo-1,3-bis(bromomethyl)benzene (15). To a solution of 2-bromo-1,3-dimethylbenzene (1.73 mL, 12.96 mmol, 1.0 eq.) and CCl₄ (14.4 mL) was added NBS (4.62 g, 25.93 mmol, 2.0 eq.) and AIBN (64 mg, 0.36 mmol, 0.03 eq.). The reaction mixture was refluxed for 6h and

allowed to cool to r.t. before filtering off the solids. The filter was washed with CCl_4 (5 mL) and the solvent was evaporated *in vacuo* to obtain a brown-red oil. The crude oil was recrystallized from hexane (14.4 mL) and left overnight. The product (2.13 g, 6.21 mmol, 48%) was obtained as white crystals). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm) δ 7.45 (d, $J = 7.56$ Hz, 2H), 7.31 (t, $J = 7.56$ Hz, 1H), 4.67 (s, 4H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3 , ppm) δ 138.6, 131.5, 128.2, 126.7, 40.0.

***N,N'*-(2-bromo-1,3-phenylene)bis(methylene))bis(*N*-isopropylpropan-2-amine) (16).** Isopropyl amine (5.43 mL, 38.7 mmol, 8.0 eq.) was added to a solution of 2-bromo-1,3-bis(bromomethyl)benzene (**15**) in benzene (9.7 mL). The reaction was heated to reflux. After 42h the white salt was filtered off and washed with benzene (2.5 mL). The combined benzene portions were evaporated, and hexane (5.8 mL) was added to precipitate unchanged starting material, which was filtered off. The solvent was evaporated after which MeOH (2.9 mL) was added to the yellow oil. The solution was cooled to -20°C for 17h and the off-yellow product (1.33 g, 3.47 mmol, 71 %) was filtered off and dried *in vacuo*. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm) δ 7.56 (d, $J = 7.6$ Hz, 2H), 7.23 (t, $J = 7.6$ Hz, 1H), 3.70 (s, 4H), 3.08 (hept, $J = 6.6$ Hz, 4H), 1.03 (d, $J = 6.5$ Hz, 24H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3 , ppm) δ 141.73, 127.96, 126.38, 124.36, 49.75, 48.84, 21.00.

$[\text{iPrNCN}^{\text{iPr}}]\text{Ni-Br}$ (17). At -56°C , *n*-BuLi (2.5 M, 1.04 mL, 2.61 mmol, 1.0 eq.) was added dropwise to a solution of (**16**) (1.00 g, 2.61 mmol, 1.0 eq) in Et_2O (15 mL). After complete addition the solution was allowed to reach r.t. before being stirred for 1h. Via canula, the orange solution was added to a suspension of $\text{Ni}(\text{acac})_2$ (670 mg, 2.61 mmol, 1.0 eq.) in Et_2O (5 mL) and the reaction was stirred for 2h at r.t. Upon addition the reaction turned brown and a precipitate ($\text{Li}(\text{acac})$) was formed. The brown mixture was filtered through celite and the resulting clear, red filtrate was stored at -20°C for 40h. No product was obtained.

5.3 Methyl Route

2-bromo-1,3-bis(bromomethyl)benzene (15).

1,1'-(2-bromo-1,3-phenylene)bis(*N,N*-dimethylmethanamine) (19). **15** (1.81 g, 5.28 mmol, 1.0 eq.) and dimethylamine hydrochloride (2.15 g, 26.4 mmol, 5.0 eq.) were dissolved in chloroform (30 mL) and TEA (40 mL). The reaction was stirred for 22 h and the white slurry was washed with water and brine. The organic phase was dried over Na_2SO_4 and the drying agent was filtered off before evaporation of the solvent. The crude, yellow oil was purified through flash column chromatography (2×8 cm, PE:EtOAc:TEA 10:1:0.3) and the product obtained as a colourless oil (0.797 g, 2.94 mmol, 55%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm) δ 7.31 (d, 2H, $J = 7.5$ Hz), 7.23 (t, 1H, $J = 6.6$ Hz), 3.54 (s, 4H), 2.29 (s, 12H). $^{13}\text{C-NMR}$ (400 MHz, DMSO-d_6 , ppm) δ 138.8, 129.6, 126.7, 64.1, 45.7.

$[\text{MeNCN}^{\text{Me}}]\text{Ni-Br}$ (20). A solution of **19** (520 mg, 1.91 mmol, 1.0 eq.), in THF (10 mL) was added dropwise to a solution of $\text{Ni}(\text{COD})_2$ (527 mg, 1.91 mmol, 1.0 eq.) at -78°C . The solution was allowed to slowly reach room temperature over 2 h and the colour changed from yellow through green to brown. The solution was filtered through a glass filter and concentrated *in vacuo*. The solids were washed with cold hexane and the product was recrystallized by dissolving the brown solids in a minimum amount of MeOH and keeping it at -20°C for four

days. The product (55 mg, 0.166 mmol, 8.7%) was obtained as red needle crystals. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm) δ 6.89 (t, 1H, $J = 8$ Hz), 6.47 (s, 2H), 3.98 (s, 4H), 2.84 (s, 10H).

HRMS-ESI(+) m/z calculated. $[\text{NCNNi} + \text{MeCN}]^+$: 290.1167; found: 290.1164. $[\text{NCNNi} - \text{Br}]^+$: 249.0902; found: 249.0900

[$^{\text{Me}}\text{NCN}^{\text{Me}}\text{Ni-Me}$ (21)]. Compound **20** (55 mg, 0.16 mmol, 1.0 eq.) was dissolved in THF (10 mL) and MeMgBr (3.0 M in Et_2O , 55 μL , 1.0 eq.) was added dropwise at -78°C . The reaction was allowed to reach r.t. and stirred overnight. After ca. 20h, the reaction had changed colour from orange to dark brown. The solvent was evaporated, and the brown solids redissolved in *n*-hexane. The solution was filtered through celite to yield a yellow filtrate, which was evaporated. A yellow solid was obtained but analysis showed no product.

Entry #	Amount of Starting Material (24) (mg):	Amount of 24 (mmol):	Equivalents of MeMgBr (in Et_2O):	Solvent:	
1	100	0.272	1.0	THF	
2	140	0.38	1.0	THF	

5.4 PyPhPy Route

1,3-di(pyridine-2-yl)benzene (23). To a three-necked 250 mL round-bottom flask equipped with a stir-bar was added *n*-BuLi (10.85 mL, 2.5M, 3.2 eq.) and dry THF (30 mL). At -78°C a solution of 2-bromopyridine (2.42 mL, 25.44 mmol, 3.0 eq.) in THF (8.5 mL) was added dropwise. The solution turned yellow and was stirred for 1h. A suspension of ZnCl_2 (4.62 g, 33.91 mmol, 4.0 eq.) in THF (30 mL) was added and the reaction mixture was allowed to reach room temperature. $\text{Pd}(\text{PPh}_3)_4$ (490 mg, 0.42 mmol, 0.05 eq.) and 1,3-dibromobenzene (1.02 mL, 8.48 mmol, 1.0 eq.) was added before heating the reaction to reflux for 18h. The reaction was terminated by addition of NH_4Cl (1.36 g, 25.44 mmol, 3.0 eq.) and H_2O (8.5 mL). The solvent was evaporated, redissolved in water and the reaction was extracted with CH_2Cl_2 (3 \times 25 mL). The combined organic phases were extracted with H_2O (3 \times 15 mL). The organic phase was dried over MgSO_4 and the drying agent was filtered off. After evaporation of the solvent *in vacuo*, the yellow crude was purified by flash column chromatography. $R_f = 0.21$ in 1:3 EtOAc:hexane. The product (1.52 g, 6.54 mmol, 77%) was obtained as a yellow, viscous oil. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6 , ppm) δ 8.82 (t, $J = 1.8$ Hz, 1H), 8.71 (ddd, 2H, $J = 4.8$ Hz, 1.8 Hz, 1.0 Hz), 8.15 (dd, 2H, $J = 7.7$ Hz, 1.8 Hz), 8.07 (dt, 2H, $J = 8.0$ Hz, 1.0 Hz), 7.91 (td, 2H, $J = 7.7$ Hz, 1.8 Hz), 7.61 (t, 1H, $J = 7.7$ Hz), 7.39 (ddd, 2H, $J = 7.5$ Hz, 4.6 Hz, 1.1 Hz). $^{13}\text{C-NMR}$ (400 MHz, DMSO-d_6 , ppm) δ 155.8, 149.6, 139.2, 137.3, 129.2, 127.1, 124.7, 122.8, 120.4.

[^{Py}NCN^{Py}]Ni-Br (24). To a solution of **23** (232 mg, 1.0 mmol, 1 eq.) in THF (19 mL) was added (DME)NiBr₂ (309 mg, 1.0 mmol, 1 eq.) inside the glovebox. Next, triethylamine (ccc mL, 10.0 mmol, 10 eq.) was added and the reaction mixture was heated at 75°C overnight. After 16 h the solvent was evaporated *in vacuo* and the yellow-orange solids were dissolved in DCM. The organic phase was washed with water and the organic phase was dried over Na₂SO₄. The drying agent was filtered off and the solvent evaporated to yield the product (105 mg, 0.285 mmol) in a 28% yield. Crystals for analysis were obtained by dissolving the brown solid in a minimum amount of DCM and letting Et₂O slowly diffuse into it. The product was obtained as dark red crystals. ¹H-NMR (400 MHz, DMSO-d₆, ppm) δ 8.74 (d, *J* = 5.6 Hz, 2H), 8.07 (t, *J* = 7.6 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 6.7 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H).

XRD data is available in the Appendix. Angles and bond distances can be seen in Figure 6.

[^{Py}NCN^{Py}]Ni-Me (25). Complex **24** was added to a Strauss flask equipped with a magnetic stir bar inside a glove box. In the fumehood, solvent was added. The flask was cooled to –78°C and a solution of MeMgBr Grignard reagent was added. The reaction mixture was allowed to reach room temperature overnight. After ca. 16h, the solvent was evaporated *in vacuo* and distilled hexane added to the solids. The clear solution was filtered through celite and the filtrate was evaporated *in vacuo*. A white solid was obtained that was analysed by NMR in a J. Young tube. Analysis indicated no product.

Entry #	Amount of Starting Material (24) (mg):	Amount of 24 (mmol):	Equivalents of MeMgBr (in Et ₂ O):	Solvent:	
1	100	0.272	1.0	THF	
2	140	0.38	1.0	THF	

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Appendix

Table 1. Data from SXRD of 24.

Empirical Formula	$C_{16}H_{11}BrN_2Ni$
Formula Weight	369.88
Temperature/K	298(2)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	8.8022(4)
b/Å	16.4169(8)
c/Å	9.2332(6)
$\alpha/^\circ$	90
$\beta/^\circ$	93.972(5)
$\gamma/^\circ$	90
Volume/Å ³	1331.04
Z	4
ρ_{calc} g/cm ³	1.846
μ/mm^{-1}	4.448
F(000)	736
2 θ range for data collection	7.079 to 59.696
Index ranges	-11 ≤ h ≤ 12 -22 ≤ k ≤ 22 -11 ≤ l ≤ 11
Reflections collected	15087
Independent reflections	3267
Data/restraints/parameters	3267/0/181
Goodness-of-fit on F ²	1.082
Final R indexes	R ₁ = 0.0456
[I>=2 σ (I)]	wR ₂ = 0.1053
Final R indexes (all data)	R ₁ = 0.0659 wR ₂ = 0.1143
Largest diff. peak / hole / e Å ⁻³	0.63 / -0.90
CCDC	2004554

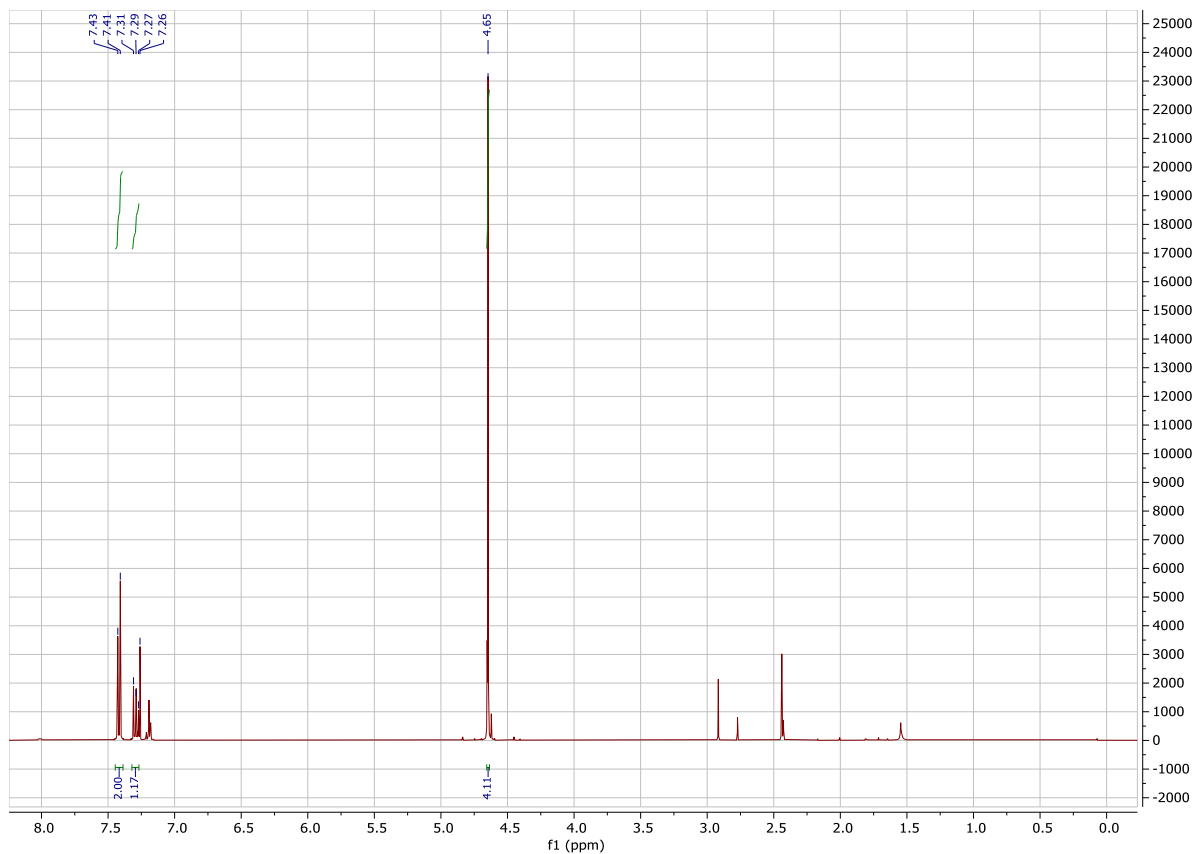


Figure 7. $^1\text{H-NMR}$ (400 MHz, CDCl_3) of **15**

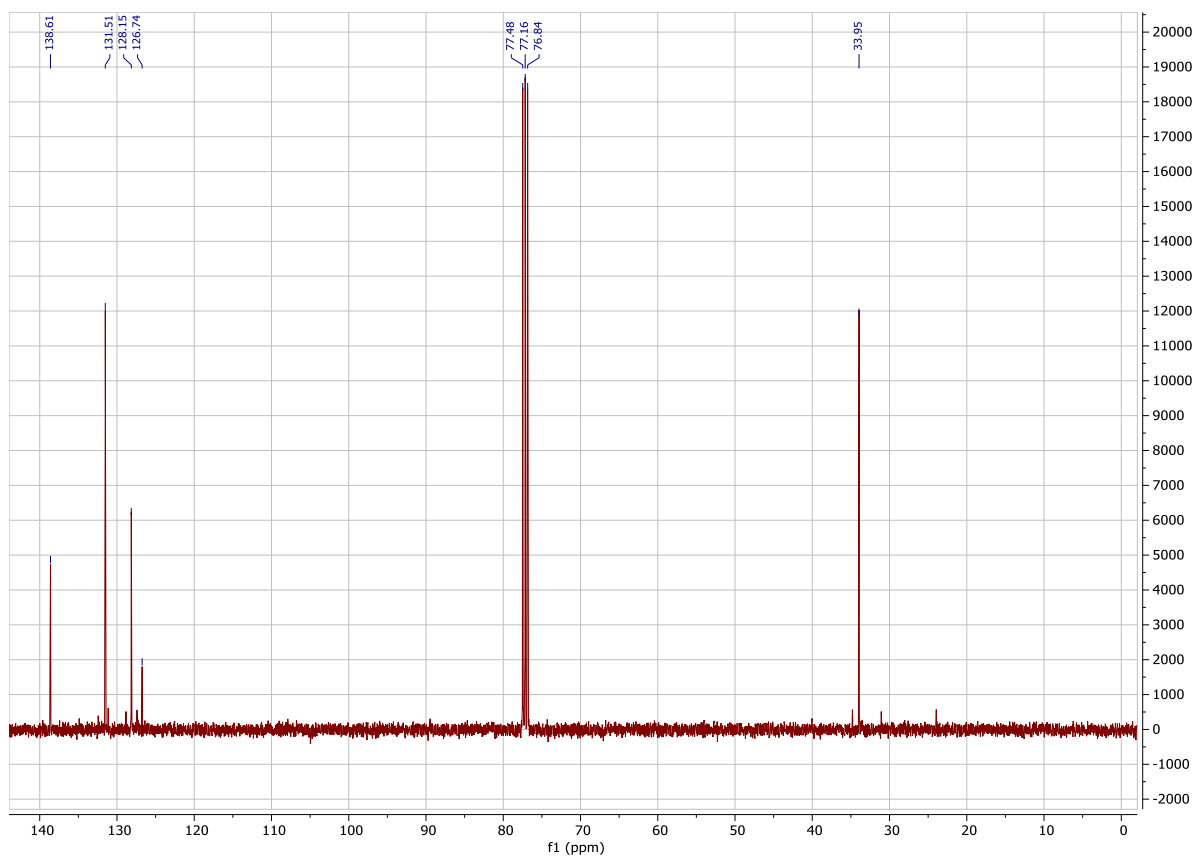


Figure 8. $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of **15**.

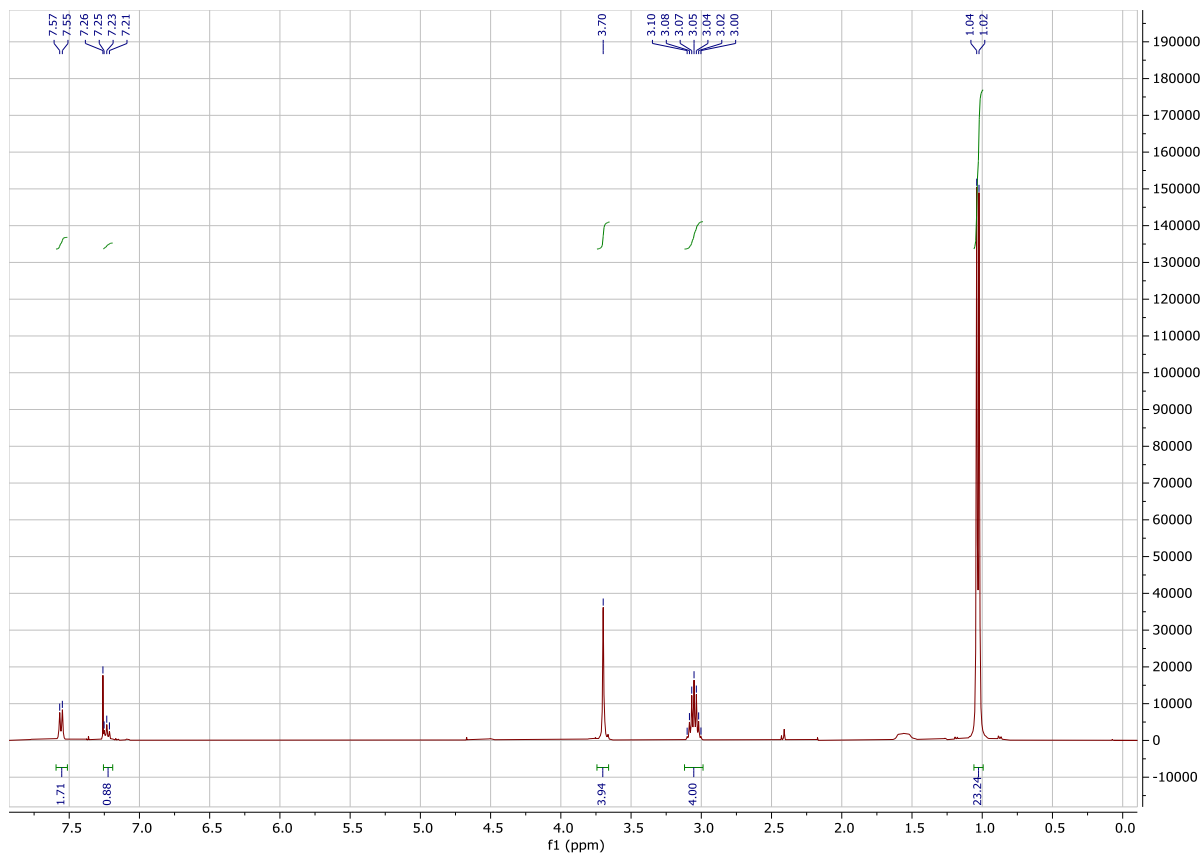


Figure 9. $^1\text{H-NMR}$ (400 MHz, CDCl_3) of **16**.

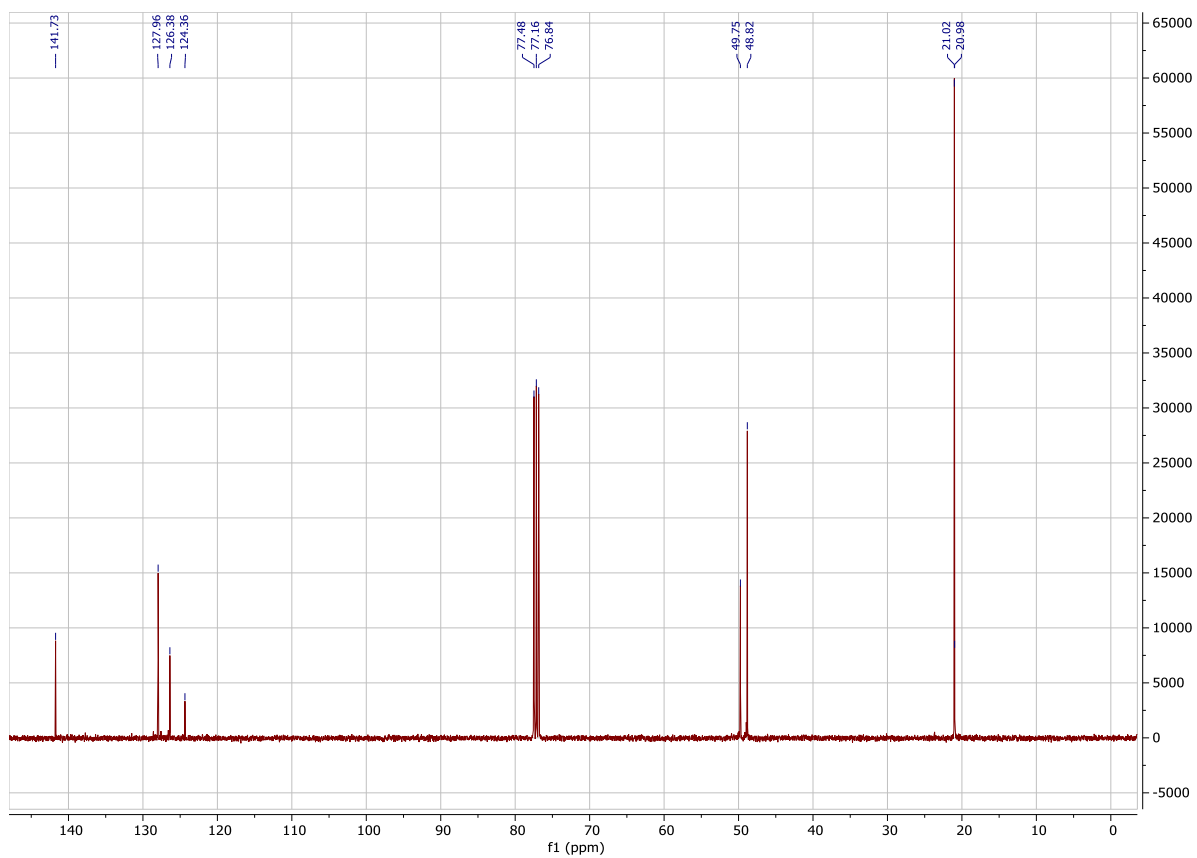


Figure 10. $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of **16**.

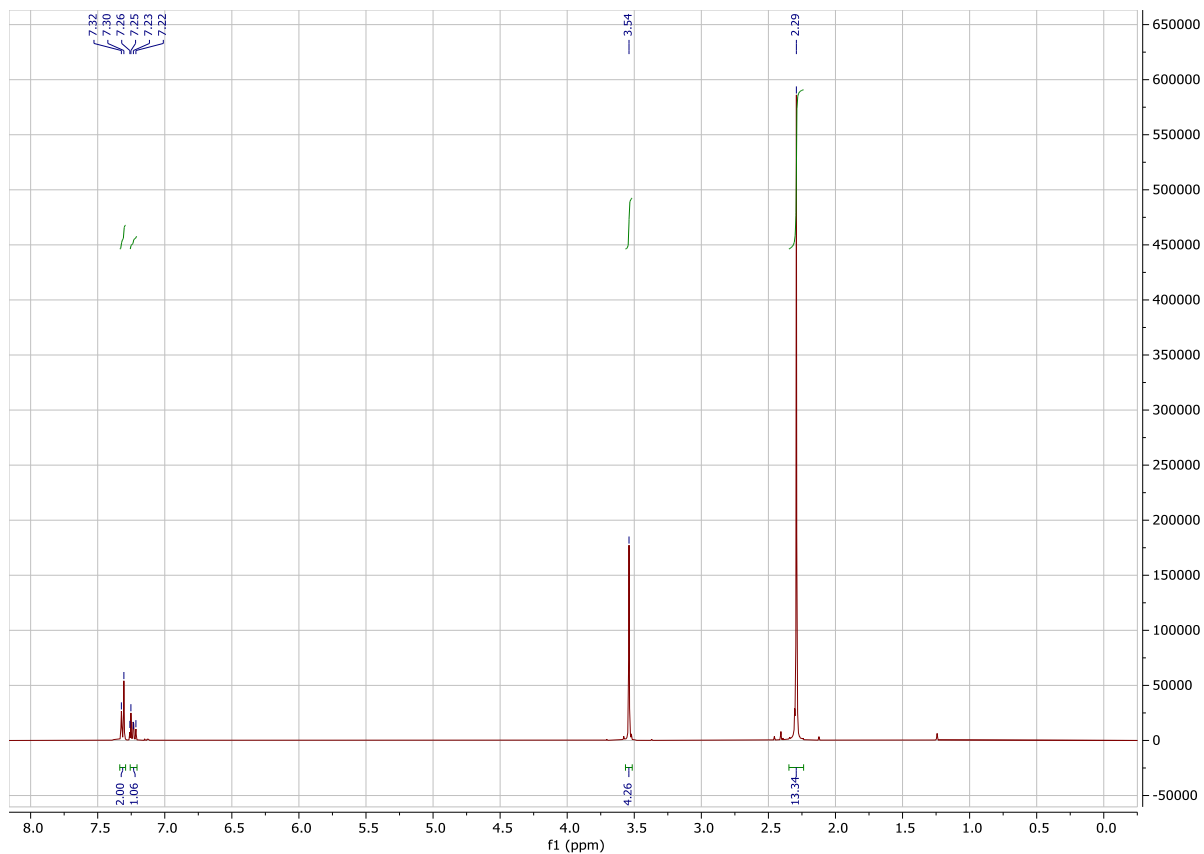


Figure 11. $^1\text{H-NMR}$ (400 MHz, CDCl_3) of **19**.

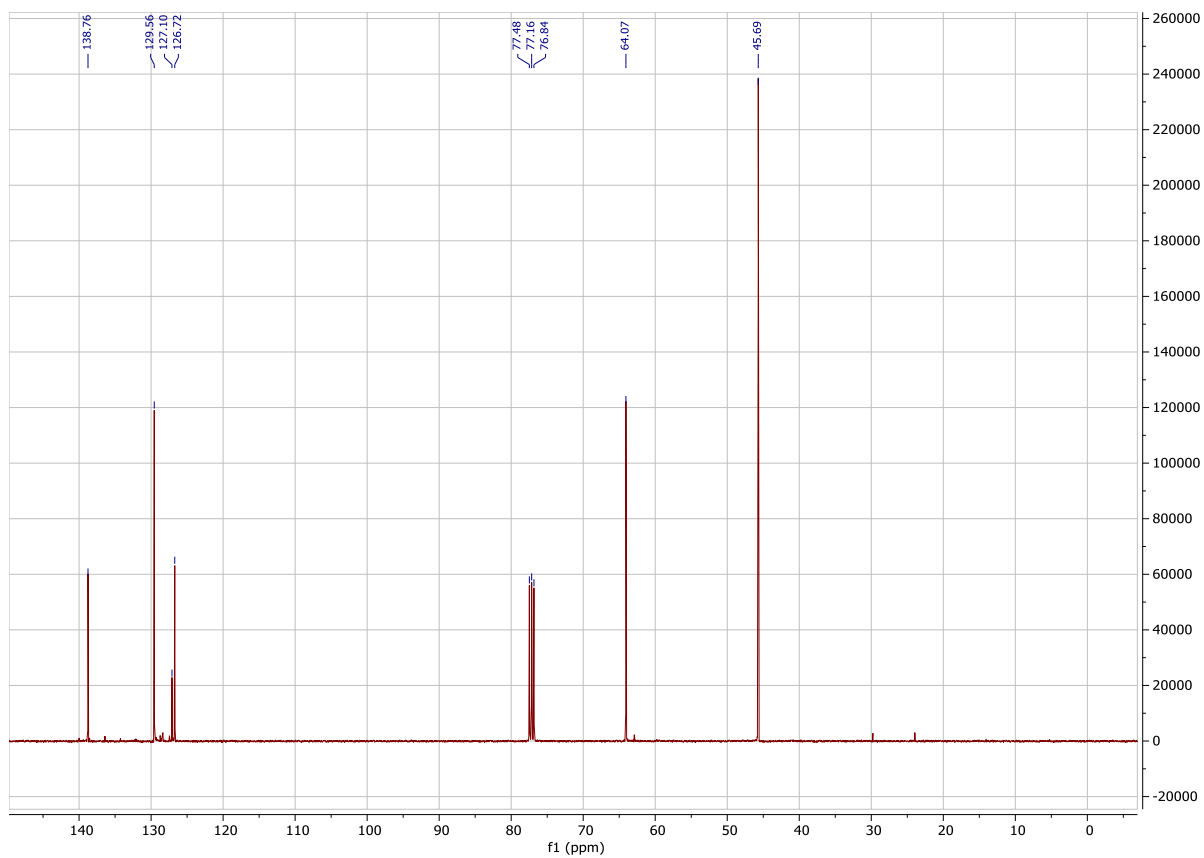


Figure 12. $^{13}\text{C-NMR}$ (400 MHz, CDCl_3) of **19**.

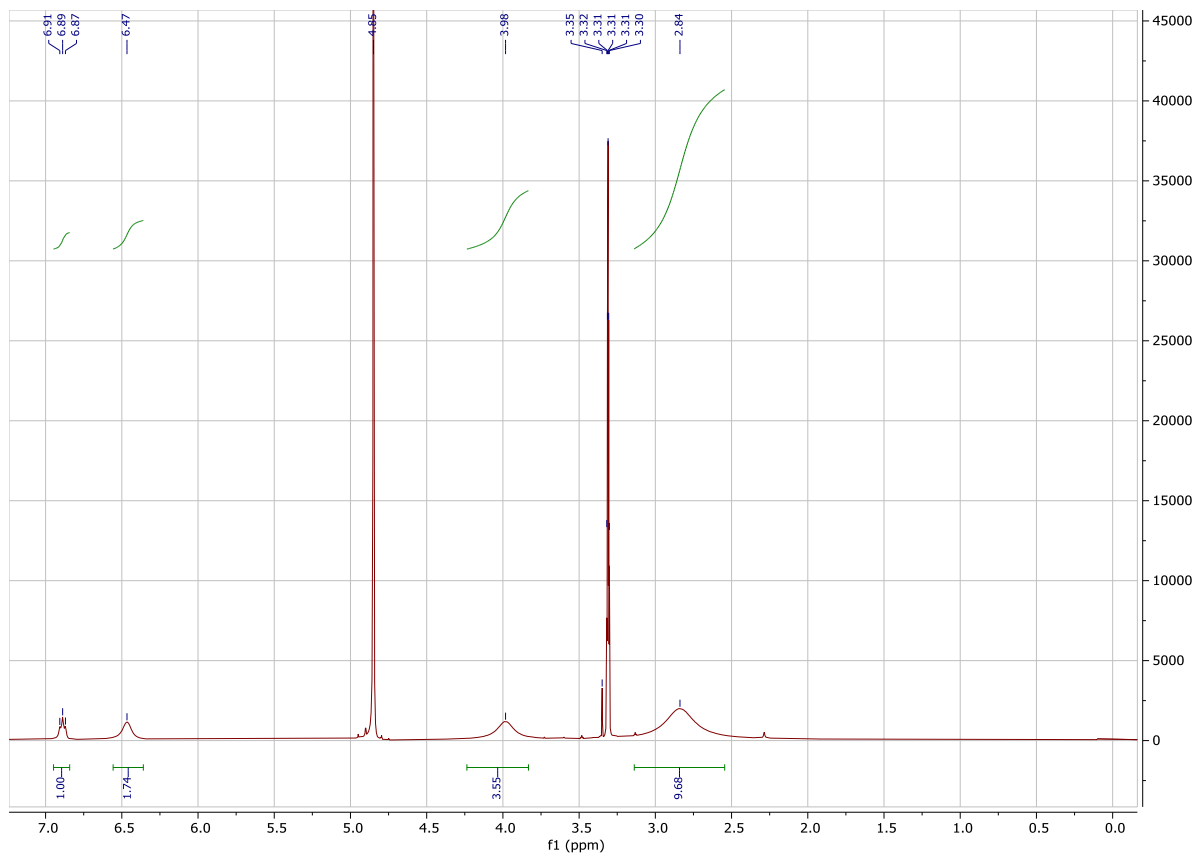


Figure 13. ¹H-NMR of 20.

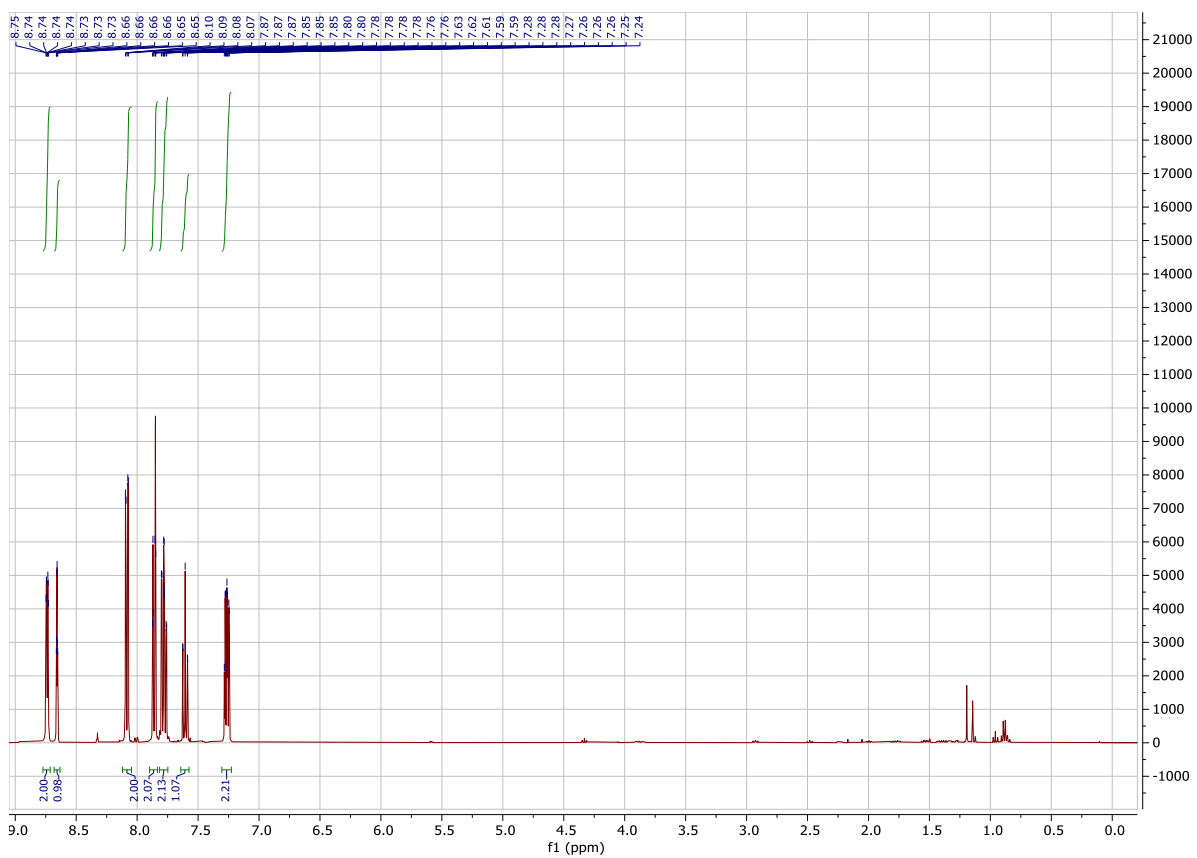


Figure 14. ¹H-NMR (400 MHz, DMSO-d₆) of 23.

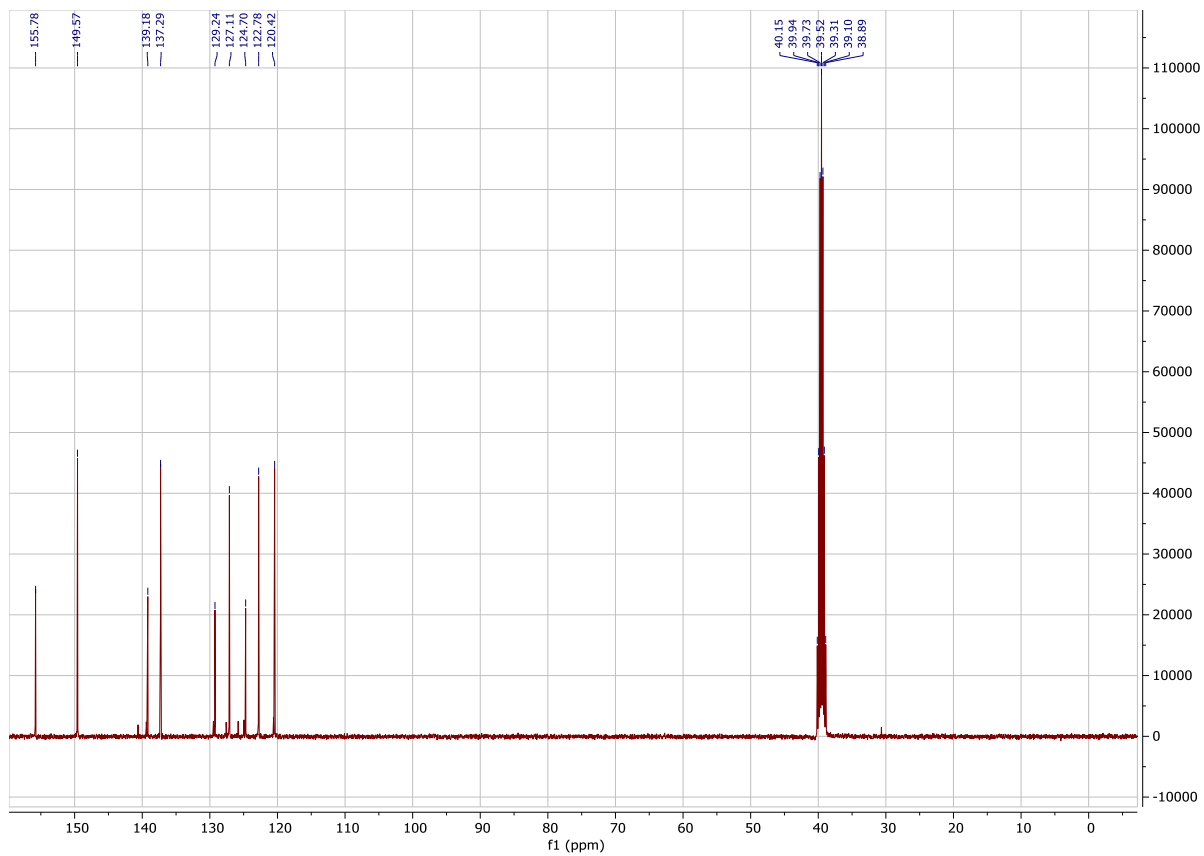


Figure 15. C-NMR of 23.

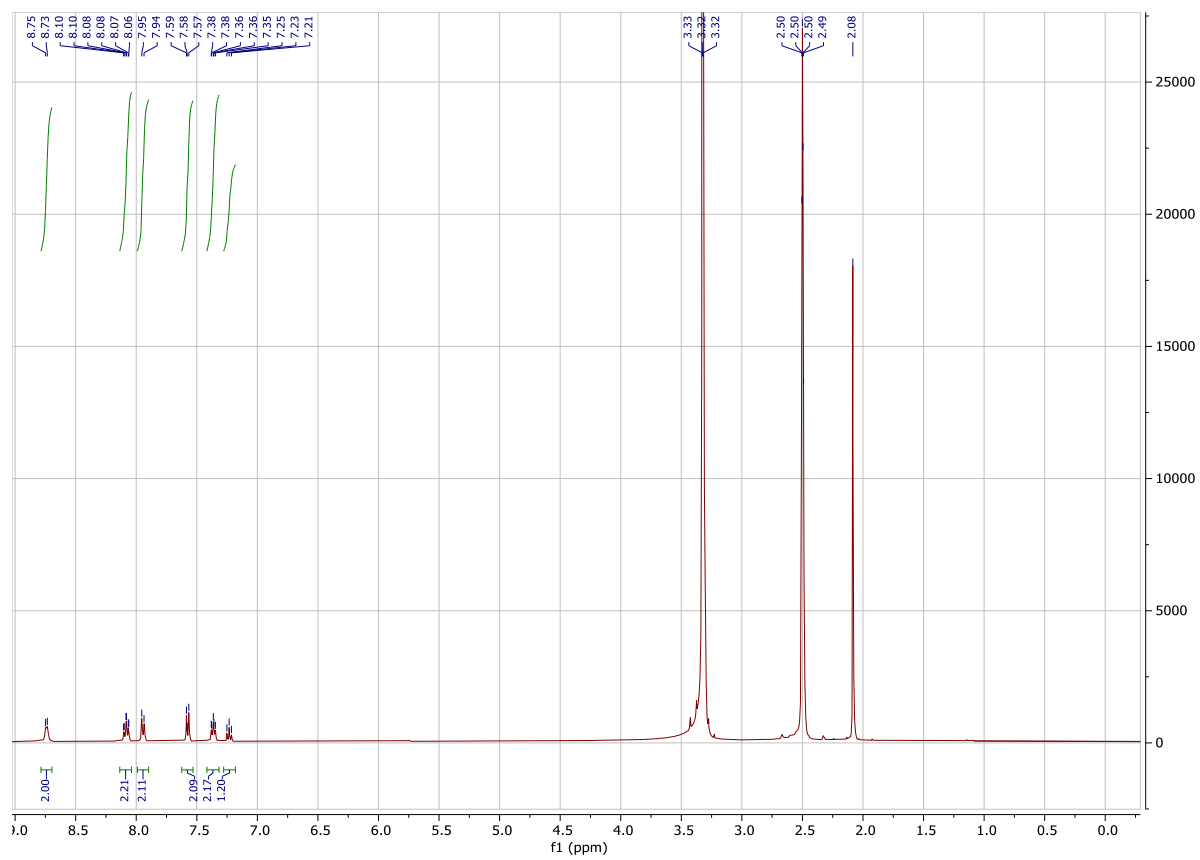
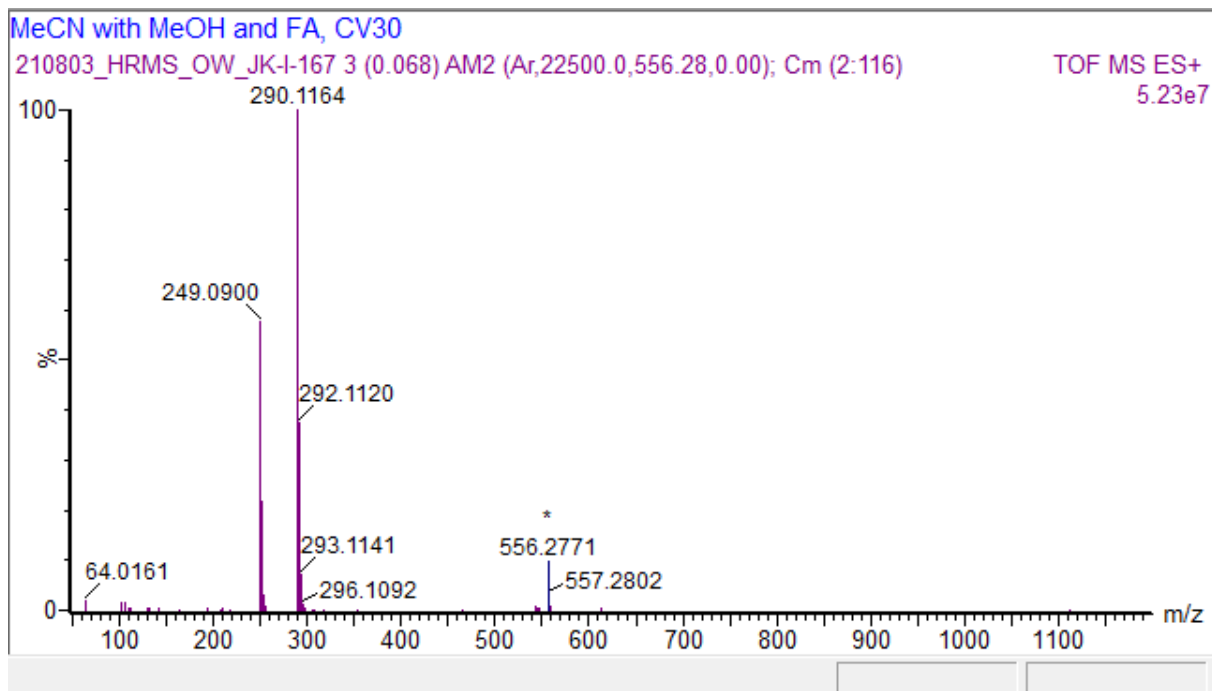


Figure 16. H-NMR (400 MHz, DMSO-d₆) of 24.



Single Mass Analysis

Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd Electron Ions

183 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-50 H: 0-100 N: 0-3 O: 0-2 58Ni: 0-1 Br: 0-1

Mass	Calc. Ma...	mDa	PPM	DBE	Formula	i.	Fit Conf %	C	H	N	O	58Ni	Br	I
249.0900	249.0902	-0.2	-0.8	5.0	C12 H19 N2 58Ni	0	46.72	12	19	2		1		
	249.0902	-0.2	-0.8	12.0	C15 H11 N3 O	0	53.28	15	11	3	1			

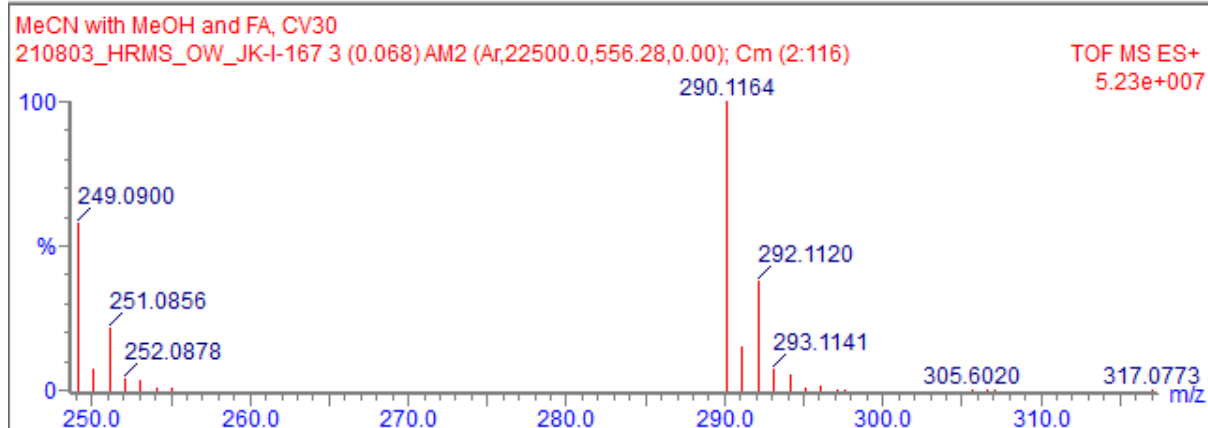


Figure 17. HRMS of 20.