Magnetic Hybrid Materials based on Co/C Nanoparticles and their Use in Catalysis

Dissertation

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Meiner Familie

“Wissenschaft ist Magie, die funktioniert.”

Kurt Vonnegut (1922 – 2007)

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Abbreviations

AAA	asymmetric allylic alkylation
Ac	acetyl-
AIBN	azobisisobutyronitrile
aq	aqueous
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Boc	*tert*-butyloxycarbonyl
conc	concentrated
dba	dibenzylideneacetone
DCC	dicyclohexyl carbodiimide
DCE	dichloroethane
DCM	dichloromethane
DEAD	diethyl azodicarboxylate
DMAP	4-dimethylaminopyridine
DMSO	dimethylsulfoxide
DPPA	diphenyl phosphoryl azide
DPPBA	diphenylphosphino benzoic acid
ee	enantiomeric excess
EI	electron impact
equiv.	equivalent(s)
ESI	electron spray ionization
h	hour(s)
HPLC	high performance liquid chromatography
i-	iso-
ICP	ionic coupled plasme
IR	infrared
Me	methyl
MeCN	acetonitrile
MW	microwave
n-	normal-
n.d.	not determined
nm	nanometer(s)
NMR	nuclear magnetic resonance
NP	nanoparticle
OMS	octamethylcyclotetrasiloxane
p-	para-
PEI	polyethyleneimine
PFMN	phosphine functionalized magnetic nanoparticles
Ph	phenyl
ppm	parts per million
Pr-	propyl-
PS	polystyrene
R	arbitrary residue
R_f	retardation factor
rac-	racemic
r.t.	room temperature
SQUID	superconducting quantum interference device
t	time
T	temperature
TEM	transmission electron microscopy
tert-	tertiary-
TH	transfer hydrogenaiton
THF	tetrahydrofurane
TLC	thinlayer chromatography
TOF	turnover frequency
TON	turnover number
TOPO	tri-octyl phosphineoxide
wt%	weight percent
XPS	X-ray photoelectron spectroscopy

A. Introduction

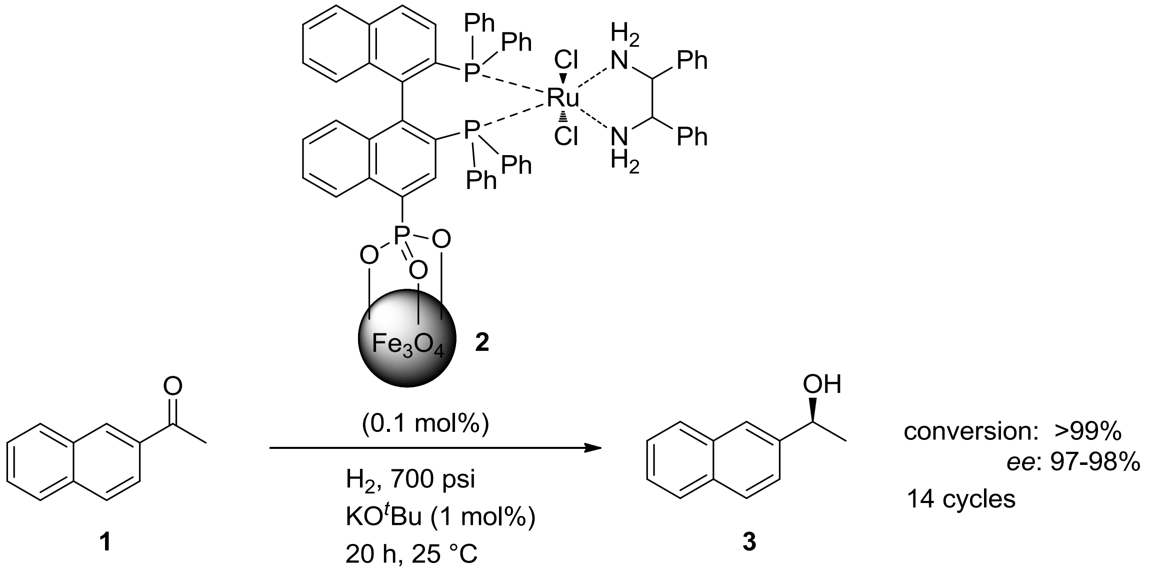
Catalysis is one of the key components of sustainable organic chemistry. While homogeneous catalysts (often transition metal complexes) can be highly active, they need to be separated from the solution after the reaction. Especially on larger scale syntheses (*e.g.* in pharmaceutical applications), the clean separation of the product from a soluble catalyst as well as other reactants is essential, to avoid (metal) contamination and maintain health and safety standards.[1] Although common separation techniques like, *e.g.* column chromatography or extraction are often effective, they are usually neither very economic nor ecological due to generation of waste solvents and chemicals. As a result, many efforts have been dedicated to improve catalyst recycling and product isolation. One approach is the use of heterogeneous catalysts using solid supports. Their main advantage compared to homogeneous catalysts is the grafting of the catalysts onto insoluble resins. Notable materials used as supports are, *e.g.* based on silica or polymeric resins (Wang or Merrifield resins[2]). However, these materials usually have a limited lifetime because of their structural lability, as they tend to get damaged easily by mechanic stresses such as magnetic stirring or during the recycling process. Furthermore, only the sites in the surface of the porous material are active, thus reducing the overall catalytic activity.[3,4] A way to circumvent these issues is the use of nanoparticle chemistry. It combines the advantages of homogeneous and heterogeneous catalysis as: "[t]he domain of nanoparticles […] lies between these two orthogonal strategies, hence this approach is sometimes called "semi-heterogeneous"."[5] Their small size (nanometer scale) provides an excellent surface to volume ratio, which enables high catalyst loadings and, therefore, good interaction of the active sites. This results in high reaction rates, even comparable to those of conventional catalysts. In order to make NPs suitable for chemical applications, they need to be inert under the applied conditions (as their low size makes them susceptible to *e.g.* oxidation, high temperatures). Moreover, NPs agglomerate to bulk materials without the aid of any stabilizing agents going hand in hand with a drop in activity.[4] The latter can be achieved through various stabilizing supports: polymers[6], silica[7], zeolites[8], carbon[9], graphene[10] or carbon nanotubes.[11] An especially interesting subclass are magnetic nanoparticles: these can be conveniently separated within a few seconds using an external magnet and the supernatant solution can then be simply decanted.[4,5,12] Thus, product contamination is avoided and the immobilized catalyst can be reused in further reactions. As above mentioned magnetic NPs also need to be chemically stable under the applied reaction conditions. This can be achieved through passivation/protection/etc. using a core-shell approach.[13] The core provides magnetic properties required for the recycling while the surrounding shell allows easy chemical functionalization to immobilize the desired catalytic system as well as creates a chemical inert environment. Furthermore, undesired metal leaching from the core into reaction solution can be avoided to a certain degree.

In the next chapters, different magnetic nanobeads, as well as strategies regarding their surface functionalization, will be described, regarding the key features of uncoated magnetic supports just as those surrounded by protective layers. Special emphasis will be put on carbon-coated cobalt nanoparticles as they have been used extensively in this thesis. Various approaches to achieve their functionalization, leading to good dispersibility in various solvents and applications in a variety of transition metal-catalyzed reactions will be highlighted.

1. Magnetic nanoparticles: materials and functionalization

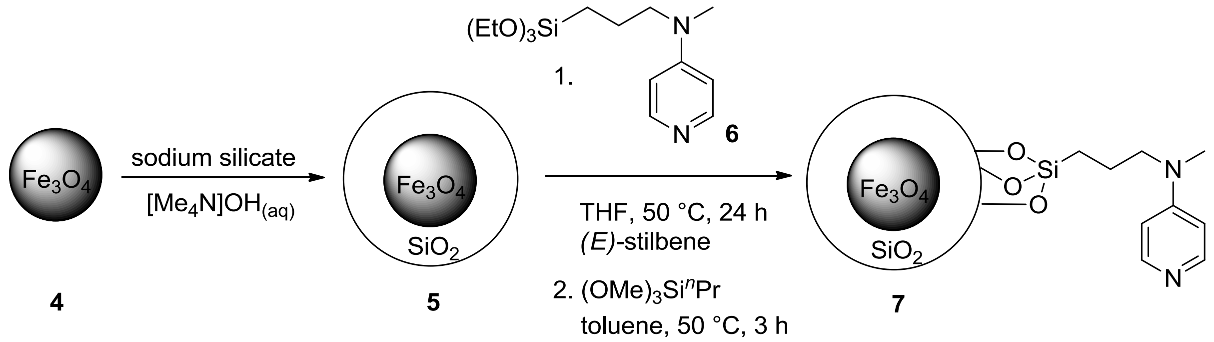
A variety of different magnetic nanomaterials have been studied over the years: NPs from elemental metals (e.g. Fe, Co, Ni), alloys (e.g. FePt, CoPt), iron oxides (FeO, Fe_2O_3, Fe_3O_4), or ferrites MFe_2O_4 (M = Co, Mn, Cu, Zn) have been investigated.[14] Typically, magnetic NPs are synthesized *via* a bottom-up approach from metal salts or other molecular precursors. Depending on the desired catalytic application, either the naked metal nanoparticle itself acts as the catalyst or it acts as a carrier for an immobilized catalyst. However, using naked nanoparticles leads to several disadvantages *e.g.* agglomeration. This can be circumvented, by encapsulating the magnetic metal core in a protective shell, which is then used to immobilize the actual catalyst.[5] Synthesis of these encapsulated NPs is usually carried out using the core-shell approach, which was first developed for the generation of Au(0)-colloids in the 1990s.[15] This method could then be transferred to the functionalization of magnetic NPs, in particular with the most commonly used magnetite- (Fe_3O_4)[5] and Co-based NPs.

Magnetite NPs have been widely employed because of their good availability and low toxicity. Additionally, because of their superparamagnetic properties, they have a low level of agglomeration as they possess no magnetic properties at all in absence of a magnetic field, but are readily magnetized by an external magnetic field. Preparation of magnetite NPs in a narrow size distribution (3–20 nm) can be achieved in a simple and reliable fashion preparation through high-temperature synthesis (265 °C) of iron (III) acetylacetoacetate in phenyl ether in the presence of alcohol, oleic acid and oleylamine.[16] Using the aforementioned core-shell methodology, a variety of surface functionalizations is possible. Lin *et al.* described the direct immobilization of a Ru(II)-BINAP-phosphonic acid on magnetite particles catalyst **2**. [17] The catalyst system was then used for the asymmetric hydrogenation of 1-acetonaphthone (**1**, scheme 1) and exhibited high catalytic activity, excellent enantioselectivity and showed great recycling capabilities by magnetic decantation via an external magnetic field.



Scheme 1: Magnetite supported Ru(II)-BINAP-phosphonic acid catalyst **2** for asymmetric hydrogenation of 1-acetonaphthone **1** exhibiting high catalytic activity (up to 50 TON h^{-1}).

Another more efficient approach is the silanization of the iron oxide surface achieved using the Stöber method.[18] The protective silica shell was introduced *via* hydrolysis of a sol-gel precursor (tetraethoxysilane) yielding shells with 2 to 100 nm thickness. This leads to the surface being terminated by silanol groups, which enables covalent attachment of linkers, ligands, metals, etc.. Moreover this protective silica shell shields the metal oxide core effectively against its surrounding environment. Hence, silica-coated magnetic nanoparticles are among the most versatile scaffolds.[5] Connon *et al.* were the first to synthesize an organocatalyst immobilized on $Fe_3O_4@SiO_2$ **5** (scheme 2) and used it in the acetylation of phenylethanol by acetic anhydride.[19] The material was shown to be active, even at loadings as low as 0.2 mol% and showed excellent catalytic activity (80% conversion after 30 iterative cycles).



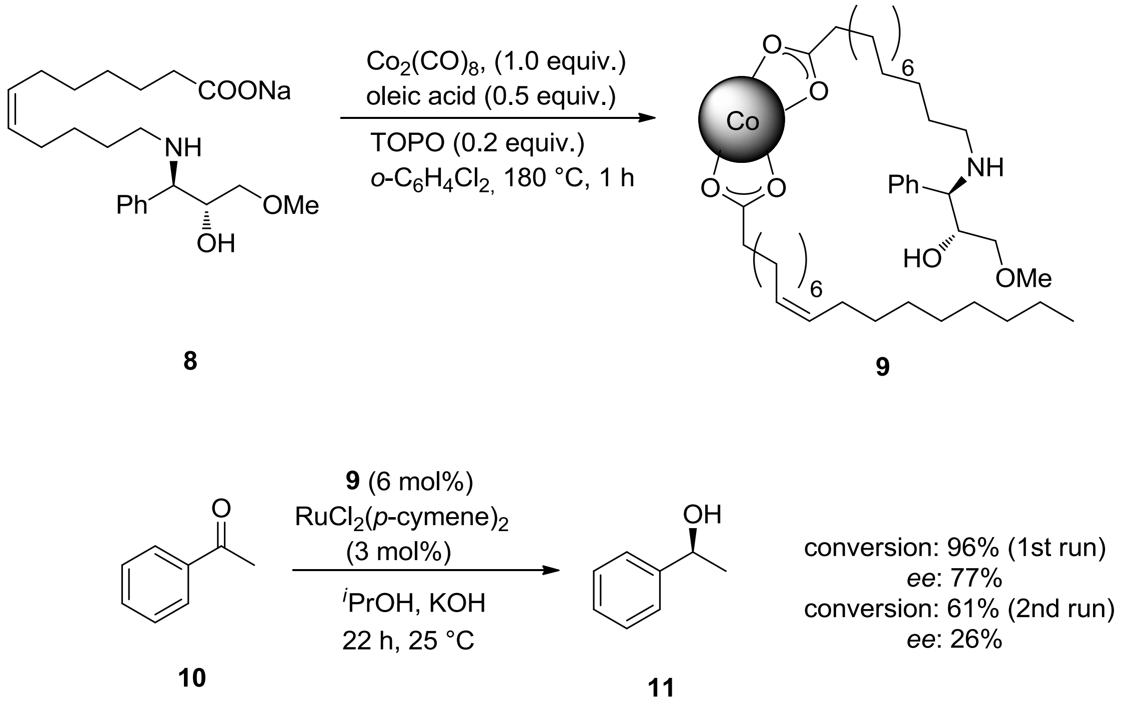
Scheme 2: First organocatalyst immobilized on silica-coated magnetite nanoparticles **5**.

In contrast to magnetite (Fe_3O_4: $M_{S,bulk} \leq 92$ emu/g), pure metals and their alloys possess by far a much higher saturation magnetization (Co: $M_{S,bulk} \leq 163$ emu/g; Fe: $M_{S,bulk} \leq 222$ emu/g),[20] but are highly sensitive to air and other exterior influences. Therefore, a suitable coating is required to protect the metal core.[5] However, the deposition of silica is more challenging due to a lack of OH- groups on the metal surface. Moreover, covalent bonds on silica can be quite labile due to hydrolysis and though is a limiting factor regarding catalytic applications. To tackle these issues, different, more stable functionalization approaches have been invented which will be described in the following chapter. A special focus was put on the contributions of the Reiser group to the field of NPs.

2. Carbon-coated cobalt nanoparticles

As aforementioned, the saturation magnetization ($M_{S,bulk}$) of nanoparticles derived from pure metals (Fe, Co) exceed the saturation magnetization of *e.g.* magnetite. As highly functionalized NPs tend to have a reduced overall magnetization, higher initial magnetization values are desirable to ensure the complete recovery of the magnetic material. However, unprotected pure metal nanoparticles are highly air-sensitive, thus requiring a strong protective shell.[5]

Pioneering work in stabilizing Co NPs was done by Pericàs and co-workers through the use of fatty acids in combination with a functionalized oleic acid (**8**) bearing chiral β-amino alcohols (scheme 3).[21]

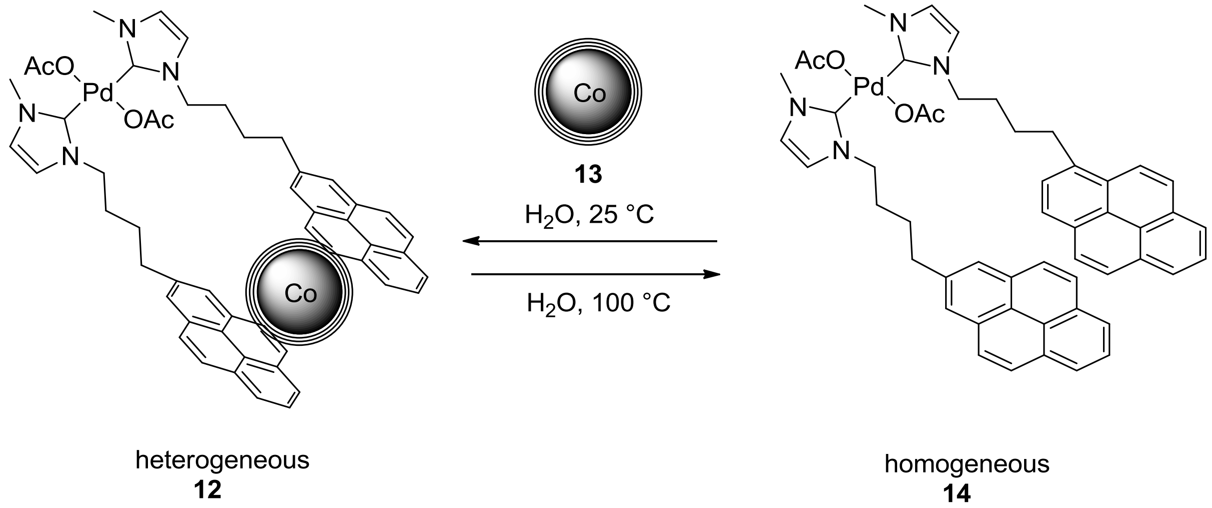


Scheme 3: Cobalt NPs functionalized by chiral amino alcohol **8** for Ru-catalyzed transfer hydrogenation of acetophenone **10**.

Good loadings of 1.4 mmol/g of amino alcohol **8** could be achieved with an average particle size of 13 nm. The so obtained NPs then served as ligands for the Ru-catalyzed transfer hydrogenation (TH) of acetophenone **10** and showed increased activity as well as selectivity compared to the free amino alcohol caused by the concave active site formed on the surface of the nanocatalyst.[21] Unfortunately, recycling proved to be less successful as both, conversion and selectivity decreased already in the second run. The cause for this was believed to be the irreversible reduction of the catalytically active Ru(II) by leached Co(0). To prevent such redox processes from happening, alternative protective shells needed to be developed which prevent leaching of the core metal. One promising approach was the encapsulation of the core metal with graphene layers.[5]

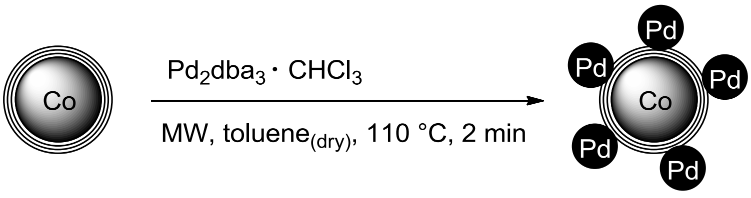
Stark *et al.* developed the first, reliable large-scale synthesis (> 30 g/h) of such carbon coated metal nanoparticles through flame spray pyrolysis *via* reduction of metal carboxylates in nitrogen filled glove boxes.[22] These NPs possess an average diameter of about 50 nm and are coated by approximately 2-4 carbon layers. Furthermore, the material shows a remarkable chemical stability against acids and bases as well as a high thermal stability. At the same time, the carbon shell prevents the labile cobalt core from oxidation. Functionalization can then be achieved either covalently (using surface modification) or non-covalently by utilizing the intrinsic π-π-stacking capabilities of the graphene layer and, *e.g.* aromatic compounds.

This interaction is especially strong in polar solvents, preventing undesired dissociation of the immobilized compounds. Controlled dissociation can be achieved *via* a catch-release strategy.[5] This methodology was used by Reiser *et al.* for non-covalently grafting a palladium complex to Co/C-NPs **13** trough pyrene tags and used the resulting material for the hydroxycarbonylation of aryl halides in water.[23] The non-covalently attached palladium complex **14** could be readily released into solution by applying high temperatures, thus the catalyst became homogeneous during the reaction at 100°C. Once the reaction was finished the mixture was then cooled down to room temperature, leading to reabsorption of the pyrene moieties on the graphene layer and, thus, recovery of the catalyst (scheme 4).



Scheme 4: Non-covalent functionalization of Co/C nanobeads **13** with pyrene-tagged palladium complex **14** via π-π stacking interactions.

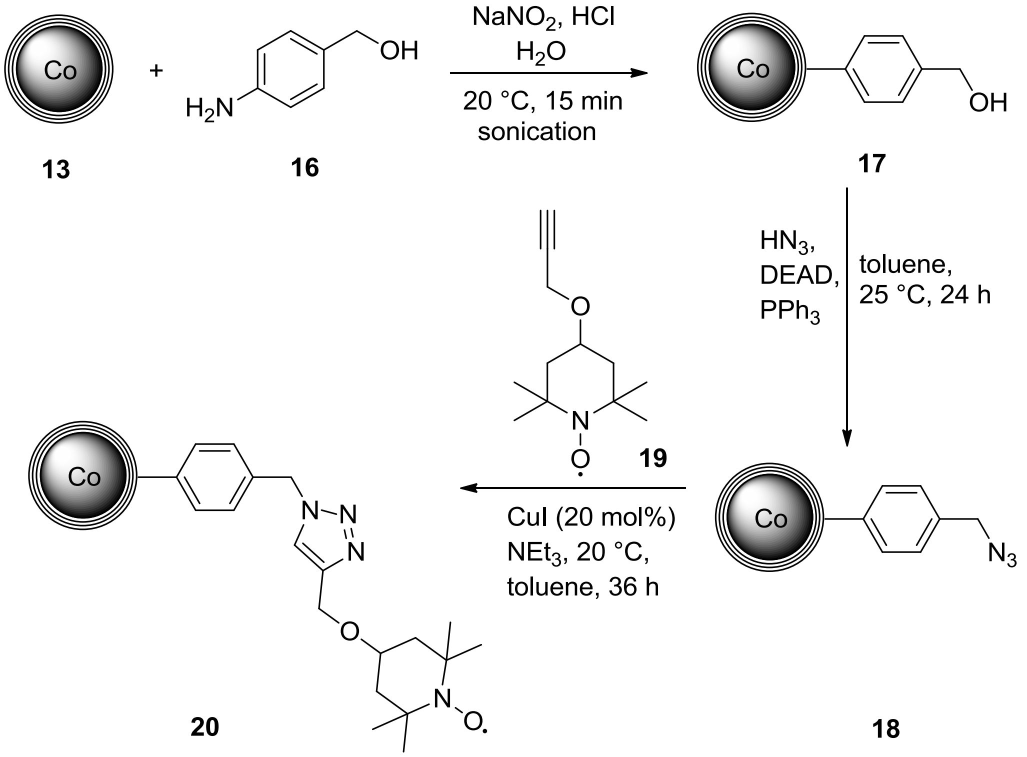
The catalyst could then be easily recovered *via* magnetic decantation and reused for at least 16 times, showing only a negligible palladium leaching. Another example for non-covalent functionalization was the direct deposition of palladium NPs on the graphene surface of carbon-coated cobalt nanobeads by Reiser *et al.* applying microwave conditions.[24] The latter was used for reduction of the palladium precursor to the desired NPs. The so obtained catalyst **15** (scheme 5) could be utilized in the hydrogenation of a variety of alkenes, displaying an impressive catalytic activity (TOF´s up to 11095 h^{-1} for hydrogenation of *trans*-stilbene). The catalyst could be easily separated with an external magnet and then reused for at least six consecutive runs with almost no loss in activity.[24]



13 **15**

Scheme 5: Pd nanoparticles deposited on Co/C nanobeads **13** via microwave irradiation for alkene hydrogenation.

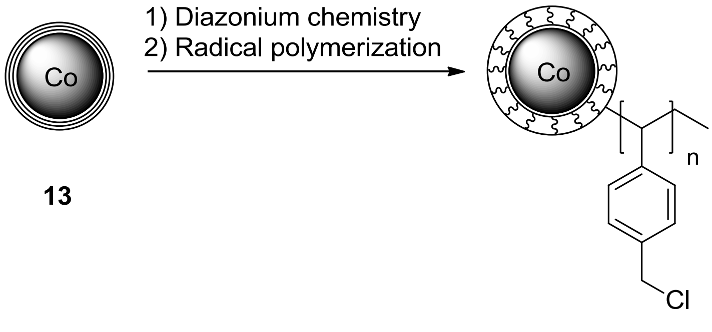
The graphene layers can also be covalently functionalized for the attachment of ligand backbones *via* C-C-bond formation. Stark and Reiser reported the covalent attachment of aryl compounds **16** on the graphene surface by decomposition of a diazonium precursor[5] following literature precedent developed for the grafting of diazonium salts on carbon surfaces (scheme 6)[25]. Subsequently, an alkyne-tagged TEMPO derivative **19** was attached to the aryl-polymer **17** *via* "click" reaction which was then used as a recyclable catalyst (**20**) for the chemoselective oxidation of primary and secondary alcohols to the corresponding aldehydes. The NP catalyst **20** could be easily recovered *via* an external magnet and used in at least 14 iterative cycles with almost no loss in catalytic activity.[26] The absence of significant Co leaching underlines the stability and inertness of the graphene layer support against oxidative conditions.



Scheme 6: Co/C nanobeads **13** functionalized via diazonium chemistry and further tagged by TEMPO **19** via "click" reaction.

However, all of the above-mentioned nanoparticles so far face the same problem of limited loading capacity (0.1-0.2 mmol/g).[20] This can be increased by covalently attaching polymers or dendrimers onto the surface *via* C-C bond formation, followed by functionalization with the desired catalyst.[5] Furthermore, this also prevents the nanomagnets from agglomeration and improves their dispersibility in various organic solvents.[20] Dendrimers can be covalently attached to the NPs using two different approaches: direct synthesis on the NP after the introduction of a linker or the grafting of a presynthesized dendrimer onto the desired NPs.[20] Both methods lead to materials with a high functional group density. Reiser *et al.* used the grafting strategy for the functionalization of Co/C nanobeads with polyester dendrons based on 2,2-bis-(hydroxymethyl) propionic acid. Starting from the previously mentioned azide functionalized Co/C beads **18**, dendrons bearing alkynes on the one side and either hydroxyl or ammonium groups on the other side were again added *via* "click" reaction. This shell led to highly functionalized NPs which formed stable particle dispersions in water.[27] However, synthesis of these materials can be quite complicated.

Polymer-functionalized nanoparticles, in contrast, are easier to synthesize than their dendrimeric analogues. Polymeric shells, which are covalently bound to carbon-coated magnetic nanobeads, can be introduced using, *e.g.* free radical polymerization. (scheme 7).

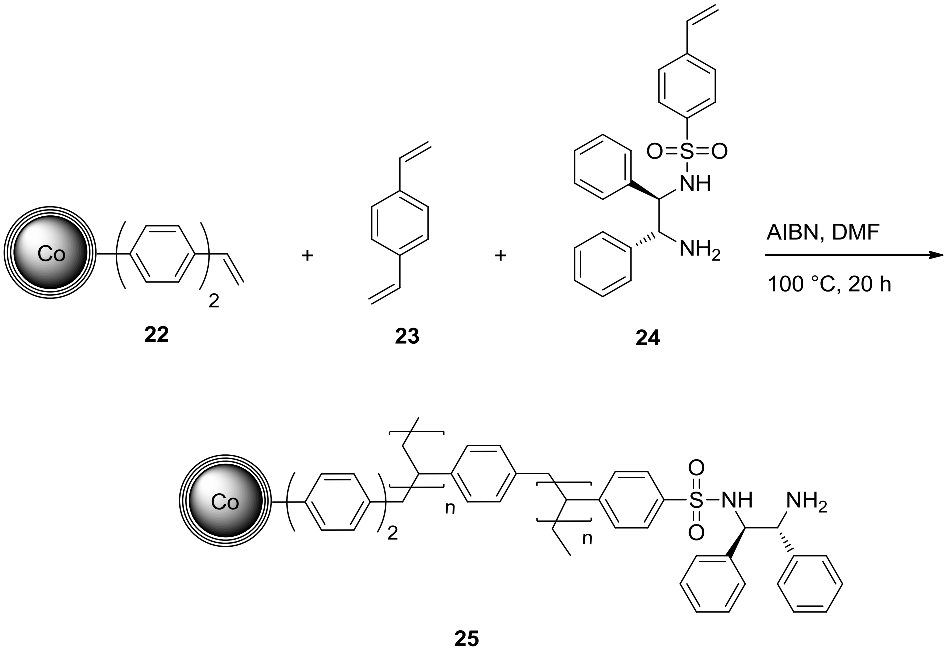


13

21

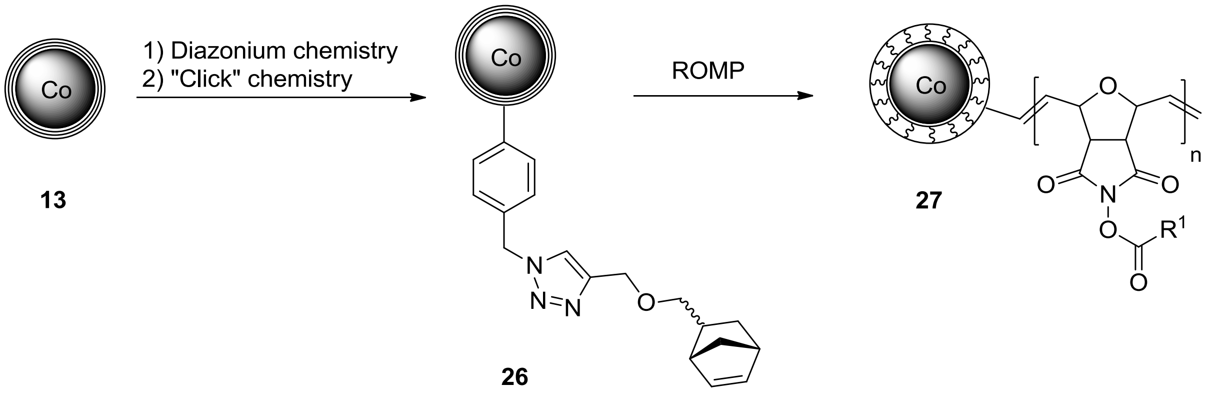
Scheme 7: Preparation of polymer-coated NPs via radical polymerization.

Stark *et al.* reported a grafting polymerization of 4-chloromethylstyrene on the surface of vinyl-functionalized Co/C particles[28] with high Cl-loadings up to 3 mmol/g. The resulting chloro-polystyrene-coated NPs **21** gave access to, *e.g.* an immobilized variant of the Jorgensen-Hayashi organocatalyst[29] or various palladium NHC complexes.[30] Furthermore, also magnetic amine-, borohydride-exchange- and Wang-aldehyde resins were amenable from magnetic poly(benzyl chloride) NPs **21**.[31] Reiser *et al.* used **21** for the immobilization of a Noyori-type ruthenium complex on Co/C nanobeads which was built up by radical copolymerization of Co/C nanoparticles bearing a polystyrene matrix **22** with divinylbenzene **23** and chiral diamine ligand **26**. This resulted in catalyst **25** which gave excellent results in the asymmetric transfer hydrogenation of various aryl ketones (81-100% yield; 91-99% *ee*). The catalyst **25** was, furthermore, recyclable for 10 consecutive runs with low Pd leaching (< 10 ppm) and almost no loss in catalytic activity (scheme 8).[32]



Scheme 8: Immobilization of a Noyori-type Ru-catalyst via radical copolymerization for asymmetric transfer hydrogenation of aryl ketones.

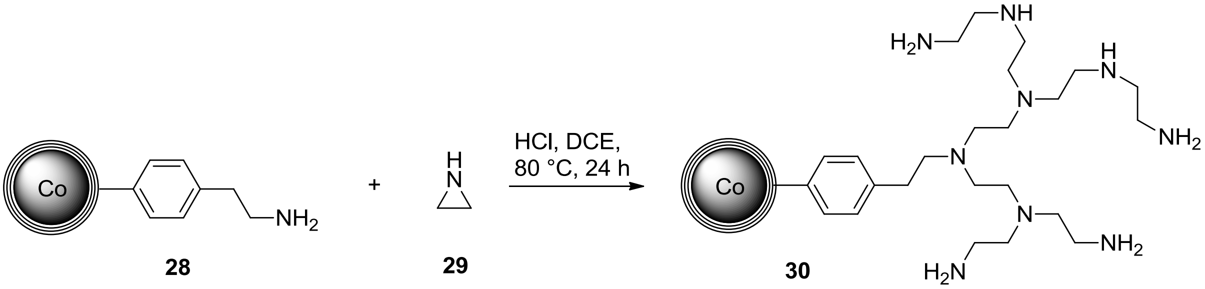
An alternative approach for the synthesis of polymer-coated NPs is the use of surface-initiated ring opening metathesis polymerization (ROMP). A versatile strategy was developed by introducing norbonene tags on the surface of Co/C NPs **13** (scheme 9).[33]



Scheme 9: Preparation of polymer-coated NPs via ROMP.

Reiser and Hanson extended this method to the synthesis of high loading, effective acylating agents for primary and secondary amines giving high yields and good recyclability. As key step for the NP preparation, norbonene tags were introduced *via* ROMP strategy to the surface of Co/C nanoparticles and further activated using a Grubbs second generation catalyst derivative.[34]

Reiser *et al*. also employed the ROMP strategy for the direct covalent synthesis of a PEI (polyethylene imine) polymer on the Co/C nanoparticles.[35] The method was adapted from Liu *et al.,* who developed the synthesis of polyethyleneimine-grafted carbon nanotubes (CNT). The latter were obtained by performing a cationic polymerization of aziridine in the presence of amine-functionalized multiwalled CNTs.[36] This approach was used during several synthetic studies for NP functionalization with different functional groups including hydroxyl, amine and ammonium terminal groups in evaluation of their water dispersibilty.[35] The PEI polymer was synthesized by direct cationic ring opening polymerization of covalently amino-functionalized Co/C particles **28** with an excess of aziridine **29**, which led to an outstanding high loading of 13 mmol/g on amino functionalities (scheme 10).



Scheme 10: Synthesis of the PEI particles **30**.[35]

The Co/C-PEI NPs **30** proved to be highly effective Hg^{2+}-scavengers for the treatment of wastewaters, which could be effectively demonstrated on a 20 L scale requiring only 6 mg of material **30**. The decontamination level proved to be acceptable for drinking water (< 30 ppb) and the system was further recyclable for at least six consecutive runs.[37] In the following chapters, the Co/C-PEI NPs will be highlighted in its capability of encapsulating Pd nanoparticles and the resulting excellent catalytic activity in a variety of Pd-catalyzed reactions.

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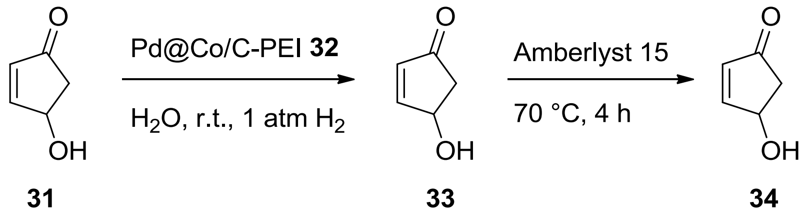
B. Main part

1. Pd(0) nanoparcticles stabilized by PEI supported Co/C nanobeads as a recyclable nanocatalyst for hydrogenations of olefins in water

A highly efficient and sustainable alternative to hydrogenate various alkenes in water with a recyclable catalyst is reported. Therefore, a poly(ethylene imine) supported Co/C hybrid material (Co/C-PEI **30**) showed a high capability to incorporate and stabilize metal nanoparticles, like palladium. The new nanocatalyst (Pd@Co/C-PEI **32**) is highly water dispersible, easily retrievable via an external magnet and thus an effective and green alternative to conventional and commercial available Pd/C. Its synthetical importance is highlighted by the facile synthesis of cyclopentenone **34**, which acts as an important building block in organic synthesis. Therefore the hydrogenation of the model substrate 4-hydroxycyclopentenone **31** to 4-hydroxycyclopentanone **33** in water was conducted and the magnetic catalyst was even efficient to be reused for seven consecutive runs without any significant loss in activity. (scheme 11).



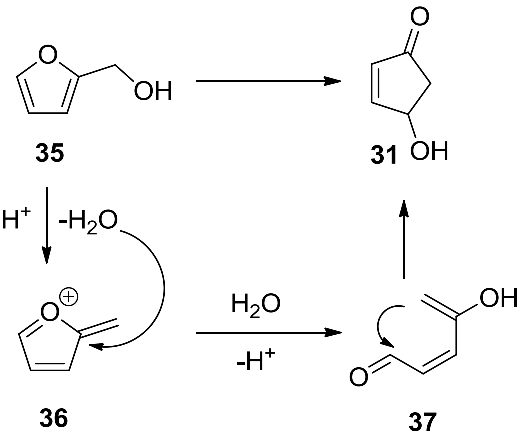
Scheme 11: Hydrogenation of **31** to **33** applying Pd@Co/C-PEI **32** and further reaction to cyclopentenone **34**.

1.1 Introduction

The catalytic hydrogenation of organic molecules is one of the most widely used methods to get access to reduced compounds, both, in academic and industrial applications. Especially with regards to green and sustainable chemistry, hydrogenation reactions with the use of molecular hydrogen and a recyclable catalyst gained a huge interest in the last decade.[1] Magnetic nanocatalysts render themselves as excellent supports for hydrogenation catalysts due to their high surface-to-volume ratio and the facile recycling *via* magnetic decantation. To point out only one example in the field of magnetic nanoparticle (NP) based hydrogenation catalysts: In 2014, Reiser *et al.* grafted the surface of magnetic Co/C nanobeads directly with Pd nanoparticles which showed exceptionally high catalytic activity in the hydrogenation of several alkenes within short reaction times. The magnetic catalyst (Pd@Co/C) was furthermore easily retrievable within few seconds *via* an external magnet and showed quite low Pd leaching (< 6 ppm per cycle) into the reaction solution.[2]

In regard to green chemistry, the use of water as a solvent for organic reactions has gained more and more interest in recent research.[3] To combine the strategy of using magnetic NPs with water as a green solvent, a catalyst needs to be capable to avoid agglomeration, thus deactivation is reduced and furthermore it needs to form stable dispersions to guarantee a good reactivity. The abovementioned nanoparticle-on-nanoparticle catalyst (Pd@Co/C), however, showed relatively poor dispersibility in water and is therefore not suitable for hydrogenations in water. In principal hydrogenation reactions in water are common for years, however, they focused on transfer hydrogenation[4] or hydrogenations in biphasic systems.[5] Often additives like small quantities of methanol or ethanol as co-solvent[6] or silanes[7] are needed, due to solvation problems. As an exceptional case, Zhang *et al.* reported an aqueous phase hydrogenation of 4-hydroxy-2-cyclopentenone during studies towards the selective synthesis of 1,3-cyclopentanediol.[8] The hydrogenation of 4-hydroxy-2-cyclopentenone could be performed at a 7 mmol scale (0.7 g) applying 0.1 g catalyst (Raney-Nickel, Ru/C, Pd/C) at 5 MPa H_2 pressure in 40 g H_2O. At room temperature subsequently 80% of 4-hydroxycyclopentanone after 1 h reaction time could be obtained. At higher temperatures dehydration to cyclopentenone and further hydrogenation to cyclopentanone (60%) and cyclopentanol was observed. With this publication in mind, the focus turned to mild hydrogenation conditions at ambient pressure without any further additives as an efficient and green alternative to Pd/C.

Furthermore, as model substrate 4-hydroxycyclopentenone was chosen, since it is not only a highly water-soluble substrate and fits into the concept of green chemistry, but is also a valuable intermediate for the synthesis of natural products and analogues.[9,10] 4-hydroxy-2-cyclopentenone **31** is generally accessible *via* furfuryl alcohol **35** (scheme 12) under conventional heating in aqueous media for 22-48 h. Reiser *et al.* developed in 2010 a microwave-assisted synthesis of 4-hydroxy-2-cyclopentenone **31** out of furfuryl alcohol **35** in water within minutes (200-210 °C, 15 bar) and was further able to transform this synthesis to a microreactor in a continuous flow setup, hence, making it amenable for large-scale synthesis in industry.[11]

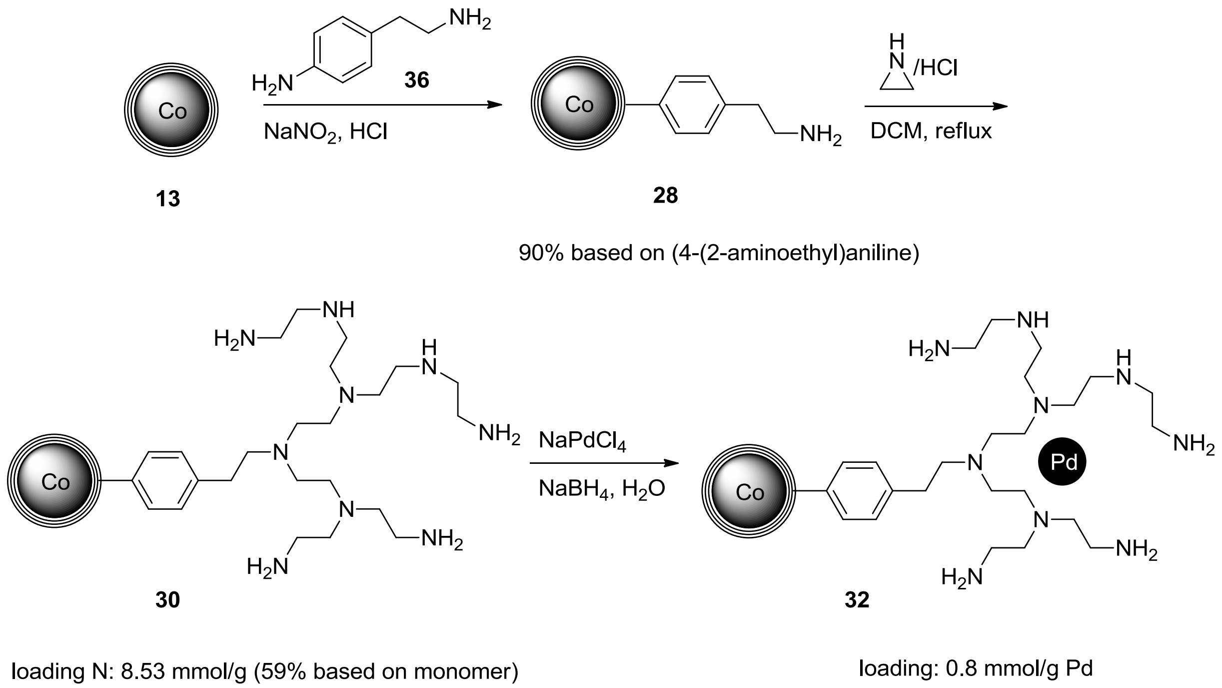


Scheme 12: Conversion of furfuryl alcohol **35** to 4-hydroxy-2-cyclopetenone **31**.

In 2014, a general one-pot synthesis of 4-hydroxy-2-cyclopentenone out of simple furanes has been reported. Noteworthy, the complete synthesis was accomplished in water applying the green oxidant singlet oxygen as an additive.[12] One possible application of 4-hydroxy-2-cyclopentenone **31** is its conversion to cyclopentenone **34**, being an intermediate used on an industrial scale, *e.g*. in fragrance production. Since, as already mentioned, 4-hydroxy-2-cyclopentenone **31** is synthesized and highly soluble in water the aim was to develop magnetically supported catalysts that would be amenable for hydrogenations in this medium.

1.2 Results and discussion

Over the last decades, carbon coated nanobeads have proven themselves as excellent scavengers, reagents, and catalysts.[13] Especially noteworthy is their high potential to act as recyclable catalysts for hydrogenation reactions.[2] In order to generate a highly water dispersible and green catalyst for hydrogenation reactions in water, the PEI polymer was attached to the Co/C nanobeads, which already showed a great capacity to catch Hg^{2+} ions in water.[14] Based on this previous investigations, Pd nanoparticles were incorporated into this system following an established procedure[15] modified by Reiser *et al.*[16], whereby the PEI polymer should stabilize the NPs from agglomeration and ensure a good dispersibility in water. The synthesis was accomplished within three steps (scheme 13): First Co/C nanobeads **13** were covalently functionalized *via* diazonium chemistry dispersing them with 4-(2-aminoethyl)aniline **36** and HCl in water. Adding a pre-cooled solution of sodium nitrite, the in situ formed aryl radical could be covalently grafted to the graphene layer of the cobalt nanobeads, yielding amino-tagged particles **28** with an amine loading of 0.06 mmol per g. Subsequently, these NPs **28** were exposed to a surface-initiated cationic polymerization of aziridine **29** to obtain PEI functionalized nanoparticles **30** with a high amino loading of 8.5 mmol/g. The latter was performed in DCM as a solvent, applying reflux conditions. After 24 h of reaction time, the polymeric NPs were stuck to the glass wall of the flask indicating the polymerization to be complete. This hybrid material forms stable dispersions in water without any sign of precipitation.



Scheme 13: Synthesis of the NP catalyst **32**; Reaction conditions: 1) 1 g **13**, 1 mmol (132 µL) 4-(2-aminoethyl)phenylaniline **36** in 15 mL H_2O, HCl_{conc} (1 mL), add 1 mmol (103.5 mg) $NaNO_2$ in 15 mL H_2O; 2) 250 mg **28**, 0.18 µmol (15 µL) HCl_{conc}, 15 mmol (778 µL) aziridine **29** in 12 mL DCM heating at 50 °C for 24 h; 3) 50 mg **30**, 50 µL HCl (1M), 0.047 mmol (5 mL) Na_2PdCl_4 solution in 2 mL H_2O, adding 0.24 mmol (8.9 mg) $NaBH_4$ in 2.5 mL H_2O.

The Pd(0) NPs were obtained adapting the method of Amali *et al.* by reduction of a Pd(II) precursor (Na_2PdCl_4) and simultaneously embedding them into the PEI polymer.[15] Pd(0) nanoparticles are common for hydrogenations and in general accessible *via* Pd(0) precursors like Pd_2dba_3 or reduction of Pd(II) reagents like $Pd(OAc)_2$ or Na_2PdCl_4 *via* microwave irradiation.[2] In this work Na_2PdCl_4 was chosen due to the structure of the applied NP polymer: At pH = 6, the free amines of the PEI-coated NPs **30** can entrap $PdCl_4^-$ ions *via* positively charged ammonium groups. These are then selectively reduced by sodium borohydride producing Pd(0) NPs. Using 5 mL of Na_2PdCl_4 (0.0094 M) and 50 mg of Co/C-PEI **30** (8.5 mmol/g) led to an excellent incorporation of 91%. The Pd loading was determined by ICP-OES as 0.8 mmol/g (8.5 wt%). The TEM picture (figure 1) verifies the formation of small Pd nanoparticles (visible as black dots) with an average size of 5 nm. They are embedded in the PEI polymer (greyish structure) which surrounds the 20-50 nm sized Co/C NPs (big black dots).

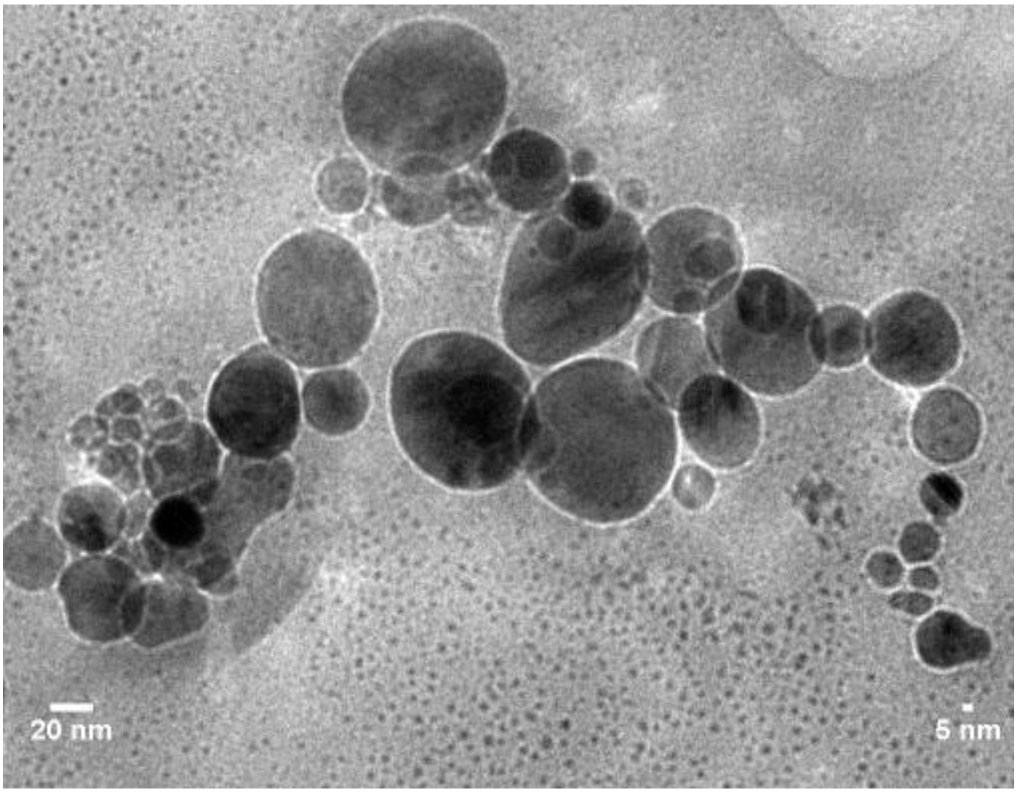


Figure 1: TEM picture of Pd@Co/C-PEI **32**.

XPS studies have been done for confirming the oxidation state of the Pd nanoparticles (figure 2). The following spectrum shows the $3d_{5/2}$ and the $3d_{3/2}$ binding energy, presumably, for Pd(0). However, the intensity is relatively low and the binding energies for Pd(0) and Pd(II) are not differing a lot, hence, it cannot be proven that only Pd(0) is present.

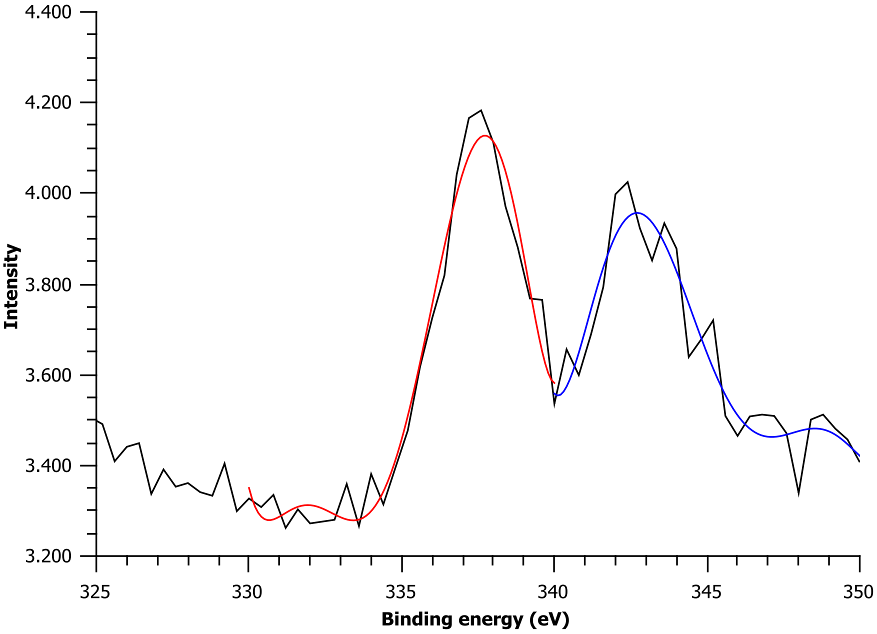
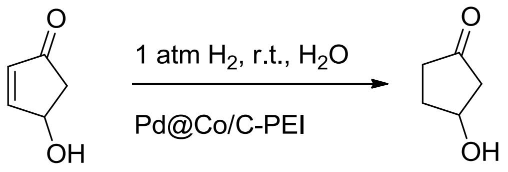


Figure 2: XPS spectrum of Pd@Co/C-PEI **32**.

As before mentioned the aim was to use this novel hybrid system **32** for the hydrogenation of the model substrate 4-hydroxy-2-cyclopentenone **31**, which is obtained from Piancatelli rearrangement in water. Benchmarking, the Pd@Co/C-PEI catalyst **32** first in the hydrogenation of **31** at ambient H_2 pressure, room temperature and water as solvent (table 1) showed full conversion after 2 h of reaction time by applying 0.5-0.1 mol% of Pd@Co/C-PEI **32**. Even with a low Pd loading of 0.01 mol% (entry 4), full conversion of the starting material could be achieved after a prolonged reaction time of 4 h. Thus, extraordinary high TONs up to 9800 compared to conventional Pd/C were reached. Furthermore, applying 0.01 mol% of the catalyst went hand in hand with an upscale of the hydrogenation reaction from 0.5 mmol to 20 mmol. Hence, high amounts of 4-hydroxycyclopentanone **33** (2 g) were accessible with relatively low amount of Pd (2.5 mg Pd@Co/C-PEI **32**).

It turned out that water was an excellent medium for the reduction of 4-hydroxy-2-cyclopentenone **31**, indeed, while the conversion was significantly lower using common solvents for hydrogenations like ethanol (88% conversion after 2 h, entry 5) Notably, control experiments were carried out to verify Pd@Co/C-PEI **32** as the catalytic active species. The reaction showed neither conversion when solely Co/C-PEI **30** was applied (entry 6), nor in the absence of any catalyst (entry 7). The achieved results were then compared with the reaction catalyzed by conventional Pd/C which is usually used for hydrogenations of organic compounds (entry 8). The latter not only showed less activity (53% yield after 18 h), but also had the problems of forming cyclopentanone as a byproduct.

Table 1: Hydrogenation studies on 4-hydroxy-2-cyclopentenone employing Pd@Co/C-PEI **32**.



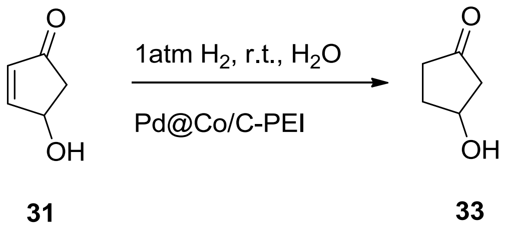
31 **33**

entry	catalyst	t [h]	Pd [mol%]	yield [%]	TOF [h^{-1}]
1	Pd@Co/C-PEI	2	0.5	97	97
2	Pd@Co/C-PEI	2	0.2	95	238
3	Pd@Co/C-PEI	2	0.1	96	480
4	Pd@Co/C-PEI	4	0.01	98	2450
5[a)]	Pd@Co/C-PEI	2	0.5	88	88
6	Co/C-PEI	2	-	-	-
7	-	2	-	-	-
8	Pd/C	18	0.1	53	21

Reaction conditions: 0.5 mmol 4-hydroxy-2-cyclopentenone **31**, 1 atm H_2, r.t., 5 mL H_2O, 0.8 mmol/g Pd@Co/C-PEI (0.5 mol%-0.1 mol%); 20 mmol 4-hydroxy-2-cyclopentenone **31**, 1 atm H_2, r.t., 8.5 mL H_2O, 0.8 mmol/g Pd@Co/C-PEI (2.5 mg, 0.01 mol%); [a)]reaction in EtOH as solvent.

In order to study recycling of the catalyst and investigate the metal leaching into the product, the reaction was performed at large scale (20 mmol). The hydrogenations were then carried out with 0.01 mol% palladium catalyst **32** and after achieving full conversion the catalyst was recycled by an external magnet and subsequently reused for a second run. Thus, seven consecutive runs were performed with no significant decrease in activity (98% to 92%) and a low palladium contamination in the isolated product, namely 3 ppm in average (table 2). In summary, 19% of the initial palladium was lost in total over the seven runs, however, no significant effect on the catalytic activity could be observed.

Table 2: Recycling studies on the hydrogenation reaction of **31** applying Pd@Co/C-PEI **32**.



entry	yield [%]	leaching Pd [ppm]	Pd loss [%]	leaching Co [ppm]
1	98	0.2	0.2	7
2	98	0.6	0.6	14
3	99	0.8	0.8	16
4	97	2.8	2.6	18
5	98	3.9	3.7	31
6	96	4.5	4.2	58
7	92	8.1	7.6	60

Reaction conditions: 20 mmol 4-hydroxy-2-cyclopentenone **31**, 1 atm H_2, r.t., 8.5 mL H_2O, 4 h, 0.4 mmol/g Pd@Co/C-PEI (5 mg, 0.01 mol%).

By contrast to the abovementioned low palladium leaching, the contamination regarding leached cobalt is significantly higher. An explanation for this observation can be found in the variation of graphene layers in the applied batch of nanoparticles received from the ETH Zürich. Small imperfections in the thin, surrounding graphene layers no longer provide the cobalt in the metal core from oxidation or the employed reaction conditions. Thus, the cobalt content in the isolated products is a lot higher than normally observed for reactions applying Co/C. Figure 3 shows a graphical representation of the obtained conversion of 4-hydroxy-2-cyclopentenone **31** in the seven following runs. The recycling experiments were performed three times each to give better evidence (represented in the error bars).

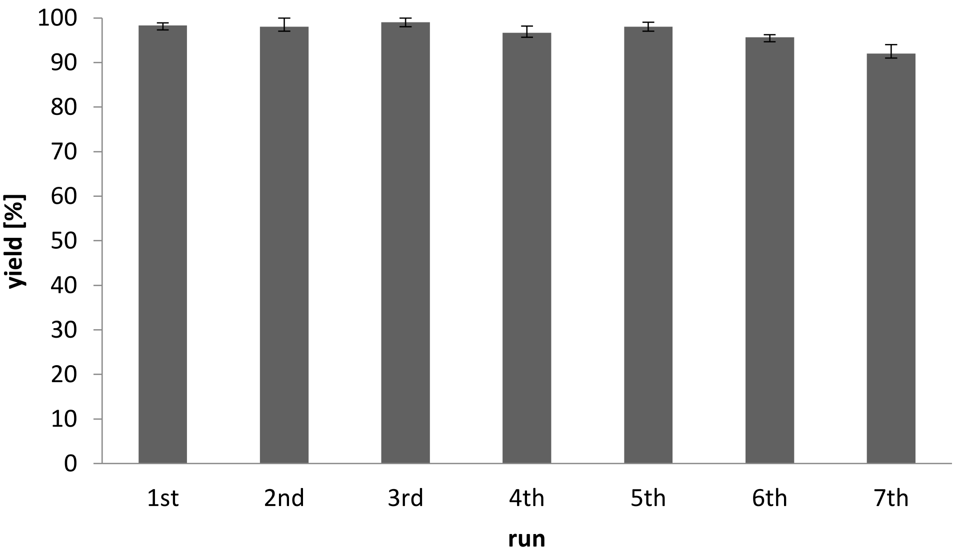
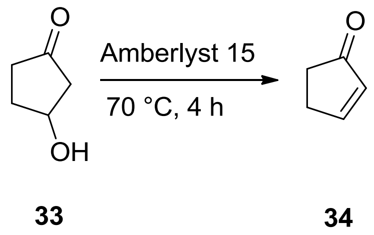


Figure 3: Recycling regarding the hydrogenation of 4-hydroxy-2-cyclopetenone graphically represented.

Having shown the excellent catalytic activity and recycling of the hybrid system Pd@Co/C-PEI **32**, the model substrate 4-hydroxy-2-cyclopentenone **31** and the corresponding alkane 4-hydroxycyclopentanone **33** were further converted to cyclopentenone **34**. As already mentioned, **34** is a valuable building block in pharmaceutical products and further an intermediate being used on industrial scale. This transformation would give a solution to the problem of energy- and time-consuming water removal before its further use. **34** is water-insoluble, in contrast to its precursors, and thus easily accessible *via* simple extraction with organic solvents.[17] 4-hydroxy-2-cyclopentenone **31** is obtained from furfuryl alcohol **35** *via* Piancatelli rearrangement[11] and is converted by hydrogenation reaction to its corresponding alkane **33** by applying the hybrid system Pd@Co/C-PEI **32** quantitatively. Noteworthy, this reaction was carried out on a 20 mmol scale, by using 0.01 mol% Pd@Co/C-PEI **32**. After magnetic decantation of the catalyst, the latter is further treated with an acidic ion exchanger, Amberlyst 15, at high temperatures of 70 °C to eliminate the hydroxy moiety (scheme 14). This gave the product cyclopentenone **34** in high yields. Thereby, the ion exchanger can also be removed easily *via* decantation and the water-insoluble **34** can be extracted (with ethyl acetate), followed by distillation to yield the isolated product. Since all these reactions can be performed in aqueous media, just with the aid of a catalyst, only water as byproduct is formed which renders the process attractive from an ecological point of view.



Scheme 14: Elimination of the hydroxyl moiety; Reaction conditions: 0.5 mmol (20 mmol) 4-hydroxy-2-cyclopentanone **33**, 30 mg (255 mg) Amberlyst 15 with c = 30 mg/mL, 1 mL (8.5 mL) H_2O, 70 °C, 4 h.

All in all, a fast and energy saving procedure for the synthesis of the technical product cyclopentenone **34** could be developed (figure 4). Key step is the hydrogenation of 4-hydroxy-2-cyclopentenone **31** in water applying our new hybrid system Pd@Co/C-PEI **32** which is reusable without any loss in activity and relatively low product contamination for at least seven consecutive runs.

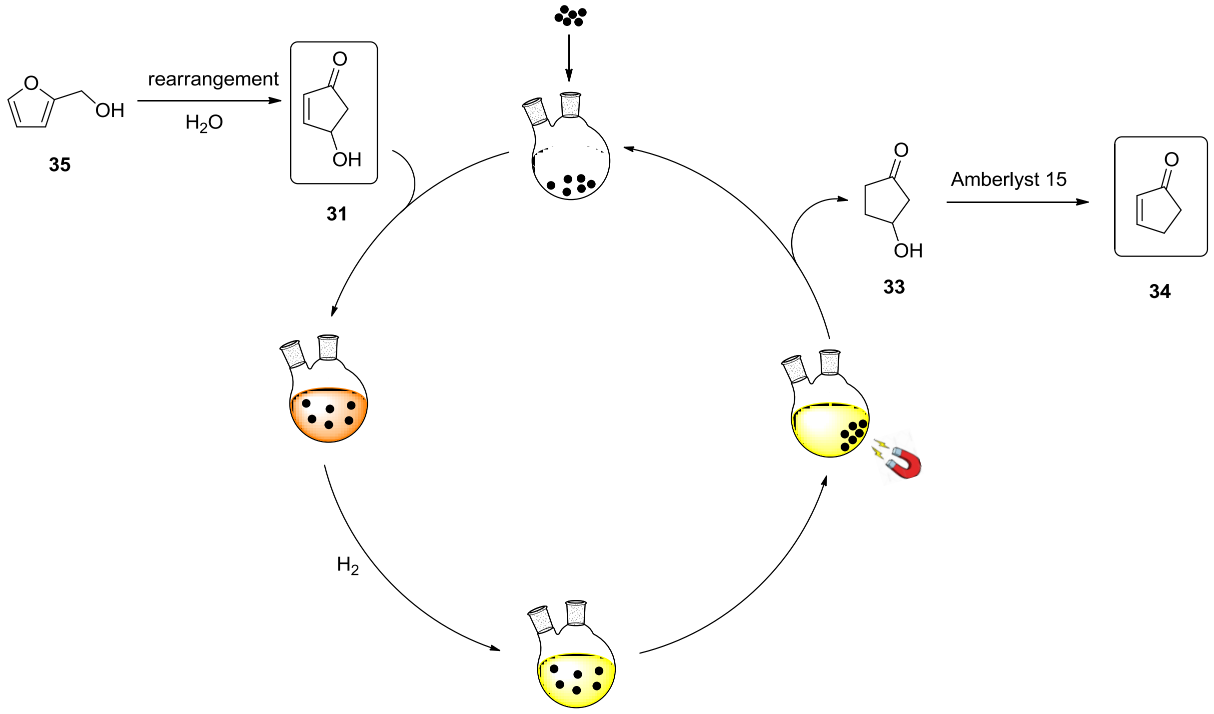
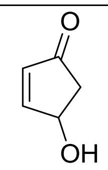
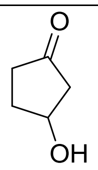
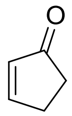
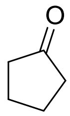
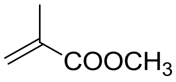
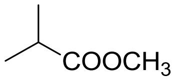
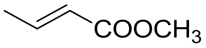
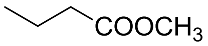
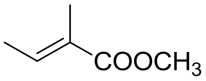
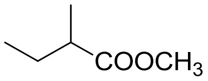
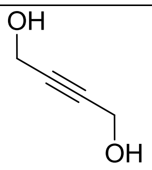
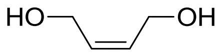
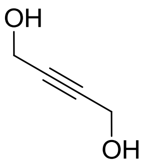
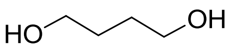
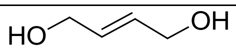
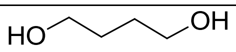


Figure 4: Cycle for transformation of 4-hydroxy-2-cyclopentenone **31** to the water insoluble cyclopentenone **34**.

In order to further validate the catalytic activity of the new hybrid material Pd@Co/C-PEI **32** and its efficiency of hydrogenating various olefins, the substrate scope was expanded and by using the same conditions as before (ambient H_2 pressure, r.t., H_2O, 0.5 mol% Pd@Co/C-PEI **32**) (table 3).

Table 3: Pd@Co/C-PEI **32** catalyzed hydrogenation reactions with various substrates.

entry	substrate	product	t [h]	yield [%]
1	 **31**	 **33**	2	97
2	 **34**	 **38**	2	95
3	 **39**	 **40**	4	98
4	 **41**	 **42**	2	96
5	 **43**	 **44**	2	98
6	 **45**	 **46**	4	97
7	 **47**	 **48**	2	51
8	 **47**	 **49**	4	96
9	 **50**	 **49**	4	96

Reaction conditions: 0.5 mmol substrate, 1 atm H_2, r.t., 5 mL H_2O, 0.8 mmol/g Pd@Co/C-PEI (4 mg, 0.5 mol%); yields are isolated yields.

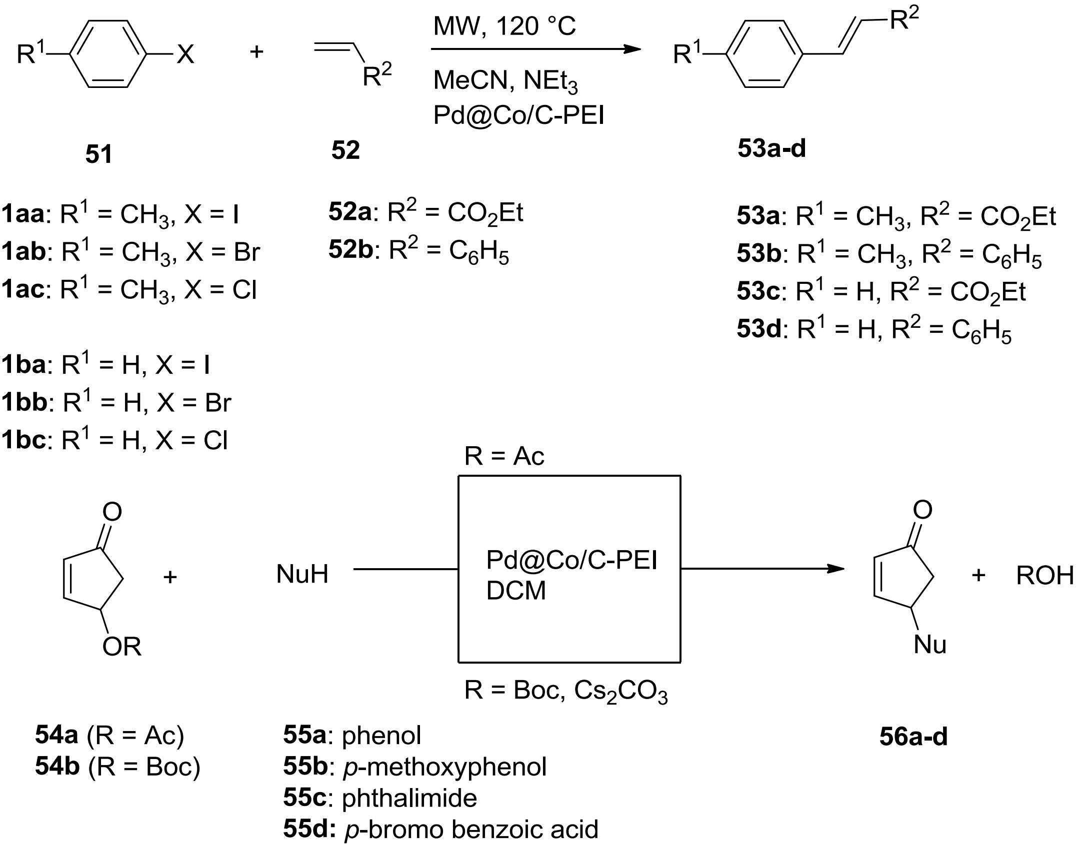
Di-or trisubstituted olefins were hydrogenated in excellent yields (entry 4,5,6). Noteworthy, especially trisubstituted olefins (entry 6) which are in general difficult to hydrogenate were completely converted in relatively short reaction times (4 h) to the corresponding alkanes by the described catalytic system, yielding good TOFs up to 50 h^{-1}. However, higher substituted alkenes **41** and **43** were easier to reduce than primary alkenes **39** (entry 4,5 compared with entry 3). Even the electron withdrawing ester group had no negative effect on the activity of the catalyst, thus, the corresponding products **40**, **42**, **44**, **46** could be obtained almost quantitative within only 2-4 hours. Furthermore, Pd@Co/C-PEI **32** was able to selectively hydrogenate the alkyne **47** to its corresponding alkene by time selection (entry 7). After 2 h only the alkene was obtained, whereby a prolonged reaction time to 4 h exclusively yielded the corresponding alkane (entry 8). In the case of entry 2, further selectivity of the preferred C-C bond reduction over the C-O bond reduction was observed. The reported catalytic system could reduce the C-C bond of cyclopentenone **34** in the presence of a carbonyl group. Worth to mention that by applying commercial Pd/C the C-O double bond, as well as the C-C bond, were completely reduced after 2 h of reaction time.

1.3 Conclusion

The catalytic activity and the suitability of the new synthesized hybrid system Pd@Co/C-PEI **32** was tested for the hydrogenation of various alkenes, especially 4-hydroxy-2-cyclopentenone **31**, in aqueous media. The NP catalyst gave excellent results for all tested substrates (di-/ tri-substituted alkenes, alkynes) and was easily recyclable for seven iterative cycles with consistent catalytic activity. Notably, the hydrogenation and further conversion to cyclopentenone **34** could be performed on large scale (20 mmol) with low amounts of nanoparticle catalyst resulting in high turnover numbers of 9800. Furthermore, it gives a green approach for this transformation to water-insoluble cyclopentenone **34** in aqueous media forming only water as a byproduct, but also avoids the high energy consuming work by evaporating the solvent. The active sites of Pd@Co/C-PEI **32** showed high stability grounding in low Pd leaching into the desired product (below 8 ppm). To sum up, with Pd@Co/C-PEI **32**, a catalytic system was found forming stable dispersions in water and thus being a promising alternative towards conventional Pd/C.

2. Pd(0) supported coupling reactions catalyzed *via* Pd@Co/C-PEI nanoparticles

The previous chapter dealt with the outstanding properties of the newly synthesized hybrid material Pd@Co/C-PEI **32** regarding its excellent stability and dispersibility in water, making it highly desirable for water-mediated hydrogenations of various alkenes/alkynes. While these reactions were all performed in water as green solvent, this catalyst is not limited to only hydrogenate double- and triple-bonds, but also finds its application in further, well-known Pd (0) catalyzed reactions. Therefore, Heck coupling reactions and Pd(0) catalyzed allylations were selected as model reactions for evaluating the catalytic activity of Pd@Co/C-PEI **32** in C-C-coupling reactions. Notably, the catalyst not only showed high dispersibility in aqueous media but also forms stable dispersions in a variety of polar solvents due to their high density of amino groups. The results showed a high catalytic activity in the selected C-C coupling reactions whereby also in this case, the nanocatalyst **32** showed good recyclability for at least five iterative runs. The catalytic activity showed no significant decrease and the Pd leaching into the reaction solution could be kept at a low level. In scheme 15 an overview over the accomplished reactions and substrate scope applying Pd@Co/C-PEI **32** is shown.



51 **52** **53a-d**

51aa: $R^1 = CH_3$, X = I
51ab: $R^1 = CH_3$, X = Br
51ac: $R^1 = CH_3$, X = Cl

51ba: $R^1 = H$, X = I
51bb: $R^1 = H$, X = Br
51bc: $R^1 = H$, X = Cl

52a: $R^2 = CO_2Et$
52b: $R^2 = C_6H_5$

53a: $R^1 = CH_3$, $R^2 = CO_2Et$
53b: $R^1 = CH_3$, $R^2 = C_6H_5$
53c: $R^1 = H$, $R^2 = CO_2Et$
53d: $R^1 = H$, $R^2 = C_6H_5$

54a (R = Ac)
54b (R = Boc)

55a: phenol
55b: *p*-methoxyphenol
55c: phthalimide
55d: *p*-bromo benzoic acid

56a-d

Scheme 15: Overview over the chosen Pd-catalyzed coupling reactions applying Pd@Co/C-PEI **32**.

2.1 Heck reactions

2.1.1 Introduction

Pd catalyzed coupling reactions are still among the most useful reactions in organic synthesis for selective C-C bond formation and insertion of aryl units which are common substructures for the drug skeletons.[15] In 2010, the significance of this new strategies to connect C-C bonds was rewarded with the Nobel Prize in chemistry to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki for their pioneering work on palladium-catalyzed cross-coupling reactions. In the 1960s, first investigations were made on this field, establishing the fundamental research. In particular, the Heck coupling reaction is extensively utilized due to its high efficiency in the synthesis of arylated olefins and the resulting widespread applications.[18] In 1974, Heck *et al.*[19] announced palladium acetate in combination with triphenylphosphine to efficiently catalyze the arylation and vinylation of aryl and vinylic iodides and bromides, respectively. Especially in the case of bromide reagents, the reaction rate could be increased a lot by the use of triphenylphosphine. Since that time, a lot of effort to investigate and optimize these reactions was done. Extensive mechanistic studies opened up various catalytic cycles[20,21], whereby recent publications claim a number of catalytic active species, including Pd NPs[22] and Pd clusters or colloids.[23-26] However, after the performed Heck reaction the Pd species are known to aggregate (precipitation of inactive Pd black) and thus, the catalytic activity of Pd catalysts is decreased.[27,28] Furthermore, they suffer from the lack of an efficient separation or recycling strategy. Therefore, especially the design of heterogeneous alternatives was one main focus, including the development of new stabilizing ligands.[29] One widely applied heterogeneous strategy to provide the Pd species from agglomeration is the use of phosphine-functionalized magnetic nanoparticles (PFMN).[18] Panahi *et al.* reported one of the most efficient catalytic systems which is based on a readily synthesized nanoparticle-anchored PFMN-Pd(OAc)$_2$ complex.[30] The catalyst was able to perform the Heck reaction of chlorobenzene with ethyl acrylate in 93% yield applying 1 mol% Pd in the presence of K_2CO_3 in DMF at 120 °C. Noteworthy, the leaching of Pd was found to be less than 1% in total (determined by ICP analysis) and the system was recyclable for at least four consecutive runs with sustained selectivity and activity. Apart from phosphine-based ligands, other chelating fragments as well as magnetic nanocomposites like ionic liquid-modified magnetic NPs could be applied to avoid undesired aggregation and deactivation of Pd NPs (*e.g.* oleic acid functionalized Fe_3O_4 NPs aiming to catalyze Heck reactions.[31] The amine functionalized NP system Pd@Co/C-PEI **32** showed that it can act as stabilizing support for the Pd species without inhibiting catalytic activity and suppressing the desired properties of the NPs themselves (see chapter 1). In addition, it combines the advantage of well-distributed and highly stabilized NPs with an easy recycling strategy due to the magnetic core of the Co/C support. Thus, the Pd@Co/-PEI system **32** was used as catalyst in Heck reactions to enable a feasible separation and reusability and further benchmarking its catalytic activity for the in general more challenging aryl bromides and chlorides. Moreover, these investigations were mainly motivated by the aim of achieving high turn over frequencies, through short reaction times and low catalyst loadings resulting in a highly recyclable catalytic system which would further suppress the formation of any aggregated Pd during the reaction.

2.1.2 Results and discussion

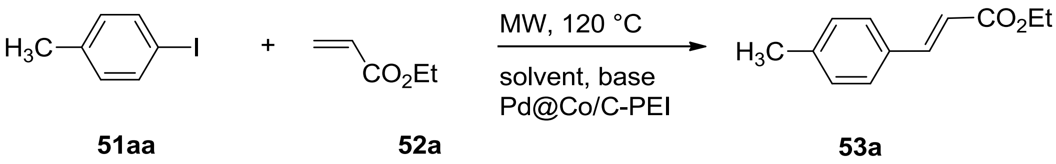
In this section, the catalytic potency of Pd@Co/C-PEI **32** regarding its activity in Heck reactions was evaluated. Adapting the reaction conditions from Diao *et al.* first investigations were conducted with *p*-iodotoluene and ethyl acrylate as model substrates. In 2011, Diao and coworkers reported a magnetic Fe_3O_4 based carbon nanocomposite with deposited Pd NPs as an efficient and recyclable catalyst for Suzuki and Heck coupling.[32]

However, magnetite (Fe_3O_4) in general has the drawbacks of a labile covalent bond formation under hydrolytic conditions which results in lower overall stability of the catalytic system. Moreover, the saturation magnetization of the, in this work highlighted graphene-coated cobalt nanobeads ($M_{S,bulk} \leq 158$ emu/g) exceed by far the magnetization of magnetite ($M_{S,bulk} \leq 92$ emu/g).[33] As highly functionalized NPs tend to have a reduced overall magnetization, higher initial magnetization values are desirable to ensure the complete recovery of the magnetic material. Due to the graphene-like carbon shell, a stable C-C bond formation is possible, for example *via* diazonium chemistry[34], which opens up a variety of functional groups.[16]

With these advantages of Co/C NPs in mind, the Pd@Co/C-PEI nanobeads **32**, which were already successfully applied as hydrogenation catalyst in chapter 1, were further examined regarding their activity in Heck reactions. Therefore, the reaction conditions reported by

Diao and co-workers were used for the initial studies: 1 equiv. aryl halide, 2 equiv. alkene, 4 equiv. K_2CO_3 in DMF at 120°C applying 0.3 mol% Pd. However, using 1 mol% Pd@Co/C-PEI **32** with *p*-iodotoluene **51aa** and ethyl acrylate **52a** as model substrates at 120 °C only led to comparably low TOFs. In order to improve the throughput capacity, microwave conditions were tested, since the Co/C nanobeads are well-known to positively contribute to the microwave heating due to their potency to absorb and re-emit the radiation.[35] The optimization studies are represented in the following table (table 4).

Table 4: Optimization studies regarding the reaction of *p*-iodotoluene 51**aa** and ethyl acrylate **52a**.



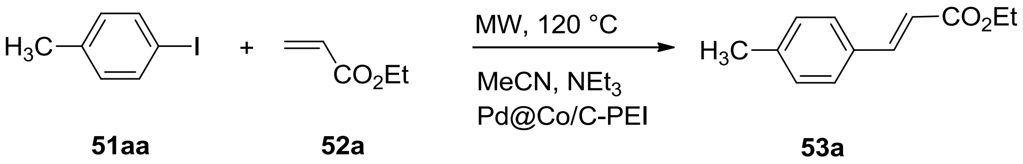
entry	catalyst	solvent	base	Pd [mol%]	time [h]	yield [%]	TOF [h^{-1}]
1[a)]	**32**	DMF	K_2CO_3	0.3	24	30	4
2[a)]	**32**	DMF	K_2CO_3	1	24	94	4
3	**32**	DMF	K_2CO_3	0.5	1	65	130
4	**32**	MeCN	K_2CO_3	0.5	24	97[b)]	8
5	**32**	MeCN	NEt_3	0.5	24	98[b)]	8
6	**32**	MeCN	NEt_3	0.5	1	99	198
7	**32**	MeCN	NEt_3	0.2	1	96	480
8	**32**	MeCN	NEt_3	0.1	1	98	980
9	**32**	MeCN	NEt_3	0.01[c)]	4	36	900
10	Co/C-PEI	MeCN	NEt_3	-	1	-	-
11	-	MeCN	NEt_3	-	1	-	-

Reaction conditions: 0.5 mmol *p*-iodotoluene **51aa**, 0.6 mmol ethyl acrylate **52a**, 0.6 mmol base in 2 mL solvent, 120 °C MW, 0.8 mmol/g Pd@Co/C-PEI **32**;[a)]0.5 mmol *p*-iodotoluene **51aa**, 1 mmol ethyl acrylate **52a**, 2 mmol K_2CO_3 in 2 mL DMF, 120 °C; [b)]conventional heating (acetonitrile, reflux); [c)]20 mmol *p*-iodotoluene.

As above mentioned, the Heck coupling applying the conditions adapted from Diao *et al.*, gave unfruitful results (entry 1 and 2). Switching from conventional heating to microwave heating showed an improvement regarding the product per time ratio (entry 3). Changing the solvent from DMF to acetonitrile resulted in even better results (entry 4) especially using microwave irradiation (entry 6). Here increasing the temperature to 120 °C (boiling point 80 °C) went hand in hand with an increase in pressure (8-10 bar) which enhanced the catalytic activity. To achieve the same effect with DMF as solvent, the applied temperature should be over 150 °C. However, undesired leaching of palladium black (non-magnetic precipitate) was discovered when temperatures above 150 °C were reached. Thus, acetonitrile was the solvent of choice. The base was further changed from K_2CO_3 to trimethylamine due to solubility issues but had no effect on catalytic activity (entry 5). Using acetonitrile as solvent and microwave conditions, the reported catalytic system showed an excellent activity allowing catalyst loadings down to 0.1 mol% (entry 8), which corresponds to high TOFs up to 980 h^{-1}. Further reduction to 0.01 mol% correlated with a decrease in the catalytic activity by 10% (entry 9), however, therefore also an upscaling to 20 mmol (4 g) was necessary. Control experiments (entry 10 and 11) verified Pd@Co/C-PEI **32** as the catalytic active species, since no conversion was observed, neither without any support nor with solely Co/C-PEI **30**.

Next, the recyclability of the reported system was investigated, using again *p*-iodotoluene **51aa** and ethyl acrylate **52a** as model substrates with 0.1 mol% Pd catalyst **32**. Thereby, special attention was paid to the metal leaching into the desired product. The five iterative Heck reactions were all stopped after one hour reaction time by separating the magnetic nanocatalyst *via* an external magnet, decanting and washing the solution and, after drying, directly reusing the NPs for the following run. Thus, five consecutive cycles could be performed without any significant loss in activity (99% to 95% yield). Furthermore, the product contamination due to the metal leaching was determined *via* ICP-OES, detecting an averagely low level of 30 ppm Pd (table 5). This corresponds to an overall Pd loss of 27%, which, however, did not have an observable negative impact regarding the product formation.

Table 5: Recycling studies regarding the reaction of *p*-iodotoluene **51aa** and ethyl acrylate **52a**.



entry	yield [%]	leaching Pd [ppm]	Pd loss [%]	leaching Co [ppm]
1	99	19	4	9
2	96	22	4	8
3	98	27	5	18
4	95	39	7	19
5	98	37	7	18

Reaction conditions: 1 mmol iodotoluene **51aa**, 1.2 mmol ethyl acrylate **52a**, 1.2 mmol triethylamine in 3 mL acetonitrile, 1 h, 120 °C, 0.46 mmol/g Pd@Co/C-PEI **32** (2 mg, 0.1 mol%).

Figure 5 shows a graphical representation of the obtained conversion of the presented reaction in the five following runs.

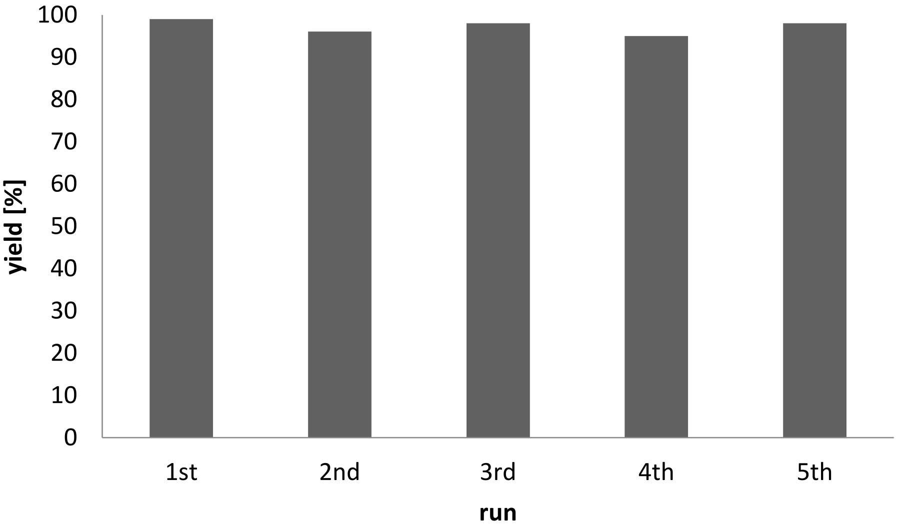
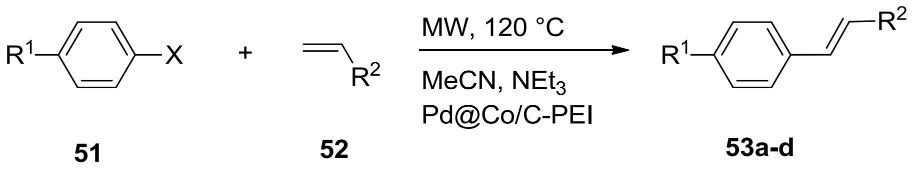


Figure 5: Recycling regarding the Heck reaction of *p*-iodotuluene **51aa** and ethyl acrylate **52a** graphically represented.

Next, the catalytic activity of the nanocatalyst **32** was further benchmarked regarding its capability to catalyze more challenging substrates like aryl bromides and aryl chlorides, which own a higher activation barrier. In table 6 an overview over the various tested aryl halides and ethyl acrylate **52a** or styrene **52b** is given.

Table 6: Various Heck reactions applying Pd@Co/C-PEI **32**.



entry	R^1	X	R^2	t [h]	Pd [mol%]	yield [%]
1	H	I	CO_2Et	1	0.1	99
2	H	I	C_6H_5	1	0.1	98
3	CH_3	I	CO_2Et	1	0.1	98
4	CH_3	I	C_6H_5	1	0.1	98
5	H	Br	CO_2Et	2	0.1	97
6	H	Br	C_6H_5	2	0.1	97
7	CH_3	Br	CO_2Et	2	0.1	97
8	CH_3	Br	C_6H_5	2	0.1	96
9	H	Cl	CO_2Et	4	0.1	22
10	H	Cl	C_6H_5	4	0.1	20
11	CH_3	Cl	CO_2Et	4	0.1	29
12	CH_3	Cl	CO_2Et	4	0.5	30
13[a)]	CH_3	Cl	CO_2Et	4	0.1	-
14	CH_3	Cl	CO_2Et	8	0.1	28
15	CH_3	Cl	C_6H_5	4	0.1	23
16	CH_3	Cl	C_6H_5	4	0.5	25
17[a)]	CH_3	Cl	C_6H_5	4	0.1	-
18	CH_3	Cl	C_6H_5	8	0.1	24

Reaction conditions: 0.5 mmol aryl halide **51**, 0.6 mmol alkene **52**, 0.6 mmol triethylamine in 2 mL acetonitrile, 120 °C, 0.8 mmol/g Pd@Co/C-PEI **32**; [a)]150 °C.

Pd@Co/C-PEI **32** showed excellent activity in the Heck reactions of aryl iodides **51aa** and **51ba** with both, ethyl acrylate **52a** and styrene **52b**, within one hour (entry 1-4). By doubling the reaction time to two hours, the more challenging aryl bromides **51ab** and **51bb** could be successfully converted to its corresponding coupling products (entry 5-8).

However, aryl chlorides **51ac** and **51bc** could only be coupled to some extent with the corresponding alkene, resulting in barely moderate yields (in average 20% yield and conversion, entry 9, 10, 11, 15). Surprisingly, the conversion could not be improved, neither by increasing the catalyst amount (entry 12, 16), nor by prolonged reaction times (entry 14, 18 This indicates some kind of catalyst poisoning which already has been reported for aryl chlorides.[36] An increase in the reaction temperature even led to a decomposition of the NP catalyst system as described above (entry 13, 17). Nevertheless, Pd@Co/C-PEI **32** was able to successfully convert aryl iodides and, what is even more interesting, also aryl bromides with a relatively low amount of catalyst within short reaction times (1-2 h), resulting in high TOFs from 480-980 h^{-1}.

In summary, Pd@Co/C-PEI **32** was examined to be a suitable catalyst for Heck reactions regarding aryl iodides, aryl bromides, and to some extent for aryl chlorides. The catalytic system could successfully catalyze these substrates with low catalyst loadings within relatively short reaction times using microwave irradiation. Furthermore, Pd@Co/C-PEI **32** showed again a great recyclability and was successfully reused for five iterative Heck cycles with consistent catalytic activity. Unfortunately, applying these relatively harsh reaction conditions, 28% of the overall Pd was lost in total, resulting in moderate contamination values for Pd and Co. Another drawback is the struggling with regard to aryl chlorides in relatively low yields. In the course of this work, none of the tested attempts led to any significant improvements.

2.2 Tsuji-Trost allylations

2.2.1 Introduction

In contrast to a huge number of publications for the Suzuki, Sonogashira and Heck coupling reactions, the field of Tsuji-Trost coupling reactions is less discussed in the recent literature.[37] However, this does not reduce its scientific importance. The Tsuji-Trost reaction has emerged as a powerful tool for the controlled introduction of various carbon-carbon and carbon-heteroatom bonds catalyzed by a variety of transition metal complexes. Within these reaction types, the key intermediate is a (π-allyl)metal complex which undergoes a nucleophilic displacement, thus, a focused introduction of an allyl group into an organic compound is possible.[38] Therefore, the same Pd catalysts are commonly used than for Heck reactions, mainly phosphine ligand based complexes like $Pd(PPh_3)_4$. A great variety of homogeneous[39-41] and heterogeneous Pd catalysts[42-44] are reported for the Tsuji-Trost allylation, however, heterogeneous alternatives offer the best option due to separation issues.[29] Thus, the focus of recent research turned to the investigation of Pd NPs immobilized on various supports.[42,45-48] In the following, one selected heterogeneous catalyst for Tsuji-Trost reactions is going to be highlighted due to its almost unique bifunctional catalytic system: Baba *et al.* published a catalytic system of tertiary amines and a diaminopalladium complex, both covalently grafted onto the same silica surface (SiO_2/diamine/Pd/NEt_2).[49] Thus, this catalyst is not only able to catalyze the reaction but also serves as an internal base. The idea behind this was to avoid any self-quenching of the base in the presence of a Lewis acid metal centre which is prevented in this approach as both catalysts are anchored on the same surface (figure 6).[50]

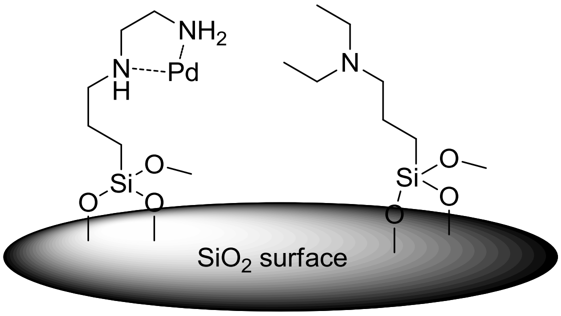
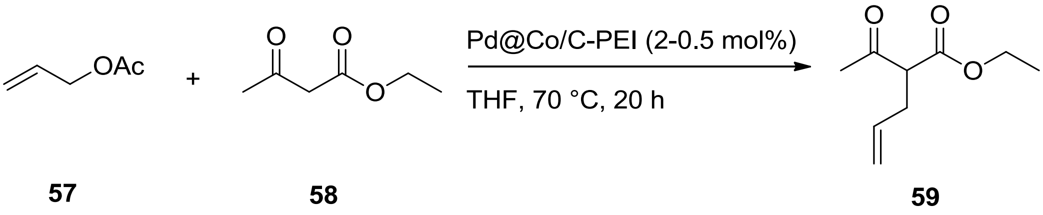


Figure 6: Surface structure of the synergistic catalytic system SiO_2/diamine/Pd/NEt_2.

The synergistic system SiO_2/diamine/Pd/NEt_2 turned out to be active and selective for the Tsuji-Trost allylation of various nucleophiles (phenols, 1,3-dicarbonyls, carboxylic acids) in THF as solvent with allyl methyl carbonate and allyl acetates. Furthermore, this bifunctional catalyst system was reusable for four times without any significant loss in both, activity and selectivity. This publication led to the idea of applying the well-studied Pd@Co/C-PEI system **32**, which possesses a basic character due to the high density of amine groups, as a recyclable heterogeneous catalyst including an internal basic system.

2.2.2 *Results and discussion*

Based on the work of Baba and co-workers regarding Pd catalyzed Tsuji-Trost allylations, the idea was to test the Pd@Co/C-PEI nanoparticles **32** as bifunctional palladium catalyst. As stated above, the high density of the amine groups may serve as an internal base. Thus, the use of an external base should be avoided in the allylic alkylations. At the same time, the palladium nanoparticles bared inside the PEI polymer catalyze the coupling of various nucleophiles with allylic compounds. In addition, the simplicity in this catalysis may be the main benefit. The Pd@Co/C-PEI NPs **32** enable the use of low catalytic amounts due to their high loading on amino groups (8.5 mmol/g), but also the outstanding high Pd content (0.8 mmol/g). In order to evaluate the catalytic activity of Pd@Co/C-PEI, the allylation of ethyl-3-oxobutanate **58** with allyl acetate **57** was chosen as model reaction. Therefore, 1.0 equiv. ethyl-3-oxobutanate **58,** 2.5 equiv. allyl acetate **57** and 2 mol% Pd catalyst **32** were dissolved in THF and heated to 70 °C for 20 h, yielding the desired product with 97%. Consequently, the catalyst amount was further reduced to 0.5 mol% without any decrease in activity (scheme 16).



Scheme 16: Pd@Co/C-PEI catalyzed reaction of ethyl-3-oxobutanate **58** with allyl acetate **57**; Reaction conditions: 2.5 mmol allyl acetate **57**, 1. mmol ethyl-3-oxobutante **58** in 4 mL THF, 20 h, 70 °C, 0.44 mmol/g Pd@Co/C-PEI **32** (2 mol%-0.5 mol%).

Worth to mention is that no additional base was necessary to efficiently perform this reaction. This result suggests that the tertiary amines of the PEI polymer are potent to replace the base. From a mechanistic point of view, a plausible reaction cycle including the catalyst as bifunctional system is proposed in figure 7.

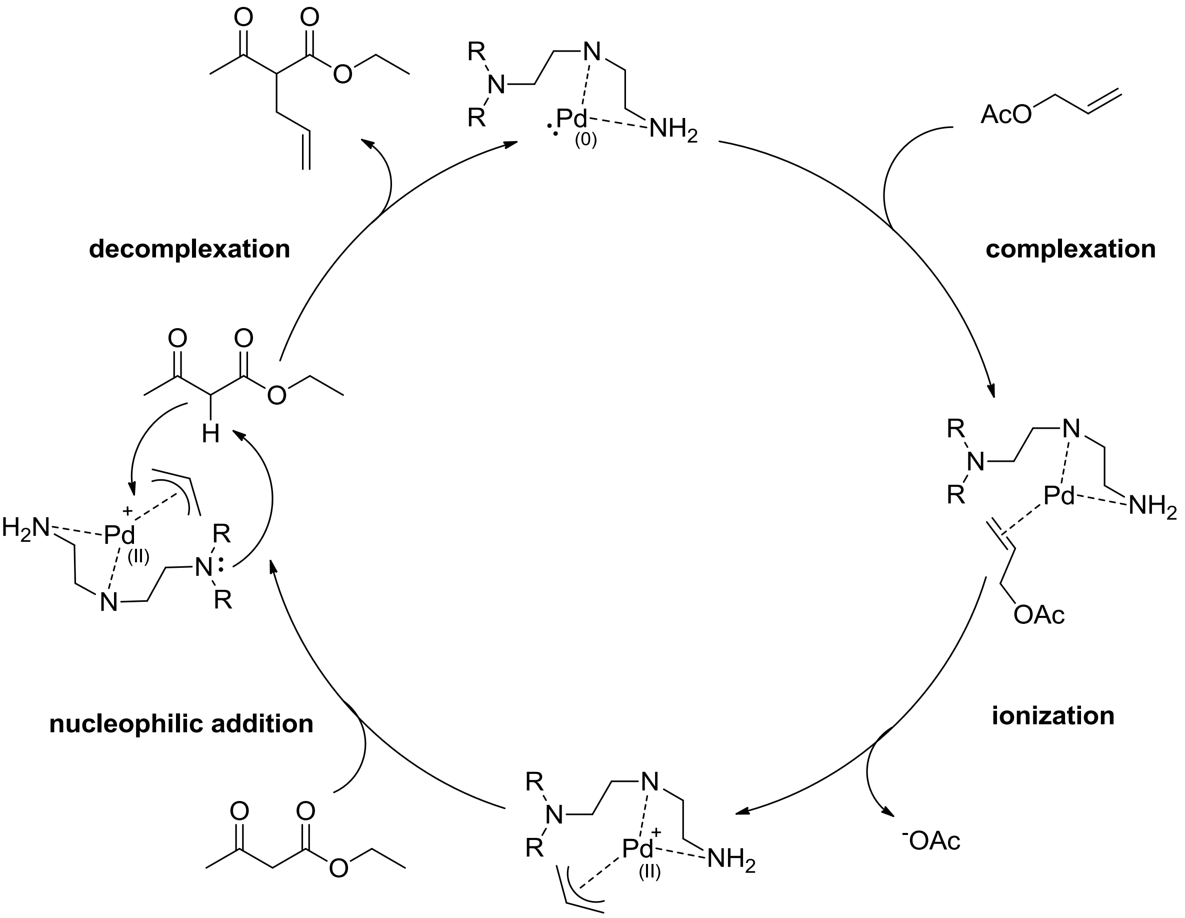
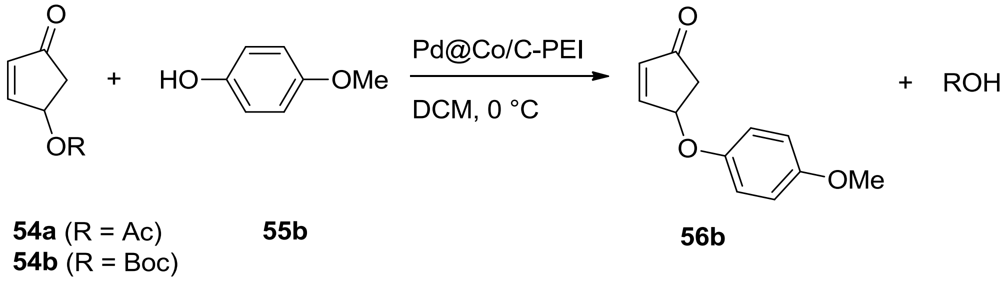


Figure 7: Proposed reaction mechanism for the nucleophilic alkylation of ethyl-3-oxobutanate **58** with allyl acetate **57** applying Pd@Co/C-PEI **32.**

The mechanism shows a proposed mechanism for the Pd catalyzed Tsuji-Trost reaction of allyl acetate **57** and ethyl-3-oxobutanate **58** involving the four fundamental steps: complexation, ionization including the cationic (π-allyl)metal complex, nucleophilic addition, and decomplexation.[38] In figure 7, the bifunctional system Pd@Co/C-PEI **32** is represented by one exemplary part of the amine polymer, including partial coordination to the Pd.

Having shown that Pd@Co/C-PEI **32** can successfully act as synergistic system for allylation reactions, the catalyst was further benchmarked regarding its efficiency towards various substrates. In chapter 1, the synthesis of 4-hydroxy-2-cyclopentenone in flow is shortly presented and its accessibility from renewable resources. The functionalization *via* Tsuji-Trost reaction with a great variety of nucleophiles renders it a versatile platform chemical in organic synthesis. Thus, protected 4-hydroxy-2-cyclopentenones **54a** and **54b** were chosen as model substrates for the following performed allylations. The first approaches were started from the corresponding acetates and *O*-Boc-derivatives with *p*-methoxyphenol **55b** as nucleophile, employing the conditions described by Baba *et al.*. However, no product formation could be observed, which may be a problem due to the applied solvent, but could also result from the reaction temperature of 70 °C (table 7, entry 1). Hence, another approach was carried out due to the previous work of the Reiser group regarding the Tsuji-Trost reaction with protected 4-hydroxy-2-cyclopentenones **54a** and **54b**, *p*-methoxyphenol **55b** and Pd@Co/C-PEI **32** in DCM as solvent at 0 °C (table 7).[51,52]

Table 7: Optimization studies regarding the reaction of protected 4-hydroxy-2-cyclopentenones **54a** and **54b** with *p*-methoxyphenol **55b** applying Pd@Co/C-PEI **32**.



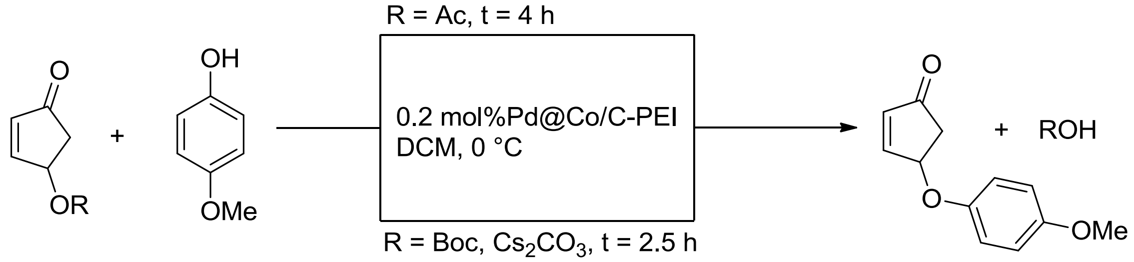
entry	R	reaction time [h]	Pd [mol%]	additives	yield [%]	TOF [h^{-1}]
1[a)]	Ac	20	1	-	-	-
2	Ac	1	1	-	40	40
3	Ac	2	1	-	82	41
4	Ac	4	1	-	98	25
5	Ac	4	0.2	-	92	115
6	Ac	4	-	-	-	-
7	Ac	4	0.1	-	46	115
8	Boc	2.5	0.2	-	-	-
9	Boc	2.5	-	-	-	-
10	Boc	2.5	0.2	Cs_2CO_3	90	180

Reaction conditions: 2.5 mmol protected 4-hydroxy-2-cyclopentenones **54a** and **54b**, 1. mmol *p*-methoxyphenol **55b** in 4 mL DCM, 0 °C, 0.44 mmol/g Pd@Co/C-PEI **32** (1 mol%-0.2 mol%) when R = Ac or 0.63 mmol/g Pd@Co/C-PEI **32** (0.2 mol%), 0.3 equiv. (97 mg) Cs_2CO_3 when R = Boc; [a)]in 4 mL THF, 20 h, 70 °C, 0.44 mmol/g Pd@Co/C-PEI **32** (1 mol%).

Applying these conditions, product formation with the acetate-derivative **54a** as starting material was observed after 1 h reaction time (entry 2). Full conversion was obtained when the reaction time was increased to 4 h (entry 4). The amount of catalyst Pd@Co/C-PEI **32** could be further reduced to 0.2 mol%, which even resulted in higher reactivity (entry 5). When lower amounts of Pd were used, no significant change regarding the TOF was noticed, however, no full conversion could be reached within the 4 h reaction time (entry 7). In contrast, the *O*-Boc-derivative **54b** only gave any product when additional Cs_2CO_3 was added (entry 8 and 10). This may give a hint that Boc-protected reactants are among more challenging substrates. These results match with those already observed in our group, which showed improvement in conversion and yield when adding catalytic amounts of Cs_2CO_3 to the Tsuji-Trost reaction of Boc-protected 4-hydroxycyclopentenone **54b** and *p*-methoxyphenol **55b**.[52] Furthermore, control experiments were conducted to verify Pd@Co/C-PEI **32** as the catalytic active species (entry 6 and 9).

After the best reaction conditions were found, the recyclability had to be tested next. The consecutive Tsuji-Trost cycles were carried out on a 1 mmol scale employing again protected 4-hydroxy-2-cyclopentenones **54a** and **54b** and *p*-methoxyphenol **55b** as model reagents, with regard to the metal leaching into the desired product. Notably, the *O*-Boc derivative needed the addition of 0.3 equiv. Cs_2CO_3. After 4 h (R = Ac) or 2.5 h (R = Boc), respectively, the Tsuji-Trost reactions were stopped by separating the magnetic nanocatalyst *via* an external magnet, decanting and washing the solution and, after drying, directly reusing the NPs for the following run. Moreover, the basic amine system was regenerated with the help of 1M K_2CO_3 solution to again deprotonate the tertiary amino groups. Thus, five iterative cycles were performed and the product contamination due to the metal leaching was analyzed *via* ICP-OES, determined as 3% total Pd loss over in each separate run (table 8) Thereby, the yield slowly decreased after each run due to the lower catalytic activity of Pd@Co/C-PEI **32**. Analyzing the Pd leaching into the reaction solution, this could not be identified as deactivation factor since it was kept at a low level in both cases, **54a** and **54b**. However, in general Pd@Co/C-PEI **32** is an effective bifunctional catalyst for Tsuji-Trost allylations, easily recyclable *via* an external magnet and can be reused at least for five consecutive runs.

Table 8: Recycling studies regarding the reaction of protected 4-hydroxy-2-cyclopentenones **54a** and **54b** with *p*-methoxyphenol **55b** applying Pd@Co/C-PEI **32**.



54a (R = Ac)
54b (R = Boc)

55b

56b

entry	yield [%]		leaching Pd [ppm]		leaching Co [ppm]	
	R = Ac	R = Boc	R = Ac	R = Boc	R = Ac	R = Boc
1	92	90	2	2	1	1
2	90	89	3	2	2	1
3	89	88	5	3	12	2
4	82	82	7	13	4	2
5	79	78	10	13	3	1

Reaction conditions: 2.5 mmol protected 4-hydroxy-2-cyclopentenones **54a** and **54b**, 1. mmol *p*-methoxyphenol **55b**, 0.3 equiv (97 mg) Cs$_2$CO$_3$ in 4 mL DCM, 0 °C, 0.44 mmol/g Pd@Co/C-PEI (5 mg, 0.2 mol%) when R = Ac or 0.63 mmol/g Pd@Co/C-PEI **32** (3 mg, 0.2 mol%) when R = Boc.

The following figure 8 represents the obtained data for all five runs in a graphical way.

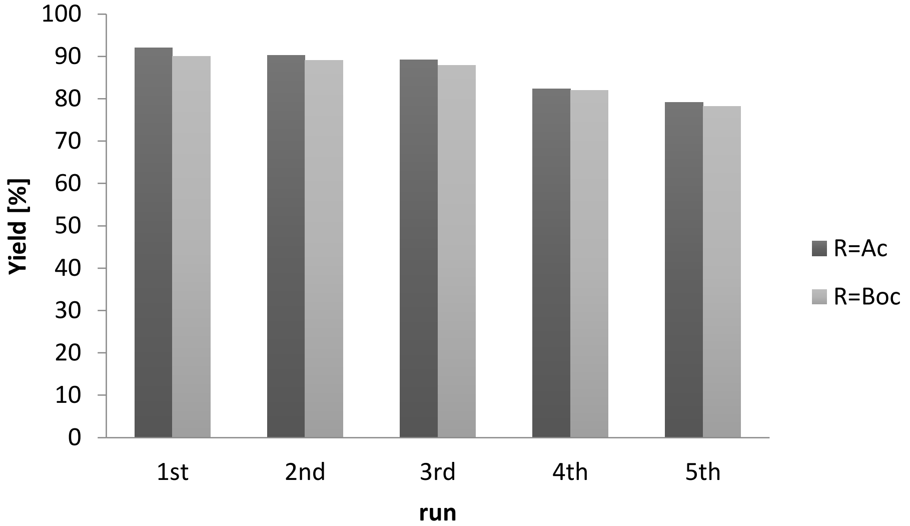
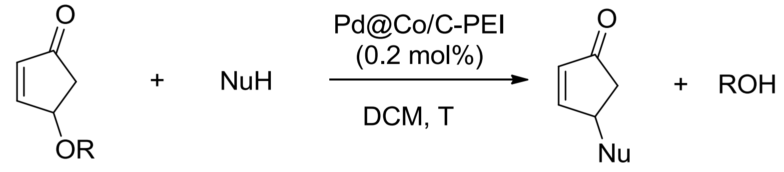


Figure 8: Recycling regarding the reaction protected 4-hydroxy-2-cyclopentenones **54a** and **54b** and *p*-methoxyphenol **55b**, graphically represented.

Now having proven the suitability of Pd@Co/C-PEI **32** for the recyclable Tsuji-Trost reaction of *p*-methoxyphenol **55b** with protected 4-hydroxy-2-cyclopentenones **54a** and **54b** several nucleophiles were tested to extend the substrate scope (table 9).

Table 9: Tsuji-Trost reaction of protected 4-hydroxy-2-cyclopentenones **54a** and **54b** with various nucleophiles.



54a (R = Ac)
54b (R = Boc)

55a: phenol
55b: *p*-methoxyphenol
55c: phthalimide
55d: *p*-bromo benzoic acid

56a-d

entry	R	NuH	T [°C]	t [h]	additives	yield [%]
1	Ac	**55a**	r.t.	2.5	-	77
2	Ac	**55a**	r.t.	4	-	89
3	Ac	**55b**	0	4	-	92
4	Ac	**55c**	r.t.	18	-	80
5	Ac	**55c**	r.t.	24	-	91
6	Ac	**55d**	0	1	-	0
7	Boc	**55a**	0	2.5	Cs_2CO_3	82
8	Boc	**55a**	0	4	Cs_2CO_3	95
9	Boc	**55a**	0	2.5	-	0
10	Boc	**55b**	0	2.5	Cs_2CO_3	90
11	Boc	**55c**	r.t.	18	Cs_2CO_3	87
12	Boc	**55c**	r.t.	24	Cs_2CO_3	94

Reaction conditions: 2.5 mmol protected 4-hydroxy-2-cyclopentenones **54a** and **54b**, 1. mmol nucleophile **55**, 0.3 equiv. (97 mg) Cs_2CO_3 in 4 mL DCM, 0.63 mmol/g Pd@Co/C-PEI **32** (3 mg, 0.2 mol%).

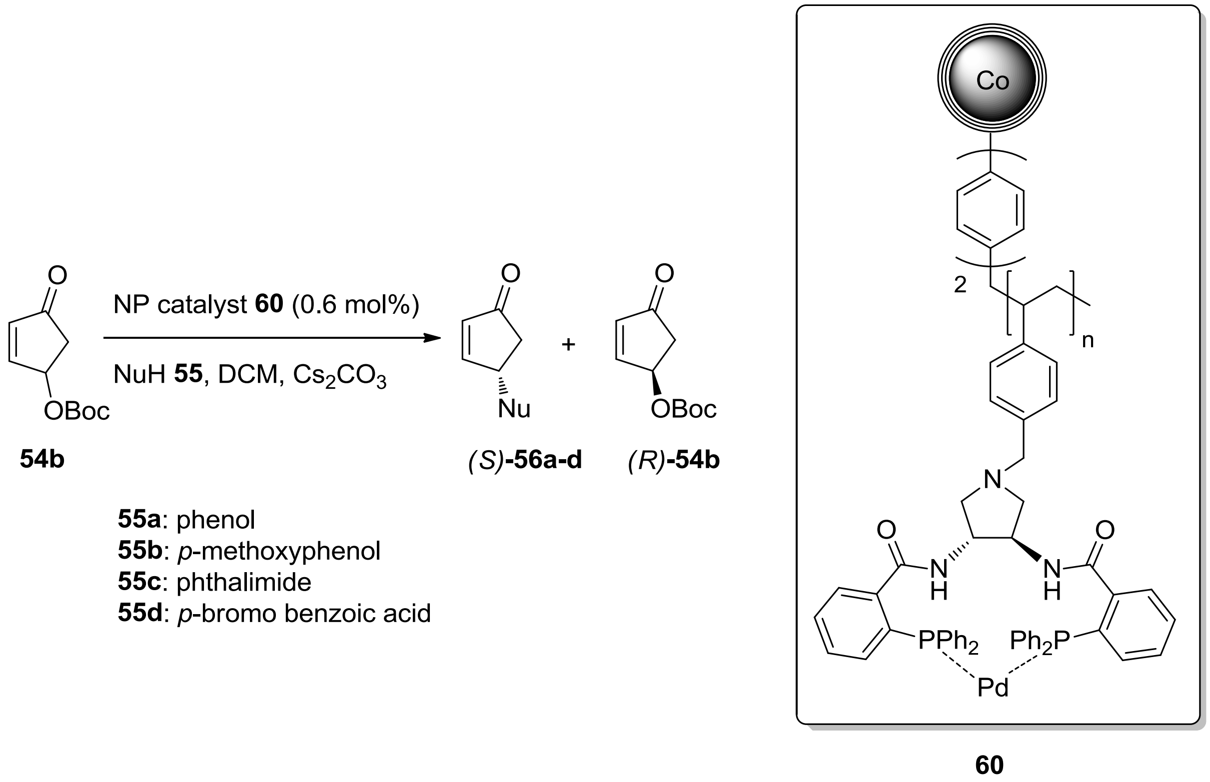
Adapting the reaction conditions from the Reiser group regarding Tsuji-Trost allylations with the acetyl- and the *O*-Boc-derivative, phenol **55a**, phthalimide **55c** and *p*-bromo benzoic acid **55d** were the nucleophiles of choice.[51] All reactions were carried out with 0.2 mol% of Pd@Co/C-PEI **32** and gave full conversion. Phenol **55a** was easily attached to the starting materials **54a** and **54b** in excellent yields (entry 2 and 8). Phthalimide **55c** also turned out to be an excellent nucleophile for the Tsuji-Trost allylation as it could be introduced in good yields by prolonged reaction times of 24 h (entry 5 and 12). However, the Boc group could only be substituted in the presence of 0.3 equiv. Cs_2CO_3 (entry 7-9), which renders the *O*-Boc-derivative **54b** among the more challenging substrates. An exception here was *p*-bromo benzoic acid **55d** due to the reaction of the carboxylic acid group with the amine functionalities of the PEI polymer (entry 6). Thus, it was no longer available for the desired Tsuji-Trost reaction.

2.3 Conclusion

To sum up, the results achieved in this chapter, Pd@Co/C-PEI **32** was not only proven to be a suitable catalyst for hydrogenation chemistry but is furthermore capable to successfully catalyze Pd-supported Heck and Tsuji-Trost coupling reactions in excellent yields. In the Heck reactions, aryl iodides (**51aa** and **51ba**) and aryl bromides (**51ab** and **51bb**) were converted quantitatively, whereas aryl chlorides (**51ac** and **51bc**) still emerged as challenging substrates and just led to 20-30% of the coupled product. Nevertheless, the catalyst was easily recyclable with an external magnet and could be reused for at least five consecutive runs with low catalyst leaching into the product. Tsuji-Trost allylations were performed with various nucleophiles **55** and protected hydroxyl-2-cyclopentenones **54a** and **54b** in excellent yields. Notably, the catalyst here acted as both, base and palladium catalyst, however, in case of Boc-protected substrates additional Cs_2CO_3 was needed in catalytic amounts to achieve any conversion. The Pd@Co/C-PEI catalyst **32** could easily be recycled with an external magnetic field and reused for at least five iterative allylation reactions. Conspicuously, the Pd leaching was significantly low with a total Pd loss of only 3%.

3. Asymmetric allylic substitutions of protected *rac*-4-hydroxycyclopentenones catalyzed by a chiral, magnetically recyclable Trost-type Pd complex*

Previous chapters dealt with Pd@Co/C-PEI **32** as a novel hybrid system for Pd catalyzed hydrogenation reactions as well as its suitability for both Heck and allylation coupling reactions. In this last chapter, the before mentioned allylations should be carried out in a chiral approach with a Trost-type ligand covalently bound to the magnetic Co/C nanobeads. As nanoparticle precursor Co/C-PS-Cl nanobeads **21** were chosen to attach the Trost type ligand *via* nucleophilic substitution. The use of these polymeric nanobeads should enhance the loading capacity and further prevent the catalytic system from agglomeration. Thus a recyclable semi-heterogeneous version of a Tsuji-Trost type catalyst **60** for the chiral resolution of Boc-protected (±)-4-hydroxy-2-cyclopentenone **54b** with various nucleophiles **55** was established (scheme 17).



Scheme 17: Chiral resolution of protected (±)-4-hydroxy-2-cyclopentenone **54** with various nucleophiles **55** applying NP catalyst **60**.

The established catalytic system was able to successfully catalyze the coupling of various nucleophiles in good to excellent enantioselectivities and thus, achieved an excellent chiral resolution on the background of the work already published in our group.[51] The catalyst

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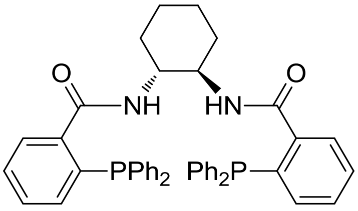
[*] Previous work on this project done by Chayan Charoenpakee during his internship in Regensburg 2016.

was furthermore recyclable for five iterative catalyst cycles without any significant loss in both, catalytic activity and enantioselectivity. Moreover, the polymeric particles turned out as an excellent environment for the attached Pd complex as the Pd leaching was kept at low leaching value.

3.1 Introduction

The previous chapter already mentioned the Tsuji-Trost allylation as a powerful and versatile tool for the formation of C-C/C-heteroatom bonds *via* palladium catalysis. A unique feature of this reaction is, if an appropriate catalyst is used, its capability of introducing chirality, thus converting molecules of any symmetry type into enantiomerically pure compounds.[38] Hence, the focus of this chapter lied on induced stereochemistry in allylic alkylations. First examples to introduce asymmetry at the allylic fragment were accomplished in 1977 by Strege *et al.*.[53] Since these pioneering efforts the asymmetric allylic alkylation has undergone a huge progress in research involving both, a broad range of substrates and nucleophiles.[38] A key role in the development of the asymmetric allylic alkylation (AAA) played the design and screening of various chiral ligands. . Those can be classified into four major groups: 1) chiral phosphines, 2) dinitrogen ligands, 3) P,N chelate ligands and 4) mixed chelate ligands. The most prominent example among those ligands might be the “classical” Tsuji-Trost ligand **61** (figure 9), which is based on readily available 2-(diphenylphosphino)benzoic acid (DPPBA) and chiral diamine.[38]



61

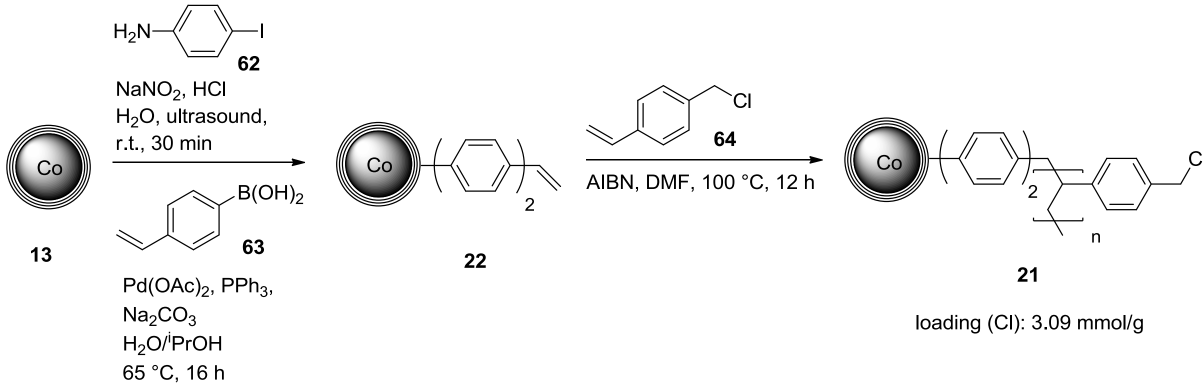
Figure 9: Design of the “classical” Tsuji-Trost ligand **61**.

Despite the huge amount of chiral ligands, the turnover numbers of these systems are in general quite low and further both, ligand and palladium, are quite expensive. Thus, their separation from the reaction media is one of the major drawbacks in the homogeneous catalysis, which can be elegantly circumvented by heterogeneous versions. Nanoparticles serve as unique support as they bridge both homogeneous and heterogeneous aspects due to their high surface-to-volume ratio, high catalytic efficiency and easy separation. A first example for asymmetric C-C coupling reaction catalyzed by nanoparticles is presented by Claudret *et al.* in 2004, who used Pd nanoparticles stabilized by asymmetric diphosphite ligands leading to a high enantioselectivity in the kinetic resolution of *rac*-3-acetoxy-1,3-diphenyl-1- propene.[54] In 2002, Han *et al*. published the immobilization of an analogue of ligand **61** on a polystyrene-based resin for Pd catalyzed asymmetric desymmetrizations.[55] This heterogeneous analogue was reported to show excellent activity and enantioselectivity. Due to its structure, it served as inspiration for the development of a novel magnetic NP version of the Trost-type ligand reported in this chapter and as a further application for the kinetic resolution of protected *rac*-4-hydroxy-2-cyclopentenone. Enantiopure 4-hydroxy-2-cyclopentenone is a versatile chiral intermediate[56] for various natural products as well as pharmaceutical drugs, e.g. prostaglandin PGE_1 methyl ester.[57] Racemic 4-hydroxy-2-cyclopentenone is achieved *via* transformation of furfuryl alcohol under acidic conditions in aqueous media, the Piancatelli rearrangement.[58] One approach to obtain chiral 4-hydroxy-2-cyclopentenone would be a kinetic resolution, here achieved due to the reaction with various nucleophiles and a Trost-type ligand which was accomplished in this chapter.

3.2 Results and discussion

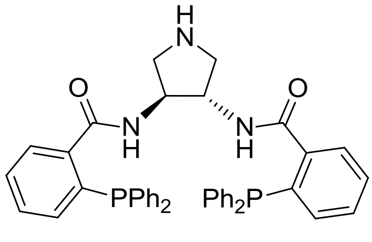
At first the above mentioned Trost-type ligand, developed by Han *et al.*, had to be pre-synthesized and was then grafted onto an appropriate type of Co/C nanobeads. Therefore, Co/C-PS-Cl nanobeads **21** were chosen since they grant not only a superior degree of functionalization due to covalent attachment of the polymer, but also a satisfying saturation magnetization (33 emu/g).[59] The polymeric shell further provides long-term stability under harsh conditions and due to the resulting high functional group loadings, it can overcome the in general low turnovers of known Tsuji-Trost catalysts. Moreover, a Trost-type ligand could easily be immobilized onto the nanobeads *via* nucleophilic substitution of the chloride. Hence, this hybrid material was chosen as magnetic support for the development of a magnetic NP-based recyclable Tsuji-Trost catalyst. Co/C-PS-Cl **21** were synthesized according to a procedure developed by Stark *et al.*[59] starting from commercially available Co/C **13** and functionalizing them with styrene moieties adapting diazonium chemistry/cross-coupling reactions. Further modifications were achieved *via* grafting polymerization of 4-chloromethylstyrene **64** with the vinyl-functionalized Co/C particles **22**. Moreover, the content of surface-bound polymer can be controlled by varying the concentration of AIBN.

Thus, applying higher amounts of AIBN (3 mol% with respect to 4-chlorostyrene) high loadings of chlorine of 3 mmol/g were achieved. Hence, a stable nanoparticle/polymer hybrid was formed (scheme 18).[59]



Scheme 18: Synthesis of Co/C-PS-Cl **21** out of unfunctionalized Co/C nanobeads **13**.

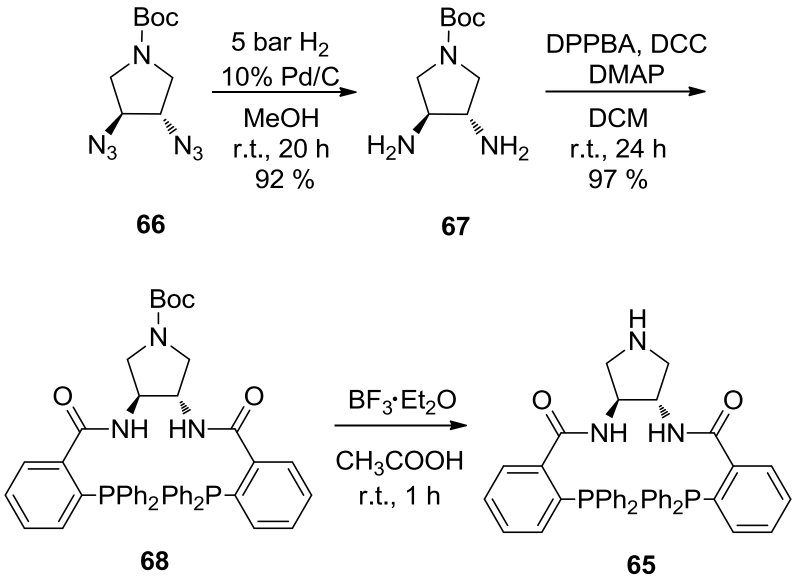
With the suitable nanoparticles **21** in hand, the approach of Han *et al.* was taken into account for pre-synthesizing the desired Trost-type ligand **65** (figure 10).[55] The free amine group of the Trost-analogue **65** should easily replace the chloride via nucleophilic substitution and thus, being anchored in the stable polymeric structure of the nanobeads **21**.



65

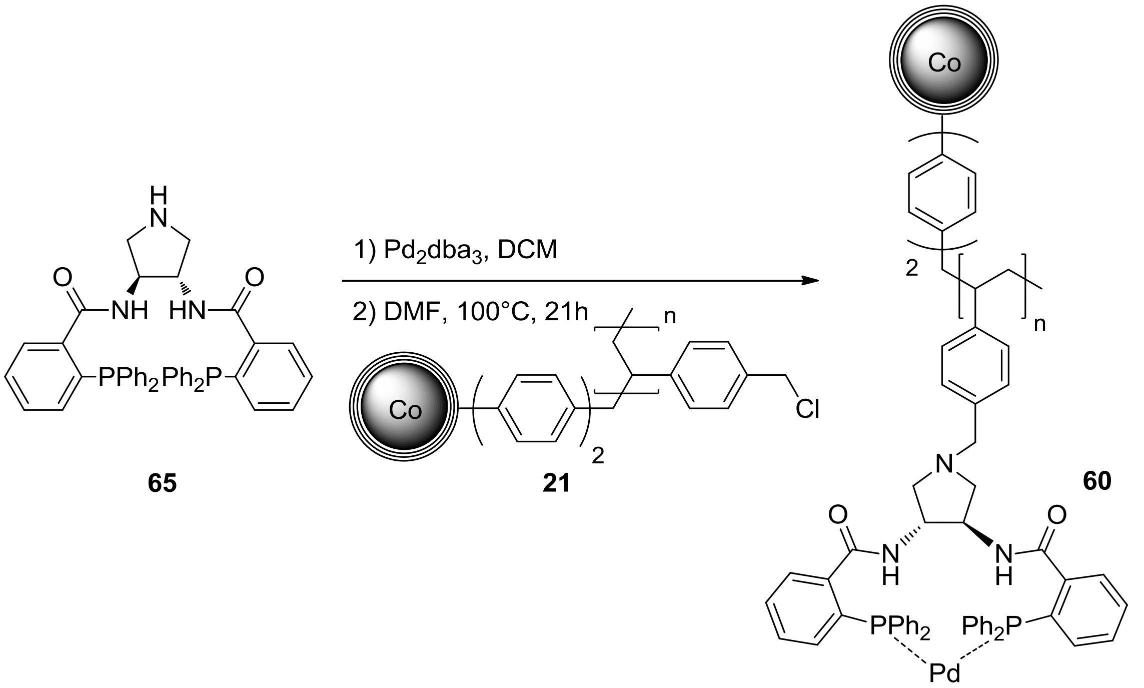
Figure 10: Trost type ligand **65** for chiral resolution of *rac*-4-hydroxy-2-cyclopentenone **54**.

This synthesis of **65** was achieved starting from enantiopure (3*S*,4*S*)-*tert*-butyl 3,4-diazidopyrrolidine-1-carboxylate **66** ($[\alpha]_D^{20} = -88.2$ (*c* 1, $CHCl_3$)) in four reaction steps (scheme 19).



Scheme 19: Reaction pathway for the synthesis of Trost type ligand **65**; Reaction conditions: 1 mmol **66**, 10 wt% (25 mg) Pd, 5 mL MeOH; 0.5 mmol **67**, 1 mmol DPPBA, 0.2 equiv DMAP (12.2 mg), 1.1 equiv. DCC (113.5 mg) in overall 10 mL DCM; 0.5 mmol **68**, 3 equiv. (0.2 mL) BF_3*Et_2O in 2 mL acetic acid, poured onto 1 g NaOAc in 5 mL ice water.

The starting material **66** was subjected to an autoclave at 5 bar for complete hydrogenation of the azide moieties to the corresponding amines of the compound **67** applying conventional palladium on charcoal as catalytic species. The second step implies amidation of the diamino functionalities with diphenylphosphino benzoic acid (DPPBA). The synthesis of this bisamide ligand **68** needed the addition of DMAP in catalytic amounts and DCC as coupling reagent (Steglich conditions). Thereby, the byproduct dicyclohexylurea was removed *via* simple filtration through a plug of celite before further purification of the crude reaction product *via* column chromatography was performed. In the last step, the Boc-group was cleaved by treatment of **68** with an excess of freshly distilled boron trifluoride diethyl etherate. After maintaining the reaction mixture at room temperature for 30 min, the crude was neutralized with sodium acetate to achieve the crude deprotected Trost-type ligand **65**.[60] The catalytic active species was finally formed by encapsulating Pd(0) using the ligand exchange method. Therefore, the unprotected Trost analogue was stirred without further purification in a solution of Pd_2dba_3 in DCM until the initial purple solution turned yellow-brown. Afterwards, the solvent was removed *via* nitrogen flow followed by addition of 50 mg Co/C-PS-Cl nanobeads **21** in DMF. The reaction mixture was heated for 21 h at 100 °C yielding the desired nanoparticle-based Trost-type complex **60** (scheme 20). Hence, the readily formed complex **65** was anchored onto the Co/C-PS-Cl beads **21**.



Scheme 20: Immobilization of the Trost analogue **65** onto Co/C-PS-Cl nanobeads **21**; Reaction conditions: 0.048 mmol (33 mg) ligand, 0.012 mmol (11 mg) Pd_2dba_3 in 10 mL DCM; 50 mg Co/C-PS-Cl, 5 mL DMF, 100 °C, 21 h.

The formation of the palladium complex before being immobilized onto the nanobeads avoids the coordination of any palladium onto the graphene shell and guarantees the palladium solely being coordinated by the Trost-type ligand. The latter was verified *via* both, elemental analysis (0.19 mmol/g ligand) and ICP-OES (0.15 mmol/g Pd). The NP version of the Trost ligand **60** was furthermore characterized using IR spectroscopy. Reliable information can be obtained by monitoring the appearing C=O band at 1620 cm^{-1} as well as the N-H band at 3300 cm^{-1} compared to Co/C-PS-Cl **21**(figure 11).

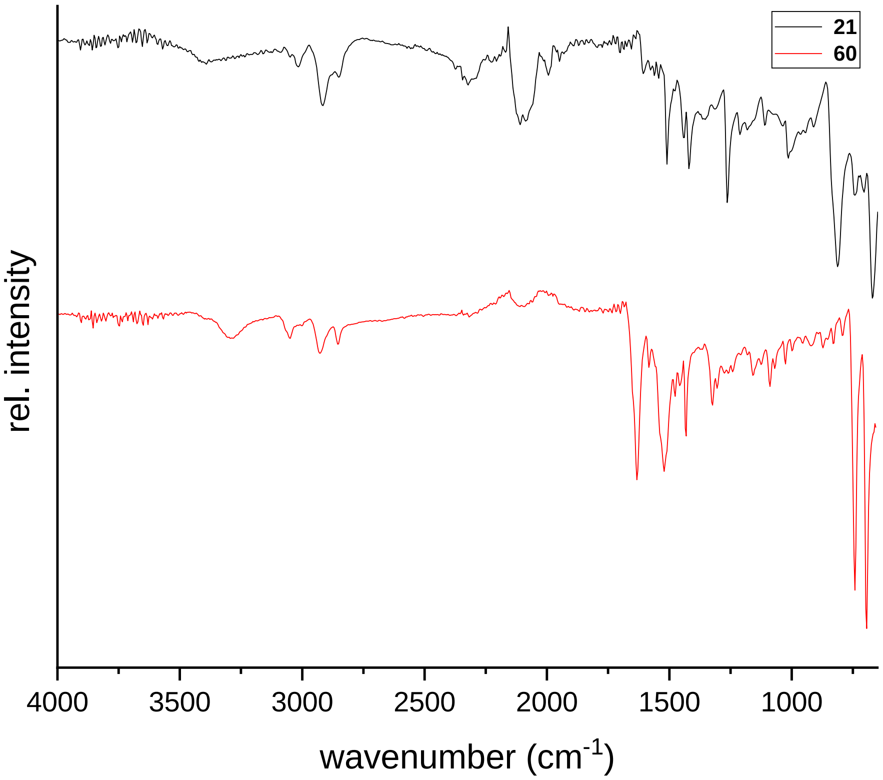
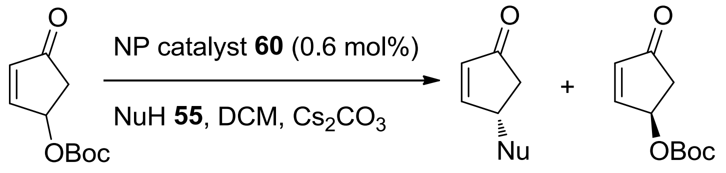


Figure 11: IR spectra of Co/C-immobilized Trost complex **60**.

To validate the catalytic activity of the immobilized Trost-catalyst it had to be tested in appropriate test reactions. As model reaction, the kinetic resolution of protected *rac*-4-hydroxy-2-cyclopentenone **54** was chosen due to its easy accessibility and versatile amenable applications in organic synthesis. Former colleagues in our group already explored the chiral resolution of protected 4-hydroxy-2-cyclopentenone **54** *via* chiral Tsuji-Trost reaction applying the "classical" Tsuji-Trost ligand **61**, Pd_2dba_3 in DCM as solvent. Low catalyst loadings (1-2 mol% Pd, 2-4 mol% **61**) led to a successful synthesis of various optically active 4-substituted-2-cyclopentenones and their further processing for natural products and biologically active 2-cyclopentenones such as guaianes, and pseudoguaianolides, was accomplished.[51] Thus, several Tsuji-Trost reactions with 0.5 mmol Boc-protected 4-hydroxycyclopentenone **54b** as model substrate and a variety of nucleophiles **55** were performed with low catalyst loadings of 0.6 mol%. The following table sums up the achieved results with the NP version of a Trost-type ligand **60** in DCM (Table 10). All reactions were carried out under nitrogen to avoid any undesired oxidation of the phosphine ligand.

Table 10: Kinetic resolution of Boc-protected *rac*-4-hydroxy-2-cyclopentenone **54b** with various nucleophiles **55**.



54b *(S)*-**56a-d** *(R)*-**54b**

55a: phenol
55b: *p*-methoxyphenol
55c: phthalimide
55d: *p*-bromo benzoic acid

entry	NuH	T [°C]	t [h]	Yield **57** [%]	*ee* [%]	Yield **55b** [%]	*ee* [%]
1	**55a**	0	1	30	80	37	>99
2	**55b**	0	2.5	37	n.d.*	45	>99
3	**55c**	r.t.	18	39	81	47	>99
4	**55d**	0	1	40	91	38	>99

Reaction conditions: 0.5 mmol protected 4-hydroxycyclopentenone **54b**, 0.24 mmol nucleophile **55**, 0.3 equiv. (23 mg) Cs_2CO_3 (based on nucleophile) in 2 mL DCM, 0.15 mmol/g NP catalyst **60** (10 mg, 0.6 mol% based on nucleophile).

In the described approaches for Tsuji-Trost reactions stoichiometric quantities of nucleophile were employed, which had been already proven to achieve a dynamic kinetic resolution regarding hydroxybutenolide or related substrates.[61] Moreover, it is already known in literature that higher optical purities are achieved when 0.5 equiv. or even less of the nucleophile are used in the case of the Boc-protected substrate. Thus 0.24 equiv. of the tested nucleophiles were subsequently employed. The carboxylic acid derivative (entry 4) gave excellent enantioselectivities among the performed Tsuji-Trost reactions which match with the reported literature: phenol **55a** and carboxylic acids are reported to be suitable nucleophiles as they provide high selectivity.[51] Phenol **55a** also proved to be a suitable nucleophile, as it gave good enantioselectivity at 0 °C within 1 h (entry 1). The successful enantioselective induction of phthalimide **55c** into the cyclopentenone moiety would even give access to carboxyclic nucleosides. This was successfully accomplished at room temperature after a reaction time of 18 h (entry 3). No prediction could be made in the case of *p*-methoxyphenol (entry 2), since the two possible enantiomers could not be separated

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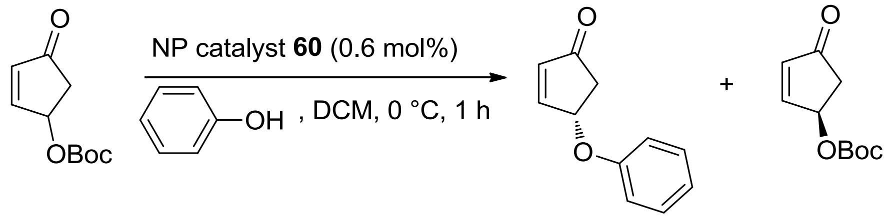
[*] $[\alpha]_D^{20} = -3.9$ (*c* 1, $CHCl_3$); literature value: $[\alpha]_D^{25} = -8.6$ (*c* 1, $CHCl_3$);

with the applied HPLC setup, however, the optical rotation indicated no successful kinetic resolution.

All in all, the nucleophiles **55a, 55c, 55d** yielded relatively high enantioselectivities regarding the substituted products **56a, 56c, 56d** compared to the classical Tsuji-Trost ligand **61**.[51] Furthermore, the enantiopure starting materials (*R*)-**54b** could be successfully re-isolated, no matter which nucleophile was applied. Remarkably, Cs_2CO_3 seemed to be an essential additive, since no conversion was observed without adding catalytic amounts of Cs_2CO_3.

After successful approaches, the focus turned to the studies towards iterative Trost reactions applying the enantioselective NP-catalyst **60**. The kinetic resolution of the *O*-Boc-derivative **54b** with phenol **55a** as nucleophile was carried out applying 0.6 mol% catalyst. After 1 h reaction time, the supernatant was decanted and the nanoparticles subjected to the next run (Table 11).

Table 11: Recycling studies towards the kinetic resolution of *boc*-protected *rac*-4-hydroxy-2-cyclopentenone **54b**.



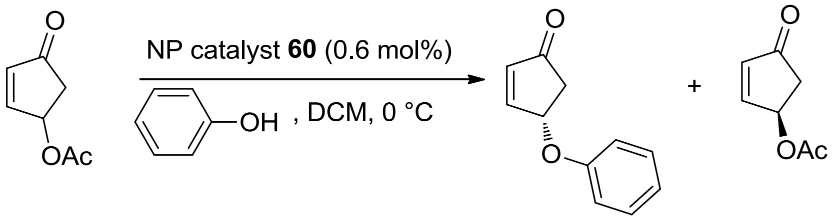
54b (*S*)-**56a** (*R*)-**54b**

entry	Yield (*S*)-**56a** [%]	*ee* [%]	Yield (*R*)-**54b** [%]	*ee* [%]	leaching Pd [ppm]	leaching Co [ppm]
1	43	84	48	>99	18	23
2	40	87	46	>99	8	8
3	42	86	44	>99	13	20
4	38	86	48	>99	6	12
5	40	85	44	>99	11	29

Reaction conditions: 0.5 mmol protected 4-hydroxy-2-cyclopentenone **54b**, 0.24 mmol nucleophile **55a**, 0.3 equiv. (23 mg) Cs_2CO_3 (based on nucleophile) in 2 mL DCM, 0.15 mmol/g NP catalyst **60** (10 mg, 0.6 mol% based on nucleophile).

Thus, five consecutive cycles without significant loss in activity were performed. Outstanding is the constant level in enantioselectivity. Furthermore, the product contamination due to Pd leaching, analyzed *via* ICP-OES was kept at low ppm values corresponding to an overall palladium loss of 3%. Overall, the NP-catalyst **60** is not only highly enantioselective and has great recycling capabilities, but is further extremely stable towards the applied conditions in the performed Tsuji Trost reactions.

As the transformation of the *O*-Boc-derivatives gave promising results regarding their nucleophilic substitutions, also one reaction with the acetyl-derivative **54a** applying phenol **55a**, as model nucleophile, was performed under the known reaction conditions (DCM, 0 °C, 1 h) (scheme 21).



54a *(S)*-**56a** *(R)*-**54a**

Scheme 21: Kinetic resolution regarding Ac-protected 4-hydroxy-2-cyclopentenone **54a**; Reaction conditions: 0.5 mmol protected 4-hydroxy-2-cyclopentenone **54a**, 0.24 mmol nucleophile **55a** in 2 mL DCM, 0.15 mmol/g NP catalyst **60** (10 mg, 0.6 mol% based on nucleophile).

The allylic substitution with substrate **54a** yielded 20% of the desired product (*S*)-**56a** with a rather low enantioselectivity of 57 %*ee*. The enantioselectivity is certainly higher than reported for the Tsuji-Trost ligand **61** (26 %*ee* after 18 h reaction time)[51], however, also the NP version did not completely succeed in the kinetic resolution of **54a**. This substrate is known to be not suitable for this kind of transformation due to a deactivation of the allyl acetate moiety by the conjugated carbonyl group.[51] Though, no further investigations regarding Ac-protected 4-hydroxy-2-cyclopentenone **54a** have been done.

3.3 Conclusion

In summary, a Trost-type ligand **65** was successfully synthesized and grafted onto polymeric nanoparticles (Co/C-PS-Cl **21**) *via* nucleophilic substitution. Furthermore, it was tested in the kinetic resolution of Boc-protected 4-hydroxy-2-cyclopentenone **54b** showing great selectivity in both substituted products and recovered starting material. Notably, the reactions were carried out applying relatively low catalyst amounts (0.6 mol%) for the included nucleophiles: phenols **55a, 55b**, carboxylic acids **55d** and nitrogen-containing heterocycles **55c**. To the best of our knowledge, it is by far the first reported, enantioselective Trost-type catalyst bound onto magnetic nanoparticles. Furthermore, the developed hybrid material turned out to be highly recyclable with an external magnetic field showing not only constant catalytic activity but also constant high enantioselectivity. Remarkably, the catalyst showed high chemical and mechanic stability, due to the polymeric character resulting in an overall Pd loss of below 3%.

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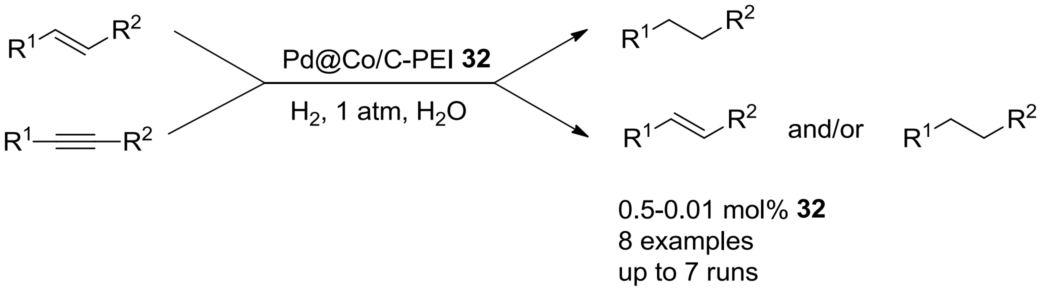
C. Summary

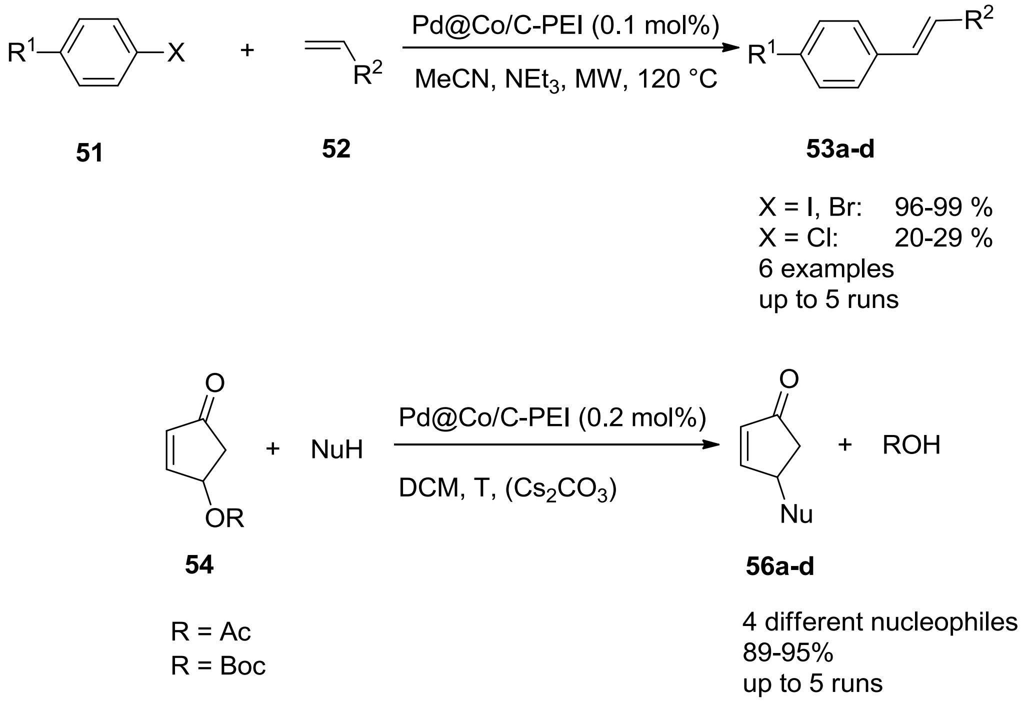
In this thesis, various polymers were introduced to Co/C nanoparticles followed by the immobilization of Pd nanoparticles or chelating ligands. They were employed in a great variety of Pd-catalzed hydrogenations, as well as C-C or C-heteroatom coupling reactions. Thereby, the excellent magnetization of unfunctionalized Co/C NPs **13** allowed a fast and easy separation of the introduced hybrid materials by an external magnetic field. The use of the polymers, additionally, enabled not only high Pd loadings, but also a good dispersibility, especially in polar solvents.

The first chapter highlighted PEI-coated Co/C nanobeads **30** as excellent supports for Pd NPs, resulting in a high Pd loading of 0.8 mmol/g (8.5 wt%). This material showed excellent catalytic activity in the hydrogenation of di-/ tri-substituted alkenes, especially 4-hydroxy-2-cyclopentenone **31**, and alkynes in water, and was easily recyclable for seven consecutive cycles showing consistent catalytic activity. Worth to mention, C-C double bonds could be selectively reduced in the presence of a C-O double bond. Further, the hydrogenation of alkynes to the corresponding alkenes could be controlled by time selection. Notably, the hydrogenation of 4-hydroxy-2-cyclopentenone **31** and transformation to water-insoluble cyclopentenone **34** in aqueous media could be performed at large scale applying a low Pd amount of 0.01 mol%, forming only water as byproduct.



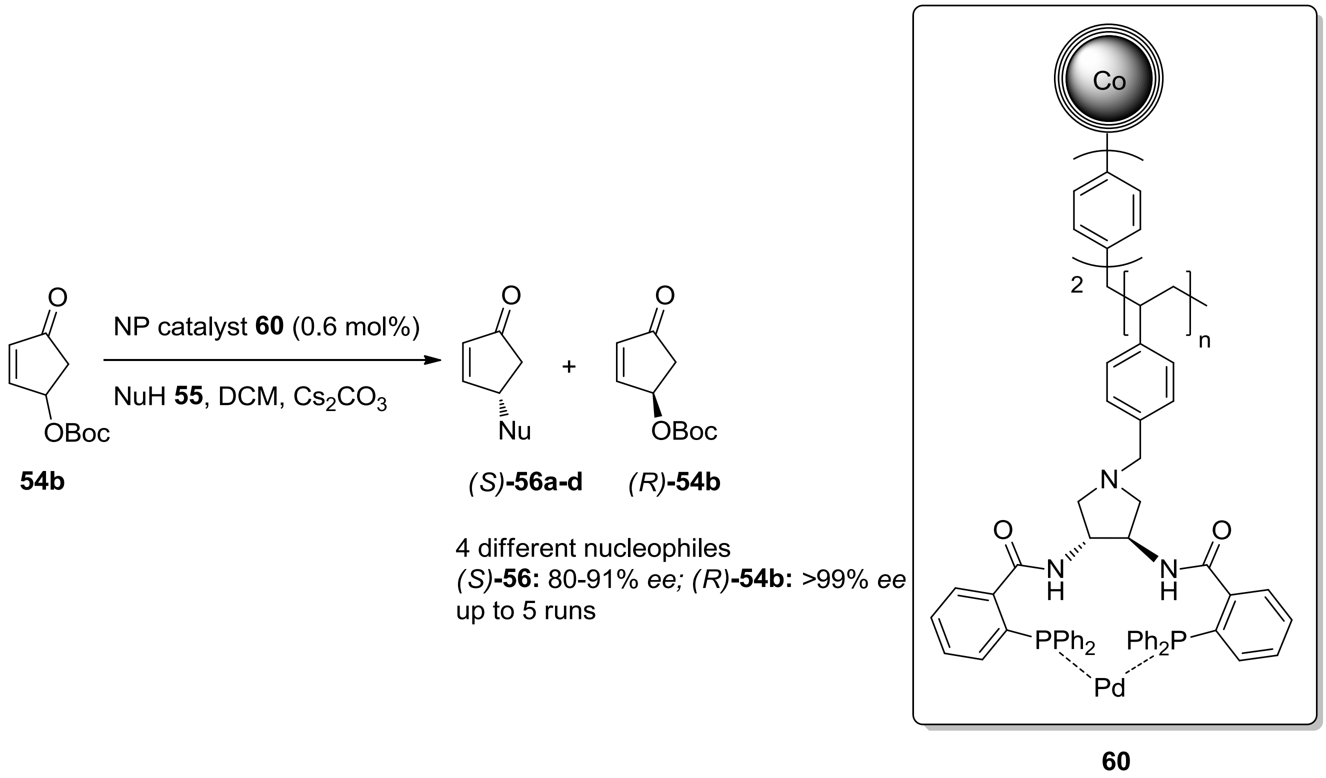
Scheme 22: Hydrogenation reactions by the use of Pd@Co/C-PEI **32** in water.

Chapter 2 extended the reaction scope, regarding the Pd@Co/C-PEI system **32**, to Pd-catalyzed Heck coupling and Tsuji-Trost allylation reactions. The Heck couplings with aryl iodides (**51aa** and **51ba**) and aryl bromides (**51ab** and **51bb**) could be performed quantitatively with 0.1 mol% Pd, whereas aryl chlorides (**51ac** and **51bc**) emerged as more challenging substrates (20-30%). The Tsuji-Trost reactions with protected 4-hydroxy-2-cyclopentenones **54a** and **54b** and various nucleophiles **55** were catalyzed in excellent yields without any external base being required. Exceptionally, the *O*-Boc-derivative needed additional Cs_2CO_3 in catalytic amounts for any conversion. Pd@Co/C-PEI **32** was easily recyclable in both reaction types for at least five iterative cycles without significant changes in catalytic activity.



Scheme 23: C-C/C- heteroatom coupling reactions by the use of Pd@Co/C-PEI **32**.

In the last chapter, a Trost-type ligand **65** was immobilized onto polystyrene-coated Co/C NPs **21** and successfully used in the kinetic resolution of Boc-protected 4-hydroxycyclopentenone **54b**. Though, C-, O-, and N- heteroatoms were introduced with good enantioselectivities with a low Pd loading of 0.6 mol%. Finally, the recycling of the applied hybrid system was studied revealing consistent activity and enantioselectivity for five consecutive runs.



4 different nucleophiles
(S)-**56:** 80-91% *ee; (R)*-**54b:** >99% *ee*
up to 5 runs

Scheme 24: Kinetic resolution of *rac*-**54b** by a NP-supported Trost-type catalyst **60.**

D. Zusammenfassung

Diese Doktorarbeit beschäftigt sich mit der Immobilisierung von Palladium Nanopartikeln oder chelatisierenden Liganden auf graphenbeschichteten Kobaltnanopartikeln, welche zusätzlich mit verschiedensten Polymeren ummantelt wurden. Diese wurden dann in einer Reihe von Palladium katalysierten Reaktionen, wie Hydrierungen, C-C und C-Heteroatom Kupplungen, als Katalysator verwendet. Die exzellente Magnetisierung unfunktionalisierter Co/C-Nanopartikel erlaubte hierbei eine schnelle und einfache Abtrennung der vorgestellten Hybridmaterialien, durch die Anlegung eines externen Magnetfeldes. Die Verwendung von Polymeren auf der Oberfläche der Partikel ermöglichte zusätzlich hohe Palladiumbeladungen, sowie eine gute Dispersionsstabilität in polaren Lösungsmitteln. Das erste Kapitel hebt polyethylenimin-beschichtete Co/C-Nanopartikel und deren erstklassige Eignung als Trägermaterial für Palladium Nanopartikel hervor, wodurch hohe Palladiumbeladungen von 0.8 mmol/g (8.5 wt%) ermöglicht wurden. Dieses Material zeigte ausgezeichnete katalytische Aktivität in der Hydrierung di- bzw. tri-substituierter Alkene, vornehmlich 4-hydroxy-2-cyclopentenone **31**, sowie der Hydrierung von Alkinen in Wasser. Des Weiteren war dieses Material leicht wiederverwendbar für sieben fortlaufende Hydrierzyklen, ohne Abnahme an katalytischer Aktivität. Besonders erwähnenswert war hierbei die selektive Reduktion von C-C- in Gegenwart von C-O-Doppelbindungen. Ebenso konnten Alkine selektiv zu ihren entsprechenden Alkenen durch Regulierung der Reaktionszeit hydriert werden. Insbesondere konnten die Hydrierung von 4-hydroxy-2-cyclopentenon **31** und dessen weitere Verarbeitung zu wasserunlöslichem cyclopentenon **34** in großem Maßstab und in wässriger Lösung durchgeführt werden. Für diese quantitative Transformation wurden nur 0.01 mol% an Pd-Katalysator benötigt und Wasser als einziges Abfallprodukt gebildet.

Kapitel 2 erweiterte die Bandbreite an, durch Pd@Co/C-PEI zugänglichen Reaktionen, zu Pd-katalysierten Heck Kupplungen und Tsuji-Trost Allylierungen. Die Heck Reaktionen mit den Iod- und Brom-substituierten Aryl-Derivaten konnten quantitativ, mit einem geringen Pd-Anteil von 0.1 mol%, durchgeführt werden, wohingegen Chlor-Aryle sich als schwerer zugänglich erwiesen. In den Tsuji-Trost Reaktionen mit geschützten 4-hydroxy-2-cyclopentenonen **54a** und **54b** und verschiedensten Nukleophilen **55** konnten exzellente Ausbeuten ohne den Zusatz einer externen Base erreicht werden. Eine Ausnahme bildeten hierbei die *O*-Boc-Derivate, welche zusätzlich katalytische Mengen an Cs_2CO_3 benötigten, damit überhaupt ein Umsatz beobachtet werden konnte. Pd@Co/C-PEI **32** konnte jedoch in beiden Reaktionstypen leicht in fünf aufeinanderfolgenden Zyklen wiederverwendet werden, ohne dabei eine Änderung in der katalytischen Aktivität zu zeigen.

Im letzten Kapitel wurde eine Variante des Trost-Liganden auf polystyrol-beschichteten Co/C-Nanopartikeln immobilisiert und erfolgreich in der kinetischen Racematspaltung von racemischem, Boc-geschütztem 4-hydroxy-2-cyclopentenon **54b** eingesetzt. Auf diese Weise konnten C-, O- und N- Nukleophile in guten Enantioselektivitäten mit einem geringen Pd-Gehalt von 0.6 mol% eingeführt werden. Letztendlich wurde die Wiederverwendbarkeit des Systems getestet. Das genutzte Hybridmaterial zeigte hierbei gute Wiederverwendbarkeit in fünf folgenden Reaktionszyklen bei gleichbleibender Reaktivität und Enantioselektivität.

E. Experimental Part

1. General Information

Commercially available reagents were used as received. Carbon coated nanoparticles were donated from Prof. W. J. Stark (ETH Zürich). They were dispersed with the help of an ultrasonic bath (Sonorex RK 255 H-R, Bandelin) and recovered with the aid of a neodymium based magnet (N48, W-12-N, Webcraft GmbH, side length 12 mm) unless otherwise indicated.

^{1}H-NMR

^{1}H NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz) and a Bruker Avance 400 spectrometer (400 MHz). All measurements were performed at ambient temperature. Chemical shifts δ are reported in parts per million [ppm] relative to the solvent signals as internal standard: $CDCl_3$ = 7.26 ppm, CD_3OD = 3.31 ppm, $(CD_3)_2SO$ = 2.50 ppm, D_2O = 4.79 ppm. Spectra were evaluated in first order and coupling constants *J* are given in Hertz [Hz]. 1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint) or doublet of doublets (dd). Splitting patterns that could not be interpreted are designated as multiplet (m).

^{13}C-NMR

^{13}C-NMR spectra were recorded on a Bruker Avance 300 (75.5 MHz) and a Bruker Avance 400 (101 MHz) spectrometer at ambient temperature. The spectra were recorded in $CDCl_3$, CD_3OD, $(CD_3)_2SO$ and D_2O. Chemical shifts are reported as δ, parts per million (ppm), relative to the center of the residual solvent signals: $CDCl_3$ = 77.16 ppm, CD_3OD = 49.00 ppm, $(CD_3)_2SO$ = 39.52 ppm.

^{31}P-NMR

^{31}P-NMR spectra were recorded on a Bruker Avance 400 (121 MHz) spectrometer at ambient temperature. The spectra were recorded in $(CD_3)_2SO$. Chemical shifts are reported as δ, parts per million (ppm).

Chiral high-performance liquid chromatography (chiral HPLC)

Chiral HPLC was performed on a Varian LC-902 Liquid Chromatograph using a Chiralcel OJ-H column (4.6 × 250 mm, 10 µm), as well as Phenomenex Lux Cellulose-1 (4.6 × 250 mm, 5 µm). The absolute configuration of the product was determined through comparison with literature values.

Column chromatography

(Flash-) Column chromatography was performed using Merck Gerduran 60 (0.063–0.200 mm) or Merck flash (0.040–0.063 mm) silica gel.

Infrared spectroscopy (IR)

Infrared spectra were recorded on an Agilent Cary 630 FT-IR spectrometer. All compounds were measured neat. The wavenumbers are reported as cm^{-1}.

Mass spectrometry (MS)

Mass spectrometry was performed in the Analytical Department of the University of Regensburg ("Zentrale Analytik") on a Jeol AccuTOF GCX, a Finnigan MAT SSQ 710 A, a Finnigan ThermoQuest TSQ 7000 and an Agilent Q-TOF 6540 UHD.

Thin layer chromatography (TLC)

Thin layer chromatography was performed on silica gel coated aluminium plates (Merck silica gel 60 F_{254} and Macherey-Nagel ALUGRAM® Xtra SIL G/UV_{254}). Visualization was accomplished with UV light (λ = 254 nm) and through the use of TLC stains, *e.g.* vanillin/sulfuric acid, followed by heating.

Optical rotation

Optical rotation values were determined using a Perkin Elmer 241 polarimeter at a wavelength of 589 nm (sodium-*d*-line) in a 1.0 dm cell with an inner volume of approximately 1 mL.

Elemental analysis

Elemental analysis was done by the microanalytical laboratory of the University of Regensburg on Vario EL III for checking the success of reactions on magnetic nanoparticles.

ICP-OES

ICP-OES (inductively coupled plasma optical emission spectrometry) was measured on a SpectroFlame EOP (Spectro) in 32% *aqua regia* solution (v/v).

XPS

XPS (X ray photoelectron spectroscopy) was measured on a Perkin-Elmer Physical Electronics PHI5700 ESCA System (Department of Physics, University of Regensburg) for verifying the oxidation state of the grafted metals.

TEM

Transmission electron microscopy (TEM) was performed on a FEI TecnaiF30 using standard TEM plates (carbon film on 400 mesh grids copper) with 3.05 mm diameter at the Department of Physics of the University of Regensburg.

2. NP-catalyzed hydrogenation reactions in water

General procedure for washing Co/C nanoparticles (13) prior use

Carbon coated cobalt nanoparticles Co/C **13** (1 g) were obtained from Turbobeads Llc, Switzerland. Prior usage they were washed in a millipore H_2O/HCl_{conc} (20 mL; 1/1) with a mechanical stirrer. The suspension was stirred for 24 h at ambient temperature. The washing solution was removed by magnetic decantation and the procedure repeated 5 times. To remove residual acid the particles were subsequently washed with millipore H_2O (5 mL) for 1 h followed by recovery of the particles with the aid of a magnet. The washing procedure was repeated until the pH of the washing solution was neutral. The NPs were washed with acetone (3x 5 mL) and diethylether (2x 5 mL) before being dried *in vacuo* to obtain 900 mg of washed carbon coated cobalt nanoparticles.

elemental microanalysis [%]: C, 7.12; H, 0.04; N, 0.

4-(2-Aminoethyl)phenyl functionalized Co/C nanoparticle (28)

To a mixture of Co/C nanoparticles **13** (1.0 g, 0.1 mmol, 1.0 equiv.) and 4-(2-Aminoethyl)phenylaniline **36** (132 µL, 1 mmol, 10 equiv.) in millipore H_2O (15 mL), HCl_{conc} (1 mL) was added to adjust a pH of 1, and then dispersed in an ultrasonic bath for 15 min. While stirring in an ice bath $NaNO_2$ (103.5 mg, 1.5 mmol, 15 equiv.) in millipore H_2O (15 mL) was added dropwise. Furthermore the suspension was dispersed another 30 min in an ultrasonic bath. Afterwards the nanoparticles were collected *via* an external magnet and the solvent was decanted. The NPs were washed with 1M NaOH (3x 5 mL), millipore H_2O (3x

5 mL), acetone (3x 5 mL), diethylether (3x 5 mL) before being dried *in vacuo* to obtain 1.01 g of Co/C-NH_2.

elemental microanalysis [%]: C, 10.27; H, 0.15; N, 0.09 – **loading** N 0.06 mmol/g.

Poly(ethylenimine) functionalized Co/C nanoparticle (30)

4-(2-Aminoethyl)phenyl functionalized Co/C nanoparticles **28** (250 mg, 0.015 mmol, 1 equiv.) were predespersed in DCM (12 mL) in an ultrasonic bath before adding aziridine **29** (778 µL, 15 mmol, 1000 equiv.) and HCl_{conc} (15 µL, 0.18 µmol, 0.012 equiv.). The mixture was then heated while stirring to 50 °C fo 24 h. Afterwards the particles were collected via an external magnet and the solvent was decanted. Furthermore the NPs were washed with DCM (3x 5 mL), millipore H_2O (3x 5 mL), DCM (3x 5 mL) before being dried *in vacuo* to obtain 276 mg of PEI functionalized NPs.

elemental microanalysis [%]: C, 27.42; H, 5.83; N, 11.95 – **loading** N 8.53 mmol/g.

Pd@Co/C-PEI (32)

PEI functionalized Co/C NPs **30** (50 mg, 0.43 mmol, 1 equiv.) were dispersed in 2 ml Millipore water by sonication for 10 min. After the pH was adjusted to 6 by 1 M HCl (50 µL), sodium tetrachloropalladate solution (5 mL, 0.047 mmol, 0.11 equiv., 0.0094 M in millipore water) was added dropwise followed by magnetic stirring for 1 h. The reduction of Pd(II) to Pd(0) was completed by adding a solution of $NaBH_4$ (8.9 mg, 0.24 mmol, 0.56 equiv.) in 2.5 mL water (0.094 M) and further stirring for 30 min. The synthesized Pd@Co/C-PEI were collected by an external magnet and washed with millipore H_2O (5x 5 mL) and *i*PrOH (2x 5 mL) before being dried *in vacuo* to obtain 56 mg of Pd@Co/C-PEI.

ICP-OES: loading Pd :0.8 mmol/g (91%; 8.5 wt%);

General procedure for hydrogenation reactions with Pd@Co/C-PEI (32)

Pd@Co/C-PEI nanoparticles **32** (0.5-0.1 mol% Pd, 0.5-2.5 µmol) and substrate (0.5 mmol) in millipore water (5 mL) were added in a Schlenk tube and further dispersed by sonication for 10 min (pH of the solution: pH 6). The Schlenk was evaporated and flushed with H_2 for ten times before being stirred under 1 atm H_2 (balloon) for a certain time. Afterwards, the catalyst was recovered via an external magnet and the product isolated as described in the following.

3-hydroxycyclopentanone (33): After a reaction time of 2 h the starting material was completely hydrogenated. The product was isolated *via* solvent evaporation under reduced pressure. The product was obtained in 97% yield (48 mg); **^{1}H-NMR** (400 MHz, D_2O): δ = 1.90-2.48 (m, 7H), 4.48 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 32.0, 35.6, 47.7, 69.7, 217.6.

Cyclopentanone (38): After a reaction time of 2 h the starting material was completely hydrogenated. The product was isolated *via* extraction with ethyl acetate (2x 2 mL) followed by distillation at 110 °C oil bath temperature (bp: 130 °C) for solvent removal. The product was obtained in 95% yield (40 mg); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.81-2.04 (m, 2H), 2.07-2.29 (m, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ = 23.2, 38.4, 218.9.

methyl propionate (40): After a reaction time of 4 h the starting material was completely hydrogenated. The product was extracted with diethyl ether (2x 2 mL) followed by solvent evaporation under reduced pressure (bp: 80 °C). The product was obtained in 98% yield (43 mg); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 1.07 (t, 3H, *J* = 7.6 Hz), 2.27 (q, 2H, *J* = 7.6 Hz), 3.60 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 9.0, 27.4, 51.5, 175.0.

methyl isobutyrate (42): After a reaction time of 2 h the starting material was completely hydrogenated. The product was extracted with diethyl ether (2x 2 mL) followed by solvent evaporation under reduced pressure (bp: 90 °C). The product was obtained in 96% yield (49 mg); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 1.14 (s, 3H), 1.16 (s, 3H), 2.54 (hept, 1H, *J* = 7.0 Hz), 3.65 (s, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 19.0, 33.9, 51.6, 177.6.

methyl butyrate (44): After a reaction time of 2 h the starting material was completely hydrogenated. The product was extracted with diethyl ether (2x 2 mL) followed by solvent evaporation under reduced pressure (bp: 102 °C). The product was obtained in 98% yield (50 mg); **^{1}H-NMR** (400 MHz, MeOD): δ = 0.94 (t, 3H, *J* = 7.4 Hz), 1.55-1.70 (m, 2H), 2.29 (t, 2H, *J* = 7.3 Hz), 3.65 (s, 3H); **^{13}C-NMR** (101 MHz, MeOD): δ = 12.5, 18.0, 35.3, 50.5, 174.5.

methyl 2-methylbutanoate (46): After a reaction time of 4 h the starting material was completely hydrogenated. The product was extracted with diethyl ether (2x 2 mL) followed by solvent evaporation under reduced pressure (bp: 118 °C). The product was obtained in 97% yield (56 mg).; **^{1}H-NMR** (400 MHz, MeOD): $\delta = 0.89$ (t, 3H, $J = 7.4$ Hz), 1.12 (d, 3H, $J = 7.0$ Hz), 1.20-1.75 (m, 2H), 2.27-2.50 (m, 1H), 3.66 (s, 1H), **^{13}C-NMR** (101 MHz, MeOD): $\delta = 10.5, 15.6, 26.5, 40.8, 50.6, 177.5$.

(*Z*)-but-2-ene-1,4-diol (48): After a reaction time of 2 h the triple bond got selectively reduced to the double bond. The solvent was removed via evaporation under reduced pressure. The mixture (2-butyne-1,4-diol and 2-butene-1,4-diol) was recrystallized from PE/EE mixture resulting in the product-containing supernatant and the precipitated starting material. The pure product was obtained via solvent evaporation of the supernatant under reduced pressure yielding 51% 2-butene-1,4-diol **48** (22 mg). After a reaction time of 4 h the starting material was completely hydrogenated to its corresponding alkane **49** in 97% yield (44 mg); **^{1}H-NMR** (300 MHz, $CDCl_3$): $\delta = 2.48$ (s, 2H), 4.22 (d, 4H, $J = 5.1$ Hz), 5.78 (ddd, 2H, $J = 5.0$ Hz, 3.8 Hz); **^{13}C-NMR** (101 MHz, $CDCl_3$): $\delta = 58.3, 131.0$.

butane-1,4-diol (49): After a reaction time of 4 h the starting material was completely hydrogenated. The product was isolated via solvent evaporation under reduced pressure. The product was obtained in 96% yield (43 mg); **^{1}H-NMR** (400 MHz, $CDCl_3$): $\delta = 1.60$-1.71 (m, 4H), 3.18 (s, 2H), 3.61-3.71 (m, 4H); **^{13}C-NMR** (101 MHz, $CDCl_3$): $\delta = 29.8, 62.6$.

Hydrogenation reaction of 4-hydroxy-2-cyclopentenone (31) with Pd@Co/C-PEI (32) on 2 g scale

Pd@Co/C-PEI nanoparticles **32** (0.01 mol% Pd; 2 µmol) and 4-hydroxy-2-cyclopentenone **31** (20 mmol) in millipore water (8.5 mL) were added in a Schlenk tube and further dispersed by sonication for 10 min (pH of the solution: pH 6). The Schlenk was evaporated and flushed with H_2 for ten times before being stirred under 1 atm H_2 (balloon) for 4 h. Afterwards, the catalyst was recovered via an external magnet and the solvent evaporated under reduced pressure. This afforded the product **33** in 98% yield (1.9 g). The spectroscopic data was according to literature.

Recycling experiments

For the recycling procedure the recovered Pd@Co/C-PEI nanoparticles **32** were subjected to the next run by simply adding the new substrate (20 mmol 4-hydroxy-2-cyclopentenone **31** as model substrate) in 8.5 mL water following the general procedure for hydrogenation on large scale described above. Thus seven consecutive runs applying 0.01 mol% of catalyst could be performed with almost any loss in activity.

Analysis of Pd leaching during recycling

The palladium leaching was determined in the catalytic hydrogenation of 4-hydroxy-2-cyclopentenone **31** using 0.01 mol% of Pd@Co/C-PEI **32** on large scale. After each run the solution was removed via magnetic decantation and completely evaporated. The residue was taken up by a defined amount of aqua regia 32% (v/v), filtered through a syringe filter and analyzed via ICP-OES. The data are given as ppm values defined as µg palladium per gramm obtained product.

Hydrogenation of 4-hydroxy-2-cyclopentenone (31) and further reaction to 2-cyclopentenone (34)

3-hydroxycyclopentanone **33** is synthesized following the general hydrogenation procedure on large scale described above. After magnetic removal of the catalyst the product solution was treated with the acidic ion exchanger Amberlyst 15 (255 mg; c = 30 mg/mL)) for elimination of the hydroxyl moiety. The resulted solution was heated for 4 h at 70 °C. Afterwards the aqueous phase was extracted with ethyl acetate (2x 5 mL). The combined organic layers were dried over $MgSO_4$ and the solvent afterwards removed by distillation (bp: 150 °C). This afforded the pure product **34** in 97 % yield (1.6 g).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.08-2.19 (m, 2H), 2.52 (ddd, 2H, *J* = 7.0 Hz, 4.7 Hz, 2.3 Hz), 5.99 (dt, 1H, *J* = 5.7 Hz, 2.2 Hz), 7.58 (dt, 1H, *J* = 5.5 Hz, 2.7 Hz); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 29.0, 34.0, 134.6, 164.8, 210.9.

3. NP-catalyzed Heck reactions

General procedure for Heck reactions applying Pd@Co/C-PEI (32)

Aryl halide **51** (0.5 mmol, 1 equiv.) in acetonitrile (2 ml), alkene **52** (0.6 mmol, 1.2 equiv.) and triethylamine (83 µl, 0.6 mmol, 1.2 equiv.) were introduced to a microwave vessel. Palladium catalyst **32** (0.5-0.1 mol% Pd, 0.5-2.5 µmol) was added, the reaction mixture dispersed via an ultrasonic bath for 10 min and then heated in a focused microwave oven to 120 °C for a certain time, depending on the aryl halide. Afterwards, water (1 ml) was added to the reaction mixture followed by extraction via diethylether (3x 2 ml). The combined organic layers were dried over $MgSO_4$ before evaporating the solvent. The crude product was purified by column chromatography and the products eluted by an appropriate hexanes/EtOAc mixture.

(*E*)-ethyl 3-(*p*-tolyl)acrylate (53a): R_f = 0.7 (hexanes:EtOAc 8:2); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 1.33 (t, 3H, *J* = 7.1 Hz), 2.36 (s, 3H), 4.26 (q, 2H, *J* = 7.1 Hz), 6.39 (d, 1H, *J* = 16.0 Hz), 7.18 (d, 2H, *J* = 8.0 Hz), 7.41 (d, 2H, *J* = 8.1 Hz), 7.66 (d, 1H, *J* = 16.0 Hz); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 14.4, 21.5, 60.4, 117.2, 128.1, 129.6, 131.8, 140.6, 144.6, 167.2.

ethyl cinnamate (53c): R_f = 0.5 (hexanes:EtOAc 7:3); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 1.34 (t, 3H, *J* = 7.1 Hz)), 4.27 (q, 2H, *J* = 7.1 Hz), 6.44 (d, 1H, *J* = 16.0 Hz), 7.31-7.41 (m, 3H), 7.46-7.51 (m, 2H), 7.69 (d, 1H, *J* = 16.0); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 14.4, 60.5, 118.3, 128.1, 128.9, 130.2, 134.5, 144.6, 167.0.

(*E*)-1,2-diphenylethene (53d): R_f = 0.7 (hexanes:EtOAc 8:2); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 7.13 (s, 2H), 7.24-7.32 (m, 2H), 7.34-7.42 (m, 4H), 7.49-7.58 (m, 4H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 126.6, 127.7, 128.8, 137.4.

(*E*)-1-methyl-4-styrylbenzene (53b): R_f = 0.6 (hexanes:EtOAc 7:3); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 7.08 (d, 2H, *J* = 2.3 Hz), 7.18 (d, 2H, *J* = 7.9 Hz), 7.22-7.29 (m, 1H), 7.36 (t, 2H, *J* = 7.6 Hz), 7.42 (d, 2H, *J* = 2.0 Hz), 7.51 (d, 2H, *J* = 7.5 Hz); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 20.8, 126.3, 126.4, 127.4, 127.8, 128.7, 129.4, 134.4, 137.5.

Recycling experiments

For the recycling procedure the recovered Pd@Co/C-PEI nanoparticles **32** were subjected to the next run by introducing new reagents (reaction of iodotoluene **51aa** with ethyl acrylate **52a** on 1 mmol scale was chosen for these experiments) to the microwave vial following the general procedure described above. Thus five consecutive runs applying 0.1 mol% catalyst were performed. Recovery of the catalyst was achieved via an external magnet.

Analysis of Pd leaching during recycling

The palladium leaching was determined in the reaction of iodotoluene **51aa** on 1 mmol scale with ethyl acrylate **52a** using 0.1 mol% of Pd@Co/C-PEI. After each run the solution was removed via magnetic decantation and completely evaporated. The residue was taken up by a defined amount of aqua regia 32% (v/v), filtered through a syringe filter and analyzed *via* ICP-OES. The data are given as ppm values defined as µg palladium per gramm obtained product.

4. NP-catalyzed Tsuji-Trost reactions

Ethyl 2-acetylpent-4-enoate (59)

In a flame dried Schlenk flask Pd@Co/C-PEI nanoparticles **32** (0.5 mol% Pd, 5 µmol)) were added under nitrogen atmosphere and further dispersed by sonication in THF (4 mL) for 10 min. Afterwards, ethyl 3-oxybutanoate **58** (130.14 mg, 1.0 mmol, 1.0 equiv.) and allyl acetate **57** (250.29 mg, 2.5 mmol, 2.5 equiv.) were added and the resulting suspension was heated under vigorous stirring to 70 °C. After 20 h the reaction was complete and after evaporating the solvent the product was afforded as colourless oil (165 mg, 0.97 mmol, 97%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.20 (t, 3H, J = 7.1 Hz), 2.17 (s, 3H), 2.52 (t, 2H, J = 7.0 Hz), 3.45 (t, 1H, J = 7.4 Hz), 4.13 (q, 2H, J = 7.1 Hz), 4.88-5.13 (m, 2H), 5.67 (ddt, 1H, J = 17.0 Hz, 10.1 Hz, 6.8 Hz).

4-(4-methoxyphenoxy)cyclopent-2-enone (56b)

In a flame dried Schlenk flask Pd@Co/C-PEI nanoparticles **32** (1-0.2 mol% Pd, 10-2 µmol) were added under nitrogen atmosphere and further dispersed by sonication in DCM (4 mL) for 10 min. Afterwards, 4-methoxyphenol **55b** (124.14 mg, 1.0 mmol, 1.0 equiv.) and 4-oxocyclopent-2-en-1-yl acetate **54a** (350.35 mg, 2.5 mmol, 2.5 equiv.) or *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate **54b** (495.54 mg, 2.5 mmol, 2.5 equiv.) were added and the resulting suspension was stirred for 4 h or 2.5 h at 0 °C. Notable, when *tert*-butyl (4-

oxocyclopent-2-en-1-yl) carbonate **54b** was used, Cs_2CO_3 (97 mg, 0.3 mmol, 0.3 equiv.) had to be added. After magnetic decantation, the solvent was evaporated and the crude product purified by column chromatography (hexanes:EtOAc 5:1).

R_f = 0.3 (hexanes/EtOAc 5:1; stains brown with vanillin); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 2.45 (dd, 1H, *J* = 18.4 Hz, 2.1 Hz), 2.84 (dd, 1H, *J* = 18.4 Hz, 6.0 Hz), 3.77 (s, 3H), 5.27-5.43 (m, 1H), 6.34 (dd, 1H, *J* = 5.7 Hz, 1.1 Hz), 6.79-6.92 (m, 4H), 7.69 (dd, 1H, *J* = 5.7 Hz, 2.3 Hz); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 41.9, 55.7, 76.1, 114.9, 116.7, 136.4, 151.3, 154.6, 161.5, 205.3.

Recycling experiments (Synthesis of 4-(4-methoxyphenoxy)cyclopent-2-enone (56b))

For the recycling procedure the recovered Pd@Co/C-PEI nanoparticles **32** were subjected to the next run by simply adding new reagents: 4-oxocyclopent-2-en-1-yl acetate **54a** (350.35 mg, 2.5 mmol, 2.5 equiv.) and 4-methoxyphenol **55b** (124.14 mg, 1.0 mmol, 1.0 equiv.) or *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate **54b**, 4-methoxyphenol **55b** (124.14 mg, 1.0 mmol, 1.0 equiv.) and Cs_2CO_3 (97 mg, 0.3 mmol, 0.3 equiv.) in 4 mL DCM under nitrogen atmosphere. Then the procedure described above was followed for five consecutive runs. Notable, the recovery of the NP base was achieved by stirring the NP in a K_2CO_3 solution (1M) after each recycling step.

Analysis of Pd leaching during recycling

The palladium leaching was determined in both the Tsuji-Trost reaction of 4-methoxyphenol **55b** with 4-oxocyclopent-2-en-1-yl acetate **54a** and the Tsuji-Trost reaction of 4-methoxyphenol **55b** with *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate **54b**. After each run the solution was removed *via* magnetic decantation and completely evaporated. The residue was taken up by a defined amount of aqua regia 32% (v/v), filtered through a syringe filter and analyzed *via* ICP-OES. The data are given as ppm values defined as µg palladium per gramm obtained product.

4-phenoxycyclopent-2-enone (56a)

In a flame dried Schlenk flask Pd@Co/C-PEI nanoparticles (0.2 mol% Pd, 2 µmol) were added under nitrogen atmosphere and further dispersed by sonication in DCM (4 mL) for 10 min. Afterwards, phenol **55a** (94.12 mg, 1.0 mmol, 1.0 equiv.) and 4-oxocyclopent-2-en-1-yl acetate **54a** (350.35 mg, 2.5 mmol, 2.5 equiv.) or *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate **54b** (495.54 mg, 2.5 mmol, 2.5 equiv.) were added and the resulting suspension was stirred for 4 h at room temperature or 4 h at 0 °C. Notable, when *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate **54b** was used, Cs_2CO_3 (97 mg, 0.3 mmol, 0.3 equiv.) had to be added. After magnetic decantation the solvent was evaporated and the crude product purified by column chromatography (hexanes:EtOAc 9:2).

R_f = 0.3 (hexanes:EtOAc 9:2; stains brown with vanillin); spectroscopic data according to literature.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 2.44 (dd, 1H, *J* = 18.4 Hz, 2.1 Hz), 2.89 (dd, 1H, *J* = 18.4 Hz, 6.0 Hz), 5.45 (ddd, 1H, *J* = 5.8 Hz, 3.5 Hz, 2.2 Hz), 6.36 (dd, 1H, *J* = 5.7 Hz, 1.3 Hz), 6.87-6.96 (m, 2H), 6.96-7.06 (m, 1H), 7.26-7.40 (m, 2H), 7.70 (dd, 1H, *J* = 5.7 Hz, 2.4 Hz).

2-(4-oxocyclopent-2-en-1-yl)isoindoline-1,3-dione (56c)

In a flame dried Schlenk flask Pd@Co/C-PEI nanoparticles **32 (**0.2 mol% Pd, 2 µmol) were added under nitrogen atmosphere and further dispersed by sonication in DCM (4 mL) for 10 min. Afterwards, isoindoline-1,3-dione **55c** (147.14 mg, 1.0 mmol, 1.0 equiv.) and 4-oxocyclopent-2-en-1-yl acetate **54a** (350.35 mg, 2.5 mmol, 2.5 equiv.) or *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate **54b** (495.54 mg, 2.5 mmol, 2.5 equiv.) were added and the resulting suspension was stirred for 24 h at room temperature. Notable when *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate **54b** was used, Cs_2CO_3 (97 mg, 0.3 mmol, 0.3 equiv.) had to be added. After magnetic decantation the solvent was evaporated and the crude product purified by column chromatography (hexanes:EtOAc 9:2).

R_f = 0.15 (hexanes:EtOAc 9:2; stains brown with vanillin); spectroscopic data according to literature.

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 2.75 (dd, 1H, *J* = 18.3 Hz, 3.4 Hz), 2.85 (dd, 1H, *J* = 18.3 Hz, 6.9 Hz), 5.49-5.58 (m, 1H), 6.44 (d, 1H, *J* = 5.7 Hz, 2.2 Hz), 7.52 (dd,1H, J = 5.7 Hz, 2.4 Hz), 7.70-7.80 (m, 2H), 7.80-7.91 (m, 2H).

5. NP-catalyzed kinetic resolution of protected *rac*-4-hydroxy-2-cyclopentenone

Synthesis of (3*R*,4*R*)-*tert*-butyl 3,4-diaminopyrrolidine-1-carboxylate (67)

(3*R*,4*R*)-*tert*-butyl 3,4-diazidopyrrolidine-1-carboxylate **66** (253.26 mg, 1 mmol) was dissolved in MeOH (5 ml) in an autoclave vessel. After adding Pd/C (10 wt%, 25 mg), the reaction mixture was stirred under 5 bar H_2 pressure for 20 h in an autoclave. After completion the mixture was filtered and washed with methanol. The solvent was removed under reduced pressure to obtain the pure product as yellow oil (185 mg, 92%).

^{1}H-NMR (400 MHz, MeOD) δ = -0.04 (s, 9H), 1.56 (dd, 2H, *J* = 16.3 Hz, 6.8 Hz), 1.72-1.93 (m, 4H), 2.18 (d, 2H, *J* = 7.4 Hz);); **^{13}C-NMR** (101 MHz, MeOD) δ = 27.3, 51.0, 51.4, 57.0, 57.5, 79.5, 155.1; **$[\alpha]_D^{20}$** = -54.6 (*c* 1, $CHCl_3$); **LRMS** (ESI): *m/z* = 202.1549 [MH^+]; calc. for $[C_9H_{19}N_3O_2]^+$ = 201.15.

Synthesis of (3*R*,4*R*)-*tert*-butyl 3,4-bis(2-(diphenylphosphino)benzamido)pyrrolidine-1-carboxylate (68)

In a flame dried Schlenk flask amino ligand **67** (100.36 mg, 0.5 mmol, 1 equiv.), DPPBA (306.29 mg, 1 mmol, 2 equiv.) and DMAP (12.2 mg, 0.1 mmol, 0.2 equiv.) were dissolved in dry DCM (8 ml) under nitrogen atmosphere. Then, DCC (113.5 mg, 0.55 mmol, 1.1 equiv.) in 2 ml DCM was added dropwise under stirring and ice cooling. Afterwards, the reaction mixture was stirred for another 24 h at room temperature. The precipitated white solid was filtered off and the solvent further evaporated to get a slight-yellow solid compound which was purified by column chromatography (hexanes:EtOAc 7:1 to 1:1). The pure product was isolated as white solid (380 mg, 0.48 mmol, 97%).

^{1}H-NMR (400 MHz, DMSO) δ = 1.41 (s, 9H), 2.94-3.38 (m, 4H), 4.31 (s, 2H), 7.01-7.89 (m, 28H), 8.63 (d, 2H, *J* = 6.8 Hz); **^{31}P-NMR** (121 Hz, DMSO) δ = -9.26; **$[\alpha]_D^{20}$** = 27.52(*c* 1, DCM); **LRMS** (ESI): *m/z* = 778.2962 [MH^+]; calc. for $[C_{47}H_{45}N_3O_4P_2]^+$ = 777.29.

Synthesis of *N*,*N*'-((3*R*,4*R*)-pyrrolidine-3,4-diyl)bis(2-(diphenylphosphino)benzamide) (65)

In a flame dried Schlenk flask (3*R*,4*R*)-*tert*-butyl 3,4-bis(2-(diphenylphosphino) benzamido)pyrrolidine-1-carboxylate **68** (388.91 mmol, 0.5 mmol, 1 equiv.) was dissolved in acetic acid (2 mL). Then, BF_3*Et_2O (0.2 mL, 1.5 mmol, 3 equiv.) was added followed by vigorous stirring for 30 min at room temperature. Afterwards, the solution was poured onto a solution of NaOAc (1 g) in ice water (5 mL). The precipitate was washed with ice water (5x 3 mL) and diethylether (5x 3 mL) and dried over P_2O_5 *in vacuo* to obtain the Tsuji-Trost type ligand. This was used without further purification for coupling with the Co/C-PS-Cl nanobeads.

Tsuji-Trost ligand functionalized Co/C-PS-Cl nanoparticles (60)

In a flame dried Schlenk flask Trost-type ligand **65** (33 mg, 0.048 mmol) and Pd_2dba_3 (11 mg, 0.012 mmol) in dry DCM (10 mL) were added under nitrogen atmosphere and stirred until the purple solution turned yellow-brown. Then, the DCM was removed under a constant flow of nitrogen. In the next step Co/C-PS-Cl **21** (50 mg) dispersed in DMF (5 mL) with the aid of an ultrasonic bath for 10 min. Then, the suspension was stirred for 21 h at 100 °C. Afterwards, the nanoparticles were collected *via* an external magnet and the solvent was decanted. The NPs were washed with DMF (3x 5 mL) and DCM (3x 5 mL) before being dried *in vacuo* to obtain 56 mg of functionalized nanoparticles.

elemental microanalysis [%]: C, 44.43; H, 3.73; N, 0.86 – **loading** ligand 0.19 mmol/g.

ICP-OES: loading Pd :0.15 mmol/g.

Kinetic resolution of *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate (54b) applying nanoparticle catalyst (60)

Under nitrogen atmosphere to a solution of *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate **54b** (99.11 mg, 0.5 mmol, 2.1 equiv.), nucleophile **55** (0.24 mmol, 1 equiv.) and Cs_2CO_3 (23 mg, 0.3 equiv.) in dry DCM (2 mL) in a flame dried Schlenk flask was added the nanoparticle catalyst **60** bearing a Tsuji-Trost type ligand (0.6 mol% Pd, 1.4 µmol). The suspension was allowed to stir for a certain time at a certain temperature until the catalyst was recovered via an external magnet. The decanted solution was further filtered to remove the Cs_2CO_3 and the solvent evaporated. The crude reaction mixture was purified by column chromatography and the products eluted by an appropriate hexanes/EtOAc mixture.

4-methoxyphenol (55b): 2.5 h at 0 °C; **R$_f$((*S*)-4-(4-methoxyphenoxy)cyclopent-2-enone)** = 0.3 (hexanes:EtOAc 5:1; stains brown with vanillin); **^{1}H-NMR** (400 MHz, CDCl$_3$) δ = 2.45 (dd, 1H, *J* = 18.4 Hz, 2.1 Hz), 2.84 (dd, 1H, *J* = 18.4 Hz, 6.0 Hz), 3.77 (s, 3H), 5.27-5.43 (m, 1H), 6.34 (dd, 1H, *J* = 5.7 Hz, 1.1 Hz), 6.79-6.92 (m, 4H), 7.69 (dd, 1H, *J* = 5.7 Hz, 2.3 Hz); **^{13}C-NMR** (101 MHz, CDCl$_3$) δ = 41.9, 55.7, 76.1, 114.9, 116.7, 136.4, 151.3, 154.6, 161.5, 205.3; **chiral HPLC analysis** (Chiracel OD-H, *n*heptane/*i*PrOH 9:1, 0.5 ml/min, 220 nm):): t$_r$ = 28.5, t$_r$ = 30.9 (literature values; not separable); **R$_f$((*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate)** = 0.5 (hexanes:EtOAc 5:1; stains dark brown with vanillin); **^{1}H-NMR** (400 MHz, CDCl$_3$) δ = 1.50 (s, 9H), 2.40 (dd, 1H, *J* = 18.7 Hz, 2.2 Hz), 2.83 (dd, 1H, *J* = 18.7 Hz, 6.4 Hz), 5.61-5.79 (m, 1H), 6.33 (dd, 1H, *J* = 5.7 Hz, 1.2 Hz), 7.59 (dd, 1H, *J* = 5.7 Hz, 2.4 Hz); **^{13}C-NMR** (101 MHz, CDCl$_3$) δ = 27.7, 41.0, 74.2, 83.3, 137.2, 152.3, 158.7, 203.7; **chiral HPLC analysis** (Chiracel OJ-H, *n*heptane/*i*PrOH 99:1, 1.0 ml/min, 215 nm): t$_r$major = 13.2 min, >99 %*ee*.

phenol (55a): 1 h at 0 °C; **R$_f$((*S*)-4-phenoxycyclopent-2-enone)** = 0.3 (hexanes:EtOAc 9:2; stains brown with vanillin); **^{1}H-NMR** (400 MHz, CDCl$_3$) δ = 2.46 (dd, 1H, *J* = 18.4 Hz, 2.1 Hz),2.89 (dd, 1H, J = 18.4 Hz, 6.0 Hz), 5.35-5.56 (m,1H), 6.37 (dd, 1H, *J* = 5.7 Hz, 1.1 Hz), 6.93 (dd, 2H, *J* = 8.7 Hz, 0.9 Hz), 7.01 (t, 1H, *J* = 7.4 Hz), 7.26-7.37 (m, 2H), 7.71 (dd, 1H, *J* = 5.7 Hz, 2.3 Hz); **^{13}C-NMR** (101 MHz, CDCl$_3$) δ = 41.9, 75.1, 115.3, 121.8, 129.8, 136.6, 157.3, 159.7, 205.1; **chiral HPLC analysis** (Phenomenex Lux Cellulose-1, *n*heptane/*i*PrOH 90:10, 1.0 ml/min, 215 nm): t$_r$major = 13.93 min, t$_r$minor = 12.78 min, 80 %*ee;* **R$_f$((*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate)** = 0.5 (hexanes:EtOAc 9:2; stains dark brown with vanillin); spectroscopic data in accordance to literature**; chiral HPLC analysis** (Chiracel OJ-H, *n*heptane/*i*PrOH 99:1, 1.0 ml/min, 215 nm): t$_r$major = 11.4 min, >99 %*ee*.

isoindoline-1,3-dione (55c): 18 h at room temperature; **R$_f$((*S*)-2-(4-oxocyclopent-2-en-1-yl)isoindoline-1,3-dione)** = (hexanes:EtOAc 9:2) = 0.15; **^{1}H-NMR** (400 MHz, CDCl$_3$) δ = 2.75 (dd, 1H, *J* = 18.3 Hz, 3.4 Hz), 2.85 (dd, 1H, *J* = 18.3 Hz, 6.9 Hz), 5.49-5.59 (m,1H), 6.44 (dd, 1H, J = 5.7 Hz, 2.2 Hz), 7.52 (dd, 1H, *J* = 5.7 Hz, 2.4 Hz), 7.72-7.78 (m, 2H), 7.83-7.89 (m, 2H); **^{13}C-NMR** (101 MHz, CDCl$_3$) δ = 39.6, 49.4, 123.6, 131.4, 134.4, 136.2, 159.6, 167.2, 205.9; **chiral HPLC analysis** (Phenomenex Lux Cellulose-1, *n*heptane/*i*PrOH 90:10, 1.0 ml/min, 215 nm): t$_r$major = 20.71 min, t$_r$minor = 22.21 min, 81 %*ee;* **R$_f$((*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate)** = 0.4 (hexanes:EtOAc 9:2; stains brown with vanillin); spectroscopic data in accordance to literature**; chiral HPLC analysis** (Chiracel OJ-H, *n*heptane/*i*PrOH 99:1, 1.0 ml/min, 215 nm): t$_r$major = 11.4 min, >99 %*ee*.

4-bromobenzoic acid (55d): 1 h at 0 °C; **R$_f$((*S*)-4-bromophenyl (4-oxocyclopent-2-en-1-yl) carbonate)** = 0.2 (hexanes:EtOAc 9:2); **^{1}H-NMR** (400 MHz, CDCl$_3$) δ = 2.48 (dd, 1H, *J* = 18.8 Hz, 2.2 Hz), 2.94 (dd, 1H, *J* = 18.8 Hz, 6.4 Hz), 6.10 (ddd, 1H, *J* = 6.1 Hz, 3.5 Hz, 2.2 Hz), 6.41 (dd, 1H, *J* = 5.7 Hz, 1.2 Hz), 7.56-7.63 (m, 2H), 7.68 (dd, 1H, *J* = 5.7 Hz, 2.4 Hz), 7.84-7.93 (m,2H)); **^{13}C-NMR** (101 MHz, CDCl$_3$) δ = 41.1, 72.7, 128.1, 128.7, 131.3, 131.9, 137.4, 158.7, 166.8, 204.3; **chiral HPLC analysis** (Phenomenex Lux Cellulose-1, *n*heptane/*i*PrOH 70:30, 0.5 ml/min, 254 nm): t$_r$major = 20.95 min, t$_r$minor = 24.60 min, 91 %*ee*; **R$_f$((*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate)** = 0.3 (hexanes:EtOAc 9:2; stains brown with vanillin); spectroscopic data in accordance to literature**; chiral HPLC analysis** (Chiracel OJ-H, *n*heptane/*i*PrOH 99:1, 1.0 ml/min, 215 nm): t$_r$major = 13.6 min, >99 %*ee*.

Analysis of Pd leaching during recycling

The palladium leaching was determined in the kinetic resolution of *tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate **54b** applying phenol **55a** as nucleophile and Cs$_2$CO$_3$ as additive as described in the general procedure above. After each run the solution was removed *via* magnetic decantation and completely evaporated. The product mixture was separated by column chromatography and both conversion and enantioselectivity were evaluated. The residue (of both reaction products) was taken up by a defined amount of aqua regia 32% (v/v), filtered through a syringe filter and analyzed *via* ICP-OES. The data are given as ppm values defined as µg palladium per gramm obtained product.

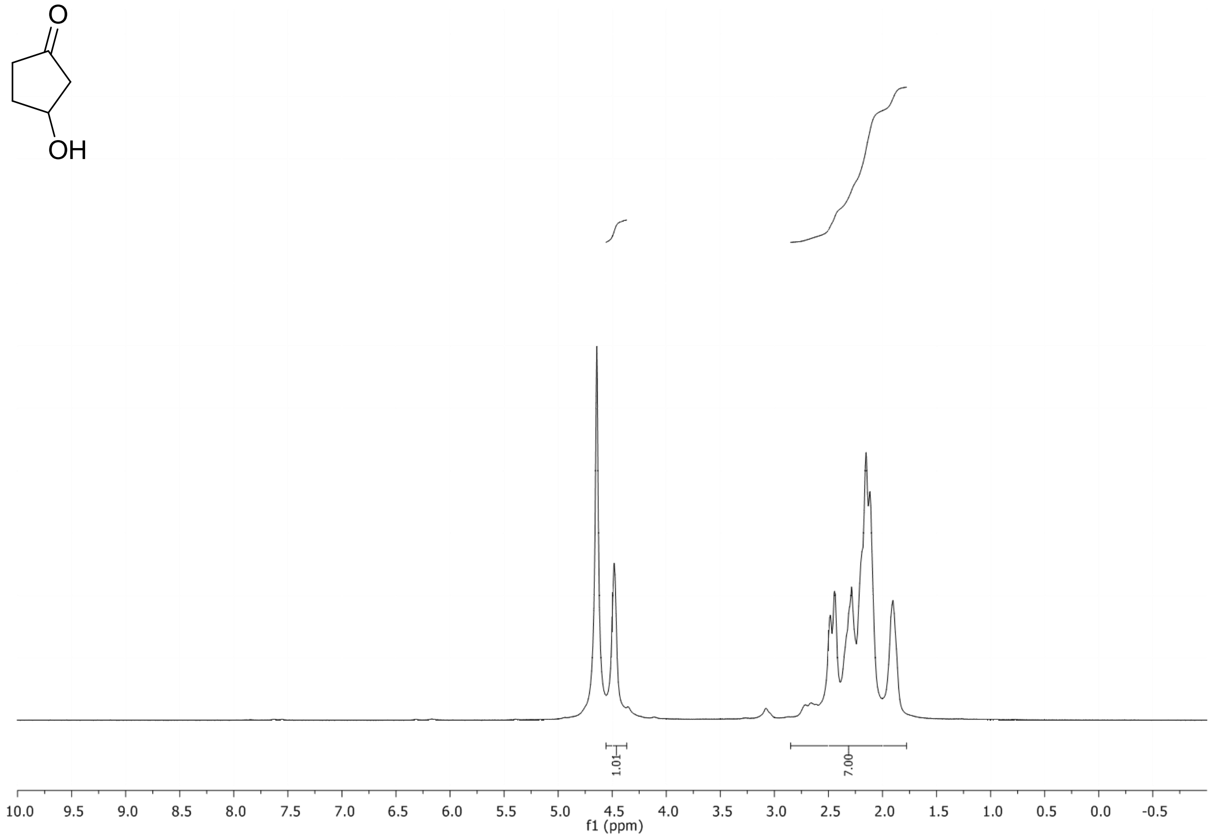
F. Appendix

1. NMR spectra

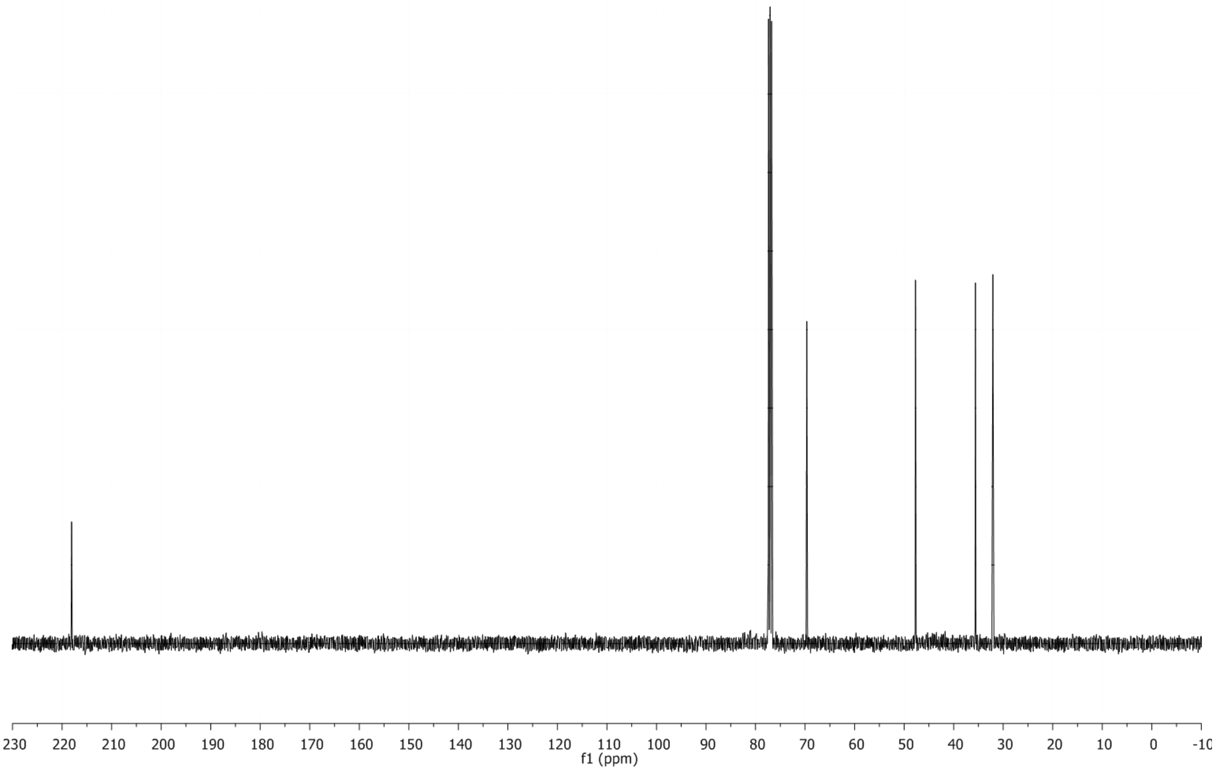
^{1}H NMR spectra	upper image
^{13} C NMR spectra	lower image

Frequency, solvent and temperature (if not ambient) are noted at the top of the spectra.

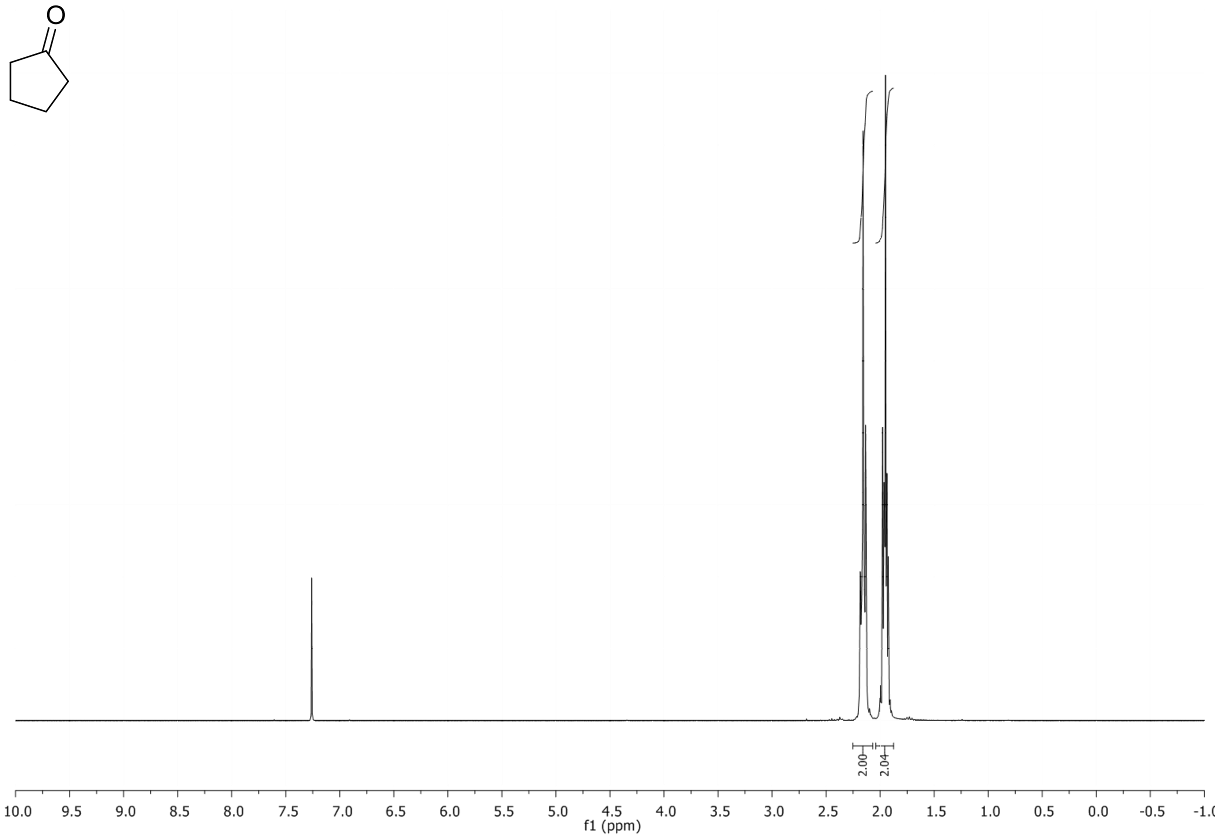
^{1}H-NMR (400 MHz, D_2O)-**33**



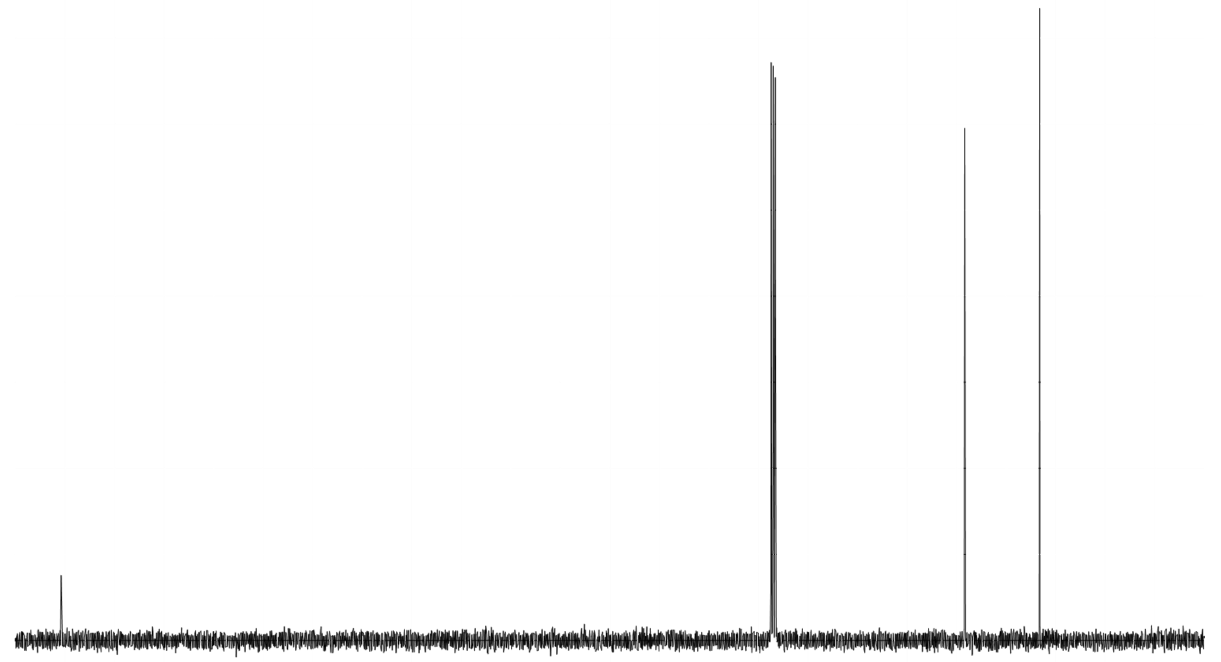
^{13}C-NMR (101 MHz, $CDCl_3$)



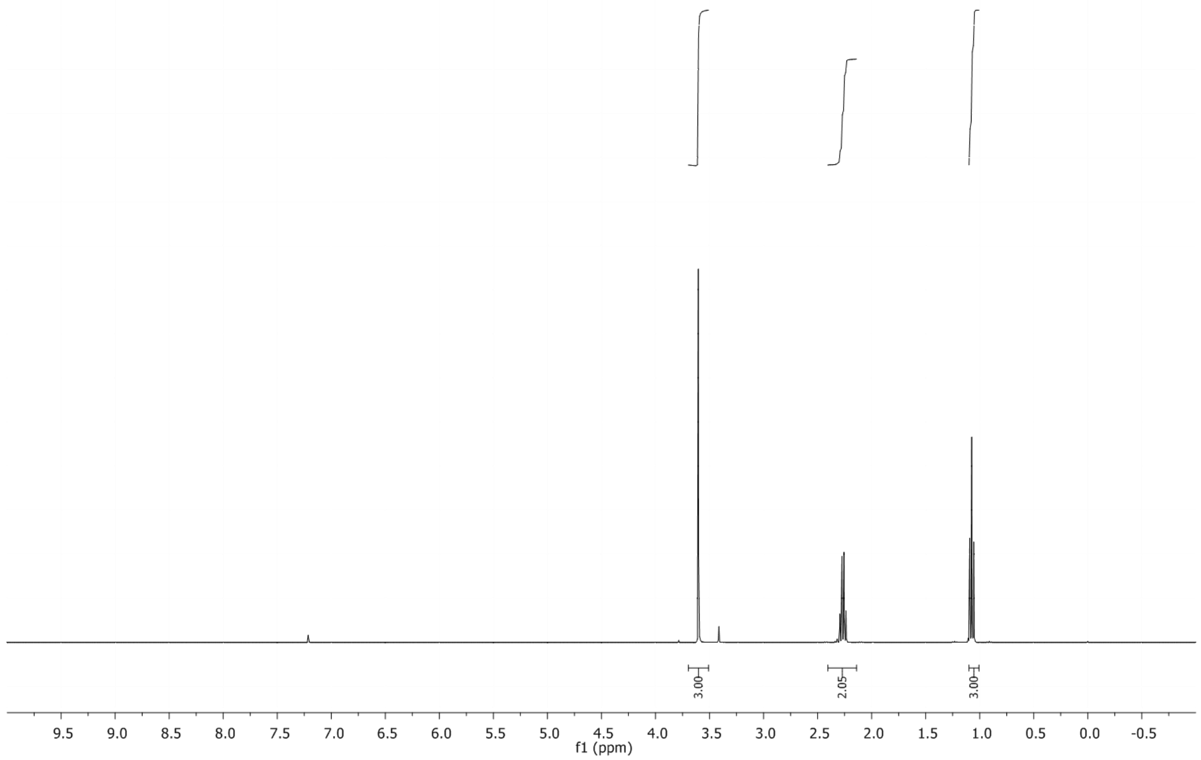
^{1}**H-NMR** (300 MHz, $CDCl_3$)-**38**



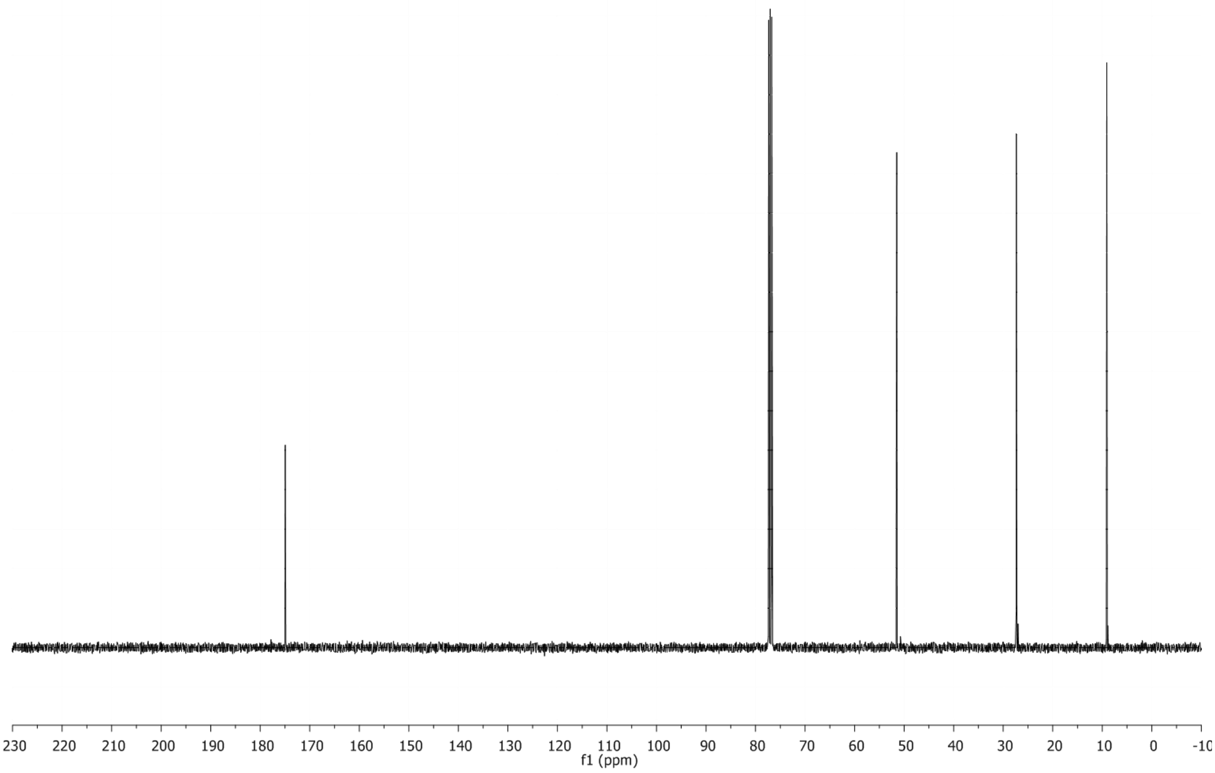
^{13}**C-NMR** (75 MHz, $CDCl_3$)



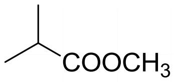
^{1}H-NMR (400 MHz, CDCl$_3$)-**40**

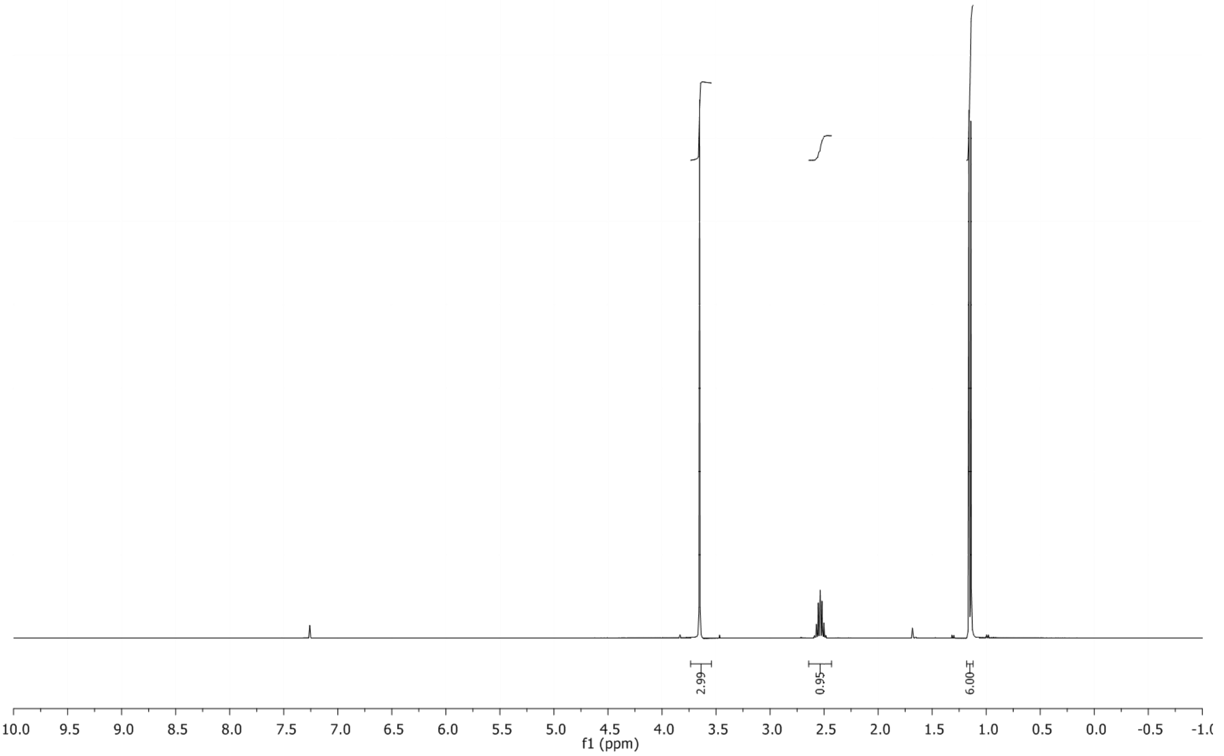


^{13}C-NMR (101 MHz, CDCl$_3$)

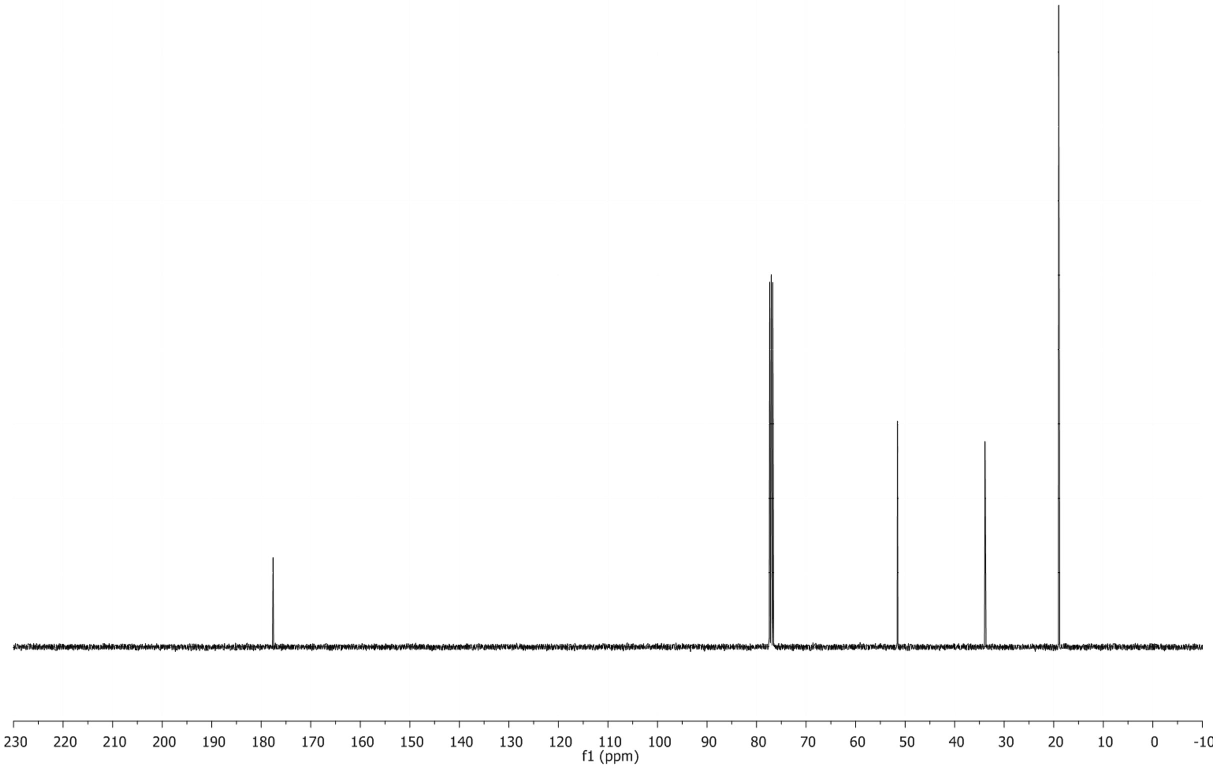


^{1}**H-NMR** (400 MHz, $CDCl_3$)-**42**

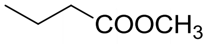


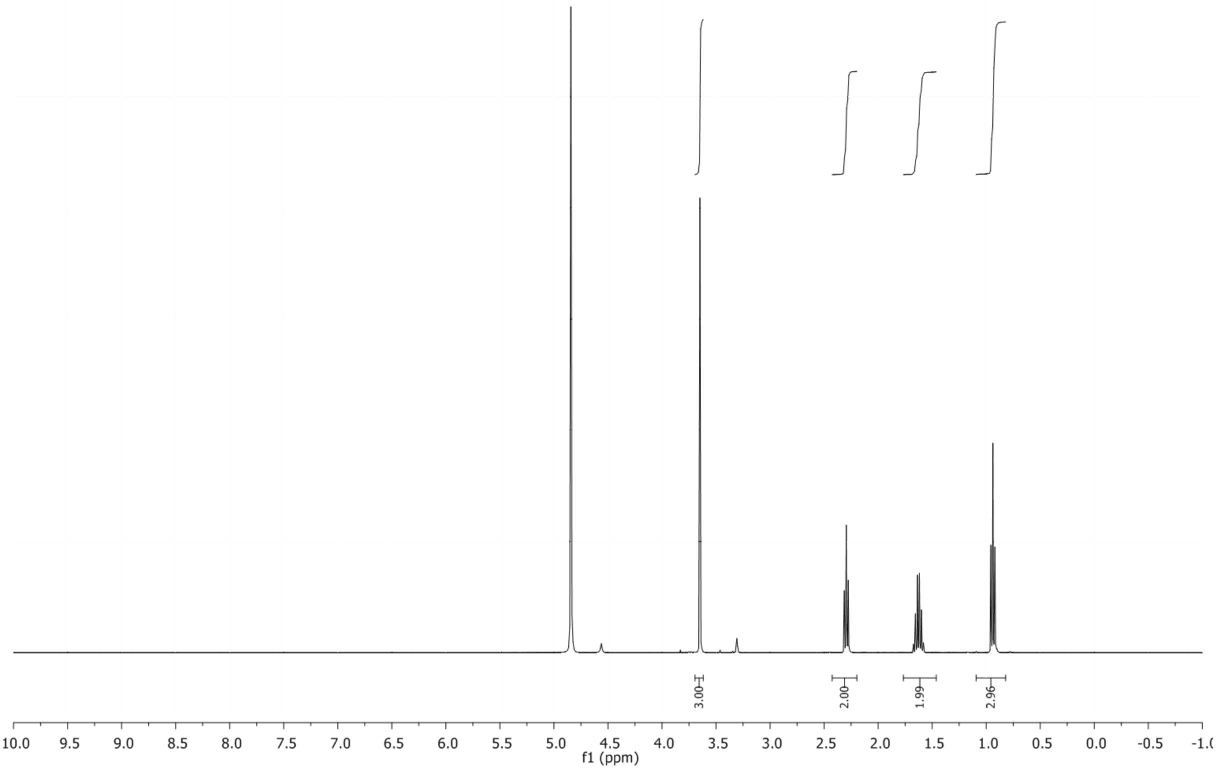


^{13}**C-NMR** (101 MHz, $CDCl_3$)

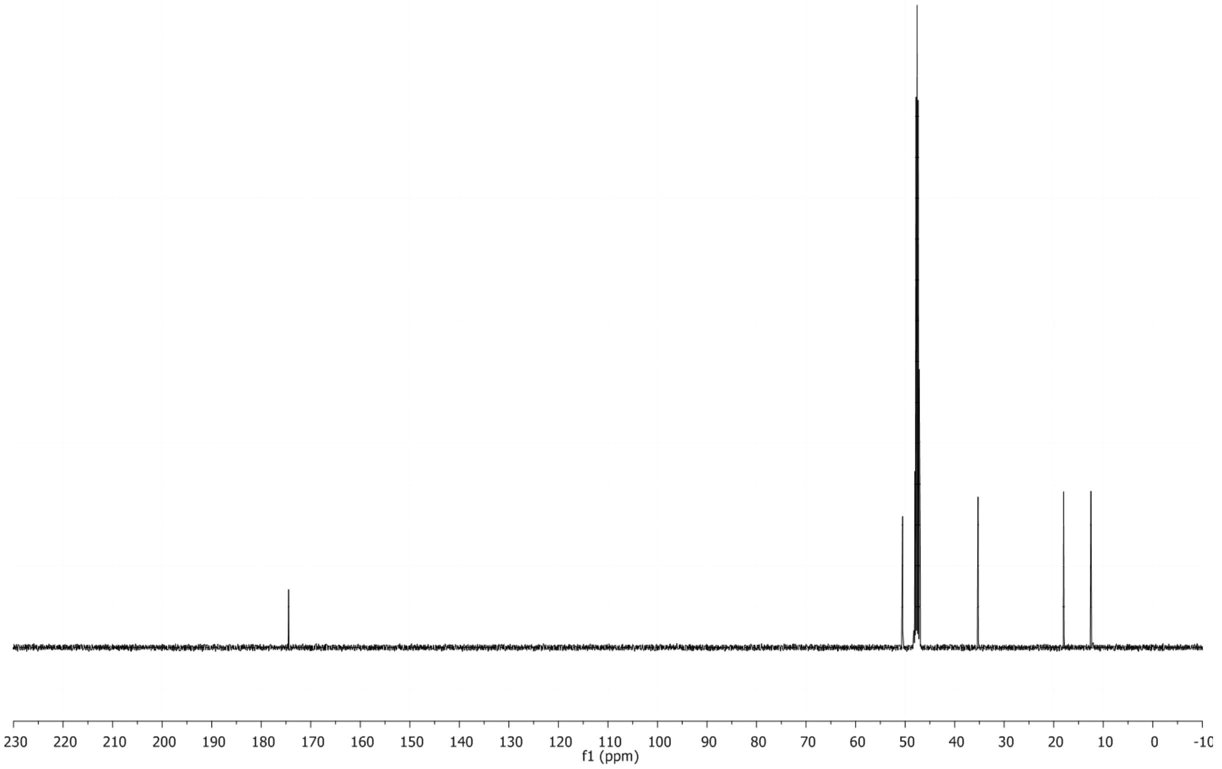


^{1}**H-NMR** (400 MHz, MeOD)-**44**

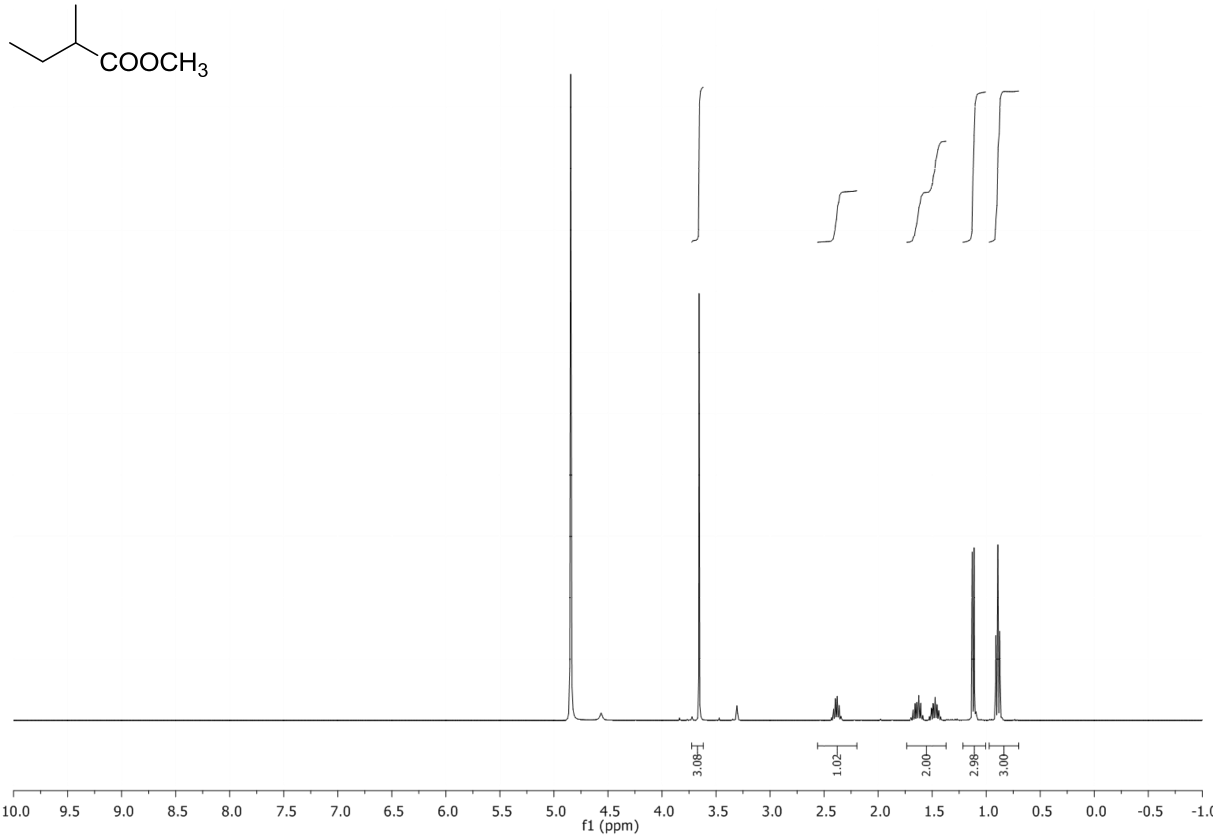




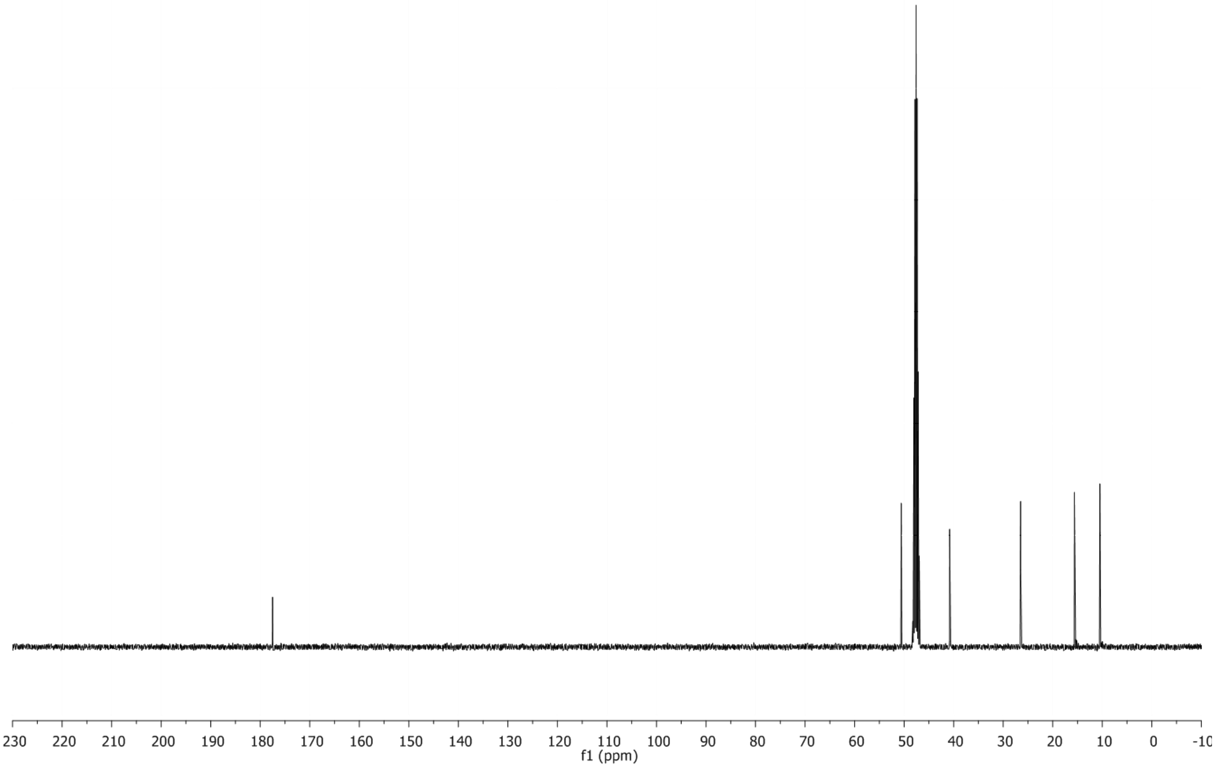
^{13}**C-NMR** (101 MHz, MeOD)



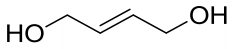
^{1}**H-NMR** (400 MHz, MeOD)-**46**

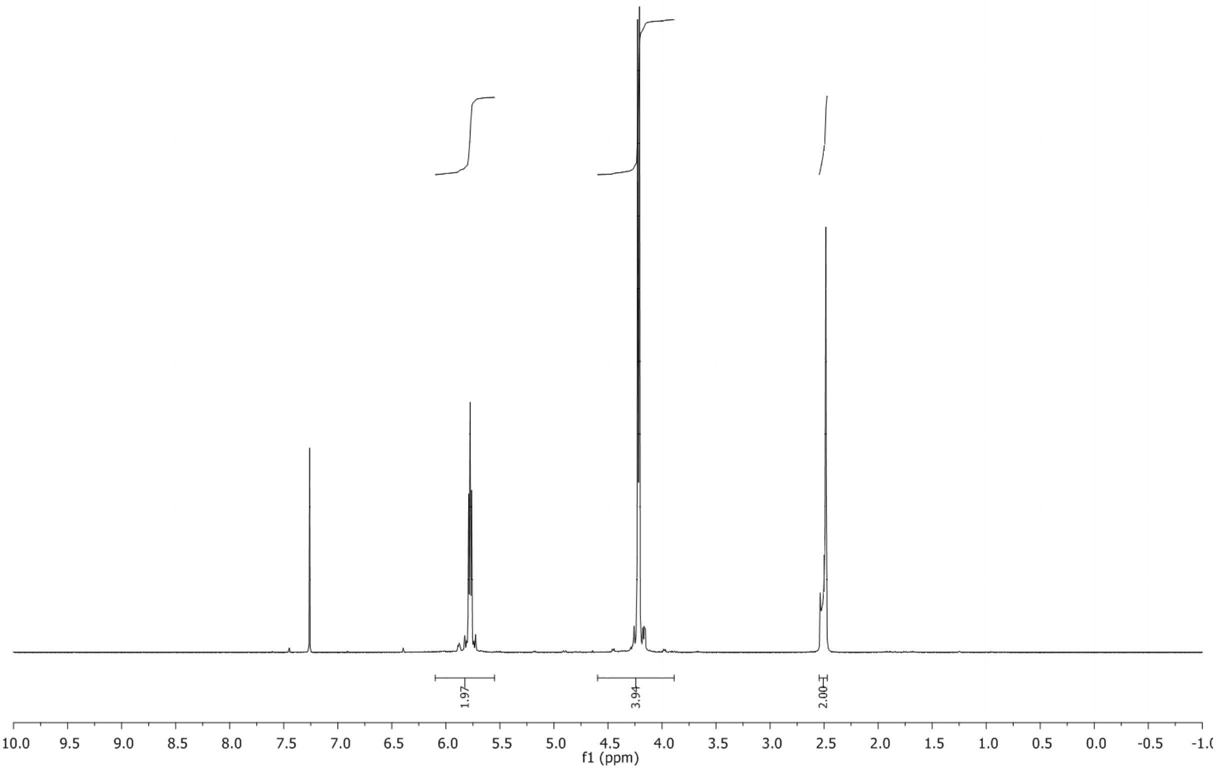


^{13}**C-NMR** (101 MHz, MeOD)

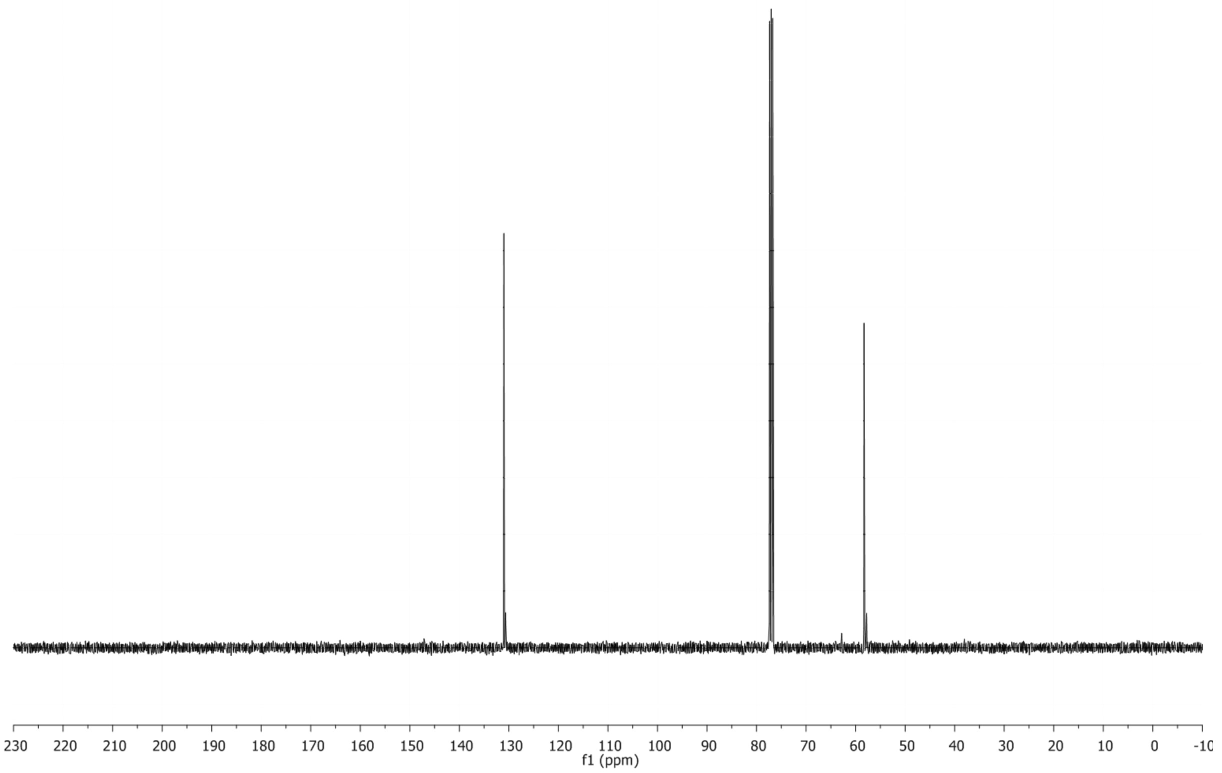


^{1}**H-NMR** (300 MHz, CDCl$_3$)-**48**

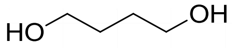


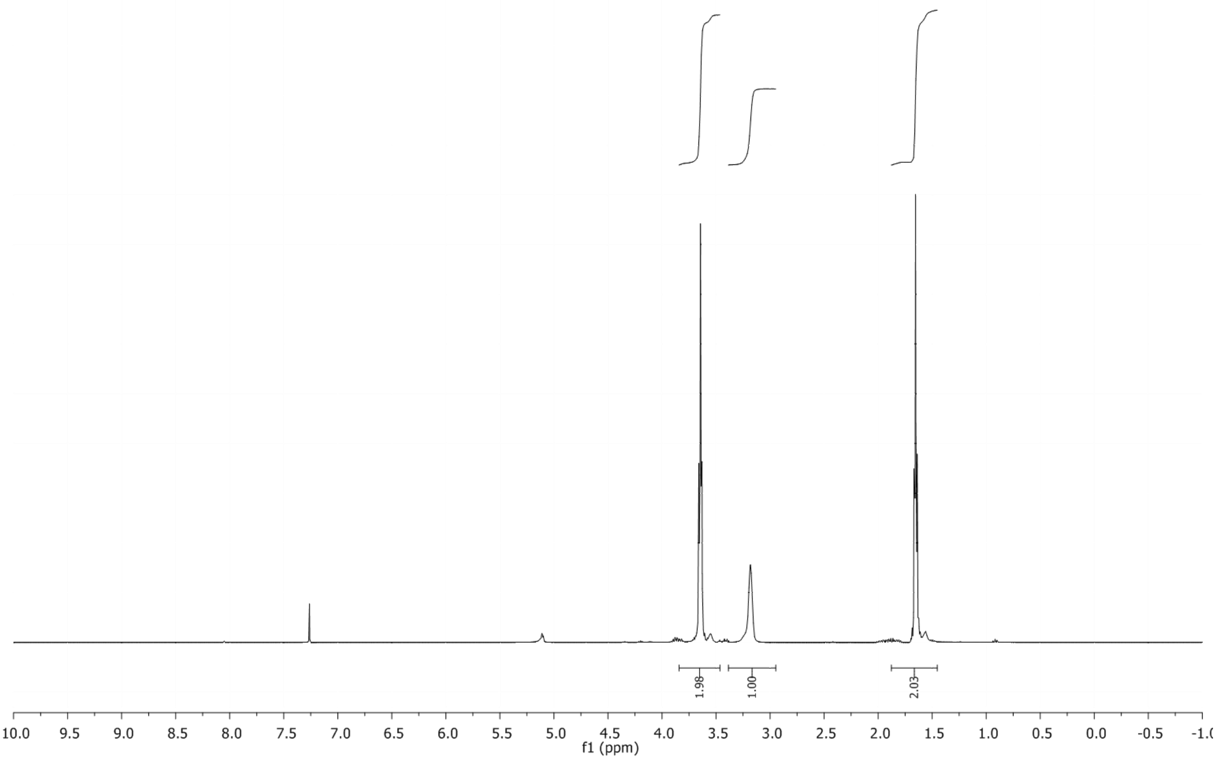


^{13}**C-NMR** (101 MHz, CDCl$_3$)

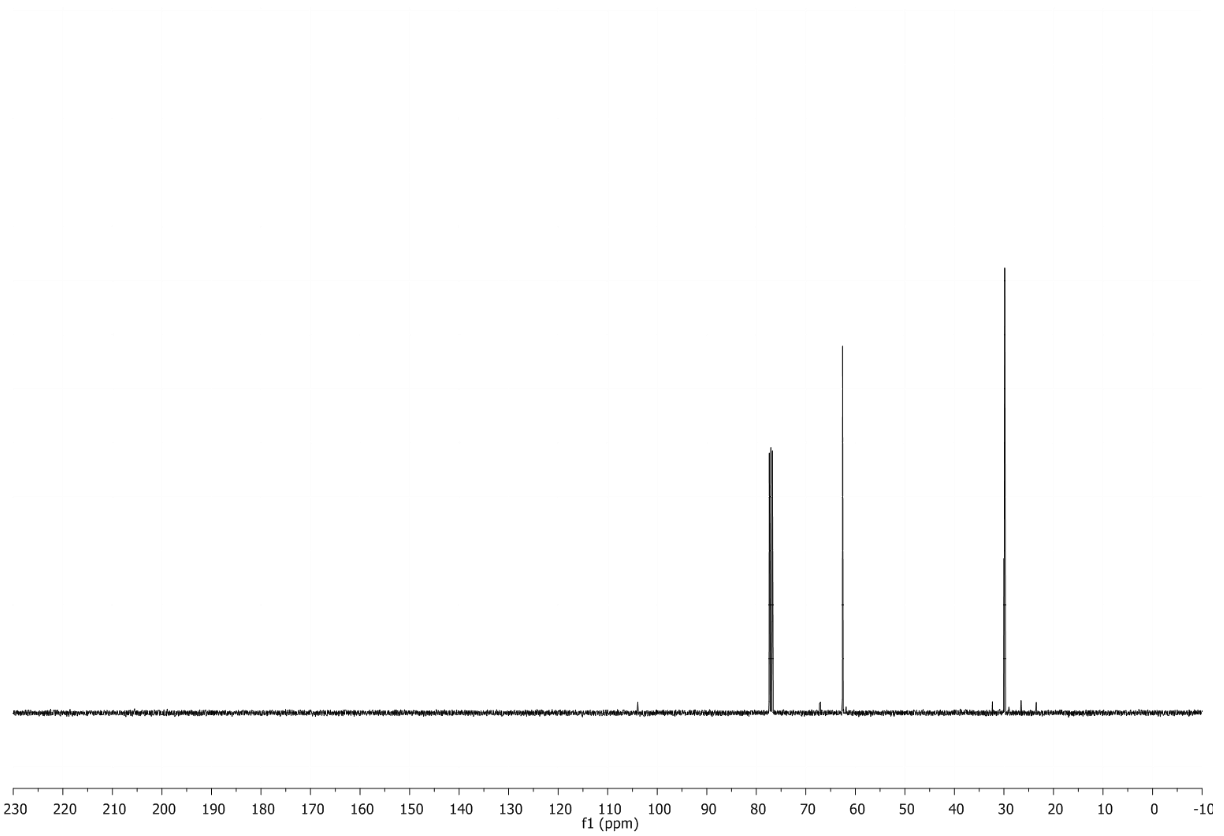


^{1}**H-NMR** (400 MHz, $CDCl_3$)-**49**

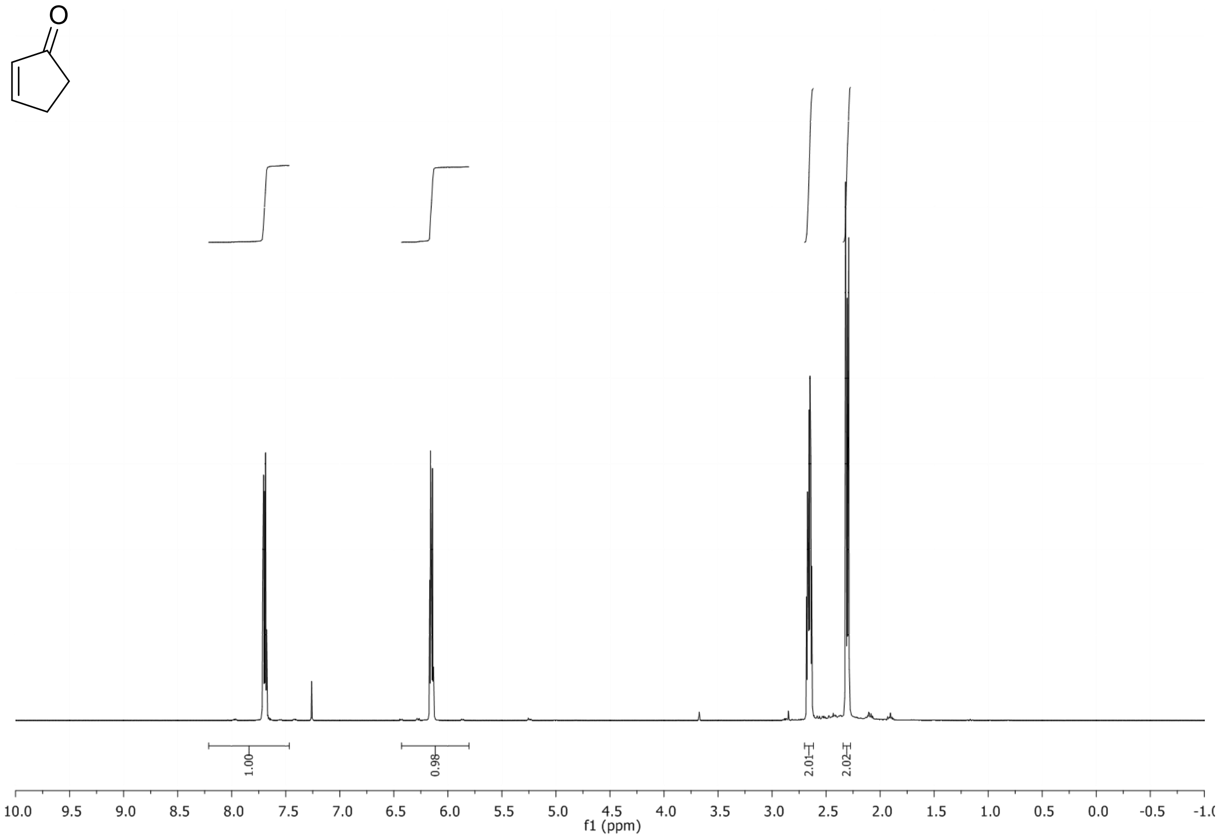




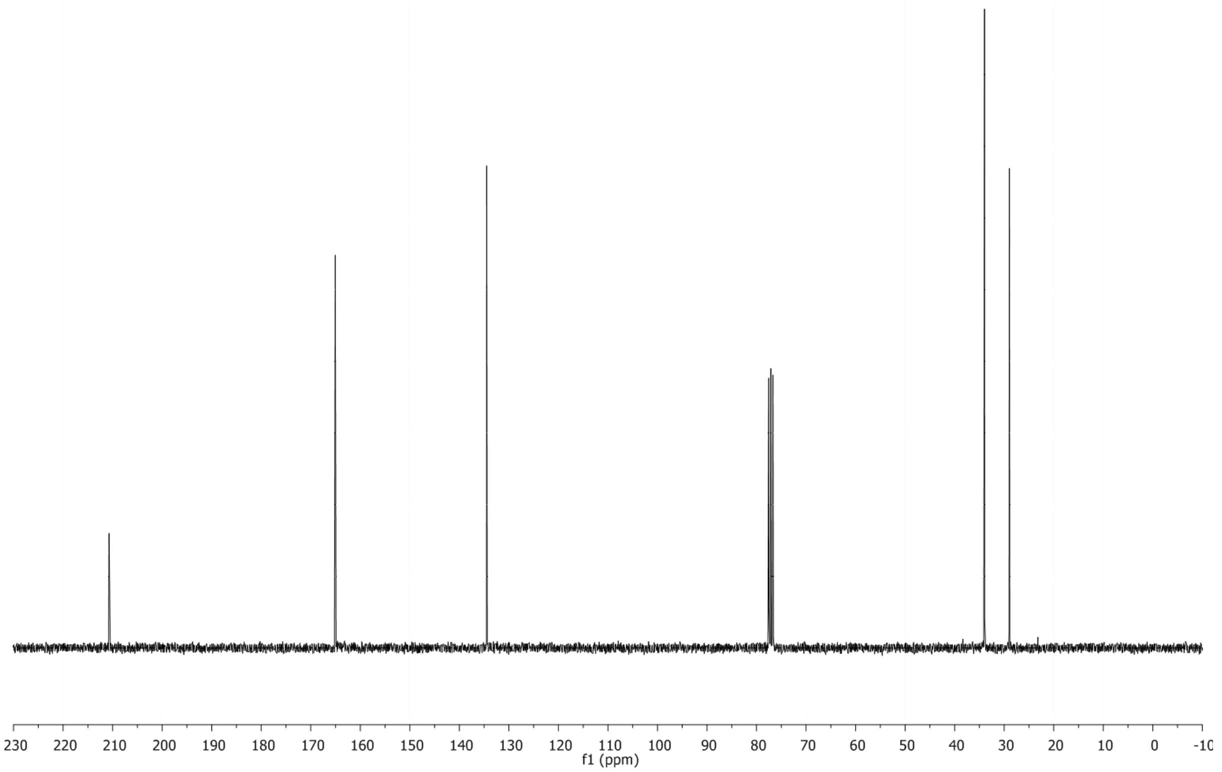
^{13}**C-NMR** (101 MHz, $CDCl_3$)



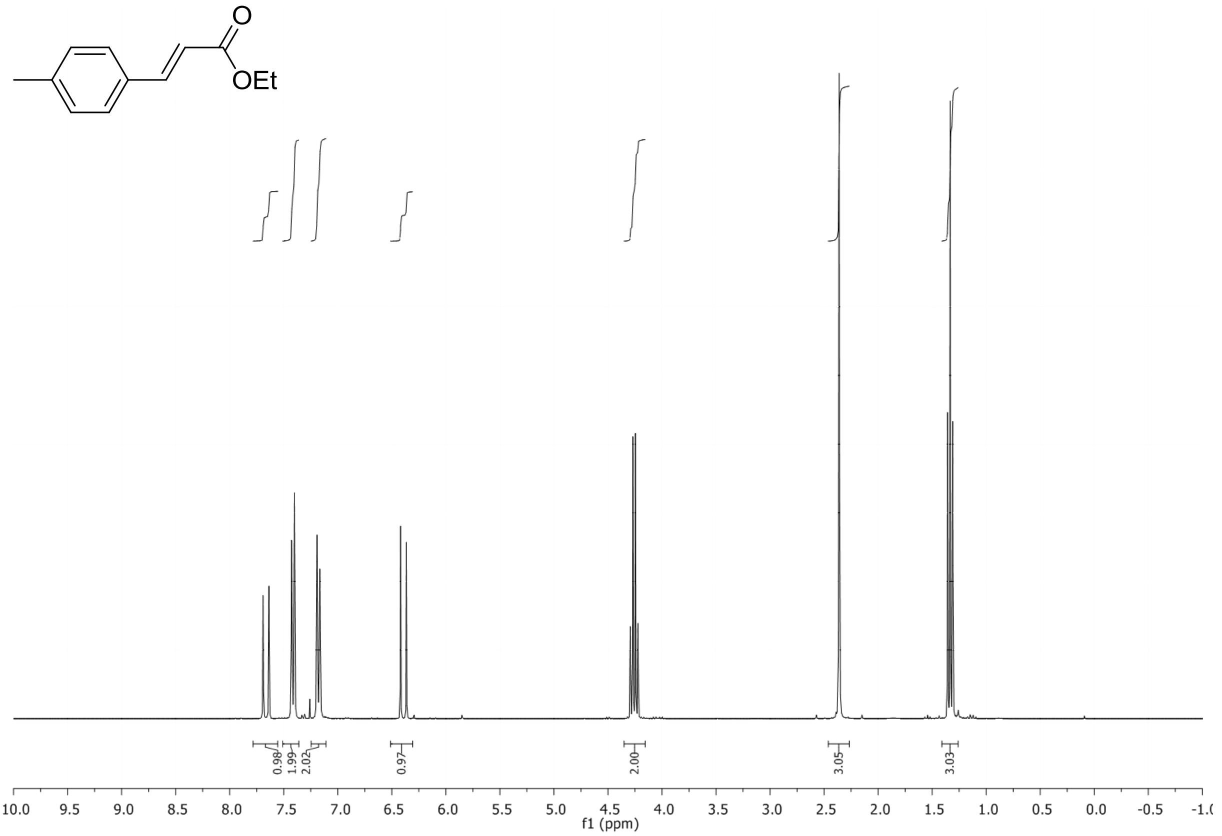
^{1}**H-NMR** (300 MHz, $CDCl_3$)-**34**



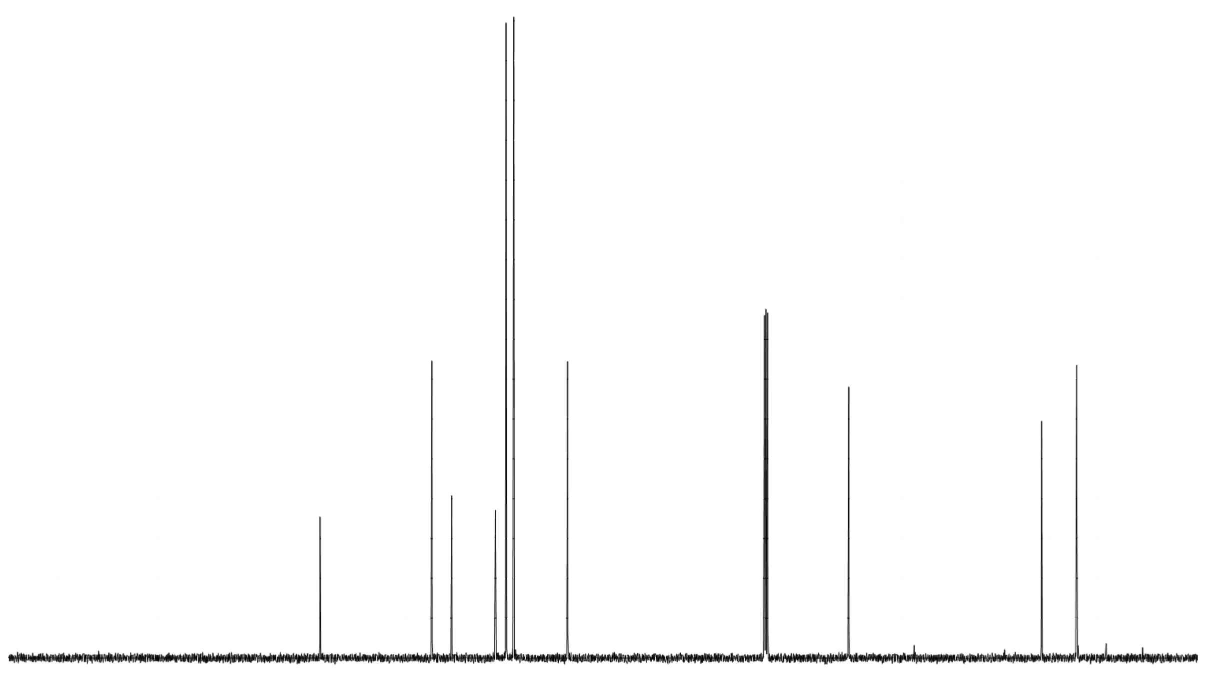
^{13}**C-NMR** (101 MHz, $CDCl_3$)



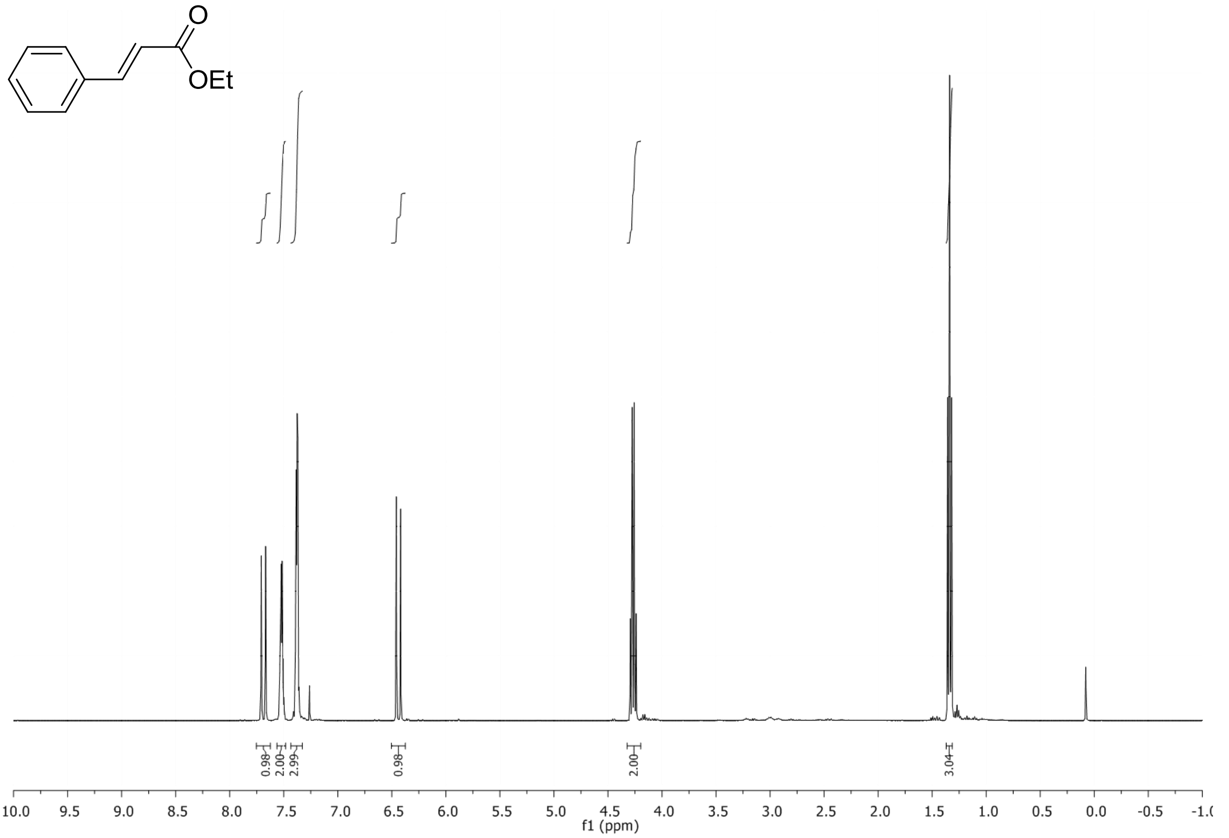
^{1}**H-NMR** (300 MHz, $CDCl_3$)-**53a**



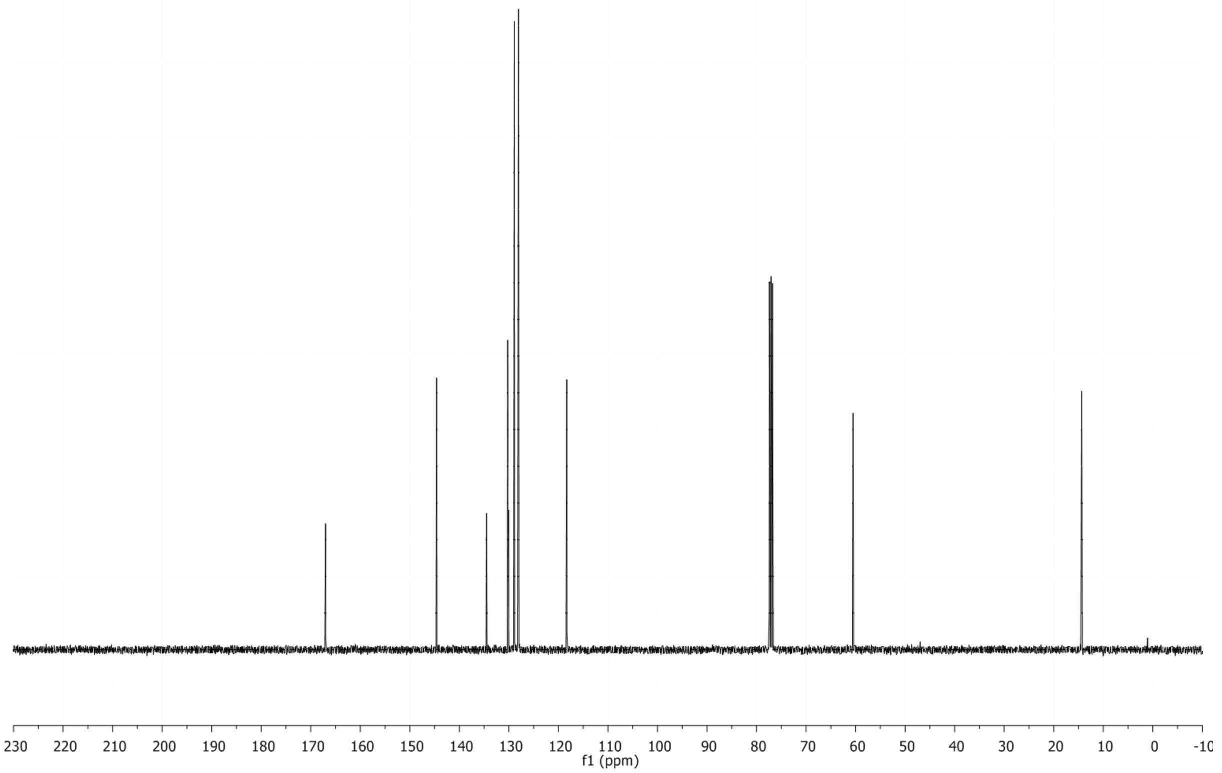
^{13}**C-NMR** (101 MHz, $CDCl_3$)



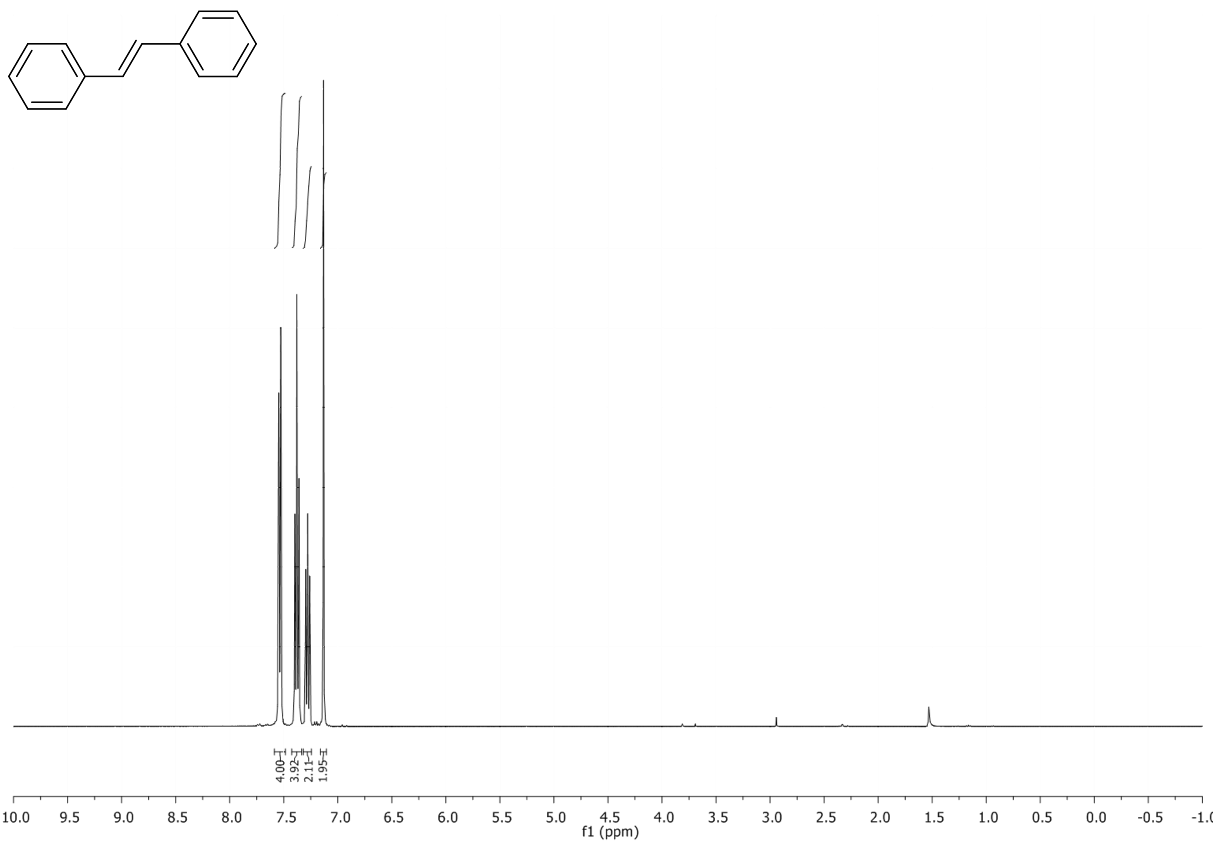
^{1}**H-NMR** (400 MHz, $CDCl_3$)-**53c**



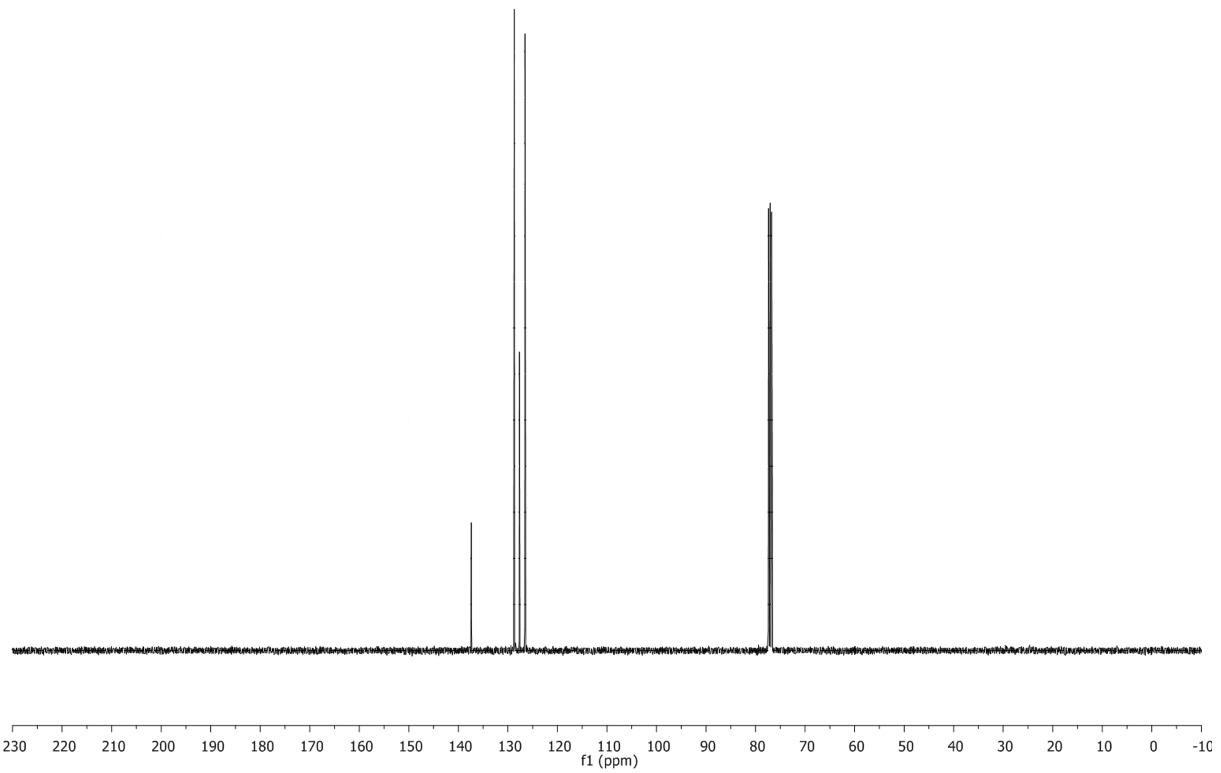
^{13}**C-NMR** (101 MHz, $CDCl_3$)



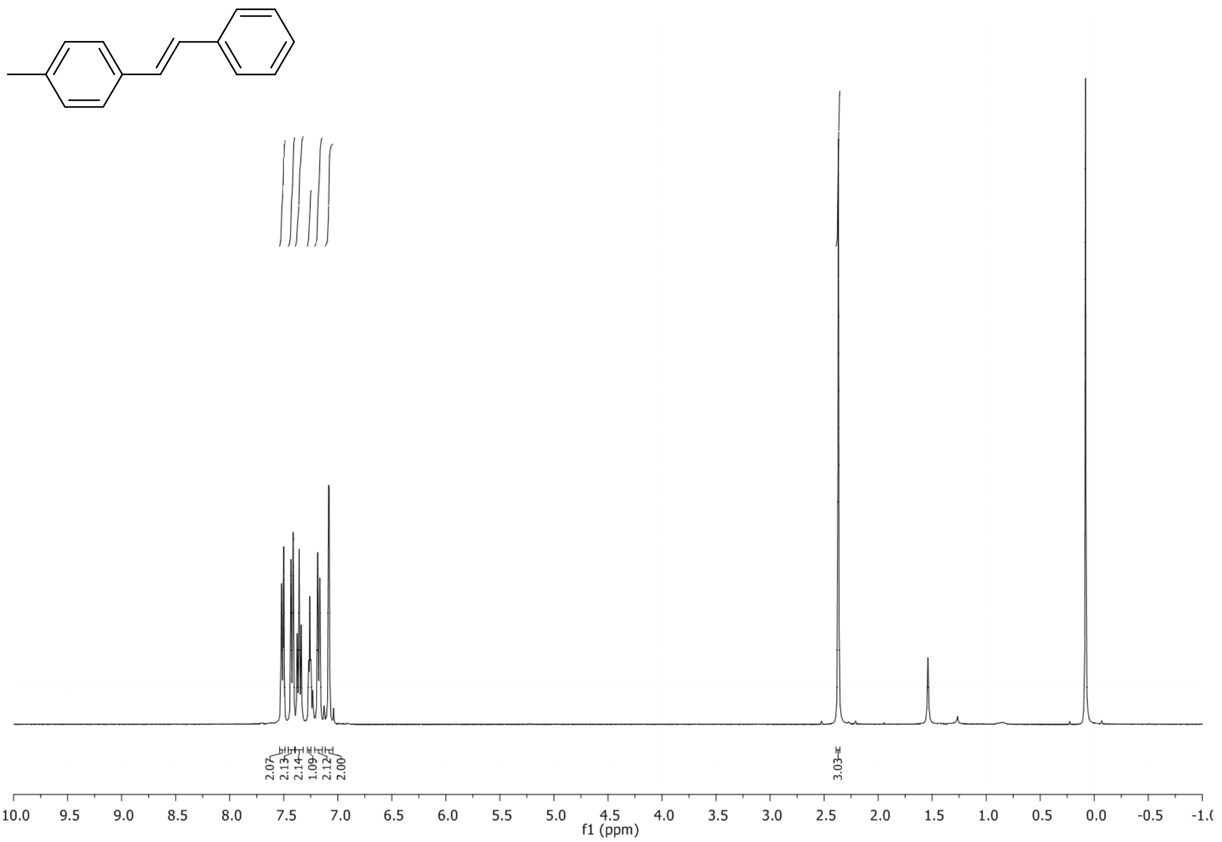
^{1}**H-NMR** (400 MHz, CDCl$_3$)-**53d**



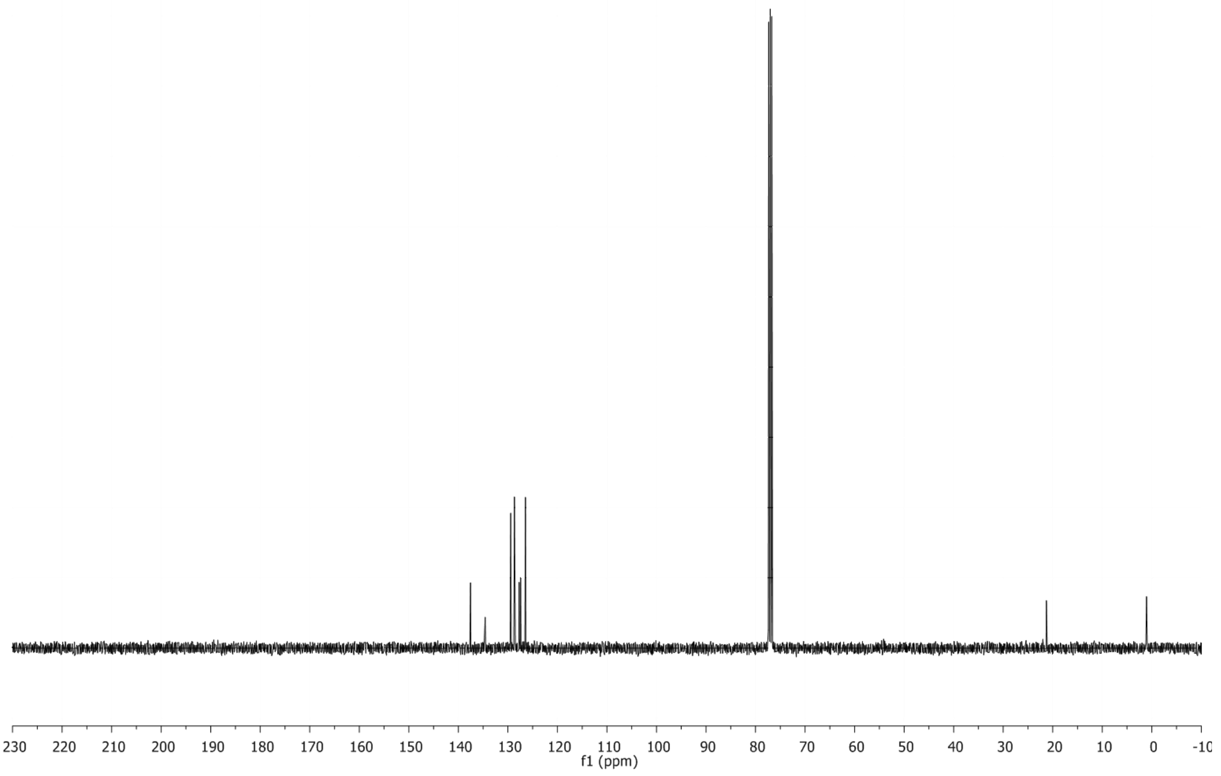
^{13}**C-NMR** (101 MHz, CDCl$_3$)



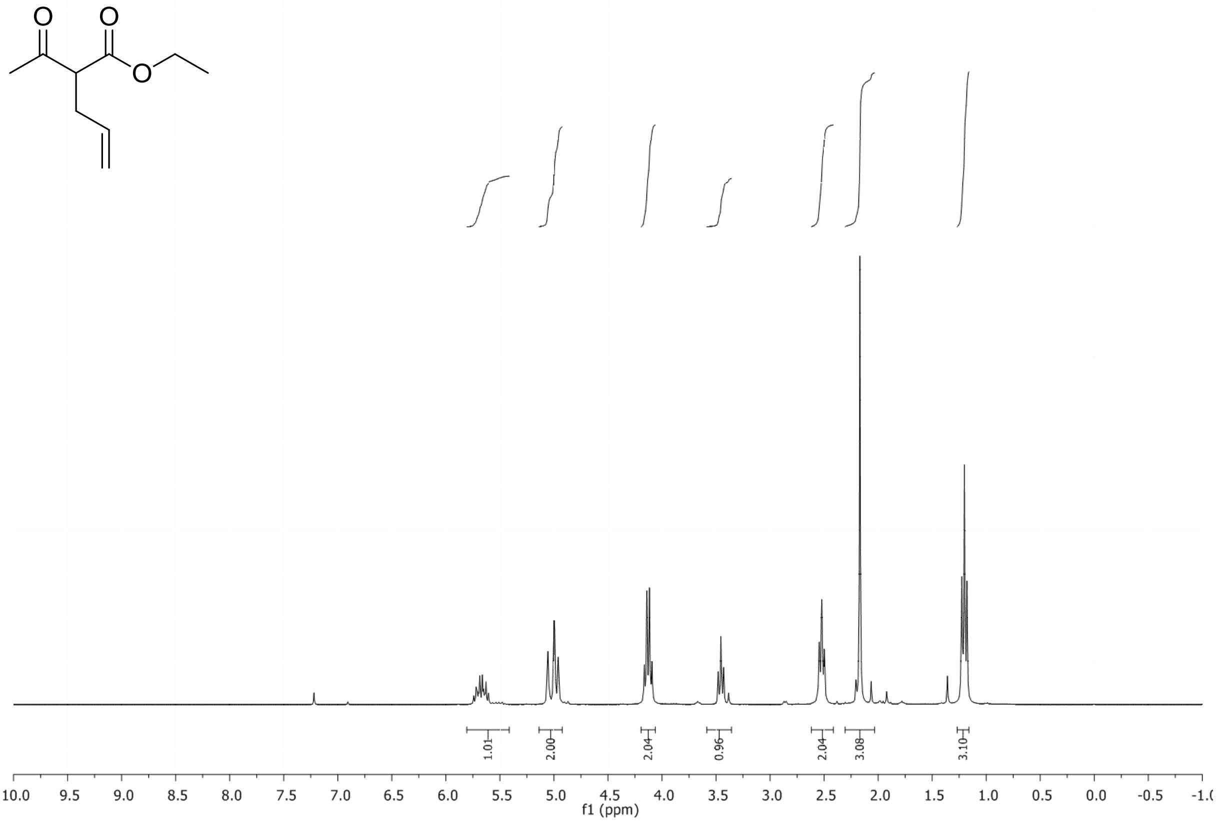
^{1}**H-NMR** (400 MHz, $CDCl_3$)-**53b**



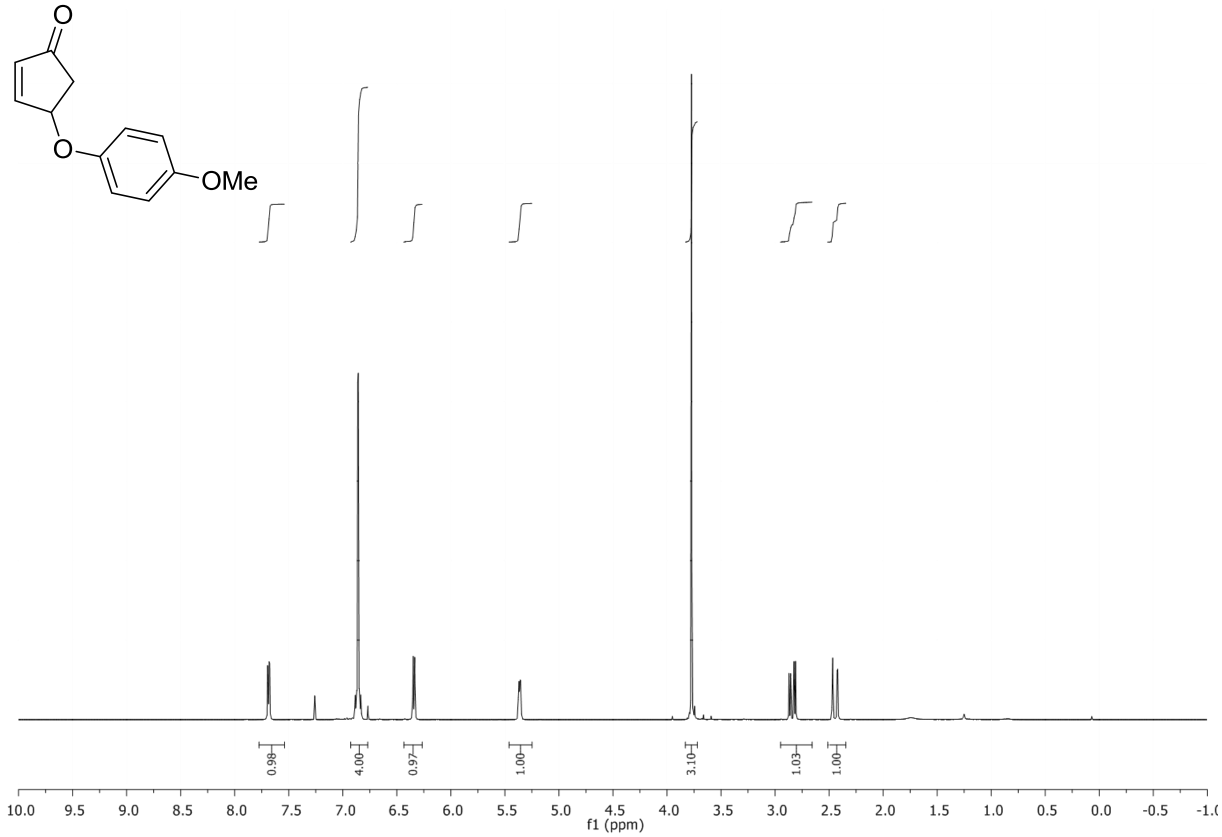
^{13}**C-NMR** (101 MHz, $CDCl_3$)



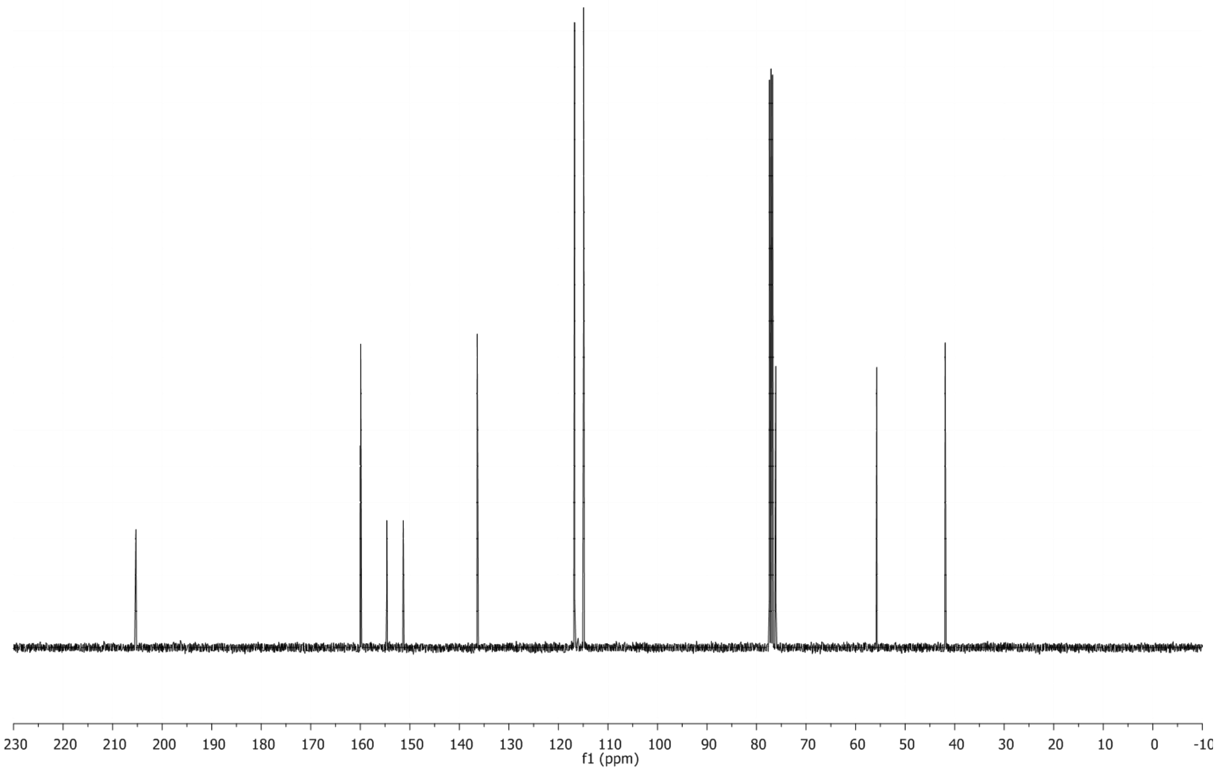
^{1}H-NMR (300 MHz, CDCl$_3$)-**59**



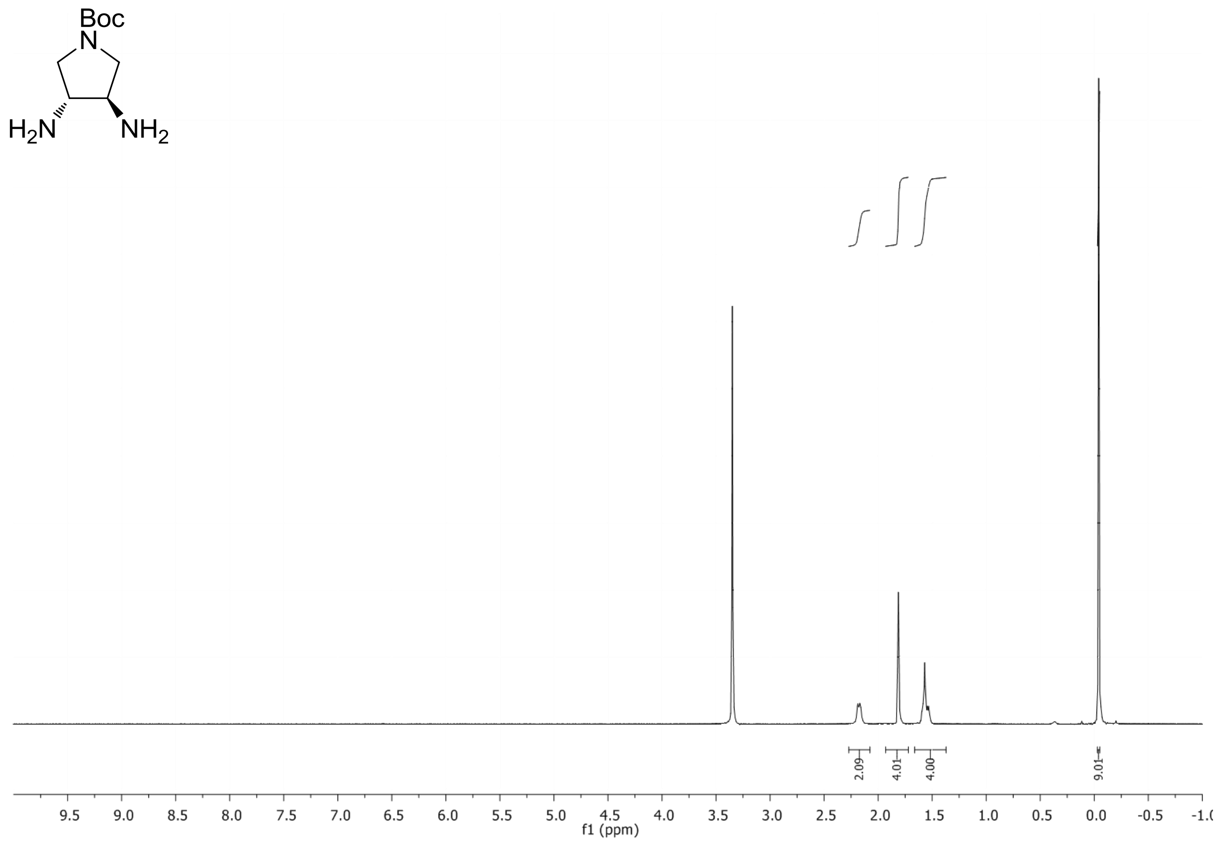
^{1}**H-NMR** (400 MHz, CDCl$_3$)-**56b**



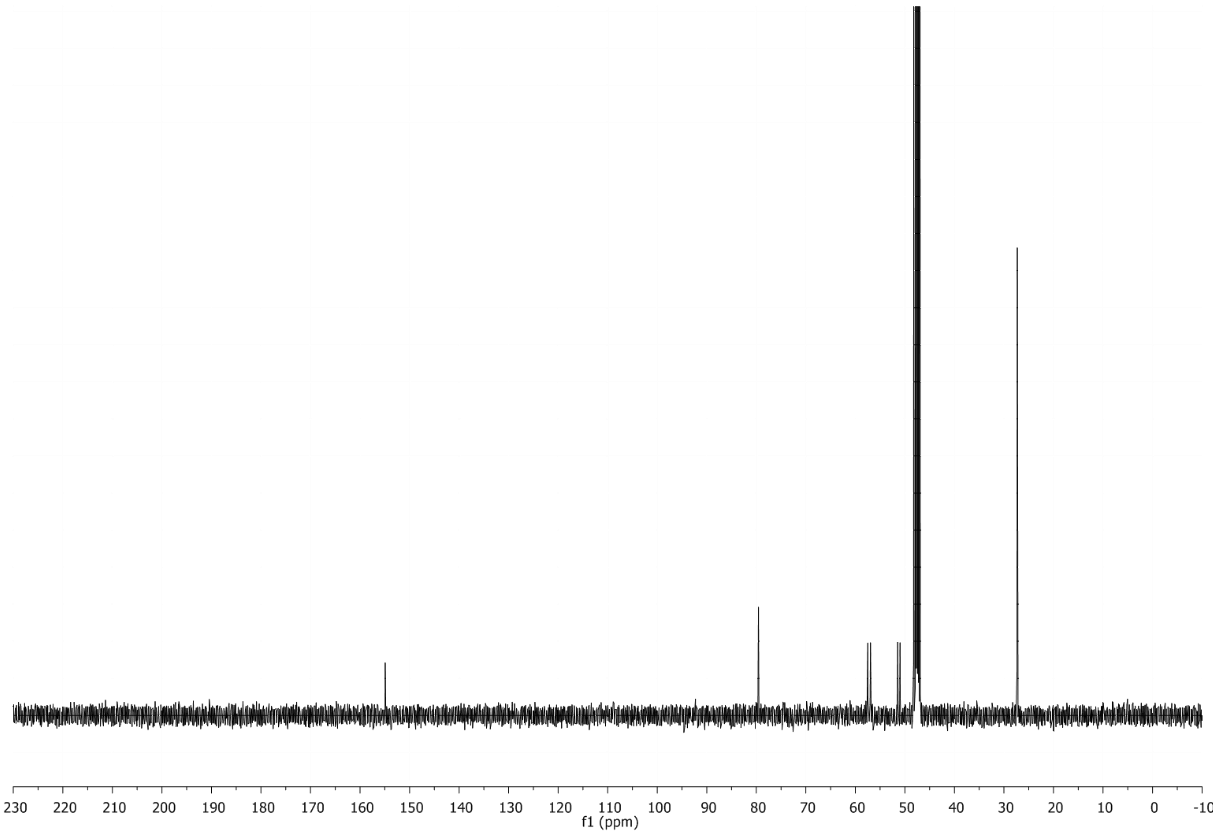
^{13}**C-NMR** (101 MHz, CDCl$_3$)



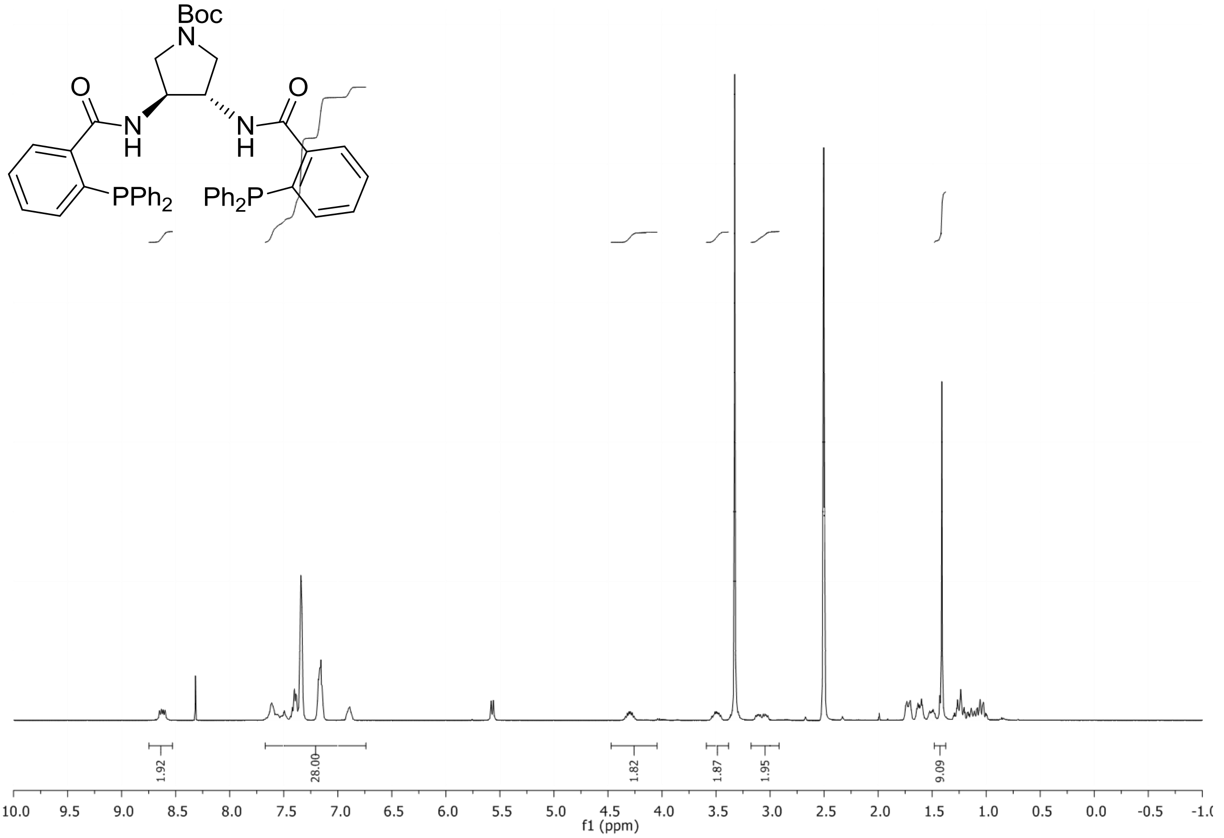
^{1}**H-NMR** (400 MHz, MeOD)-**67**



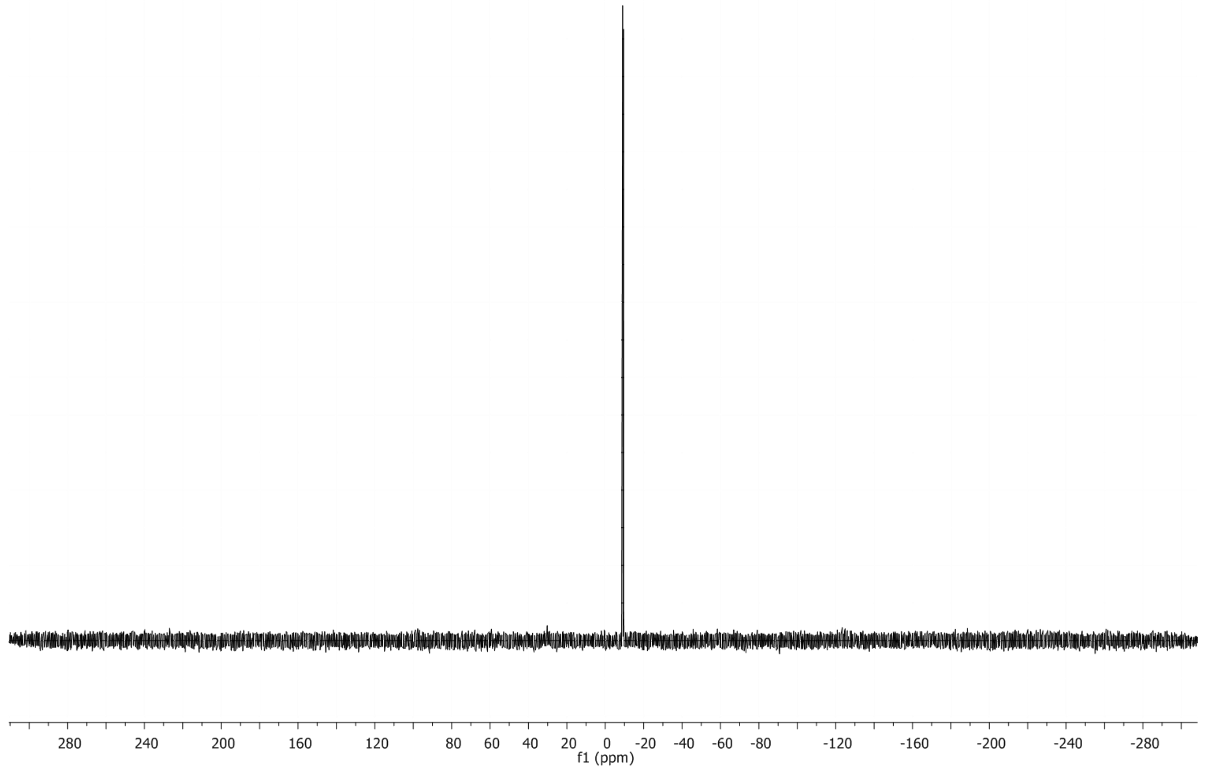
^{13}**C-NMR** (101 MHz, MeOD)



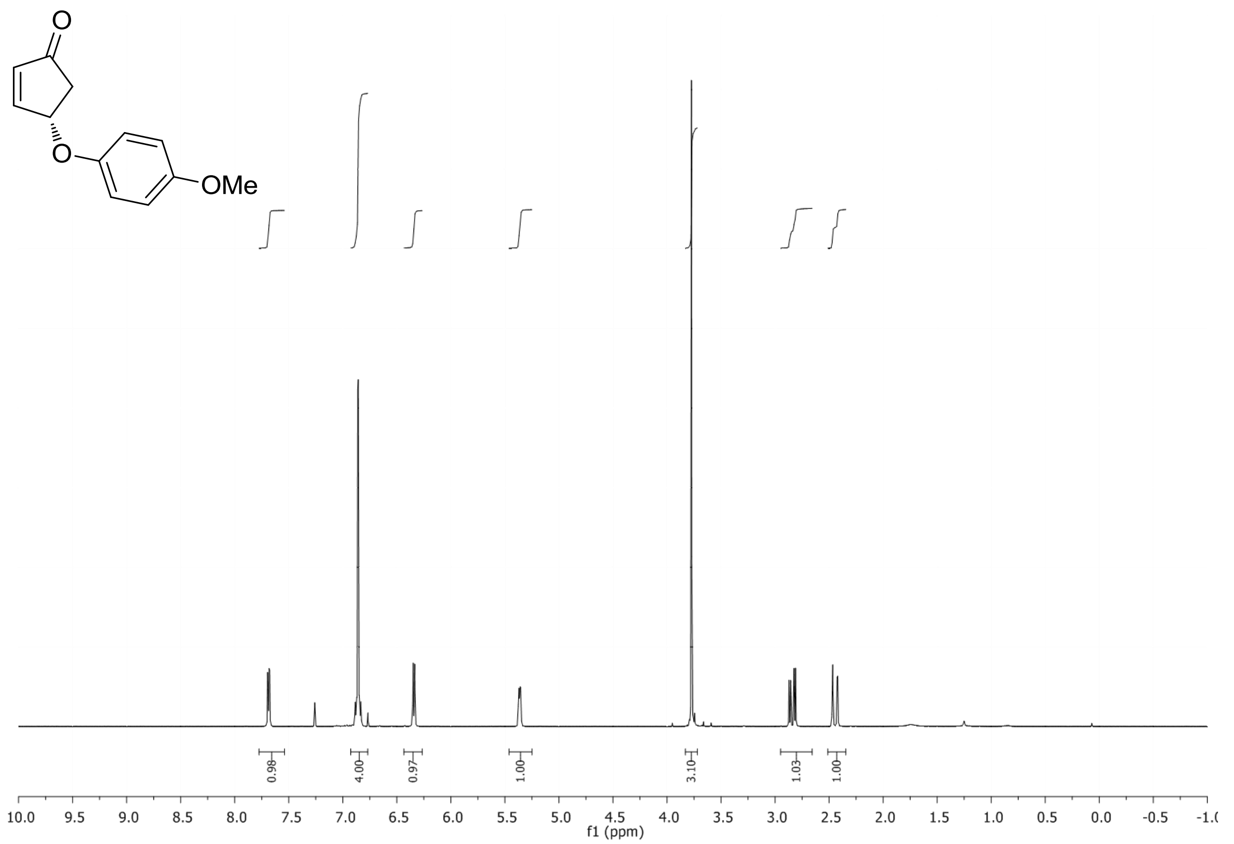
^{1}**H-NMR** (400 MHz, DMSO)-**68**



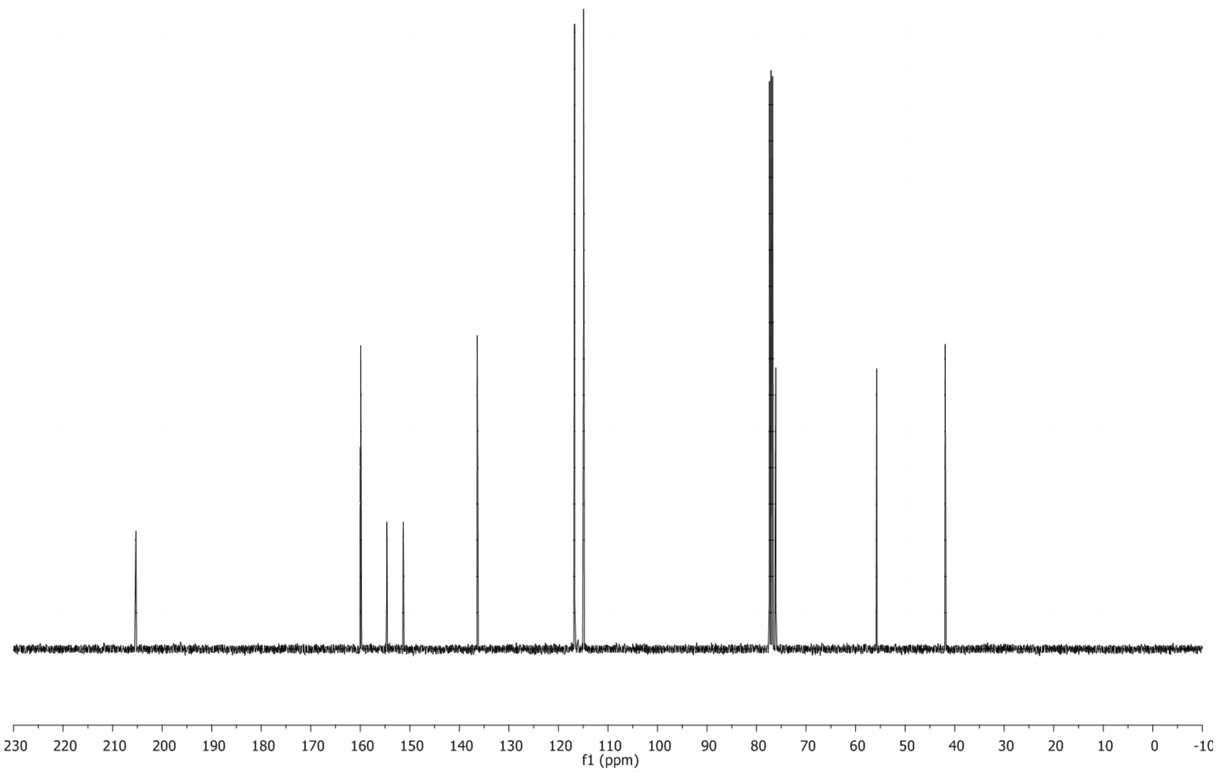
^{31}**P-NMR** (121 Hz, DMSO)



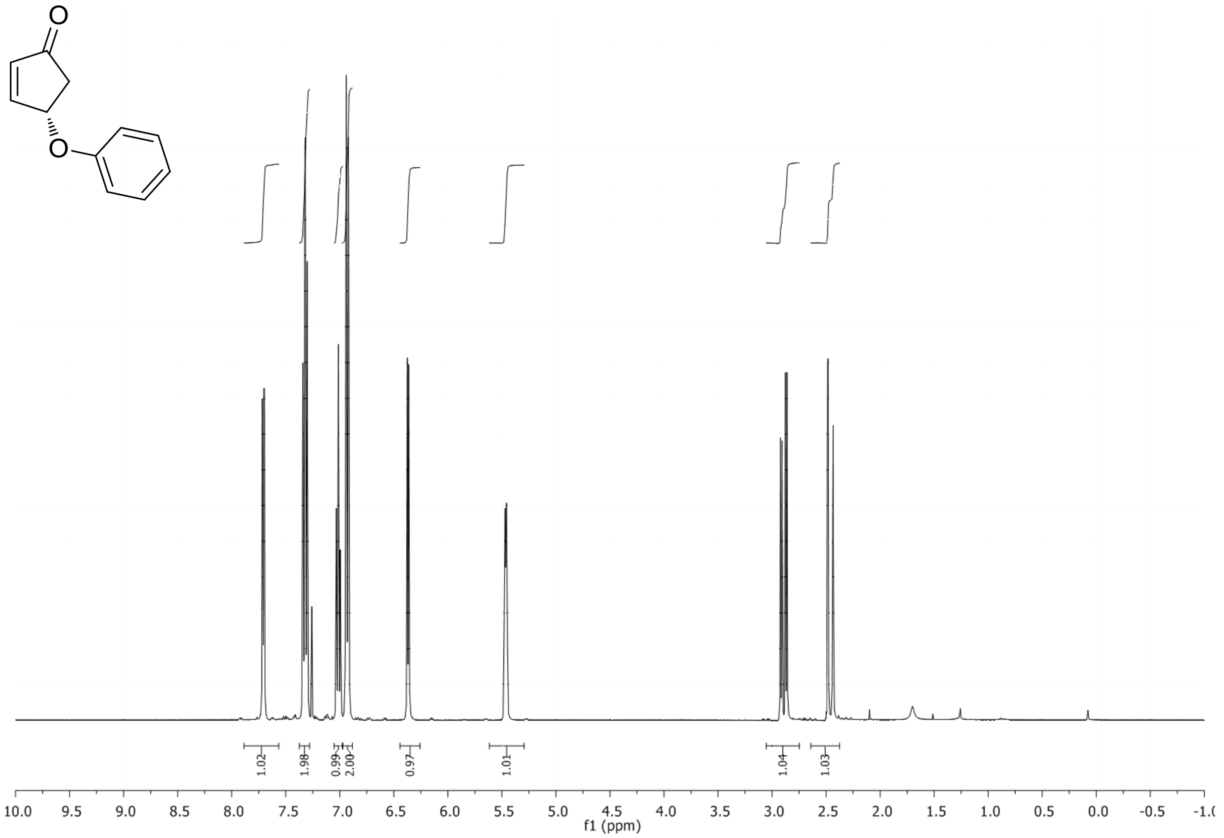
^{1}**H-NMR** (400 MHz, CDCl$_3$)-(*S*)-**56b**



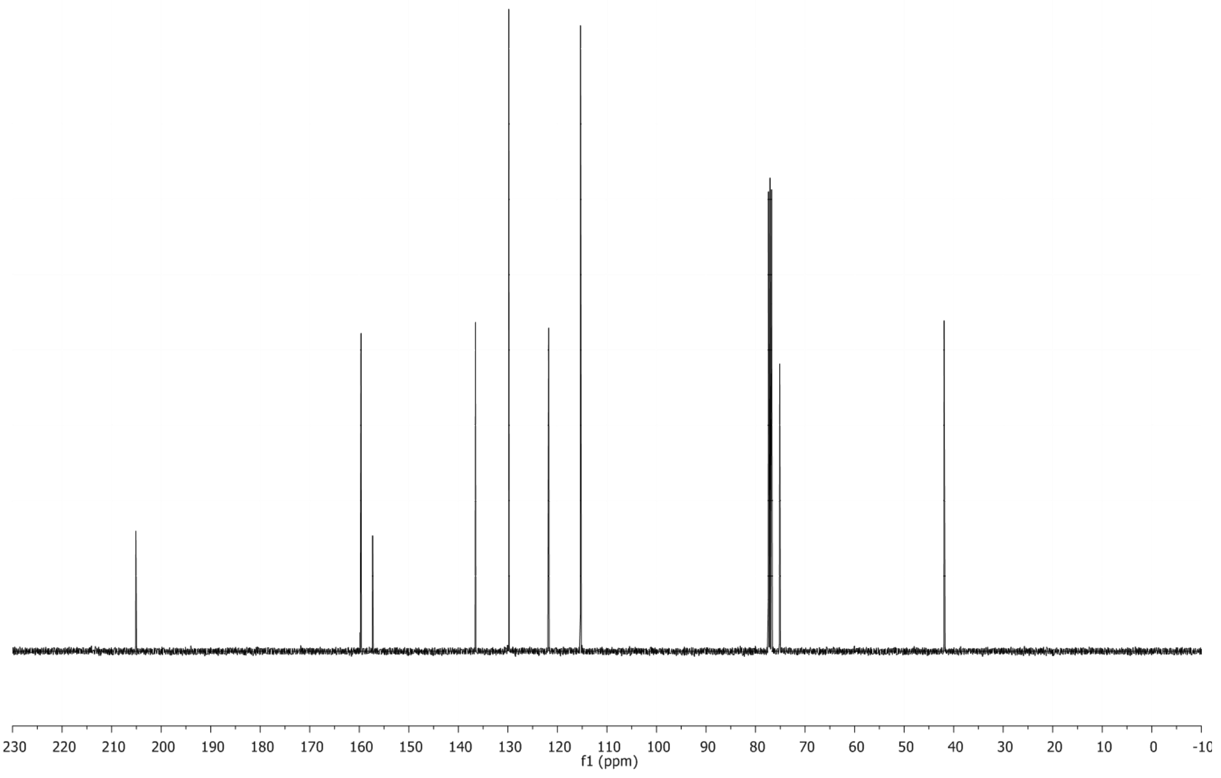
^{13}**C-NMR** (101 MHz, CDCl$_3$)



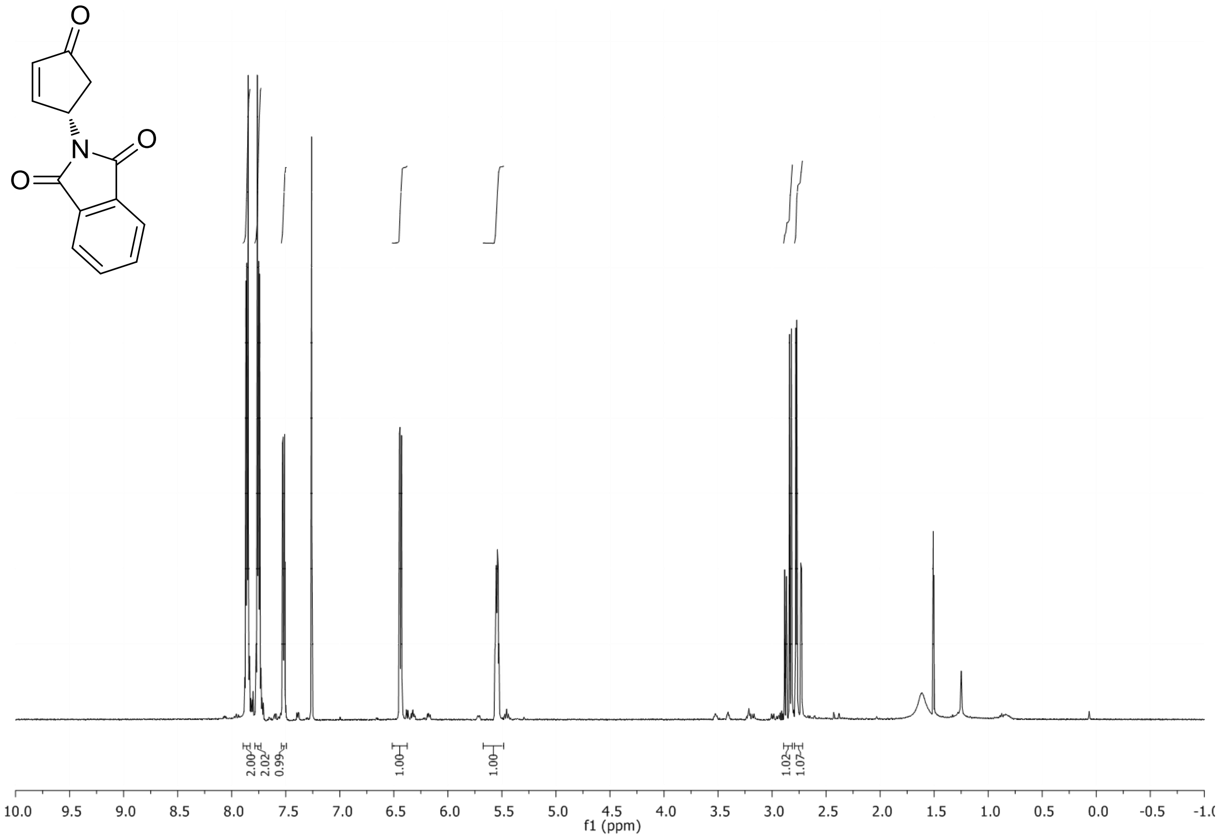
^{1}**H-NMR** (400 MHz, $CDCl_3$)-(*S*)-**56a**



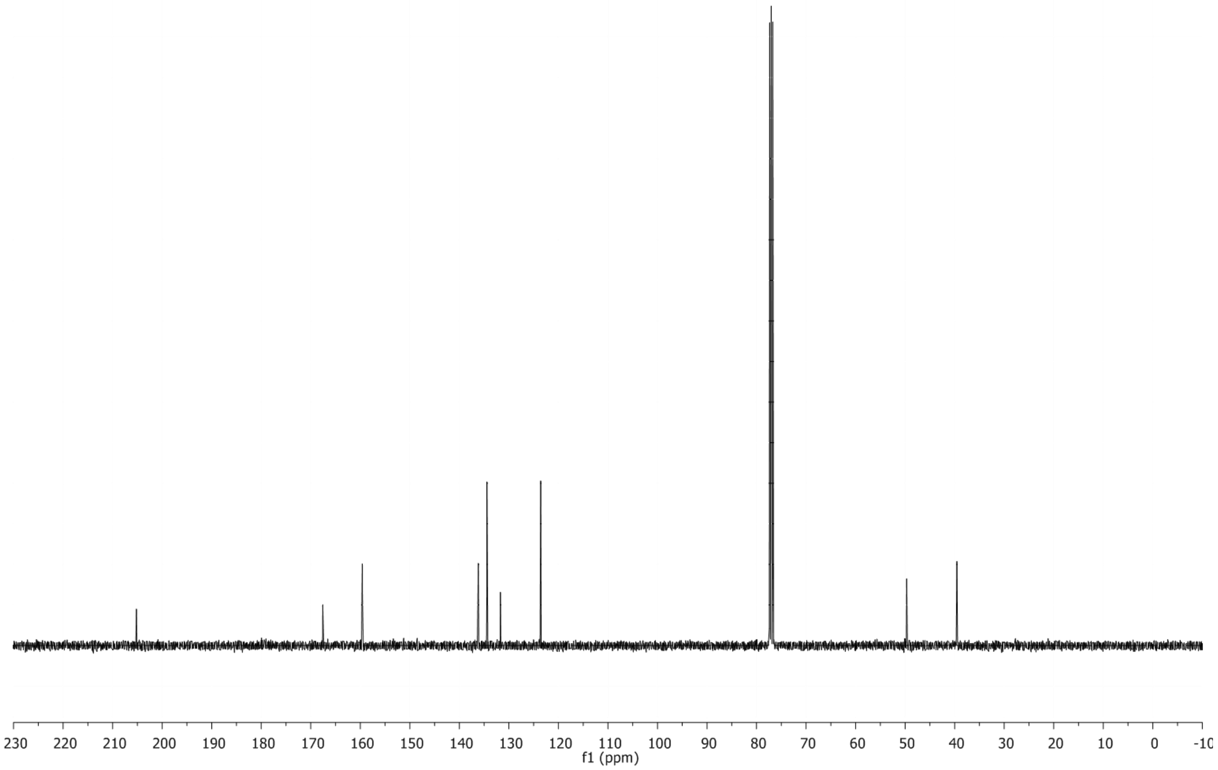
^{13}**C-NMR** (101 MHz, $CDCl_3$)



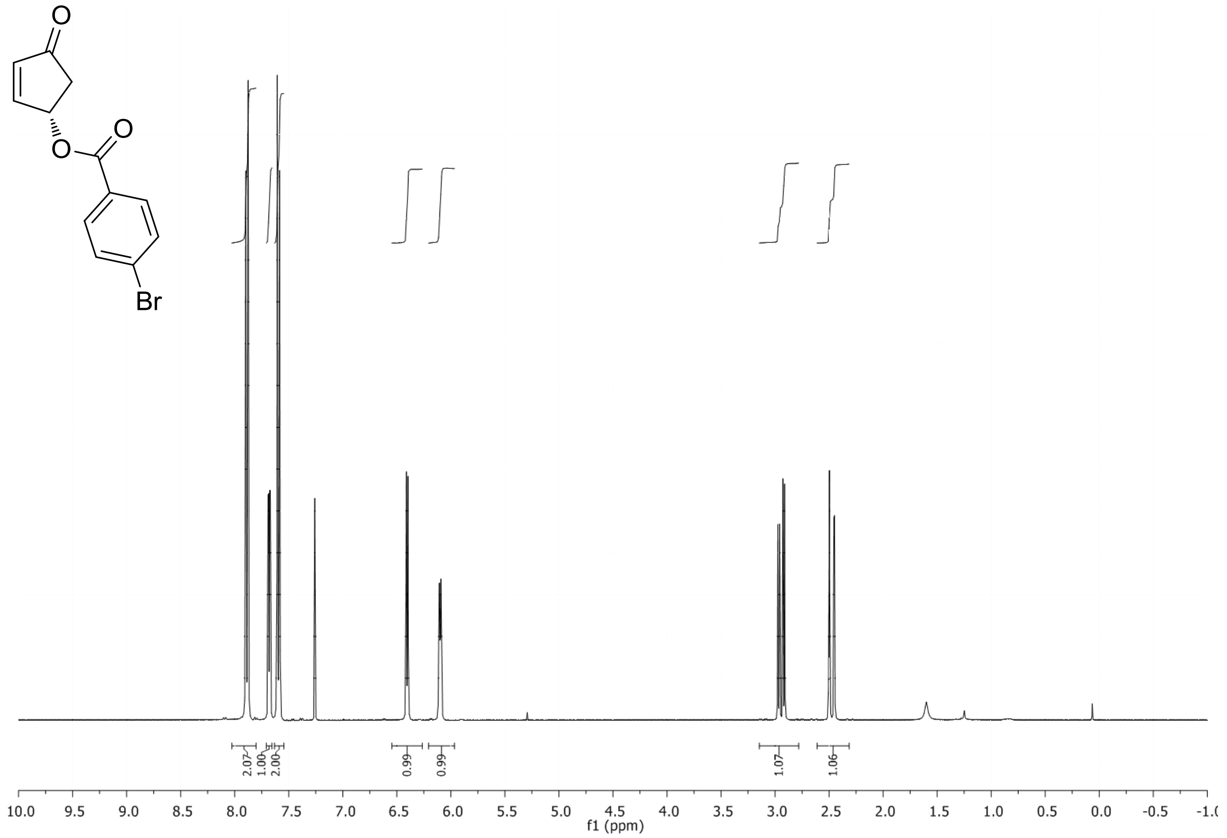
^{1}H-NMR (400 MHz, CDCl$_3$)-(*S*)-**56c**



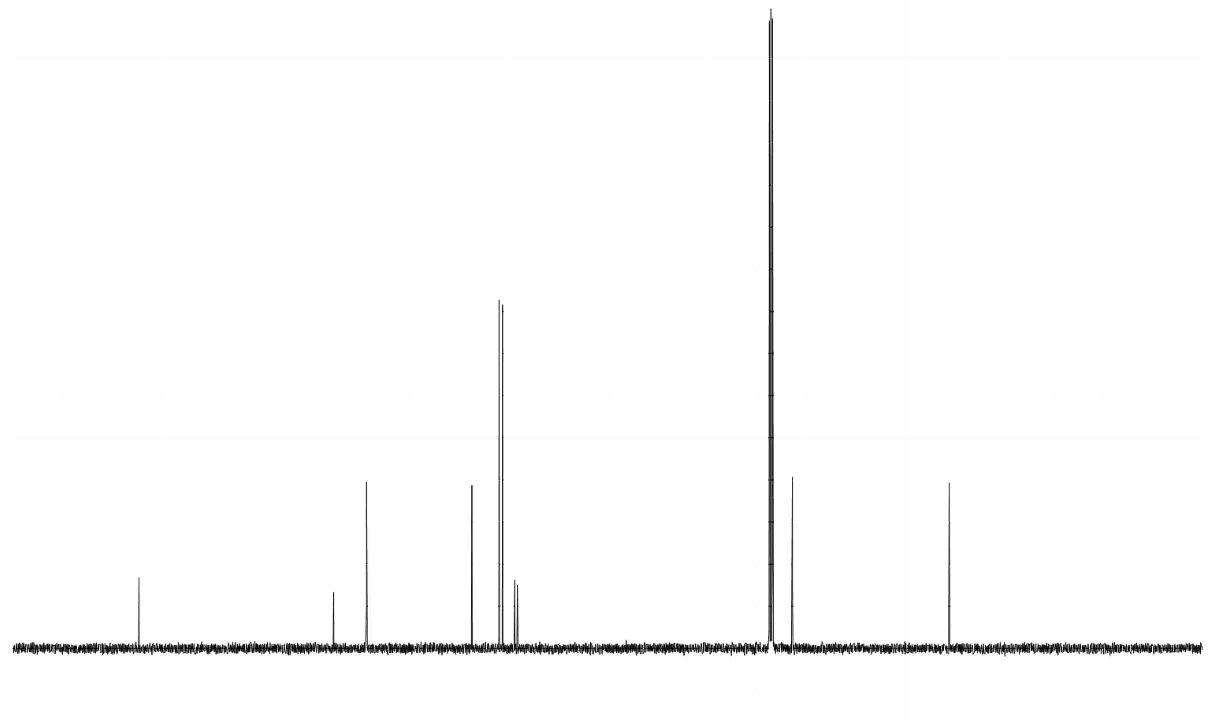
^{13}C-NMR (101 MHz, CDCl$_3$)



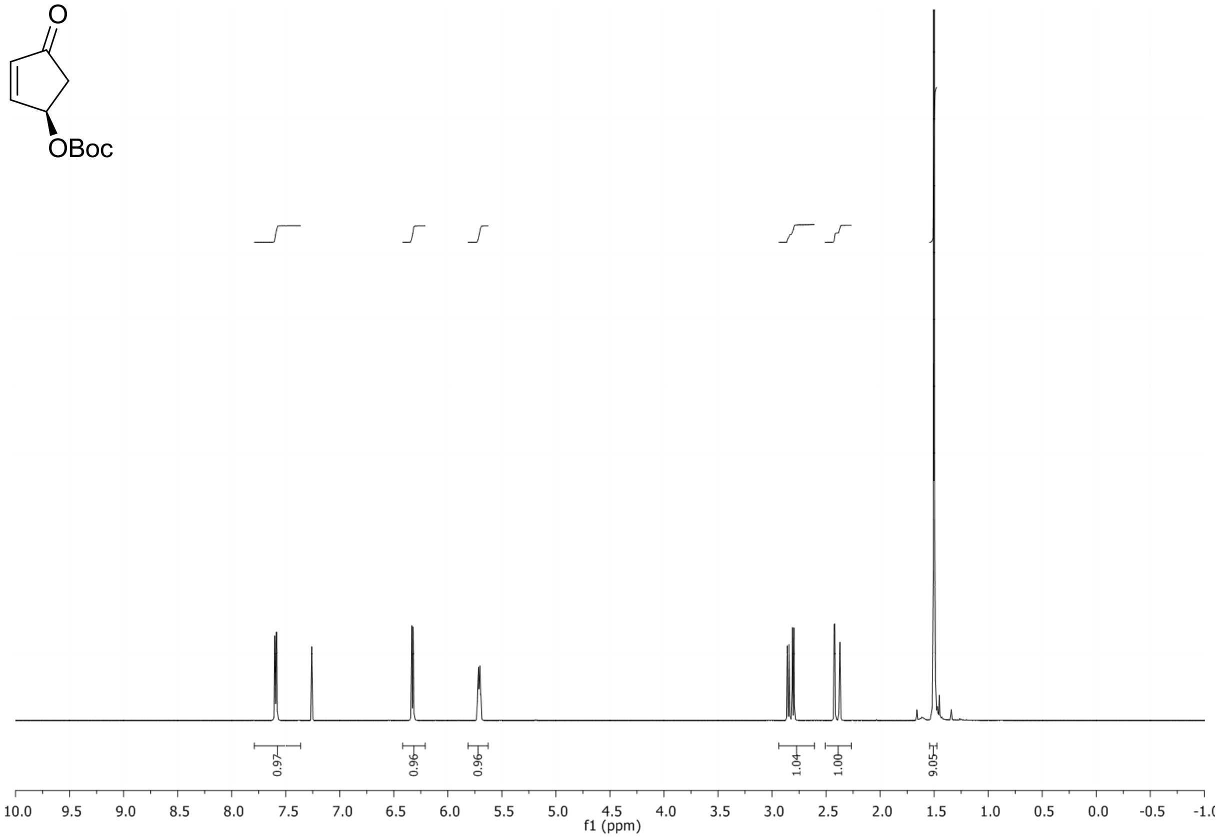
^{1}H-NMR (400 MHz, $CDCl_3$)-(*S*)-**56d**



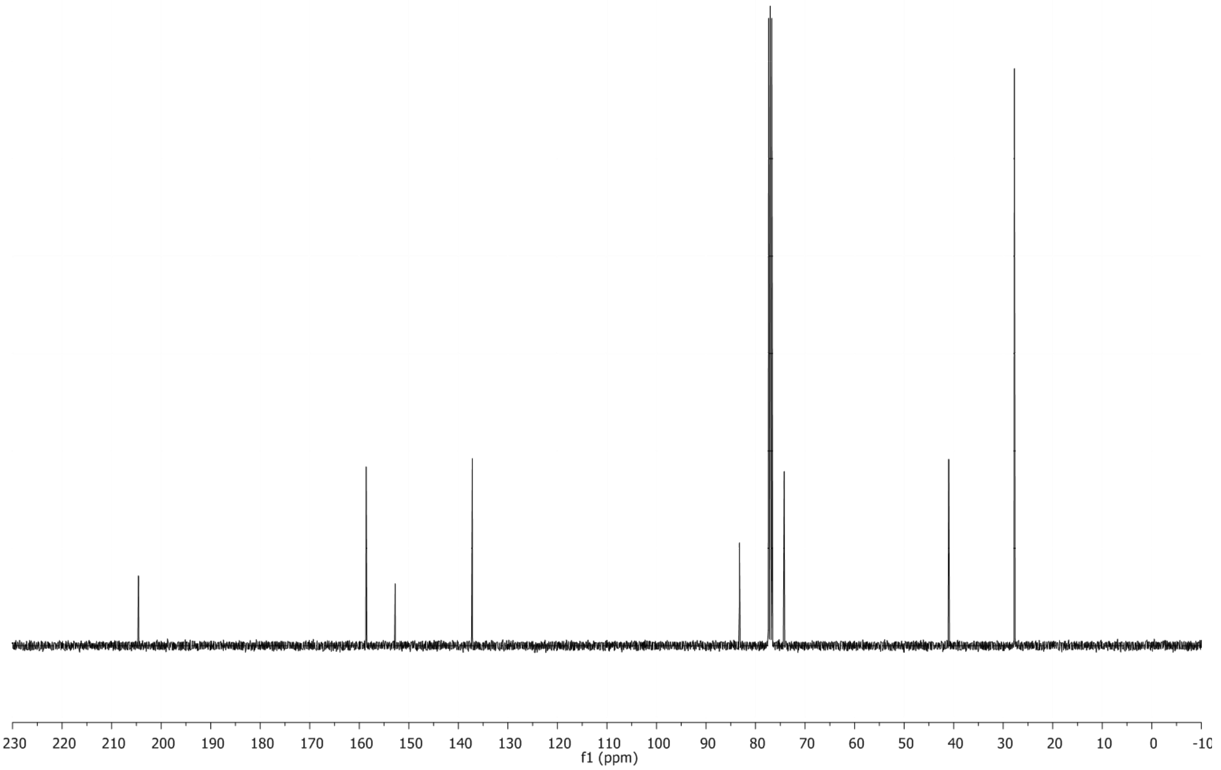
^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}**H-NMR** (400 MHz, $CDCl_3$)-(*R*)-**54a**



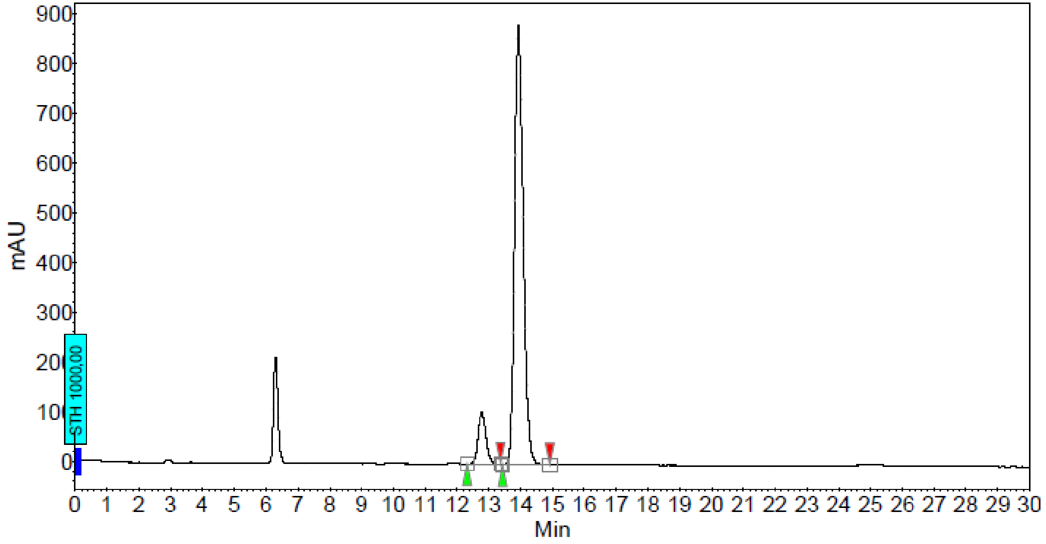
^{13}**C-NMR** (101 MHz, $CDCl_3$)



2. HPLC chromatograms

Table 10-entry 1-(*S*)-4-phenoxycyclopent-2-enone ((*S*)-56a)

BK172_2_2.DATA - PDA detector Absorbance Analog Channel 1

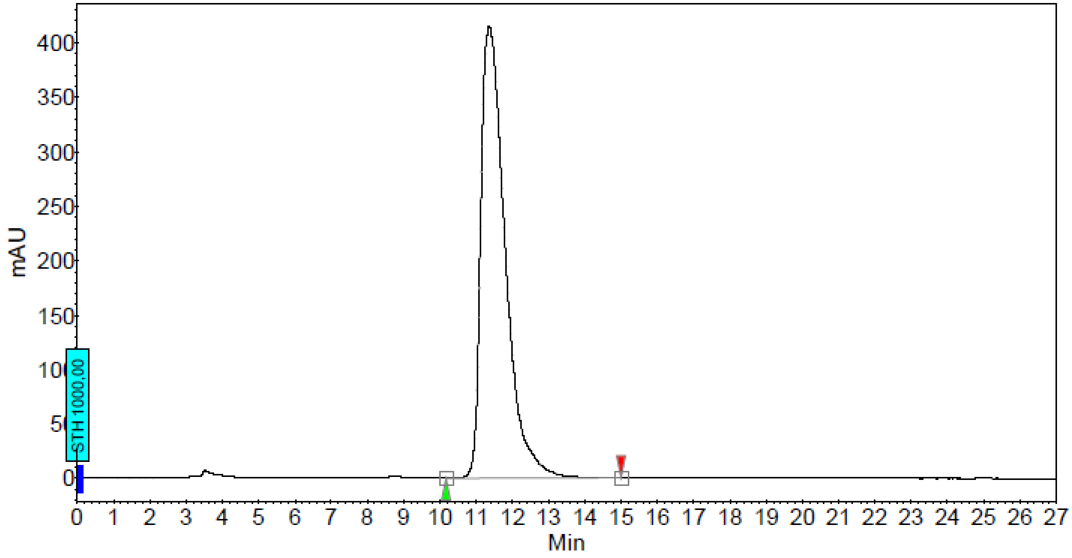


Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12,78	9,57	104,0	30,1	9,573
2	UNKNOWN	13,93	90,43	881,9	283,9	90,427
Total			100,00	985,9	314,0	100,000

Table 10-entry 1-(*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate ((*R*))-54b)

BK180-1_F1.DATA - PDA detector Absorbance Analog Channel 1

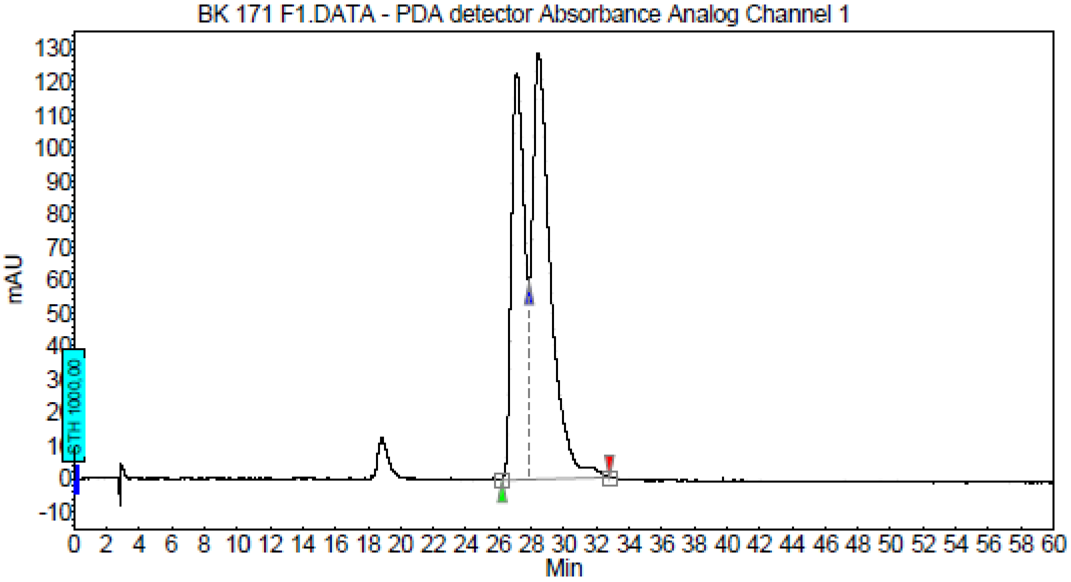


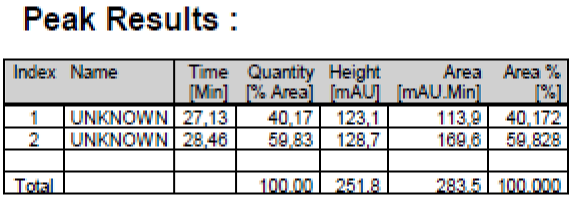
Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11,36	100,00	415,0	323,6	100,000
Total			100,00	415,0	323,6	100,000

Table 10-entry 2-(*S*)-4-(4-methoxyphenoxy)cyclopent-2-enone ((*S*)-56b)

rac-4-(4-methoxyphenoxy)cyclopent-2-enone (56b)

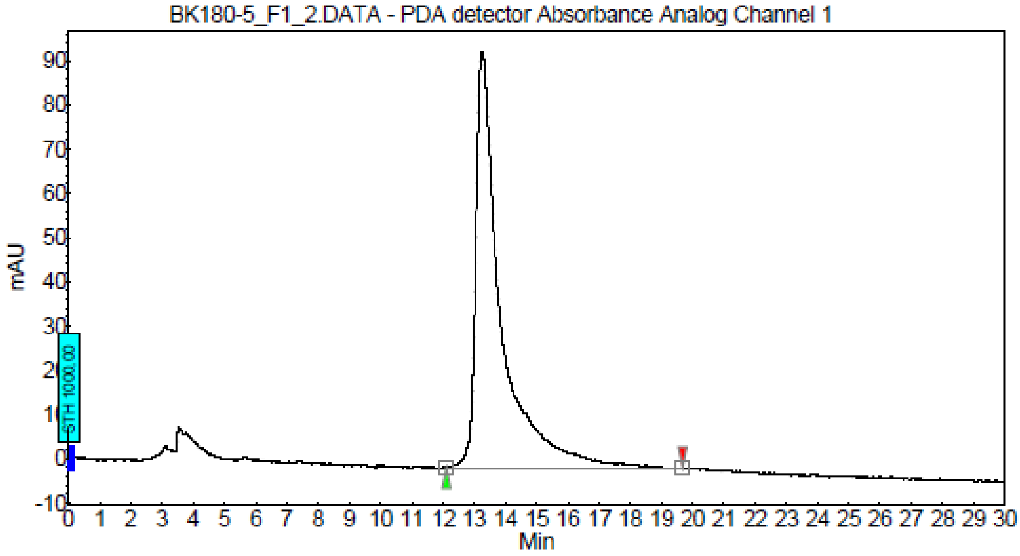


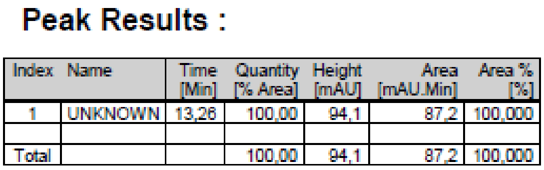


Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	27,13	40,17	123,1	113,9	40,172
2	UNKNOWN	28,46	59,83	128,7	169,6	59,828
Total			100,00	251,8	283,5	100,000

Table 10-entry 2-(*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate ((*R*))-54b)

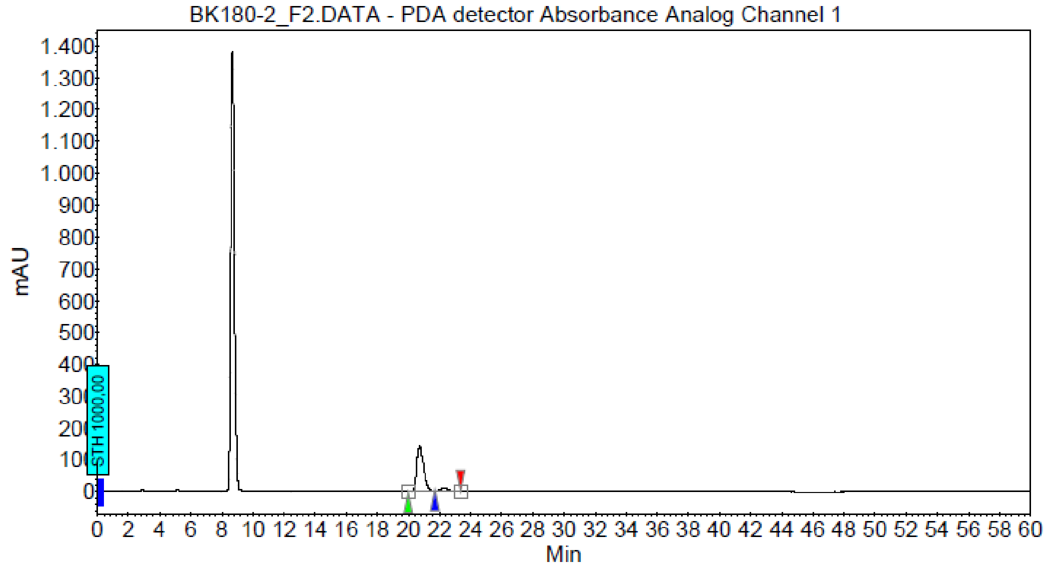




Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13,26	100,00	94,1	87,2	100,000
Total			100,00	94,1	87,2	100,000

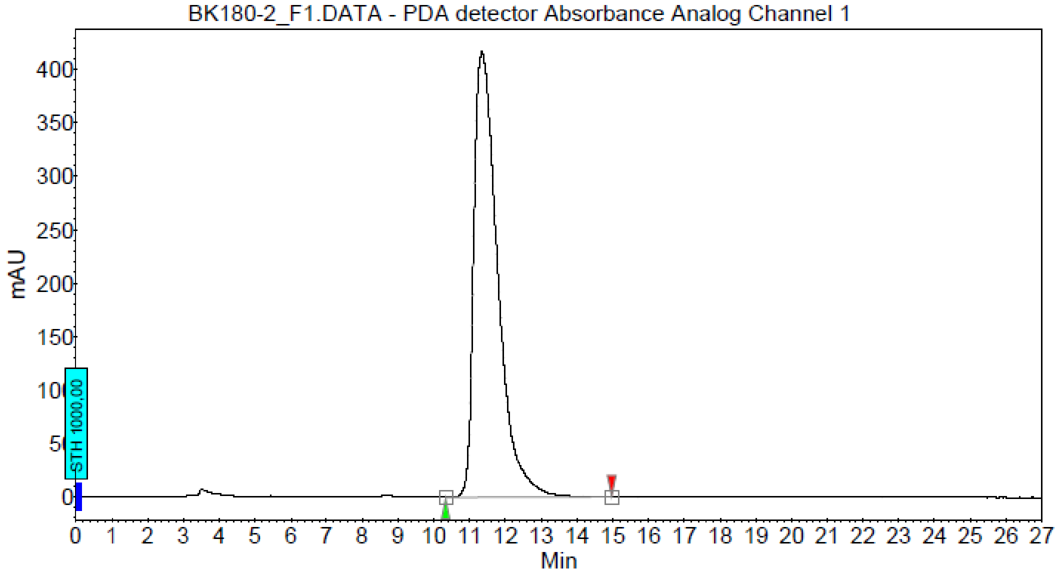
Table 10-entry 3-(*S*)-2-(4-oxocyclopent-2-en-1-yl)isoindoline-1,3-dione ((*S*)-56c)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20,71	90,35	144,7	72,9	90,347
2	UNKNOWN	22,21	9,65	13,1	7,8	9,653
Total			100,00	157,8	80,7	100,000

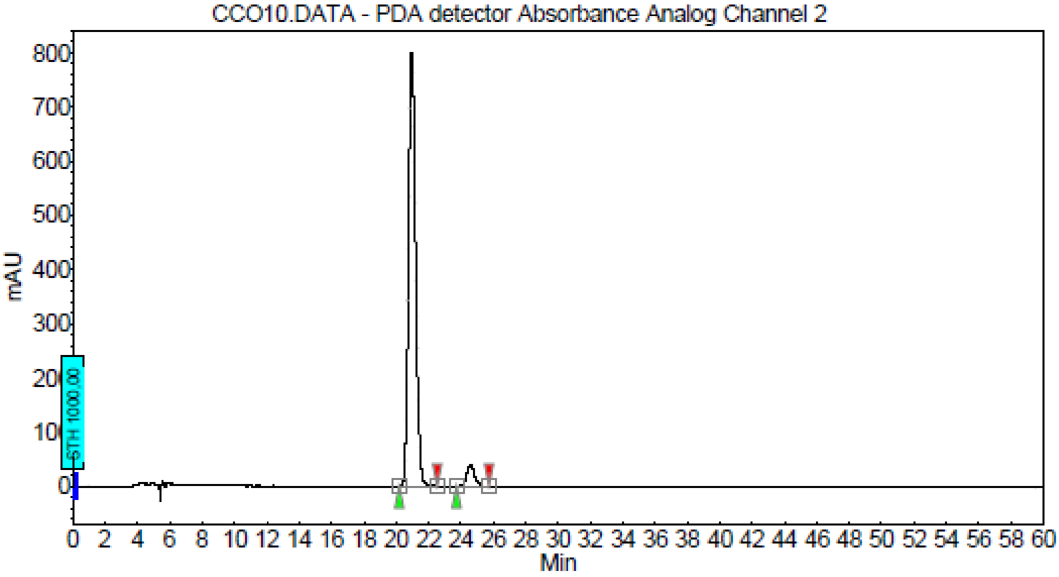
Table 10-entry 3-(*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate ((*R*))-54b)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	11,35	100,00	416,7	324,6	100,000
Total			100,00	416,7	324,6	100,000

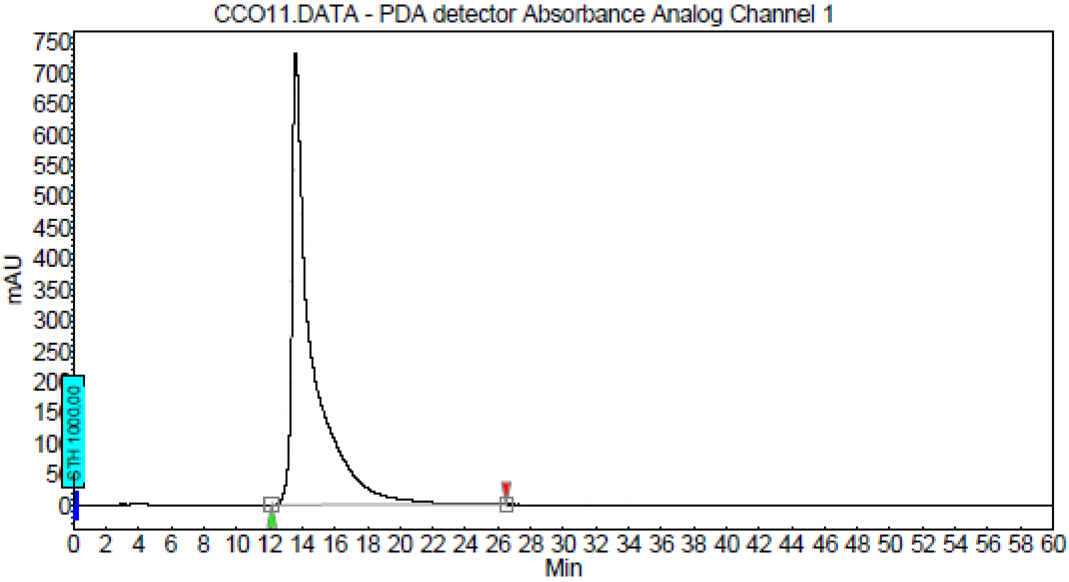
Table 10-entry 4-(*S*)-4-bromophenyl (4-oxocyclopent-2-en-1-yl) carbonate ((*S*)-56d)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	20,95	95,08	799,5	405,8	95,076
2	UNKNOWN	24,60	4,92	39,3	21,0	4,924
Total			100,00	838,8	426,8	100,000

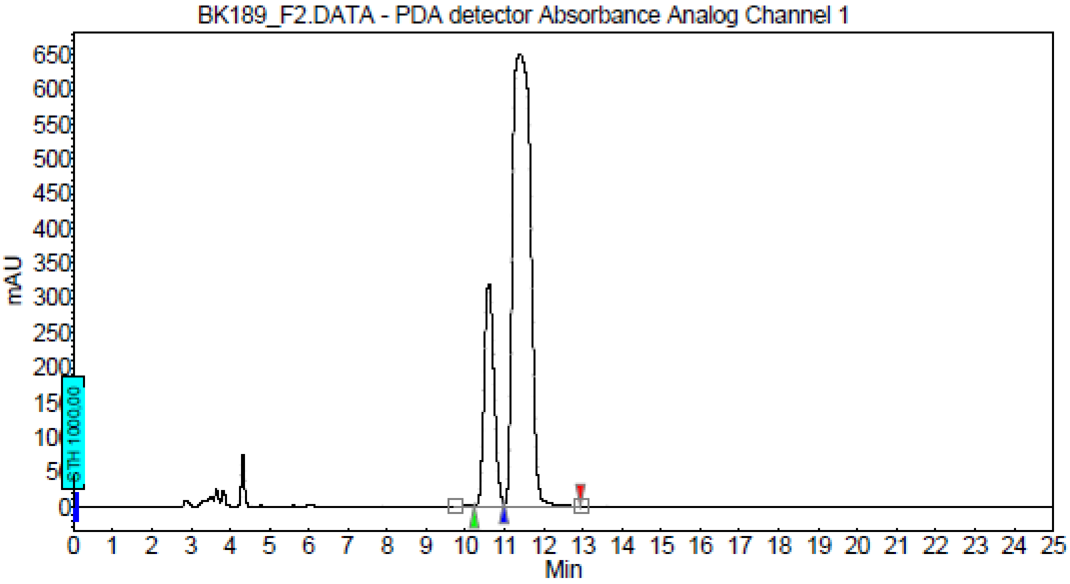
Table 10-entry 4-(*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate ((*R*))-54b)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13,60	100,00	732,2	1014,1	100,000
Total			100,00	732,2	1014,1	100,000

Scheme 21-(*S*)-4-phenoxycyclopent-2-enone ((*S*)-56a)

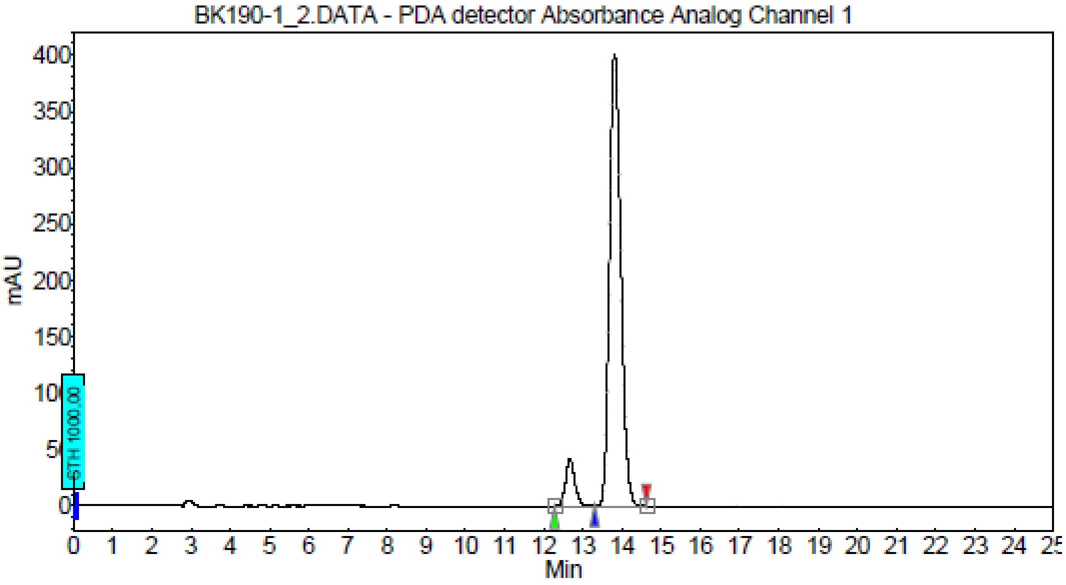


Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10,60	21,45	319,6	94,0	21,449
2	UNKNOWN	11,39	78,55	650,1	344,1	78,551
Total			100,00	969,7	438,1	100,000

Recycling studies (table 11)

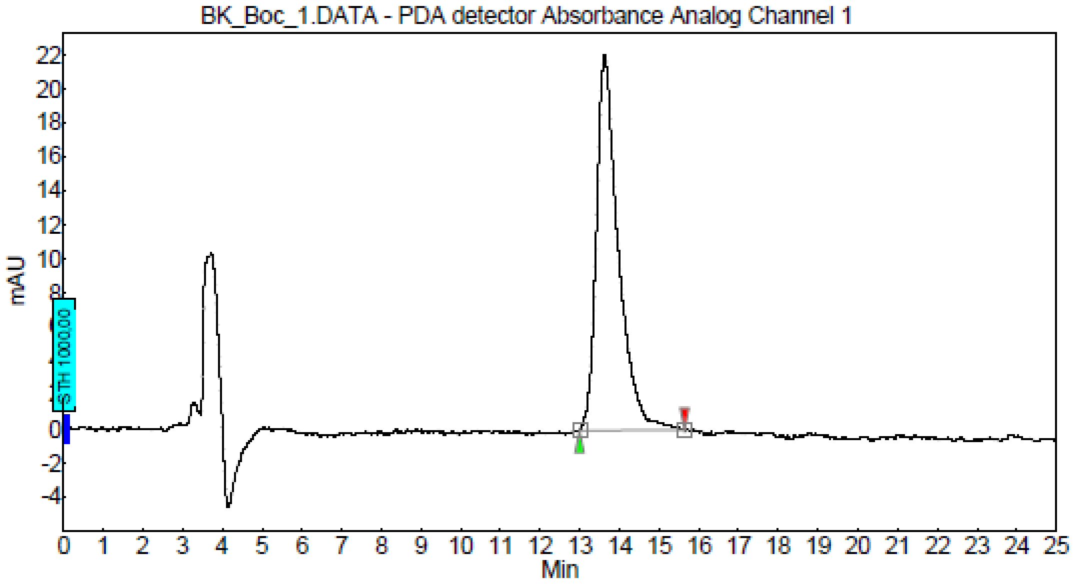
Run 1-(*S*)-4-phenoxycyclopent-2-enone ((*S*)-56a)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12,67	8,08	41,7	12,0	8,079
2	UNKNOWN	13,81	91,92	401,1	136,3	91,921
Total			100,00	442,8	148,2	100,000

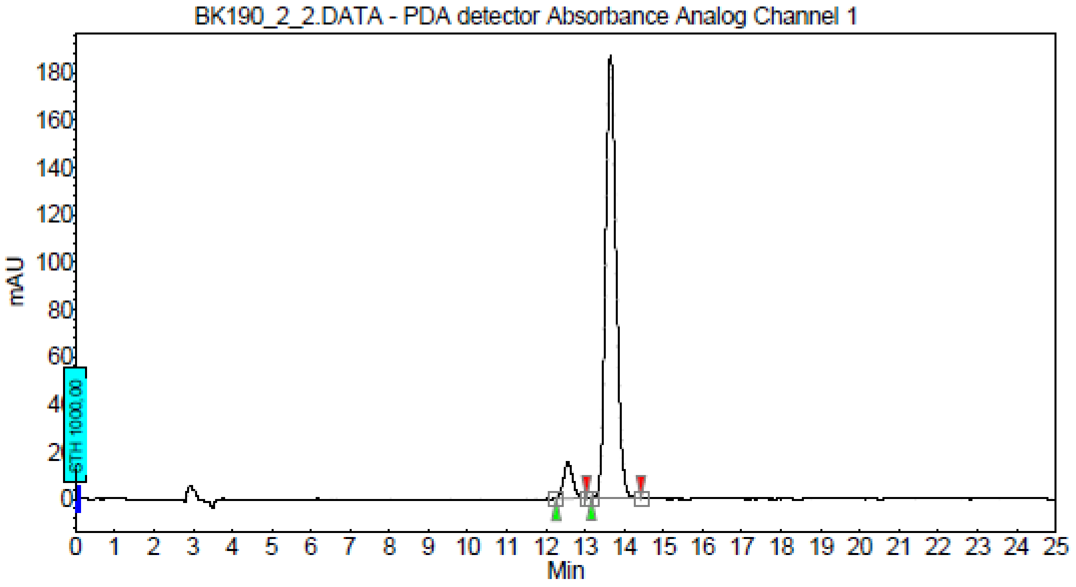
Run 1-(*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate ((*R*))-54b)

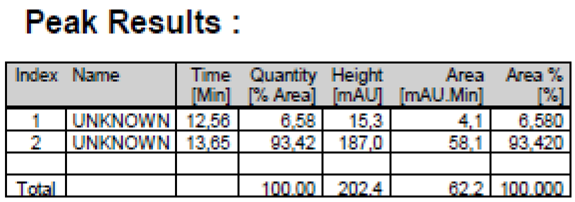


Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13,62	100,00	22,1	14,2	100,000
Total			100,00	22,1	14,2	100,000

Run 2-(*S*)-4-phenoxycyclopent-2-enone ((*S*)-56a)

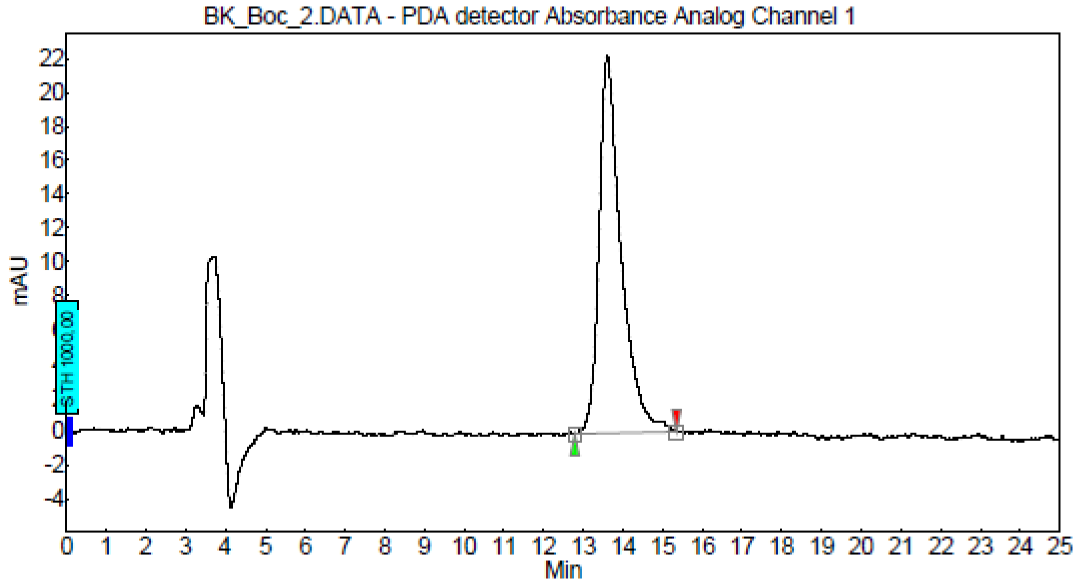


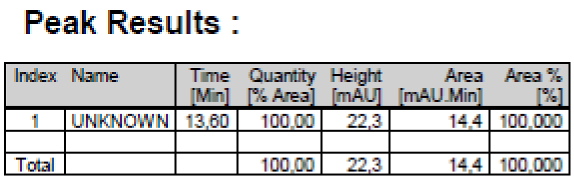


Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12,56	6,58	15,3	4,1	6,580
2	UNKNOWN	13,65	93,42	187,0	58,1	93,420
Total			100,00	202,4	62,2	100,000

Run 2-(*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate ((*R*))-54b)

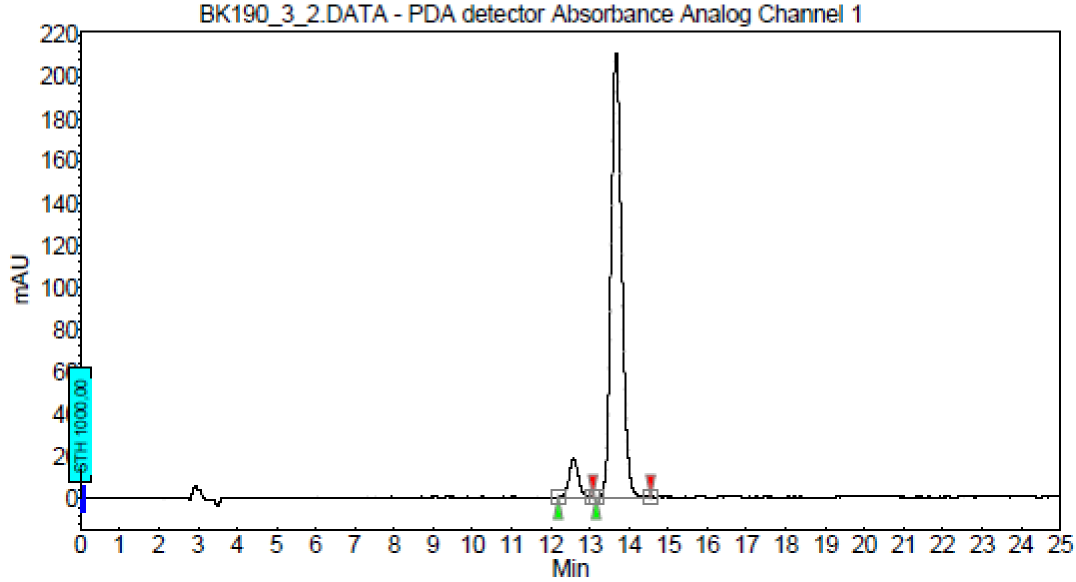




Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13,60	100,00	22,3	14,4	100,000
Total			100,00	22,3	14,4	100,000

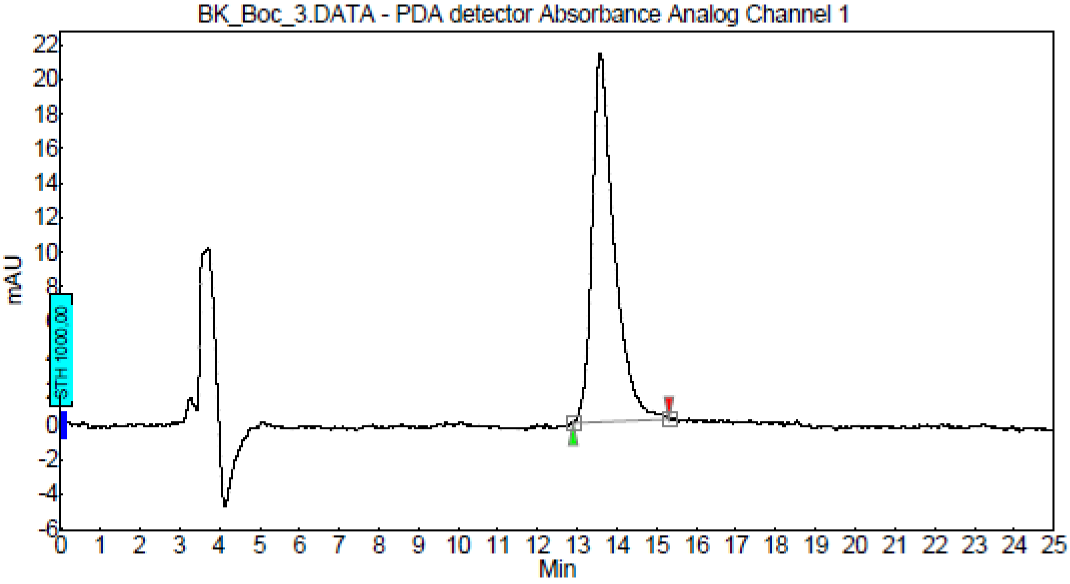
Run 3-(*S*)-4-phenoxycyclopent-2-enone ((*S*)-56a)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12,59	6,97	18,2	5,0	6,970
2	UNKNOWN	13,67	93,03	210,7	66,2	93,030
Total			100,00	228,8	71,2	100,000

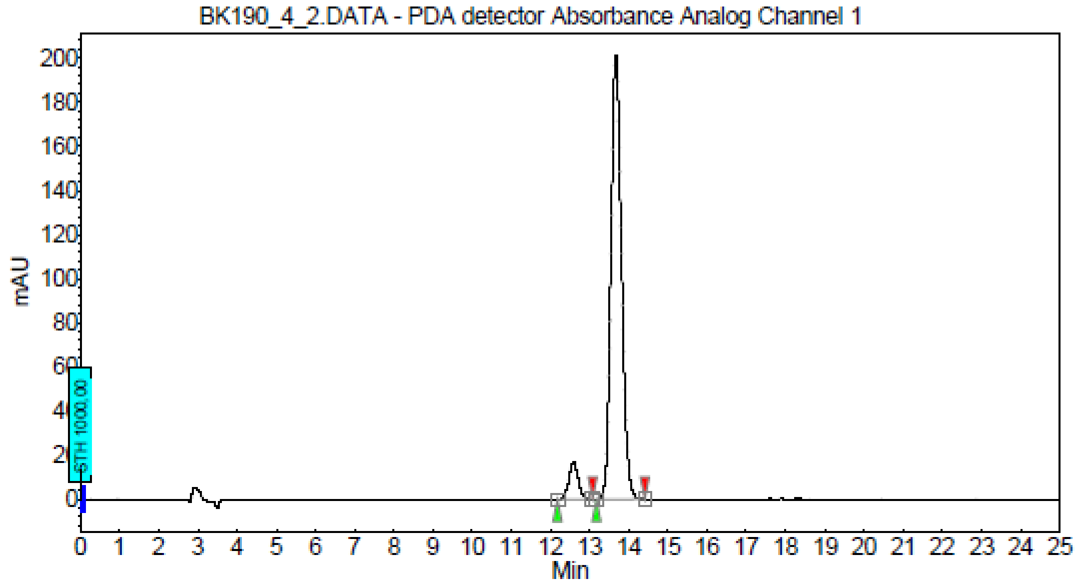
Run 3-(*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate ((*R*))-54b)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13,58	100,00	21,3	13,8	100,000
Total			100,00	21,3	13,8	100,000

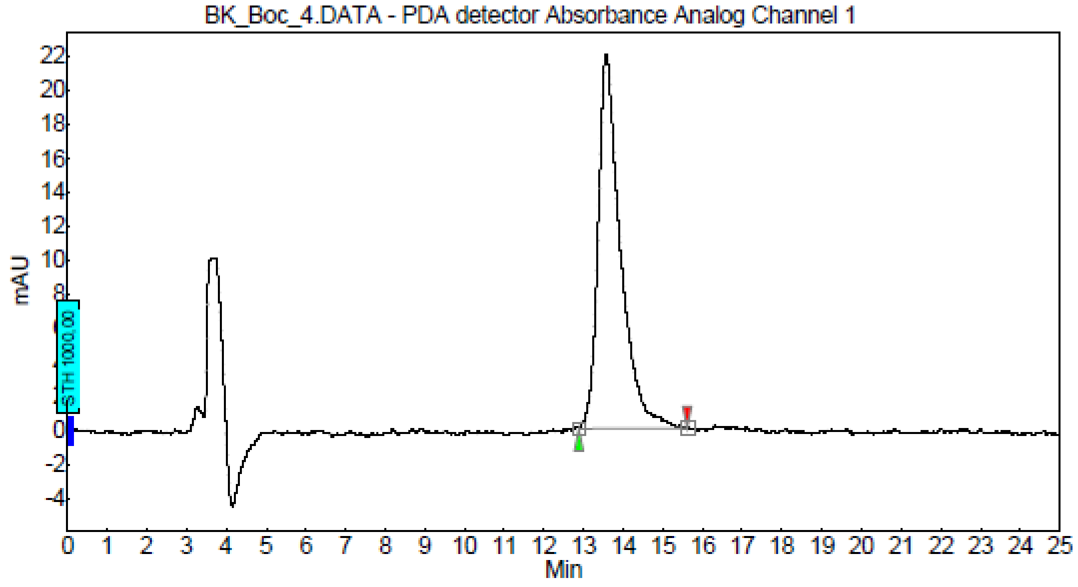
Run 4-(*S*)-4-phenoxycyclopent-2-enone ((*S*)-56a)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12,59	6,90	17,1	4,7	6,899
2	UNKNOWN	13,67	93,10	201,4	62,9	93,101
Total			100,00	218,6	67,6	100,000

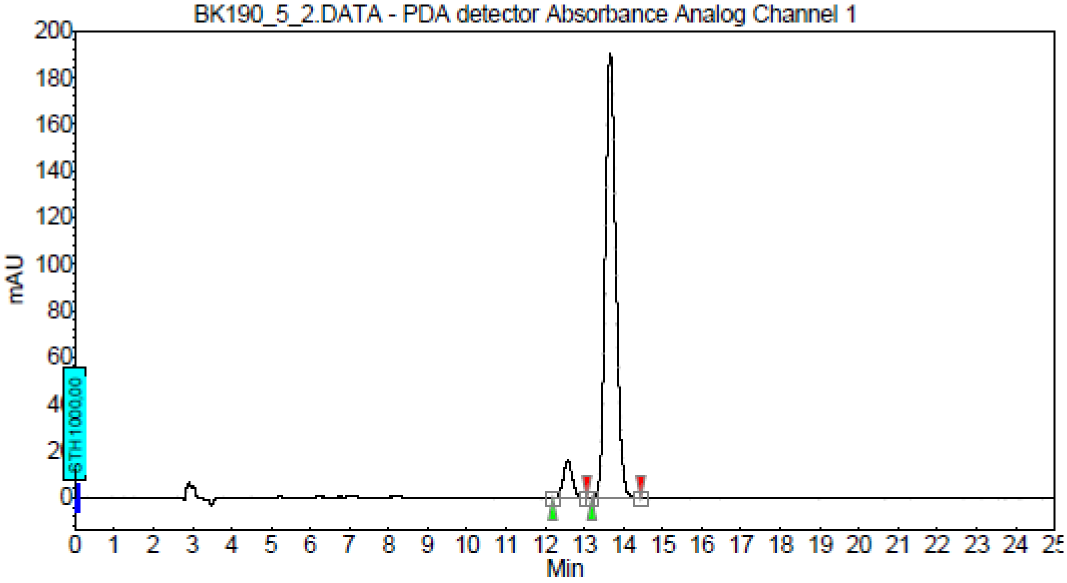
Run 4-(*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate ((*R*))-54b)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13,58	100,00	22,0	14,4	100,000
Total			100,00	22,0	14,4	100,000

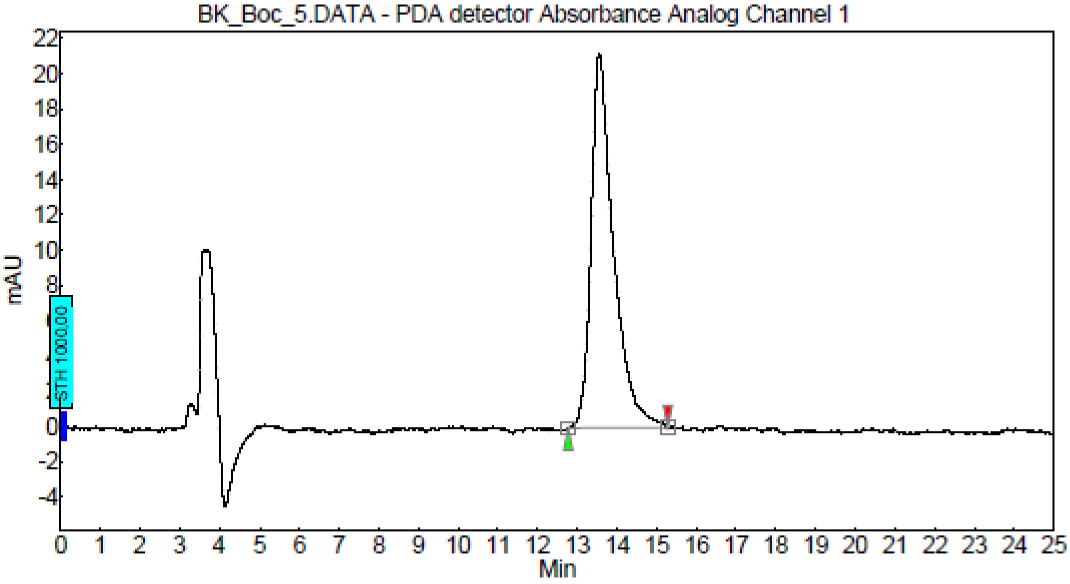
Run 5-(*S*)-4-phenoxycyclopent-2-enone ((*S*)-56a)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	12,57	7,01	16,3	4,5	7,010
2	UNKNOWN	13,66	92,99	190,7	59,3	92,990
Total			100,00	207,0	63,8	100,000

Run 5-(*R*)-*tert*-butyl (4-oxocyclopent-2-en-1-yl) carbonate ((*R*))-54b)



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	13,55	100,00	21,2	13,9	100,000
Total			100,00	21,2	13,9	100,000

Curriculum Vitae

Personal data

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10/2014 – current	PhD thesis in the research group of *Prof. Dr. O. Reiser* (University of Regensburg, Germany)
09/2014	Master of Science in chemistry
01/2014 – 09/2014	Master thesis in the research group of *Prof. Dr. O. Reiser* (University of Regensburg, Germany)
10/2012 – 09/2014	Advanced studies in chemistry (University of Regensburg, Germany)
09/2012	Bachelor of Science in chemistry
04/2012 – 07/2012	Bachelor thesis in the research group of *Prof. Dr. Burkhard König* (University of Regensburg, Germany)
10/2009 – 09/2012	Studies in chemistry (University of Regensburg, Germany)
09/2000 – 06/2009	Abitur (*A-levels*), Johann-Michael Fischer Gymnasium, Burglengenfeld, Germany.

Publications

1. C. M. Eichenseer, **B. Kastl**, M. Pericas, P. R. Hanson, O. Reiser , *ACS Sus. Chem. Eng.* **2016**, *4*, 2698-2705.

“Synthesis and Application of Magnetic Noyori-Type Ruthenium Catalysts for Asymmetric Transfer Hydrogenation Reactions in Water.”

2. **B.Kastl**, D. Dobler, O.Reiser, *Manuscript in preparation*

“Pd(0) nanocatalysts supported on functionalized magnetic Co/C nanoparticles for hydrogenations of olefins in water”

Conferences

GDCh Wissenschaftsforum 2017 – Berlin (Germany), September 10.–14., 2017.

"Carbon coated cobalt nanoparticles as supportive catalysts in allylic substitutions" (Poster).

26th ISHC Congress 2017 – Regensburg, (Germany), September 03.-08., 2017.

"Efficient allylic substitutions catalyzed by bifuntional nanoparticles" (Poster).

6th EuCheMS Chemistry Congress – Seville (Spain), September 11.–15., 2016.

"*Magnetic Hydrid Materials based on Co/C Nanoparticles and their Use in Catalysis"* (Short Oral, 5 min).

GDCh Wissenschaftsforum 2015 – Dresden (Germany), August, 30.–September, 02., 2015.

"Nanoparticle Supported Catalysis" (Poster).

Professional References

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H. Declaration

Herewith I declare that this present thesis is a presentation of my original work prepared single-handed. Wherever contributions from others are involved, all of them are marked clearly, with reference to the literature, license, and acknowledgment of collaborative research.

Regensburg, July 25, 2018

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Benjamin Kastl