New Multicomponent Polymerization Approaches to Conjugated Poly(heterocycles) and Poly(1,3-dipoles)

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Abstract

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Conjugated polymers have emerged over the last decades as an intriguing class of electronic materials with potential applications ranging from polymer-based light emitting diodes, sensors, transistors, photovoltaics and many other areas. Despite the development of many useful variants of conjugated polymers, a challenge that remains in this area is their synthesis. All except the most simple conjugated polymers are constructed by a multistep synthesis, where a complex monomer is first assembled prior to polymerization. This not only creates waste with each step, but also makes it challenging to modify polymer structures, as each monomer must be independently prepared. The objective of the research described in this thesis is to develop a new approach to prepare conjugated polymers via multicomponent polymerization reactions. These have provided tunable methods to assemble pyrrole-based conjugated polymers in one pot reactions from combinations of available substrates, such as diimines, diacid chlorides, alkynes and/or alkynes. In addition, these reactions provide access to new classes of conjugated polymers: poly(Münchnones) and poly(phospha-Münchnones).

In Chapter 2, we describe the palladium-catalyzed coupling of diimines, diacid chlorides, carbon monoxide and alkynes. This reaction provides access to families of conjugated poly(pyrroles) in one pot reactions, and with independent control of all the substituents and conjugated units. Moreover, a new class of conjugated polymer, a poly(1,3-dipole), can be isolated. The latter exhibits low electronic band-gaps, and can serve as an intermediate in the synthesis of a range of conjugated poly(heterocycles) via 1,3-dipolar cycloadditions.

Chapter 3 describes an alternative, phosphonite-mediated multicomponent synthesis of poly(pyrroles). In analogy to the results in Chapter 2, this transformation also uses diimines and diacid chloride monomers, which are in this case coupled by the addition of (catechyl)PPh rather than palladium catalyzed carbonylation. This generates another class of poly(1,3-dipole) that can react with a variety of alkynes or alkenes to form poly(pyrroles). This approach offers several advantages over the one presented in Chapter 2: the polymers exhibit higher molecular weights, it tolerates a broader scope of monomers, and it does not rely on transition metal catalysis. Notably, to the best of our knowledge, this represents the first metal-free multicomponent synthesis of conjugated polymers.

In Chapter 4, a new type of donor-acceptor conjugated polymer containing 1,3-dipole units is described: a poly(phospha-Münchnone). These can be isolated from the multicomponent polymerization of diimines, diacid chlorides and (catechyl)PPh presented in Chapter 3. UV-Vis spectroscopy shows that these polymers are low band-gap materials. Moreover, their properties can be easily tuned by choice of the diimine or diacid chloride monomers.

In Chapter 5, we studied the use of renewable starting materials in the phosphonite-mediated multicomponent polymerization presented in Chapter 3. The lignin degradation product bis-vanillin is readily incorporated into this platform to generate cross-conjugated polymers, including poly(1,3-dipoles) and poly(pyrroles). Changing the diacid chloride or the alkyne / alkene coupling partner allowed access to a range of polymers with tunable optical properties. 2,5-furandicarboxylic acid (FDCA), a monomer derived from cellulose oxidation, can also be employed as a precursor to the diacid chloride monomer. The latter provides the first example of a conjugated polymer obtained from both components of lignocellulosic biomass.

Résumé

Nouvelles Approches pour la Polymérisation à Multiples Composants de Poly(hétérocycles) et de Poly(1,3-dipôles) Conjugués

Les polymères conjugués se sont établis dans les dernières décennies en tant que matériaux électroniques ayant des applications dans multiples domaines, tel que les diodes à électroluminescence, les capteurs, les panneaux solaires… Malgré le développement de maintes variantes de polymères conjugués, leur synthèse reste un défi à relever. Tous sauf les plus simples polymères sont synthétisés en plusieurs étapes, où un monomère complexe est assemblé avant la polymérisation. Ceci non seulement génère des déchets à chaque étape, mais aussi rend très difficile la modification de la structure moléculaire du polymère, puisque chaque monomère doit être préparé indépendamment. L'objectif de la recherche décrite dans cette thèse est de développer une nouvelle approche pour la préparation de polymères conjugués avec des polymérisations à multiples composants. Ces dernières donnent accès à des polymères conjugués à base de pyrroles, à partir de composant facilement disponibles, tels que des diimines, des dichlorures d'acide et des alcènes ou des alcynes. De plus, ces réactions donnent accès à une nouvelle classe de polymères conjugués : les poly(Münchnones) et les poly(phospha-Münchnones).

Dans le Chapitre 2, nous décrivons un couplage catalysé au palladium entre des diimines, des dichlorure d'acides, du monoxyde de carbone et des alcynes. Cette réaction en récipient unique donne accès à des familles de poly(pyrroles) conjugués tout en contrôlant tous les substituants et les unités conjuguées. De plus, une nouvelle classe de polymères conjugués peut être isolée : les poly(1,3-dipôles). Ces derniers présentent des bandes interdites de basse énergie, et peuvent aussi servir d'intermédiaires dans la synthèse d'un éventail de poly(hétérocycles) via des cycloadditions 1,3-dipolaires.

Le Chapitre 3 décrit une autre synthèse à multiples composants de poly(pyrroles) induite par une phosphine. En analogie avec les résultats dans le Chapitre 2, cette transformation utilise également des diimines et des dichlorures d'acides, qui dans ce cas sont couplés par l'addition de la phosphine plutôt que par la carbonylation catalysée au palladium. Ceci génère une autre classe de poly(1,3-dipôles) qui peuvent réagir avec une variété d'alcynes ou d'alcènes pour former des poly(pyrroles). Cette approche offre plusieurs avantages comparée à celle présentée dans le Chapitre 2 : les polymères ont une plus grande masse molaire, la synthèse tolère une large gamme de monomères, et n'est pas dépendante d'un métal de transition. À notre connaissance, ceci représente la première synthèse à multiples composants de polymères conjugués sans métaux.

Dans le Chapitre 4, un nouveau type de polymère conjugué donneur-accepteur contenant des dipôles 1,3 est décrit : les poly(phospha-Münchnones). Ils peuvent être isolés lors de la synthèse à multiples composants présentées dans le Chapitre 3. Des études préliminaires de leurs propriétés par spectroscopie UV-visible montrent que ces matériaux ont une basse bande interdite. De plus, leurs propriétés peuvent être aisément modulées par le choix des monomères.

Dans le Chapitre 5, nous avons étudié l'utilisation de matériaux de départ renouvelables dans la polymérisation à multiples composants présentée dans le Chapitre 3. La di-vanilline, un produit de dégradation de la lignine, est facilement incorporée dans cette synthèse, et génère des polymères à conjugaison croisée, incluant des poly(1,3-dipôles) et des poly(pyrroles). Le changement du dichlorure d'acide ou de l'alcyne ou l'alcène permet d'accéder à un éventail de polymères avec des propriétés optiques modulables. Le 2,5-furane-diacide carboxylique, un monomère dérivé de l'oxydation de la cellulose, peut aussi être employé comme précurseur du dichlorure d'acide. En combinaison avec la di-vanilline, ceci génère un polymère incorporant les deux composants de la biomasse lignocellulosique.

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Contributions of Co-Authors

This thesis consists of six chapters. The first chapter is an introduction to this work and Chapter 6 will present conclusions and suggestions for future work. The main body includes one publication (Chapter 2) and three publications to be submitted (Chapters 3, 4, 5). All the work was carried out as part of my degree of Doctor of Philosophy in Chemistry under the supervision of Dr. Bruce Arndtsen. As such, he is the corresponding author on all manuscripts. All the experiments reported in this thesis were performed by myself with the following exceptions:

Chapter 2: I contributed equally with Dr. David Leitch and Dr. Zhi-Yong Han who conducted the initial development of the reaction and synthesized a number of the polymers reported. I optimized the polymer synthesis and performed all absorbance, fluorescence, and cyclic voltammetry analyses. Evan Keyzer, Ali Siamaki and Ashley Gefen performed preliminary monomer screening.

Chapter 3: Moritz Vollmer performed initial studies on the synthesis of polymer **3.8**.

Chapter 5: Anthony Lau reproduced the synthesis of polymer **5.4d** and characterized it by NMR and UV-Vis absorbance.

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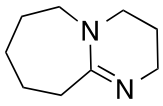
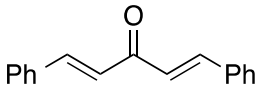
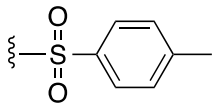
List of Abbreviations

Å	Ångström
A^3 coupling	Aldehyde-Amine-Alkyne coupling
ATRP	Atom Transfer Radical Polymerization
Ar	Aryl
Atm	Atmosphere
*n*Bu	*n*-Butyl
*t*Bu	*tert*-Butyl
n-BuLi	*n*-Butyllithium
Bn	Benzyl
BnOBz	Benzyl benzoate
bpy	2,2-Bipyridine
° C	Degrees Celsius
Cy	Cyclohexyl
CO	Carbon monoxide
CO_2	Carbon dioxide
CS_2	Carbon disulfide
DBU	
DMAc	N,N-Dimethylacetamide
DMAD	

dba	
DCM	Dichloromethane
DFT	Density Functional Theory
DOE	Department of Energy
DP	Degree of Polymerization
dppp	1,3-Bis(diphenylphosphino)propane
Et	Ethyl
EWG	Electron Withdrawing Group
FDCA	2,5-Furan Dicarboxylic Acid
GPC	Gel Permeation Chromatography
Hex	Hexyl
*c*Hex	Cyclohexyl
*i*Pr	*Iso*-Propyl
kDa	KiloDalton
MALI	Mercaptoacetic Acid Locking Imine
MALLS	Multi Angle Laser Light Scattering
MCRs	Multicomponent Coupling Reactions
Me	Methyl
Mes	Mesityl
MHz	Megahertz
MS	Molecular Sieves

mg	Milligram
mmol	Millimole
mL	Milliliter
M_n	Number Average Molecular Weight
M_w	Mass Average Molecular Weight
NMR	Nuclear Magnetic Resonance Spectroscopy
NMP	N-Methyl-2-Pyrrolidone
OPVs	Organic Photovoltaics
P3HT	Poly-3-Hexyl-Thiophene
PDI	Polydispersity Index
PEG	Polyethylene Glycol
*n*Pent	*n*-Pentyl
Ph	Phenyl
PS	Polystyrene
RAFT	Reversible Addition−Fragmentation Chain-Transfer
RI	Refractive Index
ROMP	Ring Opening Metathesis Polymerization
SEC	Size Exclusion Chromatography
TBA	Tetrabutyl Ammonium
THF	Tetrahydrofuran
o-tol	*Ortho*-Tolyl

Ts 

U4CR Ugi 4-Components Reaction

Chapter 1: Introduction
Use of Multicomponent Coupling Reactions for the Synthesis of Macromolecules

1.1 Perspective

Natural and synthetic macromolecules play an increasingly important role in our lives. These materials can be found in everything from our clothes (from natural cellulose to synthetic polyesters or polyamides), packaging (polyolefins, polyethylene terephthalate, poly-lactic acid), as structural materials (polyurethanes, polyvinyl chloride), to more advanced applications in drug delivery (dendrimers, biomaterials), optoelectronics (conjugated polymers, magnetic polymers, photosensitive polymers), and many other areas. Together, with these growing applications, the past several decades have seen extensive efforts directed towards the development of new synthetic approaches to functional materials. As a result, classic polymerization techniques (e.g. free-radical, ionic, insertion, or condensation polymerizations) have been expanded to access more diverse polymers via living polymerizations (e.g. ATRP, RAFT, insertion, ROMP), or metal-catalyzed coupling reactions, among others. Overall, these have provided well-defined polymers for an ever-growing range of applications.

Despite these many advances, one limitation in polymer synthesis is the ability to efficiently access structurally complex materials. Structural complexity has become an important tool in many current areas of polymer design, as it can provide a method to create materials with highly tuned macroscopic or molecular level features. Unfortunately, structural complexity in polymers is typically derived from the monomer(s) themselves. While many simple monomers are readily available (e.g. simple alkenes for polyolefins, simple diols or diamines for polyesters or polyamides), more complex monomers must typically first be prepared via a multistep synthesis. The latter can make the overall construction of complex, highly tuned polymers a time intensive and costly activity, and

leads to the formation of significant chemical waste with each step. In addition, this synthetic sequence must be repeated for each new variant of these polymers. These features cannot only limit access to complex macromolecules for product discovery, but also the capacity to prepare these materials on the scale often desired for synthetic polymers, which for many applications can reach into the millions of tons per year.

One approach to address these issues is to consider structurally complex polymers as synthesized from combinations of multiple simpler monomers, rather than as the polymerization product of complex monomers. The synthesis of random terpolymers and block terpolymers has been known for many decades. An alternative is to assemble multiple different monomers into a structurally more complex repeat unit; i.e. a multicomponent polymerization. Multicomponent coupling reactions (MCRs) have seen significant use in organic chemistry as a method to combine three or more simpler units into often pharmaceutically relevant products.[1-11] In contrast to the more classical multistep synthesis, MCRs can often provide a route to access structural complexity with high step- and atom-economy, minimized waste, and high modularity, where any of the three or more substrates can be tuned to create libraries of products to systematically modify their properties (e.g. in drug design). In light of these attractive features, there has been rapidly developing interest in the application of multicomponent coupling reactions to polymer synthesis: a field in which synthetic efficiency is at least as relevant. These transformations have taken a number of general forms, including the multicomponent synthesis of alternating polymers (Figure 1.1a), the multicomponent assembly of more complex units (Figure 1.1b), as well as the multicomponent formation of monomers for subsequent polymerization (Figure 1.1c).[12-15]

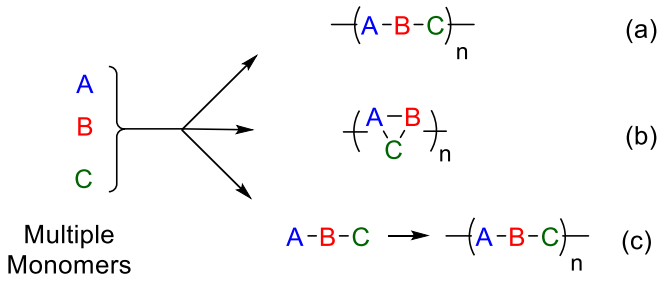


Figure 1.1 Multicomponent Approaches to Polymers

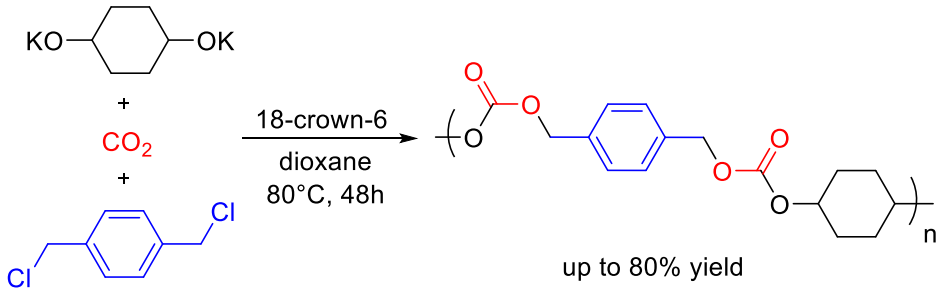
This chapter will present an overview of the use of multicomponent coupling reactions in polymer synthesis. These polymerizations will generally be divided into those that employ classic organic multicomponent coupling reactions (section 1.2), and those that use transition metal catalysis (section 1.3). Although we will highlight some examples of the multicomponent synthesis of monomers for polymer synthesis, especially where there has been significant research activity, we will focus our discussion on multicomponent polymerization reactions that provide direct access to polymers from three or more substrates (Figure 1.1a,b). This will provide the background for this thesis, which will present the development of novel multicomponent approaches to synthesize conjugated poly(heterocycles) and poly(1,3-dipoles).

1.2 Organic Multicomponent Polymerizations

A number of recent studies have employed well-established organic multicomponent coupling reactions to assemble new classes of polymers. Such transformations typically generate alternating polymers, although there are some examples of formation of more complex units (Figure 1.1b). Provided below is a highlight of important examples of these transformations.

1.2.1 Multicomponent Polymerizations with Two Diversifiable Units

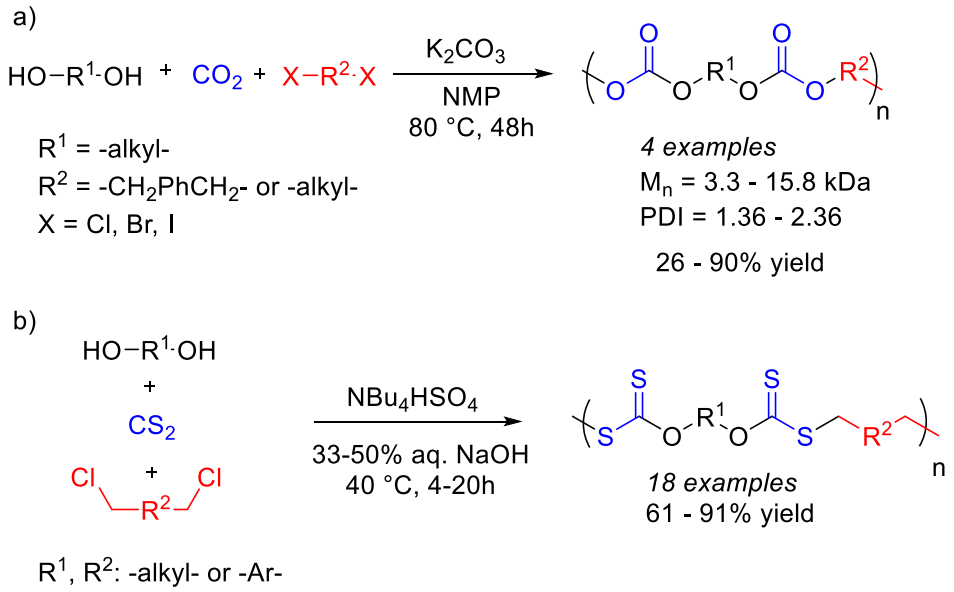
Multicomponent polymerization reactions with three or more diversifiable units offer access to the greatest level of structural diversity. Nevertheless, many of the early examples of these transformations were those involving only two tunable monomers. For example, one of the earliest reports of a multicomponent polymerization was that by Soga and coworkers in 1978, where carbon dioxide, potassium diolates, and α,α'-dihalo-p-xylene were coupled to generate polycarbonates (Scheme 1.1).[16] This transformation is believed to involve the reaction of the deprotonated diol with carbon dioxide to form a dicarbonate for subsequent slower nucleophilic addition to the benzyl chloride. No examples of the diversification of this reaction were described. The authors did not perform gel permeation chromatography (GPC), therefore, only relative viscosities were used to compare molecular weights. Rukan later used the same reaction platform to extend the scope to other benzyl halides .[17]



Scheme 1.1 Three-Component Synthesis of Polycarbonates from Carbon Dioxide

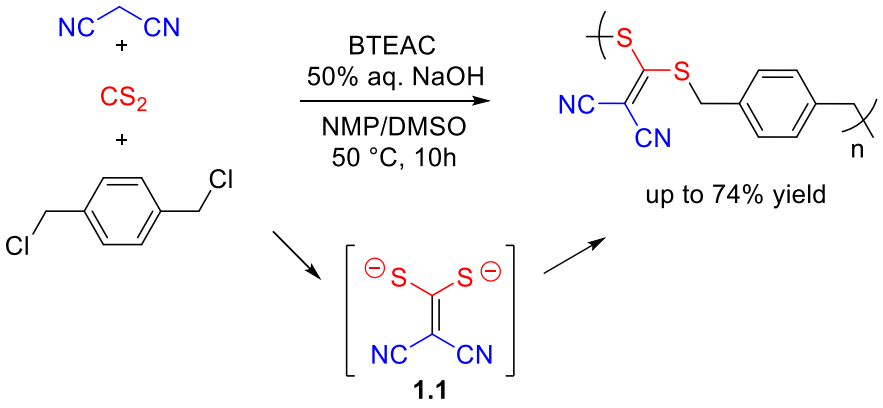
The ability of CO_2 to participate in multicomponent polymerizations has since been expanded upon by other laboratories. In 1994, Inoue and coworkers reported the generation of several different polycarbonates from CO_2, diols and dihalides (Scheme 1.2a).[18] They were able to generate four polymers from aliphatic diols and α,α'-dihalo-*p*-xylene with molecular weights up to 15.8 kDa (by GPC) using 1,4-cyclohexane diol. Alkyl-dibromides and -diiodides were also viable coupling partners, although lower yields (26-36%) and molecular weights (5.6-6.5 kDa) were obtained. Carbon disulfide can also

be employed as a monomer in this platform. Leung reported that this approach can allow the multicomponent generation of poly(S-dithiocarbonates) (Scheme 1.2b).[19] They were able to synthesize a library of 18 polymers from aliphatic and benzylic precursors. By screening this wide range of monomers, they showed that the main influence on the thermal stability of the polymers was the structure of the dihalide monomer.



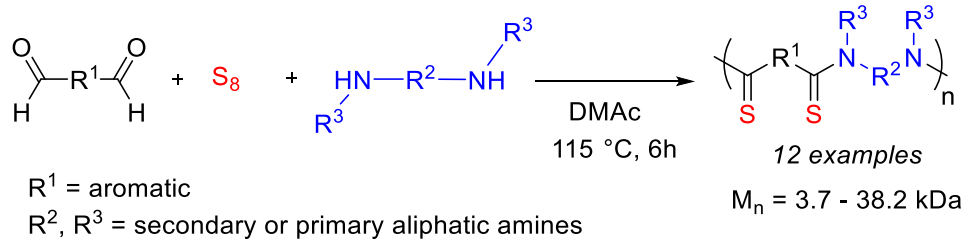
Scheme 1.2 Three-Component Synthesis of Polycarbonates and Poly(S-dithiocarbonates)

An interesting alternative use of CS_2 was reported by Suh *et al.* in 1988 for the synthesis of polysulfides from its terpolymerization with malonitrile and α,α'-dichloro-p-xylene (Scheme 1.3).[20] In this case, the reaction of CS_2 with malonitrile under phase-transfer conditions can generate an equivalent to the doubly deprotonated intermediate **1.1** for coupling with xylene monomer. No examples of diversity were shown, and only moderate yields were obtained (40-74%).



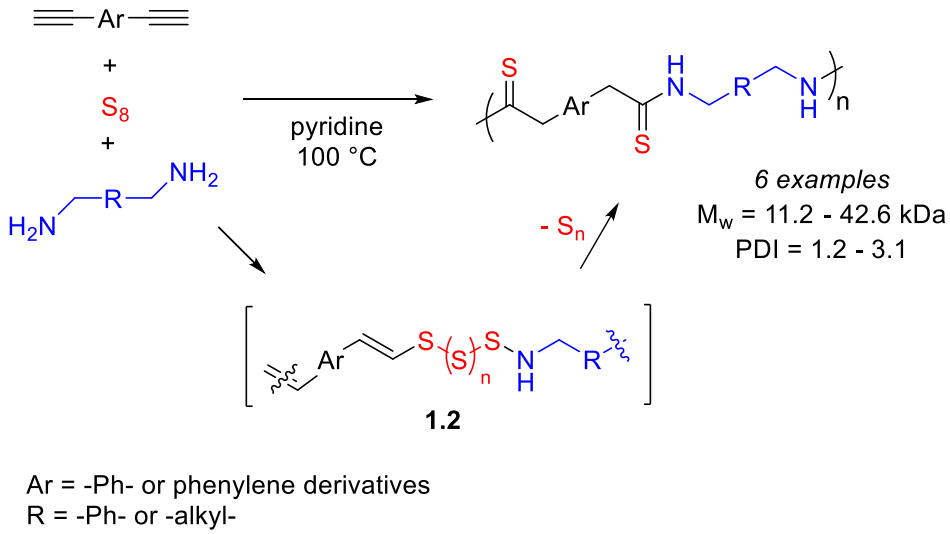
Scheme 1.3 Three-Component Synthesis of Polysulfides

Elemental sulfur has also been employed as a non-diversifiable monomer in multicomponent polymerizations. Yamamoto described in 2001 the synthesis of polythioamides from elemental sulfur, dialdehydes and diamines using the Willgerodt-Kindler reaction (Scheme 1.4).[21] The Willgerodt-Kindler reaction proceeds via the initial polycondensation of the aldehyde and the amine to form a poly(iminium) salt followed by nucleophilic attack of sulfur, which is itself activated by the amine. The authors showed that an array of aromatic dialdehydes were compatible with this reaction, including pyridine and thiophene derivatives, as well as a number of secondary aliphatic amines. Interestingly, while primary aliphatic amines lead to the precipitation of the poly(imine) intermediate and incomplete conversion under standard reaction conditions, the initial mixing of the amine with elemental sulfur prior to the addition of aldehyde allowed the generation of defect-free polythioamides.



Scheme 1.4 Willgerodt-Kindler Three-Component Synthesis of Polythioamides

Elemental sulfur has also been used in the multicomponent synthesis of polythioamides from diynes (Scheme 1.5).[22] This polymerization, reported by Tang, is proposed to occur via the nucleophilic attack of the amine on elemental sulfur to generate an amide/ polysulfide adduct which subsequently adds to the alkyne to form **1.2**. The latter can undergo elimination of sulfur and rearrangement to form the polythioamide product.[23] Using this approach, a range of solid state luminescent polymers was generated in high yields and molecular weights (up to 42.6 kDa).



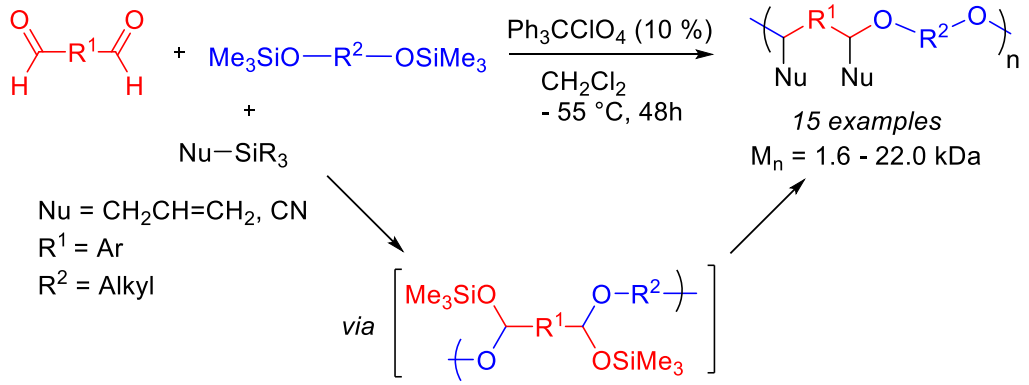
Scheme 1.5 Three-Component Synthesis of Polythioamides

1.2.2 Multicomponent Polymerizations with Three or More Diversifiable Monomers

While much of the early work on multicomponent polymerizations focused on terpolymerizations with two diversifiable monomers, research beginning in the 1990's started exploring multicomponent polymerizations with three tunable building blocks. As described below, the latter gives access to greater structural variability, and allows for the construction of more complex polymers in an efficient fashion.

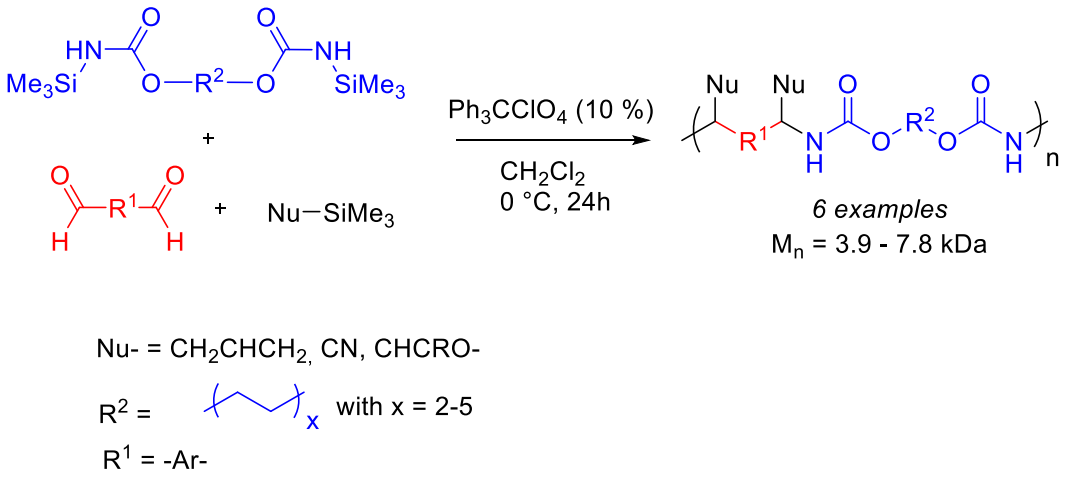
1.2.2.1 *Aldehyde- Silyl Ether-Nucleophile Coupling*

Yokozawa described in 1996 one of the first examples of a multicomponent polymerization where each of the three components could be modulated.[24] The terpolymerization of dialdehydes, bis(trimethylsilyl)ethers, and trimethylsilyl nucleophiles catalyzed by triphenylmethyl (Tr) perchlorate afforded polyethers (Scheme 1.6). The reaction is postulated to proceed via the trityl catalyzed addition of the silyl ether to the aldehyde to afford an hemiacetal, which subsequently couples with the silyl nucleophile and eliminates siloxane. In this early example, a library of polyethers (15 polymers) with side-chain containing allyl or cyano groups could be generated, and in molecular weights up to 22 kDa.



Scheme 1.6 Multicomponent Synthesis of Functionalized Polyethers

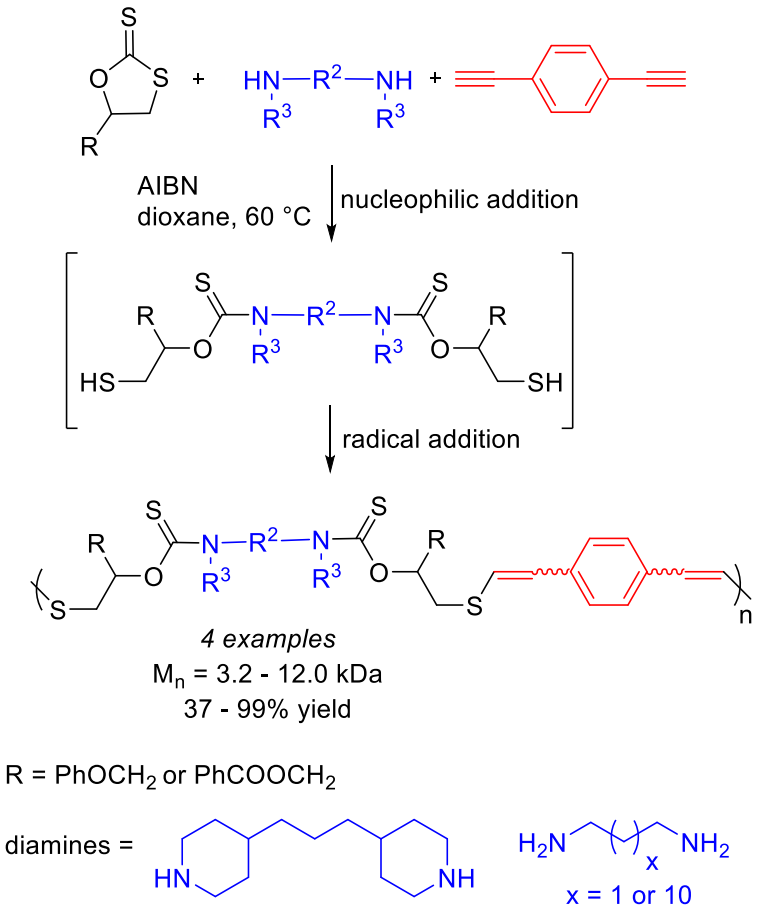
Following this initial report, Yokozawa expanded the scope of this reaction to incorporate various side chain functionalities (e.g. alkene and cyano groups),[25-27] as well as demonstrated it could be performed with N-N'-Bis(trimethylsilyl)carbamate monomers.[28] The latter provides a streamlined route to form substituted polyurethanes (Scheme 1.7).



Scheme 1.7 Multicomponent Synthesis of Polyurethanes

1.2.2.2 *Alkyne-Amine-Cyclic Dithiocarbonate Coupling*

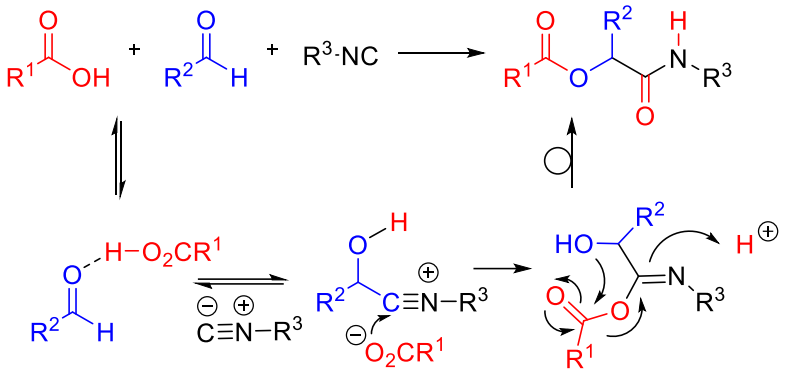
An alternative multicomponent polymerization platform was described by Endo in the three-component coupling of cyclic dithiocarbonates, diamines, and diynes.[29] As illustrated in Scheme 1.8, this reaction involved the nucleophilic addition of the amine to the dithiocarbonate to afford a mercaptourethane, followed by AIBN mediated radical addition to the alkyne. The products of this reaction were demonstrated to be rare-metal chelating polymers with moderate molecular weights (up to 12.0 kDa). Despite the potential to diversify each of the three monomers, the substrate scope was quite narrow and only four different polymers were reported.



Scheme 1.8 Multicomponent Polymerization of Diamines, Diynes, and Cyclic Dithiocarbonates

1.2.2.3 *The Passerini Reaction in Polymer Synthesis*

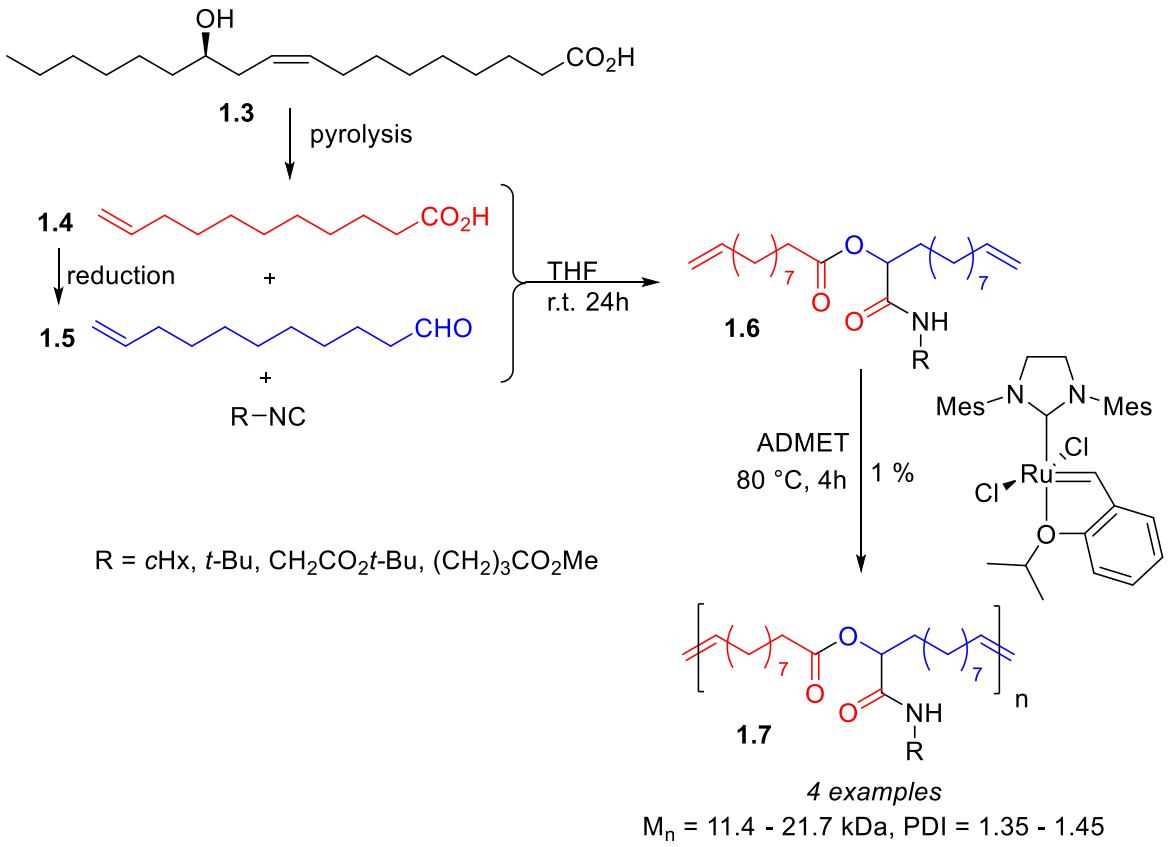
Passerini described in 1921 the one-pot, multicomponent coupling of isocyanides, aldehydes and carboxylic acids to generate α-hydroxyamides derivatives with 100% atom economy (Scheme 1.9).[30-33] This mechanistically complex reaction involves the addition of an isocyanide to an aldehyde-carboxylic acid hydrogen-bonded complex, followed by a carboxylic acid addition and a rearrangement.[34-36] Due to the ease of diversification of any of these simple substrates, the Passerini reaction has seen widespread use in organic synthesis, including the synthesis of compound libraries and various biologically relevant compounds.[11,37-40]



Scheme 1.9 Passerini Three-Component Coupling Reaction

1.2.2.3.1 Monomer Synthesis via the Passerini Reaction

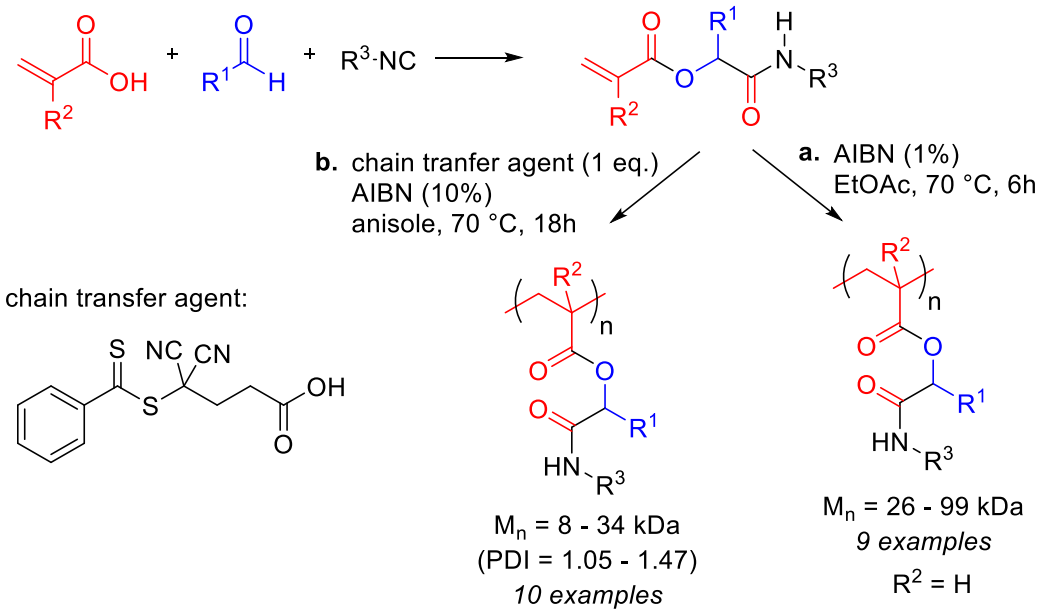
The first example of the use of the Passerini reaction for the synthesis of polymers was described by Meier and coworkers in 2011.[41] Their approach involved the multicomponent generation of olefin-containing monomers from the renewable resource ricinoleic acid (**1.3**), which is the major fatty acid in castor oil. **1.3** can be converted to 10-undecenoic acid **1.4** upon pyrolysis which can be reduced to 10-undecenal **1.5**. These two components were combined with a range of isocyanides to yield functionalized dienes **1.6** in good yields. The latter were polymerized using acyclic diene metathesis (ADMET) with the Hoveyda-Grubbs second generation catalyst to afford polymers **1.7** with molecular weights up to 21.7 kDa (Scheme 1.10). Although only one acid and one aldehyde were used in this paper, the reaction offers good diversity in the isocyanide (4 examples), and provides a novel method to generate polyesters from sustainable monomers.



Scheme 1.10 Passerini Reaction with Ricinoleic Acid Derived Monomers and ADMET Polymerization

In subsequent papers, Meier demonstrated that this platform can be exploited to generate a diverse range of polymers. This includes the use of multiple alkene-tethered carboxylic acids/aldehydes[42] and isocyanides bearing substituents that can be later converted to other functional groups (i.e. convertible isocyanides).[43] Meier also employed the Passerini reaction to synthesize acrylate monomers that can be polymerized with a radical initiator (Scheme 1.11a).[44] In this latter work, they were able to tune the cloud point of the thermoresponsive polyacrylates by changing the side chain substituents, illustrating the easy access to modular properties from MCRs. Similarly, Roth and coworkers reported the synthesis of acrylic monomers via the Passerini reaction for subsequent reversible

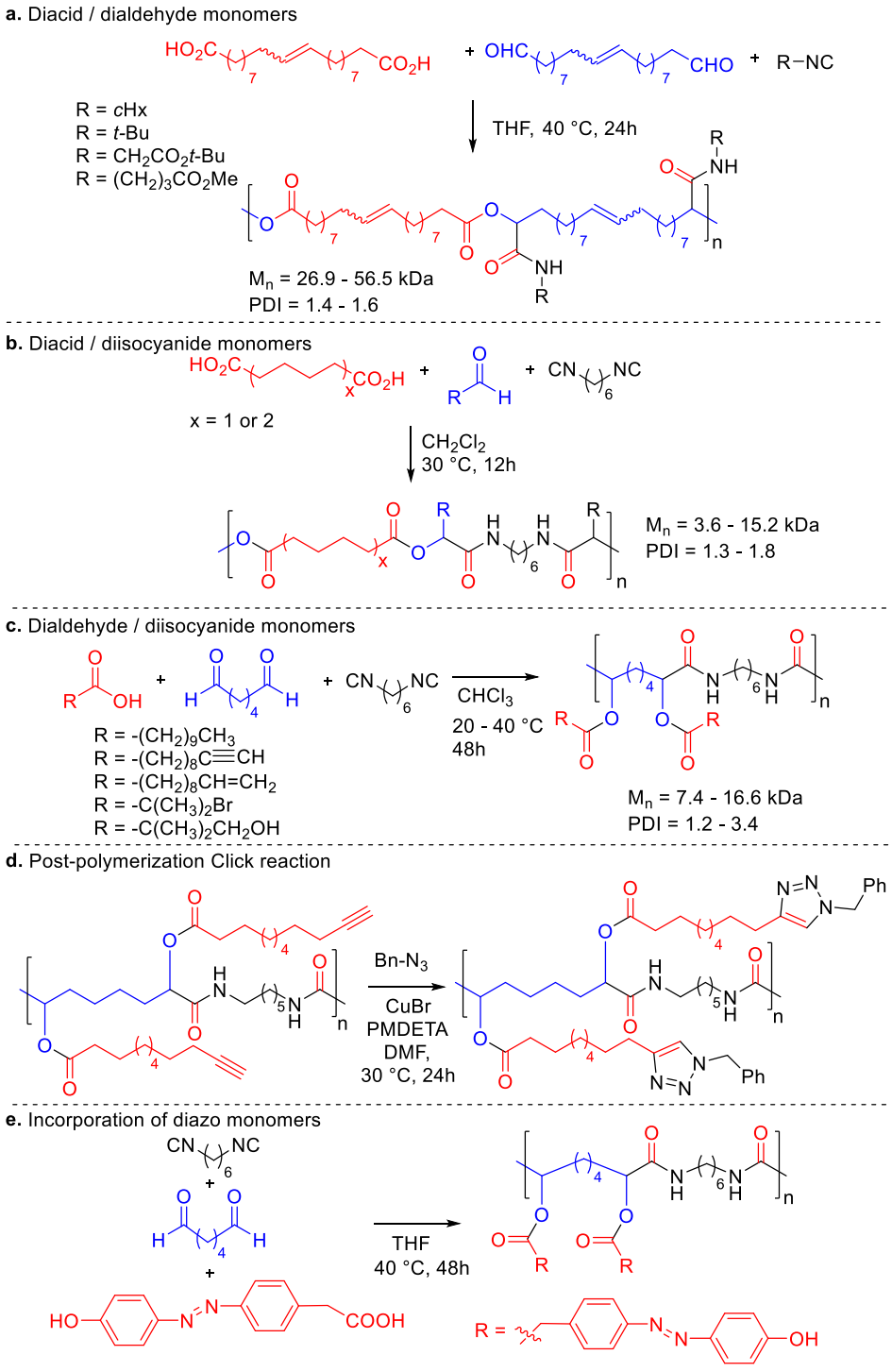
addition-fragmentation chain-transfer (RAFT) polymerization, affording polyacrylates with a narrow polydispersity (Scheme 1.11b).[45]



Scheme 1.11 Acrylate Monomer Synthesis via the Passerini Reaction

1.2.2.3.2 Multicomponent Polymerization via the Passerini Reaction

The Passerini reaction has also been used as a direct tool for polymerization. By using difunctional monomers, such as dialdehydes (A-A), dicarboxylic acids (B-B), and/or diisocyanides (C-C), a diverse variety of polymer structures can be assembled in a highly tunable fashion. Meier described the first multicomponent polyaddition based on the Passerini three-component reaction using dialdehyde, dicarboxylic acid, and isocyanide monomers (Scheme 1.12a).[41] This provided a route to complex polyesters with molecular weights up to 56.5 kDa while maintaining a surprisingly low PDI of 1.4. In this early work, they only reported the use of four different isocyanides while maintaining the same diacid and dialdehyde. Those were obtained from self-metathesis of the renewable compounds **1.4** and **1.5** (see previous section).



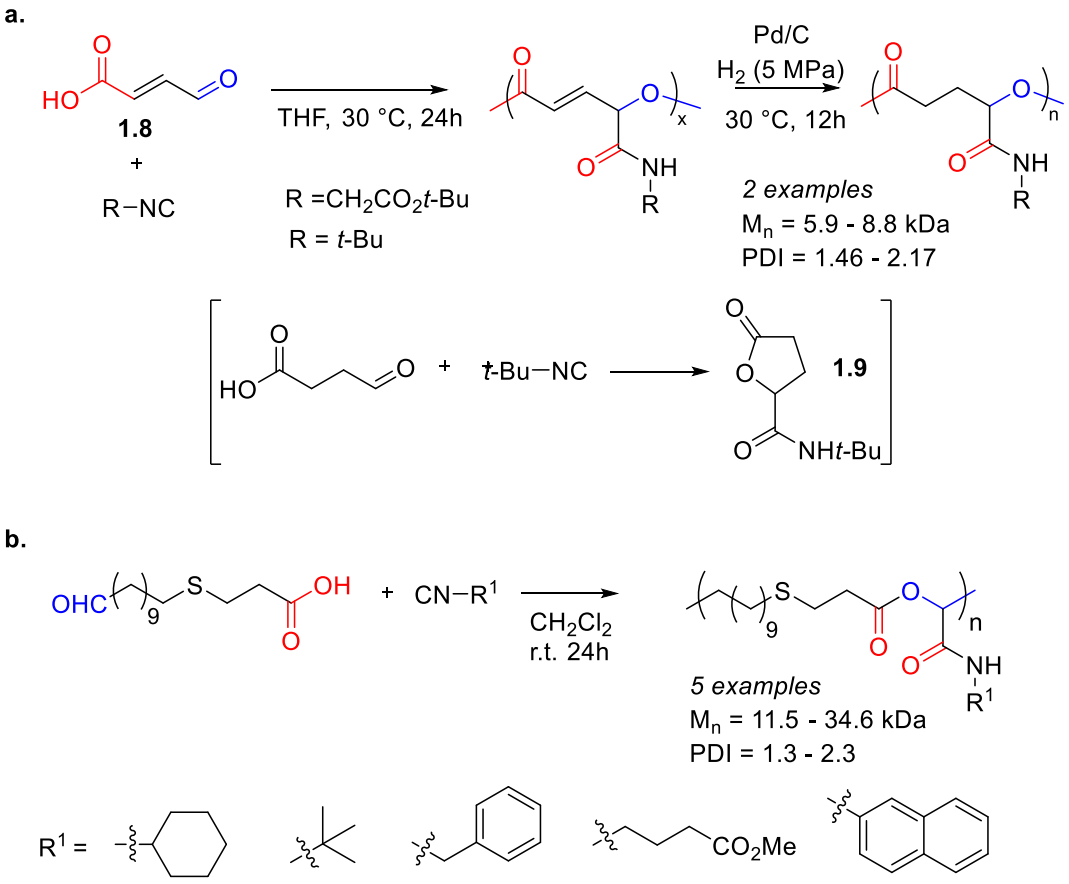
Scheme 1.12 Multicomponent Polymerization via the Passerini Reaction

In an alternative approach, Li reported the use of the Passerini reaction for the synthesis of sequence regulated poly(ester-amides) (M_n up to 15.2 kDa) from dicarboxylic acids, diisocyanides and aldehydes (Scheme 1.12b).[46] While only one polymer was synthesized in this initial report, Li subsequently described a number of variants of this reaction, including the in situ generation of the aldehyde by alcohol oxidation,[47] and the synthesis of photodegradable polymers by incorporating a photosensitive *o*-nitrobenzene functionality onto the side chain of the polymer.[48,49]

The third possibility for this polymerization from dialdehydes, diisocyanides and carboxylic acids was also reported by Li (Scheme 1.12c).[50] In this work, the authors exploited the functional group tolerance of the Passerini reaction to incorporate various alkynes, alkenes, alkyl bromides, and alcohols onto the polyamide side chain via the carboxylic acid monomer. These pendant functionalities can allow the further modification of the polymer. As an example, subjecting the polymer containing a pendant alkynyl group to CuAAC cycloaddition with benzylazide allowed the quantitative formation of triazole containing polymers (Scheme 1.12d). A similar approach was exploited by Song and coworkers for the multicomponent synthesis of polyamides with a pendant azo group (Scheme 1.12e).[51] These polymers were shown to self-assemble into nanospheres that could deform upon irradiation.

Another use of the Passerini reaction in multicomponent polymerization is to employ A-B + C monomers. Li and coworkers introduced this method in 2013 as a route to generate functionalized variants of poly(4-hydroxybutyrate) (P4HB), a biodegradable polyester (Scheme 1.13a).[52] Although this approach uses a multicomponent reaction, it does not involve three separate starting materials, and therefore does not allow access to as highly tunable structures as those in Scheme 1.12. Li noted that the saturated version of the monomer **1.8**, 4-oxobutyric acid, cannot be used directly in the polymerization due to the competing intramolecular cyclization to form the γ-butyrolactone **1.9**. In order to minimize this side reaction, the alkene-containing **1.8** was used, and the resulting polymer was hydrogenated to form a derivative of P4HB. The polymers were formed in only low

molecular weights (5.9 to 8.8 kDa), due to the presence of cyclic oligomers (confirmed by MALDI-TOF). The Meier group subsequently demonstrated that a similar approach with a longer linker minimized the formation of cyclic side products, and allowed access to much higher molecular weight polymers (up to 34.6 kDa, Scheme 1.7b).[53] The reaction was tolerant to a range of isocyanides including those with aromatic, benzylic and ester substituents.

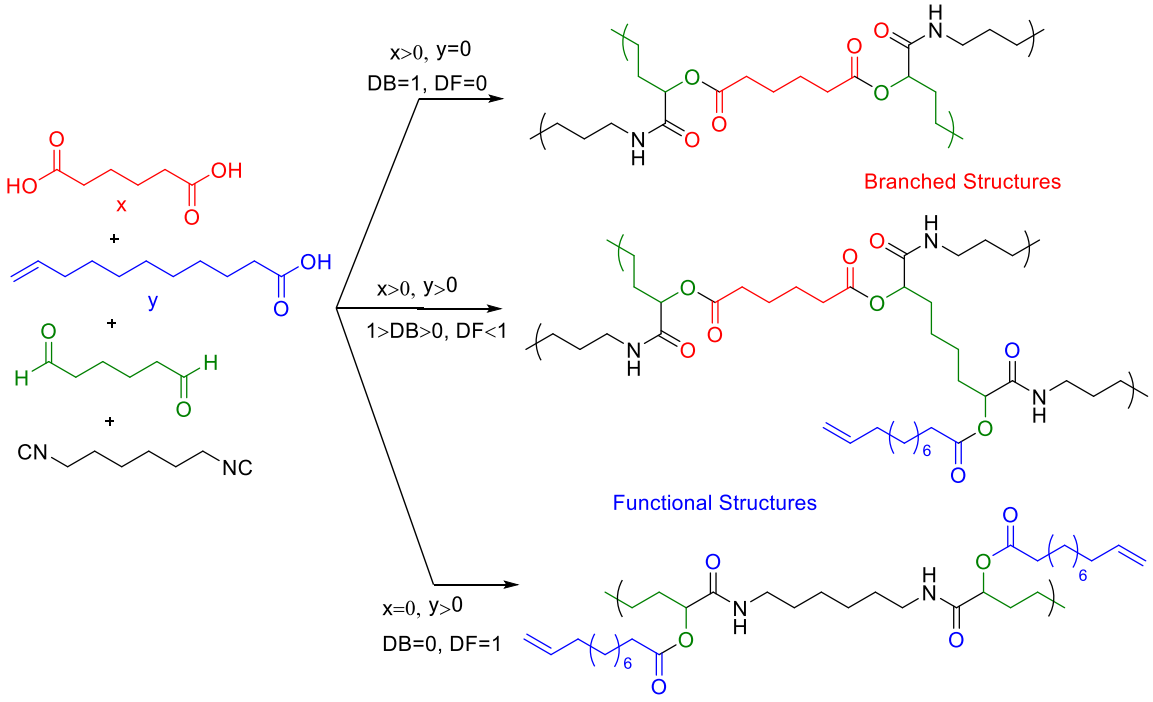


Scheme 1.13 Multicomponent Polymerization via the Passerini Reaction Using Difunctionalized Monomers

1.2.2.3.3 Complex Polymer Architectures

The three-component nature of the Passerini reaction can also make it adaptable to assemble of more complex polymer architectures. For example, Li used this reaction with

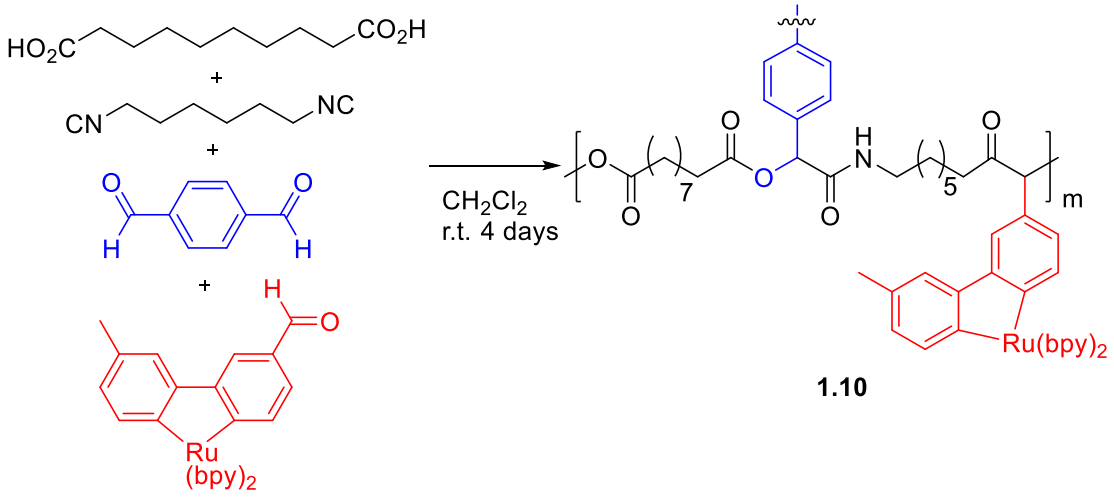
A-A + B-B + C-C type monomers to generate highly branched polymers (HBPs) with the degree of branching (DB) and functional group (DF) controlled by the use of an alkene-functionalized monocarboxylic acid (Scheme 1.14).[54] Controlling polymer branching and functional groups is important to modulate properties such as viscosity, solubility, or glass transition. While the simultaneous control of both of these factors can be difficult to achieve via traditional polymerizations without resorting to synthetically more elaborate monomers, the Passerini reaction provided precise control over the architecture of the HBPs based on the monomer feeding ratio. Unfortunately, only low molecular weights were obtained for polymers with a high degree of branching (DB = 100 %, M_n = 3.5 kDa) due to premature gelation.



Scheme 1.14 Passerini-Based Synthesis of Highly Branched Polymers

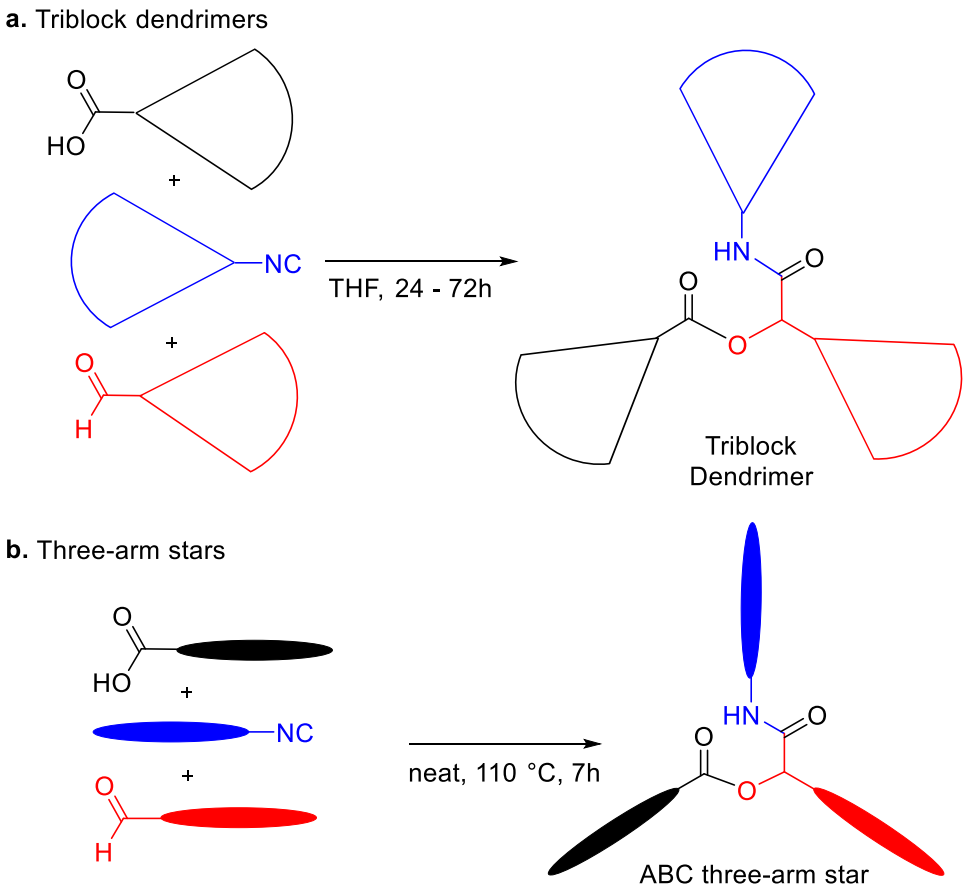
Xie used a similar approach to synthesize cross-linked polymers in which a ruthenium photocatalyst was covalently anchored from a monoaldehyde monomer (Scheme 1.15).[55] The formation of cross-linked polymers as robust and porous materials usually requires high temperature, pressure, and catalyst loading. Here, the Passerini polymerization

proceeded at room temperature to afford an insoluble cross-linked, ruthenium-containing polymer **1.10**. The latter was shown to have utility as a recyclable catalyst for the photocatalytic oxidation of sulfides.



Scheme 1.15 Cross-Linked, Ruthenium Containing Polymers via the Passerini Reaction

The high efficiency of the Passerini reaction has also been used to generate well-defined, monodisperse surface-triblock dendrimers.[56,57] Surface diblock dendrimers are well established. In contrast, dendrimers with more than two different surface functional groups are difficult to synthesize, and had not been previously reported. Rudick demonstrated that three different branched precursors incorporating aldehyde, carboxylic acid, and isocyanide functionalities can be coupled into triblock dendrimers via the Passerini reaction (Scheme 1.16a). The reaction proceeds with a 60% yield, and incorporates three different surface functional groups. The same lab reported more recently a similar convergent approach for the synthesis of three-arm stars (Scheme 1.16b).[58] These materials are typically synthesized from an asymmetric core, and each arm is functionalized in a stepwise fashion (minimum 3 steps). The Passerini reaction allows for the formation of three-arm stars in one-pot in reasonable yields (up to 75%).

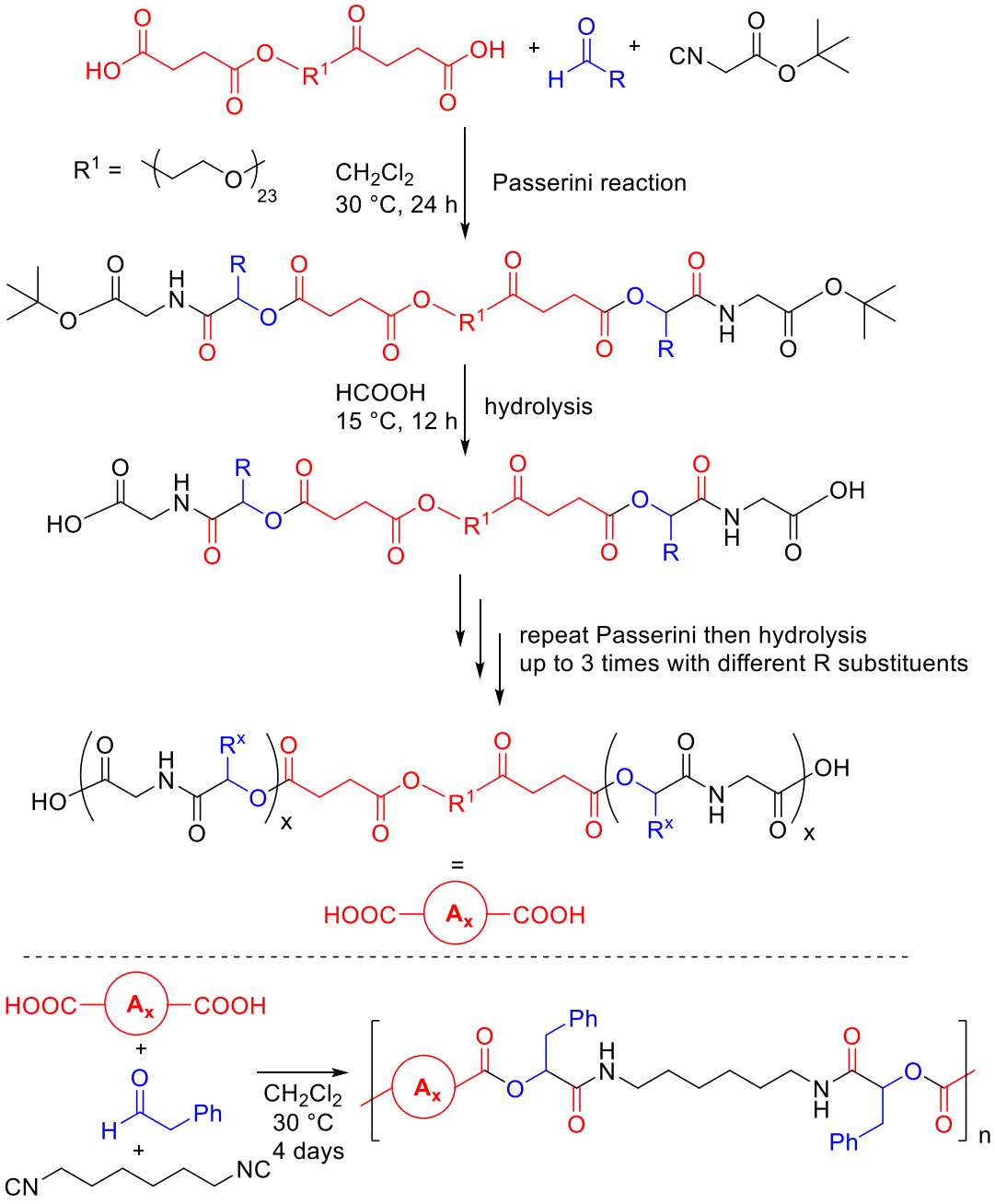


Scheme 1.16 Synthesis of Triblock Dendrimers and Three-Arm Stars via the Passerini Reaction

1.2.2.3.4 Synthesis of Sequence-Defined Polymers

The ability to generate polymers with well-defined monomer sequences, much like DNA, proteins and other biological assemblies, remains a significant challenge in polymer chemistry. The most well-established sequence-defined synthesis of polymers is the Merrifield solid phase peptide synthesis introduced in 1963.[59] Related methods to generate DNA and RNA sequences are also now established.[60-62] However, only a few methods have been reported for the synthesis of sequence-defined polymers.[63,64] In 2013, Li demonstrated that the Passerini reaction can be used to generate sequence-defined, non-biological multi-block copolymers.[65] This strategy involved sequential Passerini reactions

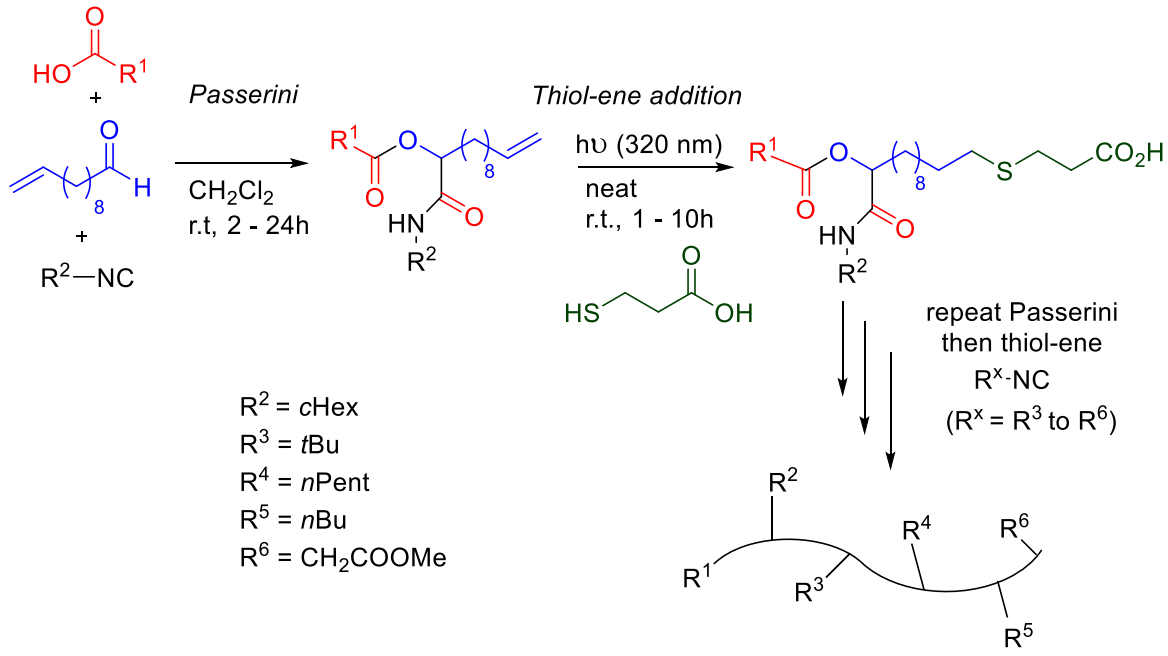
followed by a selective hydrolysis and subsequent Passerini reaction to form oligomers end-capped with carboxylic acids (Scheme 1.17). Once the sequence was generated, a copolymer was formed via a Passerini polyaddition with phenylacetaldehyde and 1,6-diisocyanohexane. They were able to obtain well-defined block copolymers in excellent yield and with M_n up to 55.3 kDa (PDI = 1.5) by using this method.



Scheme 1.17 Synthesis of Well-Defined Block Copolymers Using the Passerini Reaction

In 2014, Meier and coworkers demonstrated that the iterative application of the Passerini reaction and the thiol-ene addition could allow the sequence controlled synthesis of polymers bearing five different side chains (Scheme 1.18).[66] This approach allows for the

synthesis of macromolecules with a precise incorporation of functionalities without using protecting groups or activating reagents.[67]

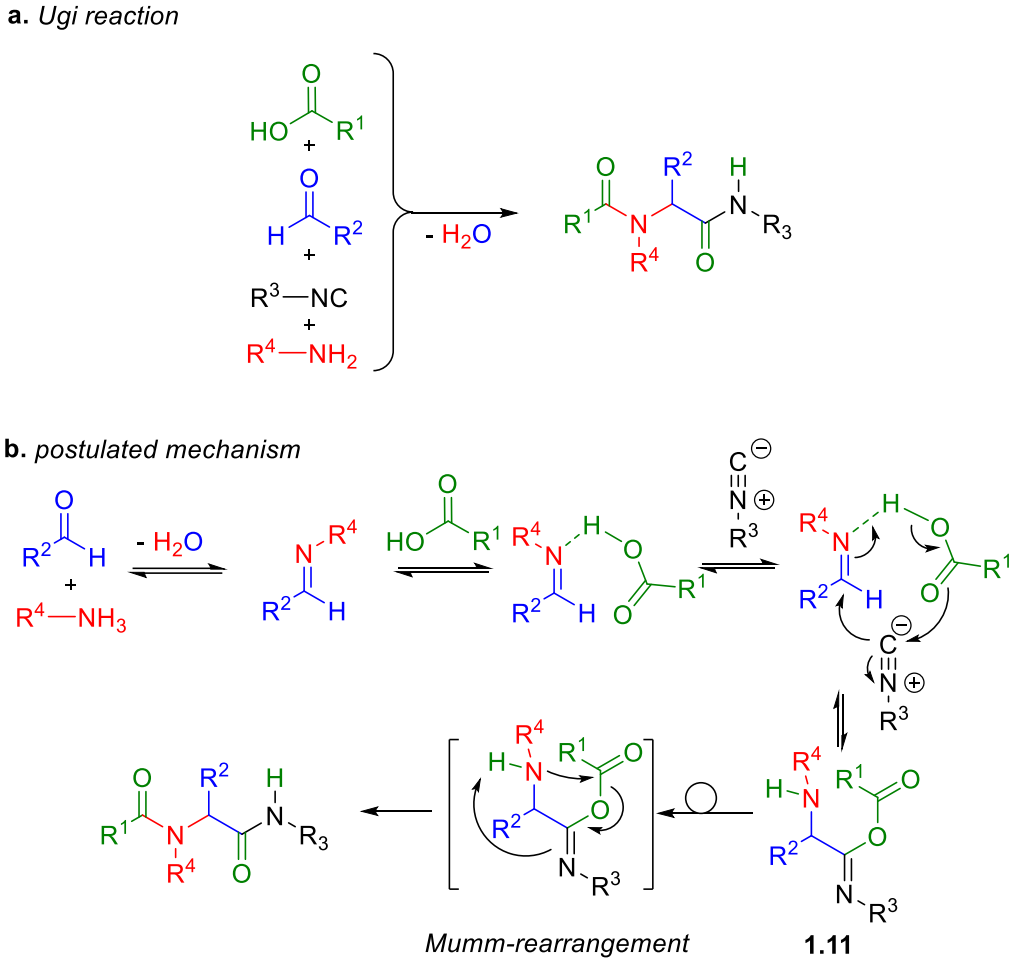


Scheme 1.18 Iterative Synthesis of Oligomers using the Passerini and Thiol-Ene Reactions

1.2.2.4 *The Ugi Reaction in Polymer Synthesis*

The Ugi reaction is among the most commonly employed multicomponent reactions in organic chemistry.[31,32,68-71] This transformation allows the coupling of aldehydes, carboxylic acids, isocyanides and amines in one-pot to generate α-amino acid derivatives (bis-amides) from four diversifiable units (Scheme 1.19a). The mechanism of this complex reaction is related to the Passerini reaction, and involves the series of equilibrium steps shown in Scheme 1.19b including the in situ formation of an imine followed by nucleophilic attack by the isocyanide. This intermediate then spontaneously reacts with the carboxylate to form **1.11**, which then undergoes the final Mumm rearrangement to afford the product.[35,72,73] The Ugi reaction is particularly useful as it allows for four degrees

of tunability, and has been heavily exploited for library formation in pharmaceutical design.[11,74-77]

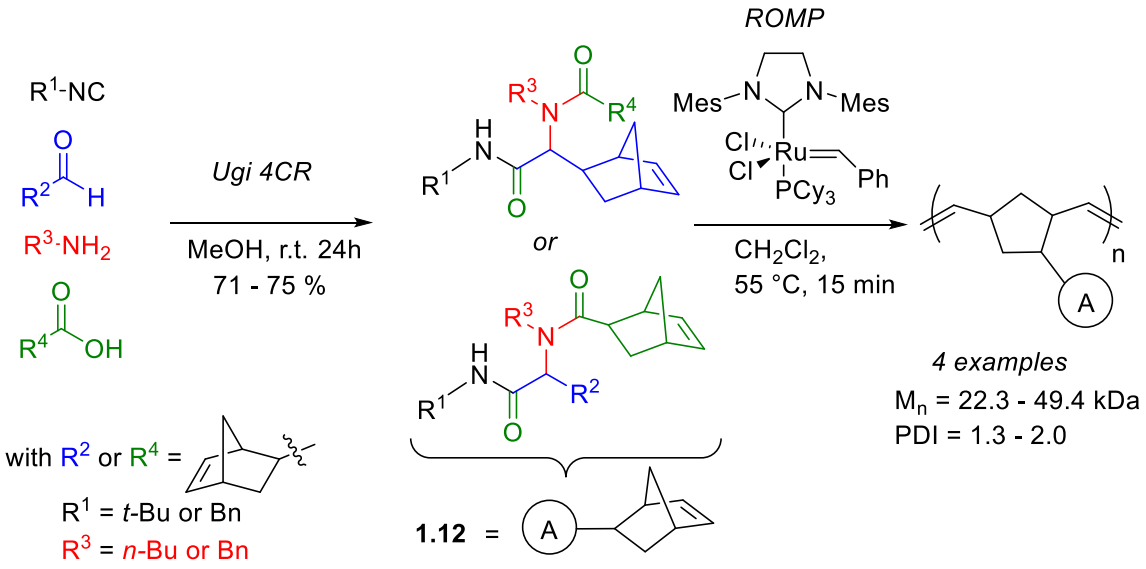


Scheme 1.19 Ugi Four-Component Coupling Reaction

1.2.2.4.1 Synthesis of Monomers via the Ugi Reaction

The first use of the Ugi reaction in polymer synthesis was once again directed towards the multicomponent assembly of monomers. This report, by Wright in 2003, exploited the Ugi reaction to synthesize dipeptide-like substituted norbornenes **1.12**.[78] Four different monomers were obtained in good yields from the reaction of isocyanides, amines, aldehydes and carboxylic acids, where one of the last two was tethered to norbornene.

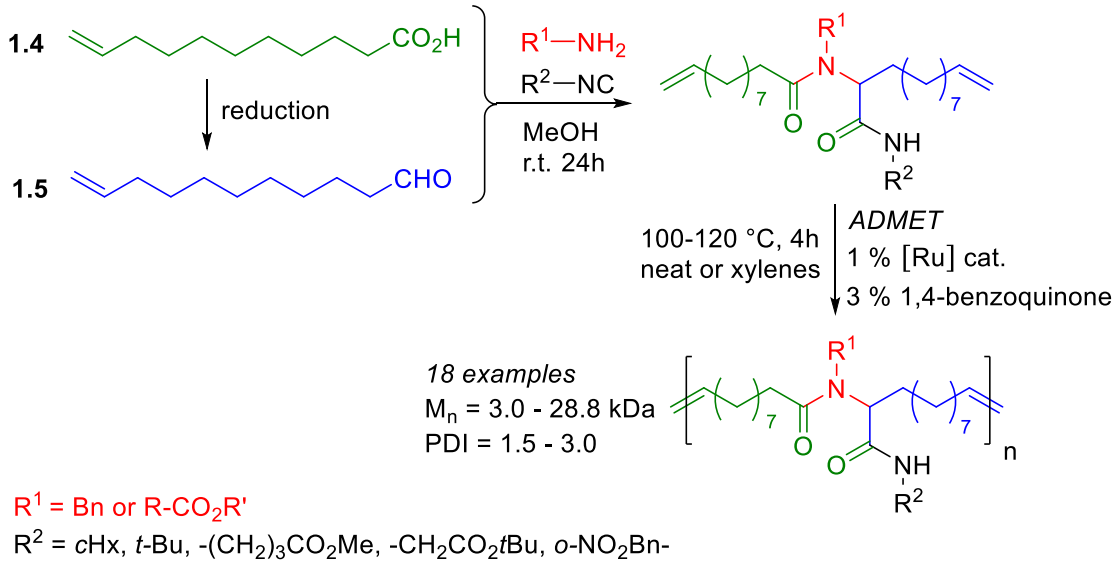
These were polymerized via ROMP using the Grubbs 2nd generation catalyst. While this process does require the synthesis of a norbornene-tethered substrate for the Ugi reaction, the use of norbornene precursors bearing enantio-enriched substituents allowed access to chiral polymers which have potential use in chiral separations.



Scheme 1.20 Synthesis of Norbornene Derivatives Using the Ugi Reaction and ROMP Polymerization

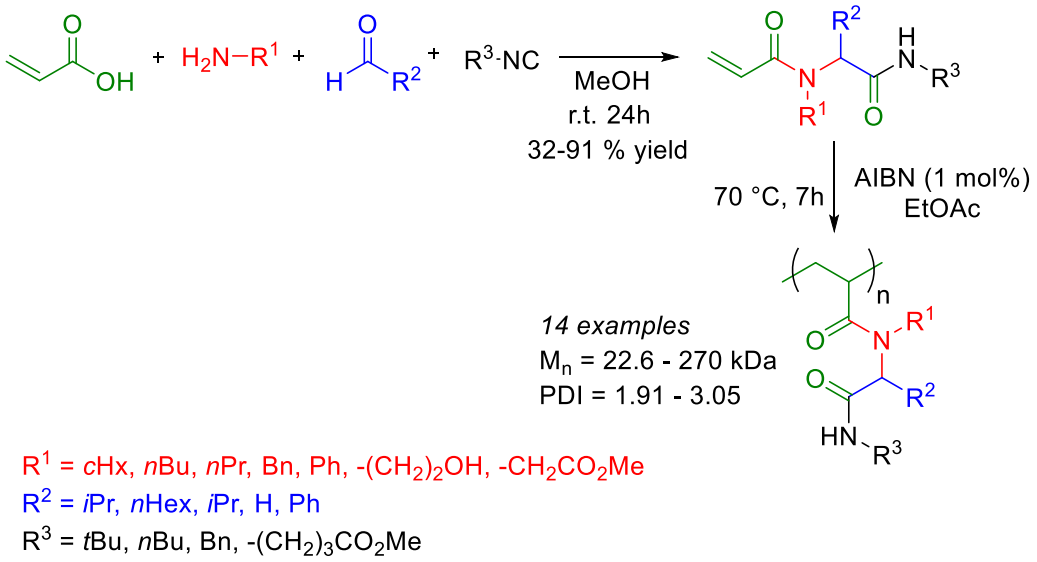
The Ugi reaction has seen recent, renewed interest for the modular synthesis of polymers.[79] In 2012, Meier employed the Ugi reaction in a similar fashion to the Passerini reaction for the synthesis of dienes precursors from ricinoleic acid (**1.4** and **1.5**) for subsequent ADMET polymerization to afford polyamides (Scheme 1.21).[80] One advantage of the Ugi reaction is that it offers an extra degree of diversification compared to the Passerini reaction. Meier exploited this to generate a library of 18 alkene containing monomers from readily available starting materials, including α-amino acid derivatives. Although the synthesis of these monomers was straightforward, the subsequent ADMET polymerization proved problematic, and each substrate had to be separately optimized (M_n = 3.0 to 28.8 kDa). The same reaction was used with convertible isocyanides to generate a range of functionalized polymers via post-polymerization modification.[43] Examples include

polymers bearing tertiary amines for application as organocatalysts, and alkenes or carboxylic acids which offer the possibility for further side chain modification (e.g. via thiol-ene, metathesis, peptide coupling, esterification, etc.).



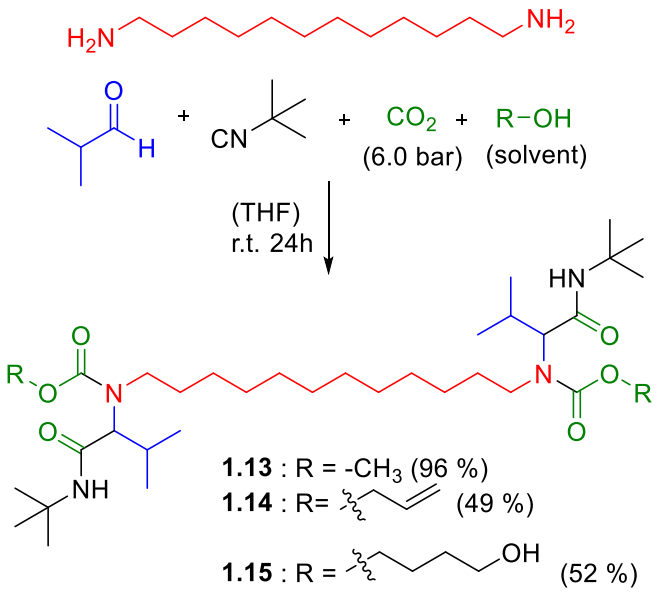
Scheme 1.21 ADMET Polymerization of Monomers Obtained via the Ugi Four-Component Reaction

Another example by the Meier lab showed the use of the Ugi reaction for the synthesis of acrylamides, which can be later polymerized via a free-radical polymerization with AIBN (Scheme 1.22).[81] By using the Ugi reaction, they were able to synthesize a library of 14 acrylamides in moderate to good yields (32 – 91%). Most monomers proved to be suitable for polymerization, and high molecular weight polyacrylamides were obtained (22.6 to 270.1 kDa). The polyacrylamides generated showed potential biocompatibility, which could open the door to biomedical applications for these new polymer scaffolds. Notably, fluorescent tags, chemical sensors or protein-reactive functionalities could also be incorporated onto the side-chain via the Ugi reaction.



Scheme 1.22 Four-Component Ugi Synthesis of Acrylamides for Free-Radical Polymerization

A variant of the Ugi reaction involves the replacement of the carboxylic acid unit with two other components: CO_2 and alcohols. This reaction proceeds in a similar fashion to the four-component Ugi reaction, where the addition of methanol to CO_2 leads to an in situ generated carboxylic acid derivative for subsequent reaction with the amine, aldehyde and isocyanide components. Unlike the typical Ugi reaction, this provides a route to generate a more reactive carbamate (rather than amide) product. This transformation was employed by the Meier group to synthesize dicarbamates monomers (Scheme 1.23).[82] Depending upon the alcohol employed, different polymerizations modes were possible with the monomers. For example, while the Lewis acid catalyzed transcarbamoylation of **1.13** (R=Me) did not afford any polymer, the diene monomer **1.14** could be coupled with 1,4-butanedithiol in the thiol-ene reaction to afford polymer in good yield and molecular weight (up to 19.3 kDa). Alternatively, the diol containing polymer **1.15** was polymerized via polycondensation with diphenyl carbonate to afford a polymer with M_n = 19.7 kDa.

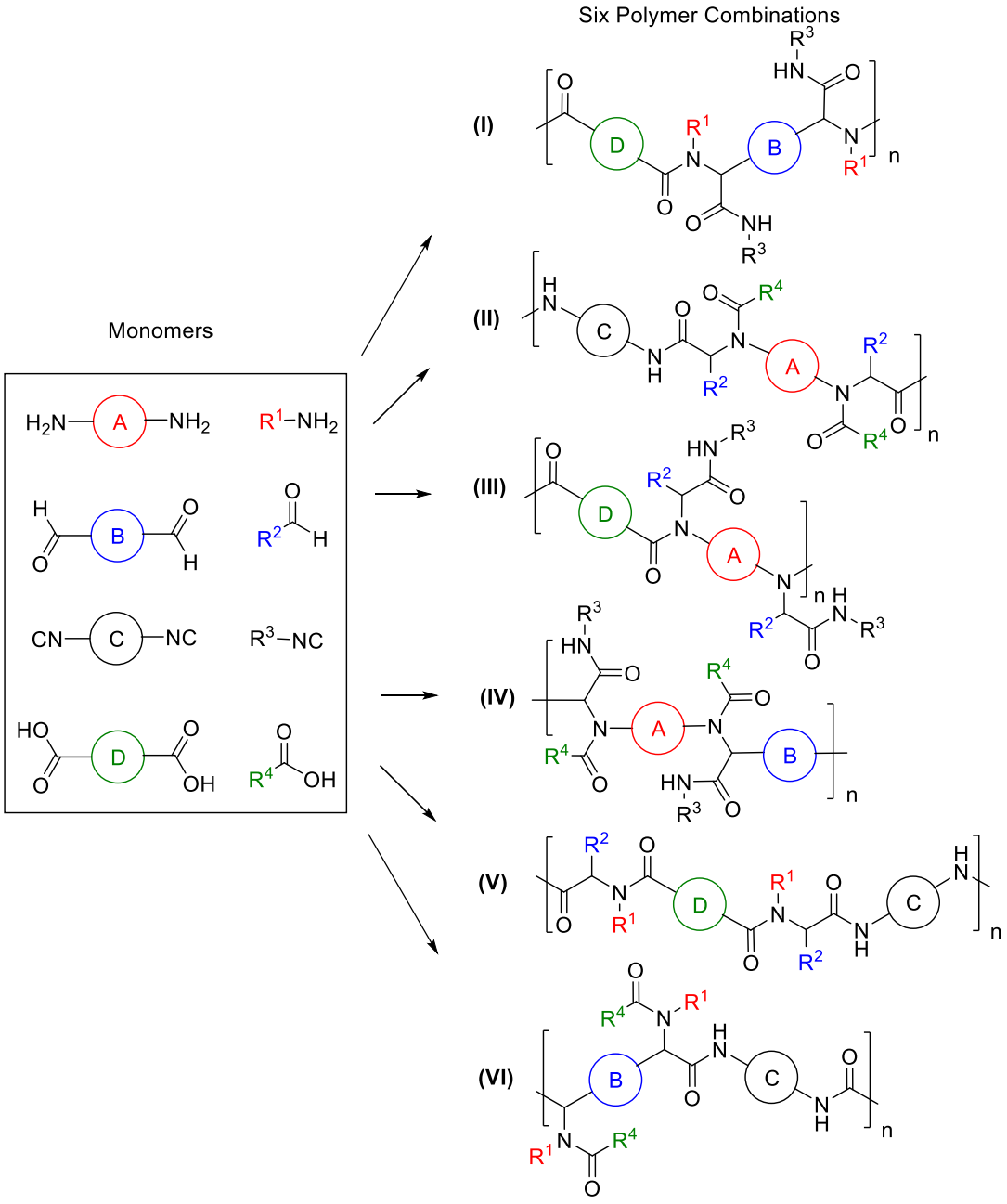


Scheme 1.23 Synthesis of Substituted Dicarbamates Using the Five-Component Ugi Reaction

1.2.2.4.2 Multicomponent Polymerization via the Ugi Reaction

More recent research has shown that the Ugi reaction can be directly applied to the multicomponent synthesis of polymers. In a proof-of-concept study, Meier and coworkers described in a single article that all six different difunctional monomer combinations can lead to linear polymers from the Ugi reaction (Scheme 1.24).[83] Molecular weights of up to 17.8 kDa were obtained with the combination of a diamine, diisocyanide, aldehyde, and carboxylic acid (combination **II**). Certain limitations were noted in these studies; a) a stepwise addition has to be performed in order to pre-form the imine and avoid the Passerini product formation; b) the solvent mixture has to be optimized for each substrate; c) the scope is limited to aldehydes that do not contain acidic α-protons; and d) in some cases, moderate yields were obtained due to the necessity to remove macrocyclic side products via multiple precipitations.

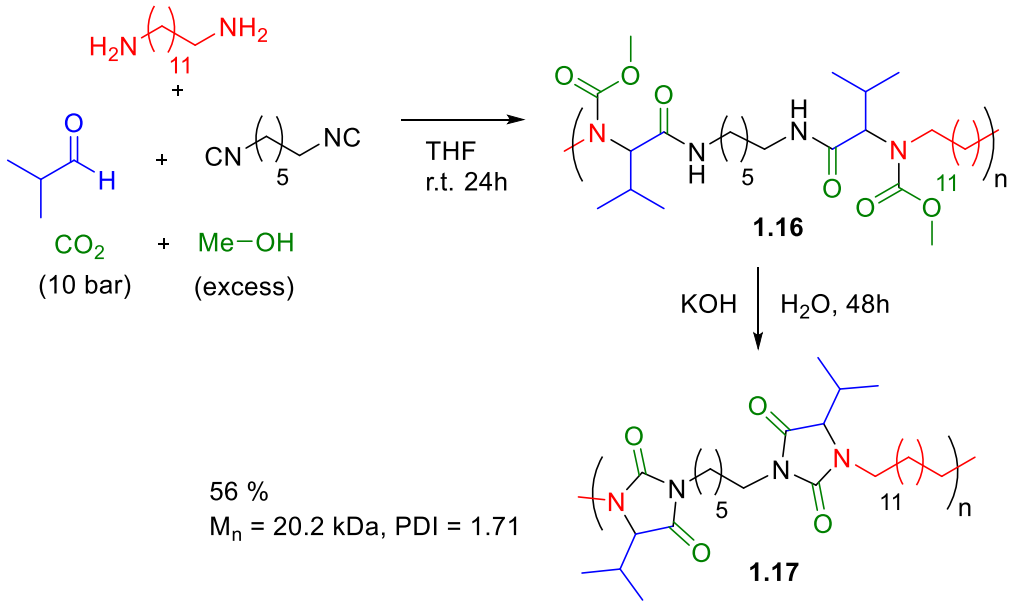
Luxenhofer expanded the scope of these Ugi polycondensation polymerizations to incorporate aromatic monomers under slightly modified reaction conditions.[84] They were also able to generate all six combinations noted in Scheme 1.24. Although certain combinations afforded poor molecular weights, monomer combination **VI** led to molecular weights as high as 44 kDa. They noted that only in this latter reaction is the backbone of the polymer formed before the final step Mumm-rearrangement in the Ugi reaction (see Scheme 1.19). This may explain the lower molecular weights observed for other substrate combinations.



Scheme 1.24 Four-Component Ugi Polycondensation in Polymer Synthesis

The five-component Ugi reaction with CO_2 and methanol has also been employed to generate polymers (Scheme 1.25). While only one variant of this transformation was reported, it provides **1.16** in one step and in good molecular weight (20.2 kDa).[82] In

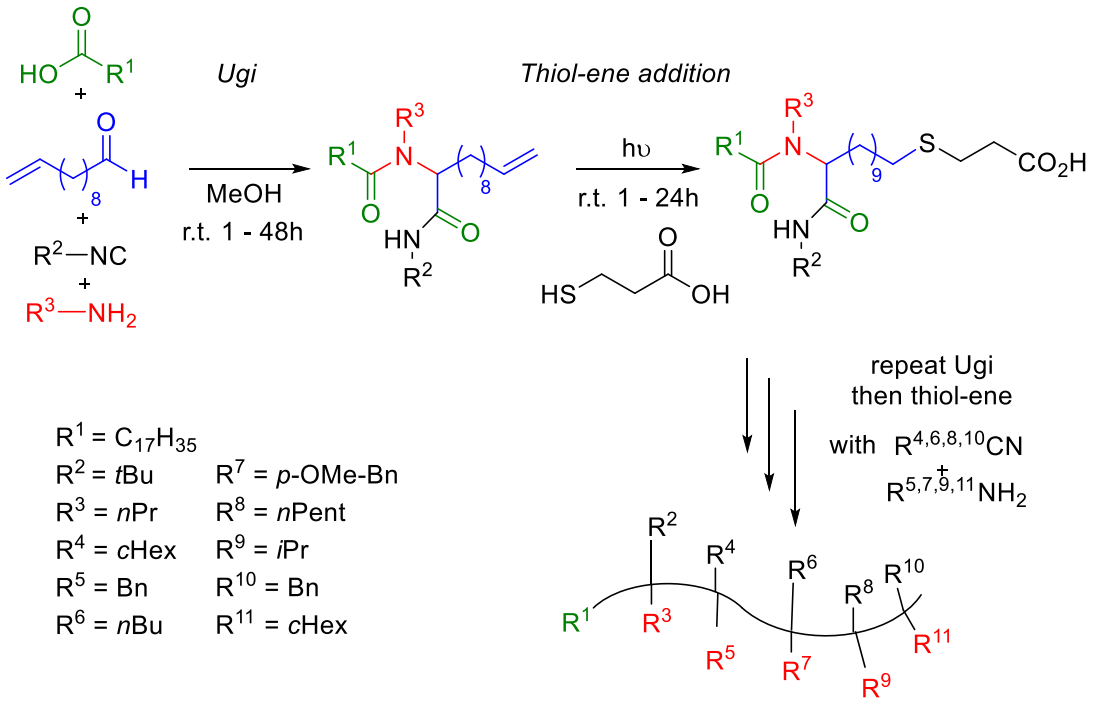
addition, when coupled with deprotection by aqueous KOH, it can allow the overall synthesis of the hydantoin containing polymer **1.17** from a diamine, diisocyanide, aldehyde, and CO_2.



Scheme 1.25 Five-Component Ugi Reaction to Synthesize Polyamides and Polyhydantoin

1.2.2.4.3 Synthesis of Sequence-Defined Polymers

Following a strategy they had already employed with the Passerini reaction, Meier and coworkers have also used the Ugi/thiol-ene reactions to generate sequence-controlled polymers (Scheme 1.26).[85] The advantage of the Ugi reaction over the Passerini is its ability to simultaneously control two side chains at each insertion, thereby allowing for a greater degree of structural diversification (e.g. with eleven distinct groups $R^{1\text{-}11}$).



Scheme 1.26 Sequential Ugi and Thiol-Ene Addition Reaction for the Synthesis of Well-Defined Oligomers

1.2.2.4.4 Post-Polymerization Functionalization via the Ugi Reaction

While not formally a topic of this chapter, it is notable that the Ugi reaction has also been used in a number of post-polymerization transformations.[79] This strategy has been explored for various applications by the Tao lab, including the synthesis of fluorescent polymers,[86] multifunctional PEGylation agents for protein conjugation,[87] and the hexa-component one-pot formation of polymer-conjugated carbon nanotubes.[88]

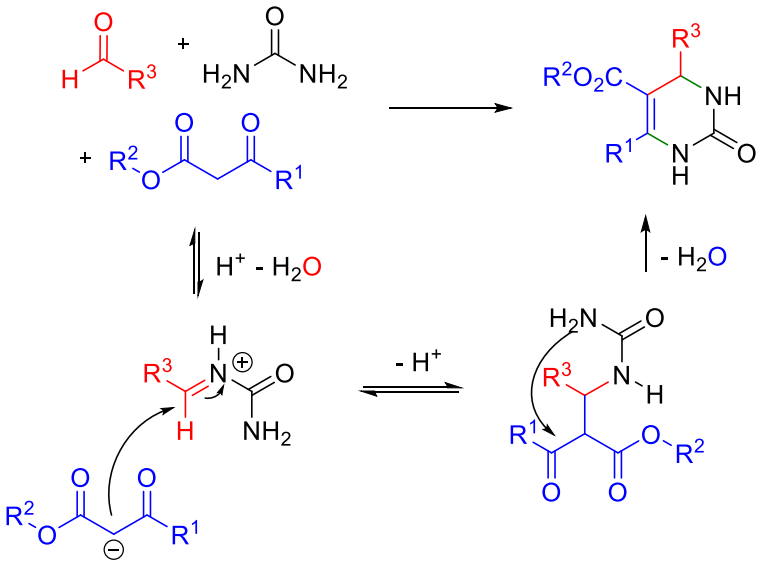
1.2.3 Cyclic Repeat Units from Multiple Monomers

The polymer structures described above are generally composed of the three monomers alternating along the polymer chain, or as substituent(s) on the backbone. An alternative use of MCRs in polymer synthesis is to assemble a more complex cyclic unit from three

different building blocks at the same time as the polymer. While this area has been much less heavily explored, a few examples of such reactions have recently emerged and are highlighted below.

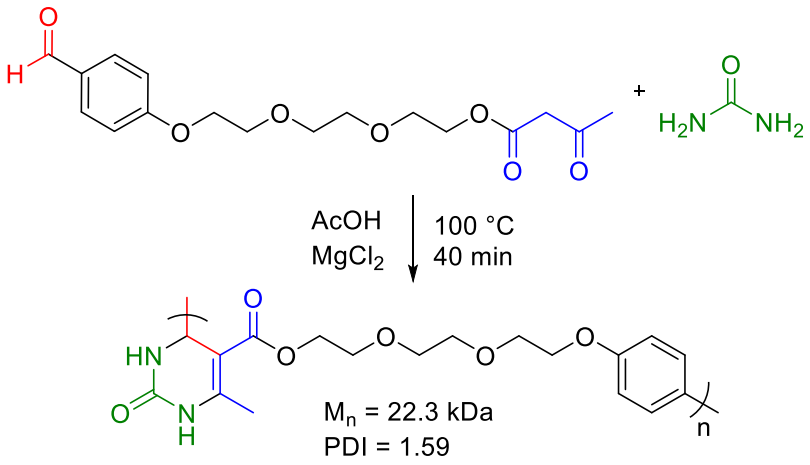
1.2.3.1 *The Biginelli and Hantzsch Reactions*

Since its discovery in 1893, the Biginelli reaction has been widely used in organic synthesis for accessing dihydropyrimidones in a modular fashion from aldehydes, ureas, and 1,3-diones (Scheme 1.27).[89-93]



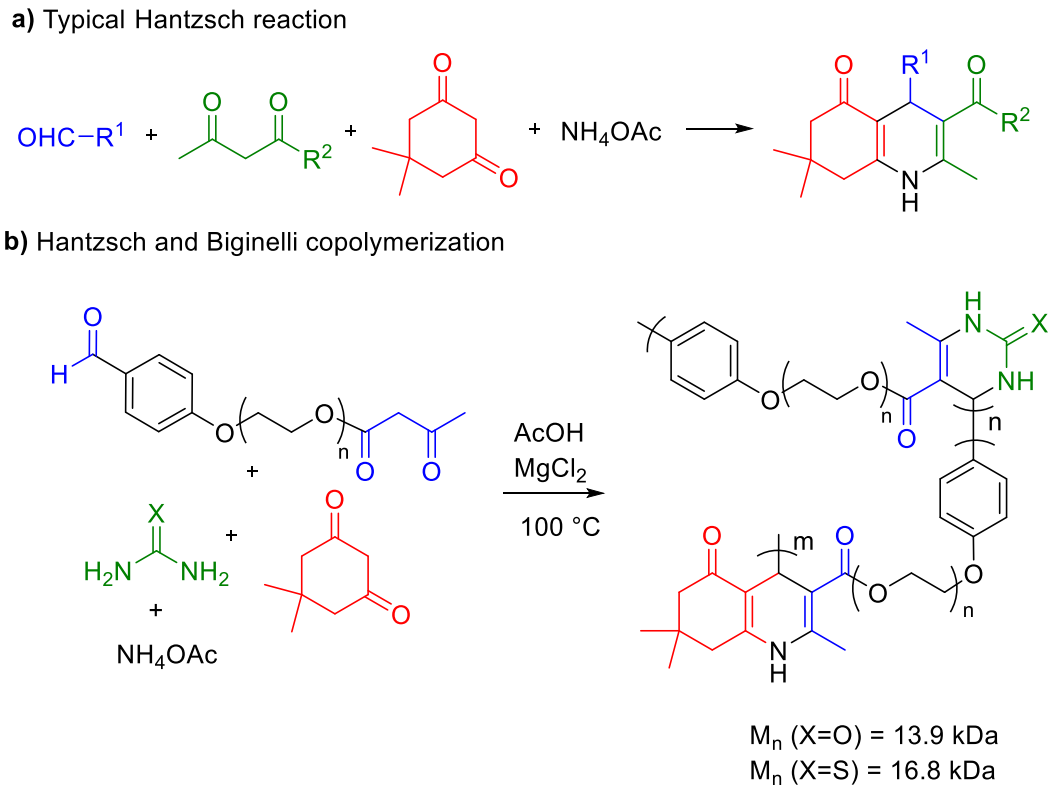
Scheme 1.27 Biginelli Three-Component Reaction

Despite its ability to efficiently access heterocyclic structures, only two examples of the use of the Biginelli reaction to generate well-defined polymers have been reported, both coming from the Tao laboratory.[94] In their first example, Tao employed an aldehyde-tethered 1,3-dione and urea to generate a dihydropyrimidone-containing polymer (Scheme 1.28).[95] The polymer was obtained on a multigram scale within 40 min at 100 °C and in good molecular weights (22.3 kDa). Although only one polymer structure was reported, this polymerization platform offers the possibility for tuning the structure by varying the tether between the aldehyde and the dione.



Scheme 1.28 Biginelli Reaction in Polymer Synthesis

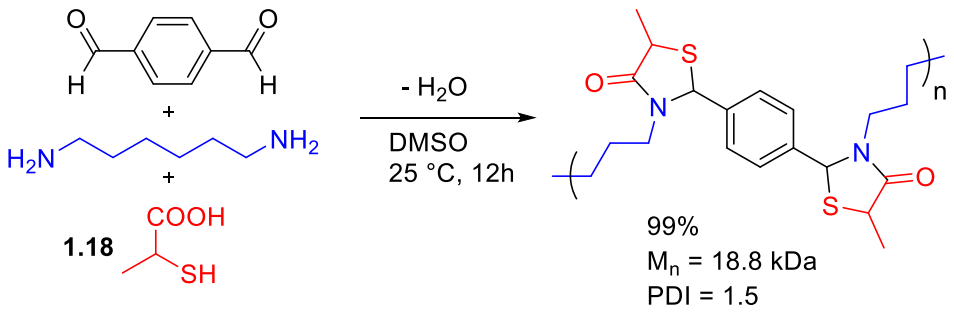
The second example by the Tao lab uses the Biginelli reaction together with a second MCR, the Hantzsch reaction, to generate random copolymers (Scheme 1.29b).[96] The Hantzsch reaction also relies upon a 1,3-dione building block, which in this case couples with an aldehyde, amine and cyclic dione to form dihydropyridines (Scheme 1.29a).[97,98] By exploiting this common unit, the authors were able to generate copolymers using a combination of five different functional units, where modulation of the ratios of functional groups can be used to tune the polymer structure.



Scheme 1.29 One-pot Copolymerization via the Biginelli and Hantzsch Reactions

1.2.3.2 *The Mercaptoacetic Acid Locking Imine (MALI) Reaction*

The mercaptoacetic acid locking imine (MALI) was first introduced by Erlenmeyer and Oberlin in 1947 to generate 4-thiazolidones from aldehydes, mercaptoacetic acids, and amines, with high atom efficiency (only loss of water), without a metal catalyst, and under mild conditions.[99] This reaction presumably proceeds via the formation of an imine intermediate followed by the addition of the mercaptoacetic acid **1.18** across the C=N bond. Its use in polymer science was first described by Tao and coworkers in 2014.[100] In this paper, the MALI reaction of dialdehydes, diamines and mercaptoacetic acid allowed the formation of a heterocycle-containing polymer with good molecular weight (M_n = 18.8 kDa, PDI = 1.5) and under mild conditions (Scheme 1.30). Despite the potential of this reaction for diversification (with three easily modified monomers), only one example of polymer structure was reported in the article.



Scheme 1.30 MALI Reaction in Multicomponent Polymerization

1.3 Metal-Catalyzed and Mediated Multicomponent Polymerizations

Metal-catalyzed and -mediated multicomponent coupling reactions provide an alternative toolbox for the synthesis of polymers. The diverse reactivity of transition-metal catalysts (e.g. ligand substitution, oxidative addition/reductive elimination, nucleophilic/electrophilic attack, migratory insertion, and cycloaddition) is well-established to provide a method to convert available, often unreactive monomers into polymers. In addition, the order of the steps that occur on the catalyst can control substrate assembly. Together, these features suggest the potential utility of metal-catalyzed multicomponent reactions in converting multiple simple and often unreactive building blocks into well-defined products.[2,101-111] While those features seem attractive, only a few examples of the applications of transition metal catalysis to multicomponent polymerizations have been reported. These are highlighted below.

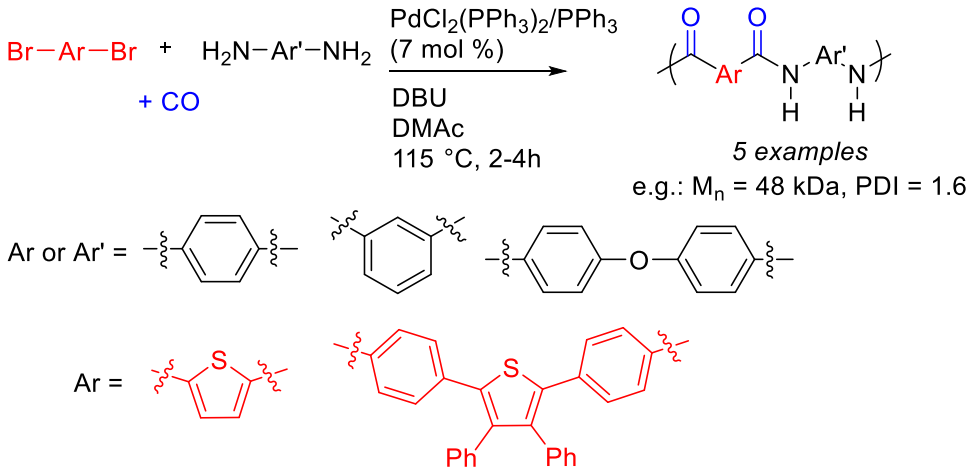
1.3.1 Multicomponent Polymerizations with Two Diversifiable Units

Similar to that noted in organic multicomponent polymerization reactions, a number of the early examples of metal-catalyzed multicomponent polymerizations involved the use of only two diversifiable units, with the third monomer often being a simple substrate such as CO or CO_2. While these only offer the possibility of tuning two building blocks,

multicomponent polymerizations based upon these building blocks can provide alternative methods to construct polyesters and polyamides from simplified substrates.

1.3.1.1 *Palladium-Catalyzed Carbonylations in Multicomponent Polymerization*

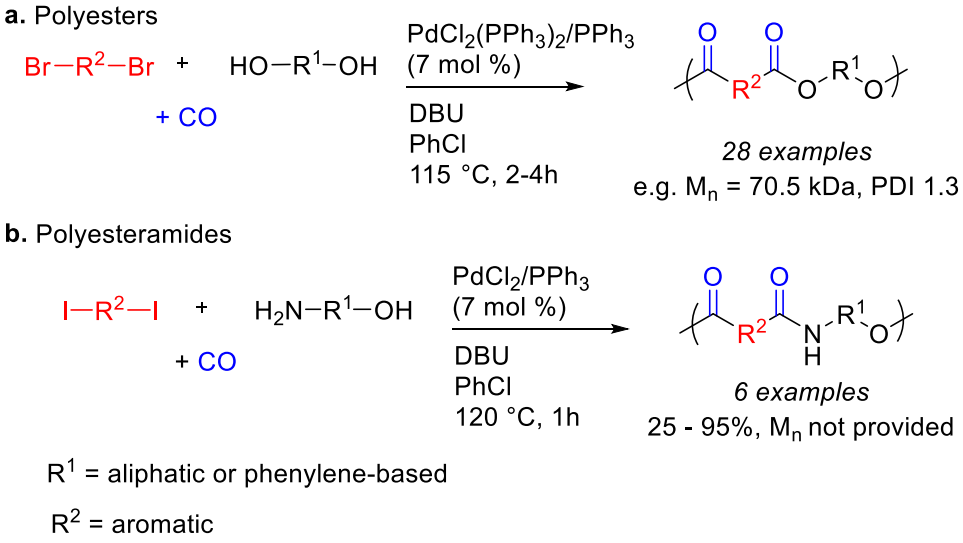
Perhaps the simplest version of a metal catalyzed multicomponent polymerization involves the use of carbonylative coupling reactions. For example, Imai described in 1988 the palladium-catalyzed carbonylative coupling of aromatic-dibromides and -diamines to generate polyamides (Scheme 1.36).[112] In addition to arene-containing monomers, they were also able to incorporate thiophene units by using 2,5-dibromothiophene. Relative to the typical synthesis of polyamides from diamines and sensitive diacid chlorides, an attractive feature of this approach is that it employs substrates that are stable and available. Since this work, a number of variants of this reaction have been reported,[113] including those with aromatic-diiodides[114] or -dichlorides,[115] and using a less expensive nickel catalyst.[116]



Scheme 1.31 Palladium-Catalyzed Carbonylative Synthesis of Polyamides

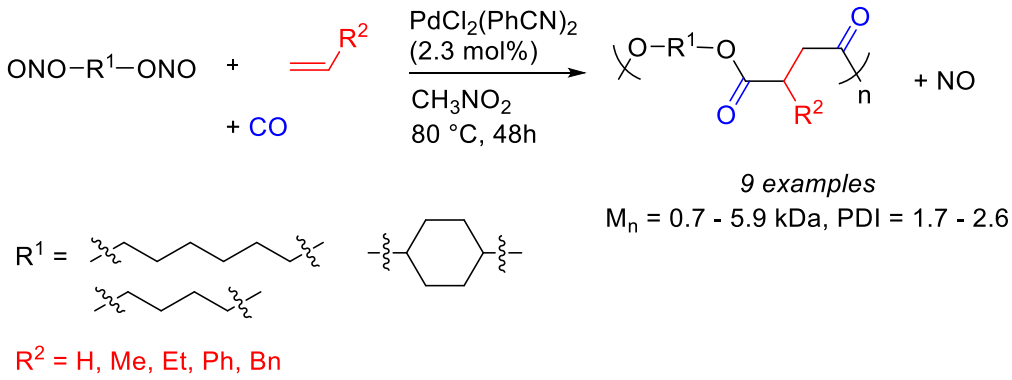
Imai also reported the synthesis of polyesters via the palladium-catalyzed carbonylation coupling of aromatic dibromides and diols (Scheme 1.32a).[117] A wide range of diols were tolerated in this reaction, including aliphatic and aromatic diols. In related work, Chaudhari described in 2001 the palladium-catalyzed carbonylative coupling of aryl diiodides with amino alcohols to generate polyesteramides (Scheme 1.32b).[118,119] Six

different polymeric structures were obtained, although the low viscosities reported indicate a low degree of polymerization.[120]



Scheme 1.32 Palladium-Catalyzed Carbonylative Multicomponent Polymerizations

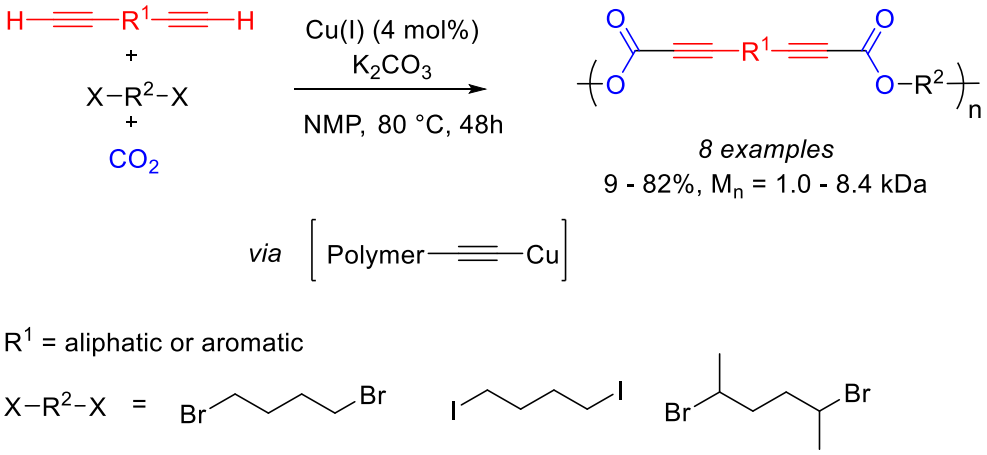
Sen reported an interesting alternative synthesis of polyesters via the palladium-catalyzed carbonylation of dinitrites and alkenes (Scheme 1.33).[121] This transformation allows for the incorporation of a side chain functionality via the use of substituted alkenes. Nine different polymers were synthesized although only in low molecular weights (M_n = 0.7 – 5.9 kDa). A drawback of this reaction is the generation of nitric oxide as a by-product, although the authors suggest this could theoretically be reused to synthesize the nitrite monomers.



Scheme 1.33 Palladium-Catalyzed Carbonylative Synthesis of Polyesters from Dinitrites and Alkenes

1.3.1.2 *Copper-Catalyzed Multicomponent Polymerizations with Carbon Dioxide*

In addition to carbonylations, CO_2 has also been employed in transition metal catalyzed multicomponent polymerization reactions. The earliest example of this transformation was reported in 1996 by Inoue and coworkers in the copper catalyzed coupling of diynes and alkyl dihalides with CO_2 to form polyesters (Scheme 1.34).[122] Much like the use of CO_2 in organic multicomponent polymerizations (section 1.2.1), this reaction presumably involves the *in situ* generation of a copper-acetylide nucleophile for sequential nucleophilic reactions with CO_2 then the alkyl halide. Dialkynes with aromatic linkers were well tolerated, affording polymers with low molecular weights. On the other hand, aliphatic dialkynes only afforded very low yields (9%). The scope of alkyl dihalides was only briefly explored, showing that alkyl iodides afforded lower yields (34%) compared to bromides (up to 82%).



Scheme 1.34 Copper-Catalyzed Three-Component Synthesis of Polyesters

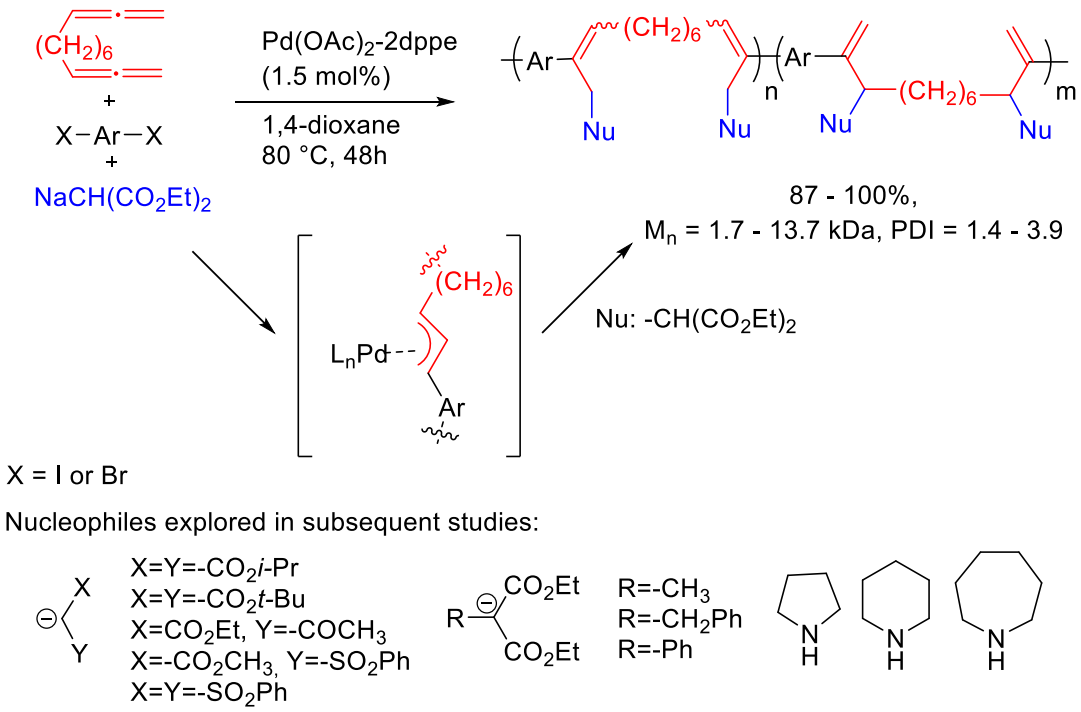
1.3.2 Multicomponent Polymerizations with Three or More Diversifiable Units

The reactions described above allow for only two degrees of flexibility. In the late 1990s, several labs started exploiting metal-catalyzed multicomponent reactions to build larger libraries of polymers from three different diversifiable units.

1.3.2.1 *Palladium-Catalyzed Multicomponent Cross-Coupling Reactions*

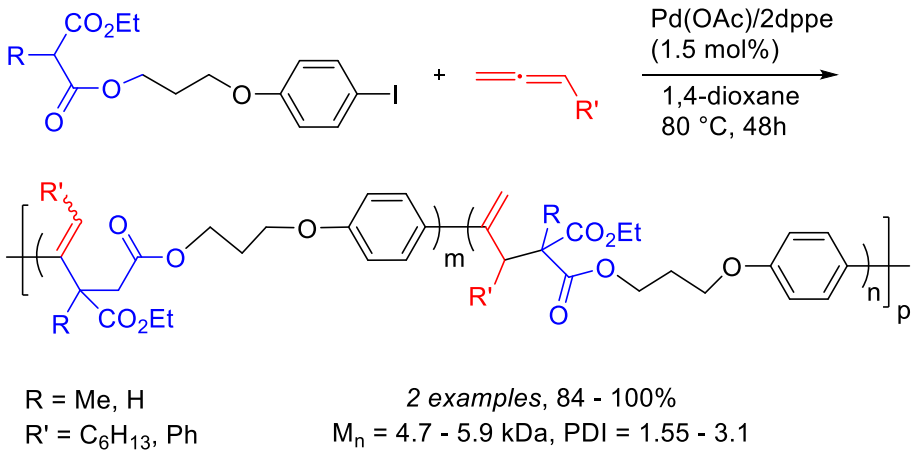
The first example of a metal-catalyzed multicomponent polymerization with three diversifiable substrates was reported by Tomita and Endo in 1996. The reaction involves the palladium-catalyzed coupling of dihaloarenes, bis-allenes and a nucleophile (sodium diethyl malonate) to generate well-defined alternating terpolymers (Scheme 1.35).[123] Similar to small molecule coupling with allenes, this reaction presumably involves the insertion of an allene into an in situ generated palladium-aryl bond to form a palladium π-allyl complex that can undergo nucleophilic attack to generate the alkene-containing polymer. Although this reaction allows the potential to modify all three coupling partners, the scope of the reaction was only briefly explored to show that longer and more rigid

linkers between the aryl halides afforded higher molecular weight polymers (M_n = 13.7 kDa), and no difference in reactivity was observed between aryl-iodides and -bromides. In a follow-up paper, the same group investigated the ability of other nucleophiles to be incorporated into the polymer.[124] Eleven different nucleophiles proved effective in the synthesis of polymers, including soft carbanions and cyclic amines. Notably, varying the nucleophile allowed modification of the decomposition and glass transition temperature of the polymers (T_{dec} = 296 – 352 °C and T_g = 28 – 73 °C).



Scheme 1.35 Palladium-Catalyzed Three-Component Polymerization with Bis-allenes

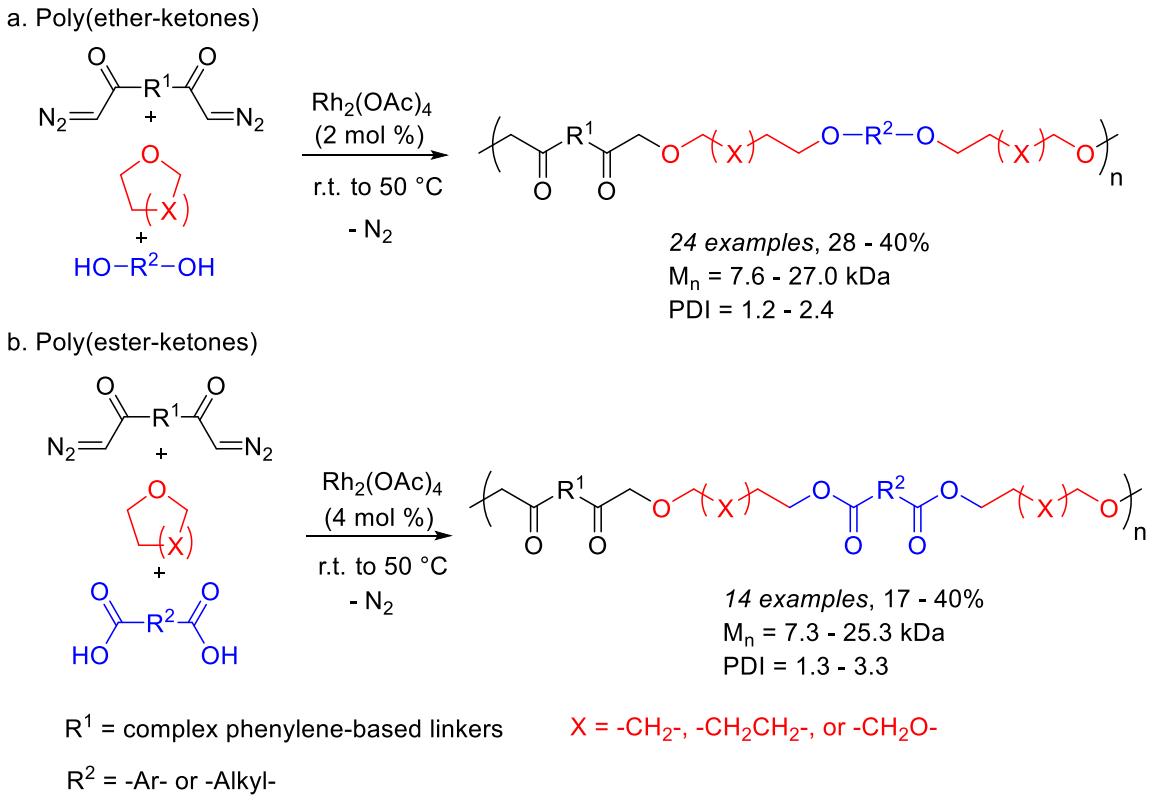
A limitation of the above reaction is the availability and stability of bis-allenes, which can be challenging to prepare. To address this, these same authors examined the palladium-catalyzed coupling of simple allenes with malonate-tethered aryl iodides.[125] Two different polymers were generated in this reaction, but in low molecular weights (up to 5.9 kDa, Scheme 1.36). Alternatively, this same work described the use of a nucleophile bearing two aryl iodide units to generate multibranched polymers (M_n up to 3.4 kDa).



Scheme 1.36 Palladium-Catalyzed Multicomponent Coupling Polymerization with Simple Allenes

1.3.2.2 *Rhodium-Catalyzed Diazoalkane-Diol-Ether Polymerizations*

Inoue and co-workers reported in 2010 that $Rh_2(OAc)_4$ can catalyze the three component polymerization of bis(diazoketones), diols, and cyclic ethers such as THF to form poly(ether-ketones) (Scheme 1.37a).[126] In this system, a rhodium-carbene complex is presumably generated from the diazo monomer, which can subsequently react as an electrophile with THF, followed by ring opening of the latter by the alcohol. While providing access to complex polymers incorporating both ketone and ether functionalities, this reaction presents some limitations: yields and molecular weights reported are low, and the cyclic ether is not fully incorporated, leading to defects in the polymer. Despite those limitations, this reaction allows good flexibility and 24 different structures were reported from a small library of starting materials. More recently, Inoue demonstrated that the diols in this reaction can be replaced with dicarboxylic acids, thereby allowing the synthesis of 14 different polyester-ketones (Scheme 1.37b).[127]

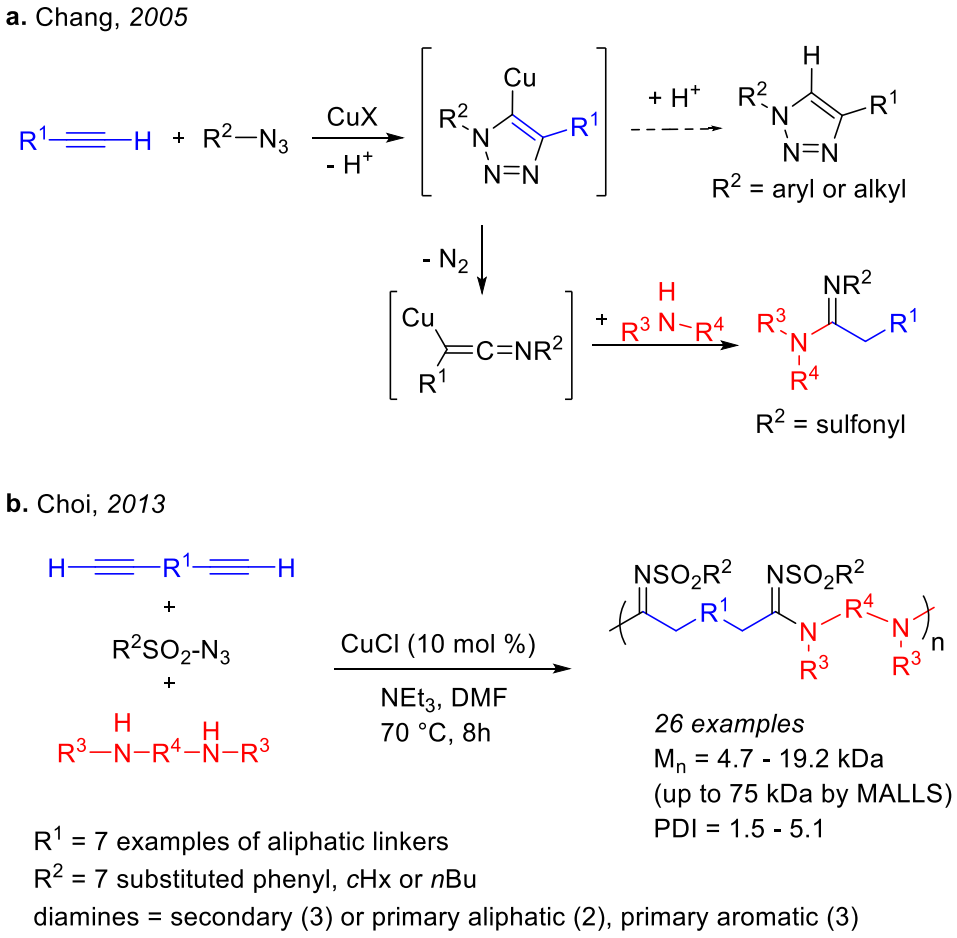


Scheme 1.37 Rhodium-Catalyzed Multicomponent Synthesis of Poly(ethers) and Poly(esters)

1.3.2.3 *Copper-Catalyzed Azide-Alkyne Cycloadditions*

The copper-catalyzed coupling of terminal alkynes and substituted azides to form triazoles proceeds in high yields, with no by-products, and high modularity/functional group compatibility (i.e., a "Click" reaction). As these are each desirable features in polymer synthesis, alkyne/azide coupling has seen significant use in assembling macromolecules.[128-132] While alkyne/azide couplings only involve two components, recent research has shown this platform can also be expanded to multicomponent reactions. Chang reported the copper-catalyzed three-component reaction of alkynes, sulfonyl azides and amines to generate sulfoamidines (Scheme 1.38a).[133] The reaction proceeds via the classic Cu-catalyzed azide-alkyne cycloaddition (CuAAC), but instead of forming the well-known triazole, undergoes thermal ring-opening via the loss of nitrogen followed by

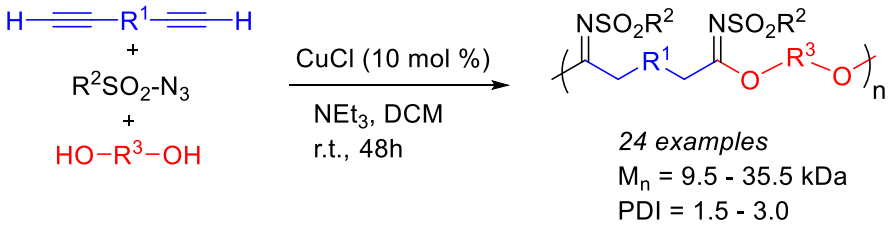
the nucleophilic attack of the amine. By using this reaction in multicomponent polymerizations with dialkynes, sulfonyl azides and diamines, Choi was able to obtain poly(N-sulfonylamidines) with molecular weights as high as 75 kDa, as determined by SEC-MALLS (Scheme 1.38b).[134] Importantly, all three monomers could be easily modulated. This allowed for the synthesis of a library of 26 poly(N-sulfonylamidines).



Scheme 1.38 Multicomponent Copper-Catalyzed Synthesis of Sulfoamidines and Poly(N-Sulfoamidines)

In a separate work, the Choi laboratory demonstrated that the same reaction with diols, instead of diamines, can be used to form a library of poly(N-sulfoimidates).[135] Again, each

of the three monomers can be modulated, allowing the build-up of 24 structurally distinct polymers in good molecular weights (between 9.5 and 33.5 kDa, Scheme 1.39).

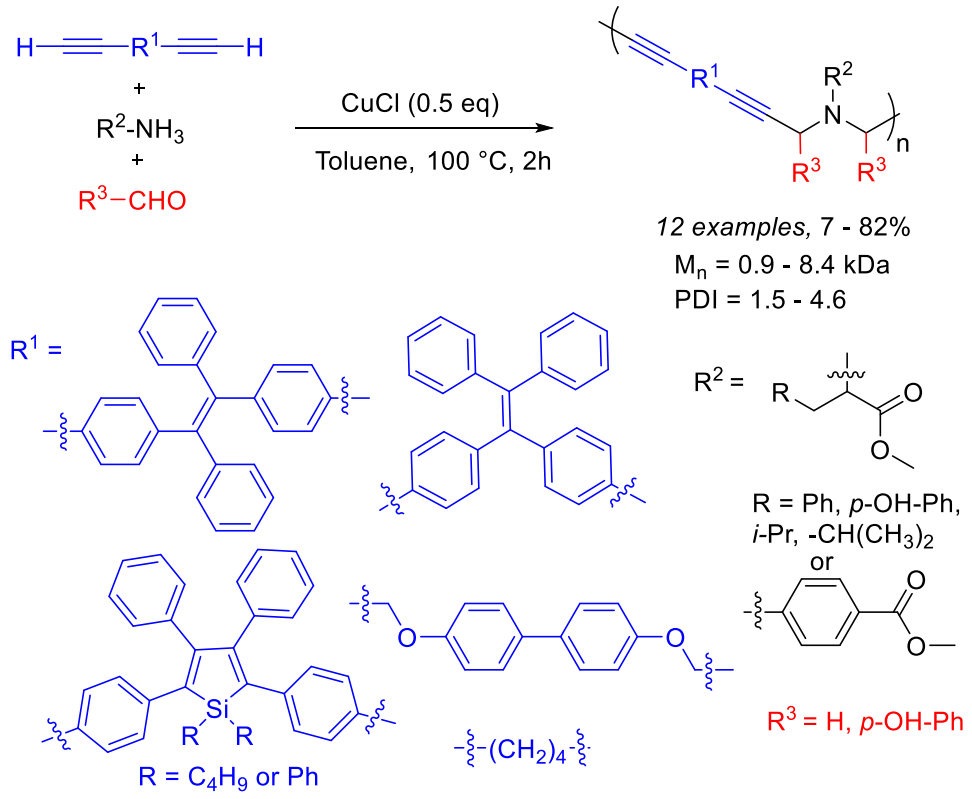


R^1 = 4 examples of aliphatic linkers, 1 example of aromatic
R^2 = 5 examples of substituted phenyls, *c*Hx
R^3 = includes 7 aliphatic, 1 benzylic, 2 aromatic, 1 chiral diol

Scheme 1.39 Copper-Catalyzed Multicomponent Synthesis of Poly(N-Sulfoimidates)

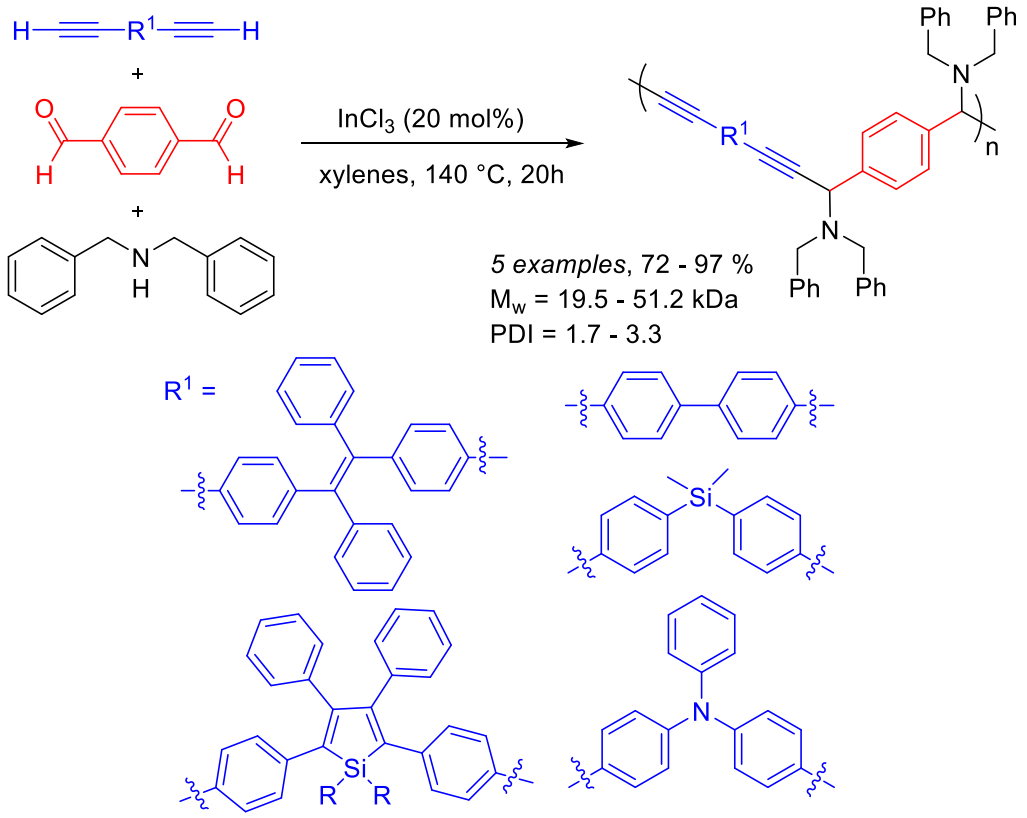
1.3.2.4 *Metal-Catalyzed A^3 Coupling Reactions*

Another copper-catalyzed MCR is the aldehyde-amine-alkyne (A^3)-coupling reaction developed by Li and co-workers.[136,137] Tang et al. applied this reaction to polymer synthesis via the coupling of diynes, primary amines and aldehydes into poly(dipropargylamines) (Scheme 1.40).[138] All three monomers could be diversified, yielding 12 different polymer structures. The advantage of this approach is to rapidly generate a library of polymers with modular properties for different applications. Examples of these included photopatterning of fluorescent polymers with a modular emission energy and explosive detection.



Scheme 1.40 Copper-Catalyzed Polymerization via an A^3-Coupling Reaction

The Tang laboratory also reported the A^3-coupling reaction of diynes, terephthaldehyde and dibenzylamine, in this case with an $InCl_3$ catalyst (Scheme 1.41).[139] Although this reaction afforded better yields and higher molecular weights than those noted in Scheme 1.40, it does not display significant structural flexibility, and only the dialkyne was modified.



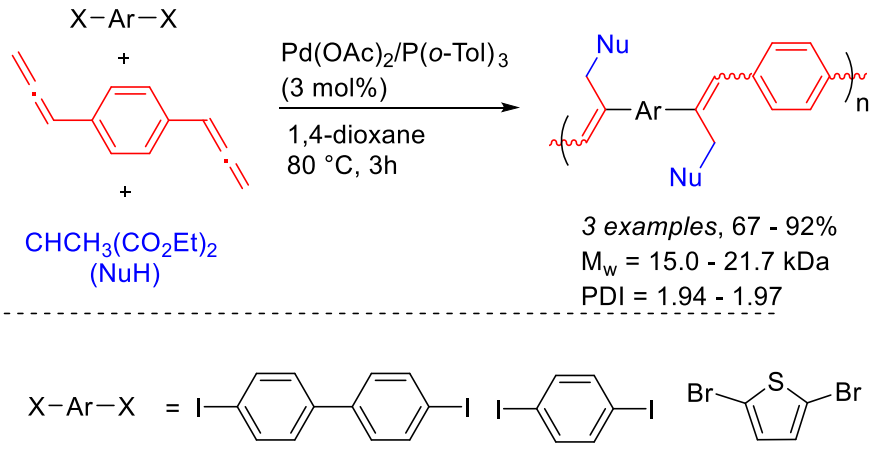
Scheme 1.41 Indium-Catalyzed Multicomponent Polymerization via an A^3-Coupling Reaction

1.3.3 Multicomponent Synthesis of Conjugated and Cross-Conjugated Polymers

One area where multicomponent polymerizations could prove useful is in the synthesis conjugated polymers. These materials have found utility in a wide range of electronic applications (e.g. transistors, solar cells, light-emitting devices, sensors).[140-147] Importantly, the electronic properties of conjugated polymers are strongly dependent upon their molecular structure; hence the necessity to easily access tunable architectures.[148-151] Nevertheless, only a very few examples of multicomponent conjugated and cross-conjugated polymer syntheses have been reported.

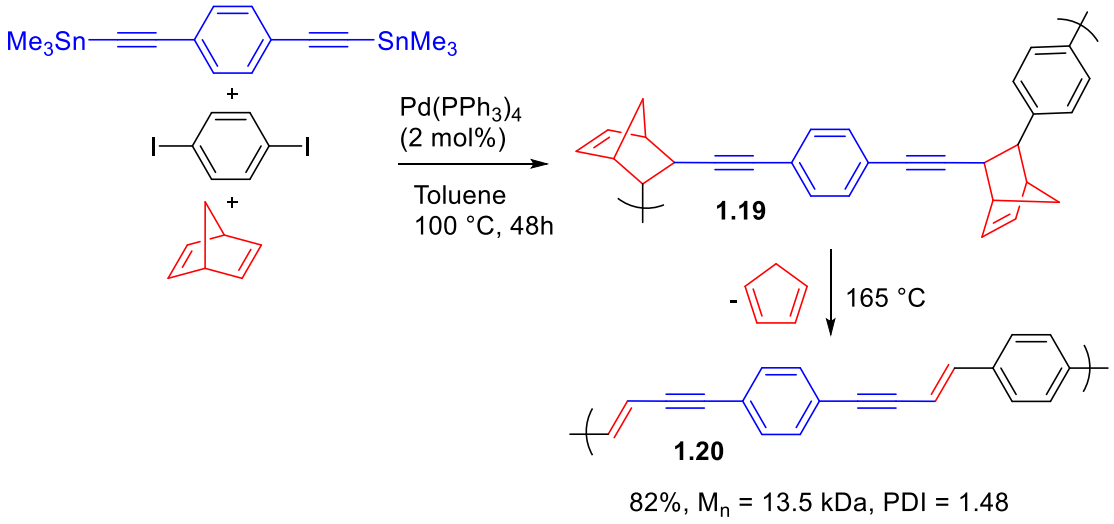
1.3.3.1 *Palladium-Catalyzed, Multicomponent Cross-Coupling Polymerizations*

Building upon their early work in palladium-catalyzed multicomponent polymerizations (section 1.3.2.1), Endo and coworkers exploited the reactivity of palladium π-allyl intermediates to synthesize conjugated poly(arylene-vinylene)s from conjugated bis-allenes, dihaloarenes and diethyl methylmalonate (Scheme 1.42).[152] Three different halogenated monomers were employed, including thiophene dibromide, without erosion of the molecular weight. Interestingly these polymers exhibited electroluminescence, which could prove useful in LED devices. Subsequent reports demonstrated that allene-tethered aryl bromides could also be used in this reaction,[153] as could chiral nucleophiles.[154] The latter was found to induce a higher order structure in the polymer.



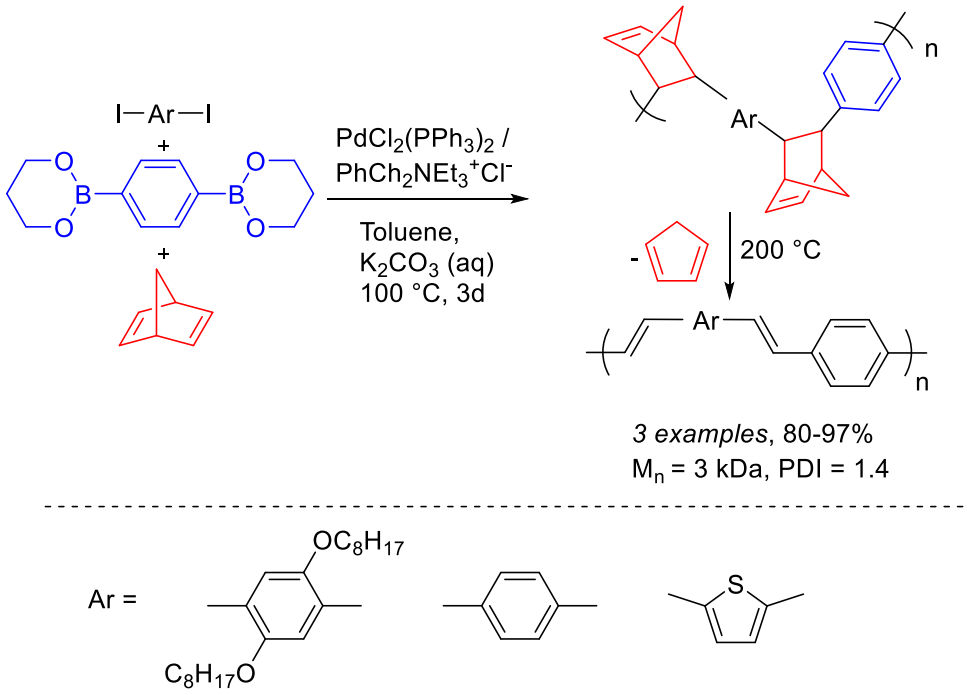
Scheme 1.42 Poly(phenylenevinylene) Synthesis via Palladium-Catalyzed Three-Component Polymerization

Tomita and Endo also reported a three-component coupling reaction between a para-diiodobenzene, norbornadiene, and a distannylated diyne to generate a soluble polynorbornene **1.19**, which upon heating undergoes a retro Diels-Alder leading to create an insoluble enyne-containing conjugated polymer **1.20** (Scheme 1.43).[155] Although this reaction should allow for the diversification of at least the distannane and the dihalide, only one polymer was synthesized.



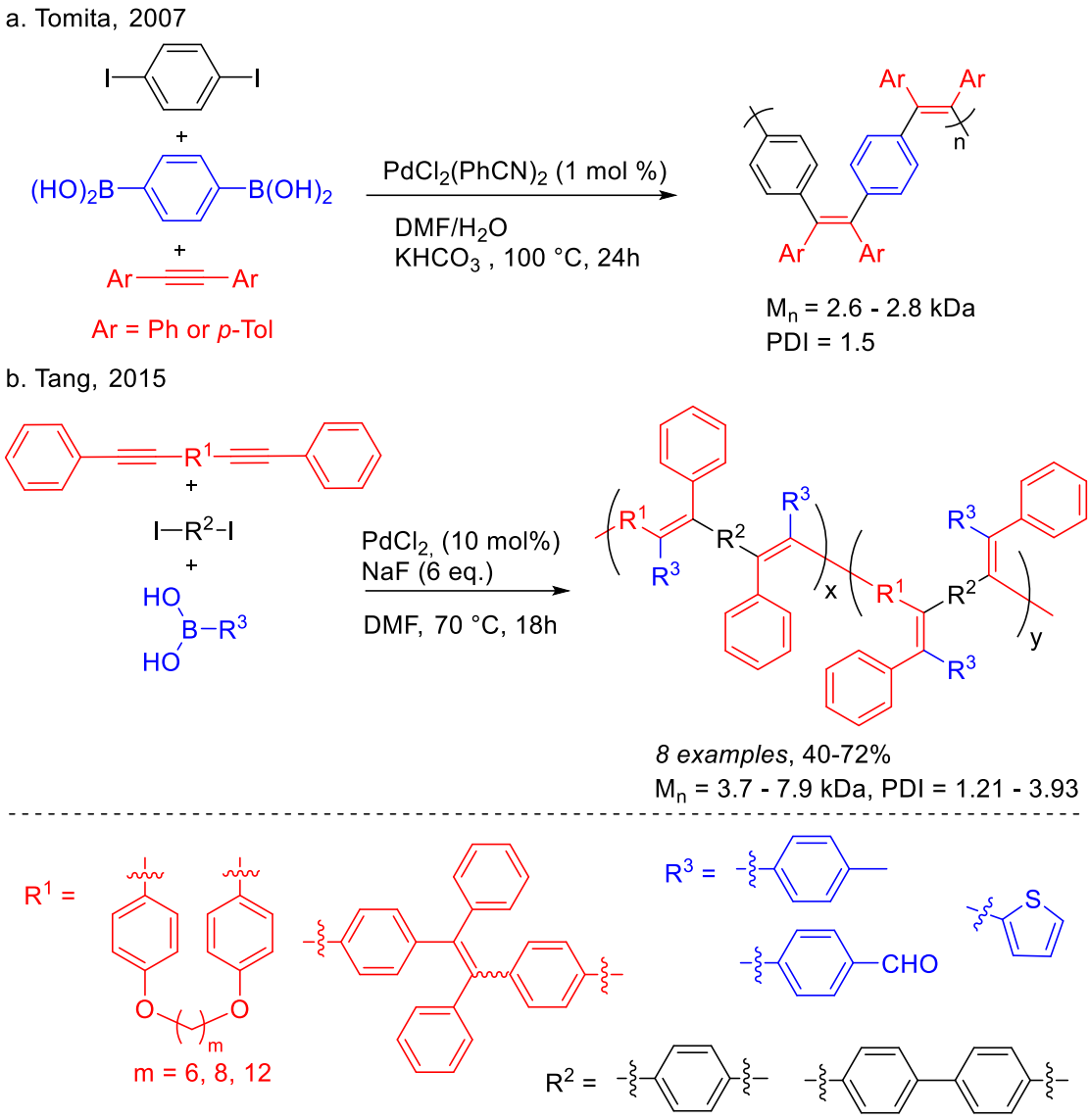
Scheme 1.43 Stille-Type Palladium-Catalyzed Three Component Polymerization

A similar approach was later described by Ishibe and Tomita with a diboronic acid (instead of a distannane) in a Suzuki-type polycoupling reaction (Scheme 1.44).[156] Good yields were obtained for the poly(phenylene vinylene) derivatives using three different diiodoarenes, although only low molecular weights were reported (ca. 3 kDa).



Scheme 1.44 Suzuki-Type Three-Component Polymerization with Norbornadiene

Tomita used another variant of the Suzuki reaction to generate conjugated poly(phenylenevinylene) (PPV) derivatives in one step from diiodobenzene, phenyl diboronic acid and alkynes (Scheme 1.45a).[157] Unfortunately, only low molecular weights were obtained due to the precipitation of the poorly soluble polymer. More recently, the Tang group used this reaction with diynes, diiodides, and boronic acids, and under similar reaction conditions obtained a small library of eight different polymers with higher molecular weights (M_n up to 7.9 kDa, Scheme 1.45b).[158] The polymers generated proved to be efficient fluorescent chemosensors for the detection of Ru^{3+} ions.

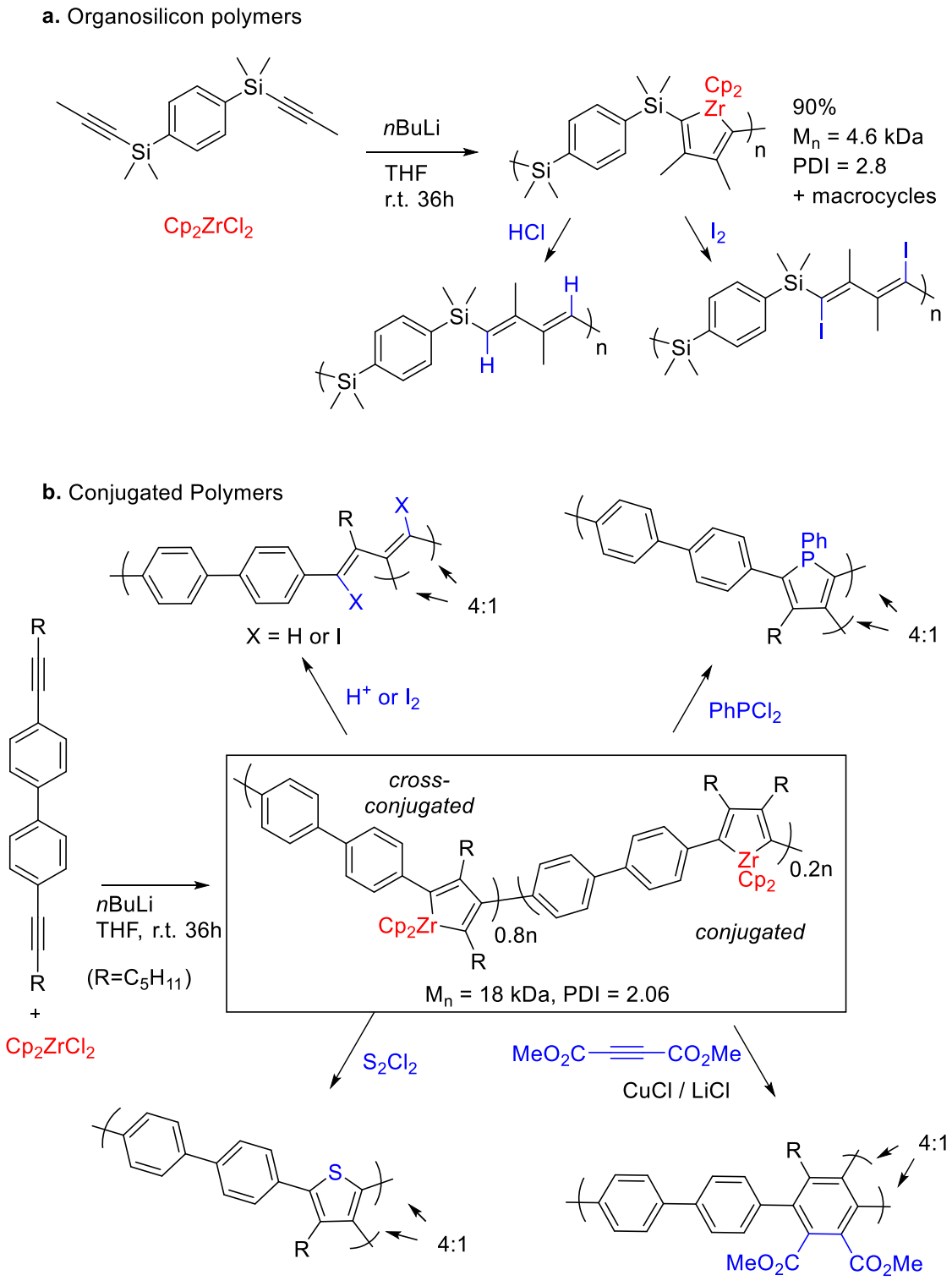


Scheme 1.45 Suzuki-Type Three-Component Polymerization with Alkynes

1.3.3.2 *Zirconocene-Mediated Cycloaddition Polymerizations*

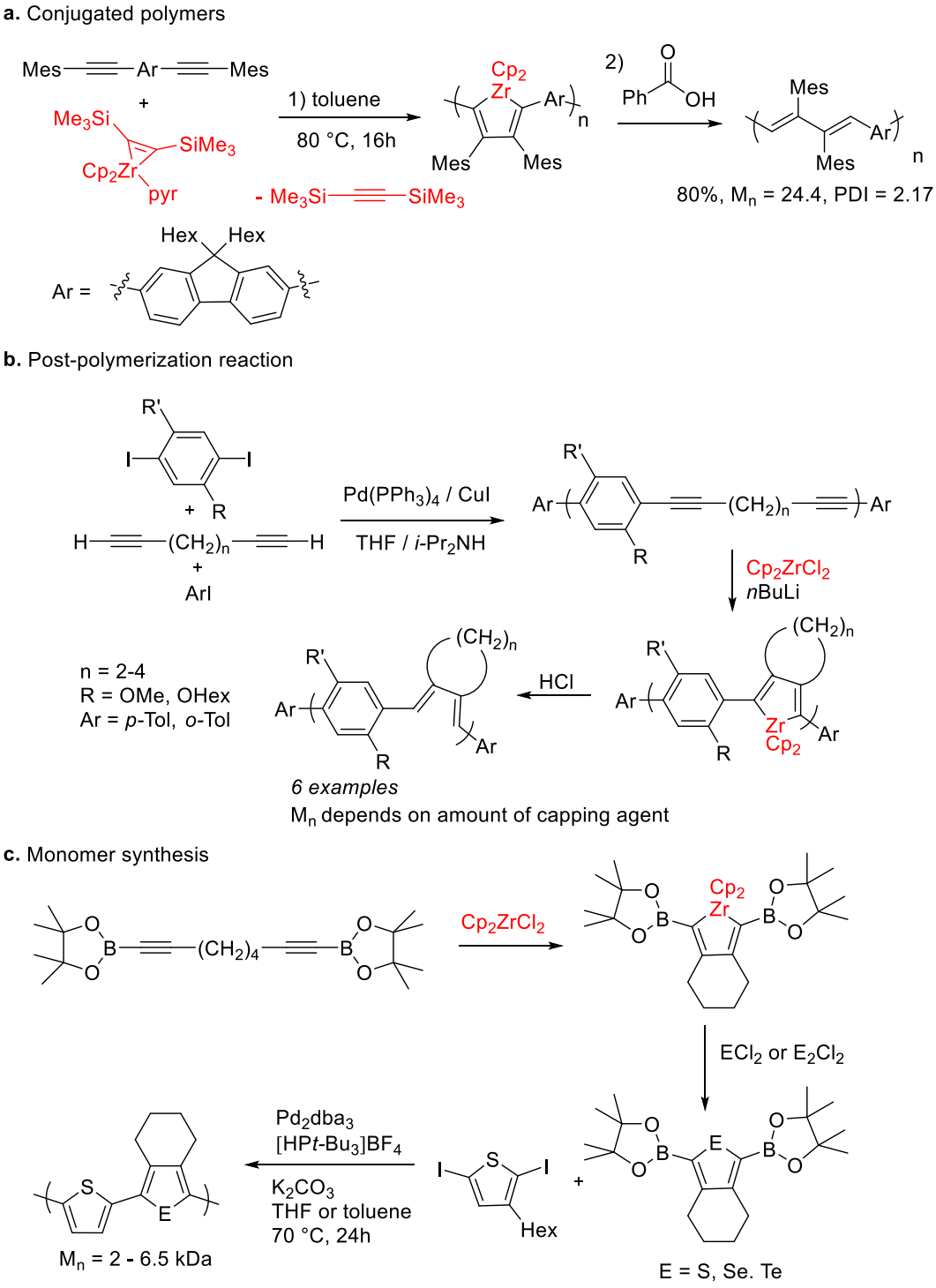
One limitation of multicomponent cross-coupling reactions is that often rely upon often metallated building blocks, and the structural complexity of the polymers is derived from the complexity of the monomers. An alternative approach to use multicomponent polymerizations is to assemble a more complex cyclic unit at the same time as the polymer. The Tilley laboratory reported an early example of this reaction in 1995 directed towards

organosilicon polymers in the zirconocene mediated cyclodimerization of diynes (Scheme 1.46a).[159] While only formally involving two different components, this transformation provides an efficient route to metallocycle polymers and macrocycles from two alkynes and "Cp_2Zr", generated in situ from Cp_2ZrCl_2 and two equivalents of *n*BuLi. Later studies showed that this approach is applicable to the synthesis of conjugated and cross-conjugated polymers mixtures. Poly(metallocycles) can be converted to a number of other polymers via either protonation or halogenation (to afford diene/arene polymers), transmetallation with $PhPCl_2$ or S_2Cl_2 to generate polyphospholes or polythiophenes, or cycloaddition with alkynes to form poly(phenylenes) (Scheme 1.46b).[160]



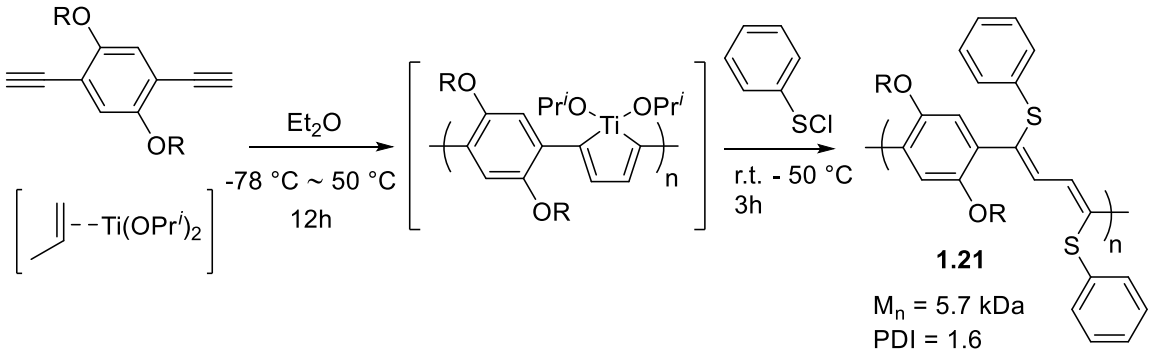
Scheme 1.46 Zirconocene-Mediated Routes to Organosilicon and Conjugated Polymers

While this report described the formation of only a single polyzirconocene intermediate, and this was in a mixture of conjugated and cross-conjugated units, subsequent studies by Tilley and other labs have expanded this approach to access a range of conjugated polymers. For example, Tilley has shown that mesityl-substituted alkynes can be used to favor the formation of conjugated polymers exclusively (Scheme 1.47a).[161] The Tilley lab has also used this reaction for the post-polymerization functionalization polyalkynes to generate a range of poly(phenylenedienylenes) with tunable band-gaps and emission energies (Scheme 1.47b).[162] In an alternative approach, Rivard has shown how the zirconocene-mediated cyclization of diynes containing organoboron substituents can be used to create monomers for cross-coupling polymerization (Scheme 1.47c).[163] By modulating the transmetallating agent, a range of novel poly(heterocycles) can be generated via this method.



Scheme 1.47 Zirconocene-Mediated Reactions for the Synthesis of Conjugated Polymers

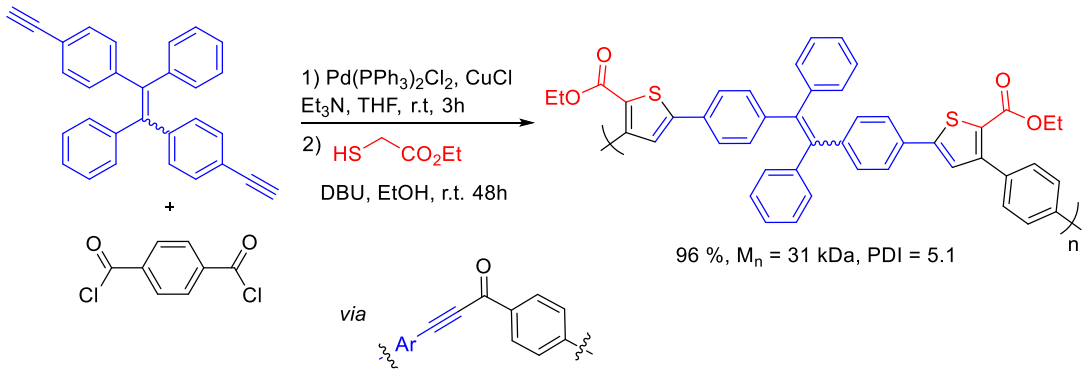
Tomita used a similar approach to construct titanium-containing conjugated polymers from diynes. In this case, transmetallation with PhSCl allowed the overall construction of **1.21** (Scheme 1.48).[164] While only one polymer was reported, the reaction could allow diversification of the dialkyne or the nucleophile.



Scheme 1.48 Conjugated Polymers via Titanacyclopentadienes

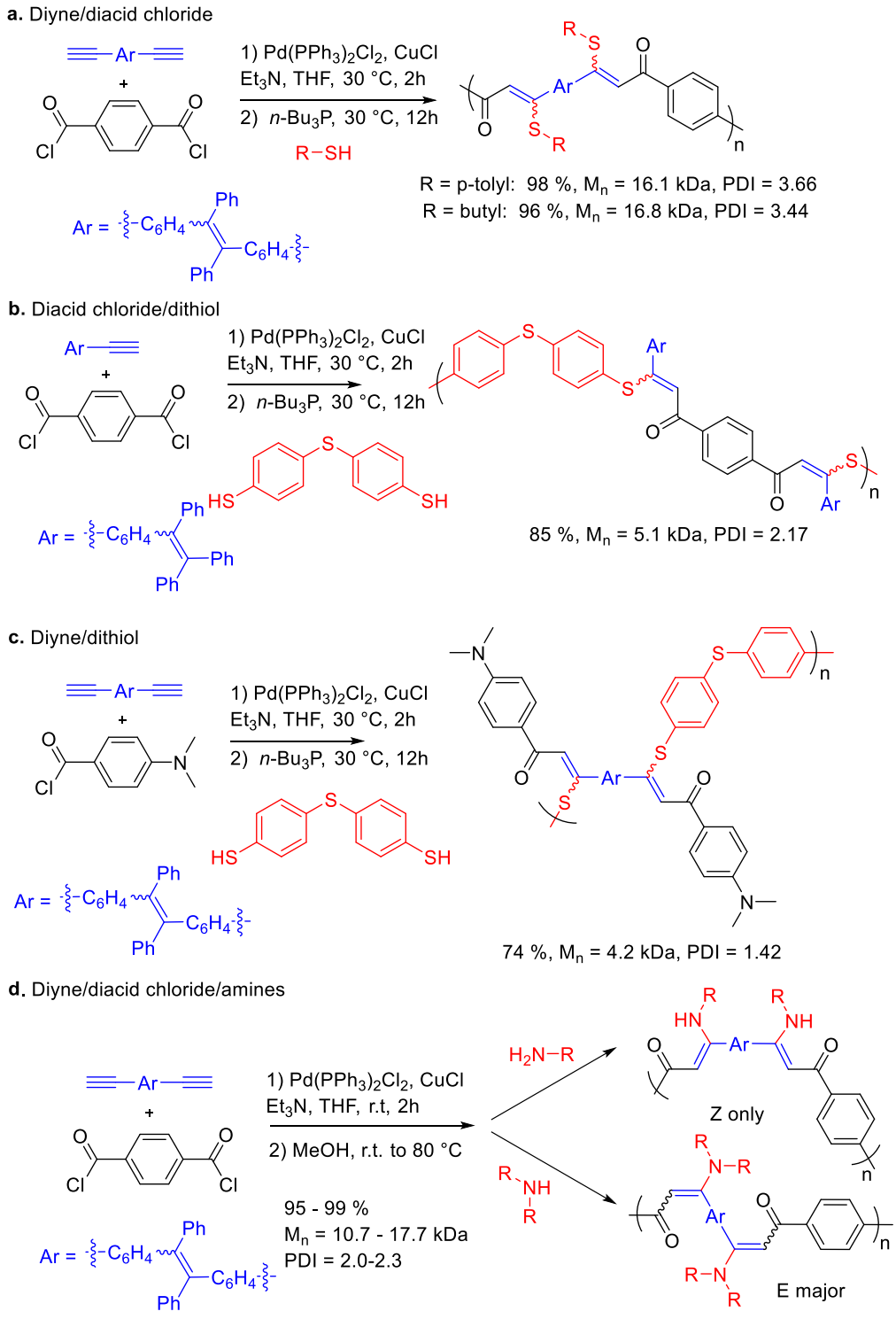
1.3.3.3 *Palladium-Catalyzed Multicomponent Polymerizations via Alkynones*

Lam and Tang have reported an approach to cross-conjugated polymers based upon the catalytic synthesis of alkynones originally described by Müller (Scheme 1.49).[165,166] This reaction uses dialkynes, terephthaloyl chloride and ethyl 2-mercaptoacetate to generate a 2,4-substituted-thiophene unit within the polymer backbone without having to presynthesize the monomer. The key catalytic step in this reaction is the palladium catalyzed coupling of the terminal alkyne with an acid chloride to form a poly-alkynone, which undergoes subsequent cycloaddition with the thiol (Fiesselmann cyclocondensation) to form fluorescent, thiophene containing polymers.



Scheme 1.49 Multicomponent Tandem Polymerization of Thiophene-Containing Polymers via Poly(alkynones)

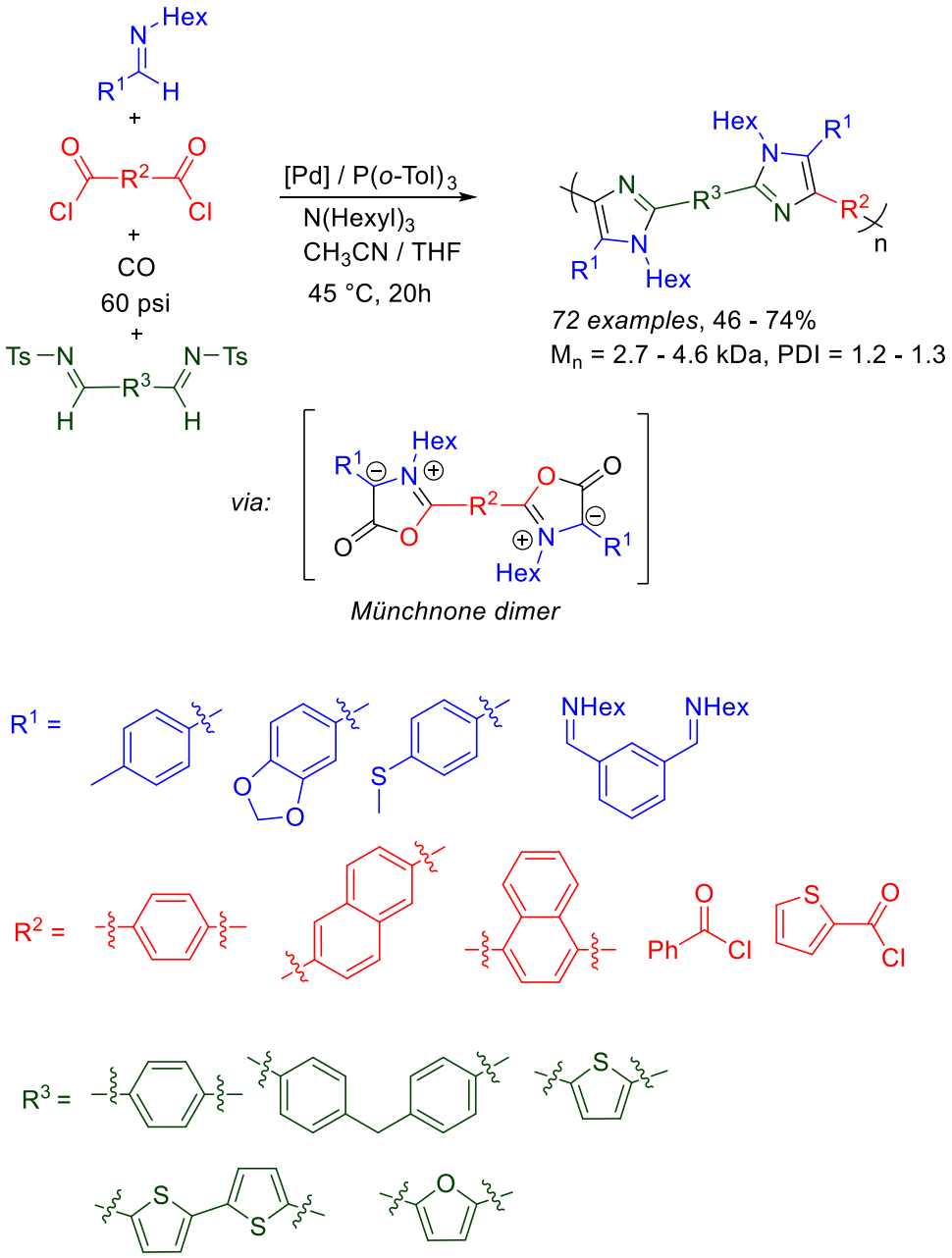
Although this initial report only described the generation of a single polymer, in a follow-up paper the same group demonstrated a number of variants of this reaction to generate cross-conjugated aromatic polyketones or non-conjugated polymers from dithiols (Scheme 1.50).[167] In these cases, simple thiols undergo a Michael addition to the ynone to yield alkene-containing polymers. This transformation can be performed in a variety of ways, including via the use of diynes/diacid chlorides (Scheme 1.50a), diacid chloride/dithiols (Scheme 1.50b), or diynes and dithiols (Scheme 1.50c). Only the combination of dialkyne, dithiol and mono-acid chloride (Scheme 1.50c) afforded low molecular weight polymers ($M_n = 4.2$ kDa). Although little variation of the starting materials was reported, the reaction could potentially be translated to a range of different monomers. In addition to thiols, primary or secondary amines can also be added to the poly(alkynone) to form poly(enaminones).[168,169] The reaction is highly selective towards the Z-isomer with primary amines, due to stabilization via hydrogen bonding, whereas with secondary amines the E-isomer is favored (Scheme 1.50d).



Scheme 1.50 Palladium-Catalyzed Multicomponent Tandem Polymerization via Alkynones

1.3.3.4 *Palladium-Catalyzed Multicomponent Polymerization via 1,3-Dipoles*

In 2011, our laboratory reported an alternative multicomponent polymerization approach to generate poly(heterocycles). This polymerization involves the palladium-catalyzed coupling of three available monomers: diimines (from dialdehydes), diacid chlorides (monomers in polyamide synthesis) and simple imines, into imidazole-based polymers (Scheme 1.51).[170] This reaction proceeds via the in situ generation of a 1,3-dipole (a Münchnone) from the carbonylative coupling of imines and acid chlorides, and polymerizes via a 1,3-dipolar cycloaddition with the diimines (*N*-tosyl substituted). A useful feature of this reaction is its tunability, as each of the three building blocks is readily generated. The latter allowed the assembly of a novel library of 72 different fluorescent, cross-conjugated materials with tunable emission energies (400 – 530 nm). However, a limitation of this approach is low molecular weights, which are typically between 3 and 4 kDa.



Scheme 1.51 Palladium-Catalyzed Multicomponent Polymerization via 1,3-Dipoles

1.4 Overview of the Thesis

The studies outlined above show that multicomponent polymerizations can provide a useful alternative approach to assemble polymers. One of the more intriguing areas in which these reactions may prove useful is in the field of conjugated polymers. These rely upon the ability to access complex polymer architectures, and tune these structures to optimize electronic properties. Both of these features are, in principal available with multicomponent polymerizations. Nevertheless, as discussed above, only a few synthetic methods allow for the multicomponent synthesis of conjugated polymers, and these typically generate either cross-conjugated polymers, use synthetic/metallated monomers, or form low molecular weight products. We explore in this thesis the use of multicomponent polymerizations to synthesize conjugated polymers with a complex and tunable repeat unit from available substrates (Figure 1.2).

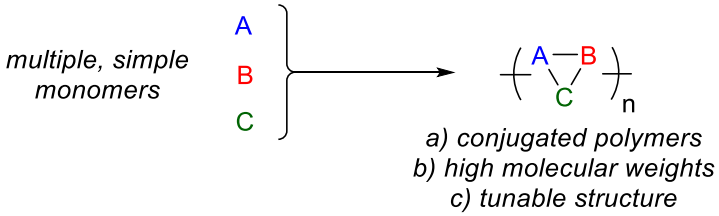


Figure 1.2 Multicomponent Polymerization of Conjugated Polymers

The results in our laboratory (section 1.3.3.4 above) demonstrate the potential broad scope of conjugated polymers available via multicomponent polymerizations in the synthesis of imidazole-based oligomers. However, these can only give access to cross-conjugated polymers and in low molecular weights. To address this, we report in Chapter 2 the palladium-catalyzed multicomponent synthesis of fully conjugated poly(heterocycles). This reaction employs available diimines, diacid chlorides, carbon monoxide and alkynes as monomers to generate families of conjugated pyrrole-based polymers with good molecular weights. In addition, a new class of conjugated polymer is reported in this work: a poly(1,3-dipole). These polymers exhibit low band-gap properties, and can be derivatized via 1,3-dipolar cycloadditions to a range of poly(heterocycles). Notably, by

changing the cycloaddition partner, the optical band-gap, fluorescence energy, quantum yield, and redox properties of the polymer products can be easily modulated.

In Chapter 3, we describe the development of an alternative, phosphonite-mediated multicomponent synthesis of conjugated poly(pyrroles). To the best of our knowledge, this represents the first metal-free multicomponent synthesis of conjugated polymers. Similar to the results in Chapter 2, this reactions involves the in situ multicomponent formation of a poly(1,3-dipole) from the combination of diimines, diacid chlorides, and (catechyl)PPh. These poly(1,3-dipoles) can then react with a variety of alkynes and alkenes to form poly(pyrroles). Notably, the polymers formed by this reaction are higher molecular weights than those formed by palladium catalysis, the reaction does not employ transition metals, and is tolerant to a much broader scope of monomers.

In Chapter 4, we describe studies on a new type of donor-acceptor conjugated polymer: a poly(phospha-Münchnone). These polymers are synthesized as intermediates in the multicomponent polymerization of diimines, diacid chlorides and (catechyl)PPh presented in chapter 3, and can be isolated and characterized. Preliminary studies show these polymers are low band-gap materials, and their properties can be modulated by the tuning the imine or acid chloride monomers.

Finally, in Chapter 5 we explored the capacity of the phosphonite-mediated multicomponent polymerization to allow for the incorporation of renewable starting materials into cross-conjugated polymers. We demonstrated that the oxidative dimerization product of vanillin, a product of lignin oxidative degradation, can be readily incorporated into this polymerization. Similarly, the acid chloride in this polymerization can be derived from 2,5-furandicarboxyaldehyde (FDCA), a monomer derived from cellulose oxidation. Together, these provide the first example of the synthesis of conjugated polymers from both components of lignocellulosic biomass.

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Chapter 2: A Palladium Catalyzed Multicomponent Coupling Approach to Conjugated Poly(1,3-Dipoles) and Polyheterocycles

2.1 Preface

This chapter describes the development of a palladium-catalyzed multicomponent synthesis of conjugated polymers. This work was published in Nature Communications (Leitch, D. C.; Kayser, L. V.; Han, Z.-Y.; Siamaki, A. R.; Keyzer, E. N.; Gefen, A.; Arndtsen, B. A. *Nat. Commun.* **2015**, *6*, 7411 - CC BY license). Preliminary experiments were performed by Ali Siamaki. The multicomponent polymerization initial development was performed by David Leitch and Zhi-Yong Han, who also synthesized a number of the polymers reported. My contribution was to optimize the reaction to afford higher molecular weight polymers, quantify the efficiency of the cycloaddition with ^{13}C-labelled polymers and perform UV-Vis absorbance, fluorescence and cyclic voltammetry measurements. Evan Keyzer and Ashley Gefen provided preliminary studies in the synthesis of the vanillin-based monomers and polymers.

2.2 Introduction

A central goal in polymer synthesis is to directly convert simple chemical building blocks into useful materials. While a wide variety of interesting and potentially important structurally complex polymers have been discovered through recent research efforts (e.g. biopolymers, advanced polymer networks, responsive materials, etc.), their synthesis via traditional methods can be sufficiently involved to limit their accessibility, especially with the efficiency often demanded in polymer synthesis. One area where structure complexity has proven particularly powerful is in the field of π-conjugated polymers. The

development of poly(heterocycles) (polypyrroles,[1] polythiophenes,[2,3] and others[4-6]) and their copolymers has sparked a renaissance in how scientists consider constructing a host of organic electronics, such as semiconductors, photovoltaic devices, sensors, and others.[7-10] A useful feature of conjugated polymers is their tunability. The modulation of substituents, conjugated heteroatoms or alternating backbone units can allow the construction of conjugated polymers with tailored electronic and other physical features. A number of powerful approaches have been developed to access conjugated polymers, including the now commonplace use of cross coupling methodologies.[11,12] While very effective, these often achieve complexity from the monomers themselves, which can in some instances require a multistep synthesis, followed by halogenation and metallation, and can make accessing varied polymer structures an iterative process. The latter have made the development of alternative methods to construct conjugated polymers an area of growing relevance.[13-15]

In principle, an attractive synthesis of complex conjugated polymers would be to consider their structure as arising directly from available monomers. A challenge is in how to accomplish this in an efficient fashion. One possibility is offered by multicomponent coupling reactions. Multicomponent reactions have been heavily exploited in organic synthesis to increase molecular complexity without the need for multistep synthetic sequences, with high efficiency and minimal waste.[16,17] When coupled with transition metal catalysis, these can provide methods to both activate and selectively couple several simple substrates directly into complex products.[18-20] Although metal catalysis is an established tool for activating typically unreactive components towards efficient polymerization (e.g. polyolefin synthesis, ring opening polymerization, etc.), the use of metal catalysis to control the coupling of multiple different monomers into new, well-defined and more complex polymer structures is much less explored. Block terpolymer synthesis is well established (**I**, Figure 2.1a), and a number of intriguing examples have recently emerged in the metal-catalyzed assembly of alternating multicomponent polymers **II**,[21-27] including the synthesis of conjugated,[22,23] and high molecular weight materials.[27] However, a method to directly convert multiple simple monomers into an entirely new polymer structure such as **III** has, to our knowledge, not been reported. Considering the variety of monomers relevant for polymerization (e.g. diamines, diacids, alkenes, alkynes,

etc), this method could provide an efficient route to access a diverse variety of structurally complex polymers, yet do so through combinations of available substrates, with high efficiency, and with facile access to structural diversity.

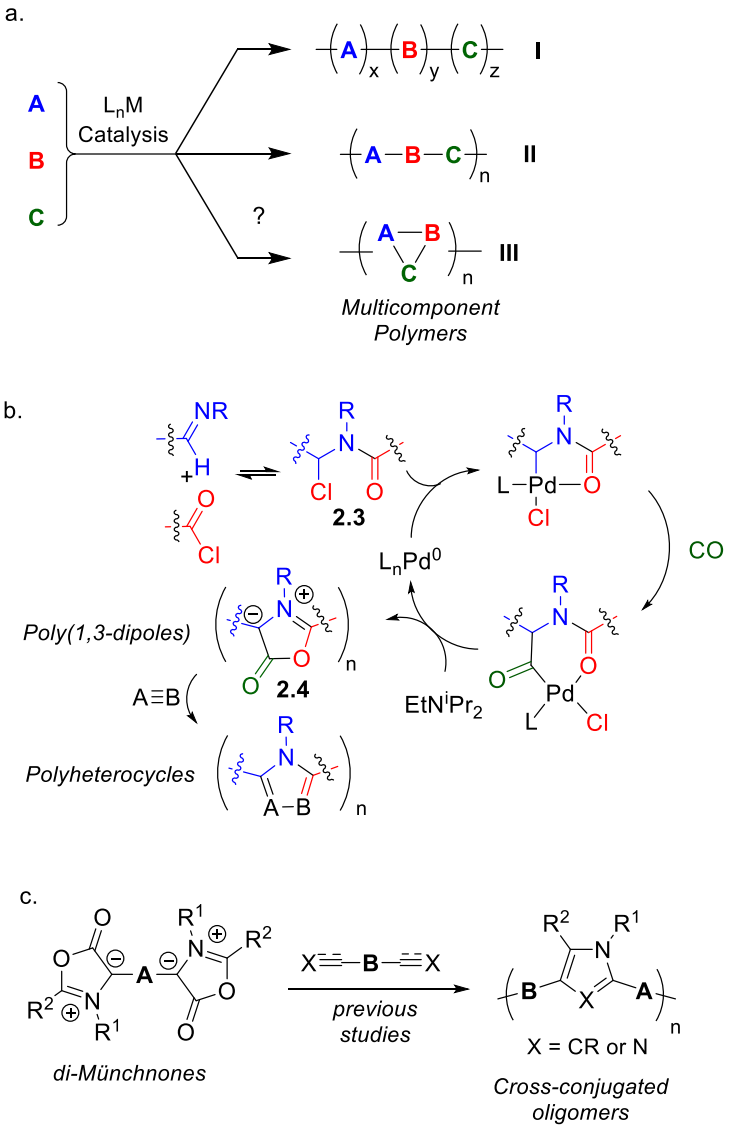


Figure 2.1 Multicomponent Approaches to Complex Polymer Synthesis. **a.** Metal-catalyzed multicomponent coupling approaches to polymers. **b.** Palladium catalyzed Münchnone formation. **c.** Previous work involving di-Münchnones in oligomer synthesis.

A polymerization as in Figure 2.1a requires a multicomponent reaction that is selective, high yielding, yet relies upon available monomers. A potential transformation that fulfills these features is the palladium catalyzed synthesis of heterocycles shown in Figure 2.1b. We have recently reported a palladium catalyzed route to generate 1,3-dipoles **2.4** (Münchnones) from imines, acid chlorides and carbon monoxide.[28,29] This reaction proceeds in high efficiency, and equally important with substrates that are all easily accessible for a polymerization: imines, acid chlorides and carbon monoxide. 1,3-dipoles, including di-Münchnones, have been used in condensation chemistry to synthesize cross-conjugated materials in low molecular weights (Figure 2.1c).[30,31] A more attractive approach suggested by this palladium catalyzed synthesis would be to couple simple diimines, diacid chlorides and CO into a novel type of mesoionic, 1,3-dipole-containing conjugated polymer **2.4**. Münchnones are known to undergo a variety of 1,3-dipolar cycloaddition reactions with unsaturated substrates (A≡B) to generate nitrogen-containing heterocycles.[32] As such, this platform would allow the assembly of various structurally distinct polymers from multiple combinations of available substrates.

We describe here our efforts towards the development of such a metal catalyzed multicomponent polymerization reaction. This has allowed the assembly π-conjugated poly(heterocycles) from multiple combinations of simple monomers: diimines, diacid chlorides, carbon monoxide, alkenes and/or alkynes. In addition to demonstrating the feasibility of this strategy, this reaction allows access to a new class of conjugated polymer in the form of a mesoionic poly(1,3-dipole). The polymers can be easily modified by cycloaddition, providing access to families of conjugated materials in one-pot, metal-catalyzed reactions.

2.3 Results and Discussion

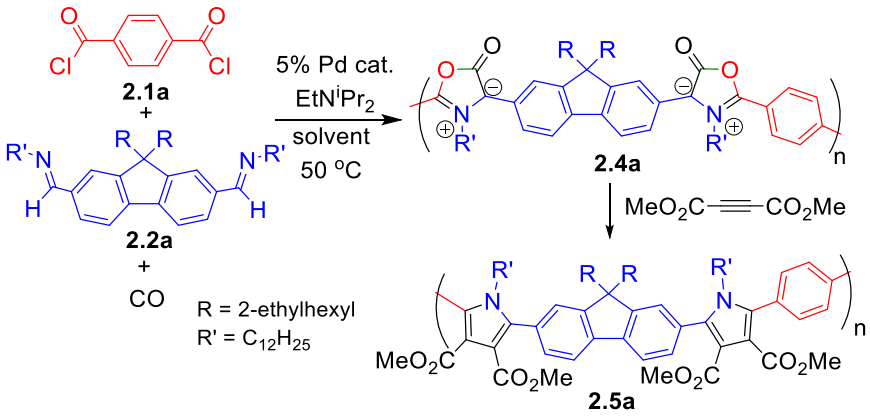
2.3.1 Multicomponent Synthesis of Conjugated Poly(Pyrroles)

As model monomers for the polymerization, we examined the palladium-catalyzed coupling of terephthaloyl chloride **2.1a**, diimine **2.2a** based on dialkylfluorene, and carbon

monoxide (Table 2.1). The efficiency of this polymerization was determined by reacting **2.4a** with the commercially available alkyne dimethylacetylene dicarboxylate (DMAD) to form the polypyrrole **2.5a**. Using simple Pd(II) sources, with or without the addition of phosphines ligands, leads to no polymerization (entries 1-4), presumably due to their slow reduction under the mild reaction conditions. Conversely, the common Pd(0) catalyst Pd_2dba_3•$CHCl_3$ (dba = dibenzylidene acetone) results in the rapid conversion of starting materials to form a poorly soluble, amorphous product (entry 7). GPC analysis shows that the THF soluble fraction contains a polymer (M_n = 7.8 kDa) but with a broad PDI (3.4). The addition of PPh_3 or PCy_3 in an attempt to attenuate the reactivity of the palladium catalyst leads instead to complete inhibition of the reaction (entries 5, 8, 9), while $P(o\text{-Tol})_3$ restores activity but yields a similarly poorly soluble product with a broad PDI (entry 10).

The low solubility and broad PDI in this product may be due to the alkene-based dba on the palladium precatalyst, which could react via cycloaddition with **2.4a** and lead to crosslinking. To circumvent this reaction, $Pd[P(o\text{-Tol})_3]_2$ was employed as a commercially available source of Pd(0) with only weakly associated, and unreactive, ligands. This catalyst leads to the near complete consumption of the reagents under mild conditions (50 ^oC, 4 atm CO), and the generation of a polymer (**2.5a**) that is soluble in common solvents (entry 11). ^1H and ^{13}C NMR and IR analysis show the conversion of the monomers into the polypyrrole **2.5a**, which has identical spectral features to independently prepared model compounds. GPC analysis shows **2.5a** to have a well-defined monomodal molecular weight distribution (PDI =1.6). The catalytic activity of $Pd[P(o\text{-Tol})_3]_2$ can be enhanced by the addition of $CuPF_6$, which presumably acts as a phosphine scavenger to generate a mono-ligated palladium catalyst (entry 12). Alternatively, simply using high CO pressure leads to a rapid and near quantitative polymerization, forming polypyrrole **2.5a** as the only observable product (entry 13). Molecular weights as high as 22.7 kDa can be obtained by increasing the concentration and reaction time (entry 14).

Table 2.1 A Multicomponent Synthesis of Conjugated Poly(Pyrroles)[a]



Entry	Catalyst	Yield[b]	M_n (kDa)	M_w (kDa)	PDI
1	$PdCl_2(PhCN)_2$	NR	-	-	-
2	$PdCl_2(PPh_3)_2$	NR	-	-	-
3	$PdCl_2(PhCN)_2$ /P(*o*-tol)$_3$	NR	-	-	-
4	$Pd(OAc)_2$	NR	-	-	-
5	$Pd(PPh_3)_4$	NR	-	-	-
6	Pd[P(*t*-Bu)$_3$]$_2$	50	2.0	3.4	1.4
7	Pd_2dba_3•$CHCl_3$	70	7.8[c]	26.5	3.4
8	Pd_2dba_3 / PPh_3	NR	-	-	-
9	Pd_2dba_3 / PCy_3	NR	-	-	-
10	Pd_2dba_3 / P(*o*-tol)$_3$	75	7.4[c]	28.1	3.8
11	Pd[P(*o*-tol)$_3$]$_2$	60	5.5	8.8	1.6
12	Pd[P(*o*-tol)$_3$]$_2$ [d]	69	7.0	10.5	1.5
13	Pd[P(*o*-tol)$_3$]$_2$[e]	85	12.7	25.2	1.9
14	Pd[P(*o*-tol)$_3$]$_2$[f]	73	22.7	56.6	2.5

[a]**2.1a** (0.10 mmol), **2.2a** (0.10 mmol), EtN^{i}Pr$_2$ (0.40 mmol), 4 atm CO, 5% Pd/pyrrole, THF, 50 °C, 24 h; then PhCOCl (0.10 mmol), 4 mL DCM, alkyne (0.40 mmol), rt, 18 h. [b]2.5a, isolated yield. [c]THF extract. [d]5 % $CuPF_6$, 30h. [e]20 bar CO, THF/MeCN: 1.9/0.6 mL, 45 °C, 30h; isolated by soxhlet extraction. [f]20 bar CO, THF/MeCN: 1.5/0.5 mL, 45 °C, 64 h

2.3.2 Multicomponent Synthesis of Poly(1,3-Dipoles)

The reaction in Table 2.1 provides a new approach to synthesize pyrrole-based conjugated polymers from combinations of substrates that are either available or monomers themselves in other polymerizations (terephthaloyl chloride, carbon monoxide, dialdehydes, alkynes). This platform can also be used to access new classes of conjugated materials. For example, the first step in the transformation in Table 2.1 also generates the 1,3-dipole containing polymer **2.4a**. 1,3-dipoles such as Münchnones are typically considered reactive intermediates and used *in situ* in synthesis. However, while performing the palladium catalyzed coupling in the absence of alkyne we noted the precipitation of a dark solid **2.4a** that can be easily isolated by washing with acetonitrile. This polymer is surprisingly stable (< 5% mass loss at up to 180 ^{o}C under nitrogen), and can be stored at low temperature in the absence of air and moisture, although they do hydrolyze in the presence of water. In order to fully characterize the moderately soluble **2.4a** by NMR analysis, it was prepared in moderate molecular weight with an imine end-capping agent (**2.4a'**, M_n = 6.7 kDa, see Experimental Section 2.5.7). Spectral analyses show all the signals for a Münchnone, including characteristic carbonyl resonances in the IR (1710 cm^{-1}) spectra and in the ^{13}C NMR (δ 160.6 ppm) and others, all of which correlate with the model di-Münchnone **2.4a"** prepared from diimine **2.2a**, toluoyl chloride and CO. **2.4a** therefore represents an unusual new class of mesoionic polymer: poly(1,3-dipoles).

Donor/acceptor conjugated polymers have become an important thrust in the recent design of polymer-based photovoltaic materials,[7,8,33] although these do not typically incorporate formal charges into the backbone. Likely as a result of this charge separation, poly-Münchnone **2.4a** is a dark purple solid, characteristic of low band-gap materials. UV-Vis analysis shows intense (molar absorptivity up to 5.0 x 10^4 $L.mol^{-1}.cm^{-1}$) and broad absorptions in most of the visible region (Figure 2.2a). These are significantly red-shifted relative to the model bis-Münchnone, and indicate that **2.4a** is highly conjugated. While the precise nature of this extended conjugation is still under investigation, the persistent charge-separated character of the mesoionic moieties creates a donor/acceptor motif on a single heterocycle, and may also provide a novel route to planarization as a mechanism to partially eliminate charge (e.g. Figure 2.2b). Estimation of the optical band-gap by

absorbance onset gives values of 1.74 eV for **2.4a'** (1.59 eV for the high molecular weight **2.4a**), and cyclic voltammetry shows a reversible reduction and an electrochemical bandgap of 1.84 eV. As such, these are a new class of low band-gap conjugated materials.

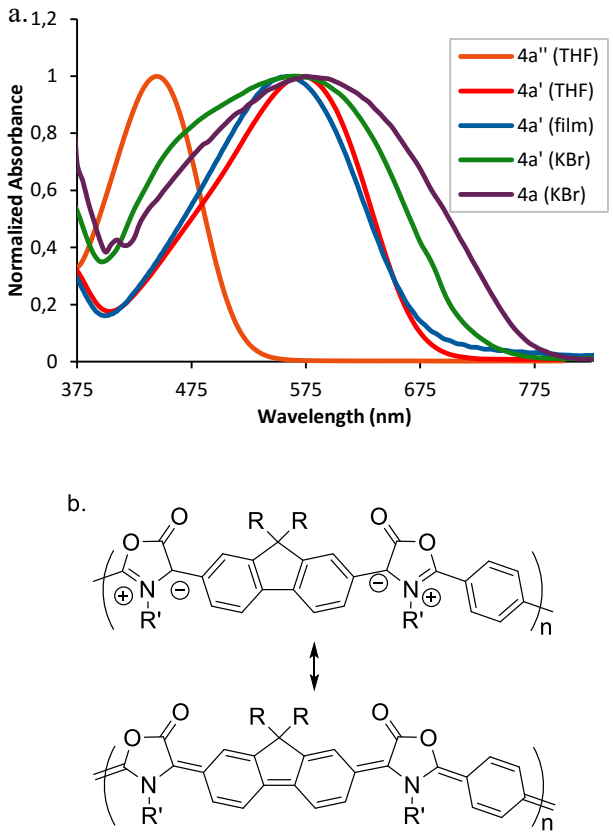


Figure 2.2 UV-Vis Spectra and Conjugation in Poly(Münchnones) **a.** UV-Vis spectra of **2.4a** (22.7 kDa), **2.4a'** (6.7 kDa) and model dimer **2.4a"** (n = 1). **b.** Potential resonance structures of 2.4a leading to planarization.

In addition to their unusual electronic properties, the synthesis of **2.4** from diimines and diacid chlorides makes it straightforward to attenuate their structure and form a range of mesoionic polymers. Examples of the structural diversity available are shown in Figure 2.3. Notably, each of the bis(acid chloride) monomers are either commercially available or easily prepared from the diacid compounds. For example, 2,5-thiophene dicarbonyl dichloride (precursor to **2.4c**) can be synthesized in one step from adipic acid, a commodity

chemical used in the production of nylon and other polyamides, while 2,5-furan dicarboxylic acid is derived from carbohydrates, and identified by the DOE as one of the top 10 bio-based renewable chemicals.[34] The diimines used can be similarly altered to incorporate carbazole (**2.4e**), a common unit in conjugated polymer production.[6] In all cases, the catalytic coupling is clean and molecular weights limited only by the solubility of the poly(1,3-dipole).

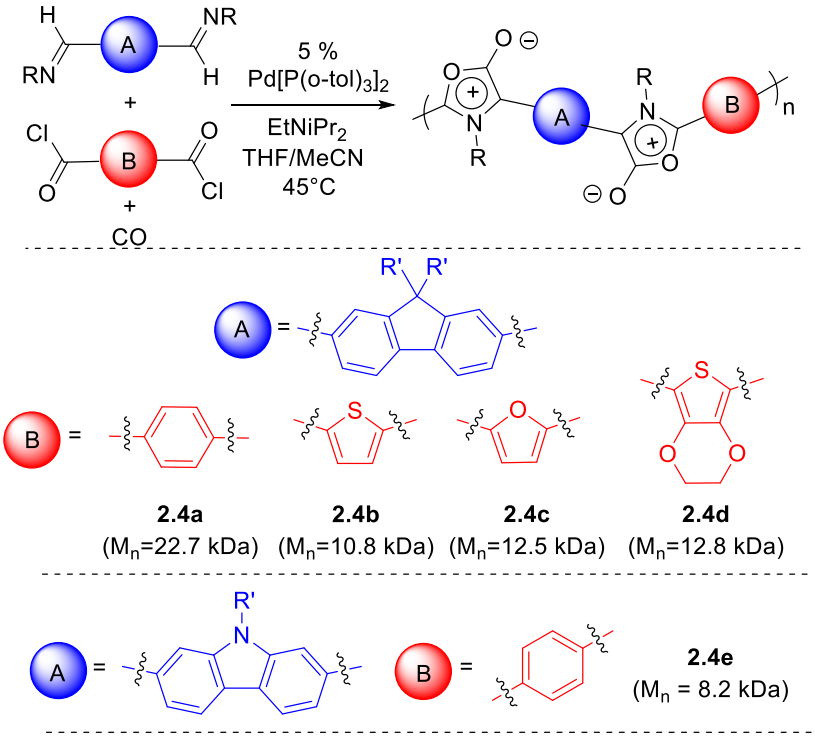


Figure 2.3 Diversity of Münchnone-Containing Polymers.

Due to the moisture sensitivity of **2.4**, molecular weight determined by conversion to poly(pyrroles) **2.5**, as in Table 2.1.

The structural manipulations translate into the properties of these polymers. For example, the disubstituted carbazole-containing polymer **2.4e** displays visible absorbances that are blue-shifted (λ_{max} of 539 nm) relative to 4a (λ_{max} of 570 nm) (Figure 2.4a). Alternatively, the thiophene-containing material **2.4b** is significantly red-shifted relative to these other polymers (absorbance onset ~768 nm), corresponding to an optical bandgap of 1.58 eV.

The latter is comparable to materials currently of interest as light harvesting materials in bulk hetero junction (BHJ) solar cells.[7,8] As such, this provides a method to both construct low band-gap conjugated polymers, and manipulate or tune their electronic properties by choice of the constituent components.

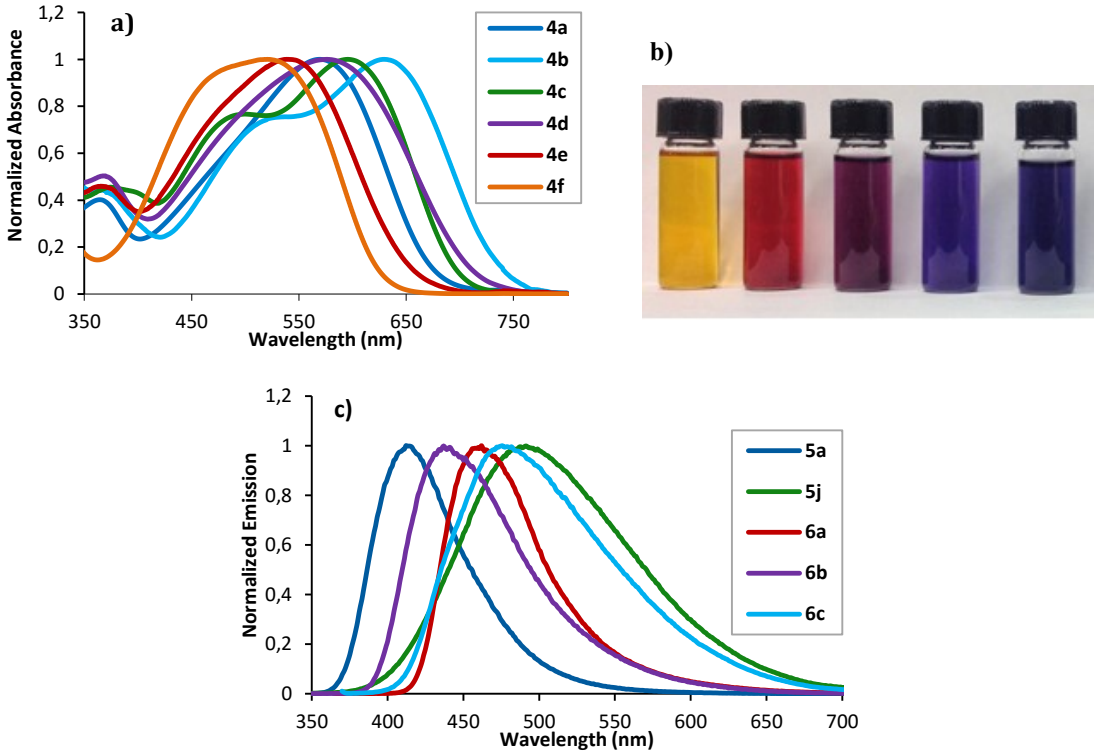


Figure 2.4 Properties of polymers **2.4'-2.6**.

Polymers **2.4a'-e'** were prepared with imine end capping at 6-8 kDa to ensure full solubility for analyses (See Experimental Section). **a.** UV-Vis absorbance spectra of poly(Münchnones) **2.4a-f** in THF. b. Polymers **2.5a**, **2.4f'**, **2.4e'**, **2.4a'**, and **2.4c'** in THF (from l to r). **c.** Fluorescence spectra of select polymers **2.5-2.6** in THF.

2.3.3 Multicomponent Synthesis of Poly(heterocycles)

These poly-Münchnones **2.4** also offer access to another, deeper level of molecular complexity: via their backbone reactivity. This can provide to our knowledge a unique route to convert one conjugated organic polymer into other backbone conjugated

polymers.[35,36,37] For example, the addition of phenyl methylpropiolate to **2.4a** results in the transformation of the purple, low band-gap poly-Münchnone into a moderate band-gap, blue emitting polypyrrole **2.5b** (Figure 2.5). ^{1}H NMR and IR analysis suggest the complete disappearance of 1,3-dipole unit in this reaction, with no observable byproducts. In order to quantify the efficiency of cycloaddition, ^{13}C-labelled polymer **2.4a** was generated from isotopically enriched terephthaloyl chloride 1,4-$C_6H_4(^{13}COCl)_2$. NMR (^{13}C) analysis shows the quantitative reaction with alkyne to form polypyrrole (>95%, see Figure 2.8 in Section 2.5.9), and is consistent with the high cycloaddition reactivity of the 1,3-dipoles. A range of pyrrole-based polymers can be formed by this reaction. For example, changing the alkyne employed can provide access to a wide variety of pyrrole-based polymers. Representative examples of these include the diester-containing polymer **2.5a** or the diketone-substituted **2.5c**. In addition to alkynes, electron-deficient alkenes are suitable dipolarophiles to form pyrroles. This can allow the facile formation of polycyclic pyrrole-based polymer **2.6a** (from cyclic alkene cycloaddition) the mono-substituted **2.6b** (from chlorocyanoethylene), or the unsubstituted polypyrrole **2.6c** with high yield. By employing different diimines and diacid chlorides, various other polypyrroles can be obtained (e.g. **2.5d**-**2.5h**). As such, this provides a platform to readily incorporate desired functionalities onto conjugated polymers, all of which emanate from a single polymer **2.4**. The reactivity of Münchnones is also not limited to pyrroles. The addition of *N*-tosyl imine forms imidazole-based conjugated polymer **2.7**, and backbone conjugation in these polymers can be easily quenched by the addition of alcohols, leading to the generation of polyamides **2.8**. Poly-Münchnones **2.4** can therefore be considered highly reactive and versatile conjugated materials, where a single polymer **2.4** can be transformed into entire families of new conjugated materials. In the case of phenyl methylpropiolate, this polymerization can be performed in a single step (Figure 2.6), allowing the orthogonal, four-component synthesis of a conjugated polymer.

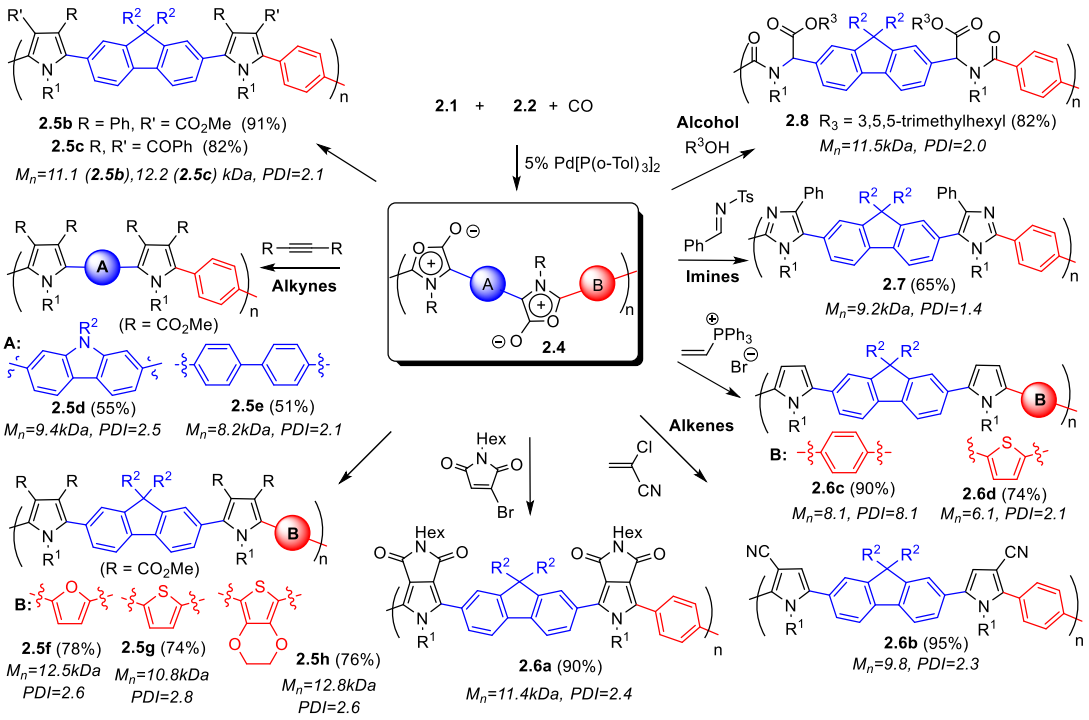


Figure 2.5 Transformation of Poly(Münchnones) into Families of Conjugated Polymers. Derivatization performed on poly-Münchnone samples of 8-12 kDa to ensure full solubility of **2.4a-e**, and allow the quantification of the cycloaddition

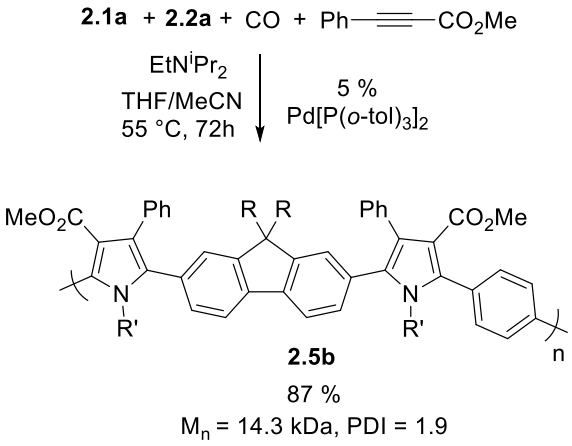


Figure 2.6 One-Pot Four Components Polymerization

This structural diversity can provide a further platform to modulate properties. For example, between polymers **2.4-2.8**, optical absorbance and polymer band-gap can be tuned across the visible spectrum, and materials can be formed that fluoresce anywhere from blue to green to not at all (Figure 2.4c, Table 2.2, and Tables 2.3 and 2.4 in Section 2.5.3 for the full list of properties). Similarly, electrochemical studies show that this cycloaddition (or lack thereof) can be used to tune HOMO energies by over 1 eV. While the primary thrust of these studies was not in product design, several of the polymers reported here display notable properties. Polypyrroles and their copolymers have attracted significant interest as electronic materials,[1,38] Three of the pyrrole-based polymers (**2.5a**, **2.6a**, **2.6b**) have good photoluminescent quantum efficiency (>35%) with emission maxima in the range of blue light (413-459 nm). Alternatively, the pyrrole-based imide-functionalized (DPPD) unit has been identified as a promising electron acceptor unit in conjugated polymers, and can be readily generated by this approach (**2.6a**),[39] while alternating pyrrole-thiophene materials such as **2.6d** represent new variants of materials found to be of use in field effect transistors.[40] The range of properties observed is a direct result of their structural diversity, which varies from the backbone conjugated heterocycles, the spacer units, to the substituents. This level of structural attenuation would require an individual synthesis for each new monomer via typical methods. In this case, each polymer is generated in one pot, from a small pool of monomers, and with minimal waste (often only HCl and CO_2).

Table 2.2 Properties of Polymers 2.5-2.8

Cpd	λ_{max} (nm)	λ_{em} (nm)	φ_{PL}	E_g^{opt} (eV)	E_g^{opt} film (eV)
2.5a	321	413	0.39	3.18	3.16
2.5b	335	492	0.27	2.91	2.87
2.5c	329	496	0.04	2.99	2.98
2.5d	325	474	0.03	2.92	2.79
2.5e	301	413	0.12	3.15	3.08
2.5f	320	459	0.14	3.08	2.97
2.5g	320	467	0.11	3.07	3.11
2.5h	321	467	0.10	3.05	2.97
2.5i	312	417	0.17	3.19	2.93
2.5j	329	473	0.02	2.88	2.92
2.6a	364	459	0.35	2.86	2.80
2.6b	345	431	0.47	3.01	2.96
2.6c	366	501	0.08	2.60	2.60
2.6d	368	497	0.06	2.63	2.47
2.7	330	467	0.12	2.98	2.80
2.8	280	-	-	3.45	3.42

Selected physical properties of **2.5-2.8** (see Tables 2.3 and 2.4 in Section 2.5.3 for further details, electrochemical studies, HOMO/LUMO energies, and for properties of polymers **2.4a-f**).

2.3.4 Synthesis of Conjugated Polymers from Vanillin

Finally, we have examined the potential of using other, renewable materials as precursors to conjugated polymers. Lignin is a major component of lignocellulosic biomass, and the world's largest renewable source of aromatic compounds, making it a potentially attractive, bio-based feedstock for π-conjugated polymers.[41] Lignin depolymerization yields a variety of aromatic building blocks, including the dialdehyde **2.9** (a dimer of vanillin). As this multicomponent polymerization employs aldehydes and carboxylic acids as monomer feedstocks, **2.9** can be incorporated in this palladium catalyzed polymerization to generate the conjugated poly-Münchnone **2.4f** (Figure 2.7). UV-Vis and electrochemical studies show that **2.4f** is a moderately low band-gap polymer (1.9 eV). As above, the dipole in **2.4f** can undergo cycloaddition reactions to generate the polypyrroles **2.5i** and **2.5j**, each

of which are blue emitting materials. These polymers are hybrid materials derived from four simple substrates: vanillin, terephthaloyl chloride, a primary amine, and carbon monoxide, and represent as far as we are aware the first use of lignin in conjugated polymer formation. Considering the versatility of this reaction, it should prove relevant for the controlled assembly of a range of renewable-based conjugated polymers.

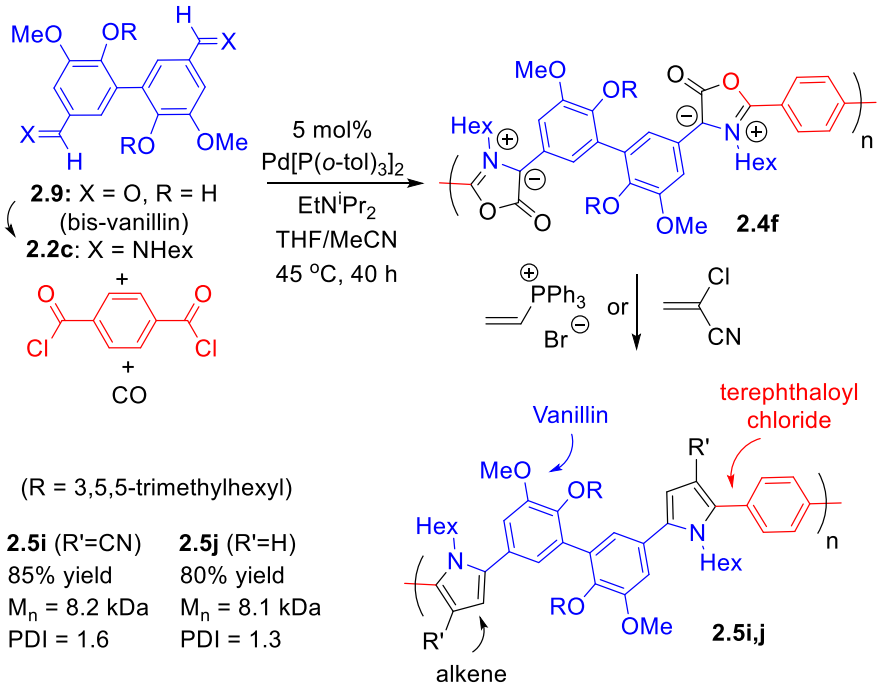


Figure 2.7 Conjugated Polymers from Vanillin

2.4 Conclusions

In summary, we have described a new type of metal-catalyzed multicomponent polymerization, which provides a method to convert combinations of monomers, such as diimines, diacid chlorides, carbon monoxide, alkynes, alkenes and alcohols, into structurally well-defined conjugated polymers. In addition, new backbone conjugated mesoionic polymers (**2.4**) can be prepared via this coupling, which can undergo efficient post-polymerization cycloaddition to generate families of conjugated materials. In light of the variety of dipolarophiles possible for cycloaddition, as well as diimines and bis(acid

chloride)s available, this can be used to construct arrays of conjugated materials, yet without the typical need to preassemble each new conjugated unit, and with the efficiency often desired in polymer synthesis. This multicomponent catalytic polymerization approach could prove equally applicable for the controlled assembly of a range of new materials from established monomers and/or other inexpensive building blocks. Experiments directed toward the latter are currently underway.

2.5 Experimental Section

2.5.1 General Methods

All reactions were carried out using standard Schlenk line and glovebox techniques under an atmosphere of oxygen- and water-free dinitrogen, unless described otherwise. Solution phase ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz Varian Mercury, 400 MHz Varian Mercury, or 500 MHz Varian VNMRS spectrometer at ambient temperature; chemical shifts are reported in parts per million (ppm) relative to the corresponding residual *protio*-solvent signal. Mass spectra were acquired by electrospray ionization (ESI). GPC was carried out on a Polymer Laboratories PL-GPC 50 with THF as the eluent and a UV-Vis absorbance detector. Samples were analyzed versus monodispersed polystyrene standards. The UV-Vis absorption of the polymers was measured in THF (polymers **2.4**) or $CHCl_3$ (polymers **2.5**-**2.8**) solutions using a 1 cm path quartz cell and also as thin films (drop cast on a glass slide) using a JASCO V670 UV-Vis-NIR spectrometer. The fluorescence measurements were performed on a Varian Eclipse Fluorometer. The relative fluorescence quantum yields were determined versus anthracene in ethanol ($\Phi_{em} = 0.27$) at slit widths of 2.5 nm. The excitation wavelength corresponds to the maxima of absorption for each polymer as per in Table 2.4. Cyclic voltammetry was performed on a CH670 potentiostat from CH-Instruments in a three-electrode cell using a 0.1M solution of $(TBA)PF_6$ in CH_3CN as an electrolyte. The polymers were drop-casted onto the working electrode. Platinum wires were used as working and counter electrodes, a $Ag/AgNO_3$ electrode was used as a reference. The scan rate was 0.1 V s^{-1} for all the measurements. All

potentials were adjusted versus ferrocene (Fc/Fc^+). The reduction and oxidation in cyclic voltammograms of polymers **2.4** were acquired separately.

UV-Vis, Fluorescence spectra and cyclic voltammograms for the polymers are available on the internet in the supporting information of the article.[42]

2.5.2 Materials

All common reagents were purchased from Aldrich and used as received, unless otherwise noted. Na_2PdCl_4 was purchased from Pressure Chemicals. P(*o*-tol)$_3$ and P(*t*-Bu)$_3$ $PdCl_2(PhCN)_2$, and $PdCl_2(PPh_3)_2$ were purchased from Strem and used as received. Common solvents (THF, Et_2O, acetonitrile, DCM) were sparged with dinitrogen and dried by passage through a column of alumina before use in air- and moisture-sensitive experiments. d^6-Benzene and $CDCl_3$ were dried over CaH_2 for at least 48 hours, then degassed by the freeze-pump-thaw method and vacuum transferred prior to use. *N*,*N*-Diisopropylethylamine, dimethyl acetylenedicarboxylate, methyl phenylpropiolate, 2-chloroacrylonitrile were distilled from CaH_2 prior to use in polymerizations. Terephthaloyl chloride was recrystallized from hexanes prior to use in polymerizations. $Pd_2dba_3CHCl_3$,[43] Pd[P(*o*-tol)$_3$]$_2$,[44] Pd[P(*t*-Bu)$_3$]$_2$,[45] 9,9-Bis(2-ethylhexyl)-2,7-fluorene dicarboxaldehyde,[46] *N*-(2-ethylhexyl)-2,7-carbazole dicarboxaldehyde,[47] 2,5-furan dicarbonyl chloride,[48] 2,5-thiophene dicarbonyl chloride,[49] 1,4-diphenylbut-2-yne-1,4-dione,[50] and 3-bromo-1-hexyl-1H-pyrrole-2,5-dione[51] were prepared according to literature procedures.

2.5.3 Supplementary Tables

Table 2.3 Properties of Poly-Münchnones 2.4a-f[a]

Cpd	λ_{max}[b] (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	E_g^{opt} film[c] (eV)	E_g^{elec} (eV)	E_{HOMO}[d] (eV)	E_{LUMO}[e] (eV)
2.4a	570	699	1.78	1.74	1.60	-4.92	-3.08
2.4b	630	768	1.62	1.58	1.29	-4.91	-3.40
2.4c	596	725	1.71	1.72	1.46	-5.03	-3.11
2.4d	576	749	1.66	1.65	1.56	-4.88	-3.16
2.4e	539	688	1.81	1.76	1.59	-4.90	-3.11
2.4f	521	649	1.91	1.88	1.66	-4.84	-3.09

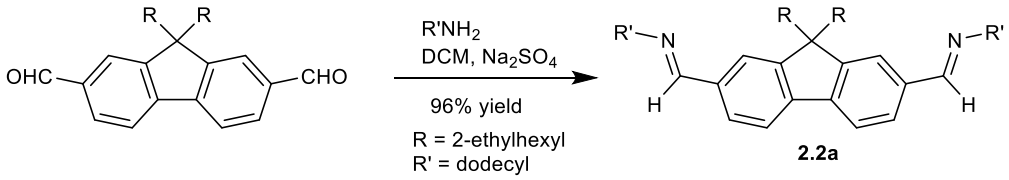
[a]Analyses of **2.4a-f** were performed on imine end-capped materials to ensure complete solubility. [b]THF solution. [c]Drop-cast polymer thin film. [d] From cathodic onset with reference to Fc/Fc^+ (E_{HOMO} = e - (*E*ox^{onset} vs Fc/Fc^+) - 4.80 eV) [e] From anodic onset with reference to Fc/Fc^+ (E_{LUMO} = e - (*E*red^{onset} vs Fc/Fc^+) - 4.80 eV).

Table 2.4 Properties of Polymers 2.5-2.8

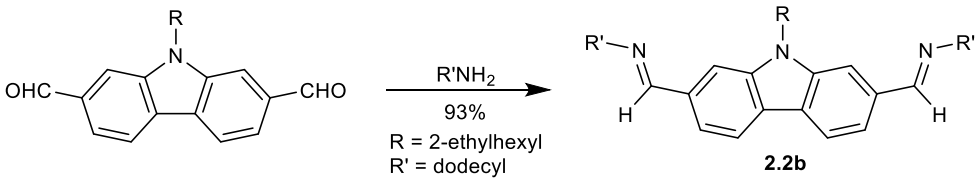
Cpd	M_n (kDa)	PDI	λ_{max}[a] (nm)	λ_{onset} (nm)	λ_{em} (nm)	φ_{PL}	E_g^{opt} (eV)	E_g^{opt} film[b] (eV)	E_{HOMO}[c] (eV)	E_{LUMO}[d] (eV)
2.5a	22.7[e]	2.5	321	391	413	0.39	3.18	3.16	-5.67	-2.51
2.5b	11.1	2.1	335	426	492	0.27	2.91	2.87	-5.57	-2.70
2.5c	12.2	2.1	329	416	496	0.04	2.99	2.98	-5.72	-2.74
2.5d	9.4	2.5	325	426	474	0.03	2.92	2.79	-5.47	-2.68
2.5e	8.2	2.1	301	395	413	0.12	3.15	3.08	-5.75	-2.67
2.5f	12.5[e]	2.6	320	403	459	0.14	3.08	2.97	-5.45	-2.48
2.5g	10.8	2.8	320	405	467	0.11	3.07	3.11	-5.61	-2.50
2.5h	12.8[e]	2.6	321	408	467	0.10	3.05	2.97	-5.51	-2.54
2.5i	8.5	1.6	312	390	417	0.17	3.19	2.93	-5.53	-2.60
2.5j	8.5	1.6	329	431	473	0.02	2.88	2.92	-5.16	-2.24
2.6a	11.4	2.4	364	434	459	0.35	2.86	2.80	-5.75	-2.95
2.6b	9.8	2.3	345	413	431	0.47	3.01	2.96	-5.80	-2.84
2.6c	8.1	1.8	366	478	501	0.08	2.60	2.60	-5.27	-2.67
2.6d	6.1	2.1	368	472	497	0.06	2.63	2.47	-5.07	-2.60
2.7	9.2	1.4	330	417	467	0.12	2.98	2.80	-5.62	-2.82
2.8	11.5	2.0	280	360	-	-	3.45	3.42	-	-

[a] $CHCl_3$ solution. [b]Drop-cast film. [c] Calculated as in Table c. [d] The anodic onset was not observed. Therefore electron affinity was calculated from the HOMO level and optical band-gap ($E_{LUMO} = E_{HOMO} + E_g^{opt}$ thin film). [e] The formation of **2.4** was performed for 64h.

2.5.4 Synthesis of Monomers

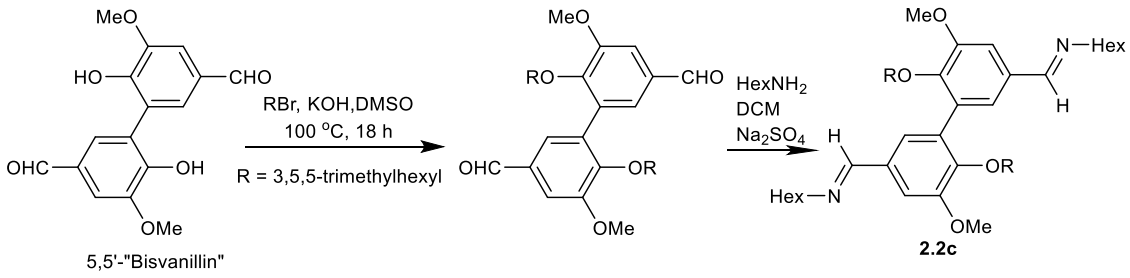


2.2a: 9,9-Bis(2-ethylhexyl)-2,7-fluorene dicarboxaldehyde (6.53 g, 14.6 mmol) and dodecylamine (5.42 g, 29.2 mmol) were dissolved in 50 mL dichloromethane. Excess Na_2SO_4 was added and the mixture stirred for 3 hours. CaH_2 was carefully added portionwise until no more effervescence was observed, then an approximate equal amount of Celite was added. The suspension was gravity filtered and the solvent removed. The resulting viscous oil was dried under vacuum at 70 °C for 18 hours to give 11.00 g of pure diimine (96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 2H), 7.73 (m, 6H), 3.63 (t, *J* = 7.0 Hz, 4H), 2.03 (m, 4H), 1.70 (m, 4H), 1.52 – 1.11 (m, 36H), 0.99 – 0.58 (m, 26H), 0.58 – 0.41 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 151.6, 143.0, 135.1, 127.5, 123.5, 120.1, 62.0, 54.9, 44.3, 34.7, 33.5, 31.9, 31.0, 29.6, 29.4, 29.4, 27.9, 27.4, 27.0, 22.7, 14.1, 14.0, 10.3. MS(ESI): $C_{55}H_{93}N_2$ $[M+H]^+$ *m/z* calcd. 781.73333; found 781.73251.



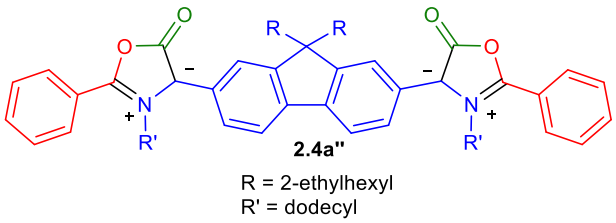
2.2b: *N*-(2-ethylhexyl)-2,7-carbazole dicarboxaldehyde (0.150 g, 0.447 mmol) and dodecylamine (0.158 g, 0.852 mmol) were dissolved in dichloromethane (2 mL). Excess Na_2SO_4 was added and the mixture stirred for 5 hours. The solution was filtered and a fresh portion of Na_2SO_4 was added. The suspension was stirred overnight. The solution was filtered and the solvent removed to give a waxy solid. This material was dried *in vacuo* at 70 °C overnight (note: solid melts at this temperature) to give a waxy off-white solid upon cooling (0.278 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.78 (s, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 4.24 (m, 2H), 3.67 (t, *J* = 7.0 Hz, 4H), 2.25 – 2.00 (m, 1H), 1.86 – 1.59 (m, 4H), 1.52 – 1.06 (m, 46H), 0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 141.9, 134.5, 124.4, 120.6, 119.5, 108.7, 61.9, 47.5, 39.2, 31.9,

31.1, 30.8, 29.7, 29.7, 29.6, 29.5, 29.4, 28.6, 27.4, 24.3, 23.0, 22.7, 14.1, 14.0, 10.9. MS(ESI): $C_{46}H_{76}N_3$ $[M+H]^+$ *m/z* calcd. 670.60338; found 670.60324.



2.2c: 5,5'-"Bisvanillin" [52] (2.50 g, 8.270 mmol) and KOH (2.125g, 37.87 mmol) were dissolved in DMSO (40 mL) at 80 °C. After 1 hour, 1-bromo-3,5,5-trimethylhexane was added. The mixture was stirred at 80 °C for 18 hours. The product was extracted with diethyl ether. The diethyl ether layer was washed with water and brine and then dried over sodium sulfate. After evaporated in vacuum, the crude product was purified by column chromatography. The resulting alkylated dialdehyde (1.045 g, 1.890 mmol) was dissolved in dichloromethane (3 mL). Hexylamine (0.383 g, 0.500 mL, 3.78 mmol) was added via syringe. Excess Na_2SO_4 was added and the mixture stirred for 5 hours. The solution was filtered and a fresh portion of Na_2SO_4 was added. The suspension was stirred overnight. The solution was filtered and the solvent removed to give a viscous yellow oil. This material was dried *in vacuo* at 70 °C overnight to give **2.2c** (1.276 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 2H), 7.44 (d, *J* = 1.4 Hz, 2H), 7.10 (m, 2H), 3.92 (s, 6H) 3.90 – 3.84 (m, 2H), 3.83 – 3.73 (m, 2H), 3.57 (t, *J* = 7.0 Hz, 4H), 1.66 (m, 4H), 1.54 (m, 2H), 1.40 – 1.14 (m, 10H), 1.05 (dd, *J* = 13.9, 3.8 Hz, 2H), 0.90 (m, 6H), 0.81 – 0.74 (m, 16H), 0.74 – 0.67 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 153.3, 148.5, 132.3, 131.4, 125.5, 108.7, 71.5, 61.7, 55.8, 51.4, 39.4, 31.7, 31.0, 29.9, 27.2, 27.0, 25.8, 25.7, 22.6, 22.2, 22.1, 14.1. MS(ESI): $C_{46}H_{77}O_4N_2$ $[M+H]^+$ *m/z* calcd. 721.58779; found 721.58677.

2.5.5 Synthesis of Model Compounds

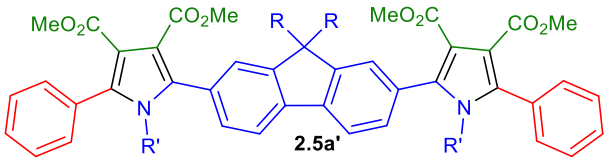


2.4a": A model bis(Münchnone) based on polymer **2.4a** was prepared as follows. Imine **2.2a** (122.2 mg, 0.200 mmol) and benzoyl chloride (56.2 mg, 46.5 µL, 0.400 mmol) were dissolved in THF (1 mL) in a Teflon-sealable thick walled reaction vessel. Then, *N*,*N*-diisopropylethylamine (103.4 mg, 145.2 µL, 0.800 mmol) and Pd[P(*o*-tol)$_3$]$_2$ (14.3 mg, 0.0200 mmol) were dissolved/suspended in THF (1 mL). This slurry was added to the imine/acid chloride solution and stirred until homogeneous. The headspace was briefly evacuated, and the reaction tube charged with 60 psi CO (gauge pressure). The mixture was heated to 50 °C for 18 hours with stirring. Afterward, the CO headspace was replaced with nitrogen, and the vessel returned to the glovebox. The resulting suspension was diluted with dichloromethane (5 mL) and transferred to a 20 mL glass vial. Excess K_3PO_4 was added and the suspension vigorously stirred for 18 hours. The suspension was filtered through Celite and the filter cake washed with dichloromethane (3 x 2 mL). The volatiles were removed *in vacuo* to give the crude product. The residue was dissolved in a minimum of acetonitrile and cooled to -35 °C to precipitate 35.2 mg of **2.4a"** (20% yield, significant product was sacrificed to obtain a pure sample; a crude ^{1}H NMR spectrum indicated complete conversion). See Supplementary Figures 1-9 for ^{1}H and ^{13}C NMR spectra of all model compounds. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 16.6, 7.2 Hz, 6H), 7.62 – 7.36 (m, 10H), 4.36 (s, 4H), 2.03 (s, 4H), 1.56 (d, J = 6.5 Hz, 2H), 1.36 – 0.60 (m, 40H), 0.52 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 151.2, 142.7, 139.2, 130.9, 129.4, 127.9, 127.3, 126.7, 126.6, 126.4, 123.4, 123.2, 123.1, 122.9, 120.0, 95.9, 55.0, 47.4, 45.3, 34.7, 33.5, 30.1, 28.8, 28.2, 26.5, 25.5, 22.8, 22.3, 14.0, 13.8, 10.2. MS(ESI): $C_{59}H_{77}O_4N_2$ $[M+H]^+$ *m*/*z* calcd. 877.58779; found 877.58724.

2.5a', 2.5b', 2.5c', 2.6a', 2.6b': Model bis(pyrrole)s were formed for spectroscopic comparison to polymers **2.5** and **2.6** in order to confirm the presence of the newly constructed pyrrole units. These compounds were obtained as follows. Imine **2.2a** (234.4 mg, 0.300 mmol) and benzoyl chloride (84.3 mg, 69.6 µL, 0.600 mmol) were dissolved in

THF (1.5 mL) in a Teflon-sealable thick walled reaction vessel. Then, *N*,*N*-diisopropylethylamine (155.1 mg, 209.0 µL, 1.20 mmol) and Pd[P(*o*-tol)$_3$]$_2$ (21.5 mg, 0.0300 mmol) were dissolved/suspended in THF (1.5 mL). This slurry was added to the imine/acid chloride solution and stirred until homogeneous. The headspace was briefly evacuated, and the reaction tube charged with 60 psi CO (gauge pressure). The mixture was heated to 50 °C for 24 hours with stirring. Afterward, the CO headspace was replaced with nitrogen, and the vessel returned to the glovebox. The mixture was diluted with THF (total volume ~6 mL) and split into six fractions, one for each of the model compounds. To each fraction was added a dipolarophile in the following amounts: dimethyl but-2-ynedioate: 28.4 mg, 24.6 µL, 0.200 mmol ethyl 3-phenylpropiolate: 32.0 mg, 29.5 µL, 0.200 mmol; 1,4-diphenylbut-2-yne-1,4-dione: 46.7 mg, 0.200 mmol; 3-bromo-1-hexyl-1H-pyrrole-2,5-dione: 28.6 mg, 0.110 mmol (also added *N*,*N*-diisopropylethylamine [12.9 mg, 17.4 µL, 0.100 mmol]); 2-chloroacrylonitrile: 11.0 mg, 10.0 µL, 0.126 mmol (also added *N*,*N*-diisopropylethylamine [12.9 mg, 17.4 µL, 0.100 mmol]).

The reaction mixtures were stirred at room temperature for 18 hours, except for that with 1,4-diphenylbut-2-yne-1,4-dione, which was heated to 50 °C for 18 hours. After the allotted reaction time, each solution was concentrated *in vacuo* and purified by flash chromatography on silica gel (details for each below). Because the six-way split of the solution of di(Münchnone), the reactions were not performed quantitatively; these compounds were sought just as models for spectroscopic comparisons with polymers **2.5** and **2.6**. The yields for the individual runs varied considerably, and were judged not representative of the reaction efficiency; the average yield was 82%.

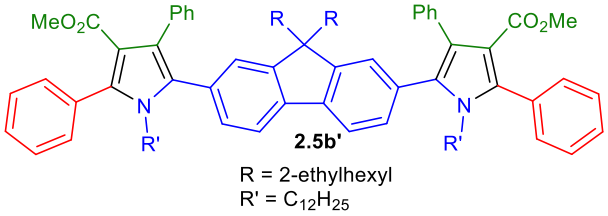


2.5a'

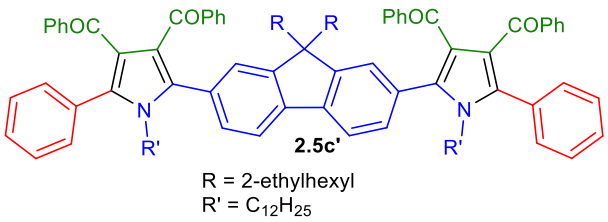
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

2.5a': ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.62 – 7.33 (m, 14H), 3.77 – 3.68 (m, 4H), 3.66 (s, 6H), 3.63 – 3.54 (m, 6H), 2.03 (m, 4H), 1.40 – 1.09 (m, 26H), 1.09 – 1.01 (m, 3H), 1.01 – 0.91 (m, 7H), 0.91 – 0.60 (m, 28H), 0.50 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 165.4, 151.1, 141.0, 136.6, 136.4, 131.1, 130.5, 129.8, 128.7, 128.2, 125.8, 125.7, 119.8, 114.8, 114.3, 55.0, 51.6, 51.4, 45.6,

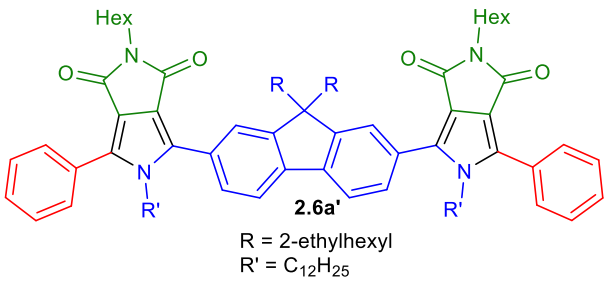
45.0, 34.8, 33.4, 31.9, 30.4, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.7, 28.4, 26.2, 26.1, 22.8, 22.7, 14.1, 14.0, 10.1. MS(ESI): $C_{81}H_{113}O_8N_2$ $[M+H]^+$ *m/z* calcd. 1241.84914; found 1241.84849.



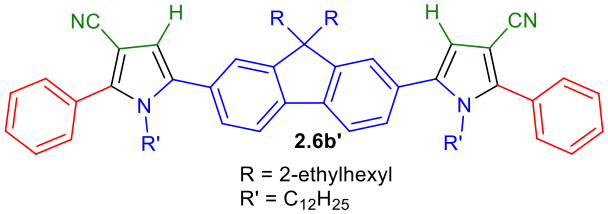
2.5b': Ratio of major to minor regioisomers (major shown): ~14.5:1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.33 (m, 12H), 7.32 – 7.24 (m, 2H), 7.20 (d, *J* = 7.1 Hz, 3H), 7.16 – 6.98 (m, 6H), 3.88 – 3.66 (m, 4H), 3.42 (s, 6H), 2.02 – 1.81 (m, 4H), 1.43 – 0.76 (m, 60H), 0.71 (t, *J* = 7.0 Hz, 6H), 0.60 (m, 4H), 0.52 – 0.33 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 151.2, 140.1, 138.2, 135.3, 132.7, 132.6, 130.7, 130.4, 128.5, 128.2, 128.0, 127.1, 126.8, 126.3, 125.8, 124.3, 119.7, 112.7, 54.5, 50.6, 46.0, 45.0, 34.9, 33.2, 33.1, 31.9, 30.6, 29.6, 29.4, 29.3, 29.2, 28.8, 28.2, 27.0, 26.3, 26.0, 25.9, 22.8, 22.7, 14.1, 10.2. MS(ESI): $C_{89}H_{117}O_4N_2$ $[M+H]^+$ *m/z* calcd. 1277.90079; found 127.89813.



2.5c': ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.54 (m, 2H), 7.48 (m, 4H), 7.45 – 7.36 (m, 10H), 7.36 – 7.27 (m, 6H), 7.27 – 7.17 (m, 4H), 7.14 – 6.99 (m, 8H), 3.91 (m, 4H), 2.02 – 1.82 (m, 4H), 1.40 – 1.10 (m, 26H), 1.07 (m, 3H), 1.00 (m, 3H), 0.94 – 0.65 (m, 22H), 0.59 (m, 12H), 0.40 – 0.24 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 192.0, 151.0, 140.8, 139.5, 137.4, 136.6, 131.7, 131.4, 131.1, 130.9, 130.3, 129.3, 128.9, 128.4, 128.2, 127.7, 127.6, 126.2, 124.2, 123.5, 119.6, 54.9, 45.4, 45.1, 34.6, 33.4, 31.9, 30.3, 29.6, 29.4, 29.3, 29.2, 28.7, 28.2, 26.2, 22.7, 14.1, 14.0, 9.9. MS(ESI): $C_{101}H_{121}O_4N_2$ $[M+H]^+$ *m/z* calcd. 1425.93209; found 1425.93277.



2.6a': ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.8 Hz, 2H), 7.75 – 7.60 (m, 8H), 7.53 (t, J = 7.5 Hz, 4H), 7.46 (t, J = 7.3 Hz, 2H), 4.31 – 4.13 (m, 4H), 3.55 (t, J = 7.2 Hz, 4H), 2.23 – 2.07 (m, 4H), 1.70 – 1.54 (m, 4H), 1.21 (m, 40H), 1.08 – 0.94 (m, 6H), 0.86 (m, 32H), 0.75 – 0.68 (m, 1H), 0.62 (m, 5H), 0.53 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 164.2, 151.5, 141.4, 134.9, 134.6, 129.6, 129.4, 129.1, 128.9, 128.7, 128.1, 124.6, 120.5, 118.8, 118.7, 55.4, 46.5, 46.5, 45.4, 45.3, 37.8, 34.8, 34.7, 33.4, 33.3, 31.9, 31.6, 31.5, 30.2, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.7, 28.2, 28.1, 26.6, 26.5, 25.9, 25.3, 22.8, 22.7, 22.6, 22.5, 14.1, 14.0, 13.9, 10.3, 10.2. MS(ESI): $C_{89}H_{127}O_4N_4$ $[M+H]^+$ *m/z* calcd. 1315.98518; found 1315.98105.



2.6b': Ratio of major to minor regioisomers (major shown): ~20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.6 Hz, 2H), 7.67 – 7.33 (m, 14H), 6.52 (s, 2H), 4.04 (m, 4H), 2.30 – 1.96 (m, 4H), 1.23 (m, 24H), 1.09 – 0.74 (m, 26H), 0.67 (m, 6H), 0.54 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 142.5, 141.2, 136.3, 132.2, 129.3, 128.8, 128.7, 128.2, 125.1, 124.9, 120.6, 117.1, 112.0, 93.1, 55.3, 45.8, 45.5, 34.8, 33.5, 33.4, 31.9, 30.2, 29.7, 29.6, 29.4, 29.3, 29.2, 28.7, 28.3, 26.6, 26.5, 26.0, 22.7, 14.1, 14.0, 10.2. MS(ESI): $C_{75}H_{102}N_4Na$ $[M+Na]^+$ *m/z* calcd.1081.79967; found 1081.79877.

2.5.6 Typical Procedure for the Synthesis of Poly-Münchnones **2.4a-e**

2.4a: In a glovebox, diimine **2.2a** (78.1 mg, 0.100 mmol) and terephthaloyl chloride **2.1a** (20.3 mg, 0.100 mmol) were dissolved with 0.5 mL of THF in a 5 mL vial. *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) and $Pd[P(o\text{-tol})_3]_2$ (7.2 mg, 0.010 mmol) were added together with 1.0 mL of THF and 0.5 mL of MeCN. The vial equipped with a stir bar was installed in a 40 mL Parr steel autoclave. The vessel was charged with

CO (20 bar) then heated at 45 °C in oil bath for 64 hours. The CO was evacuated, and the vessel was brought back into a glovebox. **2.4a** can be isolated if required by trituration and washing of the dark reaction slurry with acetonitrile (5 x 2 mL), to provide **2.4a** as a sparingly soluble purple/black solid. However, it is often more efficient and convenient to directly convert this product into polypyrrole **2.5a** by reaction with DMAD (see section VIII for detailed workup procedure) for yield and molecular weight determination: 73% yield. GPC: M_n = 22.7 kDa, PDI = 2.5. PolyMünchnone **2.4a** used for formation of polymers **2.5b, 2.5c,** and **2.6-8** was prepared in more moderate molecular weights (t = 30 h) to ensure complete product solubility for quantitative yield analysis.

2.4b: As above from **2.2a** (78.1 mg, 0.100 mmol), thiophene-2,5-dicarbonyl dichloride **2.1c** (20.9 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 ºC for 36 hours. (74% yield). GPC: M_n = 10.8 kDa, PDI = 2.8.

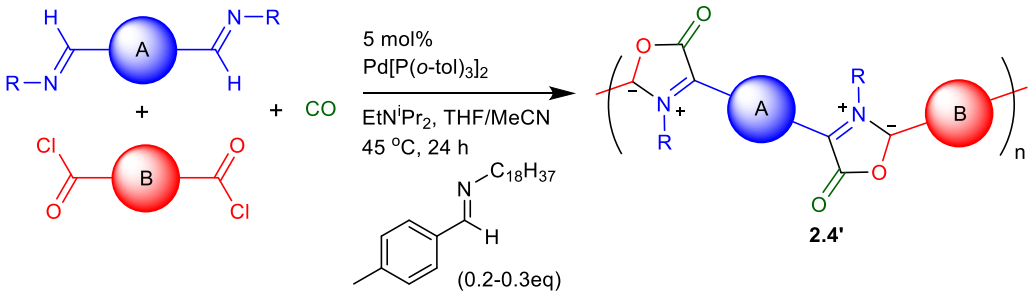
2.4c: As above from **2.2a** (78.1 mg, 0.100 mmol), furan-2,5-dicarbonyl dichloride **2.1b** (19.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.5/0.5 mL), 45 ºC for 64 hours. (78% yield). GPC: M_n = 12.5 kDa, PDI = 2.6.

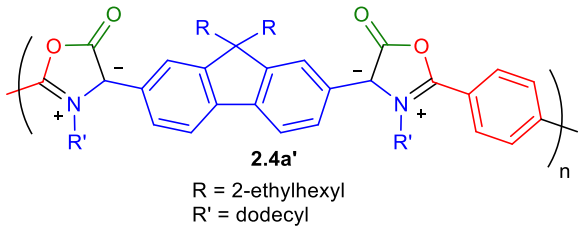
2.4d: As above from **2.2a** (78.1 mg, 0.100 mmol), 2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5,7-dicarbonyl dichloride **2.1d** (26.7 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.5/0.5 mL), 45 ºC for 64 hours. (76% yield). GPC: M_n = 12.8 kDa, PDI = 2.6.

2.4e: As above from **2.2b** (67.0 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 ºC for 21 hours. (55% yield). GPC: M_n = 9.4 kDa, PDI = 2.5.

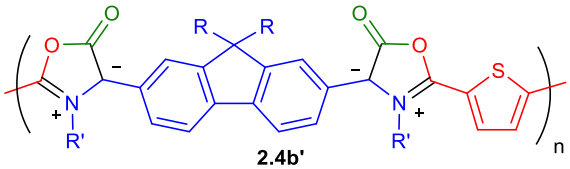
2.5.7 Synthesis of End-Capped Poly-Münchnones

For quantitative spectroscopic analysis, imine end capped polymers **2.4a-e'** were prepared as described below:





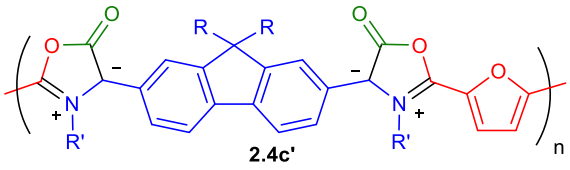
2.4a': In a glovebox, diimine **2.2a** (62.5 mg, 0.080 mmol) and (*p*-tolyl)HC=N(octadecyl) (12.7 mg, 0.04 mmol) were dissolved with 0.4 mL of THF in a 5 mL vial. Terephthaloyl chloride (20.3 mg, 0.100 mmol) was added. *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) and Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol) were added together with 1.1 mL of THF and 0.5 mL of MeCN. The vial equipped with a stir bar was installed in a 40 mL Parr steel autoclave. The vessel was charged with CO (20 bar) then heated at 45 °C in oil bath for 24 hours. The CO was evacuated, and the vessel was brought back into a glovebox. THF (~1 mL) was added to dissolve the purple residue. This darkly coloured solution was added dropwise to acetonitrile (16 mL) in a 20 mL capacity scintillation vial. The slurry thus formed was cooled to -35 °C overnight and subsequently centrifuged. The liquid layer was decanted and the solid residue triturated with acetonitrile repeatedly (3 x 2 mL). The solid product was dried *in vacuo* for 18 hours to give 80.7 mg of **2.4a'** (86% yield). GPC: M_n = 6.7 kDa, PDI = 2.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 7.25 (m, 10H), 4.40 – 4.31 (br m, 4H), 2.39 (s, 0.77H, *p*-tolyl end group), 2.09 (br m, 4H), 1.63 (br m, 4H), 1.34 – 0.54 (m, 72H). ^{13}C NMR (125 MHz, $CDCl_3$) 160.6, 151.4, 139.6, 137.3, 129.7, 128.8, 127.5, 125.0, 123.5, 120.2, 98.7, 98.3, 55.1, 47.7, 45.2, 34.7, 33.6, 31.9, 31.8, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 28.8, 28.6, 28.2, 26.6, 26.0, 14.1, 14.0, 10.2, 10.2. IR (film): λ_{CO} = 1714 cm^{-1}, λ_{CN} = 1553 cm^{-1}.



2.4b

R = 2-ethylhexyl
R' = dodecyl

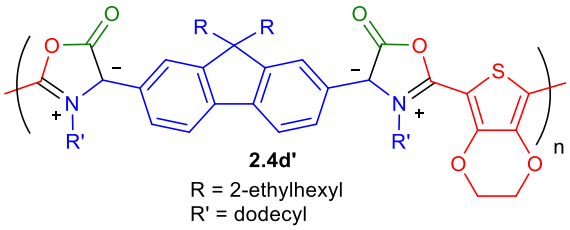
2.4b': As above from **2.2a** (54.7 mg, 0.07 mmol), thiophene-2,5-dicarbonyl dichloride, 20.9 mg, 0.1 mmol), (*p*-tolyl)HC=N(octadecyl) (22.3 mg, 0.060 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), and Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol). The reaction was heated to 45 °C for 24 hours before isolation. 89 mg (89% yield). GPC: M_n = 6.8 kDa, PDI = 2.9. ^{1}H NMR (400 MHz, $CDCl_3$) 7.76 – 7.05 (m, 8H), 4.37 – 4.26 (m, br, 4H), 2.38 (s, 0.96H, *p*-tolyl end group), 2.03 – 0.86 (m, 80H). ^{13}C NMR could not be obtained due to insufficient solubility of this polymer. Structure determined by conversion to polypyrrole **5g**.



2.4c'

R = 2-ethylhexyl
R' = dodecyl

2.4c': As above from **2.2a** (54.7 mg, 0.07 mmol), furan-2,5-dicarbonyl dichloride, 19.3 mg, 0.1 mmol), (*p*-tolyl)HC=N(octadecyl) (22.3 mg, 0.060 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), and Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol). The reaction was heated to 45 °C for 24 hours before isolation. 90 mg (90% yield). GPC: M_n = 5.7 kDa, PDI = 2.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 6.95 (m, 8H), 4.46 – 4.34 (br m, 4H), 2.38 (s, 1.30H, *p*-tolyl end group), 2.03 – 1.62 (m, 4H), 1.24 – 0.49 (m, 76H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 151.4, 139.3, 137.4, 131.6, 129.6 128.5, 126.8, 126.0, 124.4, 122.9, 120.3, 114.1, 98.5, 98.1, 55.1, 47.3, 46.8, 45.2, 34.6, 33.5, 31.9, 28.8, 28.1, 22.6, 21.2, 14.0, 10.2.

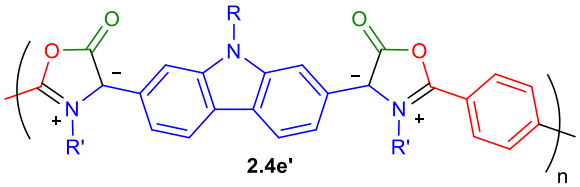


2.4d'

R = 2-ethylhexyl
R' = dodecyl

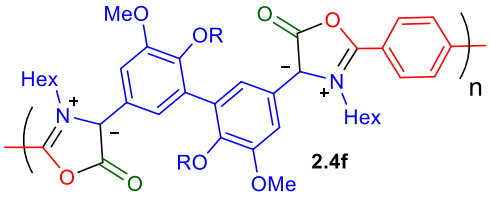
2.4d': As above from **2.2a** (54.7 mg, 0.07 mmol), 2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarbonyl dichloride, 26.7 mg, 0.1 mmol), (*p*-tolyl)HC=N(octadecyl) (22.3 mg, 0.060 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), and Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol). The reaction was heated to 45

°C for 24 hours before isolation. 92 mg (87% yield). GPC: M_n = 7.7 kDa, PDI = 2.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.21 (m, 6H), 4.50 – 4.27 (br m, 8H), 2.36 (s, 1.30H, *p*-tolyl end group), 2.02 (s, br, 2H), 1.61 (s, br, 2H), 1.24 – 0.53 (m, 76H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 160.6, 151.3, 139.5, 136.9, 134.2, 133.8, 129.6, 128.3, 126.6, 125.1, 122.9, 120.1, 64.9, 55.0, 47.5, 45.2, 34.7, 33.5, 31.8, 29.6, 28.1, 26.2, 22.6, 21.2, 14.1, 10.2.



2.4e'
R = 2-ethylhexyl
R' = dodecyl

2.4e': As above from **2.2b** (46.9 mg, 0.07 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.1 mmol), (*p*-tolyl)HC=N(octadecyl) (22.3 mg, 0.060 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), and Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol). The reaction was heated to 45 °C for only 8 hours before isolation. 78 mg (86% yield). GPC: M_n = 4.5 kDa, PDI = 2.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 7.24 (m, 10H), 4.43 – 4.28 (br m, 6H), 2.38 (s, 1.42H, *p*-tolyl end group), 1.68 – 0.85 (m, 61H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 139.0, 137.2, 129.6, 128.7, 127.3, 125.0, 123.5, 98.1, 65.9, 61.8, 53.3, 46.9, 31.8, 29.6, 29.4, 28.5, 25.9, 22.6, 21.2, 14.0, 11.0.

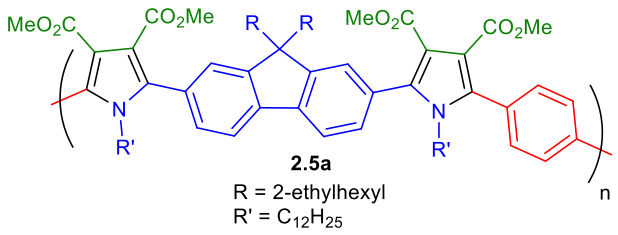


2.4f
R = 3,5,5-trimethylhexyl

2.4f': As above from **2.2c** (57.7 mg, 0.08 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), (*p*-tolyl)HC=N(octadecyl) (14.9 mg, 0.04 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), and Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol). The reaction was heated to 45 °C for only 24 hours before isolation. 72 mg (79% yield). GPC: M_n = 6.9 kDa, PDI = 1.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, br, 2H), 7.26 – 7.23 (m, 4H), 6.88 (s, br, 2H), 4.36 – 3.83 (m, 14H), 2.36 (s, 0.68H, *p*-tolyl end group), 1.66 – 0.74 (m, 56H). ^{13}C NMR (125 MHz, $CDCl_3$) δ160.6, 153.4, 145.3, 139.7, 132.6, 129.7, 128.8, 127.7, 123.6, 123.0, 112.1, 97.9, 71.9, 55.8, 51.4, 47.6, 39.5, 31.8, 31.0, 30.8, 29.9, 29.6, 29.3, 28.9, 27.2, 26.0, 25.5, 22.6, 22.3, 22.2, 14.1, 13.8.

2.5.8 General Procedure for the Synthesis of Polymers **2.5-2.8**

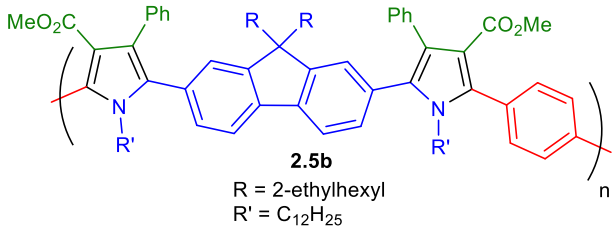
In a glovebox, diacid chloride **2.1** (0.1 mmol) and diimine **2.2** (0.100 mmol) were dissolved in 0.6 mL of THF in a 5 mL vial. *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) and Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol) in another 1.3 mL of THF and 0.6 mL of MeCN was added to the vial. The vial equipped with a stir bar was installed in a 40 mL Parr steel autoclave. The vessel was charged with CO (20 bar) and heated at 45 °C in oil bath for 21-48 hours as noted below. The CO was evacuated, and the vessel was brought back into a glovebox. 1.5 mL of THF and the appropriate dipolarophile (together with *N*,*N*-diisopropylethylamine in some cases, as noted below) was added. The reaction mixture was stirred at room temperature or 50 °C for 16 h. 0.2 mL water was added and the mixture was extracted with *o*-dichlorobenzene using a Soxhlet extractor. The solvent was removed under vacuum and the residue was dissolved with a minimum amount of hot chloroform (~ 1mL). The concentrated solution was dripped into methanol (~20 mL) to precipitate the polymer. The suspension was centrifuged, and the methanol layer decanted. The polymer was again washed with methanol (3 x 2 mL) before drying in under vacuum at 50 °C. To quantitate the conversion of **2.4** into **2.5-2.8**, ^{1}H, ^{13}C NMR and/or IR analysis were performed. For example, the ^{1}H NMR resonance for the NC*H*$_2$R in the Münchnone unit of **2.4a'** (δ 4.30-4.40 ppm) is in a unique location and can be easily monitored. This is replaced by the analogous signal in **2.5a** at δ 3.70 ppm. An example spectra of the conversion of **2.4a'** to **2.5a** is shown in Section 2.5.9 and integration shows no (< 5%) remaining Münchnone after reaction.



2.5a
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

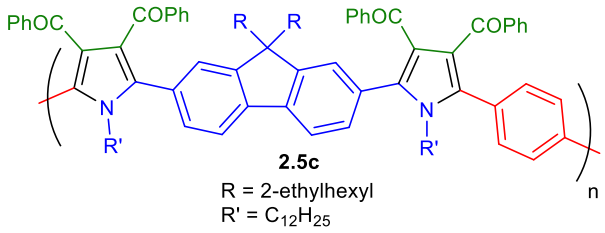
2.5a: As above from **2.2a** (78.1 mg, 0.10 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.5/0.5 mL), 45 ºC for 64 hours. The CO was evacuated, and the vessel was brought back into a glovebox. The slurry was suspended in

THF (2 mL), dimethyl but-2-ynedioate (56.8 mg, 0.400 mmol) in 3mL of THF was added, and the reaction mixture stirred at room temperature for 2 h. $CHCl_3$ (1 mL) was then added and the reaction mixture was left to stir an additional 16 h at room temperature. After the reaction was complete, 0.2 mL of water were added and the reaction mixture was heated at 120 °C for 2 days in order to hydrolyze any remaining imine or iminium salt end groups. The mixture was then filtered over loosely packed Celite. Tightly packed Celite would result in a loss of yield due to the removal of highly viscous higher molecular weight polymer. The polymer was precipitated and washed with MeOH (3x2 mL), and finally filtered through an alumina plug with chloroform as a solvent. 85 mg (73% yield). GPC: M_n = 22.7 kDa, PDI = 2.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.43 (m, 10H), 3.78 – 3.61 (m, 16H), 2.04 (s, br, 4H), 1.25 – 0.52 (m, 76H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 151.1, 141.0, 136.8, 135.6, 131.5, 130.3, 129.9, 129.6, 125.7, 119.8, 115.1, 115.0, 114.8, 54.9, 51.4, 45.5, 34.8, 33.4, 31.8, 30.6, 30.5, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.3, 26.4, 26.1, 22.7, 22.6, 14.0, 10.0.



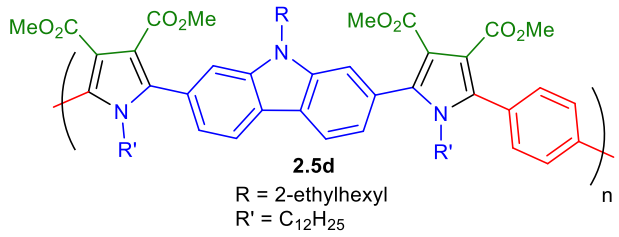
2.5b
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

2.5b: As above from **2.2a** (78.1 mg, 0.10 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 ºC for 30 hours. The cycloaddition step was carried out with methyl 3-phenylpropiolate (64.1 mg, 59.0 µL, 0.400 mmol) at 50 ºC for 16 h. 115 mg (91% yield). GPC: M_n = 11.1 kDa, PDI = 2.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 7.12 (m, 20H), 3.85 – 3.81 (m, 4H), 3.52 – 3.43 (m, 6H), 1.91 (s, br, 4H), 1.26 – 0.46 (m, 76H). ^{13}C NMR (125 MHz,/$CDCl_3$) δ 165.5, 151.2, 140.1, 137.5, 135.1, 130.7, 130.3, 127.1, 125.8, 124.6, 119.7, 113.0, 54.4, 50.4, 45.9, 45.3, 34.9, 33.1, 31.8, 30.7, 29.6, 29.5, 29.4, 29.2, 29.0, 28.2, 22.8, 22.6, 14.0, 10.2.



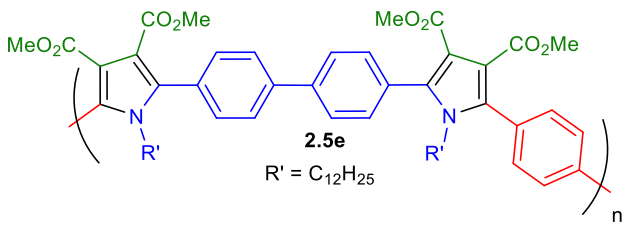
2.5c
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

2.5c: As above from **2.2a** (78.1 mg, 0.10 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 °C for 30 hours. The cycloaddition step was carried out with 1,4-diphenylbut-2-yne-1,4-dione (93.7 mg, 0.400 mmol) at room temperature for 16 h. 116 mg (82% yield). GPC: M_n = 10.6 kDa, PDI = 1.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.03 (m, 30H), 3.85 (s, br, 4H), 2.03 – 1.88 (m, 4H), 1.15 – 0.34 (m, 76H). ^{13}C NMR (125 MHz,/$CDCl_3$) δ 191.8, 151.1, 140.7, 139.3, 139.2, 139.1, 137.1, 136.9, 136.3, 131.8, 131.5, 131.2, 130.8, 129.2, 128.9, 127.7, 127.6, 126.0, 124.4, 124.3, 124.2, 123.8, 123.8, 119.7, 54.9, 45.3, 34.6, 33.4, 31.8, 30.4, 29.6, 29.5, 29.4, 29.3, 29.0, 28.1, 26.3, 26.1, 22.6, 14.1, 14.0, 13.9, 9.9.



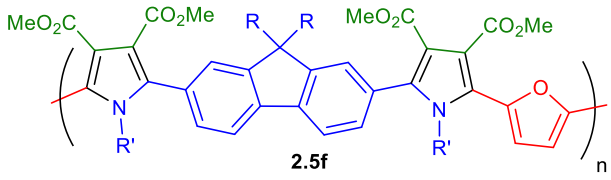
2.5d
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

2.5d: As above from **2.2b** (67.0 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 °C for 21 hours. The cycloaddition step was carried out with dimethyl but-2-ynedioate (56.8 mg, 50.0 µL, 0.400 mmol) at room temperature for 16 h. 53 mg (51% yield). GPC: M_n = 9.4 kDa, PDI = 2.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 7.26 (m, 10H), 4.21 – 3.49 (m, 18H), 1.58 – 0.84 (m, 61H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.2, 164.1, 138.0, 129.5, 127.1, 121.6, 120.1, 111.7, 53.9, 47.9, 40.3, 39.4, 37.3, 33.6, 33.6, 31.8, 30.1, 30.1, 29.6, 29.6, 29.3, 28.9, 26.9, 26.6, 22.9, 22.6, 14.2, 14.1, 13.9, 10.8.



2.5e
R' = $C_{12}H_{25}$

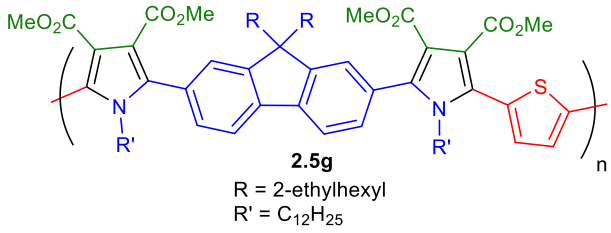
2.5e: As above from 1,1'-([1,1'-biphenyl]-4,4'-diyl)bis(N-dodecylmethanimine) (54.4 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 ºC for 48 hours. The cycloaddition step was carried out with dimethyl but-2-ynedioate (56.8 mg, 50.0 µL, 0.400 mmol) at room temperature for 16 h. 55 mg (55% yield). GPC: M_n = 8.2 kDa, PDI = 2.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 7.53 (m, 12H), 3.89 – 3.47 (m, 16H), 1.83 – 0.83 (m, 46H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 131.0, 130.4, 130.2, 126.9, 54.0, 51.7, 37.3, 37.0, 33.6, 31.8, 30.1, 30.0, 29.7, 29.5, 29.2, 28.7, 27.0, 26.6, 26.2, 26.1, 22.6, 22.3, 19.7, 14.1.



2.5f
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

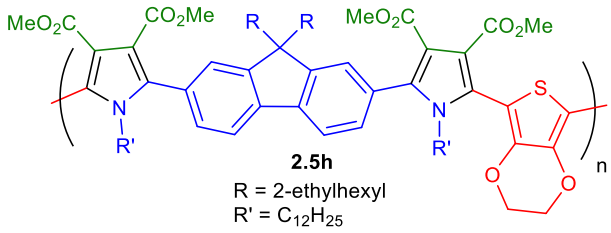
2.5f: As above from **2.2a** (78.1 mg, 0.100 mmol), furan-2,5-dicarbonyl dichloride **2.1b** (19.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.5/0.5 mL), 45 ºC for 64 hours. The CO was evacuated, and the vessel was brought back into a glovebox. The slurry was suspended in THF (2 mL), dimethyl but-2-ynedioate (56.8 mg, 0.400 mmol) in 3mL of THF was added, and the reaction mixture was stirred at room temperature for 2 h. $CHCl_3$ (1 mL) was then added and the reaction mixture was left to stir an additional 16 h at room temperature. After the reaction was complete, 0.2 mL of water were added and the reaction mixture was heated at 120 °C for 2 days in order to hydrolyze any remaining imine or iminium salt end groups. The mixture was then filtered over loosely packed Celite. Tightly packed Celite would result in a loss of yield due to the removal of highly viscous higher molecular weight polymer. The polymer was precipitated and washed with MeOH (3x2 mL) and finally filtered through an alumina plug with chloroform as a solvent. 90 mg (78% yield). GPC: M_n = 12.5 kDa, PDI = 2.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 6.31 (m, 8H), 3.91 – 3.43 (m, 16H), 2.03 (s, br, 4H), 1.38 – 0.51 (m, 76H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3,

164.4, 151.1, 144.2, 141.1, 138.4, 129.9, 129.4, 125.6, 124.3, 119.8, 117.2, 114.5, 113.5, 109.6, 55.0, 51.9, 51.3, 45.9, 34.8, 33.4, 31.8, 30.7, 29.6, 29.6, 29.3, 28.3, 26.4, 26.1, 22.6, 14.0, 10.0.



2.5g
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

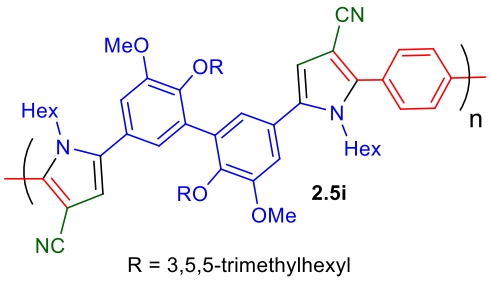
2.5g: As above from **2.2a** (78.1 mg, 0.100 mmol), thiophene-2,5-dicarbonyl dichloride **2.1c** (20.9 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 ºC for 36 hours. The cycloaddition step was carried out with dimethyl but-2-ynedioate (56.8 mg, 50.0 µL, 0.400 mmol) at room temperature for 16 h. 90 mg (74% yield). GPC: M_n = 10.8 kDa, PDI = 2.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 6.20 (m, 8H), 3.84 – 3.45 (m, 16H), 2.04 (s, br, 4H), 1.62 – 0.51 (m, 76H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 164.6, 151.2, 141.1, 137.8, 133.2, 129.9, 129.5, 126.7, 125.6, 119.8, 117.3, 114.8, 55.0, 51.7, 51.4, 45.5, 40.2, 34.9, 33.4, 31.8, 30.9, 29.6, 29.6, 29.5, 29.4, 29.2, 29.1, 28.3, 27.8, 22.8, 22.6, 14.0, 10.0.



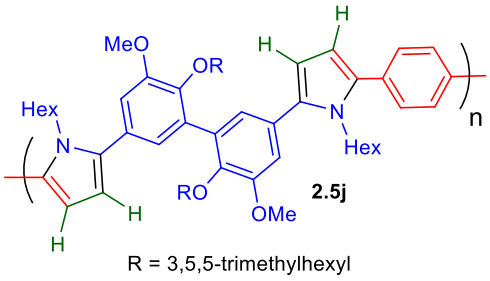
2.5h
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

2.5h: As above from **2.2a** (78.1 mg, 0.100 mmol), 2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5,7-dicarbonyl dichloride **2.1d** (26.7 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.5/0.5 mL), 45 ºC for 64 hours. The CO was evacuated, and the vessel was brought back into a glovebox. The slurry was suspended in THF (2 mL), dimethyl but-2-ynedioate (56.8 mg, 0.400 mmol) in 3mL of THF was added, and the reaction mixture was stirred at room temperature for 2 h. $CHCl_3$ (1 mL) was then added and the reaction mixture was left to stir 16 h at room temperature. After the reaction was complete, 0.2 mL of water were added and the reaction mixture was heated at 120 °C for 2 days in order to hydrolyze any remaining imine or iminium salt end groups. The mixture was then filtered over loosely

packed Celite. Tightly packed Celite would result in a loss of yield due to the removal of highly viscous higher molecular weight polymer. The polymer was precipitated and washed with MeOH (3x2mL) and finally filtered through an alumina plug with chloroform as a solvent. 94 mg (76% yield). GPC: M_n = 12.8 kDa, PDI = 2.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.40 (m, 6H), 4.28 (s, br, 4H), 3.88 – 3.42 (m, 16H), 2.03 (s, br, 4H), 1.61 – 0.51 (m, 76H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 151.0, 141.0, 139.7, 137.8, 129.9, 129.5, 125.6, 124.3, 119.7, 117.5, 115.2, 106.9, 64.6, 54.9, 51.6, 51.4, 45.5, 34.8, 33.4, 31.8, 30.7, 29.6, 29.5, 29.3, 28.3, 26.7, 26.1, 22.8, 22.6, 14.1, 10.0.

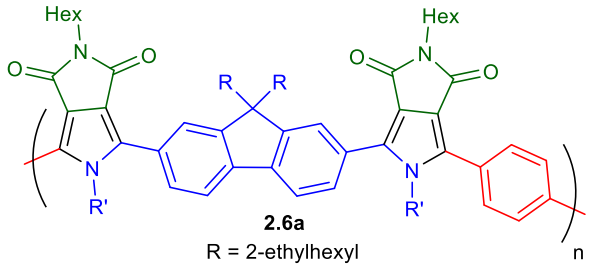


2.5i: As above from **2.2c** (72.1 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (0.75/0.25 mL), 45 °C for 40 hours. The cycloaddition step was carried out with 2-chloroacrylonitrile (35.0 mg, 32.0 µL, 0.400 mmol) and *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) at room temperature for 16 h. 75 mg (82% yield). GPC: M_n = 8.5 kDa, PDI = 1.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, br, 4H), 7.11 – 7.04 (m, br, 4H), 6.52 (s, 2H), 4.12 – 3.46 (m, 14H), 1.25 – 0.68 (m, 56H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 147.0, 142.8, 135.5, 132.8, 131.8, 129.2, 124.6, 124.2, 117.3, 113.1, 112.2, 92.9, 71.9, 56.0, 51.3, 46.0, 39.5, 31.0, 30.8, 30.1, 29.9, 29.6, 27.2, 26.0, 25.6, 22.3, 22.2, 13.8.



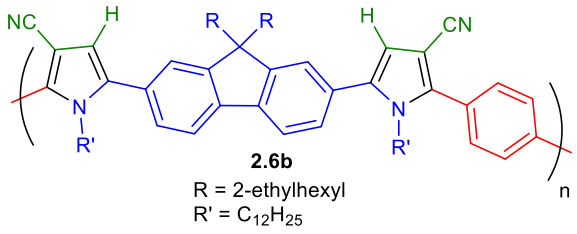
2.5j: As above from **2.2c** (72.1 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (0.75/0.25 mL), 45 °C for 40 hours. The cycloaddition step was carried out with triphenyl(vinyl)phosphonium bromide (147.7 mg, 0.400 mmol) and *N*,*N*-

diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) at room temperature for 16 h. 70 mg (80% yield). GPC: M_n = 8.1 kDa, PDI = 1.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, br, 4H), 7.04 – 7.00 (m, br, 4H), 6.27 – 6.26 (s, br, 4H), 4.13 – 3.48 (m, 14H), 1.25 – 0.69 (m, 56H). ^{13}C NMR (125 MHz, $CDCl_3$) 152.6, 145.5, 136.6, 136.0, 135.3, 132.9, 132.5, 128.9, 128.6, 120.9, 117.5, 112.3, 109.3, 71.7, 55.8, 51.4, 45.3, 39.5, 39.5, 30.8, 29.9, 29.6, 27.2, 26.6, 26.0, 22.3, 13.8.



2.6a
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

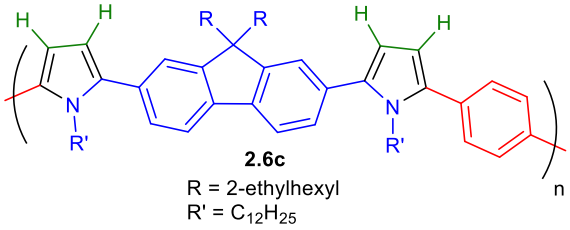
2.6a: As above from **2.2a** (78.1 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 °C for 30 hours. The cycloaddition step was carried out with 3-bromo-1-hexyl-1H-pyrrole-2,5-dione (104.1 mg, 0.400 mmol) and *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) at room temperature for 16 h. 126.8 mg (96% yield). GPC: M_n = 11.4 kDa, PDI = 2.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 7.70 (m, 10H), 4.31 (s, br, 4H), 3.57 (s, br, 4H), 2.48 (s, br, 4H), 1.63 (s, br, 4H), 1.29 – 0.56 (m, 94H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 164.0, 151.6, 141.4, 135.6, 133.8, 130.0, 129.7, 128.7, 128.0, 124.6, 120.6, 119.3, 119.0, 55.4, 46.9, 45.3, 37.9, 34.8, 33.3, 31.8, 31.4, 30.3, 29.6, 29.5, 29.4, 29.3, 28.8, 28.7, 28.1, 28.1, 26.6, 26.0, 22.7, 22.6, 22.5, 14.1, 14.0, 10.2, 10.2.



2.6b
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

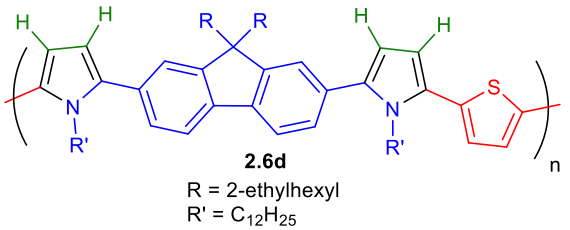
2.6b: As above from **2.2a** (78.1 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 °C for 30 hours. The cycloaddition step was carried out with 2-chloroacrylonitrile (35.0 mg, 0.400 mmol) and *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) at room temperature for 16 h. 92.4

mg (95% yield). GPC: M_n = 9.8 kDa, PDI = 2.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.55 (m, 10H), 6.61 (s, br, 2H), 4.12 (s, br, 4H), 2.14 (s, br, 4H), 1.25 – 0.56 (m, 76H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 143.0, 141.3, 135.5, 131.9 129.4, 128.8, 128.6, 125.0, 120.6, 116.8, 112.5, 93.4, 55.3, 46.0, 45.5, 34.8, 33.5, 33.4, 31.8, 29.7, 29.5, 29.4, 29.3, 28.8, 28.3, 26.6, 26.5 26.0, 22.6, 14.1, 14.0.



2.6c
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

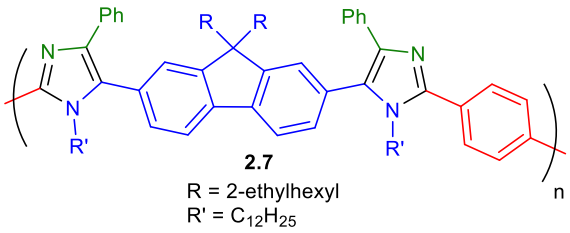
2.6c: As above from **2.2a** (78.1 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 °C for 30 hours. The cycloaddition step was carried out with triphenyl(vinyl)phosphonium bromide (147.7 mg, 0.400 mmol) and *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) at room temperature for 16 h. The product was isolated directly without Soxhlet extraction. 88 mg (95% yield). GPC: M_n = 8.1 kDa, PDI = 1.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 7.45 (m, 10H), 6.36 – 6.31 (m, 4H), 4.18 (s, br, 4H), 2.07 (s, br, 4H), 1.26 – 0.56 (m, 76H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 139.9, 137.5, 136.2, 132.6, 132.3, 128.8, 127.6, 124.6, 119.5, 109.5, 54.9, 45.5, 45.2, 34.7, 33.8, 33.6, 31.8, 30.6, 29.7, 29.6, 29.4, 29.4, 29.3, 28.9, 28.4, 28.3, 26.7, 26.6, 26.2, 22.7, 22.6, 14.1, 14.0, 10.3, 10.2.



2.6d
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

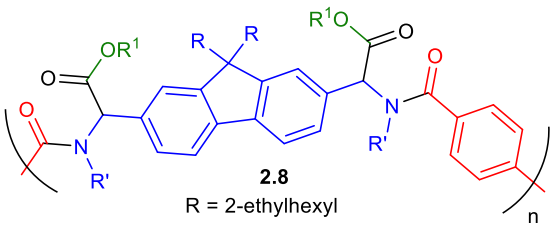
2.6d: As above from **2.2a** (78.1 mg, 0.100 mmol), thiophene-2,5-dicarbonyl dichloride **2.1c** (20.9 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 °C for 16 hours. The cycloaddition step was carried out with triphenyl(vinyl)phosphonium bromide (147.7 mg, 0.400 mmol) and *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) at room temperature for 16 h. The product was isolated directly without Soxhlet extraction. 76 mg (82% yield). GPC: M_n

= 6.1 kDa, PDI = 2.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.38 (m, 7H), 7.07 (s, br, 1H), 6.44 (s, br, 2H), 6.25 (s, br, 2H), 4.21 (s, br, 4H), 2.08 (s, br, 4H), 1.62 – 0.55 (m, 76H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 140.1, 137.5, 135.2, 134.6, 133.8, 132.3, 130.7, 130.3, 128.3, 128.0, 125.4, 124.8, 119.5, 110.7, 109.5, 68.1, 68.1, 54.9, 53.7, 45.4, 45.0, 42.0, 40.0, 34.7, 33.8, 33.5, 31.9, 30.9, 29.6, 29.6, 29.3, 28.3, 27.0, 26.8, 26.4, 22.7, 22.6, 14.2, 14.0, 10.2.



2.7
R = 2-ethylhexyl
R' = $C_{12}H_{25}$

2.7: As above from **2.2a** (78.1 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 °C for 40 hours. The cycloaddition step was carried out with *N*-benzylidene-4-methylbenzenesulfonamide (259 mg, 1.0 mmol) at room temperature for 16 h. The product was isolated directly without Soxhlet extraction. Indicated by ^{1}H NMR, the isolated product contains a very small amount of impurities containing the tosyl group. 75 mg (65% yield). GPC: M_n = 9.2 kDa, PDI = 1.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.18 (m, 20H), 3.85 – 3.47 (m, 4H), 2.05 (s, br, 4H), 1.25 - 0.52 (m, 76H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 134.8, 131.2, 129.9, 129.1, 128.6, 128.2, 126.8, 125.0, 121.1, 120.6, 55.3, 49.1, 44.4, 40.1, 34.7, 33.8, 31.8, 29.6, 29.4, 28.8, 28.1, 27.0, 22.6, 14.1, 13.9, 10.3.

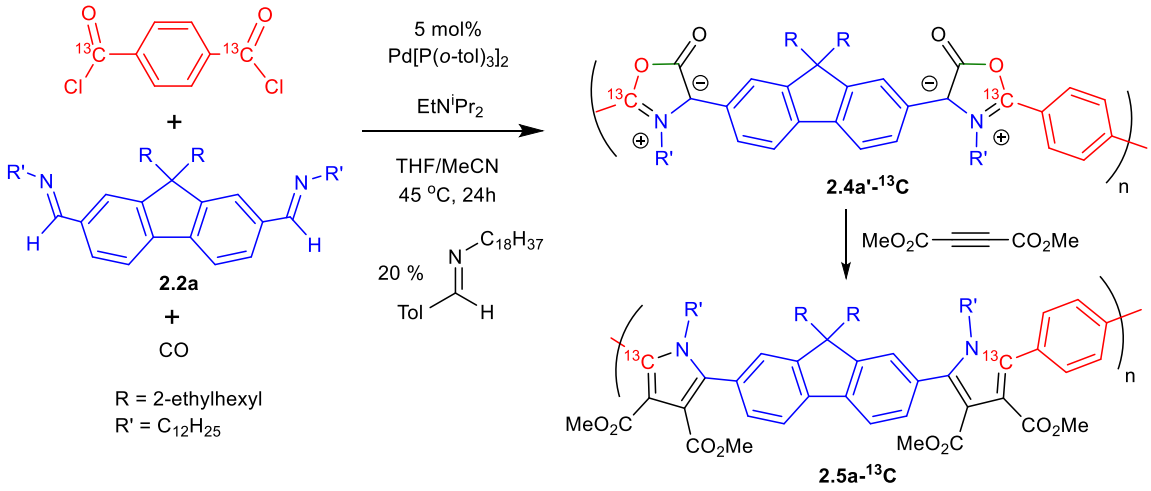


2.8
R = 2-ethylhexyl
R' = $C_{12}H_{25}$
R^1 = 3,5,5-trimethylhexyl

2.8: As above from **2.2a** (78.1 mg, 0.100 mmol), terephthaloyl chloride **2.1a** (20.3 mg, 0.10 mmol), *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol), Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol), CO (20 bar), THF/MeCN (1.9/0.6 mL), 45 °C for 30 hours. The crude polyMünchnone was quenched with 3,5,5-trimethylhexan-1-ol (57.7 mg, 0.400 mmol) at room temperature for 16 h and then heated at 70 °C for 1 hour. The crude mixture

was concentrated and precipitated in MeOH (~ 20 mL). The slurry thus formed was then centrifuged. The liquid layer was decanted and the solid residue triturated with MeOH repeatedly (3 x 2 mL). The solid product was dried *in vacu*. 103 mg (82% yield). GPC: M_n = 11.5 kDa, PDI = 2.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.52 (m, 10H), 6.04 – 5.90 (m, 2H), 4.26 – 4.20 (m, 4H), 3.31 – 3.22 (m, 2H), 2.01 - 0.52 (m, 114H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 170.3, 151.6, 140.9, 137.6, 132.9, 128.4, 126.8, 125.8, 120.0, 65.7, 64.1, 62.4, 55.0, 50.9, 47.6, 44.9, 37.6, 34.6, 33.6, 31.8, 31.0, 29.9, 29.5, 29.4, 29.3, 29.0, 28.3, 27.2, 26.6, 26.2, 22.6, 22.5, 14.1, 13.9, 10.2, 10.0.

2.5.9 Quantification of Cycloaddition with ^{13}C labelled **2.4a'**



In order to quantify the post-polymerization cycloaddition of polymers **2.4**, ^{13}C labelled polymer **2.4a'-^{13}C** was generated as follows: In a glovebox, diimine **2.2a** (62.5 mg, 0.080 mmol) and (*p*-tolyl)HC=N(octadecyl) (12.7 mg, 0.04 mmol) were dissolved with 0.4 mL of THF in a 5 mL vial. ^{13}CO-terephthaloyl chloride (20.3 mg, 0.100 mmol) was added. *N*,*N*-diisopropylethylamine (51.7 mg, 70.0 µL, 0.400 mmol) and Pd[P(*o*-tol)$_3$]$_2$ (7.2 mg, 0.010 mmol) were added together with 1.1 mL of THF and 0.5 mL of MeCN. The vial equipped with a stir bar was installed in a 40 mL Parr steel autoclave. The vessel was charged with CO (20 bar) then heated at 45 °C in oil bath for 24 hours. The CO was evacuated, and the vessel was brought back into a glovebox. THF (~1 mL) was added to dissolve the purple residue. This darkly colored solution was added dropwise to acetonitrile (16 mL) in a 20 mL capacity scintillation vial. The slurry thus formed was cooled to -35

°C overnight and subsequently centrifuged. The liquid layer was decanted and the solid residue triturated with acetonitrile repeatedly (3 x 2 mL). The solid product was dried *in vacuo* for 18 hours to give 66.2 mg of **2.4a'-^{13}C** (81% yield). Polymer **2.5a-^{13}C** was prepared as above from **2.4a'-^{13}C** (20.0 mg, 0.021 mmol) and DMAD (9 mg, 0.06 mmol). ^{13}C NMR analysis of **2.4a'-^{13}C** shows the incorporation of ^{13}C-label into the Münchnone unit (140 and 139 ppm) as the only enhanced signals in the aromatic region. After cycloaddition with DMAD, this signal is no longer present, and is replaced by ^{13}C enriched signals at 136 and 135 ppm, corresponding to the pyrrole backbone carbon. No other ^{13}C labeled signals are observed in the aromatic region, suggesting the essentially quantitative conversion (>95%) of the Münchnone unit into pyrrole.

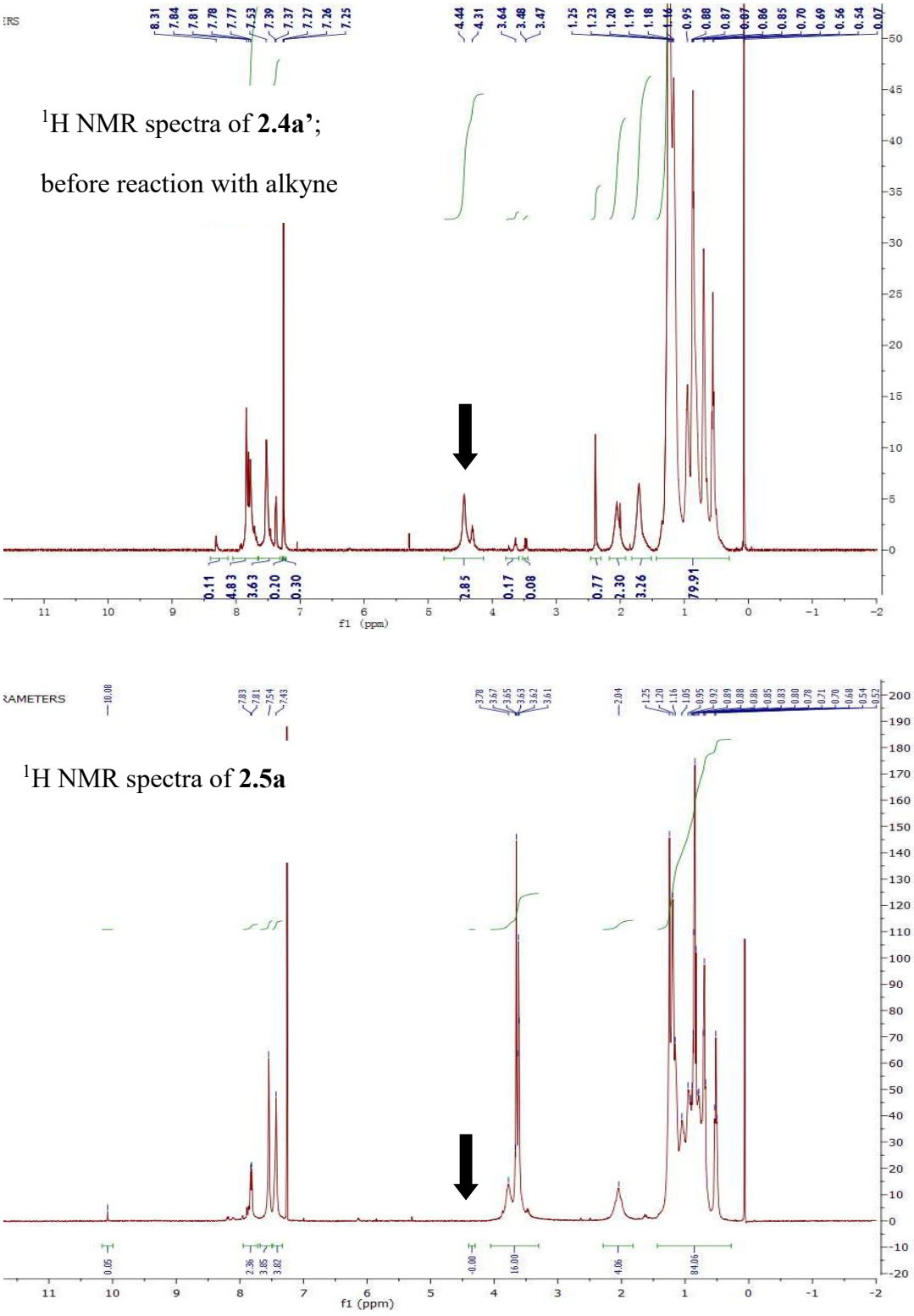


Figure 2.8a [1]H NMR spectra of **2.4a'** before and after reaction with the alkyne (**2.5a**).

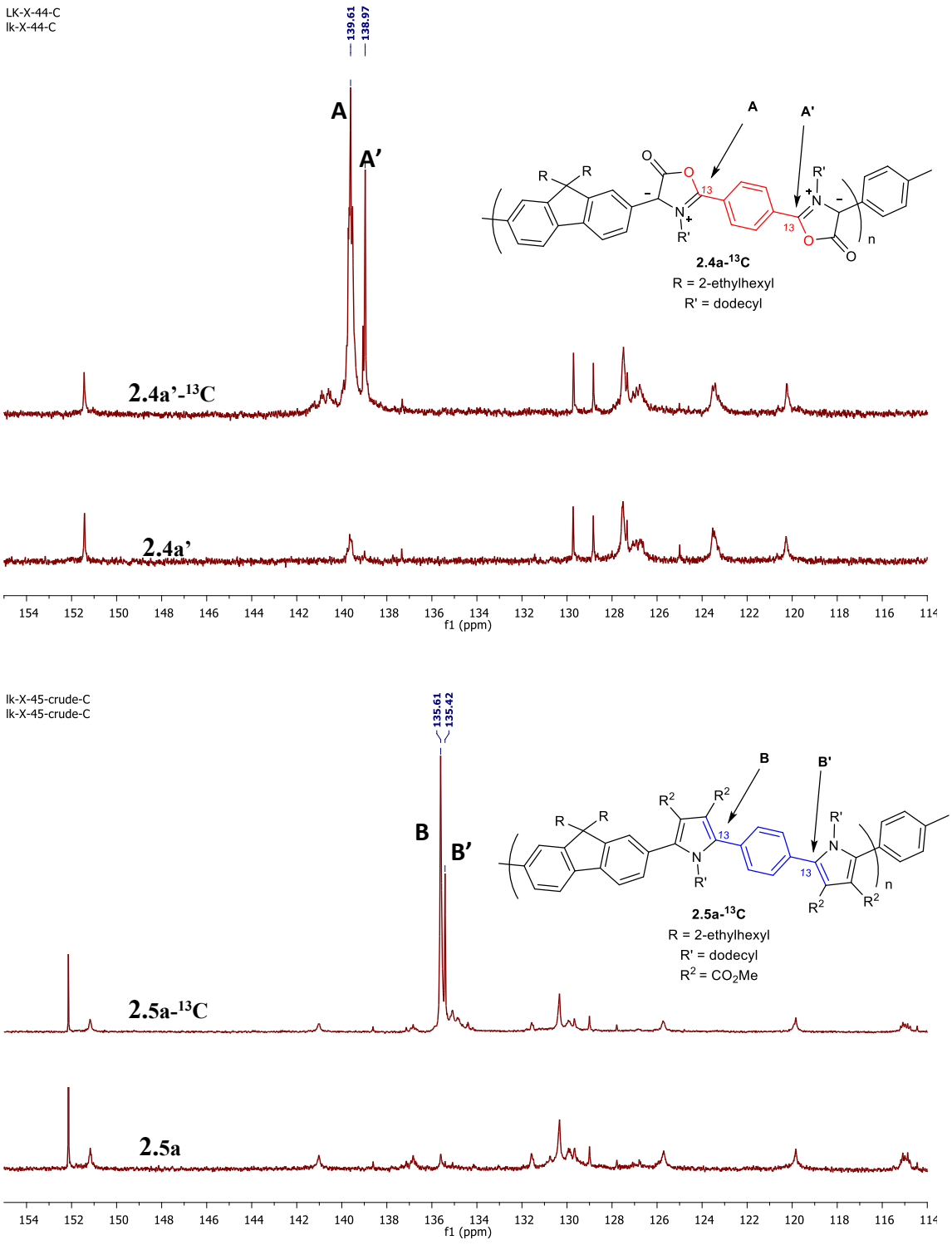


Figure 2.8b ^{13}C NMR spectra of **2.4a'-^{13}C**, **2.4a'**, **2.5a-^{13}C** and **2.5a** for the quantification of the cycloaddition.

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Chapter 3: A Metal-Free, Multicomponent Synthesis of Pyrrole-Based π-Conjugated Polymers from Imines, Acid Chlorides and Alkynes

3.1 Preface

The studies in Chapter 2 demonstrate that conjugated polymers can be synthesized via the palladium-catalyzed multicomponent reaction of diimines, diacid chlorides, carbon monoxide and alkynes/alkenes. In this chapter, we describe an alternative phosphonite-mediated multicomponent polymerization. This reaction uses diimines, diacid chlorides and (catechyl)PPh to generate poly(1,3-dipoles) which subsequently react with a range of alkynes / alkenes. This platform provides several advantages over the one in Chapter 2: higher molecular weight polymers are obtained, the reaction tolerates a broader scope of substrates, and more importantly, does not rely on a transition metal catalyst that can often be tedious to remove. To the best of our knowledge, this provides the first example of a metal-free multicomponent synthesis of conjugated polymers.

3.2 Introduction

Multicomponent coupling reactions (MCRs) have become of growing utility in synthetic chemistry.[1-10] In contrast to the more traditional multistep assembly of products, MCRs provide the potential to directly access complex structures from three or more building blocks, often with minimal waste, and with broad structural diversity. While these reactions have been most heavily exploited in small molecule organic synthesis and the generation of compound libraries of relevance to pharmaceutical development, the application of MCRs to polymer synthesis has also recently begun to attract attention.[11-14] These efforts have been directed towards the synthesis of functional condensation polymers, such as via the Passerini[15-17] and Ugi[18-21] three and four component reactions, “click”-

inspired reactions such as the mercaptoacetic acid locking imine (MALI),[22] Cu-catalyzed three-component synthesis of polyamidines,[23] A^3-coupling reactions,[24,25] and others.[26-30] Due to their high efficiency, MCRs have also been used in post-polymerization functionalization,[31-33] and in the synthesis of sequence-defined macromolecules.[34,35]

One area where multicomponent polymerization reactions could prove of significant utility is in the construction of π-conjugated polymers. Conjugated polymers have emerged as useful materials for a range of electronic applications (e.g. light-emitting devices, photovoltaics, field effect transistors, molecular sensors, charge transport, and others).[36-42] An important feature of conjugated macromolecules is their tunability, where changes to their structure or substituents can be used to create fined tuned polymers. While effective as a design tool, exploiting this tunability often results in structurally complex polymers. A number of powerful methods have been devised to construct conjugated polymers, including the now common use of palladium-catalyzed cross-coupling reactions.[43,44] Nevertheless, these achieve complexity from the monomer(s) themselves, which for many polymers can require an involved multistep synthesis. This can make access to the structural diversity, to optimize properties, an iterative, waste intensive, and often costly sequence, where each repeat unit must be synthesized prior to polymerization. These features have fueled developing interest in the design of more streamlined approaches to conjugated polymer synthesis.[45-47]

Despite the useful features of multicomponent polymerizations, only a few examples of the application of this technology to conjugated polymers have been reported. In early examples, Endo and Tomita described the use of multicomponent palladium catalyzed cross-coupling reactions to prepare alternating conjugated polymers (e.g. Figure 3.1a).[48-52] Tang and coworkers have reported several one-pot tandem three-component polymerizations for the synthesis of cross-conjugated polymers (e.g. Figure 3.1b).[53-56] And, while only involving two different monomers, Tilley, Tomita and Rivard have independently exploited the metallocene-mediated cycloaddition of alkynes followed by transmetallation to modularly generate polyheterocycles (e.g. Figure 3.1c).[57-61] Recently, we have noted that structurally more complex conjugated units can be assembled at the same time as the polymer in the palladium-catalyzed multicomponent formation of pyrrole-

based conjugated polymers (Figure 3.1d).[62] While efficient and opening access to new polymers, this latter reaction can also display limitations relative to more classic approaches to poly-heteroaromatics. Firstly, similar to cross coupling reactions, these polymerizations rely upon palladium catalysis, which can be sensitive to perform, shows scope limitations (e.g. the required use of fluorenyl imines), and can require extensive efforts to remove palladium defects from the product to minimize their influence on electronic properties. In addition, as with many multicomponent polymerizations, the molecular weights observed to date in multicomponent conjugated polymer synthesis are often moderate (typically < 15 repeat units). The latter presumably reflects the challenge of designing a multicomponent reaction with sufficient efficiency to generate high molecular weight materials.

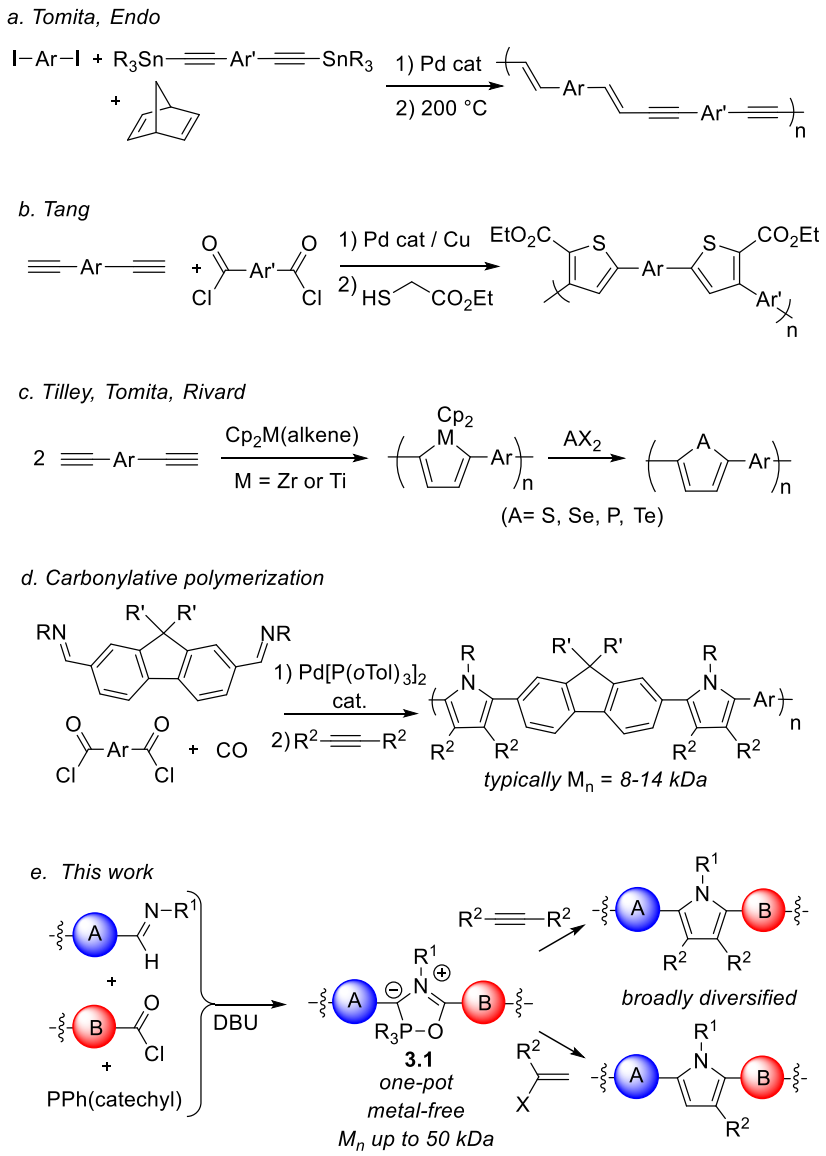


Figure 3.1 Multicomponent Approaches to π-Conjugated Polymers

In considering these issues, we have become interested in the design of a more broadly applicable multicomponent coupling reaction that incorporates a number of key features: a) it employs combinations of easily available substrates, b) is easy to perform, c) can be broadly diversified, d) does not employ transition metals, and, importantly, e) can allow the reliable synthesis of high molecular weight conjugated polymers. In this regard, we have recently reported a new multicomponent coupling reaction of imines, acid chlorides and a phosphonite ((catechyl)PPh) to generate 1,3-dipoles **3.1** (Figure 3.1e) i.e. phospha-Münchnones.[63-65] Compound **3.1** can undergo 1,3-dipolar cycloaddition with

dipolarophiles such as alkynes to generate polysubstituted pyrroles. A useful feature of this reaction for a polymerization is its synthetic simplicity, as it is a straightforward condensation of stable materials, each of which could potentially arise from available, commodity substrates (dialdehydes, diacid chlorides, alkynes or alkenes). As such, provided the efficiency of this transformation is sufficient for a polymerization, this could provide an attractive alternative to cross-coupling reactions to assemble conjugated polymers. We report below our studies towards this goal. These demonstrate that the multicomponent formation of poly-**3.1** can open a novel transition metal free route to construct π-conjugated materials from multiple monomers. This polymerization is easily performed, scalable, proceeds in high molecular weights, and displays the broadest substrate compatibility of which we are aware for a multicomponent conjugated polymer synthesis.

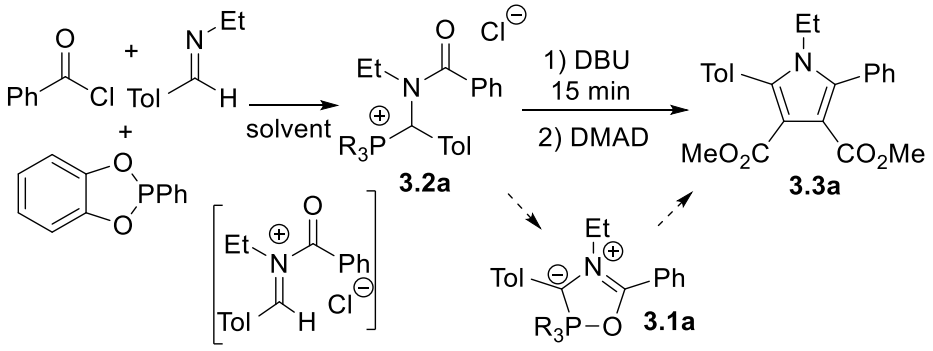
3.3 Results and Discussion

3.3.1 Stoichiometric Model Reactions

The reaction of imine, acid chloride, (catechyl)PPh and base, followed by alkyne, has been previously reported to generate pyrroles in good yields (70-90% yields), though not sufficient enough to form high molecular weight polymers.[63] Thus, prior to examination of this reaction for polymerizations, we first probed more closely the efficiency of the small molecule multicomponent coupling reaction. As illustrated in Table 3.1, monitoring this reaction by *in situ* ^{1}H NMR analysis ($CDCl_3$) shows the formation of phosphonium salt **3.2a** in 93% yield (entry 1). The addition of DBU base results in the formation of the 1,3-dipole **3.1a**, but requires the use of a large excess of base (2 equiv.), and is still incomplete (88%). Cycloaddition with dimethylacetylene dicarboxylate (DMAD) forms pyrrole in poor yield (58%). We postulated that the chloroform solvent may be partially interfering with the deprotonation reaction in this system, and lower product yields. Moreover, the generation and reactivity of the ionic intermediates in this reaction (e.g. phosphonium salt **3.2a**, 1,3-dipole **3.1a**) may show a strong dependence on solvent polarity. For example,

performing this reaction in less polar benzene results in the incomplete disappearance of the reagents and the formation of **3.2a** as an insoluble precipitate, which does not fully form either the 1,3-dipole or pyrrole (entry 2). Conversely, more polar methylene chloride or acetonitrile solvents result in the essentially quantitative formation of a soluble **3.2a** and phospha-Münchnone **3.1a** (entries 3,4), although in this case the 1,3-dipole is insoluble in acetonitrile. Interestingly, only moderate yields of pyrrole are observed upon DMAD cycloaddition in either solvent. Control experiments demonstrate that this arises in part from side reactions between the alkyne and the excess DBU employed to fully form **3.1a**. This effect can be minimized by the use of a stoichiometric amount of DBU base, but lowers the efficiency of the deprotonation of **3.2a** (92%, entry 6). Alternatively, the insolubility of **3.1a** in acetonitrile can allow its facile and quantitative removal from the reaction mixture by precipitation, and can be subsequently added to alkyne to form pyrrole in quantitative yields (entry 6). Notably, NMR analysis shows no evidence for byproducts in any of these steps, suggesting that this should be a viable platform for a polymerization (see experimental section 3.5.4).

Table 3.1 Optimization of the Multicomponent Reaction



Entry	Solvent	**3.2a** (%)	**3.1a** (%)	**3.3a** (%)
1	$CDCl_3$	93 (9h)	88[a]	58
2	C_6D_6	insoluble	78	61
3	CD_2Cl_2	99 (5h)	98	82
4	CD_3CN	98 (3h)	97	75
5	CD_2Cl_2	99 (5h)	92[b]	92
6	CD_2Cl_2[c]	99 (5h)	98	99[d]

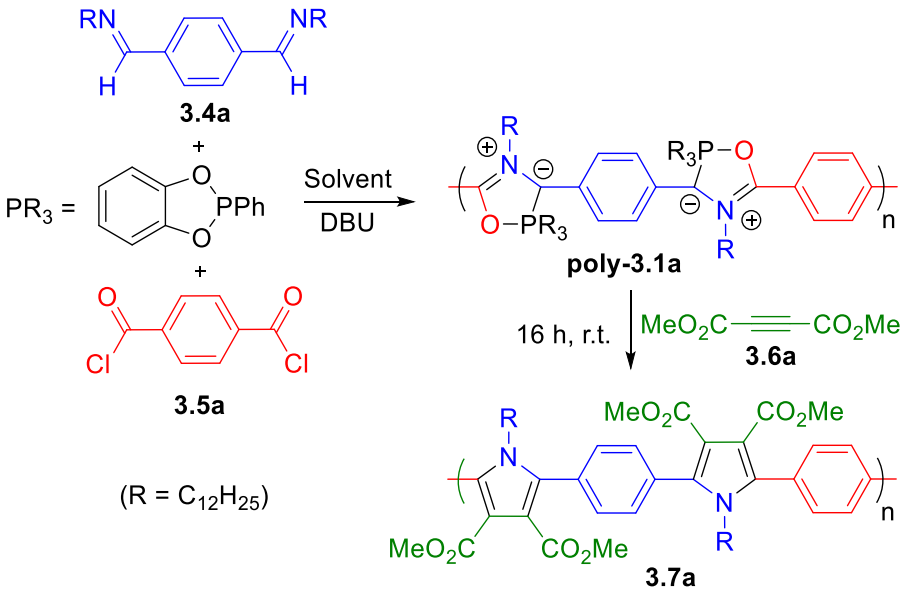
Imine (15 mg, 0.10 mmol), PhCOCl (14 mg, 0.10 mmol), (catechyl)PPh (24 mg 0.11 mmol), BnOBz standard, r.t. to form **3.2a**. Then DBU (18 mg, 0.12 mmol), 15 min to form **3.1a.** DMAD (43 mg, 0.3 mmol), 15 min to form **3.3a**. [a]DBU (0.2 mmol). [b]DBU (0.105 mmol). [c]**3.1a** precipitated before DMAD addition. [d]from **3.1a**.

3.3.2 Polymerization Chemistry

With the model reaction in hand, we next examined the ability of this chemistry to generate conjugated polymers. To do so, four simple reagents were employed: terephthaloyl chloride **3.5a**, a diimine derived from terephthaldehyde **3.4a**, (catechyl)PPh, and dimethyl acetylenedicarboxylate (**3.6a**). As shown in Table 2, the analogous reaction to that performed with model compounds above leads to the formation of the polymer **3.7a** in only moderate molecular weight (4.8 kDa, entry 1). As this molecular weight of the polymer is set during the addition of phosphine to the equilibrium generated poly(iminium salt), increasing solvent polarity (entry 2) or elevated temperatures (entries 4-6) can be used to favor this step, in the latter case leading to **3.7a** with molecular weights as high as 15.0

kDa.[66] ^{1}H and ^{31}P NMR analysis show that **3.7a** formed under the latter conditions has no detectable impurities beyond those assigned as end-groups (aldehyde (a), carboxylic acid (b) and amides (c), Figure 3.2a). In addition, the polymerization can be easily monitored by *in situ* ^{31}P NMR analysis (Figure 3.2b). These show that the polymerization is remarkably efficient at each stage of the reaction, and shows no evidence for any defects except for those representing end groups (<1%). This includes the final cycloaddition step to eliminate phosphine oxide, which is quantitative within NMR error. Interestingly, this end-group analysis suggests that this polymer is generated in higher molecular weights (M_n ~ 67 kDa) than that shown by GPC analysis. Consistent with this, GPC-MALLS-RI analysis of this same polymer reveals its absolute molecular weight is closer to 51.1 kDa, or a degree of polymerization (DP) of 120.[67] The latter is the highest molecular weight of which we are aware for a multicomponent conjugated polymer synthesis.

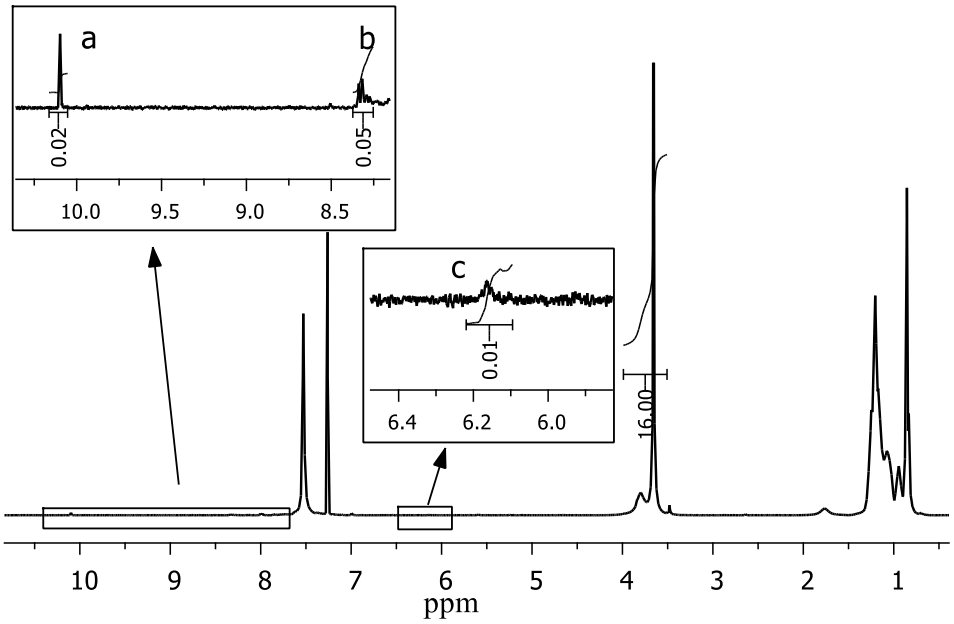
Table 3.2 Multicomponent Polymerization Development[a]



Entry	Solvent	Temp	Yield	M_n(kDa)/PDI
1	CH_2Cl_2	r.t.	71 %	4.8/1.6
2	CH_2Cl_2:CH_3CN	r.t.	68 %	8.9/1.5
3	CH_3CN	r.t.	insoluble	-
4	CH_2Cl_2	45 °C	74 %	9.4/1.9
5	CH_2Cl_2	55 °C	74 %	14.9/1.9
6	CH_2Cl_2:CH_3CN	55 °C	75 %	15.0/2.3 (51.1)[b]

[a] **3.4a** (47 mg, 0.10 mmol), **3.5a** (20 mg, 0.10 mmol), (catechyl)PPh (52 mg, 0.24 mmol), 0.6 mL of solvent, 24h, then DBU (46 mg, 0.30 mmol). **Poly-3.1a** precipitated with acetonitrile. **3.6a** (43 mg, 0.30 mmol). [b]Absolute M_n determined by GPC-MALLS.

a) ^{1}H NMR analysis of polymer **3.7a**



b) *In situ* ^{31}P NMR analysis of polymerization

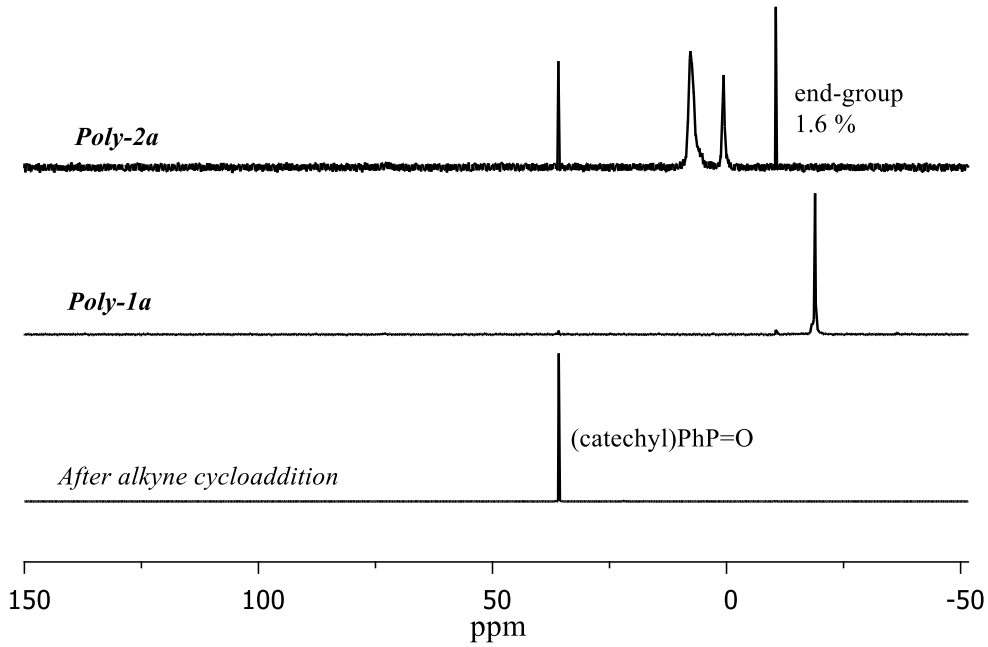
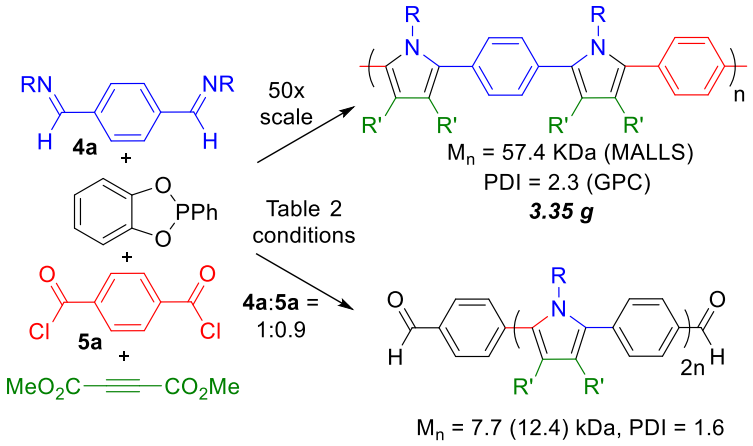


Figure 3.2 ^{1}H and ^{31}P NMR Analysis of the Polymerization. (a: aldehyde, b: carboxylic acid, c: amide end-groups in ^{1}H NMR). The signals for non-polymer bound excess (catechyl)PPh were omitted for clarity.

A feature of this reaction is its ability to access conjugated polymers without pre-synthesized conjugated units: terephthaloyl chloride **3.5a** is a monomer used in large scale polyamide production, diimine **3.4a** is derived from readily available terephthaldehyde and a primary amine, dimethylacetylene dicarboxylate (**3.6a**), an inexpensive and commercial alkyne, and (catechyl)PPh which can be easily generated from catechol and dichlorophenylphosphine.[63] As such, this represents an easily prepared conjugated polymer, which can be generated on multigram scale (Scheme 3.1). Systematic changes to the reaction conditions or stoichiometry can also be used to modulate the size and structure of **3.7a**. As an example, the use of a slight excess imine allows the generation of well-defined **3.7a** with addressable aldehyde end-groups (see experimental section 3.5.5). Alternatively, dilution of the reaction, which inhibits the equilibrium formation of iminium salt, leads to lower molecular weight materials. The polymerization can also be performed in a fully one-pot fashion by using a stoichiometric amount of base with only a slightly lower molecular weight (M_n = 10.5 kDa, see experimental section 3.5.7).



Scheme 3.1 Systematic Control of Multicomponent Polymerization

3.3.3 Polymer Diversity

As this polymerization uses available imine, acid chloride and alkyne monomers, it is straightforward to diversify. For example, as shown in Figure 3.3, a diverse range of diimines can be incorporated into this reaction. The accessibility of these monomers also makes it straightforward to tune the polymer structure. For example, as shown in Figure

3.3, a diverse range of diimines can be incorporated into this reaction. This includes carbazole (**3.4e**), fluorenyl (**3.4c)**, and biphenyl (**3.4d**) imines, which form polymers in molecular weights as high as 40 kDa. Other heterocycles can also be added into the polymer backbone, such as thiophenyl and bis-thiophenyl (**3.4g,h**). Cross-conjugated polymers can be similarly generated by the use of meta-substituted diimines (**3.4f**). Notably, these monomers are each formed from commercial and inexpensive dialdehydes. The acid chloride residue can also be modulated to incorporate a range of units. This can include thiophenyl diacid chloride (available in one step form adipic acid) (**3.5c**), furans (accessible from 2,5-furan dicarboxylic acid, a breakdown product of cellulose) (**3.5b**), as well as various other simple diacids (**3.4d-g**).

The dipolarophile can also be modulated in this reaction as a tool to tune pyrrole substituents. Excellent regioselectivities were obtained for the unsymmetrical alkynes (**3.6b,f**) and alkenes (**3.6d**) examined, which is notable compared to more classical Münchnone cycloadditions, which often leads to isomeric mixtures. This allows for the synthesis of regioregular conjugated polymers. Of note, vinylphosphonium bromide **3.6e** can be used as an acetylene equivalent to access unsubstituted pyrroles. Taken together, the diversity of the three monomers can allow the potential synthesis of over 300 structurally distinct conjugated polymers. We are aware of no other approach to conjugated polymers that provide such straightforward access to structural diversity, especially with high molecular weight control. As detailed in the experimental section (Table 3.4), analysis of the properties of these polymers shows that UV-Vis absorbance and fluorescence can be modulated by over 100 nm within the polymers generated, pyrrole fluorescent materials can be formed with fluorescence quantum efficiencies of up to 76 % for polymer $\mathbf{3.7}_{\mathbf{cfd}}$ obtained from a **3.4c**, **3.5f**, and **3.6d** combination of monomers.

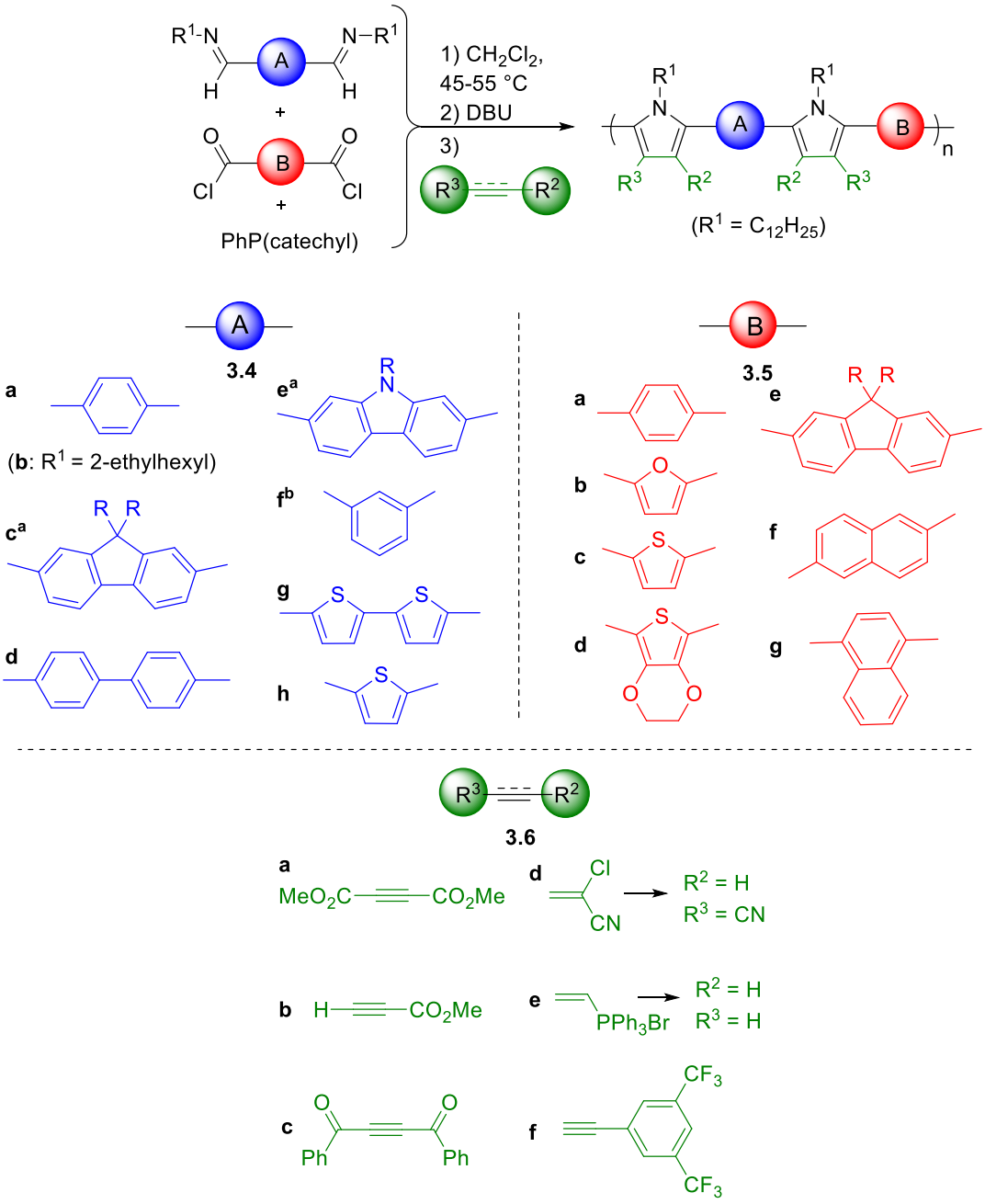


Figure 3.3 Diversity of Imine, Acid Chloride, Alkyne and Alkene Monomers. [a]R = 2-ethylhexyl. [b]R^1 = hexyl.

Table 3.3 Conjugated Polymers from Monomers Combinations[a]

Pdt	%	M_n[b]	PDI	DP	Pdt	%	M_n[b]	PDI	DP
3.7baa	63	11.3	2.1	31	**3.7cda**	74	15.1	1.8	25
3.7caa	91	25.3	2.3	43	**3.7cea**	86	34.6	1.7	41
3.7daa	98	24.4	2.3	43	**3.7cfa**	76	40.7	1.9	67
3.7eaa	66	16.3	1.7	32	**3.7cga**	87	30.1	1.7	57
3.7faa	54	14.2	2.3	33	**3.7cab**	82	18.7	2.3	36
3.7gaa	79	10.7	2.7	23	**3.7cac**	81	21.3	2.1	34
3.7haa	77	19.9	2.3	46	**3.7cad**	74	15.1	2.1	31
3.7cba	84	22.3	2.0	39	**3.7cae**	69	24.7	1.8	56
3.7cca	84	31.4	2.0	54	**3.7caf**	81	15.7	1.9	23

[a]Polymers **3.7xyz** with **x**: imine **3.4x**, **y**: acid chloride **3.5y**, and **z**: alkyne/alkene **3.6z**. Procedure of Table 3.2, entry 5: 0.10 mmol imine/acid chloride at 45-55 °C. See Experimental section for details. [b]M_n and PDI by GPC in THF vs polystyrene standards.

Pyrrole containing polymers and copolymers have attracted attention as conducting polymers for transistors, electrochromic devices, capacitors, electromagnetic shielding, and different types of sensors, although these materials are more classically generated from presynthesized pyrrole-containing monomers.[68-72] As an example, thiophene-pyrrole copolymers have been examined as field effect transistors.[73,74] Previous syntheses of these materials have involved electropolymerization[75] or multistep organic synthesis,[76,77] and formed insoluble or oligomeric materials. In contrast, as illustrated in Figure 3.4, the combination of the thiophenyl diimine **3.4h**, 2,5-thiophenedicarbonyl dichloride **3.5j** and (catechyl)PPh followed by vinyl phosphonium salt **3.6e** can allow the straightforward synthesis of the soluble alternating thiophene-pyrrole copolymer **3.8** in good molecular weight (11.0 kDa, PDI = 1.8), and no evidence of structural defects. UV-Vis analysis of **3.8** shows evidence for ordering in the solid state, while electrochemical analysis shows it is stable to reversible oxidation (See Figures 3.4b and 3.4c).

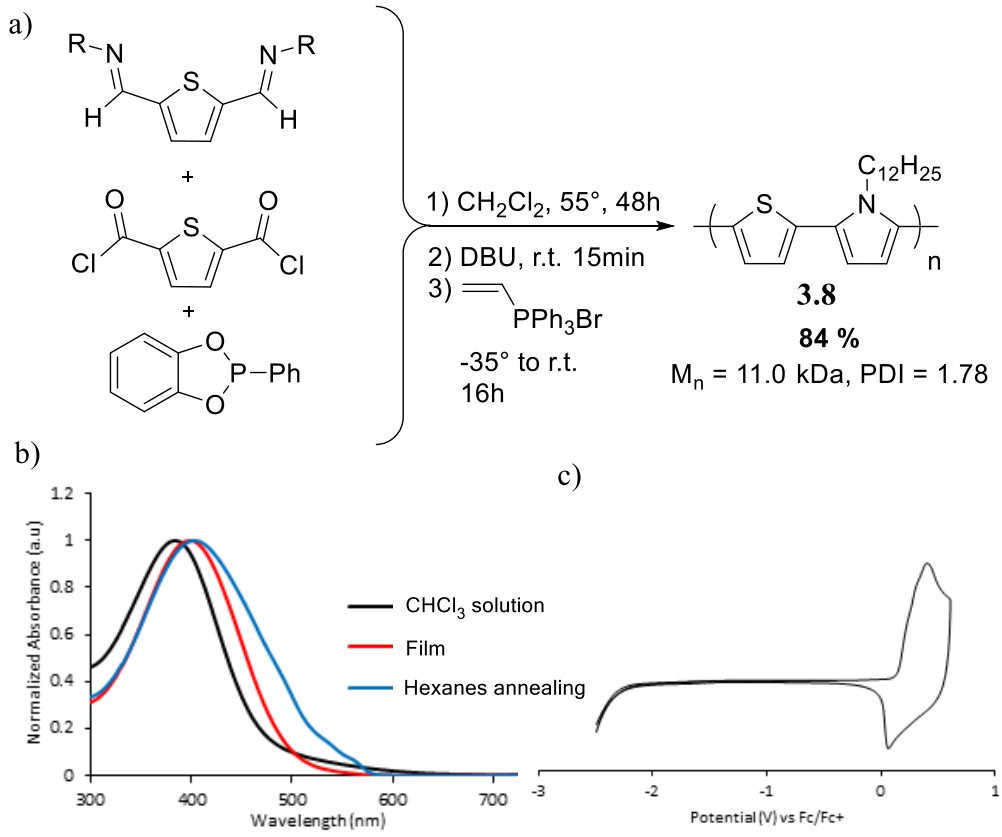


Figure 3.4 Multicomponent Synthesis of Polymer **3.8** **(a)** Synthesis of pyrrole-thiophene co-polymer. **(b)** Normalized UV-Vis in $CHCl_3$, as a thin film, and after hexanes annealing. **(c)** Cyclic voltammogram of thin film in CH_3CN (Bu_4NCl electrolyte)

3.4 Conclusions

In conclusion, we have developed a new, metal-free multicomponent synthesis of conjugated polymers. This approach allows the scalable synthesis of high molecular weight and essentially defect-free pyrrole-containing polymers directly from combinations of readily available diimines, diacid chlorides and alkynes / alkenes. The wide monomer scope of this reaction can provide a route to form libraries of conjugated polymers with tunable properties. Experiments directed towards expanding this multicomponent approach to access new polymers are currently underway.

3.5 Experimental Section

3.5.1 General Considerations

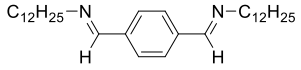
All reactions were carried out in a glovebox under a nitrogen atmosphere, unless described otherwise. Solution phase ^{1}H (400 or 500 MHz), ^{31}P (162 MHz) and ^{13}C (126 MHz) NMR spectra were recorded at ambient temperature; chemical shifts are reported in parts per million (ppm) relative to the corresponding residual *protio*-solvent signal. Mass spectra were acquired by electrospray ionization (ESI) with an orbitrap detector. The UV-Vis absorption of the polymers was measured in $CHCl_3$ solutions using a 1 cm path quartz cell on a UV-Vis spectrometer. The fluorescence quantum yields were determined versus anthracene in ethanol (Φ_{em} = 0.27) at slit widths of 2.5 nm. The excitation wavelength corresponds to the maxima of absorption for each polymer as per in Table 3.4. GPC was carried out with THF as the eluent and a UV-Vis absorbance detector. Samples were analyzed versus monodispersed polystyrene standards. Cyclic voltammetry was performed on a CH670 potentiostat from CH-Instruments in a three-electrode cell using a 0.1M solution of (TBA)PF_6 in CH_3CN as an electrolyte with the polymer drop-casted onto the working electrode. Platinum wires were used as working and counter electrodes, a $Ag/AgNO_3$ electrode was used as a reference. The scan rate was 0.1 V s^{-1} for all the measurements. All potentials were adjusted versus ferrocene (Fc/Fc^{+}).

All common reagents were purchased from Aldrich and used as received, unless otherwise noted. Common solvents (dichloromethane, acetonitrile) were sparged with dinitrogen, dried by passage through a column of alumina, and stored over activated sieves in an inert atmosphere glovebox for at least one week prior to use. $CDCl_3$ and CD_2Cl_2 were dried over CaH_2 for 24 hours, then degassed by the freeze-pump-thaw method and vacuum transferred prior to use. Dimethyl acetylenedicarboxylate, methyl phenylpropiolate, 2-chloroacrylonitrile, benzoyl chloride and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) were distilled from CaH_2. 9,9-Bis(2-ethylhexyl)-2,7-fluorene di(N-dodecylimine),[62] *N*-(2-ethylhexyl)-2,7-carbazole di(N-dodecylimine),[62] 1,3-phenyl di(N-hexylimine),[78] 2,5-furan dicarbonyl dichloride,[78] 2,5-thiophene dicarbonyl dichloride,[78] Naphthalene-2,6-dicarbonyl dichloride,[78] Naphthalene-1,4-dicarbonyl dichloride,[78] 9,9-Bis(2-ethylhexyl)-

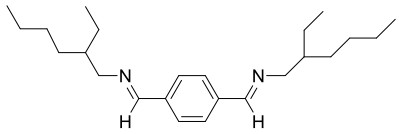
2,7-fluorene dicarbonyl dichloride,[62] 1,4-diphenylbut-2-yne-1,4-dione,[79] (catechyl)phenylphosphine,[63] N-ethyl-C-tolyl-imine,[80] were prepared according to literature procedures.

3.5.2 General Procedure for the Synthesis of Diimines

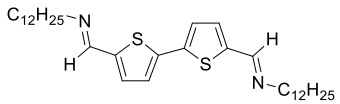
Dialdehydes (1 eq.) were dissolved in dichloromethane prior to the addition of the appropriate amines (2 eq.) and excess of anhydrous sodium sulfate. The reaction mixture was stirred for 18h. The suspension was then filtered and the solvent evaporated under vacuum. The resulting solid or oils were dried under vacuum at 70 °C for 18h to afford pure bis-imines.



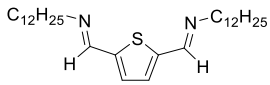
3.4a: white solid (96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 2H), 7.76 (s, 4H), 3.61 (t, J = 7 Hz, 4H), 1.70 (m, 4H), 1.68-1.25 (m, 36H), 0.87 (t, 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.12, 138.09, 77.24, 76.98, 76.73, 61.94, 31.90, 30.88, 29.65, 29.62, 29.57, 29.43, 29.33, 27.36, 22.67, 14.09. MS(ESI): $C_{32}H_{57}N_2$ $[M+H]^+$ *m/z* calcd. 469.45163; found 469.45252.



3.4b: yellow oil (94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 2H), 7.76 (s, 4H), 3.62 – 3.44 (m, 4H), 1.78 – 1.57 (m, 2H), 1.48 – 1.22 (m, 16H), 1.01 – 0.78 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.19, 138.13, 77.25, 76.99, 76.74, 65.28, 40.53, 31.38, 28.97, 24.58, 23.03, 14.10, 10.97. MS(ESI): $C_{24}H_{41}N_2$ $[M+H]^+$ *m/z* calcd. 357.32643; found 357.32662.



3.4g: brown solid (96%). Dialdehyde synthesized according to previously reported procedure.[81] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.17 (s, 4H), 3.58 (b, 4H), 1.68 (s, b, 4H), 1.31-1.25 (m, 36H), 0.87 (t, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.60, 142.01, 139.74, 130.70, 124.46, 61.46, 31.90, 30.84, 29.65, 29.62, 29.61, 29.57, 29.41, 29.34, 27.31, 22.67, 14.10. MS(ESI): $C_{34}H_{57}N_2S_2$ $[M+H]^+$ *m/z* calcd. 557.39577; found 557.39680.



3.4h: brown solid (97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.22 (s, 2H), 3.56 (td, *J* = 6.9, 0.9 Hz, 4H), 1.74 – 1.56 (m, 4H), 1.47 – 1.08 (m, 36H), 0.87 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.52, 144.80, 129.34, 61.46, 31.90, 30.82, 29.65, 29.62, 29.58, 29.42, 29.34, 27.30, 22.67, 14.10. MS(ESI): $C_{30}H_{55}N_2S$ $[M+H]^+$ *m/z* calcd. 475.40805; found 475.40844.

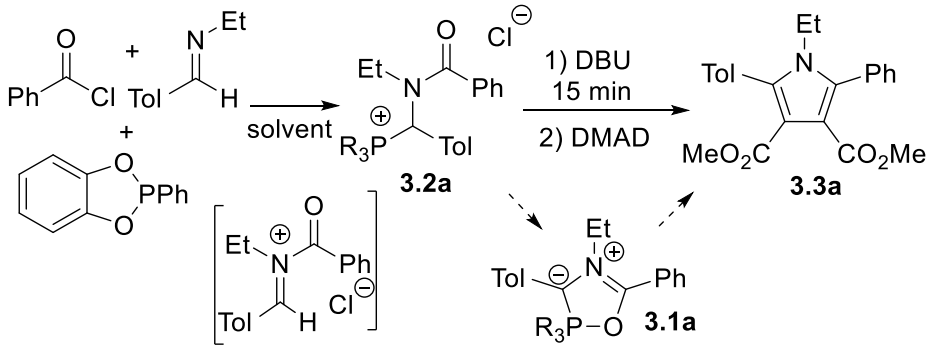
3.5.3 Supplementary Table

Table 3.4 Properties of the (Polypyrroles)

					Solution[b]				Film[c]	
Polymer	Yield %	M_n (kDa)	PDI	DP	λ_{abs} (nm)	E_{gap}[d] (eV)	λ_{em} (nm)	Φ_{em}[e]	λ_{abs} (nm)	E_{gap}[d] (eV)
3.7$_{aaa}$	74	14.9	1.9	35	296	3.45	411	0.29	297	3.34
3.7$_{baa}$	63	11.3	2.1	31	304	3.38	403	0.32	305	3.30
3.7$_{caa}$	91	25.3	2.3	43	320	3.30	411	0.55	323	3.24
3.7$_{daa}$	98	24.4	2.3	43	300	3.39	407	0.36	308	3.29
3.7$_{eaa}$	66	16.3	1.7	32	320	3.15	412	0.22	323	3.19
3.7$_{faa}$	54	14.2	2.3	33	282	3.49	406	0.28	290	3.45
3.7$_{gaa}$	79	10.7	2.7	23	345	2.94	487	0.14	353	2.71
3.7$_{haa}$	77	19.9	2.3	46	300	3.29	463	0.30	302	3.19
3.7$_{cba}$	84	22.3	2.0	39	321	3.13	460	0.37	321	3.09
3.7$_{cca}$	84	31.4	2.0	54	320	3.14	466	0.28	322	3.07
3.7$_{cda}$	74	15.1	1.8	25	320	3.08	460	0.12	319	3.15
3.7$_{cea}$	87	30.1	1.7	41	328	3.23	414	0.64	328	3.19
3.7$_{cfa}$	76	40.7	1.9	67	323	3.19	408	0.58	326	3.18
3.7$_{cga}$	86	34.6	1.7	57	320	3.22	431	0.33	323	3.16
3.7$_{cab}$	82	18.7	2.3	36	341	3.12	439	0.57	340	3.08
3.7$_{cac}$	81	21.3	2.1	31	325	2.96	485	0.02	327	3.01
3.7$_{cad}$	74	15.1	2.1	31	347	3.01	432	0.59	353	2.82
3.7$_{cae}$	69	24.7	1.8	56	369	2.89	448	0.28	376	2.79
3.7$_{caf}$	81	15.8	1.9	23	347	2.97	450	0.50	346	2.81
3.7$_{cfd}$	79	21.4	2.4	41	351	3.00	428	0.76	354	2.92
3.8	84	11.0	1.8	34	384	2.40	526	0.04	403[f]	2.17[f]

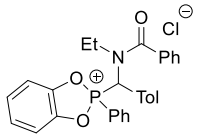
[a] Yield and properties of isolated polymers. Molecular weight (M_n), polydispersity (PDI), and degree of polymerization (DP=2n) obtained by GPC in THF versus polystyrene standards. [b] Chloroform solution. [c] Drop-casted film on glass plate. [d] Estimated from the absorption onset. [e] Calculated using an anthracene standard. [f] After hexanes vapors annealing.

3.5.4 Typical Procedure for the Stoichiometric Model Reactions



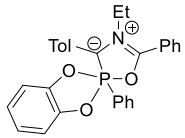
In the glovebox, imine (14.7 mg, 0.10 mmol), PhCOCl (14.1 mg, 0.10 mmol), (catechyl)PPh (23.8 mg 0.11 mmol) were added together in the appropriate deuterated solvent (as per Table 3.1) and transferred into a J-Young NMR tube. The reaction was monitored by ^{1}H and ^{31}P NMR and yields calculated versus a benzyl benzoate (BnOBz) internal standard by comparison with initial NMR (imine + BnOBz). The reaction was left at room temperature until full conversion to **3.2a**. **3.1a** is formed within 15 min at room temperature after the addition of DBU (0.105 - 0.12 mmol). DMAD (42.6 mg, 0.30 mmol) was then added at room temperature, complete conversion occurs in 15 min to yield pyrrole **3.3a**.

Isolation of the intermediates: Phosphonium salt **3.2a** can be isolated by precipitation in toluene. Phospha-Münchnone **3.1a** can be isolated by precipitation in CH_3CN. **3.3a** can be isolated by filtration through an alumina plug with $CHCl_3$ followed by crystallization at low temperature in hexanes.

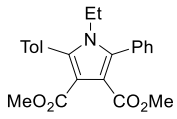


3.2a: Mixture of diastereomers: 1: 8.7: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.47 (s, 1H), 8.33 (s, 1H), 8.03 (s, 0.20H), 7.93 – 6.38 (m, 15H), 4.57 (s, 0.87H), 4.33 (s, 0.10H), 3.83 (s, 0.10H), 3.73 (s, 0.87H), 2.32 (s, 0.7H), 2.18 (s, 2.3H), 1.13 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.3 (major), -0.4 (minor). ^{13}C NMR (126 MHz, $CDCl_3$) (minor isomer's peak may not be reported) δ 170.2 (d, $^{4}J_{C\text{-}P}$ = 7.5 Hz), 146.6, 140.7 (d, $^{1}J_{C\text{-}P}$ = 159.1 Hz), 134.7, 133.6, 131.6, 131.5, 130.01, 129.9 (d, $^{4}J_{C\text{-}P}$ = 2.5 Hz), 129.6, 129.5, 129.4, 129.09 (d, $^{2}J_{C\text{-}P}$ = 17.3 Hz), 128.7,

128.6_5, 124.9 (d, $^2J_{C\text{-}P}$ = 17.3 Hz), 124.2, 123.70, 121.4, 111.5 (d, $^3J_{C\text{-}P}$ = 6.9 Hz), 59.0 (d, $^1J_{C\text{-}P}$ = 119.3 Hz), 46.3 (d, $^3J_{C\text{-}P}$ = 9.1 Hz), 21.2, 14.6. MS could not be obtained.



3.1a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (m, 2H), 7.53 (m, 2H), 7.46 – 7.35 (m, 3H), 7.35 – 7.19 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 1H), 6.72 (d, *J* = 4.2 Hz, 2H), 6.49 (s, 1H), 3.88 (q, b, *J* = 7.0 Hz, 2H), 2.37 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ -18.5. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 142.9 (d, $^1J_{C\text{-}P}$ = 225.7 Hz), 135.5 (d, $^4J_{C\text{-}P}$ = 1.8 Hz), 134.9 (d, $^{3\ or\ 4}J_{C\text{-}P}$ = 6.0 Hz), 132.8 (d, $^2J_{C\text{-}P}$ = 18.2 Hz), 129.8, 128.6 (d, $^4J_{C\text{-}P}$ = 3.7 Hz), 128.3, 128.0, 128.0_3, 127.9 (d, $^4J_{C\text{-}P}$ = 2.1 Hz), 127.8, 127.0, 121.7, 118.9, 110.7, 73.01 (d, $^1J_{C\text{-}P}$ = 261.8 Hz), 42.6 (d, $^3J_{C\text{-}P}$ = 8.0 Hz), 21.2, 15.2. MS(ESI): $C_{29}H_{23}O_3NP$ $[M+H]^+$ *m/z* calcd. 468.17231; found 468.17159.



3.3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 5H), 7.34 – 7.22 (m, 4H), , 3.72 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 3.64 (s, 3H), 2.41 (s, 3H), 0.82 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 165.4, 138.6, 136.5, 136.1, 131.1, 130.5, 130.3, 129.0, 128.7, 128.2, 127.9, 114.4, 114.3, 51.5, 51.5, 39.8, 21.4, 16.1. MS(ESI): $C_{23}H_{24}O_4N$ $[M+H]^+$ *m/z* calcd. 378.16998; found 378.16890.

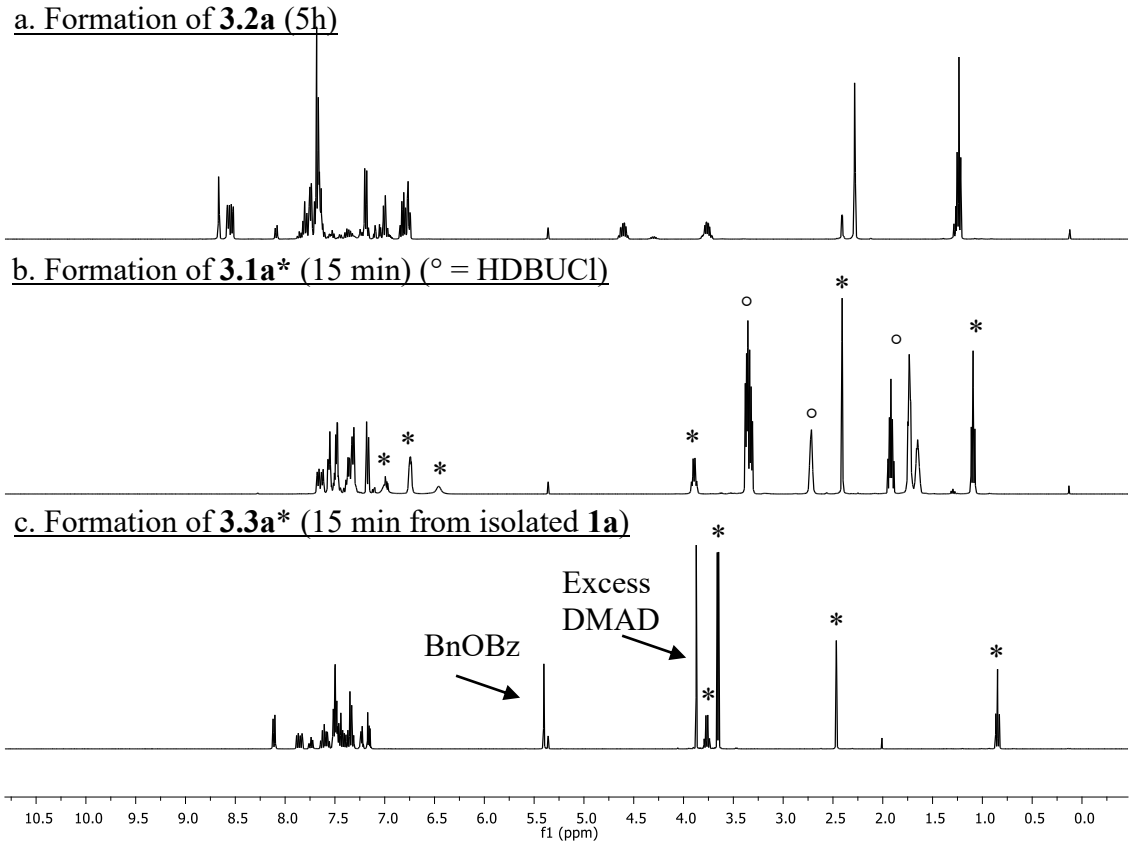


Figure 3.5. ^{1}H NMR of *In-Situ* Reaction Intermediates in CD_2Cl_2.

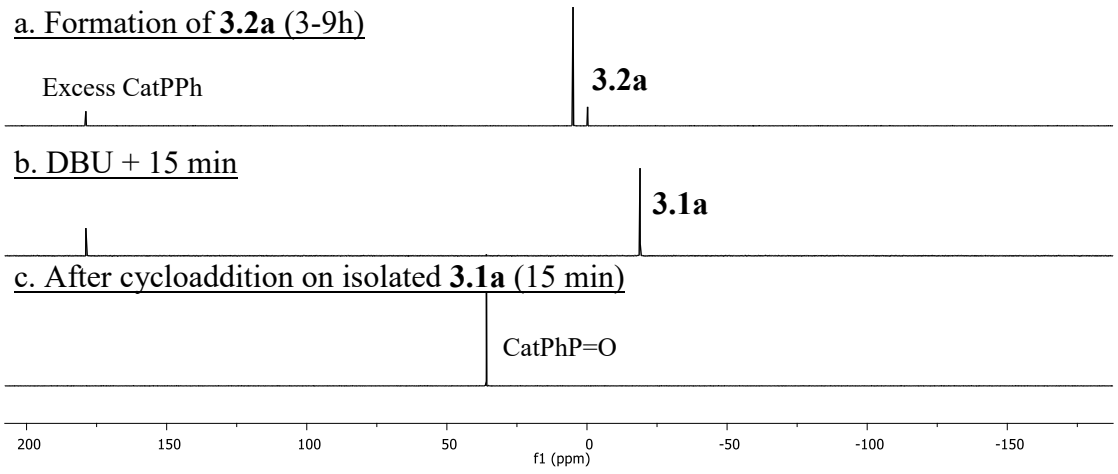
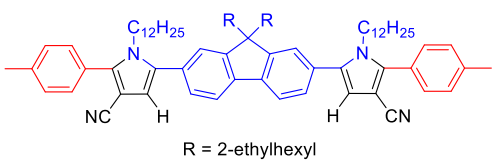


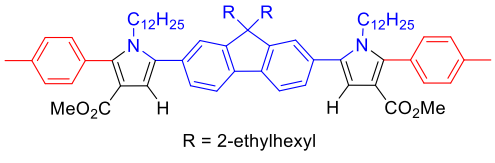
Figure 3.6. ^{31}P NMR of *In-Situ* Reaction Intermediates in CD_2Cl_2.

3.5.5 Synthesis of Model Dimers for Regioselectivity Assignment



R = 2-ethylhexyl

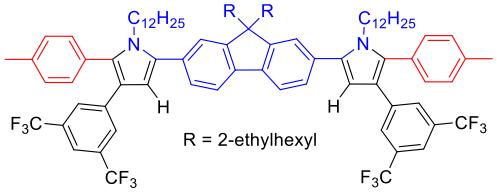
3.9a: In a glovebox, bis-imine **3.4c** (78 mg, 0.1 mmol), toluoyl chloride (34 mg, 0.22 mmol) and (catechyl)PPh (48 mg, 0.22 mmol) were dissolved with 1 mL of dichloromethane and left to stir at 45° for 1 hour before the addition of DBU (79.2 mg, 0.52 mmol). The reaction was left to stir at r.t. for 30 min before the addition of chloroacrylonitrile (**3.6d**, 19 mg, 0.22 mmol). The solution was left to react at r.t. for 18h before filtration through alumina. The volatiles were removed under vacuum and the resulting oil was washed with cold methanol to afford **3.9a** as a yellow oil (73 mg, 67 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.8 Hz, 2H), 7.48 – 7.37 (m, 8H), 7.32 (d, J = 7.9 Hz, 4H), 6.48 (s, 2H), 4.05 (t, J = 7.1 Hz, 4H), 2.44 (s, 6H), 2.23 – 1.91 (m, 4H), 1.41 – 0.44 (m, 76H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 142.7, 140.6, 139.0, 136.3, 130.7, 129.6, 129.5, 128.0, 127.2, 124.9, 120.0, 117.5, 111.9, 92.6, 55.1, 45.7, 45.0, 34.9, 33.8, 33.7, 31.9, 30.2, 29.6, 29.5, 29.4, 29.3, 29.2, 28.7, 28.4, 28.3, 26.8, 26.0, 22.8, 22.7, 21.4, 14.1, 14.0, 10.3. Although only one weak NOESY correlation was observed for the *pyrrole-H*, the exact regiochemistry had to be assigned by analogy with previously reported compounds[63] due to overlapping fluorene and tolyl proton signals. MS(ESI): $C_{77}H_{107}N_4$ $[M+H]^+$ *m/z* calcd. 1087.8490; found 1087.8530.



R = 2-ethylhexyl

3.9b: In a glovebox, bis-imine **3.4c** (95 mg, 0.12 mmol), toluoyl chloride (39 mg, 0.25 mmol) and (catechyl)PPh (58 mg, 0.27 mmol) were dissolved with 1 mL of dichloromethane and left to stir at r.t. for 18 hours before the addition of DBU (42 mg, 0.28 mmol). The resulting phospha-Münchnone dimer was precipitated and washed with cold acetonitrile (172 mg, 98 % yield). The phospha-Münchnone dimer (89 mg, 0.06 mmol) was reacted with methyl propiolate (**6b**, 15mg, 0.19 mmol) in dichloromethane at r.t. for 30 min. The reaction mixture was filtered through alumina before removal of the volatiles. The resulting oil was precipitated and washed with cold methanol (3x1 mL) to afford clean **3.9b** as a yellow oil (51 mg, 72 % yield). The product was obtained as a single regioisomer but exists as three conformational isomers due to the restricted rotation around the fluorene and pyrrole units.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.8 Hz, 2H), 7.48 (s, broad, 2H), 7.44 (dd, J = 7.8 Hz, J = 1.5 Hz, 2H), 7.35 (d, J = 8.0 Hz, 4H), 7.30 (d, J = 8.1 Hz, 4H), 6.71-6.70-6.69 (3 singlets, *pyrrole-H*, 2H), 4.03 – 3.86 (m, 4H), 3.71 (s, 6H), 2.45 (s, 6H), 2.18 – 1.88 (m, 4H), 1.38 – 0.35 (m, 78H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 151.2, 140.2, 140.1, 138.0, 135.0, 131.5, 130.5, 129.2, 128.8, 127.8, 124.9, 119.7, 113.0, 110.6, 55.0, 50.7, 45.0, 34.8, 33.7, 33.6, 31.9, 30.4, 29.6, 29.6, 29.4, 29.3, 29.2, 28.8, 28.4, 26.8, 26.7, 26.1, 22.8, 22.7, 21.4, 14.1, 14.0, 10.3, 10.2. MS(ESI): $C_{79}H_{113}N_2O_4$ $[M+H]^+$ *m/z* calcd. 1153.8695; found 1153.8702.



3.9c: Phospha-Münchnone dimer was synthesized and isolated as per the procedure described above for **3.9b**. The phospha-Münchnone dimer (84 mg, 0.06 mmol) was reacted with 1-ethynyl-3,5-bis(trifluoromethyl)benzene (**3.6f**, 41 mg, 0.17 mmol) in dichloromethane at 45° for 18h. The reaction mixture was filtered through alumina before removal of the volatiles. The resulting oil was precipitated and washed with cold methanol (3x1 mL) and hexanes (2x1 mL) to afford **3.9c** as a yellow oil (76 mg, 90 % yield). The product was obtained as a single regioisomer but exists as three conformational isomers due to the restricted rotation around the fluorene and pyrrole units. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 2H), 7.60 (s, 4H), 7.54 (s, 4H), 7.50 (dd, J = 7.8, 1.5 Hz, 2H), 7.28 (s, 8H), 6.52-6.51 (2 singlets, *pyrrole-H*, 2H), 4.13 – 3.84 (m, 4H), 2.45 (s, 6H), 2.12 (t, J = 4.6 Hz, 4H), 1.43 – 0.43 (m, 76H). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) (only one conformational isomer reported) (multiplets due to ^{19}F coupling could not be identified) δ 151.2, 140.2, 138.6, 138.3, 136.1, 133.3, 131.7, 131.4, 131.2, 130.9, 130.9, 130.6, 129.7, 129.3, 127.8, 127.0, 124.8, 124.6, 122.4, 119.9, 119.7, 118.0, 108.6, 55.1, 45.1, 34.9, 33.8, 33.7, 31.9, 30.7, 29.6, 29.6, 29.5, 29.3, 29.3, 28.8, 28.4, 28.4, 26.9, 26.8, 26.2, 22.8, 22.7, 21.3, 14.1, 14.0, 10.4, 10.3. The regiochemistry was assigned in this case by analogy with previously published results[63] as no NOESY or selective NOE signals could be observed. This is likely due to a large torsion angle between the fluorene and pyrrole units and the presence of conformational isomers. MS(ESI): $C_{91}H_{113}F_{12}N_2$ $[M+H]^+$ *m/z* calcd. 1461.8707; found 1461.8718.

3.5.6 Synthesis of Aldehyde End-Capped Poly(Pyrrole)

In a glovebox, bis-imine **3.4a** (46.9 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (18.3 mg, 0.09 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 55 °C for 24h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (45.7 mg, 0.30 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 30 min before concentrating the solution under vacuum. The resulting dark solid (**poly-3.1a**) was washed with 3x1mL of acetonitrile, dissolved/suspended in dichloromethane (10 mL) and then DMAD (42.6 mg, 0.3 mmol) was added. The reaction mixture was left to stir at r.t. for 18h in the glovebox. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) then redissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **3.7a'** as a white solid. (54.2 mg, 64 % yield). GPC: M_n = 7.7 kDa, PDI = 1.6. (SEC-MALLS: M_n = 12.4 kDa)

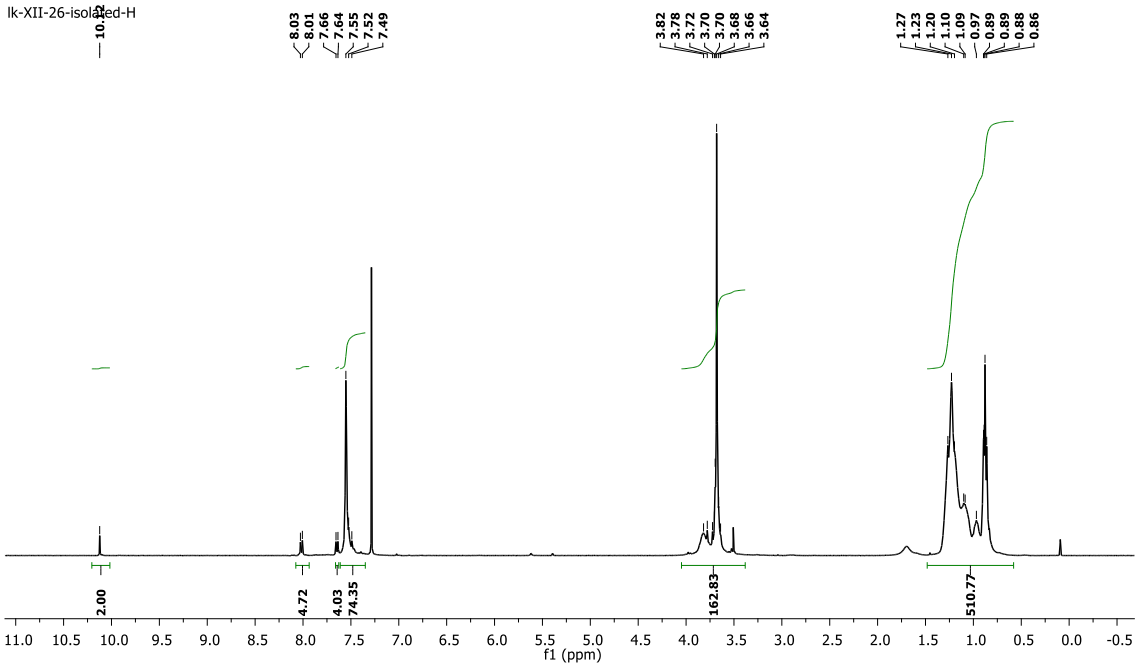
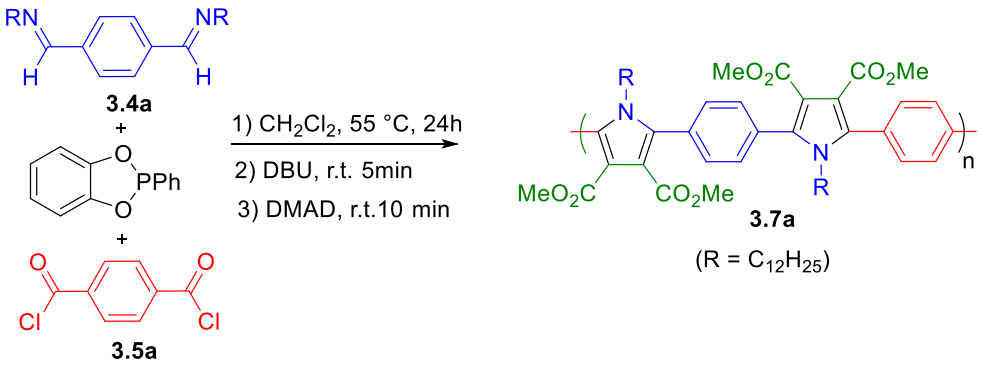


Figure 3.7 ^{1}H NMR of Polymer **3.7a'** with Well-Defined Aldehyde End-Groups.

3.5.7 One-pot Synthesis of Poly(Pyrrole) **3.7a** – *In-Situ* DMAD Cycloaddition



In a glovebox, bis-imine **3.4a** (46.9 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 55 °C for 24h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (33.5 mg, 0.22 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 5 min before addition of DMAD (85.3 mg, 0.6 mmol) was added. The reaction mixture was left to stir at r.t. for 10min. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) and hexanes (3x3 mL) then dissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **3.7a** as a white solid (73 mg, 85 % yield). GPC: M_n = 10.5 kDa, PDI = 2.1.

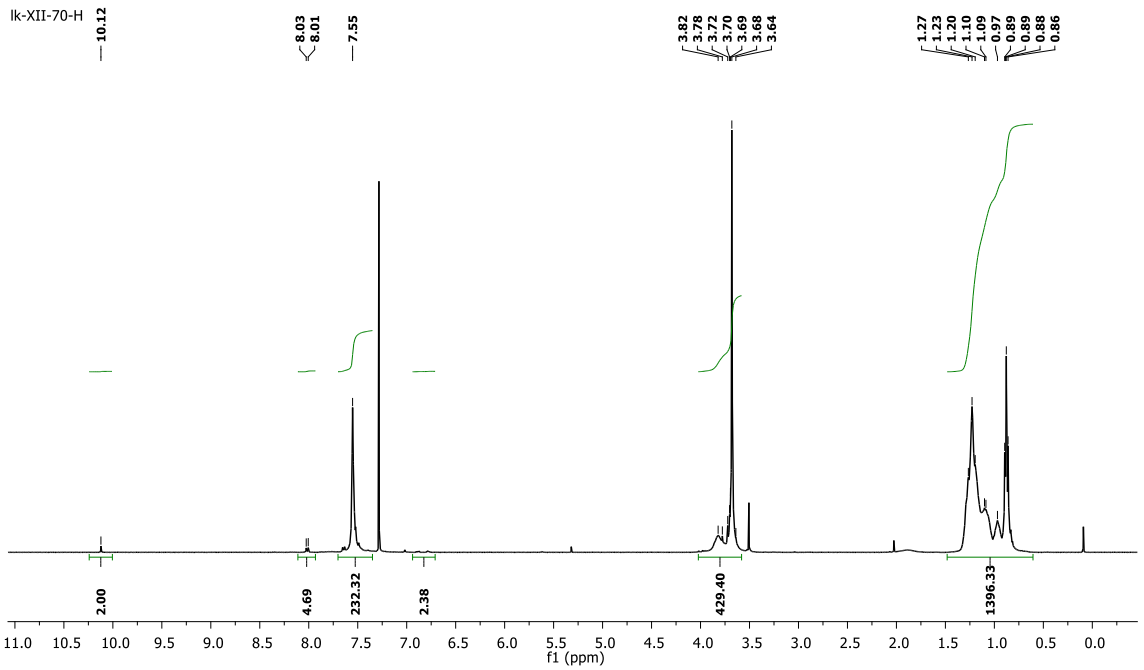


Figure 3.8 ^{1}H NMR of Polymer **3.7a** when Cycloaddition with DMAD Performed *In-Situ*

3.5.8 Multi-gram Scale Synthesis of Polymer **3.7a**

In a glovebox, bis-imine **3.4a** (2.25 g, 4.8 mmol), terephtaloyl chloride **3.5a** (970 mg, 4.8 mmol) were dissolved in 18 mL of dichloromethane and left to stir for one hour at room temperature before the addition of (catechyl)PPh (2.49 g, 11.5 mmol) in 10 mL of dichloromethane. The solution was stirred in a sealed reaction vessel at 55° for 24h. The solution was then slowly added dropwise to a solution of DBU (2.20 g, 14.4 mmol) in dichloromethane (100 mL). The reaction was left to stir at r.t. for 30 min before concentrating the solution under vacuum. The resulting dark solid (**poly-3.1a**) was washed with 4x20 mL of acetonitrile, dissolved/suspended in dichloromethane (250 mL) and then DMAD (2.05 g, 14.4 mmol) was added. The reaction was left to stir at r.t. for 18h in the glovebox. Subsequently, the reaction was brought out of the glovebox and quenched with water (2 mL). The polymer was precipitated and triturated with methanol (4x100 mL). The volatiles were removed *in vacuo* to afford the polymer **3.7a** as a white solid. (3.35 g, 82 % yield). GPC: M_n = 15.6 kDa, PDI = 1.9. (SEC-MALLS: M_n = 57.4 kDa)

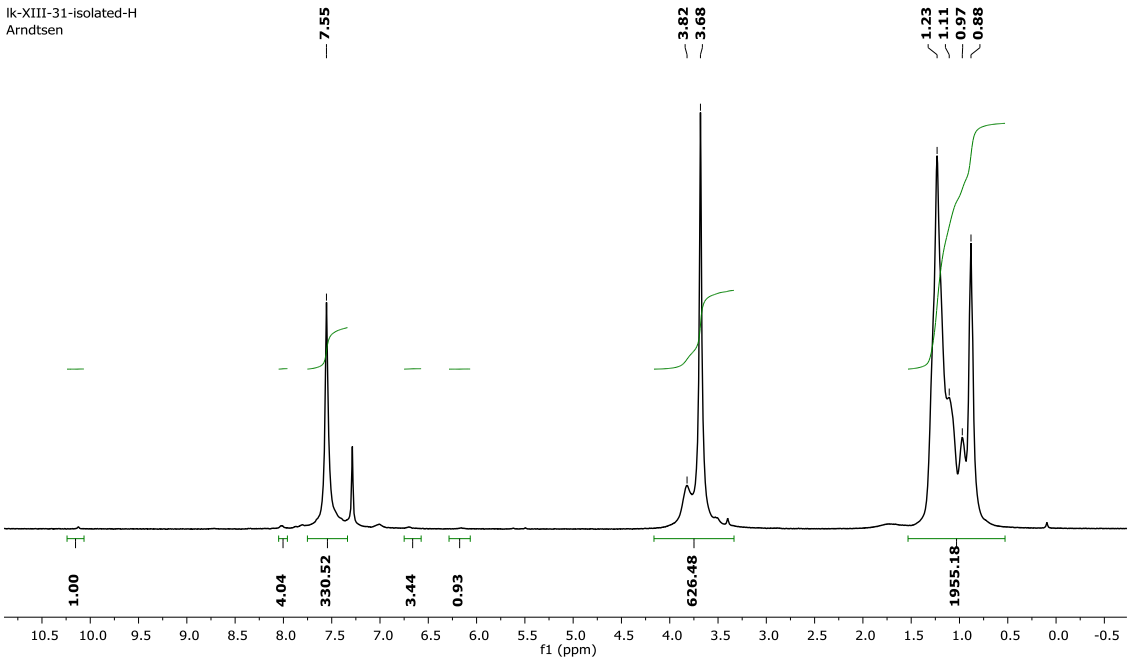
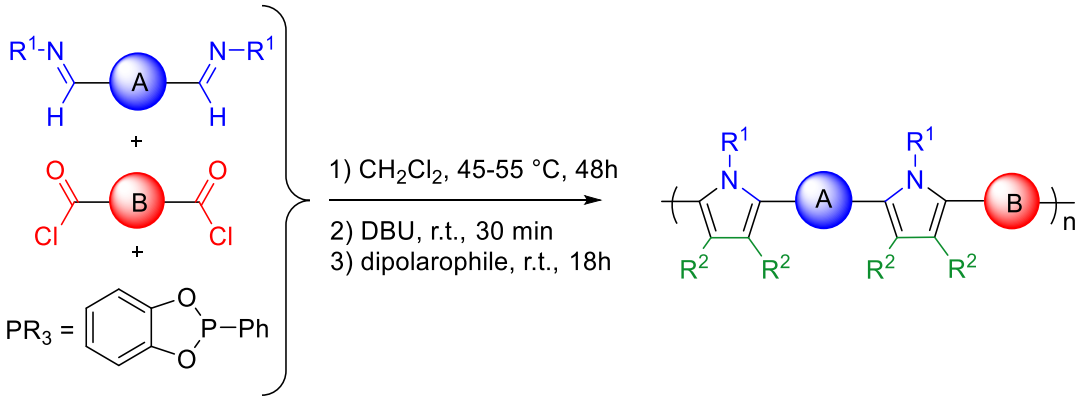


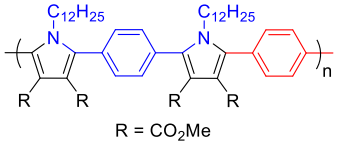
Figure 3.8 ^{1}H NMR of Polymer **3.7a** from Multi-Gram Synthesis

3.5.9 Typical Synthesis of Poly(Pyrroles)

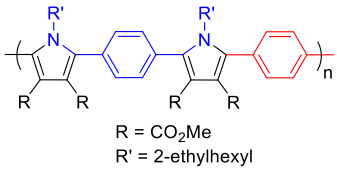


In a glovebox, a bis-imine **3.4** (0.10 mmol), a bis-acid chloride **3.5** (0.10 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane. The solution was transferred in a sealed reaction vessel and heated at 45 or 55 °C for 24 - 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (45.7 mg, 0.30 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 30 min before concentrating the solution under vacuum. The resulting dark solid (**poly-3.1a**) was washed with 3x1mL of acetonitrile, dissolved/suspended in dichloromethane (10

mL) and then the appropriate dipolarophile **3.6** (0.3 mmol) was added. In some cases, the dipolarophile is directly added to the crude solution of **poly-3.1a**. The reaction mixture was left to stir at r.t. for 18h in the glovebox. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) then redissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the clean poly(pyrroles).

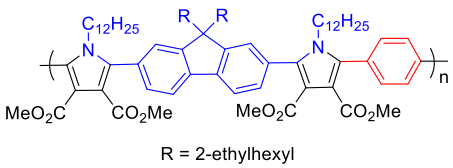


3.7a: In a glovebox, bis-imine **3.4a** (46.9 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 55 °C for 24h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (45.7 mg, 0.30 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 30 min before concentrating the solution under vacuum. The resulting dark solid (**poly-3.1a**) was washed with 3x1mL of acetonitrile, dissolved/suspended in dichloromethane (10 mL) and then DMAD **3.6a** (42.6 mg, 0.3 mmol) was added. The reaction mixture was left to stir at r.t. for 18h in the glovebox. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) then redissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **3.7a** as a white solid (63 mg, 74 % yield). GPC: M_n = 14.9 kDa, PDI = 1.9. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 8H), 3.80 (s, 4H), 3.66 (s, 12H), 1.43 – 0.72 (m, 44H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 136.0, 131.5, 130.4, 115.1, 51.5, 45.4, 31.9, 30.4, 29.6, 29.6, 29.4, 29.4, 29.3, 28.9, 26.4, 22.6, 14.1.



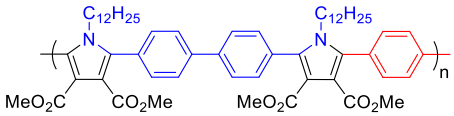
3.7$_{baa}$: In a glovebox, bis-imine **3.4b** (35.7 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 55 °C for 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (45.7 mg, 0.30 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 30 min before concentrating the solution under vacuum. The

resulting dark solid was washed with 3x1mL of acetonitrile, dissolved/suspended in dichloromethane (10 mL) and then DMAD (42.6 mg, 0.3 mmol) was added. The reaction mixture was left to stir at r.t. for 18h in the glovebox. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) then redissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **3.7$_{baa}$** as a white solid (47 mg, 63 % yield). GPC: M_n = 11.3 kDa, PDI = 2.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 4H), 3.82 (s, 4H), 3.67 (s, 12H), 1.32 – 0.60 (m, 24H), 0.46 (t, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 136.4, 131.4, 130.5, 115.4, 51.5, 49.3, 39.4, 30.2, 28.0, 23.1, 22.8, 22.6, 13.8, 10.2.

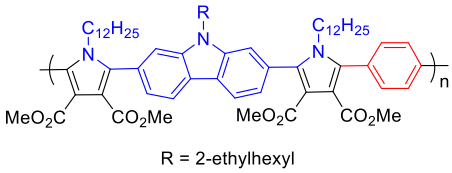


R = 2-ethylhexyl

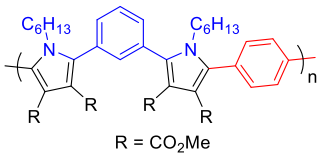
3.7$_{caa}$: Same procedure as **3.7$_{baa}$** with bis-imine **3.4c** (mg, 0.10 mmol), terephthaloyl chloride a **3.5a** (20.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 99 mg (yellow solid, 78% yield). GPC: M_n = 18.8 kDa, PDI = 2.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.7 Hz, 2H), 7.54 (s, 4H), 7.43 (s, 4H), 3.77 (s, 4H), 3.65 (s, 6H), 3.64 – 3.60 (m, 6H), 2.06 (s, 4H), 1.39 – 0.62 (m, 70H), 0.53 (t, J = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 151.1, 141.0, 136.8, 135.6, 131.5, 130.3, 129.9, 129.6, 125.7, 119.8, 115.1, 115.0, 114.8, 54.9, 51.4, 45.5, 34.8, 33.4, 31.8, 30.6, 30.5, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.3, 26.4, 26.1, 22.7, 22.6, 14.0, 10.0.



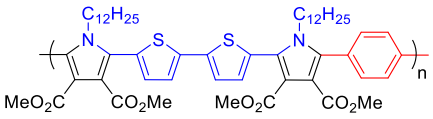
3.7$_{daa}$: Same procedure as **3.7$_{baa}$** with bis-imine **3.4d** (54.5 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 78 mg (yellow solid, 98 % yield). GPC: M_n = 24.4 kDa, PDI = 2.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 4H), 7.53 (s, 8H), 3.79 (s, 4H), 3.70 (s, 6H), 3.66 (s, 6H), 1.67 (s, 4H), 1.37 – 0.70 (m, 42H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 165.9, 141.2, 137.2, 136.4, 132.2, 131.7, 131.1, 130.9, 127.6, 115.7, 115.5, 52.4, 52.2, 45.9, 32.5, 31.1, 30.3, 30.2, 30.1, 30.0, 29.9$_6$, 29.5, 27.0, 23.3, 14.8.



3.7$_{eaa}$: In a glovebox, bis-imine **3.4e** (67.0 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of DCM in a sealed reaction vessel and heated at 45 °C for 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (45.7 mg, 0.30 mmol) in DCM (5mL). The reaction mixture was left to stir at r.t. for 30 min before concentrating the solution under vacuum. The resulting dark solid was washed with 3x1mL of acetonitrile, dissolved/suspended in DCM (10 mL) and then DMAD **3.6a** (42.6 mg, 0.3 mmol) was added. The reaction mixture was left to stir at r.t. for 18h in the glovebox. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) then redissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **3.7$_{baa}$** as a yellow solid (68 mg, 66 % yield). GPC: M_n = 16.3 kDa, PDI = 1.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.8 Hz, 2H), 7.56 (s, 4H), 7.51 (s, 2H), 7.30 (d, J = 8.2 Hz, 2H), 4.22 (s, 2H), 3.82 (s, 4H), 3.67 (s, 6H), 3.64 (s, 6H), 2.10 (s, 1H), 1.51 – 0.59 (m, 60H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 165.2, 141.1, 137.3, 135.8, 131.6, 130.4, 128.4, 122.7, 121.4, 120.3, 115.1, 114.7, 111.5, 51.7, 51.5, 47.9, 45.3, 39.5, 31.8, 31.2, 30.5, 29.5, 29.5, 29.4, 29.3, 29.3, 28.9, 28.7, 26.4, 26.3, 24.4, 23.1, 22.6, 14.1, 14.0, 11.0, 10.9.

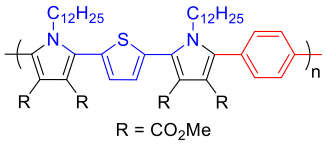


3.7$_{faa}$: Same procedure as **3.7$_{baa}$** with bis-imine **3.4f** (30.0 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD (42.6 mg, 0.3 mmol). Afforded 47 mg (white solid, 54 % yield). GPC: M_n = 14.2 kDa, PDI = 2.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 8H), 3.81 (s, 4H), 3.64 (s, 12H), 1.23 (d, J = 14.5 Hz, 4H), 1.05 (m, 4H), 0.99 – 0.79 (m, 8H), 0.71 (t, J = 7.2 Hz, 6H). ^{13}C NMR (126 MHz,$CDCl_3$) δ 165.3, 164.9, 136.3, 135.6, 132.9, 131.4, 131.1, 130.9, 130.4, 128.3, 115.2, 114.7, 51.5, 51.5, 45.2, 30.8, 30.7, 30.3, 25.9, 25.8, 22.2, 22.1, 13.7.

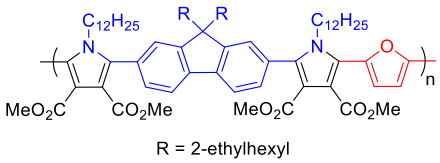


3.7$_{gaa}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4g** (55.7 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol)

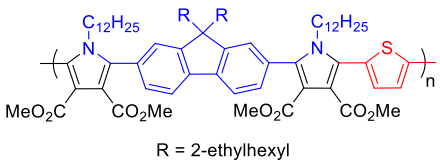
and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 74 mg (orange solid, 79 % yield). GPC: M_n = 10.7 kDa, PDI = 2.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 4H), 7.23 (d, J = 3.7 Hz, 2H), 7.11 (d, J = 3.4 Hz, 2H), 3.85 (s, 4H), 3.78 (s, 6H), 3.64 (s, 6H), 1.42 – 0.91 (m, 40H), 0.85 (t, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 164.5, 139.2, 136.9, 131.5, 131.2, 130.4, 129.4, 127.5, 123.9, 117.5, 114.8, 52.0, 51.4, 45.6, 31.9, 30.8, 29.8, 29.6, 29.6, 29.4, 29.3, 28.9, 26.4, 22.7, 14.1.



3.7$_{haa}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4h** (47.5 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 73 mg (orange solid, 77 % yield). GPC: M_n = 19.9 kDa, PDI = 2.3. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 4H), 7.20 (s, 2H), 3.87 (s, 4H), 3.74 (s, 6H), 3.64 (s, 6H), 1.46 – 0.91 (m, 40H), 0.85 (t, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 164.5, 136.9, 133.0, 131.4, 130.4, 130.0, 127.1, 117.6, 114.8, 51.8, 51.5, 45.6, 31.9, 30.8, 29.7, 29.6, 29.5, 29.3, 29.0, 26.6, 22.7, 14.1.

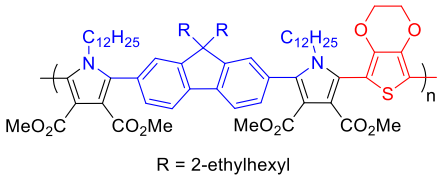


3.7$_{cba}$: Same procedure as **3.7$_{baa}$** with bis-imine **3.4c** (78.1 mg, 0.10 mmol), diacid chloride **3.5b** (19.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 97 mg (orange solid, 84 % yield). GPC: M_n = 22.3 kDa, PDI = 2.0. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 2H), 7.38 (m, 4H), 6.78 (s, 2H), 3.91 (s, 4H), 3.79 (s, 6H), 3.58 (s, 6H), 2.04 (s, 4H), 1.38 (s, 4H), 1.33 – 0.61 (m, 66H), 0.51 (t, J = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 164.6, 164.5, 164.4, 151.2, 144.2, 141.1, 138.4, 129.9, 129.4, 125.7, 124.3, 119.8, 117.2, 114.7, 114.6, 114.5, 113.6, 55.0, 51.9, 51.4, 45.9, 45.6, 34.9, 33.5, 31.9, 30.8, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 28.3, 26.4, 26.2, 22.8, 22.7, 14.1, 14.0, 10.1.



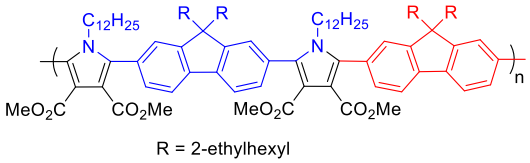
3.7$_{cca}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4c** (78.1 mg, 0.10 mmol), diacid chloride **3.5c** (20.9 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 98 mg

(orange solid, 84 % yield). GPC: M_n = 31.4 kDa, PDI = 2.0. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 2H), 7.41 (s, 4H), 7.21 (s, 2H), 3.85 (s, 4H), 3.74 (s, 6H), 3.60 (s, 6H), 2.04 (s, 4H), 1.50 – 0.61 (m, 70H), 0.52 (t, J = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $cdcl_3$) δ 165.2, 165.1, 164.8, 164.7, 164.6, 151.3, 151.2, 141.1, 137.9, 133.2, 129.9, 129.5, 126.8, 125.7, 119.9, 117.4, 117.4, 117.3, 115.0, 114.9, 114.8, 55.0, 51.8, 51.5, 45.5, 34.9, 33.5, 31.9, 31.0, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 28.4, 26.6, 26.1, 22.8, 22.7, 14.1, 14.0, 10.1.



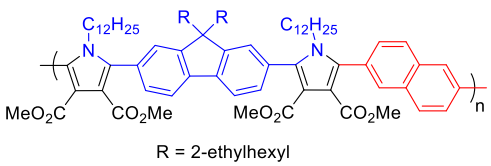
R = 2-ethylhexyl

3.7$_{cda}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4c** (78.1 mg, 0.10 mmol), diacid chloride **3.5d** (26.7 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 90 mg (yellow solid, 74 % yield). GPC: M_n = 15.1 kDa, PDI = 1.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (s, end-group), 7.80 (d, J = 7.4 Hz, 2H), 7.40 (s, 4H), 4.28 (s, 4H), 3.83 (s, 4H), 3.76 (s, 6H), 3.58 (s, 6H), 2.01 (s, 6H), 1.52 – 0.35 (m, 74H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 151.1, 141.1, 139.8, 137.9, 129.9, 129.6, 125.6, 124.4, 119.8, 117.5, 115.3, 106.9, 64.6, 55.0, 51.6, 51.4, 45.6, 34.9, 33.5, 31.9, 30.8, 29.7, 29.6, 29.3, 28.4, 26.8, 26.1, 22.8, 22.7, 14.1, 14.1, 10.1.

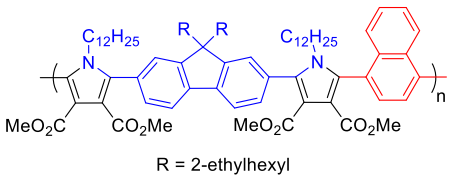


R = 2-ethylhexyl

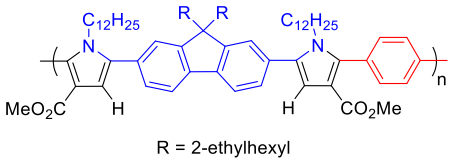
3.7$_{cea}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4c** (78.1 mg, 0.10 mmol), diacid chloride **3.5e** (51.6 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 129 mg (yellow solid, 87 % yield). GPC: M_n = 30.1 kDa, PDI = 1.7. ^{1}H NMR ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, 4H), 7.45 (s, 8H), 3.76 (s, 4H), 3.62 (s, 12H), 2.06 (s, 8H), 1.25-0.52 (m, 106H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 165.2, 151.1, 141.0, 136.5, 129.9, 125.7, 119.8, 115.0, 114.9, 114.8, 110.0, 55.0, 51.5, 45.7, 45.1, 34.9, 33.5, 31.9, 30.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.1, 28.3, 26.4, 26.1, 22.8, 22.6, 14.1, 14.1, 13.9, 10.1.



3.7$_{cfa}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4c** (78.1 mg, 0.10 mmol), diacid chloride **3.5f** (25.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 92 mg (yellow solid, 76 % yield). GPC: M_n = 40.7 kDa, PDI = 1.9. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (m, 4H), 7.84 (d, J = 7.7 Hz, 2H), 7.60 (s, 2H), 7.47 (s, 4H), 3.83 (s, 4H), 3.65 (m, 12H), 2.07 (s, 4H), 1.60 (s, 4H), 0.96 (m, 70H), 0.53 (t, J = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 165.4, 151.2, 141.1, 136.8, 136.7, 136.5, 132.7, 129.8, 129.4, 128.6, 128.3, 125.7, 119.9, 115.2, 114.6, 55.0, 51.6, 51.5, 45.6, 45.2, 34.9, 33.5, 31.9, 30.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.4, 26.3, 26.2, 22.8, 22.7, 14.1, 10.1.

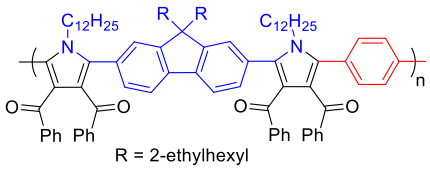


3.7$_{cga}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4c** (78.1 mg, 0.10 mmol), diacid chloride **3.5g** (25.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and DMAD **3.6a** (42.6 mg, 0.3 mmol). Afforded 105 mg (yellow solid, 86 % yield). GPC: M_n = 34.6 kDa, PDI = 1.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.74 (s, 2H), 7.66 (s, 2H), 7.55 (s, 2H), 7.49 (s, 4H), 3.67 (s, 7H), 3.47 (s, 3H), 3.42 (s, 3H), 2.09 (s, 4H), 0.89 (m, 76H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 165.5, 164.6, 151.3, 141.0, 136.6, 134.6, 134.2, 133.1, 130.5, 129.9, 129.6, 128.5, 127.0, 125.9, 119.9, 115.7, 115.2, 55.0, 51.7, 51.3, 51.0, 45.6, 35.0, 33.4, 31.9, 30.8, 29.5, 29.4, 29.3, 28.9, 28.4, 26.4, 26.2, 22.7, 22.6, 14.1, 10.1.

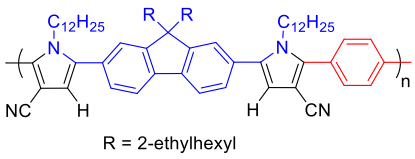


3.7$_{cab}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4c** (78.1 mg, 0.10 mmol), diacid chloride **3.5a** (20.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and alkyne **3.6b** (11.0 mg, 0.3 mmol). Afforded 75.4 mg (yellow solid, 82 % yield). GPC: M_n = 40.7 kDa, PDI = 1.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.7 Hz, 2H), 7.76 (s, 4H), 7.69 (s, 2H), 7.65 (d, J = 7.4 Hz, 2H), 6.95 (s, 2H), 4.19 (s, 4H), 3.88 (s, 6H), 2.27 (s, 4H), 1.94 (s, 4H), 1.59 – 0.79 (m, 66H), 0.75 (t, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 151.3, 151.3, 140.3, 139.1, 135.5, 132.4, 131.4, 130.4, 127.9, 124.9, 119.8, 113.5, 111.0, 55.1, 50.8, 45.4, 45.1, 34.9, 33.7, 33.6,

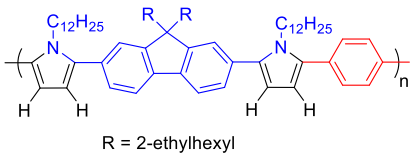
31.9, 30.6, 29.6, 29.6, 29.5, 29.3, 29.0, 28.4, 28.4, 26.9, 26.7, 26.4, 22.8, 22.7, 14.1, 14.0, 10.3, 10.3.



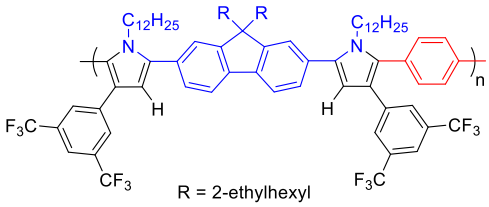
3.7$_{cac}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4c** (78.1 mg, 0.10 mmol), diacid chloride **3.5a** (20.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and alkyne **3.6c** (53.9 mg, 0.23 mmol). Afforded 102 mg (yellow solid, 81 % yield). GPC: M_n = 21.3 kDa, PDI = 2.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.00 (m, 30H), 3.86 (s, 4H), 1.90 (s, 4H), 1.69 – 0.34 (m, 76H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.1, 191.8, 151.1, 140.8, 139.4, 139.3, 137.1, 137.0, 136.8, 136.3, 131.8, 131.5, 131.2, 130.8, 130.3, 129.3, 128.9, 128.1, 127.7, 127.6, 126.5, 126.0, 124.5, 124.4, 123.8, 119.7, 54.9, 45.4, 34.6, 33.4, 31.9, 30.4, 29.6, 29.6, 29.4, 29.3, 29.0, 28.2, 26.4, 26.2, 22.7, 14.1, 14.0, 9.9.



3.7$_{cad}$: In a glovebox, bis-imine **3.4c** (78.1 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of DCM in a sealed reaction vessel and heated at 45 °C for 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (45.7 mg, 0.5 mmol) in DCM (5mL). The reaction mixture was left to stir at r.t. for 30 min before the addition of alkene **3.6d** in a DCM solution (21.9 mg, 0.25 mmol). The reaction mixture was left to stir at r.t. for 18h in the glovebox. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) then redissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **3.7$_{cad}$** as a yellow solid (72 mg, 74 % yield). GPC: M_n = 15.1 kDa, PDI = 2.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 2H), 7.71 (s, 4H), 7.46 (m, 4H), 6.55 (s, 2H), 4.14 (s, 4H), 2.10 (s, 4H), 1.64 (s, 4H), 1.37 – 0.42 (m, 72H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 141.4, 140.8, 137.3, 130.6, 130.5, 130.1, 128.1, 124.9, 120.2, 117.2, 112.4, 93.3, 55.2, 46.1, 45.0, 34.9, 33.8, 33.7, 31.9, 30.4, 29.6, 29.4, 29.3, 28.9, 28.4, 28.3, 26.9, 26.7, 26.1, 22.8, 22.7, 14.1, 14.0, 13.9, 10.4, 10.3, 10.3.

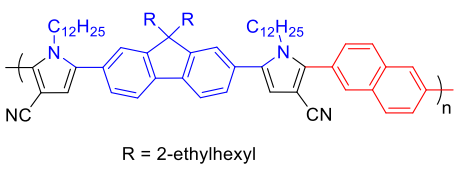


3.7$_{cae}$: In a glovebox, bis-imine **3.4c** (78.1 mg, 0.10 mmol), terephthaloyl chloride **3.5a** (20.3 mg, 0.10 mmol) and (catechyl)PPh (52 mg, 0.24 mmol) were dissolved with 0.6 mL of DCM in a sealed reaction vessel and heated at 45 °C for 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (36.5 mg, 0.25 mmol) in DCM (5mL). The reaction mixture was left to stir at r.t. for 30 min before the addition of alkene **3.6e** in a DCM solution (84.9 mg, 0.23 mmol) followed by DBU (36.5 mg, 0.25 mmol). The reaction mixture was left to stir at r.t. for 18h in the glovebox. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) and hexanes (3x3 mL) then redissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **3.7$_{cae}$** as an orange solid (55.8 mg, 69 % yield). GPC: M_n = 24.7 kDa, PDI = 1.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.55 (s, 4H), 7.49 (s, 2H), 7.46 (d, J = 7.6 Hz, 2H), 6.36 (s, 1H), 6.30 (s, 1H), 4.19 (s, 4H), 2.06 (s, 4H), 1.36 – 0.35 (m, 76H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 139.9, 137.5, 136.3, 136.2, 132.6, 132.3, 128.8, 127.7, 124.6, 119.5, 109.5, 55.0, 45.5, 45.2, 34.8, 33.8, 33.7, 31.9, 30.6, 29.6, 29.5, 29.4, 29.3, 29.0, 28.4, 28.3, 26.8, 26.6, 26.2, 22.8, 22.7, 14.1, 14.0, 10.3, 10.2.



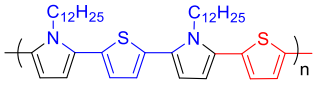
3.7$_{caf}$: Same procedure as **3.7$_{eaa}$** with bis-imine **3.4c** (78.3 mg, 0.10 mmol), diacid chloride **3.5a** (19.3 mg, 0.095 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and alkyne **3.6f** (71.4 mg, 0.3 mmol). After the addition of alkyne, the reaction mixture was stirred at 45 °C for 80h before quenching with water. Afforded 109 mg (yellow solid, 81 % yield). GPC: M_n = 15.8 kDa, PDI = 1.9. The polymer was imine end-capped to ensure solubility and avoid precipitation during cycloaddition step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 2H), 7.72 (s, 4H), 7.64 – 7.44 (m, 10H), 6.55 (s, 2H), 4.09 (s, 4H), 2.15 (s, 4H), 1.65 (s, 4H), 1.48 – 0.26 (m, 72H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 140.4, 138.7, 137.2, 132.7, 132.3, 131.6, 131.3, 131.1, 130.8, 127.8, 127.4, 126.7, 124.6, 122.4, 120.6, 120.2, 119.9, 118.4, 109.5,

55.1, 45.4, 45.2, 34.9, 33.8, 33.6, 31.9, 30.7, 29.6, 29.5, 29.4, 29.3, 29.1, 28.9, 28.4, 26.9, 26.7, 26.2, 22.8, 22.7, 14.1, 14.0, 10.3, 10.3, 10.0.



R = 2-ethylhexyl

3.7$_{cfd}$: Same procedure as **3.7$_{cad}$** with bis-imine **3.4c** (78.1 mg, 0.10 mmol), diacid chloride **3.5f** (25.3 mg, 0.10 mmol), (catechyl)PPh (51.9 mg, 0.24 mmol) and alkene **3.6d** (45.7 mg, 0.3 mmol). Afforded 83 mg (yellow solid, 79 % yield). GPC: M_n = 21.4 kDa, PDI = 2.4. ^{1}H NMR (500 Mhz, $CDCl_3$) δ 8.10 (m, 4H), 7.85 (d, 2H), 7.70 (d,2H), 7.51 (m, 4H), 6.58 (s, 2H), 4.17 (s, 4H), 2.12 (s, 4H), 1.27-0.56 (m, 72H). (500 MHz, $CDCl_3$): ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 142.1, 140.8, 137.1, 133.1, 130.5, 129.2, 128.6, 128.1, 127.6, 124.9, 120.2, 117.3, 112.3, 93.5, 55.2, 46.1, 45.1, 34.9, 33.9, 33.7, 31.9, 30.5, 29.6, 29.4, 29.3, 28.9, 28.4, 28.3$_6$, 26.9, 26.7, 26.1, 22.8, 22.7, 14.1, 14., 10.3$_3$, 10.2$_7$.



3.8: In a glovebox, bis-imine **3.4h** (47.5 mg, 0.10 mmol), diacid chloride **3.5c** (20.9 mg, 0.10 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of DCM in a sealed reaction vessel and heated at 55 °C for 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (76.1 mg, 0.5 mmol) in DCM (5mL). The reaction was diluted to 15 mL and placed in the freezer at -35 °C for 1h before the dropwise addition of alkene **3.6e** (73.8 mg, 0.20 mmol) in a cold DCM solution (4 mL). The reaction mixture was left to stir at r.t. for 18h in the glovebox. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) and hexanes (3x3 mL) then redissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **3.8** as a red solid (54 mg, 84 % yield). GPC: M_n = 11.0 kDa, PDI = 1.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 4H), 6.42 (s, 4H), 4.27 (s, 4H), 1.70-0.89 (m, 46H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.5, 128.4, 125.8, 110.8, 45.4, 31.9, 31.3, 29.6, 29.6, 29.5, 29.3, 29.1, 26.5, 26.4, 22.7, 14.1.

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Chapter 4: A Multicomponent Synthesis of Low Band-Gap, Conjugated Poly(1,3-Dipoles): Poly(Phospha-Münchnones)

4.1 Preface

In Chapter 3, we reported the multicomponent synthesis of poly(pyrroles) from diimines, diacid chlorides, (catechyl)PPh, and alkynes / alkenes. In this chapter, we describe the synthesis and characterization of the reactive intermediates: poly(phospha-Münchnones) in this polymerization. Similar to the poly(Münchnones) described in Chapter 2, preliminary studies show that poly(phospha-Münchnones) are low band-gap materials with tunable properties.

4.2 Introduction

Conjugated polymers have emerged over the last decade as interesting materials for a wide range of applications, including as sensors,[1-3] light-emitting diodes,[4-6] field-effect transistors,[7] and organic photovoltaics (OPVs).[8-10] Research in the latter area has highlighted the need for low band-gap polymers (LUMO - HOMO = E_g below 2 eV) that are capable of absorbing light in the visible region in order to harvest as much sunlight as possible.[11] One of the most well-studied conjugated polymers for photovoltaics is poly(3-hexylthiophene) (P3HT). It has a band-gap of 1.9 eV and exhibits generally high performance in bulk heterojunctions solar cells.[12] More recently, efforts have focused on the synthesis of donor-acceptor type polymers (D-A); where the donor is an electron-rich moiety and the acceptor is electron deficient.[9,13-16] These can exhibit very low band-gaps due to the presence of low energy charge transfer bands between the donor and the acceptor (Figure 4.1).

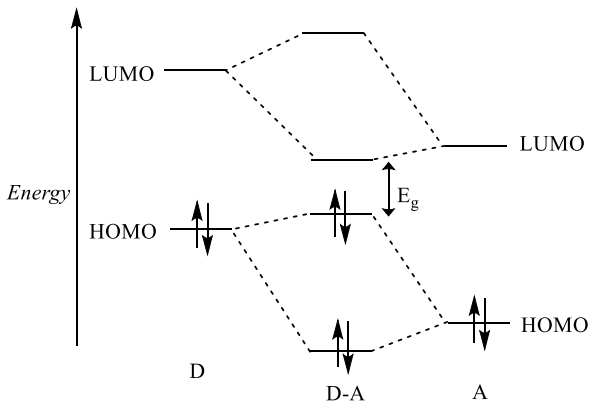
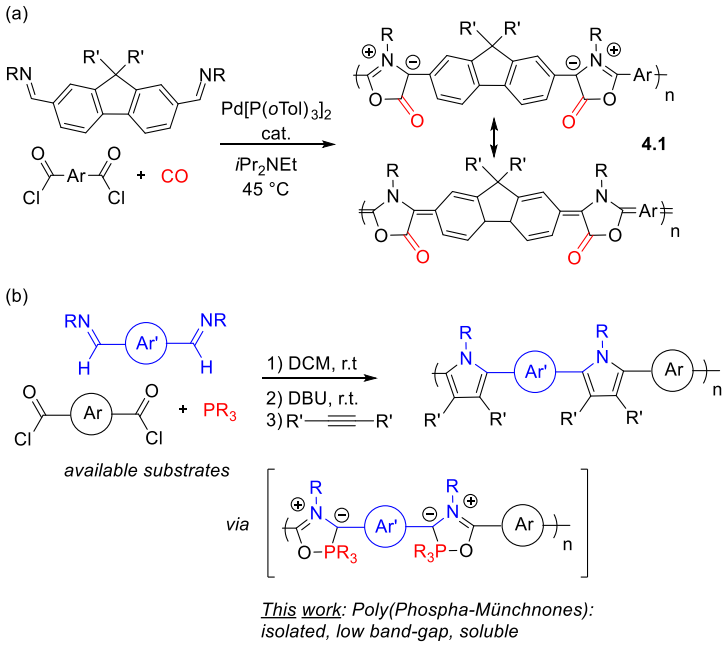


Figure 4.1 Molecular Orbital Diagram for Conjugated Donor-Acceptor Systems

Unlike P3HT, D-A polymers offer the possibility of structural modification in order to fine tune their properties, where the HOMO energy is controlled predominantly by the donor, and the LUMO by the acceptor. These polymers are typically synthesized via palladium-catalyzed cross-coupling reactions (e.g. Stille or Suzuki couplings).[17] While the latter has provided access to a broad range of high molecular weight donor-acceptor copolymers, these reactions generate stoichiometric amounts of organometallic by-products, and often require an initial multistep synthesis of the monomers. Alternative pathways to D-A polymers are therefore highly desirable to make them more commercially and environmentally attractive for large scale applications.[18] Some steps towards these goals have been described by the use of palladium-catalyzed C-H heteroarylation or ruthenium-catalyzed alkene metathesis as greener synthetic alternatives to conjugated polymers.[19-22]

A potentially attractive approach to conjugated polymer synthesis would be to consider their often complex structure as arising from combinations of more readily available monomers: i.e. a multicomponent polymerization. Multicomponent polymerizations have recently attracted attention as a method to efficiently synthesize polymers from simple reagents, and with facile access to diversification.[23-25] Despite these attractive features, only a few examples of the multicomponent synthesis of conjugated polymers have been reported.[26-29] The first report of a multicomponent synthesis of low band-gap conjugated polymers was from our lab in the palladium-catalyzed coupling of diimines, diacid chlorides and carbon monoxide (Scheme 4.1a).[30] The product of this reaction also represented a new class of conjugated polymer, a poly(1,3-dipole), or a poly(Münchnone).

As these polymers incorporate a mesoionic heterocycle into their backbone, they represent a variant of D-A conjugated polymer, which in this case have a formally charged ground state structure. Conjugated polymers incorporating separated charges along their backbone have been previously reported, and were shown to exhibit low band-gap properties.[31] These include structures based on the squaraine dye[32,33] and zwitterionic pyrrole-derived polymers.[34,35] Consistent with this, polymers **4.1** are low band-gap materials (as low as 1.58 eV). However the scope was limited to complex fluorenyl-based diimines bearing branched alkyl chains to ensure the solubility of the poly(Münchnone).



Scheme 4.1 Multicomponent Synthesis of Poly(1,3-Dipoles) **(a)** Palladium-Catalyzed Carbonylative Synthesis of Poly(Münchnones) **(b)** Metal-Free Synthesis of Poly(Pyrroles) via Poly(Phospha-Münchnones)

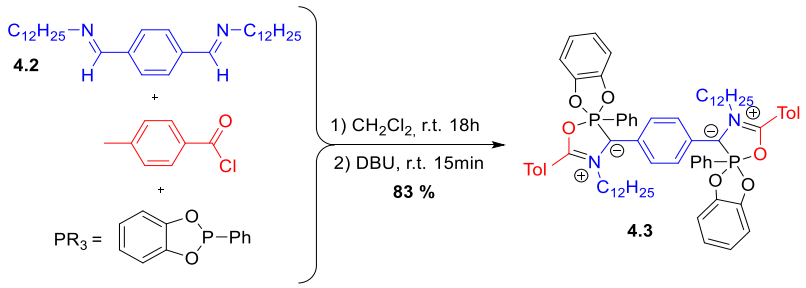
In considering approaches to address this limitation, we have recently reported a new, metal-free multicomponent polymerization platform for the synthesis of conjugated polypyrroles from diimines, diacid chlorides and alkynes (Scheme 4.1b).[36] This reaction is believed to proceed through the initial formation of another type of poly(1,3-dipole), a poly(phospha-Münchnone), although the latter was not isolated. In the present work, we

report the use of this platform to generate poly(phospha-Münchnones) as products. In addition, UV-Vis studies suggest that these polymers are low band-gap materials, and with an optical absorbance dependent on the choice of imine and acid chloride monomers.

4.3 Results and Discussion

4.3.1 Synthesis of Model Compounds

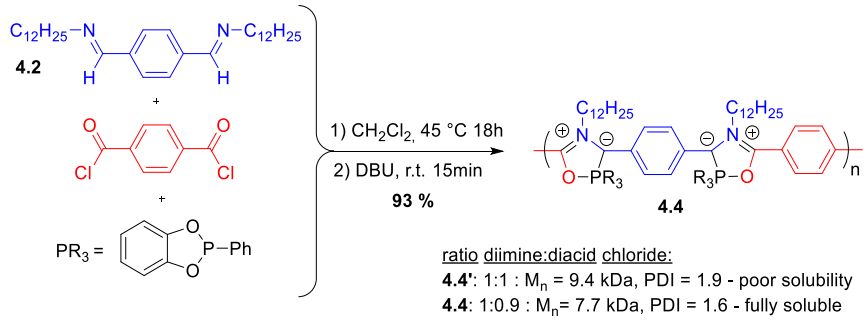
1,3-dipoles such as phospha-Münchnones are typically employed as reactive intermediates in cycloaddition reactions, rather than as isolated products. Thus, we first probed the stability and spectroscopic properties of the model dimeric compound **4.3**. This compound can be synthesized in analogy to previous reports via the multicomponent coupling of terephtaldehyde-derived imine **4.2**, *p*-toluoyl chloride, and (catechyl)PPh (Scheme 4.2). After 18h at room temperature, the addition of DBU base leads to the 1,3-dipole dimer **4.3** in near quantitative yield by in-situ ^{31}P NMR analysis. Precipitation and washing with cold acetonitrile affords **4.3** as a clean product in 83% isolated yield. ^{1}H, ^{13}C and ^{31}P NMR data are all consistent with the formulation of **4.3** as shown. In particular, the phosphorus resonance in the ^{31}P NMR is strongly shielded (δ -18.8 ppm), consistent with a five-coordinate structure in **4.3**, while in the ^{13}C NMR the ylide (72.5 ppm, $^{1}J_{C\text{-}P}$ = 259.4 Hz) and former amide carbons (149.8, $^{2}J_{C\text{-}P}$ = 19.0 Hz) both show phosphorus coupling.[37] **4.3** is stable as a solid under inert atmosphere, and can be stored at -35 °C for several months or at r.t. for a week. However, this compound reacts rapidly with water when exposed to air.



Scheme 4.2 Multicomponent Synthesis of Model Phospha-Münchnone Dimer **4.3**

4.3.2 Polymer Synthesis

A similar reaction sequence to that of Scheme 4.2 can be employed to form a polymer. As shown in Scheme 4.3, the combination of bis-imine **4.2**, (catechyl)PPh and terephthaloyl chloride in dichloromethane at 45 °C for 18h followed by deprotonation leads in the formation of **4.4'** as a dark magenta solid. Due to its moisture sensitivity, the molecular weight of **4.4'** (M_n = 9.4 kDa) was determined by its conversion to a soluble poly(pyrrole) upon reaction with dimethylacetylene dicarboxylate (DMAD).[38] Unfortunately, **4.4'** formed under these conditions is only sparingly soluble in common solvents, and full characterization and analysis could not be obtained. In order to ensure full solubility, an excess of diimine (1.1 equivalents) was used to end-cap the polymer. The latter polymer **4.4**, was obtained in excellent yield (93 %, M_n = 7.7 kDa) and is fully soluble in chlorinated solvent (e.g. dichloromethane). Multinuclear NMR analysis shows the same features as the model compound **4.4**, including a ^{31}P NMR signal at -18.97 ppm. In addition, imine end-groups can be clearly observed (^{1}H NMR: δ 8.32 (N=C*H*) and 3.63 (N-CH_2) ppm).



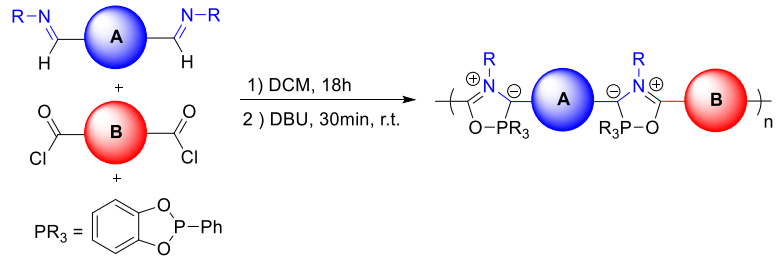
Scheme 4.3 Multicomponent Polymerization of Poly(Phospha-Münchnone) **4.4**

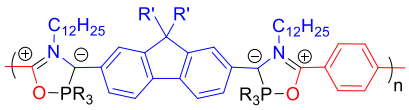
4.3.3 Diversity of Poly(Phospha-Münchnones)

An advantage of this polymerization is its ease of structural modification, as the building blocks (diimines, diacid chlorides) are readily available in multiple forms. This can provide access to a range of poly(1,3-dipoles). Examples of these are shown in Table 4.1. To ensure the full solubility of polymers **4.6**-**4.10**, the molecular weights were maintained

between 6.3 and 10.0 kDa by the use of a slight excess of the diimine. However, the branched alkyl-containing **4.5** can be formed as a soluble polymer in high molecular weight (M_n = 20.7 kDa). Examples of the heterocyclic units that can be introduced into the polymer includes thiophenes, which can be incorporated via the bis-imine (**4.6**) or diacid chloride (**4.9**), and furans (**4.8**). 3,4-ethylenedioxithiophene, the conjugated unit in PEDOT conducting polymers, can also be introduced from the diacid chloride (**4.10**), as can the planar naphtyl fragment (**4.7**). Notably, each of these materials can be isolated by precipitation in acetonitrile in high yields, and their molecular weight determined by GPC after conversion to the corresponding DMAD derived poly(pyrrole). Overall, this provides a general platform to synthesize families of 1,3-dipole containing polymers from combinations of diimines, diacid chlorides and (catechyl)PPh.

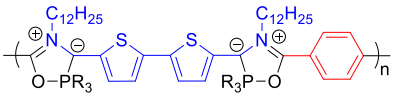
Table 4.1 Diversity of Poly(Phospha-Münchnones)





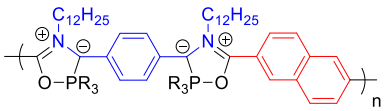
4.5: R' = 2-ethylhexyl

99 %, M_n = 20.7 kDa, PDI = 1.85



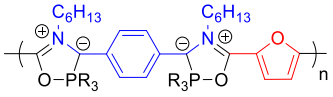
4.6

92%, M_n = 10.0 kDa, PDI = 1.8



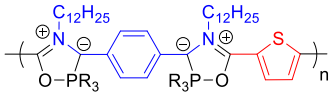
4.7

99%, M_n = 8.9 kDa, PDI = 1.6



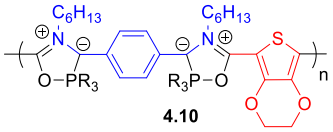
4.8

81%, M_n = 6.8 kDa, PDI = 1.6



4.9

98 %, M_n = 6.8 kDa, PDI = 1.5



4.10

89 %, M_n = 6.3 kDa, PDI = 1.8

4.3.4 UV-Vis Analysis

We have preliminarily explored the properties of these poly(phospha-Munchnones) by UV-Vis analysis. Similarly to the previously reported poly(Münchnones), the UV-Vis spectra of polymer **4.4** in chloroform shows a λ_{max} at 517 nm and band-gap of 1.89 eV (Figure 4.2 and Table 4.2).[30] The latter is significantly red-shifted compared to its model dimer **4.3** indicating extended conjugation. As we have previously noted for Münchnones, while mesoionic heterocycles do not have a stable, neutral resonance structure, the linking of these together into polymers introduces the potential for neutral, quinoid-type resonance structures as a mechanism to eliminate charge (Figure 4.2c). The latter would be expected to strongly favor planarization of **4.4**, and extended conjugation.

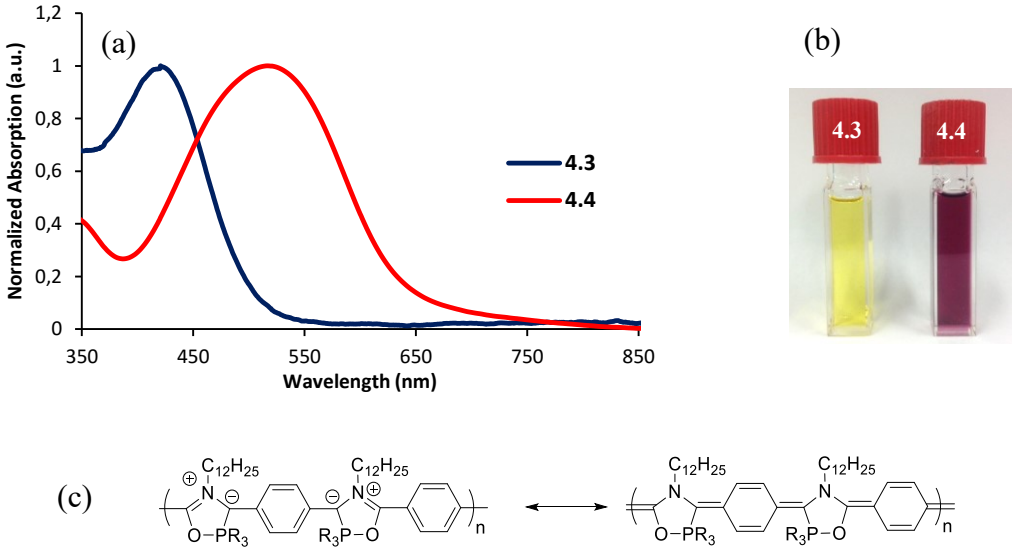
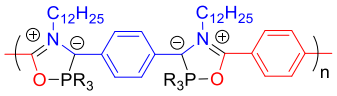
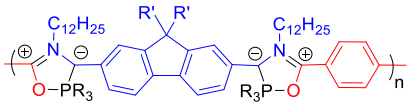
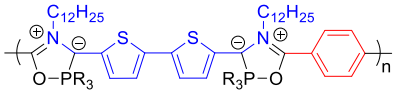
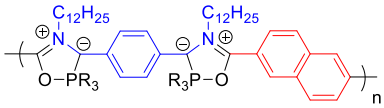
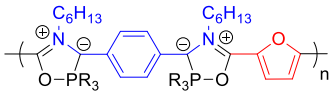
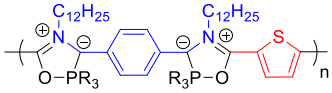
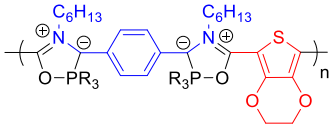


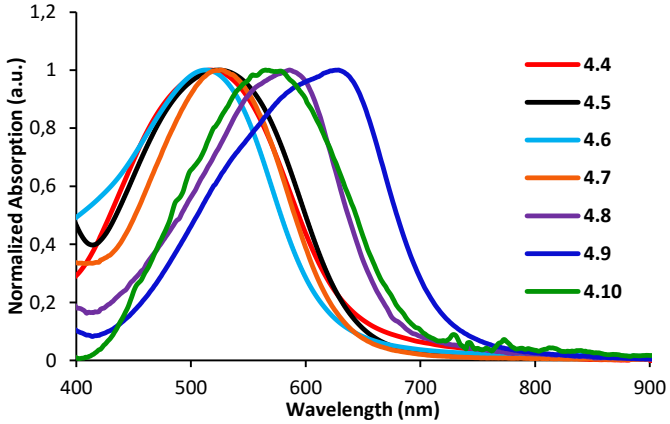
Figure 4.2 Properties of Poly(Phospha-Münchnones) **(a)** Normalized UV-Vis absorption spectra of dimer **4.3** and polymer 4.4 in chloroform **(b)** Picture of **4.3** and **4.4** in a diluted chloroform solution. **(c)** Potential resonance structures of polymer **4.4**

As shown in Figure 4.3, the optical absorbance and band-gap of these polymers shows a strong dependence upon the monomers employed. For example, the introduction of furan (polymer **4.8**) or thiophene-based linkers (polymer **4.9** and **4.10**) via the diacid chloride results in significantly red-shifted polymers compared to **4.4**. Conversely, substituents arising from the diimine (e.g. polymers **4.5** and **4.6**) do not have a major effect on absorption. While the origin of these effects are still under investigation, one reasonable rationale is that the imine substituents are incorporated *ortho* to the phosphorus in the 1,3-dipole. The large size of the PR_3 unit is expected to limit planarization of this residue, and may therefore minimize its electronic communication with the 1,3-dipole chromophore. The smaller oxygen atom on the acid chloride side of the 1,3-dipole can more easily accommodate this planarization, and may result in a stronger influence of these units on the electronic features of the 1,3-dipole. Regardless of the rationale, the structural modification of **4.4-4.10** can allow to modulate the optical energy gap between 1.67 and 1.89 eV by a simple change in constituents, and without an elaborate monomer synthesis.

Table 4.2 Absorption Properties of Poly(Phospha-Münchnones)

	Polymer, PR_3 = (catechyl)PPh	λ_{abs} (nm)	E_g (opt) (eV)
4.4		517	1.89
4.5	 R' = 2-ethylhexyl	525	1.82
4.6		513	1.87
4.7		526	1.88
4.8		586	1.77
4.9		629	1.67
4.10		585	1.74

(a)



(b)

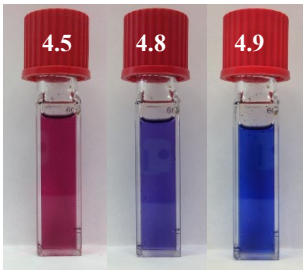


Figure 4.3 Optical Properties of Poly(Phospha-Münchnones) **(a)** Normalized UV-Vis absorption spectra in chloroform. **(b)** Pictures of polymers **4.5**, **4.8** and **4.9** in dilute chloroform solutions.

4.4 Conclusions

We have reported a multicomponent polymerization approach to generate a new class of low band-gap conjugated polymers. This reaction employs monomers that are either readily available or easily generated (diimines, diacid chlorides and (catechyl)PPh), and can be diversified to access families of poly(1,3-dipoles) in one-pot reactions and with minimal by-products. These polymers have a tunable absorption energy (λ_{max} between 513 – 629 nm), and are red-shifted from the model compounds, consistent with extended conjugation. The further study of the properties of these new polymers is currently underway.

4.5 Experimental Section

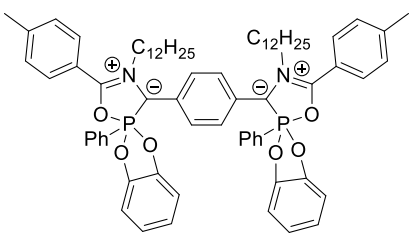
4.5.1 General Considerations

All reactions were carried out in a glovebox under a nitrogen atmosphere, unless described otherwise. Solution phase ^{1}H (400 or 500 MHz), ^{31}P (162 MHz) and ^{13}C (126 MHz) NMR spectra were recorded at ambient temperature; chemical shifts are reported in parts per million (ppm) relative to the corresponding residual *protio*-solvent signal. Mass spectra were acquired by electrospray ionization (ESI) with an orbitrap detector. The UV-Vis absorption of the polymers was measured in $CHCl_3$ solutions using a 1 cm path quartz cell on a UV-Vis spectrometer. GPC was carried out with THF as the eluent and a UV-Vis absorbance detector. Samples were analyzed versus monodispersed polystyrene standards.

All common reagents were purchased from Aldrich and used as received, unless otherwise noted. Common solvents (dichloromethane, acetonitrile) were sparged with dinitrogen, dried by passage through a column of alumina, and stored over activated molecular sieves in an inert atmosphere glovebox for at least one week prior to use. Terephthaloyl chloride was recrystallized from pentane prior to use in polymerizations. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was distilled from calcium hydride.

Catechylphenylphosphine,[37] the diacid chlorides and the diimines[30] were synthesized according to literature procedures.

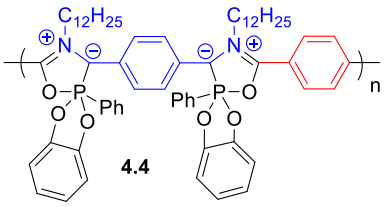
4.5.2 Synthesis of Model Dimer



4.3: (N-dodecyl)phenyldiimine **4.1** (46.9 mg, 0.10 mmol) and toluoyl chloride (34.0 mg, 0.22 mmol) were dissolved in dichloromethane (0.5 mL) in a small glass vial. Then, a solution of (catechyl)PPh (49.7 mg, 0.230 mmol) in dichloromethane (0.5 mL) was added. The solution was left to stir in the glovebox at room temperature for 18h. DBU was then added and the solution was stirred for another 15 minutes. The solvent was removed *in vacuo.* The residue was dissolved in a minimum amount of acetonitrile and cooled to -35 °C to precipitate 94.0 mg of the product **4.3** as a yellow powder (83% yield). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.79 – 7.58 (m, 4H), 7.52 – 7.22 (m, 18H), 7.01 (s, 2H), 6.74 (s, 4H), 6.48 (s, 2H), 3.91 (t, J = 7.1 Hz, 4H), 2.44 (s, 6H), 1.55 – 1.39 (m, 4H), 1.11 (m, 42H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ -18.8. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 149.8 (d, $^{2}J_{C\text{-}P}$ = 19.0 Hz), 147.9, 145.7, 143.0 (d, $^{1}J_{C\text{-}P}$ = 226.0 Hz), 140.6, 133.5, 133.3 (d, $^{2}J_{C\text{-}P}$ = 19.3 Hz), 129.4, 128.5, 128.1, 127.9 (d, $^{2}J_{C\text{-}P}$ = 18.6 Hz), 127.8 (d, $^{3}J_{C\text{-}P}$ = 11.5 Hz), 124.3, 121.6, 118.9, 110.6 (d, $^{3}J_{C\text{-}P}$ = 11.8 Hz), 110.2, 72.5 (d, $^{1}J_{C\text{-}P}$ = 259.4 Hz), 48.0 (d, $^{3}J_{C\text{-}P}$ = 7.7 Hz), 31.9, 29.6, 29.5, 29.4, 29.3_5, 29.3, 28.9, 28.8, 25.9, 22.7, 21.1, 13.9. MS could not be obtained due to the sensitivity of the compound.

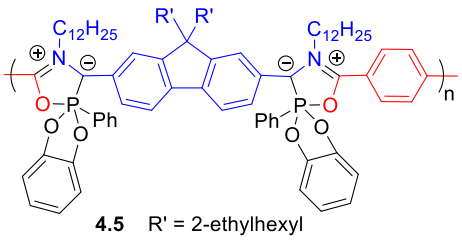
4.5.3 Synthesis of the Poly(Phospha-Münchnones)

Due to the water sensitivity of the poly(phospha-Münchnones), their molecular weights were obtained after conversion to the corresponding poly(pyrrole) by reaction with dimethyl acetylene dicarboxylate (DMAD) as previously described.[36] Rigorously dried solvents (less than 5 ppm water) and glassware must be used for the synthesis and characterization of the polymers. These must be kept under inert atmosphere at all time and can be stored at -35 °C for several months.



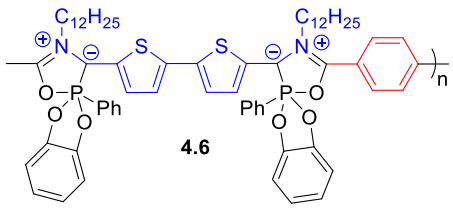
4.4

4.4: In a glovebox, (N-dodecyl)phenyldiimine (46.9 mg, 0.10 mmol), terephthaloyl chloride (18.3 mg, 0.09 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 45 °C for 18h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (36.5 mg, 0.24 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 15 min before removal of volatiles under vacuum. The resulting solid was then washed with acetonitrile 5x1 mL and dried under vacuum to afford 86 mg of **4.4** as a dark magenta solid (93 % yield). GPC: M_n = 7.7 kDa, PDI = 1.6. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.32 (end-group, s, 0.42H), 7.85 – 7.53 (m, 8H), 7.51 – 7.14 (m, 10H), 7.02 (s, 2H), 6.76 (s, 4H), 6.48 (s, 2H), 3.96 (s, 4H), 3.63 (end-group, s, 0.9H), 1.82 – 0.70 (m, 46H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ -19.0. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 160.1, 147.7, 145.5, 142.6 (d, $^1J_{C\text{-}P}$ = 225.6 Hz), 133.8 (d, $^2J_{C\text{-}P}$ = 18.0 Hz), 128.3 - 127.0 (complex, 7 signals), 126.9, 122.1, 110.8, 110.2, 75.89 (weak d, $^1J_{C\text{-}P}$ = 257.7 Hz) 61.7, 48.4, 31.9, 31.8_8, 29.7, 29.6, 29.5_6, 29.4_4, 29.4, 29.3, 29.2, 29.0, 28.8, 28.6, 27.4, 26.1, 25.8, 22.7, 13.9.



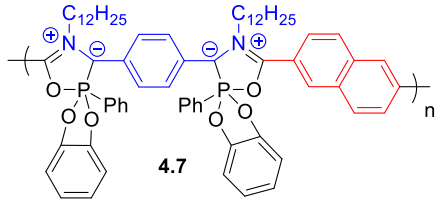
4.5 R' = 2-ethylhexyl

4.5: In a glovebox, fluorene(N-dodecyl)diimine (78.1 mg, 0.10 mmol), terephthaloyl chloride (19.3 mg, 0.095 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 45 °C for 18h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (36.5 mg, 0.24 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 15 min before removal of volatiles under vacuum. The resulting solid was then washed with acetonitrile 5x1 mL and dried under vacuum to afford 126 mg of **4.5** as a dark magenta solid (99 % yield). GPC: M_n = 20.7 kDa, PDI = 1.9. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.33 (m, 20H), 6.98 (s, 2H), 6.67 (s, 4H), 6.40 (s, 2H), 3.89 (s, 4H), 2.00 (s, 4H), 1.66 – 0.12 (m, 76H). ^{31}P NMR (162 MHz, $CDCl_3$) δ -18.9. No good ^{13}C NMR could be obtained within a reasonable time period (24h). Characterization was done by conversion with DMAD to the corresponding poly(pyrrole).



4.6

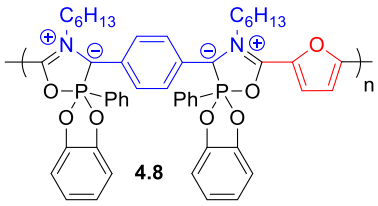
4.6: In a glovebox, bis-thiophene(N-dodecyldiimine) (55.7 mg, 0.10 mmol), terephthaloyl chloride (18.3 mg, 0.09 mmol) and (catechyl)PPh (54.5 mg, 0.25 mmol) were dissolved with 0.6 mL of dichloromethane and left to react at r.t. for 18h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (36.5 mg, 0.24 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 15 min before removal of volatiles under vacuum. The resulting solid was then washed with acetonitrile 5x1 mL and dried under vacuum to afford 93 mg of **4.6** as a dark magenta solid (92 % yield). GPC: M_n = 10.0 kDa, PDI = 1.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (imine end-group, s, 0.15H), 7.83 – 7.43 (m, 8H), 7.43 – 7.28 (m, 6H), 7.02 (m, 4H), 6.90 – 6.67 (m, 6H), 6.61 (s, 2H), 3.91 (s, 4H), 1.71 (s, 4H), 1.47 – 0.65 (m, 42H). ^{31}P NMR (81 MHz, $CDCl_3$) δ -18.4. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 145.1, 142.6, 140.8, 139.2, 137.3, 133.0, 129.1, 128.1, 128.0, 127.7, 127.5, 127.4, 122.3$_7$, 122.1, 119.3, 110.8, 48.1, 31.9, 29.6, 29.4, 29.3, 28.9, 26.3, 22.7, 14.1.



4.7

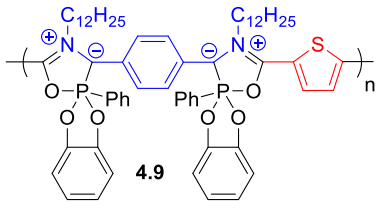
4.7: In a glovebox, (N-dodecyl)phenyldiimine (46.9 mg, 0.10 mmol), naphthalene-2,6-dicarbonyl dichloride (22.8 mg, 0.09 mmol) and (catechyl)PPh (47.6 mg, 0.22 mmol) were dissolved with 0.6 mL of dichloromethane and left to react at r.t. for 18h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (36.5 mg, 0.24 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 15 min before removal of volatiles under vacuum. The resulting solid was then washed with acetonitrile 5x1 mL and dried under vacuum to afford 97 mg of **4.7** as a dark magenta solid (99 % yield). GPC: M_n = 9.8 kDa, PDI = 1.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (imine end-group, s, 0.46H), 7.98 (s, 2H), 7.90 – 7.80 (m, 2H), 7.80 – 7.56 (m, 7H), 7.51 – 7.28 (m, 9H), 7.02 (s, 2H), 6.71 (s, 4H), 6.42 (s, 2H), 3.99 (s, 4H), 3.61 (end-group, s, 0.79H), 1.81 – 0.61 (m, 46H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.3 (CatPPh=O), -17.7, -17.9, -18.3. ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.80 (end-group), 148.0, 145.6, 143.6, 141.8, 133.8, 132.7, 128.9, 128.0, 127.9$_5$, 127.6, 127.2, 126.0, 125.3, 121.7, 119.0, 110.8, 110.2, 61.9, 48.4, 31.9, 31.1, 29.6$_7$, 29.6$_5$, 29.6$_3$,

29.6$_2$, 29.5$_9$, 29.5$_5$, 29.5$_2$, 29.5$_0$, 29.4$_2$, 29.4$_0$, 29.3$_4$, 29.3$_0$, 29.2, 29.0, 28.7, 27.4, 26.2, 25.8, 22.7, 22.6, 14.1.



4.8

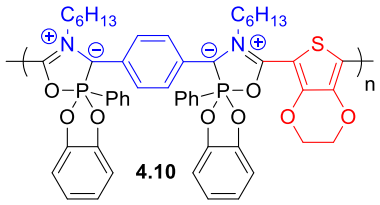
4.8: In a glovebox, phenyl(N-hexyl-diimine) (30.0 mg, 0.10 mmol), 2,5-furan diacid chloride (18.3 mg, 0.095 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 45 °C for 24h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (36.5 mg, 0.24 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 15 min before removal of volatiles under vacuum. The resulting solid was then washed with acetonitrile 5x1 mL and dried under vacuum to afford 66 mg of **4.8** as a dark purple solid (81 % yield). GPC: M_n = 6.8 kDa, PDI = 1.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 4H), 7.45 – 7.12 (m, 10H), 6.98 (s, 2H), 6.75 (m, 6H), 6.37 (s, 2H), 3.99 (s, 4H), 1.60 (s, 4H), 0.92 (m, 18H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.3 (CatechylPPh=O), -20.0. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 145.4, 143.3, 141.9, 141.5, 137.8, 133.9, 133.8, 133.1, 129.0, 128.3, 128.2, 128.0, 127.9, 122.2, 121.8, 119.1, 114.1, 110.9, 110.1, 110.0, 47.4, 31.2, 29.7, 29.4, 25.9, 22.3, 13.8.



4.9

4.9: In a glovebox, phenyl(N-dodecyl-diimine) (30.0 mg, 0.10 mmol), 2,5-thiophene diacid chloride (18.8 mg, 0.09 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 45 °C for 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (36.5 mg, 0.24 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 15 min before removal of volatiles under vacuum. The resulting solid was then washed with acetonitrile 5x1 mL and dried under vacuum to afford 91 mg of **4.9** as a dark blue solid (98 % yield). GPC: M_n = 6.8 kDa, PDI = 1.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (end-group, s, 0.16H), 7.66 (s, 8H), 7.43 – 7.14 (m, 16H), 7.01 (s, 2H), 6.71 (s, 4H), 6.39 (s, 2H), 3.90 (s, 4H), 1.67 (s, 4H), 1.38 – 0.57 (m, 42H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.3 (CatPPh=O), -10.7 (end-group, 3%), -21.5, -22.2. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 145.3, 133.9, 129.0, 128.7, 128.6, 128.0,

127.9, 123.8, 121.8, 119.2, 110.9, 110.0, 61.9, 47.8, 31.9, 31.1, 29.7, 29.6, 29.5, 29.3, 29.2, 28.8, 27.4, 26.5, 26.2, 22.7, 14.1.



4.10: In a glovebox, phenyl(N-hexyl-diimine) (30.0 mg, 0.10 mmol), 2,5-ethylenedioxythiophene diacid chloride (25.4 mg, 0.095 mmol) and (catechyl)PPh (51.9 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 45 °C for 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (36.5 mg, 0.24 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 15 min before removal of volatiles under vacuum. The resulting solid was then washed with acetonitrile 5x1 mL and dried under vacuum to afford 66 mg of **4.10** as a dark purple solid (81 % yield). GPC: M_n = 6.3 kDa, PDI = 1.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (end-group, s, 0.18H), 7.74 – 7.59 (m, 6H), 7.44 – 7.20 (m, 12H), 7.00 (s, 4H), 6.70 (s, 6H), 6.43 (s, 2H), 4.36 (s, 4H), 3.88 (s, 4H), 1.79 – 0.50 (m, 22H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.3 (catechylPPh=O), -10.65 (end-group), -17.82, -18.35. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 145.6, 133.3, 132.3, 129.0, 128.9, 128.5, 128.0, 127.8, 123.8, 122.2, 121.6, 119.0, 112.8, 112.7, 110.9, 110.0, 64.7, 61.9, 53.4, 31.7, 31.6, 31.4, 31.2, 31.0, 30.9_7, 29.7, 29.0, 28.8, 27.1, 25.9, 25.6, 22.6, 22.4, 22.2, 14.1, 13.9.

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(38) **4.4** was suspended in dichloromethane and left to react with DMAD for 18h at r.t. before quenching with water and precipitation in MeOH. The molecular weight was determined by GPC in THF in comparison to PS standards.

Chapter 5: Renewable Monomers in the Phosphonite-Based, Multicomponent Synthesis of Cross-Conjugated Polymers

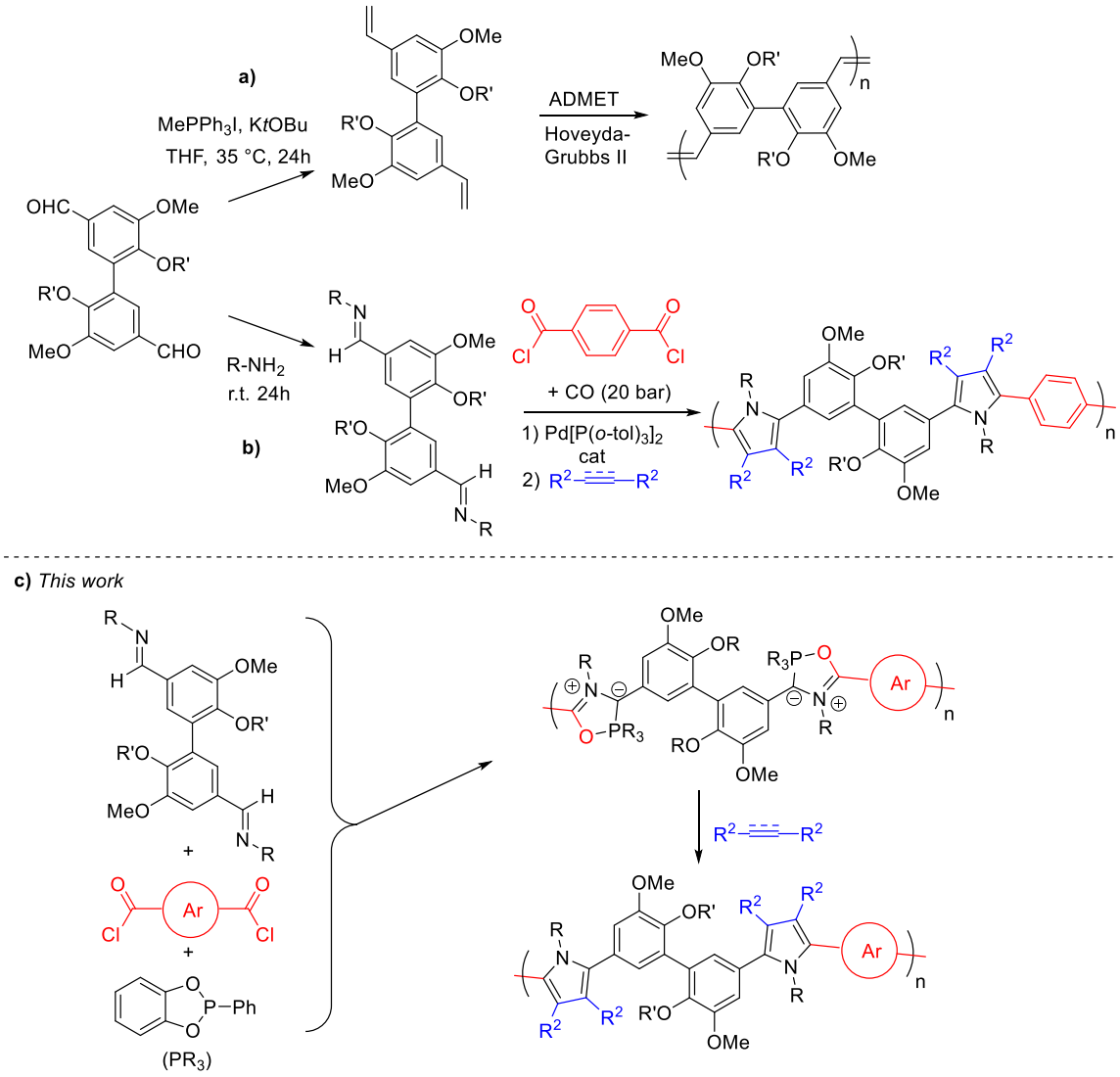
5.1 Preface

The studies in Chapters 3 and 4 demonstrate that the phosphonite-mediated multicomponent polymerization of diimines, diacid chlorides and alkynes/alkenes provides an efficient platform for the synthesis of conjugated polymers. We describe in this chapter the extension of this approach to the synthesis of cross-conjugated polymers from renewable starting materials. These studies show that bis-vanillin monomers, available from the oxidative degradation of lignin, can be used in this metal-free multicomponent polymerization. Similarly, 2,5-furandicarboxyaldehyde (FDCA), a product of cellulose oxidation, can serve as a precursor to the diimine or the diacid chloride. This provides the first example of synthesis of cross-conjugated polymer from both components of lignocellulosic biomass.

5.2 Introduction

The rapid depletion and negative environmental impact of petroleum and petroleum-derived products has become of growing concern over the past decade, and has stimulated a movement towards the design of replacement materials based upon renewable resources.[1-12] Common examples include poly-lactic acid (PLA), a biodegradable polymer derived from corn starch extracts,[13] cellulose fibers or nanocrystals,[14] and triglyceride-based monomers (fatty acids).[15,16] More recently, lignin, a complex amorphous aromatic polymer extracted from wood, has begun to attract attention as a feedstock material.[17-21] Lignin represents the world's largest renewable source of aromatics, and over 40 million tons is produced annually as a by-product of the pulp and paper industry. The most common current use of this material is to burn it for cheap energy production. As an alternative,

lignin can be depolymerized to afford small aromatic molecules such as vanillin, a well-known food flavoring agent. While vanillin can also be obtained from petroleum feedstocks, the biorefinery company *Borregaard* in Norway is currently the second largest producer of vanillin.[22] The large scale availability of vanillin from a non-edible biomass source makes it an ideal candidate for the synthesis of aromatic polymers.[23] Several examples have been reported in the literature on the polymerization of vanillin-based monomers into semi(aromatic) polyesters,[24,25] the electropolymerization of bis-vanillin,[26] or thiol-ene polymerization of alkene substituted vanillin.[27] Surprisingly, despite its aromatic nature, vanillin has only been reported twice as a precursor for the synthesis of conjugated polymers. Llevot reported the synthesis of bis-vanillin diene via a Wittig reaction followed by ADMET polymerization to obtain a cross-conjugated polymer with a molecular weight of 29.0 kDa (Scheme 5.1a).[28] Concurrent with this work, our lab reported the first example of a palladium-catalyzed multicomponent polymerization that allows for the incorporation of bis-vanillin-imine into the backbone of cross-conjugated poly(pyrroles) (Scheme 5.1b).[29]



Scheme 5.1 Synthesis of Cross-Conjugated Polymers from Vanillin Monomers

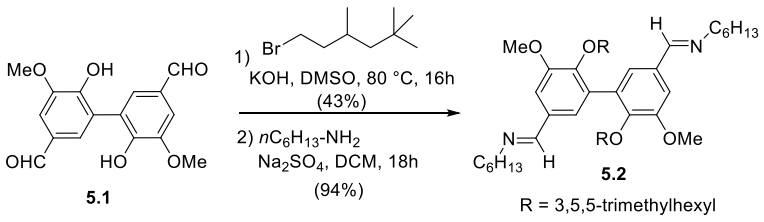
We have shown in Chapter 3 that the phosphonite-mediated multicomponent polymerization of aromatic diimines, diacid chlorides, and alkynes/alkenes can provide an alternative, non-palladium based approach to synthesize pyrrole-containing conjugated polymers. A useful feature of this reaction is its wide substrate scope, as well as the ability to access high molecular weight, low defect polymers. The reliance of this phosphonite-mediated polymerization on monomers arising from oxygenated substrates (e.g. imines from aldehydes, acid chlorides from carboxylic acids) also suggests its potential use in the conversion of bio-mass derived materials into conjugated polymers. Here, we describe the use of this phosphonite-mediated multicomponent polymerization as a metal-free method

to construct vanillin-based polymers (Scheme 5.1c). Importantly, by exploiting the tunability offered by the multicomponent polymerization, a range of hybrid polymers derived from bis-vanillin and other available monomers (e.g. with terephthaloyl chloride, alkynes, and/or alkenes) can be generated in a one pot polymerizations. This includes a cross-conjugated polymer composed of both components of lignocellulosic biomass. Moreover, we have preliminarily examined the use of cellulose-derived furan-diimines as a monomer in this polymerization.

5.3 Results and Discussion

5.3.1 Synthesis of Vanillin-Based Monomers

As we have previously communicated (Chapter 2), the diimine **5.2** can be generated in two steps from bis-vanillin (**5.1**). This sequence involves the initial alkylation of **5.1** with 1-bromo-3,5,5-trimethylhexane to form a soluble, phenol-protected dialdehyde. Conversion to the diimine by condensation with *n*-hexylamine affords **5.2** as a yellow oil in near quantitative yield (94%). By careful control of the aldehyde/amine to maintain a 1:1 ratio, no further purification is required and **5.2** is simply dried under vacuum to remove traces of solvent.

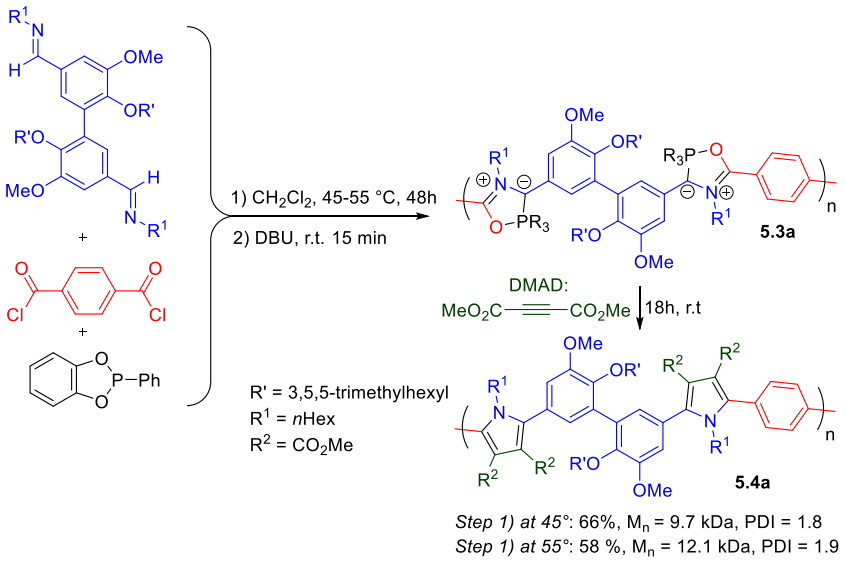


Scheme 5.2 Synthesis of Vanillin-Derived Diimine **5.2**

5.3.2 Synthesis of Polymers

5.3.2.1 *Reaction Development*

Our initial studies towards the use of the vanillin-based diimine **5.2** in polymerization involved its reaction with terephthaloyl chloride (a commodity chemical used in the synthesis of Kevlar), and (catechyl)PPh. As shown in Scheme 5.3, the reaction of these components at 45 °C for 48 h followed by deprotonation with DBU leads to the in situ formation of poly(phospha-Münchnone) **5.3a**. After precipitation and washing with acetonitrile (to remove excess DBU), the addition of dimethylacetylene dicarboxylate (DMAD) to **5.3a** results in quantitative 1,3-dipolar cycloaddition and phosphonate loss to afford the pyrrole-containing cross-conjugated polymer **5.4a** in 66% isolated yield. GPC analysis of **5.4a** shows it to have moderate molecular weight (M_n = 9.7 kDa, M_w = 17.5 kDa, PDI = 1.8). Increasing the temperature of the first step in the polymerization to 55 °C can increase this molecular weight (M_n = 12.1 kDa). The moderate yields in both of these polymerizations are likely the result of the partial solubility of the polymers in the washing solvents used for isolation (methanol and acetonitrile).



Scheme 5.3 Multicomponent Polymerization with Vanillin Bis-Imine

To assess the purity of **5.4a**, it was examined by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy (e.g. ^{1}H NMR in Figure 5.1). Of note, ^{1}H NMR spectra show only signals for the symmetrical vanillin (e.g. δ 7.02 (2H), δ 6.92 (2H)), phenylene (δ 7.45 (4H)), and pyrrole (δ 3.68 and 3.61 (12H)) units with no visible defects. Small signals corresponding to aldehyde (δ 9.87 ppm), carboxylic acid (δ 8.27 ppm) and amide (δ 6.15 ppm) end-groups are also observed. Interestingly, integration of these suggests a degree of polymerization (DP) of 82 (or M_n = 46 kDa) that is inconsistent with GPC analysis. This discrepancy may potentially arise from the presence of macrocycles, which would lead to erroneous end-group analysis, or the polystyrene standards used for GPC calibration, which may not be suitable for this type of polymer. We are currently probing the origin of this difference.

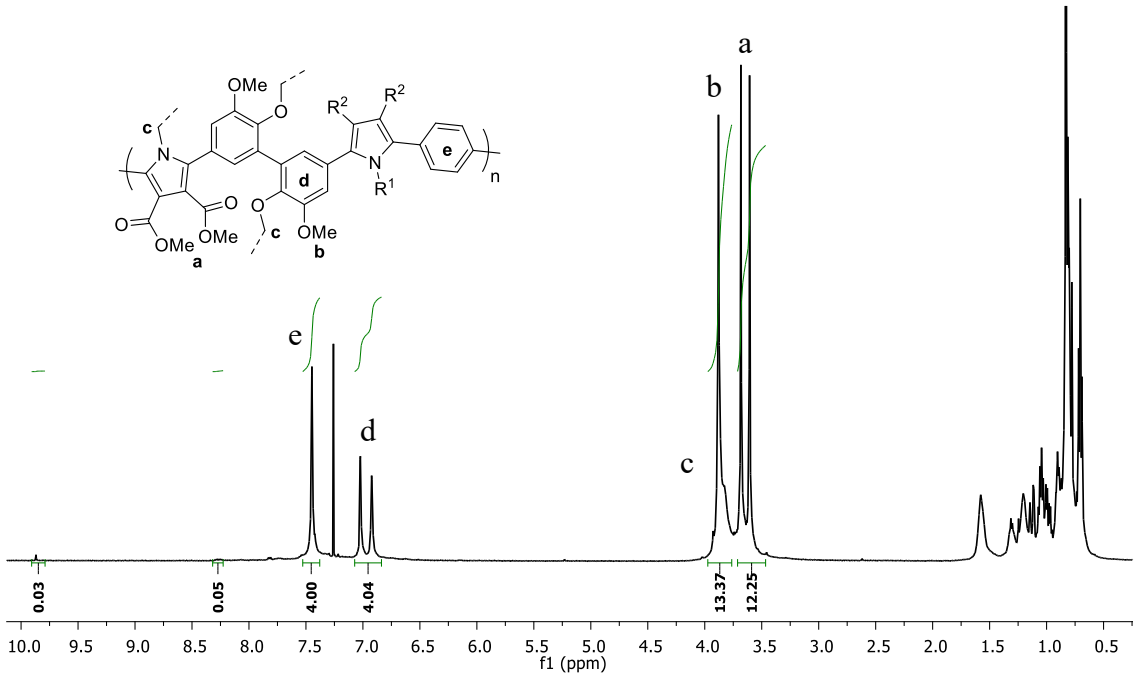


Figure 5.1 ^{1}H NMR Spectra of Polymer **5.4a**

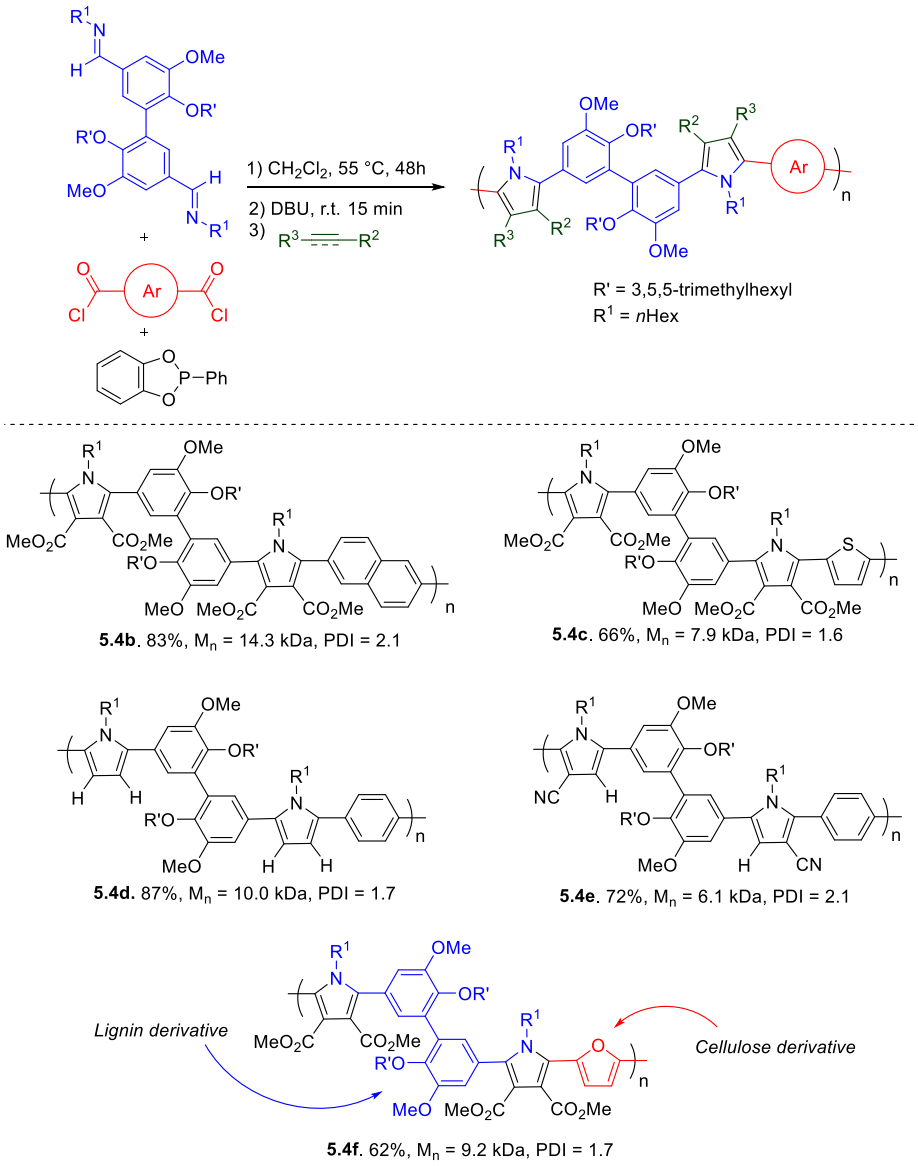
5.3.2.2 *Diversity of Vanillin-Based Poly(Pyrroles)*

In addition to the formation of **5.4a**, the availability of the other monomers in this polymerization (diacid chlorides, dipolarophiles) makes it straightforward to generate

several variants of vanillin-derived polymers (Table 5.1). For example, the use of a naphthalene-derived diacid chloride provides a route to generate the naphthalene-containing polymer **5.4b**. Thiophene can also be incorporated into the polymer from the acid chloride fragment (**5.4c**). Alternatively, as shown in polymers **5.4d** and **5.4e**, the cycloaddition reagent can modulated to include electron poor alkenes, such as vinyl triphenylphosphonium bromide (an acetylene equivalent) or 2-chlorocyanoethylene. As with DMAD, these latter also undergo clean cycloaddition to form pyrroles with varying backbone substituents.

We have also explored the use of acid chlorides that can also potentially be derived from biomass. Furan dicarboxylic acid (FDCA) has been identified by the US Department of Energy as one of the top 12 bio-mass derived renewable chemicals, and is generated from the oxidative cleavage of cellulose.[30] As shown in polymer **5.4f**, the acid chloride of FDCA can be readily incorporated into this polymerization. This latter represents what is to our knowledge the first example of a cross-conjugated polymer derived from both components of lignocellulose, while the third component, dimethylacetylene dicarboxylate, is a readily available alkyne.

Table 5.1 Diversity of Vanillin-Based Poly(Pyrroles)



5.3.3 Properties of the Polymers

Pyrrole-based conjugated polymers have been shown to be fluorescent materials of potential relevance in polymer-based LEDs.[31] As shown in Table 5.2, these lignin-based polymers are also blue emitting compounds, and the structural modifications can be exploited to modulate this emission. For example the introduction of smaller linkers such as thiophene (**5.4c**) or furan (**5.4f**) induces a red-shift in the fluorescence energy (**5.4c**: 463 nm, **5.4f**: 457 nm, **5.4a**: 414 nm). The substituents on the pyrrole can also influence on

emission energies (**5.4a**, **5.4d**. **5.4e**). In addition, these latter have a significant effect the quantum yield. Of note, the cyano-substituted **5.4e** leads to relatively high efficiencies (Φ_{em} = 0.48), whereas the unsubstituted pyrrole is a significantly less fluorescent material (Φ_{em} = 0.17).

Table 5.2 Optical Properties of the Vanillin-Based Polymers

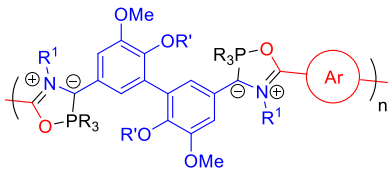
Polymer	λ_{abs} (nm)	λ_{em} (nm)	E_g (eV)	Φ_{em}
5.4a	285	414	3.42	0.30
5.4b	276	412	3.29	0.36
5.4c	290	463	3.08	0.25
5.4d	335	426	3.13	0.17
5.4e	320	434	3.30	0.48
5.4f	291	457	3.29	0.28

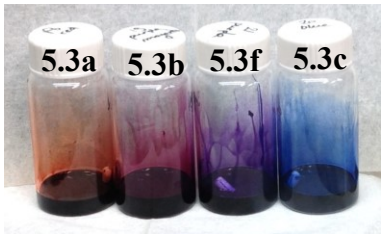
UV-Vis absorbance and fluorescence spectra measured in $CHCl_3$ solutions. Quantum yields of fluorescence determined versus an anthracene standard.

5.3.4 Vanillin-Based Poly(Phospha-Münchnones)

We have previously noted (Chapter 4) that the poly(phospha-Münchnones) intermediates in this multicomponent polymerization are an interesting class of low band-gap, donor-acceptor material that incorporate charges into the polymer backbone. We see similar features arising from the vanillin-based polymers **5.3**. Polymers **5.3a-c, f** can be isolated prior to alkyne cycloaddition as deeply colored solids by precipitation and washing with acetonitrile (Figure 5.2). These polymers are stable under inert atmosphere, but do decompose in the presence of air or moisture. The UV-Vis absorbance of **5.3** is strongly dependent upon the acid chloride employed. Thus, while the phenylene and naphthylene derived **5.3a,b** are moderate band-gap polymers, those based upon the more planarizing furan (**5.3f**) and in particular thiophene (**5.3c**) are reasonably low band-gap materials (e.g. Eg = 1.64 eV for **5.3c**).[32]

a)





b)

Polymer	λ_{abs} (nm)	E_g (eV)
5.3a	480	1.85
5.3b	523	1.87
5.3c	618	1.64
5.3f	578	1.76

c)

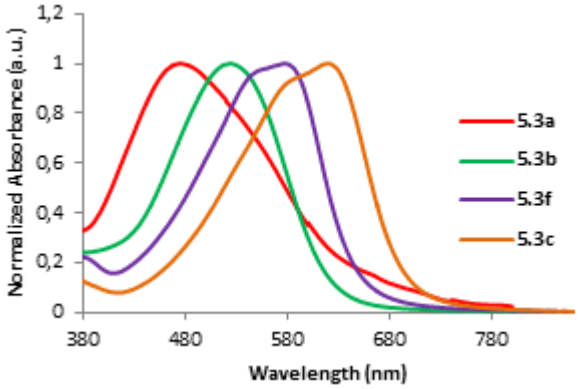


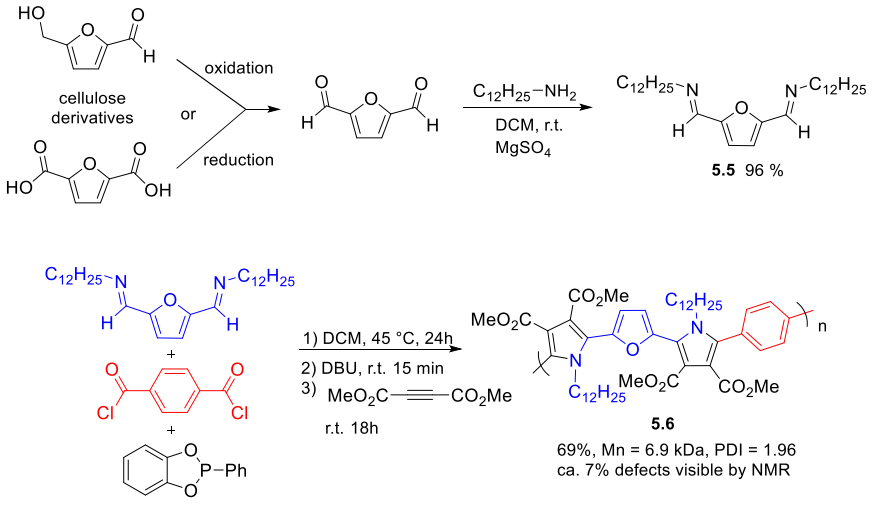
Figure 5.2 Vanillin-Based Poly(Phospha-Münchnones) **(a)** Solutions of 5.3a-c,f in dichloromethane. **(b)** UV-Vis maximum absorbance in $CHCl_3$, and calculated band-gap from the absorption onset. **(c)** UV-Vis absorbance spectra in $CHCl_3$

Taken together with the polypyrroles, this multicomponent platform can provide access to vanillin-based cross-conjugated polymers ranging from high band-gap blue-emitting polymers to lower band-gap poly(1,3-dipoles), with these properties tunable based upon the other two components.

5.3.5 Synthesis of Conjugated Polymers from Cellullose Derivatives

We have preliminarily accessed the potential of this multicomponent polymerization to employ diimines derived from cellulose-based deconstruction products: 2,5-furan dicarboxyaldehyde. This compound can be generated from 2,5-furan dicarboxylic acid (via reduction), as well as from hydroxymethylfurfural (via oxidation), which is also on the US Department of Energy list of top 12 bio-based chemicals. As illustrated in Scheme

5.4, the reaction of furan dicarboxyaldehyde with a primary amine leads to the quantitative formation of diimine **5.5**. The use of this imine in the multicomponent polymerization with terephthaloyl chloride and (catechyl)PPh, followed by the addition of DMAD, leads to the generation of the pyrrole-containing polymer **5.6** in good yield, although only moderate molecular weights (69 %, M_n = 6.9 kDa). However, preliminary assessment of the purity by ^{1}H NMR analysis shows the presence defects in the aromatic region (ca. 7%). We postulate the latter may arise from competing side reactions between the in situ generated iminium salt and the electron rich furan unit, although this has yet to be confirmed.



Scheme 5.4 Synthesis and Multicomponent Polymerization of Furan Bis-Imines

5.4 Conclusions

We have successfully incorporated vanillin-based monomers into cross-conjugated polymers via the multicomponent polymerization of vanillin derived diimines, diacid chlorides and (catechyl)PPh. Two different types of polymers were obtained using this approach: poly(1,3-dipoles) and poly(pyrroles), both of which can be generated in one-pot reactions of available substrates. Importantly, manipulation of the components in this polymerization (acid chloride and dipolarophile) can provide a tool to systematically modulate the properties of these vanillin-based polymers. Studies directed towards the

potential use of these features in the design of new classes of biomass derived electronic materials are currently underway.

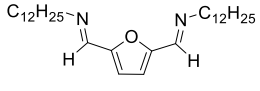
5.5 Experimental Section

5.5.1 General Considerations

All reactions were carried out in a glovebox under a nitrogen atmosphere, unless described otherwise. Solution phase ^{1}H (400 or 500 MHz), ^{31}P (162 MHz) and ^{13}C (126 MHz) NMR spectra were recorded at ambient temperature; chemical shifts are reported in parts per million (ppm) relative to the corresponding residual *protio*-solvent signal. Mass spectra were acquired by electrospray ionization (ESI) with an orbitrap detector. The UV-Vis absorption and fluorescence of the polymers was measured in $CHCl_3$ solutions using a 1 cm path quartz cell on a UV-Vis spectrometer and a fluorometer. The fluorescence quantum yields were determined versus anthracene in ethanol (Φ_{em} = 0.27) at slit widths of 2.5 nm. The excitation wavelength corresponds to the maxima of absorption for each polymer as per in Table 5.2. GPC was carried out with THF as the eluent and a UV-Vis absorbance detector. Samples were analyzed versus monodispersed polystyrene standards.

All common reagents were purchased from Aldrich and used as received, unless otherwise noted. Common solvents (dichloromethane, acetonitrile) were sparged with dinitrogen, dried by passage through a column of alumina, and stored over activated molecular sieves for at least one week in an inert atmosphere glovebox prior to use. Terephthaloyl chloride was recrystallized from pentane prior to use in polymerizations. (catechyl)PPh[33] and the diacid chlorides[29] were synthesized according to literature procedures. The bis-vanillin diimine **5.2** was synthesized according to the procedure in Chapter 2.

5.5.2 Monomer Synthesis

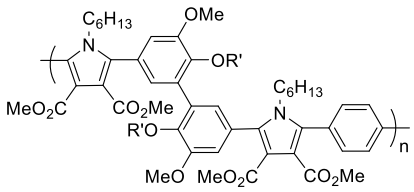


5.5

5.5: 2,5-furan dicarboxyaldehyde (462 mg, 3.73 mmol) was dissolved in dichloromethane (100 mL) under air. Dodecylamine (1.38 g, 7.45 mmol) was added followed by excess anhydrous

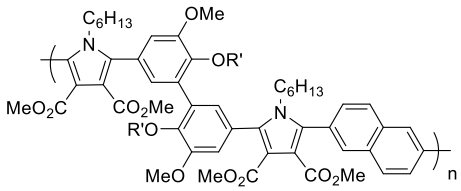
magnesium sulfate. The suspension was left to react at room temperature for 18 h. The solution was filtered and the solvent removed. The powder was dried under vaccum at 70 °C overnight to give **5.5** as a beige solid (1.64 g, 96 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 2H), 6.85 (s, 2H), 3.57 (t, *J* = 7.0 Hz, 4H), 1.67 (d, *J* = 7.1 Hz, 4H), 1.40 – 1.11 (m, 36H), 0.86 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 149.9, 113.6, 62.1, 31.9, 30.7, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 27.3, 22.7, 14.1. MS(ESI): $C_{30}H_{55}ON_2$ $[M+H]^+$ *m/z* calcd. 459.43089; found 459.43042.

5.5.3 Synthesis of Poly(Pyrroles)



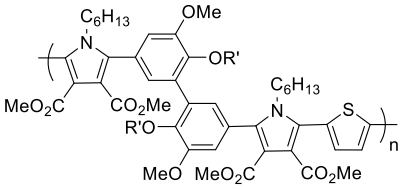
R' = 3,5,5-trimethylhexyl
5.4a

5.4a: In a glovebox, bis-vanillin diimine **5.2** (72 mg, 0.10 mmol), terephthaloyl chloride (20 mg, 0.10 mmol) and (catechyl)PPh (54.5 mg, 0.25 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 55 °C for 48 h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (61 mg, 0.40 mmol) in dichlomethane (5mL). The reaction mixture was left to stir at r.t. for 5 min before removal of solvent *in vacuo*. The resulting purple solid was washed with acetonitrile (3x 1 mL) and redissolved in dichlomethane (3 mL) before the addition of dimethyl acetylenedicarboxylate (DMAD) (85 mg, 0.6 mmol). The reaction mixture was left to stir at r.t. for 18 h. Subsequently, the reaction mixture was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x1 mL) then dissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **5.4a** as a yellow solid. (64 mg, 58 % yield). GPC: M_n = 12.1 kDa, M_w = 23.0 kDa, PDI = 1.9. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 4H), 7.02 (s, 2H), 6.92 (s, 2H), 3.88 (s + broad s, 14H), 3.68 (s, 6H), 3.61 (s, 6H), 1.58 (s, 4H), 1.40 – 0.54 (m, 54H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 165.1, 152.5, 146.7, 136.4, 135.8, 132.4, 131.5, 130.3, 125.4, 125.2, 114.9, 114.7, 114.4, 71.8, 55.9, 51.6, 51.4, 51.3, 45.3, 39.6, 31.0, 31.0, 30.3, 29.9, 29.4, 27.2, 26.1, 25.9, 22.4, 22.3, 13.8.



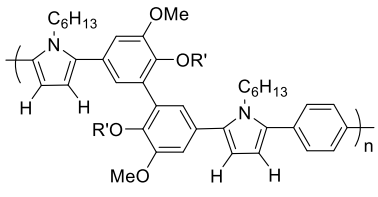
R' = 3,5,5-trimethylhexyl
5.4b

5.4b: Same procedure as **5.4a** with bis-vanillin diimine **5.2** (72 mg, 0.10 mmol) and naphthalene-2,6-dicarbonylchloride (25 mg, 0.10 mmol). Afforded polymer **5.4b** as a yellow solid. (96 mg, 83 % yield). GPC: M_n = 14.3 kDa, M_w = 30.0 kDa, PDI = 2.1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (m, 4H), 7.53 (d, J = 8.4 Hz, 2H), 7.07 (s, 2H), 6.99 (s, 2H), 3.91 (2s, 14H), 3.71 (s, 6H), 3.65 (s, 6H), 1.59 (s, 4H), 1.42 – 0.44 (m, 54H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 165.3, 152.5, 146.7, 136.6, 136.2, 132.6, 132.4, 129.7, 129.4, 128.6, 128.2, 125.5, 125.3, 114.9, 114.5, 114.4, 71.9, 55.9, 51.7, 51.6, 51.4, 45.2, 39.6, 31.0, 30.9, 30.4, 29.9, 27.2, 26.1, 25.8, 22.4, 22.1, 13.8.



R' = 3,5,5-trimethylhexyl
5.4c

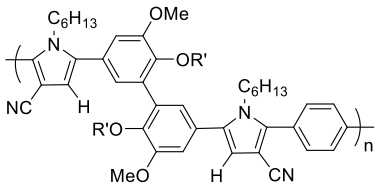
5.4c: Same procedure as **5.4a** with bis-vanillin diimine **5.2** (72 mg, 0.10 mmol) and 2,5-thiophenedicarbonyl dichloride (21 mg, 0.10 mmol). Afforded polymer **5.4c** as a yellow solid. (73 mg, 66 % yield). GPC: M_n = 7.9 kDa, M_w = 12.6 kDa PDI = 1.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (s, 2H), 6.98 (s, 2H), 6.89 (s, 2H), 3.98 – 3.76 (m, 14H), 3.69 (s, 6H), 3.66 (s, 6H), 1.58 (s, 4H), 1.43 – 0.64 (m, 54H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 164.9, 152.5, 146.9, 137.3, 133.2, 132.4, 129.8, 126.9, 125.2, 117.1, 114.7, 114.3, 71.8, 55.9, 51.6, 51.6, 51.4, 45.5, 39.6, 31.1, 31.0, 30.8, 29.9, 29.9, 27.3, 26.1, 26.0$_7$, 26.0$_6$, 25.9$_8$, 22.4, 22.3, 13.8.



R' = 3,5,5-trimethylhexyl
5.4d

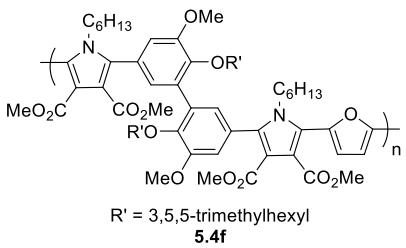
5.4d: In a glovebox, bis-vanillin diimine **5.2** (216 mg, 0.30 mmol), terephthaloyl chloride (61 mg, 0.30 mmol) and (catechyl)PPh (155.6 mg, 0.72 mmol) were dissolved with 1.8 mL of dichloromethane in a sealed reaction vessel and heated at 55 °C for 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (228 mg, 1.5 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 5 min then diluted to 15 mL and placed in the freezer at -35 °C. A cold dichloromethane solution of vinyl triphenylphosphonium bromide (222 mg, 0.6 mmol) was then added dropwise while maintaining a low temperature. The reaction mixture was left to stir at r.t. for 18h.

Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x3 mL) and hexanes (3x3 mL) then dissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **5.4d** as a yellow solid. (228 mg, 87 % yield). GPC: M_n = 17.5 kDa, M_w = 26.3 kDa, PDI = 1.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 4H), 7.04 (s, 2H), 7.00 (s, 2H), 6.26 (d, J = 5.6 Hz, 4H), 4.14 (s, 4H), 3.90 (m, 10H), 1.80 – 0.54 (m, 58H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 145.5, 136.8, 136.1, 132.9, 132.6, 129.0, 128.7, 124.1, 112.3, 109.4, 109.2, 71.7, 55.8, 51.4, 45.3, 39.6, 31.0, 31.0, 30.6, 30.0, 27.3, 26.0, 25.8, 22.3, 22.3, 13.9.



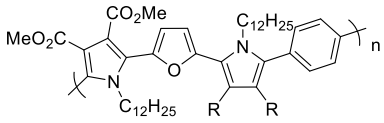
R' = 3,5,5-trimethylhexyl
5.4e

5.4e: In a glovebox, bis-vanillin diimine **5.2** (72 mg, 0.10 mmol), terephthaloyl chloride (20 mg, 0.10 mmol) and (catechyl)PPh (52 mg, 0.24 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 45 °C for 48h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (38.1 mg, 0.25 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 5 min before removal of solvent *in vacuo*. The resulting purple solid was washed with acetonitrile (3x 1 mL) and redissolved in dichloromethane (3 mL) before the addition of DBU (38.1 mg, 0.24 mmol) and 2-chloroacrylonitrile (18 mg, 0.24 mmol). The reaction mixture was left to stir at r.t. for 18h. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x1 mL) then dissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford the polymer **5.4e** as a yellow solid. (66 mg, 72 % yield). GPC: M_n = 6.1 kDa, M_w = 12.8 kDa, PDI = 2.1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 4H), 7.01 (s, 2H), 6.95 (s, 2H), 6.51 (s, 2H), 4.09 (s, 4H), 4.02 – 3.76 (m, 10H), 2.10 (s, 2H), 1.73 – 0.51 (m, 56H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 146.5, 141.2, 136.7, 132.7, 130.6, 130.0, 126.7, 124.3, 117.1, 112.6, 112.0, 93.1, 71.8, 56.0, 51.4, 46.0, 39.6, 31.0, 30.9, 30.3, 29.9, 29.4, 27.3, 26.0, 25.6, 22.3, 22.2, 14.1, 13.8.



5.4f

5.4f: Same procedure as **5.4a** with bis-vanillin diimine **5.2** (72 mg, 0.10 mmol) and 2,5-furandicarbonyl dichloride (19 mg, 0.10 mmol). Afforded polymer **5.4f** as a yellow solid. (67 mg, 62 % yield). GPC: M_n = 9.2 kDa, M_w = 15.6 kDa, PDI = 1.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.86 (end-group, s, 0.05H), 6.93 (s, 2H), 6.85 (s, 2H), 6.71 (s, 2H), 3.92 (s, 4H), 3.85 (s, broad, 10H), 3.73 (s, 6H), 3.63 (s, 6H), 1.58 (s, 4H), 1.45 – 0.46 (m, 54H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 164.7, 152.4, 146.9, 144.2, 137.8, 132.5, 125.2, 125.0, 124.5, 117.0, 114.5, 114.2, 113.5, 71.7, 55.8, 51.8, 51.5, 51.4, 45.9, 39.6, 31.1, 31.0, 30.6, 29.9, 27.3, 26.1, 26.0, 26.0, 22.4, 22.3, 22.2, 22.2, 13.8, 13.7.



5.6

5.6: In a glovebox, furan diimine **5.5** (46 mg, 0.10 mmol), terephthaloyl chloride (20 mg, 0.10 mmol) and (catechyl)PPh (55 mg, 0.25 mmol) were dissolved with 0.6 mL of dichloromethane in a sealed reaction vessel and heated at 45 °C for 24h. The solution was then slowly added dropwise to a large vial (20 mL) containing DBU (61 mg, 0.40 mmol) in dichloromethane (5mL). The reaction mixture was left to stir at r.t. for 5 min before removal of solvent *in vacuo*. The resulting purple solid was washed with acetonitrile (3x 1 mL) and redissolved in dichloromethane (3 mL) before the addition of DMAD (85.3 mg, 0.6 mmol). The reaction mixture was left to stir at r.t. for 18h. Subsequently, the reaction was brought out of the glovebox and quenched with water (0.1 mL). The polymer was precipitated and triturated with methanol (3x1 mL) then dissolved in $CHCl_3$ and filtered through an alumina plug. The volatiles were removed *in vacuo* to afford polymer **5.4a** as a brown solid. (58 mg, 69 % yield). GPC: M_n = 6.9 kDa, M_w = 13.8 kDa, PDI = 2.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 4H), 6.77 (s, 2H), 3.93 (s, 4H), 3.79 (s, 6H), 3.62 (s, 6H), 1.38 - 0.83 (m, 46H).

5.5.4 Vanillin-Based Poly(Phospha-Münchnones)

Poly(phospha-Munchnones) isolated as per the procedure described above, and prior to the cycloaddition reaction. Due to the high water sensitivity of these materials, chloroform was

rigorously dried over activated molecular sieves for a week before dissolving the polymers. UV-Vis measurements were done in an oven-dried quartz UV cell equipped with a screw-cap which was rinsed with the polymer solution (c = 0.013 mg/mL) once before acquisition.

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Chapter 6: Summary, Conclusions and Future Work

This chapter briefly summarizes the results and conclusions presented in this thesis, as well as its contribution to the field of multicomponent polymerizations. Suggestions for future work based on this research will also be reported.

6.1 Conclusions and Contributions to Knowledge

Over the last decades, Multicomponent Coupling Reactions (MCRs) have found significant utility in synthetic organic chemistry as methods to assemble products with often minimal waste, high atom economy, minimal steps and broad substrate diversity. Despite all of these advantages, MCRs have only recently gained attention in polymer science and have very rarely been applied to the synthesis of conjugated polymers (see Chapter 1). In this thesis, we presented two new multicomponent polymerization approaches to the synthesis of conjugated polymers.

In Chapter 2, we described the first metal-catalyzed multicomponent synthesis of conjugated poly(heterocycles). This palladium-catalyzed transformation provides an alternative to the more common cross-coupling polymerization, where a new, more complex, cyclic repeat unit is generated as the polymerization proceeds. An important feature of this reaction is the availability of the building blocks: diimines, diacid chlorides and dipolarophiles (e.g. alkynes, alkenes). This latter makes this both an efficient route to construct poly(heterocycles) from combinations of reagents, and a readily tunable platform. Moreover, a new type of conjugated mesoionic polymer was synthesized in this reaction: a poly(Münchnone). These poly(1,3-dipoles) are moderately low band-gap materials that can be readily tuned by varying the monomers. These results demonstrate the potential utility of multicomponent polymerizations to serve as modular platforms for the synthesis of conjugated polymers.

Chapter 3 reported an alternative, phosphonite-mediated multicomponent polymerization route to generate poly(pyrroles). To the best of our knowledge, this represents the first example of a metal-free multicomponent synthesis of conjugated polymers. This reaction uses diimines, diacid chlorides and (catechyl)PPh to generate a poly(phospha-Münchnone) intermediate that can subsequently react with alkynes or alkenes to form poly(pyrroles). Notably, this approach overcomes some of the limitations of the reaction presented in Chapter 2; it generates higher molecular weight polymers and offers a broader substrate scope tolerance. With regard to the latter, this transformation can now allow inexpensive, commodity materials (e.g. diimines based upon terephthaldehyde, terephthaloyl chloride, alkynes, etc) to be employed as monomers for direct conversion to conjugated materials. The monomers combinations reported in this chapter allows the potential generation of more than 300 different polymers, all in one-pot reactions. As an example, we synthesized a thiophene-pyrrole copolymer that could prove useful in field-effect transistors.

In Chapter 4, we described the isolation of the poly(phospha-Münchnone) intermediates introduced in Chapter 3. Preliminary UV-Vis studies showed that these poly(1,3-dipoles) have low band-gap properties similar to donor-acceptor type polymers. The band-gaps can be easily modulated by changing the diimine or diacid chloride monomers.

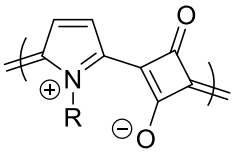
Finally, Chapter 5 presented the use of renewable starting materials in the phosphonite-mediated multicomponent synthesis of conjugated polymers. Since this reaction relies on monomers derived from oxygenated starting materials (imines from aldehydes and acid chlorides from carboxylic acids), we have shown that it can incorporate lignocellulosic derivatives such as bis-vanillin (from lignin) or furan dicarboxylic acid (FDCA from cellulose). A range of cross-conjugated polymers were obtained, which show tunable properties.

6.2 Suggestions for Future Work

6.2.1 Synthesis of New Poly(1,3-Dipoles)

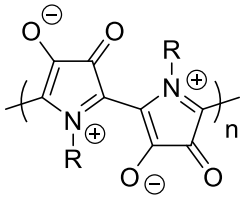
Chapters 2 and 4 introduced a new type of low band-gap conjugated polymers: poly(1,3-dipoles). Poly(Münchnones) and poly(phospha-Münchnones) both exhibit properties similar to donor-acceptor polymers presumably due to the charge separation within the polymer backbone. A similar effect had been previously noted for polymers based on the squaraine dye (Figure 6.1a),[1,2] or zwitterionic pyrrole-based polymers (Figure 6.1b).[3,4]

a. Pyrrole-derived poly(squaraines)



R = $C_{12}H_{25}$, $C_{11}H_{22}OH$

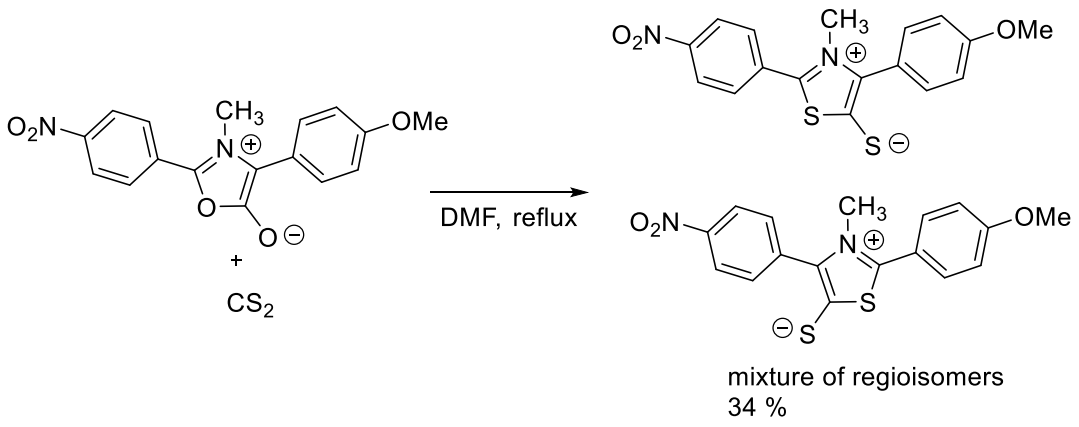
b. Pyrrole-based poly(zwitterions)



R = C_4H_9, $C_{12}H_{25}$

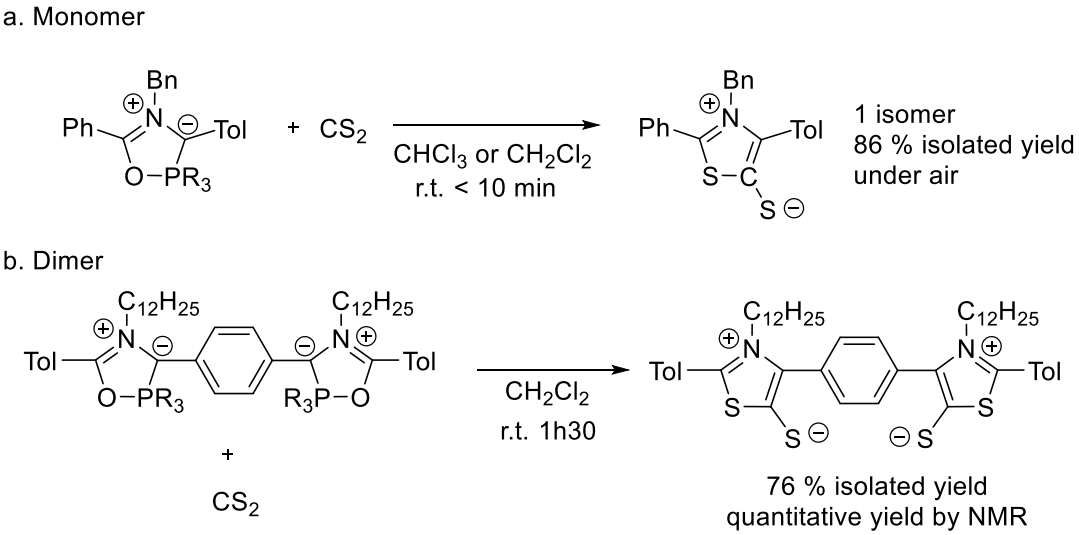
Figure 6.1 Donor-Acceptor Polymers with Charge Separated Ground States

Although poly(Münchnones) and poly(phospha-Münchnones) would be interesting candidates for application in electronic devices, their water sensitivity makes their practical use more challenging. Alternatively, other 1,3-dipoles have been found to be air stable and could lead to stable poly(1,3-dipoles). Huisgen described in 1967 the synthesis of 1,3-thiazolium-5-thiolates (sulfur analogs to Münchnones) from the cycloaddition of carbon disulfide to Münchnone (Scheme 6.1).[5] However, subsequent reports of this reaction showed that the yield is often strongly dependent on the substituents, and mixtures of regioisomers were obtained for unsymmetrical Münchnones.[6] This is undesirable for the post-polymerization cycloaddition on poly(Münchnones) as it would lead to defects in the polymer backbone.



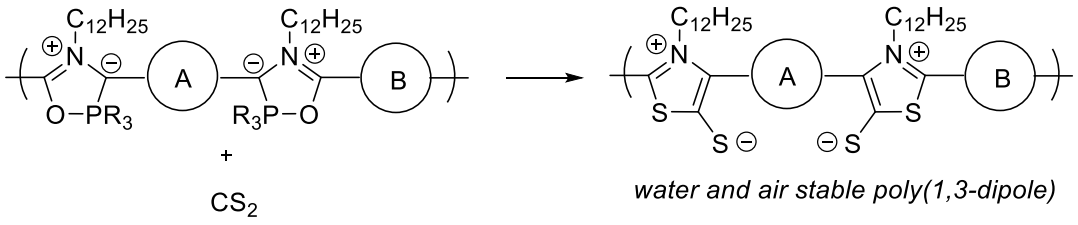
Scheme 6.1 Synthesis of 1,3-thiazolium-5-thiolates from Münchnones

A way to address this issue would be to use more reactive and selective phospha-Münchnones. These have been shown to have a stronger electronic bias across the dipole, and therefore often lead to more regioselective cycloadditions with electron poor dipolarophiles.[7] Our preliminary studies have shown that phospha-Münchnones react quantitatively with CS_2 in less than 10 min at room temperature to form 1,3-thiazolium-5-thiolates. The latter was isolated under air as a single regioisomer (Scheme 6.2a). This reaction is also applicable to model dimers (Scheme 6.2b).



Scheme 6.2 Preliminary Results on the Carbon Disulfide Cycloaddition to Phospha-Münchnones

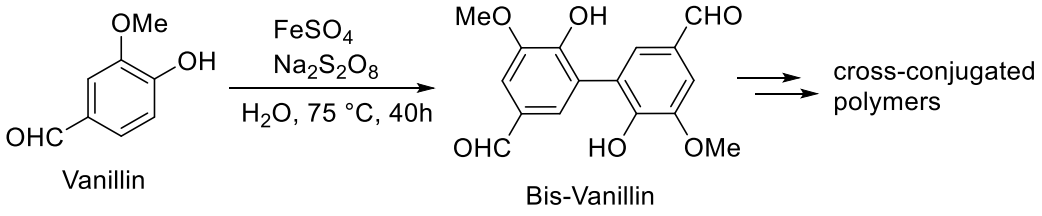
The proposed project would be to use poly(phospha-Münchnones) as intermediates in the synthesis of regioregular poly(1,3-dipoles) (Scheme 6.3). In light of the high yields obtained with the model dimer, poly(1,3-thiazolium-5-thiolates) should be easily accessible as stable poly(1,3-dipoles) and could display interesting electronic properties combined with moisture and air stability.



Scheme 6.3 Proposed Synthesis of Poly(1,3-thiazolium-5-thiolates)

6.2.2 Towards Fully Conjugated Vanillin-Based Polymers

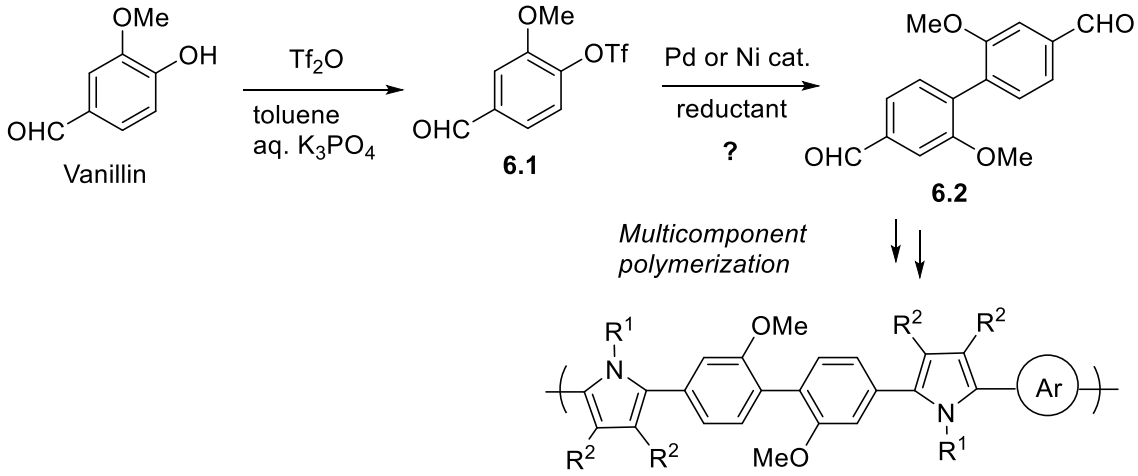
In Chapter 5, a bis-vanillin diimine was employed as a renewable monomer for the synthesis of cross-conjugated polymers. This bis-vanillin was obtained via oxidative dimerization of vanillin, and results in a 3,3'-dialdehyde (Scheme 6.4). One limitation of this reaction is its generation of cross-conjugated polymers, which are less generally useful in the field of organic electronics.[8]



Scheme 6.4 Oxidative Dimerization of Vanillin

The use of vanillin-derived monomers to assemble in fully conjugated polymers could prove more attractive. In order to achieve this, a new reaction must be developed. A

potential two-step strategy towards this is described in Scheme 6.5. The reaction of vanillin with triflic anhydride is expected to generate the aryl triflate **6.1**.[9] The palladium- or nickel-catalyzed reductive homocoupling of aryl triflates has been previously reported, although it can be more challenging with substrates bearing *ortho*-substituents.[10,11] In order to avoid the direct reduction of the aryl triflate to phenol, screening of the catalyst (palladium, nickel, and ligands) and the electron source (cathode or zinc powder) will be necessary. The use of this transformation with **6.1** would provide a two-step method to convert vanillin into the 4,4'-dialdehyde **6.2**. This dialdehyde **6.2** could serve as a precursor to bis-imines and be used in the multicomponent polymerizations presented in this thesis.



Scheme 6.5 Proposed Pathway for the Synthesis of Vanillin-Based Monomers for Conjugated Polymers

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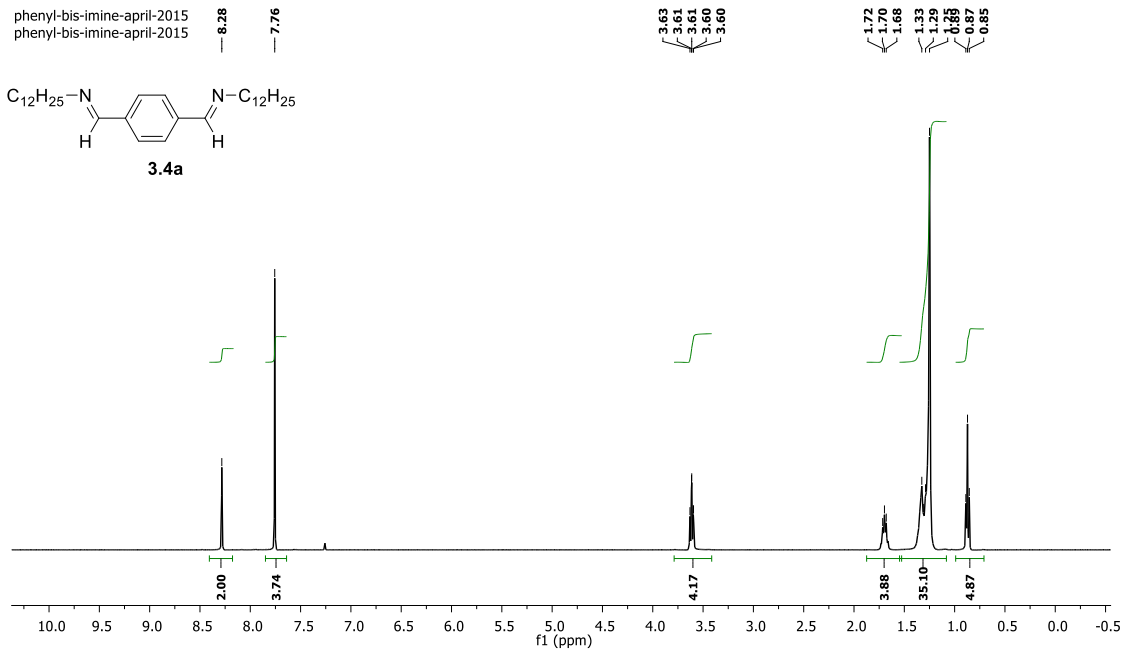
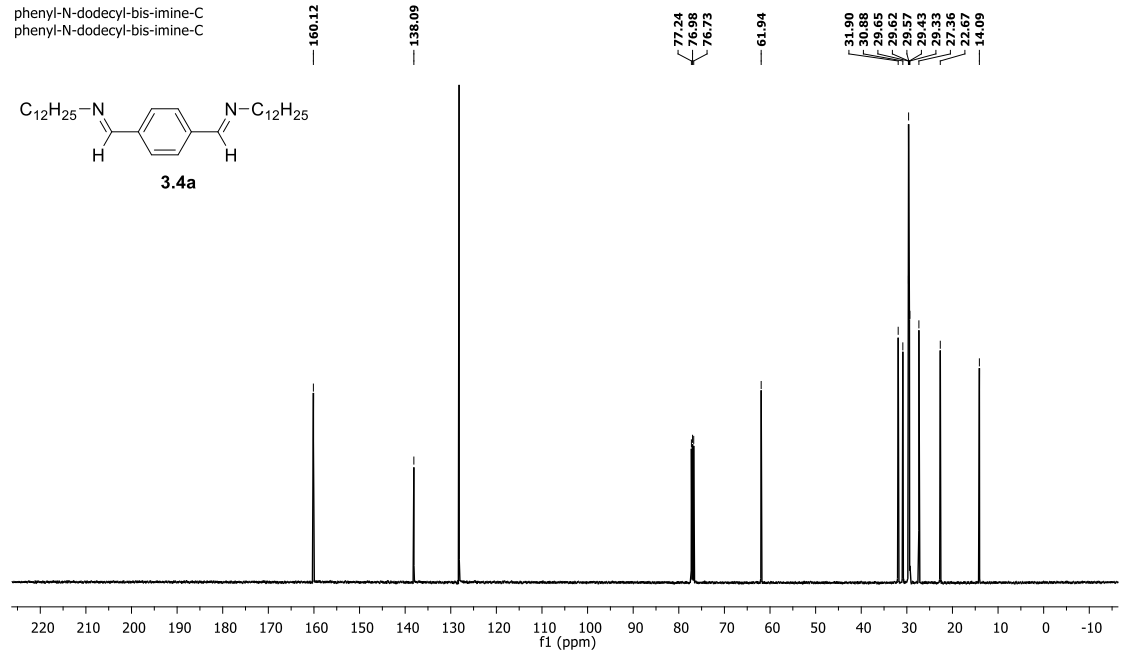
Appendix A: Spectroscopic Data for Chapter 3

A.1 ^{1}H and ^{13}C NMR of **3.4a**





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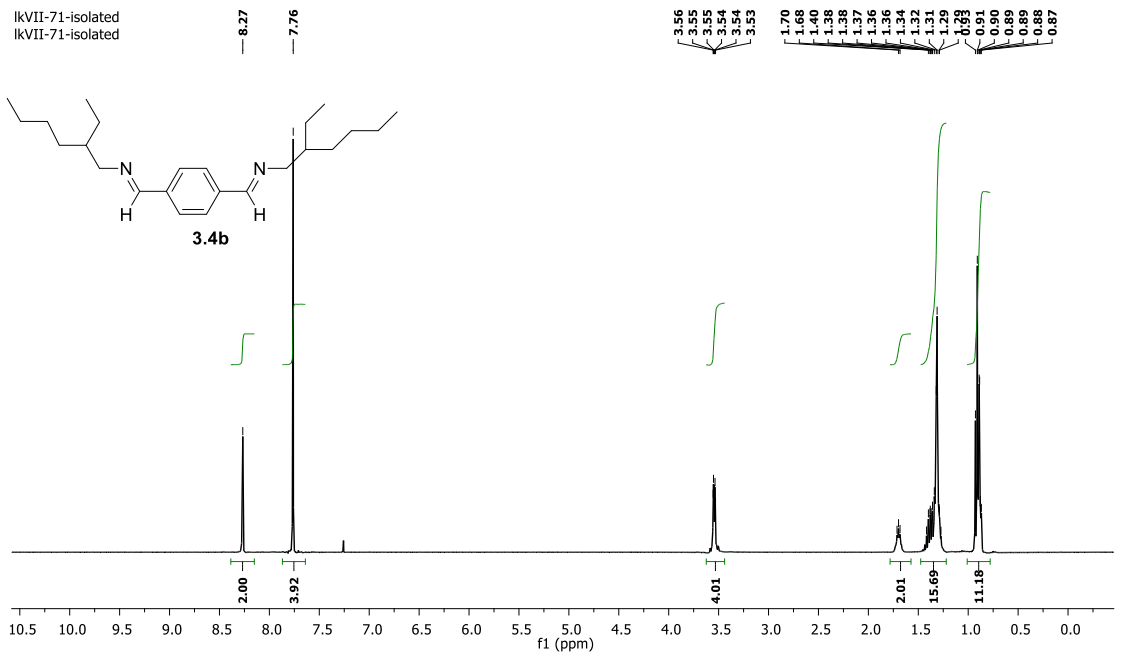
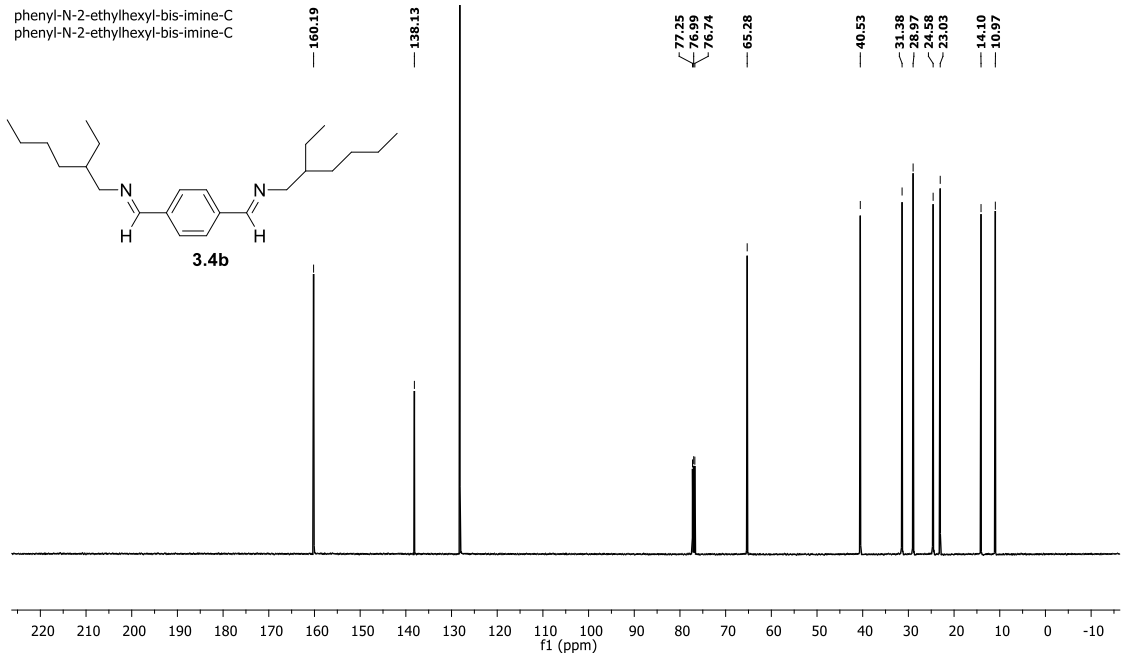
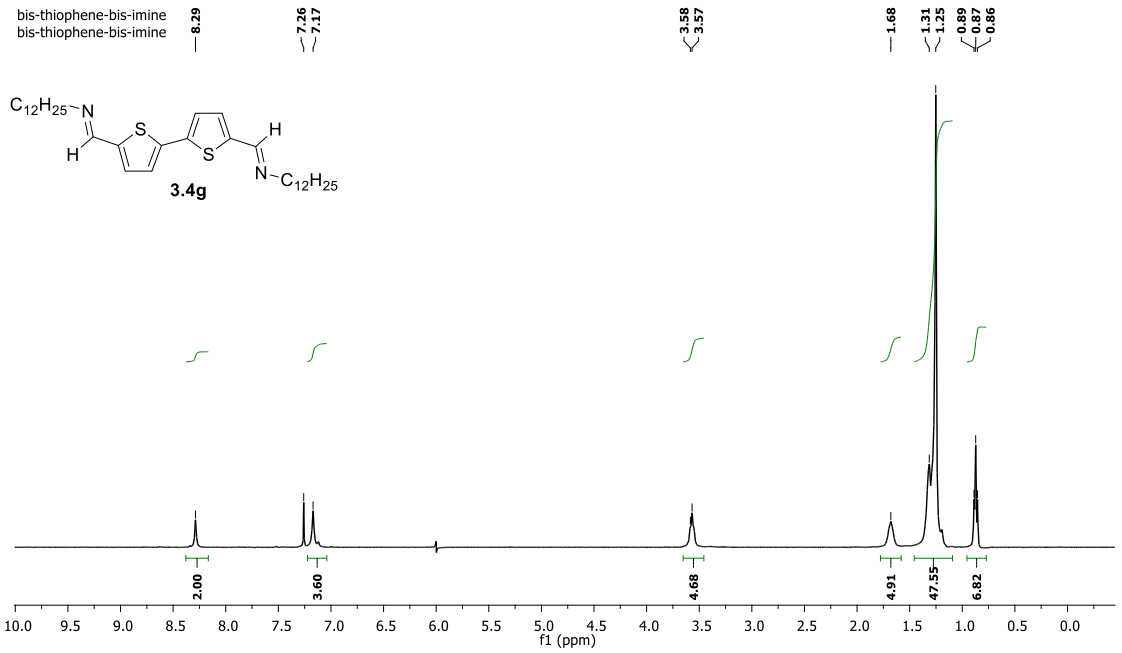
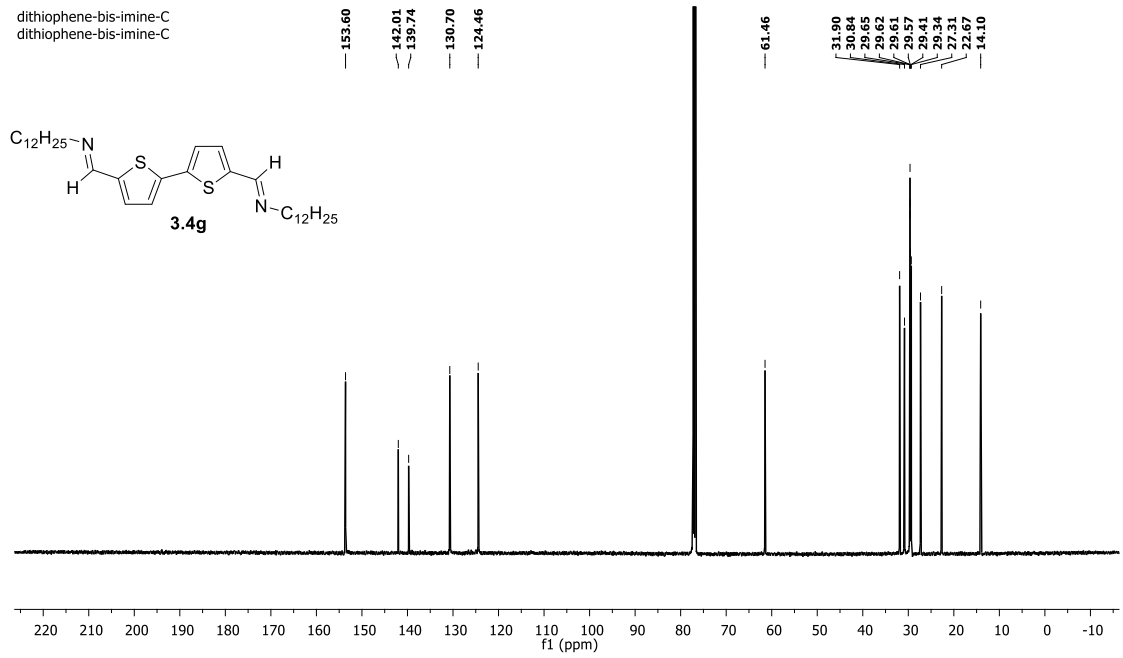


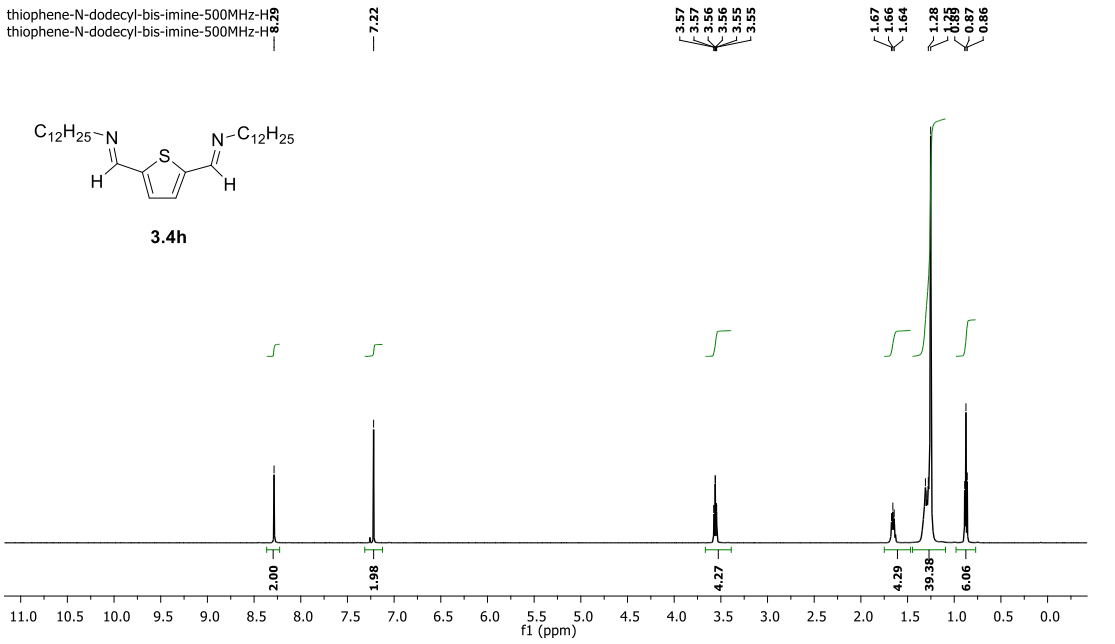


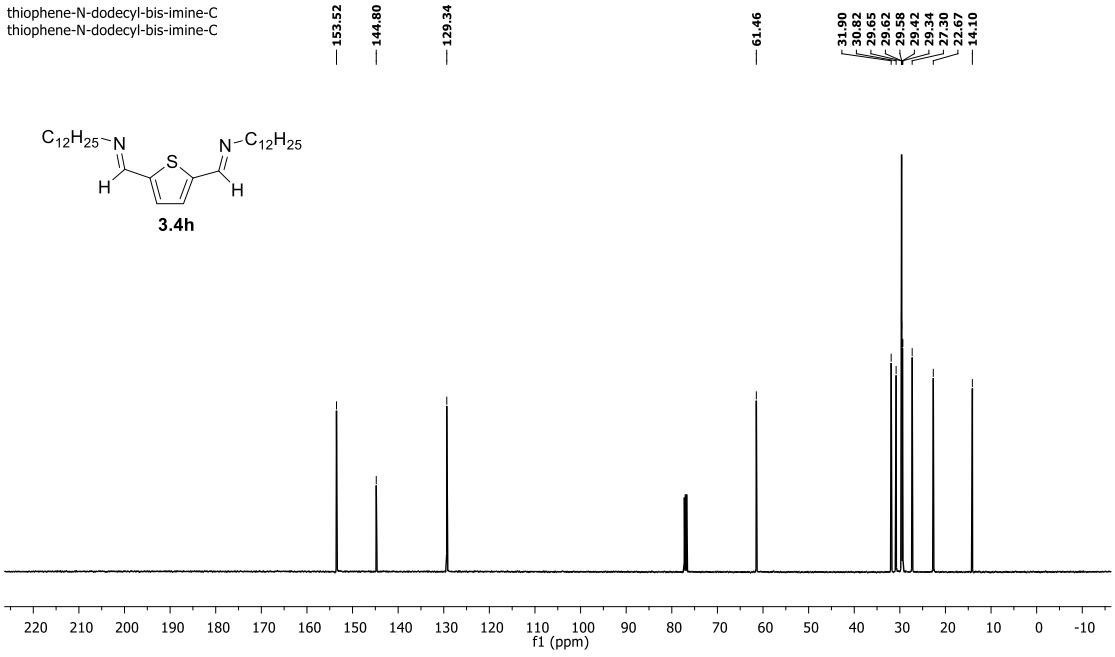
A.3 ^{1}H and ^{13}C NMR of **3.4g**



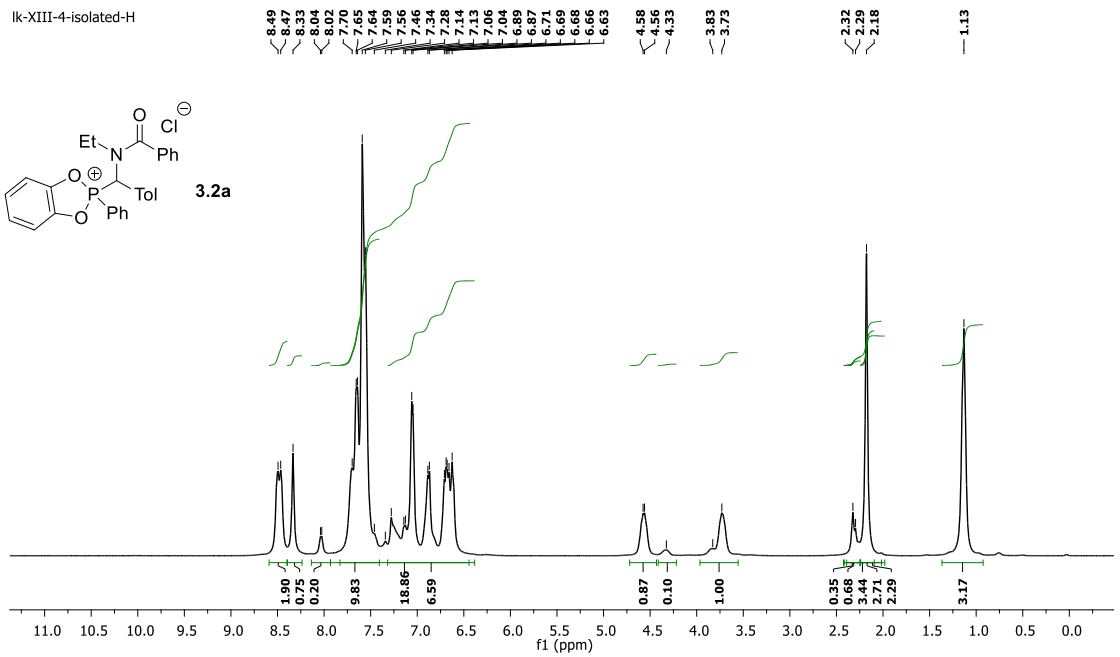


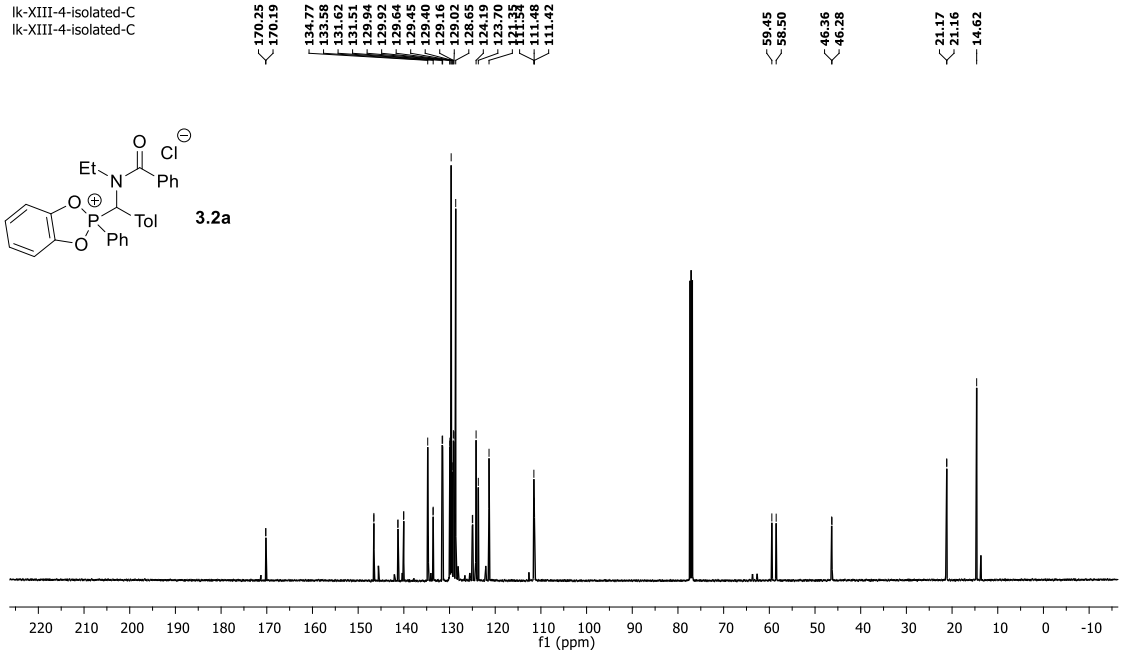
A.4 ^{1}H and ^{13}C NMR of **3.4h**

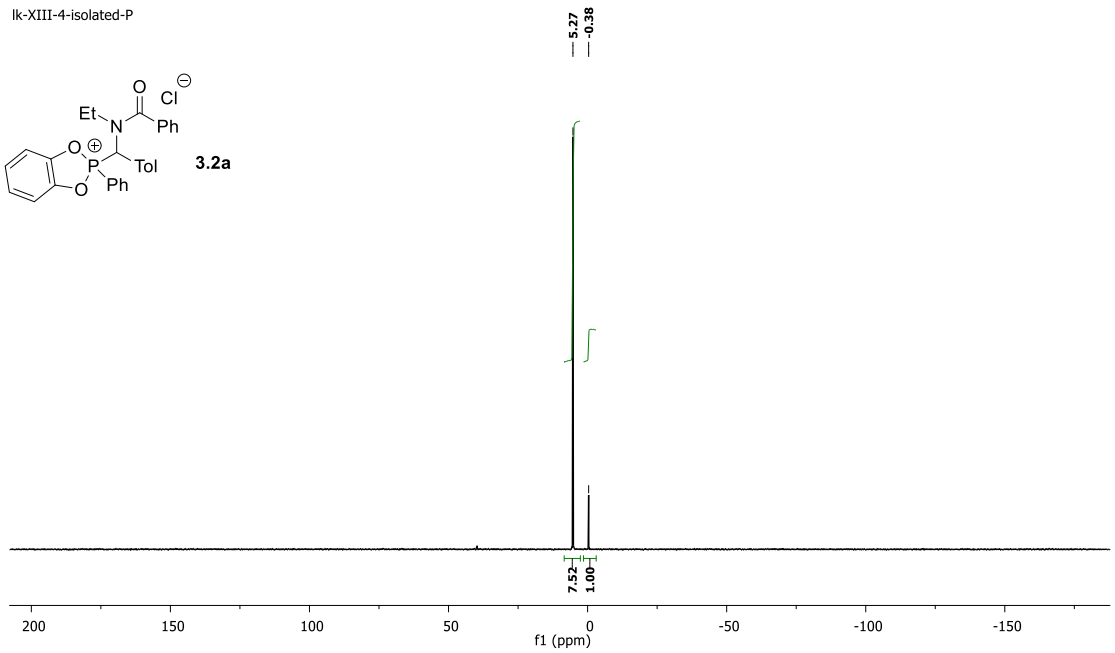




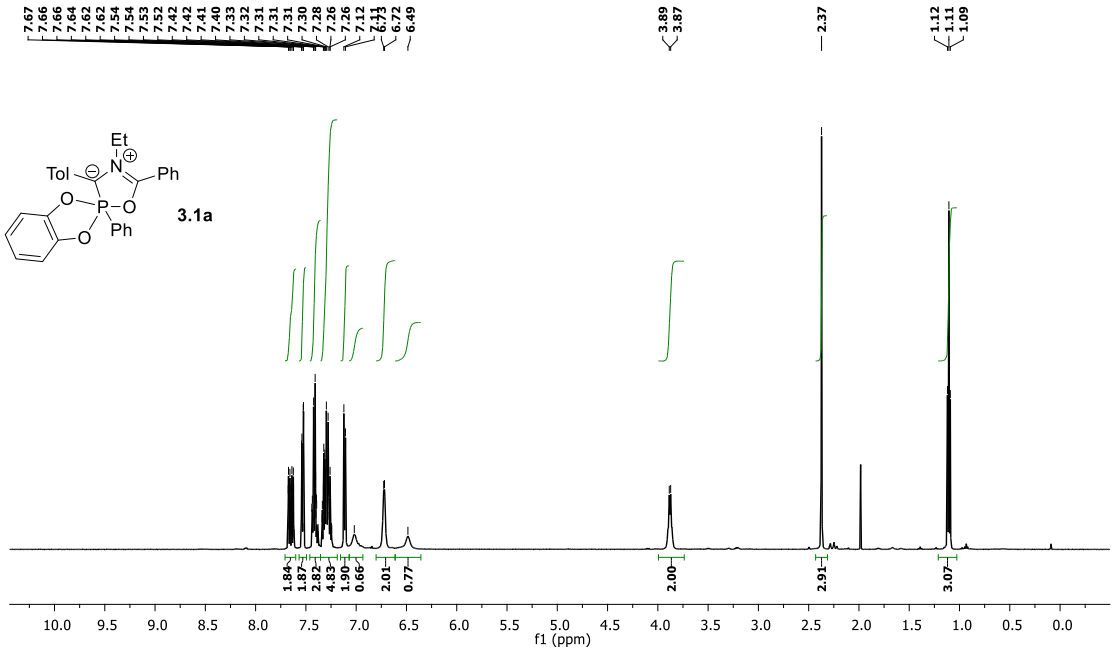
A.5 ^{1}H, ^{13}C and ^{31}P NMR of **3.2a**





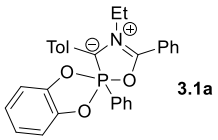


A.6 ^{1}H, ^{13}C and ^{31}P NMR of **3.1a**

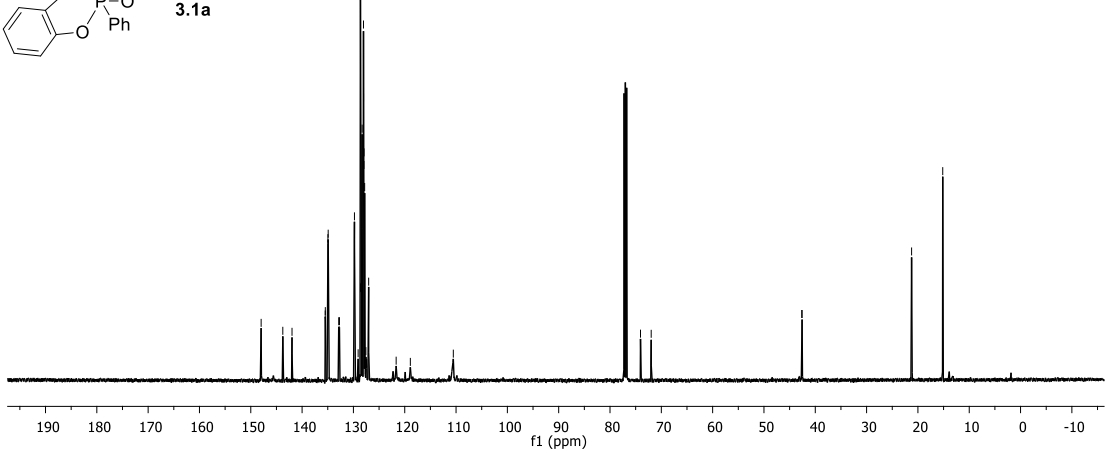


lk-XII-67-isolated-C-2
lk-XII-67-isolated-C

147.98
143.76
141.96
134.97
134.92
129.80
128.64
128.31
128.04
128.03
127.95
127.94
74.06
71.97
42.63
42.57
21.23
15.16

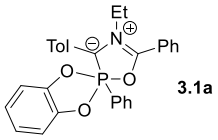


3.1a

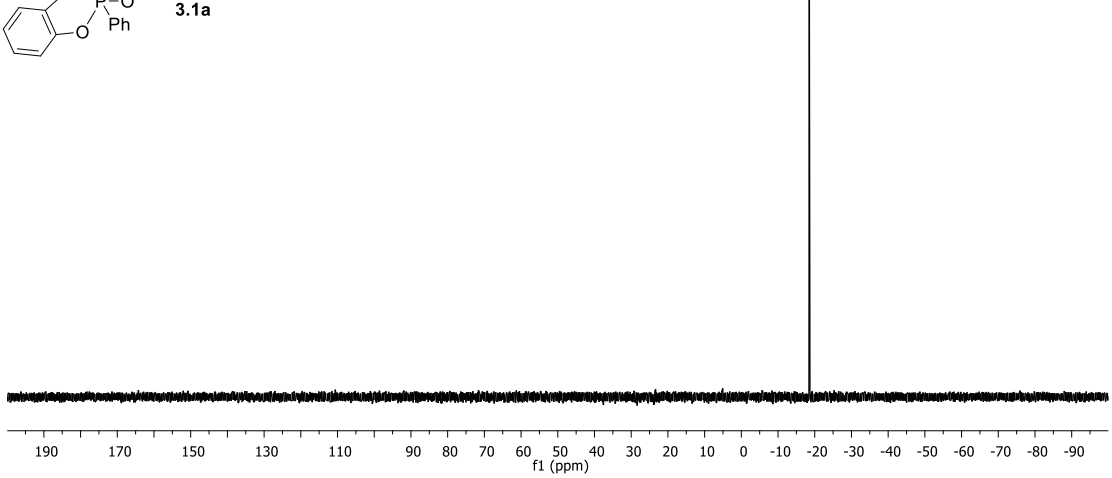


lk-XII-67-isolated-P
lk-XII-67-isolated-P

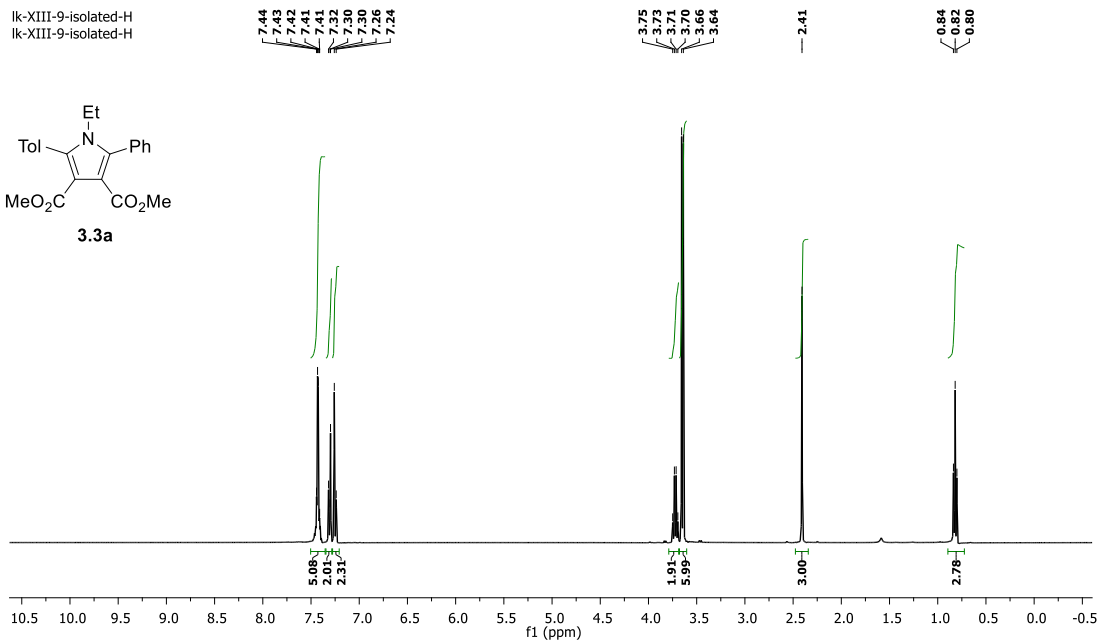
-18.52

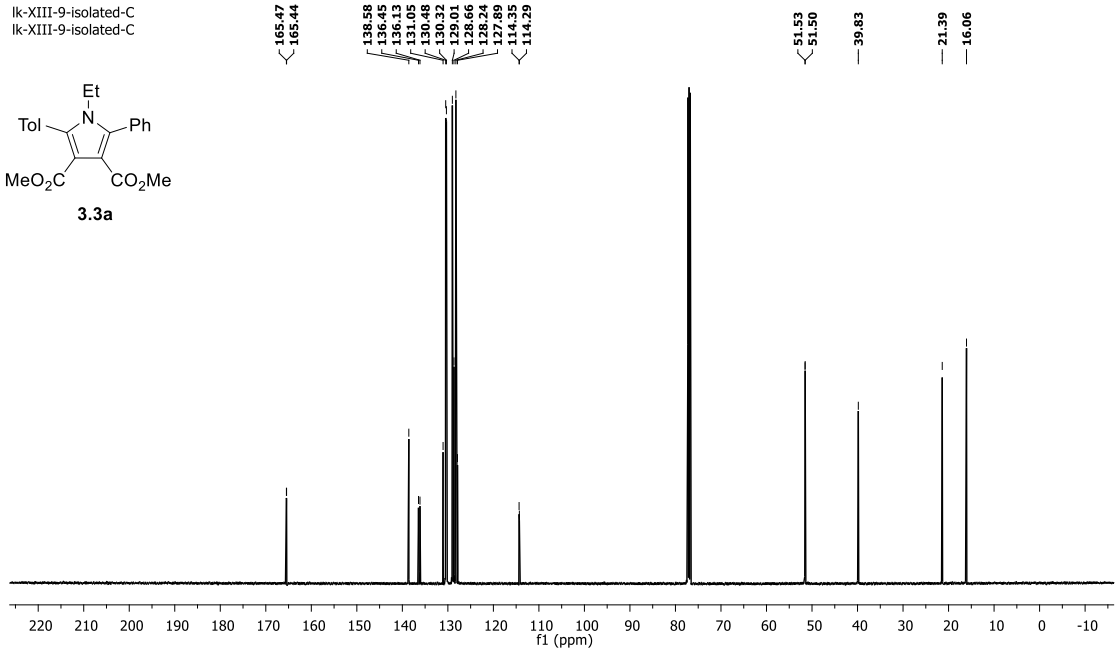


3.1a

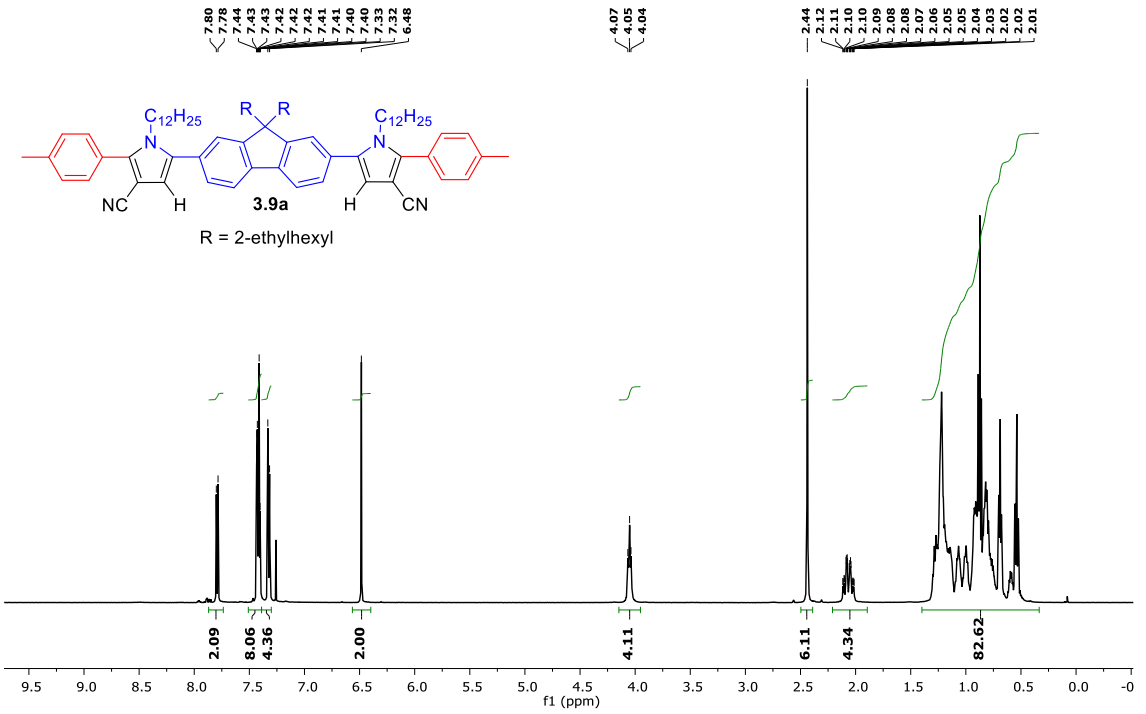


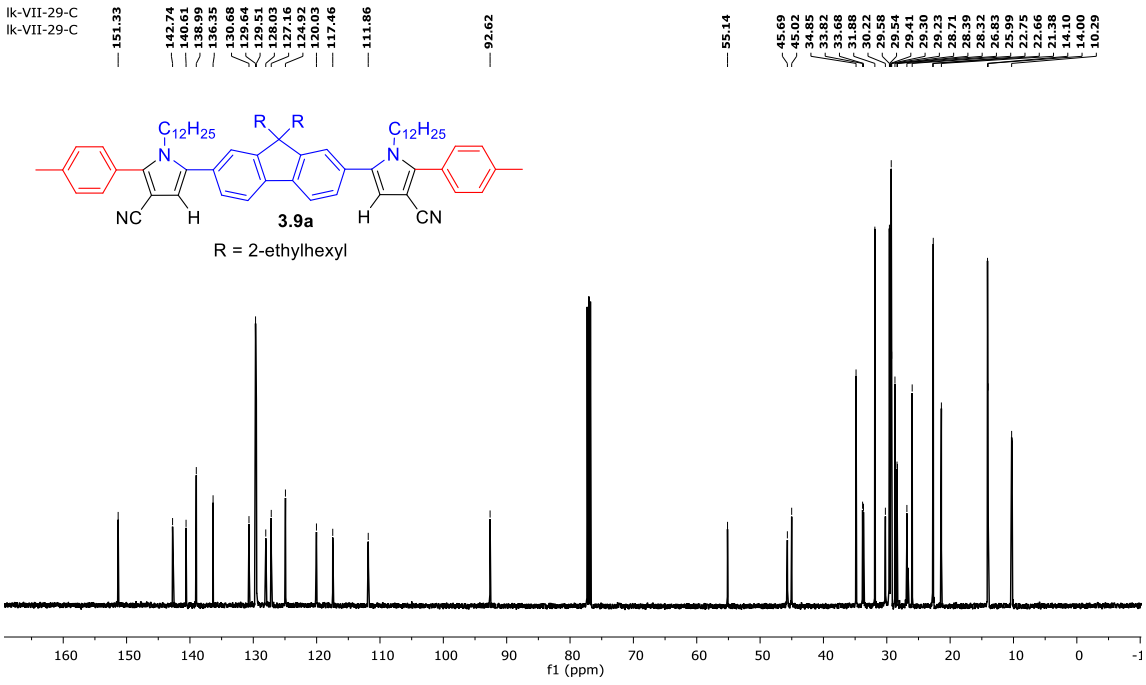
A.7 ^{1}H and ^{13}C NMR of **3.3a**

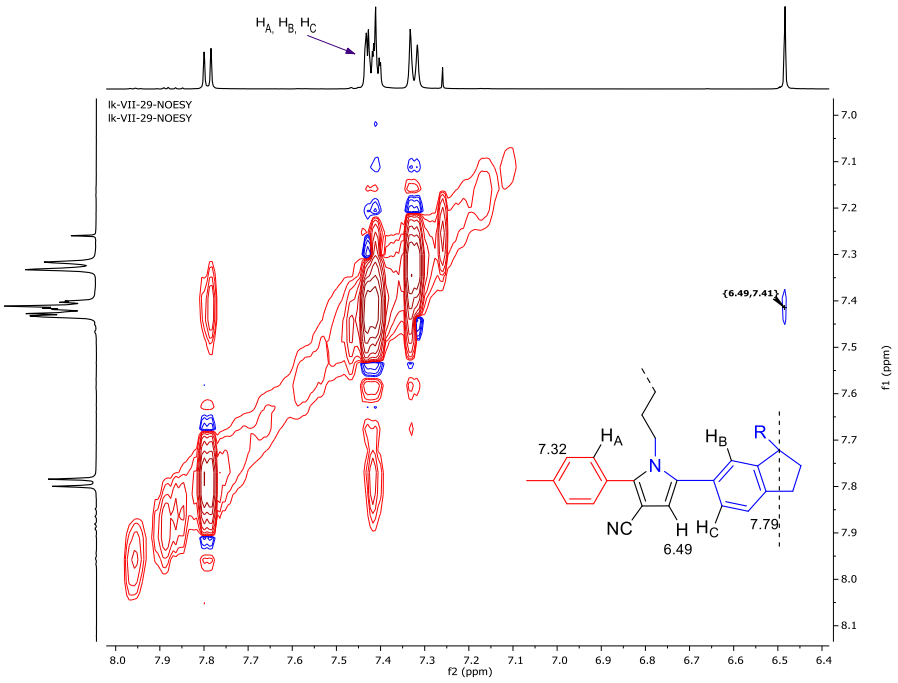




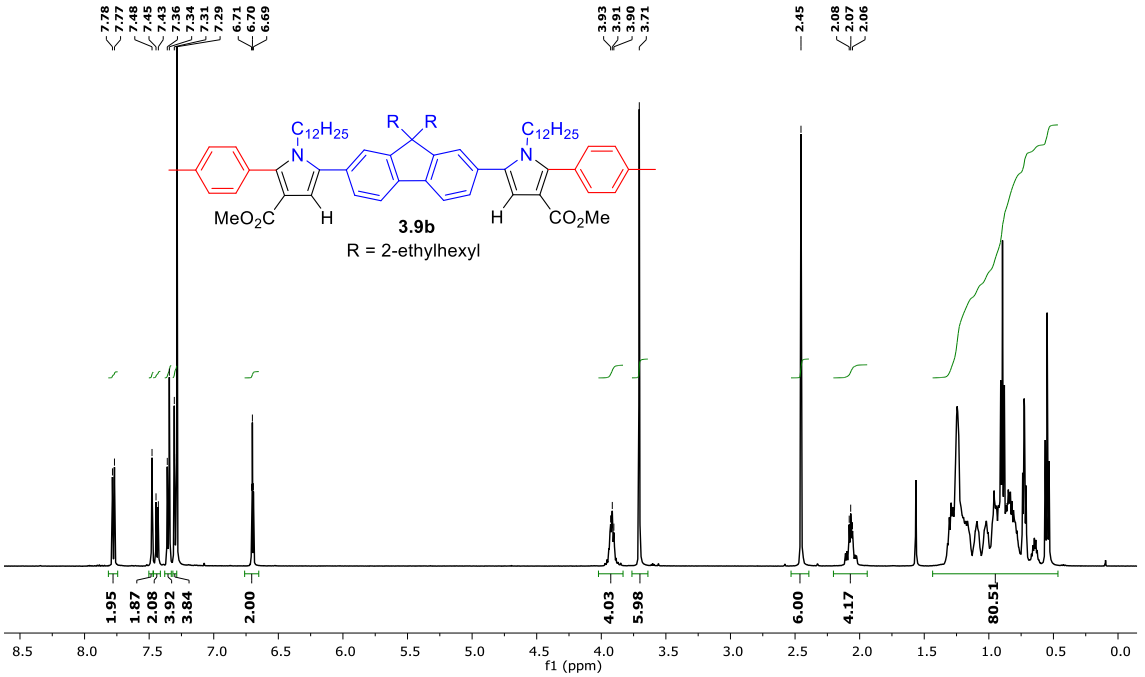
A.8 ^{1}H, ^{13}C and partial NOESY NMR of **3.9a**

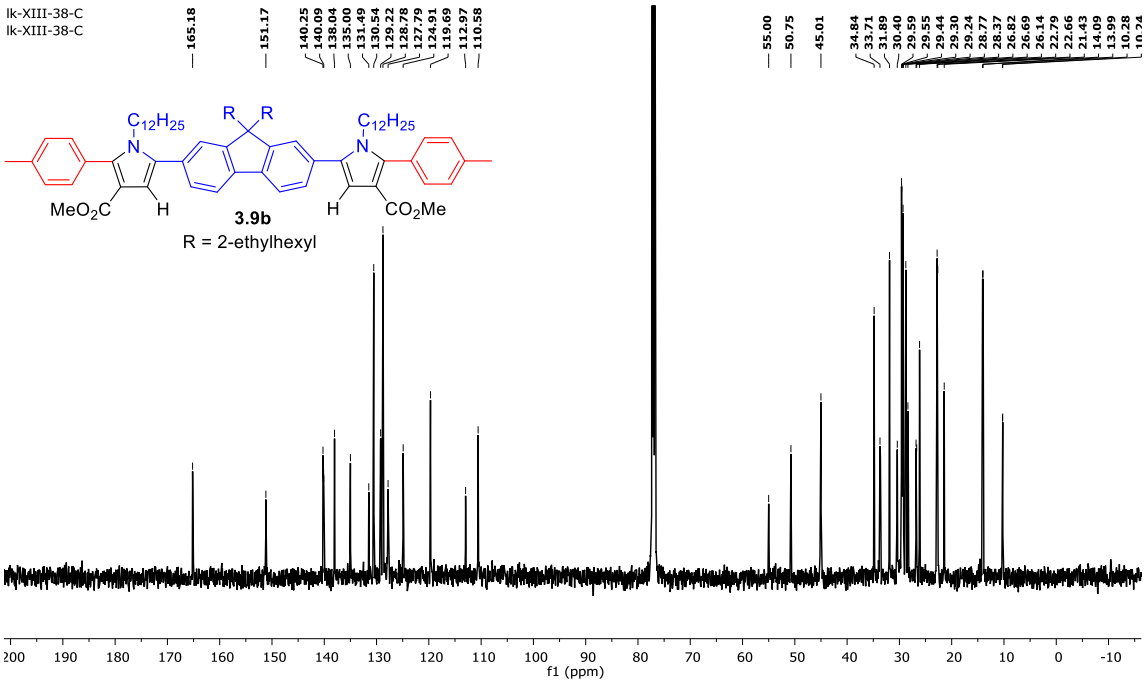


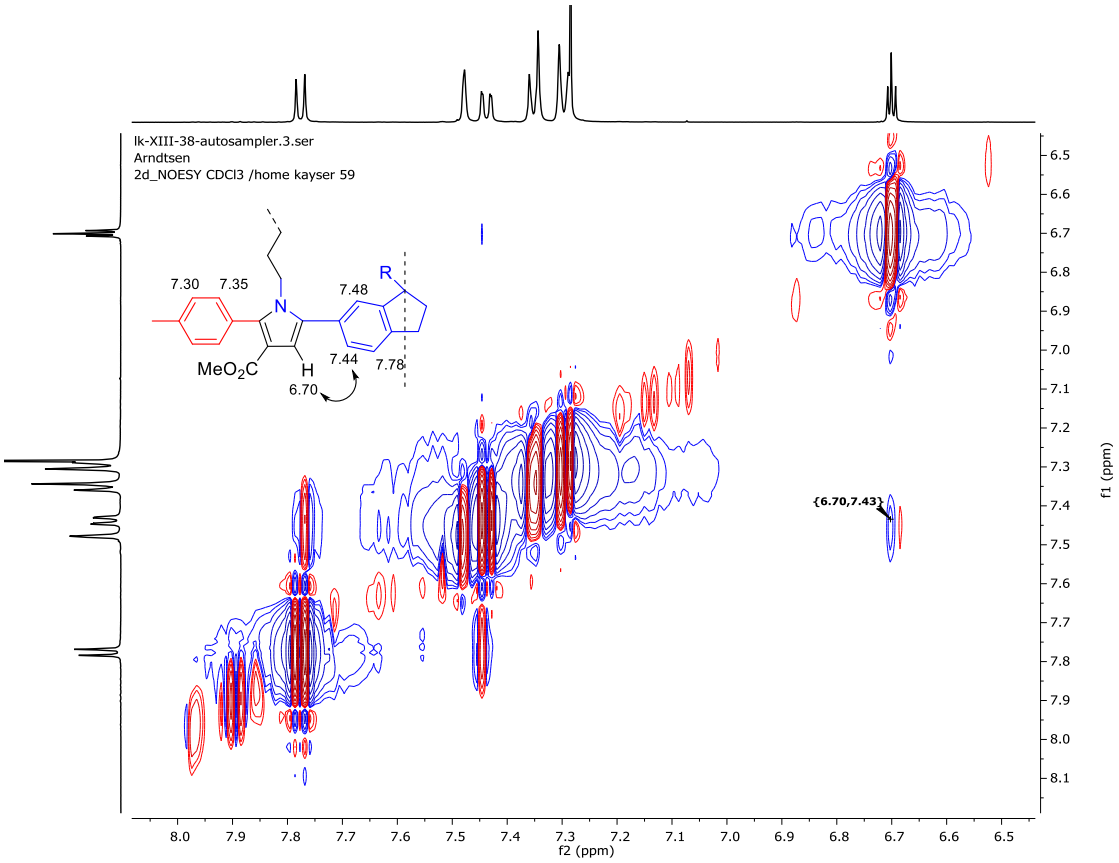



H_A, H_B, H_C
lk-VII-29-NOESY
lk-VII-29-NOESY
{6.49,7.41}
7.32
H_A
H_B
R
N
NC
H
H_C
6.49
7.79
f1 (ppm)
f2 (ppm)

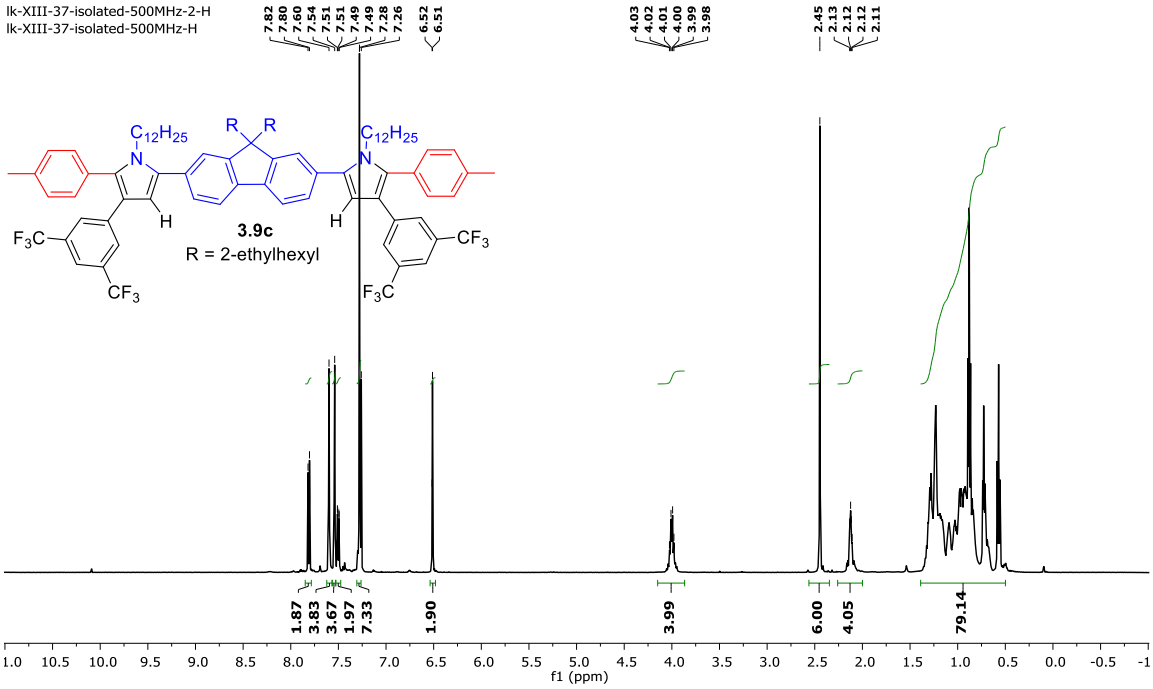
A.9 ^{1}H, ^{13}C and partial NOESY NMR of **3.9b**

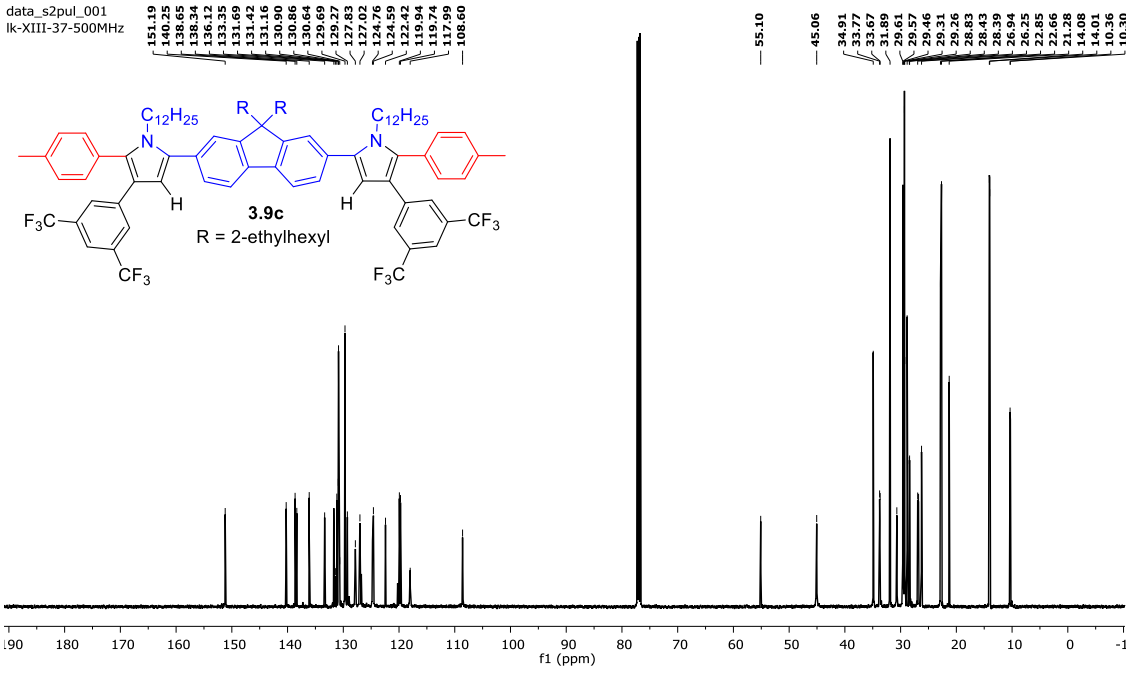




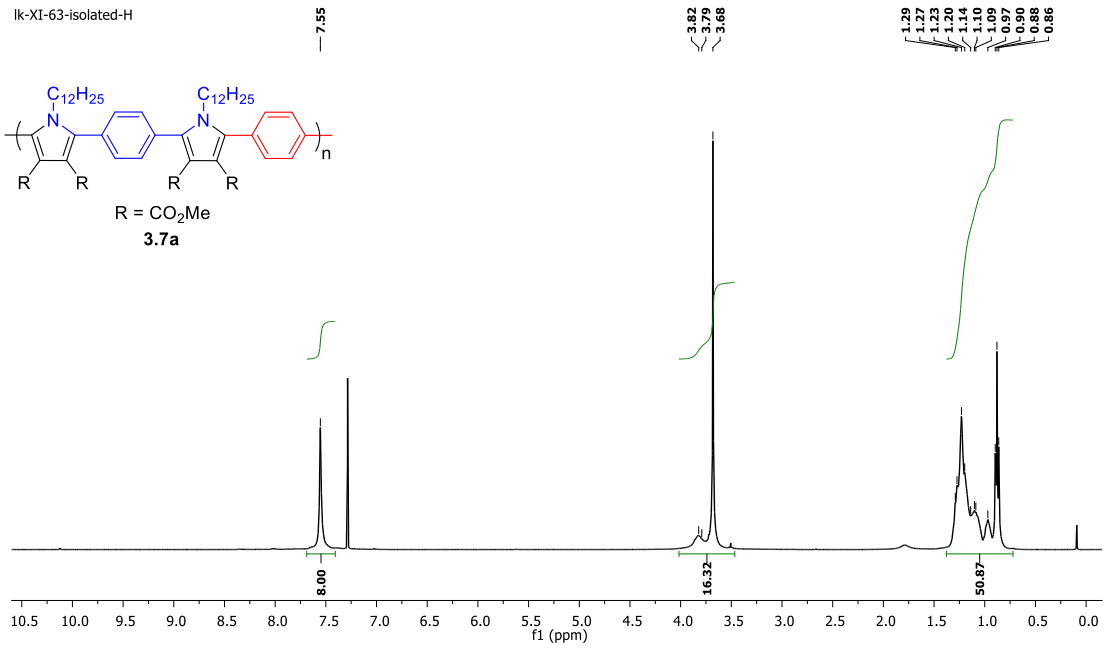

lk-XIII-38-autosampler.3.ser
Arndtsen
2d_NOESY CDCl3 /home kayser 59
7.30
7.35
7.48
R
N
MeO2C
H
6.70
7.44
7.78
{6.70,7.43}
f2 (ppm)
f1 (ppm)

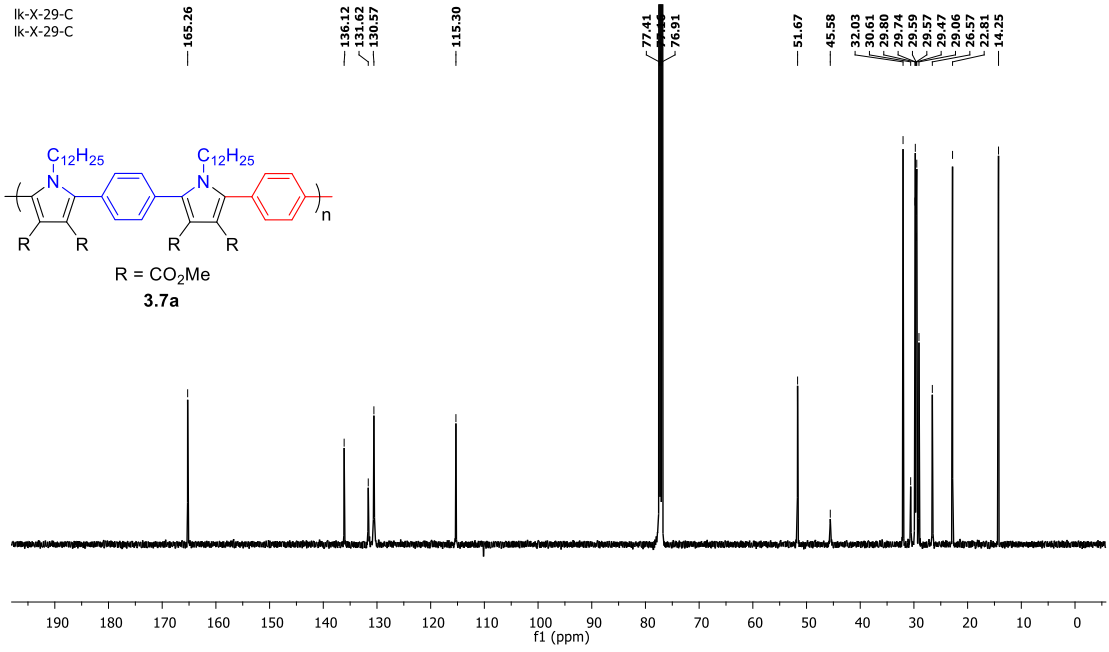
A.10 ^{1}H and ^{13}C NMR of **3.9c**



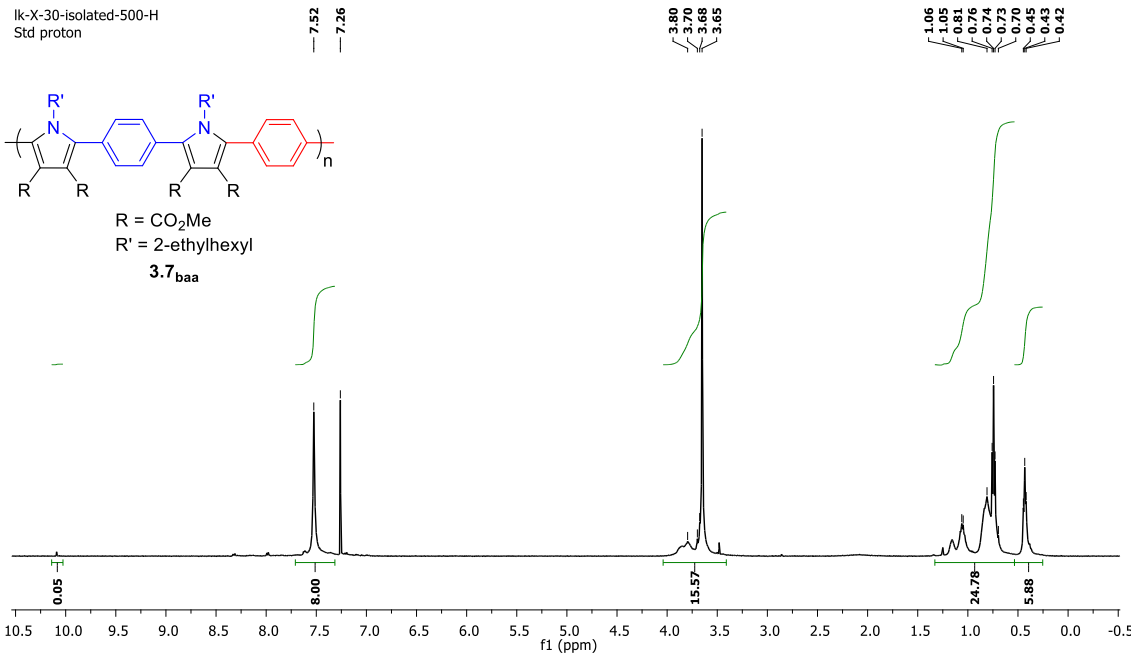


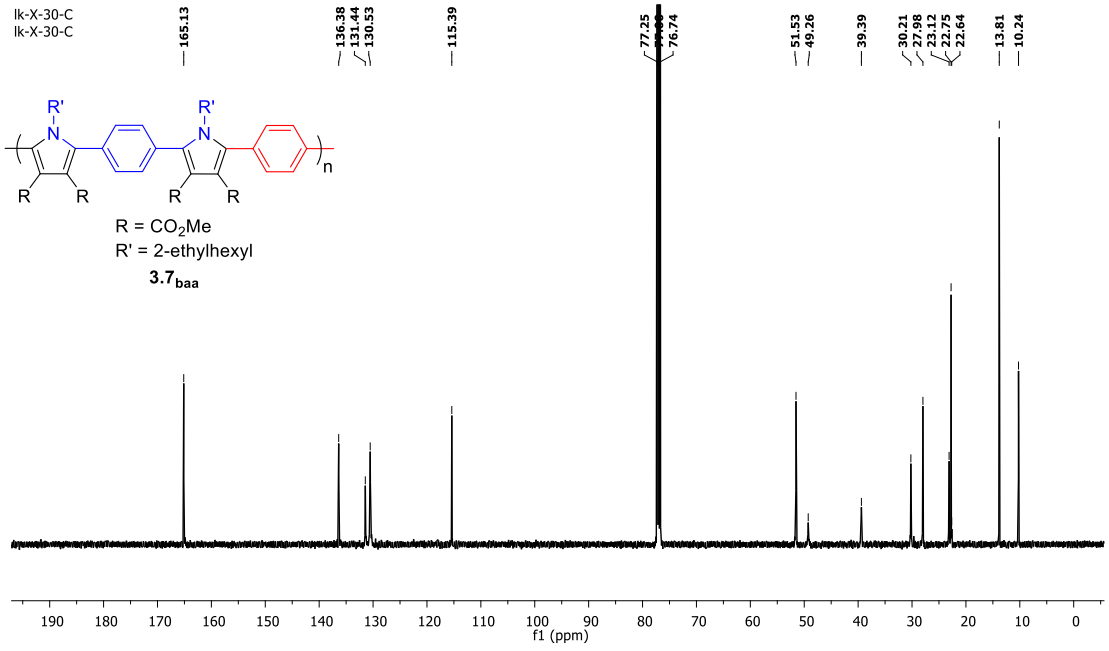
A.11 ^{1}H and ^{13}C NMR of **3.7a**



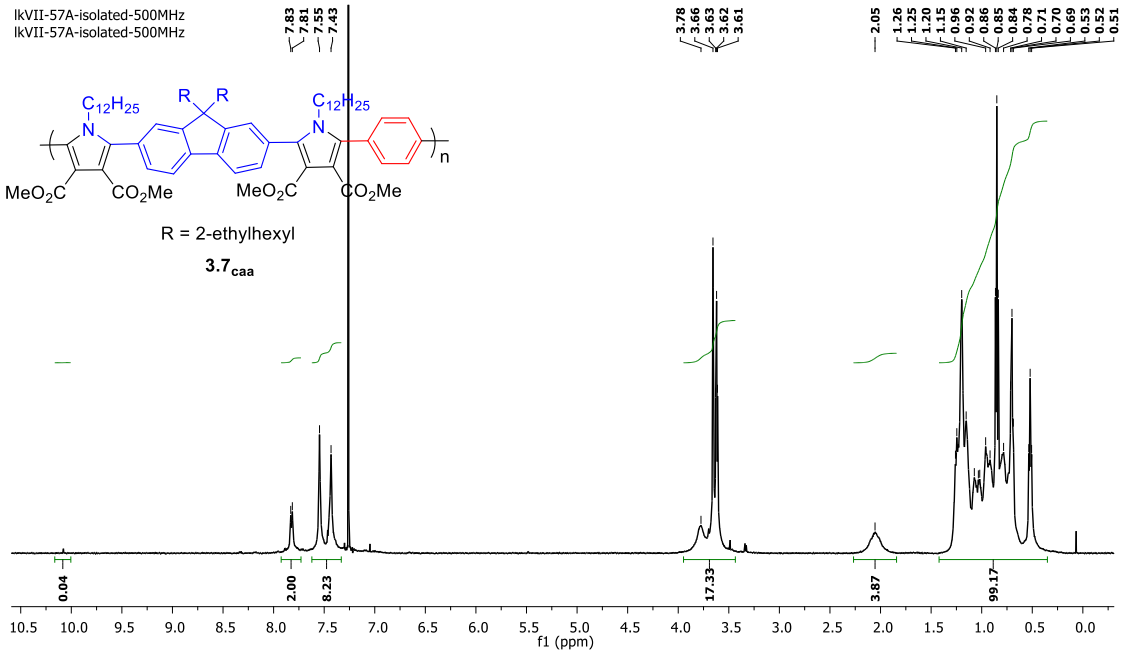


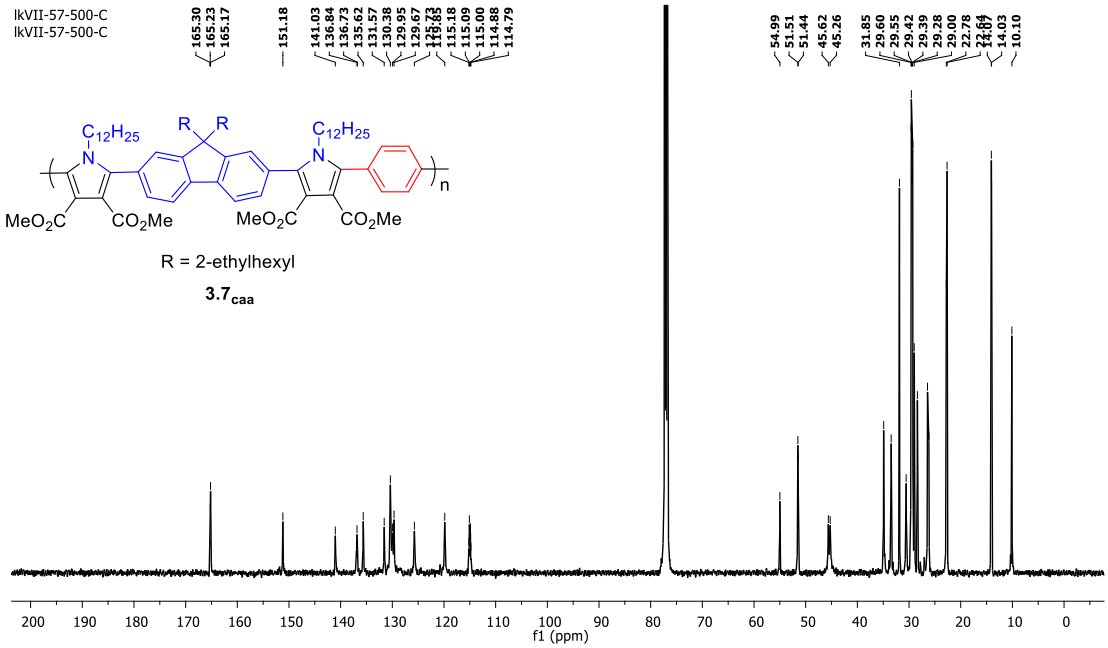
A.12 ^{1}H and ^{13}C NMR of **3.7baa**



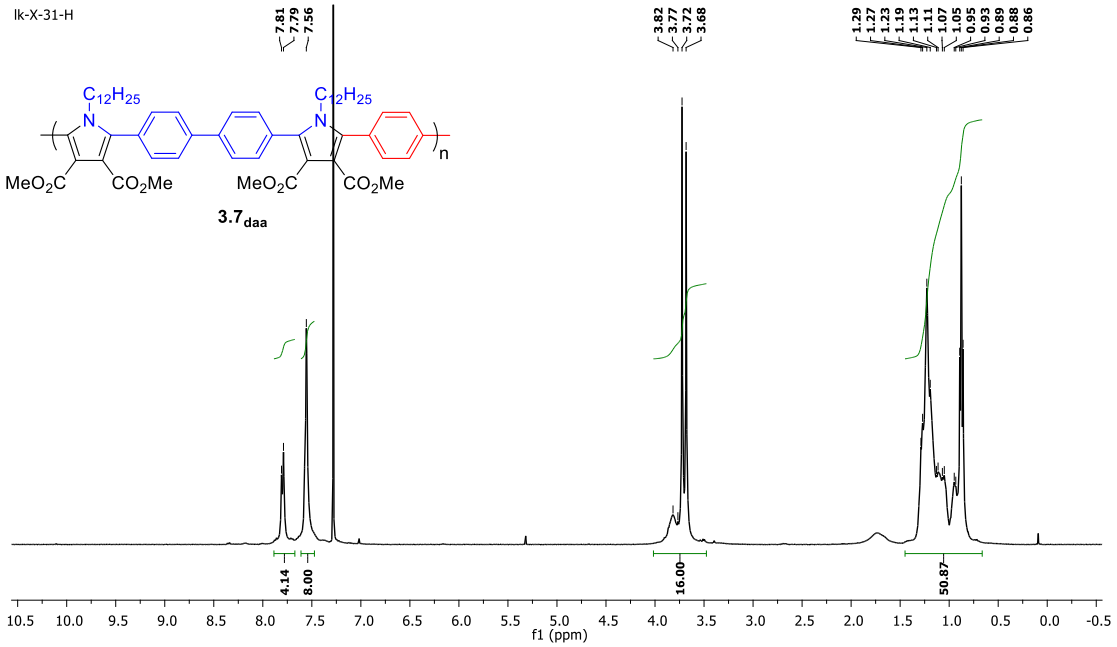


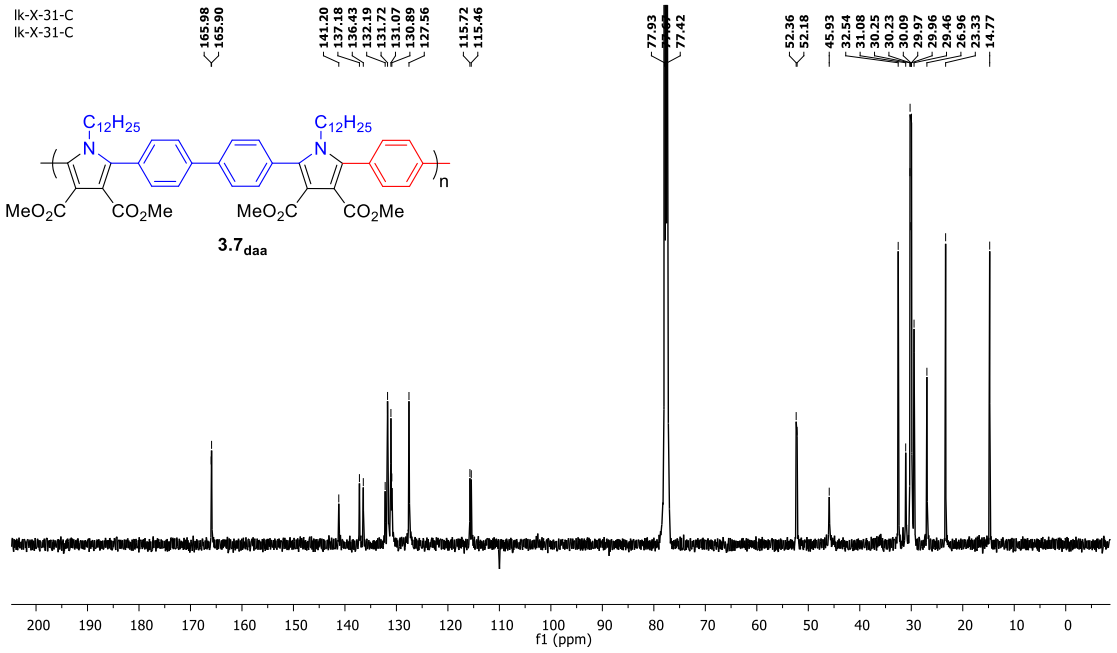
A.13 ^{1}H and ^{13}C NMR of **3.7caa**



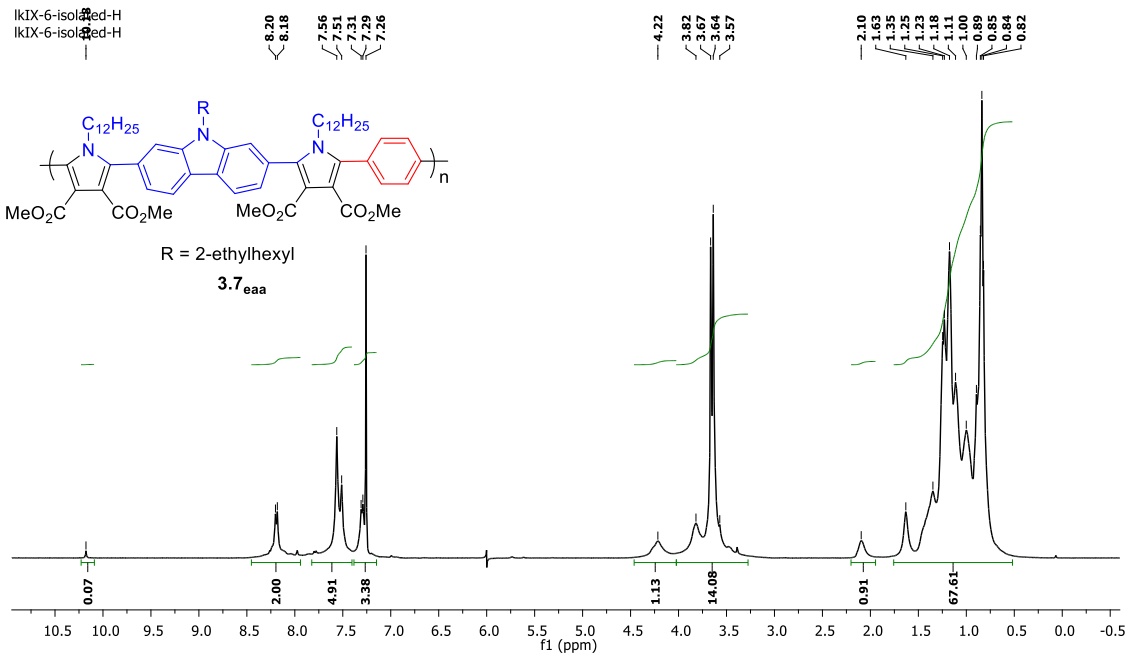


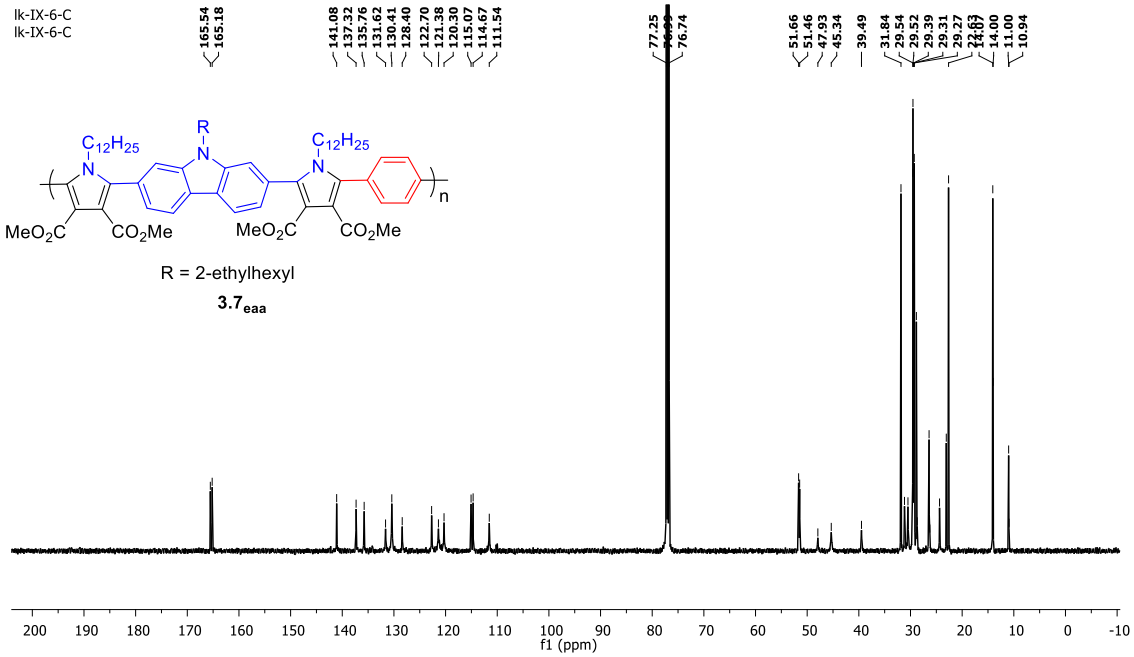
A.14 ^{1}H and ^{13}C NMR of **3.7daa**



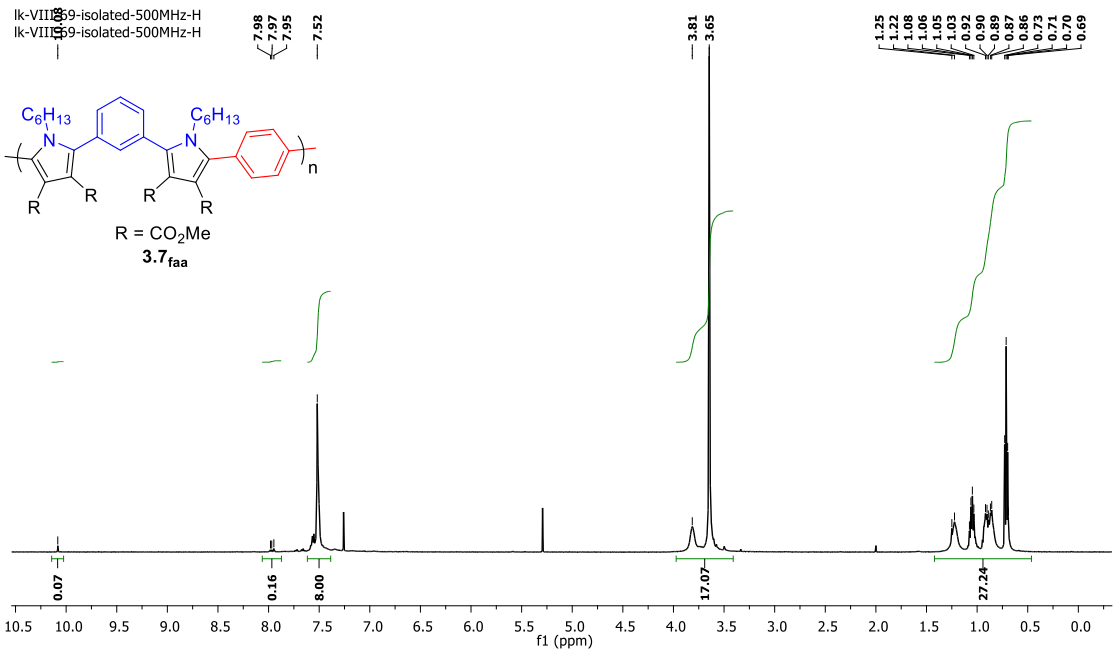


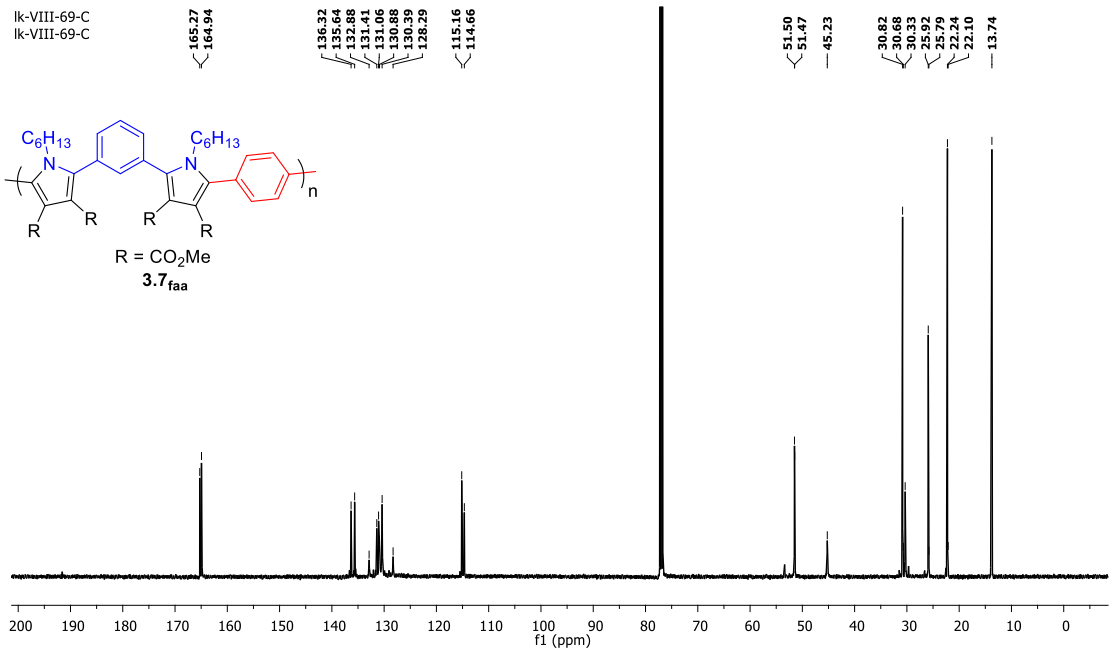
A.15 ^{1}H and ^{13}C NMR of **3.7eaa**



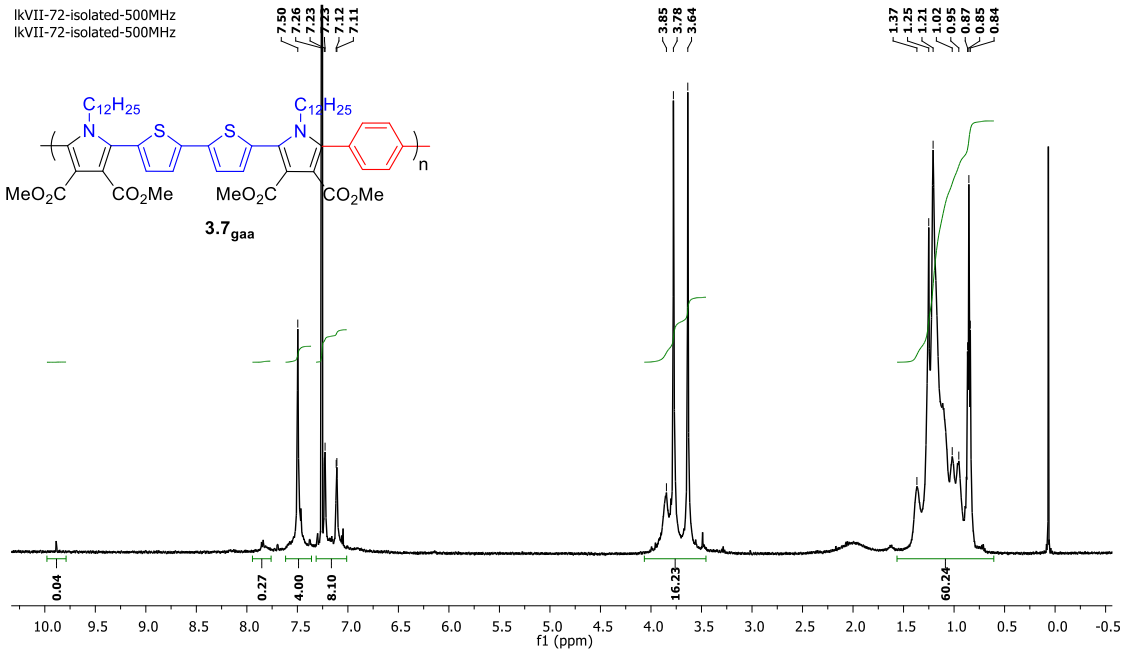


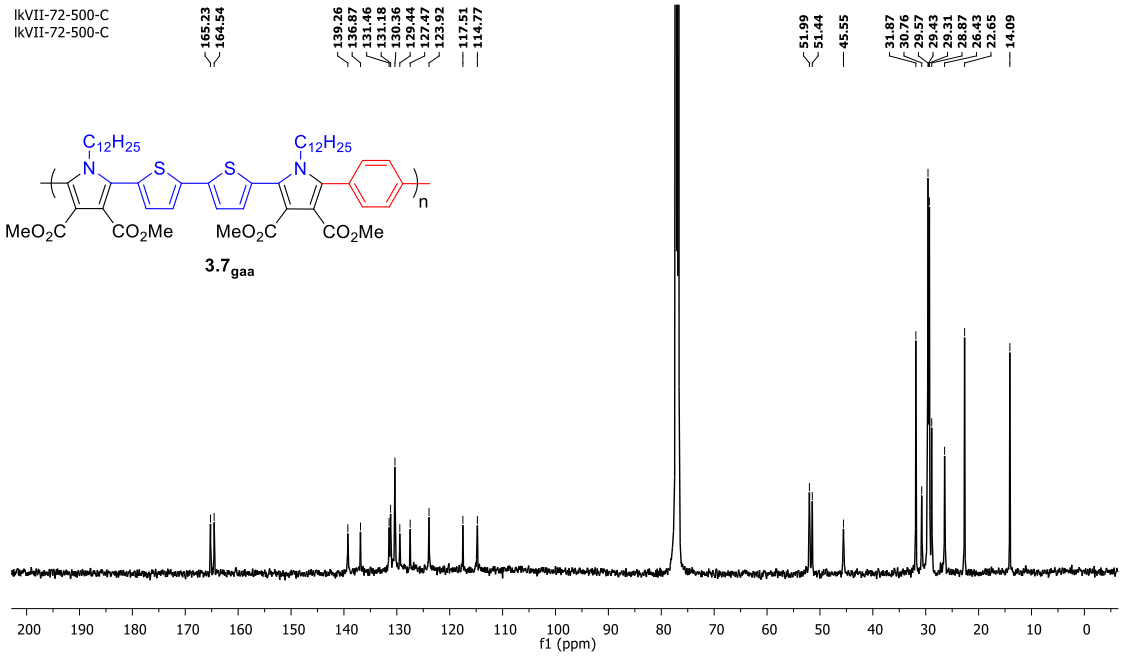
A.16 ^{1}H and ^{13}C NMR of **3.7faa**



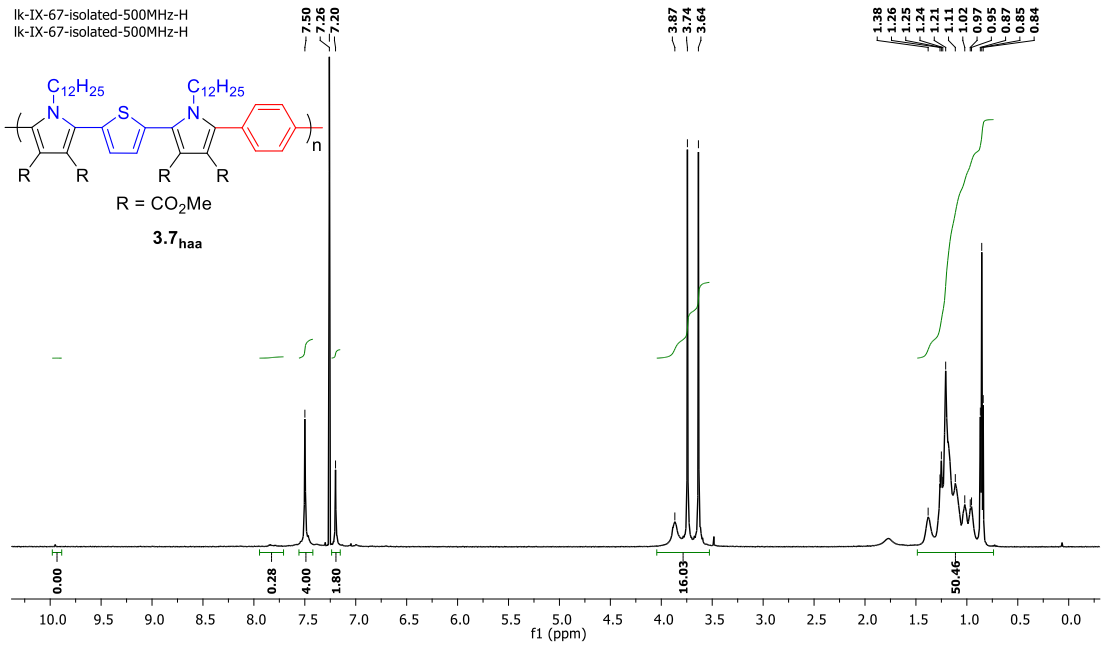


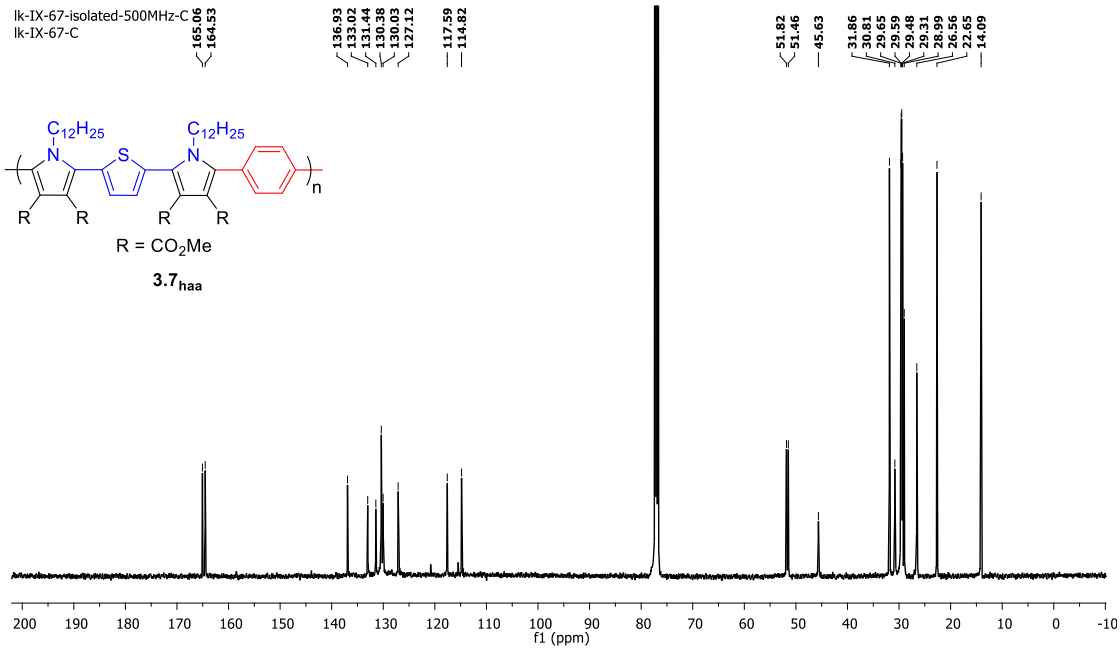
A.17 ^{1}H and ^{13}C NMR of **3.7gaa**



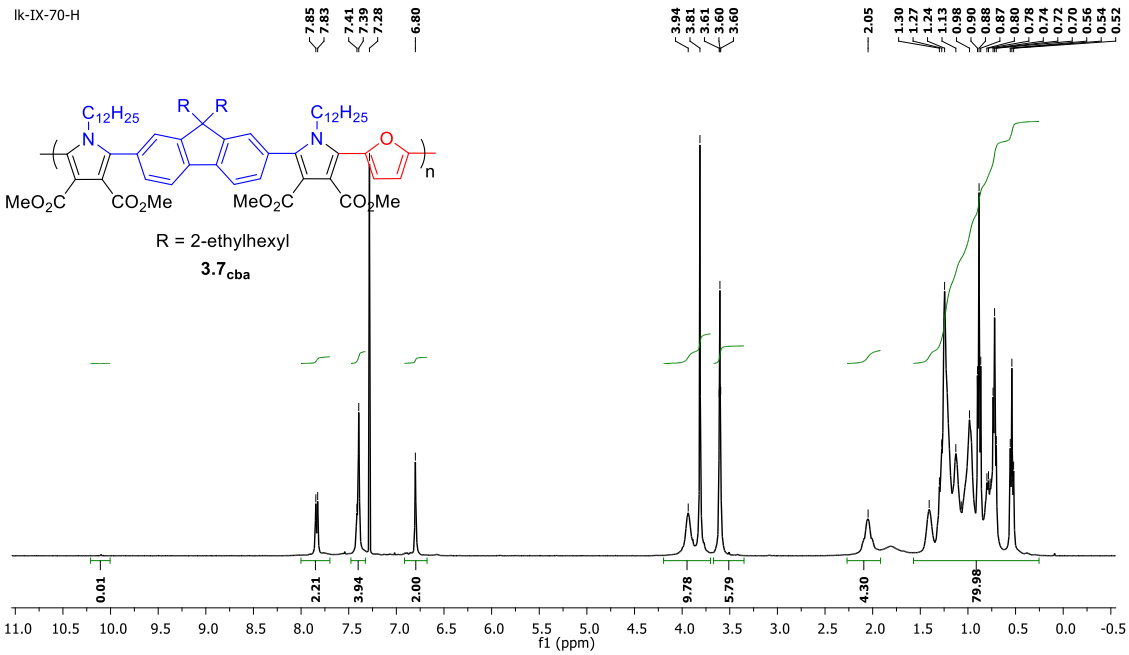


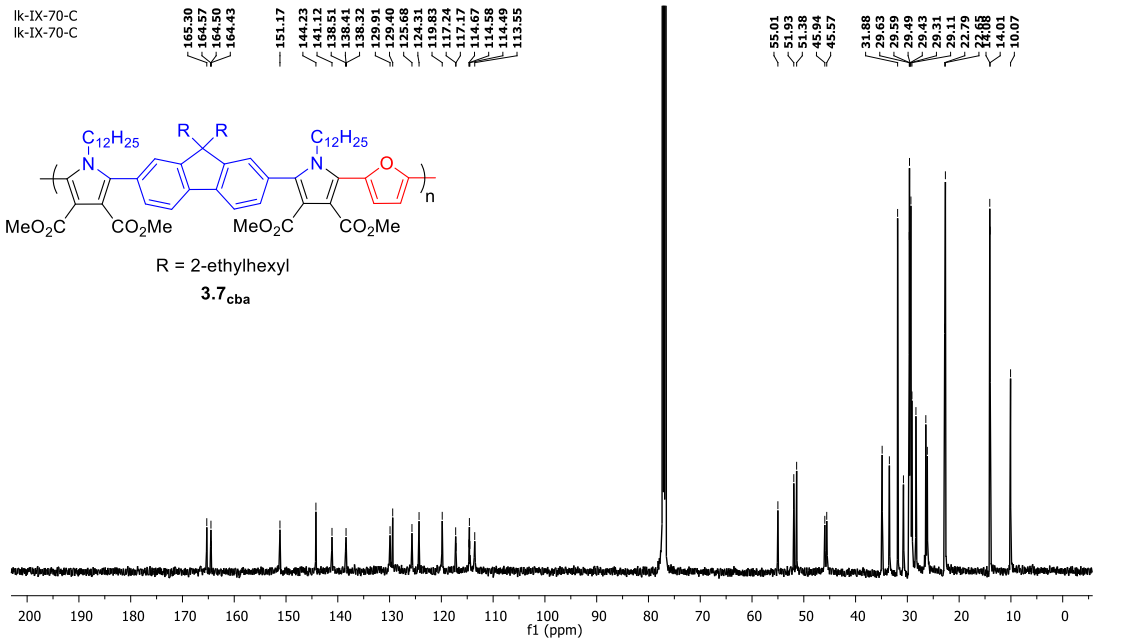
A.18 ^{1}H and ^{13}C NMR of **3.7haa**



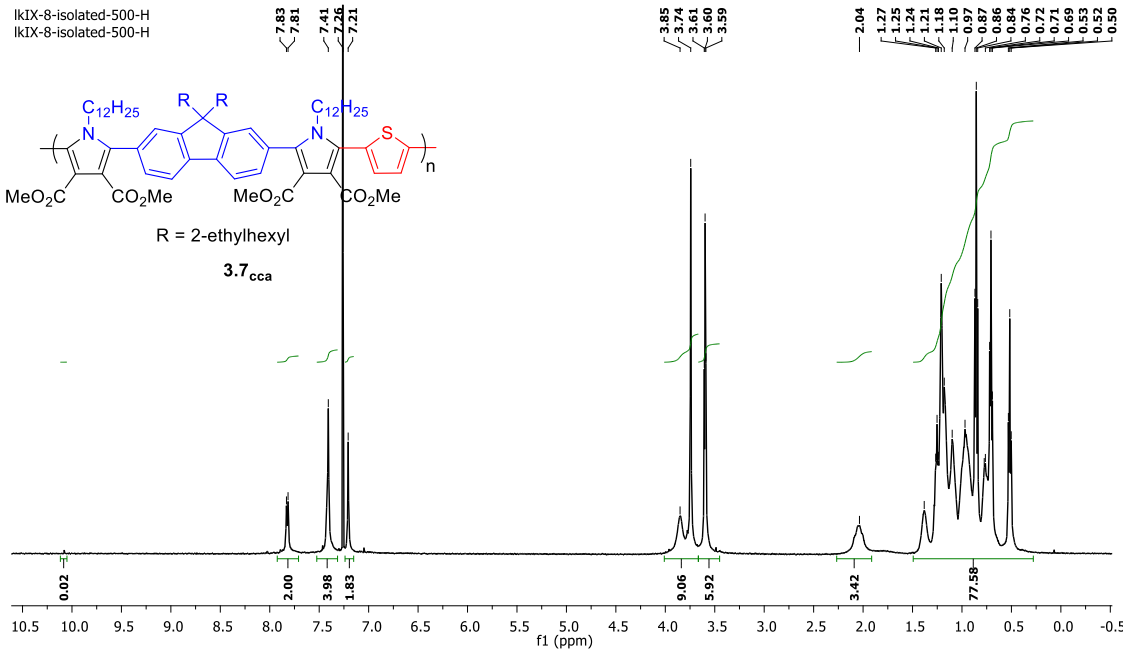


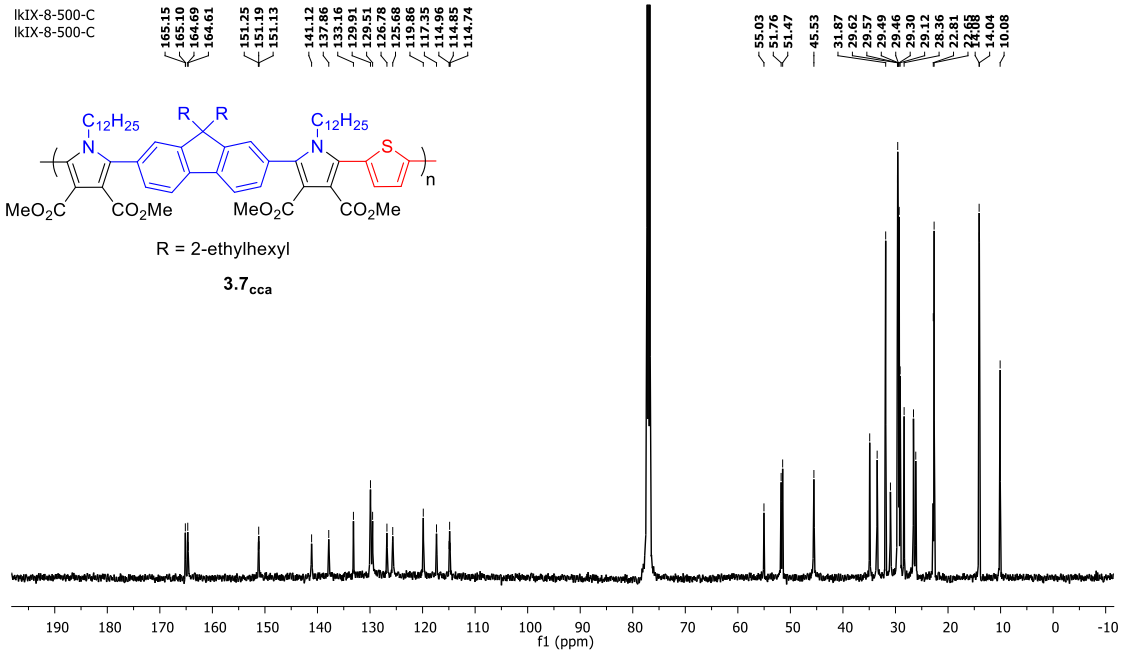
A.19 ^{1}H and ^{13}C NMR of **3.7cba**



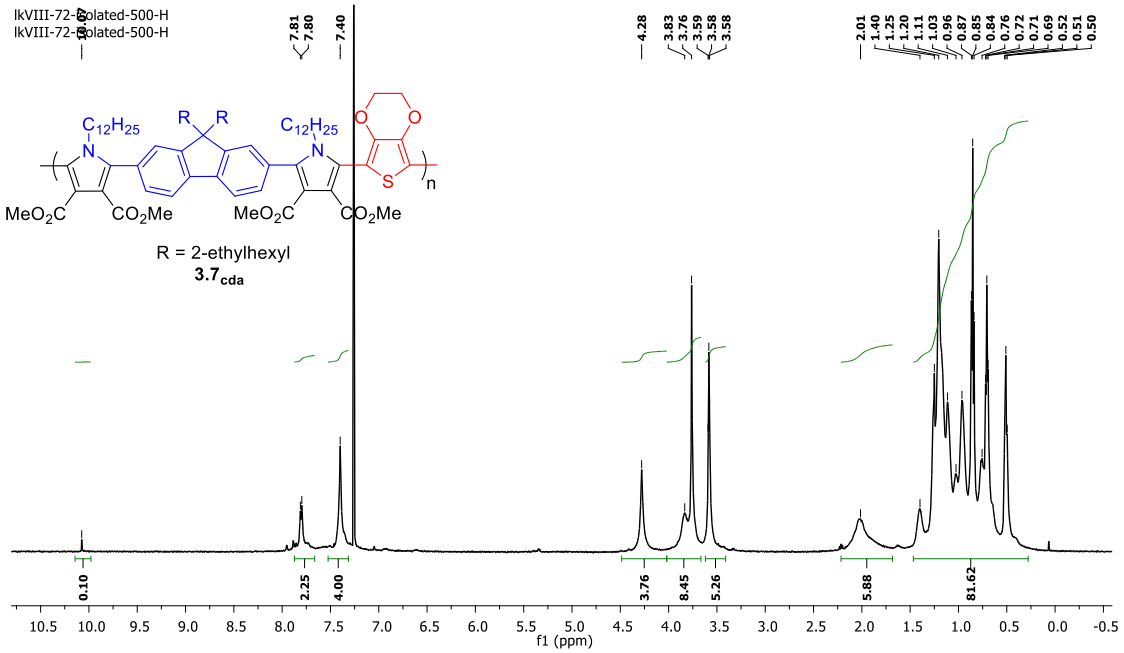


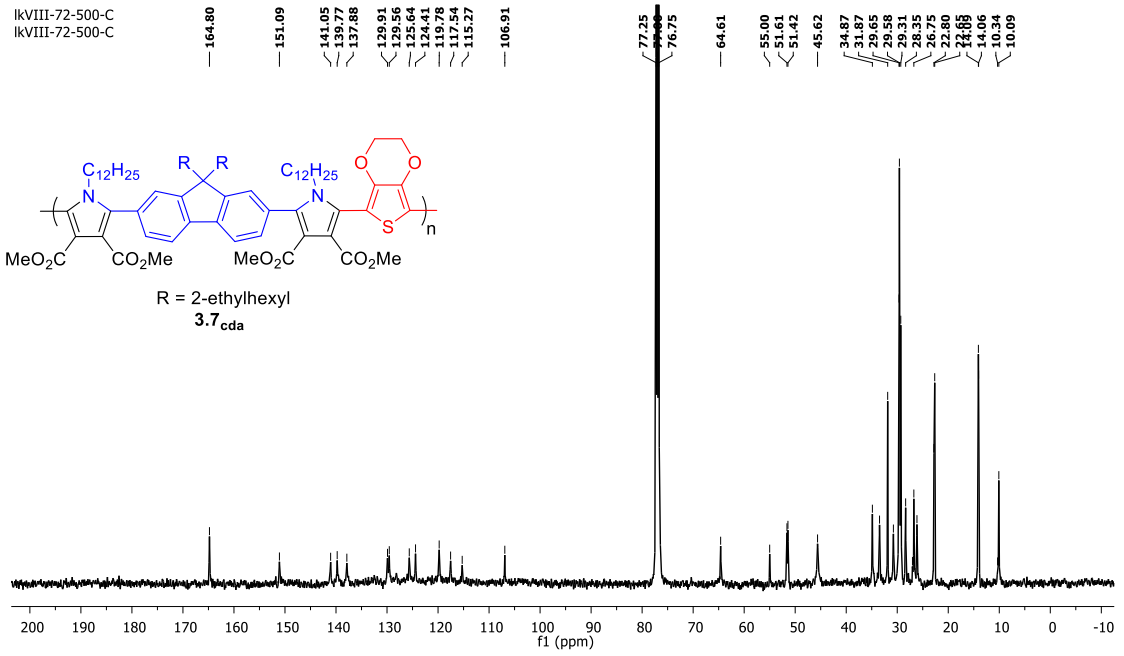
A.20 ^{1}H and ^{13}C NMR of **3.7cca**



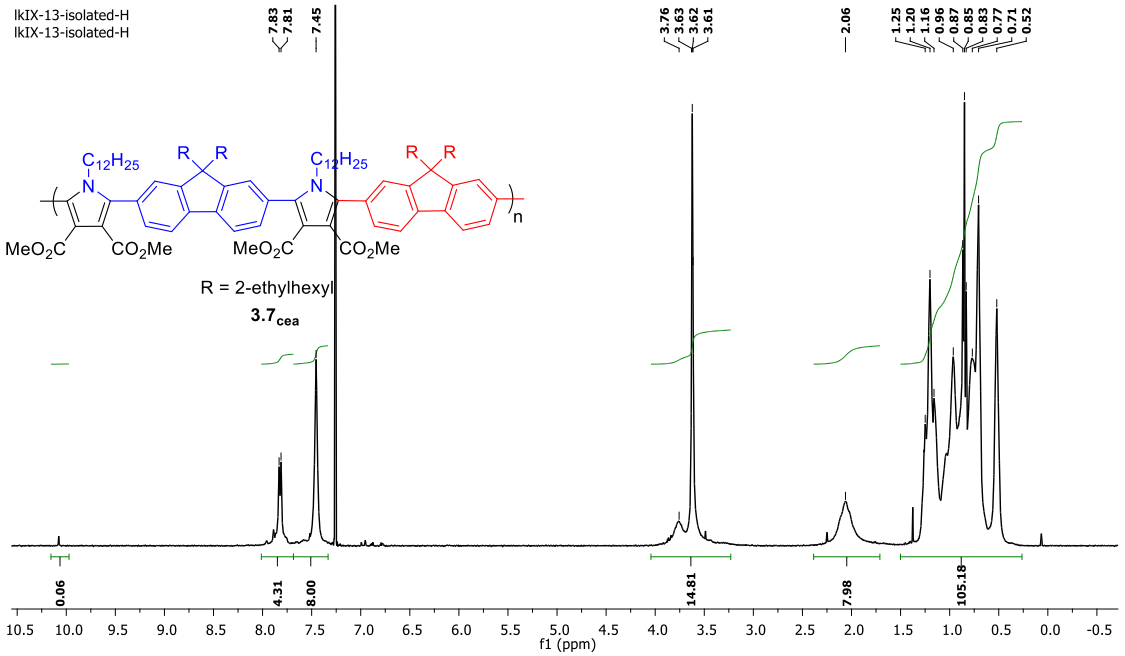


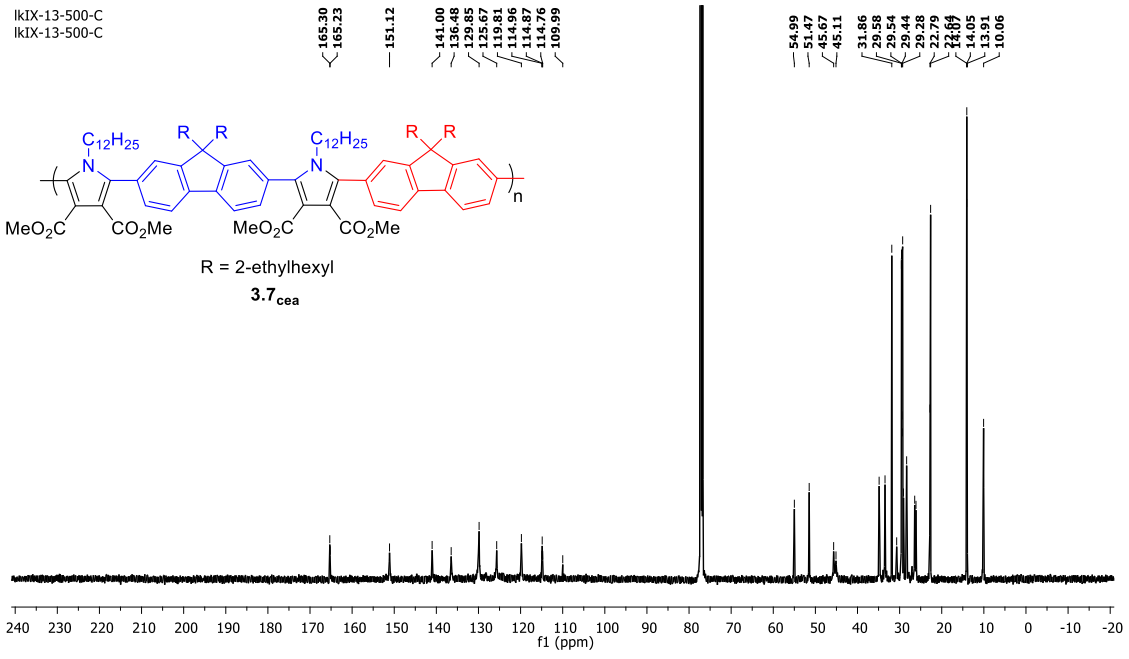
A.21 ^{1}H and ^{13}C NMR of **3.7cda**



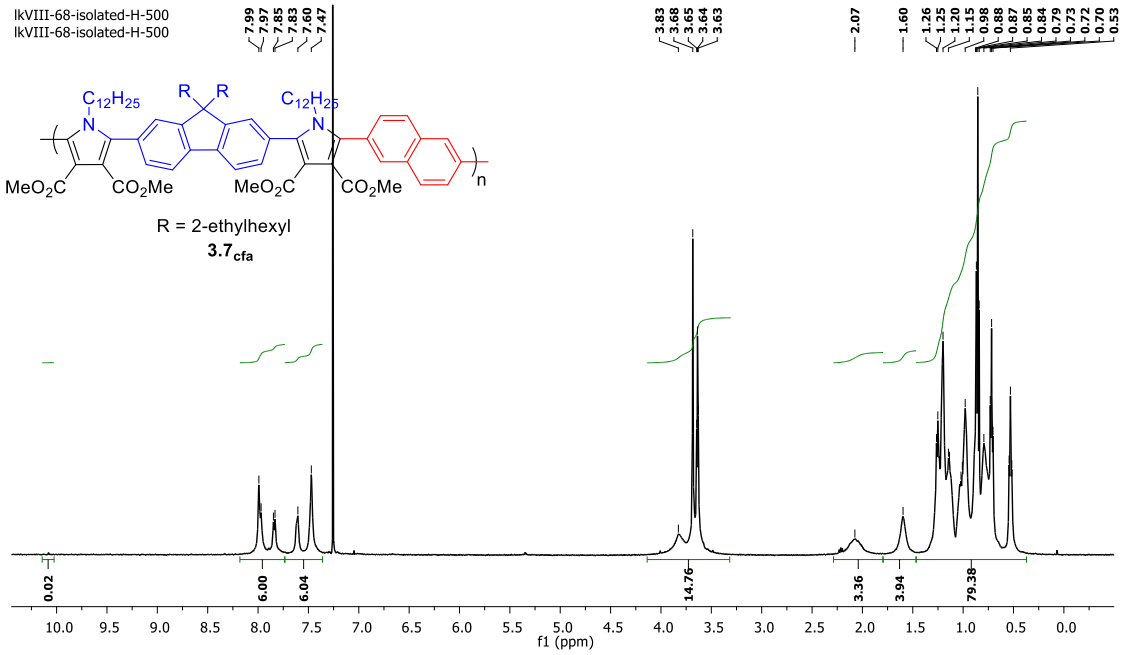


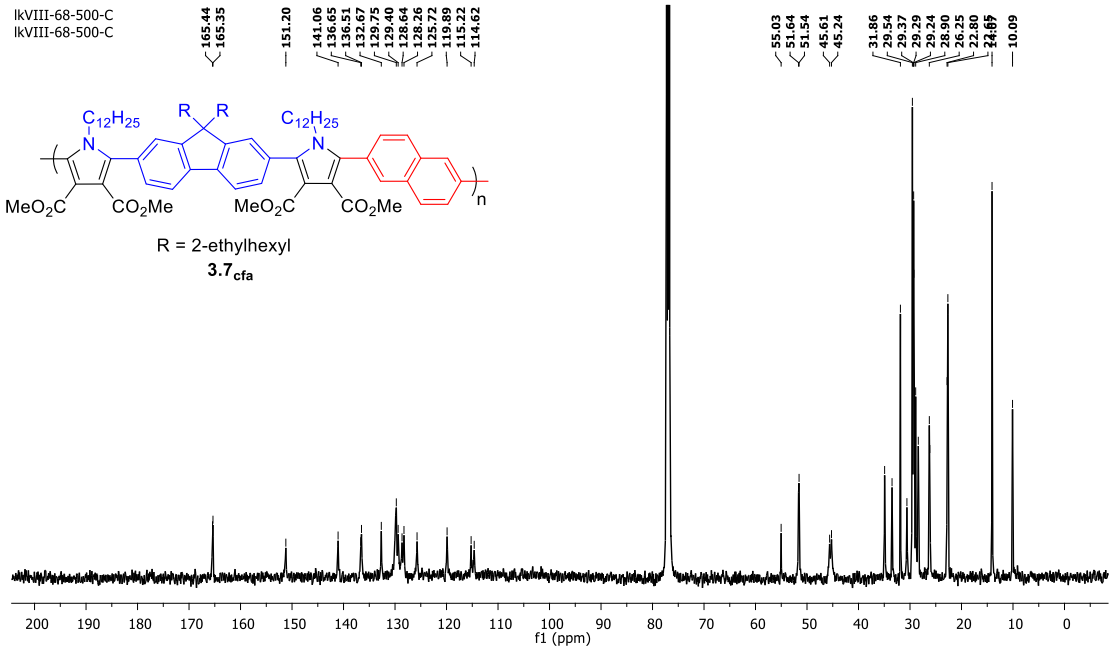
A.22 ^{1}H and ^{13}C NMR of **3.7cea**



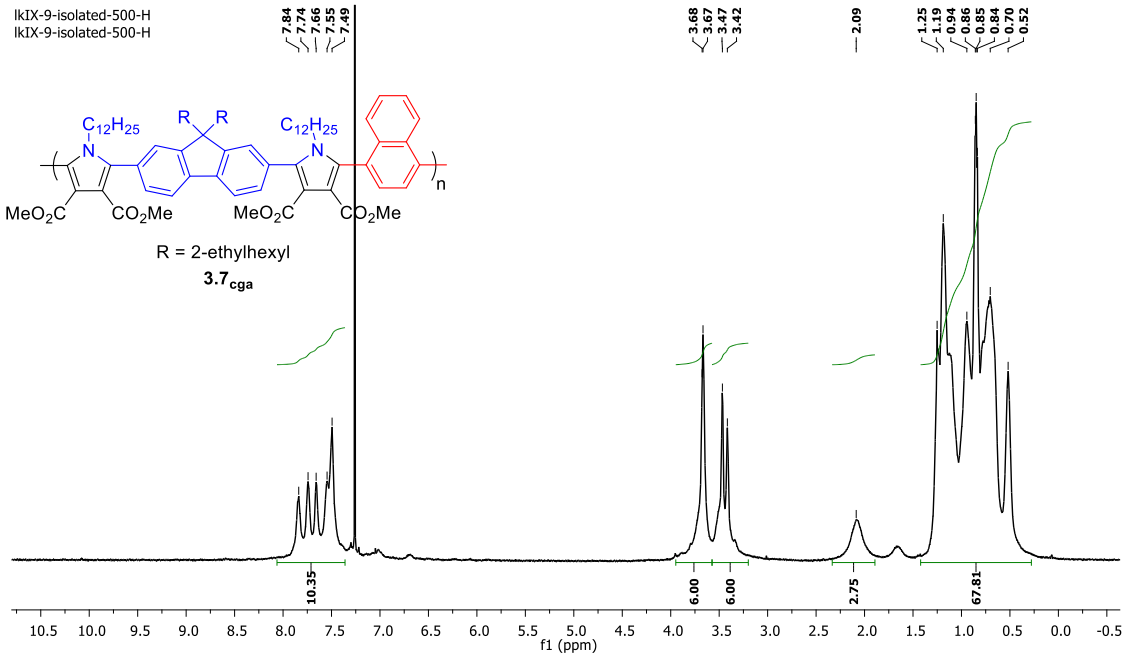


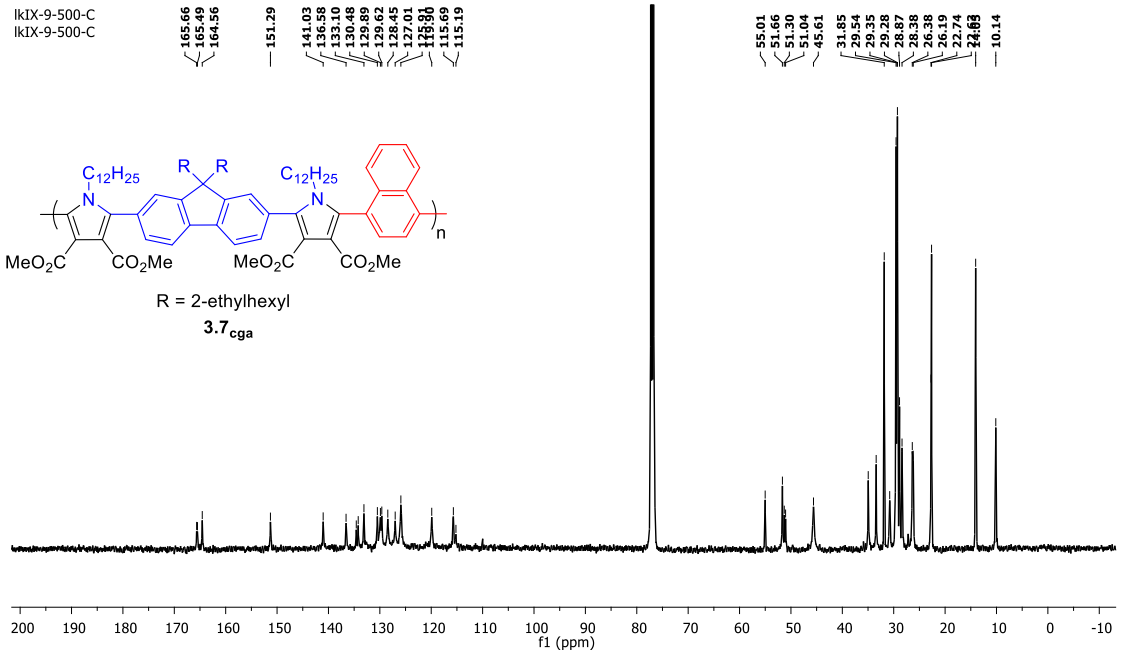
A.23 ^{1}H and ^{13}C NMR of **3.7cfa**



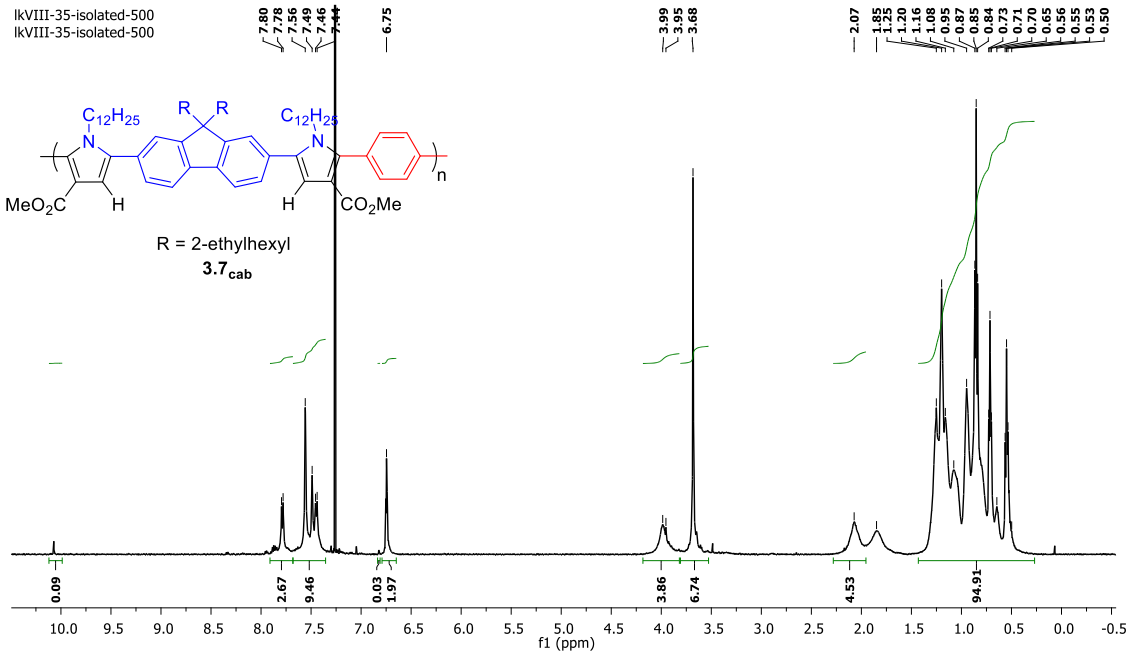


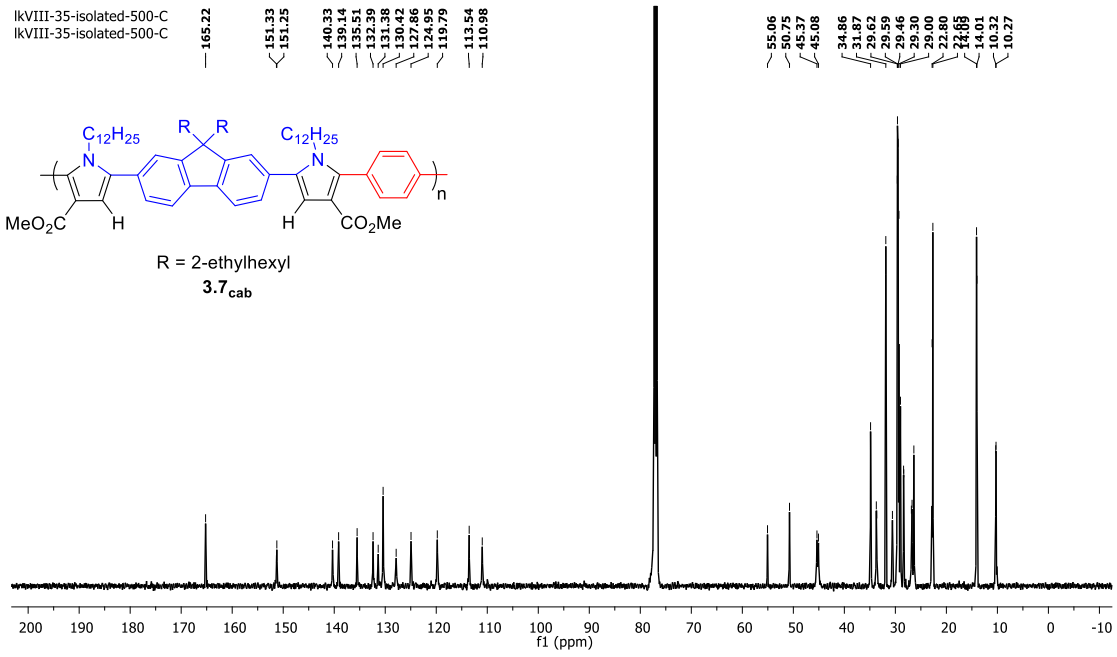
A.24 ^{1}H and ^{13}C NMR of **3.7cga**



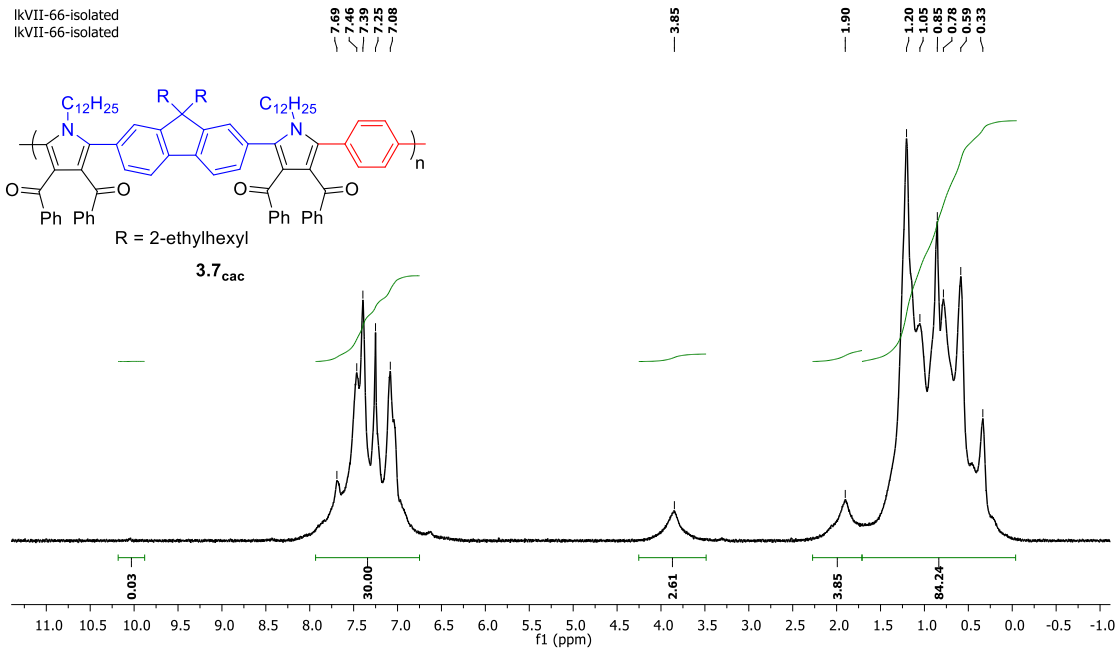


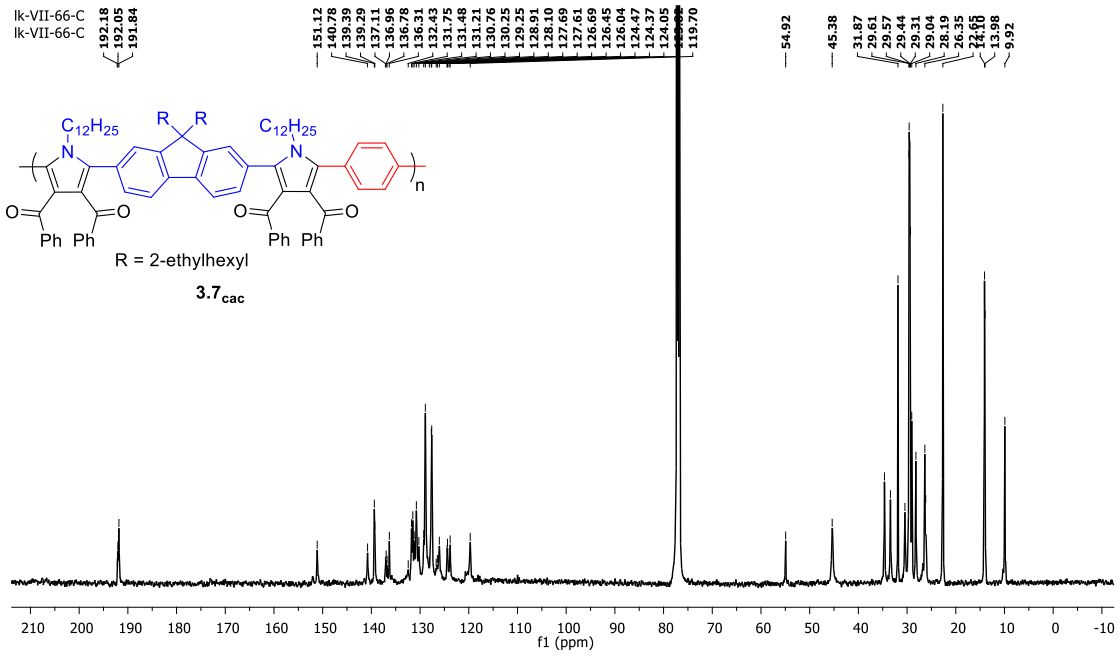
A.25 ^{1}H and ^{13}C NMR of **3.7cab**



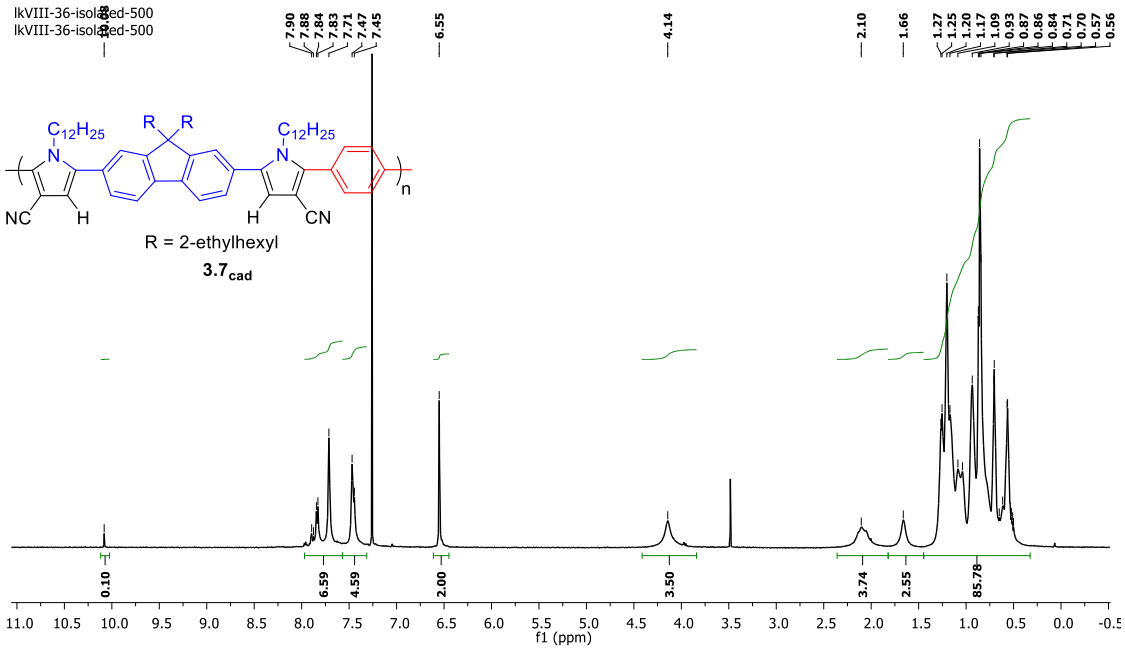


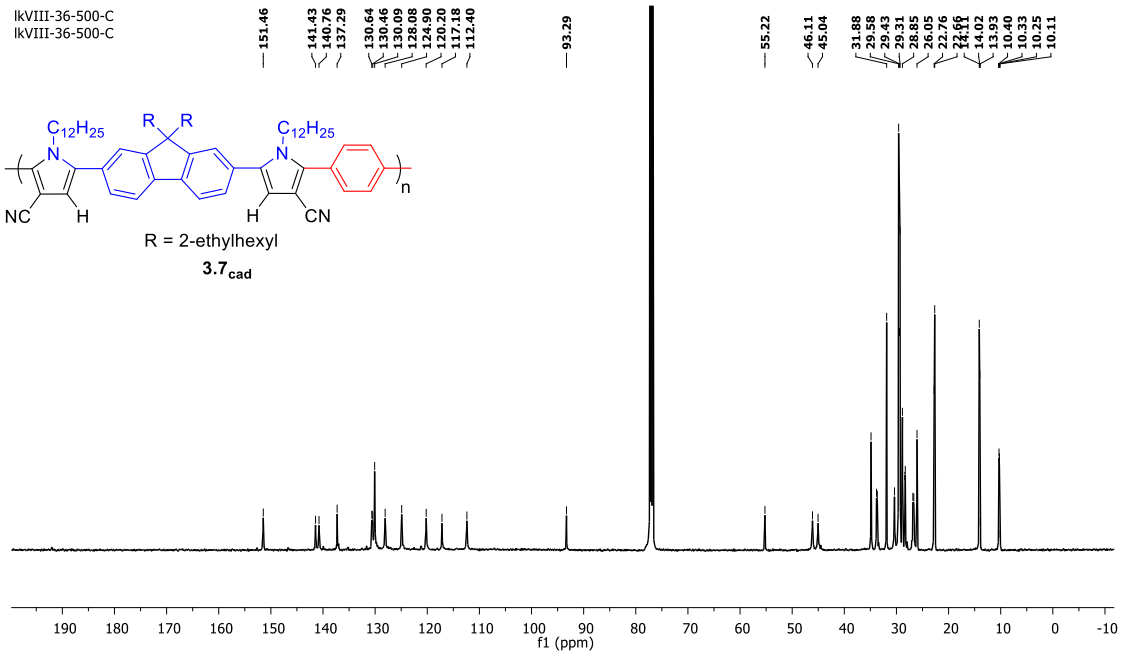
A.26 ^{1}H and ^{13}C NMR of **3.7cac**



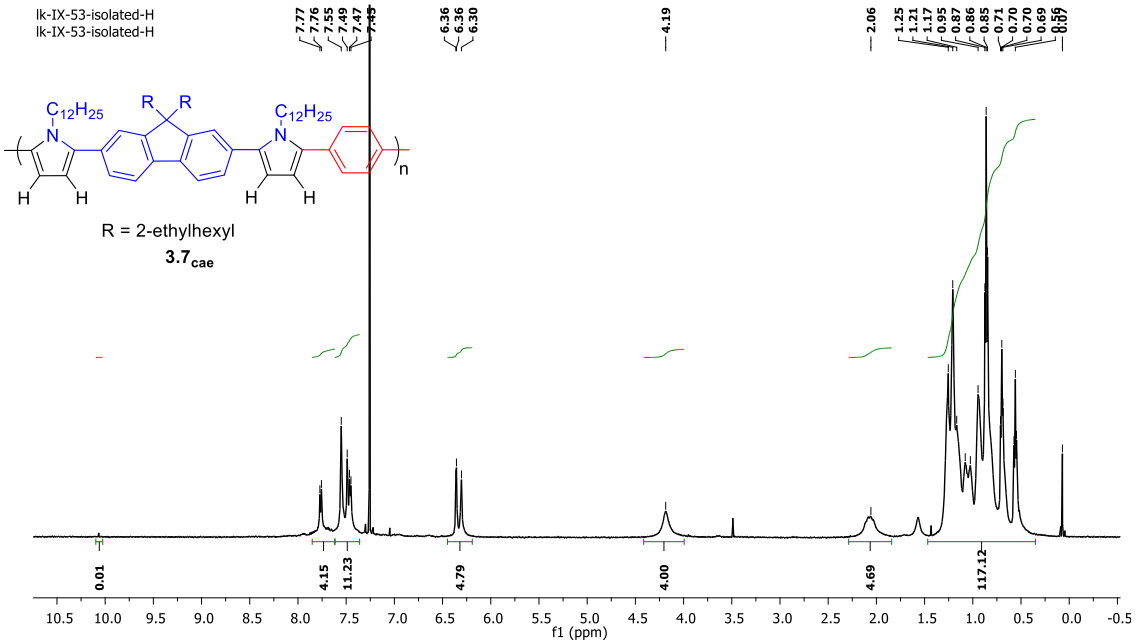


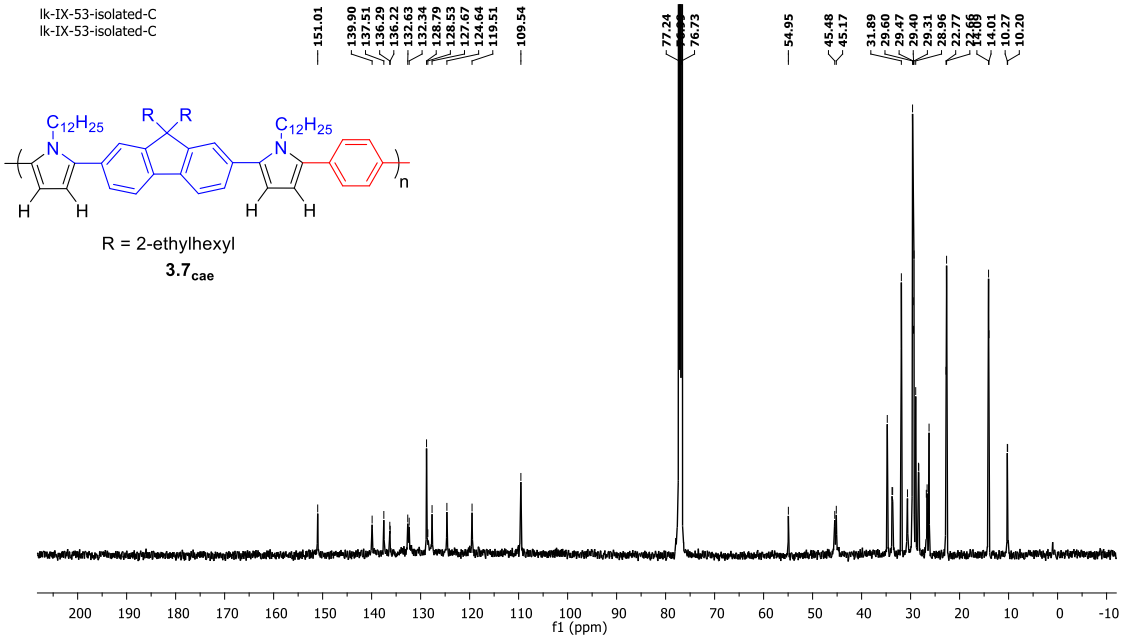
A.27 ^{1}H and ^{13}C NMR of **3.7cad**



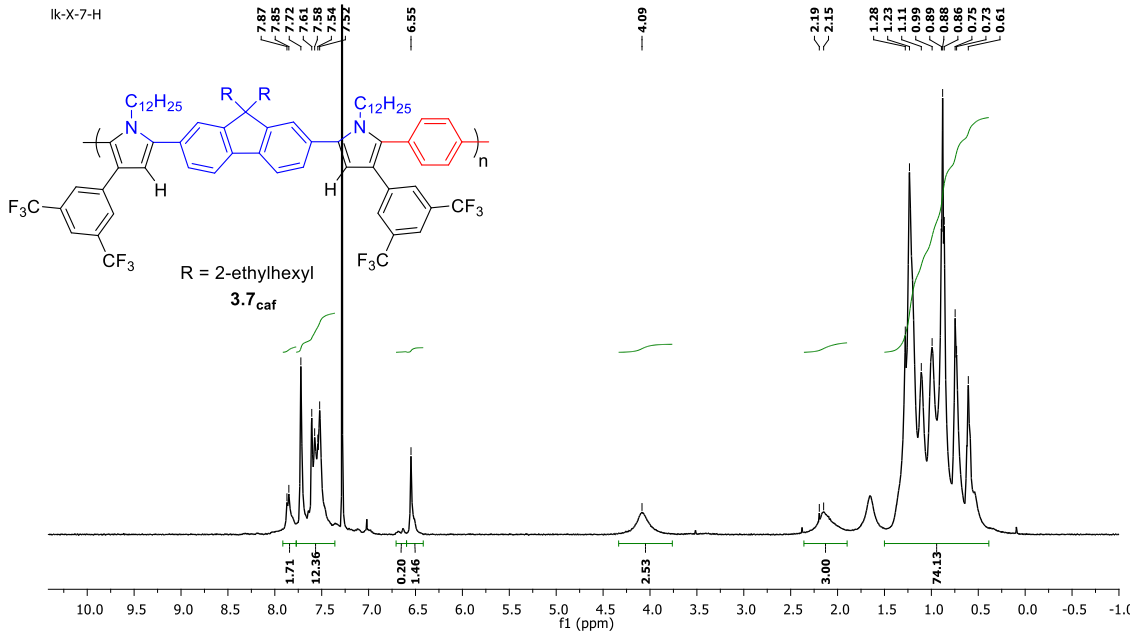


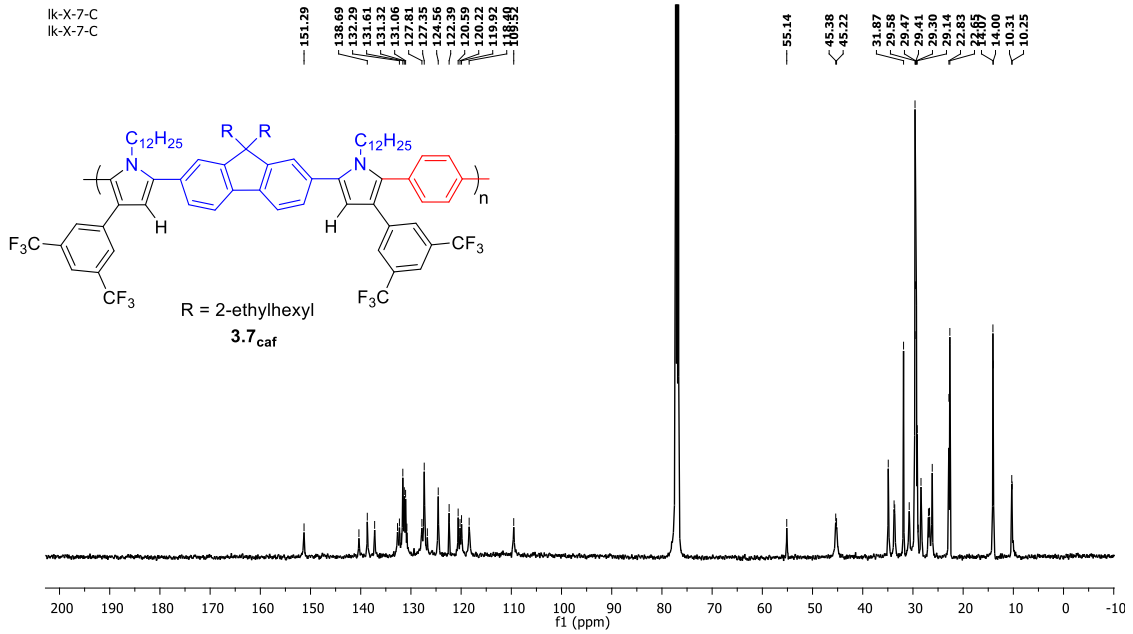
A.28 ^{1}H and ^{13}C NMR of **3.7cae**



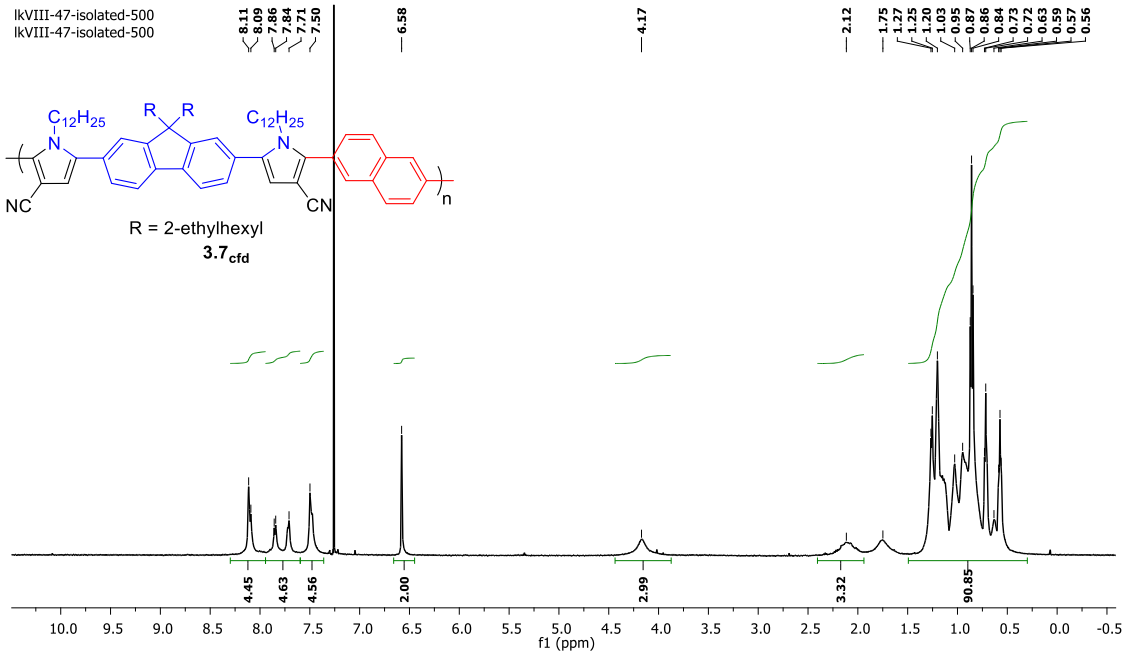


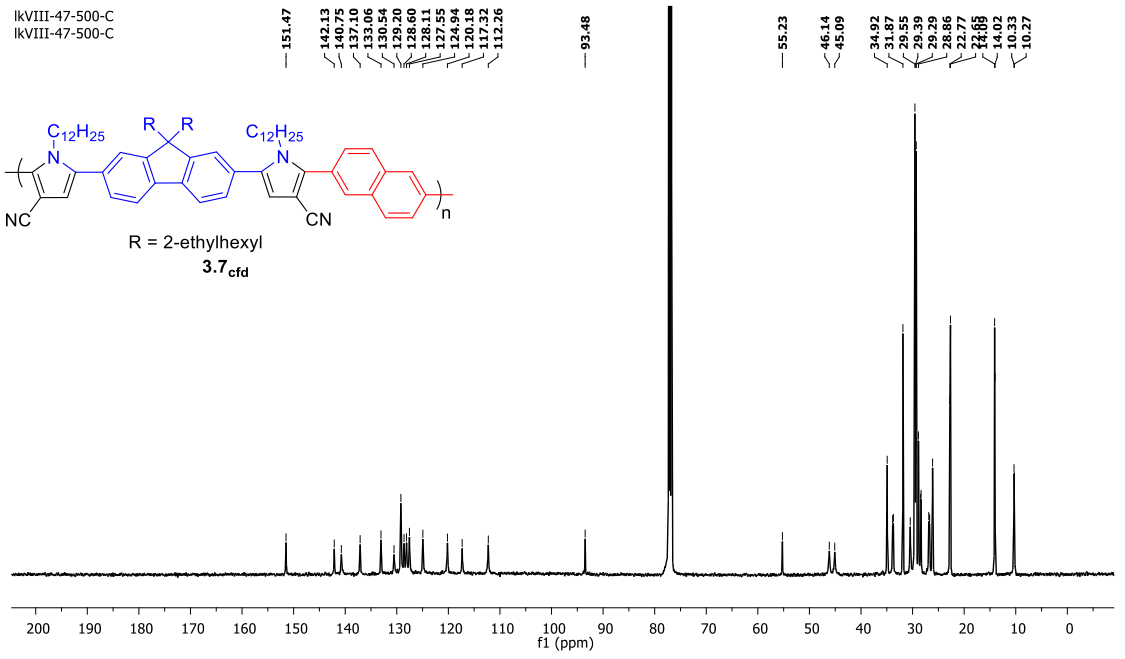
A.29 ^{1}H and ^{13}C NMR of **3.7caf**



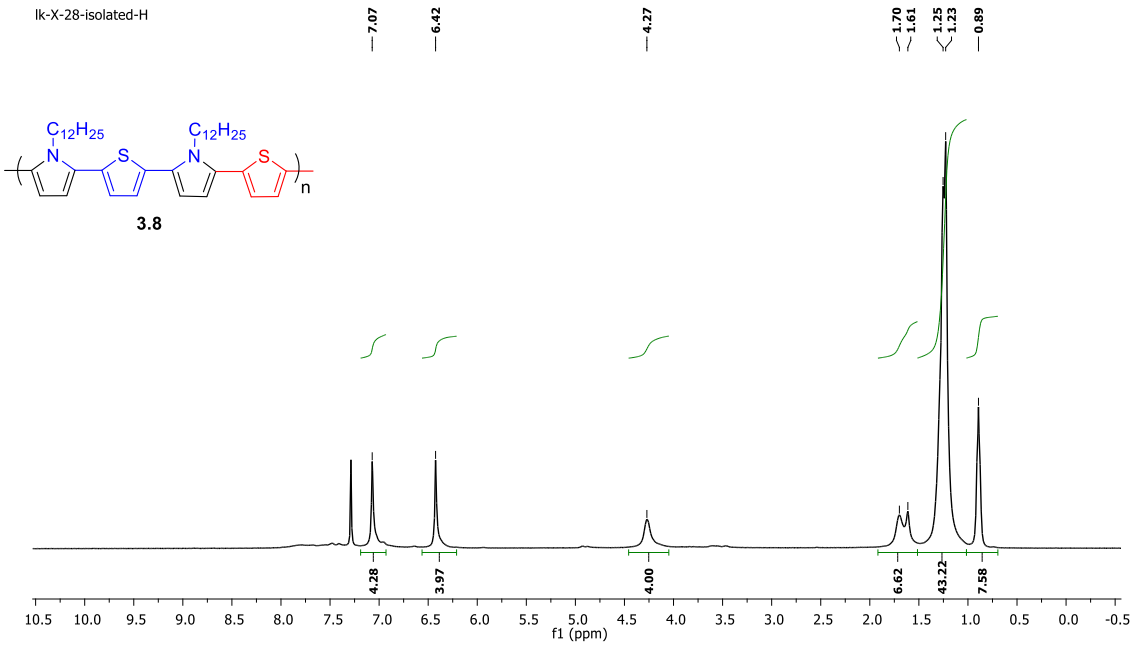


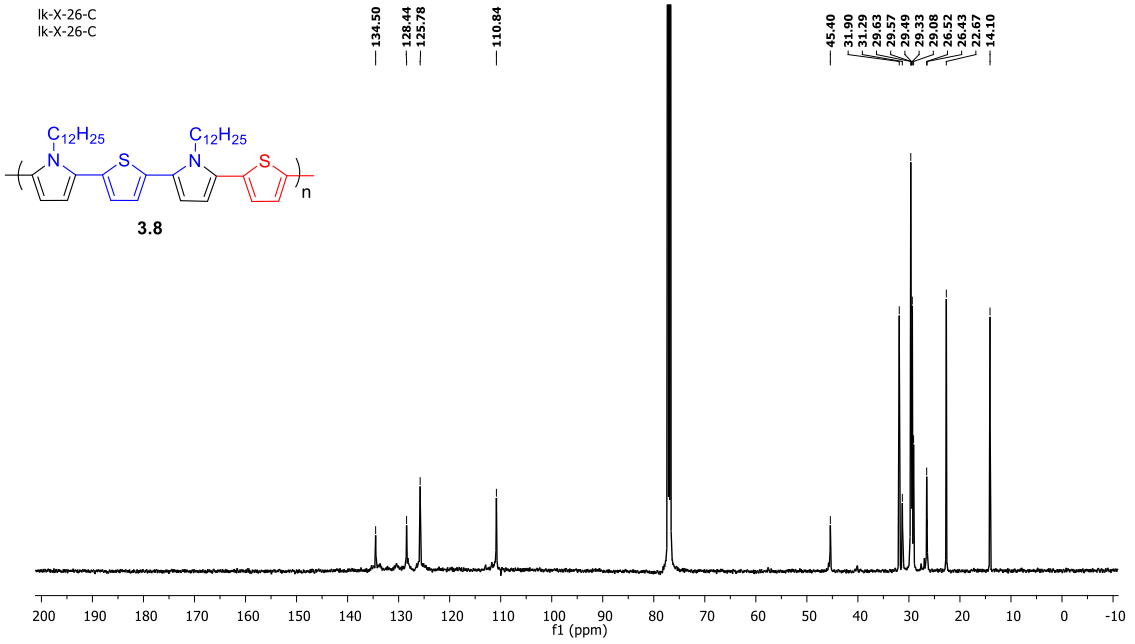
A.30 ^{1}H and ^{13}C NMR of **3.7cfd**





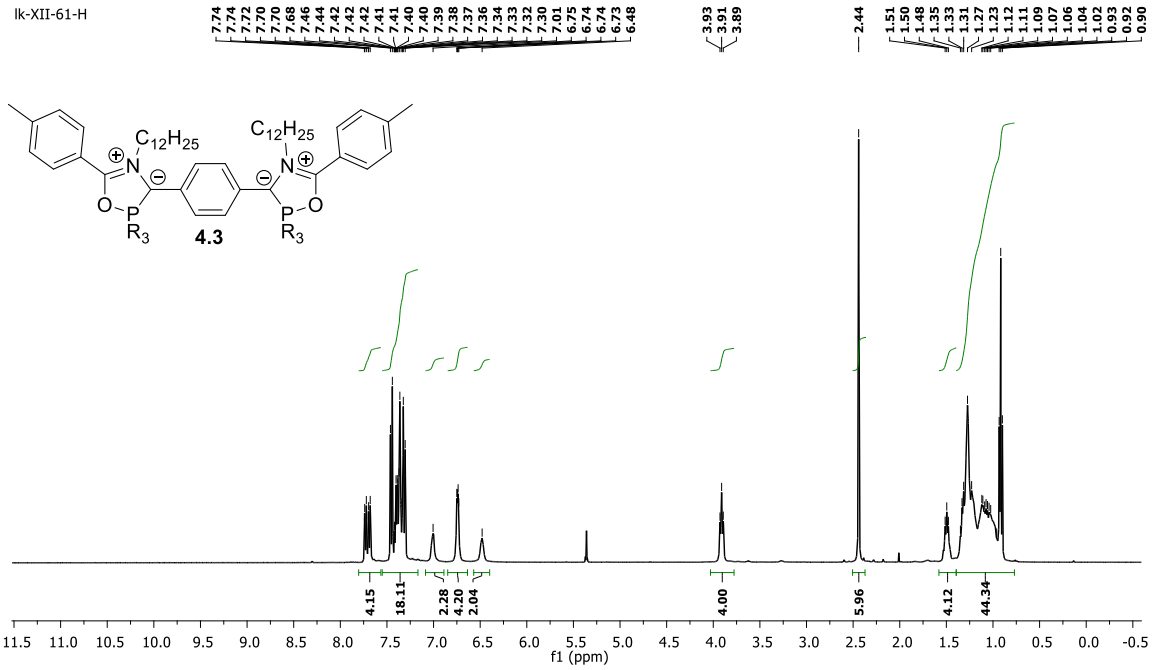
A.31 ^{1}H and ^{13}C NMR of **3.8**

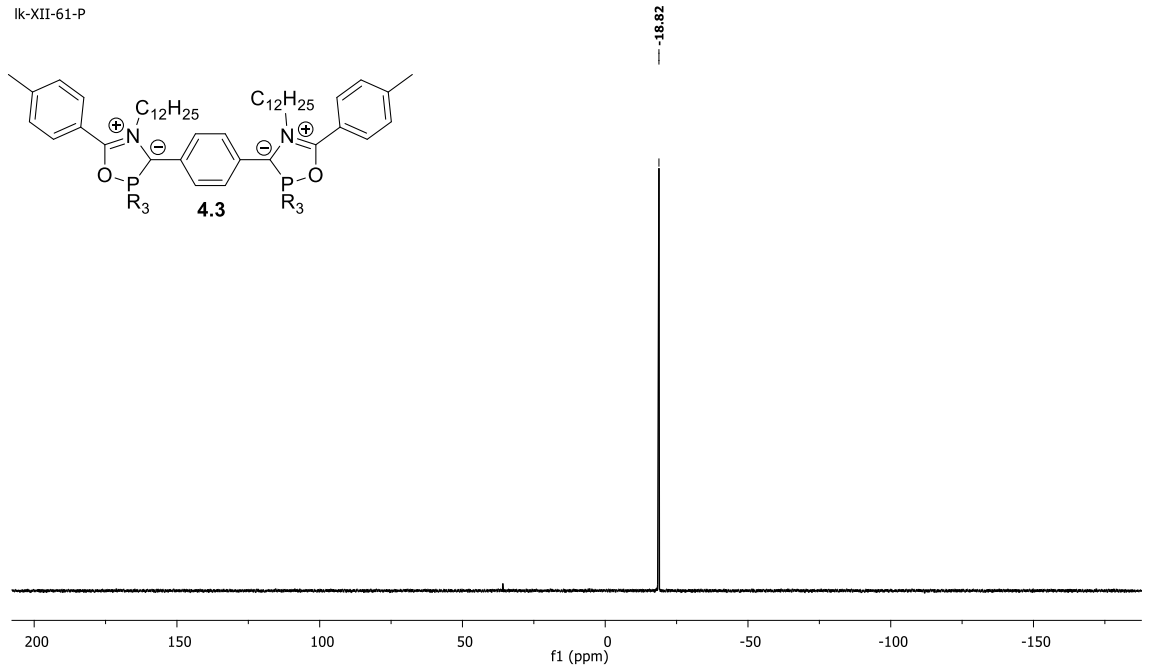


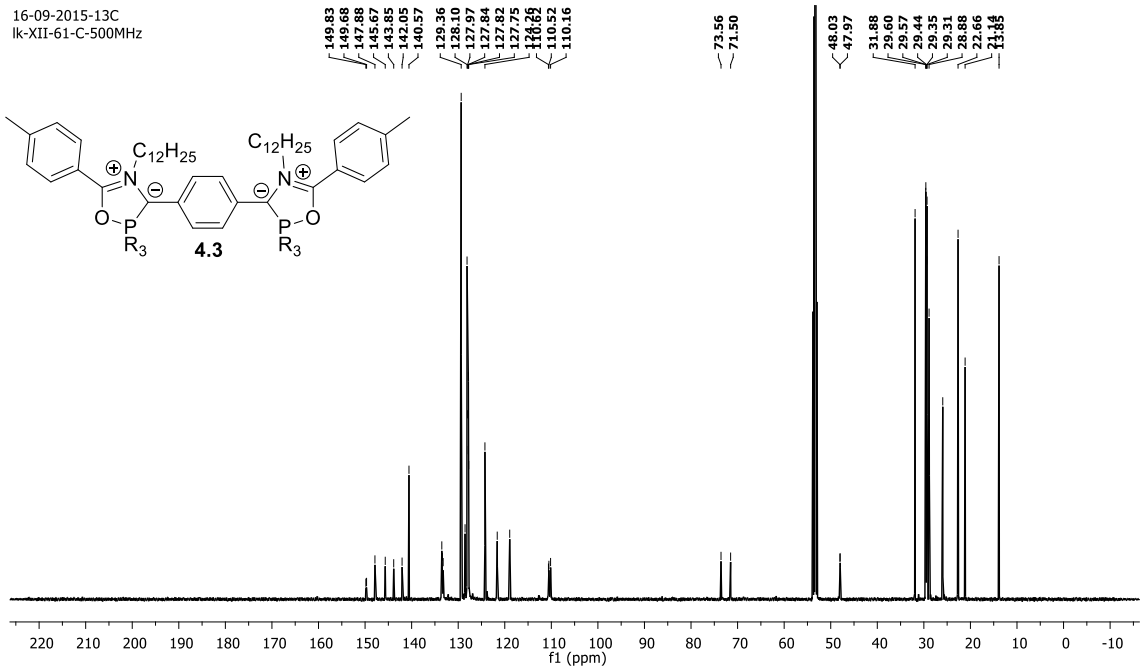


Appendix B: Spectroscopic Data for Chapter 4

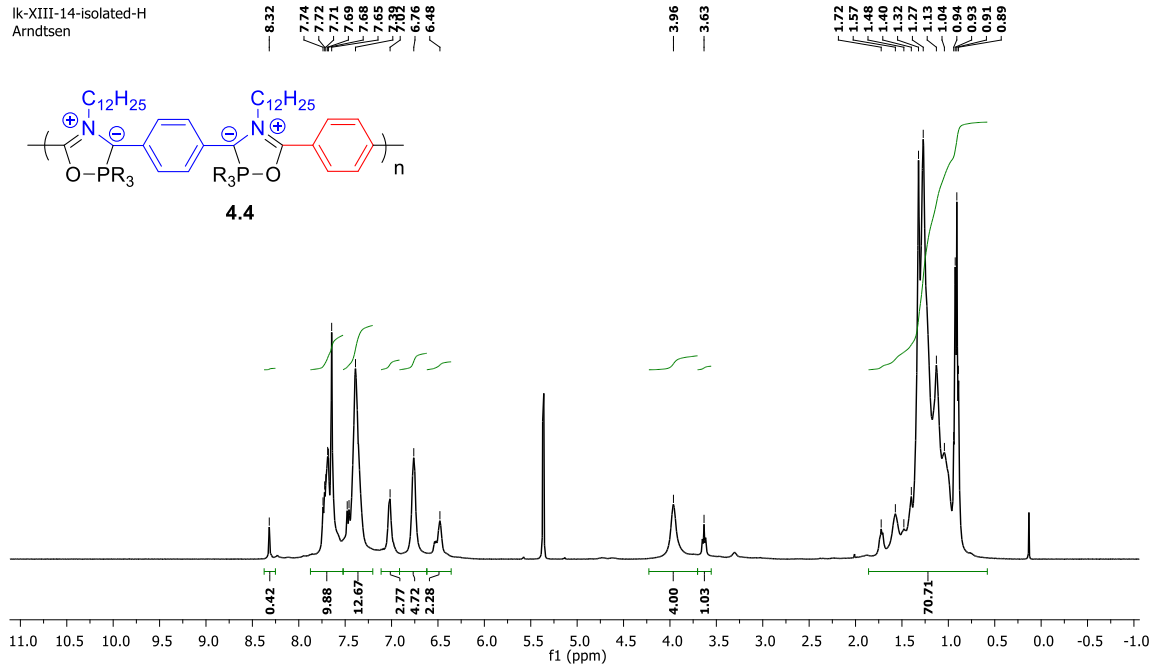
B.1 ^{1}H, ^{31}P and ^{13}C NMR of **4.3**



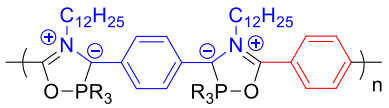




B.2 ^{1}H, ^{31}P and ^{13}C NMR of **4.4**

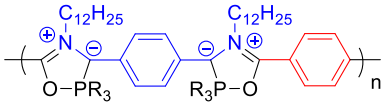


lk-XIII-14-isolated-P
Arndtsen



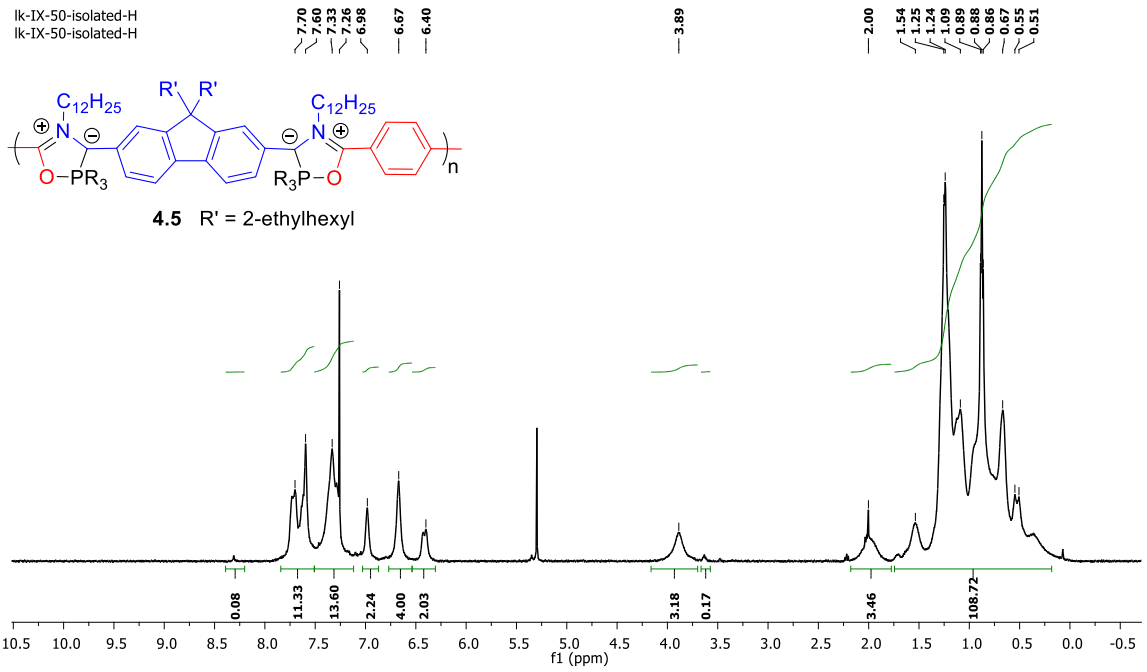
4.4

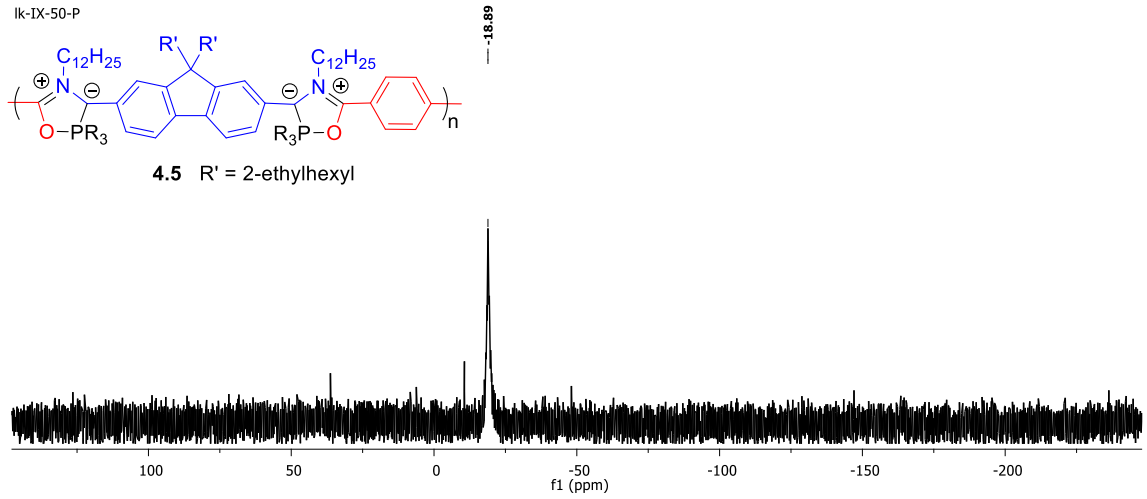
lk-XIII-14-PPM-C
lk-XIII-14-PPM-C



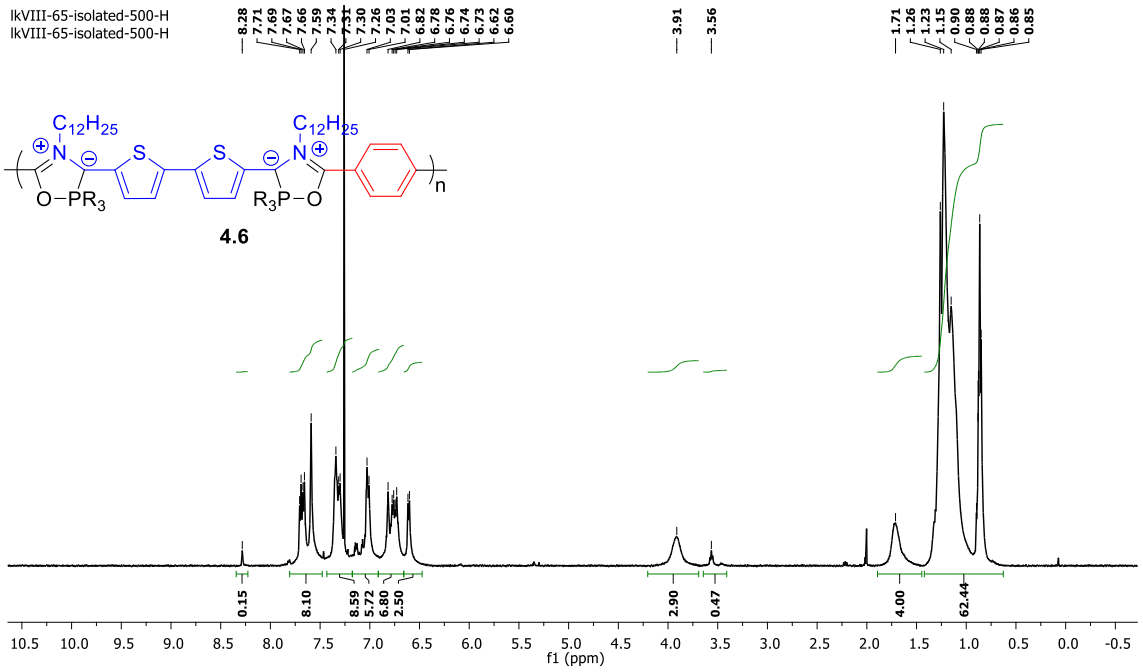
4.4

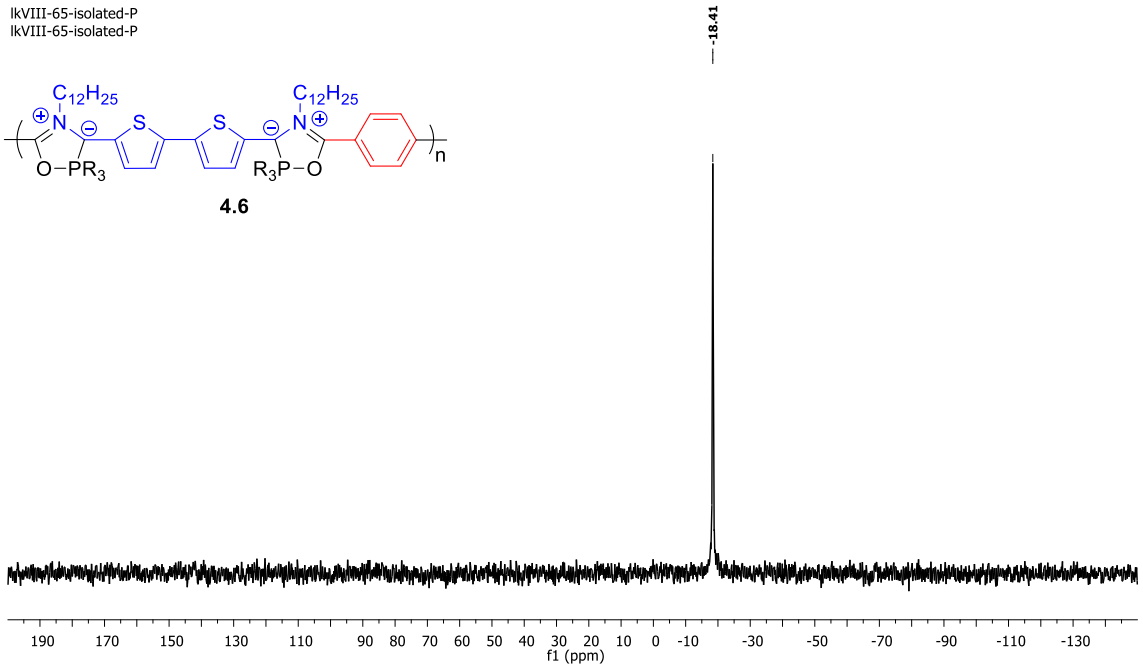
B.3 ^{1}H and ^{31}P NMR of **4.5**

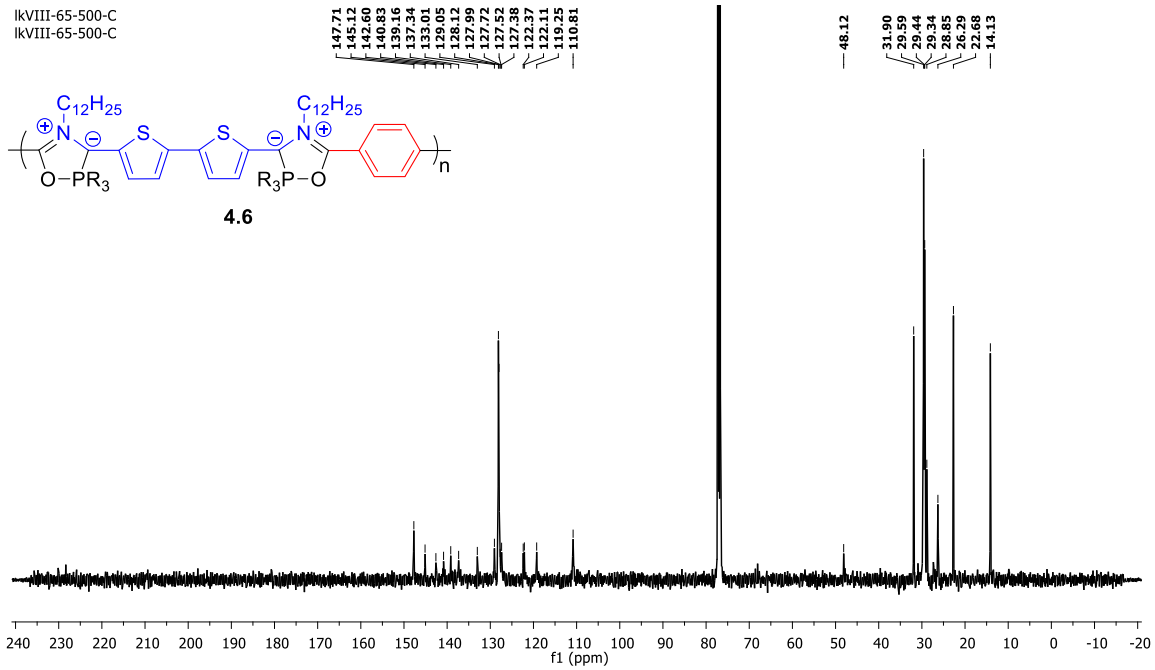




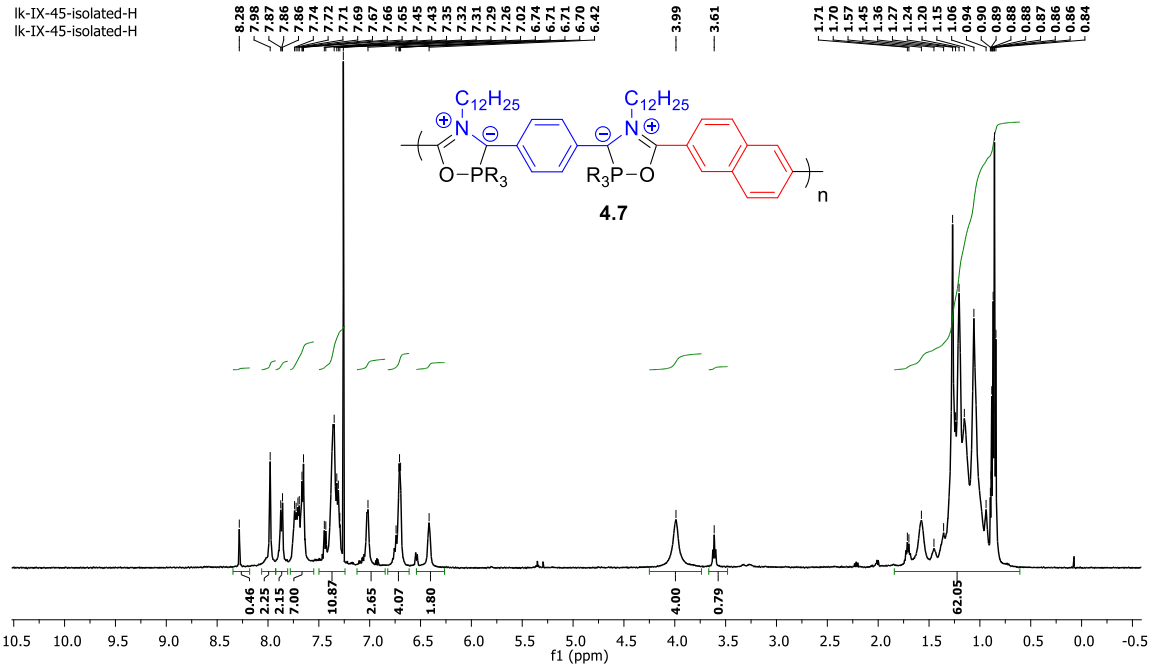
B.4 ^{1}H, ^{31}P and ^{13}C NMR of **4.6**

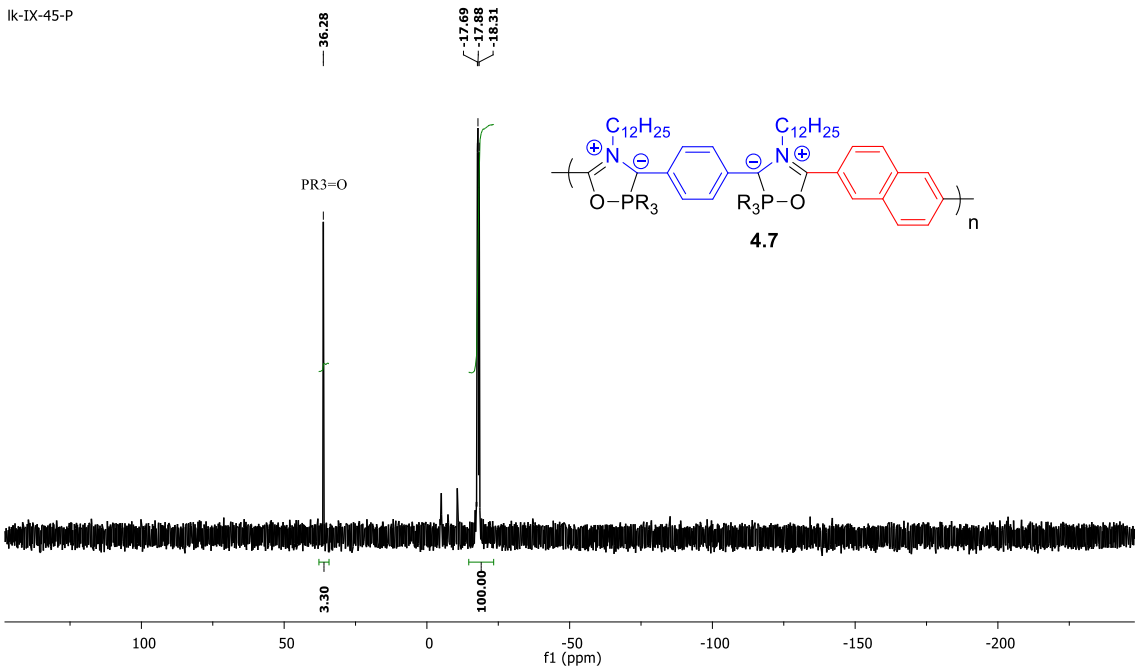


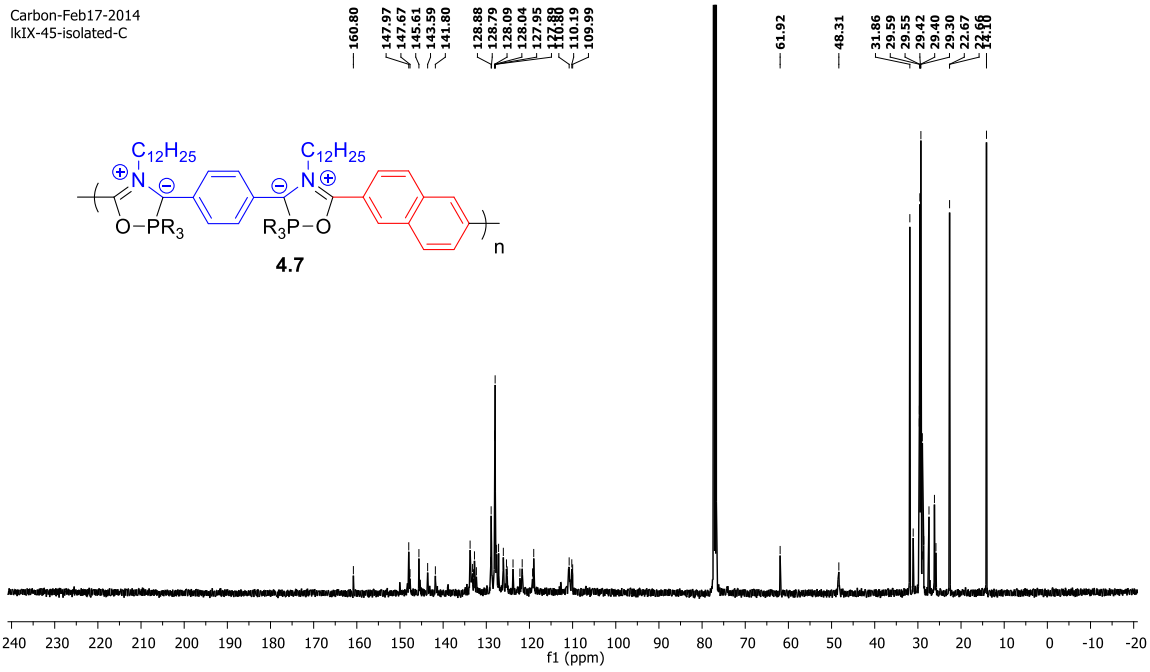




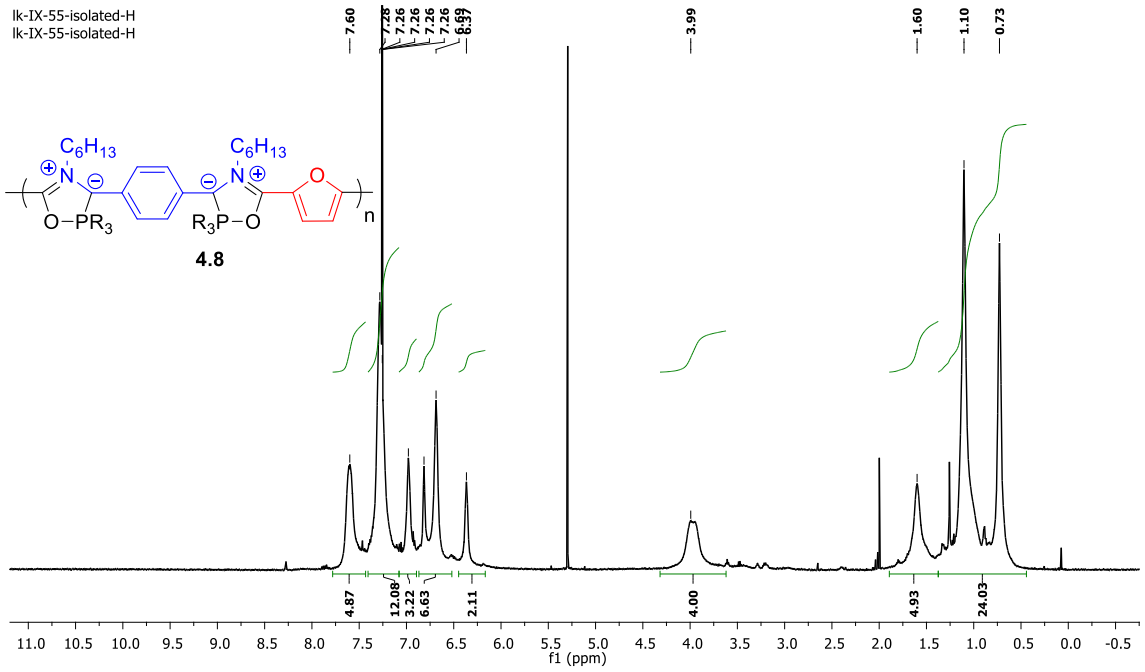
B.5 ^{1}H, ^{31}P and ^{13}C NMR of **4.7**

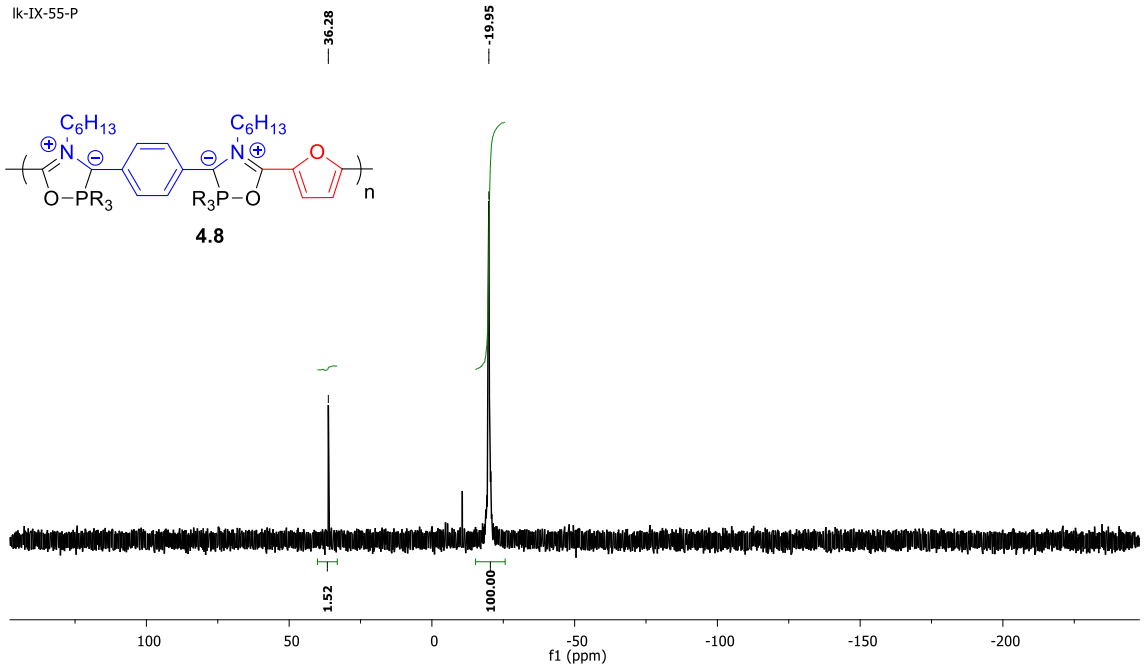


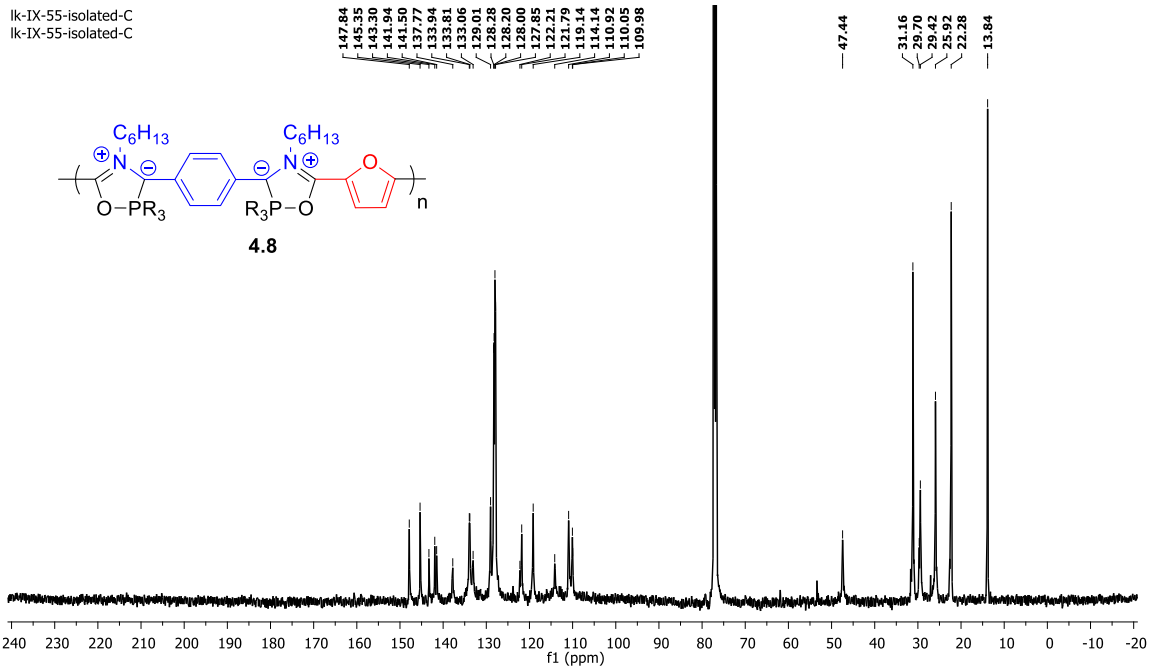

lk-IX-45-P
36.28
-17.69
-17.88
-18.31
PR3=O
3.30
100.00
100
50
0
-50
-100
-150
-200
f1 (ppm)
4.7


Carbon-Feb17-2014
lkIX-45-isolated-C
160.80
147.97
147.67
145.61
143.59
141.80
128.88
128.79
128.09
128.04
127.95
110.19
109.99
61.92
48.31
31.86
29.59
29.55
29.42
29.40
29.30
22.67
14.10
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)
4.7

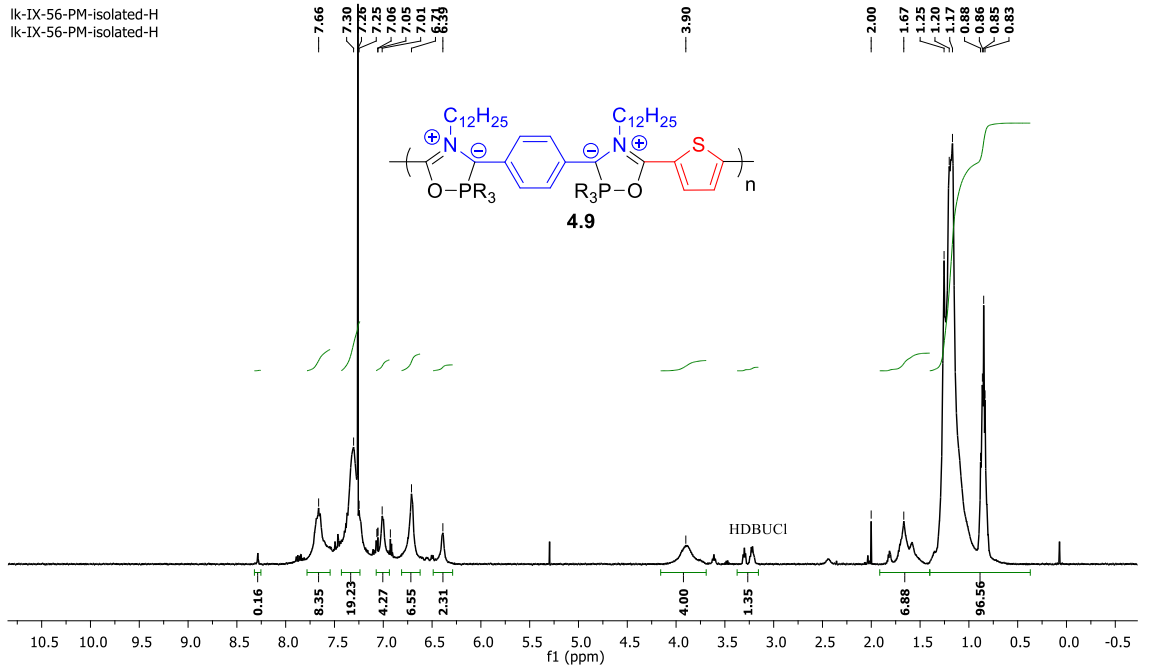
B.6 ^{1}H, ^{31}P and ^{13}C NMR of **4.8**

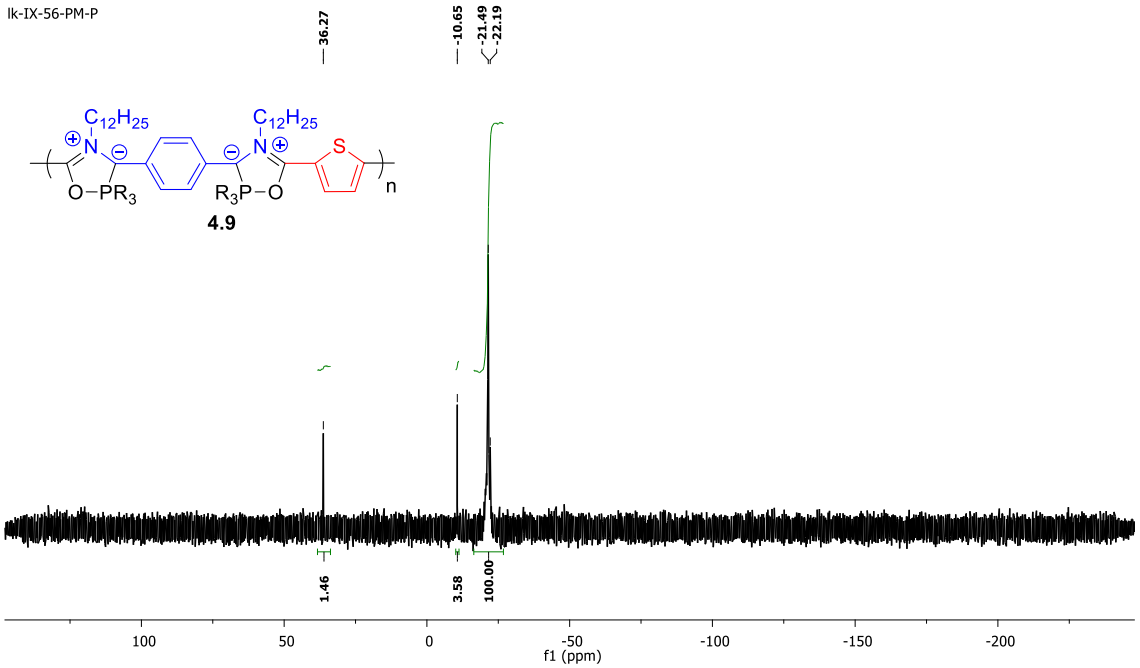


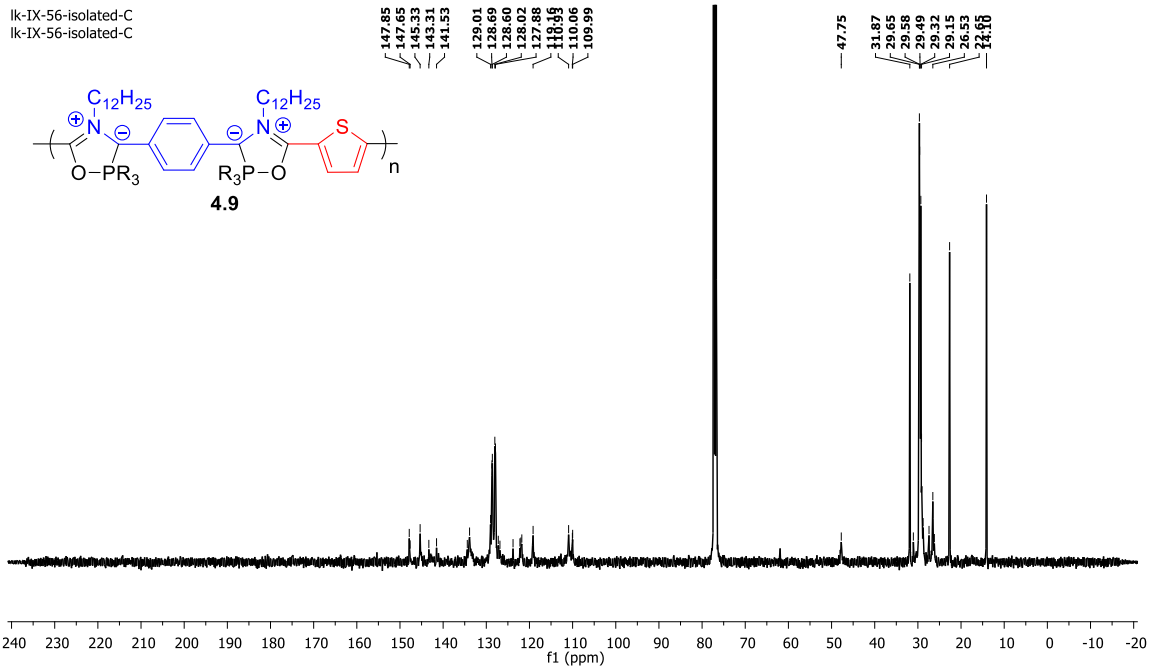




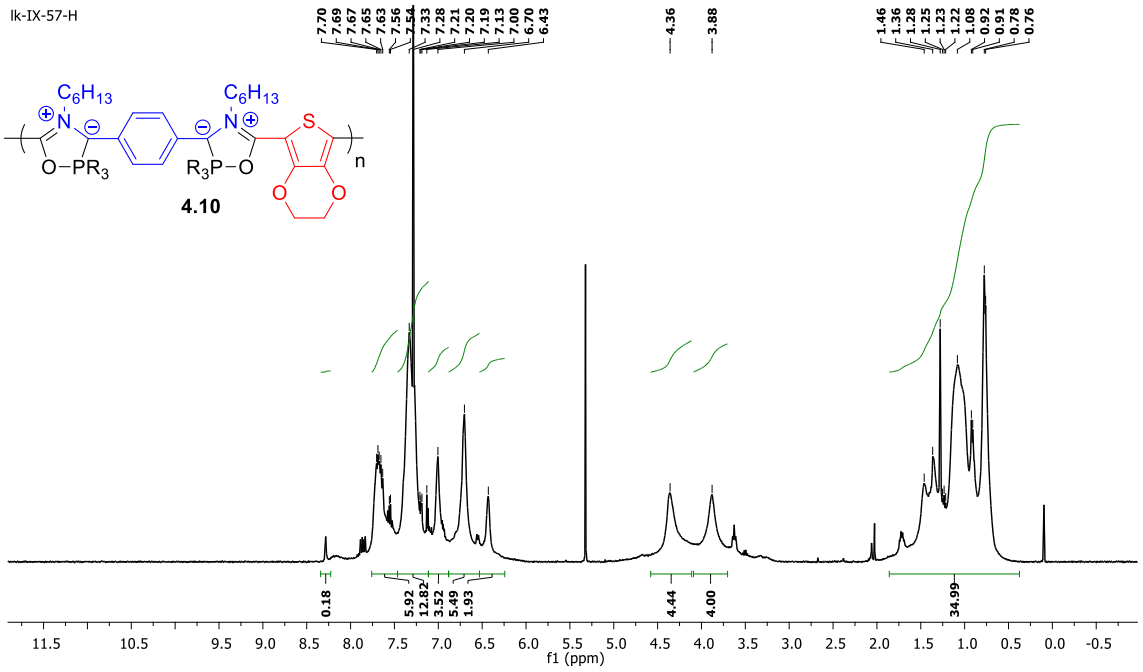
B.7 ^{1}H, ^{31}P and ^{13}C NMR of **4.9**

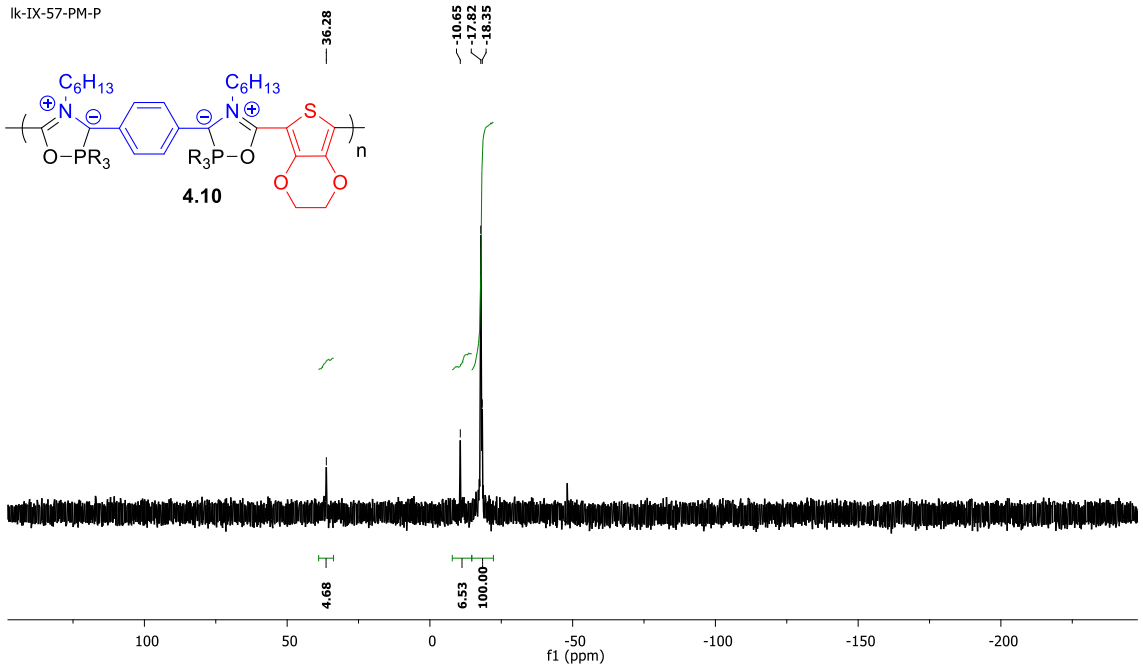


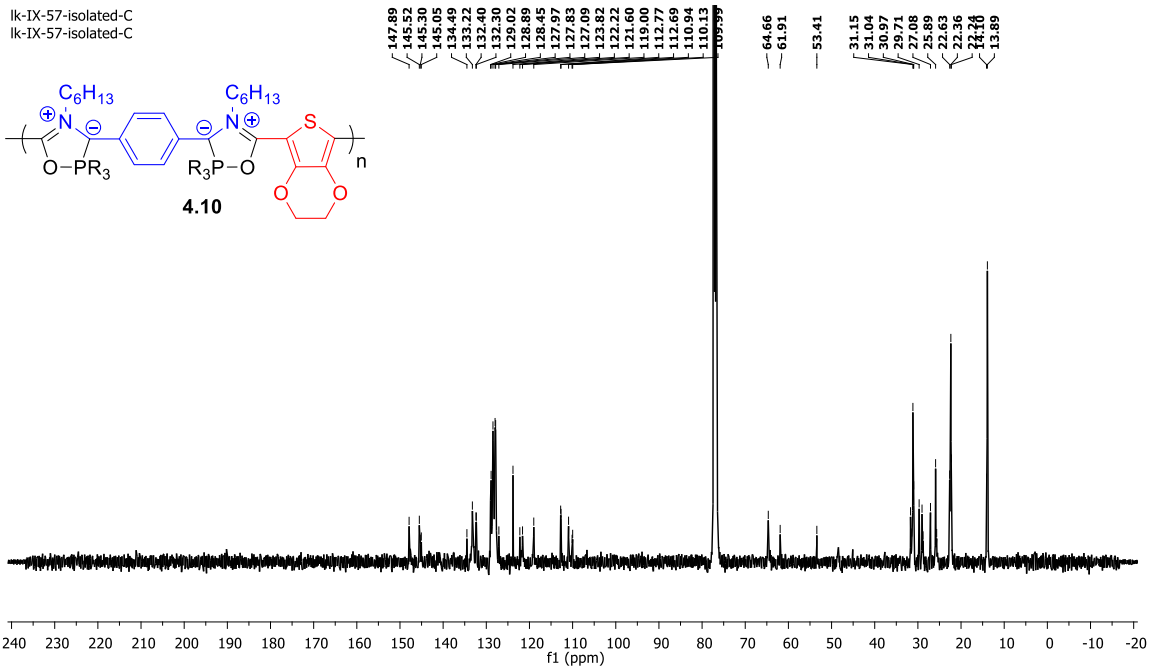

lk-IX-56-PM-P
36.27
-10.65
-21.49
-22.19
C12H25
C12H25
S
O–PR3
R3P–O
n
4.9
1.46
3.58
100.00
100
50
0
-50
-100
-150
-200
f1 (ppm)


lk-IX-56-isolated-C
lk-IX-56-isolated-C
147.85
147.65
145.33
143.31
141.53
129.01
128.69
128.60
128.02
127.88
110.06
109.99
47.75
31.87
29.65
29.58
29.49
29.32
29.15
26.53
14.10
C12H25
C12H25
S
O–PR3
R3P–O
n
4.9
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

B.8 ^{1}H, ^{31}P and ^{13}C NMR of **4.10**

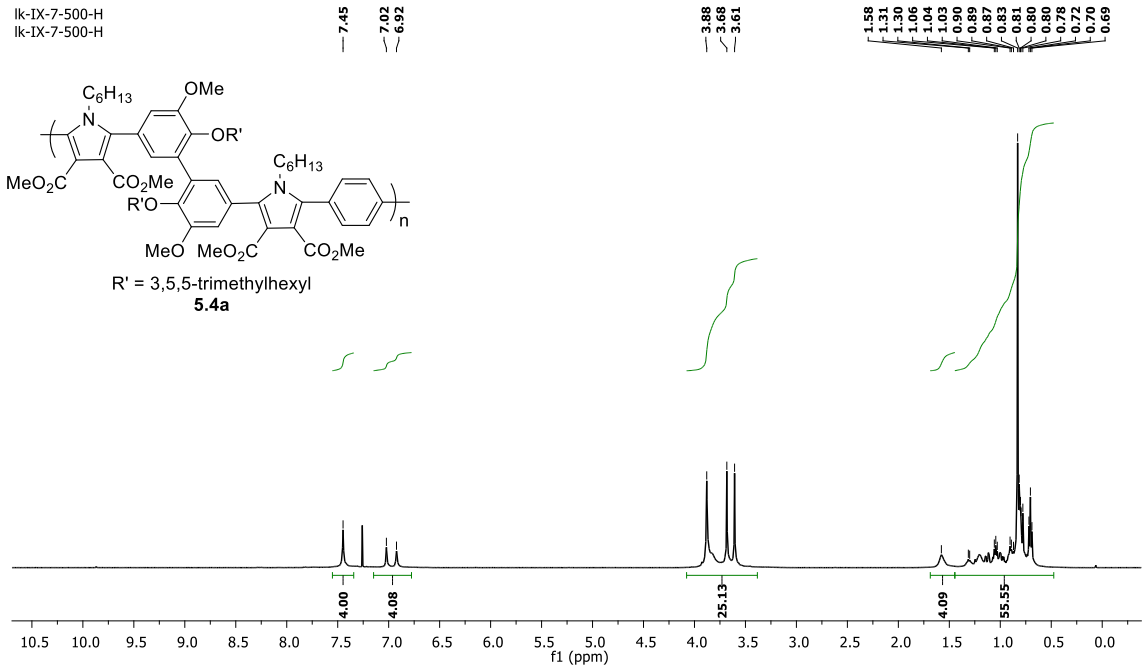


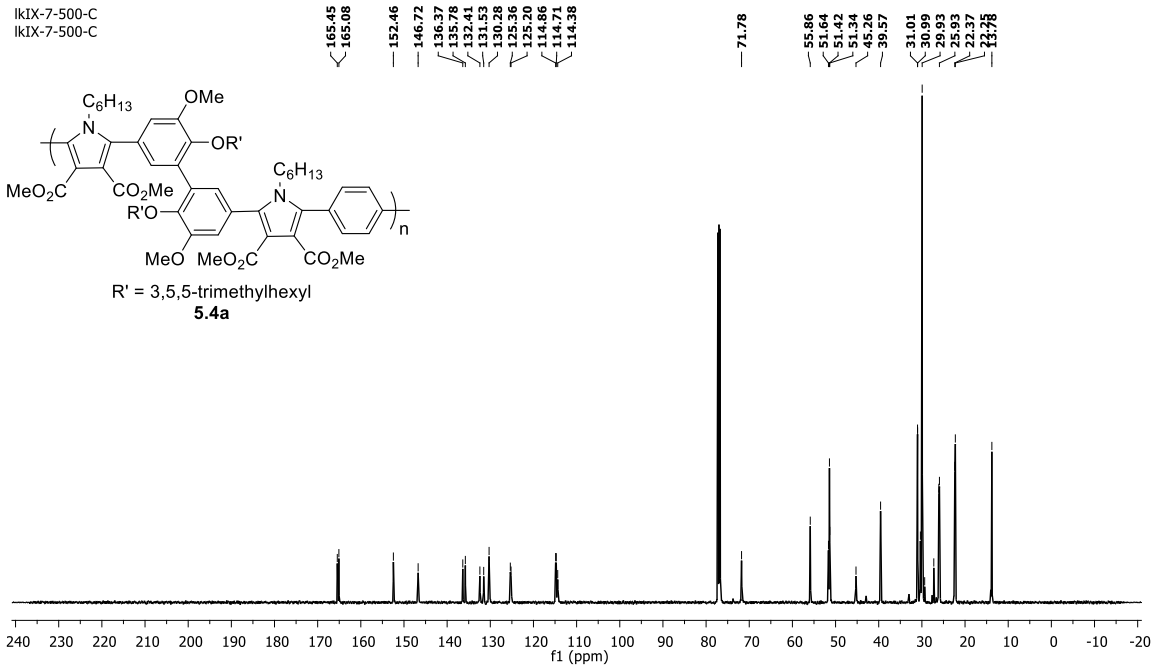



lk-IX-57-isolated-C
lk-IX-57-isolated-C
147.89
145.52
145.30
145.05
134.49
133.22
132.40
132.30
129.02
128.89
128.45
127.97
127.83
127.09
123.82
122.22
121.60
119.00
112.77
112.69
110.94
110.13
105.99
64.66
61.91
53.41
31.15
31.04
30.97
29.71
27.08
25.89
22.63
22.36
14.10
13.89
C6H13
C6H13
O−PR3
R3P−O
S
O
O
n
4.10
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

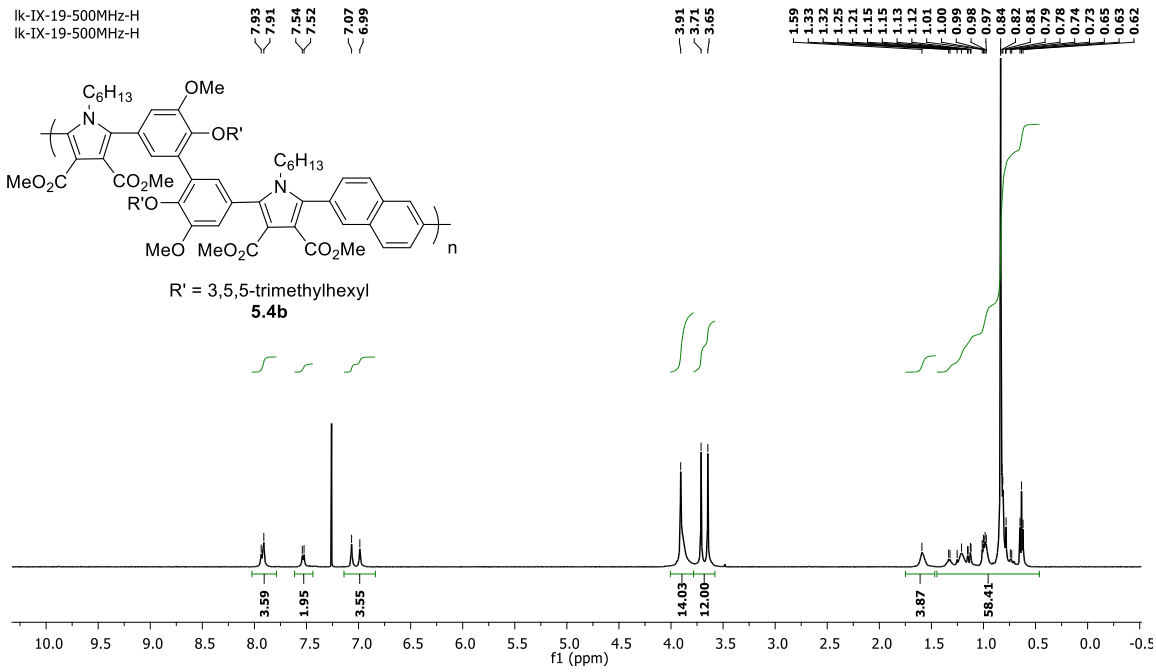
Appendix C: Spectroscopic Data for Chapter 5

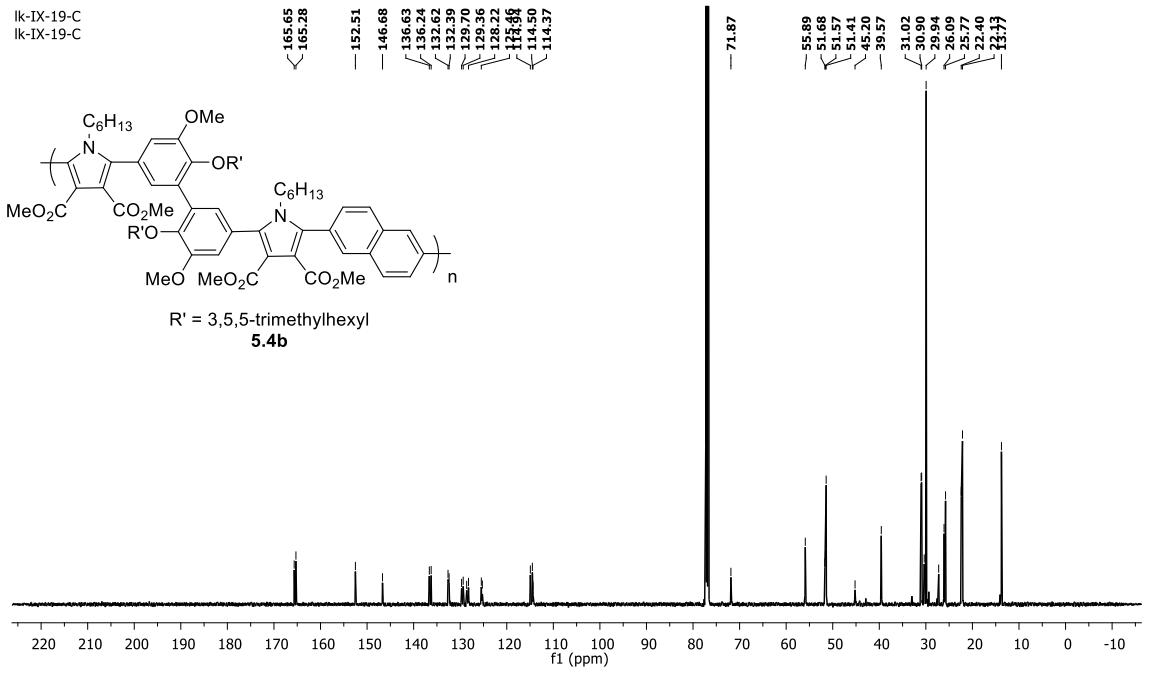
C.1 ^{1}H and ^{13}C NMR of **5.4a**



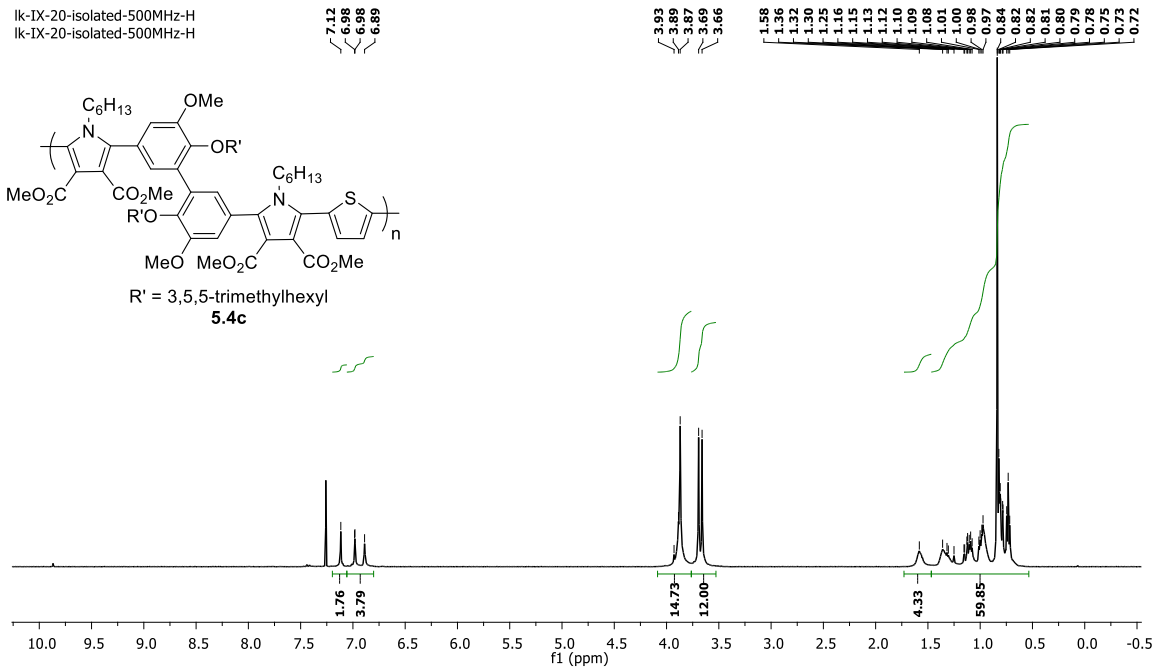


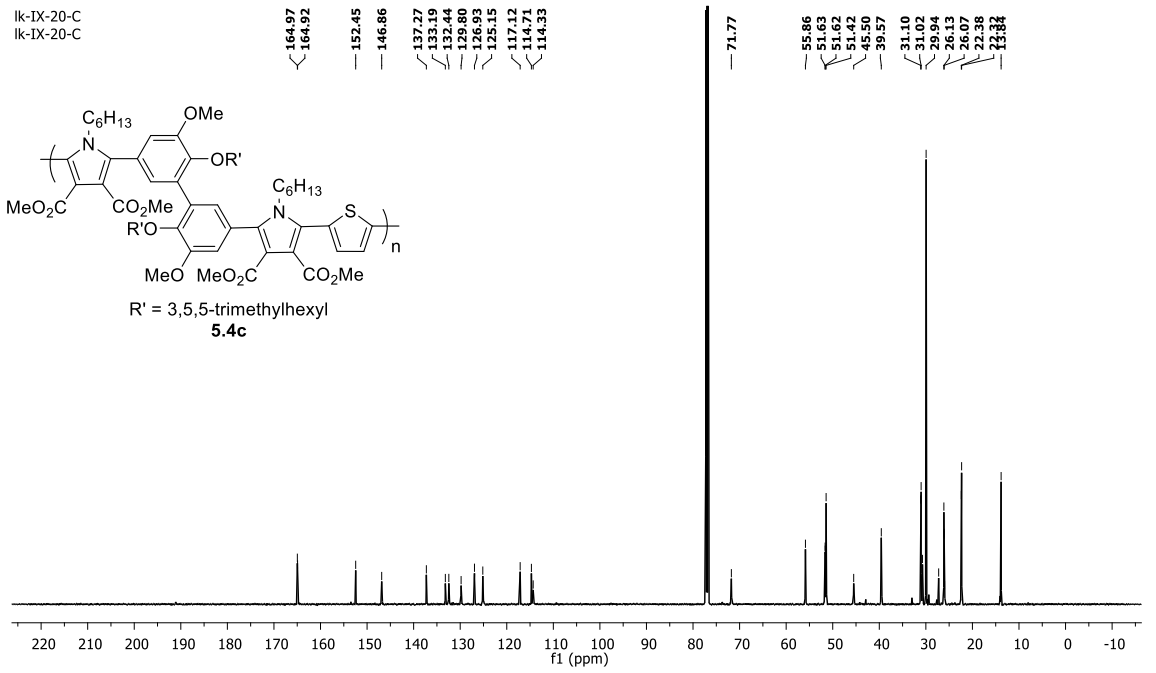
C.2 ^{1}H and ^{13}C NMR of **5.4b**



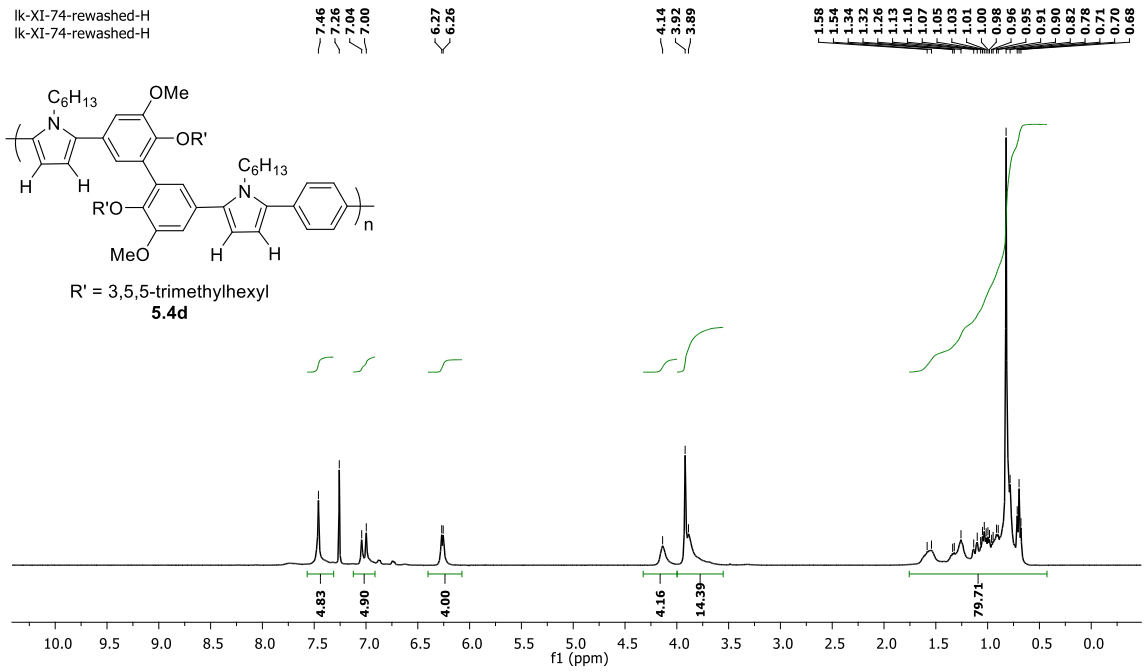


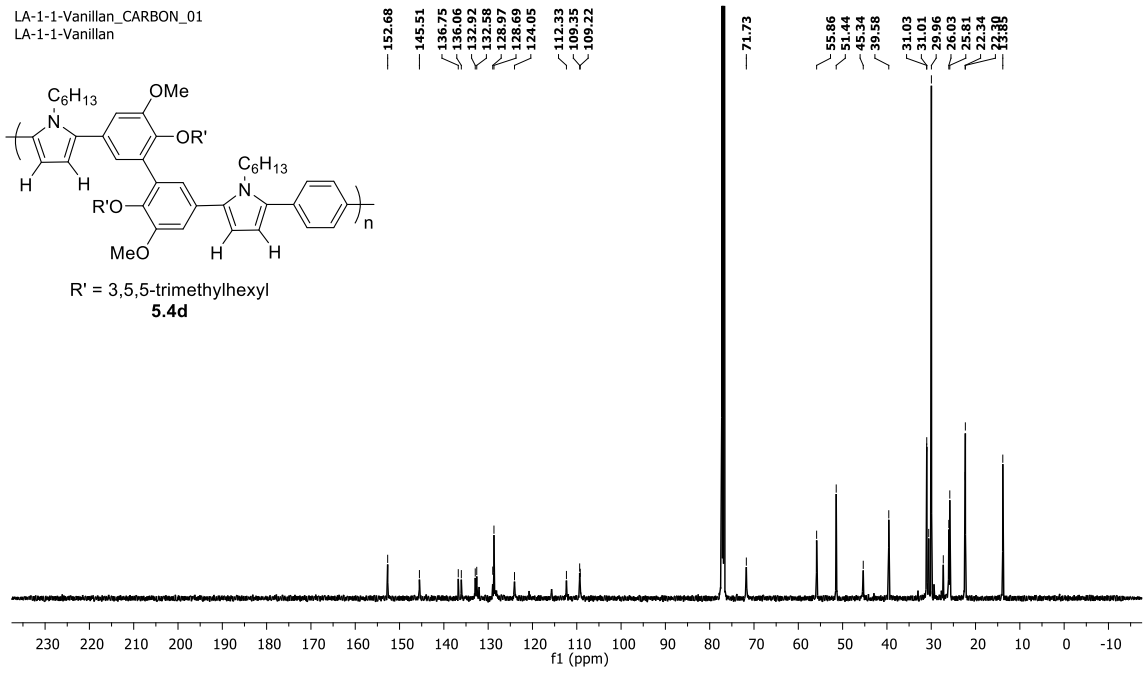
C.3 ^{1}H and ^{13}C NMR of **5.4c**



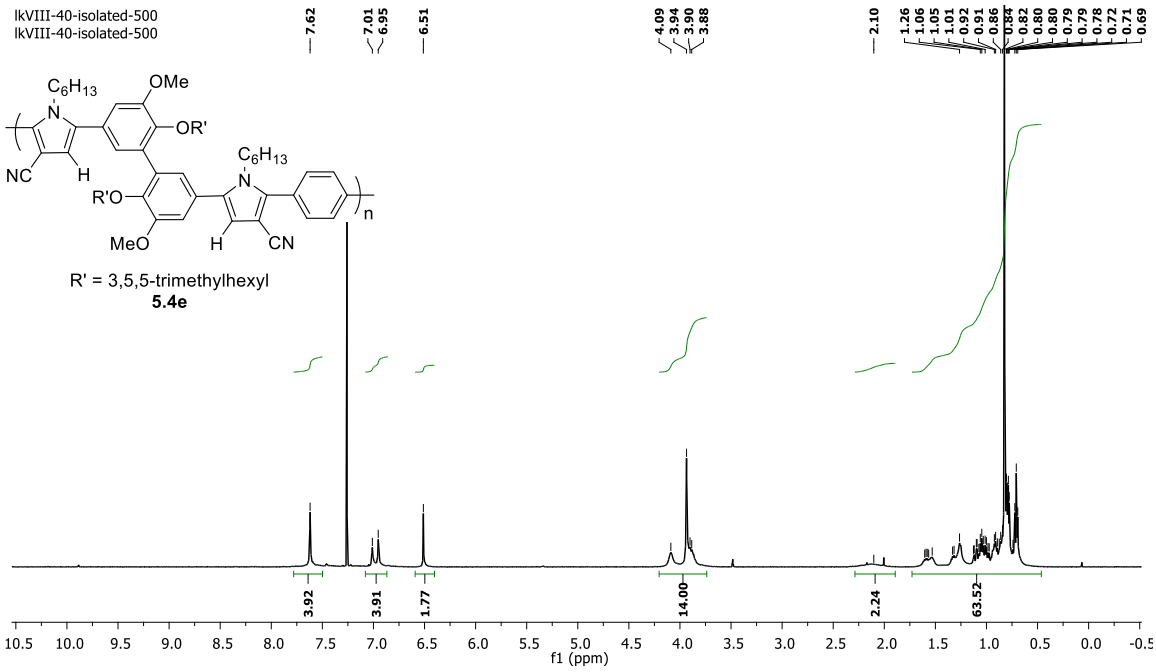


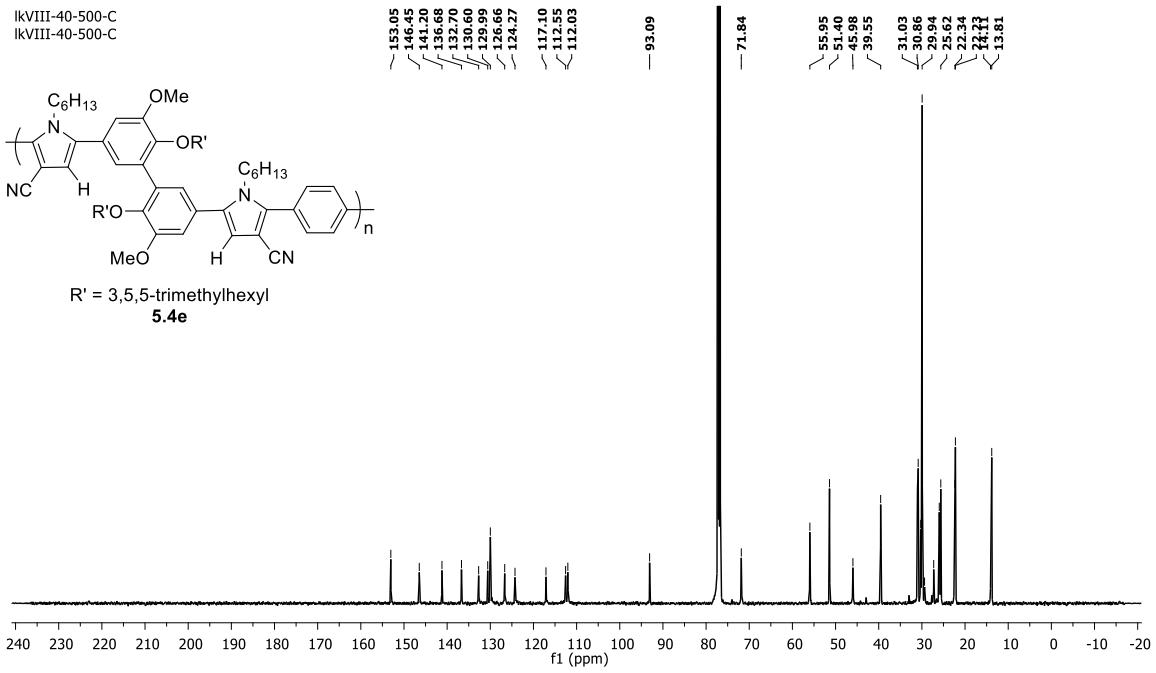
C.4 ^{1}H and ^{13}C NMR of **5.4d**



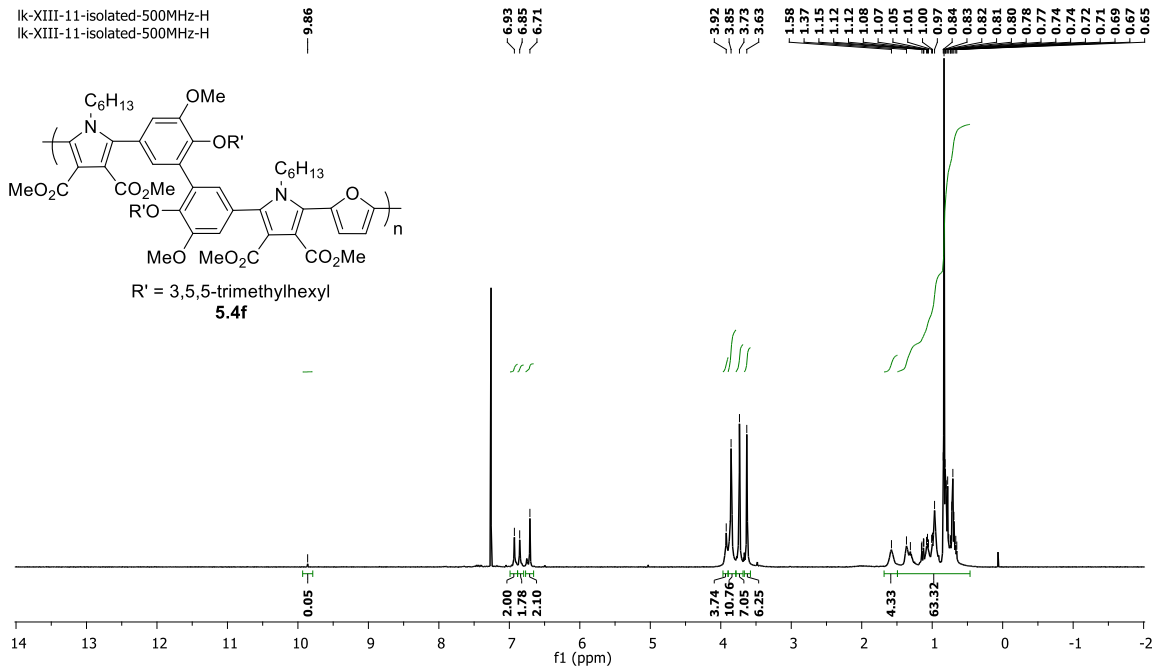


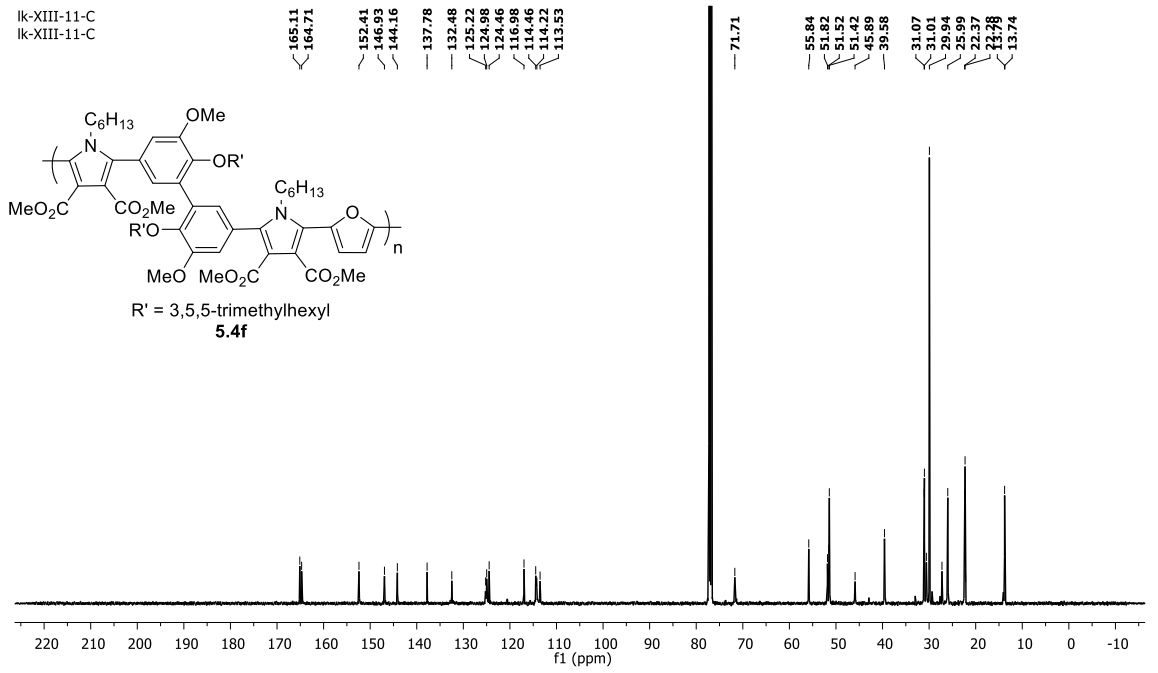
C.5 ^{1}H and ^{13}C NMR of **5.4e**



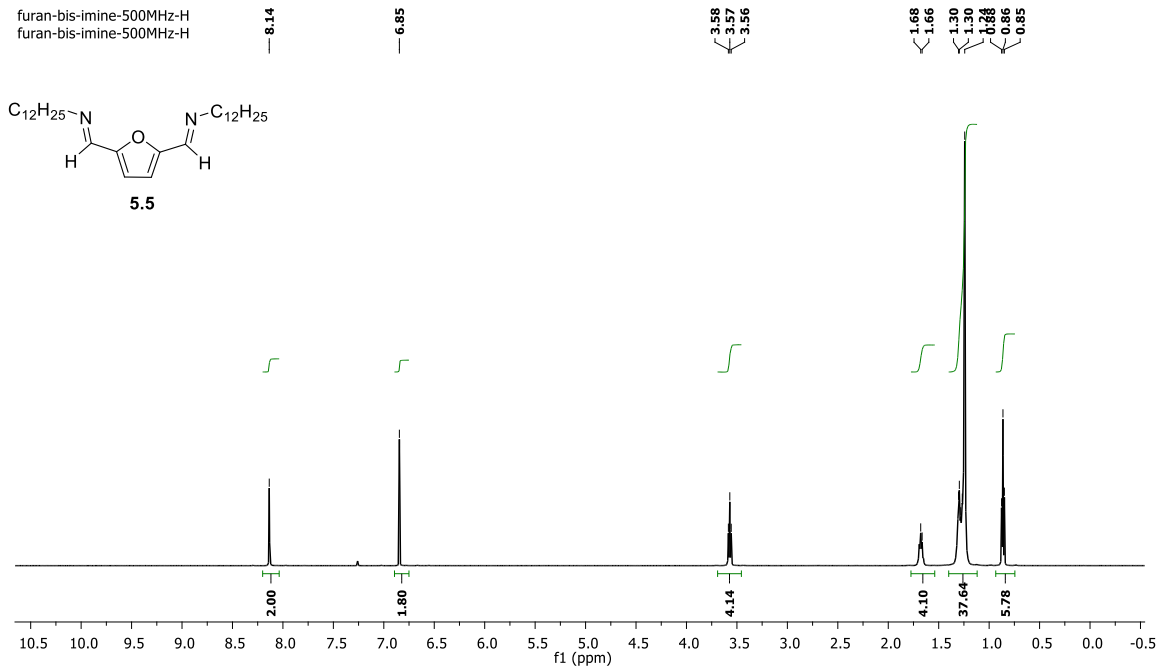


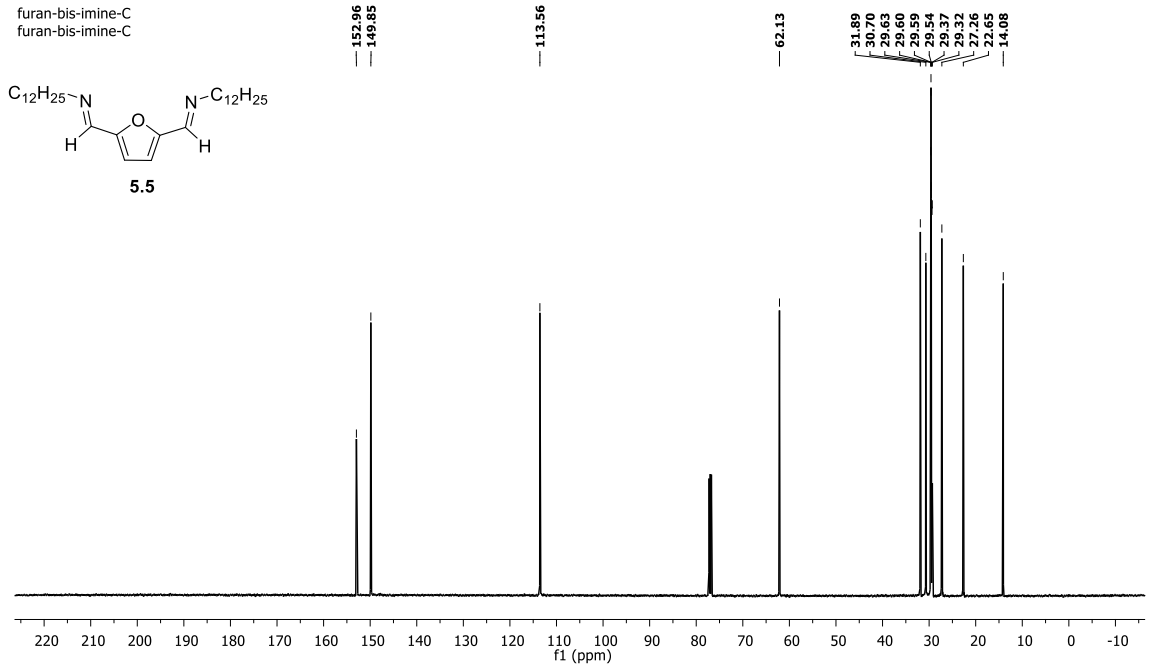
C.6 ^{1}H and ^{13}C NMR of **5.4f**





C.7 ^{1}H and ^{13}C NMR of **5.5**





C.8 ^{1}H NMR of **5.6**