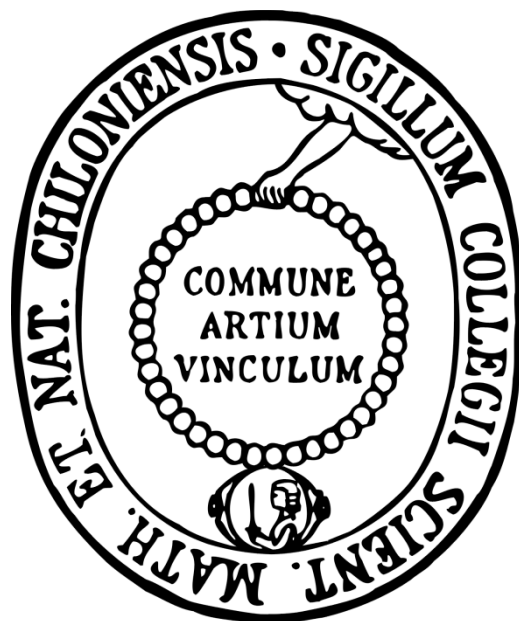

**Chemoselective Cross-Coupling Reactions as Tools
in Synthesis and Applications for Polymer Chemistry**



Dissertation

zur Erlangung des Doktorgrades

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Lu-Ying He

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First referee: Prof. Dr. Anne Staubitz

Second referee: Prof. Dr. Frank Sönnichsen

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gez. Prof. Dr. Wolfgang J. Duschl, Dekan

The work was under the supervision of

Prof. Dr. Anne Staubitz

Otto Diels Institute of Organic Chemistry

University of Kiel

Sep. 2011 to Mar. 2015

I, the undersigned, **Lu-Ying He**, declare under penalty of perjury, this dissertation
**“Chemoselective Cross-Coupling Reactions as Tools in Synthesis and Applications for
Polymer Chemistry”** is the result of my own work, apart from the advice of my
supervisor Prof. Dr. Anne Staubitz. It has been compiled and written independently by
me. It has not been previously submitted, either in whole or in part, to any other
university for any academic degree.

Place and date:

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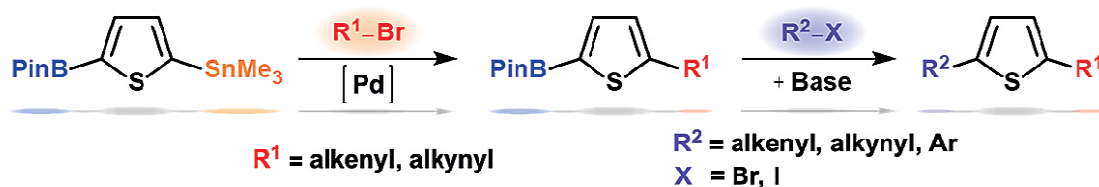
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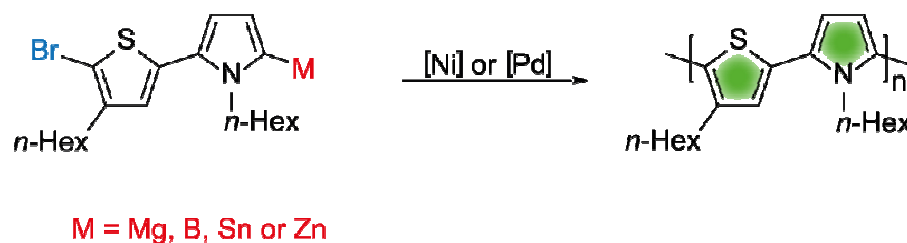
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Abstract

A nucleophile-selective cross-coupling reaction with vinyl and alkynyl bromides on a dinucleophilic thiophene bearing two metal groups, a boronic ester and a stannyl group, has been developed. The first nucleophilic site to react is the stannyl group, and subsequently, a Suzuki–Miyaura cross-coupling takes place after adding a second electrophile, base and water. The generality of the reaction was shown with various electron rich, electron neutral, electron poor vinyl bromides and alkynyl bromides. The roles typical in Sonogashira couplings or Heck reactions of the aromatic ring as the dielectrophile coupling to vinyl and alkynyl metal species are reversed, which presents a new tool for organic synthesis.

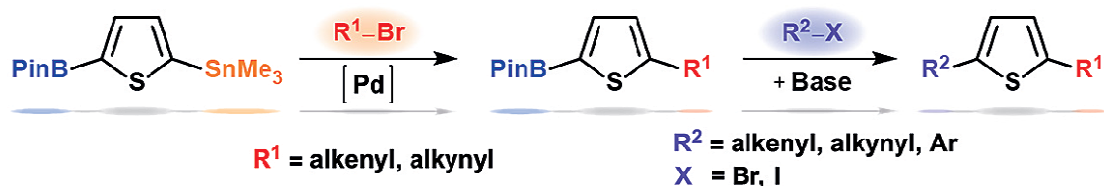


Four different difunctional thienylpyrrole monomers with a bromide group on the thienyl moiety and a metal group (Mg, B, Sn or Zn) on the pyrrole moiety were developed. Based on those monomers, π -conjugated poly(thiophene-*alt*-pyrrole)s **PTPs** were firstly synthesized via nickel and palladium catalyzed Kumada polycondensation from this A-B type monomer. The polymers were analyzed by NMR, IR, GPC, MALDI-MS, UV-vis, PL and TGA measurements.

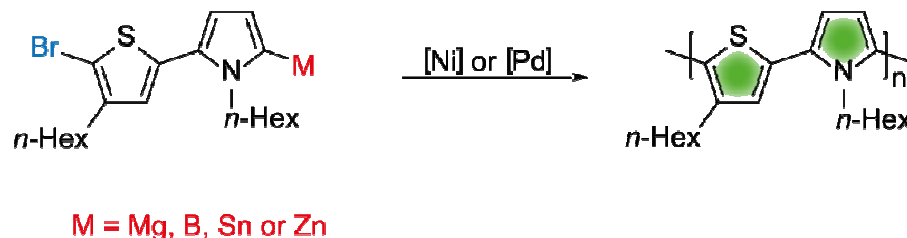


Zusammenfassung

Eine Nukleophil-selektive Kreuzkupplungsreaktion mit Vinyl- und Alkynyl-Bromiden an einem dinukleophilen Thiophen, welches mit zwei Metall-Funktionalisierungen, einem Borester- und einer Stannyl-Gruppe versehen ist, wurde entwickelt. Die erste reagierende nukleophile Seite ist die Stannyl-Gruppe mit anschließender Reaktion des Boresters im Rahmen einer Suzuki-Miyaura Kreuzkupplungsreaktion, für welche ein weiteres Nukleophil, eine Base und Wasser hinzugefügt wurden. Die Allgemeingültigkeit dieser Reaktion wurde anhand von verschiedenen elektronenreichen, -neutralen und -armen Vinyl- und Alkynyl-Bromiden gezeigt. Die typische Rollenverteilung in Sonogashira-Kupplungen und Heck-Reaktionen mit einem aromatischen Elektrophil welches mit Vinyl- und Alkynyl-Metall Spezies reagiert, sind umgekehrt, was ein neues Werkzeug in der organischen Synthese darstellt.



Es wurden vier verschiedene difunktionelle Thienyl-Pyrrol-Monomere mit einer Brom-Funktionalisierung an der Thienyl-Gruppe und einer Metall-Gruppe (Mg, B, Sn oder Zn) an dem Pyrrol-Rest entwickelt. Basierend auf diesen Monomeren konnten π -konjugierte Poly(thiophene-*alt*-pyrrol)e **PTPs** durch Nickel- und Palladium-katalysierte Kumada Polykondensationen von einem derartigen A-B Monomer synthetisiert werden. Die Polymere wurden mittels NMR, IR, GPC, MALDI-MS, UV-vis, PL und TGA Messungen analysiert.



Abbreviations

A	acceptor
ATR	attenuated total reflectance
calcd.	calculated
COSY	correlated spectroscopy
D	doublet (NMR)
D	donor
DEPT	distortionless enhancement by polarization transfer
DMF	<i>N,N</i> -dimethylformamide
EI	electron ionization
ESI	electrospray ionization
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
GPC	gel permeation chromatography
HMBC	heteronuclear multiple bond coherence
HOMO	highest occupied molecular orbital
HRMS	high resolution mass spectrometry
HSQC	heteronuclear single quantum coherence
IR	infrared
LUMO	lowest unoccupied molecular orbital
m	medium (concerning the intensity) (IR)
m	multiplet (NMR)
MALDI-MS	matrix-assisted laser desorption/ionization mass spectrometry
MEH-PPV	poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene)
M_n	number average molecular weight
MS	mass spectrometry
MTBE	methyl <i>tert</i> -butyl ether
MW	microwave
M_w	weight average molecular weight
NIS	<i>N</i> -iodosuccinimide
NMR	nuclear magnetic resonance
OFET	organic field effect transisto
OLED	organic light emitting diode
OPV	organic photovoltaic
P3AT	poly(3-alkyl)thiophene
PDI	polydispersity index
Pin	pinacol
PL	photoluminescence
PPV	polyparaphenylene vinylene
PPy	polypyrrole
PTV	poly(thienylene-vinylene)

PTP	poly(thiophene- <i>alt</i> -pyrrole)
R _f	retention factor
RFID	radio frequency identification
rr	regioregular
s	strong (concerning the intensity) (IR)
s	singlet (NMR)
T	triplet (NMR)
T _g	glass-transition temperature
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMS	tetramethylsilane
UV	ultraviolet
W	weak (concerning the intensity) (IR)

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1 Introduction

1.1 Semiconducting polymers

Since the discovery of the electrical conductivity of doped polyacetylene in 1977 by Shirakawa, MacDiarmid and Heeger,^[1] semiconducting polymers have attracted an increasing amount of attention as promising materials for the development and production of various organic electronic devices.^[2] Due to their potential advantages over inorganic materials, such as low cost, low overall weight and good mechanical flexibility organic electronics based on semiconducting polymers are a promising alternative to conventional inorganic solid state electronics. More importantly, soluble semiconducting polymers can be processed by high-throughput methodologies, such as spin-coating, inkjet printing, gravure and flexographic printing onto flexible substrates, which is crucial for the realization of cheap and large-scale roll-to-roll processing of printed electronics.^[3]

Nowadays, numerous and diverse organic electronics based on semiconducting polymers are available in the laboratory. Organic photovoltaics (OPVs) offer the exciting prospect of printable large-area solar cells. Organic field effect transistors (OFETs) are applied for low-cost and flexible electronics like radio frequency identification (RFID) tags. Organic lasers are potential compact sources of tunable, coherent light, and others. Many of the organic electronics are based on small molecule semiconductors and oligomers have even been commercially realized: for examples, organic light emitting diodes (OLEDs) are implemented in displays of mobile phones and television (Figure 1, left), and lamps using organic electroluminescence (Figure 1, right). For accelerating the market launch of polymer electronics, producing more cost effective, processable and well-defined polymers is necessary.



Figure 1. OLED TV by LG (Left) and OLED lamp by Blackbody (picture credits: press material LG^[4], with permission of Blackbody^[5])

Over the past three decades, a great number of semiconducting polymers have been synthesized and investigated towards their use in organic electronics, such as poly(*p*-phenylene vinylene) (**PPV**),^[6] poly(3-alkyl)thiophene (**P3AT**),^[7] polyfluorene (**PFO**),^[8] polypyrrole (**PPy**),^[9] polyaniline (**PANI**),^[10] and others (Figure 2). The side chains introduced in polythiophene and poly(*p*-phenylene vinylene) play a significant role in improving the solubility and processability, but they are also influencing the morphology and consequently the charge carrier mobility.^[11]

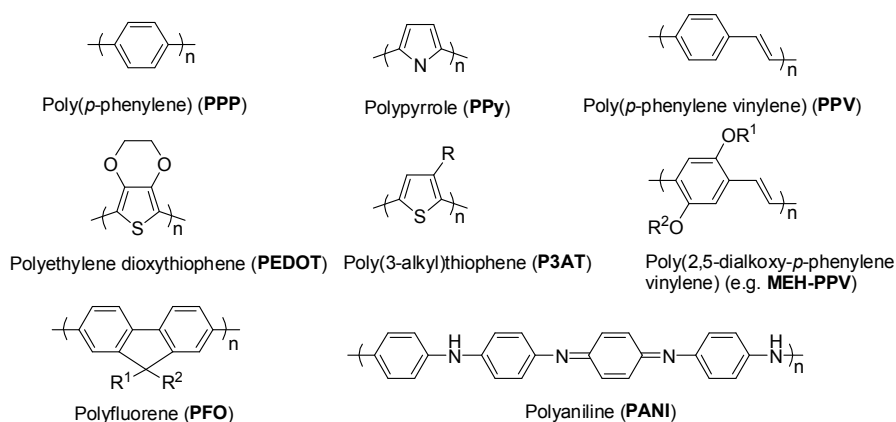


Figure 2. Molecular structures of selected important semiconducting polymers.

The reason why those polymers show semiconducting properties is the sp^2p_z hybridization of the carbon atoms in the repeat units.^[12] Semiconducting polymers are composed of σ -bonds (from sp^2 -orbitals) and alternating π -bonds (from overlapping p_z orbitals). The overlapping p_z orbitals ensure electron delocalization which makes the conjugated polymers semiconducting, as seen in band diagram (Figure 3). When the p_z orbitals of two carbon atoms are combined to form a π -bond, they split up into a bonding π -orbital (HOMO, highest occupied molecular orbital) and an anti-bonding π^*

orbital (LUMO, lowest unoccupied molecular orbital). The lower energy π -orbital (HOMO) is occupied by both p_z electrons, while the anti-bonding LUMO is empty. A consecutive combination of the p_z orbitals of two neighboring ethylene moieties leads to another two π and π^* orbitals. If all the p_z orbitals of a high molecular weight polymer are combined with each other, many increasing close energy levels result, and the gap between HOMO and LUMO is decreased. However, it is not possible to make the band gap disappear entirely even with a sufficiently long polymer chain due to the Peierls distortion, which leads to a partial localization of electrons by distorting the geometry of the polymers' backbone.^[13] The result is a small band gap ($E_g < 3$ eV) conjugated polymer which lies between that for an insulator ($E_g > 3$ eV) and a conductor ($E_g = 0$ eV). By excitation of electrons in the polymer chain, the electrons in the HOMO can be transferred into the LUMO (producing excitons) providing that the excitation energy (irradiation or thermal energy) is equal or higher than that of the band gap.

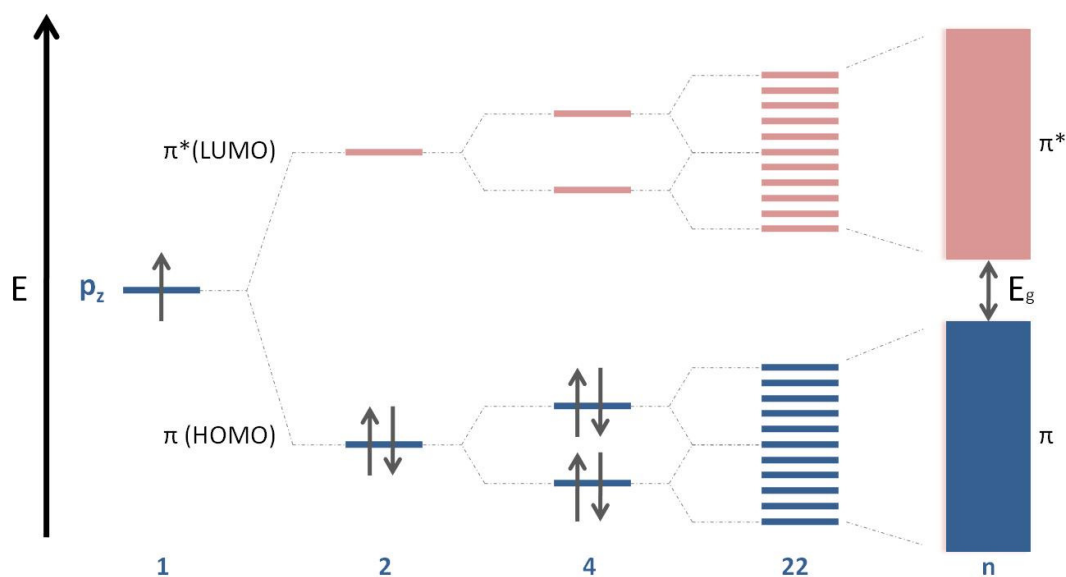


Figure 3. A schematic band diagram for semiconducting polymers (adapted from an article by Rehahn^[14]). The HOMOs and LUMOs can be described analogous to the valence and conduction bands of inorganic semiconductors.

The HOMO and LUMO energy levels and the band gap are the first of several general principles to be considered for the design of conjugated polymers for different and specific applications. For example, lower band gap conjugated polymers are more promising when considering the exciton dissociation and the absorption of sunlight for solar cells. There are three ways to narrow the band gap: 1) enlargement of the

π -systems,^[15] 2) using quinoidal instead of aromatic structures,^[16] 3) integration of donor–acceptor (D–A) functional units.^[17] Among those methods, the D–A approach is a quite efficient way to tune both the HOMO and LUMO energy levels by introducing alternative electron rich and electron poor building blocks into the polymer chain, where the HOMO is mainly located at the donor unit, and the LUMO is mainly located at the acceptor unit (Figure 4).^[18] Therefore, both HOMO and LUMO energy levels and hence the band gaps can be well tuned.^[19] There are already many semiconducting polymers containing D–A functional units (Figure 5), which have been successfully used in tailoring the properties for application in OPVs^[20] and OFETs.^[11, 21]

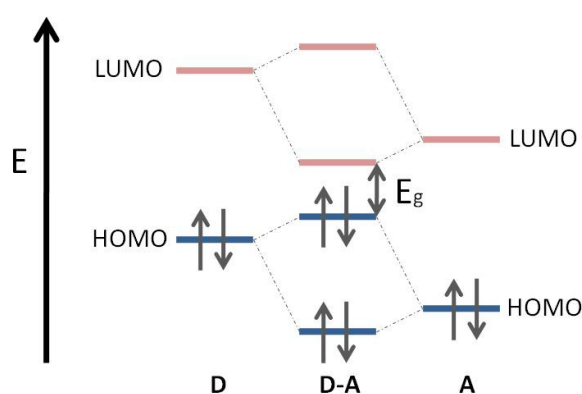


Figure 4. Hybridization of the energy levels of donor and acceptor units leads to a narrow band gap (adapted from an article by Meijer and coworkers^[22]).

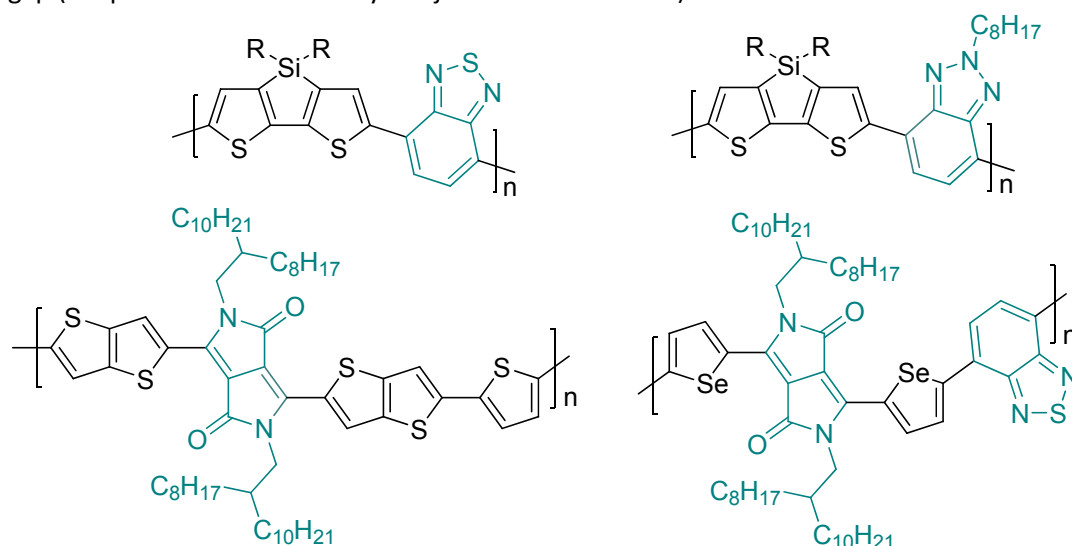


Figure 5. Some examples of low band gap semiconducting polymers contain D–A units (donor units are in black, acceptor units are in blue).^[23]

1.2 Synthesis of alternating semiconducting copolymers

The general synthetic route for preparing soluble conjugated alternating copolymers

is the transition-metal-catalyzed step growth polymerization. Mostly, these are conducted by Stille or Suzuki cross-coupling reactions between two monomers: one is functionalized with two metal groups ($M = \text{Sn}, \text{B}$), the other one with two halides ($X = \text{Br}, \text{I}$) (Figure 6). This method yields perfectly alternating copolymers, but also results in a high polydispersity index ($\text{PDI} = M_w/M_n$), poor regioselectivity when the non-symmetrical monomers contain flexible alkyl chains (Figure 7), and quite often relative small molecular weights. These parameters have a strong impact on the morphology of the resulting polymers which in turn affects the charge carrier mobility and subsequently the overall performance of the organic electronic devices.

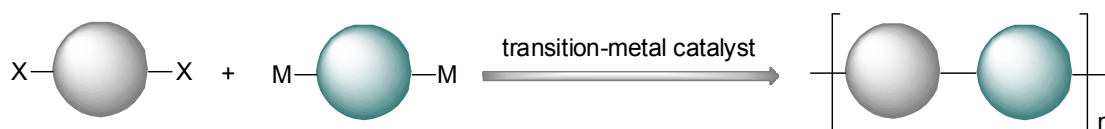


Figure 6. General method for preparing conjugated alternating copolymers by step growth polymerization.

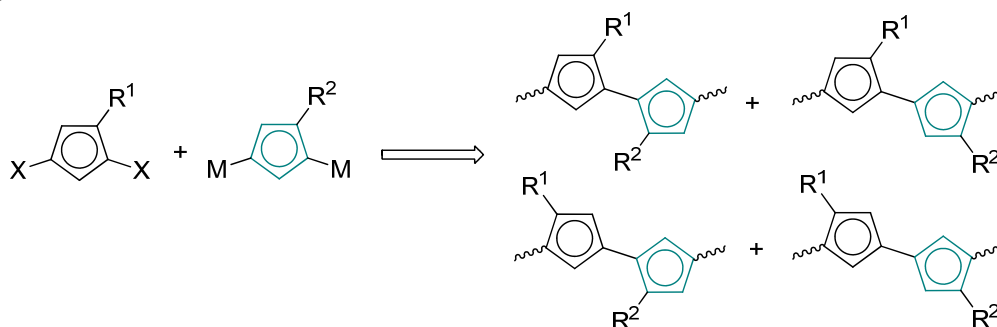
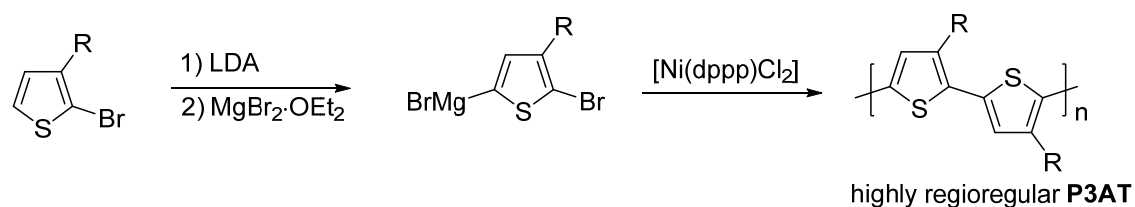


Figure 7. The four different possibilities of the coupling of two different monomers which result in the poor regioselectivity.

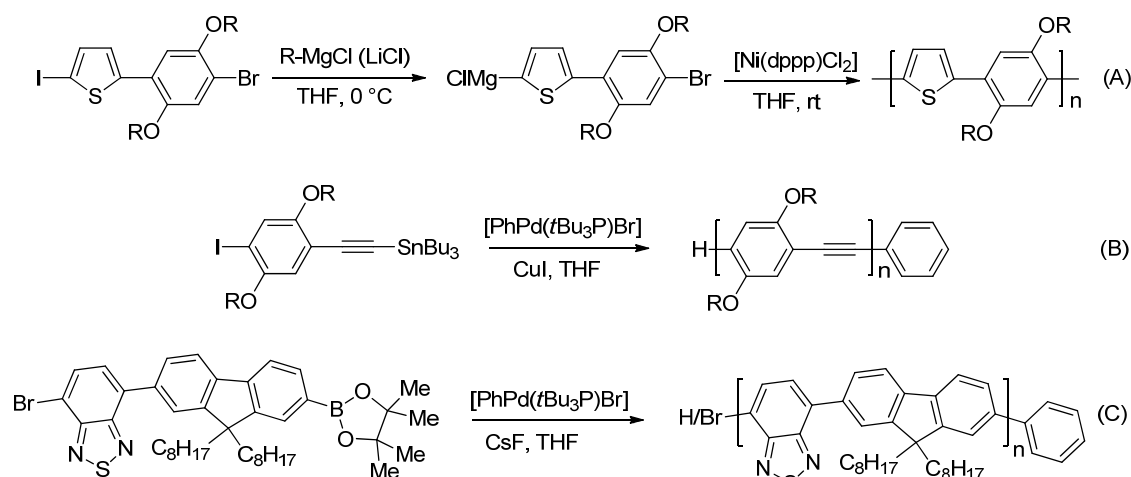
However, in 1992, a polymerization for highly regioselective poly(3-alkylthiophene)s based on a Kumada cross-coupling reaction was developed by McCullough.^[24] Here, the highly regioselective polymer was synthesized from a bifunctional monomer ($X\text{-Ar-M}$) with both a metal and a halogen functional group (Scheme 1). For over 10 years, it was believed that this reaction would follow a typical step growth mechanism until Yokozawa and coworker found that the polymerization could be described as a quasi-living chain growth in 2004.^[25] This finding was independently confirmed by McCullough in the same year. Using this method, it is not only possible to obtain a highly regioselective polymer, but also relatively narrow PDIs. It was further possible to control the molecular weight of the polymer by the amount of catalyst and the

reaction time. In addition, specific terminal groups could be introduced, and a second monomer could be added after polymerization of the first monomer to afford block copolymers. This Grignard metathesis method has been applied in the synthesis of other electron-rich polyarenes, such as polyselenophene,^[26] polyfluorene,^[27] polypyrrole,^[28] poly(dialkoxyphenylene)^[29] and poly(bithienyl- methylene)s^[30], as well as electron-deficient polymers, such as polypyridines,^[31] poly(benzotriazole)^[32] and polythiazoles.^[33] Moreover, it has been used to synthesize block^[34] and gradient copolymers.^[35] With this new method, more and more exciting and new materials are available and great progress was made in the field of organic electronics, as these regioregular polymers showed dramatically enhanced electrical properties compared to the regioirregular polymers.^[36]



Scheme 1. Chain growth polymerization for the preparation of highly regioregular **P3AT** was developed by McCullough.^[24]

Using these findings, it is highly desirable to apply the quasi-living chain growth polymerization to synthesize conjugated alternating copolymers, especially with D-A alternating units. In order to prepare the conjugated alternating copolymers by chain growth polymerization, a difunctional monomer of type X-Ar¹-Ar²-M (X = halogen, M = Mg, Zn, B, Sn and other metals) must be developed for the polycondensation. The monomers based on magnesium or zinc are generally too active for isolation and must be prepared *in situ* before being polymerized with a catalyst; While the monomers functionalized with boron or tin can be purified and isolated. However, their synthesis is rather difficult, which is an important factor why this type chain growth polymerization is not more widespread. In 2012, Bielawski and coworkers reported the first controlled, quasi-living chain-growth synthesis of a conjugated alternating copolymer, poly(thiophene-*alt-p*-phenylene), via a Kumada catalyst transfer polycondensation of a difunctional Grignard-type monomer (Scheme 2A).^[37] There were also a few conjugated alternating copolymers synthesized via a chain growth Stille or Suzuki polymerizations from pure and isolable monomers, as shown in Scheme 2(B, C).^[38]



Scheme 2. Chain growth polymerization for conjugated alternating copolymers by Kumada coupling (A),^[37] Stille coupling (B),^[38b] and Suzuki coupling (C).^{[38a]1}

Irrespective of whether a step growth or a chain growth polymerization is used to synthesize conjugated alternating copolymers, it is inevitable to form carbon-carbon bonds between two different units for making monomers or polymers. Cross-coupling reactions have evolved over the past 40 years into one of the most widely applicable methods for C-C bond formation^[39] since the discovery of the Ni-catalyzed reaction of Grignard reagents with vinyl or aryl halides in 1972.^[40] Cross-coupling reactions pervade all areas of organic synthesis^[41] from the synthesis of natural products,^[42] pharmaceuticals^[43] to agrochemicals^[44]. They are also key steps in building polymers,^[45] which can be used as organic conductor or semiconductor with novel electronic, optical or mechanical properties.

1.3 Cross-coupling reactions

Cross-coupling reactions involve an organic electrophile (R^1-X) and an organometallic nucleophile (R^2-M') in the presence of a catalyst $[M]$ (Figure 8). The catalysts most widely employed are transition metals from groups 8-10, especially complexes of palladium and nickel. Cross-coupling reactions are often classified depending on the metal or semimetal present in the nucleophile. For example, the Suzuki-Miyaura is boron-mediated, the Stille reaction is tin-mediated, the Kumada reaction is magnesium-mediated, the Negishi reaction is zinc-mediated and others. It is generally

¹ Although this article was published in 2011, which was earlier than the article by Bielawski, there was no proof that the polymerization was a quasi-living polymerization.

accepted that cross-coupling reactions follow a catalytic cycle consisting of three main steps (Figure 9): oxidative addition, transmetalation, and reductive elimination.

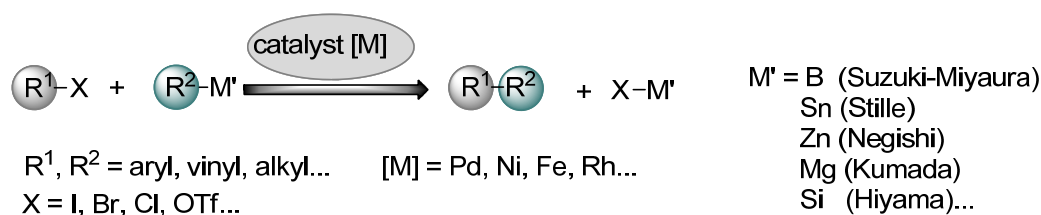


Figure 8. General cross-coupling reactions.

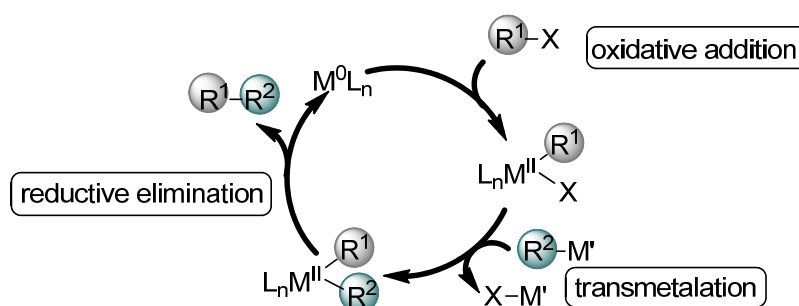


Figure 9. General catalytic cycle for cross-coupling reactions.

In the oxidative addition step, the electrophile (R^1-X) is added to the catalyst [M^0] complex to generate an [M^{II}] intermediate. There are two main pathways to obtain the intermediate (Figure 10): a concerted pathway and an S_N2 -type pathway.^[46] In the concerted pathway, $M'-C$ and $M'-X$ bonds are formed simultaneously to get a three-centered σ complex, followed by intramolecular ligand bond cleavage to form the oxidized complex. The S_N2 -type pathway is an associative bimolecular process that consists of two steps: first, nucleophilic attack by the metal center at the less electronegative atom in the electrophile leads to cleavage of the R^1-X bond, to form an cationic [$M-R^1$]⁺ species and anion X^- ; subsequently, the two charged species combine rapidly to obtain the oxidized complex.

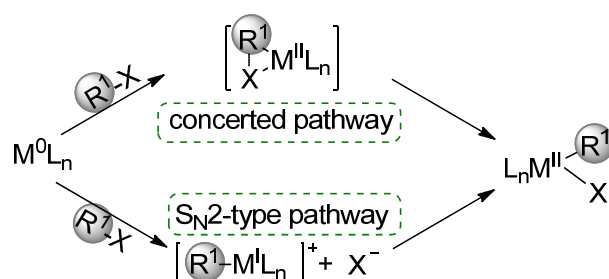


Figure 10. Proposed reaction mechanisms for oxidative addition of cross-coupling reactions.^[46]

Transmetalation is the key and most characteristic step of cross-coupling reactions. In this step, the organic group R^2 of the nucleophile (R^2-M') is transferred to the [M^{II}]

intermediate. The mechanisms depend on the particular cross-coupling reactions since they differ in the nucleophile used. The mechanisms of the Suzuki-Miyaura, and the Stille coupling reactions will be presented as they were key steps in this work. A Suzuki-Miyaura cross-coupling takes place between an organic halide (or triflate) and an organoboron species ($R^2\text{-BY}_2$) in the presence of a palladium catalyst and a base (e.g., NaOH, K_3PO_4 , Na_2CO_3 , CS_2CO_3 , $NaHCO_3$, NaOAc). For a long time, the role of the external base was not clear, and several proposals have been made.^[47] It is widely believed that the role of the base is to activate the organoboron compound by forming an organoborate species as well as to facilitate the formation of the more reactive palladium complex $[R^1\text{-PdL}_n\text{-O}^t\text{Bu}]$ from $[R^1\text{-PdL}_n\text{-X}]$ by substitution reaction (Figure 11).^[48] In addition, the reductive elimination step is also accelerated by the reaction of base with $trans\text{-}[R^1\text{PdR}^2\text{L}_2]$.^[49]

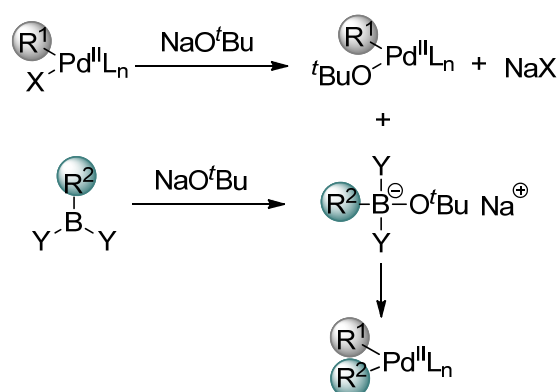


Figure 11. Proposed reaction mechanisms for transmetalation in the Suzuki-Miyaura coupling.^[46]

Stille coupling takes place between an organic halide (or triflate) and a stannane $R^2\text{-SnR}_3$. The most common types of transmetalation for the Stille coupling involve a cyclic mechanism or an open mechanism (Figure 12).^[46, 50] The cyclic process has been shown to proceed in two steps: associative ligand substitution followed by the transmetalation reaction through a cyclic transition state. Then the X group leaves bound to the tin atom, which results in a palladium complex with R^1 and R^2 present in a *cis* conformation. The open process involves the same initial addition of the organostannane to the *trans* palladium complex as the cyclic process; however, the X group does not coordinate to the tin, producing an open transition state.

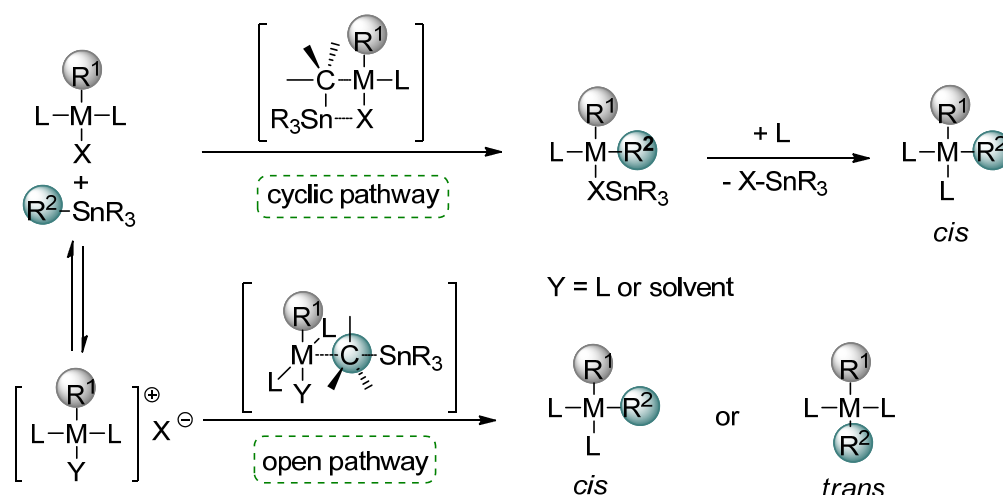


Figure 12. Proposed reaction mechanism for transmetalation in Stille coupling.^[46]

The following reductive elimination consists of the combination of R^1 and R^2 . This process requires both organic groups to occupy coordination sites *cis* to one another. Any *trans* complex resulting from transmetalation must isomerize to the *cis* intermediate before this process. A variety of mechanisms exist for reductive elimination and the generally accepted one is a concerted process (Figure 13).^[51] A cyclic three-coordinated transition state results in the final coupling product and the regeneration of the catalyst species.

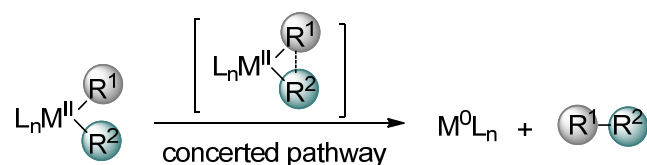


Figure 13. General mechanism for reductive elimination in cross-coupling reactions.^[46]

1.4 Undesired homo-coupling in cross-coupling reactions

Highly satisfactory cross coupling reactions are those that are generally applicable and are capable of selectively providing the desired products in high yields, while avoiding all or most of the side reactions, like homo-coupling, β -hydride elimination, isomerization and others. The most common side reactions associated with the cross-coupling reaction are undesired homo-coupling reactions to form R^1-R^1 and R^2-R^2 dimers (Figure 14). The oxidative homo-coupling leading to byproducts such as R^1-R^1 may occur if oxygen is not rigorously excluded.^[52] Besides, there are some other possible pathways leading to homo-coupled byproducts, such as 1) halogen-metal exchange between the organic halides (R^1-X) and transmetalating reagent (R^2-M'),^[53] 2)

reductive elimination between a $[M^{II}]$ complex and transmetalating reagent (R^2-M'), 3) exchange of organic groups (R^1 and R^1) between $[M^{II}R^1XL_n]$ and the transmetalating reagent (R^1-M'),^[54] 4) reductive elimination from a $[M^{III}]$ complex,^[55] 5) metathesis reaction of $[M^{II}R^1XL_n]$,^[56] 6) reactions via radical chain mechanism or reductive elimination from a $[M^{IV}]$ complex.^[57]

After oxidative addition of organic halides (R^1-X) to the $[M^0L_2]$ complex, the resulting $[M^{II}R^1XL_2]$ intermediate may undergo four reaction processes (A, B, C and D) affording homo-coupling byproducts (Figure 14):

Process A involves exchange of organic groups R^1 and R^2 between $[M^{II}R^1XL_2]$ and the transmetalating reagent R^2-M' to generate a mixture of two organometallic $[M^{II}]$ complexes $[M^{II}R^1XL_2]$ and $[M^{II}R^2XL_2]$ and two transmetalating reagents (R^1-M' and R^2-M'), from the four compounds, cross-coupled and homo-coupled products can be formed. This proposed mechanism was first described by Elsevier and coworkers for coupling reactions of organic halides with organomagnesium, -zinc and -tin reagents catalyzed by $[Pd(Ar-BIAN)]$ complex.^[54a] Other mechanisms which could in principle lead to the formation of homo-coupled byproducts were excluded according to experimental data. This process has been observed also in the $[trans-Pd(CH_2Ph)X-(PPh_3)_2]$ complexes.^[54b, 54c]

Process B involves further oxidative addition of R^1-X to $[M^I RL_n]$ generated by chemical or electrochemical reduction of $[M^{II}RXL_n]$. The reaction forms $[M^{III}R^1_2XL_n]$, which reductively eliminates R^1-R^1 . This type of process was originally proposed for the coupling of aryl chlorides by nickel catalysis and reducing metals in polar solvents by Colon and Kelsey^[55a] and expanded to palladium-catalyzed systems by Amatore and Jutand.^[55b-e]

On the other hand, process C involves metathesis of two $[M^{II}R^1XL_2]$ intermediates to give $[M^{II}R^1_2L_2]$ and $[M^{II}X_2L_2]$. The former forms R^1-R^1 on reductive elimination, and the latter can be reduced to $[M^0L_2]$ by transmetalating reagent R^2-M' to form R^2-R^2 . Similarly, Kochi^[58a, 59] proposed a metathesis of $[Ni^{III}ArX_2L_n]$ and $[Ni^{II}ArXL_n]$ in a radical chain mechanism to give $[Ni^{III}Ar_2XL_n]$ and $[Ni^{II}X_2L_n]$, of which the former underwent reductive elimination to afford biaryl compound $Ar-Ar$ and generated species, which reacts with $[Ni^{II}X_2L_n]$ to afford $[Ni^{III}Ar_2XL_n]$. Recently, Ozawa and coworkers^[58b] reported a metathesis of $[Pd^{II}styrylXL_2]$ and $[Pd^{II}styrylXL]$ generated $[Pd^{II}styryl-styrylL]$ and

$[\text{Pd}^{\text{II}}\text{X}_2\text{L}_2]$ the former gave homo-coupled byproduct 1,4-diphenylbutadiene via reductive elimination. In this reaction, $[\text{Pd}^{\text{II}}\text{styrylXL}_2]$ was generated via P-C reductive elimination of $[\text{Pd}^{\text{II}}\text{styrylXL}_2]$.

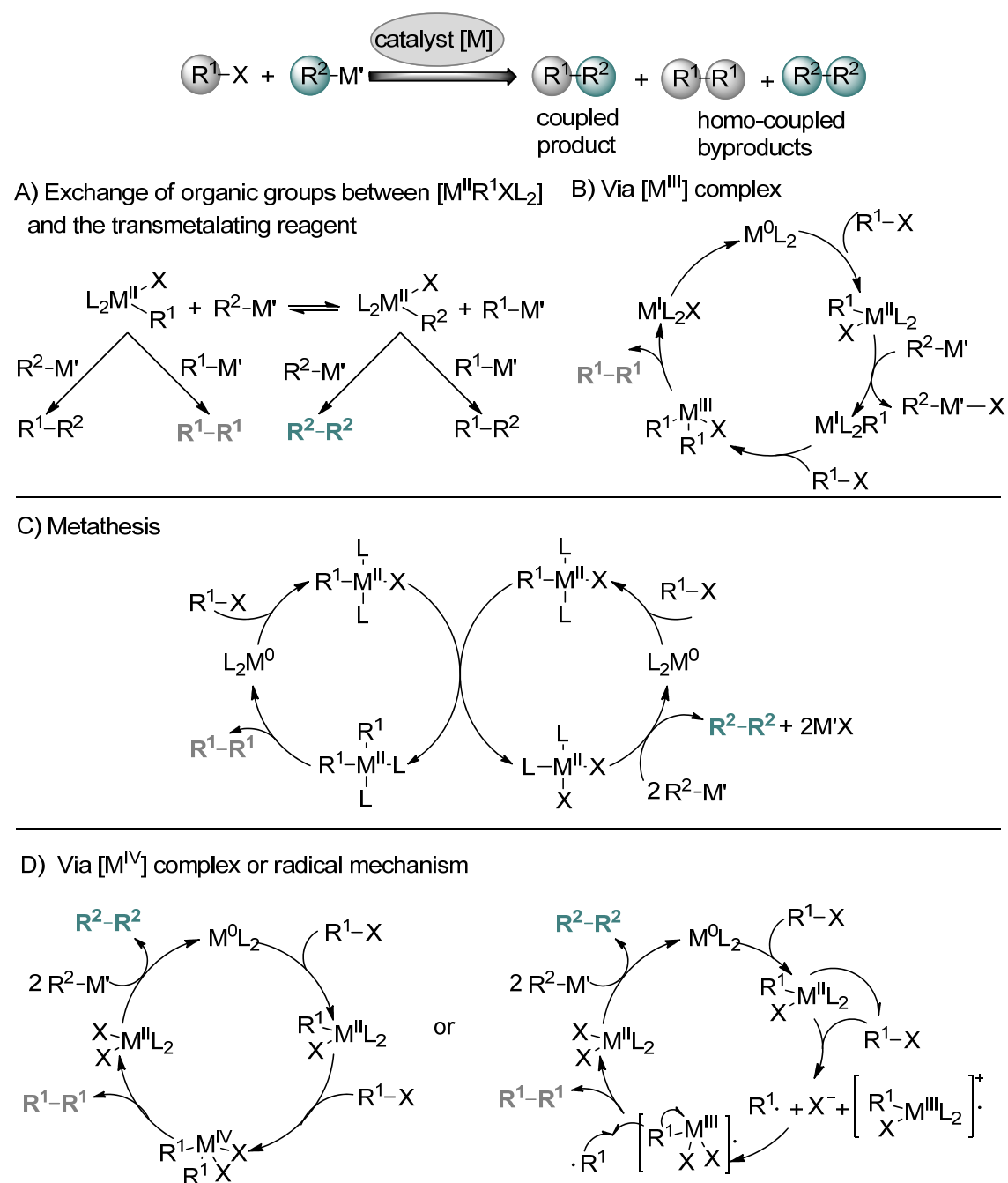


Figure 14. A selection of possible mechanisms for homo-coupling processes previously reported^[54a, 58] (adapted from an article by Weix^[58c]).

In the case of process D, two different mechanisms were proposed: two sequential oxidative addition steps to form a $[\text{M}^{\text{IV}}]$ intermediate^[60] or a radical chain mechanism.^[61]

1.5 Selective cross-coupling reactions

The optimization of reaction conditions can avoid all or most of the side reactions, which would increase the overall product yields. However, to generate highly satisfactory cross-coupling reactions for the preparation of more complex organic structures, highly selective cross-coupling reactions are essential. Research on selective cross-coupling reactions regarding the electrophiles (differentiating between X^1-R-X^2 ($X = I, Br, Cl, OTf, \text{etc.}$)) has been intensively pursued.^[62] The reactivity of the electrophilic component relies on the leaving group X ; the order of the reactivity of halides and triflates is in general $I > Br > OTf >> Cl$ for the cross-coupling reaction of boron reagents.^[63] In contrast, nucleophile selective cross-coupling reactions using dimetallic substrates have hardly been examined.^[64] Most of the reports are associated with hetero-bis-metallic alkenes containing tin/boron or boron/boron (Figure 15).^[64a-e, 64g, 64i-m] As Stille (Sn) and Suzuki-Miyaura (B) cross-coupling reactions require very different reaction conditions, the tin/boron alkenes can be used as an orthogonal Stille and Suzuki-Miyaura coupling partners in a one-pot reaction. Relying on those useful tin/boron alkenes a sequential Stille and Suzuki-Miyaura coupling strategy has been implemented in organic synthesis (Scheme 3),^[64k] which could decrease the reaction steps, improve the yield and even allow access to new compounds. The unsymmetrical boron/boron reagent could also be used in a highly selective Suzuki-Miyaura coupling, affording coupling products in which the protected boronyl group is left intact as their reactivities differentiated by the protective groups onto one of the two boron atoms.^[64a-h]

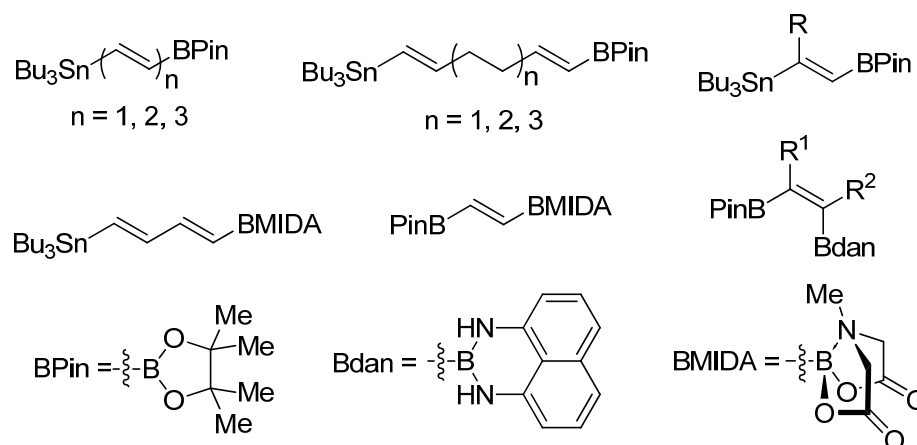
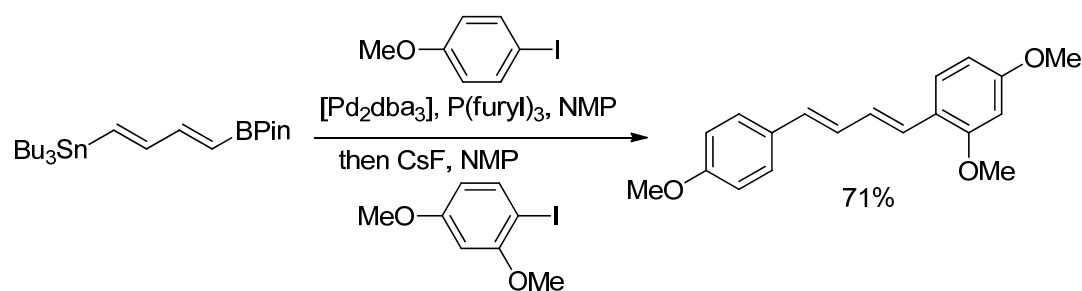


Figure 15. Some examples of hetero-bis-metallic alkenes. ^[64a-e, 64g, 64i-m]



Scheme 3. One-pot sequential Stille/Suzuki-Miyaura coupling reaction with bis-metallic butadiene.^[64k]

There are only a few examples of hetero-bis-metallic aromatic compounds for chemoselective cross-coupling reactions.^[64n-p, 65] The benzene derivative p - $\text{Bu}_3\text{Sn-C}_6\text{H}_4\text{-B(OR)}_2$ was first reported by Nemoto and coworker for a selective cross-coupling reaction with two protected nucleosides, while the boron group remained.^[64n] A nucleophile selective one pot reaction was developed recently on a new thiophene building block containing both a stannyl group and a boronic ester functional group in Staubitz' group (Figure 16A).^[64p] Furthermore, this reaction was extended to both nucleophile and electrophile selective cross-coupling reactions with aromatic rings based on the bis-metallic thiophene (Figure 16B).^[64o] For both reactions, excellent chemo-selectivity was observed in Stille coupling with mono-halogenated or di-halogenated electrophiles in high yields.

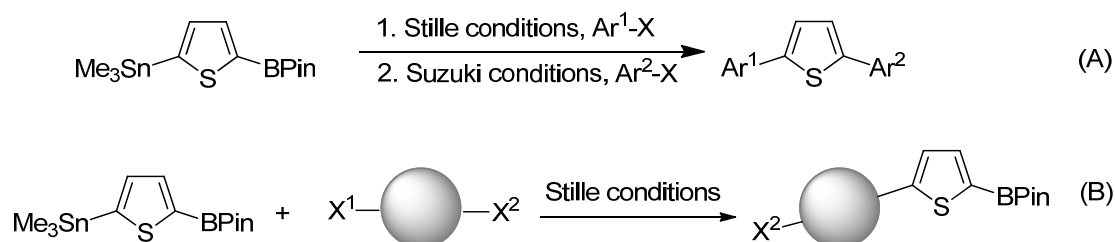


Figure 16. Selective cross-coupling reactions based on hetero-bis-metallic thiophene.^[64o, 64p]

In order to develop the nucleophile selective cross-coupling reactions, more bis-metallic substrates are essential and it is also important to extend this methodology to different types of electrophiles, such as vinyl and alkynyl halides. Double and triple bonds are also very important functional groups that can be introduced by cross-coupling methods. Vinylene and ethynylene-based materials, like poly(p -phenylene vinylene) (**PPV**), poly(thienylene-vinylene) (**PTV**), poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (**MEH-PPV**), have shown potential applications in OLEDs,^[66] OPVs,^[67] and others. Incorporating vinylene or ethynylene

linkages between the aromatic rings could increase charge carrier mobility, the degree of co-planarity, and lower the band gap of molecules.

2 Objectives

Conjugated alternating copolymers have shown promising applications in organic devices. An advantageous synthetic route for preparing soluble conjugated alternating copolymers is the quasi-living chain growth polymerization from a single monomer containing a halogen and a metal functional group (Chapter 1.2). However, the synthesis of this kind of monomers is rather difficult, which is an important factor hindering the development of the polymerization method. Therefore, in order to expand the synthetic methods for difunctionalized monomers, nucleophile selective cross-coupling reactions should be developed (Figure 17). The nucleophile should contain two different metal functional groups, which allow one metal to react in the first coupling reaction, and the other metal reacts under slightly different conditions (Chapter 3.1). As semiconducting polymers incorporating vinylene or ethynylene linkages have shown highly interesting properties, vinyl and alkynyl halogens would be introduced as electrophiles. After the first coupling reaction, further halogenation of the resulting molecule would produce a compound containing both a metal and a halogen functional group.

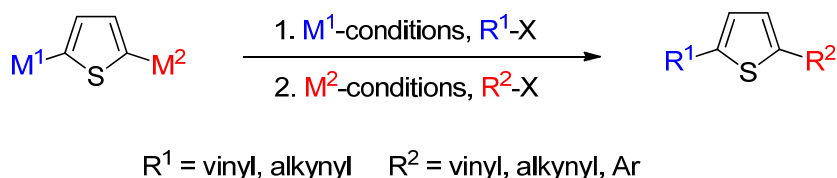
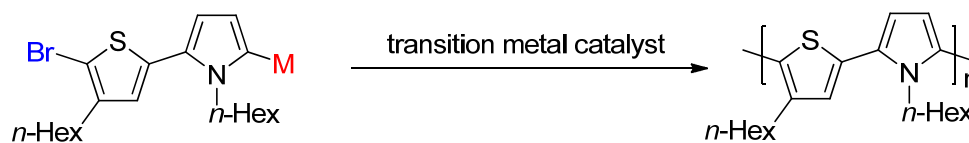


Figure 17. The nucleophile selective cross-coupling reactions between vinyl and alkynyl halogens and dinucleophilic thiophene.

Among conjugated alternating copolymers, the combination of thiophene with other heterocycles has led to distinct improvements in device performance. However, poly(thiophene-*alt*-pyrrole) have hardly been examined, even though in all the conjugated polymers, polythiophenes and polypyrroles are centrally important and have been widely investigated as potential materials for organic electronics.^[68] The common method to prepare copolymers of thiophene and pyrrole are electrochemical polymerization.^[69] However, this method may lead to significant branching and regioirregular polymers. Thus, difunctional thienylpyrrole monomers with a halogen on the thienyl moiety and a metal on the pyrrole moiety were to be prepared. This kind of monomer is highly desirable as it has the potential to make the polymerization via a

quasi-living chain growth mechanism.^[70] Based on this monomer, π -conjugated poly(thiophene-*alt*-pyrrole) **PTP** was to be synthesized (Scheme 4) and the optical and thermal properties of this polymer were to be investigated (see chapter 3.2 and 3.3).



Scheme 4. Poly(thiophene-*alt*-pyrrole) will be synthesized from dicunctionalized monomers.

3 Results and Discussion

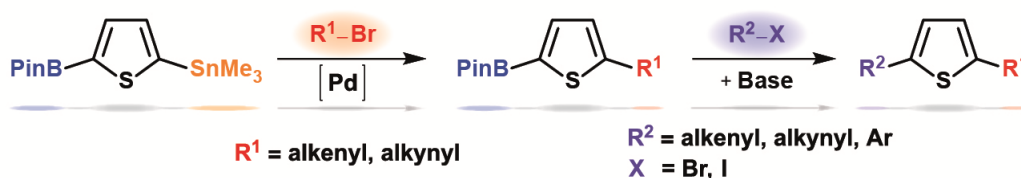
3.1 Chemoselective cross-coupling reactions

“Nucleophile Selective Cross-Coupling Reactions with Vinyl and Alkynyl Bromides on a Dinucleophilic Aromatic Substrate”

Lu-Ying He, Mathias Schulz-Senft, Birk Thiedemann, Julian Linshoeft, Paul J. Gates and Anne Staubitz, *Eur. J. Org. Chem.* **2015**, 14, DOI: 10.1002/ejoc.201500138

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A nucleophile selective cross-coupling reaction on an aromatic compound bearing two metal groups, Bpin and SnMe₃, has been developed. Previously, only aryl bromides and iodides could be used as electrophilic components, but in this work, the scope could be extended to vinyl and alkynyl bromides as electrophiles. This means that the typical roles of the aromatic ring as the dielectrophile coupling to vinyl and alkynyl metal species are reversed, presenting a new tool for organic synthesis. The first nucleophilic site to react is the stannyl group, and subsequently, a Suzuki-Miyaura cross-coupling reaction can take place on the same molecule.



Scientific contribution to this paper

In this project, I carried out almost all syntheses and the experimental work, with the following support by the coauthors: M. Schulz-Senft synthesized two alkynyl bromides (**6c** and **6d**). B. Thiedemann did three cross-coupling reactions with alkynyl bromides (**7c**, **7d** and **7e**). J. Linshoeft afforded the compound **10**. P. J. Gates recorded all high resolution mass spectra. A. Staubitz synthesized compounds **6e** and **6f**, and also corrected the manuscript.

Nucleophile-Selective Cross-Coupling Reactions with Vinyl and Alkynyl Bromides on a Dinucleophilic Aromatic Substrate

Lu-Ying He,^[a] Mathias Schulz-Senft,^[a] Birk Thiedemann,^[a] Julian Linshoef,^[a]
Paul J. Gates,^[b] and Anne Staubitz*^[a]

Keywords: Cross-coupling / Palladium / C–C coupling / Chemoselectivity / Sulfur heterocycles

A nucleophile-selective cross-coupling reaction on an aromatic compound bearing two metal groups, Bpin and SnMe₃, has been developed. Previously, only aryl bromides and iodides could be used as electrophilic components, but in this work, the scope could be extended to vinyl and alkynyl bromides as electrophiles. This means that the roles typical

in Sonogashira couplings or Heck reactions of the aromatic ring as the dielectrophile coupling to vinyl and alkynyl metal species are reversed, which presents a new tool for organic synthesis. The first nucleophilic site to react is the stannyl group, and subsequently, a Suzuki–Miyaura cross-coupling reaction can take place on the same molecule.

Introduction

Cross-coupling reactions (CCRs) of organometallic compounds R–M with organic compounds R–X have evolved into powerful and general methodologies for carbon–carbon bond formation.^[1] CCRs pervade all areas of organic synthesis^[2] from the construction of polymers,^[3] pharmaceuticals^[4] to natural products. In many cases, functional group tolerance is high, but to build up complex organic scaffolds, highly selective CCRs are essential. Research on electrophile-selective CCRs [differentiating between R–X¹ and R–X² (X = I, Br, Cl, OTf, etc.)] has been intensively pursued.^[5] For Stille reactions, the order of reactivity of halides is I > Br > Cl.^[6] However, nucleophile-selective CCRs with dimetallic (hetero)-aromatic substrates have been very rarely examined.^[7]

In our group, a nucleophile-selective one pot reaction was developed recently on a new thiophene building block that contains both a stannyl group and a boronic ester functional group.^[7c] Furthermore, this reaction was extended to both nucleophile- and electrophile-selective CCRs with aromatic rings based on a thiophene building block.^[7d] For both reactions, excellent chemoselectivity was observed in Stille CCRs with mono-halogenated or di-halogenated electrophiles in high yields.

However, the two reactions could be carried out only with aromatic electrophiles. As double and triple bonds are also very important functional groups that can be intro-

duced by cross-coupling methods, we now focussed on establishing nucleophile-selective CCRs with halogenated vinyl or alkynyl compounds.

Results and Discussion

As a test reaction, dinucleophilic thiophene **1** was cross-coupled with the commercially available β -bromostyrene (**2a/2a'** = 8:1) in toluene at 80 °C under microwave conditions with [Pd(PPh₃)₄] as the catalyst. After 1 h, the starting material was completely consumed, and the products **3a** and **3a'** were isolated in a combined yield of 36%. Although the reaction was highly selective for the nucleophile and no Suzuki–Miyaura cross-coupling occurred, two major homocoupling byproducts, the biaryl **4** in a yield of 17%, and 1,4-diphenylbutadiene **5** in yield of 10% were isolated. Oxidative homocoupling reactions leading to byproducts such as **4** may occur when oxygen is not rigorously excluded,^[8] but the reactions were performed under nitrogen with rigorous exclusion of air and a repeat experiment yielded similar results. Ozawa and co-workers have recently performed a thorough investigation into a similar reaction.^[9] When (*E*)- β -bromostyrene reacted with phenylboronic acid under Suzuki cross-coupling conditions, they also found substantial amounts of byproduct **5** as an *E/Z* mixture and biphenyl. Their detailed mechanistic studies suggested that oxidative addition of the (*E*)- β -bromostyrene to the Pd-centre was followed by a metathesis reaction with (*E*)- β -bromostyrene leading to the homocoupled styryl-styryl species **5** and [Pd(L)₂Br₂]. The latter may be reduced by the aryl–metal species present, giving rise to biaryl compounds such as **4**. This reactivity was not observed for (*Z*)- β -bromostyrene, because of the higher stability of its oxidative insertion product, (*Z*)-styryl-Pd(L)₂Br, towards reac-

[a] Otto Diels-Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, 24098 Kiel, Germany
E-mail: astaubitz@oc.uni-kiel.de
<http://www.otto-diels-institut.de/staubitz/>

[b] School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

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FULL PAPER

A. Staubitz et al.

tion with another equivalent of (*Z*)- β -bromostyrene. As the relative kinetic stabilities of the intermediates in a catalytic cycle are highly dependent on the reaction conditions, it seemed plausible that this reaction could be optimized to improve the yield of the product and minimize the amount of byproducts. Over 40 different reaction conditions were screened (solvents, catalysts, temperature, catalyst loading, reaction time, concentration; for details see the Supporting Information Table S1), all reactions were monitored and quantified by gas chromatography (GC).

Conversion and yield were highly dependent on the catalysts, solvents and temperature. It emerged that for bidentate and/or very bulky ligands, in the catalysts [Pd(dppe)Cl₂], [Pd(OAc)₂/SPhos], [Pd(dppf)Cl₂] and [Pd(P*t*Bu₃)₂], the yields were low (25, 30, 46 and 39% respectively, Table S1, entries 13–16) because considerable amounts of homocoupled byproducts **4** and **5** formed alongside other non-identified byproducts. Presumably, the intermediate styryl–Pd(L)₂Br species, which forms by oxidative addition, is very reactive towards vinyl bromides in the case of catalysts with bulky ligands. This might be because in the products of the homocoupling reaction, i.e., the complex [PdL₂Br₂] and the byproducts **4** and **5**, steric strain can be released. Therefore, [Pd(PPh₃)₄] as the least hindered catalyst (up to three ligands dissociate)^[10] proved the most suitable catalyst for this reaction (Table 1). Solvent screening of dioxane, toluene, THF, pyridine, acetonitrile and DMF (Table 1, entries 1–6) showed that DMF was the most suitable solvent, giving a combined yield of **3a** + **3a'** of 95% at 60 °C (Table 1, entry 6). However, polarity of the solvent cannot be the only parameter influencing the reaction, because the much less polar toluene, for example, also

gave a good combined yield of **3a** and **3a'** of 66% (Table 1, entry 2). The catalyst loading could be lowered to 1 mol-%, and the product was obtained in 97% yield (**3a** + **3a'**, Table 1, entry 7). The reaction was also efficient at a lower temperature of 40 °C (Table 1, entry 8); whereas 20 °C led to very long reaction times (Table 1, entries 9 and 10). Moreover, at 40 °C, fewer homocoupled byproducts were observed than at 60 °C.

Based on these results, the best reaction conditions for the nucleophile-selective CCR were a catalyst loading of [Pd(PPh₃)₄] as low as 1 mol-% in DMF as the solvent, either at 40 °C or 60 °C. The next aim was to establish whether these conditions would be suitable for a variety of vinyl (Table 2) and alkynyl bromides (Table 3) as electrophiles.

Vinyl bromides were synthesized from corresponding α , β -unsaturated carboxylic acids^[11] or carboxaldehyde^[12] in good yields (see Supporting Information for details). The alkynyl bromides were also easily available in high yields from the corresponding terminal alkynes.^[11] For both types of electrophiles, all reactions were entirely nucleophile-selective (as detectable by GC–MS and NMR spectroscopy) and generally very tolerant towards the electrophiles used. In the case of vinyl bromides, especially for electron-rich compounds, good to excellent yields of the corresponding products were obtained at 40 °C (74–77%; Table 2, **3b**, **3c** and **3e**). However, the amine **3d** could be isolated in only 43% yield because despite the higher temperature of 60 °C and a significantly longer reaction time of 168 h, the conversion to the product was low. Even longer reaction times did not improve the result, which may be caused by the binding of the amine to the Pd centre.^[13] With electron-neutral electro-

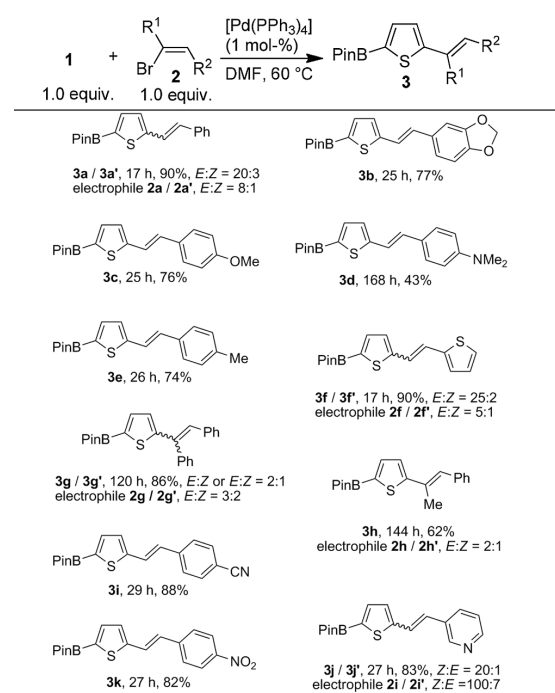
Table 1. Optimization of reaction conditions.^[a]

Entry	Solvent	Concentration [mmol/mL]	Cat. loading [mol-%]	<i>T</i> [°C]	<i>t</i> [h]	Conv. ^[b] [%]	Yield [%] ^[c]			
							3a	3a'	4	5
1	Dioxane	0.25	5	60	17	83	51	5	3	0
2	Toluene	0.25	5	60	17	91	59	7	9	6
3	THF	0.25	5	60	17	94	73	8	6	3
4	Pyridine	0.25	5	60	17	93	37	3	16	14
5	MeCN	0.25	5	60	17	100	43	10	22	14
6	DMF	0.25	5	60	17	100	83	12	2	0
7	DMF	0.25	1	60	17	100	86	11	2	0
8	DMF	0.5	1	40	17	96	86	4	1	0
9	DMF	0.5	5	20	17	40	12	0	1	0
10	DMF	0.5	5	20	65	93	70	1	4	0

[a] **1** (1.1 equiv.), **2** (1.0 equiv.). [b] Conversion is based on **2**. [c] Determined by GC with triisopropylbenzene as the internal calibration standard.

Nucleophile-Selective Cross-Coupling Reactions

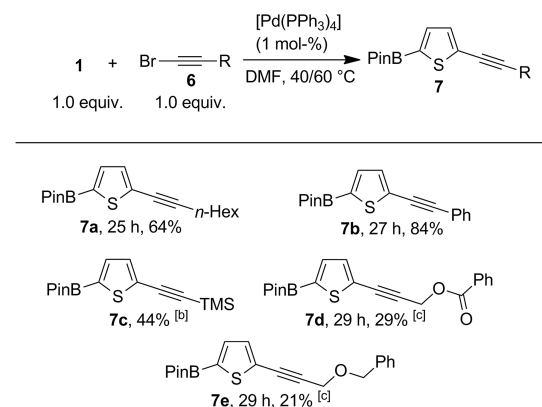
philes, β -bromostyrene **3a** and 2-(2-bromovinyl)-thiophene **3f** also gave good yields of 90%, albeit at 60 °C, i.e., 20 °C higher than for electron-rich vinyl bromides. However, the reaction to form **3g** required about seven times as long as **3e**, which can be attributed to the much greater steric hindrance due to the additional phenyl group geminal to the reacting centre. If the steric hindrance was instead provided by a methyl group (product **3h**), a longer reaction time of 144 h was required. Electron-deficient vinyl bromides gave excellent yields of the products **3i**, **3j** and **3k** in relatively short reaction times of about 30 h (88, 83 and 82%, respectively).

Table 2. Nucleophile-selective CCRs with various vinyl bromides.^[a]

[a] The reactions to obtain **3a**, **3b**, and **3d** were performed at 40 °C.

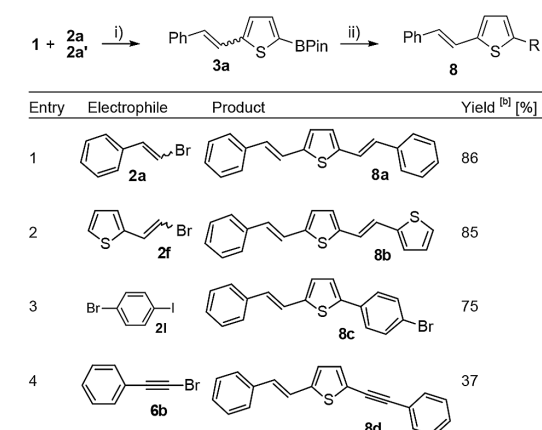
The reaction was further analysed with respect to alkynyl bromides as electrophilic coupling partners (Table 3). For alkynyl bromides with a simple *n*-hexyl (**6a**) or phenyl substituent (**6b**), the reaction gave good yields of 64 and 84%, respectively at 40 °C. However, the reaction with **6c** (*R* = TMS), only afforded **7c** in a yield of 44% (and could only be isolated as a 1:1 mixture with starting material **1**, even at a temperature of 60 °C and a significantly longer reaction time of 168 h). Although no byproduct formation was observed, the reactivity of the electrophilic component was exceedingly low. For **6d** and **6e**, both reactions were complete in 29 h at 60 °C, but the isolated yield was relatively low. In these cases, the issue was not conversion, but purification. Both products decomposed on a silica column, and it was also not possible to purify them by Kugelrohr distillation. This was a general observation for all products of

type **7** (see Supporting Information for details): If Kugelrohr distillation was not possible, then no pure products could be obtained due to over-absorption onto silica gel, possibly due to interactions of the vacant orbital on boron with nucleophilic moieties in silica gel.^[14]

Table 3. Stille CCRs of alkynyl bromides.^[a]

[a] The reactions to obtain **7a** and **7b** were performed at 40 °C, and those for **7c–7e** were performed at 60 °C. [b] As a 1:1 mixture with the starting material **1**. [c] Contains impurities, for details see the Supporting Information.

After the chemoselective Stille CCR, the products still contain a boronic ester functional group, which can be further coupled with a second electrophile by a Suzuki–Miyaura CCR. By merely adding K_2CO_3 as a base, water and a second electrophile to the reaction mixture after completion of the Stille CCR, this could be accomplished. All of these subsequent reactions were stirred at 100 °C for 6 h (Table 4). This allowed the synthesis of **8a** and **8b** in yields of 86 and 85%, respectively. The synthesis of **8b** demon-

Table 4. Chemoselective one-pot CCRs of thiophene **1**.^[a]

[a] i) **1** (1.0 equiv.), **2a + 2a'** (1.0 equiv.) $[\text{Pd}(\text{PPh}_3)_4]$ (1 mol-%), DMF, 60 °C, 17 h. ii) Electrophiles (1.0 equiv.), K_2CO_3 (2.0 equiv.), H_2O , 100 °C, 6 h. [b] Yields of isolated products.

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strates that the strategy of using a nucleophile-selective cross-coupling reaction allows very easy access to non-symmetric di-stilbene-like materials. Aryl iodides can also be used as the second electrophile and in the case of **2l**, the reaction is also highly electrophile selective as shown by the high yield of 75%. In addition, no unselectively cross-coupled byproduct could be detected by GC-MS or NMR spectroscopy. The second Suzuki-Miyaura coupling was also performed with an alkynyl bromide, **6b**, but the yield was lower in this case, reflecting the lower efficiency of such substrates in cross-coupling reactions, as described above (Table 4).

Conclusions

In conclusion, reaction conditions for a nucleophile-selective CCR between vinyl and alkynyl bromides with a dinucleophilic thiophene substrate were established. Although homocoupling of the nucleophile and electrophile, respectively, are potential competing reactions, careful optimisation of the reaction conditions led to a process in which these side reactions could be largely suppressed in all cases. These reactions are general with respect to a wide variety of electrophiles. For vinyl bromides, all products were obtained in good to excellent yields, although time and temperature needed to be adjusted from case to case. Alkynyl bromides proved more difficult electrophilic components, mainly due to purification issues, which are apparently intrinsic for these types of boronic ester containing thiophene alkynyl groups. In both cases, the resulting products are extremely versatile building blocks: they still contain a boronic ester that can be further coupled with a second electrophile by a Suzuki-Miyaura cross-coupling in one-pot reactions. Furthermore, the reactions with the alkynyl bromides provide access to aromatic alkynyl compounds, with a reversal of the roles of nucleophile and electrophile compared with Sonogashira CCRs. This makes this reaction a valuable alternative for volatile aromatic alkynyl compounds, in cases where Sonogashira couplings fail or are unselective. The main advantage of a nucleophile-selective cross-coupling reaction is that a further organometallic site remains for subsequent functionalisation reactions. This was also demonstrated: by merely adding water and a base, a Suzuki-Miyaura reaction could be added to the reaction sequence. Aryl bromides and iodides as well as vinyl bromides and alkynyl bromides react under these conditions.

Experimental Section

General Procedure for Nucleophile-selective CCRs with Various Vinyl Bromides: A solution of **1** (373 mg, 1.00 mmol), the vinyl bromide (1.00 mmol), and [Pd(PPh₃)₄] (11.6 mg, 10.0 μmol, 1 mol-%) in DMF (4 mL) was heated to 40 or 60 °C for a specific time (for details with respect to specific electrophiles see the Supporting Information). The mixture was filtered through a short plug of celite with *n*-hexane (500 mL) as the solvent. The solvent was removed in vacuo and the crude product was purified by Kugelrohr

distillation or column chromatography (for details with respect to specific electrophiles see the Supporting Information).

General Procedure for Nucleophile-selective CCRs with Various Alkynyl Bromides: A solution of **1** (373 mg, 1.00 mmol), the alkynyl bromide (1.00 mmol), and [Pd(PPh₃)₄] (11.6 mg, 10.0 μmol, 1 mol-%) in DMF (4 mL) was heated to 40 or 60 °C for a specific time (for details with respect to specific electrophiles see the Supporting Information). The mixture was filtered through a short plug of celite with *n*-hexane (500 mL) or diethyl ether (50 mL) as the solvent. The solvent was removed in vacuo and the crude product was purified by Kugelrohr distillation or column chromatography (for details with respect to specific electrophiles see the Supporting Information).

General Procedure for Chemo-selective One-pot CCR of Thiophene 1: A solution of **1** (186 mg, 500 μmol), β-bromostyrene (*E/Z* = 8:1; 91.0 mg, 500 μmol), and [Pd(PPh₃)₄] (5.78 mg, 5.00 μmol, 1 mol-%) in DMF (4 mL) was heated to 60 °C for 17 h. Then the second electrophile (500 μmol) in DMF (4 mL) was added to the solution in one portion in addition to K₂CO₃ (138 mg, 1.00 mmol) in degassed water (1 mL). The solution was heated to 100 °C for 6 h. After the solution cooled down to 20 °C, the solution was diluted with CH₂Cl₂ (8 mL) and filtered through a short plug of silica with CH₂Cl₂ (250 mL). After removing the volatile components in vacuo, the crude product was purified by column chromatography (for details with respect to specific electrophiles see the Supporting Information).

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Cross-Coupling



A nucleophile-selective one-pot cross-coupling reaction on an aromatic compound bearing both a stannyl group and a boronic ester has been developed with vinyl and alkynyl bromides as electrophiles, exploiting the different reactivity of the Stille

and Suzuki–Miyaura cross-coupling reactions. The typical roles of the aromatic ring as the dielectrophile coupling to vinyl and alkynyl metal species are reversed, which presents a new tool for organic synthesis.

L.-Y. He, M. Schulz-Senft,
B. Thiedemann, J. Linshoef, P. J. Gates,
A. Staubitz* 1–6

Nucleophile-Selective Cross-Coupling Reactions with Vinyl and Alkynyl Bromides on a Dinucleophilic Aromatic Substrate

Keywords: Cross-coupling / Palladium / C–C coupling / Chemoselectivity / Sulfur heterocycles

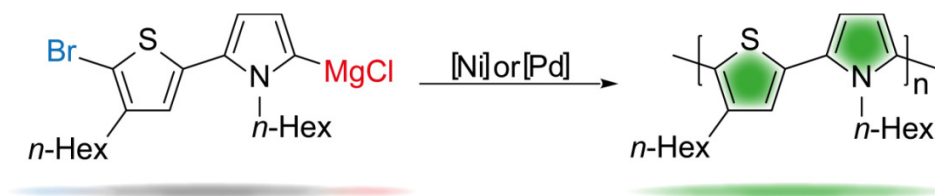
3.2 Difunctional thienylpyrroles for alternating copolymers

3.2.1 Grignard-type thienylpyrrole for alternating poly(thiophene-*alt*-pyrrole)

“Synthesis of Poly(thiophene-*alt*-pyrrole) from a Difunctionalized Thienylpyrrole by Kumada Polycondensation”

Lu-Ying He, Sara Urrego-Riveros, Paul J. Gates, Christian Näther, Maren Brinkmann, Volker Abetz and Anne Staubitz, *Tetrahedron*, 2015, *submitted*.

A difunctional thienylpyrrole monomer with a bromide on the thienyl moiety and a magnesium halide on the pyrrole moiety was prepared via chemo-selective magnesium-iodine exchange. Based on this monomer, π -conjugated alternating poly(thiophene-*alt*-pyrrole) **PTP** was synthesized via nickel and palladium catalyzed Kumada polycondensation. The optical and thermal properties of this polymer have been investigated and suggested a wide band gap polymer, with a very low T_g for such materials.



Scientific contribution to this paper

In this project, I carried out all syntheses and the experimental work, with the following support by the coauthors: S. Urrego-Riveros helped to synthesize some starting materials (**1**, **3**, **4**, **11**). P. J. Gates recorded most of the high resolution mass spectra and MALDI-MS spectra. C. Näther carried out all thermal analyses. M. Brinkmann and V. Abetz helped to carry out some GPC measurements. A. Staubitz and I wrote the manuscript together.



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Synthesis of Poly(thiophene-*alt*-pyrrole) from a Difunctionalized Thiénylpyrrole by Kumada Polycondensation

Lu-Ying He^a, Sara Urrego-Riveros^a, Paul J. Gates^b, Christian Näther^c, Maren Brinkmann^d, Volker Abetz^{d, e} and Anne Staubitz^{a, *}

^a Otto Diels-Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, Kiel 24098 Germany

^b School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

^c Institute for Inorganic Chemistry, University of Kiel, Otto-Hahn-Platz 6, Kiel, 24118 Germany

^d Helmholtz-Zentrum Geesthacht, Institute of Polymer Research, Max-Planck-Str. 1, Geesthacht 21502, Germany

^e Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, Hamburg 20146, Germany,

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ABSTRACT

A difunctional thiénylpyrrole monomer with a bromide on the thiényl moiety and a magnesium halide on the pyrrole moiety was prepared via chemo-selective magnesium-iodine exchange. Based on this monomer, a π -conjugated alternating poly(thiophene-*alt*-pyrrole) PTP was synthesized via nickel and palladium catalyzed Kumada polycondensation. The optical and thermal properties of this polymer have been investigated and suggested a wide band gap polymer, with a very low T_g for such polymers.

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Introduction

Conjugated polymers have attracted extensive attention because of their potential industrial applications, due to their unique semiconducting and optoelectronic properties.¹⁻³ Among the conjugated polymers, polythiophenes and polypyrroles are centrally important and have been widely investigated as potential materials for organic electronics.⁴⁻⁸ The properties of polythiophene and polypyrrole are different: polypyrrole has a larger band gap (ca. 3 eV⁹ compared to ca. 2 eV for polythiophene¹⁰), resulting in a relatively low conductivity,^{11,12} and has a lower oxidation potential,^{13,14} which makes it highly reactive toward oxygen. As the copolymerization of the monomer containing several distinct units can lead to an interesting combination of the properties observed in the corresponding homopolymers,¹⁵⁻¹⁸ it is interesting to obtain copolymers that contain both heterocycles simultaneously. Cava and coworker described the poly(thienylpyrrole) showed tailored electroactive properties.¹⁹

Copolymers of thiophene and pyrrole have mainly been prepared via electrochemical polymerization of 2,5-di(thiophen-2-yl)-1*H*-pyrrole derivatives.²⁰⁻³⁰ However, this method may lead to significant branching and regioirregular polymers. In addition,

organometallic polycondensations have recently been employed to obtain copolymers via a bis(trimethylstannyl)thiophene monomer and a dibromo pyrrole monomer.³¹⁻³³ However, the polymers obtained by the Stille polycondensation had a very low molecular weight. There was no report on preparing poly(thiophene-*alt*-pyrrole) via a single monomer which contains a metal functional group and a halogen group. However, this kind of monomer is highly desirable as it has the potential to proceed via a quasi-living chain growth mechanism.³⁴⁻⁴³ Herein, we report the highly chemo-selective synthesis of difunctional thiénylpyrrole monomer containing a metal functional group and a bromo group. Based on the monomer, π -conjugated alternating poly(thienylpyrrole) was prepared via palladium catalyzed Kumada polycondensation.

Results and Discussion

Synthesis of the pre-monomer 4

The precursor monomer 4 was synthesized by an electrophile-selective Stille cross-coupling⁴⁴ between the 2-bromo-3-hexyl-5-iodothiophene 1 and the tributyltin substituted pyrrole 2, followed by iodination of the pyrrole unit with an excess *N*-iodosuccinimide (NIS) in a yield of 62% over two steps.

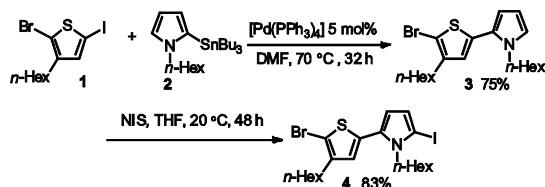
* Corresponding author. Tel.: +49-431-880-3697; fax: +49-431-880-1558; e-mail: astaubitz@oc.uni-kiel.de

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Although we initially planned to use **3** directly as a monomer precursor by lithiation through deprotonation as a lithiated monomer or followed by lithium-metal exchange if required, several metalation experiments using lithium diisopropylamide (LDA), and 1-lithio-2,2,6,6-tetramethyl-piperidine (LTMP) failed (For details see in the SI).

Scheme 1. Synthesis of precursor monomer **4**.



A more reliable route seemed to be the lithiation of **4** by iodine-lithium exchange using different alkyl lithium reagents such as *n*-BuLi, *t*-BuLi or MeLi under different conditions (Table 1) (For details see the SI). In order to analyze the success of the lithiation procedure, the lithiated heterocycles were quenched with MeI, which could be easily identified by gas chromatography-mass spectrometry (GC-MS) and ¹H NMR spectroscopy. However, lithiation and quenching with MeI did not give the product 2-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-5-methyl-1*H*-pyrrole; on the contrary, 2-bromo-1-hexyl-5-(4-hexyl-5-methylthiophen-2-yl)-1*H*-pyrrole **5** was obtained as main product. This suggests a “halogen dance reaction”,⁴⁵ in which the initial iodo-lithium exchange on the pyrrole moiety was followed by bromination from the brominated thiophene moiety. This observation is unusual because in hexylthiophene, a bromide substituent is much more favoured in the 2 position adjacent to the *n*-hexyl group, but metallation is favoured in the 5 position (which in **4** is blocked by the pyrrole).⁴⁶⁻⁴⁸ In addition, *n*-BuLi and *t*-BuLi (entries 1-3) also gave another byproduct 1-hexyl-2-(4-hexyl-5-methylthiophen-2-yl)-5-iodo-1*H*-pyrrole **6**. This is a consequence of a bromo-lithium exchange without a halogen dance. Although MeLi just gave trace amount of **6** (entry 4), other unidentified compounds was shown from the NMR (For details see in the SI).

Table 1. Lithiation of precursor monomer **4**.

entry	lithium reagents	solvents	T (°C)	ratio ^a 5 : 6
1	<i>n</i> -BuLi	THF	-78	6 : 1
2	<i>n</i> -BuLi	THF	-100	10 : 1
3	<i>t</i> -BuLi	Me-THF	-129	0.5 : 1
4	MeLi	THF	-78	>99:1 ^b

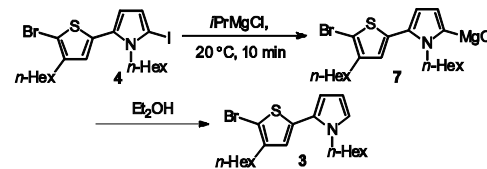
^a Estimated by ¹H NMR spectroscopy and identified by GC-MS.
^b A trace amount of compound **6** was detected only by GC-MS.

Synthesis of the Grignard type monomer **7**

Surprisingly then, the Grignard-type monomer **7** could be synthesized by treating the precursor monomer **4** with 1 equiv of

*i*PrMgCl at 20 °C for 10 min via a fast magnesium-iodine exchange reaction (100% yield based on analytical GC with analysis of the protonated species **3** (Scheme 2). The metalation occurred selectively at the α-position of the thiophene, leaving the aryl bromide intact.

Scheme 2. Synthesis of Grignard-type monomer **7** by magnesium-iodine exchange.



Synthesis of poly(thiophene-*alt*-pyrrole) (PTP) with **7**

Based on the Grignard-type monomer **7**, polymerization was carried out firstly by the addition of 2 mol% of [Ni(dppp)Cl₂] at 20 °C for 24 h. These conditions are well established for the synthesis of well-defined poly(3-hexylthiophene) by Kumada catalyst-transfer condensation polymerization.^{34,35} However, the yield was only 65% and the molecular weight of the polymer (M_n = 3.9 kDa, M_w/M_n = 1.5, GPC calibrated against polystyrene) was also quite low. Analysis of the polymer by MALDI-TOF revealed a series of peaks suggesting an isopropyl end group (Figure 1A). This could arise from quenching the metallated monomer by isopropyl iodide, which is the product from the previous magnesium-iodine exchange. In view of the fact that this reaction was not observed without a transition metal catalyst, also it is more likely that this end group arises as a cross-coupling product. This problem has been reported for other polymers, such as poly(9,9-dioctylfluorene).⁴⁹ In that case, the use of the magnesium complex [tBuMgCl·LiCl·15-crown-5] as the metallating species prevented any further substitution most likely because the *tert*-butyl cation is more stable compared to isopropyl cation. Treatment of **4** with 1 equiv of [tBuMgCl·LiCl·15-crown-5] at 20 °C for 10 min in THF gave **7** (100% yield based on analytical GC-MS with analysis of the protonated species **3**). The polymerization was then carried out by adding of 2 mol% of [Ni(dppp)Cl₂] to the reaction mixture. After 24 h at 20 °C the polymer was obtained in a yield of 43% (M_n = 6.3 kDa, M_w/M_n = 1.5, with a conversion of 99%). The MALDI-TOF MS spectra of the oligomer showed no evidence for a *tert*-butyl end group, with H/H, H/Br and Br/Br being the major end groups (Figure 1B). The obtained Br/Br terminated polymer was presumably as a result of the dissociation of the associated Ni⁰-arene π complexes according the proposed mechanism by Yokozawa^{50,53} and McClough.^{54,55} Although preventing the quenching reaction of polymerization, the relatively high polydispersity and only moderate yield led us to analyze further reaction conditions.

Palladium catalysts are generally less reactive than nickel catalysts for Kumada coupling with alkyl halides. In this instance, we decided to use [Pd(*t*Bu₃P)₂] as catalyst as it has been shown to be a suitable catalyst for chain growth polymerization of alternating copolymers based on Stille or Suzuki coupling reactions.^{56,43} Although inefficient at 20 °C, (Table 2, entry 1) this catalyst was more efficient at 50 °C. The reaction was performed in the etheral solvents MTBE, DME, THF, and dioxane (Table 2, entries 2-5). In all cases, polymeric products were obtained. The highest molecular weight polymer was obtained by using MTBE as solvent (Table 2, entry 3) with a

Figure 1. MALDI-TOF MS spectra of the poly(pyrrrole-*alt*-thiophene): (A) polymer synthesized with *i*PrMgCl and [Ni(dppp)Cl₂]; (B) polymer synthesized with *t*BuMgCl, LiCl, 15-crown-5 and [Ni(dppp)Cl₂]; (C) polymer synthesized with *i*PrMgCl and [Pd(*t*Bu₃P)₂] (Table1, entry 6); (D) polymer synthesized with [*i*PrMgCl·LiCl] and [Pd(*t*Bu₃P)₂] (Table1, entry 10).

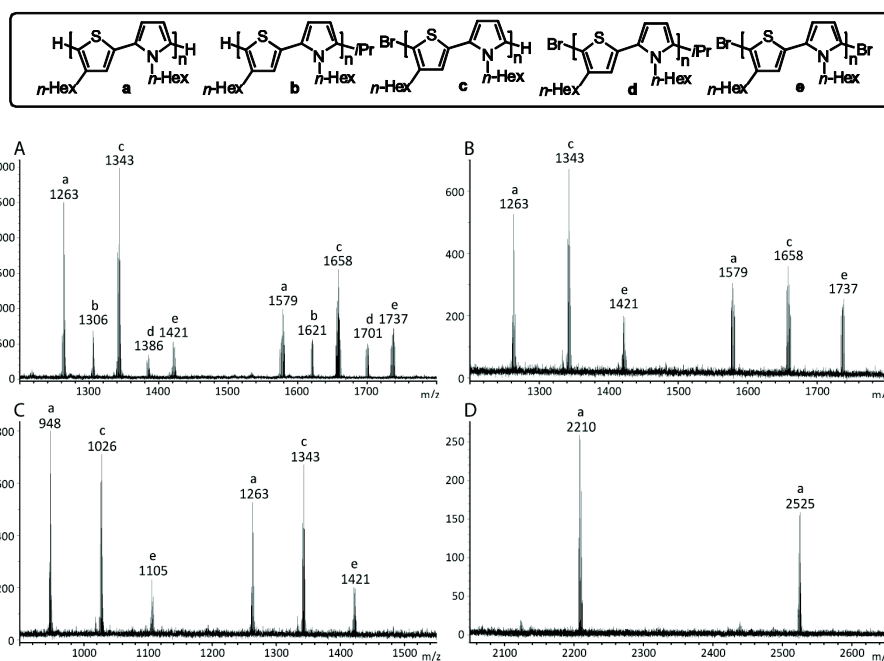
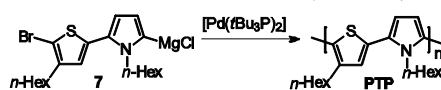


Table 2. Polymerization of **7** with various ether solvents and different catalyst loadings^a



entry	cat. loading [mol%]	solvent	T (°C)	time (h)	yield (%)	M_n^b	M_w/M_n^b	Expected M_n^c
1	2	MTBE	20	24	-	-	-	15700
2	2	MTBE	50	18	91	7700	1.6	15700
3	2	DME	50	18	38	4000	1.5	15700
4	2	THF	50	18	49	5000	1.6	15700
5	2	Dioxane	50	18	73	5600	1.6	15700
6	2	MTBE	50(MW)	6.5	94	13200	2.2	15700
7	1	MTBE	50(MW)	5	14	1700	1.4	31500
8	2	MTBE	50(MW)	5	27	2100	1.4	15750
9	5	MTBE	50(MW)	5	97	17800	2.8	6300
10	5	MTBE/LiCl	50(MW)	5	99	29500	4.6	6300

^a The polymerizations were carried out by treatment of **4** with 1.0 eq. of *i*PrMgCl at 20 °C for 10 min to form **7**, followed by addition of [Pd(*t*Bu₃P)₂].

^b Estimated by GPC calibrated against a polystyrene standard (eluent: CHCl₃, 1 mL/min).

^c If the polymerization was a quasi-living chain-growth polymerization.

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weight average molecular weight of $M_n = 7700$. However, in all cases, the polymers' polydispersities were relatively high between 1.5 and 1.6 and molecular weights stayed below the expected molecular weights, which should not be expected for living polymerizations. To increase the rate of polymerization, the reaction in 4 mL of MTBE was conducted under microwave irradiation at 50 °C for 6.5 h. The conversion was 100% and 94% of the polymer was obtained with a higher molecular weight than under thermal conditions ($M_n = 13.2$ kDa, $M_w/M_n = 2.2$) (Table 2, entry 6). Different catalysts loadings (1, 2, 5 mol%) were also investigated for the polymerization catalyzed by $[\text{Pd}(\text{tBu}_3\text{P})_2]$ at 50 °C for 5 h under microwave irradiation (Table 1, entry 7-9), 5 mol% of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ afforded the longest polymer chain ($M_n = 17.8$ kDa, $M_w/M_n = 2.9$). In general, higher catalyst loadings gave higher yields and polymers with higher molecular weights, but also with increased polydispersities (M_w/M_n), which is counter indicative of a quasi-living chain growth polymerization. The polymers synthesized with $[\text{Pd}(\text{tBu}_3\text{P})_2]$ also had H/H, H/Br and Br/Br end groups (Figure 1C), which proves the polymerization process did not undergo the quenching with isopropyl iodide. However, the dissociation of the associated Pd⁰-arene π complexes occurred, which could lead to the Br/Br terminated polymer. Stefan and coworkers reported the palladium-mediated polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene proceeded by a step-growth mechanism and with lower regioirregularity as various side reactions of dissociated Pd(0) catalyst.⁵⁷ It has been shown the addition of LiCl to Kumada catalyst transfer polycondensation could have beneficial effects on the chain-growth polymerization characteristics of aryl-Gignard monomers.^{41,36} Bielawski and coworkers reported the addition of LiCl led to controlled chain-growth polymerization of 2-(4-bromo-2,5-bis(2-ethylhexyloxy)phenyl)-5-chloromagnesio-thiophene to afford poly(thiophene-*alt-p*-phenylene).⁴¹ However, in our case, LiCl did not show this effect; on the contrary, the M_w/M_n (4.6) value was much higher with much bigger M_n (29500) (Table 2, entry 10). The polymer had only H/H as the main end group in the presence of LiCl (Figure 1D). Based on these results, the best reaction conditions for the polymerization of **7** was 2 mol% of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ in MTBE as the solvent at 50 °C for 6.5 h under microwave irradiation.

The conversion vs. time plot (Figure 2A) shows that the polymerization of **7** catalyzed by 2 mol% of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ in 5 mL of MTBE at 50 °C under microwave conditions went smoothly in the first 390 min, up to a conversion of about 70%. However, after 390 min, the apparent conversion increased sharply and reached 100% in 25 min. The M_n and M_w/M_n values of the crude PTP (without purification by precipitation and fractionation) at each conversion in this polymerization were analyzed by GPC to evaluate the polymerization in detail. The M_n values did not increase in proportion to the conversion, and the M_n increased sharply toward the end of the reaction. Both of these observations suggest a step-growth polymerization. The M_w/M_n values of the collected polymer samples increased along with the consumption of monomer.

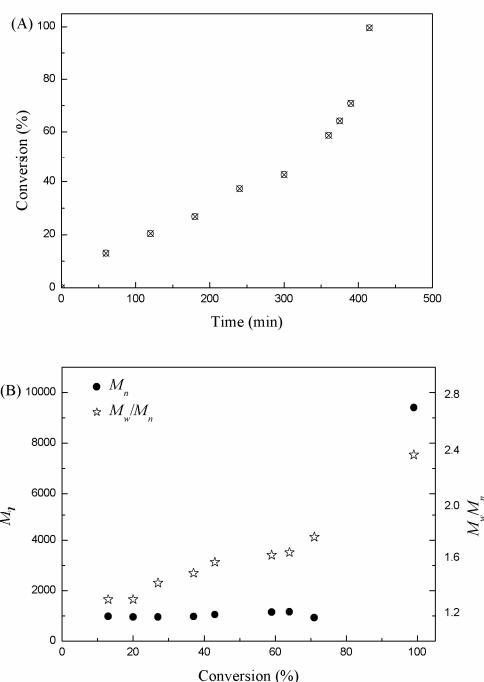


Figure 2. Conversion vs. time (A), and M_n and M_w/M_n vs. conversion (B) plots for the polymerization of **7** with 2 mol% of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ in MTBE ($[4]_0 = 0.1$ mol/L) at 50 °C under microwave conditions. The conversion was defined as amount of compound **3** (from the quenching of a sample with ethanol) and determined by GC using naphthalene as internal calibration standard.

Optical Properties of PTP

The polymer samples were analyzed with respect to their absorption properties and their photoluminescence spectra (Figure 3, a representative example of a polymer prepared under the conditions of Table 2, entry 6). The absorption spectra of **4** in diethyl ether solution showed maximal peaks at 306 nm. The absorption peaks of the polymers PTP (Table 2, entries 6, 9 10) in diethyl ether solution were all observed at ca. 348 nm, largely irrespective of the chain length obtained. If the polymers were processed as a film prepared by spin-coating, the absorption peaks were all at ca. 354 nm. The absorption bands of the polymer PTP in both solution and processed as a film were relatively narrow compared to regioregular poly(3-alkylthiophene) (rr-P3AT) ($\lambda_{\text{max}} \approx 450$ nm).⁵⁸ This may be attributed to the effect of steric interactions of neighboring *n*-hexyl groups that reduce the conjugation length of the polymers. In fact, DFT calculations suggest a torsion angle between the planes of the two heterocycles of ca. -143 ° in the *anti*-conformation of thiophene and pyrrole and 46 ° for the *syn*-conformation. These values are similar in the tetramers in all possible conformations (see Supporting Information). Irrespective of the chain length obtained (Table 2, entries 6, 9 10), the ether solutions of PTP all give a bright-green fluorescence with the maximum emission wavelength of ca. 487 nm, corresponding to the onset of π - π^* transition of the electronic absorption spectra, which is at significantly higher energy than the rr-P3AT ($\lambda_{\text{max}} \approx 570$ nm).⁵⁸

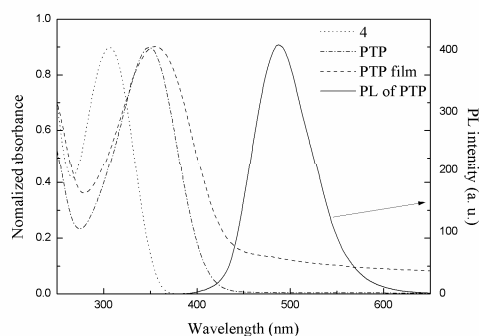


Figure 3. UV-vis spectra of 4 and PTP in diethyl ether and as a film, PL spectra ($\lambda_{\text{exc}} = 348 \text{ nm}$) of PTP in diethyl ether.

Thermal behavior of the polymer PTP

The thermal stability of the polymer (a representative example of a polymer prepared under the conditions of Table 2, entry 6) was studied by thermogravimetric analysis (TGA) under N_2 at a heating rate of $4 \text{ }^\circ\text{C}/\text{min}$ (Figure 4). The polymer showed a 2% weight loss at $201 \text{ }^\circ\text{C}$ and a 38% weight loss at $451 \text{ }^\circ\text{C}$. The first mass loss might be traced back to the removal of volatile species from the polymer, whereas the second mass loss can be due to the decomposition of the polymer. On the other hand, a DSC thermogram suggested a glass transition temperature at ca. $-14 \text{ }^\circ\text{C}$ (see SI), which is quite low comparing to other semiconducting polymers. This lower transition temperature may be caused by the torsion between thiophene and pyrrole, which renders the material very flexible.

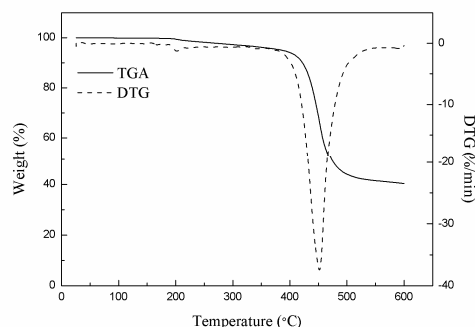


Figure 4. TGA and DTG curves of PTP.

Conclusions

A difunctional thienylpyrrole monomer containing a magnesium group and a bromo group was synthesized via a chemo-selective halogen-magnesium exchange. All halogen lithium exchange reactions on the dihalogenated starting material (with bromide on the thiophenyl moiety and iodide on the pyrrole moiety) proved unselective, leading to halogen dance or quenching with the alkyl halide that forms *in situ*. By using a magnesiated monomer, alternating copolymers PTP containing 3-alkylthiophene and *N*-alkylpyrrole was prepared by palladium catalyzed Kumada polycondensation. The molecular weights were high and a moderate polydispersity was found. The M_n vs. conversion plot indicated that the polymerization proceeded via a step-growth mechanism, presumably due to the dissociation of

the associated Pd^0 -arene π complexes. The absorption bands of the polymer PTP in both solution and processed as a film were relatively very narrow due to the effect of steric interactions of neighboring *n*-hexyl groups that reduce the conjugation length of the polymers. This study highlights the difficulties for introducing pyrroles into semiconducting polymers. It points out optimal reaction conditions for the selective metallation of pyrroles in spite of the presence of competing thiophenes. The optical and thermal properties suggest a wide band gap polymer, with a very low T_g for such materials.

Experimental section

General Methods and Materials

All syntheses were carried out using standard Schlenk techniques or in glovebox under a dry and inert nitrogen atmosphere unless stated otherwise. Glassware and NMR-tubes were dried in an oven at $200 \text{ }^\circ\text{C}$ for at least 2 h prior to use. Reaction vessels were heated under vacuum and purged with nitrogen three times before adding reagents.

All solvents that were used for reactions were used freshly distilled after refluxing for several hours over the specified drying agent under nitrogen and were stored in a J. Young's tube. If no drying agent is noted, the solvents were used for chromatography only and distilled for purification purposes.

Instruments and measurements

^1H NMR and ^{13}C NMR spectra were recorded at 300 K . ^1H NMR spectra were recorded on a Bruker DRX 500 (500 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker DRX 500 (125 MHz) spectrometer. All ^1H NMR and ^{13}C NMR spectra were referenced against the residual solvent peak. The exact assignment of the peaks was proved by ^1H , ^{13}C DEPT and two-dimensional NMR spectroscopy such as ^1H COSY, ^{13}C HSQC or $^1\text{H}/^{13}\text{C}$ HMBC when possible.

IR spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer with a A531-G Golden-Gate-ATR-unit. Ultra High resolution EI mass spectra were run on a VG Analytical Autospec apparatus. MALDI-MS analyses were performed using Bruker Daltonics UltrafleXtreme 2. The analyte (DCM, 1 mg/ml) was pre-mixed with the Dithranol matrix (MeOH, 10 mg/ml) in a 1:1 (v/v) ratio immediately prior to analysis. UV/Vis spectra were recorded on a Perkin Elmer Lambda14 spectrometer. Luminescence spectra were recorded on a Perkin Elmer LS55 spectrometer.

M_n and M_w were determined on a Viscotek GPCmax VE2001, equipped with a Viscotek VE3580 RI detector (columns: ViscotekLT5000L 300 x 7.8 mm and LT4000L 300 x 7.8 mm).

The DTA-TG measurements were performed in Al_2O_3 crucibles using a Netzsch STA-409CD instrument. All measurements were performed under N_2 and were corrected for buoyancy and current effects. The instruments were calibrated using standard reference material, DSC investigations were performed with the DSC 204/1/F from Netzsch and the DSC 1 Star System with STARe Excellence Software from Mettler-Toledo AG. The measurements were performed in Al pans and the instruments were calibrated using standard reference materials.

GC-MS analysis was performed on a Hewlett Packard 5890A gas chromatograph, equipped with a Hewlett Packard 5972A mass selective detector and an Agilent Technologies dimethylpolysiloxane column (19091S-931E, nominal length 15 m, 0.25 mm diameter, 0.25 μm grain size).

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Tetrahedron

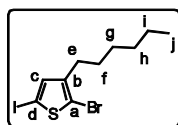
GC analysis was performed on an Agilent Technologies 6890N gas chromatograph, equipped with an Agilent Technologies 7683 Series Injector, an Agilent Technologies (5 %-phenyl)-methylpolysiloxane column (19091J-413, nominal length 30 m, 0.32 mm diameter, 0.25 μ m grain size) and a flame ionization detector (FID).

Reactions under microwave irradiation were carried out using a Biotage® Initiator+ SP Wave synthesis system, with continuous irradiation power from 0 to 300 W (Organic Synthesis Mode). The temperature was measured with an external IR sensor during microwave heating. All reactions were carried out in 5 mL oven-dried Biotage microwave vials sealed with an aluminum/Teflon® crimp top, which can be exposed to a maximum of 250 °C and 20 bar internal pressure.

For chromatographic purifications, silica gel (Macherey-Nagel Inc., grain size 0.040–0.063 mm) was used. Thin layer chromatography was performed using pre-coated plates from Macherey-Nagel Inc., ALUGRAM® Xtra SIL G/UV254. Chromatographic purification for compounds (3, 4, 5, 6, 8) were carried out using an Interchim Puriflash 430 system, where cartridges by Interchim (silica HC, grain size 50 μ m, 40g, 80 g or 120 g) were used.

Synthesis

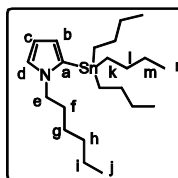
2-Bromo-3-hexyl-5-iodothiophene (1)



2-Bromo-3-hexyl-5-iodothiophene was prepared similarly to a method described by Koeckelberghs and co-workers⁵⁹ and was modified as follows: 2-bromo-3-hexylthiophene (5.00 g, 20.2 mmol) (For the synthetic procedure and analytic data see in the SI) was dissolved in a mixture of chloroform (100 mL) and acetic acid (50 mL) and shielded from light under an air atmosphere. Then, *N*-iodosuccinimide (6.75 g, 30.0 mmol) was added in one portion. The reaction was stirred for 16 h at 20 °C. The solution was poured into water (100 mL) and the water phase was extracted with *n*-hexane (3 x 100 mL). The combined organic phases were washed with aqueous NaOH (2 M, 1 x 500 mL), water (2 x 200 mL), brine (1 x 100 mL) and were dried over MgSO₄. After the solvent was removed *in vacuo*, the crude product was purified by Kugelrohr distillation (110 °C, 1.7 x 10⁻¹ mbar) to get 6.8 g (89%, lit.⁵⁹ 78%) of the product as yellow oil.

¹H NMR (500 MHz, CDCl₃): δ = 6.96 (s, 1 H, H-c), 2.52 (t, ³J = 7.6 Hz, 2 H, H-e), 1.59–1.50 (m, 2 H, H-f), 1.37–1.24 (m, 6 H, H-g, h, i), 0.89 (t, ³J = 6.7 Hz, 3 H, H-j) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 144.3 (C-b), 138.0 (C-c), 111.7 (C-a), 71.0 (C-d), 31.6, 29.6, 29.2, 28.8 (C-e, f, g, h), 22.6 (C-i), 14.1 (C-j) ppm. HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₁₀H₁₄BrIS]⁺ 371.9044; Found 371.9032. IR (ATR): ν = 2953 (m), 2923 (s), 2854 (s), 1534 (w), 1456 (m), 1403 (m), 1377 (w), 1275 (w), 1261 (w), 1191 (w), 1095 (w), 995 (s), 909 (w), 826 (s), 750 (s), 724 (m), 694 (w), 650 (w), 578 (w), 470 (s) cm⁻¹.

1-Hexyl-2-(tributylstannyl)-1H-pyrrole (2)



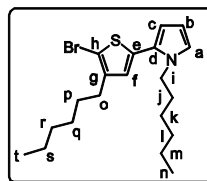
(For the synthetic procedure and analytic data see in the SI) was

n-Butyllithium (12.48 mL, 31.20 mmol, 2.50 M in hexanes) was added to a stirred solution of *N,N,N',N'*-tetramethyl-ethane-1,2-diamine (4.710 g, 31.20 mmol) in *n*-hexane (90 mL) at 0 °C within 5 min. The reaction mixture was stirred for 1 h at 0 °C. *N*-(*n*-hexyl)-pyrrole (3.620 g, 24.00 mmol)

added dropwise to the solution at this temperature over the course of 10 min. The reaction mixture was allowed to warm up to 20 °C and stirred for 18 h. The reaction mixture was cooled back to 0 °C and tri-*n*-butyltin chloride (10.28 g, 36.00 mmol) was added dropwise over the course of 20 min and warm up to 20 °C and stirred for another 8 h. Then the reaction was quenched with saturated NH₄Cl aqueous solution (50 mL). The aqueous layer was extracted with *n*-hexane (3 x 50 mL) and the combined organic phases were washed with water (3 x 100 mL). The organic phase was dried over MgSO₄ and the solvent was removed *in vacuo*. The crude product was filtered over silica gel (which was pretreated by stirring it in a 5% Et₃N in *n*-hexane solution to deactivate it). After removal of the solvent, the mixture was purified by bridge distillation (190 °C, 5 mbar) to receive 9.7 g (91 %) of colorless oil.

¹H NMR (500 MHz, CDCl₃): δ = 6.90 (t, ³J = 1.9 Hz, 1 H, H-d), 6.32–6.15 (m, 2 H, H-b, c), 3.83 (t, ³J = 7.6 Hz, 2 H, H-e), 1.77–1.71 (m, 2 H, H-f), 1.55–1.49 (m, 6 H, H-k), 1.36–1.28 (m, 12 H, H-g, h, i, l), 1.06–1.02 (m, 6 H, H-m), 0.90 (t, ³J = 7.3 Hz, 12 H, H-j, n) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 131.6 (C-a), 123.9 (C-d), 118.6 (C-b/c), 108.5 (C-b/c), 51.5 (C-e), 32.4, 31.6 (C-f, g), 29.1 (C-k), 27.3, 26.7, 22.5 (C-h, i, l), 13.9, 13.6 (C-j, n), 10.3 (C-m) ppm. ¹¹⁹Sn NMR (187 MHz, CDCl₃): δ = -64.0 ppm. HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₂H₄₄NSn]⁺ 441.2434; Found 441.2418. IR (ATR): ν = 2955 (m), 2925 (s), 2854 (m), 1510 (w), 1462 (m), 1417 (w), 1376 (w), 1282 (m), 1072 (m), 1001 (w), 960 (w), 864 (w), 765 (m), 749 (m), 710 (s), 690 (m), 665 (m), 613 (w), 596 (m), 504 (m) cm⁻¹.

2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-1H-pyrrole (3)

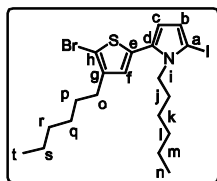


[Pd(PPh₃)₄] (866 mg, 750 μ mol) was added to a solution of 1-hexyl-2-(tributylstannyl)-1H-pyrrole (6.60 g, 15.0 mmol) and 2-bromo-3-hexyl-5-iodothiophene (5.60 g, 15.0 mmol) in DMF (60 mL) at 20 °C. The reaction mixture was stirred at 70 °C for 32 h and then poured into water (100 mL). The aqueous layer was extracted with diethyl ether (3 x 50 mL) and the combined organic phase was washed with water (3 x 80 mL) before drying over MgSO₄. The volatiles were removed *in vacuo*. The crude product was purified by column chromatography over silica gel (*n*-hexane/DCM 14:1, R_f = 0.51) to obtain 4.50 g (76%) of a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ = 6.73 (t, ³J = 2.2 Hz, 1 H, H-a), 6.67 (s, 1 H, H-f), 6.23 (dd, ³J = 3.6 Hz, ⁴J = 1.7 Hz, 1 H, H-c), 6.14 (t, ³J = 3.2 Hz, 1 H, H-b), 3.94 (t, ³J = 7.5 Hz, 2 H, H-i), 2.55 (t, ³J = 7.5 Hz, 2 H, H-o), 1.72–1.66 (m, 2 H, H-j), 1.62–1.56 (m, 2 H, H-p), 1.38–1.22 (m, 12 H, H-k, l, m, q, r, s), 0.91–0.84 (m, 6 H, H-n, t) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 142.2 (C-g), 134.6 (C-e), 126.5 (C-f), 125.8 (C-d), 122.9 (C-a), 110.4 (C-c), 107.9 (C-b), 107.7 (C-h), 47.5 (C-i), 31.7, 31.5, 31.4 (C-j, k, l), 29.7, 29.6 (C-o, p), 28.9, 26.4, 22.6, 22.5 (C-m, q, r, s), 14.1, 14.0 (C-n, t) ppm. HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₀H₃₀BrNS]⁺ 395.1282; Found 395.1275. IR (ATR): ν = 2955 (m), 2925 (s), 2854 (m), 1573 (w), 1525 (w), 1457 (m), 1432 (m), 1408 (w), 1377 (w), 1291 (m), 1195 (m), 1113 (w), 1071 (m), 1032 (w), 1002 (w), 835 (m), 783 (m), 750 (m), 710 (s), 643 (w), 612 (m), 584 (w), 497 (w), 478 (w) cm⁻¹.

2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-5-iodo-1H-pyrrole (4)

N-Iodo-succinimide (896 mg, 4.00 mmol) was added in one portion to a stirred solution of 2-(5-bromo-4-hexylthiophen-2-yl)-



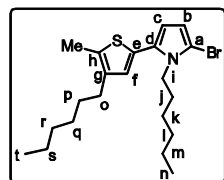
1-hexyl-1*H*-pyrrole (794 mg, 2.00 mmol) in THF (15 mL) at 20 °C. The reaction was stirred at 20 °C for 48 h. The reaction mixture was quenched with an aqueous solution of Na₂S₂O₃ (1 M, 10 mL) and the organic phase was extracted with diethyl ether (3 x 15 mL) before drying it over MgSO₄. The solvent was removed *in vacuo*. The crude product was purified by column chromatography over silica gel (*n*-hexane, R_f = 0.64) to give 866 mg (83%) of a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ = 6.78 (s, 1 H, H-f), 6.33 (d, ³J = 3.8 Hz, 1 H, H-c), 6.23 (d, ³J = 3.8 Hz, 1 H, H-b), 4.02 (t, ³J = 7.8 Hz, 2 H, H-i), 2.59 (t, ³J = 7.5 Hz, 2 H, H-o), 1.64-1.57 (m, 4 H, H-j, p), 1.38-1.21 (m, 12 H, H-k, l, m, q, r, s), 0.91-0.86 (m, 6 H, H-n, t) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 143.7 (C-g), 135.8 (C-e), 129.6 (C-d), 128.5 (C-f), 119.8 (C-c), 114.1 (C-b), 109.3 (C-h), 72.8 (C-a), 49.0 (C-i), 32.8, 32.4, 32.1 (C-j, k, l), 30.8, 30.4, 29.8 (C-o, p, q), 27.1 (C-m), 23.7, 23.5 (C-r, s), 14.4, 14.3 (C-n, t) ppm. HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₀H₂₉BrNS]⁺ 521.0249; Found 521.0238. IR (ATR): ν = 2954 (s), 2924 (s), 2854 (s), 1573 (w), 1521 (w), 1455 (s), 1402 (s), 1375 (m), 1288 (m), 1199 (m), 1102 (w), 1035 (w), 1002 (w), 967 (w), 867 (w), 839 (m), 754 (s), 725 (m), 661 (w), 584 (w), 475 (w) cm⁻¹.

Typical procedure of lithiation of precursor monomer 4

4 (261 mg, 0.50 mmol) was added in one portion to THF (15 mL) and the solution was cooled to -78 °C. *n*-BuLi (0.2 mL, 0.50 mmol, 2.5 M in hexanes) was added dropwise to the solution over the course of 1 min and stirred for 10 min. Then MeI (426 mg, 0.2 mL, 3 mmol) was added in one portion and stirred for 2 h at -78 °C. The reaction was quenched with water (5 mL) and the aqueous phase was extracted with ether (2 x 15 mL). The combined organic phase was dried over MgSO₄. The solvent was removed *in vacuo* and the crude product was checked by GC-MS and NMR. The isolated products are shown as follows:

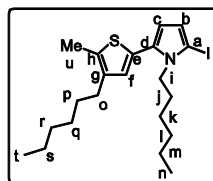
2-Bromo-1-hexyl-5-(4-hexyl-5-methylthiophen-2-yl)-1*H*-pyrrole (5)



¹H NMR (500 MHz, MeOD): δ = 6.72 (s, 1 H, H-f), 6.14 (d, ³J = 3.8 Hz, 1 H, H-b/c), 6.11 (d, ³J = 3.8 Hz, 1 H, H-b/c), 4.05-3.95 (m, 2 H, H-i), 2.53 (t, ³J = 7.5 Hz, 2 H, H-o), 2.34 (s, 3 H, H-u), 1.65-1.54 (m, 4 H, H-j, p), 1.38-1.19 (m, 12 H, H-k, l, m, q, r, s), 0.93-0.83 (m, 6 H, H-n, t) ppm. ¹³C NMR (126 MHz, MeOD): δ = 139.8 (C-g), 133.7 (C-h), 131.1 (C-e), 129.3 (C-a/d), 129.2 (C-f), 111.6 (C-b/c), 111.4 (C-b/c), 103.7 (C-a/d), 46.9 (C-i), 31.8 (C-j/p), 31.6 (C-j/p), 29.0 (C-o), 32.9, 32.4, 30.0, 27.1, 23.7, 23.6 (C-k, l, m, q, r, s), 14.4, 14.3 (C-t, n), 12.7 (C-u) ppm. HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₇H₃₇BrNS]⁺ 409.1339; Found 409.1442. IR (ATR): ν = 2954 (s), 2924 (s), 2855 (s), 1458 (s), 1428 (m), 1402 (w), 1377 (m), 1289 (m), 1194 (m), 1158 (w), 1109 (w), 1030 (w), 961 (w), 892 (w), 839 (m), 750 (vs) cm⁻¹.

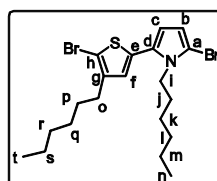
1-Hexyl-2-(4-hexyl-5-methylthiophen-2-yl)-5-iodo-1*H*-pyrrole (6)

¹H NMR (500 MHz, MeOD): δ = 6.70 (s, 1 H, H-f), 6.29 (d, ³J = 3.7 Hz, 1 H, H-b/c), 6.16 (d, ³J = 3.7 Hz, 1 H, H-b/c), 4.03-3.98 (m, 2 H, H-i), 2.53 (t, ³J = 7.5 Hz, 2 H, H-o), 2.34 (s, 3 H, H-u),



1.65-1.53 (m, 4 H, H-j, p), 1.38-1.19 (m, 12 H, H-k, l, m, q, r, s), 0.93-0.83 (m, 6 H, H-n, t) ppm. ¹³C NMR (126 MHz, MeOD): δ = 139.7 (C-g), 133.9 (C-h), 131.1 (C-d/e), 131.1 (C-d/e), 129.2 (C-f), 119.5 (C-b/c), 113.2 (C-b/c), 71.2 (C-a), 49.0 (C-i), 32.1 (C-j/p), 31.6 (C-j/p), 29.0 (C-o), 32.9, 32.4, 30.0, 27.1, 23.7, 23.6 (C-k, l, m, q, r, s), 14.4, 14.3 (C-t, n), 12.7 (C-u) ppm. HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₇H₃₂BrNS]⁺ 457.1300; Found 457.1292. IR (ATR): ν = 2954 (s), 2924 (s), 2855 (s), 1458 (s), 1420 (m), 1396 (w), 1376 (m), 1289 (m), 1194 (m), 1158 (w), 1102 (w), 1030 (w), 961 (w), 889 (w), 839 (m), 752 (vs) cm⁻¹.

2-Bromo-5-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-1*H*-pyrrole (8)



¹H NMR (500 MHz, MeOD): δ = 6.80 (s, 1 H, H-f), 6.22 (d, ³J = 3.8 Hz, 1 H, H-b/c), 6.16 (d, ³J = 3.8 Hz, 1 H, H-b/c), 4.06-4.01 (m, 2 H, H-i), 2.63-2.56 (2 H, H-o), 1.67-1.57 (m, 4 H, H-j, p), 1.41-1.20 (m, 12 H, H-k, l, m, q, r, s), 0.94-0.84 (m, 6 H, H-n, t) ppm. ¹³C NMR (126 MHz, MeOD): δ = 143.8 (C-g), 135.8 (C-e), 128.5 (C-f), 127.9 (C-d), 112.4 (C-b/c), 112.0 (C-b/c), 109.0 (C-h), 105.0 (C-a), 46.9 (C-i), 32.8, 32.4, 31.8, 30.8, 30.4, 29.9, 27.1, 23.7, 23.6 (C-j, k, l, m, o, p, q, r, s), 14.4, 14.3 (C-t, n) ppm. HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₆H₂₉Br₂NS]⁺ 473.0388; Found 473.0411. IR (ATR): ν = 2955 (s), 2925 (s), 2856 (s), 1577 (w), 1524 (w), 1461 (s), 1411 (m), 1378 (w), 1290 (m), 1202 (m), 1111 (w), 1034 (w), 971 (w), 869 (w), 839 (m), 751 (vs) cm⁻¹.

General procedure for polymerization of 7

In a microwave vial, *i*PrMgCl (0.25 mL, 2.00 M in THF, 0.50 mmol) was added dropwise to a solution of precursor monomer 4 (261 mg, 0.50 mmol) in dry MTBE (3.0 mL) via a hamilton syringe in the glove box at 20 °C over the course of 1 min. After stirring the reaction mixture for 10 min at 20 °C, a solution of [Pd(*i*Bu₃P)₂] (5.11 mg, 10.0 μmol) in MTBE (1.0 mL) was added to the reaction mixture. The reaction mixture was heated up to 50 °C under microwave irradiation and stirred for 5 h. Then the reaction mixture was quenched with H₂O (10 mL) and the aqueous phase was extracted with diethyl ether (2 x 20 mL). The combined organic layer was washed with brine (1 x 20 mL) and dried with MgSO₄. The volatiles were removed *in vacuo* to give the crude product. This was dissolved in diethyl ether (0.5 mL) and the solution was added dropwise into methanol (200 mL) with vigorous stirring to remove the low molecular weight compounds. The precipitated polymer was extracted by soxhlet extractor with MeOH (200 mL) for 5 h. For removal from the Soxhlet extractor, the solid polymer was refluxed by diethyl ether (100 mL). The volatiles were removed *in vacuo* and product was dried under reduced pressure for 16 h give the polymer as orange to red brown viscous solid.

¹H NMR (600 MHz, CDCl₃): δ = 6.97 (s, 1 H, H-f), 6.41 (d, ³J = 3.6 Hz, 1 H, H-b/c), 6.26 (d, ³J = 3.6 Hz, 1 H, H-b/c), 4.17-3.92 (m, 2 H, H-i), 2.66-2.46 (m, 2 H, H-o), 1.64-1.51 (m, 4 H, H-j, p), 1.35-1.09 (m, 12 H, H-k, l, m, q, r, s), 0.88 (t, ³J = 6.8 Hz, 3 H,

8

Tetrahedron

H-n/t), 0.81 (t, $^3J = 7.1$ Hz, 3 H, H-n/t) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 142.8$ (C-g), 134.9 (C-e), 128.1 (C-a/d), 127.6 (C-h), 126.7 (C-a/d), 126.3 (C-f), 112.0 (C-b/c), 110.0 (C-b/c), 45.3 (C-i), 31.7 (C-k/l/m/q/r/s), 31.2 (C-k/l/m/q/r/s), 31.0 (C-j/p), 30.7 (C-j/p), 29.1 (C-o), 29.1 (C-k/l/m/q/r/s), 26.3 (C-k/l/m/q/r/s), 22.6 (C-k/l/m/q/r/s), 22.4 (C-k/l/m/q/r/s), 14.1 (C-n/t), 13.9 (C-n/t) ppm. IR (ATR): $\nu = 2953$ (s), 2923 (s), 2854 (s), 1458 (s), 1402 (m), 1376 (m), 1308 (m), 1193 (m), 1033 (m), 873 (w), 839 (m), 762 (m), 723 (m), 684 (w), 637 (w), 567 (w) cm^{-1} .

Procedure for the kinetics study

In a microwave vial, PrMgCl (0.25 mL, 2.00 M in THF, 0.50 mmol) was added dropwise to a solution of precursor monomer 4 (261 mg, 0.50 mmol) and naphthalene (64.1 mg, 0.50 mmol, used as an internal standard for GC analysis to analyze the conversion) in dry MTBE (3.0 mL) via a hamilton syringe in the glove box at 20 °C over the course of 1 min. After stirring the reaction mixture for 10 min at 20 °C, a solution of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ (5.11 mg, 10.0 μmol) in MTBE (2.0 mL) was added to the reaction mixture. After the 60 min, 120 min, 180 min, 240 min, 300 min, 360 min, 375 min, 390 min, 415 min, 440 min, a sample (0.3 mL) was taken out of the reaction mixture. 0.1 mL of the solution was quenched with 2 droplets of ethanol. The quenched solution was diluted with 3 mL of THF, 2 mL of the solution was filtered with a syringe filter (0.45 μm) and used for GC analysis. The other 0.2 mL of reaction mixture was quenched with ethanol (1 mL) and diluted with Et_2O (4 mL) and water (2 mL). After shaking the vial, the layers were separated. The organic phase was dried over MgSO_4 and filtered with a syringe filter (0.45 μm). Half of the solvent was removed *in vacuo*, diluted in chloroform (HPCL grade, 2 mL) and used for GPC analysis. The other half of the solvent was removed *in vacuo*, diluted in deuterated benzene for NMR analysis.

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References and notes

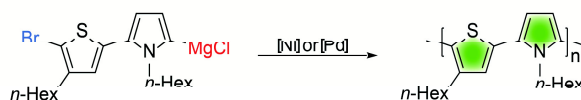
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60. The peak is overlapping with the solvent peak.

Graphical Abstract

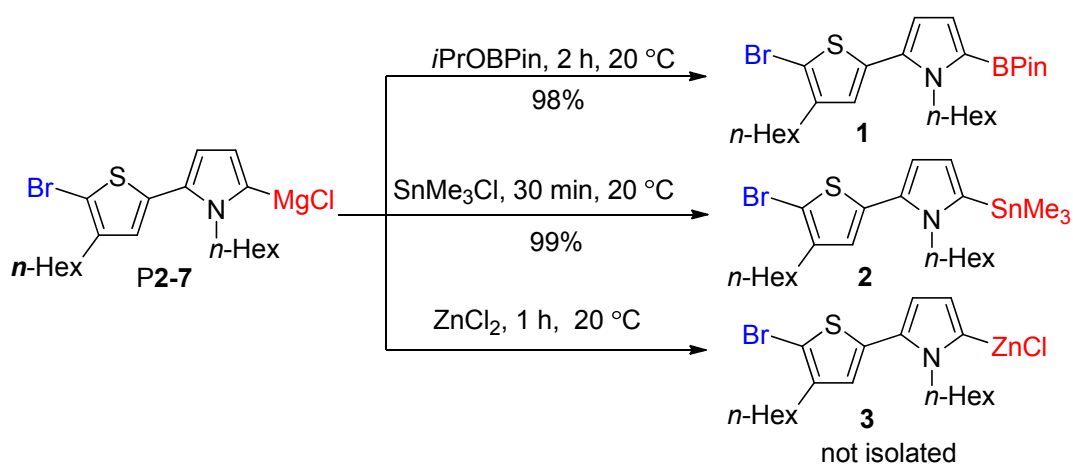
**Synthesis of Poly(thiophene-*alt*-pyrrole)
from a Difunctionalized Thiénylpyrrole by
Kumada Polycondensation**

Lu-Ying He, Sara Urrego-Riveros, Paul J. Gates, Christian Näther, Maren Brinkmann, Volker Abetz and Anne Staubitz *

Otto Diels-Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, Kiel 24098 Germany

3.2.2 More stable difunctionalized thienylpyrroles for poly(thiophene-*alt*-pyrrole)

Except the difunctional monomer based on magnesium, other difunctional monomers with zinc, boron, or tin could also be used for polymerization by Negishi coupling, Suzuki coupling and Stille coupling respectively. Moreover, the monomers with boron or tin can be purified and isolated. The monomers containing other different metal functional groups (BPin for **1**, SnMe₃ for **2**, ZnCl for **3**) were prepared by transmetallation from Grignard-type monomer **P2-7**² in excellent yields (Scheme 5). Suzuki-type monomer **1** was prepared in an excellent yield of 98% by quenching Grignard-type monomer **P2-7** with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Stille-type monomer **2** was prepared in an excellent yield of 99% by quenching Grignard-type monomer **P2-7** with trimethyltin chloride. For the two transmetallation reactions, there was no need to do further purification after the work up, which also proves the iodo-magnesium exchange to Grignard-type monomer **P2-7** was quantitative. Negishi-type monomer **3** was synthesized by quenching Grignard-type monomer **P2-7** with zinc chloride at 20 °C for 1 h.



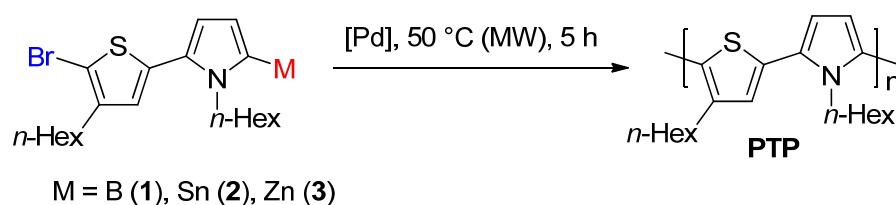
Scheme 5. Synthesis of monomers **1**, **2** and **3** by transmetalation from Grignard-type monomer **P2-7**.

Monomer **1**, **2** and **3** were firstly polymerized by 5 mol% of [Pd(*t*Bu₃P)₂] in MTBE at 50 °C under microwave irradiation for 5 h (Table 1, entries 1, 3, 5). This set of conditions was for the polymerization of Grignard-type monomer **P2-7** (Chapter 3.2.1). For the Suzuki-type polycondensation of **1**, additional 10 eq. of K₃PO₄ in H₂O was used

² **P** stands for “publication”, **2** is the number of subsection where the publication appears and **4** is the number of the molecule in the publication. The follows are the same.

as a base. The Suzuki-type polymerization just afforded oligomers ($M_n = 1600$) in a yield of 30%, perhaps due to the poor immiscibility of MTBE and water (Table 1, entry 1). In fact, when MTBE was replaced by THF to increase the solubility of K_3PO_4 , the yield reached 56% and M_n was ca. 5600 (Table 1, entry 2). For Stille polycondensation of **2**, the condition afforded 82% of yield, and a higher M_n with a relative low PDI ($M_n = 7.3$ kDa, PDI = 1.9) (Table 1, entry 3). When replacing the solvent with DMF, no polymerization was observed (Table 1, entry 4). For Negishi-type polycondensation of **3**, the condition gave the longest polymer chain ($M_n = 12.3$ kDa, PDI = 2.3) (Table 1, entry 5). The polymerization was also efficient when the catalyst loading was reduced to 2 mol% (Table 1, entry 6).

Table 1. The polymerization of **1**, **2** and **3**^a.



entry	Poly-mer	Mono-mer	catalyst	cat. loading [mol%]	solvent	yield (%)	M_n^a	M_w/M_n^a	expected M_n^b
1	PTP1	1 ^c	$[Pd(tBu_3P)_2]$	5	MTBE	30	1600	1.4	6300
2	PTP1	1 ^c	$[Pd(tBu_3P)_2]$	5	THF	56	5600	1.6	6300
3	PTP2	2	$[Pd(tBu_3P)_2]$	5	MTBE	82	7300	1.9	6300
4	PTP2	2	$[Pd(PPh_3)_4]$	5	DMF	-	-	-	6300
5	PTP3	3	$[Pd(tBu_3P)_2]$	5	MTBE	95	12300	2.3	6300
6	PTP3	3	$[Pd(tBu_3P)_2]$	2	MTBE	97	10000	2.0	15700

^a Estimated by GPC based on polystyrene standard (eluent: $CHCl_3$, 1 mL/min). ^b If the polymerization was a quasi-living chain-growth polymerization. ^c additional 10 eq. of K_3PO_4 in 1 mL of degassed H_2O was added into the reaction.

The polymers were analyzed with respect to their absorption properties (Figure 18, three representative examples of polymers prepared under the conditions of Table 1, entries 2, 3, 5). The absorption spectra of the isolable monomers **1** and **2** in diethyl ether solution all showed maximum peaks at ca. 306 nm. The absorption peaks of the polymers **PTP1-PTP3** in diethyl ether solution were all observed at 348 nm, irrespective of the monomer they were prepared from (**1**, **2**, and **3**). If the polymers were processed as films by spin-coating, the absorption maximal peak were all at 354 nm. The absorption bands of the polymer **PTP** in both solution and processed as a film were

relatively very narrow compared to regioregular poly(3-alkylthiophene) (rr-P3AT) ($\lambda_{\max} \approx 450$ nm).^[71] This may be attributed to the effect of steric interactions of neighboring *n*-hexyl groups that reduce the conjugation length of the polymers (see chapter 3.2.1).

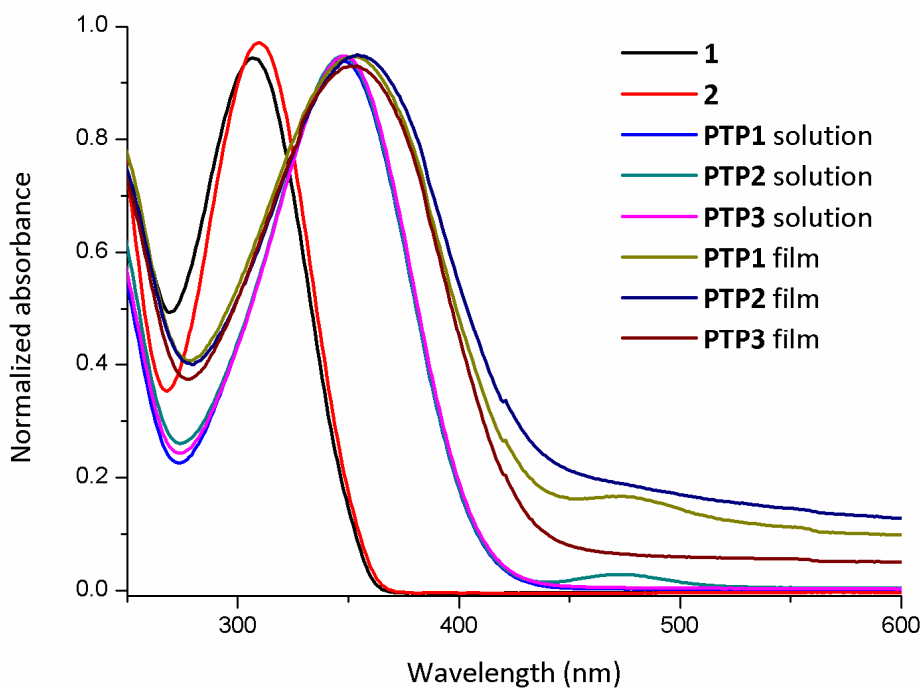


Figure 18. UV-vis spectra of monomer **1**, **2** and **PTP1- PTP3** in diethyl ether and as films.

Irrespective of the chain length obtained (Table 1, entries 2, 3, 5), the ether solutions of **PTP1-PTP3** all give a bright-green fluorescence with the maximum emission wavelength of ca. 487 nm (Figure 19), corresponding to the onset of π - π^* transition of the electronic absorption spectra, which is at significantly higher energy than the rr-P3AT ($\lambda_{\max} \approx 570$ nm).^[71]

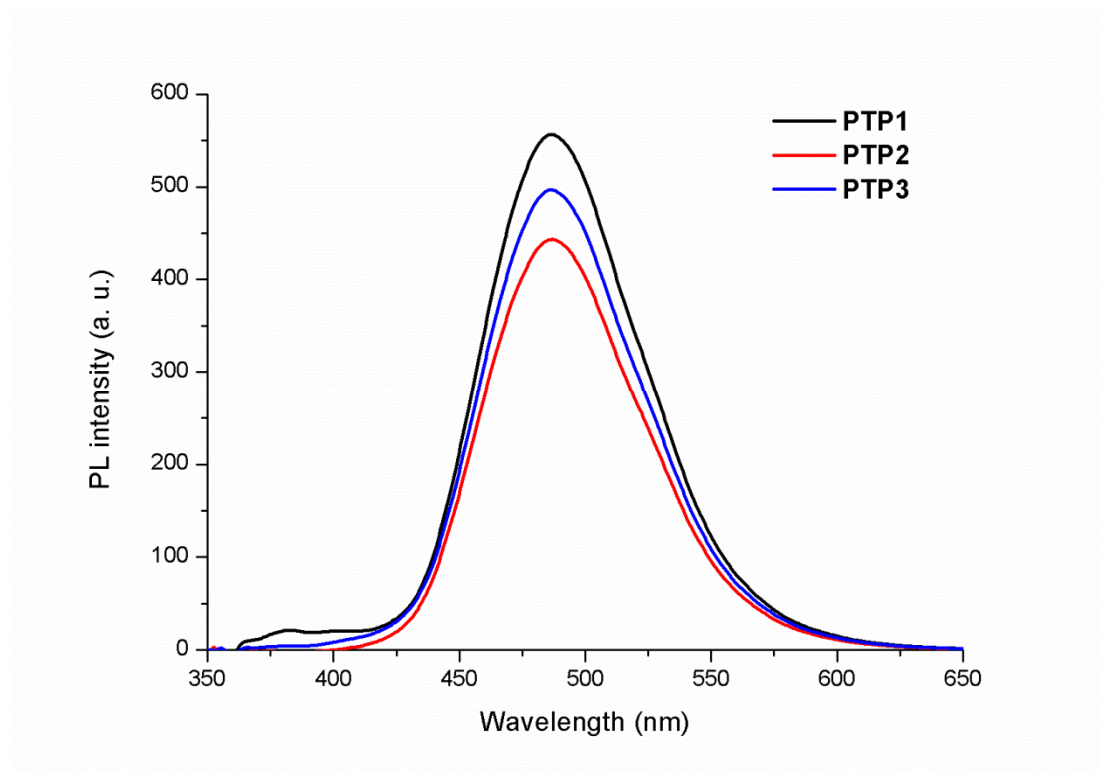


Figure 19. PL spectra ($\lambda_{\text{exc}} = 348 \text{ nm}$) of **PTP1**- **PTP3** in diethyl ether.

In conclusion, three difunctional thienylpyrrole monomers containing a different metal group and a bromo group were synthesized in high yields via transmetalation. By using these monomers, alternating copolymers **PTP** containing 3-alkylthiophene and *N*-alkylpyrrole were prepared by palladium catalyzed Kumada polycondensation. The molecular weights of **PTP1** and **PTP2** were not sufficiently high, suggesting that the conditions for the polymerization need to be optimized. The absorption bands of all polymers in both solution and solid film were relatively narrow due to the effect of steric interactions of neighboring *n*-hexyl groups that reduce the conjugation length of the polymers.

3.3 Bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-Bu₃P)₂] – a Versatile Catalyst

“Bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-Bu₃P)₂]”

Lu-Ying He, *Synlett* **2015**, 26.

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During my research on the synthesis of poly(pyrrole-*alt*-thiophene), a crucial step was to develop a synthetic route towards the polymer based on the monomer which contains both nucleophilic (metal) and electrophilic (halogen) functional groups. Bis(tri-*tert*-butylphosphine)palladium(0), [Pd(*t*Bu₃P)₂], has shown the best efficiency, resulting in high yields, and giving a high molecular weight polymer via Kumada polycondensation (Chapter 3.2). In order to highlight also other important applications of [Pd(*t*Bu₃P)₂], a short “Spotlight” was submitted and accepted for publication to the journal *Synlett*.

Bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-Bu₃P)₂]

Lu-Ying He

Otto-Diels-Institut für Organische Chemie, University of Kiel, Otto-Hahn-Platz 4, 24098 Kiel, Germany
lhe@oc.uni-kiel.de

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Lu-Ying He was born in Sichuan, China, in 1986. She obtained her B.Sc. from Southwest University in 2008, China and studied at South China University of Technology from 2008 to 2011. Currently, she is working towards her Ph. D. at the Otto-Diels-Institute for Organic Chemistry under supervision of Prof. Dr. Anne Staubitz. Her research focuses on transition-metal-catalyzed cross-coupling reactions and semiconducting polymers with alternating heterocycle units.



Introduction

The catalyst bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-Bu₃P)₂, **1**, CAS: 53199-31-8] is a colorless, air-sensitive solid. It must be manipulated in a glove box or under inert gas. [Pd(*t*-Bu₃P)₂] (**1**) contains bulky, electron-rich tertiary phosphine ligands [*t*-Bu₃P]. In a palladium-catalyzed cross-coupling reaction, they promote the oxidative addition as they can stabilize higher oxidation states. Reductive elimination is also facilitated because of the bulky ligands. Thus **1** has been shown to be superior in transition-metal-catalyzed cross-coupling reactions compared to the classical [Pd(Ph₃P)₄] catalyst. [Pd(*t*-Bu₃P)₂] is not only efficient for typical cross-coupling reactions, such as Stille, Negishi, Suzuki, Heck, Sonogashira, or Buchwald–Hartwig aminations, with electrophiles R-X (X = Cl, Br, I, OTf, SO₂Cl and others), but also for cross-coupling of organolithium reagents,¹ alkenylgermanes,² alkali-metal silanolates,³ trior-

gano-indium reagents⁴ and others. Moreover, it has been used for arylations of hydro-siloxanes,⁵ decarboxylative cross-coupling reactions,⁶ carbonylations and amino-carbonylations,⁷ carboindinations,⁸ C-H functionalizations,⁹ cyanations,¹⁰ methylenation of olefins¹¹ and annulation reactions.¹² In recent years, **1** has become one of the best new-generation catalysts and plays an important role in organic synthesis.

[Pd(*t*-Bu₃P)₂] is commercially available and can also be prepared by treating [Pd(η⁵-C₅H₅)(η³-C₃H₅)] with the ligand [*t*-Bu₃P] in *n*-hexane at room temperature for 3 h.¹³ The pale red crude product can be recrystallized from *n*-hexane at –20 °C to give pure colorless crystals.

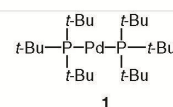
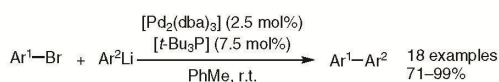
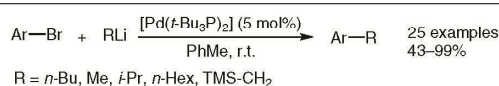


Figure 1 Bis(tri-*tert*-butylphosphine)palladium

Table 1 The Use of Bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-Bu₃P)₂]

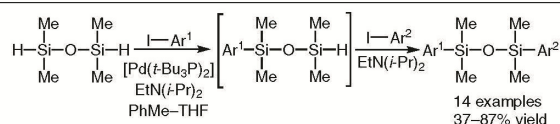
[Pd(*t*-Bu₃P)₂]-Catalyzed Cross-Coupling of Organolithium Reagents
Feringa and coworkers reported [Pd(*t*-Bu₃P)₂]-catalyzed cross-coupling reactions between alkyllithium reagents and a variety of aryl- and alkenylbromides under mild conditions.¹ Those cross-coupling reactions are highly selective, avoiding lithium–halogen exchange and homocoupling side reactions. The authors also extended the cross-coupling reactions to (hetero)aryllithium reagents by using the in situ prepared catalyst [Pd₂(dba)₃] and [*t*-Bu₃P] as ligand.



[Pd(*t*-Bu₃P)₂]-Catalyzed Cross-Coupling of Alkali-Metal Silanolates
A broadly applicable protocol for the [Pd(*t*-Bu₃P)₂]-catalyzed cross-coupling of a wide range of alkali metal arylsilanolates with various aryl halides was developed.³ This method also applied to the cross-coupling of heteroarylsilanolates.

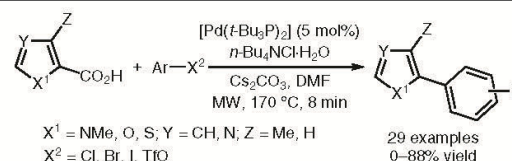


[Pd(*t*-Bu₃P)₂]-Catalyzed Arylation of Hydrosiloxanes
Symmetrical and unsymmetrical siloxanes were synthesized by [Pd(*t*-Bu₃P)₂]-catalyzed arylation of hydrosiloxanes.⁵ This method was a one-pot process and showed high functional group tolerance. It was also exploited to perform triple arylations.

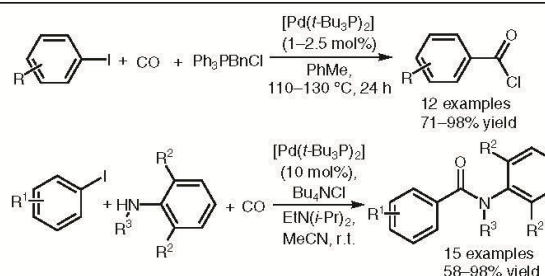


[Pd(*t*-Bu₃P)₂]-Catalyzed Decarboxylative Cross-Coupling Reaction

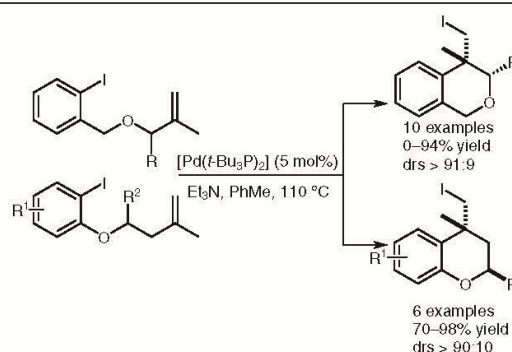
Forgione, and Bilodeau and coworkers developed a procedure for highly selective Pd-catalyzed decarboxylative cross-coupling reactions between heteroaromatic carboxylic acids and various aryl halides in the presence of a reactive C-H group.⁶ This process provides a valuable alternative for other cross-coupling reactions, in cases where appropriate cross-coupling partners are not commercially available and hard to be synthesized.

**[Pd(*t*-Bu₃P)₂]-Catalyzed Carbonylation and Aminocarbonylation**

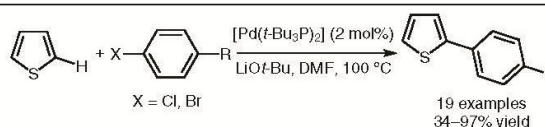
Traditional methods to synthesize acid chloride involve toxic reagents, such as PCl₃, thionyl chloride and oxalyl chloride. Quesnel and Arndtsen described a new method to construct acid chlorides via the [Pd(*t*-Bu₃P)₂]-catalyzed carbonylation of aryl iodides under mild conditions.⁷ The decisive step of the process was reductive elimination of [(*t*-Bu₃P)(CO)Pd(COAr)Cl], which was facilitated by the combination of the bulky, electron-rich [*t*-Bu₃P], the phosphine chloride and CO coordination. This method was exploited to perform traditional aminocarbonylation of aryl iodides under exceptionally mild conditions (ambient temperature and pressure).

**[Pd(*t*-Bu₃P)₂]-Catalyzed Carboiodination**

Various functionalized chromans and isochromans were prepared via the intramolecular [Pd(*t*-Bu₃P)₂]-catalyzed carboiodination of alkenyl aryl iodides in the presence of an amine base Et₃N.⁸ Those cyclizations had a broad functional group tolerance and showed high diastereo-selectivities, which was thought to originate from the minimization of axial-axial interactions in the carbopalladation step.

**[Pd(*t*-Bu₃P)₂]-Catalyzed C-H Functionalization**

Tamba and coworkers described a facile [Pd(*t*-Bu₃P)₂]-catalyzed C-H arylation of heteroarene compounds with aryl bromides and aryl chlorides in the presence of LiOt-Bu as a base.⁹



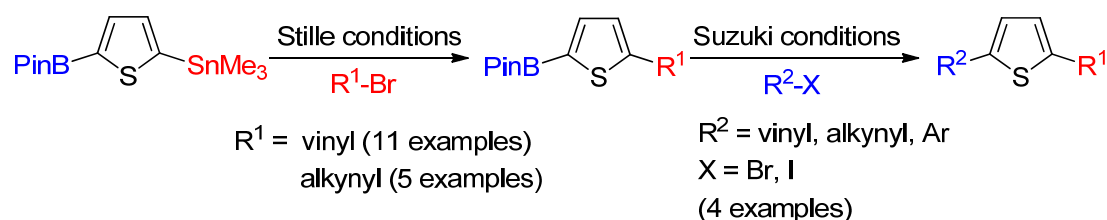
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4 Summary and Outlook

Nucleophile selective cross-coupling reactions

To access more building blocks for semiconducting polymers, especially for conjugated alternating copolymers containing vinylene or ethynylene linkages, nucleophile selective cross-coupling reactions with vinyl and alkynyl bromides on a dinucleophilic aromatic substrate were successfully developed. Homo-coupling reaction of the nucleophile and the electrophile respectively has shown to be potential competing side reactions (Scheme 6). After systematically optimizing over 40 different reaction conditions (solvents, catalysts, reaction temperature, time, catalyst loading and concentration of reaction mixture), the side reactions could be largely suppressed in all cases, and fully nucleophile selective cross-coupling reactions could be achieved. Here, only the tin reacted in the first Stille coupling reaction in high yields, and the boronic ester stayed intact. The optimal reaction conditions for the initial Stille coupling are general over a wide variety of electron rich, electron neutral and electron poor vinyl bromides (11 examples). Moreover, these reaction conditions are also efficient for alkynyl bromides, even though the purification has proven to be difficult (5 examples).

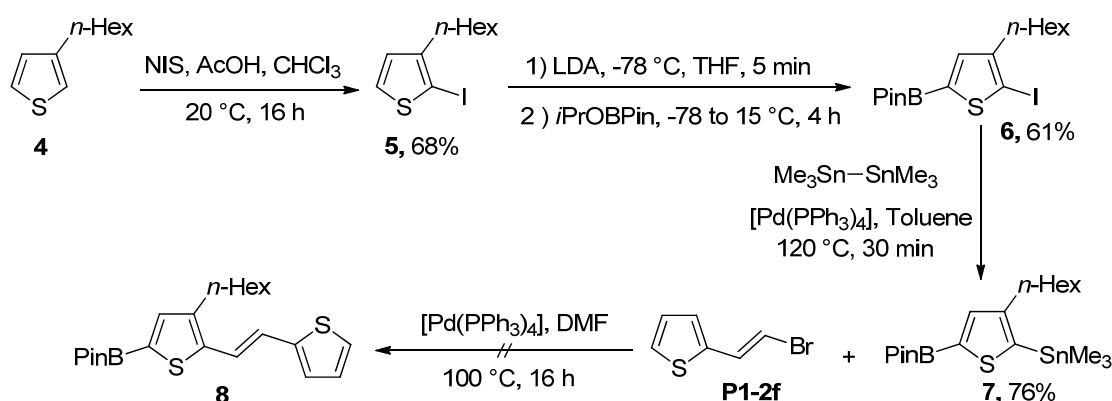


Scheme 6. Nucleophile selective cross-coupling reactions with vinyl and alkynyl bromides on a dinucleophilic aromatic substrate were developed after optimizing over 40 reaction conditions.

In both cases, the resulting products are extremely versatile building blocks: 1) they still contain a boronic ester functional group that can be further coupled with a second electrophile by a Suzuki–Miyaura cross-coupling in a one-pot reaction (4 examples). By merely adding a base, water and a second electrophile to the reaction mixture after completion of the Stille cross-coupling reaction, this could be accomplished. 2) a further halogenation of the resulting molecule would produce a compound which contains a boronic ester and a halogen functional group, which could be used as monomers for quasi-living chain growth polymerization to make poly(*p*-phenylene

vinylene) **PPV** and poly(*p*-phenylene ethynylene) **PPE** analogues. However, these kinds of polymers are hardly soluble, which has a negative impact on their processability. To increase the solubility, one *n*-hexyl chain was introduced to thiophene moiety **7** (Scheme 7). However, the cross-coupling reaction between **7** and 2-(2-bromovinyl)-thiophene did not proceed even under microwave irradiation, which may be due to the steric hinderance of the *n*-hexyl chain.

In future work, further optimizations need to be conducted to obtain higher yields of the product **8**. After obtaining the monomer, the conditions for polymerization and the kinetics of polymerization need to be investigated.

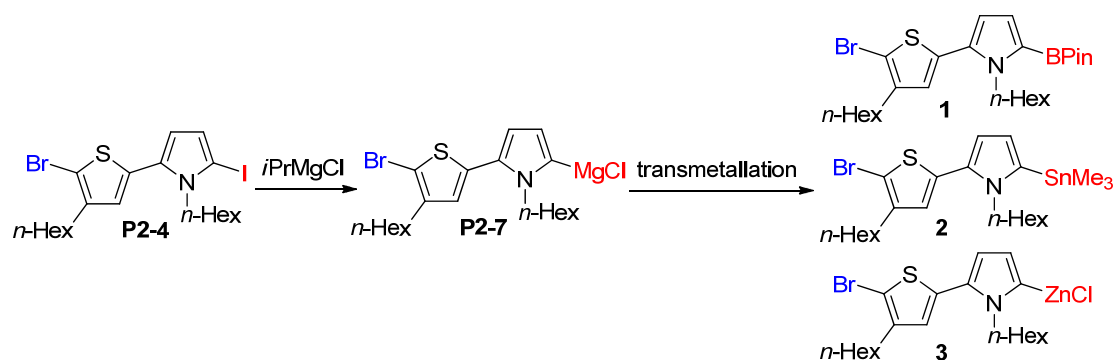


Scheme 7. Synthesis of dinucleophilic thiophene **7** with a *n*-hexyl side chain and attempted cross-coupling with 2-(2-bromovinyl)-thiophene.

Difunctionalized thienopyrrole monomers for poly(thiophene-*alt*-pyrrole)

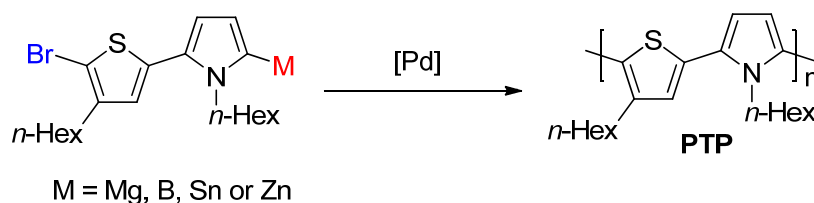
The most common way to make conjugated alternating copolymers is to cross-couple two co-monomers; one containing two halogen functional groups, and one containing two metal groups. A newly developed approach to make alternating copolymers is via a single monomer which contains both a metal functional group and a halogen group in only one molecule. This kind of monomer is highly desirable as it has the potential to make the polymerization via a quasi-living chain growth mechanism.

In this work, four different thienopyrrole monomers containing both a metal group (Mg, B, Sn or Zn) and a bromo group were synthesized in high yields via a chemo-selective halogen-magnesium exchange and subsequent transmetalation (Scheme 8).



Scheme 8. Synthesis of dicunctionalized monomers via halogen-magnesium exchange and subsequent transmetalation.

By using these difunctionalized monomers, copolymers poly(thiophene-*alt*-pyrrole) **PTP** containing alternating 3-alkylthiophene and *N*-alkylpyrrole were prepared by palladium catalyzed Kumada, Suzuki, Stille or Negishi polycondensation respectively after optimizing the reaction conditions (Scheme 9). The molecular weights were high and a moderate polydispersity was found. However, the kinetics study of the polymerization of **P2-7** indicated that the polymerization proceeded via a step-growth mechanism, and the optical and thermal properties of the polymers suggested a wide band gap polymer, with a very low T_g for such materials.



Scheme 9. Synthesis of **PTP** from difunctionalized monomers

For further work, I suggest to decrease the steric interactions of neighboring *n*-hexyl groups, by replacing them with smaller alkyl chains, thus improving the conjugation length and to decrease the band gap. The alkyl chain at the *N*-position could be replaced by a less flexible chain, like acetylenic side chain, which was reported by Yamamo and coauthors.^[72] This monomer could further combine an electron poor heterocycle, like benzothiadiazole to make a D-A monomer. The polymer from D-A monomer could also lower the band gap significantly.

5 Experimental Section

5.1 Supporting information for *Eur. J. Org. Chem.* 2015, 14.

Eur. J. Org. Chem. 2015 · ISSN 1099-0690

SUPPORTING INFORMATION

DOI: 10.1002/ejoc.201500138

Title: Nucleophile-Selective Cross-Coupling Reactions with Vinyl and Alkynyl Bromides on a Dinucleophilic Aromatic Substrate

Author(s): Lu-Ying He, Mathias Schulz-Senft, Birk Thiedemann, Julian Linshoef, Paul J. Gates, Anne Staubitz*

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Abbreviations

A	area
anhyd.	anhydrous
Ar	aryl
ATR	attenuated total reflectance
calcd.	calculated
CI	chemical ionization
COSY	correlated spectroscopy
d	doublet (NMR)
DEPT	distortionless enhancement by polarization transfer
DMF	<i>N,N</i> -dimethylformamide
dppe	1,2- <i>bis</i> (diphenylphosphino)ethane
dppf	1,1'- <i>bis</i> (diphenylphosphino)ferrocene
EI	electron ionization
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
HSQC	heteronuclear single quantum coherence
HPLC	high-performance liquid chromatography
IR	infrared
m	medium (concerning the intensity) (IR)
m	multiplet (NMR)
M.p.	melting point
MS	mass spectrometry
MW	microwave
n	amount of substance
NBS	<i>N</i> -bromosuccinimide
NMR	nuclear magnetic resonance
Pin	pinacol
RF	response factor
R _t	retardation factor
s	strong (concerning the intensity) (IR)
s	singlet (NMR)
SPhos	2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl
t	triplet (NMR)
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMS	tetramethylsilane
w	weak (concerning the intensity) (IR)

General Methods and Materials

All syntheses were carried out using standard Schlenk techniques or in glovebox under a dry and inert nitrogen atmosphere unless stated otherwise. Glassware and NMR-tubes were dried in an oven at 200 °C for at least 2 h prior to use. Reaction vessels were heated under vacuum and purged with nitrogen three times before adding reagents.

Analyses

¹H NMR, ¹³C NMR, ¹¹B NMR and ¹¹⁹Sn NMR spectra were recorded at 300 K. ¹H NMR spectra were recorded on a Bruker DRX500 (500 MHz) spectrometer or Bruker Avance 600 (600 MHz) spectrometer. ¹³C NMR spectra were recorded on a Bruker DRX 500 (125 MHz) spectrometer or Bruker Avance 600 (150 MHz) spectrometer. ¹¹B NMR and ¹¹⁹Sn NMR spectra were recorded on a Bruker DRX 500 (160 MHz) spectrometer. All ¹H NMR and ¹³C NMR spectra were referenced against the residual solvent peak. ¹¹B NMR spectra were referenced against BF₃·OEt₂ in CDCl₃, the reference of the ¹¹⁹Sn NMR spectra was calculated based on the ¹H NMR signal of TMS. ²⁹Si NMR spectra were recorded on a Bruker DRX 500 (99 MHz) spectrometer and the reference was calculated based on the ¹H NMR signals of CHCl₃.

The exact assignment of the peaks was proven by ¹H, ¹³C DEPT and two-dimensional NMR spectroscopy such as ¹H COSY, ¹H/¹³C HSQC or ¹H/¹³C HMBC when possible.

IR spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer with a A531-G Golden-Gate-ATR-unit. Ultra High resolution ESI mass spectra were recorded on a Bruker Daltonics Apex IV Fourier transform Ion Cyclotron resonance mass spectrometer. The high resolution EI mass spectra were run on a VG Analytical Autospec apparatus.

All melting points were recorded on a LG1586 Electrothermal® IA6304 capillary melting point and are uncorrected.

GC-MS analysis was performed on a Hewlett Packard 5890A gas chromatograph, equipped with a Hewlett Packard 5972A mass selective detector (EI at 70 eV) and an Agilent Technologies dimethylpolysiloxane column (19091S-931E, nominal length 15 m, 0.25 mm diameter, 0.25 µm grain size). Helium was used as the carrier gas.

GC analysis was performed on an Agilent Technologies 6890N gas chromatograph, equipped with an Agilent Technologies 7683 Series Injector, an Agilent Technologies (5 %-phenyl)-methylpolysiloxane column (19091J-413, nominal length 30 m, 0.32 mm diameter, 0.25 µm grain size) and a flame ionization detector (FID). Nitrogen was used as the carrier gas.

Reactions under microwave irradiation were carried out using a Biotage® Initiator + SP Wave synthesis system, with continuous irradiation power from 0 to 400 W (Organic Synthesis Mode). The temperature was measured with an external IR sensor during microwave heating. All reactions were carried out in 2 mL oven-dried Biotage microwave vials sealed with an aluminum/Teflon® crimp top, which can be exposed to a maximum of 250 °C and 20 bar internal pressure.

Chemicals

All reagents were used without further purification unless noted otherwise.

Compound	Supplier	Purity	Comment
(Bromomethyl)triphenylphosphonium bromide	Sigma-Aldrich Inc.	98%	
(<i>E</i>)-3-(3-Pyridyl)acrylic acid	Alfa Aesar Inc.	98%	
(<i>E</i>)-4-Nitrocinnamic acid	Alfa Aesar Inc.	98%	
[Pd(dppe)Cl ₂]	Strem Chemicals Inc.	98%	
[Pd(dppf)Cl ₂]	Sigma-Aldrich Inc.	>98%	
[Pd(OAc) ₂]	Strem Chemicals Inc.	>98%	
[Pd(PPh ₃) ₄]	ABCR Inc.	99%	
[Pd(PtBu ₃) ₂]	Strem Chemicals Inc.	>98%	
1,3,5-Triisopropylbenzene	Alfa Aesar Inc.	96%	distilled
1-Bromo-4-iodobenzene	Fluka Inc	≥ 97%	
2,5-Dibromothiophene	Alfa Aesar Inc.	95%	
3-(2-Thienyl)acrylic acid	Alfa Aesar Inc.	99%	
3,4-(Methylenedioxy)cinnamic acid	Alfa Aesar Inc.	98%	

3-Pyridinecarboxaldehyde	Sigma-Aldrich Inc.	97% (GC)	
4-Cyanobenzaldehyde	Alfa Aesar Inc.	97%	
4-Dimethylaminobenzaldehyde	Alfa Aesar Inc.	98%	
4-Methoxycinnamic acid	ABCR Inc.	98%	
4-Methyl-2-pentenoic acid	Alfa Aesar Inc.	98+%	
4-Methylcinnamic acid	ABCR Inc.	99%	
AgNO ₃	Merck Inc.	99.9%	
Ammonium chloride	Grüssing Inc.	99.5%	
Benzyl bromide	TCI Inc.	98% (GC)	
Bromine	Acros Inc.	99.99%	
β-Bromostyrene	Alfa Aesar Inc.	96%	distilled
<i>n</i> -Butyllithium	Acros Inc.	2.5 M in <i>n</i> hexane	
<i>n</i> -Butylmagnesium chloride	Fischer Scientific Inc.	20 wt% in THF/Toluene	
Cyclohexanecarboxaldehyde	Alfa Aesar Inc.	99%	
Ethynyltrimethylsilane	Sigma-Aldrich Inc.	98%	
Iodosobenzene diacetate	Alfa Aesar Inc.	98%	
Isopropylmagnesium chloride	Sigma-Aldrich Inc.	2.0 M in THF	
Magnesium sulfate	Grüssing Inc.	99%	
Malonic acid	Alfa Aesar Inc.	98%	
α-Methylcinnamic acid	Alfa Aesar Inc.	97%	
Methylolithium	Acros Inc.	1.6 M in diethyl ether	
NBS	Sigma-Aldrich Inc.	99%	
Octyne	Fluka Inc.	>98%	
α-Phenylcinnamic acid	Alfa Aesar Inc.	98%	
Pinacol	ABCR Inc.	99%	
Potassium carbonate	AppliChem GmbH	Pure Ph. Eur., USP	
Potassium <i>t</i> butoxide	Acros Inc.	97%	
Propargyl alcohol	Alfa Aesar Inc.	99%	
Propargyl benzoate	VWR Inc.	98%	
Sodium	Merck Inc.	≥ 99%	
Sodium chloride	Grüssing Inc.	99.5%	
Sodium hydrid	Merck Inc.	60% in mineral oil	
Sodium sulfate	Grüssing Inc.	99%	
SPhos	Strem Chemicals Inc.	>98%	
Tetraethylammonium bromide	Alfa Aesar Inc.	99%	
Thiophene	VWR Inc.	99%	distilled
TMEDA	Acros Inc.	99.5%	
Triethylamine	Acros Inc.	99%	distilled from CaH ₂
Triisopropyl borate	Strem Chemicals Inc.	>98%	
Trimethyltin chloride	Acros Inc.	99%	

Solvents

All solvents for reactions were used freshly distilled after refluxing for several hours over the specified drying agent under nitrogen and were stored in a J. Young's tube. If no drying agent is noted, the solvents were used for chromatography only and distilled for purification purposes.

Solvent	Supplier or grade before distillation, drying procedure if applicable
Acetone	BCD, technical grade, not distilled
Acetonitrile	Sigma Aldrich, HPLC-grade; Degassed by three freeze-pump-thaw cycles, stored over 3 Å

	molecular sieves
Cyclohexane	BCD, technical grade
DCM	BCD, technical grade, Dried over phosphorus pentoxide, stored over 3 Å molecular sieves
Diethyl ether	BCD, technical grade
Dioxane	Grüssing; Dried over sodium with benzophenone as an indicator; Degassed by three freeze-pump-thaw cycles, stored over 3 Å molecular sieves
DMF	ABCR, anhydrous, amine free; 99.9%; contained molecular sieves
Ethyl acetate	BCD, technical grade
<i>n</i> hexane	WALTER CMP, technical grade; Dried over sodium with benzophenone as an indicator; stored over 3 Å molecular sieves
<i>n</i> pentane	WALTER CMP, technical grade
Pyridine	Sigma Aldrich; Dried over calcium hydride; Degassed by three freeze-pump-thaw cycles, stored over 3 Å molecular sieves
THF	Sigma Aldrich; Dried over LiAlH ₄ with benzophenone as an indicator; Degassed by three freeze-pump-thaw cycles, stored over 3 Å molecular sieves
Toluene	Sigma Aldrich, anhydrous, 99.9 %

Chromatography

For chromatographic purifications, silica gel (Macherey-Nagel Inc., grain size 0.040 - 0.063 mm) was used. Thin layer chromatography was performed using pre-coated plates from Macherey-Nagel Inc., ALUGRAM[®]Xtra SIL G/UV254. Chromatographic purification for compounds (2a-2d, 2f, 2i-2k, 3a-3c, 3i, 3j, 6e, 6f, 7d, 7e, 8a, 8b, 8c, 8d) were carried out using an InterchimPuriflash 430 system, in which cartridges by Interchim (silica HC, grain size 50 µm, 40 g, 80 g or 120 g) were used.

GC Optimization Reactions

The yields for the optimization reactions were determined by GC by a multiple point internal standard method, using 1,3,5-triisopropylbenzene as a standard. The following equation was used for the calculation of the yields for substance **3a**, **4** and **5**.

$$n(\text{analyte}) = \frac{A(\text{analyte})}{A(\text{standard})} \times \frac{n(\text{standard})}{RF}$$

Where n is the amount of substance, A is the integrated area and RF is a system specific response factor. For the calibration curve, known amounts of the analyte and 1,3,5-triisopropylbenzene were used. The response factor RF was obtained from the slope of the resulting calibration curve (Figures SI 1, SI 3 and SI 4).

For substance **3a'**, the yield for the optimization reactions was determined by GC and NMR because it could not be isolated. The GC and NMR were measured at the same time. First, the amount of substance **3a** was calculated from the known RF and then the amount of substance **3a'** was calculated based on the ratio of **3a'** and **3a** which was obtained from the NMR measurement. The following equation was used for the calculation of the amount of substance **3a'**. The yields for substance **3a'** were calculated by the last equation like substance **3a**, **4** and **5**. The response factor RF was obtained from the slope of the resulting calibration curve (Figure SI 2).

$$n(3b) = r \times \frac{A(3a)}{A(\text{standard})} \times \frac{n(\text{standard})}{1.1291}$$

Where r is the ratio between the amount of substance **3a'** and **3a**.

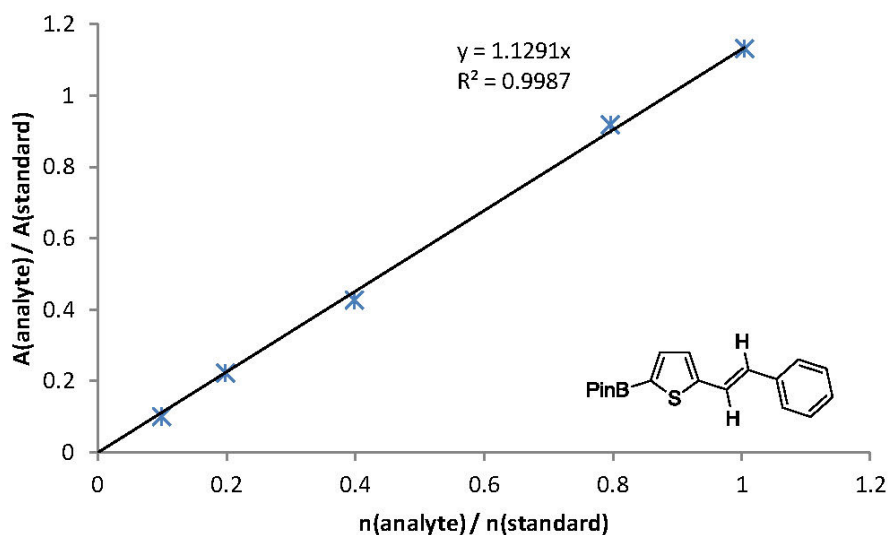


Figure SI 1. Calibration curve for (*E*)-4,4,5,5-tetramethyl-2-(5-styryl)thiophene-2-yl)-1,3,2-dioxaborolane **3a**, using 1,3,5-triisopropylbenzene as an internal standard.

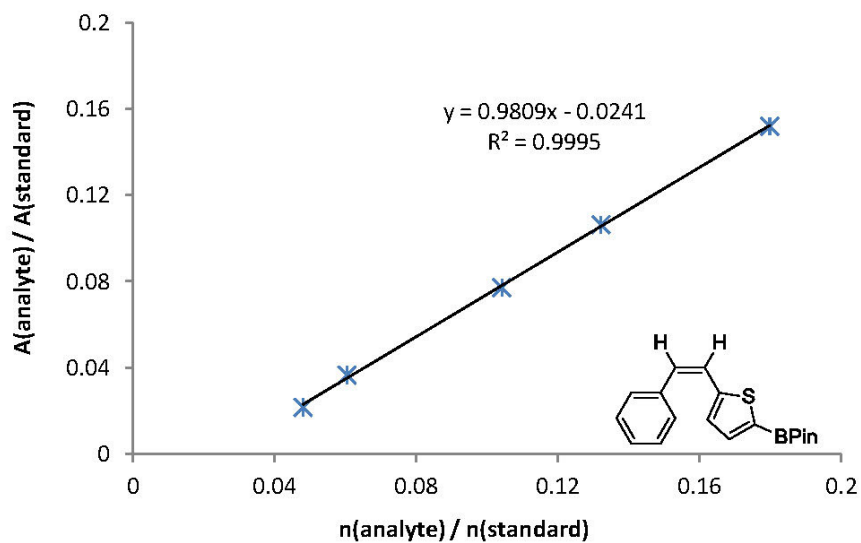


Figure SI 2. Calibration curve for Z-4,4,5,5-tetramethyl-2-(5-styryl)thiophene-2-yl)-1,3,2-dioxaborolane **3a'**, using 1,3,5-triisopropylbenzene as an internal standard.¹

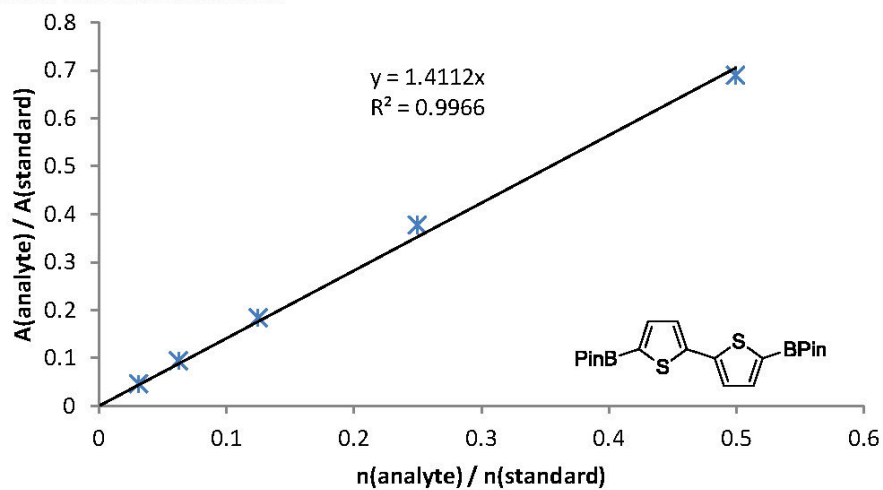


Figure SI 3. Calibration curve for 5,5'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene **4** using 1,3,5-triisopropylbenzene as an internal standard.

¹The standard line does not go through 0: because of the indirect determination of the Z product, the errors for each individual measurement are higher than for the other compounds (**3a**, **4** and **5**), which were calibrated directly.

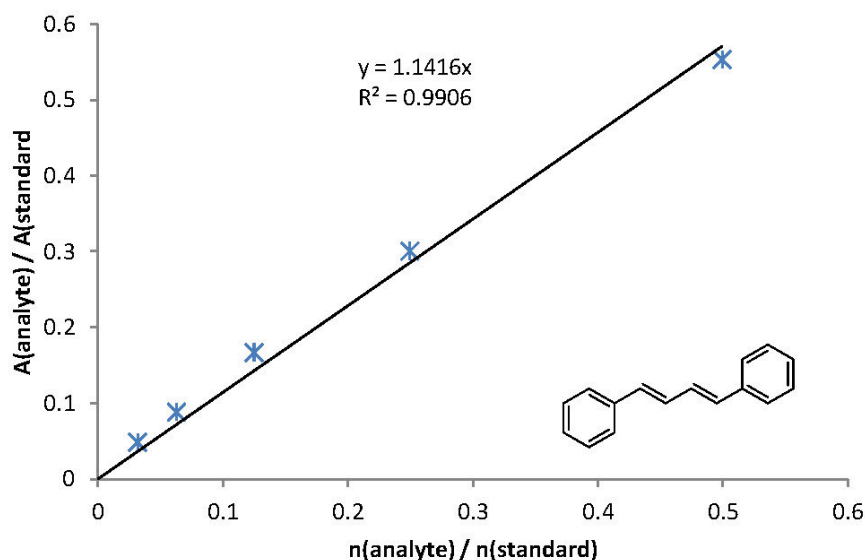


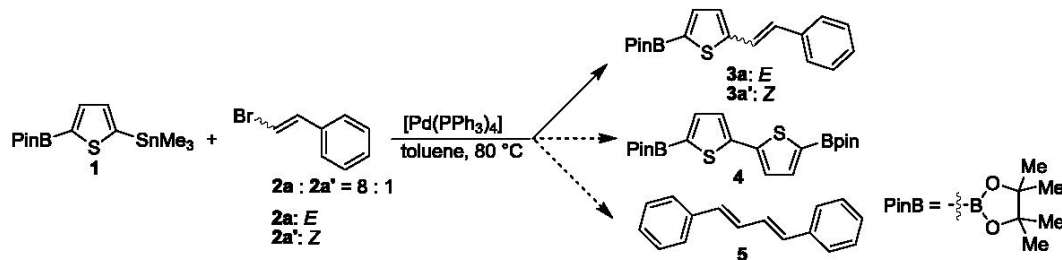
Figure SI 4. Calibration curve for 1,4-diphenylbuta-1,3-diene **5** using 1,3,5-triisopropylbenzene as an internal standard.

General procedure for the optimization reactions:

A solution of **1** (205 mg, 0.550 mmol), β -bromostyrene (*E* / *Z* = 8 / 1) (91 mg, 0.50 mmol), the catalyst (1-10 mol%) and the internal standard 1,3,5-triisopropylbenzene (100 μ L, 84.5 mg, 414 μ mol) was heated to the required temperature for the specified time, in the specified solvents (1-4 mL) (Table SI 1). After certain time intervals, a sample (0.2 mL) was taken from each reaction vessel and diluted with CHCl_3 (10 mL). About 2 mL was filtered through a short plug of silica (5 x 3 mm) using a syringe filter and then used for GC analysis.

For all specific reaction conditions, the parameters are shown in Table SI 1.

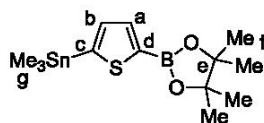
Table SI 1. Optimization reactions for the synthesis of **3a** and **3a'**.



entry	solvent / mL	catalyst	loading [mol%]	T [°C]	t [h]	conversion [%]	yield [%]	
							3a : 3a' : 4 : 5	
1	Dioxane / 4	[Pd(PPh ₃) ₄]	5	60	17	83	51:5:3:0	
2	DMF / 4	[Pd(PPh ₃) ₄]	5	60	17	100	83:12:2:0	
3	Toluene / 4	[Pd(PPh ₃) ₄]	5	60	17	91	59:7:9:6	
4	THF / 4	[Pd(PPh ₃) ₄]	5	60	17	94	73:8:6:3	
5	Pyridine / 4	[Pd(PPh ₃) ₄]	5	60	17	93	37:3:16:14	
6	Acetonitrile / 4	[Pd(PPh ₃) ₄]	5	60	17	100	43:10:22:14	
7	Dioxane / 4	[Pd(PPh ₃) ₄]	5	65	17	91	67:1:3:0	
8	Dioxane / 4	[Pd(PPh ₃) ₄]	5	65	26	95	72:3:3:0	
9	Toluene / 4	[Pd(PPh ₃) ₄]	5	65	17	96	54:5:8:5	
10	Toluene / 4	[Pd(PPh ₃) ₄]	5	65	26	100	57:9:8:6	
11	THF / 4	[Pd(PPh ₃) ₄]	5	65	17	100	62:7:5:3	

12	THF / 4	[Pd(PPh ₃) ₄]	5	65	26	100	65:10:5:4
13	DMF / 4	[Pd(dppe)Cl ₂]	5	60	16	100	23:2:16:8
14	DMF / 4	[Pd(OAc) ₂]/ SPhos	5 10	60	16	100	23:7:26:13
15	DMF / 4	[Pd(dppf)Cl ₂]	5	60	16	100	43:3:9:4
16	DMF / 4	[Pd(PtBu ₃) ₂]	5	60	16	100	35:4:4:1
17	DMF / 4	[Pd(PPh ₃) ₄]	2.5	60	16	100	81:12:2:0
18	DMF / 4	[Pd(PPh ₃) ₄]	1	60	17	100	86:11:2:0
19	DMF / 4	[Pd(PPh ₃) ₄]	1	60	6	100	78:9:2:0
20	DMF / 4	[Pd(PPh ₃) ₄]	5	40	17	97	87:5:1:0
21	DMF / 4	[Pd(PPh ₃) ₄]	5	40	22	98	78:6:1:0
22	DMF / 2	[Pd(PPh ₃) ₄]	5	40	17	97	80:5:1:0
23	DMF / 2	[Pd(PPh ₃) ₄]	5	40	22	98	83:6:1:0
24	DMF / 1	[Pd(PPh ₃) ₄]	5	40	17	97	87:6:1:0
25	DMF / 1	[Pd(PPh ₃) ₄]	5	40	22	97	78:7:1:0
26	DMF / 4	[Pd(PPh ₃) ₄]	2	40	17	95	86:5:1:0
27	DMF / 4	[Pd(PPh ₃) ₄]	2	40	20	97	92:5:1:0
28	DMF / 4	[Pd(PPh ₃) ₄]	2	40	26	98	87:6:1:0
29	DMF / 4	[Pd(PPh ₃) ₄]	2	40	41	>99	92:9:1:0
30	DMF / 2	[Pd(PPh ₃) ₄]	1	40	17	96	86:4:1:0
31	DMF / 2	[Pd(PPh ₃) ₄]	1	40	20	96	88:5:1:0
32	DMF / 2	[Pd(PPh ₃) ₄]	1	40	26	97	90:7:1:0
33	DMF / 2	[Pd(PPh ₃) ₄]	1	40	41	>99	93:9:1:0
34	DMF / 2	[Pd(PPh ₃) ₄]	5	20	17	40	12:0:1:0
35	DMF / 2	[Pd(PPh ₃) ₄]	5	20	41	93	77:1:2:0
36	DMF / 2	[Pd(PPh ₃) ₄]	5	20	65	93	70:1:4:0
37	DMF / 2	[Pd(PPh ₃) ₄]	10	20	17	38	7:0:0:0
38	DMF / 2	[Pd(PPh ₃) ₄]	10	20	41	50	18:0:1:0
39	DMF / 2	[Pd(PPh ₃) ₄]	10	20	65	92	64:1:2:0
40	THF / 4	[Pd(OAc) ₂]/ SPhos	5 10	60	16	100	10:4:37:35
41	THF / 4	[Pd(PtBu ₃) ₂]	5	60	16	100	25:1:21:24
42	Dioxane / 4	[Pd(OAc) ₂]/ SPhos	5 10	60	16	100	10:5:39:35
43	Dioxane / 4	[Pd(PtBu ₃) ₂]	5	60	16	100	34:2:15:19
44	Toluene / 4	[Pd(PtBu ₃) ₂]	5	60	16	100	24:1:22:28

Syntheses

4,4,5,5-Tetramethyl-2-(5-(trimethylstannyl)thiophen-2-yl)-1,3,2-dioxaborolane (1)^[1]

Methylolithium (625 μL , 1.00 mmol, 1.60 M in diethyl ether) was added within 10 min to a suspension of 2,5-bis(trimethylstannyl)thiophene (410 mg, 1.00 mmol) in THF (6 mL) at $-100\text{ }^{\circ}\text{C}$. The slightly yellow solution was stirred for 2 h at $-78\text{ }^{\circ}\text{C}$. 2-*iso*Propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **8** (186 mg, 1.00 mmol) was slowly added at this temperature and stirred for 1 h. Then the reaction mixture was warmed to $20\text{ }^{\circ}\text{C}$ within 12 h without removing the cooling bath and was then quenched with water (50 mL). The aqueous layer was washed with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine (1 x 20 mL) and dried over MgSO_4 . The solvent was removed *in vacuo* and the crude product was purified by sublimation² ($30\text{ }^{\circ}\text{C}$, 2×10^{-2} mbar) to afford the product (205 mg, 55%; Lit: 55%) as a colorless solid.

Note: the compound was unstable to silica gel chromatography.

¹H NMR (500 MHz, CDCl_3): δ = 7.79 (d, 1 H, ³J = 3.2 Hz, H-a/b), 7.33 (d, 1 H, ³J = 3.2 Hz, H-a/b), 1.37 (s, 12 H, H-f), 0.40 (s, 9 H, H-g) ppm.

¹³C NMR (126 MHz, CDCl_3): δ = 146.5 (C-c), 137.8 (C-a/b), 136.3 (C-a/b), 84.1 (C-e), 24.9 (C-f), -8.1 (C-g) ppm.³

¹¹⁹Sn NMR (187 MHz, CDCl_3): δ = -26.8 ppm.

¹¹B NMR (160 MHz, CDCl_3): δ = 28.8 ppm.

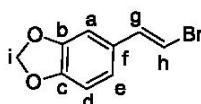
HRMS (ESI-FTMS) *m/z*: $[\text{M} + \text{Na}]^+$ Calcd for $[\text{C}_{13}\text{H}_{23}\text{BO}_2\text{SSn} + \text{Na}]^+$ 397.0426; Found 397.0432.

IR (ATR): ν = 2978 (m), 2920 (w), 1510 (s), 1418 (s), 1331 (s), 1254 (m), 1138 (s), 1064 (s), 1021 (m), 957 (m), 928 (m), 853 (m), 820 (m), 770 (s), 665 (s), 533 (s) cm^{-1} .

M. p.: $84\text{ }^{\circ}\text{C}$.

The NMR data are in agreement with our previous work.^[1]

(E)-5-(2-Bromovinyl)benzo[d][1,3]dioxole (2b)



Tetraethylammonium bromide (2.30 g, 11.0 mmol) was added to a stirred suspension of iodobenzene diacetate (3.54 g, 11.0 mmol) in anhydrous DCM (35 mL). The reaction mixture was stirred at $25\text{ }^{\circ}\text{C}$ for 5 min and then (*E*)-3,4-(methylenedioxy)cinnamic acid (1.92 g, 10.0 mmol) was added in one portion and stirred for 15 h at $25\text{ }^{\circ}\text{C}$. The reaction mixture was diluted with DCM (80 mL) and washed successively with aqueous NaHSO_3 (10%, 3 x 50 mL), aqueous NaHCO_3 (10% 3 x 50 mL), H_2O (2 x 50 mL) and brine (1 x 50 mL). The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (*n*hexane, R_f = 0.28) and recrystallized in *n*hexane at $-30\text{ }^{\circ}\text{C}$ to afford the product (1.97 g, 87%) as a colorless solid.

¹H NMR (500 MHz, CDCl_3): δ = 7.00 (d, ³J = 13.9 Hz, 1 H, H-g), 6.81 (s, 1 H, H-a), 6.76 (m, 2 H, H-e,d), 6.59 (d, ³J = 13.9 Hz, 1 H, H-h), 5.96 (s, 1 H, H-i) ppm.

¹³C NMR (126 MHz, CDCl_3): δ = 148.3 (C-b/c), 147.9 (C-b/c), 136.8 (C-g), 130.4 (C-f), 121.0 (C-e), 108.6 (C-d), 105.6 (C-a), 104.7 (C-h), 101.4 (C-i) ppm.

²The starting material, as well as the monostannylated and monoboronated species were sublimed first ($25\text{ }^{\circ}\text{C}$, 2×10^{-2} mbar).

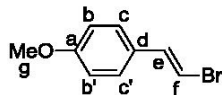
³The carbon atom bound to boron was not visible due to the high quadrupole moment of the boron nucleus, the same as other similar compounds.

HRMS (EI-sector) m/z : $[M]^+$ Calcd for $[C_9H_7BrO_2]^+$ 225.9629; Found 225.9631.

IR (ATR): $\tilde{\nu}$ = 3087 (m), 3008 (w), 2910 (m), 2778 (w), 1608 (w), 1500 (m), 1485 (m), 1433 (m), 1349 (m), 1242 (s), 1186 (s), 1103 (m), 1031 (s), 923 (s), 820 (m), 765 (s), 605 (m), 508 (s), 459 (m) cm^{-1} .

M.p.: 55 °C.

(E)-1-(2-Bromovinyl)-4-methoxybenzene (2c)



(E)-1-(2-Bromovinyl)-4-methoxybenzene was prepared similarly to a method described by Jaya Prakash Das et al.^[3] and was modified as follows:

Triethylamine (70.0 μ L, 0.50 mmol) was added to a stirred solution of (E)-4-methoxycinnamic acid (1.78 g, 10.0 mmol) in DCM (50 mL). After stirring the reaction mixture for 5 min at 23 °C, N-bromosuccinimide (1.96 g, 11.0 mmol) was added in one portion. The reaction mixture was stirred for another 2.5 h and quenched with saturated aqueous solution of $NaHCO_3$ (20 mL). The organic phase was washed with water (2 x 20 mL), brine (1 x 20 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by column chromatography over silica gel (*n*hexane, R_f = 0.28) to afford the product (1.89 g, 89%, Lit.^[3]: 90%) as a colorless solid.

1H NMR (500 MHz, $CDCl_3$): δ = 7.23 (d, 3J = 9.8 Hz, 2 H, H-c, c'), 7.04 (d, 3J = 14.0 Hz, 1 H, H-e), 6.85 (d, 3J = 9.8 Hz, 2 H, H-b, b'), 6.61 (d, 3J = 14.0 Hz, 1 H, H-f), 3.81 (s, 3 H, H-g) ppm.

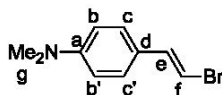
^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.7 (C-a), 136.6 (C-e), 128.8 (C-d), 127.4 (C-c, c'), 114.2 (C-b, b'), 104.0 (C-f), 55.3 (C-g) ppm.

HRMS (EI-sector) m/z : $[M]^+$ Calcd for $[C_9H_9BrO]^+$ 211.9837; Found 211.9841.

IR (ATR): $\tilde{\nu}$ = 3067 (m), 3020 (w), 2957 (w), 2932 (w), 2837 (m), 1601 (m), 1507 (m), 1457 (m), 1303 (m), 1253 (m), 1173 (m), 1026 (m), 949 (s), 835 (s), 774 (s), 710 (m), 524 (s), 467 (m) cm^{-1} .

M.p.: 52 °C.

(E)-4-(2-Bromovinyl)-N,N-dimethylaniline (2d)



(E)-4-(2-Bromovinyl)-N,N-dimethylaniline was prepared similarly to a method described by Fursule et al.^[2] and was modified as follows:

Iodosobenzene diacetate (3.54 g, 11.0 mmol) was added to a stirred suspension of tetraethylammonium bromide (2.30 g, 11.0 mmol) in anhydrous DCM (100 mL). The reaction mixture was stirred at 23 °C for 5 min and then (E)-3-(4-(Dimethylamino)phenyl)acrylic acid (1.91 g, 10.0 mmol) was added in one portion and stirred at 23 °C for 19 h. The reaction mixture was diluted with DCM (100 mL) and washed successively with aqueous $NaHSO_3$ (10%, 3 x 80 mL), aqueous $NaHCO_3$ (10%, 3 x 80 mL), H_2O (2 x 80 mL) and brine (1x 100 mL). The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (*n*hexane / ethyl acetate: 9 / 1, R_f = 0.35) to afford the product (1.16 g, 51%, Lit.^[2]: 91%) as a colorless solid.

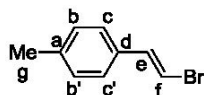
1H NMR (600 MHz, $CDCl_3$): δ = 7.18 (d, 3J = 8.7 Hz, 2 H, H-c, c'), 7.00 (d, 3J = 13.9 Hz, 1 H, H-e), 6.66 (s, 2 H, br, H-b, b'), 6.51 (d, 3J = 13.9 Hz, 1 H, H-f), 2.97 (s, 6 H, H-g) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.4 (C-a), 136.9 (C-e), 127.1 (C-c, c'), 124.3 (C-d), 112.3 (C-b, b'), 101.5 (C-f), 40.4 (C-g) ppm.

HRMS (EI-sector) m/z : $[M]^+$ Calcd for $[C_{10}H_{12}NBr]^+$ 225.0153; Found 225.0154.

IR (ATR): $\tilde{\nu}$ = 3069 (m), 2892 (w), 2805 (w), 1599 (m), 1513 (m), 1439 (m), 1330 (m), 1276 (m), 1232 (m), 1183 (m), 1064 (m), 947 (s), 926 (m), 817 (s), 766 (9s), 750 (s), 518 (s) cm^{-1} .

M.p.: 105 °C.

(E)-1-(2-Bromovinyl)-4-methylbenzene (2e)

(E)-1-(2-Bromovinyl)-4-methylbenzene was prepared similarly to a method described by Fursule et al.^[2] and was modified as follows:

Tetraethylammonium bromide (920 mg, 4.40 mmol) was added to a stirred suspension of iodobenzene diacetate (1.42 g, 4.40 mmol) in anhydrous DCM (50 mL). The reaction mixture was stirred at 25 °C for 5 min and then (E)-4-methylcinnamic acid (650 mg, 4.00 mmol) was added and stirred at 25 °C for 15 h in one portion. The reaction mixture was diluted with DCM (100 mL) and washed successively with aqueous NaHSO₃ (10%, 3 x 50 mL), aqueous NaHCO₃ (10%, 3 x 50 mL), H₂O (2 x 50 mL) and brine (1 x 50 mL). The organic layer was dried over MgSO₄ and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (*n*hexane, R_f = 0.64) and recrystallized in *n*hexane at -30 °C to afford the product (315 mg, 40%, Lit.^[2]: 92%) as a colorless solid.

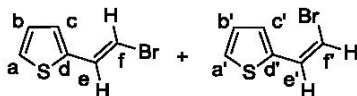
¹H NMR (500 MHz, CDCl₃): δ = 7.19 (d, ³J = 8.1 Hz, 2 H, H-c, c'), 7.13 (d, ³J = 8.1 Hz, 2 H, H-b, b'), 7.06 (d, ³J = 14.0 Hz, 1 H, H-e), 6.71 (d, ³J = 14.0 Hz, 1 H, H-f), 2.33 (s, 3 H, H-g) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 138.2 (C-a), 137.0 (C-e), 133.2 (C-d), 129.5 (C-b, b'), 126.0 (C-c, c'), 105.4 (C-f), 21.2 (C-g) ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₉H₉Br]⁺ 195.9888; Found 195.9884.

IR (ATR): $\tilde{\nu}$ = 3069 (m), 3025 (w), 2913 (m), 2854 (w), 1601 (m), 1508 (m), 1446 (w), 1225 (m), 1194 (m), 949 (s), 936 (s), 825 (s), 768 (s), 723 (m), 501 (s) cm⁻¹.

M.p.: 40 °C.

(E)-2-(2-Bromovinyl)thiophene and (Z)-2-(2-bromovinyl)thiophene (2f)

2-(2-Bromovinyl)thiophene was prepared similarly to a method described by Jaya Prakash Das et al.^[3] and was modified as follows:

Triethylamine (28.0 μL, 200 μmol) was added to a stirred solution of (E)-3-(2-thienyl) acrylic acid (616 mg, 4.00 mmol) in DCM (20 mL). After being stirred for 5 min at 23 °C, *N*-bromosuccinimide (748 mg, 4.20 mmol) was added in one portion. The reaction mixture was stirred for another 4 h and quenched with saturated aqueous solution of NaHCO₃ (10 mL). The organic phase was washed with water (2 x 7 mL) and brine (1 x 10 mL), and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica gel (*n*hexane, R_f = 0.51) to afford the product (430 mg, 57%, Lit.^[3]: 80%) as light yellow oil. The product contained the *E* and *Z* isomers in 5 / 1 *E* / *Z* ratio.

Note: The product decomposed under air atmosphere, which may be caused by oxygen or light.

For (E)-2-(2-Bromovinyl)thiophene

¹H NMR (500 MHz, CDCl₃): δ = 7.22–7.20 (m, 1 H, H-a), 7.19 (d, ³J = 14.0 Hz, 1 H, H-e/f), 6.99–6.94 (m, 2 H, H-b,c), 6.63 (d, ³J = 14.0 Hz, 1 H, H-e/f) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 139.9 (C-d), 130.2 (C-e/f), 127.4 (C-b/c), 126.0 (C-b/c), 125.1 (C-a), 105.2 (C-e/f) ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₆H₅BrS]⁺ 187.9295; Found 187.9293.

For (Z)-2-(2-bromovinyl)thiophene:

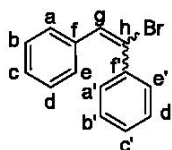
¹H NMR (500 MHz, CDCl₃): δ = 7.39 (d, ³J = 5.1 Hz 1 H, H-a'), 7.33–7.29 (m, 2 H, H-c', e'/f'), 7.07 (dd, ³J = 5.1, 3.6 Hz, 1 H, H-b'), 6.32 (d, ³J = 7.9 Hz, 1 H, H-e'/f') ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 138.0 (C-d'), 130.1 (C-e'/f'), 126.9 (C-a'), 126.3 (C-b', c'), 104.1 (C-e'/f') ppm.

For the mixture:

IR (ATR): $\tilde{\nu}$ = 3105 (w), 3060 (m), 1601 (w), 1421(w), 1238 (s), 1211 (m), 1041 (w), 925 (s), 854 (m), 828 (m), 764 (s), 733 (m), 692 (s), 586 (m), 507 (m), 489 (m) cm^{-1} .

1-Bromoethene-1,2-diylidibenzene (2g)



Tetraethylammonium bromide (2.30 g, 11.0 mmol) was added to a stirred suspension of iodosobenzene diacetate (3.54 g, 11.0 mmol) in anhydrous DCM (35 mL). The reaction mixture was stirred at 25 °C for 5 min and then α -phenylcinnamic acid (2.24 g, 10.0 mmol) was added in one portion and stirred for 15 h at 25 °C. The reaction mixture was diluted with DCM (80 mL) and washed successively with aqueous NaHSO_3 (10%, 3 x 50 mL), aqueous NaHCO_3 (10%, 3 x 50 mL), H_2O (2 x 50 mL) and brine (1 x 50 mL). The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The residue obtained was purified by Kugelrohr distillation (100 °C, 2.6 mbar) to afford the product (1.20 g, 53%) as yellow oil. The product contained the *E* and *Z* isomer in a 3 / 2 or 2 / 3 ratio, but it could not be determined which the major isomer was.

E or *Z* isomer:

$^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ = 7.74–7.70 (m, 2 H), 7.68–7.64 (m, 2 H), 7.44–7.31 (m, 6 H), 7.26 (s, 1 H, H-g) ppm.

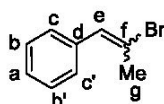
$^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ = 7.44–7.31 (m, 5 H), 7.26 (s, 1 H, H-g), 7.16–7.11 (m, 3 H), 7.00–6.95 (m, 2 H) ppm.⁴

$^{13}\text{C NMR}$ (126 MHz, CD_2Cl_2): δ = 141.4, 140.0 (C-f/h/f'), 136.7, 136.4 (C-f/h/f'), 133.5, 130.4 (C-g), 129.6, 129.5, 129.2, 129.1, 129.0, 128.7, 128.6, 128.5, 128.1, 127.9 (C-a-e, C-a'-e'), 124.3, 123.6 (C-f/h/f') ppm.⁵

HRMS (EI-sector) *m/z*: $[\text{M}]^+$ Calcd for $[\text{C}_{14}\text{H}_{11}\text{Br}]^+$ 258.0044; Found 258.0040.

IR (ATR): $\tilde{\nu}$ = 3080 (w), 3055 (m), 3024 (m), 1598 (w), 1494 (m), 1444 (m), 1165 (w), 1074 (m), 1029 (m), 926 (m), 887 (m), 755 (s), 688 (s), 564 (m), 537(m), 504 (m) cm^{-1} .

(2-Bromoprop-1-en-1-yl)benzene (2h)



Tetraethylammonium bromide (2.30 g, 11.0 mmol) was added to a stirred suspension of iodosobenzene diacetate (3.54 g, 11.0 mmol) in anhydrous DCM (35 mL). The reaction mixture was stirred at 25 °C for 5 min and then α -methylcinnamic acid (1.92 g, 10.0 mmol) was added in one portion and stirred for 15 h at 25 °C. The reaction mixture was diluted with DCM (80 mL) and washed successively with aqueous NaHSO_3 (10%, 3 x 50 mL), aqueous NaHCO_3 (10%, 3 x 50 mL), H_2O (2 x 50 mL) and brine (1 x 50 mL). The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The residue obtained was purified by Kugelrohr distillation (65 °C, 3 mbar) to afford the product (1.10 g, 56%) as light yellow oil. The product contained *E* and *Z* isomer in 2 / 1 or 1 / 2 ratio, but it could not be determined which the major isomer was.

$^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ = 7.57–7.52 (m, 2 H), 7.38–7.33 (m, 6 H), 7.30–7.25 (m, 3 H), 7.25–7.22 (m, 4 H), 6.98 (s, 2 H, H-e), 6.76 (s, 1 H, H-e), 2.49 (d, 3J = 1.4 Hz, 3 H, H-g), 2.46 (d, 3J = 1.4 Hz, 6 H, H-g) ppm.⁶

⁴ The peaks of *Z*- and *E*-isomer could not be analyzed because of the overlap of signals.

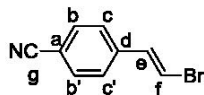
⁵ The peaks belong to both *E*- and *Z*-isomer; The peaks of *Z*- and *E*-isomer could not be analyzed because of the overlap of signals.

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 136.9 (C-d), 136.7 (C-d), 132.6, 129.1, 128.8, 128.7, 128.4, 128.3, 127.9, 127.6, 124.1 (C-f), 122.4 (C-f), 30.8 (C-g), 25.2 (C-g) ppm.⁷

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_9\text{H}_9\text{Br}]^+$ 195.9888; Found 195.9888.

IR (ATR): $\tilde{\nu}$ = 3081 (w), 3057 (w), 3024 (m), 2952 (w), 2916 (m), 1632 (w), 1494 (m), 1435 (m), 1276 (m), 1066 (s), 916 (m), 847 (m), 749 (s), 695 (s), 553 (s), 501 (s), 433 (m) cm^{-1} .

(E)-4-(2-Bromovinyl)benzonitrile (2i)



Iodosobenzene diacetate (5.50 g, 17.0 mmol) was added to a stirred suspension of tetraethylammonium bromide (3.55 g, 17.0 mmol) in anhydrous DCM (100 mL). The reaction mixture was stirred at 25 °C for 5 min and then (E)-3-(4-cyanophenyl) acrylic acid (2.60 g, 15.0 mmol) was added in one portion and refluxed for 26 h. The reaction mixture was diluted with DCM (150 mL) and washed successively with aqueous NaHSO_3 (10%, 3 x 100 mL), aqueous NaHCO_3 (10%, 3 x 100 mL), H_2O (2 x 100 mL) and brine (1 x 100 mL). The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (*n*hexane / ethyl acetate: 9 / 1, R_f = 0.25) to afford the product (890 mg, 29%) as a colorless solid.

^1H NMR (500 MHz, CDCl_3): δ = 7.77 (d, 3J = 8.5 Hz, 2 H, H-c, c'), 7.66 (d, 3J = 8.5 Hz, 2 H, H-b, b'), 7.10 (d, 3J = 8.3 Hz, 1 H, H-e), 6.63 (d, 3J = 8.3 Hz, 1 H, H-f) ppm.

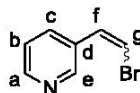
^{13}C NMR (126 MHz, CDCl_3): δ = 139.4 (C-d), 132.0 (C-b, b'), 130.9 (C-e), 129.5 (C-c, c'), 118.7 (C-g), 112.7 (C-a), 110.1 (C-f) ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_9\text{H}_8\text{NBr}]^+$ 206.9684; Found 206.9682.

IR (ATR): $\tilde{\nu}$ = 3075 (m), 3011 (m), 2916 (w), 2227 (m), 1604 (m), 1501 (m), 1405 (m), 1325 (s), 1288 (m), 1178 (m), 1113 (m), 1021 (m), 918 (m), 858 (s), 824 (s), 752 (s), 732 (s), 685 (s), 567 (s), 548 (s), 484 (m) cm^{-1} .

M.p.: 47 °C.

3-(2-Bromovinyl)pyridine (2j)



3-(2-Bromovinyl)pyridine was prepared similarly to a method described by Hayford et al.^[4] and was modified as follows: A mixture of bromomethyltriphenylphosphonium bromide (2.62 g, 6.00 mmol) and potassium *t*butoxide (673 mg, 6.00 mmol) in THF (40 mL) was cooled to -78 °C and stirred at the indicated temperature for 1 h. A solution of 3-pyridine carboxaldehyde (500 μL , 5.30 mmol) in THF (5 mL) was then added via a syringe in 5 minutes. The reaction mixture was stirred another 5 h at -78 °C. Then the mixture was diluted with 50 mL of petroleum ether, and filtered under vacuum. The solvent was removed *in vacuo* and the crud product was purified by column chromatography over silica gel (*n*hexane / ethyl acetate: 5:1, R_f = 0.35) to afford the product (455 mg, 49%, Lit.^[4]: 91%) as light yellow oil. The product contained *Z* and *E* isomer in 100 / 7 *Z* / *E* ratio.

^1H NMR (*Z* isomer)(500 MHz, CDCl_3): δ = 8.77(d, 3J = 2.1 Hz, 1 H, H-e), 8.55 (dd, 3J = 4.8 Hz, 4J = 1.5 Hz, 1 H, H-a), 8.15 (dt, 3J = 8.0 Hz, 4J = 1.8 Hz, 1 H, H-c), 7.32 (d, 3J = 8.0 Hz, 3J = 4.8 Hz, 1 H, H-b), 7.07 (d, 3J = 8.2 Hz, 1 H, H-f), 6.59 (d, 3J = 8.2 Hz, 1 H, H-g) ppm.

⁶ The peaks belong to both *E*- and *Z*-isomer; The ^1H NMR spectrum of these isomers cannot be analysed because of the overlap.

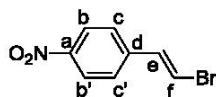
⁷ It was not possible to analyse the peaks because of the overlap of the peaks of *Z*- and *E*-isomer.

^{13}C NMR (Z isomer)(126 MHz, CDCl_3): δ = 150.4 (C-e), 149.2 (C-a), 135.5 (C-c), 131.0 (C-d), 129.2 (C-f), 123.0 (C-b), 109.2 (C-g) ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_7\text{H}_6\text{BrN}]^+$ 182.9684; Found 182.9683.

IR (ATR): $\tilde{\nu}$ = 3078 (n), 1616 (w), 1567 (m), 1472 (m), 1409 (s), 1324 (s), 1185 (m), 1124 (m), 1024 (s), 954 (m), 954 (s), 835 (m), 807 (s), 697 (vs), 625 (vs), 574 (s), 516 (m) cm^{-1} .

(E)-1-(2-Bromovinyl)-4-nitrobenzene (2k)



(E)-1-(2-Bromovinyl)-4-nitrobenzene was prepared similarly to a method described by Fursule et al.^[2] and was modified as follows:

Iodosobenzene diacetate (6.44 g, 20.0 mmol) was added to a stirred suspension of tetraethylammonium bromide (4.18 g, 20.0 mmol) in anhydrous DCM (50 mL). The reaction mixture was stirred at 23 °C for 5 min and then (E)-4-nitrocinnamic acid (2.89 g, 15.0 mmol) was added in one portion and refluxed for 46 h. The reaction mixture was diluted with DCM (100 mL) and washed successively with aqueous NaHSO_3 (10%, 3 x 50 mL), aqueous NaHCO_3 (10%, 3 x 50 mL), H_2O (2 x 50 mL) and brine (1 x 100 mL). The organic layer was dried over MgSO_4 and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (n-hexane / ethyl acetate: 9 / 1, R_f = 0.35) to afford the product (1.16 g, 31%, Lit.^[2]: 89%) as a colorless solid.

^1H NMR (500 MHz, CDCl_3): δ = 8.24 (d, 3J = 8.8 Hz, 2 H, H-b, b'), 7.83 (d, 3J = 8.8 Hz, 2 H, H-c, c'), 7.16 (d, 3J = 8.3 Hz, 1 H, H-e), 6.68 (d, 3J = 8.3 Hz, 1 H, H-f) ppm.

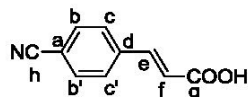
^{13}C NMR (126 MHz, CDCl_3): δ = 147.2 (C-a), 141.3 (C-d), 130.7 (C-e), 129.7 (C-c, c'), 123.5 (C-b, b'), 110.7 (C-f) ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_8\text{H}_6\text{BrNO}_2]^+$ 226.9582; Found 226.9581.

IR (ATR): $\tilde{\nu}$ = 3080 (m), 1607 (m), 1592 (m), 1508 (m), 1407 (m), 1333 (s), 1315 (m), 1276 (m), 1221 (m), 1106 (m), 1011 (w), 936 (w), 854 (s), 811 (m), 765 (s), 708 (m), 677 (s), 574 (m), 509 (s) cm^{-1} .

M.p.: 46 °C.

(E)-3-(4-Cyanophenyl)acrylic acid (2l)



(E)-3-(4-Cyanophenyl)acrylic acid was prepared similarly to a method described by Legoabe et al.^[5] and was modified as follows:

To a stirred solution of 4-formylbenzonitrile (2.62 g, 20.0 mmol) and malonic acid (2.29 g, 22.0 mmol) in pyridine (10 mL), piperidine (0.2 mL, 2.0 mmol) was added at 23 °C. The reaction mixture was heated to 80 °C for 18 h. After cooling down to 23 °C, the reaction mixture was poured into ice-cooled aqueous hydrochloric acid (100 mL, 1 N) and a colorless solid precipitated. This precipitate was filtered and washed with cooled water. Recrystallisation from aqueous ethanol (1:2) at 30 °C afforded the product (2.84 g, 82%) as a colorless solid.

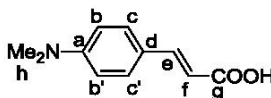
^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ = 7.90–7.83 (m, 4 H, H-c, b, c', b'), 7.63 (d, 3J = 16.1 Hz, 1 H, H-e), 6.69 (d, 3J = 16.1 Hz, 1 H, H-f) ppm.

^{13}C NMR (126 MHz, $\text{DMSO}-d_6$): δ = 167.2 (C-g), 141.9 (C-e), 138.8 (C-d), 132.7 (C-b, b'), 128.9 (C-c, c'), 122.9 (C-f), 118.6 (C-a/h), 112.1 (C-a/h) ppm.

HRMS (ESI-FTMS) m/z : $[\text{M} - \text{H}]^+$ Calcd for $[\text{C}_{10}\text{H}_6\text{NO}_2]^+$ 172.0404; Found 172.0399.

IR (ATR): $\tilde{\nu}$ = 2824 (w), 2559 (w, br), 2225 (m), 1682 (s), 1623 (s), 1561 (m), 1509 (m), 1422 (m), 1308 (s), 1285 (m), 1229 (m), 981 (s), 910 (m), 836 (s), 822 (s), 749 (m), 679 (m), 542 (s), 482 (m), 452 (m) cm^{-1} .

M.p.: 253 °C.

(E)-3-(4-(Dimethylamino)phenyl)acrylic acid (2m)

(E)-3-(4-(Dimethylamino)phenyl)acrylic acid was prepared similarly to a method described by Zhang et. al.^[6] and was modified as follows:

To a stirred solution of 4-dimethylaminobenzaldehyde (2.98 g, 20.0 mmol) and malonic acid (2.29 g, 22.0 mmol) in pyridine (10 mL) was added piperidine (200 μ L, 2.00 mmol) at 23 °C. The reaction mixture was heated to 80 °C for 25 h. After cooling down to 23 °C, the reaction mixture was poured into ice-cooled aqueous hydrochloric acid (50 mL, 1 N) and yellow solid precipitated. The yellow precipitate was filtered and washed with cooled water and acetone to afford the product (2.81 g, 74%) as a yellow solid.

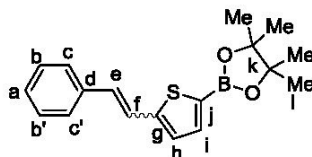
¹H NMR (500 MHz, DMSO-*d*₆): δ = 11.93 (s, 1 H, H-g), 7.45–7.49 (m, 3 H, H-c, c', e), 6.70 (d, 2 H, H-b, b'), 6.20 (d, 1 H, H-f), 2.96 (s, 6 H, H-h) ppm.

¹³C NMR (126 MHz, DMSO-*d*₆): δ = 168.6 (C-g), 152.1 (C-a), 145.1 (C-e), 130.2 (C-c, c'), 122.0 (C-d), 113.4 (C-f), 112.3 (C-b, b'), 40.3 (C-h)⁸ppm.

HRMS (ESI-FTMS) *m/z*: [M - H]⁺ Calcd for [C₁₁H₁₂NO₂]⁺ 190.0874; Found 190.0878.

IR (ATR): $\tilde{\nu}$ = 2805 (w, br), 1667 (m), 1593 (m), 1523 (m), 1434 (m), 1419 (m), 1367 (m), 1308 (m), 1260 (m), 1227 (m), 1186 (m), 987 (m), 941 (m), 813 (s), 748 (m), 675 (m), 530 (s), 480 (m) cm⁻¹.

M.p.: 225 °C.

4,4,5,5-Tetramethyl-2-(5-styrylthiophen-2-yl)-1,3,2-dioxaborolane (3a)

A solution of **1** (373 mg, 1.00 mmol), β -bromostyrene (*E* / *Z* = 8 / 1) (182 mg, 1.00 mmol), [Pd(PPh₃)₄] (11.6 mg, 10.0 μ mol, 1 mol%) in DMF (4 mL) was heated to 60 °C for 17 h. The mixture solution was filtered over a short plug of celite using *n*hexane (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by Kugelrohr distillation (145 °C, 9.2 x 10⁻² mbar) to yield the product (281 mg, 90%) as a yellow solid. The product contained *E* and *Z* isomer in 20 / 3 *E* / *Z* ratio.

¹H NMR (500 MHz, CDCl₃): δ = 7.56–7.50 (m, 3 H, H-c, c', h/i), 7.42–7.37 (m, 2 H, H-b, b'), 7.35–7.28 (m, 2 H, H-a, f), 7.20 (d, ³*J* = 3.6 Hz, 1 H, H-h/i), 7.08 (d, ³*J* = 16.2 Hz, 1 H, H-e), 1.38 (s, 12 H, H-l) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 149.7 (C-i), 138.1 (C-h/i), 137.2 (C-d), 130.1 (C-e), 129.1 (C-b, b'), 128.3 (C-a), 127.6 (C-h/i), 126.8 (C-c, c'), 121.8 (C-f), 84.55 (C-k), 25.0 (C-l) ppm.

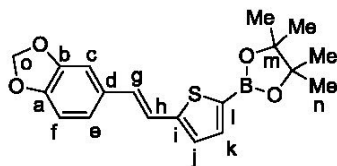
¹¹B NMR (160 MHz, CDCl₃): δ = 28.74 ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₁₈H₂₁BO₂S]⁺ 312.1355; Found 312.1359.

IR (ATR): $\tilde{\nu}$ = 2978 (m), 1522 (m), 1495 (m), 1458 (m), 1370 (m), 1327 (s), 1266 (m), 1239 (m), 1138 (s), 1061 (s), 1011 (m), 950 (s), 852 (s), 808 (s), 745 (m), 689 (s), 660 (s), 585 (m), 526 (m) cm⁻¹.

M.p.: 77 °C.

⁸The peak of the C-H signal overlapped with the residual H signal of the NMR solvent peak.

(E)-2-(5-(2-(Benzo[d][1,3]dioxol-5-yl)vinyl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

A solution of **1** (373 mg, 1.00 mmol), (*E*)-5-(2-bromovinyl)benzo[d][1,3]dioxole **2b** (227 mg, 1.00 mmol), [Pd(PPh₃)₄] (11.6 mg, 10.0 μmol, 1 mol%) in DMF (4 mL) was heated to 40 °C for 25 h. The mixture solution was filtered over a short plug of silica gel using diethyl ether (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel (*n*pentane / diethyl ether: 85 / 15, R_f = 0.47) to afford the product (274 mg, 77%) as a yellow solid.

¹H NMR (500 MHz, CDCl₃): δ = 7.51 (d, ³J = 3.6 Hz, 1 H, H-j/k), 7.11–7.05 (m, 2 H, H-j/k, h), 7.01 (s, 1 H, H-c), 6.93 (d, ³J = 16.1 Hz, 1 H, H-g), 6.90 (d, ³J = 8.0 Hz, 1 H, H-e), 6.78 (d, ³J = 8.0 Hz, 1 H, H-f), 5.97 (s, 2 H, H-o), 1.35 (s, 12 H, H-n) ppm.

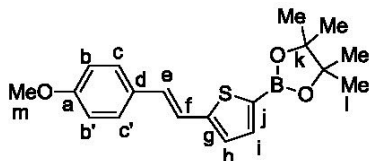
¹³C NMR (126 MHz, CDCl₃): δ = 149.7 (C-i), 148.2 (C-a/b), 147.5 (C-a/b), 137.8 (C-j/k), 131.3 (C-d), 129.6 (C-g), 126.7 (C-j/k), 121.6 (C-e), 119.9 (C-h), 108.5 (C-f), 105.4 (C-c), 101.2 (C-o), 84.1 (C-m), 24.8 (C-n) ppm.

¹¹B NMR (160 MHz, CDCl₃): δ = 28.88 ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₁₉H₂₁BO₄S]⁺ 356.1253; Found 356.1250.

IR (ATR): $\tilde{\nu}$ = 2976 (m), 1603 (m), 1525 (m), 1503 (m), 1490 (s), 1447 (s), 1372 (m), 1349 (s), 1310 (m), 1254 (s), 1210 (m), 1138 (s), 1062 (m), 1036 (s), 939 (s), 853 (s), 839 (m), 810 (s), 683 (m), 661 (s), 617 (m), 578 (w), 519 (w), 471 (w), 442 (m) cm⁻¹.

M.p.: 91 °C.

(E)-2-(5-(4-Methoxystyryl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

A solution of **1** (373 mg, 1.00 mmol), (*E*)-1-(2-bromovinyl)-4-methoxybenzene **2c** (213 mg, 1.00 mmol), [Pd(PPh₃)₄] (11.6 mg, 10.0 μmol, 1 mol%) in DMF (4 mL) was heated to 40 °C for 25 h. The mixture solution was filtered over a short plug of silica gel using diethyl ether (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel (*n*pentane / diethyl ether: 92 / 8, R_f = 0.21) to afford the product (260 mg, 76%) as a yellow solid.

¹H NMR (500 MHz, CDCl₃): δ = 7.52 (d, ³J = 3.5 Hz, 1 H, H-h/i), 7.41 (d, ³J = 8.9 Hz, 2 H, H-c, c'), 7.16–7.09 (m, 2 H, H-e/f, h/i), 6.98 (d, ³J = 16.1 Hz, 1 H, H-e/f), 6.89 (d, ³J = 8.9 Hz, 2 H, H-b, b'), 3.85–3.82 (s, 3 H, H-m), 1.36 (s, 12 H, H-l) ppm.

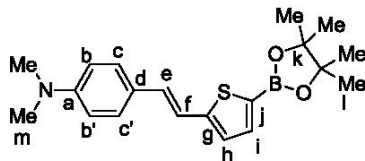
¹³C NMR (126 MHz, CDCl₃): δ = 159.5 (C-a), 150.0 (C-g), 137.8 (C-h/i), 129.6 (C-d), 129.5 (C-e/f), 127.8 (C-b, b'), 126.5 (C-h/i), 119.5 (C-e/f), 114.2 (C-c, c'), 84.1 (C-k), 55.3 (C-m), 24.8 (C-l) ppm.

¹¹B NMR (160 MHz, CDCl₃): δ = 29.02 ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₁₉H₂₃BO₃S]⁺ 342.1461; Found 342.1456.

IR (ATR): $\tilde{\nu}$ = 2979 (m), 1602 (m), 1509 (s), 1457 (s), 1377 (m), 1356 (s), 1333 (s), 1295 (s), 1252 (s), 1172 (m), 1134 (s), 1065 (s), 1031 (m), 1016 (m), 952 (s), 850 (s), 815 (s), 745 (m), 683 (m), 660 (s), 587 (m), 531 (m), 471 (m), 443 (m) cm⁻¹.

M.p.: 98 °C.

(E)-N,N-Dimethyl-4-(2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)vinyl)aniline (3d)

A solution of **1** (373 mg, 1.00 mmol), (*E*)-4-(2-bromovinyl)-*N,N*-dimethylaniline **2d** (226 mg, 1.00 mmol), [Pd(PPh₃)₄] (11.6 mg, 10.0 μmol, 1 mol%) in DMF (4 mL) was heated to 60 °C for 168 h. The mixture solution was filtered over a short plug of celite using diethyl ether (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by Kugelrohr distillation (170 °C, 7.9 x 10⁻² mbar) to yield the product (151 mg, 43%) as a yellow solid.

¹H NMR (500 MHz, CDCl₃): δ = 7.50 (d, ³J = 3.5 Hz, 1 H, H-h/i), 7.36 (d, ³J = 8.8 Hz, 2 H, H-c, c'), 7.08–7.02 (m, 2 H, H-f, h/i), 6.96 (d, ³J = 16.1 Hz, 1 H, H-e), 6.70 (d, ³J = 8.8 Hz, 2 H, H-b, b'), 2.99 (s, 6 H, H-m), 1.35 (s, 12 H, H-l) ppm.

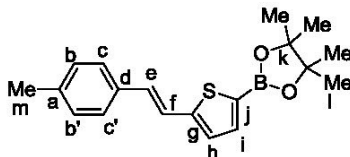
¹³C NMR (126 MHz, CDCl₃): δ = 150.8 (C-g), 150.3 (C-a), 137.8 (C-h/i), 130.3 (C-e), 127.6 (C-c, c'), 125.7 (C-f/h/i), 125.1 (C-d), 117.3 (C-f/h/i), 112.4 (C-b, b'), 84.0 (C-k), 40.4 (C-m), 24.8 (C-l) ppm.

¹¹B NMR (160 MHz, CDCl₃): δ = 28.59 ppm.

HRMS (ESI-FTMS) *m/z*: [M + H]⁺ Calcd for [C₂₀H₂₇BNO₂S]⁺ 356.1854; Found 356.1858; [M + Na]⁺ Calcd for [C₂₀H₂₆BNO₂Na S]⁺ 378.1673; Found 378.1676.

IR (ATR): ν̄ = 2977 (m), 2911 (w), 1601 (s), 1518 (s), 1455 (s), 1357 (s), 1335 (s), 1302 (s), 1270 (m), 1232 (m), 1183 (m), 1167 (m), 1139 (s), 1065 (s), 1015 (m), 954 (s), 853 (s), 809 (s), 752 (w), 684 (m), 662 (s), 586 (m), 529 (m), 443 (m) cm⁻¹.

M.p.: 155 °C.

(E)-4,4,5,5-Tetramethyl-2-(5-(4-methylstyryl)thiophen-2-yl)-1,3,2-dioxaborolane (3e)

A solution of **1** (373 mg, 1.00 mmol), (*E*)-1-(2-bromovinyl)-4-methylbenzene **2a** (197 mg, 1.00 mmol), [Pd(PPh₃)₄] (11.6 mg, 10.0 μmol, 1 mol%) in DMF (4 mL) was heated to 40 °C for 26 h. The mixture solution was filtered over a short plug of silica gel using diethyl ether (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel (*n*pentane / ether: 95 / 5, R_f = 0.32) to afford the product (241 mg, 74%) as a yellow solid.

¹H NMR (500 MHz, CDCl₃): δ = 7.52 (d, ³J = 3.6 Hz, 1 H, H-i), 7.36 (d, ³J = 8.1 Hz, 2 H, H-c, c'), 7.20 (d, ³J = 16.1 Hz, 1 H, H-f), 7.15 (d, ³J = 8.1 Hz, 2 H, H-b, b'), 7.11 (d, ³J = 3.6 Hz, 1 H, H-h), 7.00 (d, ³J = 16.1 Hz, 1 H, H-e), 2.35 (s, 3 H, H-m), 1.35 (s, 12 H, H-l) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 149.8 (C-g), 137.8 (C-a), 137.7 (C-i), 134.0 (C-d), 129.9 (C-e), 129.4 (C-b, b'), 126.8 (C-j), 126.4 (C-c, c'), 120.6 (C-f), 84.1 (C-k), 24.8 (C-l), 21.3 (C-m) ppm.

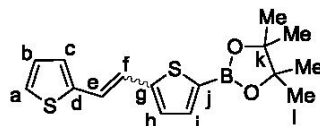
¹¹B NMR (160 MHz, CDCl₃): δ = 28.69 ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₁₉H₂₃BO₂S]⁺ 326.1512; Found 326.1510.

IR (ATR): ν̄ = 2976 (m), 1606 (w), 1525 (m), 1511 (s), 1456 (s), 1355 (s), 1327 (s), 1310 (s), 1270 (m), 1137 (s), 1062 (s), 1011 (m), 952 (s), 851 (s), 814 (s), 685 (m), 663 (s), 586 (m), 529 (m), 485 (m), 439 (m) cm⁻¹.

M.p.: 108 °C.

4,4,5,5-Tetramethyl-2-(5-(2-(thiophen-2-yl)viny)thiophen-2-yl)-1,3,2-dioxaborolane (3f)



A solution of **1** (373 mg, 1.00 mmol), 2-(2-bromovinyl)thiophene **2f** (*E* / *Z* 5 / 1) (189 mg, 1.00 mmol), [Pd(PPh₃)₄] (11.6 mg, 10.0 μmol, 1 mol%) in DMF (4 mL) was heated to 60 °C for 17 h. The mixture solution was filtered over a short plug of celite using *n*hexane (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by Kugelrohr distillation (140 °C, 1.2 × 10⁻¹ mbar) to yield the product (286 mg, 90%) as a yellow solid.⁹ The product contained *E* and *Z* isomer in about 25 / 2 *E* / *Z* ratio.

¹H NMR (600 MHz, CDCl₃): δ = 7.51 (d, ³J = 3.6 Hz, 1 H, H-i), 7.20 (d, ³J = 5.0 Hz, 1 H, H-a), 7.13 (d, ³J = 15.9 Hz, 1 H, H-f), 7.10 (d, ³J = 3.6 Hz, 1 H, H-h), 7.07–7.04 (m, 2 H, H-e, c), 7.00–6.98 (dd, ³J = 5.0 Hz, ³J = 3.5 Hz, 1 H, H-b), 1.35 (s, 12 H, H-l) ppm.

¹³C NMR (150 MHz, CDCl₃): δ = 149.0 (C-g), 142.2 (C-d), 137.8 (C-i), 127.7 (C-b), 127.1 (C-h), 126.5 (C-c), 124.7 (C-a), 122.9 (C-f), 121.1 (C-e), 84.1 (C-k), 24.8 (C-l) ppm.

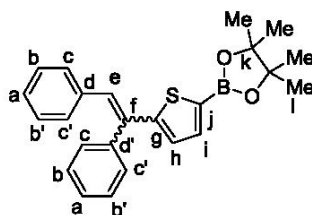
¹¹B NMR (160 MHz, CDCl₃): δ = 28.97 ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₁₆H₁₆BO₂S₂]⁺ 318.0919; Found 318.0917.

IR (ATR): ν̄ = 3110 (w), 2978 (m), 1530 (m), 1511 (m), 1458 (m), 1422 (m), 1371 (m), 1345 (s), 1295 (s), 1268 (m), 1213 (m), 1167 (m), 1136 (s), 1061 (s), 1011 (m), 999 (m), 959 (m), 933 (s), 902 (m), 852 (s), 814 (s), 794 (m), 763 (m), 721 (s), 682 (m), 660 (s), 589 (m), 521 (m), 436 (m)cm⁻¹.

M.p.: 87 °C.

2-(5-(1,2-Diphenylvinyl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)



A solution of **1** (373 mg, 1.00 mmol), 1-bromoethene-1,2-diyl)dibenzene **2g** (*E* / *Z* or *Z* / *E* 3 / 2) (259 mg, 1.00 mmol), [Pd(PPh₃)₄] (11.6 mg, 10.0 μmol, 1 mol%) in DMF (4 mL) was heated to 60 °C for 120 h. The mixture solution was filtered over a short plug of celite using *n*hexane (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by Kugelrohr distillation (170 °C, 5.2 × 10⁻² mbar) to yield the light yellow solid product (334 mg, 86%). The product contained *E* and *Z* isomer in a ratio of about 2 / 1.

¹H NMR (500 MHz, DMSO-*d*₆): δ = 7.54–6.96 (m, 23 H), 1.28, 1.27 (s, 21 H, H-l) ppm.

¹³C NMR (126 MHz, DMSO-*d*₆): δ = 154.7, 148.6, 142.6, 139.5, 138.4, 138.3, 136.9, 136.4, 135.7, 134.3, 131.3, 130.4, 129.8, 129.7, 129.6, 129.5, 128.9, 128.7, 128.6, 128.5, 128.0, 127.8, 127.6, 127.5, 126.9 (C-a-i), 84.6, 84.5 (C-k), 25.1, 25.0 (C-l) ppm.¹⁰

¹¹B NMR (160 MHz, DMSO-*d*₆): δ = 28.80 ppm.

HRMS (ESI-FTMS) *m/z*: [M + H]⁺ Calcd for [C₂₄H₂₆BO₂S]⁺ 389.1745; Found 389.1743; [M + Na]⁺ Calcd for [C₂₄H₂₅BO₂NaS]⁺ 411.1565; Found 411.1557.

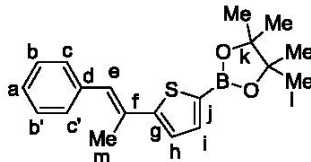
⁹ The product decomposed on a silica column.

¹⁰ The peaks belong to both *E*- and *Z*-isomer; it was impossible to analyze the peaks of ¹H NMR and ¹³C NMR spectra because the overlap of signals.

IR (ATR): $\tilde{\nu}$ = 2978 (m), 2930 (w), 1598 (w), 1524 (m), 1491 (m), 1445 (s), 1371 (s), 1348 (s), 1326 (s), 1267 (s), 1212 (w), 1140 (s), 1061 (s), 1013 (m), 957 (m), 925 (m), 852 (s), 813 (m), 752 (s), 715 (m), 693 (s), 663 (s), 619 (w), 577 (m), 556 (m), 515 (m), 436 (m) cm^{-1} .

M.p.: 42 °C.

(E)-4,4,5,5-Tetramethyl-2-(5-(1-phenylprop-1-en-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane (3h)



A solution of **1** (373 mg, 1.00 mmol), (2-bromoprop-1-en-1-yl)benzene **3h** (*E* / *Z* or *Z* / *E* 2 / 1) (197 mg, 1.00 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (11.6 mg, 10.0 μmol , 1 mol%) in DMF (4 mL) was heated to 60 °C for 144 h. The mixture solution was filtered over a short plug of celite using *n*hexane (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by Kugelrohr distillation (130 °C, 7.7×10^{-2} mbar) and recrystallized in *n*hexane at -80 °C to yield the product (202 mg, 62%) as a colorless solid.

$^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ = 7.50 (d, 3J = 3.6 Hz, 1 H, H-i), 7.39–7.35 (m, 4 H, H-b, b', c, c'), 7.29–7.24 (m, 1 H, H-a), 7.23 (d, 3J = 3.6 Hz, 1 H, H-h), 7.10 (d, 3J = 1.3 Hz, 1 H, H-e), 2.31 (d, 3J = 1.3 Hz, 3 H, H-m), 1.34 (s, 12 H, H-l) ppm.

$^{13}\text{C NMR}$ (126 MHz, CD_2Cl_2): δ = 155.1 (C-g), 137.9 (C-i), 137.8 (C-d), 131.4 (C-f), 129.6, 128.6 (C-b, b', c, c'), 127.6 (C-e), 127.2 (C-a), 125.0 (C-h), 84.5 (C-k), 25.0 (C-l), 17.7 (C-m) ppm.

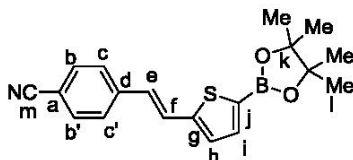
$^{11}\text{B NMR}$ (160 MHz, CD_2Cl_2): δ = 28.71 ppm.

HRMS (EI-sector) *m/z*: $[\text{M}]^+$ Calcd for $[\text{C}_{19}\text{H}_{23}\text{BO}_2\text{S}]^+$ 326.1512; Found 326.1513.

IR (ATR): $\tilde{\nu}$ = 2979 (m), 1618 (w), 1599 (w), 1525 (s), 1494 (m), 1456 (s), 1383 (s), 1332 (s), 1290 (s), 1271 (s), 1213 (w), 1139 (s), 1071 (s), 1047 (m), 1017 (m), 959 (m), 918 (w), 853 (s), 805 (s), 756 (m), 710 (m), 694 (s), 664 (s), 619 (w), 595 (w), 578 (w), 497 (m), 462 (w), 441 (m) cm^{-1} .

M.p.: 71 °C.

(E)-4-(2-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)vinyll) benzonitrile (3i)



A solution of **1** (373 mg, 1.00 mmol), (*E*)-4-(2-bromovinyl)benzonitrile **2i** (208 mg, 1.00 mmol), $\text{Pd}(\text{PPh}_3)_4$ (11.6 mg, 10.0 μmol , 1 mol%) in DMF (4 mL) was heated to 60 °C for 29 h. The mixture solution was filtered over a short plug of silica gel using diethyl ether (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel (*n*pentane / diethyl ether: 85 / 15, R_f = 0.30) to afford the product (295 mg, 88%) as a light yellow solid.

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ = 7.61 (d, 3J = 8.3 Hz, 2 H, H-b, b'), 7.46 (d, 3J = 8.3 Hz, 2 H, H-a, a'), 7.42 (d, 3J = 3.6 Hz, 1 H, H-h/i), 7.00 (d, 3J = 3.6 Hz, 1 H, H-h/i), 6.80 (d, 3J = 12.2 Hz, 1 H, H-f), 6.55 (d, 3J = 12.2 Hz, 1 H, H-e), 1.31 (s, 12 H, H-l) ppm.

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ = 145.3 (C-g), 141.9 (C-d), 137.1 (C-h/i), 132.3 (C-b, b'), 130.0 (C-h/i), 129.5 (C-c, c'), 128.1 (C-e), 125.2 (C-f), 119.0 (C-m), 111.1 (C-a), 84.2 (C-k), 24.7 (C-l) ppm.

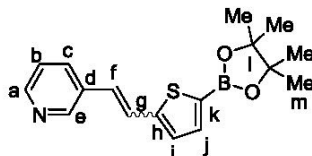
$^{11}\text{B NMR}$ (160 MHz, CDCl_3): δ = 28.77 ppm.

HRMS (EI-sector) *m/z*: $[\text{M}]^+$ Calcd for $[\text{C}_{19}\text{H}_{20}\text{BNO}_2\text{S}]^+$ 337.1308; Found 337.1310.

IR (ATR): $\tilde{\nu}$ = 2984 (w), 2969 (s), 2227 (m), 1623 (w), 1603 (m), 1518 (m), 1504 (m), 1395 (m), 1371 (m), 1345 (s), 1327 (s), 1265 (m), 1211 (w), 1139 (s), 1065 (s), 1016 (m), 957 (m), 875 (s), 849 (s), 826 (m), 809 (s), 753 (m), 733 (m), 682 (m), 660 (s), 592 (m), 557 (s), 468 (w), 432 (m) cm^{-1} .

M.p.: 117 °C.

3-(2-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)vinyl)pyridine (3j)



A solution of **1** (373 mg, 1.00 mmol), 3-(2-bromovinyl)pyridine **2k** (*Z* / *E* 100 / 7) (184 mg, 1.00 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (11.6 mg, 10.0 μmol , 1 mol%) in DMF (4 mL) was heated to 60 °C for 27 h. The mixture solution was filtered over a short plug of celite using *n*hexane (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by Kugelrohr distillation (120 °C, 5.3×10^{-2} mbar) to get the product (261 mg, 83%) as white solid. The product contained *Z* and *E* isomer in 20 / 1 *Z* / *E* ratio.

$^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ = 8.58–8.55 (m, 1 H, H-e), 8.53 (dd, $^3J = 4.8$ Hz, $^4J = 1.7$ Hz, 1 H, H-a), 7.69–7.63 (m, 1 H, H-c), 7.38 (d, $^3J = 3.6$ Hz, 1 H, H-j), 7.31–7.27 (m, 1 H, H-b), 7.03 (d, $^3J = 3.6$ Hz, 1 H, H-i), 6.85 (d, $^3J = 12.0$ Hz, 1 H, H-g), 6.57 (d, $^3J = 12.0$ Hz, 1 H, H-f), 1.29 (s, 12 H, H-m) ppm.

$^{13}\text{C NMR}$ (126 MHz, CD_2Cl_2): δ = 150.2 (C-e), 149.1 (C-a), 146.1 (C-h), 137.2 (C-j), 136.3 (C-c), 133.4 (C-d), 130.5 (C-i), 126.8 (C-f), 125.5 (C-g), 123.7 (C-b), 84.5 (C-l), 24.9 (C-m) ppm.

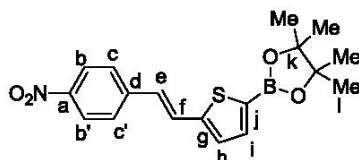
$^{11}\text{B NMR}$ (160 MHz, CD_2Cl_2): δ = 28.63 ppm.

HRMS (EI-sector) *m/z*: $[\text{M}]^+$ Calcd for $[\text{C}_{17}\text{H}_{20}\text{BNO}_2\text{S}]^+$ 313.1308; Found 313.1310.

IR (ATR): $\tilde{\nu}$ = 2973 (m), 2927 (w), 1522 (m), 1627 (m), 1476 (m), 1423 (m), 1356 (m), 1271 (w), 1206 (m), 1182 (s), 1140 (vs), 1001 (s), 979 (vs), 942 (s), 863 (m), 812 (m), 770 (s), 691 (vs), 653 (vs), 596 (m), 564 (m), 471 (m) cm^{-1} .

M.p.: 59 °C.

(*E*)-4,4,5,5-Tetramethyl-2-(5-(4-nitrostyryl)thiophen-2-yl)-1,3,2-dioxaborolane (3k)



A solution of **1** (373 mg, 1.00 mmol), (*E*)-1-(2-bromovinyl)-4-nitrobenzene **2j** (228 mg, 1.00 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (11.6 mg, 10.0 μmol , 1 mol%) in DMF (4 mL) was heated to 60 °C for 27 h. The mixture solution was filtered over a short plug of silica gel using diethyl ether (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by column chromatography (*n*pentane / diethyl ether: 85 / 15, $R_f = 0.30$) to afford the product (293 mg, 82%) as a red solid.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 8.18 (d, $^3J = 8.5$ Hz, 2 H, H-b, b'), 7.52 (d, $^3J = 8.5$ Hz, 2 H, H-a, a'), 7.43 (d, $^3J = 3.6$ Hz, 1 H, H-i), 7.02 (d, $^3J = 3.6$ Hz, 1 H, H-h), 6.84 (d, $^3J = 12.2$ Hz, 1 H, H-f), 6.58 (d, $^3J = 12.2$ Hz, 1 H, H-e), 1.31 (s, 12 H, H-l) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 147.0 (C-a), 145.2 (C-g), 144.0 (C-d), 137.1 (C-i), 130.3 (C-h), 129.7 (C-c, c'), 127.7 (C-e), 125.7 (C-f), 123.9 (C-b, b'), 84.2 (C-k), 24.7 (C-l) ppm.

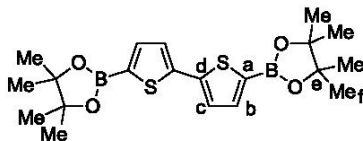
$^{11}\text{B NMR}$ (160 MHz, CDCl_3): δ = 28.83 ppm.

HRMS (ESI-FTMS) *m/z*: $[\text{M} + \text{Na}]^+$ Calcd for $[\text{C}_{18}\text{H}_{20}\text{BNO}_4\text{NaS}]^+$ 380.1102; Found 380.1105.

IR (ATR): $\tilde{\nu}$ = 2982 (m), 2928 (w), 1618 (w), 1592 (m), 1523 (m), 1508 (s), 1454 (m), 1357 (m), 1338 (s), 1299 (s), 1266 (m), 1208 (w), 1138 (s), 1103 (m), 1065 (m), 1012 (m), 955 (m), 890 (m), 852 (s), 830 (m), 809 (s), 759 (s), 729 (m), 693 (m), 662 (s), 579 (m), 470 (m), 439 (m) cm^{-1} .

M.p.: 112 °C.

5,5'-bis(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene (**4**)



1 (373 mg, 1.00 mmol), **9** (336 mg, 1.00 mmol), and [Pd(PPh₃)₄] (57.8 mg, 50.0 μmol) were dissolved in toluene (2 mL). The reaction mixture was heated to 100 °C by microwave irradiation for 4 h and colorless crystals precipitated. Subsequently, the mixture was dissolved in diethyl ether (10 mL) and filtered through a short plug of celite. The solvent was removed *in vacuo* and the crude product was purified by column chromatography (*n*hexane / diethyl ether: 10 / 1, R_f = 0.21) to afford the product (218 mg, 52%) as a colorless solid.

¹H NMR (500 MHz, CDCl₃): δ = 7.49 (d, ³J = 3.6 Hz, 2 H, H-b/c), 7.31 (d, ³J = 3.6 Hz, 2 H, H-b/c), 1.34 (s, 24 H, H-f) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 144.0 (C-d), 138.3 (C-b/c), 126.0 (C-b/c), 84.7 (C-e), 25.0 (C-f) ppm.

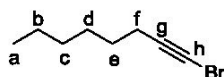
¹¹B NMR (160 MHz, CDCl₃): δ = 28.68 ppm.

HRMS (ESI-FTMS) *m/z*: [M + H]⁺ Calcd for [C₂₀H₂₈B₂O₄S]⁺ 419.1695; Found 419.1695.

IR (ATR): ν̄ = 2981 (m), 2933 (w), 1515 (m), 1435 (m), 1330 (s), 1251 (m), 1136 (s), 1075 (m), 1020 (m), 958 (m), 850 (s), 807 (s), 750 (s), 661 (s), 578 (w), 429 (m) cm⁻¹.

M.p.: 201 °C.

1-Bromo-1-octyne (**6a**)



This compound was prepared by a literature method.^[7]

To a stirred solution of 1-octyne (1.47 mL, 10.0 mmol) in acetone (263 mL), in a flask which was shielded rigorously from light, solid AgNO₃ (510 mg, 3.00 mmol) and *N*-bromo-succinimide (2.5 g, 14.0 mmol) were added in one portion under an air atmosphere. After stirring for 3 h at 22 °C, the reaction mixture was diluted with water (200 mL) and extracted with *n*hexane (3 x 200 mL). The combined extracts were washed with brine (1 x 300 mL) and dried over MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by column chromatography over silica gel (*n*hexane, R_f = 0.82) to afford the product (1.40 g, 74%, Lit.^[7]: 80%) as colorless oil.¹¹

¹H NMR (500 MHz, CDCl₃): δ = 2.20 (t, ³J = 7.2 Hz, 2 H, H-f), 1.56–1.44 (m, 2 H, H-e), 1.40–1.23 (m, 6 H, H-b,c,d), 0.89 (t, ³J = 6.9 Hz, 3 H, H-a) ppm.

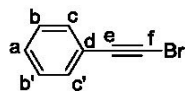
¹³C NMR (126 MHz, CDCl₃): δ = 80.5 (C-g), 37.4 (C-h), 22.5, 28.3, 28.5, 31.3 (C-b,c,d,e), 19.7 (C-f), 14.0 (C-a) ppm.

HRMS (EI-sector) *m/z*: No spectrum could be obtained either by EI or ESI.

IR (ATR): ν̄ = 2958 (m), 2956 (s), 2929 (m), 1430 (m), 1430 (w), 1378 (w), 1327 (w), 750 (w), 725 (m), 409 (w) cm⁻¹.

The NMR data agree with the literature.^[7]

¹¹ The product was volatile.

(Bromoethynyl)benzene (6b)^[8]

This compound was prepared by a literature method.^[8]

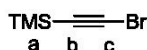
To a stirred solution of ethynylbenzene (1.02 g, 10.0 mmol) in acetone (50 mL), in a flask which was shielded rigorously from light, solid AgNO₃ (84.0 mg, 500 μmol) and *N*-bromosuccinimide (2.53 g, 14.0 mmol) were added in one portion under an air atmosphere. After stirring for 6 h at 22 °C, the solvent was removed *in vacuo* and the crude product was purified by column chromatography over silica gel (*n*hexane, R_f = 0.53) to afford the product (1.70 g, 90%; Lit.: [8]) as yellow oil.

¹H NMR (600 MHz, CDCl₃): δ = 7.47–7.43 (m, 2 H, H-c, c'), 7.36–7.29 (m, 2 H, H-a, b, b') ppm.

¹³C NMR (151 MHz, CDCl₃): δ = 132.0 (C-c, c'), 128.7 (C-a), 128.3 (C-b, b'), 122.7 (C-d), 80.0 (C-e), 49.7 (C-f) ppm.

HRMS (ESI-FTMS) *m/z*: [M]⁺ Calcd for [C₈H₆Br]⁺ 179.9575; Found 179.9574.

IR (ATR): $\tilde{\nu}$ = 3062 (w), 2818 (w), 2199 (m), 1595 (m), 1485 (s), 1442 (m), 1070 (m), 1026 (m), 915 (m), 751 (vs), 687 (vs), 611 (s), 519 (vs) cm⁻¹.

(Bromoethynyl)trimethylsilane (6c)

This compound was prepared by a literature method.^[9]

n-BuMgCl (9.49 mL, 15.0 mmol) was added dropwise over the period of 10 min to the stirred solution of ethynyltrimethylsilane (1.47 g, 15.0 mmol) in THF (45 mL) at 20 °C. The solution stirred for 18 h at 20 °C. Then the solution was cooled to -78 °C and stirred for 1 h before bromine (770 μL, 15.0 mmol) was added dropwise over the period of 10 min. Then the solution warmed up to 20 °C. The reaction mixture was quenched slowly with 2 M of Na₂S₂O₃ aqueous solution (15 mL). The yellow solution became colorless and was stirred for additional 5 min. The organic layer was washed with brine (3 x 50 mL) and dried over MgSO₄. The solvent was removed *in vacuo* and the crude product was purified Kugelrohr distillation (60–80 °C, 100 mbar) to afford (1.41 g, 69%, Lit.^[9]: 56%) of colorless oil.

¹H NMR (500 MHz, CDCl₃): δ = 0.18 (s, 9 H, H-a) ppm.

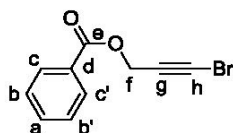
¹³C NMR (125 MHz, CDCl₃): δ = 87.1 (C-b), 61.6 (C-c), 0.1 (C-a) ppm.

²⁹Si NMR (99 MHz, CDCl₃): δ = (-15.50 – -15.85) ppm.¹²

²⁹Si [¹H] DEPT NMR (99 MHz, CDCl₃): δ = 15.67 (s, Si-(CH₃)₃) ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₅H₆BrSi]⁺ 177.9636; Found 177.9637.

IR (ATR): $\tilde{\nu}$ = 2962 (m), 2125 (s), 1251 (s) cm⁻¹.¹³

3-Bromoprop-2-yn-1-yl benzoate (6d)

To the mixture of propargyl benzoate (2.40 g, 15.0 mmol) and *N*-bromosuccinimide (3.26 g, 12.0 mmol) in 10 mL of acetone, AgNO₃ (127 mg, 750 μmol) was added in one portion and the mixture was stirred at 20 °C for 3 h. After

¹² The expected ²J Si-H coupling constant with 6.6 Hz was observed, but the signal/noise ratio is too low to see the complete multiplet.

¹³ No peak at about 3300 cm⁻¹, corresponding to CC-H valence vibration.

removing the solvent *in vacuo*, the residue was dissolved in a mixture of water (30 mL) and *n*pentane (30 mL). The aqueous phase was extracted with *n*pentane (3 x 30 mL). The organic layers were combined and the solvent was removed *in vacuo*. The crude product was purified by column chromatography over silica gel (DCM / *n*pentane: 1 / 1, R_f = 0.4) to afford the product (2.83 g, 79%) as colorless oil.

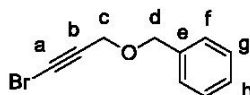
$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 8.09–8.05 (m, 2 H, H-c,c'), 7.61–7.56 (m, 1 H, H-a), 7.48–7.43 (m, 2 H, H-b,b'), 4.95 (s, 2 H, H-f) ppm.

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ = 165.9 (C-d), 135.5 (C-a), 130.0 (C-c,c'), 129.5 (C-d), 128.6 (C-b,b'), 74.3 (C-g), 53.4 (C-f), 47.4 (C-h) ppm.¹⁴

HRMS (EI-sector) m/z : $[M]^+$ Calcd for $[\text{C}_{10}\text{H}_7\text{BrO}_2]^+$ 239.9609; Found 239.9614.

IR (ATR): $\tilde{\nu}$ = 3064 (w), 2946 (w), 2226 (m) cm^{-1} .

Benzylprop-(3-bromo-2-ynyl) ether (6e)



To the mixture of benzylprop-2-ynyl ether (2.19 g, 15.0 mmol), and *N*-bromosuccinimide (3.26 g, 18.0 mmol) in acetone (15 mL), AgNO_3 (127 mg, 750 μmol) was added and the mixture was stirred at 24 °C for 3 h under exclusion of light. After GC-MS indicated the completion the reaction, the solvent was evaporated. The residue was dissolved in a mixture of water (100 mL) and *n*pentane (100 mL). After phase separation, the aqueous phase was extracted with pentane (100 mL). The organic layers were combined, dried over Na_2SO_4 and the solvent was removed *in vacuo*. The product was purified by column chromatography (silica, eluent: gradient of *n*pentane to ethyl acetate; R_f = 0.2) and was obtained as colorless oil (2.31 g, 68%).

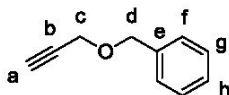
$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 7.45–7.27 (m, 5 H, H-f,g,h), 4.60 (s, 2 H, H-d), 4.20 (s, 2 H, H-c) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 137.2 (C-e), 128.5 (C-f/g), 128.1 (C-f/g), 127.9 (C-h), 76.2 (C-a/b), 71.7 (C-d), 58.0 (C-c), 46.1 (C-a/b) ppm.

HRMS (EI-sector) m/z : $[M]^+$ Calcd for $[\text{C}_{10}\text{H}_8\text{BrO}]^+$ 224.9738; Found 224.9740.

IR (ATR): $\tilde{\nu}$ = 3039 (w), 2854 (m), 2213 (m), 1087 (s), 1073 (s), 736 (s), 696 (s) cm^{-1} .

Benzylprop-2-ynyl ether (6f)



This compound was prepared by a literature method.^[10]

Propargylic alcohol (2.24 g, 40.0 mmol) in DMF (15 mL) was added in portion over 15 min to a suspension of NaH (60% in mineral oil, 1.62 g, 40.4 mmol) in DMF (35 mL) at 0 °C. After 30 min, benzyl bromide (6.91 g, 40.4 mmol) was added in one portion, the cooling bath removed and the resulting mixture was stirred at 22 °C for 22 h. The mixture was then diluted by ethyl acetate (200 mL) and washed by HCl 1N (200 mL) and dried over Na_2SO_4 . The reaction mixture was then concentrated and purified by a short filter column chromatography (silica: 0.040-0.063 mm, 230-400 mesh; eluent: *n*pentane; For TLC: *n*pentane / DCM = 8 / 2, R_f impurity = 0.76; R_f product = 0.50). The product (4.93 g, 84%, Lit.^[10]: 100%)¹⁵ was received as a colorless oil and stored in the fridge at 4 °C.

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ = 7.42–7.28 (m, 5 H, H-f,g,h), 4.62 (s, 2 H, H-d), 4.18 (d, 4J = 2.4 Hz, 2 H, H-c), 2.47 (t, 4J = 2.4 Hz, 1 H, H-a) ppm.

$^{13}\text{C NMR}$ (151 MHz, CDCl_3): δ = 137.4 (C-e), 128.6 (C-f/g), 128.3 (C-f/g), 128.1 (C-h), 79.8 (C-b), 74.7 (C-a), 71.7 (C-d), 57.2 (C-c) ppm.

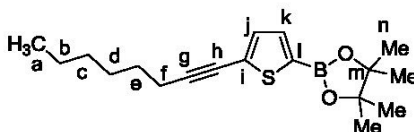
¹⁴ A signal with a negative intensity at 70.8 ppm is due to an artifact which occurred during the measurement.

¹⁵ The product is very volatile and should not be placed under a vacuum of below 10 mbar at 45 °C.

HRMS: No spectrum could be obtained either by EI or ESI.

IR (film): $\tilde{\nu}$ = 3291, 2856, 1073, 696 cm^{-1} .

4,4,5,5-Tetramethyl-2-(5-(oct-1-y-n-1-y)thiophen-2-yl)-1,3,2-dioxaborolane (7a)



A solution of **1** (373 mg, 1.00 mmol), 1-bromo-1-octyne **6a** (189 mg, 1.00 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (11.6 mg, 10.0 μmol , 1 mol%) in DMF (4 mL) was heated to 40 °C for 25 h. The mixture solution was filtered over a short plug of celite using *n*hexane (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by Kugelrohr distillation (125 °C, 5.0×10^{-2} mbar) to yield the product (204 mg, 64%) as a colorless oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 7.45 (d, 3J = 3.6 Hz, 1 H, H-j/k), 7.15 (d, 3J = 3.6 Hz, 1 H, H-j/k), 2.43 (t, 3J = 7.1 Hz, 2 H, H-f), 1.64–1.57 (m, 2 H, H-e), 1.47–1.41 (m, 2 H, H-e), 1.36–1.29 (m, 16 H, H-b, c, n), 0.91 (t, 3J = 6.9 Hz, 3 H, H-a) ppm.

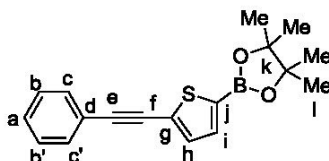
$^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 136.8 (C-j/k), 131.9 (C-j/k), 130.9 (C-i), 96.2 (C-g), 84.1 (C-m), 73.8 (C-h), 31.3 (C-c), 28.6 (C-d/e), 28.4 (C-d/e), 24.7 (C-n), 22.5 (C-b), 19.8 (C-f), 14.0 (C-a) ppm.

$^{11}\text{B NMR}$ (160 MHz, CDCl_3): δ = 28.41 ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{18}\text{H}_{27}\text{BO}_2\text{S}]^+$ 318.1825; Found 318.1823.

IR (ATR): $\tilde{\nu}$ = 7978 (w), 2930 (m), 2858 (w), 2227 (w), 1523 (m), 1456 (s), 1372 (m), 1352 (s), 1289 (s), 1270 (m), 1213 (m), 1140 (s), 1064 (s), 1016 (m), 998 (w), 957 (m), 852 (s), 810 (s), 749 (w), 724 (w), 686 (m), 664 (s), 579 (m), 444 (m) cm^{-1} .

4,4,5,5-Tetramethyl-2-(5-(phenylethynyl)thiophen-2-yl)-1,3,2-dioxaborolane (7b)



A solution of **1** (186 mg, 500 μmol), (bromoethynyl)benzene **6b** (90.5 mg, 500 μmol), $[\text{Pd}(\text{PPh}_3)_4]$ (5.80 mg, 0.50 μmol , 1 mol%) in DMF (2 mL) was heated to 40 °C for 27 h. The mixture solution was filtered over a short plug of celite using *n*hexane (500 mL) as solvent. The solvent was removed *in vacuo* and the crude product was purified by Kugelrohr distillation (110 °C, 6.2×10^{-2} mbar) to afford the product (130 mg, 84%) as a colorless solid.

$^1\text{H NMR}$ (600 MHz, CDCl_3): δ = 7.54–7.50 (m, 3 H, H-c, c', i), 7.37–7.33 (m, 3 H, H-a, b, b'), 7.31 (d, 3J = 3.6 Hz, 1 H, H-h), 1.35 (s, 12 H, H-l) ppm.

$^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ = 137.0 (C-i), 132.9 (C-h), 131.5 (C-c, c'), 129.8 (C-g), 128.6 (C-a), 128.4 (C-b, b'), 122.8 (C-d), 94.4 (C-e), 84.3 (C-k), 82.7 (C-f), 24.8 (C-l) ppm.

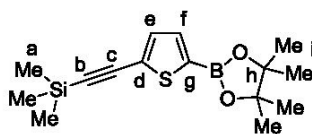
$^{11}\text{B NMR}$ (160 MHz, CDCl_3): δ = 28.70 ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{18}\text{H}_{18}\text{BO}_2\text{S}]^+$ 310.1198; Found 310.1192.

IR (ATR): $\tilde{\nu}$ = 2977 (m), 1527 (m), 1492 (s), 1453 (s), 1355 (vs), 1337 (vs), 1314 (vs), 1249 (s), 1138 (vs), 1067 (m), 1012 (m), 958 (m), 912 (m), 852 (s), 813 (s), 748 (vs), 684 (s), 660 (s), 580 (m), 517 (m) cm^{-1} .

M.p.: 104 °C.

Trimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)ethynyl)silane (7c)



A solution of **1** (746 mg, 2.00 mmol), (bromoethynyl)trimethylsilane **6c** (340 mg, 2.00 mmol), [Pd(PPh₃)₄] (23.0 mg, 20.0 μmol, 1 mol%) in DMF (8 mL) was heated to 60 °C for 7 d. The mixture solution was filtered over a short plug of celite using diethyl ether (50 mL) as eluent. The solvent was removed *in vacuo* and the crude product (1.03 g) was purified by Kugelrohr distillation (70 °C, 2 x 10⁻¹ mbar) to afford a mixture (50 / 50) of **1** (starting material) and product (533 mg). A subsequent column chromatography (*n*hexane / ethyl acetate: 97 / 3, R_f = 0.9) led to decomposition. Calculated yield from ¹H NMR after first Kugelrohr distillation: 267 mg, 44% (with 44% of remaining starting material **1**). Other purification attempts using silica or alumina as a stationary phase or preconditioning the column with 5 % NEt₃ failed and it appeared that the product decomposes on the column.

¹H NMR (500 MHz, CDCl₃): δ = 7.44 (d, ³J = 3.6 Hz, 1 H, H-f), 7.25 (d, ³J = 3.6 Hz, 1 H, H-e), 1.33 (s, 12 H, H-i), 0.25 (s, 9 H, H-a) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 136.8 (C-f), 133.7 (C-e), 129.8 (C-d), 100.4 (C-b) 97.7 (C-c), 84.1 (C-h), 24.9 (C-i), -8.1 (C-a) ppm.¹⁶

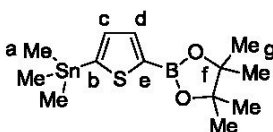
¹¹B NMR (160 MHz, CDCl₃): δ = 28.73 ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₀H₂₁O₄BS]⁺ 368.1254; Found 368.1256.

IR (ATR): Not measured due to a mixture of product and by-products.

M.p.: Not measured due to a mixture of product and by-products.

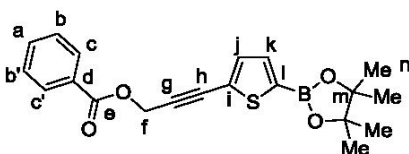
Data from the remaining starting material in the spectrum for comparative purposes:



¹H NMR (500 MHz, CDCl₃): δ = 7.76 (d, ³J = 3.3 Hz, 1 H, H-d), 7.29 (d, ³J = 3.3 Hz, 1 H, H-c), 1.34 (s, 12 H, H-g), 0.37 (s, 9 H, H-a) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 146.5 (C-b), 137.8 (C-d), 136.3 (C-c), 84.5 (C-f), 24.9 (C-g), -8.2 (C-a) ppm.

3-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)prop-2-yn-1-yl benzoate (7d)



A solution of **1** (372.9 mg, 2.000 mmol), 3-bromoprop-2-yn-1-yl benzoate **6d** (239.1 mg, 2.000 mmol), [Pd(PPh₃)₄] (11.60 mg, 10 μmol, 1 mol%) in DMF (8 mL) was heated to 60 °C for 29 h. The mixture was filtered over a short plug of celite using diethyl ether (50 mL) as eluent. The solvent was removed *in vacuo* and ca. half of the crude product (328.0 mg of 871.0 mg) was purified by column chromatography (*n*hexane / ethyl acetate: 4 / 1, R_f = 0.8) to yield the

¹⁶Intensity of quarternary thiophene carbon atom (g) were too low for detection.

product (140.0 mg, 43%) with low amounts of impurities. A subsequent column chromatography (gradient from *n*hexane / ethyl acetate: 98 / 2 to 1 / 1; $R_f = 0.1$ [98 / 2]) led to fewer impurities, but the yield deteriorated (81.00 mg, 11%). Other purification attempts using alumina as a stationary phase or preconditioning the column with 5 % NEt_3 failed and it appeared that the product decomposes on the column.

Yield extrapolated from whole sample: 29%.

$^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 8.11\text{--}8.08$ (m, 2 H, H-c), 7.60–7.56 (m, 1 H, H-a), 7.47 (d, $^3J = 3.6$ Hz, 1 H, H-k), 7.46–7.43 (m, 2 H, H-b), 7.29 (d, 1 H, 3.6 Hz, H-j), 5.18 (s, 2 H, H-f), 1.33 (s, 12 H, H-n) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3): $\delta = 166.0$ (C-e), 137.0 (C-k), 134.0 (C-j), 133.4 (C-a), 130.0 (C-c), 129.7 (C-d), 128.6 (C-b), 128.1 (C-a), 88.5 (C-g), 84.5 (C-m), 80.1 (C-h), 53.5 (C-f), 24.9 (C-n) ppm.

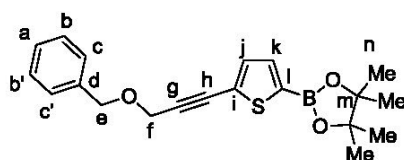
$^{11}\text{B NMR}$ (160 MHz, CDCl_3): $\delta = 28.41$ ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{20}\text{H}_{21}\text{O}_4\text{BS}]^+$ 368.1254; Found 368.1256.

IR (ATR): Not measured due to a mixture of product and by-products.

M.p.: Not measured due to a mixture of product and by-products.

2-(5-(3-(Benzyloxy)prop-1-yn-1-yl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7e)



A solution of **1** (746 mg, 2.00 mmol), (3-bromoprop-2-yn-1-yl)oxy)methyl)benzene **6e** (450 mg, 2.00 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (23.0 mg, 20.0 μmol , 1 mol%) in DMF (8 mL) was heated to 60 °C for 29 h (when the reaction was completed as indicated by NMR). The mixture was filtered over a short plug of celite using diethyl ether (50 mL) as eluent. The solvent was removed *in vacuo* and the ca. half of the crude product (386 mg of 734 mg) was purified by column chromatography (gradient from *n*hexane / ethyl acetate: 98 / 2 to 1 / 1; $R_f = 0.1$ [98:2]) to yield a mixture of the product (80.0 mg, 11%) and low amounts of some other impurities as light green oil. Other purification attempts using alumina as a stationary phase or preconditioning the column with 5% NEt_3 failed and it appeared that the product decomposes on the column.

Yield extrapolated from whole sample: 21%.

$^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 7.48$ (d, $^3J = 3.6$ Hz, 1 H, H-k), 7.40–7.34 (m, 5 H, H-a,b,c), 7.26 (d, $^3J = 3.6$ Hz, 1 H, H-j) 4.66 (s, 2 H, H-e), 4.42 (s, 2 H, H-f), 1.34 (s, 12 H, H-n) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3): $\delta = 137.5$ (C-d), 137.0 (C-k), 133.5 (C-j), 132.6 (C-l), 129.1 (C-i), 128.6 (C-b/c), 128.4 (C-b/c), 128.1 (C-a), 90.6 (C-g), 84.5 (C-m), 80.0 (C-h), 71.9 (C-e), 58.2 (C-f), 24.9 (C-n) ppm.

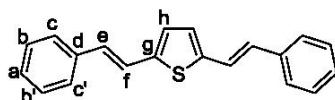
$^{11}\text{B NMR}$ (160 MHz, CDCl_3): $\delta = 28.29$ ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{20}\text{H}_{23}\text{O}_3\text{BS}]^+$ 354.1461; Found 354.1463.

IR (ATR): Not measured due to a mixture of product and by-products.

M.p.: Not measured due to a mixture of product and by-products.

2,5-Di((*E*)-styryl)thiophene (8a)



A solution of **1** (186 mg, 0.500 mmol), β -bromostyrene (*E* / *Z* 8:1) (91.0 mg, 0.500 mmol), and $[\text{Pd}(\text{PPh}_3)_4]$ (5.78 mg, 5.00 μmol , 1 mol%) in DMF (4 mL) was heated to 60 °C for 17 h. Then, β -bromostyrene (*E* / *Z* = 8 / 1) (91.0 mg, 0.50 mmol) in DMF (4 mL) was added to the solution in one portion, followed by a solution of K_2CO_3 (138 mg, 1.00 mmol).

in degassed water (1 mL) also in one portion. The solution was heated to 100 °C for 6 h. After it cooled down to 20 °C, the solution was diluted with DCM (8 mL) and filtered through a short plug of silica with DCM (250 mL). After removing the volatiles *in vacuo*, the crude product was purified by column chromatography (*n*pentane / DCM: 9 / 1, $R_f = 0.33$) to afford the product (124 mg, 86%) as yellow solid.

$^1\text{H NMR}$ (600 MHz, CD_2Cl_2): $\delta = 7.49$ (d, $^3J = 7.6$ Hz, 4 H, H-c, c'), 7.39–7.34 (m, 4 H, H-b, b'), 7.26 (t, $^3J = 7.4$ Hz, 2 H, H-a), 7.23 (d, $^3J = 16.1$ Hz, 2 H, H-f), 7.00 (s, 2 H, H-h), 6.94 (d, $^3J = 16.1$ Hz, 2 H, H-e) ppm.

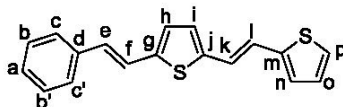
$^{13}\text{C NMR}$ (151 MHz, CD_2Cl_2): $\delta = 142.3$ (C-g), 137.4 (C-d), 129.2 (C-b, b'), 128.8 (C-e), 128.1 (C-a), 127.7 (C-h), 126.7 (C-c, c'), 122.2 (C-f) ppm.

HRMS (EI-sector) *m/z*: $[\text{M}]^+$ Calcd for $[\text{C}_{20}\text{H}_{16}\text{S}]^+$ 288.0973; Found 288.0980.

IR (ATR): $\bar{\nu} = 3056$ (w), 3018 (w), 1621 (w), 1595 (m), 1488 (w), 1442 (m), 1236 (m), 1073 (w), 1041 (m), 950 (vs), 886 (w), 842 (w), 793 (vs), 745 (s), 689 (vs), 592 (m), 549 (vs), 524 (m), 468 (m) cm^{-1} .

M.p.: 187 °C.

2-((*E*-Styryl)-5-((*E*-2-(thiophen-2-yl)vinyl)thiophene (8b)



A solution of **1** (186 mg, 0.500 mmol), β -bromostyrene (*E* / *Z* = 8 / 1) (91.0 mg, 0.500 mmol), and $[\text{Pd}(\text{PPh}_3)_4]$ (5.78 mg, 5.00 μmol , 1 mol%) in DMF (4 mL) was heated to 60 °C for 17 h. Then, 2-(2-bromovinyl)thiophene **2f** (*E* / *Z* = 5 / 1) (94.0 mg, 0.500 mmol), in DMF (4 mL) was added to the solution in one portion, followed by a solution of K_2CO_3 (138 mg, 1.00 mmol) in degassed water (1 mL), also in one portion. The solution was heated to 100 °C for 6 h. After the solution cooled down to 20 °C, it was diluted with DCM (8 mL) and filtrated through a short plug of silica with DCM (250 mL). After removing the volatiles *in vacuo*, the crude product was purified by column chromatography (*n*pentane / DCM: 95 / 5, $R_f = 0.30$) to afford the product (125 mg, 85%) as yellow solid.

$^1\text{H NMR}$ (600 MHz, CD_2Cl_2): $\delta = 7.42$ (d, $^3J = 7.3$ Hz, 2 H, H-c, c'), 7.38–7.34 (m, 2 H, H-b, b'), 7.22–7.13 (m, 3 H, H-a, e/f/k/l/h/i/n/o/p), 7.03–7.01 (m, 1 H, H-h/i/n/o/p), 7.01–6.93 (m, 3 H, H-e/f/k/l/h/i/n/o/p), 6.92 (d, $^3J = 3.7$ Hz, 1 H, H-h/i/n/o/p), 6.89 ((d, $^3J = 3.7$ Hz, 1 H, H-h/i/n/o/p), 6.86 (d, $^3J = 16.1$ Hz, 1 H, H-e/f/k/l) ppm.¹⁷

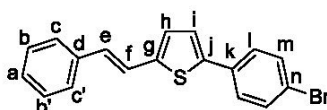
$^{13}\text{C NMR}$ (151 MHz, CD_2Cl_2): $\delta = 142.8$, 142.3, 141.8 (C-g/f/m), 137.3 (C-d), 129.2 (C-b, b'), 128.9, 128.2, 128.1, 127.8, 127.6 (C-a/e/f/k/l/h/i/n/o/p), 126.7 (C-c, c', h/i/n/o/p), 125.0, 122.1, 122.0, 121.8 (C-e/f/k/l/h/i/n/o/p) ppm.

HRMS (EI-sector) *m/z*: $[\text{M}]^+$ Calcd for $[\text{C}_{18}\text{H}_{14}\text{S}_2]^+$ 294.0537; Found 294.0534.

IR (ATR): $\bar{\nu} = 3064$ (w), 3018 (w), 1787 (w), 1594 (m), 1492 (m), 1446 (m), 1420 (m), 1364 (w), 1282 (w), 1226 (m), 1074 (w), 1040 (m), 941 (vs), 855 (m), 810 (s), 789 (s), 746 (s), 689 (vs), 575 (m), 544 (s), 466 (m) cm^{-1} .

M.p.: 143 °C

(*E*)-2-(4-bromophenyl)-5-styrylthiophene (8c)



A solution of **1** (186 mg, 0.500 mmol), β -bromostyrene (*E* / *Z* = 8 / 1) (91.0 mg, 0.500 mmol), and $[\text{Pd}(\text{PPh}_3)_4]$ (5.78 mg, 5.00 μmol , 1 mol%) in DMF (4 mL) was heated to 60 °C for 17 h. Then, 1-bromo-4-iodobenzene (141 mg, 0.50 mmol) in DMF (4 mL) was added to the solution in one portion, followed by a solution of K_2CO_3 (138 mg, 1.00 mmol) in degassed water (1 mL), also in one portion. The solution was heated to 100 °C for 6 h. After it cooled down to 20 °C, the solution was diluted with DCM (8 mL) and filtrated through a short plug of silica with DCM (250 mL). After removing the volatiles

¹⁷ It was not possible to distinguish all of the peaks because of peak overlap. The same was the case for the $^{13}\text{C NMR}$ spectrum.

in vacuo, the crude product was purified by column chromatography (*n*pentane / DCM: 95 / 5, $R_f = 0.41$) to afford the product (128 mg, 75%) as yellow solid.

$^1\text{H NMR}$ (600 MHz, CD_2Cl_2): $\delta = 7.54\text{--}7.47$ (m, 6 H, H-c, c' l, m), 7.39–7.34 (m, 2 H, H-b, b'), 7.29–7.20 (m, 3 H, H-a, f, h), 7.07 (d, $^3J = 3.7$ Hz, 1 H, H-i), 6.97 (d, $^3J = 16.1$ Hz, 1 H, H-e) ppm.

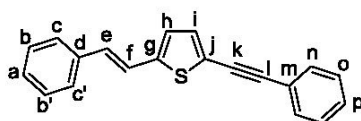
$^{13}\text{C NMR}$ (151 MHz, CD_2Cl_2): $\delta = 143.2$ (C-g), 141.9 (C-k), 137.3 (C-d), 133.6 (C-j), 132.4 (C-l/m), 129.2 (C-b, b'), 129.0 (C-e), 128.2 (C-a), 128.0 (C-i), 127.5 (C-l/m), 126.7 (C-c, c'), 124.6 (C-h), 122.0 (C-f), 121.7 (C-n) ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{26}\text{H}_{13}\text{BrS}]^+$ 339.9921; Found 339.9926.

IR (ATR): $\tilde{\nu} = 3066$ (w), 3018 (w), 1593 (w), 1482 (m), 1444 (m), 1399 (m), 1276 (m), 1235 (w), 1116 (m), 1075 (m), 1006 (m), 948 (s), 820 (s), 795 (vs), 747 (vs), 689 (vs), 568 (m), 552 (m), 503 (s), 469 (m) cm^{-1} .

M.p.: 170 °C.

(*E*)-2-(phenylethynyl)-5-styrylthiophene (8d)



A solution of **1** (186 mg, 0.500 mmol), β -bromostyrene (*E* / *Z* = 8 / 1) (91.0 mg, 0.500 mmol), and $[\text{Pd}(\text{PPh}_3)_4]$ (5.78 mg, 5.00 μmol , 1 mol%) in DMF (4 mL) was heated to 60 °C for 17 h. Then, (bromoethynyl)benzene **6b** (90.5 mg, 0.50 mmol), in DMF (4 mL) was added to the solution in one portion, followed by a solution of K_2CO_3 (138 mg, 1.00 mmol) in degassed water (1 mL), also in one portion. The solution was heated to 100 °C for 6 h. After it cooled down to 20 °C, the solution was diluted with DCM (8 mL) and filtrated through a short plug of silica with DCM (250 mL). After removing the volatiles *in vacuo*, the crude product was purified by column chromatography (*n*pentane, $R_f = 0.25$) to afford the product (51 mg, 37%) as yellow solid.

$^1\text{H NMR}$ (600 MHz, CD_2Cl_2): $\delta = 7.56\text{--}7.51$ (m, 2 H, H-n), 7.50 (d, $^3J = 7.5$ Hz, 2 H, H-c, c'), 7.31–7.35 (m, 5 H, H-b, b', o, p), 7.28 (t, $^3J = 7.4$ Hz, 1 H, H-a), 7.24–7.18 (m, 2 H, H-f, i), 7.01 (d, $^3J = 3.7$ Hz, 1 H, H-h), 6.97 (d, $^3J = 16.1$ Hz, H-e) ppm.

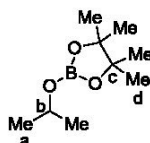
$^{13}\text{C NMR}$ (151 MHz, CD_2Cl_2): $\delta = 145.0$ (C-g), 137.1 (C-d'), 133.2 (C-i), 131.7 (C-n), 129.7 (C-e), 129.2, 129.0, 128.9 (C-b, b', o, p), 128.4 (C-a), 126.8 (C-h, c), 123.2 (C-m), 122.1 (C-i), 121.6 (C-f), 94.5 (C-l), 83.3 (C-k) ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{20}\text{H}_{14}\text{S}]^+$ 286.0816; Found 286.0814.

IR (ATR): $\tilde{\nu} = 3053$ (w), 3016 (w), 1592 (m), 1520 (m), 1485 (m), 1442 (m), 1276 (m), 1224 (m), 1189 (m), 1070 (m), 1029 (m), 952 (s), 914 (m), 885 (w), 839 (w), 797 (s), 747 (vs), 688 (vs), 599 (m), 543 (m), 523 (m), 465 (w) cm^{-1} .

M.p.: 152 °C.

2-*iso*Propyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*i*PrO-BPin) (9)



For the convenience of the reader, the data are reproduced from the supporting information of work by Linshoef et al.^[1] in our group.

2-*iso*Propyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared similarly to a method described by Andersen et al.^[11] and was modified as follows.

Tri-*iso*propyl borate (31.8 g, 169 mmol) and pinacol (20.0 g, 169 mmol) in *n*hexane (50 mL) were heated to 90 °C (external temperature) and an *iso*propanol / hexane azeotrope was removed by distillation within 16 h. The residue was distilled (90 °C oil bath, 16 mbar) to afford the product (26.9 g, 86%, Lit.^[11]: 92%) as colorless, air and moisture sensitive oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 4.29 (septet, 3J = 6.2 Hz, 1 H, H-b), 1.20 (s, 12 H, H-d), 1.15 (d, 3J = 6.2 Hz, 6 H, H-a) ppm.

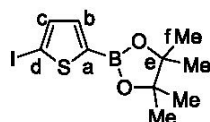
$^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 82.5 (C-c), 67.4 (C-b), 24.6 (C-d), 24.4 (C-a) ppm.

$^{11}\text{B NMR}$ (160 MHz, CDCl_3): δ = 21.8 ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_9\text{H}_{10}\text{BO}_3]^+$ 186.1427; Found 186.1420.

IR (ATR): $\tilde{\nu}$ = 2979 (w), 1504 (w), 1473 (w), 1444 (m), 1373 (w), 1345 (w), 1319 (m), 1148 (m), 1121 (m), 958 (w), 905 (s), 852 (m), 727 (s), 672 (m), 648 (m) cm^{-1} .

2-(5-Iodothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)



A solution of diisopropylamine (7.08 g, 70.0 mmol) in THF (200 mL) was cooled to $-78\text{ }^\circ\text{C}$ and *n*Butyllithium (20.0 mL, 50.0 mmol) was added dropwise over the course of 1 h. The mixture was warmed to $0\text{ }^\circ\text{C}$ with in 30 min by replacing the dry ice bath with ice bath. Then the reaction mixture was cooled again to $-78\text{ }^\circ\text{C}$ and stirring was continued for 5 min. 2-Iodothiophene (10.5 g, 50.0 mmol) in THF (20 mL) was added over the course of 25 min and the reaction mixture was stirred for 1 h at $-78\text{ }^\circ\text{C}$. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10.2 g, 55.0 mmol) was added dropwise within 30 min to the orange-brown suspension and the reaction mixture was stirred for 19 h while it was allowed to warm to $20\text{ }^\circ\text{C}$ without removal of the cooling bath. The reaction was quenched with a saturated solution of ammonium chloride (50 mL) and the aqueous layer was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were dried over MgSO_4 . The volatiles were removed *in vacuo* to obtain the product (16.7 g, 99%) of oil that crystallized after 18 h at $5\text{ }^\circ\text{C}$ to give a pale yellow solid.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 7.29 (d, 3J = 3.6 Hz, 1 H, H-b/c), 7.27 (d, 3J = 3.6 Hz, 1 H, H-b/c), 1.33 (s, 12 H, H-f) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 138.5 (C-b/c), 138.3 (C-b/c), 84.3 (C-e), 81.5 (C-d), 24.7 (C-f) ppm.

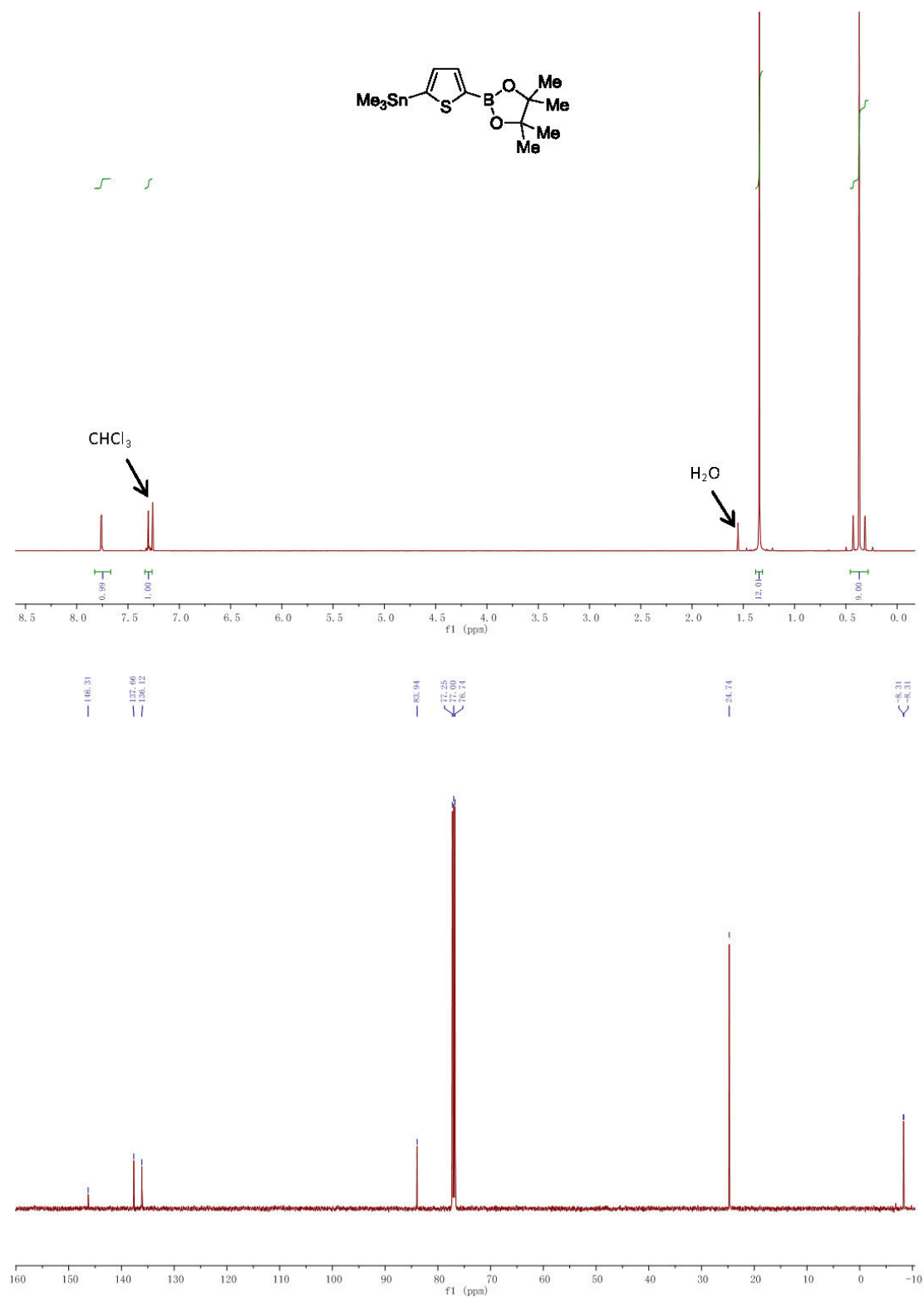
$^{11}\text{B-NMR}$ (160 MHz, CDCl_3): δ = 28.2 ppm.

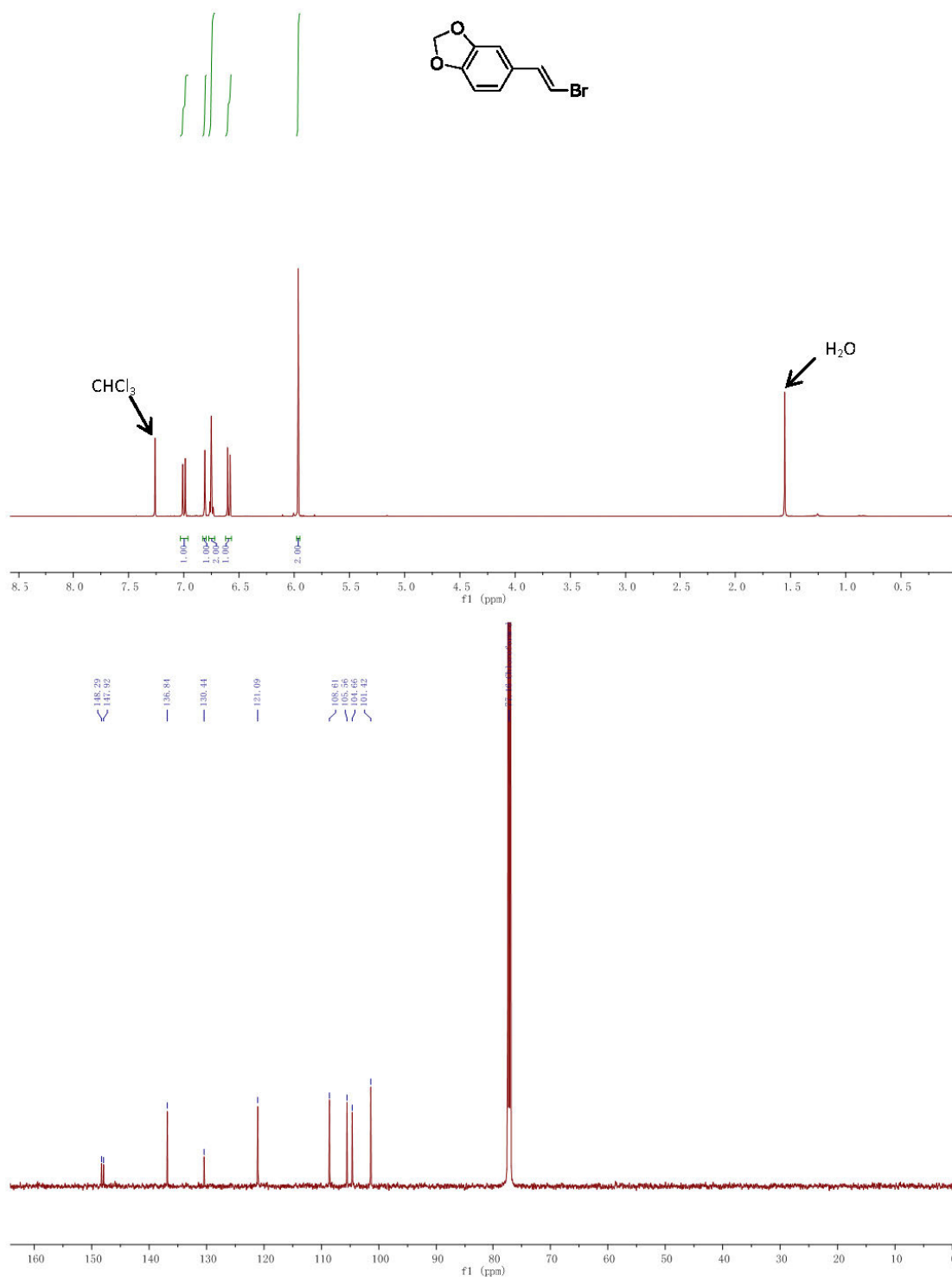
HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{10}\text{H}_{14}\text{O}_2\text{BIS}]^+$ 335.9852; Found 335.9851.

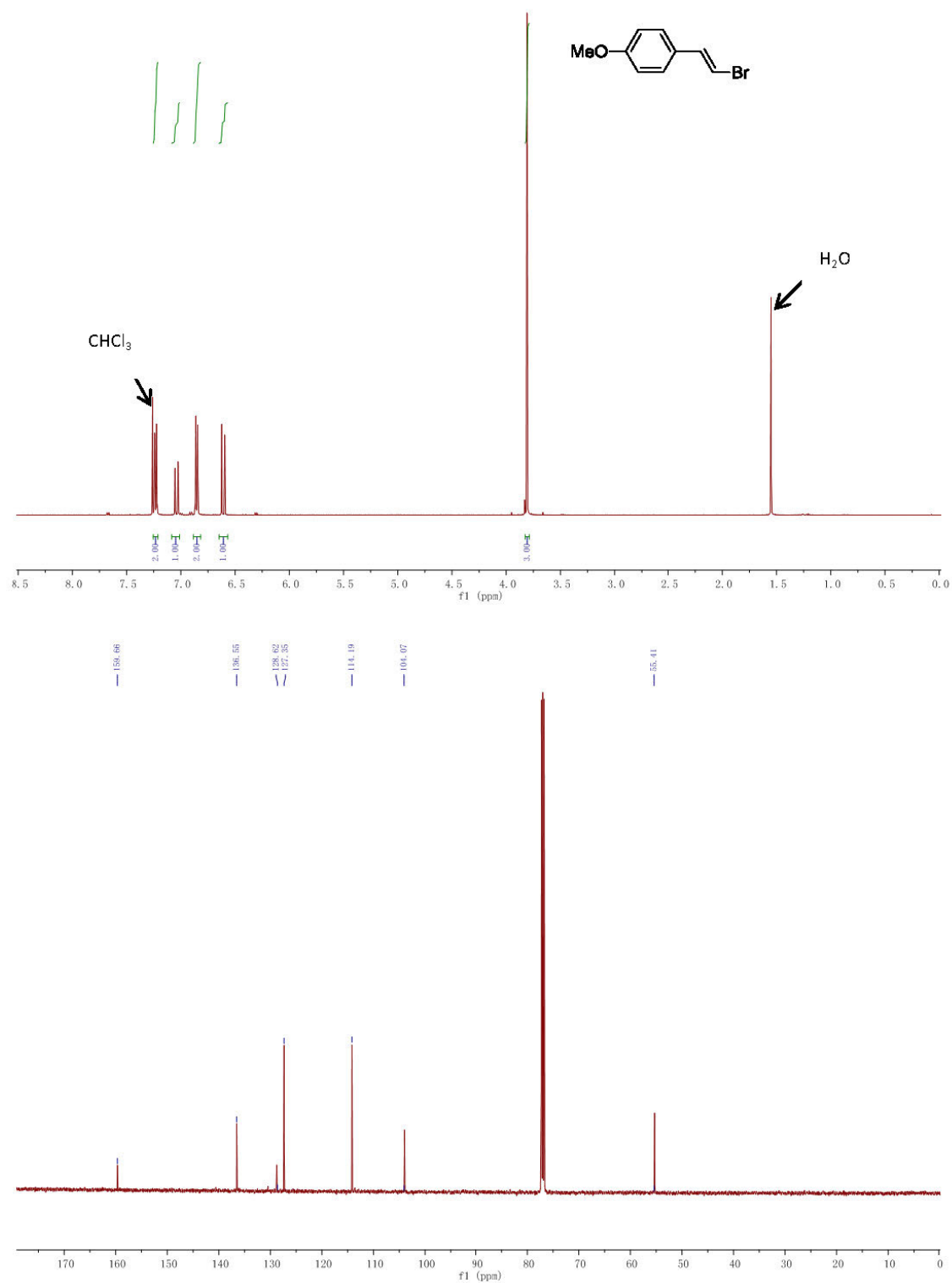
IR (ATR): $\tilde{\nu}$ = 2978 (m), 2929 (w), 1516 (s), 1414 (s), 1341 (s), 1322 (s), 1266 (m), 1136 (s), 1065 (m), 1019 (m), 849 (s), 815 (m), 798 (m), 661 (s), 430 (s) cm^{-1} .

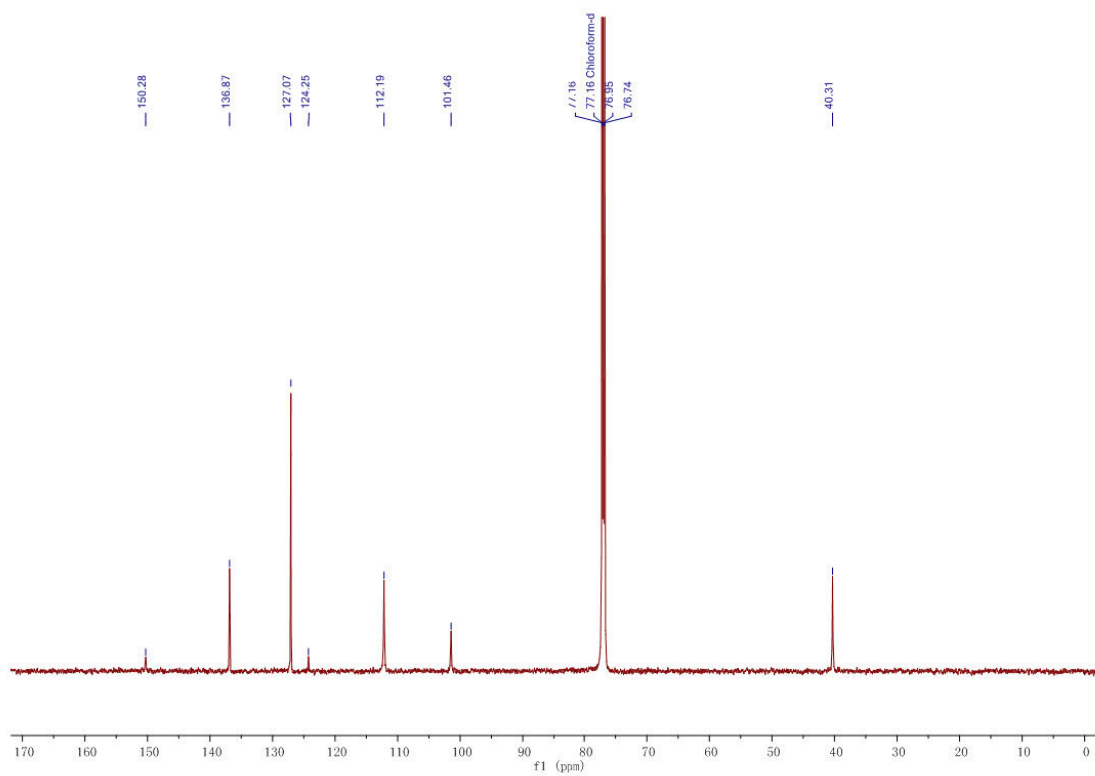
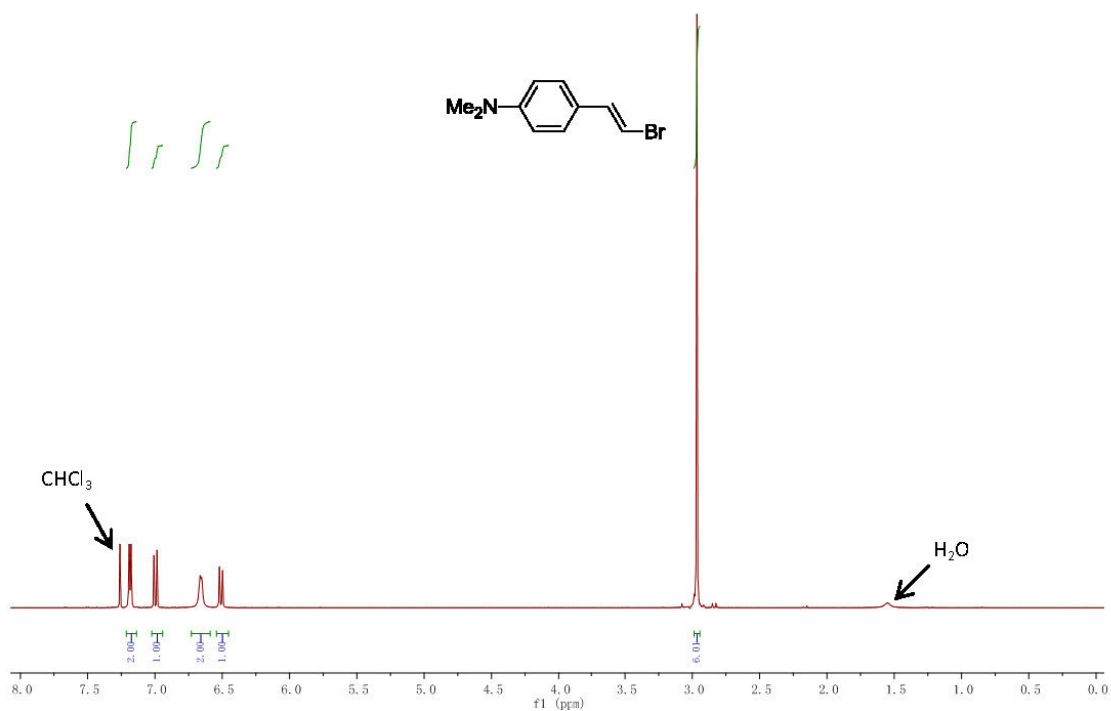
M.p.: $43\text{ }^\circ\text{C}$.

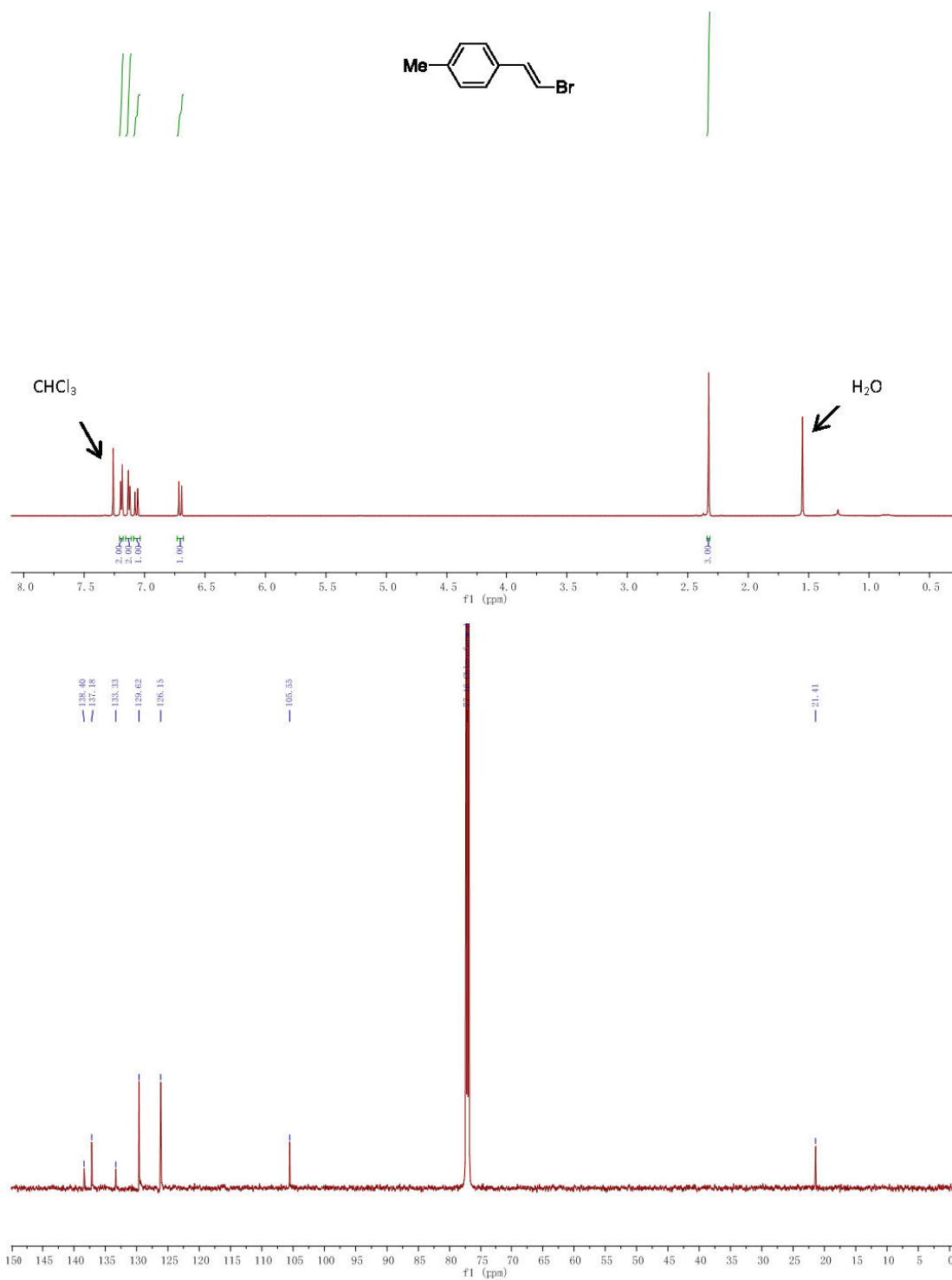
NMR Spectra (^1H NMR spectra followed by ^{13}C { ^1H } NMR spectra)
4,4,5,5-Tetramethyl-2-(5-(trimethylstannyl)thiophen-2-yl)-1,3,2-dioxaborolane (1)



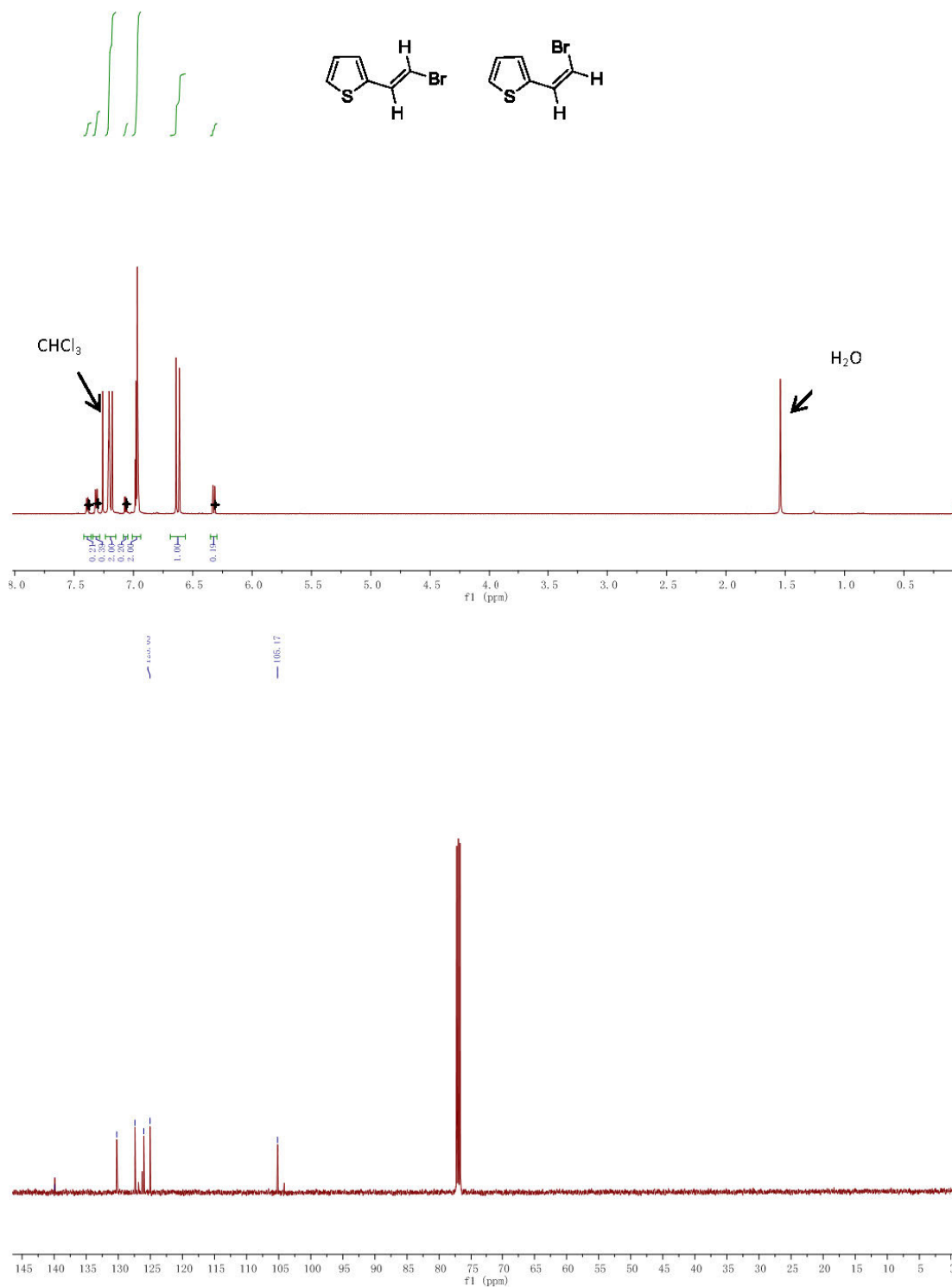
(E)-5-(2-Bromovinyl)benzo[d][1,3]dioxole (2b)

(E)-1-(2-Bromovinyl)-4-methoxybenzene (2c)

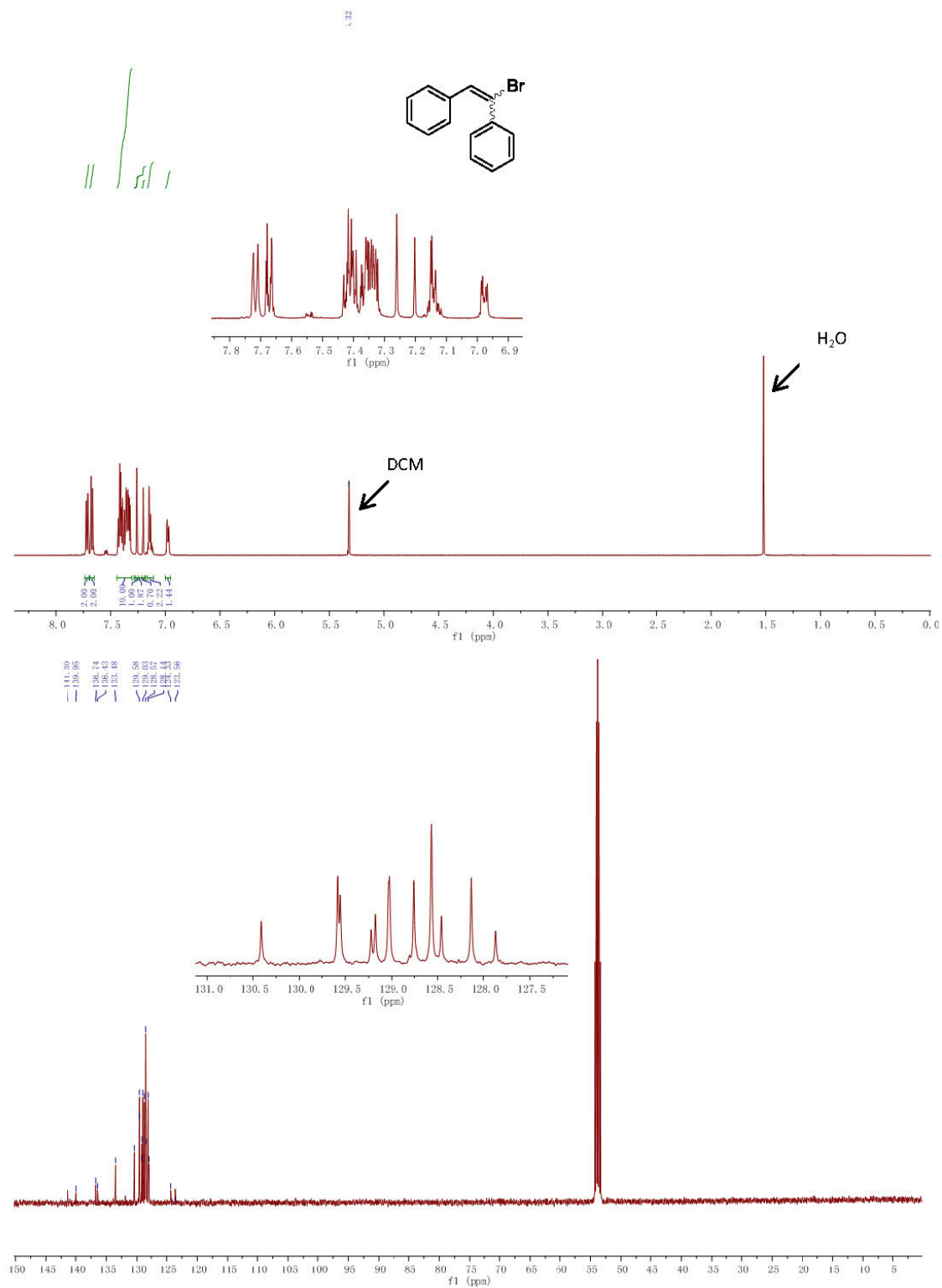
(E)-4-(2-Bromovinyl)-N,N-dimethylaniline (2d)

(E)-1-(2-Bromovinyl)-4-methylbenzene (2e)

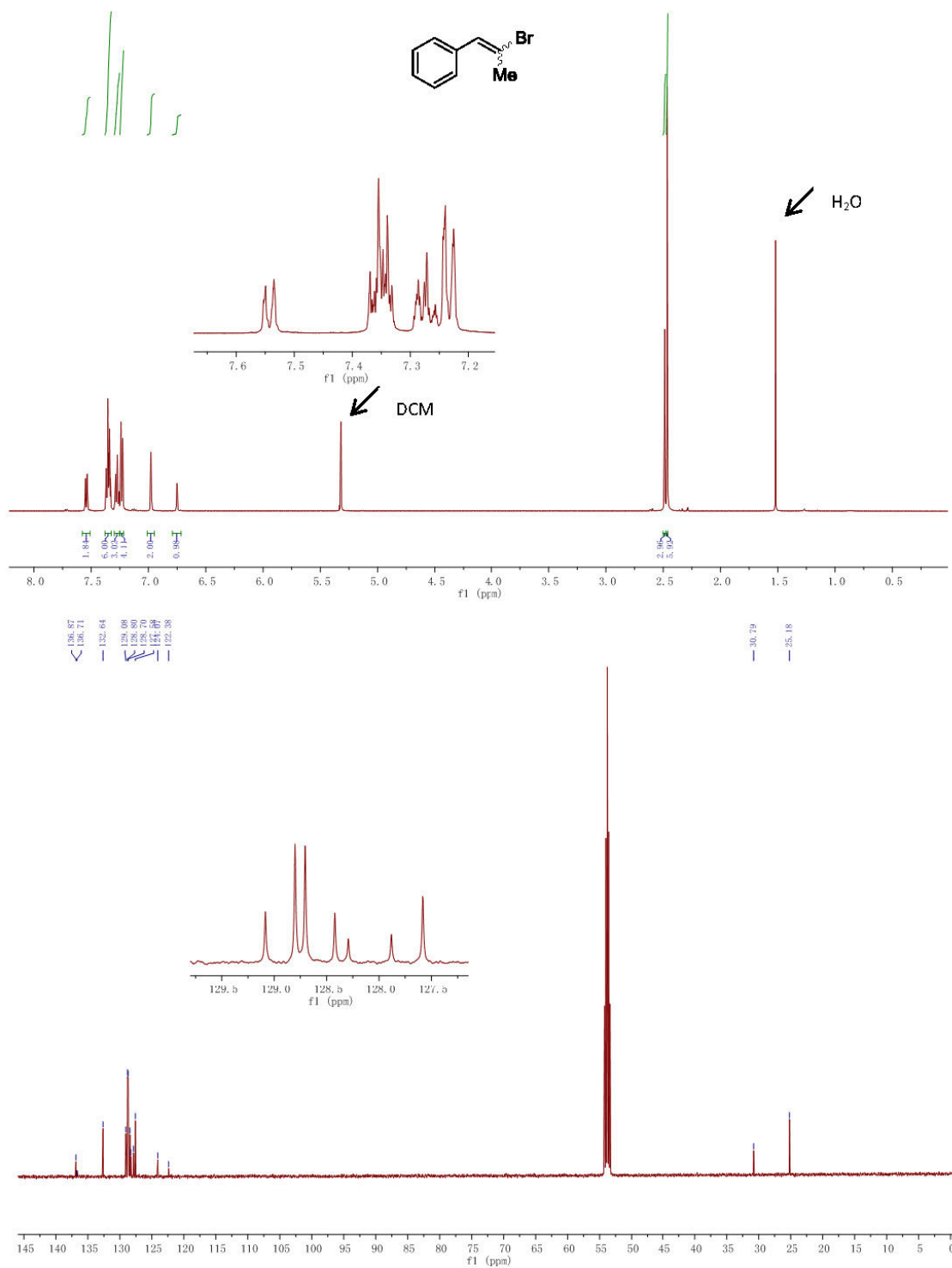
2-(2-Bromovinyl)thiophene, (Z)-2-(2-bromovinyl)thiophene (*) (2f)

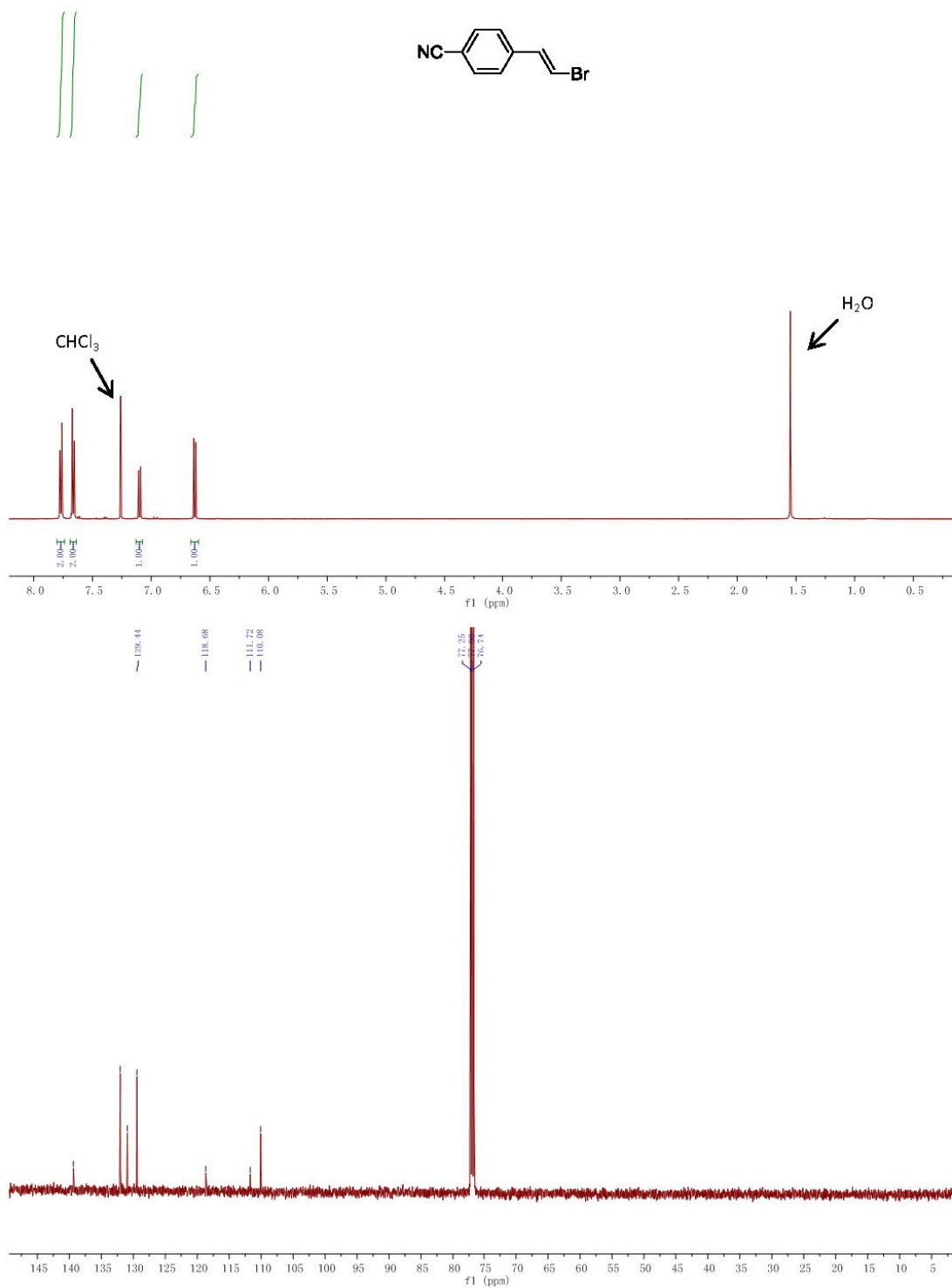


(1-Bromoethene-1,2-diyl)dibenzene (2g)

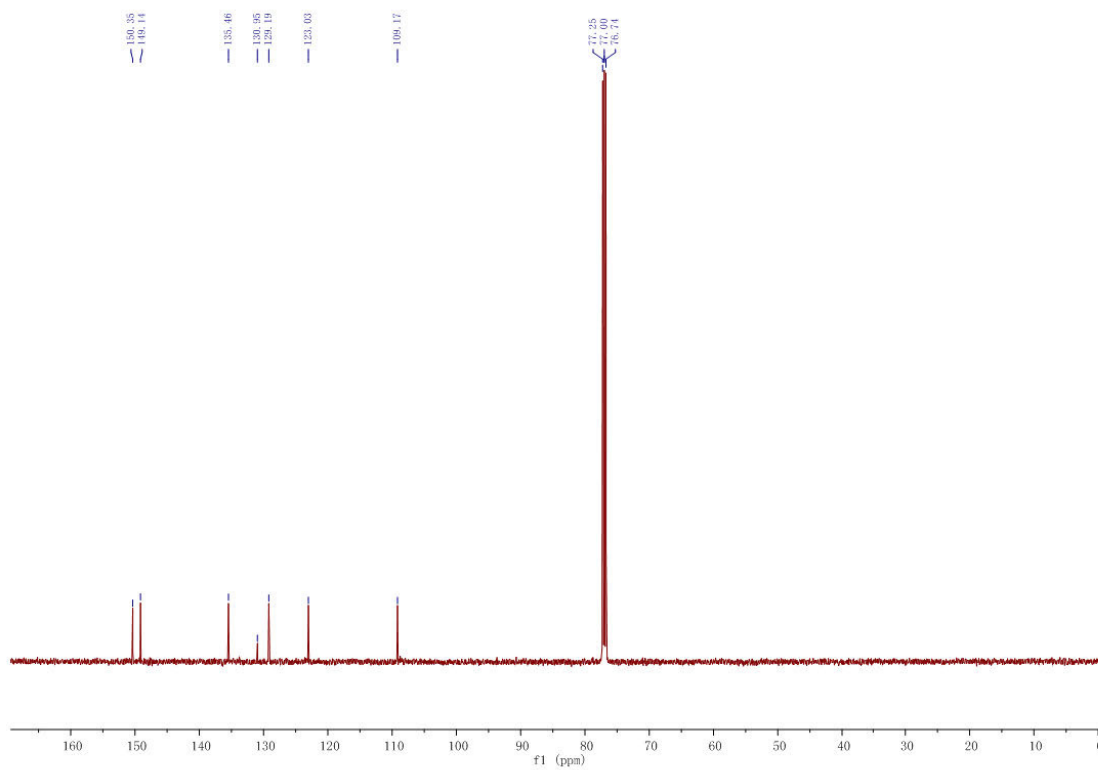
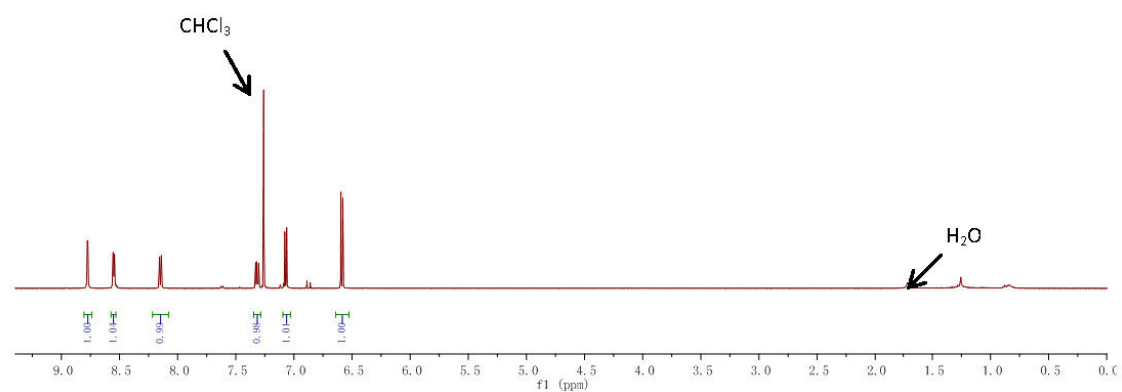
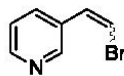
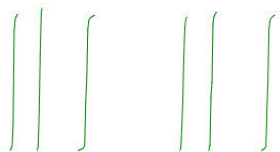


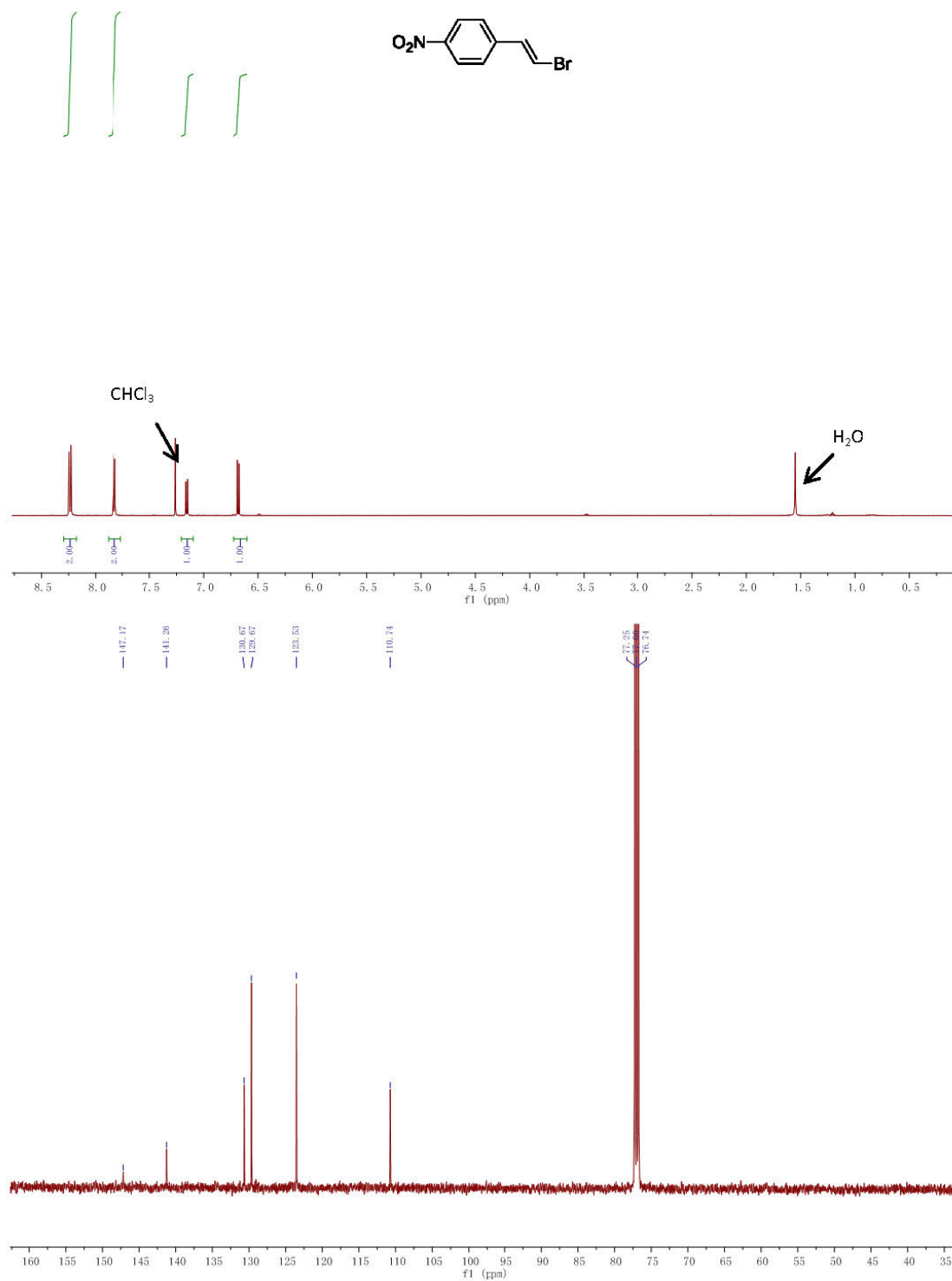
(2-Bromoprop-1-en-1-yl)benzene (2h)

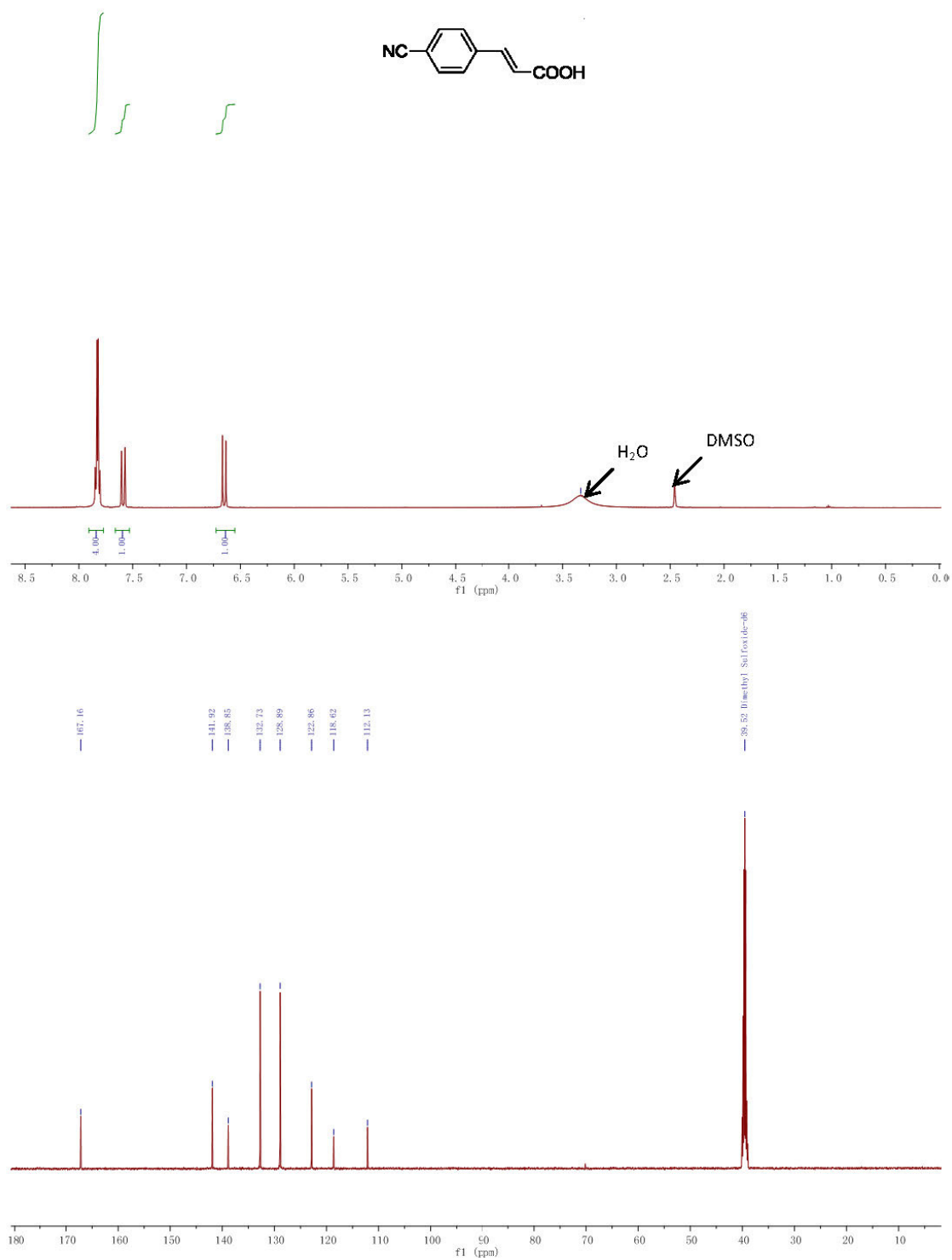


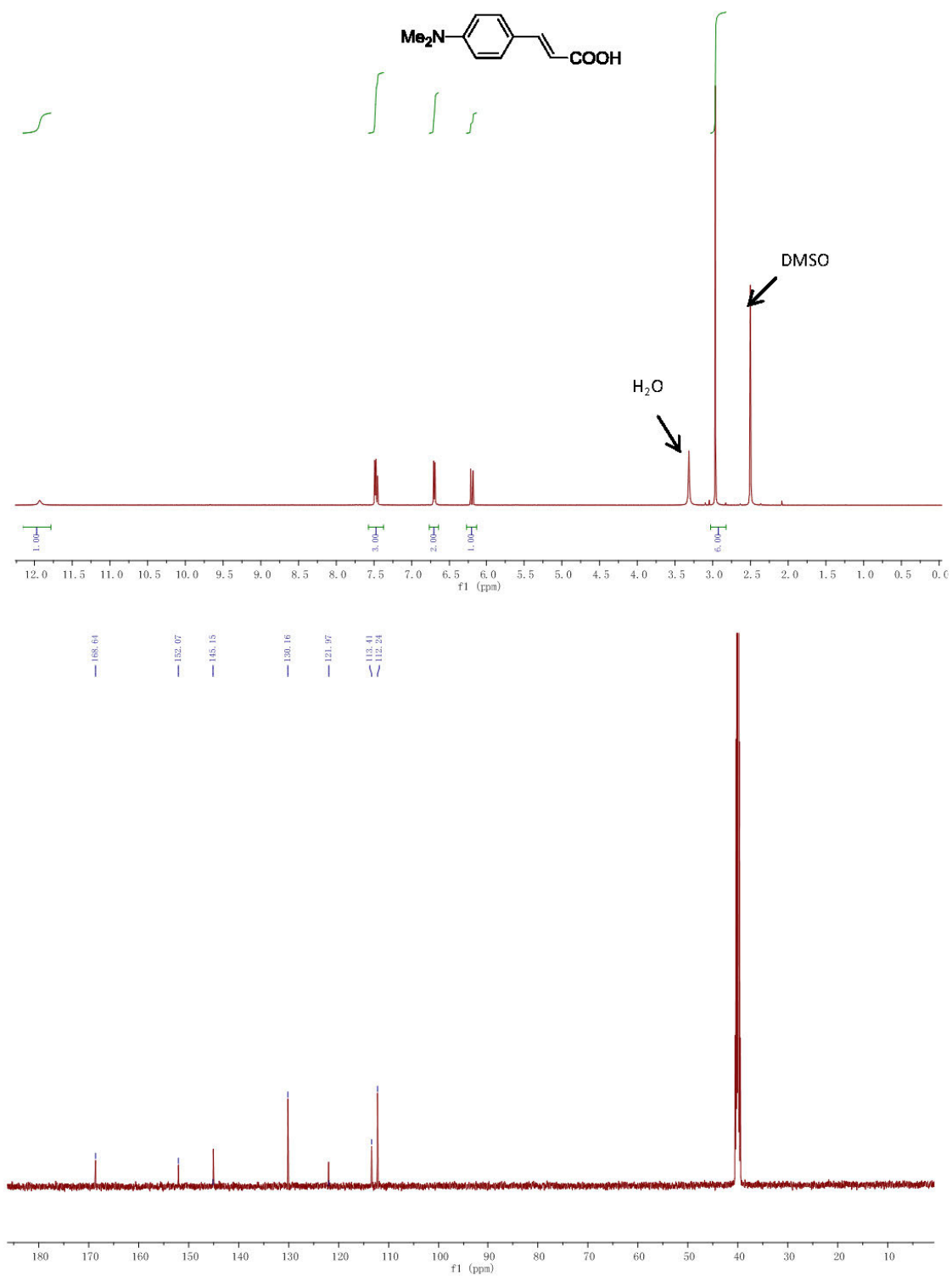
(E)-4-(2-Bromovinyl)benzonitrile (2i)

3-(2-Bromovinyl)pyridine (2j)

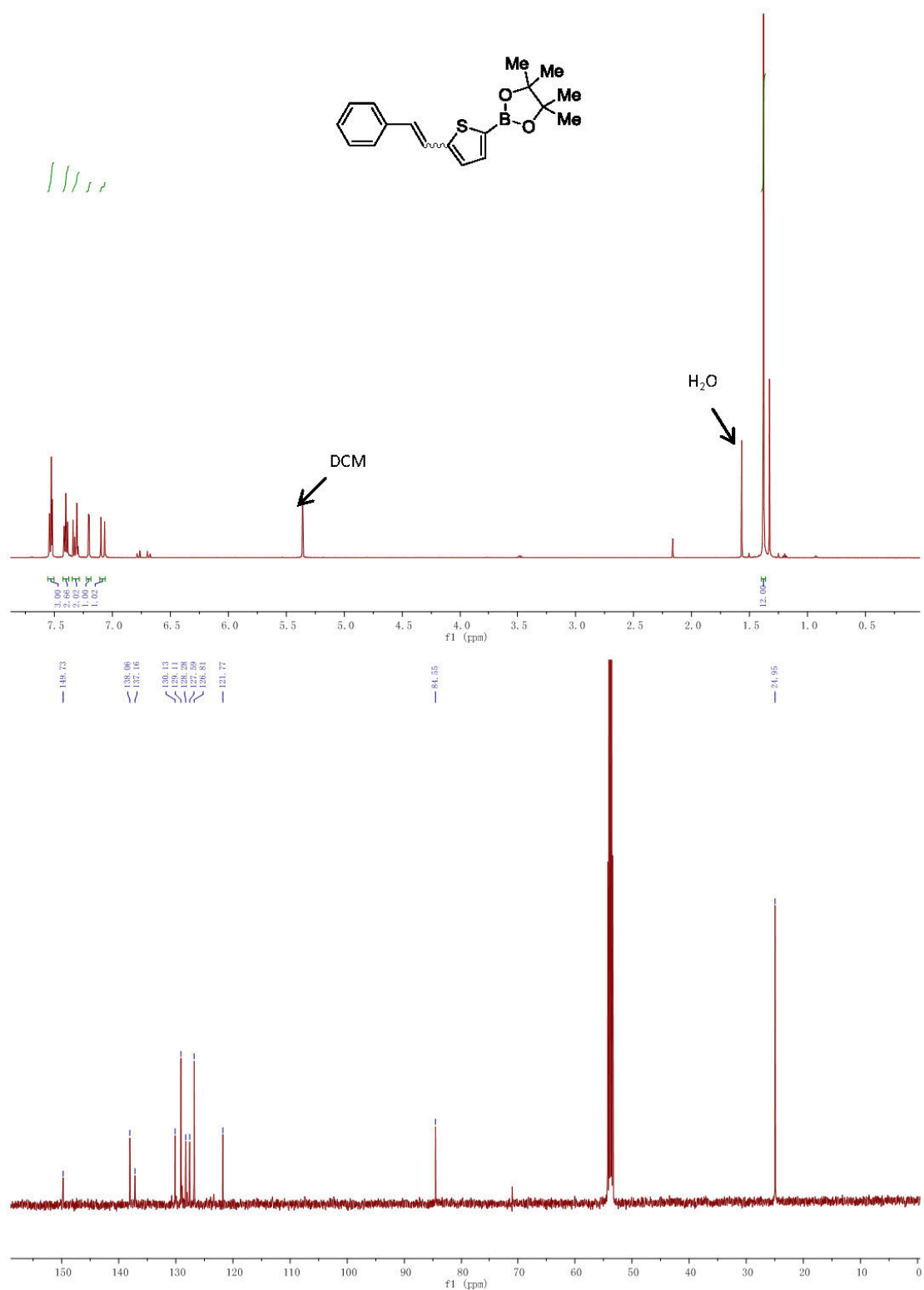


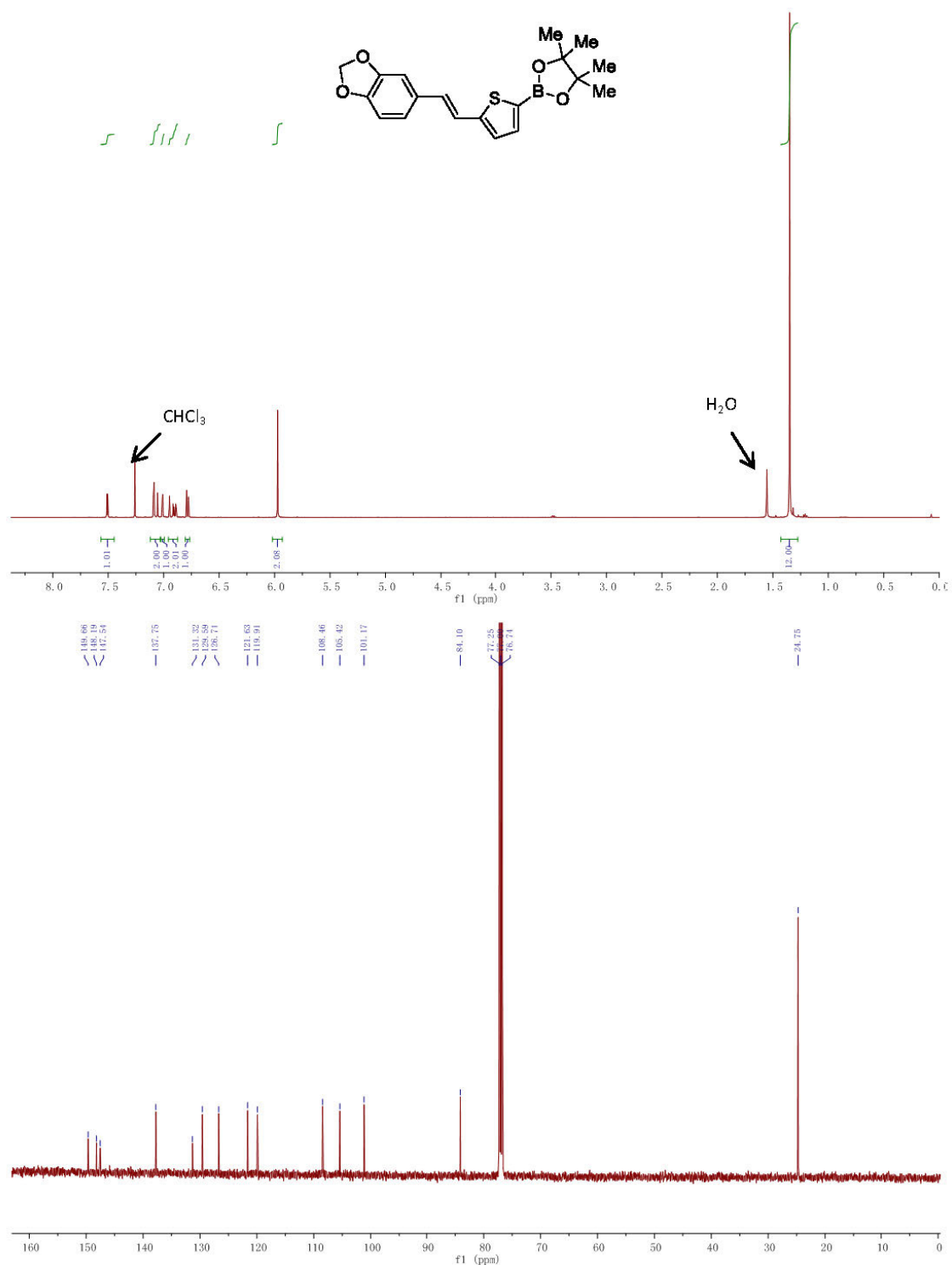
(E)-1-(2-Bromovinyl)-4-nitrobenzene (2k)

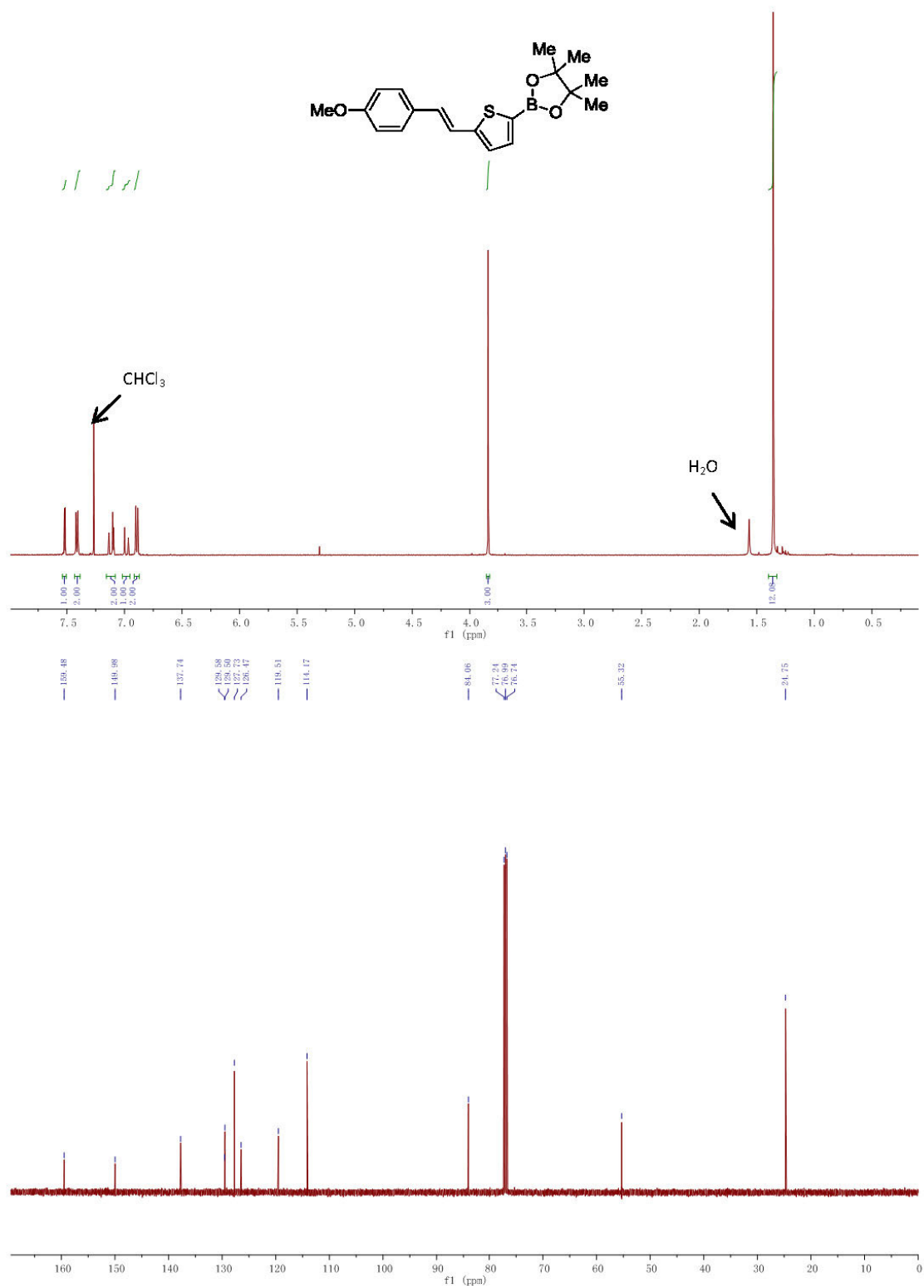
(E)-3-(4-Cyanophenyl)acrylic acid (2l)

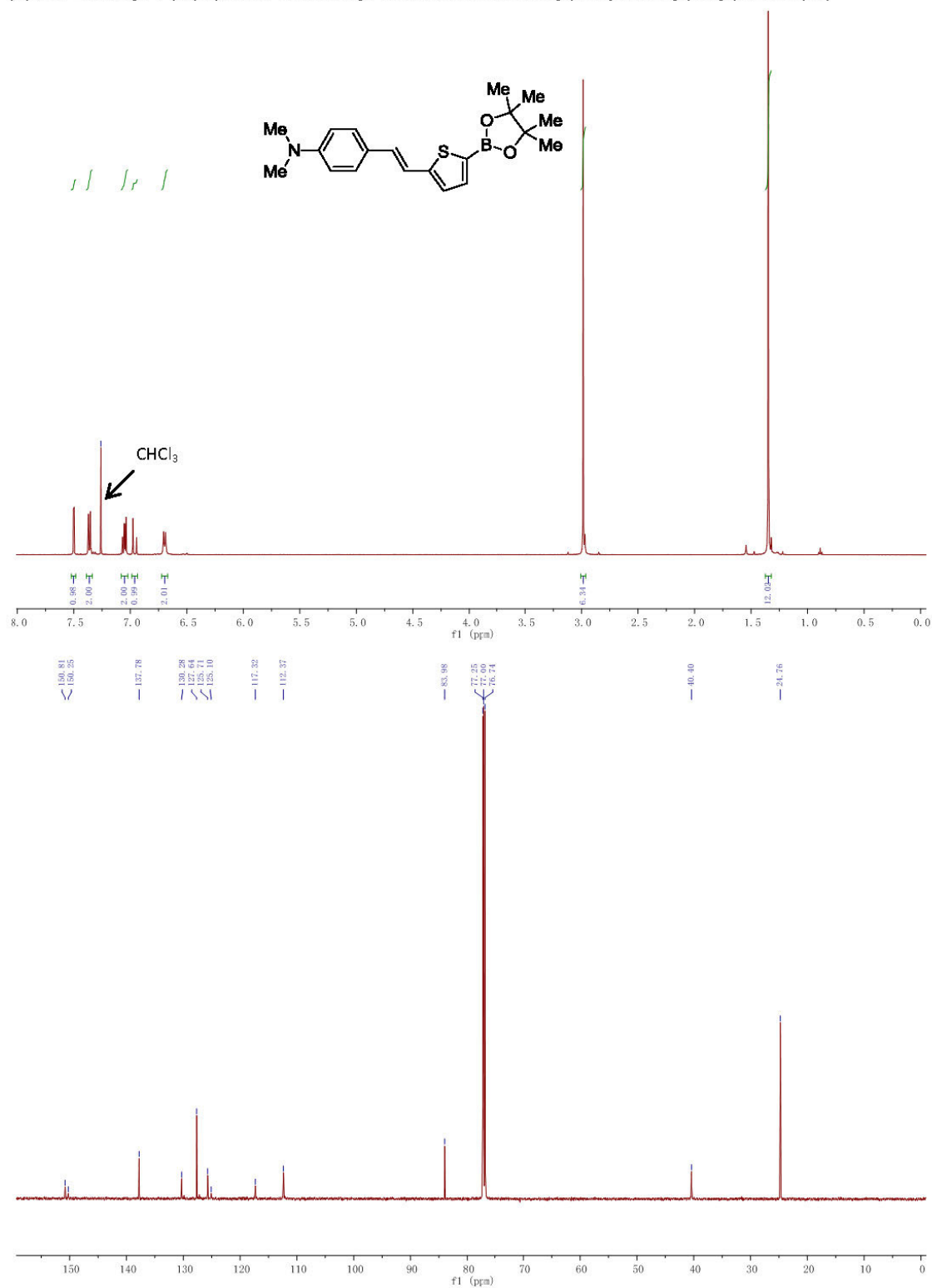
(E)-3-(4-(Dimethylamino)phenyl)acrylic acid (2m)

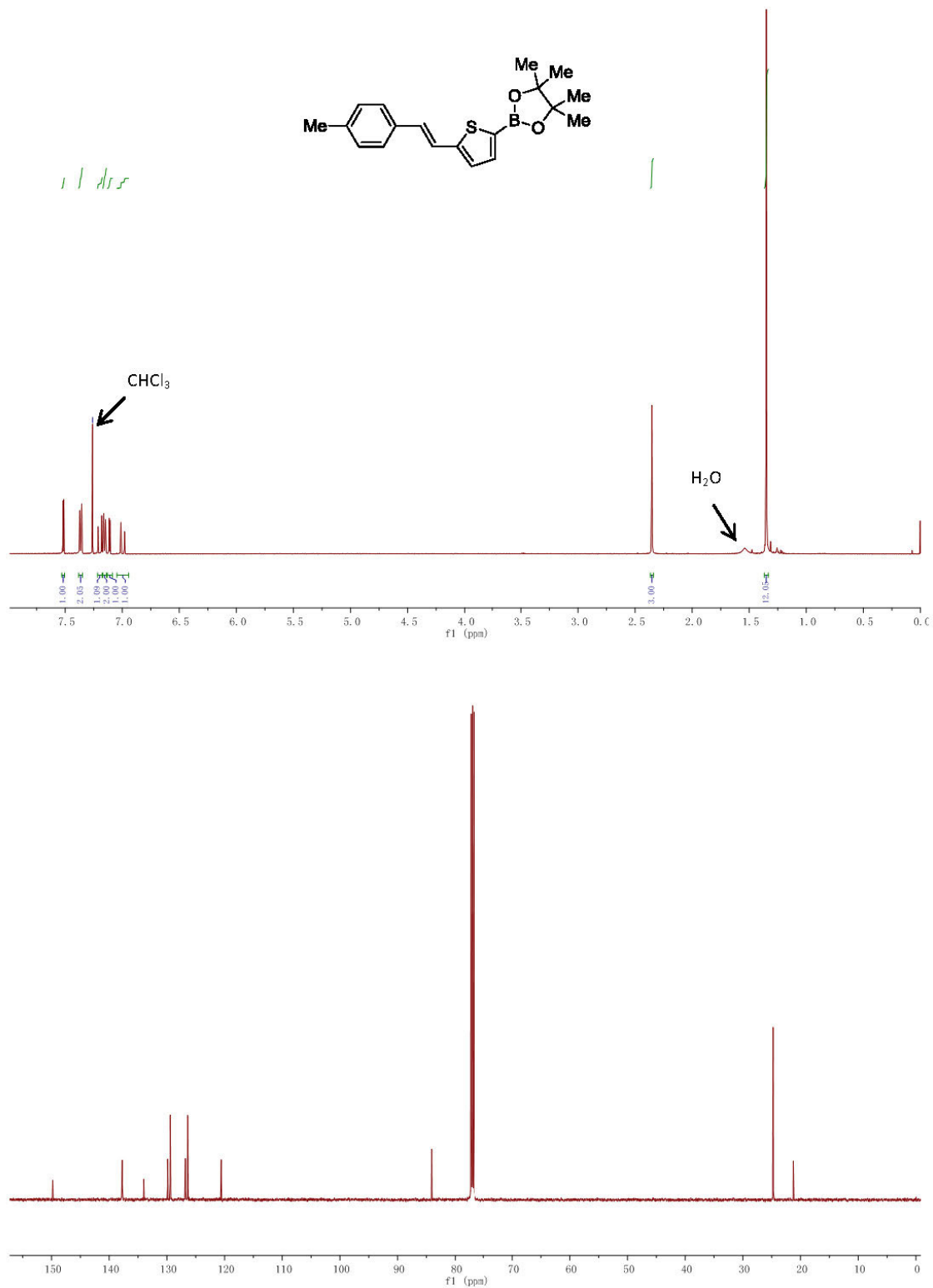
4,4,5,5-Tetramethyl-2-(5-styrylthiophen-2-yl)-1,3,2-dioxaborolane (3a)



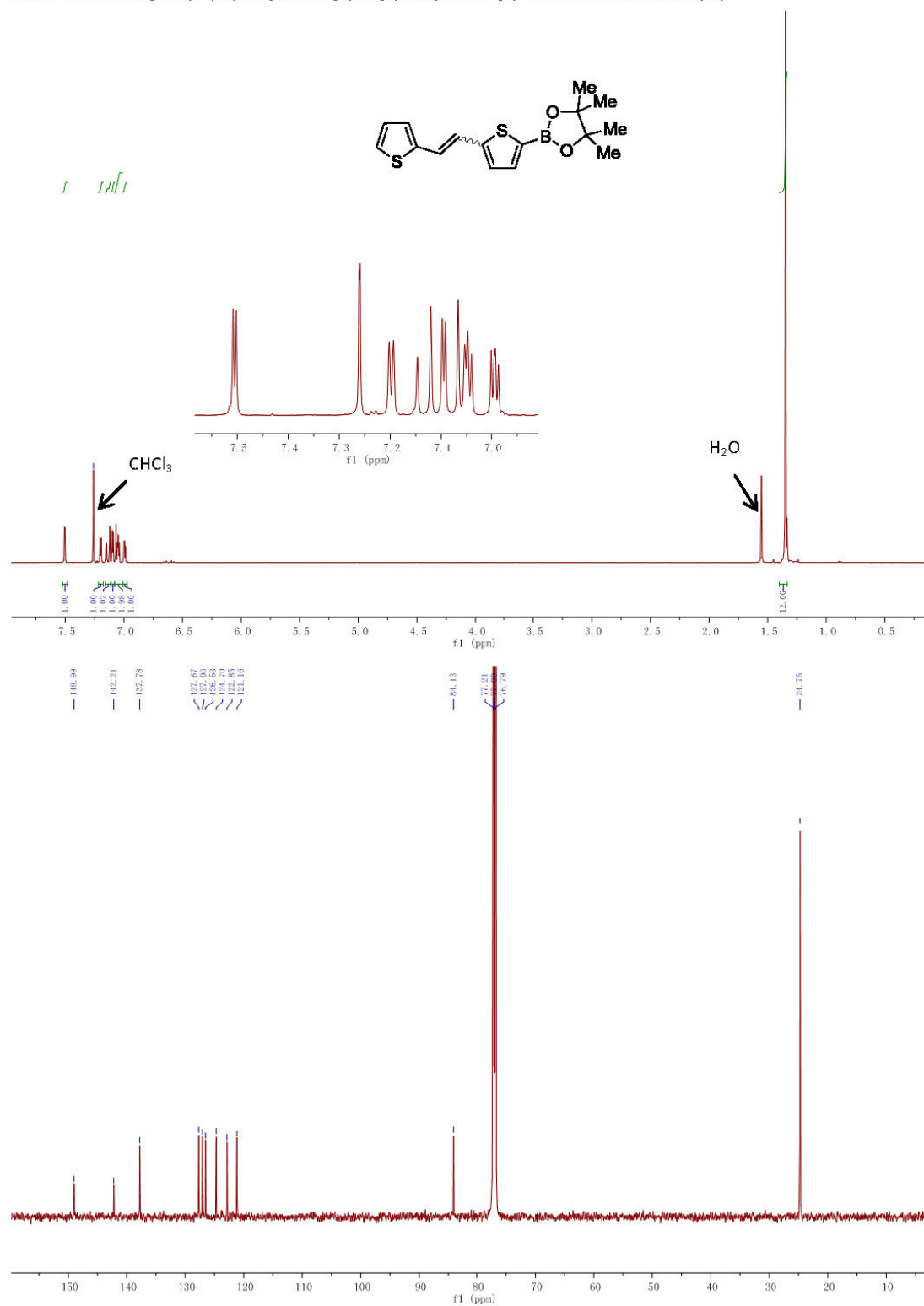
(E)-2-(5-(2-(Benzo[d][1,3]dioxol-5-yl)vinyl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

(E)-2-(5-(4-Methoxystyryl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)

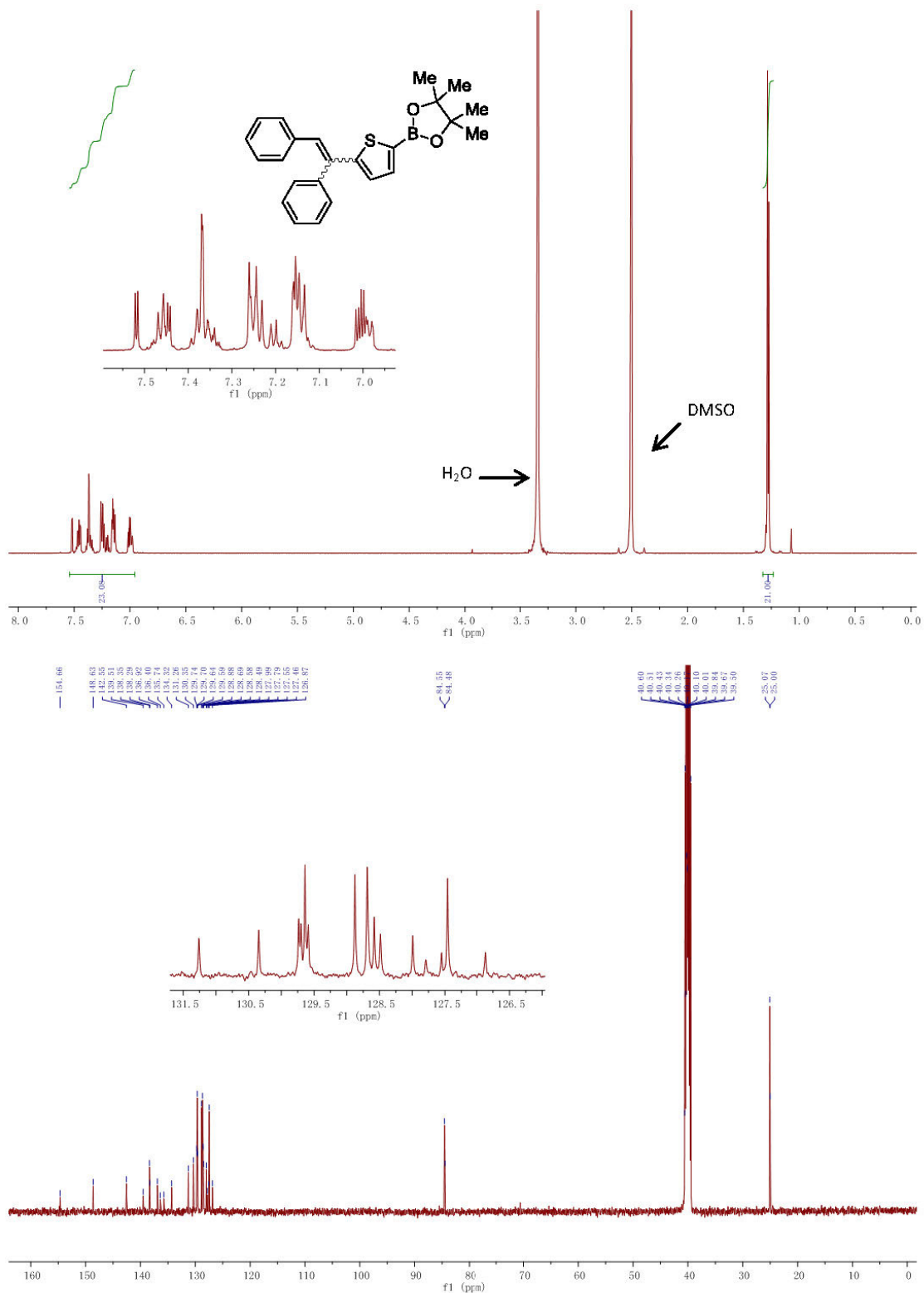
(E)-N,N-Dimethyl-4-(2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)vinyl)aniline (3d)

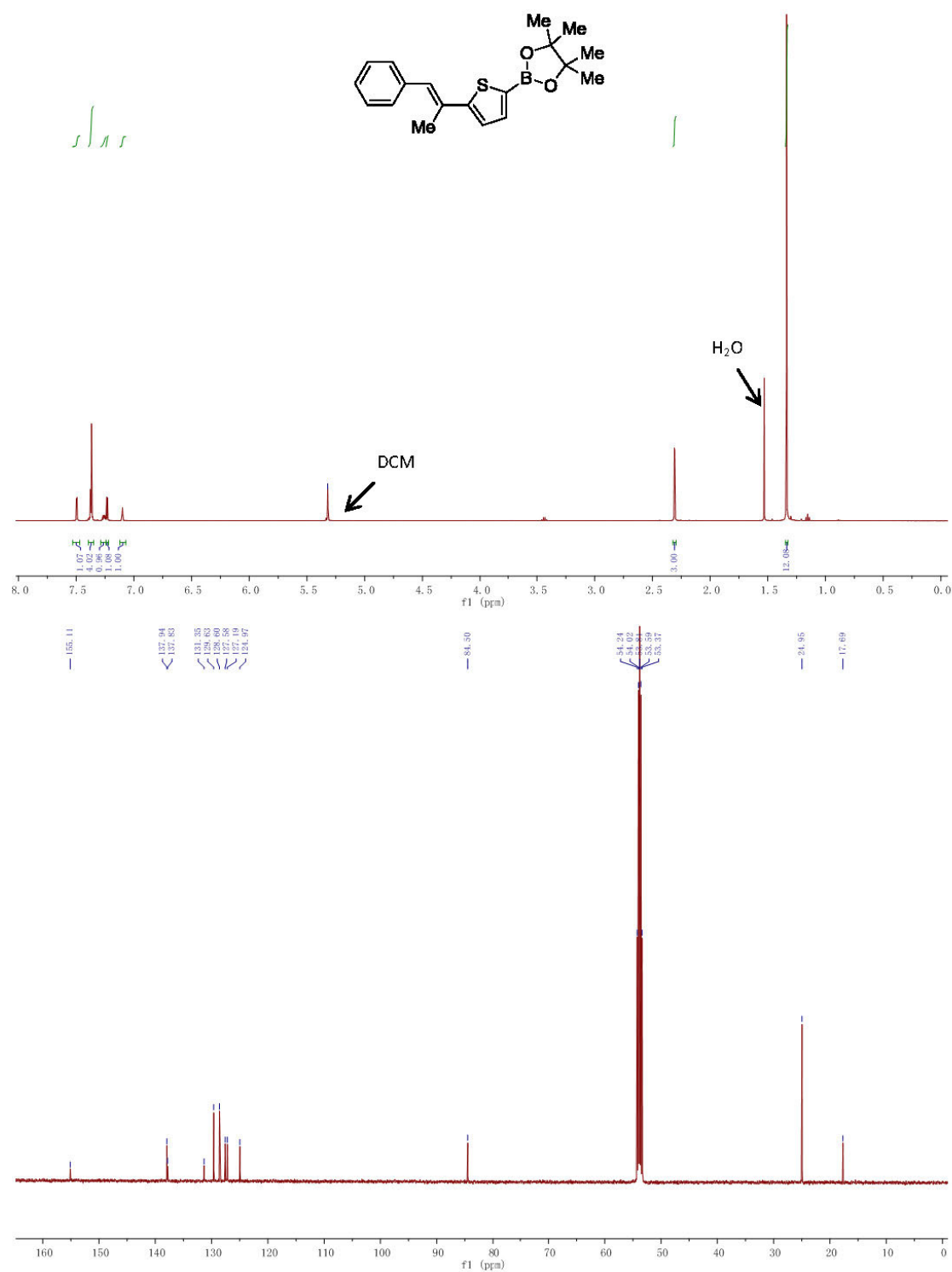
(E)-4,4,5,5-Tetramethyl-2-(5-(4-methylstyryl)thiophen-2-yl)-1,3,2-dioxaborolane (3e)

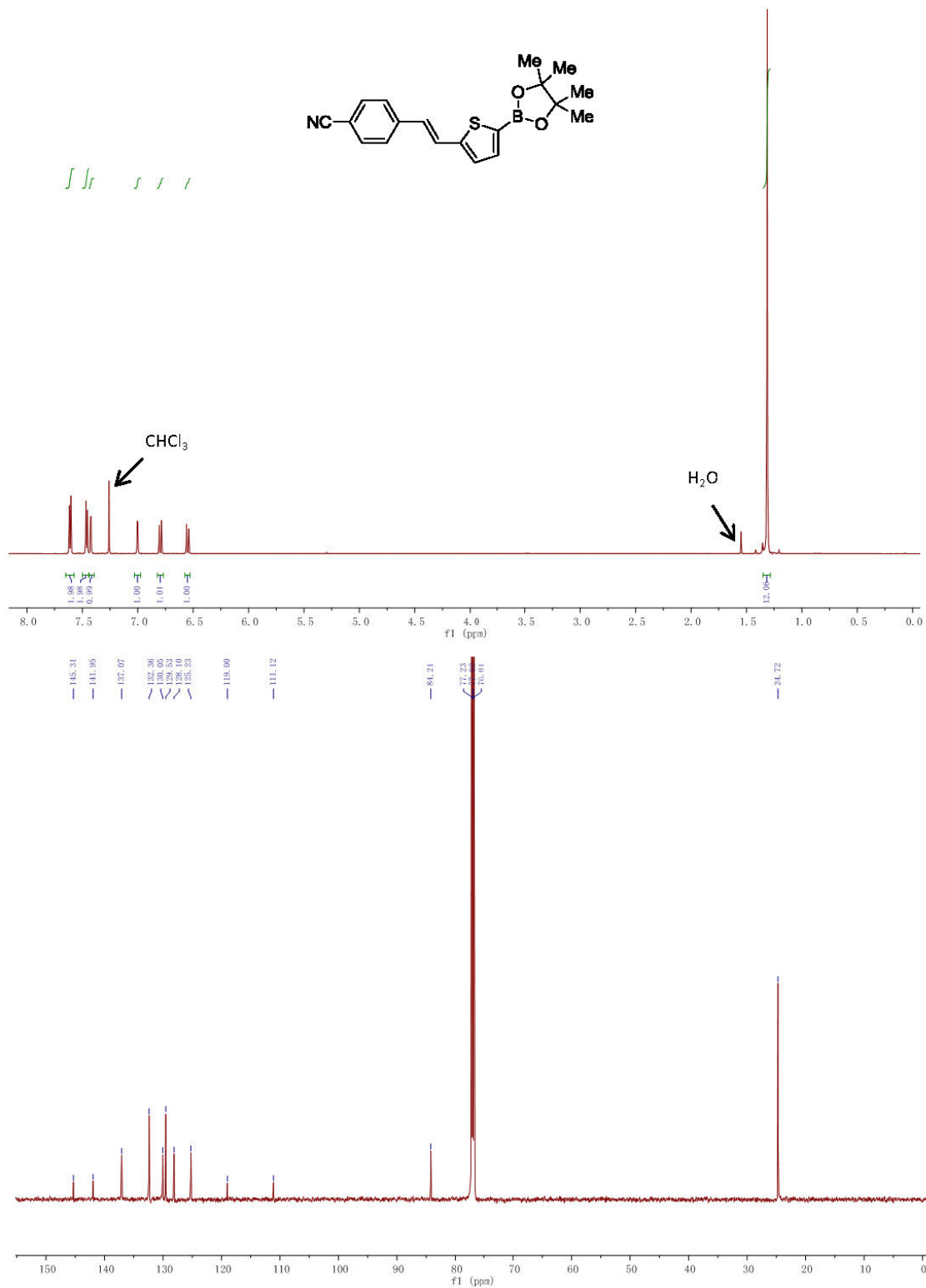
4,4,5,5-Tetramethyl-2-(5-(2-(thiophen-2-yl)vinyl)thiophen-2-yl)-1,3,2-dioxaborolane (3f)



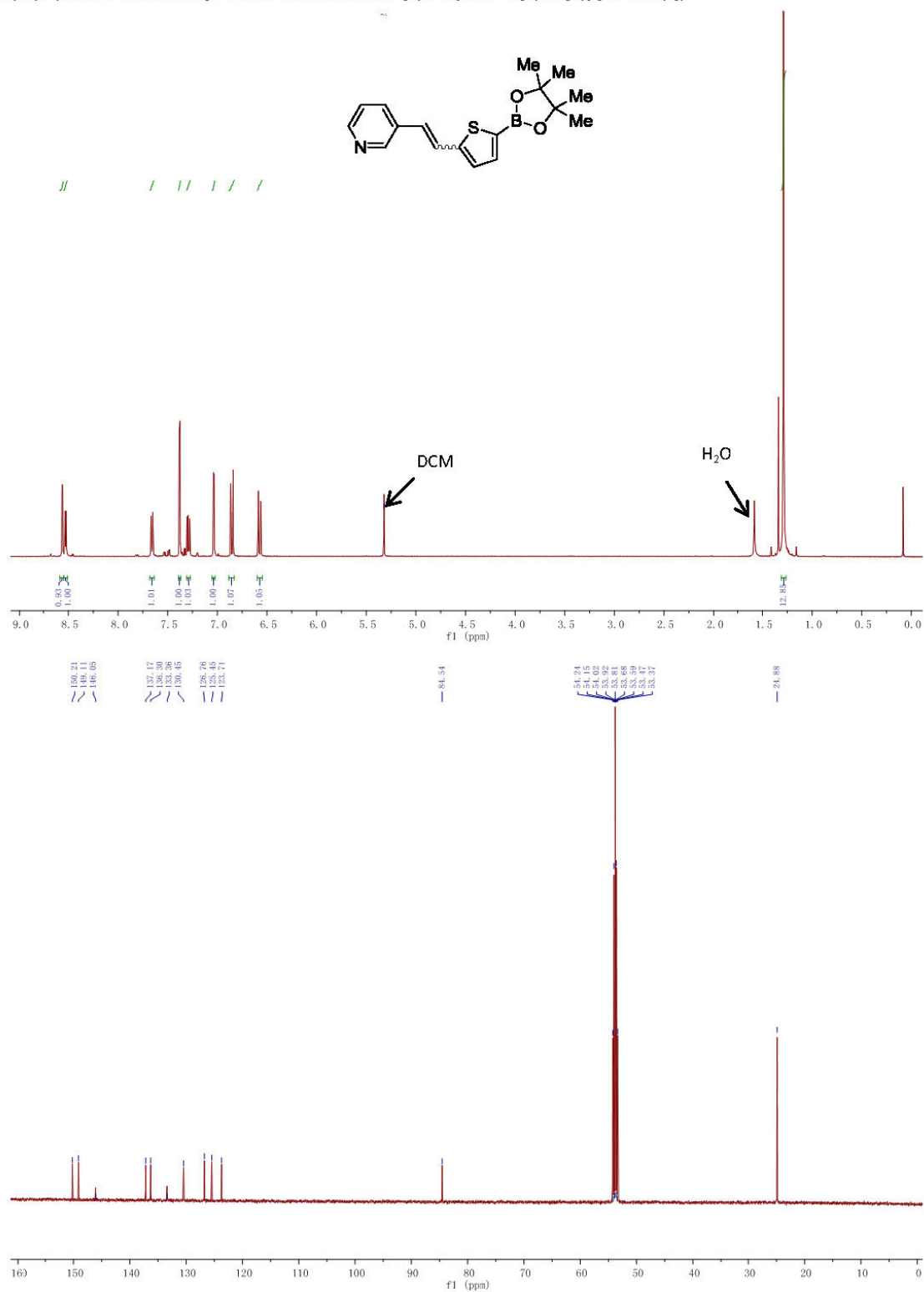
2-(5-(1,2-Diphenylvinyl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

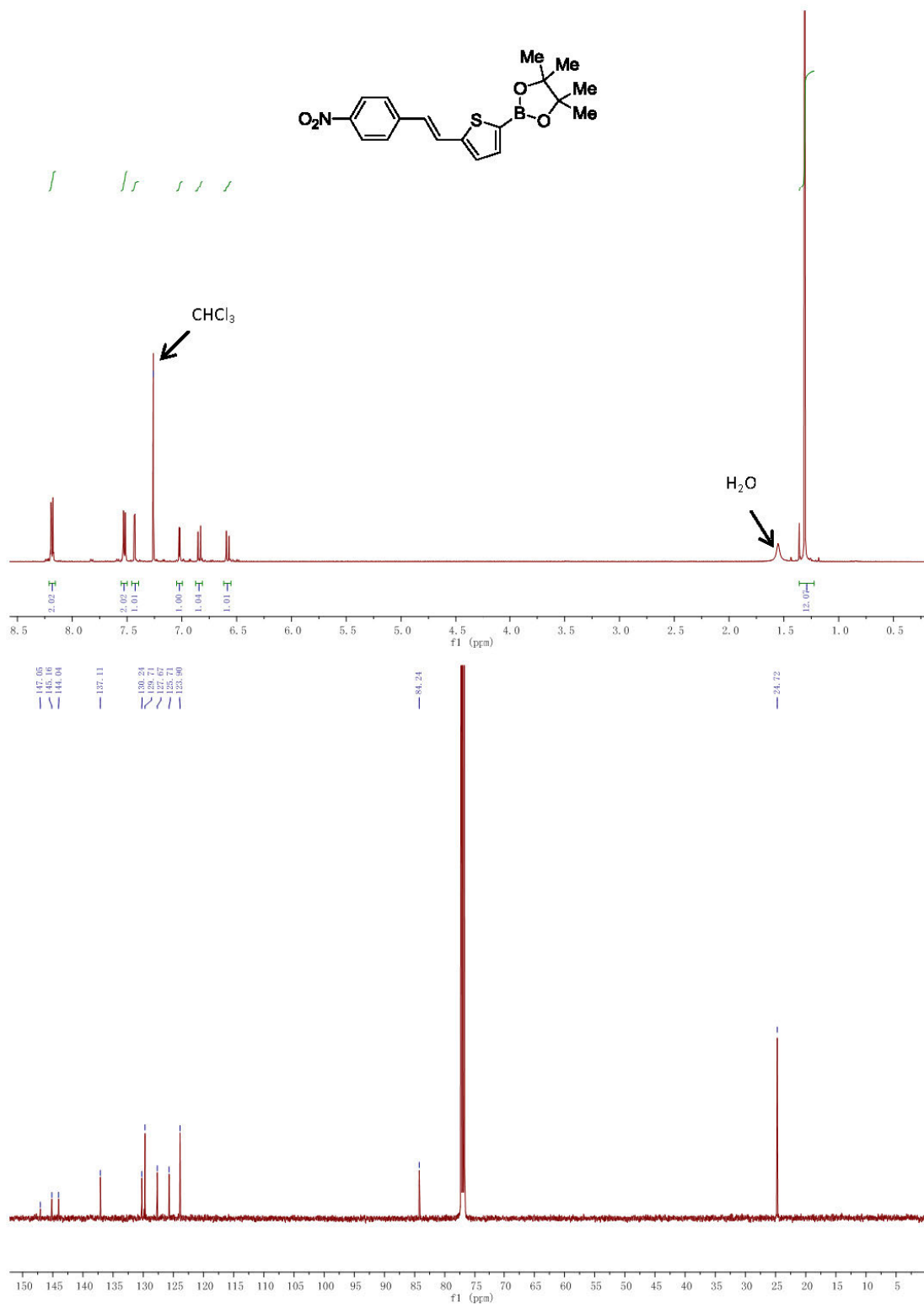


(E)-4,4,5,5-Tetramethyl-2-(5-(1-phenylprop-1-en-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane (3h)

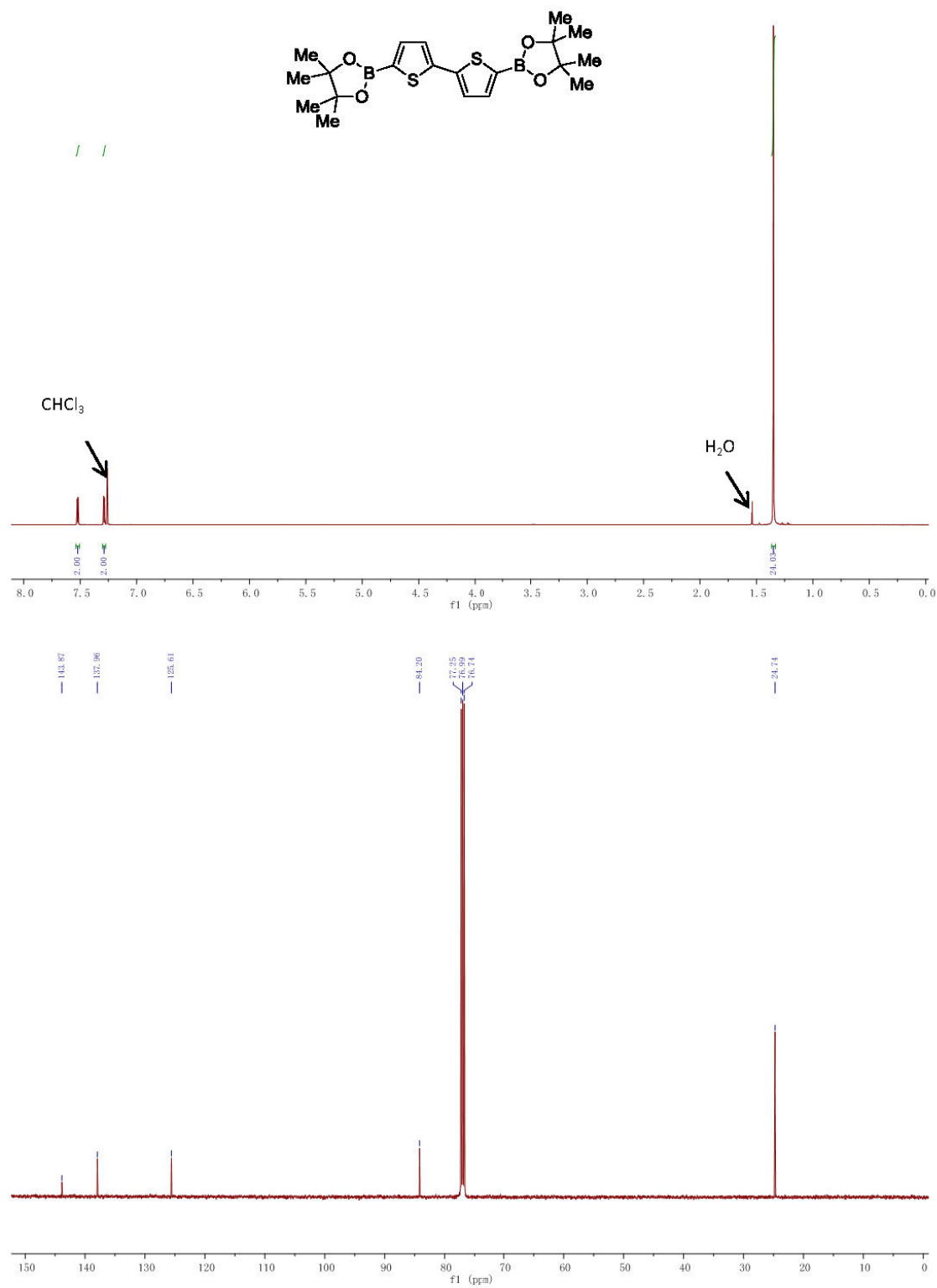
(E)-4-(2-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)vinyl)-benzonitrile (3i)

3-(2-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)vinyl)pyridine (3j)

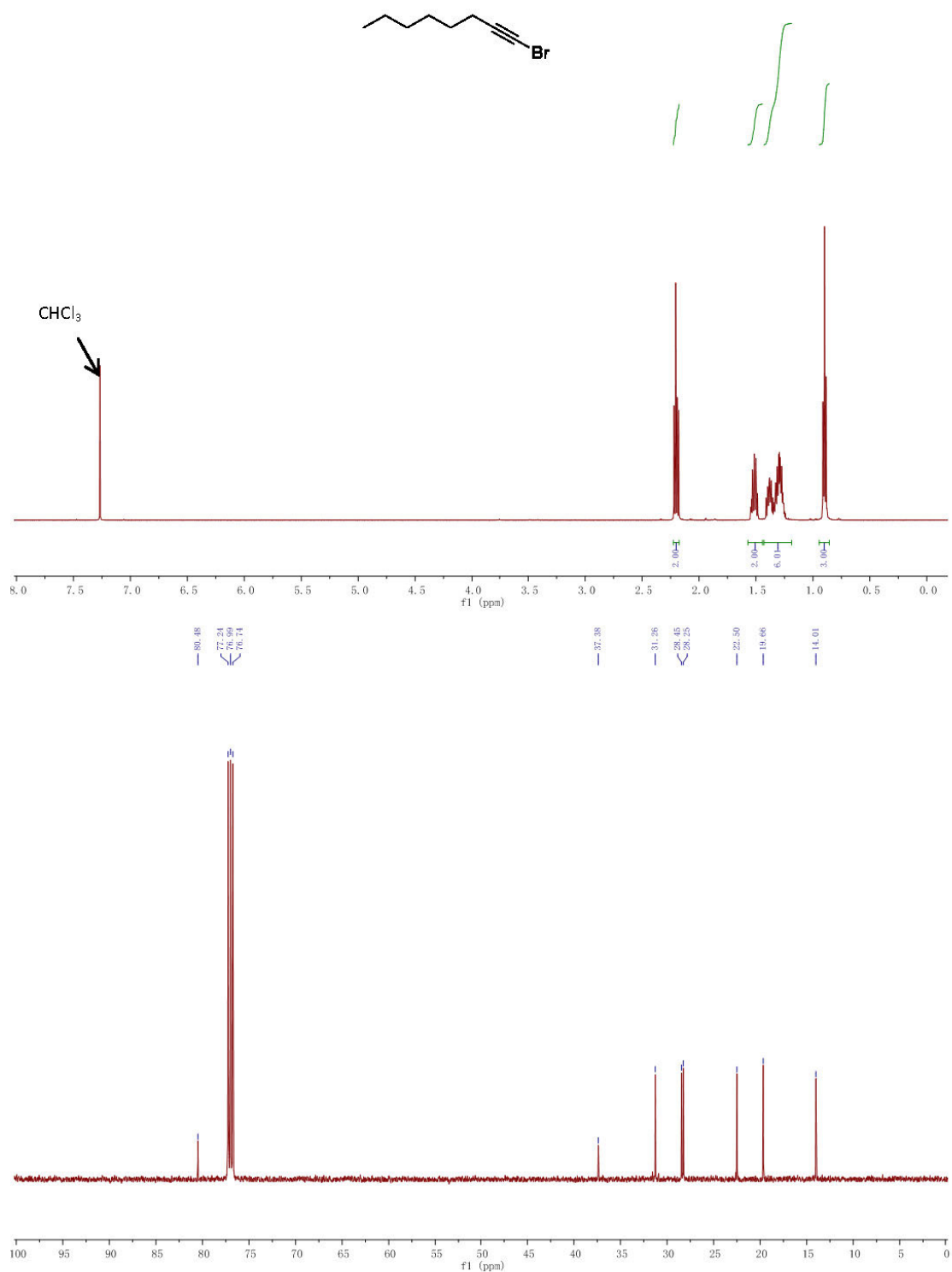


(E)-4,4,5,5-Tetramethyl-2-(5-(4-nitrostyryl)thiophen-2-yl)-1,3,2-dioxaborolane (3k)

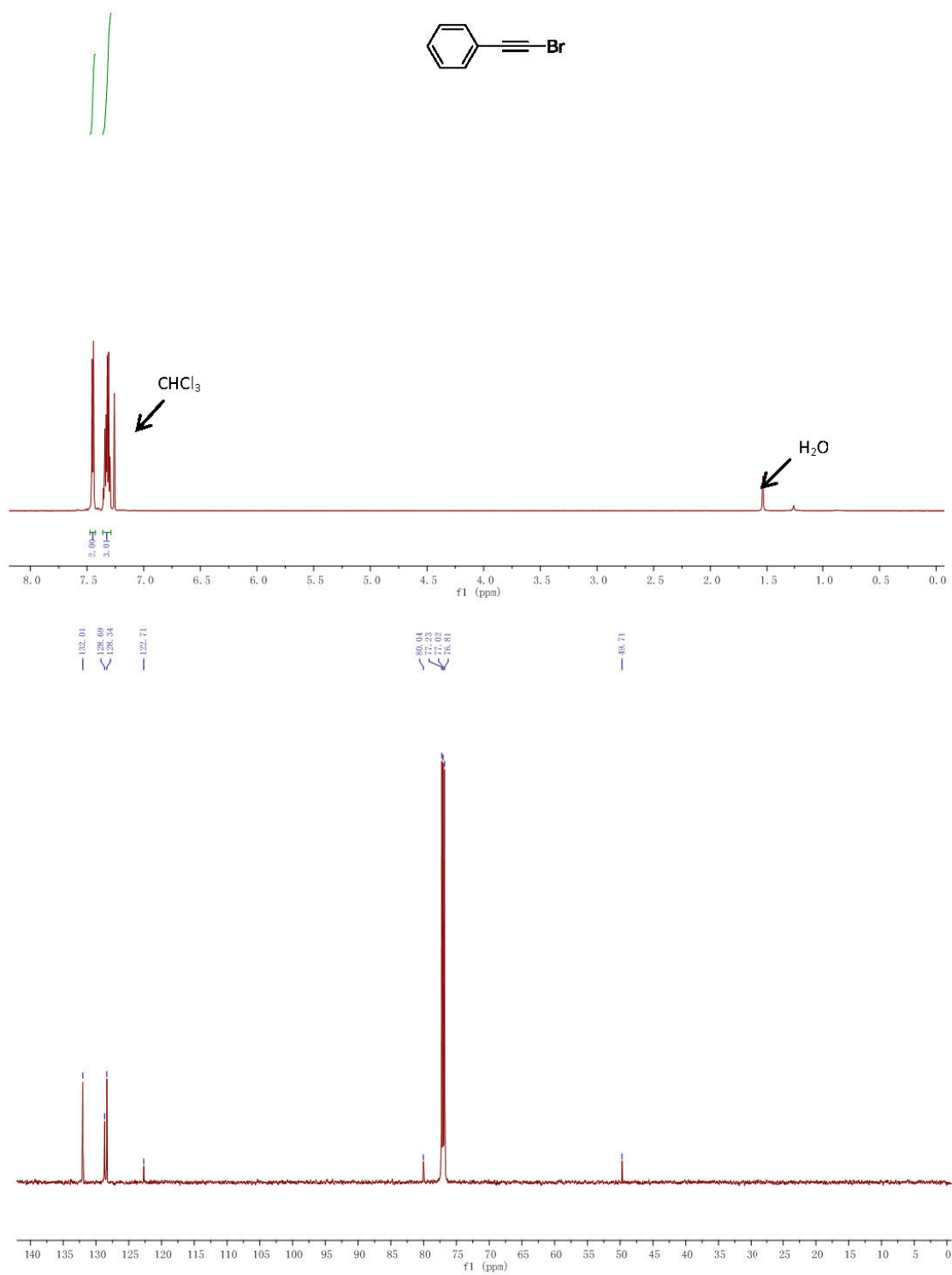
5,5'-bis(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene (4)



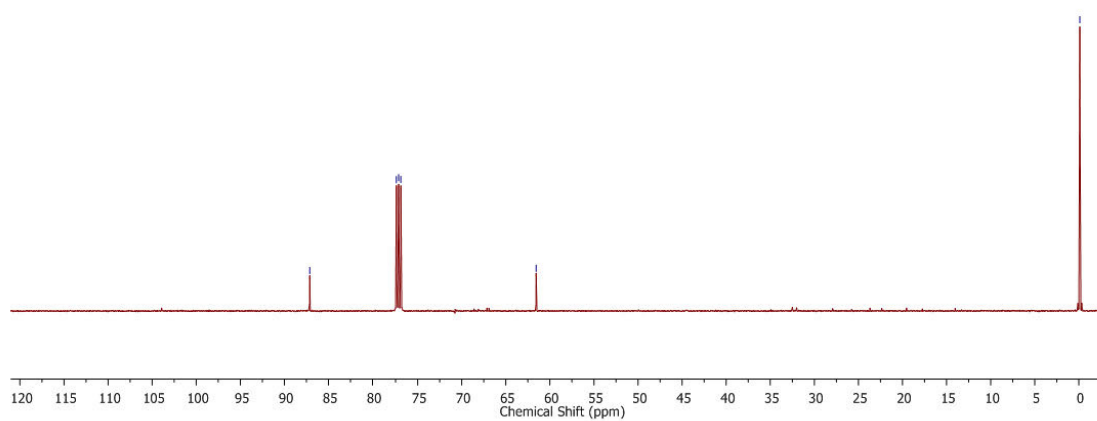
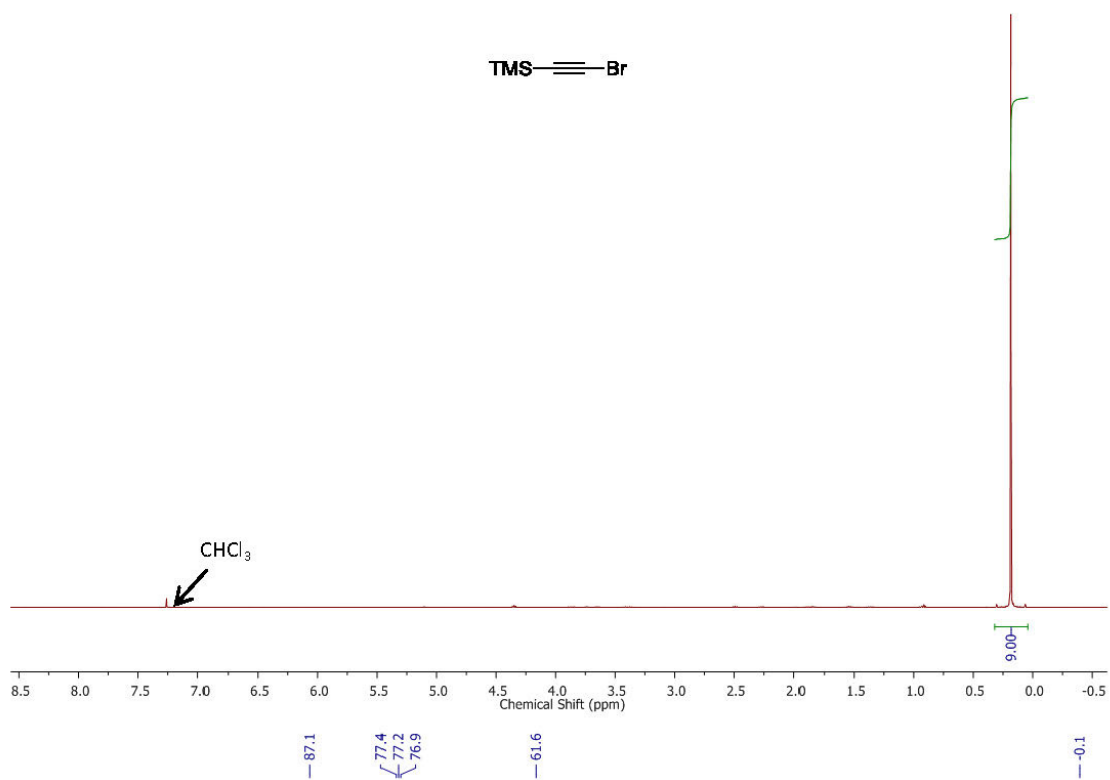
1-Bromo-1-octyne (6a)



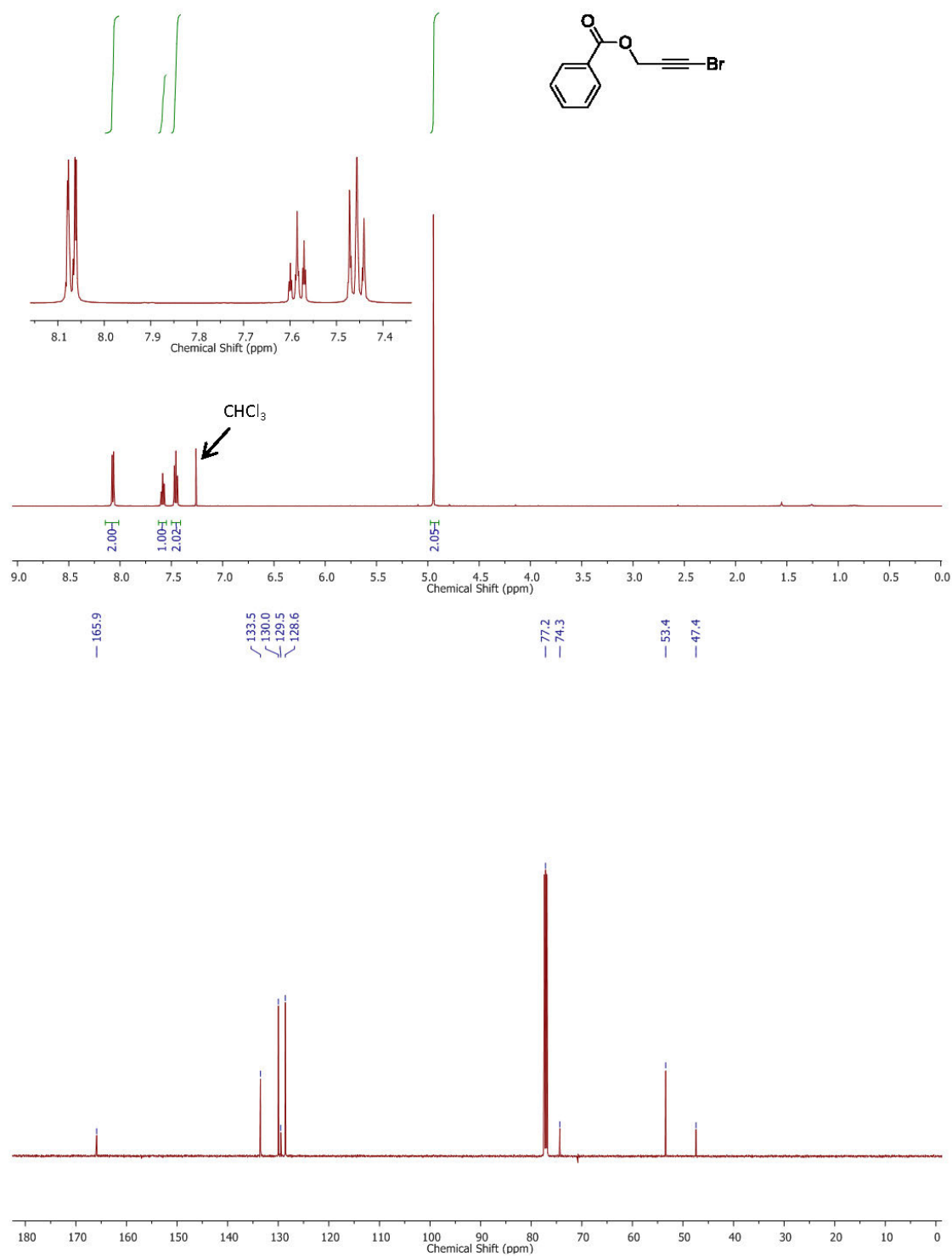
(Bromoethynyl)benzene (6b)



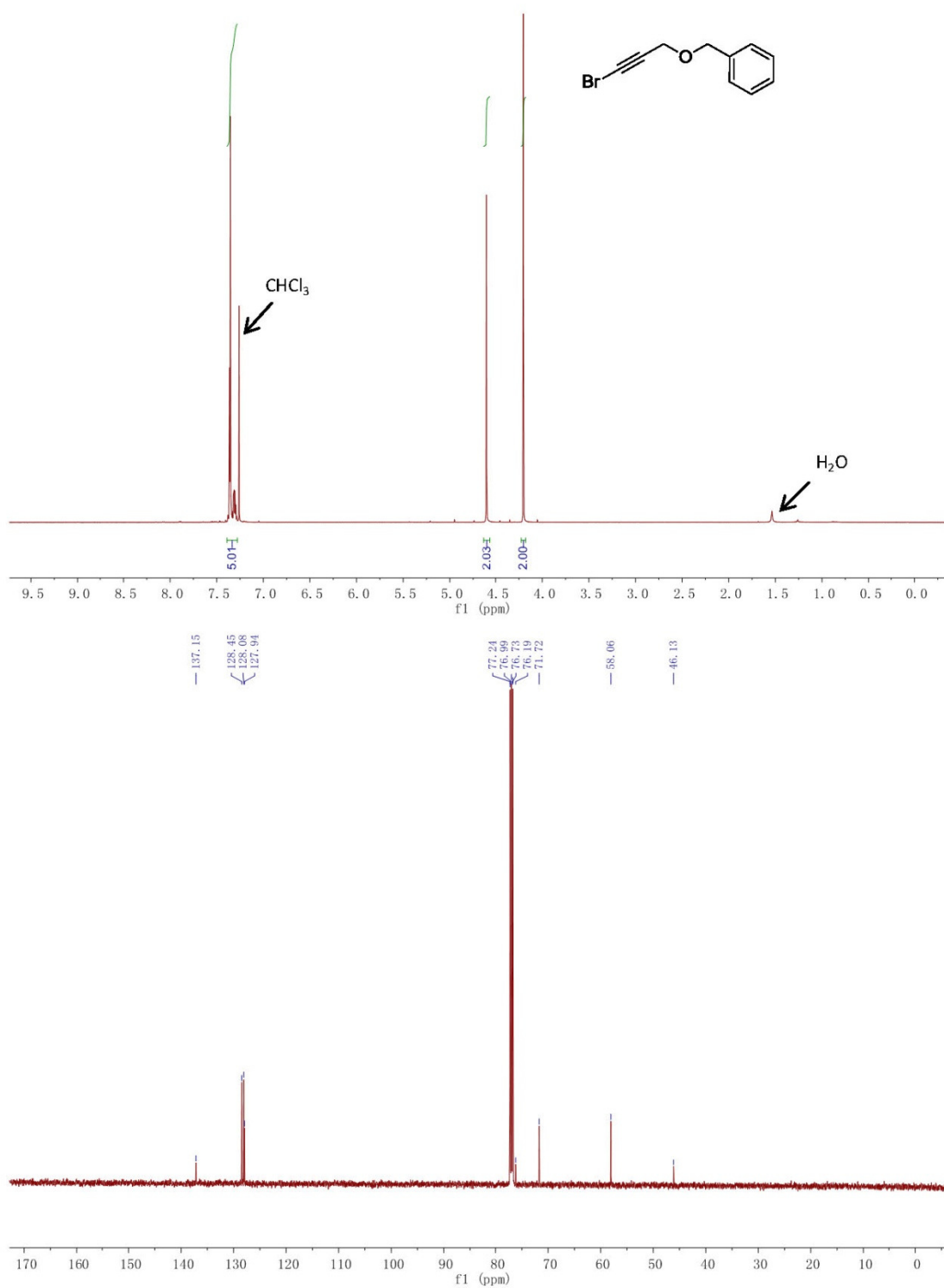
(Bromoethynyl)trimethylsilane (6c)



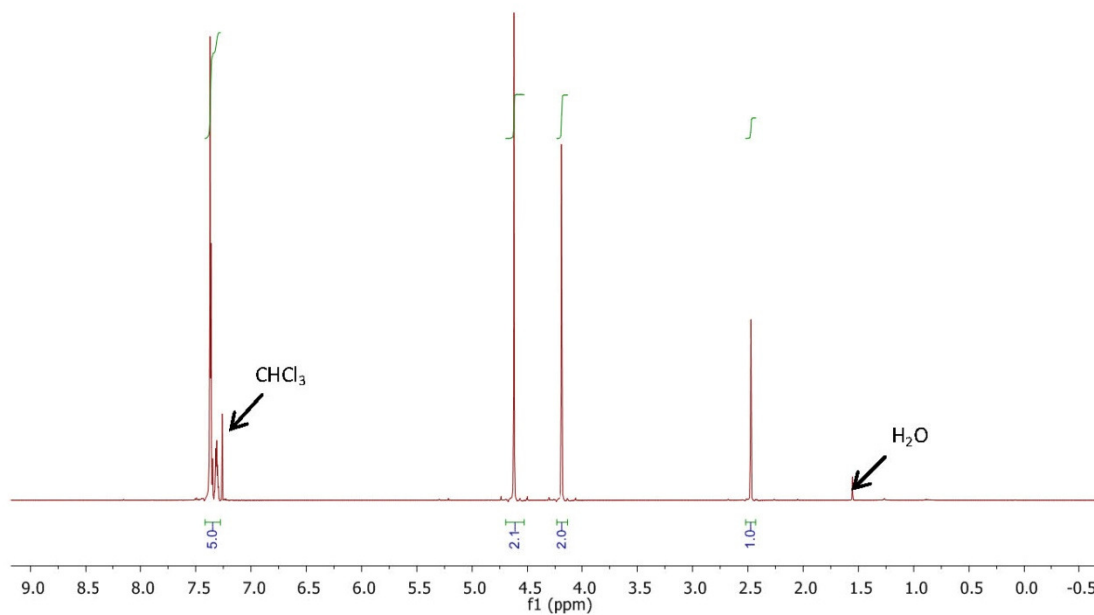
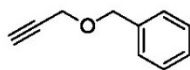
3-Bromoprop-2-yn-1-yl benzoate (6d)



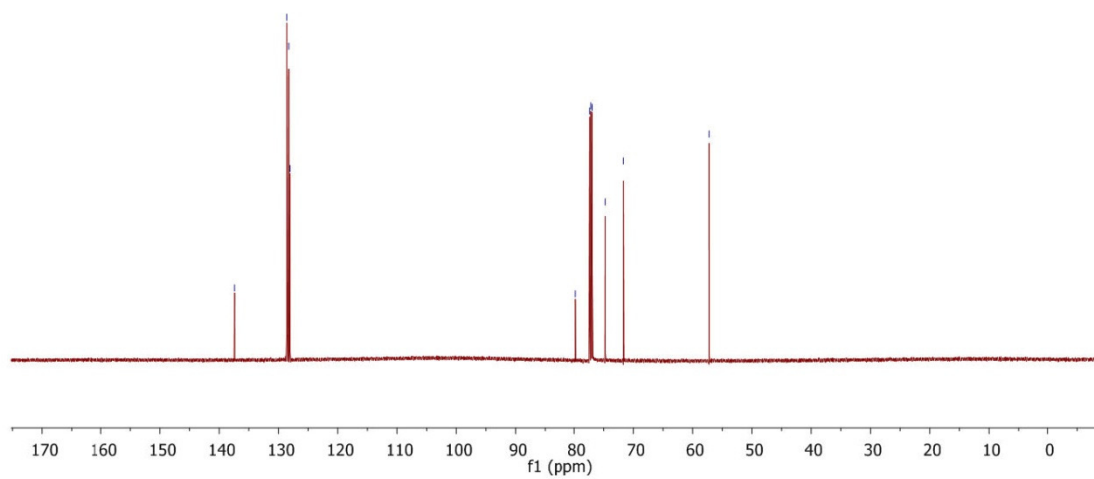
Benzylprop-(3-bromo-2-ynyl) ether (6e)



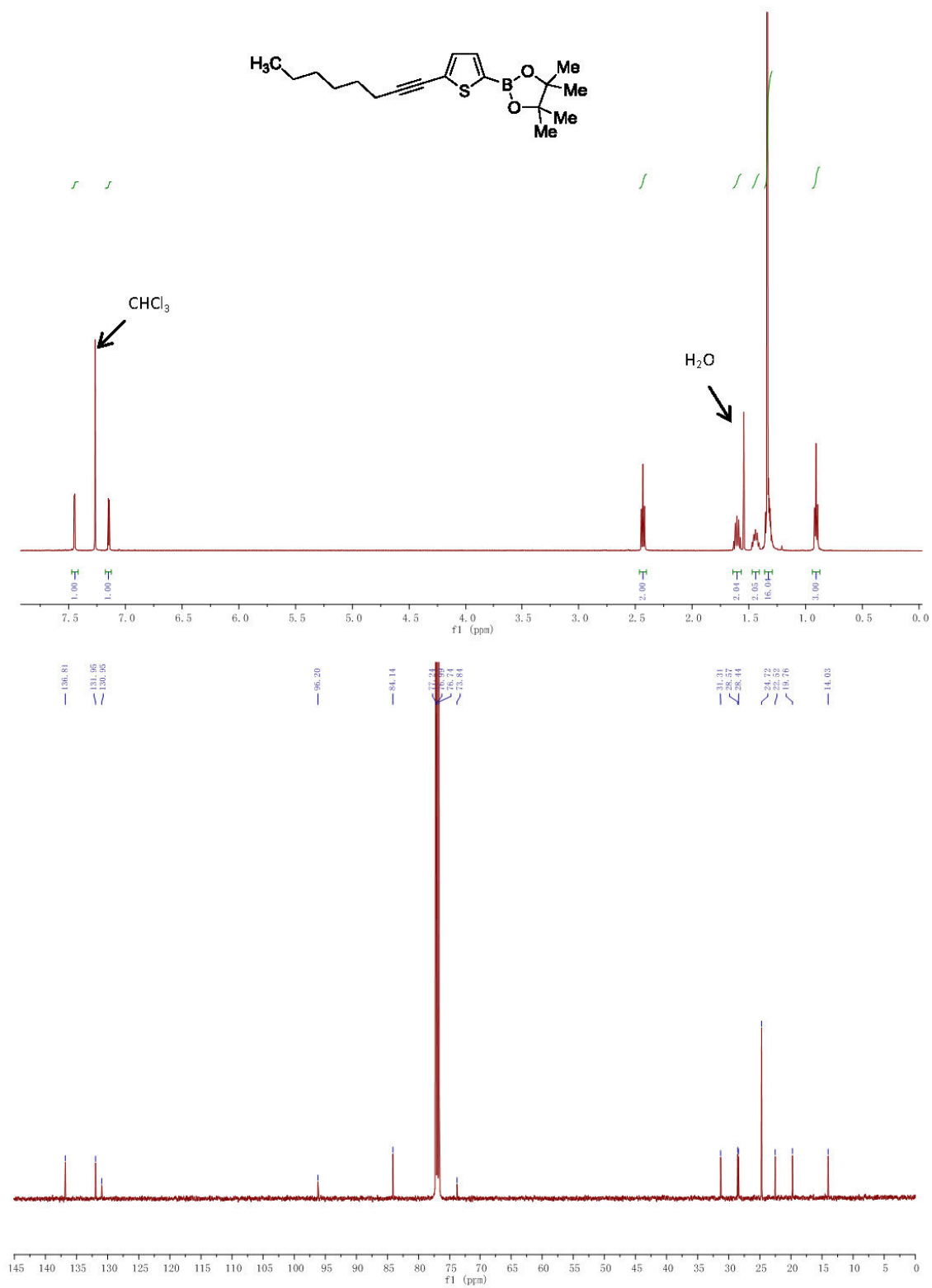
Benzylprop-2-ynyl ether (6f)



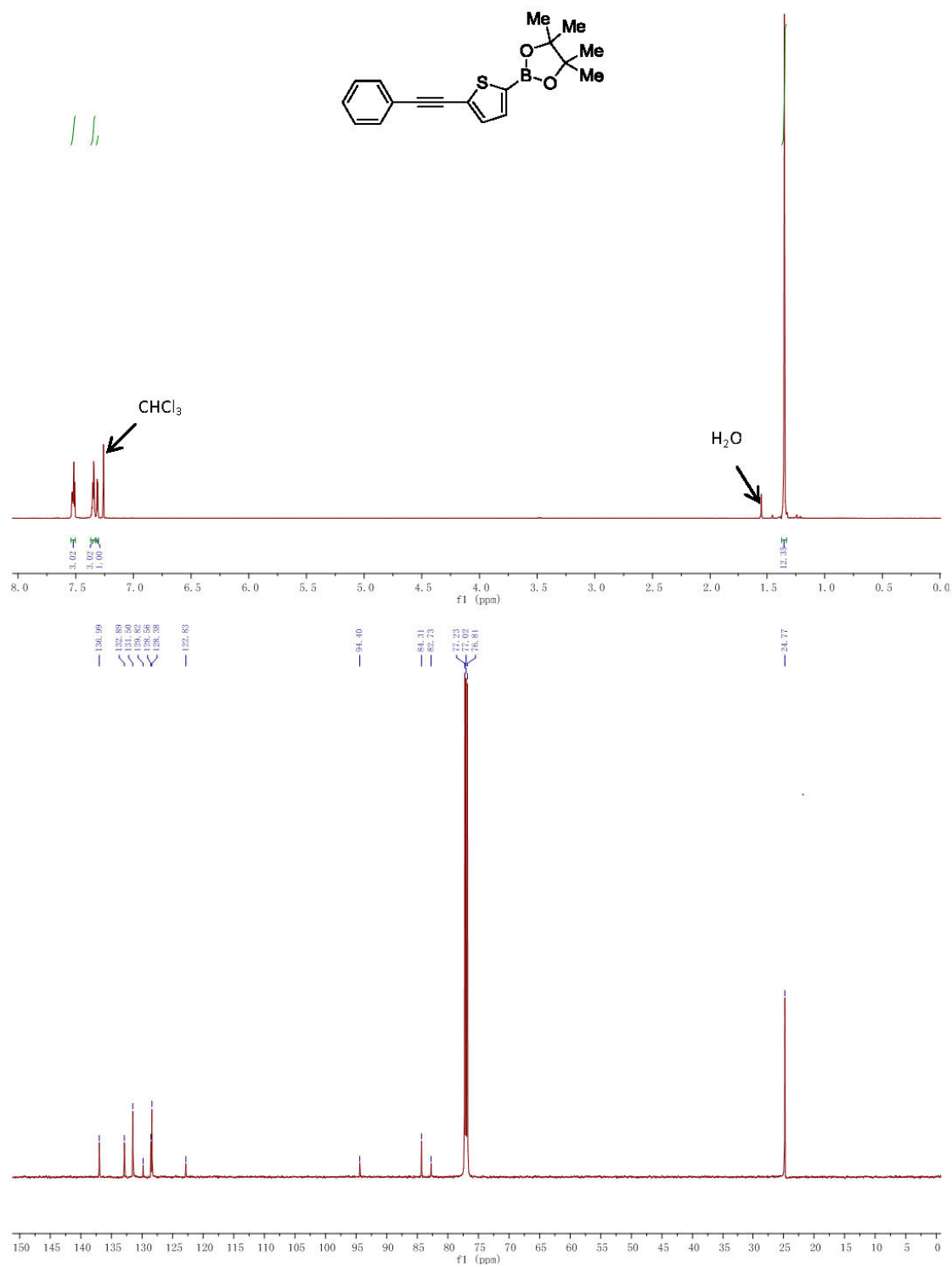
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128.6
128.3
128.1
79.8
77.4
77.2
76.9
74.7
71.7
57.2



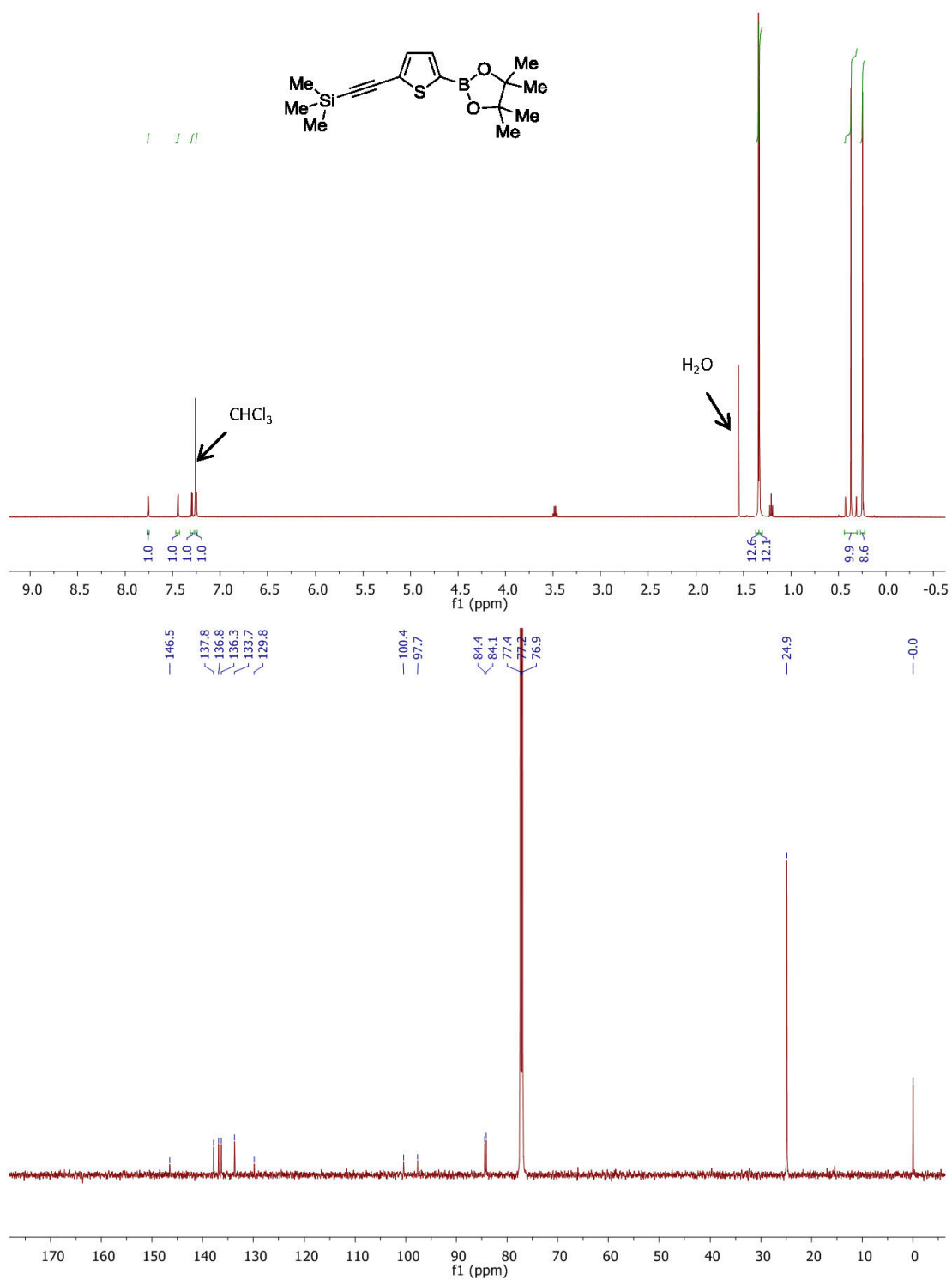
4,4,5,5-Tetramethyl-2-(5-(oct-1-yn-1-yl)thiophen-2-yl)-1,3,2-dioxaborolane (7a)



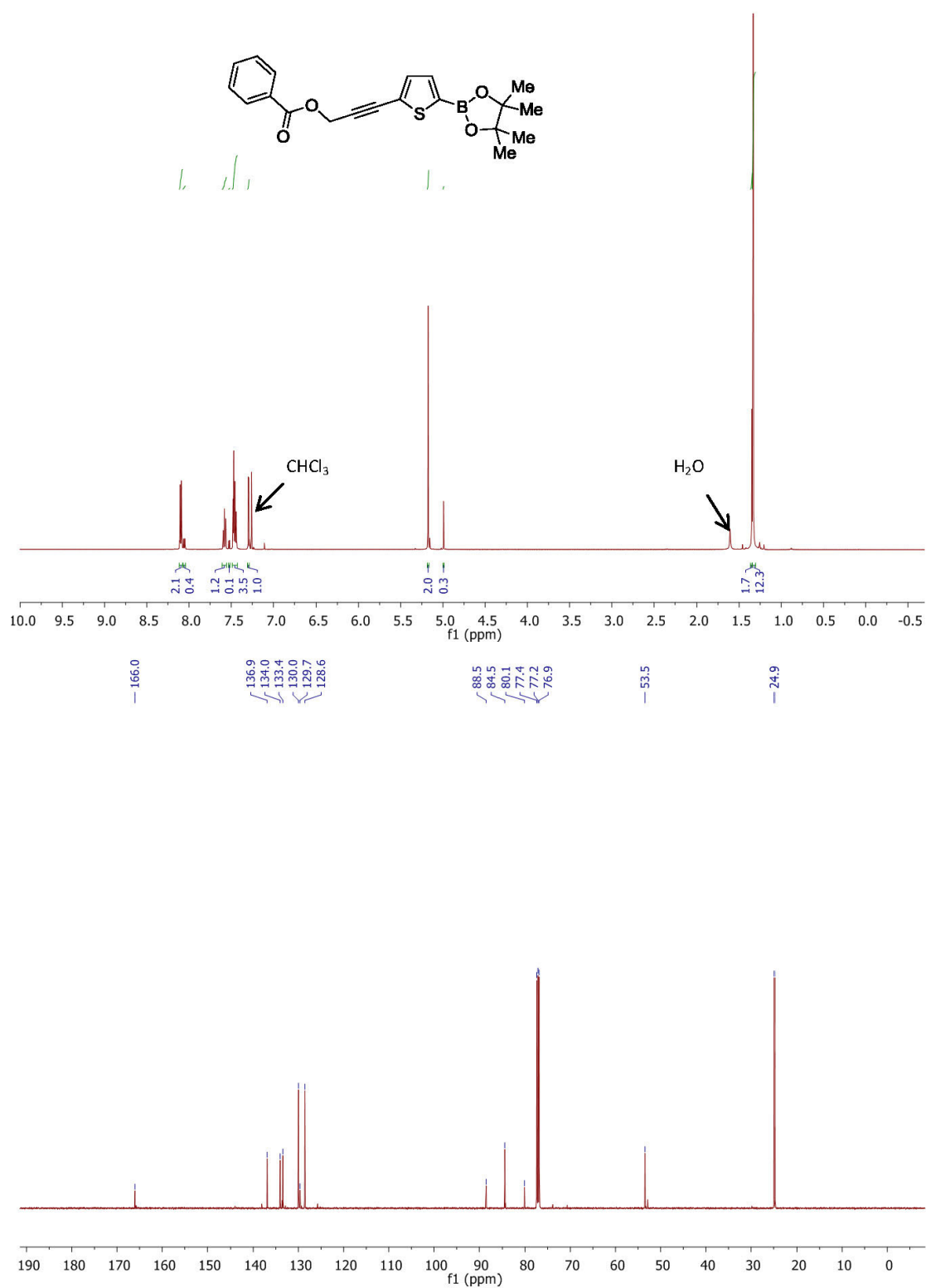
4,4,5,5-Tetramethyl-2-(5-(phenylethynyl)thiophen-2-yl)-1,3,2-dioxaborolane (7b)



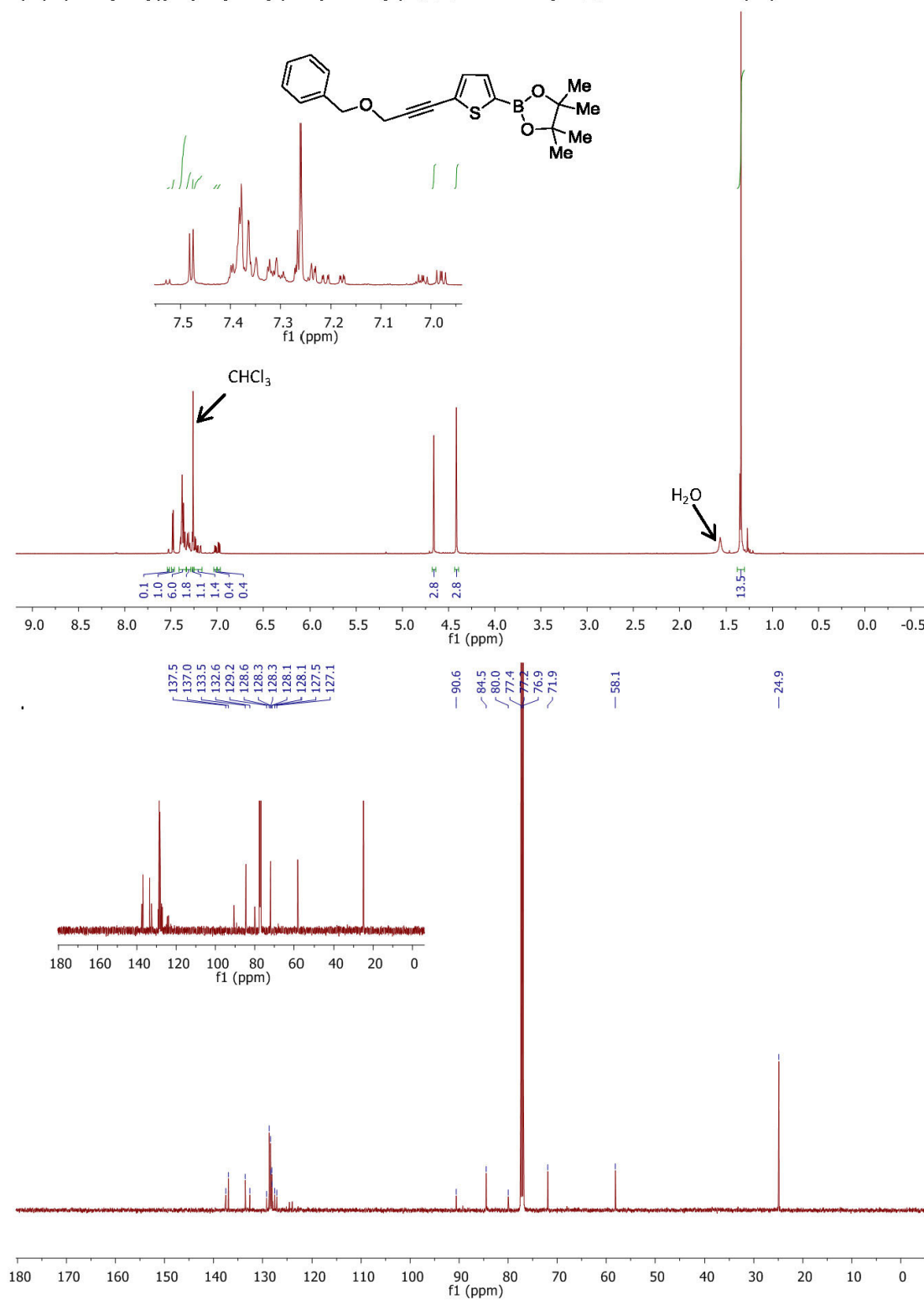
Trimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)ethynyl)silane (7c)

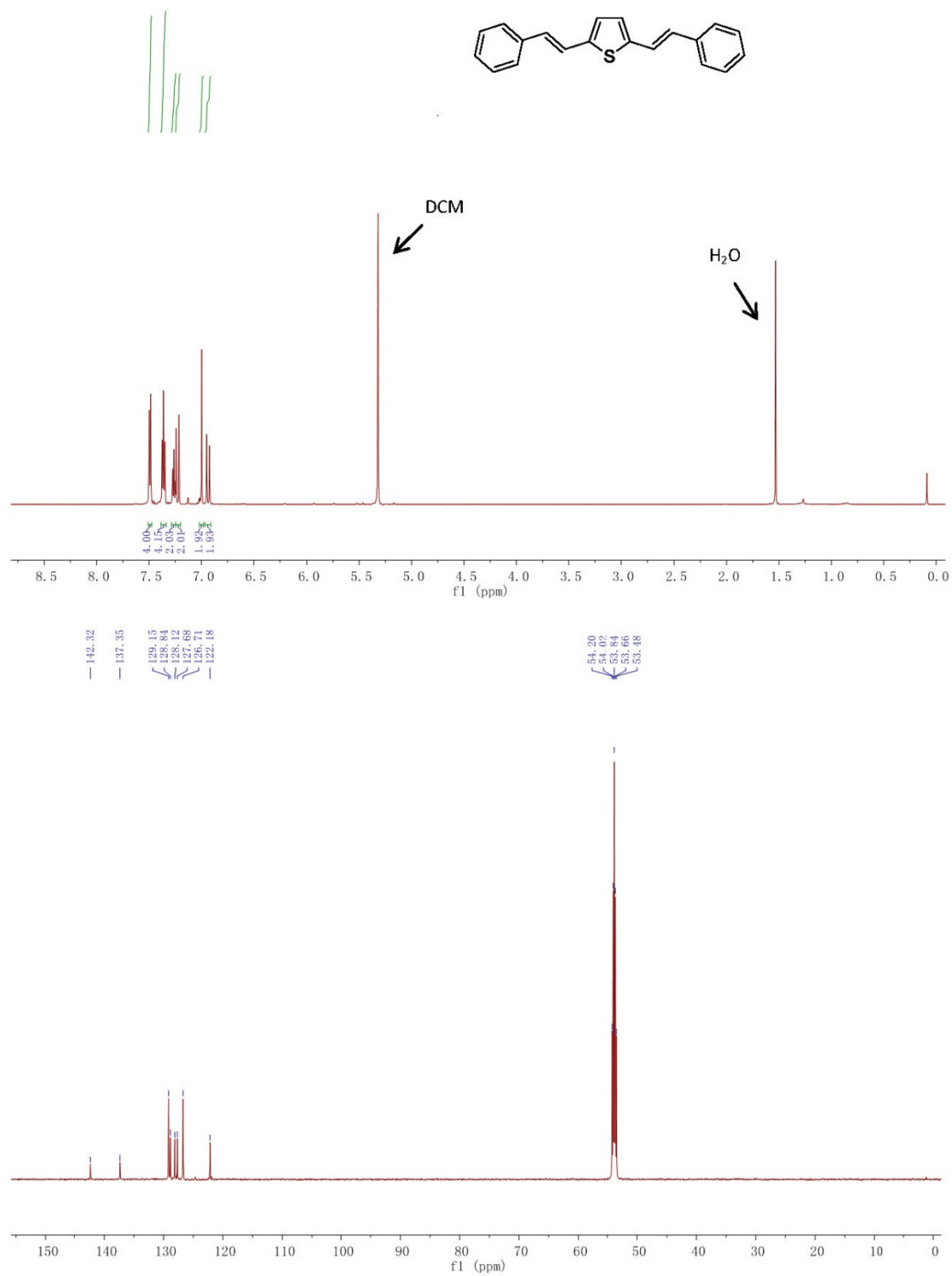


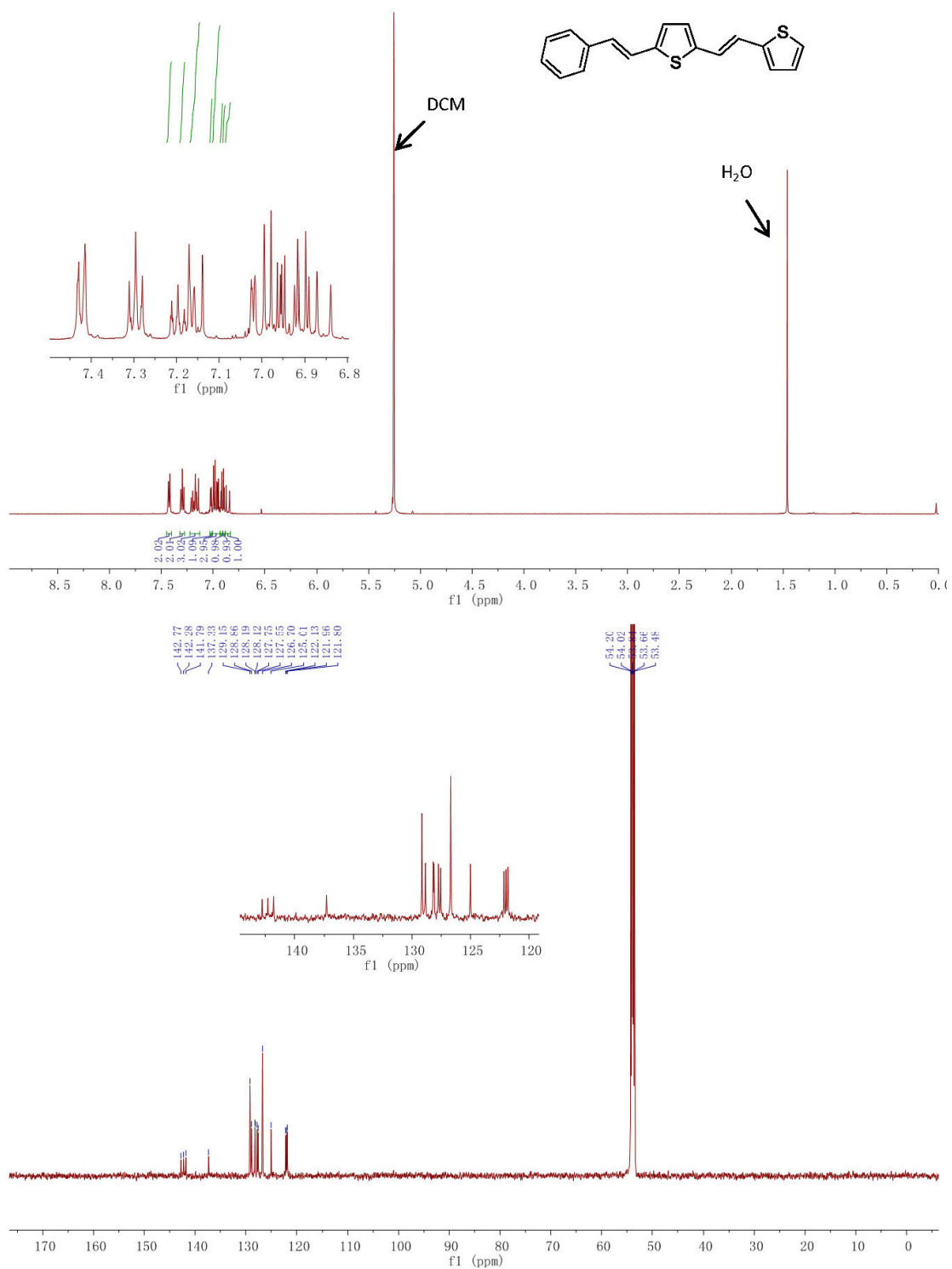
3-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)prop-2-yn-1-ylbenzoate (7d)

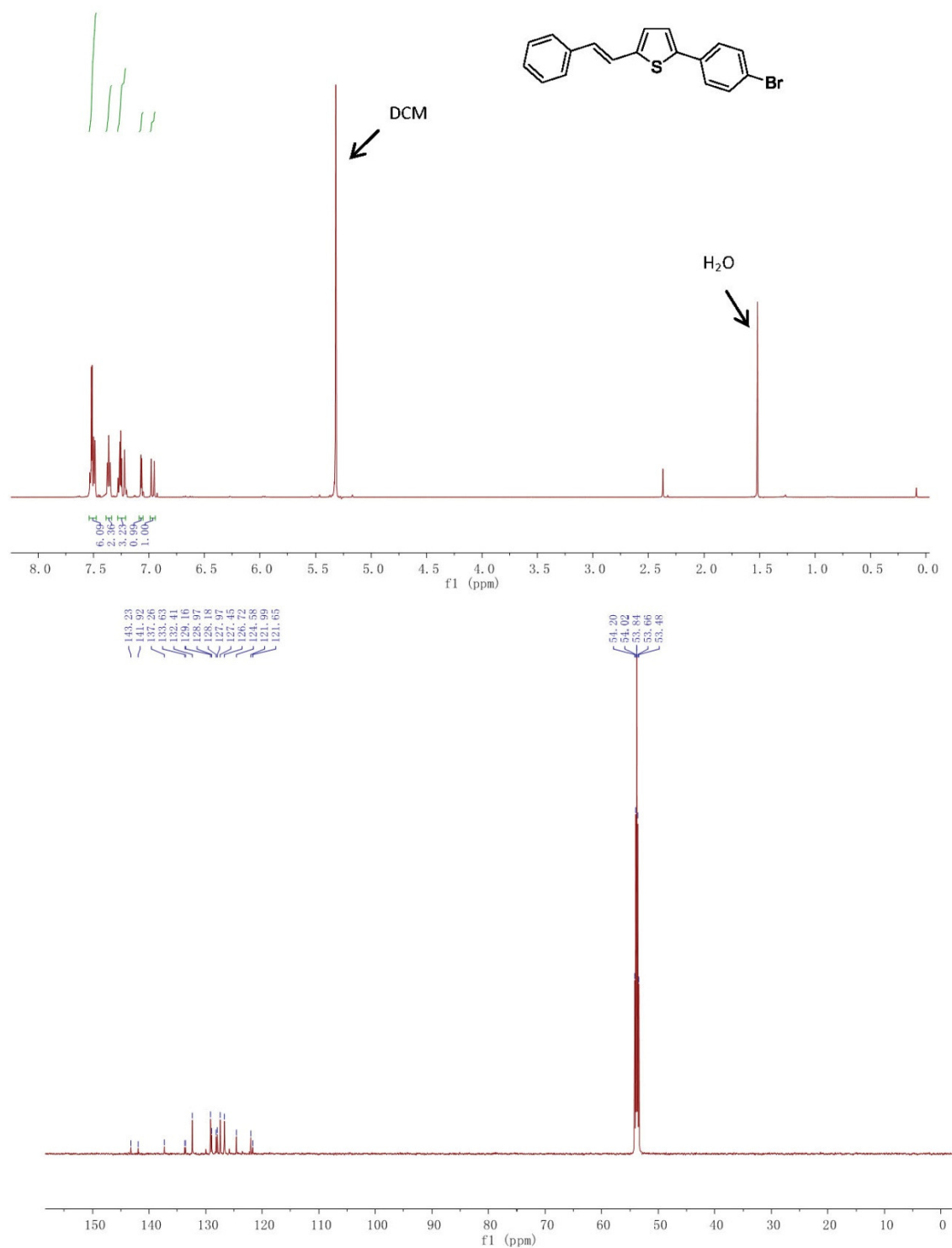


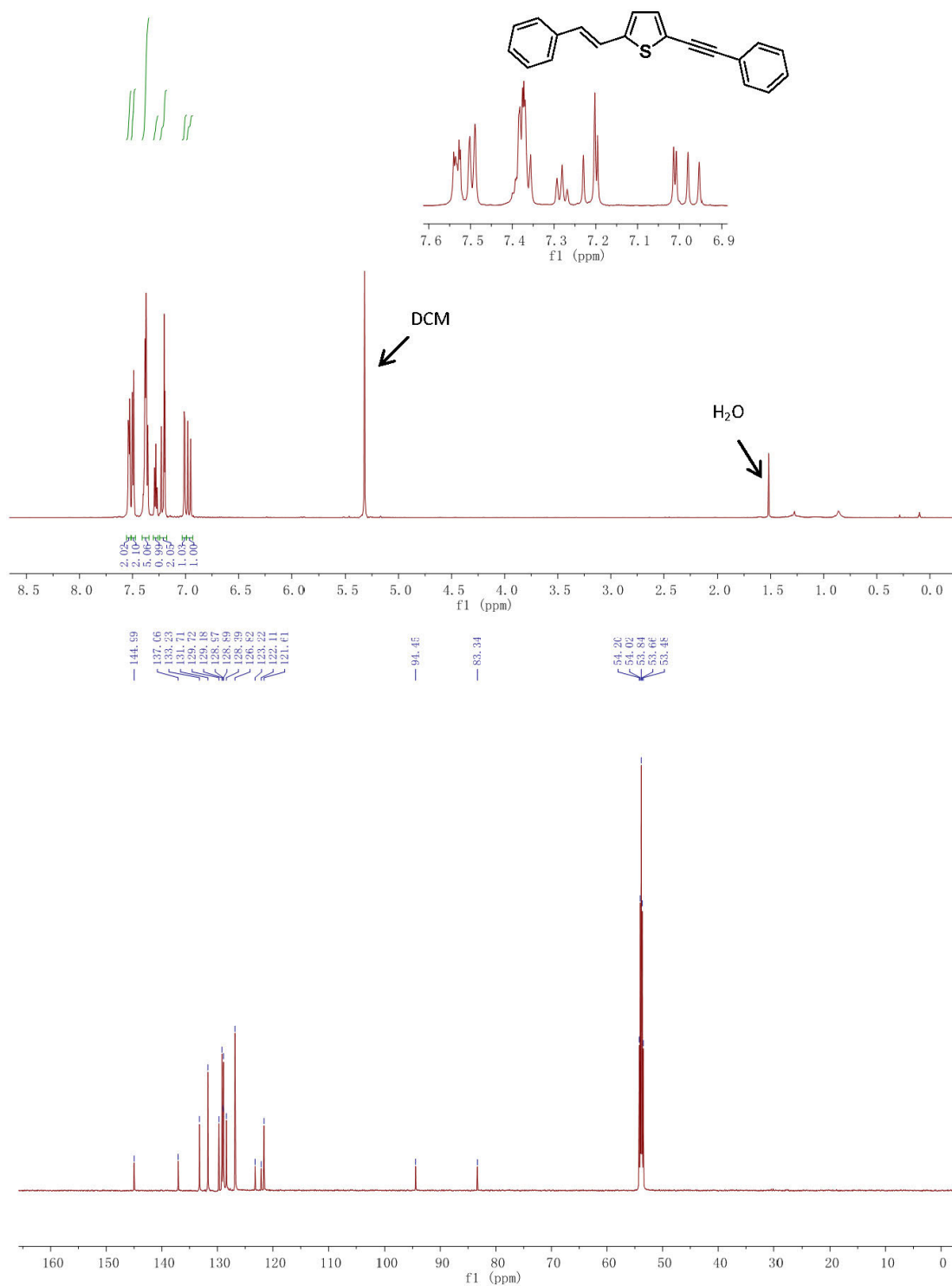
2-(5-(3-(Benzyloxy)prop-1-yn-1-yl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7e)

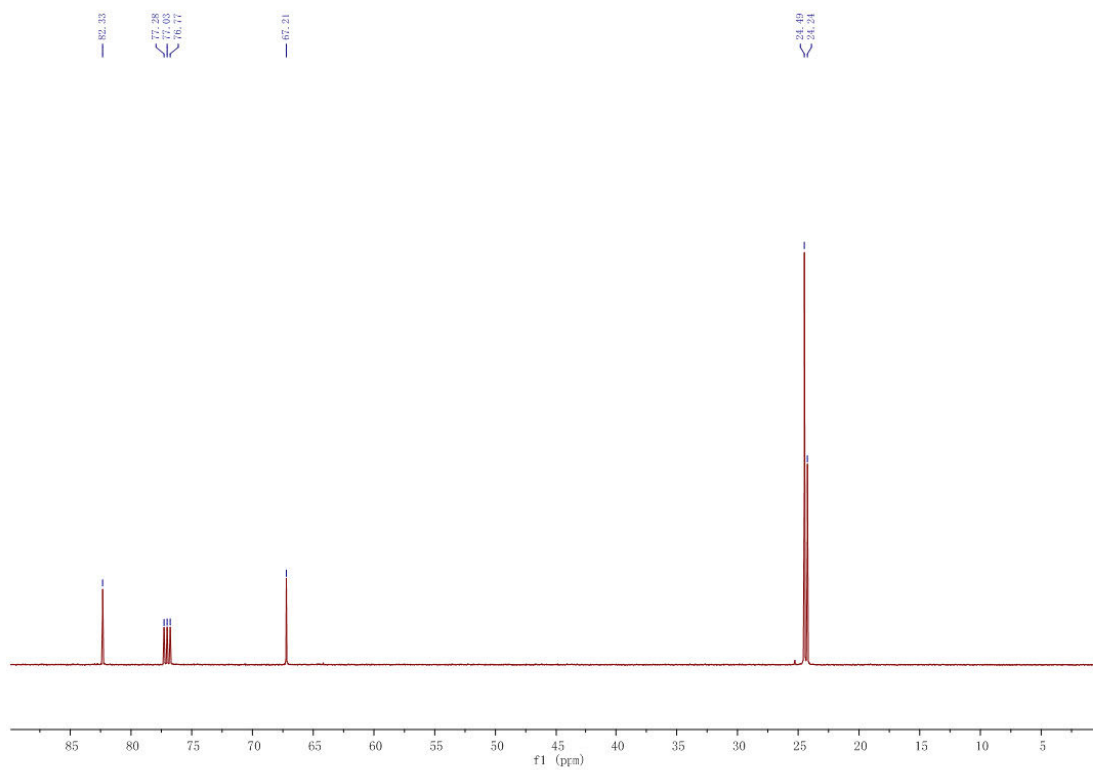
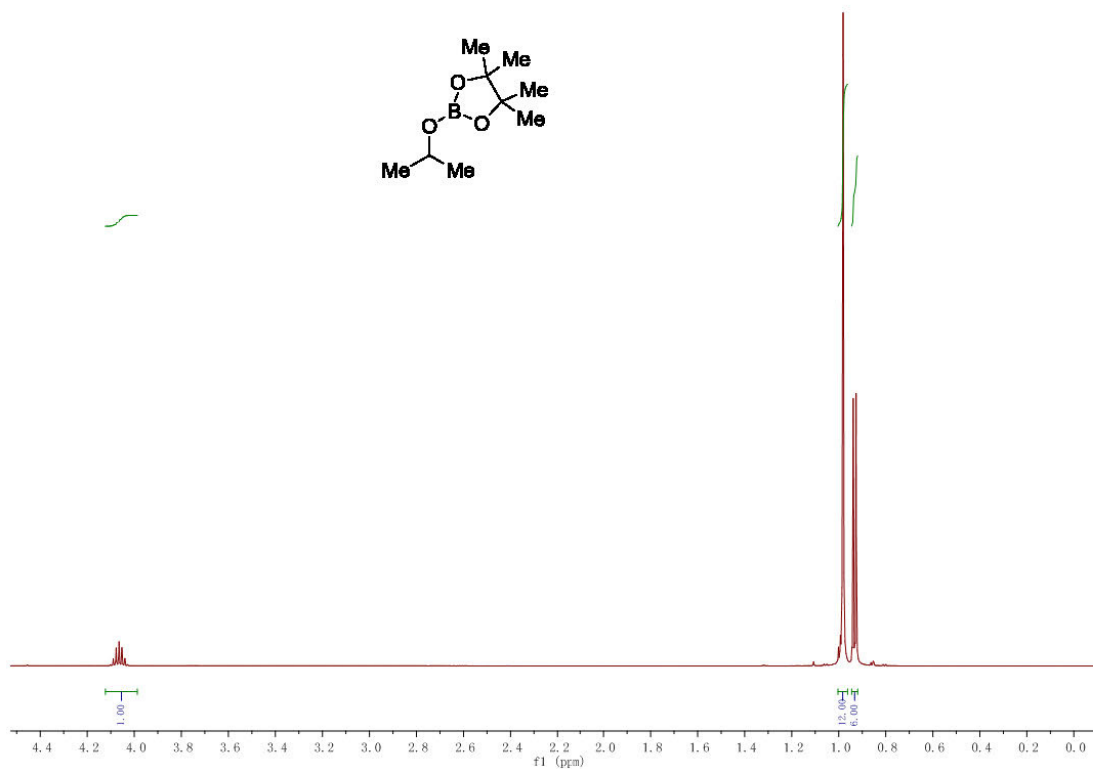
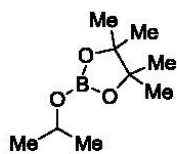


2,5-Di(*E*-styryl)thiophene (8a)

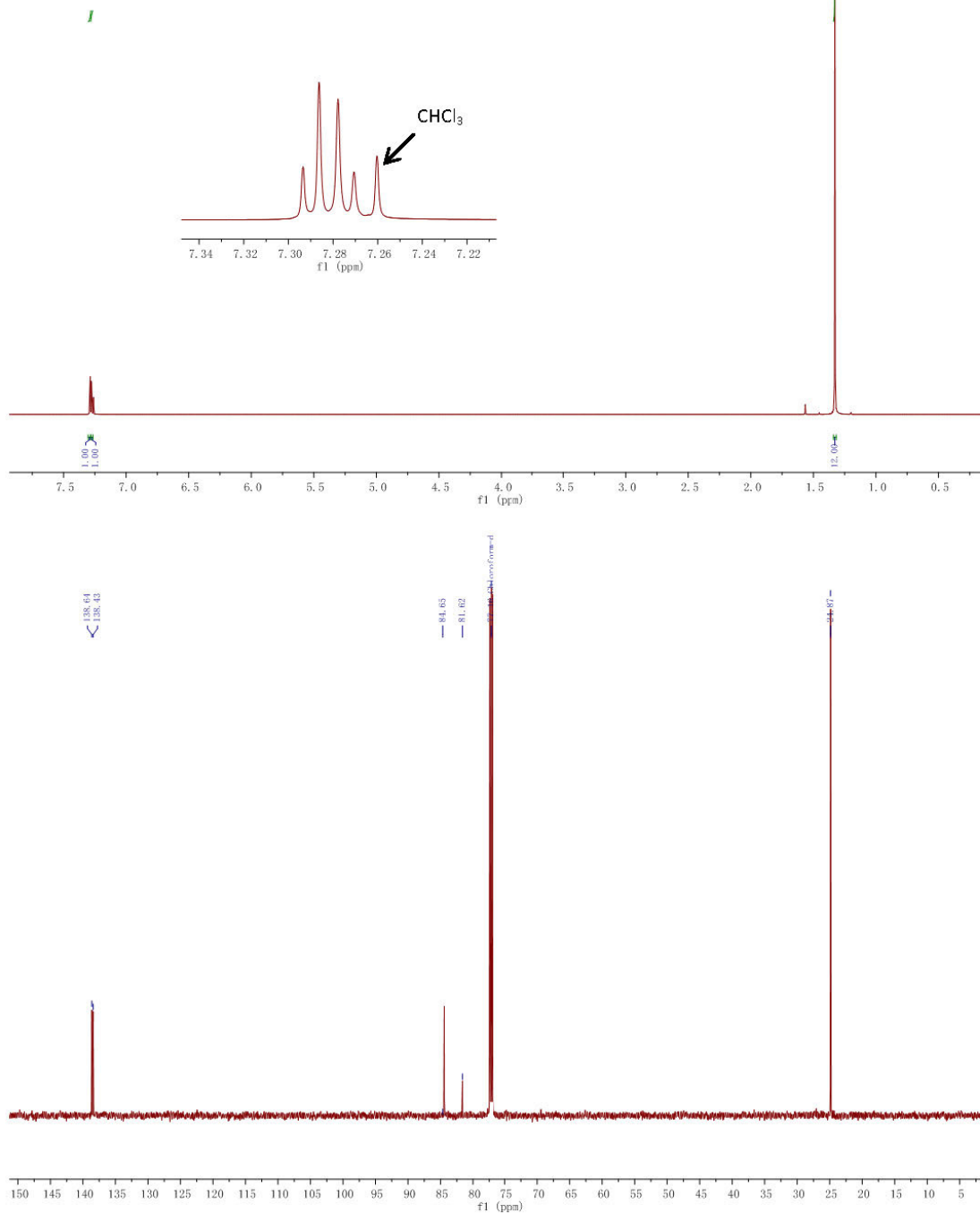
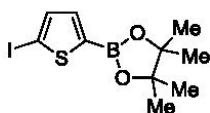
2-((*E*-Styryl)-5-((*E*-2-(thiophen-2-yl)vinyl)thiophene (8b)

(E)-2-(4-Bromophenyl)-5-styrylthiophene (8c)

(E)-2-(Phenylethynyl)-5-styrylthiophene (8d)

2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*i*PrO-BPin) (9)

2-(5-Iodothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)



References

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5.2 Supporting information for *Tetrahedron* 2015, submitted.**Supporting Information**

for

**Synthesis of Poly(thiophene-*alt*-pyrrole) from a Difunctionalized
Thienylpyrrole by Kumada Polycondensation**

Lu-Ying He^a, Sara Urrego-Riveros^a, Paul J. Gates^b, Christian Näther^c, Maren Brinkmann^d,
Volker Abetz^{d,c} and Anne Staubitz^{a,*}

^a *Otto Diels-Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, Kiel 24098 Germany*

^b *School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK*

^c *Institute for Inorganic Chemistry, University of Kiel, Otto-Hahn-Platz 6, Kiel, 24118 Germany*

^d *Helmholtz-Zentrum Geesthacht, Institute of Polymer Research, Max-Planck-Str. 1, Geesthacht 21502, Germany*

^e *Institute of Physical Chemistry, University of Hamburg, Grindelallee 117, Hamburg 20146, Germany,*

* Corresponding author. Tel.: +49-431-880-3697; fax: +49-431-880-1558; e-mail: astaubitz@oc.uni-kiel.de

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Abbreviations

A	area
anhyd.	anhydrous
Ar	aryl
ATR	attenuated total reflectance
calcd.	calculated
CI	chemical ionization
COSY	correlated spectroscopy
d	doublet (NMR)
DEPT	distortionless enhancement by polarization transfer
DMF	<i>N,N</i> -dimethylformamide
dppe	1,2- <i>bis</i> (diphenylphosphino)ethane
dppf	1,1'- <i>bis</i> (diphenylphosphino)ferrocene
EI	electron ionization
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
HMBC	heteronuclear multiple bond coherence
HPLC	high-performance liquid chromatography
HSQC	heteronuclear single quantum coherence
IR	infrared
m	medium (concerning the intensity) (IR)
m	multiplet (NMR)
MALDI-TOF-MS	matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
M_n	number average molecular weight
M_w	weight average molecular weight
M.p.	melting point
MS	mass spectrometry
MTBE	Methyl <i>tert</i> -butyl ether
MW	microwave
n	amount of substance
RF	response factor
R_f	retention factor
s	strong (concerning the intensity) (IR)
s	singlet (NMR)
SPhos	2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl
t	triplet (NMR)
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMS	tetramethylsilane
w	weak (concerning the intensity) (IR)

Materials**Chemicals**

All reagents were used without further purification unless noted otherwise.

Compound	Supplier	Purity	Comment
Thiophene	Alfa Aesar Inc.	99 %	
Br ₂	Acros Inc.	99+ %	
HBr(48%)	Fisher Scientific	48%	
Natriumthiosulfat	Grüssing Inc.	97 %	
Zinc	J.T.Baker B.V. - Deventer-Holland	-	
Acetic acid	Grüssing Inc.	99.5 %	
Magnesium	Merck Inc.	>99%	
1-Bromohexane	Sigma-Aldrich Inc.	98%	
Ni(dppp)Cl ₂	ABCR Inc.	99%	
<i>N</i> -Bromosuccinimide	Sigma-Aldrich Inc.	98%	
<i>N</i> -iodosuccinimide	molekula	95%	
Pyrrole	Sigma-Aldrich Inc.	98%	
NaH	Acros Inc.	60% disperse in oil	
<i>n</i> -Butyllithium	Acros Inc.	2.5 M in hexane	
Tributyltin chloride	Acros Inc.	95 %	
Tetramethylethyldiamine	Acros Inc.	99.5 %	
Magnesium sulfate	Grüssing Inc.	99 %	
[Pd(PPh ₃) ₄]	ABCR Inc.	99 %	
[Pd(P ^{<i>t</i>} Bu ₃) ₂]	Strem Chemicals Inc.	>98 %	
Sodium	Merck Inc.	≥ 99 %	
Sodium chloride	Grüssing Inc.	99.5 %	
15-Crown-5	VWR Inc.	98%	
Isopropylmagnesium chloride solution	Sigma-Aldrich Inc.	2 M in THF	
LiCl	Sigma-Aldrich Inc.	99%	

Solvent	Supplier or grade before distillation, drying procedure if applicable
CHCl ₃	VWR Inc., HPLC grade
Diethyl ether	BCD, technical grade
DMF	ABCR, anhydrous, amine free; 99.9%; contains amine and molecular sieves
Hexane	WALTER CMP, technical grade, sodium with benzophenone as an indicator; stored over 3 Å molecular sieves
THF	Sigma Aldrich; Dried over LiAlH ₄ with benzophenone as an indicator, degassed by three freeze-pump-thaw cycles stored over 3 Å molecular sieves
MTBE	Sigma Aldrich; HPLC grade, sodium with benzophenone as an indicator; degassed by three freeze-pump-thaw cycles, stored over 3 Å molecular sieves in the glovebox
Dioxane	Grüssing; Dried over sodium with benzophenone as an indicator; degassed by three freeze-pump-thaw cycles, stored over 3 Å molecular sieves in the glovebox

GC Calibration

The conversion for the polymerization was determined by GC by a multiple point internal standard method, using naphthalene as a standard. The following equation was used for the calculation of the conversion of substances **3**, and **4**.

$$n(\text{analyte}) = \frac{A(\text{analyte})}{A(\text{standard})} \times \frac{n(\text{standard})}{RF}$$

where n is the amount of substance, A is the integrated area and RF is a system specific response factor. For the calibration curve, known amounts of the analytical naphthalene were used. The response factor RF was obtained from the slope of the resulting calibration curve (Figures SI 1 and SI 2).

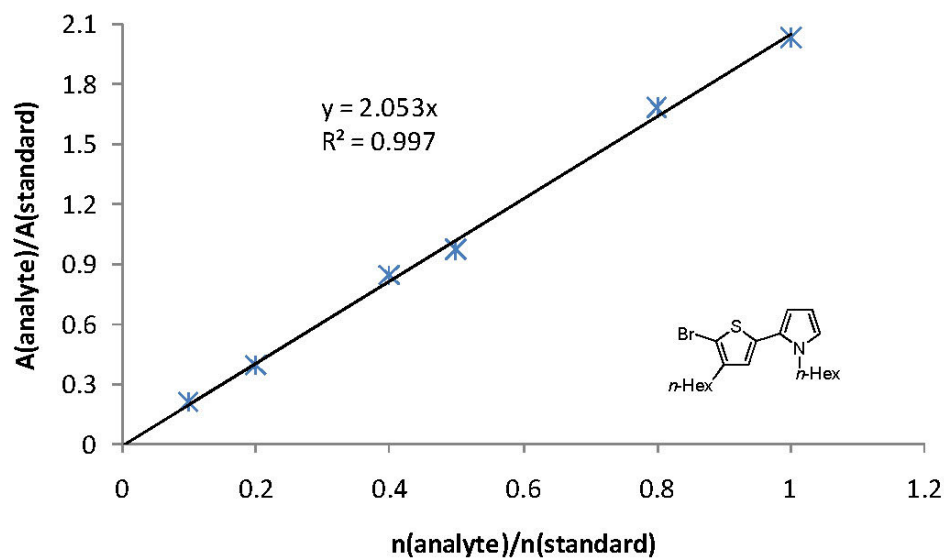


Figure SI 1. Calibration curve for 2-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-1H-pyrrole **3** using naphthalene as an internal standard.

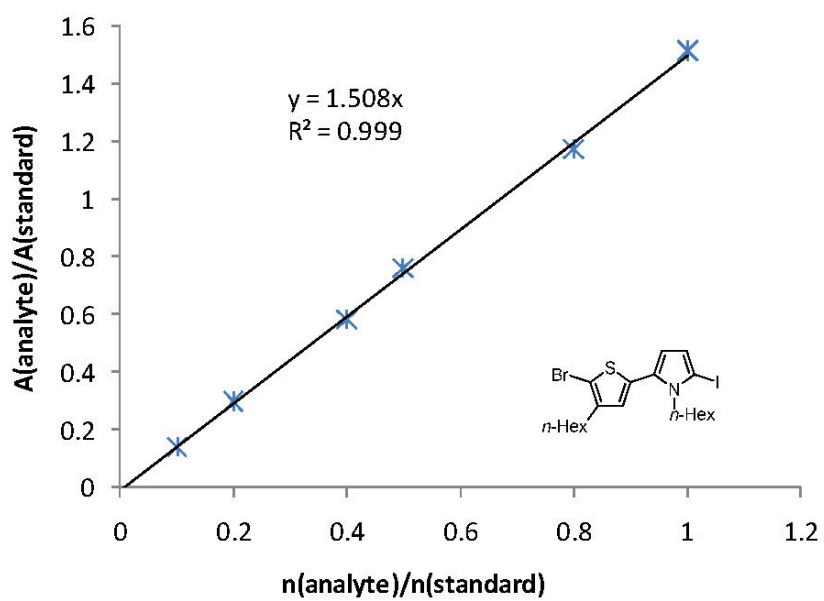


Figure SI 2. Calibration curve for 2-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-5-iodo-1*H*-pyrrole **4** using naphthalene as an internal standard.

Lithiation of compound **3** with LDA

Diisopropylamine (111 mg, 155 μ L, 1.10 mmol) was added to THF (10 mL) in one portion. The solution was cooled to 0 $^{\circ}$ C and *n*-BuLi (0.40 mL, 1.00 mmol, 2.5 M in hexanes) was added dropwise in 2 min. After stirring for 20 min at 0 $^{\circ}$ C, the solution was cooled to -78 $^{\circ}$ C and stirring was continued for another 5 min. To this reaction mixture a solution of **3** (397 mg, 1.00 mmol) in anhydrous THF (3 mL) was added via a syringe over the course of 5 min. The reaction mixture was stirred for 6 h at -78 $^{\circ}$ C,* and warmed up 20 $^{\circ}$ C without moving the cooling bath and stirred another 12 h at 20 $^{\circ}$ C. MeI (426 mg, 0.200 mL, 3.00 mmol) was added in one portion. The reaction was quenched with water (5 mL) and the aqueous phase was extracted with ether (2 \times 15 mL). The combined organic phase was dried over MgSO₄. The solvent was removed *in vacuo* and the crude product was checked by GC-MS. The GC-MS spectra showed that there was no product detected and still a substantial amount of starting material left; some products from side reactions were also found, such as the quenched products from lithiation of both bromo and iodo groups and halogen dance reaction, which gave 1-hexyl-2-(4-hexylthiophen-2-yl)-1H-pyrrole and 2-bromo-5-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-1H-pyrrole respectively.

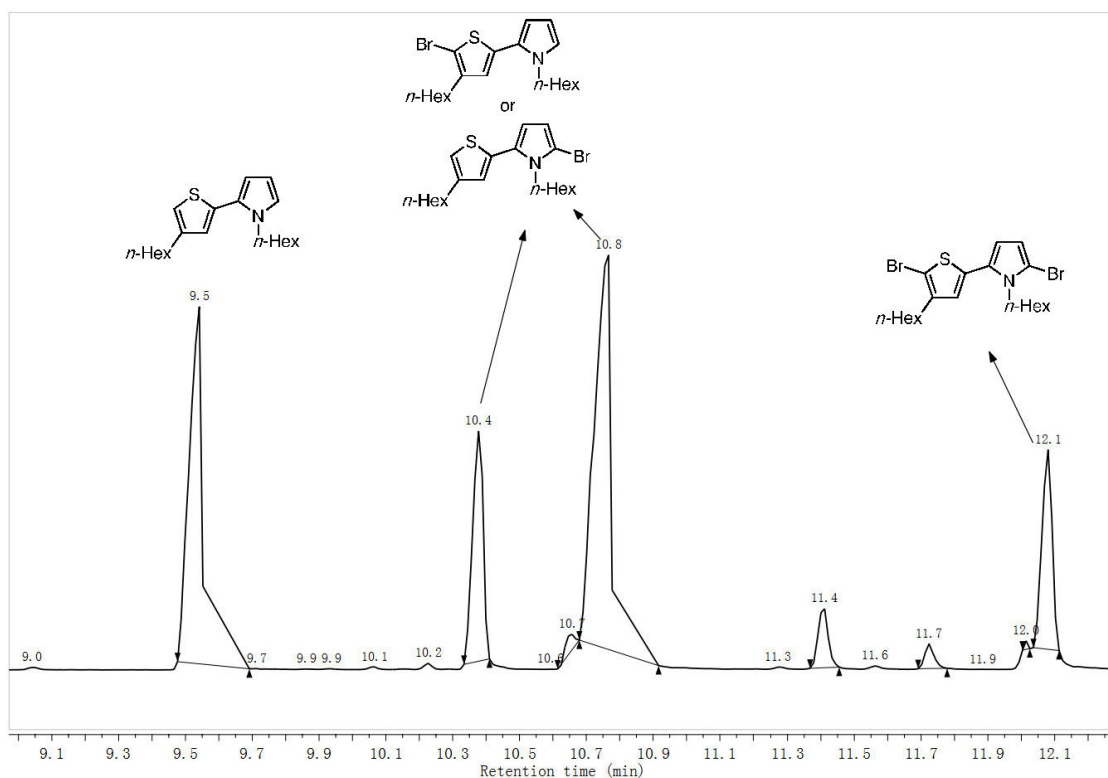
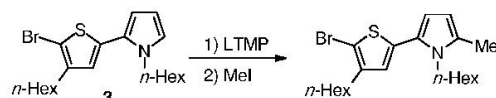


Figure SI 3. GC-MS trace of the lithiation of compound **3** with LDA.

* No product found by GC-MS analysis.

Lithiation of compound **3** with LTMP

2,2,6,6-Tetramethylpiperidine (141 mg, 187 μ L, 1.10 mmol) was added to THF (10 mL) in one portion. The solution was cooled to 0 $^{\circ}$ C and *n*-BuLi (0.40 mL, 1.00 mmol, 2.5 M in hexanes) was added dropwise in 2 min. After stirring for 20 min at 0 $^{\circ}$ C, the solution was cooled to -78 $^{\circ}$ C and stirring was continued for another 5 min. To this reaction mixture a solution of **3** (397 mg, 1.00 mmol) in anhydrous THF (3 mL) was added via a syringe over the course of 5 min. The reaction mixture was stirred for 4 h at -78 $^{\circ}$ C,[†] and warmed up 0 $^{\circ}$ C and stirred another 2 h at 0 $^{\circ}$ C. MeI (426 mg, 0.200 mL, 3.0 mmol) was added in one portion. The reaction was quenched with water (5 mL) and the aqueous phase was extracted with ether (2 x 15 mL). The combined organic phase was dried over MgSO₄. The solvent was removed *in vacuo* and the crude product was analyzed GC-MS and ¹H NMR spectroscopy. This showed that the crude product contained a some product, but also substantial amounts of starting material; and products of side reactions. These were lithiation of both bromo and iodo groups and halogen dance reaction, which gave 1-hexyl-2-(4-hexylthiophen-2-yl)-1H-pyrrole and 2-bromo-5-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-1H-pyrrole respectively.

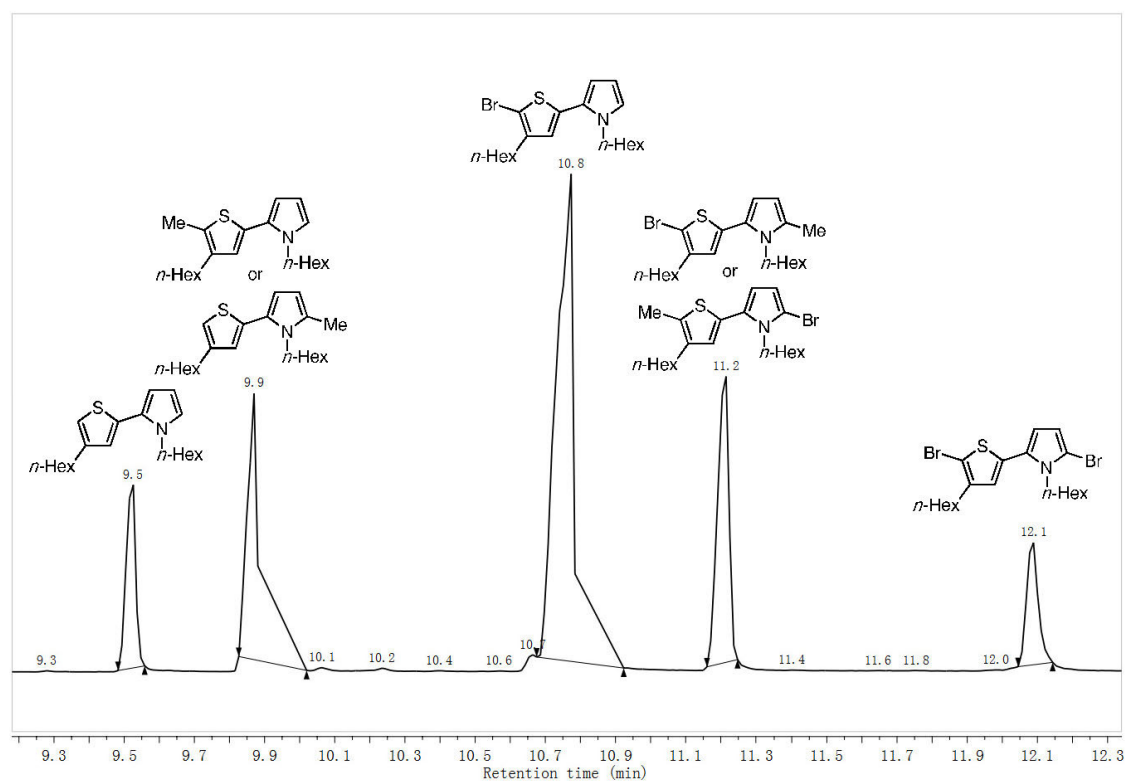


Figure SI 4. GC-MS trace of the lithiation of compound **3** with LTMP.

[†] The GC-MS showed there was a little product, but still a lot of starting mater left and side reactions happened, like lithiation of bromo group and halogen dance reaction.

NMR spectra of crude products obtained via the lithiation of precursor monomer **4**.

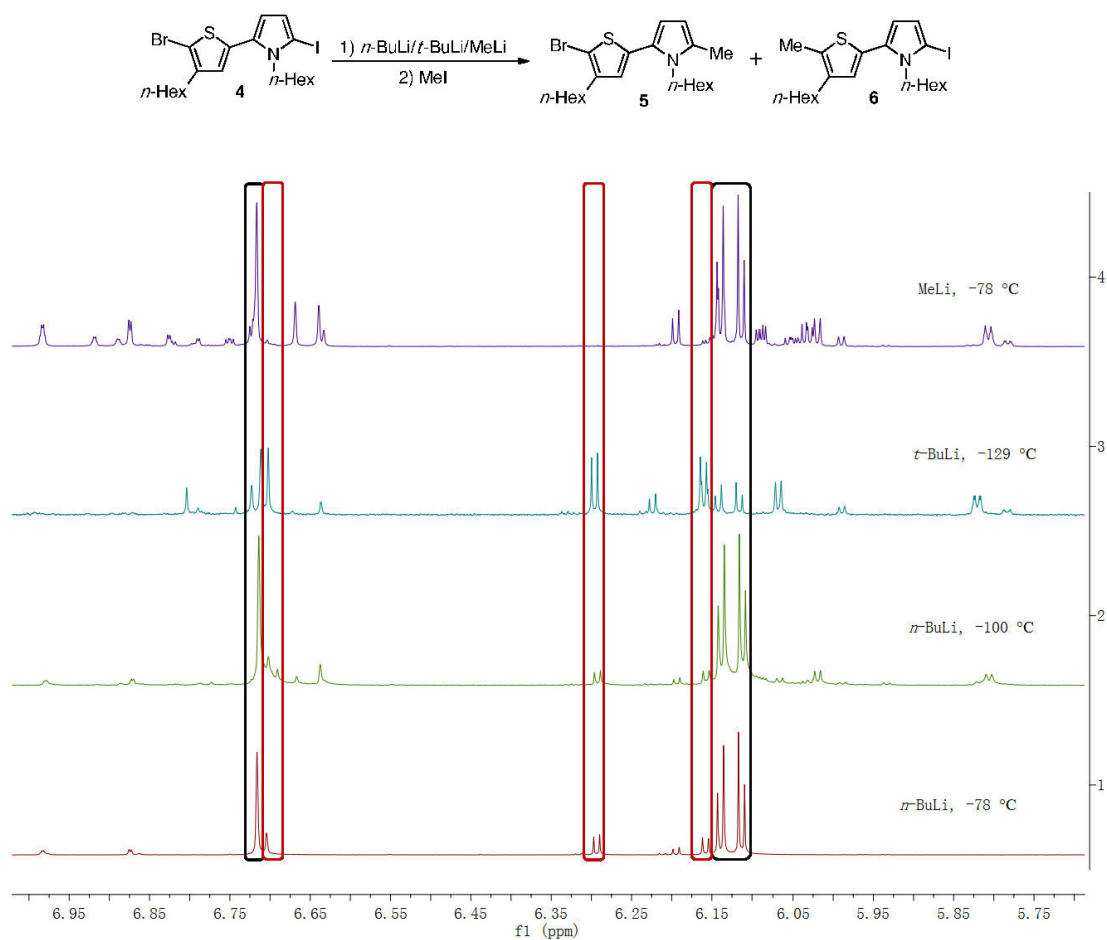
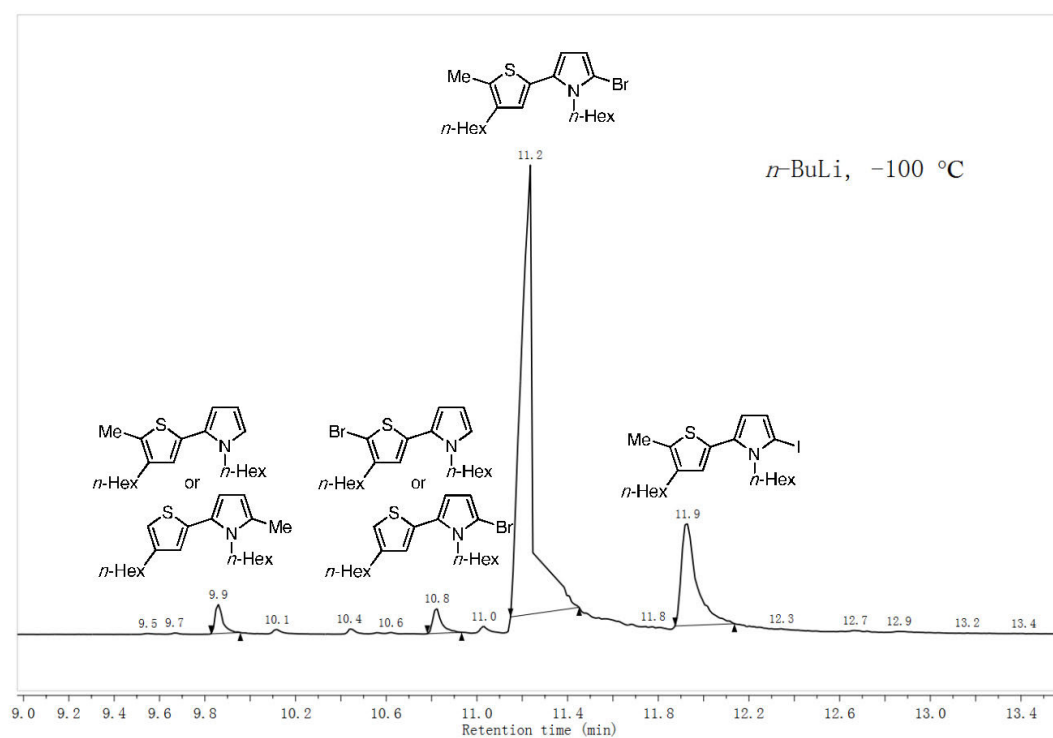
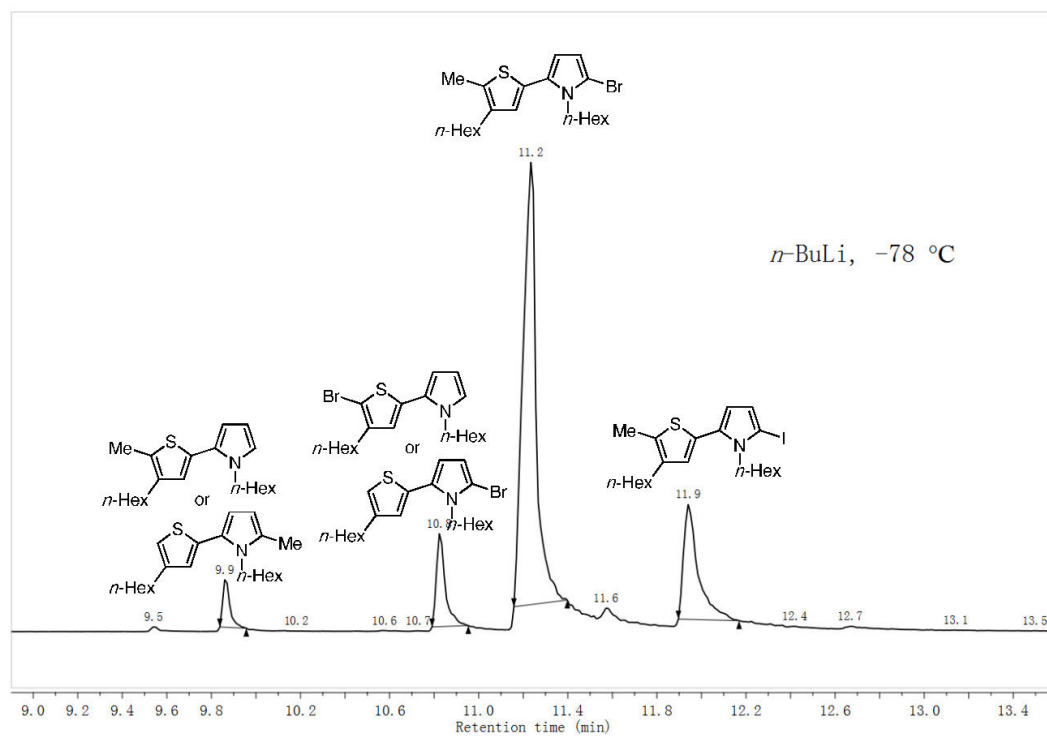


Figure SI 5. Signals from compound **5** are marked by the black box, signals from compound **6** are marked by a red box.

GC-MS spectra of crude products obtained via the lithiation of precursor monomer4.



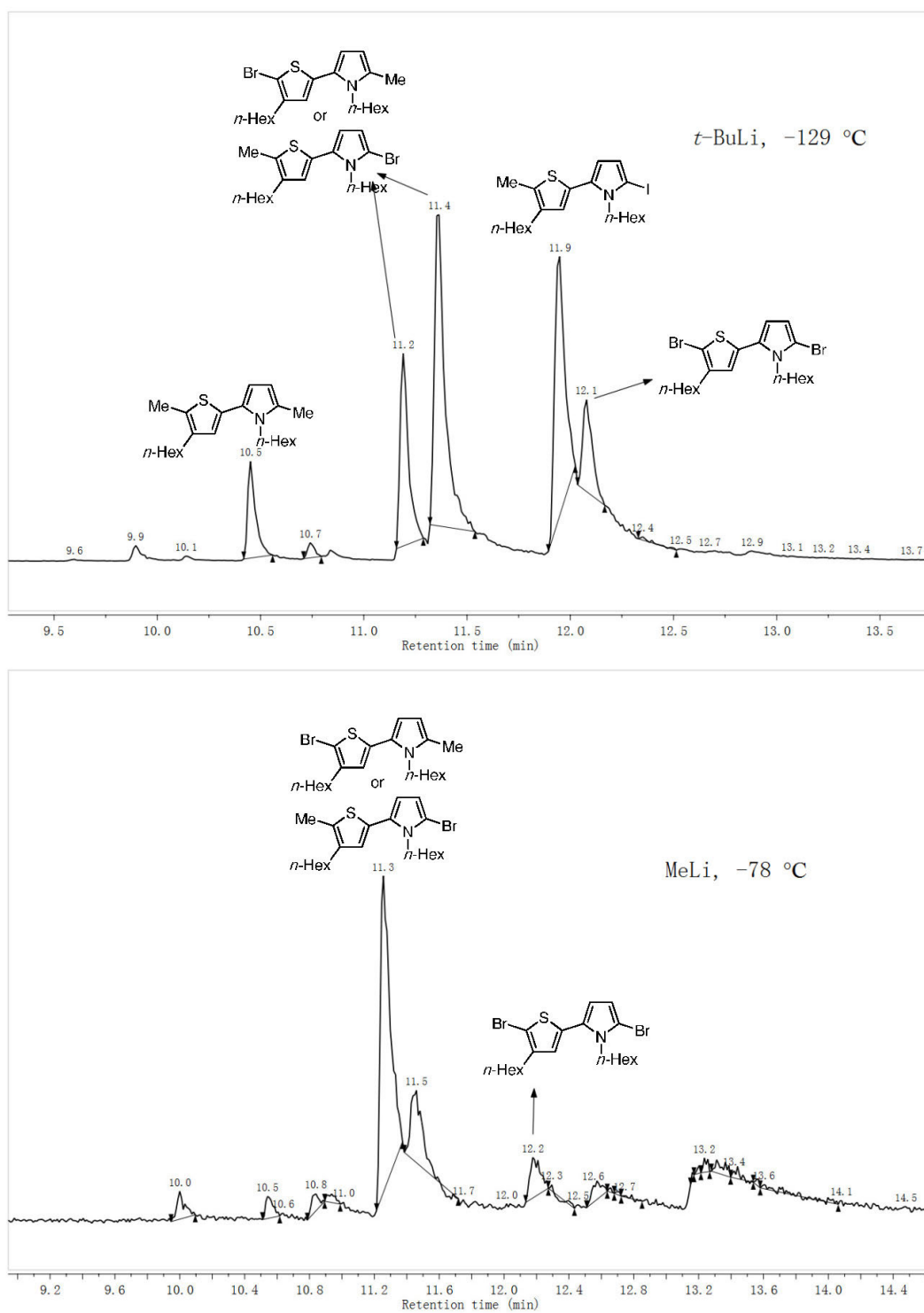
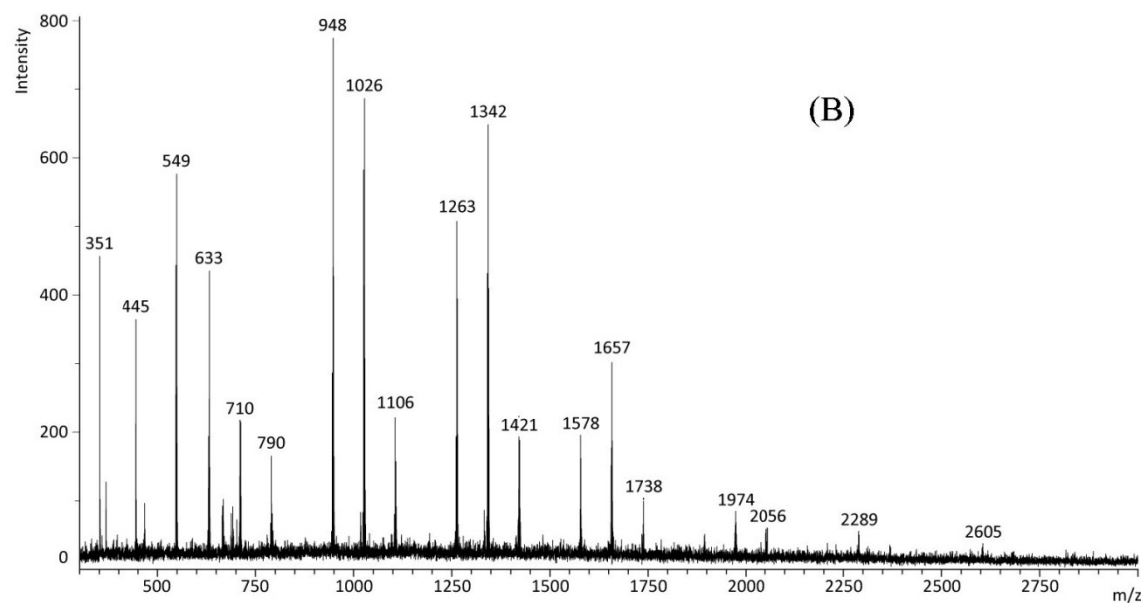
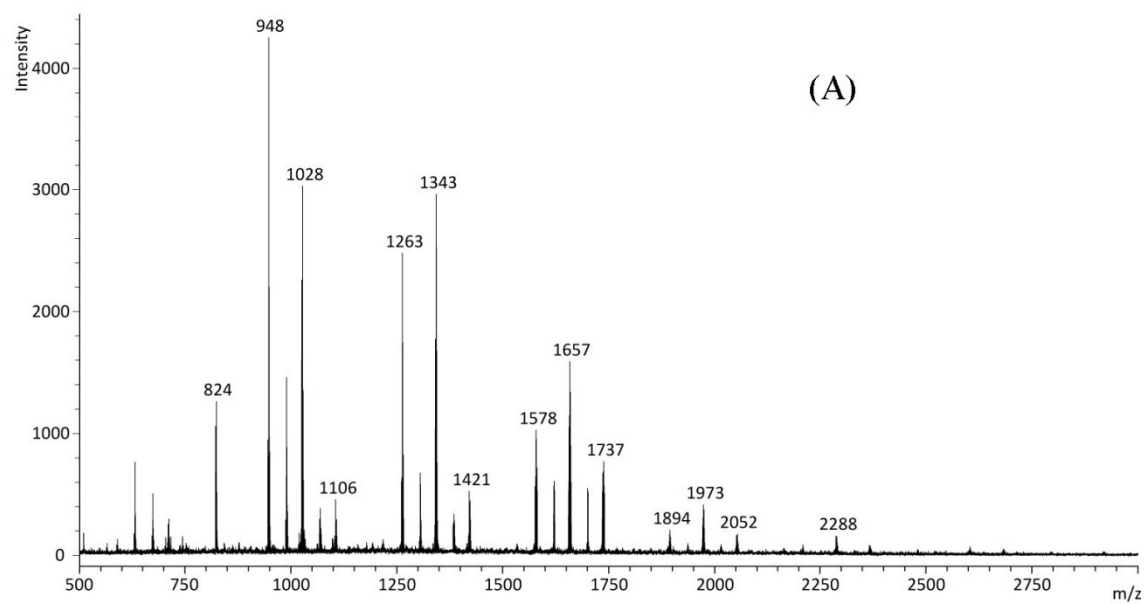


Figure SI 6. Lithiation of precursor monomer 4.

MALDI-TOF MS spectra of the poly(thiophene-*alt*-pyrrole)

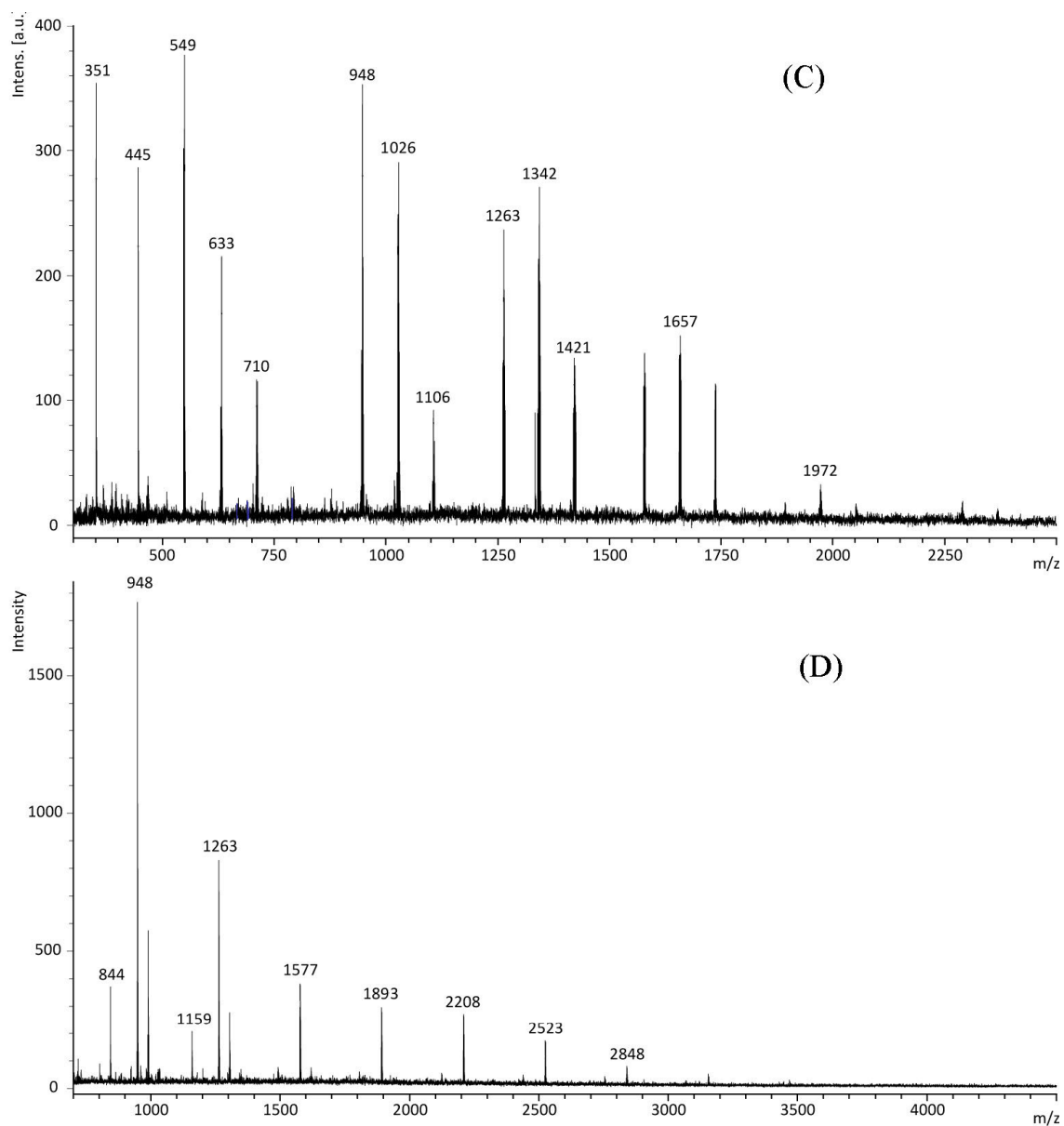


Figure SI 7. (A) polymer synthesized with $i\text{PrMgCl}$ and $[\text{Ni}(\text{dpp})\text{Cl}_2]$; (B) polymer synthesized with $t\text{BuMgCl}\cdot\text{LiCl}$, 15-crown-5 and $[\text{Ni}(\text{dpp})\text{Cl}_2]$; (C) polymer synthesized with $i\text{PrMgCl}$ and $[\text{Pd}(t\text{Bu}_3\text{P})_2]$ (Table1, entry 6); (D) polymer synthesized with $[i\text{PrMgCl}\cdot\text{LiCl}]$ and $[\text{Pd}(t\text{Bu}_3\text{P})_2]$ (Table1, entry 10).

NMR spectra for the kinetic study of the polymerization of **7**.

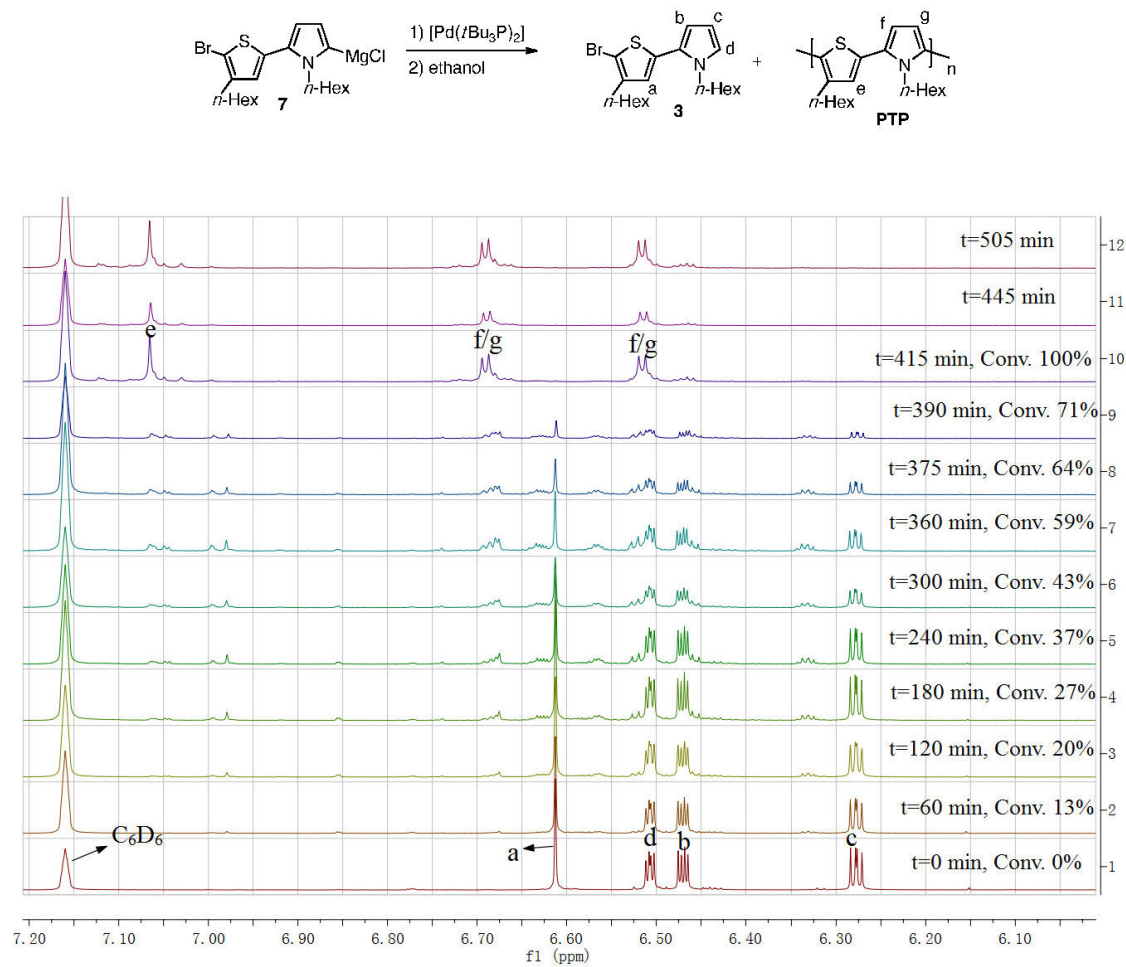
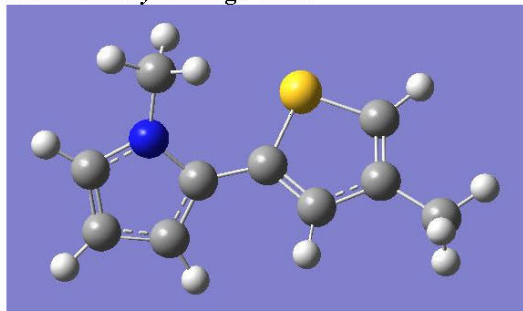


Figure SI 8. ^1H NMR spectra from the polymerization reaction

DFT calculations

The geometry of the compounds was optimized at the B3LYP level,^{1,2} using the Programme Gaussian 9.0, revision D01.³ The results were visualized with the program GaussView 5.0.⁴ The 6-31+G(d,p) basis set was used for Li, C, N and H.⁵⁻⁷ To estimate the key thermochemical properties, full geometry optimization was followed by vibrational frequency calculations. These confirmed that true minima (only positive frequencies) or transition states (one negative frequency) were obtained. They also allowed to obtain corrections for zero-point energy, internal energy, and free energy (at 298.15K) in the rigid-rotor harmonic oscillator limit. For comparison, the electronic energies, E , the zero-point energy corrected energies E_{ZPE} (at 0 K), enthalpies ΔH (at 298.15 K), and free energies ΔG (at 298.15 K) are given in atomic units. To appreciate the torsions, the dihedral angles between the planes of the heterocycles are also given. They were always measured from the heteroatom in one cycle across the connecting carbon atoms to the heteroatom in the adjacent cycle. The coordinates are presented in Å.

Monomer in *syn*-configuration

Atom nr.	Atom	x	y	z
1	C	-3.598011	-1.246702	0.012960
2	C	-2.258699	-1.204840	-0.313036
3	C	-1.913209	0.158935	-0.467949
4	C	-3.051563	0.920677	-0.230352
5	N	-4.082897	0.038196	0.065238
6	H	-4.250180	-2.084216	0.213849
7	H	-1.608559	-2.059755	-0.432671
8	H	-0.951142	0.563373	-0.748607
9	C	-3.170226	2.371058	-0.245436
10	C	-2.235189	3.271107	0.209321
11	S	-4.502387	3.235767	-1.006723
12	C	-2.564639	4.643856	-0.026557
13	H	-1.334425	2.951682	0.722156
14	C	-3.768943	4.772169	-0.665021
15	H	-4.280034	5.684721	-0.940609
16	C	-5.449810	0.378405	0.425345
17	H	-5.462057	1.227292	1.112130

18	H	-6.053174	0.631808	-0.452678
19	H	-5.902971	-0.480739	0.923414
20	C	-1.697239	5.797404	0.400344
21	H	-1.532374	5.792614	1.484005
22	H	-0.710965	5.750282	-0.075605
23	H	-2.150607	6.756074	0.135029

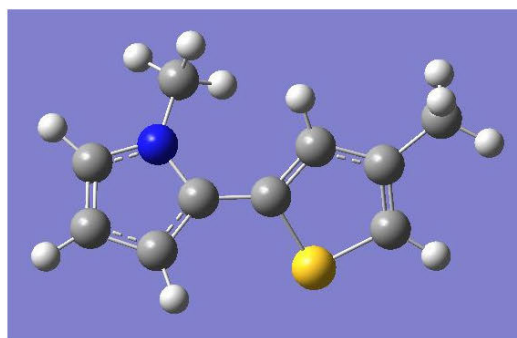
$$E = -840.643588092$$

$$E_{ZPE} = -840.458298$$

$$\Delta H = -840.445818$$

$$\Delta G = -840.496644$$

$$\text{Dihedral angle: } -45.5^\circ$$

Monomer in *anti*-configuration

Atom nr.	Atom	x	y	z
1	C	-3.605147	-1.291963	0.094243
2	C	-2.256375	-1.191437	0.363850
3	C	-1.929047	0.184999	0.336123
4	C	-3.089271	0.896898	0.053031
5	N	-4.114292	-0.029976	-0.098288
6	H	-4.248410	-2.156843	0.020982
7	H	-1.586735	-2.016029	0.562381
8	H	-0.962269	0.630086	0.524716
9	C	-3.268247	2.332067	-0.092675
10	C	-4.308638	3.152079	0.282426
11	S	-1.994621	3.286961	-0.835666
12	C	-4.100221	4.540213	-0.003661
13	H	-5.191178	2.785787	0.794802
14	C	-2.885147	4.757695	-0.595831
15	H	-2.459849	5.702955	-0.904792
16	C	-5.496824	0.244773	-0.448259
17	H	-6.104891	0.475075	0.434262
18	H	-5.546309	1.090913	-1.135711
19	H	-5.917813	-0.634293	-0.940628
20	C	-5.094478	5.619736	0.330222
21	H	-6.047630	5.459137	-0.187219
22	H	-5.311473	5.644268	1.404469
23	H	-4.721261	6.606067	0.042611

$$E = -840.627807000$$

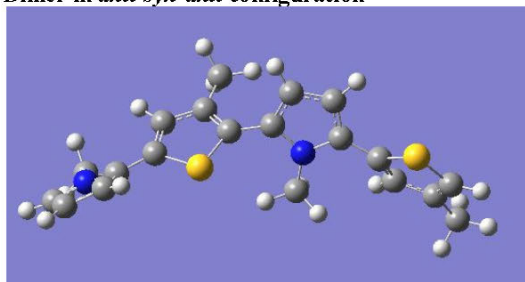
$$E_{ZPE} = -840.441907$$

$$\Delta H = -840.429540$$

$$\Delta G = -840.479843$$

Dihedral angle: -143.0°

Dimer in *anti-syn-anti* configuration



Atom	Atom	x	y	z
	C	-3.651073	-1.161035	0.403877
	C	-3.205025	-1.031856	1.702670
	C	-3.019031	0.349781	1.941613
	C	-3.360278	1.036893	0.781412
	N	-3.744597	0.088456	-0.160178
	H	-3.909465	-2.039178	-0.169979
	H	-3.037668	-1.841370	2.398617
	H	-2.696246	0.815003	2.862336
	C	-3.327620	2.467105	0.528524
	C	-4.152505	3.267606	-0.229244
	S	-2.088087	3.444493	1.291111
	C	-3.812732	4.656633	-0.217012
	H	-5.016837	2.886890	-0.761431
	C	-2.710831	4.926228	0.566415
	C	-4.140699	0.330218	-1.536454
	H	-5.207685	0.566900	-1.619982
	H	-3.566209	1.160762	-1.950354
	H	-3.936788	-0.566749	-2.124799
	C	-4.594345	5.693707	-0.977746
	H	-4.596368	5.476860	-2.052588
	H	-5.641196	5.715837	-0.653146
	H	-4.175251	6.690579	-0.828745
	C	-2.121195	6.228333	0.885813
	C	-2.633235	7.241372	1.684421
	C	-1.701738	8.299075	1.693630
	H	-3.577941	7.194811	2.207019
	C	-0.625476	7.924839	0.896224
	H	-1.793958	9.247946	2.202662
	C	0.581035	8.682433	0.600753
	C	1.309073	8.808675	-0.560871
	S	1.292298	9.678487	1.861176
	C	2.425468	9.700780	-0.464891
	H	1.035085	8.311698	-1.484498
	C	2.527374	10.250502	0.785022
	H	3.262289	10.962219	1.136119
	N	-0.884717	6.651389	0.411586
	C	-0.026065	5.887905	-0.480625

38	H	-0.216394	4.824221	-0.342139
39	H	-0.211192	6.139920	-1.531267
40	H	1.018860	6.097425	-0.248301
41	C	3.354540	10.001887	-1.610134
42	H	3.872531	9.098330	-1.952549
43	H	2.809342	10.406473	-2.470730
44	H	4.114659	10.732993	-1.322841

$$E = -1680.06131435$$

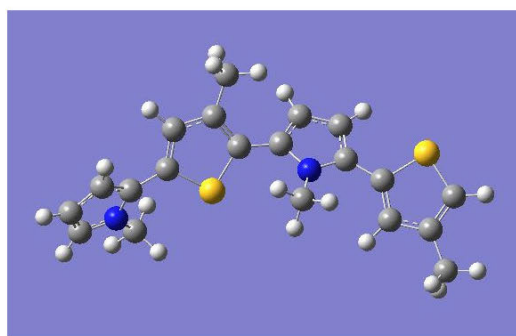
$$E_{ZPE} = -1679.709231$$

$$\Delta H = -1679.684762$$

$$\Delta G = -1679.765134$$

Dihedral angle: -145.6° , 73.4° , -142.6°

Dimer in *syn-syn-anti* conformation



Atom Nr.	Atom	x	y	z
1	C	-3.565279	-1.293821	0.097448
2	C	-2.762197	-1.139530	-1.013422
3	C	-2.623066	0.251230	-1.232852
4	C	-3.345189	0.916819	-0.247902
5	N	-3.920592	-0.051866	0.565219
6	H	-3.914304	-2.185457	0.597710
7	H	-2.333214	-1.938468	-1.601238
8	H	-2.082825	0.737150	-2.032802
9	C	-3.469255	2.352782	-0.055342
10	C	-2.489437	3.291424	-0.279852
11	S	-4.976680	3.161192	0.347485
12	C	-2.909311	4.648701	-0.145892
13	H	-1.474383	3.009153	-0.537712
14	C	-4.244125	4.759276	0.194966
15	C	-4.727125	0.168755	1.755013
16	H	-4.300406	0.970412	2.361342
17	H	-5.760252	0.432465	1.505588
18	H	-4.734928	-0.749306	2.345375
19	C	-1.974874	5.810533	-0.353762
20	H	-1.259200	5.899821	0.472683
21	H	-1.390134	5.679315	-1.270815
22	H	-2.521233	6.753339	-0.421252
23	C	-4.993964	5.964188	0.526768
24	C	-4.672014	6.968652	1.432386

1	C	-5.714025	7.915942	1.418214	24	C	-4.750411	6.940122	1.478737
2	H	-3.794452	6.972583	2.062661	25	C	-5.795050	7.884699	1.438255
3	C	-6.670675	7.482825	0.506234	26	H	-3.904929	6.928669	2.151484
4	H	-5.800621	8.801157	2.032158	27	C	-6.701289	7.474877	0.466873
5	C	-7.925626	8.118452	0.145075	28	H	-5.920931	8.751414	2.071088
6	C	-9.153849	7.575297	-0.160530	29	C	-7.928381	8.146385	0.067614
7	S	-8.018781	9.871842	0.097103	30	C	-8.115043	9.504160	-0.050926
8	C	-10.177969	8.541646	-0.421276	31	S	-9.459664	7.312745	-0.179336
9	H	-9.340858	6.507295	-0.157766	32	C	-9.458741	9.896367	-0.348256
10	C	-9.706469	9.822098	-0.305314	33	H	-7.296172	10.207417	0.055652
11	H	-10.257654	10.743761	-0.433970	34	C	-10.288744	8.812474	-0.456097
12	N	-6.221629	6.287909	-0.039719	35	H	-11.342356	8.806270	-0.700747
13	C	-6.821147	5.595780	-1.173117	36	N	-6.223849	6.295047	-0.084733
14	H	-6.031442	5.146258	-1.776362	37	C	-6.770172	5.630154	-1.261997
15	H	-7.505809	4.802765	-0.854199	38	H	-5.959686	5.137533	-1.799828
16	H	-7.374436	6.313437	-1.779630	39	H	-7.520288	4.878273	-0.997370
17	C	-11.599193	8.181467	-0.761512	40	H	-7.233438	6.371437	-1.914295
18	H	-11.652303	7.596646	-1.687267	41	C	-9.890822	11.325324	-0.539580
19	H	-12.057411	7.575934	0.028986	42	H	-9.708612	11.920055	0.362937
20	H	-12.213863	9.075259	-0.896053	43	H	-9.338435	11.802916	-1.357034
21					44	H	-10.956689	11.390944	-0.773118

$$E = -1680.06245192$$

$$E_{ZPE} = -1679.710327$$

$$\Delta H = -1679.685933$$

$$\Delta G = -1679.765589$$

Dihedral angles: -43.8°, -55.3°, -145.0°

Dimer in *syn-syn-syn* conformation

Atom	x	y	z
C	-3.545984	-1.283615	0.014435
C	-2.685902	-1.101936	-1.048593
C	-2.542473	0.293789	-1.230152
C	-3.319054	0.934829	-0.270625
N	-3.931842	-0.053640	0.489557
H	-3.916896	-2.187260	0.475865
H	-2.222691	-1.886204	-1.630149
H	-1.963302	0.799185	-1.989804
C	-3.459336	2.365832	-0.053902
C	-2.473947	3.312254	-0.213012
S	-4.987126	3.160361	0.295103
C	-2.905575	4.664837	-0.070462
H	-1.446787	3.038729	-0.429027
C	-4.255313	4.763489	0.210154
C	-4.802066	0.137679	1.638946
H	-4.411210	0.925721	2.285934
H	-5.821009	0.404949	1.340059
H	-4.838769	-0.793843	2.206699
C	-1.967779	5.834092	-0.210867
H	-1.278896	5.897260	0.640365
H	-1.353674	5.733695	-1.112647
H	-2.514067	6.777725	-0.265371
C	-5.024779	5.958731	0.533063

$$E = -1680.06154718$$

$$E_{ZPE} = -1679.709623$$

$$\Delta H = -1679.685105$$

$$\Delta G = -1679.765260$$

Dihedral angles: -43.5°, -55.6°, 45.7°

Dimer in *anti-anti-anti* configuration

This hypothetical structure could not be optimized as it was either too high in energy or did not exist as a stable structure.

DSC heating and cooling curves for PTP at 3 °C/min under N₂.

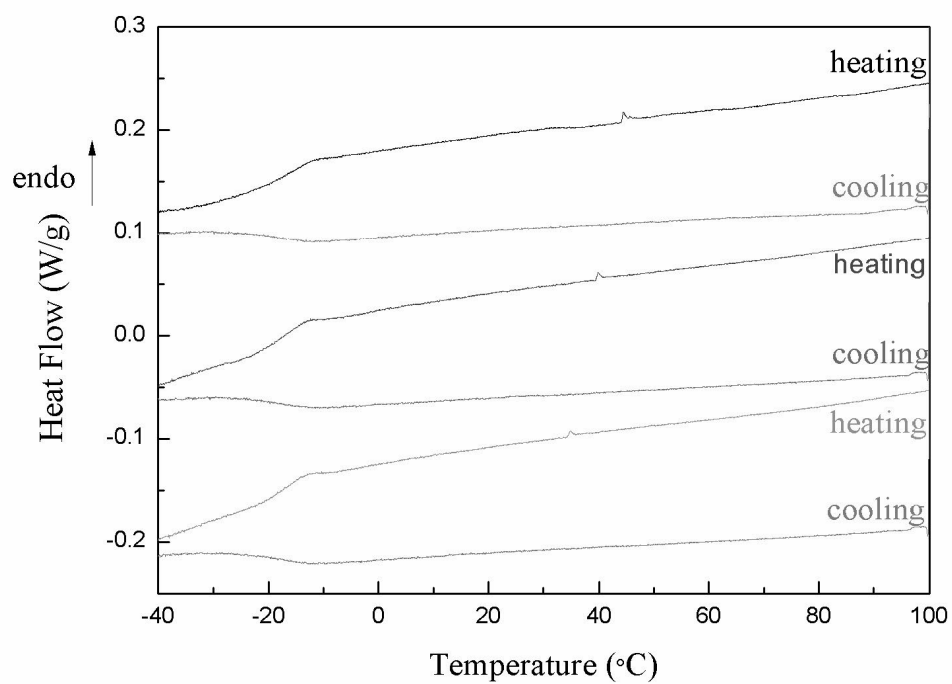


Figure SI 9. A sample of the polymer was subjected to DSC using three heating and cooling samples. All three measurements suggest a T_g of ca. -14 °C.

Synthesis**3-Bromothiophene (9)**

3-Bromothiophene was prepared similar to a method described by Bjørnholm et al.⁸ and was modified as follows: To a solution of thiophene (16.0 mL, 200 mmol), 48% aqueous HBr (100 mL) and diethyl ether (25 mL), a solution of bromine (33.4 mL, 650 mmol) in 48% aqueous HBr (80 mL) was added under vigorous stirring in a dropwise fashion within 3.5 h by using an addition funnel at 22 °C. The reaction mixture was stirred for another 19 h at 22 °C. Then the mixture was quenched by an aqueous saturated solution of Na₂S₂O₃ (150 mL). The aqueous layer was extracted with dichloromethane (3 x 100 mL). The combined organic phases were washed with brine (150 mL) and dried over MgSO₄. The solvent was removed *in vacuo* to receive a red brown oil, which was used in the subsequent step without further purification.

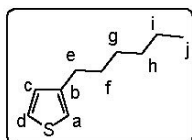
Zinc (52.5 g, 800 mmol) was dispersed in a mixture of water (240 mL) and acetic acid (50 mL) and heated to reflux for 30 min. Then the oil bath was removed and the red brown oil from the reaction described above was dissolved in acetic acid (50 mL) and added dropwise over the course of 3 h. After completion of the addition, the reaction mixture was heated up for another 4 h to reflux. The solution was filtered and the filter cake washed with *n*-hexane (50 mL). Then the aqueous phase was extracted with *n*-hexane (3 x 150 mL). The combined organic phase was dried over MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by vigreux distillation (50 °C, 6 mbar) to receive 15.6 g (48%, lit.⁸ 21%) of slightly yellow oil.

¹H NMR (500 MHz, CDCl₃): δ = 7.28 (dd, ³J = 5.1 Hz, ⁴J = 3.2 Hz, 1 H, H-d), 7.24 (dd, ⁴J = 3.2 Hz, ⁴J = 1.3 Hz, 1 H, H-a), 7.03 (dd, ³J = 5.1 Hz, ⁴J = 1.3 Hz, 1 H, H-c) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 130.0 (C-c), 126.6 (C-d), 122.7 (C-a), 110.0 (C-b) ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₄H₃BrS]⁺ 161.9139; Found 161.9143.

IR (ATR): $\tilde{\nu}$ = 3110 (m), 1493 (s), 1442 (w), 1399 (w), 1353 (m), 1195 (m), 1085 (m), 973 (w), 880 (s), 845 (s), 797 (w), 758 (vs), 677 (m), 621 (w), 584 (s) cm⁻¹.

3-Hexylthiophene (10)

3-Hexylthiophene was prepared similarly to a method described by Ng et al.⁹ and was modified as follows: magnesium (2.55 g, 105 mmol) was stirred without solvent under nitrogen for 1 h in order to activate the surface. A solution of 1-bromohexane (14.9 g, 90.0 mmol) in dry diethyl ether (75 mL) was added dropwise to a suspension of the activated magnesium in diethyl ether (45 mL) within 1 h at 20 °C. The reaction mixture was heated to reflux for another 1 h. The resulting Grignard reagent was added to 3-bromothiophene (12.23 g, 75.00 mmol) and [Ni(dppp)Cl₂] (81 mg, 15 mmol, 0.2 mol%) in diethyl ether (45 mL) at 0 °C via syringe over the course of 30 min and the mixture was stirred for 4 h at 20 °C. The reaction mixture was quenched with aqueous hydrochloric acid (1 M, 60 mL) at 0 °C. Then the aqueous layer was extracted with diethyl ether (4 x 50 mL). The combined organic layers were dried over MgSO₄ and the volatiles were removed *in vacuo*. The residue was purified by vigreux distillation (110 °C, 6 mbar) to yield 10.2 g (81%, lit.⁹ 71%) of colorless oil.

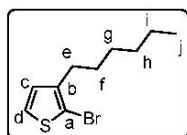
¹H NMR (500 MHz, CDCl₃): δ = 7.24 (dd, ³J = 4.9 Hz, ⁴J = 2.9 Hz, 1 H, H-d), 6.95 (dd, ³J = 4.9 Hz, ⁴J = 1.2 Hz, 1 H, H-c), 6.93 (dd, ⁴J = 2.9 Hz, ⁴J = 1.2 Hz, 1 H, H-a), 2.64 (t, ³J = 7.6 Hz, 2 H, H-e), 1.66-1.60 (m, 2 H, H-f), 1.38-1.30 (m, 6 H, H-g, h, i), 0.91 (t, ³J = 7.0 Hz, 3 H, H-j) ppm.

^{13}C NMR (126 MHz, CDCl_3): δ = 143.3 (C-b), 128.3 (C-c), 125.0 (C-d), 119.8 (C-a), 31.7, 30.5, 30.3, 29.0 (C-e, f, g, h), 22.6 (C-i), 14.1 (C-j) ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{10}\text{H}_{16}\text{S}]^+$ 168.0973; Found 168.0972.

IR (ATR): $\tilde{\nu}$ = 2995 (m), 2925 (s), 2855 (m), 1537 (w), 1478 (m), 1409 (w), 1377 (w), 1234 (w), 1153 (w), 1079 (w), 936 (w), 855 (m), 834 (m), 769 (s), 680 (m), 660 (w), 632 (m), 577 (w) cm^{-1} .

2-Bromo-3-hexylthiophene (11)



2-Bromo-3-hexylthiophene was prepared similarly to a method described by Carlsen et al.¹⁰ and was modified as follows: 3-hexylthiophene (12.0 g, 71.3 mmol) was dissolved in glacial acetic acid (100 mL) under an air atmosphere. Then NBS (12.7 g, 71.5 mmol) was added in one portion. The reaction mixture was stirred for 2.5 h at 22 °C. Then the solution was poured into water (200 mL) and diethyl ether (250 mL). After extraction, the organic phase was separated and washed with aqueous NaOH (2 M, 5 x 150 mL), followed by water (3 x 150 mL). The organic layer was dried over MgSO_4 and then the solvent was removed *in vacuo*. The crude product was purified by vigreux distillation (130 °C, 4×10^{-2} mbar) to receive 13.5 g (77%, lit.¹⁰ 92%) of light yellow oil.

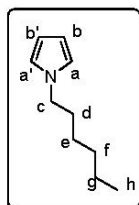
^1H NMR (500 MHz, CDCl_3): δ = 7.18 (d, $^3J = 5.6$ Hz, 1 H, H-d), 6.79 (d, $^3J = 5.6$ Hz, 1 H, H-c), 2.56 (t, $^3J = 7.6$ Hz, 2 H, H-e), 1.60-1.54 (m, 2 H, H-f), 1.36-1.27 (m, 6 H, H-g, h, i), 0.88 (t, $^3J = 7.0$ Hz, 3 H, H-j) ppm.

^{13}C NMR (126 MHz, CDCl_3): δ = 142.0 (C-b), 128.2 (C-c), 125.1 (C-d), 108.8 (C-a), 31.6, 29.7, 29.4, 28.9 (C-e, f, g, h), 22.6 (C-i), 14.1 (C-j) ppm.

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{10}\text{H}_{15}\text{BrS}]^+$ 246.0078; Found 246.0086.

IR (ATR): $\tilde{\nu}$ = 2995 (m), 2924(s), 2855(m), 1539(w), 1457 (m), 1409(m), 1377 (w), 1275(w), 1261(w), 1228(w), 1087(w), 991(s), 874(w), 829(m), 764(s), 750(s), 711(s), 683(s), 634(s), 580(m), 466(w) cm^{-1} .

1-Hexyl-1H-pyrrole (12)



1-Hexyl-1H-pyrrole was prepared similarly to a method described by Piomelli et al.¹¹ and was modified as follows: pyrrole (10.0 mL, 144 mmol) was added dropwise over the course of 30 min at 0 °C to a stirred solution of sodium hydride (10.7g of 60% mineral oil dispersion, 267 mmol) in DMF (320 mL). After hydrogen evolution had ceased, 1-bromohexane (29.6 mL, 210 mmol) was added in one portion. The reaction mixture was allowed to warm up to 20 °C within 15 min by removing the cooling bath and it was stirred at 20 °C for 9 h. The reaction was quenched by adding water (80 mL). DCM (100 mL) was added and the organic layer was washed with water (6 x 300 mL) and dried over MgSO_4 . After the solvent was removed *in vacuo*, the product (17.54 g, 81%) was obtained by vigreux distillation (115 °C, 6 mbar) as colorless oil.

^1H NMR (500 MHz, CDCl_3): δ = 6.68 (a t, $^{12}J = 2.1$ Hz, 2 H, H-a, a'), 6.16 (a t, $^{12}J = 2.1$ Hz, 2 H, H-b, b'), 3.89 (t, $^3J = 7.2$ Hz, 2 H, H-c), 1.81-1.76 (m, 2 H, H-d), 1.36-1.32 (m, 6 H, H-e, f, g), 0.92 (t, 3 H, $^3J = 6.8$ Hz, H-h) ppm.

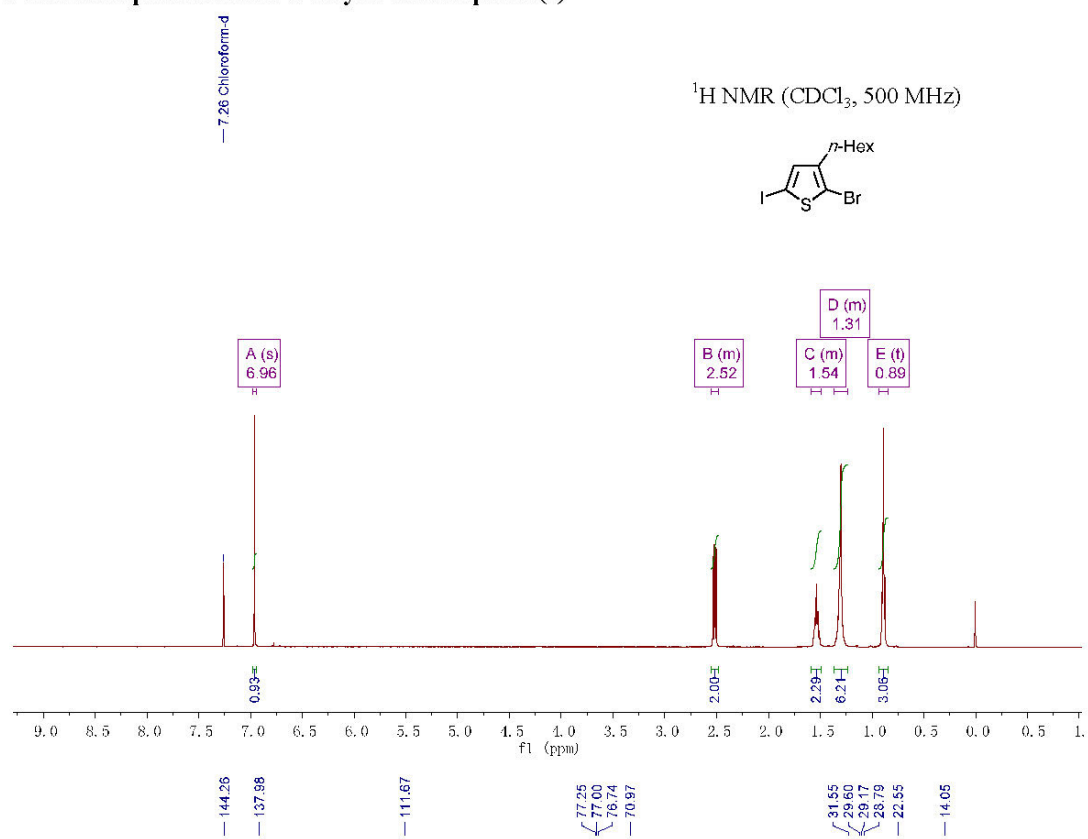
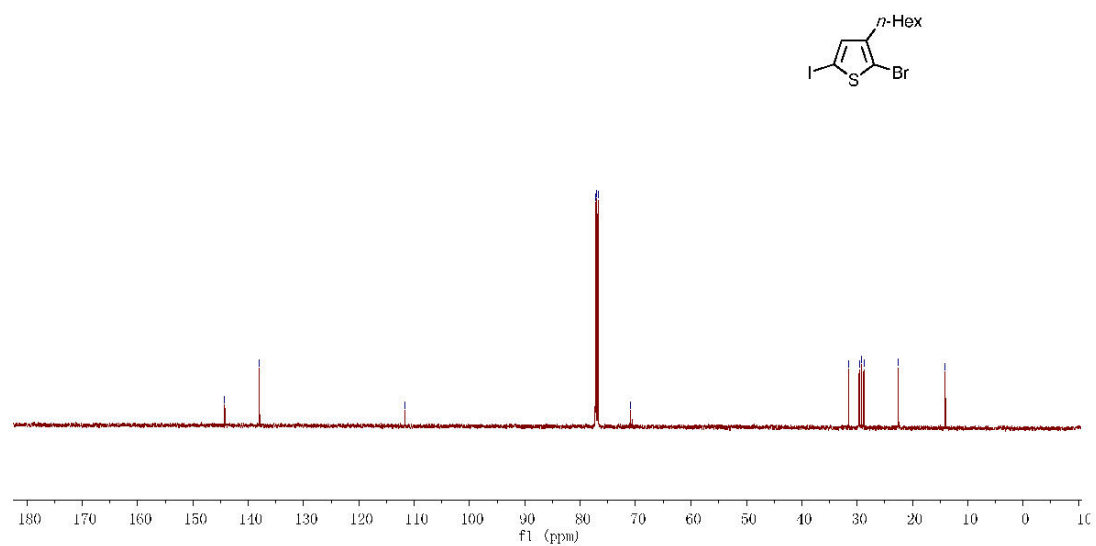
^{13}C NMR (126 MHz, CDCl_3): δ = 120.5 (C-a, a'), 107.8 (C-b, b'), 49.7 (C-c), 31.6 (C-d), 31.4 (C-e), 26.5 (C-f), 22.5 (C-g), 14.0 (C-h) ppm.

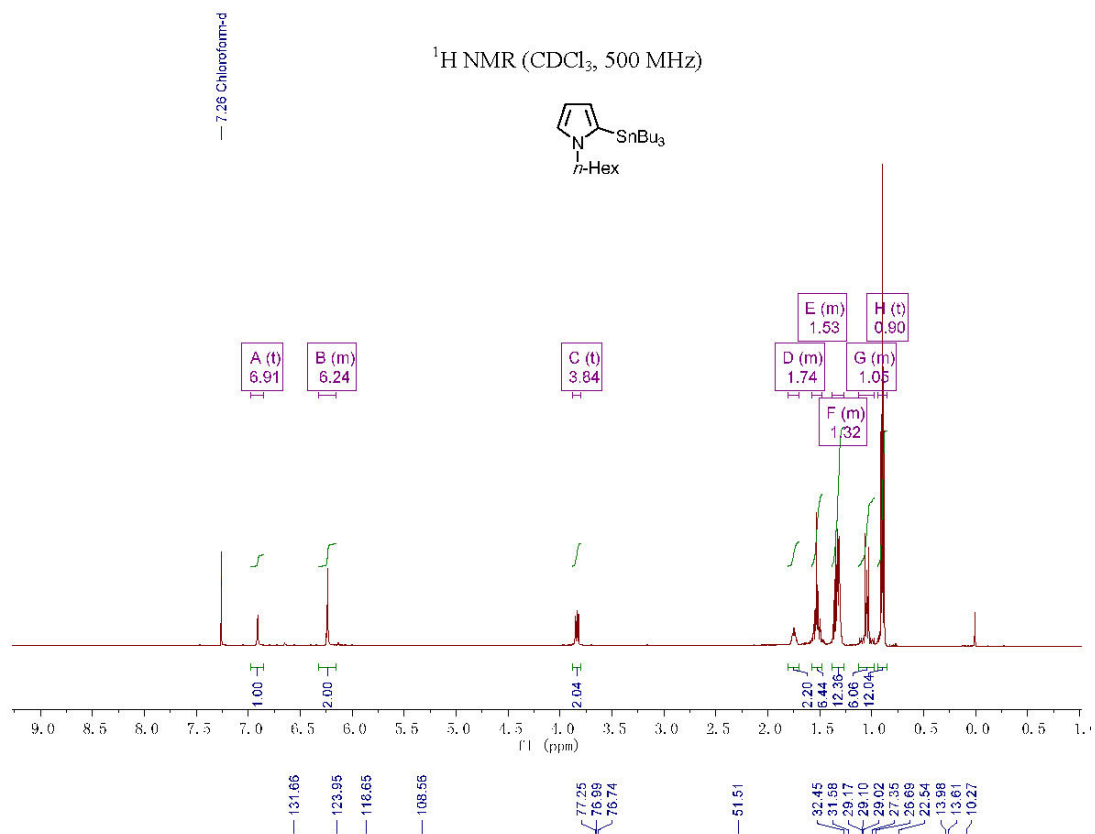
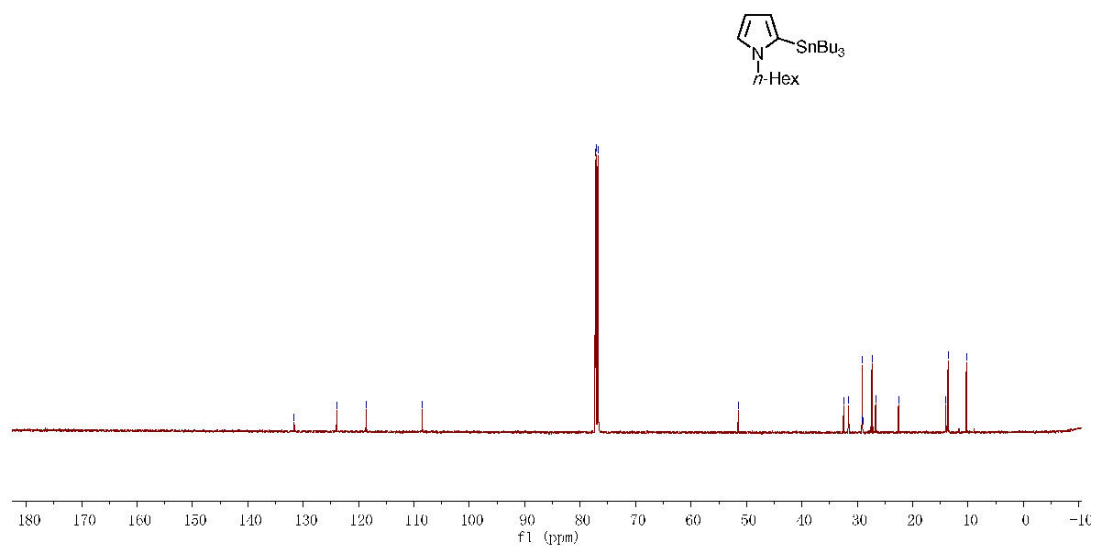
HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{10}\text{H}_{17}\text{N}]^+$ 151.1361; Found 151.1363.

IR (ATR): $\tilde{\nu}$ = 2957 (m), 2928 (s), 2858 (m), 1537 (w), 1500 (s), 1465 (w), 1377 (w), 1281 (s), 1088 (s), 1063 (m), 968 (w), 716 (vs), 650 (w), 616 (s) cm^{-1} .

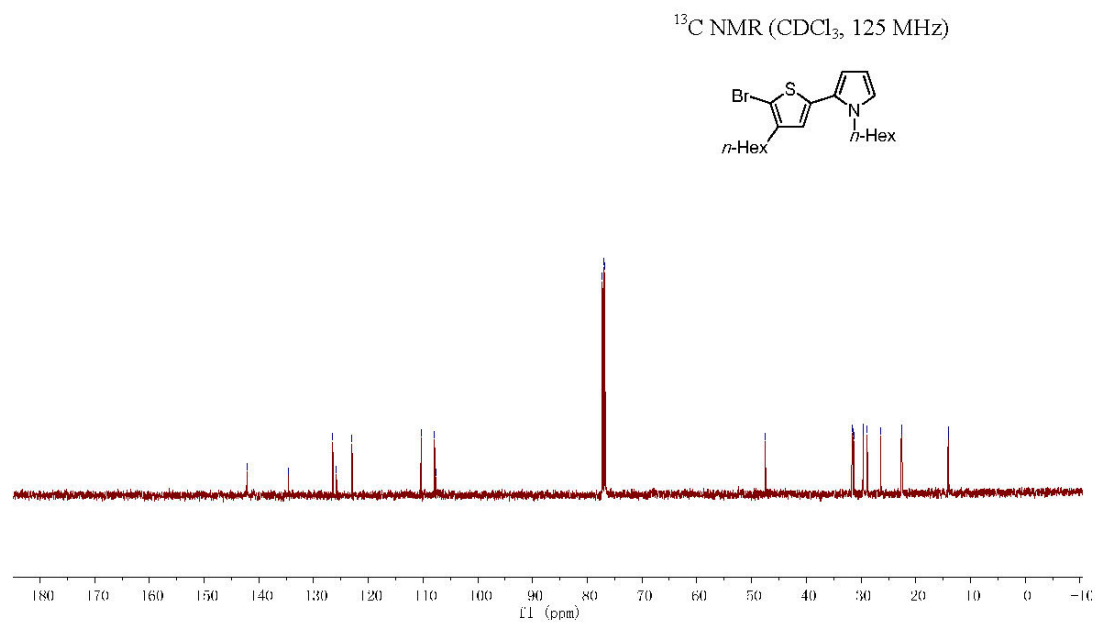
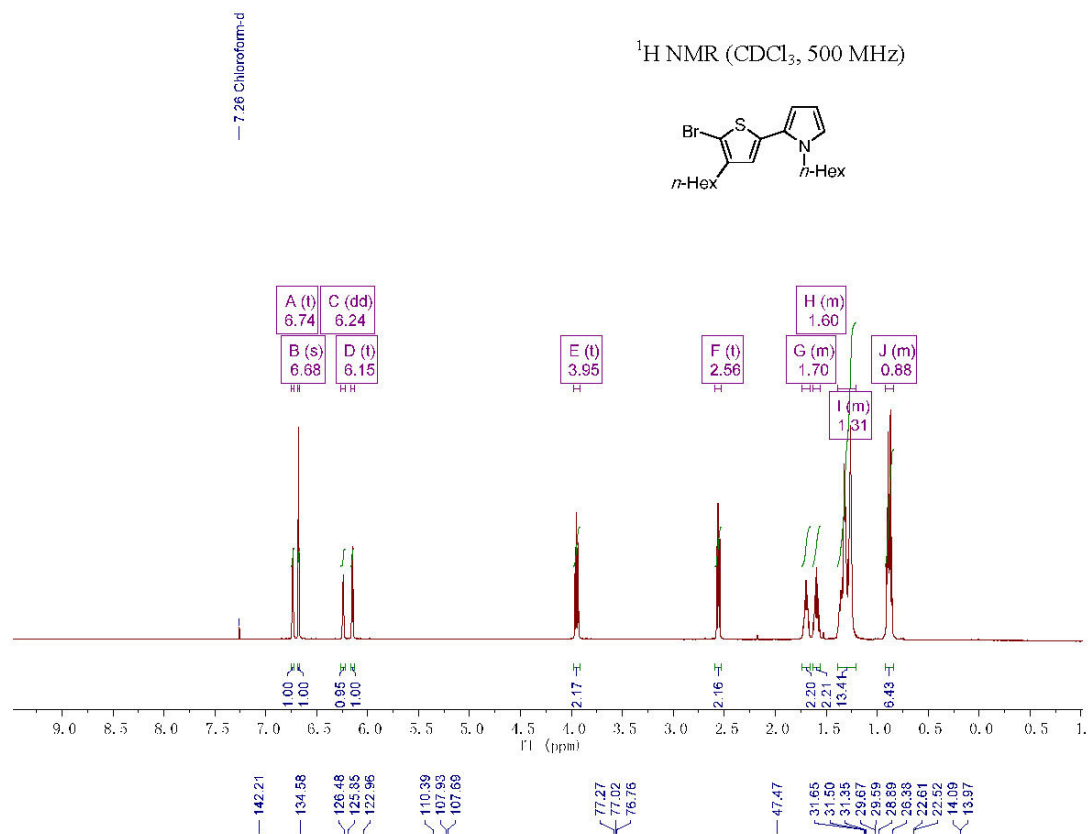
NMR Spectra

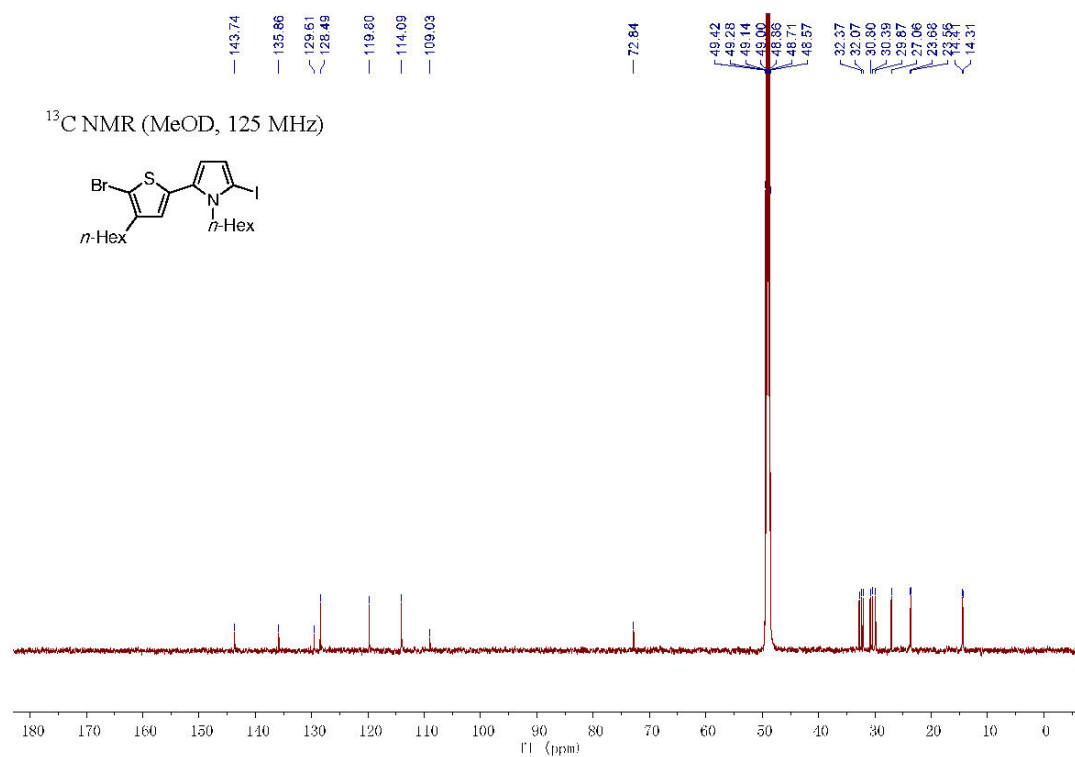
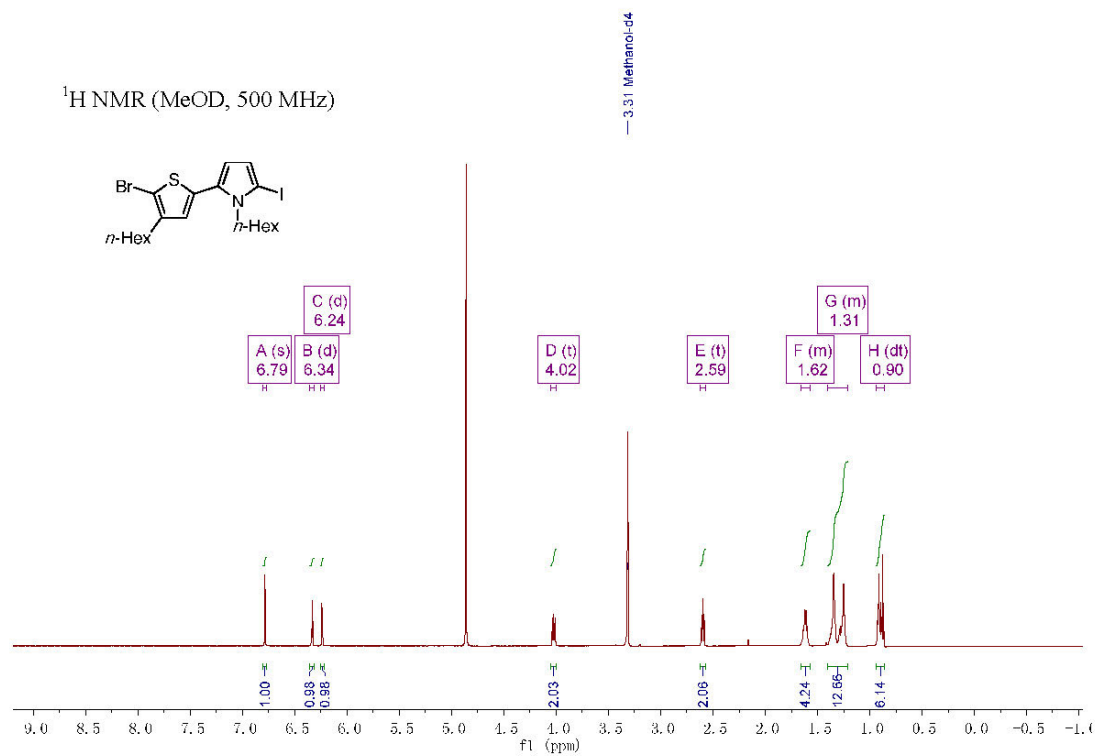
3-Bromothiophene2-Bromo-3-hexyl-5-iodothiophene (1)

¹³C NMR (CDCl₃, 125 MHz)

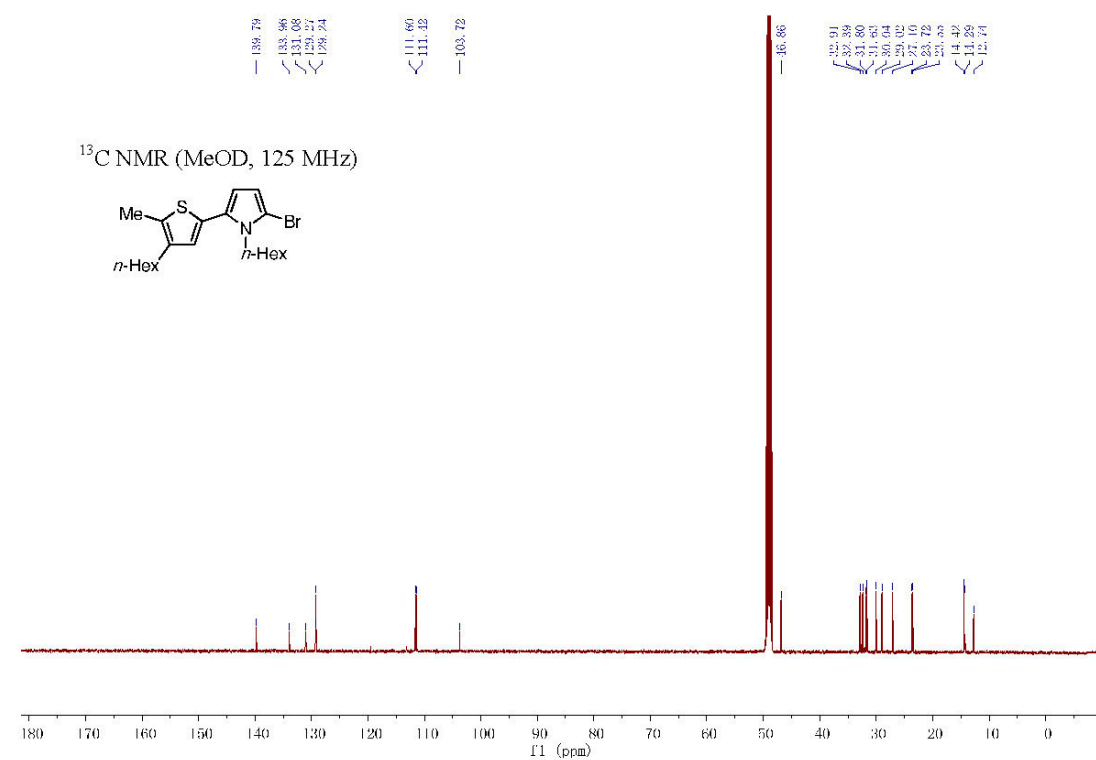
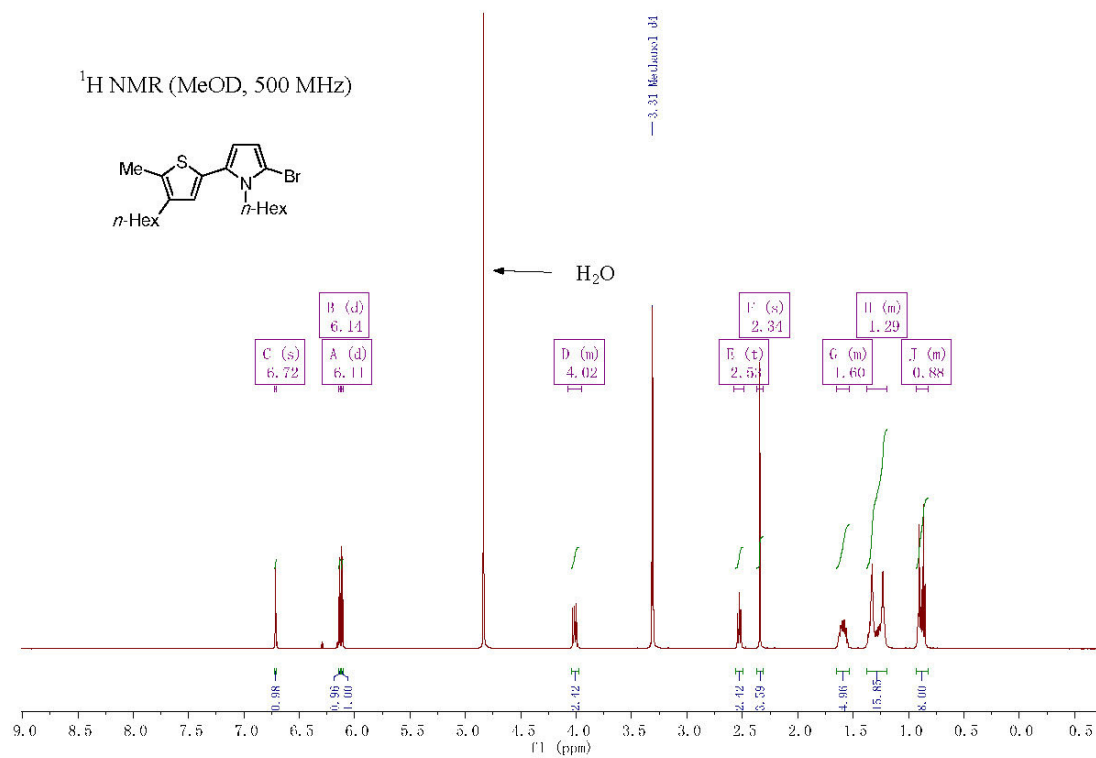
1-Hexyl-2-(tributylstannyl)-1*H*-pyrrole (2)¹³C NMR (CDCl₃, 125 MHz)

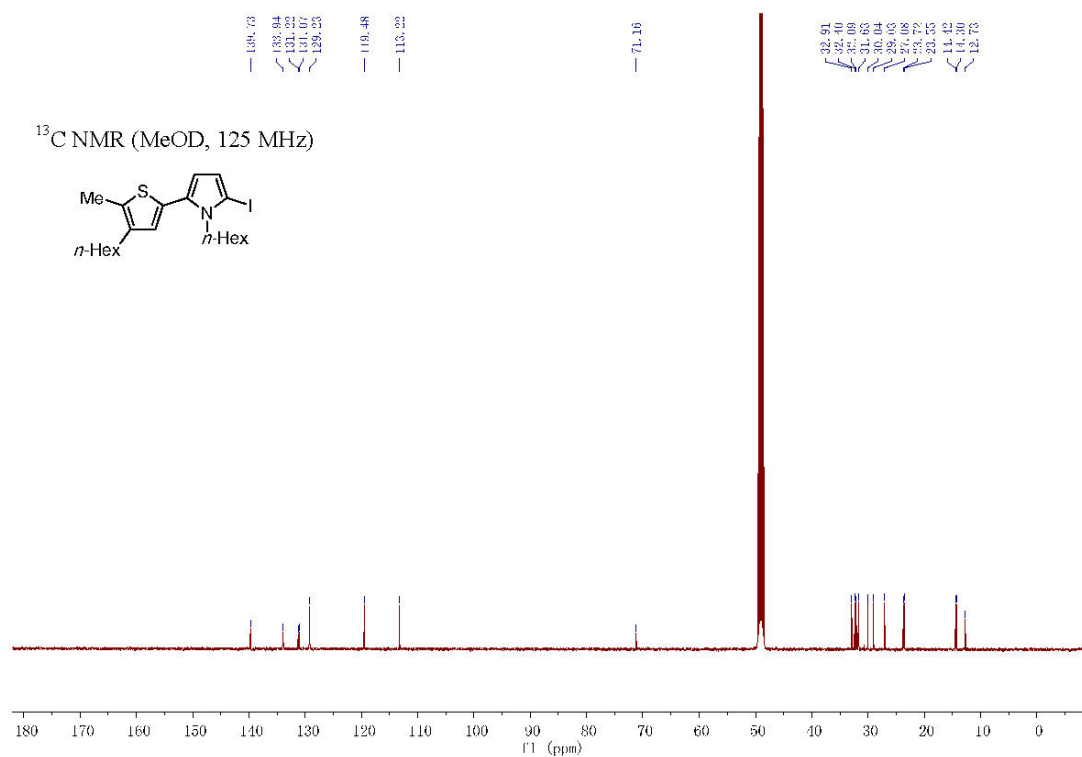
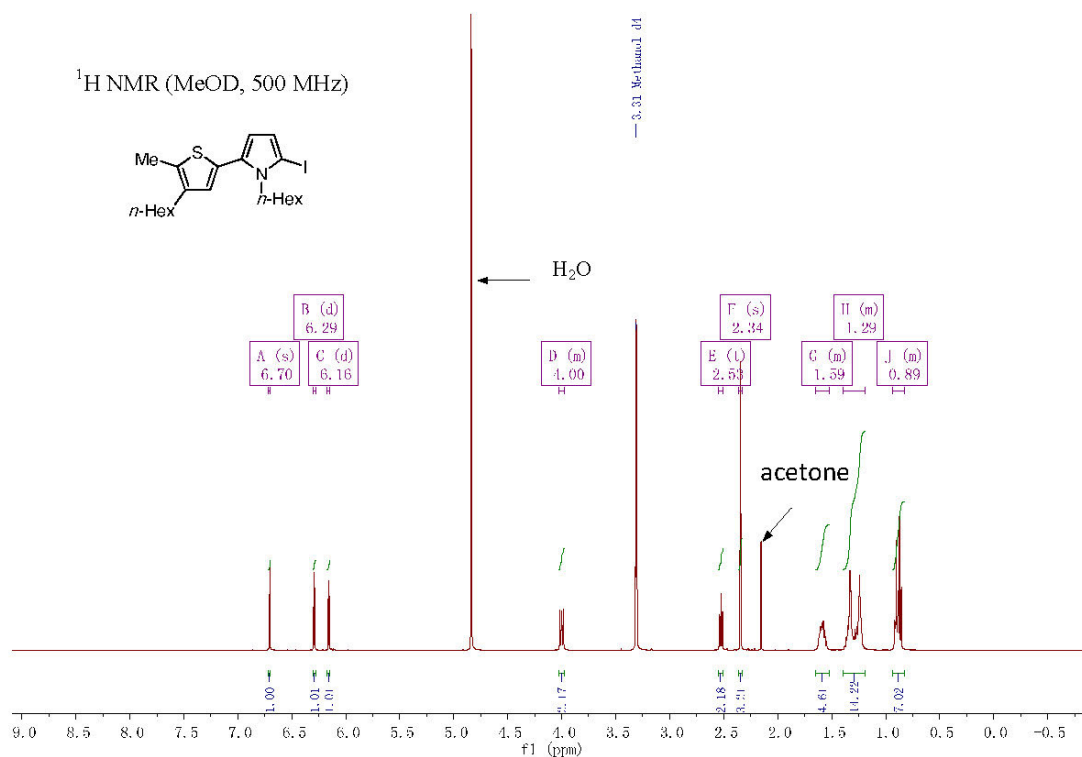
2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-1H-pyrrole (3)



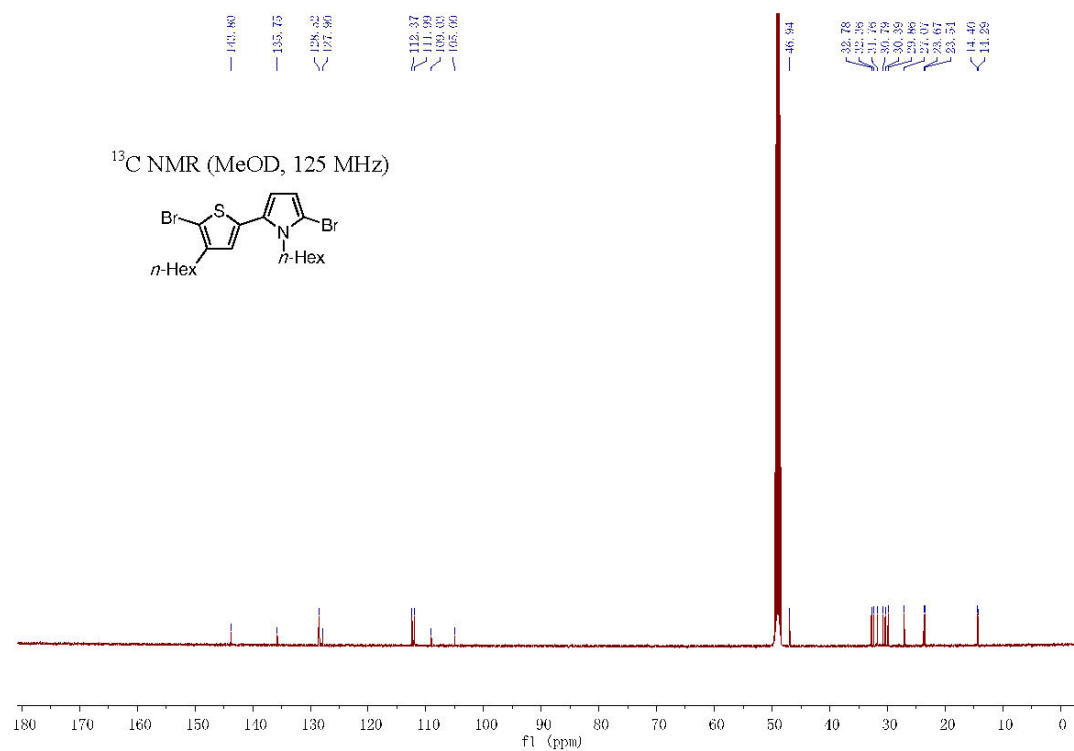
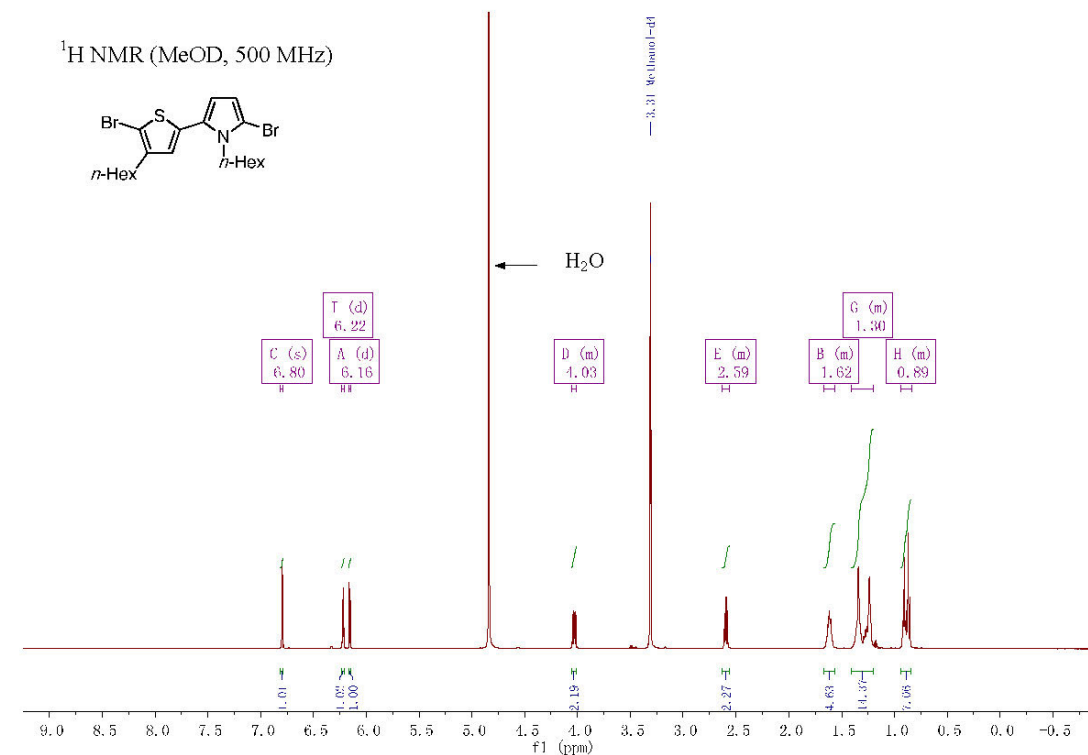
2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-5-iodo-1*H*-pyrrole (4)

2-Bromo-1-hexyl-5-(4-hexyl-5-methylthiophen-2-yl)-1H-pyrrole (5)

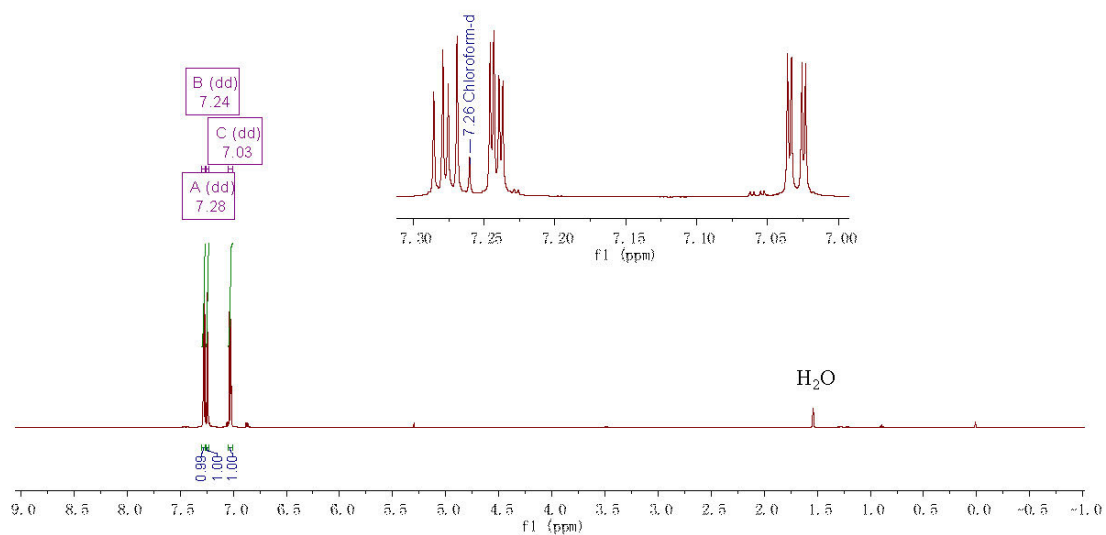
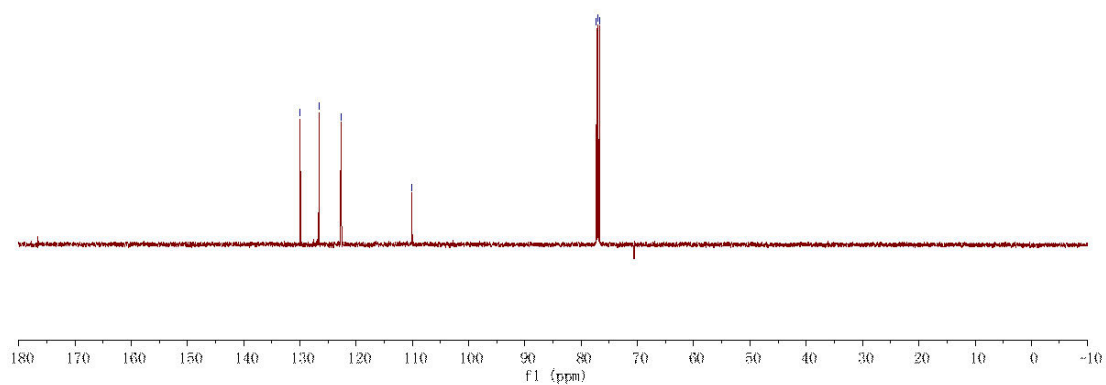


1-Hexyl-2-(4-hexyl-5-methylthiophen-2-yl)-5-iodo-1*H*-pyrrole (**6**)

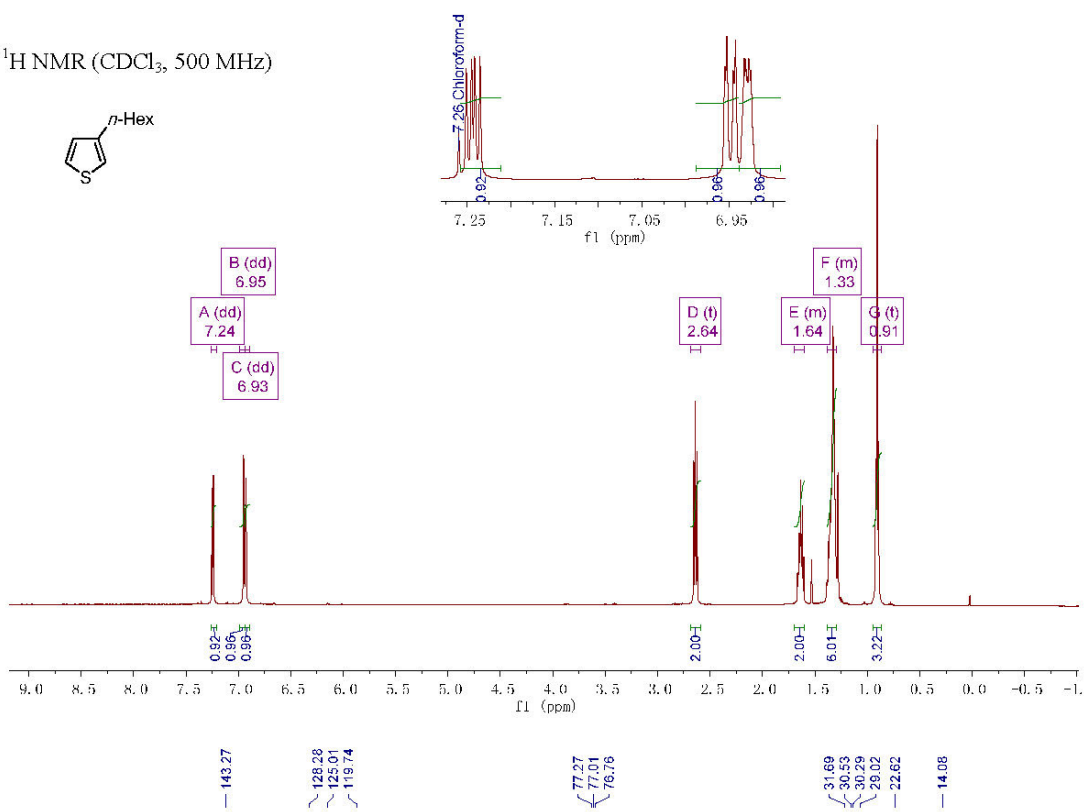
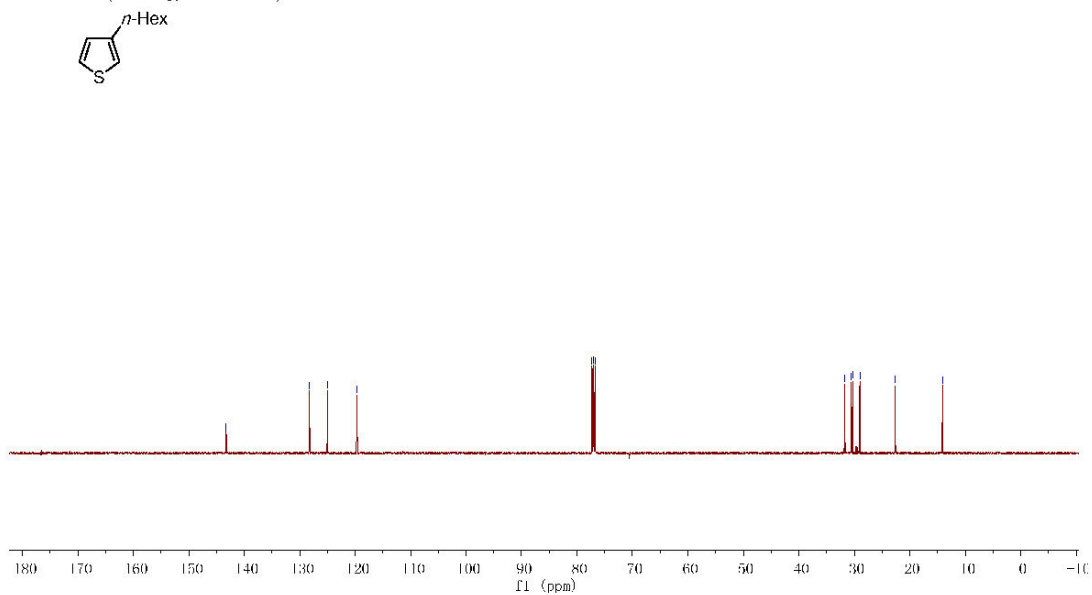
2-Bromo-5-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-1H-pyrrole (8)



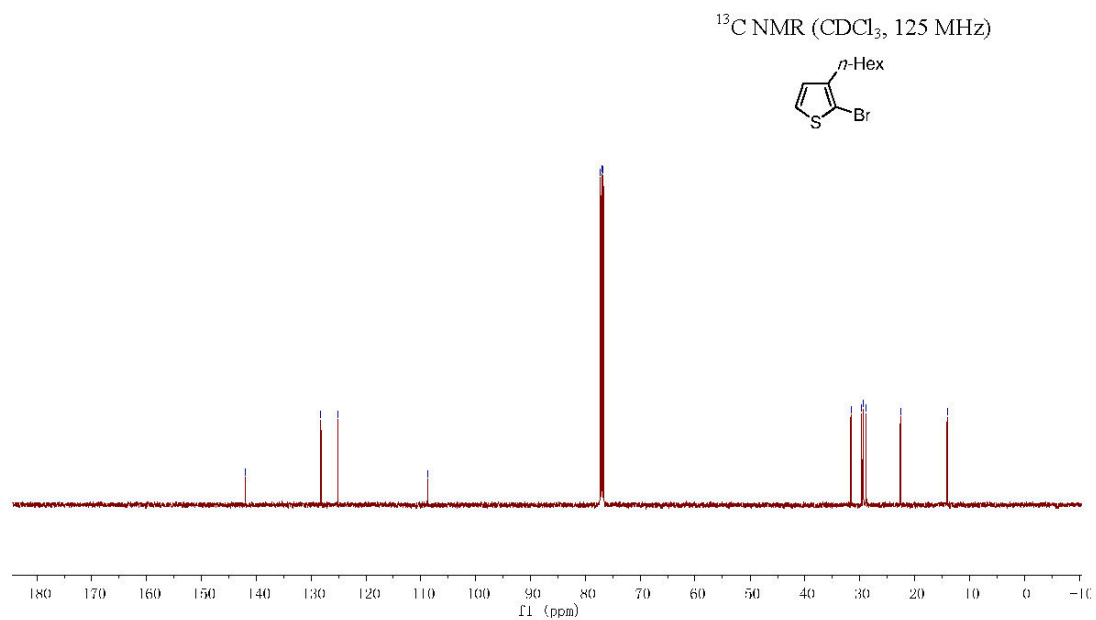
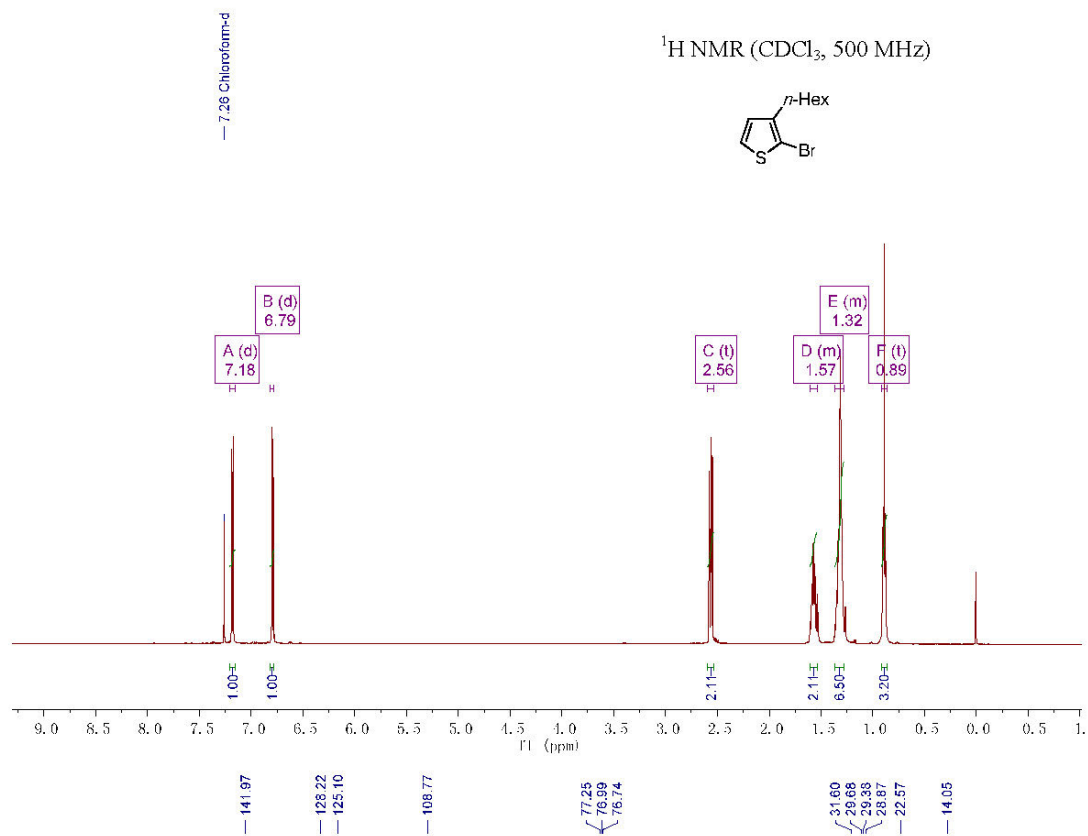
3-Bromothiophene (9)

 ^1H NMR (CDCl_3 , 500 MHz) ^{13}C NMR (CDCl_3 , 125 MHz)

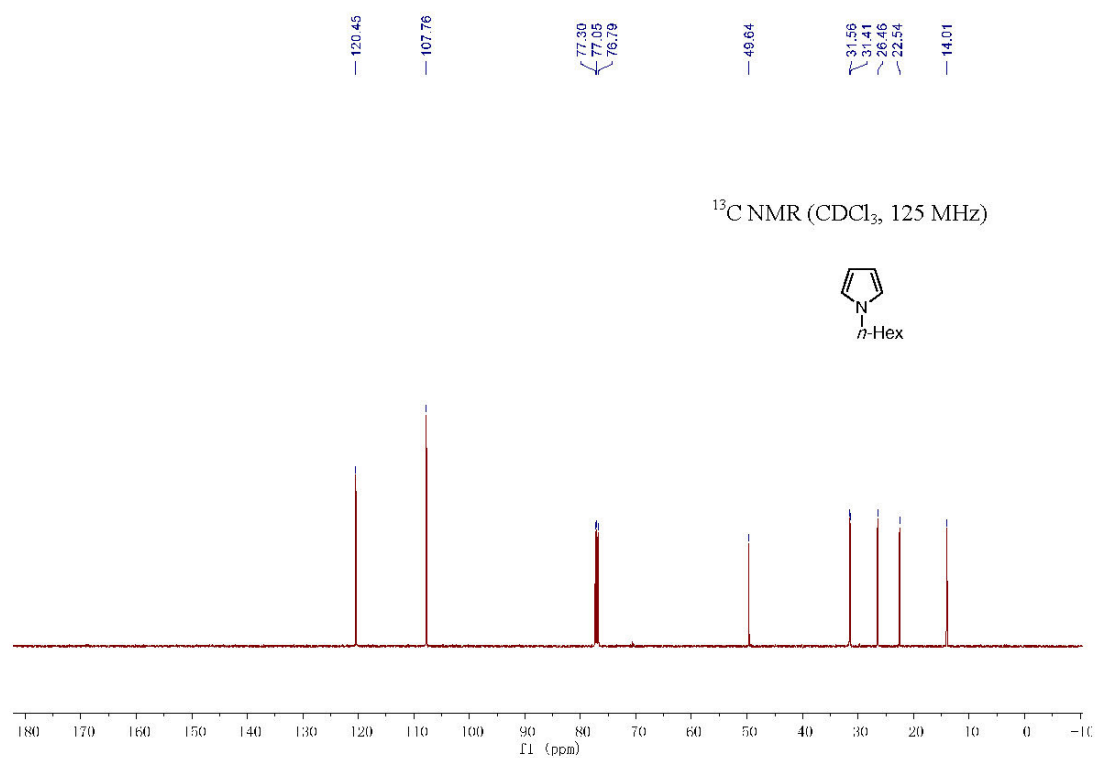
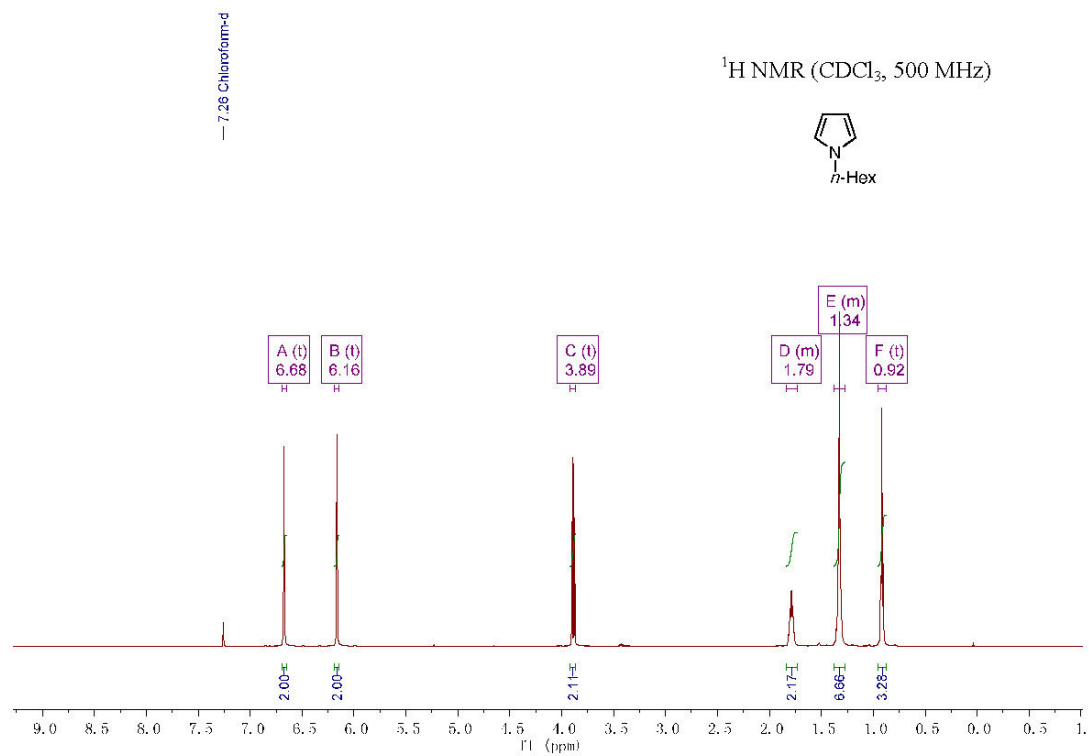
3-Hexylthiophene (10)

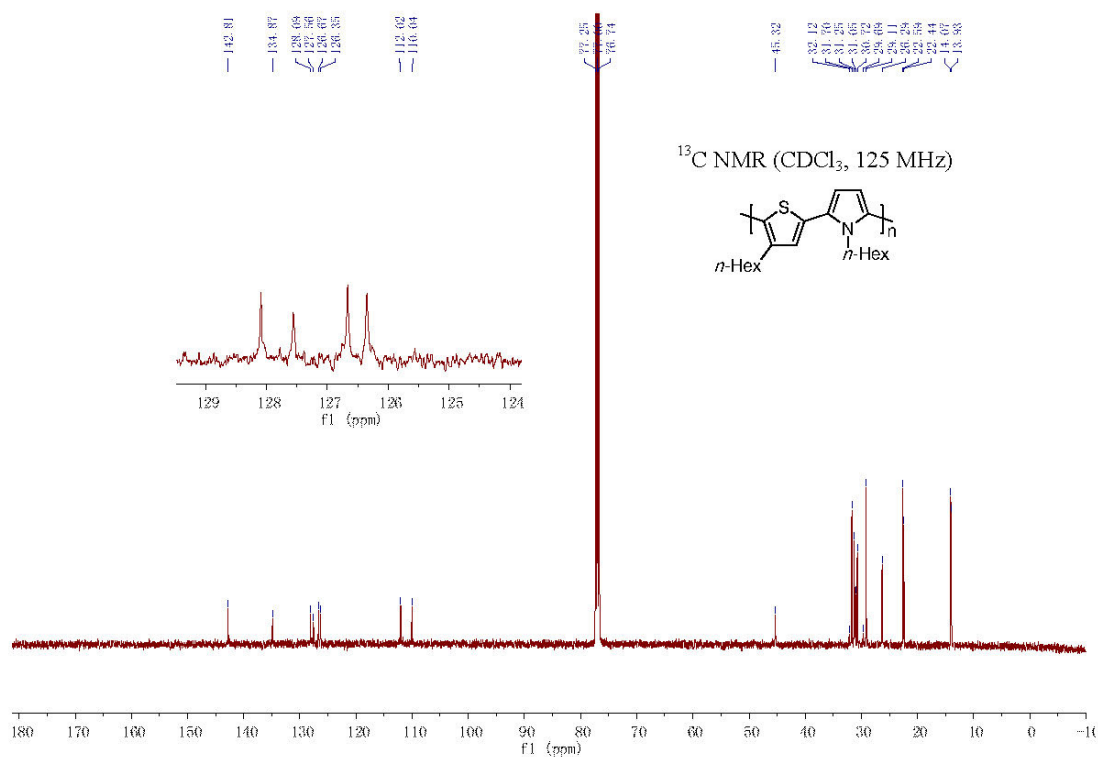
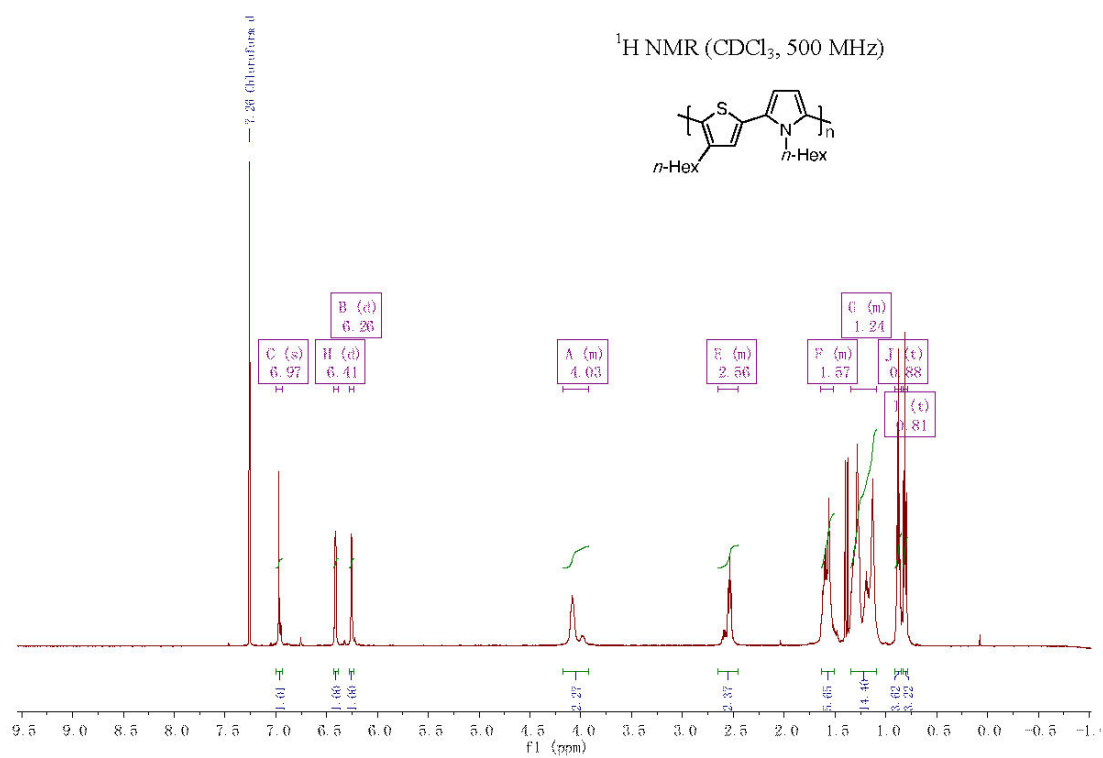
 ^1H NMR (CDCl_3 , 500 MHz) ^{13}C NMR (CDCl_3 , 125 MHz)

2-Bromo-3-hexylthiophene (11)



1-Hexyl-1H-pyrrole (12)



Poly(thiophene-*alt*-pyrrole) (PTP) (of Table 2, entry 9)

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4. Gaussian, Inc. 340 Quinnipiac St Bldg 40, Wallingford, CT 06492 USA, Copyright 2000-2008 Semichem. Inc. Authors: R. D. Dennington II, T. A. Keith, J. M. Millan.
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5.3 General methods and materials for unpublished syntheses

All syntheses were carried out using standard Schlenk techniques or in glovebox under a dry and inert nitrogen atmosphere unless stated otherwise. Glassware and NMR-tubes were dried in an oven at 200 °C for at least 2 h prior to use. Reaction vessels were heated under vacuum and purged with nitrogen three times before adding reagents.

Analyses

^1H NMR, ^{13}C NMR, ^{11}B NMR and ^{119}Sn NMR spectra were recorded at 300 K. ^1H NMR spectra were recorded on a Bruker DRX 500 (500 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker DRX 500 (125 MHz) spectrometer. ^{11}B NMR and ^{119}Sn NMR spectra were recorded on a Bruker DRX 500 (160 MHz) spectrometer. All ^1H NMR and ^{13}C NMR spectra were referenced against the residual solvent peak. ^{11}B NMR spectra were referenced against $\text{BF}_3\cdot\text{OEt}_2$ in CDCl_3 , the reference of the ^{119}Sn NMR spectra was calculated based on the ^1H NMR signal of TMS. The exact assignment of the peaks was proved by ^1H , ^{13}C DEPT and two-dimensional NMR spectroscopy such as ^1H COSY, ^{13}C HSQC or $^1\text{H}/^{13}\text{C}$ HMBC when possible.

IR spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer with a A531-G Golden-Gate-ATR-unit. Ultra High resolution ESI mass spectra were recorded on a Bruker Daltonics Apex IV Fourier transform Ion Cyclotron resonance mass spectrometer. High resolution EI mass spectra were run on a VG Analytical Autospec apparatus. UV/Vis spectra were recorded on a Perkin Elmer Lambda14 spectrometer. Luminescence spectra were recorded on a Perkin Elmer LS55 spectrometer.

M_n and M_w were determined on a Viscotek GPCmax VE2001, equipped with a Viscotek VE3580 RI detector (columns: ViscotekLT5000L 300 x 7.8 mm and LT4000L 300 x 7.8 mm).

GC-MS analysis was performed on a Hewlett Packard 5890A gas chromatograph, equipped with a Hewlett Packard 5972A mass selective detector and an Agilent Technologies dimethylpolysiloxane column (19091S-931E, nominal length 15 m, 0.25 mm diameter, 0.25 μm grain size).

GC analysis was performed on an Agilent Technologies 6890N gas chromatograph, equipped with an Agilent Technologies 7683 Series Injector, an Agilent Technologies

(5 %-phenyl)-methylpolysiloxane column (19091J-413, nominal length 30 m, 0.32 mm diameter, 0.25 μm grain size) and a flame ionization detector (FID).

Reactions under microwave irradiation were carried out using a Biotage[®] Initiator+ SP Wave synthesis system, with continuous irradiation power from 0 to 300 W (Organic Synthesis Mode). The temperature was measured with an external IR sensor during microwave heating. All reactions were carried out in 5 mL oven-dried Biotage microwave vials sealed with an aluminum/Teflon[®] crimp top, which can be exposed to a maximum of 250 °C and 20 bar internal pressure.

Chemicals

All reagents were used without further purification unless noted otherwise.

Compound	Supplier	Purity
<i>n</i> -Butyllithium	Acros Inc.	2.5 M in hexane
Tributyltin chloride	Acros Inc.	95 %
Tetramethylethyldiamine	Acros Inc.	99.5 %
Magnesium sulfate	Grüssing Inc.	99 %
[Pd(PPh ₃) ₄]	ABCR Inc.	99 %
[Pd(PtBu ₃) ₂]	Strem Chemicals Inc.	>98 %
Diisopropylamine	Fischer Scientific Inc.	99%
Trimethyltin chloride	Sigma-Aldrich Inc.	-
Isopropylmagnesium chloride solution	Sigma-Aldrich Inc.	2 M in THF
N-iodosuccinimide	Molekula Inc.	95%
Acetic acid	Grüssing Inc.	99.5 %
Natriumthiosulfat	Grüssing Inc.	97 %
Potassium phosphate tribasic	Sigma-Aldrich Inc.	97%
Iodine	Acros Inc.	99.5%
Hexamethyldistannane	Sigma-Aldrich Inc.	99%

Solvents

All solvents that were used for reactions were used freshly distilled after refluxing for several hours over the specified drying agent under nitrogen and were stored in a J. Young's tube. If no drying agent is noted, the solvents were used for chromatography only and distilled for purification purposes.

Solvent	Supplier or grade before distillation, drying procedure if applicable
CHCl ₃	VWR Inc., HPLC grade

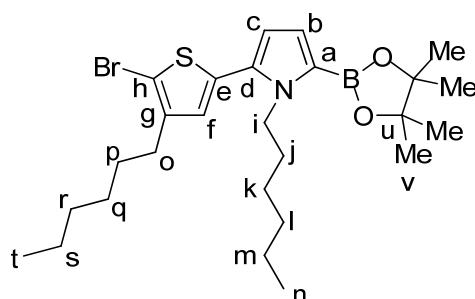
Diethyl ether	BCD, technical grade
DMF	ABCR, anhydrous, amine free; 99.9%; contains amine and molecular sieves
<i>n</i> -Hexane	WALTER CMP, technical grade, sodium with benzophenone as an indicator; stored over 3 Å molecular sieves
THF	Sigma Aldrich; Dried over LiAlH ₄ with benzophenone as an indicator, degassed by three freeze-pump-thaw cycles stored over 3 Å molecular sieves
MTBE	Technical grade, sodium with benzophenone as an indicator; degassed by three freeze-pump-thaw cycles, stored over 3 Å molecular sieves in the glovebox
Toluene	AlfaAesar Inc., anhydrous, 99.8%

Chromatography

For chromatographic purifications, silica gel (Macherey-Nagel Inc., grain size 0.040-0.063 mm) was used. Thin layer chromatography was performed using pre-coated plates from Macherey-Nagel Inc., ALUGRAM[®]Xtra SIL G/UV254. Chromatographic purification for compounds **6** and **10** were carried out using an InterchimPuriflash 430 system, where cartridges by Interchim (silica HC, grain size 50 µm, 40g, 80 g or 120 g) were used.

5.4 Unpublished synthesis

5.4.1 2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (1)



*i*PrMgCl (0.50 mL, 2.0 M in THF, 1.00 mmol) was added dropwise over 1 min. to a solution of 2-(5-bromo-4-hexyl-thiophen-2-yl)-1-hexyl-5-iodo-1*H*-pyrrole **P2-4** (522 mg, 1.00 mmol) in dry THF (8 mL) via a hamilton syringe at 20 °C in the glove box. After stirring 10 min at 20 °C, *i*PrOBPin (205 mg, 1.10 mmol) was added in one portion to the solution and stirred for about 2 h at 20 °C in the glove box. The reaction mixture was removed out from the glove box, quenched with water and extracted with *n*-hexane (3 x 10 mL). The combined solution was dried with MgSO₄. The volatiles were removed *in vacuo* and 511 mg (98%) of light yellow oil was obtained without further purification.

¹H NMR (500 MHz, CDCl₃): δ = 6.80 (d, ³*J* = 3.7 Hz, 1 H, H-b/c), 6.73 (s, 1 H, H-f), 6.26 (d, ³*J* = 3.7 Hz, 1 H, H-b/c), 4.30-4.15 (m, 2 H, H-i), 2.63-2.50 (m, 2 H, H-o), 1.72-1.56 (m, 4 H, H-j, p), 1.38-1.24 (m, 24 H, H-k, l, m, q, r, s, v), 0.93-0.85 (m, 6 H, H-n, t) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 142.2 (C-g), 134.3 (C-e), 131.5 (C-d), 127.0 (C-f), 121.7 (C-b/c), 111.1 (C-b/c), 109.3 (C-h), 83.2 (C-u), 46.8 (C-i), 32.6, 31.6, 31.4, 29.6, 29.5, 28.9, 26.3, 22.6, 22.5, (C-j, k, l, m, o, p, q, r, s), 24.7 (C-v), 14.0, 13.9(C-t,n) ppm.³

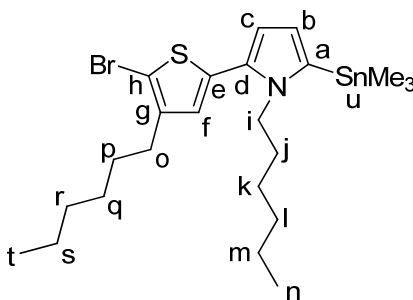
¹¹B NMR (160 MHz, CDCl₃): δ = 27.6 ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₆H₄₁BNO₂SBr]⁺ 521.2134; Found 521.2150.

IR (ATR): $\tilde{\nu}$ = 2954 (s), 2924 (s), 2854 (s), 1573 (w), 1521 (w), 1455 (s), 1402 (s), 1375 (m), 1288 (m), 1199 (m), 1102 (w), 1035 (w), 1002 (w), 967 (w), 867 (w), 839 (m), 754 (s), 725 (m), 661 (w), 584 (w), 475 (w) cm⁻¹.

³³ The carbon atom bound to boron was not visible due to the high quadrupole moment of the boron nucleus.

5.4.2 2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-5-(trimethylstannyl)-1H-pyrrole (2)



*i*PrMgCl (0.50 mL, 2.0 M in THF, 1.00 mmol) was added dropwise over 1 min to a solution of 2-(5-bromo-4-hexylthiophen-2-yl)-1-hexyl-5-iodo-1H-pyrrole **P2-4** (522 mg, 1.00 mmol) in dry THF (8 mL) of via a syringe at 20 °C in the glove box. After stirring for 10 min at 20 °C, trimethyltin chloride (219 mg, 1.10 mmol) was added in one portion to the solution and the reaction mixture was stirred for 30 min at 20 °C in the glove box. The reaction mixture was removed out from the glove box and quenched with water and extracted with *n*-hexane (3 x 10 mL). The combined solution was dried with MgSO₄. The volatiles were removed *in vacuo* and 552 mg (99%) of light yellow oil were obtained without further purification.

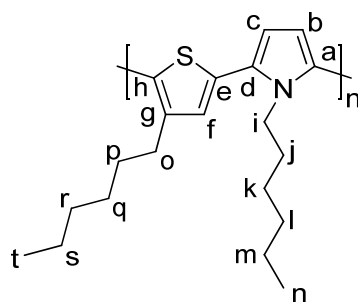
¹H NMR (500 MHz, CDCl₃): δ = 6.68 (s, 1 H, H-f), 6.33 (d, ³J = 3.4 Hz, 1 H, H-b/c), 6.27 (d, ³J = 3.4 Hz, 1 H, H-b/c), 3.98-3.92 (m, 2 H, H-i), 2.59-2.53 (m, 2 H, H-o), 1.68-1.55 (m, 4 H, H-j, p), 1.36-1.23 (m, 12 H, H-k, l, m, q, r, s), 0.93-0.82 (m, 6 H, H-n, t), 0.34 (s, 9 H, H-u) ppm.

¹³C NMR (126 MHz, CDCl₃): δ = 142.1 (C-g), 135.3, 134.9 (C-a, e), 129.6 (C-d), 126.4 (C-f), 118.4 (C-b/c), 111.6 (C-b/c), 107.7 (C-h), 49.3 (C-i), 32.5, 31.6, 31.4, 29.7, 29.6, 28.9, 26.5, 22.6, 22.5, (C-j, k, l, m, o, p, q, r, s), 14.1, 13.9 (C-t, n), -8.3 (C-u) ppm.

¹¹⁹Sn NMR (187 MHz, CDCl₃): δ = -52.07 ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₃H₃₈NSnSBr]⁺ 559.0930; Found 559.0934.

IR (ATR): $\tilde{\nu}$ = 2954 (s), 2924 (s), 2854 (s), 1573 (w), 1521 (w), 1455 (s), 1402 (s), 1375 (m), 1288 (m), 1199 (m), 1102 (w), 1035 (w), 1002 (w), 967 (w), 867 (w), 839 (m), 754 (s), 725 (m), 661 (w), 584 (w), 475 (w) cm⁻¹.

5.4.3 General procedure for polymerization of **1** (PTP1)

In a microwave vial, a solution of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ (12.8 mg, 25.0 μmol) in THF (1.0 mL) was added to a solution of **1** (261 mg, 0.50 mmol) in THF (2.0 mL) at 20 °C in the glove box. Then a solution of K_3PO_4 (10.6 mg, 5.00 mmol) in degassed H_2O (1 mL) was added in the reaction mixture in one portion. The reaction mixture was heated and stirred at 50 °C under microwave irradiation for 5 h. Then the reaction mixture was quenched with H_2O (10 mL) and the water phase was extracted with diethyl ether (2 x 20 mL). The combined organic layer was washed with brine (1 x 20 mL) and dried with MgSO_4 . The volatiles were removed *in vacuo* to give the crude product. The crude product was dissolved in diethyl ether (0.5 mL) and the solution was added dropwise into methanol (200 mL) with vigorous stirring to remove the low molecular weight compounds. The precipitated polymer was extracted by soxhlet extractor with methanol (200 mL) for 5 h. For removing from the Soxhlet extractor, the solid polymer was refluxed with diethyl ether (100 mL). The volatiles were removed *in vacuo* and product was dried under reduced pressure for 18 h to give the polymer as black green viscous solid.⁴

¹H NMR (500 MHz, CDCl_3): δ = 6.97 (s, 1 H, H-3), 6.41 (d, 3J = 3.6 Hz, 1 H, H-2), 6.26 (d, 3J = 3.6 Hz, 1 H, H-1), 4.17-3.92 (m, 2 H, H-a), 2.66-2.46 (m, 2 H, H-g), 1.64-1.51 (m, 4 H, H-b, h), 1.35-1.09 (m, 12 H, H-c, d, e, l, j, k), 0.88 (t, 3J = 6.8 Hz, 3 H, H-f), 0.81 (t, 3J = 7.1 Hz, 3 H, H-l) ppm.

¹³C NMR (126 MHz, CDCl_3): δ = 142.8 (C-g), 134.9, 128.1, 127.6, 126.7, 126.3, 112.0, 110.0, 45.3, 32.1, 31.7, 31.2, 31.0, 30.7, 29.7, 29.1, 26.3, 22.6, 22.4, 14.1, 13.9 ppm. **IR** (ATR): $\tilde{\nu}$ = 2953 (s), 2923 (s), 2854 (s), 1458 (s), 1402 (m), 1376 (m), 1308 (m), 1193 (m), 1071 (m), 1033 (m), 873 (w), 839 (m), 762 (m), 715 (m), 684 (w), 637 (w), 567 (w) cm^{-1} .

⁴ The analytical data of polymer are the same with the polymerization of **2** and **3**, so they will not be written in the procedures for them.

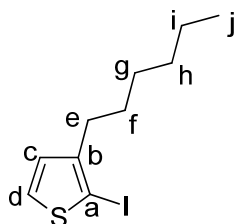
5.4.4 General procedure for polymerization of **2** (PTP2)

In a microwave vial, a solution of [Pd(*t*Bu₃P)₂] (12.8 mg, 25.0 μmol) in MTBE (1.0 mL) was added to the solution of **2** (279 mg, 0.50 mmol) in MTBE (1.0 mL) at 20 °C in the glove box. The reaction mixture was stirred and heated at 50 °C under microwave irradiation for 5 h. Then the reaction mixture was quenched with H₂O (10 mL) and the water phase was extracted with diethyl ether (2 x 20 mL), then the combined organic layer was washed with brine (1 x 20 mL) and dried with MgSO₄. The volatiles were removed *in vacuo* to give a crude product. The crude product was dissolved in diethyl ether (0.5 mL) and the solution was added dropwise into methanol (200 mL) with vigorous stirring to remove the low molecular-weight compounds. The precipitated polymer was extracted by Soxhlet extraction with methanol (200 mL) for 5 h. For removing from the Soxhlet extractor, the solid polymer was refluxing with diethyl ether (100 mL). The volatiles were removed *in vacuo* and product was dried under reduced pressure for 18 h to give the polymer as black green viscous solid.

5.4.5 General procedure for polymerization of 3 (PTP3)

In a microwave vial, *i*PrMgCl (0.25 mL, 2.0 M in THF, 0.50 mmol) was added dropwise to a solution of precursor monomer **P2-4** (261 mg, 0.50 mmol) in MTBE (3.0 mL) via a Hamilton syringe at 20 °C over the course of 1 min in glove box. Then anhydrous ZnCl₂ (68.1 mg, 0.50 mmol) was added to the reaction mixture at 20 °C in one portion. After stirring the reaction mixture for 1 h at 20 °C, a solution of [Pd(*t*Bu₃P)₂] (12.8 mg, 25.0 μmol) in MTBE (1.0 mL) was added to the reaction mixture. The reaction mixture was heated and stirred at 50 °C under microwave irradiation for 5 h. Then the reaction mixture was quenched with H₂O (10 mL) and the aqueous phase was extracted with diethyl ether (2 x 20 mL), then the combined organic layer was washed with brine (1 x 20 mL) and dried with MgSO₄. The volatiles were removed *in vacuo* to give the crude product. The crude product was dissolved in diethyl ether (0.5 mL) and the solution was added dropwise into methanol (200 mL) with vigorous stirring to remove the low molecular-weight compounds. The precipitated polymer was extracted by soxhlet extractor with methanol (200 mL) for 5 h. In order to remove it from the Soxhlet extractor, the solid polymer was subjected to refluxing diethyl ether (100 mL). The volatiles were removed *in vacuo* and product was dried under reduced pressure for 18 h to give the polymer as black green viscous solid.

5.4.6 2-Iodo-3-hexylthiophene (5)



N-Iodosuccinimide (6.7 g, 30 mmol) was added in one portion to 3-*n*-hexylthiophene (5.0 g, 40 mmol) in the mixture of glacial acetic acid (50 mL) and CHCl_3 (50 mL) at 20 °C. The reaction mixture was stirred for 16 h. Then NaOH aqueous solution (1 M, 50 mL) was added to the reaction mixture over ice bath and $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution (0.5 M, 50 mL) was added afterwards. The aqueous phase was extracted with diethyl ether (3 x 50 mL) and the combined organic layers were dried over MgSO_4 . The solvent was removed *in vacuo* and the crude product was purified by Kugelrohr distillation (100 °C, 5×10^{-1} mbar) to afford 6.5 g (68%) of the product as orange oil.

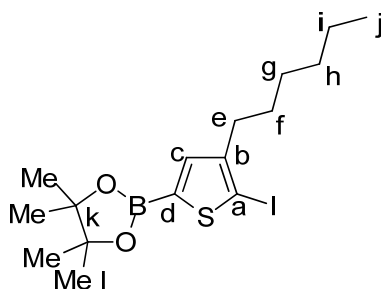
$^1\text{H NMR}$ (500 MHz, CDCl_3): δ = 7.38 (d, 3J = 5.5 Hz, 1 H, H-d), 6.75 (d, 3J = 5.5 Hz, 1 H, H-c), 2.55 (t, 3J = 7.7 Hz, 2 H, H-e), 1.61-1.52 (m, 2 H, H-f), 1.39-1.27 (m, 6 H, H-g, h, i), 0.89 (t, 3J = 6.9 Hz, 3 H, H-j) ppm.

$^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ = 147.2 (C-b), 130.3 (C-d), 127.9 (C-c), 73.9 (C-a), 32.1, 31.6, 30.0, 28.9, 22.6 (C-e, f, g, h, i), 14.1 (C-j) ppm.

HRMS (EI-sector) m/z : $[M]^+$ Calcd for $[\text{C}_{10}\text{H}_{15}\text{S}]^+$ 293.9939; Found 293.9941.

IR (ATR): $\tilde{\nu}$ = 2954 (m), 2924 (s), 2854 (s), 1687 (w), 1528 (w), 1456 (m), 1397 (m), 1227 (w), 963 (w), 828 (m), 713 (s), 684 (m), 634 (s), 578 (m) cm^{-1} .

5.4.7 2-(4-Hexyl-5-iodothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



A solution of diisopropylamine (1.5 g, 15 mmol) in THF (80 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and *n*-butyllithium (6.0 mL, 15 mmol, 2.5 M in hexanes) was added dropwise in 10 min. The reaction mixture was warmed to $0\text{ }^{\circ}\text{C}$ by removing the cooling bath in 30 min. Then the reaction mixture was cooled back to $-78\text{ }^{\circ}\text{C}$ and stirred for 5 min. 2-Iodo-3-hexylthiophene (4.4 g, 15 mmol) was added over dropwise in 10 min and the reaction mixture was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$. *i*PrOBPin (2.8 g, 15 mmol) was added dropwise in 10 min to the orange-brown suspension and the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 15 minutes. Then the cooling bath was removed and the mixture was stirred for another 4 h at $15\text{ }^{\circ}\text{C}$. The reaction mixture was quenched with H_2O (50 mL). The aqueous layer was extracted with DCM (3 x 70 mL) and the combined organic was dried over MgSO_4 . The solvent was removed *in vacuo* and the mixture was purified by column chromatography over silica gel (gradient from *n*-pentane / ethylacetate: 95 / 5 to 1 / 1; $R_f = 0.48$ [95 / 5]) to afford 3.87 g (61%) of the product as a red brown oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 7.24$ (s, 1 H, H-c), 2.54 (t, $^3J = 7.7$ Hz, 2 H, H-e), 1.62-1.52 (m, 2 H, H-f), 1.37-1.26 (m, 18 H, H-g, h, i, l), 0.89 (t, $^3J = 6.9$ Hz, 3 H, H-j) ppm.

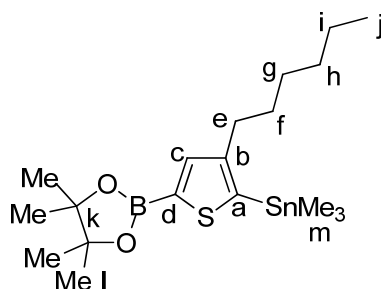
$^{13}\text{C NMR}$ (126 MHz, CDCl_3): $\delta = 148.6$ (C-b), 137.5 (C-c), 84.2 (C-k), 82.7 (C-a), 31.9, 31.6, 29.9, 28.9, 22.6 (C-e, f, g, h, i), 24.7 (C-l), 14.1 (C-j) ppm.⁵

IR(ATR): $\tilde{\nu} = 2978$ (w), 2955 (w), 2926 (m), 2855 (w), 1540 (m), 1428 (s), 1370 (m), 1327 (s), 1294 (s), 1267 (s), 1139 (vs), 1025 (m), 956 (w), 851 (s), 768 (w), 749 (w), 684 (w), 663 (s), 577 (w) cm^{-1} .

HRMS (EI-sector) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{16}\text{H}_{26}\text{BIO}_2\text{S}]^+$ 420.0791; Found 420.0795.

⁵ C-d was not visible due to the high quadruple moment of the B nucleus, same as other similar compounds.

5.4.8 (3-Hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethyl stannane (7)



2-(4-Hexyl-5-iodothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **6** (840 mg, 2.00 mmol), [Pd(PPh₃)₄] (12 mg, 10 μmol) and hexamethyldistannane (689 mg, 2.10 mmol) was dissolved in toluene (4 mL) at 20 °C. The reaction mixture was heated to 120 °C under microwave irradiation and stirred for 30 min. Then the reaction mixture was poured in to H₂O (10 mL) and the aqueous phase was extracted with DCM (3 x 15 mL). The combined organic was dried over MgSO₄ and the solvent was removed *in vacuo*. The crude product was purified by Kugelrohr distillation (130 °C, 3 x 10⁻² mbar) to afford 692 mg (76%) of the product as red brown oil.

¹H NMR (500 MHz, CDCl₃): δ = 7.61 (s, 1 H, H-c), 2.67-2.59 (m, 2 H, H-e), 1.63-1.54 (m, 2 H, H-f), 1.39-1.25 (m, 18 H, H-g, h, i, l), 0.89 (t, ³J = 6.9 Hz, 3 H, H-j), 0.37 (s, 9 H, H-m) ppm.

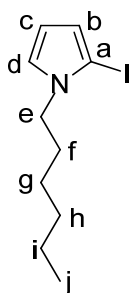
¹³C NMR (126 MHz, CDCl₃): δ = 152.2 (C-b), 141.0 (C-a), 139.0 (C-c), 83.9 (C-m), 32.2, 32.1, 31.7, 29.3, 22.6, (C-e, f, g, h, i), 24.7 (C-l), 14.1 (C-j), -8.1 (C-m) ppm.

¹¹B NMR: δ = 28.8 ppm.

¹¹⁹Sn NMR: δ = -35.7 ppm.

HRMS (ESI-FTMS) *m/z*: [M + Na]⁺ Calcd for [C₁₉H₃₅BNaO₂SSn]⁺ 481.1370; Found 481.1358.

IR(ATR): $\tilde{\nu}$ = 2977 (w), 2926 (m), 1526 (m), 1423 (m), 1369 (m), 1322 (s), 1267 (m), 1142 (s), 982 (m), 853 (s), 771 (s), 665 (s), 529 (s) cm⁻¹.

5.4.9 1-Hexyl-2-iodo-1*H*-pyrrole (9)

n-Butyllithium (10 mL, 25 mmol, 2.5 M in hexanes) was added to a stirred solution of *N,N,N',N'*-tetramethyl-ethane-1,2-diamine (3.80 mL, 25.0 mmol) in *n*-hexane (30 mL), at 0 °C during the course of 5 min and stirred for 1h. *N*-(*n*-hexyl)-pyrrole (3.0 g, 20 mmol) was added dropwise in 15 min to the solution at 0 °C. The reaction mixture was warmed up to 20 °C and stirred for 18 h. Then the reaction mixture was cooled back to -78 °C and THF (45 mL) was added. A solution of iodine (5.0 g, 20 mmol) in THF (30 mL) was added in 1.5 h by syringe pump and stirred for about 30 min at -78 °C. The reaction mixture was quenched with saturated NH₄Cl aqueous solution (20 mL) and Na₂S₂O₃ aqueous solution (0.5 M, 100 mL). The aqueous layer was extracted with diethyl ether (3 x 60 mL) and the combined organic layers were washed with brine (1 x 150 mL). The organic layer was dried with MgSO₄ and the solvent was removed *in vacuo*. The remaining dark brown liquid was purified by Kugelrohr distillation (65 °C, 6.5 x 10⁻² mbar) to give 4.5 g (83%) of light yellow liquid.

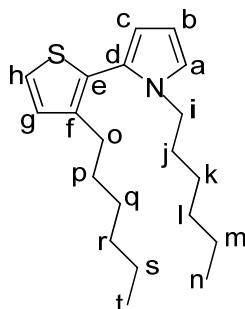
¹H NMR (600 MHz, CDCl₃): δ = 6.82 (t, 1 H, ³*J* = 2.3 Hz, H-d), 6.32 (dd, ³*J* = 3.5 Hz, 1.7 Hz, 1 H, H-c), 6.16 (t, ³*J* = 3.3 Hz, 1 H, H-b), 3.86 (t, 2 H, ³*J* = 7.4 Hz, H-e), 1.75-1.68 (m, 2 H, H-f), 1.36-1.27 (m, 6 H, H-g, h, i), 0.89 (t, 3 H, ³*J* = 6.8 Hz, H-j) ppm.

¹³C NMR (150 MHz, CDCl₃): δ = 123.8 (C-d), 118.3 (C-c), 110.6 (C-b), 68.2 (C-a), 50.7 (C-e), 31.4, 31.3 (C-f, g), 26.2 (C-h), 22.5 (C-i), 14.0 (C-j) ppm.

HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₁₀H₁₆I]⁺ 277.0327; Found 277.0322.

IR (ATR): $\tilde{\nu}$ = 2955 (m), 2927 (s), 2856 (m), 1515 (w), 1460 (s), 1428 (s), 1377 (m), 1282 (s), 1119 (w), 1065 (m), 986 (w), 874 (w), 772 (m), 701 (vs), 613 (s) cm⁻¹.

5.4.10 1-Hexyl-2-(3-hexylthiophen-2-yl)-1H-pyrrole (10)



[Pd(PPh₃)₄] (115 mg, 100 μmol) was added to a solution of 2-tri-*n*-butyltin-*N*-(*n*-hexyl)-pyrrole **P2-2** (880 mg, 2.00 mmol) and 2-bromo-3-*n*-hexylthiophene (496 mg, 2 mmol) in DMF (6 mL) at 20 °C. The reaction mixture was heated to 70 °C for 48 h and then poured into water (20 mL). The solution was extracted with diethyl ether (3 x 20 mL) and the organic extracts were washed with brine (3 x 20 mL) before dried with MgSO₄. The volatiles were removed *in vacuo*. The crude product was purified by column chromatography over silica gel (*n*-pentane, R_f = 0.25) to give 304 mg (48%) of yellow liquid.

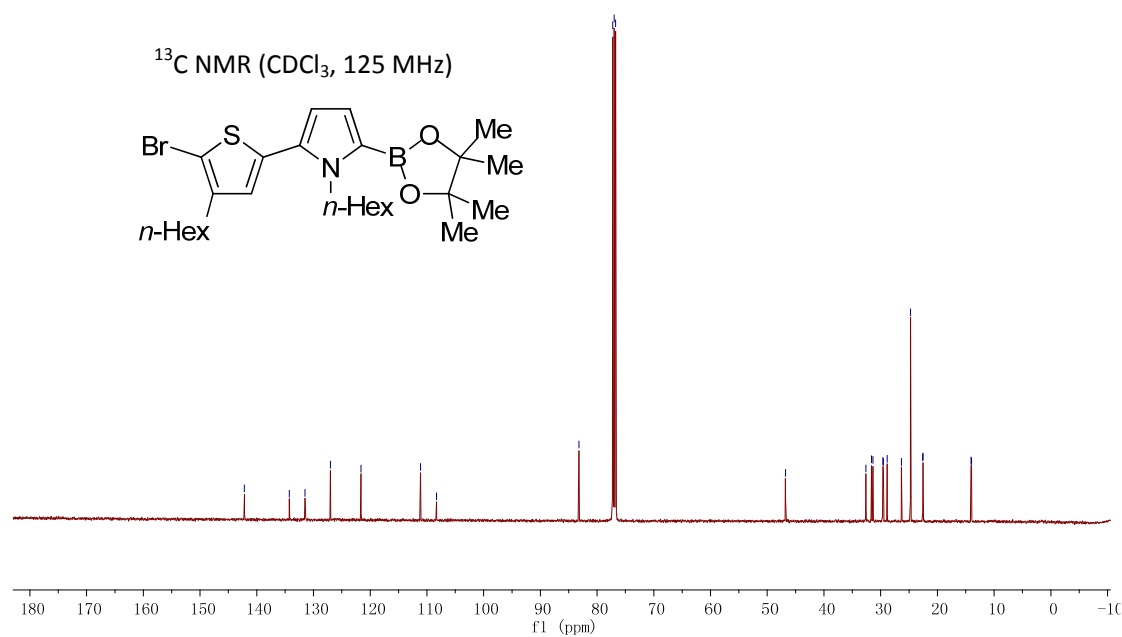
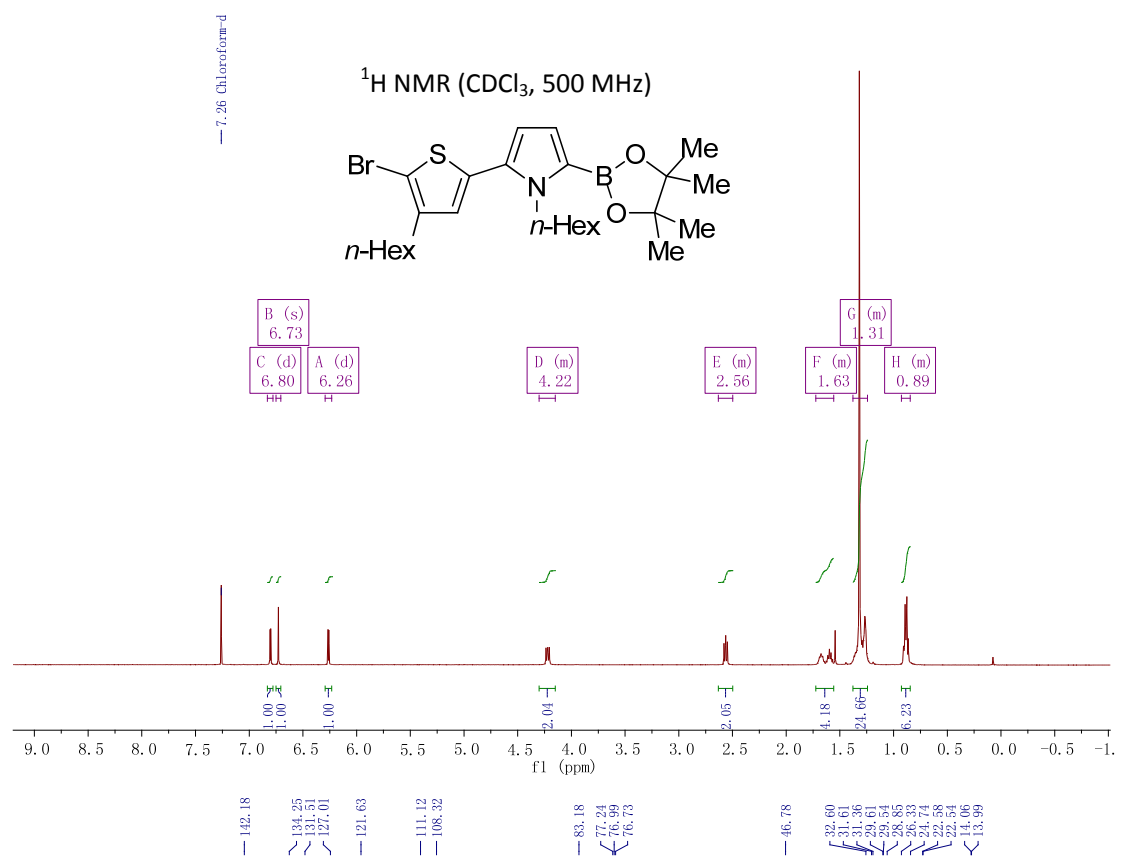
¹H NMR (500.1 MHz, CD₃OD): δ = 7.35 (d, 1 H, ³J = 5.3 Hz, H-h), 6.98 (d, 1 H, ³J = 5.3 Hz, H-g), 6.80 (dd, 1 H, ³J = 2.8 Hz, ³J = 1.8 Hz, H-a), 6.12 (dd, 1 H, ³J = 3.5 Hz, ³J = 2.8 Hz, H-b), 6.0 (dd, 1 H, ³J = 3.5, ³J = 1.8 Hz, H-c), 3.78 (t, 2 H, ³J = 7.3 Hz, H-i), 2.45 (t, 2 H, ³J = 7.7 Hz, H-o), 1.61-1.47 (m, 4 H, H-j, p), 1.31-1.12 (m, 12 H, H-k, l, m, q, r, s), 0.82-0.87 (m, 6 H, H-n, t) ppm.

¹³C NMR (125.8 MHz, CDCl₃): δ = 143.4 (C-f), 129.7 (C-e), 129.3 (C-g), 126.1 (C-h), 125.5 (C-d), 123.0 (C-a), 112.3 (C-c), 108.4 (C-d), 48.0 (C-i), 32.7, 32.4, 31.7, 30.1, 29.8, 27.3, 23.6, 23.5 (C-o-s, C-i-m) 14.4, 14.3 (C-n, t) ppm.

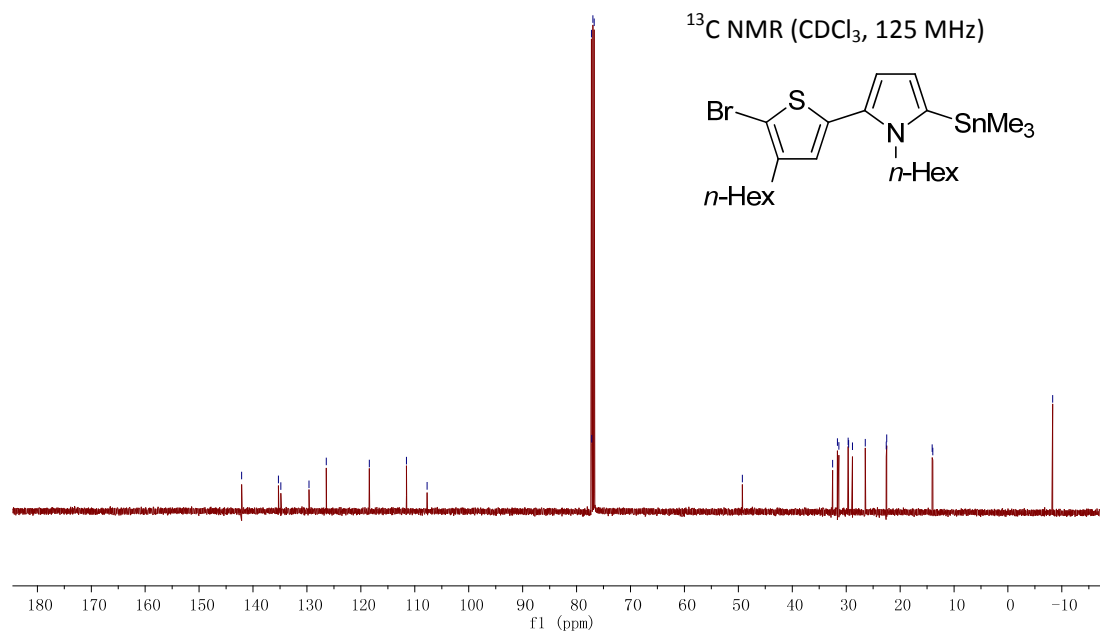
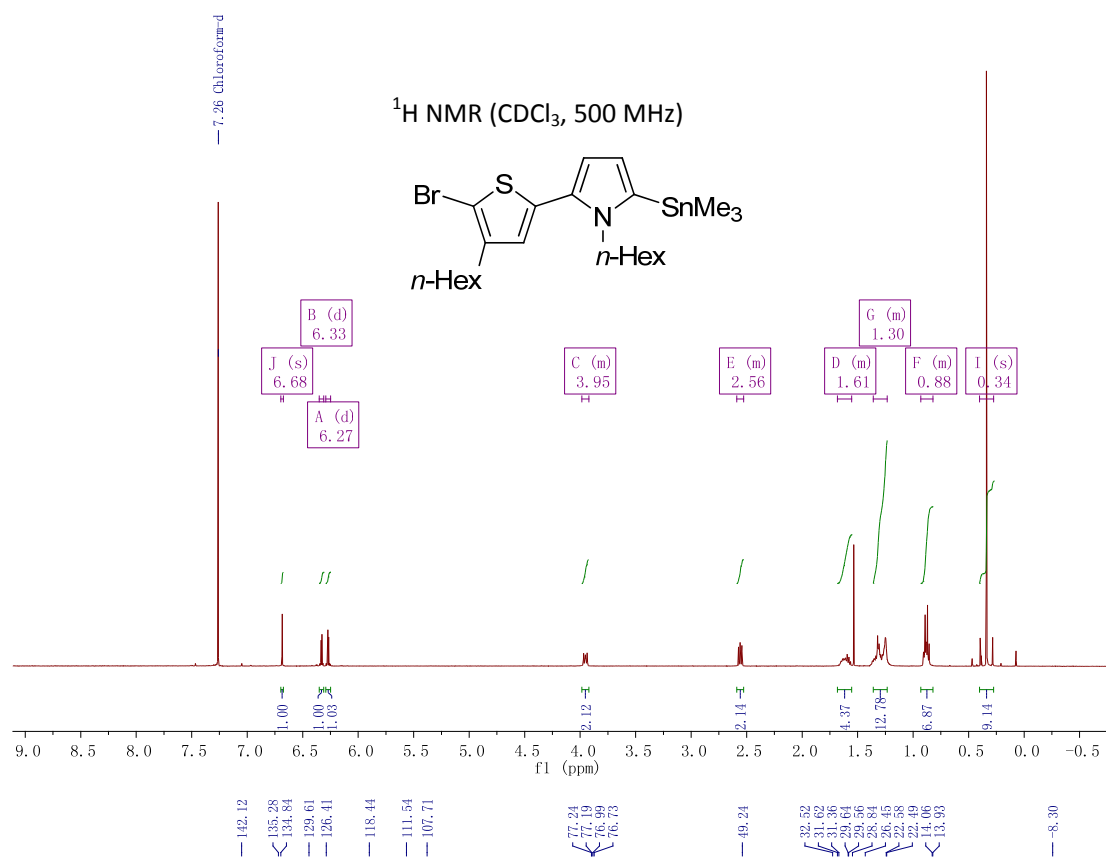
HRMS (EI-sector) *m/z*: [M]⁺ Calcd for [C₂₀H₃₁NS]⁺ 317.2177; Found 317.2180.

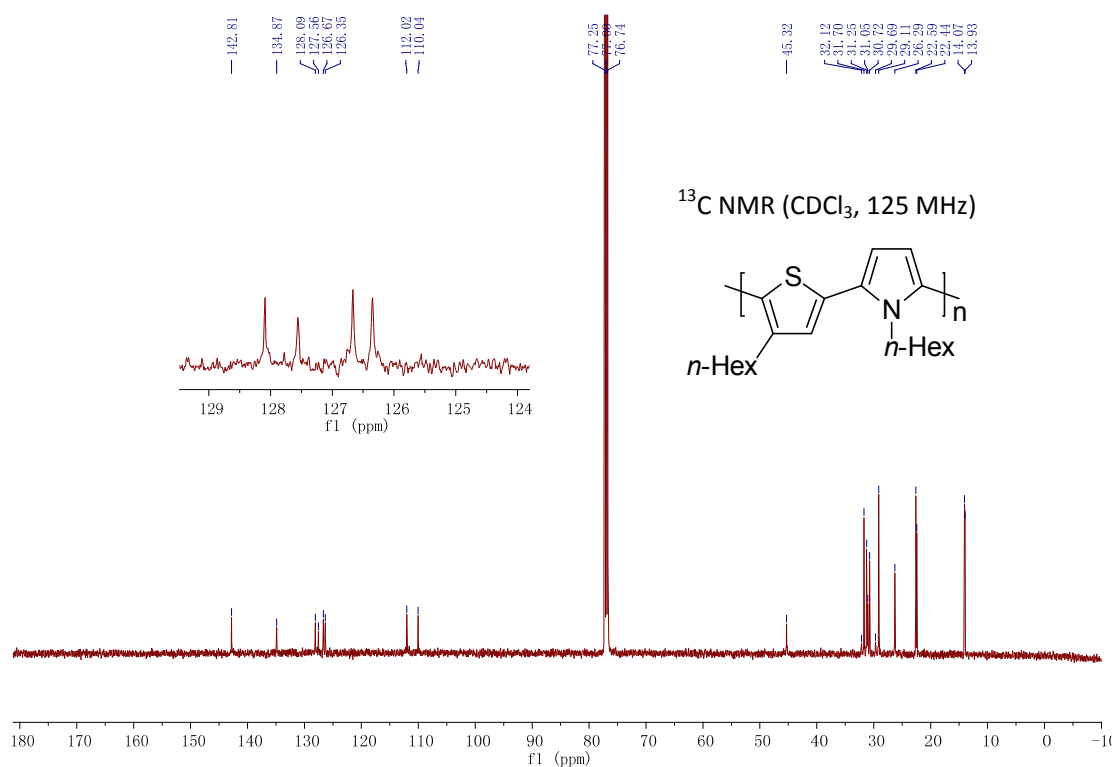
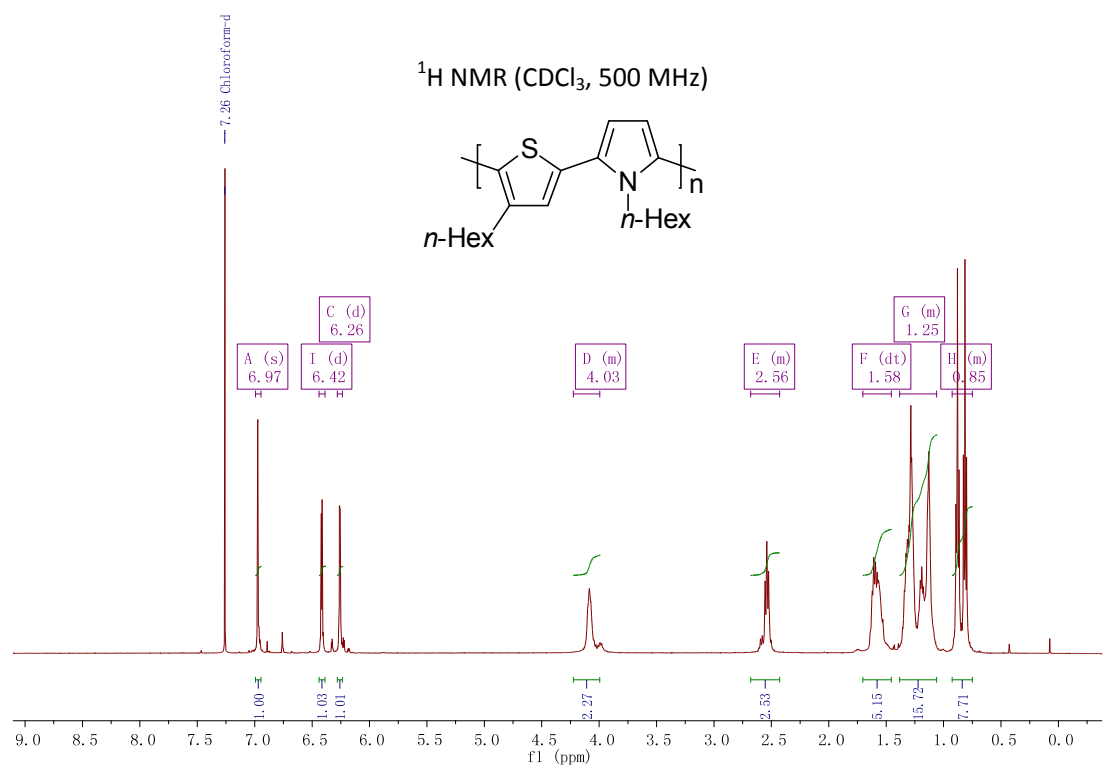
IR (ATR): $\tilde{\nu}$ = 2955 (m), 2925 (s), 2856 (s), 1466 (m), 1428 (m), 1377 (m), 1300 (m), 1232 (w), 1070 (m), 1030 (w), 929 (w), 834 (w), 784 (m), 709 (vs), 669 (m), 614 (m) cm⁻¹.

5.5 NMR spectra

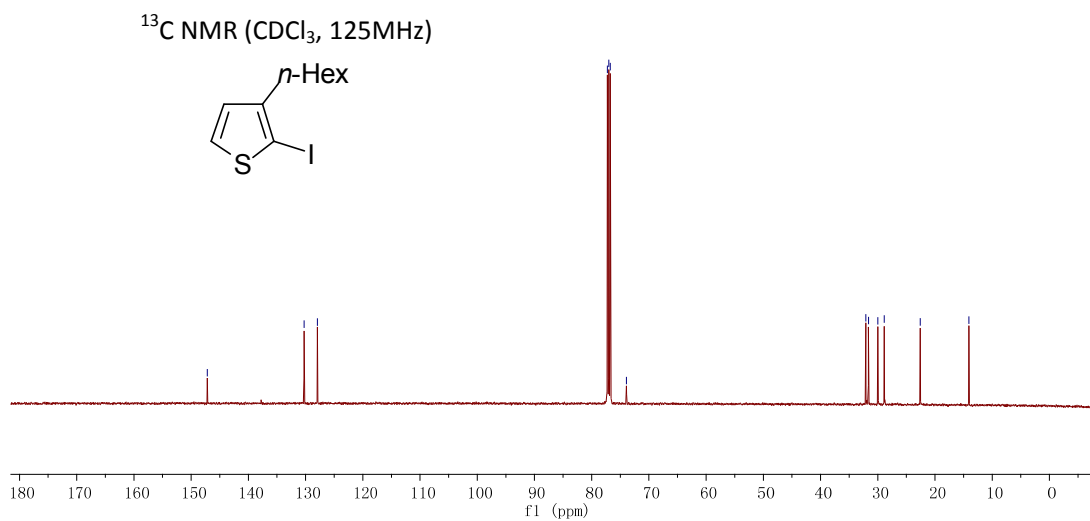
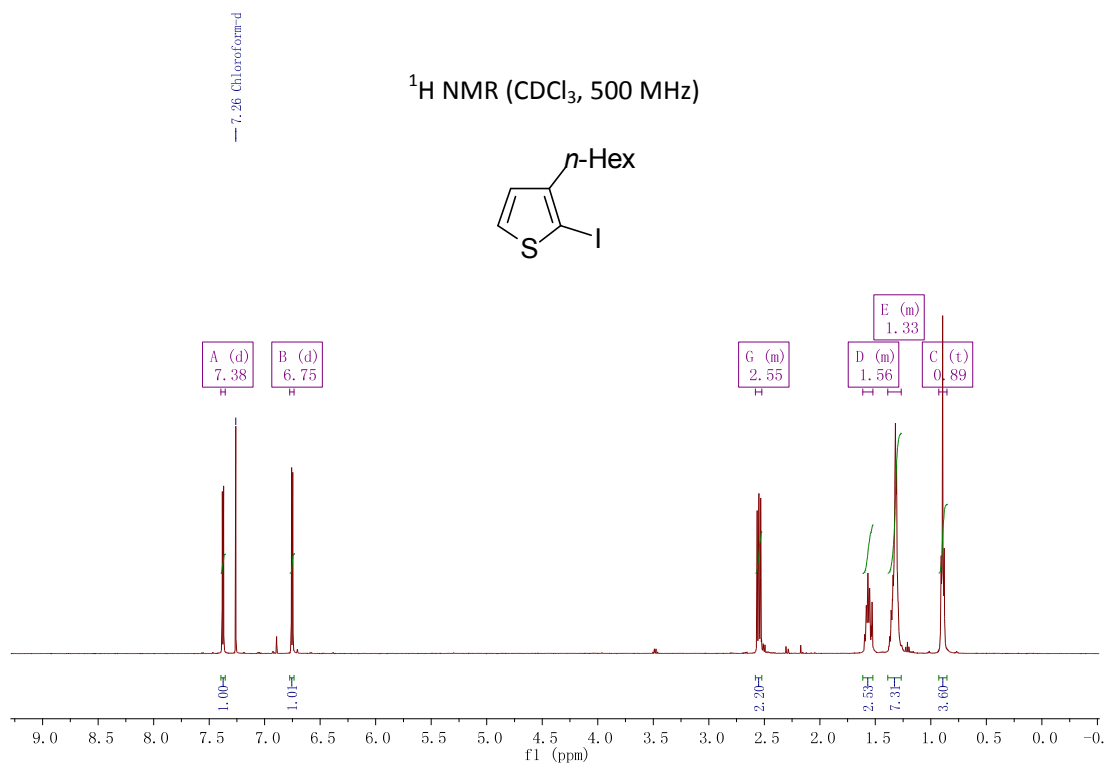
2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (**1**)

2-(5-Bromo-4-hexylthiophen-2-yl)-1-hexyl-5-(trimethylstannyl)-1H-pyrrole (2)

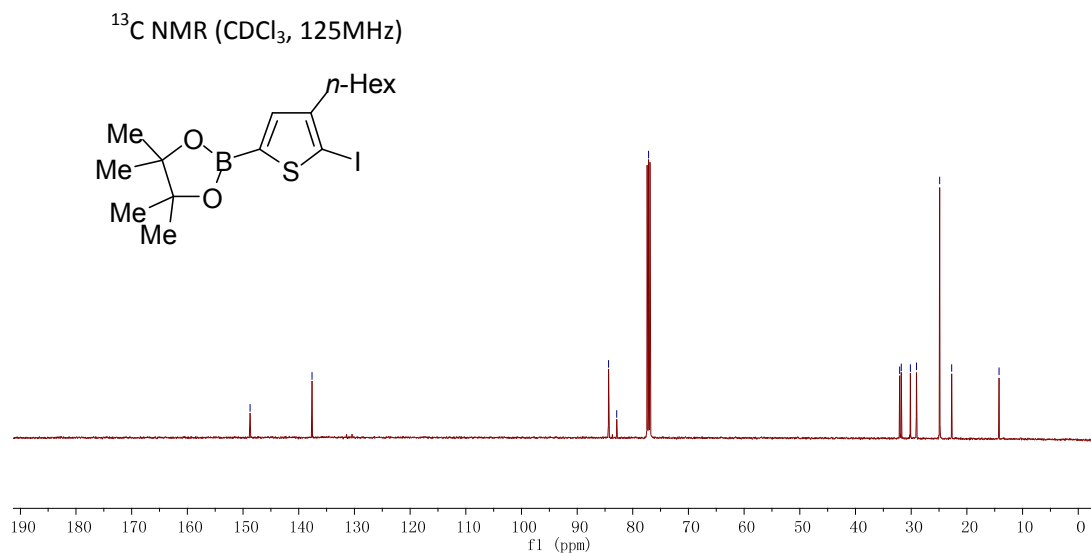
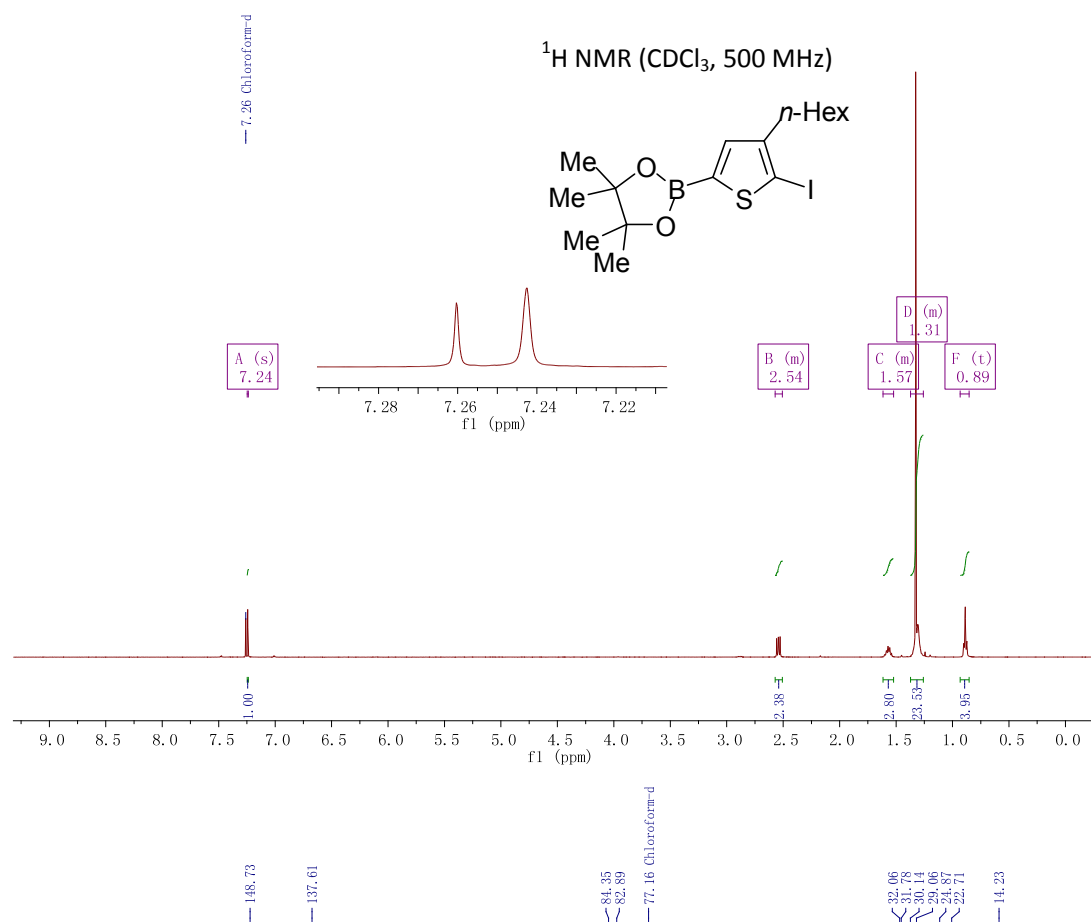


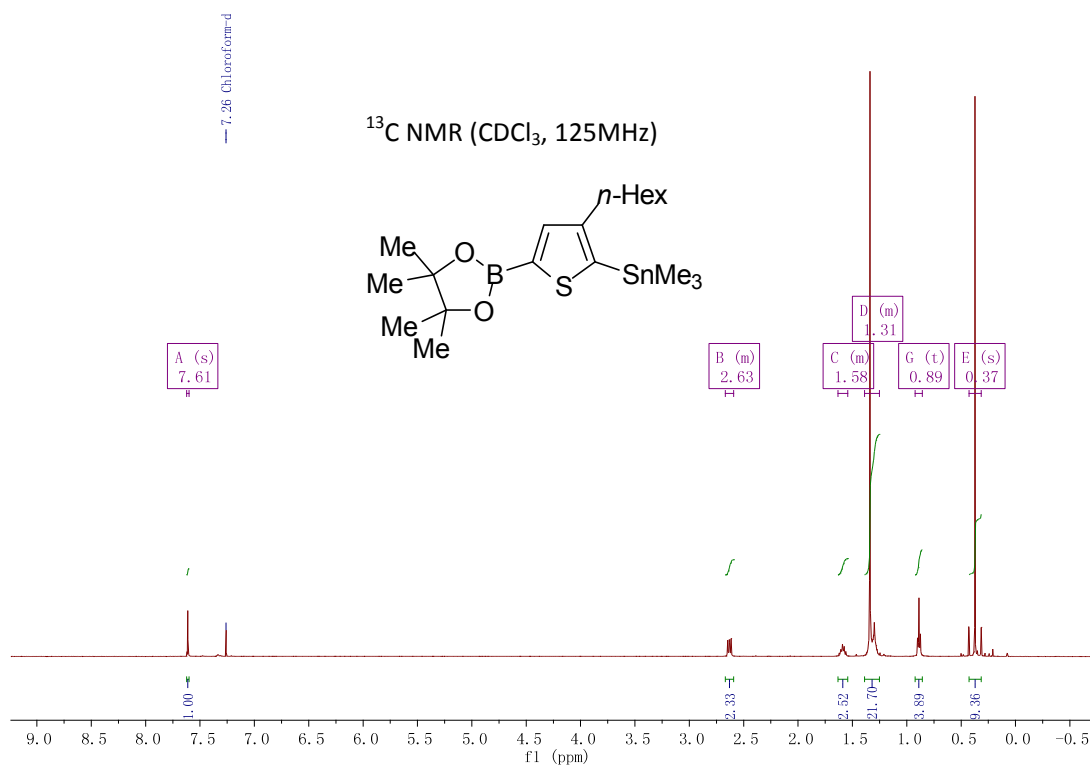
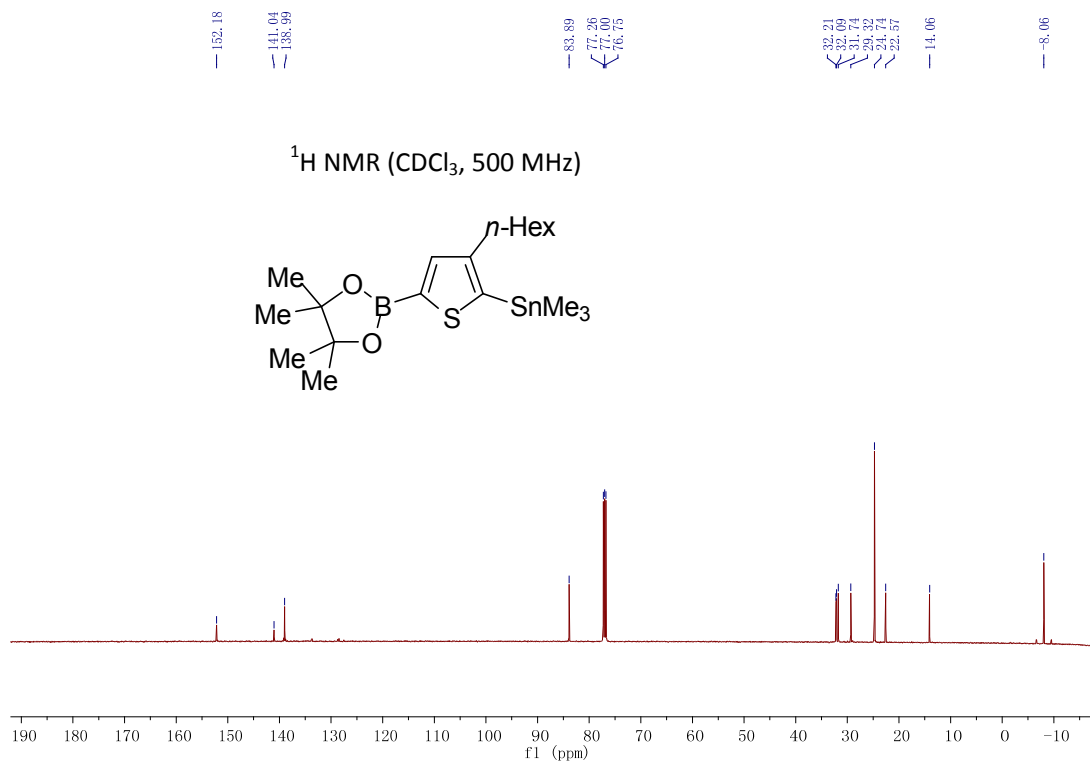
Poly(thiophene-*alt*-pyrrole) (PTP) (Table 2, entry 9)

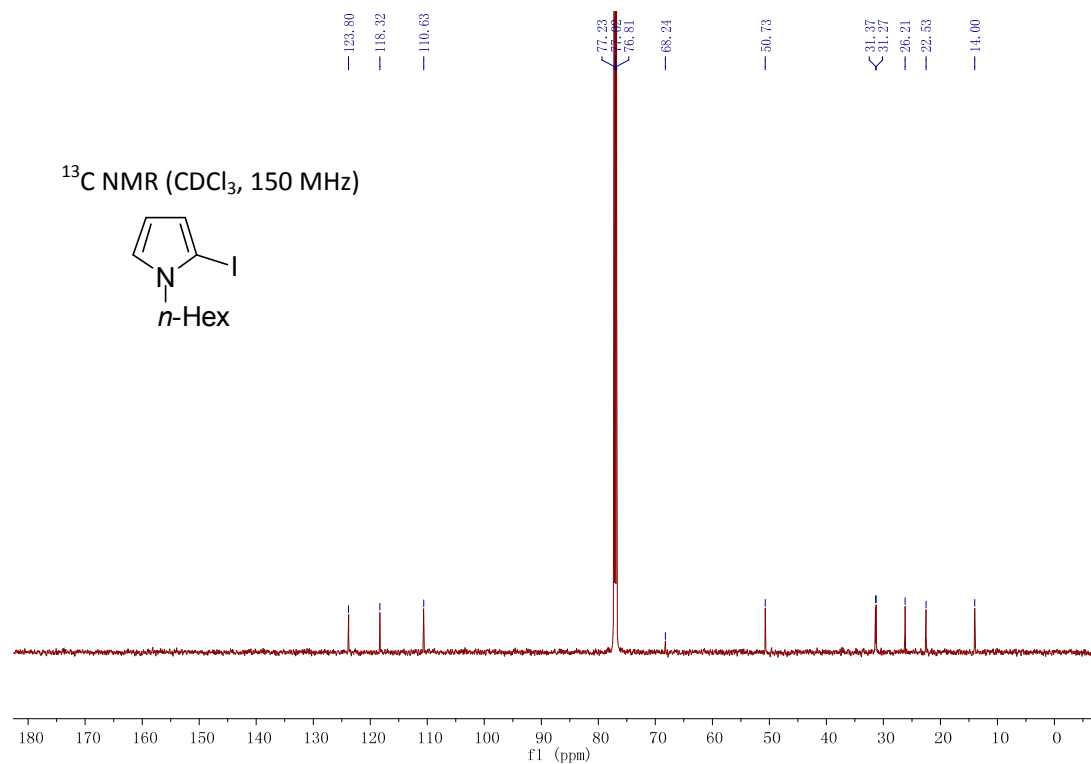
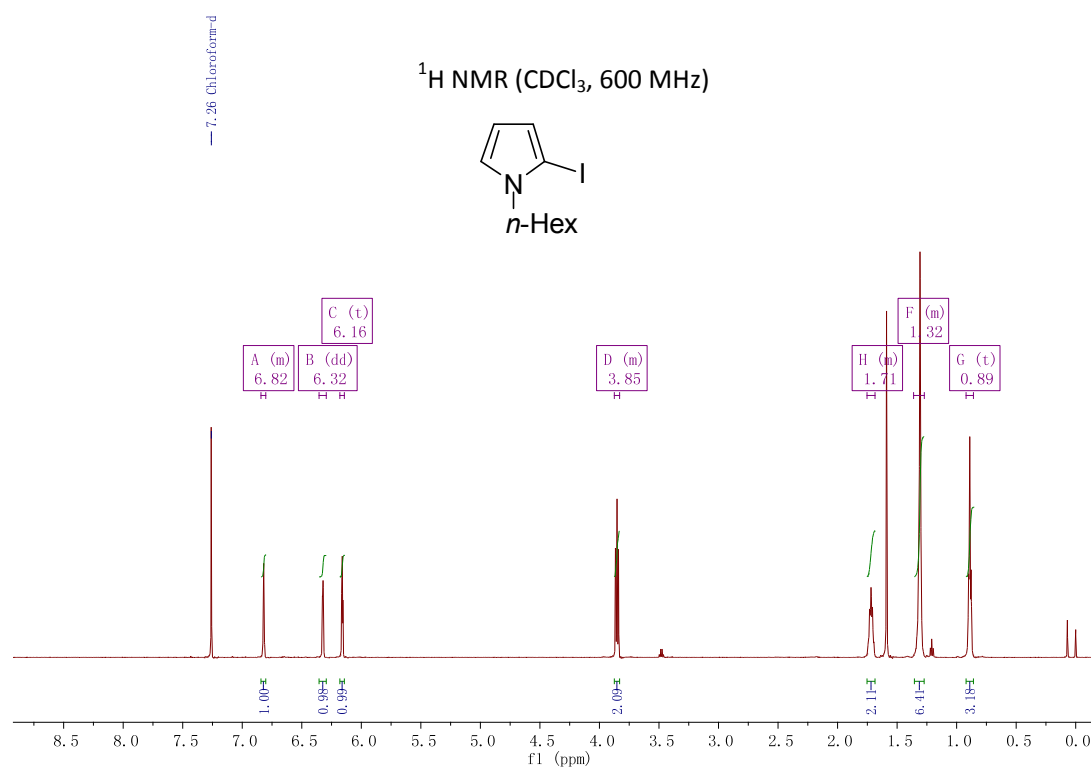
2-(4-Hexyl-5-iodothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)



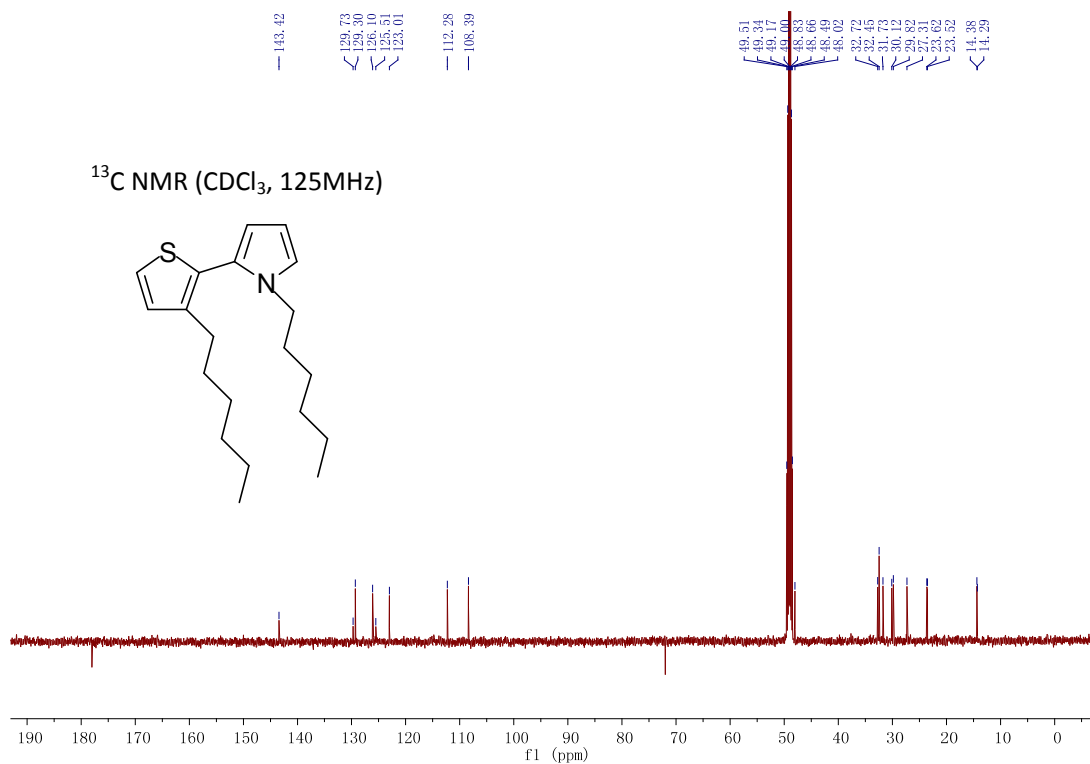
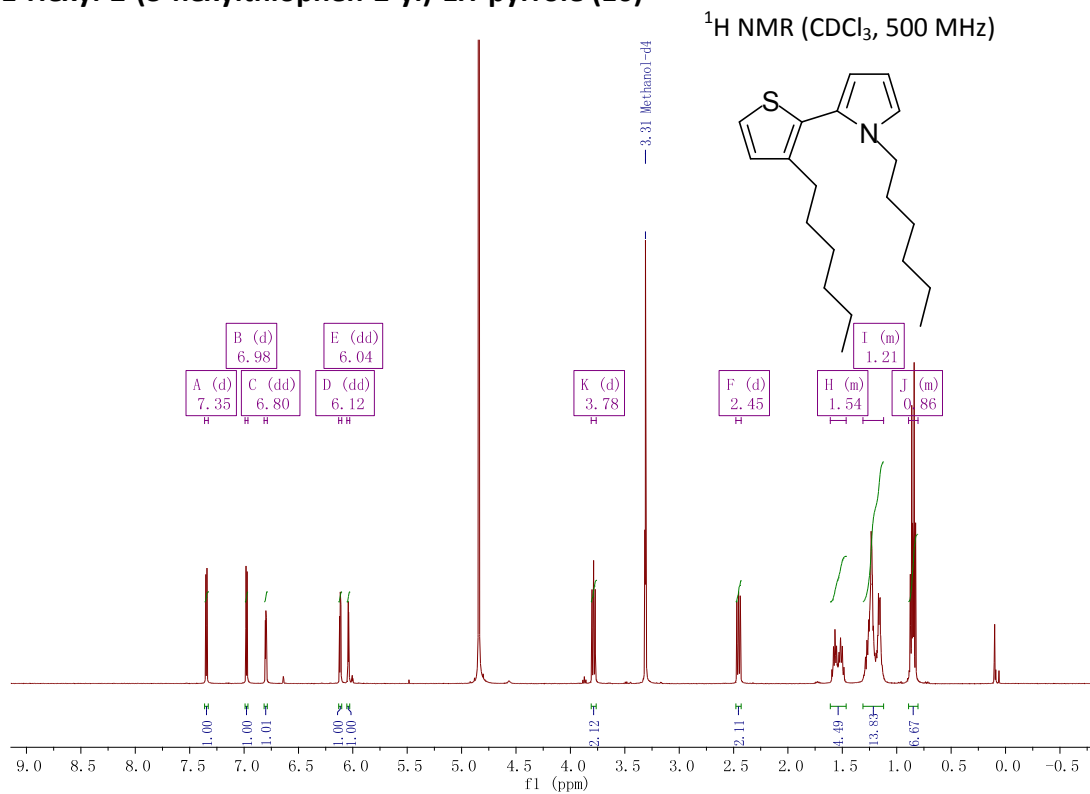
2-(4-Hexyl-5-iodothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6)



(3-Hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethylstannane (7)

1-Hexyl-2-iodo-1*H*-pyrrole (9)

1-Hexyl-2-(3-hexylthiophen-2-yl)-1H-pyrrole (10)



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