การสังเคราะห์พอลิฟีนิลีนเอไทนิลีนโดยใช้แคลเซียมคาร์ไบด์

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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SYNTHESIS OF POLY(PHENYLENEETHYNYLENE)S USING CALCIUM CARBIDE

Miss Nopparat Thavornsin

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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Thesis Title	SYNTHESIS OF POLY(PHENYLENEETHYNYLENE)S USING CALCIUM CARBIDE
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Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Assistant Professor Sumrit Wacharasundhu, Ph.D.
Thesis Co-advisor	Associate Professor Mongkol Sukwattanasinitt, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

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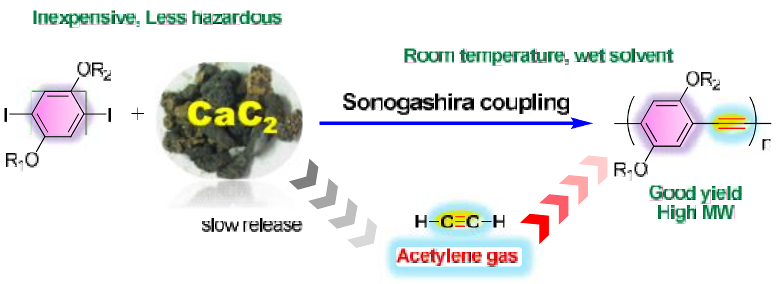
นพรัตน์ ถาวรสิน: การสังเคราะห์พอลิฟีนิลีนเอไทนิลีนโดยใช้แคลเซียมคาร์ไบด์ (SYNTHESIS OF POLY(PHENYLENEETHYNYLENE)S USING CALCIUM CARBIDE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ. ดร. สัมฤทธิ์ วัชรสินธุ์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : รศ.ดร. มงคล สุขวัฒนาสินิทธิ์, 112 หน้า.

งานวิจัยนี้มุ่งเน้นที่จะพัฒนาการสังเคราะห์พอลิฟีนิลีนเอไทนิลีน (PPEs) จากการใช้แคลเซียมคาร์ไบด์ ซึ่งเป็นวัตถุดิบหลักทางเคมีและแอริลไดไอโอไดด์ ทำปฏิกริยาคัปปลิงเร่งด้วยแพลลาเดียม ปฏิกิริยาดำเนินไปได้ด้วยดีที่อุณหภูมิห้องด้วยสภาวะที่ไม่รุนแรงและใช้สารตั้งต้นที่สามารถหาซื้อได้ง่ายและมีราคาถูก ให้ร้อยละผลได้ของ PPEs เป็นที่น่าพอใจ 60-93 เปอร์เซ็นต์หลังจากตกตะกอนสองครั้งด้วยเมทานอล นอกจากนี้ยังสามารถเตรียม PPEs ที่ประกอบด้วยหมู่แทนที่ที่หลากหลายเช่น บิลทอกซี, ออกทิลออกซี, เอทิลเฮกซิลออกซี, เมทิลไดเอทอกซี และ ออกซีโพรพานอลได้อีกด้วย โดยให้ร้อยละผลได้ของ PPEs สูงมาก 71-93 เปอร์เซ็นต์ ข้อมูลทางGPC ของ PPEs ที่สังเคราะห์ได้แสดงให้เห็นถึงดัชนีการกระจายน้ำหนักโมเลกุลของพอลิเมอร์ที่แคบเปลี่ยนแปลงในช่วง 2.0 ถึง 2.5 และมีองศาการเกิดพอลิเมอร์สูงอยู่ในช่วงตั้งแต่ 35 ถึง 130 เมื่อเปรียบเทียบผลที่ได้กับวิธีการสังเคราะห์ PPEs แบบเดิมพบว่า PPEs ที่สังเคราะห์ได้มีสมบัติที่เท่ากับหรือดีกว่าในด้านขององศาการเกิดพอลิเมอร์และการกระจายตัวของพอลิเมอร์ เป็นที่น่าสนใจอย่างยิ่งเมื่อ PPEs ที่พิสูจน์เอกลักษณ์ด้วย NMR ระบุว่าไม่มีการเกิดโฮโมคัปปลิงของแอลไคน์ในโครงสร้างของพอลิเมอร์ ชี้ให้เห็นว่า PPEs ที่ได้ไม่มีความบกพร่อง อีกทั้งยังศึกษาสมบัติกายภาพทางแสงของ PPEs ที่สังเคราะห์ได้พบว่ามีประสิทธิภาพควอนตัมสูง (0.34 - 0.71)



สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..

ปีการศึกษา 2555.................................... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..............................

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม..............................

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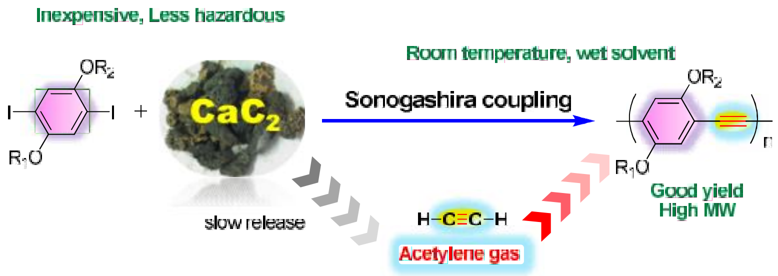
Our research focused on the development of the synthesis of poly(phenylene-ethynylene)s (PPEs) from primary chemical feed stock calcium carbide and aryl diiodides via the Pd-catalyst cross coupling reaction. The reaction proceeds smoothly at ambient temperature with all commercially inexpensive reagents to generate the PPEs in satisfactory yields (60-93%) after double precipitation with methanol. Moreover, a number of PPEs which containing various substituent such as butyloxy, octyloxy, ethyhexyloxy, methyl diethoxy and oxypropanol are successfully prepared in excellent yields (71-93%). The GPC data of the resulting PPEs show the narrow polydispersity index (PDI) vary from 2.0 to 2.5 and high degree of polymerization (DP) ranging from 35 to 130. When compare these data with the conventional method, it indicates that our PPE show equal or better properties in term of DP and PDI. Interestingly, NMR characterizations of PPEs indicate that no homocoupling of alkyne in the PPE structure suggesting defect free PPEs is obtained from this method. The photophisical properties of prepared PPEs are also investigated showing high quantum efficiency of the polymers (0.34 - 0.71).



Field of Study : Petrochemistry and Polymer Science
Academic Year : 2012..................................

Student's Signature ....
Advisor's Signature ....
Co-advisor's Signature ....

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LIST OF ABBREVIATIONS

Ar	Aromatic
br	Broaden (NMR)
calcd	Calculated
CaC_2	Calcium carbide
$CDCl_3$	Deuterated chloroform
CH_2Cl_2	Methylene chloride
^{13}C NMR	Carbon-13 nuclear magnetic resonance
Cs_2Co_3	Caesium carbonate
CuI	Copper iodided
d	Doublet (NMR)
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicycloundec-7-ene
dd	Doublet of doublet (NMR)
DMSO	Dimethyl sulfoxide
DMSO-*d*6	Deuterated dimethyl sulfoxide
DP_n	Degree of polymerization
equiv	Equivalent (s)
EtOAc	Ethyl acetate
FT-IR	Fourier transform infrared spectroscopy
g	Gram (s)
h	Hour
^1H NMR	Proton nuclear magnetic resonance
H_2SO_4	Sulfuric acid
Hz	Hertz
J	Coupling constant
K_2CO_3	Potassium carbonate
m	Multiplet (NMR)
mg	Milligram (s)
min	Minute (s)
mL	Milliliter (s)

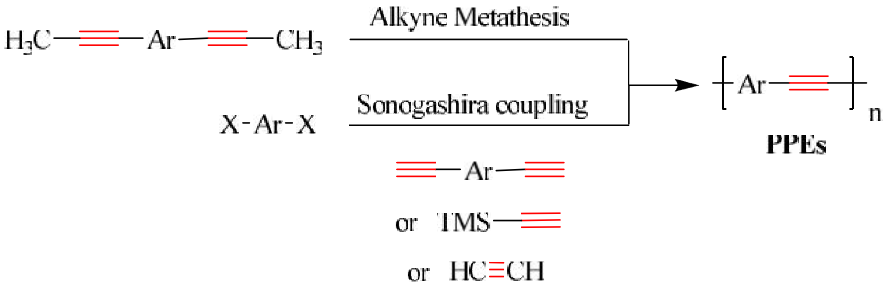
mmol	Millimole
M	Molar
MeCN	Acetonitrile
MeOH	Methanol
M.W.	Molecular weight
$NaSO_4$	Sodium sulfate
NMR	Nuclear magnetic resonance
PAEs	Poly(aryleneethynylene)s
Pd	Palladium
$PdCl_2(PPh_3)_2$	Bis(triphenylphosphine)palladium(II) chloride
$Pd(PPh_3)_4$	Tetrakis(triphenylphosphine)palladium(0)
PDI	Polydispersity index
ppm	Parts per million
PPEs	Poly(phenyleneethynylene)s
rt	Room temperature
s	Singlet (NMR)
t	Triplet (NMR)
TEA	Triethylamine
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Trimethysilyl
UV	Ultraviolet
%	Percent
δ	Chemical shift
°C	Degree Celsius
ε	Molar absorptivity
λ	Lambda
Φ_f	Fluorescence quantum efficiency

CHAPTER I

INTRODUCTION

1.1 Introduction

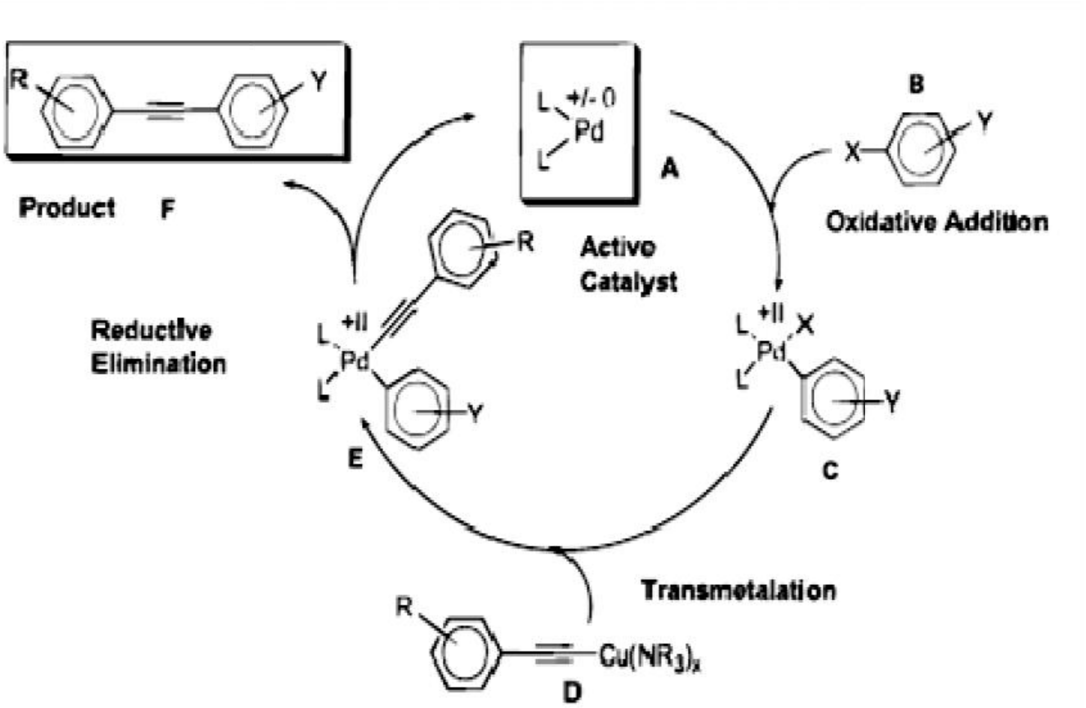
Poly(phenyleneethynylene)s (PPEs) are rigid rod *pi*-conjugated polymer consisting benzene ring and alkyne linker in each repeat units which can be offers a great opportunity to decorate the backbone with various pendants. They find wide uses in many fields such as semiconductor devices [1], molecular wire [2-4], photovoltatic device [5] and molecular electronics [6-7]. Moreover, PPEs display attractive photophysical properties in absorption and emission [8], making them as and an popular fluorophore in sensor application [2, 9-10]. Synthetically, there are currently two general methods available to make PPEs. The first one is the alkyne metathesis [11] which is powerful tool for preparing PPE in high yield and high molecular weight polymer. However, it requires high reaction temperature, high pressure and expensive catalyst such as molybdenum hexacarbonyl ($Mo(Co)_6$) or metalcarbyne catalyzed [8]. Hence, this synthetic method is not favored and less possible to be practical in the industrial scale and laboratory work. While the second one is the most popular method, Pd catalyzed coupling reaction. Its popularity can be attributed to its mild reaction conditions, remarkable functional group tolerance, and high often quantitative yield [12]. This reaction involves the coupling of dihaloarenes to various acetylene sources such as diethynylarenes, protected acetylenes and acetylene gas (Scheme 1.1) which have been reported in many literatures. The results show formation of PPEs in high yield with high to excellent molecular weight. However, these methods have several disadvantages such as multiple step synthesis and high cost material. Although, acetylene gas is appreciably more economical but the major drawback of acetylene gas is its high flammability and complicated instrument set up. Recently, calcium carbide (CaC_2) has been used as an acetylene sources for synthesis of small acetylenic molecules [13-15] since its ease to handle and negligible price. Thus, we are interested to synthesize PPEs using calcium carbide as starting material in the presence of commercially available reagents under mild condition which have not been reported in any literature. Furthermore, compatibility of the reaction with various side chain substituted aryl dihalobenzene and comparison study in term molecular weight and quality of PPEs from CaC_2 and conventional methods are being tested in this work.



Scheme 1.1 General synthetic method for PPEs

1.2 Introduction of Pd-catalyzed polymerizations

Historically, the Pd-catalyzed coupling of terminal alkynes to aromatic bromides or iodides in amine solvents has been known since 1975 [16], so called the Sonogashira cross-coupling reaction. Later, these reactions were first applied for the synthesis of PPEs [16-19] by Giesa and Schulz [20] in 1990. Machanistically, the reaction involves a palladium-mediated cross coupling between a sp^2 hybridized carbon and a sp-hybridized carbon to create a single bond and a conjugated bridge. Its popularity can be attributed to its mild reaction conditions, remarkable functional group tolerance, and high often quantitative yield. The reaction is catalytic in palladium and copper and requires a stoichiometric equivalent of base. The generally accepted mechanism of this reaction is depicted in Scheme 1.2 [12, 17, 20-21] begins with a Pd^0 species **A** undergoing oxidative addition to the aryl–X bond of **B** to form the intermediate **C**. Transmetalation with the Cu acetylide **D** leads to the diorgano-Pd species **E**, which undergoes reductive elimination to yield the product **F**, and regenerating **A**.

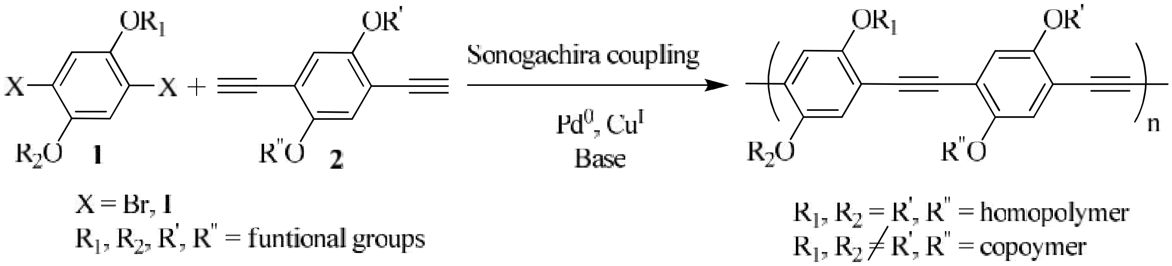


Scheme 1.2 Catalytic cycle of Sonogashira coupling

Currently, PPEs polymerizations employ several acetylene sources as starting material coupling with diharoarene such as diethynylarene, TMS-acetylene and acetylene gas. Thus, the utilization of each acetylene sources for synthesis of PPE will be reviewed and demonstrated in the next topic.

1.2.1 Diethynylarene as acetylene source

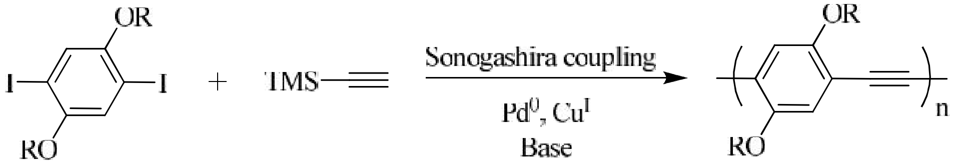
The use of diethynylarene **1** coupling with dihaloarene **2** is the most popular method to produce PPEs both homo– and copolymerization corresponding to side chain substituted benzene ring (Scheme 1.3). Those PPEs are prepared under this method gave high yield with degree of polymerization (DP) approximate 20-50. [8]



Scheme 1.3 Synthesis of PPEs from diethynylarene

1.2.2 TMS-acetylene as acetylene source

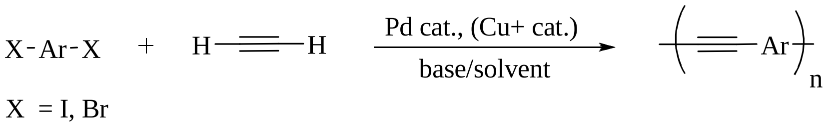
PPE polymerization used protected acetylene have also been reported in several literatures [22-25]. The advantage of this strategy is the one-pot synthesis was required to complete the reaction. Mechanistically, the coupling reaction of iodide and terminal alkyne occurs initially and then deprotected trimethylsilane by *in situ* hydrolysis, and again coupling with iodide. Rate limiting of this reaction is deprotection step which can be restrained the occurrence of diyne defect [23]. The resultant PPEs showed high degree of polymerization (DP ≈ 70-80) and narrow polydispersity index (PDI ≈ 1.5-3.0).



Scheme 1.4 Synthesis of PPEs from TMS-acetylene

1.2.3 Acetylene gas as acetylene source

Dihaloarene can also be polymerized directly with acetylene gas (Scheme 1.5) via Sonogashira coupling reaction. This strategy is one of the most effective process yielding polymer in good yields and high compatibility of diharoarene starting materials. The resultant polymers showed high molecular weight and high purity absence diyne formation [26].



Scheme 1.5 Synthesis of PPEs from acetylene gas

As mentioned above, we found that all acetylene source is effective reagent which can be produced PPEs in high yield with moderate to high molecular weight. However, there are several disadvantages which can be demonstrated in Table 1.1.

Table 1.1 Disadvantages of conventional acetylene source

Entry	**Acetylene sources**	**Disadvantages**
1	Diethynylarene	1) Multiple step process, the diiodobenzene and the dialkynylbenzene have to be synthesized 2) 5-10% alkyne homocoupling, end group presented in PPE backbone
2	TMS-acetylene	1) High cost material
3	Acetylene gas	1) High flamibility 2) Complicated experiment setup 3) Required expensive reactor 4) Needed close attention during the process

Recently, calcium carbide (CaC_2) has been used as a new acetylene source for synthesis of small acetylenic molecules [13-15] since its ease to handle and its negligible price. Thus we are interested in the synthesis of PPEs using alternative acetylene source, calcium carbide as starting material in the presence of commercially available reagents under mild condition.

1.3 Introduction of calcium carbide

Calcium carbide (CaC_2) is a flammable compound producing by the reaction of calcium oxide with carbon in an electric furnace at temperatures in the range 1,800° to 2,100°C [27] (Scheme 1.6a). The basic chemical process was discovered since in 1888 [28]. Pure calcium carbide is colorless, but most of the material is produced industrially, and is somewhat impure, giving it a black or grayish-white color. Typically, the carbide product produced generally contains around 80% calcium carbide by weight with the less rest such as CaO, Ca_3P_2, CaS, Ca_3N_2, SiC, etc [27]. Due to its inexpensive price and domestically availability, it has been widely used. The most important application of calcium carbide is the production of flammable gas acetylene by reacted with water (Scheme 1.6b). It also is used to produce calcium cyanamide ($CaCN_2$) by reacting with nitrogen at about 1,000°C (Scheme 1.6c), used as a fertilizer and a source of ammonia [27] and others such as use for incubation of agricultural products [29-30], production of PVC [31-32], use as a chemical reagent or cutting fuel in the iron (foundry) and steel industries, use as a low-priced fuel, and use in chemical synthesis [33-36].

$$\mathrm{CaO + 3C} \xrightarrow{1{,}800\text{-}2{,}100\ ^{0}\mathrm{C}} \mathbf{CaC_2} + \mathrm{CO} \quad \text{- - - - - - - - - - -} \quad \text{(a)}$$

$$\mathrm{CaC_2 + 2H_2O} \xrightarrow{\qquad\qquad} \mathbf{C_2H_2} + \mathrm{Ca(OH)_2} \quad \text{- - - - - - - -} \quad \text{(b)}$$

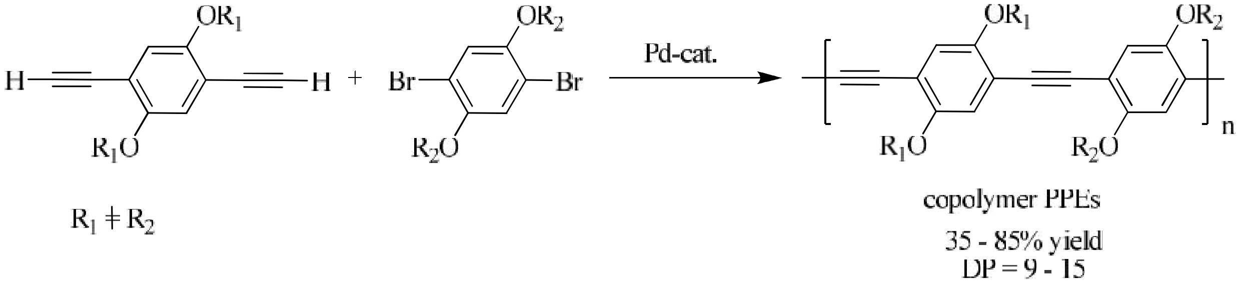
$$\mathrm{CaC_2 + N_2} \xrightarrow{\qquad\qquad} \mathbf{CaCN_2} + \mathrm{C} \quad \text{- - - - - - - - - - -} \quad \text{(c)}$$

Scheme 1.6 Production of a) calcium carbide, b) acetylene gas, c) calcium cyanamide

1.4 Literature reviews

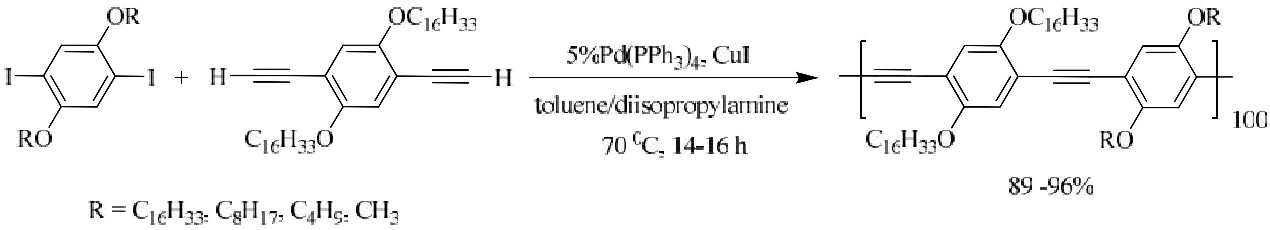
1.4.1 Synthesis of PPEs from diethynylarene

In 1990, Giesa and Schulz were the first to utilize the Sonogashira coupling to make dialkoxy-PPEs and some other PAEs [20]. The authors employed dibromoarenes in combination with diethynylarenes in these Pd-catalyzed coupling reactions to afford copolymer PPEs in good yield with low molecular weight (DP = 9-15) (Scheme 1.7). Their PAEs were purplish-grey or chocolate colored, suggesting significant defects of alkyne homocoupling, end group or phosphine salt formation [8].



Scheme 1.7 Synthesis of PPEs from dihaloarene and diethynylarene

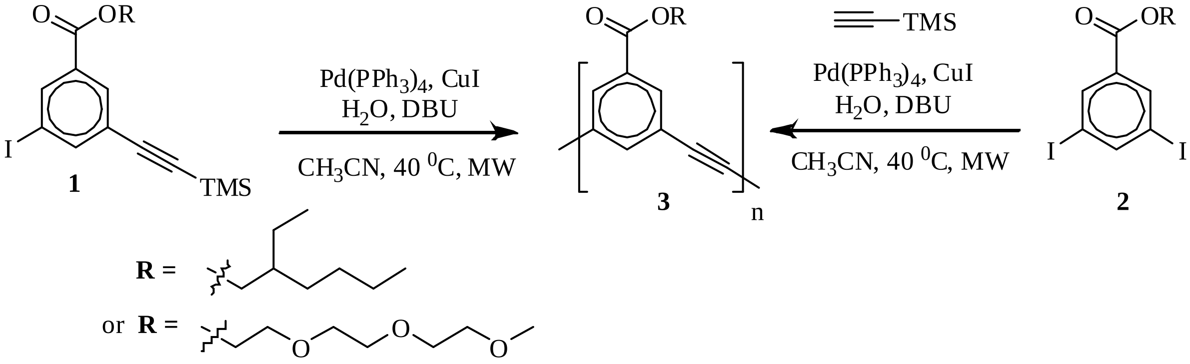
In 1995, Swager and co-workers prepared soluble conjugated rigid-rod poly(p-phenyleneethynylene)s in high yields (89 – 96%) by coupling aryl acetylene with aryl diiodide at 70 ^{0}C for 14-16 h (Scheme 1.8). The result showed PPEs containing R = 50% C_4H_9 and 50% CH_3 had the highest molecular weight (98,000 Da.) or degree of polymerization (DP = 100). Moreover, they found the variations in monomer ratios can be used to adjust the molecular weights of the polymers. By adjusting the monomer stoichiometry closer to unity, high molecular weight polymers can be synthesized [37].



Scheme 1.8 Synthesis of PPEs from dihaloarene and diethynylarene

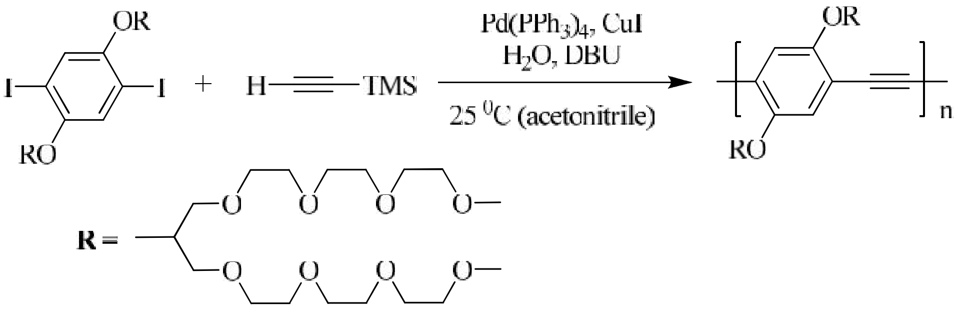
1.4.2 Synthesis of PPEs from TMS-acetylene

In 2004, Khan and Hecht [23] reported the synthesis of poly(*m*-phenyleneethynylene)s from coupling reaction of **1** or **2** with TMSA (Scheme 1.9), by using 6 mol% Pd(PPh_3)$_4$, 10 equiv. of water, microwave irradiation at 40 °C for 4 h, and the use of a highly concentrated reaction mixture. The resulting polymers **3** showed respectable chain-lengths (DP ~ 80) with no signals at two point: $80.6 \geq \delta \geq 79.7$ and $75.4 \geq \delta \geq 74.7$ ppm that could be attributed to diyne defects. The success of this reaction is due to the amount of water which is necessary to deprotect the silylated acetylene. This step was hypothesized that represented the rate-limiting step of this reaction.



Scheme 1.9 Synthesis of P*m*PEs from dihaloarene and TMS acetylene

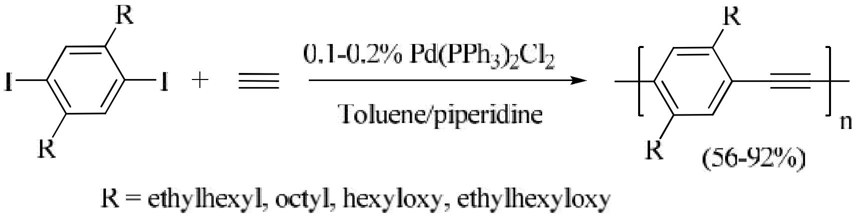
In 2005, Khan and co-workers [22] demonstrated a practical synthetic route to a non-ionic, non-protic, amphiphilic PPE derivative using two branched ethyleneglycol (OEG) as side chain which should render the backbone soluble in the variety of media including water. The reaction involved Sonogashira coupling of aryl iodides with TMS acetylene at room temperature for 3 days to form polymer in 83% yield with high degree of polymerization (DP = 30), narrow polydispersity index (PDI = 2.0) and performed high quantum yields which can be explained by the absence of diacetylene defects. Moreover, the resulting PPE displayed good solubility in a wide range of different solvents, most importantly in water (0.7 mg. mL^{-1}).



Scheme 1.10 Synthesis of P*m*PEs from dihaloarene and TMS acetylene

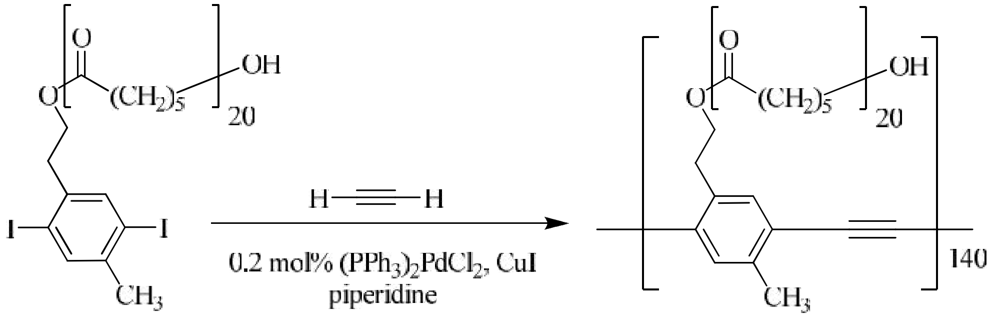
1.4.3 Synthesis of PPEs from acetylene gas

In 2002, Bunz and co-workers [26] developed the use of acetylene gas for poly(*p*-phenyleneethynylene)s synthesis (Scheme 1.11). Varieties of PPEs have been polymerized in mild condition, catalyst loading 0.1- 0.2% Pd(PPh$_3$)Cl$_2$ were sufficient for this strategy. In addition, they found the best solvent to be a 1:1 mixture of toluene and piperidine and optimum molar ratio of diiodobenzene to acetylene gas was between 1.0 and 1.1. These stoichiometries utilizing monomer yielded polymers of exceptionally high yields and high quality with degree of polymerization as high as 316 for R = ethylhexyloxy.



Scheme 1.11 Synthesis of PPEs from dihaloarene and acetylene gas

In 2003, Wang and co-worker [38] reported the synthesis of PPE with macromolecular side chains via Pd-catalyzed coupling reaction of grafted side chain macromonomer with acetylene gas furnishing a deep-yellow, flaky material after precipitation from methanol. The reaction gave 78% yield of polymer with very high degree of polymerization of 140 repeating units and displayed the signals of the alkyne carbons at 92 ppm.

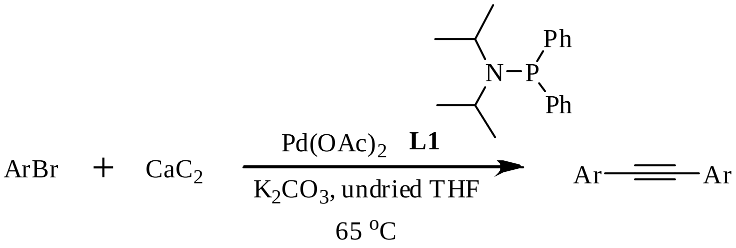


Scheme 1.12 Synthesis of PPEs from dihaloarene and acetylene gas

1.4.4 The uses of calcium carbide in organic synthesis

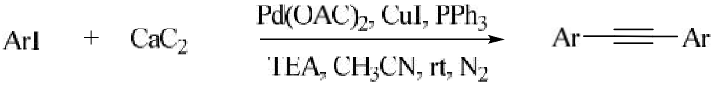
Calcium carbide is the primary feed stock for generate series of acetylene source which used in organic synthesis. This low cost effective material, calcium carbide is more economical carbon source than the acetylene gas for 500 times and also have several advantages in term of experiment due to its solid state such as its ease to handle, facile experiment setup and stock it safely. Thus in recent year, the utilizations of calcium carbide for Pd-catalyzed coupling reaction are being developed continuously.

In 2006, Zhang [15] reported the synthesis of diarylethynes via copper free Pd-catalyzed coupling reaction of aryl bromides from calcium carbide (Scheme 1.13). The reaction gave moderate to high yields for aryl bromide containing electron-donating substituents. However, low yield were obtained in the case of electron-deficient aryl bromide. However, this process required an amino phosphine ligand which was not commercially available. Thus, this method is inconvenient in laboratory and cannot be practical in the industrial.

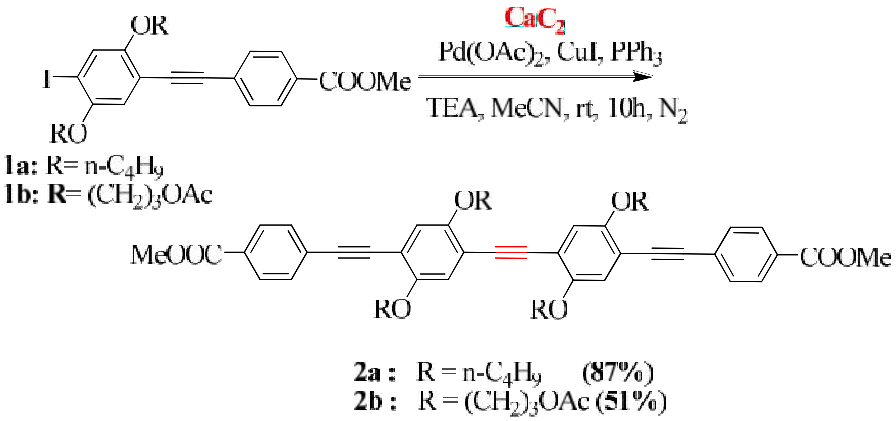


Scheme 1.13 The previous use of calcium carbide in diarylethynes synthesis

In 2011, Chuentragool and co-workers [13] were successfully developed the synthesis of diarylethyne using calcium carbide as alkyne source coupling with varieties of aryl iodide via Sonogashira coupling reaction (Scheme 1.14). The reactions were carried out under mild conditions in undried acetonitrile, used inexpensive and commercially available reagents such as $Pd(OAc)_2$, CuI, PPh_3 and TEA to afford the symmetrical diarylethynes in excellent yields as high as 99% by only a simple filtration through a bed of silica gel. The reaction not only proceeds with excellent yield but also tolerates a wide range of functional groups. Moreover, this reaction was first accomplished for the synthesis of highly functionalized oligo (phenyleneethynylenes) in good yields (51-87%) (Scheme 1.15).

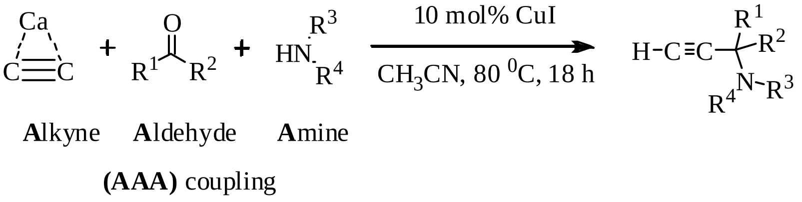


Scheme 1.14 Synthesis of diarylethynes from calcium carbide



Scheme 1.15 Synthesis of oligo (phenyleneethynylenes) from calcium carbide

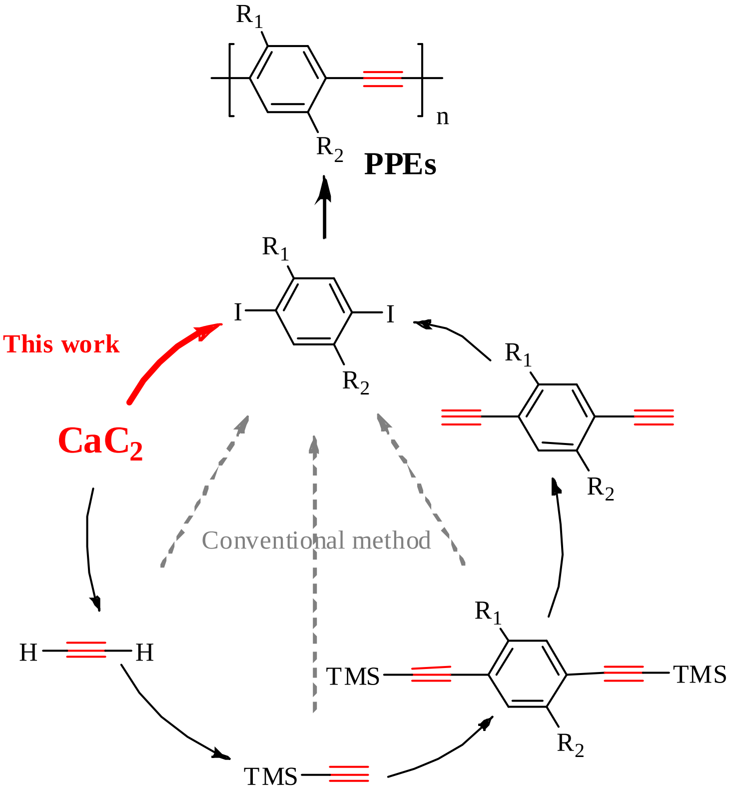
In 2012, Lin and co-workers [14] successfully prepared mono-substituted aminopropynes and related compounds directly from calcium carbide with the corresponding amine and aldehyde or ketone via alkyne, aldehyde, amine (AAA) coupling using CuI as catalyst as shown in Scheme 1.16. The yields of monosubstituted aminopropyne products with a terminal alkyne function ranged from good to high yields (68-86%). However, no reaction was observed for primary amines. This may be due to the lower activity of imine intermediates for primary amines compared to iminium intermediates for secondary amines.



Scheme 1.16 Synthesis of aminopropynes from calcium carbide

1.5 Objective of this research

From all relevant research above, the effective synthesis of small acetylenic molecules have been reported by utilizing calcium carbide as alkyne source, but there was no report that use calcium carbide which is easy to handle, high efficiency and low cost for the synthesis of acetylenic polymers such as PPEs. In fact, calcium carbide is a primary feed stock, for the large scale production acetylene gas, TMS-acetylene and even diethynylarene. Thus, this work aim to use directly calcium carbide as alternative reagent coupling with aryl diiodides via Sonogashira coupling reaction focusing on milder condition to synthesize PPEs with high yield, high molecular weight and high quality (Scheme 1.17 below). This work is going to study the reaction optimization including the effect of palladium sources, catalyst loading, substrate concentration, base and solvents. Also, molecular weight and photophysical properties are being determined to compare with PPEs from conventional method.



Scheme 1.17 Objective of this research

CHAPTER II

EXPERIMENTAL

All reagents were purchased from Sigma-Aldrich, Fluka® (Switzerland) or Merck® (Germany) and used without further purification. Analytical thin-layer chromatography (TLC) was performed on Kieselgel F-254 pre-coated plastic TLC plates from EM Science. Visualization was performed with a 254 nm ultraviolet lamp. Gel column chromatography was carried out with silica gel (60, 230-400 mesh) from ICN Silitech. Elemental (C, H, N) analysis was performed on PE 2400 series II (Perkin-Elmer, USA). The ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 or Bruker 400 in $CDCl_3$ and DMSO-d_6. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards: chloroform (δ 7.26 for ^{1}H, δ 77.00 for ^{13}C) and DMSO-d_6 (δ 2.50 for ^{1}H, δ 39.52 for ^{13}C). Coupling constants (J) are reported in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triple), q (quartet), bs (broad singlet), m (multiplet). Fourier transform infrared spectra were acquired on Nicolet 6700 FT-IR spectrometer equipped with a mercury-cadminum telluride (MCT) detector (Nicolet, USA). All polymer solutions were filtered through 0.45 μm syringe filters prior to use. Polymer molecular weights were determined by Waters 600 controller chromatograph equipped two HR (waters), column (HR1 and HR4) at 35 ^{o}C and a reflective index detector (waters 2414). Tetrahydrofuran was used as an eluent with the flow rate of 1.0 mL/min (3mg/mL sample concentrations). Sample injection volume was 50 µL. Polystyrenes (996-188,000 Da.) were used as standards for calibration. The UV-Visible spectra were obtained from a Varian Cary 50 UV-Vis spectrophotometer (Varian, USA) using $CHCl_3$ and DMSO as a solvent and recorded the spectra from 200 nm to 600 nm at ambient temperature. Fluorescence emission spectra and fluorescence quantum efficiency were acquired by using Perkin Elmer precisely LS 45, quinine sulphate in 0.1 M H_2SO_4 ($\Phi_f = 0.54$) was used as the standard.

2.1 Initial observation

Table 3.1 Initial observation using 4-iodotoluene: A 100 mL round bottom flask with a magnetic stir bar was charged with 200.0 mg of 4-iodotoluene (1 equiv), CaC_2 (6 equiv), palladium sources such as $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$ and $Pd(OAc)_2$ (0.05 equiv), CuI (0.10 equiv) and PPh_3 (0.10 equiv) in THF 12 mL. The solution was stirred and degassed with N_2 for 5 minutes. Then, TEA was added (6 mL). The mixture was stirred at room temperature for 20 h. The reaction mixture was then filtrated through a filter paper and washed with CH_2Cl_2. The filtered was evaporated under vacuum and separated by column chromatography using 100% hexane as the eluent to give 1,2-dip-tolylethyne in corresponding yields.

1,4-dibutoxy-2,5-diiodobenzene (2a)

Compound 1a: To a stirred suspension of KOH (4.58 g, 81.72 mmol) and hydroquinone (2.00 g, 18.16 mmol) in DMF (15 mL) was added dropwise butyl bromide (9.95 g, 72.64 mmol). The mixture was stirred at room temperature for overnight. The mixture was extracted three times with CH_2Cl_2. The combined organic phase was washed with water, brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 8.82 g (18.16 mmol, 76%) of **1a** as a light brown solid: ^1H NMR (400 MHz, *$CDCl_3$*) δ ppm 6.82 (s, 4H), 3.90 (t, *J* = 6.5 Hz, 4H),1.77-1.70 (m, 4H), 1.52-1.43 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 153.7, 115.9, 68.9, 32.0, 19.7, 14.3.

Compound 2a: To a stirred of **1a** (4.00 g, 17.99 mmol) in MeOH (30 mL) at temperature below 15 ^0C was added dropwise iodine(I) chloride (12.76 g, 78.61 mmol) and the mixture was stirred reflux for 1 day under pressure of N_2. The mixture was extracted three times with CH_2Cl_2. The combined extract was washed with aqueous $Na_2S_2O_3$, water, and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to afford 6.25 g (17.99 mmol, 74%) of **2a** as a white solid. ^1H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.17 (s, 2H), 3.93 (t, *J* = 6.4 Hz, 4H), 1.82-1.75

(m, 4H), 1.58-1.49 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ ppm 153.2, 123.2, 86.6, 70.4, 31.6, 19.6, 14.1. This spectral data agreed with the results reported in the literature [37].

2.2 Pd-catalyst coupling reaction using calcium carbide as a starting material.

2.2.1 Optimization conditions

General procedure for purification of poly(1,4-dibutoxy-*p*-phenylene ethynylene) (3a) (procedure A): After the reaction proceeded completely, the reaction mixture was then filtered through a cotton wool and washed with CH_2Cl_2 several times until the color of polymer solution disappear. The filtrated was evaporated under vacuum and precipitated by dropping the solution into 150 mL of MeOH. The precipitate that formed was collected by centrifuge, washed repeatedly with MeOH and evaporated under vacuum to give poly(1,4-dibutoxy-*p*-phenyleneethynylene) **(3a)** in corresponding yields. After that the desired product was characterized by ^{1}H, ^{13}CNMR spectroscopy, FT-IR and elemental analysis (EA) and then determined the molecular weight by gel permeation chromatography (GPC).

Table 3.2 Catalyst loading and substrate concentration: A 100 mL round bottom flask with a magnetic stir bar was charged with 150.0 mg of 1,4-dibutoxy-2,5-diiodobenzene (2a) (1 equiv), CaC_2 (6 equiv), $Pd(OAc)_2$ (0.01, 0.05, 0.10 and 0.20 equiv), CuI and PPh_3 (2 times of the $Pd(OAc)_2$ equivalent). The mixture was degassed with N_2 for 30 seconds and then the solvent mixture of TEA/THF in ratio 1:2 were added corresponding to substrate concentration (0.05, 0.10 and 0.20 M). The reaction mixture was stirred under N_2 at rt for 20 h and then purified the desired product according to general procedure A to give orange powder of PPE **3a** in corresponding yields.

Table 3.3 Amount of CaC_2 and TEA: A 100 mL round bottom flask with a magnetic stir bar was charged with 150.0 mg of 1,4-dibutoxy-2,5-diiodobenzene (2a) (1 equiv), CaC_2 (3 or 6 equiv), $Pd(OAc)_2$ (0.05 equiv), CuI (0.10 equiv) and PPh_3 (0.10 equiv). The mixture was degassed with nitrogen for 30 seconds and then added MeCN (3 or 6 mL) or THF (3 or 4 mL). It must be noted that volume of solvent corresponding to concentration at 0.05 M. The solution was stirred and degassed with N_2 for 5 minutes and then TEA was added (3 or 6 equiv and 2 mL). The reaction mixture was stirred under N_2 at rt for 20 h and then purified the desired product according to general procedure A to give orange powder of PPE **3a** in corresponding yields.

Table 3.4 Base and solvent screening: A 100 mL round bottom flask with a magnetic stir bar was charged with 150.0 mg of 1,4-dibutoxy-2,5-diiodobenzene (2a) (1 equiv), CaC_2 (6 equiv), $Pd(OAc)_2$ (0.05 equiv), CuI (0.10 equiv) and PPh_3 (0.10 equiv). The mixture was degassed with nitrogen for 30 seconds and then the mixture of base/solvent in ratio 1:2 were added by fixed concentration at 0.05 M. The reaction mixture was stirred under N_2 at rt for 20 h and then purified the desired product according to general procedure A to give orange powder of PPE **3a** in corresponding yields.

2.2.2 Monomer (2a) and polymer (3a) characterization

PPE 3a: A 100 mL round bottom flask with a magnetic stir bar was charged with 2a (150 mg, 0.31 mmol), palladium(II)acetate (3.37 mg, 0.015 mmol), copper iodide (5.90 mg, 0.031 mmol), triphenylphosphine (8.13mg, 0.031 mmol), calcium carbide (119.22 mg, 1.86 mmol) and DBU (2 mL) in THF (4 mL). The solution mixture was carried out under positive pressure of N_2 filled in rubber balloons. The mixture was stirred at room temperature for 20 hours and then purified the desired product according to general procedure A. This reaction gave 53.5 mg (0.22 mmol, 71%) of 3a-3 as a yellow orange powder. GPC (vs.polystyrene standards in tetrahydrofuran): $M_w = 20{,}168$, $M_w/M_n = 2.3$, $DP_n = 36$. ^1H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.01 (br, 2H), 4.04 (br, 4H), 1.83 (br, 4H), 1.55 (br, 4H), 0.99 (br, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 153.7, 117.6, 114.6, 91.8, 69.7, 31.6, 19.4, 14.1. IR (neat, cm^{-1}) 2954, 2929, 2869, 2200, 2157, 1768, 1721, 1595.

2.2.3 Comparative study between other conventional methods with CaC_2 method

Part I: Synthesis section

1) *Preparation of 1,4-dibutoxy-2,5-diethynylbenzene* ***(2a-H)***

Compound 2a-TMS: A 100 mL round bottom flask with a magnetic stir bar was charged with 1,4-dibutoxy-2,5-diiodobenzene (2a) (1.00 g, 2.11 mmol), $PdCl_2(PPh_3)_2$ (28 mg, 0.04 mmol), CuI (15 mg, 0.07 mmol), PPh_3 (21 mg, 0.08 mmol). The mixture was added with THF (5 mL) and TEA (1.21 g, 12.00 mmol). The mixture was stirred for 5 minutes and then added ethynyltrimethylsilane (0.63 g, 6.42 mmol). The reaction mixture was stirred under N_2 at rt for 4 days. The mixture was extracted three times with CH_2Cl_2/NH_4Cl. The combined organic phase was dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography using 100% hexane as eluent to provide 0.52 g (1.26 mmol, 62%) of **2a-TMS** as a bright yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 6.89 (s, 2H), 3.95 (t, *J* = 6.3 Hz, 4H), 1.80 – 1.73 (m, 4H), 1.56 – 1.49 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 6H), 0.25 (s, 18H). This spectral data agreed with the results reported in the literature [39].

Compound 2a-H: A 100 mL round bottom flask with a magnetic stir bar was charged with 2a-TMS (0.52 g, 1.26 mmol). The mixture was added with 20% K_2CO_3 (35 mg, 0.25 mmol), CH_2Cl_2 (5 mL) and MeOH (5 mL). The reaction mixture was stirred under N_2 at rt for 4 h. The mixture was extracted three times with CH_2Cl_2. The combined organic phase was washed three times with NH_4Cl and washed again with H_2O and then dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 0.28 g (1.05 mmol, 83%) of **2a-H** as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ ppm 6.95 (s, 2H), 3.98 (t, *J* = 6.5 Hz, 4H), 3.33 (s, 2H), 1.82 – 1.75 (m, 4H), 1.56 – 1.47 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 6H). This spectral data agreed with the results reported in the literature [39].

*2) Synthesis of PPE **3a** from various acetylene sources*

Synthesis of PPE 3a-1 from diethynylarene (2a-H) [40]**:** A 100 mL round bottom flask with a magnetic stir bar was charged with 2a (100.0 mg, 0.21 mmol), 2a-H (59.62 mg, 0.22 mmol), $PdCl_2(PPh_3)_2$ (0.29 mg, 0.42×10^{-3} mmol), CuI (0.08 mg, 0.42×10^{-3} mmol). The mixture was added with solvent mixture of TEA/toluene in ratio 1:2. The solution was stirred at rt under N_2 atmosphere for 12 h and then purifying the desired product according to general procedure A. This reaction gave 48.51 mg (0.20 mmol, 95%) of **3a-1** as an orange powder. ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.02 (s, 2H), 4.06-4.03 (t, 4H), 4.05 (t, *J* = 6.1 Hz, 4H), 1.85 (dt, *J* = 13.8, 6.9 Hz, 4H), 1.58 (dt, *J* = 13.9, 6.9 Hz, 4H), 1.00 (t, *J* = 7.1 Hz, 6H).

Synthesis of PPE 3a-2 from TMS acetylene [22]**:** A 100 mL round bottom flask with a magnetic stir bar was charged with **2a** (150.0 mg, 0.31 mmol), $Pd(PPh_3)_4$ (17.34 mg, 0.015 mmol), CuI (5.90 mg, 0.031 mmol). The mixture was added with solvent mixture of MeCN/THF and stirred for 30 seconds. Then, the solution mixture was added with TMS-acetylene (36.53 mg, 0.37 mmol) and DBU (0.28 g, 1.86 mmol), respectively. The solution was stirred at rt under N_2 atmosphere for 3 days and then purified the desired product according to general procedure A. This reaction gave 75.9 mg (0.31 mmol, 100%) of **3a-2** as a yellow greenish powder. GPC (vs.polystyrene standards in tetrahydrofuran): M_w = 9,669, M_w/M_n = 2.3, DP_n = 17. ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.02 (s, 2H), 4.04 (br, 4H), 1.84 (br, 4H), 1.56 (br, 4H), 1.00 (br, 6H).

2.3 Preparation of aryl diiodides

Compound 2b [37, 41]

1b: To a stirred solution of hydroquinone (2.00 g, 18.16 mmol), KOH (4.59 g, 81.72 mmol) in DMF (15 mL). The solution was added dropwise with n-octyl bromide (14.03 g, 72.64 mmol). The mixture was stirred at room temperature for overnight. The mixture was extracted three times with CH_2Cl_2. The combined organic phase was washed with water, brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to afford 3.05 g (18.16 mmol, 50%) of **1b** as a white powder: ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 6.81 (s, 4H), 3.89 (t, *J* = 6.6 Hz, 4H),1.78-1.71 (m, 4H), 1.47-1.40 (m, 4H), 1.32-1.28 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 153.7, 115.9, 69.2, 32.3, 29.9, 29.9, 29.7, 26.5, 23.1, 14.6.

2b: To a stirred of 1b (3.00 g, 8.98 mmol) in MeOH (20 mL) at temperature below 15 ^{0}C was added dropwise iodine(I) chloride (6.37 g, 39.25 mmol) and the mixture was stirred reflux for 1 day under pressure of N_2. The mixture was extracted three times with CH_2Cl_2. The combined extract was washed with aqueous $Na_2S_2O_3$, water, and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to afford 1.89 g (8.98 mmol, 36%) of **2b** as a white powder. ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.17 (s, 2H), 3.92 (t, *J* = 6.4 Hz, 4H), 1.83 – 1.75 (m, 4H), 1.54 – 1.44 (m, 4H), 1.39 – 1.24 (m, 16H), 0.89 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 152.9, 122.9, 86.4, 70.4, 31.8, 29.3, 29.2, 29.2, 26.0, 22.7, 14.1.

Compound 2c [42]

1c: To a stirred solution of hydroquinone (2.00 g, 18.16 mmol), KOH (4.59 g, 81.72 mmol) in dried DMSO (15 mL). The solution was added dropwise with 2-ethylhexyl bromide (14.03 g, 72.64 mmol). The mixture was stirred at room temperature for overnight. The mixture was extracted three times with CH_2Cl_2. The combined organic phase was washed with water, brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to afford 5.59 g (18.16 mmol, 92%) of **1c** as a colorless oil. ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 6.83 (s, 4H), 3.79 (d, *J* = 4.5 Hz, 4H), 1.69 (dd, *J* = 11.2, 5.4 Hz, 2H), 1.56 – 1.21 (m, 16H), 1.06 – 0.85 (m, 12H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 153.7, 115.6, 71.5, 39.8, 30.8, 29.4, 24.1, 23.3, 14.3, 11.3.

2c: To a stirred of 1c (0.50 g, 1.49 mmol), in MeOH (35 mL) at temperature below 15 ^{0}C was added dropwise iodine(I) chloride (1.07 g, 5.96 mmol) and the mixture was stirred reflux for 1 day under pressure of N_2.The mixture was extracted three times with CH_2Cl_2. The combined extract was washed with aqueous $Na_2S_2O_3$, water, and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to afford 0.69 g (1.49 mmol, 78%) of **2c** as a colorless oil. ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.15 (s, 2H), 3.83 (d, *J* = 5.4 Hz, 4H), 1.72 (m, 2H), 1.59 – 1.38 (m, 8H), 1.36 – 1.24 (m, 8H), 0.91 (m, 12H). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ ppm 152.4, 121.9, 85.6, 71.9, 39.0, 30.0, 28.6, 23.5, 22.5, 13.6, 10.8.

Compound 2e [43]

1d: To a stirred solution of hydroquinone (1.00 g, 9.08 mmol), KOH (3.40 g, 60.4 mmol) in dried DMSO (10 mL). The solution was added dropwise with n-ethylhexyl bromide (0.58 g, 3.02 mmol). The mixture was stirred at room temperature for overnight. The mixture was extracted three times with CH_2Cl_2. The combined organic phase was washed with water, brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to afford 0.51 g (3.02 mmol, 77%) of **1d** as an colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, *J* = 6.7 Hz, 4H), 5.20 (s, 1H), 3.78 (d, *J* = 5.9 Hz, 2H), 1.73-1.67 (m, 1H), 1.53 – 1.38 (m, 4H), 1.33-1.31 (m, 4H), 0.94-0.91 (t, 6H). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ ppm 153.6, 149.3, 116.1, 115.8, 71.5, 39.5, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1.

1e: To a stirred solution of 1d (0.51 g, 2.31 mmol) in dried THF (15 mL) was charged with MeI (0.98 g, 6.94 mmol) and then added NaH (0.11 g, 4.62 mmol). The reaction mixture was stirred for 12 h at 70 ^{0}C and finally dropped with MeOH (5 mL). The reaction mixture was extracted with CH_2Cl_2 (3× 50) and the combined organic layers were dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 0.46 g (2.31 mmol, 85%) of **1e** as an colorless oil. ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 6.85 (s, 4H), 3.86 – 3.65 (m, 5H), 1.75-1.69 (m, 1H), 1.57 – 1.30 (m, 8H), 0.96-0.88 (m, 6H) ^{13}C NMR (101 MHz, *CDCl$_3$*) δ ppm 152.7, 152.2, 114.5, 113.6, 70.3, 54.7, 38.5, 29.6, 28.1, 22.9, 22.1, 13.0, 10.1.

2e: A solution of 1e (0.15 g, 0.65 mmol), H_5IO_6 (0.07 g, 0.33 mmol) and I_2 (0.33 g, 1.30 mmol) in 1.5 mL acetic acid, 1 mL sulphuric acid and 2 mL water was stirred at 70 ^{0}C for 12 h. After cooling, the mixture was extracted with CH_2Cl_2 (3×50). The organic layer was washed with aqueous $Na_2S_2O_3$, water, and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 0.19 g (0.65 mmol, 60%) of **2e** as a colorless oil. ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.19 (s, 1H), 7.16 (s, 1H), 3.82 (d, *J* = 3.0 Hz, 5H), 1.79 – 1.68 (m, 1H), 1.60 – 1.40 (m, 4H), 1.35 (dd, *J* = 23.2, 19.7 Hz, 4H), 0.97 – 0.88 (m, 6H). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ ppm 153.3, 153.2, 122.6, 121.7, 86.3, 85.6, 72.5, 57.3, 39.6, 30.6, 29.2, 24.1, 23.1, 14.2, 11.3.

Compound 2f [44]

1f: To a stirred suspension of K_2CO_3 (4.5 g, 32.56 mmol) and hydroquinone (1 g, 9.08 mmol) in MeCN (10 mL) was added dropwise 3-chloropropan-1-ol (2.58 g, 27.25 mmol). The mixture was refluxed overnight. The mixture was extracted with CH_2Cl_2 (3× 50) and the combined organic layers were dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 1.26 g (9.08 mmol, 76%) of **1f** as a white powder. ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 6.83 (s, 4H), 4.07 (t, *J* = 5.9 Hz, 4H), 3.86 (t, *J* = 5.9 Hz, 4H), 2.10 – 1.98 (m, 4H),1.89 (s, 2H). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ ppm 153.0, 115.4, 66.5, 60.5, 31.9.

2f: To a stirred of 1f (1.50 g, 5.64 mmol) in MeOH (15 mL) at temperature below 15 ^{0}C was added dropwise iodine(I) chloride (4.57 g, 28.18 mmol) and the mixture was stirred reflux for 1 day under pressure of N_2.The mixture was extracted three times with CH_2Cl_2. The combined extract was washed with aqueous $Na_2S_2O_3$, water, and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to afford 2.64 g (5.52 mmol, 98%) of **2f** as a white solid. ^{1}H NMR (400 MHz, *DMSO*) δ ppm 7.33 (s, 2H), 4.52 (s, 2H), 4.01 (t, *J* = 6.2 Hz, 4H), 3.58 (t, *J* = 5.9 Hz, 4H), 1.83 (p, *J* = 6.2 Hz, 4H). ^{13}C NMR (101 MHz, *DMSO*) δ ppm 152.3, 122.4, 86.9, 66.8, 57.3, 32.1.

Compound 2h [45]

1g: To a stirred solution of diethyleneglycol monomethylether (10.38 g, 86.31 mmol) and DMAP in CH_2Cl_2 (150 mL) was charged with triethylamine (25.00 mL, 178 mmol). The reaction mixture was stirred at 0 ^{0}C for 10 min and then dropwise with mesylchloride (10.92 g, 95.2 mmol). The reaction mixture was stirred at room temperature for 2 h. The mixture was extracted with CH_2Cl_2 (3× 50) and the combined organic layers were dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 15.47 g (78.0 mmol, 90%) of **1g** as a light yellow oil. ^{1}H NMR (400 MHz, *CDCl*$_3$) δ ppm 4.33 (t, *J* = 4.60 Hz, 2H), 3.72 (t, *J* = 4.40 Hz, 2H), 3.60 (t, *J* = 4.40 Hz, 2H), 3.49 (t, *J* = 4.60 Hz, 2H), 3.32 (s, 3H), 3.02 (s, 3H).

1h: To a stirred solution of hydroquinone (1.53 g, 13.89 mmol) and KOH (2.44 g, 43.5 mmol) in DMF (30 mL) was added with 1g (5.81 g, 29.3 mmol). The reaction mixture was stirred at 60 ^{0}C for 20 h. The reaction mixture was extracted with CH_2Cl_2 / 0.1 M HCl and the combined organic phase was washed with water (10×100), dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 4.21 g (13.34 mmol, 96%) of **1h** as a brown oil. ^{1}H NMR (400 MHz, *CDCl*$_3$) δ ppm 6.80 (s, 4H), 4.05 (t, *J* = 5.00 Hz, 4H), 3.79 (t, *J* = 4.80 Hz, 4H), 3.68 (t, *J* = 4.60 Hz, 4H), 3.54 (t, *J* = 4.60 Hz, 4H), 3.35 (s, 6H).

2h: A solution of 1h (0.50 g, 1.59 mmol), H_5IO_6 (0.18 g, 0.79 mmol) and I_2 (0.80 g, 3.18 mmol) in acetic acid (4.5 mL), sulfuric acid (3 mL) and water (6 mL) was stirred at 70 ^{0}C for 12 h. After cooling, the mixture was extracted with CH_2Cl_2 (3×50). The organic layer was washed with aqueous $Na_2S_2O_3$, water, and brine, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 0.59 g (1.04 mmol, 66%) of **2h** as a white powder. ^{1}H NMR (400 MHz, *CDCl*$_3$) δ ppm 7.23 (s, 2H), 4.11 (t, *J* = 4.80 Hz, 4H), 3.89 (t, *J* = 4.80 Hz, 4H), 3.78 (t, *J* = 4.40 Hz, 4H), 3.58 (t, *J* = 4.40 Hz, 4H), 3.40 (s, 6H). ^{13}C NMR (101 MHz, *CDCl*$_3$) δ ppm 153.4, 123.8, 86.6, 72.3, 71.3, 70.6, 69.8, 60.7, 59.3.

Compound 2i: To a stirred solution of 2f (0.10 g, 0.21 mmol) and DMAP in pyridine (1.5 mL) was charged with acetic anhydride (0.08 g, 0.84 mmol). The reaction mixture was stirred reflux for 3 h under pressure of N_2. The reaction mixture was extracted with EtOAc / H_2O and the combined organic phase was washed with water (3×100), dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 0.11 g (0.20 mmol, 96%) of **2i** as an warm white powder. ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.18 (s, 2H), 4.32 (t, *J* = 6.2 Hz, 4H), 4.02 (t, *J* = 6.0 Hz, 4H), 2.17 - 2.11 (m, 4H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 171.0, 152.8, 122.9, 86.3, 66.7, 61.2, 28.6, 21.0.

Compound 2j: To a stirred solution of 2f (0.10 g, 0.21 mmol) and DMAP in pyridine (1.5 mL) was charged with hexanoic anhydride (0.22 g, 1.05 mmol). The reaction mixture was stirred reflux for 3 h under pressure of N_2. The reaction mixture was extracted with EtOAc / H_2O and the combined organic phase was washed with water (3×100), dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 0.14 g (0.21 mmol, 99%) of **2j** as a colorless solid**.** ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.16 (s, 2H), 4.31-4.28 (t, *J* = 6.3 Hz, 4H), 4.01-3.98 (t, *J* = 6.0 Hz, 4H) , 2.30-2.27 (t, *J* = 7.6 Hz, 4H), 2.14-2.08 (m, 4H), 1.63-1.56 (m, 4H), 1.29-1.25 (m, 8H), 0.87-0.84 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 173.8, 152.8, 122.9, 86.4, 66.8, 61.0, 34.3, 31.4, 28.7, 24.7, 22.4, 14.0.

Compound 2k: To a stirred solution of 2f (1.00 g, 2.09 mmol), *p*-toluenesulfonyl chloride (1.60 g, 8.36 mmol) and DMAP in dried CH_2Cl_2 (10 mL) was charged with pyridine (0.66 g, 8.36 mmol). The reaction mixture was stirred at room temperature for 3 h under pressure of N_2. The reaction mixture was extracted with EtOAc / H_2O and the combined organic phase was washed with water (3×100), dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 1.04 g (1.32 mmol, 63%) of **2k** as a white powder. ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.76 (d, *J* = 8.0 Hz, 4H), 7.24 (d, *J* = 7.9 Hz, 4H), 7.00 (s, 2H), 4.32 (t, *J* = 5.8 Hz, 4H), 3.89 (t, *J* = 5.6

Hz, 4H), 2.36 (s, 6H), 2.18 – 2.10 (m, 4H). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ ppm 152.3, 144.8, 132.9, 129.9, 127.9, 122.5, 86.0, 66.9, 65.2, 28.9, 21.7.

Compound 2l: To a stirred solution of 2k (20 mg, 0.02 mmol), NaN_3 (31.20 mg, 0.48 mmol) in dried DMF (0.5 mL). The reaction mixture was stirred at 105 ^{o}C for 12 h under pressure of N_2. The reaction mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water (3×50), dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide quantitative of **2l** as a white solid. ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.18 (s, 2H), 4.02 (t, *J* = 5.8 Hz, 4H), 3.60 (t, *J* = 6.6 Hz, 4H), 2.09 – 2.02 (m, 4H). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ ppm 152.8, 123.0, 86.4, 66.9, 48.3, 28.8.

Compound 2m: To a stirred solution of 2l (0.18 g, 0.34 mmol), PPh_3 (0.45 g, 1.70 mmol) in THF 5 mL. Water (2.5 mL) was added and the resulting mixture was heated at 80 ^{o}C for 2 h. The solvent was then removed *in vacuo* and the residue was purified by column chromatography using 100% methanol as eluent to give 0.13 g (0.34 mmol, 99%) of **2m** as a white solid. ^{1}H NMR (400 MHz, *MeOD*) δ ppm 7.21 (s, 2H), 3.95 (t, *J* = 5.9 Hz, 4H), 2.84 (t, *J* = 6.8 Hz, 4H), 1.91 – 1.85 (m, 4H). ^{13}C NMR (101 MHz, *MeOD*) δ ppm 154.3, 124.1, 87.0, 69.6, 39.9, 32.7.

Compounds 2n and 2o: To a stirred solution of 2k (0.20 g, 0.25 mmol), sodium bromide (0.13 g, 1.27 mmol) in dried acetone (10 mL).The reaction mixture was stirred reflux for 24 h under pressure of N_2. The reaction mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water (3×100), dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 0.15 g (0.16 mmol, 65%) of **2n** as a white solid. ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.21 (s, 2H), 4.09 (t, *J* = 5.6 Hz, 2H), 3.69 (t, *J* = 6.4 Hz, 2H), 2.33 (p, *J* = 5.9 Hz, 2H).^{13}C NMR (101 MHz, *CDCl$_3$*) δ ppm 152.9, 123.1, 86.5, 67.8, 32.4, 30.2. Furthermore, this reaction provided **2o** as minor product in 34% yield. ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 7.76 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.21 (d, 2H), 7.16 (s, 1H), 7.01 (s, 1H), 4.32 (t, *J* = 5.9 Hz, 2H), 4.08 (t, *J* = 5.6 Hz, 2H), 3.87 (t, *J* = 5.6 Hz, 2H), 3.69 (t, *J* = 6.3 Hz, 2H), 2.35 (s, 3H), 2.16 – 2.10

(m, 2H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 152.7, 152.5, 144.9, 133.0, 130.0, 128.0, 123.0, 122.6, 86.3, 86.2, 67.7, 67.1, 65.3, 32.4, 30.2, 29.0, 26.6, 21.8.

2.4 Preparation of PPEs (3a-3o) from monomers (2a-2o)

Table 3.6 PPEs substrate applicability

General procedure for polymerization of aryl diiodides (procedure B) (3b-3h): A 100 mL round bottom flask with a magnetic stir bar was charged with aryl diiodides (1 equiv.), palladium catalyst (0.05 equiv.), copper catalyst (0.1 equiv.), triphenylphosphine (0.1 equiv.), calcium carbide (6 equiv.) in 1:2 mixture of base and solvent. All reactions were carried out under positive pressure of N_2 filled in rubber balloons. The mixture was stirred at room temperature for 20 h. The solution mixture was then filtered through a cotton wool using methylene chloride as eluent, concentrated to a small volume and precipitated by dropping the solution into 150 mL of methanol. The precipitate that formed was collected by centrifuge, washed repeatedly with methanol and evaporated under vacuum.

PPE3b [40]**:** Synthesis as declared in procedure B using 2b (100 mg, 0.17 mmol), palladium(II)acetate (1.9 mg, 0.008 mmol), copper iodide (3.24 mg, 0.017 mmol), triphenylphosphine (4.46 mg, 0.017 mmol), calcium carbide (65.38 mg, 1.02 mmol) and DBU (1 mL) in THF (2 mL) to afford 47.27 mg (0.13 mmol, 78%) of **3b** as an orange solid. GPC (vs.polystyrene standards in tetrahydrofuran): M_w = 40972, M_w/M_n = 2.40, DP_n = 48, ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 6.99 (br, 2H), 4.00 (br, 4H), 1.83 (br, 4H), 1.49 (br, 4H), 1.27 (br, 20H), 0.86 (br, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 153.7, 117.6, 114.5, 91.6, 69.9, 32.0, 29.6, 29.5, 29.5, 26.2, 22.8, 14.2. IR (neat, cm^{-1}) 2922, 2850, 2186, 2157, 1733, 1597.

PPE3c [26]**:** Synthesis as declared in procedure B using 2c (100 mg, 0.17 mmol), palladium(II)acetate (1.9 mg, 0.008 mmol), copper iodide (3.24 mg, 0.017 mmol), triphenylphosphine (4.46 mg, 0.017 mmol), calcium carbide (65.38 mg, 1.02 mmol) and DBU (0.5 mL) in THF (1 mL) to afford 50.36 mg (0.14 mmol, 83%) of **3c** as a yellow fiber. GPC (vs.polystyrene standards in tetrahydrofuran): M_w = 91300, M_w/M_n = 2.00, DP_n = 128, ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 6.99 (s, 2H), 3.89 (s, 4H), 1.81 (s, 2H), 1.53 (s, 8H), 1.33 (s, 8H), 0.98 (s, 5H), 0.88 (s, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 153.6, 116.6, 114.1, 91.5, 71.9, 39.5, 30.5, 29.0, 23.9, 22.9, 13.9, 11.2. IR (neat, cm^{-1}) 2954, 2921, 2869, 2855, 2203, 2159, 1642, 1592. Elemental Analysis = Calc. C: 80.84, H: 10.18, Found. C: 80.86, H: 10.11.

PPE3e: Synthesis as declared in procedure B using 2e (100 mg, 0.20 mmol), palladium(II)acetate (2.25 mg, 0.01 mmol), copper iodide (3.81 mg, 0.02 mmol), triphenylphosphine (5.25 mg, 0.02 mmol), calcium carbide (76.92 mg, 1.20 mmol) and DBU (1.34 mL) in THF (2.66 mL) to afford 48.28 mg (0.19 mmol, 93%) of **3e** as a yellow-green powder. GPC (vs.polystyrene standards in tetrahydrofuran): M_w = 26915, M_w/M_n = 2.21, DP_n = 47, ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.05 (s, 1H), 3.90 (br, 4H), 1.80 (br, 1H), 1.73 – 1.19 (br, 8H), 0.96-0.88 (br, 5H), ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 153.9, 153.7, 117.0, 115.1, 91.5, 71.7, 56.3, 39.5, 30.4, 29.0, 23.8, 22.9, 13.9, 11.1. IR (neat, cm^{-1}) 2954, 2924, 2872, 2855, 2198, 2159, 1663, 1642, 1603, 1546. Elemental Analysis = Calc. C: 79.03, H: 8.58, Found. C: 79.05, H: 8.59.

PPE3f: Synthesis as declared in procedure B using 2f (100 mg, 0.21 mmol), palladium(II)acetate (2.36 mg, 0.01 mmol), copper iodide (4.00 mg, 0.02 mmol), triphenylphosphine (5.51 mg, 0.02 mmol), calcium carbide (80.77 mg, 1.26 mmol) and DBU (1.33 mL) in THF (2.66 mL) to afford 48.40 mg (0.20 mmol, 93%) of **3f** as a dark-orange solid. ^{1}H NMR (400 MHz, *DMSO*) δ ppm 7.15 (s, 2H), 4.57 (br, 4H), 4.14 (br, 4H), 3.64 (br, 4H), 1.91 (br, 4H), ^{13}C NMR (101 MHz, *DMSO*) δ ppm 152.9, 116.9, 113.6, 91.6, 66.2, 57.4, 32.2. IR (neat, cm^{-1}) 3313, 2929, 2874, 2184, 2159, 1735, 1713, 1598.

PPE3h: Synthesis as declared in procedure B using 2h (100 mg, 0.18 mmol), palladium(II)acetate (2.02 mg, 0.009 mmol), copper iodide (3.43 mg, 0.018 mmol), triphenylphosphine (4.72 mg, 0.018 mmol), calcium carbide (69.23 mg, 1.08 mmol) and DBU (1.16 mL) in THF (2.24 mL) to afford 52.43 mg (0.16 mmol, 87%) of **3h** as an orange film. GPC (vs.polystyrene standards in tetrahydrofuran): M_w = 26975, M_w/M_n = 1.56, DP_n = 51, ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 7.05 (s, 2H), 4.24 (br, 4H), 3.92 (br, 4H), 3.77 (br, 4H), 3.53 (br, 4H), 3.35 (s, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 154.1, 118.6, 115.2, 92.0, 72.5, 71.5, 70.2, 59.5. IR (neat, cm^{-1}) 2921, 2872, 2817, 2198, 2159, 1721, 1666, 1633, 1600. Elemental Analysis = Calc. C: 64.27, H: 7.19, Found. C: 64.17, H: 6.92.

2.5 Preparation of diiodo heterocyclic compounds (2p-2s)

Compound 2p: To a stirred solution of carbazole (5.0 g, 29.9 mmol) in acetic acid (50 mL) was added potassium iodide (6.6 g, 39.8 mmol). Then, potassium iodate (9.6 g, 44.9 mmol) was added in small portions over a period of 5 min and the resulting mixture was refluxed for 20 min. The reaction was allowed to cool to room temperature and diluted with EtOAc (50 mL) and water (50 mL). The aqueous layer was separated and extracted with EtOAc (2 × 50 mL). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a brown solid residue. The crude product was purified by crystallization from acetone and hexane to yield **2p** as light brown crystals. (12.3 g, 98%). ^{1}H NMR (400 MHz, DMSO-*d6*) δ ppm 11.56 (s, 1H), 8.58 (s, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J*= 8.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-*d*6) δ ppm 138.7, 134.0, 129.1, 123.8, 113.5, 81.8.

Compound 2q [46]**:** To a stirred solution of 2p (0.20 g, 0.48 mmol), sodium hydride (0.15 g, 6.20 mmol) in dried DMF (0.5 mL) was added with 2-ethylhexyl bromide (0.18 g, 0.96 mmol). The reaction mixture was stirred at rt for 1 h. The reaction mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water (3×100), dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 0.20 g (0.39 mmol, 80%) of **2q** as bright yellow oil. ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 8.28 (d, *J* = 1.4 Hz, 2H), 7.68 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 4.01 (dd, *J* = 7.2, 2.4 Hz, 2H), 1.95 (dt, *J* = 11.3, 5.5 Hz, 1H), 1.26

(d, *J* = 7.2 Hz, 8H), 0.88 (dd, *J* = 14.3, 6.7 Hz, 6H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 140.0, 134.5, 129.3, 124.0, 111.2, 81.8, 47.6, 39.4, 31.1, 28.9, 24.5, 23.1, 14.1, 11.0.

Compound 2r [47]**:** To a stirred solution of 2p (0.50 g, 1.19 mmol), sodium hydride (0.37 g, 15.51 mmol) in dried DMF (1 mL) was added with n-octyl bromide (0.46 g, 2.38 mmol). The reaction mixture was stirred at rt for 1 h. The reaction mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water (3×100), dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 0.55 g (1.04 mmol, 88%) of **2r** as colorless oil. ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 8.32 (d, *J* = 1.3 Hz, 2H), 7.71 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 4.21 (t, *J* = 7.2 Hz, 2H), 1.85 – 1.76 (m, 2H), 1.26 (t, *J* = 13.2 Hz, 10H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, *$CDCl_3$*) δ ppm 139.7, 134.7, 129.5, 124.2, 111.0, 81.8, 43.4, 31.9, 29.4, 29.3, 29.0, 27.4, 22.7, 14.2.

Compound 2s [48]**:** To a stirred solution of 2,3-di hydrothieno[3,4-b][1,4]dioxine (24 mg, 0.17 mmol) in dried CH_2Cl_2 (0.5 mL) was added with iodine(I)chloride (0.11 g, 0.68 mmol) and pyridine (94 mg, 1.19 mmol). The reaction mixture was stirred at rt for 1 h. The reaction mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with aqueous $Na_2S_2O_3$, water, brine and dried over Na_2SO_4, concentrated *in vacuo* and purified by column chromatography to provide 11.6 mg (0.03 mmol, 17%) of **2s** as a warm white solid. ^{1}H NMR (400 MHz, *$CDCl_3$*) δ ppm 4.26 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 131.0, 129.0, 65.3, 65.3, 65.1, 65.0.

2.6 Preparation PAEs (3q-3s) from monomers (2q-2s)

Table 3.7 Preparation of PAEs

PPE3q: Synthesis as declared in procedure B using **2q** (60 mg, 0.11 mmol), palladium(II)acetate (1.23 mg, 5.5×10^{-3} mmol), copper iodide (2.11 mg, 0.011 mmol), triphenylphosphine (2.90 mg, 0.011 mmol), calcium carbide (42.30 mg, 0.66 mmol) and DBU (0.73mL) in THF (1.46 mL) to afford 19.46 mg (0.064 mmol, 59%) of **3q** as a deep brown powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.29 (br, 2H), 7.67 (br, 2H), 7.33 (br, 2H), 4.10 (br, 1H), 2.05 (br, 3H), 1.67 (br, 6H), 1.25 (br, 6H). IR (neat, cm^{-1}) 2924, 2858, 2159, 1628, 1598, 1406.

PPE3r: Synthesis as declared in procedure B using **2r** (100 mg, 0.19 mmol), palladium(II)acetate (2.16 mg, 9.5×10^{-3} mmol), copper iodide (3.62 mg, 0.019 mmol), triphenylphosphine (5.00 mg, 0.019 mmol), calcium carbide (73.07 mg, 1.14 mmol) and DBU (1.20 mL) in THF (2.40 mL) to afford 50.42 mg (0.17 mmol, 87%) of **3r** as a deep brown powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.30 (br, 2H), 7.68 (br, 2H), 7.31 (br, 2H), 4.22 (br, 2H), 1.81 (br, 2H), 1.23 (br, 10H), 0.84 (br, 6H).

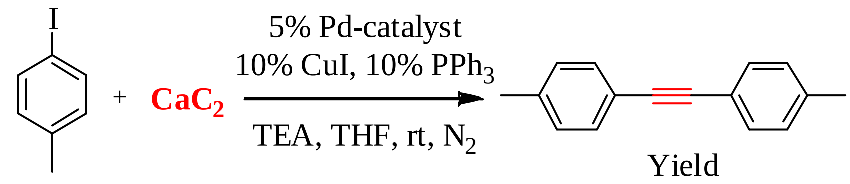
CHAPTER III

RESULTS AND DISCUSSION

3.1 Initial observation

Usually, it is well known that the reactivity of aryl iodides in oxidative addition to palladium is much greater than other halo-aryl compounds and the oxidative addition is believed to be the rate determining steps in most Sonogashira coupling [19]. Therefore, coupling reactions of aryl iodide and calcium carbide to produce the phenylene ethynylene were first tested under common Sonogashira coupling reaction in order to see the efficient of the possibility of this process. The results are summarized in Table 3.1. Pd catalyst systems were screened by focusing on type of Pd source which has been known to use for preparation of good quality of PPEs. Based on a number of literatures [13, 22-23, 26, 37], THF/TEA was typically utilized as solvent for the coupling. Thus, 4-iodotoluene and calcium carbide were subjected to Sonogashira coupling using various Pd sources in THF/TEA with CuI and PPh_3 under inert atmosphere. $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ gave low yield of 1,2-dip-tolylethyne (34 and 43% yield respectively) along with the recovered starting 4-iodotoluene. In contrast, $Pd(OAc)_2$ was efficient to complete the conversion of starting 4-iodotoluene into the desired 1,2-dip-tolylethyne in 77% yield making this Pd salt the best choice for this coupling reaction. Further optimization for PPEs synthesis was thus based mainly on $Pd(OAc)_2$.

Table 3.1 Initial observation[a]



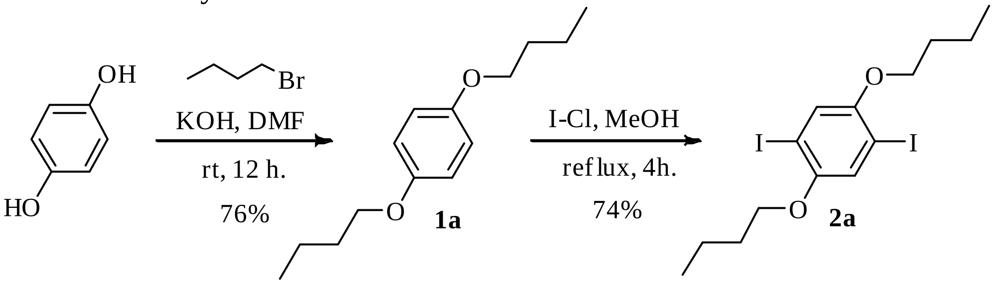
Pd-catalyst	Yield[b]
$PdCl_2(PPh_3)_2$	34%
$Pd(PPh_3)_4$	43%
$Pd(OAc)_2$	77%

[a] All reactions were carried out with 4-iodotoluene (1 equiv), CaC_2 (6 equiv), $Pd(OAc)_2$ (5%), CuI (10%), PPh_3 (10%) was degassed with N_2 for 30 sec. Then, the mixture of THF and TEA with ratio 2:1 was added to the reaction mixture and stirred under N_2 at rt for 20 hr. [b] Isolated yield.

1,4-dibutoxy-2,5-diiodobenzene (2a)

For optimization of polymerization conditions, 1,4-dibutoxy-2,5-diiodobenzene **(2a)** was selected as a model monomer due to its convenient synthesis. The flexible butyl substituent can also increase the solubility of the corresponding PPEs in common organic solvents such as THF that will facilitate the synthesis and characterization.

Compound **1a** was synthesized by alkylation of hydroquinone with butyl bromide in DMF giving the desired compound in 76% yield (Scheme 3.1). Consequently, the iodination of **1a** by iodine(I)chloride in methanol under reflux condition leading to the formation of **2a** in 74% yield as a white solid .



Scheme 3.1 Synthesis of compound **2a**

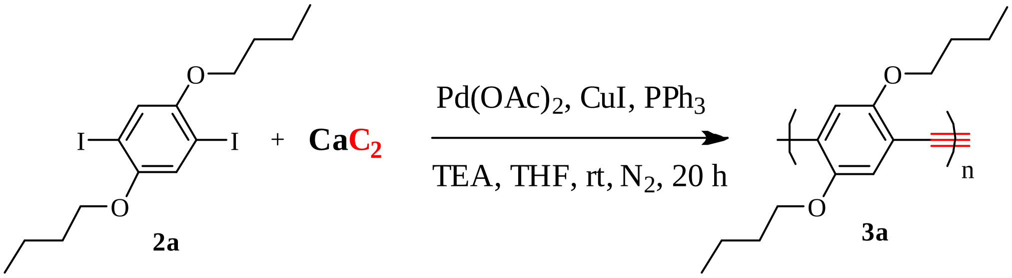
3.2 Pd-catalyst coupling reaction using calcium carbide as a starting material.

3.2.1 Optimization conditions

1) Catalyst loading and substrate concentration

With compound **2a** in hands, the optimization investigation was carried out first by varying the amount of $Pd(OAc)_2$ and monomer concentration. The polymerization was performed under a typical in THF at room temperature in the presence of calcium carbide, CuI, PPh_3 and TEA under N_2 atmosphere. The results were summarized in Table 3.2

Table 3.2 Catalyst loading and substrate concentration[a]



2a

3a

entry	$Pd(OAc)_2$ (mol%)	**2a** Conc. (M)	Yield[b]	M_w (GPC)	DP_n (GPC)	M_w/M_n (GPC)
1[c]	1	0.05	N.A.	-	-	-
2[c]	1	0.10	N.A.	-	-	-
3[c]	1	0.20	N.A.	-	-	-
4	5	0.05	84%	11,737	21	2.3
5	5	0.10	93%	9,291	15	2.5
6	5	0.20	73%	6,327	13	1.9
7[d]	10	0.05	31%	7416	15	1.8
8[d]	10	0.10	66%	7,952	12	2.6
9[d]	20	0.05	56%	6,012	11	2.2

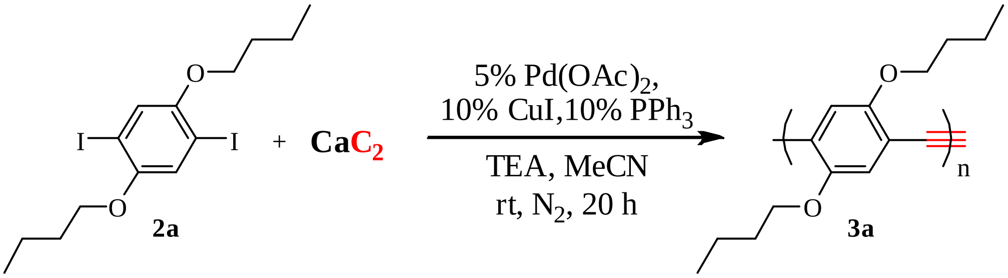
[a]All the reaction used 1,4-dibutoxy-2,5-diiodobenzene 1 equiv., CaC_2 6 equiv., TEA/THF (1:2), $Pd(OAc)_2/CuI/PPh_3$ (1:2:2). [b]Isolated yield by single precipitation from $MeOH/CH_2Cl_2$, [c]Incomplete conversion of **2a**, [d]Partially dissolved in CH_2Cl_2, N.A. = not available.

The results in Table 3.2 demonstrate that 1% of $Pd(OAc)_2$ loading is insufficient for complete conversion of the starting materials. It produced oligomer with low molecular weight (entry 1). Although, we increased substrate concentration from 0.05-0.2, the desired PPEs was not reprecipitated out in $MeOH/CH_2Cl_2$ (entries 1-3) suggesting the formation of oligomer or small molecular weight PPEs. However, this problem was solved by increasing amount of $Pd(OAc)_2$ up to 5%mol. It gave 84% yield with high degree of polymerization (DP_n = 21) without remaining any starting material **2a** (entry 4). We attempted to increase the polymerization efficiency by increasing amount of $Pd(OAc)_2$ and substrate concentration. Unfortunately, the results were disappointed. Yields and molecular weight were dropped when increasing both factors (entries 5-9). We hypothesized that lower yield and molecular weight is due to the formation of high molecular weight polymer which cause the poor solubility in CH_2Cl_2. Thus, only partially soluble of polymer could be analyzed by GPC and precipitate out in small proportion. From the above mentioned, we concluded that 5% $Pd(OAc)_2$ is suitable to drive the reaction completely and 0.05 M was the optimal concentration.

2) Amount of CaC_2 and TEA

In this section, we used 1,4-dibutoxy-2,5-diiodobenzene (1 equiv) coupling with various amounts of CaC_2 by fixing the concentration at 0.05 M and amount of $Pd(OAc)_2$ at 5%mol, CuI 10%mol and PPh_3 10%mol in TEA and MeCN as base/solvent system. [13] All the reactions were carried out under nitrogen atmosphere for 20 h and the results were summarized in Table 3.3

Table 3.3 Amount of CaC_2 and TEA



entry	CaC_2 (equiv.)	TEA	Yield[a]	M_w (GPC)	DP_n (GPC)	M_w/M_n (GPC)
1	3	3 equiv.	N.A.	-	-	-
2	3	6 equiv.	N.A.	-	-	-
3	6	6 equiv.	29%	2,776	7	1.61
4 [b]	6	6 equiv.	N.A.	-	-	-
5 [c]	6	6 equiv.	N.A.	-	-	-
6 [d]	6	6 equiv.	63%	5,004	10	1.9
7 [e]	3	2 mL	23%	5,969	12	2.0
8 [e]	6	2 mL	84%	11,737	21	2.3

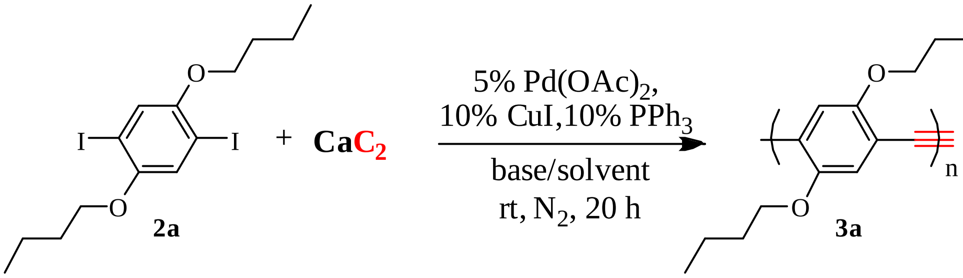
[a] Isolated yield by single precipitation from MeOH/ CH_2Cl_2, [b] added 10% H_2O, [c] Heated at 60 °C, [d] added 50% THF, [e] THF as solvent, N.A. = not available.

The results in Table 3.3 indicated that 6 equiv of CaC_2 is sufficient to drive the polymerization reaction without recovery of any starting material and when we added THF as co-solvent gave better results in comparison with MeCN was used alone or mixed with water. This is due to THF could improve solubility of starting material and the PPE product (entries 3-4, 6). However, degree of polymerization remained low ($DP_n = 10$) when TEA were used at only 6 equivalent (entry 6). To increase the degree of polymerization, we hypothesized that amount of base 6 equiv might be inadequate for coupling reaction, because base is significant to drive the formation of a π-alkyne complexation [19]. Therefore, we decided to use excess TEA combined with THF as mixed solvent (entry 8). It showed the most effective condition giving satisfactory yield along with the highest degree of polymerization. When the reaction was carried out at 60 °C, the reaction was inefficient along with an almost recovery of starting material. This is likely due to the instability of the palladium complex intermediates under this condition (entry 5). In conclusion, we found that the best condition of base/solvent system was a ratio 1:2 which produced the highest degree of polymerization.

3) Type of base and solvent

For the next optimization study, a number of bases and solvents were tested for the polymerization of 1,4-dibutoxy-2,5-diiodobenzene (1 equiv) in the presence of CaC_2 (6 equiv), 5% $Pd(OAc)_2$, 10% CuI, 10% PPh_3 in the mixture of base/solvent in a ratio 1:2 under nitrogen atmosphere at room temperature for 20 h. The results were summarized in Table 3.4

Table 3.4 Base and solvent screening



entry	Base/solvent	Yield[a]	M_w (GPC)	DP_n (GPC)	M_w/M_n (GPC)
1	TEA/THF	84%	11,737	21	2.3
2	TEA/MeCN	90%	6,888	13	2.1
3	TEA/DMF	N.A.	-	-	-
4	DIPEA/THF	N.A.	-	-	-
5	DBU/THF	71%	20,168	36	2.3
6	K_2CO_3/THF	N.A.	-	-	-
7	Cs_2CO_3/THF	N.A.	-	-	-

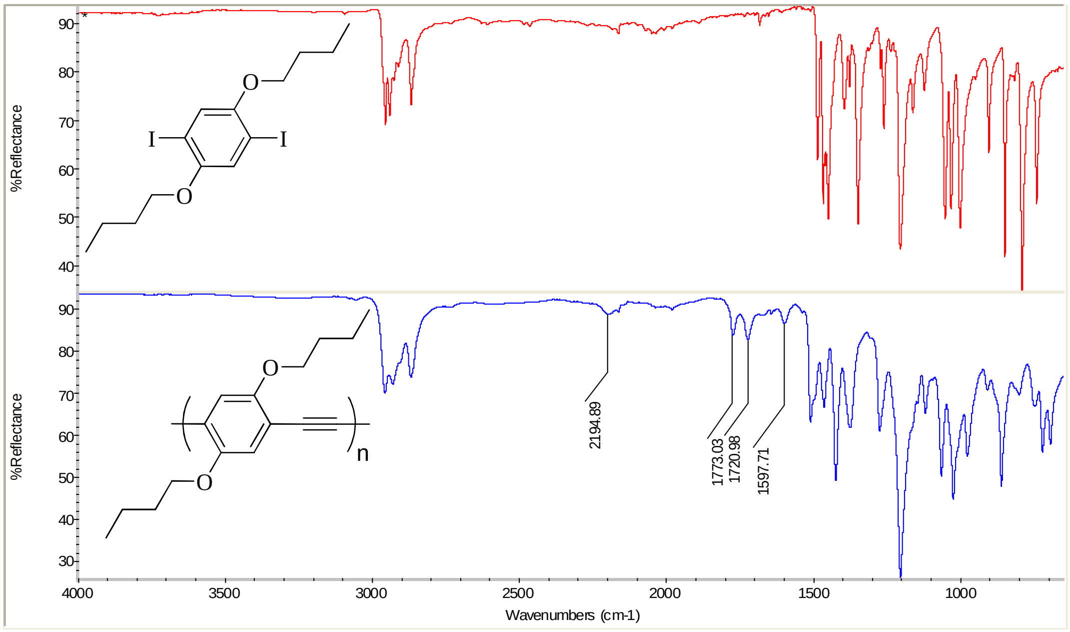
[a] Isolated yield by single precipitation from CH_3OH/CH_2Cl_2, N.A. = not available.

The results in table 3.4 showed that TEA as effective base to coupling reaction in both solvents, THF and MeCN (entries 1, 2). Although MeCN gave desired polymer with the highest yield but in terms of degree of polymerization remained low (DP_n = 13) in comparison with THF (DP_n = 21). The cause of the result was the poor solubility of starting material in MeCN. Hence, we selected THF as the best solvent for screen type of base next (entries 1, 4-7). The results indicate that inorganic base is inefficient causing incomplete conversion of starting material (entries 6, 7) while DBU was the most effective base giving satisfactory yield of yellow-orange solid of **3a** along with the highest degree of polymerization (entry 5) in comparison with TEA. Therefore, we decided that the best solvent and base system were THF and DBU, respectively. Notably, the slightly lower yield is due to the high molecular weight portion of polymer was poorly soluble in CH_2Cl_2 solvent which is needed for the precipitation.

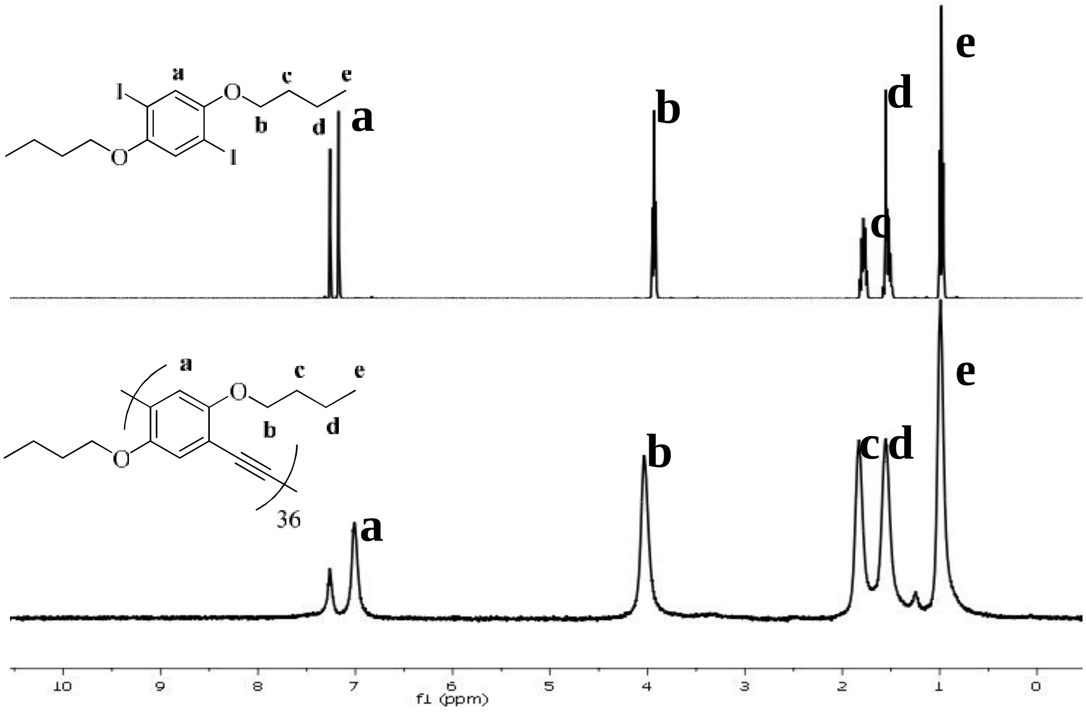
For all conditions screening, the optimized conditions is the treatment of 1,4-dibutoxy-2,5-diiodobenzene **2a** (1 equiv), CaC_2 (6 equiv), $Pd(OAc)_2$ (5%mol), PPh_3 (10%mol), CuI (10%mol) in the mixture of base/solvent in a ratio 1:2 at room temperature under a nitrogen atmosphere for 20 h. Under these optimized conditions, complete conversion of starting material **2a** to desired product **3a** which was isolated by single precipitation from $MeOH/CH_2Cl_2$ gave satisfactory yield (71 - 90%) along with high degree of polymerization in the range of 13 -36. It must be noted that the structural confirmation and molecular weight determination of monomer **2a** and PPE **3a** using FT-IR, ^1H and ^{13}C NMR spectroscopy will be further discussion in the next section.

3.2.2 Monomer (2a) and polymer (3a) characterization

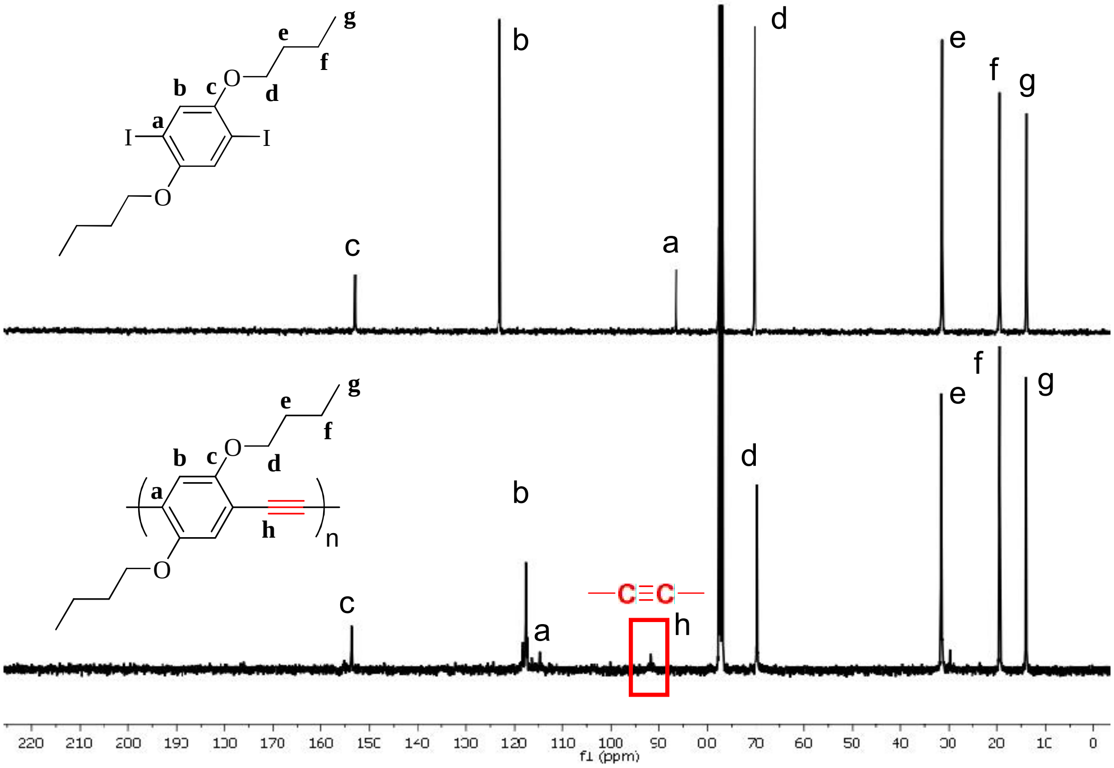
To confirm the conversion of aryl diiodide monomer **2a** into PPE **3a** which consisted of conjugated alkyne π-systems in the backbone of the polymer structure, we investigated by stacking FT-IR and ^1H, ^{13}C NMR spectra of aryl diiodide monomer **2a** with PPE **3a** derived from optimized condition with the hope that alkyne signal would show up (Figure 3.1-3.3).



%Reflectance
90
80
70
60
50
40
30
O
I
I
O
n
2194.89
1773.03
1720.98
1597.71
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)



a
b
c
d
e
I
I
O
O
36
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

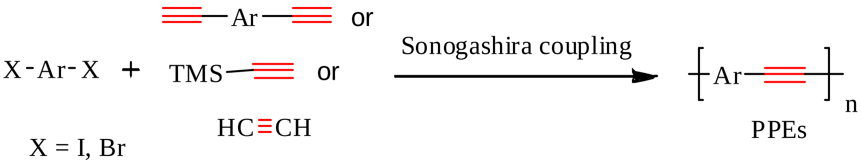


g
e
f
c
O
d
b
a
I
I
O
b
c
a
d
e
f
g
e
g
f
O
c
b
d
a
h
n
O
b
d
c
a
—C≡C—
h
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

result suggesting the high molecular weight = 20168 Da., degree of polymerization (DP_n) = 36 with narrow polydispersity index (PDI) = 2.40. Even though the new carbon source, calcium carbide is proven to be suitable starting material for PPE with high yield and molecular weight but the question arising from these discovery is, can this method are able to replace those previous conventional methods. Therefore, in the next section, we decided to prepare PPE from the known procedure and compared those PPEs with our PPE from the optimized condition.

3.2.3 Comparative study between other conventional methods with CaC_2 method

Generally, the most efficient method for synthesized PPEs is Sonogashira cross-coupling reaction because of its mild reaction condition and remarkable functional group tolerance [12]. The reaction involves the coupling of dihaloarenes to acetylene source such as diethynylarenes, protected acetylenes and acetylene gas (Scheme 3.2) [26]. However, herein we selected only diethynylarenes and TMS acetylenes as acetylene source due to its ease to handle and non flammability unlike an acetylene gas.



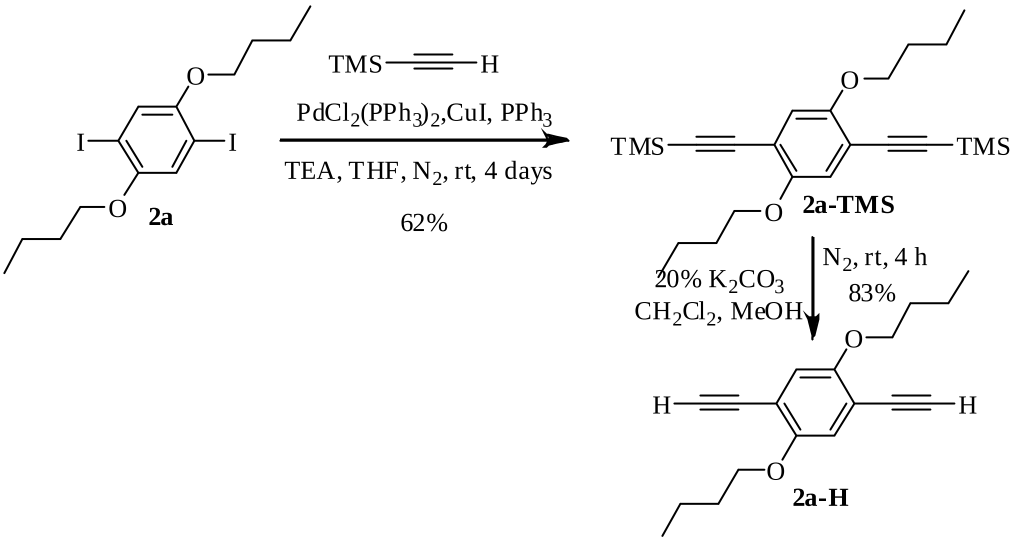
Scheme 3.2 The conventional methods for synthesis of PPEs

Initially, we prepared diethynylarene **(2a-H)** according to literature procedures and TMS-acetylene was obtained from commercial suppliers.

Part I: Synthesis section

1) *Preparation of 1,4-dibutoxy-2,5-diethynylbenzene* ***(2a-H)***

Compound **2a-TMS** was synthesized by Sonogashira reaction of **2a** with ethynyl trimethylsilane in THF in the presence of $PdCl_2(PPh_3)_2$ to give a white solid as desired product in 62% yield (Scheme 3.3). Then, deprotection of trimethylsilyl group took place smoothly upon the treatment of K_2CO_3 in CH_2Cl_2/MeOH to obtain terminal alkyne **2a-H** in 83% yield.



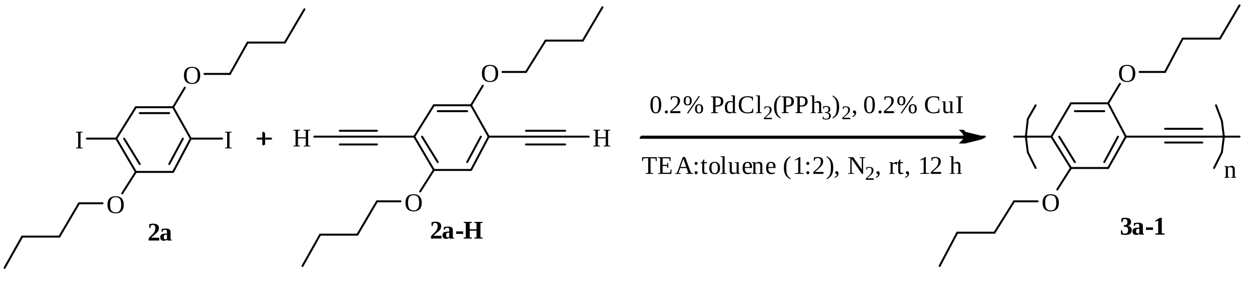
Scheme 3.3 Synthesis of compound **2a-H**

*2) Synthesis of PPE **3a** from various acetylene sources*

We synthesized series of PPE including **3a, 3a-1 and 3a-2** from difference acetylene sources. PPE **3a-1** and **3a-2** were synthesized from conventional method using diethynylarene **(2a-H)** or TMS acetylene respectively as starting material with aryl diiodide **2a** (Scheme 3.4-3.5) according to previous reported procedure [40]. While, PPE **3a** was synthesized under our optimized condition using CaC_2 as acetylene source.

Synthesis of PPE 3a-1 from diethynylarene (2a-H)

PPE **3a-1** was synthesized by Sonogashira coupling of **2a** with **2a-H** in TEA/toluene. The mixture was stirred under N_2 atmosphere at room temp for 12 h. TLC indicated the complete consumption of starting material **2a**. After filtration and precipitation with methanol, orange powder of **3a-1** was received in 95% yield (Scheme 3.4).

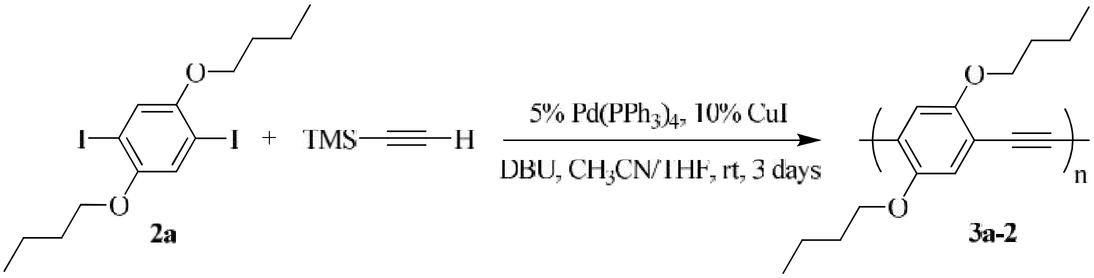


2a **2a-H** **3a-1**

Scheme 3.4 Synthesis of PPE **3a-1**

Synthesis of PPE 3a-2 from TMS acetylene

On the other hands, PPE **3a-2** was synthesized by Sonogashira coupling of **2a** with TMS acetylene using $Pd(PPh_3)_4$ and CuI as catalyst and DBU as base. The mixture was stirred in CH_3CN/THF under N_2 atmosphere at room temp for 3 days. After the routine workup method yellow greenish powder of **3a-2** were precipitated in 100% yield (Scheme 3.5).



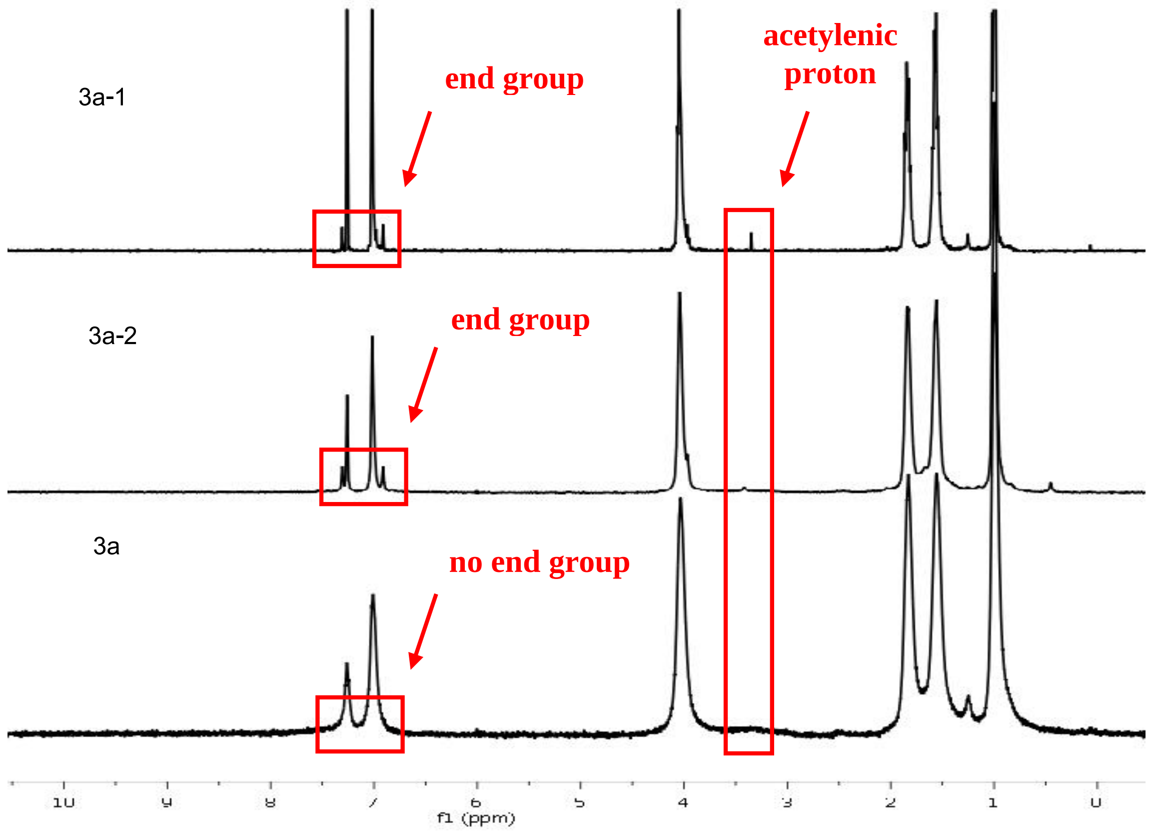
2a **3a-2**

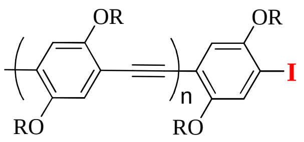
Scheme 3.5 Synthesis of PPE **3a-2**

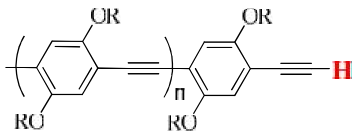
Part II: Comparative study

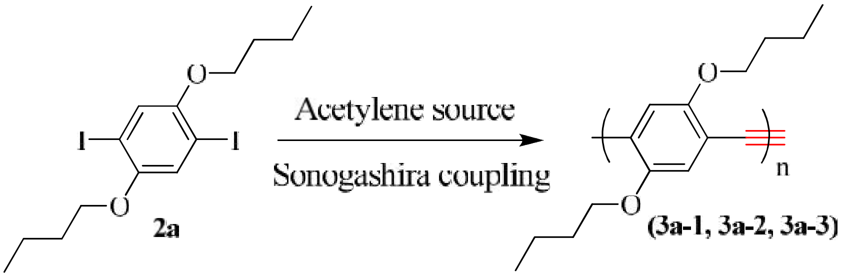
*1) Polymer **3a-1, 3a-2** and **3a** characterization*

With all the PPE **3a, 3a-**1 and **3a-2** in hand, we then compared ^{1}H NMR spectra of all polymers by stacking NMR spectra of three methods (Figure 3.4). We found that PPE **3a-1** and **3a-2** derived from terminal alkyne and TMS-acetylene method, respectively displayed small peaks in the near 3.5 ppm region of the acetylenic proton and a weak additional signal appears in the aromatic region while PPE **3a** derived from


3a-1
end group
acetylenic proton
3a-2
end group
3a
no end group
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

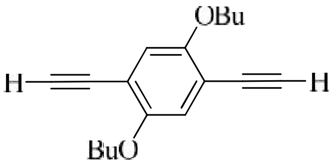

OR
OR
I
n
RO
RO


OR
OR
H
n
RO
RO



2a

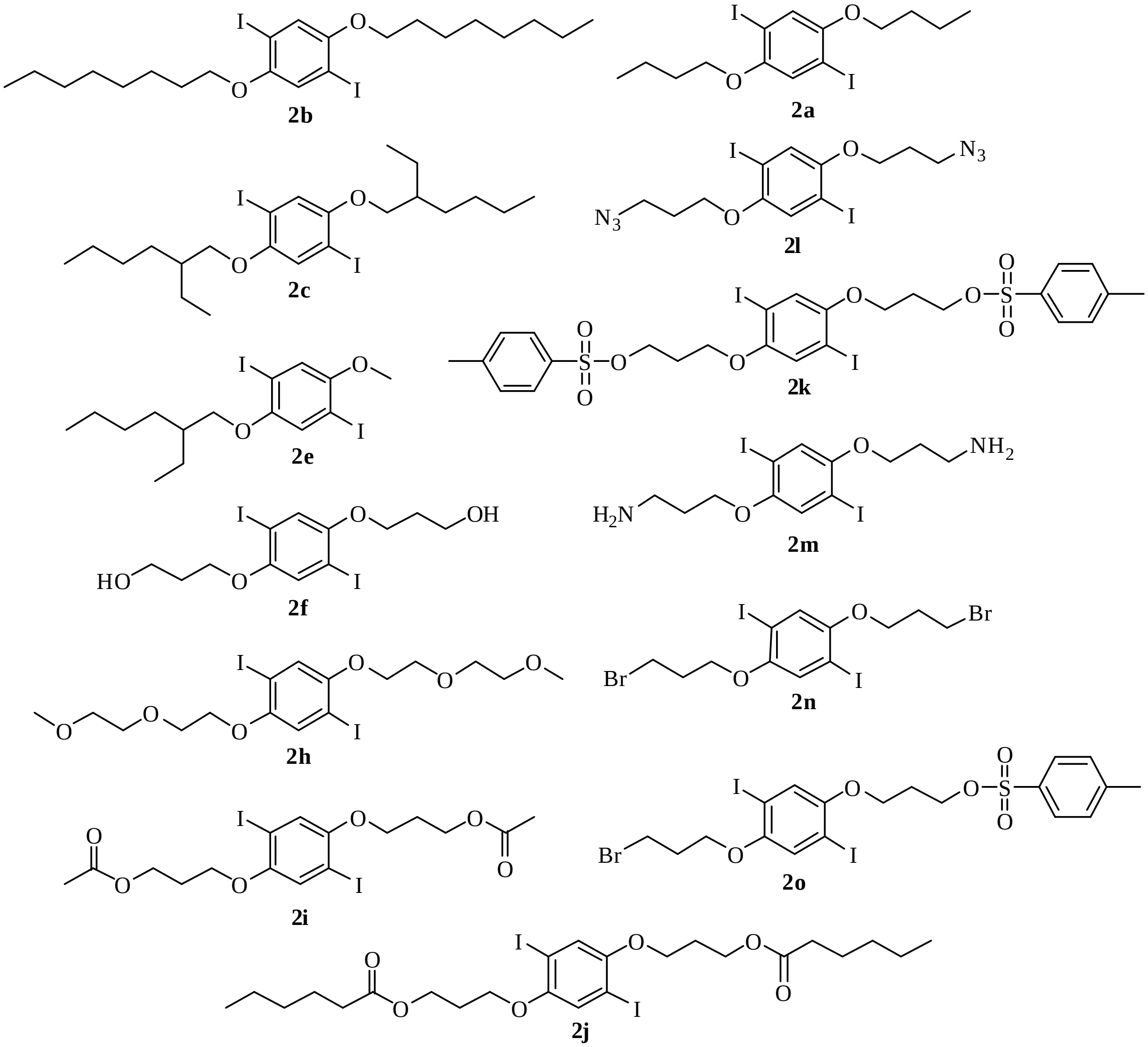
(3a-1, 3a-2, 3a-3)

entry	Acetylene sources	PPEs	Yield[b]	M_w	DP_n	M_w/M_n
1		**3a-1**	95%	-	-	-
2	$TMS-C\equiv C-H$	**3a-2**	100%	9,669	17	2.3
3	CaC_2	**3a-3**	71%	20,168	36	2.4

panel of aryl diiodides carrying various side chains in order to study the generality of this condition.

3.3 Preparation of aryl diiodides.

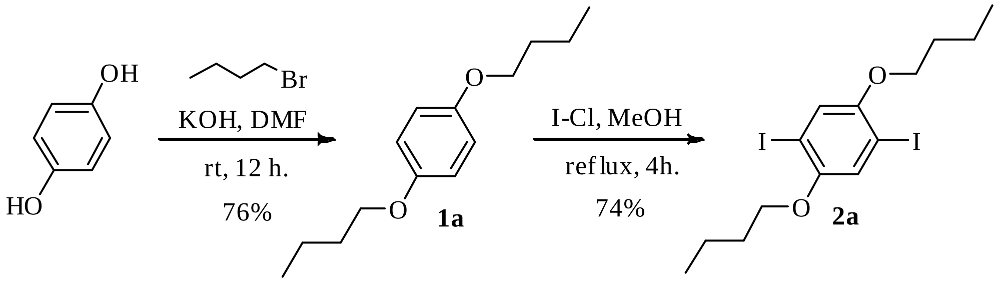
We synthesized twelve aryl diiodides **(2a-2j)** for testing substrate applicability of our optimized condition (Scheme 3.6). All of aryl diiodides were prepared according to literatures. The synthesis of such compounds will be discussed in this section.



Scheme 3.6 Diiodoarenes used in this section.

Compound 2a

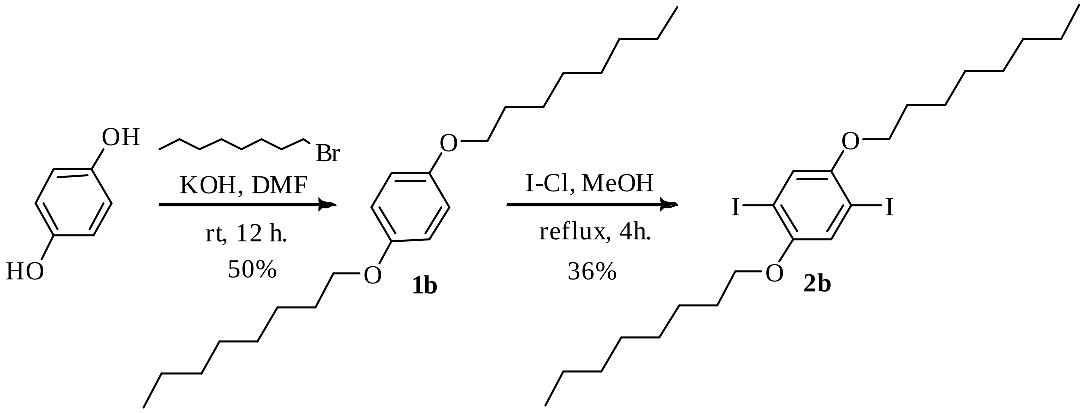
Compound 1a was synthesized by alkylation of hydroquinone and butyl bromide in DMF (76% yield) (Scheme 3.7). Then, the iodination by iodine(I)chloride in methanol gave compound **2a** in 74% yield after purification by column chromatography.



Scheme 3.7 Synthesis of compound **2a**

Compound 2b

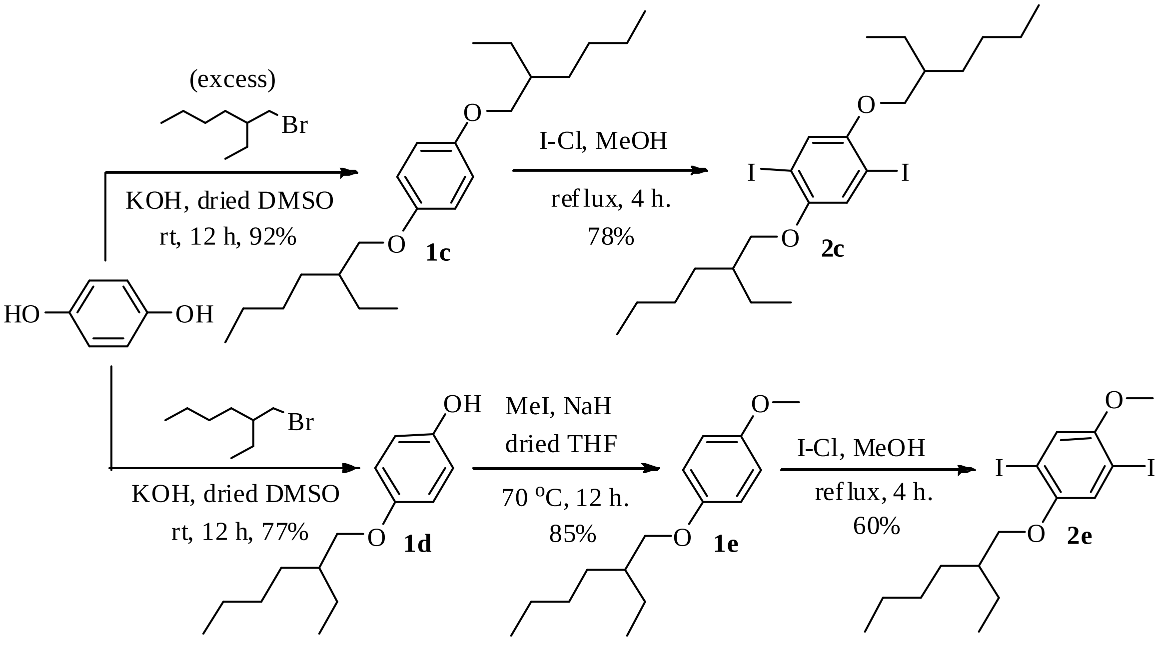
Similar to above method, reaction of hydroquinone with octyl bromide and KOH in DMF at ambient temperature for 12 h produced compound 1b in 50% yield. Then, the iodination by iodine(I)chloride in methanol generated compound **2b** in 36% yield (Scheme 3.8).



Scheme 3.8 Synthesis of compound **2b**

Compounds 2c and 2e

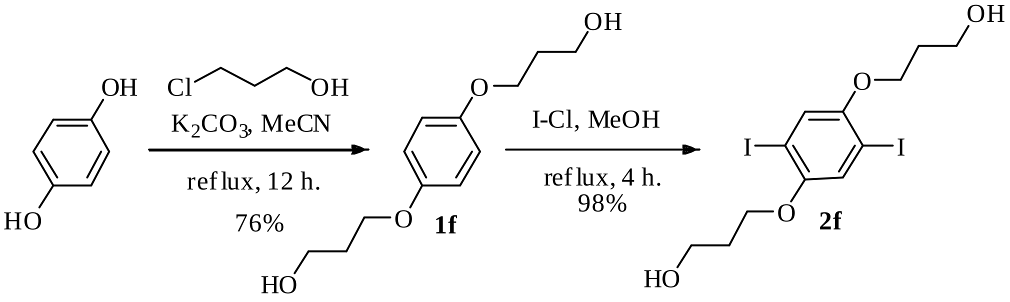
To synthesize compounds **2c** and **2e,** we first carefully reacted 2-ethylhexyl bromide with hydroquinone in dried DMSO providing dialkylated 1c and monoalkylated 1d in 92% and 77% yield, respectively. Then, 1d was further methylated by methyl iodide to give 1e in 85% yield. Finally, the iodination of 1c and 1e were subjected to the routine iodination with iodine(I)chloride in methanol to obtain **2c** and **2e** in 78 and 85% yield, respectively (Scheme 3.9).



Scheme 3.9 Synthesis of compounds **2c** and **2e**

Compound 2f

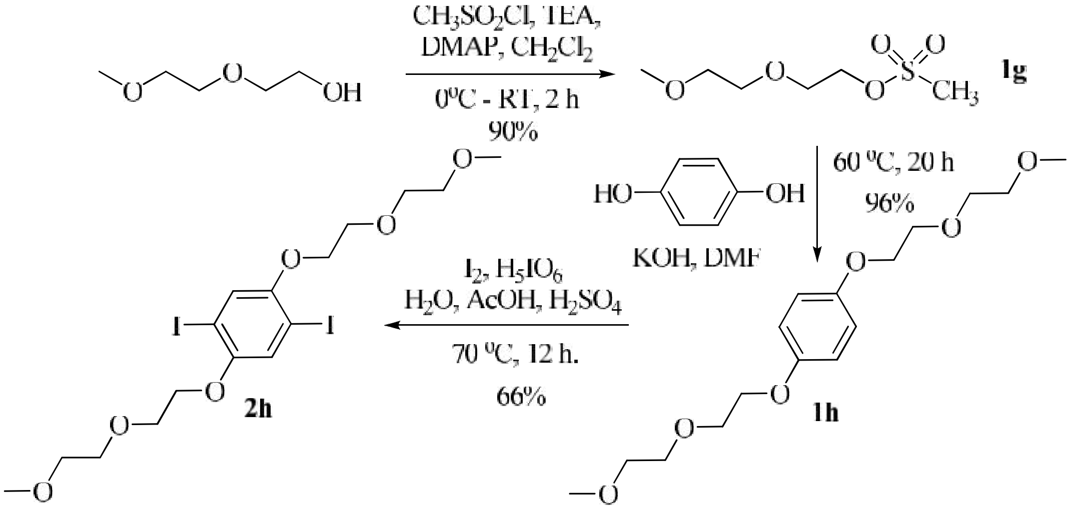
To test the compatibility of our method with alcohol substrate, we decided to prepare compound **2f.** We reacted 3-chloropropane-1-ol with hydroquinone in MeCN resulting in the formation of compound 1f in 76% yield. Then, iodination by iodine(I)chloride in methanol gave compound **2f** in 98% yield (Scheme 3.10).



Scheme 3.10 Synthesis of compound **2f**

Compound 2h

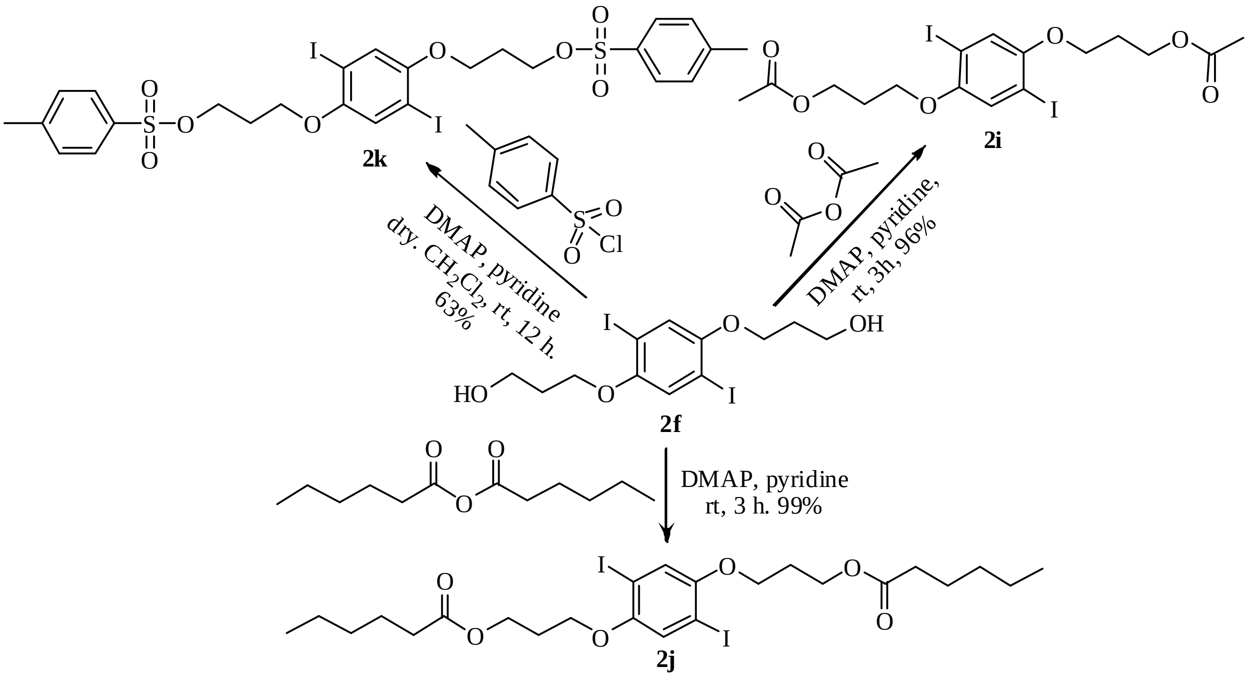
Compound **2h** were synthesized in order to prove that polyoxygenic substrate did not affect the reaction condition. We first activated hydroxyl group on diethyleneglycol monomethylether with mesylchloride to obtain 1g in 90% yield. Then, 1g was reacted with hydroquinone in DMF at 60 ^{0}C for 20 h to generate 1h in 96%. Finally, iodination by iodine(II) gave **2h** in 66% yield (Scheme 3.11).



Scheme 3.11 Synthesis of compound **2h**

Compounds 2i, 2j and 2k

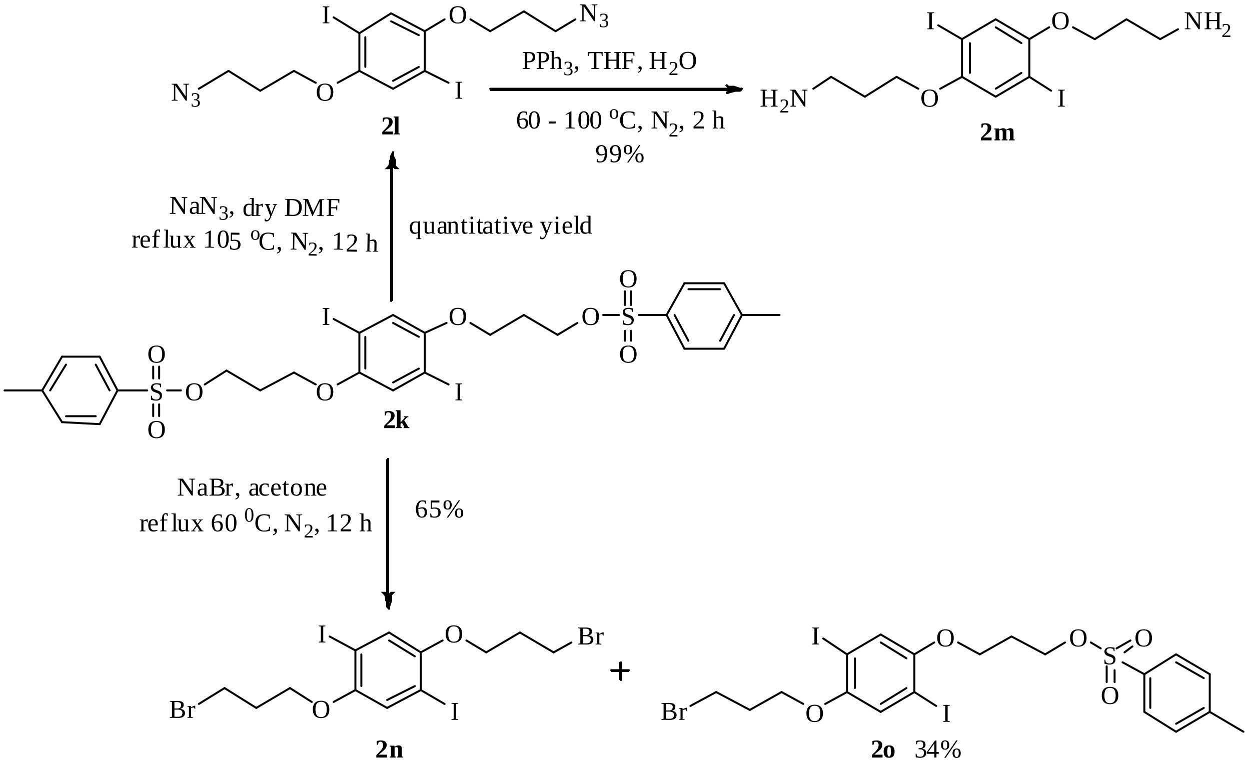
To confirm that our condition is the gentle reaction that allows the substrate carrying sensitive functional group to react, we decided to prepare compounds 2i, 2j and 2k. Compounds **2i** and **2j** were easily generated from esterification of 2f with acetic or hexanoic anhydride in pyridine and refluxing for 3 h to obtain 96 and 99% yield, respectively. On the other hand, 2f was reacted with *p*-toluenesulfonylchloride in dried CH_2Cl_2 resulting in formation of compound **2k** in 63% yield (Scheme 3.12).



Scheme 3.12 Synthesis of compounds **2i, 2j** and **2k**

Compounds 2l, 2m, 2n and 2o

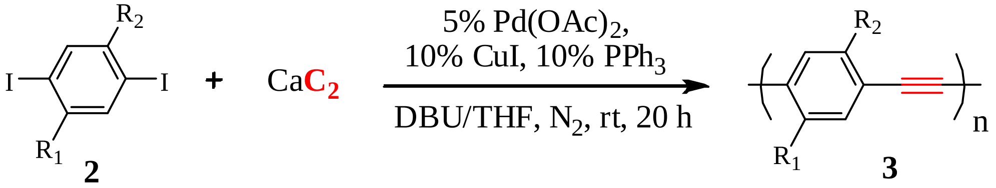
To demonstrate the high compatibility of various functional groups in our method, reactive group substituted aryldiiodide were synthesized. Reaction of 2k with NaN_3 in dried DMF was refluxed for 12 h to give diazide compound **2l** in quatitative yield (Scheme 3.13). Then, the reduction of 2l by triphenylphosphine in THF/H_2O to afford compound **2m** in 99% yield. On the other hand, compound **2n** was generated from bromination of 2k gave in 65% yield. Furthermore, we obtained compound **2o** as minor product from bromination in 34% yield.

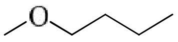
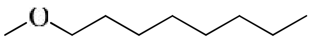
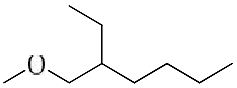
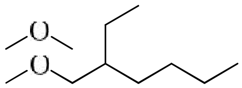
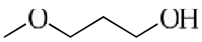
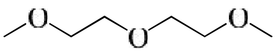
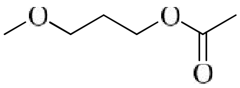
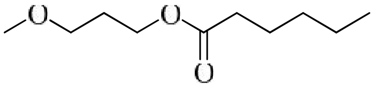
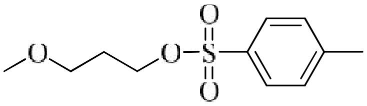
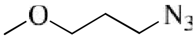
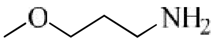
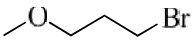
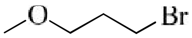
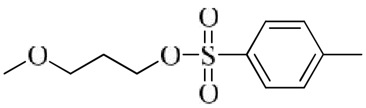


Scheme 3.13 Synthesis of compounds **2l, 2m, 2n** and **2o**

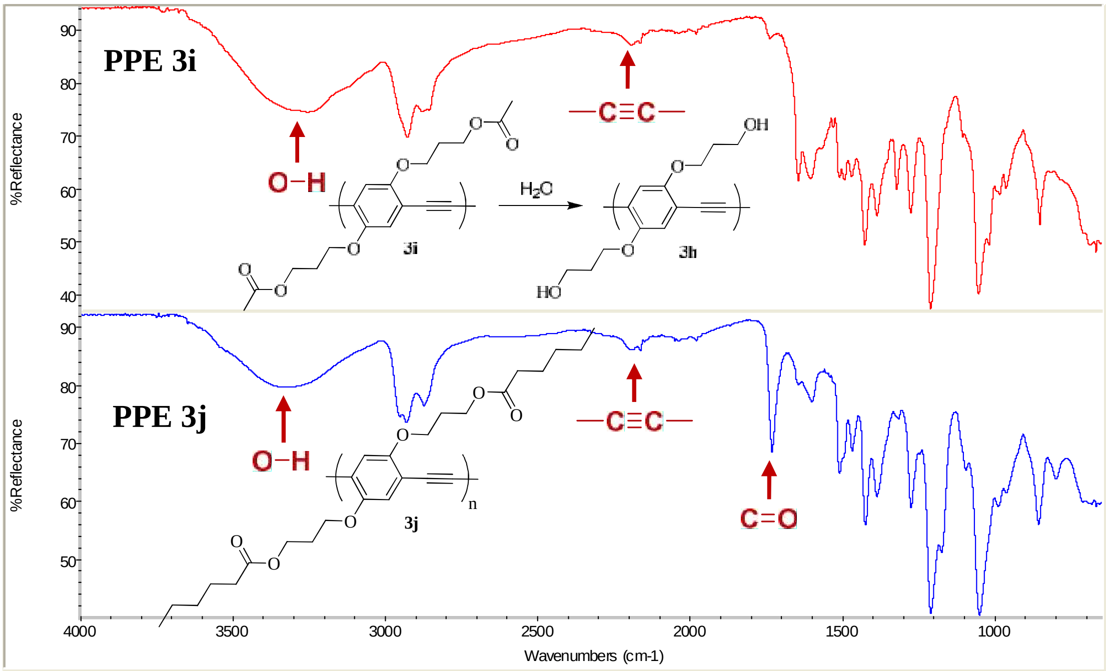
3.4 Preparation PPEs (3a-3o) from monomers (2a-2o)

With all the diiodo benzene (2a-2o) in hands, we next studied the generality of our reaction. Therefore, a series of aryl diiodides (2a-2o) which were prepared according to section 3.4 were subjected to the coupling reaction with CaC_2 under the optimized reaction conditions: aryl diiodides **2a-2o** (1 equiv), CaC_2 (6 equiv), $Pd(OAc)_2$ (5%mol), PPh_3 (10%mol), CuI (10%mol) in the mixture of DBU/THF in a ratio 1:2 and reaction proceeded smoothly at room temperature under a nitrogen atmosphere for 20 h to give the corresponding PPEs **3a-3o**. The results were summarized in Table 3.6.



entry	PPE **3**	yield^{a}	M_w^{b} (Da)	DP_n^{b}	M_w/M_n^{b}
1	**3a;** $R_1=R_2=$ 	71%	20,168	36	2.3
2	**3b;** $R_1=R_2=$ 	78%	40,972	48	2.4
3	**3c;** $R_1=R_2=$ 	83%	91,300	128	2.0
4	**3e;** $R_1=$ $R_2=$ 	93%	26,915	47	2.2
5	**3f;** $R_1=R_2=$ 	93%	N.D.	N.D.	N.D.
6	**3h;** $R_1=R_2=$ 	87%	26,975	51	1.5
7	**3i;** $R_1=R_2=$ 	66%	N.D.	N.D.	N.D.
8	**3j;** $R_1=R_2=$ 	63%	N.D.	N.D.	N.D.
9	**3k;** $R_1=R_2=$ 	N.A.	-	-	-
10	**3l;** $R_1=R_2=$ 	93%	N.D.	N.D.	N.D.
11	**3m;** $R_1=R_2=$ 	N.A.	-	-	-
12	**3n;** $R_1=R_2=$ 	N.A.	-	-	-
13	**3o;** $R_1=$  $R_2=$ 	N.A.	-	-	-

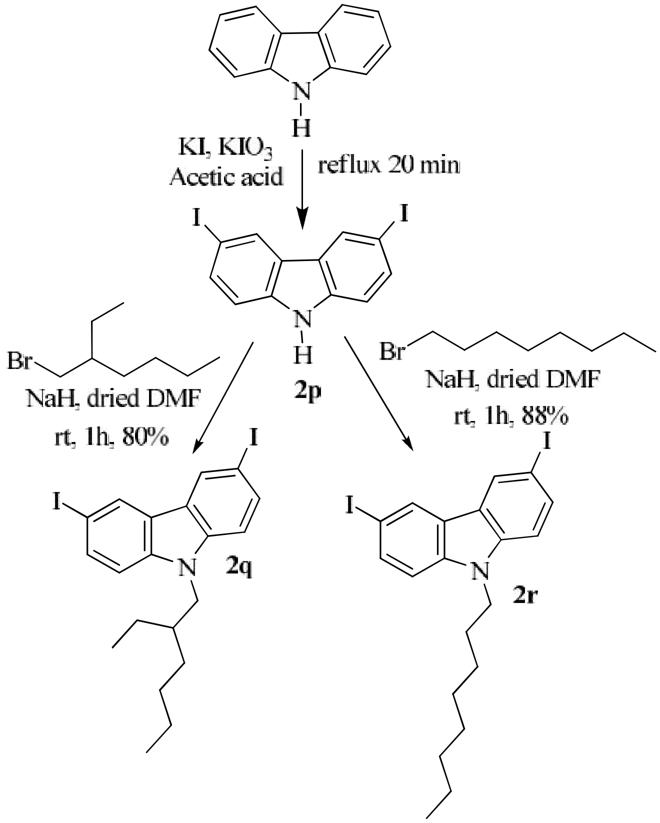
The aryl diiodides bearing a symmetrically alkoxy chain (R_1=R_2) such as butoxy (2a), octyloxy (2b) and ethylhexyloxy (2c) yielded the desired PPEs in good to excellent yields (71 - 83%) (entries 1-3). In addition, GPC data indicated that PPEs **3a** and **3b** showed higher molecular weight as compared with previous report [40]. Particularly, diiodo benzene carrying ethylhexyloxy side chain (2c) gave the highest molecular weight (entry 3). This is due to steric hindrance of side chain which had an impact on π-π stacking formation leading to excellent solubility of **3c** in the reaction medium. Moreover, the polymerization condition was efficient for unsymmetrical aryl diiodide. As seen in entry 4, PPE **3e** was successful coupling in excellent yield (93%) although, the molecular weight was significantly decreased when compared with produce asymmetrical PPE **3c**. We hypothesized that the unsymmetrical side chain induced conformation of polymer to be arranged in helical form. This is due to steric interaction along the polymer backbone. Surprisingly, aryl diiodides containing oxygeneous substituents such as **2f** and **2h** were able to tolerate and proceed smoothly under the polymerization condition giving the desired PPEs **3f** and **3h** in excellent yields (entries 5, 6). Compound **2h** gave PPE **3h** with high degree of polymerization (DP_n=32) and narrow polydispersity index (PDI=1.5). Unfortunately, the molecular weight of PPE **3f** could not be measured by GPC because it is insoluble in THF. In the case of aryl diiodides **2i** and **2j** containing ester group, we found that ester group did not survive in the reaction as they could not afford the target PPEs **3i** and **3j** (entries 7, 8). FT-IR spectra shown in Figure 3.5 indicated that all ester groups of PPE **3i** disappeared and it was hydrolyzed to alcohol side chain yielding the PPE **3f.** The corresponding to the signal of –OH stretching which displayed at 3300 nm^{-1} were detected and signal at 1750 nm^{-1} of C=O stretching disappeared. In the case of diiodo benzene 2j, the hexyl ester moiety in PPE **3j** were hydrolyzed partially as seen in Scheme 3.19 which showed the signals of C=O and –OH stretching at 1750 nm^{-1} and 3300 nm^{-1}, respectively. This is due to the reaction consisting of water from undried THF which could drive the hydrolysis of ester. Unfortunately, the presence of protecting group **3k**, amine **3m**, bromide **3n** and even unsymmetrical with difference functional group **3o** substituents were not suitable for this reaction because they formed only oligomer with


PPE 3i
O–H
C≡C
H2O
3i
3h
OH
HO
PPE 3j
O–H
C≡C
C=O
3j
n
%Reflectance
90
80
70
60
50
40
%Reflectance
90
80
70
60
50
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

3.5 Preparation of diiodo heterocyclic compounds (2p-2s)

Compounds 2p, 2q and 2r

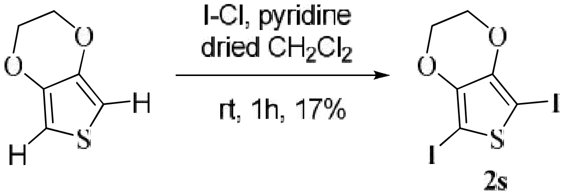
Compounds **2p, 2q** and **2r** were synthesized in order to see the potential of our method that may be applicable for PAEs synthesis from diiodo heterocyclic compound. Initially, we prepared compound **2p** which is an important starting material to produce TNT sensory material by iodination of carbazole with potassium iodide to give 98% yield. Then, alkylation of 2p using 2-ethylhexyl bromide or octyl bromide in pyridine provided compound **2q** and **2r** in 80% and 88% yield, respectively (Scheme 3.14).



Scheme 3.14 Synthesis of compounds **2q** and **2r**

Compound 2s

To study the effect of sulfur atom on our reaction, we prepared compound **2s** by iodination of 2,3-dihydrothieno[3,4-b][1,4]dioxine using iodine(I)chloride in dried CH_2Cl_2 to afford compound **2s** in 17% yield (Scheme 3.15). We can observe the ^1H NMR signal of carbon at dioxine shifting to down field after iodination.

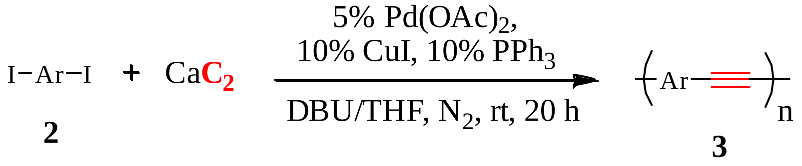


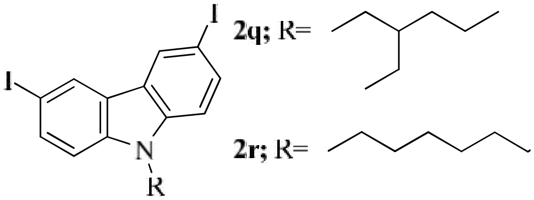
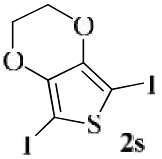
Scheme 3.15 Synthesis of compound **2s**

3.6 Preparation of PAEs (3q-3s) from monomers (2q-2s)

Typically, poly(aryleneethynylene)s or PAEs were synthesized from Sonogashira coupling reaction of aryl dihalide with terminal alkyne or TMS acetylene. Hence, we are interested to synthesize PAEs from new carbon source calcium carbide under our optimized condition. The prepared diiodoarene such as 2q, 2r and 2s were subjected to above mentioned condition in order to determine the efficiency of this reaction. The results are summarized in Table 3.7.

Table 3.7 Preparation of PAEs



entry	aryl diiodides **2**	PPE **3**	yield[a]	M_w[b] (GPC)	DP_n[b] (GPC)	M_w/M_n[b] (GPC)
1		**3q**	59%	N.D.	N.D.	N.D.
		3r	87%	N.D.	N.D.	N.D.
2		**3s**	N.A.	-	-	-

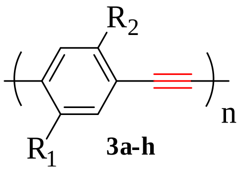
[a]Isolated yield by precipitation from MeOH/CH$_2$Cl$_2$. [b]Determined with GPC using universal calibration with standard polystyrene. N.D.= non dissolved in THF, N.A.= not available

The results in Table 3.7 indicated that monomers **2q** and **2r** could be used for synthesis of PAEs **3q** and **3r** appearing as a deep brown powder in satisfactory yields. However, the molecular weight could not be determined because of both PPEs were poor by soluble in THF. While, monomer **2s** could not be polymerized to give polymer with molecular weight high enough to precipitate out from the reaction mixture, although the starting material **2s** was completely consumed under this condition.

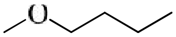
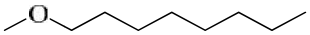
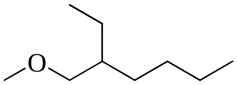
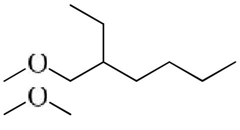
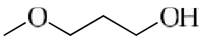
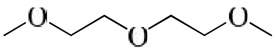
3.7 Color appearance

In this section, we observed the color appearance of PPEs in different environment such as solid state, in solution and under black-light. The appearance is presented in Table 3.8.

Table 3.8 Color appearance of PPEs **3a-3h**



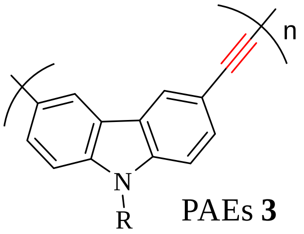
3a-h

entry	PPEs	solid state[a]	solution[b]	under black-light[b]
1	**3a;** R_1=R_2= 			
2	**3b;** R_1=R_2= 			
3	**3c;** R_1=R_2= 			
4	**3e;** R_1= R_2= 			
5	**3f;** R_1=R_2= 			
6	**3h;** R_1=R_2= 			

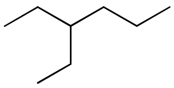
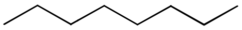
[a]Isolated yield by precipitation from MeOH/CH_2Cl_2. [b]Dissolved in chloroform except **3f** was dissolved in DMSO.

The photograph of each PPE in Table 3.8 demonstrated that the alkoxy substituted PPEs are yellow-orange to deep orange powder suggesting that PPEs are defect free corresponding to Bunz et al. [51] In the case of PPEs solution, we first dissolved PPEs **3a-3e, 3h** in chloroform and PPE **3f** in DMSO. We observed the color of PPE solution by naked eye and found that typically all polymers gave yellow greenish emission in chloroform under visible light, while under black-light they showed greenish-blue colored emission. Furthermore, we investigated color appearance of synthesized PAEs **(3q** and **3r)** as seen in the Table 3.9.

Table 3.9 Color appearance of PAEs **3q** and **3r**

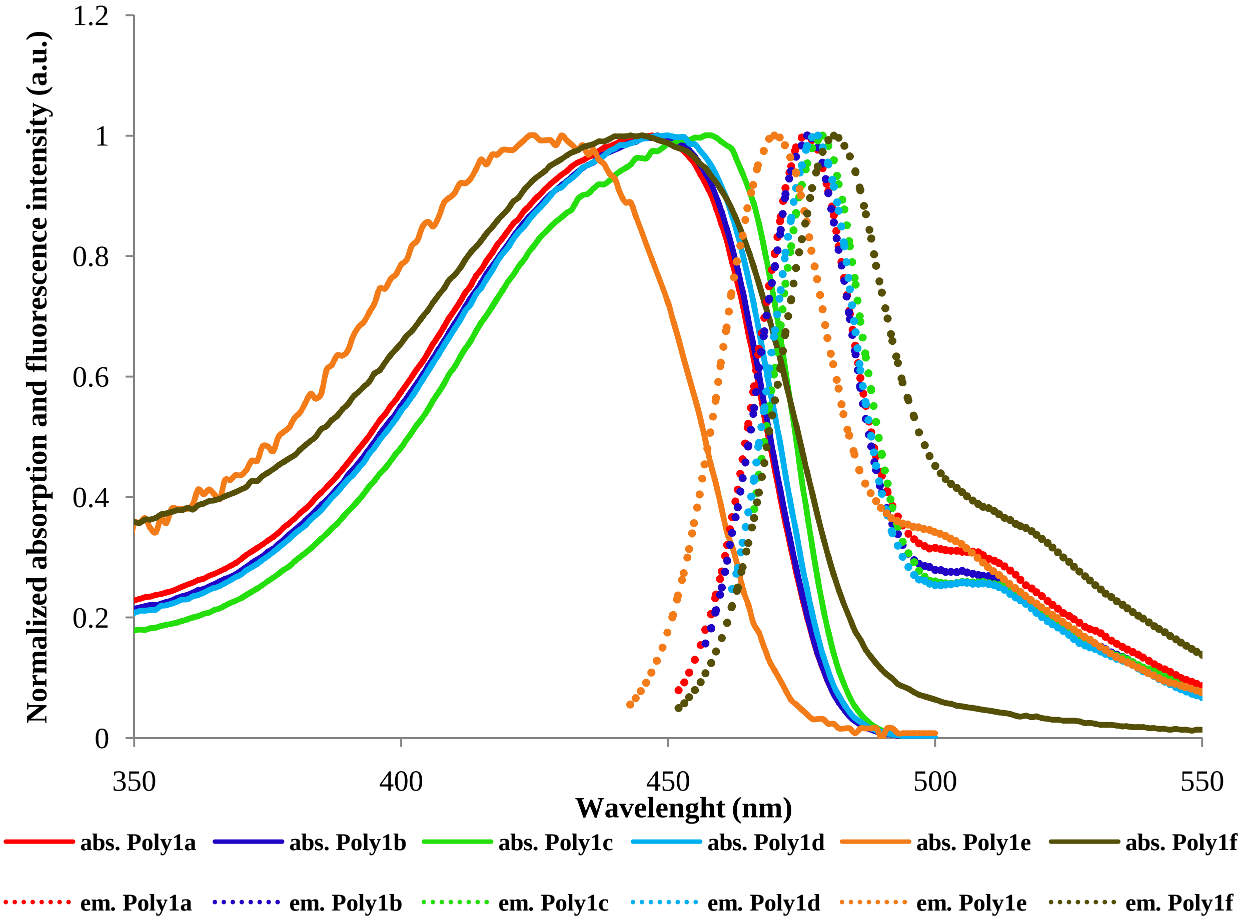


PAEs **3**

entry	PAEs	solid state^a	In solution^b	under black-light^b
1	**3q;** R= 			
2	**3r;** R= 			

^{a}Isolated yield by precipitation from MeOH/CH_2Cl_2. ^{b}Dissolved in $CHCl_3$

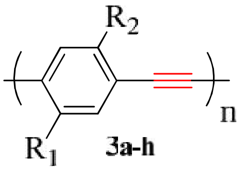
PAEs **3q** appears as deep brown powder similar to PAEs **3r** and both were dissolved in chloroform giving light brown solution under visible light. Surprisingly, appearance of PAEs solution was investigated under black-light showing strong light blue emission.



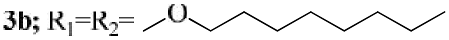
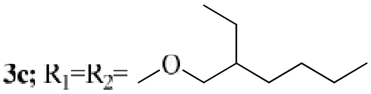
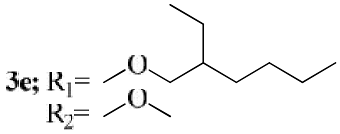
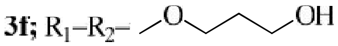
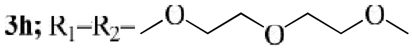
Normalized absorption and fluorescence intensity (a.u.)
1.2
1
0.8
0.6
0.4
0.2
0
350
400
450
500
550
Wavelenght (nm)
abs. Poly1a
abs. Poly1b
abs. Poly1c
abs. Poly1d
abs. Poly1e
abs. Poly1f
em. Poly1a
em. Poly1b
em. Poly1c
em. Poly1d
em. Poly1e
em. Poly1f

The normalized intensity of absorption and fluorescence spectra of PPEs **3a-3h** are presented in Figure 3.6 and tabulated in Table 3.10. The photophysical properties of the polymers including maximum absorption wavelength (λ_{abs}), maximum emission wavelength (λ_{em}), molar absorptivity (ε) and fluorescence quantum efficiency (Φ_f) were determined as presented in Table 3.10.

Table 3.10 Photophysical properties of PPEs **3a-3h**[a]



3a-h

entry	polymer **3**	λ_{abs}/nm	λ_{em}/nm	log ε	Φ_f
1		447	476	4.32	0.65
2		448	476	4.30	0.66
3		458	479	4.41	0.71
4		450	478	4.02	0.67
5		445[b]	481[b]	4.11[b]	0.34[b]
6		430	470	4.02	0.67

[a]All reaction was dissolved in $CHCl_3$ and used quinine sulfate as reference standard. [b]Performed in DMSO

The results in Table 3.10 summarized that all polymers showed maximum wavelength of absorption around 445 – 458 nm, except PPE **3h** which showed maximum wavelength at 430 nm which is similar to the reported case of a PPE bearing ethylene glycol side chain [22] and showed the emission maximum around 480 nm, representing a rather small stoke shift due to the rigid conformation of polymers (Figure 3.6). The fact that the absorption spectra and the absorption maxima of the polymers appeared at almost the same wavelength suggested that these polymers have a similar π-conjugated system. Moreover, all polymers were found to have high molar absorptivity (ε) which were reported in log ε around 4.00-4.40. The fluorescence quantum efficiency (Φ_f) were determined by using a comparative method with well-characterized standard samples of known quantum yield values and had the emission range cover in emission of compound. For all PPEs, quinine sulfate in 0.1 M H_2SO_4 ($\Phi_f = 0.54$) was used as the standard and gave relatively high quantum efficiencies (0.34-0.71). The observed high quantum yields can be explained by the absence of diacetylene defects due to our robust method of polymer preparation. [23]

CHAPTER IV

CONCLUSION

Poly(phenyleneetynylene)s (PPEs) were successfully synthesized directly from primary chemical feed stock calcium carbide as carbon triple bond source. The synthesis involves coupling reaction between aryl diodides with calcium carbide via a Pd-catalyzed coupling reaction. Under the optimized conditions, PPEs are prepared in excellent yields after precipitation with methanol. To test the functional group compatibility, the aryl diiodides containing oxygenic or alkoxy side chains are subjected to polymerization reaction and the desired PPE obtained in good yields along with high molecular weight and high quality. Unfortunately, aryl diiodides containing sensitive or reactive functional groups such as ester, bromo or tosyl were not suitable for polymerization under this optimized condition giving the small oligomer of ethylene phenylene. Moreover, we demonstrate that poly(aryleneethynylene)s (PAEs) containing heterocyclic ring such as thiophene and carbazole can be synthesized from this reaction in satisfactory yields. Photophysical properties of these PPEs show the absorption and emission maximum around 445 and 480 nm respectively with high molar absorptivity between 4.02-4.41 and high quantum efficiency in the range of 0.34-0.71. In comparison with the conventional method using acetylene gas or protected acetylene as starting material, our method offers several advantages such as 1) low cost starting material 2) convenient experimental setup 3) less hazardous. Therefore, this novel synthetic would be great alternative processor the preparation of high quality PPEs in laboratory and industrial aspect.

REFERENCES

[1] Kuroda, K., and Swager, T. M. Synthesis of a Nonionic Water Soluble Semiconductive Polymer. Chemical Communications (2003) : 26–27.

[2] Swager, T. M. The Molecular Wire Approach to Sensory Signal Amplification. Accounts of Chemical Research 31 (1998) : 201-207.

[3] Zhou, Q., and Swager, T. M. Fluorescent Chemosensors Based on Energy Migration in Conjugated Polymers: The Molecular Wire Approach to Increased Sensitivity. Journal of the American Chemical Society 117 (1995) : 12593-12602.

[4] Wilson, J. N. Bangcuyo, C. G. Erdogan, B. Myrick, M. L., and Bunz, U. H. F. Nanostructuring of Poly(aryleneethynylene)s: Formation of Nanotowers, Nanowires, and Nanotubules by Templated Self-Assembly. Macromolecules 36 (2003) : 1426-1428.

[5] Geng, J. X., and Zeng, T. Y. Influence of Single-Walled Carbon Nanotubes Induced Crystallinity Enhancement and Morphology Change on Polymer Photovoltaic Devices. Journal of the American Chemical Society 128 (2006) : 16827-16833.

[6] Seminario, J. M. Zacarias, A. G., and Tour, J. M. Molecular Alligator Clips for Single Molecule Electronics. Studies of Group 16 and Isonitriles Interfaced with Au Contacts. Journal of the American Chemical Society 121 (1999) : 411-416.

[7] Tour, J. M. Kozaki, M., and Seminario, J. M. Molecular Scale Electronics: A Synthetic/Computational Approach to Digital Computing. Journal of the American Chemical Society 120 (1998) : 8486-8493.

[8] Bunz, U. H. F. Poly(aryleneethynylene)s. Macromolecular Rapid Communications 30 (2009) : 772–805.

[9] Yang, J. S., and Swager, T. M. Fluorescent Porous Polymer Films as TNT Chemosensors: Electronic and Structural Effects. Journal of the American Chemical Society 120 (1998) : 11864-11873.

[10] Yang, J. S., and Swager, T. M. Porous Shape Persistent Fluorescent Polymer Films: An Approach to TNT Sensory Materials. Journal of the American Chemical Society 120 (1998) : 5321.

[11] Bunz, U. H. F. Poly(*p*-phenyleneethynylene)s by Alkyne Metathesis. Accounts of Chemical Research 34 (2001) : 998-1010.

[12] Veller, B. V., and Swager, T. M. Poly(aryleneethynylene)s. In M. Leclerc et al. (eds.), Design and Synthesis of Conjugated Polymers, pp. 175-180. Federal Republic of Germany, 2010.

[13] Chuentragool, P. Vongnam, K. Rashatasakhon, P. Sukwattanasinitt, M., and Wacharasindhu, S. Calcium Carbide As a Cost-Effective Starting Material for Symmetrical Diarylethynes via Pd-Catalyzed Coupling Reaction. Tetrahedron 67 (2011) : 8177-8182.

[14] Lin, Z. Yu, D. Sum, Y. N., and Zhang, Y. Synthesis of Functional Acetylene Derivatives from Calcium Carbide. ChemSusChem 5 (2012) : 625-628.

[15] Zhang, W., and others. The Use of Calcium Carbide in One-pot Synthesis of Symmetric Diaryl Ethynes. Chemical Communications (2006) : 4826-4828.

[16] Sonogashira, K. Tohda, Y., and Hagihara, N. A Convenient Synthesis of Acetylene: Catalytic Substitutions of Acetylenic Hydrogen with Bromoalkane, Iodoaerenes and Bromopyridines. Tetrahedron Letters 16 (1975) : 4467-4470.

[17] Bunz, U. H. F. Poly(aryleneethynylene)s: Syntheses, Properties, Structures, and Applications. Chemical Reviews 100 (2000) : 1605-1644.

[18] Bunz, U. H. F. Synthesis and Structure of PAEs. Advances in Polymer Science 177 (2005) : 1-52.

[19] Chinchilla, R., and Najera, C. The Sonogashira Reaction: A Booming Methodology in Synthetic Organic Chemistry. *Chemical Reviews* 107 (2007) : 874-922.

[20] Giesa, R., and Schulz, R. C. Soluble Poly(l,4-phenyleneethynylene)s. Makromolekulare Chemie 191 (1990) : 857–867.

[21] Nielsen, K. T. Bechgaard, K., and Krebs, F. C. Removal of Palladium Nanoparticles from Polymer Materials. Macromolecules 38 (2005) : 658-659.

[22] Khan, A. Muller, S., and Hecht, S. Practical Synthesis of An Amphiphilic, Non-Ionic Poly(paraphenyleneethynylene) Derivative With a Remarkable Quantum Yield in Water. Chemical Communications (2005) : 584-586.

[23] Khan, A., and Hecht, S. Microwave-Accelerated Synthesis of Lengthy and Defect-Free Poly(*m*-phenyleneethynylene)s via ABA and A2 + BBA Polycondensation Routes. Chemical Communications 2004 : 300-301.

[24] Hecht, S., and Khan, A. Intramolecular Cross-Linking of Helical Folds: An Approach to Organic Nanotubes. Angewandte Chemie International Edition 42 (2003) : 6021 –6024.

[25] Khan, A., and Hecht, S. Functional Organic Nanotubes from Hollow Helical Scaffolds. Synthetic Metals 147 (2004) : 37-42.

[26] Wilson, J. N. Waybright, S. M. McAlpine, K., and Bunz. U. H. F. Acetylene Gas: A Reagent in the Synthesis of High Molecular Weight Poly(p-phenyleneethynylene)s Utilizing Very Low Catalyst Loadings. Macromolecules 35 (2002) : 3799-3800.

[27] Patnaik, P. Handbook of Inorganic Chemical Compounds. Lindenwood, NJ : McGraw-Hill Professional Publication, 2003.

[28] Morehead, J. T., and Chalmot, G. D. The Manufacture of Calcium Carbide. Journal of the American Chemical Society 18 (1896) : 311–331.

[29] Abeles, F. B., and Gahagan, H. E. III. Abscission: The Role of Ethylene, Ethylene Analogues, Carbon Dioxide, and Oxygen. Plant Physiology 43 (1968) : 1255–1258.

[30] Mworia, E. G., et al. Low-Temperature-Modulated Fruit Ripening is Independent of Ethylene in 'Sanuki Gold' Kiwifruit. Journal of Experimental Botany 63 (2012) : 963–971.

[31] Dun, Y. Troubles in the PVC industry. Hong Kong Trade Development Council, 2006.

[32] Greenwood, N., and Earnshaw, A. Chemistry of The Elements 2nd Ed. United Kingdom : Pergamon Press, 1997.

[33] Pang, L. L., et al. Synthesis of Carbon Spheres via a Low-Temperature Metathesis Reaction. Journal of Physical Chemistry C 112 (2008) : 12134-12137.

[34] Cataldo, F. A Method for Synthesizing Polylynes in Solution. Carbon 43 (2005) : 2792-2800.

[35] Jiang, Y. Kuang, C., and Yang, Q. The Use of Calcium Carbide in the Synthesis of 1-Monosubstituted Aryl 1,2,3-Triazole via Click Chemistry. Synlett 19 (2009) : 3163-3166.

[36] Ray, F. E. Sawicki, E., and Borum, O.H. Cancer Research Laboratory. University of Florida 74 (1952) : 1247-1249.

[37] Swager, T. M. Gil, C. J., and Wrighton, M. S. Fluorescence Studies of Poly(phenylene ethyny1ene)s: The Effect of Anthracene Substitution. Journal of Physical Chemistry 99 (1995) : 4886-4893.

[38] Wang, Y. Erdogan, B. Wilson, J. N., and Bunz, U. H. F. Grafted Conjugated Polymers: Synthesis and Characterization of A Polyester Side Chain Substituted Poly(*para*phenylene ethynylene). Chemical Communications (2003) : 1624-1625.

[39] Harriman, A. Mallon, L. J. Elliot, K. J. Haefele, A. Ulrich, G., and Ziessel, R. Length Dependence for Intramolecular Energy Transfer in Three- and

Four-Color Donor-Spacer-Acceptor Arrays. Journal of the American Chemical Society 131 (2009) : 13375–13386.

[40] Shinar et al. Fabrication of Poly(phenyleneethnylene) Light-Emitting Diodes. U.S. Patent 5,334,539, August 2, 1994.

[41] Weder, C., and Wrighton, M. S. Efficient Solid-State Photoluminescence in New Poly(2,5-dialkoxy-p-phenyleneethynylene)s. Macromolecules 29 (1996) : 5157-5165.

[42] Egbe, D. A. M. Roll, C. P. Birckner, E. Grummt, U. W. Stockmann, R., and Klemm, E. Side Chain Effects in Hybrid PPV/PPE Polymers. Macromolecules 35 (2002) : 3825-3837.

[43] Lucht, B. L. Mao, S. S. H., and Tilley, T. D. A Zirconocene-Coupling Route to Substituted Poly(p-phenylenedienylene)s: Band Gap Tuning via Conformational Control. Journal of the American Chemical Society 120 (1998) : 4354-4365.

[44] Crisp, G. T., and Bubner, T. P. Preparation of Sterically Constrained Arylalkyne Oligomers. Tetrahedron 53 (1997) : 11899–11912.

[45] Li, J. Kendig, C. E., and Nesterov, E. E. Chemosensory Performance of Molecularly Imprinted Fluorescent Conjugated Polymer Materials. Journal of the American Chemical Society 129 (2007) : 15911-15918.

[46] Iraqi, A., and Wataru, I. 3,6-Linked 9-Alkyl-9H-Carbazole Main-Chain Polymers: Preparation and Properties. Journal of Polymer Science Part A: Polymer Chemistry 42 (2004) : 6041–6051.

[47] Maegawa, Y. Goto, Y. Inagaki, S., and Shimada, T. A Useful Procedure for Diiodination of Carbazoles and Subsequent Efficient Transformation to Novel 3,6 Bis(triethoxysilyl) Carbazoles Giving Mesoporous Materials. Tetrahedron Letters 47 (2006) : 6957–6960.

[48] Meng, H., et al. Solid-State Synthesis of a Conducting Polythiophene via an Unprecedented Heterocyclic Coupling Reaction. Journal of the American Chemical Society 125 (2003) : 15151-15162.

[49] Moroni, M., and Moigne, J. L. Rigid Rod Conjugated Polymers for Nonlinear Optics Characterization and Linear Optical Properties of Poly(arylene-ethyny1ene) Derivatives. Macromolecules 27 (1994) : 562-571.

[50] Rubin, Y. Lin, S. S. Knobler, C. B. Anthony, J. Boldi, A. M., and Diederich, F. Solution-Spray Flash Vacuum Pyrolysis: A New Method for the Synthesis of Linear Poliynes with Odd Numbers of C-C Bonds from Substituted 3,4-Dialkynyl-3-cyclobutene-1,2-diones. Journal of the American Chemical Society 113 (1991) : 6943-6949.

[51] Kloppenburg, L, Song, D., and Bunz, U. H. F. Alkyne Metathesis with Simple Catalyst Systems: Poly(p-phenyleneethynylene)s. Journal of the American Chemical Society 120 (1998) : 7973-7974.

Appendix

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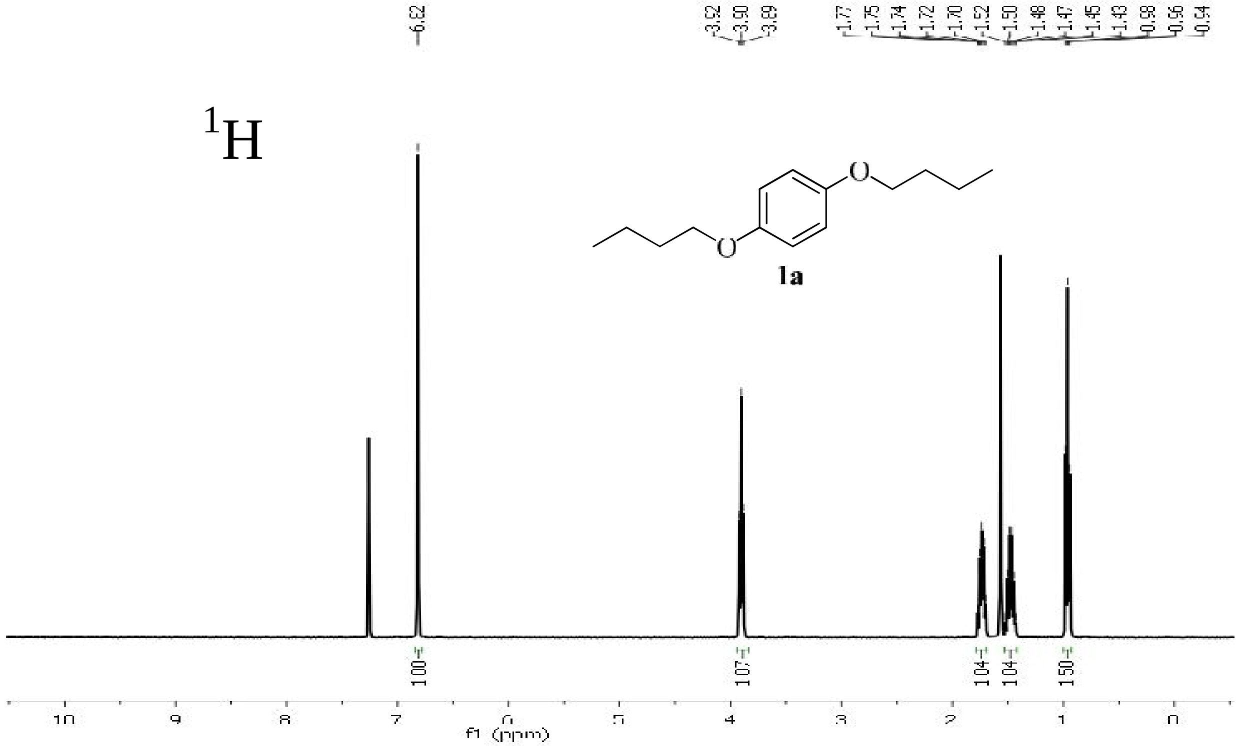

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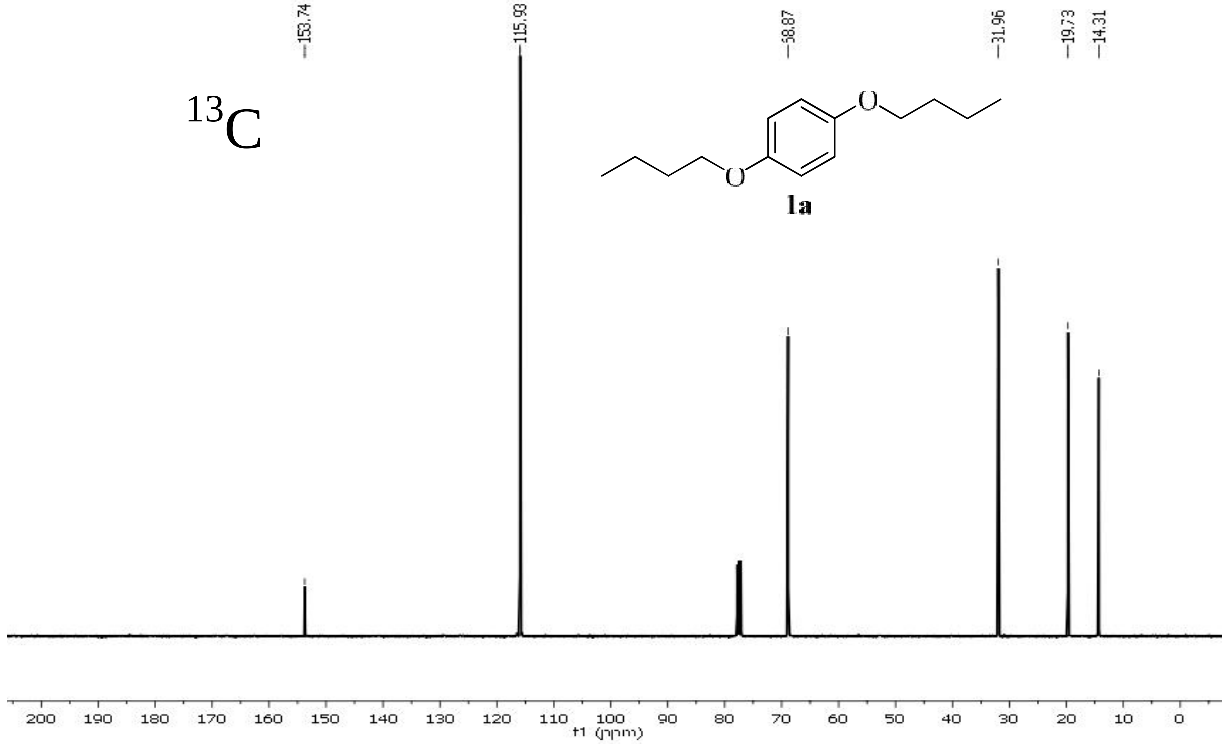
3.92
3.90
3.89
1.77
1.75
1.74
1.72
1.70
1.52
1.50
1.48
1.47
1.45
1.43
0.98
0.96
0.94
1a
1.00
1.07
1.04
1.04
1.50
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

^{13}C



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115.93
68.87
31.96
19.73
14.31
1a
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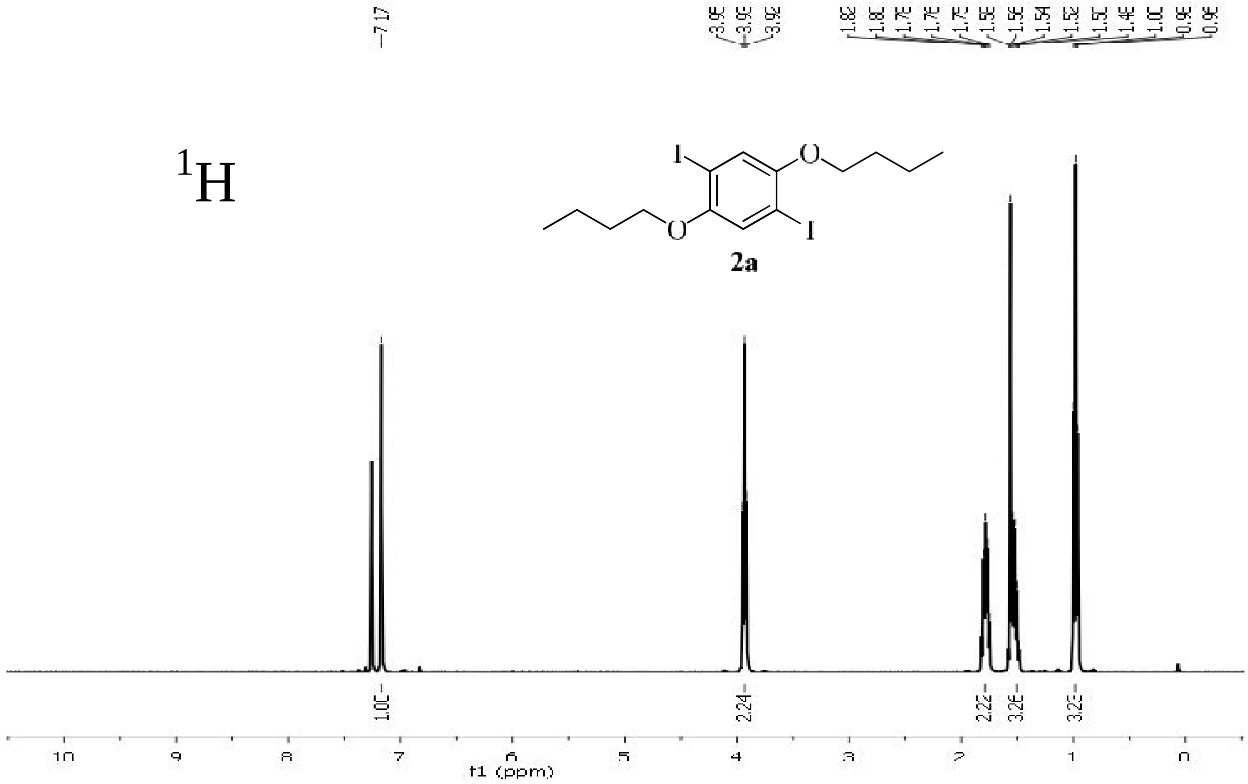
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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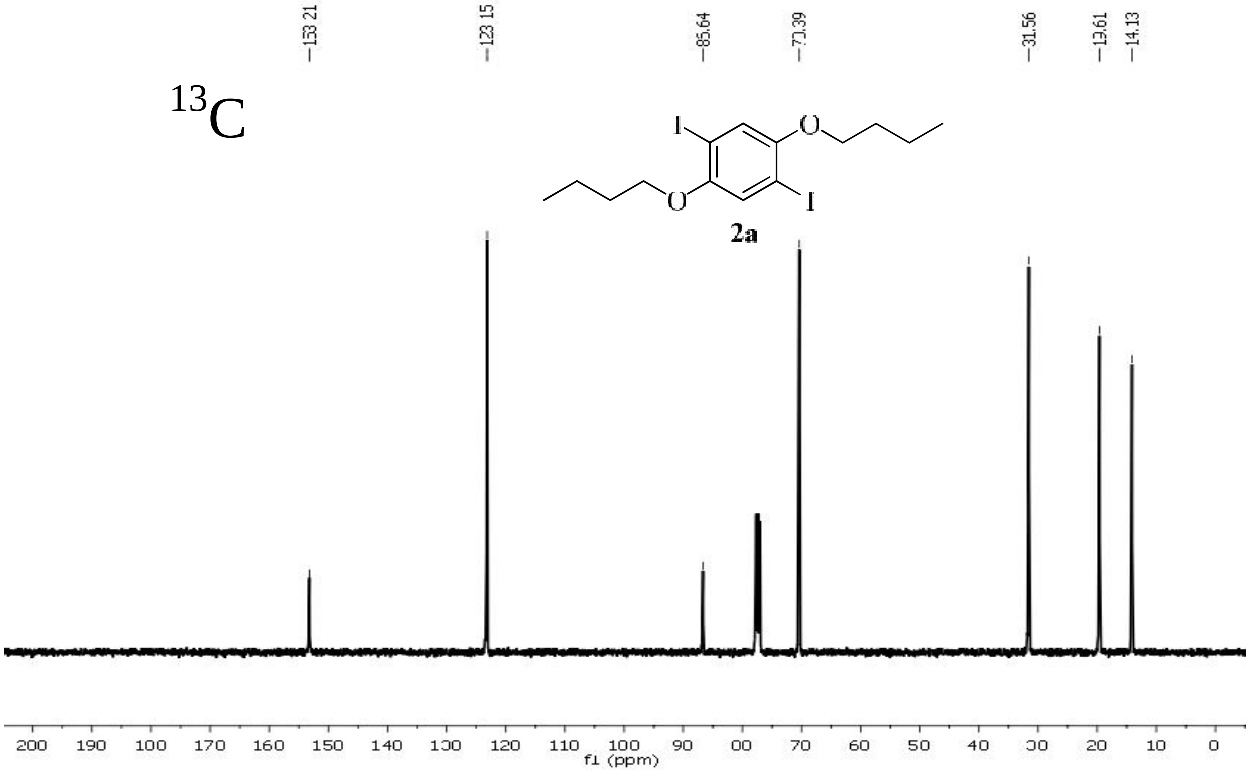
3.95
3.93
3.92
1.82
1.80
1.78
1.76
1.75
1.58
1.56
1.54
1.52
1.50
1.48
1.00
0.98
0.96
^{1}H
I
O
O
I
2a
1.00
2.24
2.22
3.26
3.23
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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123.15
86.64
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19.61
14.13
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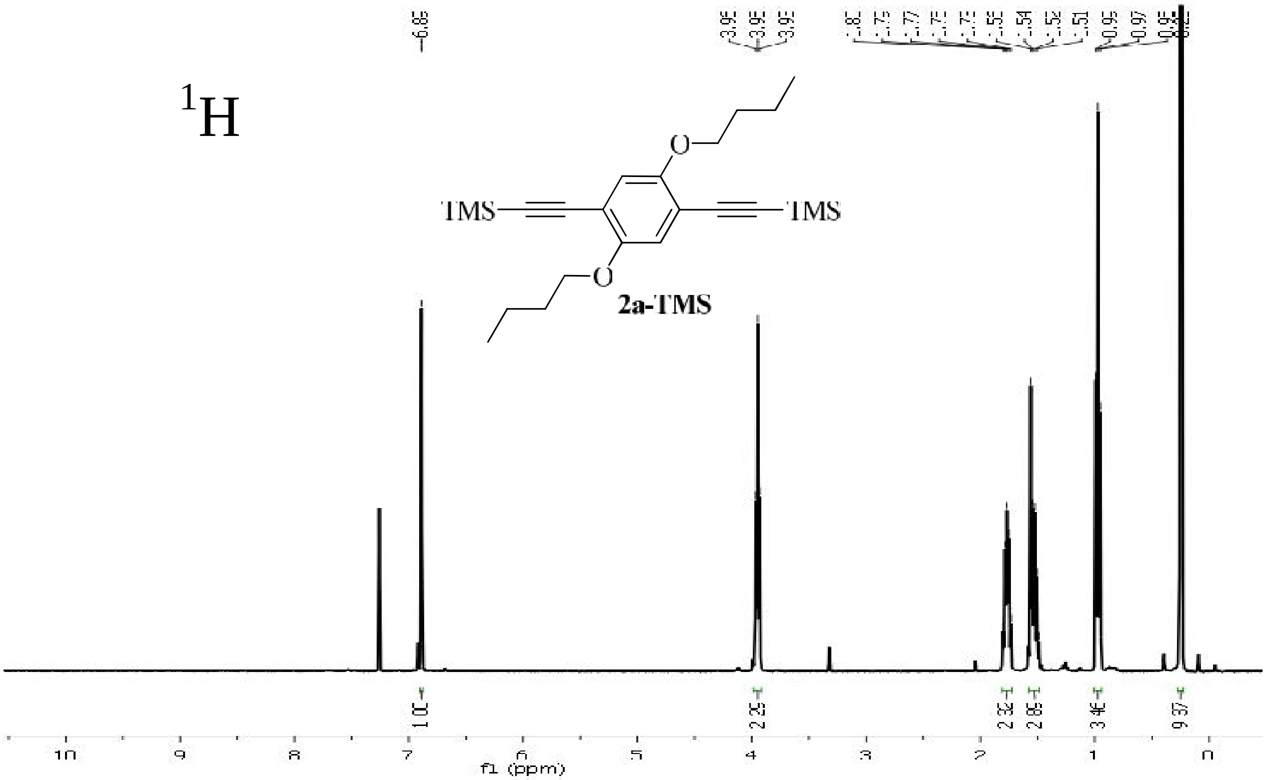
O
O
I
2a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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1.81
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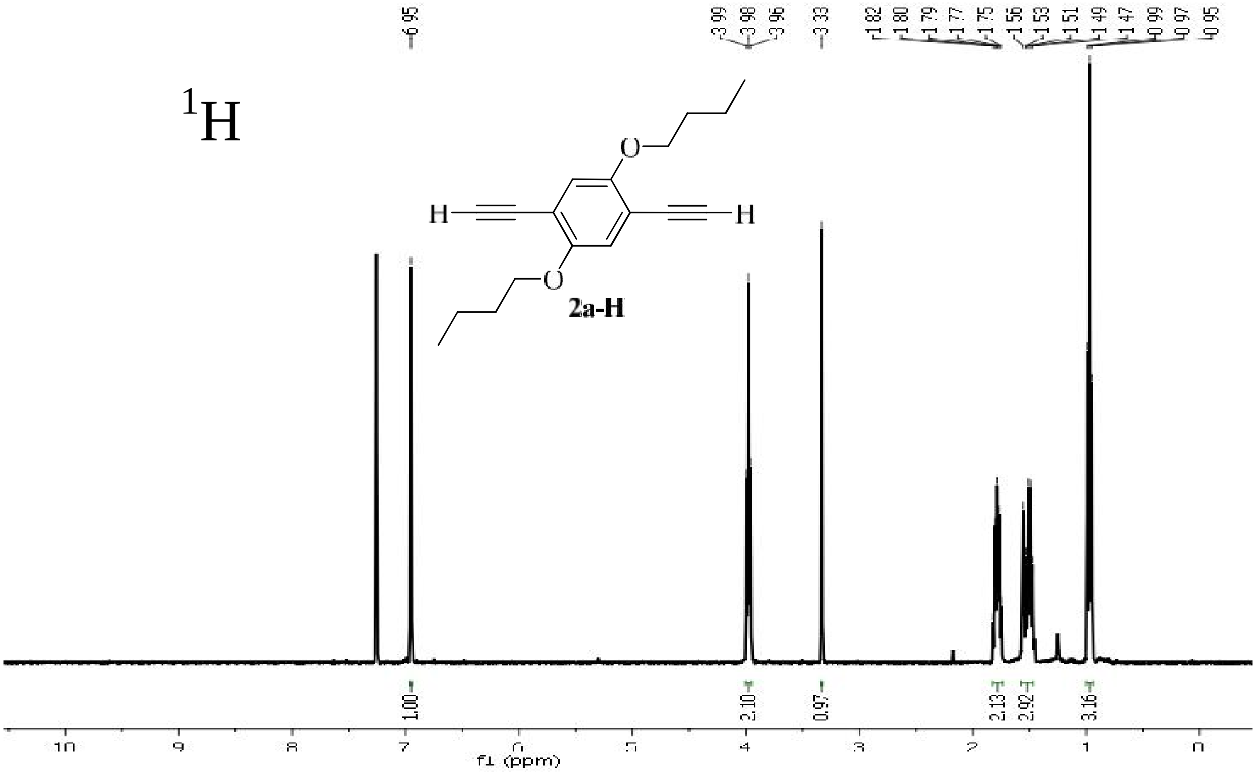
1.73
1.55
1.54
1.52
1.51
0.99
0.97
0.95
0.25
TMS
TMS
O
O
2a-TMS
1.00
2.29
2.32
2.85
3.46
9.37
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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3.98
3.96
3.33
1.82
1.80
1.79
1.77
1.75
1.56
1.53
1.51
1.49
1.47
0.99
0.97
0.95
H
H
O
O
2a-H
1.00
2.10
0.97
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3.16
10
9
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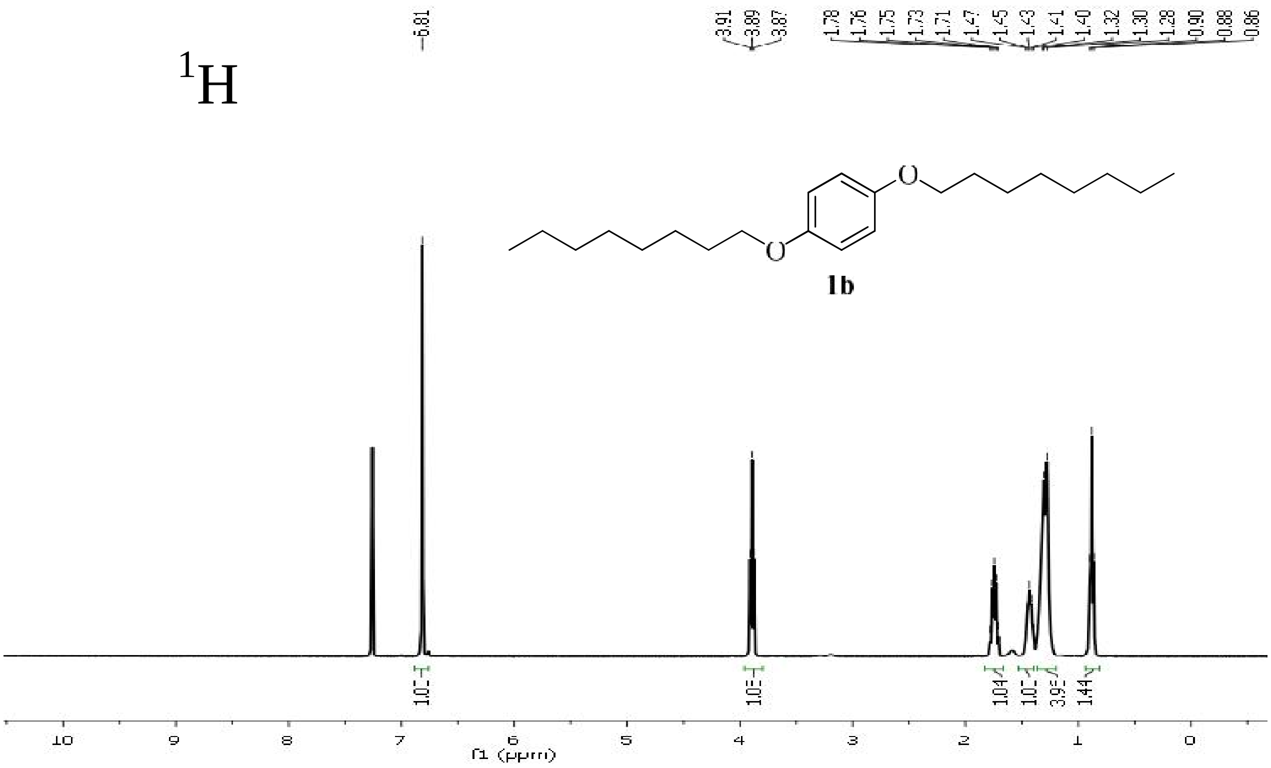
7
6
5
4
3
2
1
0
f1 (ppm)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3.91
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3.87
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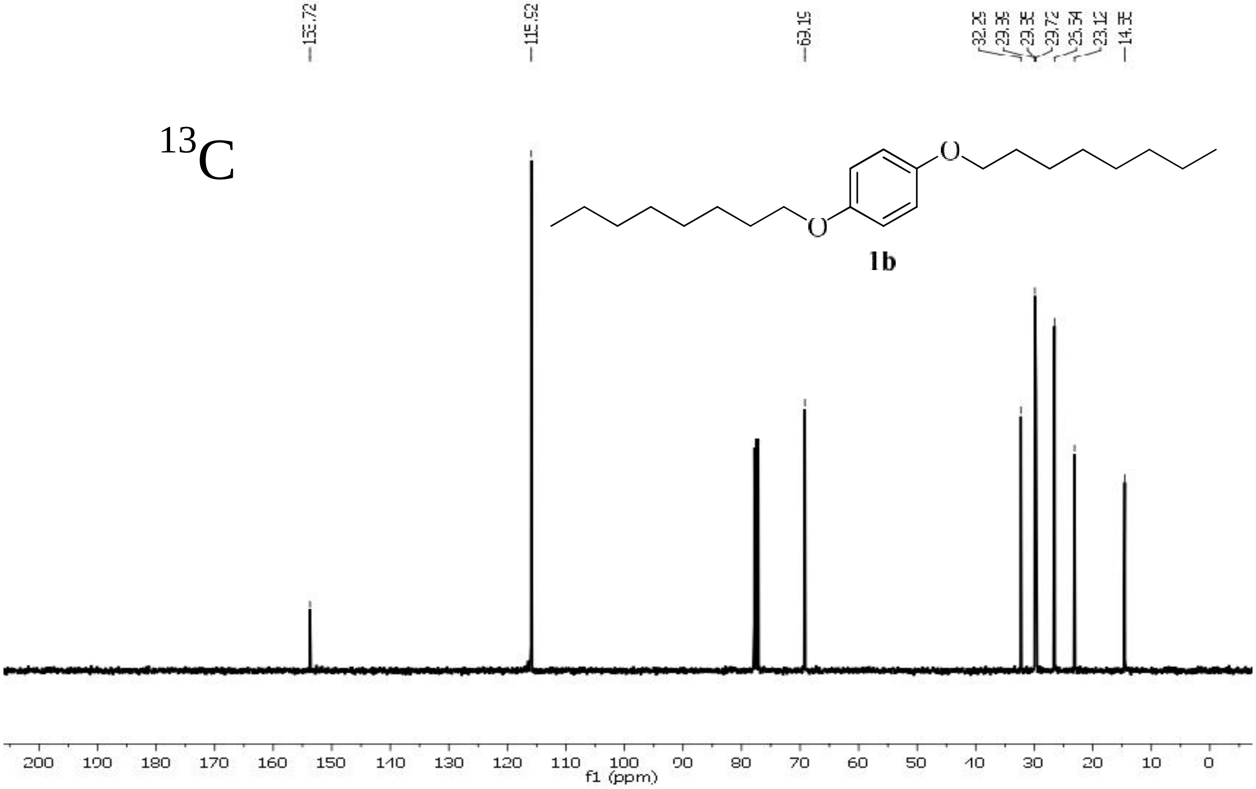
1.76
1.75
1.73
1.71
1.47
1.45
1.43
1.41
1.40
1.32
1.30
1.28
0.90
0.88
0.86
O
O
1b
1.07
1.05
1.04
1.07
3.95
1.44
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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23.12
14.55
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O
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200
190
180
170
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150
140
130
120
110
100
90
80
70
60
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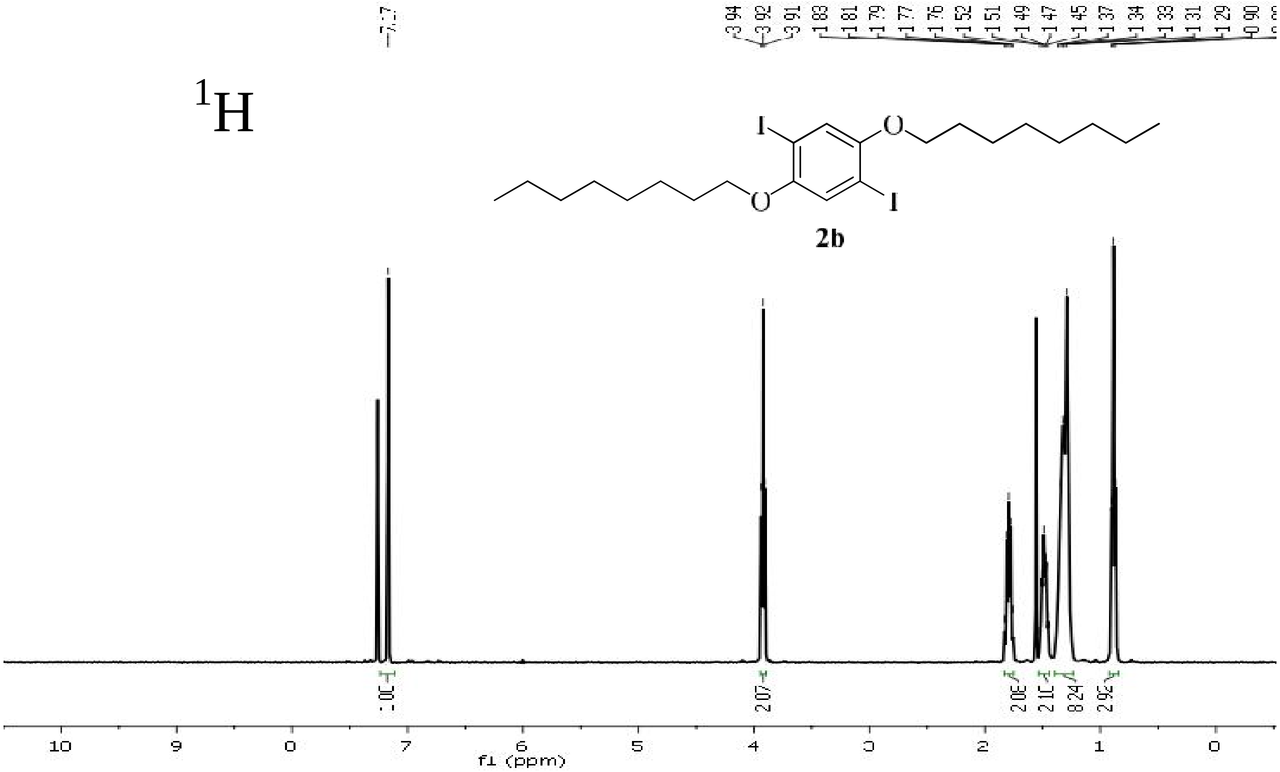
20
10
0
f1 (ppm)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1.76
1.52
1.51
1.49
1.47
1.45
1.37
1.34
1.33
1.31
1.29
0.90
I
O
O
I
2b
1.00
2.07
2.08
2.10
8.24
2.92
10
9
8
7
6
5
4
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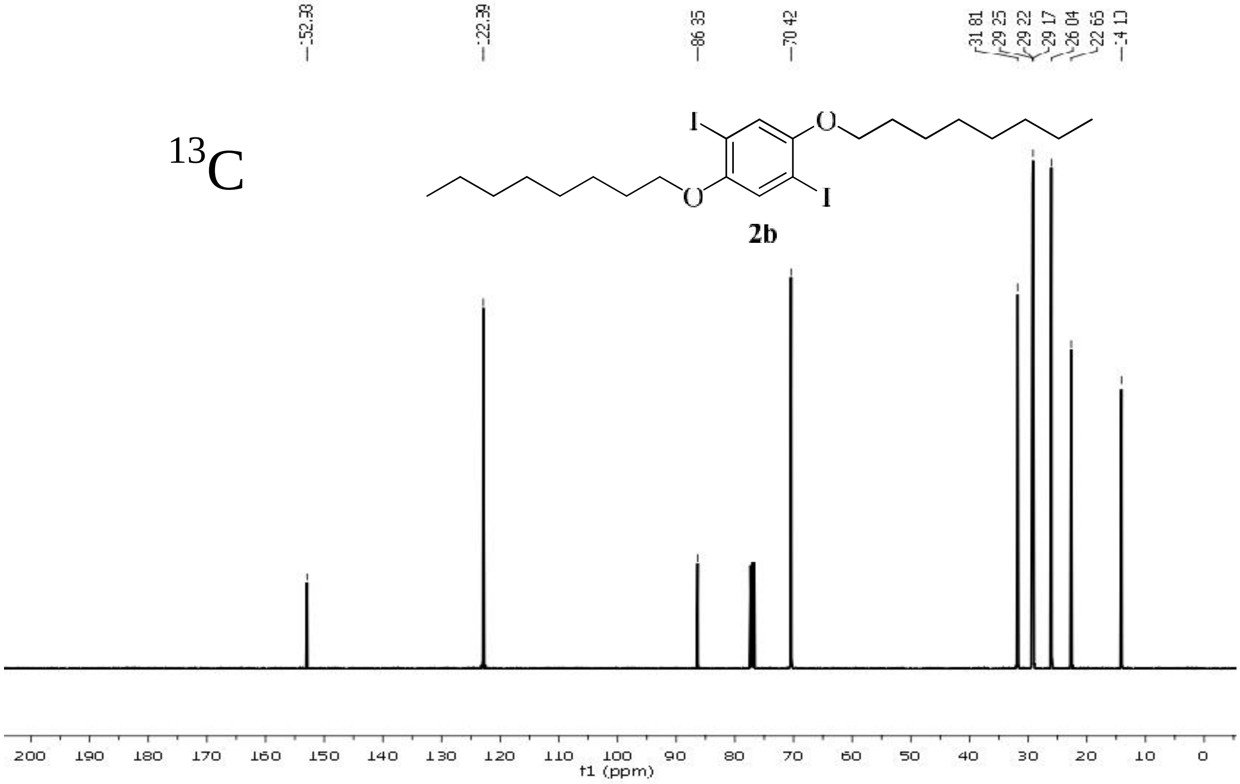
2
1
0
f1 (ppm)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70.42
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29.22
29.17
26.04
22.65
14.13
13C
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O
O
I
2b
200
190
180
170
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150
140
130
120
110
100
90
80
70
60
50
40
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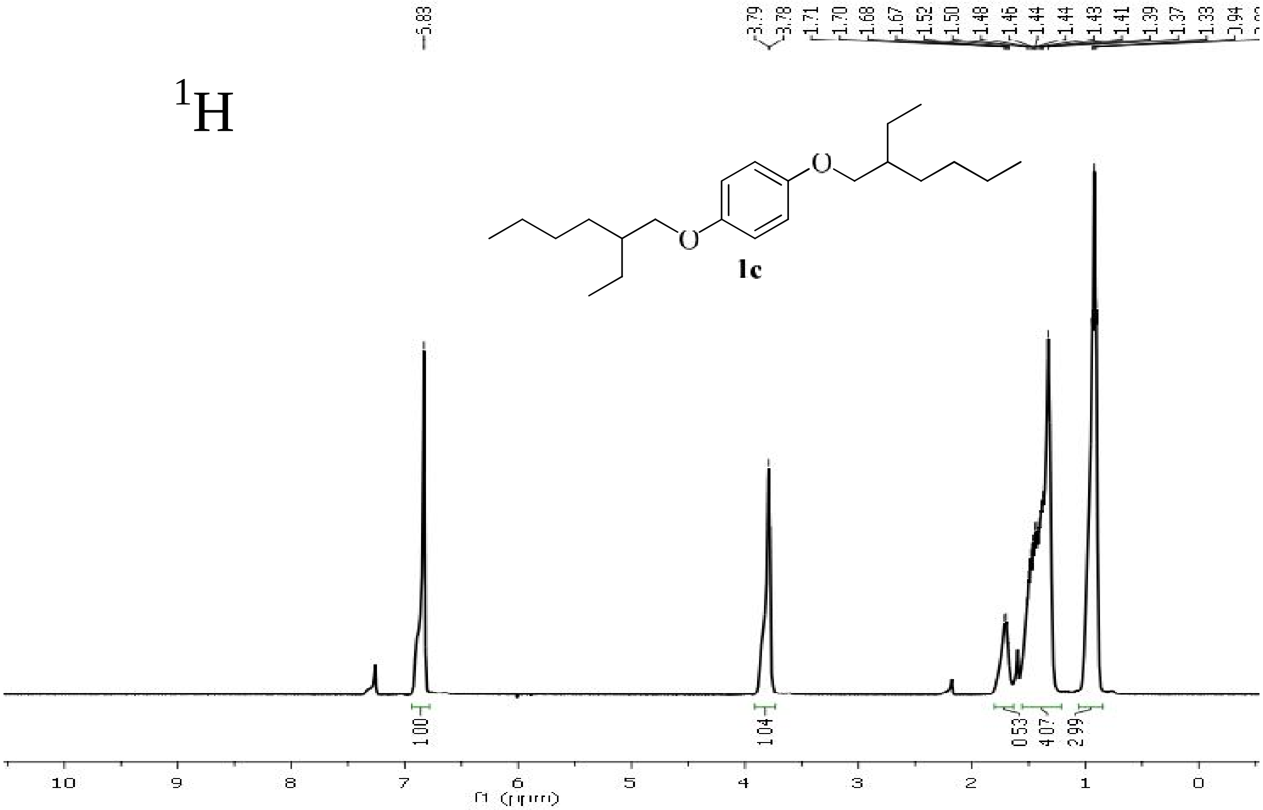
20
10
0
f1 (ppm)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1.50
1.48
1.46
1.44
1.44
1.43
1.41
1.39
1.37
1.33
0.94
1.00
1.04
0.53
4.07
2.99
10
9
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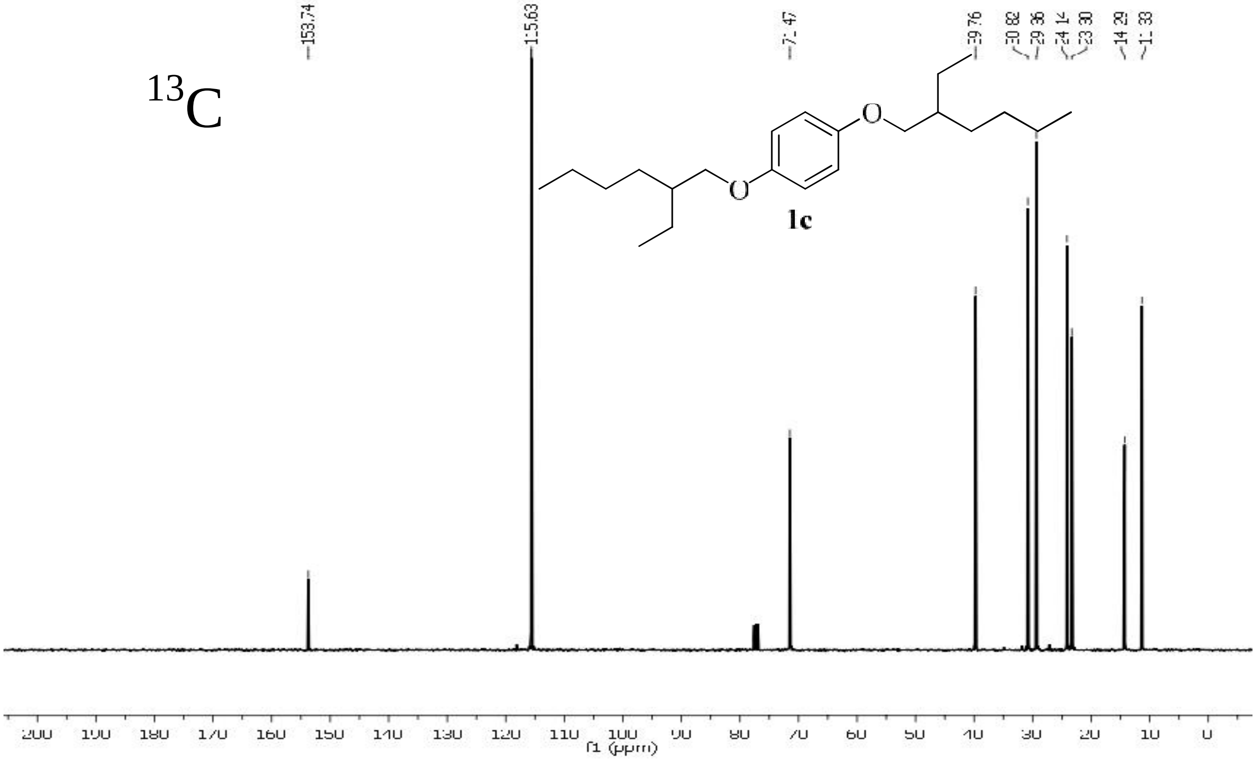
7
6
5
4
3
2
1
0
f1 (ppm)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14.29
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200
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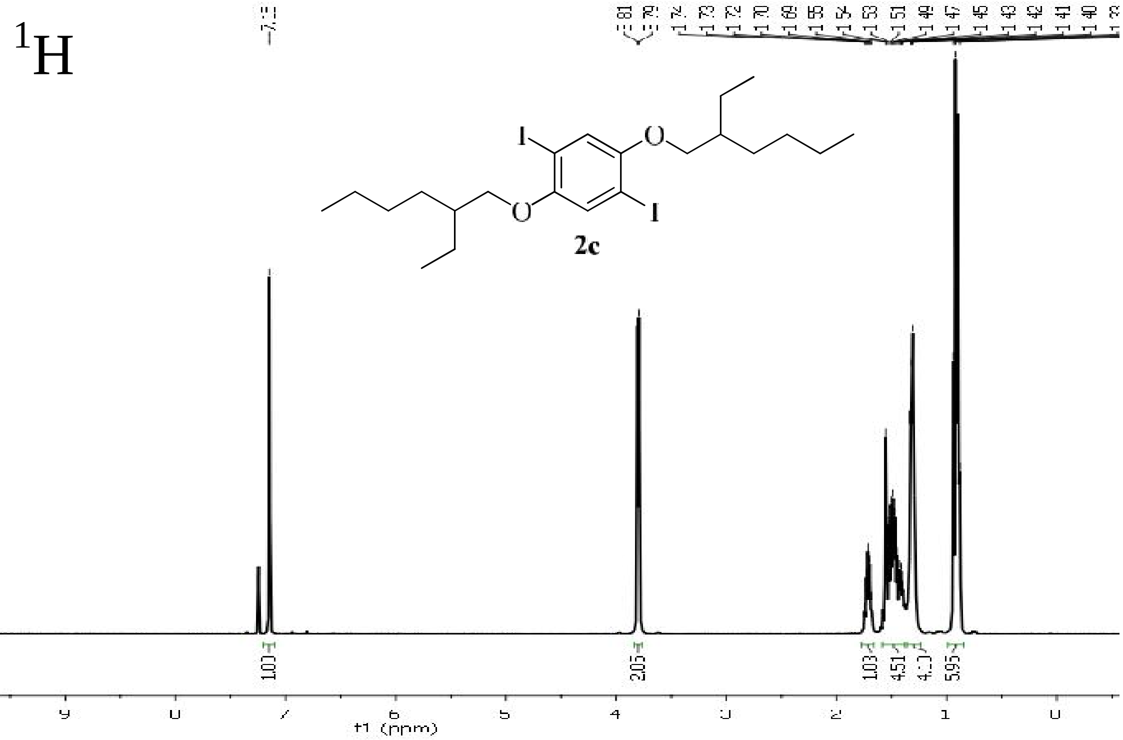
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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1.70
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1.55
1.54
1.53
1.51
1.49
1.47
1.45
1.43
1.42
1.41
1.40
I
O
I
O
2c
1.00
2.05
1.03
4.51
4.50
5.95
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

13C
152.39
121.39
85.60
71.85
33.93
30.03
23.57
23.43
22.54
13.63
10.75
I
O
I
O
2c
200
190
180
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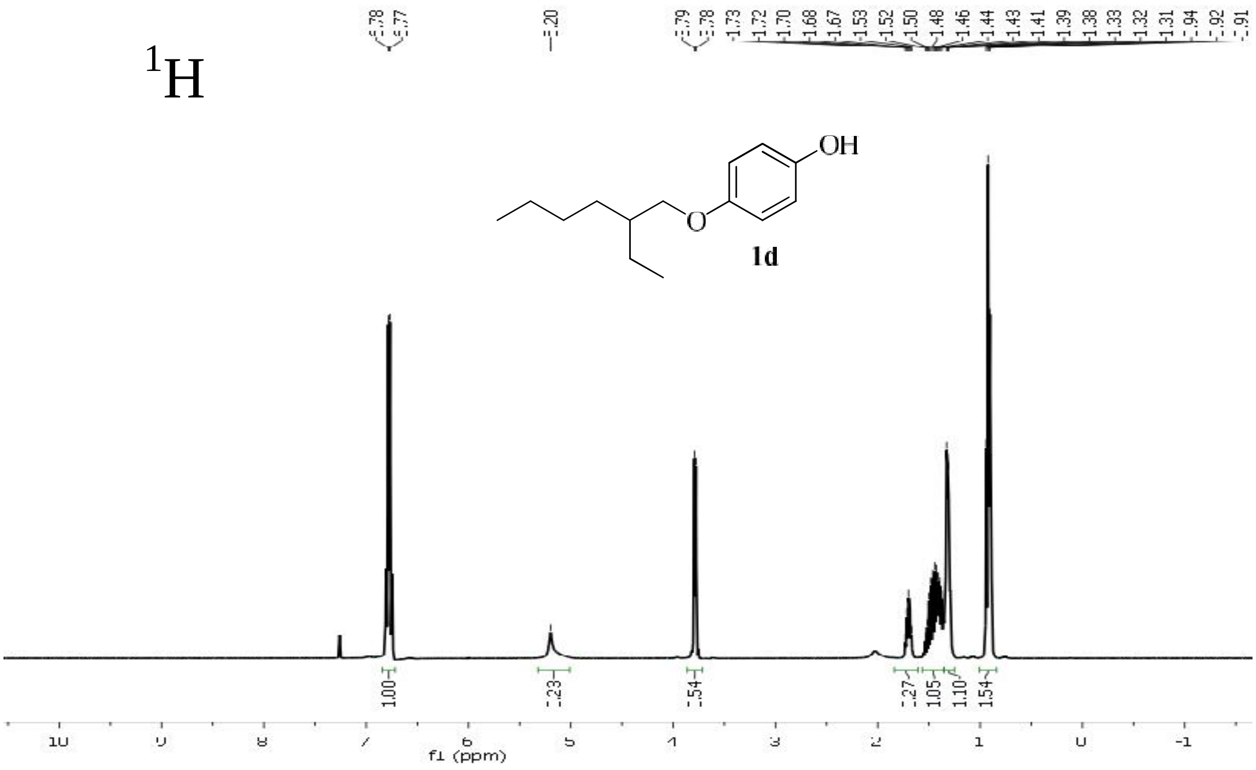
0
f1 (ppm)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1.50
1.48
1.46
1.44
1.43
1.41
1.39
1.38
1.33
1.32
1.31
0.94
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0.91
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O
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0.54
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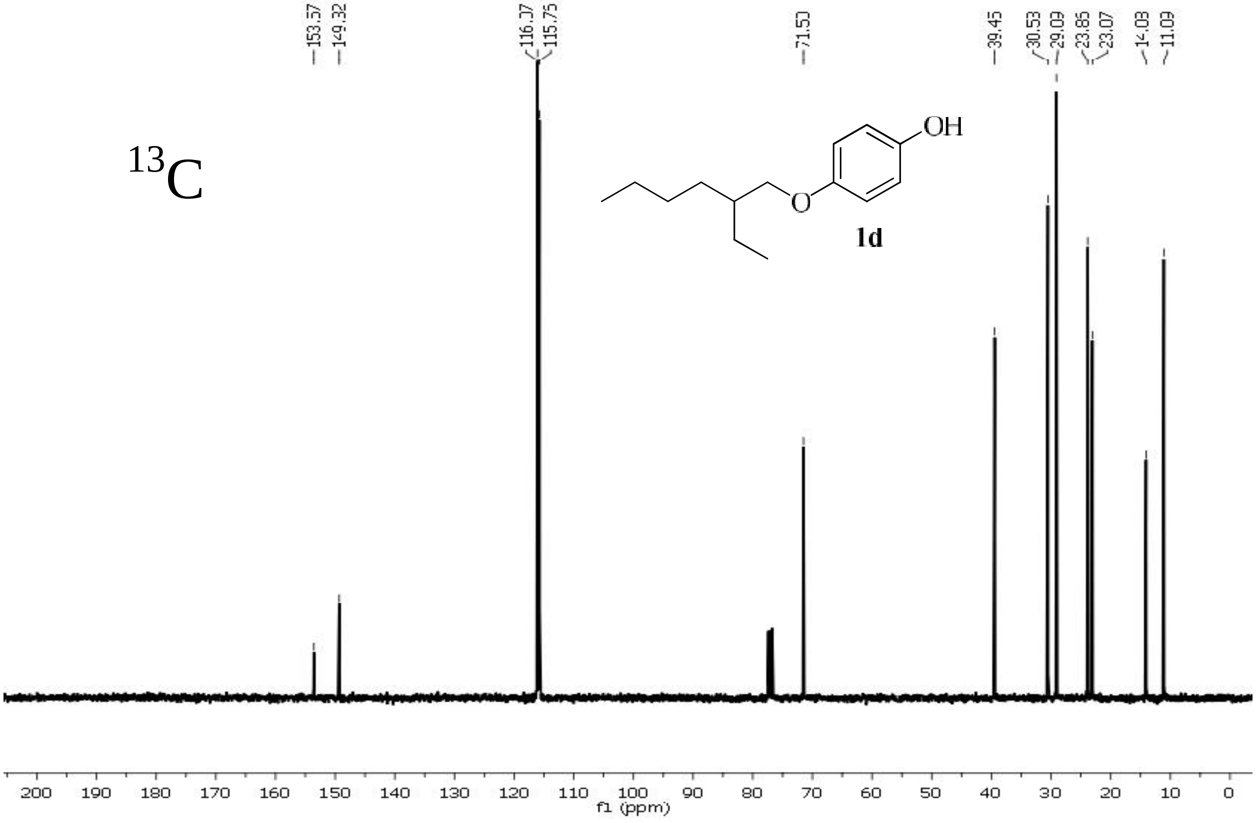
0
-1
f1 (ppm)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11.09
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O
1d
200
190
180
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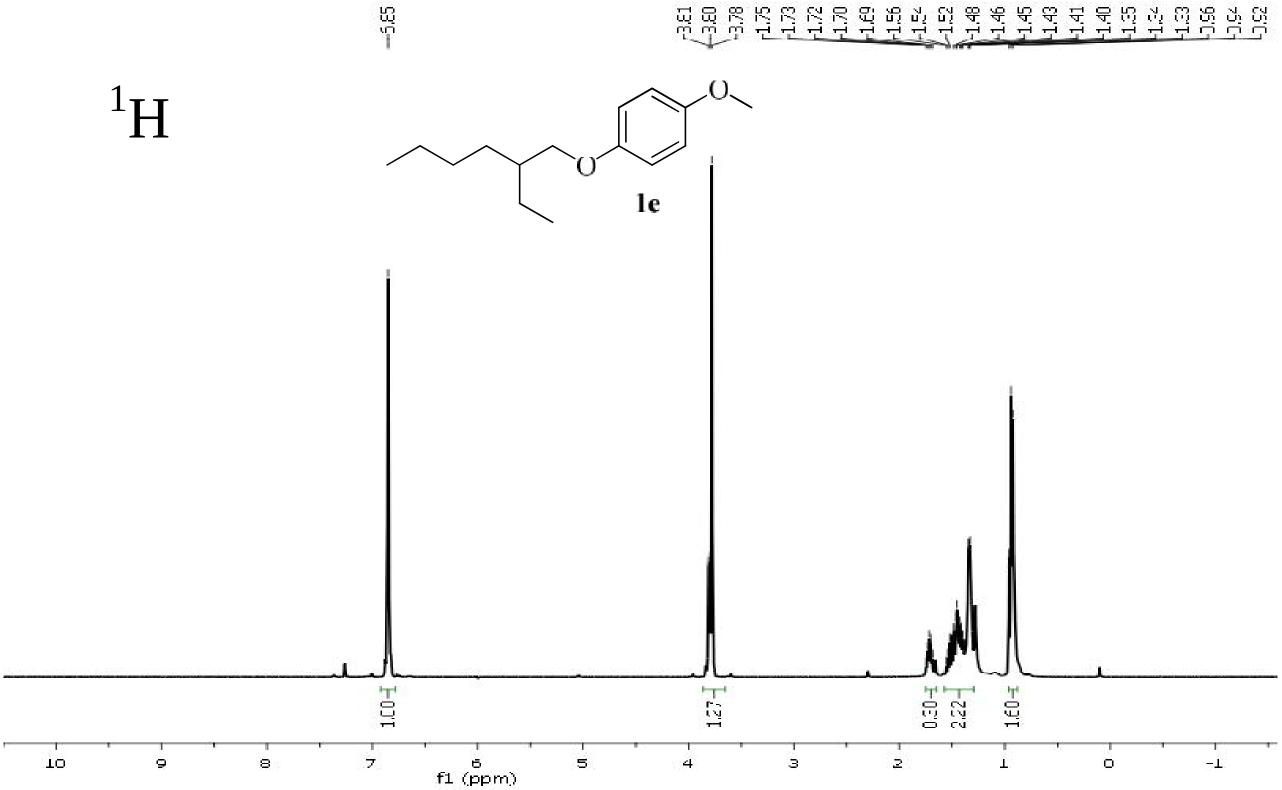
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1.34
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0.96
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3
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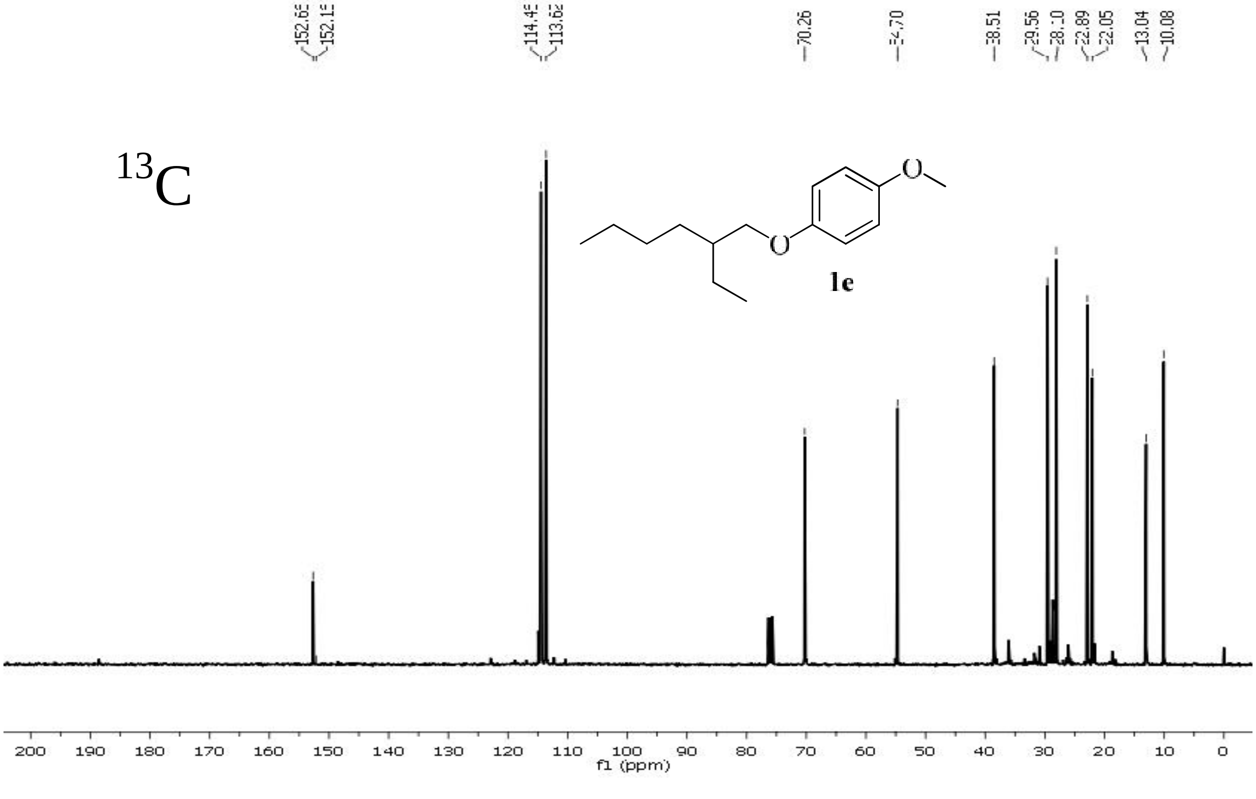
f1 (ppm)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200
190
180
170
160
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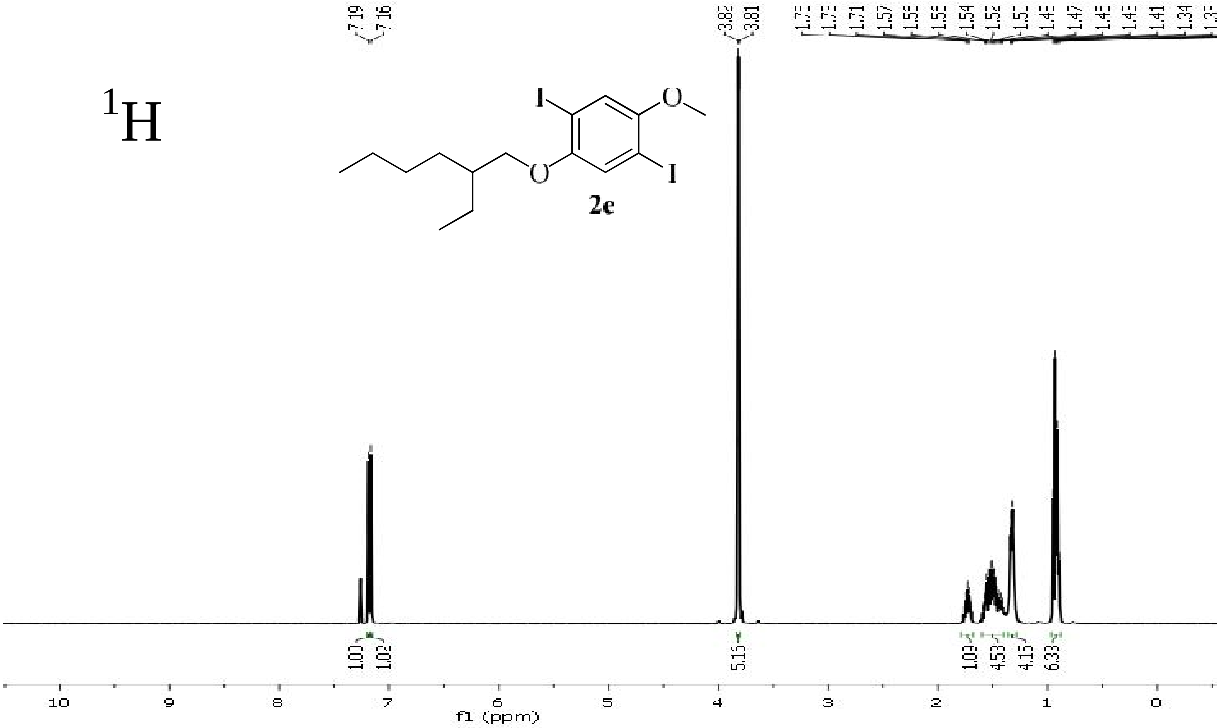
f1 (ppm)

^{1}H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1.02
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1.09
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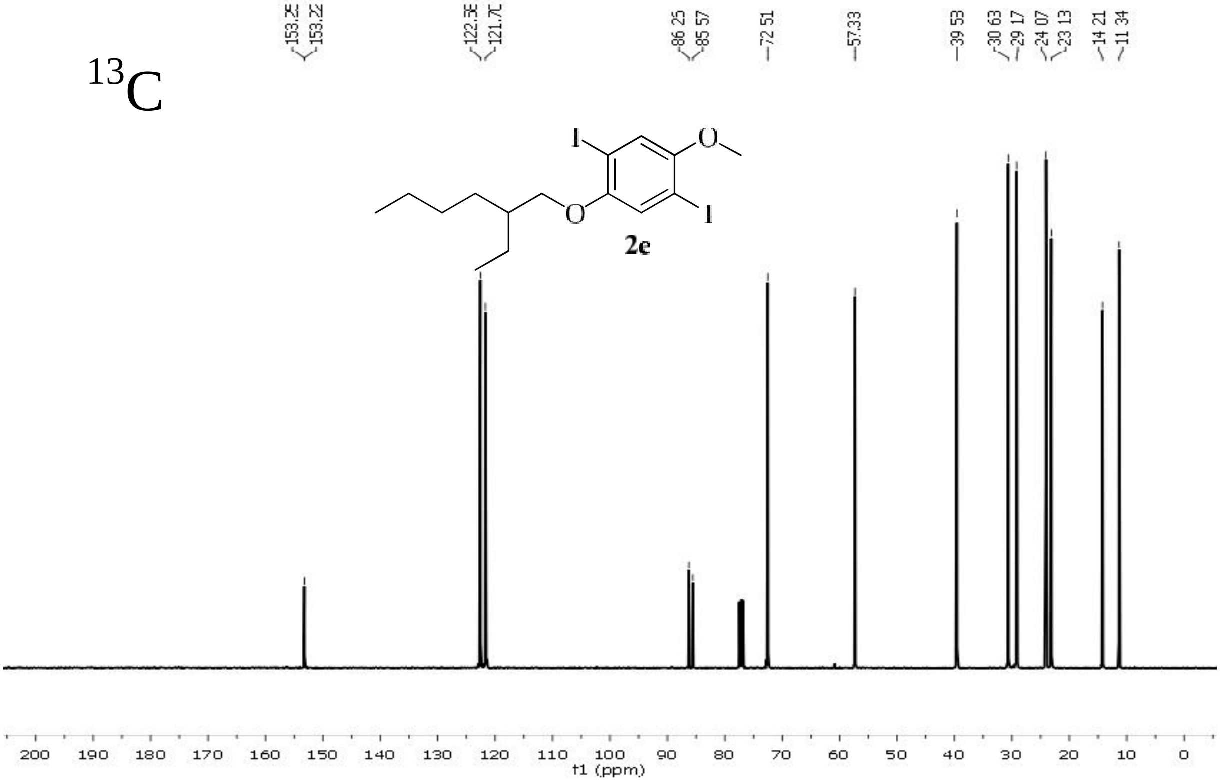
f1 (ppm)

^{13}C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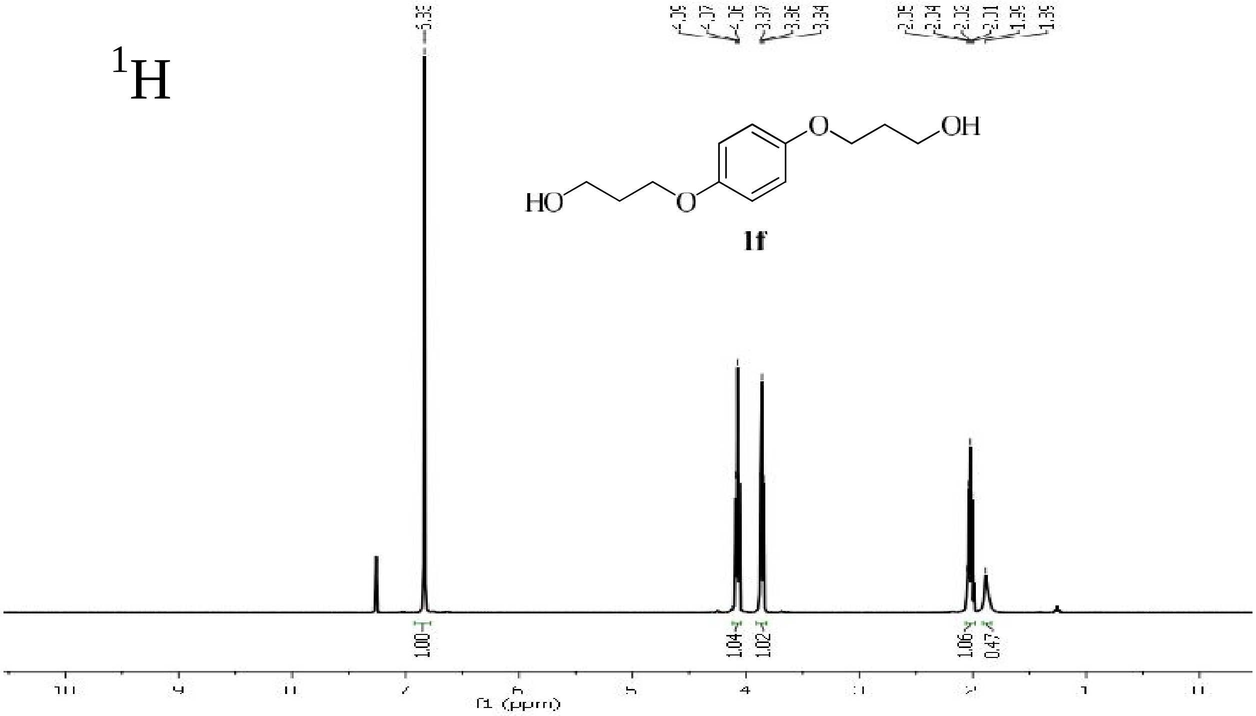
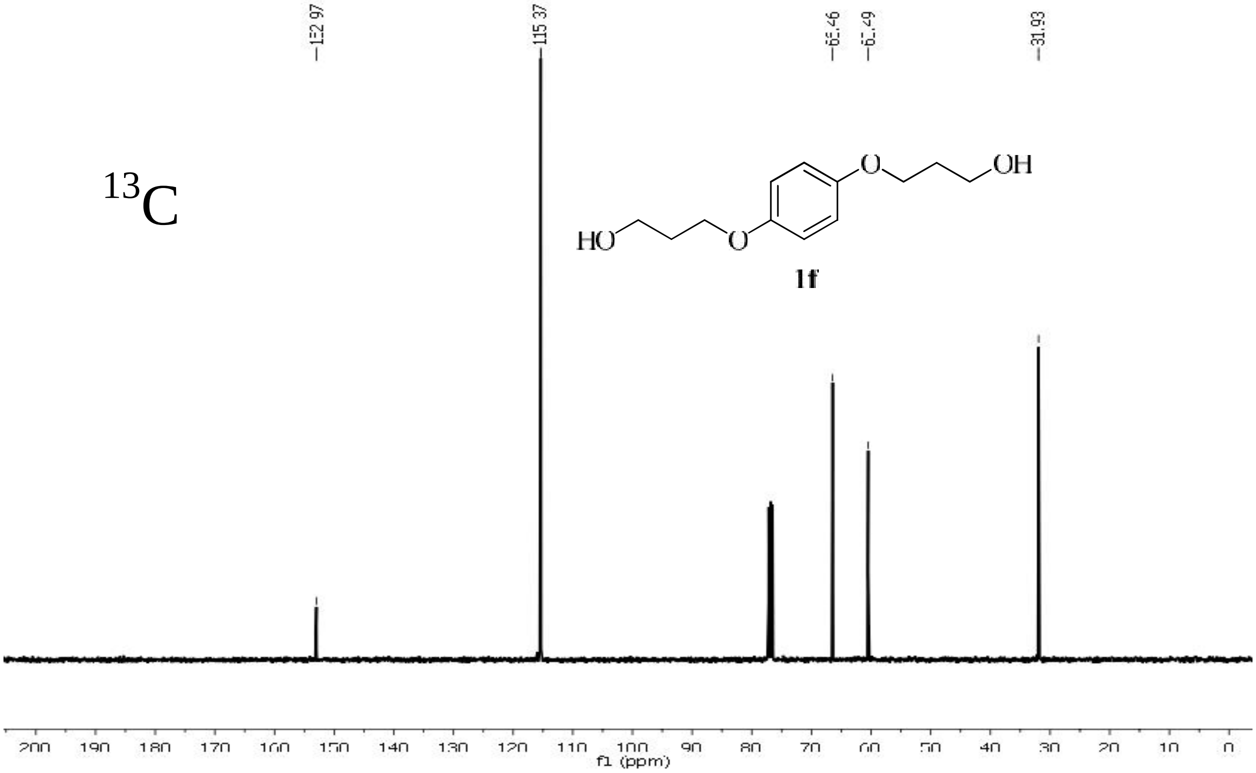
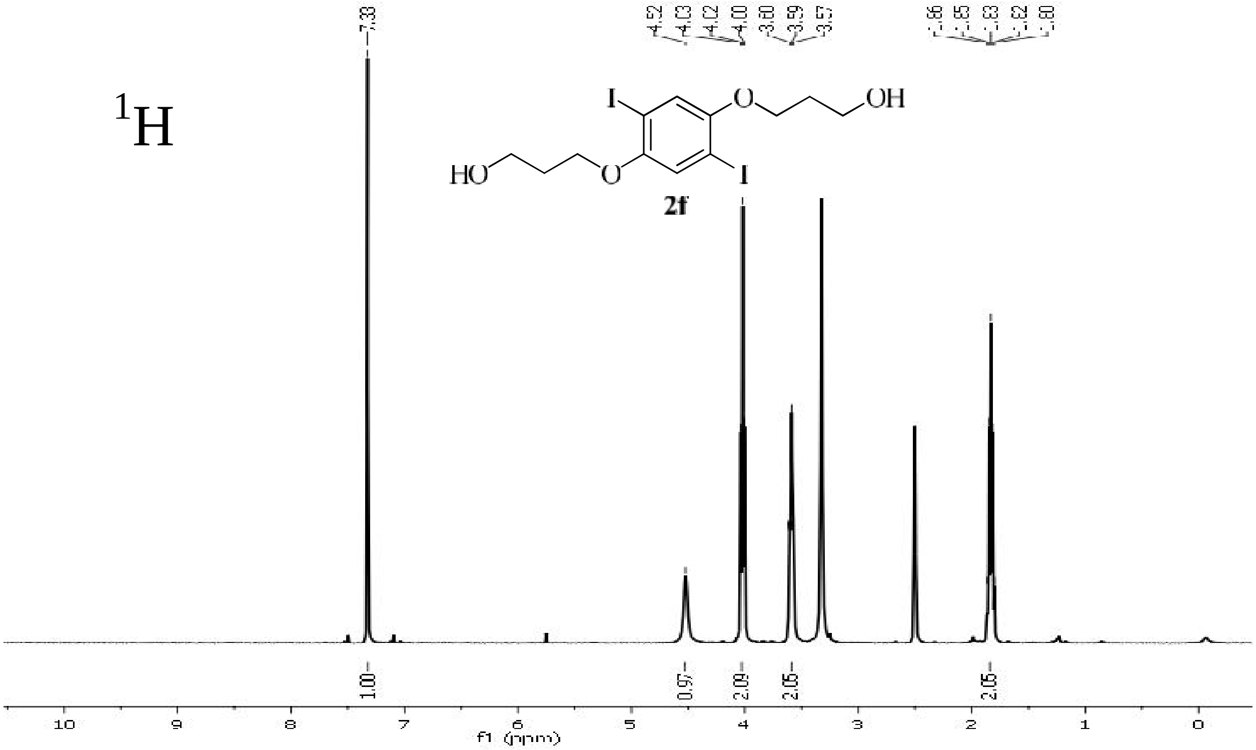
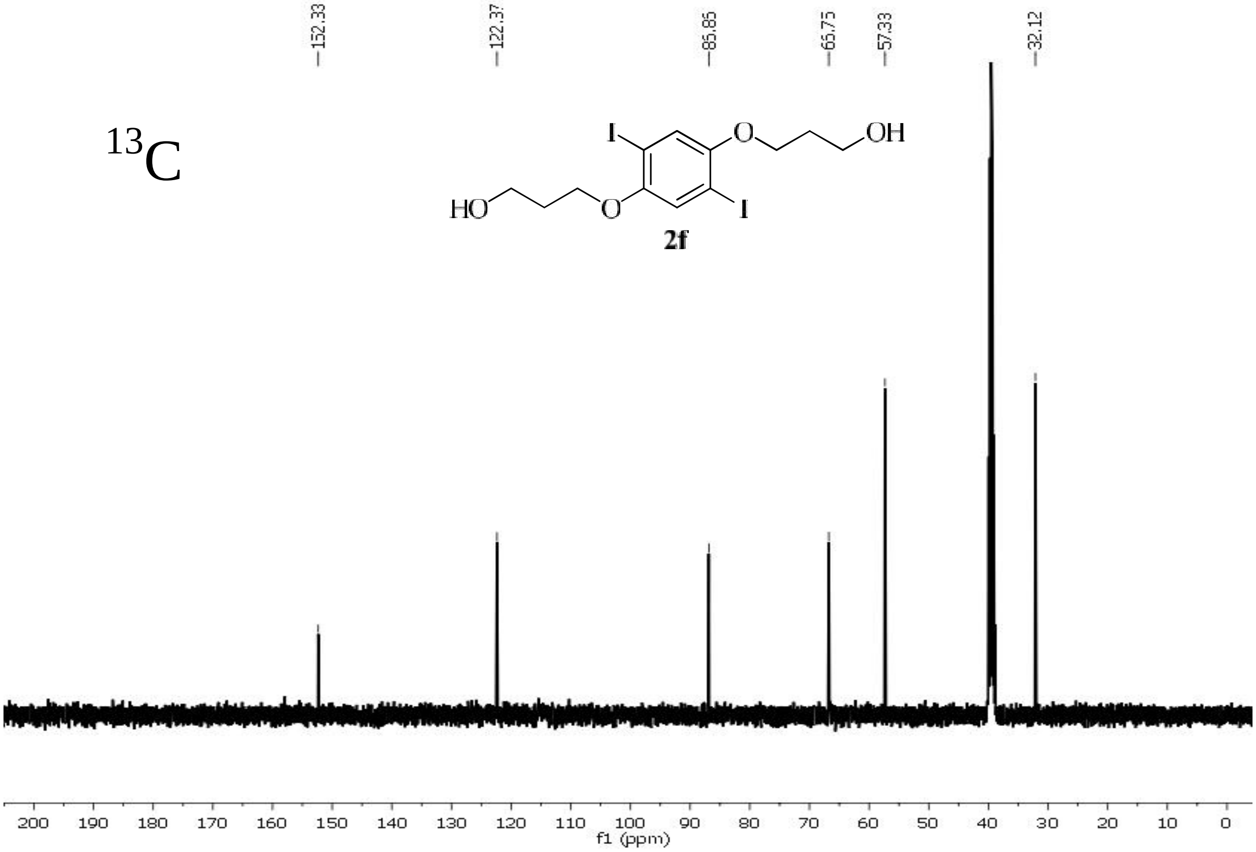
f1 (ppm)


1H
6.83
4.09
4.07
4.06
3.87
3.86
3.84
2.05
2.04
2.02
2.01
1.89
1.89
HO
O
O
OH
1f
1.00
1.04
1.02
1.06
0.47
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

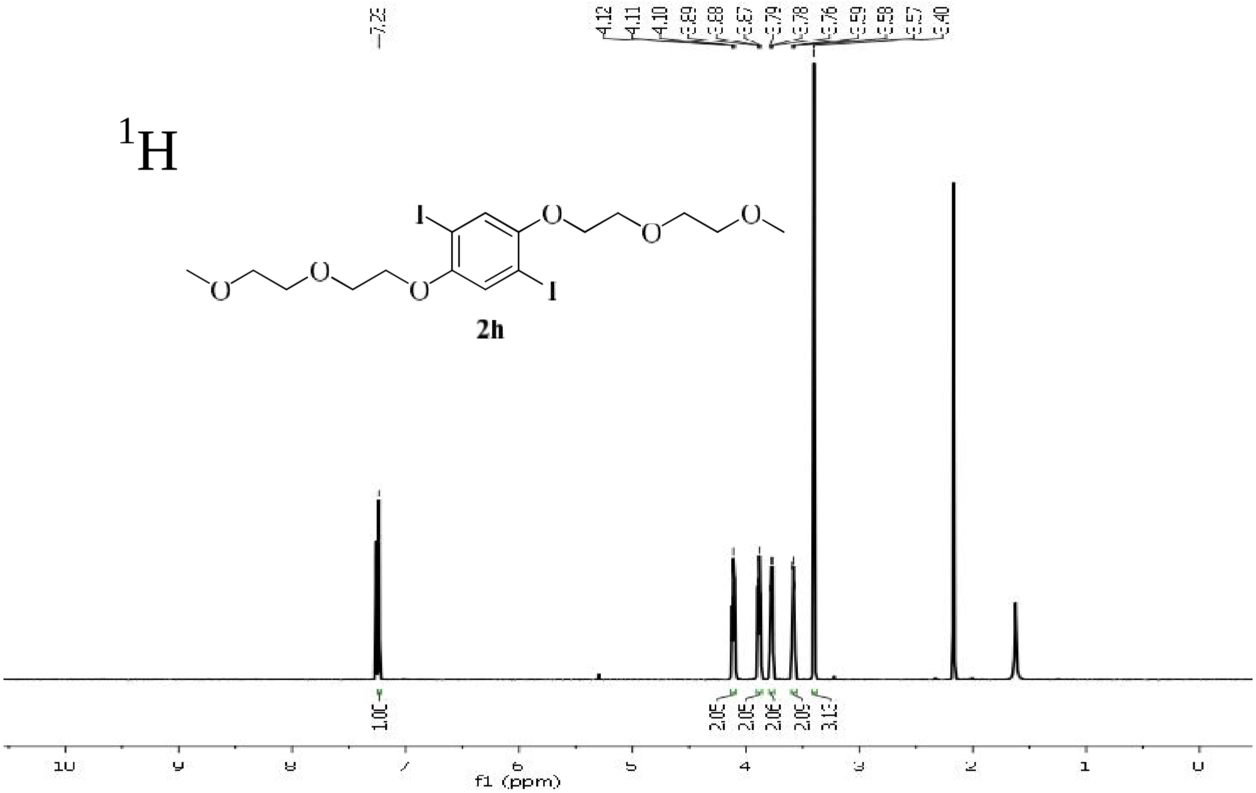

13C
152.97
115.37
66.46
60.49
31.93
HO
O
O
OH
1f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

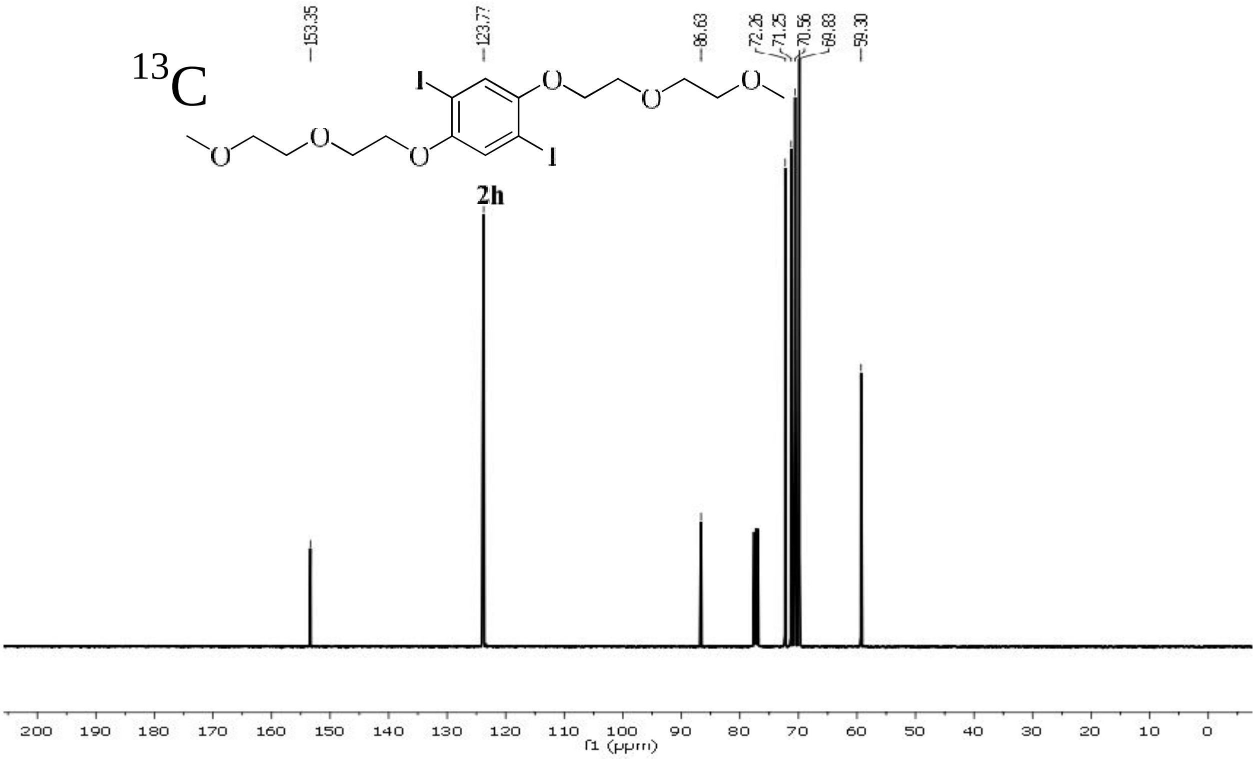


1H
7.33
4.52
4.03
4.02
4.00
3.60
3.59
3.57
1.86
1.85
1.83
1.82
1.80
I
O
OH
HO
O
I
2f
1.00
0.97
2.09
2.05
2.05
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

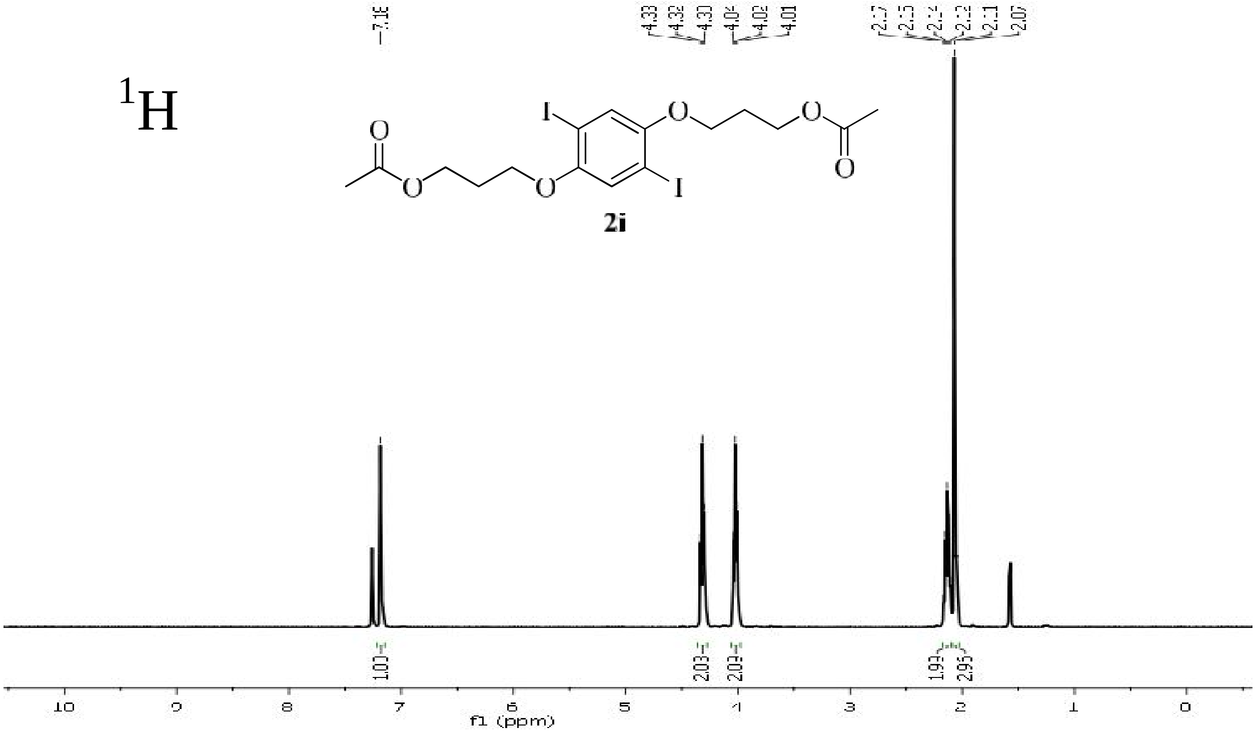


13C
152.33
122.37
85.85
65.75
57.33
32.12
I
O
OH
HO
O
I
2f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H
7.25
4.12
4.11
4.10
3.89
3.88
3.87
3.79
3.78
3.76
3.59
3.58
3.57
3.40
I
O
O
O
O
O
O
I
2h
1.00
2.05
2.05
2.06
2.09
3.13
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

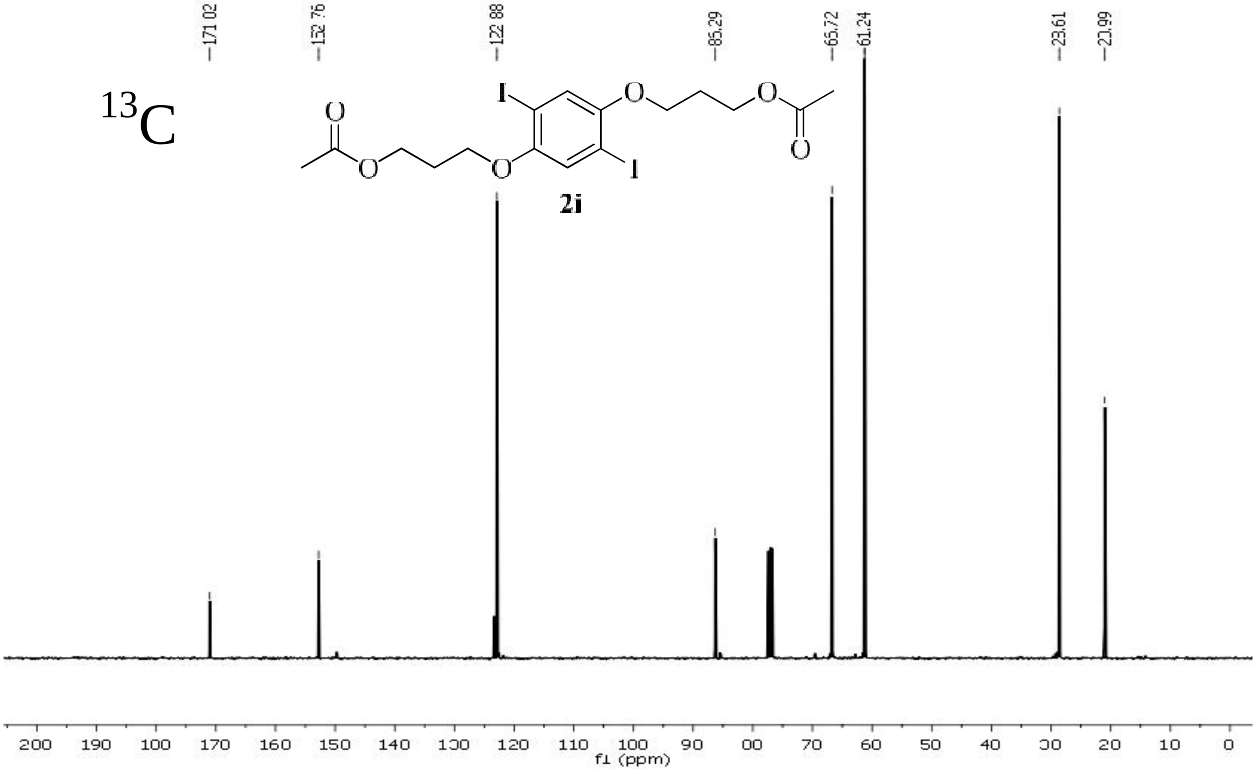

13C
153.35
123.77
86.63
72.26
71.25
70.56
69.83
59.30
I
O
O
O
O
O
O
I
2h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H

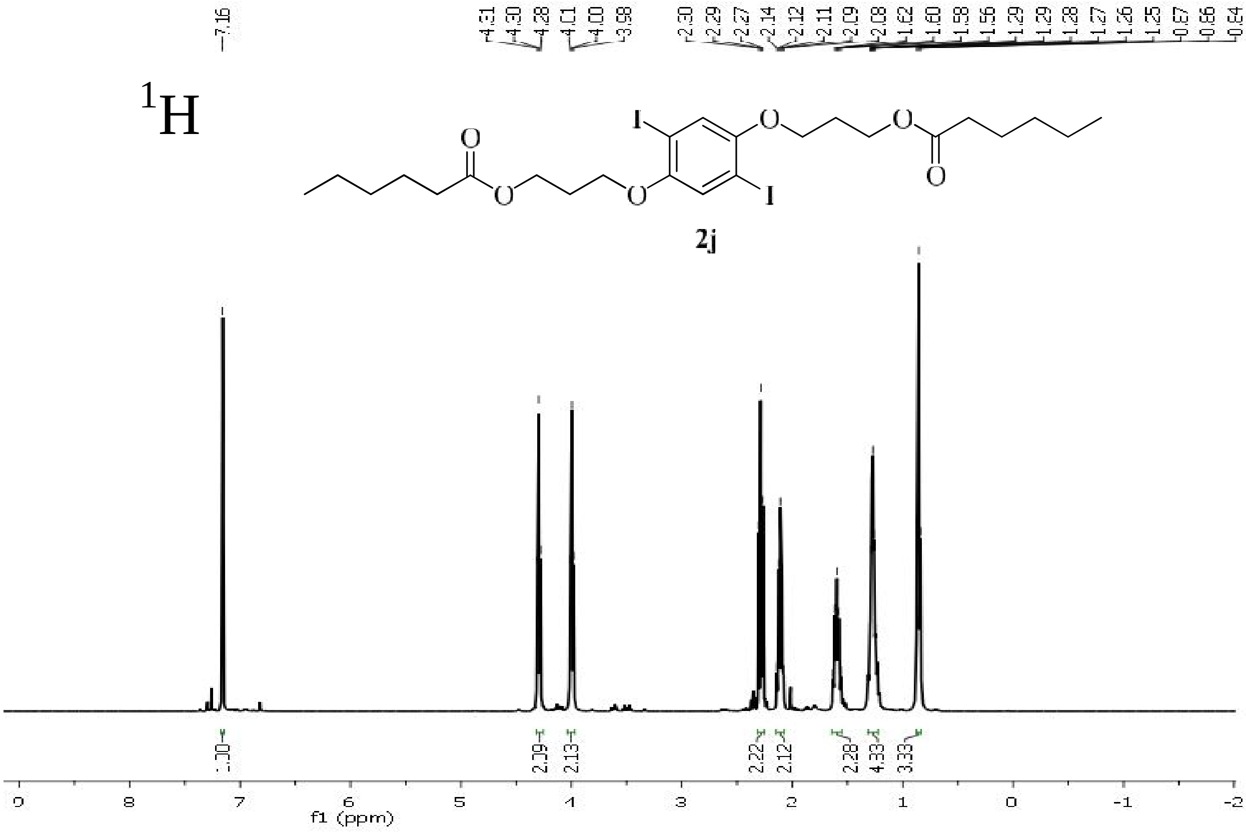


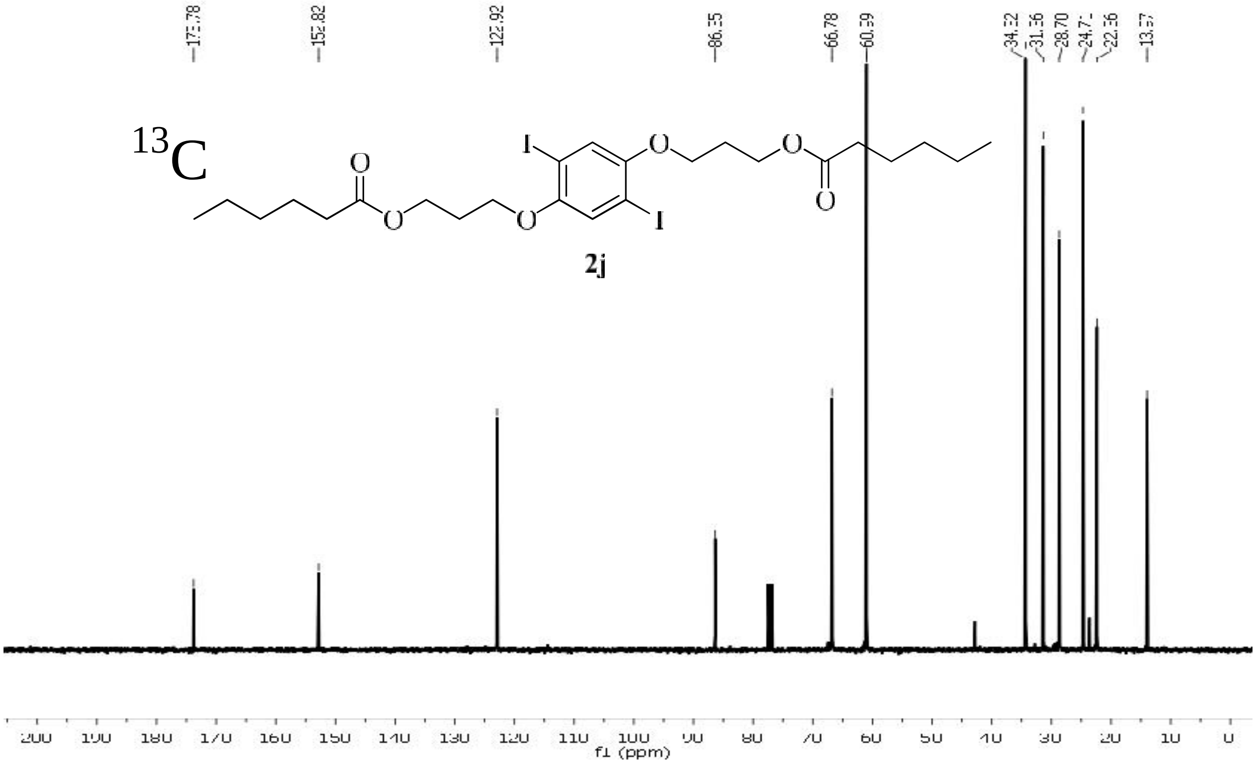
7.16
4.33
4.32
4.30
4.04
4.02
4.01
2.17
2.15
2.14
2.12
2.11
2.07
I
O
O
O
O
O
O
I
2i
1.00
2.03
2.04
1.93
2.95
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

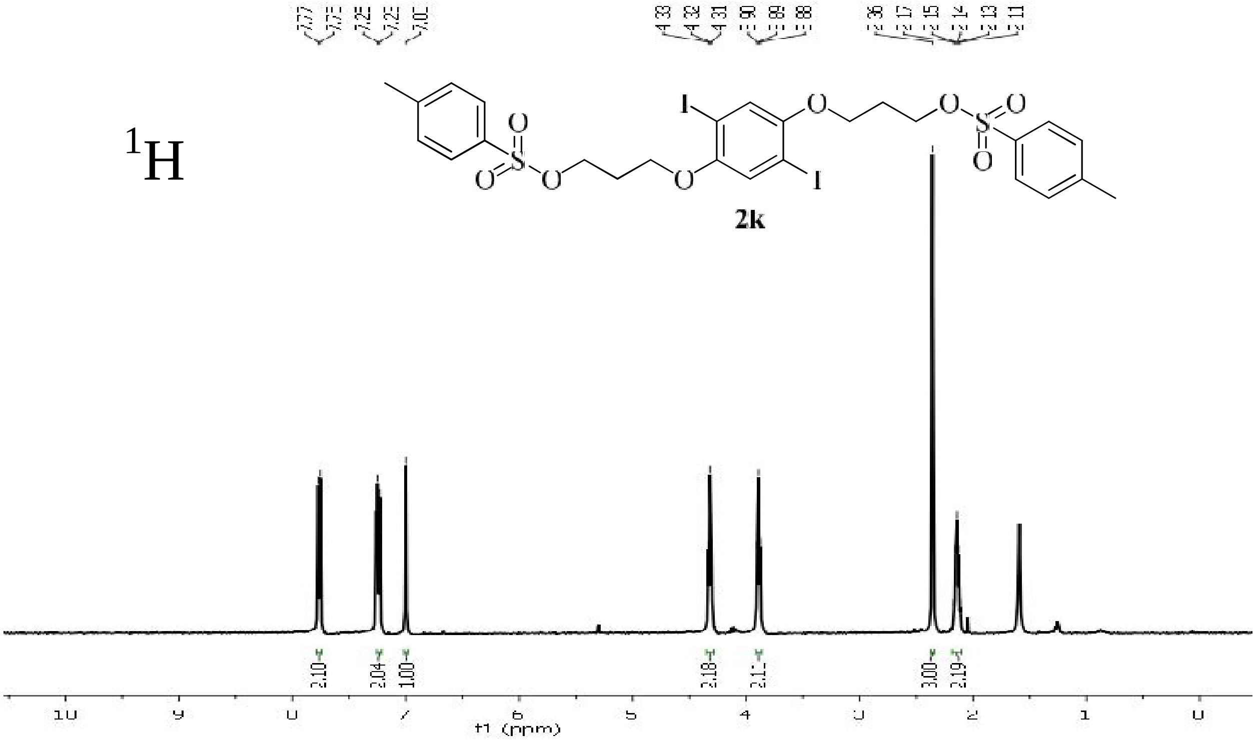
^{13}C

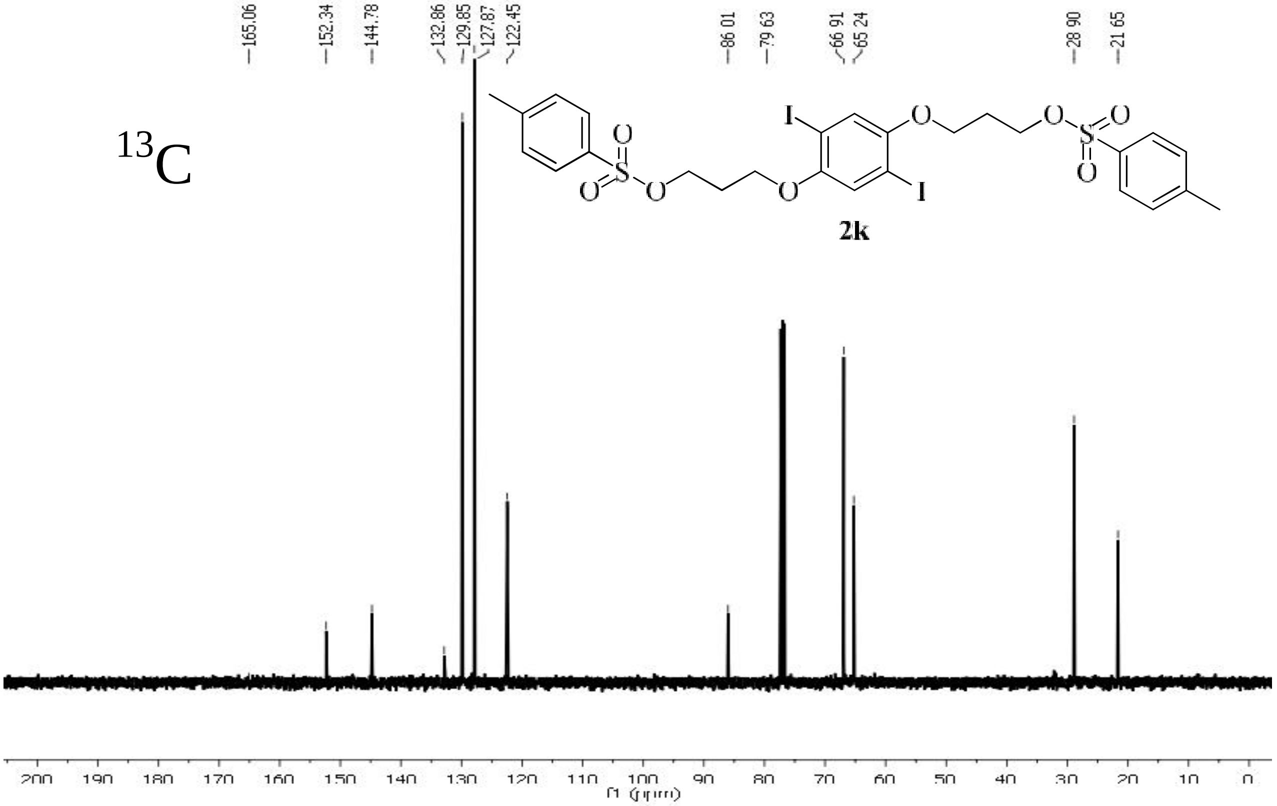


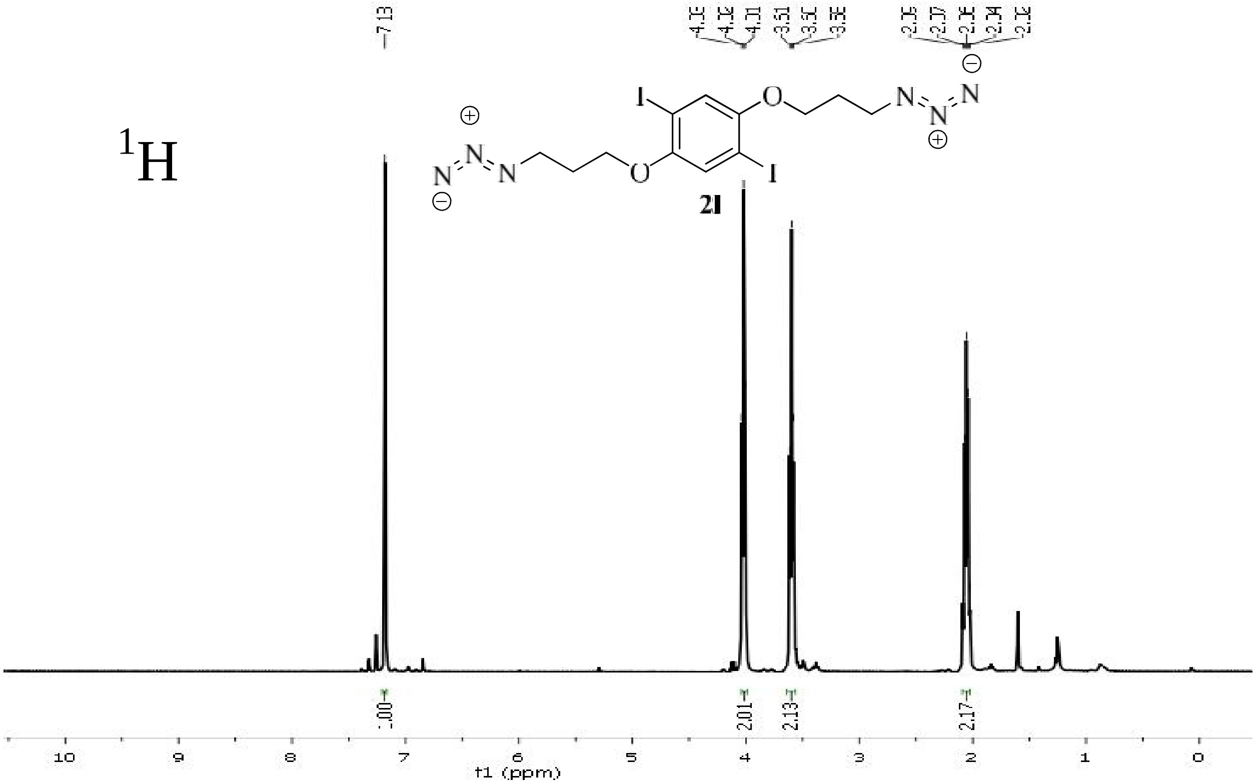
171.02
152.76
122.88
85.29
65.72
61.24
28.61
20.99
I
O
O
O
O
O
O
I
2i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

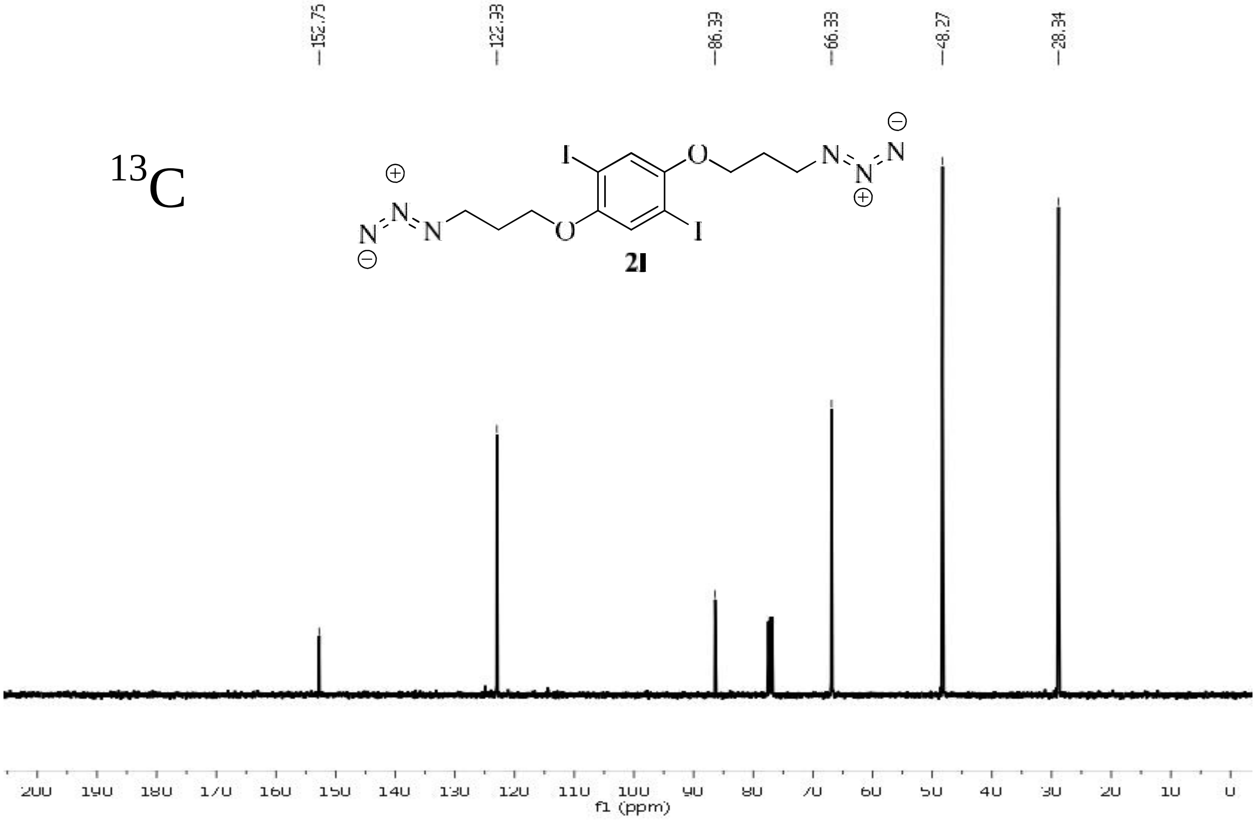

7.16
4.31
4.30
4.28
4.01
4.00
3.98
2.30
2.29
2.27
2.14
2.12
2.11
2.09
2.08
1.62
1.60
1.58
1.56
1.29
1.29
1.28
1.27
1.26
1.25
0.87
0.86
0.84
^{1}H
I
O
O
O
O
I
O
O
2j
1.00
2.09
2.13
2.22
2.12
2.28
4.33
3.33
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

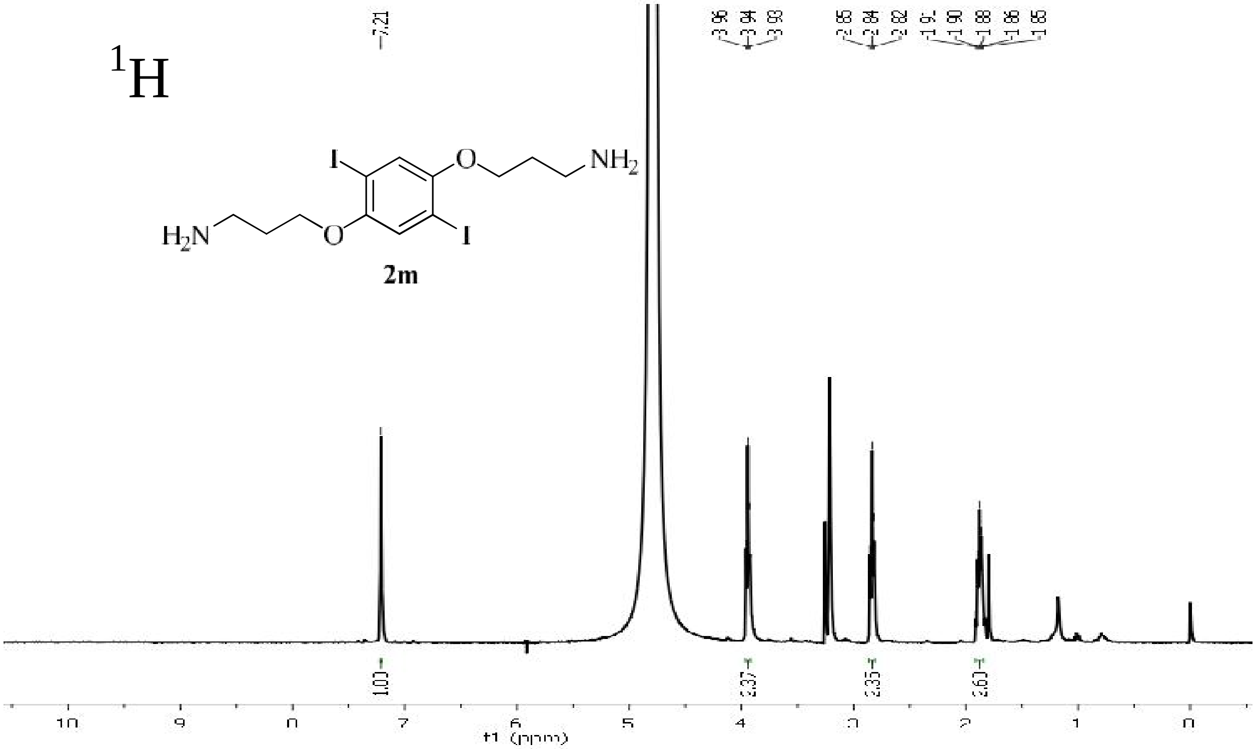

173.78
152.82
122.92
86.35
66.78
60.39
34.32
31.36
28.70
24.7
22.36
13.57
^{13}C
I
O
O
O
O
I
O
O
2j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H
7.77
7.75
7.25
7.23
7.03
4.33
4.32
4.31
3.90
3.89
3.88
2.36
2.17
2.15
2.14
2.13
2.11
I
O
O
S
O
O
O
O
S
O
O
I
2k
2.10
2.04
1.00
2.18
2.11
3.00
2.19
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

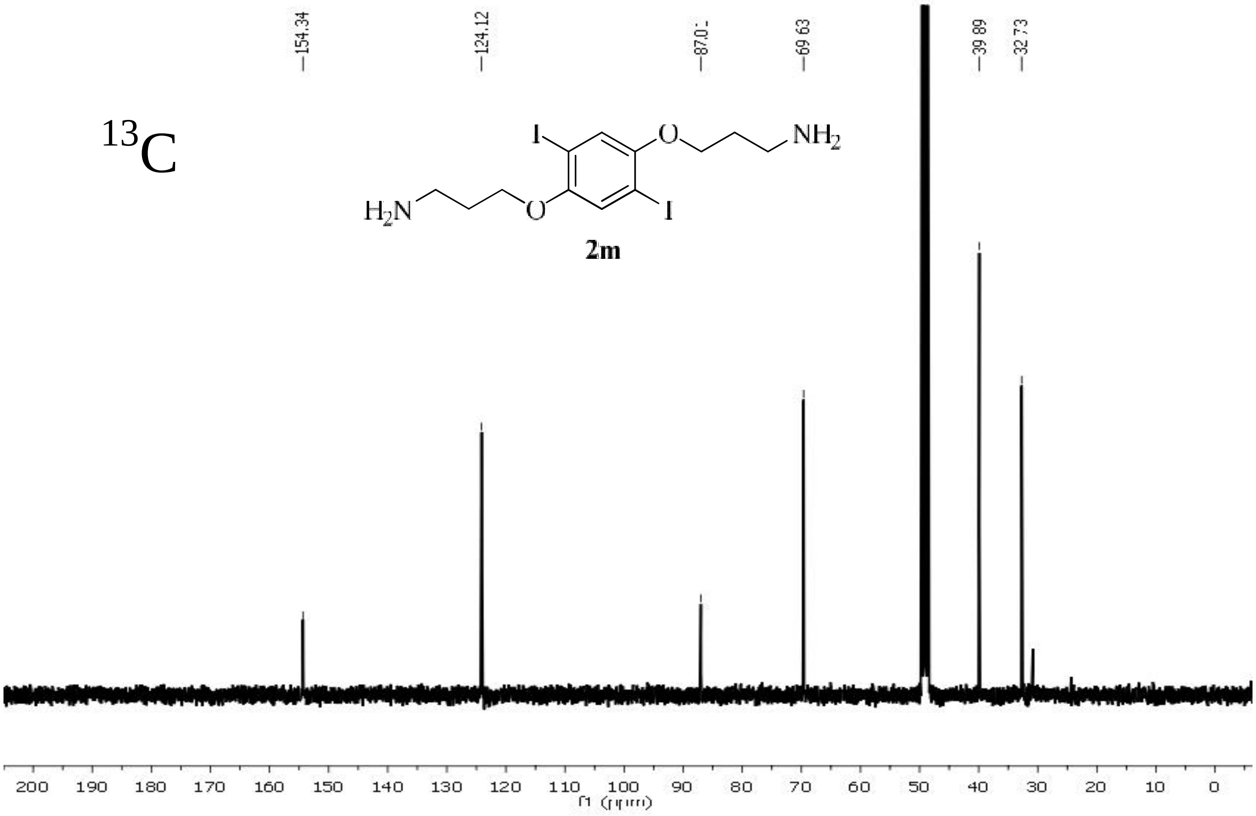

13C
165.06
152.34
144.78
132.86
129.85
127.87
122.45
86.01
79.63
66.91
65.24
28.90
21.65
I
O
O
S
O
O
O
O
S
O
O
I
2k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H
7.13
4.03
4.02
4.01
3.59
3.58
3.56
2.08
2.07
2.06
2.04
2.03
I
O
N
N
N
2l
1.00
2.01
2.13
2.17
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


152.75
122.33
86.39
66.33
48.27
28.34
13C
I
O
N
N
N
2l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

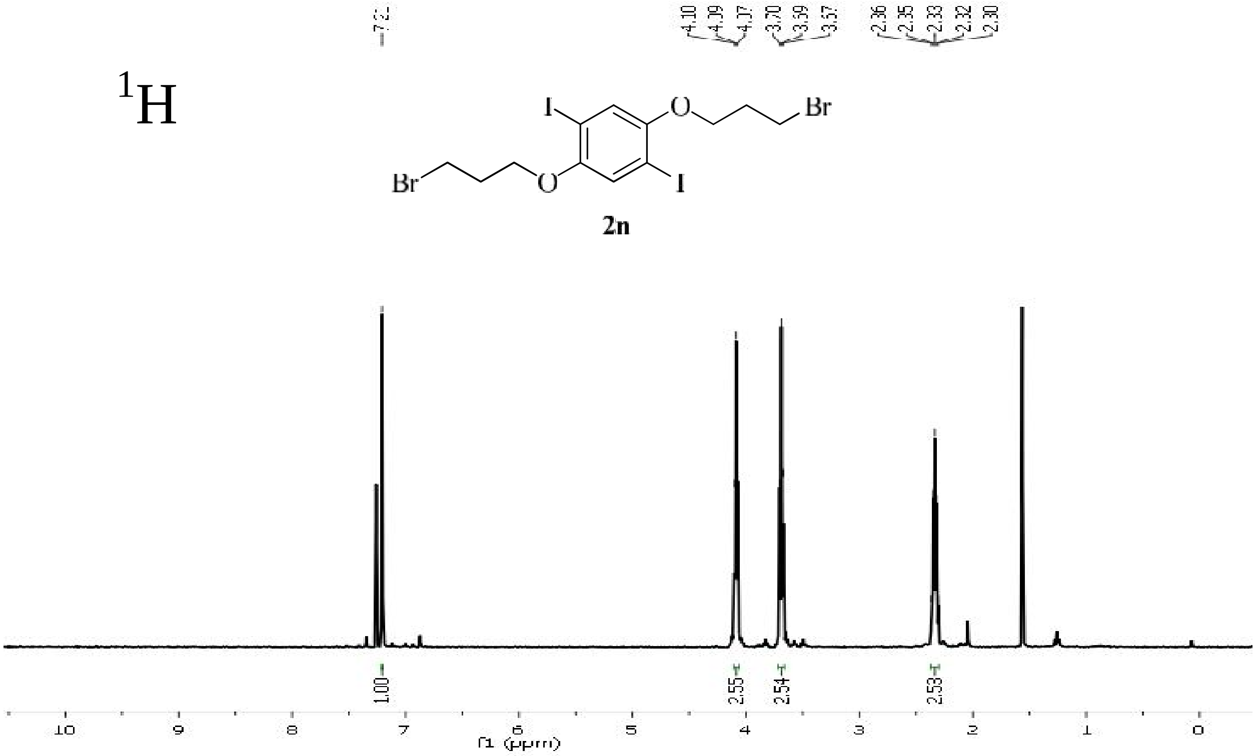


1H
7.21
3.96
3.94
3.93
2.85
2.84
2.82
1.91
1.90
1.88
1.86
1.85
I
O
NH2
H2N
O
I
2m
1.00
2.37
2.35
2.60
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)



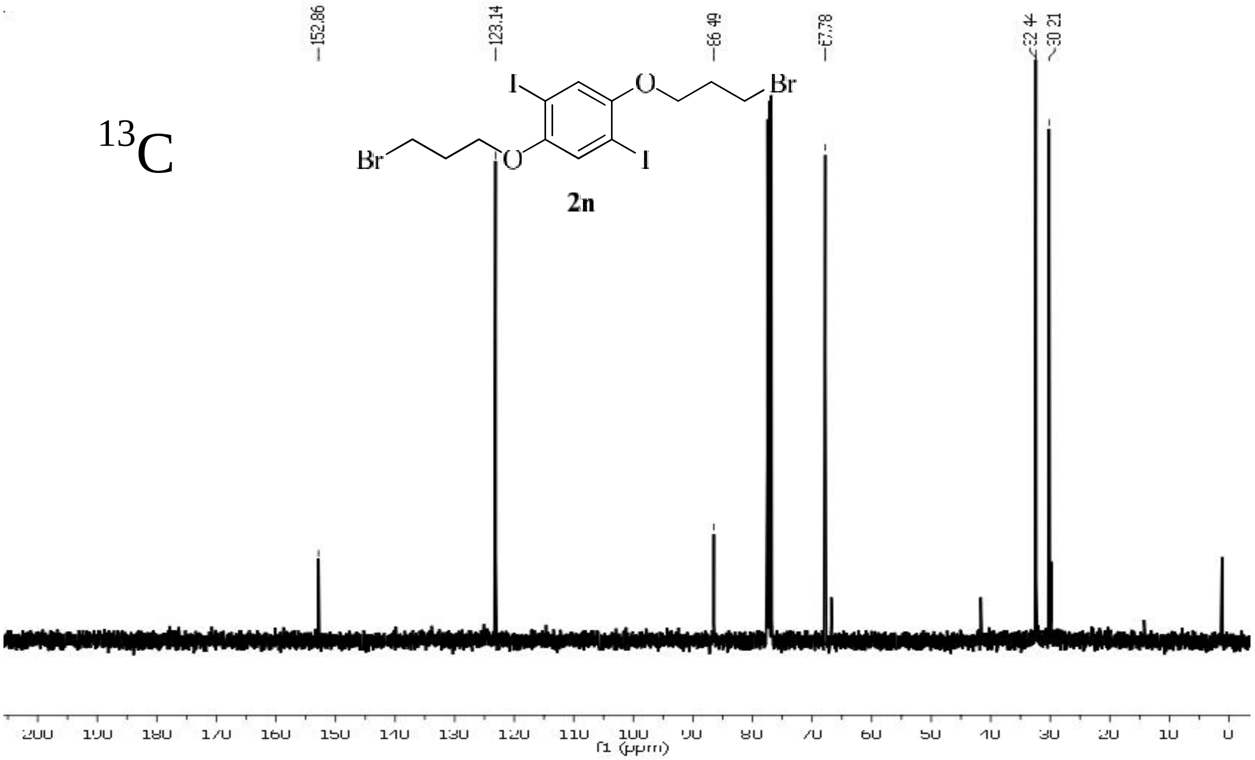
13C
154.34
124.12
87.01
69.63
39.89
32.73
I
O
NH2
H2N
O
I
2m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H

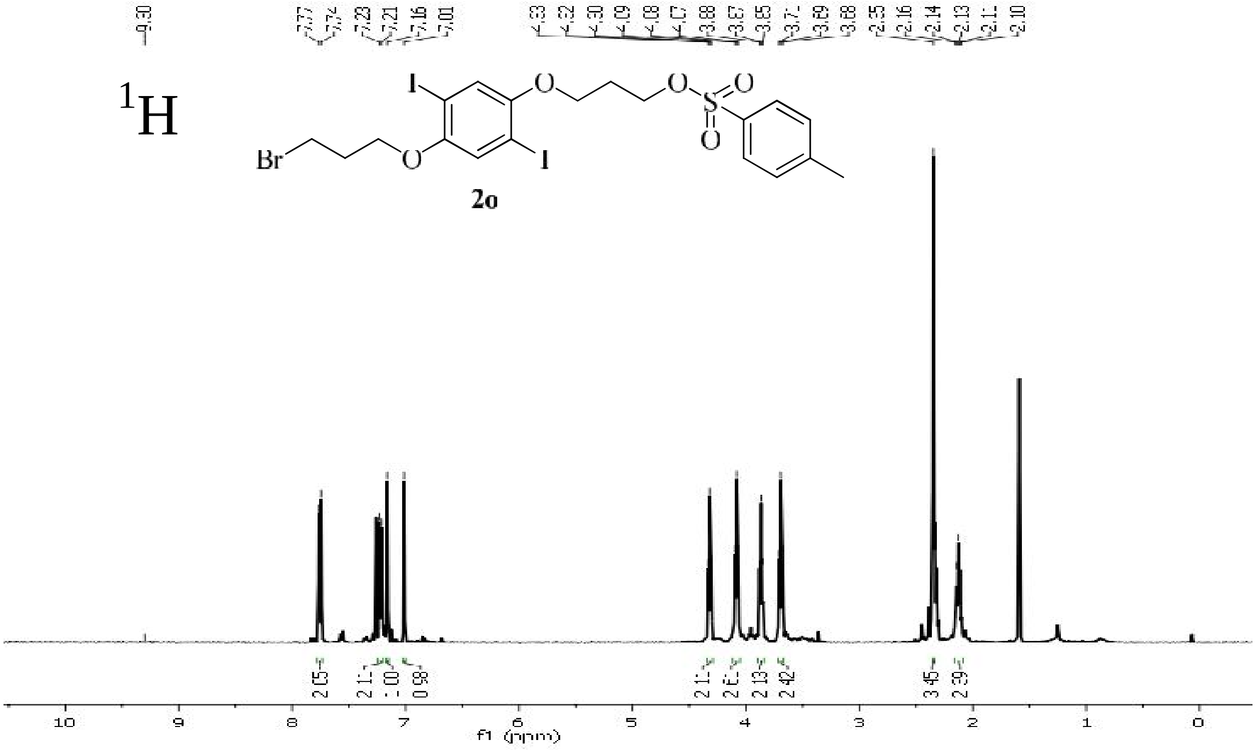

2n

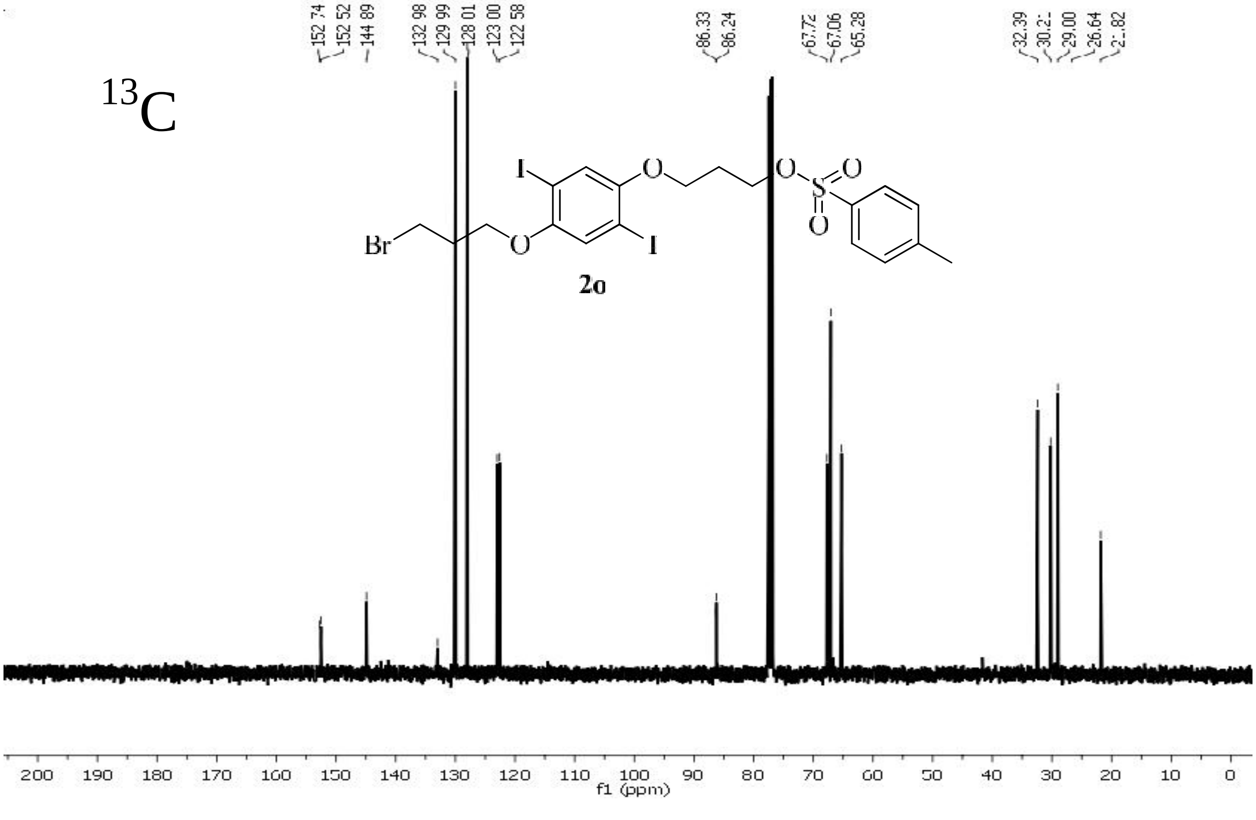
7.21
4.10
4.09
4.07
3.70
3.69
3.67
2.36
2.35
2.33
2.32
2.30
I
O
Br
Br
O
I
1.00
2.55
2.54
2.53
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

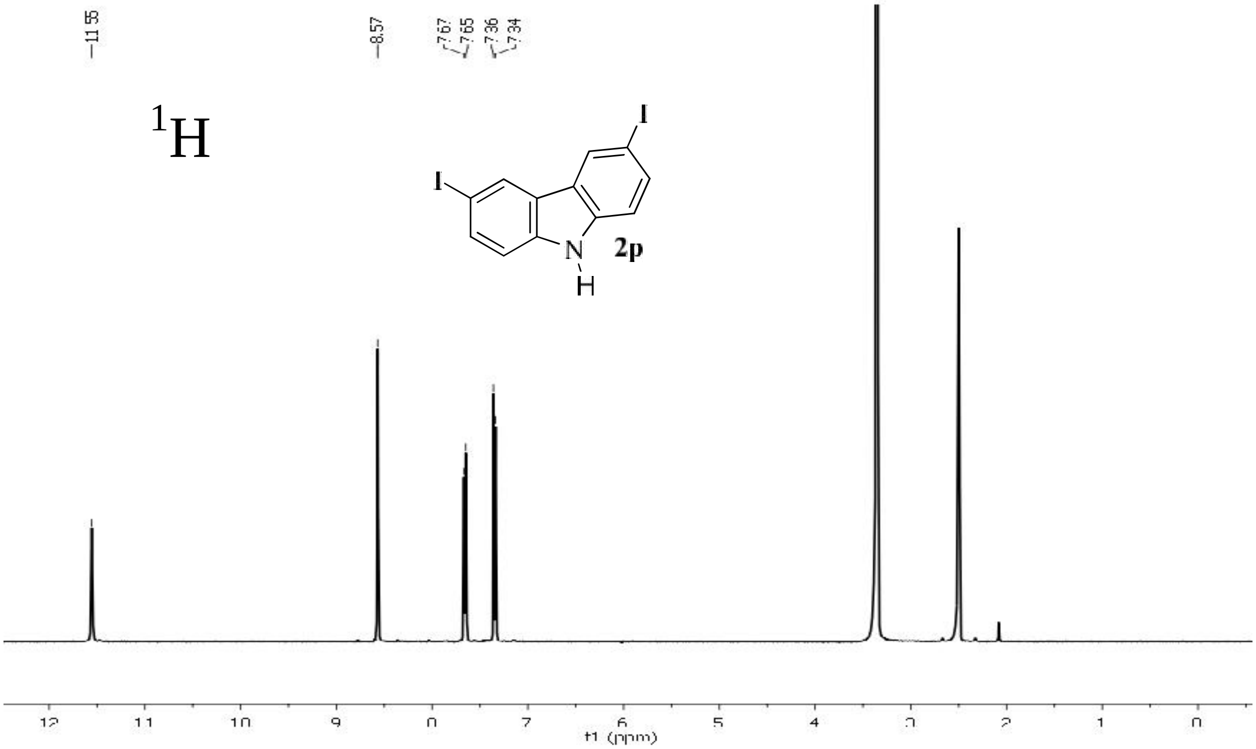
^{13}C

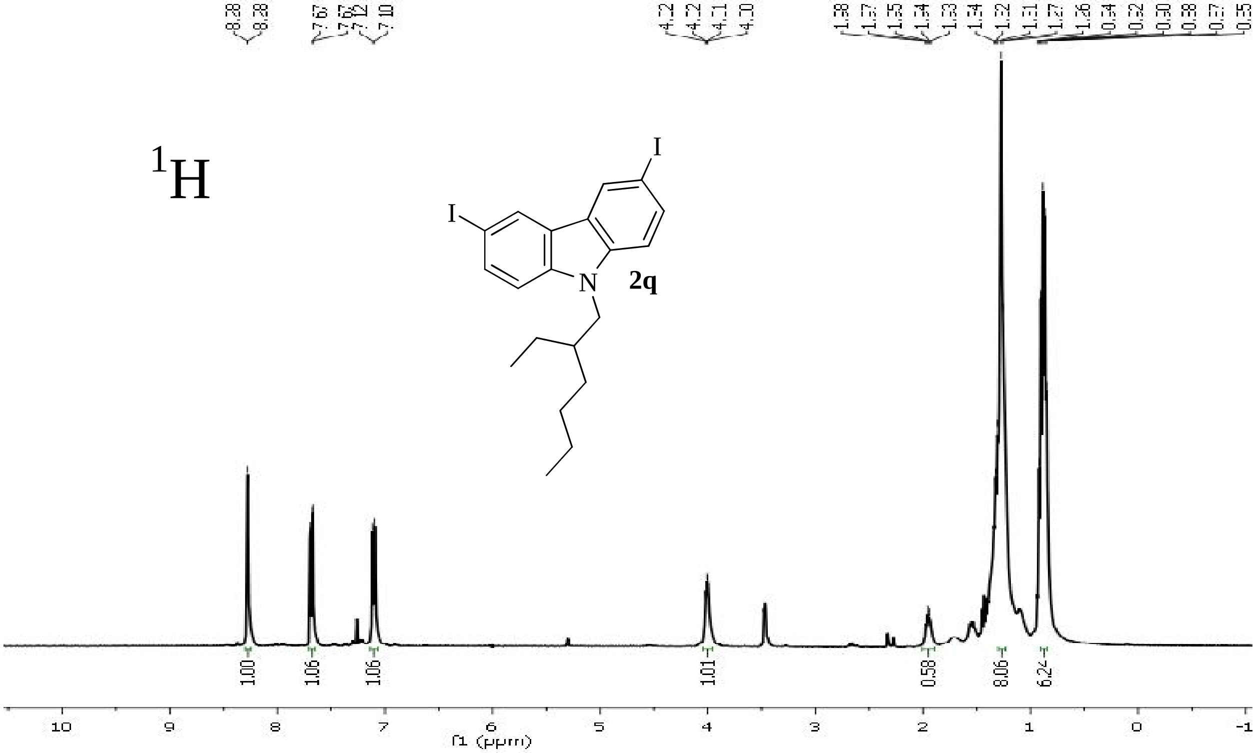

2n

152.86
123.14
86.49
67.78
32.44
30.21
I
O
Br
Br
O
I
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

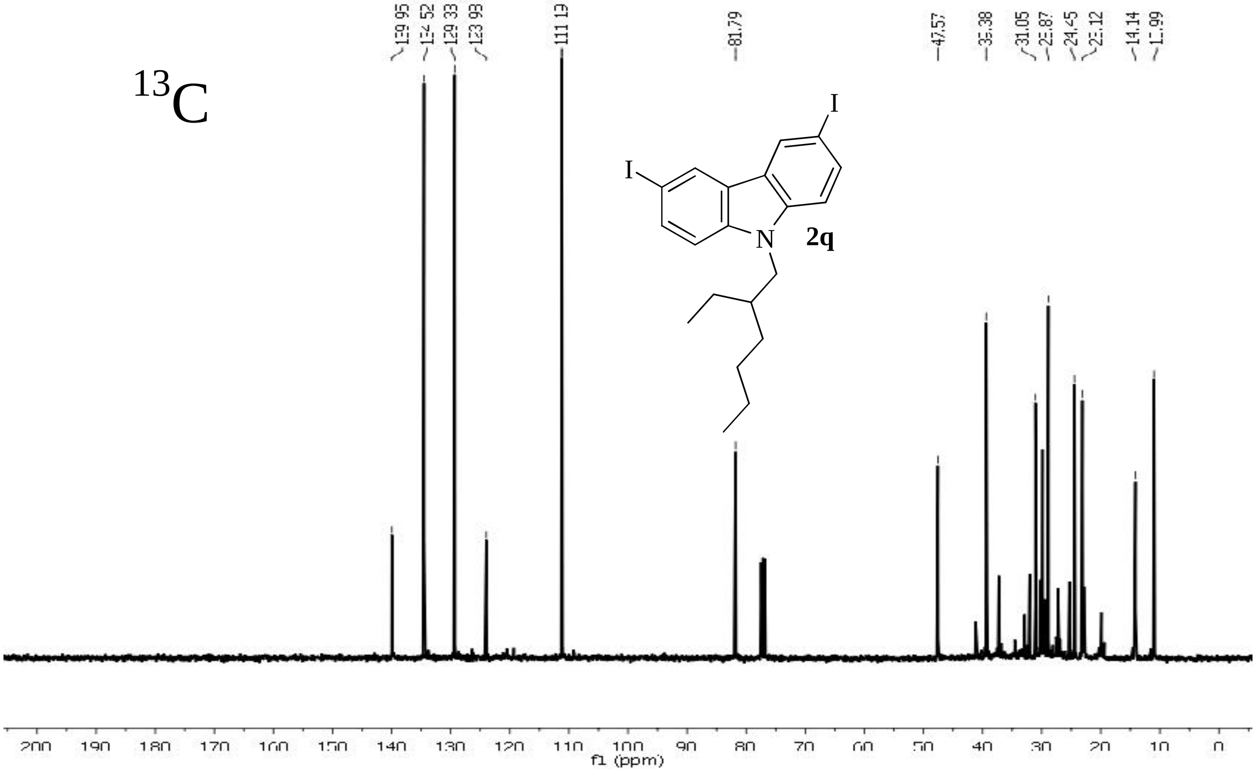

1H
2o
9.30
7.77
7.74
7.23
7.21
7.16
7.01
4.33
4.32
4.30
4.09
4.08
4.07
3.88
3.87
3.85
3.71
3.69
3.68
2.35
2.16
2.14
2.13
2.11
2.10
2.05
2.11
1.00
0.98
2.11
2.6
2.13
2.42
3.45
2.59
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


13C
2o
152.74
152.52
144.89
132.98
129.99
128.01
123.00
122.58
86.33
86.24
67.72
67.06
65.28
32.39
30.2
29.00
26.64
21.82
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

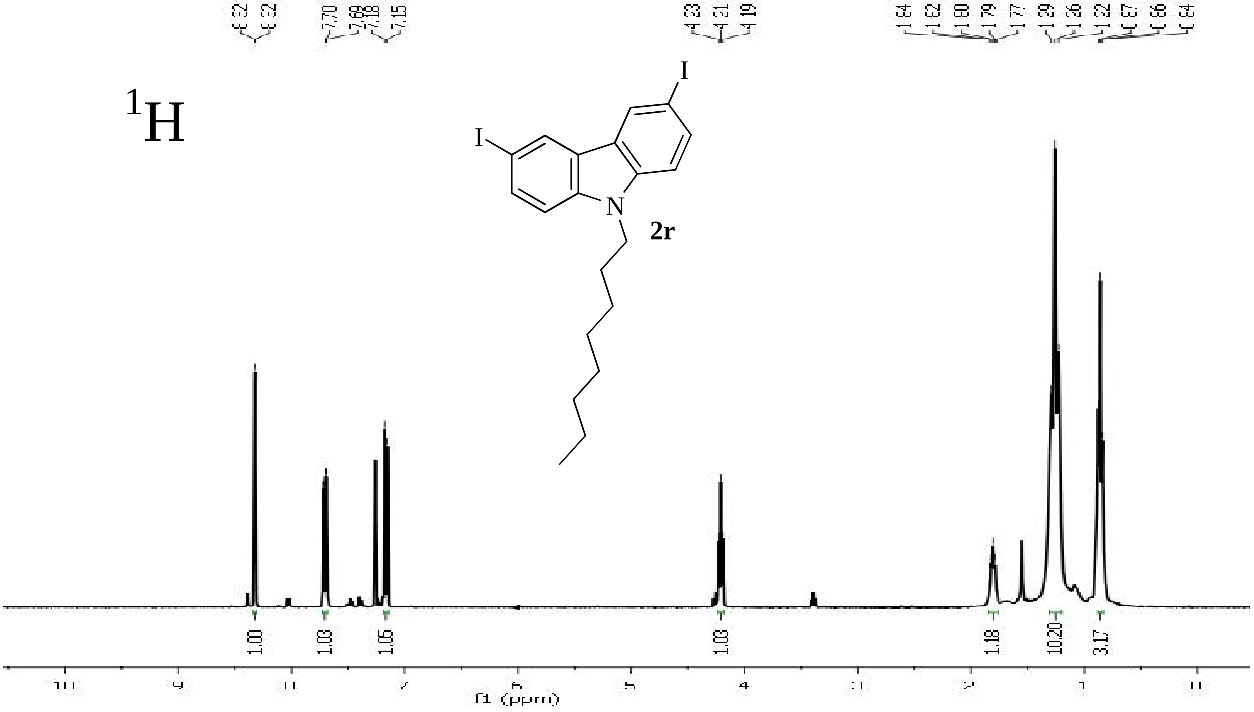

11.55
8.57
7.67
7.65
7.36
7.34
1H
I
I
N
H
2p
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


8.28
8.28
7.67
7.67
7.12
7.10
4.02
4.02
4.01
4.00
1.98
1.97
1.95
1.94
1.93
1.34
1.32
1.31
1.27
1.26
0.94
0.92
0.90
0.88
0.87
0.85
1H
I
I
N
2q
1.00
1.06
1.06
1.01
0.58
8.06
6.24
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

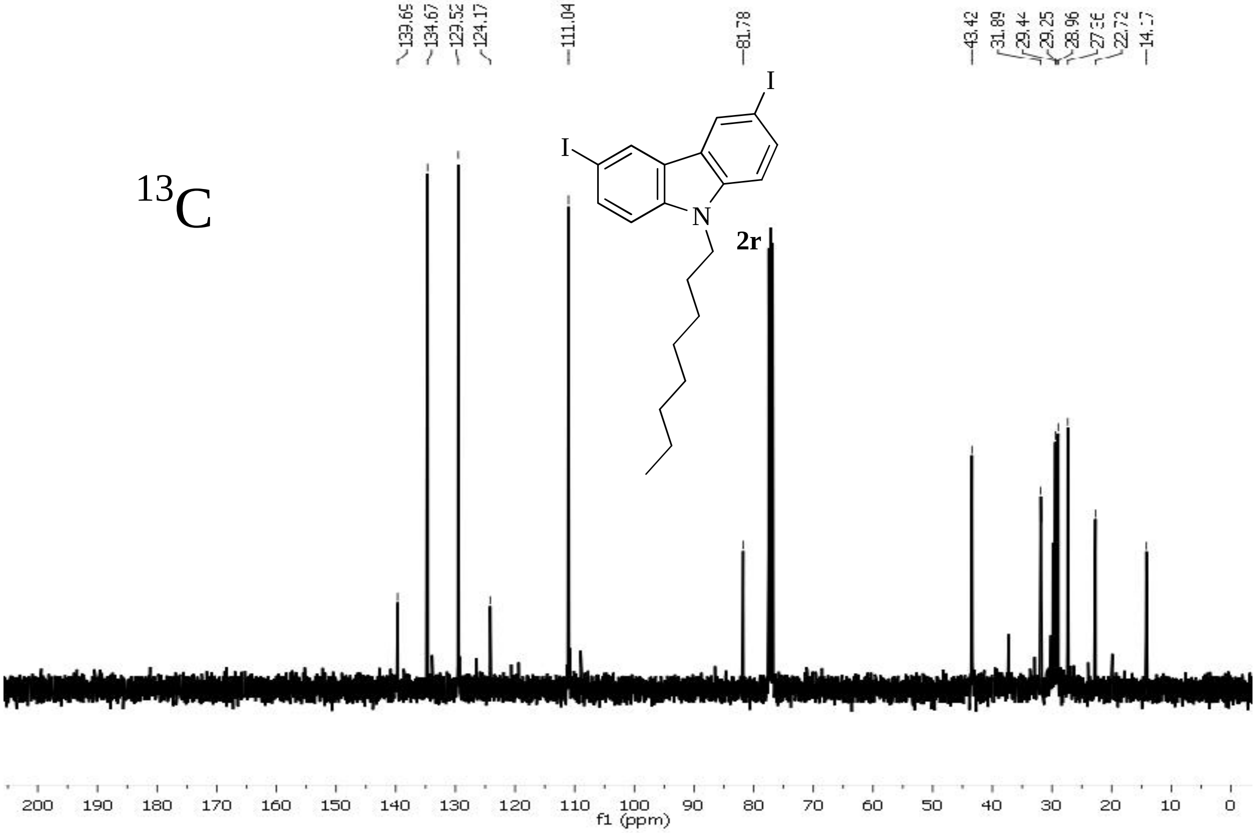
^{13}C


139.95
134.52
129.33
123.93
111.13
81.79
47.57
39.38
31.05
28.87
24.45
23.12
14.14
10.99
I
I
N
2q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H

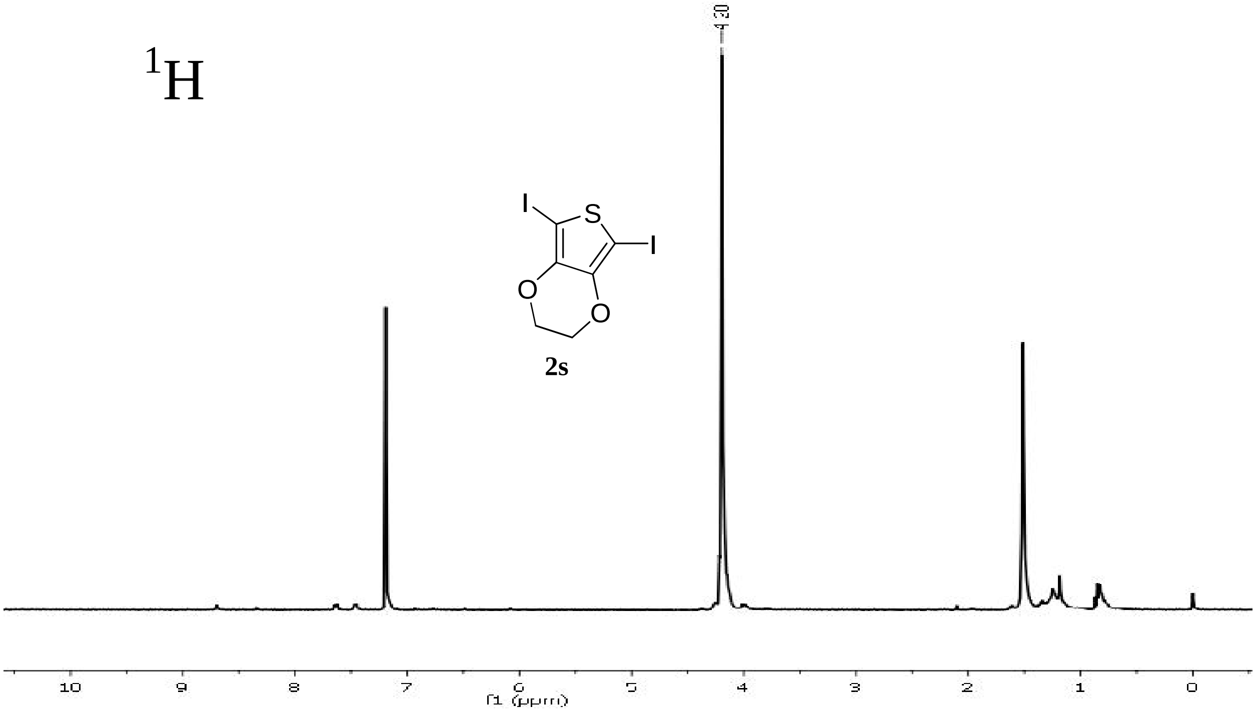

8.32
8.32
7.70
7.69
7.18
7.15
4.23
4.21
4.19
1.84
1.82
1.80
1.79
1.77
1.29
1.26
1.22
0.87
0.86
0.84
I
I
N
2r
1.00
1.03
1.05
1.03
1.18
10.20
3.17
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

^{13}C


139.65
134.67
129.52
124.17
111.04
81.78
43.42
31.89
29.44
29.25
28.96
27.36
22.72
14.17
I
I
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

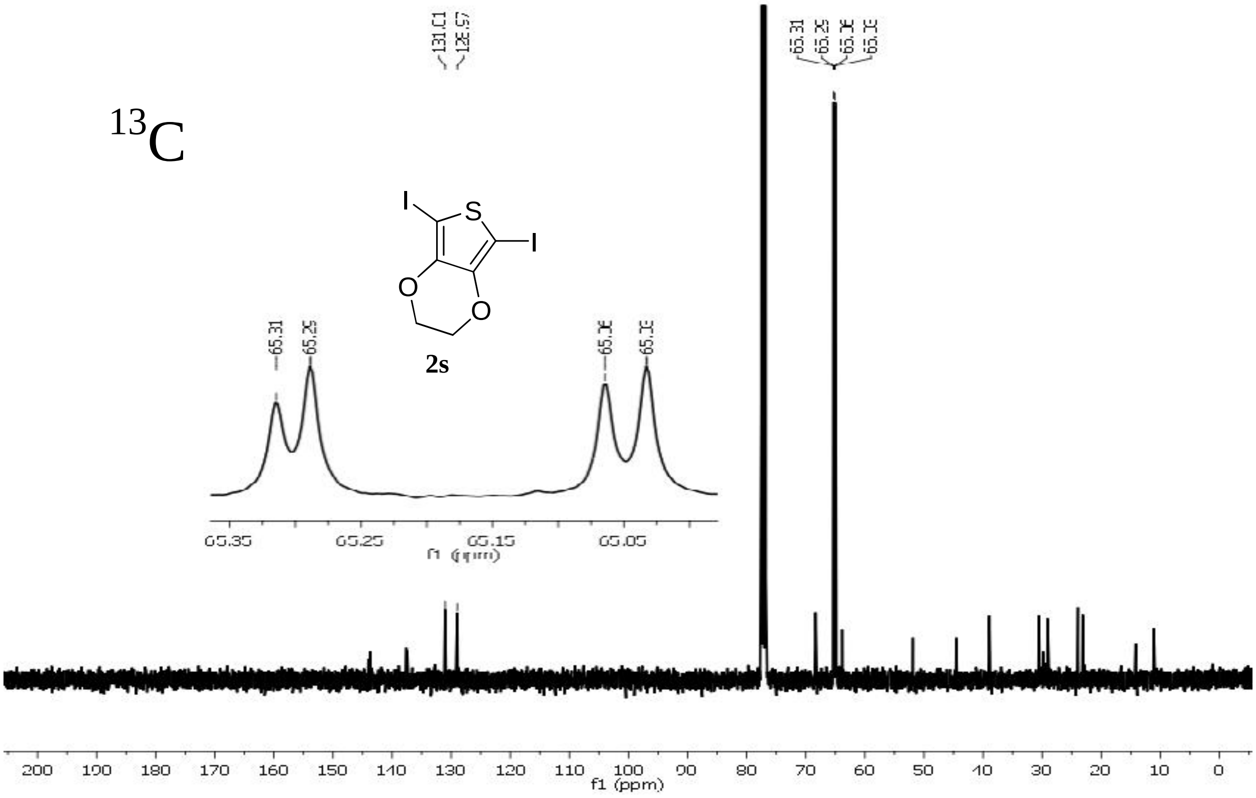
2r

^{1}H


4.20
I
S
I
O
O
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

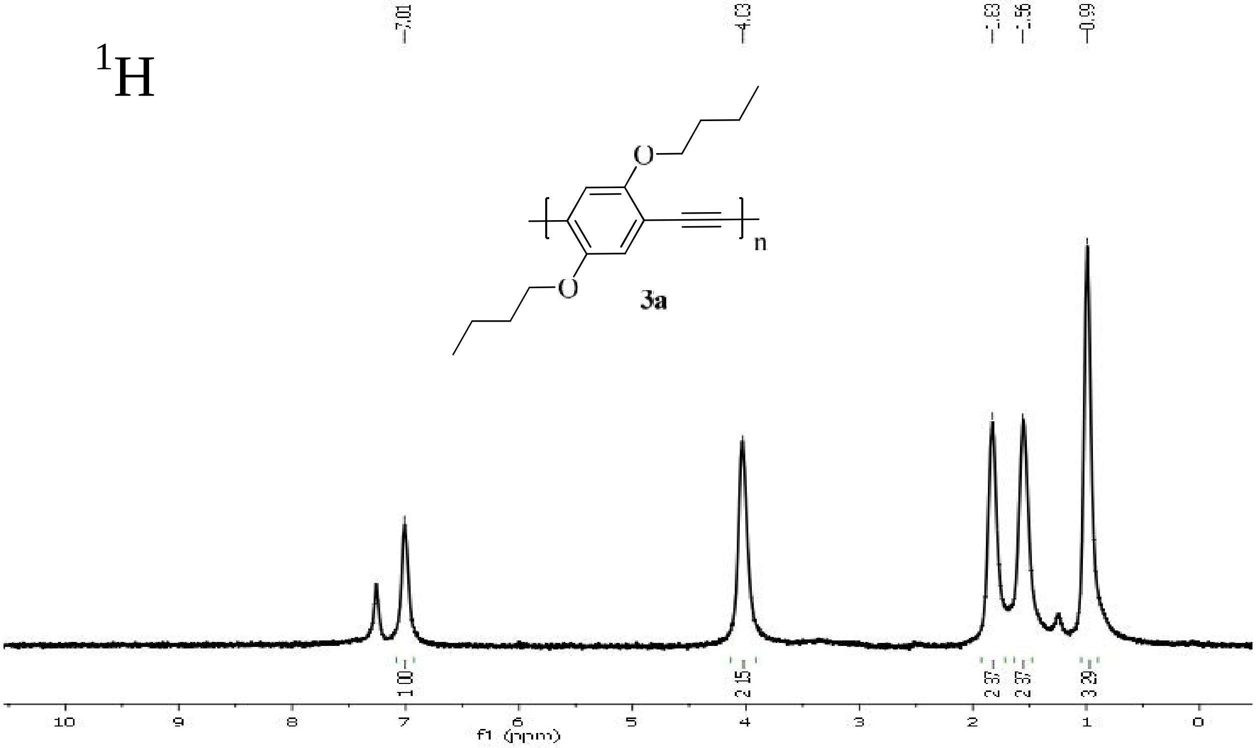
2s

^{13}C

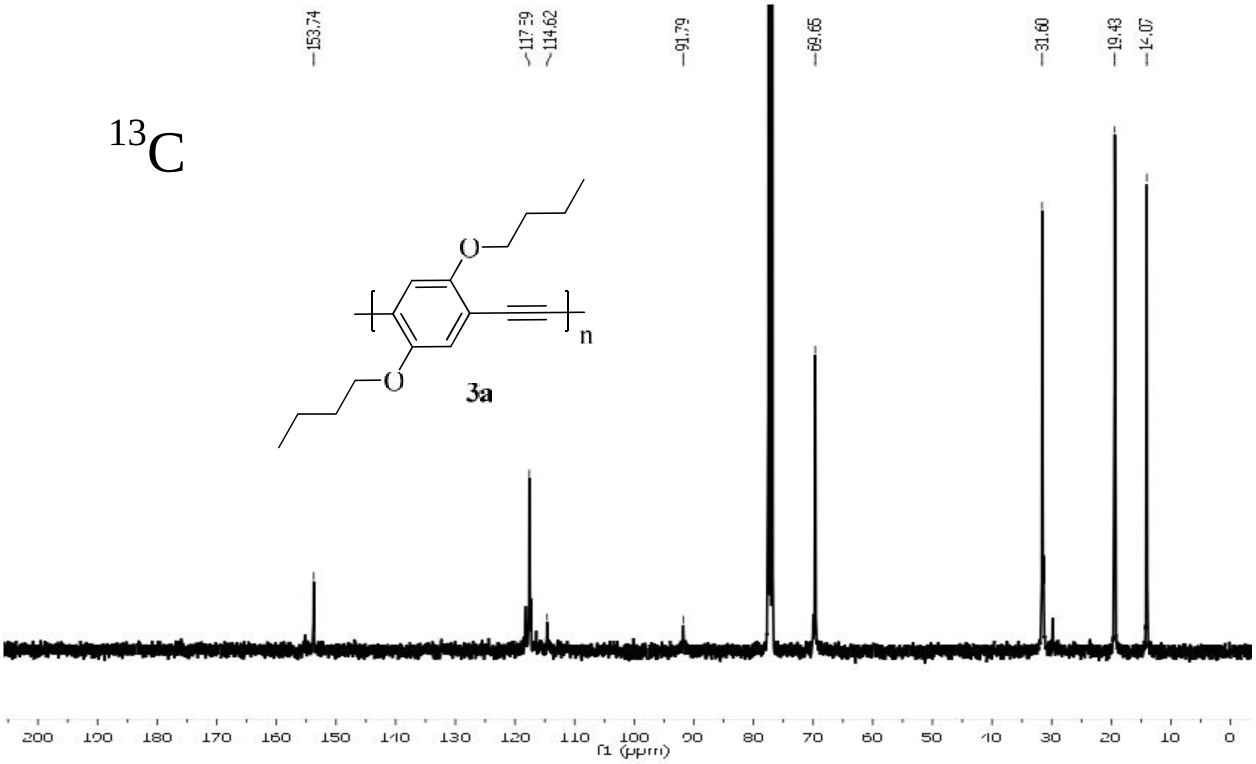

131.01
128.57
65.31
65.25
65.06
65.03
I
S
I
O
O
65.31
65.25
65.06
65.03
65.35
65.25
65.15
65.05
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

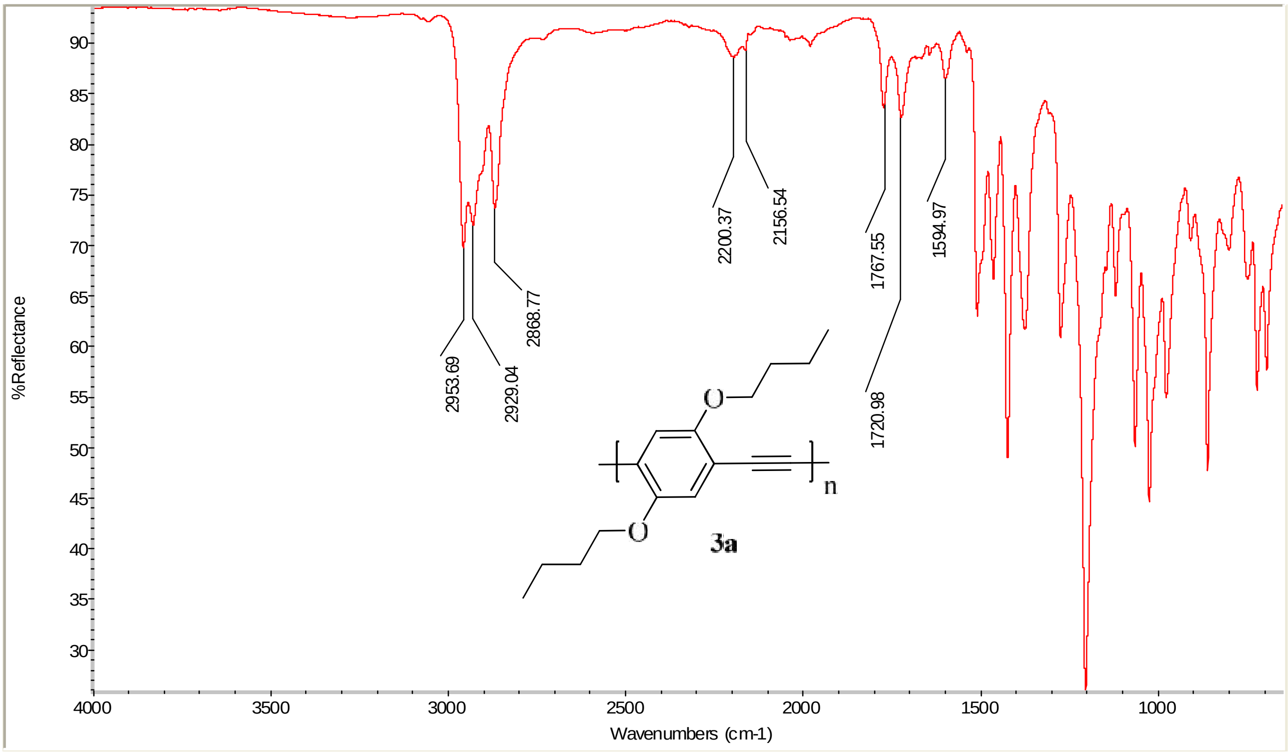
2s

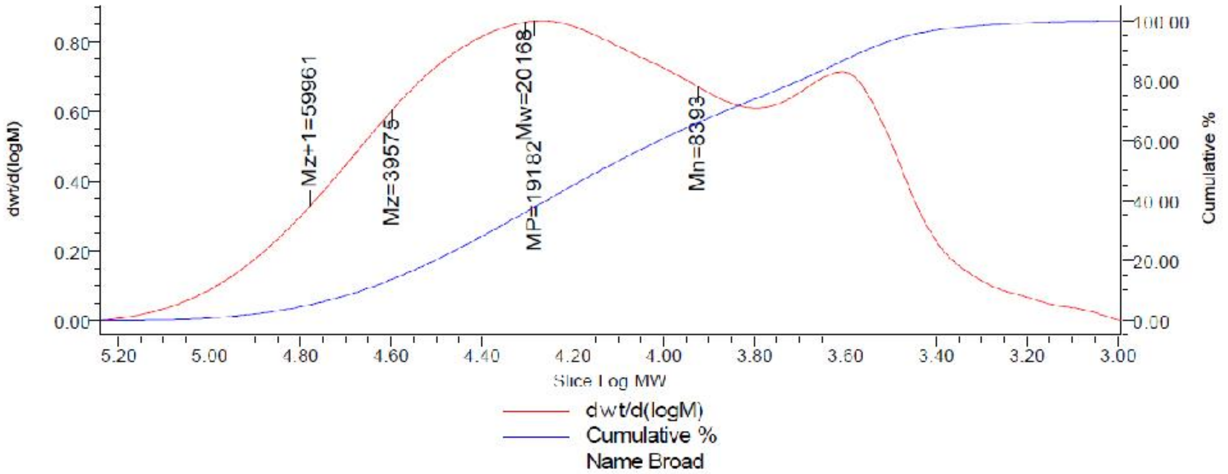
^{1}H


7.01
4.03
1.83
1.56
0.99
O
O
n
1.00
2.15
2.37
2.37
3.39
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

3a

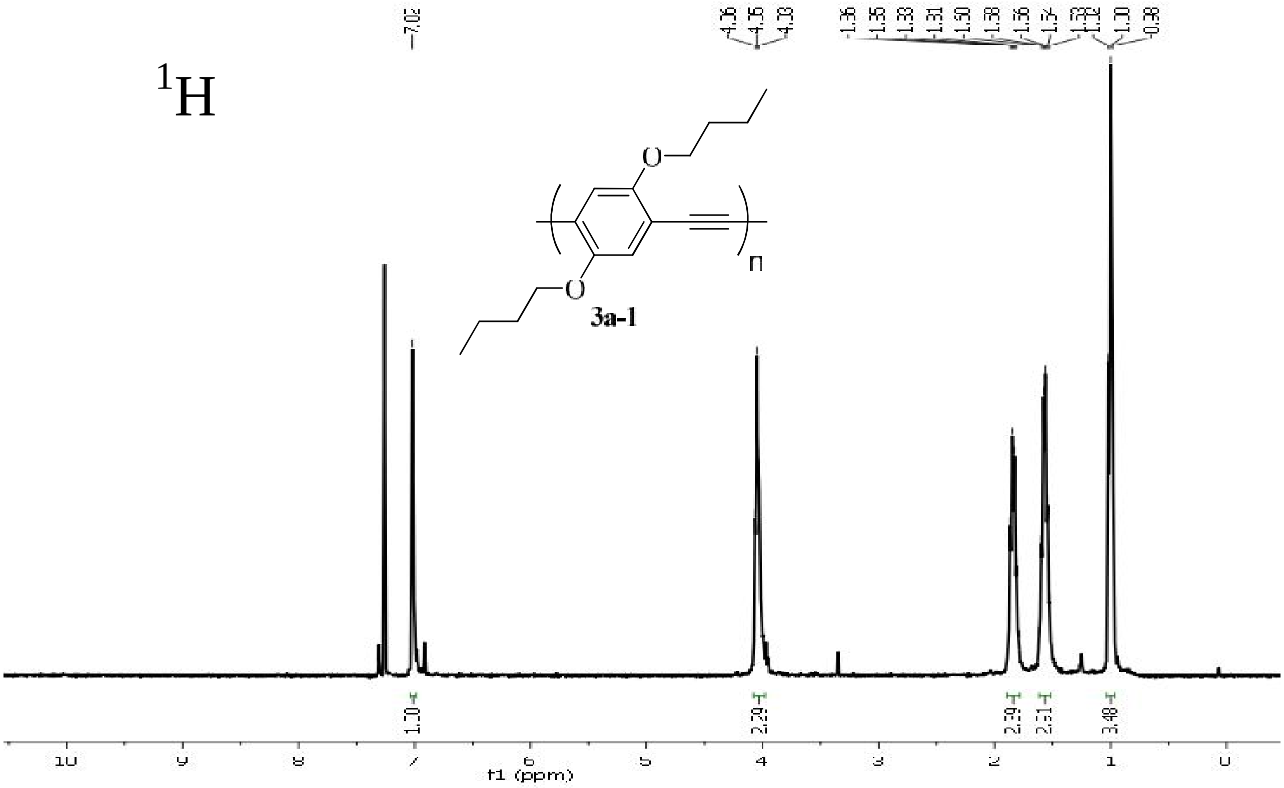

13C
153.74
117.59
114.62
91.79
69.65
31.60
19.43
14.07
O
O
n
3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


%Reflectance
90
85
80
75
70
65
60
55
50
45
40
35
30
2953.69
2929.04
2868.77
2200.37
2156.54
1767.55
1720.98
1594.97
O
O
n
3a
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

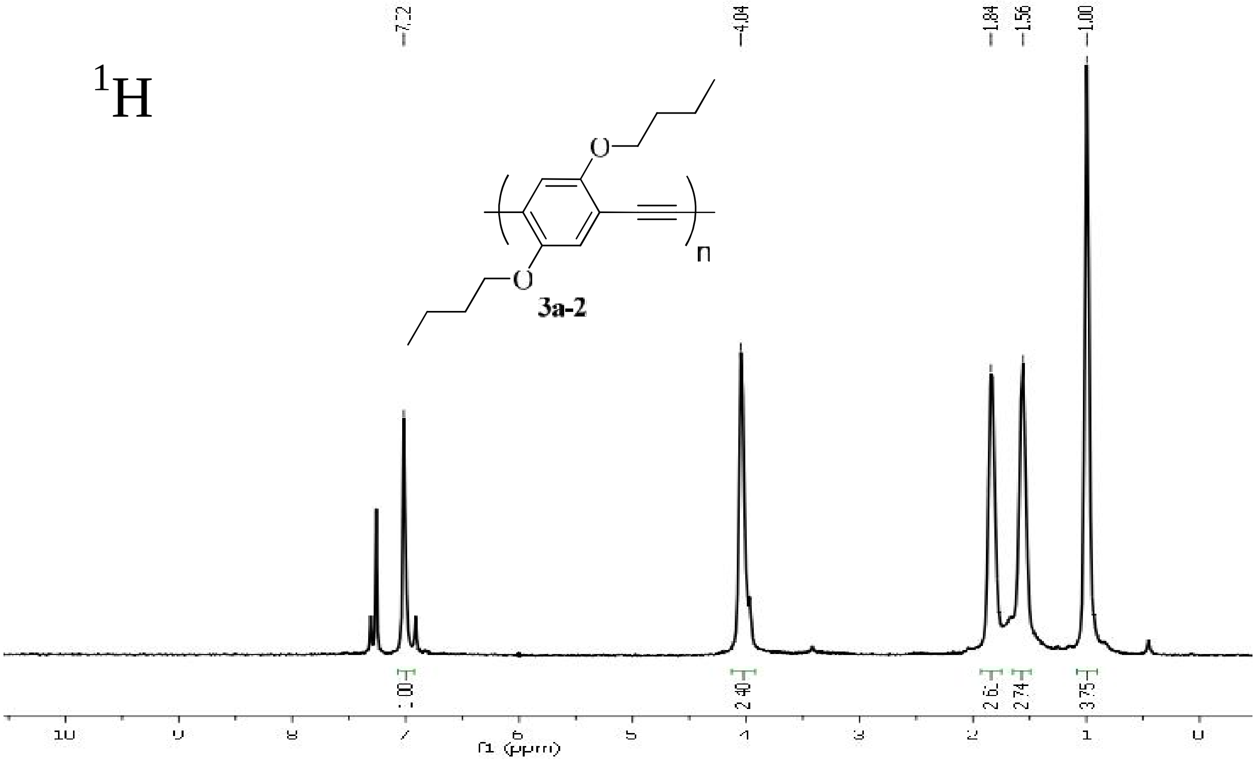


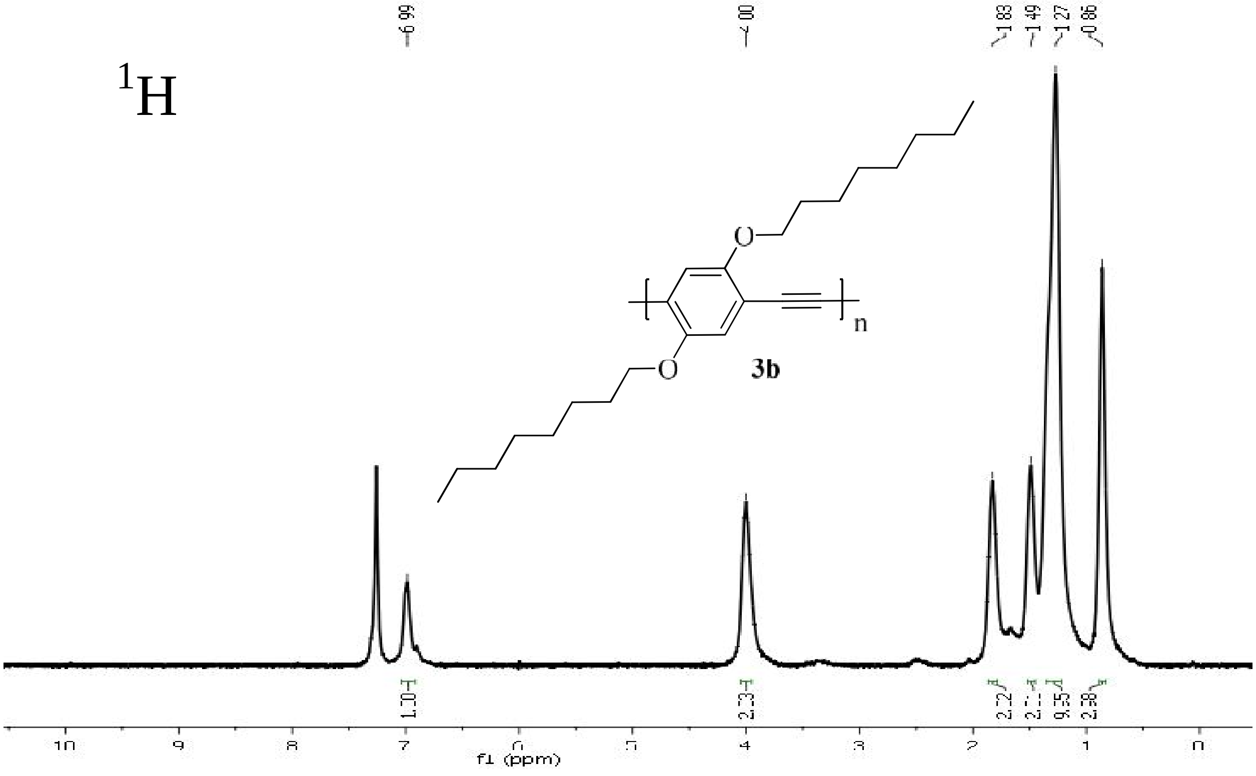
GPC Results / Process Channel ver 1
Processed Channel Descr.:

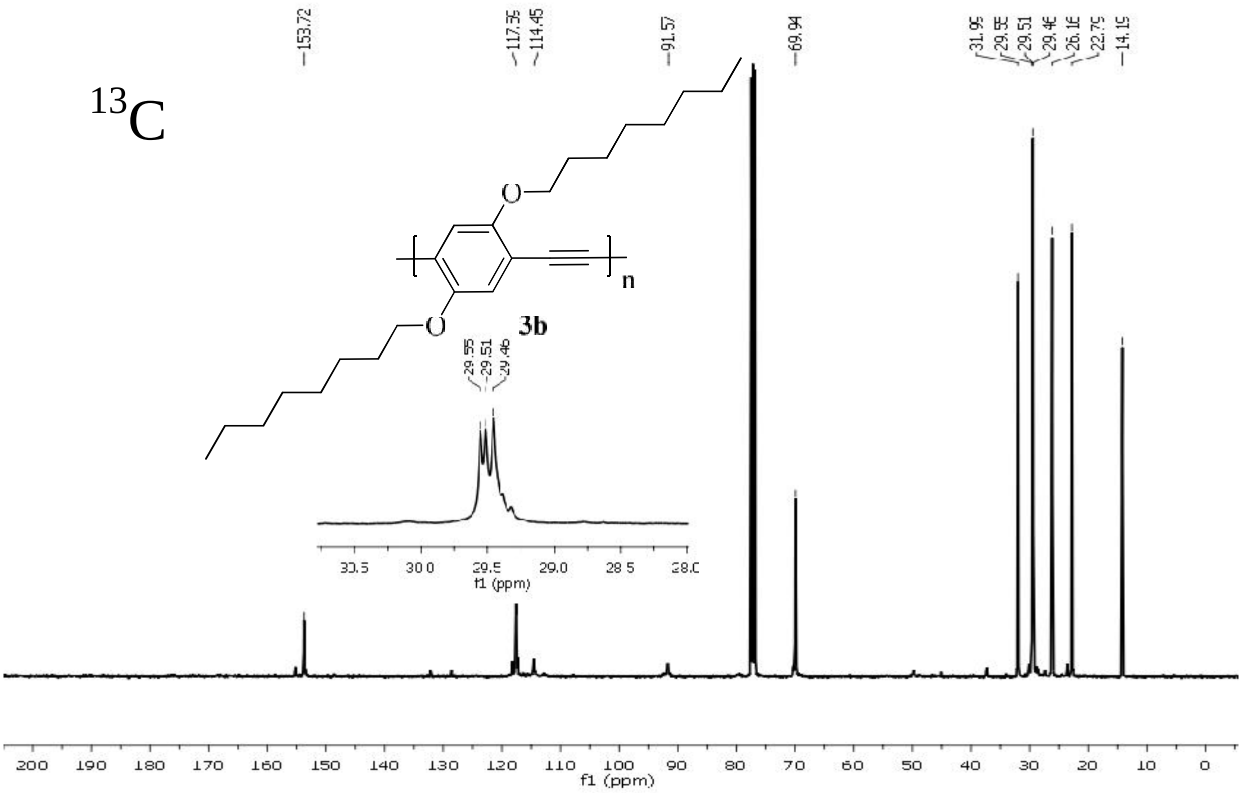
	Peak Name	Retention Time (min)	% Area	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Area (µV*sec)	Height (µV)
1	Broad	14.197	100.00	8393	20168	19182	39575	59961	2.402898	10781539	55584



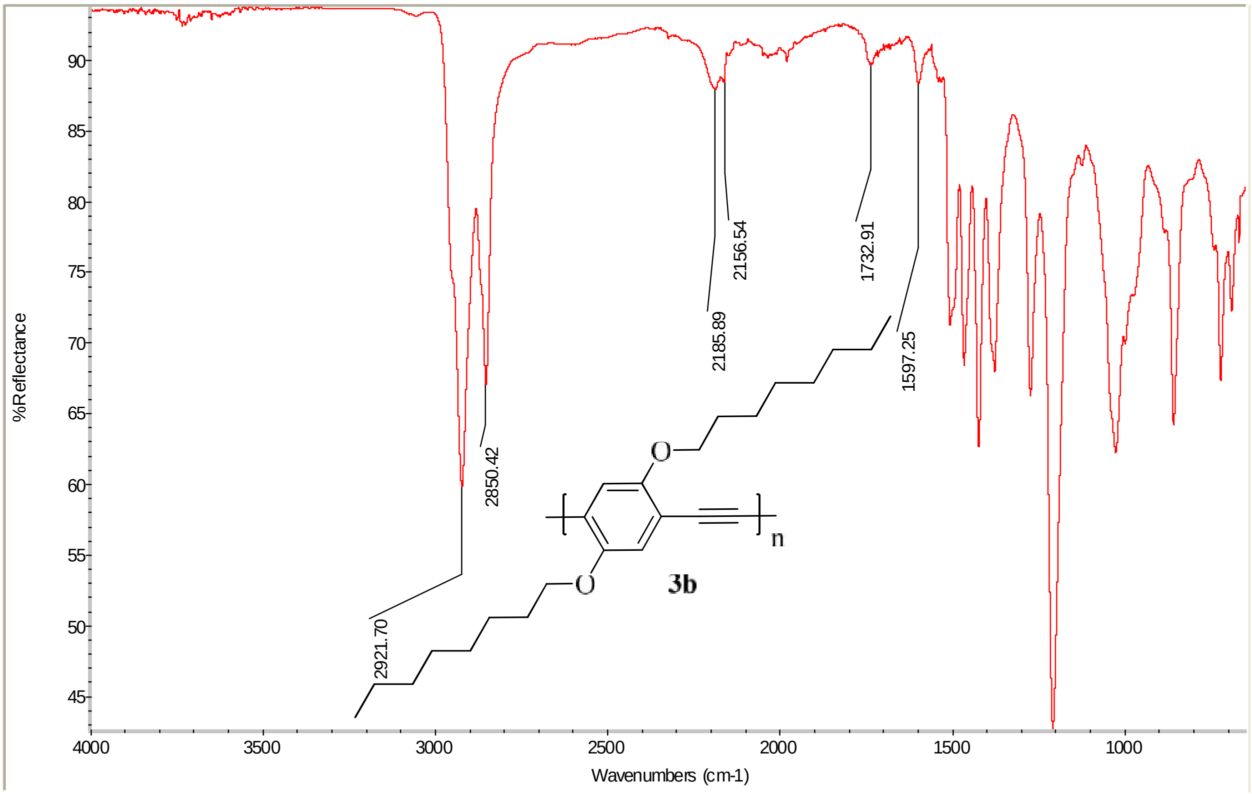
3a-1


1H
3a-2
n
O
O
7.22
4.04
1.84
1.56
1.00
1.00
2.40
2.6
2.74
3.75
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

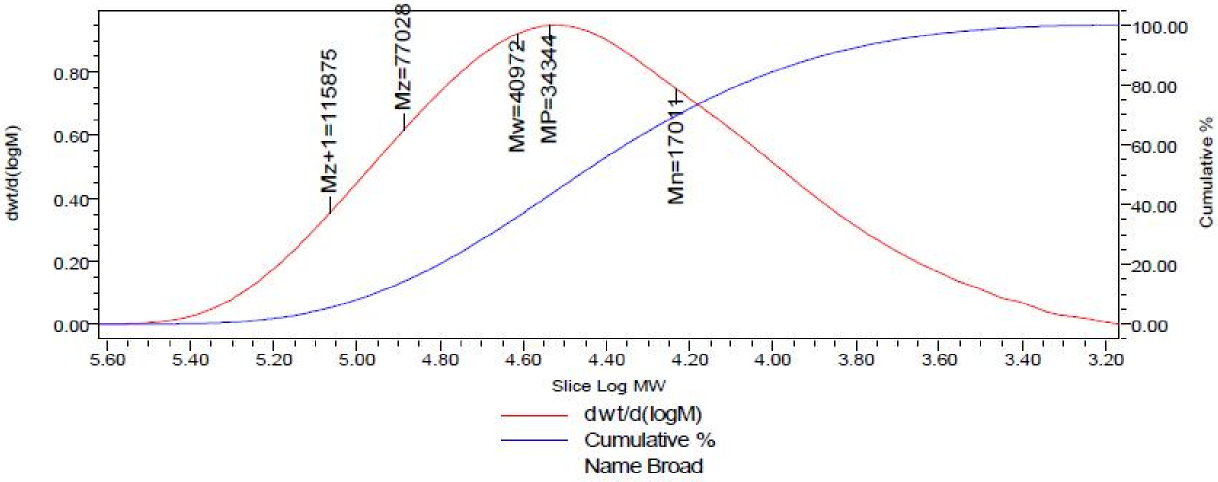

1H
3b
n
O
O
6.99
4.00
1.83
1.49
1.27
0.86
1.00
2.33
2.22
2.11
9.55
2.98
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)



13C
153.72
117.35
114.45
91.57
69.94
31.95
29.55
29.51
29.46
26.16
22.79
14.19
O
O
n
3b
29.55
29.51
29.46
30.5
30.0
29.5
29.0
28.5
28.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



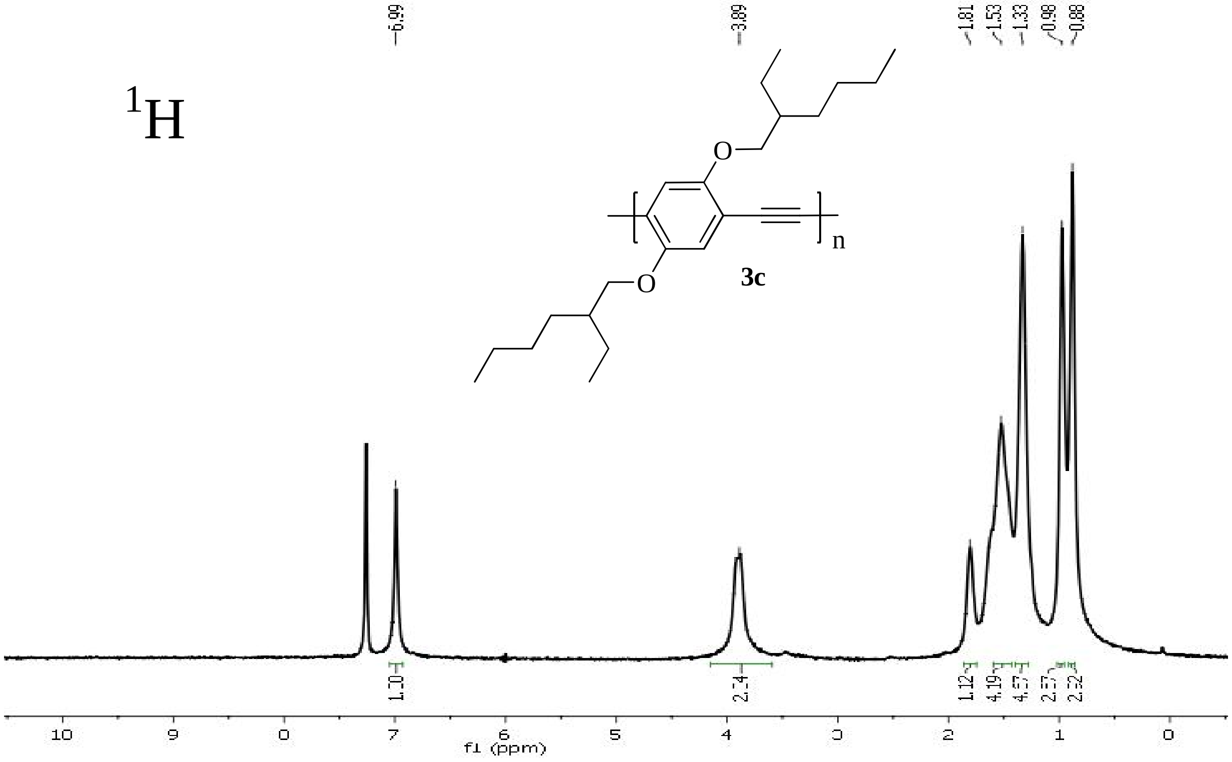
%Reflectance
90
85
80
75
70
65
60
55
50
45
2921.70
2850.42
2185.89
2156.54
1732.91
1597.25
O
O
n
3b
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

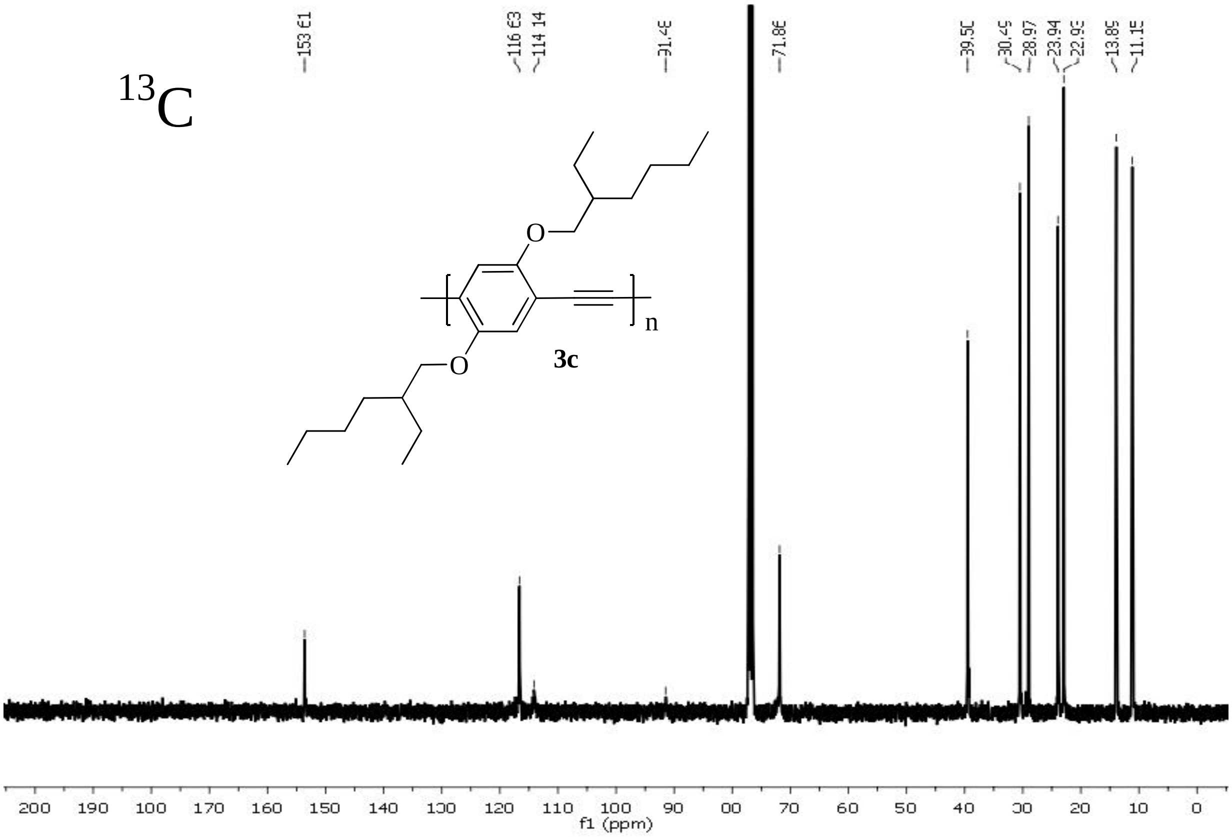


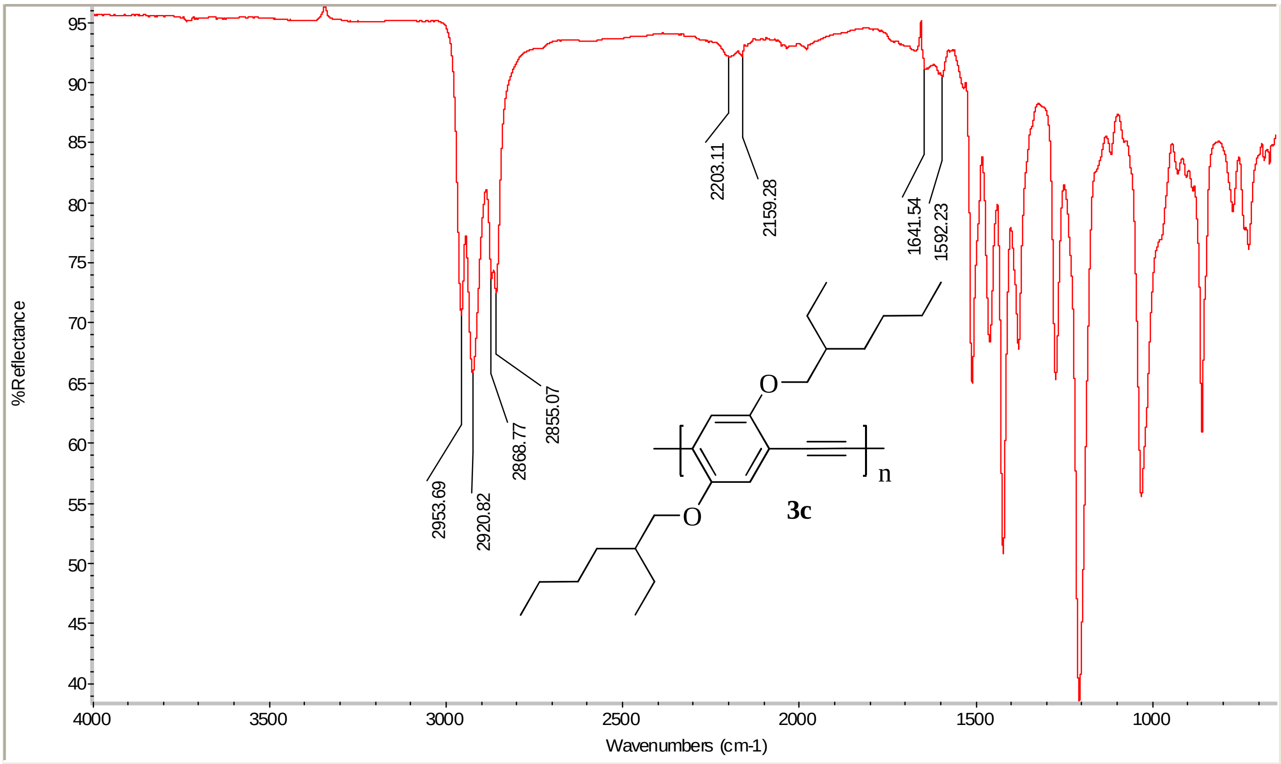
GPC Results / Process Channel ver 1

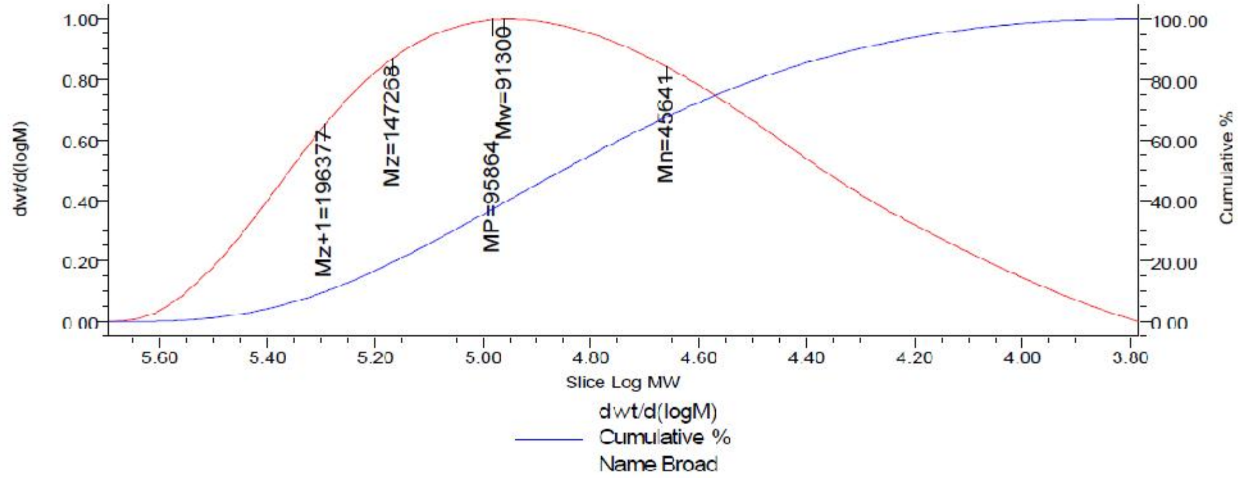
Processed Channel Descr.:

	Peak Name	Retention Time (min)	% Area	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Area (µV*sec)	Height (µV)
1	Broad	13.505	100.00	17011	40972	34344	77028	115875	2.408563	13429190	78971



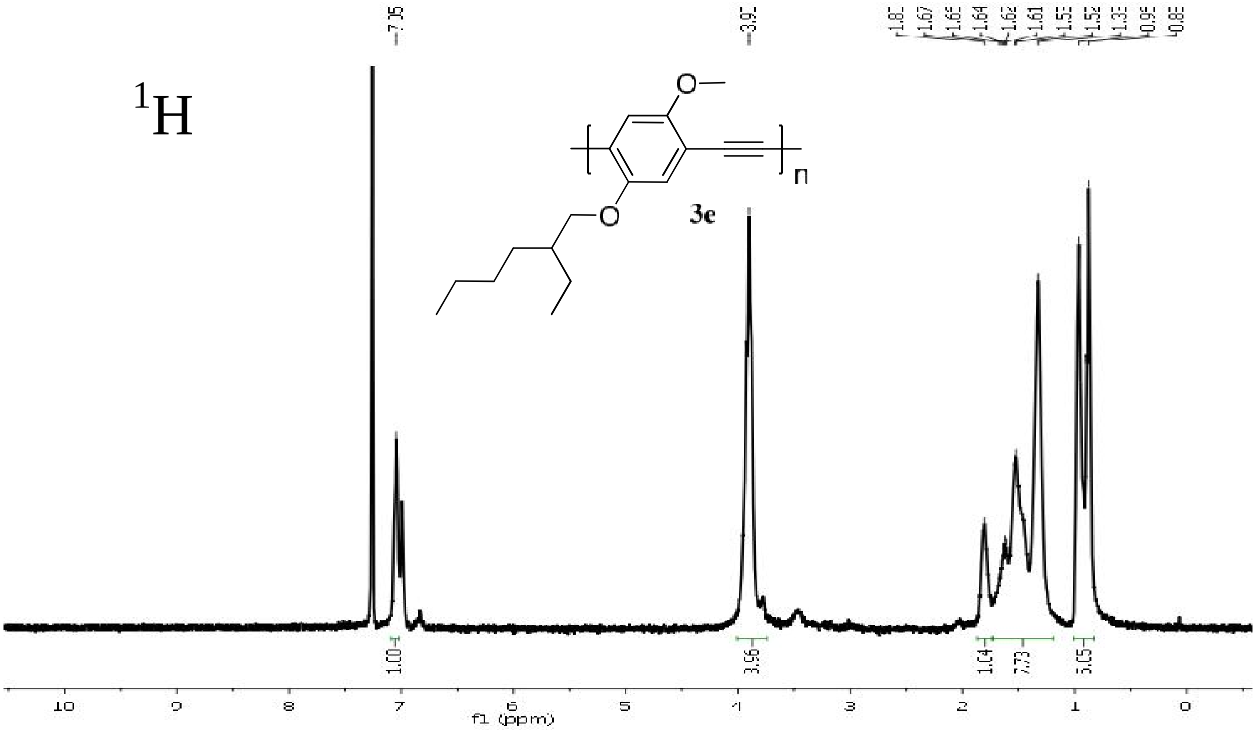

^{13}C
153.61
116.63
114.14
91.48
71.86
39.50
30.45
28.97
23.94
22.93
13.89
11.15
O
O
n
3c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

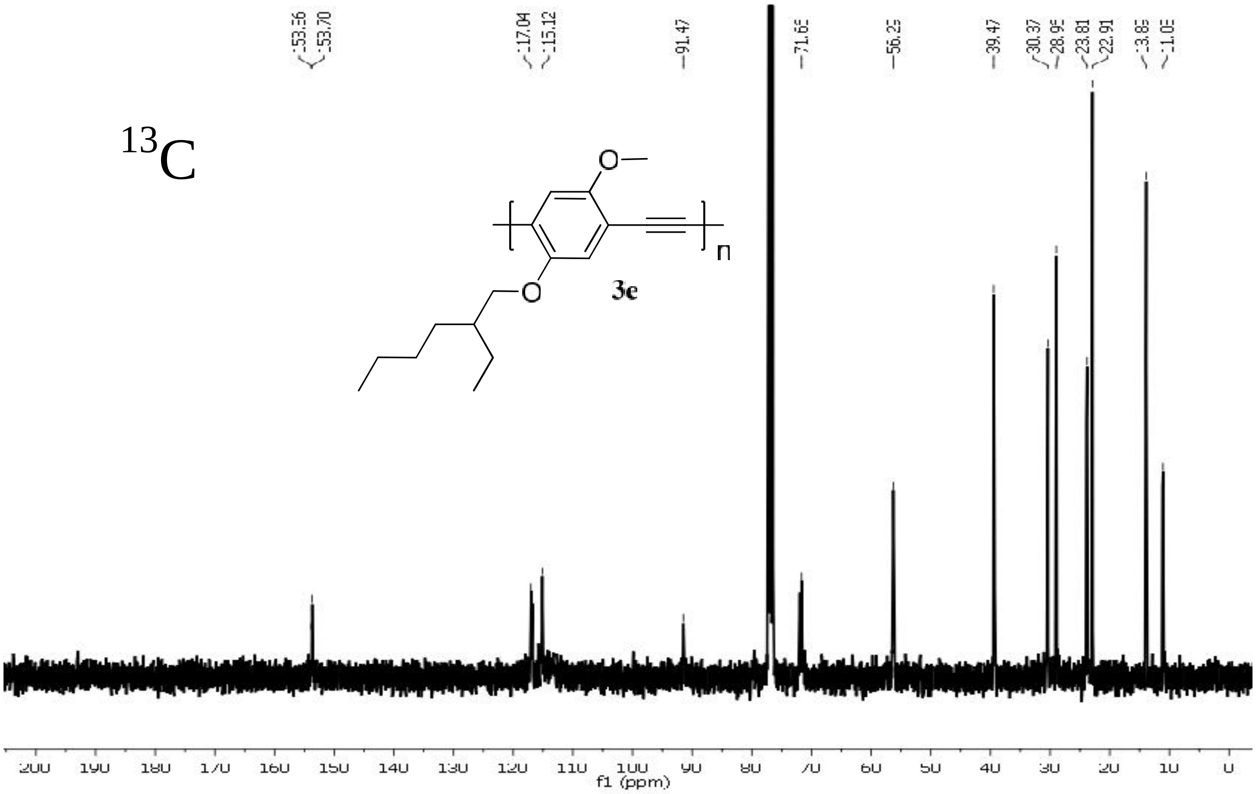

95
90
85
80
75
70
65
60
55
50
45
40
%Reflectance
2953.69
2920.82
2868.77
2855.07
2203.11
2159.28
1641.54
1592.23
O
O
n
3c
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)



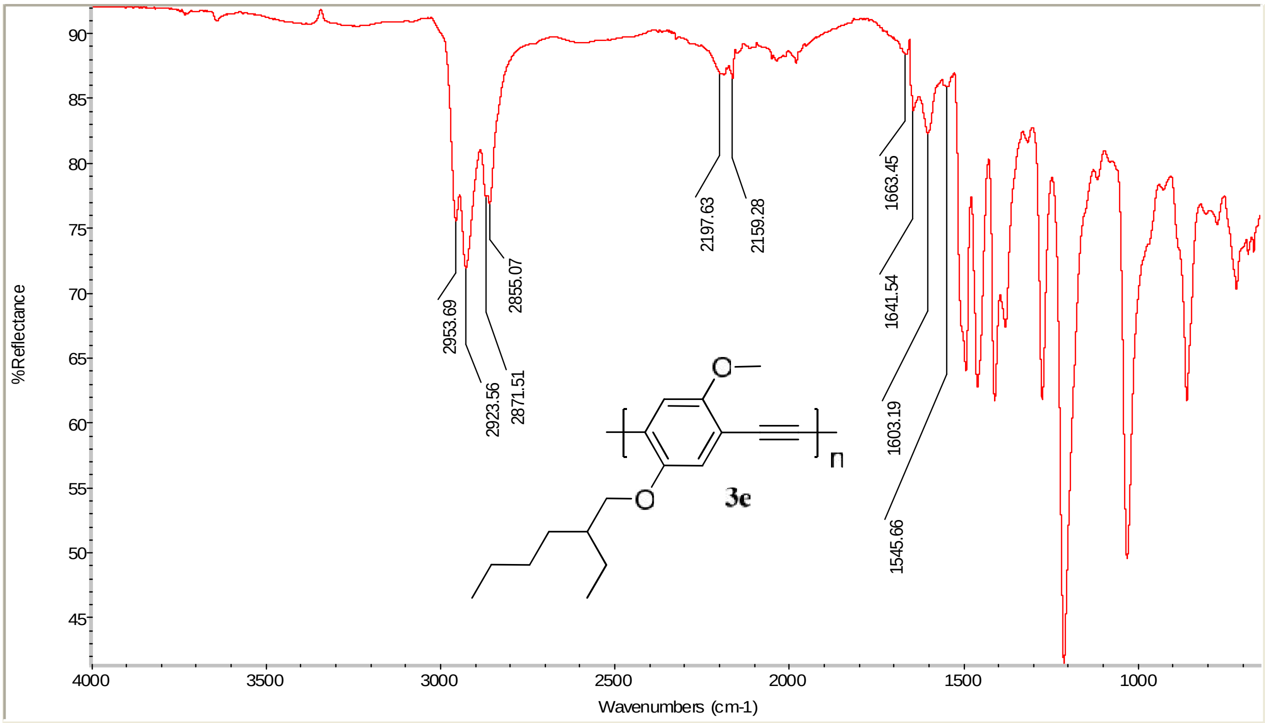
GPC Results / Process Channel ver 1
Processed Channel Descr.:

	Peak Name	Retention Time (min)	% Area	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Area (µV*sec)	Height (µV)
1	Broad	12.350	100.00	45641	91300	95864	147268	196377	2.000407	6807957	57982

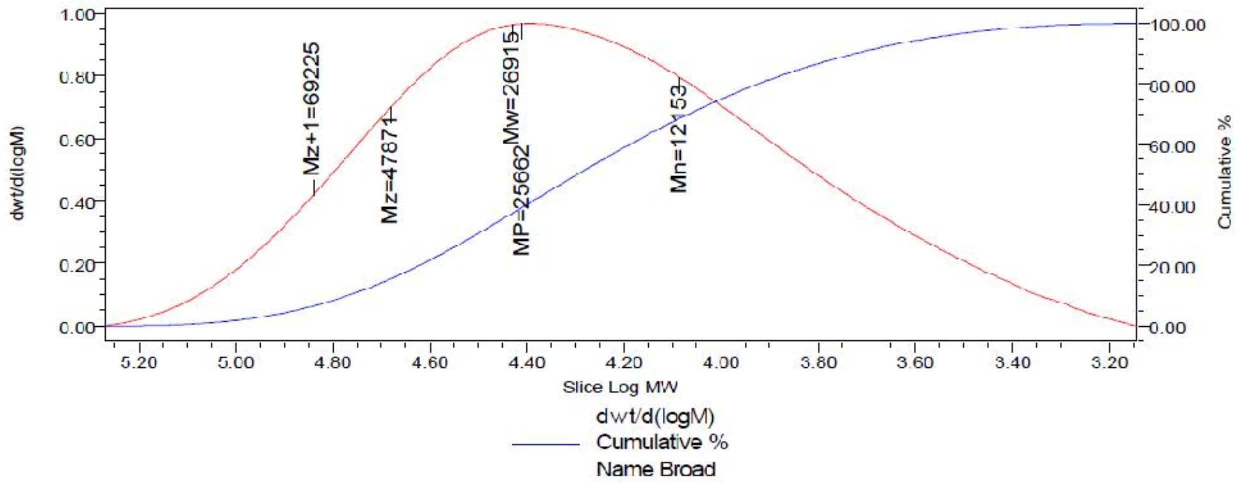




^{13}C
153.56
153.70
117.04
115.12
91.47
71.65
56.23
39.47
30.37
28.95
23.81
22.91
13.85
11.03
O
O
n
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



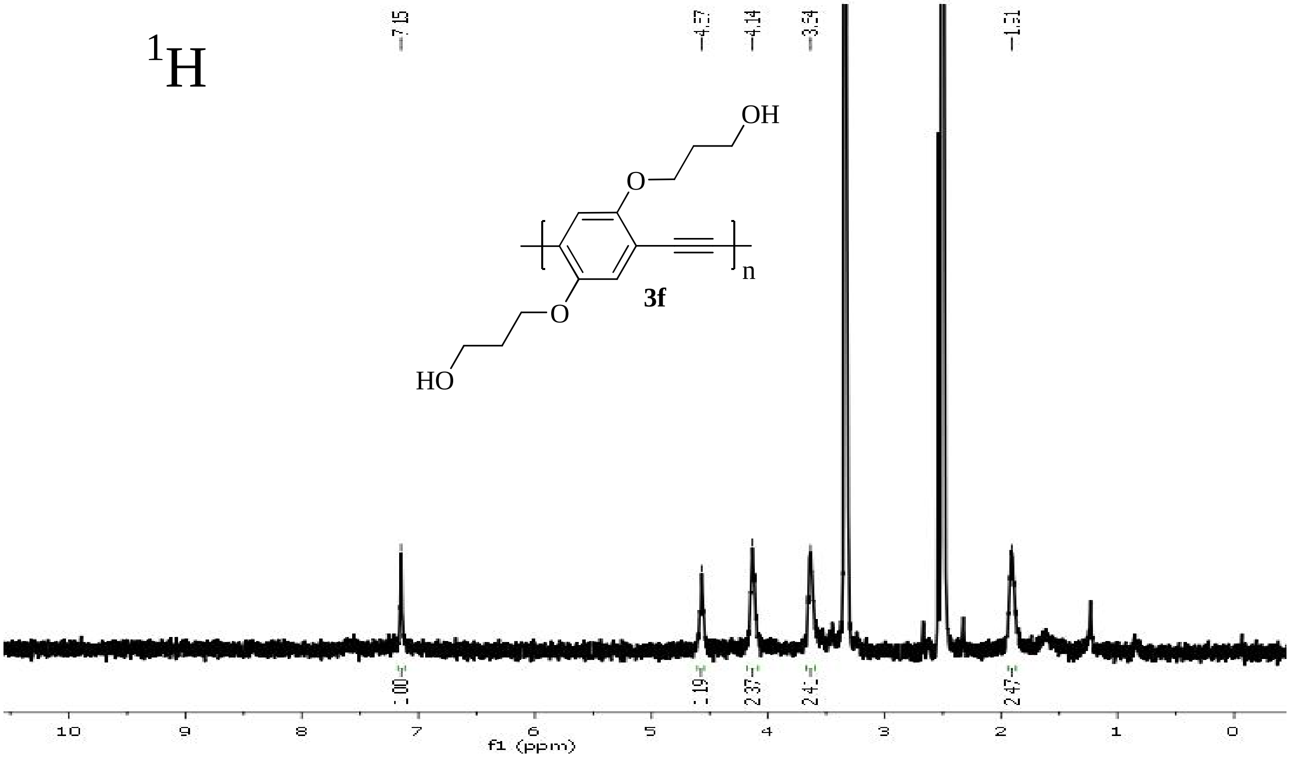
%Reflectance
90
85
80
75
70
65
60
55
50
45
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
2953.69
2923.56
2871.51
2855.07
2197.63
2159.28
1663.45
1641.54
1603.19
1545.66
O
O
n
3e

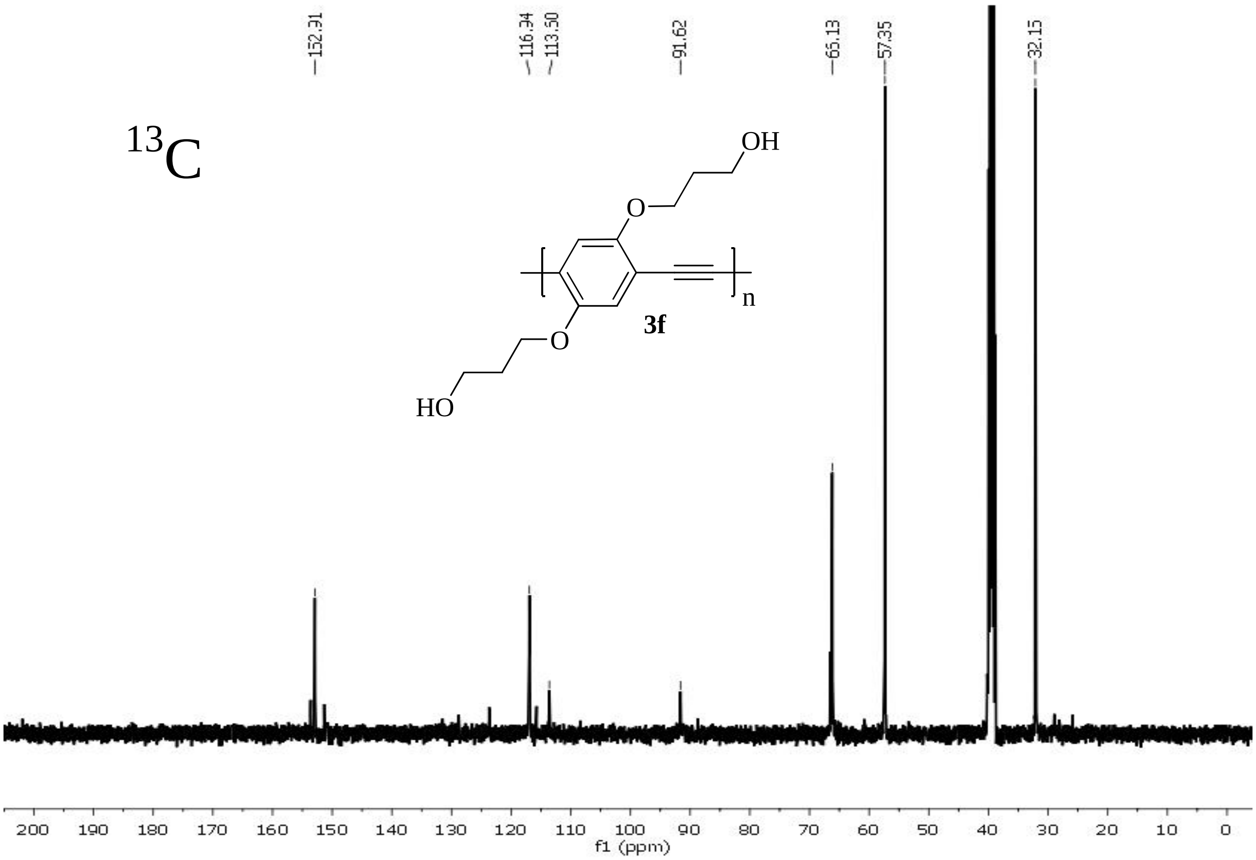


GPC Results / Process Channel ver 1

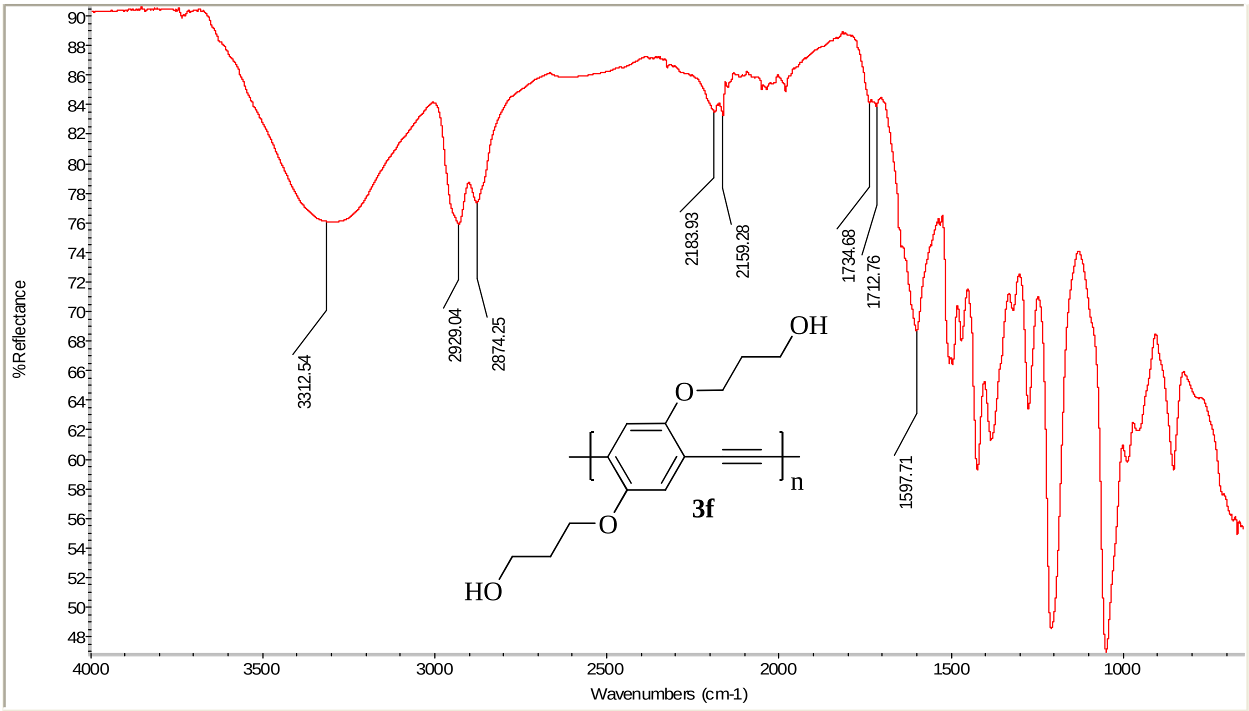
Processed Channel Descr.:

	Peak Name	Retention Time (min)	% Area	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Area (µV*sec)	Height (µV)
1	Broad	13.762	100.00	12153	26915	25662	47871	69225	2.214675	30964678	182729

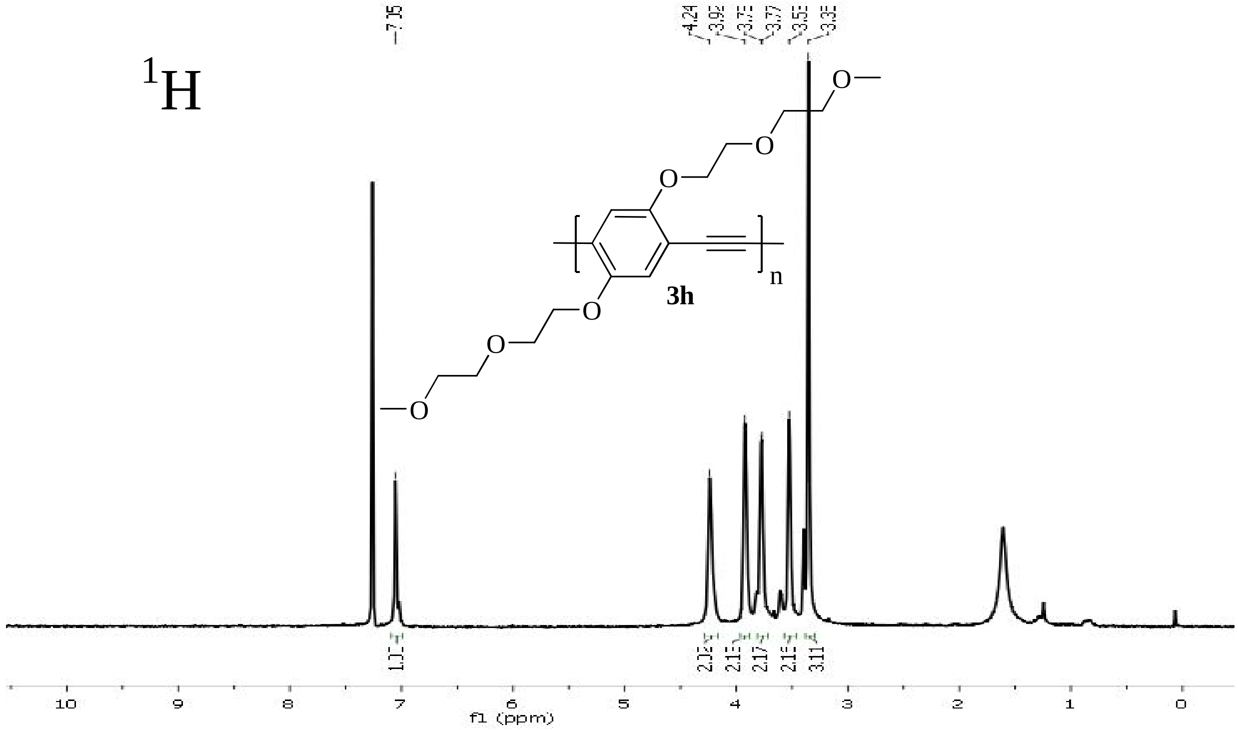




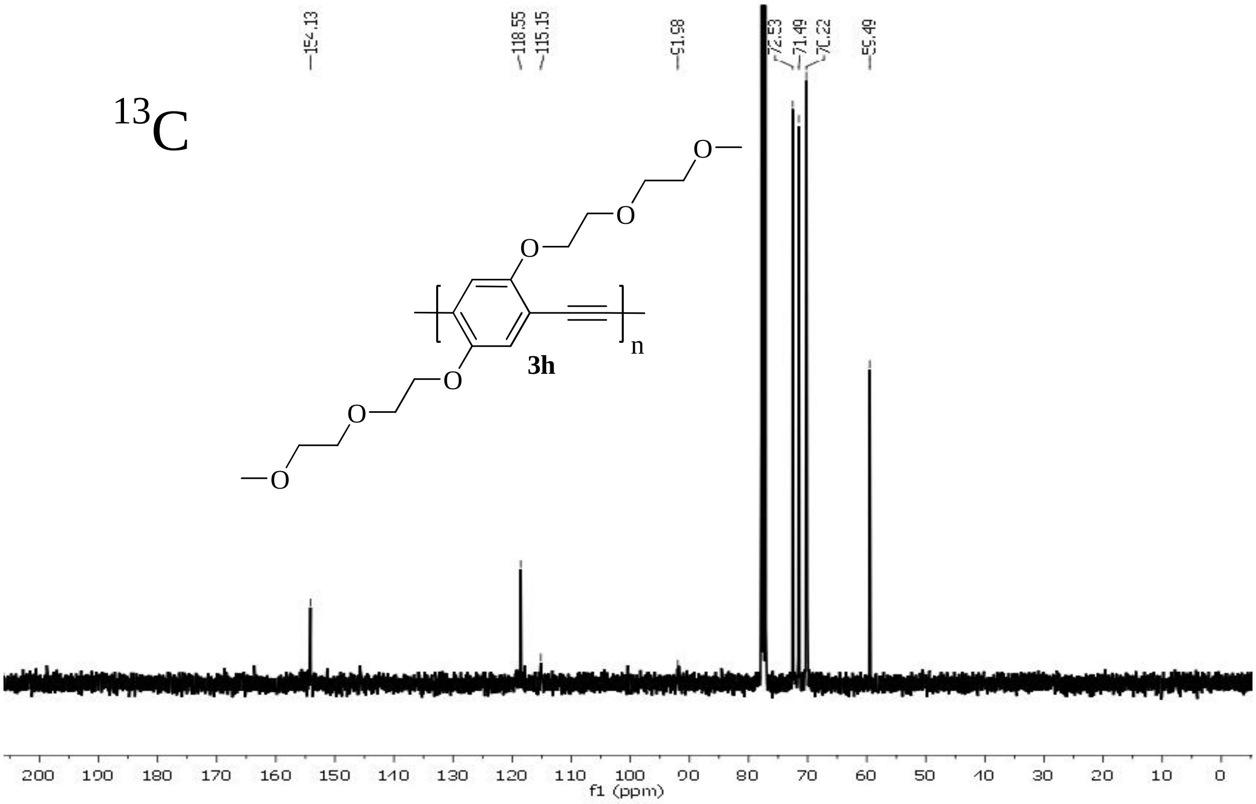
^{13}C
152.31
116.34
113.50
91.62
65.13
57.35
32.15
OH
O
O
HO
n
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



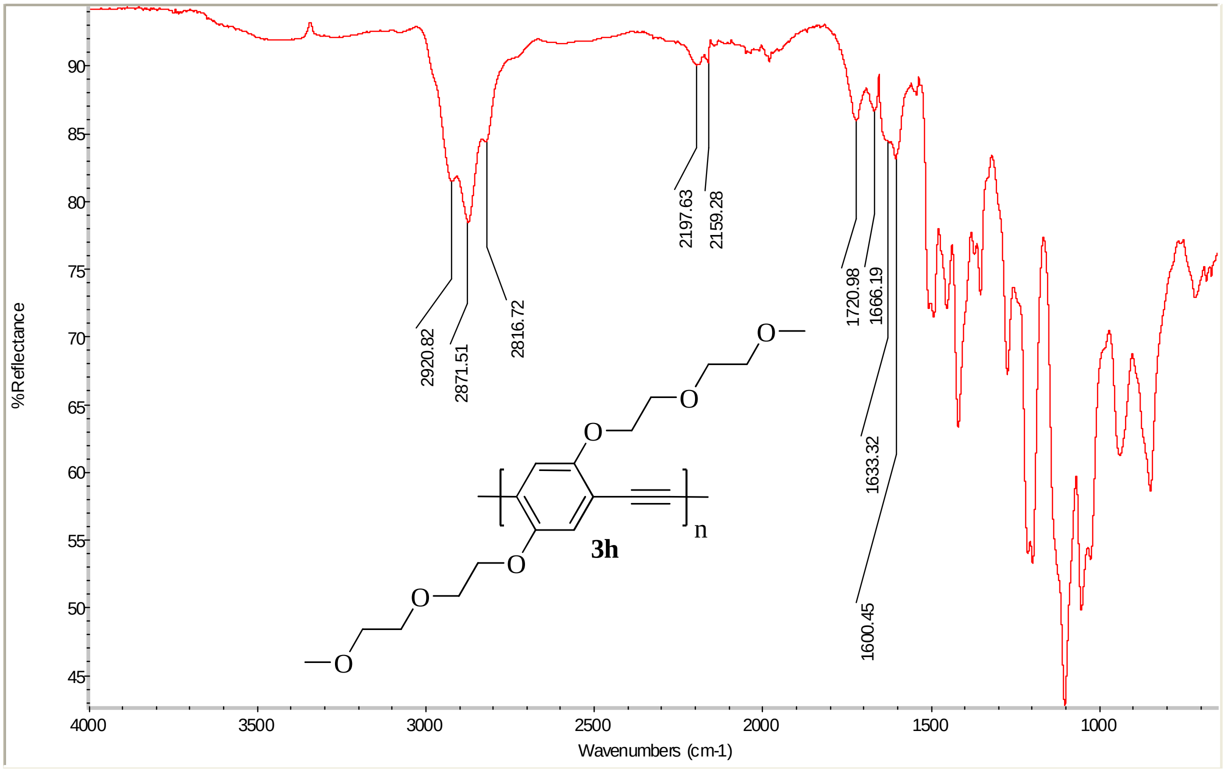
%Reflectance
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
3312.54
2929.04
2874.25
2183.93
2159.28
1734.68
1712.76
1597.71
OH
O
O
HO
n
3f
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

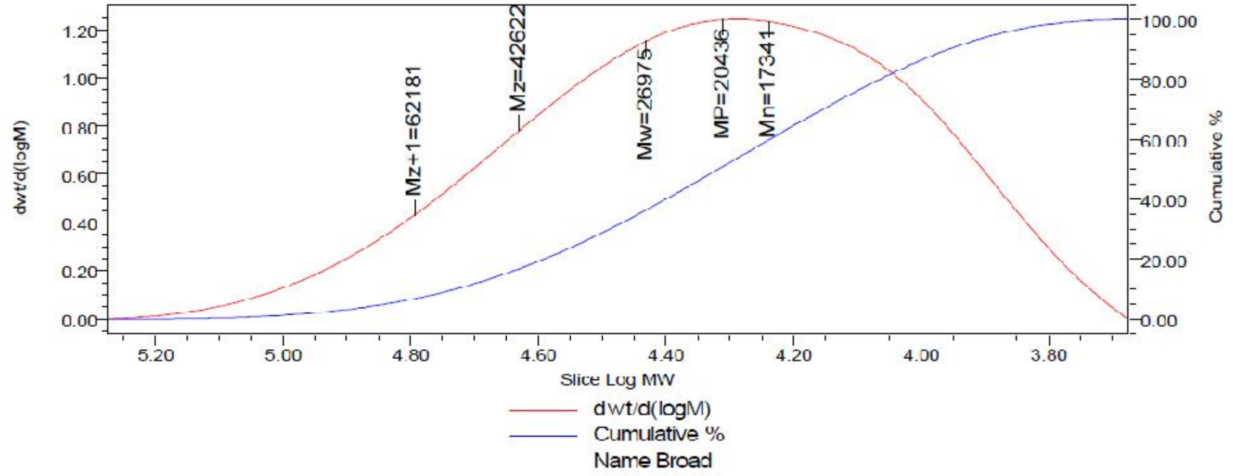


^{1}H
3h
n
7.05
4.24
3.92
3.78
3.77
3.53
3.35
1.00
2.08
2.15
2.17
2.15
3.11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)



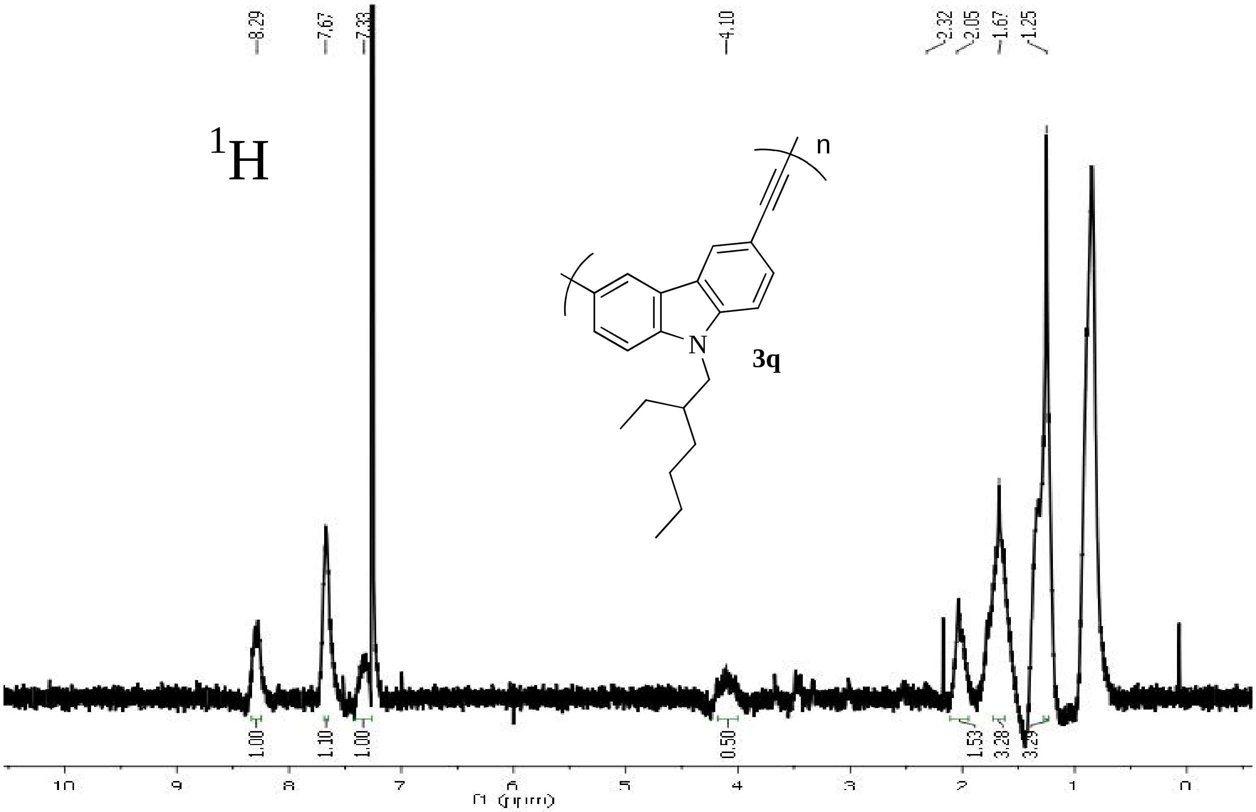
^{13}C
3h
n
154.13
118.55
115.15
91.98
72.53
71.49
70.22
59.49
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



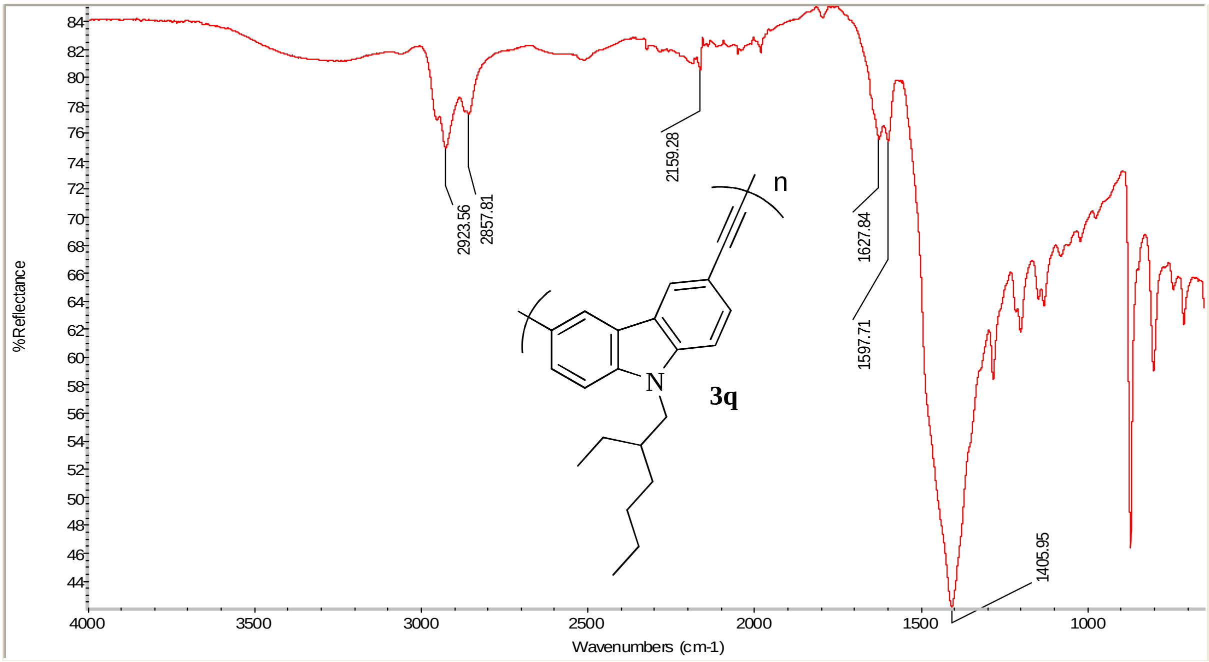


GPC Results / Process Channel ver 1
Processed Channel Descr.:

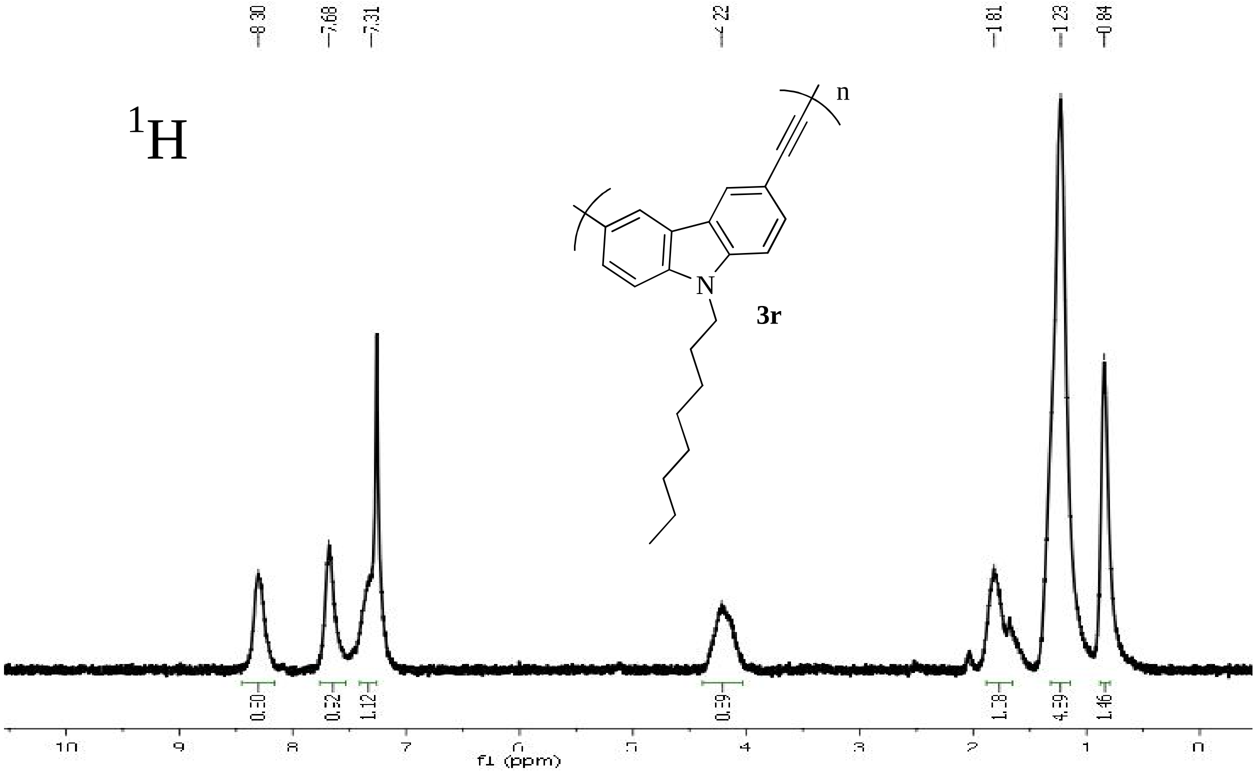
	Peak Name	Retention Time (min)	% Area	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Area (µV*sec)	Height (µV)
1	Broad	14.033	100.00	17341	26975	20436	42622	62181	1.555623	4498672	33659



1H
8.29
7.67
7.33
4.10
2.32
2.05
1.67
1.25
n
N
3q
1.00
1.10
1.00
0.50
1.53
3.28
3.29
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)



84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
%Reflectance
2923.56
2857.81
2159.28
1627.84
1597.71
1405.95
n
N
3q
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)



1H
8.30
7.68
7.31
4.22
1.81
1.23
0.84
n
N
3r
0.50
0.52
1.12
0.59
1.38
4.39
1.46
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

วทศ 0803-2554

ศูนย์เครื่องมือวิจัยวิทยาศาสตร์และเทคโนโลยี จุฬาลงกรณ์มหาวิทยาลัย
อาคารสถาบัน 3 จุฬาลงกรณ์ ซอย 62 พญาไท กรุงเทพฯ 10330 โทร. 218-8030-2, 254-0211 โทรสาร (662) 254-0211

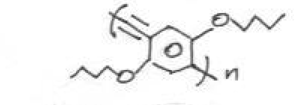
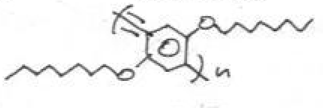
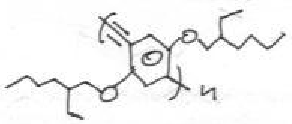
SCIENTIFIC AND TECHNOLOGICAL RESEARCH EQUIPMENT CENTRE CHULALONGKORN UNIVERSITY
CHULALONGKORN SOI 62 PHAYA-THAI ROAD BANGKOK 10330 THAILAND TEL. 218-8030-2, 254-0211 FAX: (662) 254-0211

รายงานเลขที่ 686/2555 **หน้า 1/2**

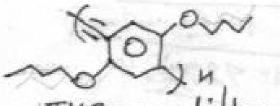
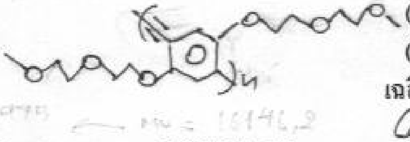
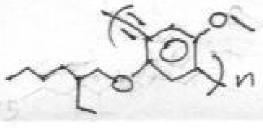
รายงานผลการวิเคราะห์

ตัวอย่าง	สารเคมี
ใบส่งตัวอย่าง	S552484
เจ้าของตัวอย่าง	นายเชียรชัย ชุปวา
วัตถุประสงค์	วิเคราะห์ปริมาณธาตุคาร์บอน ไฮโดรเจน และไนโตรเจน
เครื่องมือวิเคราะห์	CHNS/O Analyzer (PE2400 SeriesII)
วิธีวิเคราะห์	Gaseous products freed by pyrolysis in high-purity oxygen and were chromatographically separated by frontal analysis with quantitatively detected by thermal conductivity detector.
วันที่วิเคราะห์	6 สิงหาคม 2555

ผลการวิเคราะห์

ตัวอย่างที่	**ชื่อตัวอย่าง**		**%C**	**%H**	**%N**
1	NTV-EA-148	(1)	70.11	7.20	...
		(2)	70.21	7.17	...
		(3)	70.26	7.16	...
		เฉลี่ย	**70.19**	**7.18**	**...**
		Calc.	78.65	8.25	
2	NTV-EA-166	(1)	73.95	9.19	...
		(2)	74.03	9.11	...
		(3)	74.08	9.07	...
		เฉลี่ย	**74.02**	**9.12**	**...**
		Calc.	80.84	10.17	
3	NTV-EA-190	(1)	80.94	10.04	...
		(2)	80.74	10.23	...
		(3)	80.89	10.05	...
		เฉลี่ย	**80.86**	**10.11**	**...**
		Calc.	80.84	10.18	

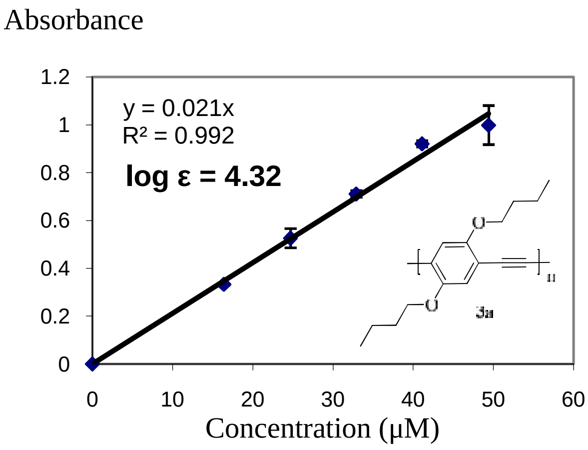
อธ/อพ

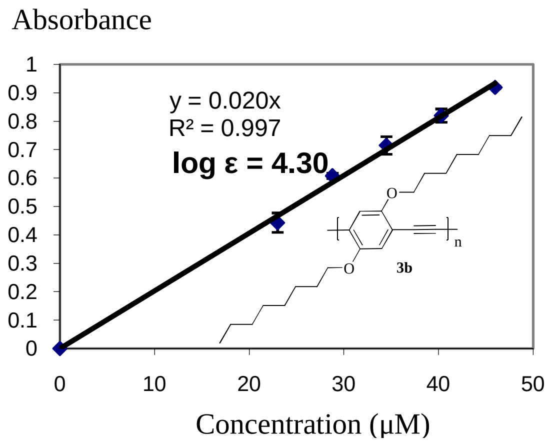
ตัวอย่างที่	ชื่อตัวอย่าง		%C	%H	%N
4	NTV-EA-192	(1)	71.80	6.96	…
		(2)	71.68	7.24	…
		(3)	71.97	7.07	…
		เฉลี่ย	**71.82**	**7.09**	**...**
	TMS-condition	Calc.	78.65	8.25	
5	NTV-EA-194	(1)	63.98	6.98	…
		(2)	64.31	6.87	…
		(3)	64.21	6.90	...
		เฉลี่ย	**64.17**	**6.92**	**...**
		Calc.	64.27	7.19	
6	NTV-EA-233	(1)	78.86	8.55	…
		(2)	79.28	8.59	…
		(3)	79.00	8.63	...
		เฉลี่ย	**79.05**	**8.59**	**...**
		Calc.	79.03	8.58	

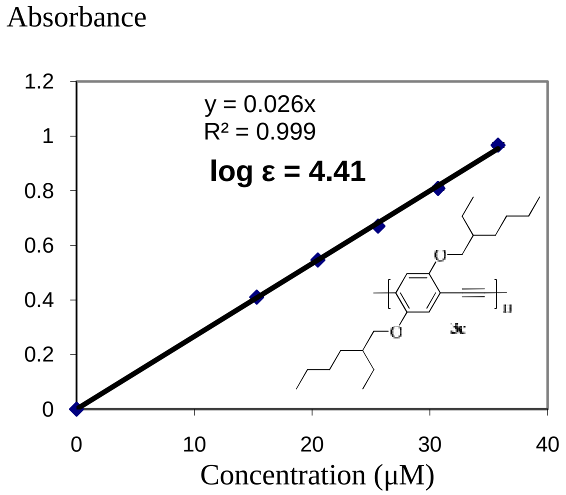
(นางสาว อัมพร อึ้งปกรณ์แก้ว)
ผู้วิเคราะห์

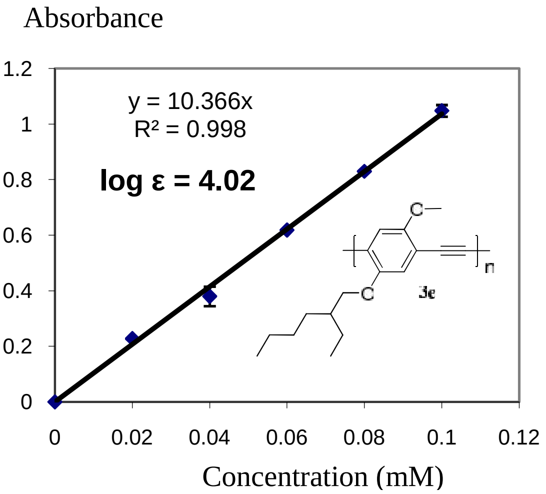
(นาง สุนันท์ รังษีกาญจน์ส่อง)
หัวหน้าฝ่ายวิเคราะห์

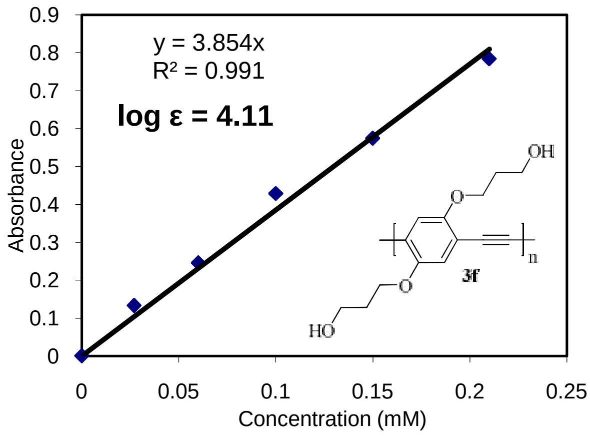
(รศ.ดร. อมร เพชรสม)
รักษาการแทนผู้อำนวยการ


Absorbance
y = 0.021x
R² = 0.992
log ε = 4.32
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
Concentration (μM)
O
O
n
3a

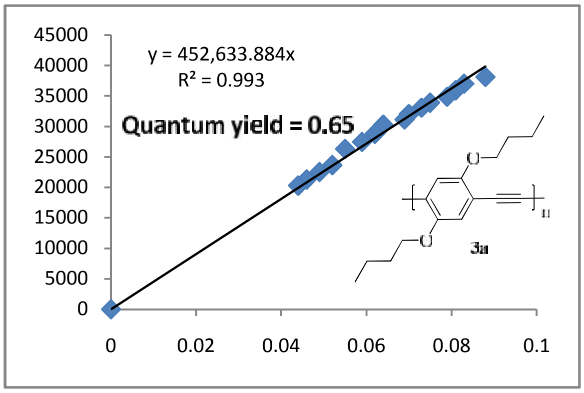

Absorbance
y = 0.020x
R² = 0.997
log ε = 4.30
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
Concentration (μM)
O
O
n
3b

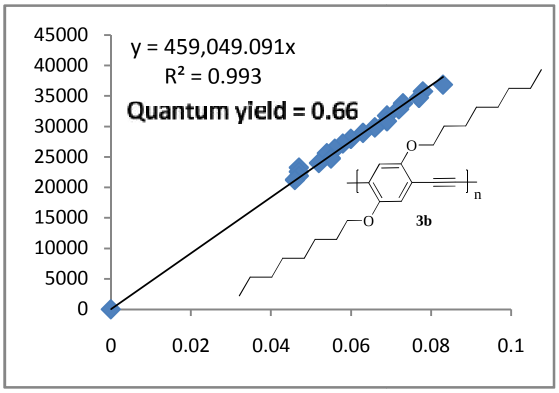

Absorbance
y = 0.026x
R² = 0.999
log ε = 4.41
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
Concentration (μM)
O
O
n
3c

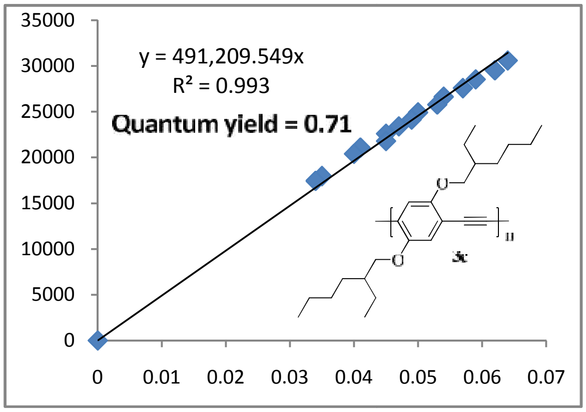

Absorbance
y = 10.366x
R² = 0.998
log ε = 4.02
1.2
1
0.8
0.6
0.4
0.2
0
0
0.02
0.04
0.06
0.08
0.1
0.12
Concentration (mM)
C
C
n
3e

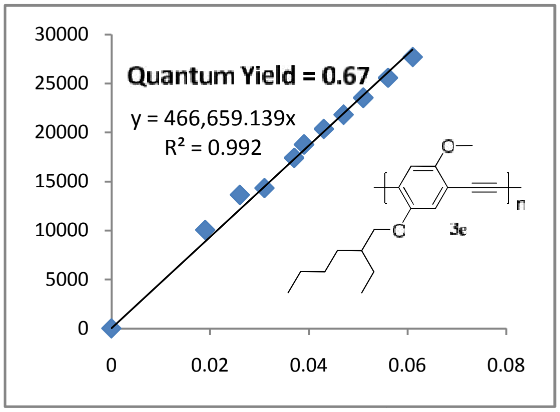

y = 3.854x
R² = 0.991
log ε = 4.11
Absorbance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.05
0.1
0.15
0.2
0.25
Concentration (mM)
OH
O
O
HO
n
3f

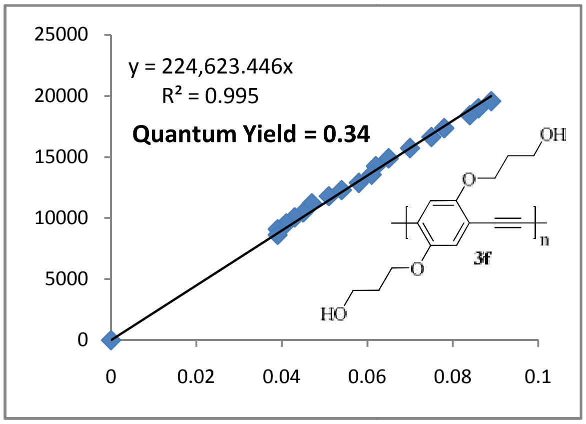
Quantum yield











VITAE

Miss Nopparat Thavornsin was born on March 14, 1988 in Bangkok, Thailand. She got a Bachelor's Degree of Science in Industry Chemical from King Mongkut's Institute of Technology Ladkrabang in 2010. Then, she started her a Master's Degree in Petrochemistry and Polymer Science program at Chulalongkorn University. She had presented her research on "Synthesis of Poly(phenylene ethynylene)s using Calcium Carbide" in 7th Mathematics and Physical Sciences Graduate Congress 2011 and The Pure and Applied Chemistry International Conference (PACCON 2012). Then, she went to Japan Advanced Institute of Science and Technology (JAIST) to associate in JASSO program for 42 days. After that, she came back to presented her research in the topic of "Synthesis of Poly(phenyleneethynylene)s from the Cost Effective Calcium Carbide as Acetylene Surrogate" in The Pure and Applied Chemistry International Conference (PACCON 2013) by poster presentation. Part of this work also submitted in the international journal, Macromolecules.

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