Master's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

Kristine Olsen Strandheim

Synthesis and Characterization of BODIPY Dyes for Optoelectronic Applications

Master's thesis in Organic Chemistry
Supervisor: Solon Economopoulos
September 2019

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Declaration

I hereby declare that the work presented in this master's thesis has been conducted individually. The study has been conducted in accordance with the rules and regulations for the integrated master's degree in Industrial Chemistry and Biotechnology (Master of Science degree, 5 years) at the Norwegian University of Science and Technology. The work has been performed from January 2019 to September 2019.

Trondheim, September 11, 2019

Kristine Olsen Strandheim

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Preface

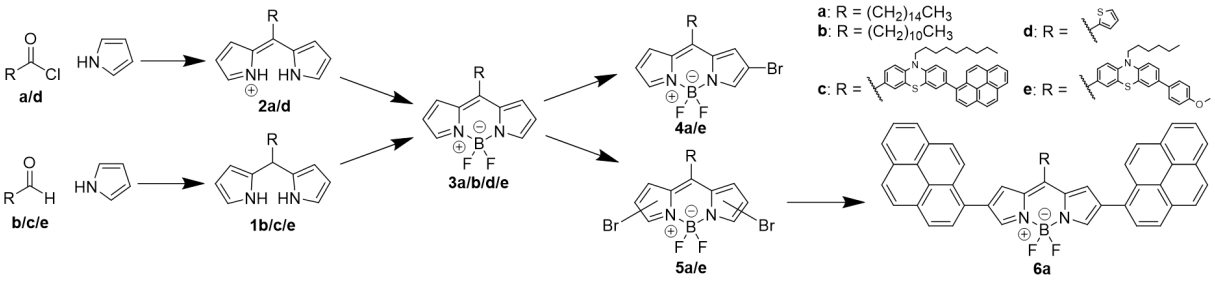
The presented work, "Synthesis and Characterization of BODIPY Dyes for Optoelectronic Applications", has been performed at the Department of Chemistry, Norwegian University of Science and Technology (NTNU).

I would like to thank my supervisor, Assoc. Prof. Solon Economopoulos, for accepting me as part of his research team and giving me the opportunity to work under his tutelage. The encouragement and guidance along the way have truly been appreciated.

Many thanks to Dr. Sigvart Evjen for inspiration and crazy ideas, and my boyfriend, Magnus Gryteselv, for being there for me and supporting me through challenging periods.

Abstract

The objective of the project was to synthesize novel boron dipyrromethene difluoride (F-BODIPY) chromophores. The synthetic pathway toward the target chromophores are depicted in Scheme 1. The finished dyes were to be used for different optoelectronic applications targeting solar cells. The one-pot reaction has been used to make BODIPY dyes **3a**/**d** from acid chlorides **a**/**d** and pyrrole, and the two step reaction with dipyrromethanes **1b**/**c**/**e** as intermediates, has been used to synthesize the BODIPY dyes **3b**/**e**.



Scheme 1: Synthesis of F-BODIPYs **3** from pyrrole and acid chloride or aldehyde. Top left: One-pot reaction with dipyrromethene **2a**/**d** as a theoretical intermediates. Bottom left: Two-step reaction with dipyrromethanes **1b**/**c**/**e** as intermediates, and BODIPYs **3b**/**e** as products. Right: Bromination reactions performed on BODIPYs **3a** and **3e**. Suzuki cross-coupling of 2,6-dibrominated BODIPY **5a** and pyrene-1-boronic acid.

The initial one-pot reactions were successful, BODIPY **3a** was synthesized, but low yields and challenging work up limited the applicability of the approach. A new modified one-pot method gave higher yield (10%) and less aggregated reaction mixture.

The two step route applied on dodecanal (**b**) gave a 90% yield of dipyrromethane **1b** in the first step, but no yield of BODIPY **3b** in the second step. Phenothiazine aldehyde **e** had good results with a yield of 73% and 89% for the first and second step, respectively.

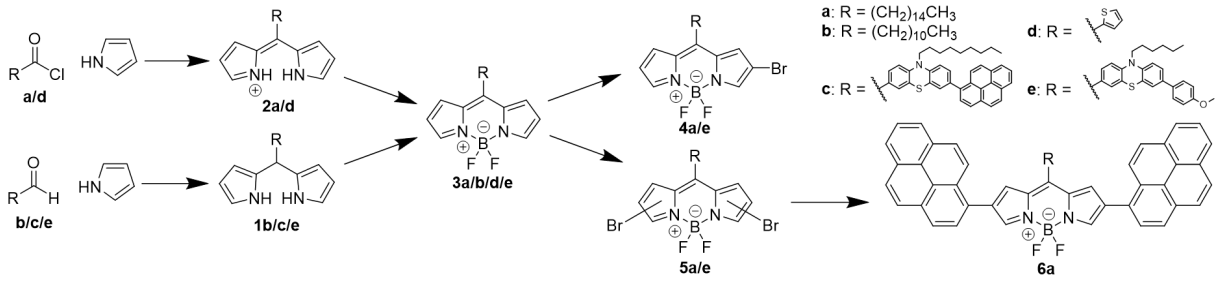
Bromination of BODIPYs **3a** and **3e** have been performed. Meso-alkyl BODIPY **3a** had a yield of 38% and 27% of 2-mono- and 2,6-dibrominated BODIPY, respectively, Scheme 1. Bromination of meso-phenothiazine BODIPY **3e** resulted in problems with overbromination. At lower temperatures, a mixture of α, β-mono- and dibrominated BODIPYs were obtained.

A Suzuki cross-coupling between 2,6-dibrominated BODIPY **5a** and pyrene-1-boronic acid was attempted at mild temperature. Issues with stability led to no product being formed.

Optical and electrochemical characterization of the purified chromophores was performed, alongside standard structural characterization by COSY, HSQC and HMBC as well as ^{1}H and ^{13}C NMR experiments.

Sammendrag

Målet for dette masterprosjektet var å syntetisere nye kromoforer basert på bor dipyrrometen difluorid (F-BODIPY) kromoforen. Reaksjonsruten mot de ønskede kromoforene er vist i skjema 2. De ferdige fargestoffene skulle brukes for optoelektroniske formål rettet mot solceller. "One-pot"-reaksjonen har blitt brukt for å lage BODIPY-fargestoffene **3a**/**d** fra syreklorider **a**/**d** og pyrrol, og to-trinns reaksjonen med dipyrrometaner **1b**/**c**/**e** som mellomprodukt, har blitt brukt til å lage BODIPY-fargestoffer **3b**/**e**.



Skjema 2: Syntese av F-BODIPY **3** fra pyrrol og syreklorid eller aldehyd. Topp venstre: "One-pot"-reaksjon med dipyrrometen **2a**/**d** som et teoretisk intermediat. Bunn venstre: To-trinns reaksjon med dipyrrometaner **1b**/**c**/**e** som mellomprodukter, og BODIPY-fargestoffene **3b**/**c**/**e** som produkter. Høyre: Bromineringsreaksjon utført på BODIPY kromoforene **3a** og **3e**. Suzuki koblingsreaksjon mellom 2,6-dibrominert BODIPY **5a** og pyren-1-borsyre.

De innledende "one-pot"-reaksjonene var vellykket, BODIPY-produktet **3a** ble laget, men lavt utbytte og utfordrende etterarbeid (work up) begrenset prosedyrens anvendbarhet. En ny, modifisert "one-pot"-metode ga høyere utbytte (10 %) og mindre sammenklumpet reaksjonsblanding.

Totrinns prosedyren utført med dodecanal (**b**) ga 90 % utbytte av dipyrrometan **1b** i det første trinnet, men ikke noe utbytte av BODIPY **3b** i det andre trinnet. Fenotiazinaldehyd **e** ga gode resultater med et utbytte på henholdsvis 73 % og 89 % for første og andre trinn.

Brominering av BODIPY **3a** og **3e** har blitt utført. Meso-alkyl-BODIPY **3a** hadde et utbytte på 38 % og 27 % av henholdsvis 2-mono- and 2,6-dibrominert BODIPY, skjema 2. Brominering av meso-fenotiazin-BODIPY **3e** resulterte i problemer med overbrominering. Ved lavere temperaturer ble en blanding av α,β-mono- og dibrominerte produkter dannet.

En Suzuki-krysskoblingsreaksjon mellom 2,6-dibrominert meso-alkyl BODIPY **5a** og pyren-1-borsyre ble forsøkt ved mild temperatur. Problemer med stabilitet ledet til at produkt ikke ble dannet.

Optisk og elektrokjemisk karakterisering av rene kromoforer ble utført, i tillegg til standard struktur karakterisering ved hjelp av COSY, HSQC og HMBC samt ^{1}H og ^{13}C NMR eksperimenter.

Symbols and abbreviations

Ar	aromatic
BHJSC	bulk heterojunction solar cell
BODIPY	boron dipyrromethene
br	broad (NMR)
brs	broad singlet (NMR)
cat.	catalyst
CD_2Cl_2	deuterated dichloromethane
$CDCl_3$	deuterated chloroform
$(CHCl)_2$	1,2-dichloroethane
CH_2Cl_2	dichloromethane
conc.	concentrated
corr.	corrected
COSY	Correlated Spectroscopy
cps	counts per second
δ	chemical shift [ppm]
δ^+	delta positive charge (carbonyl carbon)
d	doublet (NMR)
DCM	dichloromethane
dd	doublet of doublets (NMR)
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DIPEA	*N,N*-diisopropylethylamine (Hünig's base)
DMF	dimethylformamide
DPMa	dipyrromethane
DPMe	dipyrromethene
DSSC	dye-sensitized solar cell
EDG	electron donating group
eq.	equivalent
et al.	et alia (and others)
Et_2O	diethyl ether
Et_3N	triethylamine
EtOAc	ethyl acetate
EWG	electron withdrawing group
F-BODIPY	boron dipyrromethene difluoride
F-BODIPY	4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene

HMBC	Heteronuclear Multiple Bond Correlation
HSQC	Heteronuclear Single Quantum Coherence
Hz	hertz
i-Pr	*iso*-propyl
IR	Infrared Spectroscopy
J	coupling constant [Hz]
KS-x	reaction number x performed by Kristine Strandheim (author)
L	ligand
m	multiplet (NMR)
m	meta
Me	methyl
min	minutes
mL	milliliter
mmol	millimol
NBS	*N*-bromosuccinimide
nm	nanometer
NMR	Nuclear Magnetic Resonance
Nu	nucleophile
o	ortho
obsd	observed
p	para
η	efficiency
Ph	phenyl
ppm	parts per million
PV	photovoltaic
quint	quintet (NMR)
Rf	retention factor (TLC)
RT	room temperature
rx.	reaction
s	singlet (NMR)
t	triplet (NMR)
TFA	trifluoroacetic acid
TLC	Thin Layer Chromatography
Å	Ångström (1 Å = 0.1 nm)

List of compounds

General numbering of compounds

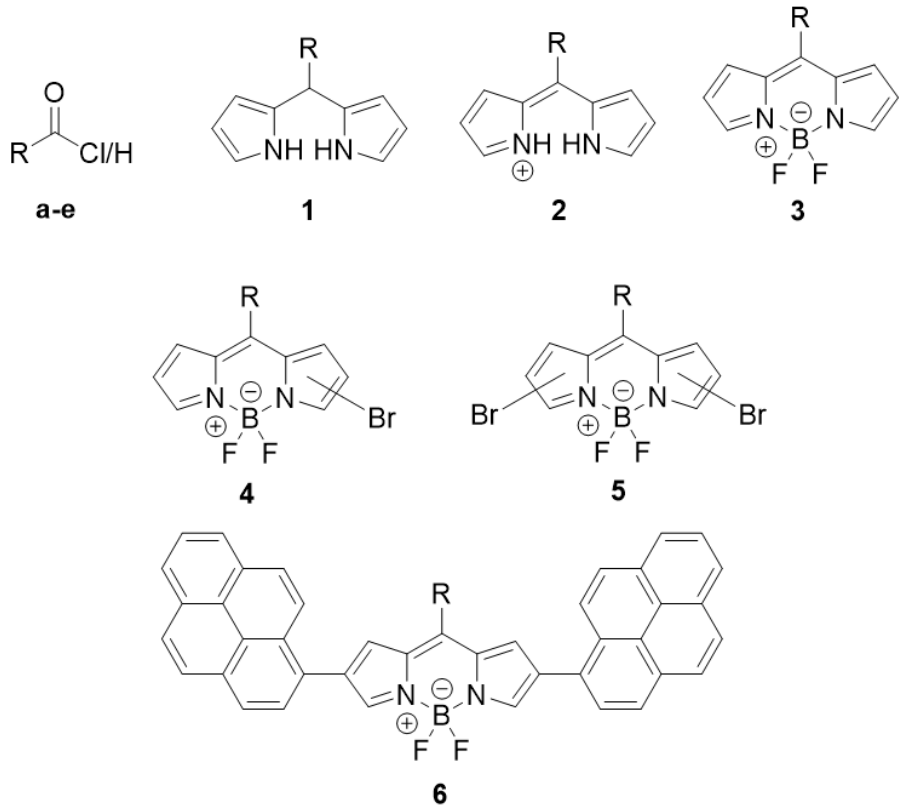


Figure 3: All compounds that have been synthesized or attempted synthesized, during the project and master assignment, have been given a number and a letter. The number corresponds to one of the basic forms 1 to 6 shown above, while the letter a to e refers to the side chain R coming from the initial acid chloride or aldehyde substrate. Aldehyde substrates are used in two step reactions to form BODIPYs **3** with dipyrromethanes **1** (DPMa) as intermediate products. Acid chlorides yield BODIPYs **3** directly from one-pot synthesis with dipyrromethenes **2** (DPMe) as theoretical intermediates.

BODIPYs from palmitoyl chloride (a)

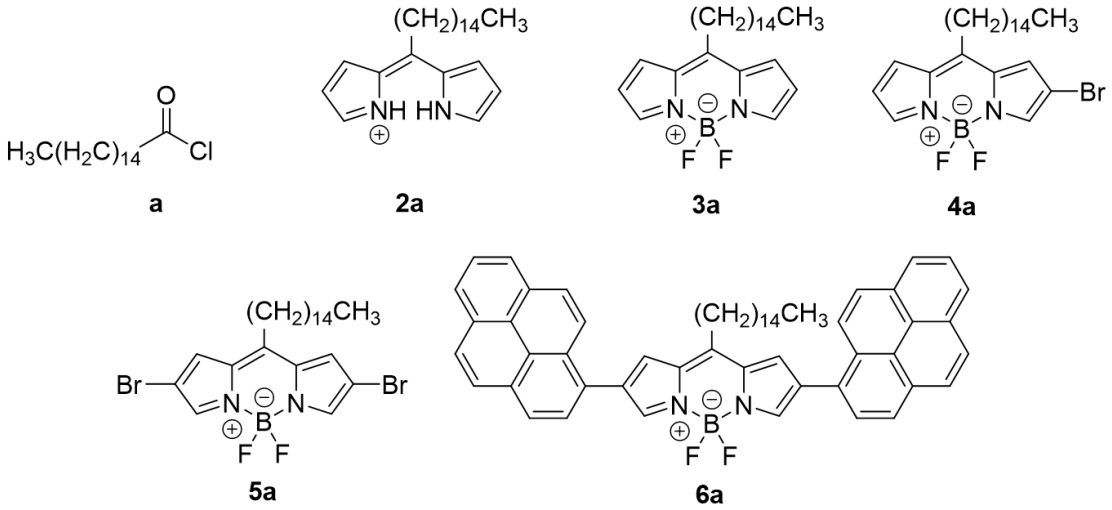


Figure 4: BODIPY and pre-BODIPY compounds synthesized and attempted synthesized with pentadecyl side chain from starting substrate palmitoyl chloride (**a**).

Previous BODIPYs from dodecanal (b) and phenothiazine aldehyde (c)

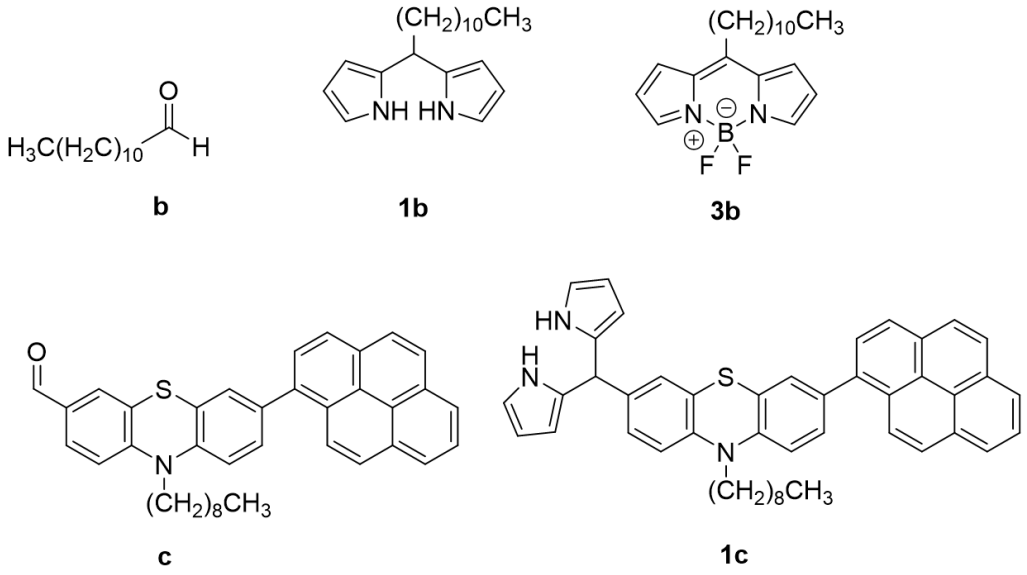


Figure 5: BODIPY and pre-BODIPY compounds synthesized and attempted synthesized during the project assignment with undecyl side chain from starting substrate dodecanal (**b**) and a phenothiazine side chain from starting substrate 10-nonyl-7-(pyren-2-yl)-10*H*-phenothiazine-3-carbaldehyde (**c**).

BODIPY from 2-thiophenecarbonyl chloride (d)

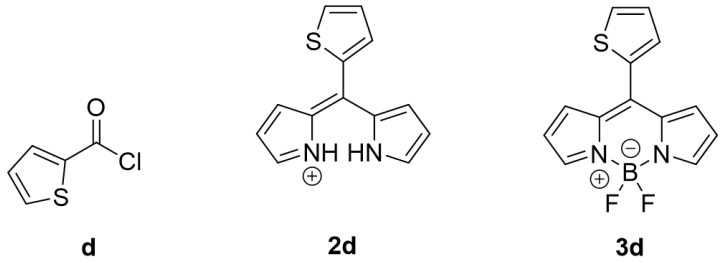


Figure 6: BODIPY and pre-BODIPY compounds attempted synthesized with thiophene-2-yl side chain from starting substrate 2-thiophenecarbonyl chloride (**d**).

BODIPYs from phenothiazine aldehyde (e)

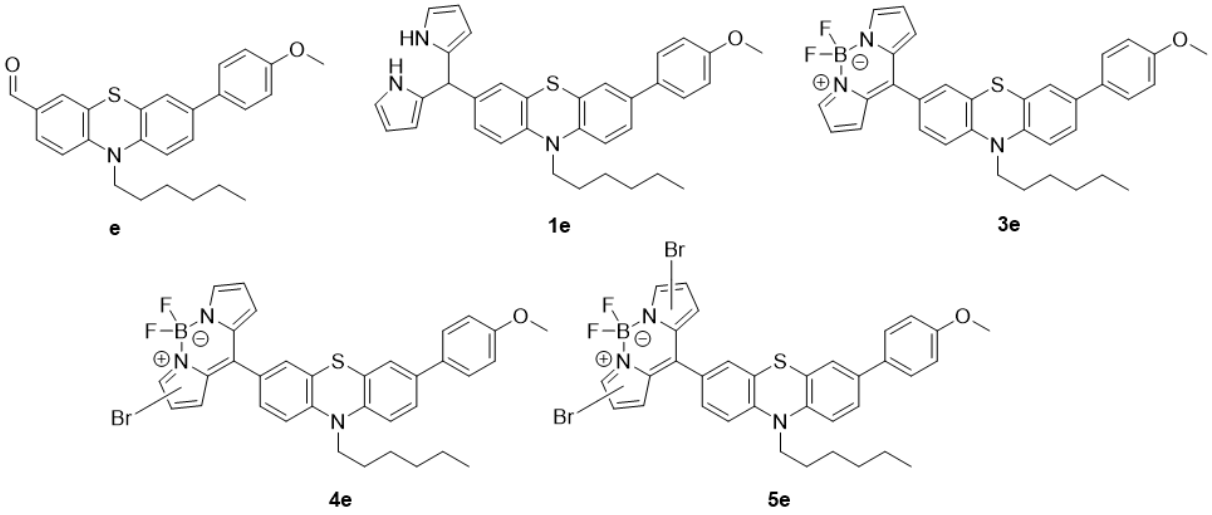


Figure 7: BODIPY-phenothiazine multichromophores synthesized from starting substrate 10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazine-3-carbaldehyde (**e**).

Contents

Chapter 1

Introduction

The first BODIPY dyes were reported in 1968 by Treibs and Kreuzer.[1] The discoverers of this unique family of dyes noted their bright green color and highly fluorescent character.[1] The dyes were not thoroughly investigated until the 1980s when their potential utilization as biological labeling agents were suggested.[2,3]

In general the F-BODIPY dyes absorb strongly in the UV-region, and have sharp emission peaks with high quantum yields.[3] The dyes are relatively insensitive to the pH and polarity of their environment, making them reasonably stable under physiological conditions.[3] Since the 80s many different applications of BODIPY dyes have been discovered, and some have been commercialized.[2] The research applications range from chemo-sensors, labeling reagents and photodynamic therapy agents to tunable laser dyes and organic photovoltaics.[2–7]

Most of the previous research efforts have been focused on to 1,3,5,7-tetramethylated F-BODIPYs, because of their ease of synthesis and functionalization.[2] The scientific interest is currently on removing these methyl substituents to enable higher conjugation and planarity of the F-BODIPYs.[8] Longer conjugation and greater planarity could yield fluorophores that absorb and emit in the red visible (Vis) to near infrared (NIR) spectral range.[8] Stable dyes with sharp absorption and fluorescence emission bands in these regions, combined with high fluorescence quantum yields and high molar absorption coefficients, may find extensive use in many different fields, such as optical engineering, analytical chemistry, sensing applications, and materials science.[8]

1.1 Aim of project

The aim of this master's project is to look into synthesis of 1,3,5,7-unsubstituted F-BODIPY dyes for optoelectronic applications. The main focus of the assignment has been on testing and development of synthetic routes for synthesis of different α,β-unsubstituted BODIPYs, as well as 2-mono- and 2,6-dibromination of said BODIPYs. Brominated chromophores are to be coupled with π-spacers (to enhance absorption properties) and different anchoring groups to facilitate attachment to graphene (covalently and non-covalently) or TiO_2. The research group's main interest concerns exploration of the properties of new BODIPY graphene hybrid materials.

This master's project is a continuum of the project assignment "*Synthesis and Characterization of BODIPY Dyes for Optoelectronic Applications*" performed autumn 2018 by Kristine Olsen Strandheim (current author).[9] The project is a continuation of work done on dyes and carbon nanomaterials performed by Assoc. Prof. Solon Economopoulos and others during his research career at Cyprus University of Technology, National Hellenic Research Foundation (NHRF) and Norwegian University of Science and Technology (NTNU). As well as work performed by Hans-Petter Larsen,[10] during his synthesis project in TKJ4130 spring 2018. Previous work include, but are not limited to, BODIPYs, phenothiazines, multichromophores and graphene hybrid materials.[6,11–15]

Chapter 2

Theory

In the following chapter a brief theoretical background for the project is given. The first section is on properties, use and research on F-BODIPY materials. The second section focuses on different approaches for synthesis of F-BODIPY dyes, while functionalization of BODIPYs is discussed in the third part. A brief overview on synthesis and properties of graphene and graphene hybrid materials is presented in section four.

2.1 Properties of BODIPY dyes and derivatives

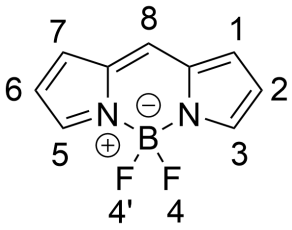


Figure 2.1: F-BODIPY core with numbered positions. 3,5 are α-positions, 1,2,6,7 are β-positions and 8 is the meso-position.

The unsubstituted F-BODIPY frame is shown in Figure 2.1, the position numbering system is derived from *s*-indacene.[2,3] F-BODIPY is an abbreviation of boron dipyrromethene difluoride. However, the IUPAC name of the compound family is 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene.[5] All of the numbered positions 1 to 8 can be chemically modified.[2]

The optoelectronic properties of F-BODIPY dyes can be affected by the substituents on the core structure.[5] Figure 2.2 and Figure 2.3 show how substituents in the meso-position affects fluorescence quantum yield (Φ) and shift the absorption and emission maxima. Φ is the ratio of emitted and absorbed light, often determined versus fluorescein in 0.1 N NaOH ($\Phi = 0.90$) as reference.[5] In general, electron donating groups (EDG) blue shifts the absorption and emission maxima, while electron withdrawing groups (EWG) red shifts the maxima. A red shift of maxima can also be achieved by increased conjugation.[5,8]

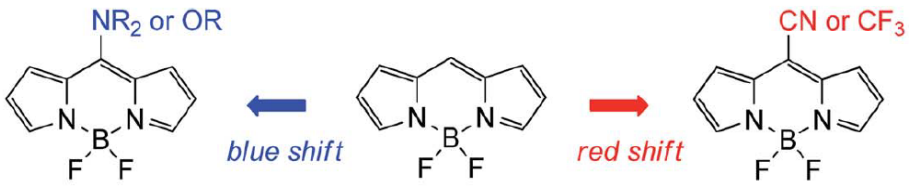


Figure 2.2: Effect of meso-substituent on shift of absorption and emission maxima for F-BODIPY dyes. R is in this context an abbreviation for an unspecified alkyl group.[5]

Meso-alkylation with saturated carbon chains does usually not affect optical properties compared with unsubstituted F-BODIPY dye. The exception being meso-*tert*-butyl

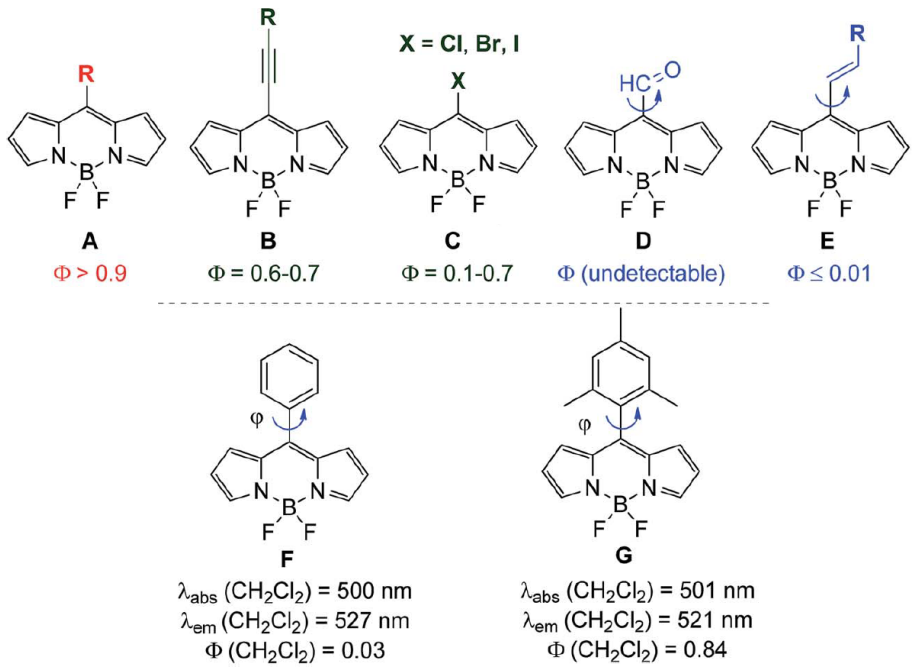


Figure 2.3: Effect of meso-substituent on fluorescence quantum yield (Φ) in F-BODIPY dyes. R is in this context an abbreviation for an unspecified alkyl group.[5]

F-BODIPY, due to distorted planarity of the core moiety.[5] Planar dyes often have problems with solubility and aggregation, which is why an anti-aggregation moiety is usually incorporated.[15] A dye design based on phenothiazine, previously made for DSSC (dye-sensitized solar cell) applications at NTNU,[15] is shown in Figure 2.4. Auxiliary donors and π-spacers are introduced to push the absorption towards the infrared region of the electromagnetic spectrum.[15] Multichomophores with phenothiazine and F-BODIPY units have previously been reported by several research groups with promising results regarding absorption.[16–19] A common approach to functionalization of F-BODIPY dyes is selective halogenation, followed by a coupling reaction.[2]

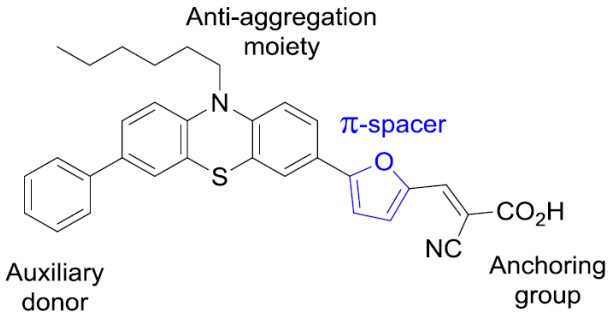
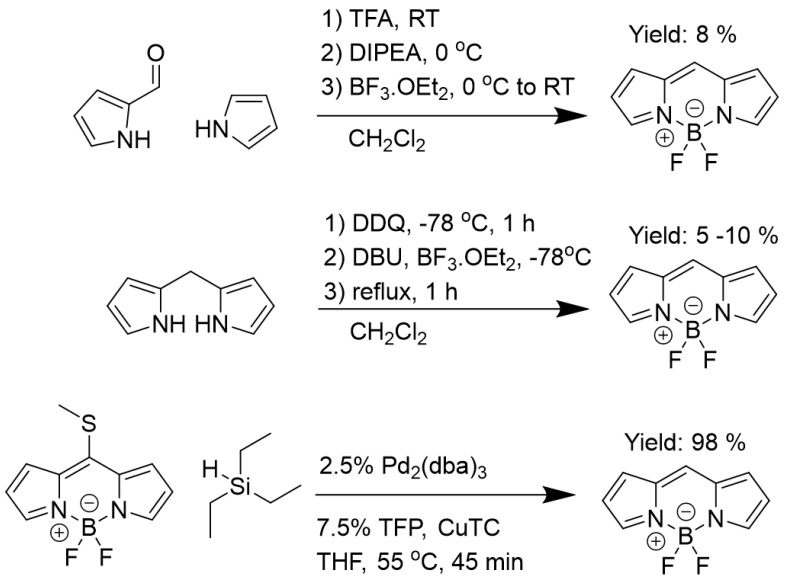


Figure 2.4: Example of dye design for attachment to TiO_2 for dye-sensitized solar cell (DSSC) applications.[15]

2.2 Synthesis of α, β-unsubstituted F-BODIPY dyes

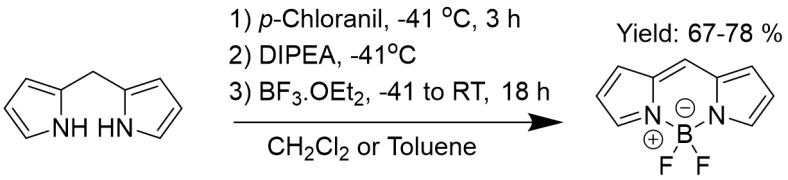
Synthesis of the fully unsubstituted F-BODIPY

Most of the developments in F-BODIPY chromophores have been focused on 1,3,5,7-tetramethylated derivatives, as they are easier to synthesize and chemically modify.[2] Surprisingly, the unsubstituted F-BODIPY core was not reported until 2009. In 2009 it was reported by three different research groups,[20–22] using three different approaches, see Scheme 2.5. A condensation reaction between pyrrole and pyrrole-2-carboxaldehyde followed by borylation was reported, with a yield of 8%.[20] An oxidation of dipyrromethane followed by borylation was reported, with a yield of 5-10%.[21] Additionally, a rather different approach with dethiomethylation of 8-thiomethyl F-BODIPY by palladium catalysis was reported.[22] The yield of the dethiomethylation was 98%, but synthesis of 8-thiomethyl F-BODIPY is a prerequisite.



Scheme 2.5: First reported procedures of fully unsubstituted F-BODIPY. From top to bottom: Condensation reaction between pyrrole and pyrrole-2-carboxaldehyde followed by borylation.[20] Oxidation of dipyrromethane followed by borylation.[21] Dethiomethylation of 8-thiomethyl F-BODIPY by palladium catalysis.[22]

A fourth research group made further developments in the synthesis of the fully unsubstituted F-BODIPY by oxidation of dipyrromethane.[23] The yield was increased from 8% to 67-78% by use of a weaker oxidant, higher temperature (-41 °C instead of -78 °C) and different base, as shown in Scheme 2.5 and Scheme 2.6.

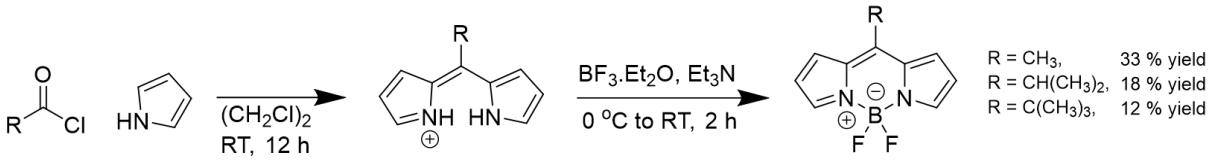


Scheme 2.6: Improved synthesis of fully unsubstituted F-BODIPY by oxidation and borylation of dipyrromethane.[23]

Synthesis of α,β-unsubstituted meso-alkylated F-BODIPY

Only a handful of α,β-unsubstituted meso-alkylated F-BODIPY dyes have been reported. Of 863 α,β-unsubstituted meso-substituted F-BODIPY dyes only 13 have acyclic carbon chains (SciFinder, 03.12.18). Of the 13 compounds; 7 have alkyl chains, of which the longest chain is *n*-pentyl. Both *n*-pentyl and *n*-butyl meso-substituted F-BODIPYs have been synthsized from other F-BODIPY dyes through alkylation with organolithium reagents or reduction of double bond.[24,25]

A one-pot synthesis of meso-substituted F-BODIPY dyes from pyrrole and acid chlorides has previously been reported.[26] Several meso-alkylated F-BODIPY dyes have been reported by this method,[5,26] as shown in Scheme 2.7. Acid chloride is used as both electrophile and a source of *in situ* generated acid catalyst (HCl). A simplified mechanism for the one-pot reaction is proposed in Figure 2.8.



Scheme 2.7: Meso-alkylated F-BODIPY dyes synthesized from pyrrole and acid chloride in a one-pot reaction.[5,26]

A one-pot procedure, similar to the previously reported procedures,[5,26] have been shown to yield poor results using a long chained acid chloride (palmitoyl chloride, **a**).[9] Several weaknesses of the procedure have been identified, and is presented thoroughly in the Results and Discussion of this master's thesis and the previous project report.[9]

An alternative approach, to a one-pot formation of α,β-unsubstituted meso-alkylated F-BODIPY, is a two-step reaction with a dipyrromethane (DPMa) as an intermediate product. The method have previously been used to make α,β-unsubstituted meso-thiophene F-BODIPYs for functionalization into a copolymer for near infrared polymer light harvesters for bulk heterojunction (BHJ) organic photovoltaics.[27] The first step of the two-step reaction is a condensation between pyrrole and an aldehyde to form a dipyrromethane (DPMa) **1**, see Scheme 2.9 and Figure 2.10. The chain of the aldehyde becomes the meso-substituent in the final F-BODIPY product. The second reaction is

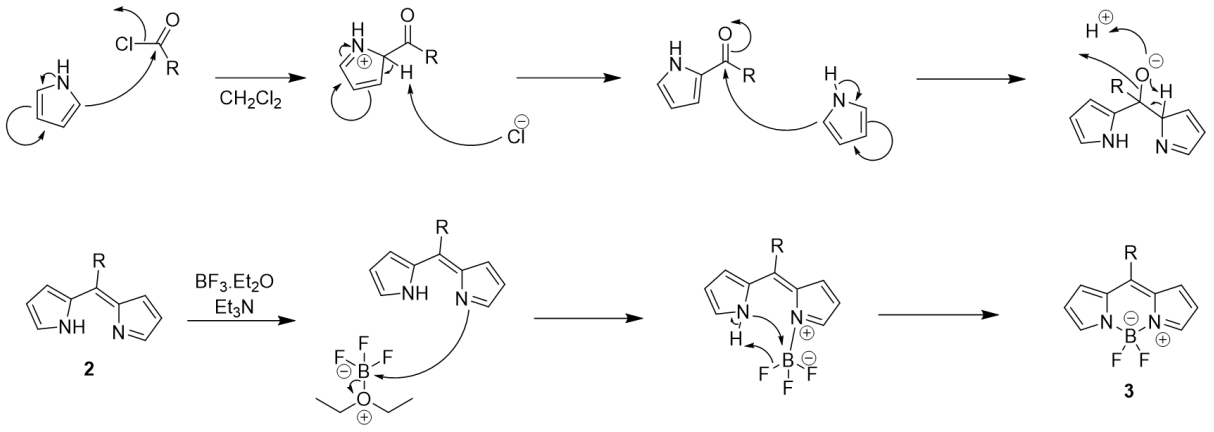
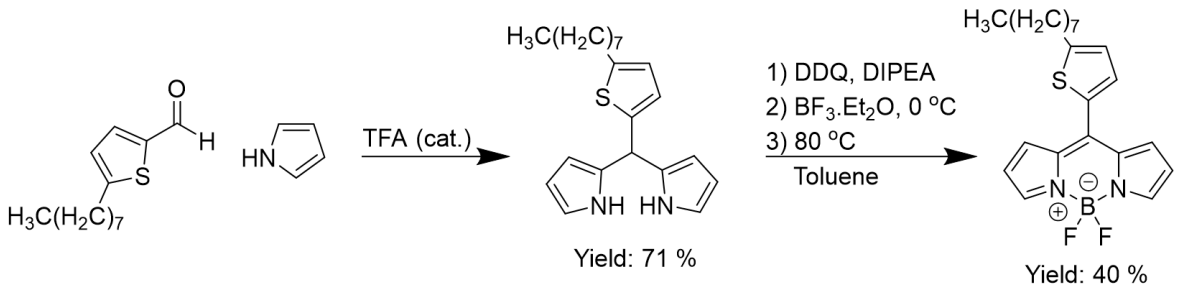


Figure 2.8: Proposed simplified mechanism for one-pot condensation reaction between pyrrole and acid chloride to form dipyrromethene (DPMe) **2**, followed by borylation to give F-BODIPY **3**.

an oxidation and borylation of the DPMa **1**, as shown in Scheme 2.9 and Figure 2.11. With a yield of 71% for the first step, and 40% for the second step, the overall yield of the meso-thiophene BODIPY is 28%. The yields of two step procedures in general are better than the presented yields of the one-pot procedures for meso-alkylated BODIPYs. However, two reactions and work ups are required as opposed to one.



Scheme 2.9: Two-step reaction to form a α,β-unsubstituted meso-thiophene F-BODIPY. Condensation reaction between pyrrole and aldehyde will form a dipyrromethane (DPMa). DPMa is then oxidized by DDQ and borylated.[27]

Condensation reactions with pyrrole and dodecanal **b**, inspired by reported procedures,[27] have been performed to give DPMa **1b**.[9] The obtained DPMa product **1b** has been observed to decompose in air at room temperature (RT). The decomposition is slow, but can be observed as a change in color from yellow to dark brown over time. The DPMa **1b**, obtained from the condensation reaction in the first step, was oxidized with DDQ. No BODIPY product was formed from the borylation following the oxidation. The alkylated DPMa **1b**, and related intermediate products, have shown a lower stability than initially anticipated by the research group.[9] The synthesis of meso-alkylated BODIPYs does not seem to be comparable with the compounds previously reported,[27] see Scheme 2.9. It can

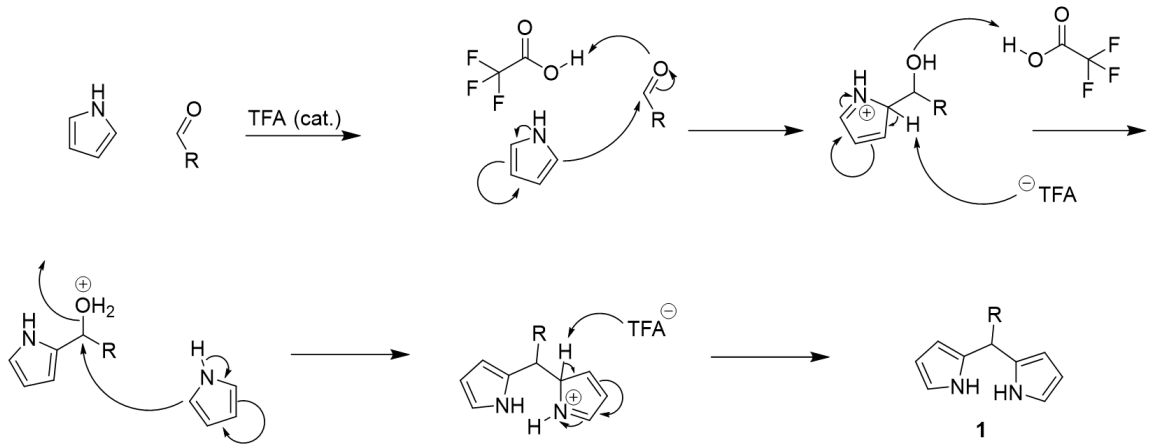


Figure 2.10: Proposed simplified mechanism for condensation reaction between pyrrole and aldehyde to form dipyrromethane (DPMa) **1**.

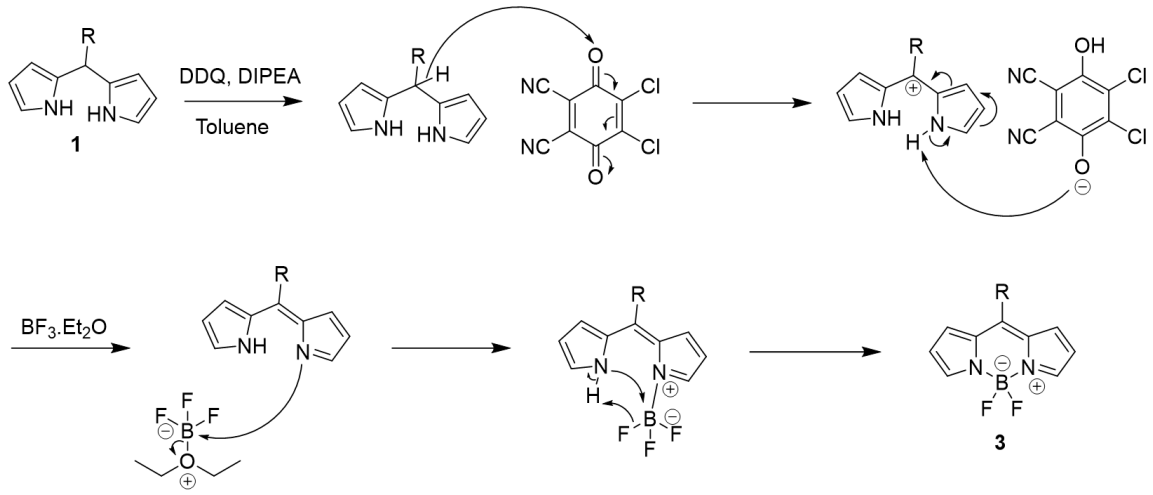


Figure 2.11: Proposed simplified mechanism for oxidation of dipyrromethane (DPMa) **1** followed by borylation to give F-BODIPY **3**.

be deduced that the electron-rich thiophene substituent is much more stabilizing to the cationic intermediate product than an alkyl group, mechanism shown in Figure 2.11.

2.3 Functionalization of BODIPY dyes

Electrophilic substitution of 2,6-positions

Aromatic rings are able to react as nucleophile in electrophilic aromatic substition (EAS). This reaction is often used as the principal reaction of aromatic functionalization. In the case of BODIPY, an EAS can take place in order to replace the H-atoms of the core moiety. Although F-BODIPY do not fulfill Hückel's rule it is viewed as an aromatic system.

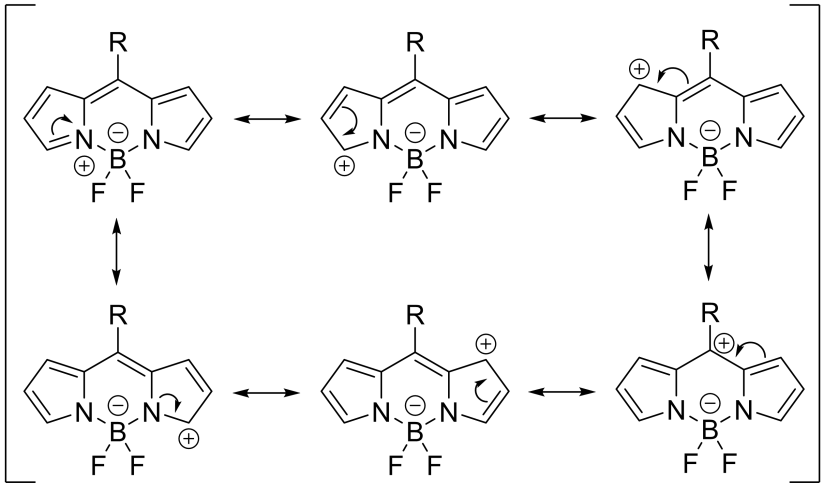


Figure 2.12: Resonance structures of the BODIPY core moiety, the bottom and top left structures are in resonance due to free rotation of the meso-bond.

The resonance structures of an α, β-unsubstituted BODIPY are shown in Figure 2.12. The resonance structures are important when determining where an electrophilic substitution will take place. Due to the partial positive charge on C-atoms in 1,3,5,7-positions the 2,6-positions are the preferred reaction sites of an EAS. Depending on electrophile, the aromatic system is either activated or deactivated for further EAS reactions when the initial substitution has taken place.

In the case of bromination, the bromine substituent is weakly deactivating to further attacks. The deactivating substitute effect of bromine is beneficial in regards to the risk of over-bromination of a substrate, making regioselective reactions easier to perform. Likewise, the meso-substituent can have an activating or deactivating effect as illustrated in Figure 2.13.

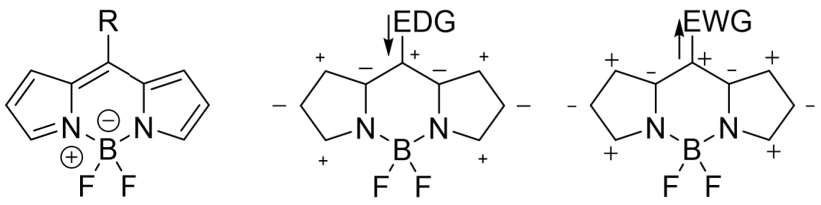
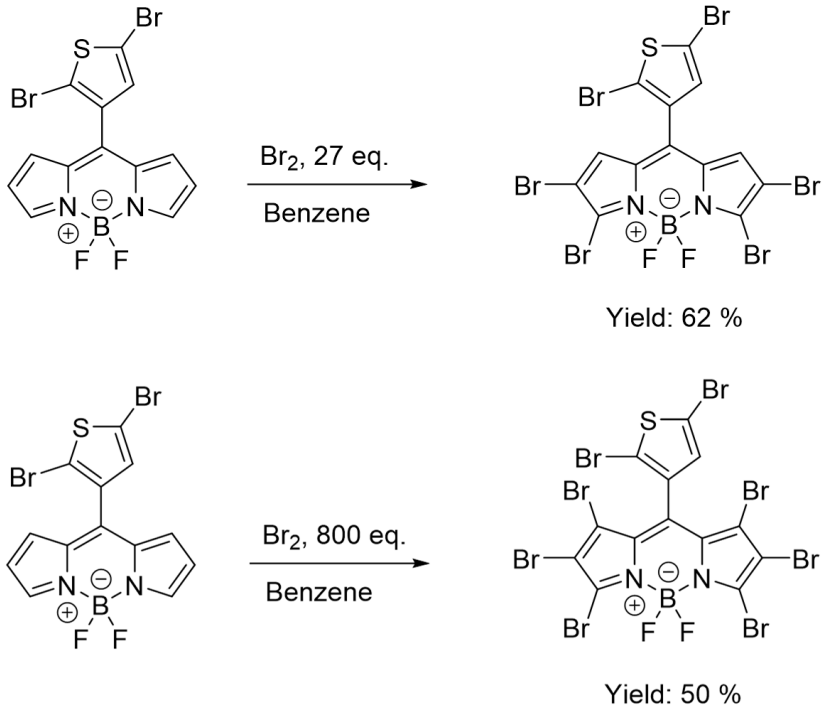


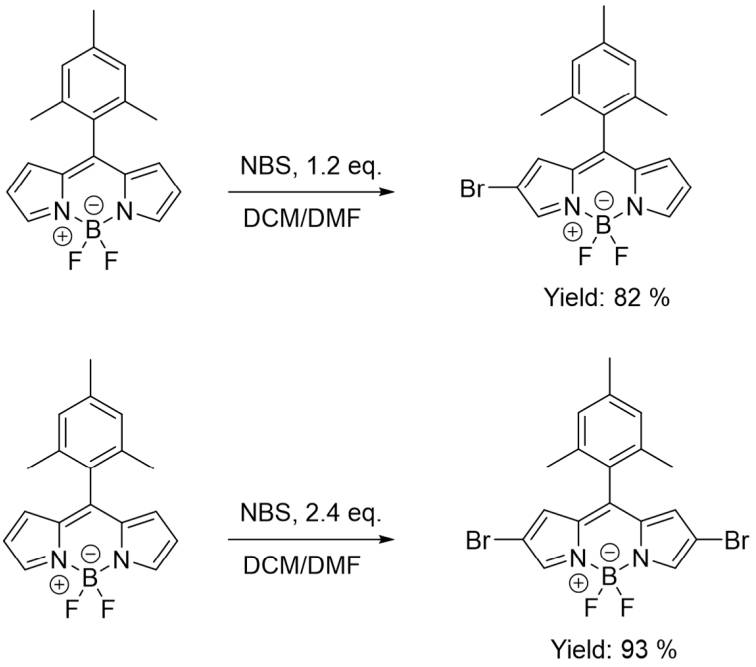
Figure 2.13: The subtituent effect of electron rich and electron deficient meso-substituents on the carbon atoms of the BODIPY core system. EDG = Electron Donating Group, EWG = Electron Withdrawing Group

2,6-Halogenated BODIPYs have traditionally been synthesized from 1,3,5,7-tetramethylated BODIPYs, or by halogenation of the DPMa precursor. The blocking effect of the methyl groups is beneficial regarding the specificity of the reaction. Regioselective halogenation of α,β-unsubstituted F-BODIPYs was first achieved in 2008,[28] and later improved.[29]



Scheme 2.14: Top: First regioselective halogenation of α,β-unsubstituted F-BODIPY. Bottom: Full bromination of α,β-unsubstituted F-BODIPY.[28]

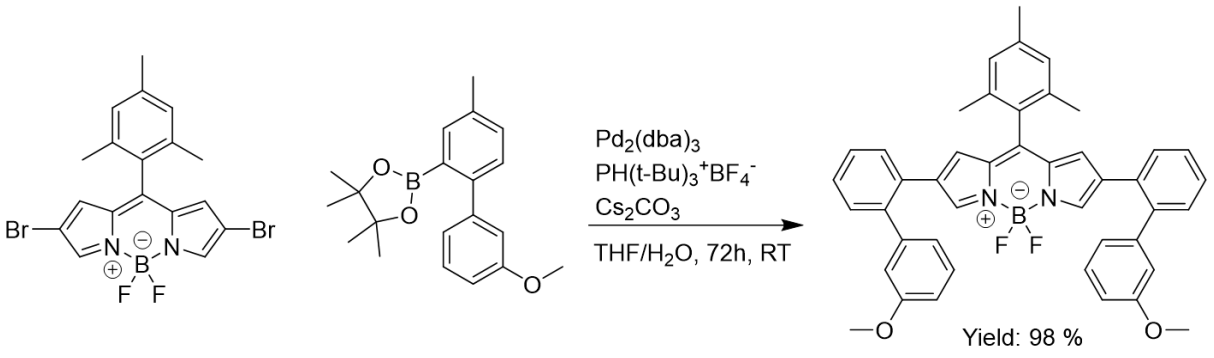
The initial experiments with Br_2 in benzene yielded tetra- and hexabrominated BODIPYs,[28] see Scheme 2.14. Dibrominated BODIPYs proved difficult to isolate.[28] A different bromination procedure involving *N*-bromosuccin-imide (NBS) in a 1:1 mixture of dichloromethane (DCM) and dimethylformamide (DMF) allowed for the isolation of both mono- and dibrominated BODYIPYs,[29] Scheme 2.15.



Scheme 2.15: Improved regioselective halogenation of α,β-unsubstituted F-BODIPYs.[29]

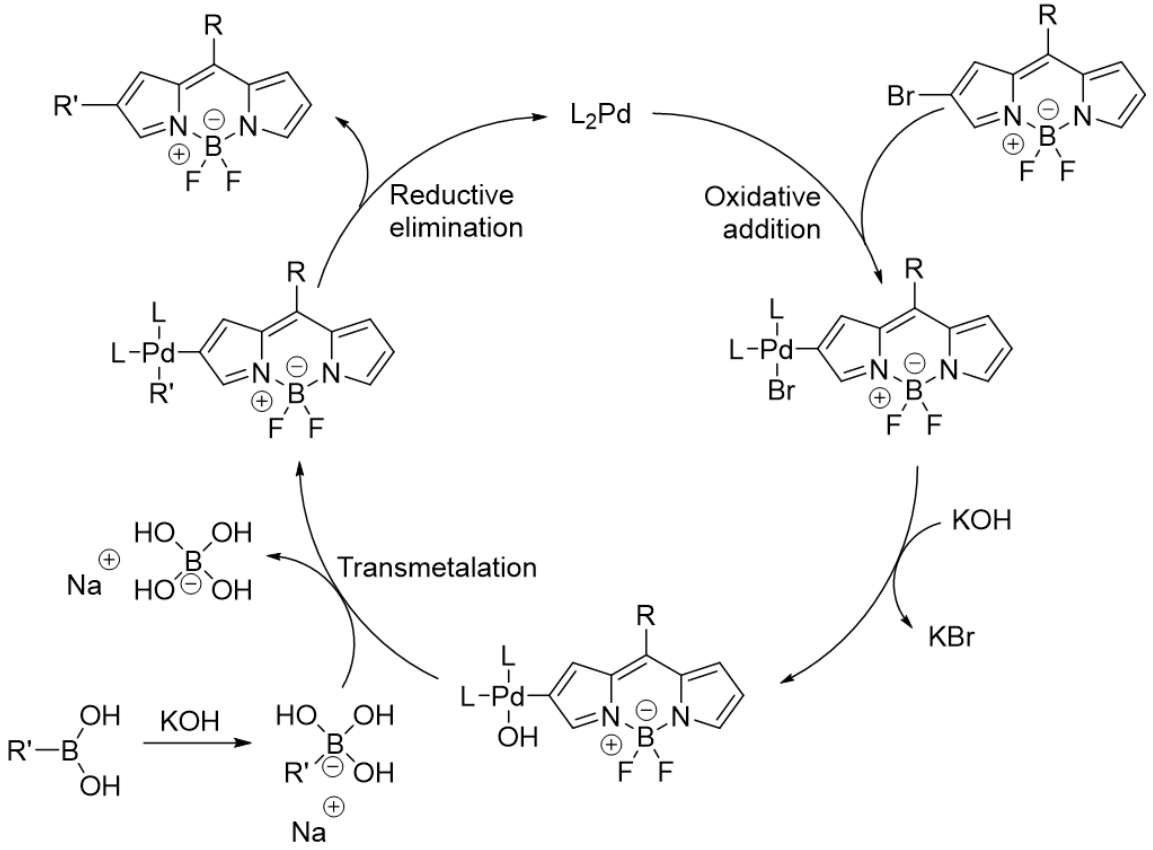
Nucleophilic substitution of leaving groups in 2,6-positions

Mono- and dibrominated BODIPYs make good substrates for different cross-coupling reactions, of which Suzuki coupling is one of the most famous. In 2010 Richard F. Heck, Ei-ichi Negishi and Akira Suzuki were awarded the Nobel Prize in Chemistry for their effort into developing palladium-catalyzed cross-coupling reactions. The different coupling reactions pose efficient means of creating new carbon-carbon bonds. While the oxidative addition and reductive elimination mechanisms are reasonably well understood, and are presumably fundamentally common processes for all cross-coupling reactions of organometallics, less is known about the transmetalation step, see Scheme 2.17. The cross-coupling reactions are excellent at extending the degree of π-electron conjugation and for attachment of, for example, anchoring groups.



Scheme 2.16: Suzuki cross-coupling reaction on 2,6-dibrominated BODIPY.[30]

A room temperature (RT) Suzuki cross-coupling reaction on 2,6-dibrominated meso-mesityl BODIPY have been achieved with a 98% yield.[30] The reaction is shown in Scheme 2.16. Both boronic acid substrates and pinacol boronate substrates, as shown in the catalytic cycle (Scheme 2.17) and the coupling reaction (Scheme 2.16), respectively, are common in Suzuki cross-coupling reactions.



Scheme 2.17: Example of catalytic cycle of cross-coupling reaction with monobrominated BODIPY substrate. Inspired by Miyaura and Suzuki (1995).[31]

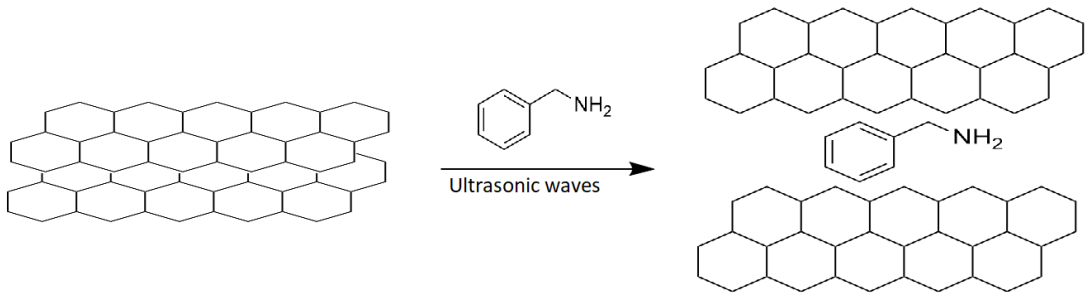
2.4 Graphene and graphene hybrid materials

The BODIPY chromophores, once properly functionalized, can be coupled with graphene. Depending on anchoring system the dyes can be covalently or non-covalently bound to the graphene sheets.

Preparation of graphene

The term graphene is used to refer to single layers of graphite, but it may also be used prefixed by 'monolayer', 'bilayer' or 'few-layer'. Graphene is made up by sp^2-hybridized carbon atoms arranged in a hexagonal lattice with partially filled p-orbitals.[32] The partially filled p-orbitals make graphene an excellent conductor. In graphite, the layers are held together by van der Waals interactions and each layer is spaced by 3.41 Å (0.341 nm).[33] Graphene can be produced by a wide variety of methods, at different expenses and of varying quality.[34] Some scalable methods are molecular assembly, liquid-phase exfoliation, reduction of graphene oxide, and graphene grown on silicon carbide (SiC),[34] see Figure 2.19. Chemical vapor deposition (CVD) and mechanical exfoliation of graphene are not considered to be suitable methods for mass-production.

Liquid-phase exfoliation from bulk graphite is the most economical way to achieve larger quantities of single layer graphene.[33] Graphite can be separated into mono to few-layer sheets of graphene by ultrasonication with an exfoliating agent in a suitable solvent. The exfoliating agent can be a solvent in itself, such as benzylamine or N-methyl-2-pyrrolidone (NMP).[33,35] An example with benzylamine as solvent and exfoliating agent is shown in Scheme 2.18.



Scheme 2.18: Exfoliation of graphite by ultrasonication in benzylamine. The double bonds of graphene are excluded for simplicity.

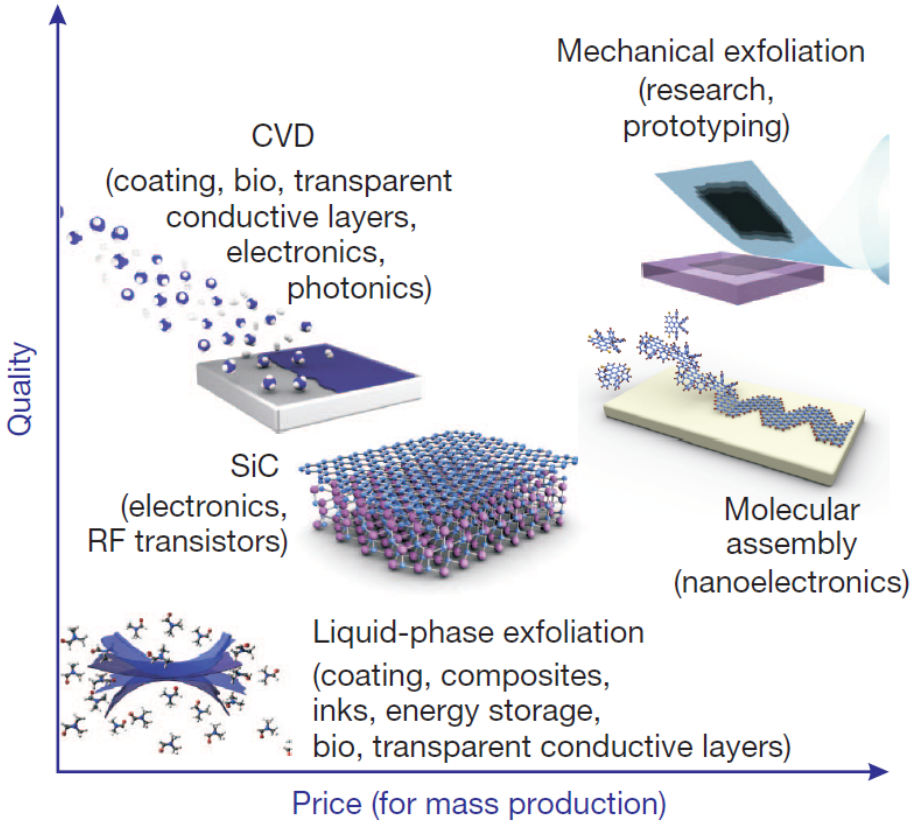


Figure 2.19: Price versus quality of graphene produced by different production techniques, chemical vapor deposition (CVD), mechanical exfoliation, molecular assembly, liquid-phase exfoliation, and graphene grown on silicon carbide (SiC).[34]

Functionalization of Graphene

The structure and electronic properties of pristine graphene, as well as the interaction of graphene sheets with atoms and molecules, have been studied extensively.[36] Several ways of attachment of organic functional groups have been developed, each with possible advantages and drawbacks.

Covalent binding to Graphene

Functionalization of graphene sheets with organic functional groups has been developed for a range of different purposes. The main purpose is the dispersibility of graphene in common organic solvents, which is usually obtained after attachment of certain organic groups.[36] Dispersion of graphene sheets is important to facilitate formation of nanocomposite materials with graphene. Organic functional groups, such as chromophores, offer new properties that could be combined with the properties of graphene. When organic molecules are covalently attached to the surface of graphene, its extended aromatic character is perturbed, enabling the control of its electronic properties.[36] The development of

a band gap through chemical doping is a powerful tool for the use of graphene in nanoelectronic devices.[37] The organic covalent functionalization reactions of graphene sheets include two general routes:

- Formation of covalent bonds between dienophiles or free radicals and C=C bonds of graphene
- Formation of covalent bonds between organic functional groups and the oxygen groups of graphene oxide (GO)

Non-covalent binding to Graphene

Non-covalent functionalization of graphene sheets by π-interactions (as in the case of carbon nanotubes) is an attractive method, as it offers the possibility of attaching functional groups to graphene without disturbing the electronic network.[36,38,39] Non-covalent intermolecular interactions involving π-systems are crucial to the stabilization of proteins, DNA-protein complexes, enzyme-drug complexes, organic supramolecules, and functional nanomaterials.[36,40–44] The π-systems involved in these interactions are relevant in the context of nanomaterial design and fabrication of nanodevices, as small changes in the electronic characteristics of the π-systems can lead to dramatic effects in the structure and properties of the nanosystem.[36,44–46]

Chapter 3

Results and Discussion

In the following chapter results from both the master's project and the project assignment are presented. A brief background on the previous projects and experiments are given in the first section. The second section is focused on ^{1}H NMR investigations of the BODIPY **3a** primarily performed during the project assignment, but with added in-depth discussion and insight regarding the one-pot synthesis. The line of thought from the second section is taken further in the third section. Newly developed experimental reactions, which have been carried out in the starting phase of the master's project, are presented along with a discussion of interesting findings. The fourth section focuses on two-step reactions, an alternative approach to synthesis of F-BODIPY dyes. Bromination and Suzuki cross-coupling of the synthesized BODIPY chromophores are presented and discussed in the fifth and sixth section, respectively. An overview of performed reactions is included in Table 3.7 in the seventh section. Lastly, optical and electrochemical properties of some of the synthesized products are presented in the eighth section.

3.1 Previous experiments

Prior to this master's project, BODIPY **3a** was synthesized by Hans-Petter Larsen,[10] see Figure 3.1 and Scheme 3.3. The resulting brown solid was transferred to the project assignment "*Synthesis and Characterization of BODIPY Dyes for Optoelectronic Applications*",[9] performed and written by Strandheim (current author) autumn 2018. Initial separation issues, poor yields and alternative reactions were looked into and discussed in the project assignment.[9] Thin Layer Chromatography (TLC) of the BODIPY-mixture obtained from Hans-Petter Larsen is shown in Figure 3.2. BODIPY dyes are often highly fluorescent molecules, and as such **3a** shows a characteristic green fluorescence even at low concentrations. The pink fluorescent byproduct has been identified as a pyrroyl BODIPY dye previously reported,[26] see Figure 3.1.

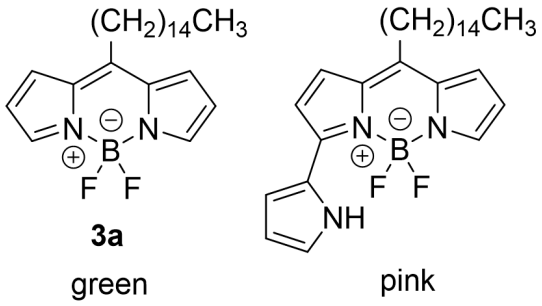


Figure 3.1: BODIPY **3a** and pink fluorescent pyrroyl BODIPY dye previously reported.[26]

Subsequent one-pot syntheses, inspired by reported procedures,[26] have been performed to make additional BODIPY **3a**, see Scheme 3.3. Washing, filtering and drying of the reaction mixtures have been challenging due to aggregation. Emulsions made the work slow,

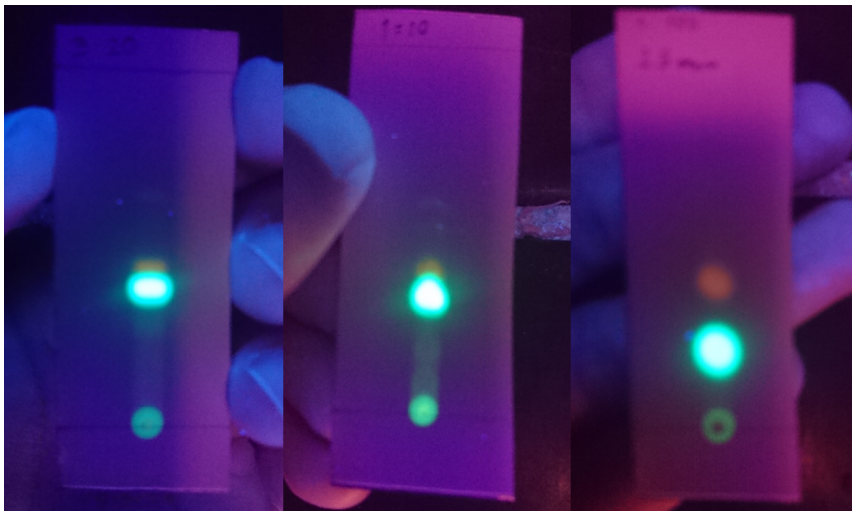
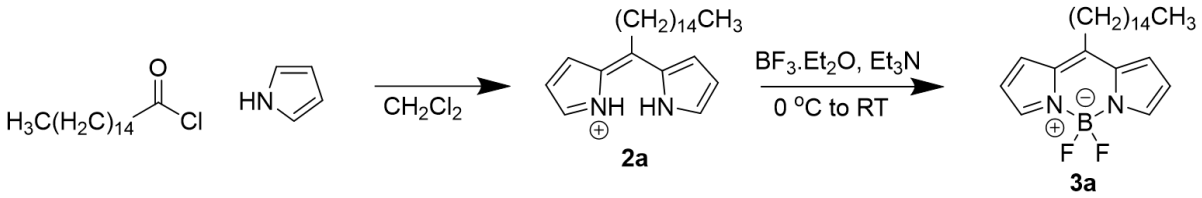


Figure 3.2: TLC of BODIPY product made by Hans Petter Larsen. The solvent systems are ethyl acetate/*n*-pentane 3:20, 1:10 and 1:100 from left to right, respectively. The right most TLC plate was left in the TLC chamber for 25 minutes. The green fluorescent compound is product **3a** and the pink fluorescent compound is a byproduct.

and all equipment had to be cleaned with chromosulfuric acid after use. ^{1}H NMR spectra of test samples from the resulting crudes showed that they contained trace amounts of BODIPY, barely visible in the spectra. The bright fluorescence of the BODIPY dye makes it hard to estimate yields by TLC.



Scheme 3.3: One-pot synthesis of BODIPY **3a** from pyrrole and palmitoyl chloride. DPMe **2a** is a theoretical intermediate which is not worked up, base and borylation agent is usually added after 12 hours reaction time.

A difference between the one-pot reactions performed by Larsen and Strandheim,[9,10] and the reported procedures,[26] is the choice of solvent. DCM (dichloromethane) have been used by Larsen and Strandheim instead of 1,2-dichloroethane, due to availability. A one-pot reaction with 1,2-dichloroethane have later been performed by Susanne Hansen Troøyen and John Fjeldsbø Landa under supervision by the author, but no evident difference was found regarding solvent.

3.2 Investigation of the one-pot synthesis of BODIPY 3a by ^{1}H NMR experiments

Table 3.1: Compositions of reagents and solvent for the NMR reaction experiments 1, 2 and 3. *N,N*-diisopropylethylamine is abbreviated DIPEA. Palmitoyl chloride (**a**) is abbreviated p. chlor.

NMR exp.	P. chlor. [mL]	Pyrrole [mL]	DIPEA [mL]	$BF_3 \cdot Et_2O$ [mL]	CD_2Cl_2 [mL]
1	0.017	0.008	-	-	1
2	0.1	0.05	-	-	1.2
3	0.1	0.05	0.1	0.15	0.6

Several weaknesses of the one-pot procedure have been identified,[9] which is also presented in this Section of the master's thesis. During the project assignment,[9] three *in situ* ^{1}H NMR experiments were carried out to facilitate a deeper understanding of the one-pot procedure. Compositions of said ^{1}H NMR experiments are given in Table 3.1. Starting materials pyrrole and palmitoyl chloride were dissolved in CD_2Cl_2 under nitrogen atmosphere. In the first ^{1}H NMR experiment modest concentrations (typical of a normal NMR sample) were used, and ^{1}H NMR spectra were recorded at given intervals. The spectra primarily showed formation of 1-(1*H*-pyrrol-2-yl)hexadecan-1-one, the intermediate formed after the first nucleophilic attack by pyrrole on palmitoyl chloride (**a**), see mechanism in Figure 3.4.

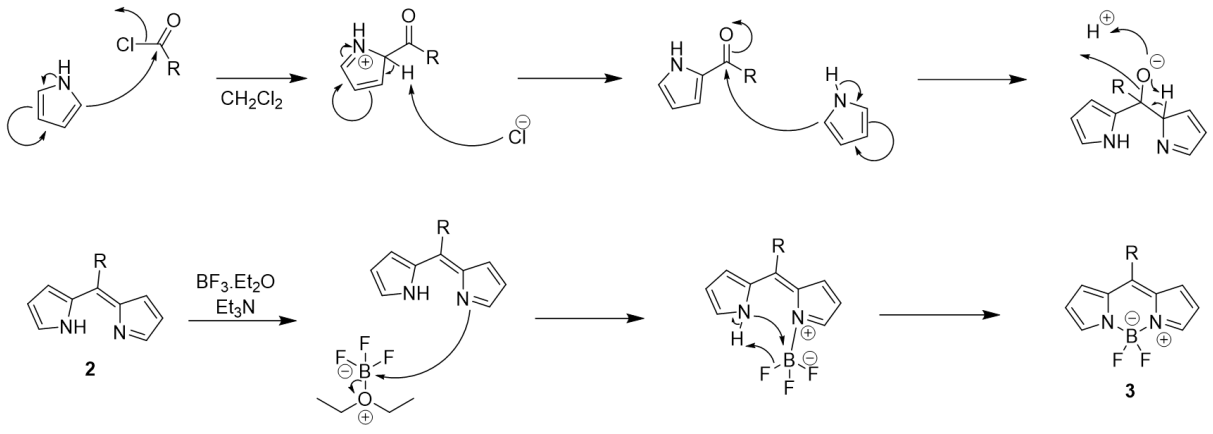


Figure 3.4: Proposed simplified mechanism for condensation reaction between pyrrole and acid chloride, followed by borylation.

In the second ^{1}H NMR experiment the concentrations were set to mimic the concentration of actual one-pot reactions. An overview of composition of some of the different one-pot reactions is given in Table 3.2. When comparing the ^{1}H NMR spectra from the

first and second NMR experiment it is evident that concentration of reagents is an important factor impacting reaction rate, which is common for inter-molecular reactions. Byproducts is also more prominent in the second experiment. In the original one-pot procedure amine and $BF_3 \cdot Et_2O$ are added after 12 hours.[26] Figure 3.5 and Figure 3.6 show parts of the ^{1}H NMR spectrum from the second NMR experiment obtained after 12 hours reaction time.

It has not been possible to confirm the formation of DPMe **2a** due to lack of comparable spectra. The free base of fully unsubstituted DPMe is known to be unstable above -40 °C.[23,47] An ^{1}H NMR spectrum of fully unsubstituted DPMe complexed with HCl in $CDCl_3$ have been reported.[23] However, match up with the spectrum is challenging. The reason behind the uncertainty is partly the difference in meso-substituent and deuterated solvent, but also shifting of the spectrum peaks due to high concentration of different molecular species in the NMR sample used in the second ^{1}H NMR experiment.

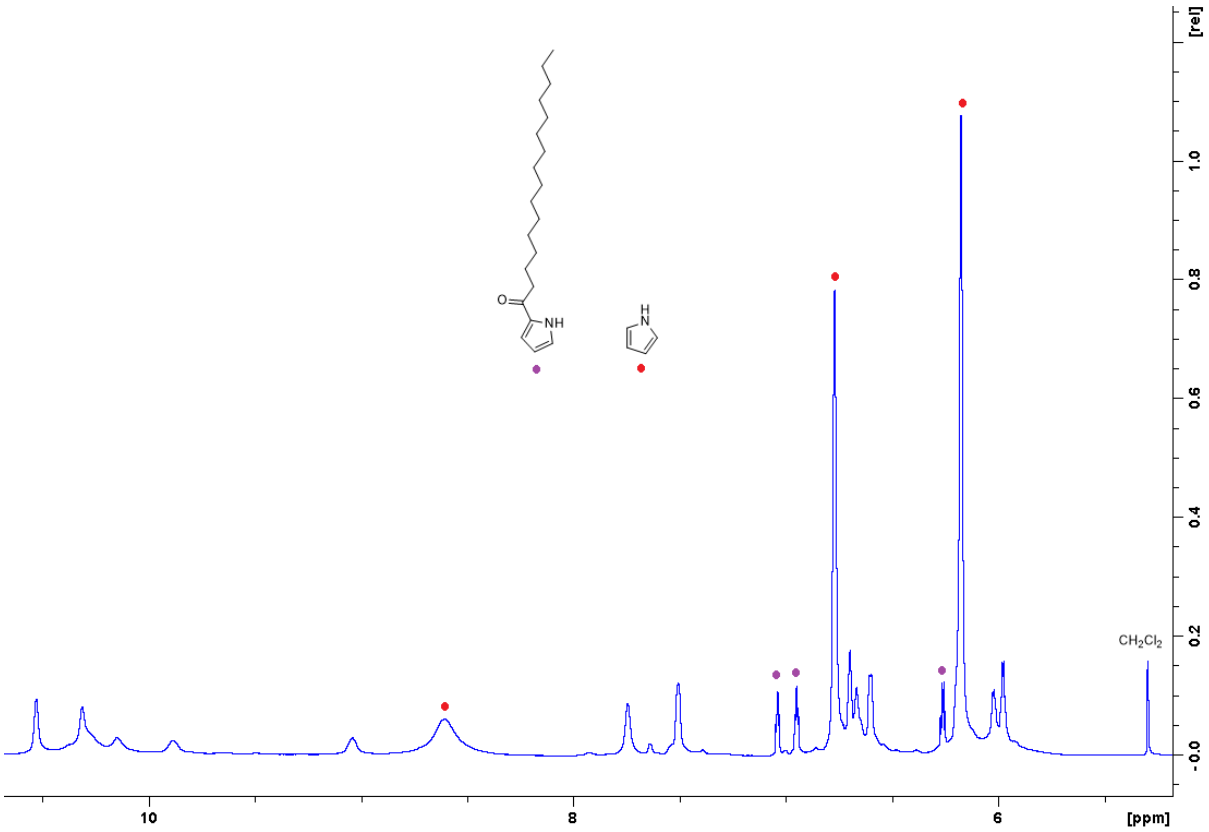


Figure 3.5: Aromatic region of the ^{1}H NMR spectrum from NMR experiment nr. 2. Pyrrole and palmitoyl chloride were dissolved in CD_2Cl_2 under nitrogen atmosphere and reacted for 12 hours. Red dots show the peaks from aromatic and nitrogen bonded H-atoms on pyrrole. Purple dots show peaks from aromatic bonded H-atoms on 1-(1*H*-pyrrol-2-yl)hexadecan-1-one. The other peaks are unknown.

The overall yields in the one-pot reactions are low due to poor specificity of the reaction. From *in situ* NMR observation, it appears that the initial pyrrole attack on the

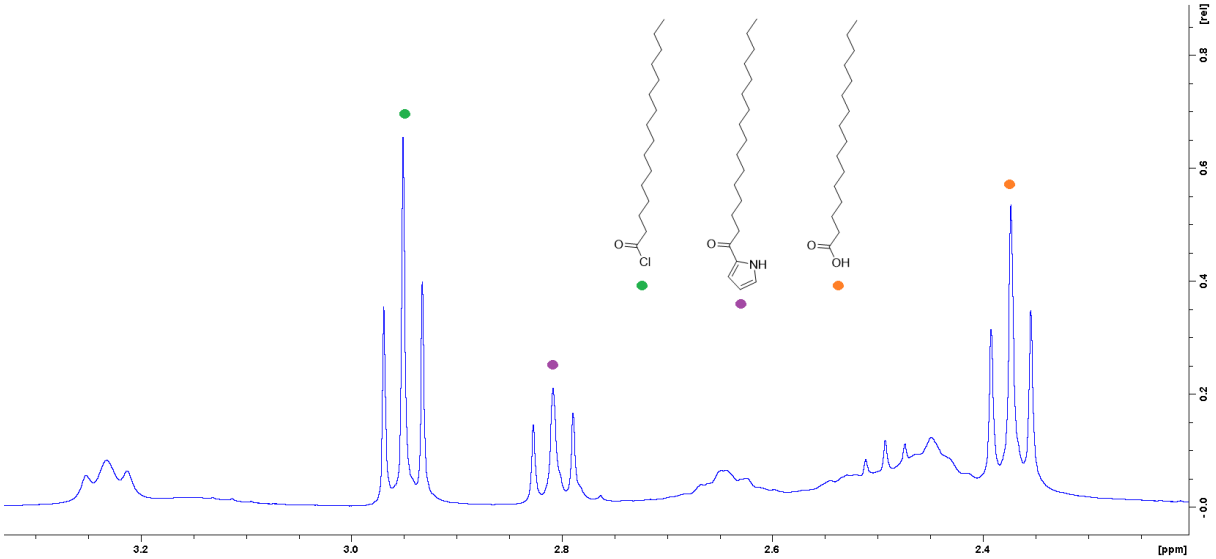


Figure 3.6: Parts of the alkyl region of the ^{1}H NMR spectrum from the second NMR experiment. Pyrrole and palmitoyl chloride were dissolved in CD_2Cl_2 under nitrogen atmosphere and reacted for 12 hours. Narrow triplets are signals from the CH_2-group closest to C=O. Green dot shows peaks from the H-atoms on palmitoyl chloride. Purple dot shows peaks from the H-atoms on 1-(1*H*-pyrrol-2-yl)hexadecan-1-one. Orange dot shows peaks from the H-atoms on palmitic acid. The other peaks are unknown.

acid chloride is the rate limiting step, see proposed mechanism in Figure 3.4. The ketone intermediate is the first to be visible in the ^{1}H NMR spectra, but remains at low concentrations as the reactants are consumed. The concentration of the ketone intermediate is stable after 2-3 hours.

Palmitic acid has been observed in gram quantities during work up of the one-pot reactions targeting BODIPY **3a**. Water, which is known to react with acid chlorides, is formed *in situ*, making palmitic acid an expected side product. Both, water present at reaction start and water formed *in situ*, are expected to react with palmitoyl chloride (**a**). ^{1}H NMR spectra of crude and visual examination of the reactions suggest that palmitic acid typically is the major product of the one-pot reaction. One pyrrole molecule might react with several acid chlorides, due to the pyrrole being unsubstituted. 2,4-Dimethylsubstituted pyrrole, as used for 1,3,5,7-tetramethylated BODIPYs does not polymerize in reaction with carbonyls. Pyrrole can also polymerize with itself, which is the reason for distillation of the reagent prior to the reaction. The pyrroyl BODIPY, previously described,[26] might arise from either dimerized pyrrole or a nucleophilic attack by pyrrole on intermediate or finished BODIPY. However, the yields of the pyrroyl BODIPY byproduct have not been high enough to rise concern regarding pyrrole concentration.

Due to synthetic challenges, reports of α,β-unsubstituted meso-alkylated BODIPYs are few, as shown in Section 2.2, and pointed out by another research group,[2] illustrated by the following quote:

"The absorption- and fluorescence-spectroscopic properties of members of the Bodipy family are highly influenced by the extent of electron delocalization around the central cyanine framework and, in a modest way, by the donor and acceptor characteristics of the pyrrole substituents. It is, in fact, quite rare for Bodipy dyes to lack alkyl substituents at the pyrrole groups."

The absence of alkyl-substituents on pyrrole makes the BODIPY products more attractive as potential candidates for organic optoelectronic applications in different types of solar cells.

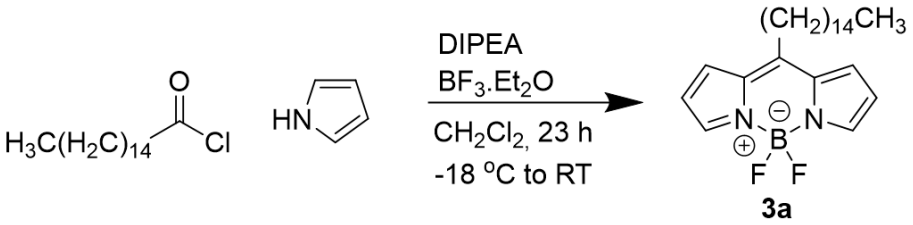
In the third ^{1}H NMR experiment (Table 3.1) *N,N*-diisopropylethylamine (DIPEA) and $BF_3 \cdot Et_2O$ were added together with pyrrole and palmitoyl chloride (**a**) from the start, to see if F-BODIPY would be formed. In the original one-pot synthesis the first part of the reaction is acid catalysed, and in the second part base is added, partly due to formation of HF. The ^{1}H NMR spectra of the third NMR experiment showed that F-BODIPY **3a** was made in comparable or better yields than previously performed one-pot procedures. This exciting find probably depends on intricate interactions and interdependencies between pH, *in situ* formed water and HF, substrates, solvents, reactants and intermediates, as well as temperature, among other things.

The main concern of the one-pot reaction regarding yield of α,β-unsubstituted meso-alkylated BODIPY seems to be degradation and polymerization of starting material and intermediate products. By reducing the time from reaction start to addition of base and borylation agent, and by reducing temperature, less of the intermediates and substrates is lost to degradation and polymerization. Based on experience from the reactions previously carried out, and knowledge from literature search and the ^{1}H NMR experiments, a modified one-pot reaction was designed.

3.3 Modified one-pot synthesis of BODIPY core

Experiment KS-9 was the first step toward a viable one-pot synthesis, see Scheme 3.7. Distilled pyrrole (5.0 mL, 2.2 eq.), palmitoyl chloride (10.0 mL, 1 eq.), DIPEA (10 mL) and $BF_3 \cdot Et_2O$ (14 mL, drop-wise) were added to DCM (120 mL) under nitrogen atmosphere at -18 °C (ice/acetone bath). Compared with previous one-pot reactions the reaction mixture was easier to work with, and equipment no longer needed to be cleaned with chromosulfuric acid after use. The reaction yield was 10%, which was considerably higher than the two previous attempts at the one-pot synthesis. In the project assignment it was concluded that:

"A logical next step would be to add palmitoyl chloride drop-wise (slow enough to prevent a build-up) to a reaction mixture of excess pyrrole, $BF_3 \cdot Et_2O$ and DIPEA. The $BF_3 \cdot Et_2O$ is sensitive to water and could react with the water formed in situ instead of palmitoyl chloride, thereby increasing the yield." [9]



Scheme 3.7: Modified one-pot synthesis of BODIPY **3a** from pyrrole and palmitoyl chloride, (KS-9).

In the next experiment, KS-10, these thoughts were taken into account. DIPEA (20 mL) and $BF_3 \cdot Et_2O$ (5 mL, drop-wise) were added to distilled pyrrole (36.0 mL, 31 eq.) under nitrogen atmosphere at -18 °C (ice/acetone bath). Palmitoyl chloride (5.0 mL, 1 eq.) in DCM (20 mL) was added drop-wise over 6 hours. The reaction mixture was left stirring in the ice/acetone bath for 23 hours total, and was allowed to reach ambient temperature. More $BF_3 \cdot Et_2O$ (15 mL) was added drop-wise after 7 hours reaction time, due to low formation of BODIPY (TLC). The finished reaction was not successful, due to low yield of the target BODIPY.

A key difference between the two reactions, KS-9 and KS-10, was the pH. The pH of the first reaction (KS-9, at reaction stop) was between 1 and 2, whereas the second reaction (KS-010, at reaction stop) with more added base had a pH between 4 and 5. The reason more base was added was due to concerns regarding the hydrofluoric acid formed *in situ* from $BF_3 \cdot Et_2O$. However, a highly acidic environment seem important to drive the reaction forward. In the proposed mechanism of the one-pot synthesis, Figure 3.4, a proton source is needed during the final step of the condensation reaction.

An alternative way of dealing with *in situ* produced water was proposed. The addition of anhydrous $MgSO_4$ might keep the acid chloride from oxidizing. In experiment KS-11, DIPEA (10 mL), distilled pyrrole (8 mL, 3.5 eq.) and palmitoyl chloride (10 mL, 1 eq., drop-wise) were added to DCM (100 mL) with anhydrous $MgSO_4$ (8 g) under nitrogen atmosphere at -18 °C (ice/acetone bath). $BF_3 \cdot Et_2O$ (14 mL) was added drop-wise over 45 minutes. The reaction mixture was left stirring in the ice/acetone bath for 43 hours total, and was allowed to reach ambient temperature.

Table 3.2: Compositions of reagents and solvent for the modified one-pot experiments. Palmitoyl chloride (**a**) is abbreviated p. chlor.

Rx.	**P. chlor.** [mL]	**Pyrrole** [mL]	**DIPEA** [mL]	**$BF_3 \cdot Et_2O$** [mL]	**CH_2Cl_2** [mL]	**Yield** %
KS-9	10	5	10	14	120	10
KS-10	5	35	20	20	20	-
KS-11	10	8	10	14	100	4

Table 3.3: Overview of one-pot reactions performed during the master and project assignment. - = trace amounts, * = unknown

Rx.	**Product**	**Rx. time** [h]	**Yield** [g]	**Yield** %
KS-2	3a	14.5+14.5	-	-
KS-3	3a	14.5	*	*
KS-9	3a	23	1.278	10
KS-10	3a	22	-	-
KS-11	3a	43	0.489	4
KS-15	3d	408	-	-

Experiment KS-9 and KS-11 is similar in composition as shown in Table 3.2, but the yield in KS-11 is approximately half of that in KS-9, Table 3.3. The main difference is the addition of $MgSO_4$ as an *in situ* drying agent in KS-11. The difference in yield might indicate that water plays an important role in the reaction mechanism, besides being detrimental to the acid chloride and borylation agent. In the proposed mechanism of the one-pot synthesis, shown in Figure 3.4, protonated water molecules can act as a proton source during the final step of the condensation reaction. Water molecules likely influences several of the steps of the mechanism. However, these interactions are not easily explained without advanced computational models, extending beyond the scope of this master's project.

The instability of the investigated meso-alkyated BODIPYs led to a search for alternative meso-substituents with stronger electron donating properties. 2-thiophenecarbonyl

chloride (**d**) was chosen as a candidate for the one-pot synthesis. 5-octylthiophene-2-carbaldehyde has previously been used for two-step reactions.[27] Product yields of the previously reported two step reaction were 71% and 40% for the first and second step, respectively,[27] giving an overall yield of 28%. The reactions are presented in Section 2.2 and are are shown in Scheme 2.9.

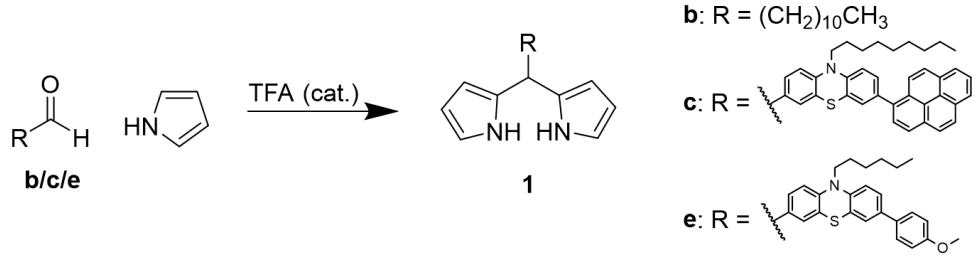
In experiment KS-15 distilled pyrrole (1.5 mL, 2.3 eq.), 2-thiophene-carbonyl chloride (1 mL, 1 eq.), DIPEA (0.6 mL, drop-wise) and $BF_3 \cdot Et_2O$ (1.8 mL, drop-wise) were added to DCM (12 mL) with $MgSO_4$ (0.8 g) under nitrogen atmosphere at -18 °C (ice/acetone bath). More DIPEA (0.6 mL, drop-wise) was added 30 minutes after the addition of $BF_3 \cdot Et_2O$. The reaction mixture was left stirring for 17 days, and was allowed to reach ambient temperature. The reaction was left this long due to illness, and was not worked up because of decomposition of the product.

Two different one-pot procedures with 2-thiophenecarbonyl chloride (**d**) were performed under the supervision of the author. One of the reactions was performed by Mats Solberg Nes as part of his master's project, and the other reaction was performed by Susanne Hansen Troøyen and John Fjeldsbø Landa during their synthesis project in TKJ4130. Nes's reaction was performed similar to KS-15 only without the $MgSO_4$, while Troøyen and Fjeldsbø's reaction was performed in close comparison to the original one-pot procedure.[26] An overview of the one-pot reactions performed by the author is given in Table 3.3.

Common for all three one-pot reactions, with 2-thiophenecarbonyl chloride (**d**), were low yields and a much slower convertion rate compared with one-pot reactions with meso-alkylated BODIPY. Even though thiophene is a more stabilizing meso-substituent than an alkyl chain, the initial nucleophilic attack of the pyrrole on the acid chloride is less favored, likely driving the increase in total reaction time. The reason the nucleophilic attack is less favored is the electron donating character of the thiophene ring, lowering the delta positive charge (δ^+) of the carbonyl carbon.

3.4 Two-step synthesis of BODIPY core

An alternative approach to the one-pot synthesis is a two-step procedure. The two-step synthesis differs from the one-pot synthesis in that the acid chloride is switched with an aldehyde, and pyrrole is used as the solvent. An acid catalyst has to be added as HCl is no longer formed *in situ*. Instead of forming a dipyrromethene (DPMe) **2**, a dipyrromethane (DPMa) **1** is synthesized. The DPMa **1** is more stable and can be worked up and purified. The DPMa **1** is oxidized to form a tertiary carbocation, which is deprotonated and becomes a DPMe **2**. The DPMe **2** is then borylated with $BF_3 \cdot Et_2O$, for reaction mechanisms see Figure 2.10 and Figure 2.11 in the theory.



Scheme 3.8: First step of a two-step synthesis of BODIPY **3**. Dipyrromethanes **1** are made from pyrrole and aldehydes.

Condensation reactions with pyrrole and aldehyde, inspired by reported procedures,[27] have been performed both during the project assignment and master's project. Overview of the two-step reactions is given in Table 3.4. The earliest reactions, KS-4 and KS-5, gave lower yields than expected for similar compounds. The relatively low yields obtained led to an investigation of the dodecanal (**b**) used in the experiments. ^{1}H NMR samples revealed that the dodecanal (**b**) was only 33% pure. When accounting for the low purity of the starting material the yields improve substantially, from 28% and 33% to 77% and 90% for KS-4 and KS-5, respectively. Heating the reaction and increasing the reaction time of KS-5 compared with KS-4 seem to have impacted the yield of DPMa **1b** positively. Unfortunately, the uncertainty in purity of the starting material is high. Ideally the reactions should have been performed again with new dodecanal (**b**) to gain more accurate yields. Reactions with new dodecanal (**b**) were not carried out due to time constraints. The alkylated DPMa **1b** and related intermediate products exhibited lower stability than initially anticipated.

Phenothiazine aldehyde **c** was included in the project assignment in order to make a multichromophore with both BODIPY and phenothiazine. Phenothiazine is a chromophore that the solar cell lab at NTNU has years of experience with,[15] and is expected to positively affect the optical properties of the resulting molecule without sacrificing solubility, due to the alkyl chain incorporated. The chosen phenothiazine aldehyde already

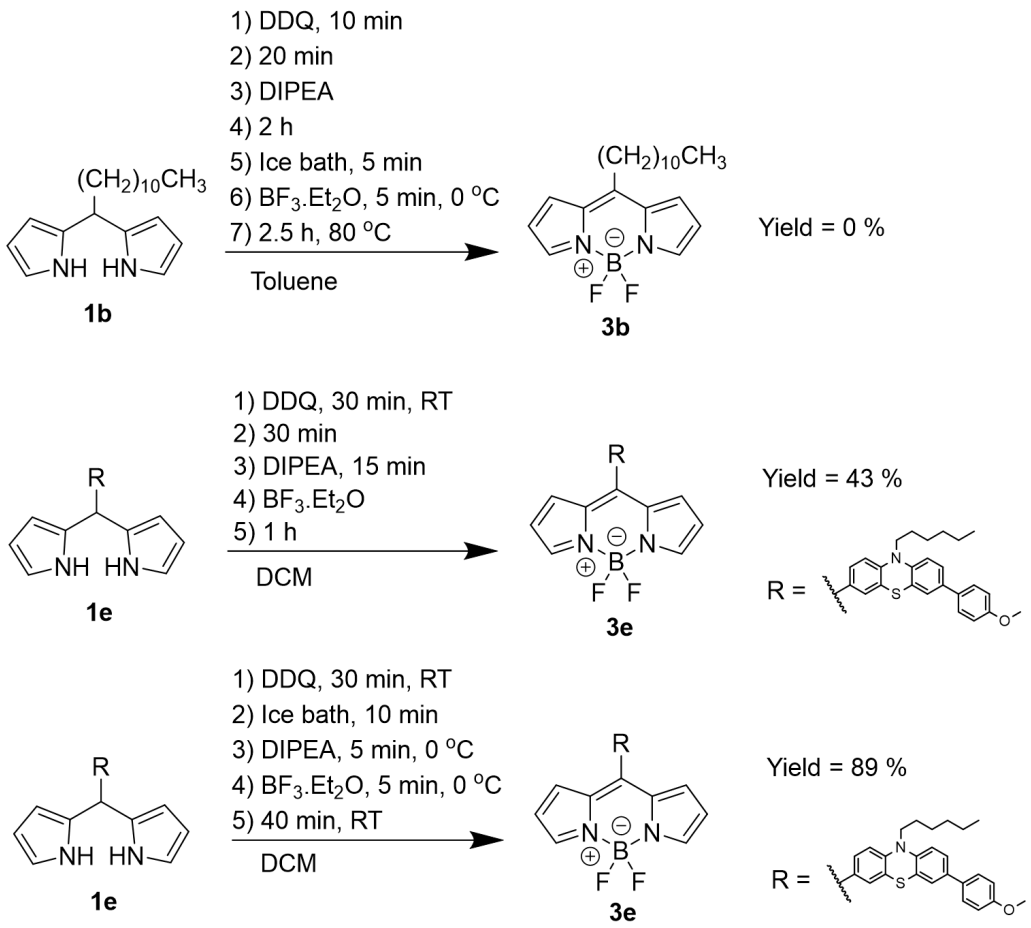
Table 3.4: Overview of two step reactions performed during the master and project assignment. * = unknown

Rx.	**Product**	**Rx. time** [h]	**Yield** [g]	**Yield** %	**Corr. yield** %
KS-4	1b	1.5	0.452	28	77
KS-5	1b	2.5	2.661	33	90
KS-6	1c	0.83	*	*	
KS-7	3b	4.5	0	0	
KS-8	3b	7.33	0	0	
KS-16	1e	1.33	1.926	73	
KS-17	3e	2.25	0.048	43	
KS-18	3e	1.5	0.486	89	
KS-20	3e	98	0.361	28	

has a potential anchoring group, which can be utilized for non-covalent interactions with graphene. A small scale test reaction was carried out on approximately 120 mg starting material **c**, but the DPMa **1c** was not worked up. The work up was not prioritized due to time constraints and initial discouraging results in the second step of the two-step reaction, see KS-7 and KS-8 in Table 3.4.

During the master assignment the two-step procedure was reevaluated and an alternative phenothiazine aldehyde (**e**) was tried. Reactions were influenced by reported synthetic procedures on phenothiazine BODIPYs.[48] The first step, condensation reaction with aldehyde **e**, pyrrole and trifluoroacetic acid (TFA, acid catalyst), was successfully carried out with a yield of 73%, which is comparable to the calculated yield of DPMa **1b**. The TLC-system used was not able to separate DPMa **1e** and the intermediate alcohol product, see mechanism in Figure 2.10. Due to overlap, the reaction was stopped before completion. The yield could probably have been pushed higher by extending the reaction time by 15-45 minutes. Overall the first reaction of the two-step synthesis is efficient and reliable.

The second step of the two step reaction is a lot more sensitive to reaction time, concentration, temperature and sequence of addition. The DPMa **1b**, obtained from the first two-step condensation reactions (KS-4 and KS-5), was oxidized with DDQ at RT, see Scheme 3.9. No product was formed following the oxidation and borylation, due to decomposition of the starting and intermediate products, confirmed by ^{1}H NMR. Subsequent reactions on DPMa **1e**, performed during the master's project, have been a lot more successful. Based on a similar reaction on phenothiazine DPMa,[48] KS-17 was performed with phenothiazine DPMa **1e** to a yield of 43%, see Scheme 3.9. Comparing experiment KS-17 and KS-8, solvent has been changed from toluene to DCM, the addition of DDQ was slower, DIPEA was added much closer in time to $BF_3 \cdot Et_2O$, the reaction



Scheme 3.9: Second step of a two-step synthesis of BODIPY **3**. Dipyrromethanes **1** are oxidized and borylated to from BODIPY **3**. The reactions, KS-8, KS-17 and KS-18 from top to bottom, respectively, illustrate progression made on the second step of the two-step synthesis.

was not heated, and the overall time and concentration used was lower. The ice bath was left out, as it was not used in reported procedures for phenothiazine BODIPYs.[48]

When performing experiment KS-18, an ice bath was introduced, the number of DDQ equivalents was reduced from 1.4 to 1.06, and time usage was further reduced. Seemingly most important were the reduction in DDQ usage and the time between drop-wise addition of DIPEA and $BF_3 \cdot Et_2O$. Small adjustments led to more than a two-fold increase in yield of BODIPY **3e** from 43% to 89% (KS-17 to KS-18). Using the experience from KS-17 and KS-18, BODIPY **3b** most likely could have been obtained at a lower yield. A milder oxidant such as *p*-chloranil can potentially be used, and performing the oxidation at a lower temperature might also improve yields. However, stability issues make the meso-alkyl BODIPY dyes less likely to be useful for optoelectronic applications.

The last performed second step reaction, KS-20, was supposed to replicate the success of KS-18 (89% yield). However, DIPEA was not available at the time of reaction. Instead of DIPEA, triethylamine (Et_3N) was used. Et_3N was chosen because of availability, and its use in the original one-pot procedure.[26] The substitution of the base decreased the

conversion rate of the reaction substantially. As observed in earlier oxidation reactions with DDQ, time is important in relation to yield due to decomposition. In stead of having a 1.5 hour reaction with 89% yield, KS-20 became a 98 hour reaction with 28% yield. DIPEA is a bulky, hindered base and a poor nucleophile compared with Et_3N. Due to the steric hinderence DIPEA is more selectively targeting readily available (not hindered) acidic protons than Et_3N. The difference in affinity between DIPEA and Et_3N might be the main reason or part of the reason behind the reduced conversion rate.

3.5 Bromination of BODIPYs

All bromination reactions have been carried out with recrystallized NBS. NBS was chosen over Br_2 due of safety and convenience, as well as it being the preferred choice in most literature procedures. No bromination procedures are published on α,β-unsubstituted meso-alkylated F-BODIPYs (SciFinder, 05.09.19). In 29 of 31 dibromination procedures the meso-substituent is a phenyl group with different substituents, the two other procedures have thiomethyl and 5-oktyl 2-thiophenyl as meso-substituents. The NTNU chromophore research groups have no previous experience with bromination of α,β-unsubstituted BODIPYs. The degree of regioselectivity of the bromination step was unknown.

The large scale of the initial one-pot reactions, performed with palmitoyl chloride (**a**), allowed BODIPY **3a** to be attained in high enough quantities to start bromination, despite modest yields. An overview of all bromination reactions is given in Table 3.5. The first bromination reaction, KS-12, had a descent total yield of 65%, when considering both 2-monobrominated BODIPY **4a** (38%) and 2,6-dibrominated BODIPY **5a** (27%). Both mono- and dibrominated BODIPYs are wanted. However, dibrominated BODIPYs have a wider range of applications, for instance polymers in bulk heterojunction solar cells (BHJSCs).

Table 3.5: Overview of the bromination reactions performed.

Rx.	**Product**	**Rx. time** [h]	**Yield** [g]	**Yield** %	**Corr. yield** %
KS-12	4a+5a	27	0.103+0.052	63+27	38+27
KS-13	4a+5a	4	0.068+0.143	16+29	8+29
KS-19	4e+5e	25	0.001+0.008	2+13	
KS-21	4e+5e	72	0.293+0.125	33+13	

It is easier to attain adequate amounts of brominated BODIPY, if the bromination reaction is led towards one major product. More NBS was added in the next reaction, KS-13, in order to obtain more 2,6-dibrominated BODIPY. Although the reaction time of KS-13 was shorter, much more of the intermediates/products were decomposed when more equivalents (eq.) of NBS was added (3.1 eq. added over 3.5 hours, instead of 2.7 eq. over 3 hours). The yield of 2,6-dibrominated BODIPY **5a** increased from 27% to 29%. Meanwhile, the yield of 2-monobrominated BODIPY **4a** dropped from from 38% to 8%. An initial thought was the possibly of over-bromination, but NMR spectra showed convincing results of dealkylation, or perhaps rather the left-over alkyl chain after disintegration of the BODIPY core moiety. The NMR results support the hypothesis that meso-alkyl BODIPYs **3a** and **3b**, and related intermediates and brominated products, are unsuitable chromophores for optoelectronic applications, due to low stability.

The first bromination of phenothiazine BODIPY **3e**, KS-19, was performed at a small scale, 45 mg starting material, in order to assess the progression of the reaction as more equivalents of NBS was added (3.7 eq., 2 separate additions). Along with mono- and dibrominated BODIPY seemingly one other compound was forming together with the two others. NMR spectra showed the compound to likely be an over-brominated product. Unfortunately, exact structure elucidation was hard and deemed unnecessary at this point.

In order to combat the over-bromination problem it was decided to slow down the next bromination reaction, KS-21, by decreasing the temperature from RT to 0 °C. NBS (2.4 eq.) was added over 3 hours and the reaction was allowed to reach ambient temperature. The reaction was stopped and worked up after 72 hours, giving a total yield of 46%. Due to illness the reaction was left longer than initially planed, which might have affected the yield. A somewhat surprising find was the mixture of different mono- and dibrominated BODIPYs. By lowering the temperature, the equilibrium between the kinetic product and the thermodynamic product had shifted. By extensive use of column chromatography and NMR experiments most of the products were identified and characterised, se Table 3.6 and Figure 3.10.

Table 3.6: ^{1}H NMR and ^{13}C NMR results for different bromination products of BODIPY **3e**. $\mathbf{4e}_{\alpha}$ and $\mathbf{4e}_{\beta}$ are monobrominated products with bromine in 3- and 2-position, respectively. $\mathbf{5e}_{\alpha,\beta}$ and $\mathbf{5e}_{\beta}$ are dibrominated products. s = singlet, d = doublet, dd = doublet of doublets

NMR	**3-**	**5-**	**2-**	**6-**	**1-**	**7-**
3e	7.91(s) 143.4		6.54(dd) 118.2		7.01(d) 131.0	
$\mathbf{4e}_{\alpha}$	Br -	7.96(s) -	6.51(d) -	6.59(dd) -	6.84(d) -	7.02(d) -
$\mathbf{4e}_{\beta}$	7.75(s) 141.3	7.95(s) 145.2	Br 105.6	6.57(dd) 119.2	6.93(s) 129.7	7.05(d) 132.6
$\mathbf{5e}_{\alpha,\beta}$	Br 135.6	7.77(s) 141.9	6.56(d) 122.9	Br 106.3	6.97(d) 129.7	6.94(s) 132.7
$\mathbf{5e}_{\beta}$	7.81(s) 143.2		Br 106.8		7.03(s) 131.1	

The product ratio was 1:1.3 for dibrominated BODIPYs $\mathbf{5e}_{\beta}$ and $\mathbf{5e}_{\alpha,\beta}$, respectively. Trace amounts of $\mathbf{4e}_{\alpha}$ were found together with $4e_{\beta}$. The distribution between the different mono- and dibrominated BODIPYs is interesting, in the sense that $\mathbf{4e}_{\alpha}$ seem to be more activated than $\mathbf{4e}_{\beta}$ toward further bromination. Traces of what could be BODIPY $\mathbf{5e}_{\alpha}$ were seen in the NMR spectra, but the findings were difficult to confirm. The product distribution agrees with a gradual increase in temperature, shifting the main bromination

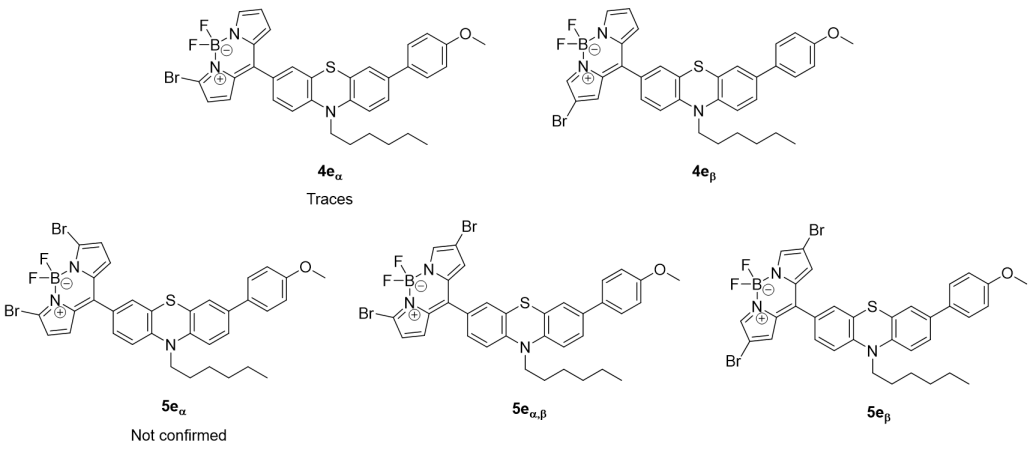
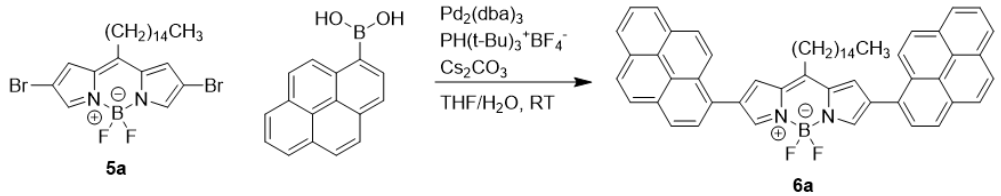


Figure 3.10: Possible mono- and dibrominated BODIPYs made from phenothiazine BODIPY **3e**.

target from α to β hydrogens. Decreasing the temperature to avoid over-bromination turned out to be counterproductive toward the goal of getting one major product.

3.6 Suzuki coupling of brominated BODIPYs

A Suzuki coupling of a pyrene chromophore onto the dibrominated BODIPY **5a** was attempted, see Scheme 3.11. BODIPY **6a** is an attractive candidate as the pyrene moieties should provide non-covalent anchoring groups for graphene nanosheets, yielding readily available nanoensembles. The BODIPY dye would enrich the electron accepting properties of the carbon nanomaterial with desirable light harvesting capabilities from both the BODIPY core and the pyrene side-groups. The alkyl chain should provide adequate solubility in common organic solvents to the graphene hybrid material.



Scheme 3.11: Attempted Suzuki coupling of BODIPY **5a** and pyrene-1-boronic acid.

Unfortunately, due to low quantities of dibrominated starting material **5a**, only one reaction was attempted with no identifiable product. The poor stability of the meso-alkylated BODIPYs made Suzuki coupling even at RT impossible. The only solution, as the author sees it, is opting for more stable BODIPYs, in which higher conjugation and/or strong EDGs at the meso-position is desirable.

3.7 Overview of performed reactions

All reactions performed during the project and master assignment are listed chronologically in Table 3.7. Compounds are listed in Figure 3.12. The main focus of the project and master assignment has been on testing and development of synthetic routes for synthesis of different α,β-unsubstituted BODIPYs, as well as bromination of said BODIPYs. Although the BODIPY core is known for its chemical tailoring and a plethora of possibilities, it has become evident that different meso-substituted (EDG, EWG, conjugation) BODIPYs require tailored reaction conditions and pathways.

Table 3.7: Overview of reactions performed by the author during the project and master assignment. Reactions KS-2 to KS-9 are performed during the project assignment. - = trace amounts, * = unknown

Rx.	**Product**	**Rx. time** [h]	**Yield** [g]	**Yield** %	**Corr. yield** %
KS-2	3a	14.5+14.5	-	-	
KS-3	3a	14.5	*	*	
KS-4	1b	1.5	0.452	28	77
KS-5	1b	2.5	2.661	33	90
KS-6	1c	0.83	*	*	
KS-7	3b	4.5	0	0	
KS-8	3b	7.33	0	0	
KS-9	3a	23	1.278	10	
KS-10	3a	22	-	-	
KS-11	3a	43	0.489	4	
KS-12	4a+5a	27	0.103+0.052	63+27	38+27
KS-13	4a+5a	4	0.068+0.143	16+29	8+29
KS-14	6a	114	-	-	
KS-15	3d	408	-	-	
KS-16	1e	1.33	1.926	73	
KS-17	3e	2.25	0.048	43	
KS-18	3e	1.5	0.486	89	
KS-19	4e+5e	25	0.001+0.008	2+13	
KS-20	3e	98	0.361	28	
KS-21	4e+5e	72	0.293+0.125	33+13	

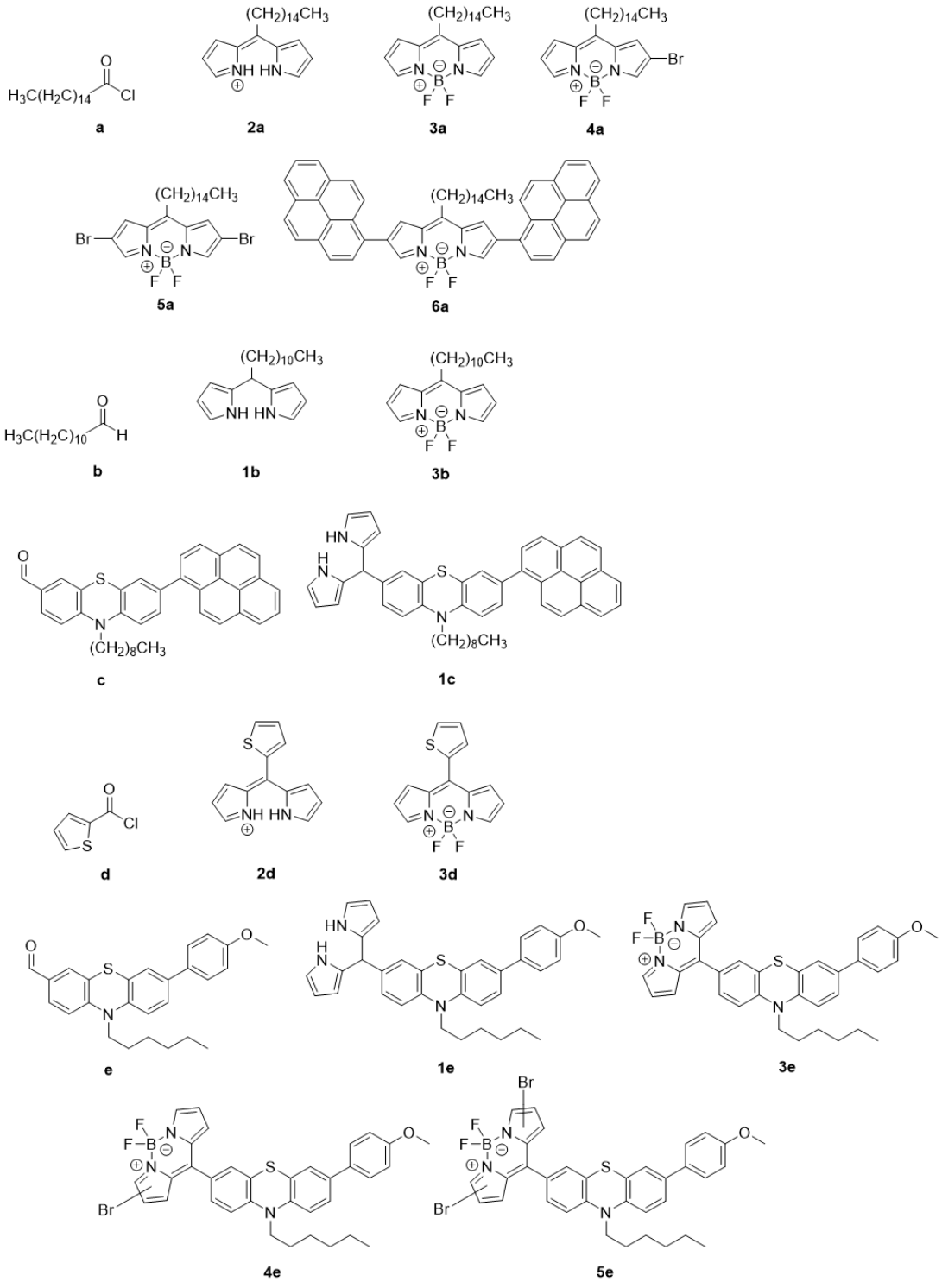


Figure 3.12: Overview of all synthesized and attempted synthesized products and starting materials (acid chlorides or aldehydes **a**-**e**).

3.8 Photophysical properties of synthesized compounds

Absorption (UV-Vis) and emission (Photoluminescence) spectra of synthesized compounds **3a**, **5a**, **1e**, **3e**, **4e** and **5e** in solution (acetone) are shown in Figure 3.13 and Figure 3.14. A redshift of both absorbance and emission maxima can be seen as a clear trend regarding increased bromination of the compounds, see Table 3.8. For both meso-alkylated BODIPY **3a** and meso-phenothiazine BODIPY **3e** a redshift of approximately 36 nm is observed for the 2,6-dibrominated counterparts **5a** and **5e**, respectively.

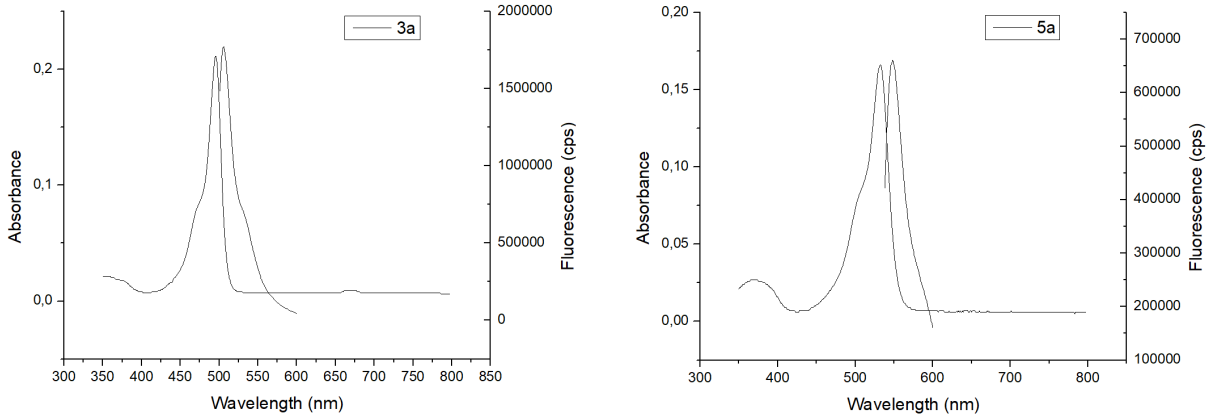


Figure 3.13: UV-visible absorbance and emission spectra of meso-alkyl BODIPY **3a** and 2,6-dibrominated meso-alkyl BODIPY **5a**, from left to right, respectively.

The meso-alkylated BODIPYs in general possess a blueshifted absorbance maxima compared with the meso-phenothiazine BODIPYs. BODIPYs with EDGs in meso-position have blueshifted absorbance maxima compared with BODIPYs with EWGs in meso-position, according to literature data presented in the theory, see Figure 2.2. The difference in absorbance maxima might seem to (incorrectly) indicate that the alkyl-group is a slightly better EDG than the phenothiazine-group. However, the redshift of meso-phenothiazine BODIPY **3e** compared with meso-alkyl BODIPY **3a**, is likely due to higher conjugation, as phenothiazine is considered an electron rich chromophore and strong EDG.[8,48]

Bromine is special in the sense that it is electron withdrawing due to its high electronegativity, but can also be electron donating due to π back-bonding. On phenyl rings bromine is an ortho, para directing group although its a weak EWG. In brominated BODIPY the electron withdrawing effect of bromine is likely causing the redshift.

Observation of the BODIPY chromophores **3a** and **3e**, under 366 nm UV-light, as well as emission spectra, show strong fluorescence for the meso-alkylated BODIPY **3a** and no fluorescence for the meso-phenothiazine BODIPY **3e**. The observations, supported by

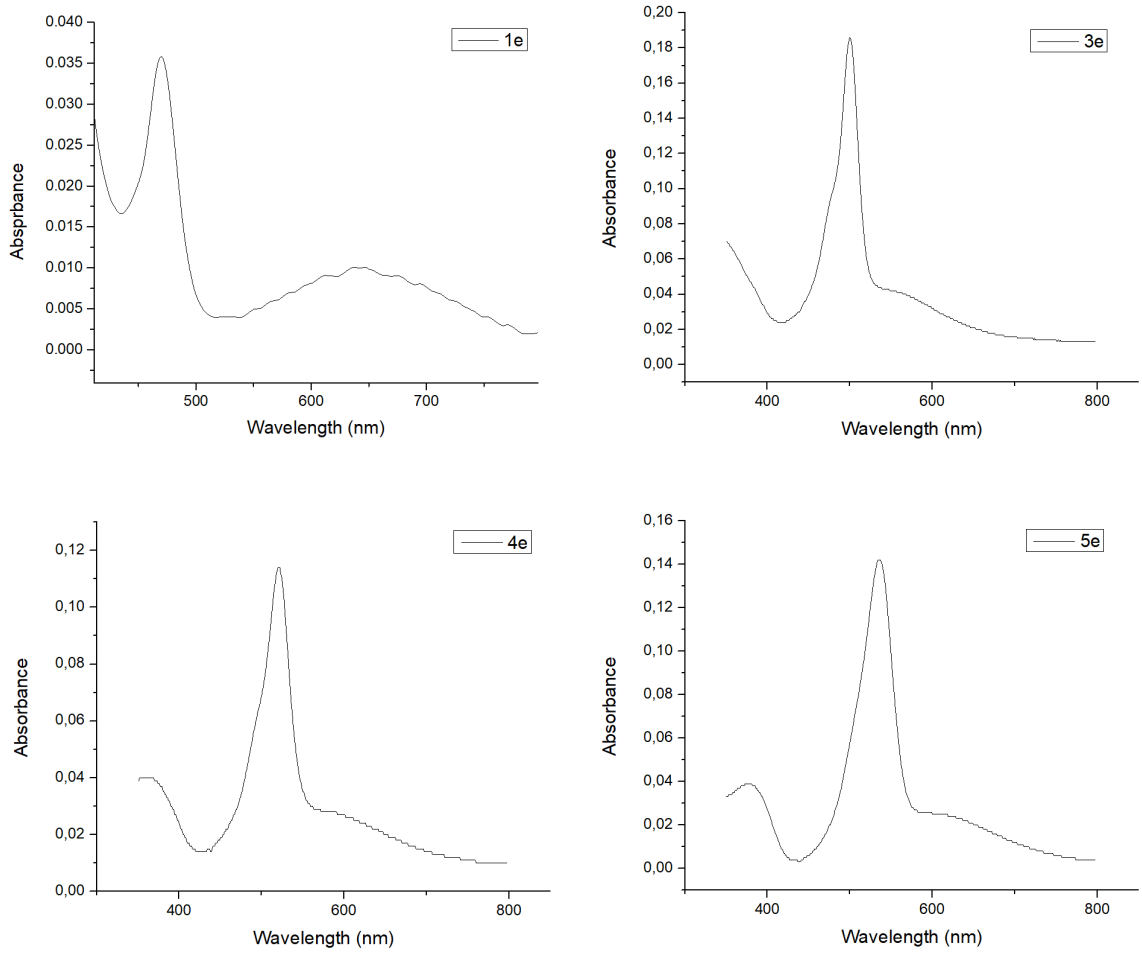


Figure 3.14: UV-visible absorbance spectra of phenothiazine DPMa **1e**, meso-phenothiazine BODIPY **3e**, 2-monobrominated and 2,6-dibrominated meso-phenothiazine BODIPY **4e** and **5e**, top left to bottom right, respectively.

existing data and literature values,[5,48] make it logical to assume that the fluorescence quantum yield (Φ) of **3a** is high. The difference in fluorescence between **3a** and **3e** is to some extent expected, due to previous reports of distorted planarity of the BODIPY chromophore when bonded with phenothiazine at the meso-position.[48] Distorted planarity as cause of low fluorescence have previously been described.[5]

Voltammetry examination of BODIPY **5a**, in solution (DCM), displays a characteristic reversible reduction at -1.7 V and an irreversible oxidation at 0.8 V, as shown in the voltammogram in Figure 3.15. The resulting HOMO and LUMO values from the onsets yield 5.7 eV and 3.5 eV, respectively. The voltammogram displays characteristics in accordance with other similar BODIPY dyes in the literature.[11] The electrochemical bandgap calculated (2.2 eV) is in excellent agreement with the optical bandgap, found from the onset of the absorption spectra (2.2 eV).

Table 3.8: Absorbance and emission maxima of specified compounds. In all compounds but **1e** the maxima is due to the BODIPY unit. Redshift is observed with increased bromination.

Comp.	**Absorbance** λ_{max} [nm]	**Emission** λ_{max} [nm]
3a	495	506
5a	532	548
1e	470	-
3e	500	-
$4e_{\beta}$	521	-
$5e_{\beta}$	536	-

The synthesized chromophores do not possess any notable film forming properties which prevented the study of the optoelectochemical properties in solid state, therefore characterization in solution is preferred.

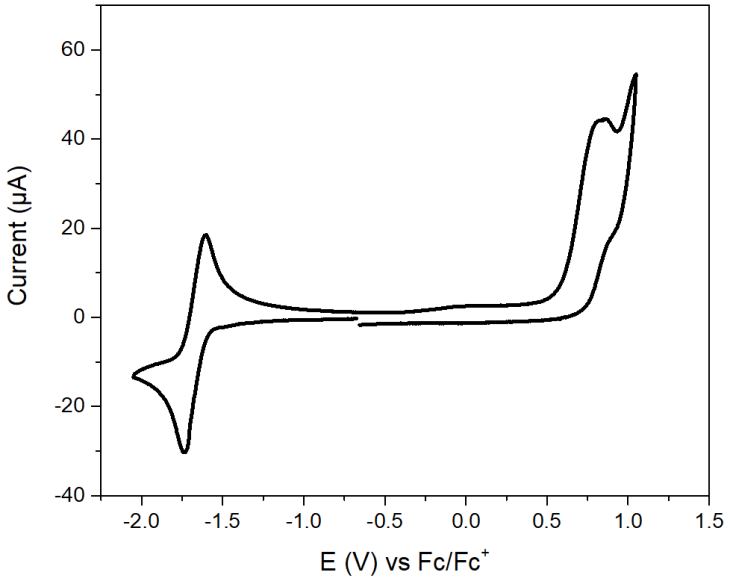


Figure 3.15: Electrochemical measurements of 2,6-dibrominated meso-alkyl BODIPY **5a**. Cyclic voltammetry (200 mV/s scan rate) on **5a** in solution (0.1 M TBAPF6 in DCM). All potentials are *vs* Fc/Fc^{+}.

Chapter 4

Conclusion

A previously reported one-pot synthesis,[26] with minor modifications, has been attempted in order to make α,β-unsubstituted meso-alkylated BODIPY **3a**. The procedure has given unsatisfactory results, being difficult to work up and having modest yields. ^{1}H NMR experiments yielded greater insight into the reactions and side reactions of the condensation reaction between pyrrole and palmitoyl chloride (**a**). BODIPY **3a** was shown to form when all reactants (pyrrole, palmitoyl chloride, DIPEA and $BF_3 \cdot Et_2O$) were mixed at reaction start. A main cause of the modest yields has been identified as the hydrolysis of palmitoyl chloride (**a**) by water formed *in situ*.

A new one-pot method was developed based on NMR experiments, literature search and previous experience with BODIPYs. The new method proved to be better, by having a higher yield (10%) and less aggregated reaction mixture. Bromination of meso-alkyl BODIPY **3a** yielded 2-mono-brominated BODIPY **4a** (38%) and 2,6-dibrominated BODIPY **5a** (27%). Subsequent Suzuki cross-coupling of BODIPY **5a** and pyrene-1-boronic acid, showed that the stability of the meso-alkylated BODIPYs was too low to provide usable quantities of the target molecules for research applications. The one-pot procedure, both original and modified, has been shown unfit for acid chlorides with an EDG in α-position to the carbonyl, as the case with 2-thiophenecarbonyl chloride (**d**).

The two step route to meso-alkylated BODIPY had good yields in the first step, 71% and 90% for DPMa **1b**. The second step could not be performed at RT with DDQ as oxidizing agent. The two-step procedure has worked well with phenothiazine aldehyde **e**, with a yield of 73% for DPMa **1e** and 89% for BODIPY **3e**. The yield of DPMa **1e** is likely to be improvable as the first step has only been performed once. Bromination reactions on phenothiazine BODIPY **3e** had challenges with over-bromination and regioselectivity.

Optical characterization of the synthesized BODIPYs provided useful insight into the role of different meso-substituents. Strong fluorescence was observed for the meso-alkylated BODIPY **3a**, while no fluorescence was observed for the meso-phenothiazine BODIPY **3e**. Voltammetry of BODIPY **5a** showed characteristic reversible reduction (-1.7 V) and irreversible oxidation (0.8 V). The electrochemical bandgap was in agreement with the optical bandgap (2.2 eV).

Important insights:

- Alkyl chain in meso-position yield unstable BODIPY products
- Hydrolysis of the starting acid chloride in one-pot reactions is an important loss mechanism
- The two-step synthesis is preferable to the one-pot reaction
- Limiting equivalents of DDQ and reaction time used in the second step of the two-step reaction is beneficial
- Meso-phenothiazine BODIPYs do not exhibit intense characteristic fluorescence
- Lowering the temperature of bromination reactions from RT to 0 °C impact the equilibrium between kinetic and thermodynamic product
- TLC- and NMR-samples from bromination reactions must be quenched with aqueous $Na_2S_2O_3$-solution before preparation

4.1 Further work

A lot of work for possible new BODIPY projects remain. It is important to keep in mind that the work on BODIPY chromophores just started at NTNU, and as such little previous experience was available at the starting point of the author's project and master assignment.

A logical follow up of this master, would be to focus on the two-step procedure for making new BODIPYs. Preferably BODIPYs with higher stability should be chosen, at least in the start. The largest hurdle of the project and master's assignment has been focusing on too unstable and hard to make products, before enough experience with the BODIPY chromophore was acquired.

It is the authors opinion that the one-pot procedure can be further optimized. However, because of the complexity of the reaction it is difficult to predict the outcome, and a suitable yet stable product might be hard to come by due to the "EWG-preferance" of the initial nucleophilic attack. A possible solution to the decreased reactivity might be to substantially increase the amount of pyrrole used or substitute the DCM with pyrrole entirely. Bromination of phenothiazine BODIPY **3e** (or similar BODIPYs) can also likely be improved. Alternative low temperature bromination of BODIPYs at α-position(s) might be of scientific interest.

Chapter 5

Experimental section

5.1 General methods

Commercial grade reagents were used as supplied by the manufacturer, unless otherwise stated. Dry solvents were collected from a solvent purification system (MB SPS-800 Solvent Purification System). All reactions were monitored using NMR and thin-layer chromatography (TLC, silica gel 60 F254, 0.25 mm thickness). The TLC plates were developed by UV-light. Flash chromatography was carried out using silica gel (Sigma Aldrich silica gel 60, 0.040-0.063 mm). Reported yields are corrected for solvent and impurities.

NMR spectra were recorded using a 400 MHz NMR spectrometer (Bruker Avance III HD NMR spectrometer, Nanaobay electronics). Spectra are presented with acquisition parameters. ^{1}H chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (TMS $\delta = 0.0$) as the internal standard. Peaks are characterized as s (singlets), brs (broad singlets), d (doublets), t (triplets), q (quartets), quint (quintets), sept (septets) or m (multiplets). Coupling constants (J) are given in Hertz (Hz). The values of the chemical shifts were determined by COSY, HSQC and HMBC as well as ^{1}H and ^{13}C NMR experiments.

Electrochemistry studies were performed using a standard three-electrode cell under argon atmosphere. All measurements were performed with Ar bubbling into the electrochemical cell for 15 min. 10 sec prior to the measurements, the Ar was turned to "blanket-mode". Platinum wire (99.99%) was used as working electrode and platinum gauze (55 mesh, 99.9%) as counter electrode. Silver/silver chloride was used as a reference electrode. Tetrabutylammonium hexafluorophosphate (0.1 M, $TBAPF_6$, 98%) was used as electrolyte and was recrystallized three times from acetone and dried in vacuum at approximately 100 °C before each experiment. Measurements were recorded using an EG&G Princeton Applied Research potensiostat/galvano-stat Model Verstastat 3 connected to a personal computer running VersaStudio software. The scan rate was kept constant for all CV runs at 200 mV/s. All results were calibrated using commercially available ferrocene (purified by sublimation) as internal standard. Samples were measured in DCM. To calculate HOMO/LUMO levels, using the potentials obtained, the following equations[49] were used:

$$E_{HOMO} = -(E_{[ox\ vs\ Fc/Fc+]} + 5.1)(eV) \tag{5.1}$$

$$E_{LUMO} = -(E_{[red\ vs\ Fc/Fc+]} + 5.1)(eV) \tag{5.2}$$

For HOMO-LUMO estimations, the onset of the peak was considered.

Modified procedures for one-pot synthesis of BODIPYs

Experiment KS-9

Synthesis of BODIPY **3a**: Distilled pyrrole (5.0 mL, 72 mmol, 2.2 eq.), palmitoyl chloride (10.0 mL, 33 mmol, 1 eq.), DIPEA (10 mL) and $BF_3 \cdot Et_2O$ (14 mL, drop-wise) were added to DCM (120 mL) under nitrogen atmosphere at -18 °C (ice/acetone bath). The reaction mixture was left stirring in the bath for 23 hours, and was allowed to reach ambient temperature. The reaction was washed with aqueous NaOH-solution (0.1 M, 4 × 200 mL) and filtered. The reaction mixture was washed with distilled water (400 mL), dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. The crude product (9.60 g) was filtered through silica gel (ethyl acetate/*n*-pentane, 1:5 v/v) and evaporated under reduced pressure. The product was purified by column chromatography on silica gel (gradient ethyl acetate/*n*-pentane, 1:100 to 1:25, v/v). A red/green oil/solid with green surface was obtained with a yield of 10% (1.28 g, 3.2 mmol).*

BODIPY **3a**, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.84 (s, 2 CH), 7.27 (d, 2 CH, J = 4.2), 6.55-6.51 (m, 2 CH), 2.92 (t, CH_2, J = 8.0), 1.78 (qui, CH_2, J = 7.7), 1.49-1.39 (m, CH_2), 1.39-1.17 (m, 12 CH_2), 0.88 (t, CH_3, J = 6.7)

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 151.3 (C), 143.3 (2 CH), 135.2 (2 C), 127.8 (2 CH), 117.9 (2 CH), 33.9 (CH_2), 31.9 (CH_2), 31.2 (CH_2), 30.1 (CH_2), 29.7-29.6 (6CH_2) 29.4-29.3 (3 CH_2), 22.7 (CH_2), 14.1 (CH_3)

R_f (1:5 ethyl acetate/*n*-pentane): 0.77

*Performed during the project assignment, included for explanatory purposes.

Experiment KS-10

Synthesis of BODIPY **3a**: DIPEA (20 mL) and $BF_3 \cdot Et_2O$ (5 mL, drop-wise) were added to distilled pyrrole (36.0 mL, 519 mmol, 31 eq.) under nitrogen atmosphere at -18 °C (ice/acetone bath). Palmitoyl chloride (5.0 mL, 16.5 mmol, 1 eq.) in DCM (20 mL) was added drop-wise over 6 hours. The reaction mixture was left stirring in the ice/acetone bath for 23 hours total, and was allowed to reach ambient temperature. $BF_3 \cdot Et_2O$ (15 mL) was added drop-wise after 7 hours reaction time. The reaction was not worked up.

Experiment KS-11

Synthesis of BODIPY **3a**: DIPEA (10 mL), distilled pyrrole (8 mL, 115 mmol, 3.5 eq.) and palmitoyl chloride (10 mL, 33 mmol, 1 eq., drop-wise) were added to DCM (100 mL) with anhydrous $MgSO_4$ (8 g) under nitrogen atmosphere at -18 °C (ice/acetone bath). $BF_3 \cdot Et_2O$ (14 mL) was added drop-wise over 45 minutes. The reaction mixture was left stirring in the ice/acetone bath for 43 hours total, and was allowed to reach ambient temperature. The reaction was washed with aqueous NaOH-solution (0.1 M, 4 × 200 mL) and filtered. The reaction mixture was washed with distilled water (400 mL), dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. The crude product

(10.24 g) was filtered through silica gel (ethyl acetate/*n*-pentane, 1:20 v/v). The product was dissolved in n-pentane, filtered and partially evaporated before it was purified by column chromatography on silica gel (gradient ethyl acetate/*n*-pentane, 1:100 to 1:25, v/v). A red/green oil/solid was obtained with a yield of 4% (0.4888 g, 1.2 mmol).

Experiment KS-15

Synthesis of BODIPY **3d**: Distilled pyrrole (1.5 mL, 2.16 mmol, 2.3 eq.), 2-thiophenecarbonyl chloride (1 mL, 0.94 mmol, 1 eq.), DIPEA (0.6 mL, drop-wise) and $BF_3 \cdot Et_2O$ (1.8 mL, drop-wise) were added to DCM (12 mL) with $MgSO_4$ (0.8 g) under nitrogen atmosphere at -18 °C (ice/acetone bath). More DIPEA (0.6 mL, drop-wise) was added 30 minutes after the addition of $BF_3 \cdot Et_2O$. The reaction mixture was left stirring in the ice/acetone bath for 17 days, and was allowed to reach ambient temperature.*

*The reaction was left this long due to illness, and was not worked up because of decomposition of the product.

Brominations of BODIPY 3a for synthesis of mono- and dibrominated BODIPYs 4a and 5a

Experiment KS-12

Synthesis of BODIPY **4a** and **5a**: BODIPY **3a** (136 mg, 0.34 mmol, 1 eq.) was dissolved in a solvent mixture of DCM (12 mL) and DMF (12 mL) under nitrogen atmosphere at RT. Recrystallized NBS (164 mg, 0.92 mmol, 2.7 eq.) in DCM (10 mL) was added drop-wise over 3 hours. The reaction was stopped after 27 hours, and the mixture evaporated under reduced pressure. The crude was purified by column chromatography on silica gel (gradient ethyl acetate/*n*-hexane, 1:100, v/v). A pink solid identified as the dibrominated product **5a** was obtained with a yield of 27% (51.8 mg, 0.093 mmol), and a dark purple solid identified as the monobrominated product **4a** and several impurities was obtained with a yield of 63% (103.2 mg, 0.214 mmol).*

*The purple product mixture is estimated to be 60% pure, giving a corrected yield of 38% (62 mg, 0.13 mmol)

Bodipy **4a**, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.91 (s, CH), 7.69 (s, CH), 7.34 (d, CH, $J = 4.3$), 7.20 (s, CH), 6.59 (d, CH, $J = 4.1$), 2.88 (t, CH_2, $J = 7.9$), 1.76 (qui, CH_2, $J = 7.7$), 1.47-1.38 (m, CH_2), 1.37-1.16 (m, 12 CH_2), 0.88 (t, CH_3, $J = 6.7$)

Bodipy **5a**, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.75 (s, 2 CH), 7.27 (s, 2 CH), 2.83 (t, CH_2, $J = 8.0$), 1.76 (qui, CH_2, $J = 7.8$), 1.47-1.38 (m, CH_2), 1.37-1.17 (m, 12 CH_2), 0.88 (t, CH_3, $J = 6.7$)

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 151.2 (C), 143.5 (2 CH), 134.9 (2 C), 128.2 (2 CH), 106.7 (2 CBr), 33.9 (CH_2), 31.9 (CH_2), 31.5 (CH_2), 30.1 (CH_2), 29.7-29.3 (9 CH_2), 22.7 (CH_2), 14.1 (CH_3)

Experiment KS-13

Synthesis of BODIPY **4a** and **5a**: BODIPY **3a** (352 mg, 0.875 mmol, 1 eq.) was dissolved in a solvent mixture of DCM (25 mL) and DMF (25 mL) under nitrogen atmosphere at RT. Recrystallized NBS (486 mg, 2.73 mmol, 3.1 eq.) in DCM (25 mL) was added drop-wise over 3.5 hours under stirring. The reaction was stopped after 4 hours. The reaction mixture was diluted with DCM (50 mL), and washed with aqueous $Na_2S_2O_3$-solution (10 wt%, 100 mL) and distilled water (3 × 100 mL). The organic phase was dried over $MgSO_4$, decanted and evaporated under reduced pressure. The crude was dissolved in n-pentane, filtered, partially evaporated under reduced pressure and purified by column chromatography on silica gel (gradient ethyl acetate/*n*-pentane, 1:100 to 1:25, v/v). A pink solid identified as the dibrominated product **5a** was obtained with a yield of 29% (143.0 mg, 0.255 mmol), and a dark purple solid identified as the monobrominated product **4a** and several impurities was obtained with a yield of 16% (67.5 mg, 0.140 mmol).*

*The purple product mixture is estimated to be 50% pure, giving a corrected yield of 8% (33.8 mg, 0.070 mmol)

Suzuki coupling of BODIPY 5a and pyrene-1-boronic acid

Experiment KS-14

Synthesis of BODIPY **6a**: A degassed solvent mixture of THF (60 mL) and distilled water (0.4 mL) was added to BODIPY **5a** (143 mg, 0.255 mmol, 1 eq.), pyrene-1-boronic acid (160 mg, 0.650 mmol, 2.5 eq.), $Pd_2(dba)_3$ (23 mg), $[(t\text{–Bu})_3PH]BF_4$ (30 mg) and Cs_2CO_3 (345 mg) by cannulation. The reaction mixture was stirred at RT for 114 hours under nitrogen atmosphere. The reaction mixture was filtered through a cilite-pad and evaporated under reduced pressure. The crude was purified by column chromatography on silica gel (gradient DCM/*n*-pentane, 1:50 to 1:5, v/v).

Procedure for synthesis of dipyrromethane (DPMa) 1e

Experiment KS-16

Synthesis of DPMa **1e**: 10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazine-3-carbaldehyde **(e)** (2.05 g, 4.91 mmol, 1 eq) was dissolved in distilled pyrrole (18.0 mL, 260 mmol, 53 eq) and the mixture was degassed under nitrogen atmosphere for 1 hour. Trifluoroacetic acid (0.05 mL) was added and the reaction stirred for 15 minutes. The reaction mixture was diluted with DCM (100 mL) and washed with aqueous NaOH-solution (0.1 M, 3 × 100 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude was purified by column chromatography on silica gel (gradient ethyl

acetate/*n*-pentane, 1:5 to 1:2, v/v). An orange oil was obtained with a yield of 73% (1.926 g, 3.61 mmol).

DPMa **1e**, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.90 (brs, 2 NH), 7.46-7.41 (m, 2 CH), 7.33-7.29 (m, CH), 7.28 (d, CH, J = 2.1), 7.00-6.96 (m, 2 CH), 6.96-6.91 (m, 2 CH), 6.87 (d, CH, J = 8.4), 6.79 (d, CH, J = 8.2), 6.70-6.67 (m, 2 CH), 6.17-6.13 (m, 2 CH), 5.94-5.91 (m, 2 CH), 5.37 (s, CH), 3.83 (s, ceCH3), 3.82 (t, CH_2, J = 7.2), 1.81 (quint, CH_2, J = 7.4), 1.48-1.38 (m, CH_2), 1.34-1.28 (m, 2 CH_2), 0.88 (t, CH_3, J = 7.1)

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 158.9 (C), 144.1 (C), 143.8 (C), 136.1 (C), 135.2 (C), 132.6 (C), 132.3 (2 C), 127.5 (2 CH), 127.3 (CH), 127.2 (CH), 125.5 (CH), 125.5 (CH), 124.8 (C), 124.7 (C), 117.2 (2 CH), 115.4 (CH), 115.3 (CH), 114.2 (2 CH), 108.5 (2 CH), 107.2 (2 CH), 55.4 (CH_3), 47.5 (CH_2), 43.1 (CH), 31.5 (CH_2), 26.9 (CH_2), 26.7 (CH_2), 22.6 (CH_2) , 14.0 (CH_3)

R_f (1:5 ethyl acetate/*n*-pentane): 0.75

Procedures for synthesis of BODIPY 3e

Experiment KS-17

Synthesis of BODIPY **3e**: Dipyrromethane **1e** (100 mg, 0.19 mmol, 1 eq.) in dry DCM (18 mL) was added DDQ (59 mg, 0.26 mmol, 1.4 eq.) in dry DCM (3.5 mL) drop-wise over 30 minutes under nitrogen atmosphere with stirring. DIPEA (0.15 mL, drop-wise) was added after 1 hour total reaction time and the mixture was stirred for 15 minutes before drop-wise addition of $BF_3 \cdot Et_2O$ (0.11 mL). The reaction was stopped after 2 hours and 15 minutes total reaction time. The reaction mixture was diluted with DCM (100 mL) and washed with aqueous NaOH-solution (0.1 M, 5 × 50 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude was purified by column chromatography on silica gel (*n*-hexane/DCM, 1:2, v/v). A dark purple oil/solid was obtained with a yield of 43% (47.8 mg, 0.083 mmol).

Bodipy **3e**, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.91 (s, 2 CH), 7.49-7.42 (m, 2 CH), 7.40-7.34 (m, 2 CH), 7.34-7.30 (m, 2 CH), 7.00 (d, 2 CH, J = 4.0), 6.98-6.91 (m, 4 CH), 6.56-6.52 (m, 2 CH), 3.91 (t, CH_2, J = 7.3), 3.84 (s, CH_3), 1.88 (quint, CH_2, J = 7.4), 1.49 (quint, CH_2, J = 7.3), 1.38-1.32 (m, 2 CH_2), 0.90 (t, CH_3, J = 7.3)

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 159.1 (C), 148.0 (C), 146.3 (C), 143.4 (2 CH), 142.5 (C), 136.2 (C), 134.5 (2 C), 132.2 (C), 131.0 (2 CH), 130.6 (CH), 129.4 (CH), 127.8 (C), 127.5 (2 CH), 125.8 (CH), 125.6 (CH), 124.6 (C), 124.0 (C), 118.2 (2 CH), 115.9 (CH), 114.7 (CH), 114.3 (2 CH), 55.4 (CH_3), 47.9 (CH_2), 31.5 (CH_2), 26.8 (CH_2), 26.6 (CH_2), 22.6 (CH_2), 14.0 (CH_3)

R_f (100 % DCM): 0.35

Experiment KS-18

Synthesis of BODIPY **3e**: Dipyrromethane **1e** (500 mg, 0.94 mmol, 1 eq.) in dry DCM (100 mL) was added DDQ (225 mg, 0.99 mmol, 1.06 eq.) in dry DCM (25 mL) drop-wise over 30 minutes under nitrogen atmosphere with stirring. The reaction was stirred for 10 minutes before it was chilled in an ice bath. DIPEA (0.75 mL) and $BF_3 \cdot Et_2O$ (0.55 mL) was added drop-wise. The ice bath was removed and the reaction was stirred for 30 minutes before it was stopped after 1.5 hours total reaction time. The reaction mixture was partly evaporated under reduced pressure. The crude was purified by column chromatography on silica gel (*n*-hexane/DCM, 1:1, v/v). A dark purple oil/solid was obtained with a yield of 89% (485.8 mg, 0.84 mmol).

Experiment KS-20

Synthesis of BODIPY **3e**: Dipyrromethane **1e** (1.205 g, 2.26 mmol, 1 eq.) in dry DCM (240 mL) was added DDQ (520 mg, 2.29 mmol, 1.01 eq.) in dry DCM (60 mL) drop-wise over 70 minutes under nitrogen atmosphere with stirring. The reaction was chilled in an ice bath, NEt_3 (1.2 mL) and $BF_3 \cdot Et_2O$ (1.3 mL) was added drop-wise. The ice bath was removed and the reaction was stopped after 98 hours total reaction time. The reaction mixture was partly evaporated under reduced pressure. The crude was purified by column chromatography on silica gel (gradient *n*-pentane/DCM, 1:1 to 2:3, v/v). A dark purple oil/solid was obtained with a yield of 28% (360.7 mg, 0.62 mmol).*

*NEt_3 was used instead of DIPEA, which is believed to be the main reason for the low conversion rate and yield. DIPEA was not available at the time of the reaction.

Brominations of BODIPY 3e for synthesis of mono- and dibrominated BODIPYs 4e and 5e

Experiment KS-19

Synthesis of BODIPY **4e** and **5e**: BODIPY **3e** (45.0 mg, 0.078 mmol, 1 eq.) was dissolved in a solvent mixture of DCM (2.5 mL) and DMF (2.5 mL) under nitrogen atmosphere at RT. Recrystallized NBS (42.6 mg, 0.24 mmol, 3.1 eq.) in DCM (5 mL) was added drop-wise over 1 hour under stirring. After 22 hours more recrystallized NBS (7.7 mg, 0.043 mmol, 0.56 eq.) in DCM (1 mL) was added drop-wise over 10 minutes. The reaction was stopped after 25 hours total reaction time. The reaction mixture was washed with aqueous $Na_2S_2O_3$-solution (10 wt%, 10 mL) and distilled water (3 × 10 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude was purified by column chromatography on silica gel (*n*-pentane/DCM, 1:1, v/v). A purple solid identified as the dibrominated product **5e**$_\beta$ was obtained with a yield of 13% (7.7 mg, 0.010 mmol), and a dark purple solid identified as the monobrominated product **4e**$_\beta$ and several impurities was obtained with a yield of 2% (1.1 mg, 0.0017 mmol).

Bodipy **4e**$_\beta$, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.95 (s, CH), 7.75 (s, CH), 7.48-7.42 (m, 2 CH), 7.36-7.30 (m, 3 CH), 7.26 (d, CH, J = 2.0), 7.05 (d, CH, J = 4.2), 6.97-6.89 (m, 5 CH), 6.59-6.56 (m, CH), 3.89 (t, CH_2, J = 7.2), 3.83 (s, CH_3), 1.86 (quint, CH_2, J = 7.4), 1.48 (quint, CH_2, J = 7.2), 1.38-1.32 (m, 2 CH_2), 0.90 (t, CH_3, J = 7.3)

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 159.2 (C), 148.4 (C), 146.1 (C), 145.2 (CH), 142.2 (C), 141.3 (CH), 136.3 (C), 134.9 (C), 133.9 (C), 132.6 (CH), 132.1 (C), 130.7 (CH), 129.7 (CH) 129.3 (CH), 127.6 (2 CH), 127.3 (C), 125.9 (CH), 125.6 (CH), 124.8 (C), 123.8 (C), 119.2 (CH), 116.0 (CH), 114.8 (CH), 114.3 (2 CH), 105.6 (CBr), 55.4 (CH_3), 48.0 (CH_2), 31.5 (CH_2), 26.8 (CH_2), 26.6 (CH_2), 22.6 (CH_2), 14.0 (CH_3)

R_f (100 % DCM): 0.48

Bodipy **5e**$_\beta$, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.81 (s, 2 CH), 7.50-7.44 (m, 2 CH), 7.39-7.34 (m, 2 CH), 7.34-7.29 (m, 2 CH), 7.03 (s, 2 CH), 6.99-6.92 (m, 4 CH), 3.93 (t, CH_2, J = 7.3), 3.85 (s, CH_3), 1.88 (quint, CH_2, J = 7.2), 1.50 (quint, CH_2, J = 7.3), 1.39-1.33 (m, 2 CH_2), 0.91 (t, CH_3, J = 7.0)

R_f (100 % DCM): 0.58

R_f (1:2 Et_2O/*n*-pentane): 0.38

Experiment KS-21

Synthesis of BODIPY **4e** and **5e**: BODIPY **3e** (770 mg, 1.33 mmol, 1 eq.) was dissolved in a solvent mixture of DCM (35 mL) and DMF (35 mL) under nitrogen atmosphere at RT. The mixture was cooled in an ice bath, and recrystallized NBS (578 mg, 3.25 mmol, 2.4 eq.) in DCM (25 mL) was added drop-wise over 3 hours under stirring. and was allowed to reach ambient temperature. in the ice bath the reaction was stopped after 72 hours total reaction time. The reaction mixture was washed with aqueous $Na_2S_2O_3$-solution (10 wt%, 200 mL) and distilled water (3 × 200 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude was purified by column chromatography on silica gel (gradient *n*-hexane/DCM, 3:2 to 1:2, v/v). BODIPY $\mathbf{5}_{\alpha,\beta}$ and $\mathbf{5}_{\beta}$ was identified in fraction 2-13 with a combined yield of 13% (124.9 mg, 0.13 mmol). BODIPY $\mathbf{4}_{\beta}$ and traces of $\mathbf{4}_{\alpha}$ was identified in fraction 15-18 with a yield of 33% (292.9 mg, 0.44 mmol). Fractions 2-13 with BODIPY $\mathbf{5}_{\alpha,\beta}$ and $\mathbf{5}_{\beta}$ was purified twice by column chromatography on silica gel (Et_2O/*n*-pentane, 1:2, v/v).

Bodipy $\mathbf{5e}_{\alpha,\beta}$, ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.77 (s, CH), 7.49-7.44 (m, 2 CH), 7.38-7.31 (m, 3 CH), 7.27 (d, CH, J = 2.1), 6.99-6.92 (m, 6 CH), 6.57 (d, CH, J = 4.5), 3.92 (t, CH_2, J = 7.3), 3.85 (s, CH_3), 1.88 (quint, CH_2, J = 7.3), 1.49 (quint, CH_2, J = 7.3), 1.39-1.32 (m, 2 CH_2), 0.90 (t, CH_3, J = 7.0)

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 159.2 (C), 148.5 (C), 145.9 (C), 142.2 (C), 141.9 (CH), 136.4 (C), 135.6 (CBr), 133.7 (C), 133.5 (C), 132.7 (CH), 132.1 (C), 130.7 (CH), 129.7 (CH), 129.2 (CH), 127.6 (2 CH), 126.6 (C), 125.9 (CH), 125.6 (CH), 125.0 (C), 123.8 (C), 122.9 (CH), 116.0 (CH), 114.8 (CH), 114.3 (2 CH), 106.3 (CBr), 55.4 (CH_3), 48.0 (CH_2), 31.5 (CH_2), 26.8 (CH_2), 26.7 (CH_2), 22.6 (CH_2), 14.0 (CH_3)

R_f (100 % DCM): 0.58

R_f (1:2 Et_2O/*n*-pentane): 0.29

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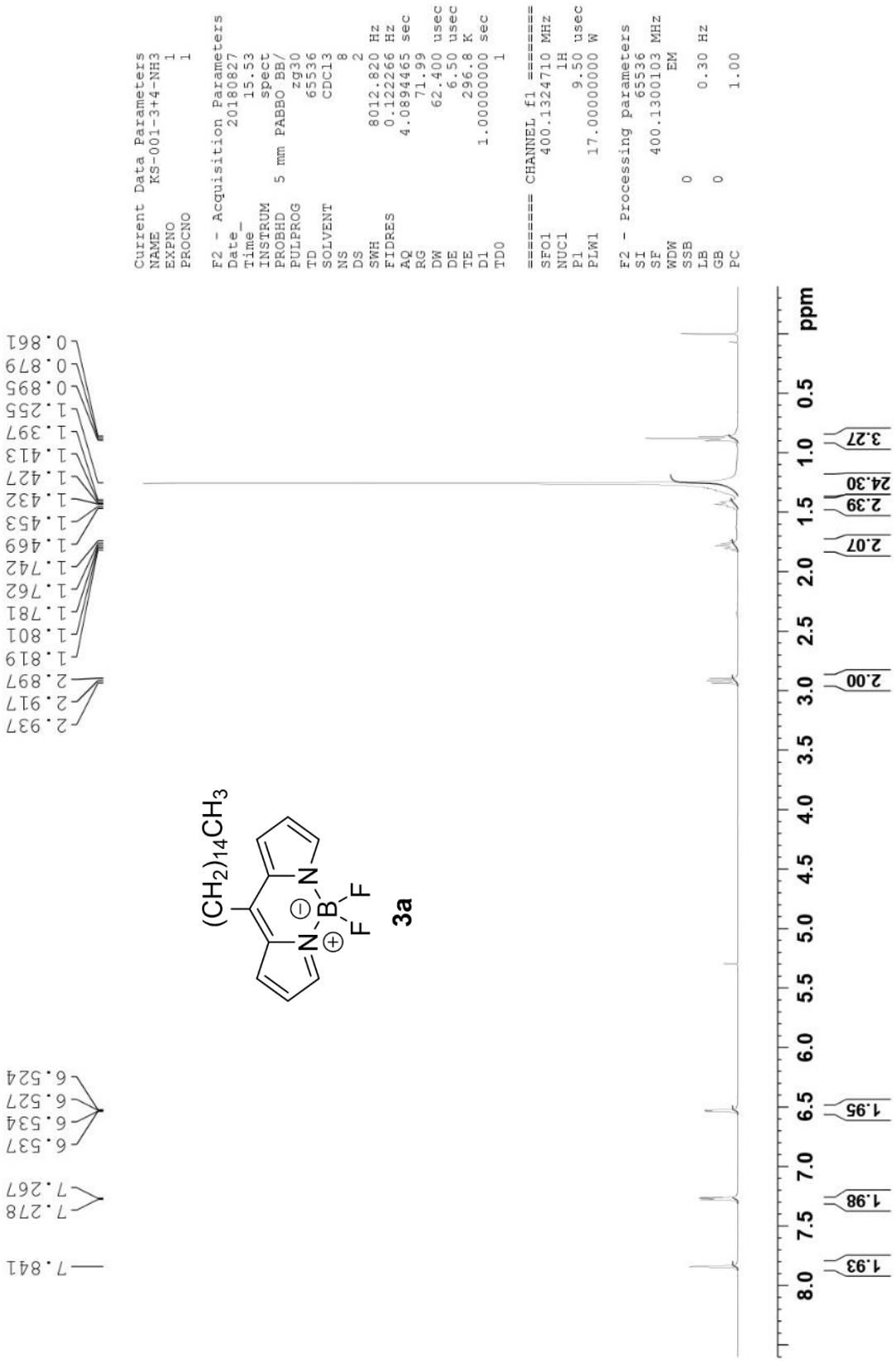
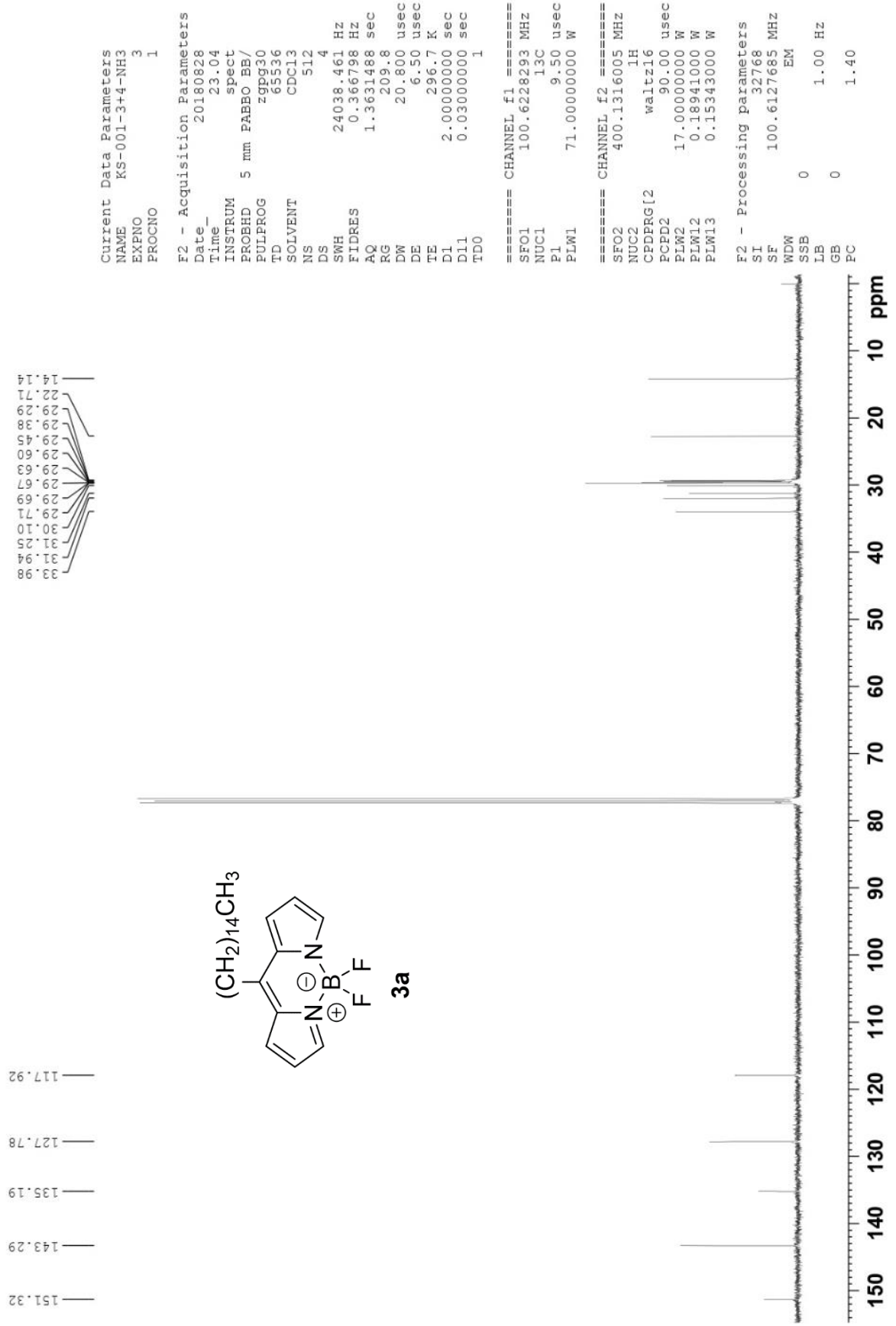
Appendices

A Spectra of BODIPY **3a**

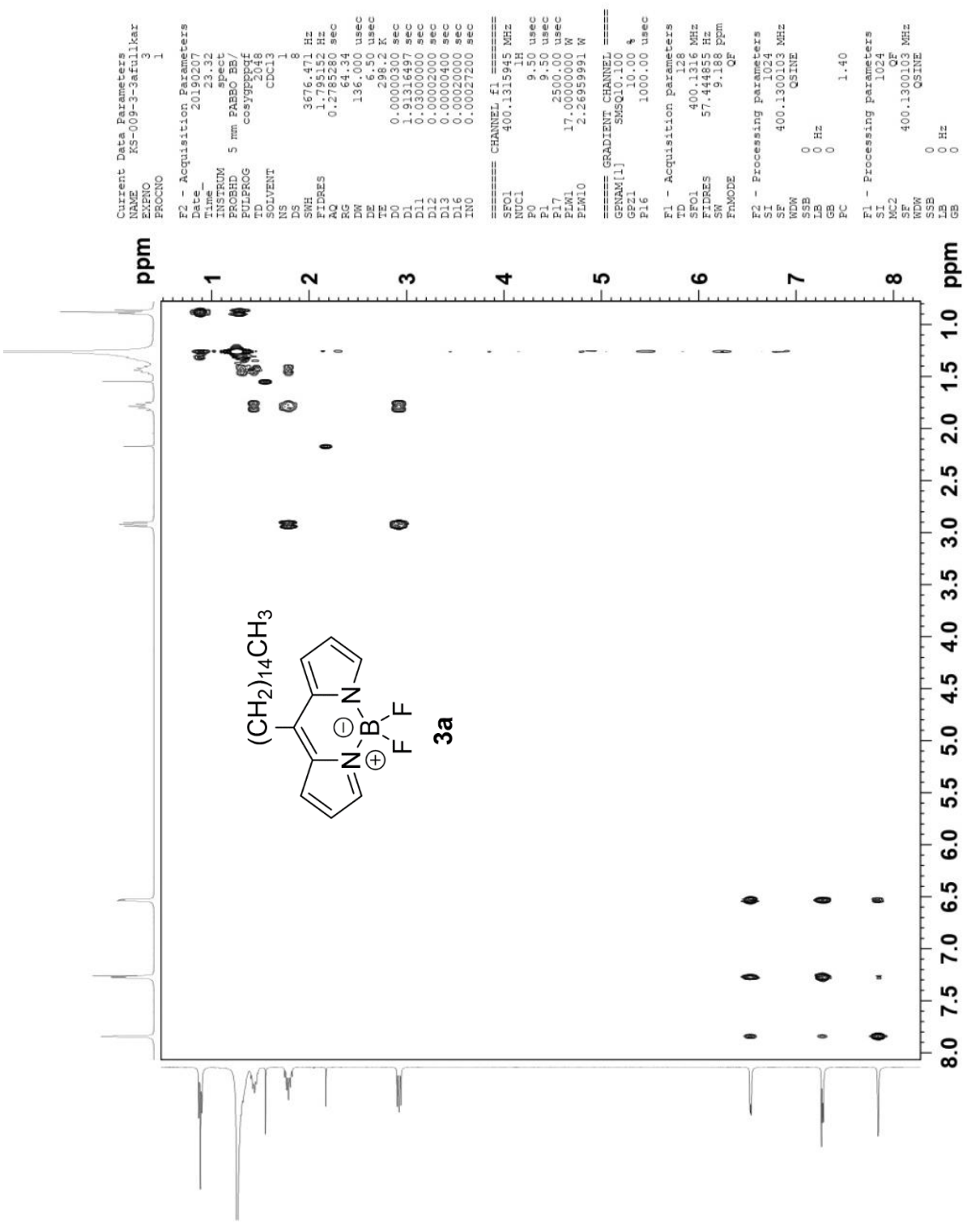
A1 ^{1}H NMR spectrum of BODIPY **3a**



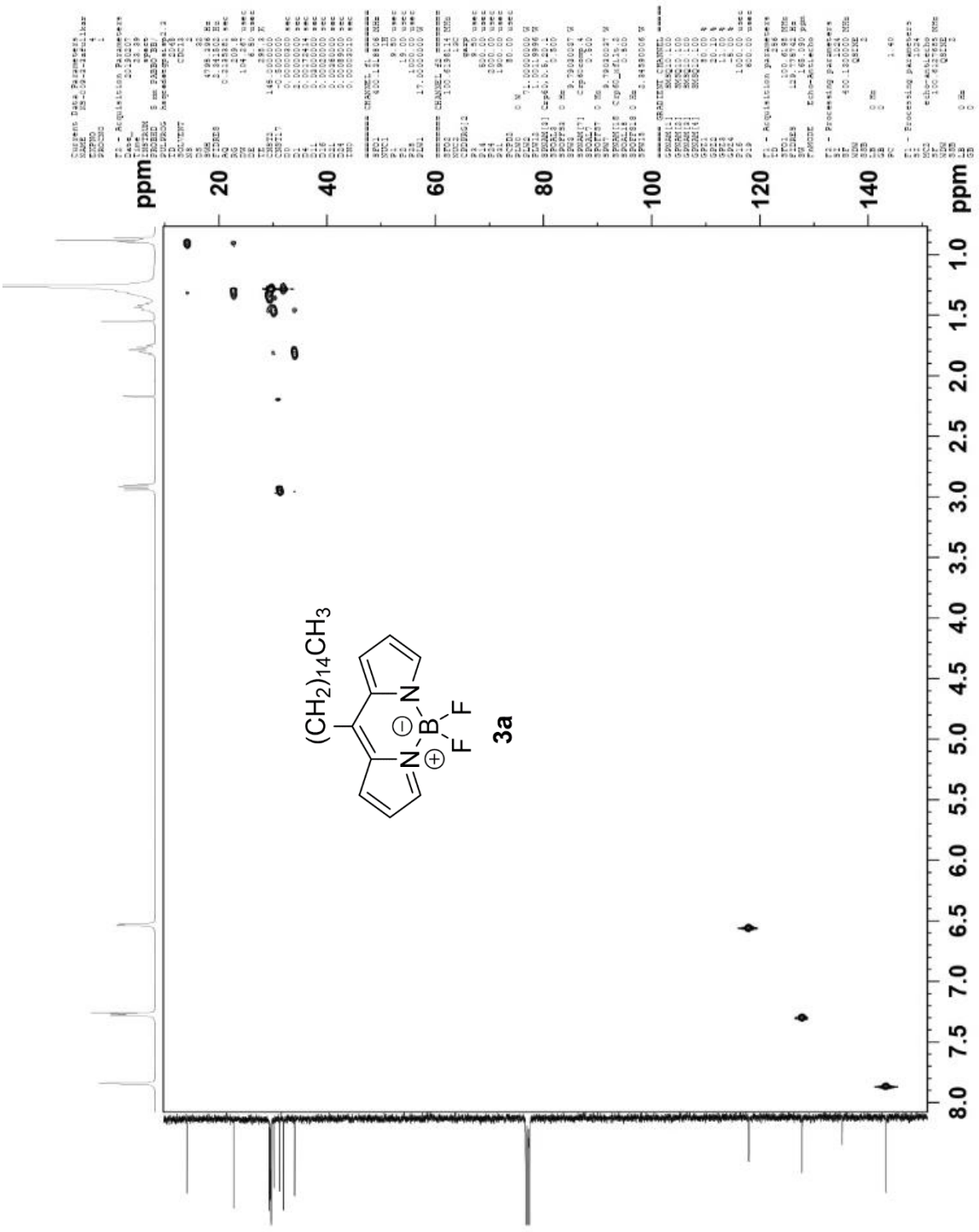
A2 ^{13}C NMR spectrum of BODIPY **3a**



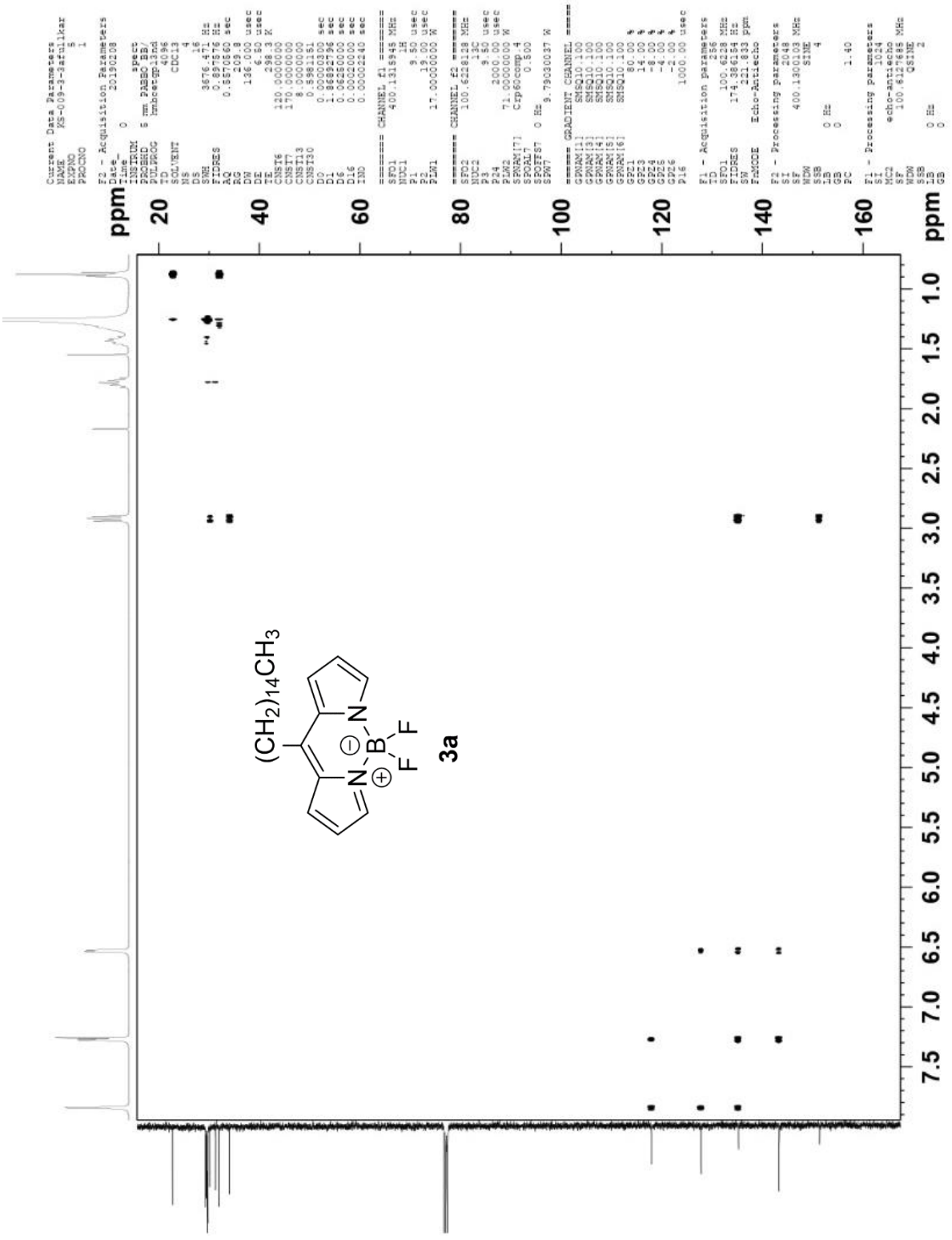
A3 COSY spectrum of BODIPY **3a**



A4 HSQC spectrum of BODIPY **3a**

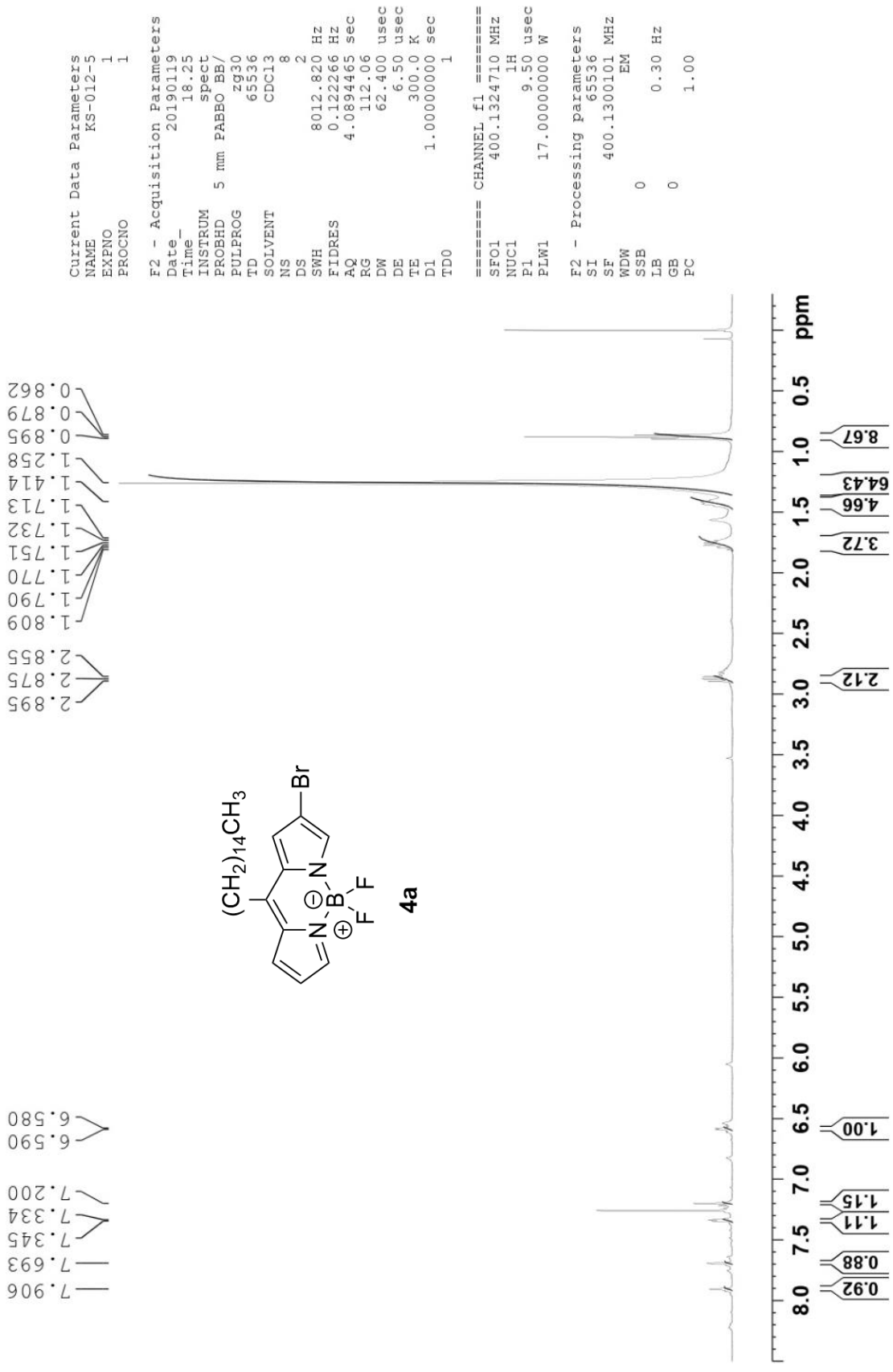


A5 HMBC spectrum of BODIPY **3a**



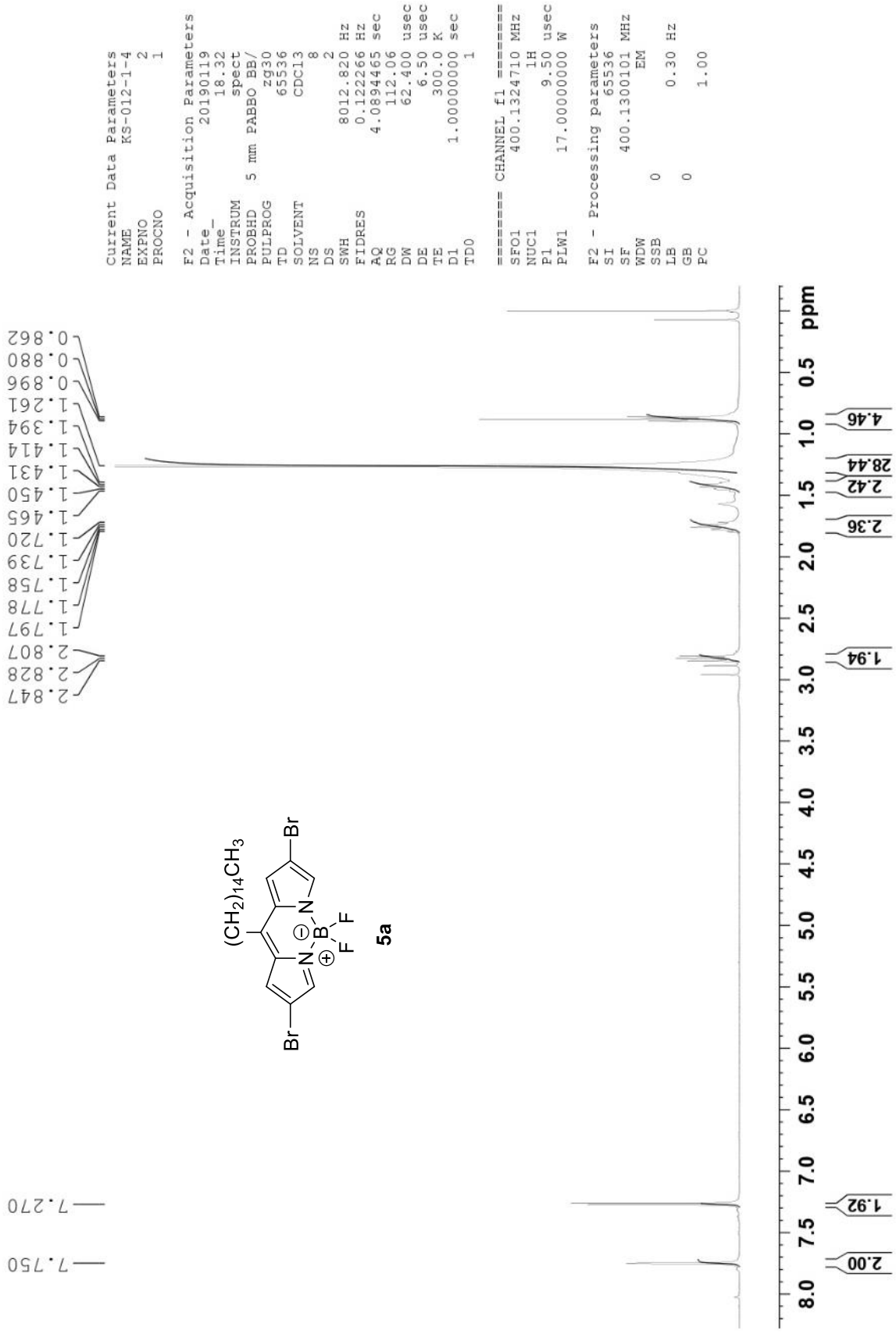
B Spectrum of BODIPY **4a**

B1 ^{1}H NMR spectrum of BODIPY **4a**

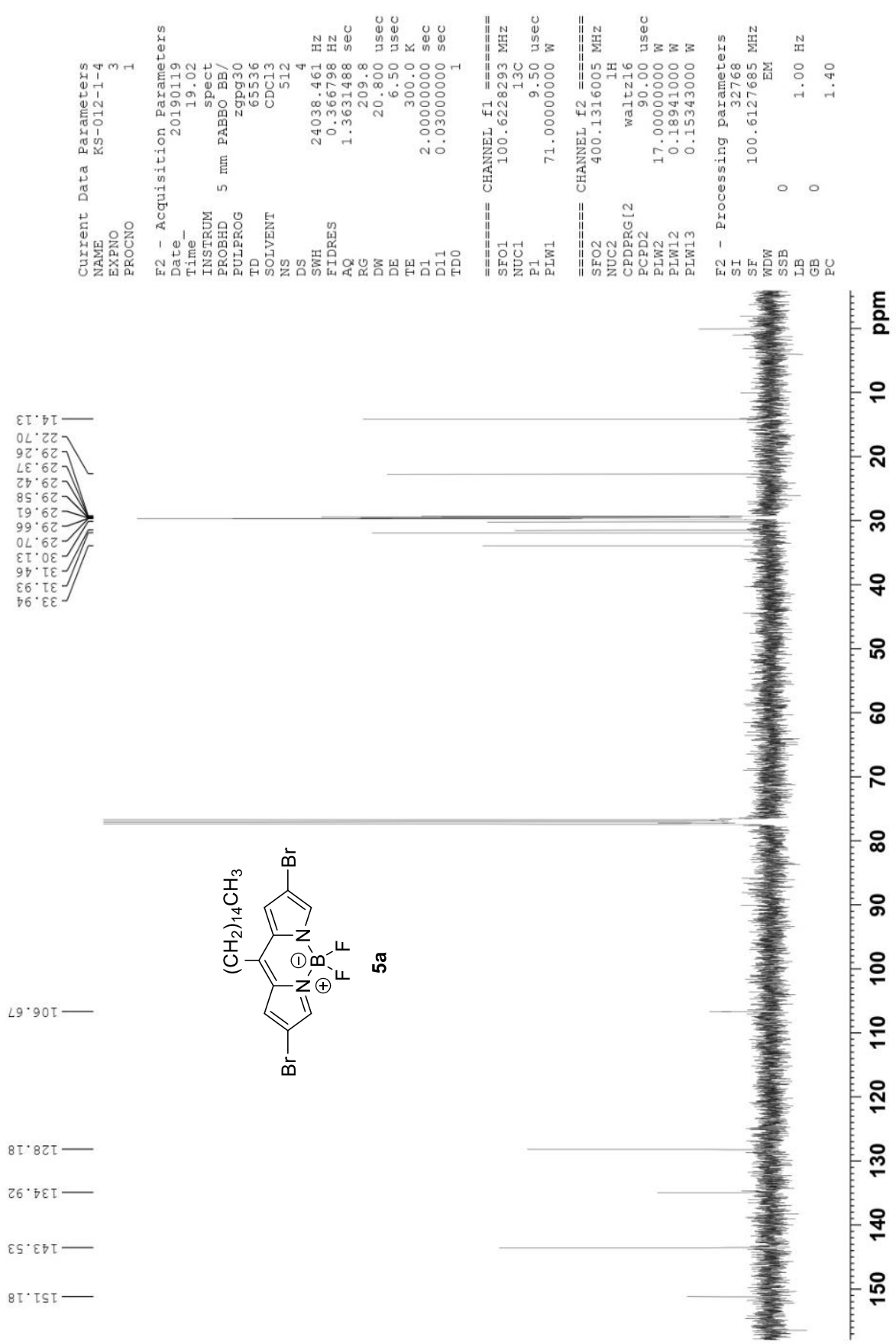


C Spectra of BODIPY **5a**

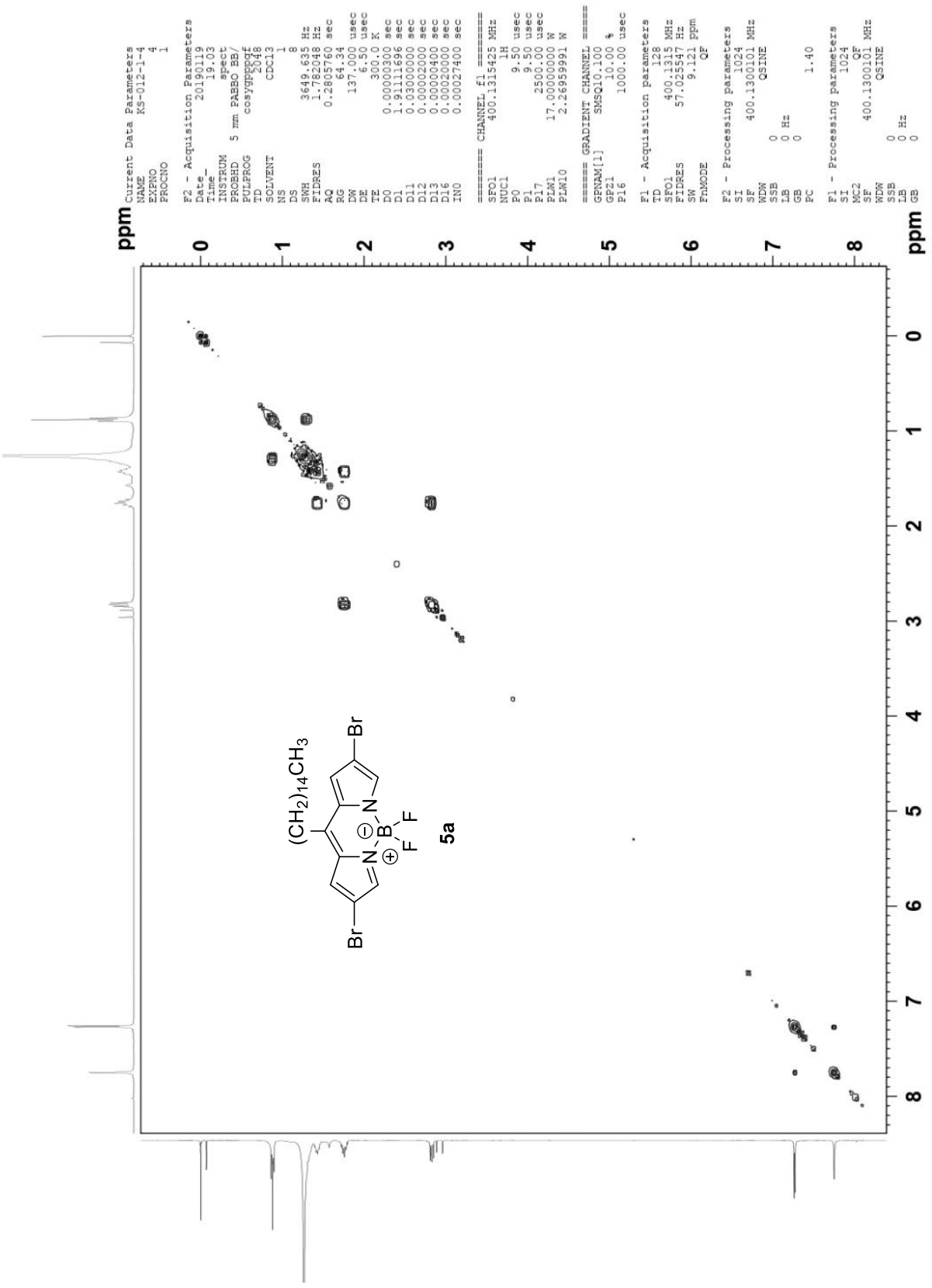
C1 ^{1}H NMR spectrum of BODIPY **5a**



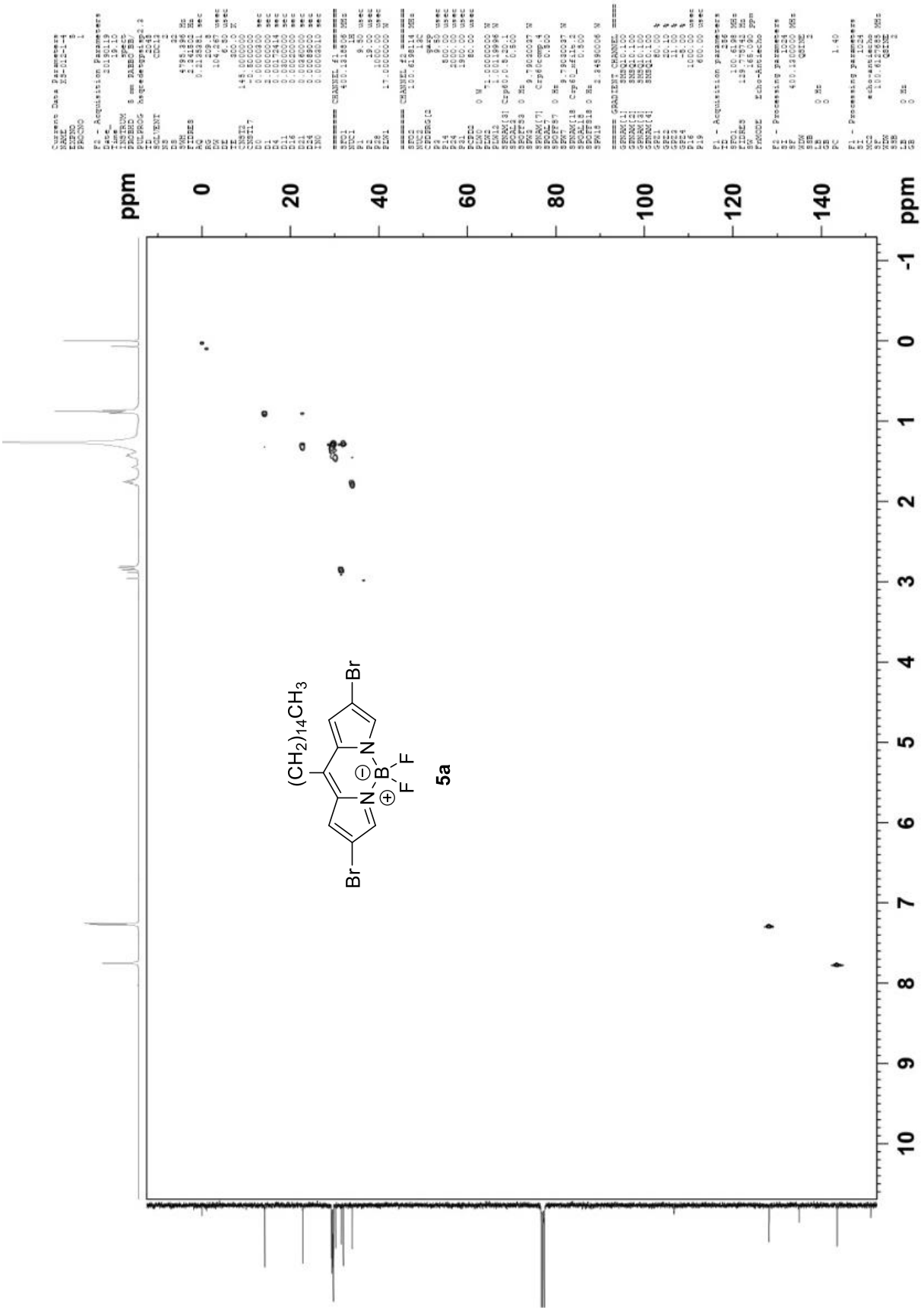
C2 ^{13}C NMR spectrum of BODIPY **5a**



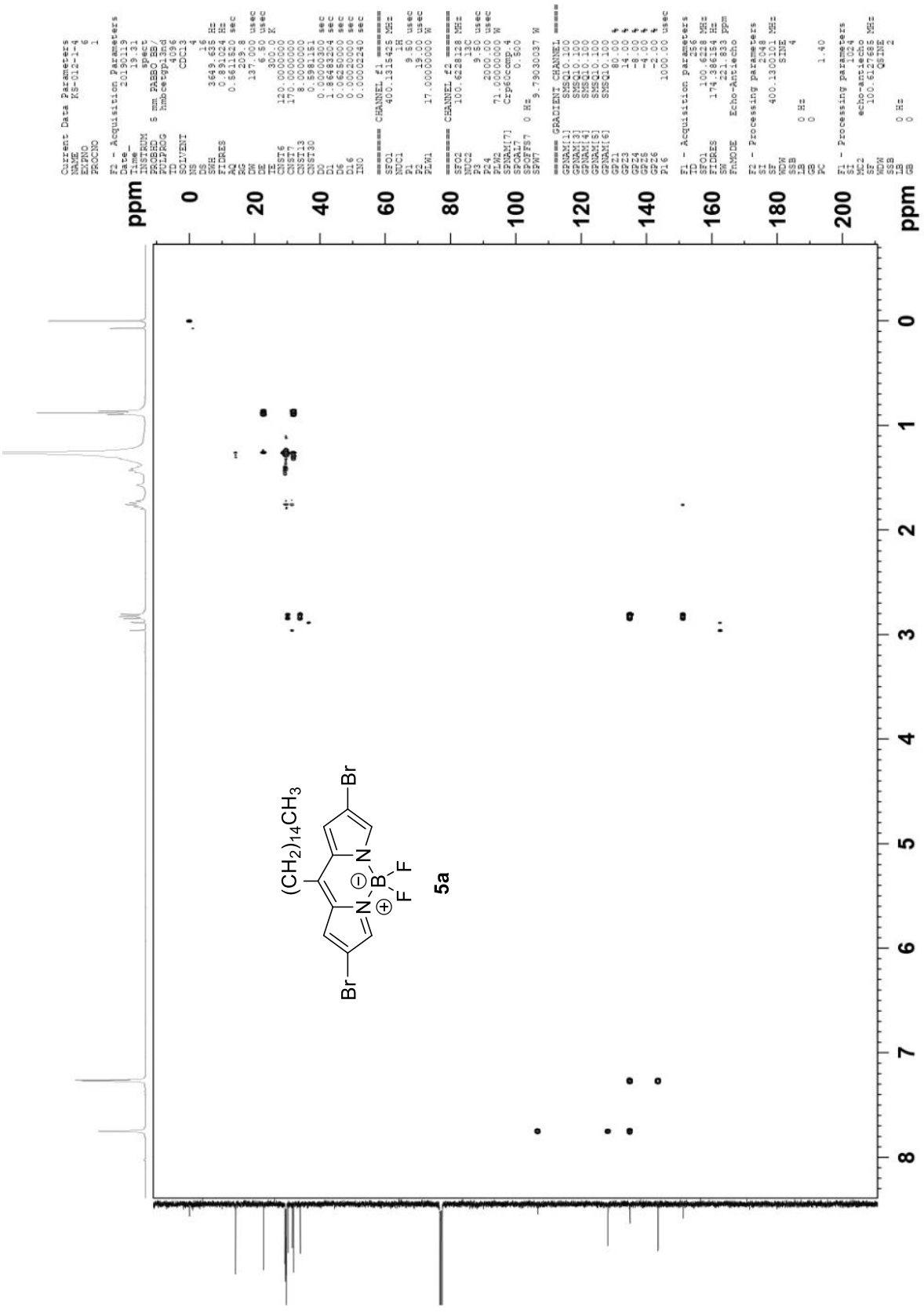
C3 COSY spectrum of BODIPY **5e**



C4 HSQC spectrum of BODIPY **5a**

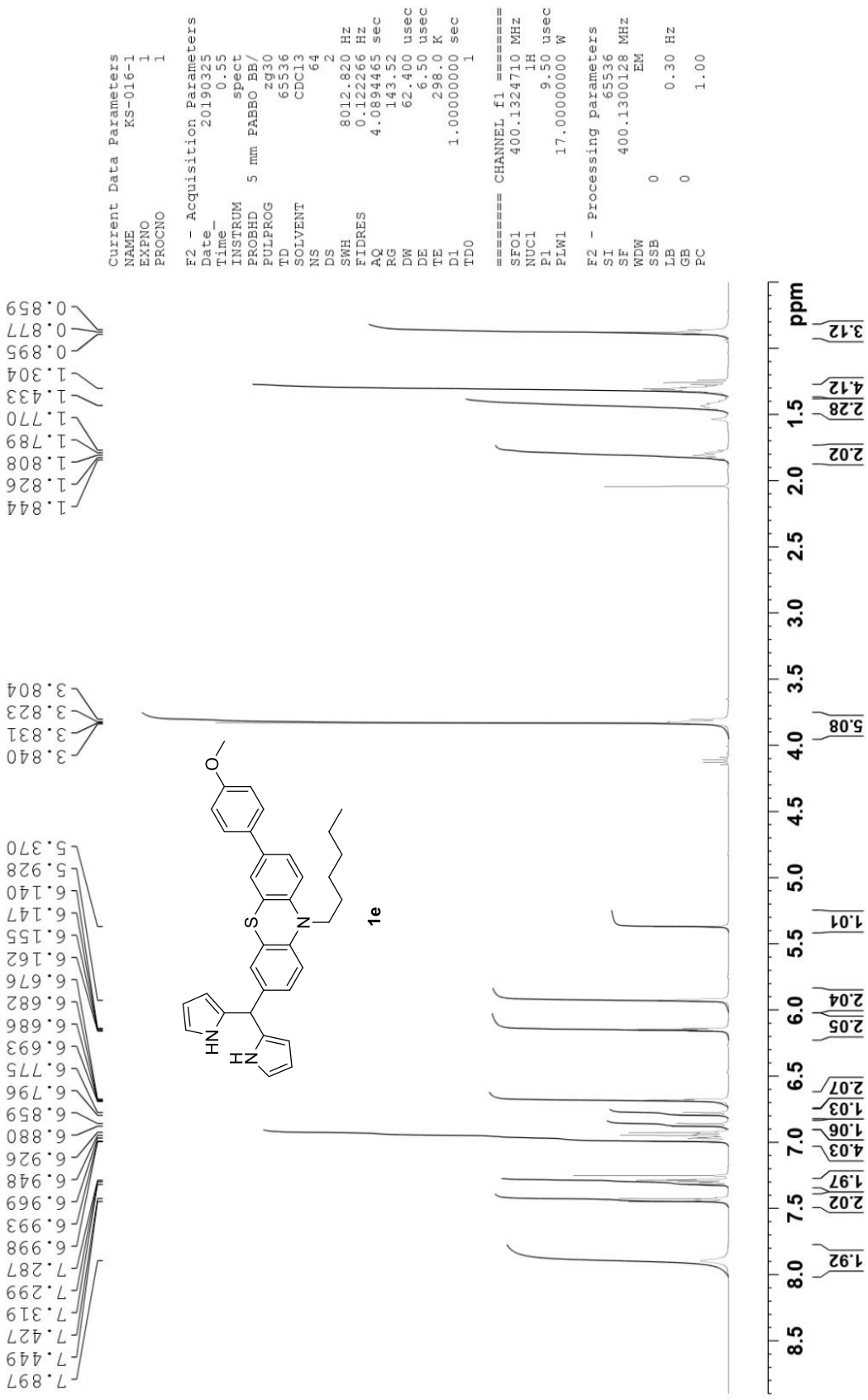


C5 HMBC spectrum of BODIPY **5a**

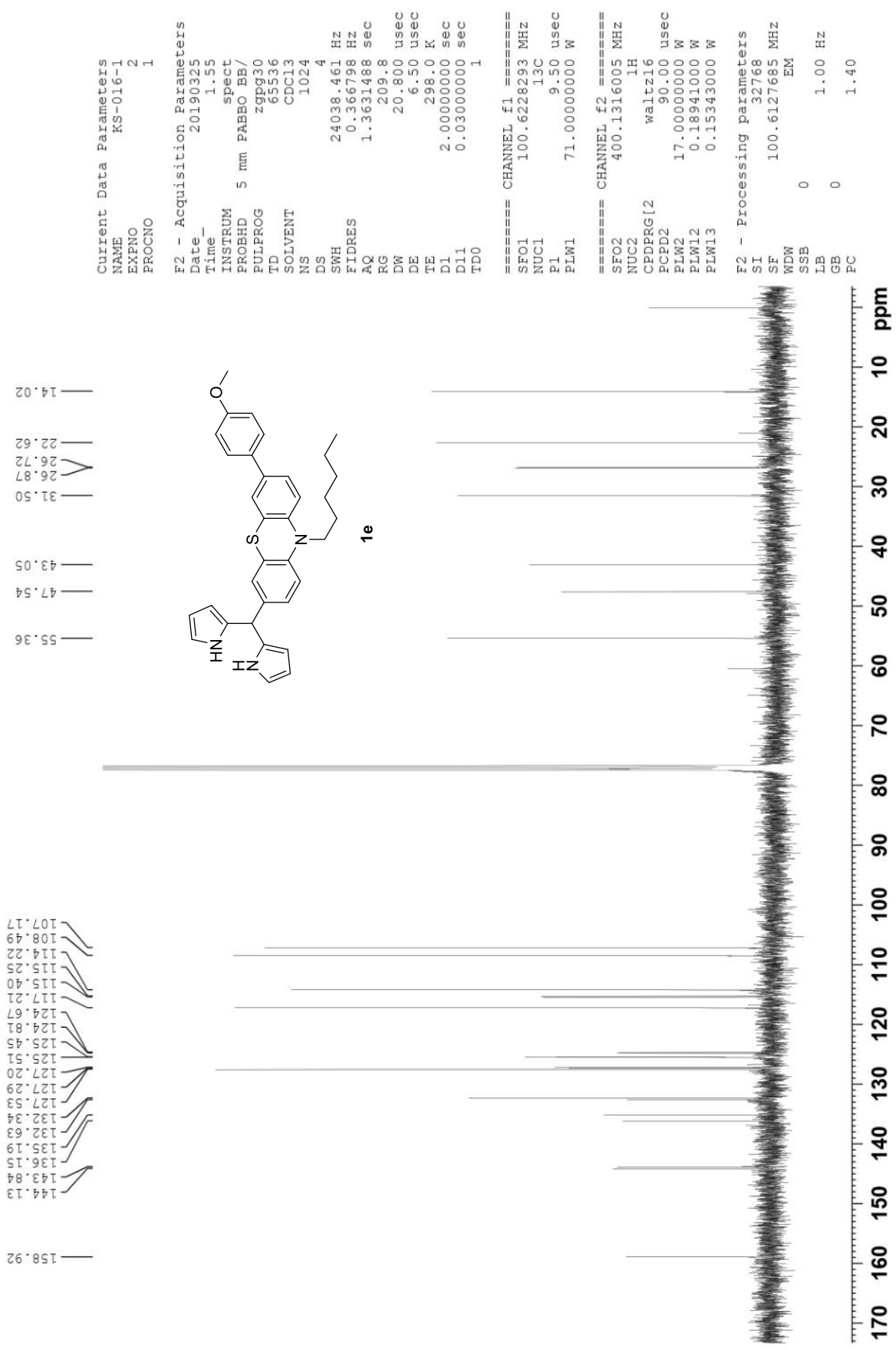


D Spectra of DPMa **1e**

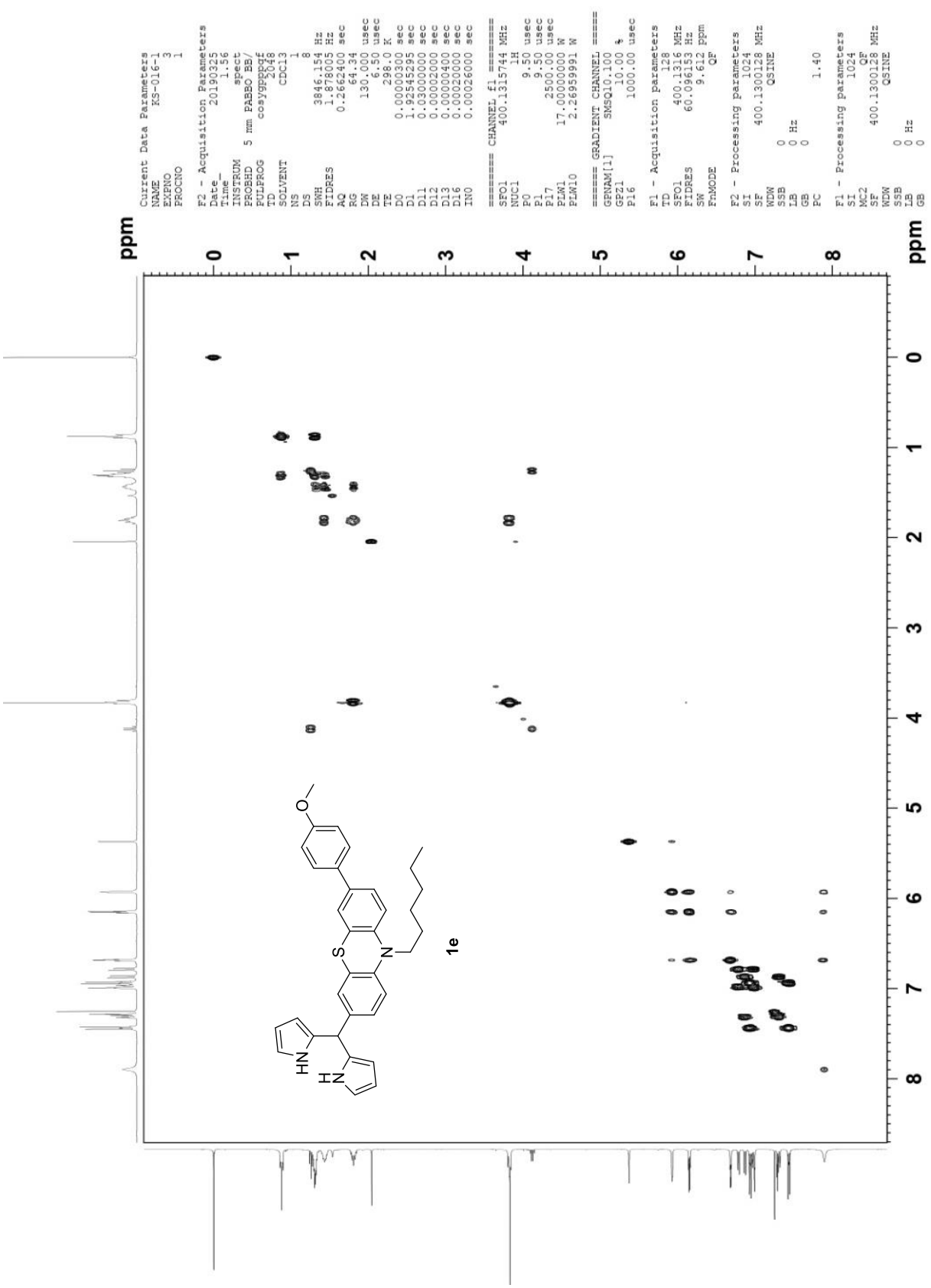
D1 ^{1}H NMR spectrum of DPMa **1e**



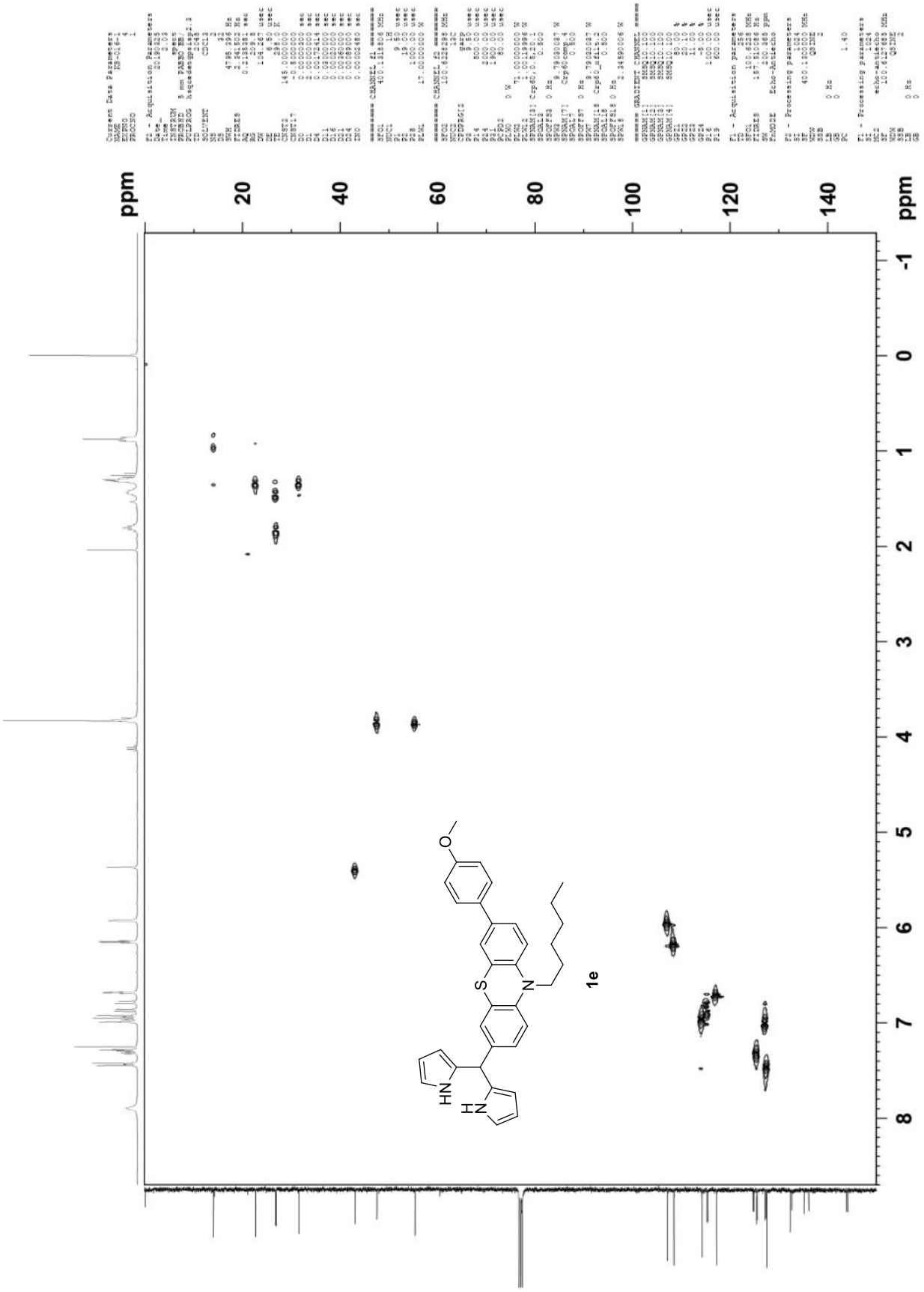
D2 ^{13}C NMR spectrum of DPMa **1e**



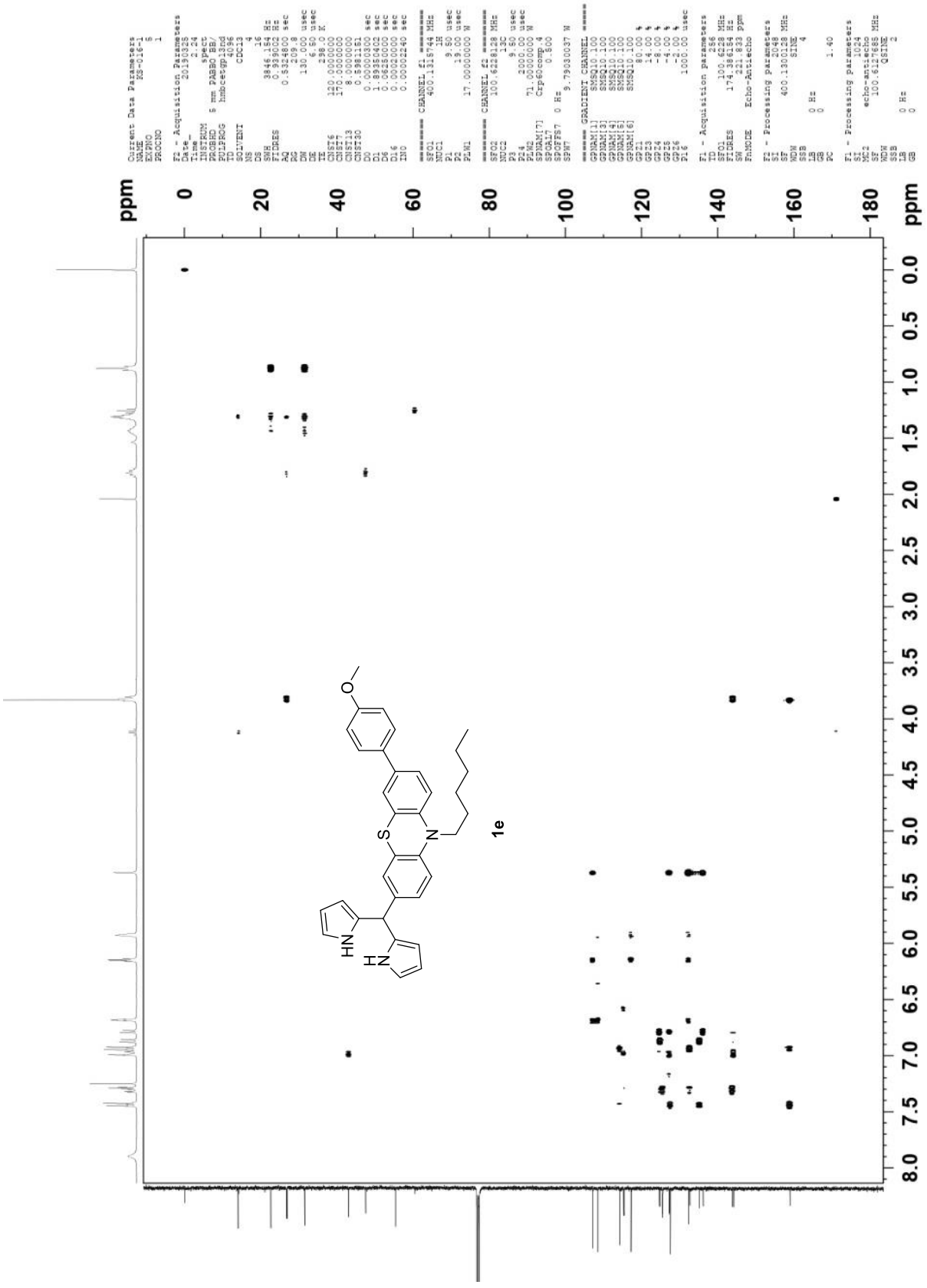
D3 COSY spectrum of DPMa **1e**



D4 HSQC spectrum of DPMa **1e**

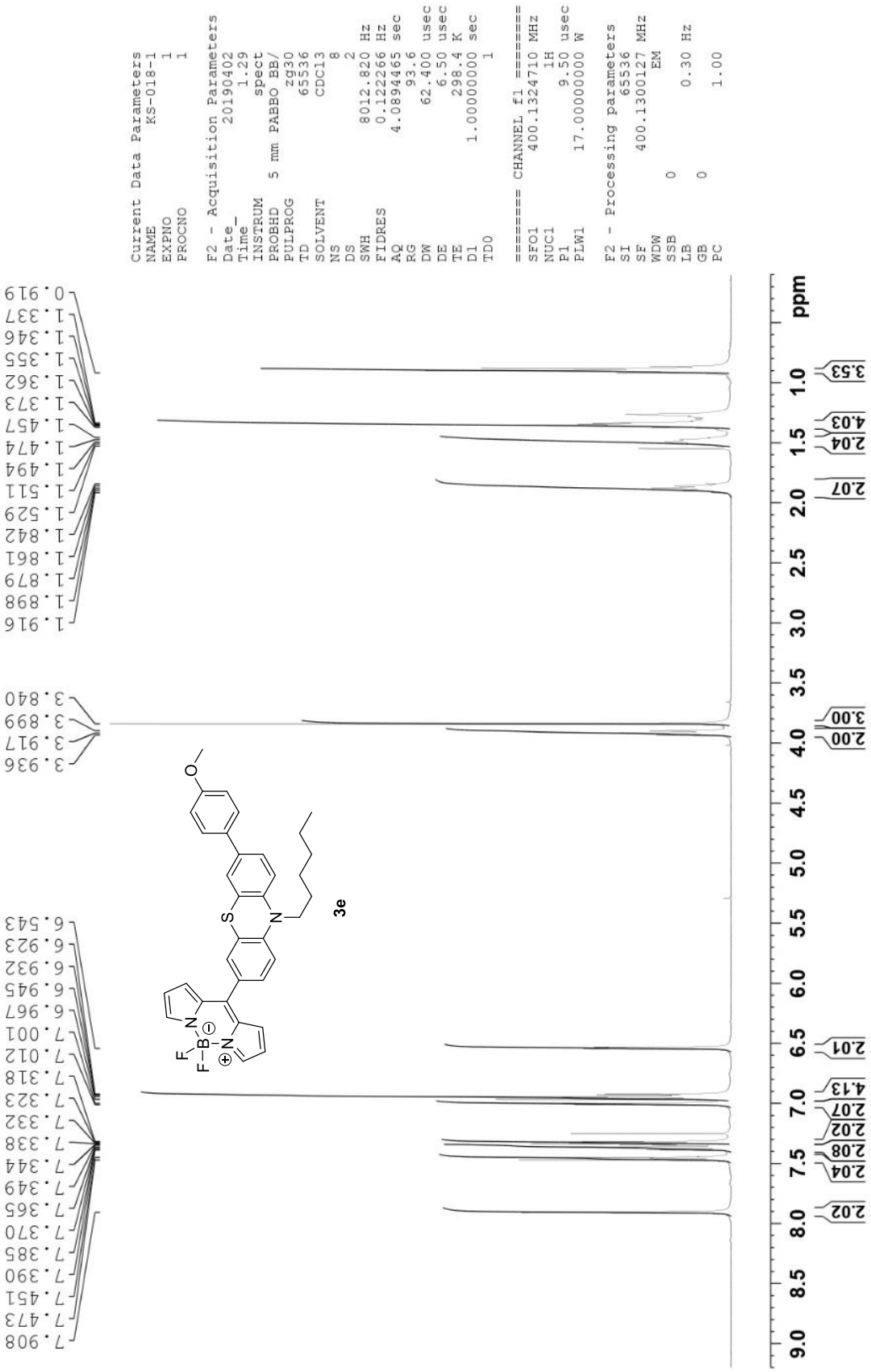


D5 HMBC spectrum of DPMa **1e**

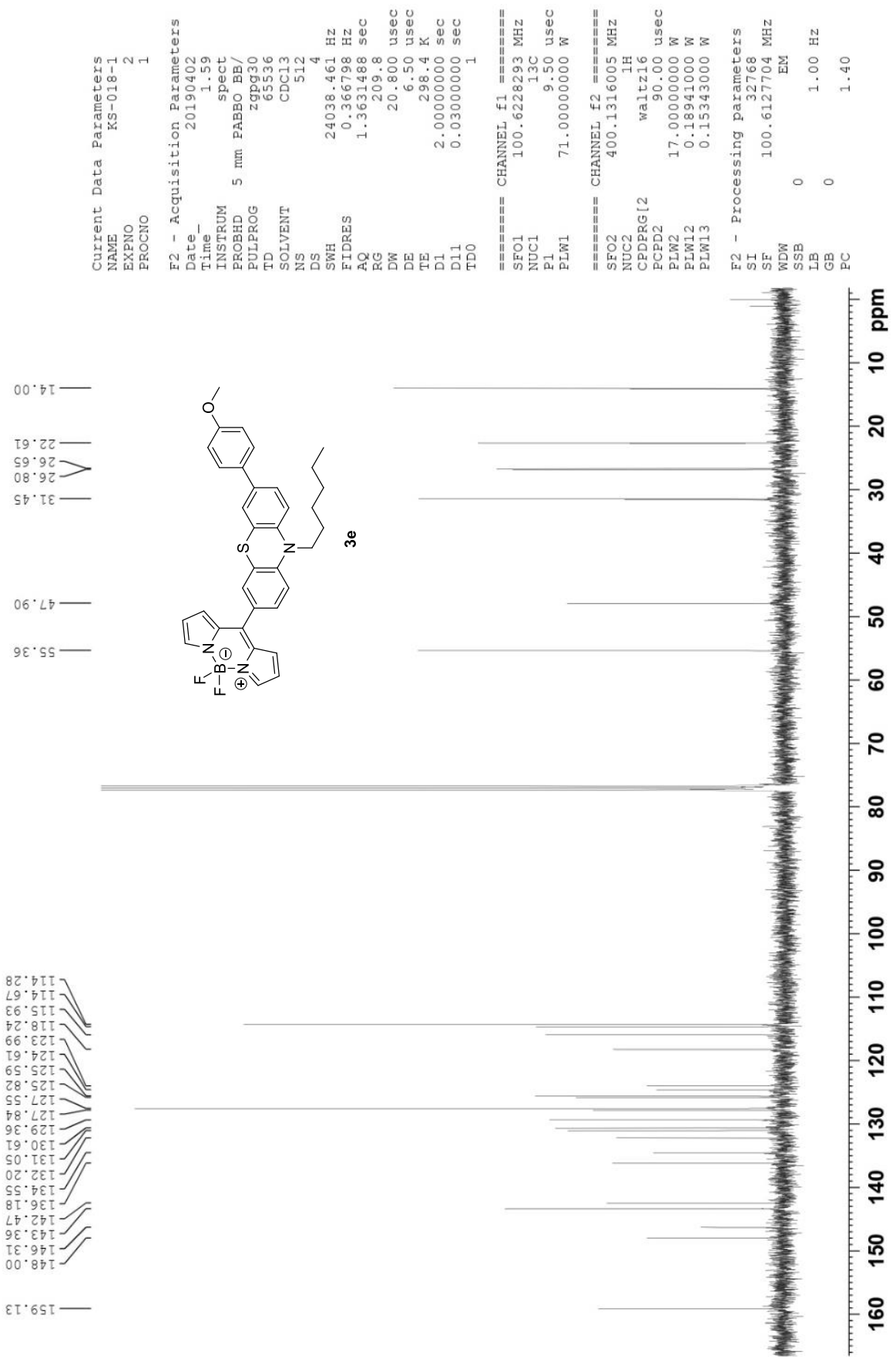


E Spectra of BODIPY **3e**

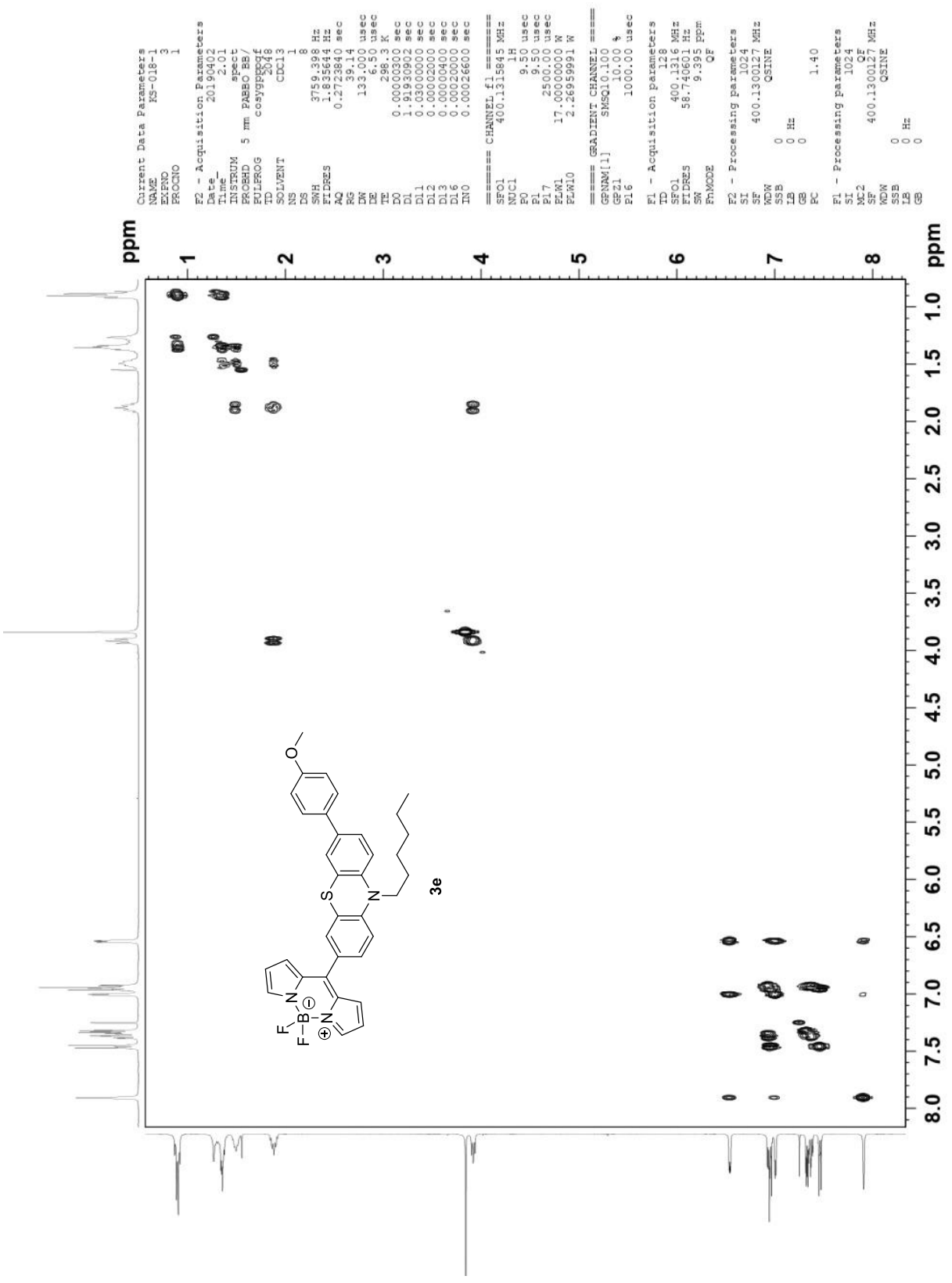
E1 ^{1}H NMR spectrum of BODIPY **3e**



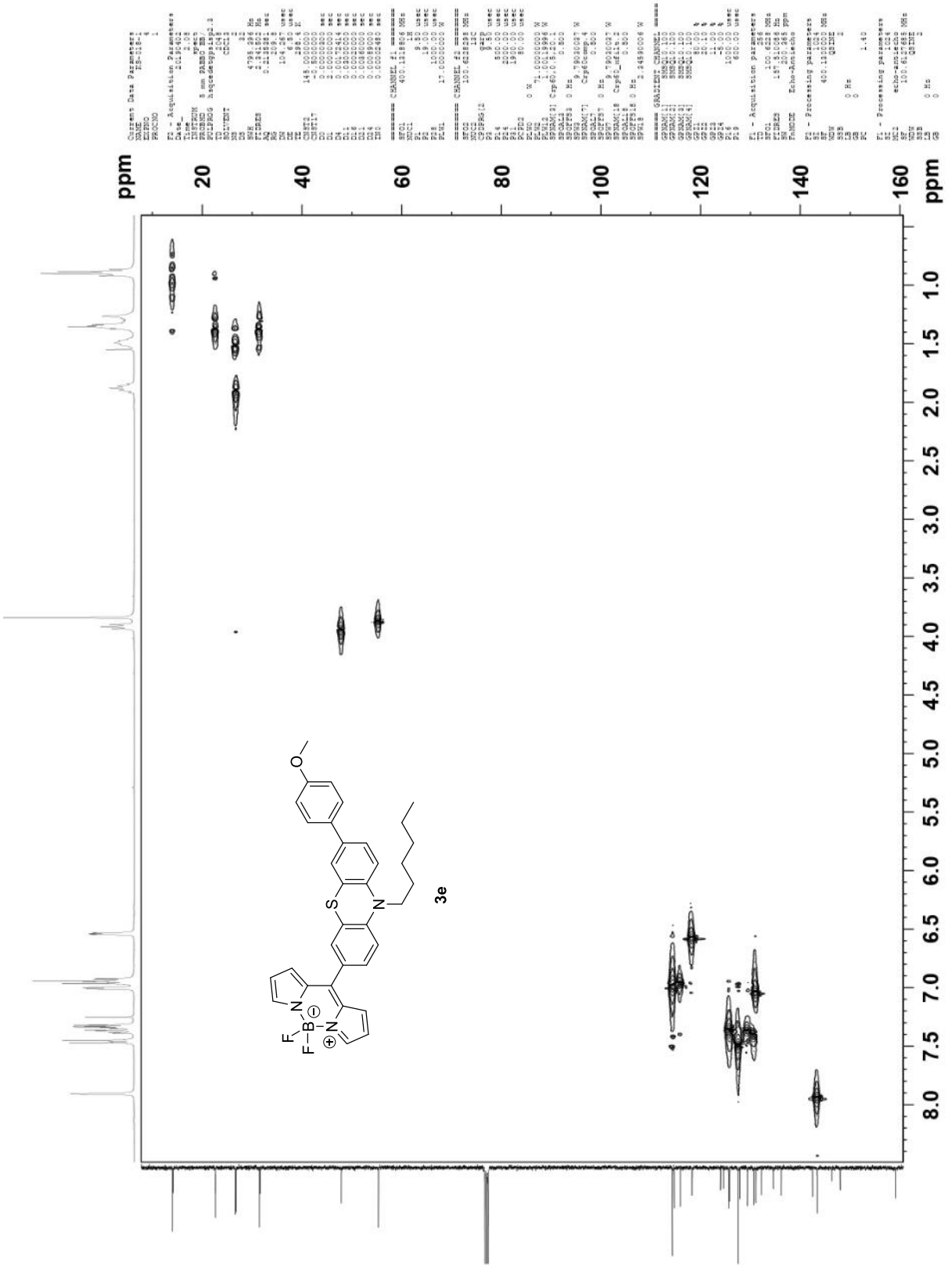
E2 ^{13}C NMR spectrum of BODIPY **3e**



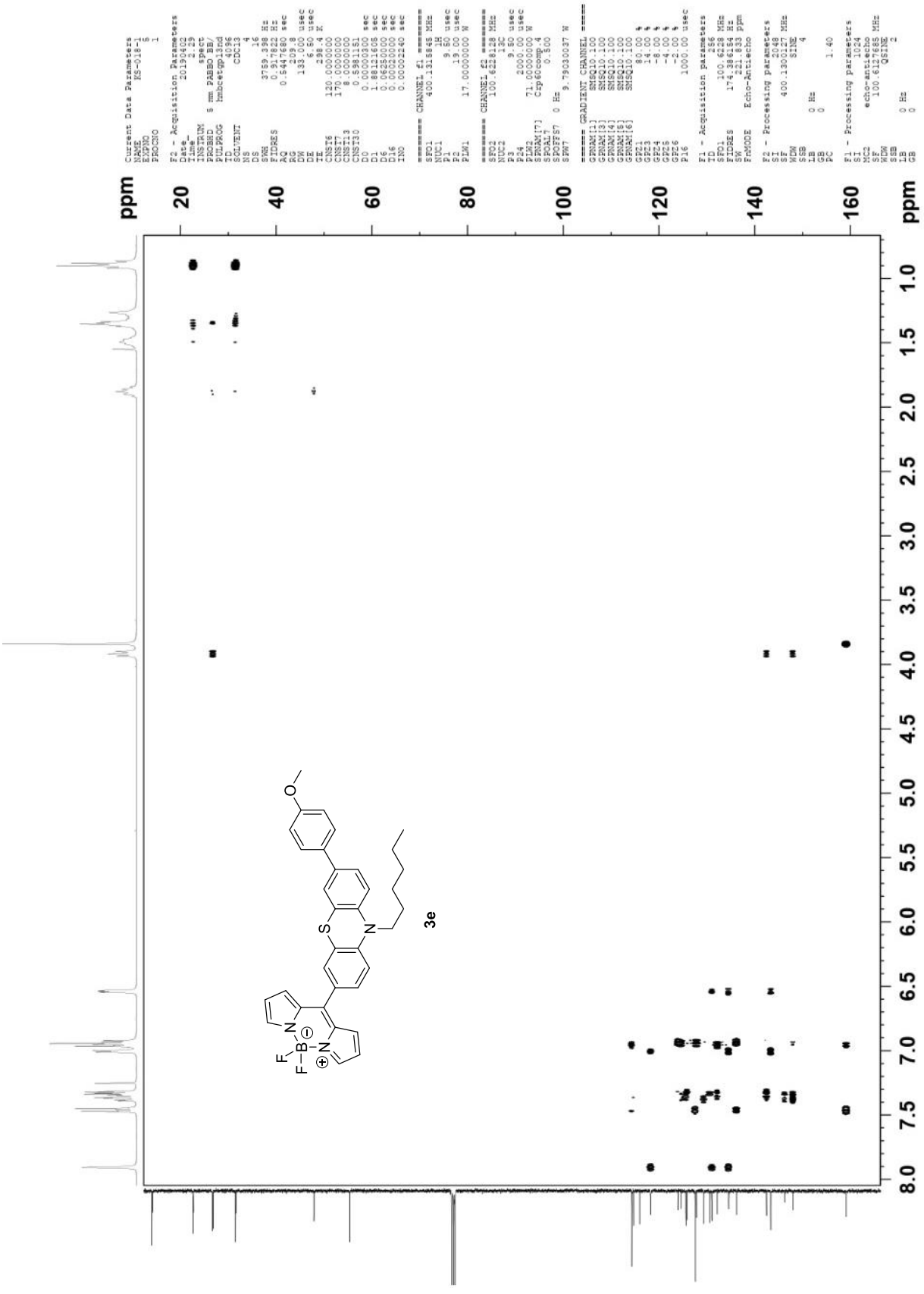
E3 COSY spectrum of BODIPY **3e**



E4 HSQC spectrum of BODIPY **3e**

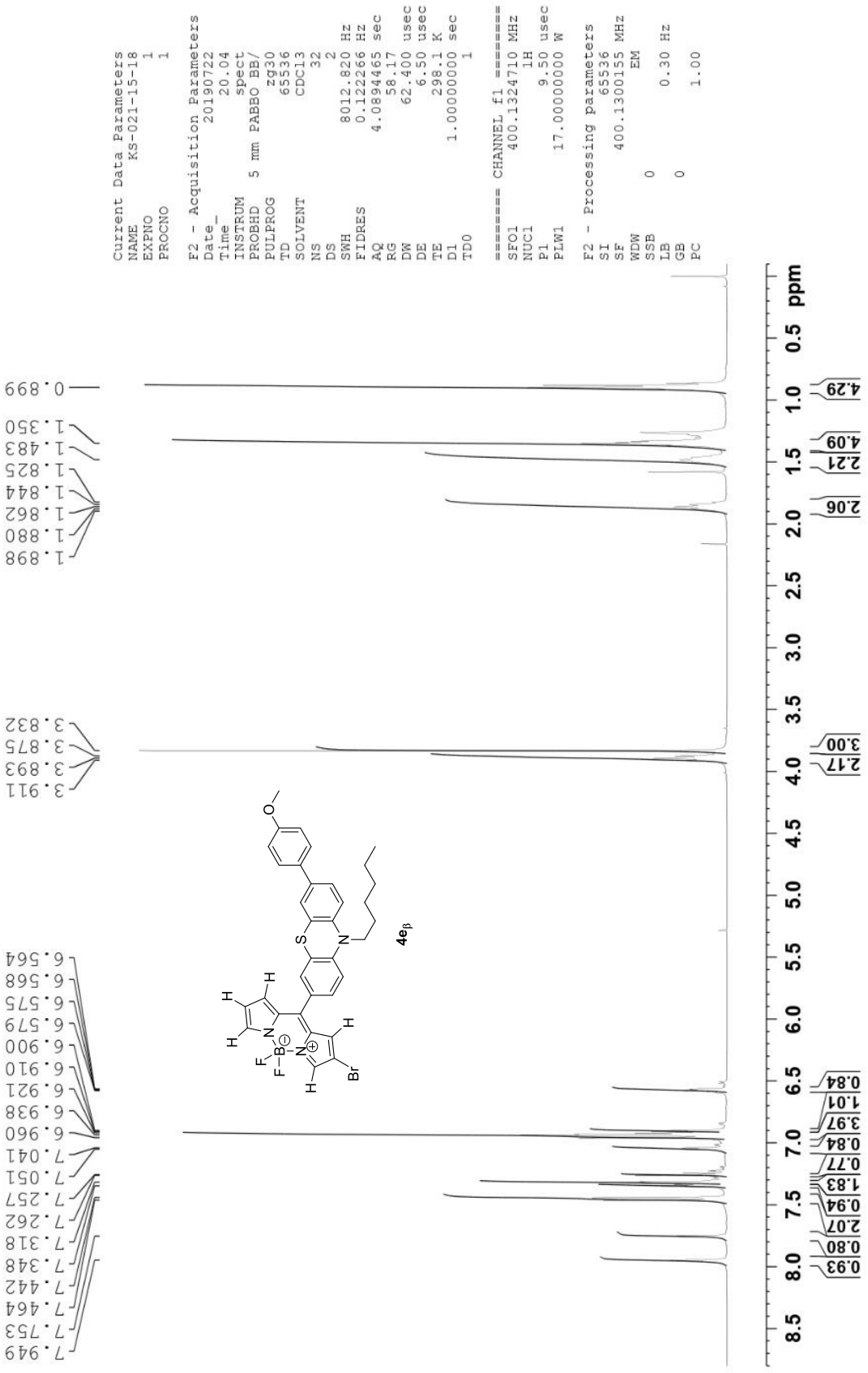


E5 HMBC spectrum of BODIPY **3e**

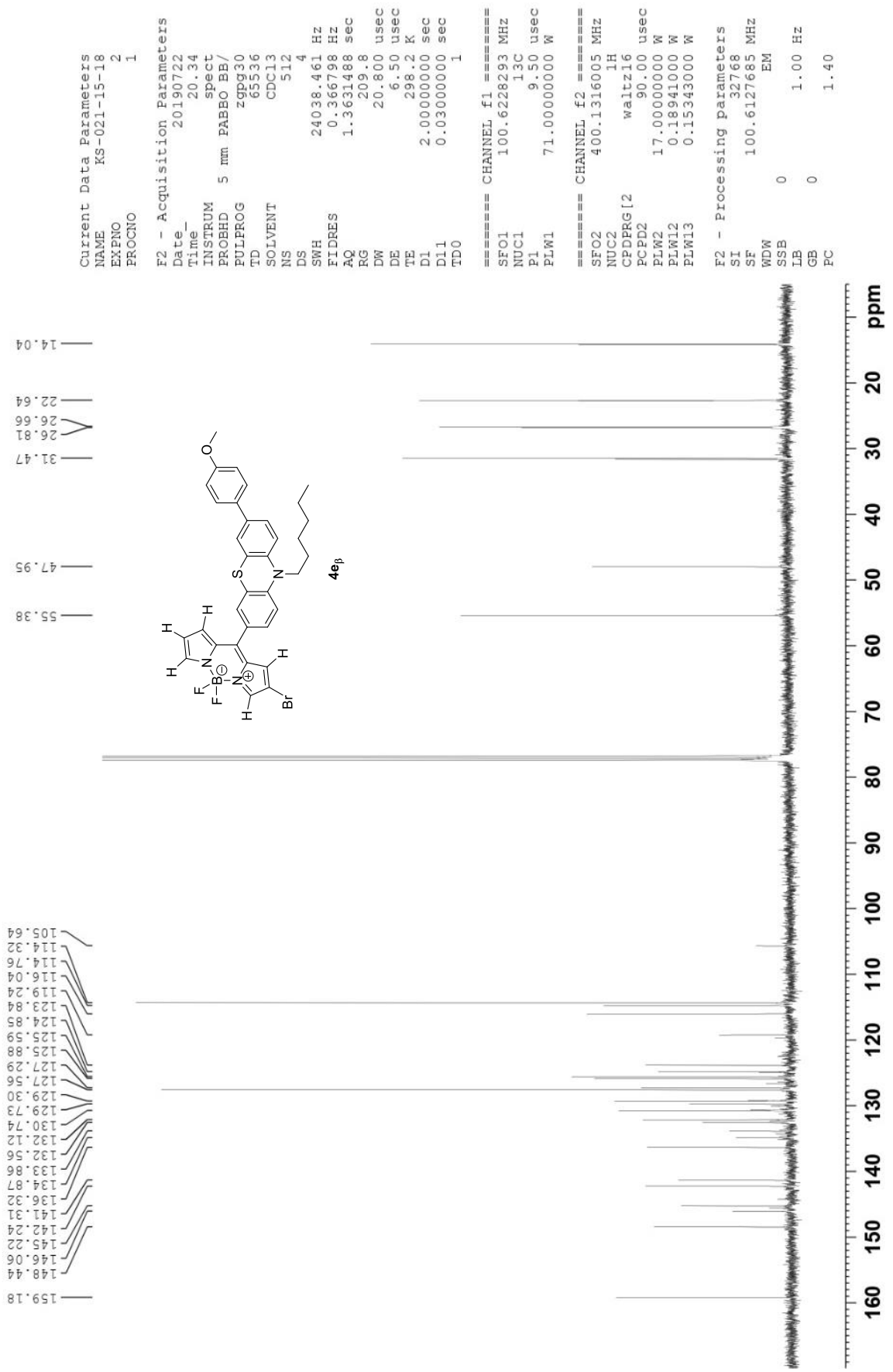


F Spectra of BODIPY **4eβ**

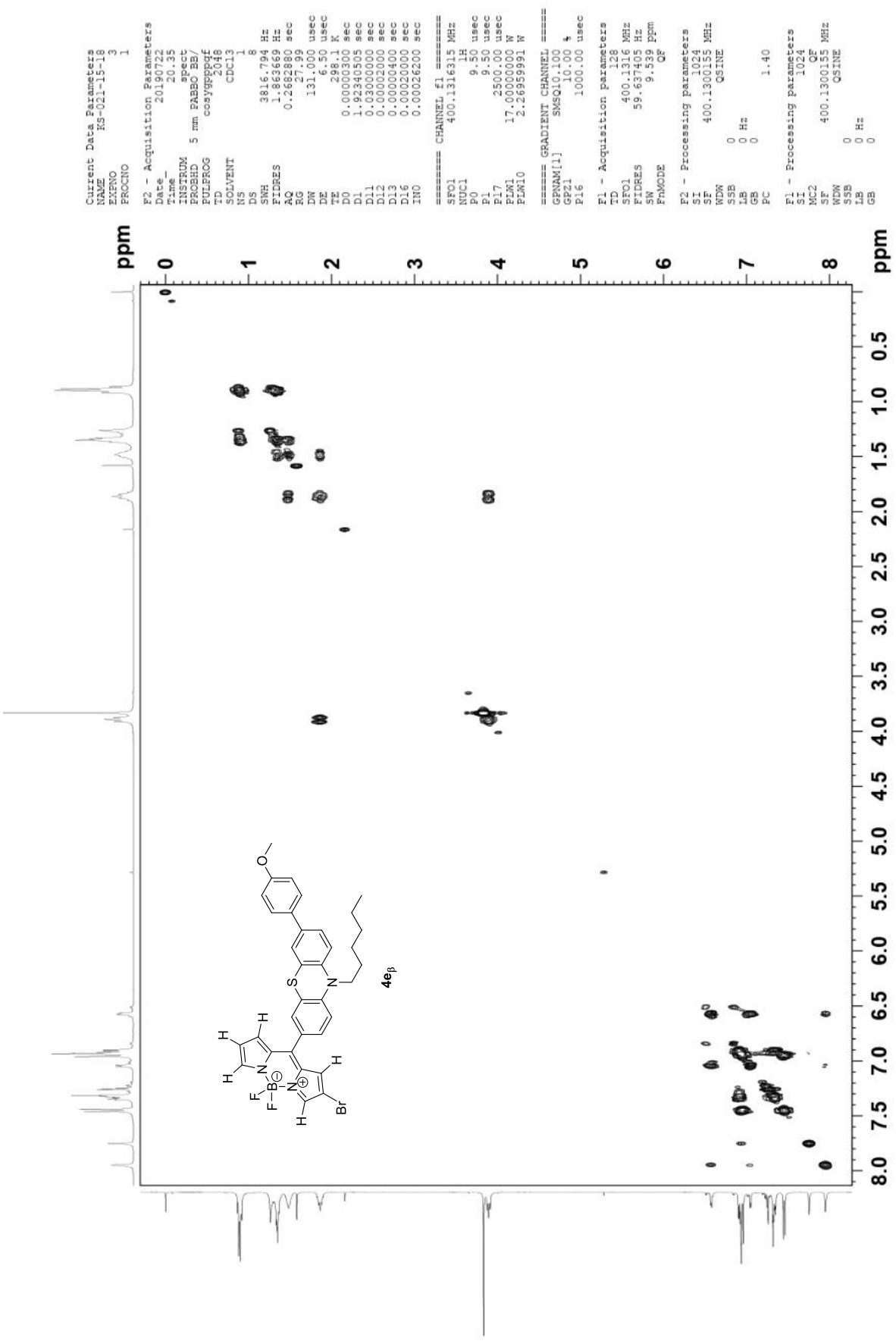
F1 ^{1}H NMR spectrum of BODIPY **4eβ**



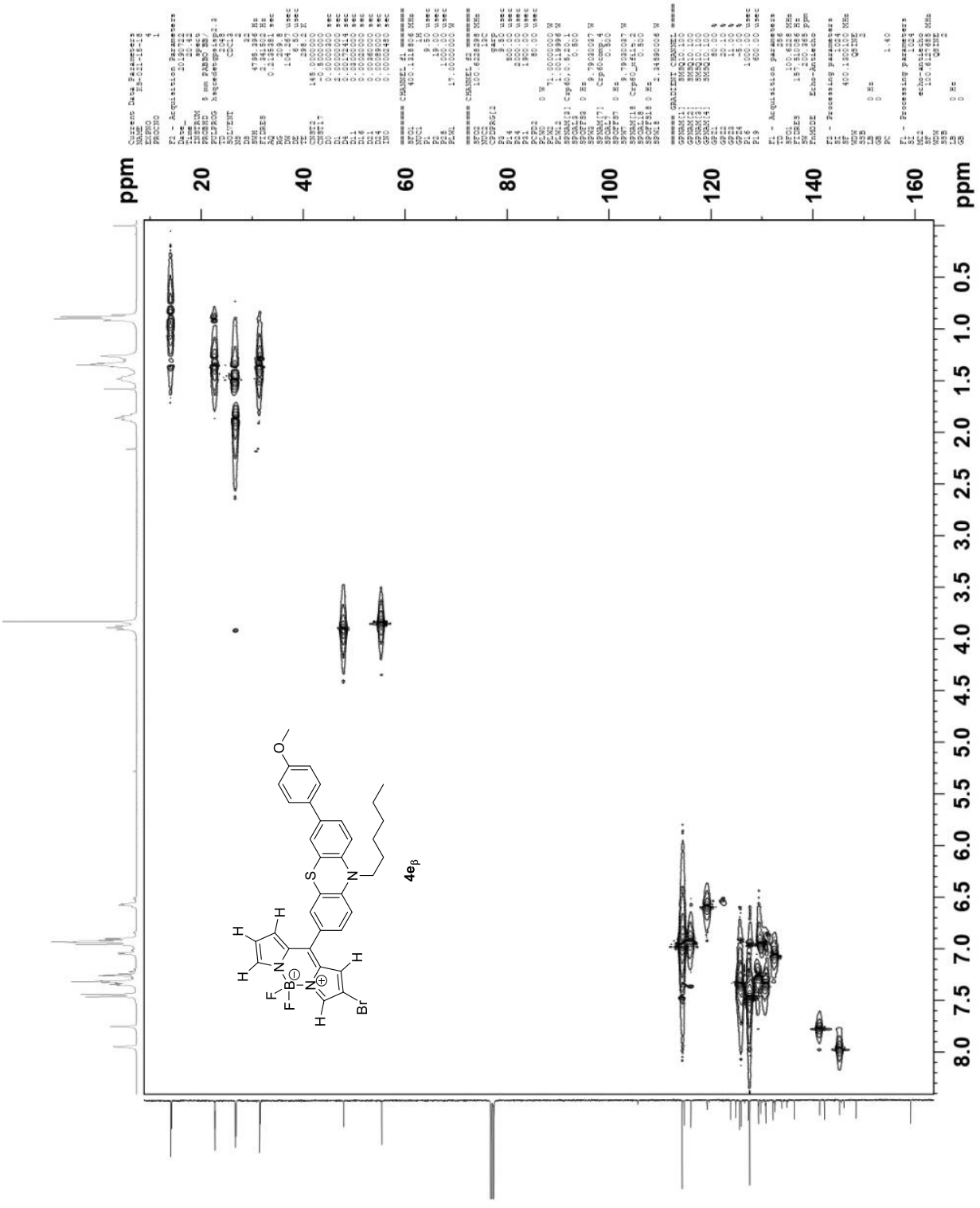
F2 ^{13}C NMR spectrum of BODIPY **4eβ**



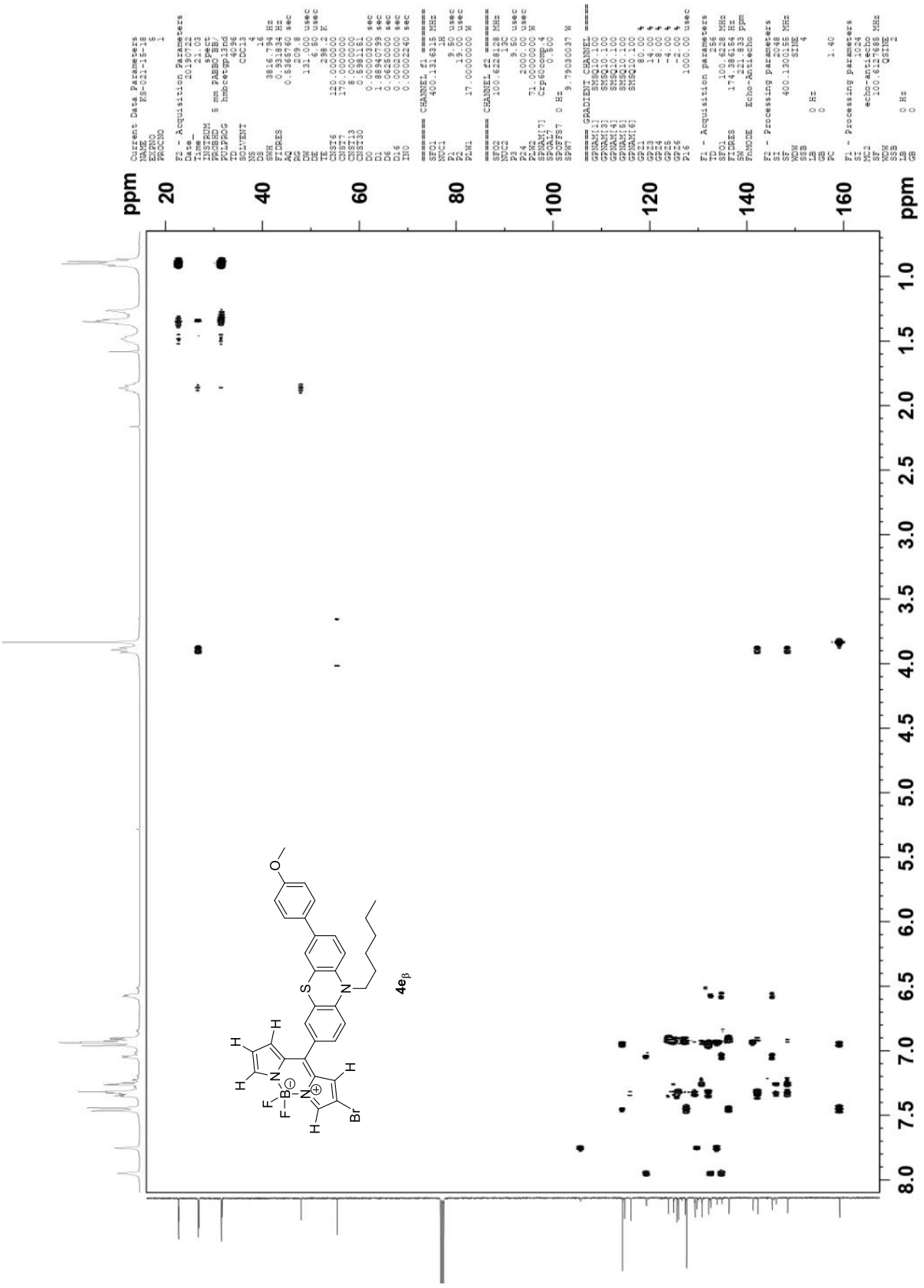
F3 COSY spectrum of BODIPY **4eβ**



F4 HSQC spectrum of BODIPY **4eβ**

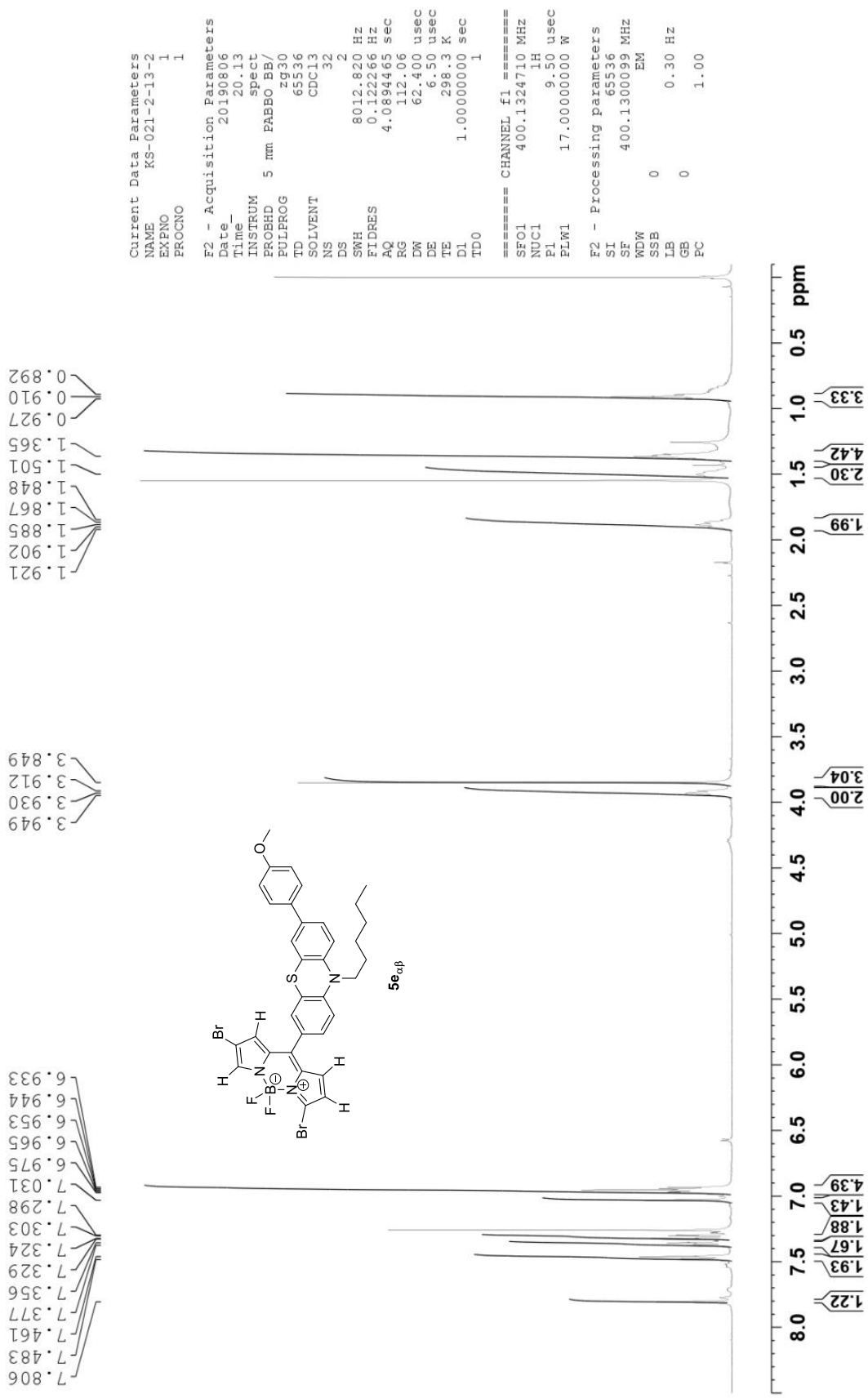


F5 HMBC spectrum of BODIPY **4eβ**

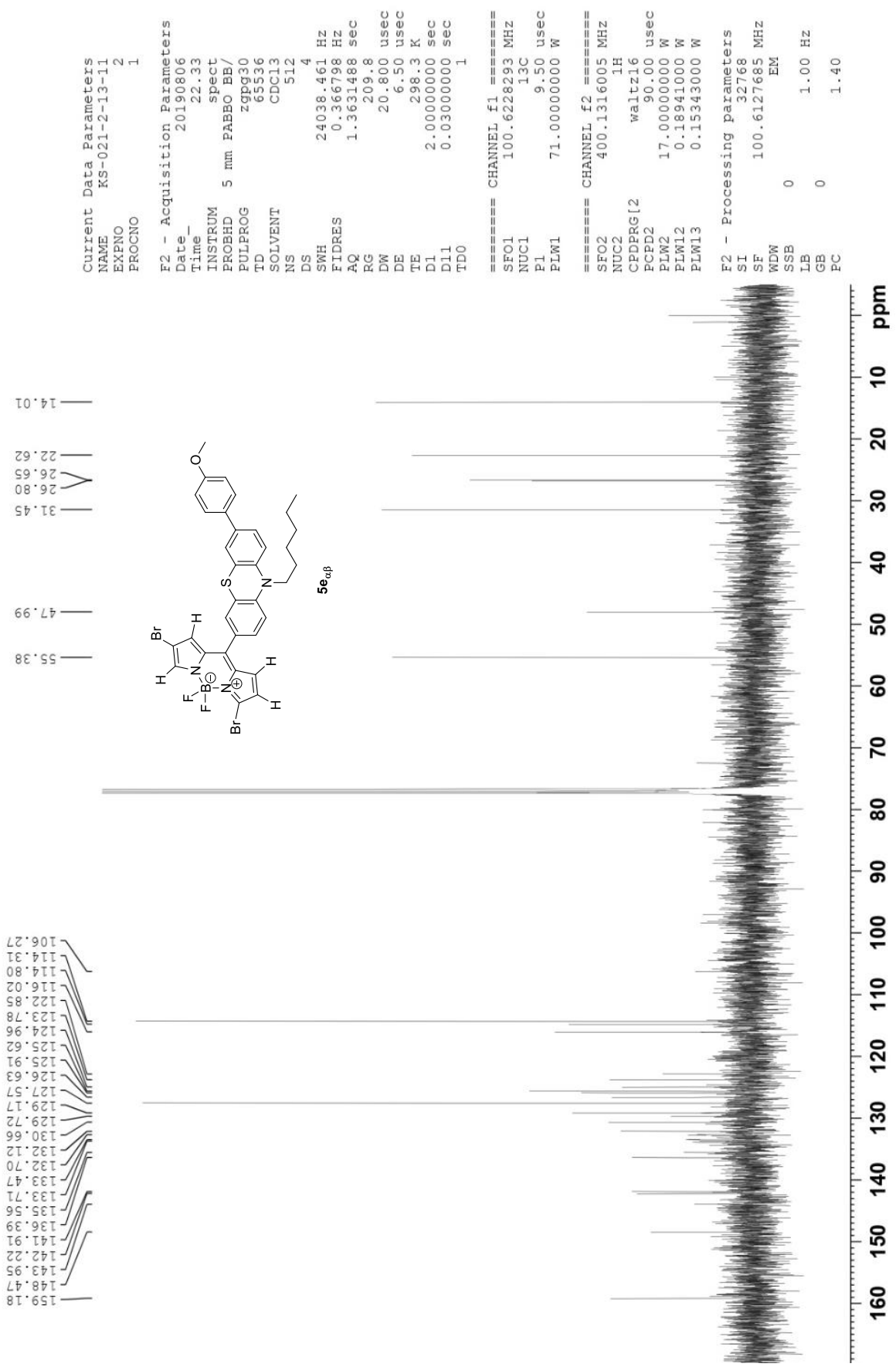


G Spectra of BODIPY **5e$_{\alpha\beta}$**

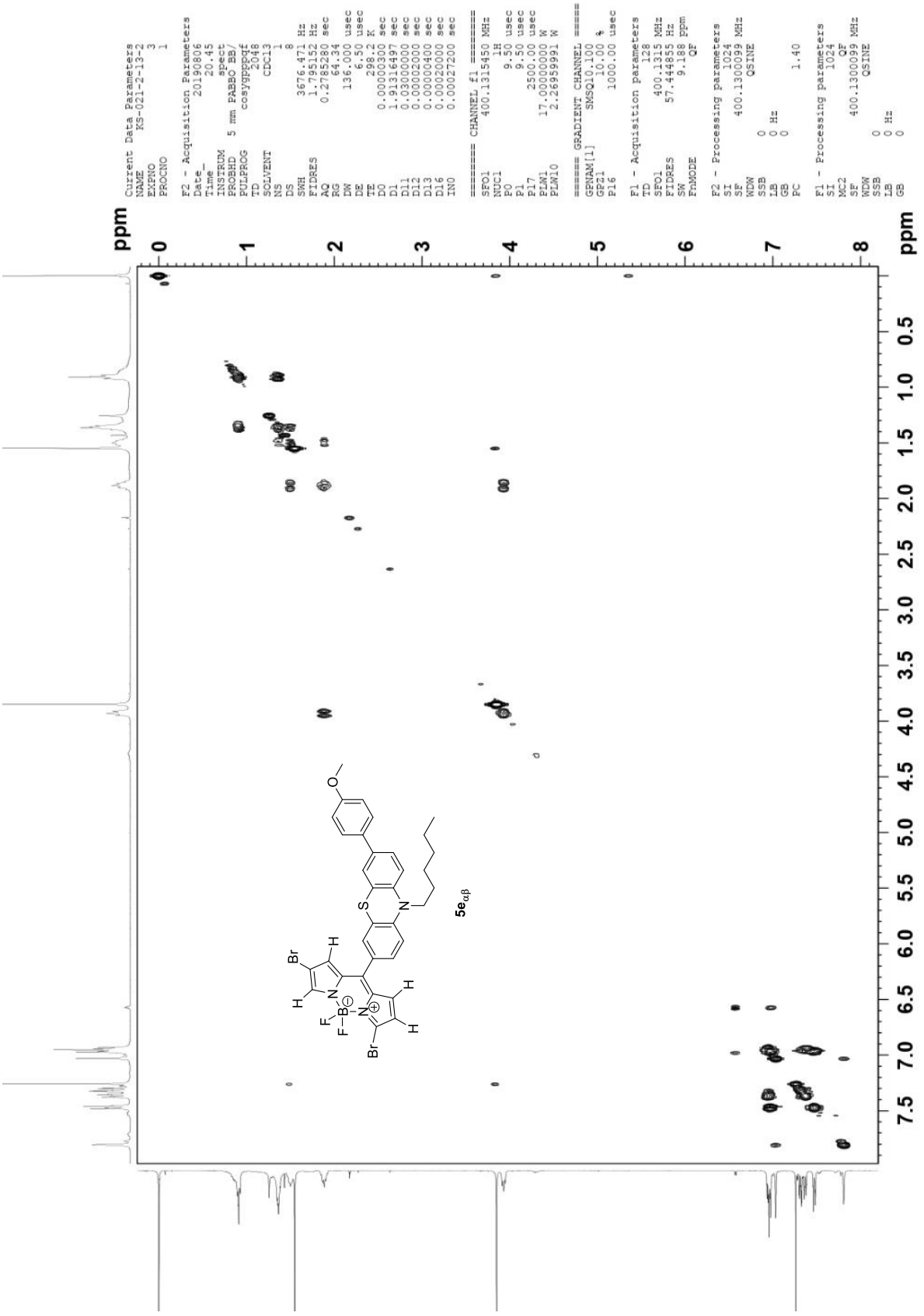
G1 ^{1}H NMR spectrum of BODIPY **5e$_{\alpha\beta}$**



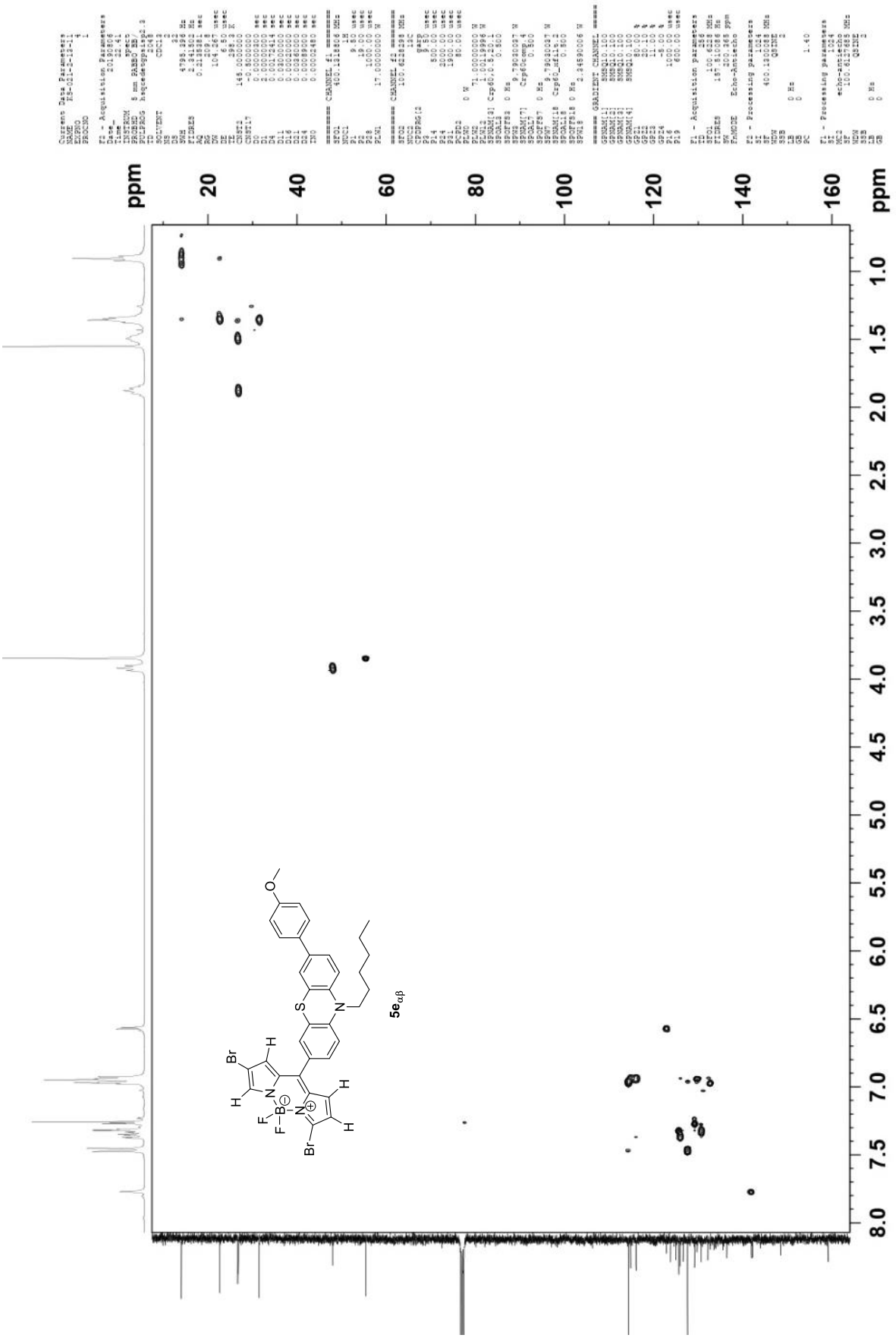
G2 ^{13}C NMR spectrum of BODIPY **5e$_{\alpha\beta}$**



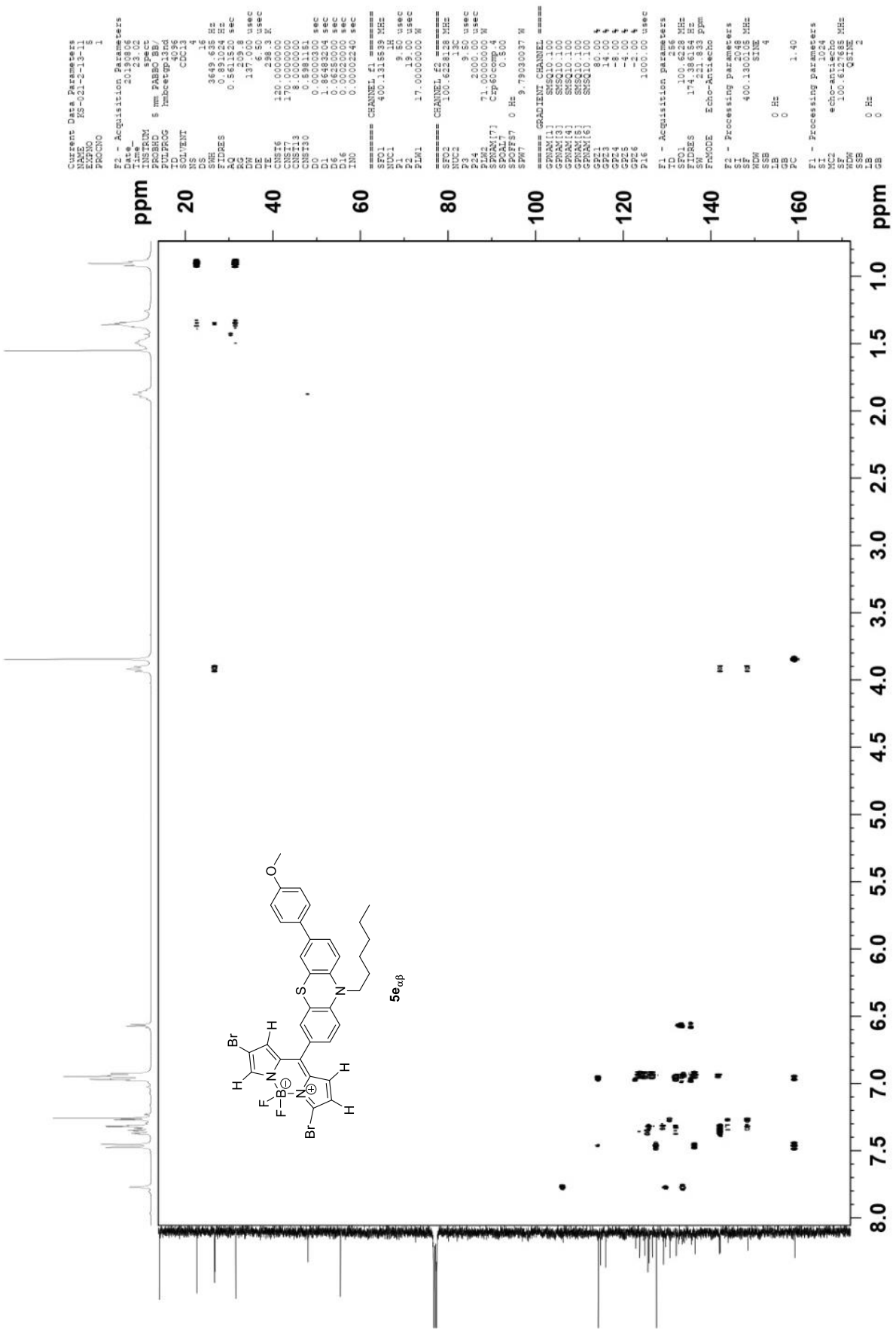
G3 COSY spectrum of BODIPY **5e$_{\alpha\beta}$**



G4 HSQC spectrum of BODIPY **5e$_{\alpha\beta}$**

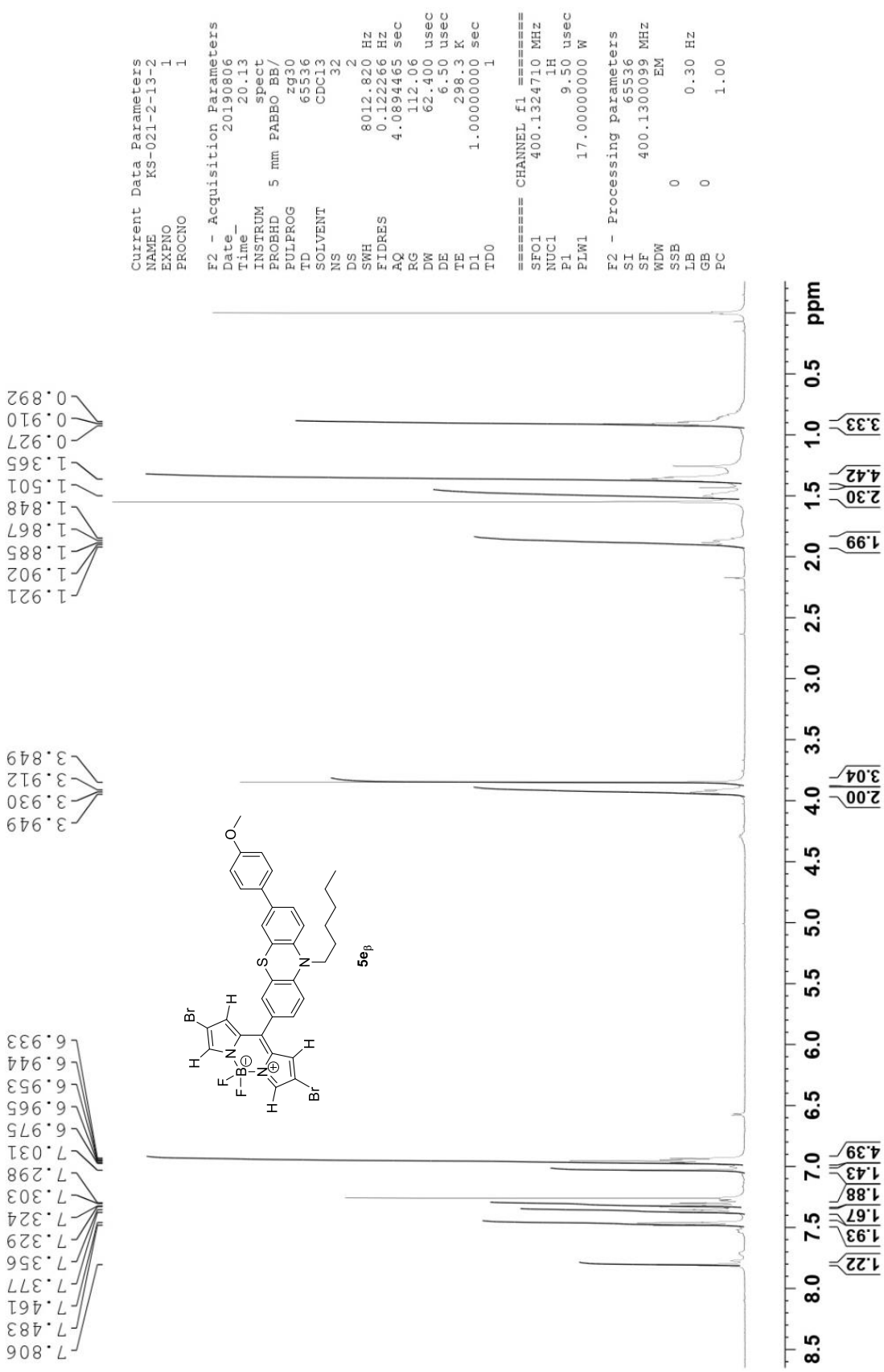


G5 HMBC spectrum of BODIPY **5e$_{\alpha\beta}$**

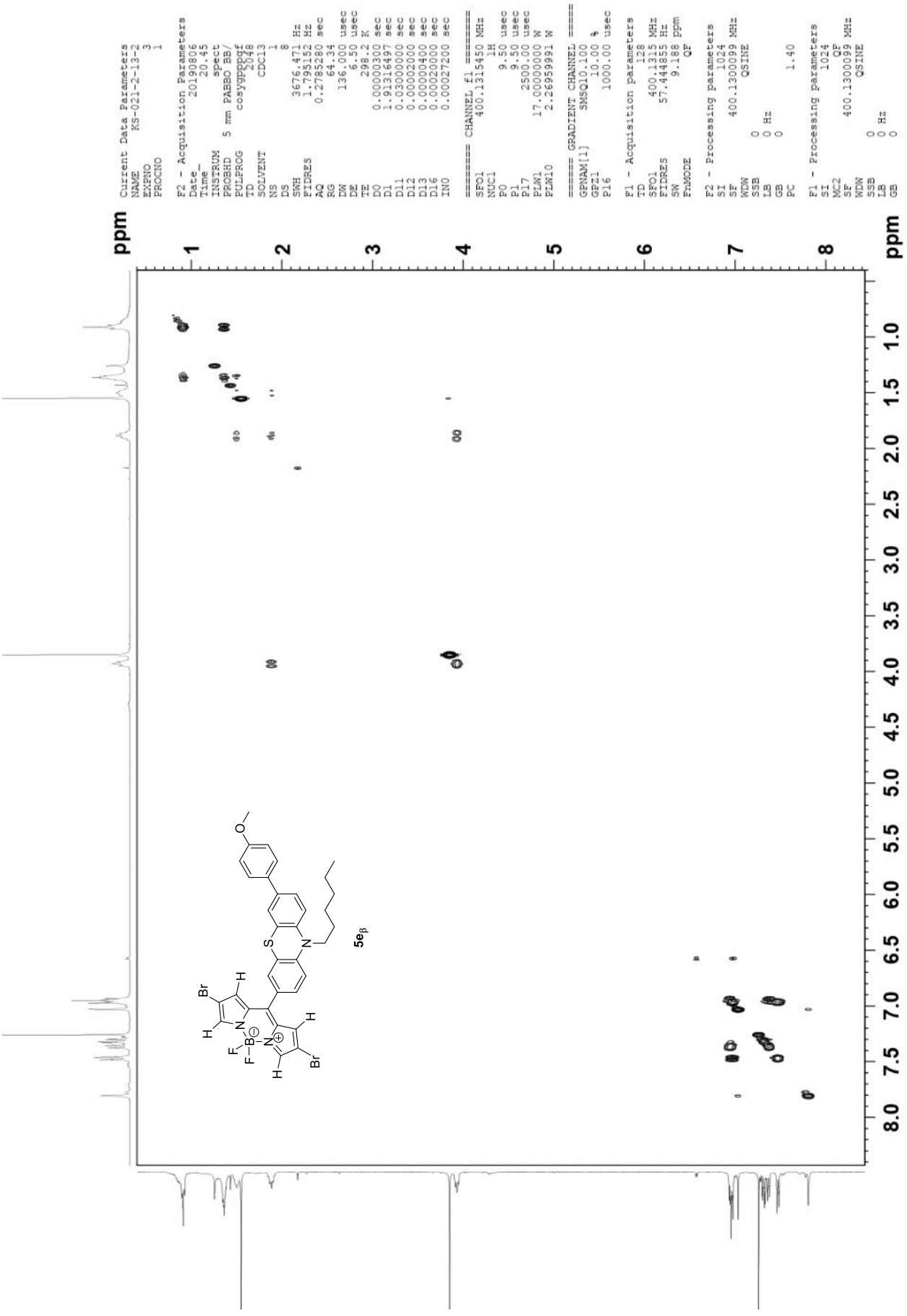


H Spectra of BODIPY **5eβ**

H1 ^{1}H NMR spectrum of BODIPY **5eβ**



H2 COSY spectrum of BODIPY **5eβ**



Kristine Olsen Strandheim

Synthesis and Characterization of BODIPY Dyes for Optoelectronic Applications

NTNU
Norwegian University of
Science and Technology