SUPRAMOLECULAR BODIPY DYE ARCHITECTURES FOR ADVANCED LIGHT-
HARVESTING AND ENERGY TRANSFER APPLICATIONS

by

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AUTHOR'S DECLARATION

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ABSTRACT

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Shape-persistent phenylacetylene macrocycles have been explored in a number of optoelectronic and light-harvesting applications, including two-photon absorption. Likewise, BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes) dyes have also been extensively used in material applications, owing to their tunable, intense absorption and sharp emission spectra exhibiting high quantum yields. Combining these two architectures, this thesis presents a derivative where a BODIPY is contained orthogonally within the phenylacetylene-macrocycle. This structure was inspired by photosystem II antennae complexes where energy is absorbed by antennae complexes and funneled down to a reaction centre. Specifically, this family of molecules uses the phenylacetylene macrocycle to harvest the light and transfer it to the BODIPY core, and this has been observed by examining the fluorescence emission from the BODIPY (Figure 1). This novel dye design if coupled to a donor (**D**) and acceptor (**A**) capable of anchoring to TiO₂ could be modified to become a π -spacer (*i.e.* D- π -A motif) for dye-sensitized solar cells resulting in panchromatic absorption, and ultimately more efficient devices.

Figure 1

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DEDICATION

I would like to dedicate this dissertation to my parents for their endless support, guidance and blessings who educated and shaped me into the person I currently am.

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LIST OF ABBREVIATIONS

<i>o</i> -	Ortho position (position 2 on benzene ring)
Ac ₂ O	Acetic anhydride
AcOH	Acetic acid
AES	Electrophilic aromatic substitution
AIE	Aggregation induced emission
Al	Aluminum
BF ₃ .OEt ₂	boron trifluoride diethyletherate
BODIPY	4,4-Difluoro-4-bora-3a,4a-diaza- <i>s</i> -indacene
CDCl ₃	Deuterated chloroform
CH ₂ Cl ₂	Dichloromethane
CHCl ₃	Chloroform
CuI	Copper (I) iodide
Cu(I)Cl	Copper (I) chloride
CV	Cyclic voltammetry
d	Doublet (NMR peak descriptor)
DART	Direct analysis in real time
DCE	Dichloroethane
DCM	Dichloromethane
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DRET	Dexter resonance energy transfer
DFT	Density Functional Theory
DIPEA	<i>N,N</i> -diisopropylethylamine
DMF	Dimethyl formamide
DSSC	Dye-sensitized solar cell
EDG	Electron donating group
EET	Excitation energy transfer
EI	Electron impact
ET	Energy transfer

eq	Equivalent
ESI	Electrospray ionization
Et ₂ O	Diethyl ether
EtOAc	Ethyl acetate
EtOH	Ethanol
eV	Electron volt
EWG	Electron withdrawing group
ϵ	Molar absorptivity ($\text{M}^{-1}\text{cm}^{-1}$)
FF	Fill factor
FMOs	Frontier molecular orbitals
FRET	Forster resonance energy transfer
g	Gram
h	Hour
H ₂ O	Water
H ₂ SO ₄	Sulfuric acid
HCl	Hydrochloric acid
Hex	Hexanes
NH ₄ Cl	Ammonium chloride
HNEt ₂	Diethylamine
HNO ₃	Nitric acid
HOMO	Highest occupied molecular orbital
HRMS	High resolution mass spectrometry
Hz	Hertz
I	Intensity
I ₂	Iodine
<i>J</i>	Coupling constant (NMR)
<i>J</i> _{SC}	Short circuit current
K ₂ CO ₃	Potassium carbonate
KF	Potassium fluoride
KI	Potassium iodide

KIO ₄	Potassium periodate
KMnO ₄	Potassium permanganate
KOH	Potassium hydroxide
LUMO	Lowest unoccupied molecular orbital
<i>m/z</i>	Mass to charge ratio
MeI	Iodomethane (aka methyl iodide)
MeOH	Methanol
mg	Milligram
MgSO ₄	Magnesium sulfate
MHz	Megahertz
min	Minutes
mL	Millilitre
MLCT	Metal-to-ligand charge transfer
mmol	Millimole
η	Efficiency
N ₂	Nitrogen gas
Na ₂ CO ₃	Sodium carbonate
NaHCO ₃	Sodium bicarbonate
Na ₂ S ₂ O ₃	Sodium thiosulfate
NaIO ₄	Sodium periodate
NaNO ₂	Sodium nitrite
NaOH	Sodium hydroxide
NBS	<i>N</i> -bromosuccinimide
<i>n</i> -BuLi	<i>n</i> -Butyl lithium
NEt ₃	Triethylamine
NIS	<i>N</i> -iodosuccinimide
NMR	Nuclear magnetic resonance
NO ₂	Nitrogen dioxide (nitro group)
ON	Overnight
<i>P</i> -	Para position (position 4 on benzene ring)

PCC	Pyridinium chlorochromate
PdCl_2	Palladium (II) chloride
$\text{PdCl}_2(\text{PPh}_3)_2$	Bis(triphenylphosphine)palladium chloride
PE	Petroleum ether
P_{in}	Incident power
POCl_3	Phosphoryl chloride (aka phosphorus oxychloride)
PPh_3	Triphenylphosphine
ppm	Parts per million
PSII	Photosystem II
PV	Photovoltaic
R_f	Retention factor
RT	Room temperature
TD-DFT	Time Dependent Density Functional Theory
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TiO_2	Titanium dioxide
TMS-acetylene	Ethynyl(trimethyl)silane (aka trimethylsilyl acetylene)
TPA	Triphenylamine
TPE	Tetraphenylethene
V_{oc}	Open circuit voltage
UV	Ultra violet
Vis	Visible
Zn	Zinc
δ	Chemical shift
λ_{max}	Wavelength at maximum absorption

LIST OF NUMBERED COMPOUNDS

1.1

1.2

1.3

1.4

3.1

3.2

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Chapter 1: Introduction

1.1. Solar Energy and the Environment

Humanity's insatiable demand for energy (13 terawatts (TW) in 2006) will likely increase to 30 TW by 2050. Currently, 85% of our global energy is generated from the combustion of fossil fuels, and this has led to the depletion of available reserves (needed for other applications) and has led to significant adverse effects on the environment. In order to address this issue, humanity must mitigate its consumption of fossil fuels with non-carbonaceous energy sources, and this represents one of the greatest technological (and social) challenges of our time.^{1,2}

Of the major non-carbonaceous energy forms (wind, hydroelectric, biomass, geothermal, tidal, nuclear and solar), photovoltaic energy is the most likely source to meet our energy demands. Solar energy has a low environmental impact and gifts the earth surface with 183,000 TW of energy.^{3,4} Unfortunately, the problem with photovoltaic technology is that it currently is more expensive than the conventional sources, and as such, modern solar cells must be improved upon.

Photovoltaic technology can be broadly divided into three generations. The first two generations of solar cells are based on either single-crystal silicon or thin-film (amorphous silicon (a-Si), Cd-Te, Ga-As, GaInAs, etc) technologies. The first two generations are highly efficient and robust owing to their inorganic nature, but their applications are limited due to either cost and/or the use of hazardous materials in these technologies. In order to replace traditional energy sources and expand our solar market to the TW scale, a substantial change in technology is required. To this end, third generation photovoltaic materials are being investigated to complement existing technologies. One of the most efficient next/third generation photovoltaic cells is the dye-sensitized solar cell (DSSC).⁵ DSSCs have drawn considerable attention due to their interesting and promising conversion efficiencies (exceeding 13%).⁶⁻⁹

1.2. Dye-Sensitized Solar Cells (DSSCs)

The original dye-sensitized concept was first reported in the late 1960s when Gerischer and Tributsch worked on the sensitization of an organic dye (perylene) with an n-type zinc oxide semiconductor; however, the perylene showed poor power conversion.^{10,11} A significant

breakthrough was achieved when Grätzel and co-workers reported a DSSC (1991) with an efficiency of 7.1%.⁵ Since this time, DSSCs have improved considerably and are considered as promising alternatives for photovoltaic conversion of solar energy.

In a DSSC, an electrically conducting glass substrate is coated with a thin (10-25 μm) porous layer of titanium dioxide (TiO_2) nanoparticles to create a modified anode. This anode is then further modified by adsorbing a dye molecule to the titania surface (Figure 1.1a). A platinized glass cathode seals the cell, and an electrolyte solution is added completing the cell fabrication (Figure 1.1b).

Figure 1.1. a) Construction of a DSSC device, and b) a representative optically transparent cell made in our labs; c) operational model of a Grätzel's cell (DSSC) with the arrows showing the movement of electrons: 1) light absorption and electron excitation from HOMO to LUMO of dye. 2) Electron injection from S^* into the TiO_2 semiconductor. 3) Electron percolates through the TiO_2 and external load where it ultimately reduces the electrolyte. 4) Regeneration of dye by electrolyte

From an operational point of view (Figure 1.1c), when a photon is absorbed by the dye molecule (1), an electron is excited from HOMO (S) to the LUMO (S^*). The excited electron has the thermodynamic driving force to be injected into conduction band of TiO_2 (2). The electron percolates through the anode (3) and external load where it then reduces the redox-active electrolyte. The electrolyte then regenerates the dye (4) allowing the cycle to continue. As with

any voltaic cell, there are four main components that affect the performance of the DSSCs: the photosensitizing dye, anode, cathode and electrolyte.^{12,13} The dye is generally considered the powerhouse of the cell and the most likely source of cell deterioration and as such will be the major focus with this thesis and its attempt to make a more efficient DSSC dye.

1.2.1. Efficiency of DSSC

The efficiency (η) of a solar cell, which gives the overall conversion of sunlight to electrical energy, is given by the short circuit current (J_{sc}), open circuit voltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (P_{in}) as according to the following equation.

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

where the fill factor is the ratio of the maximum power of the cell per unit area and P_{in} is the power of the incident radiation at AM (air mass) 1.5 (typically 1000 W/m²). To a first approximation, the V_{oc} is related to the energy difference between conduction band of the semiconductor and electrolyte redox couple. Conversely, the J_{sc} is related to the efficacy of the dye injecting electrons into the semiconductor. The J_{sc} depends on the relative energy levels of the sensitizers and the kinetics of the electron-transfer processes at electrolyte/dye/semiconductor interface. During operation, certain undesirable things may happen. For example, the electrons from excited state (S^*) can either decay back to the ground state or the electrons after being injected to TiO_2 , can go to the electrolyte or back to the dye directly without passing through the external circuit and reduce its performance. This short circuiting process is called recombination.

1.3. Anatomy of DSSC dyes

With dyes being a key component in the DSSC architecture, the past two decades has observed a tremendous variation in structure-property investigation when considering the electronic and optical properties of molecular dyes. To this end, two major classes of DSSC dyes have emerged; namely, transition metal-based dyes and organic dyes.

Owing to the original success of the Gratzel cell, ruthenium polypyridyl complexes such as the **Black dye** and **N719** (Figure 1.2) received considerable attention and have been pushed to conversion efficiencies (η) >11%.¹⁴⁻¹⁶ However, the poor absorption beyond 600 nm, cost and low natural abundance of ruthenium,¹⁷ has shifted the paradigm towards organic-based dyes like Sun's dye that achieved more modest conversion efficiencies of (η) >7%.¹⁸ Organic dyes are advantageous because they offer a large diversity in the molecular structure and can be synthesized using a diverse library of reactions. It is also possible to more readily tune the absorption, emission and electrochemical properties through suitable molecular design strategies.¹⁹

Figure 1.2. a) Black dye b) N719 c) Sun's dye

In general, all dyes can be distilled to a requisite structure that contains a redox-active donor (D) that is coupled through a conjugated linker (π) to an acceptor (A) capable of anchoring to TiO₂¹⁸⁻²² (D- π -A molecular structure, Figure 1.3).

Figure 1.3. Organic dye motif for DSSCs

1.3.1. Redox active donors

The donor part of the dye molecule should be robustly redox-active and should be able to effectively inject an electron into TiO_2 . In metal based dyes, this is typically the role of the redox-active metal and a metal-to-ligand charge transfer driven process. However, in organic based dyes, the triphenylamine (TPA) group has been found to be a promising redox active donor for photovoltaic materials owing to its excellent electron-donating ability, high hole-transporting properties and stability. The TPA moiety can also be readily functionalized/tuned and the propeller-shaped molecular structure of TPA also suppresses the recombination of injected electron from TiO_2 to the redox couple. As such, TPA and its derivatives have been extensively used in metal-free organic dyes for DSSCs.²³⁻²⁵

1.3.2. π -spacers

The donor and acceptor parts of the dye molecule are connected through π -spacers. These spacers are significant as they increase the photocross-section of dye and charge separation in the excited state. In transition metal based dyes, the polypyridyl ligands typically play the role of π -spacer, but in organic systems thiophenes have been extensively employed.

The π -spacer also dramatically influences the wavelength of absorption. To a first approximation, dyes obey the 1D *particle-in-a-box* model, and therefore extension of the box (conjugated system) leads to a decrease in the HOMO-LUMO gap (π - π^* ; Figure 1.4). More generally, however, adjusting the length of the conjugated spacer tunes the energy of the frontier molecular orbitals (FMOs) and concomitantly shifts the absorption profile for the desired application.²⁶

Figure 1.4. Decrease in energy gap by increasing conjugation length

Thiophenes as the π -conjugated unit are desirable owing to their chemical and environmental stability as well as their electronic tunability.^{18,27,28} However, the challenge of using thiophenes as π -spacers is that with increased numbers of thiophene units there is a stronger propensity for intermolecular π - π interactions leading to dye aggregation ultimately decreasing the efficiency of organic dyes.^{23,29} Dye aggregation should be minimized in order to obtain maximum performance and this could be done by appropriate structural modifications.^{30,31} Substituting different alkyl groups on the π -conjugated oligothiophene units^{23,32} show inhibited dye aggregation and improved efficiency.

1.3.3. Acceptors/anchor

For an efficient DSSC, the dye must bind strongly to the surface of the TiO_2 semiconductor and covalent bonding interactions provide the strongest linkage between the dye and the TiO_2 .³³

Although silane (SiX_3 or SiOX_3), sulfonate (SO_3^-) and phosphonic acids have been used as anchoring groups, carboxylic acids have become the standard anchoring group owing to their ability to effectively bind to the semiconductor with relative stability and ease of synthesis.^{34,35} Furthermore, carboxylic acid derivatives (*i.e.*, ester, acetic anhydride, acid chloride, or amide) have also been used. Cyanoacetic acid is the most common organic acceptor because of its strong electron-withdrawing effect within the dye motif that improves charge separation in organic systems. Carboxylic acid groups can bind to the TiO_2 surface via different binding modes as shown in figure 1.5.^{36,37}

Figure 1.5. Binding modes for carboxylate unit on TiO_2 surface

1.3.4. Designing effective organic dyes

While designing dyes for DSSC applications, it is important to first understand how molecules absorb light. Dyes should be deliberately designed to absorb strongly in the visible and near IR regions of the electromagnetic spectrum, because that is where the greatest photon flux resides in the solar spectrum. Furthermore, in order to favor electron injection into the semiconductor upon photon absorption, significant charge separation must occur between the ground and excited state (Figure 1.6 a & b). In organic metal-free dyes, the charge transfer sensitization is driven by a π -to- π^* transition. As shown in Figure 1.6, when a photon is absorbed, the electron density in the HOMO, located principally on the redox-active donor portion (TPA), is excited towards the π^* orbital of the dye (*i.e.*, cyanoacetic acid) through a π -spacer (thiophene). The electron is then injected from the π^* orbital into the semiconductor (Figure 1.6c).

Figure 1.6. Electronic redistribution between HOMO and LUMO (a, b), leading to charge injection into the semiconductor (c) upon photoexcitation of Sun's Dye¹⁸

In order for charge transfer to take place, a molecule's propensity to absorb light in the UV-Vis-NIR is a significant quantity. When designing a dye with an intense absorption envelope, the efficacy of light absorption directly relates to the molar extinction coefficient (ϵ). The molar extinction coefficient incorporates two physical quantities: (1) optical cross-section and (2) the probability of absorption (Figure 1.7). The optical cross-section is proportional to the size of the molecule, while the probability directly relates to quantum mechanics and probability of an optical transition. The most probable absorption ($S \rightarrow S^*$) corresponds to a transition between the two electronic states with the best wave function overlap (Frank-Condon Principle).³⁸ The dichotomy here pertains to the polarizability (μ) operator (transition dipole moment). Polarizability represents a molecule's propensity to undergo charge redistribution upon photon absorption. However, with greater charge redistribution, there is necessarily less wave function overlap between ground and excited states (Figure 1.6). Therefore, the π -spacer is critical for negotiating wave function overlap and it suggests that there is an optimal length and type of π -spacer needed in dye design. Furthermore, this suggests that the use of theoretical density functional theory (DFT) calculations, and time dependent (TD-DFT) can be advantageous when designing an effective dye.

Figure 1.7. Factors affecting the extinction coefficient (ϵ)

1.3.5. Designing organic dyes inspired by Nature

The sensitization of metal-free organic dyes was first studied in 1994.^{39,40} Squaraine dyes (Figure 1.8) were used to study the performance of the DSSC. It was observed that the cell showed low conversion efficiencies of 0.05-0.7%. It was found that the poor conversion efficiencies were due to very high back-electron transfer and very low singlet fluorescence quantum yields of the symmetrical squaraine sensitizers. Since then, different types of organic sensitizers have been studied for application in DSSCs.

Figure 1.8. Squaraine dye [bis(2,4,6-trihydroxyphenyl)squaraine]

Naturally inspired porphyrin-based dyes have long been pursued for their photophysical properties, but recently have been shown to be promising candidates for DSSC applications as well. The intrinsic advantages of porphyrin-based dyes are their rigid molecular structures with large absorption coefficients in the visible region and their many reaction sites capable of fine tuning of the optical, physical, electrochemical properties of porphyrins.⁴¹ The rational design of porphyrin dyes involve creating a redox stable push-pull system, which has now led to the highest

validated power conversion efficiencies in DSSC dyes; 12%⁴² (Figure 1.9a) and 13%⁷ (Figure 1.9b), respectively.

Figure 1.9. Porphyrin-based dyes for DSSC applications

The extensive investigations on porphyrin dyes as light sensitizers is inspired by natural photosynthetic systems. Porphyrins are found in a variety of important biological systems and their functions range from oxygen transfer to electron transfer (cytochrome c, cytochrome oxidase) to energy conversion (chlorophyll during photosynthesis). The propensity of porphyrins to be efficient sensitizers is due to its cavity which can fit a variety of metals.^{8,41}

1.4. Artificial synthesis and more of Nature's inspiration for dye design

Plants require sunlight for photosynthesis. During photosynthesis, CO₂ and water are converted into carbohydrates and oxygen by a network of proteins and electron transfer chains, all driven by light, and corresponding proton gradients.^{43,44} The process of plant-based photosynthesis is illustrated in Figure 1.10.

Figure 1.10. Natural photosynthesis; sunlight harvesting by plants

During photosystem II (PSII), a photon is absorbed by chlorophyll and the energy is used to excite an electron. The excited electron is carried by mobile quinone-based carriers and are utilized to reduce NADP⁺ to NADPH. At the same time the proton gradient is generated in lumen which drives the ATP synthesis. Both the NADPH and ATP are used during the Calvin cycle to generate carbohydrates.⁴⁵

When contrasting DSSC design with PSII, a DSSC can be envisaged as a simplified mimic to natural photosynthesis. During photosynthesis, an electron is excited (by photon of light) from the reaction center and is replaced by the oxidation of H₂O (Figure 1.11a). However, in the case of DSSC the electron gets excited from the HOMO of the dye, and is replaced by the electrolyte (Figure 1.11b). Therefore, much can be garnered and gained by mimicking PSII for DSSC optimization.

Figure 1.11. An analogy between harvesting light by plants (a) and DSSC (b)

Another possible DSSC inspiration from photosynthesis is the concept of using multiple redox-active chromophores for energy and electron transfer. Over simplified in the above prose, when the photon is absorbed by PSII it is seldom the reaction centre that absorbs the photon but rather a complex series of antennae dyes. These antenna molecules are porphyrin rings or carotenoids that direct and regulate excitation energy flow (Figure 1.12a). As a result, the absorbed energy gets transferred to the neighboring molecules through the process of Forrester resonance energy transfer (FRET); ultimately funneling down toward the reaction centre dimer. This process keeps on going until the energy in the reaction centre is sufficient when finally, an electron is excited to the charge transfer chain (Figure 1.12b). As such, Nature's light-harvesting capabilities depend on supramolecular chromophores for capturing, transferring and converting solar energy.⁴⁶

Figure 1.12. a) The carotenoids and antennae complexes used in the b) Förster resonance energy transfer (FRET) during photosynthesis⁴⁵

Another key structural feature in this FRET process is that rigid protein frameworks facilitate rapid energy transfer from highly-conjugated antenna complexes to the reaction centre, and based on this inspiration mimicking antenna scaffolds has become a popular pursuit towards solar energy production.⁴⁷ To this end, there has been considerable interest in developing intensely absorbing rigid dyestuffs capable of mimicking this natural behaviour.

1.5. Phenylacetylene macrocycles

One family of chromophore capable of acting as antennae complexes are the shape-persistent phenylacetylene macrocycles.⁴⁸ Owing to their intense light absorption, these extended π -structures have been explored in a number of optoelectronic and light-harvesting applications,⁴⁹ and the synthesis of large macrocycles with well-defined geometries has garnered considerable interest in the recent years.⁵⁰⁻⁵³ Their architectures have similarity to natural light harvesting complexes which can collect light and transfer its energy through excitation energy transfer (EET) processes.^{54,55} Increasing interest in π -conjugated macrocycles is attributed to the their promising application in material science,⁵⁶ in host-guest systems,⁵⁷ storage devices,⁵⁸ digital computation,⁵⁹ molecular rotors.⁶⁰⁻⁶²

Compound **1.1** represents a simple phenylacetylene macrocycle (**PAM**). The size of **PAM** can be changed from several angstroms to several nanometers, and different functional groups can be

incorporated to tune the electronic properties of the macrocycles.⁶³ Owing to their ease of synthesis and self-assembling capabilities, they have become promising building blocks for a variety of supramolecular structures. Acetylene-based macrocycles have also been used for the synthesis of complex rigid macrocyclic scaffolds having chromophores contained within them (*vide infra*),^{64,65} and these macrocycles have an interior and exterior that can be substituted with functional groups making them attractive structures for organic materials.⁶⁶

1.1

PAMs can have various conformations due to the existence of ring-strain energy within the molecules. Their rigid backbones give rise to large number of molecular surfaces and often results in well-organized structures. Phenylacetylene macrocycles, with different numbers of phenylacetylene units (ranging from 4 to 9) were studied and it was found that macrocycles with 4, 5 and 6 repeat units adopt only a planar conformation. However, when the size of macrocycle exceeds 6 units, the distorted conformations (boat-like or chair-like) become predominant, being energetically more favored.⁶³

1.5.1. Synthesis of phenylacetylene macrocycles

Synthesis of macrocycles is generally carried out using cross-coupling reactions between sp - or sp^2 - hybridized carbon atoms. This has been done with a variety of palladium cross-coupling reactions like Sonogashira cross-coupling⁶⁷⁻⁶⁹, Negishi cross-coupling⁷⁰, Heck reaction⁷¹ *etc.* These coupling reactions generally give high yields in individual steps and show high tolerance

towards functional groups. A general mechanism of the Sonogashira cross-coupling reactions is shown in Figure 1.13.

Figure 1.13. General mechanism for Sonogashira Cross-Coupling reaction

During palladium catalysed cross-coupling, a palladium catalyst begins the cycle as Pd⁰. Oxidative addition with an aryl halide results in an intermediate species and palladium is converted from Pd⁰ to Pd^{II}. During the transmetallation step, the halide is replaced with a terminal deprotonated alkyne yielding a Pd^{II} species. The reductive elimination results in C-C bond formation between the aryl and alkyne carbon and Pd^{II} is converted to Pd⁰ again allowing it to continue into another cycle. In general, the other cross-coupling reactions follow a similar mechanism, and the difference with the Sonogashira reaction is that copper is used as a co-catalyst to lower the pKa of the terminal acetylene, ultimately permitting transmetallation.

Although coupling reactions provide a large variety in the synthesis of macrocycles, they also involve a large number of synthetic steps which are kinetically controlled. The ring closing step requires dilute conditions (< 1 mM) and the overall yield in these reaction is often quite low.^{72,73} The yield of the macrocycle drops with the increasing size of the macrocycle. The low yield is due to the irreversible nature of the reactions so that the undesired bond formation cannot be avoided.⁶⁴

In order to overcome the problem of low yield, people have used an alternative approach based on dynamic covalent chemistry (DCC), which prepares macrocycles in high yield.⁷⁴ This approach overcomes the formation of undesired products because of its reversible nature. Examples of this approach are the metathesis reactions (imine metathesis⁷⁵ and alkyne metathesis⁷⁶) which, under thermodynamically controlled conditions, have synthesized macrocycles in high yield. Zhang and Moore have summarized the kinetically controlled and thermodynamically controlled synthesis of shape-persistent macrocycles.⁶⁴

1.5.2. Phenylacetylene macrocycles and energy transfer

Macrocycles have the ability to absorb light energy and redistribute the charge density to other parts of the molecule. This could be done either through bonding or through space. The process of light-harvesting and energy transfer was demonstrated by the following study which

shows the π -conjugated polymeric wires (poly(phenylene-ethynylene-butadiynylene)) covalently encapsulated by conjugated macrocycle.⁷⁷

Molecule **1.2** is a polymeric species where the polymer chain runs through a covalently bound macrocycle. The energy absorbed by the macrocycle is transferred to and concentrated in the wire core (Figure 1.14). The absorption for the macrocycle polymer (1, c, black line) shows two absorption peaks at 337 and 442 nm which correlates to the absorption of macrocycle (3, a, blue line) and the polymer (2, b, green line). The binding of macrocycle to the polymer could slightly change the individual absorption. The emission of the macrocycle (a, blue dotted line) overlaps with the absorption of polymer 2. Energy transfer occurs and as a result the emission of macrocycle polymer 1 is identical to that of the core polymer 2 and is independent of the excitation wavelength. The temporal rise in the emission of the acceptor provides the ultimate confirmation that the EET did occur within the molecule and that the emission occurs from the core.

Figure 1.14. Absorption and emission spectra molecule **1.2**, along with its components.⁷⁷ Figure reproduced with permission from *Angewandte Chemie-International Edition* **2007**, 46, 3450. Copyright 2007 John Wiley and Sons.

1.5.3. Macrocycles and two photon absorption

Due to the large conjugation length, phenylacetylene macrocycles can exhibit two photon absorption *i.e.* two photons are used to excite an electron. In the following study a phenylacetylene

macrocycle derivative **1.3** with triphenylamine units was reported.⁷⁸ Macrocycle **1.3** showed an enlarged two-photon absorption cross-section.

The absorption and emission spectra of three compounds along with the reference TPA are shown in Figure 1.15. All the three compounds show maximum absorption at ~ 380 nm which corresponds to the $\pi-\pi^*$ transition. Absorption ~ 300 nm relates to that of TPA and it decreases from dimer to tetramer and almost diminishes in case of macrocycle **1.3**. This shows complete electron delocalization through TPA and ethynyl segment in **1.3**. Also, the maximum absorption shows red-shifting from dimer to macrocycle which corresponds to the extended conjugation length in the molecular backbone. The emission spectra ~ 430 nm shows a similar trend with slight onset emission redshift from **1** to **3** which can be attributed to the more extended conjugation.

The two-photon absorption was measured by a Z-scan technique which uses a femtosecond laser source. Macrocycle **1.3** showed a two-photon absorption cross-section peak at 650 nm which is less than 760 nm (double wavelength of their linear absorption maxima). This could possibly be

due to the fact that the two-photon excitation might populate the molecule to a higher energy excited state with larger probability as compared to that by one-photon excitation.⁷⁸ Compared with regular phenylacetylene macrocycles, **1.3** showed an extended cross-section due to its more branched structure.

Figure 1.15. Absorption and emission of dimer (**1**), tetramer (**2**) and macrocycle (**1.3**), along with the reference triphenylamine.⁷⁸ Figure reproduced with permission from *Tetrahedron Lett.* **2012**, 53, 4885. Copyright 2012 Elsevier.

In another study, the shape persistent symmetrical structure of phenylacetylene macrocycle was used to synthesis a two-photon absorption macrocycle **1.4**.⁷⁹ The macrocycle had dibutylamino- (Bu_2N) and butoxy- (BuO) as the donor groups which increased the long-wavelength absorption maxima and the Stokes shift. When compared to the absorption maximum of unsubstituted phenylacetylene macrocycle, **1.4** witnessed an increase of ~ 110 nm in the absorption maximum which was attributed entirely to the presence of donor groups. Because more rigid fluorophores are typically more fluorescent⁸⁰ (because rigid structures provide a better wavefunction overlap in excited and ground states), macrocycle **1.4** was shown to be strongly fluorescent. The two-photon excitation spectrum of **1.4** showed a similar pattern except the

wavelength was doubled relative to the one photon spectrum which is the evidence that the macrocycle experiences two-absorption absorption.

1.4

More recently, structure-property relationships of acetylene-linked perylene bisimide (PBI) macrocycles were studied.⁸¹ The PBI macrocycles were found to be promising candidates for artificial light-harvesting systems. Macrocycles with three to six PBI units (**1.5** has three PBI) were synthesized and it was observed that the macrocycles with three and four PBI units were more rigid molecules and they showed a well-defined geometry. With increased ring size the structures became more distorted; the fluorescence lifetimes became shorter and their distributions became broader. On the other hand, the smaller ring size macrocycles (with PBI units 3-4) showed higher

photostability and efficient excitation energy transfer (EET). These properties were attributed to their well-defined and planar structures.

1.5

1.6. BODIPY dyes

BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) dyes have similarity to porphyrins and can be generally considered as demi-porphyrins. They were first discovered by Treibs and Kreuzer in 1968.⁸² BODIPY has been used in a variety of advanced material applications due to its highly desirable properties such as high absorption coefficients, sharp emission peaks exhibiting high quantum yields, and chemical stability under wide range of conditions. Their fluorescence characteristics can further be changed by modifying their structures. The generic core and its relative positions are shown in Figure 1.16. Owing to these characteristics, as well as their stability to physiological conditions and insensitivity to the polarity and pH of the surrounding environment⁸³, they have found a wide range of applications in labelling proteins^{84,85} and DNA⁸³, for imaging events in cells and whole organisms, chemosensors, fluorescent switches, laser dyes, dye sensitized solar cells and organic photovoltaics (OPVs).⁸⁶

Figure 1.16. BODIPY core and its relative positions

1.6.1. General synthesis of BODIPY

Dipyrranes are precursors for the synthesis of BODIPYs. The most relevant synthetic methodologies aimed at developing efficient synthetic routes, as well as achieving wider structural diversity of dipyrromethane derivatives, have been summarized in a review by Pereira and co-workers.⁸⁷ Dipyrranes also constitute important building blocks in the synthesis of porphyrins, corroles, chlorins, calix[4]pyrroles, porphodimethenes, and dipyrinato complexes. The 2012 review by Gryko *et al.* explains the most practical and useful synthetic methodologies for the synthesis of the above mentioned compounds starting with dipyrranes.⁸⁸ Bessette and Hanan⁸⁶ have focused on summarizing the recent developments in the use of materials based on dipyrromethene and azadipyrromethenes, especially their BF_2 derivatives (BODIPY and aza-BODIPY), for organic photovoltaic (OPV) applications.⁸⁶

In general, BODIPY can be prepared using two main synthetic routes: 1) The pyrrole is reacted with an aldehyde through a double electrophilic aromatic substitution and condensation to create a dipyrrolemethane. This step is facilitated by using trifluoroacetic acid (TFA) which creates an electrophilic centre (Scheme 1.1). This intermediate is then oxidized using DDQ or *p*-chloranil, and reacted with an organic base and boron trifluoride diethyletherate ($\text{BF}_3 \cdot \text{OEt}_2$) to form BODIPY.^{83,89}

Scheme 1.1. A general scheme for the synthesis of BODIPY using an aldehyde

The other alternative route uses an acid chloride which reacts with pyrrole to make a dipyrin core that then reacts with a base and BF₃·OEt₂ to form BODIPY (Scheme 1.2).^{83,90}

Scheme 1.2. General synthetic approach to BODIPY using acid chlorides

1.6.2. Tuning BODIPY

The electronic properties of BODIPY can be tuned by substituting its various positions. The *meso*-position sits on the mirror plane of BODIPY and can be readily modified using different aldehydes and acid chloride derivatives. Unfortunately, while this is the synthetically easiest position to modify, it also has the smallest effect on the optical properties of the dye, because the mirror plane does not significantly interact with the BODIPY π -system. The use of aromatic substituents minimally extends conjugation and only a slight broadening of the absorption profile is observed, unless a redox active species is added.⁹¹ Bañuelos and co-workers systematically studied modification at the *meso*-position to test the photochemical properties influenced by

substituents on the *meso*-position. It was observed that the alkyl substituents do not affect the absorption profile significantly; however, there can be a slight blue shift of the λ_{max} owing to inductive effects of the alkyl substituent increasing the electron density on the *meso* carbon.⁹¹

In addition, the Koivisto group has extensively studied tuning BODIPY using the 2,6-positions. The 2,6-positions of BODIPY are the most electronegative positions and can undergo electrophilic addition reactions to yield a variety of derivatives.

Modification at the 3, 5-positions has also been extensively studied. Electron donating groups have been attached at the 5-position and a non-linear push-pull system has been developed with the donor at the 5-position of the BODIPY core and acceptor at the 3-position.⁹² Recently Ziessel group prepared BODIPY derivatives substituted on the 5-position and described unsymmetrical triads constructed from extended BODIPY dyes, diketopyrrolopyrrole (DPP) dyes, with electron donor fragments containing triarylamines. The assemblies are such that each module maintains its individual optical and redox properties. The use of phenyl-alkyne-phenyl or phenyl-alkyne-thienyl spacer units is favorable for weak electronic interaction between the modules.⁹³

Finally, the boron centre can be substituted by replacing fluoride atoms with various groups. Alkyl groups can be introduced to the boron centre through the use of aryl Grignards or aryl lithiums to displace the fluoride atoms.⁹⁴⁻⁹⁶ Alkoxide substituents can be introduced through aluminum trichloride in the desired alcohol whereas alkyne groups can also be added by using an acetylide anion to displace fluoride.⁹⁵ Generally speaking the substitution of fluoride with aryl or alkyne groups have the least effect on absorption and emission properties owing to the fact that boron centre does not affect the conjugation on BODIPY core. However, boron substitution has an impact on the fluorescence which decreases by replacing fluoride with bulky alkyl groups.⁹⁴⁻⁹⁶

1.6.3. BODIPYs in photovoltaics

One of the limitations of organic dyes is their narrow high-energy absorption bands. In order to improve the DSSC performance, organic dyes should possess panchromatic absorption envelopes extending into the near-infrared (NIR). Encouraged by the excellent photophysical properties and efficient electron transfer in BODIPY dyes, efforts to include them as non-innocent π -spacers (which have absorption and emission properties) within the DSSCs dye motif have been growing.⁹⁷

In the first attempts, BODIPY dyes were found to be ineffective sensitizers for DSSC applications.^{98,99} Akkaya and coworkers investigated a small set of BODIPY dyes possessing Type II (Figure 1.7) D-A motifs.¹⁰⁰⁻¹⁰³ This was a surprising choice for a first generation dye, because substitution at the *meso*-position results in poor electronic communication with the BODIPY core, and when D-A motifs are added at the *meso*-position, energy-transfer “cassettes” typically result; in general energy transfer through the BODIPY core tends to be less efficient in both Type I & II motifs. Conversely, extremely fast energy transfer is observed when transition moments are aligned (Figure 1.17; Type III).^{90,95,104} Therefore, BODIPY motifs of Type III are more suitable for DSSC applications. One method of incorporating BODIPY into a Type III motif is presented by dyes **1.6** and **1.7**.

Figure 1.17. Type I, II and III donor (D)/acceptor (A) motifs in BODIPY dyes for DSSC applications

One of the challenges in working with BODIPY DSSC dyes could be due to poor charge separation in the dominant optical transition.⁹⁰ However, inclusion of a D-A profile across BODIPY broadens and bathochromically shifts the BODIPYs absorption envelope. The Koivisto group recently reported the use of BODIPY as a non-innocent π -spacer in DSSC dyes (**1.6**).⁹⁰ Using TPA donors and cyanoacetic acid acceptors at the 2,6 positions lead to a broadening profile and panchromatic light-harvesting, and a significant improvement in device performance. This has been pushed even further via the use of a phenothiazine (PTZ) moiety as electron donor resulting in an efficiency of over 5% (**1.7**).¹⁰⁴

1.6.4. Energy transfer in BODIPYs

In the previous sections, discussion has focused on the absorption properties of individual chromophores. Although BODIPY exhibit strong absorption properties, it also possesses a relatively narrow absorption window. One strategy to overcome this limitation is to make a dyad chromophore system where BODIPY can be attached to another chromophore. In this dyad assembly, each component absorbs at a different wavelength and upon absorption of light, one chromophore transfers the absorbed energy to the other chromophore. Thus a dyad assembly leads to a panchromatic absorption. As a result, BODIPYs have been used in multi-component molecular arrays that demonstrate electronic energy transfer (EET) over large distances. These molecular arrays feature the positioning of individual units to directed EET along the molecular axis or along another preferred pathway.¹⁰⁵

The assembly of two or more BODIPY derivatives have been made and studied for energy transfer. To this end BODIPY triads photosensitizers **1.8**¹⁰⁶ and **1.9**¹⁰⁷ exhibited enhanced intramolecular resonance energy transfer. Likewise, diketopyrrolopyrrole π -bridges combined with a BODIPY dimer (**1.10**) permitted the harvesting of low energy photons via intramolecular energy transfer.

BODIPY dyes have been substituted with polycyclic aromatic hydrocarbons (PAHs), which in turn transfer energy upon excitation to the BODIPY core. The influence of the orientation between the *meso*-donor and BODIPY-acceptor on electronic energy transfer has been studied using a molecule with two nearly perpendicular chromophores. This has been achieved by substituting the *meso*-position with anthracenyl unit¹⁰⁸ (**1.11**), phenanthrene unit¹⁰⁹ (**1.12**), perpendicular oligothiophene donor¹¹⁰ (**1.13**), -thienyl and furyl donor¹¹¹ (**1.14**). A linear molecular dyad was synthesised by attaching a anthracenyl-based unit¹¹² (**1.15**) and pyrene–thiophene energy donor¹¹³ (**1.16**) linked *via* a triazole unit to a BODIPY energy acceptor. The

donor to acceptor separation distance is around 20 Å. Emission from the donor originates from a mixed π - π^* and partial charge-transfer state and overlaps favourably with the absorption profile for the acceptor.

A BODIPY was directly linked to an aza-BODIPY at the β -position aza-BODIPY. Owing to the direct linking of the two entities, ultrafast energy transfer was witnessed from BODIPY donor to aza-BODIPY acceptor (**1.17**).¹¹⁴ Circularly polarized luminescence *via* intramolecular energy transfer was observed when three moieties having different effects were used: (i) BODIPY acts as the chromophore, (ii) BINOL as the chiral perturbing moiety, and (iii) tetraphenylethene (TPE) as the aggregative induced emission (AIE) and UV-absorbing moiety (**1.18**).¹¹⁵

A recent study combined two energy transfer processes, dark resonance energy transfer (DRET) and fluorescence resonance energy transfer (FRET), in one polarity sensitive donor-acceptor system (Figure 1.18).¹¹⁶ The DRET and FRET was studied in organic and aqueous media respectively. In aqueous media, the FRET process was observed. This is because the generation of emissive TPE donor is strongly polarity dependent, due to its aggregation-induced emission (AIE) feature. However, in tetrahydrofuran (THF), the DRET process was observed. This is because TPE fragment of the dye are non-emissive. Photophysical results were similar both in aqueous and organic media with the exception that the TPE fragments of the dye were non-emissive in organic media.

Figure 1.18. Dark resonance energy transfer (DRET) and fluorescence resonance energy transfer (FRET) in one polarity sensitive donor-acceptor system.¹¹⁶ Figure reproduced with permission from *Chemistry - A European Journal* **2016**, 22, 736. Copyright 2016 John Wiley and Sons.

Owing to the large free volume within macrocycles it is possible to bind organic substrates within the cavity and this can influence the properties of both the macrocycle host and guest depending on the nature of the functional groups attached to the macrocycle. Aromatic macrocycles as supramolecular hosts can increase the energy transfer efficiencies owing to their stronger binding affinities to aromatic guests *via* π stacking¹¹⁷ and hydrophobic effect.¹¹⁸ The Levine group studied the use of aromatic organic macrocycle as supramolecular hosts to observe non-covalent energy transfer.¹¹⁹ They synthesized macrocycle **1.19** that was electronically

dissymmetric. The electronic dissymmetry allowed the electron-rich analyte to bind near the electron-deficient component of the macrocycle and an electron-deficient fluorophore was inserted near the electron-rich part of the macrocycle. Benzo[*a*]pyrene was taken as a donor **D** and BODIPY as the accepting fluorophore **A**. The binding was quantified by measuring the changes in the emission spectra of donor molecule (benzo[*a*]pyrene). An increase in the emission of donor molecule was observed with increasing the concentration of macrocycle **1.19**.

Macrocycle **1.19** was also investigated for its ability to promote energy transfer from donor **D** to fluorescent acceptor **A**. It was observed that the acceptor emission increased (Figure 1.19A) by adding the donor molecules and that was due to the energy transfer from the donor to the

fluorophore acceptor. Also, a decrease in the donor emission was observed when a competing energy acceptor was added (Figure 1.19B).

Figure 1.19. Energy transfer in macrocycle **1.19** (A and B). F_{DA} and F_D are the integrated emission of the donor in the presence and absence of acceptors whereas I_{DA} and I_A are the integrated emission of the fluorophore in the presence and absence of analyte.¹¹⁹ Figure reproduced with permission from *Chem. Commun.* **2013**, 49, 8259. Copyright 2013 Royal Society of Chemistry.

Inspired by the natural photosynthetic systems, researchers have investigated the BODIPY and porphyrin assemblies in covalent and non-covalent arrays. In these assemblies, light is harvested by more than one chromophore and the excitation energy is transferred to the acceptor unit by the antenna effect. In general, the porphyrins absorb in 400 – 450 nm (Soret band) and 550 – 650 nm (weak to medium Q bands). The inherent problem of porphyrin's poor absorptivity in the blue-green region (450-550 nm) can be overcome by linking it with BODIPY which absorbs strongly in blue-green region (near 500 nm).¹²⁰⁻¹²⁴

The efficiency of the intramolecular energy transfer in antennae assemblies depends on the extent of electronic coupling between the chromophores which could be modulated either by the bridge or the special orientation of the units.^{125,126} Triazole bridged BODIPY-Zn or BODIPY-Ni porphyrin conjugates containing one BODIPY and one porphyrin (dyad, **1.20**¹²⁷ and **1.21**¹²⁸), three BODIPYs and one porphyrin (tetrad, **1.22**¹²⁸) and four BODIPYs and one porphyrin (pentad, **1.23**¹²⁸) were studied. The absorption spectra shows increase of roughly three and four times in the BODIPY (donor) π - π^* transition. The fluorescence studies showed a strong emission from the porphyrin unit when excited at 495 nm (where the BODIPY absorbs strongly), supporting an

energy transfer from BODIPY to the porphyrin unit and the efficiencies were recorded with more than 90%.

Both covalent¹²⁹ (**1.24**) and non-covalent¹³⁰ (**1.25**) architectures incorporating BODIPY, a Zn porphyrin and squaraine units were also studied for panchromatic absorption. By combining the squaraine unit (which absorbs in the region of 600-700 nm) with BODIPY and porphyrin units, the researchers were able to absorb in the entire visible spectrum. In this dye design, the squaraine served as an EWG and anchor to TiO₂ nanoparticle in DSSC, while simultaneously the squaraine also serves as a light harvesting chromophore. The BODIPY dye lacking the imidazole moiety (**1.24**) displayed no enhancement in DSSC performance despite panchromatic absorption, and the ϵ -values were higher than that of **1.25**. However, the BODIPY dye bearing an imidazole moiety non-covalently bound (**1.25**) increased the efficiency of the DSSC to 4%; highlighting the importance of the supramolecular assembly for efficient energy transfer.

1.7. Resonance Energy Transfer

Energy transfer (ET) occurs when one molecule or moiety serves to donate energy to another acceptor molecule or molecular substituent. Förster provided the first rationale of this process as the energy released from an excited donor could simultaneously excite the ground-state

acceptor based on the Coulombic interaction between these two chemical groups.¹³¹ Dexter provided another mechanism by which an excited donor group transfer energy to the acceptor group due to hopping of electrons to accomplish the non-radiative process.¹³² The processes of Dexter and Förster resonance energy transfer are depicted in Figure 1.20.

Figure 1.20. Dexter (top) and Förster (bottom) processes of energy transfer (ET)

Energy transfer have found wide range of applications in biological systems. The precise location and nature of the interactions between specific molecular species in living cells is of major interest in many areas of biological research.¹³³ Energy transfer have also been extensively studied for material applications e.g. photovoltaics⁸ (for panchromatic absorption) and light-emitting diodes and fluorescent sensors etc.¹³⁴

1.7.1. Förster (Fluorescence) Resonance Energy Transfer (FRET)

FRET is non-radiative resonance energy transfer. Unlike observing traditional fluorescence behavior, FRET involves the excitation of the donor (or auxillary chromophore) that transfers its energy “through space” to the acceptor (fluorophore). For FRET to happen, the donor’s emission band must have sufficient overlap with the acceptor’s adsorption band (Figure 1.21a). Also, the emission dipole of the donor

and the absorption dipole of the acceptor must be at the same frequency (wavelength) in order to be in resonance.^{133,135,136} It is essentially a two-step version of the same excitation and emission process. The energy absorbed by the donor molecule perturbs charge distribution of the acceptor (if the two states are correctly oriented and the molecules are close in space) resulting in the acceptor being excited. This results in the relaxation of donor without emission of a photon and thus radiationless transfer of energy to the acceptor occurs (Figure 1.21b). The acceptor can eventually relax to its ground state by emitting a photon of longer wavelength.^{133,137,138}

Figure 1.21. a) An overlap between emission of the donor and absorbance of the acceptor as a requirement of FRET and b) the mechanism of FRET from donor to acceptor

A typical distance range for FRET is 10-100 Angstroms ($\text{\AA}$)^{138,139} and it is used as a technique to monitors the distance between different fluorescent probes typically attached to macromolecules. FRET can be employed to monitor either binding interactions between different molecules or conformational changes within the same molecule. This technique can be used both *in vitro* and *in vivo*.¹³³

The efficiency of energy transfer (E_T) is a measure of the fraction of photons absorbed by the donor that are transferred to the acceptor and is evaluated as shown in Equation 1.1.

$$E_T = 1 - (T_{DA}/T_D) \text{ ----- Equation 1.1}$$

where T_{DA} is the donor lifetime in the presence of the acceptor and T_D is the donor lifetime in the absence of the acceptor.

Besides spectral overlap between the donor emission and acceptor absorption spectra and the relative orientation of the donor and acceptor transition dipole moments, the other factors effecting the rate

of energy transfer include quantum yield of the donor and the distance separating the donor and acceptor molecules. According to Förster's theory, the rate of energy transfer is given by the Equation 1.2.

$$K_T = (1/T_D) \cdot [R_0/r]^6 \text{ ----- Equation 1.2}$$

where R_0 is the Förster critical distance, T_D is the donor lifetime in the absence of the acceptor, and r is the distance separating the donor and acceptor chromophores. The Förster critical distance is the maximal separation length between donor and acceptor molecules under which resonance energy transfer will still occur. The value of R_0 may be calculated from the following expression given by Equation 1.3.

$$R_0 = 2.11 \times 10^{-2} \cdot [\kappa^2 \cdot J(\lambda) \cdot \eta^{-4} \cdot Q_D]^{1/6} \text{ ----- Equation 1.3}$$

where κ -squared is a factor describing the relative orientation in space between the transition dipoles of the donor and acceptor, $J(\lambda)$ is the overlap integral in the region of the donor emission and acceptor absorbance spectra (with the wavelength expressed in nanometers), η represents the refractive index of the medium, and Q_D is the quantum yield of the donor.

1.7.2. Dexter Resonance Energy Transfer (DRET)

Dexter energy transfer involves transfer of excitation energy from donor to acceptor due to hopping of electrons *via* a non-radiative path.¹³² The Dexter exchange energy transfer is generally associated with fluorescence quenching mechanism (quenching implies any physical process or molecular state that decreases the molecular fluorescence). DRET requires an overlap between the wavefunctions of both donor and acceptor ($\langle \Psi_0/\Psi_1 \rangle$). This typically requires π -resonance interactions between neighbors. The overlap of wavefunctions also implies that the excited donor and ground-state acceptor should be close enough so the exchange could happen. DRET can only occur at short distances and is generally observed within a distance of 10 Å.^{132,134,140}

Dexter energy transfer is a process that two molecules (intermolecular) or two parts of a molecule (intramolecular) bilaterally exchange their electrons (not formally considered electron transfer). The exchange mechanism could be through a singlet-singlet energy transfer ($^1D^* + ^1A \rightarrow ^1D + ^1A^*$) in which a singlet group produces another singlet group (Figure 1.22a) or through a triplet-triplet energy transfer ($^3D^* + ^1A \rightarrow ^1D + ^3A^*$) in which a triplet group produces another triplet group (Figure 1.22b).^{141,142}

Figure 1.22. Electron exchange mechanism during DRET; a) singlet-singlet energy transfer and b) triplet-triplet energy transfer

Even if there are competing mechanisms between Forster and Dexter mechanisms often a supplementary Dexter contribution will go unnoticed. Also the possibility of quenching by electron transfer (depending on the nature of D and A) should not be overlooked, especially in polar solvents that support this process.¹⁴³

1.8. Objectives

In order to mimic photosynthesis and design better organic based dyes for dye-sensitized solar cell (DSSC) applications,¹⁴⁴ this research is aimed at combining the phenylacetylene macrocycle and BODIPY motifs to create and explore a family of non-innocent π -spacers that could be used in DSSC dye motif for light-harvesting applications. While this thesis does not produce DSSC dyes, the hypothesis is that upon absorption of light, the phenylacetylene macrocycle will transfer energy to the BODIPY core, thereby increasing the effective absorption envelope. The objective can be categorized into four sub-sections.

1. Synthesize a novel π -spacer amenable for integration into a DSSC dye (D- π -A) motif. This involves the synthesis of BODIPY-phenylacetylene macrocycles in which the BODIPY resides inside and aligned orthogonally to the phenylacetylene macrocycle. Alignment of BODIPY orthogonal to the macrocycle is significant because it minimizes the chance of Dexter energy transfer owing to the lack of orbital overlap. As a result, the energy transfer in this structural design is hypothesized to operate through a Förster mechanism (see section 1.7 for details).
2. Explore energy transfer behavior in order to elucidate the potential for desirable energy transfer within the molecule and to ascertain if energy transfer results in enhancing the absorption envelope.
3. Systematically tune the phenylacetylene-BODIPY dyad by adding donor groups to the macrocycle with the hope of tuning the frontier molecular orbitals, and absorption envelope.
4. Begin synthetic modifications toward DSSC applications where the BODIPY-macrocycle π -spacer would be incorporated within a D- π -A motif.

Chapter 2: BODIPY-Phenylacetylene Macrocycles for Enhanced Light-Harvesting and Energy Transfer Applications

2.1. Introduction

As stated in the thesis objectives, an orthogonal BODIPY-phenylacetylene macrocycle was the idealized structure sought in order to study energy transfer and evaluate the efficacy of this building block as a π -spacer for light harvesting applications. The hypothesis is that upon absorption of light, the phenylacetylene macrocycle would effectively transfer energy to the BODIPY core, thereby increasing the effective absorption envelope of the dye. To this end, the synthesis, characterization and evaluation of physicochemical properties of an orthogonal phenylacetylene macrocycle-BODIPY dyad are described herein.

A proposed design of the target BODIPY-macrocycle is shown in Figure 2.1, where the BODIPY is tethered and oriented orthogonally within the cavity of the macrocycle. To make this proposed target molecule, a variety of strategies were attempted and employed. To this end, a symmetric macrocycle can be broken down into four parts: two arms, one top BODIPY containing unit, and a bottom cap (Figure 2.1b). The top BODIPY unit should have structural features capable of connecting the phenylacetylene arms. The phenylacetylene arms are intended to extend the π -conjugation and provide a large enough cavity to support the BODIPY unit and close the ring using the bottom cap.

Figure 2.1. A proposed design of the orthogonal BODIPY-phenylacetylene macrocycle (a) and its assembly from building blocks (b)

Subsections 2.2.1 – 2.2.3 of this thesis describe the synthesis of the various building blocks designed for the construction of a BODIPY-phenylacetylene macrocycle and the attempted synthesis using the “bottom cap-*up*” (2.2.4) approach. Owing to synthetic limitations, a top BODIPY-*down* approach was employed (2.2.6), which required the synthesis of new building blocks (2.2.5), but ultimately led to the formation of a desirable BODIPY-phenylacetylene macrocycle dyad and derivatives (*vide infra*).

2.2. Synthesis

2.2.1. A retrosynthetic analysis of BODIPY-phenylacetylene macrocycle

A retrosynthetic approach for the synthesis of BODIPY-phenylacetylene macrocycle is proposed in Scheme 2.1. According to this approach, the small building blocks (**2.15** and **2.19**) are reacted to yield TMS-protected U-shape molecule (**2.20**) which is then deprotected (**2.21**) and reacted with desired BODIPY-cap (**2.9**) to yield the desired product (**2.22**). The building blocks are selected such that the BODIPY is enclosed in the macrocycle.

Scheme 2.1. A retrosynthetic approach for the synthesis of BODIPY-Phenylacetylene macrocycle

2.2.2. Synthesis of top BODIPY cap

The first step towards the synthesis of the BODIPY cap was to make an appropriate aldehyde. As such, 4-*tert*-butyl-2,6-diiodobenzaldehyde (**2.4**) was synthesized using a modified literature method.¹⁴⁵ The individual steps starting from 4-*tert*-butyltoluene (which is commercially available) are summarized in Scheme 2.2. Substitution of 4-*tert*-butyltoluene with iodine by electrophilic aromatic substitution produced compound **2.1**, which was then oxidized with KMnO₄ to yield acetate **2.2**. The acetate was hydrolyzed to the alcohol **2.3**, which was oxidized to the corresponding benzaldehyde **2.4** using Pyridinium chlorochromate (PCC). The overall yield of **2.4** over the 4 steps was 36%.

Scheme 2.2. Synthesis of substituted benzaldehyde **2.4**

The next step in the preparation of the BODIPY-cap was the preparation of a substituted pyrrole *i.e.* 2,4-dimethyl-1*H*-pyrrole (**2.6**). Ethylacetoacetate was converted to a diester **2.5** using the Paul-Knorr synthesis, followed by a decarboxylation of **2.5** using KOH to yield **2.6** according to Scheme 2.3. Although **2.6** has been previously reported¹⁴⁶, this sequence has been optimized to be more effective. The separation of the pyrrole in the presence of ethylene glycol is achieved

using vacuum distillation at 60 °C over a period of 3 hours. The overall yield of the product over two steps was 43%.

Scheme 2.3. Synthesis of Pyrrole **2.6**

The oxidation of benzaldehyde **2.4** to benzoic acid **2.7** was attempted with the hope that it could be converted to the acid chloride **2.8** (because the synthesis of BODIPY from acetyl chloride yield high). The acid chloride could then be reacted with pyrrole **2.6** to yield BODIPY **2.9** according to Scheme 2.4. However, this reaction failed en route to **2.7**. One fraction was recovered as the starting material whereas, the rest of the fractions were some unidentified intermediates. One of the potential reasons for this failed reaction could be the purification and isolation. The purification of carboxylic acid using chromatography could have been a determining factor as carboxylic acids have a strong affinity for the stationary phase.

Scheme 2.4. Expected oxidation of **2.4** to the corresponding benzoic acid, acetyl chloride and BODIPY

After a failed attempt to convert aldehyde to acetyl chloride, the aldehydes **2.4** was reacted with pyrrole **2.6** to make BODIPY (Scheme 2.5). Following a protocol for a similar BODIPY,¹⁴⁷ the reaction conditions were adjusted to prepare BODIPY derivative **2.9**.

Scheme 2.5. Synthesis of BODIPY **2.9**

This novel compound **2.9** was fully characterized by ¹H NMR, ¹³C NMR, ¹¹B NMR, ¹⁹F NMR, and mass spectrometry. This high symmetry compound (**2.9**) has a simple NMR spectrum (Figure 2.2). There are two sets of methyl protons (b and c) and a set of *tert*-butyl protons in the aliphatic region. One set of methyl protons (c) is strongly shielded which could be due to the orthogonal phenyl ring. There is also a set of two equivalent protons in the aromatic region. Integration gives the exact number of protons for BODIPY **2.9**. The NMR spectra (¹³C NMR, ¹¹B NMR and ¹³C NMR) can be found in appendices.

Figure 2.2. ¹H NMR spectrum of BODIPY **2.9** in CDCl₃

2.2.3. Synthesis of phenylacetylene arm

With the BODIPY fragment in hand, the next step was to prepare the phenylacetylene arms. The first step was the preparation of ((3-azidophenyl)ethynyl)trimethylsilane compound with butane (1:1) (**2.11**), the synthesis is depicted in Scheme 2.6. Compound **2.10** was prepared from 3-iodoaniline using diazonium chemistry followed by the reaction with (trimethylsilyl)acetylene (TMS-acetylene) through a Sonogashira cross-coupling to yield **2.11**. All the steps were fully characterized by NMR spectroscopy, in agreement with literature characterization.¹⁴⁸

Scheme 2.6. Synthesis of compound **2.11**

Diethyl-triazine (N_3Et_2) is an interesting functional group because it is referred to as a masked iodide and can be readily converted using iodomethane (MeI). Compounds **2.12** and **2.13** were obtained from compound **2.11** according to the reactions outlined in Scheme 2.7. The corresponding yields for **2.12** and **2.13** were 82% and 73% respectively. Both compounds **2.12** and **2.13** were characterized by ^1H NMR spectroscopy and the data agreed with literature values.¹⁴⁸

Scheme 2.7. Synthesis of compounds **2.12** and **2.13**

Continuing with the protection/deprotection strategy, **2.12** and **2.13** were reacted together using a Sonogashira cross-coupling followed by the reaction with iodomethane to yield compound **2.15**.¹⁴⁸ The synthesis of compound **2.15** is depicted in Scheme 2.8, with an overall yield of 66%.

Scheme 2.8. Synthesis of arm **2.15** towards the macrocycle

2.2.4. Synthesis of bottom-cap

The synthesis of the next building block (bottom-cap **2.19**) is elaborated in Scheme 2.9 and the sequence had an overall yield of 31%. The first step, which yields **2.16** requires iodination of 4-*tert*-butylaniline which was achieved using the piranha solution (H_2O_2 & H_2SO_4).¹⁴⁹ Deamination of the aromatic ring was then achieved using diazonium chemistry. In a reported literature method, this was done by reacting **2.16** with *tert*-butylnitrite in DMF.¹⁵⁰ As *tert*-butylnitrite was not readily available, NaNO_2 with a strong acid was used successfully in EtOH. The reaction worked well and the product (**2.17**) was characterized by ^1H NMR and the data agreed with the literature. The Sonogashira cross-coupling reaction with TMS-acetylene yielded **2.18** followed by the deprotection of TMS groups to yield **2.19**.

Scheme 2.9. Synthesis of building block **2.19** for the synthesis of macrocycle

2.2.5. Synthesis of BODIPY-macrocycle (bottom-up approach)

A bottom up approach used for assembling the U-shape molecule starting from a bottom cap is illustrated in Figure 2.3. The U-shape molecule then react with the top BODIPY cap to

cyclize the ring. This approach is in accordance with the retrosynthetic strategy shown in Scheme 2.1.

Figure 2.3. A cartoon showing the synthetic strategy of making BODIPY-macrocycle using bottom up – approach cyclization of the ring

To carry out the synthesis according to the bottom-up approach, both building blocks **2.15** and **2.19** were reacted together *via* a Sonogashira cross-coupling to yield product **2.20** as outlined in Scheme 2.10. This TMS-protected derivative **2.20** was characterized using ^1H NMR and ^{13}C NMR spectroscopy. The ^1H NMR (given in appendices) did not provide conclusive information as the aromatic protons have significant overlap. However, the TMS protons and aromatic protons were integrated according to the structure. ^{13}C NMR resolved clean enough to show all 25 distinct carbons. Also, the high resolution mass spectral data provided evidence for this compound as the experimental mass was consistent with the calculated one. The next step was the deprotection of the terminal TMS groups to get compound **2.21**. Also, the appearance of two terminal alkyne protons at 3.10 ppm in the ^1H NMR and the disappearance of the TMS protons suggested the formation of the terminal alkyne derivative **2.21**.

Scheme 2.10. Synthesis of pre-macrocycle U-shape molecule **2.21**

The next, and perhaps the most critical, step was the synthesis of the target BODIPY-macrocycle **2.22**, depicted in Scheme 2.11. The alkyne derivative **2.21** was reacted with BODIPY **2.9** through a Sonogashira cross-coupling to afford the BODIPY-macrocycle **2.22**. This reaction was done under high dilution in order to avoid competitive polymerization. However, this reaction failed to yield the desired product. This failure was believed to be linked to steric crowding of the methyl groups on BODIPY **2.9**, and the Sonogashira cross-coupling being too demanding at the reaction centre. A few fractions were obtained but none of them were characterized as the starting material or the product.

Scheme 2.11. Synthesis of BODIPY macrocycle **2.22**

To check the validity of this hypothesis, the same reaction was attempted with ethynyl benzene instead of **2.21** (Scheme 2.12). While the steric demands were similar to that of the macrocycle formation, the number of bond forming reactions was also similar when using ethynyl benzene. Again this reaction failed to show any indication of coupling at all. This led us to conclude that sterics proximate to the BODIPY core were prohibiting the coupling reaction.

Scheme 2.12. Sonogashira cross-coupling reaction of ethynylbenzene with BODIPY **2.9**

2.2.6. Synthesis of a new BODIPY cap

In order to overcome this steric problem, an unsubstituted BODIPY was synthesized using a similar strategy as shown in Scheme 2.4, the only difference being that pyrrole (Sigma Aldrich) rather than dimethyl pyrrole was used. The preparation of unsubstituted BODIPY **2.24** is illustrated in Scheme 2.13.

Scheme 2.13. Synthesis of unsubstituted BODIPY **2.24**

BODIPY **2.24** was successfully synthesized and characterized. ¹H NMR spectroscopy (Figure 2.4) integrates for eight aromatic protons along with nine protons belonging to the *tert*-butyl group (Figure 2.4). Also, the ¹³C NMR spectrum was clean (given in appendices) and showed the exact number of equivalent carbons. However, the yield dropped significantly during this step. The best yield for this unsubstituted BODIPY **2.24** was 16% as compared to 35% in the case of tetramethyl BODIPY (**2.9**).

Figure 2.4. ^1H NMR of BODIPY **2.24** in CDCl_3

Another strategy to minimize steric hindrance was to move the demanding coupling reaction farther from the BODIPY core. To this end, TMS-acetylene was reacted with BODIPY **2.24** to yield **2.25** according to Scheme 2.14. At first, this reaction was carried out using route A (Scheme 2.14) but the overall yield over the last two steps (to make **2.24** and **2.25**) was 7.7%. This lower yield was mainly due to the first step, because the synthesis of BODIPY is typically a low yielding reaction. To improve the yield during these steps, an alternative attempt was made by reacting di-iodobenzaldehyde **2.4** with TMS-acetylene to yield the TMS-protected benzaldehyde **2.26** which was then reacted with pyrrole to yield the TMS-protected BODIPY **2.25**. The overall yield using this route (illustrated by route B, Scheme 2.14) was 26.4%, which became the preferred method of making **2.25**.

Scheme 2.14. Synthesis of TMS-protected BODIPY **2.25** by two different routes (A and B)

2.2.7. Synthesis of BODIPY-macrocycle (top-down approach)

Moving the coupling reaction farther from the BODIPY crowded core makes it more amenable to construct the macrocycle through a top-down approach, rather than making U-shape molecule **2.21**. This top-down construction strategy depicted by the cartoon is shown in Figure 2.5.

Figure 2.5. A cartoon showing the synthetic strategy of making BODIPY-macrocycle using top-down approach cyclization of the ring

With **2.25** in hand, further reactions were carried out to connect the BODIPY unit with a phenylacetylene arm **2.15**. The first step was the deprotection of **2.25** to yield the terminal alkyne BODIPY **2.27** (73%) which was then reacted with the previously made phenylacetylene arm **2.15** to yield the pre-macrocycle U-shape molecule **2.28**. Deprotection of **2.28** yielded pre-macrocycle **2.29**. Both of these steps (shown in Scheme 2.15) yielded products with good yields (83% and 71%, respectively).

Scheme 2.15. Synthesis of pre-macrocycle BODIPY derivative **2.29**

To cyclize the ring, BODIPY derivative **2.29** was then reacted with 1-(*tert*-butyl)-3,5-diiodobenzene **2.17** using a Sonogashira cross-coupling reaction to yield the BODIPY-macrocycle **2.30** as illustrated by Scheme 2.16. In order to avoid polymerization during this step, the reaction was done at mM concentration (*i.e.* under high dilution).

Scheme 2.16. Synthesis of BODIPY-macrocycle **2.30**

Due to a large number of aromatic protons, it was difficult to characterize product **2.30** with certainty using NMR spectroscopy. ^1H NMR showed the overlap of *tert*-butyl protons with the solvent peak (hexanes and/or grease) at 1.26 which made it difficult to integrate properly. However, ^1H NMR confirmed the disappearance of terminal alkyne protons. Also, distortionless enhancement by polarization transfer (DEPT-90) ^{13}C NMR showed the disappearance of the terminal alkyne which were converted to quaternary carbons. These two pieces of evidence gave the indication that something happened but the number of protons were not integrating according to the desired structure. After extensive characterisation efforts, it was determined that the iodo-derivative **2.17** never reacted with the **2.29**. Instead, both the terminal alkynes coupled to each other through a Glaser-type coupling process and resulted in a BODIPY-phenylacetylene macrocycle **2.31** with five phenyl rings instead of six, as illustrated by Scheme 2.17. This was not our initial target. However, it was still a BODIPY-macrocycle with BODIPY orthogonal to macrocycle and it served our purpose for energy transfer studies.

Scheme 2.17. Synthesis of BODIPY-macrocycle **2.31**

2.2.8. Characterization of BODIPY-macrocycle

The product **2.31** was further purified by column chromatography and ^1H NMR spectroscopy showed 12 peaks in the aromatic region with each peak representing two equivalent protons (24 protons in total). Also, *tert*-butyl protons were integrated for nine protons as shown in Figure 2.6. This integration justifies all the protons in **2.31**. The ^{13}C NMR spectrum (shown in appendices) also satisfies the number of carbons in **2.31**.

Figure 2.6. ^1H NMR of BODIPY-macrocycle **2.31** in CDCl_3

The final confirmation of the BOBIPY-macrocycle (**2.31**) was achieved by x-ray crystallography (Figure 2.7; single crystals were grown from saturated DCM:Hex (1:2) solutions). In the solid state, the dihedral angle between the BODIPY and attached phenyl ring is 118° , suggesting that the two chromophores are not truly orthogonal. However, in solution ^1H -NMR displayed equivalent environments throughout the macrocycle and BODIPY suggesting that there is a significant amount of rotational freedom for the BODIPY within the cavity, but not enough for it to adopt a coplanar conformation within the macrocycle (*vide infra*, DFT).

Figure 2.7. Crystal structure of BODIPY-macrocycle **2.31**. (ORTEP, 30% thermal ellipsoids). Hydrogen atoms and solvent molecules have been removed for clarity

2.2.9. Proposed mechanism for the synthesis of BODIPY-phenylacetylene macrocycle

The product **2.31** was likely formed during the initiation step of an attempted Sonogashira cross-coupling reaction. $\text{PdCl}_2(\text{PPh}_3)_2$ was used as Pd source; the Pd^{2+} state needs to undergo reductive elimination before it enters the catalytic cycle. During this initiation step, the macrocycle was likely formed. While a thorough study of the mechanism was not carried out, a proposed mechanism for the cyclization of macrocycle during the initiation step is illustrated in Figure 2.8 whereas the general mechanism for the Sonogashira cross-coupling reaction is discussed in chapter 1 (Figure 1.13).

Figure 2.8. Proposed mechanism for the synthesis of product during the initiation step of Sonogashira cross-coupling reaction.

In the case where $PdCl_2(PPh_3)_2$ is used as a catalyst, Pd is in its Pd^{II} state. Both of the Cl^- ions are labile, Pd can form a bond with the terminal alkyne in the presence of a base. Both the terminal alkynes come off during the reductive elimination step and form a homodimer. This is likely the reason for getting a five membered macrocycle rather than the originally desired intermolecular product. Kinetics favour this step rather than the cross-coupling reaction and the iodo-derivative never gets a chance to react with the terminal alkyne (Figure 2.8).

This proposed mechanism also makes sense in terms of product yield. Because 13-15 mole percent of the Pd catalyst was used, the product had a similar yield. If in fact this is the case, then the presence of di-iodo derivative **2.17** is not required. This hypothesis is further discussed in Section 2.2.10).

2.2.10. Synthesis of control macrocycle

In order to conduct energy transfer studies, a control macrocycle **2.34** was needed and synthesized. This control macrocycle has similar structural features to **2.31** except missing the BODIPY. The terminal alkyne derivative **2.19** and arm **2.15** were reacted through a Sonogashira cross-coupling reaction to yield a TMS-protected pre-macrocycle derivative **2.32** followed by deprotection of the TMS groups to yield **2.33**. Cyclization of **2.33** was carried out using the same strategy as for the parent BODIPY-macrocycle **2.31** and a control macrocycle **2.34** was successfully synthesized. The reaction sequence is shown in Scheme 2.18.

Scheme 2.18. Synthesis of control macrocycle **2.34**

In this instance, di-iodo derivative **2.17** was added to keep the procedure exactly the same as the one used for making BODIPY-phenylacetylene macrocycle **2.31**. The yield (17%) was similar to the parent macrocycle **2.31**.

2.2.11. Synthesis of more rigid BODIPY-macrocycle: back to tetramethyl BODIPY

According to the X-ray crystal data of BODIPY-macrocycle **2.31**, the BODIPY was inside the macrocycle but not exactly orthogonal to the macrocycle. This observation led us to make a more sterically hindered BODIPY, one that was previously attempted using the bottom-up approach. In this instance, tetramethyl BODIPY **2.36** was required rather than the unsubstituted

BODIPY **2.27** (Scheme 2.19). The synthesis was similar to the one employed to make the parent BODIPY-macrocycle **2.31**. A tetramethyl BODIPY derivative (**2.36**) was made as a top BODIPY unit. To achieve **3.6**, dimethyl pyrrole **2.6** was reacted with TMS-protected aldehyde **2.26** to produce the TMS-acetylene derivative of BODIPY (**2.35**) which was then deprotected using KF to yield a terminal alkyne BODIPY **2.36**.

Scheme 2.19. Synthesis of alkyne derivative of tetramethyl BODIPY **2.36**

The next step was to make the rigid BODIPY-macrocycle **2.39** using BODIPY **2.36**, and the phenylacetylene arm **2.15** to yield **2.37**, followed by the deprotection of **2.37** to yield **2.38**. This time, the last step (cyclization of macrocycle) was carried out without the addition of the di-iodo-*tert*-butyl phenyl unit **2.17** to prove our previous hypothesis (*i.e.* the reaction does not require the presence of di-iodo derivative **2.17**). According to expectations, the cyclization step yielded BODIPY-macrocycle **2.39**. A similar yield was obtained for this BODIPY-macrocycle **2.39**. Scheme 2.20 shows the synthesis of the rigid BODIPY-phenylacetylene macrocycle **2.39**. In addition, it was pleasing that moving the coupling reaction away from the BODIPY core permitted the opportunity to synthesize the original methylated BODIPY target.

Scheme 2.20. Synthesis of BODIPY-macrocycle with tetramethyl BODIPY **2.39**

2.2.12. Other synthetic attempts towards making BODIPY-phenylacetylene macrocycles

This section explains additional syntheses that were explored towards making BODIPY-phenylacetylene macrocycles. When previously discussed syntheses were not working, an attempt was made to prepare a macrocycle with an aldehyde group inside its cavity with the hope that this aldehyde could be converted to BODIPY at a later stage. Towards this end, **2.26** was deprotected to yield **2.40** which was then reacted with arm **2.15** to yield the TMS-protected U-shape molecule **2.41** as shown in Scheme 2.21. The deprotection step (to yield **2.40**) worked well (spectroscopic data is given in the appendices). However, the next step which was the Sonogashira cross-coupling between the deprotected aldehyde **2.40** and the arm **2.15** did not produce any desired product. Six

different fractions were collected but none of them were the product. Most of the fractions showed peaks in the aromatic region but the aldehyde proton was missing.

Scheme 2.21. Attempted synthesis of aldehyde **2.41**

An alternative route was explored to make the aldehyde bearing macrocycle (Scheme 2.22). According to this approach, the TMS-protected aldehyde **2.26** was first protected to get **2.42**, which was then deprotected to **2.43**, which was then reacted with arm **2.15** to yield the protected version of **2.41**. A pure fraction of **2.44** was obtained with a 79% yield which was then deprotected to yield **2.45**. All of these steps yielded the products in good yield. NMR data of all these protected products (**2.42**, **2.43**, **2.44** and **2.45**) are presented in the appendices.

Scheme 2.22. Synthesis of protected aldehyde derivative of terminal alkyne **2.45**

A macrocycle from **2.45** was never pursued beyond this step for several reasons. Firstly, because this route involved more steps with the most critical (typically lowest yielding) step remaining, it was deemed a less desirable route. Secondly, because the deprotection of the aldehyde involve reflux, the macrocycle might decompose at high temperature. Lastly, the BODIPY-macrocycle was successfully synthesized while this route was being pursued. Despite this route never being used to make the BODIPY-macrocycle, it still could serve as an alternative approach for future studies.

2.3. Results and Discussion

2.3.1. Photophysical properties of controlled BODIPY and controlled macrocycle

Absorption and emission data were collected in DCM. The control BODIPY (**2.24**) has a maximum absorption at 515 nm and when excited at its maximum absorption, emission is observed at 533 nm (Figure 2.9a). When the control macrocycle (**2.34**) is excited at 287 nm (maximum absorption wavelength), the emission is observed at 333 nm (Figure 2.9b).

Figure 2.9. Absorption (blue solid line) and emission (orange dotted line) of BODIPY **2.24** (a) and macrocycle **2.34** (b).

2.3.2. Photophysical properties of BODIPY-phenylacetylene macrocycle **2.31**

Absorption data collected in DCM solutions and time-dependent density functional theory (TD-DFT) assigned transitions (labelled according to orbitals in Figure 2.11) are provided in Figure 2.10. Similar to most BODIPY derivatives, building block **2.24**, has a strong absorption at 515 nm, and a hypsochromic shoulder; the remainder of the spectrum is relatively featureless. In **2.31**, these BODIPY absorptions are slightly blue-shifted (510 nm), and a series of strong absorptions owing to the macrocycle are present below 350 nm.

Figure 2.10. Absorption spectra of BODIPY-phenylacetylene macrocycle, **2.31** and benchmark BODIPY **2.24**, in DCM. Dominant optical transitions have been assigned using TD-DFT

DFT calculations (B3LYP, 6-31G) of the frontier molecular orbitals (FMOs) for **2.31** are presented in Figure 2.11. The minimized DFT structure possesses a slightly bowl-shaped phenylacetylene macrocycle, consistent with the observed structure in the solid-state X-ray crystal. Unlike the solid-state structure, the optimized DFT structure sees the BODIPY essentially orthogonal to the attached phenyl ring with a dihedral angle of 89.97°. In addition, most FMOs predominantly have electron density on the macrocycle, except the HOMO-2 and HOMO-1 which have significant contributions localised on the BODIPY portion of the molecule, and the LUMO is localised exclusively on the BODIPY.

Figure 2.11. DFT calculated frontier molecular orbitals for BODIPY-macrocycle, **2.31**

TD-DFT calculations were performed to elucidate the nature of the observed absorption behaviour. Consistent with the assignments in Figure 2.9, the largest optical transition (292 nm) was assigned as the HOMO to LUMO+2. This absorption is localized on the macrocycle and these intense $\pi-\pi^*$ absorptions arise from optical transitions that possess significant electron density overlap between the ground and excited state. All optical transitions below 350 nm are dominated by strong $\pi-\pi^*$ absorptions localised predominantly on the macrocycle. Absorptions centred at 510 nm, are due to optical transitions that are primarily localized on the BODIPY (HOMO-1 to LUMO), and are consistent with previous studies.¹⁵¹

2.3.3. Energy transfer in BODIPY-macrocycle

Emission data of the BODIPY-macrocycle **2.31** was also collected in DCM and is presented in Figure 2.12. When comparing the emission of the parent BODIPY-macrocycle **2.31** to the control macrocycle **2.34**, distinct differences emerge with respect to the fluorophore. Upon

excitation of **2.34** at 287 nm (Figure 2.9b), emission from the macrocycle results in a Stokes shift of 46 nm. Conversely, when **2.31** is excited at 292 nm, emission appears to originate from the BODIPY portion of the molecule resulting in a ‘Stokes-like’ shift of 236 nm (Figure 2.12). Irrespective of the excitation wavelength (292, 487 or 510 nm) an emission from BODIPY and proportional to the absorption extinction coefficient, is observed at 528 nm. This is consistent with Kasha’s rule (which states that emission is always from the lowest excited state and is thus at longer wavelength as compared to absorption wavelength) where one would expect fluorescence from the lowest excited state, (i.e. the LUMO which is located predominantly on the BODIPY portion of the molecule).

Figure 2.12. Absorption (blue solid line) and emission (dotted lines, orange when excited at 292 nm, black when excited at 487 nm and green when excited at 510 nm) of macrocycle **2.31**

Besides the emission scan (Figure 2.12), an excitation scan of **2.31** was run by choosing the emission wavelength at 528 nm. As shown in Figure 2.13, excitation data of **2.31** resembles its absorption profile.

Figure 2.13. Absorption and excitation (emission observed @ 528 nm) spectra of **2.31** in DCM

Presumably when light is absorbed by molecule **2.31**, the macrocycle part of the molecule is excited, which in turn transfers its absorbed energy to the BODIPY core. Emission from BODIPY irrespective of the excitation wavelength throughout the absorption profile suggests that there is an energy transfer from the macrocycle to the BODIPY core.

These results are consistent with other previously reported oligomeric phenylacetylene architectures, where exciton accumulation was observed in π -conjugated wires sheathed by phenylacetylene macrocycles, despite the wire not being conjugated to the macrocycle.⁷⁷ More recently, energy transfer has been observed in coordination driven structures with BODIPYs installed on the periphery.¹⁵² Using non-covalent host-guest complexes, it was shown that highly efficient energy transfer is observed from a guest to the BODIPY containing host.¹⁵³ Combining these popular phenylacetylene macrocycle and BODIPY motifs, our work demonstrates that effective supramolecular energy transfer can occur between these intensely absorbing chromophores. Moreover, this motif should be suitable as a π -spacer for DSSC applications as the orthogonal nature of our structure has ideal energy transfer from the macrocycle to the BODIPY core of the molecule and could be modified for panchromatic absorption.

2.3.4. Emission profile of **2.31** at variable concentrations

The BODIPY-phenylacetylene macrocycle (**2.31**) shows energy transfer from the macrocycle to the BODIPY core as can be seen upon excitation of the macrocyclic portion of the compound, and an emission characteristic of BODIPY (Figure 2.12). To eliminate co-concentration dependence as a variable on the emission profile, the emission data at different concentrations of **2.31** was collected. It was observed that intensity of the emission is directly proportional to the concentration (Figure 2.14) suggesting no significant concentration behavior. In Figure 2.14, a blue solid line represents the absorption profile of BODIPY-macrocycle **2.31** and the dotted lines represents the emission data for different concentrations of **2.31** (with the concentrations decreasing from 1 to 4).

Figure 2.14. Absorption spectrum (solid blue line) and emission spectra (dotted lines) of **2.31** with decreasing concentrations from 1-4

2.3.5. Absorption/Emission studies of rigid BODIPY-macrocycle **2.39**

Photophysical studies were performed on **2.39** and are summarized in Figure 2.15. The absorption profile of **2.39** was similar to that of **2.31** with the exception that the molar extinction coefficient (ϵ) of the BODIPY portion was much higher ($60000 \text{ M}^{-1}\text{cm}^{-1}$) than the one in the parent BODIPY-macrocycle **2.31** ($40000 \text{ M}^{-1}\text{cm}^{-1}$). This increase in ϵ -value is probably due to the fact that the BODIPY containing four methyl groups, is more rigid and orthogonal to the macrocycle and hence leads to higher absorption.

The emission data is represented by the dotted line in Figure 2.15. The BODIPY-macrocycle **2.39** was excited at different wavelengths (290 nm, 306 nm, 335 nm, and 510 nm) but the excitation was only observed from the BODIPY core, regardless of the excitation wavelength. This also supports the occurrence of energy transfer within the molecules.

Figure 2.15. Absorption (blue solid line) and emission (dotted lines, orange when excited at 290 nm, black when excited at 306 nm, pink when excited at 335 nm and green when excited at 510 nm) of BODIPY-macrocycle **2.39**

Absorption and emission data for BODIPY-macrocycles (**2.31** and **2.39**) and the control subunits (**2.24** and **2.34**) along with their respective fluorescence quantum yields is summarized in Table 2.1. The fluorescence quantum yield for parent BODIPY unit **2.24** was low (0.12) and the control macrocycle **2.34** emitted at 333 nm. However, when they were attached together to make a BODIPY-phenylacetylene, they were highly fluorescent and exhibited excellent fluorescence quantum yields (0.89 and 0.91 for **2.31** and **2.39** respectively).

Table 2.1. Absorption and Emission Data for the BODIPY fluorophore in benchmark molecule **2.24** and macrocycle derivative **2.31**

Compound	Absorption ^a		Fluorescence ^b	
	λ_{ab} (nm)	$\epsilon \times 10^4$ M ⁻¹ cm ⁻¹	λ_{em} (nm)	Quantum Yield
2.24	515	3.50	533	0.12
2.31	510	4.00	528	0.89
2.34	287	11.5	333	N/A
2.39	510	6.00	530	0.91

^a Low energy absorptions of BODIPY in DCM from UV-Vis. ^b Measurements were made in DCM. ^cQuantum yield for BODIPY (**2.24**) and BODIPY-macrocycle (**2.31**), were determined at 22°C relative to Rhodamine 6G in ethanol (QY = 0.95) using a Luminescence Spectrophotometer LS50B (Perkin Elmer).

2.4. Summary and Conclusion

In this chapter a BODIPY-phenylacetylene macrocycle was synthesized where BODIPY is enclosed in and orthogonal to the phenylacetylene macrocycle. Various synthetic strategies were used to make the target molecule **2.31**. However, a successful synthetic strategy (top-down approach) showed that cyclizing the ring at the bottom was a more effective way to close the ring. Also the steric effect on BODIPY does not allow the Sonogashira cross-coupling reaction to take place in the case that the ring is closed at the top (bottom-up approach).

After the synthesis of the parent BODIPY-phenylacetylene macrocycle **2.31**, the control macrocycle **2.34** was made to carry out the energy transfer studies. Upon excitation at 287 nm, the control macrocycle **2.34** emits at 333 nm with a Stokes shift of 46 nm. However, when the BODIPY-phenylacetylene macrocycle **2.31** is excited at λ_{max} (292 nm), the emission is from the BODIPY core and a Stokes shift of 236 nm is observed. It is also observed that emission always occurs from the BODIPY core, irrespective of the excitation wavelength which suggests that there is an energy transfer from the macrocycle to the BODIPY core. The process of energy transfer from the macrocycle to BODIPY is depicted in Figure 2.15.

Figure 2.16. An energy transfer process within the BODIPY-macrocycle

A more rigid BODIPY-phenylacetylene macrocycle **2.39** was made which also showed energy transfer from the macrocyclic part to the BODIPY core. The BODIPY core in **2.39** is more orthogonal to the macrocycle as compared to **2.31** which is attributed to the steric effect of the tetramethyl groups on BODIPY in the case of **2.39**. It was also observed that both of the BODIPY-phenylacetylene macrocycles **2.31** and **2.39** exhibit excellent fluorescence quantum yields (0.89 and 0.91 respectively).

The BODIPY-phenylacetylene macrocycle design possesses a macrocycle orthogonal to the BODIPY unit and upon excitation, energy transfer is observed from the macrocyclic part of the compound to the BODIPY core. However, this dye design was intended to be used for light harvesting applications for which it should be able to absorb in the visible region of the solar spectrum. The BODIPY core absorbs around 500 nm but the macrocycle absorbs around 300 nm. This led the study to modify the macrocyclic part of the BODIPY-phenylacetylene to red-shift its absorption profile. To this end, modified BODIPY-phenylacetylene macrocycles were studied as discussed in Chapter 3.

2.5. Experimental

2.5.1. General considerations

Unless stated otherwise, all reagents were purchased from Sigma Aldrich except PdCl₂ (Pressure Chemical Co., Pittsburg, PA). PdCl₂ was reacted with PPh₃ to make catalyst PdCl₂(PPh₃)₂. Purification by column chromatography was carried out using silica (Silicycle: ultrapure flash silica). Analytical thin-layer chromatography was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Silicycle) and visualized under UV light. Routine ¹H, ¹³C{¹H}, ¹¹B{¹H}, and ¹⁹F NMR spectra were recorded at 400, 100, 128 and 376 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to a residual nondeuterated solvent (CHCl₃) for ¹H and ¹³C nuclei and boron trifluoride diethyletherate (BF₃•OEt₂) (¹¹B nucleus; δ = 0 ppm), C₆F₆ (¹⁹F nucleus; δ = 0 ppm). Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; q = quartet and br = broad. High resolution mass spectrometry (HRMS) results were obtained from Queens University, Kingston Ontario. Electron impact (EI) mass spectrometry and Electrospray ionization (ESI) techniques were used for the ionization; time of flight (TOF) was used for analysis. UV-Vis data was taken using Cary Series UV-Vis-NIR Spectrophotometer from Agilent Technologies and DCM (having the onset peak at 230 nm) was used as the solvent. The GAUSSIAN 09 computational package¹⁵⁴ was used to perform ground-state geometry optimization calculations employing Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr non-local correlation functional B3LYP¹⁵⁵⁻¹⁵⁷ and 6-31G basis set was used for all the atoms. Time-dependent density functional theory calculations were also performed using this methodology, and the first 200 singlet excited states were calculated. Calculations by the first-principles method were used to obtain accurate excitation energies and oscillator strengths. The solvent was modelled with the polarizable continuum model using DCM as the solvent.¹⁵⁸

2.5.2. Synthesis

The synthetic procedure of each compound is given below. General synthetic steps have been used unless otherwise mentioned in the procedure.

2.1

2,6-diiodo-4-*tert*-butyltoluene (2.1). In a 500 mL round bottom flask, 4-*tert*-butyltoluene (4.74 g, 32.0 mmol), KIO₄ (7.36 g, 32.0 mmol), I₂ (15.0 g, 59.0 mmol), AcOH (40 mL), CHCl₃ (30 mL), H₂SO₄ (12 mL), and H₂O (12 mL) were taken and the mixture was heated to 90°C for 24 h. The reaction mixture was then cooled to room temperature (RT) and extracted with Hex:Et₂O (1:1). Washing the organic phase with a saturated sodium bicarbonate (NaHCO₃) solution followed by removal of solvent (*in vacuo*) gave product **2.1** as a light orange oil (10.25 g, 80 %). The spectroscopic data agreed with the literature.¹⁵⁹ ¹H NMR (CDCl₃, 400 MHz): δ = 7.84 (s, 2H), 2.73 (s, 3H), 1.29 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 152.39, 139.82, 136.83, 99.53, 34.53, 34.01, 31.16.

2.2

4-(*tert*-butyl)-2,6-diiodobenzyle acetate (2.2). To a stirred solution of **2.1** (4.85 g, 12.1 mmol) in H₂SO₄ (3.3 mL), AcOH (20 mL), and Ac₂O (40 mL), 2.49 g (15.8 mmol) of KMnO₄ were slowly added over a period of 3 hours while keeping the temperature at 40 °C. The mixture was stirred for 1 day at the same temperature. The mixture was poured into water and extracted with Et₂O. The organic layer was washed with 10% NaOH solution and then with brine. The organic phase was dried over anhydrous MgSO₄, filtered and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using Hex:DCM (1:1) as the eluent to give 4-*tert*-

butyl-2,6-diiodobenzyl acetate (**2.2**) as a yellow viscous liquid (3.30 g, 60%). The spectroscopic data agreed with the literature.¹⁴⁵ ¹H NMR (CDCl₃, 400 MHz): δ = 7.86 (s, 2H), 5.40 (s, 2H), 2.13 (s, 3H), 1.28 (s, 9H).

2.3

(4-(*tert*-butyl)-2,6-diiodophenyl)methanol (2.3). To a stirred solution of the acetate **2.2** (1.39 g, 3.14 mmol) in MeOH (25 mL) was slowly added K₂CO₃ (0.122 g, 1.05 mmol) and the mixture was stirred at RT for 3 hours. The reaction mixture was quenched by the addition of 2 M HCl. The mixture was extracted with Et₂O and the organic fraction was washed with brine, dried over MgSO₄, filtered and the solvent was removed under reduced pressure to yield product **2.3** as a yellow viscous liquid (1.10 g, 84%). The spectroscopic data agreed with the literature.¹⁴⁵ ¹H NMR (CDCl₃, 400 MHz): δ = 7.82 (s, 2H), 5.00 (d, 2H), 2.10 (t, 1H), 1.27 (s, 9H).

2.4

4-(*tert*-butyl)-2,6-diiodobenzaldehyde (2.4). To a stirred solution of alcohol **2.3** (1.03 g, 2.48 mmol) in DCM (20.0 mL) was added PCC (1.54 g, 7.20 mmol) and the mixture was stirred overnight at RT. The solvent was removed under reduced pressure and the residue was chromatographed using Hex:DCM (1:1) as the eluent to give product **2.4** as a yellow solid (0.91 g, 89%). The spectroscopic data agreed with the literature.¹⁴⁵ ¹H NMR (CDCl₃, 400 MHz): δ = 9.76 (s, 1H), 8.00 (s, 2H), 1.32 (s, 9H).

2.5

Diethyl-3,5-dimethyl-1H-pyrrole-2,4-dicarboxylate (2.5). Ethyl acetoacetate (20.0 mL, 154 mmol) was added to glacial AcOH (70 mL) and the solution was cooled in an ice bath. In another flask, a solution of NaNO₂ (12.2 g, 177 mmol) in H₂O (20 mL) was cooled in an ice bath and added drop wise to the first mixture, maintaining an internal temperature of 6–10 °C. The resulting yellow solution was stirred overnight at RT and ethyl acetoacetate (23.0 mL, 178 mmol) was added to the mixture. Zinc powder (22.6 g, 344 mmol) was obtained and a minimum amount was added in small portions to increase the internal temperature of the mixture to 65 °C. The mixture was then cooled to 0 °C and the ice bath was removed. Zinc powder was added in small portions to increase the internal temperature of the mixture to 70 °C and the remaining Zn was added slowly maintaining the internal temperature between 60–80 °C. After the last addition of zinc powder, the mixture was refluxed for 24 hours and poured onto ice. The solids were filtered and washed with H₂O. The crude material was recrystallized from hot EtOH, affording product **2.5** as an off-white solid (29.7 g, 80%). The spectroscopic data agreed with the literature.¹⁶⁰ ¹H NMR (CDCl₃, 400 MHz): δ = 9.09 (s, 1H), 4.30 (q, 4H), 2.56 (s, 3H), 2.51 (s, 3H), 1.37 (t, 6H).

2.6

2,4-dimethyl-1H-pyrrole (2.6). Under an atmosphere of N₂, pyrrole-dicarboxylate **2.5** (15.0 g) was dissolved in ethylene glycol (~75.0 mL) and KOH (11.7 g, 156.7 mmol) was slowly added. The mixture was heated to 160 °C for 3 hours. After being cooled to room temperature, the product was distilled off under vacuum, affording product **2.6** as an oxygen sensitive dark oil (3.22 g, 54%). The spectroscopic data agreed with the literature.¹⁴⁶ ¹H NMR (CDCl₃, 400 MHz): δ = 7.62 (s, 1H), 6.41 (s, 1H), 5.76 (s, 1H), 2.24 (s, 3H), 2.09 (s, 3H).

2.9

10-(4-(*tert*-butyl)-2,6-diiodophenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5H-4λ⁴,5λ⁴-

dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (2.9). To a solution of dimethylpyrrole **2.6** (0.5 mL, 4.4 mmol, 2 eq) in dry DCM (100.0 mL), the benzaldehyde **2.4** (0.91 g, 2.2 mmol) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, 0.70 g of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was added and the mixture was stirred overnight (if the TLC analysis (4:1 PE:EtOAc + 1P triethylamine) revealed incomplete oxidation, more DDQ (0.5 eq) was added). Upon completion of the reaction, 3.0 mL of *N,N*-diisopropylethylamine (DIPEA) and 3.5 mL of boron trifluoride diethyletherate (BF₃OEt₂) were added and left to react overnight. The resulting mixture was concentrated *in vacuo*, redissolved in EtOAc, and washed with water. The aqueous layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. Silica column chromatography (using toluene as a solvent) yielded product **2.9** as orange powder (515 mg, 36 %). ¹H NMR (CDCl₃, 400 MHz): δ = 7.93 (s, 2H), 6.01 (s, 2H), 2.58 (s, 6H), 1.45 (s, 6H), 1.33 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 156.46, 156.17, 144.95, 141.52, 139.67, 137.11, 129.99, 121.30, 96.67, 34.66, 31.13, 14.91, 13.90. ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.49-1.00. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -146.37 (q). HRMS (DART-TOF): calcd for C₂₃H₂₅BF₂I₂N₂ 632.0168; found 632.0185.

2.10

1-azido-3-iodobenzene compound with butane (1:1) (2.10). To a solution of 3-iodoaniline (1.00 g, 4.57 mmol) in concentrated HCl (35%, 6.0 mL), was added a solution of NaNO₂ (0.347 g, 5.03 mmol) in H₂O (1.0 mL) at 0 °C. After stirring at 0 °C for 30 min, the resulting mixture was added

dropwise slowly at 0 °C to a suspension of K₂CO₃ (5.05 g, 36.9 mmol), HNEt₂ (0.50 g, 5.03 mmol), and H₂O (18.52 mL). The reaction mixture was then warmed to room temperature and stirred for 1 hour. After extraction with EtOAc, the organic layer was evaporated, and the residue was chromatographed using Hex:EtOAc (15:1, *R_f* = 0.69) as the eluent to give product **2.10** as a red oil (1.04 g, 97%). The spectroscopic data agreed with the literature.¹⁴⁸ ¹H NMR (CDCl₃, 400 MHz): δ = 7.78 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 3.75 (q, *J* = 9.0 Hz, 4H), 1.25 (br. 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 152.36 (C), 133.45 (CH), 130.15 (CH), 128.75 (CH), 120.24 (CH), 94.46 (C), 48.73 (CH₂), 41.15 (CH₂), 14.31 (CH₃), 11.13 (CH₃).

2.11

((3-azidophenyl)ethynyl)trimethylsilane compound with butane (1:1) (2.11). To a mixture of iodobenzene **2.10** (2.00 g), PdCl₂(PPh₃)₂ (0.23 g, 0.34 mmol) and CuI (0.13 g, 0.67 mmol) catalysts in THF:NEt₃ (12.0 mL) was added the trimethylsilyl acetylene (TMS-acetylene) (0.98 g, 7.33 mmol). The mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was removed *in vacuo*, and the residue was chromatographed using Hex:EtOAc (20:1) as the eluent to yield product **2.11** as a yellow oil (1.65 g, 92% yield). The spectroscopic data agreed with the literature.¹⁴⁸ ¹H NMR (CDCl₃, 400 MHz): δ = 7.53 (s, 1H), 7.35-7.37 (m, 1H), 7.20-7.25 (m, 2H), 3.75 (q, 4H), 1.26 (br, 6H), 0.25 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 150.95, 128.48, 128.26, 123.60, 123.31, 105.50, 93.17, 48.27, 41.05, 13.32, 12.45, -0.09.

2.12

1-azido-3-ethynylbenzene compound with butane (1:1) (2.12). The TMS-protected alkyne **2.11** (1.65 g, 6.02 mmol) was dissolved in THF:MeOH (26 mL, 1:1) and stirred with excess of KF (1.05 g, 18.1 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered and the solvent evaporated *in vacuo*. The residue was chromatographed using Hex:DCM (4:1) as the eluent to give product **2.12** in good yield (0.99 g, 92%). The spectroscopic data agreed with the literature.¹⁴⁸ ¹H NMR (CDCl₃, 400 MHz): δ = 7.56 (s, 1H), 7.39-7.43 (m, 1H), 7.22-7.29 (m, 2H), 3.76 (q, 4H), 3.05 (s, 1H), 1.26 (t, 6H).

2.13

((3-iodophenyl)ethynyl)trimethylsilane (2.13). Ethynylbenzene **2.12** (1.00 g, 3.70 mmol) and MeI (20.0 mL) were sealed in a heavy walled flask (microwave tube) and heated to 120 °C for 12 hours. The reaction mixture was quenched with water; extracted with DCM, dried over MgSO₄ and filtered. The solvent was removed *in vacuo* and the pure product was isolated by column chromatography using pure hexanes (R_f = 0.65) as the eluent to yield product **2.13** in decent yield (0.81 g, 77%). The spectroscopic data agreed with the literature.¹⁴⁸ ¹H NMR (CDCl₃, 400 MHz): δ = 7.82 (s, 1H), 7.64 (d, 1H), 7.41 (d, 1H), 7.024 (t, 1H), 0.245 (s, 9H).

2.14

((3-((3-azidophenyl)ethynyl)phenyl)ethynyl)trimethylsilane compound with butane (1:1) (2.14). To a mixture of compound **2.13** (2.00 g, 6.66 mmol), PdCl₂(PPh₃)₂ (0.30 g, 0.26 mmol) and CuI (0.10 g, 0.52 mmol) in THF:NEt₃ (24 mL, 2:1) was added **2.12** (1.48 g, 7.33 mmol). The mixture was stirred at RT overnight. The solution was filtered, the filtrate was poured into 1M HCl, and extracted with EtOAc. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was removed *in vacuo*, and the residue was chromatographed using Hex:EtOAc (20:1, *R_f* = 0.42) as the eluent to give product **2.14** as a yellow oil (2.06 g, 83%). The spectroscopic data agreed with the literature.¹⁴⁸ ¹H NMR (CDCl₃, 400 MHz): δ = 7.65 (s, 1H), 7.58 (s, 1H), 7.46 (d, 1H), 7.38-7.41 (m, 2H), 7.25-7.31 (m, 3H), 3.77 (q, 4H), 1.27 (s, 6H), 0.25 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 151.16, 134.92, 131.42, 131.34, 128.74, 128.25, 128.05, 123.66, 123.38, 123.30, 123.20, 121.07, 104.17, 94.79, 90.38, 87.89, 48.36, 40.93, 13.42, 12.13, -0.13.

2.15

((3-((3-iodophenyl)ethynyl)phenyl)ethynyl)trimethylsilane (2.15). Compound **2.14** (0.69 g, 2.52 mmol) and MeI (7.0 mL) were sealed in a heavy walled microwave vial under an atmosphere of nitrogen (N₂) and heated to 120 °C for 12 hours. The reaction mixture was cooled and quenched with water; extracted with DCM, dried over MgSO₄ and filtered. The solvent was removed *in vacuo* and the pure product was isolated by column chromatography using Hex:DCM (3:2) as the eluent to give product **2.15** with 80% yield (0.59 g). The spectroscopic data agreed with the literature.¹⁴⁸ ¹H NMR (CDCl₃, 400 MHz): δ = 7.88 (s, 1H), 7.63-7.68 (m, 2H), 7.41-7.48 (m, 3H), 7.26-7.30 (m, 1H), 7.08 (t, 1H), 0.25 (s, 9H).

2.16

4-(*tert*-butyl)-2,6-diiodoaniline (2.16). To *tert*-butylaniline (1.00 g) was added 2 eq. of KI (2.22 g, 13.4 mmol), 4 eq. of 30% H₂O₂ (4.0 mL) and 2 eq. of H₂SO₄ (2.0 mL) (H₂SO₄ and H₂O₂ were added together-piranha solution) in MeOH and left to stir overnight at RT. The organic layer was extracted with hexane/Et₂O (1:1), washed with NaHCO₃, filtered, and dried over MgSO₄. The solvent was removed *in vacuo* and the residue was chromatographed using pure hexane (*R_f* = 0.28) as the eluent to give product **2.16** as a light orange liquid (2.0 g, 74%). The spectroscopic data agreed with the literature.¹⁴⁹ ¹H NMR (CDCl₃, 400 MHz): δ = 7.61 (s, 2H), 4.46 (s, 2H), 1.24 (s, 9H).

2.17

1-(*tert*-butyl)-3,5-diiodobenzene (2.17). To a solution of 4-(*tert*-butyl)-2,6-diiodoaniline **2.16** (3.00 g, 7.48 mmol) in 10 mL of EtOH, concentrated H₂SO₄ (1.5 mL) and NaNO₂ (1.16) were added and the mixture was reflux for 8 hours. After addition of Et₂O, the organic layer was separated, washed, and dried over MgSO₄. The solvents were removed *in vacuo* and the residue was chromatographed using hexanes as the eluent to give product **2.17** as a slightly yellow oil (1.99 g, 69%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.47 (t, 1H), 7.43 (d, 2H), 1.28 (s, 9H).

2.18

((5-(*tert*-butyl)-1,3-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (2.18). To a mixture of diiodobenzene **2.17** (0.36 g, 0.94 mmol), PdCl₂(PPh₃)₂ (0.12 g, 0.17 mmol) and CuI (0.06 g, 0.33 mmol) in THF:NEt₃ (9.0 mL, 2:1) was added the TMS-acetylene (0.38 g, 2.00 mmol). The mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was removed *in vacuo*, and the residue was chromatographed using Hex:EtOAc (20:1) as the eluent to give product **2.18** (0.26 g, 84%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.42 (s, 2H), 1.29 (br, 9H), 0.25 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 151.33, 132.74, 129.17, 122.88, 104.71, 94.08, 34.65, 31.06, 0.05.

2.19

1-(*tert*-butyl)-3,5-diethynylbenzene (2.19). The alkyne **2.18** (1.65 g, 6.02 mmol) was dissolved in MeOH (13.0 mL) and THF (13.0 mL) and stirred with excess KF (0.41 g, 3 × 18.05 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered and the solvent removed *in vacuo*. The residue was chromatographed using Hex:DCM (2:1) as the eluent to give product **2.19** as a yellow liquid (0.87 g, 72%). The spectroscopic data agreed with the literature.¹⁵⁰ ¹H NMR (CDCl₃, 400 MHz): δ = 7.51 (d, 2H), 7.45 (t, 1H), 3.07 (s, 2H), 1.31 (s, 9H).

((((((5-(*tert*-butyl)-1,3-phenylene)bis(ethyne-2,1-diyl))bis(3,1-phenylene))bis(ethyne-2,1-diyl))bis(3,1-phenylene))bis(ethyne-2,1-diyl))bis(trimethylsilane) (**2.20**). To a mixture of *tert*-butyl-3,5-diethynylbenzene **2.19** (0.07 g), PdCl₂(PPh₃)₂ and CuI in THF:NEt₃ (9.0 mL) was added **2.15** (0.28 g, 0.86 mmol). The mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was removed *in vacuo*, and the residue was chromatographed using Hex:EtOAc (20:1) as the eluent to give product **2.20** as a light orange solid. ¹H NMR (CDCl₃, 400 MHz): δ = 7.71 (s, 2H), 7.65 (s, 2H), 7.56 (s, 1H), 7.54 (s, 2H), 7.52-7.42 (m, 8H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 1.36 (s, 9H), 0.25 (s, 18H). ¹³C NMR (CDCl₃, 100 MHz): δ = 135.09, 134.69, 132.51, 131.80, 131.77, 131.51, 131.49, 131.41, 129.85, 129.00, 128.55, 128.38, 123.54, 123.42, 123.26, 122.99, 89.73, 89.41, 89.12, 89.06, 88.75, 88.51, 34.78, 30.92, -0.09. HRMS (DART-TOF): calcd for C₅₂H₄₆Si₂ 726.3138; found 726.3153.

3,3'-((5-(*tert*-butyl)-1,3-phenylene)bis(ethyne-2,1-diyl))bis(((3-ethynylphenyl)ethynyl)benzene) (2.21). The alkyne **2.20** (0.38 g, 0.5 mmol) was dissolved in MeOH (5.0 mL) and THF (5.0 mL) and stirred with excess (5 eq) KF (0.15 g, 2.6 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered, and the solvent removed *in vacuo*. The residue was chromatographed using Hex:DCM (2:1) as the eluent to give product **2.21** as an off-white liquid (0.21 g, 70%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.73 (t, 2H), 7.67 (t, 2H), 7.57-7.45 (m, 11H), 7.37-7.30 (m, 4H), 3.10 (s, 2H), 1.37 (s, 9H). HRMS (EI-TOF): *m/z* 582.2355 ([MH]⁺), calcd for C₄₆H₃₀: *m/z* 582.2348.

2.22

Attempted synthesis of BODIPY-phenylacetylene macrocycle 2.22. The BODIPY **2.9** (66 mg, 0.105 mmol) was dissolved in 120 mL of THF:NEt₃ (2:1) in a 500 mL round bottom flask and sparged for 20 min followed by the addition of PdCl₂(PPh₃)₂ (42 mg, 0.060 mmol) and CuI (22 mg, 0.120 mmol). The terminal alkyne derivative **2.21** (70 mg, 0.119 mmol) was added to the mixture and the resulting mixture was stirred at RT and monitored with the TLC. All the starting materials disappeared after 24 hours. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue

was chromatographed using various combination of solvents. However, the desired product **2.22** was not isolated.

Attempted synthesis of 2.23. The BODIPY **2.9** (300 mg, 0.500 mmol) was dissolved in 350 mL of THF:NEt₃ (2:1) in a 500 round bottom flask and sparged for 30 minutes followed by the addition of PdCl₂(PPh₃)₂ (75 mg) and CuI (40 mg). The terminal alkyne derivative **2.21** (123 mg, 1.2 mmol) was added to the mixture and the resulting mixture was stirred at RT and monitored with the TLC. All the starting materials disappeared after 24 hours. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using various combination of solvents. However, the NMR spectra did not show any evidence for product **2.23**.

10-(4-(*tert*-butyl)-2,6-diiodophenyl)-5,5-difluoro-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (2.24). To a solution of pyrrole (0.36 g, 5.3 mmol, 2.2 eq) in dry DCM (100 mL), 2,6-diiodo-4-*tert*-butylbenzaldehyde **2.4** (1.0 g, 2.42 mmol, 1 eq) was added followed

by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (0.82 g, 1.5 eq) was added and the mixture was stirred for ~3 hours. After TLC analysis revealed the completion of oxidation, DIPEA (3.0 mL) and BF₃OEt₂ (3.5 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography using toluene (*R_f* = 0.42) as the eluent, yielded product **2.24** as orange powder (237 mg, 17 %). ¹H NMR (CDCl₃, 400 MHz): δ = 7.96 (s, 2H), 7.95 (s, 2H), 6.71 (d, *J* = 4.0 Hz, 2H), 6.52 (d, *J* = 4.0 Hz, 2H), 1.36 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 156.09, 150.07, 145.16, 138.73, 136.62, 134.47, 129.99, 119.07, 96.11, 34.72, 31.02. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -145.85 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.27 (t, *J_{FB}* = 28 Hz). HRMS (ESI-TOF): *m/z* 556.95364 ([M-F]⁻), calcd for C₁₉H₁₇BF₂N₂: *m/z* 556.95527.

2.25

10-(4-(*tert*-butyl)-2,6-bis((trimethylsilyl)ethynyl)phenyl)-5,5-difluoro-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (2.25). BODIPY derivative **2.24** (440 mg, 0.700 mmol) was dissolved in THF:NEt₃ (4.5 mL, 2:1) in a 250 mL flask followed by the addition of PdCl₂(PPh₃)₂ (48 mg, 0.070 mmol), CuI (27 mg, 0.140 mmol) and TMS-acetylene (175 mg, 1.72 mmol). The mixture was stirred overnight at RT. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (2:1, *R_f* = 0.40) as the eluent to yield product **2.25** as a greenish solid (282 mg, 78%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.90 (s, 2H), 7.56 (s, 2H),

6.78 (d, $J = 4.0$ Hz, 2H), 6.46 (d, $J = 4.0$ Hz, 2H), 1.36 (s, 9H), -0.04 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 152.64, 144.89, 143.95, 136.44, 135.56, 130.95, 129.16, 123.58, 118.02, 102.40, 100.54, 34.84, 30.99, -0.63$. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -145.45$ (q). ^{11}B NMR (CDCl_3 , 128 MHz): $\delta = 0.28$ (t, $J_{\text{FB}} = 28$ Hz). HRMS (EI-TOF): m/z 516.2411 ($[\text{MH}]^+$), calcd for $\text{C}_{29}\text{H}_{35}\text{BF}_2\text{N}_2\text{Si}_2$: m/z 516.2400.

2.26

4-(tert-butyl)-2,6-bis((trimethylsilyl)ethynyl)benzaldehyde (2.26). Benzaldehyde **2.4** (1.0 g, 2.42 mmol) was dissolved in THF: NEt_3 (18 mL, 2:1) in a 250 mL flask followed by the addition of $\text{PdCl}_2(\text{PPh}_3)_2$ (0.168 g, 0.24 mmol), CuI (0.09 g, 0.48 mmol) and TMS-acetylene (0.52 g, 5.31 mmol). The mixture was stirred overnight at RT. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:EtOAc (19:1, $R_f = 0.70$) as the eluent to yield product **2.26** as an orange-yellow crystalline solid (0.78 g, 91%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 10.59$ (s, 1H), 7.52 (s, 2H), 1.32 (s, 9H), 0.29 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 190.24, 156.00, 134.74, 131.64, 124.78, 101.92, 101.29, 35.05, 30.76, -0.21$. HRMS (EI-TOF): m/z 354.1831 ($[\text{MH}]^+$), calcd for $\text{C}_{21}\text{H}_{30}\text{OSi}_2$: m/z 354.1835.

2.27

10-(4-(*tert*-butyl)-2,6-diethynylphenyl)-5,5-difluoro-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (2.27). BODIPY derivative **2.25** (0.16 g, 0.30 mmol) was dissolved in MeOH:THF (8 mL, 1:1) and stirred with excess KF (0.09 g, 5 eq). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered, and the solvent evaporated *in vacuo*. The residue was chromatographed using Hex:DCM (2:1, *R_f* = 0.29) as the eluent to give product **2.27** as a red solid (82 mg, 73%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.92 (s, 2H), 7.65 (s, 2H), 6.75 (d, *J* = 4.0 Hz, 2H), 6.48 (d, *J* = 4.0 Hz, 2H), 2.99 (s, 2H), 1.38 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 152.81, 144.56, 143.89, 135.61, 130.73, 130.52, 122.74, 118.47, 82.09, 80.69, 34.82, 30.97. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -145.70 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.31 (t, *J_{FB}* = 28 Hz). HRMS (EI-TOF): *m/z* 372.1605 ([MH]⁺), calcd for C₂₃H₁₉BF₂N₂: *m/z* 372.1609.

2.28

10-(4-(*tert*-butyl)-2,6-bis((3-((3-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (2.28). To a solution of BODIPY derivative **2.27** (100 mg, 0.258 mmol) in 3 mL of THF:NEt₃ (2:1), PdCl₂(PPh₃)₂ (18 mg, 0.0258 mmol) and CuI (10 mg, 0.052 mmol) were added as catalysts followed by the addition of 208 mg (0.516 mmol) of TMS-protected-*tert*-butyl, 3,5-phenylacetylene **2.15**. The mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and

filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (1:1, R_f = 0.26) as the eluent to give the product as a red solid (196 mg, 83%). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.98 (s, 2H), 7.71-7.64 (m, 4H), 7.48-7.37 (m, 8H), 7.31-7.29 (m, 2H), 7.24-7.20 (m, 2H), 7.08-7.06 (m, 2H), 6.92-6.91 (d, J = 4.0 Hz, 2H), 6.51-6.50 (d, J = 4.0 Hz, 2H), 1.45 (s, 9H), 0.26 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 153.00, 144.50, 135.61, 135.05, 134.67, 134.44, 131.74, 131.63, 131.58, 1312.1, 129.26, 128.57, 128.52, 128.38, 123.73, 123.51, 123.29, 123.27, 122.70, 118.55, 104.11, 95.03, 93.90, 89.09, 88.94, 87.77, 34.95, 31.07, -0.09. ^{19}F NMR (CDCl_3 , 376.5 MHz): δ = -145.48 (q). ^{11}B NMR (CDCl_3 , 128 MHz): δ = 0.48 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): m/z 897.3664 ($[\text{M}-\text{F}]^-$), calcd for $\text{C}_{61}\text{H}_{51}\text{BFN}_2\text{Si}_2$: m/z 897.3662.

2.29

10-(4-(*tert*-butyl)-2,6-bis((3-((3-ethynylphenyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (2.29). Compound **2.28** (150 mg, 0.161 mmol) was dissolved in MeOH:THF (6.0, 1:1 mL) and reacted with excess KF (50 mg, 0.803 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO_4 , filtered, and the solvent evaporated under reduced pressure. The residue was chromatographed using Hex:DCM (1:1, R_f = 0.33) as the eluent to give product **2.29** as a red viscous liquid (88 mg, 71%). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.99 (s, 2H), 7.69-7.66 (m, 4H), 7.53-7.45 (m, 4H), 7.41-7.38 (m, 4H), 7.34-7.30 (m, 2H), 7.25-7.21 (m, 2H), 7.10-7.08 (m, 2H), 6.92-6.91 (d, J = 4.0 Hz, 2H), 6.51-6.50 (d, J = 4.0

The chemical structure shows a macrocyclic complex. At the center is a boron atom (B) coordinated by two nitrogen atoms (N) in a bipyridine-like ligand. The boron atom is also bonded to two fluorine atoms (F). The macrocycle is composed of four phenyl rings connected by ethynyl groups. One of the phenyl rings is substituted with a tert-butyl group.

2.32

((((5-(*tert*-butyl)-1,3-phenylene)bis(ethyne-2,1-diyl))bis(3,1-phenylene))bis(ethyne-2,1-diyl))bis(3,1-phenylene))bis(ethyne-2,1-diyl))bis(trimethylsilane) (**2.32**). To a solution of **2.19** (0.307 g, 1.684 mmol) in 18 mL of THF:NEt₃ (2:1), PdCl₂(PPh₃)₂ (18 mg, 0.0258 mmol) and CuI (10 mg, 0.052 mmol) were added as catalysts followed by the addition of 1.30 g (3.536 mmol) of TMS-protected-*tert*-butyl, 3,5-phenylacetylene (**2.15**). The mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:EtOAc (19:1, *R_f* = 0.6) as the eluent to give product **2.32** as a light-yellow solid (1.144 g, 93%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.73 (t, *J* = 1.2 Hz, 2H), 7.68 (t, *J* = 1.2 Hz, 2H), 7.55-7.43 (m, 11H), 7.37-7.33 (t, *J* = 7.6 Hz, 2H), 7.32-7.28 (t, *J* = 7.6 Hz, 2H), 1.37 (s, 9H), 0.27 (s, 18H). ¹³C NMR (CDCl₃, 100 MHz): δ = 151.7, 134.7, 131.8, 131.7, 131.5, 131.5, 131.4, 129.0, 128.5, 128.4, 123.6, 123.6, 123.5, 123.3, 123.0, 104.1, 95.1, 89.7, 89.1, 89.1, 88.5, 34.7, 31.1, -0.1. HRMS (ESI-TOF): *m/z* 727.3257 ([M+H]⁺), calcd for C₅₂H₄₇Si₂: *m/z* 727.3222.

2.33

3,3'-((5-(*tert*-butyl)-1,3-phenylene)bis(ethyne-2,1-diyl))bis(((3-ethynylphenyl)ethynyl)benzene) (2.33). Compound **2.32** (1.144 g, 1.573 mmol) was dissolved in 22 mL of MeOH:THF (1:1) and reacted with excess KF (0.75 g, 7.866 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered and the solvent evaporated under reduced pressure. The residue was chromatographed using Hex: EtOAc (15:1, *R_f* = 0.4) as the eluent to give product **2.33** as an off-white solid (362 mg, 39%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.73 (s, 2H), 7.68 (s, 2H), 7.55-7.46 (m, 11H), 7.37-7.30 (m, 4H), 3.11 (s, 2H), 1.37 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 151.8, 135.2, 134.7, 132.0, 131.9, 131.9, 131.5, 131.4, 129.0, 128.6, 128.5, 123.6, 123.4, 123.4, 123.0, 122.6, 89.8, 89.2, 89.0, 88.5, 82.7, 77.9, 34.8, 31.1. HRMS (ESI-TOF): *m/z* 583.2454 ([M+H]⁺), calcd for C₄₆H₃₁: *m/z* 583.2426.

2.34

Synthesis of controlled macrocycle 2.34. Pre-macrocycle **2.33** (250 mg, 0.134 mmol) was dissolved in THF:NEt₃ (130 mL, 2:1) and sparged with N₂ for 15 minutes. PdCl₂(PPh₃)₂ (9.0 mg, 0.013 mmol) and CuI (5.0 mg, 0.027 mmol) were added as catalysts followed by the addition of **2.17** and the mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:Et₂O (9:1, *R_f* = 0.63) as the eluent to give product **2.34** as a pink solid (13.5 mg, 17%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.97 (s, 2H), 7.85 (s, 2H), 7.69 (s, 1H), 7.54-7.44 (m, 8H), 7.37-7.30 (m, 6H), 1.37 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 151.8, 139.5, 136.8, 133.0, 130.8, 130.6, 130.1, 129.8, 128.7, 128.6, 128.5, 123.8, 123.7, 123.3, 123.1, 122.3, 90.2, 90.0, 89.4, 88.6, 82.5, 75.2, 34.8, 31.2. HRMS (EI-TOF): *m/z* 580.2187 ([MH]⁺), calcd for C₄₆H₂₈: *m/z* 580.2191.

2.35

10-(4-(*tert*-butyl)-2,6-bis((trimethylsilyl)ethynyl)phenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (2.35). To a solution of pyrrole **2.6** (0.82 g, 8.59 mmol, 2.5 eq) in dry DCM (120 mL), benzaldehyde derivative **2.26** (1.22 g, 3.44 mmol, 1

eq) was added followed by a catalytic amount of trifluoroacetic acid (TFA). After overnight stirring of the resulting reddish solution, DDQ (1.17 g, 1.5 eq) was added and the mixture was stirred for ~3 hours. After the TLC analysis revealed the completion of oxidation, DIPEA (3.6 mL) and BF₃OEt₂ (4.2 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, redissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography using toluene (*R_f* = 0.69) as the eluent, yielded product **2.35** as orange powder (0.91 g, 42 %). ¹H NMR (CDCl₃, 400 MHz): δ = 7.52 (s, 2H), 5.94 (s, 2H), 2.54 (s, 6H), 1.45 (s, 6H), 1.33 (s, 9H), 0.02 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 156.64, 156.17, 143.91, 141.52, 139.67, 137.11, 130.37, 121.34, 96.67, 89.71, 85.33, 34.67, 31.45, 14.76, 13.59, -0.01. ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.76 (t, *J_{FB}* = 32 Hz). ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -146.36 (q). HRMS (DART-TOF): calcd for C₃₃H₄₃BF₂N₂Si₂ 572.3026; found 572.3029.

2.36

10-(4-(*tert*-butyl)-2,6-diethynylphenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (2.36). BODIPY derivative **2.35** (0.275 g, 0.48 mmol) was dissolved in MeOH:THF (10 mL, 1:1) and stirred with excess KF (0.14 g, 5 eq). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered, and the solvent evaporated *in vacuo*. The residue was chromatographed using pure toluene (*R_f* = 0.49) as the eluent to give product **2.36** as a reddish solid (0.134 g, 65%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.64 (s, 2H), 5.98 (d, *J*=4.0 Hz, 2H), 3.01 (s, 2H), 2.57 (s, 6H), 1.44 (s, 6H), 1.36 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 158.14, 157.13, 142.27, 140.21, 138.99, 138.44, 130.71, 122.84, 96.06, 88.56, 86.66,

34.23, 31.37, 14.36, 13.38. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -146.55$ (q). ^{11}B NMR (CDCl_3 , 128 MHz): $\delta = 0.82$ (t, $J_{\text{FB}} = 83$ Hz). HRMS (EI-TOF): m/z 428.2241 ($[\text{MH}]^+$), calcd for $\text{C}_{27}\text{H}_{27}\text{BF}_2\text{N}_2$: m/z 428.2235.

2.37

10-(4-(*tert*-butyl)-2,6-bis((3-((3-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (2.37). To a solution of BODIPY derivative **2.36** (409 g, 0.955 mmol) in 11 mL of THF: NEt_3 (2:1), $\text{PdCl}_2(\text{PPh}_3)_2$ (67 mg, 0.096 mmol) and CuI (36 mg, 0.191 mmol) were added as catalysts followed by the addition of 803 mg (0.2006 mmol) of TMS-protected-phenylacetylene derivative **2.15**. The mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (1:1, $R_f = 0.70$) as the eluent to give product **2.37** as a red solid (725 mg, 78%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.68$ (s, 4H), 7.51-7.42 (m, 8H), 7.33-7.20 (m, 6H), 6.00 (s, 2H), 2.62 (s, 6H), 1.57 (s, 6H), 1.44 (s, 9H), 0.28 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 155.43, 152.97, 142.24, 140.19, 139.19, 137.43, 137.29, 135.10, 134.70, 131.90, 131.77, 131.69, 131.55, 130.72, 129.89, 129.13, 128.51, 128.39, 125.1, 123.51, 123.30, 123.19, 123.03, 122.98, 121.01, 104.15, 95.01, 93.05, 89.08, 89.02, 87.49, 34.90, 31.19, 22.68, 14.74, 14.15, 13.68, -0.06$. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -146.24$ (q). ^{11}B NMR (CDCl_3 , 128 MHz):

$\delta = 1.00$ (t, $J_{FB} = 30$ Hz). HRMS (ESI-TOF): m/z 972.4284 ($[M-F]^-$), calcd for $C_{65}H_{59}BFN_2Si_2$: m/z 972.4278.

2.38

10-(4-(*tert*-butyl)-2,6-bis((3-((3-ethynylphenyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (2.38). Compound **2.37** (958 mg, 0.984 mmol) was dissolved in MeOH:THF (20 mL 1:1) and reacted with excess KF (286 mg, 4.921 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated *in vacuo*. The residue was chromatographed using Hex:EtOAc (9:1, $R_f = 0.23$) as the eluent to give product **2.38** as a reddish viscous liquid (555 mg, 68%). 1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.79$ (s, 4H), 7.75-7.72 (m, 4H), 7.50-7.46 (m, 6H), 7.38-7.28 (m, 4H), 6.03 (s, 2H), 3.15 (s, 2H), 2.66 (s, 6H), 1.61 (s, 6H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 155.38, 152.95, 152.93, 142.20, 139.15, 137.33, 135.36, 135.12, 134.70, 131.91, 131.88, 131.75, 131.52, 129.08, 128.47, 128.46, 123.44, 123.17, 122.96, 122.95, 122.45, 121.02, 92.99, 89.18, 88.81, 87.47, 82.74, 77.79, 34.88, 31.16, 14.73, 13.66$. ^{19}F NMR ($CDCl_3$, 376.5 MHz): $\delta = -146.30$ (q). ^{11}B NMR ($CDCl_3$, 128 MHz): $\delta = 0.46$ (t, $J_{FB} = 30$ Hz). HRMS (EI-TOF): m/z 828.3490 ($[MH]^+$), calcd for $C_{59}H_{43}BF_2N_2$: m/z 828.3487.

2.39

Synthesis of rigid BODIPY-macrocycle 2.39. BODIPY pre-macrocycle **2.38** (199 mg, 0.240 mmol) was dissolved in 120 mL of THF:NEt₃ (2:1) and sparged with N₂ for 15 minutes. PdCl₂(PPh₃)₂ (25 mg, 0.036 mmol) and CuI (46 mg, 0.240 mmol) were added as catalysts followed by the addition of **2.17** and the mixture was stirred overnight at RT. The solution was filtered, the solvent removed from the filtrate, redissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (2:1, *R_f* = 0.35) as the eluent to give product **2.39** as a dark red solid (32 mg, 16%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.72 (s, 2H), 7.68 (s, 2H), 7.57-7.49 (m, 6H), 7.43- 7.35 (m, 6H), 7.28-7.24 (m, 2H), 6.01 (s, Hz, 2H), 2.63 (s, 6H), 1.57 (s, 6H), 1.43 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 155.39, 152.92, 142.18, 139.13, 135.35, 134.65, 132.25, 131.46, 129.02, 128.60, 128.44, 123.64, 122.95, 122.05, 121.03, 93.01, 89.44, 88.68, 87.50, 80.89, 74.39, 34.88, 31.15, 14.75, 13.66. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -146.9 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.99 (t, *J_{FB}* = 31 Hz).

2.40

4-(tert-butyl)-2,6-diethynylbenzaldehyde (2.40). TMS-protected benzaldehyde **2.26** (0.8 g) was dissolved in 30 mL of THF:MeOH (1:1) and stirred with excess KF (1.07 g, 5 eq). The reaction

was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered, and the solvent evaporated *in vacuo*. The residue was chromatographed using Hex:DCM (1:1, R_f = 0.25) as the eluent to give product **2.40** as a yellowish liquid. ¹H NMR (CDCl₃, 400 MHz): δ = 10.61 (s, 1H), 7.62 (s, 2H), 3.43 (s, 2H), 1.33 (s, 9H). HRMS (EI-TOF): m/z 210.1051 ([MH]⁺), calcd for C₁₅H₁₄O: m/z 210.1045.

2.41

4-(tert-butyl)-2,6-bis((3-((3-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)benzaldehyde (2.41). To a mixture of **2.40** (0.22 g), PdCl₂(PPh₃)₂ (0.041) and CuI (0.023) in THF:NEt₃ (9.0 mL, 2:1), TMS-protected-tert-butyl, 3,5-phenylacetylene **2.15** (0.52 g) was added. The mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, redissolved in EtOAc, and washed with an NH₄Cl solution. The extract was washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using various solvent mixtures but Hex:DCM (1:1) was found to be the best. However, pure product was never obtained. NMR data showed that there was no product in the crude.

2.42

((5-(*tert*-butyl)-2-(1,3-dioxolan-2-yl)-1,3-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (2.42). Benzaldehyde **2.26** (2.31 g, 6.5 mmol) and ethylene glycol (2.84, 183 mmol) were dissolved in 44 mL of toluene in a 250 mL round bottom flask and *p*-toluenesulfonic acid (0.03 g, 0.2 mmol) was added. The flask was equipped with a Dean-Stark trap and the mixture was refluxed overnight. After being cooled to RT, the mixture was neutralized with aqueous Na₂CO₃ and the organic layer was separated and dried over MgSO₄. After removal of volatiles *in vacuo*, the crude material was purified via column chromatography using pure hexane (*R_f* = 0.26) as the eluent to afford product **2.42** as a yellow oil (2.07 g, 80%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.47 (s, 2H), 6.38 (s, 1H), 4.28 (t, *J* = 8.0 Hz, 2H), 4.07 (t, *J* = 8.0 Hz, 2H), 1.29 (s, 9H), 0.26 (s, 18H). ¹³C NMR (CDCl₃, 100 MHz): δ = 151.83, 137.30, 131.73, 122.82, 102.92, 102.01, 98.36, 66.35, 34.53, 30.92, 0.03. HRMS (EI-TOF): *m/z* 398.2091 ([MH]⁺), calcd for C₂₃H₃₄O₂Si₂: *m/z* 398.2097.

2.43

2-(4-(*tert*-butyl)-2,6-diethynylphenyl)-1,3-dioxolane (2.43). Protected aldehyde **4.42** (0.453 g) was dissolved in 20 mL of THF:MeOH (1:1) and stirred with excess KF (0.33 g, 5 eq) overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered, and the solvent evaporated under reduced pressure. The residue was chromatographed using Hex:EtOAc (15:1, *R_f* = 0.21) as the eluent to give product **2.43** as a light yellow solid (0.262 mg, 91%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.55 (s, 2H), 6.42 (s, 1H),

4.28 (t, $J = 7.0$ Hz, 2H), 4.07 (t, $J = 7.0$ Hz, 2H), 3.30 (s, 2H), 1.29 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 152.18, 138.09, 132.07, 121.99, 101.85, 81.50, 81.39, 66.34, 34.54, 30.89$. HRMS (EI-TOF): m/z 254.1300 ($[\text{MH}]^+$), calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$: m/z 254.1307.

2.44

((((((5-(*tert*-butyl)-2-(1,3-dioxolan-2-yl)-1,3-phenylene)bis(ethyne-2,1-diyl))bis(3,1-phenylene))bis(ethyne-2,1-diyl))bis(3,1-phenylene))bis(ethyne-2,1-diyl))bis(trimethylsilane) (2.44). To a mixture of **2.43** (0.262 g, 1.03 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.072, 0.103 mmol) and CuI (0.039, 0.206 mmol) in 11 mL of $\text{THF}:\text{NEt}_3$ (1:1), TMS-protected-*tert*-butyl, 3,5-phenylacetylene **2.15** (0.91 g, 2.27 mmole) was added. The mixture was stirred at RT for 6 hours. The solution was filtered, the solvent removed from the filtrate, redissolved in EtOAc, and washed with an NH_4Cl solution. The extract was washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:EtOAc (15:1, $R_f = 0.28$) as the eluent to give product **2.44** in good yield (0.65 g, 79%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.71$ (t, $J = 4.0$ Hz, 2H), 7.67 (t, $J = 0.4$ Hz, 2H), 7.60 (s, 2H), 7.53-7.43 (m, 8H), 7.37-7.26 (m, 4H), 6.54 (s, 1H), 4.37 (t, $J = 8.0$ Hz, 2H), 4.14 (t, $J = 8.0$ Hz, 2H), 1.36 (s, 9H), 0.27 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 152.22, 135.09, 134.46, 131.80, 131.52, 131.48, 131.40, 131.32, 123.74, 123.58, 123.48, 123.22, 122.89, 104.07, 102.30, 95.11, 92.51, 89.20, 89.04, 88.33, 66.45, 34.67, 31.00, 26.93, 25.30, -0.08$. HRMS (ESI-TOF): m/z 799.34357 ($[\text{M}+\text{H}]^+$), calcd for $\text{C}_{55}\text{H}_{51}\text{O}_2\text{Si}_2$: m/z 799.34221.

2.45

2-(4-(*tert*-butyl)-2,6-bis((3-((3-ethynylphenyl)ethynyl)phenyl)ethynyl)phenyl)-1,3-dioxolane (2.45). Compound **2.44** (0.65 g, 0.899 mmol) was dissolved in 12 mL of THF:MeOH (1:1) and stirred with excess KF (0.43 g, 5 eq). The reaction was left to stir at RT for 5 hours. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered and the solvent removed *in vacuo*. The residue was chromatographed using Hex:EtOAc (9:1, *R_f* = 0.25) as the eluent to give product **2.45** as a green viscous liquid (0.307 g, 59%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.72 (t, *J* = 4.0 Hz, 2H), 7.68 (t, *J* = 4.0 Hz, 2H), 7.60 (s, 2H), 7.53-7.46 (m, 8H), 7.38-7.30 (m, 4H), 6.53 (s, 1H), 4.36 (t, *J* = 8.0 Hz, 2H), 4.14 (t, *J* = 8.0 Hz, 2H), 3.11 (2H), 1.35 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 152.24, 136.68, 135.16, 134.48, 132.02, 131.89, 131.50, 131.45, 131.33, 128.59, 128.50, 102.29, 92.49, 89.18, 89.02, 88.34, 82.71, 77.90, 66.44, 34.67, 30.99. HRMS (ESI-TOF): *m/z* 655.26499 ([M+H]⁺), calcd for C₄₉H₃₅O₂: *m/z* 655.26316.

Chapter 3: Synthesis of Modified BODIPY-Phenylacetylene Macrocycles Designed to Tune the Absorption Profile

3.1. Introduction

As discussed in the previous chapter, a BODIPY-phenylacetylene macrocycle (**2.31**) was successfully made with a BODIPY contained within the macrocycle. Also, fluorescence studies showed that there was energy transfer from the macrocycle to the BODIPY. The macrocyclic part of the molecule (**2.31**) absorbs light in the UV region with a maximum absorption at 292 nm. However, for DSSC applications this is less than ideal, because few photons penetrate our atmosphere at this wavelength. To design a dye for DSSC applications, it needs to be modified such that the macrocyclic part absorbs appreciably in the visible (or near IR)¹⁶¹ (*i.e.* a red-shift in the absorption profile is required). The solar spectrum and photon flux diagrams are shown in Figure 3.1 and provide insight into how many photons of a given wavelength are striking the earth's surface during daylight hours.

Figure 3.1. Solar irradiance and inset of photon flux

In principle, macrocycles could be systematically tuned by modifying electronic properties and conjugation lengths. To further red-shift the absorption profile of the macrocycle in **2.31**, a strategy was taken to tune the electronic density on the phenylacetylene arm **2.15**. The inclusion of electron donating and withdrawing groups can create a push-pull system and potentially broaden of the absorption profile. Figure 3.2 depicts the macrocycle modifications aimed to red shift the absorption envelope.

Figure 3.2. A proposed design of the modified phenylacetylene arm (a) and its assembly with other building blocks to modified BODIPY-phenylacetylene macrocycle (b). EDG represents electron donating group whereas EWG represents electron withdrawing group

Before starting this proposed synthesis, an unsubstituted phenylacetylene arm (**3.1**) and its modified counterpart (**3.4**), (shown in Figure 3.3) were made and their absorption properties were studied, as a proof of concept.

Figure 3.3. Unsubstituted phenylacetylene **3.1** and its modified counterpart **3.4** with electron donating and accepting groups attached

UV-Vis data for both compounds **3.1** and **3.4** are shown in Figure 3.4. The absorption profile of the unsubstituted phenylacetylene **3.1** shows dominant absorption below 300 nm. However, attaching EDG and EWG red shifts the absorption profile significantly within the phenylacetylene arm **3.4** beyond 350 nm. Also, a broadened absorption (300-425 nm) is observed, which could be attributed to charge transfer between the EDG and EWG.

Figure 3.4. UV/Vis data for unsubstituted phenylacetylene arm **3.1** (dotted line) and modified phenylacetylene arm **3.4** (solid line)

DFT calculations were also run on the proposed modified BODIPY-phenylacetylene macrocycle and FMOs are shown in Figure 3.5. As it can be seen in Figure 3.5, the HOMO is localized on the donor part of the macrocycle whereas the LUMO stays on the acceptor unit. Based on electronic density splitting between these FMOs, it was hypothesized that upon absorption of a photon, electron density shifts from the lower part of the macrocycle (donor) to the upper side (acceptor) and eventually gets transferred to the BODIPY core.

Figure 3.5. DFT calculations on proposed modified BODIPY-phenylacetylene macrocycle (depicted by Figure 3.2b)

With DFT data in hand and experimental evidence to suggest that modification of the phenylacetylene arm (**3.4**) could permit a similar redshift in the absorption envelope of **2.31** modified BODIPY-phenylacetylene macrocycles were synthesized and studied using UV-Vis and fluorescence to determine if this is a viable approach (*vide infra*).

3.2. Synthesis

3.2.1. Synthesis of control phenylacetylene arms

The first step in the synthesis was the preparation of the control phenylacetylene arm. Towards this end, an unsubstituted phenylacetylene arm **3.1** and its substituted derivative **3.4** were made. Synthesis of the unsubstituted phenylacetylene arm **3.1** was carried out by a Sonogashira cross-coupling between iodobenzene and ethynylbenzene (Scheme 3.1). Synthesis of **3.1** has been extensively studied in literature. A few articles have reported the synthesis of **3.1** *via* the Sonogashira cross-coupling reaction. However, they used a different protocol. In one such study, palladium nanoparticles supported on Smopex metal scavengers as catalysts have been used to synthesize **3.1**.¹⁶² Gold and palladium combined for the Sonogashira coupling have also been used.^{163,164} Instead of following the literature methods, CuI and $\text{PdCl}_2(\text{PPh}_3)_2$ catalysts together were used at RT and the product was obtained with 91% yield.

Scheme 3.1. Synthesis of unsubstituted phenylacetylene arm **3.1**

Similar to **3.1**, various methods have been reported in literature for the synthesis of **3.4**. However, a general Sonogashira cross-coupling protocol was used to make a substituted derivative of **3.1**. Synthesis of **3.4** was carried out according to Scheme 3.2. In the first step, 4-iodoanisole was reacted with TMS-acetylene to yield **3.2**, followed by deprotection to yield **3.3**. Sonogashira cross-coupling reaction of **3.3** with 1-iodo-4-nitrobenzene yielded **3.4**.

Scheme 3.2. Synthesis of substituted phenylacetylene arm **3.4**

3.2.2. Attempted synthesis of new modified phenylacetylene arms: D—A arms

The first step towards the synthesis of the modified BODIPY-phenylacetylene macrocycle was the synthesis of the modified phenylacetylene arm. Because a red-shift was required in the macrocyclic part of the parent BODIPY-phenylacetylene macrocycle (**2.31**), the modification was required with phenylacetylene arms and the top BODIPY cap was kept the same. A cartoon showing this proposed design of the modified phenylacetylene arm is shown in Figure 3.6.

Figure 3.6. A proposed design of the modified phenylacetylene arm

To make the desired modified phenylacetylene arm (Figure 3.6), a donor (EDG) and acceptor (EWG) were required. The donor and acceptor units were designed in such a way that reacted them together could give the desired phenylacetylene arm. A proposed retrosynthesis is given in Scheme 3.3.

Scheme 3.3. A retrosynthetic scheme towards the synthesis of modified phenylacetylene arm **3.5** starting with donor **3.11** and acceptor **3.15**

As shown in Scheme 3.3, the donor **3.11** and acceptor **3.15** were required to make the modified arm **3.5**. The synthesis of donor **3.11** was carried out according to Scheme 3.4. The first step was the synthesis of **3.7**, which has been reported in literature. One of the methods used 1-iodo-2-methoxybenzene (2-iodoanisole) as a starting material.¹⁶⁵ Fuming HNO₃ was used to install a nitro-group (NO₂) on 2-iodoanisole. To carry out this step, concentrated HNO₃ was used instead of fuming HNO₃ owing to its unavailability but this reaction failed to work. However, the same step was carried out using another literature method where they used oxidative iodination of deactivated arenes in concentrated H₂SO₄ with I₂/NaIO₄ or KI/NaIO₄.¹⁶⁶ This method was followed with the exception that KIO₄ was used instead of NaIO₄ and the product was obtained in 75% yield.

The next step was the reduction of NO₂ to NH₂ to yield **3.8** and several literature methods for the reduction of the NO₂ group were available. The Zn powder with glacial AcOH was used to carry out this step, but it failed to yield the desired product (**3.8**). Another method was pursued by using SnCl₂.¹⁶⁷ This method worked but the yield was low. The best yield for this reaction was obtained by using a patent method¹⁶⁸ where they used Fe and NH₄Cl as shown in Scheme 3.4.

The next step in the synthesis of donor group **3.11** was to convert **3.8** to its triazine derivative **3.9** which was carried out *via* diazonium chemistry (yield of 73%). Compound **3.9** was then reacted with TMS-acetylene through a Sonogashira Cross-coupling reaction to yield **3.10** in good yield (70%). Reaction of TMS-protected triazine derivative **3.10** with CH₃I yielded **3.11** in 89% yield.

Scheme 3.4. Synthesis of donor part of the modified phenylacetylene arm

With the donor group in hand, the next step was the synthesis of acceptor group **3.15**. However, the synthesis of **3.15** was found to be challenging. The most suitable precursor was 5-iodo-2-nitroaniline (**3.12**) which could be converted to **3.15** using known methodologies as shown in Scheme 3.5.

Scheme 3.5. Synthesis of acceptor unit **3.15** from 5-Iodo-2-nitroaniline (**3.12**)

The precursor **3.12** was commercially available from Synquest Labs, but was too expensive (USD. \$2260 per 5 g) to purchase, particularly for something meant to be a low cost technology. A literature search revealed that only a few methods were available to make a bromo counterpart (**3.16**) of **3.12**. Additionally, the literature methods were from patents.^{169,170} With no other option

available, patent methods were attempted to make **3.12** from 1-iodo-4-nitrobenzene (actual method used 1-bromo-4-nitrobenzene instead of 1-iodo-4-nitrobenzene). However, this reaction failed to yield the desired product (**3.12**). The reaction was then carried out on 1-bromo-4-nitrobenzene; again this step failed to yield **3.16**. Some variations were made to the reagents (e.g. $\text{NH}_2\text{OBn.HCl}$ and $\text{NH}_2\text{OH.HCl}$ were used instead of $\text{NH}_2\text{OMe.HCl}$) and reaction conditions (e.g. variations in temperature). All the efforts to synthesize it from different routes and reagents were in unsuccessful.

Scheme 3.6. Synthesis of compounds **3.12** and **3.16** starting with 1-iodo-4-nitrobenzene and 1-bromo-4-nitrobenzene respectively

With the failure of reactions to prepare **3.12**, the effort to make acceptor unit **3.15** was not pursued further. However, an alternative strategy to build the arm stepwise starting with the BODIPY cap was under taken (*vide infra*).

3.2.3. Stepwise synthesis of modified phenylacetylene arm starting with BODIPY-cap

After an unsuccessful attempt to make modified phenylacetylene arm **3.5** from donor **3.11** and acceptor **3.15** groups, a new strategy starting with the top BODIPY cap and attaching an acceptor and then donor part (i.e. a gradual top-down strategy) to get to BODIPY-A-D pre-macrocycle was adopted. The cyclization of pre-macrocycle can yield the desired modified

BODIPY-phenylacetylene macrocycle. This strategy of stepwise synthesis starting with the BODIPY cap is depicted by a cartoon shown in Figure 3.7.

Figure 3.7. A stepwise strategy for the synthesis of modified BODIPY-phenylacetylene arm.

The same BODIPY cap (**2.27**) was used to start the synthesis as shown in Scheme 3.7. A new acceptor precursor **3.18** was selected for reacting with BODIPY **2.27**. The synthesis of **3.18** was challenging too. However, the first step which involved the nitration of 1,3-diiodobenzene (Scheme 3.7) was previously reported.^{171,172} Both of the literature methods involve the reaction of fuming HNO₃ with 1,3-diiodobenzene at 0 °C to yield the desired product (**3.17**). This procedure was followed to get **3.17** with the exception that instead of using fuming HNO₃, concentrated HNO₃ (70%) was used. It was noticed that the reaction does not proceed no matter how long it is stirred. However, this reaction worked when 1,3-diiodobenzene was heated to reflux with concentrated HNO₃ for 12 hours and afforded the product **3.17** in nearly quantitative yield (96%).

The next step was the synthesis of **3.18** which was achieved by reacting **3.17** with TMS-acetylene *via* Sonogashira cross-coupling as shown in Scheme 3.1. This apparently simple looking reaction happened to be one of the most difficult reactions. Because there were two iodo-groups on the same molecule, reacting one group selectively over the other was problematic. The idea behind this proposed reaction was that the steric effect of the NO₂ group might hinder the reaction at the *ortho*-position and hence prefer the reaction at the *para*-position.

Scheme 3.7. Synthesis of iodo-derivative with EWG (nitro) group (**3.6**)

The crude NMR showed impure product. The TLC showed two superimposing spots that were not separated by any solvent mixture. The two fractions were separated after extensive column chromatography using hexane as an eluent. One of the fractions was characterized as mono-substituted derivative (**3.18**) whereas the second fraction was a di-substituted derivative where both of the iodo-groups were replaced with TMS-acetylene. A 2D NMR (HMBC) spectrometry was used to confirm if the TMS-acetylene was at the *para*-position (*para* to NO₂).

The next step was the reaction of this new acceptor unit **3.18** with the previously made terminal alkyne BODIPY **2.27** using the Sonogashira cross-coupling reaction to yield **3.19** (Scheme 3.6). While the reaction was successful, the purification step was relatively difficult. Also, a few strange observations were made during this reaction; a) fluorescence was quenched b) the yield dropped unexpectedly, c) a dark red solid (insoluble to all available solvents) was obtained as a by-product. Generally speaking, a Sonogashira cross-coupling works in good to excellent yields. However, in the case of BODIPY, the Sonogashira reaction give yields somewhere from 50-70%. Surprisingly for this reaction to make **3.19**, the yield dropped to 13%.

As shown in Scheme 3.8, the next step was the deprotection of **3.19** to **3.20** which was obtained in 45% yield. Compound **3.20** was then reacted with donor unit **3.11** to yield TMS-protected macrocycle precursor **3.21**. This reaction seemed to proceed but a pure product was never obtained. The cleanest fraction obtained after column chromatography showed the ¹H NMR integrating for more than desired number of protons. Additionally, no clear results were obtained by mass spectrum (mass spectrum can be found in the appendices). Although the product was not pure, the next step was still attempted with hope to get the deprotected derivative **3.22**. This was assumed based on the observation that TMS-protected BODIPY derivatives were almost always

greasy and that deprotection might yield a pure product. However, this reaction failed to yield **3.22**. NMR studies failed to show any sign of product and further characterization was halted.

Scheme 3.8. Attempted synthesis of U-shape molecule **3.22** towards modified BODIPY-macrocycle

The failure of the above mentioned reactions were attributed to the decomposition of BODIPY during all preparation steps.

3.2.4. Modified phenylacetylene arms and its assembly with top BODIPY-cap

To overcome this problem, a more stable BODIPY (tetramethyl BODIPY) **2.36** was reacted with acceptor group **3.18** to yield **3.23** (Scheme 3.9). A clean product was obtained by column chromatography. However, same observations were made as in the case of **3.19**. The yield during this step was low (13%) and the fluorescence was quenched.

Scheme 3.9. Reaction of acceptor unit with tetramethyl-BODIPY to get **3.23**

It was thought that the presence of NO₂ at the *ortho*-position might be the reason for quenching of the fluorescence and also the lower yield. To study if that is the case, the same reaction was attempted with a donor group (methoxy derivative **3.9**) rather than nitro derivative **3.18** to yield **3.17** (Scheme 3.8). Although the yield was better (21%) than that of **3.19** and **3.23**, it was still low and unsatisfactory with seven more steps to get the desired product. As a result of low yielding reactions, this approach was abandoned at this stage.

Scheme 3.10. Synthesis of BODIPY cap with donor group (**3.24**)

3.2.5. Synthesis of new phenylacetylene arms and macrocycle: mono-donor arms

As a result of the above mentioned failed attempts to make the modified phenylacetylene arms with donor and acceptor groups, the new strategy was to make a modified arm with only donor groups attached. This new arm is shown by a cartoon in Figure 3.8.

Figure 3.8. A cartoon showing a mono-donor phenylacetylene arm

This new arm **3.26** was made according to Scheme 3.11. The donor group **3.11** was reacted with previously made triazine alkyne **2.12** to yield **3.25** which was then reacted with iodomethane to yield the mono-donor phenylacetylene arm **3.26**. Both of the steps gave products in good yields. Spectroscopic data for both of **3.25** and **3.26** is given in the appendices.

Scheme 3.11. Synthesis of mono-donor arm **3.26**

The next step was to attach arm **3.26** to the BODIPY cap **2.27** and subsequently cyclize the ring as shown in Scheme 3.12. The first step involved the reaction of terminal alkyne BODIPY **2.27** with new phenylacetylene arm **3.26** to yield **3.27**. Deprotection of **3.27** resulted in a U-shape molecule **3.28** which upon cyclization afforded the modified macrocycle **3.29**. All of these compounds were fully characterized and the spectroscopic data is given in appendices.

Scheme 3.12. Synthesis of modified BODIPY-macrocycle **3.29**

During the cyclization step, stoichiometric CuI was used and a yield of 23% was obtained which is an improvement from previous attempts for the cyclization step. Also, the bottom cap **2.17** was not used this time. This was the first time when the cyclization step was carried out without adding the bottom cap. However, the end result was the same. This adds to the evidence for the proposed mechanism during the cyclization step (Figure 2.16).

3.2.6. Synthesis of another mono-donor arm with donor group towards the BODIPY-cap

Another phenylacetylene arm was made with mono-donor with donor groups on the upper side (towards BODIPY cap). Attaching this arm to the BODIPY cap could give a BODIPY-phenylacetylene macrocycle with donor group on the top side of the macrocycle. The motivation for this structure was to study how the process of energy transfer differs in both cases (one where the donor group is on the lower side of the macrocycle and the other where it is on the upper side). A cartoon representing this kind of modified phenylacetylene arm is shown in Figure 3.9.

Figure 3.9. A cartoon representing a mono-donor phenylacetylene are with donor group on top

To make this new mono-donor arm (shown in Figure 3.9), a new donor group (**3.32**) made from 5-iodo-2-methoxyaniline in three steps (as shown in Scheme 3.13) was required. 5-iodo-2-methoxyaniline was obtained from Alfa Aesar and converted to triazine derivative **3.30** *via* diazonium chemistry which was further reacted with TMS-acetylene through Sonogashira cross-coupling to yield **3.31**. Finally, the deprotection of **3.31** with KF yielded **3.32**. All of the steps gave high yields. The spectroscopic data is shown in appendices.

Scheme 3.13. Synthesis of alkyne derivative **3.32**

To make the desired arm **3.34**, methoxy alkyne derivative **3.32** was reacted with **2.13** to yield **3.33**. The next step was the conversion of triazine to iodo group (**3.34**) which was achieved by reacting **3.33** with iodomethane. The synthetic steps to make **3.34** are depicted in Scheme 3.14.

Scheme 3.14. Synthesis of compound **3.34**

Both of the derivatives, **3.33** and **3.34**, were made in excellent yields (92% and 93% respectively). They were fully characterized by spectroscopic techniques and the data is given in the appendices. The modified phenylacetylene arm **3.34** was then used to build the second modified BODIPY-phenylacetylene macrocycle **3.37** using a reaction Scheme 3.15. All of these steps were similar to the one described in Scheme 3.12. All of the intermediates as well as the product (**3.37**) were fully characterized and the spectroscopic data is given in the appendices.

Scheme 3.15. Synthesis of modified BODIPY-macrocycle **3.37**

3.2.6. Synthesis of new phenyl acetylene arms and macrocycle: *bis*-donor arms

After the successful synthesis of two modified BODIPY-phenylacetylene macrocycles (one with mono-donor groups on the lower side of the macrocycle (**3.29**) and the other with mono-donor on the upper side of the macrocycle (**3.36**)), another macrocycle with *bis*-donor groups was made. For this purpose, a modified phenylacetylene arm with *bis*-donor groups was needed. A cartoon showing the new arm with *bis*-donor groups is shown in Figure 3.10.

Figure 3.10. A design of a modified phenylacetylene arm with *bis*-donor group

The synthesis of the *bis*-donor arm is shown in Scheme 3.16. Both of the precursors (**3.32** and **3.11**) have been previously made and reacting them using Sonogashira cross-coupling protocol yielded **3.38** which was converted to the desired arm (**3.39**) by heating with iodomethane.

Scheme 3.16. Synthesis of compound **3.39**

The next step was the reaction of *bis*-donor arm **3.39** and BODIPY **2.27** to yield new modified BODIPY-phenylacetylene macrocycle **3.42** as according to Scheme 3.17. The first step was to make the TMS-protected U-shape molecule **3.40** which upon deprotection yielded a pre-8macrocycle molecule **3.41**. Cyclization of **3.41** using a previously explored protocol yielded the desired product **3.42**. Each step was fully characterized and the spectroscopic data for each step is given in the appendices.

Scheme 3.17. Synthesis of modified BODIPY-macrocycle **3.42**

3.2.7. Characterization of modified macrocycles with mono- and *bis*-donor arms

NMR spectroscopy was used as a preliminary technique to characterize the modified BODIPY-phenylacetylene macrocycles (**3.29**, **3.37** and **3.42**). ¹H NMR, ¹³C NMR, ¹¹B NMR, ¹⁹F NMR and DEPT-90 ¹³C NMR (where appropriate) were used for the characterization. The ¹H NMR and crystal structure data of compound **3.29** are given in Figures 3.11 and 3.12, respectively. The ¹H NMR featured the integration of 22 aromatic protons, besides six methyl and nine *tert*-butyl protons (Figure 3.11).

Figure 3.11. ¹H NMR spectrum of compound **3.29**

The detailed spectroscopic data (can be found in the appendices) helped in characterizing the desired product **3.29**. However, the final evidence was an X-ray crystal structure determination. The crystal structure was grown using DCM:Hex (1:2) and letting it evaporate slowly. The crystal structures of the modified macrocycles can found in Figure 3.12. It is clear that the BODIPY resides inside the macrocycle and is orthogonal to the macrocycle.

Figure 3.12. Crystal structure of compound **3.29** (ORTEP, 30% thermal ellipsoids). Hydrogen atoms and solvent molecules have been removed for clarity

The ^1H NMR spectra of compounds **3.37** and **3.42** are given in Figures **3.13** and **3.14** respectively and justifies the structures completely. The rest of characterization is given in the appendices.

Figure 3.13. ¹H NMR spectrum of compound **3.37**

The identity of **3.37** was again confirmed by x-ray crystallography (Figure 3.14).

Figure 3.14. Crystal structure of compound **3.37** (ORTEP, 30% thermal ellipsoids). Hydrogen atoms and solvent molecules have been removed for clarity

Figure 3.15. ¹H NMR spectrum of compound **3.42**

3.3. Results and Discussion

3.3.1. Photophysical properties of modified BODIPY-phenylacetylene macrocycle **3.29**

The absorption data of compound **3.29** was collected in a DCM solution (Figure 3.16). The macrocyclic part of compound **3.29** absorbs at 296 nm along with a sharp absorption at 367 nm whereas the BODIPY portion exhibits a typical BODIPY absorption at 511 nm with a shoulder at 487 nm. When **3.29** is excited at 296 nm, the emission is observed from BODIPY core at 528 nm.

Figure 3.16. UV-Vis spectra of **3.29** & **2.31**; fluorescence emission spectrum from **3.29**

The TD-DFT (6-31G*) was used to assign transitions in FMOs of compound **3.29**. Table 3.1 summarizes these transitions. In the table, f represents the oscillator strength and is a relative

value for intensity of the absorption. Orbital contributions (Cont. (%)) represents the percent contribution of a particular set of orbitals involved in the transition. The highest value of oscillator strength represents the transition at 296 nm which is in accordance with the absorption profile and is assigned to the HOMO-1 to LUMO+1 transition. The FMOs of compound **3.29** are shown in Figure 3.17. The second highest absorption is due to the BODIPY core which is assigned to the HOMO-2 to LUMO transition.

Table 3.3. Assignment of transitions based on TDDFT for macrocycle **3.29**

Compound	$\lambda(\text{nm})$ exp.	$\lambda(\text{nm})$ calc.	f	Active MOs	Cont.(%)
3.29	511	414	0.468	HOMO-2 $\rightarrow$ LUMO	88.8
				HOMO-3 $\rightarrow$ LUMO	7.5
	486	363	0.014	HOMO-3 $\rightarrow$ LUMO	67.9
				HOMO $\rightarrow$ LUMO	11.6
	367	329	0.811	HOMO $\rightarrow$ LUMO+1	48.8
				HOMO $\rightarrow$ LUMO+2	10.6
	313	293	0.257	HOMO-1 $\rightarrow$ LUMO+4	23.7
				HOMO $\rightarrow$ LUMO+5	12.7
	296	288	1.971	HOMO-1 $\rightarrow$ LUMO+1	34.8
				HOMO $\rightarrow$ LUMO+4	13.1

Figure 3.17. FMOs of compound 3.29

3.3.2. Photophysical properties of modified BODIPY-phenylacetylene macrocycle **3.37**

The absorption data of compound **3.37** is shown in Figure 3.18. The macrocyclic part of the compound **3.37** absorbs at 297 nm along with a shoulder at 337 nm whereas the BODIPY part exhibits a typical BODIPY absorption at 511 nm. Upon excitation of **3.37** at 297 nm, the emission is observed from the BODIPY core (528 nm).

Figure 3.18. UV-Vis spectra of **3.37** & **2.31**; fluorescence emission spectrum from **3.37**

The TD-DFT (6-31G*) was used to assigned transitions in FMOs of compound **3.37**. Table 3.2 summarizes these transitions. The highest value of oscillator strength represents the transition at 297 nm which is in accordance with the absorption profile and is assigned to the HOMO-1 to LUMO+1 transition. The FMOs of compound **3.37** are shown in Figure 3.19. The second highest absorption is from the BODIPY core which is assigned to the HOMO-2 to LUMO transition.

Table 3.2. Assignment of transitions based on TDDFT for macrocycle **3.37**

Compound	$\lambda(\text{nm})$ exp.	$\lambda(\text{nm})$ calc.	f	Active MOs			Cont.(%)
3.37	511	415	0.448	HOMO-2	→	LUMO	82.1
				HOMO	→	LUMO	8.7
	486	380	0.032	HOMO	→	LUMO	57.1
				HOMO-3	→	LUMO	20.7
	337	315	0.393	HOMO-3	→	LUMO+1	36.3
				HOMO-4	→	LUMO+1	8.5
	313	301	1.646	HOMO-1	→	LUMO+2	28.0
				HOMO	→	LUMO+3	31.1
	297	286	2.290	HOMO-1	→	LUMO+1	27.9
				HOMO	→	LUMO+4	27.0

Figure 3.19. FMOs of compound 3.37

3.3.3. Photophysical properties of modified BODIPY-phenylacetylene macrocycle **3.42**

The absorption data of compound **3.42** is shown in Figure 3.20. The macrocyclic part of compound **3.42** shows a maximum absorption at 301 nm and it extends to 380 nm. The absorption from the BODIPY core (511 nm) resembles the other two modified macrocycles with a shoulder at 487 nm. Upon excitation of **3.42** at 297 nm, the emission is observed from the BODIPY core (534 nm).

Figure 3.20. UV-Vis spectra (DCM) of **3.42** & **2.31**; fluorescence emission spectrum from **3.42**

The TD-DFT (6-31G*) was used to assigned transitions in FMOs of compound **3.42**. Table 3.3 summarizes these transitions. The highest value of oscillator strength represents the transition at 301 nm which is in accordance with the absorption profile and is assigned to the HOMO to LUMO+4 transition. The FMOs of compound **3.42** are shown in Figure 3.21. The second highest absorption is from the BODIPY core which is assigned to the HOMO-3 to LUMO transition.

Table 3.3. Assignment of transitions based on TDDFT for macrocycle **3.42**

Compound	$\lambda(\text{nm})$ exp.	$\lambda(\text{nm})$ calc.	f	Active MOs			Cont.(%)
3.42	512	415	0.446	HOMO-3	→	LUMO	56.0
				HOMO-2	→	LUMO	37.8
	487	383	0.032	HOMO	→	LUMO	44.8
				HOMO-3	→	LUMO	23.5
	367	330	0.774	HOMO-2	→	LUMO+1	18.6
				HOMO	→	LUMO+1	48.6
	348	303	1.277	HOMO-1	→	LUMO+2	25.3
				HOMO	→	LUMO+3	18.9
	317	292	1.018	HOMO-1	→	LUMO+1	29.3
				HOMO	→	LUMO+4	12.1
				HOMO-11	→	LUMO	16.7
	300	283	1.269	HOMO-1	→	LUMO+5	24.0
				HOMO	→	LUMO+4	24.5

Figure 3.21. FMOs of compound 3.42

3.3.4. Emission profile of 3.29 at variable concentrations

All of the modified macrocycles (**3.29**, **3.37** and **3.42**) show energy transfer from the macrocycle to the BODIPY core as can be seen upon excitation of the macrocyclic portion of the compound, and an emission characteristic of BODIPY. To eliminate co-concentration dependence as a variable on the emission profile, the emission data at different concentrations of **3.29** was collected. It was observed that intensity of the emission is directly proportional to the concentration (Figure 3.22) suggesting no significant concentration behavior. In Figure 3.22, a blue solid line represents the absorption profile of modified BODIPY-macrocycle **3.29** and the dotted lines represent the emission data for different concentrations of **3.29** (with the concentrations decreasing from 1 to 4). This trend was consistent with the other modified macrocycles (**3.37** and **3.42**) as well.

Figure 3.22. Absorption spectrum (solid blue line) and emission spectra (dotted lines) of **3.29** with decreasing concentrations from 1-4

3.4. Summary and Conclusion

In this chapter an attempt was made to modify the previously made BODIPY-phenylacetylene macrocycle **2.31** in which the energy transfer is observed from macrocycle to the BODIPY core. The macrocycle in **2.31** absorbs around 300 nm and to red-shift the absorption envelop of the macrocycle part, it was modified by attaching donor (although acceptor groups were also explored) on the phenylacetylene arms. An attempt to implement a push-pull strategy between the donor and acceptor groups was unsuccessful owing to synthetic difficulties. However, the modified macrocycles were successfully made by substituting mono-donor groups (on one side of the macrocycle) and *bis*-donor groups (on both sides of the macrocycle).

The absorption studies show that the modified BODIPY-phenylacetylene macrocycle with *bis*-donor group (**3.42**) displayed a more red-shifted absorption profile as compared to those with mono-donor groups (**3.29** and **3.37**). The absorption envelope in **3.42** was extended up to 380 nm which indicates a bathochromic shift of about 50 nm as compared to the parent BODIPY-phenylacetylene macrocycle **2.31**. TD-DFT calculations were performed to assign the dominant transitions in the FMOs of the modified macrocycles. The fluorescence studies showed the energy transfer from the macrocycle to the BODIPY upon excitation of the macrocyclic part. However, a curious concentration dependent emission was observed for the family of methoxy-substituted macrocycles (**3.29**, **3.37** & **3.42**) from 380-450 nm which increases with decreasing the concentration of the modified BODIPY-phenylacetylene macrocycle.

3.5. Experimental

3.5.1. General considerations

Unless stated otherwise, all reagents were purchased from Sigma Aldrich except PdCl₂ (Pressure Chemical Co., Pittsburg, PA). PdCl₂ was reacted with PPh₃ to make catalyst PdCl₂(PPh₃)₂. Purification by column chromatography was carried out using silica (Silicycle: ultrapure flash silica). Analytical thin-layer chromatography was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Silicycle) and visualized under UV light. Routine ¹H, ¹³C {¹H}, ¹¹B {¹H} and ¹⁹F NMR spectra were recorded at 400, 100, 128 and 376 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to a residual nondeuterated solvent (CHCl₃) for ¹H and ¹³C nuclei and BF₃•OEt₂ (¹¹B nucleus; δ = 0 ppm) C₆F₆ (¹⁹F nucleus; δ = 0 ppm). Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; q = quartet and br = broad. High resolution mass spectrometry (HRMS) results were obtained from Queens University, Kingston Ontario. Electron impact (EI) mass spectrometry and Electrospray ionization (ESI) techniques were used for the ionization; time of flight (TOF) was used for analysis. UV-Vis data was taken using Cary Series UV-Vis-NIR Spectrophotometer from Agilent Technologies and dichloromethane (having the onset peak at 230 nm) was used as the solvent. The GAUSSIAN 09 computational package¹⁵⁴ was used to perform ground-state geometry optimization calculations employing Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr non-local correlation functional B3LYP¹⁵⁵⁻¹⁵⁷ and 6-31G basis set was used for all the atoms. Time-dependent density functional theory calculations were also performed using this methodology, and the first 200 singlet excited states were calculated. Calculations by the first-principles method were used to obtain accurate excitation energies and oscillator strengths. We modelled the solvent with the polarizable continuum model using DCM as the solvent.¹⁵⁸

3.5.2. Synthesis

The synthetic details of each compound are given below. General synthetic steps have been used unless otherwise mentioned in the procedure.

3.1

1,2-diphenylethyne (3.1). Iodobenzene (2.40 g, 11.75 mmol) was dissolved in 104 mL of THF:NEt₃ (1:1) and sparged with nitrogen for 15 min. PdCl₂(PPh₃)₂ (0.344 g, 0.490 mmol) and CuI (0.186 g, 0.979 mmol) were added followed by the addition of phenylacetylene (1.0 g, 9.79 mmol). The resulting mixture was stirred overnight at RT. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using pure hexanes (*R_f* = 0.31) to yield product **3.1** as a light yellow crystalline solid (1.59 g, 91%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.66-7.64 (m, 2 H), 7.45-7.42 (m, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 131.72, 128.46, 128.36, 123.40, 89.54.

3.2

((4-methoxyphenyl)ethynyl)trimethylsilane (3.2). Iodoanisole (1.0 g) was dissolved in 50 mL of THF:NEt₃ (1:1) and sparged with nitrogen for 15 min. PdCl₂(PPh₃)₂ (0.150 g, 0.214 mmol) and CuI (0.081 g, 0.427 mmol) were added as catalysts followed by the addition TMS-acetylene (0.504 g, 5.127 mmol). The resulting mixture was stirred overnight at RT. The solution was then filtered,

the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:EtOAc (14:1, $R_f = 0.38$) to yield the pure product (**3.2**). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.40$ (d, $J = 8.0$ Hz, 2H), 6.80 (d, $J = 8.0$ Hz, 2H), 3.76 (s, 3H), 0.26 (s, 9H).

3.3

1-ethynyl-4-methoxybenzene (3.3). Protected alkyne **3.2** (1 g, 4.89 mmol) was dissolved in 50 mL of THF:MeOH (1:1) and reacted with excess KF (0.85 g, 3 eq). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO_4 , filtered, and the solvent evaporated under reduce pressure to yield the pure product (**3.3**) in good yield (0.51 g, 79%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.43$ (d, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 8.0$, 2H), 3.81 (s, 3H), 3.00 (s, 1H).

3.4

1-methoxy-4-((4-nitrophenyl)ethynyl)benzene (3.4). 1-iodo-4-nitrobenzene (0.678 g, 2.72 mmol) was dissolved in 24 mL of THF: NEt_3 (1:1) and sparged with nitrogen for 15 minutes. $\text{PdCl}_2(\text{PPh}_3)_2$ (0.08 g, 0.113 mmol) and CuI (0.043 g, 0.227) were added as catalysts followed by the addition of terminal alkyne derivative **3.3** (0.30 g, 2.27 mmol). The mixture was stirred overnight at RT. The solution was filtered, the solvent removed from the filtrate, dissolved in

EtOAc, and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (2:1, R_f = 0.40) to give the product (**3.4**) as a fluffy yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 8.22 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 160.45, 146.70, 133.46, 131.99, 130.71, 123.63, 114.23, 114.13, 95.17, 86.66, 55.37.

3.7

2-iodo-1-methoxy-4-nitrobenzene (3.7). Powdered I_2 (5.47 g, 21.55 mmol) and KIO_4 (2.1492 g, 9.344 mmol) were added slowly portion wise to 95% H_2SO_4 (118 mL) and were stirred for 30 minutes at 30 °C to give a dark brown iodinating solution containing 1.1 equivalents of the I^+ intermediate. The mixture was added over a period of 45 minutes to a mixture of 4-nitroanisole (6.0 g, 39.18 mmol) in a minimal amount of sulfuric acid. The solution was stirred until the reaction was quenched (about 15 minutes). The reaction mixture was poured slowly into stirred ice water (1200 mL) and filtered using vacuum filtration. The crude solid was dried using a glass plug and then air dried in the dark. Recrystallization from MeOH yielded the product as a fluffy white solid (8.24 g, 75%). ^1H NMR (CDCl_3 , 400 MHz): δ = 8.67 (d, J = 2.68 Hz, 1H), 8.26 (dd, J = 2.68, 9.08 Hz, 1H), 6.86 (d, J = 9.08 Hz, 1H), 3.99 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 149.74, 139.98, 138.22, 126.41, 100.16, 87.59. HRMS (EI-TOF): m/z 374.8246, calcd for $\text{C}_6\text{H}_3\text{I}_2\text{NO}_2$: m/z 374.8253.

3.8

3-iodo-4-methoxyaniline (3.8). Nitrobenzene derivative **3.7** (4 g, 14.34 mmol) was dissolved in methanol (50 mL) in a 500 mL flask followed by the addition of a solution of NH_4Cl (3.83 g, 71.7

mmol) in water (40 mL) and powdered Fe (2.36 g, 42.2 mmol). The mixture was refluxed for 3.5 h. The precipitates formed were filtered off and the filtrate was evaporated until the MeOH was removed. After diluting with water and alkalisation with Na₂CO₃ the mixture was extracted with EtOAc. The organic layer was extracted with brine, water, and dried over MgSO₄. The solvent was evaporated in *vacuo*, and the residue was chromatographed using Hex: EtOAc (2:1, *R_f* = 0.40) to yield the product as a brown viscous liquid (3.68 g, 50%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.15 (d, *J* = 1.92 Hz, 1H), 6.68-6.62 (m, 2H), 3.79 (s, 3H), 3.42 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 151.59, 141.45, 126.18, 116.16, 112.46, 86.73, 57.10. HRMS (EI-TOF): *m/z* 374.8246, calcd for C₆H₃I₂NO₂: *m/z* 374.8253.

3.9

(*E*)-3,3-diethyl-1-(3-iodo-4-methoxyphenyl)triaz-1-ene (3.9). To a solution of aniline derivative **3.8** (3.0 g, 13.7 mmol) in concentrated HCl (35%, 17.7 mL) was added a solution of NaNO₂ (1.04 g, 15.07 mmol) in water (3.0 mL) at 0 °C. After stirring at 0°C for 30 min, the resulting mixture was added dropwise slowly at 0 °C to a suspension of K₂CO₃ (15.27 g, 110.51 mmol), diethylamine (1.49 g, 20.4 mmol), and water (55.5 mL). The reaction mixture was then warmed to room temperature and stirred for 1.5 hours. After extraction with EtOAc, the solvent was evaporated in *vacuo*, and the residue was chromatographed using hex: EtOAc (15:1, *R_f* = 0.42) to yield the product as orange/red liquid (4.78 g, 75%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.89 (d, *J* = 2.36 Hz, 1H), 7.35 (dd, *J* = 2.36, 8.72 Hz, 1H), 6.78 (d, *J* = 2.36, 8.72 Hz, 1H), 3.86 (s, 3H), 3.73 (q, *J* = 7.12 Hz, 4H), 1.25 (t, *J* = 7.12 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 155.72, 146.24, 130.59, 121.90, 110.80, 86.22, 56.65, 12.90. HRMS (EI-TOF): *m/z* 333.0331, calcd for C₁₁H₁₆IN₃O: *m/z* 333.0338

3.10

(*E*)-3,3-diethyl-1-(4-methoxy-3-((trimethylsilyl)ethynyl)phenyl)triaz-1-ene (3.10). Triazine derivative **3.9** (2.75 g, 8.25 mmol) was dissolved in THF:NEt₃ (138 mL, 2:1) in a 500 mL flask followed by the addition of PdCl₂(PPh₃)₂ (290 mg, 0.41 mmol), CuI (157 mg, 0.82 mmol), and TMS-acetylene (0.97 g, 9.90 mmol). The mixture was stirred overnight at RT. The solution was filtered, the solvent removed from the filtrate, re-dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex: EtOAc (15:1, *R_f* = 0.40) to yield the product as an orange viscous liquid (1.55 g, 70%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.53 (d, *J* = 2.40 Hz, 1H), 7.34 (dd, *J* = 2.40, 8.84 Hz, 1H), 6.81 (d, *J* = 8.84 Hz, 1H), 3.87 (s, 3H), 3.72 (q, *J* = 7.2 Hz, 4H), 1.24 (t, *J* = 7.2 Hz, 6H), 0.26 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 158.09, 144.62, 125.60, 122.30, 112.36, 110.99, 101.59, 97.96, 56.16, 12.87, 0.12. HRMS (EI-TOF): *m/z* 303.1762, calcd for C₁₆H₂₅N₃OSi: *m/z* 303.1767.

3.11

((5-iodo-2-methoxyphenyl)ethynyl)trimethylsilane (3.11). TMS-acetylene substituted triazine derivative **3.10** (1.0 g, 3.30 mmol) and methyl iodide (5 mL) were sealed in a heavy walled flask (microwave tube) and heated to 120 °C for 12 hours. The reaction mixture was quenched with water, extracted with DCM, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the crude was chromatographed using pure hexane (*R_f* = 0.65) to yield the product as yellow viscous liquid (0.97 g, 89%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.71 (d, *J* = 2.20 Hz, 1H), 7.53 (dd, *J* = 2.20, 8.76 Hz, 1H), 6.61 (d, *J* = 8.76 Hz, 1H), 3.83 (s, 3H), 0.26 (s, 9H). ¹³C NMR (CDCl₃,

100 MHz): δ = 160.21, 142.14, 138.56, 114.92, 112.85, 100.15, 99.44, 81.68, 55.97, -0.02. HRMS (EI-TOF): m/z 329.9932, calcd for $C_{12}H_{15}IOSi$: m/z 329.9937.

3.12

Attempted synthesis of 5-iodo-2-nitroaniline (3.12). The mixture of *t*-BuOK (5.63, 5 eq) and CuCl (0.1 g, 0.1 eq) ethylene glycol dimethylether (1,2-dimethoxyethane) (18.58 ml) is prepared at 0 °C under a nitrogen atmosphere. The 1-iodo-4-nitrobenzene (2.5 g, 1 eq) and $NH_2OBn \cdot HCl$ (2.56, 1.6 eq) was added in DMF (10 ml). To this the above DME solution mixture was added drop wise over 30 minutes at 0 °C. After completion of the addition, the cooling bath was removed and the contents stirred at RT for 6h. The completion of the reaction was monitored by TLC. The yellow coloured solid product was obtained after thorough purification with ice water. The solid was filtered and dried over vacuum. Purification was attempted by flash chromatography (using various solvent mixtures), a pure compound was never obtained. The starting material was recovered in high yield (~80%) which means the reaction never took place.

3.16

5-bromo-2-nitroaniline (3.16). To a solution of *t*-BuOK (11.80g, 4.25 eq) and Cu(I)Cl (0.25 g, 0.1 eq) in 1,2-dimethylethane (37.17 ml), stirred at 0 °C under nitrogen, a solution of 1-bromo-4-nitrobenzene (5.0 g, 1 eq) and $NH_2OMe \cdot HCl$ (1.08 g, 1.25 eq) in DMF (20 ml) were added dropwise over 103 min. The cooling bath was removed and the mixture was allowed to react at room temperature for 3h. The mixture was diluted with ethyl acetate (185.86 mL) and washed with saturated aqueous ammonium chloride. The organic layer was dried over $MgSO_4$, filtered, and the

solvent were removed *in vacuo*. Purification was tried by flash chromatography (using various solvent mixtures); however, a pure compound was never obtained. Most of the starting material was recovered at the end as in the case of its iodo-counterpart **3.12**.

3.17

2,4-diiodo-1-nitrobenzene (3.17). 1,3-diodobenzene (6.45 g, 19.55 mmol) was dissolved in HNO₃ (45 mL) in a 250 mL round bottom flask and the mixture was refluxed overnight. The resulting mixture was carefully poured into water and extracted with CH₂Cl₂. The organic extracts were washed successively with saturated NaHCO₃ solution, and brine. Drying over anhydrous MgSO₄ and removal of solvent gave a yellow fluffy solid that was purified by flash chromatography using Hex-EtOAc (15:1, *R_f* = 0.50) as the eluent to give the nitro derivative **b** as a crystalline yellow solid (7.04 g, 96%). ¹H NMR (CDCl₃, 400 MHz): δ = 8.43 (d, *J* = 1.8 Hz, 1H), 7.82 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ = 149.74, 139.98, 138.22, 126.41, 100.16, 87.59. HRMS (EI-TOF): *m/z* 374.8246, calcd for C₆H₃I₂NO₂: *m/z* 374.8253.

3.18

((3-iodo-4-nitrophenyl)ethynyl)trimethylsilane (3.18). 2,4-diiodo-nitrobenzene (**3.17**) (3.70 g, 9.88 mmol) was dissolved in THF:NEt₃ (116 mL, 2:1) in a 250 mL flask followed by the addition of PdCl₂(PPh₃)₂ (347 mg, 0.49 mmol), CuI (188 mg, 0.99 mmol) and TMS-acetylene (0.97 g, 9.88

mmol). The mixture was stirred overnight at RT. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:EtOAc (19:1, $R_f = 0.56$) to yield the product as an orange/yellow viscous liquid (1.19 g, 35%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.11$ (s, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 0.26 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 144.88, 132.07, 129.03, 125.15, 101.02, 100.97, 88.01, 86.02, -0.37$. HRMS (EI-TOF): m/z 344.9688 ($[\text{MH}]^+$), calcd for $\text{C}_{11}\text{H}_{12}\text{NO}_2\text{Si}$: m/z 344.9682.

3.19

10-(4-(*tert*-butyl)-2,6-bis((2-nitro-5-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (3.19). Compound **3.18** (887 mg, 2.569 mmol) was dissolved in 15 mL of THF: NEt_3 (2:1) and the mixture was sparged for 15 minutes. After 15 minutes, $\text{PdCl}_2(\text{PPh}_3)_2$ (36 mg, 0.051 mmol) and CuI (20 mg, 0.103 mmol) were added as catalysts followed by the addition of the BODIPY derivative **2.27** (383 mg, 1.028 mmol) and the mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (2:1, $R_f = 0.22$) to give the product as a dark red solid (105 mg, 13%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.97$ (s, 2H), 7.95 (s, 2H), 7.78 (s, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.16 (s, 2H), 6.90 (d, $J = 4.0$ Hz, 2H), 6.52 (d, $J = 4.0$ Hz, 2H), 1.45 (s, 9H), 0.31 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 153.50, 147.49, 144.82, 143.62, 138.57, 135.81, 135.49, 131.69, 131.12, 130.72, 128.85, 124.71, 123.24, 118.76, 118.21, 101.63, 101.00, 94.76$,

89.55, 35.03, 31.03, -0.36. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -144.48$ (q). ^{11}B NMR (CDCl_3 , 128 MHz): $\delta = 0.65$ (t, $J_{\text{FB}} = 28$ Hz). HRMS (ESI-TOF): m/z 829.26599 ($[\text{M}-\text{F}]^-$), calcd for $\text{C}_{45}\text{H}_{41}\text{O}_4\text{N}_4\text{BF}_2\text{Si}_2$: m/z 806.2727 (measured MS has an extra Na).

3.20

10-(4-(*tert*-butyl)-2,6-bis((5-ethynyl-2-nitrophenyl)ethynyl)phenyl)-5,5-difluoro-5H-4,5'-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (3.20). Compound **3.19** (100 mg, 0.124 mmol) was dissolved in MeOH:THF (4 mL, 1:1) and reacted with excess KF (36 mg, 0.620 mmol). The reaction was left to stir for 5 hours at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO_4 , filtered, and the solvent evaporated *in vacuo*. The residue was chromatographed using Hex: DCM (2:1, $R_f = 0.33$) as the eluent to give the product as a red viscous liquid (37 mg, 45%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.97$ (d, $J = 8.0$ Hz, 4H), 7.79 (s, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 2.0$ Hz, 2H), 6.52 (d, $J = 2.0$ Hz, 2H), 3.34 (s, 2H), 1.45 (s, 9H). HRMS (ESI-TOF): m/z 663.20400 ($[\text{M}+\text{H}]^+$), calcd for $\text{C}_{39}\text{H}_{26}\text{BF}_2\text{O}_4\text{N}_4$: m/z 663.20097.

3.21

10-(4-(*tert*-butyl)-2,6-bis((5-((4-methoxy-3-((trimethylsilyl)ethynyl)phenyl)ethynyl)-2-nitrophenyl)ethynyl)phenyl)-5,5-difluoro-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (3.21). BODIPY derivative **3.20** (144 mg, 0.386 mmol) and compound **3.11** (333 mg, 0.964 mmol) were dissolved in 13 mL of THF:NEt₃ (2:1) and the resulting mixture was sparged for 20 minutes. After the addition of catalysts, PdCl₂(PPh₃)₂ (18 mg, 0.0258 mmol) and CuI (10 mg, 0.052 mmol), the mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using pure toluene (*R_f* = 0.15) to give the product as a red solid (32.6 mg, 10.5%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.99 (s, 4H), 7.81 (s, 2H), 7.68 (m, 4H), 7.44 (m, 4H), 7.20 (s, 2H), 6.91 (d, *J* = 4.0 Hz, 4H), 6.62 (d, *J* = 2.0 Hz, 2H), 6.53 (d, *J* = 2.0 Hz, 2H), 3.93 (s, 6H), 1.46 (s, 9H), 0.27 (s, 18H) – In this spectrum, the protons were integrating for more than the desired number of protons which means the product was not pure. HRMS: No clear results for MS

3.22

10-(4-(*tert*-butyl)-2,6-bis((5-((4-methoxy-3-((trimethylsilyl)ethynyl)phenyl)ethynyl)-2-nitrophenyl)ethynyl)phenyl)-5,5-difluoro-5*H*-4 κ^4 ,5 κ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (3.22). Compound **3.21** (88 mg, 0.083 mmol) was dissolved in MeOH:THF (2 mL, 1:1) and reacted with excess KF (24 mg, 0.412 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered, and the solvent evaporated *in vacuo*. The residue was chromatographed using Hex: DCM (1:1) but no product was obtained. The following NMR data was obtained which proves that it was not the product. ¹H NMR (CDCl₃, 400 MHz): δ = 7.91 (d, *J* = 4.0 Hz, 2H), 7.56 (s, 2H), 7.18 (d, *J* = 4.0, 2H), 6.78 (d, *J* = 2.0 Hz, 2H), 6.46 (d, *J* = 2.0 Hz, 2H), 1.36 (s, 9H), -0.04 (s, 18H). ¹³C NMR (CDCl₃, 100 MHz): No data was obtained. ¹⁹F NMR (CDCl₃, 376.5 MHz,): No data was obtained. ¹¹B NMR (CDCl₃, 128 MHz): No data was obtained. HRMS; showed random peaks and no sign of product. Raw data (spectroscopic) is given in the appendices.

3.23

10-(4-(tert-butyl)-2,6-bis((2-nitro-5-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5H-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (3.23).

BODIPY derivative **2.36** (75 mg, 0.175 mmol) and compound **3.18** (121 mg, 0.350 mmol) were dissolved in 6 mL of THF:NEt₃ (2:1) and the resulting mixture was sparged under nitrogen for 15 minutes. After the addition of PdCl₂(PPh₃)₂ (6 mg, 0.009 mmol) and CuI (3 mg, 0.018 mmol), the mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (2:1, *R_f* = 0.31) to give the product as a red solid (22 mg, 13%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.96 (d, *J* = 8.0 Hz, 2H), 7.76 (s, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.28 (s, 2H), 6.00 (s, 2H), 2.61 (s, 2H), 1.53 (s, 2H), 1.42 (s, 9H), 0.28 (s, 18H). ¹³C NMR (CDCl₃, 100 MHz): δ = 147.50, 144.81, 138.57, 131.70, 131.13, 130.72, 128.85, 127.20, 124.71, 123.24, 118.73, 118.21, 101.63, 101.00, 94.76, 89.55, 77.21, 35.03, 31.21, 31.02, -0.37. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -145.48 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.56 (t, *J_{FB}* = 32 Hz). HRM (EI-TOF): *m/z* 862.3361 ([M-F]⁻), calcd for C₆₁H₅₁BFN₂Si₂: *m/z* 862.3353.

3.24

Synthesis of 3.24. Triazine derivative **3.9** (489 mg, 1.467 mmol) was dissolved in 10 mL of THF:NEt₃ (2:1) and the mixture was sparged for 15 minutes. PdCl₂(PPh₃)₂ (18 mg, 0.0258 mmol) and CuI (10 mg, 0.052 mmol) were added as catalysts followed by the addition of BODIPY **2.26** (218 mg 0.587 mmol). The mixture was stirred at RT for 6 hours. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:EtOAc (5:1, *R_f* = 0.35) to yield the

product as a red solid (96 mg, 21%). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.87 (s, 2H), 7.67 (s, 2H), 7.28 (d, J = 2.0 Hz, 2H), 7.20 (d, J = 2.0 Hz, 2H), 6.91 (d, J = 4.0 Hz, 2H), 6.74 (s, 1H), 6.71 (s, 1H), 6.45 (d, J = 4.0 Hz, 2H), 3.73 (q, J = 7.0, 7.0 Hz, 8H), 3.70 (s, 6H), 1.42 (s, 9H), 1.26 (t, J = 7.0 Hz, 12H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 157.85, 152.44, 144.64, 143.80, 135.99, 134.19, 131.21, 130.59, 129.30, 124.94, 124.30, 122.54, 118.11, 111.82, 110.93, 91.18, 90.84, 56.09, 34.87, 31.09, 30.91. ^{19}F NMR (CDCl_3 , 376.5 MHz): δ = -144.48 (q). ^{11}B NMR (CDCl_3 , 128 MHz): δ = 0.62 (t, J_{FB} = 29 Hz). HRMS: No data was obtained.

3.25

((5-((3-azidophenyl)ethynyl)-2-methoxyphenyl)ethynyl)trimethylsilane compound with butane (1:1) (3.25). To a mixture of compound **3.11** (1.00 g, 3.028 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.106 g, 0.151 mmol) and CuI (0.058 mg, 0.303 mmol) in $\text{THF}:\text{NEt}_3$ (15 mL, 2:1) was added **2.12** (0.735 g, 3.634 mmol). The mixture was stirred at room temperature for 3 hours. The solution was filtered, the solvent was removed from the filtrate, dissolved in EtOAc and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was removed *in vacuo*, and the residue was chromatographed using $\text{Hex}:\text{EtOAc}$ (9:1, R_f = 0.5) to give the product as a yellow viscous liquid (1.232 g, 94%). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.63 (d, J = 2.0 Hz, 1H), 7.56 (s, 1H), 7.45 (dd, J = 2.0, 8.5 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 3.90 (s, 3H), 3.77 (q, J = 7.0 Hz, 4H), 1.27 (t, J = 7.0 Hz, 6H), 0.27 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 160.06, 151.20, 137.40, 133.28, 128.75, 128.01, 123.64, 123.23, 120.79, 115.66, 112.69, 110.71, 100.29, 99.12, 88.89, 87.88, 55.99, 0.03. HRMS (EI-TOF): m/z 403.2069 ($[\text{MH}]^+$), calcd for $\text{C}_{24}\text{H}_{29}\text{N}_3\text{OSi}$: m/z 403.2080.

3.26

((5-((3-iodophenyl)ethynyl)-2-methoxyphenyl)ethynyl)trimethylsilane (3.26). Compound **3.25** (1.469 g, 3.641 mmol) and MeI (5.0 mL) were sealed in a heavy walled microwave vial and heated to 120 °C for 8 h. The reaction mixture was cooled and quenched with water; extracted with DCM, dried with MgSO₄, and filtered. The solvent was removed *in vacuo* and the pure product was isolated by column chromatography using Hex:EtOAc (9:1, *R_f* = 0.30) to yield a product as light yellow liquid (1.285 g, 82%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.86 (s, 1H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.44 (t, *J* = 7.0 Hz, 2H), 7.06 (t, *J* = 7.0 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 3H), 0.28 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 160.40, 140.03, 137.44, 137.06, 133.33, 130.54, 129.85, 125.48, 114.91, 112.87, 110.78, 100.11, 99.38, 93.72, 89.87, 86.81, 56.01, 0.05. HRMS (EI-TOF): *m/z* 430.0240 ([MH]⁺), calcd for C₂₀H₁₉OISi: *m/z* 430.0250.

3.27

10-(4-(tert-butyl)-2,6-bis((3-((4-methoxy-3-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-5H-4H,5H-tetrahydro-1,2,4-triazole

dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (3.27). To a solution of BODIPY derivative **2.27** (300 mg, 0.806 mmol) in 15 mL of THF:NEt₃ (2:1), Pd(PPh₃)₄ (93 mg, 0.081 mmol) and CuI (31 mg, 0.161 mmol) were added as catalysts followed by the addition of 763 mg (1.773 mmol) of TMS-protected iodo-derivative **3.26**. The mixture was stirred at RT for 6 hours. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (1:1, *R_f* = 0.44) to give the product as a red solid (394 mg, 50%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.97 (s, 2H), 7.67 (s, 2H), 7.61 (s, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.37 (m, 4H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.92 (d, 4.0 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 4.0 Hz, 2H), 3.91 (s, 6H), 1.44 (s, 9H), 0.27 (s, 18H). ¹³C NMR (CDCl₃, 100 MHz): δ = 160.27, 152.96, 144.48, 137.39, 134.29, 133.42, 131.45, 131.24, 129.23, 128.46, 123.63, 122.76, 112.76, 110.79, 100.18, 99.26, 93.99, 89.10, 87.73, 87.54, 77.22, 56.01, 34.94, 31.07, 0.02. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -145.44 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.47 (t, *J_{FB}* = 28 Hz). HRMS (ESI-TOF): *m/z* 977.39260 ([M+H]⁺), calcd for C₆₃H₅₆BF₂N₂O₂: *m/z* 977.39360.

3.28

10-(4-(tert-butyl)-2,6-bis((3-((3-ethynyl-4-methoxyphenyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-5H-4^κ,5^κ-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (3.28). Compound **3.27** (390 mg, 0.399 mmol) was dissolved in MeOH:THF (8.0, 1:1 mL) and reacted with excess KF (116 mg, 1.998 mmol). The reaction was left to stir for 2.5 hours at RT. The reaction mixture was poured into water and extracted with DCM. The organic layer was dried over MgSO₄, filtered, and

the solvent evaporated *in vacuo*. The residue was chromatographed using Hex: DCM (1:2, R_f = 0.43) as the eluent to give the product as a red viscous liquid (82 mg, 25%). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.97 (s, 2H), 7.67 (s, 2H), 7.63 (d, J = 2.0 Hz, 2H), 7.51 (dd, J = 2.0, 9.0 Hz, 2H) 7.37 (d, J = 9.0 Hz, 2H), 7.34 (s, 2H), 7.20 (t, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 4.0 Hz, 2H), 6.89 (d, J = 8.0, 2H), 6.50 (d, J = 4.0 Hz, 2H), 3.93 (s, 6H), 3.32 (s, 2H), 1.44 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 160.55, 152.98, 144.49, 137.30, 134.37, 133.79, 131.46, 131.26, 131.13, 129.21, 128.47, 123.74, 123.55, 122.65, 115.36, 111.67, 110.81, 93.98, 88.90, 87.76, 81.66, 79.11, 77.21, 56.05, 34.95, 31.07. ^{19}F NMR (CDCl_3 , 376.5 MHz): δ = -145.43 (q). ^{11}B NMR (CDCl_3 , 128 MHz): δ = 0.48 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): m/z 833.31819 ($[\text{M}+\text{H}]^+$), calcd for $\text{C}_{57}\text{H}_{40}\text{BF}_2\text{N}_2\text{O}_2$: m/z 833.31454.

3.29

Modified BODIPY-macrocycle 3.29. BODIPY pre-macrocycle **3.28** (82 mg, 0.098 mmol) was dissolved in THF: NEt_3 (98 mL, 2:1) and sparged with N_2 for 30 minutes. $\text{PdCl}_2(\text{PPh}_3)_2$ (34 mg, 0.049 mmol) and CuI (19 mg, 0.098 mmol) were added as catalysts and the mixture was stirred at RT for 34 hours. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (1:1, R_f = 0.29) to give the product as a dark red solid (19 mg, 23%). ^1H NMR (CDCl_3 , 400 MHz): δ = 8.12 (s, 2H), 8.10 (s, 2H), 7.68 (s, 2H), 7.38 (dd, J = 4 Hz, 8Hz, 2H), 7.33 (s, 2H), 7.31 (s, 2H), 7.23 (t, J = 8 Hz, 2H), 7.10 (s, 2H), 6.94 (d, J = 4.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 6.49 (s, 2H), 3.93 (s, 6H), 1.45 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 159.91, 152.89, 144.76, 141.90, 137.05, 135.61, 131.94, 131.02, 129.87, 129.57, 129.09, 128.19, 123.96, 123.82, 122.71, 118.57, 112.48, 110.73, 94.04, 89.80, 88.37, 88.07, 79.60, 78.93, 77.22, 56.03, 34.94,

31.08. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -145.86$ (q). ^{11}B NMR (CDCl_3 , 128 MHz): $\delta = 0.71$ (t, $J_{\text{FB}} = 28$ Hz). HRMS (ESI-TOF): m/z 811.29202 ($[\text{M}-\text{F}]^-$), calcd for $\text{C}_{57}\text{H}_{37}\text{BFN}_2\text{O}_2$: m/z 811.29266.

3.30

2-azido-4-iodo-1-methoxybenzene compound with butane (1:1) (3.30). To a solution of 5-iodo-2-methoxyaniline (1.0 g, 4.570 mmol) in concentrated HCl (35%, 6 mL) was added a solution of NaNO_2 (0.35 g, 5.02 mmol) in water (1.0 mL) at 0°C . After stirring at 0°C for 30 min, the resulting mixture was added dropwise slowly at 0°C to a suspension of K_2CO_3 (5.09 g, 36.84 mmol), diethylamine (0.5 g, 6.80 mmol), and water (18 mL). The reaction mixture was then warmed to room temperature and stirred for 1.5 hours. After extraction with EtOAc, the solvent was evaporated *in vacuo*, and a pure product was obtained as a brown viscous liquid (1.31 g, 86%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.58$ (d, $J = 2.4$ Hz, 1H), 7.37 (dd, $J = 2.4, 8.8$, 1H), 6.67 (d, $J = 8.8$, 1H), 3.86 (s, 3H), 3.78 (q, $J = 7.12$, 4H), 1.28 (t, $J = 7.12$, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 153.06, 142.41, 134.20, 127.18, 114.52, 83.84, 56.44, 14.11, 12.20$. HRMS (EI-TOF): m/z 333.0332, calcd for $\text{C}_6\text{H}_3\text{I}_2\text{NO}_2$: m/z 333.0338.

3.31

((3-azido-4-methoxyphenyl)ethynyl)trimethylsilane compound with butane (1:1) (3.31).

Triazine derivative **3.30** (1.31 g, 3.932 mmol) was dissolved in THF:NEt₃ (12 mL, 2:1) in a 100 mL flask and was sparged for 15 minutes followed by the addition of PdCl₂(PPh₃)₂ (0.138 g, 0.197 mmol), CuI (0.075 mg, 0.393 mmol) and TMS-acetylene (0.463 g, 4.718 mmol). The mixture was stirred overnight at RT. The solution was filtered, the solvent removed from the filtrate, re-dissolved in EtOAc, and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:EtOAc (15:1, *R_f* = 0.25) to yield the product as light brown viscous liquid (1.10 g, 92%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.39 (d, *J* = 2.0 Hz, 1H), 7.22 (dd, *J* = 2.0, 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 3.78 (q, *J* = 7.12, 7.12, 4H), 1.27 (t, *J* = 7.12, 6H), 0.23 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 153.52, 144.46, 140.64, 129.80, 122.21, 115.40, 111.79, 105.64, 91.95, 56.22, 30.90, 0.10. HRMS (EI-TOF): *m/z* 303.1762, calcd for C₁₆H₂₅N₃OSi: *m/z* 303.1767.

3.32

2-azido-4-ethynyl-1-methoxybenzene compound with butane (1:1) (3.32). The TMS-protected alkyne **3.31** (1.10 g, 3.625 mmol) was dissolved in MeOH (7 mL) and THF (7 mL) and stirred with excess KF (0.63 g, 10.874 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over MgSO₄, filtered and the solvent evaporated *in vacuo*. The residue was chromatographed using Hex:EtOAc (9:1, *R_f* = 0.41) as the eluent to give the product (0.641 g, 76%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.44 (d, *J* = 2.0 Hz, 1H), 7.25 (dd, *J* = 1.6, 8.2 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 3.76 (q, *J* = 7.2 Hz, 4H), 2.98 (s, 1H), 1.27 (t, *J* = 6.0 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 153.69, 140.78, 129.85, 122.33, 114.32, 111.98, 84.07, 75.38, 56.25, 12.86. HRMS (EI-TOF): *m/z* 231.1380, calcd for C₁₃H₁₇N₃O: *m/z* 231.1372.

3.33

((3-((3-azido-4-methoxyphenyl)ethynyl)phenyl)ethynyl)trimethylsilane compound with butane (1:1) (3.33). To a mixture of compound **2.13** (1.00 g, 3.331 mmol) in THF:NEt₃ (15 mL, 2:1), PdCl₂(PPh₃)₂ (0.117 g, 0.167 mmol) and CuI (0.063 g, 0.333 mmol) catalysts were added followed by the addition of **3.32** (0.925 g, 3.997 mmol). The mixture was stirred at room temperature for 10 hours. The solution was filtered, the filtrate was dissolved in EtOAc and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was removed *in vacuo*, and the residue was chromatographed using Hex:EtOAc (9:1, *R_f* = 0.31) to give the product as a light yellow viscous liquid (1.236 g, 92%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.63 (s, 1H), 7.45 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.27 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 3.81 (q, *J* = 7.0 Hz, 4H), 1.29 (t, *J* = 7.0 Hz, 6H), 0.25 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 153.51, 140.84, 134.89, 131.36, 131.13, 129.39, 128.25, 124.01, 123.36, 121.87, 115.26, 112.05, 104.32, 94.73, 90.47, 86.87, 56.28, -0.07. HRMS (EI-TOF): *m/z* 403.2088 ([MH]⁺), calcd for C₂₄H₂₉N₃OSi: *m/z* 403.2080.

3.34

((3-((3-iodo-4-methoxyphenyl)ethynyl)phenyl)ethynyl)trimethylsilane (3.34). Compound **3.33** (1.163 g, 2.883 mmol) and MeI (5.0 mL) were sealed in a heavy walled microwave vial under nitrogen and heated to 120 °C for 12 h. The reaction mixture was cooled and quenched with water; extracted with DCM, dried with MgSO₄ and filtered. The solvent was removed *in vacuo* and the pure product was isolated by column chromatography using Hex:EtOAc (9:1, *R_f* = 0.63) to yield the product as a yellowish liquid (1.154 g, 93%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.97 (s, 1H), 7.62 (s, 1H), 7.48-7.40 (m, 3H), 7.29-7.25 (m, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 0.25 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 158.36, 142.40, 134.93, 133.00, 131.51, 131.33, 128.34, 123.50, 123.42, 117.20, 104.12, 94.98, 88.22, 85.52, 56.45, -0.09. HRMS (EI-TOF): *m/z* 430.0248 ([MH]⁺), calcd for C₂₀H₁₉OISi: *m/z* 430.0250.

3.35

10-(4-(tert-butyl)-2,6-bis((2-methoxy-5-((3-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-5H-4,4',5,5'-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (3.35). To a solution of BODIPY derivative **2.27** (300 mg, 0.806 mmol) in 12 mL of THF:NEt₃ (2:1), PdCl₂(PPh₃)₂ (57 mg, 0.081 mmol) and CuI (31 mg, 0.161 mmol) were added as catalysts followed by the addition of 763 mg (1.773 mmol) of TMS-protected iodo-derivative **3.34**. The mixture was stirred at RT for 12 hours. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (1:1, *R_f* = 0.52) to give the product as a red solid (200 mg, 25%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.94 (s, 2H), 7.68

(s, 2H), 7.47 (d, $J = 7.0$ Hz, 2H), 7.41-7.35 (m, 4H), 7.29-7.26 (m, 4H), 6.91 (d, $J = 4.0$ Hz, 2H), 6.74 (d, $J = 9.0$ Hz, 2H), 6.48 (d, $J = 4.0$ Hz, 2H), 3.73 (s, 6H), 1.44 (s, 9H), 0.26 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 160.00, 144.07, 136.90, 134.88, 133.38, 131.45, 131.34, 131.16, 129.41, 128.34, 123.70, 123.41, 115.13, 112.15, 110.69, 94.83, 91.61, 90.03, 89.01, 87.60, 77.21, 55.90, 34.92, 31.08, -0.08$. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -144.75$ (q). ^{11}B NMR (CDCl_3 , 128 MHz): $\delta = 0.45$ (t, $J_{\text{FB}} = 28$ Hz). HRMS (ESI-TOF): m/z 977.39111 ($[\text{M}+\text{H}]^+$), calcd for $\text{C}_{63}\text{H}_{56}\text{BF}_2\text{N}_2\text{O}_2$: m/z 977.39360.

3.36

10-(4-(tert-butyl)-2,6-bis((5-((3-ethynylphenyl)ethynyl)-2-methoxyphenyl)ethynyl)phenyl)-5,5-difluoro-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (3.36). Compound **3.35** (200 mg, 0.205 mmol) was dissolved in MeOH:THF (6.0, 1:1 mL) and reacted with excess KF (59 mg, 1.023 mmol). The reaction was left to stir for 2 hours at RT. The reaction mixture was poured into water and extracted with DCM. The organic layer was dried over MgSO_4 , filtered, and the solvent evaporated *in vacuo*. The residue was chromatographed using Hex:DCM (1:2, $R_f = 0.57$) as the eluent to give the product as a red sticky solid (103 mg, 61%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.95$ (s, 2H), 7.69 (s, 2H), 7.64 (s, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.37 (dd, $J = 2.5, 8.5$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 2.5$ Hz, 2H), 6.91 (d, $J = 4.0$ Hz, 2H), 6.75 (d, $J = 8.5$ Hz, 2H), 6.49 (d, $J = 4.0$ Hz, 2H), 3.74 (s, 6H), 3.09 (s, 2H), 1.44 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 160.01, 152.72, 144.11, 136.97, 134.94, 133.40, 131.82, 131.57, 131.16, 129.38, 128.46, 123.99, 123.85, 122.41, 115.06, 112.16, 110.69, 91.64, 90.05, 89.17, 87.45, 82.89, 77.67, 77.21, 55.91, 34.93, 31.08$. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -144.77$ (q).

^{11}B NMR (CDCl_3 , 128 MHz): $\delta = 0.46$ (t, $J_{\text{FB}} = 28$ Hz). HRMS (ESI-TOF): m/z 813.30798 ($[\text{M}-\text{F}]^-$), calcd for $\text{C}_{57}\text{H}_{39}\text{BFN}_2\text{O}_2$: m/z 813.30831.

3.37

Modified BODIPY-macrocycle 3.37. BODIPY pre-macrocycle **3.36** (103 mg, 0.124 mmol) was dissolved in $\text{THF}:\text{NEt}_3$ (124 mL, 2:1) and sparged with N_2 for 30 minutes. $\text{PdCl}_2(\text{PPh}_3)_2$ (44 mg, 0.062 mmol) and CuI (24 mg, 0.124 mmol) were added as catalysts and the mixture was stirred at RT for 32 hours. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc , and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using Hex:DCM (1:1, $R_f = 0.35$) to give the product as a red solid (25 mg, 24%). ^1H NMR CDCl_3 , 400 MHz): $\delta = 8.11$ (m, 4H), 7.71 (s, 2H), 7.40- 7.33 (m, 6H), 7.30 (t, $J = 4.0$ Hz, 2H), 7.06 (d, $J = 2.0$ Hz, 2H), 6.94 (d, $J = 4.0$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 2H), 6.49 (d, $J = 4.0$ Hz, 2H), 3.92 (s, 6H), 1.44 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 159.17$, 144.58, 139.81, 139.13, 129.96, 129.19, 128.31, 124.08, 123.87, 122.59, 115.58, 112.18, 110.35, 92.01, 90.32, 89.75, 88.23, 82.56, 75.13, 55.95, 34.97, 31.08. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -145.90$ (q). ^{11}B NMR (CDCl_3 , 128 MHz): $\delta = 0.70$ (t, $J_{\text{FB}} = 28$ Hz). HRMS (ESI-TOF): m/z 811.29349 ($[\text{M}-\text{F}]^-$), calcd for $\text{C}_{57}\text{H}_{37}\text{BFN}_2\text{O}_2$: m/z 811.29266.

3.38

((5-((3-azido-4-methoxyphenyl)ethynyl)-2-methoxyphenyl)ethynyl)trimethylsilane

compound with butane (1:1) (3.38). To a mixture of compound **3.11** (0.85 g, 2.574 mmol) in THF:NEt₃ (12 mL, 2:1) was added **3.32** (0.655 g, 2.831 mmol) and the mixture was sparged for 20 minutes. Catalysts, PdCl₂(PPh₃)₂ (0.090 g, 0.129 mmol) and CuI (0.049 g, 0.257 mmol), were added and the mixture was stirred at room temperature for 11 hours. The solution was filtered, the solvent removed from the filtrate, redissolved in EtOAc and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was removed *in vacuo*, and the residue was chromatographed Hex:AcOEt (9:1, R_f = 0.29) to give the product as a off-white solid (0.74 g, 66%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.61 (s, 1H), 7.44 (s, 1H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.79 (q, *J* = 7.0 Hz, 4H), 1.28 (t, *J* = 7.0 Hz, 6H), 0.27 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 159.87, 153.30, 140.82, 137.22, 133.12, 129.21, 121.72, 115.96, 115.62, 112.63, 112.09, 110.72, 100.39, 99.00, 88.86, 86.69, 56.29, 55.96, 12.88, 0.04. HRMS (EI-TOF): *m/z* 433.2190, calcd for C₂₅H₃₁N₃O₂Si: *m/z* 433.2186.

3.39

((5-((3-iodo-4-methoxyphenyl)ethynyl)-2-methoxyphenyl)ethynyl)trimethylsilane (3.39).

Compound **3.38** (0.74 g, 1.707 mmol) and MeI (3.5 mL) were sealed in a heavy walled microwave vial and heated to 120°C for 8 h. The reaction mixture was cooled and quenched with water; extracted with DCM, dried with MgSO₄ and filtered. The solvent was removed *in vacuo* and the pure product was isolated by column chromatography using Hex:EtOAc (9:1, *R_f* = 0.38) to yield the product as white fluffy solid (0.676 g, 86%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.93 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.44 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.41 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 6H), 0.27 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 160.13, 158.11, 142.24, 137.28, 133.12, 132.79, 117.58, 115.33, 112.78, 110.75, 110.44, 100.19, 99.23, 88.12, 86.69, 85.49, 56.43, 55.99, 0.02. HRMS (EI-TOF): *m/z* 460.0361, calcd for C₂₁H₂₁O₂Si: *m/z* 460.0356.

10-(4-(tert-butyl)-2,6-bis((2-methoxy-5-((4-methoxy-3-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)-5,5-difluoro-5H-414,514-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (3.40). BODIPY derivative **2.27** (220 mg, 0.591 mmol) was dissolved in 9 mL of THF:NEt₃ (2:1) and sparged for 20 minutes followed by the addition was Pd(PPh₃)₄ (68 mg, 0.059 mmol), CuI (23 mg, 0.118 mmol) and compound **3.39** (680 mg, 1.478). The mixture was stirred at RT for 6 hours. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc and washed with an NH₄Cl solution. The extract was then washed with brine, dried over MgSO₄, and filtered. The solvent was evaporated *in vacuo*,

and the residue was chromatographed using Hex:DCM (1:3, R_f = 0.40) to give the product as a red solid (360 mg, 59%). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.94 (s, 2H), 7.68 (s, 2H), 7.61 (d, J = 2.5 Hz, 2H), 7.46 (dd, J = 2.5, 8.5 Hz, 2H), 7.34 (dd, J = 2.5, 8.5 Hz, 2H), 7.28-7.24 (m, 2H), 6.91 (d, J = 4.0 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 6.48 (d, J = 4.0 Hz, 2H), 3.89 (s, 6H), 3.72 (s, 6H), 1.44 (s, 9H), 0.28 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 160.02, 159.76, 152.69, 144.97, 144.09, 137.20, 136.75, 133.28, 133.18, 129.38, 124.05, 115.64, 115.51, 112.67, 112.08, 110.82, 110.69, 100.36, 99.09, 91.56, 90.16, 87.49, 77.25, 55.99, 55.88, 31.09, 0.05. ^{19}F NMR (CDCl_3 , 376.5 MHz): δ = -145.23 (q). ^{11}B NMR (CDCl_3 , 128 MHz): δ = 0.65 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): m/z 1036.40987 ($[\text{M}-\text{F}]^-$), calcd for $\text{C}_{65}\text{H}_{59}\text{BF}_2\text{N}_2\text{O}_4\text{Si}_2$: m/z 1036.40690.

3.41

10-(4-(tert-butyl)-2,6-bis((5-((3-ethynyl-4-methoxyphenyl)ethynyl)-2-methoxyphenyl)ethynyl)phenyl)-5,5-difluoro-5H-4,5-dipyrrolo[1,2-c:2',1'-

f][1,3,2]diazaborinine (3.41). Compound **3.40** (353 mg, 0.341 mmol) was dissolved in MeOH:THF (7 mL, 1:1) and reacted with excess KF (99 mg, 1.704 mmol). The reaction was left to stir for 2 hours. The reaction mixture was poured into water and extracted with DCM. The organic layer was dried over MgSO_4 , filtered and the solvent evaporated *in vacuo*. The residue was chromatographed using Hex:DCM (1:3, R_f = 0.30) as the eluent to give the product as a red viscous liquid (100 mg, 28%). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.94 (s, 2H), 7.68 (s, 2H), 7.62 (d, J = 2.0 Hz, 2H), 7.51 (dd, J = 2.0, 8.5 Hz, 2H), 7.35 (dd, J = 2.0, 8.5 Hz, 2H), 7.26 (s, 2H), 6.91-6.87 (m, 4H), 6.73 (d, J = 8.5 Hz, 2H), 6.48 (d, J = 2.0 Hz, 2H), 3.93 (s, 6H), 3.73 (s, 6H), 3.31 (s, 2H), 1.43 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 160.29, 159.77, 152.69, 144.09, 137.10, 136.82, 135.95, 133.63, 133.19, 131.16, 129.36, 124.02, 118.34, 115.83, 115.42, 112.10, 111.57, 110.81,

110.67, 91.58, 90.14, 87.63, 87.29, 81.53, 79.24, 56.03, 55.89, 34.92, 31.08. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -144.76$ (q). ^{11}B NMR (CDCl_3 , 128 MHz): $\delta = 0.63$ (t, $J_{\text{FB}} = 30$ Hz). HRMS (ESI-TOF): m/z 893.33438 ($[\text{M}+\text{H}]^+$), calcd for $\text{C}_{59}\text{H}_{44}\text{BF}_2\text{N}_2\text{O}_4$: m/z 893.33567.

3.42

Modified BODIPY-macrocycle 3.42. BODIPY pre-macrocycle **3.41** (93 mg, 0.104 mmol) was dissolved in $\text{THF}:\text{NEt}_3$ (105 mL, 2:1) and sparged with N_2 for 45 minutes. $\text{PdCl}_2(\text{PPh}_3)_2$ (8.3 mg, 0.012 mmol) and CuI (4.5 mg, 0.024 mmol) were added as catalysts and the mixture was stirred at RT for 21 hours. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc , and washed with an NH_4Cl solution. The extract was then washed with brine, dried over MgSO_4 , and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using $\text{Hex}:\text{DCM}$ (1:2, $R_f = 0.26$) to give the product as a dark red solid (21 mg, 23%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 8.10$ (s, 2H), 8.05 (d, $J = 2.0$ Hz, 2H), 7.70 (s, 2H), 7.36 (dd, $J = 2.0, 8.5$ Hz, 2H), 7.31 (dd, $J = 2.0, 8.5$ Hz, 2H), 7.03 (d, $J = 2.0$ Hz, 2H), 6.93 (d, $J = 4.0$ Hz, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 6.76 (d, $J = 8.5$ Hz, 2H), 6.48 (d, $J = 4.0$ Hz, 2H), 3.92 (s, 6H), 3.91 (s, 6H), 1.44 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 159.51, 158.84, 152.66, 144.62, 141.53, 138.79, 135.20, 131.55, 131.09, 129.21, 128.95, 128.92, 128.91, 123.89, 118.50, 116.16, 116.00, 112.36, 112.10, 110.67, 110.31, 91.94, 90.40, 88.16, 88.13, 79.74, 78.86, 56.00, 55.92, 34.96, 31.06$. ^{19}F NMR (CDCl_3 , 376.5 MHz): $\delta = -145.84$ (q). ^{11}B NMR (CDCl_3 , 128 MHz): $\delta = 0.87$ (t, $J_{\text{FB}} = 28$ Hz). HRMS (ESI-TOF): m/z 890.31413 ($[\text{M}+\text{H}]^+$), calcd for $\text{C}_{59}\text{H}_{41}\text{BF}_2\text{N}_2\text{O}_4$: m/z 890.31220.

Chapter 4: Functionalizing BODIPY Dyes for DSSC Applications

4.1. Introduction

Ultimately, this research sought to develop a dye suitable for light-harvesting applications. To this end, a BODIPY-phenylacetylene macrocycle could be appended with a donor (*e.g.* triphenylamine) and accepting group (*e.g.* cyanoacetic acid groups derived from aldehydes), allowing it to effectively integrate into the DSSC. The donor groups could be added to the aforementioned family of dyes in a variety of ways, and two strategies are depicted in Figure 4.1.

Figure 4.1. Proposed design for the attachment of donor groups to the BODIPY-phenylacetylene macrocycle; a) donor (D) and acceptor (A) groups are attached to BODIPY, b) D and A attached to macrocycle

In the pursuit of these modified dyes, a number of small benchmark compounds were prepared. As the synthesis of a BODIPY-phenylacetylene macrocyclic dye was not realized, the information collated here will be of value for future DSSC dye design, as it builds on the Koivisto group's previous work towards dye design (Figure 4.2).⁹⁰ It should also be noted that this work was conducted concurrently to macrocycle synthesis, and as such it was performed in anticipation of integrating these building blocks into the previously discussed macrocyclic scaffolds.

Figure 4.2. Using BODIPY as a π -spacer with donor and acceptor groups for DSSC applications

This chapter describes supplementary syntheses, physicochemical characterization of compounds indirectly related to the objectives of this thesis. This chapter is divided into three sections. Section 4.2.1 describes the attempts to make DSSC dyes using BODIPYs as π -spacers. These attempts were not performed on BODIPY-macrocycle **2.31** but were explored using simpler π -spacers. Section 4.2.2 describes the synthesis of *meso*-substituted BODIPYs by putting electron donating groups on both the methylated-BODIPY (tetra-methyl BODIPY) and unsubstituted BODIPY. Additionally, the physicochemical properties of *meso*-substituted BODIPYS were studied and are discussed in 4.3 (results and discussion). In addition, section 4.2.3 describes electrophilic addition reactions in the presence of BODIPY alkyne species.

followed by electrophilic aromatic substitution (bromination) to yield **4.2**. Lithiation of **4.2** and quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane gave boronic ester **4.3** which serves as a suitable precursor (to be used later) for a Suzuki coupling reaction.

Scheme 4.2. Synthesis of donor chromophore **4.3**

To test this retrosynthetic methodology (Scheme 4.1), before reacting on the BODIPY-phenylacetylene macrocycle π -spacer, a trial was performed using a simpler BODIPY (Scheme 4.3).⁹⁰ For this purpose, pentamethyl BODIPY **4.4** was made from acetyl chloride and iodinated to yield **4.5** as shown in Scheme 4.5. The reaction of iodo-BODIPY **4.5** with **4.3** through a Suzuki cross-coupling reaction yielded **4.6**. The next two steps involve the formylation of **4.6** to yield **4.7** and the addition of a cyanoacetic acid anchor group using a Knoevenagel condensation reaction to give the D- π -A dye motif **4.8**.

Scheme 4.3. Synthesis of DSSC dye **4.8** with a with D- π -A dye motif

Although dye **4.8** was already reported in literature,⁹⁰ it was resynthesized as a benchmark compound for this thesis. This exercise also aided in becoming familiar with the challenges involved in the synthesis of BODIPY dyes.

In anticipation of a U-shape Sonogashira coupling (see section 2.2.4), building block **2.9** was converted into **4.10** (Scheme 4.4). The first step was the substitution of one side of the BODIPY with an aldehyde *via* a Vilsmeier-Haack reaction to yield **4.9**. The electrophilic addition reaction was done to get the iodo derivative of **4.10**. Iodo-BODIPY derivative **4.10** was then reacted with **4.3** *via* a Suzuki cross-coupling reaction to incorporate the donor group on BODIPY

(**4.11**) but this reaction failed to yield the desired product. It was assumed that this failure could be due to competitive reactions with two other iodo groups on the phenyl ring located at the *meso*-position of BODIPY **4.10**.

Scheme 4.4. Synthesis of aldehyde derivative **4.10** as a precursor to D- π -A dye motif

In order to minimize wasting important building blocks, the above failed reaction was further investigated using a simple phenyl ring at the *meso*-position (**4.12**). BODIPY **4.12** was synthesized from benzaldehyde and 2,4-dimethyl-1*H*-pyrrole. BODIPY **4.12** was then formylated to **4.13** followed by iodination to yield **4.14**. Iodo- BODIPY **4.14** was then reacted with donor unit **4.3** to yield **4.15**. Again, the Suzuki cross-coupling reaction failed to yield **4.15**. This result was discouraging as it was counter to our previous iodide hypothesis. At this point, this particular protocol was abandoned owing to concurrent breakthroughs in macrocycle synthesis (see section 2.2.6 and 2.2.10).

Scheme 4.5. Synthesis of BODIPY-aldehyde with phenyl group at *meso*-position (**4.15**)

Another possible strategy is to perform the iodination and the Suzuki cross-coupling reaction before the formyl group is appended to BODIPY. Although, this route was never pursued, a proposed synthetic scheme (similar to retrosynthesis) for the synthesis of DSSC dye is given in Scheme 4.6.

a BODIPY having donor (D) substituted at the *meso*-position as an electron donating group is shown in Figure 4.3.

Figure 4.3. A cartoon **a)** showing a donor (**D**) substituted at the *meso*-substitution of BODIPY and how this building block is a subset of dye scaffold **b)** and generic structures of unsubstituted-BODIPY (**c**) and methylated-BODIPY (**d**) where the donor is attached as R.

BODIPYs (Figure 4.3) were made using appropriate benzaldehydes, most of which were commercially available except 4-(*bis*(4-methoxyphenyl)amino)benzaldehyde (**4.16**) which was synthesized according to Scheme 4.7.

Scheme 4.7. Synthesis of benzaldehyde **4.16**

Scheme 4.8 summarizes the synthesis of various unsubstituted-BODIPYs having R groups at the *meso*-position. Similar reaction conditions were in each case and exceptions and differences are reported in the experimental section. Physicochemical properties for these donor BODIPY building blocks are highlighted in Section 4.3.

Scheme 4.8. Synthesis of unsubstituted-BODIPYs from their respective aldehydes and unsubstituted pyrrole

Likewise, Scheme 4.9 shows the synthesis of various methylated-BODIPYs starting with the appropriate aldehydes and 2,4-dimethyl-1*H*-pyrrole. The same reagents were used for all of the BODIPYs. Also, similar reaction conditions were used, unless otherwise stated in the experimental section. Physicochemical properties for these donor BODIPY building blocks are highlighted in Section 4.3.

Scheme 4.9. Synthesis of methylated-BODIPYs from their respective aldehydes and 2,4-dimethyl-1H-pyrrole.

4.2.3. Iodination and Formylation on the 2,6-positions of *meso*-substituted BODIPYs

One serious concern was whether the phenylacetylene portion of the macrocycle would be able to tolerate electrophilic addition reactions to the BODIPY core; a critical necessity in our long term synthetic methodology. Figure 4.4, shows a generic *meso*-substituted BODIPY with 2,6-positions available for the iodination and/or formylation reaction. Another important consideration was whether unsubstituted-BODIPY cores would be able to effectively undergo *mono*-iodination. To this end, trial reactions were done as shown in Scheme 4.11.

Figure 4.4. A cartoon showing iodination and formylation reactions at the 2,6-positions of a *meso*-substituted BODIPY

With the knowledge that iodination reactions work fairly well on methylated-BODIPY (e.g. **4.3** and **4.12**), it was desirable to check if the iodination reaction works the same way on unsubstituted-BODIPY. Pleasingly, an iodination reaction was carried out successfully on **4.20** using NIS (Scheme 4.11) to yield its iodo derivative **4.27**, and minimal di-iodo product was observed.

Scheme 4.10. Iodination of BODIPY **4.20** to yield the iodo-derivative **4.27**

The iodination and formylation reactions were also attempted using a TMS-protected alkyne BODIPY **2.35** to check its tolerance to these reaction conditions. Both the iodination and formylation reactions on **2.35** worked fairly well and are shown in Scheme 4.12. Both the formylation and iodination reactions can be done interchangeably. The iodination and formylation reactions were studied on different BODIPYs ranging from less bulky groups at the *meso*-position (**4.4**, **4.12** and **4.17**) to more sterically hindered groups (**2.9**, **4.9**). In each case, the result was the same *i.e.* good yields during all these reactions, regardless of how bulky the group is at the *meso*-position; however, if the iodination is done before the Vilsmeier-Haack formylation, the overall yield drops.

Scheme 4.11. Synthesis of iodo and formyl derivatives of **2.35** through electrophilic addition (**4.28**) and Vilsmeier-Haack formylation reaction (**4.29**) in the presence of alkyne substituted BODIPY

4.3. Results and Discussion

The unsubstituted and methylated BODIPYs previously discussed were investigated for their structure-property relationships with respect to how the influence of strong electron donating groups at the *meso*-position can alter the physical properties of these dyes. Unless otherwise noted, these molecules were studied in DCM solutions and the physicochemical properties (electrochemical, absorption and theoretical (by DFT) have been collated and appear in Table 4.1 and 4.2.

Table 4.1. Physicochemical properties of unsubstituted-BODIPYs with various groups at *meso*-position.

BODIPY Dye	E _{1/2} (ox) V vs NHE ^a	E _{1/2} (red) V vs NHE ^a	λ _{ab} (nm) ^b (ε × 10 ⁴ M ⁻¹ cm ⁻¹)	Dominant Transition (FMO)
4.17	2.02	-0.57	497 (6.0)	HOMO to LUMO
4.18	2.07	-0.62	499 (5.5)	HOMO to LUMO
4.19	2.06	-0.66	500 (4.2)	HOMO to LUMO
4.20	2.03 -	-0.68 -	498 (2.8) 406 (0.6)	HOMO to LUMO

^a CV data was collected using 0.1 M NBu₄PF₆ DCM solutions at 100 mVs⁻¹ and referenced to a [Fc]/[Fc]⁺ internal standard followed by conversion to NHE; [Fc]/[Fc⁺] = +765 mV vs. NHE in DCM; ^b low energy or visible transitions from UV-Vis of BODIPY family in DCM.

Table 4.2. Physicochemical properties of methylated-BODIPYs with various groups at *meso*-position.

BODIPY	E _{1/2} (ox)	E _{1/2} (red)	λ _{ab} (nm) ^b	Dominant Transition
Dye	V vs NHE ^a	V vs NHE ^a	(ε × 10 ⁴ M ⁻¹ cm ⁻¹)	(FMO)
4.4	1.53	-	497 (7.0)	HOMO to LUMO
4.12	1.51	-	502 (4.8)	HOMO to LUMO
4.23	1.55	-	501 (2.7)	HOMO to LUMO

4.24	1.51	-	499 (3.6)	HOMO to LUMO
4.25	0.76 2.06	- -	503 (6.1) 277 (4.5)	HOMO to LUMO
4.26	0.91 1.42 1.82	- - -	501 (3.8) 310 (1.4) 293 (1.6)	HOMO to LUMO

^a CV data was collected using 0.1 M NBu₄PF₆ DCM solutions at 100 mVs⁻¹ and referenced to a [Fc]/[Fc]⁺ internal standard followed by conversion to NHE; [Fc]/[Fc⁺] = +765 mV vs. NHE in DCM; ^b low energy or visible transitions from UV-Vis of BODIPY family in DCM.

4.3.1. Absorption behaviour of *meso*-substituted BODIPYs

The UV-Vis data of unsubstituted-BODIPYs (Figure 4.5) shows that the absorption is not significantly red-shifted by changing the aryl groups (EDG) at the *meso*-position compared to the parent BODIPY **4.17**. However, when a redox active species is present at the *meso*-position a charge transfer band results (**4.22** from 525-625 nm). The charge transfer band is from the excited TPA unit which likely donates electron density to excited BODIPY core.

Figure 4.5. UV-Vis absorption data for unsubstituted BODIPYs

A similar trend was observed in the case of methylated BODIPYs. Only modest changes were observed and a slight red-shift in absorption occurred by attaching different EDGs as compared to parent BODIPY **4.4** (Figure 4.6). One intriguing difference however, was that now charge transfer band was not prominent in **4.26**. One hypothesis for this observation could be due to the fact that the methyl-substitution maintains a rigorous orthogonality between the BODIPY and TPA π -systems, effectively prohibiting significant charge transfer.

Figure 4.6. UV-Vis absorption data for methylated BODIPYs

4.3.2. Theoretical investigation (DFT/TD-DFT) of *meso*-substituted BODIPYs

DFT calculations for both families of building blocks have been summarized in Figures 4.7 and 4.8. Lending support to the previous hypothesis (*vide supra*), when comparing the optimized geometries of **4.22** and **4.26**, the methylated BODIPY has the TPA unit strictly orthogonal, while the non-methylated derivative **4.22** has the plane canted by about 70°. This seems to have a significant impact on the optical properties as the HOMOs reside on the BODIPY cores whereas in the case of LUMOs, the electron density is localized on the *meso*-substituted aryl groups. This trend is found with all BODIPY derivatives except **4.22** and **4.26** which have HOMOs lying on the TPA unit and LUMO at the *meso*-position. This supports the rationale for the observed charge transfer as shown in Figure 4.5. The end result is that the new HOMO is on the TPA unit and the LUMO is on the *meso*-position of BODIPY.

Figure 4.7. TD-DFT calculations on unsubstituted BODIPYs (3-21G). Dominant optical transitions have been highlighted with a dashed line, and the secondary contribution highlighted with a solid line.

The TD-DFT calculations were used to assign the dominant transitions which are shown in Table 4.1 and Table 4.2. The dominant transitions (denoted by dotted arrows) in all the cases were from HOMO to LUMO. The secondary transitions (denoted by solid arrows) in FMOs are also shown. In either case the transitions involve the shift of electron density from the BODIPY core to the *meso*-position.

Figure 4.8. TD-DFT calculations on methylated-BODIPYs (3-21G). Dominant optical transitions have been highlighted with a dashed line, and the secondary contribution highlighted with a solid line.

4.3.3. Electrochemical behaviour of *meso*-substituted BODIPYs

Cyclic voltammetry (CV) is used as an electroanalytical technique to study redox active behaviour of analytes. It is a quantitative and qualitative technique, which can be used to determine the formal potential of a half-reaction or the stability of a redox species. A reversible oxidation potential allows for the determination of the HOMO energy and a reversible reduction allows for the determination of the LUMO energy; however, these are solvent and supporting electrolyte dependent approximations. The HOMO-LUMO gap can be calculated by taking the difference between the HOMO and LUMO potentials.

The cyclic voltammetry experiment is carried out by applying a control potential to the analyte. The experiment involves three electrodes connected to a potentiostat and inserted into a solution consisting of a supporting electrolyte and the analyte (the solvent must have an electrochemical window larger than the potential region which the sample is run through). A cyclic voltammogram (potential-current curve) is generated when a potentiostat varies the potential of the working electrode with respect to the reference electrode.^{173,174} The counter-electrode is required to complete the circuit *i.e.* during the working electrode's anodic sweep (oxidative mode), the counter-electrode acts as a cathode (reductive mode) and *vice versa*.¹⁷⁴

Cyclic voltammetry (CV) data (summarized in Table 4.1 and Table 4.2) show a quasi-reversible oxidation for unsubstituted BODIPYs which is due to BODIPY oxidation occurring close to the solvent decomposition edge of the voltammogram (Figure 4.9). In these derivatives, there is also an observable quasi-reversible reduction. This reduction is not typically observed in our methylated BODIPY derivatives; however, the LUMO of unsubstituted BODIPYs lies within the solvent window and is reduced before the solvent (Figure 4.9). The two dotted lines in Figure 4.9 represent the DCM solvent stability window in our electrochemical studies.

Figure 4.9. HOMO-LUMO energy gap for methylated BODIPY and unsubstituted BODIPY having donor group (R) at the *meso*-position. The two dotted lines represent the solvent window

In the case of more electron-rich methylated-BODIPYs, HOMOs lie within the solvent window and these derivatives are reversibly oxidized (Figure 4.9). Additionally, methylated-BODIPYs possess a fully reversible oxidation owing to substitution at their 1,3,5 and 7 positions which prevents decomposition (Table 4.1 and Table 4.2). A representative voltammogram for *meso*-substituted BODIPYs is shown in Figure 4.10 (see appendices for detailed CV data). The oxidation potential ($E_{1/2}$) is determined by calculating the average of the anodic (E_a) and cathodic (E_p) potentials.

Figure 4.10. A reversible cyclic voltammogram (CV) of **4.12**; E_a represents the anodic peak, E_c represents cathodic peak and $E_{1/2}$ represents formal redox potential (oxidation potential).

The CV data also shows that it is slightly harder to reduce the unsubstituted BODIPYs when strong EDGs are attached (Table 4.1). This increase in the reduction potential is attributed to the destabilization of the LUMO. Unsurprisingly, TPA substituted BODIPYs (*i.e.*, **4.26**) observes more than one oxidation events owing to the TPA group that is readily oxidized; however, it is interesting to note that in both the methylated and non-methylated derivatives the trimethoxy-substituted derivative is also redox active and while it may not demonstrate any unique behaviour optically, it could be leveraged as a redox-active donor. Finally, consistent with the DFT and UV-Vis data, it is also observed that the HOMOs of methylated-BODIPYs are only modestly perturbed to higher energy as compared to their unsubstituted counterparts.

4.4. Summary and conclusion

In this chapter, based on previously reported dye design strategy, a series of model reactions were explored towards making a D- π -A dye motif. During these attempted reactions, it was observed that the Suzuki cross-coupling reactions pose a challenge in the presence of a BODIPY aldehydes. Avoiding Suzuki cross-coupling reactions on formylated BODIPYs, the best strategy could be to iodinate a BODIPY first, attach a donor group to it through Suzuki cross-coupling, and then formylate it *via* a Vilsmeier-Haack formylation reaction.

A number of unsubstituted-BODIPYs and methylated BODIPYs having different donor groups at the *meso*-position were synthesized and studied for their physicochemical properties. The HOMOs lie on the BODIPY core in most of the BODIPYs except two which have TPA donor groups. In the BODIPYs with TPA donor groups at the *meso*-position have HOMOs which reside on the TPA unit and a new HOMO is created. However, similar to the rest of the BODIPYs, the LUMOs resides on the *meso*-position. It was also observed that LUMO energy increases with the increased electronic density at the *meso*-position. Additionally, unsubstituted BODIPYs decompose upon oxidation resulting in quasi-reversible oxidations whereas, the methylated BODIPYs are not prone to decomposition and witness a reversible oxidation.

Formylation and iodination reactions were studied at 2,6-positions of various BODIPYs. It was concluded that both reactions work reasonably well regardless of the presence of bulky groups on the BODIPY, and should not pose a significant challenge in dye integration moving forward. However, the formylation reaction can be done more selectively as compared to iodination which is prone to competition reactions when both the 2 and 6-positions are available on BODIPY. If the iodination reaction is required before the Vilsmeier-Haack formylation reaction, keeping the iodinating agent (NIS) as a limiting reagent can help increase the yield during the iodination reaction.

4.5. Experimental

4.5.1. General considerations

Unless stated otherwise, all reagents were purchased from Sigma Aldrich except PdCl₂ (Pressure Chemical Co., Pittsburg, PA). PdCl₂ was reacted with PPh₃ to make catalyst PdCl₂(PPh₃)₂. Purification by column chromatography was carried out using silica (Silicycle: ultrapure flash silica). Analytical thin-layer chromatography was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Silicycle) and visualized under UV light. Routine ¹H, ¹³C{¹H}, ¹¹B{¹H} and ¹⁹F NMR spectra were recorded at 400, 100, 128 and 376 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to a residual nondeuterated solvent (CHCl₃) for ¹H and ¹³C nuclei and BF₃•OEt₂ (¹¹B nucleus; δ = 0 ppm) C₆F₆ (¹⁹F nucleus; δ = 0 ppm). Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; q = quartet and br = broad. High resolution mass spectrometry (HRMS) results were obtained from Queens University, Kingston Ontario. Electron impact (EI) mass spectrometry and Electrospray ionization (ESI) techniques were used for the ionization; time of flight (TOF) was used for analysis. UV-Vis data was taken using Cary Series UV-Vis-NIR Spectrophotometer from Agilent Technologies and dichloromethane (having the onset peak at 230 nm) was used as the solvent. The GAUSSIAN 09 computational package¹⁵⁴ was used to perform ground-state geometry optimization calculations employing Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr non-local correlation functional B3LYP¹⁵⁵⁻¹⁵⁷ and 6-31G basis set was used for all the atoms. Time-dependent density functional theory calculations were also performed using this methodology, and the first 200 singlet excited states were calculated. Calculations by the first-principles method were used to obtain accurate excitation energies and oscillator strengths. We modelled the solvent with the polarizable continuum model using DCM as the solvent.¹⁵⁸

4.5.2. Synthesis

The synthetic details for each compound are given below. General synthetic steps have been used unless otherwise mentioned in the procedure.

4-methoxy-N-(4-methoxyphenyl)-N-phenylaniline (4.1). Under an atmosphere of N_2 , *p*-iodoanisole (6.35 g, 27 mmol), aniline (1.0 mL, 11 mmol) and 1,10-phenanthroline (0.39 g, 2.2 mmol) were solubilized in 20 mL of toluene. The solution was heated to 100 °C followed by the addition of CuCl (0.22 g, 2.2 mmol) and KOH (4.9 g, 87 mmol). The resulting mixture was refluxed overnight. After being cooled to room temperature, 3 mL of glacial AcOH and 15 mL of toluene were added. The mixture was washed with H_2O once and extracted with toluene. The combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was purified via column chromatography using Hex:EtOAc (9:1, R_f = 0.6) to yield the product as a yellow solid (3.80 g, 46%). NMR data agreed with the literature values. 1H NMR ($CDCl_3$, 400 MHz): δ = 7.17 (t, J = 8.0 Hz, 2H), 7.05 (m, 4H), 6.94 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 8.0 Hz, 1H), 6.84-6.80 (m, 4H), 3.80 (s, 6H).

4-bromo-*N,N*-bis(4-methoxyphenyl)aniline (4.2). Under an atmosphere of N₂, 4-methoxy-*N*-(4-methoxyphenyl)-*N*-phenylaniline **4.1** (1.98 g, 6.48 mmol) was dissolved in 46 mL of THF:EtOAc (26:20) and *N*-bromosuccinimide (1.38 g, 7.78 mmol) was added in one portion. The flask was covered with Al foil and the mixture was stirred overnight. Volatiles were removed *in vacuo* and the crude was purified via column chromatography using Hex:EtOAc (9:1, *R_f* = 0.5) as the eluent affording the desired product as a yellowish solid (2.46 g, 99%). NMR data agreed with the literature values.¹⁷⁵ ¹H NMR (CDCl₃, 400 MHz): δ = 7.24 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 4H), 6.83 (d, *J* = 8.0 Hz, 4H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 6H).

4.3

4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (4.3). Under an atmosphere of N₂, 4-bromo-*N,N*-bis(4-methoxyphenyl)aniline **4.2** (2.46 g, 6.40 mmol) was dissolved in 23 mL of dry THF and the solution was cooled to -78 °C. While keeping the temperature at -78 °C, *n*BuLi (1.6M, 4.8 mL, 7.63 mmol) was added dropwise and the mixture was stirred for 30 min at the same temperature. 2-isopropoxy-4,4',5,5'-tetramethyl-[1,3,2]-dioxaborolane (1.9 mL, 9.66 mmol) was added in one portion and the mixture was stirred at -78 °C for 30 min. The mixture was allowed to warm to room temperature and stir overnight. 5.0 mL of MeOH were added and volatiles were removed *in vacuo*. The crude product was purified via column chromatography using Hex:EtOAc (9:1, *R_f* = 0.4) as the eluent, affording the desired product as a brown solid (0.96 g, 35%). NMR data agreed with the literature values.¹⁷⁶ ¹H NMR (CDCl₃, 400 MHz): δ = 7.60 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 4H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 4H), 3.80 (s, 6H), 1.32 (s, 12H).

4.4

5,5-difluoro-1,3,7,9,10-pentamethyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (4.4). In a 250 Schlenk flask, under an atmosphere of N₂, acetyl chloride (3.23 g, 41.1 mmol) was added dropwise at room temperature over 30 minutes to a solution of pyrrole (1.70 g, 17.9 mmol) in 10 mL of dry DCM. The mixture was refluxed for 1 hour and after cooling to room temperature, 50 mL of hexanes was added to the mixture. Volatiles were removed *in vacuo* and 120 mL of dry DCM were added. NEt₃ (7.0 mL) was added and the mixture was stirred for 10 min. BF₃·OEt₂ (9.4 mL) was added dropwise and stirred for 1 hour at RT. The mixture was washed with NaHCO₃ and the organic layer was dried over MgSO₄, filtered and concentrated *in vacuo*. The oily residue was chromatographed using Hex:DCM (1:1, R_f = 0.62). The resulting solid was recrystallized in DCM:MeOH to yield the product as a dark red solid (3.13 g, 37%). NMR data agreed with the literature values.⁹⁰ ¹H NMR (CDCl₃, 400 MHz): δ = 6.05 (s, 2H), 2.58 (s, 3H), 2.52 (s, 6H), 2.42 (s, 6H).

4.5

5,5-difluoro-2-iodo-1,3,7,9,10-pentamethyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (4.5). BODIPY 4.4 (126 mg, 0.481 mmol) was dissolved in ~10 mL of DCM and NIS (97 mg, 0.433 mmol) was added. The mixture was stirred at room temperature for 40 hours with the flask covered with Al foil. Volatiles were removed *in vacuo* and the crude material was purified via column chromatography using Hex:DCM (1:1) as the eluent affording the desired product as a red solid (137 mg, 71%). NMR data agreed with the literature values.⁹⁰

^1H NMR (CDCl_3 , 400 MHz): δ = 6.12 (s, 1H), 2.61 (s, 3H), 2.60 (s, 3H), 2.53 (s, 3H), 2.46 (3H), 2.43 (s, 3H).

4-(5,5-difluoro-1,3,7,9,10-pentamethyl-5H-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-2-yl)-N,N-bis(4-methoxyphenyl)aniline (4.6). Iodo-BODIPY **4.5** (100 mg, 0.258 mmol) and TPA derivative **4.3** (133 mg, 0.309 mmol) were dissolved in 15 mL of THF:H₂O (9:1) and the solution was sparged for 10 minutes under an atmosphere of N₂. K₂CO₃ (178 mg, 1.289 mmol) and Pd(PPh₃)₄ (30 mg, 0.026 mmol) were added and the mixture was refluxed for 36 hours under an N₂ atmosphere. After being cooled to room temperature, 10 mL of H₂O were added and the organic layer was separated. The aqueous layer was extracted with Et₂O and the combined organic layers were dried over MgSO₄, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using DCM (R_f = 0.7) as the eluent, affording the desired product as a pink viscous liquid (21.3 mg, 15%). NMR data agreed with the literature values.⁹⁰ ^1H NMR (CDCl_3 , 400 MHz): δ = 7.11 (m, 4H), 6.97 (m, 4H), 6.85 (m, 4H), 6.06 (s, 1H), 3.80 (s, 6H), 2.63 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H), 2.34 (s, 3H).

8-(4-(bis(4-methoxyphenyl)amino)phenyl)-5,5-difluoro-1,3,7,9,10-pentamethyl-5H-5 λ^4 ,6 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine-2-carbaldehyde (4.7). An oven dried schlenk flask

was charged with DMF (1 mL), and DCE (3 mL). The solution was cooled to 0 °C under nitrogen and POCl₃ (1 mL) was added over 5 min. The solution was stirred an additional 5 min before being warmed to room temperature. After 30 min of stirring at RT, a solution of BODIPY **4.6** (21 mg, 0.038 mmol) in 3 mL of DCE was added in one portion. The reaction was stirred for 3 hours at room temperature and monitored by TLC for consumption of the starting material. The solution was slowly poured onto 40 mL of saturated aqueous NaHCO₃ at 0 °C then warmed to room temperature and stirred for overnight. The organic layer was extracted with DCM and solvents were removed *in vacuo*. The residue was purified by column chromatography using DCM as the eluent (*R_f* = 0.15) to remove the impurities and then column was flushed with a DCM:EtOAc (9:1) mixture to yield the product (15 mg, 68%). NMR data agreed with the literature values.⁹⁰ ¹H NMR (CDCl₃, 400 MHz): δ = 10.11 (s, 1H), 7.12 (m, 4H), 6.96 (m, 4H), 6.87 (m, 4H), 3.81 (s, 6H), 2.79 (s, 3H), 2.75 (s, 3H), 2.74 (s, 3H), 2.55 (s, 3H), 2.39 (s, 3H).

(E)-3-(8-(4-(bis(4-methoxyphenyl)amino)phenyl)-5,5-difluoro-1,3,7,9,10-pentamethyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-2-yl)-2-cyanoacrylic acid (4.8). Aldehyde **4.7** (25 mg, 0.042 mmol) was dissolved in a minimal amount of CHCl₃ and cyanoacetic acid (7 mg, 0.084 mmol) and piperidine (1 mg, 0.011 mmol) were added. The mixture was refluxed overnight and after being cooled to RT, the organic layer was washed with 1N HCl. Volatiles were removed *in vacuo*. Purification was done by dissolving the purple crude solid in 16 mL of Hex:DCM (1:1) and left to recrystallize at room temperature. ¹H NMR data is consistent with previously reported.⁹⁰

4.9

10-(4-(tert-butyl)-2,6-diiodophenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5H-5 λ^4 ,6 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine-2-carbaldehyde (4.9). An oven dried schlenk flask was charged with DMF (10 mL), and DCE (30mL). The solution was cooled to 0 °C under an atmosphere of N₂ and POCl₃ was added over 5 minutes. The solution was stirred for an additional 5 minutes before being warmed to room temperature. After 30 minutes stirring at room temperature, a solution of BODIPY **2.9** (0.26 g, 0.413 mmol) in 30 mL of DCE was added in one portion. The reaction was stirred for 3 hours at room temperature and monitored by TLC for consumption of starting material. The solution was slowly poured onto 400 mL of saturated aqueous NaHCO₃ at 0 °C then warmed to room temperature and left to stir overnight. The organic layer was extracted with DCM and solvents were removed *in vacuo*. The residue was purified by column chromatography using DCM as the eluent (*R_f* = 0.42) yielding the product as an orange solid (0.23 g, 87%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.04 (s, 1H), 7.97 (s, 2H), 6.19 (s, 1H), 2.85 (s, 3H), 2.65 (s, 3H), 1.74 (s, 3H), 1.50 (s, 3H), 1.34 (s, 9H).

4.10

10-(4-(tert-butyl)-2,6-diiodophenyl)-5,5-difluoro-8-iodo-1,3,7,9-tetramethyl-5H-5 λ^4 ,6 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine-2-carbaldehyde (4.10). Formyl-BODIPY **4.9** (224

mg, 0.34 mmol) was dissolved in 35 mL of DCM and *N*-iodosuccinimide (81.0 mg, 0.36 mmol) was added. The mixture was stirred at room temperature for 12 h with the flask covered with Al foil. Volatiles were removed *in vacuo* and the crude material was purified *via* column chromatography using DCM as the eluent (R_f = 0.48) affording the desired product as an orange solid (220 mg, 82%). ^1H NMR (CDCl_3 , 400 MHz): δ = 10.05 (s, 1H), 7.98 (s, 2H), 2.86 (s, 3H), 2.74 (s, 3H), 1.75 (s, 3H), 1.52 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 185.74, 161.68, 158.69, 157.11, 146.83, 146.30, 143.51, 138.91, 137.45, 132.36, 128.46, 126.84, 96.05, 88.53, 34.83, 31.06, 16.63, 14.20, 13.50, 11.07. ^{19}F NMR (CDCl_3 , 376.5 MHz): δ = -144.59 (q). ^{11}B NMR (CDCl_3 , 128 MHz): δ = 0.57 (t, J_{FB} = 32 Hz).

8-(4-(bis(4-methoxyphenyl)amino)phenyl)-10-(4-(tert-butyl)-2,6-diiodophenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5H-5 λ^4 ,6 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine-2-carbaldehyde (4.11). BODIPY **4.10** (100 mg, 0.26 mmol) and TPA derivative **4.3** (150 mg, 0.39 mmol) were dissolved in 40 mL of THF:H₂O (9:1) and the solution was sparged for 10 min with N₂. K₂CO₃ (182 mg, 1.30 mmol) and Pd(PPh₃)₄ (30 mg, 0.026 mmol) were added and the mixture was refluxed for 12 hours under an atmosphere of N₂. After being cooled to room temperature, 50 mL of H₂O were added and the organic layer was separated. The aqueous layer was extracted with Et₂O and the combined organic layers were dried over MgSO₄, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using Hex:DCM (1:1) as the eluent but none of the fractions contained the desired product. NMR studies showed no product.

4.12

5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-

f][1,3,2]diazaborinine (4.12). To a solution of 2,4-dimethyl-1H-pyrrole (0.56 g, 8.33 mmol, 2.2 eq) in dry DCM (100 mL), benzaldehyde (0.3 g, 3.33 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, 2,3-dichloro-5,6-dicyanobenzoquinone (1.13 g, 1.5 eq) was added and the mixture was stirred for ~3 hours. After TLC analysis revealed the completion of oxidation, DIPEA (3.0 mL) and BF₃.OEt₂ (3.5 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (toluene, *R_f* = 0.46) yielded the product as an orange powder (291 mg, 30 %). ¹H NMR (CDCl₃, 400 MHz): δ = 7.47 (m, 3H), 7.26 (m, 2H), 5.97 (s, 2H), 2.55 (s, 6H), 1.37 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 155.42, 143.17, 141.78, 134.98, 131.45, 129.15, 128.98, 127.94, 121.25, 14.57, 14.33. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -146.16 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.90 (t, *J_{FB}* = 32 Hz).

4.13

5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-

f][1,3,2]diazaborinine-2-carbaldehyde (4.13). An oven dried schlenk flask was charged with DMF (5.0 mL), and DCE (15 mL). The solution was cooled to 0 °C under nitrogen and POCl₃ (6.0

mL) was added over 5 minutes. The solution was stirred an additional 5 minutes before being warmed to room temperature. After 30 minutes stirring at room temperature, a solution of BODIPY **4.12** (80 mg, 0.25 mmol) in 15 mL of DCE was added in one portion. The reaction was stirred for 3 hours at room temperature and monitored by TLC for consumption of the starting material. The solution was slowly poured onto 240 mL of saturated aqueous NaHCO₃ at 0 °C then warmed to RT and stirred overnight. The organic layer was extracted with DCM and solvents were removed *in vacuo*. The residue was purified by column chromatography using DCM as the eluent (*R_f* = 0.15) yielding the product as an orange solid (78 mg, 90%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.01 (s, 1H), 7.54-7.52 (m, 3H), 7.30-7.27 (m, 2H), 6.15 (s, 1H), 2.82 (s, 3H), 2.62 (s, 3H), 1.65 (s, 3H), 1.42 (3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 185.88, 161.62, 156.54, 147.27, 143.59, 142.94, 134.19, 129.54, 127.73, 126.37, 124.01, 123.98, 43.43, 30.90, 14.81, 11.54.

4.14

5,5-difluoro-8-iodo-1,3,7,9-tetramethyl-10-phenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine-2-carbaldehyde (4.14). Formyl-BODIPY **4.13** (79 mg, 0.22 mmol) was dissolved in 24 mL of DCM and NIS (56 mg, 0.25 mmol) was added. The mixture was stirred at room temperature for 12 hours with the flask covered with Al foil. Volatiles were removed *in vacuo* and the crude material was purified via column chromatography using DCM as the eluent (*R_f* = 0.2) affording the desired product as an orange red solid. ¹H NMR (CDCl₃, 400 MHz): δ = 10.02 (s, 1H), 7.56 (m, 3H), 7.28 (m, 2H), 2.83 (s, 3H), 2.71 (s, 3H), 1.66 (s, 3H), 1.43 (s, 3H).

8-(4-(bis(4-methoxyphenyl)amino)phenyl)-5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5H-5 λ^4 ,6 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine-2-carbaldehyde (4.15). Iodo BODIPY derivative **4.14** (82 mg, 0.172 mmol) and TPA derivative **4.3** (111 mg, 0.257 mmol) were dissolved in 27 mL of THF:H₂O (9:1) and the solution was sparged for 10 min under an atmosphere of N₂. K₂CO₃ (44 mg, 0.318 mmol) and Pd(PPh₃)₄ (20 mg, 0.017 mmol) were added and the mixture was refluxed for 12 hours under N₂. After being cooled to room temperature, 12 mL of H₂O were added and the organic layer was separated. The aqueous layer was extracted with Et₂O and the combined organic layers were dried over MgSO₄, filtered, and volatiles were removed *in vacuo*. Purification of the crude material was attempted *via* column chromatography using Hex:DCM (1:1) as the eluent but there was no separation. Another column was run with Hex:EtOAc (19:1) but still no separation was achieved. The ¹H NMR was not very clean and the crude was never characterized as a pure product. ¹H NMR data is shown in appendices.

4-(bis(4-methoxyphenyl)amino)benzaldehyde (4.16). An oven dried schlenk flask was charged with DMF (20 mL), and DCE (60 mL). The solution was cooled to 0 °C and POCl₃ (24 mL) was added over 5 minutes. The solution was stirred for an additional 5 min before being warmed to room temperature. After 30 minutes stirring at room temperature, a solution of *bis*-methoxy-TPA

4.1 (0.611 g, 2 mmol) in 60 mL of DCE was added in one portion. The reaction was stirred for 3 hours at room temperature and monitored by TLC for consumption of starting material. The solution was slowly poured into 800 mL of saturated aqueous NaHCO₃ at 0 °C then warmed to RT and stirred overnight. The organic layer was extracted with DCM and solvents were removed *in vacuo*. The residue was purified by column chromatography using DCM as the eluent (*R_f* = 0.5) yielding the product as a yellowish solid. ¹H NMR (CDCl₃, 400 MHz): δ = 9.75 (s, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 4H), 6.89 (d, *J* = 8.5 Hz, 4H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.81. HRMS (EI-TOF): *m/z* 333.1361 ([MH]⁺), calcd for C₂₁H₁₉O₃N: *m/z* 333.1365.

4.17

5,5-difluoro-10-methyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (4.17). To a solution of pyrrole (1.90 g, 28.4 mmol, 2.5 eq) in dry DCM (200 mL), acetaldehyde (0.5 g, 11.35 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (3.86 g, 17.03 mmol, 1.5 eq) was added and the mixture was stirred for ~3 hours. After TLC analysis revealed the completion of oxidation, DIPEA (14 mL) and BF₃OEt₂ (14 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography using pure toluene (*R_f* = 0.32) yielded the product as an orange powder (0.54 g, 23 %). ¹H NMR (CDCl₃, 400 MHz): δ = 7.85 (s, 2H), 7.31 (d, *J* = 4.0 Hz, 2H), 6.55 (d, *J* = 4.0 Hz, 2H), 2.64 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 145.86, 143.42, 133.55, 128.01, 117.96, 16.14. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -145.93 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.12 (t, *J_{FB}* = 27 Hz).

4.18

5,5-difluoro-10-phenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (4.18). To a solution of pyrrole (1.58 g, 23.6 mmol, 2.5 eq) in dry DCM (250 mL), benzaldehyde (1.0 g, 9.42 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (3.21 g, 1.5 eq) was added and the mixture was stirred for ~3 hours. After TLC analysis revealed the completion of oxidation, DIPEA (17 mL) and BF₃OEt₂ (20 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (toluene, *R_f* = 0.34) yielded the product as an orange powder (228 mg, 9%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.95 (s, 2H), 7.57 (m, 5H), 6.95 (d, *J* = 4.0 Hz, 2H), 6.56 (d, *J* = 4.0 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 147.41, 144.14, 134.98, 133.81, 131.63, 130.76, 130.49, 128.45, 118.52. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -145.07 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.29 (t, *J_{FB}* = 28 Hz).

4.19

10-(4-(*tert*-butyl)phenyl)-5,5-difluoro-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (4.19). To a solution of pyrrole (1.03 g, 15.41 mmol, 2.5 eq) in dry DCM (200 mL), 4-(*tert*-

butyl)benzaldehyde (1.0 g, 6.16 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (2.10 g, 1.5 eq) was added and the mixture was stirred for ~3 hours. After TLC analysis revealed the completion of oxidation, DIPEA (15 mL) and BF₃OEt₂ (17.5 mL) were added. After stirring for 12 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (toluene, *R_f* = 0.50) yielded the product a red solid (168 mg, 8.4%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.93 (s, 2H), 7.55-7.48 (m, 4H), 6.98 (d, *J* = 4.0 Hz, 2H), 6.54 (d, *J* = 4.0 Hz, 2H), 1.41 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ = 154.52, 147.77, 143.71, 134.96, 131.68, 131.02, 130.55, 125.47, 118.32, 35.01, 31.25. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -145.02 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 1.21 (t, *J_{FB}* = 32 Hz).

4.20

10-(4-ethoxyphenyl)-5,5-difluoro-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (4.20). To a solution of pyrrole (1.12 g, 16.65 mmol, 2.5 eq) in dry DCM (200 mL), 4-ethoxybenzaldehyde (1.0 g, 6.66 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (2.25 g, 1.5 eq) was added and the mixture was stirred for ~6 hours. After TLC analysis revealed the completion of oxidation, DIPEA (8 mL) and BF₃OEt₂ (10.5 mL) were added. After stirring for 12 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by column chromatography, using toluene (*R_f* = 0.26) as the eluent, yielded the product (a bright red solid) in decent yield (0.54 g, 26%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.92 (s, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 4.0 Hz, 2H), 6.55 (d, *J* = 4.0 Hz, 2H), 4.14 (t, *J* = 7.0 Hz, 2H), 1.49 (t, *J* = 7.0 Hz, 2H). ¹³C NMR (CDCl₃,

100 MHz): δ = 161.56, 147.53, 143.34, 134.84, 132.46, 131.36, 126.15, 118.25, 114.51, 63.84, 14.76. ^{19}F NMR (CDCl_3 , 376.5 MHz): δ = -145.14 (q). ^{11}B NMR (CDCl_3 , 128 MHz): δ = 0.29 (t, J_{FB} = 28 Hz). HRMS (EI-TOF): m/z 312.1245 ($[\text{MH}]^+$), calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{OBF}_2$: m/z 312.1246.

4.21

5,5-difluoro-10-(3,4,5-trimethoxyphenyl)-5H-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-c:2',1'-

f][1,3,2]diazaborinine (4.21). To a solution of pyrrole (0.85 g, 12.7 mmol, 2.5 eq) in dry DCM (150 mL), 3,4,5-trimethoxybenzaldehyde (1.0 g, 5.10 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (1.74 g, 1.5 eq) was added and the mixture was stirred for ~6 hours. After TLC analysis revealed the completion of oxidation, DIPEA (7.0 mL) and BF_3OEt_2 (8.5 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc, and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification by column chromatography (DCM, R_f = 0.40) yielded the product as an orange red solid (201 mg, 11%). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.92 (s, 2H), 7.03 (d, J = 4.0 Hz), 6.80 (s, 2H), 6.55 (d, J = 4.0 Hz, 2H), 3.95 (s, 3H), 3.88 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 153.10, 147.22, 144.01, 140.39, 134.81, 131.44, 129.10, 118.52, 108.22, 61.06, 56.38. ^{19}F NMR (CDCl_3 , 376.5 MHz): δ = -145.13 (q). ^{11}B NMR (CDCl_3 , 128 MHz): δ = 0.25 (t, J_{FB} = 28 Hz). HRMS (EI-TOF): m/z 358.1309 ($[\text{MH}]^+$), calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3\text{BF}_2$: m/z 358.1300.

4.22

4-(5,5-difluoro-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)-N,N-bis(4-methoxyphenyl)aniline (4.22). To a solution of pyrrole (0.50 g, 7.50 mmol, 2.5 eq) in dry DCM (100 mL), 4-(bis(4-methoxyphenyl)amino)benzaldehyde **4.16** (1.0 g, 3.00 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (1.02 g, 1.5 eq) was added and the mixture was stirred for ~3 hours. After TLC analysis revealed the completion of oxidation, DIPEA (3.0 mL) and BF₃OEt₂ (3.5 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc, and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (DCM, *R_f* = 0.40) yielded the product a reddish solid (68 mg, 8.5%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.88 (s, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 4H), 7.06 (d, *J* = 4.0 Hz, 2H), 6.95-6.90 (m, 6H), 6.54 (d, *J* = 4.0 Hz, 2H), 3.83 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 157.16, 151.89, 142.28, 139.17, 132.54, 130.88, 127.89, 124.65, 117.52, 117.28, 115.08, 108.53, 55.53. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -145.33 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 1.20 (t, *J_{FB}* = 32 Hz). HRMS (EI-TOF): *m/z* 495.1929 ([MH]⁺), calcd for C₂₉H₂₄N₃O₂BF₂: *m/z* 495.1939.

4.23

10-(4-(*tert*-butyl)phenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (4.23). To a solution of 2,4-dimethyl-1*H*-pyrrole (0.79 g, 8.33 mmol, 2.5 eq) in dry DCM (120 mL), 4-(*tert*-butyl)benzaldehyde (0.54 g, 3.33 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (1.13 g, 1.5 eq) was added and the mixture was stirred for ~3 hours. After TLC analysis revealed the completion of oxidation, DIPEA (4.0 mL) and BF₃OEt₂ (4.7 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc, and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (toluene, *R_f* = 0.52) yielded product as a crystalline red solid (529 mg, 42%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.49 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.97 (s, 2H), 2.55 (s, 6H), 1.37 (s, 9H), 1.36 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 155.19, 152.44, 143.23, 142.27, 131.88, 131.63, 127.51, 125.89, 121.08, 34.78, 31.40, 14.57, 14.24. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -146.34 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.79 (t, *J_{FB}* = 32 Hz).

4.24

10-(4-ethoxyphenyl)-5,5-difluoro-1,3,7,9-tetramethyl-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (4.24). To a solution of 2,4-dimethyl-1*H*-pyrrole (0.79 g, 8.32 mmol, 2.5 eq) in dry DCM (120 mL), 4-ethoxybenzaldehyde (0.5 g, 3.33 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (1.13 g, 1.5 eq) was added and the mixture was stirred for ~3 hours. After TLC analysis revealed the completion of oxidation, DIPEA (4.0 mL) and BF₃OEt₂ (4.7 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc and washed with water. The

water layer was extracted with EtOAc, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (toluene, R_f = 0.41) yielded the product as a red powder (367 mg, 30%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.15 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 5.97 (s, 2H), 4.09 (q, J = 7.0 Hz, 2H), 2.55 (s, 6H), 1.46 (t, J = 7.0 Hz, 3H), 1.43 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 159.52, 155.23, 143.18, 141.96, 131.87, 129.18, 126.91, 121.09, 115.04, 63.56, 14.78, 14.56. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -146.33 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.78 (t, J_{FB} = 33 Hz).

5,5-difluoro-1,3,7,9-tetramethyl-10-(3,4,5-trimethoxyphenyl)-5H-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (4.25). To a solution of 2,4-dimethyl-1H-pyrrole (1.21 g, 12.7 mmol, 2.5 eq) in dry DCM (150 mL), 3,4,5-trimethoxybenzaldehyde (1.00 g, 5.10 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (1.74 g, 1.5 eq) was added and the mixture was stirred for ~6 hours. After TLC analysis revealed the completion of oxidation, DIPEA (7.0 mL) and BF₃OEt₂ (8.5 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (toluene, R_f = 0.30) yielded pure product (1.01 g, 48%). ¹H NMR (CDCl₃, 400 MHz): δ = 6.52 (s, 2H), 6.00 (s, 2H), 3.91 (s, 3H), 3.82 (s, 6H), 2.55 (s, 6H), 1.53 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 155.63, 154.21, 143.06, 141.35, 138.69, 131.34, 130.09, 129.03, 128.22, 125.29, 121.21, 105.18, 61.34, 56.38, 14.58, 14.23. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -146.33 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.75 (t, J_{FB} = 32 Hz).

4.26

4-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)-N,N-bis(4-methoxyphenyl)aniline (4.26). To a solution of 2,4-dimethyl-1*H*-pyrrole (0.33 g, 4.89 mmol, 2.5 eq) in dry DCM (60 mL), 4-(*bis*(4-methoxyphenyl)amino)benzaldehyde **4.16** (0.65 g, 1.95 mmol, 1 eq) was added followed by a catalytic amount of TFA. After overnight stirring of the resulting reddish solution, DDQ (0.66 g, 1.5 eq) was added and the mixture was stirred for ~3 hours. After TLC analysis revealed the completion of oxidation, DIPEA (2.7 mL) and BF₃OEt₂ (3.0 mL) were added. After stirring for 6 hours, the mixture was concentrated *in vacuo*, dissolved in EtOAc, and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification by column chromatography (toluene, *R_f* = 0.22) yielded the pure product (139 mg, 13%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.08 (d, *J* = 8.0 Hz, 4H), 7.02 (s, 4H), 6.87 (d, *J* = 8.0 Hz, 4H), 6.00 (s, 2H), 3.81 (s, 6H), 2.56 (s, 6H), 1.59 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ = 156.20, 155.05, 149.42, 143.05, 142.48, 140.46, 138.20, 137.88, 131.91, 129.06, 128.65, 128.25, 126.82, 126.13, 125.32, 116.38, 114.87, 55.50, 14.65, 14.58. ¹⁹F NMR (CDCl₃, 376.5 MHz): δ = -146.55 (q). ¹¹B NMR (CDCl₃, 128 MHz): δ = 0.88 (t, *J_{FB}* = 33 Hz). HRMS (EI-TOF): *m/z* 551.2571 ([MH]⁺), calcd for C₃₃H₃₂N₃O₂BF₂: *m/z* 551.2556.

4.27

Synthesis of iodo-BODIPY 4.27. BODIPY **4.20** (234 mg, 0.75 mmol) was dissolved in 15 mL of DCM, followed by the addition of NIS (84 mg, 0.374 mmol). The mixture was stirred at RT for 40 hours and the flask covered with Al foil. Volatiles were removed *in vacuo* and the crude material was purified *via* column chromatography using Hex:DCM (1:1, R_f = 0.6) as the eluent affording the desired product as a red solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 7.97 (s, 1H), 7.82 (s, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.06-7.03 (m, 4H), 6.61 (d, J = 4.0 Hz, 1H), 4.14 (q, J = 7.0 Hz, 2H), 1.49 (t, J = 7.0 Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 161.90, 146.77, 146.01, 145.06, 135.92, 132.89, 132.52, 125.72, 119.32, 114.72, 63.92, 14.73. ^{19}F NMR (CDCl_3 , 376.5 MHz): δ = -144.99 (q). ^{11}B NMR (CDCl_3 , 128 MHz): δ = -0.02 (t, J_{FB} = 27 Hz).

4.28

10-(4-(*tert*-butyl)-2,6-bis((trimethylsilyl)ethynyl)phenyl)-5,5-difluoro-2-iodo-1,3,7,9-tetramethyl-5H-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (4.28). BODIPY **2.35** (170 mg, 0.27 mmol) was dissolved in a minimum amount of dry DCM and NIS (61 mg, 0.27 mmol) was added. The mixture was stirred at RT for 12 hours and the flask was covered with Al foil. Volatiles were removed *in vacuo* and the crude material was purified *via* column chromatography using Hex:DCM (2.5:1, R_f = 0.23) as the eluent affording the desired product as

an orange-red solid (90 mg, 44%). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.53 (s, 2H), 6.02 (s, 1H), 2.62 (s, 3H), 2.56 (s, 3H), 1.47 (s, 6H), 1.34 (s, 9H), -0.02 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 157.31, 153.72, 152.94, 144.34, 142.22, 138.24, 129.13, 122.94, 121.49, 102.04, 100.04, 58.49, 34.67, 31.59, 26.92, 25.28, 15.72, 14.11, -0.67. HRMS (EI-TOF): m/z 698.1991 ($[\text{MH}]^+$), calcd for $\text{C}_{33}\text{H}_{42}\text{N}_2\text{BF}_2\text{Si}_2$: m/z 698.1992.

Synthesis of 4.29. To an oven dried schlenk flask, DMF (10 mL) and DCE (30mL) were added under an atmosphere of N_2 , and the solution was cooled to 0 °C. After stirring the solution at 0 °C for 5 minutes, POCl_3 was added, the solution was stirred an additional 5 min at same temperature and then mixture was warmed to room temperature. After 30 min of stirring at RT, a solution of BODIPY (0.26 g, 1 mmol) in 30 mL of DCE was added in one portion. The reaction was stirred for 3 hours at RT. The solution was slowly poured onto 400 mL of saturated NaHCO_3 at 0 °C and the resulting mixture was stirred overnight at RT. The organic layer was extracted with DCM, dried over MgSO_4 , and solvents were removed *in vacuo*. The residue was purified by column chromatography using DCM as the eluent (R_f = 0.42) yielding the product as an orange-red solid. ^1H NMR (CDCl_3 , 400 MHz): δ = 10.01 (s, 1H), 7.54 (s, 2H), 6.11 (s, 1H), 2.78 (s, 3H), 2.66 (s, 3H), 1.60 (s, 3H), 1.39 (3H).

Chapter 5: Summary, Conclusions and Future Work

The synthesis of BODIPY-phenylacetylene macrocycles where BODIPY is enclosed within a phenylacetylene macrocycle have been reported herein. Various synthetic strategies were used to make the target molecules; however, a successful synthetic strategy (*top-down* approach) showed that cyclizing the ring at the bottom was the most effective way to close the ring (chapter 2).

Upon synthesis of the BODIPY-phenylacetylene macrocycle **2.31**, a control macrocycle **2.34** was made as a benchmark to appreciate energy transfer studies. The control macrocycle (**2.34**) was not fluorescent in the visible spectrum and upon excitation (287 nm), it emitted at 333 nm with a Stokes shift of 46 nm. However, when the BODIPY-phenylacetylene macrocycle **2.31** is excited at its λ_{max} (292 nm), the emission is exclusively from the BODIPY core with a Stokes shift of 236 nm. It is also observed that emission always occurs from the BODIPY core, irrespective of the excitation wavelength which suggests that there is an energy transfer from the macrocycle to the BODIPY. The process of energy transfer from the macrocycle to BODIPY is depicted in Figure 5.1.

Figure 5.1. An energy transfer process within the BODIPY-macrocycle

Following the parent BODIPY-phenylacetylene macrocycle **2.31**, a more rigid BODIPY-phenylacetylene macrocycle **2.39** was made which also showed energy transfer from the macrocycle to the BODIPY core. The BODIPY core in **2.39** is more rigidly orthogonal to the macrocycle as compared to **2.31** which is attributed to the steric effect of the BODIPY methyl

groups. It was also observed that both BODIPY-phenylacetylene macrocycles **2.31** and **2.39** exhibit excellent fluorescence quantum yields (0.89% and 0.91% for **2.31** and **2.39**, respectively).

The BODIPY-phenylacetylene macrocycle design possesses a macrocycle orthogonal to the BODIPY unit and upon excitation, energy transfer is observed from the macrocyclic part of the compound to the BODIPY core. However, the macrocyclic part of the molecule (**2.31**) absorbs light around 300 nm which is less than ideal for solar applications, because few photons penetrate our atmosphere at this wavelength. For photovoltaic applications, the dye needs to be modified such that the macrocycle absorbs appreciably in the visible (*i.e.* a red-shift in the absorption profile is required). To this end, modifying the macrocyclic part of the BODIPY-phenylacetylene to red-shift the absorption profile was explored and modified BODIPY-phenylacetylene macrocycles were studied as examined in Chapter 3. A bathochromic shift in the absorption envelope was achieved by attaching donor and acceptor groups on the phenylacetylene arms. An attempt to implement a push-pull strategy between donor and acceptor groups was unsuccessful owing to synthetic difficulties; however, the modified macrocycles were successfully made by substituting *mono*-donor groups (on one side of the macrocycle) (**3.29** and **3.37**) and *bis*-donor groups (on both sides of the macrocycle) (**3.42**).

The absorption studies show that the modified BODIPY-phenylacetylene macrocycle with *bis*-donor group (**3.42**) displayed the most red-shifted profile when compared with the *mono*-donor groups (**3.29** and **3.37**). The absorption envelope of compound **3.42** was extended up to 380 nm which indicates a bathochromic shift of about 50 nm as compared to the parent BODIPY-phenylacetylene macrocycle **2.31**. The fluorescence studies showed the energy transfer from the macrocycle to the BODIPY upon excitation of the macrocycle.

In anticipation of converting these BODIPY π -spacers into a D- π -A dye motif for DSSC applications, a number of unsubstituted-BODIPYs and methylated BODIPYs having different donor groups at the *meso*-position were synthesized and studied for their physicochemical properties (Chapter 4). The HOMOs lie on the BODIPY core in most of the BODIPYs except two of them (**4.22** and **4.26**) which have TPA donor groups attached at the *meso*-position and the HOMOs reside on the TPA unit. However, similar to the rest of the BODIPYs, the LUMOs reside on the *meso*-position. It was also observed that LUMO energy increases with increased electronic density at the *meso*-position. Additionally, unsubstituted BODIPYs decompose upon oxidation

which results in quasi-reversible oxidation whereas, the methylated BODIPYs are not prone to decomposition and possess a reversible oxidation. Furthermore, formylation and iodination reactions were studied at the 2,6-positions of various BODIPYs. It was observed that both reactions work fairly well regardless of the presence of bulky groups on the BODIPY. However, the formylation reaction can be done more selectively as compared to iodination which is more prone to competition reactions when both the 2- and 6-positions are available on BODIPY. If the iodination reaction is required before the Vilsmeier-Haack formylation reaction, keeping the iodinating agent (NIS) as a limiting reagent can help increase the yield during the iodination reaction.

The BODIPY-phenylacetylene macrocycles were made to mimic to energy transfer processes found in Nature. However, the BODIPY-phenylacetylene macrocycles outlined in this studied will not be effective DSSC dyes owing to the fact that the DSSC is supposed to be an economically viable technology and this synthesis is not economical. It could be used for academic purposes but unlikely useful for a commercial project.

Based on the current work, the future work is suggested to include, but is not limited to:

1. The optimization of cyclization step using varying amounts of CuI and PdCl₂(PPh₃)₂. This may include a systematic study of how the concentration affects the yield. This might lead to a new catalytic protocol for the cyclization step. Additionally, this kind of systematic study could be done on some other macrocycle which is more easily made.
2. Time resolved (femtosecond) fluorescence studies to determine the rate and efficiency of energy transfer between the BODIPY and the macrocycle (see section 1.7 for details).
3. In order to further appreciate the nature of energy transfer (Forster vs Dexter), a rotaxane based on this design could be readily prepared removing the possibility for Dexter (through bond) energy transfer, leading to a direct comparison with this work.
4. A DSSC dye (D- π -A) can be made using the BODIPY-macrocycle as a proof of concept. It is hypothesized that the proposed dye design could also have structural benefits amenable for the DSSCs as well. The structural benefits of the target molecules are summarized in Figure 5.2. A simple D- π -A dye motif without macrocycle (Figure 5.2A) is compared to the D- π -A dye motif with the macrocycle (Figure 5.2B). In the absence of macrocycle (Figure 5.2A), the electrolyte can come in contact with the TiO₂ semiconductor and a

recombination/short circuit event can occur. However, the presence of macrocycle (Figure 5.2B) reduces the possibility of recombination by passivating the surface between the electrolyte and TiO_2 .

Figure 5.2. Cartoon showing the decrease in the rate recombination and energy transfer from the macrocycle to the spacer

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Table A1. Crystal data and structure refinement for **2.31**.

Identification code	d14142twin	
Empirical formula	C ₅₆ H ₃₅ B Cl ₂ F ₂ N ₂	
Formula weight	855.57	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7852(4) Å	α = 86.895(2)°.
	b = 13.7533(4) Å	β = 85.724(2)°.
	c = 25.2899(10) Å	γ = 89.541(2)°.
Volume	4428.0(3) Å ³	
Z	4	
Density (calculated)	1.283 Mg/m ³	
Absorption coefficient	1.709 mm ⁻¹	
F(000)	1768	
Crystal size	0.130 x 0.120 x 0.080 mm ³	
Theta range for data collection	1.754 to 67.969°.	
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, 0 ≤ l ≤ 29	
Reflections collected	16017	
Independent reflections	16017 [R(int) = 0.0687]	
Completeness to theta = 67.679°	96.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7530 and 0.6786	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	16017 / 9 / 1179	
Goodness-of-fit on F ²	1.023	
Final R indices [I > 2σ(I)]	R1 = 0.0672, wR2 = 0.1680	
R indices (all data)	R1 = 0.0928, wR2 = 0.1863	
Extinction coefficient	0.00051(9)	
Largest diff. peak and hole	0.496 and -0.779 e.Å ⁻³	

Table A2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2.31**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1A)	4432(3)	5425(2)	6346(1)	51(1)
F(2A)	2823(2)	6102(2)	6267(1)	53(1)
N(1A)	4291(3)	7174(3)	6318(1)	32(1)
N(2A)	4095(3)	6273(3)	5520(2)	34(1)
C(1A)	5185(3)	7718(3)	5472(2)	28(1)
C(2A)	4922(3)	7844(3)	6013(2)	31(1)
C(3A)	5127(3)	8625(3)	6336(2)	33(1)
C(4A)	4617(4)	8405(4)	6827(2)	41(1)
C(5A)	4117(4)	7513(3)	6804(2)	38(1)
C(6A)	3780(4)	5639(3)	5176(2)	39(1)
C(7A)	4223(4)	5864(3)	4667(2)	40(1)
C(8A)	4864(4)	6663(3)	4698(2)	35(1)
C(9A)	4769(3)	6934(3)	5231(2)	31(1)
C(10A)	5912(3)	8422(3)	5169(2)	28(1)
C(11A)	5628(3)	8984(3)	4721(2)	26(1)
C(12A)	6351(3)	9612(3)	4446(2)	30(1)
C(13A)	7377(3)	9712(3)	4588(2)	30(1)
C(14A)	7654(3)	9153(3)	5035(2)	31(1)
C(15A)	6945(3)	8524(3)	5319(2)	28(1)
C(16A)	7312(3)	7934(3)	5755(2)	30(1)
C(17A)	7646(3)	7427(3)	6101(2)	32(1)
C(18A)	7974(3)	6714(3)	6488(2)	31(1)
C(19A)	8895(4)	6816(4)	6746(2)	39(1)
C(20A)	9217(4)	6075(4)	7094(2)	45(1)
C(21A)	8632(4)	5223(4)	7181(2)	43(1)
C(22A)	7709(4)	5111(3)	6928(2)	34(1)
C(23A)	7389(4)	5864(3)	6584(2)	32(1)
C(24A)	7095(4)	4238(4)	6993(2)	38(1)
C(25A)	6538(4)	3540(3)	7006(2)	36(1)

C(26A)	5801(4)	2765(3)	6981(2)	36(1)
C(27A)	5970(4)	1828(3)	7217(2)	43(1)
C(28A)	5230(5)	1115(4)	7185(2)	48(1)
C(29A)	4339(5)	1298(4)	6921(2)	46(1)
C(30A)	4163(4)	2213(3)	6682(2)	37(1)
C(31A)	4908(4)	2943(3)	6721(2)	34(1)
C(32A)	3304(4)	2432(3)	6363(2)	40(1)
C(33A)	2672(4)	2676(4)	6051(2)	41(1)
C(34A)	1999(4)	2970(4)	5672(2)	40(1)
C(35A)	1459(4)	3243(4)	5325(2)	40(1)
C(36A)	834(4)	3624(3)	4914(2)	37(1)
C(37A)	-85(4)	3154(4)	4792(2)	41(1)
C(38A)	-694(4)	3586(4)	4416(2)	45(1)
C(39A)	-429(4)	4466(4)	4159(2)	40(1)
C(40A)	492(4)	4936(3)	4270(2)	35(1)
C(41A)	1121(4)	4505(3)	4646(2)	33(1)
C(42A)	778(4)	5885(4)	4042(2)	36(1)
C(43A)	1072(4)	6696(3)	3925(2)	34(1)
C(44A)	1487(3)	7662(3)	3859(2)	33(1)
C(45A)	1015(4)	8417(4)	3569(2)	43(1)
C(46A)	1446(4)	9343(4)	3542(2)	47(1)
C(47A)	2343(4)	9529(3)	3791(2)	37(1)
C(48A)	2831(3)	8778(3)	4078(2)	31(1)
C(49A)	2394(3)	7859(3)	4110(2)	30(1)
C(50A)	3780(4)	8922(3)	4323(2)	31(1)
C(51A)	4610(3)	8944(3)	4532(2)	29(1)
C(52A)	8160(3)	10369(3)	4248(2)	34(1)
C(53A)	7672(4)	11377(4)	4167(3)	53(1)
C(54A)	8388(5)	9919(4)	3714(2)	57(2)
C(55A)	9187(4)	10477(4)	4505(2)	52(1)
B(1A)	3880(4)	6212(4)	6123(2)	38(1)
F(1B)	4875(2)	707(2)	8649(1)	49(1)
F(2B)	3189(2)	1250(2)	8701(1)	50(1)
N(1B)	4571(3)	2429(3)	8674(2)	30(1)
N(2B)	4179(3)	1351(3)	9466(2)	30(1)

C(1B)	5265(3)	2787(3)	9509(2)	28(1)
C(2B)	5124(3)	3034(3)	8980(2)	27(1)
C(3B)	5405(4)	3886(3)	8659(2)	31(1)
C(4B)	5014(4)	3787(3)	8174(2)	39(1)
C(5B)	4509(4)	2882(3)	8195(2)	36(1)
C(6B)	3777(4)	639(3)	9814(2)	36(1)
C(7B)	4091(4)	761(3)	10318(2)	37(1)
C(8B)	4729(4)	1570(3)	10287(2)	34(1)
C(9B)	4784(3)	1945(3)	9756(2)	30(1)
C(10B)	5927(3)	3415(3)	9805(2)	26(1)
C(11B)	5536(3)	3908(3)	10255(2)	25(1)
C(12B)	6201(3)	4495(3)	10512(2)	27(1)
C(13B)	7263(3)	4613(3)	10346(2)	28(1)
C(14B)	7633(3)	4128(3)	9905(2)	30(1)
C(15B)	6994(3)	3535(3)	9633(2)	28(1)
C(16B)	7460(3)	3025(3)	9199(2)	32(1)
C(17B)	7896(3)	2583(3)	8852(2)	33(1)
C(18B)	8344(4)	1946(3)	8464(2)	33(1)
C(19B)	9352(4)	2097(4)	8218(2)	39(1)
C(20B)	9784(4)	1414(4)	7877(2)	45(1)
C(21B)	9226(4)	610(4)	7776(2)	39(1)
C(22B)	8212(4)	450(3)	8010(2)	36(1)
C(23B)	7769(4)	1136(3)	8347(2)	34(1)
C(24B)	7602(4)	-388(4)	7932(2)	40(1)
C(25B)	7013(4)	-1074(4)	7926(2)	40(1)
C(26B)	6270(4)	-1847(3)	7968(2)	34(1)
C(27B)	6478(4)	-2742(3)	7745(2)	42(1)
C(28B)	5730(4)	-3474(4)	7815(2)	44(1)
C(29B)	4804(4)	-3343(3)	8111(2)	40(1)
C(30B)	4589(4)	-2449(3)	8342(2)	36(1)
C(31B)	5313(4)	-1700(3)	8263(2)	36(1)
C(32B)	3655(4)	-2297(3)	8680(2)	39(1)
C(33B)	2946(4)	-2121(3)	9001(2)	38(1)
C(34B)	2189(4)	-1877(3)	9384(2)	39(1)
C(35B)	1523(4)	-1657(3)	9724(2)	38(1)

C(36B)	774(4)	-1338(3)	10128(2)	35(1)
C(37B)	-193(4)	-1805(3)	10230(2)	39(1)
C(38B)	-924(4)	-1457(3)	10605(2)	40(1)
C(39B)	-729(4)	-634(3)	10873(2)	36(1)
C(40B)	232(3)	-153(3)	10771(2)	31(1)
C(41B)	978(4)	-525(3)	10402(2)	34(1)
C(42B)	475(3)	738(3)	10998(2)	33(1)
C(43B)	748(3)	1515(3)	11119(2)	33(1)
C(44B)	1167(3)	2465(3)	11185(2)	31(1)
C(45B)	631(4)	3178(4)	11469(2)	39(1)
C(46B)	1077(4)	4087(4)	11495(2)	43(1)
C(47B)	2052(4)	4306(3)	11247(2)	35(1)
C(48B)	2598(3)	3590(3)	10963(2)	27(1)
C(49B)	2155(3)	2679(3)	10938(2)	30(1)
C(50B)	3615(3)	3764(3)	10701(2)	30(1)
C(51B)	4468(3)	3830(3)	10472(2)	27(1)
C(52B)	7979(3)	5220(3)	10652(2)	36(1)
C(53B)	7502(8)	6239(6)	10717(5)	49(3)
C(54B)	8032(11)	4755(10)	11214(4)	71(5)
C(55B)	9049(7)	5385(9)	10368(5)	59(4)
C(52C)	7979(3)	5220(3)	10652(2)	36(1)
C(53C)	7400(8)	5749(9)	11105(4)	52(3)
C(54C)	8735(8)	4496(7)	10913(5)	47(3)
C(55C)	8549(10)	5979(8)	10291(4)	51(3)
B(1B)	4184(4)	1398(4)	8858(2)	33(1)
Cl(1)	1281(3)	-1925(2)	7426(1)	150(1)
Cl(2)	2366(2)	-288(2)	7777(1)	95(1)
C(1S)	1520(6)	-1246(7)	7929(3)	86(2)
Cl(4)	8794(4)	6274(3)	12687(2)	146(3)
Cl(3)	7878(2)	4475(2)	12471(1)	132(1)
C(2S)	7696(7)	5556(7)	12803(4)	154(6)
Cl(4A)	8050(8)	6622(4)	12447(3)	102(3)
Cl(3A)	7878(2)	4475(2)	12471(1)	132(1)
C(2SA)	7696(7)	5556(7)	12803(4)	154(6)

Table A3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **2.31**.

F(1A)-B(1A)	1.403(6)
F(2A)-B(1A)	1.381(6)
N(1A)-C(5A)	1.340(6)
N(1A)-C(2A)	1.391(6)
N(1A)-B(1A)	1.546(7)
N(2A)-C(6A)	1.348(6)
N(2A)-C(9A)	1.396(6)
N(2A)-B(1A)	1.527(7)
C(1A)-C(9A)	1.395(6)
C(1A)-C(2A)	1.404(6)
C(1A)-C(10A)	1.489(6)
C(2A)-C(3A)	1.421(6)
C(3A)-C(4A)	1.379(7)
C(3A)-H(3AA)	0.9500
C(4A)-C(5A)	1.394(7)
C(4A)-H(4AA)	0.9500
C(5A)-H(5AA)	0.9500
C(6A)-C(7A)	1.387(7)
C(6A)-H(6AA)	0.9500
C(7A)-C(8A)	1.384(7)
C(7A)-H(7AA)	0.9500
C(8A)-C(9A)	1.415(6)
C(8A)-H(8AA)	0.9500
C(10A)-C(11A)	1.405(6)
C(10A)-C(15A)	1.411(6)
C(11A)-C(12A)	1.392(6)
C(11A)-C(51A)	1.422(6)
C(12A)-C(13A)	1.394(6)
C(12A)-H(12A)	0.9500
C(13A)-C(14A)	1.400(6)
C(13A)-C(52A)	1.535(6)
C(14A)-C(15A)	1.390(6)

C(14A)-H(14A)	0.9500
C(15A)-C(16A)	1.438(6)
C(16A)-C(17A)	1.191(6)
C(17A)-C(18A)	1.430(6)
C(18A)-C(23A)	1.394(6)
C(18A)-C(19A)	1.401(6)
C(19A)-C(20A)	1.389(7)
C(19A)-H(19A)	0.9500
C(20A)-C(21A)	1.394(7)
C(20A)-H(20A)	0.9500
C(21A)-C(22A)	1.397(7)
C(21A)-H(21A)	0.9500
C(22A)-C(23A)	1.394(6)
C(22A)-C(24A)	1.435(7)
C(23A)-H(23A)	0.9500
C(24A)-C(25A)	1.198(7)
C(25A)-C(26A)	1.435(7)
C(26A)-C(31A)	1.375(7)
C(26A)-C(27A)	1.412(7)
C(27A)-C(28A)	1.378(8)
C(27A)-H(27A)	0.9500
C(28A)-C(29A)	1.377(8)
C(28A)-H(28A)	0.9500
C(29A)-C(30A)	1.390(7)
C(29A)-H(29A)	0.9500
C(30A)-C(31A)	1.402(7)
C(30A)-C(32A)	1.432(7)
C(31A)-H(31A)	0.9500
C(32A)-C(33A)	1.204(7)
C(33A)-C(34A)	1.377(7)
C(34A)-C(35A)	1.200(7)
C(35A)-C(36A)	1.433(7)
C(36A)-C(41A)	1.394(7)
C(36A)-C(37A)	1.407(7)
C(37A)-C(38A)	1.380(8)

C(37A)-H(37A)	0.9500
C(38A)-C(39A)	1.375(7)
C(38A)-H(38A)	0.9500
C(39A)-C(40A)	1.401(6)
C(39A)-H(39A)	0.9500
C(40A)-C(41A)	1.395(7)
C(40A)-C(42A)	1.437(7)
C(41A)-H(41A)	0.9500
C(42A)-C(43A)	1.195(7)
C(43A)-C(44A)	1.431(7)
C(44A)-C(45A)	1.397(7)
C(44A)-C(49A)	1.398(6)
C(45A)-C(46A)	1.388(7)
C(45A)-H(45A)	0.9500
C(46A)-C(47A)	1.380(7)
C(46A)-H(46A)	0.9500
C(47A)-C(48A)	1.399(6)
C(47A)-H(47A)	0.9500
C(48A)-C(49A)	1.382(6)
C(48A)-C(50A)	1.424(6)
C(49A)-H(49A)	0.9500
C(50A)-C(51A)	1.221(6)
C(52A)-C(55A)	1.521(7)
C(52A)-C(54A)	1.524(7)
C(52A)-C(53A)	1.526(7)
C(53A)-H(53A)	0.9800
C(53A)-H(53B)	0.9800
C(53A)-H(53C)	0.9800
C(54A)-H(54A)	0.9800
C(54A)-H(54B)	0.9800
C(54A)-H(54C)	0.9800
C(55A)-H(55A)	0.9800
C(55A)-H(55B)	0.9800
C(55A)-H(55C)	0.9800
F(1B)-B(1B)	1.391(6)

F(2B)-B(1B)	1.382(6)
N(1B)-C(5B)	1.339(6)
N(1B)-C(2B)	1.397(5)
N(1B)-B(1B)	1.542(6)
N(2B)-C(6B)	1.357(6)
N(2B)-C(9B)	1.401(5)
N(2B)-B(1B)	1.535(7)
C(1B)-C(2B)	1.386(6)
C(1B)-C(9B)	1.409(6)
C(1B)-C(10B)	1.483(6)
C(2B)-C(3B)	1.421(6)
C(3B)-C(4B)	1.374(7)
C(3B)-H(3BA)	0.9500
C(4B)-C(5B)	1.403(6)
C(4B)-H(4BA)	0.9500
C(5B)-H(5BA)	0.9500
C(6B)-C(7B)	1.384(7)
C(6B)-H(6BA)	0.9500
C(7B)-C(8B)	1.380(6)
C(7B)-H(7BA)	0.9500
C(8B)-C(9B)	1.408(6)
C(8B)-H(8BA)	0.9500
C(10B)-C(15B)	1.409(6)
C(10B)-C(11B)	1.414(6)
C(11B)-C(12B)	1.396(6)
C(11B)-C(51B)	1.436(6)
C(12B)-C(13B)	1.399(6)
C(12B)-H(12B)	0.9500
C(13B)-C(14B)	1.382(6)
C(13B)-C(52C)	1.523(6)
C(13B)-C(52B)	1.523(6)
C(14B)-C(15B)	1.400(6)
C(14B)-H(14B)	0.9500
C(15B)-C(16B)	1.424(6)
C(16B)-C(17B)	1.197(6)

C(17B)-C(18B)	1.436(6)
C(18B)-C(23B)	1.397(6)
C(18B)-C(19B)	1.400(6)
C(19B)-C(20B)	1.392(7)
C(19B)-H(19B)	0.9500
C(20B)-C(21B)	1.368(7)
C(20B)-H(20B)	0.9500
C(21B)-C(22B)	1.399(7)
C(21B)-H(21B)	0.9500
C(22B)-C(23B)	1.395(6)
C(22B)-C(24B)	1.427(7)
C(23B)-H(23B)	0.9500
C(24B)-C(25B)	1.214(7)
C(25B)-C(26B)	1.426(7)
C(26B)-C(27B)	1.396(7)
C(26B)-C(31B)	1.404(7)
C(27B)-C(28B)	1.389(7)
C(27B)-H(27B)	0.9500
C(28B)-C(29B)	1.370(7)
C(28B)-H(28B)	0.9500
C(29B)-C(30B)	1.405(6)
C(29B)-H(29B)	0.9500
C(30B)-C(31B)	1.387(7)
C(30B)-C(32B)	1.438(7)
C(31B)-H(31B)	0.9500
C(32B)-C(33B)	1.202(7)
C(33B)-C(34B)	1.370(7)
C(34B)-C(35B)	1.213(7)
C(35B)-C(36B)	1.432(7)
C(36B)-C(41B)	1.384(6)
C(36B)-C(37B)	1.398(7)
C(37B)-C(38B)	1.382(7)
C(37B)-H(37B)	0.9500
C(38B)-C(39B)	1.385(6)
C(38B)-H(38B)	0.9500

C(39B)-C(40B)	1.401(6)
C(39B)-H(39B)	0.9500
C(40B)-C(41B)	1.398(6)
C(40B)-C(42B)	1.426(6)
C(41B)-H(41B)	0.9500
C(42B)-C(43B)	1.189(6)
C(43B)-C(44B)	1.439(6)
C(44B)-C(45B)	1.392(6)
C(44B)-C(49B)	1.394(6)
C(45B)-C(46B)	1.386(7)
C(45B)-H(45B)	0.9500
C(46B)-C(47B)	1.380(7)
C(46B)-H(46B)	0.9500
C(47B)-C(48B)	1.400(6)
C(47B)-H(47B)	0.9500
C(48B)-C(49B)	1.386(6)
C(48B)-C(50B)	1.431(6)
C(49B)-H(49B)	0.9500
C(50B)-C(51B)	1.198(6)
C(52B)-C(55B)	1.508(8)
C(52B)-C(54B)	1.533(9)
C(52B)-C(53B)	1.537(8)
C(53B)-H(53D)	0.9800
C(53B)-H(53E)	0.9800
C(53B)-H(53F)	0.9800
C(54B)-H(54D)	0.9800
C(54B)-H(54E)	0.9800
C(54B)-H(54F)	0.9800
C(55B)-H(55D)	0.9800
C(55B)-H(55E)	0.9800
C(55B)-H(55F)	0.9800
C(52C)-C(55C)	1.504(8)
C(52C)-C(53C)	1.531(8)
C(52C)-C(54C)	1.539(8)
C(53C)-H(53G)	0.9800

C(53C)-H(53H)	0.9800
C(53C)-H(53I)	0.9800
C(54C)-H(54G)	0.9800
C(54C)-H(54H)	0.9800
C(54C)-H(54I)	0.9800
C(55C)-H(55G)	0.9800
C(55C)-H(55H)	0.9800
C(55C)-H(55I)	0.9800
Cl(1)-C(1S)	1.665(9)
Cl(2)-C(1S)	1.720(8)
C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900
Cl(4)-C(2S)	1.721(10)
Cl(3)-C(2S)	1.752(11)
C(2S)-H(2S1)	0.9900
C(2S)-H(2S2)	0.9900
Cl(4A)-C(2SA)	1.722(10)
Cl(3A)-C(2SA)	1.752(11)
C(2SA)-H(2S3)	0.9900
C(2SA)-H(2S4)	0.9900
C(5A)-N(1A)-C(2A)	107.7(4)
C(5A)-N(1A)-B(1A)	126.9(4)
C(2A)-N(1A)-B(1A)	125.3(4)
C(6A)-N(2A)-C(9A)	107.2(4)
C(6A)-N(2A)-B(1A)	126.9(4)
C(9A)-N(2A)-B(1A)	125.5(4)
C(9A)-C(1A)-C(2A)	119.5(4)
C(9A)-C(1A)-C(10A)	121.4(4)
C(2A)-C(1A)-C(10A)	119.1(4)
N(1A)-C(2A)-C(1A)	120.9(4)
N(1A)-C(2A)-C(3A)	108.0(4)
C(1A)-C(2A)-C(3A)	130.9(4)
C(4A)-C(3A)-C(2A)	106.5(4)
C(4A)-C(3A)-H(3AA)	126.8

C(2A)-C(3A)-H(3AA)	126.8
C(3A)-C(4A)-C(5A)	107.7(4)
C(3A)-C(4A)-H(4AA)	126.1
C(5A)-C(4A)-H(4AA)	126.1
N(1A)-C(5A)-C(4A)	110.1(4)
N(1A)-C(5A)-H(5AA)	124.9
C(4A)-C(5A)-H(5AA)	124.9
N(2A)-C(6A)-C(7A)	110.8(4)
N(2A)-C(6A)-H(6AA)	124.6
C(7A)-C(6A)-H(6AA)	124.6
C(8A)-C(7A)-C(6A)	107.0(4)
C(8A)-C(7A)-H(7AA)	126.5
C(6A)-C(7A)-H(7AA)	126.5
C(7A)-C(8A)-C(9A)	107.3(4)
C(7A)-C(8A)-H(8AA)	126.4
C(9A)-C(8A)-H(8AA)	126.4
C(1A)-C(9A)-N(2A)	121.0(4)
C(1A)-C(9A)-C(8A)	131.2(4)
N(2A)-C(9A)-C(8A)	107.8(4)
C(11A)-C(10A)-C(15A)	117.2(4)
C(11A)-C(10A)-C(1A)	122.8(4)
C(15A)-C(10A)-C(1A)	119.9(4)
C(12A)-C(11A)-C(10A)	120.1(4)
C(12A)-C(11A)-C(51A)	117.5(4)
C(10A)-C(11A)-C(51A)	122.4(4)
C(11A)-C(12A)-C(13A)	123.1(4)
C(11A)-C(12A)-H(12A)	118.4
C(13A)-C(12A)-H(12A)	118.4
C(12A)-C(13A)-C(14A)	116.4(4)
C(12A)-C(13A)-C(52A)	120.7(4)
C(14A)-C(13A)-C(52A)	122.7(4)
C(15A)-C(14A)-C(13A)	121.6(4)
C(15A)-C(14A)-H(14A)	119.2
C(13A)-C(14A)-H(14A)	119.2
C(14A)-C(15A)-C(10A)	121.4(4)

C(14A)-C(15A)-C(16A)	118.0(4)
C(10A)-C(15A)-C(16A)	120.5(4)
C(17A)-C(16A)-C(15A)	177.2(5)
C(16A)-C(17A)-C(18A)	172.3(5)
C(23A)-C(18A)-C(19A)	119.1(4)
C(23A)-C(18A)-C(17A)	118.5(4)
C(19A)-C(18A)-C(17A)	122.2(4)
C(20A)-C(19A)-C(18A)	120.1(5)
C(20A)-C(19A)-H(19A)	119.9
C(18A)-C(19A)-H(19A)	119.9
C(19A)-C(20A)-C(21A)	120.1(5)
C(19A)-C(20A)-H(20A)	120.0
C(21A)-C(20A)-H(20A)	120.0
C(20A)-C(21A)-C(22A)	120.5(4)
C(20A)-C(21A)-H(21A)	119.7
C(22A)-C(21A)-H(21A)	119.7
C(23A)-C(22A)-C(21A)	118.8(4)
C(23A)-C(22A)-C(24A)	118.5(4)
C(21A)-C(22A)-C(24A)	122.6(4)
C(18A)-C(23A)-C(22A)	121.3(4)
C(18A)-C(23A)-H(23A)	119.4
C(22A)-C(23A)-H(23A)	119.4
C(25A)-C(24A)-C(22A)	174.0(5)
C(24A)-C(25A)-C(26A)	173.6(5)
C(31A)-C(26A)-C(27A)	119.4(5)
C(31A)-C(26A)-C(25A)	118.8(4)
C(27A)-C(26A)-C(25A)	121.8(5)
C(28A)-C(27A)-C(26A)	119.2(5)
C(28A)-C(27A)-H(27A)	120.4
C(26A)-C(27A)-H(27A)	120.4
C(29A)-C(28A)-C(27A)	121.1(5)
C(29A)-C(28A)-H(28A)	119.4
C(27A)-C(28A)-H(28A)	119.4
C(28A)-C(29A)-C(30A)	120.6(5)
C(28A)-C(29A)-H(29A)	119.7

C(30A)-C(29A)-H(29A)	119.7
C(29A)-C(30A)-C(31A)	118.4(5)
C(29A)-C(30A)-C(32A)	123.6(5)
C(31A)-C(30A)-C(32A)	117.8(4)
C(26A)-C(31A)-C(30A)	121.3(4)
C(26A)-C(31A)-H(31A)	119.3
C(30A)-C(31A)-H(31A)	119.3
C(33A)-C(32A)-C(30A)	171.8(5)
C(32A)-C(33A)-C(34A)	176.6(6)
C(35A)-C(34A)-C(33A)	176.4(6)
C(34A)-C(35A)-C(36A)	176.8(5)
C(41A)-C(36A)-C(37A)	119.4(5)
C(41A)-C(36A)-C(35A)	118.8(4)
C(37A)-C(36A)-C(35A)	121.7(5)
C(38A)-C(37A)-C(36A)	119.2(5)
C(38A)-C(37A)-H(37A)	120.4
C(36A)-C(37A)-H(37A)	120.4
C(39A)-C(38A)-C(37A)	121.7(5)
C(39A)-C(38A)-H(38A)	119.2
C(37A)-C(38A)-H(38A)	119.2
C(38A)-C(39A)-C(40A)	119.8(5)
C(38A)-C(39A)-H(39A)	120.1
C(40A)-C(39A)-H(39A)	120.1
C(41A)-C(40A)-C(39A)	119.2(4)
C(41A)-C(40A)-C(42A)	118.1(4)
C(39A)-C(40A)-C(42A)	122.6(5)
C(36A)-C(41A)-C(40A)	120.6(4)
C(36A)-C(41A)-H(41A)	119.7
C(40A)-C(41A)-H(41A)	119.7
C(43A)-C(42A)-C(40A)	170.1(5)
C(42A)-C(43A)-C(44A)	171.6(5)
C(45A)-C(44A)-C(49A)	118.8(4)
C(45A)-C(44A)-C(43A)	123.3(4)
C(49A)-C(44A)-C(43A)	117.9(4)
C(46A)-C(45A)-C(44A)	119.6(4)

C(46A)-C(45A)-H(45A)	120.2
C(44A)-C(45A)-H(45A)	120.2
C(47A)-C(46A)-C(45A)	121.1(5)
C(47A)-C(46A)-H(46A)	119.4
C(45A)-C(46A)-H(46A)	119.4
C(46A)-C(47A)-C(48A)	120.0(4)
C(46A)-C(47A)-H(47A)	120.0
C(48A)-C(47A)-H(47A)	120.0
C(49A)-C(48A)-C(47A)	118.9(4)
C(49A)-C(48A)-C(50A)	118.9(4)
C(47A)-C(48A)-C(50A)	122.2(4)
C(48A)-C(49A)-C(44A)	121.6(4)
C(48A)-C(49A)-H(49A)	119.2
C(44A)-C(49A)-H(49A)	119.2
C(51A)-C(50A)-C(48A)	173.3(5)
C(50A)-C(51A)-C(11A)	174.0(5)
C(55A)-C(52A)-C(54A)	108.8(4)
C(55A)-C(52A)-C(53A)	108.5(4)
C(54A)-C(52A)-C(53A)	109.9(5)
C(55A)-C(52A)-C(13A)	112.4(4)
C(54A)-C(52A)-C(13A)	108.3(4)
C(53A)-C(52A)-C(13A)	108.9(4)
C(52A)-C(53A)-H(53A)	109.5
C(52A)-C(53A)-H(53B)	109.5
H(53A)-C(53A)-H(53B)	109.5
C(52A)-C(53A)-H(53C)	109.5
H(53A)-C(53A)-H(53C)	109.5
H(53B)-C(53A)-H(53C)	109.5
C(52A)-C(54A)-H(54A)	109.5
C(52A)-C(54A)-H(54B)	109.5
H(54A)-C(54A)-H(54B)	109.5
C(52A)-C(54A)-H(54C)	109.5
H(54A)-C(54A)-H(54C)	109.5
H(54B)-C(54A)-H(54C)	109.5
C(52A)-C(55A)-H(55A)	109.5

C(52A)-C(55A)-H(55B)	109.5
H(55A)-C(55A)-H(55B)	109.5
C(52A)-C(55A)-H(55C)	109.5
H(55A)-C(55A)-H(55C)	109.5
H(55B)-C(55A)-H(55C)	109.5
F(2A)-B(1A)-F(1A)	109.2(4)
F(2A)-B(1A)-N(2A)	111.3(4)
F(1A)-B(1A)-N(2A)	110.1(4)
F(2A)-B(1A)-N(1A)	110.8(4)
F(1A)-B(1A)-N(1A)	109.4(4)
N(2A)-B(1A)-N(1A)	106.0(4)
C(5B)-N(1B)-C(2B)	107.7(4)
C(5B)-N(1B)-B(1B)	127.6(4)
C(2B)-N(1B)-B(1B)	124.5(4)
C(6B)-N(2B)-C(9B)	106.5(4)
C(6B)-N(2B)-B(1B)	127.7(4)
C(9B)-N(2B)-B(1B)	124.7(4)
C(2B)-C(1B)-C(9B)	119.8(4)
C(2B)-C(1B)-C(10B)	119.2(4)
C(9B)-C(1B)-C(10B)	121.0(4)
C(1B)-C(2B)-N(1B)	121.3(4)
C(1B)-C(2B)-C(3B)	131.0(4)
N(1B)-C(2B)-C(3B)	107.6(4)
C(4B)-C(3B)-C(2B)	107.2(4)
C(4B)-C(3B)-H(3BA)	126.4
C(2B)-C(3B)-H(3BA)	126.4
C(3B)-C(4B)-C(5B)	107.3(4)
C(3B)-C(4B)-H(4BA)	126.4
C(5B)-C(4B)-H(4BA)	126.4
N(1B)-C(5B)-C(4B)	110.3(4)
N(1B)-C(5B)-H(5BA)	124.9
C(4B)-C(5B)-H(5BA)	124.9
N(2B)-C(6B)-C(7B)	110.7(4)
N(2B)-C(6B)-H(6BA)	124.7
C(7B)-C(6B)-H(6BA)	124.7

C(8B)-C(7B)-C(6B)	107.3(4)
C(8B)-C(7B)-H(7BA)	126.3
C(6B)-C(7B)-H(7BA)	126.3
C(7B)-C(8B)-C(9B)	107.2(4)
C(7B)-C(8B)-H(8BA)	126.4
C(9B)-C(8B)-H(8BA)	126.4
N(2B)-C(9B)-C(8B)	108.2(4)
N(2B)-C(9B)-C(1B)	120.0(4)
C(8B)-C(9B)-C(1B)	131.6(4)
C(15B)-C(10B)-C(11B)	117.8(4)
C(15B)-C(10B)-C(1B)	119.2(4)
C(11B)-C(10B)-C(1B)	123.0(4)
C(12B)-C(11B)-C(10B)	120.0(4)
C(12B)-C(11B)-C(51B)	117.1(4)
C(10B)-C(11B)-C(51B)	122.9(4)
C(11B)-C(12B)-C(13B)	122.5(4)
C(11B)-C(12B)-H(12B)	118.8
C(13B)-C(12B)-H(12B)	118.8
C(14B)-C(13B)-C(12B)	116.8(4)
C(14B)-C(13B)-C(52C)	122.0(4)
C(12B)-C(13B)-C(52C)	121.1(4)
C(14B)-C(13B)-C(52B)	122.0(4)
C(12B)-C(13B)-C(52B)	121.1(4)
C(13B)-C(14B)-C(15B)	122.7(4)
C(13B)-C(14B)-H(14B)	118.7
C(15B)-C(14B)-H(14B)	118.7
C(14B)-C(15B)-C(10B)	120.2(4)
C(14B)-C(15B)-C(16B)	118.5(4)
C(10B)-C(15B)-C(16B)	121.3(4)
C(17B)-C(16B)-C(15B)	176.3(5)
C(16B)-C(17B)-C(18B)	172.7(5)
C(23B)-C(18B)-C(19B)	119.7(4)
C(23B)-C(18B)-C(17B)	118.5(4)
C(19B)-C(18B)-C(17B)	121.8(4)
C(20B)-C(19B)-C(18B)	119.4(4)

C(20B)-C(19B)-H(19B)	120.3
C(18B)-C(19B)-H(19B)	120.3
C(21B)-C(20B)-C(19B)	120.6(4)
C(21B)-C(20B)-H(20B)	119.7
C(19B)-C(20B)-H(20B)	119.7
C(20B)-C(21B)-C(22B)	121.1(4)
C(20B)-C(21B)-H(21B)	119.4
C(22B)-C(21B)-H(21B)	119.4
C(23B)-C(22B)-C(21B)	118.7(4)
C(23B)-C(22B)-C(24B)	117.5(4)
C(21B)-C(22B)-C(24B)	123.8(4)
C(22B)-C(23B)-C(18B)	120.5(4)
C(22B)-C(23B)-H(23B)	119.8
C(18B)-C(23B)-H(23B)	119.8
C(25B)-C(24B)-C(22B)	171.6(5)
C(24B)-C(25B)-C(26B)	174.2(5)
C(27B)-C(26B)-C(31B)	119.8(4)
C(27B)-C(26B)-C(25B)	122.5(4)
C(31B)-C(26B)-C(25B)	117.7(4)
C(28B)-C(27B)-C(26B)	119.5(5)
C(28B)-C(27B)-H(27B)	120.3
C(26B)-C(27B)-H(27B)	120.3
C(29B)-C(28B)-C(27B)	121.1(5)
C(29B)-C(28B)-H(28B)	119.4
C(27B)-C(28B)-H(28B)	119.4
C(28B)-C(29B)-C(30B)	119.9(5)
C(28B)-C(29B)-H(29B)	120.0
C(30B)-C(29B)-H(29B)	120.0
C(31B)-C(30B)-C(29B)	119.7(4)
C(31B)-C(30B)-C(32B)	118.3(4)
C(29B)-C(30B)-C(32B)	121.9(5)
C(30B)-C(31B)-C(26B)	119.9(4)
C(30B)-C(31B)-H(31B)	120.0
C(26B)-C(31B)-H(31B)	120.0
C(33B)-C(32B)-C(30B)	172.6(5)

C(32B)-C(33B)-C(34B)	175.8(5)
C(35B)-C(34B)-C(33B)	179.5(6)
C(34B)-C(35B)-C(36B)	176.2(5)
C(41B)-C(36B)-C(37B)	119.2(4)
C(41B)-C(36B)-C(35B)	120.0(4)
C(37B)-C(36B)-C(35B)	120.8(4)
C(38B)-C(37B)-C(36B)	119.8(4)
C(38B)-C(37B)-H(37B)	120.1
C(36B)-C(37B)-H(37B)	120.1
C(37B)-C(38B)-C(39B)	121.2(4)
C(37B)-C(38B)-H(38B)	119.4
C(39B)-C(38B)-H(38B)	119.4
C(38B)-C(39B)-C(40B)	119.7(4)
C(38B)-C(39B)-H(39B)	120.2
C(40B)-C(39B)-H(39B)	120.2
C(41B)-C(40B)-C(39B)	118.8(4)
C(41B)-C(40B)-C(42B)	117.4(4)
C(39B)-C(40B)-C(42B)	123.7(4)
C(36B)-C(41B)-C(40B)	121.4(4)
C(36B)-C(41B)-H(41B)	119.3
C(40B)-C(41B)-H(41B)	119.3
C(43B)-C(42B)-C(40B)	170.7(5)
C(42B)-C(43B)-C(44B)	171.1(5)
C(45B)-C(44B)-C(49B)	119.0(4)
C(45B)-C(44B)-C(43B)	123.7(4)
C(49B)-C(44B)-C(43B)	117.3(4)
C(46B)-C(45B)-C(44B)	119.8(4)
C(46B)-C(45B)-H(45B)	120.1
C(44B)-C(45B)-H(45B)	120.1
C(47B)-C(46B)-C(45B)	121.5(4)
C(47B)-C(46B)-H(46B)	119.3
C(45B)-C(46B)-H(46B)	119.3
C(46B)-C(47B)-C(48B)	119.0(4)
C(46B)-C(47B)-H(47B)	120.5
C(48B)-C(47B)-H(47B)	120.5

C(49B)-C(48B)-C(47B)	119.6(4)
C(49B)-C(48B)-C(50B)	118.4(4)
C(47B)-C(48B)-C(50B)	122.0(4)
C(48B)-C(49B)-C(44B)	121.1(4)
C(48B)-C(49B)-H(49B)	119.5
C(44B)-C(49B)-H(49B)	119.5
C(51B)-C(50B)-C(48B)	174.5(5)
C(50B)-C(51B)-C(11B)	173.5(4)
C(55B)-C(52B)-C(13B)	113.2(5)
C(55B)-C(52B)-C(54B)	112.8(7)
C(13B)-C(52B)-C(54B)	109.0(6)
C(55B)-C(52B)-C(53B)	105.6(7)
C(13B)-C(52B)-C(53B)	109.6(5)
C(54B)-C(52B)-C(53B)	106.4(7)
C(52B)-C(53B)-H(53D)	109.5
C(52B)-C(53B)-H(53E)	109.5
H(53D)-C(53B)-H(53E)	109.5
C(52B)-C(53B)-H(53F)	109.5
H(53D)-C(53B)-H(53F)	109.5
H(53E)-C(53B)-H(53F)	109.5
C(52B)-C(54B)-H(54D)	109.5
C(52B)-C(54B)-H(54E)	109.5
H(54D)-C(54B)-H(54E)	109.5
C(52B)-C(54B)-H(54F)	109.5
H(54D)-C(54B)-H(54F)	109.5
H(54E)-C(54B)-H(54F)	109.5
C(52B)-C(55B)-H(55D)	109.5
C(52B)-C(55B)-H(55E)	109.5
H(55D)-C(55B)-H(55E)	109.5
C(52B)-C(55B)-H(55F)	109.5
H(55D)-C(55B)-H(55F)	109.5
H(55E)-C(55B)-H(55F)	109.5
C(55C)-C(52C)-C(13B)	111.2(5)
C(55C)-C(52C)-C(53C)	107.3(7)
C(13B)-C(52C)-C(53C)	113.6(5)

C(55C)-C(52C)-C(54C)	112.3(7)
C(13B)-C(52C)-C(54C)	106.2(5)
C(53C)-C(52C)-C(54C)	106.3(6)
C(52C)-C(53C)-H(53G)	109.5
C(52C)-C(53C)-H(53H)	109.5
H(53G)-C(53C)-H(53H)	109.5
C(52C)-C(53C)-H(53I)	109.5
H(53G)-C(53C)-H(53I)	109.5
H(53H)-C(53C)-H(53I)	109.5
C(52C)-C(54C)-H(54G)	109.5
C(52C)-C(54C)-H(54H)	109.5
H(54G)-C(54C)-H(54H)	109.5
C(52C)-C(54C)-H(54I)	109.5
H(54G)-C(54C)-H(54I)	109.5
H(54H)-C(54C)-H(54I)	109.5
C(52C)-C(55C)-H(55G)	109.5
C(52C)-C(55C)-H(55H)	109.5
H(55G)-C(55C)-H(55H)	109.5
C(52C)-C(55C)-H(55I)	109.5
H(55G)-C(55C)-H(55I)	109.5
H(55H)-C(55C)-H(55I)	109.5
F(2B)-B(1B)-F(1B)	110.1(4)
F(2B)-B(1B)-N(2B)	110.8(4)
F(1B)-B(1B)-N(2B)	110.1(4)
F(2B)-B(1B)-N(1B)	110.4(4)
F(1B)-B(1B)-N(1B)	109.7(4)
N(2B)-B(1B)-N(1B)	105.6(3)
Cl(1)-C(1S)-Cl(2)	115.9(4)
Cl(1)-C(1S)-H(1S1)	108.3
Cl(2)-C(1S)-H(1S1)	108.3
Cl(1)-C(1S)-H(1S2)	108.3
Cl(2)-C(1S)-H(1S2)	108.3
H(1S1)-C(1S)-H(1S2)	107.4
Cl(4)-C(2S)-Cl(3)	109.8(5)
Cl(4)-C(2S)-H(2S1)	109.7

Cl(3)-C(2S)-H(2S1)	109.7
Cl(4)-C(2S)-H(2S2)	109.7
Cl(3)-C(2S)-H(2S2)	109.7
H(2S1)-C(2S)-H(2S2)	108.2
Cl(4A)-C(2SA)-Cl(3A)	116.7(6)
Cl(4A)-C(2SA)-H(2S3)	108.1
Cl(3A)-C(2SA)-H(2S3)	108.1
Cl(4A)-C(2SA)-H(2S4)	108.1
Cl(3A)-C(2SA)-H(2S4)	108.1
H(2S3)-C(2SA)-H(2S4)	107.3

Symmetry transformations used to generate equivalent atoms:

Table A4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2.31**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1A)	73(2)	32(2)	48(2)	9(1)	-14(2)	5(1)
F(2A)	45(2)	61(2)	52(2)	-4(2)	4(1)	-16(1)
N(1A)	35(2)	29(2)	31(2)	1(2)	-5(2)	3(2)
N(2A)	35(2)	29(2)	37(2)	-1(2)	-4(2)	2(2)
C(1A)	28(2)	25(2)	33(2)	-3(2)	-7(2)	8(2)
C(2A)	31(2)	31(2)	30(2)	0(2)	-3(2)	6(2)
C(3A)	36(3)	33(2)	31(2)	-2(2)	-9(2)	4(2)
C(4A)	48(3)	41(3)	35(3)	-6(2)	-6(2)	3(2)
C(5A)	43(3)	38(3)	34(3)	4(2)	0(2)	5(2)
C(6A)	41(3)	27(2)	50(3)	-4(2)	-16(2)	0(2)
C(7A)	46(3)	33(3)	42(3)	-7(2)	-11(2)	5(2)
C(8A)	41(3)	30(2)	35(3)	-4(2)	-6(2)	7(2)
C(9A)	33(2)	26(2)	33(2)	0(2)	-7(2)	5(2)
C(10A)	30(2)	22(2)	32(2)	-7(2)	-4(2)	3(2)
C(11A)	28(2)	20(2)	30(2)	-3(2)	-4(2)	3(2)
C(12A)	34(2)	27(2)	29(2)	1(2)	-7(2)	4(2)
C(13A)	32(2)	24(2)	34(2)	-4(2)	-3(2)	3(2)
C(14A)	27(2)	30(2)	35(2)	-1(2)	-9(2)	4(2)
C(15A)	31(2)	24(2)	31(2)	-4(2)	-8(2)	6(2)
C(16A)	29(2)	27(2)	35(2)	-2(2)	-2(2)	4(2)
C(17A)	31(2)	31(2)	32(2)	-4(2)	-2(2)	0(2)
C(18A)	34(2)	32(2)	26(2)	-3(2)	-4(2)	5(2)
C(19A)	43(3)	38(3)	37(3)	-2(2)	-11(2)	-3(2)
C(20A)	42(3)	48(3)	47(3)	7(2)	-18(2)	-3(2)
C(21A)	47(3)	46(3)	38(3)	5(2)	-17(2)	6(2)
C(22A)	37(2)	35(3)	31(2)	-1(2)	-2(2)	1(2)
C(23A)	36(2)	33(2)	28(2)	-4(2)	-3(2)	3(2)
C(24A)	45(3)	42(3)	26(2)	-2(2)	-1(2)	5(2)
C(25A)	43(3)	30(2)	35(3)	0(2)	-2(2)	-1(2)

C(26A)	45(3)	33(2)	31(2)	-4(2)	4(2)	0(2)
C(27A)	59(3)	33(3)	37(3)	-2(2)	-12(2)	7(2)
C(28A)	67(4)	25(2)	51(3)	2(2)	-12(3)	0(2)
C(29A)	68(4)	31(3)	41(3)	-1(2)	-5(2)	-8(2)
C(30A)	46(3)	34(2)	31(2)	-3(2)	-2(2)	2(2)
C(31A)	41(3)	31(2)	31(2)	-6(2)	1(2)	6(2)
C(32A)	46(3)	33(3)	39(3)	-5(2)	1(2)	-3(2)
C(33A)	45(3)	36(3)	42(3)	-5(2)	0(2)	2(2)
C(34A)	40(3)	36(3)	43(3)	-10(2)	1(2)	1(2)
C(35A)	43(3)	34(3)	44(3)	-13(2)	1(2)	2(2)
C(36A)	40(3)	34(3)	39(3)	-15(2)	3(2)	4(2)
C(37A)	47(3)	33(3)	44(3)	-14(2)	3(2)	-8(2)
C(38A)	43(3)	45(3)	47(3)	-14(2)	-2(2)	-9(2)
C(39A)	38(3)	42(3)	40(3)	-11(2)	-4(2)	-4(2)
C(40A)	32(2)	34(2)	41(3)	-13(2)	1(2)	-2(2)
C(41A)	30(2)	31(2)	39(3)	-11(2)	-2(2)	-4(2)
C(42A)	33(2)	38(3)	38(3)	-7(2)	2(2)	0(2)
C(43A)	30(2)	36(3)	38(3)	-8(2)	-5(2)	-2(2)
C(44A)	28(2)	37(3)	35(3)	-7(2)	-2(2)	-2(2)
C(45A)	39(3)	45(3)	50(3)	-7(2)	-22(2)	-1(2)
C(46A)	49(3)	39(3)	54(3)	1(2)	-24(3)	5(2)
C(47A)	45(3)	30(2)	38(3)	-2(2)	-14(2)	0(2)
C(48A)	32(2)	33(2)	28(2)	-6(2)	-5(2)	0(2)
C(49A)	29(2)	30(2)	31(2)	-3(2)	-5(2)	3(2)
C(50A)	34(2)	27(2)	31(2)	-5(2)	-3(2)	2(2)
C(51A)	32(2)	23(2)	31(2)	-2(2)	-2(2)	2(2)
C(52A)	29(2)	37(2)	37(2)	1(2)	-7(2)	-3(2)
C(53A)	46(3)	33(3)	78(4)	11(3)	-5(3)	-5(2)
C(54A)	60(4)	63(4)	47(3)	-2(3)	5(3)	-19(3)
C(55A)	38(3)	61(4)	58(3)	11(3)	-13(2)	-16(3)
B(1A)	39(3)	34(3)	41(3)	4(2)	-4(2)	-4(2)
F(1B)	66(2)	29(1)	50(2)	-11(1)	9(1)	5(1)
F(2B)	42(2)	56(2)	53(2)	-2(1)	-10(1)	-22(1)
N(1B)	24(2)	28(2)	36(2)	-9(2)	0(2)	-1(2)
N(2B)	27(2)	24(2)	40(2)	-4(2)	1(2)	-5(2)

C(1B)	27(2)	22(2)	35(2)	-4(2)	0(2)	-2(2)
C(2B)	23(2)	25(2)	32(2)	-7(2)	3(2)	-3(2)
C(3B)	34(2)	26(2)	33(2)	-3(2)	3(2)	-5(2)
C(4B)	54(3)	32(2)	30(2)	1(2)	3(2)	-6(2)
C(5B)	45(3)	36(2)	27(2)	-5(2)	1(2)	-2(2)
C(6B)	36(3)	25(2)	48(3)	-3(2)	3(2)	-7(2)
C(7B)	45(3)	25(2)	40(3)	1(2)	6(2)	-6(2)
C(8B)	39(3)	26(2)	35(2)	-2(2)	-1(2)	4(2)
C(9B)	28(2)	25(2)	36(2)	-6(2)	1(2)	-2(2)
C(10B)	21(2)	20(2)	37(2)	1(2)	1(2)	-3(2)
C(11B)	25(2)	20(2)	31(2)	1(2)	-1(2)	-4(2)
C(12B)	27(2)	20(2)	33(2)	1(2)	-2(2)	-1(2)
C(13B)	23(2)	19(2)	42(3)	2(2)	-5(2)	-5(2)
C(14B)	21(2)	27(2)	43(3)	-1(2)	-3(2)	0(2)
C(15B)	27(2)	21(2)	35(2)	-2(2)	0(2)	1(2)
C(16B)	23(2)	28(2)	43(3)	-3(2)	0(2)	0(2)
C(17B)	29(2)	29(2)	42(3)	0(2)	-1(2)	2(2)
C(18B)	39(3)	27(2)	32(2)	1(2)	-2(2)	2(2)
C(19B)	32(2)	40(3)	43(3)	-6(2)	4(2)	-6(2)
C(20B)	36(3)	47(3)	50(3)	-7(2)	11(2)	3(2)
C(21B)	37(3)	43(3)	36(3)	-8(2)	4(2)	7(2)
C(22B)	41(3)	36(3)	31(2)	-1(2)	-1(2)	6(2)
C(23B)	33(2)	33(2)	35(2)	-2(2)	-3(2)	5(2)
C(24B)	47(3)	36(3)	38(3)	-10(2)	-6(2)	4(2)
C(25B)	45(3)	42(3)	33(3)	-7(2)	-3(2)	8(2)
C(26B)	40(3)	33(2)	28(2)	-2(2)	-5(2)	3(2)
C(27B)	42(3)	39(3)	43(3)	-4(2)	1(2)	11(2)
C(28B)	53(3)	37(3)	39(3)	-10(2)	6(2)	-1(2)
C(29B)	50(3)	32(3)	39(3)	-4(2)	-1(2)	3(2)
C(30B)	42(3)	38(3)	28(2)	-1(2)	-1(2)	10(2)
C(31B)	48(3)	30(2)	32(2)	-4(2)	-6(2)	4(2)
C(32B)	51(3)	34(2)	34(3)	0(2)	-7(2)	7(2)
C(33B)	46(3)	32(2)	36(3)	-1(2)	-5(2)	8(2)
C(34B)	44(3)	33(3)	40(3)	2(2)	-9(2)	9(2)
C(35B)	40(3)	33(2)	40(3)	2(2)	-4(2)	2(2)

C(36B)	36(3)	30(2)	37(3)	3(2)	-1(2)	4(2)
C(37B)	47(3)	30(2)	40(3)	-4(2)	-3(2)	-5(2)
C(38B)	41(3)	32(3)	46(3)	1(2)	3(2)	-14(2)
C(39B)	38(3)	31(2)	38(3)	0(2)	3(2)	-9(2)
C(40B)	31(2)	27(2)	33(2)	2(2)	-4(2)	-6(2)
C(41B)	30(2)	31(2)	39(3)	2(2)	-1(2)	-3(2)
C(42B)	29(2)	32(3)	37(2)	-1(2)	-1(2)	-6(2)
C(43B)	28(2)	36(3)	35(2)	0(2)	0(2)	-6(2)
C(44B)	30(2)	30(2)	31(2)	-2(2)	2(2)	-9(2)
C(45B)	34(3)	41(3)	42(3)	-10(2)	9(2)	-5(2)
C(46B)	41(3)	38(3)	48(3)	-16(2)	16(2)	-1(2)
C(47B)	33(2)	35(2)	36(3)	-6(2)	4(2)	-5(2)
C(48B)	23(2)	30(2)	29(2)	0(2)	0(2)	-1(2)
C(49B)	26(2)	29(2)	34(2)	-1(2)	-1(2)	-1(2)
C(50B)	32(2)	27(2)	31(2)	-3(2)	0(2)	-7(2)
C(51B)	27(2)	22(2)	30(2)	-1(2)	1(2)	-8(2)
C(52B)	28(2)	35(3)	45(3)	-5(2)	-8(2)	-1(2)
C(53B)	44(6)	32(6)	74(9)	-26(5)	-9(6)	-5(4)
C(54B)	73(10)	76(9)	67(9)	4(7)	-40(8)	-16(8)
C(55B)	25(6)	54(8)	102(10)	-39(7)	8(6)	-19(5)
C(52C)	28(2)	35(3)	45(3)	-5(2)	-8(2)	-1(2)
C(53C)	40(6)	58(8)	61(8)	-26(6)	-11(5)	6(5)
C(54C)	53(7)	41(6)	52(7)	-3(5)	-26(6)	5(5)
C(55C)	54(7)	47(7)	54(7)	-4(5)	-13(5)	-16(6)
B(1B)	29(3)	27(3)	42(3)	-7(2)	1(2)	-4(2)
Cl(1)	235(3)	117(2)	91(2)	-13(1)	38(2)	-86(2)
Cl(2)	98(1)	99(1)	88(1)	-24(1)	14(1)	-20(1)
C(1S)	62(4)	134(7)	58(4)	16(4)	4(3)	-12(4)
Cl(4)	111(4)	110(3)	209(6)	-17(3)	56(4)	-35(3)
Cl(3)	152(2)	146(2)	96(2)	3(2)	6(2)	-22(2)
C(2S)	192(12)	75(6)	171(10)	34(6)	111(9)	32(6)
Cl(3A)	152(2)	146(2)	96(2)	3(2)	6(2)	-22(2)
C(2SA)	192(12)	75(6)	171(10)	34(6)	111(9)	32(6)

Table A5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2.31**.

	x	y	z	U(eq)
H(3AA)	5534	9188	6233	40
H(4AA)	4608	8792	7127	50
H(5AA)	3712	7192	7090	46
H(6AA)	3317	5111	5269	47
H(7AA)	4109	5533	4356	47
H(8AA)	5288	6971	4414	42
H(12A)	6136	9992	4148	36
H(14A)	8343	9204	5147	37
H(19A)	9301	7392	6684	47
H(20A)	9837	6150	7273	54
H(21A)	8863	4714	7414	52
H(23A)	6759	5796	6412	39
H(27A)	6587	1691	7395	51
H(28A)	5335	487	7349	57
H(29A)	3842	794	6902	56
H(31A)	4793	3574	6563	41
H(37A)	-283	2546	4966	49
H(38A)	-1313	3268	4333	54
H(39A)	-868	4754	3907	47
H(41A)	1751	4815	4720	40
H(45A)	403	8298	3392	52
H(46A)	1119	9858	3349	56
H(47A)	2628	10167	3768	45
H(49A)	2717	7349	4308	36
H(53A)	6999	11318	4010	79
H(53B)	8145	11787	3929	79
H(53C)	7558	11674	4511	79
H(54A)	7736	9880	3535	86

H(54B)	8679	9264	3770	86
H(54C)	8894	10324	3493	86
H(55A)	9044	10713	4863	79
H(55B)	9637	10944	4290	79
H(55C)	9543	9844	4529	79
H(3BA)	5791	4423	8762	37
H(4BA)	5075	4245	7878	47
H(5BA)	4171	2628	7910	43
H(6BA)	3340	128	9723	44
H(7BA)	3901	362	10628	45
H(8BA)	5069	1825	10570	40
H(12B)	5922	4827	10812	32
H(14B)	8349	4200	9781	36
H(19B)	9738	2660	8283	47
H(20B)	10472	1508	7714	54
H(21B)	9532	152	7542	47
H(23B)	7071	1051	8499	40
H(27B)	7127	-2849	7548	50
H(28B)	5863	-4075	7653	52
H(29B)	4308	-3857	8162	48
H(31B)	5163	-1089	8410	44
H(37B)	-346	-2361	10043	46
H(38B)	-1572	-1788	10679	48
H(39B)	-1244	-398	11125	43
H(41B)	1639	-214	10339	40
H(45B)	-39	3041	11645	47
H(46B)	704	4571	11687	51
H(47B)	2349	4932	11269	42
H(49B)	2530	2193	10748	36
H(53D)	7378	6540	10366	73
H(53E)	7987	6643	10891	73
H(53F)	6836	6185	10934	73
H(54D)	7321	4609	11367	106
H(54E)	8367	5207	11435	106
H(54F)	8442	4150	11198	106

H(55D)	8970	5652	10006	89
H(55E)	9430	4765	10355	89
H(55F)	9441	5845	10560	89
H(53G)	7025	5273	11350	78
H(53H)	6898	6214	10959	78
H(53I)	7908	6099	11295	78
H(54G)	8331	4015	11142	71
H(54H)	9200	4849	11126	71
H(54I)	9156	4164	10637	71
H(55G)	8889	5670	9982	77
H(55H)	9082	6289	10483	77
H(55I)	8048	6472	10172	77
H(1S1)	1812	-1673	8210	103
H(1S2)	845	-984	8078	103
H(2S1)	7078	5912	12676	185
H(2S2)	7563	5403	13189	185
H(2S3)	6945	5606	12927	185
H(2S4)	8100	5505	13122	185

Table A6. Crystal data and structure refinement for **3.29**.

Identification code	d1689_a	
Empirical formula	C ₅₉ H ₄₁ B Cl ₄ F ₂ N ₂ O ₂	
Formula weight	1000.55	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.4441(9) Å	α = 67.977(4)°.
	b = 13.8945(9) Å	β = 69.106(4)°.
	c = 15.6741(10) Å	γ = 86.313(4)°.
Volume	2527.6(3) Å ³	
Z	2	
Density (calculated)	1.315 Mg/m ³	
Absorption coefficient	2.554 mm ⁻¹	
F(000)	1032	
Crystal size	0.120 x 0.060 x 0.040 mm ³	
Theta range for data collection	3.259 to 67.476°.	
Index ranges	-16 ≤ h ≤ 15, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18	
Reflections collected	29660	
Independent reflections	8880 [R(int) = 0.0649]	
Completeness to theta = 67.476°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7529 and 0.5381	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8880 / 0 / 636	
Goodness-of-fit on F ²	1.042	
Final R indices [I > 2σ(I)]	R1 = 0.0538, wR2 = 0.1432	
R indices (all data)	R1 = 0.0750, wR2 = 0.1578	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.421 and -0.647 e.Å ⁻³	

Table A7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3.29**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	2245(2)	5149(2)	1866(2)	67(1)
F(2)	3110(2)	3743(1)	2415(2)	66(1)
O(1)	-1144(2)	3142(1)	622(1)	31(1)
O(2)	3276(2)	-574(1)	922(1)	30(1)
N(1)	2506(2)	4806(2)	3383(2)	30(1)
N(2)	4021(2)	5442(2)	1784(2)	33(1)
C(1)	4058(2)	5794(2)	3172(2)	24(1)
C(2)	3054(2)	5263(2)	3759(2)	26(1)
C(3)	2397(2)	5104(2)	4737(2)	32(1)
C(4)	1463(2)	4566(2)	4950(2)	38(1)
C(5)	1558(2)	4394(2)	4097(2)	38(1)
C(6)	4618(3)	5717(3)	830(2)	45(1)
C(7)	5544(3)	6323(3)	584(2)	48(1)
C(8)	5489(2)	6430(2)	1445(2)	34(1)
C(9)	4542(2)	5880(2)	2193(2)	28(1)
C(10)	4583(2)	6356(2)	3558(2)	23(1)
C(11)	5553(2)	6063(2)	3701(2)	23(1)
C(12)	6046(2)	6658(2)	4006(2)	25(1)
C(13)	5612(2)	7525(2)	4196(2)	22(1)
C(14)	4646(2)	7796(2)	4068(2)	23(1)
C(15)	4132(2)	7229(2)	3750(2)	24(1)
C(16)	6202(2)	8137(2)	4528(2)	25(1)
C(17)	7298(2)	8574(2)	3718(2)	34(1)
C(18)	6371(2)	7391(2)	5469(2)	32(1)
C(19)	5595(2)	9034(2)	4739(2)	30(1)
C(20)	3170(2)	7560(2)	3576(2)	25(1)
C(21)	2379(2)	7800(2)	3384(2)	27(1)
C(22)	1486(2)	8034(2)	3063(2)	24(1)
C(23)	1073(2)	9005(2)	2900(2)	29(1)

C(24)	273(2)	9234(2)	2512(2)	31(1)
C(25)	-125(2)	8506(2)	2283(2)	29(1)
C(26)	268(2)	7523(2)	2455(2)	25(1)
C(27)	1078(2)	7291(2)	2848(2)	26(1)
C(28)	-124(2)	6757(2)	2212(2)	29(1)
C(29)	-402(2)	6122(2)	1980(2)	30(1)
C(30)	-649(2)	5360(2)	1654(2)	27(1)
C(31)	-1451(2)	5463(2)	1271(2)	29(1)
C(32)	-1646(2)	4739(2)	925(2)	28(1)
C(33)	-1027(2)	3892(2)	945(2)	26(1)
C(34)	-200(2)	3782(2)	1322(2)	26(1)
C(35)	-33(2)	4507(2)	1677(2)	27(1)
C(36)	-1920(2)	3267(2)	166(2)	36(1)
C(37)	507(2)	2973(2)	1299(2)	28(1)
C(38)	1186(2)	2366(2)	1280(2)	29(1)
C(39)	2018(2)	1742(2)	1277(2)	29(1)
C(40)	2766(2)	1221(2)	1309(2)	29(1)
C(41)	3692(2)	700(2)	1415(2)	27(1)
C(42)	3949(2)	-222(2)	1225(2)	25(1)
C(43)	4848(2)	-704(2)	1362(2)	28(1)
C(44)	5488(2)	-285(2)	1682(2)	28(1)
C(45)	5252(2)	631(2)	1865(2)	28(1)
C(46)	4346(2)	1109(2)	1727(2)	28(1)
C(47)	3475(2)	-1546(2)	778(2)	33(1)
C(48)	5897(2)	1083(2)	2192(2)	28(1)
C(49)	6394(2)	1488(2)	2484(2)	28(1)
C(50)	6885(2)	2010(2)	2881(2)	25(1)
C(51)	7698(2)	1593(2)	3236(2)	32(1)
C(52)	8107(2)	2103(2)	3663(2)	34(1)
C(53)	7715(2)	3019(2)	3746(2)	29(1)
C(54)	6908(2)	3450(2)	3393(2)	25(1)
C(55)	6506(2)	2948(2)	2949(2)	26(1)
C(56)	6459(2)	4391(2)	3486(2)	26(1)
C(57)	6033(2)	5154(2)	3562(2)	25(1)
C(1S)	-1483(4)	8519(3)	6262(3)	70(1)

Cl(1)	-504(1)	8270(1)	5300(1)	84(1)
Cl(2)	-2173(1)	9608(1)	5842(1)	75(1)
C(2S)	1542(3)	600(3)	-165(3)	50(1)
Cl(3)	2163(1)	1773(1)	-1167(1)	53(1)
Cl(4)	1452(1)	-401(1)	-576(1)	49(1)
B(1)	2944(3)	4753(3)	2347(3)	39(1)

Table A8. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **3.29**.

F(1)-B(1)	1.371(4)
F(2)-B(1)	1.376(4)
O(1)-C(33)	1.355(3)
O(1)-C(36)	1.430(3)
O(2)-C(42)	1.350(3)
O(2)-C(47)	1.444(3)
N(1)-C(5)	1.342(4)
N(1)-C(2)	1.395(3)
N(1)-B(1)	1.546(4)
N(2)-C(6)	1.334(4)
N(2)-C(9)	1.393(3)
N(2)-B(1)	1.558(4)
C(1)-C(2)	1.395(4)
C(1)-C(9)	1.397(4)
C(1)-C(10)	1.484(3)
C(2)-C(3)	1.409(4)
C(3)-C(4)	1.372(4)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.405(5)
C(4)-H(4A)	0.9500
C(5)-H(5A)	0.9500
C(6)-C(7)	1.398(5)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.388(4)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.402(4)
C(8)-H(8A)	0.9500
C(10)-C(15)	1.406(3)
C(10)-C(11)	1.410(4)
C(11)-C(12)	1.394(4)
C(11)-C(57)	1.435(3)
C(12)-C(13)	1.391(3)

C(12)-H(12A)	0.9500
C(13)-C(14)	1.390(4)
C(13)-C(16)	1.529(3)
C(14)-C(15)	1.400(4)
C(14)-H(14A)	0.9500
C(15)-C(20)	1.428(4)
C(16)-C(19)	1.522(3)
C(16)-C(17)	1.535(4)
C(16)-C(18)	1.536(4)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(21)	1.201(4)
C(21)-C(22)	1.434(4)
C(22)-C(23)	1.393(4)
C(22)-C(27)	1.395(4)
C(23)-C(24)	1.381(4)
C(23)-H(23A)	0.9500
C(24)-C(25)	1.383(4)
C(24)-H(24A)	0.9500
C(25)-C(26)	1.397(4)
C(25)-H(25A)	0.9500
C(26)-C(27)	1.398(4)
C(26)-C(28)	1.441(4)
C(27)-H(27A)	0.9500
C(28)-C(29)	1.196(4)
C(29)-C(30)	1.438(4)
C(30)-C(31)	1.386(4)
C(30)-C(35)	1.398(4)

C(31)-C(32)	1.385(4)
C(31)-H(31A)	0.9500
C(32)-C(33)	1.394(4)
C(32)-H(32A)	0.9500
C(33)-C(34)	1.410(4)
C(34)-C(35)	1.384(4)
C(34)-C(37)	1.427(4)
C(35)-H(35A)	0.9500
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-C(38)	1.201(4)
C(38)-C(39)	1.371(4)
C(39)-C(40)	1.205(4)
C(40)-C(41)	1.430(4)
C(41)-C(46)	1.383(4)
C(41)-C(42)	1.416(4)
C(42)-C(43)	1.388(4)
C(43)-C(44)	1.386(4)
C(43)-H(43A)	0.9500
C(44)-C(45)	1.400(4)
C(44)-H(44A)	0.9500
C(45)-C(46)	1.396(4)
C(45)-C(48)	1.429(4)
C(46)-H(46A)	0.9500
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-C(49)	1.195(4)
C(49)-C(50)	1.428(4)
C(50)-C(51)	1.397(4)
C(50)-C(55)	1.397(4)
C(51)-C(52)	1.385(4)
C(51)-H(51A)	0.9500
C(52)-C(53)	1.380(4)

C(52)-H(52A)	0.9500
C(53)-C(54)	1.392(4)
C(53)-H(53A)	0.9500
C(54)-C(55)	1.394(4)
C(54)-C(56)	1.439(4)
C(55)-H(55A)	0.9500
C(56)-C(57)	1.198(4)
C(1S)-Cl(1)	1.745(4)
C(1S)-Cl(2)	1.757(5)
C(1S)-H(1SA)	0.9900
C(1S)-H(1SB)	0.9900
C(2S)-Cl(4)	1.764(3)
C(2S)-Cl(3)	1.772(4)
C(2S)-H(2SA)	0.9900
C(2S)-H(2SB)	0.9900

C(33)-O(1)-C(36)	117.3(2)
C(42)-O(2)-C(47)	117.7(2)
C(5)-N(1)-C(2)	107.3(2)
C(5)-N(1)-B(1)	127.1(2)
C(2)-N(1)-B(1)	125.6(2)
C(6)-N(2)-C(9)	107.4(2)
C(6)-N(2)-B(1)	126.8(2)
C(9)-N(2)-B(1)	125.9(2)
C(2)-C(1)-C(9)	120.9(2)
C(2)-C(1)-C(10)	119.8(2)
C(9)-C(1)-C(10)	119.0(2)
N(1)-C(2)-C(1)	120.8(2)
N(1)-C(2)-C(3)	107.8(2)
C(1)-C(2)-C(3)	131.3(2)
C(4)-C(3)-C(2)	107.9(3)
C(4)-C(3)-H(3A)	126.0
C(2)-C(3)-H(3A)	126.0
C(3)-C(4)-C(5)	106.4(3)
C(3)-C(4)-H(4A)	126.8

C(5)-C(4)-H(4A)	126.8
N(1)-C(5)-C(4)	110.6(3)
N(1)-C(5)-H(5A)	124.7
C(4)-C(5)-H(5A)	124.7
N(2)-C(6)-C(7)	111.0(3)
N(2)-C(6)-H(6A)	124.5
C(7)-C(6)-H(6A)	124.5
C(8)-C(7)-C(6)	106.0(3)
C(8)-C(7)-H(7A)	127.0
C(6)-C(7)-H(7A)	127.0
C(7)-C(8)-C(9)	107.6(3)
C(7)-C(8)-H(8A)	126.2
C(9)-C(8)-H(8A)	126.2
N(2)-C(9)-C(1)	120.2(2)
N(2)-C(9)-C(8)	108.0(2)
C(1)-C(9)-C(8)	131.5(2)
C(15)-C(10)-C(11)	118.7(2)
C(15)-C(10)-C(1)	119.7(2)
C(11)-C(10)-C(1)	121.6(2)
C(12)-C(11)-C(10)	119.2(2)
C(12)-C(11)-C(57)	119.2(2)
C(10)-C(11)-C(57)	121.6(2)
C(13)-C(12)-C(11)	122.8(2)
C(13)-C(12)-H(12A)	118.6
C(11)-C(12)-H(12A)	118.6
C(14)-C(13)-C(12)	117.5(2)
C(14)-C(13)-C(16)	122.9(2)
C(12)-C(13)-C(16)	119.6(2)
C(13)-C(14)-C(15)	121.5(2)
C(13)-C(14)-H(14A)	119.2
C(15)-C(14)-H(14A)	119.2
C(14)-C(15)-C(10)	120.3(2)
C(14)-C(15)-C(20)	120.1(2)
C(10)-C(15)-C(20)	119.5(2)
C(19)-C(16)-C(13)	112.6(2)

C(19)-C(16)-C(17)	108.8(2)
C(13)-C(16)-C(17)	109.0(2)
C(19)-C(16)-C(18)	109.0(2)
C(13)-C(16)-C(18)	108.7(2)
C(17)-C(16)-C(18)	108.7(2)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-C(15)	175.1(3)
C(20)-C(21)-C(22)	173.1(3)
C(23)-C(22)-C(27)	119.8(2)
C(23)-C(22)-C(21)	121.4(2)
C(27)-C(22)-C(21)	118.6(2)
C(24)-C(23)-C(22)	119.9(2)
C(24)-C(23)-H(23A)	120.1
C(22)-C(23)-H(23A)	120.1
C(23)-C(24)-C(25)	120.6(2)
C(23)-C(24)-H(24A)	119.7
C(25)-C(24)-H(24A)	119.7
C(24)-C(25)-C(26)	120.4(2)

C(24)-C(25)-H(25A)	119.8
C(26)-C(25)-H(25A)	119.8
C(25)-C(26)-C(27)	119.0(2)
C(25)-C(26)-C(28)	121.4(2)
C(27)-C(26)-C(28)	119.5(2)
C(22)-C(27)-C(26)	120.3(2)
C(22)-C(27)-H(27A)	119.9
C(26)-C(27)-H(27A)	119.9
C(29)-C(28)-C(26)	176.9(3)
C(28)-C(29)-C(30)	175.5(3)
C(31)-C(30)-C(35)	118.3(2)
C(31)-C(30)-C(29)	122.2(2)
C(35)-C(30)-C(29)	119.4(2)
C(32)-C(31)-C(30)	121.1(2)
C(32)-C(31)-H(31A)	119.4
C(30)-C(31)-H(31A)	119.4
C(31)-C(32)-C(33)	120.5(2)
C(31)-C(32)-H(32A)	119.8
C(33)-C(32)-H(32A)	119.8
O(1)-C(33)-C(32)	125.4(2)
O(1)-C(33)-C(34)	115.5(2)
C(32)-C(33)-C(34)	119.1(2)
C(35)-C(34)-C(33)	119.3(2)
C(35)-C(34)-C(37)	119.0(2)
C(33)-C(34)-C(37)	121.7(2)
C(34)-C(35)-C(30)	121.7(2)
C(34)-C(35)-H(35A)	119.1
C(30)-C(35)-H(35A)	119.1
O(1)-C(36)-H(36A)	109.5
O(1)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
O(1)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(38)-C(37)-C(34)	172.5(3)

C(37)-C(38)-C(39)	174.0(3)
C(40)-C(39)-C(38)	176.0(3)
C(39)-C(40)-C(41)	171.1(3)
C(46)-C(41)-C(42)	119.4(2)
C(46)-C(41)-C(40)	118.4(2)
C(42)-C(41)-C(40)	122.1(2)
O(2)-C(42)-C(43)	124.5(2)
O(2)-C(42)-C(41)	116.1(2)
C(43)-C(42)-C(41)	119.4(2)
C(44)-C(43)-C(42)	120.2(2)
C(44)-C(43)-H(43A)	119.9
C(42)-C(43)-H(43A)	119.9
C(43)-C(44)-C(45)	121.1(3)
C(43)-C(44)-H(44A)	119.4
C(45)-C(44)-H(44A)	119.4
C(46)-C(45)-C(44)	118.3(2)
C(46)-C(45)-C(48)	119.3(2)
C(44)-C(45)-C(48)	122.5(2)
C(41)-C(46)-C(45)	121.5(2)
C(41)-C(46)-H(46A)	119.2
C(45)-C(46)-H(46A)	119.2
O(2)-C(47)-H(47A)	109.5
O(2)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
O(2)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(49)-C(48)-C(45)	176.7(3)
C(48)-C(49)-C(50)	174.0(3)
C(51)-C(50)-C(55)	119.1(2)
C(51)-C(50)-C(49)	122.3(2)
C(55)-C(50)-C(49)	118.6(2)
C(52)-C(51)-C(50)	120.0(2)
C(52)-C(51)-H(51A)	120.0
C(50)-C(51)-H(51A)	120.0

C(53)-C(52)-C(51)	120.7(3)
C(53)-C(52)-H(52A)	119.7
C(51)-C(52)-H(52A)	119.7
C(52)-C(53)-C(54)	120.3(3)
C(52)-C(53)-H(53A)	119.8
C(54)-C(53)-H(53A)	119.8
C(53)-C(54)-C(55)	119.1(2)
C(53)-C(54)-C(56)	122.2(2)
C(55)-C(54)-C(56)	118.7(2)
C(54)-C(55)-C(50)	120.7(2)
C(54)-C(55)-H(55A)	119.6
C(50)-C(55)-H(55A)	119.6
C(57)-C(56)-C(54)	176.2(3)
C(56)-C(57)-C(11)	176.1(3)
Cl(1)-C(1S)-Cl(2)	112.7(2)
Cl(1)-C(1S)-H(1SA)	109.1
Cl(2)-C(1S)-H(1SA)	109.1
Cl(1)-C(1S)-H(1SB)	109.1
Cl(2)-C(1S)-H(1SB)	109.1
H(1SA)-C(1S)-H(1SB)	107.8
Cl(4)-C(2S)-Cl(3)	111.42(19)
Cl(4)-C(2S)-H(2SA)	109.3
Cl(3)-C(2S)-H(2SA)	109.3
Cl(4)-C(2S)-H(2SB)	109.3
Cl(3)-C(2S)-H(2SB)	109.3
H(2SA)-C(2S)-H(2SB)	108.0
F(1)-B(1)-F(2)	110.0(3)
F(1)-B(1)-N(1)	110.0(3)
F(2)-B(1)-N(1)	110.7(3)
F(1)-B(1)-N(2)	109.7(3)
F(2)-B(1)-N(2)	110.3(3)
N(1)-B(1)-N(2)	106.0(2)

Symmetry transformations used to generate equivalent atoms:

Table A9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3.29**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	57(1)	95(2)	55(1)	-11(1)	-42(1)	-10(1)
F(2)	111(2)	36(1)	58(1)	-26(1)	-28(1)	-11(1)
O(1)	38(1)	27(1)	37(1)	-14(1)	-21(1)	1(1)
O(2)	32(1)	29(1)	37(1)	-18(1)	-16(1)	5(1)
N(1)	33(1)	23(1)	41(1)	-9(1)	-23(1)	0(1)
N(2)	39(1)	33(1)	37(1)	-18(1)	-21(1)	5(1)
C(1)	27(1)	19(1)	34(2)	-10(1)	-21(1)	7(1)
C(2)	29(1)	22(1)	35(2)	-10(1)	-21(1)	4(1)
C(3)	33(2)	25(1)	39(2)	-10(1)	-18(1)	4(1)
C(4)	29(2)	32(2)	48(2)	-9(1)	-14(1)	2(1)
C(5)	31(2)	30(2)	56(2)	-11(1)	-23(1)	1(1)
C(6)	56(2)	50(2)	42(2)	-27(2)	-23(2)	7(2)
C(7)	50(2)	54(2)	38(2)	-22(2)	-10(2)	8(2)
C(8)	34(2)	32(2)	40(2)	-16(1)	-14(1)	4(1)
C(9)	31(1)	26(1)	37(2)	-16(1)	-20(1)	8(1)
C(10)	25(1)	19(1)	28(1)	-9(1)	-13(1)	0(1)
C(11)	25(1)	20(1)	29(1)	-10(1)	-13(1)	4(1)
C(12)	23(1)	23(1)	34(2)	-13(1)	-16(1)	4(1)
C(13)	22(1)	20(1)	27(1)	-10(1)	-10(1)	1(1)
C(14)	26(1)	18(1)	28(1)	-9(1)	-13(1)	3(1)
C(15)	24(1)	22(1)	27(1)	-9(1)	-13(1)	4(1)
C(16)	27(1)	20(1)	30(1)	-11(1)	-12(1)	0(1)
C(17)	28(2)	32(1)	45(2)	-18(1)	-10(1)	-3(1)
C(18)	39(2)	29(1)	40(2)	-15(1)	-25(1)	6(1)
C(19)	33(2)	24(1)	39(2)	-16(1)	-16(1)	4(1)
C(20)	28(1)	19(1)	32(2)	-10(1)	-15(1)	2(1)
C(21)	28(1)	24(1)	33(2)	-12(1)	-15(1)	4(1)
C(22)	20(1)	24(1)	29(1)	-10(1)	-10(1)	3(1)
C(23)	27(1)	25(1)	39(2)	-16(1)	-14(1)	5(1)

C(24)	27(1)	26(1)	46(2)	-16(1)	-19(1)	11(1)
C(25)	25(1)	30(1)	35(2)	-13(1)	-15(1)	7(1)
C(26)	21(1)	24(1)	29(1)	-11(1)	-9(1)	1(1)
C(27)	23(1)	23(1)	33(2)	-10(1)	-11(1)	3(1)
C(28)	24(1)	30(1)	38(2)	-16(1)	-14(1)	5(1)
C(29)	25(1)	29(1)	39(2)	-14(1)	-14(1)	5(1)
C(30)	23(1)	25(1)	33(2)	-12(1)	-11(1)	1(1)
C(31)	27(1)	23(1)	36(2)	-11(1)	-13(1)	4(1)
C(32)	25(1)	28(1)	32(2)	-9(1)	-15(1)	2(1)
C(33)	26(1)	23(1)	29(1)	-9(1)	-12(1)	-1(1)
C(34)	25(1)	23(1)	29(1)	-8(1)	-11(1)	2(1)
C(35)	24(1)	26(1)	33(2)	-10(1)	-15(1)	2(1)
C(36)	41(2)	35(2)	41(2)	-16(1)	-25(1)	0(1)
C(37)	31(1)	26(1)	31(2)	-11(1)	-15(1)	4(1)
C(38)	32(2)	26(1)	33(2)	-12(1)	-16(1)	5(1)
C(39)	32(2)	28(1)	33(2)	-14(1)	-15(1)	5(1)
C(40)	33(2)	27(1)	30(2)	-13(1)	-13(1)	4(1)
C(41)	28(1)	25(1)	29(1)	-11(1)	-10(1)	6(1)
C(42)	27(1)	24(1)	26(1)	-10(1)	-10(1)	1(1)
C(43)	31(1)	23(1)	32(2)	-14(1)	-12(1)	6(1)
C(44)	28(1)	26(1)	33(2)	-11(1)	-14(1)	4(1)
C(45)	31(1)	24(1)	29(1)	-10(1)	-12(1)	2(1)
C(46)	31(1)	23(1)	32(2)	-14(1)	-12(1)	4(1)
C(47)	40(2)	29(1)	37(2)	-18(1)	-17(1)	2(1)
C(48)	31(1)	23(1)	30(2)	-10(1)	-11(1)	5(1)
C(49)	32(1)	24(1)	30(2)	-12(1)	-10(1)	4(1)
C(50)	26(1)	22(1)	27(1)	-11(1)	-7(1)	-1(1)
C(51)	32(2)	22(1)	44(2)	-15(1)	-15(1)	7(1)
C(52)	30(2)	29(1)	48(2)	-15(1)	-21(1)	8(1)
C(53)	30(1)	28(1)	36(2)	-14(1)	-17(1)	3(1)
C(54)	26(1)	21(1)	27(1)	-10(1)	-9(1)	3(1)
C(55)	28(1)	23(1)	28(1)	-10(1)	-11(1)	3(1)
C(56)	29(1)	26(1)	30(2)	-13(1)	-14(1)	2(1)
C(57)	27(1)	26(1)	31(1)	-14(1)	-16(1)	4(1)
C(1S)	89(3)	69(3)	51(2)	-24(2)	-22(2)	-10(2)

Cl(1)	74(1)	103(1)	74(1)	-45(1)	-8(1)	-18(1)
Cl(2)	91(1)	67(1)	81(1)	-29(1)	-43(1)	-8(1)
C(2S)	49(2)	60(2)	57(2)	-34(2)	-24(2)	7(2)
Cl(3)	66(1)	40(1)	75(1)	-29(1)	-44(1)	17(1)
Cl(4)	53(1)	42(1)	66(1)	-24(1)	-34(1)	9(1)
B(1)	49(2)	33(2)	46(2)	-12(2)	-33(2)	-1(2)

Table A10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3.29**.

	x	y	z	U(eq)
H(3A)	2571	5329	5173	38
H(4A)	870	4351	5554	46
H(5A)	1025	4037	4034	46
H(6A)	4438	5527	378	54
H(7A)	6098	6603	-44	57
H(8A)	6000	6807	1515	41
H(12A)	6706	6463	4088	30
H(14A)	4328	8381	4200	28
H(17A)	7703	8000	3588	51
H(17B)	7690	8950	3934	51
H(17C)	7200	9052	3113	51
H(18A)	6850	6869	5315	48
H(18B)	5681	7043	5967	48
H(18C)	6688	7786	5724	48
H(19A)	6001	9397	4954	45
H(19B)	4895	8763	5260	45
H(19C)	5496	9521	4138	45
H(23A)	1342	9509	3055	34
H(24A)	-7	9897	2400	37
H(25A)	-668	8677	2008	35
H(27A)	1352	6625	2968	32
H(31A)	-1875	6040	1246	34
H(32A)	-2205	4820	673	33
H(35A)	515	4423	1943	32
H(36A)	-1883	2715	-89	53
H(36B)	-1775	3948	-378	53
H(36C)	-2635	3223	654	53
H(43A)	5024	-1323	1236	33

H(44A)	6098	-626	1778	34
H(46A)	4175	1731	1849	33
H(47A)	2928	-1716	568	49
H(47B)	3451	-2102	1399	49
H(47C)	4181	-1480	271	49
H(51A)	7971	961	3185	38
H(52A)	8662	1819	3901	40
H(53A)	7998	3358	4046	35
H(55A)	5970	3247	2690	31
H(1SA)	-1143	8637	6684	83
H(1SB)	-2000	7900	6672	83
H(2SA)	1959	379	276	60
H(2SB)	816	723	219	60

Table A11. Torsion angles [$^{\circ}$] for **3.29**.

C(5)-N(1)-C(2)-C(1)	-177.5(2)
B(1)-N(1)-C(2)-C(1)	4.8(4)
C(5)-N(1)-C(2)-C(3)	0.4(3)
B(1)-N(1)-C(2)-C(3)	-177.3(2)
C(9)-C(1)-C(2)-N(1)	-0.2(4)
C(10)-C(1)-C(2)-N(1)	174.4(2)
C(9)-C(1)-C(2)-C(3)	-177.6(3)
C(10)-C(1)-C(2)-C(3)	-2.9(4)
N(1)-C(2)-C(3)-C(4)	-0.4(3)
C(1)-C(2)-C(3)-C(4)	177.2(3)
C(2)-C(3)-C(4)-C(5)	0.3(3)
C(2)-N(1)-C(5)-C(4)	-0.2(3)
B(1)-N(1)-C(5)-C(4)	177.4(3)
C(3)-C(4)-C(5)-N(1)	0.0(3)
C(9)-N(2)-C(6)-C(7)	0.8(4)
B(1)-N(2)-C(6)-C(7)	-178.7(3)
N(2)-C(6)-C(7)-C(8)	-0.9(4)
C(6)-C(7)-C(8)-C(9)	0.7(4)
C(6)-N(2)-C(9)-C(1)	174.8(3)
B(1)-N(2)-C(9)-C(1)	-5.7(4)
C(6)-N(2)-C(9)-C(8)	-0.3(3)
B(1)-N(2)-C(9)-C(8)	179.2(3)
C(2)-C(1)-C(9)-N(2)	0.7(4)
C(10)-C(1)-C(9)-N(2)	-174.0(2)
C(2)-C(1)-C(9)-C(8)	174.5(3)
C(10)-C(1)-C(9)-C(8)	-0.2(4)
C(7)-C(8)-C(9)-N(2)	-0.2(3)
C(7)-C(8)-C(9)-C(1)	-174.6(3)
C(2)-C(1)-C(10)-C(15)	-66.2(3)
C(9)-C(1)-C(10)-C(15)	108.6(3)
C(2)-C(1)-C(10)-C(11)	116.5(3)
C(9)-C(1)-C(10)-C(11)	-68.7(3)

C(15)-C(10)-C(11)-C(12)	-1.4(4)
C(1)-C(10)-C(11)-C(12)	175.9(2)
C(15)-C(10)-C(11)-C(57)	177.2(2)
C(1)-C(10)-C(11)-C(57)	-5.5(4)
C(10)-C(11)-C(12)-C(13)	1.3(4)
C(57)-C(11)-C(12)-C(13)	-177.4(2)
C(11)-C(12)-C(13)-C(14)	-0.2(4)
C(11)-C(12)-C(13)-C(16)	180.0(2)
C(12)-C(13)-C(14)-C(15)	-0.7(4)
C(16)-C(13)-C(14)-C(15)	179.1(2)
C(13)-C(14)-C(15)-C(10)	0.6(4)
C(13)-C(14)-C(15)-C(20)	-176.7(2)
C(11)-C(10)-C(15)-C(14)	0.5(4)
C(1)-C(10)-C(15)-C(14)	-176.9(2)
C(11)-C(10)-C(15)-C(20)	177.8(2)
C(1)-C(10)-C(15)-C(20)	0.4(4)
C(14)-C(13)-C(16)-C(19)	2.3(4)
C(12)-C(13)-C(16)-C(19)	-177.9(2)
C(14)-C(13)-C(16)-C(17)	-118.5(3)
C(12)-C(13)-C(16)-C(17)	61.3(3)
C(14)-C(13)-C(16)-C(18)	123.1(3)
C(12)-C(13)-C(16)-C(18)	-57.1(3)
C(27)-C(22)-C(23)-C(24)	-0.9(4)
C(21)-C(22)-C(23)-C(24)	174.5(3)
C(22)-C(23)-C(24)-C(25)	0.0(4)
C(23)-C(24)-C(25)-C(26)	0.9(4)
C(24)-C(25)-C(26)-C(27)	-0.9(4)
C(24)-C(25)-C(26)-C(28)	-179.3(3)
C(23)-C(22)-C(27)-C(26)	0.9(4)
C(21)-C(22)-C(27)-C(26)	-174.6(2)
C(25)-C(26)-C(27)-C(22)	0.0(4)
C(28)-C(26)-C(27)-C(22)	178.4(2)
C(35)-C(30)-C(31)-C(32)	0.4(4)
C(29)-C(30)-C(31)-C(32)	177.4(3)
C(30)-C(31)-C(32)-C(33)	-0.7(4)

C(36)-O(1)-C(33)-C(32)	4.2(4)
C(36)-O(1)-C(33)-C(34)	-175.5(2)
C(31)-C(32)-C(33)-O(1)	-179.7(3)
C(31)-C(32)-C(33)-C(34)	0.0(4)
O(1)-C(33)-C(34)-C(35)	-179.3(2)
C(32)-C(33)-C(34)-C(35)	0.9(4)
O(1)-C(33)-C(34)-C(37)	4.1(4)
C(32)-C(33)-C(34)-C(37)	-175.6(2)
C(33)-C(34)-C(35)-C(30)	-1.3(4)
C(37)-C(34)-C(35)-C(30)	175.3(3)
C(31)-C(30)-C(35)-C(34)	0.6(4)
C(29)-C(30)-C(35)-C(34)	-176.4(3)
C(47)-O(2)-C(42)-C(43)	3.2(4)
C(47)-O(2)-C(42)-C(41)	-176.3(2)
C(46)-C(41)-C(42)-O(2)	-179.9(2)
C(40)-C(41)-C(42)-O(2)	0.9(4)
C(46)-C(41)-C(42)-C(43)	0.5(4)
C(40)-C(41)-C(42)-C(43)	-178.6(3)
O(2)-C(42)-C(43)-C(44)	-179.6(2)
C(41)-C(42)-C(43)-C(44)	-0.1(4)
C(42)-C(43)-C(44)-C(45)	-0.5(4)
C(43)-C(44)-C(45)-C(46)	0.6(4)
C(43)-C(44)-C(45)-C(48)	-179.8(3)
C(42)-C(41)-C(46)-C(45)	-0.5(4)
C(40)-C(41)-C(46)-C(45)	178.7(3)
C(44)-C(45)-C(46)-C(41)	-0.1(4)
C(48)-C(45)-C(46)-C(41)	-179.7(3)
C(55)-C(50)-C(51)-C(52)	1.0(4)
C(49)-C(50)-C(51)-C(52)	-176.5(3)
C(50)-C(51)-C(52)-C(53)	0.3(4)
C(51)-C(52)-C(53)-C(54)	-0.6(4)
C(52)-C(53)-C(54)-C(55)	-0.4(4)
C(52)-C(53)-C(54)-C(56)	178.5(3)
C(53)-C(54)-C(55)-C(50)	1.7(4)
C(56)-C(54)-C(55)-C(50)	-177.2(2)

C(51)-C(50)-C(55)-C(54)	-2.0(4)
C(49)-C(50)-C(55)-C(54)	175.6(2)
C(5)-N(1)-B(1)-F(1)	56.1(4)
C(2)-N(1)-B(1)-F(1)	-126.7(3)
C(5)-N(1)-B(1)-F(2)	-65.7(4)
C(2)-N(1)-B(1)-F(2)	111.5(3)
C(5)-N(1)-B(1)-N(2)	174.7(2)
C(2)-N(1)-B(1)-N(2)	-8.1(4)
C(6)-N(2)-B(1)-F(1)	-53.2(4)
C(9)-N(2)-B(1)-F(1)	127.4(3)
C(6)-N(2)-B(1)-F(2)	68.2(4)
C(9)-N(2)-B(1)-F(2)	-111.3(3)
C(6)-N(2)-B(1)-N(1)	-171.9(3)
C(9)-N(2)-B(1)-N(1)	8.6(4)

Symmetry transformations used to generate equivalent atoms:

Table A12. Crystal data and structure refinement for **3.37**.

Identification code	d1690_a_sq	
Empirical formula	C ₅₇ H ₃₇ B F ₂ N ₂ O ₂	
Formula weight	830.69	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.8320(5) Å	α = 77.650(2)°.
	b = 13.6752(5) Å	β = 74.953(2)°.
	c = 18.0475(7) Å	γ = 73.617(2)°.
Volume	2448.18(18) Å ³	
Z	2	
Density (calculated)	1.127 Mg/m ³	
Absorption coefficient	0.583 mm ⁻¹	
F(000)	864	
Crystal size	0.170 x 0.100 x 0.080 mm ³	
Theta range for data collection	2.565 to 67.460°.	
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21	
Reflections collected	84458	
Independent reflections	8542 [R(int) = 0.0771]	
Completeness to theta = 67.460°	97.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7529 and 0.6460	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8542 / 0 / 583	
Goodness-of-fit on F ²	1.039	
Final R indices [I > 2σ(I)]	R1 = 0.0474, wR2 = 0.1177	
R indices (all data)	R1 = 0.0687, wR2 = 0.1298	
Extinction coefficient	0.00129(17)	
Largest diff. peak and hole	0.328 and -0.314 e.Å ⁻³	

Table A13. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3.37**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	3884(1)	6615(1)	8022(1)	72(1)
F(2)	5719(2)	5402(1)	7626(1)	69(1)
O(1)	4195(1)	12548(1)	6524(1)	44(1)
O(2)	9894(1)	4996(1)	3621(1)	44(1)
N(1)	5902(2)	7150(1)	7444(1)	39(1)
N(2)	4737(2)	6622(1)	6649(1)	36(1)
C(1)	6119(2)	7826(1)	6070(1)	29(1)
C(2)	6428(2)	7768(1)	6787(1)	32(1)
C(3)	7255(2)	8240(1)	7002(1)	39(1)
C(4)	7218(2)	7911(2)	7782(1)	51(1)
C(5)	6387(2)	7240(2)	8035(1)	51(1)
C(6)	3952(2)	6207(1)	6417(1)	44(1)
C(7)	3945(2)	6557(1)	5631(1)	44(1)
C(8)	4763(2)	7226(1)	5370(1)	35(1)
C(9)	5268(2)	7266(1)	6007(1)	30(1)
C(10)	6746(2)	8455(1)	5374(1)	28(1)
C(11)	7579(2)	7985(1)	4740(1)	29(1)
C(12)	8212(2)	8568(1)	4102(1)	31(1)
C(13)	8067(2)	9618(1)	4057(1)	30(1)
C(14)	7226(2)	10081(1)	4684(1)	32(1)
C(15)	6564(2)	9530(1)	5329(1)	30(1)
C(16)	8810(2)	10253(1)	3380(1)	35(1)
C(17)	9470(2)	9664(2)	2695(1)	42(1)
C(18)	7856(2)	11254(2)	3095(1)	50(1)
C(19)	9877(2)	10531(2)	3654(1)	53(1)
C(20)	5694(2)	10056(1)	5945(1)	31(1)
C(21)	4990(2)	10478(1)	6471(1)	33(1)
C(22)	4151(2)	10876(1)	7151(1)	32(1)
C(23)	3739(2)	11939(1)	7181(1)	37(1)

C(24)	2935(2)	12289(2)	7850(1)	46(1)
C(25)	2535(2)	11605(2)	8488(1)	47(1)
C(26)	2930(2)	10546(2)	8477(1)	41(1)
C(27)	3748(2)	10194(1)	7802(1)	36(1)
C(28)	2511(2)	9812(2)	9124(1)	45(1)
C(29)	2189(2)	9157(2)	9633(1)	48(1)
C(30)	1894(2)	8304(2)	10200(1)	44(1)
C(31)	1045(2)	8438(2)	10923(1)	50(1)
C(32)	796(2)	7588(2)	11455(1)	55(1)
C(33)	1367(2)	6606(2)	11284(1)	56(1)
C(34)	2221(2)	6458(2)	10566(1)	50(1)
C(35)	2474(2)	7311(2)	10029(1)	47(1)
C(36)	3911(2)	13634(1)	6542(1)	52(1)
C(37)	2838(2)	5448(2)	10363(1)	56(1)
C(38)	3393(3)	4650(2)	10125(1)	59(1)
C(39)	4044(3)	3777(2)	9797(1)	57(1)
C(40)	4620(2)	3050(2)	9471(1)	54(1)
C(41)	5346(2)	2282(2)	8990(1)	46(1)
C(42)	5420(2)	1234(2)	9240(1)	54(1)
C(43)	6105(2)	534(2)	8744(1)	56(1)
C(44)	6717(2)	855(2)	7997(1)	48(1)
C(45)	6662(2)	1898(2)	7737(1)	41(1)
C(46)	5977(2)	2609(2)	8239(1)	44(1)
C(47)	11141(2)	4552(2)	3155(1)	55(1)
C(48)	7285(2)	2269(2)	6966(1)	42(1)
C(49)	7771(2)	2659(1)	6337(1)	40(1)
C(50)	8300(2)	3218(1)	5614(1)	34(1)
C(51)	9166(2)	2734(1)	5006(1)	35(1)
C(52)	9690(2)	3302(1)	4330(1)	37(1)
C(53)	9371(2)	4371(1)	4246(1)	34(1)
C(54)	8475(2)	4876(1)	4841(1)	31(1)
C(55)	7950(2)	4294(1)	5514(1)	33(1)
C(56)	8152(2)	5976(1)	4773(1)	32(1)
C(57)	7863(2)	6892(1)	4760(1)	31(1)
B(1)	5033(2)	6417(2)	7470(2)	45(1)

Table A14. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **3.37**.

F(1)-B(1)	1.377(3)
F(2)-B(1)	1.385(3)
O(1)-C(23)	1.360(2)
O(1)-C(36)	1.435(2)
O(2)-C(53)	1.361(2)
O(2)-C(47)	1.437(2)
N(1)-C(5)	1.348(3)
N(1)-C(2)	1.391(2)
N(1)-B(1)	1.542(3)
N(2)-C(6)	1.333(3)
N(2)-C(9)	1.396(2)
N(2)-B(1)	1.549(3)
C(1)-C(9)	1.393(2)
C(1)-C(2)	1.400(3)
C(1)-C(10)	1.485(2)
C(2)-C(3)	1.409(3)
C(3)-C(4)	1.378(3)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.391(3)
C(4)-H(4A)	0.9500
C(5)-H(5A)	0.9500
C(6)-C(7)	1.398(3)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.379(3)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.412(3)
C(8)-H(8A)	0.9500
C(10)-C(11)	1.409(2)
C(10)-C(15)	1.414(2)
C(11)-C(12)	1.393(3)
C(11)-C(57)	1.432(2)
C(12)-C(13)	1.387(2)

C(12)-H(12A)	0.9500
C(13)-C(14)	1.398(2)
C(13)-C(16)	1.524(3)
C(14)-C(15)	1.390(3)
C(14)-H(14A)	0.9500
C(15)-C(20)	1.435(2)
C(16)-C(17)	1.527(3)
C(16)-C(19)	1.533(3)
C(16)-C(18)	1.544(3)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(21)	1.194(2)
C(21)-C(22)	1.434(3)
C(22)-C(27)	1.391(3)
C(22)-C(23)	1.403(2)
C(23)-C(24)	1.382(3)
C(24)-C(25)	1.378(3)
C(24)-H(24A)	0.9500
C(25)-C(26)	1.392(3)
C(25)-H(25A)	0.9500
C(26)-C(27)	1.397(3)
C(26)-C(28)	1.434(3)
C(27)-H(27A)	0.9500
C(28)-C(29)	1.195(3)
C(29)-C(30)	1.428(3)
C(30)-C(35)	1.390(3)
C(30)-C(31)	1.403(3)
C(31)-C(32)	1.382(3)

C(31)-H(31A)	0.9500
C(32)-C(33)	1.374(3)
C(32)-H(32A)	0.9500
C(33)-C(34)	1.401(3)
C(33)-H(33A)	0.9500
C(34)-C(35)	1.391(3)
C(34)-C(37)	1.433(3)
C(35)-H(35A)	0.9500
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-C(38)	1.198(3)
C(38)-C(39)	1.372(3)
C(39)-C(40)	1.196(3)
C(40)-C(41)	1.430(3)
C(41)-C(46)	1.391(3)
C(41)-C(42)	1.393(3)
C(42)-C(43)	1.375(3)
C(42)-H(42A)	0.9500
C(43)-C(44)	1.377(3)
C(43)-H(43A)	0.9500
C(44)-C(45)	1.393(3)
C(44)-H(44A)	0.9500
C(45)-C(46)	1.392(3)
C(45)-C(48)	1.433(3)
C(46)-H(46A)	0.9500
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-C(49)	1.199(3)
C(49)-C(50)	1.430(3)
C(50)-C(51)	1.395(3)
C(50)-C(55)	1.396(2)
C(51)-C(52)	1.378(3)
C(51)-H(51A)	0.9500

C(52)-C(53)	1.388(2)
C(52)-H(52A)	0.9500
C(53)-C(54)	1.402(3)
C(54)-C(55)	1.385(3)
C(54)-C(56)	1.430(2)
C(55)-H(55A)	0.9500
C(56)-C(57)	1.200(2)

C(23)-O(1)-C(36)	117.79(16)
C(53)-O(2)-C(47)	117.33(15)
C(5)-N(1)-C(2)	107.36(18)
C(5)-N(1)-B(1)	126.25(18)
C(2)-N(1)-B(1)	126.14(17)
C(6)-N(2)-C(9)	107.27(16)
C(6)-N(2)-B(1)	126.75(18)
C(9)-N(2)-B(1)	125.97(16)
C(9)-C(1)-C(2)	120.00(17)
C(9)-C(1)-C(10)	120.44(16)
C(2)-C(1)-C(10)	119.52(16)
N(1)-C(2)-C(1)	120.96(17)
N(1)-C(2)-C(3)	107.91(17)
C(1)-C(2)-C(3)	131.12(18)
C(4)-C(3)-C(2)	107.38(19)
C(4)-C(3)-H(3A)	126.3
C(2)-C(3)-H(3A)	126.3
C(3)-C(4)-C(5)	107.05(19)
C(3)-C(4)-H(4A)	126.5
C(5)-C(4)-H(4A)	126.5
N(1)-C(5)-C(4)	110.3(2)
N(1)-C(5)-H(5A)	124.8
C(4)-C(5)-H(5A)	124.8
N(2)-C(6)-C(7)	110.67(18)
N(2)-C(6)-H(6A)	124.7
C(7)-C(6)-H(6A)	124.7
C(8)-C(7)-C(6)	107.03(18)

C(8)-C(7)-H(7A)	126.5
C(6)-C(7)-H(7A)	126.5
C(7)-C(8)-C(9)	106.89(18)
C(7)-C(8)-H(8A)	126.6
C(9)-C(8)-H(8A)	126.6
C(1)-C(9)-N(2)	120.88(16)
C(1)-C(9)-C(8)	130.97(18)
N(2)-C(9)-C(8)	108.14(16)
C(11)-C(10)-C(15)	117.82(16)
C(11)-C(10)-C(1)	120.34(14)
C(15)-C(10)-C(1)	121.82(15)
C(12)-C(11)-C(10)	120.34(15)
C(12)-C(11)-C(57)	118.48(16)
C(10)-C(11)-C(57)	121.04(16)
C(13)-C(12)-C(11)	122.47(16)
C(13)-C(12)-H(12A)	118.8
C(11)-C(12)-H(12A)	118.8
C(12)-C(13)-C(14)	116.79(17)
C(12)-C(13)-C(16)	122.89(16)
C(14)-C(13)-C(16)	120.30(15)
C(15)-C(14)-C(13)	122.60(16)
C(15)-C(14)-H(14A)	118.7
C(13)-C(14)-H(14A)	118.7
C(14)-C(15)-C(10)	119.95(16)
C(14)-C(15)-C(20)	119.78(15)
C(10)-C(15)-C(20)	120.26(16)
C(13)-C(16)-C(17)	112.13(15)
C(13)-C(16)-C(19)	108.81(16)
C(17)-C(16)-C(19)	108.46(16)
C(13)-C(16)-C(18)	110.16(15)
C(17)-C(16)-C(18)	108.08(17)
C(19)-C(16)-C(18)	109.14(17)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5

C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(21)-C(20)-C(15)	178.3(2)
C(20)-C(21)-C(22)	173.80(19)
C(27)-C(22)-C(23)	119.00(17)
C(27)-C(22)-C(21)	119.36(16)
C(23)-C(22)-C(21)	121.64(17)
O(1)-C(23)-C(24)	125.24(17)
O(1)-C(23)-C(22)	115.05(16)
C(24)-C(23)-C(22)	119.72(19)
C(25)-C(24)-C(23)	120.64(18)
C(25)-C(24)-H(24A)	119.7
C(23)-C(24)-H(24A)	119.7
C(24)-C(25)-C(26)	121.04(19)
C(24)-C(25)-H(25A)	119.5
C(26)-C(25)-H(25A)	119.5
C(25)-C(26)-C(27)	118.2(2)
C(25)-C(26)-C(28)	122.58(19)
C(27)-C(26)-C(28)	119.21(18)
C(22)-C(27)-C(26)	121.42(17)
C(22)-C(27)-H(27A)	119.3
C(26)-C(27)-H(27A)	119.3

C(29)-C(28)-C(26)	176.0(2)
C(28)-C(29)-C(30)	174.6(2)
C(35)-C(30)-C(31)	119.2(2)
C(35)-C(30)-C(29)	118.78(19)
C(31)-C(30)-C(29)	122.0(2)
C(32)-C(31)-C(30)	119.9(2)
C(32)-C(31)-H(31A)	120.0
C(30)-C(31)-H(31A)	120.0
C(33)-C(32)-C(31)	120.8(2)
C(33)-C(32)-H(32A)	119.6
C(31)-C(32)-H(32A)	119.6
C(32)-C(33)-C(34)	120.0(2)
C(32)-C(33)-H(33A)	120.0
C(34)-C(33)-H(33A)	120.0
C(35)-C(34)-C(33)	119.3(2)
C(35)-C(34)-C(37)	118.8(2)
C(33)-C(34)-C(37)	121.9(2)
C(30)-C(35)-C(34)	120.7(2)
C(30)-C(35)-H(35A)	119.6
C(34)-C(35)-H(35A)	119.6
O(1)-C(36)-H(36A)	109.5
O(1)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
O(1)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(38)-C(37)-C(34)	173.9(3)
C(37)-C(38)-C(39)	175.7(3)
C(40)-C(39)-C(38)	176.3(3)
C(39)-C(40)-C(41)	172.2(3)
C(46)-C(41)-C(42)	119.4(2)
C(46)-C(41)-C(40)	118.0(2)
C(42)-C(41)-C(40)	122.6(2)
C(43)-C(42)-C(41)	120.0(2)
C(43)-C(42)-H(42A)	120.0

C(41)-C(42)-H(42A)	120.0
C(42)-C(43)-C(44)	120.8(2)
C(42)-C(43)-H(43A)	119.6
C(44)-C(43)-H(43A)	119.6
C(43)-C(44)-C(45)	120.2(2)
C(43)-C(44)-H(44A)	119.9
C(45)-C(44)-H(44A)	119.9
C(46)-C(45)-C(44)	119.2(2)
C(46)-C(45)-C(48)	118.58(18)
C(44)-C(45)-C(48)	122.24(19)
C(41)-C(46)-C(45)	120.45(19)
C(41)-C(46)-H(46A)	119.8
C(45)-C(46)-H(46A)	119.8
O(2)-C(47)-H(47A)	109.5
O(2)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
O(2)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(49)-C(48)-C(45)	174.7(2)
C(48)-C(49)-C(50)	174.4(2)
C(51)-C(50)-C(55)	118.41(18)
C(51)-C(50)-C(49)	122.86(16)
C(55)-C(50)-C(49)	118.73(17)
C(52)-C(51)-C(50)	120.99(16)
C(52)-C(51)-H(51A)	119.5
C(50)-C(51)-H(51A)	119.5
C(51)-C(52)-C(53)	120.17(17)
C(51)-C(52)-H(52A)	119.9
C(53)-C(52)-H(52A)	119.9
O(2)-C(53)-C(52)	124.54(17)
O(2)-C(53)-C(54)	115.55(15)
C(52)-C(53)-C(54)	119.90(18)
C(55)-C(54)-C(53)	119.14(15)
C(55)-C(54)-C(56)	119.98(16)

C(53)-C(54)-C(56)	120.81(17)
C(54)-C(55)-C(50)	121.34(17)
C(54)-C(55)-H(55A)	119.3
C(50)-C(55)-H(55A)	119.3
C(57)-C(56)-C(54)	176.5(2)
C(56)-C(57)-C(11)	177.45(19)
F(1)-B(1)-F(2)	110.08(19)
F(1)-B(1)-N(1)	110.95(19)
F(2)-B(1)-N(1)	110.00(18)
F(1)-B(1)-N(2)	110.67(18)
F(2)-B(1)-N(2)	109.35(19)
N(1)-B(1)-N(2)	105.69(17)

Symmetry transformations used to generate equivalent atoms:

Table A15. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3.37**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	59(1)	103(1)	53(1)	-4(1)	-1(1)	-34(1)
F(2)	89(1)	36(1)	87(1)	19(1)	-45(1)	-19(1)
O(1)	54(1)	24(1)	50(1)	-10(1)	-12(1)	-2(1)
O(2)	48(1)	31(1)	44(1)	-5(1)	-7(1)	2(1)
N(1)	43(1)	35(1)	39(1)	-3(1)	-13(1)	-6(1)
N(2)	34(1)	23(1)	50(1)	-2(1)	-12(1)	-7(1)
C(1)	27(1)	19(1)	42(1)	-7(1)	-13(1)	1(1)
C(2)	33(1)	24(1)	40(1)	-5(1)	-12(1)	-3(1)
C(3)	40(1)	33(1)	49(1)	-10(1)	-21(1)	-3(1)
C(4)	61(1)	48(1)	53(1)	-13(1)	-29(1)	-6(1)
C(5)	62(1)	49(1)	41(1)	-4(1)	-23(1)	-5(1)
C(6)	40(1)	26(1)	68(2)	-6(1)	-14(1)	-11(1)
C(7)	39(1)	33(1)	69(2)	-15(1)	-22(1)	-7(1)
C(8)	33(1)	24(1)	49(1)	-9(1)	-15(1)	-1(1)
C(9)	30(1)	19(1)	42(1)	-4(1)	-12(1)	-3(1)
C(10)	26(1)	21(1)	38(1)	-6(1)	-13(1)	-3(1)
C(11)	27(1)	22(1)	40(1)	-8(1)	-13(1)	-1(1)
C(12)	28(1)	25(1)	40(1)	-9(1)	-10(1)	-1(1)
C(13)	27(1)	26(1)	40(1)	-6(1)	-12(1)	-3(1)
C(14)	31(1)	21(1)	45(1)	-8(1)	-11(1)	-3(1)
C(15)	28(1)	22(1)	40(1)	-7(1)	-12(1)	-2(1)
C(16)	34(1)	28(1)	44(1)	-7(1)	-6(1)	-8(1)
C(17)	40(1)	38(1)	45(1)	-7(1)	-3(1)	-6(1)
C(18)	53(1)	30(1)	54(1)	-1(1)	-3(1)	-3(1)
C(19)	50(1)	58(1)	59(1)	-15(1)	-6(1)	-26(1)
C(20)	32(1)	21(1)	43(1)	-7(1)	-10(1)	-4(1)
C(21)	33(1)	24(1)	42(1)	-6(1)	-12(1)	-3(1)
C(22)	29(1)	29(1)	41(1)	-12(1)	-12(1)	-1(1)
C(23)	38(1)	29(1)	44(1)	-10(1)	-14(1)	-2(1)

C(24)	46(1)	36(1)	56(1)	-21(1)	-12(1)	4(1)
C(25)	44(1)	47(1)	49(1)	-20(1)	-9(1)	0(1)
C(26)	37(1)	45(1)	43(1)	-12(1)	-12(1)	-4(1)
C(27)	35(1)	34(1)	41(1)	-11(1)	-11(1)	-3(1)
C(28)	40(1)	51(1)	44(1)	-13(1)	-9(1)	-6(1)
C(29)	42(1)	56(1)	44(1)	-14(1)	-9(1)	-6(1)
C(30)	40(1)	54(1)	38(1)	-8(1)	-9(1)	-10(1)
C(31)	45(1)	61(1)	43(1)	-17(1)	-6(1)	-9(1)
C(32)	54(1)	69(2)	40(1)	-12(1)	-2(1)	-15(1)
C(33)	64(2)	65(2)	37(1)	-6(1)	-6(1)	-19(1)
C(34)	55(1)	53(1)	42(1)	-8(1)	-12(1)	-10(1)
C(35)	43(1)	56(1)	40(1)	-12(1)	-7(1)	-7(1)
C(36)	72(2)	24(1)	64(2)	-12(1)	-24(1)	-2(1)
C(37)	68(2)	54(1)	43(1)	-5(1)	-14(1)	-11(1)
C(38)	73(2)	58(2)	44(1)	-4(1)	-15(1)	-12(1)
C(39)	68(2)	51(1)	49(1)	-6(1)	-15(1)	-9(1)
C(40)	59(1)	53(1)	49(1)	-5(1)	-15(1)	-13(1)
C(41)	45(1)	46(1)	50(1)	-6(1)	-14(1)	-13(1)
C(42)	58(1)	52(1)	52(1)	2(1)	-10(1)	-22(1)
C(43)	64(2)	40(1)	62(2)	-1(1)	-8(1)	-22(1)
C(44)	50(1)	39(1)	57(1)	-7(1)	-11(1)	-16(1)
C(45)	39(1)	37(1)	49(1)	-1(1)	-15(1)	-14(1)
C(46)	44(1)	39(1)	53(1)	-4(1)	-19(1)	-11(1)
C(47)	53(1)	54(1)	46(1)	-10(1)	-5(1)	0(1)
C(48)	42(1)	32(1)	56(1)	-6(1)	-18(1)	-8(1)
C(49)	42(1)	27(1)	53(1)	-4(1)	-19(1)	-7(1)
C(50)	36(1)	26(1)	47(1)	-5(1)	-20(1)	-5(1)
C(51)	39(1)	21(1)	50(1)	-9(1)	-20(1)	0(1)
C(52)	39(1)	27(1)	46(1)	-14(1)	-16(1)	3(1)
C(53)	35(1)	26(1)	39(1)	-6(1)	-15(1)	1(1)
C(54)	30(1)	21(1)	44(1)	-10(1)	-18(1)	1(1)
C(55)	32(1)	26(1)	42(1)	-9(1)	-12(1)	-3(1)
C(56)	30(1)	25(1)	42(1)	-7(1)	-13(1)	-2(1)
C(57)	30(1)	24(1)	40(1)	-7(1)	-12(1)	-2(1)
B(1)	47(1)	38(1)	47(1)	3(1)	-12(1)	-10(1)

Table A16. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3.37**.

	x	y	z	U(eq)
H(3A)	7747	8701	6670	47
H(4A)	7675	8105	8090	62
H(5A)	6189	6894	8552	61
H(6A)	3465	5738	6741	53
H(7A)	3467	6369	5333	53
H(8A)	4952	7590	4860	42
H(12A)	8765	8234	3680	37
H(14A)	7101	10801	4668	38
H(17A)	9898	10110	2264	64
H(17B)	8805	9453	2528	64
H(17C)	10132	9052	2852	64
H(18A)	8318	11613	2621	75
H(18B)	7538	11701	3498	75
H(18C)	7107	11084	2986	75
H(19A)	10326	10974	3232	79
H(19B)	10517	9899	3804	79
H(19C)	9470	10897	4101	79
H(24A)	2655	13009	7870	55
H(25A)	1982	11859	8943	57
H(27A)	4034	9474	7786	44
H(31A)	640	9113	11047	60
H(32A)	224	7683	11945	66
H(33A)	1182	6029	11653	67
H(35A)	3050	7214	9540	56
H(36A)	4310	13979	6039	79
H(36B)	4274	13751	6950	79
H(36C)	2955	13916	6647	79
H(42A)	4997	1003	9753	65

H(43A)	6157	-181	8919	67
H(44A)	7178	363	7658	57
H(46A)	5940	3321	8068	53
H(47A)	11548	5104	2841	82
H(47B)	11005	4142	2812	82
H(47C)	11719	4108	3493	82
H(51A)	9398	2003	5060	42
H(52A)	10271	2961	3919	44
H(55A)	7339	4634	5917	39

Table A17. Torsion angles [$^{\circ}$] for **3.37**.

C(5)-N(1)-C(2)-C(1)	179.10(16)
B(1)-N(1)-C(2)-C(1)	4.5(3)
C(5)-N(1)-C(2)-C(3)	0.0(2)
B(1)-N(1)-C(2)-C(3)	-174.61(17)
C(9)-C(1)-C(2)-N(1)	0.5(2)
C(10)-C(1)-C(2)-N(1)	-177.22(14)
C(9)-C(1)-C(2)-C(3)	179.38(17)
C(10)-C(1)-C(2)-C(3)	1.7(3)
N(1)-C(2)-C(3)-C(4)	-0.3(2)
C(1)-C(2)-C(3)-C(4)	-179.30(18)
C(2)-C(3)-C(4)-C(5)	0.5(2)
C(2)-N(1)-C(5)-C(4)	0.3(2)
B(1)-N(1)-C(5)-C(4)	174.92(18)
C(3)-C(4)-C(5)-N(1)	-0.5(2)
C(9)-N(2)-C(6)-C(7)	0.1(2)
B(1)-N(2)-C(6)-C(7)	-178.81(17)
N(2)-C(6)-C(7)-C(8)	-0.4(2)
C(6)-C(7)-C(8)-C(9)	0.4(2)
C(2)-C(1)-C(9)-N(2)	-1.7(2)
C(10)-C(1)-C(9)-N(2)	176.00(14)
C(2)-C(1)-C(9)-C(8)	176.95(17)
C(10)-C(1)-C(9)-C(8)	-5.4(3)
C(6)-N(2)-C(9)-C(1)	179.04(16)
B(1)-N(2)-C(9)-C(1)	-2.0(3)
C(6)-N(2)-C(9)-C(8)	0.14(19)
B(1)-N(2)-C(9)-C(8)	179.11(16)
C(7)-C(8)-C(9)-C(1)	-179.12(17)
C(7)-C(8)-C(9)-N(2)	-0.37(19)
C(9)-C(1)-C(10)-C(11)	-60.7(2)
C(2)-C(1)-C(10)-C(11)	117.00(18)
C(9)-C(1)-C(10)-C(15)	121.05(18)
C(2)-C(1)-C(10)-C(15)	-61.3(2)

C(15)-C(10)-C(11)-C(12)	1.1(2)
C(1)-C(10)-C(11)-C(12)	-177.18(15)
C(15)-C(10)-C(11)-C(57)	176.87(16)
C(1)-C(10)-C(11)-C(57)	-1.5(2)
C(10)-C(11)-C(12)-C(13)	0.4(3)
C(57)-C(11)-C(12)-C(13)	-175.47(16)
C(11)-C(12)-C(13)-C(14)	-1.2(3)
C(11)-C(12)-C(13)-C(16)	176.79(16)
C(12)-C(13)-C(14)-C(15)	0.5(3)
C(16)-C(13)-C(14)-C(15)	-177.53(16)
C(13)-C(14)-C(15)-C(10)	1.0(3)
C(13)-C(14)-C(15)-C(20)	-178.78(16)
C(11)-C(10)-C(15)-C(14)	-1.8(2)
C(1)-C(10)-C(15)-C(14)	176.51(16)
C(11)-C(10)-C(15)-C(20)	177.98(16)
C(1)-C(10)-C(15)-C(20)	-3.7(3)
C(12)-C(13)-C(16)-C(17)	12.6(2)
C(14)-C(13)-C(16)-C(17)	-169.50(16)
C(12)-C(13)-C(16)-C(19)	-107.4(2)
C(14)-C(13)-C(16)-C(19)	70.5(2)
C(12)-C(13)-C(16)-C(18)	133.01(19)
C(14)-C(13)-C(16)-C(18)	-49.1(2)
C(36)-O(1)-C(23)-C(24)	5.3(3)
C(36)-O(1)-C(23)-C(22)	-174.33(17)
C(27)-C(22)-C(23)-O(1)	179.10(16)
C(21)-C(22)-C(23)-O(1)	-0.1(3)
C(27)-C(22)-C(23)-C(24)	-0.6(3)
C(21)-C(22)-C(23)-C(24)	-179.79(18)
O(1)-C(23)-C(24)-C(25)	-179.50(19)
C(22)-C(23)-C(24)-C(25)	0.1(3)
C(23)-C(24)-C(25)-C(26)	0.0(3)
C(24)-C(25)-C(26)-C(27)	0.3(3)
C(24)-C(25)-C(26)-C(28)	-178.7(2)
C(23)-C(22)-C(27)-C(26)	0.9(3)
C(21)-C(22)-C(27)-C(26)	-179.88(17)

C(25)-C(26)-C(27)-C(22)	-0.7(3)
C(28)-C(26)-C(27)-C(22)	178.25(18)
C(35)-C(30)-C(31)-C(32)	0.1(3)
C(29)-C(30)-C(31)-C(32)	-179.6(2)
C(30)-C(31)-C(32)-C(33)	-0.3(4)
C(31)-C(32)-C(33)-C(34)	0.5(4)
C(32)-C(33)-C(34)-C(35)	-0.5(3)
C(32)-C(33)-C(34)-C(37)	179.9(2)
C(31)-C(30)-C(35)-C(34)	-0.1(3)
C(29)-C(30)-C(35)-C(34)	179.6(2)
C(33)-C(34)-C(35)-C(30)	0.3(3)
C(37)-C(34)-C(35)-C(30)	179.8(2)
C(46)-C(41)-C(42)-C(43)	-0.4(3)
C(40)-C(41)-C(42)-C(43)	178.3(2)
C(41)-C(42)-C(43)-C(44)	-0.4(4)
C(42)-C(43)-C(44)-C(45)	0.8(4)
C(43)-C(44)-C(45)-C(46)	-0.4(3)
C(43)-C(44)-C(45)-C(48)	179.9(2)
C(42)-C(41)-C(46)-C(45)	0.8(3)
C(40)-C(41)-C(46)-C(45)	-177.89(19)
C(44)-C(45)-C(46)-C(41)	-0.5(3)
C(48)-C(45)-C(46)-C(41)	179.30(19)
C(55)-C(50)-C(51)-C(52)	1.5(3)
C(49)-C(50)-C(51)-C(52)	-177.65(18)
C(50)-C(51)-C(52)-C(53)	0.7(3)
C(47)-O(2)-C(53)-C(52)	-22.3(3)
C(47)-O(2)-C(53)-C(54)	156.24(17)
C(51)-C(52)-C(53)-O(2)	176.08(17)
C(51)-C(52)-C(53)-C(54)	-2.4(3)
O(2)-C(53)-C(54)-C(55)	-176.77(16)
C(52)-C(53)-C(54)-C(55)	1.8(3)
O(2)-C(53)-C(54)-C(56)	0.2(2)
C(52)-C(53)-C(54)-C(56)	178.79(17)
C(53)-C(54)-C(55)-C(50)	0.4(3)
C(56)-C(54)-C(55)-C(50)	-176.58(16)

C(51)-C(50)-C(55)-C(54)	-2.0(3)
C(49)-C(50)-C(55)-C(54)	177.13(17)
C(5)-N(1)-B(1)-F(1)	59.5(3)
C(2)-N(1)-B(1)-F(1)	-126.92(19)
C(5)-N(1)-B(1)-F(2)	-62.6(3)
C(2)-N(1)-B(1)-F(2)	111.0(2)
C(5)-N(1)-B(1)-N(2)	179.50(17)
C(2)-N(1)-B(1)-N(2)	-6.9(2)
C(6)-N(2)-B(1)-F(1)	-55.4(3)
C(9)-N(2)-B(1)-F(1)	125.85(19)
C(6)-N(2)-B(1)-F(2)	66.0(3)
C(9)-N(2)-B(1)-F(2)	-112.7(2)
C(6)-N(2)-B(1)-N(1)	-175.57(16)
C(9)-N(2)-B(1)-N(1)	5.7(2)

Symmetry transformations used to generate equivalent atoms:

Figure A1. ^1H NMR spectrum of compound **2.9** in CDCl_3

Figure A2. ¹³C NMR spectrum of compound **2.9** in CDCl₃

Figure A3. ^{11}B NMR spectrum of compound **2.9** in CDCl_3

Figure A4. ^{19}F NMR spectrum of compound **2.9** in CDCl_3

Figure A5. ¹H NMR spectrum of compound **2.17** in CDCl₃

Figure A6. ¹H NMR spectrum of compound **2.18** in CDCl₃

Figure A7. ¹³C NMR spectrum of compound **2.18** in CDCl₃

Figure A8. ^1H NMR spectrum of compound **2.19** in CDCl_3

Figure A9. ¹H NMR spectrum of compound **2.20** in CDCl₃

Figure A10. ^{13}C NMR spectrum of compound 2.20 in CDCl_3

Figure A11. DEPT-90 NMR spectrum of compound **2.20** in CDCl_3

Figure A13. ^1H NMR spectrum of compound **2.23** in CDCl_3

Figure A14. ^1H NMR spectrum of compound **2.24** in CDCl_3

Figure A15. ¹³C NMR spectrum of compound **2.24** in CDCl₃

Figure A16. ¹⁹F NMR spectrum of compound **2.24** in CDCl₃

Figure A17. ^{11}B NMR spectrum of compound **2.24** in CDCl_3

Figure A18. ¹H NMR spectrum of compound **2.25** in CDCl₃

Figure A19. ¹³C NMR spectrum of compound **2.25** in CDCl₃

Figure A20. ^{19}F NMR spectrum of compound **2.25** in CDCl_3

Figure A21. ^{11}B NMR spectrum of compound **2.25** in CDCl_3

Figure A22. ¹H NMR spectrum of compound **2.26** in CDCl₃

Figure A23. ¹³C NMR spectrum of compound **2.26** in CDCl₃

Figure A24. ¹H NMR spectrum of compound **2.27** in CDCl₃

Figure A25. ¹³C NMR spectrum of compound **2.27** in CDCl₃

Figure A26. ¹⁹F NMR spectrum of compound **2.27** in CDCl₃

Figure A27. ^{11}B NMR spectrum of compound **2.27** in CDCl_3

Figure A28. ¹H NMR spectrum of compound **2.28** in CDCl₃

Figure A30. DEPT-90 NMR spectrum of compound **2.28** in CDCl_3

Figure A31. ^{19}F NMR spectrum of compound **2.28** in CDCl_3

Figure A32. ^{11}B NMR spectrum of compound **2.28** in CDCl_3

Figure A33. ¹H NMR spectrum of compound **2.29** in CDCl₃

Figure A34. ¹³C NMR spectrum of compound **2.29** in CDCl₃

Figure A35. DEPT-90 NMR spectrum of compound **2.29** in CDCl_3

Figure A36. ^{19}F NMR spectrum of compound **2.29** in CDCl_3

Figure A37. ^{11}B NMR spectrum of compound **2.29** in CDCl_3

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Figure A40. DEPT-90 NMR spectrum of compound **2.31** in CDCl_3

Figure A41. ^{19}F NMR spectrum of compound **2.31** in CDCl_3

Figure A42. ^{11}B NMR spectrum of compound **2.31** in CDCl_3

Figure A43. ¹H NMR spectrum of compound **2.32** in CDCl₃

Figure A44. ¹³C NMR spectrum of compound **2.32** in CDCl₃

Figure A45. ¹H NMR spectrum of compound **2.33** in CDCl₃

Figure A46. ^{13}C NMR spectrum of compound **2.33** in CDCl_3

Figure A48. ¹³C NMR spectrum of compound **2.34** in CDCl₃

Figure A49. ^1H NMR spectrum of compound **2.35** in CDCl_3

Figure A50. ^{11}B NMR spectrum of compound **2.35** in CDCl_3

Figure A51. ¹⁹F NMR spectrum of compound **2.35** in CDCl₃

Figure A52. ^1H NMR spectrum of compound **2.36** in CDCl_3

Figure A53. ^{19}F NMR spectrum of compound **2.36** in CDCl_3

Figure A54. ^{11}B NMR spectrum of compound **2.36** in CDCl_3

Figure A55. ¹H NMR spectrum of compound **2.37** in CDCl₃

Figure A56. ¹³C NMR spectrum of compound **2.37** in CDCl₃

Figure A57. ¹⁹F NMR spectrum of compound **2.37** in CDCl₃

Figure A58. ^{11}B NMR spectrum of compound **2.37** in CDCl_3

Figure A59. ¹H NMR spectrum of compound **2.38** in CDCl₃

Figure A61. ¹⁹F NMR spectrum of compound **2.38** in CDCl₃

Figure A62. ^{11}B NMR spectrum of compound **2.38** in CDCl_3

Figure A63. ^1H NMR spectrum of compound **2.39** in CDCl_3

Figure A64. ^{13}C NMR spectrum of compound **2.39** in CDCl_3

Figure A65. DEPT-90 NMR spectrum of compound **2.39** in CDCl_3

Figure A66. ^{19}F NMR spectrum of compound **2.39** in CDCl_3

Figure A67. ^{11}B NMR spectrum of compound **2.39** in CDCl_3

Figure A68. ^1H NMR spectrum of compound **2.40** in CDCl_3

Figure A69. ¹H NMR spectrum of compound **2.41** in CDCl₃

Figure A70. ¹H NMR spectrum of compound **2.42** in CDCl₃

Figure A71. ¹³C NMR spectrum of compound **2.42** in CDCl₃

Figure A72. ¹H NMR spectrum of compound **2.43** in CDCl₃

Figure A73. ¹³C NMR spectrum of compound **2.43** in CDCl₃

Figure A75. ¹³C NMR spectrum of compound **2.44** in CDCl₃

Figure A76. ¹H NMR spectrum of compound **2.45** in CDCl₃

Figure A77. ¹³C NMR spectrum of compound **2.45** in CDCl₃

Figure A78. ¹H NMR spectrum of compound **3.1** in CDCl₃

Figure A79. ¹³C NMR spectrum of compound **3.1** in CDCl₃

Figure A80. ^1H NMR spectrum of compound **3.2** in CDCl_3

Figure A81. ¹H NMR spectrum of compound **3.3** in CDCl₃

Figure A82. ¹H NMR spectrum of compound **3.4** in CDCl₃

Figure A83. ^{13}C NMR spectrum of compound **3.4** in CDCl₃

Figure A84. ¹H NMR spectrum of compound **3.7** in CDCl₃

Figure A85. ¹H NMR spectrum of compound **3.8** in CDCl₃

Figure A86. ^{13}C NMR spectrum of compound **3.8** in CDCl_3

Figure A87. ¹H NMR spectrum of compound **3.9** in CDCl₃

Figure A88. ¹³C NMR spectrum of compound **3.9** in CDCl₃

Figure A89. ¹H NMR spectrum of compound **3.10** in CDCl₃

Figure A90. ¹H NMR spectrum of compound **3.11** in CDCl₃

Figure A91. ¹³C NMR spectrum of compound **3.11** in CDCl₃

Figure A92. ¹H NMR spectrum of compound **3.17** in CDCl₃

Figure A93. ¹³C NMR spectrum of compound **3.17** in CDCl₃

Figure A94. ¹H NMR spectrum of compound **3.18** in CDCl₃

Figure A96. ¹H NMR spectrum of compound **3.19** in CDCl₃

Figure A97. ¹³C NMR spectrum of compound **3.19** in CDCl₃

Figure A98. ¹H NMR spectrum of compound **3.20** in CDCl₃

Figure A99. ¹H NMR spectrum of compound **3.21** in CDCl₃

Figure A100. ¹H NMR spectrum of compound **3.23** in CDCl₃

Figure A101. ¹³C NMR spectrum of compound **3.23** in CDCl₃

Figure A102. ¹H NMR spectrum of compound **3.24** in CDCl₃

Figure A103. ^{13}C NMR spectrum of compound **3.24** in CDCl_3

Figure A104. ¹H NMR spectrum of compound **3.25** in CDCl₃

Figure A105. ¹³C NMR spectrum of compound 3.25 in CDCl₃

Figure A106. ¹H NMR spectrum of compound **3.26** in CDCl₃

Figure A107. ¹³C NMR spectrum of compound **3.26** in CDCl₃

Figure A108. ¹H NMR spectrum of compound **3.27** in CDCl₃

Figure A109. ¹³C NMR spectrum of compound 3.27 in CDCl₃

Figure A110. ^{11}B NMR spectrum of compound **3.27** in CDCl_3

Figure A111. ^{19}F NMR spectrum of compound **3.27** in CDCl_3

Figure A112. ¹H NMR spectrum of compound **3.28** in CDCl₃

Figure A113. ¹³C NMR spectrum of compound **3.28** in CDCl₃

Figure A114. ^{11}B NMR spectrum of compound **3.28** in CDCl_3

Figure A115. ^{19}F NMR spectrum of compound **3.28** in CDCl_3

Figure A117. ¹³C NMR spectrum of compound **3.29** in CDCl₃

Figure A118. ^{11}B NMR spectrum of compound **3.29** in CDCl_3

Figure A119. ¹⁹F NMR spectrum of compound **3.29** in CDCl₃

Figure A120. ¹H NMR spectrum of compound **3.30** in CDCl₃

Figure A121. ^{13}C NMR spectrum of compound **3.30** in CDCl_3

Figure A122. ¹H NMR spectrum of compound **3.31** in CDCl₃

Figure A123. ¹³C NMR spectrum of compound **3.31** in CDCl₃

Figure A124. ¹H NMR spectrum of compound 3.32 in CDCl₃

Figure A125. ¹³C NMR spectrum of compound **3.32** in CDCl₃

Figure A126. ¹H NMR spectrum of compound 3.33 in CDCl₃

Figure A127. ¹³C NMR spectrum of compound **3.33** in CDCl₃

Figure A128. ¹H NMR spectrum of compound **3.34** in CDCl₃

Figure A129. ¹³C NMR spectrum of compound **3.34** in CDCl₃

Figure A130. ¹H NMR spectrum of compound **3.35** in CDCl₃

Figure A131. ^{13}C NMR spectrum of compound 3.35 in CDCl_3

Figure A132. ^{11}B NMR spectrum of compound **3.35** in CDCl_3

Figure A133. ^{19}F NMR spectrum of compound **3.35** in CDCl_3

Figure A134. ¹H NMR spectrum of compound **3.36** in CDCl₃

Figure A135. ^{13}C NMR spectrum of compound **3.36** in CDCl_3

Figure A136. ^{11}B NMR spectrum of compound **3.36** in CDCl_3

Figure A137. ^{19}F NMR spectrum of compound **3.36** in CDCl_3

Figure A138. ¹H NMR spectrum of compound **3.37** in CDCl₃

Figure A140. ^{11}B NMR spectrum of compound **3.37** in CDCl_3

Figure A141. ^{19}F NMR spectrum of compound **3.37** in CDCl_3

Figure A142. ¹H NMR spectrum of compound **3.38** in CDCl₃

Figure A144. ^1H NMR spectrum of compound **3.39** in CDCl_3

Figure A145. ¹³C NMR spectrum of compound **3.39** in CDCl₃

Figure A147. ^{13}C NMR spectrum of compound **3.40** in CDCl_3

Figure A148. ¹H NMR spectrum of compound **3.41** in CDCl₃

Figure A149. ^{13}C NMR spectrum of compound **3.41** in CDCl_3

Figure A150. DEPT-90 spectrum of compound **3.41** in CDCl_3

Figure A151. ^{11}B NMR spectrum of compound **3.41** in CDCl_3

Figure A152. ^{19}F NMR spectrum of compound **3.41** in CDCl_3

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Figure A155. ^{19}F NMR spectrum of compound **3.42** in CDCl_3

Figure A156. ^1H NMR spectrum of compound **4.9** in CDCl_3

Figure A157. ^1H NMR spectrum of compound **4.10** in CDCl_3

Figure A158. ¹³C NMR spectrum of compound **4.10** in CDCl₃

Figure A159. ^{11}B NMR spectrum of compound **4.10** in CDCl_3

Figure A160. ¹⁹F NMR spectrum of compound **4.10** in CDCl₃

Figure A161. ^1H NMR spectrum of compound **4.11** in CDCl_3

Figure A162. ^1H NMR spectrum of compound **4.12** in CDCl_3

Figure A163. ¹³C NMR spectrum of compound **4.12** in CDCl₃

Figure A164. ^{19}F NMR spectrum of compound **4.12** in CDCl_3

Figure A165. ^{11}B NMR spectrum of compound **4.12** in CDCl_3

Figure A166. ^1H NMR spectrum of compound **4.13** in CDCl_3

Figure A167. ^{13}C NMR spectrum of compound **4.13** in CDCl_3

Figure A168. ^1H NMR spectrum of compound **4.14** in CDCl_3

Figure A169. ^1H NMR spectrum of compound **4.15** in CDCl₃

Figure A170. ¹H NMR spectrum of compound **4.16** in CDCl₃

Figure A171. ^1H NMR spectrum of compound **4.17** in CDCl_3

Figure A172. ^{13}C NMR spectrum of compound **4.17** in CDCl_3

Figure A173. ^{19}F NMR spectrum of compound **4.17** in CDCl_3

Figure A174. ^{11}B NMR spectrum of compound **4.17** in CDCl_3

Figure A175. ¹H NMR spectrum of compound **4.18** in CDCl₃

Figure A176. ^{13}C NMR spectrum of compound **4.18** in CDCl_3

Figure A177. ^{19}F NMR spectrum of compound **4.18** in CDCl_3

Figure A178. ^{11}B NMR spectrum of compound **4.18** in CDCl_3

Figure A179. ¹H NMR spectrum of compound **4.19** in CDCl₃

Figure A180. ¹³C NMR spectrum of compound **4.19** in CDCl₃

Figure A181. ¹⁹F NMR spectrum of compound **4.19** in CDCl₃

Figure A182. ^{11}B NMR spectrum of compound **4.19** in CDCl_3

Figure A183. ¹H NMR spectrum of compound **4.20** in CDCl₃

Figure A184. ^{13}C NMR spectrum of compound **4.20** in CDCl_3

Figure A185. ^{19}F NMR spectrum of compound **4.20** in CDCl_3

Figure A186. ^{11}B NMR spectrum of compound **4.20** in CDCl_3

Figure A187. ¹H NMR spectrum of compound **4.21** in CDCl₃

Figure A188. ¹³C NMR spectrum of compound **4.21** in CDCl₃

Figure A189. ^{19}F NMR spectrum of compound **4.21** in CDCl_3

Figure A190. ^{11}B NMR spectrum of compound **4.21** in CDCl_3

Figure A191. ^1H NMR spectrum of compound **4.22** in CDCl_3

Figure A192. ^{13}C NMR spectrum of compound **4.22** in CDCl_3

Figure A193. ^{11}B NMR spectrum of compound **4.22** in CDCl_3

Figure A194. ¹H NMR spectrum of compound **4.23** in CDCl₃

Figure A195. ¹³C NMR spectrum of compound **4.23** in CDCl₃

Figure A196. ^{19}F NMR spectrum of compound **4.23** in CDCl_3

Figure A197. ^{11}B NMR spectrum of compound **4.23** in CDCl_3

Figure A198. ¹H NMR spectrum of compound **4.24** in CDCl₃

Figure A199. ¹³C NMR spectrum of compound **4.24** in CDCl₃

Figure A200. ^{19}F NMR spectrum of compound **4.24** in CDCl_3

Figure A201. ^{11}B NMR spectrum of compound **4.24** in CDCl_3

Figure A202. ^1H NMR spectrum of compound **4.25** in CDCl_3

Figure A203. ^{13}C NMR spectrum of compound **4.25** in CDCl_3

Figure A204. ^{19}F NMR spectrum of compound **4.25** in CDCl_3

Figure A205. ^{11}B NMR spectrum of compound **4.25** in CDCl_3

Figure A206. ^1H NMR spectrum of compound **4.26** in CDCl_3

Figure A207. ¹³C NMR spectrum of compound **4.26** in CDCl₃

Figure A208. ^{19}F NMR spectrum of compound **4.26** in CDCl_3

Figure A209. ^{11}B NMR spectrum of compound **4.26** in CDCl_3

Figure A210. ¹H NMR spectrum of compound **4.27** in CDCl₃

Figure A211. ¹³C NMR spectrum of compound **4.27** in CDCl₃

Figure A212. ^{19}F NMR spectrum of compound **4.27** in CDCl_3

Figure A213. ^{11}B NMR spectrum of compound **4.27** in CDCl_3

Figure A214. ^1H NMR spectrum of compound **4.28** in CDCl_3

Figure A215. ¹³C NMR spectrum of compound 4.28 in CDCl₃

Figure A216. HRMS (EI-TOF) spectrum of compound **2.9**

Figure A217. HRMS (EI-TOF) spectrum of compound **2.15**, a) full spectrum, b) zoomed-in

Figure A218. HRMS (EI-TOF) spectrum of compound **2.20**

Figure A219. HRMS (EI-TOF) spectrum of compound **2.25**, a) full spectrum, b) zoomed-in

Figure A220. HRMS (EI-TOF) spectrum of compound **2.26**, a) full spectrum, b) zoomed-in

Figure A221. HRMS (EI-TOF) spectrum of compound **2.27**, a) full spectrum, b) zoomed-in

Figure A222. HRMS (FTMS-ESI) spectrum of compound **2.28**

Figure A223. HRMS (EI-TOF) spectrum of compound **2.29**, a) full spectrum, b) zoomed-in

Figure A224. HRMS (EI-TOF) spectrum of compound **2.31**, a) full spectrum, b) zoomed-in

Figure A225. HRMS (FTMS-ESI) spectrum of compound **2.32**, a) full spectrum, b) zoomed-in

Figure A226. HRMS (FTMS-ESI) spectrum of compound **2.33**, a) full spectrum, b) zoomed-in

Figure A227. HRMS (EI-TOF) spectrum of compound **2.34**, a) full spectrum, b) zoomed-in

Figure A228. HRMS (EI-TOF) spectrum of compound **2.35**, a) full spectrum, b) zoomed-in

Figure A229. HRMS (EI-TOF) spectrum of compound **2.40**, a) full spectrum, b) zoomed-in

Figure A230. HRMS (EI-TOF) spectrum of compound **2.42**, a) full spectrum, b) zoomed-in

Figure A231. HRMS (EI-TOF) spectrum of compound **2.43**, a) full spectrum, b) zoomed-in

Figure A232. HRMS (ESI-TOF) spectrum of compound **2.44**, a) full spectrum, b) zoomed-in

Figure A233. HRMS (ESI-TOF) spectrum of compound **2.45**, a) full spectrum, b) zoomed-in

Figure A234. HRMS (EI-TOF) spectrum of compound **3.10**, a) full spectrum, b) zoomed-in

Figure A235. HRMS (EI-TOF) spectrum of compound **3.11**, a) full spectrum, b) zoomed-in

Figure A236. HRMS (ESI-TOF) spectrum of compound **3.19**, a) full spectrum, b) zoomed-in

Figure A237. HRMS (ESI-TOF) spectrum of compound **3.20**, a) full spectrum, b) zoomed-in

Figure A238. HRMS (FTMS-ESI) spectrum of compound **3.21**

Figure A239. HRMS (EI-TOF) spectrum of compound **3.25**, a) full spectrum, b) zoomed-in

Figure A240. HRMS (EI-TOF) spectrum of compound **3.26**

Figure A241. HRMS (ESI-TOF) spectrum of compound **3.27**

Figure A242. HRMS (ESI-TOF) spectrum of compound **3.28**

Figure A243. HRMS (ESI-TOF) spectrum of compound **3.29**

Figure A244. HRMS (EI-TOF) spectrum of compound **3.33**, a) full spectrum, b) zoomed-in

Figure A245. HRMS (EI-TOF) spectrum of compound **3.34**, a) full spectrum, b) zoomed-in

Figure A246. HRMS (ESI-TOF) spectrum of compound **3.35**, a) full spectrum, b) zoomed-in

Figure A247. HRMS (FTMS-ESI) spectrum of compound **3.36**

Figure A248. HRMS (ESI-TOF) spectrum of compound **3.37**

Figure A249. HRMS (ESI-TOF) spectrum of compound **3.40**

Figure A250. HRMS (ESI-TOF) spectrum of compound **3.41**

Figure A251. HRMS (ESI-TOF) spectrum of compound **3.42**, a) full spectrum, b) zoomed-in

Figure A252. HRMS (EI-TOF) spectrum of compound **4.20**

Figure A253. HRMS (EI-TOF) spectrum of compound **4.21**

Figure A254. HRMS (EI-TOF) spectrum of compound **4.22**

Figure A255. HRMS (EI-TOF) spectrum of compound **4.26**

Figure A256. HRMS (EI-TOF) spectrum of compound **4.28**

Figure A257. CV of compound **4.17**

Figure A258. CV of compound **4.18**

Figure A259. CV of compound **4.19**

Figure A260. CV of compound **4.20**

Figure A261. CV of compound **4.21**

Figure A262. CV of compound **4.22**

Figure A263. CV of compound **4.4**

Figure A264. CV of compound **4.12**

Figure A265. CV of compound **4.23**

Figure A266. CV of compound **4.24**

Figure A267. CV of compound **4.25**

Figure A268. CV of compound **4.26**

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