

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

**Design, Synthesis and Evaluation of Photoswitches for  
Molecular Solar Thermal Energy Storage Systems**

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[Artistic drawing by Mariza Mone illustrating a treehouse with an integrated  
MOST system]

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## Abstract

To meet the future energy demands and handle climate changes, new sustainable energy sources must be developed. Over the last decades, great scientific progress on harvesting solar energy has been made, but storing the energy is still a challenge. One way to store solar energy is in a compound that absorbs solar energy while being converted to a metastable isomer through a photoisomerization process, a technique referred to as molecular solar thermal energy storage (MOST). In this work, the norbornadiene/quadracyclane system, a promising candidate for MOST, was evaluated and new synthetic methods were developed to obtain a series of novel norbornadiene derivatives in an efficient way. Photophysical characterization of the series revealed a better solar spectrum match and high energy storage densities (114–124 kJ/mol) compared to previous series. Quantum yields for the photoisomerization processes were between 28–58% and the half-lives of the photoisomers in the range of hours to days. Solvent effects on the norbornadiene/quadracyclane system were studied, showing a pronounced effect on both the half-lives of the photoisomers and on the photoisomerization process when going from polar to non-polar solvents. Additionally, bicyclooctadiene derivatives were synthesized and for the first time evaluated as MOST candidates. The series exhibited very high storage densities (143–153 kJ/mol) compared to the corresponding norbornadiene derivatives (52–63 kJ/mol) and could switch back and forth for 645 cycles without significant degradation. The absorption profile and half-lives of the photoisomers need further improvement for MOST applications, but the molecular engineering concepts presented here can be used to develop future MOST systems based on the bicyclooctadiene/tetracyclooctane system. Altogether, this work illustrates the importance of detailed molecular design and the importance of the local environment of the photoswitches for obtaining desired MOST properties.

**Keywords:** Molecular solar thermal energy storage, Solar fuels, Solar energy, Energy storage and release, Energy conversion, Diels-Alder reaction, Photoswitches, Norbornadiene, Quadracyclane, Bicyclooctadiene, Tetracyclooctane.

# List of Publications

The thesis is based on the following appended papers:

## Paper I

**A Convenient Route to 2-Bromo-3-chloronorbornadiene and 2,3-Dibromonorbornadiene.** Anders Lennartson, Maria Quant, Kasper Moth-Poulsen. *Synlett*, **2015**, 26, 1501-1504.

## Paper II

**Low Molecular Weight Norbornadiene Derivatives for Molecular Solar-Thermal Energy Storage.** Maria Quant, Anders Lennartson, Ambra Dreos, Mikael Kuisma, Paul Erhart, Karl Börjesson, Kasper Moth-Poulsen. *Chemistry – a European Journal*, **2016**, 22, 13265-13274.

## Paper III

**Solvent Effects on the Absorption Profile, Kinetic Stability, and Photoisomerization Process of the Norbornadiene–Quadricyclanes System.** Maria Quant, Alice Hamrin, Anders Lennartson, Paul Erhart, Kasper Moth-Poulsen. *Journal of Physical Chemistry C*, **2019**, 123, 7081-7087.

## Paper IV

**Synthesis, Characterization and Computational Evaluation of Bicyclooctadienes Towards Molecular Solar Thermal Energy Storage.** Maria Quant, Andreas Erbs Hillers-Bendtsen, Shima Ghasemi, Máté Erdélyi, Zhihang Wang, Lidiya Muhammad, Nina Kann, Kurt V. Mikkelsen, Kasper Moth-Poulsen. *Submitted manuscript*

Additional publications not included in the thesis:

**Macroscopic Heat Release in a Molecular Solar Thermal Energy Storage System.**

Zhihang Wang, Anna Roffey, Raul Losantos, Anders Lennartson, Martyn Jevric, Anne U. Petersen, Maria Quant, Ambra Dreos, Xin Wen, Diego Sampedro, Karl Börjesson, Kasper Moth-Poulsen. *Energy and Environmental Science*, **2019**, *12*, 187-19.

**Scalable Synthesis of Norbornadienes via in situ Cracking of Dicyclopentadiene using Continuous Flow Chemistry.**

Jessica Orrego-Hernández, Helen Hölzel, Maria Quant, Zhihang Wang, Kasper Moth-Poulsen. *European Journal of Organic Chemistry*, **2021**, 5335-5358.

**Benchmark Investigation of the Structural and Thermochemical Properties of a Series of [2.2.2]-Bicyclooctadienes Photoswitches.**

Andreas Erbs Hillers-Bendtsen, Maria Quant, Kasper Moth Poulsen, Kurt V. Mikkelsen. *Submitted manuscript*

# Contribution Report

## Paper I

Second author. I performed the synthesis of 2-bromo-3-chloronorbornadiene and 2,3-dibromonorbornadiene. Contributed to writing the manuscript.

## Paper II

First author. I performed the synthesis of most of the compounds, the kinetic study of the back-conversion and the quantum yield measurements. I wrote the main part of the manuscript.

## Paper III

First author. I performed most of the experiments. I wrote the main part of the manuscript.

## Paper IV

First author. I performed the synthesis of most of the compounds, the kinetic study of the back conversion and the NMR analysis. I wrote the main part of the manuscript.

## List of Abbreviations

AM – air mass coefficient

BOD – bicyclooctadiene

Bu – butyl

DIPA – diisopropylamine

HOMO – highest occupied molecular orbital

LUMO – lowest unoccupied molecular orbital

Me – methyl

MOST – molecular solar thermal energy storage

NBD – norbornadiene

NMP – *N*-methyl-2-pyrrolidone

NMR – nuclear magnetic resonance

TCO – tetracyclooctane

THF – tetrahydrofuran

Ts – tosyl

TS – transition state

RuPhos – dicyclohexylphosphino-2',6'-diisopropoxybiphenyl

QC – quadricyclane

QY – quantum yield

UV – ultraviolet

Vis – visible

# Table of Contents

## Chapter 1

<b>Introduction.....</b>	<b>1</b>
--------------------------	----------

## Chapter 2

<b>Molecular Solar Thermal Energy Storage .....</b>	<b>3</b>
---	----------

2.1 Photoswitches for MOST Energy Storage .....	5
---	---

2.1.1 The Norbornadiene/Quadricyclane System.....	7
---	---

2.1.2 The Bicyclooctadiene/Tetracyclooctane System.....	11
---	----

## Chapter 3

<b>Aim and Scope.....</b>	<b>13</b>
---------------------------	-----------

## Chapter 4

<b>Methods for Synthesis and Characterization .....</b>	<b>15</b>
---	-----------

4.1 Synthesis of Norbornadiene Derivatives and Bicyclooctadiene Derivatives.....	15
--	----

4.1.1 Sonogashira and Suzuki Cross-Coupling Reactions .....	18
---	----

4.2 Absorption Spectra and Quantum Yield Measurements .....	19
---	----

4.3 Kinetic Study of the Back-Conversion.....	23
---	----

## Chapter 5

<b>Synthesis and Photophysical Characterization of Norbornadiene Derivatives and Quadricyclane Derivatives .....</b>	<b>25</b>
--	-----------

5.1 Synthesis of Norbornadiene Derivatives.....	25
---	----

5.1.1 Synthesis of 2-Bromo-3-chloronorbornadiene .....	25
--	----

5.1.2 Synthesis of Donor/Acceptor-Substituted Norbornadiene Derivatives via Cross-Coupling Reactions.....	27
---	----

5.2 Photophysical Characterization of Donor/Acceptor- Substituted Norbornadiene Derivatives .....	29
---	----

## Chapter 6

<b>Solvent Effects on Derivatives of the Norbornadiene/Quadricyclane System .....</b>	<b>33</b>
---	-----------

6.1 Absorption Spectra of the Norbornadiene Derivatives .....	34
---	----

6.2 Stability of the Quadricyclane Derivatives .....	35
--	----

6.3 Photoisomerization Process.....	36
-------------------------------------	----

## Chapter 7

<b>Exploring the Bicyclooctadiene/Tetracyclooctane System for MOST Energy Storage ..</b>	<b>39</b>
--	-----------

7.1 Synthesis of Bicyclooctadiene Derivatives .....	39
---	----



7.1.1 Attempted One Step Approach Towards Synthesis of Donor/Acceptor- Substituted Bicyclooctadiene Derivatives .....	39
7.1.2 Synthesis of Donor/Acceptor Substituted Bicyclooctadiene Derivatives via Diels-Alder Reaction Followed by Cross-coupling Reactions.....	43
7.2 Photophysical Characterization of Donor/Acceptor- Substituted Bicyclooctadiene Derivatives .....	47
<b>Chapter 8</b>	
<b>Conclusion and Outlook .....</b>	<b>51</b>
8.1 Contributions to the Field of MOST Energy Storage .....	52
8.2 Reflections on Future Development of Photoswitches for MOST Systems .....	53
<b>Acknowledgment.....</b>	<b>55</b>
<b>Bibliography .....</b>	<b>56</b>



# Chapter 1

## Introduction

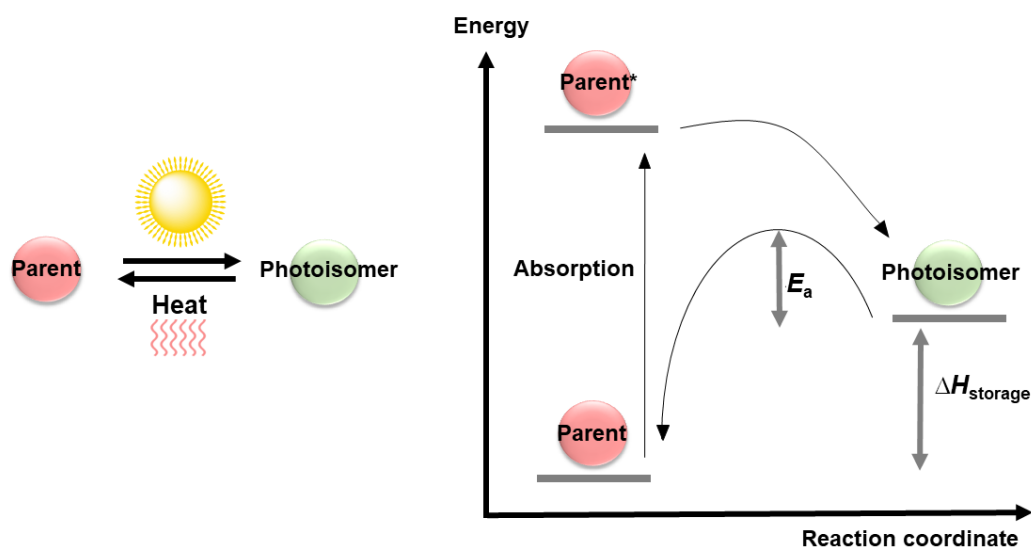
To counteract the challenges caused by pollution and climate change, fossil fuel consumption must decrease, and fossil fuels must be replaced by sustainable energy sources. The need for renewable and emission free energy sources is therefore increasing. Alternative energy sources, such as wind turbines and hydroelectric power, serve as good substitutes for fossil fuels, but their implementation in society is geographically restricted. Harvesting energy from the sun is another possibility, and research in solar energy has shown substantial progress over the last decades. Solar photovoltaics are now installed worldwide and in 2019 the capacity reached around 633 gigawatts in the world.<sup>1</sup> Also, improving the efficiency of solar cells is a constantly ongoing area of research and the world record today is 47.1%.<sup>2</sup> One area that remains a challenge is to find efficient ways of storing the solar energy. Successful strategies such as batteries,<sup>3</sup> phase change materials,<sup>4</sup> and hydrogen storage through water splitting,<sup>5</sup> are available but this is not sufficient to meet the future energy demand.<sup>6</sup> Also, many of the known storage solutions are based on rare materials and new solar energy storage concepts based on more abundant materials need to be developed. A less explored strategy is called molecular solar thermal energy storage (MOST), a technique based on photoswitches, molecules that upon light irradiation undergo a reversible structural change.<sup>7</sup> In this approach, the solar energy is captured and stored in the molecules as chemical energy, which on demand can be triggered to release the energy as heat. This thesis concerns the development of new compounds for molecular solar thermal energy storage.



# Chapter 2

## Molecular Solar Thermal Energy Storage

The concept of molecular solar thermal energy storage (MOST) is based on molecules that can absorb and store energy from the sun and on demand release the energy as heat.<sup>8, 9</sup> The molecules involved are photoswitches. A schematic illustration of a MOST system and a simplified energy diagram are presented in Figure 1. The parent compound of the photoswitch absorbs a photon and becomes excited (parent\*). After excitation, a chemical transformation occurs, and the parent compound is converted to a photoisomer. It is in the photoisomer that the energy is stored and the amount of energy that can be stored is defined by the energy difference between the parent compound and the photoisomer ( $\Delta H_{\text{storage}}$ ). The storage time is defined by the energy barrier for the back conversion ( $E_a$ ), where a high barrier provides long storage times and low barrier short storage times. The energy is released as heat in the back-conversion, where the parent compound is regenerated from the photoisomer. The back-conversion can for example be triggered by a catalyst or by applying heat.<sup>7, 8</sup>



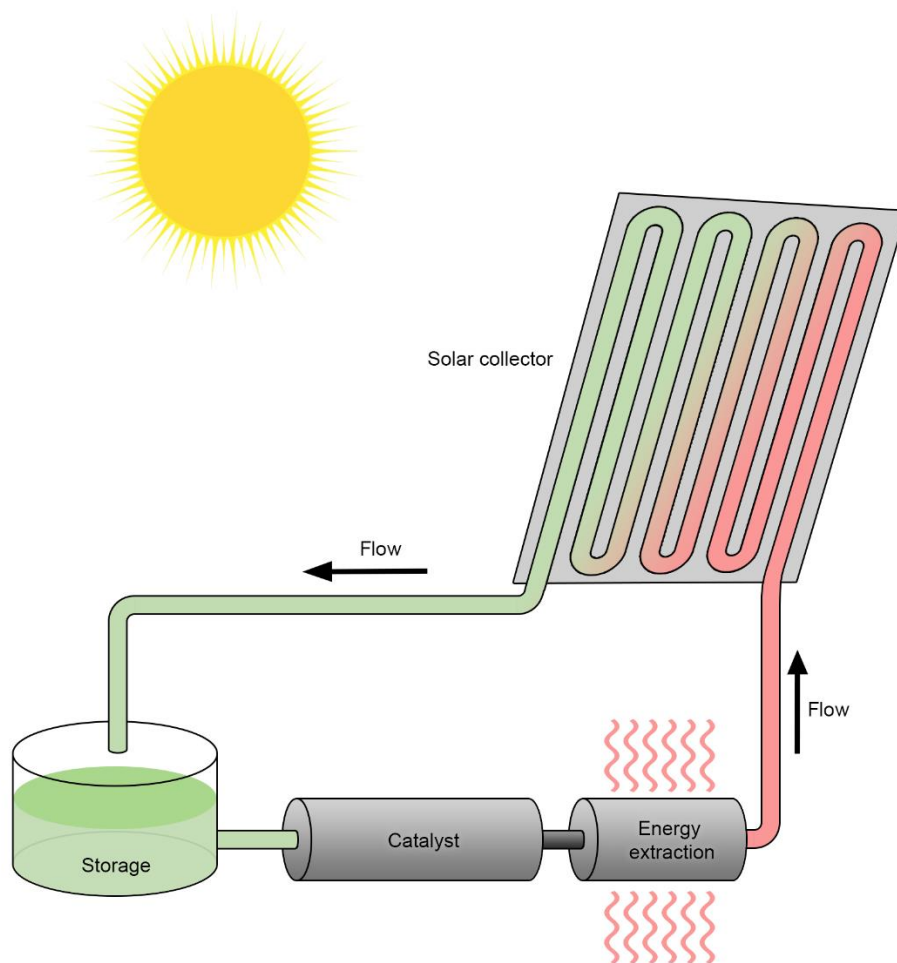
**Figure 1.** Schematic illustration of a MOST system and a simplified energy diagram.

For an efficient MOST system, there are several criteria that must be met, where some of the most crucial are listed below.<sup>10</sup>

- 1) The parent compound should absorb light in the part of the solar spectrum, so that the sun can drive the reaction.
- 2) The photoisomer should not absorb in the same range as the parent compound to avoid overlap in absorption spectra.
- 3) The energy difference between the parent compound and the photoisomer ( $\Delta H_{\text{storage}}$ ) should be large, so that a large amount of energy can be stored in the system.
- 4) The energy barrier for the uncatalyzed back conversion ( $E_a$ ) should be high to ensure that the photoisomer can be stored for a certain period of time.
- 5) The photoisomerization should proceed with a high quantum yield.
- 6) The system should be robust and function for many cycles.

In addition to these fundamental requirements, it is preferable to have a compound that has a low-molecular weight, in order to achieve a high energy density. From an environmental standpoint, the compound should also be synthesized in an efficient way from non-toxic and abundant starting materials.

To clarify how a MOST system could be integrated in future devices, a schematic illustration of one possible application is presented in Figure 2. In this device, the compound is in a closed system in the form of a liquid or dissolved in a solvent. At the solar light collector site, the parent compound becomes exposed to sunlight and is converted to the photoisomer that is transported to and kept in a storage container. When the energy should be released, the photoisomer is pumped over a catalyst that lowers the energy barrier of the back conversion, so that the back-conversion reaction is triggered. The photoisomer is then back-converted to the parent compound and the stored energy is released as heat. The thermal energy is captured at the energy extraction site, where it can be used to heat water for example.



**Figure 2.** Schematic illustration of how a MOST system could be integrated into a device.

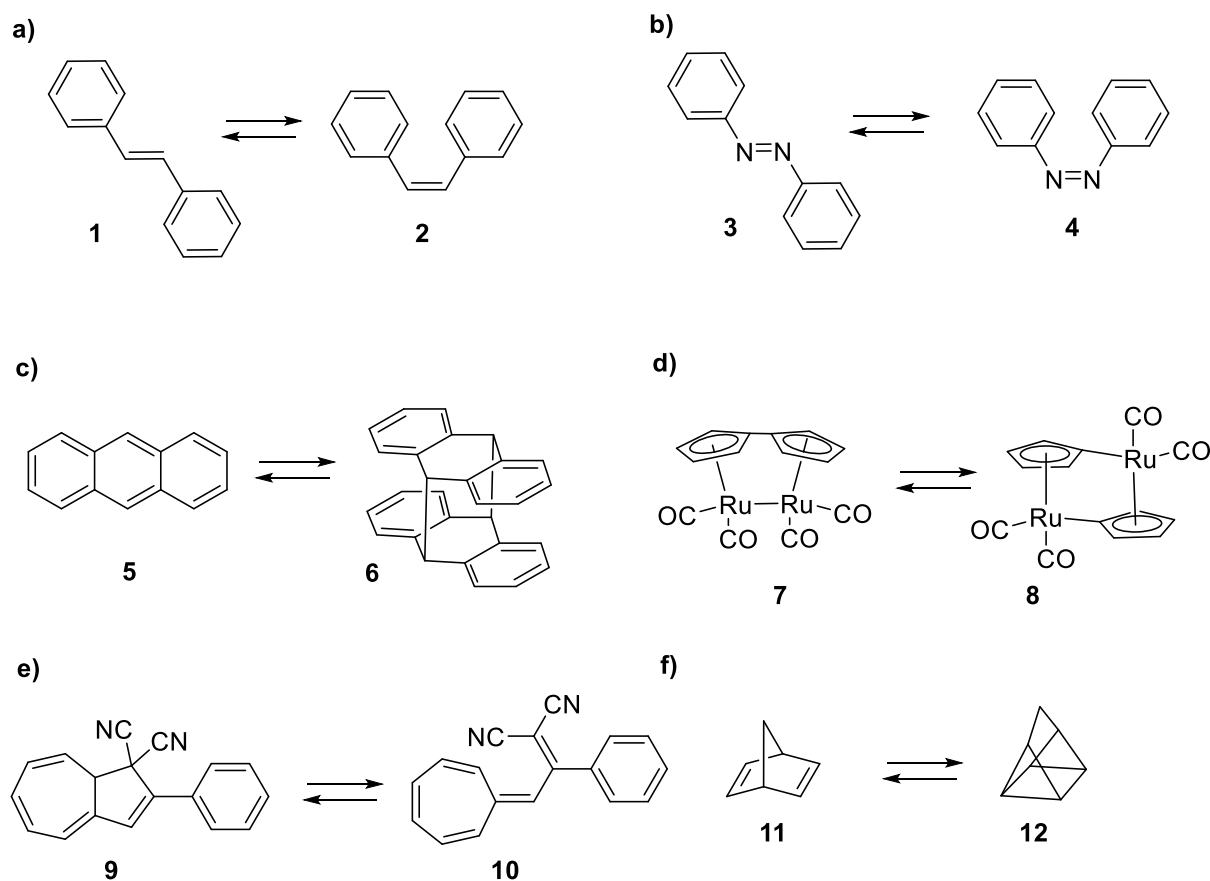
## 2.1 Photoswitches for MOST Energy Storage

One of the first observations of a photoswitch was reported in 1867 by Fritzsche,<sup>11</sup> with the discovery that an orange solution containing tetracene could be bleached when exposed to sunlight. Once the solution was placed in the dark, the orange color was recovered.<sup>11</sup> The behavior of the tetracene solution is an example of photochromism, where a reversible change of a photoswitch occurs upon exposure to light. The term photochromism was coined from the Greek words *phos* (light) and *chroma* (colour) and can be describe as positive or negative photochromism.<sup>12</sup> In a photoswitch with positive photochromism, the parent compound absorbs photons of higher energy than the photoisomer, while in a photoswitch with negative photochromism, the conditions are opposite.<sup>13</sup> Also, photoswitches are classified into two subgroups, *T-types*, where the back-conversion is triggered thermally or *P-types*, where light triggers the reaction.

Photoswitches can be either in organic and inorganic materials and can also be found in biological systems, such as for example our visual system.<sup>14</sup> Photoswitches have been utilized in a wide range of applications, where some examples are biosensing,<sup>15</sup> imaging,<sup>16</sup> and single molecular electronics.<sup>17, 18</sup> A well know application can be found in photochromic sunglasses.<sup>19</sup> The lens typically contains silver halides, that upon exposure to sunlight are reduced to generate elemental silver. Since elemental silver is colored, the lens becomes dark. Once the sunglasses are not exposed to sunlight anymore, the reverse reaction (oxidation) occurs and the lens becomes transparent again.<sup>14, 19</sup>

Several requirements must be fulfilled to obtain an efficient MOST system and not all molecular photoswitches are suitable compounds. Still, many photoswitches have been proposed as MOST candidates and some of the most common examples are shown in Figure 3. The first two photoswitches, stilbene (**1**) and azobenzene (**3**), (Figure 3a and 3b) operate through the same general mechanism, where they undergo an *E-Z* isomerization upon irradiation.<sup>20, 21</sup> Stilbenes absorb light in the region of 300–700 nm, but the storage energy for the unsubstituted system is low, around 5 kJ/mol.<sup>21, 22</sup> For unsubstituted azobenzene, the storage energy is higher, around 40 kJ/mol, and the fact that it also absorbs in the visible region and releases heat when back-converted, has made it widely studied.<sup>20</sup> An interesting modification to the azobenzene system is to covalently attach it to carbon allotropes, so that the molecules become close-packed, thereby stabilizing the *E* isomer. In these types of systems, the storage energies were increased by around 30%, but at the price of lowering the barrier for the back-conversion.<sup>23, 24 25</sup> Another photoswitch is anthracene (**5**) (Figure 3c). The photoconversion process where it dimerizes through a [4+4]-cycloaddition was studied already in the beginning of 1900s.<sup>26, 27</sup> The anthracene system fulfills some crucial MOST criteria, including a solar spectrum match, but the half-lives and storage energies need improvement.<sup>28</sup> Recent developments with anthracene derivatives have, as in the azobenzene system, focused on attachment to nanoscale templates.<sup>29</sup> The fulvalene diruthenium system (**7**) can also undergo a reversible photoisomerization when irradiated with light in the visible region.<sup>30, 31</sup> The mechanism was first believed to be concerted, but has lately been found to proceed via two short-lived intermediates starting with breaking the ruthenium-ruthenium bond. Despite the fact that the system is robust, it has issues such as low quantum yields and low solubility. In addition, heavy metals such as ruthenium are not optimal for MOST applications.





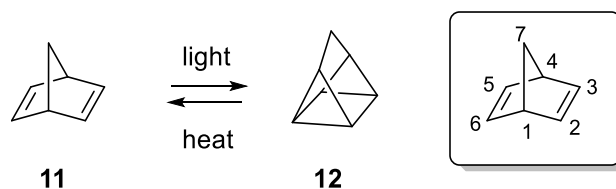
**Figure 3.** Examples of photoswitches for MOST applications and their photoisomerization processes: **a)** stilbene and the *E-Z* isomerization process; **b)** azobenzene and the *E-Z* isomerization process; **c)** anthracene and the dimerization process; **d)** tetracarbonyl-fulvalene-diruthenium and the photoisomerization; **e)** dihydroazulene and the formation to the photoisomer vinylheptafulvene; **f)** norbornadiene and the formation of the photoisomer quadricyclane.

The dihydroazulene (**9**) system has also been evaluated as a candidate for MOST, since a reversible ring opening towards vinylheptafulvene (**10**) takes place upon irradiation.<sup>32, 33</sup> The final photoswitch in Figure 3 is norbornadiene/quadricyclane (**11/12**), which is the main topic of this thesis.

### 2.1.1 The Norbornadiene/Quadricyclane System

Bicyclo[2.2.1]hepta-2,5-diene (**11**), commonly known as norbornadiene (NBD), is a rigid bridged bicyclic organic compound that contains two double bonds. Norbornadiene was first discovered and synthesized in the beginning of the 1950s.<sup>7, 34</sup> Norbornadiene is thermally stable, but as described by the Woodward-Hoffman rules,<sup>35, 36</sup> irradiation with UV-light breaks

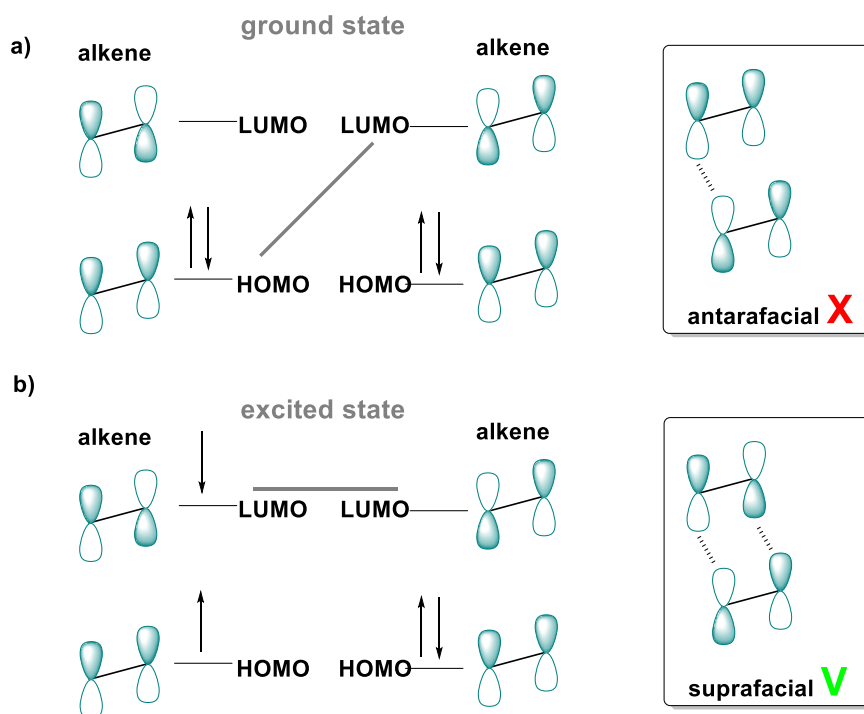
the double-bonds, leading to a [2+2]-cycloaddition. As a result, the photoisomer tetracyclo[3.2.0.0.0]heptane, known as quadricyclane (QC), is formed (Scheme 1).



**Scheme 1.** The photoisomerization process where norbornadiene (**11**) is converted to quadricyclane (**12**), and the back conversion where **12** is converted to **11** and the energy is released as heat. The numbering of the norbornadiene scaffold is presented to the right.

Frontier molecular orbitals can predict the outcome of the Woodward-Hoffman rules<sup>35, 36</sup> and illustrate why [2+2]-cycloaddition reactions are photochemically allowed but not thermally allowed (Figure 4).<sup>37</sup> In the ground state electron configuration, where thermally allowed reactions occurs, the HOMO-LUMO interactions are antarafacial. According to Woodward-Hoffman rules, antarafacial interactions are *forbidden* and associated with a high energy barrier. However, in the first excited state electron configuration, after exposure to light, the interaction instead takes place between the LUMO and LUMO and the approach is suprafacial, a reaction that is *allowed*.

The photoisomerization reaction in norbornadiene derivatives was first reported in carboxylic acid derivatives of norbornadiene. In 1961, Dauben *et al.*<sup>38</sup> observed the photoisomerization of norbornadiene to quadricyclane upon irradiation of UV-light.<sup>38, 39</sup> Quadricyclane is a strained metastable compound with a strain energy of 402 kJ/mol, which is more than two times higher than for norbornadiene, with a strain energy of 145 kJ/mol.<sup>40, 41</sup> Unsubstituted quadricyclane has an energy storage density of around 90 kJ/mol (0.98 MJ/kg) and the energy in quadricyclane can be released as heat by triggering the back-reaction to regenerate norbornadiene.<sup>42</sup> The most common way to trigger the back-conversion is by applying either heat<sup>43</sup> or a catalyst,<sup>43, 44</sup> but there are examples where back-conversion has been triggered by light<sup>45, 46</sup> or electrochemically.<sup>47-49</sup>

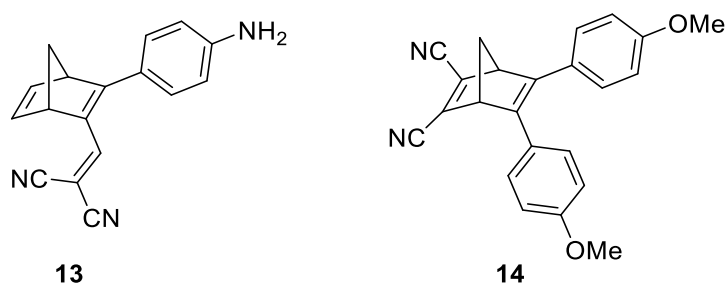


**Figure 4.** Illustration of frontier molecular orbitals involved in [2+2]-cycloaddition reactions for a) ground state electron configuration and b) first excited state electron configuration.<sup>37</sup>

Besides storing large amounts of energy, the norbornadiene/quadricyclane system can be stored for long periods of time, since the half-life of quadricyclane is 14 hours at 140 °C.<sup>50</sup> However, the drawback with the system is that the sunlight on earth cannot drive the isomerization reaction, since norbornadiene only absorbs radiation of wavelengths below 300 nm and therefore fails to fulfil a fundamental requirement for MOST. The ideal absorption onset for a MOST system is 656 nm and therefore the absorption spectra of norbornadiene derivatives must be redshifted towards longer wavelengths.<sup>51</sup> Additionally, unsubstituted norbornadiene has a low quantum yield of around 5% and to achieve maximum solar energy conversion efficiency in MOST, the quantum yield should be close to unity.<sup>51, 52</sup>

Nevertheless, the properties of norbornadiene can be altered by modifying the structure via substitution. A successful strategy, especially when it comes to obtaining solar spectrum match, is to introduce electron donating and electron withdrawing groups in the vinylic positions to create a so-called push-pull system. In the 1980s and the 1990s, the Yoshida group<sup>52, 53</sup> and the Bren/Dubonosov group,<sup>43, 54-57</sup> designed and synthesized a great number of norbornadiene derivatives with electron donating and electron withdrawing substituents. Two examples of donor/acceptor norbornadiene derivatives are illustrated in Figure 5. The donor and acceptor substituents can communicate either through direct conjugation, if attached to the same double

bond (**13**), or through homo conjugation, if attached to different double bonds (**14**). An advantage with such a system is that the conjugation will be lost once the quadricyclane derivative is formed. As a result, the quadricyclane derivative will have a different absorption spectrum with absorption-onset at an appreciably longer wavelength than the norbornadiene derivative, which is also a requirement for an efficient MOST system.



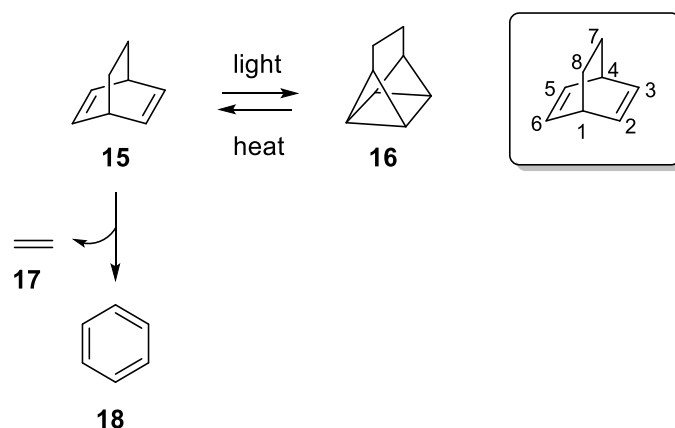
**Figure 5.** Donor/acceptor norbornadiene derivatives **13** and **14**, synthesized by the Bren/Dubonosov group<sup>54</sup> and the Yoshida group<sup>53</sup> respectively. In **13**, the donor/acceptor groups communicate through direct conjugation, versus in **14**, where they communicate through homo-conjugation.

The absorption onset for **13** and **14** are 620 nm and 667 nm, respectively, illustrating the great effect that the donor/acceptor substituents have on red-shifting the absorption spectra. However, for an efficient MOST system, there are of course more properties to consider than the absorption spectra. Both **13** and **14** have low quantum yields and the half-lives of the corresponding quadricyclane derivatives are short.

By looking at the simplified energy diagram in Figure 1, it is understandable that properties of norbornadiene and quadricyclane are correlated, since they are valences isomers of the same molecular system. Thus, modifications of norbornadiene affects several parameters. A major challenge in developing norbornadiene derivatives for efficient MOST systems is to optimize one parameter without compromising other important parameters. For example, a trend in the norbornadiene/quadricyclane system is that as the absorption of the norbornadiene derivative is red-shifted, the half-life of the quadricyclane derivative tends to decrease.<sup>9</sup> In order to address these challenges, the norbornadiene/quadricyclane system has to be further explored and more norbornadiene derivatives with other substitution patterns must be synthesized and evaluated for a deeper understanding of the correlation between substituents and MOST properties.

## 2.1.2 The Bicyclooctadiene/Tetracyclooctane System

An alternative photoswitch that has never been evaluated for MOST energy storage is [2.2.2] bicyclooctadiene (BOD, **15**), Scheme 2). Bicyclooctadiene is a bicyclic compound that contains two double bonds per molecule. Compared to norbornadiene, it contains an additional carbon atom at the bridge. The photophysical properties of bicyclooctadiene derivatives and the corresponding photoisomers have been less explored than norbornadiene derivatives since the system is known to be unstable. Tetracyclooctane derivatives (**16**) are usually short-lived, and bicyclooctadiene derivatives can thermally degrade into aromatic byproducts through a retro-Diels-Alder reaction. As illustrated in Scheme 2, bicyclooctadiene can degrade to form ethene (**17**) and benzene (**18**).<sup>58-60 61</sup>



**Scheme 2.** The photoisomerization process, where bicyclooctadiene (**15**) is converted to tetracyclooctane (**16**), and the corresponding back-conversion, along with the retro-Diels-Alder reaction to form benzene (**18**) and ethene (**17**). The numbering of the bicyclooctadiene scaffold is presented to the right.

Results from a computational study on bicyclooctadiene showed very promising results regarding the storage densities.<sup>62</sup> Bicyclooctadiene was predicted to have a storage density of 1.77 MJ/kg, which is significantly higher than for norbornadiene (0.98 MJ/kg). These results encouraged us to further explore the bicyclooctadiene/tetracyclooctane system for MOST.



# Chapter 3

## Aim and Scope

Although genuine effort has been made, an ideal photoswitch for MOST applications has not yet been identified and photoswitches must be further developed and characterized. Several research questions regarding the norbornadiene/quadracyclane system are still not answered and need to be addressed and clarified. The aim of this work is mainly to explore if it is possible to improve the properties of the norbornadiene/quadracyclane system for MOST energy storage. The first question to be answered is:

*Is it possible to improve the properties of norbornadiene by introducing new types of donor/acceptor substituents at the C2 and C3 positions?*

In order to answer this research question, we set out to develop new efficient synthetic protocols to obtain norbornadiene derivatives, since already established methods do not always deliver the desired norbornadiene derivatives and employ toxic starting materials with restricted use in many countries.<sup>63</sup> Once a new norbornadiene derivative has been synthesized, the next step is to characterize the compound photophysically, to explore the properties and important requirements needed for a MOST system.

Secondly, photoswitches such as azobenzene,<sup>64-66</sup> stilbene,<sup>67, 68</sup> tetracarbonyl-fulvalene-diruthenium,<sup>69</sup> and dihydroazulene<sup>33, 70</sup> are known to be affected by solvents, but in this regard not much is known about norbornadiene derivatives. For practical use of a norbornadiene derivatives in a MOST system like the one illustrated in Figure 2, a solvent is likely to be used. Therefore, the second question in this work is:

*Does the solvent affect the properties of derivatives of the norbornadiene/quadracyclane system?*

Finally, bicyclooctadiene, a structurally different photoswitch compared to norbornadiene but that operates through the same general isomerization mechanism, has never been evaluated for MOST purposes. Reasons could be that the photoisomers are known to be unstable and that bicyclooctadiene derivatives can degrade to aromatic byproducts, a side reaction not possible in the norbornadiene derivatives.<sup>58, 60, 71</sup> During the past years, approaches to stabilize

quadricyclane have been realized and plenty of knowledge regarding the structure/properties relationship has been gained.<sup>72,73</sup> Therefore, the final questions in this work are the following:

*Can bicyclooctadiene be substituted with donor/acceptor groups at the C2 and C3 positions?*

*Can bicyclooctadiene derivatives be evaluated as MOST candidates and will they exhibit properties for MOST energy storage?*

The outline for the rest of the thesis will be based on four papers, but first synthetic methods and methods used for photophysical characterization will be presented in Chapter 4. In Chapter 5, based on **Paper I** and **Paper II**, synthesis and evaluation of norbornadiene derivatives as MOST candidates will be describe. Chapter 6, based on **Paper III**, includes a study where solvent effects of the norbornadiene/quadricyclane system were investigated. Thereafter in Chapter 7, based on **Paper IV**, the synthesis and evaluation of bicyclooctadiene derivatives will be described. Finally, a conclusion and outlook are presented in Chapter 8.

In all papers, computations are included. The outcome of these computations will be presented, since they are important for the understanding of the function of the presented systems, but since the work was made by co-authors, discussions regarding computational methods is outside of the scope of this thesis.

For simplicity, target compounds are named NBD1-6, QC1-6, BOD1-4, and TCO1-4. All other compounds in the thesis are numbered according to their order of appearance in the text.



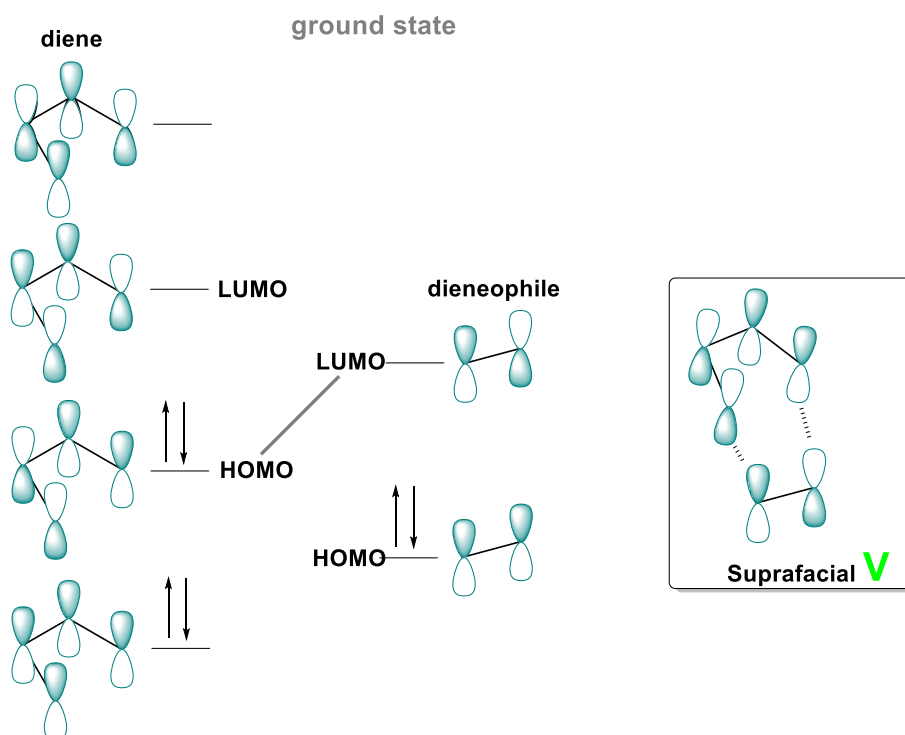
# Chapter 4

## Methods for Synthesis and Characterization

This chapter will give an overview of the methods used throughout the thesis for synthesis and photophysical characterization of the photoswitches. The basic techniques for measuring the absorption profiles and quantum yields, followed by the kinetic study of the back-conversion, will be described.

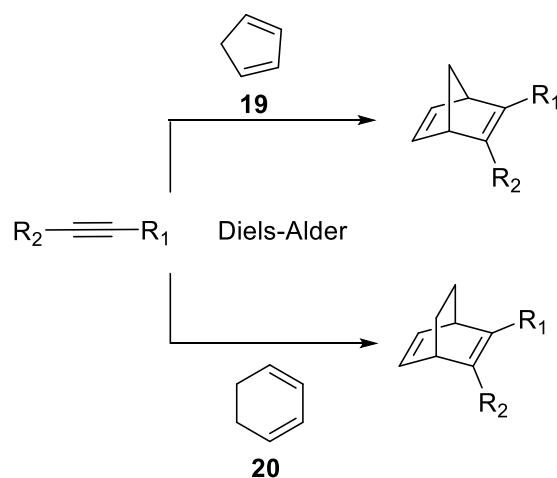
### 4.1 Synthesis of Norbornadiene Derivatives and Bicyclooctadiene Derivatives

A useful transformation in organic chemistry is the Diels-Alder reaction, where dienes react with alkenes to provide cyclohexene derivatives.<sup>74</sup> The reaction was developed by Otto Diels and Kurt Alder and they were awarded the Nobel prize in 1950 for their discovery of this reaction.<sup>75</sup> The reaction is a [4+2]-cycloaddition that, according to Woodward-Hoffman rules,<sup>35, 36</sup> is thermally allowed (Figure 6).



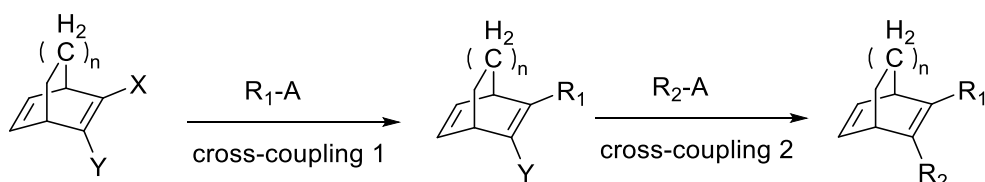
**Figure 6.** Illustration of frontier molecular orbitals involved in [4+2]-cycloaddition reactions for ground state electron configuration

The Diels-Alder reaction can be carried out with alkynes and 1,3-cyclopentadiene (**19**) or 1,3-cyclohexadiene (**20**) derivatives, which provides a way of synthesizing norbornadiene derivatives or bicyclooctadiene derivatives (Scheme 3).<sup>76</sup>



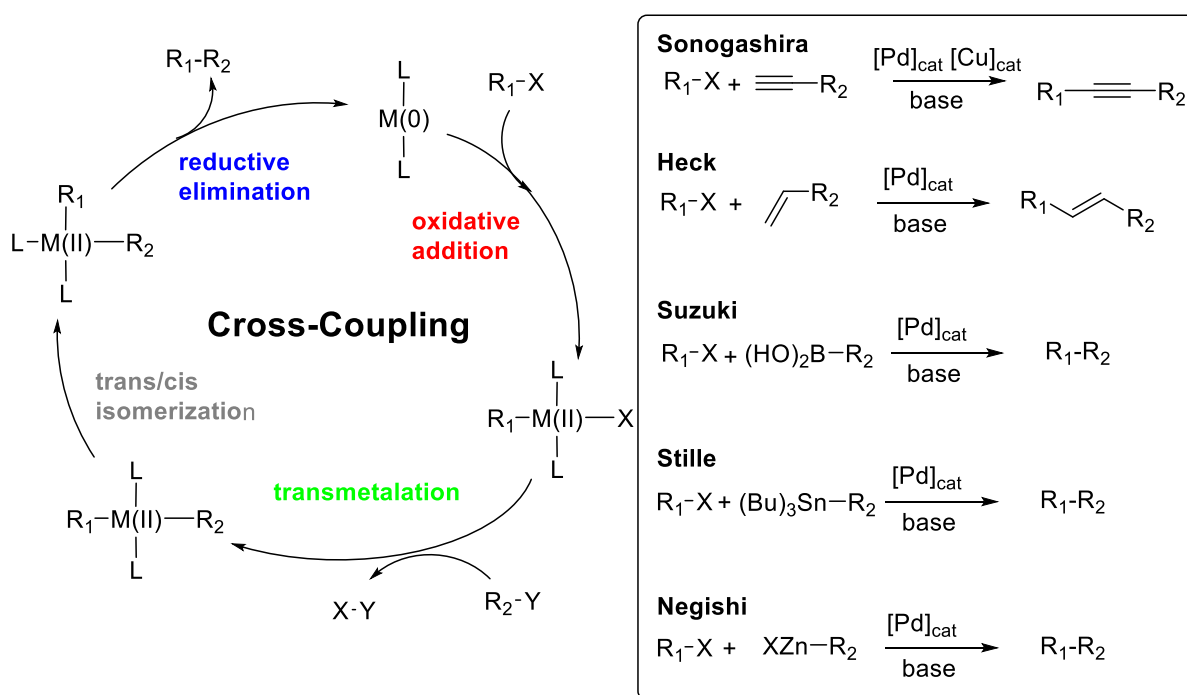
**Scheme 3.** Diels-Alder reaction between alkynes and 1,3-cyclopentadiene (**19**) or 1,3-cyclohexadiene (**20**) to obtain norbornadiene derivatives or bicyclooctadiene derivatives.

However, the varieties of photoswitches that can be synthesized through the Diels-Alder reaction are limited, since the reaction usually requires electron deficient dienes and electron rich alkynes. Also, in many cases the reaction requires high temperatures and long reaction times.<sup>37</sup> A different approach to synthesize substituted norbornadiene derivatives and bicyclooctadiene derivatives is via cross-coupling reactions, starting from a halogenated compound (Scheme 4). If the compound carries two different halogen substituents, two consecutive cross-coupling reactions can be performed to introduce two different substituents.<sup>77-79</sup>



**Scheme 4.** Introduction of substituents via cross-coupling reactions starting from halogenated compounds.  $R_1$  and  $R_2$  represents donor and acceptor groups,  $X$  and  $Y$  different halogens and  $A$  the second coupling partner.

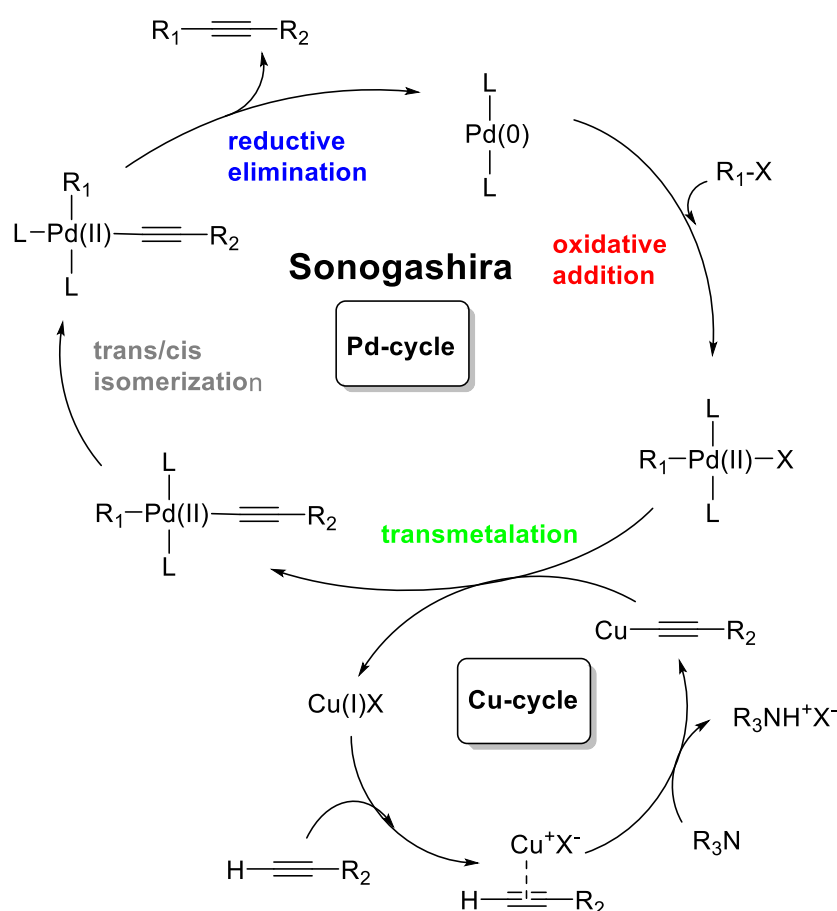
In cross-coupling reactions, organometallic catalysts are utilized to connect hydrocarbon fragments. As illustrated in Scheme 5, a cross-coupling reaction generally begins with an oxidative addition of one of the hydrocarbon fragments ( $R_1$ ) to the metal atom of the catalyst.<sup>77</sup> The second step is a transmetalation, where the other hydrocarbon fragment ( $R_2$ ) binds to the metal atom. Finally, a reductive elimination occurs, and the coupled product ( $R_1$ - $R_2$ ) is released, and the catalyst is regenerated. Commonly used catalysts include palladium complexes and one of the hydrocarbons is usually an aryl halide or another type of organic halide. The second hydrocarbon fragment varies depending on the nature of the reaction. In the Sonogashira reaction,<sup>80</sup> the second hydrocarbon fragment is an alkyne and in the Heck reaction<sup>81</sup> it is an alkene, while in the Suzuki coupling<sup>82, 83</sup> it is a boronic acid. The Stille coupling<sup>84</sup> and the Negishi coupling<sup>85</sup> are other well-known coupling reactions, where organotin and organozinc compounds are used as the second coupling partner. Because of the structural variety of the coupling partners, many types of different compounds can be synthesized, therefore making cross-coupling reactions very useful in organic synthesis.



**Scheme 5.** General mechanism for cross-coupling reactions, starting with oxidative addition, followed by transmetalation and reductive elimination, along with examples of some well-known coupling reactions.<sup>77</sup>

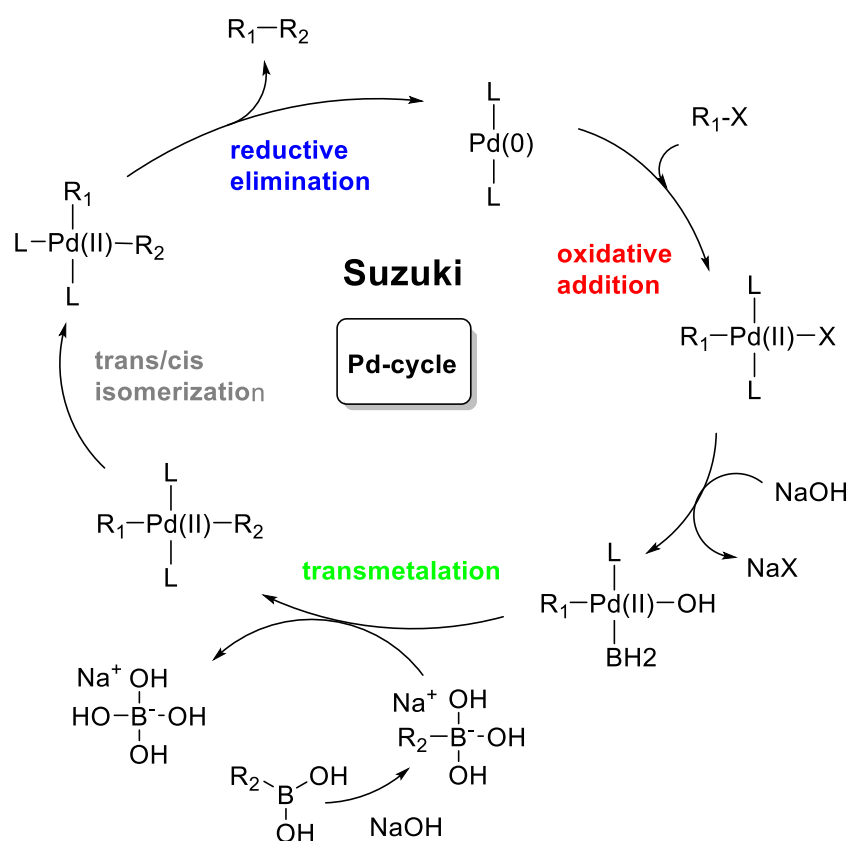
### 4.1.1 Sonogashira and Suzuki Cross-Coupling Reactions

In this thesis, two cross-coupling methods, the Sonogashira and Suzuki reaction were employed to obtain norbornadiene derivatives and bicyclooctadiene derivatives. Their generally accepted mechanisms are illustrated in Scheme 6 and 7. In the Sonogashira reaction, terminal alkynes are coupled with aryl halides or vinyl halides to form new carbon-carbon bonds. In the mechanism (Scheme 6), two catalytic cycles are involved, the “Pd-cycle” and the “Cu-cycle” where copper serves as a co-catalyst.<sup>86</sup> The copper catalyst forms a copper acetylide *in situ* from the alkyne, that increases the acidity of the terminal proton. Consequently, the “Cu-cycle” facilitates the transmetalation step. However, it is in the “Pd-cycle” that the carbon-carbon bond is formed via the general key steps for cross-coupling reactions, oxidative addition, transmetalation, trans/cis isomerization and reductive elimination. The Sonogashira reaction is usually performing well at room temperature and under nitrogen atmosphere since the presence of oxygen can induce homocoupling of the terminal alkynes. Triethylamine or diisopropylamine are common bases for the reaction.



**Scheme 6.** Mechanism for the Sonogashira reaction with copper as a co-catalyst.<sup>86</sup>

In the Suzuki reaction, an organic halide is coupled with a boronic acids to create a new carbon-carbon bond (Scheme 7).<sup>87</sup> A great advantage with the Suzuki reaction is that boronic acids are less toxic and more environmentally friendly than the organotin and organozinc reagents used in the Stille<sup>84</sup> and Negishi<sup>85</sup> coupling reactions. The Suzuki coupling can also be carried out in water as solvent, which enables water soluble substrates to participate in the reaction. As illustrated in Scheme 7, a base such as sodium hydroxide, cesium fluoride or potassium carbonate is required in the reaction.



**Scheme 7.** Mechanism for the Suzuki reaction.<sup>87</sup>

## 4.2 Absorption Spectra and Quantum Yield Measurements

The photoswitches described in this thesis undergo a chemical transformation once exposed to electromagnetic radiation that fits the absorption profile of the photoswitch. In a UV/Vis spectroscopy experiment, the absorption as a function of the wavelengths is measured and typically a solution of the photoswitch is exposed to light. The fraction of the intensity of the

incident and the transmitted light is measured to obtain the transmittance. The transmittance is correlated to the absorbance according to equation 4.1, where  $T$  is the transmittance and  $A$  is the absorbance.<sup>37</sup>

$$T = 10^{-A} \quad (4.1)$$

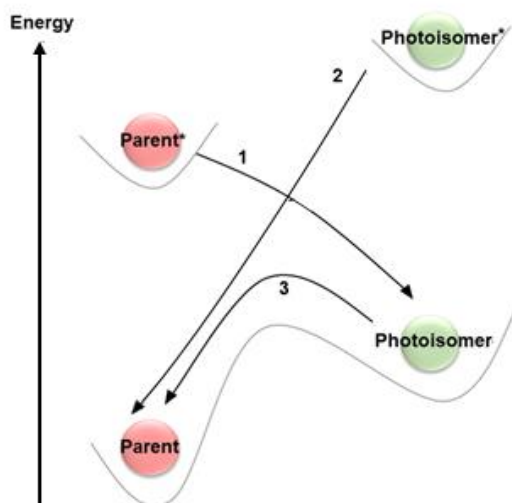
Another way to express the absorbance is by the molar extinction coefficient from the Lambert Beers Law (Equation 4.2), where  $A$  is the absorbance,  $\varepsilon$  the molar extinction coefficient,  $l$  is the path length of the light through the solution and  $c$  is the concentration.

$$A = \varepsilon \cdot l \cdot c \quad (4.2)$$

In the case where the absorption of light causes a chemical transformation, the quantum yield describes the efficiency of the process. The quantum yield ( $\phi$ ) is defined as the number of converted molecules ( $N_{converted\ molecules}$ ) divided by the number of absorbed photons ( $N_{absorbed\ photons}$ ) according to equation 4.3.

$$\phi = \frac{N_{converted\ molecules}}{N_{absorbed\ photons}} \quad (4.3)$$

The quantum yield can be measured by UV/Vis spectroscopy, and for photoswitches such as norbornadiene and bicyclooctadiene, there are three processes that can occur simultaneously (Figure 7).<sup>88</sup>



**Figure 7.** Three processes that can take place for a photoswitch. Process 1 and 2 illustrate the conversion of the parent compound to the photoisomer or vice versa after being excited by light. Process 3 illustrates the thermal conversion of the photoisomer back to the parent compound.

Firstly, the parent compound can be excited (parent\*) upon irradiation and converted to the photoisomer through process 1. Secondly, the photoisomer can also be excited and converted to the parent compound via process 2. Finally, in the third process, the photoisomer can be back-converted to the parent compound thermally, by applying heat. When expressing the rate equation for the photoisomerization from the parent compound to the photoisomer, all processes must be considered (Equation 4.4). In the rate equation,  $[Parent]$  is the concentration of the parent compound,  $\phi_{parent}$  and  $\phi_{photoisomer}$  are the quantum yields for the photoisomerization process 1 and 2 respectively,  $I$  is the photon flux,  $\beta_{parent}$  and  $\beta_{photoisomer}$  are the fractions of the absorbed photons by the parent compound and the photoisomers,  $N_A$  is Avogadro's number,  $V$  is the volume,  $k_t$  is the rate constant of the thermal conversion from the photoisomer to the parent compound and  $[photoisomer]$  is the concentration of the photoisomer.

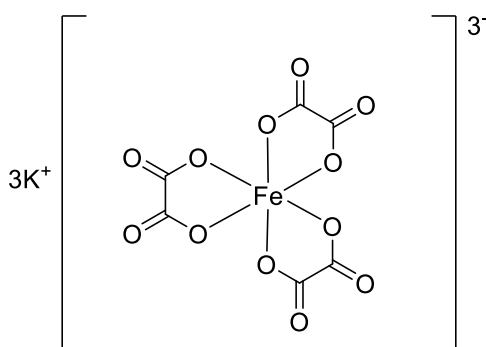
$$\frac{d[parent]}{dt} = -\frac{\phi_{parent} \cdot I \cdot \beta_{parent}(t)}{N_A \cdot V} + \frac{\phi_{photoisomer} \cdot I \cdot \beta_{photoisomer}(t)}{N_A \cdot V} + k_t [photoisomer] \quad (4.4)$$

Nevertheless, the expression and thereby the measurements of the photoisomerization process of the parent compound to the photoisomer (process 1) can be simplified by making some assumptions. Firstly, by performing the experiment at a low temperature, the thermal back-

conversion will be slow during the measurements and process 3 can be negligible. Secondly, by having a concentrated sample of the parent compound with an absorbance of over 2 at the irradiation wavelength, it can be assumed that more than 99% of the photons will be absorbed by the parent compound and almost none by the photoisomer; thus process 2 can be negligible. By making these assumptions and applying the Lambert-Beers law (Equation 4.2) to the rate expression (Equation 4.4), a linear dependence will be obtained (Equation 4.5) where  $[Parent]$  is the concentration of the parent compound,  $[Parent]_0$  is the initial concentration of the parent compound,  $\phi_{parent}$  is the quantum yield,  $I$  is the photon flux of,  $N_A$  is Avogadro's number,  $V$  is the volume and  $t_{irr}$  is the irradiation time.<sup>88</sup>

$$[Parent] = [Parent]_0 - \frac{\phi_{parent} \cdot I}{N_A \cdot V} \cdot t_{irr} \quad (4.5)$$

Consequently, the quantum yield can be obtained by stepwise irradiation of the parent compound and measuring the decrease in concentration by UV/Vis spectroscopy. However, the photon flux of the irradiation source must be known. Since it can fluctuate and decrease with time, it should be determined prior to the quantum yield measurements. The photon flux can be measured by chemical actinometry, a photochemical process where the quantum yield is known. A commonly used actinometer is potassium trioxalatoiron(III) (Figure 8), which decomposes and forms  $Fe^{2+}$  upon irradiation.<sup>89,90</sup> The amount of formed  $Fe^{2+}$ , and thereby the photon flux, can be determined by reacting it with phenanthroline to obtain a colored compound, detectable by UV/Vis spectroscopy.



**Figure 8.** Potassium trioxalatoiron(III) complex.



### 4.3 Kinetic Study of the Back-Conversion

The temperature of a chemical reaction affects the rate, and the correlation can be described either empirically by the Arrhenius equation (Equation 4.6) or by the Eyring equation, that follows from transition state theory (Equation 4.7), where  $k$  is the rate constant,  $A$  is constant for each chemical reaction,  $E_a$  is the activation energy,  $R$  is the universal gas constant,  $T$  is the absolute temperature,  $\kappa$  is the transmission coefficient,  $k_B$  is Boltzmann's constant,  $h$  is Planck's constant,  $\Delta S^\ddagger$  is the entropy of activation and  $\Delta H^\ddagger$  is the enthalpy of activation.

$$k = Ae^{-E_a/RT} \quad (4.6)$$

$$k = \frac{\kappa k_B T}{h} e^{(\Delta S^\ddagger/R)} e^{-(\Delta H^\ddagger/RT)} \quad (4.7)$$

UV/Vis spectroscopy can be utilized to measure the rate constants by monitoring the concentration of the formed species. For a reaction that follows first order kinetics, the formation of the species (X) will have an exponential decay according to the integrated rate law (Equation 4.8), where  $[X]$  is the concentration of the formed species,  $[X]_0$  is the initial concentration,  $k$  is the rate constant and  $t$  is the reaction time.

$$[X] = [X]_0 e^{-kt} \quad (4.8)$$

The thermal back-conversion of the photoswitches norbornadiene and bicyclooctadiene follows first order kinetics, and by measuring the rate constants at different temperatures, information on the stability of the corresponding photoisomers can be obtained. With rate constants at different temperatures in hand, an Eyring plot can be constructed according to the linear form of equation 4.7 (Equation 4.9), where the slope and intercept will provide information about the enthalpy and entropy of activation.

$$\ln \left( \frac{kh}{k_B T} \right) = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \frac{\Delta S^\ddagger}{R} \quad (4.9)$$

Thereafter, extrapolation of the Eyring plot can provide the rate constant at any temperature. The rate constant at 25 °C can be used to compare the stability of different photoisomers by calculating the half-life according to equation 4.10, where,  $t_{1/2}$  is the half-life and  $k$  is the rate constant.

$$t_{1/2} = \frac{\ln(2)}{k} \quad (4.10)$$

## 4.4 Cycling Studies

In order to study the robustness of photoswitches, a cycling study can be performed. By irradiating a sample of the parent compound, it will be converted to the photoisomer and by applying heat the parent compound will be regenerated. Therefore, the study can be carried out by altering irradiation with heating. The results are analyzed with UV/Vis spectroscopy and if no degradation has occurred, the absorption spectrum of the parent compound should be identical before and after the cycling. If there is a difference in the spectra, the amount of degradation can be determined.

# Chapter 5

## Synthesis and Photophysical Characterization of Norbornadiene Derivatives and Quadricyclane Derivatives

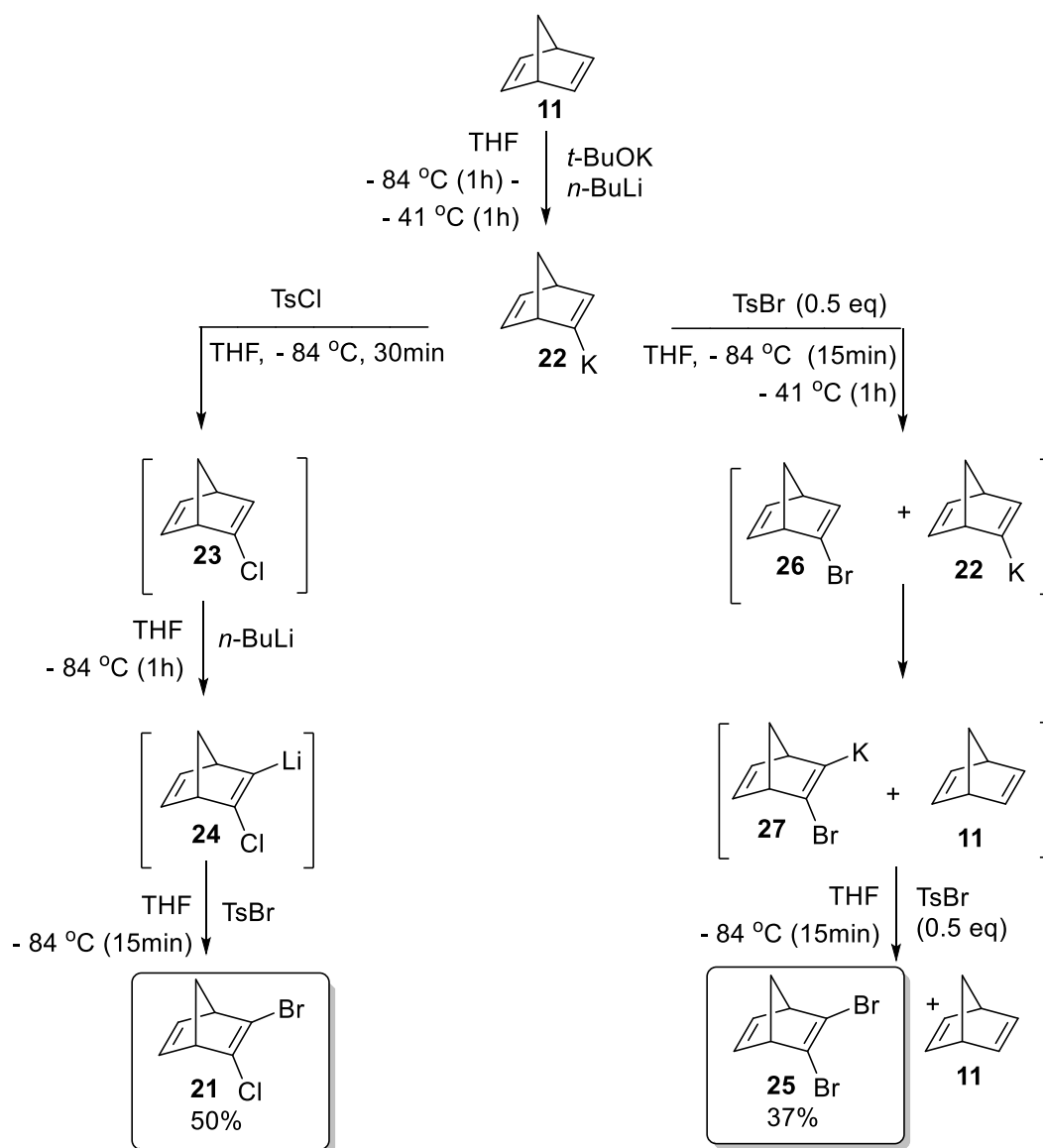
### 5.1 Synthesis of Norbornadiene Derivatives

The scope of norbornadiene derivatives that can be synthesized through the Diels-Alder reaction is limited due to the electronic demands of the reaction. Therefore, we wanted to explore cross-coupling reactions to obtain new donor/acceptor norbornadiene derivatives for MOST evaluation. For that approach, 2-bromo-3-chloronorbornadiene is an important starting material and an efficient synthesis was required. A drawback with already published procedures<sup>63, 91, 92</sup> towards 2-bromo-3-chloronorbornadiene is that the procedures use highly toxic or carcinogenic reagents and consequently we wanted to develop a new and efficient procedure towards 2-bromo-3-chloronorbornadiene.

#### 5.1.1 Synthesis of 2-Bromo-3-chloronorbornadiene

In **Paper I**, a new strategy towards the synthesis of 2-bromo-3-chloronorbornadiene (**21**) was developed (Scheme 8). The procedure was inspired by work from Tranmer *et al.*<sup>63</sup> and started with deprotonation of norbornadiene (**11**) by slowly adding *n*-butyllithium (*n*-BuLi) to a solution of **11** and potassium *tert*-butoxide (*t*-BuOK) in dry THF. The first step provided the metalated norbornadiene (**22**), which was treated with *p*-toluenesulfonyl chloride (TsCl) to give 2-chloronorbornadiene, **23**. Without isolating **23**, an *in situ* deprotonation to form **24** was carried out using *n*-butyllithium. In the final step, *p*-toluenesulfonyl bromide (TsBr) was added to provide the desired 2-bromo-3-chloronorbornadiene (**21**), which could be extracted from the reaction mixture. After purification, **21** was isolated in a yield of 50% which is close to the yield of 49% published by Tranmer *et al.*<sup>63</sup> However, our route has several advantages: 1) use of the carcinogenic brominating agent 1,2-dibromoethane is avoided, 2) the reaction times are significantly reduced, and 3) the reaction can be performed as a one-pot process without isolating the intermediates. Finally, if the yield is based on consumed norbornadiene **11**, which is the most expensive starting material, our yield was 42% compared to the 12% yield obtained by the previous protocol.

Having found a synthetic procedure for **21**, the route was adapted to synthesize 2,3-dibromonorbornadiene (**25**). In the procedure, *p*-toluenesulfonyl bromide was added to **22** to provide a mixture of 2-bromonorbornadiene (**26**) and metalated norbornadiene **22**. In the following step, **22** acted as base and deprotonated **26** to provide **27**. Another 0.5 equivalents of *p*-toluenesulfonyl bromide was added to the reaction mixture to obtain the final product **25** in a yield of 37% after **11** was recovered via distillation.

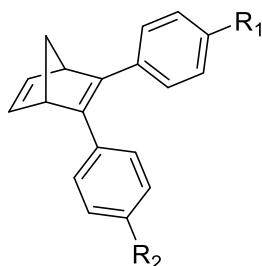


**Scheme 8.** Route towards 2-bromo-3-chloronorbornadiene (**21**) and 2,3-dibromonorbornadiene (**25**).

### 5.1.2 Synthesis of Donor/Acceptor-Substituted Norbornadiene Derivatives via Cross-Coupling Reactions

With **21** in hand, the next step towards new norbornadiene derivatives was to introduce the electron donating and electron accepting substituents. In **Paper II**, we were interested in synthesizing a series of donor/acceptor norbornadiene derivatives with low molecular weight to afford high storage densities. A series of norbornadiene derivatives containing a cyano acceptor and aryl-ethynyl donor substituents became the targets compounds for **Paper II**. The cyano group was selected as acceptor group, since it is one of the lightest with a molecular weight of 27 g/mol. We were interested in the ethynyl linker between the core of the norbornadiene and the donor group, as we speculated that this could reduce the steric hindrance we had observed by conformational analysis on previously synthesized diaryl-substituted norbornadiene derivatives (Table 1).<sup>93</sup> Reducing the steric hindrance that forces the aromatic substituents out of the plane could allow for better orbital overlap and a more red-shifted absorption profile. Also, the conjugation could be extended, which also can contribute to red-shifting the absorption.

**Table 1.** Diaryl-substituted norbornadiene derivatives and their molecular weight (MW), absorption onset ( $\lambda_{onset}$ ), absorption maxima ( $\lambda_{max}$ ) and molar extinction coefficient at the absorption maximum ( $\epsilon_{max}$ ).<sup>93</sup>



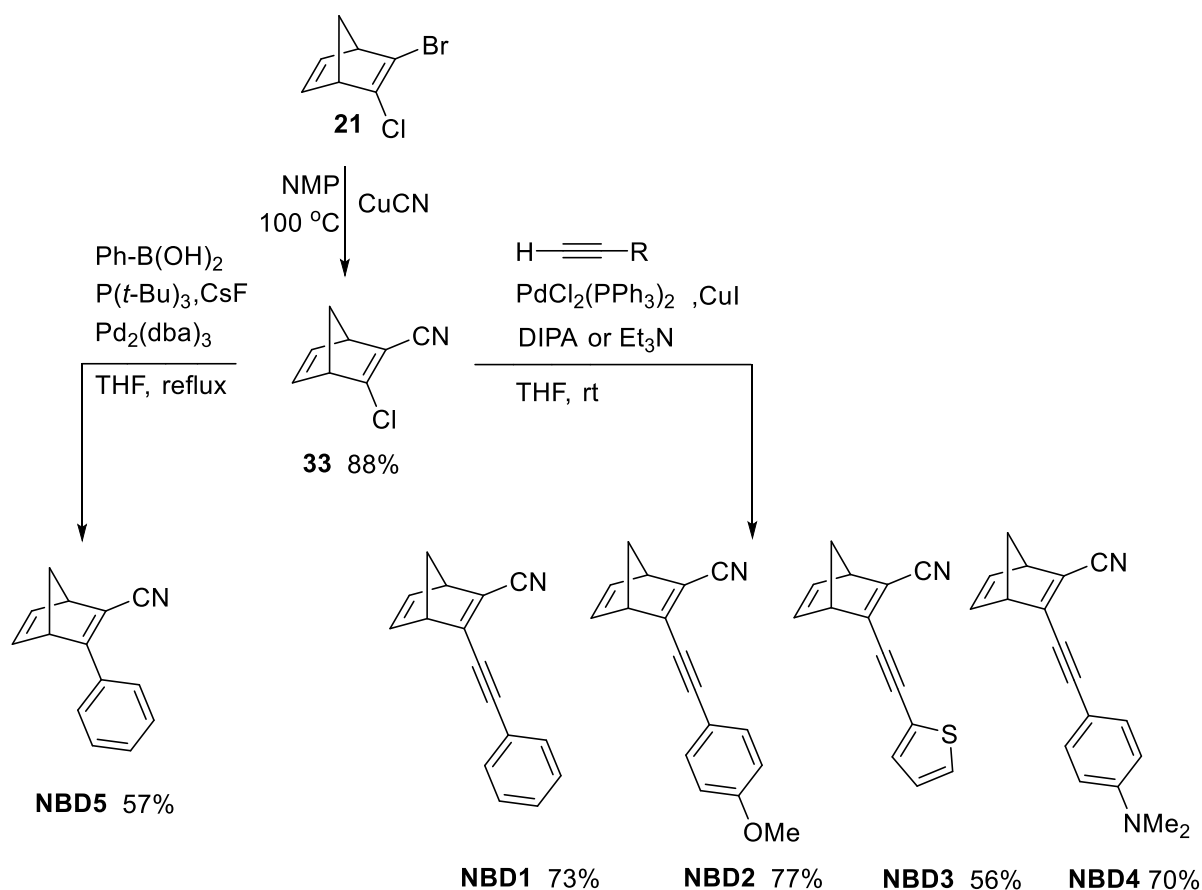
	R <sub>1</sub>	R <sub>2</sub>	MW [g/mol]	$\lambda_{onset}$ <sup>[a]</sup> [nm]	$\lambda_{max}$ [nm]	$\epsilon_{max}$ [M <sup>-1</sup> cm <sup>-1</sup> ]
<b>28</b>	H	H	244.33	389	308	8.0 x 10 <sup>3</sup>
<b>29</b>	H	OMe	274.36	402	309	9.0 x 10 <sup>3</sup>
<b>30</b>	CF <sub>3</sub>	OMe	342.36	414	318	7.2 x 10 <sup>3</sup>
<b>31</b>	CN	OMe	299.37	431	350	9.5 x 10 <sup>3</sup>
<b>32</b>	CF <sub>3</sub>	NMe <sub>2</sub>	355.40	462	365	10.1 x 10 <sup>3</sup>

[a] Absorption onsets are defined as  $\log\epsilon=2$

2-Bromo-3-chloronorbornadiene (**21**), synthesized in **Paper I**, was utilized to prepare a series of donor/acceptor-substituted norbornadiene derivatives containing a cyano acceptor and an aryl-ethynyl donor group (Scheme 9). In the first step, the cyano acceptor group was introduced

by adding copper(I) cyanide (CuCN) to a solution of **21** and after purification, 2-bromo-3-cyanonorbornadiene (**33**) was isolated to a yield of 88%. With **33** in hand, the next step was to introduce the electron donating groups through a cross-coupling reaction. To obtain ethynyl substituted norbornadiene derivatives, a Sonogashira reaction was performed at room temperature using dichlorobis(triphenylphosphine)palladium(II) in anhydrous THF. For all ethynyl derivatives, the reaction proceeded smoothly. After 2–4 hours, the reactions were completed and NBD1–4 were obtained in satisfactory yields of 56–77% following purification.

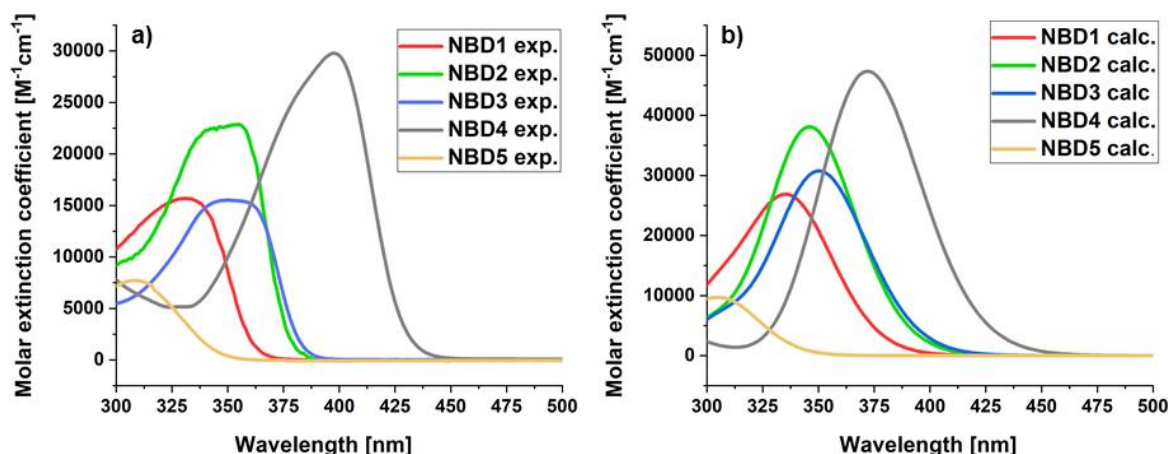
Furthermore, a Suzuki cross-coupling was carried out to synthesize a reference compound without the ethynyl-linker to allow comparison between the systems. The reaction was carried out between **33** and phenylboronic acid in refluxing THF. After purification, NBD5 was obtained in a yield of 57%.



**Scheme 9.** Routes towards donor/acceptor-substituted norbornadiene derivatives (NBD1–NBD5).

## 5.2 Photophysical Characterization of Donor/Acceptor-Substituted Norbornadiene Derivatives

In order to evaluate the MOST properties for the new series of norbornadiene derivatives (NBD1–NBD5), photophysical characterization was carried out. The UV/Vis spectra of NBD1 to NBD5 were recorded in toluene and compared to the spectra obtained by computational methods. (Figure 9, Table 2). The experimental and calculated spectra were in very good agreement, which confirms the possibility of predicting reliable absorption spectra for similar norbornadiene derivatives with other substituents. Regarding the absorption spectra, the experimentally obtained absorption onset for the norbornadiene derivatives with the ethynyl linker were similar for NBD2 and NBD3 (391 and 395 nm), lower for NBD1 (374 nm) and considerable higher for NBD4 (456 nm).



**Figure 9.** UV/Vis absorption spectra for NBD1 (red), NBD2 (green), NBD3 (blue), NBD4 (grey) and NBD5 (yellow): **a)** experimentally obtained in toluene; **b)** calculated.

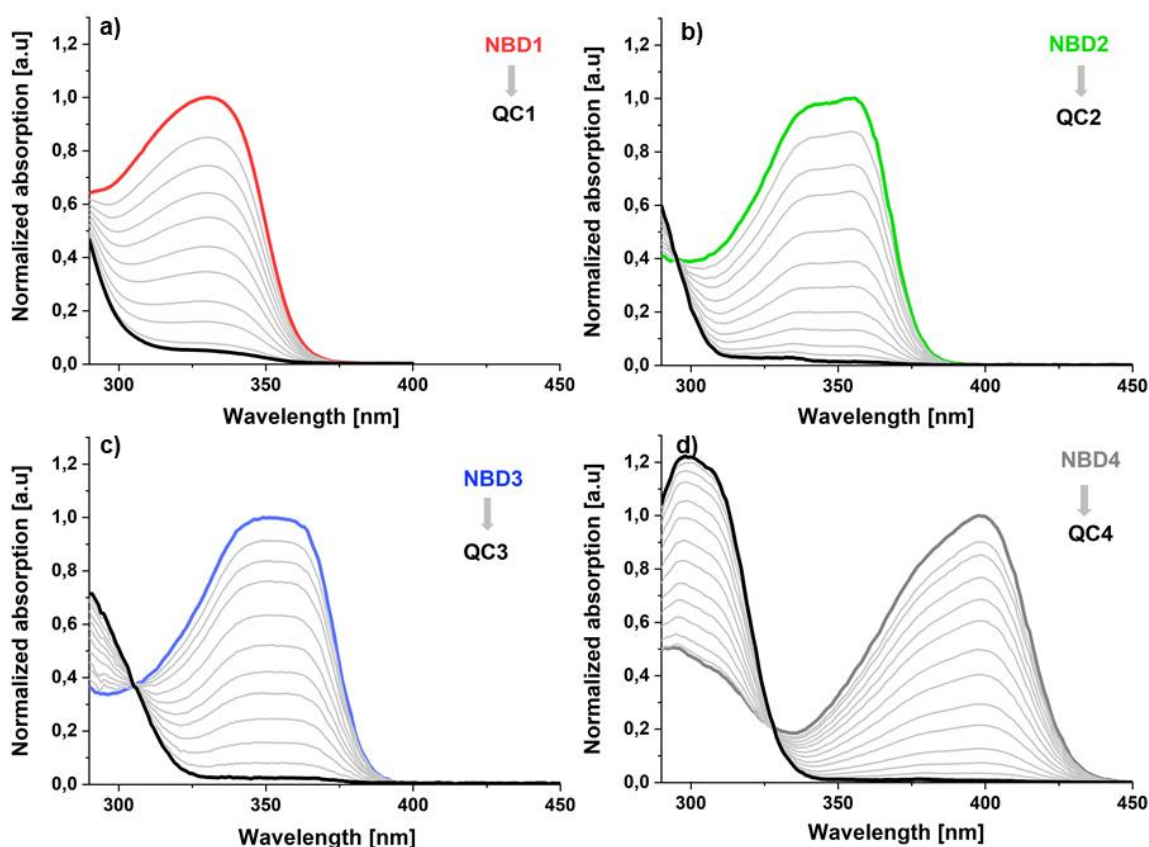
**Table 2.** Experimental (exp.) and calculated (calc.) absorption onset ( $\lambda_{onset}$ ), absorption maxima ( $\lambda_{max}$ ) and molar extinction coefficient at the absorption maximum ( $\epsilon_{max}$ ) for NBD1 to NBD5.

NBD	$\lambda_{onset}$ <sup>[a]</sup> exp. [nm]	$\lambda_{max}$ exp. [nm]	$\epsilon_{max}$ exp. [M <sup>-1</sup> cm <sup>-1</sup> ]	$\lambda_{max}$ calc. [nm]	$\epsilon_{max}$ calc. [M <sup>-1</sup> cm <sup>-1</sup> ]
NBD1	374	331	15.7 x 10 <sup>3</sup>	335	26.9 x 10 <sup>3</sup>
NBD2	391	355	22.9 x 10 <sup>3</sup>	346	38.1 x 10 <sup>3</sup>
NBD3	395	340	15.5 x 10 <sup>3</sup>	350	30.8 x 10 <sup>3</sup>
NBD4	456	398	29.8 x 10 <sup>3</sup>	372	47.3 x 10 <sup>3</sup>
NBD5	358	308	7.72 x 10 <sup>3</sup>	304	9.69 x 10 <sup>3</sup>

[a] Absorption onsets are defined as  $\log \epsilon = 2$

Consequently, NBD4 has the best solar spectrum match in these series, and the effect of introducing a *p*-dimethylaminophenyl group as the electron donating substituent is large. Regarding NBD5, the compound without an ethynyl linker between the core of the norbornadiene and the donor group, the onset was much lower (358 nm) and the molar extinction coefficient was also lower compared to the other norbornadiene derivatives. Insights from electronic structure calculations proposed that the ethynyl-linker between the donor groups and the norbornadiene core minimized the distortion of the conjugated  $\pi$  system, causing a red-shift in the absorption (compare NBD1 and NBD5). Also, the dipole strength of the HOMO/LUMO transition is enhanced by the ethynyl-linker, which resulted in the large increase in the molar extinction coefficient.

The norbornadiene derivatives were converted to their corresponding quadricyclane derivatives (QC1-QC5) by irradiation and the photoisomerization processes were monitored by UV/Vis spectroscopy (Figure 10).



**Figure 10.** Stepwise irradiation (grey) of norbornadiene derivatives (colored) to the corresponding quadricyclane derivatives (black) in toluene monitored by UV/Vis spectroscopy: **a)** NBD1 (red), **b)** NBD2 (green), **c)** NBD3 (blue), and **d)** NBD4 (grey).



The overlap in spectra between the norbornadiene derivatives and the corresponding quadricyclane derivatives was very small for all compounds, which is a great advantage, fulfilling an important MOST criterion of not competing over photons between the two isomers. Regarding NBD4, the compound with the best solar spectrum match, the photoisomer displayed negligible absorbance above 350 nm. To demonstrate that the sun can drive the photoisomerization of NBD4, it was exposed to a 1.5 AM standard solar simulator and full conversion was obtained. Isobestic points were observed in the spectra of NBD1–NBD4 and their corresponding quadricyclane derivatives, indicating that only two species were present in the solutions. No isobestic point was observed for NBD5 due to overlap with absorption of the solvent. However, it is expected to follow the same trend as NBD1–NBD4.

Quantum yields for the photoisomerization processes and half-lives of the quadricyclane derivatives were measured and the results are presented in Table 3. The quantum yield was highest (58%) for NBD5, the norbornadiene derivative without an ethynyl-linker, almost twice as high as for NBD4 (28%). Regarding the half-lives, the measurements show a major difference between the compounds with an ethynyl-linker and the compound without this moiety. The half-life of NBD5 was 55 days at ambient temperature, while the others have half-lives of less than 24 hours. By comparing NBD1 to NBD4, it was clear that the half-life of the quadricyclane derivative was affected as the absorption was red-shifted. NBD1 had the lowest onset (374 nm) and the longest half-life (22 h), while NBD4 had the highest onset (456 nm) and the shortest half-life (5 h).

Furthermore, the storage energies were measured by differential scanning calorimetry and compared to the calculated values. All systems showed exothermic peaks, and for QC4 and QC5 one exothermic peak was obtained, corresponding to a heat release of 103 and 122 kJ/mol (0.39 MJ/kg and 0.63 MJ/kg), respectively. These values were higher than for norbornadiene with a storage energy of 90 kJ/mol. For QC1 to QC3, two exothermic peaks were obtained, most likely due to a complex phase behavior of a mixture of both norbornadiene derivatives and quadricyclane derivatives. Therefore, it was not possible to precisely determine any experimental values in these cases. The calculated values for QC1 to QC3 were also high, between 118 and 121 kJ/mol.

**Table 3.** Measured quantum yields ( $\Phi$ ), half-lives ( $t_{1/2}$ ) at 25 °C in toluene calculated from extrapolating Eyring plots and experimental (exp.) along with calculated (calc.) storage energies ( $\Delta H_{\text{storage}}$ ) for NBD1 to NBD5.

<b>NBD/QC</b>	<b><math>\Phi</math> [%]</b>	<b><math>t_{1/2}</math> [h]</b>	<b><math>\Delta H_{\text{storage}}</math> exp. [MJ/kg]</b>	<b><math>\Delta H_{\text{storage}}</math> calc. [MJ/kg]</b>	<b><math>\Delta H_{\text{storage}}</math> calc. [kJ/mol]</b>
<b>NBD1/QC1</b>	39	22.0	-	0.55	118
<b>NBD2/QC2</b>	38	15.8	-	0.49	121
<b>NBD3/QC3</b>	47	7.43	-	0.53	119
<b>NBD4/QC4</b>	28	5.05	0.39	0.48	124
<b>NBD5/QC5</b>	58	1320	0.63	0.59	114

# Chapter 6

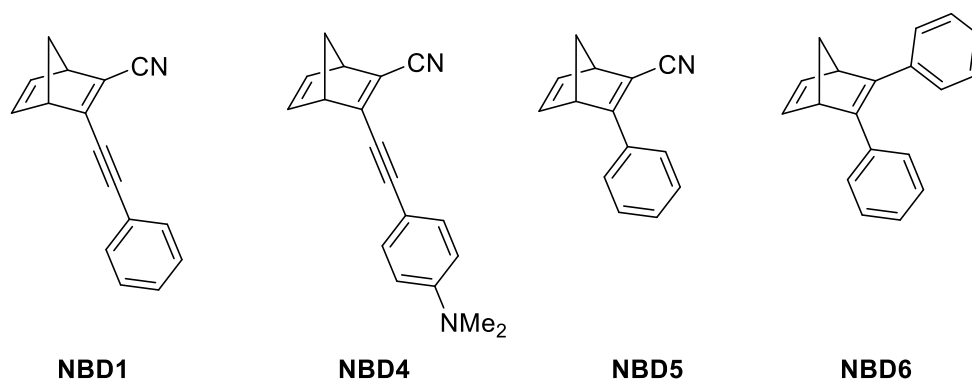
## Solvent Effects on Derivatives of the Norbornadiene/Quadricyclane System

Since altering the substituent pattern of compounds affects the properties, engineering the molecular structure of a photoswitch is usually a primary strategy when it comes to optimizing for MOST purposes. A parameter that has been much less explored, especially for the norbornadiene/quadricyclane system, is the local environment of the photoswitch.

As illustrated in Figure 2, a possible way of integrating a MOST system in a device is to pump a photoswitch through a closed system. For these types of applications, a liquid system is required, and despite that solvent free systems theoretically can provide higher efficiencies, not all compounds are liquids at the operating temperature and pressure of such a device. Consequently, solvents will play an important role when developing MOST systems.

Solvents are known to influence the properties of several potential MOST photoswitches such as azobenzene,<sup>64-66</sup> stilbene,<sup>67, 68</sup> tetracarbonyl-fulvalene-diruthenium<sup>69</sup> and dihydroazulene.<sup>33, 70</sup> We were therefore interested in evaluating potential solvent effects on the norbornadiene/quadricyclane system.

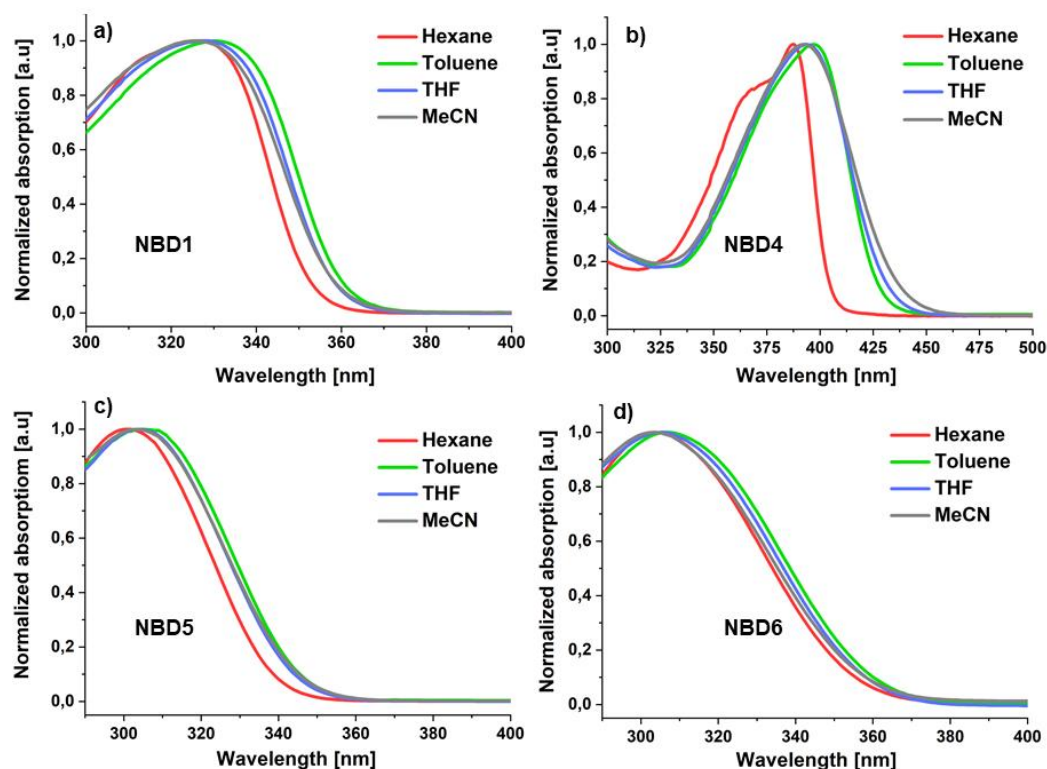
In **Paper III**, a selection of norbornadiene derivatives (NBD1, NBD4, NBD5 and NBD6: Figure 11) were photophysically characterized in four commonly used solvents, toluene, tetrahydrofuran (THF), hexane and acetonitrile (MeCN). Our choice of norbornadiene derivatives was based on a series of structurally different molecules. Two norbornadiene derivatives substituted with cyano acceptor groups and alkynyl substituted aromatic donor groups, NBD1 and NBD4, were investigated. Also, one norbornadiene derivative with a cyano acceptor group and aromatic donor group NBD5 and one comparatively more symmetrical norbornadiene derivative substituted with phenyl groups NBD6 were investigated. The chosen solvents have UV-transparency in the region where the norbornadiene derivatives are absorbing.



**Figure 11.** Structurally different norbornadiene derivatives for selected for studying solvent effects.

## 6.1 Absorption Spectra of the Norbornadiene Derivatives

The UV/Vis absorption spectra for the norbornadiene derivatives were recorded in the different solvents (Figure 12, and Table 1, **Paper III**) and for all norbornadiene derivatives there was a minor change in the peak position in the different solvents. The trend with the small shifts does not seem to be strongly related to polarity of the solvent, as in this case a higher absorption maximum would have been expected in hexane compared to toluene. What stands out in the measured UV/Vis absorption spectra is the shape of the peaks in hexane, particularly for NBD4. The effect in this case is due to the dimethylamino substituent on the donor group of NBD4, since this behavior is not observed for NBD3 which otherwise is structurally similar. Greater solvatochromic effects can be expected when hydrogen-bonding interactions take place between the solute and the solvent. Therefore, larger effects might have been observed if NBD4 would have carried a less substituted amino group and been dissolved in a protic solvent. Regarding the onset, there was a clear shift in hexane compared to the other solvents for NBD1, NBD4 and NBD5, whereas for NBD6 the effect was less pronounced. The spectra were also obtained computationally in toluene (see appended **Paper III**, Figure 2) and are in good agreement with the experimental data.



**Figure 12.** Measured UV/Vis spectra in hexane (red), toluene (green), THF (blue) and MeCN (grey) for a) NBD1, b) NBD4, c) NBD5 and d) NBD6.

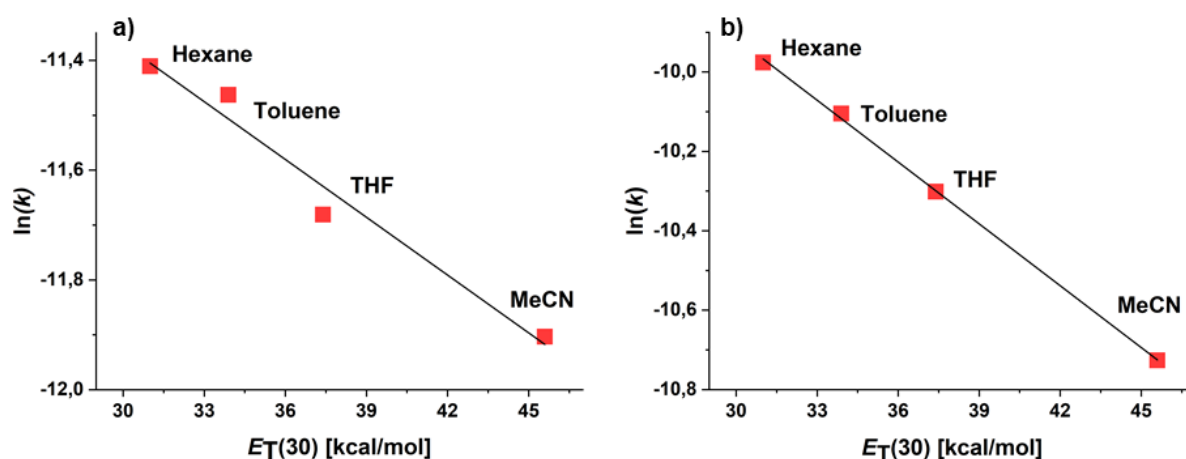
## 6.2 Stability of the Quadricyclane Derivatives

To evaluate the solvent effects on the thermal stability of the quadricyclane derivatives, a kinetic study was performed. The norbornadiene derivatives were dissolved in different solvents and converted to the corresponding quadricyclane derivatives by irradiation. The rate constants of the back-conversion were measured at several temperatures and the half-lives at 25° C were calculated. The results for QC1 and QC4 are presented in Table 4, but for practical reasons, no reliable data were obtained for QC5 and QC6, where the high temperatures and prolonged heating periods resulted in partial degradation of the compounds or evaporation of solvents.

**Table 4.** Half-lives ( $t_{1/2}$ ) at 25 °C in different solvents for QC1 and QC2 calculated from extrapolating Eyring plots.

QC	$t_{1/2}$ hexane [h]	$t_{1/2}$ toluene [h]	$t_{1/2}$ THF [h]	$t_{1/2}$ MeCN [h]
QC1	17	18	23	29
QC4	4.1	4.7	5.7	8.8

The results for QC1 and QC4 showed that changing the solvent had a great effect on the thermal stability of the quadricyclane derivatives. For QC1 and QC4, the back-conversions were faster in non-polar solvents than in polar solvents. In fact, the half-life was as much as two times larger in acetonitrile than in hexane for QC4. To explore if there was a linear trend, the rate constant for the back-conversion of QC1 and QC4 were correlated to the polarity of the solvent by plotting  $\ln(k)$  at 25 °C against the empirical solvent parameters,  $E_T(30)$ , of the solvents (Figure 13). The empirical solvent parameter is defined as the transition energy of dissolved *N*-phenolate betaine dye measured in kcal/mol (hexane 31.0 kcal/mol (130 kJ/mol), toluene 33.9 kcal/mol (142 kJ/mol), tetrahydrofuran 37.4 kcal/mol (157 kJ/mol) and acetonitrile 45.6 kcal/mol (191 kJ/mol)).<sup>94</sup> As Figure 13 illustrates, a linear trend was obtained for both QC1 and QC4. These results make it possible to alter the kinetic stability by changing the solvents and also to predict the half-lives of these compounds in different solvents.



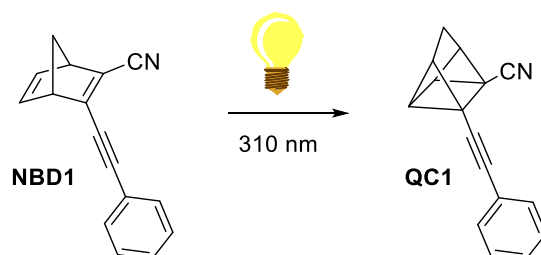
**Figure 13.** Plot of  $\ln(k)$  at 25°C against the empirical solvent parameters  $E_T(30)$  of the solvents for a) QC1 and b) QC4.

### 6.3 Photoisomerization Process

Since the solvent had such a large effect on the thermal stability of QC1 and QC4, we were curious to evaluate if the solvents also affected the photoisomerization process from the norbornadiene derivatives to quadricyclane derivatives. A qualitative NMR study was performed, where NBD1 and NBD4 were dissolved in deuterated solvents (toluene- $d_6$ ,  $CDCl_3$  and MeCN- $d_3$ ) using the same concentration (3.3 mg/mL) and volume (3 mL) for all samples. The samples were irradiated with a 405 nm LED for NBD4 and a 310 nm LED for NBD1. The photoisomerization process was monitored by NMR spectroscopy, and the results are presented

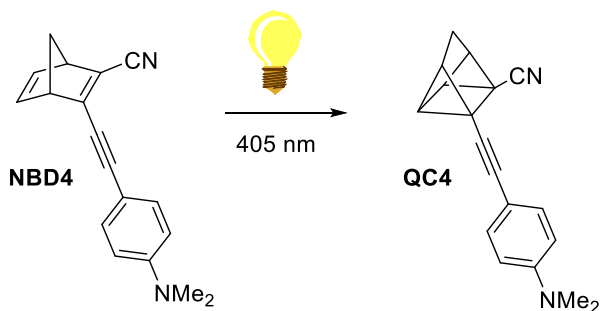
in Tables 5 and 6. For NBD4, there is a large difference between the solvents. After 7.5 minutes, the compound was completely converted to QC4 in toluene- $d_6$ , but only 38% converted in  $CDCl_3$ . In MeCN- $d_3$ , no conversion at all was observed, even after 51 minutes of irradiation. For NBD1, there is also a difference in the rate of the photoisomerization reaction and the process seems to proceed faster in polar solvents, in contrast to NBD4. A complicating factor when interpreting the results from the experiment is that 310 nm is at the borderline of where toluene starts absorbing, hence there is a possibility that some of the photons were absorbed by the solvent and not by the compound. Also, for NBD1, the back-conversion is faster in toluene than it is in MeCN, which can contribute to the lower conversion rate. For a quantitative comparison of the solvent effects on the photoisomerization, the quantum yields in MeCN were measured using UV/Vis spectroscopy and correlated to the quantum yields in toluene. For NBD4, the quantum yield was 3% in MeCN compared to 28% in toluene, which is a large difference. For NBD1, the difference was again smaller, and considering the limits of experimental error makes it difficult to draw any conclusions, except that the solvent effects are less pronounced for NBD1 than for NBD4. An explanation can be that NBD1 has a more symmetrical substitution pattern and therefore the quantum yield is less affected of the solvent polarity. NBD4 is more polar than NBD1, and the excited state is more polar than the ground state due charge transfer in the donor-acceptor structure, which might explain the large effect of solvent polarity.

**Table 5.** Photoisomerization of NBD1 to QC1 in toluene-*d*<sub>6</sub>, CDCl<sub>3</sub>, and MeCN-*d*<sub>3</sub>. A 310 nm LED was used as irradiation source and the process was monitored by <sup>1</sup>H-NMR spectroscopy.



Irradiation time [min]	Conversion Toluene- <i>d</i> <sub>6</sub> [%]	Conversion CDCl <sub>3</sub> [%]	Conversion MeCN- <i>d</i> <sub>3</sub> [%]
1.5	6	11	12
3	10	15	17
4.5	14	20	28
6	19	24	30
7.5	22	28	36
17	49	58	71

**Table 6.** Photoisomerization of NBD4 to QC4 in Toluene-*d*<sub>6</sub>, CDCl<sub>3</sub>, and MeCN-*d*<sub>3</sub>. A 405 nm LED was used as irradiation source and the process was monitored by <sup>1</sup>H-NMR spectroscopy.



Irradiation time [min]	Conversion Toluene- <i>d</i> <sub>6</sub> [%]	Conversion CDCl <sub>3</sub> [%]	Conversion MeCN- <i>d</i> <sub>3</sub> [%]
1.5	24	9	0
3	47	15	0
4.5	67	22	0
6	86	31	0
7.5	100	38	0
17	-	90	0
51	-	-	0



# Chapter 7

## Exploring the Bicyclooctadiene/Tetracyclooctane System for MOST Energy Storage

Our interest in the bicyclooctadiene/tetracyclooctane was sparked from the predicted storage density of 1.77 MJ/kg, a higher value than for norbornadiene (0.98 MJ/kg).<sup>62</sup> In **Paper IV**, we wanted to synthesize and evaluate a series of bicyclooctadiene derivatives both experimentally and computationally. Our idea regarding the design of the bicyclooctadiene derivatives was to implement the knowledge gained concerning the norbornadiene/quadracyclane systems and we therefore wanted to prepare a series of donor/acceptor bicyclooctadiene derivatives. Consequently, a synthetic procedure had to be developed, which will be presented in the upcoming section followed by the characterization of a series of novel bicyclooctadiene derivatives for MOST.

### 7.1 Synthesis of Bicyclooctadiene Derivatives

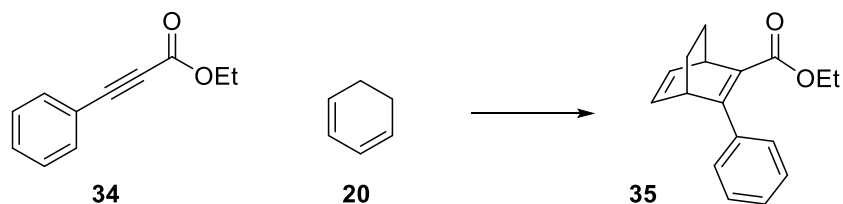
One way of synthesizing bicyclooctadiene derivatives is through the Diels-Alder reaction between alkynes and cyclohexadiene. As in the case of norbornadiene derivatives, if the alkyne is substituted with both an electron accepting and electron donating group, a donor/acceptor bicyclooctadiene derivative can be obtained in one step. Alternatively, electron accepting and electron donating group can be introduced via cross-coupling reactions.

#### 7.1.1 Attempted One Step Approach Towards Synthesis of Donor/Acceptor- Substituted Bicyclooctadiene Derivatives

As a starting point and to explore the reaction conditions for Diels-Alder reaction, a test reaction between ethyl 3-phenylpropiolate (**34**) and 1,3-cyclohexadiene was performed (Table 7) using conventional heating in a sealed vial. The result showed that the reaction was favored by an excess of the diene, since the yield is higher in entry 4 than in entry 3 or 2. The different solvents did not influence the outcome much and the reaction that was performed in the absence of solvent gave almost the same conversion yield as in toluene. Long reaction times were required for product formation, but the formation of the product never exceeded 30%. A scale-up reaction of entry 5 was performed to further analyze the outcome and to isolate the product. The crude NMR spectra of the scaled-up reaction indicated that several compounds were

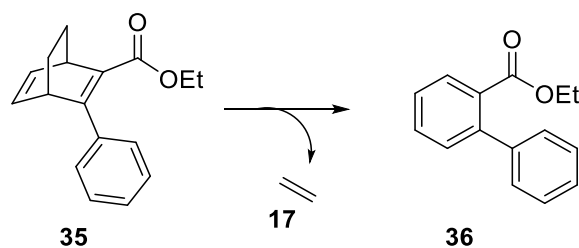
present in the reaction mixture, the bicyclooctadiene derivative (**35**), the two starting materials (**34** and **20**), but also the aromatic byproduct (**36**), formed via a retro-Diels-Alder reaction (Scheme 10). Column chromatography was performed and while the aromatic biproduct could be obtained with high purity, the bicyclooctadiene derivative could not be isolated in pure form, even after several attempts with different eluent systems and gradients.

**Table 7.** Optimization of reaction conditions of ethyl 3-phenylpropiolate (**34**) and 1,3-cyclohexadiene (**20**) to form ethyl-3-phenylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate (**35**).



Entry	Solvent	Diene equivalent	Temperature [°C]	Time [h]	Product formation [%]
<b>1</b>	chlorobenzene	2	110	18	19
				45	19
<b>2</b>	toluene	1.5	160	4	0
				23	14
				42	14
<b>3</b>	toluene	4.5	160	4	13
				23	17
				42	17
<b>4</b>	toluene	9	160	4	– <sup>[a]</sup>
				23	22
				42	27
				78	30
<b>5</b>	neat	9	160	21	23
				48	26
				72	29

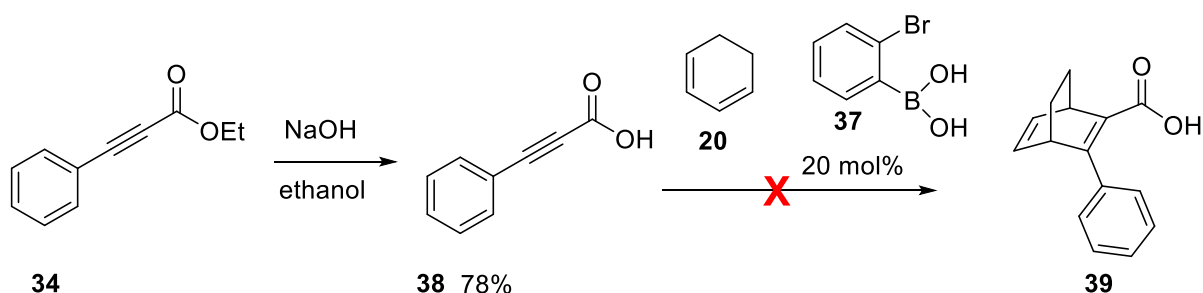
[a](–) The quality of the NMR spectra was too low to analyze the product formation



**Scheme 10.** Retro-Diels-Alder reaction of **35** to form byproduct **36** and ethene (**17**).

Clearly, the high temperatures and long reaction times favored the retro-Diels-Alder reaction since in entry 5, the byproduct yield (**36**) was 35% after 72 hours and the product yield (**35**) was 29%. When the reaction was kept running for 5 days, the product yield was still 29% but the byproduct yield had increased to 48%.

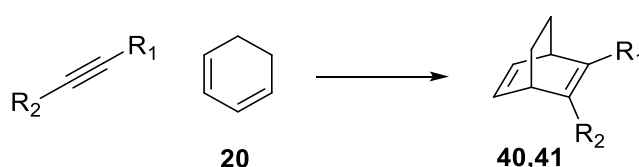
The next strategy was to add a catalyst to the reaction to allow a lower reaction temperature in order to avoid the formation of the retro-Diels-Alder product. Aluminum chloride was added to a reaction between ethyl 3-phenylpropiolate (**34**) and 1,3-cyclohexadiene (**20**) using the same conditions as in Table 6, entry 5, except that parallel reactions were performed at room temperature and 50°C, respectively. Unfortunately, the NMR spectra indicated that polymerization had occurred, and no product formation was observed. A procedure from Zheng *et al.*<sup>95</sup> has been successful in catalyzing Diels-Alder reactions between carboxylic acids and dienes with boronic acid catalysts (**37**), and therefore, as shown in Scheme 11, a reaction was carried out where **34** was first hydrolyzed to the corresponding acid (**38**), before the catalyzed Diels-Alder reaction was performed. However, no product (**39**) was formed after 24 hours.



**Scheme 11.** Attempted two-step reaction schemes to obtain bicyclooctadiene derivative **39**.

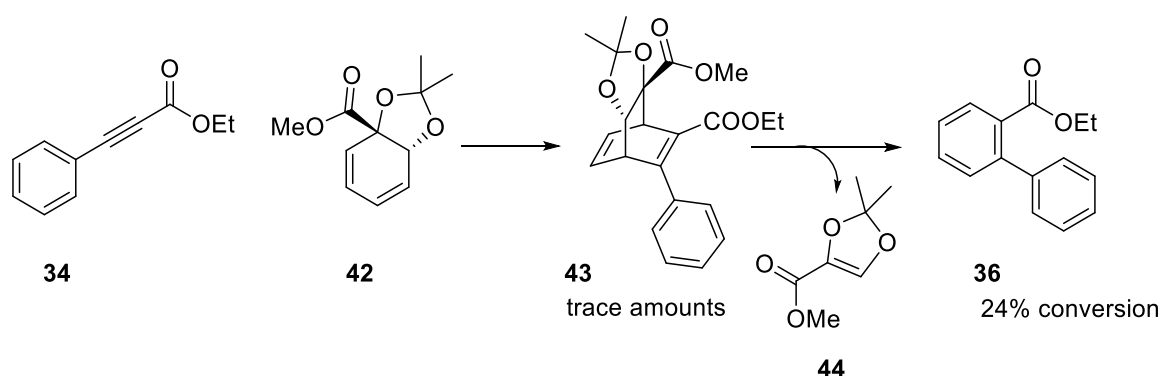
The Diels-Alder reaction is favored with electron deficient alkynes and therefore 1,3-cyclohexadiene was reacted with two slightly more electron deficient alkynes, containing a trifluoromethyl group or a cyano group (Table 8). In entry 1, no reaction occurred at 25 °C and when the temperature was increased to 100 °C the crude NMR spectrum indicated that the retro-Diels-Alder product had been formed, since there were many signals in the aromatic region of the NMR spectrum. In entry 2, no product was formed after 24 hours at 60 °C. The NMR spectrum indicated that only starting materials were present in the reaction mixture.

**Table 8.** Reaction scheme of testing different alkynes in the Diels-Alder reaction.



Entry	Solvent	R <sub>1</sub>	R <sub>2</sub>	Temperature [°C]	Product formation [%]
1	neat	Ph	COCF <sub>3</sub>	25	0
				100	-
2	neat	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	CN	60	0

Furthermore, since the formation of the aromatic ring and ethene drives the retro-Diels-Alder reaction towards the byproduct, an idea was to use a highly substituted cyclohexadiene that would result in a leaving group less stable than ethene, due to ring strain (Scheme 12). Methyl 2,2-dimethylbenzodioxole-carboxylate (**42**) has previously been synthesized by our collaborators<sup>96</sup> and was provided to us to test in the Diels-Alder reaction.



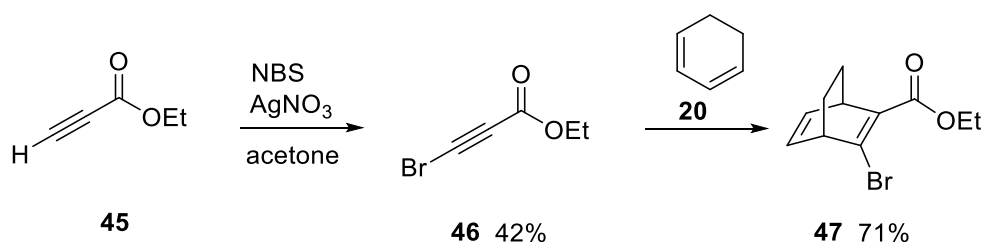
**Scheme 12.** Diels-Alder reaction between ethyl phenylpropiolate (**34**) and a substituted cyclohexadiene (**42**).

The reaction between **34** and **42** was carried out at 100 °C in the absence of solvent, using 1 equivalent of the diene. After 24 hours, 24% of the byproduct **36** had been formed and not even traces of the product could be found in the reaction mixture according to the NMR spectrum, indicating that **44** was stable enough to drive the reaction towards **36**. Lower temperatures resulted in only starting material present in the reaction mixture.

To summarize, the high temperatures required for the Diels-Alder to proceed with an alkyne substituted with both a donor and acceptor group strongly favored the retro-Diels-Alder byproduct formation. When lowering the temperature, the reactivity was too low, and no reaction occurred. We therefore needed to find a different strategy towards donor/acceptor bicyclooctadiene derivatives.

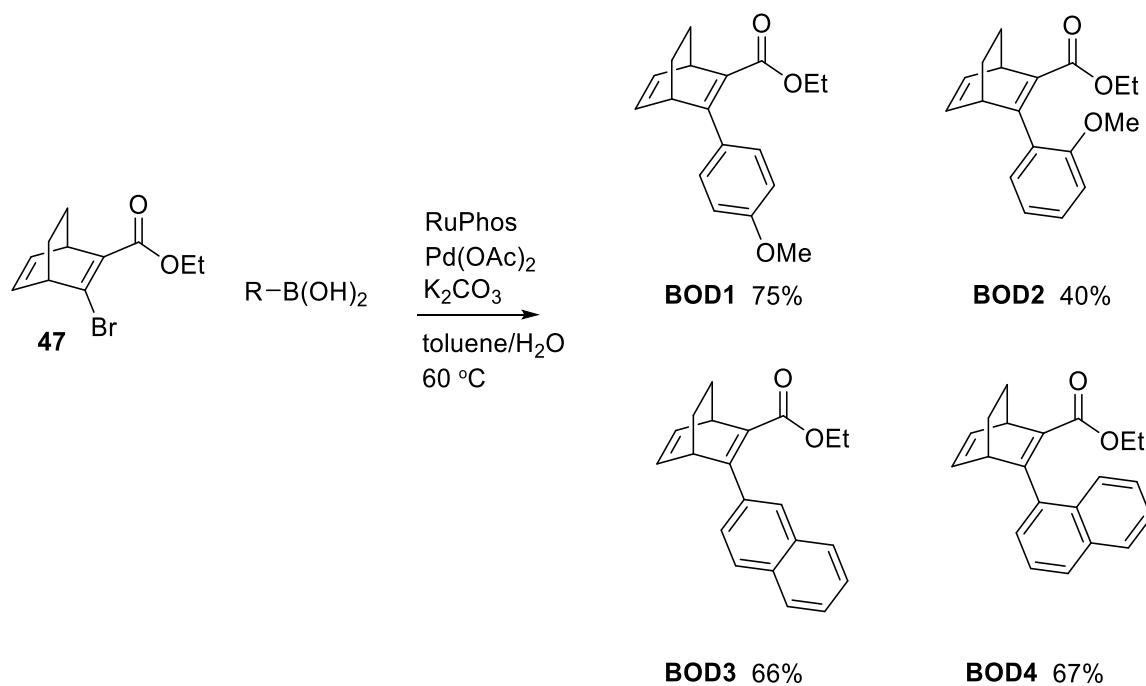
### 7.1.2 Synthesis of Donor/Acceptor Substituted Bicyclooctadiene Derivatives via Diels-Alder Reaction Followed by Cross-coupling Reactions.

Our new strategy aimed to perform the Diels-Alder reaction with an alkyne substituted with an acceptor group and a halogen, similar to what Bosse *et al.*<sup>97</sup> have reported, and thereafter carry out a palladium-catalyzed cross-coupling reaction to introduce the donor group. Ethyl propiolate (**45**) was brominated with *N*-bromosuccinimide (NBS) to produce ethyl-3-bromopropiolate (**46**). Thereafter, **46** was treated with cyclohexadiene in a Diels-Alder reaction at 60 °C to afford ethyl-3-bromobicyclo[2.2.2]octa-2,5-diene-2-carboxylate (**47**) in a yield of 71% (Scheme 13).



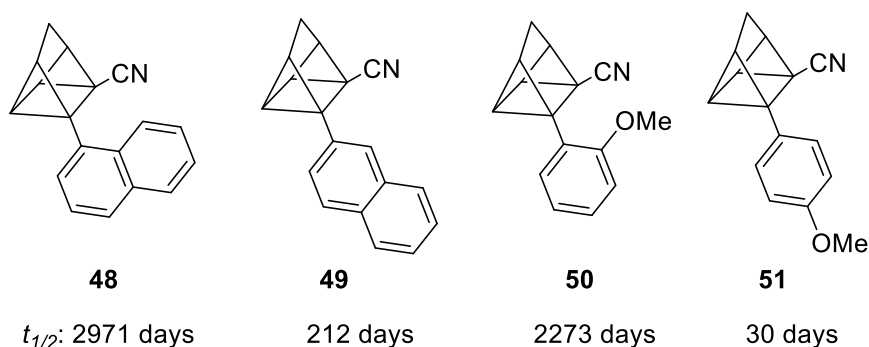
**Scheme 13.** Bromination reaction followed by Diels-Alder reaction to provide ethyl-3-bromobicyclo[2.2.2]octa-2,5-diene-2-carboxylate (**41**)

Compound **47** was used directly in a Suzuki reaction with boronic acids in a toluene and water mixture. The reaction temperatures were kept under 60 °C to avoid occurrence of a retro-Diels-Alder reaction and a series of bicyclooctadiene derivatives were successfully synthesized in 40 to 75% yields (Scheme 14). The choice of donor groups was based on finding a substituent to increase the stability of the corresponding photoisomer.



**Scheme 14.** Synthesis of bicyclooctadiene derivatives (BOD1–BOD4) via Suzuki cross-coupling.

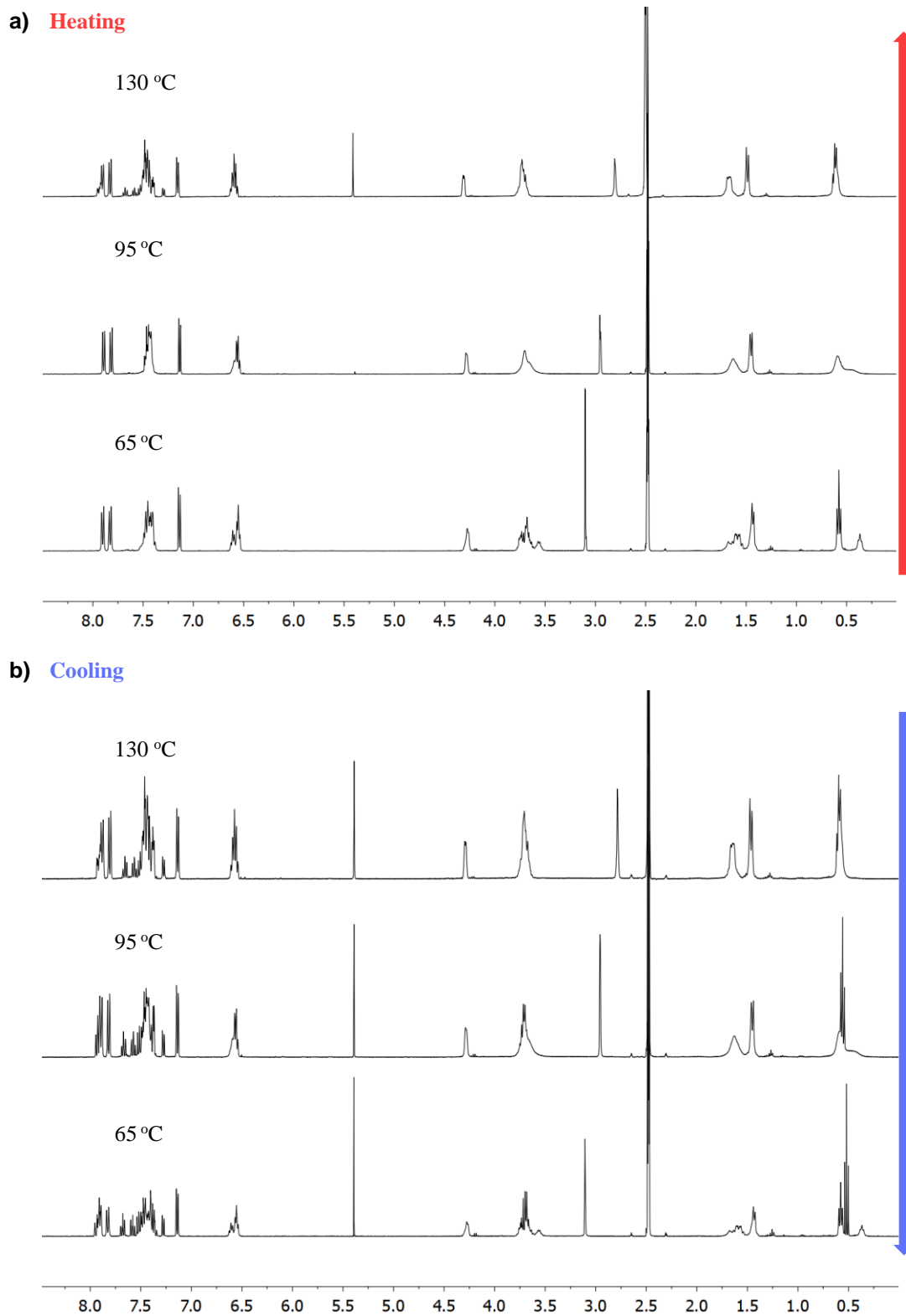
For similar norbornadiene derivatives (Figure 14) with identical donor groups, the half-lives of the corresponding photoisomer increased 32 times when adding a 1-naphthyl group (**48**) instead of a 2-naphthyl group (**49**) and 76 times by placing the methoxy group at the *ortho* position (**50**) instead of in the *para* position (**51**) of the phenyl group.<sup>72, 44</sup>



**Figure 14.** A series of quadricyclane derivatives and their half-lives at 25 °C, determined from Eyring parameters.<sup>72, 44</sup>

BOD4 was isolated as two rotamers at room temperature, due to hindered rotation around the single bond that connects the naphthyl group with the bicyclooctadiene core. To confirm that rotamers were isolated, variable temperature NMR spectroscopy was performed in DMSO at

three different temperatures of 65 °C, 95 °C and 130 °C (Figure 15). As the temperature was increased, peaks from the rotamers started to coalesce and at 130 °C, only signals from a single compound were observed. However, quickly after heating the sample up to 130 °C, the bicyclooctadiene derivative started to degrade and new peaks in aromatic region and also a new triplet at around 0-1 ppm appeared. These peaks are from the aromatic byproduct formed through a retro-Diels-Alder reaction. The sample was cooled down and the new peaks in the aromatic region remained, while signals from the different rotamers reappeared.

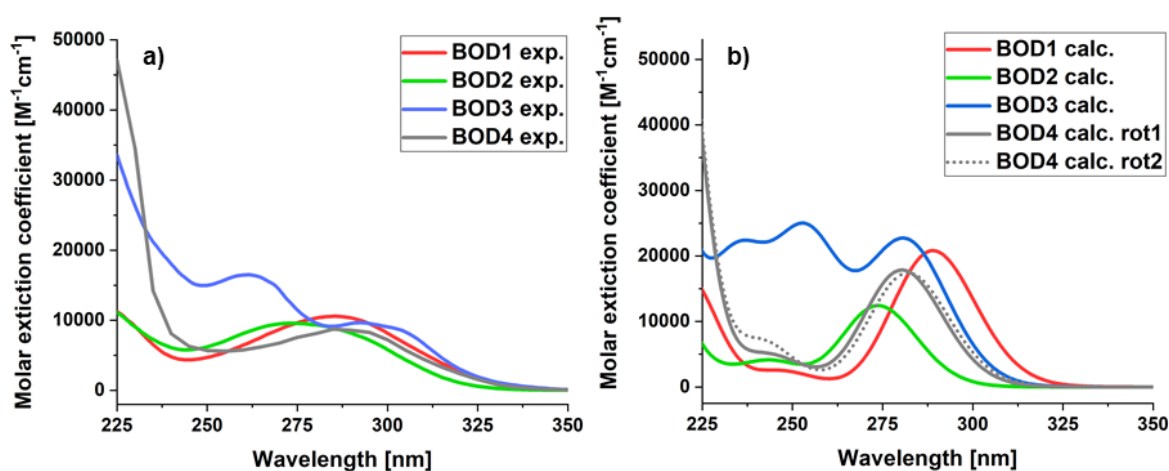


**Figure 15.**  $^1\text{H}$ -NMR spectra of BOD4 at 3 different temperatures. **a)** heating up the sample **b)** cooling down the sample.



## 7.2 Photophysical Characterization of Donor/Acceptor-Substituted Bicyclooctadiene Derivatives

The UV/Vis spectra of BOD1 to BOD4 were obtained both experimentally in acetonitrile and by computational methods (Figure 16 and Table 9). For BOD4, UV/Vis spectra for both rotamers were calculated. The experimental and calculated spectra are in good agreement, except that the calculated spectra are slightly shifted towards higher wavelengths. As expected, due to similar structures, the absorption profiles for BOD1 and BOD2 are very similar, with an onset of 350 nm and 338 nm, respectively. The maxima are at 285 nm and 274 nm and the molar extinction coefficients around  $10000 \text{ M}^{-1}\text{cm}^{-1}$  for both BOD1 and BOD2.



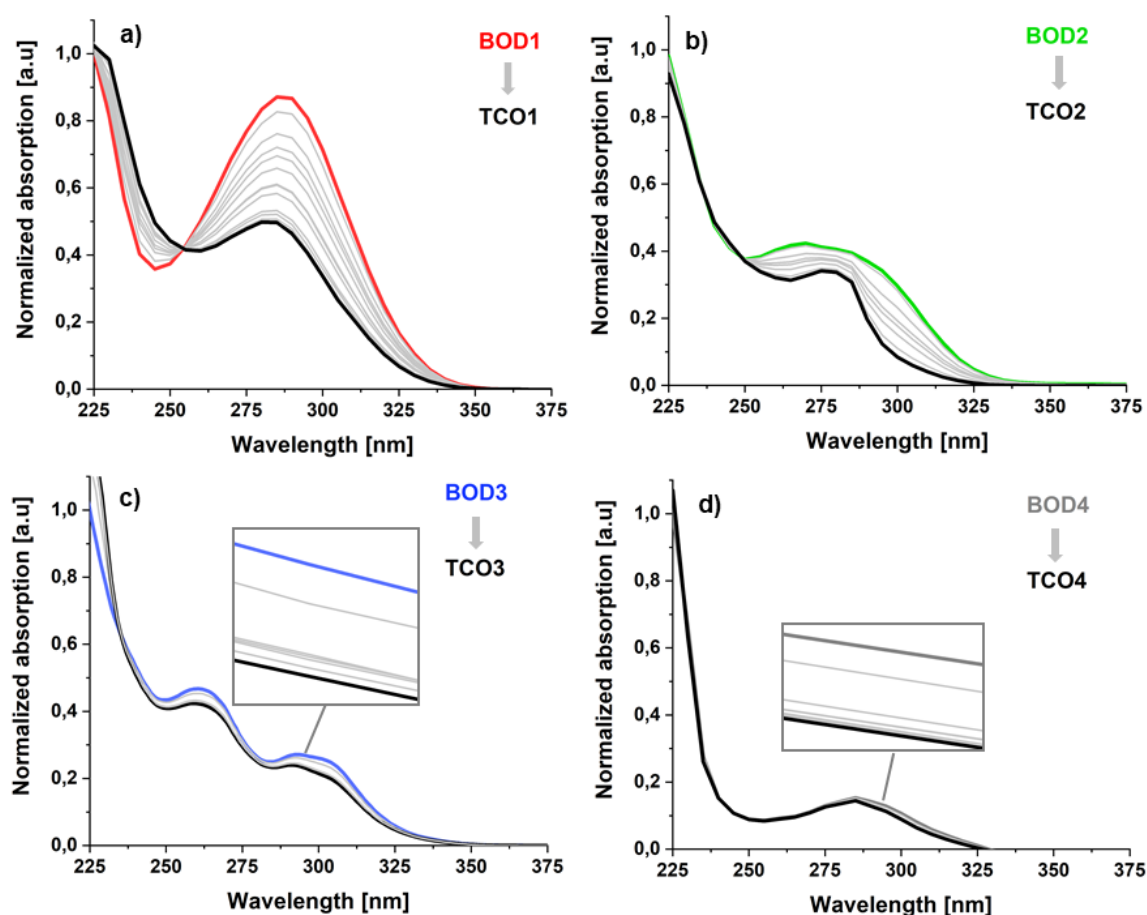
**Figure 16.** UV/Vis absorption spectra for BOD1 (red), BOD2 (green), BOD3 (blue), and BOD4 both rotamers (rot) (grey) **a)** obtained experimentally in acetonitrile, **b)** calculated.

**Table 9.** Experimental (exp.) and calculated (calc.) absorption onset ( $\lambda_{\text{onset}}$ ), absorption maxima ( $\lambda_{\text{max}}$ ) and molar extinction coefficient at the absorption maxima ( $\epsilon_{\text{max}}$ ) for BOD1 to BOD4.

BOD	$\lambda_{\text{onset}}^{\text{[a]}}$ exp. [nm]	$\lambda_{\text{max}}$ exp. [nm]	$\epsilon_{\text{max}}$ exp. [ $\text{M}^{-1}\text{cm}^{-1}$ ]	$\lambda_{\text{max}}$ calc. [nm]	$\epsilon_{\text{max}}$ calc. [ $\text{M}^{-1}\text{cm}^{-1}$ ]
BOD1	350	285	$10.6 \times 10^3$	289	$20.8 \times 10^3$
BOD2	338	274	$9.59 \times 10^3$	274	$12.4 \times 10^3$
BOD3	350	292	$9.67 \times 10^3$	281	$22.7 \times 10^3$
		262	$16.5 \times 10^3$	253	$25.0 \times 10^3$
BOD4	348	285	$8.76 \times 10^3$	280 <sup>[b]</sup>	$17.9 \times 10^3$ <sup>[b]</sup>
				282 <sup>[c]</sup>	$17.1 \times 10^3$ <sup>[c]</sup>

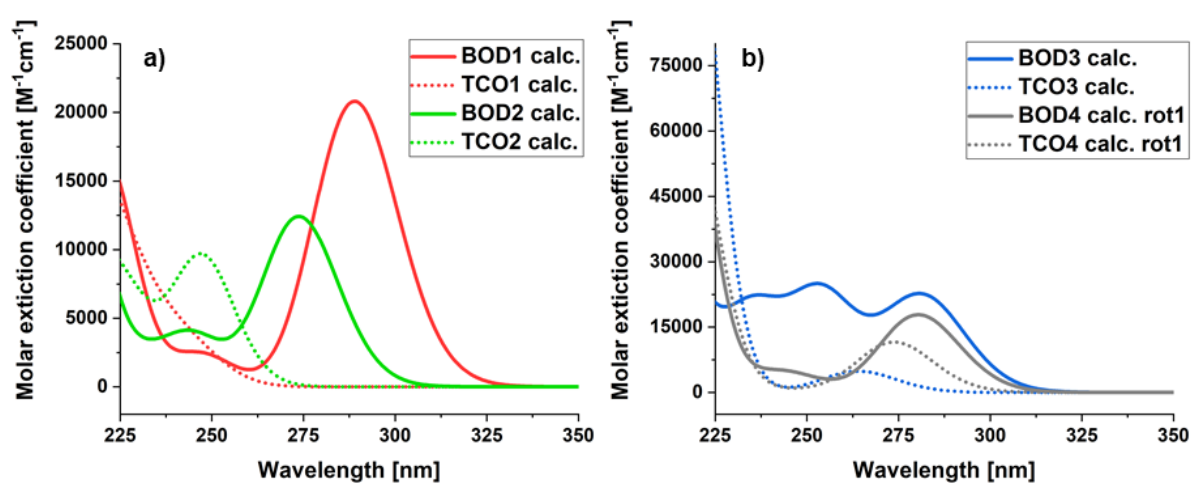
[a]Absorption onsets are defined as  $\log \epsilon = -2$ , [b]data for rotamer1, [c]data for rotamer2

Regarding BOD3 and BOD4, the spectra are not as similar as for BOD1 and BOD2, and within the range of the measurements, BOD3 has two absorption maxima at 292 nm and 262 nm, respectively, while BOD4 has one maximum at 285 nm. The absorption onsets are at 350 nm and 348 nm, respectively, and the molar extinction coefficients are similar around the first absorption maximum. In the calculated spectrum for BOD4, rotamer 1 has a slightly redshifted absorption profile (onset 9 nm, maxima 7 nm) otherwise the spectra are identical with rotamer 2. All bicyclooctadiene derivatives were irradiated to obtain the corresponding tetracyclooctane derivatives (Figure 17). For all bicyclooctadiene derivatives, a change in the absorption spectra was obtained after irradiation, but the effect was less for BOD3 and BOD4 compared to BOD1 and BOD2. A possible explanation could be a greater overlap in the absorption spectra for BOD3/TCO3 and BOD4/TCO4 compared to for BOD1/TCO1 and BOD2/TCO2.



**Figure 17.** Stepwise irradiation (grey) of bicyclooctadiene derivatives (colored) to the corresponding tetracyclooctane derivatives (black) in acetonitrile monitored by UV/Vis spectroscopy. **a)** BOD1 (red), **b)** BOD2 (green), **c)** BOD3 (blue) and **d)** BOD4 (grey).

The computed spectra of all bicyclooctadiene derivatives and tetracyclooctane derivatives are presented in Figure 18. Additionally, isosbestic points were observed for all the systems. To confirm that tetracyclooctane derivatives were formed, low temperature NMR spectroscopy was performed directly after irradiation and peaks from the tetracyclooctane derivatives were identified in all cases (see appended **Paper IV**, SI, Figure S3.22-S3.20). Also, a cycling study for all derivatives of the bicyclooctadiene/tetracyclooctane system were carried out and all compounds were able to switch back and forth with little degradation. A long-term cycling study was performed on the BOD1/TCO1 system and it could be cycled for 645 cycles with only 0.01% degradation.



**Figure 18.** Calculated spectra of bicyclooctadiene derivatives and the corresponding tetracyclooctane derivatives. **a)** BOD1/TCO1 (red/dashed red) and BOD2/TCO2 (green/dashed green) and **b)** BOD3/TCO3 (blue/dashed blue) and BOD4 rotamer1/TCO4 rotamer1 (grey/dashed grey)

The quantum yields of the photoisomerization process and half-lives of the tetracyclooctane derivatives were measured in toluene (Table 10). The quantum yields for BOD2 and BOD4 were measured to 14 and 19%, respectively, and for BOD1 and BOD3, no values could be obtained due to fast back-conversion. Regarding the half-lives, TCO1 and TCO3 have half-lives of around 10 seconds and 6 seconds, respectively, at room temperature while TCO2 and TCO4 have half-lives of 100 and 276 seconds, respectively. The effect on the half-lives from the substitution pattern was large, for the methoxy substituted compounds the half-life is around 10 times longer when the methoxy group is placed in the *ortho* position (TCO2) compared to the *para* position (TCO1). For the compounds with the naphthyl group, the effect is even larger and the half-life for TCO4 is around 55 times longer than for TCO3. The half-lives were also measured in acetonitrile and the difference from toluene was very small and

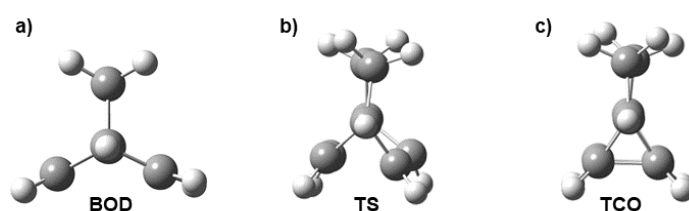
could be neglected. Furthermore, since a critical challenge with the bicyclooctadiene/tetracyclooctane system is the degradation via retro-Diels-Alder reactions, the heat tolerance was tested experimentally. All bicyclooctadiene derivatives were dissolved in toluene and heated to 75 °C for 1 hour. NMR analysis showed that no degradation had occurred, and the heating did not induce the retro-Diels-Alder reaction to form the corresponding aromatic byproducts.

**Table 10.** Measured quantum yields ( $\Phi$ ), half-lives ( $t_{1/2}$ ) at 25 °C in toluene calculated from extrapolating Eyring plots and experimental (exp.) along with calculated (calc.) storage energies ( $\Delta H_{\text{storage}}$ ) for BOD1 to BOD4.

BOD/TCO	$\Phi$ <sup>[a]</sup> [%]	$t_{1/2}$ [s]	$\Delta H_{\text{storage}}$ calc. [MJ/kg]	$\Delta H_{\text{storage}}$ calc. [kJ/mol]
<b>BOD1/TCO1</b>	-	10.1	0.51	146
<b>BOD2/TCO2</b>	14	99.6	0.53	152
<b>BOD3/TCO3</b>	-	5.7	0.51	156
<b>BOD4/TCO4</b>	19	276	0.47 <sup>[b]</sup> 0.47 <sup>[c]</sup>	142 <sup>[b]</sup> 142 <sup>[c]</sup>
<b>NBD1/QC1</b>	x	x	0.22	59
<b>NBD2/QC2</b>	x	x	0.21	57
<b>NBD3/QC3</b>	x	x	0.21	62
<b>NBD4/QC4</b>	x	x	0.18 <sup>[b]</sup> 0.16 <sup>[c]</sup>	51 <sup>[b]</sup> 46 <sup>[c]</sup>

[a] (-) values could not be measured for BOD1 and BOD2 due to short half-lives (x) NBD1-NBD4 were only evaluated computationally. [b] data for rotamer1, [c] data for rotamer2.

The storage energies were calculated for all derivatives of the bicyclooctadiene/tetracyclooctane system and also for the corresponding derivatives of the norbornadiene/quadracyclane systems, for comparison (Table 10). For all bicyclooctadiene derivatives, the storage densities were over two times higher than for the corresponding norbornadiene derivatives. One possible explanation could be the structure of the bicyclooctadiene/tetracyclooctane system (Figure 19). The transition state (TS) and tetracyclooctane feature a larger degree of staggering, compared to bicyclooctadiene, explaining the larger destabilization due to ring strain, which causes high storage densities.



**Figure 19.** Calculated structures of **a)** bicyclooctadiene **b)** the transition state and **c)** tetracyclooctane.

# Chapter 8

## Conclusion and Outlook

The overall aim of the work presented in this thesis was to develop and improve molecular photoswitches for molecular solar thermal energy storage applications. In the major part of the thesis, derivatives of the norbornadiene/quadracyclane system were investigated, where the first part focused on synthesis. A new synthetic route towards 2-bromo-3-chloronorbornadiene was developed. The yield of the overall reaction was 50%, which is in the same range as previous published procedures, but with the advantage that the carcinogenic brominating agent 1,2-dibromoethane could be avoided. The synthesis is also easy to scale up and can be performed in one day without isolating the intermediates. With 2-bromo-3-chloronorbornadiene in hand, a new series of donor/acceptor norbornadiene derivatives were synthesized through a cyanation step, followed by a Sonogashira or Suzuki cross-coupling reaction. Photophysical characterization revealed that norbornadiene derivatives with cyano acceptor groups and ethynyl-substituted aromatic donor groups (NBD1–NBD5) show a good solar spectrum match with absorption onsets of 374 to 456 nm and high energy storage densities between 114 and 121 kJ/mol. However, as the ethynyl-linker is introduced, the half-life and the quantum yield decreases, which becomes clear when comparing NBD1 and NBD5. The series of norbornadiene derivatives answered the first research question in this work “*Is it possible to improve the properties of norbornadiene by introducing new types of donor/acceptor substituents at the C2 and C3 positions?*” New donor/acceptor groups at the C2 and C3 positions can improve properties for MOST, but optimizing all parameters at once is a challenge.

In the second part of the thesis, the solvent effects on some derivatives of the norbornadiene/quadracyclane system were investigated. For NBD4, which has an unsymmetrical substitution pattern, the effect was large, and the half-life was almost doubled in going from a non-polar solvent (hexane) to a polar solvent (acetonitrile). The photoisomerization process was also affected and the quantum yields were higher in toluene than in acetonitrile. For the more symmetrically substituted norbornadiene derivatives, the effect was less pronounced. These findings shows that the local environment of the system

affects the properties and answers the second research question of this work “*Does the solvent affect the properties of derivatives of the norbornadiene/quadracyclane system?*”

The final part of this thesis involves a new type of photoswitch, based on the bicyclooctadiene scaffold. In the aim two research questions were asked “*Can bicyclooctadiene be substituted with donor/acceptor groups at C2 and C3 position?*” and “*Can bicyclooctadiene derivatives be evaluated as a MOST candidate and will they exhibit properties for MOST energy storage?*” In this work the questions were answered and a series of donor/acceptor bicyclooctadiene derivatives were synthesized and for the first time evaluated for MOST energy storage purposes. The photophysical characterization revealed half-lives of 6–276 s, absorption onsets of 228–350 nm and quantum yields of 14–19%. The system was able to switch for 645 cycles with almost no degradation. Derivatives of the bicyclooctadiene/tetracyclooctane system showed computationally very high energy storage densities of up to 151 kJ/mol, among one of the highest for all known photoswitches.

## 8.1 Contributions to the Field of MOST Energy Storage

The results from **Paper I** and **Paper II**, published in 2015 and 2016, have already contributed to the future development of MOST systems. The new synthetic procedures towards 2-bromo-3-chloronorbornadiene and 2,3-dibromonorbornadiene have been widely used in our group in the synthesis of new series of norbornadienes.<sup>18, 98</sup> Despite the fact that the Diels-Alder approach towards norbornadiene derivatives requires fewer steps than our method, it has a limited scope and obtaining the desired starting material can be troublesome. Therefore, our new strategy serves as a versatile alternative. The norbornadiene derivatives from **Paper II** inspired the design for future series of norbornadiene derivatives resulting in some of our top candidates with both good solar-spectrum match and long half-lives.<sup>72</sup> Thus, the work contributed to solving the issue of red-shifting the absorption spectra and retain long half-lives of the photoisomers. Also, NBD4 have been further used in a hybrid device combining solar and water heating and a three-input molecular keypad lock.<sup>46, 99</sup>

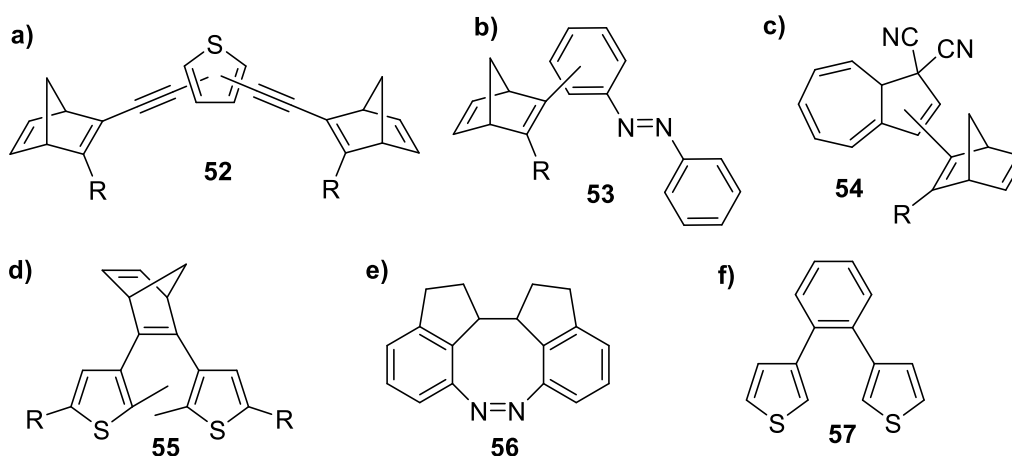
The solvent study in **Paper III** contributed with the knowledge that the local environment of the system is as important as engineering the molecule. Also, we have seen other examples where the heat-release causes a degradation due to polymerization in neat liquids that is not observed in dilute solutions of the same norbornadiene derivative, also showing the importance of the local environment.<sup>100</sup> The greatest contributions from **Paper II** are that solvents can affect both the quantum yields and the stability of the photoisomer. In many previous

publications, the quantum yields of the norbornadiene derivative to quadricyclane derivative formation are presented in a way that it is easy for the reader to believe it is an intrinsic property of the compound.

The results from **Paper IV**, the most recent paper presented in this thesis, showed that bicyclooctadiene derivatives substituted with donor/acceptor groups could be synthesized. A relatively small change in the bridge position (comparing norbornadiene and bicyclooctadiene) resulted in a large improvement of the storage density. Even though the obtained series of bicyclooctadiene derivatives will need further improvements for practical use in MOST energy storage systems, it is a great inspiration for future design. Synthesizing more bicyclooctadiene derivatives will be a future project in our research group.

## 8.2 Reflections on Future Development of Photoswitches for MOST Systems

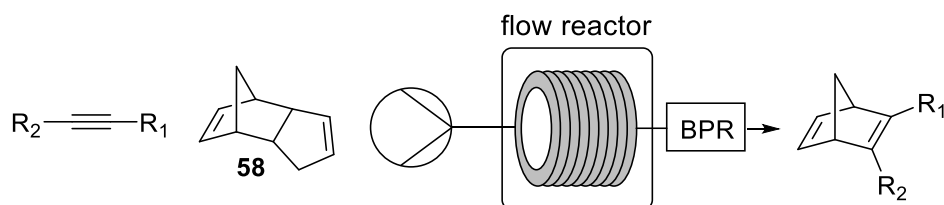
Regarding the design of photoswitches for MOST energy storage, there is still much more to explore and learn. In the norbornadiene system, other substituent patterns on other positions as well as on the bridge should be explored, to learn more about the structure/property relationship. Work on dimeric norbornadiene derivatives (**53**)<sup>98</sup> and norbornadiene derivatives combined with other photoswitches such as azobenzene derivatives (**54**)<sup>101</sup> or dihydroazulene derivatives (**55**)<sup>102</sup> and norbornadiene-bridged diarylethenes derivatives (**56**),<sup>103</sup> have also been explored recently. Regarding other photoswitches, ongoing research on diindane diazocine derivatives (**57**)<sup>104, 105</sup> and dithenylbenzene derivatives (**58**)<sup>106</sup> have shown promising results for MOST energy storage purposes (Figure 20).



**Figure 20.** a) Dimeric norbornadiene derivatives, norbornadiene derivatives combined with b) azobenzene derivative and c) dihydroazulene derivatives, d) norbornadiene-bridged diarylethenes derivatives, e) diindane diazocine derivatives, and f) dithenylbenzene derivatives

Furthermore, combining MOST with different techniques such as phase-change materials,<sup>107, 108</sup> photon-upconversion,<sup>109, 110</sup> and water heating<sup>99</sup> are some examples of ongoing research in the field.

Finally, one area that cannot be forgotten and must be explored further as the next step towards a future MOST system is the scalability of the synthesis. In our group, a method using flow chemistry for scaling up the synthesis of norbornadiene derivatives in a research lab environment has been developed.<sup>111</sup> This method allows us to produce several grams of norbornadiene derivatives within a few hours. However, for a MOST system to be integrated in society, the synthesis should efficiently produce kilograms of material and be environmentally friendly with non-toxic starting materials that are not too expensive.



**Scheme 15.** Diels-Alder reaction with *in situ* cracking of dicyclopentadiene (59) to synthesize norbornadiene derivatives in large scale using a flow reactor.<sup>111</sup>



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