Universität Regensburg

PHOTOCATALYTIC SINGLE-ELECTRON TRANSFER REACTIONS: THE PHOTO-MEERWEIN ARYLATION

Dissertation

zur Erlangung des Doktorgrades der Naturwissenschaften

(Dr. rer. nat.)

an der Fakultät für Chemie und Pharmazie

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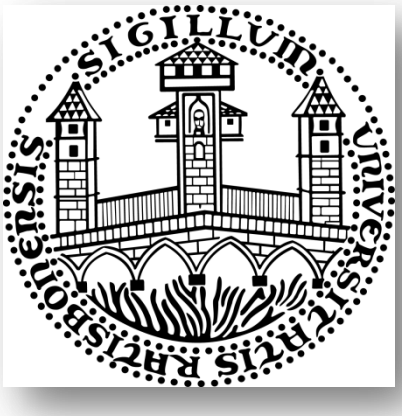

vorgelegt von

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„Das Staunen ist der Anfang der Erkenntnis."

Platon

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Meiner lieben Sophie

TABLE OF CONTENTS

1 EARLY PIONEERS OF ORGANIC PHOTOCHEMISTRY

A summary of the beginnings of organic photochemistry from a synthetic point of view is presented. Accidentally discovered reactions driven by light as well as systematic studies on the behavior of light towards matter leading to the development of a new branch of chemistry are discussed. A shortened version of the text has been published in the textbook "Chemical Photocatalysis":

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1.1 Prologue

"When oil will have been all burned in our prodigal industries, it may become necessary, even on social grounds, to come to exploit solar energy."[1] This foresightful statement fits perfectly into modern debates at the beginning of the twenty-first century about the necessity of using renewable energies and sustainable chemistry, but is in fact more than one hundred years old, written by Giacomo Ciamician, an early pioneer of organic photochemistry. He was a visionary chemist who was invaluable in developing photochemistry, an upcoming science at the beginning of the twentieth century. Apart from his credits to discover several new photochemical reactions, he was the first to establish a systematic study on the behavior of light towards matter. He realized nature as being the role model in terms of the conversion of sunlight into chemical energy and stood up for the use of synthetic methods as mild as those nature uses. In this respect, Ciamician can be considered as the inventor of the concept of green chemistry. He was also interested in using photochemical processes on an industrial scale since he realized fossil fuels as not being inexhaustible.[2]

Although the development of synthetic methods using light-energy has attracted much attention during the last decade, chemical transformations under the influence of light are known for more than 200 years. In 1790, **Joseph Priestley (1733 – 1800)** exposed partially filled vials of "spirit of nitre" (nitric acid) to sunlight and observed a reddish color, which was attributed to the formation of nitrogen dioxide (Figure 1). This first photochemical reaction in the gas phase marks the beginning of photochemistry.[3] Moreover, Priestley is given credit for discovering basic principles of photosynthesis, the most important photochemical process for living organisms on earth based on the transformation of light energy into chemical energy. He *"fully ascertained the influence of light in the production of dephlogisticated air* (oxygen) *in water by means of a green substance,"* which was identified as tiny plants.[3, 4] After **Nicholas Theodore de Saussure (1767 – 1845)** had shown in 1804 that the influence of light causes plants to consume water and carbon dioxide and to generate oxygen, a fundamental understanding of the process of photosynthesis in green plants had been discovered.[3, 5]

Figure 1: Joseph Priestley, English philosopher, chemist, and physicist.[a]

1.2 From Photochemistry of Halogens to Photography

Halogens played an important role in early photochemical experiments. The English chemist **Sir Humphry Davy (1778 – 1829)** used sunlight to produce phosgene out of a mixture of chlorine and carbon dioxide in 1812.[6] **Michael Faraday (1791 – 1867)**, an assistant to Humphry Davy, continued studies on the behavior of chlorine towards light and found in 1821 that sunlight promoted the addition of chlorine to ethylene to form 1,2-dichloroethane and the addition to benzene to give 1,2,3,4,5,6-hexachlorocyclohexane.[7, 8] **John W. Draper (1811 – 1882)**, the first President of the American Chemical Society, reported the formation of "*pure hydrochloric acid gas*" after a violent reaction between hydrogen and chlorine initiated by a beam of sunlight. [8, 9] During his studies of halogens and their salts Humphry Davy discovered the light sensitivity of silver iodide, which created the chemical basis for the process of photography.

An appropriate technique to make photography manageable was developed by the French painter **Louis Daguerre (1787 – 1851)**. He used silver iodide coated plates made from a silver plated piece of copper which had been fumed with iodine

[a] H. D. Roth, The Beginnings of Organic Photochemistry. *Angew. Chem. Int. Ed.* **1989**, *28*, 1193-1207. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

vapor. Light was focused on these plates by a *camera obscura*. The breakthrough came with the observation that the image could be brought to permanent visibility by chemical means. Treatment of the latent image with mercury fumes followed by removal of access silver iodide with sodium chloride or sodium thiosulphate solution as a fixer shortened exposure times from hours to minutes.[10, 11] The invention was announced to the French Academy of Sciences by the physicist **François Arago (1786 – 1853)**.[12] The year 1839 is considered as the birth of chemical photography. For decades, photography was the most important application of photochemical processes.

1.3 Single Discoveries in Photochemistry

The following years were characterized by accidental discoveries of photochemical reactions. Several researchers contributed to the new field of photochemistry by discovering single reactions. Among the first reaction types were reductions, cycloadditions and photodimerizations, homolytic cleavage of molecules, geometric isomerizations, light-induced halogenations, and photoreductions of carbonyl compounds.

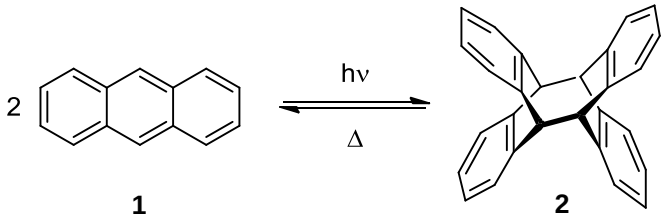
Reduction

As early as 1831, **Johann Wolfgang Döbereiner (1780 – 1849)** reported the light-induced reduction of metal ions by oxalic acid.[3, 13] In the case of an aqueous solution of oxalic acid and iron(III) oxide irradiated by sunlight, he obtained carbon dioxide and humboldtite, a basic iron(II) oxide. Similarly, he reduced salts of platinum, silver and iridium. In each case, the result was checked by control experiments in the dark. Unfortunately, he was not able to report the first photoreaction of a ruthenium compound, whose complexes today serve as powerful photocatalysts, since ruthenium was discovered thirteen years later in 1844.

Cycloaddition

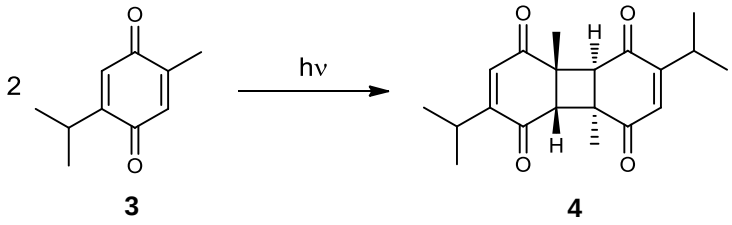
Carl Julius Fritzsche (1808 – 1871) observed the light sensitivity of anthracene in 1867: *"When a cold, saturated solution* [of anthracene] *is exposed to*

sunlight, microscopic crystals begin to precipitate."[3, 14] Control experiments in the dark proved that indeed a light reaction occurred and that the original material could be regenerated by heating the photoproduct to the melting point (Scheme 1). However, it took another twenty-five years to recognize the photoproduct **2**, being the dimer of anthracene **1**, as a result of a [4+4]-cycloaddition.[15] In this case, the photoreaction was discovered due to the fact that the photoproduct was less soluble than the starting material.



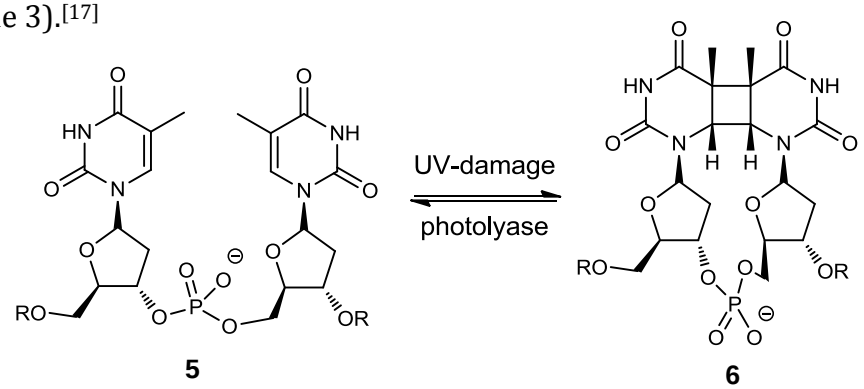
Scheme 1: Anthracene dimerization as a result of photochemical [4+4]–cycloaddition.

In 1877, **Carl Theodor Liebermann (1842 – 1914)**, a German chemist working in Berlin and known for the synthesis of the dye alizarine, observed the conversion of yellow crystals of thymoquinone **3** (2-isopropyl-5-methylbenzo-quinone) into a white, hardly soluble photoproduct **4** in sunlight within four days (Figure 2).[16] This was the first example of a [2+2]-cycloaddition of a quinone and an important step in solid-state photochemistry (Scheme 2).



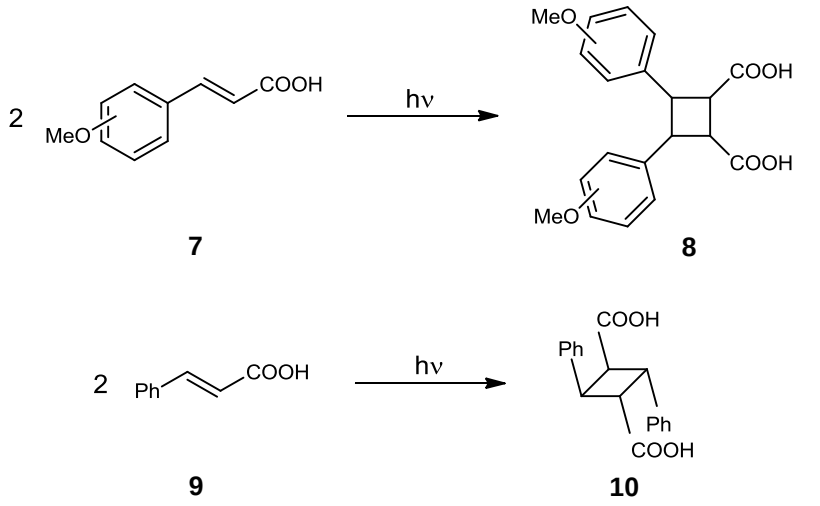
Scheme 2: The first photochemical [2+2]–cycloaddition.

Photochemical [2+2]-cycloaddition is an important but undesired reaction in living organisms. Light-induced photodimerization of thymine causes DNA damage. Fortunately, the enzyme photolyase is able to regenerate both DNA bases (Scheme 3).[17]



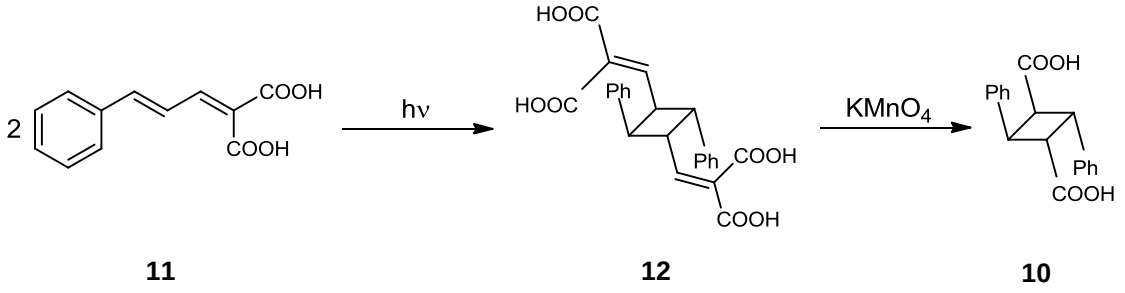
Scheme 3: Photochemical DNA damage: thymine dimerization caused by UV light.

Although Liebermann dealt also with photodimerization of olefinic compounds, credit for the discovery of the first photodimerization of a styrene derivative in 1895 has to be given to **J. Bertram** and **R. Kürsten**, two chemists working in industry. They were the first to report a light-induced reaction of β-methyl-coumaric acid crystals **7** which was found to rearrange after 14 days of irradiation with sunlight to form a white powder. Analysis yielded the photoproduct being the dimer of β-methylcoumaric acid. Moreover, the structure of the product was predicted correctly since the researchers noticed the disappearance of the double bonds and a four-membered cyclobutane ring being formed. Analogously, a photo-dimerization of cinnamic acid **9** to α-truxillic acid **10** was studied (Scheme 4).[18]



Scheme 4: The first reported photochemical dimerization of a styrene derivative.

From these extensive studies, their conclusions were more precise and deeper in understanding than the almost simultaneous examinations of Liebermann on the photodimerization of styrene derivatives and diolefin dicarboxylic acids such as cinnamylidenemalonic acid **11**, whose structure had not been clarified until 1902 at Liebermann's instance (Scheme 5).[19-21]



Scheme 5: Photodimerization of cinnamylidenemalonic acid.

It is worth mentioning that Liebermann was the first to test artificial light sources since early photochemists used sunlight as the only and most important source of radiation at that time. He found his photoreactions also took place by using an electric arc lamp or candlelight instead of sunlight.[20]

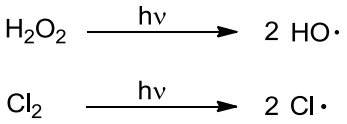
Figure 2: Carl Theodor Liebermann, a pioneer of solid-state photochemistry.[b]

Homolytic Cleavage

In 1877, the same year when Liebermann reported the dimerization of thymoquinone, the American scientists **Sir Arthur H. Downes (1851 – 1938)** and **Thomas P. Blunt (1842 – 1929)** recognized the effect of light upon organisms.[22] It could be shown that parts of the sunlight are able to kill bacteria. Their ongoing research on therapeutic application of sunlight resulted in the 1903's Nobel Prize in Physiology and Medicine *"for the treatment of diseases … by means of concentrated light rays"* that was awarded to Niels Finsen.[8] Two years later, in 1879, Downes and Blunt published a paper in Nature entitled "the effect of sunlight upon hydrogen peroxide".[23] Its topic was profound: for the first time, photochemical free-radical formation was proposed. On the basis of their observation that hydrogen peroxide in solution is completely destroyed after ten months of irradiation, they concluded a homolytic bond cleavage of H_2O_2 into two hydroxyl radicals. Similarly, a cleavage of the chlorine molecule into the free radicals was

[b] H. D. Roth, The Beginnings of Organic Photochemistry. *Angew. Chem. Int. Ed.* **1989**, *28*, 1193-1207. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

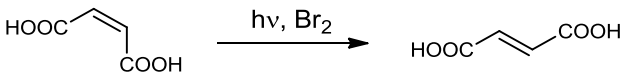
proposed (Scheme 6). The modernity of their description is remarkable since the concept of electron pair bonds was introduced several decades later. Moreover, the existence of free radicals had not been shown by Moses Gomberg until the year 1900. Although the discovery made by Downes and Blunt had been published in a major journal, it had not found great attention and was rediscovered only very recently after it had been overlooked for more than 130 years.[8]



Scheme 6: Photochemical radical formation by homolytic cleavage of hydrogen peroxide and chlorine.

Geometric Isomerization

Cis-trans isomerization is one of the most common photochemical reactions. The first geometric isomerization of olefins was reported by **William Henry Perkin (1838 – 1907)** in 1881 (Figure 3). He irradiated 2-alkoxycinnamic acid and obtained the *"β-isomer."*[24] Later, Liebermann found out that iodine accelerates the photochemical *cis-trans* isomerization of aromatic unsaturated acids such as δ-phenylpentadienoic acid.[20] **Johannes Wislicenus (1835 – 1902)** was able to extend the method to nonaromatic systems. Amongst others, when he irradiated maleic acid **13** in an aqueous solution of bromine, fumaric acid **14** was obtained (Scheme 7).[3, 25] It is no surprise that in these early days the biochemical relevance of this kind of reaction could not have been evaluated. But as we know today, the discovery of geometric isomerization is of high importance in the process of vision of vertebrates. The basic photochemical process herein is the isomerization of 11-*cis*-retinal to its all-*trans*-form. Retinal is a powerful absorber and a prosthetic group of the photoreceptor molecule rhodopsin.[26]



13 **14**

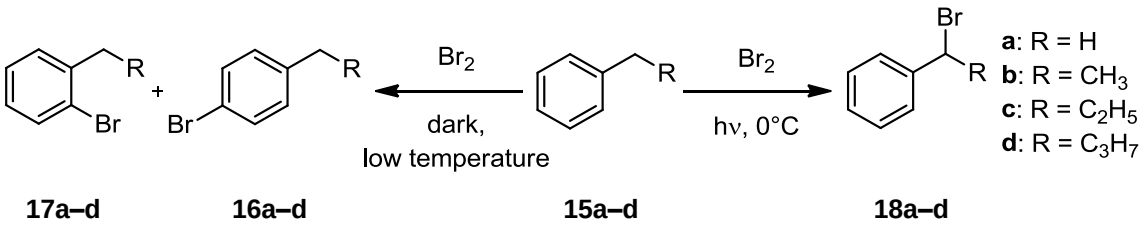
Scheme 7: Geometric isomerization of maleic to fumaric acid upon irradiation.

Figure 3: William Henry Perkin. He examined the first light-induced geometric isomerizations.[c]

Light-Induced Halogenation

Halogens played an important role in **Julian Schramm's (1852 – 1926)** photochemical experiments in Lemberg as well. Between 1884 and 1888 he studied the light-induced bromination of alkylbenzenes **15** and found out *"that light and darkness work in the same way as elevated and low temperatures, respectively."*[27] At that time it was known that the selectivity of a halogenation reaction is temperature-dependent: at low temperatures, the aromatic ring is halogenated while at elevated temperatures a substitution reaction occurs at the alkyl side chain. The new aspect of his work was the finding that the halogenation reaction can be carried out with light and that the selectivity can be controlled using light or darkness: irradiation with sunlight or magnesium light led to products substituted in the side chain whereas reactions in the dark gave products substituted at the aromatic ring (Scheme 8).[28-32] Moreover, Schramm was the first to realize the potential of this type of reaction for industrial application.[30] Today, photochlorination is an important tool in industrial synthesis.

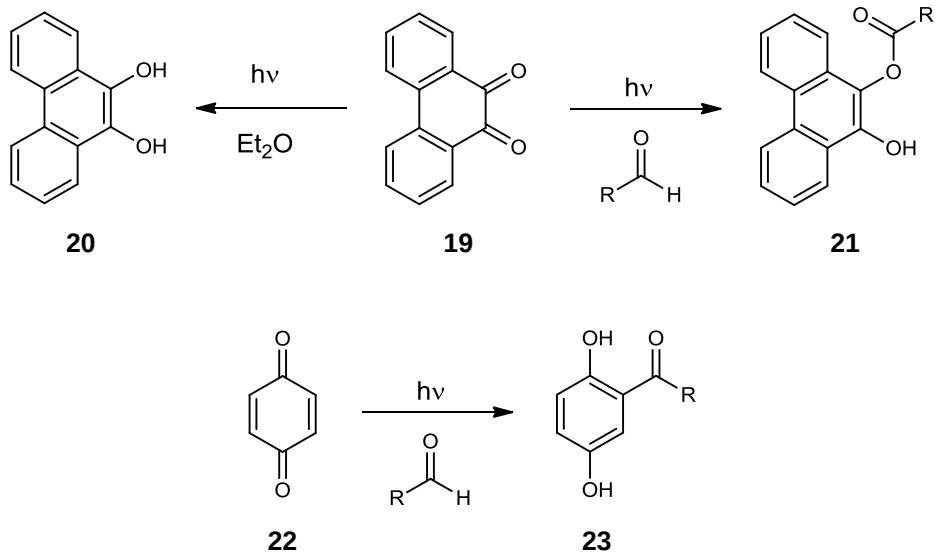
[c] H. D. Roth, The Beginnings of Organic Photochemistry. *Angew. Chem. Int. Ed.* **1989**, *28*, 1193-1207. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.



Scheme 8: Selectivity of alkylbenzene halogenation under different conditions.

Photoreduction of Carbonyl Compounds

An impressive example of an accidental discovery of a new reaction is given by **Heinrich Klinger (1853 – 1945)**. During his attempts to convert benzil to isobenzil in an aqueous solution of ether, he observed the unexpected formation of crystals. A close examination showed that the outcome of the reaction was not reproducible. Looking for the unknown parameter, he realized that *"some of the tubes were exposed to sunlight in the morning hours."* The crystals were identified as a molecular complex of benzil and benzoin. Hence, in 1886, Klinger had observed the first light-mediated reduction of a keto group to the corresponding alcohol. Analogously, phenanthrenequinone **19** could be reduced to phenanthrene-hydroquinone **20** (Scheme 9).[33] A subsequent study of different ketones led to interesting results. Especially when ether as the solvent was replaced by various aldehydes, the outcome of the photoreaction was different. Under the influence of light, the ketone and the aldehyde formed a new photoproduct. In case of phenanthrenequinone, the ketone underwent reduction followed by esterification of the oxidized aldehyde to give **21**.[34] *para*-Benzoquinone was also reduced under these conditions, but behaved differently. A new carbon-carbon bond was formed instead of an ester (Scheme 9).[35] The intermolecular photoreaction of *para*-benzo-quinone **22** with benzaldehyde, for example, resulted in the formation of the new photoproduct 2,5-dihydroxybenzophenone **23** (R = phenyl).[36] Klinger called these reactions *"synthesis by sunlight"* and observed a *"synthetic effect of light"* which he compared to photosynthesis in living plants.[34, 37] By means of colored filter solutions, he found out that his photoreactions worked best in blue light whereas photosynthesis was most efficient using red light. Moreover, he performed his reactions in special glassware such as tubes and capillaries for ideal irradiation conditions. Heinrich Klinger is considered to be the first to use photoreactions for synthetic purposes.[3]



Scheme 9: Photoreduction of ketones.

1.4 Photochemistry of Santonin

The longest known photoreaction of an organic compound is the rearrangement of santonin **24**, a sesquiterpene that was formerly used as an anthelmintic drug, but is today replaced by less toxic agents.[3] In 1834, **Hermann Trommsdorff (1811 – 1884)**, a pharmacist in Erfurt (Germany), observed a color change of santonin crystals from white to yellow followed by crystal burst after exposure to sunlight.[38] In addition, he examined the wavelength dependency of the reaction by means of a prism. He found out that the yellow color of the crystals appeared after irradiation with direct sunlight as well as with violet and blue rays, but not with green, yellow or red beams. Looking back, this was a remarkable result for the first half of the nineteenth century, since not much was known about the nature of light at that time.

The understanding of photophysical effects was poorly developed. But a very important physical principle had been found by the German chemist **Theodor von Grotthuß (1785 – 1822)** in 1817 and, some years later in 1842, independently from this work, by the aforementioned American **John W. Draper**. It says that light must be absorbed by a substance in order for a photochemical reaction to take place. Today, their observation is known as the Grotthuß-Draper law or the first law of photochemistry.[39]

Further investigations by Trommsdorff led to the result that santonin and its photoproduct were isomers. However, both structures could not be determined exactly with the analytical methods of these days. The problem remained unsolved. Several years later, **Fausto Alessandro Sestini (1839 – 1904)**, an Italian chemist working in Rome, was faced with the problem of santonin and its photoreaction (Figure 4). Sestini was the first among a series of excellent Italian photochemists, often considered to be the founder of photochemistry in Italy, whose development was closely related with the photoreaction of santonin. Italy, as it turned out, would become a center of research for photochemical reactions. In contrast to Trommsdorff's experiments in the solid state, Sestini examined the photoreaction of santonin, $C_{15}H_{18}O_3$, in solution.[40-42] He obtained "photosantonin", a diethyl ester. Irradiation in acetic acid yielded photosantonic acid **28**, $C_{15}H_{20}O_4$, as the final product.

Figure 4: Fausto Alessandro Sestini, the originator of photochemistry in Italy. [d]

Through Sestini, **Stanislao Cannizzaro (1826 – 1910)** became introduced to photochemistry (Figure 5).[43, 44] Cannizzaro and co-workers discovered an additional intermediate of the reaction which they called isophotosantonic acid and whose structure had been determined to be $C_{15}H_{22}O_5$.[45-49] In summary, Sestini and Cannizzaro discovered basic structural elements of santonin and its

[d] H. D. Roth, The Beginnings of Organic Photochemistry. *Angew. Chem. Int. Ed.* **1989**, *28*, 1193-1207. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

photoproduct such as the lactone and the acid moiety. But it was only in the middle of the 20th century when the structure of santonin, its intermediates and the mechanism of its formation had been elucidated.[50-55] In all, from its first description to the final solution, it took 130 years for the problem of the santonin photorearrangement to be solved.

Figure 5: Stanislao Cannizzaro. He introduced Ciamician and Silber to photochemistry. [e]

Today we know that santonin **24** and photosantonic acid **28** have different crystal structures, which offer an explanation for Trommsdorff's observation that sunlight causes crystals of santonin to burst. The pathway for the rearrangement is the following: from its excited state, parts of the santonin molecule undergo ring-contraction from a six-membered to a five-membered ring to form lumisantonin **25**. Lumisantonin is not stable and forms another six-membered ring out of a five- and a three-membered ring. The resulting structure **26** undergoes ring-opening to form a ketene **27** which yields the final product after water addition. Photosantonic acid **28** is thus the irradiation-hydration product (Scheme 10).[51, 53, 54]

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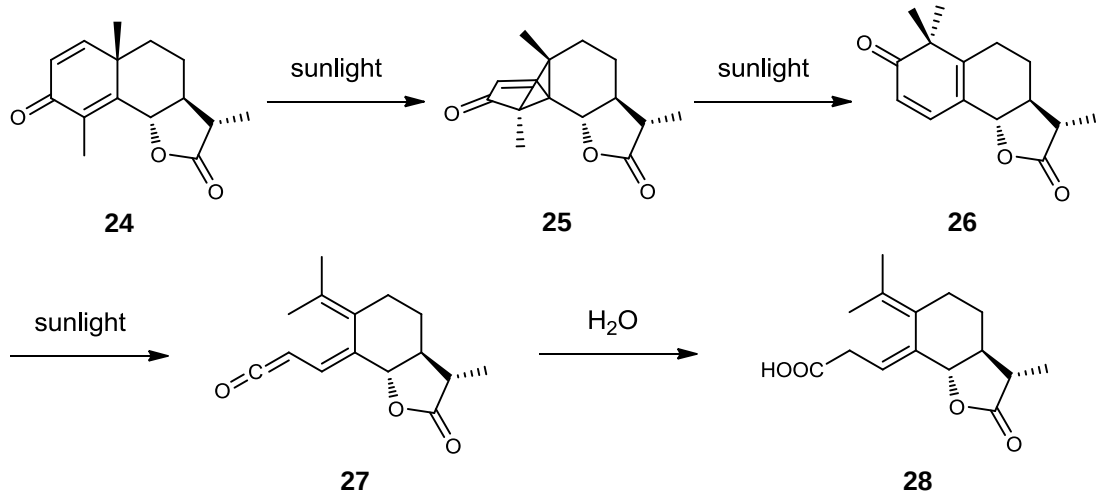
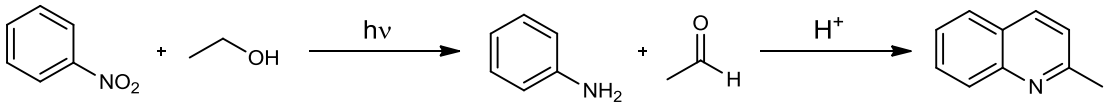


Scheme 10: Photorearrangement of santonin to photosantonic acid.

In his laboratory in Rome, Cannizzaro introduced Giacomo Ciamician, Paul Silber and Emanuele Paternò to photochemistry, all becoming researchers who had great influence in the development of this new branch of chemistry.[49] **Giacomo Ciamician (1857 – 1922)** was an Italian chemist of Armenian descent who joined the Cannizzaro group in 1881 where he, too, was faced with the problem of the santonin reaction (Figure 6). In summer 1885, he started the first photochemical examinations.[56] Soon the German **Paul Silber (1851 – 1932)** joined his projects and became his co-worker for the next 30 years, until World War I ended their partnership.[57] The skills of both researchers, with *"Ciamician as the genial and critical research director"* and *"Silber as the skilled and patient experimenter"*, being able to isolate and identify even labile photoproducts, made this collaboration *"a profitable partnership"*.[58]

Figure 6: Giacomo Ciamician (left) and Paul Silber (right). Their work surpassed any previous effort in photochemistry.[f]

They discovered the photoreduction of nitrobenzene **29** to aniline **31** and 2-methylquinoline **33** in an alcoholic solution after five months of solar irradiation and found out that a solution of *para*-benzoquinone in ethanol is converted to the corresponding hydroquinone and acetaldehyde (Scheme 11).[56, 57] Although the work had been carried out independently from Klinger's photoreduction of ketones in Bonn (Germany), the latter was several months faster in publishing his results and claimed this field for his own research, which was possible in the nineteenth century. Thus, Ciamician's and Silber's first excursion in the field of organic photochemistry had come to a sudden end. They did not continue their work in photochemistry for the next 14 years.



29 **30** **31** **32** **33**

Scheme 11: Photoreduction of nitrobenzene to aniline. The oxidation product, acetaldehyde, undergoes condensation with the reduction product, aniline, to form 2-methylquinoline under acidic conditions during the work-up process.

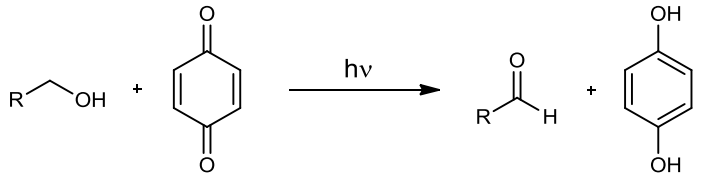
[f] Reprinted with permission from: N. D. Heindel, M. A. Pfau, A profitable partnership: Giacomo Ciamician and Paul Silber. *J. Chem. Educ.* **1965**, *42*, 383. Copyright 1965 American Chemical Society.

1.5 Ciamician – A Systematic Study

Restarting in 1900, Ciamician and Silber conducted the first systematic study of the behavior of organic compounds toward light.[58] This was the most complete study of the effect of light on chemical reactions at that time. The variety of photochemical reactions reported by Ciamician and Silber had been published in a series of 34 papers called "Chemische Lichtwirkungen" (chemical actions of light) between 1900 and 1915.[59-92] The reactions can be divided into several groups according to their mechanism: intermolecular hydrogen abstraction by excited carbonyls, hydrogen abstraction by nitro compounds, fragmentations, polymerizations and condensations, autooxidations, and rearrangements.[93, 94]

Hydrogen Abstraction by Excited Carbonyls

The first and largest group of reactions deals with oxidation and reduction reactions as a result of hydrogen transfer initiated by excited carbonyls. Ciamician's earliest photochemical experiment, the photochemistry of quinone and alcohol, is a light-mediated redox reaction. In its most general form, an alcohol **34** reacts with *para*-benzoquinone **35** to give an aldehyde **36** as the oxidation product and hydroquinone **37** as the reduction product under irradiation with sunlight (Scheme 12).

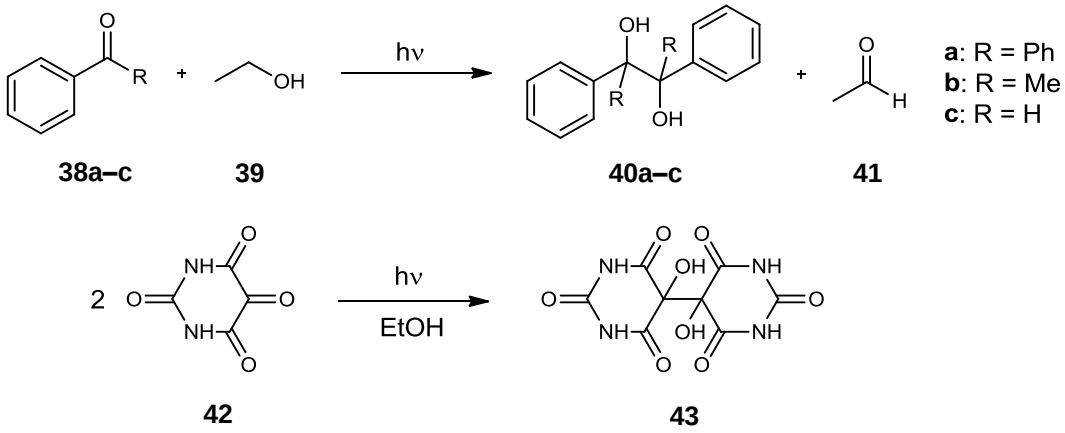


34 **35** **36** **37**

Scheme 12: Light-mediated redox reaction of carbonyls in alcoholic solution.

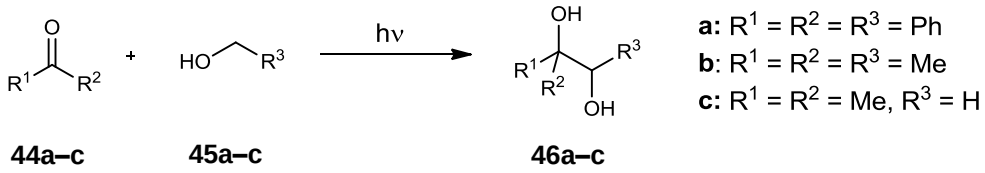
The reaction is of synthetic value in both directions. As far as the oxidative side is concerned, a mild and selective oxidation of primary alcohols to aldehydes was found. Ethanol was found to be oxidized to acetaldehyde and benzylalcohol to benzaldehyde, for example. Secondary alcohols were oxidized to ketones, e. g. isopropanol to acetone or glucose to glucosone, the oxidation product of the 2'-hydroxy group of glucose giving the corresponding ketone. Furthermore, polyalcohols were oxidized to sugars, as demonstrated by the reactions of glycerol to glyceraldehyde, erythrol to erythrose, and mannitol to mannose.

Taking the reducing side, benzoquinone was transformed to hydroquinone. The reduction was also successful for a range of other carbonyls. Benzo- and acetophenone **38a** and **38b**, respectively, were found to undergo photopinacolization, since aromatic ketones underwent clean bimolecular reduction to pinacols **40a** and **40b** in the presence of an alcohol as a reducing agent. Benzaldehyde **38c** and its derivatives gave hydrobenzoins **40c** and alloxane **42** was converted to alloxantin **43** in a reductive dimerization reaction after two months of irradiation (Scheme 13). These reactions were of preparative interest.



Scheme 13: Photopinacolization of carbonyls.

In a similar way, the reaction was used for the light-driven reductive alkylation of ketones. The reaction worked well with aliphatic ketones and alcohols but was particularly efficient when aromatic ketones or alcohols were used. Benzophenone **44a** in the presence of benzylalcohol **45a**, for example, gave the alkylated product triphenylethylene glycol **46a** (Scheme 14).

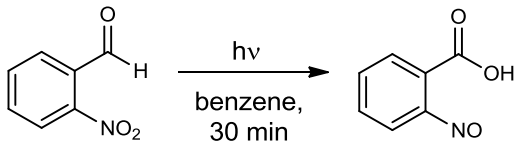


Scheme 14: Light-induced reductive alkylation of ketones.

Hydrogen Abstraction by Excited Nitro Compounds

Another group of photooxidants for both inter- and intramolecular reactions is the nitroaromatics. They were found to be reduced to the corresponding anilines upon irradiation in alcohols (see Scheme 11 above). In a detailed study it was shown that the reaction proceeds stepwise through the formation of nitroso and hydroxylamine intermediates. Of particular importance was the fast intra-

molecular reaction of *ortho*-nitrobenzaldehyde **47** to *ortho*-nitrosobenzoic acid **48** (Scheme 15). A few minutes of irradiation were sufficient to get complete conversion whereas most other conversions typically were in the time scale of months or even years. Nowadays, intramolecular hydrogen abstraction by a nitro group is widely used in terms of the *ortho*-nitrobenzyl moiety as a photoremovable protecting group.



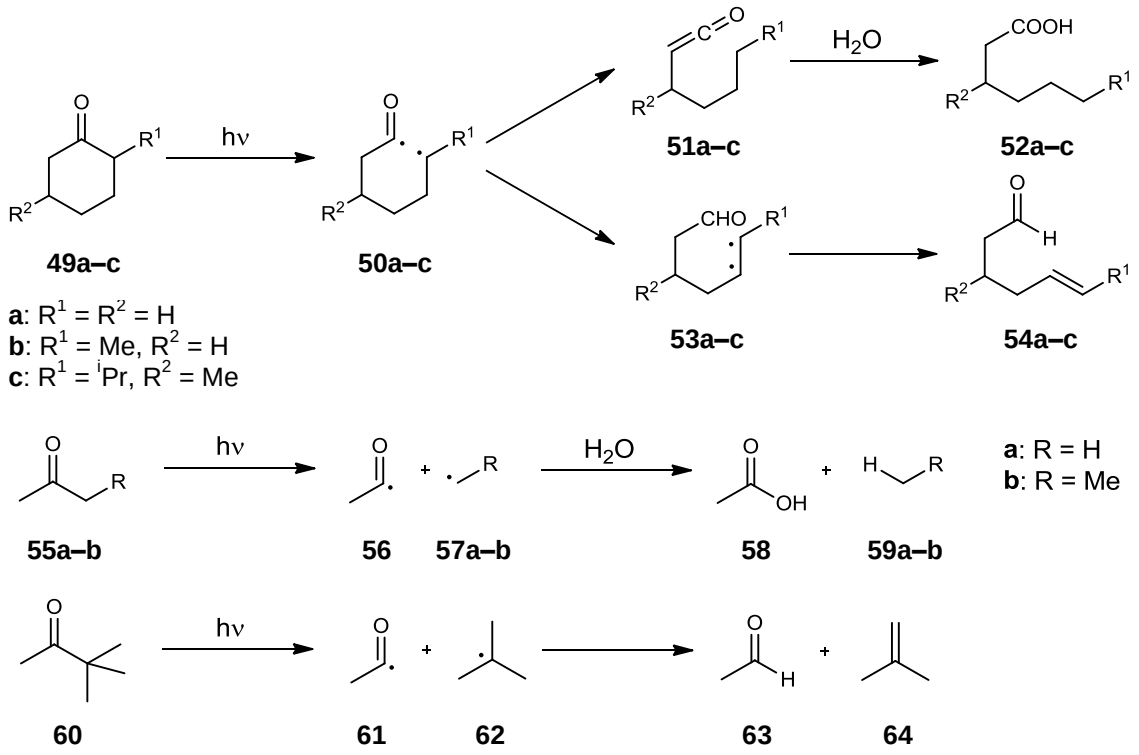
47 **48**

Scheme 15: Intramolecular hydrogen abstraction by nitro compounds.

Fragmentations

Ciamician and Silber also used sunlight for bond-cleavage. Again, carbonyl compounds had been found to be active towards this reaction pathway. In aqueous solutions of cyclic ketones, the carbon-carbon bond adjacent to the carbonyl group was cleaved leading to two different products: open-chain saturated acids and unsaturated aldehydes. For example, the cleavage of cyclohexanone **49a** yielded hexanoic acid **52a** and ω-hexenal **54a**. This reaction was noticed to be an appropriate process for the synthesis of fatty acids out of cyclic ketones. In the reaction of 2-methylcyclohexanone **49b** or menthone **49c**, the regioselectivity of the cleavage could be clearly determined: the higher substituted carbon-carbon bond adjacent to the carbonyl group was found to break (Scheme 16).

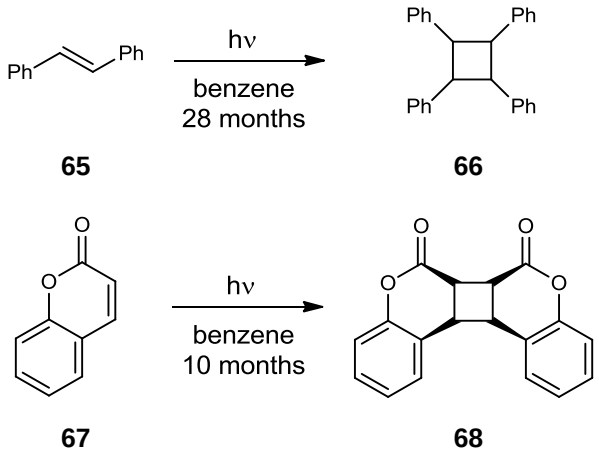
α-Cleavage was also found to occur in aliphatic ketones. Irradiation of an aqueous solution of acetone **55a** gave acetic acid **58** and methane **59a** – a formal hydrolysis of the carbon-carbon bond. α-Cleavage is today known as the Norrish Type I reaction. The name was established after detailed examinations in the gas phase by the English chemist **Ronald George Wreyford Norrish (1897 – 1978)** in the 1930s.[55, 95-98] With pinacolin **60** (3,3-dimethylbutan-2-one), acetic aldehyde **63** and isobutylene **64** was obtained. The latter product was the result of a Norrish Type II reaction, as it was called later (Scheme 16). The identification of all products must be attributed to the extraordinary experimental skills of the scientists since it was very difficult to characterize aliphatic aldehydes at that time.



Scheme 16: α-Cleavage of carbonyls: Norrish Type I and II reaction.

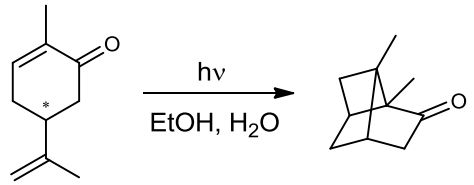
Polymerizations and Condensations

Reactions forming new bonds were summarized as *"polymerization and condensation reactions"*. The term polymerization included the formation of dimers as it is the case in [2+2]-cycloaddition reactions of unsaturated compounds. Additional substrates undergoing this kind of transformation have been reported by Ciamician and Silber in reactions demanding skill and patience. The dimerization of stilbene **65** in solution was reported after two years and four months of irradiation. A coumarin dimer **68** was found whose *syn* head-to head structure was finally proven in 1962 (Scheme 17).[99]



Scheme 17: Intermolecular [2+2]-cycloaddition reactions in solution.

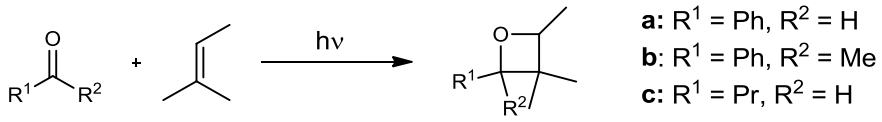
Besides intermolecular [2+2]-cycloadditions, the first intramolecular reaction was found in case of the monoterpene ketone carvone **69**, which gave an isomeric product in a clean reaction, whose structure could not be determined exactly by Ciamician and Silber. They proposed the tricyclic product carvonecamphor **70** to be formed. The proposal was found to be correct in 1957 (Scheme 18).[100]



69 **70**

Scheme 18: Intramolecular [2+2]-cycloaddition of carvone to carvonecamphor.

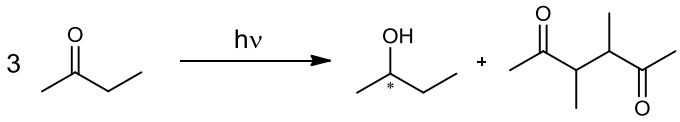
A similar reaction including the [2+2]-cycloaddition of an olefin and a carbonyl group giving oxetanes **73** was discovered by another important Italian pioneer of photochemistry, **Emanuele Paternò (1847 – 1935)**, in Rome in 1909.[101] The reaction was improved in 1954 by the Swiss-American chemist **George Hermann Büchi (1921 – 1998)** and is today known as the Paternò–Büchi reaction (Scheme 19).[102]



71a–c **72** **73a–c**

Scheme 19: Paternò-Büchi reaction : [2+2]-cycloaddition of carbonyls and olefins.

Another reaction of synthetic importance was discovered irradiating 2-butanone **74**. Beside the reduction product 2-butanol **75**, an interesting condensation product as a result of oxidative dimerization was identified: 3,4-dimethylhexane-2,5-dione **76**. This 1,4-diketone could be used for the synthesis of pyrrol derivatives (Scheme 20).

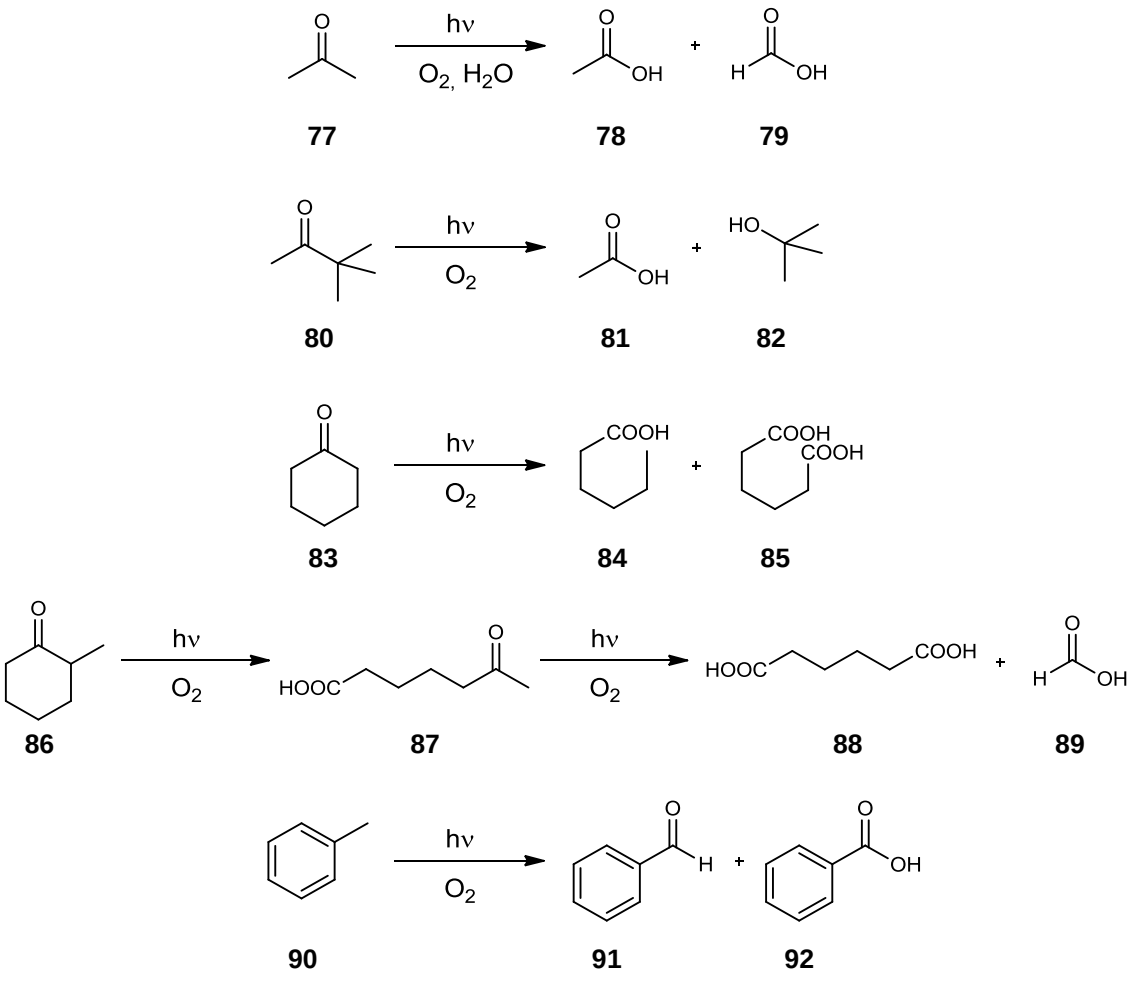


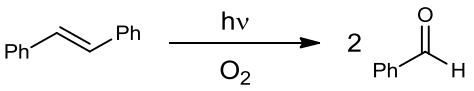
74 **75** **76**

Scheme 20: Radical dimerization of methylethylketone.

Autooxidations

In addition to oxidation reactions caused by irradiation of carbonyls, a variety of light-induced oxidations involving molecular oxygen have been treated. In some cases, different products were found in presence or absence of molecular oxygen. In the above-mentioned α-cleavage of acetone, formic acid **79** was found instead of methane when oxygen was present in the reaction vessel. Highly substituted aliphatic ketones gave tertiary alcohols **82**. Cyclic ketones were oxidatively cleaved giving carboxylic and dicarboxylic acids **84** and **85** under aerobic conditions. 2-Substituted cyclic ketones yielded ketoacids **87** who themselves underwent a second cleavage, resulting in the corresponding carboxylic acids **88** and **89**. Alkylated aromatic compounds such as toluene were oxidized to benzaldehyde **91** and benzoic acid **92** whereas in the absence of oxygen the dimer 1,2-diphenyl-ethane was obtained. Finally, stilbene **93** was converted to benzaldehyde in the presence of light and oxygen. The mechanism was explained by addition of an activated oxygen molecule to the double bond of stilbene forming a dioxetane intermediate followed by cleavage of the four-membered ring (Scheme 21).



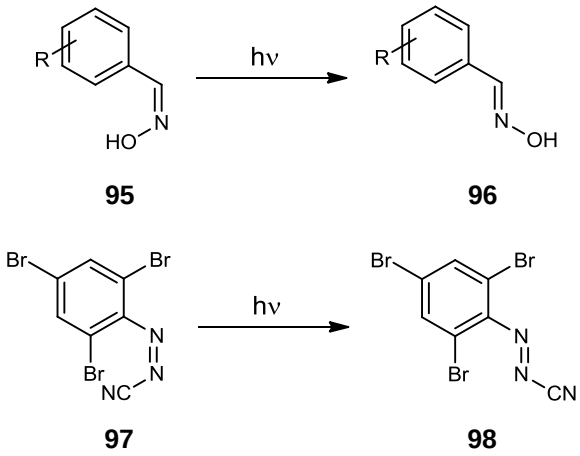


93 **94**

Scheme 21: Autooxidation reactions.

Rearrangements

Finally, unsaturated compounds were studied in consideration of their behavior towards light. Geometric isomerization was known to occur in olefins. Additionally, Ciamician and Silber studied similar isomerizations of carbon-nitrogen- and nitrogen-nitrogen double bonds such as the *syn-anti* isomerization of oximes **95** and the isomerization of cyanoazo derivatives **97** (Scheme 22).[94]



95 **96**

97 **98**

Scheme 22: *Syn-anti* isomerization of oximes and cyanoazo derivatives.

The synthetic progress of light-driven reactions was still accompanied by a lack of mechanistic understanding. Ciamician tried to give his work an interdisciplinary character by combining aspects of theoretical chemistry, physical chemistry, and biology. However, physics made great progress at the beginning of the twentieth century. **Johannes Stark (1874 – 1957)** and **Albert Einstein (1879 – 1955)** formulated the second law of photochemistry between 1908 and 1913, which is also known as quantum equivalence law.[55] It says that in primary photochemical processes, each absorbed quantum of radiation causes one equivalent of a chemical reaction. Nevertheless, a deep mechanistic and theoretical understanding of Ciamician's and Silber's photoreactions was still not possible. The theory about electronically excited states was yet to come. From today's point of view, the mechanistic background of all reactions involving carbonyls, for example, is the

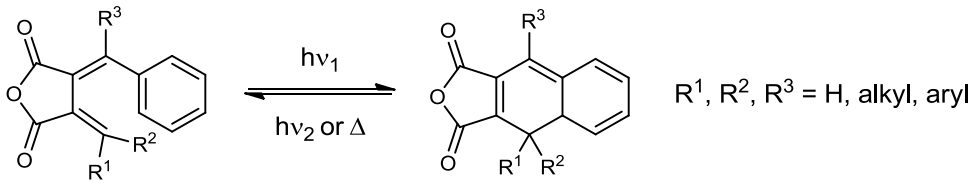
high reactivity of their triplet state with regard to fast hydrogen abstraction generating C-centered radicals.[93]

The value of Ciamician's and Silber's work is not only described by the numerous new photoreactions they discovered, but also by Ciamician's attempt to establish photochemistry as a science of its own. He summarized all the work known so far.[1] Moreover, in 1912, he drew a visionary picture about future applications of light-driven reactions.[2] Emphasizing the interdisciplinary character of his work he found parallels with biology. *"For plants, light is the source of energy. Through the intervention of chlorophyll, green plants accumulate solar energy and transform it into chemical energy … Chemistry in the laboratory differs from chemistry of organisms not in the materials, but in the reagents used. It is thus apparent that the further advancement of biology requires that all of the compounds present in nature can be produced by using only reagents present in nature, rather than agents that do not belong to the living world."*[1, 93] An understanding of chemical reactions in organisms was seen to be of high importance for the progress of man-made chemistry.[103] In organic synthesis, photochemistry was seen to be able to imitate the mild conditions of biochemical reactions.[94] Photochemistry could be used for the synthesis of fine chemicals. Special attention was paid to reactions leading to natural products, as could be shown in the synthesis of sugars or fatty acids. Moreover, it was realized that complex structures like the tricyclic compound carvonecamphor **70** could be photochemically generated in one step out of simple structures (carvone **69**).

Ciamician found several examples where light as a mild agent served as a susbstitute for strong reagents and harsh conditions. The selective oxidation of alcohols to aldehydes by benzoquinone was seen as an alternative for strong agents like bromine or nitric acid. Photopinacolization was considered to be similar to the aldol reaction with the difference that no base was required. The oxidative cleavage of stilbene by means of light was found to be able to replace ozone. And the α-cleavage of ketones could avoid harsh cleavage with permanganate.

Additionally, Ciamician drew the picture of a photochemical industry. In times where coal was the backbone of the industry he recognized fossil fuels not being

inexhaustible whereas light energy offered a lasting supply to industrialization.[93] He already predicted solar home heating, photo-electric batteries and the production of solar fuels.[2, 58] In a way, this kind of chemistry refers to what is today called "green" or "sustainable chemistry," although the terms were proposed later. But as we know, his request to exploit solar energy as the only lasting form of energy came too early. The visionary picture of *"The Photochemistry of the Future"* from 1912 did not find its breakthrough in industry, but its ideas were shared by other scientists. The German chemist **Hans Stobbe (1860 – 1938)** for example, was also campaigning for a bigger role of photochemistry. He is best known for his pioneering studies on the photochromism of fulgides **99**, a light-induced color change of organic dyes.[104, 105]



99 **100**

Scheme 23: Photochromism of fulgides.

The beginning of the twentieth century remains as a time of great progress in photochemistry since many types of photoreactions were already known. Besides Ciamician's and Silber's summary of photochemical reactions, several books appeared. In 1912, **Alfred Benrath (1871 – 1969)** from Königsberg (Germany) published a "Lehrbuch der Photochemie" (Textbook of Photochemistry).[106] **Ivan Plotnikov (1878 – 1955)**, a Russian photochemist, wrote several books, for example, "Photochemische Versuchstechnik" (1911), "Grundriss der Photochemie", and "Lehrbuch der allgemeinen Photochemie."[107] He gave a summary of the development of photochemistry where he noticed a "pre-scientific period up to about 1850" and a "second period of lively advancement" mainly combined with the development of photography. According to him, no earlier than at the beginning of the twentieth century had photochemistry begun its full development.[94]

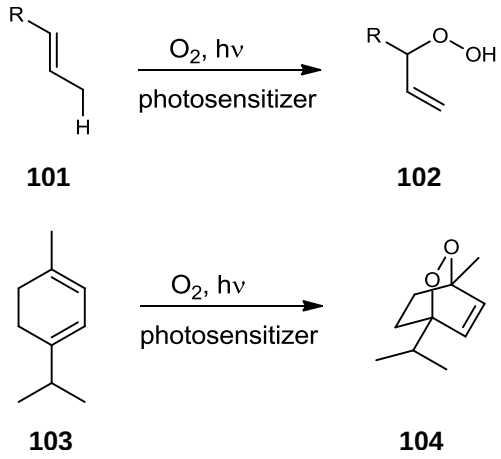
1.6 Developments in the Twentieth Century

World War I marked a break in many respects. A number of research activities had come to a sudden end. Many excellent results had to be rediscovered. Later on, many researchers continued in the field of organic photochemistry. Among them should be named only a few: **Günther Otto Schenck (1913–2003)** discovered the Schenck reaction, which is a photosensitized diastereoselective ene reaction of alkenes **101** with singlet oxygen that affords allylic hydroperoxides **102** (Figure 7).[108]

Figure 7: Günther Otto Schenk and his pilot plant for the production of ascaridol in his garden in Heidelberg (1949).[g]

He is also known for his work on the theory of photosensitization and chemical engineering in the field of solar photochemistry.[109] In 1944, he used chlorophyll from spinach leaves as photosensitizers for the selective oxidation of α-terpinene **103** to produce ascaridol **104** via a cycloaddition of oxygen and the diene.[110] This drug was urgently needed at that time as an anthelmintic to fight ascaris infections in humans. To address this, Schenck constructed an open-air solar irradiation pilot plant for the methylene blue-sensitized production of ascaridol (Scheme 24). Later, he became involved in the technical development of water disinfection by UV irradiation.[109]

[g] K. Schaffner, Günther Otto Schenck (1913-2003): A Pioneer of Radiation Chemistry. *Angew. Chem. Int. Ed.* **2003**, *42*, 2932-2933. DOI: 10.1002/anie.200390509. Copyright © 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Reproduced with permission.



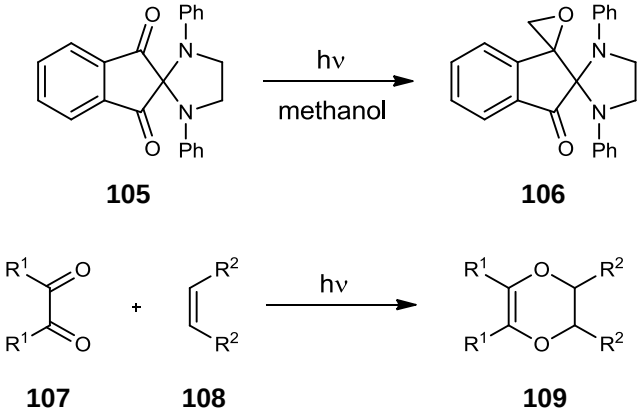
Scheme 24: Schenck-ene reaction and synthesis of ascaridol.

The area of solid-state photochemistry that Liebermann had opened was enlarged by **Gerhard Martin Julius Schmidt (1919 – 1971)**, a German scientist working at the Weizmann Institute in Israel who was familiar with the fields of organic chemistry, crystallography, and spectroscopy (Figure 8). This constellation led to the discovery of "topochemistry." The term means that solid-state reactions are determined by the geometry of the reactant lattice. In other words, reactions in the solid state occur with a minimum amount of atomic or molecular movement. [111, 112]

Figure 8: Gerhard M. J. Schmidt, a pioneer of solid-state photochemistry.[h]

[h] D. Ginsburg, Gerhard M. J. Schmidt 1919-1971. *Israel Journal of Chemistry*. **1972**, *10*, 59-72. Copyright © 1972 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Reproduced with permission.

Another scientist of international significance is the German **Alexander Schönberg (1892 – 1985)**.[113] He emigrated to Egypt in 1937 due to unsafe political circumstances in Germany (Figure 9). In Egypt, his work on solar photochemistry was favored by reason of an annual availability of 3500 hours of sunshine.[114] Besides many photochemical reactions he described the photochemical epoxidation of a carbonyl group in methanol[115] and the addition of olefins to *o*-quinones to give 1,4-dioxenes, which is today known as "Schönberg addition."[116]



Scheme 25: Photochemical epoxidation of carbonyls and Schönberg addition.

But he is most famous for his book "Preparative Organic Photochemistry".[117] This book is the last portrait of photochemistry as it was before the theory of electronically excited states came up.[94] It uses an order different from that of today's textbooks. Nowadays, textbooks show a theoretically based classification. It is an interesting fact that many photochemical reactions were discovered although the underlying physical principles of all these processes were unexplored. Early photochemists did not know about the nature of light and its effect on organic molecules to create electronically excited states. The development of physical chemistry and spectroscopy, particularly time-resolved spectroscopy, made concepts like quantization of energy, electronically excited singlet and triplet states and deactivation of excited states via electron transfer available, which could explain the mechanisms of many photoreactions.[55, 118]

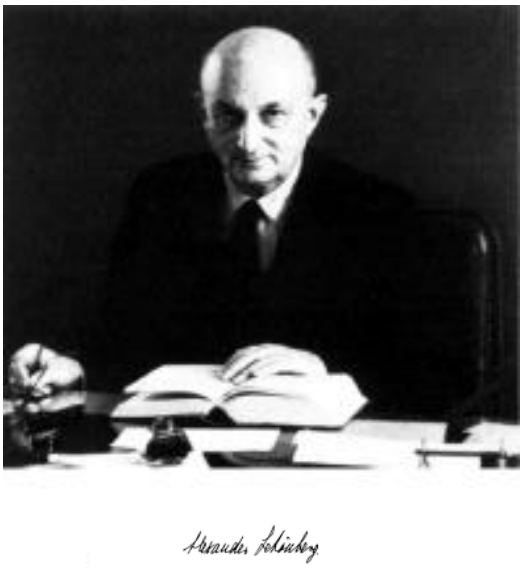


Figure 9: Photochemistry in Egypt: Alexander Schönberg. [i]

All pioneers of photochemistry have created the basis for today's research concerning light-mediated chemical transformations. Today, the need of an improved disposal of solar energy is reflected in the discussion about "green chemistry" and the implementation of renewable energies. Maybe someday Ciamician's hundred-year-old vision of the exploitation of solar energy will come true: *"And if in a distant future the supply of coal will become completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines."* [2]

[i] Reprinted with permission from: E. Singer, Alexander Schönberg 1892-1985. *Chem. Ber.* **1987**, *120*, I-XIX. Copyright © 1987 Deutsche Bunsen-Gesellschaft für physikalische Chemie e.V.

1.7 Key Steps in Early Organic Photochemistry

Table 1: Important steps in photochemistry.

Name	Year	Contribution to Photochemistry
Joseph Priestley	1790	First reported photoreaction
Nicholas de Saussure	1804	Principles of photosynthesis
Humphry Davy	1812	Photochemistry of halogens
Michael Faraday	1821	
Louis Daguerre	1839	Photography
François Arago		
Johann W. Döbereiner	1831	Photoreduction of metal salts
Carl Julius Fritzsche	1867	Dimerization of anthracene
Carl T. Liebermann	1877	First [2+2]-cycloaddition; artificial light sources
Arthur Downes	1879	Photochemical radical formation
Thomas Blunt		
William Henry Perkin	1881	Geometric Isomerization
Johannes Wislicenus		
Julian Schramm	1884	Light-induced halogenation of alkylbenzenes
Heinrich Klinger	1886	Photoreduction of carbonyls; photochemistry for synthetic purpose
Bertram and Kürsten	1895	Dimerization of styrene derivatives
Hermann Trommsdorff	1834	Photorearrangement of santonin; wavelength dependency of photoreactions
Theodor v. Grotthuß	1817	First Law of Photochemistry
John W. Draper	1842	
Fausto A. Sestini	1870s	Santonin rearrangement
Stanislao Cannizzaro	1880s	
Ciacomo Ciamician	1900	Systematic study of the behavior of light towards matter
Paul Silber		
Hans Stobbe	1908	photochromism of fulgides
Johannes Stark	1908	Second Law of Photochemistry (Quantum Equi-
Albert Einstein	1913	valence Law)

Emanuele Paternò	1909	Paternò-Büchi reaction
George H. Büchi	1954	
Ivan Plotnikov	1911	Textbooks on photochemistry
Alfred Benrath	1912	
Ronald G. W. Norrish	1930s	α-cleavage of carbonyls in gas phase
Günther Otto Schenck	1940s	Photosensitization; Schenck-ene-reaction
Gerhard M. J. Schmidt	1960s	Solid-state photochemistry; topochemistry
Alexander Schönberg	1968	New photoreactions; textbook “Preparative Organic Photochemistry”

1.8 References

[1] G. Ciamician, Sur Les Actions Chimique De La Lumière. *Bull. Soc. Chim. France* **1908**, *4*, i.

[2] G. Ciamician, The Photochemistry of the Future. *Science* **1912**, *36*, 385-394.

[3] H. D. Roth, The Beginnings of Organic Photochemistry. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1193-1207.

[4] J. Priestley, *Experiments and Observations on Different Kinds of Air*, Birmingham, **1790**.

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2 PHOTOCATALYTIC ARYLATION OF ALKENES, ALKYNES, ENONES, AND HETEROARENES WITH DIAZONIUM SALTS: THE PHOTO-MEERWEIN ARYLATION

An atom-economical and efficient radical arylation of olefins, acetylenes, enones, and *N*-heteroarenes in presence of $[Ru(bpy)_3]^{2+}$ or eosin Y as a photocatalysts under irradiation with visible light or direct sunlight using diazonium salts is reported. The easy procedure is distinguished by high yield, low catalyst loading, mild conditions, and broad scope.

The results of this chapter have been published:

D. P. Hari, P. Schroll, B. König, Metal-Free, Visible-Light-Mediated Direct C–H Arylation of Heteroarenes with Aryl Diazonium Salts. *Journal of the American Chemical Society* **2012**, *134*, 2958-2961.

P. Schroll, D. P. Hari, B. König, Photocatalytic Arylation of Alkenes, Alkynes and Enones with Diazonium Salts. *Chemistry Open* **2012**, *1*, 130-133.

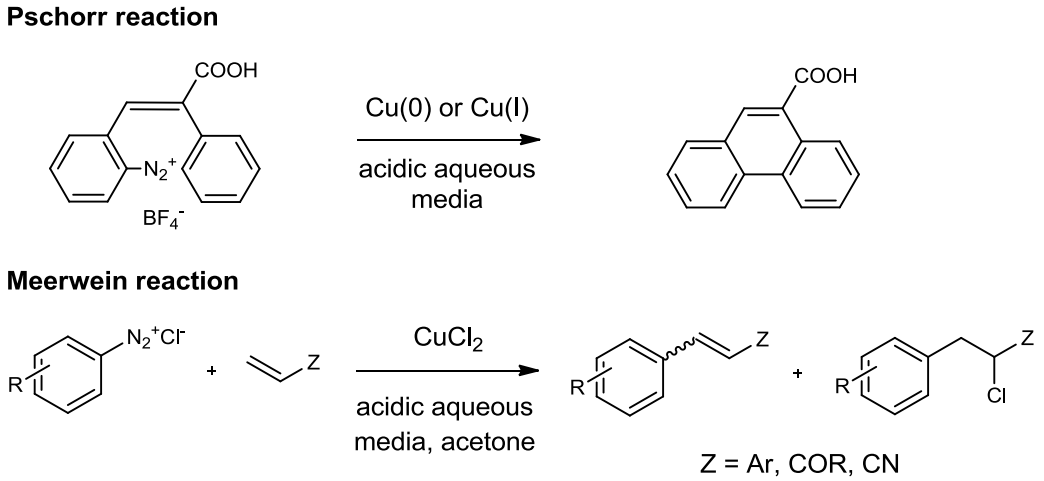
P. Schroll, B. König, Visible light-mediated arylation of unsaturated compounds with diazonium salts. *European Photochemistry Association Newsletter* **2012**, *83*, 49-51.

Author contributions:
Durga Prasada Rao Hari synthesized the arylated five-membered heterocycles and worked on the Meerwein addition reaction and the synthesis of benzothiophenes. Michal Majek performed the quantum yield determinations.

2.1 Introduction

Carbon–carbon bond formation by sp^2–sp^2 or sp^2–sp cross coupling reactions are key transformations in organic synthesis.[119-123] Many methods, typically involving transition metal catalysis, are known, and the recent recognition of Richard F. Heck, Ei-ichi Negishi and Akira Suzuki by the Royal Swedish Academy of Sciences (Stockholm, Sweden) when they were awarded the Nobel Prize in Chemistry (2010) underlines the importance of metal-catalyzed cross-coupling reactions.[124]

However, long before the triumph of the palladium-catalyzed cross-coupling reaction, such as the Heck (1972) and Sonogashira (1975) reactions,[125, 126] methods for arylation of alkenes and alkynes were known. The Meerwein arylation, developed in 1939, is a copper-catalyzed coupling of an aryl diazonium salt with an unsaturated compound.[127-130] Even earlier, in 1896, an intramolecular variant of this reaction was reported, today known as the Pschorr reaction.[131-134] A radical mechanism is discussed for both cases by reversible oxidation of copper(I) to copper(II). However, several drawbacks have prevented the broader application of these reactions in organic synthesis: the reaction yields are typically low (20–40%), high catalyst loadings are required (15–20 mol%), and side products are formed under the aqueous reaction conditions (Scheme 26).



Scheme 26: Pschorr- and Meerwein reaction.[j]

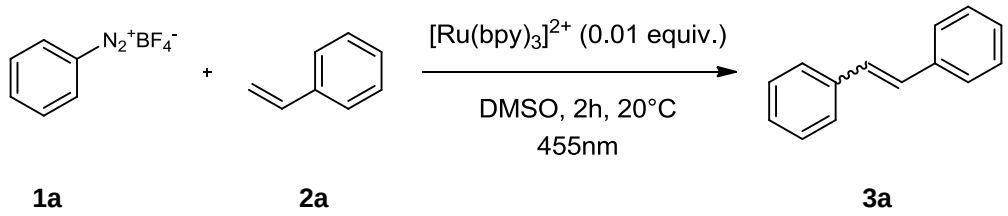
[j] The original Meerwein protocol starts from Cu(II). $CuCl_2$ reacts with acetone to form CuCl as the active catalyst.

Besides the use of copper(I) cations for the reduction of aryl diazonium salts, Fe(II) and Ti(III) have also been used as reducing agents. Reduction by metal cations and electrochemical reduction leads to homolytic dediazoniation generating aryl radicals.[135-137] In addition, aryl radicals can be obtained by photoinduced electron transfer.[138, 139] Organometallic photocatalysts such as 2,2′-bipyridine (bpy)-containing ruthenium complexes (e.g., $[Ru(bpy)_3]^{2+}$) are known to undergo one-electron transfer reactions.[140] Visible light-induced photoredox catalysis offers the possibility of initiating organic transformations with high selectivities under mild conditions, as demonstrated by MacMillan, Yoon, Stephenson, and many others.[141-155] Current reports describe the photocatalytic formation of carbon–carbon,[156-159] carbon–phosphorus[160, 161], carbon–sulfur[162], or carbon–nitrogen bonds.[163] More recently, visible-light photocatalysis has entered the field of palladium-catalyzed cross-coupling reactions. In 2007, Akita reported the acceleration of copper-free Sonogashira-type reactions by adding a photocatalyst.[164] Sanford *et al*. reported a merger of palladium-catalyzed C–H functionalization and visible-light photocatalysis. In their approach, aryl radicals were obtained from the photocatalytic reduction of arenediazonium salts by the aid of $[Ru(bpy)_3]^{2+}$ and subsequently used in palladium-catalyzed C–H arylation reactions.[165] Direct C–H arylation of five-membered heteroarenes with aryl diazonium salts was achieved using eosin Y and visible light.[166]

Combining the fields of photoredox catalysis and cross-coupling reactions, we report the intermolecular visible light-mediated arylation of unsaturated compounds catalyzed by $[Ru(bpy)_3]^{2+}$ or eosin Y as photocatalysts. The process is atom economical and efficient, and therefore suitable to improve the classic Meerwein arylation protocol significantly.

2.2 Results and Discussion

The photocatalytic reaction of phenyldiazonium tetrafluoroborate (**1a,** $E_{1/2red}$ = +0.30 V vs. SCE in sulfolane[167]) with freshly distilled styrene (**2a**) in the presence of $[Ru(bpy)_3]^{2+}$ under inert atmosphere and irradiation with a blue high-power light-emitting diode (LED, λ_{max} = 455 ± 15 nm, *P* = 3.0 W) at ambient temperature gave stilbene (**3a**), which is the formal substitution product of a styrene's vinylic hydrogen atom by the aryl residue of the diazonium salt (Scheme 27).



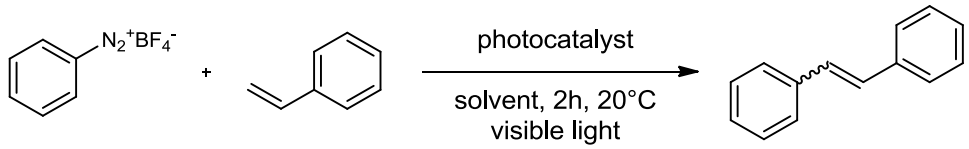
Scheme 27: Photoredox-catalyzed reaction of aryl diazonium salts with styrene.

Optimization

In the absence of the photocatalyst or without light, no coupling product was obtained. The use of dry polar aprotic solvents, such as *N*,*N*-dimethylformamide (DMF) or dimethylsulfoxide (DMSO) and a fivefold excess of styrene gave the best results. Higher concentrations of styrene resulted in the formation of oligomers and polymers, while at lower concentrations the lifetime of the aryl radical was too short for the diffusion-controlled reaction with the alkene to occur. Several photocatalysts were screened, but perylene bisimide and rose bengal gave only low yields. Eosin Y (5 mol%) gave a moderate yield of 44%, while $[Ru(bpy)_3]^{2+}$ (1 mol%) afforded the product stilbene in up to 87% yield.

Catalyst loadings of $[Ru(bpy)_3]^{2+}$ exceeding 1 mol% showed stronger absorption and decreased the yield due to reduced penetration depth of the light beam resulting in a smaller photoactive layer (Table 2). $[Ru(bpy)_3]^{2+}$ exhibits unique photochemical properties: absorption of blue light (λ_{max} = 452 nm, see Figure 11), high chemical stability, long lifetime of the photoexcited state, and high quantum yield of its formation.[140, 168-172]

Table 2: Photo-Meerwein arylation – optimization of reaction conditions.[a]



1a **2a** **3a**

Entry	Catalyst (mol%)[b]		2a (eq.) [c]	λ (nm)[d]	Solvent[e]	Yield (%)[f]
1	-	-	10	455	DMSO	-
2	$[Ru(bpy)_3]^{2+}$	1	10	-	DMSO	-
3	$[Ru(bpy)_3]^{2+}$	1	10	455	$CHCl_3$	-
4	$[Ru(bpy)_3]^{2+}$	1	10	455	THF	25
5	$[Ru(bpy)_3]^{2+}$	1	10	455	DMF	55
6	$[Ru(bpy)_3]^{2+}$	1	10	455	DMSO	62
7	$[Ru(bpy)_3]^{2+}$	1	5	455	DMSO	87
8	$[Ru(bpy)_3]^{2+}$	1	2	455	DMSO	71
9	$[Ru(bpy)_3]^{2+}$	1	1	455	DMSO	67
10	Perylene Bisimide	5	5	525	DMF[g]	3
11	Rose Bengal	5	5	525	DMSO	11
12	Eosin Y	5	5	525	DMSO	44
13	$[Ru(bpy)_3]^{2+}$	0.5	5	455	DMSO	77
14	$[Ru(bpy)_3]^{2+}$	2	5	455	DMSO	67
15	$[Ru(bpy)_3]^{2+}$	5	5	455	DMSO	64

[a] *Reaction conditions:* arenediazonium salt (0.2 mmol), styrene (0.2 – 2.0 mmol, 0.02 – 0.23 mL), photocatalyst (0.5 – 5.0 mol%), solvent (0.77 – 0.98 mL), inert atmosphere. [b] Amount relative to the amount of diazonium salt. [c] Distilled. Equivalents with respect to the amount of diazonium salt. [d] Irradiation with high-power LED (λ_{max} = 455 nm ± 15 nm, P = 3.0 W or λ_{max} = 525 nm ± 20 nm, P = 1.0 W). [e] Absolute. [f] Yields were determined by integration of the peaks in the gas chromatogram and are the sum of the *cis* and *trans* isomers. [g] Catalyst: *N*,*N*'-di(2-hexyl)heptyl-perylene-3,4,9,10-tetracarboxylic bisimide; not soluble in DMSO.

Kinetics

Monitoring of the reaction kinetics revealed an ideal reaction time of two hours. Further irradiation did not lead to an increase of product formation. The *trans* isomer was initially formed as the major product, but then partially isomerized to the *cis* isomer upon irradiation (Figure 10). We attribute the partial isomerization to a sensitization process involving the photocatalyst since stilbene itself does not absorb blue light.[173]

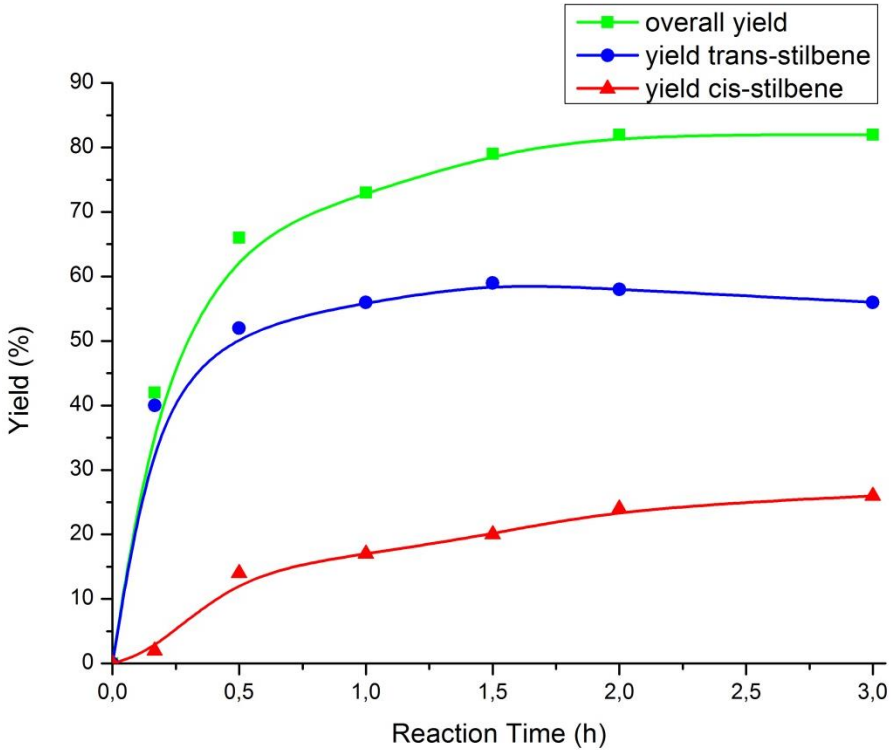
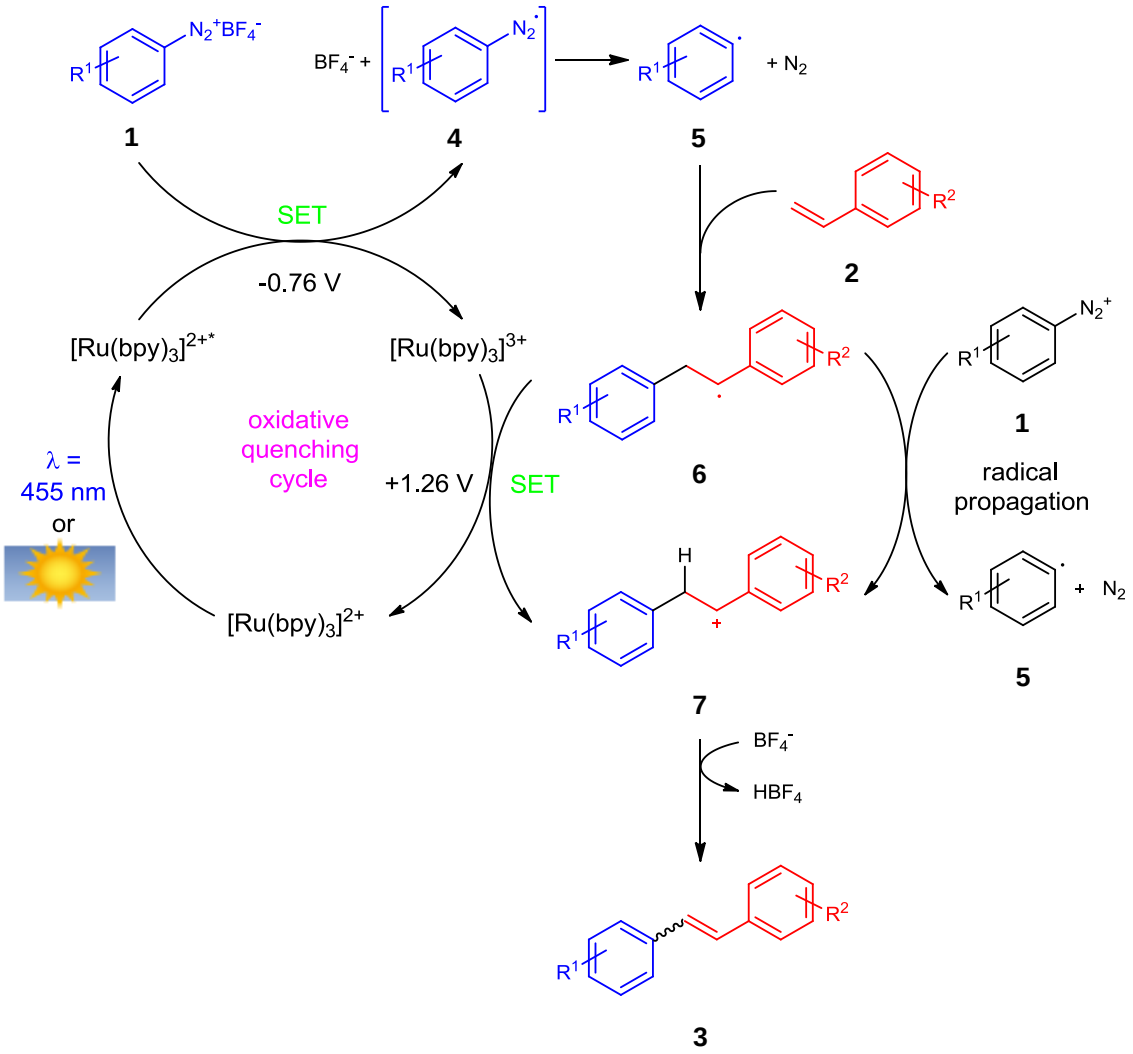


Figure 10: Kinetics for the photoredox arylation of styrene. *Reaction conditions:* arenediazonium salt (0.2 mmol), styrene (1.0 mmol, 115 µL), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2.0 µmol, 0.01 equiv.), DMSO (885 µL), high-power LED (λ_{max} = 455 nm ± 15 nm, *P* = 3.0 W), inert atmosphere, 20°C. Yields were determined by integration of the peaks in the gas chromatogram and are the sum of the *cis* and *trans* isomers.

Mechanism

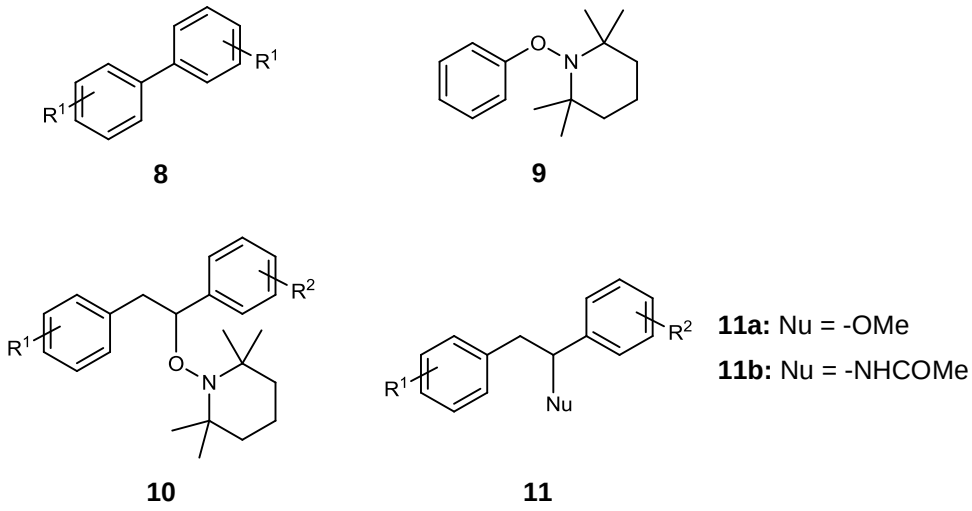
A radical pathway including one-electron oxidation and reduction steps is likely for the photoredox arylation. A mechanistic model for the arylation of unsaturated compounds using the oxidative quenching cycle of $[Ru(bpy)_3]^{2+*}$ is proposed (Scheme 28). Excitation of the metal complex with blue light leads to an electron-transfer from the metal ion to the ligand (MLCT).[140] The negatively charged aromatic ligand and the positively charged aryl diazonium ion interact via Coulomb attraction or via π-stacking. Strongly electrophilic diazonium compound **1** acts as irreversible oxidative quencher,[174] and an electron is transferred to the diazonium ion (SET, single electron transfer) generating a labile aryl diazenyl radical **4** that releases dinitrogen in a homolytic dediazoniation process to form a highly reactive aryl radical **5** as the key intermediate.[135] At the same time, the photocatalyst is oxidized to give $[Ru(bpy)_3]^{3+}$ in its ground state. The attack of neutral radical **5** to the double bond of styrene **2** gives stabilized benzylic radical **6**

which is oxidized to a carbenium ion **7** either by return of an electron to the oxidized photocatalyst $[Ru(bpy)_3]^{3+}$ ($E_{1/2red}$ = +1.26V vs. SCE) and simultaneously closing the catalytic cycle, or by transferring an electron to another diazonium ion **1** to initiate a radical chain mechanism. Product **3** is formed after deprotonation. Absorption of another photon initiates a new catalytic cycle. The radical chain pathway has been proven for selected substrates. Quantum yields $\Phi > 1$ were found for styrenes and heteroarenes, but not for acetylenes.[175] The similarity in the mechanism compared to a classic copper-catalyzed Meerwein arylation justifies the name "Photo-Meerwein" arylation for the photoredox process.[176]



Scheme 28: Proposed mechanism for the photoredox arylation of unsaturated compounds using diazonium salts.

Evidence for the proposed reaction pathway is given by various trapping products (Scheme 29). Compound **8**, the radical dimer of aryl radical **5** was detected via mass spectrometry. Additionally, 2,2,6,6-tetramethylpiperidine nitroxide (TEMPO) adducts **9** and **10** were identified when irradiating the reaction mixture and TEMPO, which indicates the presence of aryl and benzyl radical intermediates **5** and **6**, respectively. In presence of nucleophiles, addition products **11** were formed, suggesting the existence of a carbenium ion intermediate **7**.



Scheme 29: Trapping products in the Photo-Meerwein arylation.

A double functionalization of the olefin moiety was observed in presence of a nucleophile (**11**, Scheme 29). Two covalent bonds were formed in one photocatalytic reaction. Methanol, for example, added to the intermediary formed benzylic cation yielding the corresponding methylether **11a**. The benzylic cation was also trapped by acetonitrile and water, yielding amides **11b**. This result was shown in the early reports of Cano-Yelo[177] and later work by our group.[178] The Meerwein arylation-addition reaction is thus a versatile method for the intermolecular amino-arylation of alkenes.

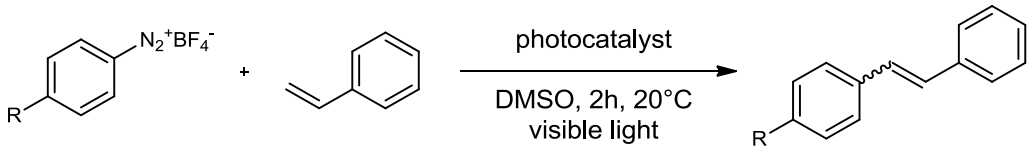
Following the mechanistic proposal, both electron transfer processes – the quenching of the photocatalyst and the back electron transfer for its regeneration – lead to useful chemical transformations, making the photoredox arylation of olefins highly efficient. In many other photocatalytic processes, only one half-reaction is a useful chemical reaction, whereas the other half-reaction creates a stoichiometric amount of waste resulting from the destruction of a sacrificial electron donor or acceptor.

Another benefit of the arylation reaction is its atom economy: all atoms, with the exception of molecular nitrogen as the leaving group, the counter ion and a proton, appear in the product molecule. The choice of the counterion is crucial in several respects: boron tetrafluoride (BF_4^-) as a non-nucleophilic and non-redox-active counter ion significantly stabilizes the diazonium ion, increases the solubility in organic solvents compared to the corresponding halides, avoids the formation of addition products and does not disturb the electron-transfer steps in the catalytic cycle. In all, the use of tetrafluoroborates in place of halides and the absence of nucleophiles lead to exclusive formation of the arylation-elimination product in which the double bond appears untouched after the reaction due to a radical addition-elimination mechanism.

Scope of Diazonium Salts

The scope of the reaction was explored using a set of substituted aryl diazonium salts **1** and unsaturated compounds **2** under optimized reaction conditions: $[Ru(bpy)_3]^{2+}$ as the photocatalyst with a loading of 1 mol%, DMSO as the solvent, a fivefold excess of olefin **2**, a nitrogen atmosphere, blue-light irradiation, ambient temperature, and a two hour reaction time. A range of different substituted arenediazonium salts was examined in the arylation of styrene, including electron-withdrawing and donating groups. Since the half-wave reduction potentials of all *para*-substituted diazonium salts were within the range of the excited photocatalyst's reducing ability ($E_{1/2red}$ = -0.76 V vs. SCE), $[Ru(bpy)_3]^{2+*}$ was able to photochemically form highly reactive aryl radicals that could subsequently be trapped by π-electron donors **2** (Table 3).[135, 174, 177, 179-181]

Table 3: Scope of aryl diazonium salts.[a]



1b–f **2a** **3b–f**

Entry	Reactant	$E_{1/2,red}$[b]	R	Product	Yield[c] (%)[d]	(%)[e]	(%)[f]
1	**1b**	+0.14 V	MeO	**3b**	83	64	80
2	**1c**	+0.25 V	Me	**3c**	68	65	70
3	**1d**	+0.35 V	Cl	**3d**	72	39	51
4	**1e**	+0.38 V	Br	**3e**	94	-	66
5	**1f**	+0.45 V	O_2N	**3f**	66	58	52

[a] *Reaction conditions:* arenediazonium salt (0.2 mmol), styrene (1.0 mmol, 115 µL), DMSO (885 µL, absolute), inert atmosphere. [b] Have-wave reduction potential of diazonium salts in sulfolane vs. SCE. See: R. M. Elofson, F. F. Gadallah, *J. Org. Chem.* **1969**, *34*, 854-857. [c] Yields were determined by integration of the peaks in the gas chromatogram and are the sum of the *cis* and *trans* isomers. [d] Catalyst: $[Ru(bpy)_3]^{2+}$ (0.01 equiv.), irradiation with high-power LED (λ_{max} = 455 nm ± 15 nm, *P* = 3.0 W), *T* = 20°C. [e] Catalyst: $[Ru(bpy)_3]^{2+}$ (0.01 equiv.), irradiation with sunlight, *T* = 37°C. [f] Catalyst: Eosin Y (0.075 equiv.), irradiation with high-power LED (λ_{max} = 525 nm ± 20 nm, *P* = 1.0 W), *T* = 20°C.

The coupling products **3b–f** were obtained in good to excellent yields of 66–94%, which was attributed to the appearance of an intermediary formed benzylic radical. Several functional groups including ether, alkyl, nitro and halide groups were tolerated in this reaction, but aryl diazonium salts derived from aminophenols led to decomposition of the starting material. Carbon-halide bonds remained untouched even when the stronger reducing catalyst *fac*-$Ir(ppy)_3$ was used providing access to halogen-substituted stilbenes **3d–e** in one step, which can be further functionalized. The reaction regioselectively took place at the diazonium moiety since halides were more difficult to reduce.

Direct sunlight was sufficient to drive the reaction. The yields under these conditions — radiation angle of 37° on the roof of our institute at 48° 59' N, 12° 6' E at noon on October 1st, 2011 — were similar to those of defined laboratory conditions using high-power light-emitting diodes as source of radiation.

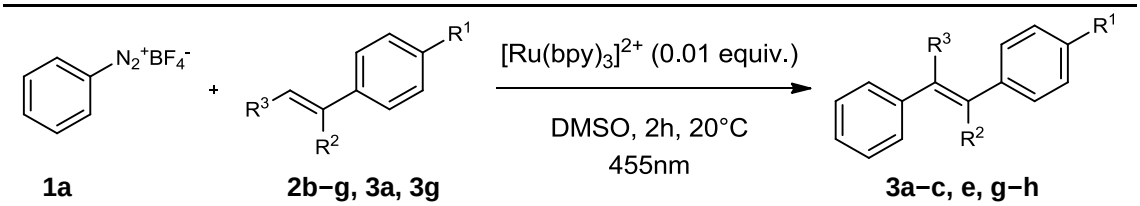
The coupling of arenediazonium salts **1b–f** with styrene also proceeded metal-free using the xanthene dye Eosin Y and green light (λ_{max} = 525 ± 20 nm). Eosin Y

exhibits similar electrochemical properties compared to $[Ru(bpy)_3]^{2+}$.[157] Substituted stilbenes **3b–f** were obtained in 51–80% yield. Notably, the arylation reaction was observed to be *trans*-selective. A higher catalyst loading of 7.5 mol% was necessary since bleaching indicated a loss of active catalyst that underwent ring-closure from the colored open form to its colorless and inactive lactone form.

Arylation of Alkenes

Among several π-electron donors, a variety of styrene derivatives bearing functional groups at the aromatic ring or at the double bond could be effectively coupled (Table 4).

Table 4: Arylation of styrene derivatives.[a]



1a **2b–g, 3a, 3g** **3a–c, e, g–h**

Entry	Reactant	R^1	R^2	R^3	Product	Yield (%)[b]
1	**2b**	MeO	H	H	**3b**	73
2	**2c**	Me	H	H	**3c**	64
3	**2d**	Br	H	H	**3e**	63
4	**2e**	H	H	NO_2	**3a**[c]	37
5	**2f**	H	H	COOH	**3a**[d]	49
6	**3a**	H	H	Ph	**3g**	12
7	**3g**	H	Ph	Ph	**3h**	38
8	**2g**	H	Ph	H	**3g**	71

[a] *Reaction conditions:* phenyl diazonium salt (0.2 mmol), styrene derivative (1.0 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2.0 µmol), DMSO (1.0 mL, absolute), irradiation with high-power LED (λ_{max} = 455 nm ± 15 nm, *P* = 3.0 W), inert atmosphere. [b] Yields were determined by integration of the peaks in the gas chromatogram. [c] Elimination of NO_2. [d] Elimination of CO_2.

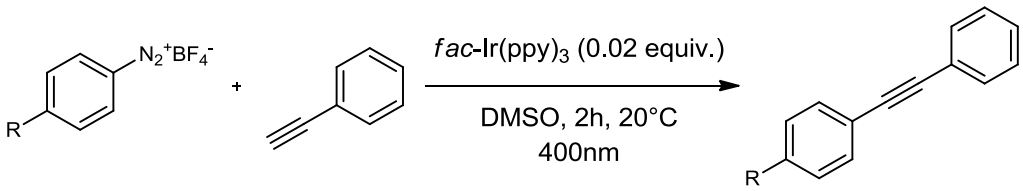
Different substituted stilbenes could be synthesized in good yields out of styrenes with substituents at the aromatic moiety (Entries 1 – 3). Since arylation exclusively occurred in the β-position of styrene, reactants already bearing β-substituents were shown to undergo arylation less effectively. In cases where β-nitrostyrene **2e** or cinnamic acid **2f** was used as the reactant, the coupling was

accompanied by defunctionalization, yielding *trans*-stilbene **3a** as a result of the loss of CO_2 or NO_2, respectively (Entries 4 – 5). The arylation of *trans*-stilbene **3a** gave triphenylethene **3g** in poor yield. Conversion of **3g** into tetraphenylethene **3h** was possible, but steric hindrance allowed only moderate yield. In contrast, the reaction of 1,1-diphenylethene **2h** was much more efficient due to a stabilized double-benzylic radical intermediate (Entries 6 – 8).

Arylation of Alkynes

Phenylacetylene underwent sp^2–sp coupling with aryl radicals to form diphenylacetylene in moderate yields, which could be attributed to the reduced reactivity of the triple bond compared to styrene (Table 5).

Table 5: Arylation of phenylacetylene.[a]

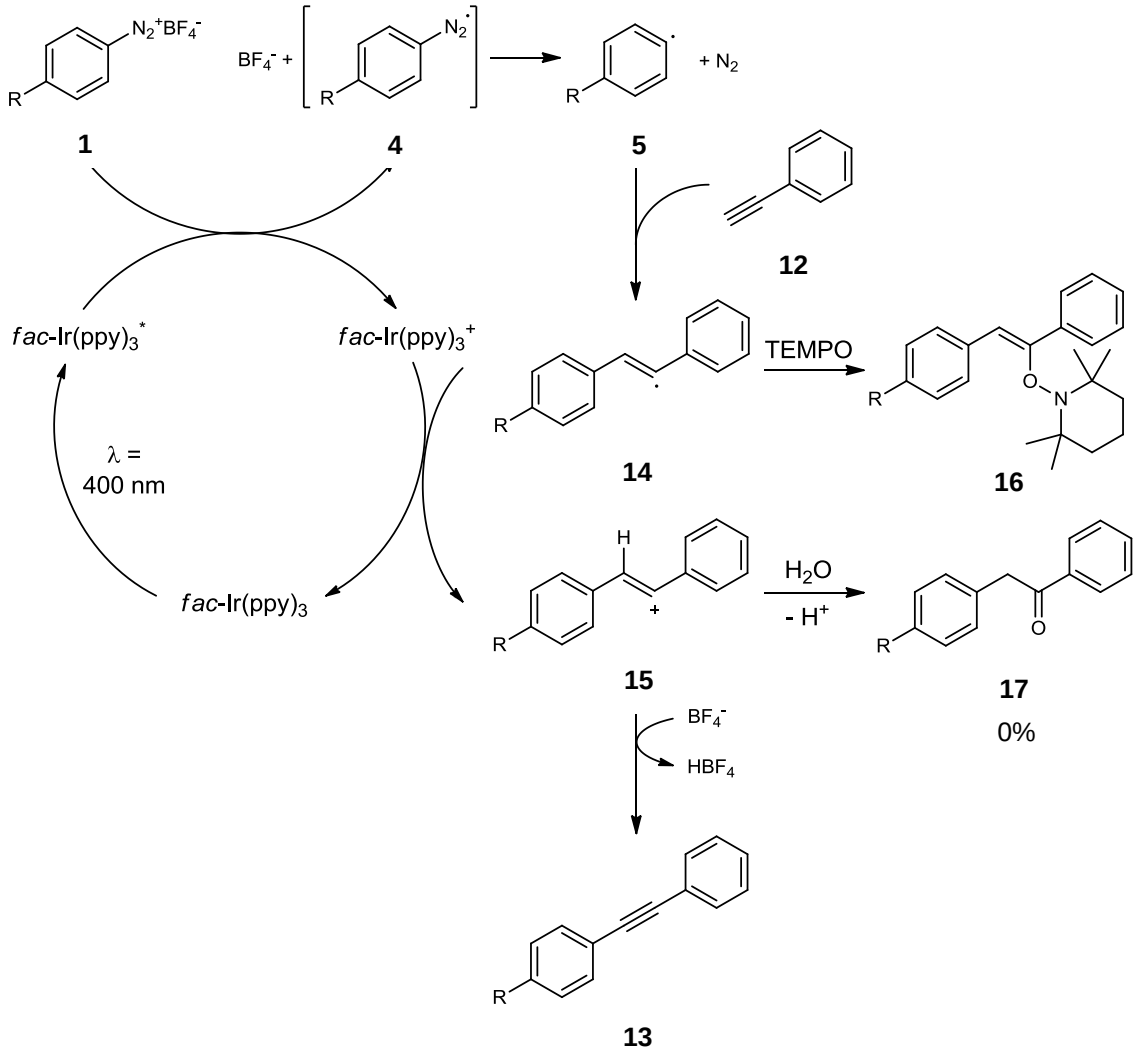


1 **12** **13a–c**

Entry	Reactant	R	Product	Yield (%)[b]
1	**1b**	MeO	**13a**	47
2	**1d**	Cl	**13b**	48
3	**1e**	Br	**13c**	34

[a] *Reaction conditions:* arenediazonium salt (0.2 mmol), phenylacetylene (1.0 mmol), *fac*-Ir(ppy)$_3$ (4.0 µmol), DMSO (1.0 mL, absolute), irradiation with high-power LED (λ_{max} = 400 nm ± 10 nm, *P* = 1.2 W), inert atmosphere. [b] Yields were determined by integration of the peaks in the gas chromatogram.

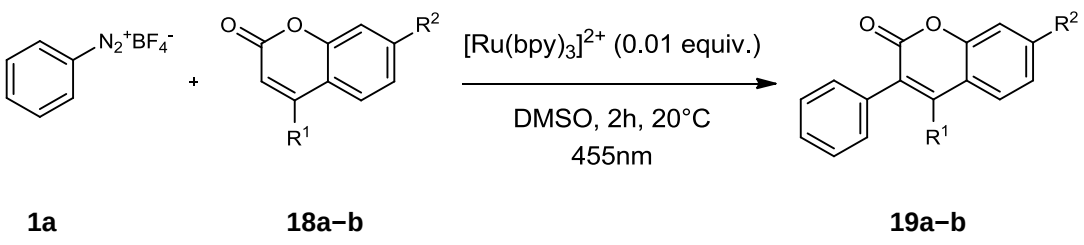
As far as the mechanism was concerned, the reaction proceeded through a vinyl radical intermediate **14** which has been trapped by TEMPO to form adduct **16**. The method was suitable for arylation of terminal alkynes (Scheme 30). Attempts to intermolecularly trap the vinylic carbenium ion **15** with water to yield the enol that tautomerizes to the corresponding ketone **17** remained unsuccessful. However, the intramolecular trapping of the vinylic radical turned out to become a suitable method for the formation of benzothiophenes and phenanthrenes.[182, 183]



Scheme 30: Vinylic intermediates in the arylation of terminal alkynes.

Arylation of Cyclic Enones

Enones such as coumarin **18** or *para*-benzoquinone **20** were arylated in good to excellent yields. Coumarin yielded 3-arylated photoproducts as proven by a control experiment with an additional substituent in 4-position. Blocking the 4-position gave the arylated coumarin anyway (Scheme 31).



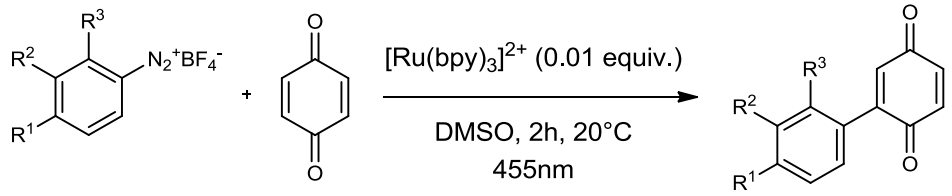
1a **18a–b** **19a–b**

19a: R^1 = H, R^2 = H; 63%
19b: R^1 = CH_3, R^2 = OH; 75%

Scheme 31: Arylation of coumarins.

The influence of the substitution pattern at the diazonium salt on the arylation efficiency was examined for *para*-benzoquinone (Table 6). The arylation reaction worked nicely with electron-donating as well as with electron-withdrawing groups. Electronic effects were found to have a minor influence on the yield of the reaction. Slightly decreased yields as a result of steric influence were observed for *meta*- and *ortho*-substituted arenediazonium salts.

Table 6: Arylation of *para*-benzoquinone.[a]



1a–p **20** **21a–p**

Entry	Reactant	R^1	R^2	R^3	Product	Yield (%)[b]
1	**1a**	H	H	H	**21a**	89
2	**1b**	MeO	H	H	**21b**	72
3	**1c**	Me	H	H	**21c**	76
4	**1e**	Br	H	H	**21e**	71
5	**1f**	O_2N	H	H	**21f**	88
6	**1g**	I	H	H	**21g**	70
7	**1h**	EtOOC	H	H	**21h**	76
8	**1i**	F_3C	H	H	**21i**	78
9	**1j**	H	MeO	H	**21j**	63
10	**1k**	H	Br	H	**21k**	71
11	**1l**	H	O_2N	H	**21l**	72
12	**1m**	H	H	Me	**21m**	79
13	**1n**	H	H	NO_2	**21n**	58
14	**1o**	H	H	CN	**21o**	47
15	**1p**	H	H	CF_3	**21p**	61

[a] *Reaction conditions:* arenediazonium salt (0.2 mmol), *para*–benzoquinone (1.0 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2.0 µmol), DMSO (1.0 mL, absolute), irradiation with high-power LED (λ_{max} = 455 nm ± 15 nm, *P* = 3.0 W), inert atmosphere. [b] Yields of the isolated products are given.

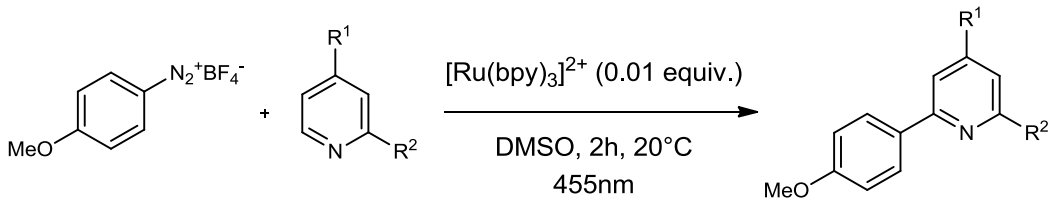
The arylation of cyclic enones demonstrates an additional advantage of the Photo-Meerwein reaction compared to transition metal-based arylation reactions:

the above-mentioned protocol allows arylation of rigid cyclic olefins in vinylic position due to a radical mechanism. A competing Heck reaction fails since it needs an H-atom in a *syn* relationship for the elimination step to occur. Tolerance of halides and vinylic arylation of cyclic olefins make the Photo-Meerwein arylation an orthogonal strategy to well-established transition metal-catalyzed reactions.

C–H Arylation of *N*-Heteroarenes

The Photo-Meerwein reaction was successfully applied to the arylation of five-membered[166] and six-membered heteroaromatic compounds. The direct arylation of heteroarenes is a powerful tool in the one-step synthesis of functionalized aromatic compounds (Table 7).

Table 7: Arylation of pyridines.[a]



1b **22a–c** **23a–c**

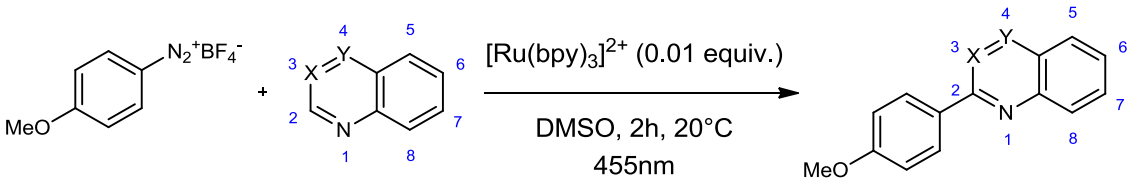
Entry	Reactant	R^1	R^2	Product	Yield (%)[b]
1	**22a**	H	H	**23a**	82
2	**22b**	CF_3	H	**23b**	79
3	**22c**	H	Br	**23c**	71

[a] *Reaction conditions:* 4-methoxybenzenediazonium salt (0.2 mmol), *N*-heteroarene (1.0 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2.0 µmol), DMSO (1.0 mL, absolute), irradiation with high-power LED (λ_{max} = 455 nm ± 15 nm, *P* = 3.0 W), inert atmosphere. [b] Yields of the isolated products are given.

Pyridine **22a** was arylated in good yields. Arylation occurred adjacent to the heteroatom through radical addition, formation of an *N*-centered amino radical and subsequent one-electron oxidation and deprotonation. The substitution pattern was ascertained by 2D-NMR experiments (COSY and NOESY). The method was suitable for the fast and efficient one-step synthesis of unsymmetrically substituted phenylpyridines, as has been exemplified on the basis of substituted pyridines **22b** and **22c**. A non-catalytic direct arylation was excluded by control

reactions in the dark or without catalyst, experiments that yielded no arylation products. The reaction therefore provides a considerable advantage to the direct thermal arylations that require a large excess of heteroarene, elevated temperatures, and long reaction times.[184] A similar reaction that generate the related 2,2′-bipyridines was unsuccessful since the diazotization of 2-amino-pyridine failed. The required diazonium salt is known to undergo rapid hydrolysis.[185, 186] This method was next extended to larger heteroaromatic systems. Quinoline **24a** as well as quinoxaline **24b** underwent clean arylation. Quinazoline **24c** offers two non-equal positions adjacent to the nitrogen atom. Hence, multiple isomers were obtained. Interestingly, the 4-arylated isomer was not isolated, but the 8-arylated isomer which had been formed via a tertiary radical intermediate (Table 8).

Table 8: Arylation of *N*-heteroarenes.[a]



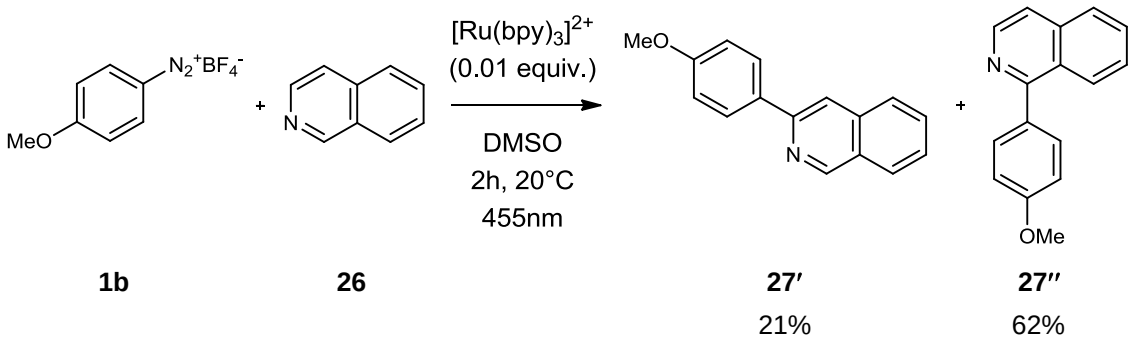
1b **24a–c** **25a–c**

Entry	Reactant	X	Y	Product	Yield (%)[b]
1	**24a**	C	C	**25a**	73
2	**24b**	C	N	**25b**	68
3	**24c**	N	C	**25c′**, **25c″**	76[c]

[a] *Reaction conditions:* 4-methoxybenzenediazonium salt (0.2 mmol), *N*-heteroarene (1.0 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2.0 µmol), DMSO (1.0 mL, absolute), irradiation with high-power LED (λ_{max} = 455 nm ± 15 nm, *P* = 3.0 W), inert atmosphere. [b] Isolated yields are given. [c] Two isomers were obtained: 2-(4-methoxyphenyl)quinazoline **25c′** (28%), 8-(4-methoxyphenyl)-quinazoline **25c″** (48%).

Additionally, the unsymmetrical molecule isoquinoline **26** gave two regioisomers as arylation products (Scheme 32). [k]

[k] After the experimental work had been finished, a paper from a competing group was published presenting similar results. See: D. Xue, Z.-H. Jia, C.-J. Zhao, Y.-Y. Zhang, C. Wang, J. Xiao, Direct Arylation of *N*-Heteroarenes with Aryldiazonium Salts by Photoredox Catalysis in Water. *Chem. Eur. J.* **2014**, *20*, 2960-2965.



1b **26** **27′** 21% **27″** 62%

Scheme 32: Arylation of isoquinoline.

2.3 Conclusions

In conclusion, we have developed an efficient visible light-mediated intermolecular arylation of π-electron donors by photoredox catalysis. The homogeneous Photo-Meerwein reaction proceeds at ambient temperature through photocatalytically generated aryl radicals from one-electron reduction of arenediazonium salts, with subsequent addition to olefinic substrates. Back-electron transfer and elimination gave sp^2-sp^2 and sp^2-sp carbon coupling products, respectively. The procedure was highly atom-economical, experimentally simple and characterized by high yields, low catalyst loadings and mild conditions. The photocatalyst eosin Y was a suitable metal-free alternative to $[Ru(bpy)_3]^{2+}$. Visible light-emitting high-power LEDs as well as sunlight were suitable sources of radiation. The reaction scope comprised a range of different substituted arenediazonium salts and tolerated a multitude of functional groups with the notable exceptions of strongly basic or nucleophilic substituents. Unsaturated compounds such as alkenes, alkynes, enones, and *N*-heteroarenes were effectively coupled. The method is suitable for the late-stage modification of heteroarenes. Tolerance of halides and vinylic arylation of cyclic olefins make the Photo-Meerwein arylation an orthogonal strategy to the well-established Heck reaction. The photoredox procedure improves the classic Meerwein arylation protocol significantly to make it more applicable to organic synthesis.

2.4 Experimental Part

2.4.1 General

Instruments, Methods, and Materials

Solvents and substrates. Commercial reagents and starting materials were purchased from Aldrich, Fluka, VWR or Acros and used without further purification. Other starting materials were prepared as reported. Solvents were used as *p. a.* grade or dried and distilled prior to use as described in common methods if required by the experimental procedure.[187]

Irradiation sources. High-power LEDs of different colors were used for irradiation experiments: Philips LUXEON® Rebel (purple, λ_{max} = 400 ± 10 nm, 1000 mA, *P* = 1.2 W), Philips LUXEON® Rebel LXML-TRo1-0225 (blue, λ_{max} = 455 ± 15 nm, 700 mA, *P* = 3.0 W), OSRAM® Oslon SSL 80 LD H9GP-3T3U-35 high-power LED lamp (royal-blue, λ_{max} = 455 ± 15 nm, 700 mA, *P* = 1.12 W), and Philips LUXEON® Rebel (green, λ_{max} = 525 ± 20 nm, 145 lm @700mA, *P* = 1.0 W).

Reaction monitoring. All reactions were monitored by thin layer chromatography (TLC) on alumina plates coated with silica gel (Merck silica gel plates 60 F_{254}, 0.2 mm) and visualized by UV light excitation (λ = 254 nm or λ = 366 nm). Preparative thin layer chromatography (PTLC) was performed on glass plates (20 × 20 cm) coated with silica gel 60 F_{254} (20 g, particle size 40–63 µm).

Chromatography. Flash column chromatography was carried out on a Biotage Isolera One automated flash purification system with UV/Vis detector using Sigma Aldrich MN silica gel 60 M (particle size 40–63 µm). Gas Chromatography was done on a GC 7890 from Agilent Technologies. Injector temperature (splitinjection: 40:1 split): 250°C. Detection temperature: 300°C (FID). A capillary column (Varian Factor Four VF-5MS / 30 m × 0.25 mm / 0.2 µm film) was used. Carrier gas: Helium with a flow rate of 1 mL / min. GC measurements were made and investigated via integration of the signals obtained. Authentic samples and internal standards were used for calibration. The GC oven temperature program adjustment was the follows: the initial temperature of 40°C was kept for 3 minutes. Then the

temperature increased constantly at a rate of 15°C / min for 16 minutes. The final temperature was 280°C. This temperature was kept for 5 minutes.

NMR spectroscopy. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 (^{1}H: 300.1 MHz, ^{13}C: 75.5 MHz, T = 300 K) and a Bruker Avance 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, T = 300 K) spectrometer equipped with a robotic sampler. Data for ^{1}H-NMR are reported as follows: chemical shift, multiplicity, integration, and coupling constant. Chemical shifts are reported in δ [ppm] relative to tetramethylsilane (TMS) as the external standard. Characterization of the signals: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, m = multiplet, bs = broad singlet. The relative number of protons is determined by integration. Coupling constants *J* are given in Hertz [Hz]. Data for ^{13}C-NMR are reported in terms of chemical shift. Error of reported values: chemical shift 0.01 ppm for ^{1}H-NMR, 0.1 ppm for ^{13}C-NMR, coupling constant 0.1 Hz. The solvent used is reported for each spectrum.

Mass spectrometry. Mass spectra were recorded on Finnigan MAT95 (EI-MS), Finnigan MAT SSQ 710 A (CI-MS), Agilent Q-TOF 6540 UHD (ESI-MS) or ThermoQuest Finnigan TSQ 7000 (ESI-MS) spectrometer.

Absorption spectroscopy. UV/Vis absorption spectra were recorded using a Varian Cary BIO 50 UV/VIS/NIR spectrometer and 10 mm quartz cuvettes (Hellma).

Cyclic voltammetry. CV has been measured with an Autolab potentiostat using a glassy carbon working electrode, a platinum wire as the counter electrode, and a silver wire as the reference electrode. Tetrabutylammonium tetrafluoroborate (c = 0.1 M) was the conducting salt unless otherwise noted. The solvent is reported for each cyclic voltammogram. The step potential was 50 mV / s. The concentration of analytes was 0.01 M. Ferrocene (c = 0.01 M) was used as the internal standard. The solution was degassed before the measurement by a stream of argon.

Yields. All yields reported are averages of at least two experimental runs.

Absorption Spectra of Frequently Used Photocatalysts

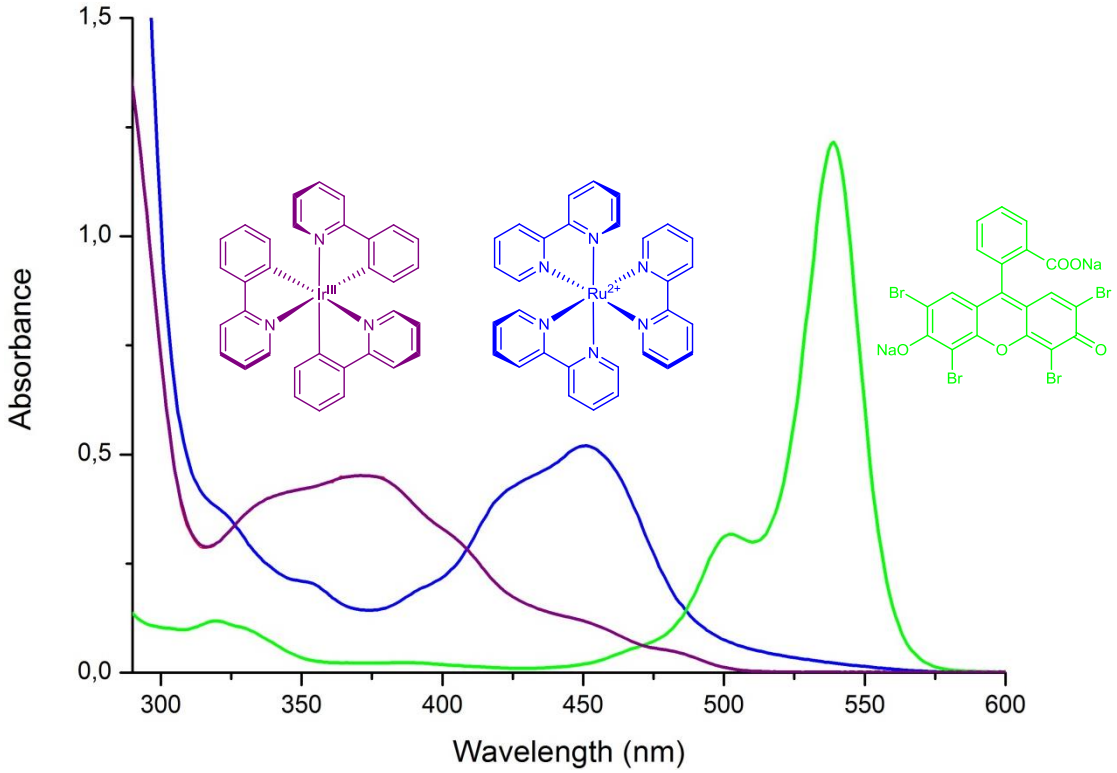


Figure 11: Absorption spectra of different photocatalysts: *fac*-Ir(ppy)$_3$ (purple), [Ru(bpy)$_3$]$^{2+}$ (blue), and Eosin Y (green). All spectra were recorded in acetonitrile (c = 2 · 10^{-5} M).

Emission Spectra of High-Power Light-Emitting Diodes

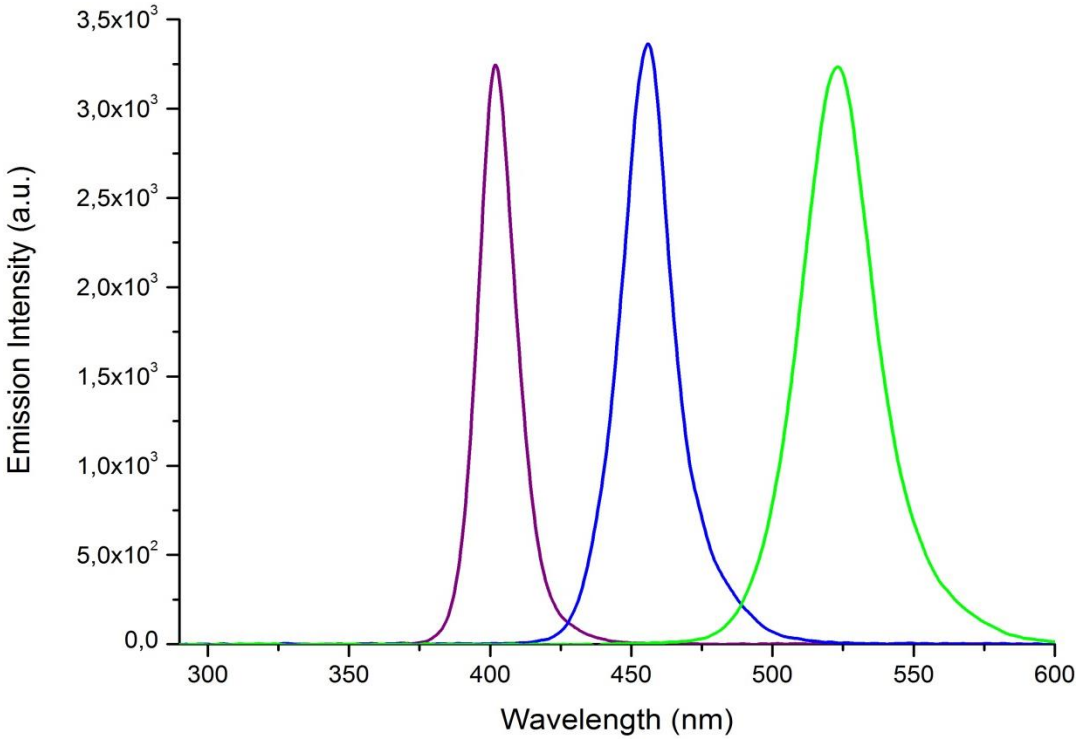


Figure 12: Emission spectra of LEDs of different colors. Left: purple (λ_{max} = 400 ± 10 nm), middle: blue (λ_{max} = 455 ± 15 nm), and right: green (λ_{max} = 525 ± 20 nm) LED.

Irradiation Setup for Photocatalytic Experiments

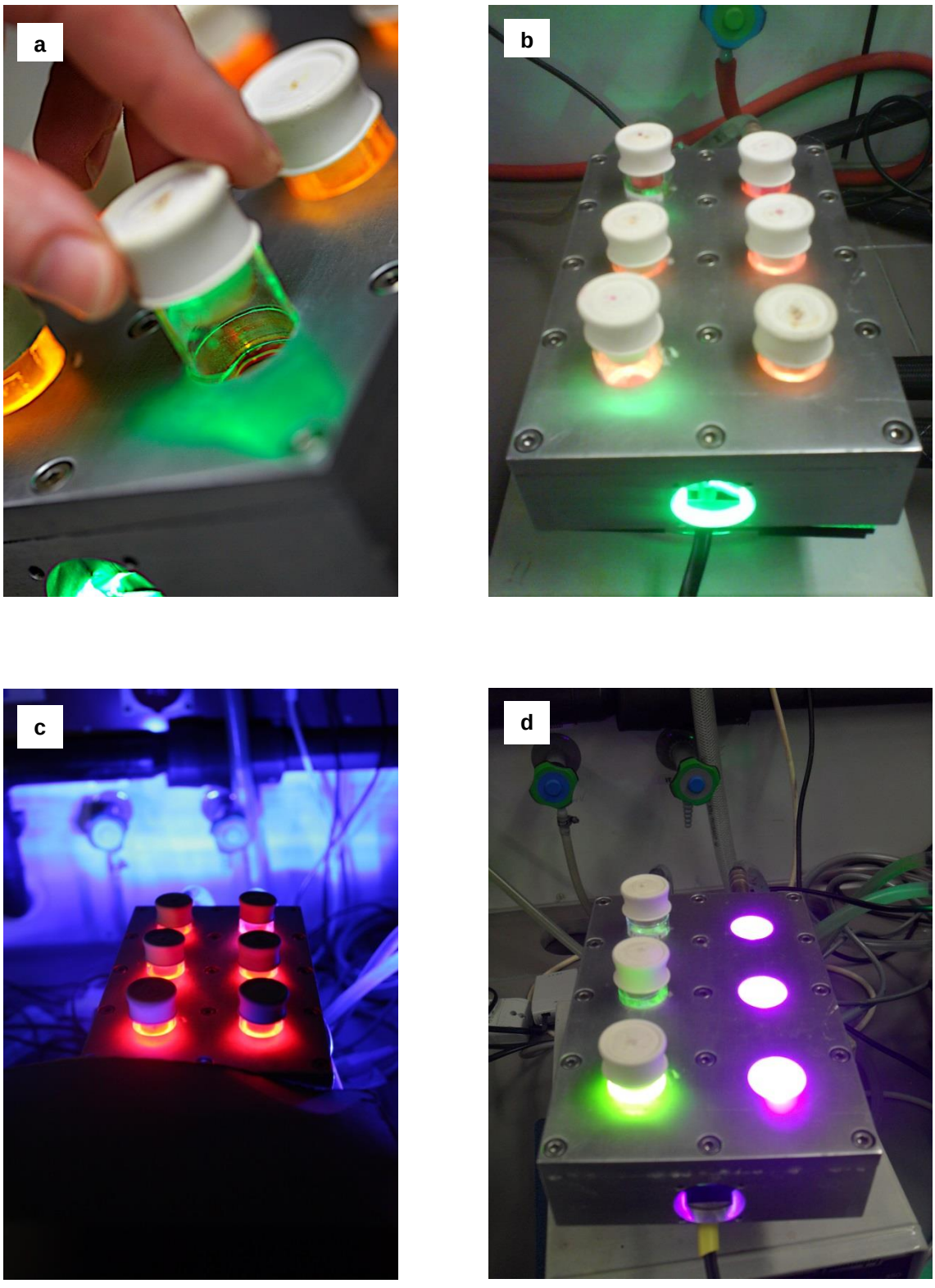


Figure 13: Irradiation setup. Sealed vessels in a cooling block were irradiated on an exchangeable array with six high power LEDs. [1]

[1] Photograph a) was taken by Johannes Beutler, photographs b), c), and d) by Peter Schroll.

***General Procedure for the Preparation of Arenediazonium Tetrafluoroborates* 1a – p[188]**

The appropriate aniline (1.0 equiv., 10 mmol) was dissolved in a mixture of distilled water (6 mL) and hydrofluoroboric acid (32%, 1.0 equiv., 10 mmol, 5.3 mL). After cooling the reaction mixture to 0°C sodium nitrite (1.0 equiv., 10 mmol, 0.69 g) in water (1.5 mL) was added dropwise. The mixture was stirred for two hours and the resulting thick precipitate was collected by filtration. Purification of the diazonium tetrafluoroborate was achieved by repeated dissolving in a minimum amount of acetone and precipitation by addition of diethyl ether until the product was obtained as a white solid. The product was filtered, washed three times with diethyl ether and dried in vacuo.

General Procedure for Photocatalytic Arylation Reactions in Homogeneous Solution

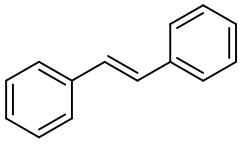
A 5 mL reaction vessel with a magnetic stirring bar was equipped with $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.01 equiv., 2.0 µmol, 1.5 mg), freshly prepared arene-diazonium tetrafluoroborate **1** (1.0 equiv., 0.2 mmol), unsaturated compound **2** (5.0 equiv., 1.0 mmol), and dry DMSO (1.0 mL). The mixture was degassed by "freeze-pump-thaw" technique (three cycles) and irradiated with a blue high-power LED (λ_{max} = 455 ± 15 nm, P = 3.0 W) for two hours. A constant temperature of 20°C was adjusted by a cooling block. Nitrogen evolution was observed right after the start of irradiation. The yield of the reaction was determined via pathway a) or b).

a) *GC-analysis:* The reaction mixture was filtered and a sample for GC analysis was prepared by diluting the reaction mixture (500 µL) with DMSO (250 µL) and a stock solution of naphthalene (250 µL, β = 15 mg/mL in DMSO) as the standard. The yield was determined by integration of the peaks in the gas chromatogram.
b) *Isolation and purification:* The reaction mixture was diluted with water (4 ml) and extracted with diethyl ether (3 × 5 mL). The combined organic layer was concentrated in vacuum. Traces of water were removed by lyophilization. Purification of the crude product was achieved by preparative thin-layer

chromatography on silica gel 60 F_{254} or flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent.

2.4.2 Photoproducts

trans-Stilbene (3a)[189]



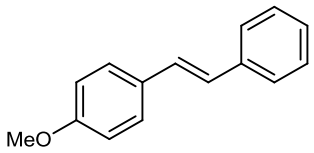
3a

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.17 (s, 2H), 7.28 – 7.36 (m, 2H), 7.37 – 7.46 (m, 4H), 7.53 – 7.61 (m, 4H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 126.7, 127.8, 128.8, 137.5.

MS (EI): *m/z* (%) = 180.1 (100) [$M^{\bullet+}$].

(*E*)-1-Methoxy-4-styrylbenzene (3b)[190]



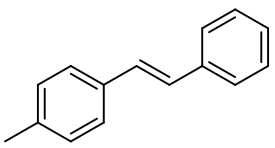
3b

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.77 (s, 3H), 6.95 (m, 2H), 7.09 (d, *J* = 16.5 Hz, 1H), 7.19 (d, *J* = 16.5 Hz, 1H), 7.24 (d, *J* = 7.5, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.55 (m, 4H).

^{13}C-NMR (100 MHz, $CDCl_3$): 55.2, 114.0, 126.2, 126.5, 127.1, 127.6, 128.1, 128.5, 130.1, 137.6, 159.2.

MS (EI): *m/z* (%) = 210.1 (100) [$M^{\bullet+}$], 195.1 (13) [$M^{\bullet+} - CH_3^{\bullet}$].

(*E*)-1-Methyl-4-styrylbenzene (3c)[189]



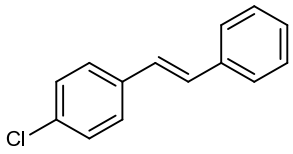
3c

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.38 (s, 3H), 7.05 (d, *J* = 16.5 Hz, 1H), 7.13 (d, *J* = 16.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.29 (m, 1H), 7.34 - 7.39 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.52 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 21.4, 126.5, 126.6, 127.5, 127.8, 128.7, 128.8, 129.4, 129.5, 134.7, 137.7.

MS (EI): *m/z* (%) = 194.1 (100) [$M^{\bullet+}$], 179.1 (85) [$M^{\bullet+} - CH_3^{\bullet}$].

(*E*)-1-Chloro-4-styrylbenzene (3d)[190]



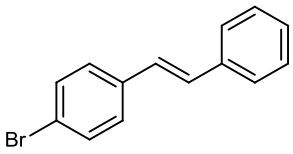
3d

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.04 (d, *J* = 18.5 Hz, 1H), 7.10 (d, *J* = 18.5 Hz, 1H), 7.28 (t, *J* = 6.9 Hz, 1H), 7.33 (m, 2H), 7.37 (t, *J* = 6.9 Hz, 2H), 7.44 (m, 2H), 7.51 (d, *J* = 6.9 Hz, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 126.6, 127.4, 127.7, 127.9, 128.7, 128.8, 129.3, 133.2, 135.9, 137.0.

MS (EI): *m/z* (%) = 214.1 (70) [$M^{\bullet+}$], 179.1 (100) [$M^{\bullet+} - Cl^{\bullet}$].

(*E*)-1-Bromo-4-styrylbenzene (3e)[190]



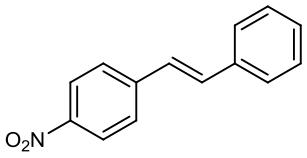
3e

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.51 (d, *J* = 12.2 Hz, 1H), 6.64 (d, *J* = 12.2 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.23 (m, 5H), 7.34(d, *J* = 8.4 Hz, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 121.3, 126.6, 127.4, 127.9, 128.0, 128.8, 129.4, 131.8, 136.3, 137.0.

MS (EI): *m/z* (%) = 258.0 (40) [$M^{\bullet+}$], 178.1 (100) [$M^{\bullet+} - Br^{\bullet}$].

(*E*)-1-Nitro-4-styrylbenzene (3f)[190]



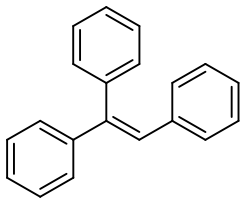
3f

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.14 (d, *J* = 16.3 Hz, 1H), 7.28 (d, *J* = 16.3 Hz, 1H), 7.29 – 7.46 (m, 3H), 7.56 (m, 2H), 7.64 (m, 2H), 8.22 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 124.3, 126.4, 127.0, 127.2, 129.0, 129.1, 133.5, 136.3, 144.0,146.9.

MS (EI): *m/z* (%) = 225.1 (86) [$M^{\bullet+}$], 178.1 (100) [$M^{\bullet+}$ – HNO_2].

Triphenylethene (3g)[191, 192]



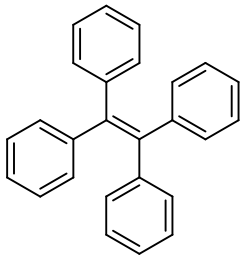
3g

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.00 (s, 1H), 7.03 – 7.08 (m, 2H), 7.11 – 7.17 (m, 3H), 7.21 – 7.25 (m, 2H), 7.30 – 7.38 (m, 8H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 126.9, 127.5, 127.6, 127.7, 128.1, 128.3, 128.4, 128.8, 129.7, 130.5, 137.5, 140.5, 142.7, 143.6.

MS (EI): *m/z* (%) = 256.2 (100) [$M^{\bullet+}$], 179.2 (31) [$M^{\bullet+}$ – $C_6H_5^+$].

Tetraphenylethene (3h)[193]



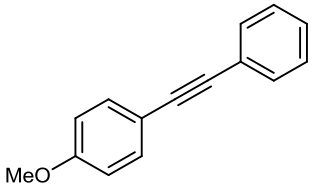
3h

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.01 – 7.06 (m, 8H), 7.08 – 7.13 (m, 12H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 126.5, 127.8, 131.5, 141.1, 143.9.

MS (EI): *m/z* (%) = 332.2 (100) [$M^{\bullet+}$].

1-Methoxy-4-(phenylethynyl)benzene (13a)[193]



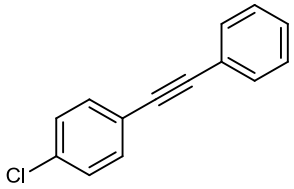
13a

^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 3.79 (s, 3H), 6.09 (m, 2H), 7.40 (m, 3H), 7.48 – 7.53 (m, 4H).

^{13}C-NMR (100 MHz, DMSO-d_6): δ [ppm] = 55.3, 87.9, 89.5, 114.2, 114.4, 122.7, 128.4, 128.7, 131.2, 132.9, 159.6.

MS (EI): *m/z* (%) = 208.2 (100) [$M^{\bullet+}$], 193.1 (48) [$M^{\bullet+} - CH_3^{\bullet}$], 165.1 (40) [$M^{\bullet+} - CH_3^{\bullet} - CO$].

1-Chloro-4-(phenylethynyl)benzene (13b)[194]



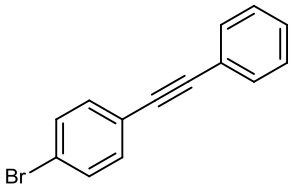
13b

^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 7.40 – 7.45 (m, 3H), 7.47 – 7.51 (m, 2H), 7.53 – 7.59 (m, 4H).

^{13}C-NMR (100 MHz, DMSO-d_6): δ [ppm] = 88.1, 90.3, 121.1, 122.0, 128.8, 128.9, 129.0, 131.4, 133.1, 133.5.

MS (EI): *m/z* (%) = 212.1 (100) [$M^{\bullet+}$], 176.1 (35) [$M^{\bullet+} - Cl^{\bullet}$].

1-Bromo-4-(phenylethynyl)benzene (13c)[195]



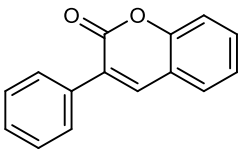
13c

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.33 – 7.36 (m, 3H), 7.38 – 7.42 (m, 2H), 7.46 – 7.51 (m, 2H), 7.53 – 7.56 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 88.4, 90.6, 122.4, 122.6, 123.0, 128.5, 128.6, 131.7, 131.8, 133.2.

MS (EI): *m/z* (%) = 256.0 (100) [$M^{\bullet+}$], 176.0 (75) [M – HBr]$^{\bullet+}$.

3-Phenyl-2*H*-chromen-2-one (19a)[196]



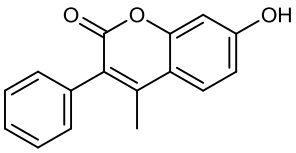
19a

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.27 – 7.33 (m, 1H), 7.35 – 7.39 (m, 2H), 7.42 – 7.46 (m, 2H), 7.52 – 7.57 (m, 2H), 7.69 – 7.73 (m, 2H), 7.82 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 116.5, 119.7, 124.5, 127.9, 128.4, 128.5, 128.6, 128.9, 131.4, 134.7, 139.9, 153.6, 160.6.

MS (EI): *m/z* (%) = 222.1 (100) [$M^{\bullet+}$], 194.1 (78) [$M^{\bullet+}$ – $CO^{\bullet}$].

7-Hydroxy-4-methyl-3-phenyl-2*H*-chromen-2-one (19b)[197]



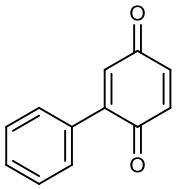
19b

^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 2.20 (s, 3H), 6.75 (d, $^{4}J_{H,H}$ = 2.4 Hz, 1H), 6.85 (dd, $^{3}J_{H,H}$ = 8.8 Hz, $^{4}J_{H,H}$ = 2.4 Hz, 1H), 7.26 – 7.31(m, 2H), 7.37 – 7.46 (m, 3H), 7.67 (d, $^{3}J_{H,H}$ = 8.8 Hz, 1H), 10.54 (s, 1H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 16.4, 102.0, 112.4, 113.1, 122.4, 127.2, 127.7, 128.1, 130.4, 134.9, 148.3, 153.9, 160.3, 160.9.

MS (EI): *m/z* (%) = 252.1 (100) [$M^{\bullet+}$], 224.1 (84) [$M^{\bullet+}$ – $CO^{\bullet}$].

[1,1′-Biphenyl]-2,5-dione (21a)[198, 199]



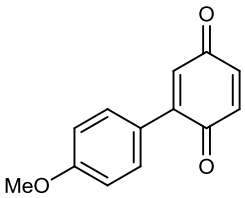
21a

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.83 – 6.89 (m, 3H), 7.42 – 7.51 (m, 5H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 127.9, 128.7, 129.4, 130.3, 132.8, 136.4, 137.2, 142.2, 187.8, 188.7.

MS (EI): *m/z* (%) = 184.1 (100) [$M^{\bullet+}$], 156.1 (60) [$M^{\bullet+} - CO^{\bullet}$], 128.1 (48) [$M^{\bullet+} - 2CO^{\bullet}$].

4′-Methoxy-[1,1′-biphenyl]-2,5-dione (21b)[200]



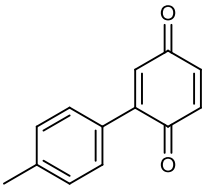
21b

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.85 (s, 3H), 6.78 (s, 1H), 6.80 – 6.82 (m, 2H), 6.92 – 6.99 (m, 2H), 7.44 – 7.51 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.5, 114.2, 125.0, 130.9, 131.1, 136.3, 137.1, 145.2, 161.4, 187.1, 187.7.

MS (EI): *m/z* (%) = 214.1 (100) [$M^{\bullet+}$], 186.1 (19) [$M^{\bullet+} - CO^{\bullet}$].

4′-Methyl-[1,1′-biphenyl]-2,5-dione (21c)[200, 201]



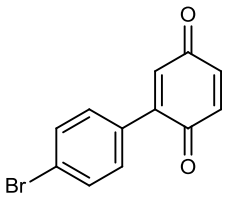
21c

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.40 (s, 3H), 6.81 – 6.86 (m, 3H), 7.26 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2H), 7.39 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 21.5, 129.3, 129.5, 129.9, 132.1, 136.4, 137.2, 140.7, 146.0, 187.0, 187.8.

MS (EI): *m/z* (%) = 198.0 (100) [$M^{\bullet+}$], 183.0 (12) [$M^{\bullet+} - CH_3^{\bullet}$], 170.1 (38) [$M^{\bullet+} - CO^{\bullet}$].

4′-Bromo-[1,1′-biphenyl]-2,5-dione (21e)[202]



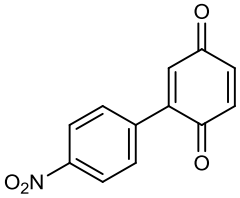
21e

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.83 – 6.87 (m, 3H), 7.32 – 7.39 (m, 2H), 7.55 – 7.62 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 125.1, 130.9, 131.6, 132.0, 132.8, 136.5, 137.2, 145.0, 186.4, 187.5.

MS (EI): *m/z* (%) = 262.0 (10) [$M^{\bullet+}$], 183.1 (100) [$M^{\bullet+} - Br^{\bullet}$].

4′-Nitro-[1,1′-biphenyl]-2,5-dione (21f)[200]



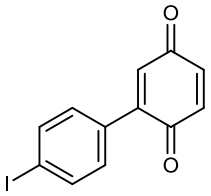
21f

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.87 – 6.96 (m, 3H), 7.62 – 7.69 (m, 2H), 8.25 – 8.33 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 123.8, 130.4, 134.2, 136.7, 137.1, 138.9, 144.0, 148.8, 185.7, 187.0.

MS (EI): *m/z* (%) = 229.0 (74) [$M^{\bullet+}$], 212.1 (80) [$M^{\bullet+} - OH^{\bullet}$], 183.1 (72) [$M^{\bullet+} - HNO_2$].

4′-Iodo-[1,1′-biphenyl]-2,5-dione (21g)[200]



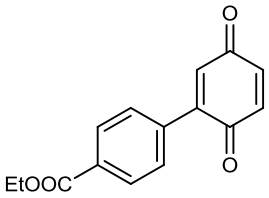
21g

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.80 – 6.91 (m, 3H), 7.19 – 7.24 (m, 2H), 7.77 – 7.82 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 127.1, 131.0, 132.2, 132.8, 136.5, 137.2, 137.9, 145.1, 186.3, 187.5.

MS (EI): *m/z* (%) = 310.0 (30) [$M^{\bullet+}$], 183.0 (100) [$M^{\bullet+} - I^{\bullet}$].

Ethyl 2′,5′-dioxo-2′,5′-dihydro-[1,1′-biphenyl]-4-carboxylate (21h)[203]



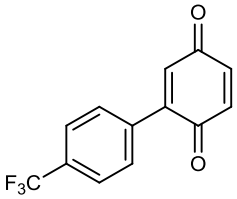
21h

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.41 (t, $^3J_{H,H}$ = 7.1 Hz, 3H), 4.40 (q, $^3J_{H,H}$ = 7.1 Hz, 2H), 6.84 – 6.91 (m, 3H), 7.51 – 7.57 (m, 2H), 8.08 – 8.13 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 14.3, 61.3, 129.3, 129.6, 130.2, 131.8, 133.4, 136.4, 137.1, 145.1, 166.0, 186.1, 187.3.

MS (EI): *m/z* (%) = 256.1 (34) [$M^{\bullet+}$], 228.1 (20) [$M^{\bullet+} - C_2H_4$], 211.0 (82) [$M^{\bullet+} - C_2H_5O^{\bullet}$].

4′-(Trifluoromethyl)-[1,1′-biphenyl]-2,5-dione (21i)[200]



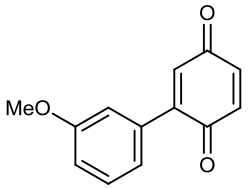
21i

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.85 – 6.93 (m, 3H), 7.59 (dd, $^{3}J_{H,H}$ = 8.8 Hz, $^{4}J_{H,H}$ = 0.7 Hz, 2H), 7.71 (dd, $^{3}J_{H,H}$ = 8.8 Hz, $^{4}J_{H,H}$ = 0.7 Hz, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 122.1, 125.6, 129.8, 132.3, 133.8, 136.2, 136.6, 137.1, 144.8, 186.2, 187.3.

MS (EI): *m/z* (%) = 252.0 (83) [$M^{\bullet+}$], 233.0 (14) [$M^{\bullet+} - F^{\bullet}$], 224.0 (35) [$M^{\bullet+}$ – CO].

3′-Methoxy-[1,1′-biphenyl]-2,5-dione (21j)[204]



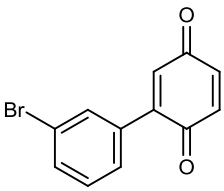
21j

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.84 (s, 3H), 6.79 – 6.89 (m, 3H), 6.98 – 7.02 (m, 2H), 7.03 – 7.07 (dt, $^{3}J_{H,H}$ = 7.7 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 1H), 7.36 (dd, $^{3}J_{H,H}$ = 8.9 Hz, $^{3}J_{H,H}$ = 7.7 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.5, 114.9, 116.0, 121.8, 129.8, 132.9, 134.0, 136.3, 137.2, 145.9, 159.6, 186.7, 187.8.

MS (EI): *m/z* (%) = 214.1 (100) [$M^{\bullet+}$], 199.1 (64) [$M^{\bullet+} - CH_3^{\bullet}$], 171.1 (38) [$M^{\bullet+} - CH_3^{\bullet} - CO^{\bullet}$].

3′-Bromo-[1,1′-biphenyl]-2,5-dione (21k)[200]



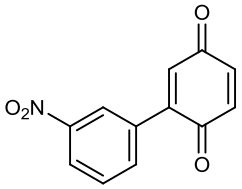
21k

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.83 – 6.87 (m, 3H), 7.32 (t, $^{3}J_{H,H}$ = 7.8 Hz, 1H), 7.39 (dt, $^{3}J_{H,H}$ = 7.8 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H), 7.57 (dt, $^{3}J_{H,H}$ = 7.8 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H), 7.62 (t, $^{4}J_{H,H}$ = 1.7 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 122.7, 128.0, 130.2, 132.2, 133.2, 133.3, 134.7, 136.5, 137.1, 144.7, 186.2, 187.4.

MS (EI): *m/z* (%) = 262.0 (5) [$M^{\bullet+}$], 183.0 (100) [$M^{\bullet+}$ – $Br^{\bullet}$], 155.1 (15) [$M^{\bullet+}$ – $Br^{\bullet}$ – $CO^{\bullet}$], 127.1 (11) [$M^{\bullet+}$ – $Br^{\bullet}$ – 2$CO^{\bullet}$].

3′-Nitro-[1,1′-biphenyl]-2,5-dione (21l)[203]



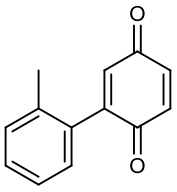
21l

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.89 – 6.96 (m, 3H), 7.65 (t, $^3J_{H,H}$ = 8.0 Hz, 1H), 7.80 – 7.84 (dt, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H), 8.32 (ddd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.9 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H), 8.37 (t, $^4J_{H,H}$ = 1.9 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 123.1, 124.4, 124.8, 129.8, 134.0, 134.2, 135.2, 136.8, 137.1, 143.8, 185.8, 187.0.

MS (EI): *m/z* (%) = 229.1 (73) [$M^{\bullet+}$], 212.1 (68) [$M^{\bullet+}$ – $OH^{\bullet}$], 183.1 (87) [$M^{\bullet+}$–$NO_2^{\bullet}$].

2′-Methyl-[1,1′-biphenyl]-2,5-dione (21m)[200]



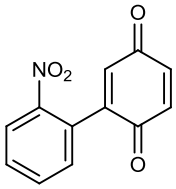
21m

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.18 (s, 3H), 6.72 (d, $^3J_{H,H}$ = 2.0 Hz, 1H), 6.86 d, $^3J_{H,H}$ = 2.0 Hz, 1H), 6.87 (s, 1H), 7.04 – 7.14 (m, 2H), 7.26 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 20.5, 126.0, 129.4, 129.7, 130.6, 131.1, 134.7, 136.5, 136.7, 137.0, 148.6, 186.3, 187.9.

MS (EI): *m/z* (%) = 198.1 (100) [$M^{\bullet+}$], 197.1 (54) [$M^{\bullet+}$ – $H^{\bullet}$].

2′-Nitro-[1,1′-biphenyl]-2,5-dione (21n)[205]



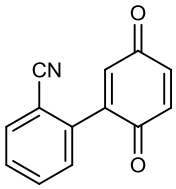
21n

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.82 (dd, $^{4}J_{H,H}$ = 1.6 Hz, $^{5}J_{H,H}$ = 0.8 Hz, 1H), 6.87 – 6.89 (m, 2H), 7.39 (dd, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 1.4 Hz, 1H), 7.66 (dt, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 1H), 7.75 (dt, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 1.4 Hz, 1H), 8.21 (dd, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 125.0, 129.0, 131.1, 131.4, 131.9, 134.3, 136.8, 137.1, 147.1, 148.3, 184.7, 187.1.

MS (EI): *m/z* (%) = 229.1 (1) [$M^{\bullet+}$], 212.1 (8) [$M^{\bullet+}$ – $OH^{\bullet}$], 199.1 (11) [$M^{\bullet+}$ – $NO^{\bullet}$], 183.1 (71) [$M^{\bullet+}$ – $NO_2^{\bullet}$].

2′,5′-Dioxo-2′,5′-dihydro-[1,1′-biphenyl]-2-carbonitrile (21o)[202]



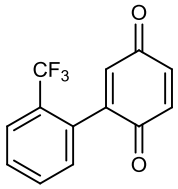
21o

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.89 – 6.95 (m, 3H), 7.40 (dd, $^{3}J_{H,H}$ = 7.7 Hz, $^{4}J_{H,H}$ = 0.9 Hz, 1H), 7.57 (dt, $^{3}J_{H,H}$ = 7.7 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 1H), 7.69 (dt, $^{3}J_{H,H}$ = 7.7 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 1H), 7.79 (dd, $^{3}J_{H,H}$ = 7.7 Hz, $^{4}J_{H,H}$ = 0.9 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 112.7, 117.5, 130.0, 130.6, 132.8, 133.5, 135.5, 136.5, 136.8, 136.9, 144.3, 185.1, 186,8.

MS (EI): *m/z* (%) = 209.1 (64) [$M^{\bullet+}$], 181.1 (23) [$M^{\bullet+}$ – $CO^{\bullet}$].

2′-(Trifluoromethyl)-[1,1′-biphenyl]-2,5-dione (21p)[200]



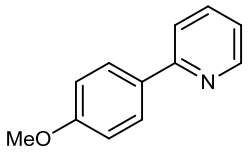
21p

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 6.73 (dd, $^{4}J_{H,H}$ = 1.7 Hz, $^{5}J_{H,H}$ = 0.5 Hz, 1H), 6.82 – 6.91 (m, 2H), 7.23 (dd, $^{3}J_{H,H}$ = 7.3 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 1H), 7.59 (m, 2H), 7.76 (dd, $^{3}J_{H,H}$ = 7.5 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 122.1, 126.6, 126.7, 129.6, 129.7, 130.7, 131.8, 134.6, 136.7, 136.8, 146.5, 185.9, 187.1.

MS (EI): *m/z* (%) = 252.1 (85) [$M^{\bullet+}$], 224.0 (32) [$M^{\bullet+}$ – $CO^{\bullet}$].

2-(4-Methoxyphenyl)pyridine (23a)[206]



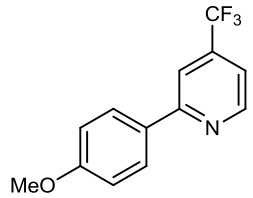
23a

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.87 (s, 3H), 6.98 – 7.02 (m, 2H), 7.17 (ddd, $^{3}J_{H,H}$ = 6.9 Hz, $^{3}J_{H,H}$ = 4.8 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H), 7.65 – 7.74 (m, 2H), 7.93 – 7.97 (m, 2H), 8.65 (ddd, $^{3}J_{H,H}$ = 4.8 Hz, $^{4}J_{H,H}$ = 1.7 Hz, $^{5}J_{H,H}$ = 1.0 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.5, 114.2, 120.0, 121.6, 128.3, 132.1, 136.8, 149.7, 157.2, 160.6.

MS (EI): *m/z* (%) = 185.1 (100) [$M^{\bullet+}$], 170.1 (30) [$M^{\bullet+} - CH_3^{\bullet}$], 142.1 (35) [$M^{\bullet+} - CH_3^{\bullet} - CO^{\bullet}$].

2-(4-Methoxyphenyl)-4-(trifluoromethyl)pyridine (23b)[207]



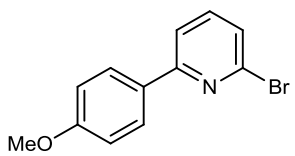
23b

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.88 (s, 3H), 7.00 – 7.05 (m, 2H), 7.38 (dd, $^{3}J_{H,H}$ = 5.1 Hz, $^{4}J_{H,H}$ = 1.4 Hz, 1H), 7.86 (d, $^{4}J_{H,H}$ = 1.4 Hz, 1H), 7.97 – 8.02 (m, 2H), 8.81 (d, $^{3}J_{H,H}$ = 5.1 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.6, 114.3, 114.5, 115.3, 116.9, 128.3, 128.5, 130.8, 150.6, 158.5, 161.3.

MS (EI): *m/z* (%) = 253.1 (100) [$M^{\bullet+}$].

2-Bromo-6-(4-methoxyphenyl)pyridine (23c)[208]



23c

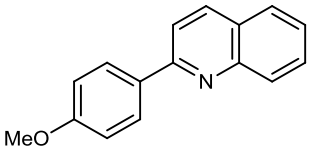
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.86 (s, 3H), 6.86 (dd, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 1.6 Hz, 1H), 6.95 – 7.00 (m, 2H), 7.14 (dd, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 1.6 Hz, 1H),

7.33 (t, $^{3}J_{H,H}$ = 7.9 Hz, 1H), 7.51 – 7.54 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.4, 112.2, 112.6, 114.3, 119.4, 128.3, 129.9, 130.7, 161.1, 166.9.

MS (EI): *m/z* (%) = 263.0 (100) [$M^{\bullet+}$].

2-(4-Methoxyphenyl)quinoline (25a)[209]



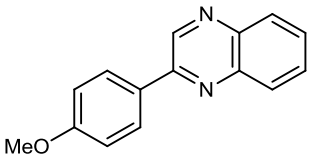
25a

^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.90 (s, 3H), 7.05 – 7.09 (m, 2H), 7.55 (ddd, $^{3}J_{H,H}$ = 8.1 Hz, $^{3}J_{H,H}$ = 6.9 Hz, $^{4}J_{H,H}$ = 1.0 Hz, 1H), 7.77 (ddd, $^{3}J_{H,H}$ = 8.5 Hz, $^{3}J_{H,H}$ = 6.9 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 1H), 7.84 (dd, $^{3}J_{H,H}$ = 8.1 Hz, $^{4}J_{H,H}$ = 1.3 Hz, 1H), 7.87 (d, $^{3}J_{H,H}$ = 8.7 Hz, 1H), 8.12 – 8.17 (m, 2H), 8.23 (dd, $^{3}J_{H,H}$ = 8.5 Hz, $^{4}J_{H,H}$ = 1.0 Hz, 1H), 8.27 (d, $^{3}J_{H,H}$ = 8.7 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 55.6, 114.6, 118.9, 126.6, 127.0, 127.7, 128.5, 129.3, 130.6, 130.8, 138.1, 147.0, 156.7, 161.5.

MS (EI): *m/z* (%) = 235.1 (100) [$M^{\bullet+}$], 220.1 (25) [$M^{\bullet+} - CH_3^{\bullet}$], 192.1 (30) [$M^{\bullet+} - CH_3^{\bullet} - CO^{\bullet}$].

2-(4-Methoxyphenyl)quinoxaline (25b)[210]



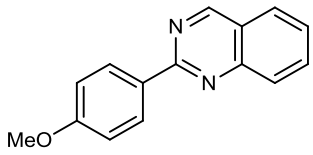
25b

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.90 (s, 3H), 7.06 – 7.11 (m, 2H), 7.68 – 7.79 (m, 2H), 8.07 – 8.13 (m, 2H), 8.15 – 8.20 (m, 2H), 9.29 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.6, 114.7, 129.0, 129.1, 129.2, 129.4, 129.5, 130.3, 141.4, 142.5, 143.2, 151.6, 161.6.

MS (EI): *m/z* (%) = 237.1 (100) [MH^{+}].

2-(4-Methoxyphenyl)quinazoline (25c′)[211]



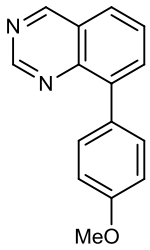
25c′

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.91 (s, 3H), 7.02 – 7.08 (m, 2H), 7.58 (dt, $^{3}J_{H,H}$ = 8.1 Hz, $^{4}J_{H,H}$ = 1.0 Hz, 1H), 7.85 – 7.92 (m, 2H), 8.04 (dd, $^{3}J_{H,H}$ = 8.1 Hz, $^{4}J_{H,H}$ = 1.0 Hz, 1H), 8.55 – 8.60 (m, 2H), 9.43 (d, $^{4}J_{H,H}$ = 0.6 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.6, 114.1, 123.5, 127.0, 127.3, 128.6, 130.3, 130.9, 134.2, 151.0, 160.6, 161.0, 162.0.

MS (EI): *m/z* (%) = 237.1 (100) [MH^+].

8-(4-Methoxyphenyl)quinazoline (25c′′)[212]



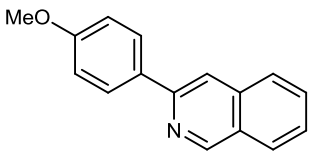
25c′′

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.89 (s, 3H), 7.04 – 7.09 (m, 2H), 7.64 – 7.69 (m, 2H), 7.72 (dd, $^{3}J_{H,H}$ = 8.1 Hz, $^{3}J_{H,H}$ = 7.2 Hz, 1H), 7.91 (dd, $^{3}J_{H,H}$ = 8.1 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 1H), 7.94 (dd, $^{3}J_{H,H}$ = 7.2 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 1H), 9.37 (s, 1H), 9.44 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.5, 114.0, 125.7, 126.4, 127.9, 130.1, 131.8, 134.2, 139.9, 148.0, 155.2, 159.7, 160.7.

MS (EI): *m/z* (%) = 237.1 (100) [MH^+].

3-(4-Methoxyphenyl)isoquinoline (27′)[213]



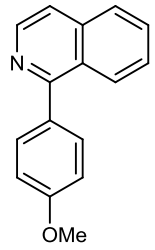
27′

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.89 (s, 3H), 7.02 – 7.07 (m, 2H), 7.65 – 7.72 (m, 3H), 7.86 (dd, $^{3}J_{H,H}$ = 8.5 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H), 8.03 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.50 – 8.55 (m, 2H), 9.26 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.6, 114.7, 120.9, 123.5, 126.6, 127.2, 127.5, 127.8, 128.4, 128.6, 128.9, 143.0, 152.1, 160.1.

MS (EI): *m/z* (%) = 235.2 (100) [$M^{\bullet+}$], 220.1 (23) [$M^{\bullet+} - CH_3^{\bullet}$], 192.2 (21) [$M^{\bullet+} - CH_3^{\bullet} - CO^{\bullet}$].

1-(4-Methoxyphenyl)isoquinoline (27′′)[214]



27′′

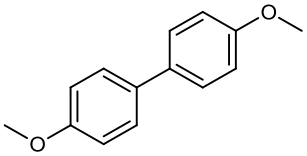
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 3.89 (s, 3H), 7.04 – 7.09 (m, 2H), 7.53 (ddd, $^{3}J_{H,H}$ = 8.2 Hz, $^{3}J_{H,H}$ = 5.7 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 1H), 7.60 (d, $^{3}J_{H,H}$ = 5.7 Hz, 1H), 7.63 – 7.70 (m, 3H), 7.86 (d, $^{3}J_{H,H}$ = 8.2 Hz, 1H), 8.14 (d, $^{3}J_{H,H}$ = 8.2 Hz, 1H), 8.59 (d, $^{3}J_{H,H}$ = 5.7 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 55.5, 113.9, 119.6, 126.8, 127.1, 127.2, 127.8, 130.0, 131.4, 132.2, 137.0, 142.3, 160.1, 160.5.

MS (EI): *m/z* (%) = 235.1 (93) [$M^{\bullet+}$], 234.1 (100) [$M^{\bullet+} - H^{\bullet}$].

2.4.3 Trapped Intermediates

4,4'-Dimethoxy-1,1'-biphenyl (8)[215] (R^1 = OMe)

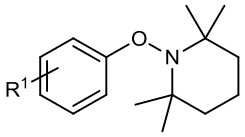


8

Only minor amount of the product was obtained that did not allow a spectroscopic characterization and product isolation.

MS (EI): *m/z* (%) = 214.1 (100) [$M^{\bullet+}$], 199.1 (32) [$M^{\bullet+} - CH_3^{\bullet}$], 183.1 (3) [$M^{\bullet+} - OCH_3^{\bullet}$], 107.1 (11) [$M^{\bullet+} - C_7H_7O^{\bullet}$].

2,2,6,6-Tetramethyl-1-phenoxypiperidine (9)[207] (R^1 = H)

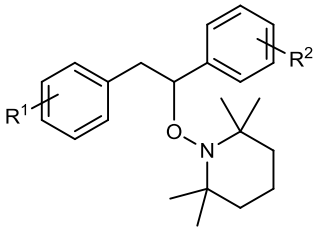


9

Only minor amount of the product was obtained that did not allow a spectroscopic characterization and product isolation.

MS (CI): *m/z* (%) = 234.2 (100) [MH^+].

1-(1,2-Diphenylethoxy)-2,2,6,6-tetramethylpiperidine (10)[216] (R^1 = R^2 = H)

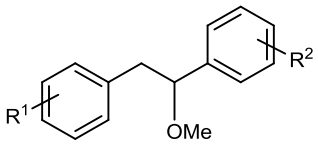


10

Only minor amount of the product was obtained that did not allow a spectroscopic characterization and product isolation.

MS (ESI): *m/z* (%) = 338.2 [MH^+].

(1-Methoxyethane-1,2-diyl)dibenzene (11a)[217] (R^1 = R^2 = H)



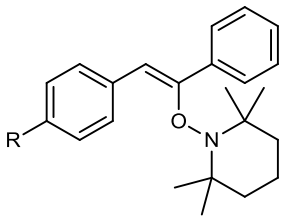
11a

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 2.89 (dd, ^2J = 13.8 Hz, ^3J = 5.9 Hz, 1H), 3.10 (dd, ^2J = 13.8 Hz, ^3J = 6.5 Hz, 1H), 3.19 (s, 3H), 4.33 (dd, ^3J = 6.5 Hz, ^3J = 5.9 Hz, 1H), 7.15 – 7.35 (m, 10 H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 44.9, 56.9, 85.2, 126.3, 126.9, 127.7, 128.2, 128.4, 129.6, 138.6, 141,8.

MS (EI): *m/z* (%) = 212.1 (1) [$M^{\bullet+}$], 181.1 (4) [$(M - OCH_3^{\bullet})^+$], 121.1 (100) [$M^+ - C_7H_7^+$], 91.1 (14) [$C_7H_7^+$], 77.1 (18) [$C_6H_5^+$].

1-((1,2-diphenylvinyl)oxy)-2,2,6,6-tetramethylpiperidine (16) (R = H)



16

Only minor amount of the product was obtained that did not allow a spectroscopic characterization and product isolation.

MS (ESI): *m/z* (%) = 336.2 [MH^+].

2.5 References

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3 PHOTOCATALYTIC SURFACE PATTERNING OF MODIFIED CELLULOSE USING DIAZONIUM SALTS AND VISIBLE LIGHT

Coumarin-functionalized cellulose sheets were chemically modified using a visible-light-catalyzed Photo-Meerwein arylation. Use of a photomask to pattern the surface resulted in directly visible images and allowed spatial resolution.

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Author contributions:
Charlie Fehl synthesized the coumarin-linked cellulose. Stephan Dankesreiter performed the solid-state UV/Vis absorption measurements. Photographs were taken by Johannes Beutler and Peter Schroll.

3.1 Introduction to Surface Modification

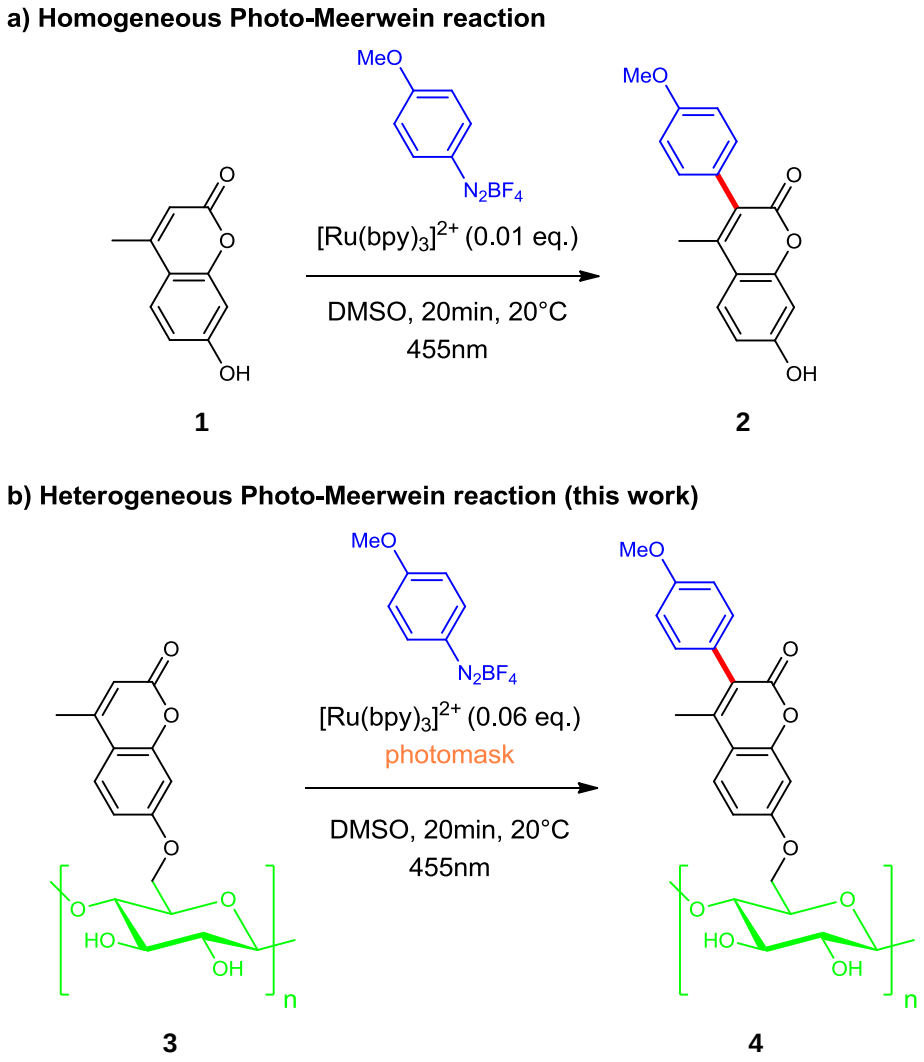
The selective functionalization of surfaces is important in many research areas. Creating defined mono- or multilayer structures requires surface patterning techniques with resolutions spanning from macroscopic to sub-nanometer scales.[218, 219] Patterned surfaces allow the development of sensor materials,[220] shape-changing materials,[221] microelectronic devices such as light-emitting displays[222] and plastic electronics,[223] as well as the production of photonic crystals,[224, 225] and are important for the study of cells.[226, 227]

The range of patterning techniques is large and can be divided into printing methods,[228] direct writing techniques,[219] electrochemical[229-231] and photochemical methods.[232] Printing methods do not require masks and include screen printing,[219] nanoimprinting,[233] microcontact printing by a stamp that transfers an inked material to the substrate,[234-236] and ink-jet printing where a jet of a polymer solution breaks up into droplets, which are deposited onto a surface and form a pattern when the solvent evaporates.[219, 228] Direct writing allows a resolution down to the submicrometer range by nanografting:[237] the tip of a scanning probe microscope scratches the surface. In photolithography, a monomer- or polymer-coated surface is exposed to photoirradiation in order to trigger photopolymerization or –decomposition.[219, 232, 238]

Modifications have been accomplished on a diverse array of surface materials. Depending on their application, it may be necessary to functionalize conductors, semiconductors, or insulators. Important materials in this respect are metals (gold), glass, carbon, graphene sheets,[239] inorganic quantum dots (CdSe,[240] TiO_2), bionanomaterials, and polymers (PVC, PET). Existing polymers can be modified with one of the above-mentioned methods, or polymerization can be initiated on a surface. Aryl radicals can induce polymerization or bind directly to the surface. Both processes have been used for surface functionalization.[241, 242]

3.2 Results and Discussion

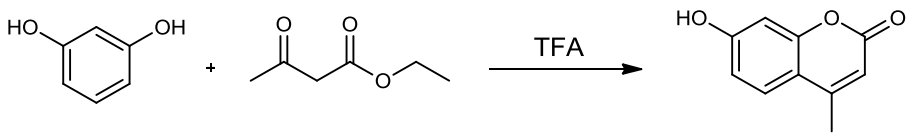
We have previously described the Photo-Meerwein arylation reaction for the homogeneous cross-coupling of an aryl diazonium salt with an unsaturated compound, activated by means of a photocatalyst and visible light (Scheme 33a). The reaction works both inter- and intramolecularly, and is suitable for the arylation of π-electron donors such as olefins, enones, enol esters, alkynes, and heteroarenes as well as σ-electron donors with various functionalized arenediazonium salts.[166, 176, 243-247] In contrast to thermal or chemical initiation of the aryl radical formation, light allows spatial control of the reaction on surfaces. We describe here the selective patterning of a modified cellulose surface using a heterogeneous visible light photocatalyzed Meerwein reaction (Scheme 33b).



Scheme 33: Homogeneous and heterogeneous Photo-Meerwein arylation.

A prerequisite for accomplishing spatial resolution is the covalent immobilization of one of the two coupling partners on the surface.[248] Suitably modified surfaces can undergo selective coupling in the presence of a solution of the second coupling partner and the photocatalyst, using a photomask to limit the irradiation area. Only irradiated parts of the surface will undergo carbon–carbon bond formation, which leads to a patterned arylated surface that can be detected by optical methods.

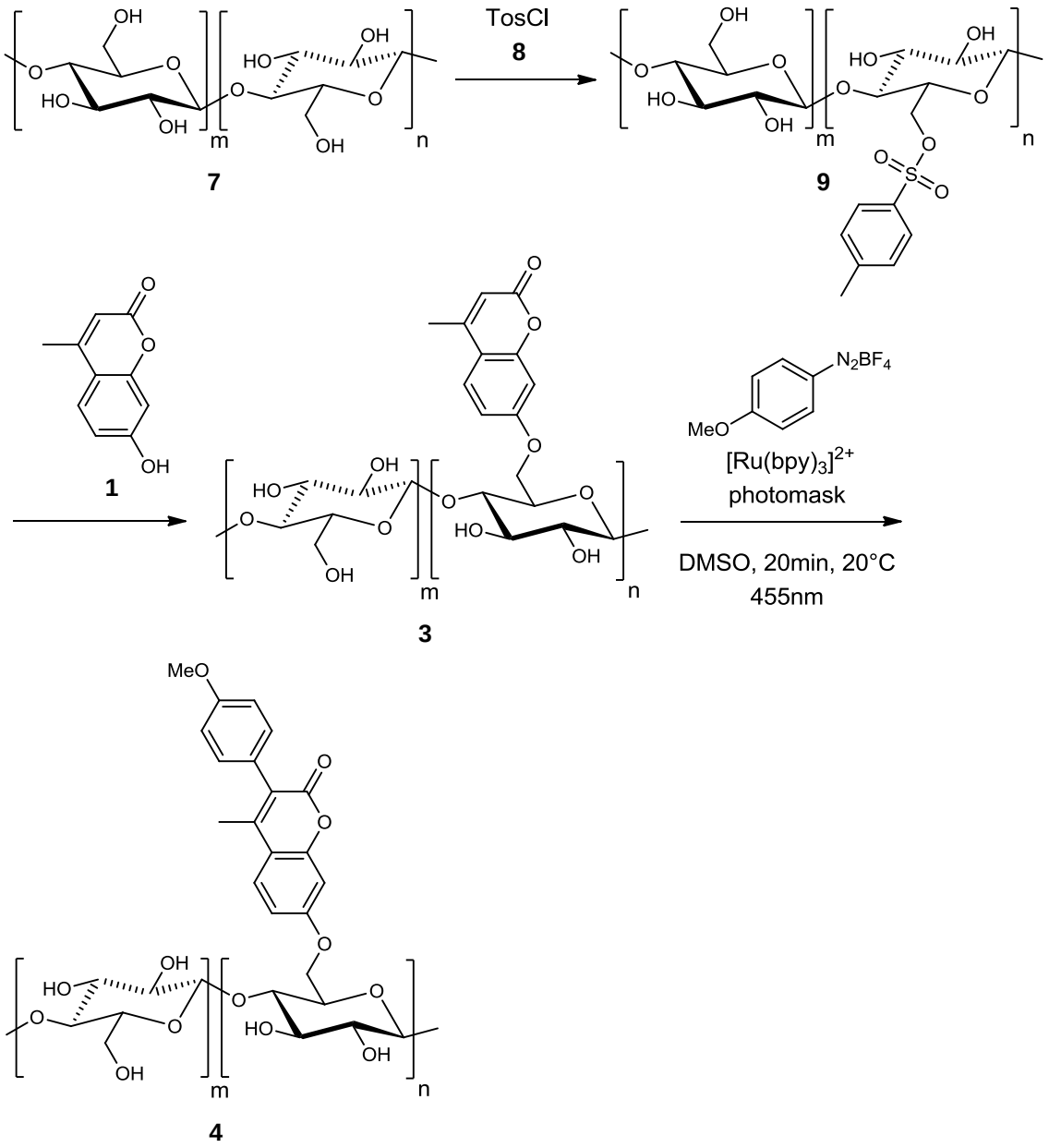
Coumarins react in a Photo-Meerwein arylation with diazonium salts in high yields.[243] The absorption and emission of the chromophore are sensitive to the local environment of the molecule,[249] which includes perichromic shifts by surface immobilization.[250] Although the parent coumarin itself absorbs only ultraviolet light, a suitable polar surface will shift the absorption considerably towards the visible region. The photocatalytic arylation of the coumarin chromophore causes an additional red-shift, easily detectable by the naked eye. We therefore selected coumarins such as **1** to functionalize a surface for subsequent photo-patterning, as the arylation reaction can be visually monitored by a color change (Scheme 34).[251]



5 **6** **1**

Scheme 34: Synthesis of substituted coumarins.

The non-conducting surface material cellulose **7** contains several hydroxyl moieties able to serve as anchors for the covalent attachment of unsaturated chromophore **1**. The 7-hydroxy group of **1** represents the linker for attachment to the cellulose polymer. From the various hydroxyl groups in cellulose, the 6′-hydroxyl group is the most reactive.[252] Coumarin derivative **1** was attached to the 6′-hydroxyl group of cellulose by tosylation and subsequent reaction with **1** to yield modified cellulose **3** (Scheme 35). The loading of cellulose with coumarin **1** was determined gravimetrically to be 21% ± 3% with respect to the amount of glucose monomers as the average of three independent experiments. The method is suitable for the modification of larger cellulose sheets. In our case, standard filter paper (45 mm in diameter) proved convenient for modification.



Scheme 35: Synthesis of functionalized cellulose sheets. A loading of 21% coumarin per glucose monomer unit indicates a ratio of *m* : *n* of about 4 : 1.

Cellulose filter paper sheets functionalized in this way were then used for photocatalytic experiments. Modified cellulose was soaked with a 0.25 M solution of *p*-methoxyphenyldiazonium tetrafluoroborate and $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bi-pyridyl) in DMSO. A nontransparent photomask covering part of the area was placed on the filter paper, and the setup was irradiated for 20 minutes with a blue high-power light-emitting diode (λ_{max} = 455 nm, *P* = 1.12 W, 700 mA). The filter paper was rinsed in methanol, water, and acetone, and dried in air. A pattern was immediately visible on the surface, as shown in Figure 14.

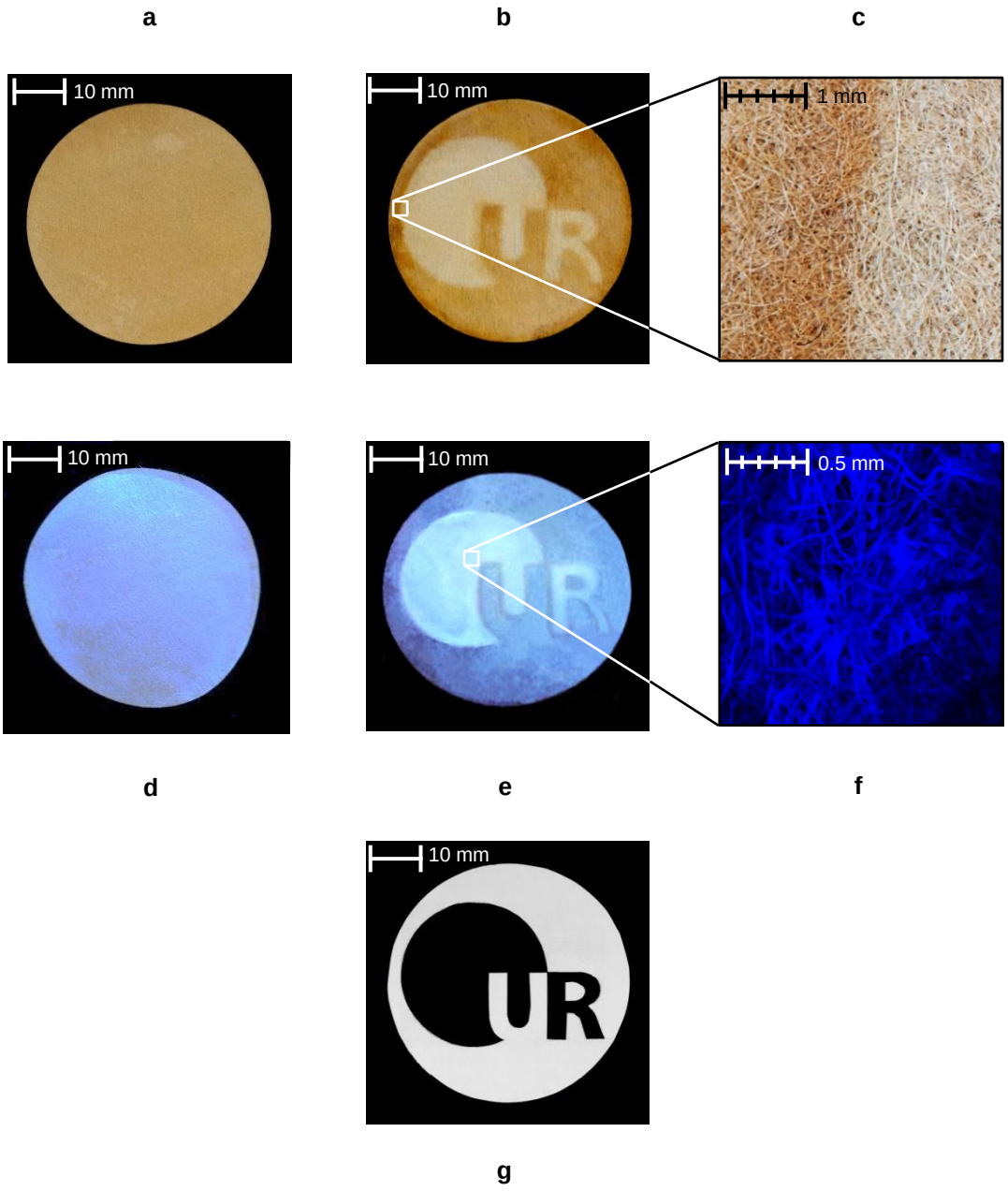


Figure 14: Patterning of modified cellulose sheets. Photographs of (a) coumarin-functionalized cellulose sheet before and (b) after photoreaction with an arenediazonium salt and $[Ru(bpy)_3]^{2+}$ as a photocatalyst through a photomask, (c) magnified boundary between illuminated and dark cellulose, (d) fluorescence emission (λ_{ex} = 366 nm) before and (e) after photoreaction through a photomask, (f) fluorescence emission of magnified cellulose fibers, (g) non-transparent white photomask on black background.

We attribute the absorption property changes to the photocatalytic arylation reaction that proceeded in irradiated areas, but not in surface areas of the cellulose sheet that were covered by the photomask. The reaction proceeded equally well with eosin Y as a metal-free photocatalyst, but the contrast of the image was lower

in this case because removal of the dye eosin Y was less effective. The reaction occured at the 3-position of coumarin **3**. The 4-methyl group in **3** had little effect on the molecule's absorption maximum, but gave additional stabilization of the intermediary formed radical, which was both in tertiary and benzylic position. A schematic description of the image formation is given in the following figure.

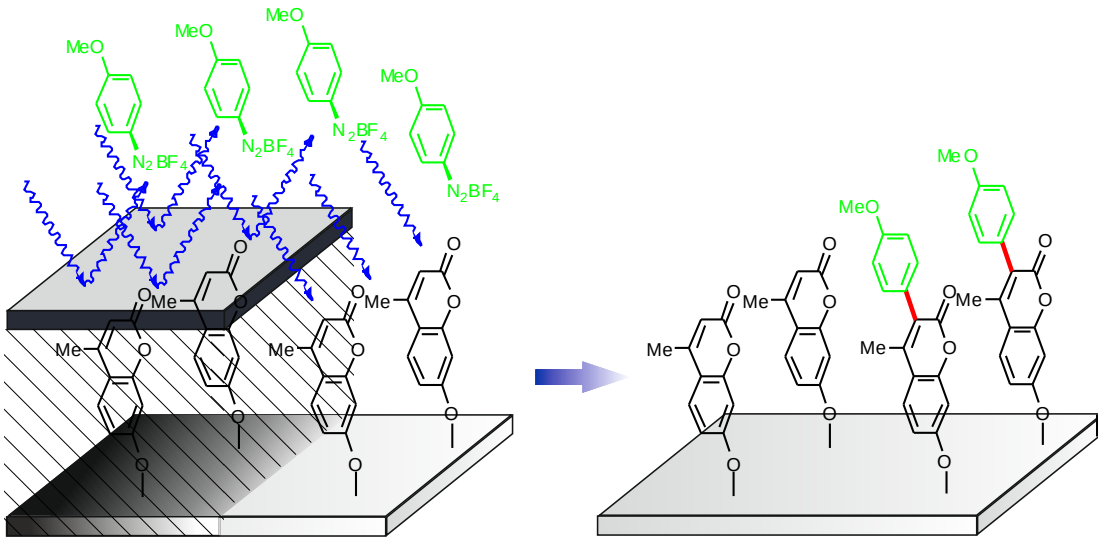


Figure 15: Schematic molecular description of image formation throughout the photoreaction. A non-transparent photomask covers part of the coumarin-modified cellulose surface. Photocatalytic arylation is only possible in irradiated parts of the surface.

Control experiments using an identical setup without either photocatalyst, aryl diazonium salt, or light showed no pattern formation on the surface, which indicated that all three reagents were indispensable for a successful photoreaction. Absorption and emission spectra of the functionalized cellulose sheets have been measured before and after the reaction. Diffuse UV/Vis reflectance spectra of the paper samples were recorded and converted into absorption spectra by applying the Kubelka–Munk transformation. Coumarin-functionalized cellulose **3** showed two absorption bands at 322 and 401 nm. After arylation, the bands of **4** were red-shifted to 349 and 404 nm, respectively. Fluorescence measurements of the cellulose paper samples (excitation wavelength λ_{ex} = 404 nm) showed two emission maxima at 421 and 496 nm before and at 438 and 505 nm after the photoreaction (Figure 16).

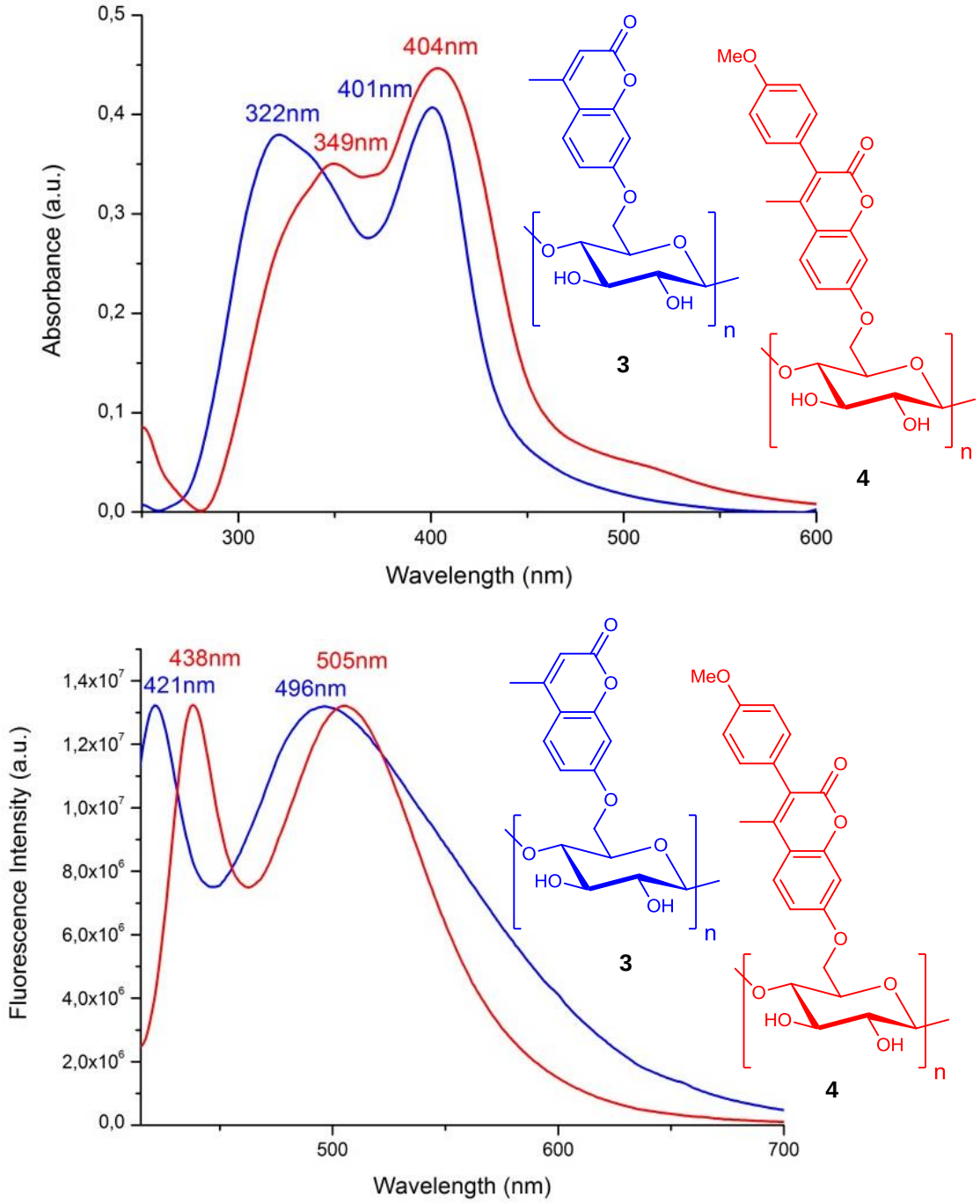


Figure 16: Absorption (top) and emission spectra (bottom) of immobilized coumarins before (blue) and after (red) the photoreaction.

For comparison, an analogous arylation reaction was performed in a homogeneous DMSO solution (Figure 17). 7-Hydroxy-4-methyl-2*H*-chromen-2-one **1** and the corresponding arylated photoproduct **2** showed absorption bands in DMSO at 292 and 318 nm before and 289 and 329 nm after the photoreaction. The absorption bands could be assigned to a π–π* transition.[253] The large bathochromic shift of about 80 nm in the heterogeneous reaction compared to the

smaller changes in the homogeneous case was rationalized by the polar environment of the cellulose surface. The emission spectrum in DMSO (excitation wavelength λ_{ex} = 318 nm) of the photoproduct **2** showed two maxima at 396 and 484 nm, while the corresponding peaks of reactant **1** were at 359 and 424 nm.

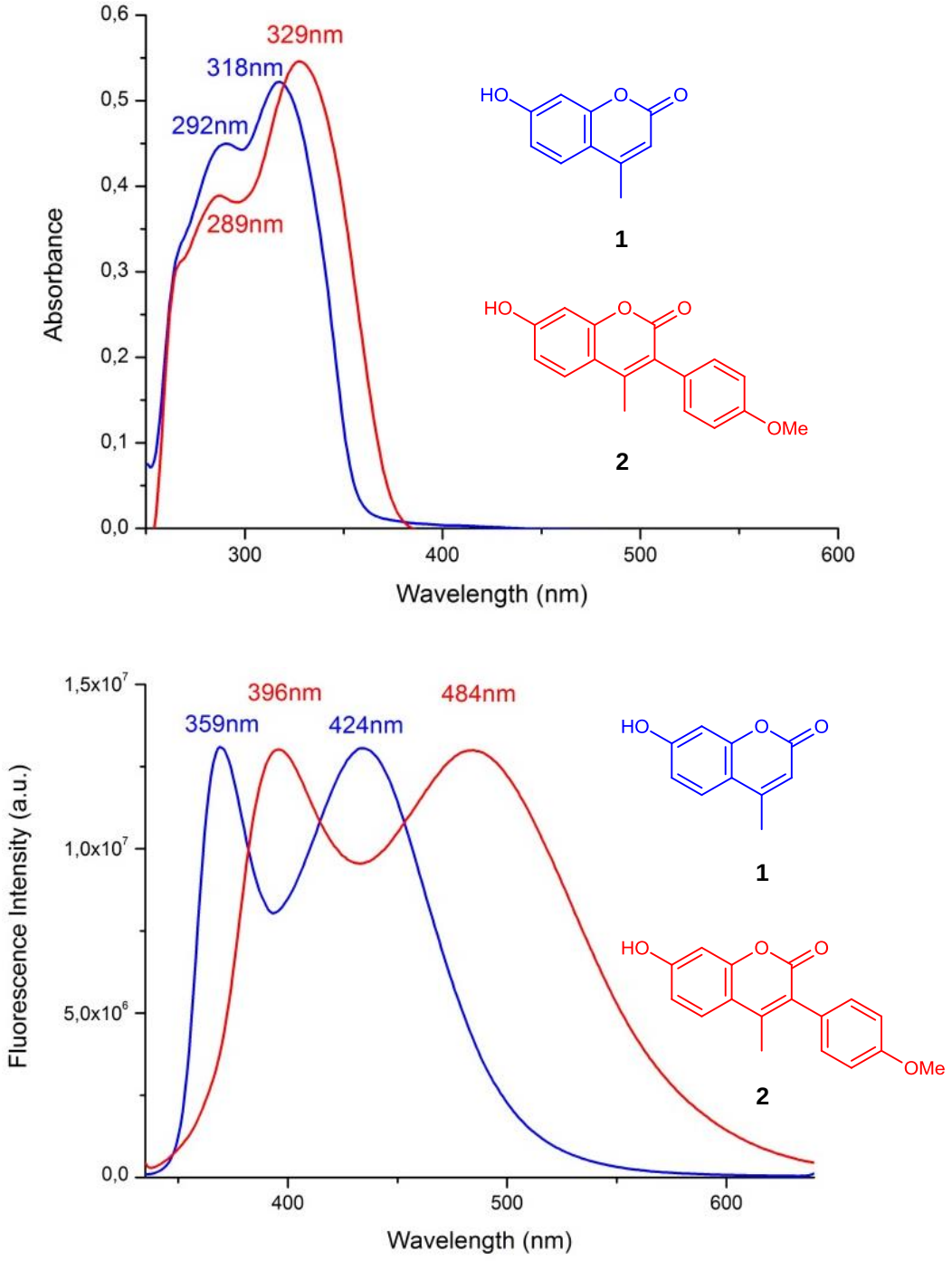
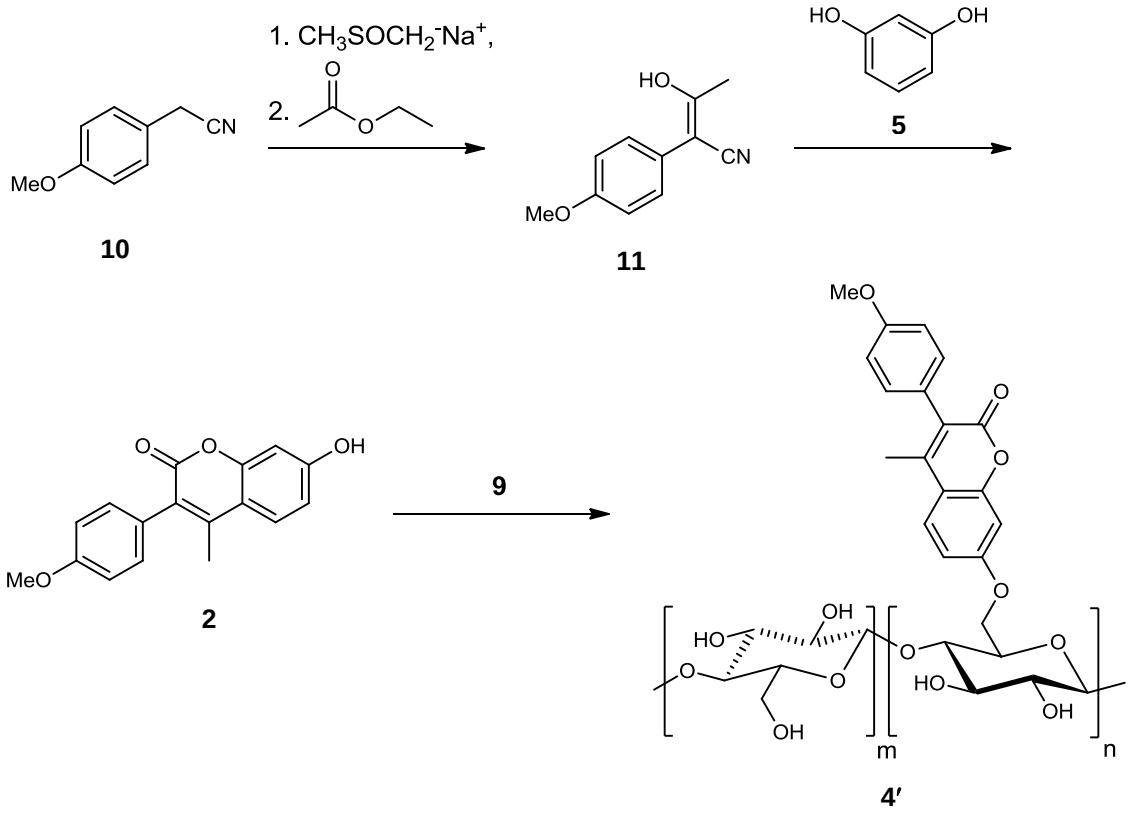


Figure 17: Absorption (top) and emission spectra spectra (bottom) of coumarins in homogeneous solution before (blue) and after (red) the photoreaction. **2** was obtained from a homogeneous Photo-Meerwein arylation out of **1**. Absorption and emission spectra were measured in DMSO ($c = 4 \cdot 10^{-5}$ M).

As an additional proof of the formation of the 3-arylated photoproduct on cellulose, the arylated coumarin **2** was attached to cellulose to give **4′** for comparison (Scheme 36). 7-Hydroxy-3-(4-methoxyphenyl)-4-methyl-2*H*-chromen-2-one **2** was immobilized in the same manner as that described in Scheme 35. An absorption spectrum of this sample was recorded and showed, within the error of the measurement, identical absorption maxima as the material of the heterogeneous photoreaction, which confirmed the proposed formation of the arylated photoproduct (Figure 18).



Scheme 36: Synthesis of an authentic sample **4′** for comparison with photocatalytically generated product **4**.

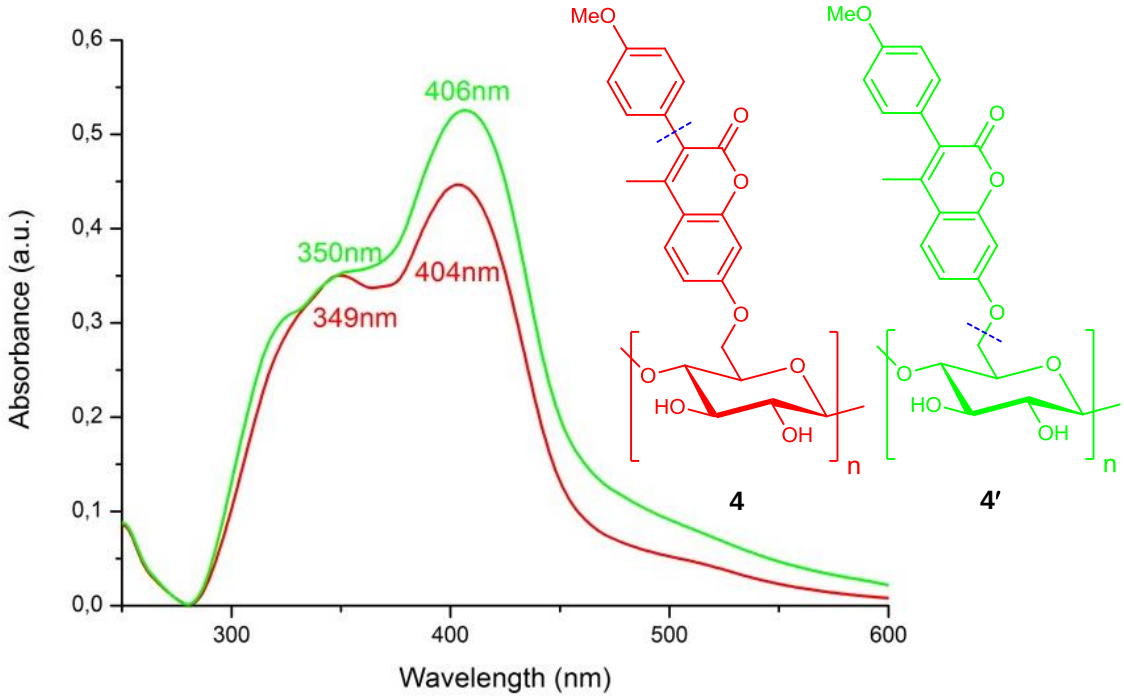


Figure 18: Absorption spectra of photocatalytically arylated immobilized coumarin **4** and independently prepared authentic sample **4′**.

3.3 Conclusions

Aryl radicals have previously been used for the direct modification of metal surfaces and polymer grafting on surfaces. We have extended the scope of such surface modifications to the arylation of coumarin-functionalized cellulose sheets by using a heterogeneous Photo-Meerwein arylation reaction. The catalytic process generated aryl radicals from diazonium salts in the presence of a photocatalyst upon irradiation with visible light. Such arylation of the coumarin altered the photophysical properties of the chromophore, which led to an image observable with the naked eye. The application of this spatially-controlled surface arylation protocol to diverse surface media bearing alkene or alkyne groups and a large variety of diazonium salts as aryl radical precursors can be readily envisaged.

3.4 Experimental Part

3.4.1 Instruments, Methods, and Materials

Solvents and substrates. Commercial reagents and starting materials were purchased from Aldrich, Fluka, VWR or Acros and used without further purification. Other starting materials were prepared as reported. Solvents were used as *p. a.* grade or dried and distilled prior to use as described in common methods if required by the experimental procedure.[187]

Irradiation source. Visible light irradiation was performed with an OSRAM® Oslon SSL 80 LD H9GP-3T3U-35 high-power LED lamp (royal-blue, λ_{max} = 455 ± 15 nm, 700 mA, P = 1.12 W).

Reaction monitoring. All reactions were monitored by thin layer chromatography (TLC) on alumina plates coated with silica gel (Merck silica gel plates 60 F_{254}, 0.2 mm) and visualized by UV light excitation (λ = 254 nm or λ = 366 nm), by naked eye, or staining with appropriate stains (anisaldehyde or *ortho*-phosphomolybdic acid). Preparative thin layer chromatography (PTLC) was performed on homemade glass plates (20 × 20 cm) coated with silica gel 60 F_{254} with ~15% calcium sulfate and fluorescent indicator (20 g, particle size 40–63 μm, Fluka).

Chromatography. Flash column chromatography was carried out on a Biotage Isolera One automated flash purification system with UV/Vis detector using Sigma Aldrich MN silica gel 60 M (particle size 40–63 μm).

NMR spectroscopy. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 (^{1}H: 300.1 MHz, ^{13}C: 75.5 MHz, T = 300 K) and a Bruker Avance 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, T = 300 K) spectrometer equipped with a robotic sampler. Data for ^{1}H-NMR are reported as follows: chemical shift, multiplicity, integration, and coupling constant. Chemical shifts are reported in δ [ppm] relative to tetramethylsilane (TMS) as the external standard. Characterization of the signals: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, m = multiplet, bs = broad singlet. The relative number of protons is determined by integration. Coupling

constants *J* are given in Hertz [Hz]. Data for ^{13}C-NMR are reported in terms of chemical shift. Error of reported values: chemical shift 0.01 ppm for ^{1}H-NMR, 0.1 ppm for ^{13}C-NMR, coupling constant 0.1 Hz. The solvent used is reported for each spectrum.

Mass spectrometry. Electron-impact (EI-MS) and chemical ionisation (CI-MS) mass spectra were measured on a Finnigan TSQ 710 spectrometer, and electronspray ionization (ESI-MS) mass spectra were measured on a ThermoQuest Finnigan TSQ 7000 spectrometer.

Absorption spectroscopy. UV/Vis spectra in solution were recorded on a Cary BIO 50 UV/Vis/NIR spectrometer (Varian). A 10 mm quartz cuvette from Hellma was used. Diffuse UV/Vis reflectance spectra for solid samples were recorded using an Omega 20 spectrometer (Bruins Instruments, Puchheim, Germany). Reflectance spectra were transformed into absorption spectra by Kubelka-Munk transformation.[254]

Fluorescence spectroscopy. Fluorescence spectra were recorded on a FluoroMax®-4 fluorescence spectrofluorometer (Horiba). Liquid samples were measured using cuvettes. Fluorescence spectra of cellulose sheets were obtained using a solid sample holder, which ensures an accurate positioning of the substrate for the measurement.

Infrared spectroscopy. IR spectra of solid samples were recorded on a BIO-RAD Excalibur IR spectrometer.

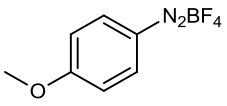
Microscopy. Microscopic pictures have been recorded on a Makroskop M420 (Wild Heerbrugg).

Yields. All yields reported are averages of at least two experimental runs.

3.4.2 Synthesis of Substrates

p-Methoxybenzenediazonium tetrafluoroborate[255, 256]

4-Methoxyaniline (1.0 equiv., 15 mmol, 1.85 g) was dissolved in a mixture of distilled water (6 mL) and hydrofluoroboric acid (32%, 1.0 equiv., 15 mmol, 8.0 mL). After cooling the reaction mixture to 0°C sodium nitrite (1.0 equiv., 15 mmol, 1.0 g) in water (2.0 mL) was added dropwise. The mixture was stirred for two hours and the resulting thick precipitate was collected by filtration. Purification of the diazonium tetrafluoroborate was achieved by repeated dissolving in a minimum amount of acetone and precipitation by addition of diethyl ether until the product was obtained as a white solid. The product was filtered, washed three times with diethyl ether and dried in vacuo to yield 1.85 g (56%) of a white solid.



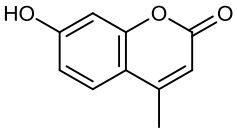
^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 4.04 (s, 3H), 7.46 – 7.51 (m, 2H), 8.59 – 8.64 (m, 2H).

^{13}C-NMR (101 MHz, DMSO-d_6): δ [ppm] = 57.5, 103.4, 117.3, 136.1, 168.8.

MS (ESI): *m/z* (%) = 135.0 (100) [M^+], 175.9 (14) [M^+ + MeCN].

7-Hydroxy-4-methyl-2*H*-chromen-2-one (1)

7-Hydroxy-4-methyl-2*H*-chromen-2-one was synthesized by using the Pechmann reaction:[251, 257] Recorcinol (1.0 equiv., 9.1 mmol, 1.0 g) and ethyl acetoacetate (1.0 equiv., 9.1 mmol, 1.15 mL) were dissolved in trifluoroacetic acid (6 mL) in a round bottom flask at ambient temperature. The solution was stirred for 24 h. The mixture was quenched by addition of ice-cold water (20 ml). After one hour at 0°C, a precipitate was formed that was filtered off in a sintered filter and washed with water (2 × 5 mL), and dried under high vacuum. Traces of water were removed by lyophilization. Yield: 1.4 g (89%) of **1** (white solid).



1

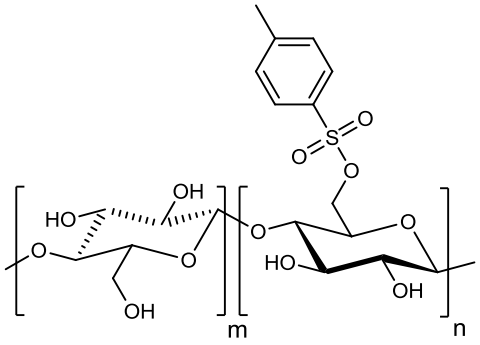
^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 2.35 (d, $^{4}J_{H,H}$ = 1.1 Hz, 3H), 6.12 (d, $^{4}J_{H,H}$ = 1.1 Hz, 1H), 6.70 (d, $^{4}J_{H,H}$ = 2.4 Hz, 1H), 6.79 (dd, $^{3}J_{H,H}$ = 8.7 Hz, $^{4}J_{H,H}$ = 2.4 Hz, 1H), 7.58 (d, $^{3}J_{H,H}$ = 8.7 Hz, 1H), 10.52 (s, 1H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 18.0, 102.1, 110.1, 111.9, 112.7, 126.5, 153.4, 154.7, 160.2, 161.0.

MS (ESI): *m/z* (%) = 176.1 (100) [$M^{\bullet+}$], 148.1 (85) [$M^{\bullet+}$ – $CO^{\bullet}$].

Tosylated cellulose (9)

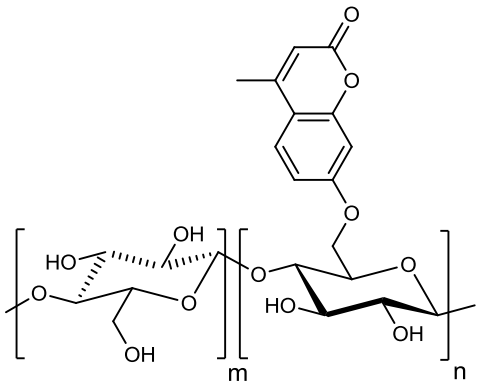
Cellulose was tosylated following a literature-known procedure:[252, 258] Cellulose (filter paper, 45 mm diameter, 110 mg, 0.61 mmol with respect to amount of glucose, 1.0 equiv.) was submerged in a mixture of $NaOH_{aq}$ (20%, 20 mL) and THF (10 mL) and cooled to 0°C. Tosyl chloride (1.5 equiv., 0.92 mmol, 175 mg) in THF (10 mL) was added dropwise. The mixture was stirred for 24 hours and allowed to warm to ambient temperature. The filter paper was washed with water (3 × 15 mL) and acetone (3 × 15 mL), and dried under high vacuum for three hours.



9

Coumarin-linked cellulose (3)

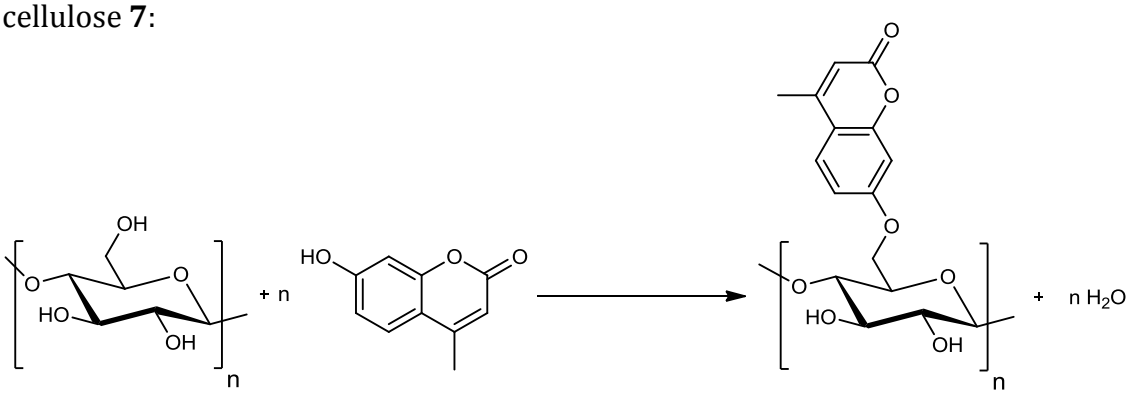
A flask was filled with DMF (dry, 30 mL) and coumarin derivative **1** (3.0 equiv. with respect to the amount of filter paper, 1.8 mmol, 0.42 g), potassium carbonate (6.0 equiv., 3.7 mmol, 0.51 g) and tosylated filter paper and heated to 90°C for 24 hours. After that, it was washed with ethanol (3 × 15 mL), and dried under high vacuum. The procedure was also performed with arylated coumarin **2**.



3

Determination of Filter Loading

Equation for immobilization of 7-hydroxy-4-methyl-2*H*-chromen-2-one **1** on cellulose **7**:



7 **1** **3**

Calculation of filter loading x_i from gravimetric data:

$$x_i = \frac{n(\mathbf{3})}{n(\mathbf{7})}$$

Note: Molar mass of glucose in cellulose polymer M(**7**) is 162.05 g·mol^{-1}, since condensation of glucose monomers (M = 180.06 g·mol^{-1}) to give the cellulose polymer liberates water.

Results from three independent experiments:

$$x_1 = 24.3\%, x_2 = 20.1\%, x_3 = 18.4\%$$

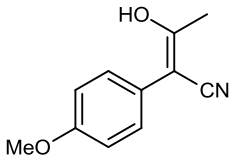
Arithmetic mean x $$x = \frac{\sum_{i=1}^{n} x_i}{n} = 21.0\%$$

Standard deviation s $$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x)^2}{n-1}} = 3.0\%$$

Filter loading x is determined to be 21% ± 3%.

(*Z*)-3-Hydroxy-2-(4-methoxyphenyl)but-2-enenitrile (11)

The molecule was synthesized according to literature.[259] An oven-dried 100 mL flask was filled with nitrogen and equipped with DMSO (55 mL). NaH (60% suspension in paraffin oil, 1.02 equiv., 100 mmol, 4.0 g) was added in portions and the mixture was heated to 75°C for 30 minutes, until hydrogen evolution had ceased. The solution was cooled to 20°C and *p*-methoxyphenylacetonitrile (1.0 equiv., 98 mmol, 13.3 mL) was added rapidly while keeping the temperature below 25°C. The mixture was stirred for five minutes. Ethyl acetate (1.0 equiv., 98 mmol, 9.7 mL) was added to the yellow solution and the temperature was kept below 20°C. The solution was allowed to warm to ambient temperature and stirred for two hours. The mixture was poured into ice-water (280 mL) and extracted with dichloromethane (4 × 50 mL). The turbid aqueous layer was filtered and acidified with acetic acid (8 mL). After one hour in the fridge, the white precipitate was filtered off, washed with water, and dried under vacuo to yield 16.4 g (89%) of product **11**.



11

^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 2.30 (s, 3H), 3.74 (s, 3H), 6.92 (d, $^{3}J_{H,H}$ = 8.8 Hz, 2H), 7.53 (d, $^{3}J_{H,H}$ = 8.8 Hz, 2H), 11.31 (s, 1H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 21.6, 55.1, 86.2, 113.7, 114.1, 125.1, 128.3, 157.5, 166.7.

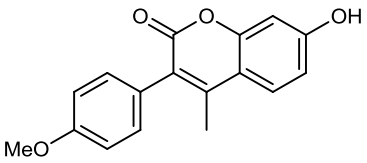
R_F (PE/EE 5:1) = 0.13.

MS (EI): *m/z* (%) = 189.1 (10) [$M^{\bullet+}$], 147.1 (100) [$M^{\bullet+}$ – O=C=CH_2], 132.1 (34) [$M^{\bullet+}$ – O=C=CH_2 – $CH_3^{\bullet}$].

7-Hydroxy-3-(4-methoxyphenyl)-4-methyl-2*H*-chromen-2-one (2)

The molecule was synthesized according to literature.[259] A 50 ml double-necked flask with stirring bar and thermometer was filled with sulfuric acid (97%, 11 ml) and cooled to 5 °C. (*Z*)-3-hydroxy-2-(4-methoxyphenyl)but-2-enenitrile **11** (1.0 equiv., 35 mmol, 6.62 g) and resorcinol (1.0 equiv., 35 mmol, 3.85 g) were

mixed in a mortar and added in small portions over 70 minutes with vigorous stirring. After removal of the cooling bath, stirring was continued for another 68 h. The viscous mixture was poured into water (60 mL) and ice (60 g). An orange honey-like tar separated. The supernatant was removed and the tar was heated to reflux with sulfuric acid (10% in water, 170 mL). A clear solution was decanted and refluxed for two hours. After cooling to 0°C, a solid precipitated which was collected and boiled in ethanol (150 mL). After that, the solution was mixed with water (300 mL). Crystallization was completed in an ice-bath. Pale yellow crystals were collected by filtration, and dried under high vacuo to yield 1.1 g (11%) of **2**.



2

^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 2.21 (s, 3H), 3.79 (s, 3H), 6.73 (d, $^{4}J_{H,H}$ = 2.4 Hz, 1H), 6.82 (dd, $^{3}J_{H,H}$ = 8.8 Hz, $^{4}J_{H,H}$ = 2.4 Hz, 1H), 6.95 – 7.01 (m, 2H), 7.17 – 7.24 (m, 2H), 7.64 (d, $^{3}J_{H,H}$ = 8.8 Hz, 1H), 10.51 (s, 1H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 16.4, 55.1, 101.9, 112.5, 113.0, 113.5, 122.0, 126.9, 127.1, 131.6, 148.1, 153.8, 158.7, 160.5, 160.7.

MS (ESI): *m/z* (%) = 283.1 (100) [MH^+], 587.2 (8) [$2MNa^+$].

R_F (PE/EE 3:1) = 0.18.

3.4.3 Photocatalytic Experiments

General Procedure for Photocatalytic Arylation in Homogeneous Solution

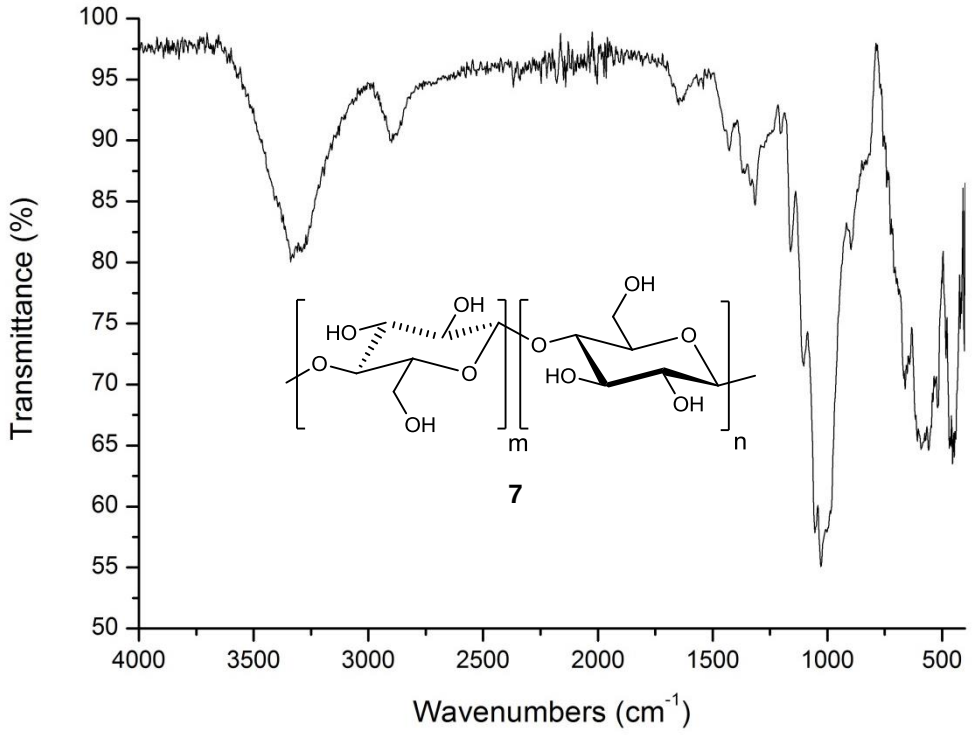
A 5 mL reaction vessel with a magnetic stirring bar was equipped with $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.01 equiv., 2.0 µmol, 1.5 mg), aryl diazonium tetraflouroborate (1.0 equiv., 0.2 mmol), unsaturated compound **1** (5.0 equiv., 1.0 mmol), and dry DMSO (1.0 mL). The mixture was degassed by "freeze-pump-thaw" technique (three cycles) and irradiated with a blue high-power LED (λ_{max} = 455 ± 15 nm, 700 mA, *P* = 1.12 W) for 20 minutes at 20°C. The reaction mixture was diluted with water (4 ml) and extracted with diethyl ether (3 × 5 mL). The combined organic

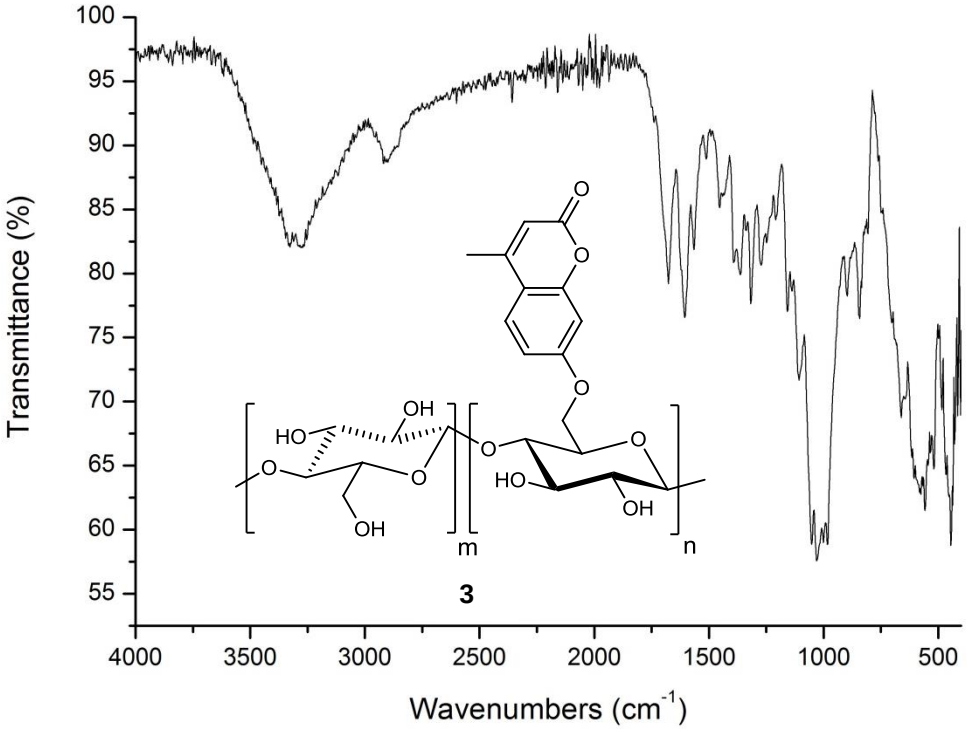
layer was concentrated in vacuo. Traces of water were removed by lyophilization. Purification of the crude product was achieved by preparative thin-layer chromatography on silica gel 60 F_{254} (petroleum ether/ethyl acetate, 3:1).

General Procedure for Heterogeneous Photocatalytic Arylation

A dry, coumarin-linked cellulose polymer (filter paper; loading: 21% ± 3% corresponding to 0.13 mmol of immobilized coumarin derivative **1**) was put on aluminum foil. A solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.06 equiv., 8.5 µmol, 6.4 mg) and *p*-methoxyphenyl diazonium tetraflouroborate (0.15 mmol, 33.3 mg) in dry DMSO (0.6 mL) was applied to the paper. A non-transparent photomask was fit over the paper, and a high-power blue light-emitting diode (LED; λ_{max} = 455 ± 15 nm, 700 mA, P = 1.12 W) propped over the setup and initiated for 20 minutes. After that, the mask was removed and the polymer was subsequently washed with methanol, water, and acetone, and dried in the air. The pattern was visible on the polymer.

3.4.4 Spectroscopic Data





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4 PHOTOCATALYTIC α-OXYAMINATION OF STABLE ENOLATES, SILYL ENOL ETHERS, AND 2-OXO-ALKANE PHOSPHONIC ESTERS

Fast α-oxyamination of stable enolates, silyl enol ethers, and *in situ* deprotonated dialkyl 2-oxoalkane phosphonates and diphenyl-2-oxoalkyl phosphine oxides was performed in the presence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) as a photocatalyst, 2,2,6,6-tetramethylpiperidine nitroxide (TEMPO), and visible light. The key step was a light-induced one-electron oxidation of TEMPO into the 2,2,6,6-tetramethyl-piperidine-1-oxoammonium ion ($TEMPO^+$), which was nucleophilically attacked to yield α-functionalized carbonyl compounds. The reaction time was significantly reduced by the use of photomicroreactor technique.

Publication:

P. Schroll, and B. König, Photocatalytic α-Oxyamination of Stable Enolates, Silyl Enol Ethers and 2-Oxoalkane Phosphonic Esters. *European Journal of Organic Chemistry* **2014**, *in print*.

Author Contributions:
Peter Schroll is the only author. Synthesis of starting materials, photochemical reactions and measurements was done by P.S.. Photographs were taken by Maria Cherevatskaya and Peter Schroll.

4.1 Introduction

Catalytic and stoichiometric one-electron oxidation reactions of different classes of substrates are well established.[260-263] For such oxidations, visible-light photocatalysis has recently been widely applied to provide the necessary redox energy. Photocatalytic oxidation of alkenes by using 9-mesityl-10-methyl-acridinium perchlorate and subsequent intra- or intermolecular trapping of the resulting radical cation with nucleophiles, such as alcohols, amines, and carboxylates, is an example that was described by Nicewicz *et al*.[264-268] The generation of carbon-centered radicals $R^{\bullet}$ through one-electron oxidation of borates of the type $R–BX_3^-K^+$ induced by photoredox catalysis followed by reaction with permanent radicals, electron-deficient alkenes, or alkynes was reported by different groups.[269-271]

Enolates and their equivalents are another class of important building blocks in synthetic organic transformations that can be oxidized. Dependent on the oxidant, they yield either an α-carbonyl radical or an α-carbonyl carbenium ion intermediate. With a stoichiometric amount of the weak one-electron oxidant *tris*-(*p*-methoxyphenyl)aminium hexafluoroantimonate (E = +0.51 V vs. saturated calomel electrode, SCE), α-carbonyl radicals are obtained from stable enolates. Two equivalents of the stronger oxidizing agent *tris*-(1,10-phenanthroline)iron(III) hexafluorophosphate {$Fe^{III}(phen)_3(PF_6)_3$, E = +1.08 V vs. SCE} afforded α-carbonyl cations as a result of two subsequent one-electron oxidation steps.[272-274] The Jahn group reported the oxidation of ester enolates with $CuCl_2$ or ferrocenium ions and subsequent trapping of the α-ester radicals with 2,2,6,6-tetramethylpiperidine nitroxide (TEMPO).[275-277] All of these reactions allow α-functionalization of carbonyls through an oxidative pathway.

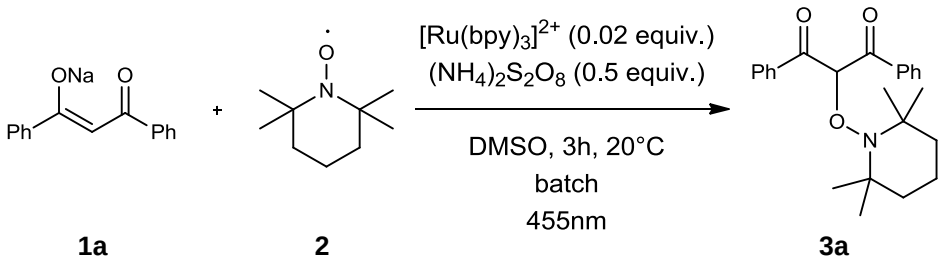
TEMPO catalyzes a variety of oxidation reactions.[278] An important application as reagent is the oxidation of alcohols to aldehydes or carboxylic acids.[279, 280] The catalytically active species was found to be the 2,2,6,6-tetramethylpiperidine-1-oxoammonium ion (**2′**, $TEMPO^+$), which is generated in the presence of an oxidant. The oxoammonium ion can react with enolates to give, for example, alkoxyamines.[281] More recently, $TEMPO^+$ was prepared photocatalytically with

visible light by using organic dyes, dye-sensitized titanium dioxide, and transition-metal complexes based on ruthenium and copper. Following this procedure, the TEMPO-mediated aerobic photocatalytic oxidation of alcohols to aldehydes was reported both heterogeneously and homogeneously.[282-287]

1,3-Dicarbonyl compounds have also been the target of one-electron oxidation reactions[288] and have been used in TEMPO-mediated oxidation with the use of visible light.[289, 290] The oxidation of the enol form occurs in the presence of TEMPO (2 equiv.) to afford α-oxyaminated products. However, reaction times of 24 – 36 hours are necessary and different reaction pathways have been proposed considering either a light-induced disproportionation reaction of TEMPO to yield $TEMPO^+$ and $TEMPO^-$ or the reduction of the enol form. We apply now stable enolates in the reaction with photocatalytically generated $TEMPO^+$ to lead to significantly reduced reaction times. The proposed reaction mechanism was supported by control experiments by using different trapping reagents.

4.2 Results and Discussion

We started our investigations by treating a 1:1 mixture of the stable enolate **1a** with TEMPO **2** in the presence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) as a photocatalyst and ammonium peroxodisulfate as an oxidant. Dry DMSO turned out to be the solvent of choice to dissolve all of the ionic compounds. Irradiation with a blue high-power light-emitting diode (LED, λ_{max} = 455 ± 15 nm, P = 3.0 W) at ambient temperature afforded desired α-oxyaminated product **3a** in 87% yield (Scheme 37). Control reactions in the dark gave only trace amounts of product **3a**. Without the photocatalyst, a background reaction yielding 4% of α-oxyaminated product occured. The results exclude efficient direct oxidation of TEMPO by ammonium peroxodisulfate.



Scheme 37: Photocatalytic α-oxyamination of stable enolates.

Optimization

Full conversion was achieved after three hours of irradiation. Hence, the reaction of the enolate was much faster than that of the enol, which required at least 24 hours for conversion. By using ammonium peroxodisulfate as the terminal oxidant, the amount of TEMPO could be reduced to one equivalent. Without peroxodisulfate, a second equivalent of TEMPO was necessary for full conversion of the enolate. A catalyst loading of 2 mol% was found to be optimal. Different photocatalysts were screened: Eosin Y gave the α-oxyamination product in 37% yield under green light (λ_{max} = 525 ± 20 nm) irradiation. 9-Mesityl-10-methyl-acridinium perchlorate ("Fukuzumi's dye") as a strongly oxidizing photocatalyst gave the product in 64% yield. However, additional unidentifiable side products were obtained. The product was obtained in 70% yield by using 2,4,6-triphenylpyrylium tetrafluoroborate as the photocatalyst. Both the acridinium and the pyrylium dyes were excited with purple light (λ_{max} = 400 ± 10 nm). The best results were obtained with $[Ru(bpy)_3]^{2+}$, which yielded α-oxyaminated product **3a** in 87% yield in a clean reaction. Although enolates are potential ligands for ruthenium ions, the photocatalyst remained stable under these conditions.[291] The reaction time was further reduced by applying flow chemistry in a photomicroreactor (Figure 19).

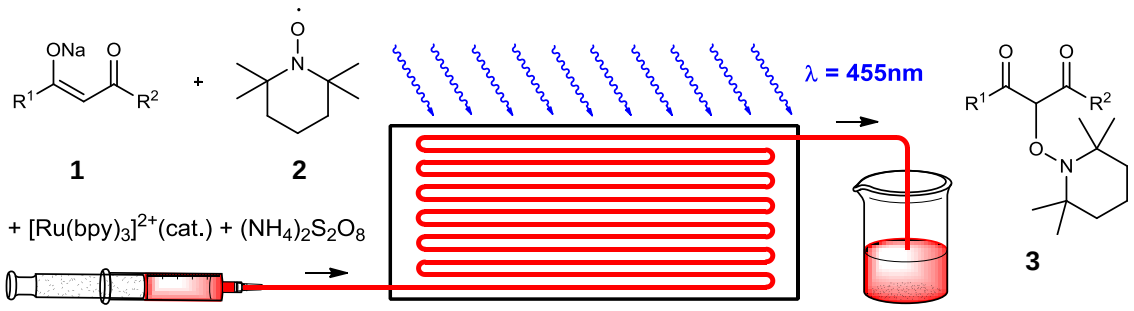


Figure 19: Photooxidation in a microreactor.

The benefits of flow photochemistry have been discussed through many examples in the literature.[292-298] Compared to the batch reaction, the reaction in a glass capillary offers a larger irradiation surface.

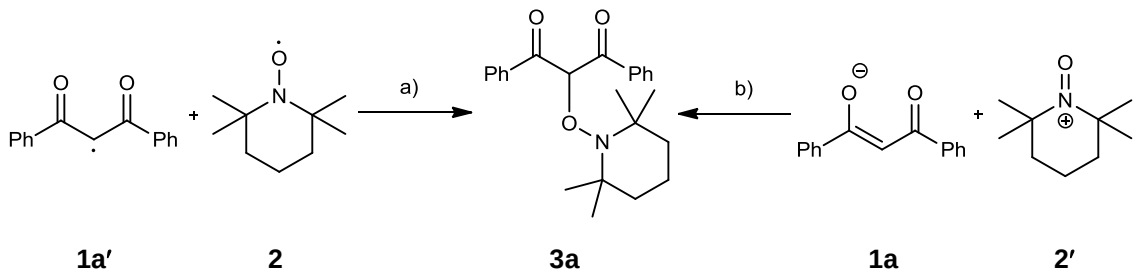
By using Equation (1) for the penetration depth l of light, a layer of l = 1.0 mm depth contributes to the photoreaction for $\varepsilon = 2.1 \cdot 10^3$ $M^{-1}cm^{-1}$ and $c = 2.0 \cdot 10^{-3}$ M in which ε is the molar extinction coefficient and c the concentration of the chromophore $[Ru(bpy)_3]^{2+}$.[299, 300]

$$l = \frac{1}{\varepsilon \cdot c \cdot ln10} \quad (1)$$

All of the reaction mixture was exposed to light upon pumping the solution through the irradiated glass capillary of 0.5 mm radius. Switching from batch to a microreactor setup therefore shortened the reaction time from three hours to ten minutes and increased the yield of the α-oxyaminated product to 93%. Despite the fact that oxygen was an appropriate oxidant for the reaction, the sealed conditions in the microreactor demanded ammonium peroxodisulfate as a nongaseous electron acceptor.

Mechanism

The α-oxyaminated product may be obtained by two different reaction pathways: (a) oxidation of the enolate to the α-carbonyl radical followed by radical recombination with the TEMPO radical or (b) TEMPO oxidation and subsequent nucleophilic attack of the enolate (Scheme 38).[281] The structure of the product allows no distinction between the two reaction pathways.

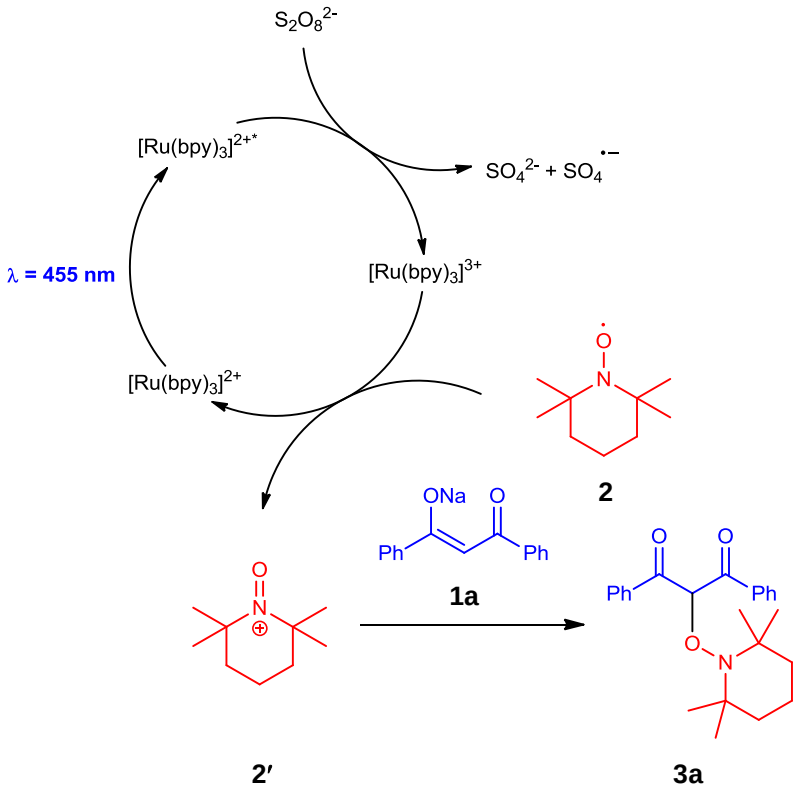


Scheme 38: Generation of α-oxyaminated 1,3-dicarbonyls by (a) radical recombination or (b) nucleophilic attack of the enolate to the oxoammonium ion.

The oxidation potentials of enolate **1a** and TEMPO **2** were determined by cyclic voltammetry to be +0.61 V and +0.68 V vs. SCE in DMSO, respectively. Both cyclic voltammograms show an irreversible oxidation wave (see the Experimental Part). The potentials of the enolate and TEMPO are identical within the error of the measurement and both lie within the photocatalyst's oxidizing ability. Distinction as to which compound is photooxidized is therefore not possible.

However, considering the reactivity of the postulated intermediates, the two mechanisms should be different. In case of enolate oxidation to the corresponding α-carbonyl radical, other radical trapping reagents should be applicable. Therefore, different π– and σ–electron donors were added to the enolate, but no coupling product was observed with styrene, furan, thiophene, *N*-methylpyrrole, or dimethyldisulfide (five equiv. each). Moreover, no dimerization product resulting from radical recombination of two α-carbonyl radicals was detected. Even if a catalytic amount of TEMPO (10 mol%) was added to initiate the oxidation, no reaction was observed with the exception of a small amount of α-oxyaminated product corresponding to the amount of TEMPO added. The presence of TEMPO is essential for the reaction. The absence of any addition product of a postulated α-carbonyl radical and π– or σ–electron donors or the formation of radical dimerization products indicates the one-electron oxidation of TEMPO to the corresponding 2,2,6,6-tetramethylpiperidine-1-oxoammonium ion ($TEMPO^+$) as the key step of the reaction.

On the basis of these results, the following mechanism is proposed: After excitation of the photocatalyst by blue light, ammonium peroxodisulfate acts as an oxidative quencher to form the strongly oxidizing species $[Ru(bpy)_3]^{3+}$.[179] The oxidant is reduced to sulfate and a sulfate radical anion that is capable of accepting an additional electron.[301] Regeneration of the photocatalyst is achieved by oxidizing TEMPO radical **2** to the corresponding oxoammonium ion **2′**. Finally, enolate **1a** attacks the oxidized species in a nucleophilic manner to produce α-oxyaminated product **3a** (Scheme 39).

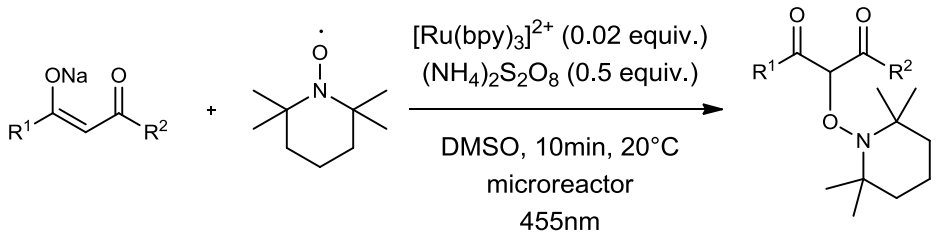


Scheme 39: Proposed mechanism for the α-oxyamination of stable enolates.

Scope

Stable enolates are easily accessible from 1,3-diketones by deprotonation with sodium hydride in diethyl ether at room temperature. Under these conditions, the (*Z*)-enolate is formed selectively.[302] A range of enolates were tested in the α-oxyamination reaction (Table 9).

Table 9: Photooxidation reaction of stable enolates with TEMPO.[a]

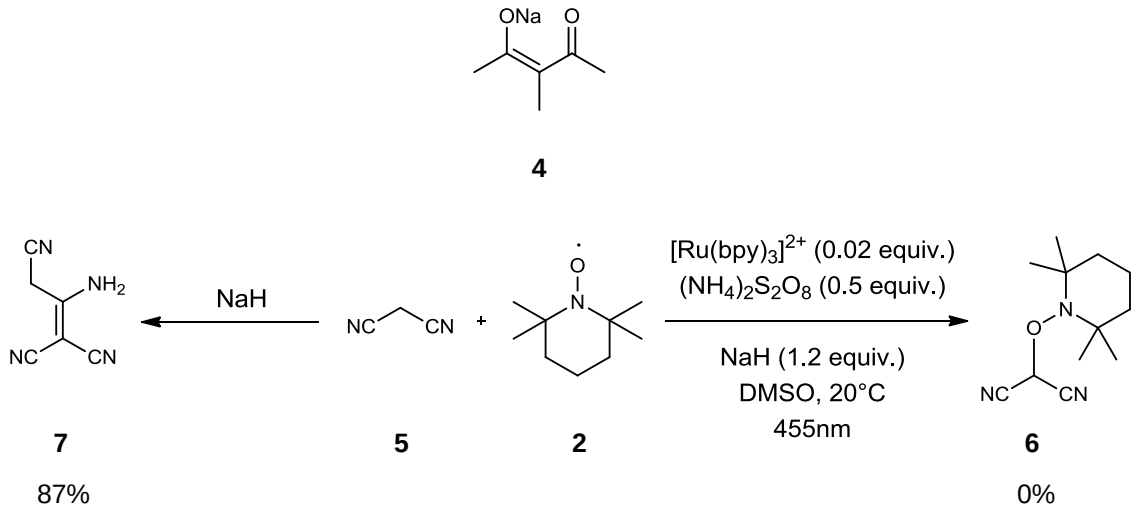


1a–e **2** **3a–e**

Entry	Reactant	R^1	R^2	Product	Yield (%)[b]
1	**1a**	Ph	Ph	**3a**	93
2	**1b**	Ph	Me	**3b**	81
3	**1c**	Me	Me	**3c**	82
4	**1d**	Ph	OEt	**3d**	96
5	**1e**	Me	OEt	**3e**	86

[a] *Reaction conditions:* Enolate (0.6 mmol), TEMPO (0.6 mmol), $(NH_4)_2S_2O_8$ (0.3 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.012 mmol), DMSO (6.0 mL, absolute), photo-microreactor, irradiation with eight high-power LEDs (λ_{max} = 455 ± 15 nm, *P* = 3.0 W). [b] Yields of the isolated products are given.

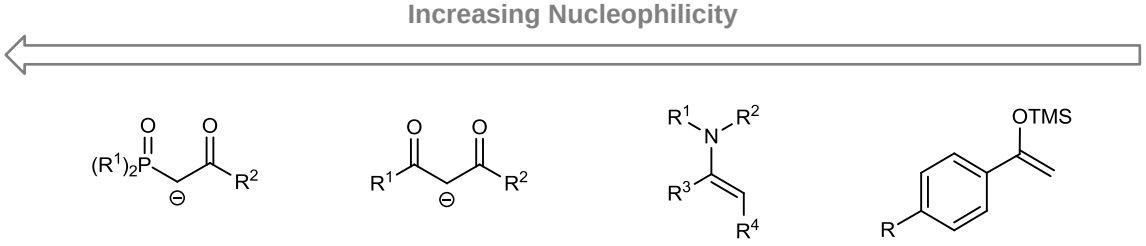
The α-oxyamination proceeded smoothly with 1,3-diketo- and β-keto ester enolates **1a–e**. The scope of the reaction was limited to β-keto enolates without substitution at the α-carbon atom: enolate **4** is more basic, which led to decomposition in DMSO solution before irradiation was started. The same applied to enolates of simple aldehydes and ketones, and this limits the scope of the method. Malononitrile **5** did not afford the oxyaminated product. In the presence of a strong base, self-condensation occurred instead, which resulted in the formation of 2-amino-1,1,3-tricyanopropene dimer **7** (Scheme 40).[303, 304]



Scheme 40: Limitations in the oxyamination reaction.

According to the mechanistic proposal (Scheme 39), the enolate reacts as a nucleophile. Oxyamination was therefore expected to proceed also with other nucleophiles.

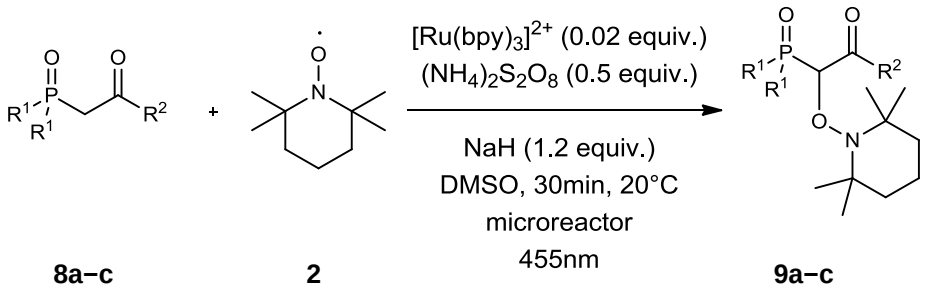
To prove the hypothesis, other classes of nucleophiles were examined in the reaction with photocatalytically generated $TEMPO^+$. The nucleophiles were selected by using Mayr's nucleophilicity scale (Scheme 41).[305-308]



Scheme 41: Selected examples from Mayr's nucleophilicity scale.

The principle of α-oxyamination of carbon nucleophiles was extended to β-keto phosphine oxides and β-keto alkyl phosphonic esters. After preparing these enolates *in situ* by treatment with sodium hydride, nucleophilic attack to the photocatalytically generated oxoammonium ion occurred. Product **9a** could only be identified in trace amounts, but compounds **8b** and **8c** gave desired products **9b** and **9c** in yields of 68 and 57%, respectively. The reaction time was 30 minutes (Table 10).

Table 10: Oxyamination of organophosphorus compounds.[a]



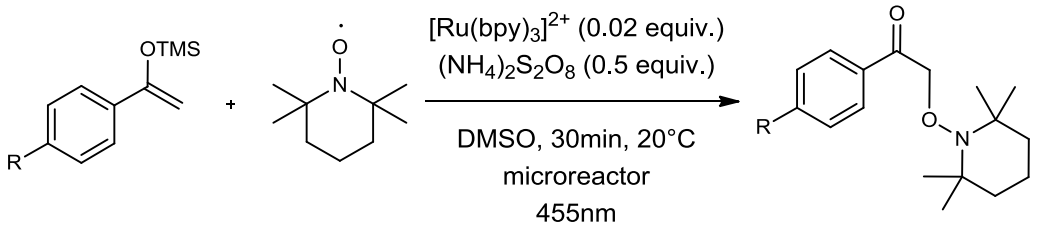
8a–c **2** **9a–c**

Entry	Reactant	R¹	R²	Product	Yield (%)[b]
1	**8a**	Ph	OEt	**9a**	trace
2	**8b**	Ph	Ph	**9b**	68
3	**8c**	EtO	Ph	**9c**	57

[a] *Reaction conditions:* Organophosphorus compound (0.6 mmol), NaH (0.72 mmol), TEMPO (0.6 mmol), $(NH_4)_2S_2O_8$ (0.3 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.012 mmol), DMSO (6.0 mL, absolute), photomicroreactor, irradiation with eight high-power LEDs (λ_{max} = 455 ± 15 nm, *P* = 3.0 W). [b] Yields of the isolated products are given.

Enamines have already been successfully used in oxyamination reactions. After hydrolysis, α-functionalized carbonyls were obtained.[309, 310] Therefore, related silyl enol ethers were examined as nucleophilic carbonyl derivatives.[311] These enolate equivalents were converted in 30 minutes under photooxidation conditions into the corresponding α-oxyaminated products **11a–c** in good yields (Table 11).

Table 11: Oxyamination of silyl enol ethers.[a]



10a–c **2** **11a–c**

Entry	Reactant	R	Product	Yield (%)[b]
1	**10a**	Me	**11a**	64
2	**10b**	H	**11b**	65
3	**10c**	Cl	**11c**	77

[a] *Reaction conditions:* Silyl enol ether (0.3 mmol), TEMPO (0.3 mmol), $(NH_4)_2S_2O_8$ (0.15 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.006 mmol), DMSO (3.0 mL, absolute), photomicroreactor, irradiation with eight high-power LEDs (λ_{max} = 455 ± 15 nm, *P* = 3.0 W). [b] Yields of the isolated products are given.

4.3 Conclusions

A fast and efficient visible-light-mediated oxyamination procedure of β-keto enolates was developed. The method was suitable for α-oxyamination of stable enolates, silyl enol ethers, β-keto phosphine oxides, and β-keto alkyl phosphonic esters. The reaction proceeded through light-induced one-electron oxidation of 2,2,6,6-tetramethylpiperidine nitroxide (TEMPO), which was followed by attack of the nucleophile; this led to α-functionalized carbonyls. The scope of the method was limited by the basicity of the enolate, as basic compounds decomposed under the reaction conditions. The use of flow chemistry in a photomicroreactor reduced the reaction time significantly.

4.4 Experimental Part

4.4.1 Instruments, Methods, and Materials

Solvents and substrates. Commercial reagents and starting materials were purchased from Aldrich, Fluka, VWR or Acros and used without further purification. Other starting materials were prepared as reported. Solvents were used as *p. a.* grade or dried and distilled prior to use as described in common methods if required by the experimental procedure.[187]

Irradiation source. Visible light irradiation was performed using LED lamps OSRAM® Oslon SSL 80 LD H9GP-3T3U-35 (royal-blue, λ_{max} = 455 ± 15 nm, 700 mA, P = 1.12 W), Philips LUXEON® Rebel LXML-TRo1-0225 (blue, λ_{max} = 455 ± 15 nm, 700 mA, P = 3.0 W), Philips LUXEON® Rebel (green, λ_{max} = 525 ± 20 nm, 145 lm @700mA, P = 1.0 W), and Philips LUXEON® Rebel (purple, λ_{max} = 400 ± 10 nm, 1000 mA, P = 1.2 W).

Microreactor. A microreactor system LTF-V (MR-Lab Series) from Little Things Factory GmbH (Elsoff, Germany) was used for photocatalytic experiments. Dimensions: 115 × 60 × 6 mm. Diameter of channel: 1.0 mm. Volume: 1.7 mL. Continuous flow was adjusted by a syringe pump (LA–100, Landgraf Laborsysteme HLL GmbH, Langenhagen, Germany).

Reaction monitoring. All reactions were monitored by thin-layer chromatography (TLC) on alumina plates coated with silica gel (Merck silica gel plates 60 F_{254}, 0.2 mm) and visualized by UV light excitation (λ = 254 nm) or by naked eye.

Chromatography. Flash column chromatography was carried out on a Biotage Isolera One automated flash purification system with UV/Vis detector using Sigma Aldrich MN silica gel 60 M (particle size 40–63 μm).

NMR spectroscopy. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 (^{1}H: 300.1 MHz, ^{13}C: 75.5 MHz, T = 300 K) and a Bruker Avance 400 (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, T = 300 K) spectrometer equipped with a robotic sampler. Data for ^{1}H-NMR are reported as follows: chemical shift, multiplicity, integration, and coupling constant. Chemical shifts are reported in δ [ppm] relative to tetramethylsilane (TMS) as the external standard. Characterization of the

signals: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets, m = multiplet, bs = broad singlet. The relative number of protons is determined by integration. Coupling constants *J* are given in Hertz [Hz]. Data for ^{13}C-NMR are reported in terms of chemical shift. Error of reported values: chemical shift 0.01 ppm for ^{1}H-NMR, 0.1 ppm for ^{13}C-NMR, coupling constant 0.1 Hz. The solvent used is reported for each spectrum.

Mass spectrometry. Electron-impact (EI-MS) and chemical ionisation (CI-MS) mass spectra were measured on a Finnigan TSQ 710 spectrometer, and electronspray ionization (ESI-MS) mass spectra were measured on a ThermoQuest Finnigan TSQ 7000 spectrometer.

Melting points. Melting points were determined with an OptiMelt MPA100 automated melting point system (Stanford Research Systems) and are uncorrected.

Cyclic voltammetry. CV has been measured with an Autolab potentiostat using a glassy carbon working electrode, a platinum wire as the counter electrode, and a silver wire as the reference electrode. Tetrabutylammonium tetrafluoroborate (c = 0.1 M) was the conducting salt unless otherwise noted. The solvent is reported for each cyclic voltammogram. The step potential was 50 mV / s. The concentration of analytes was 0.01 M. Ferrocene (c = 0.01 M) was used as the internal standard. The solution was degassed before the measurement by a stream of argon.

Yields. All yields reported are averages of at least two experimental runs.

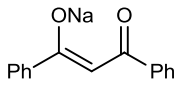
4.4.2 Synthesis of Substrates

General Procedure for the Synthesis of Sodium Enolates* 1a–e *derived from 1,3-Diketones

The 1,3-diketone (1.0 equiv., 10 mmol) was dissolved in dry diethyl ether (20 mL) at room temperature. Sodium hydride (1.0 equiv., 10 mmol, 0.40 g, 60% suspension in paraffin oil) was added in portions. After gas evolution had ceased, the mixture was stirred for 30 minutes at ambient temperature. A yellowish

precipitate was formed that was filtered, washed with cold diethyl ether (2 × 20 mL), and dried in vacuo.

Sodium (*Z*)-3-oxo-1,3-diphenylprop-1-en-1-olate (1a)[312]



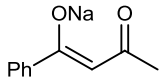
1a

86%, yellowish crystals

^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 6.35 (s, 1H), 7.30 – 7.40 (m, 6H), 7.80 – 7.91 (m, 4H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 90.4, 126.6, 127.8, 128.9, 144.1, 182.1.

Sodium (*Z*)-3-oxo-1-phenylbut-1-en-1-olate (1b)[281]



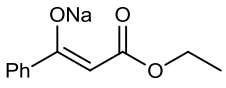
1b

67%, yellowish crystals

^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 1.81 (s, 3H), 5.62 (s, 1H), 7.20 – 7.35 (m, 2H), 7.63 – 7.83 (m, 3H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 29.7, 93.6, 126.4, 127.6, 128.6, 144.0, 180.1, 188.4.

Sodium (*Z*)-3-ethoxy-3-oxo-1-phenylprop-1-en-1-olate (1d)[281]



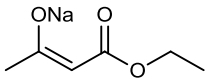
1d

40%, white crystals

^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 1.13 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3H), 3.90 (q, $^{3}J_{H,H}$ = 7.1 Hz, 2H), 4.99 (s, 1H), 7.24 – 7.32 (m, 3H), 7.65 – 7.73 (m, 2H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 15.1, 56.0, 78.0, 126.1, 127.5, 128.2, 144.3, 169.6, 180.0.

Sodium (*Z*)-4-ethoxy-4-oxobut-2-en-2-olate (1e)[281]



1e

63%, white crystals

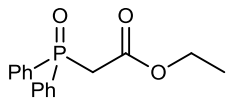
^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 1.07 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3H), 1.59 (s, 3H), 3.81 (q, $^{3}J_{H,H}$ = 7.1 Hz, 2H), 4.25 (s, 1H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 15.1, 29.0, 55.6, 80.1, 168.8, 185.4.

***General Procedure for the Synthesis of Phosphine Oxides and Alkyl Phosphonic Esters* 8a–c**

Phosphine oxides of type $(R^1)_2R^2P{=}0$ (**8a** and **8b**) and alkyl phosphonic esters of type $(R^1O)_2R^2P{=}0$ (**8c**) were synthesized using the Arbuzov reaction.[187] Ethyl diphenylphosphinite (1.0 equiv., 10 mmol, 2.16 mL) or triethyl phosphite (1.0 equiv., 10 mmol, 1.71 mL) was added to the alkyl bromide (1.0 equiv., 10 mmol) and heated to 160°C for two hours. Ethyl bromide as the byproduct was removed from the reaction mixture by distillation by the use of a Vigreux column. Reaction monitoring was achieved using thin layer chromatography. Phosphine oxides were purified by recrystallization from ethanol. Alkyl phosphonic esters were purified by flash column chromatography on silica gel using (petroleum ether/ethyl acetate, 1:1).

Ethyl 2-(diphenylphosphoryl)acetate (8a)[313]



8a

97%, white crystals, mp = 72°C (lit.: 75 – 76°C)

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.02 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3H), 3.49 (d, $^{2}J_{P,H}$ = 14.9 Hz, 2H), 3.99 (q, $^{3}J_{H,H}$ = 7.1 Hz, 2H), 7.43 – 7.57 (m, 6H), 7.73 – 7.84 (m, 4H).

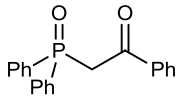
^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 13.9, 39.3 (d, $^1J_{C,P}$ = 60.6 Hz), 61.7, 128.8 (d, $^3J_{C,P}$ = 12.4 Hz), 131.3 (d, $^2J_{C,P}$ = 9.9 Hz), 131.8 (d, $^1J_{C,P}$ = 104.0 Hz), 132.4 (d, $^4J_{C,P}$ = 2.9 Hz), 166.3 (d, $^2J_{C,P}$ = 5.3 Hz).

^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ [ppm] = 27.6.

MS (ESI): *m/z* (%) = 289.1 (100) [MH^+], 577.2 (31) [$2MH^+$].

R_f (PE/EA 1:1) = 0.1.

2-(Diphenylphosphoryl)-1-phenylethanone (8b)[314]



8b

79%, colorless crystals, mp = 137°C (lit.: 140°C)

^{1}H-NMR (300 MHz, MeOD): δ [ppm] = 4.42 (d, $^2J_{P,H}$ = 14.4 Hz, 2H), 7.36 – 7.45 (m, 2H), 7.47 – 7.69 (m, 7H), 7.75 – 7.80 (m, 2H), 7.81 – 7.85 (m, 2H), 7.89 – 8.03 (m, 2H).

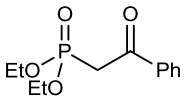
^{13}C-NMR (75 MHz, MeOD): δ [ppm] = 42.2 (d, $^1J_{C,P}$ = 63.3 Hz), 129.7 (d, $^3J_{C,P}$ = 12.4 Hz), 130.0 (d, $^3J_{C,P}$ = 8.9 Hz), 132.1 (d, $^2J_{C,P}$ = 10.1 Hz), 133.0, (d, $^1J_{C,P}$ = 104.4 Hz), 133.7, (d, $^5J_{C,P}$ = 1.3 Hz), 133.5, (d, $^4J_{C,P}$ = 2.8 Hz), 134.8, 138.4 (d, $^4J_{C,P}$ = 1.6 Hz), 194.3 (d, $^2J_{C,P}$ = 6.5 Hz).

^{31}P{^{1}H}-NMR (121 MHz, MeOD): δ [ppm] = 32.2.

MS (ESI): *m/z* (%) = 321.1 (100) [MH^+], 641.2 (20) [$2MH^+$].

R_f (PE/EA 1:1) = 0.12.

Diethyl (2-oxo-2-phenylethyl)phosphonate (8c)[315]



8c

39%, colorless oil

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.22 (t, $^3J_{H,H}$ = 7.1 Hz, 6H), 3.58 (d, $^2J_{P,H}$ = 22.7 Hz, 2H), 4.08 (dq, $^3J_{P,H}$ = 14.2 Hz, $^3J_{H,H}$ = 7.1 Hz, 4H), 7.37 – 7.46 (m, 2H), 7.48 – 7.56 (m, 1H), 7.92 – 7.99 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 16.2 (d, $^3J_{C,P}$ = 6.3 Hz), 38.4 (d, $^1J_{C,P}$ = 129.9 Hz), 62.6 (d, $^2J_{C,P}$ = 6.5 Hz), 128.6, 129.0, 133.7, 136.5 (d, $^3J_{C,P}$ = 2.0 Hz), 192.0 (d, $^2J_{C,P}$ = 6.6 Hz).

^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ [ppm] = 20.6.

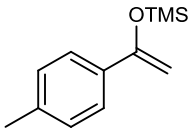
MS (ESI): *m/z* (%) = 257.1 (100) [MH^+], 535.2 (7) [$2MNa^+$].

R_f (PE/EA 1:1) = 0.14.

***General Procedure for the Synthesis of Silyl Enol Ethers* 10a–c**

Silyl enol ethers were prepared according to a modified literature procedure.[316] The enolizable ketone (1.0 equiv., 17 mmol), triethylamine (1.2 equiv., 21 mmol, 2.91 mL) and trimethylchlorosilane (1.2 equiv., 21 mmol, 2.65 mL) were dissolved in acetonitrile (10 mL). A solution of sodium iodide (1.2 equiv., 21 mmol, 3.15 g) in acetonitrile (30 mL) was added dropwise over 15 minutes at ambient temperature. The mixture was stirred for another 15 minutes. A white precipitate ($Et_3NH^+I^-$) was formed throughout the reaction. Ice-water (20 mL) was added to redissolve the salt. Cold *n*-pentane (20 mL) was added and the pentane layer was separated. The reaction mixture was extracted with cold *n*-pentane (2 × 20 mL). The combined organic layer was washed with saturated NH_4Cl-solution (20 mL), dried over magnesium sulfate and concentrated in vacuo. Further purification was achieved by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 19:1) to provide the product as yellow compound.

Trimethyl((1-(p-tolyl)vinyl)oxy)silane (10a)[317]



10a

37%, yellow crystals, mp = 90°C (lit.: 90 – 92°C)

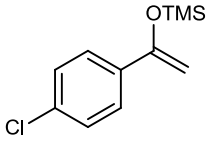
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.29 (s, 9H), 2.37 (s, 3H), 4.41 (d, $^2J_{H,H}$ = 1.6 Hz, 1H), 4.90 (d, $^2J_{H,H}$ = 1.6 Hz, 1H), 7.12 – 7.17 (m, 2H), 7.46 – 7.54 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 0.2, 21.3, 90.5, 125.3, 128.9, 134.9, 138.2, 155.8.

MS (EI): *m/z* (%) = 206.1 (18) [$M^{\bullet+}$], 191.1 (100) [$M^{\bullet+} - CH_3^{\bullet}$].

R_f (PE/EA 8:1) = 0.80.

((1-(4-Chlorophenyl)vinyl)oxy)trimethylsilane (10c)[317]



10c

22%, yellowish crystals, mp = 116°C (lit.: 112 – 117°C)

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.28 (s, 9H), 4.45 (d, $^2J_{H,H}$ = 1.9 Hz, 1H), 4.90 (d, $^2J_{H,H}$ = 1.9 Hz, 1H), 7.26 – 7.33 (m, 2H), 7.49 – 7.56 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 0.2, 91.5, 126.7, 128.4, 134.1, 136.1, 154.8.

MS (EI): *m/z* (%) = 226.1 (22) [$M^{\bullet+}$], 225.1 (26) [$M^{\bullet+} - H^{\bullet}$], 211.1 (40) [$M^{\bullet+} - CH_3^{\bullet}$], 191.1 (100) [$M^{\bullet+} - Cl^{\bullet}$].

R_f (PE/EA 8:1) = 0.84.

4.4.3 Glass Microreactor and Irradiation Setup

The microreactor **LTF-V** (Little Things Factory GmbH, Elsoff, Germany) consists of a borosilicate glass platter (dimensions: 115 x 60 x 6 mm, diameter of channel: 1.0 mm, volume: 1.7 mL) placed in a homemade cooling block. Eight blue high-power LEDs (λ_{max} = 455nm ± 15 nm, P = 3.0 W) were used as source of radiation. Irradiation from both sides was achieved by a mirror on the bottom. The solution was pumped through the microreactor with a syringe pump (LA–100, Landgraf Laborsysteme HLL GmbH, Langenhagen, Germany).

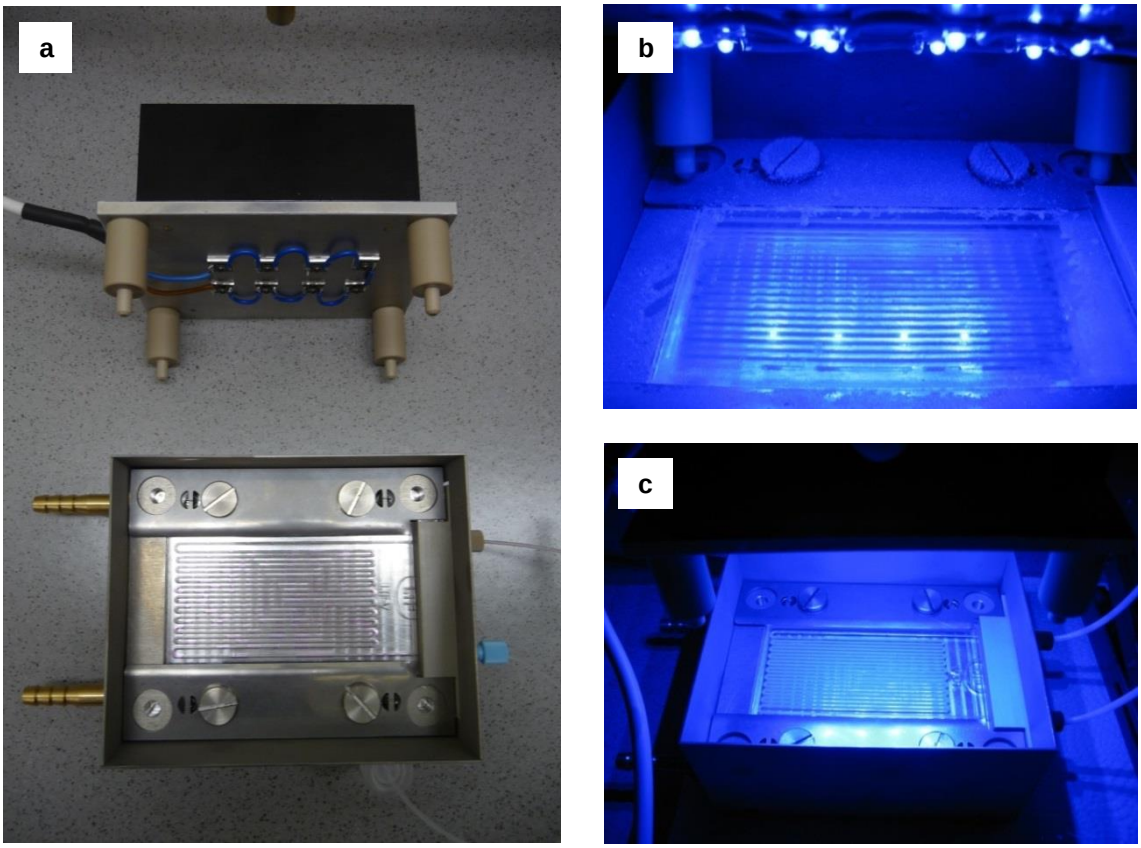


Figure 20: Photomicroreactor irradiation setup. [m]

[m] Photograph a) was taken by Peter Schroll, photographs b) and c) were taken by Maria Cherevatskaya.

4.4.4 Photocatalytic Experiments

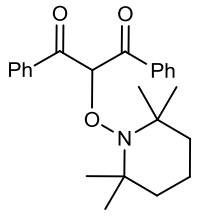
General Procedure A for Photocatalytic α-Oxyamination Reactions of Stable Nucleophiles

A 10 mL flask was equipped with $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.02 equiv., 0.012 mmol, 9.0 mg), nucleophile (1.0 equiv., 0.6 mmol), TEMPO (1.0 equiv., 0.6 mmol, 93.8 mg), ammonium peroxodisulfate (0.5 equiv., 0.3 mmol, 68.5 mg), and dry DMSO (6.0 mL). The mixture was transferred to a glass microreactor (115 × 60 × 6 mm, diameter of capillary: 1.0 mm) by a syringe and was irradiated with an array of eight blue high-power LEDs (λ_{max} = 455 ± 15 nm, P = 3.0 W) for ten minutes. The temperature in the microreactor was kept at 20°C. After that, the reaction mixture was diluted with water (5 mL) and extracted with diethyl ether (3 × 5 mL). The combined organic layer was concentrated in vacuo. Purification of the crude product was achieved by flash column chromatography (petroleum ether/ethyl acetate, 19:1). General Procedure A has been used for α-oxyamination of sodium enolates and silyl enol ethers.

General Procedure B for Photocatalytic α-Oxyamination Reactions of in situ generated Nucleophiles

General Procedure B differed from General Procedure A by initial addition of sodium hydride (1.2 equiv., 0.72 mmol, 50 mg, 60% suspension in paraffin oil). α-Oxyamination reactions of organophosphorus compounds were performed following General Procedure B.

1,3-Diphenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propane-1,3-dione (3a)[289]



3a

93%, colorless crystals, mp = 86°C

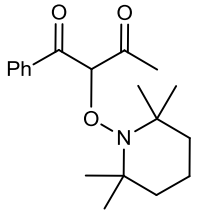
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.95 (s, 6H), 1.13 (s, 6H), 1.23 – 1.34 (m, 2H), 1.38 – 1.47 (m, 4H), 6.29 (s, 1H), 7.39 – 7.47 (m, 4H), 7.49 – 7.59 (m, 2H), 8.16 – 8.22 (m, 4H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 17.1, 20.4, 33.1, 40.2, 60.3, 99.3, 128.6, 130.3, 133.8, 134.8, 195.2.

MS (ESI): *m/z* (%) = 380.2 (100) [MH^+].

R_f (PE:EA 8:1) = 0.60.

1-Phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butane-1,3-dione (3b)[281]



3b

81%, colorless crystals, mp = 66 °C (lit.: 67°C)

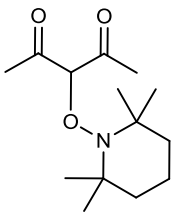
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.82 (s, 3H), 1.04 (s, 3H), 1.06 (s, 3H), 1.25 (s, 3H), 1.32 – 1.41 (m, 4H), 1.44 – 1.52 (m, 2H), 2.23 (s, 3H), 5.59 (s, 1H), 7.41 – 7.49 (m, 2H), 7.52 – 7.60 (m, 1H), 8.05 – 8.12 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 17.0, 20.2, 26.8, 32.9, 40.1, 60.0, 100.2, 128.6, 129.9, 133.9, 134.8, 195.3, 203.7.

MS (ESI): *m/z* (%) = 318.2 (100) [MH^+].

R_f (PE:EA 8:1) = 0.66.

3-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)pentane-2,4-dione (3c)[289]



3c

82%, colorless oil

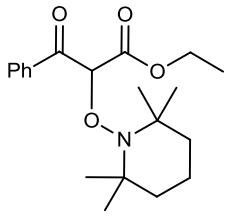
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.97 (s, 6H), 1.20 (s, 6H), 1.36 – 1.47 (m, 4H), 1.51 – 1.65 (m, 2H), 2.22 (s, 6H), 4.93 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 17.0, 20.3, 27.2, 33.1, 40.3, 60.2, 101.8, 204.0.

MS (ESI): *m/z* (%) = 256.2 (100) [MH^+].

R_f (PE:EA 8:1) = 0.58.

Ethyl 3-oxo-3-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3d)[281]



3d

96%, white needles, mp = 63 °C (lit.: 63°C)

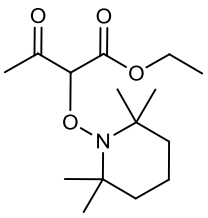
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.81 (s 3H), 0.97 (s, 3H), 1.12 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3H), 1.16 (s, 3H), 1.27 (s, 3H), 1.32 – 1.41 (m, 2H), 1.43 – 1.58 (m, 4H), 4.15 (q, $^{3}J_{H,H}$ = 7.1 Hz, 2H), 5.40 (s, 1H), 7.39 – 7.49 (m, 2H), 7.51 – 7.60 (m, 1H), 8.08 – 8.17 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 14.0, 17.0, 20.3, 33.2, 40.1, 60.1, 61.7, 92.9, 128.6, 129.9, 133.7, 134.5, 168.3, 193.7.

MS (ESI): *m/z* (%) = 348.2 (100) [MH^+].

R_f (PE:EA 8:1) = 0.54.

Ethyl 3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanoate (3e)[281]



3e

86%, colorless oil

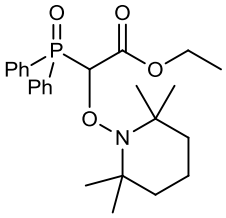
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.99 (s, 3H), 1.05 (s, 3H), 1.19 (s, 6H), 1.28 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3H), 1.35 – 1.49 (m, 4H), 1.52 – 1.63 (m, 2H), 2.31 (s, 3H), 4.21 (q, $^{3}J_{H,H}$ = 7.1 Hz, 2H), 4.80 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 14.2, 17.1, 20.3, 26.7, 32.7, 33.2, 40.3, 61.8, 93.8, 168.0, 203.3.

MS (ESI): *m/z* (%) = 286.2 (100) [MH^+].

R_f (PE/EA 8:1) = 0.57.

Ethyl-2-(diphenylphosphoryl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy) acetate (9a)



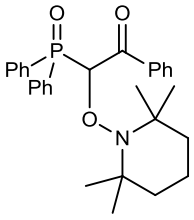
9a

Only a minor amount of the product was obtained that did not allow a spectroscopic characterization and product isolation.

MS (ESI): *m/z* (%) = 444.2 (100) [MH^+].

R_f (PE/EA 1:1) = 0.72.

2-(Diphenylphosphoryl)-1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethanone (9b)



9b

68%, colorless oil

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.87 (s, 6H), 1.09 (s, 3H), 1.14 – 1.31 (m, 7H), 1.34 – 1.44 (m, 2H), 6.34 (d, $^{2}J_{P,H}$ = 16.3 Hz, 1H), 7.18 – 7.28 (m, 3H), 7.29 – 7.36 (m,

2H), 7.41 – 7.57 (m, 5H), 7.61 – 7.66 (m, 1H), 7.68 – 7.74 (m, 2H), 8.09 – 8.19 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 16.9, 24.0, 36.0, 40.9, 56.0, 89.3 (d, $^1J_{C,P}$ = 65.7 Hz), 128.0 (d, $^3J_{C,P}$ = 12.1 Hz), 128.2 (d, $^3J_{C,P}$ = 12.5 Hz), 128.4, 128.9, 130.3 (d, $^1J_{C,P}$ = 100.7 Hz), 130.6 (d, $^1J_{C,P}$ = 101.1 Hz), 131.8 (d, $^4J_{C,P}$ = 2.9 Hz), 132.1 (d, $^2J_{C,P}$ = 9.5 Hz), 132.2132.7 (d, $^2J_{C,P}$ = 10.0 Hz), 133.2, 137.1 (d, $^3J_{C,P}$ = 1.2 Hz), 198.5 (d, $^2J_{C,P}$ = 5.5 Hz).

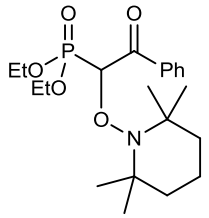
^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ [ppm] = 30.8.

MS (ESI): *m/z* (%) = 476.2 (100) [MH^+].

HRMS (ESI) *m/z*: calcd. for $C_{29}H_{35}NO_3P$ [MH^+]: 476.2355, found: 476.2362.

R_f (PE/EA 1:1) = 0.48.

Diethyl(2-oxo-2-phenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl) phosphonate (9c)



9c

57%, colorless oil

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 0.84 (s, 3H), 1.06 (s, 3H), 1.13 (t, $^3J_{H,H}$ = 7.1 Hz, 3H), 1.25 (s, 3H), 1.29 (t, $^3J_{H,H}$ = 7.1 Hz, 3H), 1.36 – 1.42 (m, 4H), 1.50 (s, 3H), 1.73 – 1.87 (m, 2H), 4.05 (pquint, $^3J_{H,H}$ = 7.1 Hz, $^3J_{P,H}$ = 7.1 Hz, 2H), 4.17 (pquint, $^3J_{H,H}$ = 7.1 Hz, $^3J_{P,H}$ = 7.1 Hz, 2H), 5.70 (d, $^2J_{P,H}$ = 19.7 Hz, 1H), 7.46 (pt, $^3J_{H,H}$ = 7.3 Hz, 2H), 7.56 (t, $^3J_{H,H}$ = 7.3 Hz, 1H), 8.03 (d, $^3J_{H,H}$ = 7.3 Hz, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 16.1 (d, $^3J_{C,P}$ = 6.5 Hz), 16.4 (d, $^3J_{C,P}$ = 6.1 Hz), 17.0, 20.3, 34.2, 40.9, 60.0, 62.8 (d, $^2J_{C,P}$ = 7.0 Hz), 63.5 (d, $^2J_{C,P}$ = 6.7 Hz), 87.7, (d, $^1J_{C,P}$ = 66.4 Hz)128.6, 129.2, 133.3, 137.1 (d, $^3J_{C,P}$ = 1.3 Hz), 196.3 (d, $^2J_{C,P}$ = 3.0 Hz).

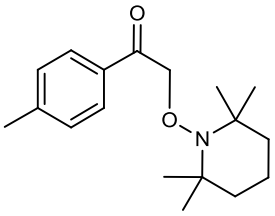
^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): δ [ppm] = 16.2.

MS (ESI): *m/z* (%) = 412.2 (100) [MH^+].

HRMS (ESI) *m/z*: calcd. for $C_{21}H_{35}NO_5P$ [MH^+]: 412.2253, found: 412.2256.

R_f (PE/EA 1:1) = 0.59.

2-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)-1-(p-tolyl)ethanone (11a)[318]



11a

64%, colorless oil

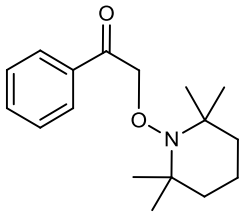
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.17 (s, 12H), 1.23 – 1.36 (m, 4H), 1.43 – 1.51 (m, 2H), 2.41 (s, 3H), 5.09 (s, 2H), 7.50 – 7.55 (m, 1H), 7.68 – 7.74 (m, 1H), 7.81 – 7.87 (m, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 17.2, 20.4, 21.3, 31.7, 39.9, 60.2, 81.4, 120.7, 128.2, 128.7, 129.4, 197.9.

MS (ESI): *m/z* (%) = 290.2 (100) [MH^+].

R_f (PE/EA 19:1) = 0.40.

1-Phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethanone (11b)[318, 319]



11b

65%, colorless oil

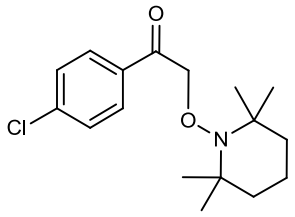
^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.18 (s, 12H), 1.23 – 1.32 (m, 4H), 1.42 – 1.52 (m, 2H), 5.12 (s, 2H), 7.40 – 7.51 (m, 2H), 7.52 – 7.61 (m, 1H), 7.90 -7.97 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 17.1, 20.4, 32.9, 39.8, 60.3, 81.4, 128.1, 128.7, 129.1, 133.4, 197.5.

MS (ESI): *m/z* (%) = 276.2 (100) [MH^+].

R_f (PE/EA 8:1) = 0.60.

1-(4-Chlorophenyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethanone (11c)



11c

77%, colorless oil

^{1}H-NMR (300 MHz, $CDCl_3$): δ [ppm] = 1.16 (s, 12H), 1.42 – 1.52 (m, 4H), 1.53 – 1.63 (m, 2H), 5.05 (s, 2H), 7.40 – 7.47 (m, 2H), 7.86 – 7.92 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ [ppm] = 17.2, 20.4, 33.0, 39.8, 60.3, 81.6, 129.1, 129.7, 133.8, 139.8, 195.0.

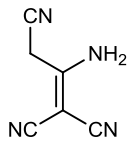
MS (ESI): *m/z* (%) = 310.2 (100) [MH^+].

HRMS (ESI) *m/z*: calcd. for $C_{17}H_{25}ClNO_2$ [MH^+]: 310.1574, found: 310.1574.

R_f (PE/EA 19:1) = 0.46.

Additional product

2-Amino-1,1,3-tricyanopropene (8)[303, 304]



7

87%, reddish powder, mp = 170 °C (lit.: 170 – 172°C)

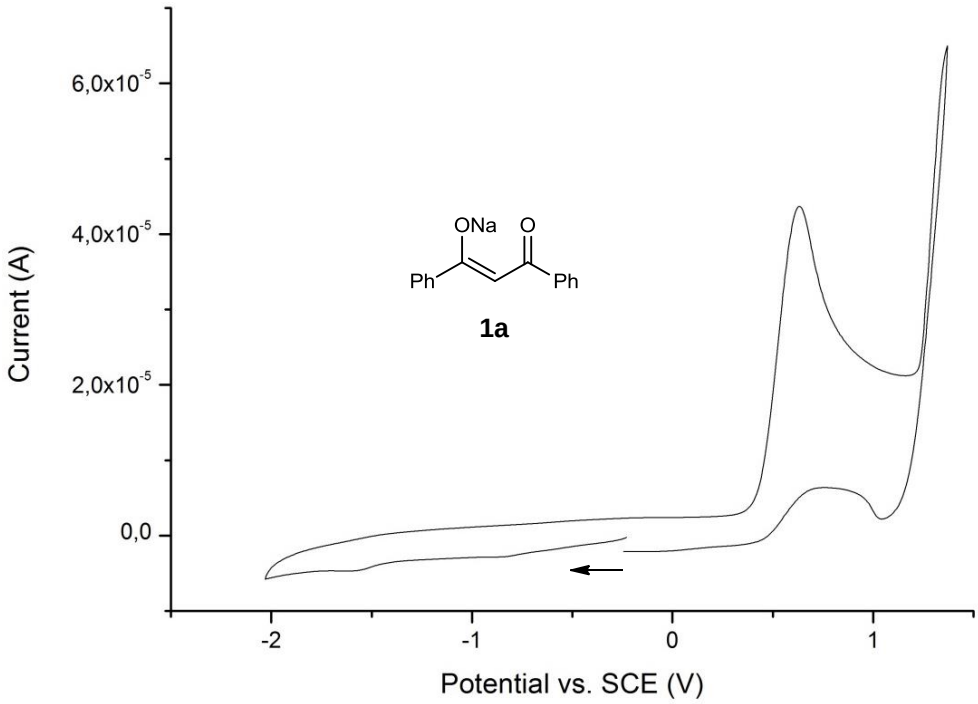
^{1}H-NMR (300 MHz, DMSO-d_6): δ [ppm] = 3.37 (s, 2H), 5.10 (bs, 2H).

^{13}C-NMR (75 MHz, DMSO-d_6): δ [ppm] = 30.9, 45.0, 122.3, 124.0, 130.5, 163.7.

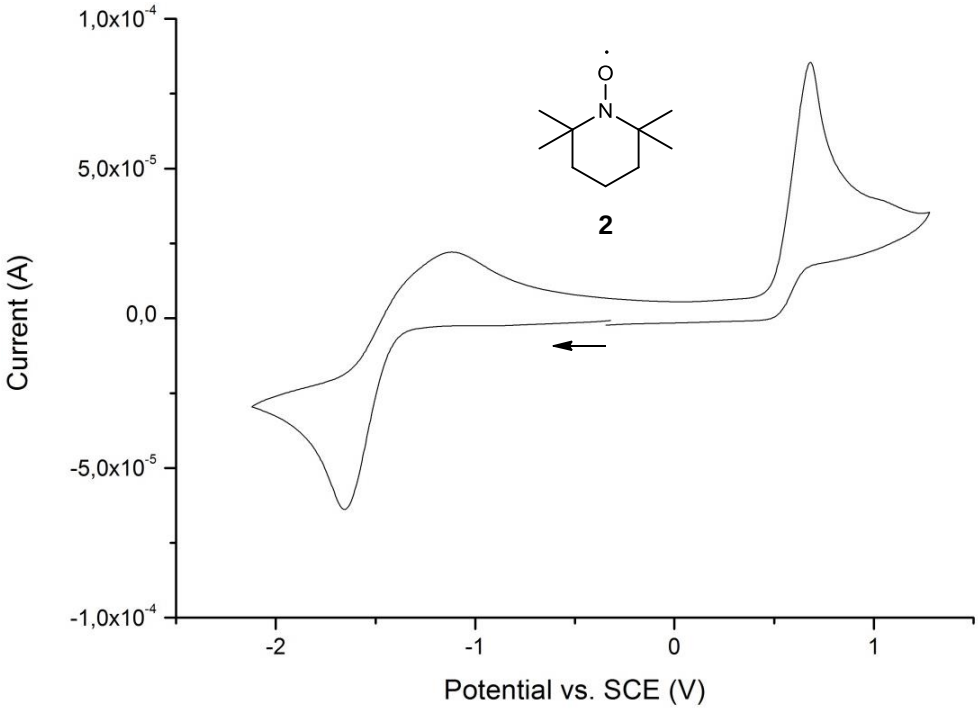
MS (ESI): *m/z* (%) = 133.0 (100) [MH^+].

4.4.5 Cyclic Voltammograms

Sodium (Z)-3-oxo-1,3-diphenylprop-1-en-1-olate (1a) in DMSO

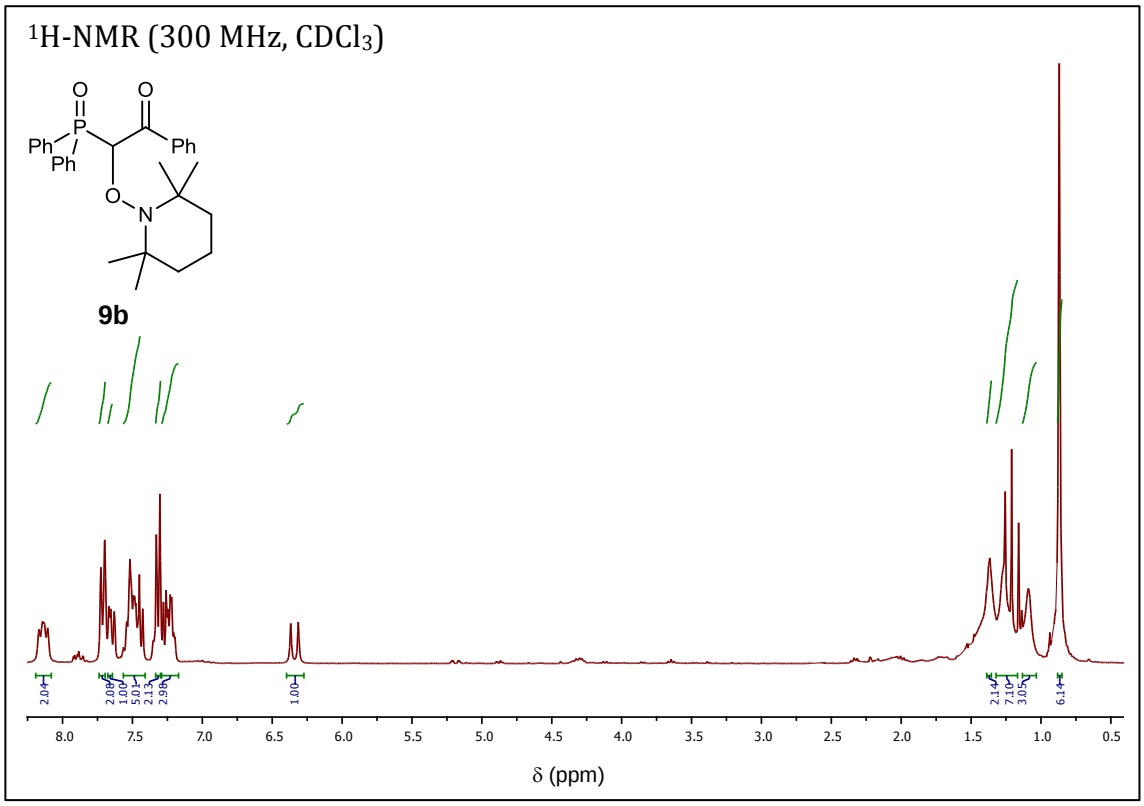


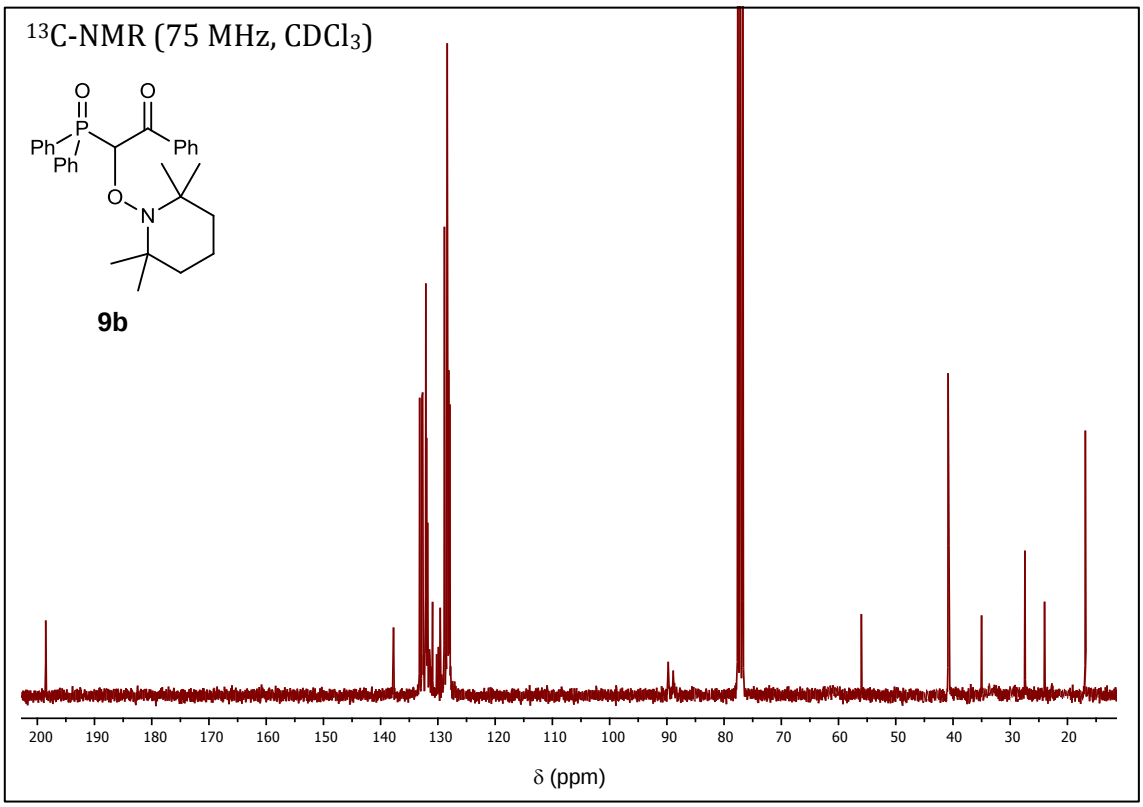
2,2,6,6-Tetramethylpiperidine nitroxide (TEMPO, 2) in DMSO

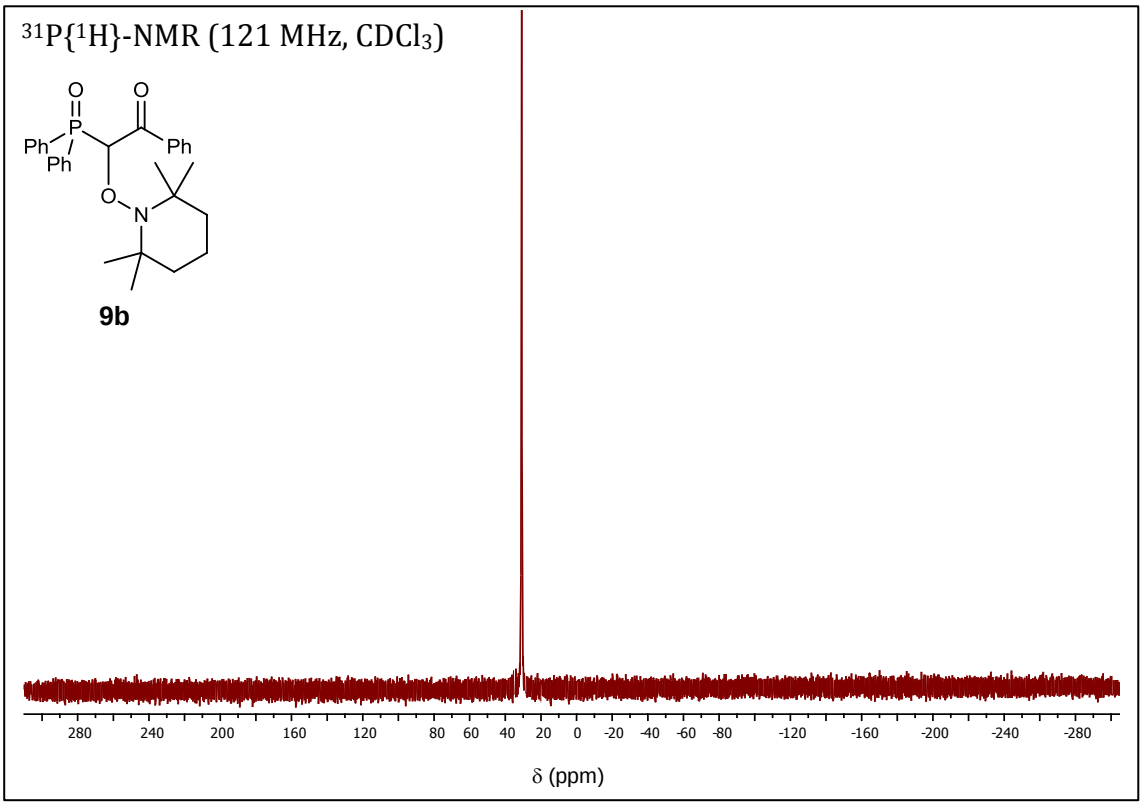


4.4.6 NMR Spectra

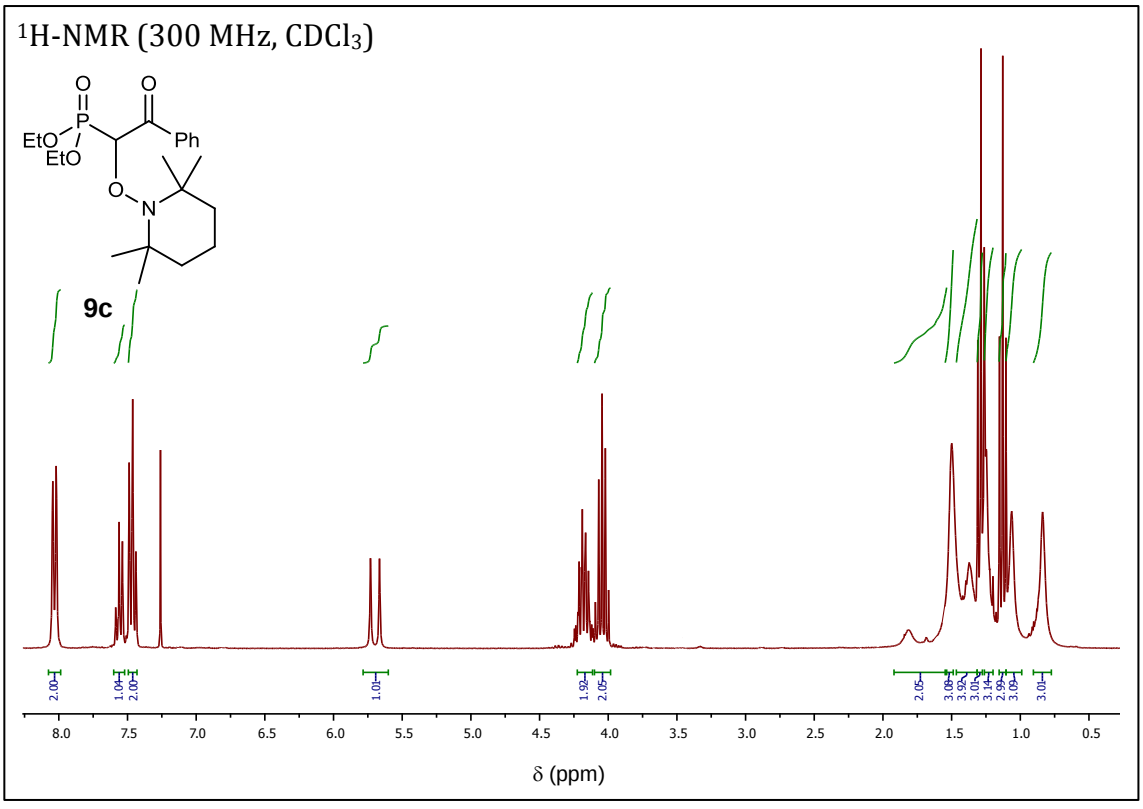
2-(Diphenylphosphoryl)-1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethanone (9b)

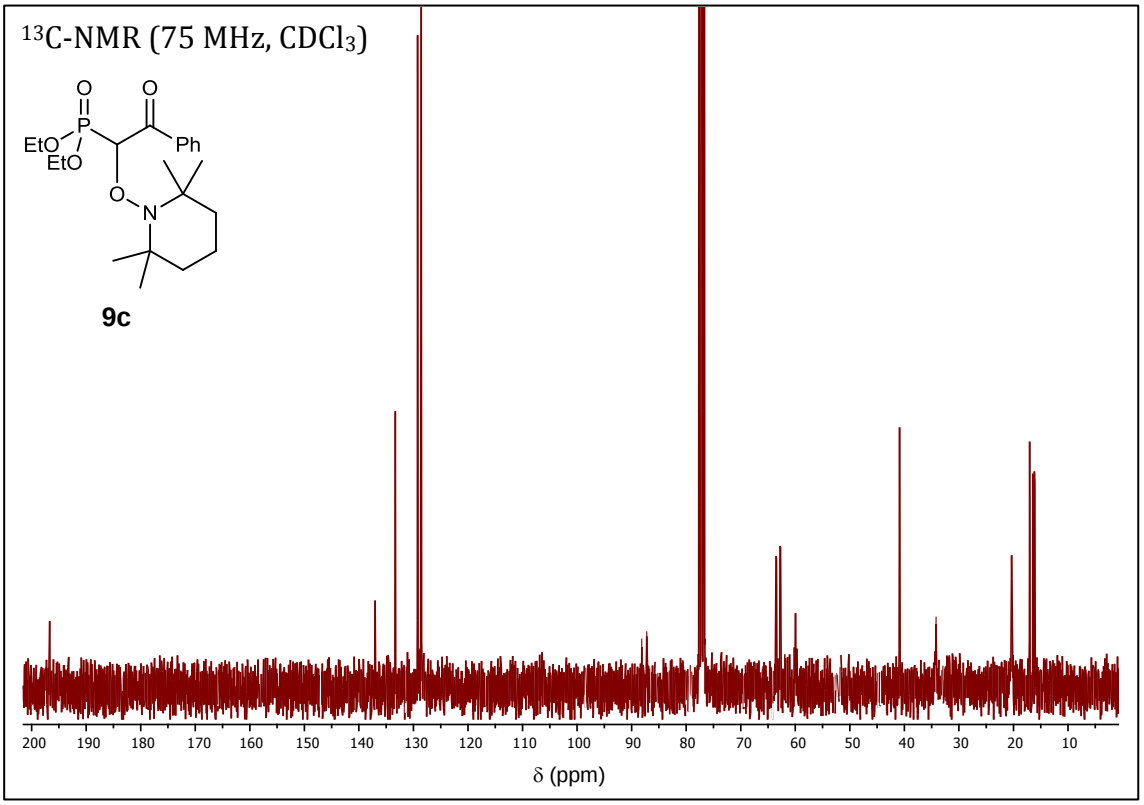


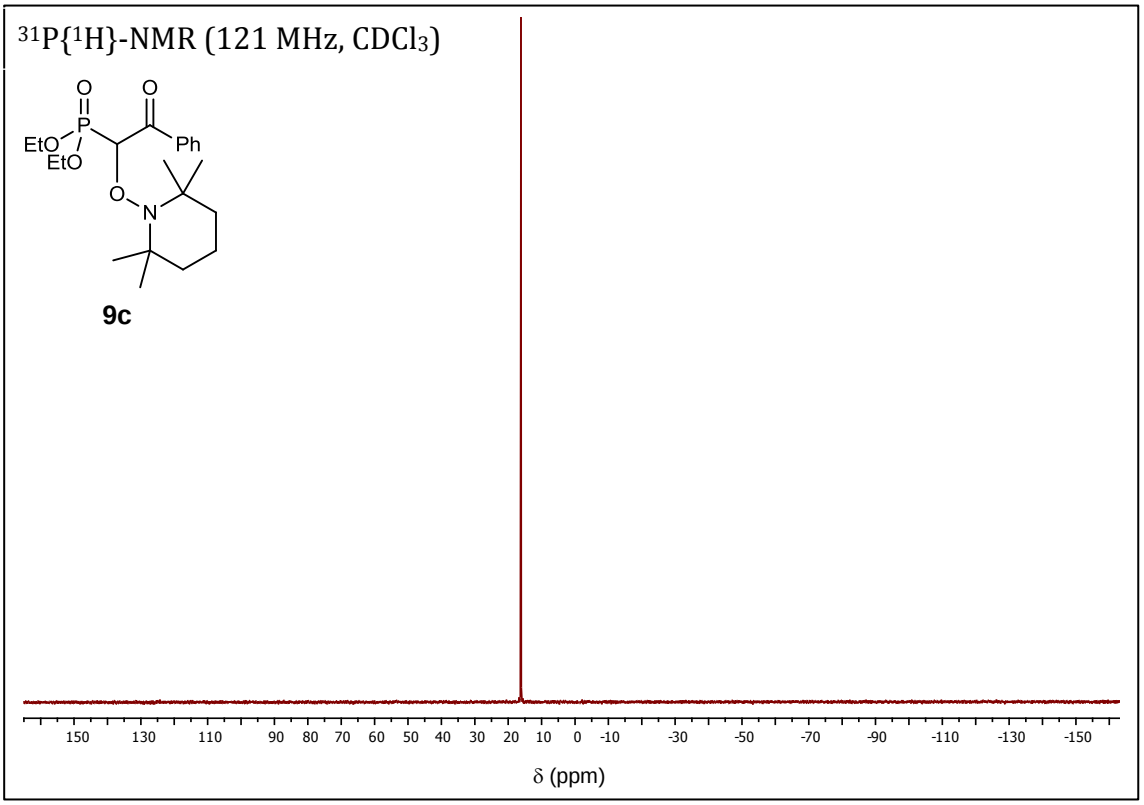




Diethyl(2-oxo-2-phenyl-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl) phosphonate (9c)

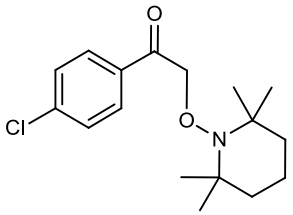



13C-NMR (75 MHz, CDCl3)
O
O
P
EtO
EtO
Ph
O
N
9c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)


31P{1H}-NMR (121 MHz, CDCl3)
O
O
P
EtO
EtO
Ph
O
N
9c
150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150
δ (ppm)

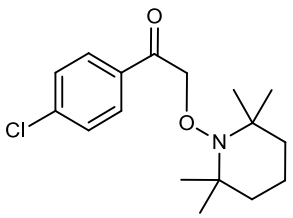
1-(4-Chlorophenyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethanone (11c)

^{1}H-NMR (300 MHz, $CDCl_3$)



11c

^{13}C-NMR (75 MHz, $CDCl_3$)



11c

4.5 References

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5 SUMMARY

The thesis deals with the development of photoredox catalysis by visible light-mediated single-electron transfer reactions for application in synthetic organic chemistry.

Chapter 1 represents a synopsis concerning the beginnings of organic photochemistry from a synthetic point of view. The discovery of the first chemical reactions driven by light are presented alongside their importance in biology (photosynthesis) and technical applications (photography). The section discusses accidentally discovered single photochemical reactions as well as the Ciamician's first systematic study on the behavior of light towards matter which led to the development of this new branch of chemistry. Moreover, chapter 1 highlights the discovery of certain basic physical principles which helped to explain the results and observations of early photochemical reactions.

Chapter 2 describes the homogeneous Photo-Meerwein reaction, a visible light-driven intermolecular arylation of π-electron donors by aryl radicals. Aryl radicals as the key intermediates were generated through photocatalytic one-electron reduction of arenediazonium cations by redox-active transition metal-based and metal-free chromophores as photocatalysts. Control Experiments confirmed the photocatalytic nature of the reaction. The Photo-Meerwein arylation was found to proceed through radical addition to unsaturated substrates, oxidation of the intermediate, and deprotonation to give the unsaturated arylated product. Investigations with respect to the substrate scope of the method showed high tolerance toward a multitude of functional groups. A large number of arene-diazonium salts was effectively coupled in the direct arylation of olefins, acetylenes, enones, and *N*-heteroarenes. Further characteristics of this photo-catalytic C-C coupling reaction include high yields, low catalyst loadings, and mild conditions.

A heterogeneous Photo-Meerwein reaction is presented in chapter 3. Cellulose sheets were chemically modified by covalent attachment of coumarin as a chromophore to make the surface sensitive to the Photo-Meerwein conditions. The

use of a mask to pattern the surface resulted in directly visible images and allowed spatial resolution throughout the photocatalyzed reaction, since arylation occurred only in irradiated parts and not in parts covered by the non-transparent photomask. Arylation altered the photophysical properties of the chromophore and led to an image observable with both spectroscopic methods and the naked eye.

The last section (chapter 4) deals with a visible light-mediated α-oxyamination reaction as a result of a one-electron oxidation in the presence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) as a photocatalyst. The required redox energy arose from the electronic excitation of the photocatalyst with visible light. 2,2,6,6-Tetramethylpiperidine nitroxide (TEMPO) was found to be photocatalytically oxidized to the oxoammonium ion ($TEMPO^+$) and was subsequently trapped by various nucleophiles to yield α-functionalized carbonyl compounds. The reaction time was significantly reduced by the use of microreactor technique.

6 ZUSAMMENFASSUNG

Die vorliegende Arbeit beschäftigt sich mit der Entwicklung und Anwendung von Einelektronentransferreaktionen in der organischen Synthese, die durch sichtbares Licht angetrieben werden.

Kapitel 1 stellt eine Übersicht über die Anfänge der organischen Photochemie aus synthetischer Sicht dar. Es wird die Entdeckung der ersten lichtgetriebenen chemischen Reaktionen behandelt und deren Wichtigkeit in Biologie (Photosynthese) und Technik (Fotografie) hervorgehoben. Der Abschnitt diskutiert sowohl einzelne zufällig entdeckte photochemische Reaktionen als auch die erste systematische Studie hinsichtlich des Verhaltens von Licht gegenüber Materie durch Giacomo Ciamician, die zur Entwicklung eines neuen Zweigs der Chemie führte. Darüber hinaus betont Kapitel 1 die Entdeckung fundamentaler physikalischer Prinzipien, die dazu beitrugen, die Ergebnisse und Beobachtungen früher photochemischer Reaktionen zu erklären.

Kapitel 2 beschreibt die homogene Photo-Meerwein Arylierung, eine durch sichtbares Licht angetriebene intermolekulare Arylierung von π-Elektronendonoren durch Arylradikale. Arylradikale als Schlüsselintermediate wurden durch photokatalytische Einelektronenreduktion von Aryldiazoniumkationen durch redoxaktive übergangsmetallbasierte sowie metallfreie Chromophore als Photokatalysatoren erzeugt. Kontrollexperimente bekräftigten den photokatalytischen Charakter der Reaktion. Die Photo-Meerwein Arylierung verläuft über eine radikalische Addition an ungesättigte Substrate, Oxidation des Zwischenprodukts sowie Deprotonierung zum ungesättigten arylierten Produkt. Untersuchungen hinsichtlich der Substratbreite der Methode zeigten eine hohe Toleranz gegenüber einer Vielzahl von funktionellen Gruppen. Eine große Zahl an Aryldiazoniumsalzen konnte effektiv in der direkten Arylierung von Olefinen, Acetylenen, Enonen und *N*-Heteroaromaten gekuppelt werden. Weitere Charakteristiken dieser photokatalytischen C-C-Bindungsknüpfungsreaktion bestehen in hohen Ausbeuten, niedrigen Katalysatorbeladungen und milden Reaktionsbedingungen.

Die heterogene Photo-Meerwein Reaktion wird in Kapitel 3 behandelt. Cellulosebögen wurden mittels kovalenter Anknüpfung des Chromophors Cumarin chemisch modifiziert und somit für die Bedingungen einer Photo-Meerwein Reaktion zugänglich gemacht. Durch Verwendung einer Schablone während der photokatalytischen Reaktion entstanden unmittelbar sichtbare Bilder. Die Methode gestattete eine räumliche Auflösung der Reaktion, da die Arylierung nur an bestrahlten Teilen der Oberfläche stattfand, nicht jedoch an solchen, die durch die lichtundurchlässige Fotomaske bedeckt waren. Die Arylierung veränderte die photophysikalischen Eigenschaften des Chromophors und führte zur Entstehung zweifarbiger Bilder, die sowohl mit spektroskopischen Methoden als auch mit bloßem Auge beobachtbar war.

Der letzte Abschnitt (Kapitel 4) befasst sich mit einer durch sichtbares Licht angetriebenen α-Oxyaminierungsreaktion, die das Ergebnis einer Einelektronenoxidation in Gegenwart des Photokatalysators $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) darstellt. Die benötigte Redoxenergie stammte dabei aus der elektronischen Anregung des Photokatalysators mit sichtbarem Licht. Es konnte gezeigt werden, dass das 2,2,6,6-Tetramethylpiperidinyloxylradikal (TEMPO) photokatalytisch zum Oxoammoniumion ($TEMPO^+$) oxidiert wird und nachfolgend von verschiedenen Nucleophilen abgefangen werden kann. Die Methode dient damit zur Synthese von α-funktionalisierten Carbonylen. Durch Verwendung eines Mikroreaktors konnte die Reaktionszeit erheblich verkürzt werden.

7 ABBREVIATIONS

A	aq	aqueous
B	bpy	2,2′-bipyridyl
	bs	broad singlet
C	cat.	catalytic amount
	calcd.	calculated
	CI-MS	chemical ionization mass spectrometry
	COSY	correlated spectroscopy
	CV	cyclic voltammetry
D	d	doublet
	DCM	dichloromethane
	dd	doublet of doublets
	DE	diethyl ether
	DMF	*N*,*N*-dimethylformamide
	DMSO	dimethylsulfoxide
	dquint	doublet of quintets
	dt	doublet of triplets
E	E	redox potential
	EA	ethyl acetate
	EI-MS	electron impact mass spectrometry
	equiv.	equivalents
	ESI-MS	electron spray ionization mass spectrometry
	Et	ethyl
	ET	electron transfer
F	Φ	quantum yield
	fac	facial (isomer)
G	GC	gas chromatography
H	$\{^1H\}$	Proton decoupled NMR spectra
	HRMS	high-resolution mass spectrometry
	Hz	Hertz

I	IC	internal conversion
	IR	infrared
	ISC	intersystem crossing
J	*J*	coupling constant
K	K	Kelvin
L	λ	wavelength
	LED	light-emitting diode
M	m	multiplet
	M	molar ($mol \cdot L^{-1}$)
	Me	methyl
	MeCN	acetonitrile
	MeO	methoxy
	MLCT	metal-to-ligand charge transfer
	MS	mass spectrometry
	m/z	mass-to-charge-ratio
N	nm	nanometer
	NMR	nuclear magnetic resonance
	NOESY	nuclear Overhauser enhancement spectroscopy
P	*P*	power
	PE	petroleum ether
	Ph	phenyl
	ppm	parts per million
	ppy	phenylpyridine
	Pr	*n*-propyl
	pquint	pseudo quintet
	pt	pseudo triplet
	PTLC	preparative thin layer chromatography
Q	q	quartet
	quint	quintet
R	R	generic substituent
	R_f	retention factor
	rt	room temperature
S	s	singlet

	SCE	saturated calomel electrode
	SET	single electron transfer
T	*T*	temperature
	t	triplet
	TEMPO	2,2,6,6-tetramethylpiperidine nitroxide
	TFA	trifluoroacetic acid
	THF	tetrahydrofuran
	TLC	thin layer chromatography
	TMS	trimethylsilyl
	TosCl	tosyl chloride, 4-toluenesulfonyl chloride
	tt	triplet of triplets
U	UV	ultraviolet
V	Vis	visible
	vs.	versus
W	W	Watt
X	X	generic substituent
Y	Y	generic substituent
Z	z	number of charges

8 APPENDIX

8.1 Publications

P. Schroll, and B. König, Photocatalytic α-Oxyamination of Stable Enolates, Silyl Enol Ethers, and 2-Oxoalkane Phosphonic Esters. *European Journal of Organic Chemistry* **2014**, *in print*. DOI: 10.1002/ejoc.201403433.

P. Schroll, C. Fehl, S. Dankesreiter, B. König, Photocatalytic Surface Patterning of Cellulose Using Diazonium Salts and Visible light. *Journal of Organic & Biomolecular Chemistry* **2013***, 11,* 6510-6514. DOI: 10.1039/c3ob40990b.

P. Schroll, Early Pioneers of Organic Photochemistry; In: Chemical Photocatalysis (Editor: Burkhard König). *Walter de Gruyter GmbH & Co. KG, Berlin/Boston,* **2013**, 3-18. ISBN: 978-3-11-026924-6.

P. Schroll, B. König, Visible Light Mediated Arylation of Unsaturated Compounds with Diazonium Salts. *European Photochemistry Association Newsletter* **2012**, *83*, 49-51.

P. Schroll, D. P. Hari, B. König, Photocatalytic Arylation of Alkenes, Alkynes and Enones with Diazonium Salts. *Chemistry Open* **2012**, *1*, 130-133. DOI: 10.1002/open.201200011.

D. P. Hari, P. Schroll, B. König, Metal-Free, Visible-Light-Mediated Direct C–H Arylation of Heteroarenes with Aryl Diazonium Salts. *Journal of the American Chemical Society* **2012**, *134*, 2958-2961. DOI: 10.1021/ja212099r.
Highlighted in *Synfacts* 2012, 8(4), 0441, DOI: 10.1055/s-0031-1290582.

P. Schroll, B. König, 1,3-Bis(pyren-1-yl)imidazolium chloride (IPyr·HCl). *Molbank* **2011**, M729. DOI: 10.3390/M729.

8.2 Conferences

4th European Association for Chemical and Molecular Sciences Chemistry Congress, Prague, Czech Republic, **2012**. *Poster presentation*.

Evonik Meets Science, Darmstadt, Germany, **2012**.

4th International Summer School Supramolecular Systems in Chemistry and Biology, Regensburg, Germany, **2011**.

8.3 Poster Presentations

P. Schroll, A. Eisenhofer, D. Sanchez, B. König, C-C and C-X coupling using π-conjugated organic photocatalysts. Graduate School 1626 – Chemical Photocatalysis, Munich, Germany, **2012**.

P. Schroll, D. P. Hari, B. König, Photocatalytic Arylation of Unsaturated Compounds with Diazonium Salts. 4th EuCheMS Chemistry Congress, Prague, Czech Republic, **2012**.

Curriculum Vitae

Peter Schroll

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Date of birth	October 13th, 1984
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Nationality	German
Family status	Unmarried
Languages	German, English, French

Education

11/2010 – present	Graduate student in the group of Prof. Dr. Burkhard König, Institute of Organic Chemistry, University of Regensburg, Germany Dissertation: "Photocatalytic Single-Electron-Transfer Reactions: The Photo-Meerwein Arylation"
10/2008 – 09/2010	Studies of Chemistry, University of Regensburg, Germany Master thesis: "New *N*-Heterocyclic Carbene Ligands for Application in Photocatalysis"
10/2005 – 09/2008	Studies of chemistry, University of Regensburg, Germany Bachelor thesis: "Synthesis of an Aldehyde Intermediate for the Preparation of Ketoalkenes from *Echinacea pallida*"
09/1995 – 06/2004	Grammar school, Leonhard-Wagner-Gymnasium, Schwab-münchen, Germany
03/2012	Internship "Spectroelectrochemistry", University of Reading, United Kingdom

02/2002 – 05/2002	Student exchange to Québéc, Canada
06/2000	Student exchange to Eastbourne, United Kingdom

Teaching Experience

2010 – 2014	Teaching assistant in laboratory courses for undergraduate students of chemistry, biology, biochemistry, and medicine; supervision of bachelor theses; supervision of trainees and undergraduate students

Research Fellowships

01/2012 – 12/2014	Stipend of the Evonik Foundation
08/2012	GDCh travel grant for the 4th EuCheMS Chemistry Congress in Prague, Czech Republic
10/2010 – 12/2011	Research fellowship of the Deutsche Forschungsgemeinschaft (DFG) (GRK 1626, Chemical Photocatalysis)

Regensburg, December 4th, 2014

9 INDEX

9.1 List of Figures

9.2 List of Schemes

9.3 List of Tables

9.4 Subject Index