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The photocycloaddition of arenes and allenes.

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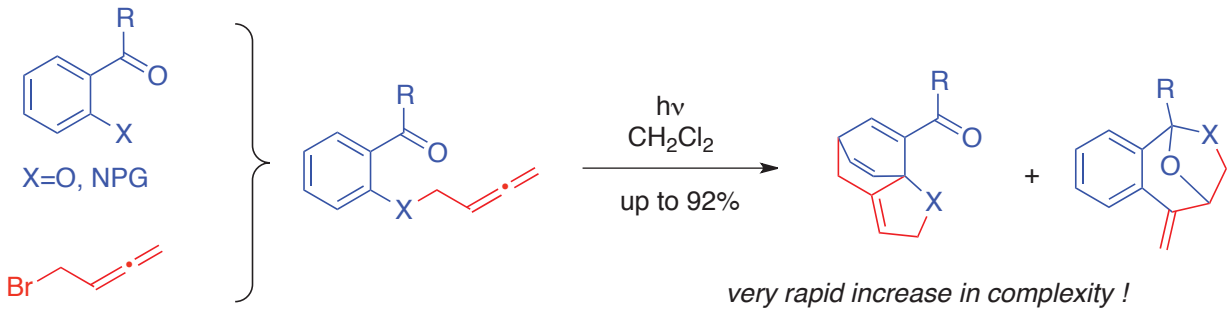
TOC Graphic



Abstract

In the present work, we report on a new intramolecular para-cycloaddition of arenes with allenes, yielding attractive rigid scaffolds bearing several reactive functionalities to build in further diversity. Bicyclo[2.2.2]octadiene-type products and benzoxepine acetals are formed in this reaction, in ratios and yields depending on the substitution pattern on the aromatic ring, the nature of the chromophore and the tether. This unprecedented reaction has remarkable features that distinguishes it from many other photochemical transformations: it is particularly robust with respect to substituents, it can be scaled up without notable loss of efficiency, and it can lead to structures with high complexity in low to good yields. All photochemical precursors could be synthesized readily in three steps. We confirmed the compatibility of the nitrogen atom in the photocycloaddition step, which gives access to bicyclo[2.2.2]octadiene scaffold with two points that allow further diversification. This reaction was scaled up to multigram quantities without erosion of the typically high yields in photocycloadducts. Sequential deprotection of the N- or the C-terminus of bicyclic amino acids gave access to two

conformationally constrained unnatural amino acids with different disposition of the two anchor points.

INTRODUCTION

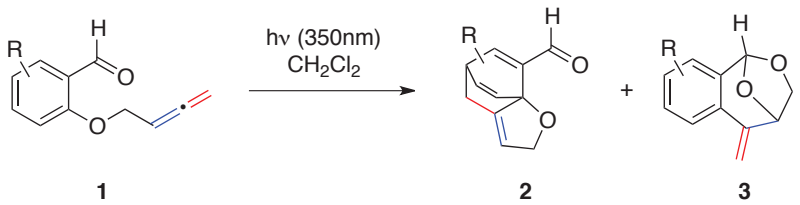
Cycloadditions are very powerful and versatile synthetic tools. They are, by essence, atom-economical, and may lead to the simultaneous formation of several bonds, thus allowing a rapid increase in molecular complexity. Aromatic rings are, however, remarkably resistant to cycloadditions, and very few reactions are capable to exploit them in such processes. Activation by transition metal complexes is one way of conferring an alkene or diene character to aromatic rings, but the main approach is the photochemical excitation. [1,2,3,4,5]

While the *meta* photocycloaddition is very well established[6,7] and has been applied many times in organic synthesis, [8] the *ortho*-[9,10] and particularly the *para*- versions[11] have not yet gained much attention as they occur rarely and usually with low yield. However, these two modes also have the potential to create significant complexity, with the formation of a new ring and up to four new stereocenters.

Among the few examples leading to *para* products in high yield, the benzil-sensitized intramolecular photocycloaddition of a cinnamoylamide and a benzamide moiety leads quantitatively to a bicyclo[2.2.2]octadiene core.[12] The proposed mechanism involves the reaction of the olefininic partner with the *ipso* position of the aromatic ring, leading to a *spiro* biradical intermediate, which then recombines towards the final compound. Interestingly, similar enamides with a naphthyl moiety undergo preferably an *ortho* photocycloaddition.[13] There are earlier reports on the *para* cycloadditions of benzene with allene and 1,2-cyclononadiene, but no yields were mentioned, and the reaction, to the best of our knowledge, was neither further studied nor exploited in synthesis,[14] to the notable exception

of the reaction of 1,1-dimethylallene with 2-phenyl-1-pyrrolium cation reported by Mariano *et al.* which gave significant yields of cycloadducts.[15]

In a preliminary communication, we reported on a very robust intramolecular *para*-cycloaddition of aromatic aldehydes with allenes, which is remarkably tolerant of a variety of substituents on either the allene or the arene partners (Scheme 1).[16] In the present work, we explore the scope and limitation of this reaction, in particular by studying the influence of the chromophore and the nature of the allene tether. This reaction was used to prepare a series of rigid and highly complex cores, bearing several branching points and reactive functionalities, different features that are attractive for diversity-oriented synthesis (DOS).[17]

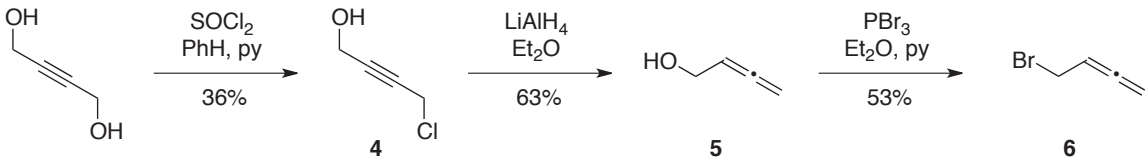


Scheme 1. Intramolecular photocycloadditions of allenyl salicylaldehydes.

RESULTS AND DISCUSSION

Preparation of the substrates

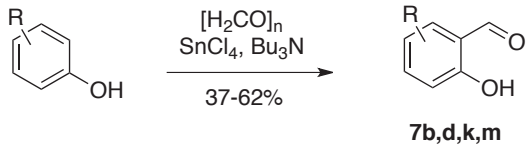
The allene bromide **6** was prepared according to a known two-step sequence (Scheme 2), starting from but-2-yne-1,4-diol which was monochlorinated with thionyl chloride into **4** and then isolated by distillation. Reduction with lithium aluminium hydride gave the allenyl alcohol **5**,[18] which was converted to the allenyl bromide **6** by reaction with phosphorous tribromide.[19]



Scheme 2. Preparation of allenyl bromide **6**.

The salicylaldehydes **7a-p** were either commercially available or prepared from the corresponding phenol precursor by a highly selective tin tetrachloride-catalyzed *ortho*-formylation (Table 1).[20]

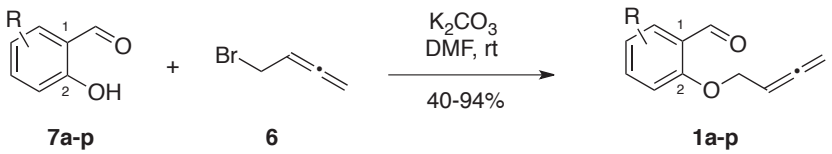
Table 1. Preparation of salicylaldehydes.



Product	R=	isolated yield
7b	3-Me	52 %
7d	3-^{t}Bu	62 %
7k	3,5-Me_2	37 %
7m	3,6-Me_2	42 %

The allenyl bromide **6** was then coupled to variously substituted salicylaldehyde derivatives **7a-p** by a simple nucleophilic displacement in the presence of a weak base, to give the 2-(buta-2,3-dienyloxy)benzaldehyde derivatives **1a-p** in moderate to excellent yields (Table 2).

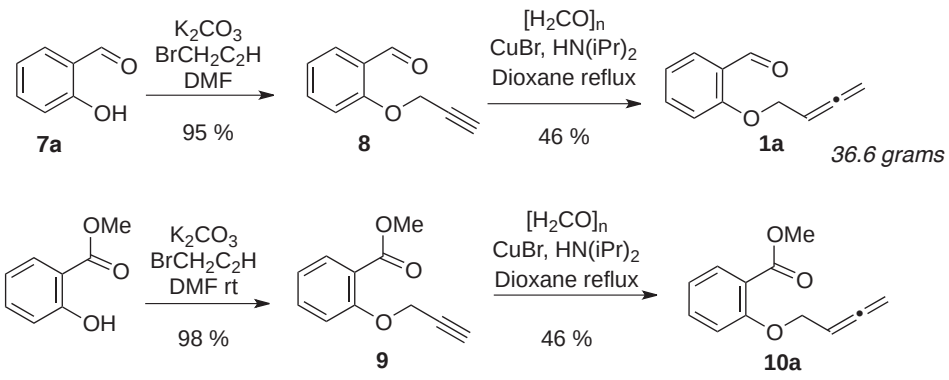
Table 2. Synthesis of allenyloxybenzaldehydes.



Entry	Product	R=	isolated yield
1	**1a**	H	86 %
2	**1b**	3-Me	70 %
3	**1c**	3-OMe	100 %
4	**1d**	3-^{t}Bu	51 %
5	**1e**	4-Me	60 %
6	**1f**	4-OMe	67 %

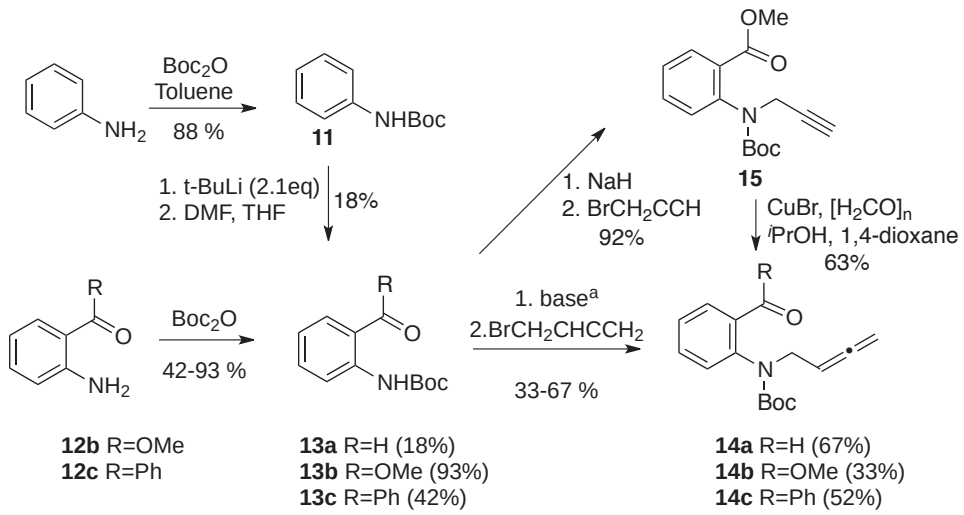
7	**1g**	5-Me	55 %
8	**1h**	5-OMe	75 %
9	**1i**	5-^{t}Bu	59 %
10	**1j**	5-Cl	88 %
11	**1k**	3,5-Me_2	63 %
12	**1l**	3,5-^{t}Bu_2	67 %
13	**1m**	3,6-Me_2	84 %
14	**1n**	4,5-CH_2O_2	89 %
15	**1o**	4-OAc, 5-OMe	40 %
16	**1p**	4-OMe, 5-OAc	94 %

This two-component synthetic route is attractive because of its simplicity, which makes it amenable to the rapid production of an array of photocycloaddition precursors. However, its scale up would require large amounts of bromoallene **6**, the preparation of which is quite cumbersone and globally low-yielding (12% over three steps). Thus we looked for an alternative route, taking advantage of the Crabbé homologation.[21] The salicylic aldehyde **7a** was first alkylated in high yield with propargyl bromide (Scheme 3), and subsequently homologated into allene **1a**. This latter reaction was carried out twice starting with 40 g of **8** yielding in total 36.6 g of photocycloaddition precursor **1a**. Likewise, the methyl ester derivative **10a** was synthesized on a 22 g scale from methyl salicylate by nearly quantitative propargylation, followed by the Crabbé homologation.



Scheme 3. Multigram scale preparation of the allene precursors

As nitrogen is a central element in biologically active molecules, we were interested in including it in our cycloaddition precursor, and to further explore the scope and limitation of this new reaction, considering other types of heteroatoms in the tether. Of particular interest were sulfur and the frequently photochemistry-unfriendly nitrogen atom.[22] If the latter would be compatible, non natural polycyclic amino acids could be obtained in one step from the simple allenylic precursors. Very recently, the thermal counterpart of this reaction was exploited by Vanderwal *et al.* with an amide-tethered allene, exploiting the pioneering work of Himbert *et al.*, who reported intramolecular thermal arene-allene cycloadditions.[23] Thus, the *N*-Boc analogue of allene **1** was prepared in a three-steps sequence starting from aniline (Scheme 3). Protection of the amine with *tert*-butyl dicarbonate into **6** was followed by a quite low-yielding monoformylation,[24] and subsequent allenylation with allenyl bromide, led to the photocycloaddition precursor **14a**. The ester analogue **14b** was prepared by a closely related route, but without the problematic formylation step, taking advantage of the commercially available methyl anthranilate **12b**, which was protected and allenylated (Scheme 4).[25,26]



Scheme 4. Preparation of the cycloaddition precursors. a) K_2CO_3 for **14a**, NaH for **14b,c**.

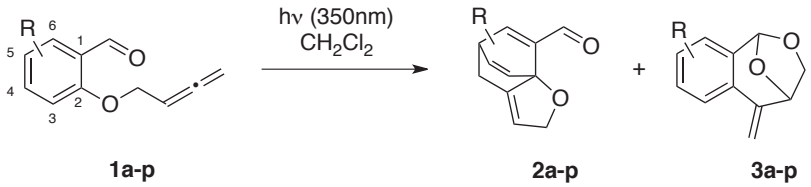
Surprisingly, the allenylation of **13b** failed to proceed with the reaction conditions applied earlier for the benzaldehyde **13a**. Hypothesizing that potassium carbonate was a too weak base, we first

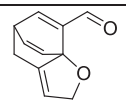
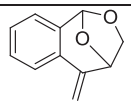
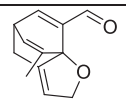
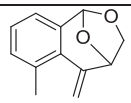
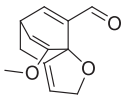
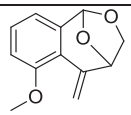
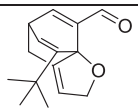
successfully used cesium carbonate and activation of the bromide by the addition of sodium iodide. However, we finally settled for sodium hydride at lower temperature, as a comparable efficiency was observed but for a significantly lower cost. As we had developed an alternative route amenable to scale up,[Error! Bookmark not defined.] we also prepared **14b** by a Crabbé homologation of alkyne **15**, itself obtained by direct propargylation of carbamate **13b**. The overall yield of this sequence is satisfactory, and it was carried out up to a scale of 30 grams. The benzophenone derivative **14c** was also prepared by the protection of **12c**, followed by allenylation.

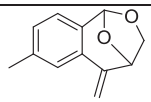
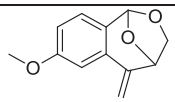
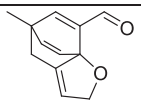
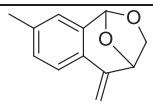
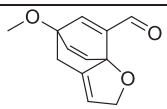
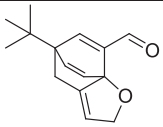
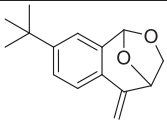
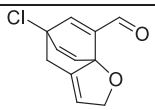
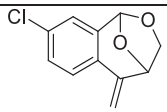
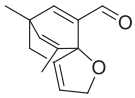
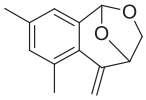
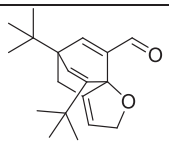
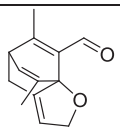
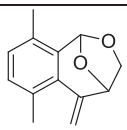
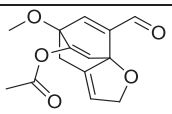
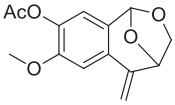
Photochemistry with an oxygen-containing tether

The allenylsalicylaldehyde derivatives **1a-o** were irradiated at 350 nm (Rayonet®, quartz glassware) in dry and degassed dichloromethane at room temperature, and the benzoxepine and dihydrofuran-fused bicyclo[2.2.2]octadiene products **2a-p** and **3a-p** were observed in varying proportions (Table 3).

Table 3. Spectroscopic and isolated yields of irradiation products.



				Spectroscopic experiments			Preparative experiments		
Entry	**1**	**2**	**3**	Time[a]	**2**[a]	**3**[a]	Time[b]	**2**[b]	**3**[b]
1	**1a**			110 min	38%	21%	6 h	19%	15%
2	**1b**			40 min	52%	20%	8 h	10%	13%
3	**1c**			19 min	67%	19%	1.3 h	67%	24%
4	**1d**			40 min	84%	0%	3 h	65%	0%

5	**1e**			200 min	0%	19%	18 h	0%	14%
6	**1f**			525 min	0%	21%	27 h	0%	21%
7	**1g**			80 min	56%	15%	16 h	34%	11%
8	**1h**			60 min	58%	0%	12.5 h	23%	0%
9	**1i**			60 min	58%	11%	13.5 h	63%	20%[c]
10	**1j**			120 min	30%	34%	2.5 h	28%	40%
11	**1k**			30 min	73%	20%	3 h	61%	12%
12	**1l**			30 min	84%	0%	1 h	94%	0%
13	**1m**			120 min	13%	36%	4 h	14%	35%
14	**1o**			90 min	86%	0%	1.5 h	69%	0%
15	**1p**			380 min	0%	19%	48 h	0%	15%[c]

[a]11mM solution, yields determined by ^{1}H-NMR. [b] Preparative scale and isolated yields. [c] Isolated product not totally pure, yield corrected by ^{1}H-NMR.

In order to better compare the values, small scale irradiation under normalized conditions (11 mM in dichloromethane) were performed, and the conversion was monitored by NMR analysis.[27] The reactions were not performed directly in the NMR tube, as deuterated solvents express a different vibrational pattern and may therefore show a non-negligible influence on the non-radiative relaxation of the excited state and may alter the outcome of photochemical reactions.[28] The reaction was also carried out on a preparative scale (0.15-0.79 mmol), and the identity of the products were established by full spectroscopic analyses; the identity of the core structures was confirmed by X-ray analysis of **2l** and **3b**.[16]

Substitution on position 3 of the aromatic ring with electron releasing substituents (Table 3, entries 2-4) accelerates the reaction considerably and enhances the formation of the *para*-photocycloaddition product, whereas the substituents on the position 4 show an opposite effect. For example irradiation of the 4-methyl- or 4-methoxy-substituted analogue leads to remarkably longer reaction times and no formation of the bicyclo[2.2.2]octadiene product (Table 3, entries 5 and 6). On the other hand, substitution at position 5 with electron donating groups leads to shorter reaction times and higher yields of bicyclo[2.2.2]octadienes (Table 3, entries 7 - 9). However the effect is not as strong as for the same substituents on position 3. Interestingly, 5-chloro and 3,6-dimethyl (Table 3, entries 10 and 13) are the only substituents which could enhance the formation of the benzoxepine product. For the substitution with a *tert*-butyl group at position 3 a counterintuitive sterical influence is observed, completely suppressing the formation of the benzoxepine product (Table 3, entries 4 and 12). Additionally, the reaction time is considerably decreased; the bicyclo[2.2.2]octadiene compound **2l** is obtained in a very high yield in one hour on a 100 mg scale. On the other hand, irradiation of **1n** does not yield any photocycloaddition compounds and leads to complete decomposition of the starting material.

Throughout this study Rayonet lamps have been used and replaced as their intensity considerably weakens over their lifetime. Thus, since the irradiation intensity was not consistent, actinometric

measurements were not made and quantum yields are not accessible. However clear trends emerged from these experiments, since overall efficiency varied by a factor up to 50.

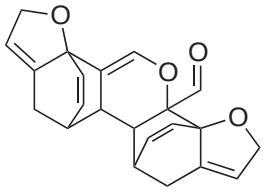
The UV-Vis spectra of the derivatives substituted at position 5 show also red-shifted absorptions (Figure 1, supplementary information). This bathochromic shift could also account for the shorter irradiation times. As the precursors **1** usually show weak absorbance at long wavelength, the 350 nm-centered emission of the fluorescent lamps overlaps only with the tail of the band.

Shortening the irradiation wavelength does not, however, lead to a substantial increase in yield, as shown by the individual monitoring of each compounds arising from **1a** under irradiation at 254 nm (Figure 2, supplementary information). The benzoxepine compound **3a** is relatively photostable at this wavelength, to the contrary of the bicyclo-octadiene derivative **2a**. This experiment also confirms that both compounds are not precursors of each other.

The reaction was nominally carried out in dichloromethane, but we studied the influence of various solvents, such as acetonitrile-d_3, acetone-d_6, methanol-d_4, benzene-d_6 and toluene-d_8 (Figure 3, supplementary information). Dichloromethane, acetonitrile and methanol showed the best results with similar conversion and reaction times; however, dichloromethane shows in all cases the highest yields for the benzoxepine. The photocycloaddition does also take place in acetone, but slower conversion and considerably lower yields for the benzoxepine compound are observed. Benzene and toluene are poor solvents for this photocycloaddition as yields of the benzoxepine compound are low and the bicyclo[2.2.2]octadiene does not form at all in toluene. Deuteration of dichloromethane has no apparent effect on the conversion, at least for **1a**.

This cycloaddition is compatible with multigram scale execution; **1a** was irradiated in 5 batches containing each 9.1 g of starting material in 1.5 L of dichloromethane. Overall, more than 10 g of the final compound **2a** could be produced. The reaction was usually stopped at a conversion of around 60

%, at which point *ca* 20 % of the bicyclo[2.2.2]octadiene product **2a** was formed; further irradiation usually did not lead to a significant increase of product. From each batch, *ca* 30 % of starting material **1a** could be recovered, together with *ca* 10 % of the benzoxepine **3a**. The isolation of **2a** at this scale needed special care, as the bicyclo[2.2.2]octadiene **2a** tends to form its dimer **16** by an apparent hetero-Diels-Alder reaction. The dimerization was observed when the crude reaction mixture was stored at 4 °C overnight, when the monomer was concentrated from a mixture of hexane and ethyl acetate in the rotatory evaporator, or when the monomer was heated in isopropanol.

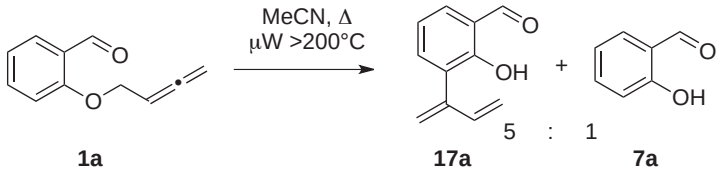


16

This side reaction can however be avoided if the crude mixture is purified immediately after the irradiation by flash chromatography with dichloromethane and ether as solvent mixture. The pure compound can be stored in a freezer over several months without observable dimerization. On the other hand, this high reactivity can be exploited for further modification of the core; this will be published in due course.

Thermal reaction

In order to confirm the photochemical nature of the reaction, it was also attempted under thermal conditions. Therefore the starting material was heated in a microwave oven (Biotage Initiator, single mode, sealed vessel). The starting material **1a** is thermally stable up to 190°C, and some conversion to the product **17** as well as the cleavage of the allenyl to the salicylic aldehyde **7a** is observed above 200°C (Scheme 5). Product **17a** is formed by an apparent Claisen rearrangement,[29] which has already been observed with arylallenyl ethers.[30]

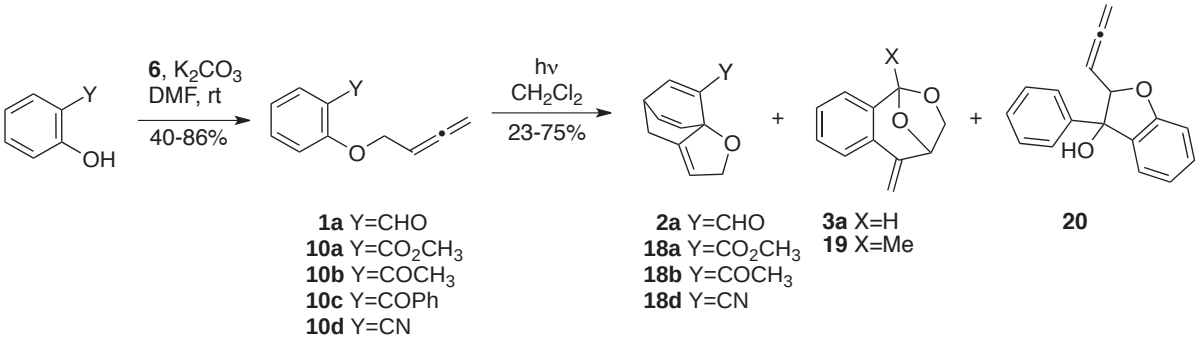


Scheme 5. Thermal reaction of **1a**.

Other chromophores

The reaction is not limited to benzaldehyde derivatives, and other functional groups were examined (Table 4). The Y substituent is an intrinsic part of the chromophore, thus it has a considerable influence on the absorbance (Figure 4, supplementary information); on the other hand, due to the sensitivity of the bicyclo[2.2.2]octadiene to shorter wavelentgths, the change of the irradiation towards more energetic light is detrimental. Therefore three different groups were probed: ester, nitrile and ketone were chosen, taking into account the previously mentioned constrains.

Table 4. Synthesis and photolysis of other precursors.



Entry	Y=	**allene**	**bicyclo[2.2.2]octadiene**	**benzoxepine**	**other**
1	CHO	**1a** (86%)	**2a** (19%)	**3a** (15%)	
2	COMe	**10b** (40%)	**18b** (21%)	**19** (45%)	
3	COPh	**10c** (46%)	-	-	**20** (75%)
4	CO_2Me	**10a** (48%)	**18a** (24%)	-	
5	CN	**10d** (65%)	**18d** (32%)		

As the UV spectra of the methyl benzoate **10a** shows a hypsochromic shift the irradiation was carried out at 300 nm instead of 350 nm and the product **18a** was isolated in 24 % of yield (Table 4, entry 4; this product rapidly degrades after isolation). The *para* photocycloaddition product is the major formed compound and no benzoxepine-like structure was observed. Along with the main compound, a side product could also be isolated from the crude mixture in 6 % yield, and was tentatively identified by proton-NMR as the Claisen-rearranged product **17b**.

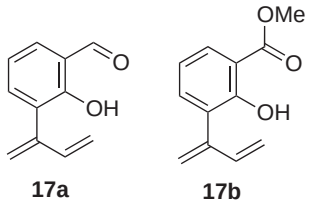


Figure 5. The Claisen rearrangement side products.

Likewise, an analoguous side product, tentatively assigned to **17a** was also isolated from the irradiation of 2-(buta-2,3-dienyloxy)-benzaldehyde **1a** at 254 nm in 6 % yield as well as in the thermal conversion of **1a** upon heating above 200 °C (*vide supra*). The formation of this product could be explained by a photoinduced Claisen rearrangement,[31] but to our knowledge, there are no earlier reports on such reactions with allenes.

The benzonitrile **10d**, as it was already the case for the methyl benzoate **10a,** absorbs at shorter wavelengths than the benzaldehydes. Therefore the irradiation was carried out at 300 nm instead of 350 nm, leading to the isolation of **18d** in 32 % yield. No other photocycloaddition product could be detected. However, traces of the byproduct arising from the Claisen rearrangement were also observed in the crude reaction mixture.

The UV spectra of the acetophenone **10b** shows a slight shift of the absorption to shorter wavelengths, but this effect is less pronounced than for the former two examples. Therefore the starting material can still be excited in the Rayonet reactor at 350 nm, and the benzoxepine **19** was isolated in 45 %, together

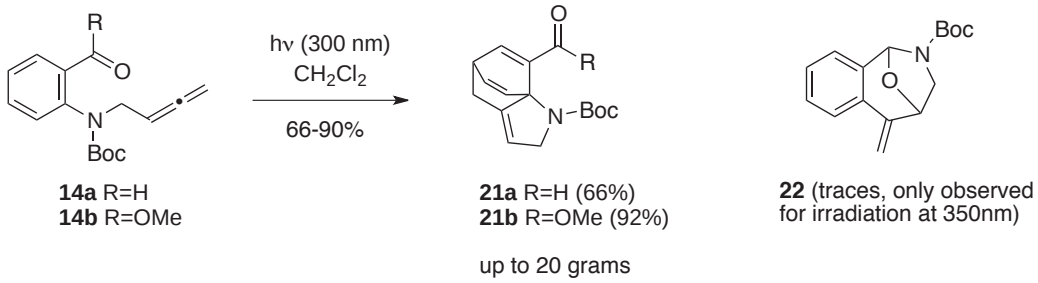
with the bicyclo[2.2.2]octadiene **18b** in a 21 % yield. The ketone and the aldehyde are the only functional group for which we could isolate the benzoxepine products.

As more substituted aliphatic ketones would be prone to Norrish-type I reactions, we turned our attention to the benzophenone analogue **10c**. Photolysis of this substrate would not only open the access to new products but also converges with the work of Griesbeck *et al*., where the photocycloaddition of allyloxy-substituted benzophenone undergo intramolecular photocycloadditions upon irradiation, leading to a benzoxepine and a diastereoisomeric mixture of dihydrobenzofurans.[32] Surprisingly, none of our previously observed compounds were formed. On the other hand, the reaction is very fast and completely regioselective towards a diastereoisomeric mixture of dihydrobenzofurans **15** in high yield (75%). The advantage of the ester and nitriles is the formation of single photoproducts, the bicyclo[2.2.2]octadiene derivatives (Table 5, entries 4 and 5).

Photochemistry with a nitrogen-containing tether

These results motivated us to further explore the scope and limitation of this new reaction, considering other types of heteroatoms in the tehter, in particular the frequently photochemistry-unfriendly nitrogen atom.[22,33] The UV spectrum of the *N*-Boc precursor **14a** is slightly shifted towards shorter wavelengths with respect to its oxygen-containing analogue **1**. The photocycloaddition step was nevertheless carried out at 350 nm, yielding the two photocycloaddition products **21a** and **22** (Scheme 6). However, ^{1}H-NMR spectra of both cycloadducts are poorly resolved and suggest the presence of rotamers. This hypothesis could unfortunately not be confirmed by ^{1}H-NMR spectroscopy at higher temperature (up to 60 °C).[34] On the other hand, when **14a** was irradiated at 300 nm for 2 hours in dichloromethane, the bicyclo[2.2.2]octadiene product **21a** was obtained in good yield, without other regioisomer. Likewise, irradiation of **14b** gave smoothly the cycloadduct **21b** in very high yield, which shows a similar rotamer pattern as for **21a**. This reaction is compatible with larger scale experiments; thus, irradiation

of up to 20 g of compound **14b** in 1.5 L of dichloromethane lead to the isolation of the photocycloadduct **21b** in very high yield (92 %).



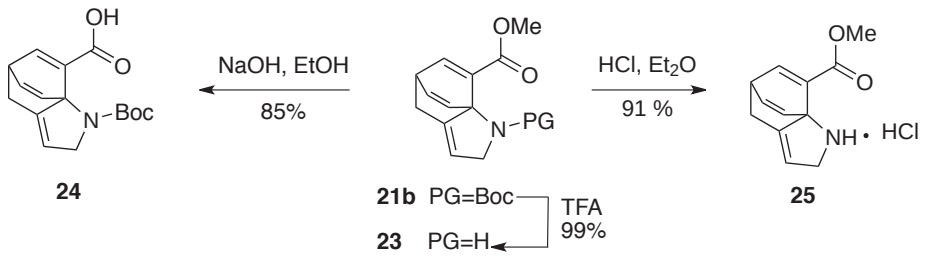
Scheme 6. Photocycloaddition of nitrogen-containing allenes

Since we suspected that the rotamers arise from the *N*-Boc group, we subjected the products to acidic hydrolysis (Scheme 7).

The deprotection of **21a** in trifluoroacetic acid seems to proceed well by TLC analysis; however the isolation of the free amine failed, despite attempts of chromatography on neutral alox, on silica gel eluted with dichloromethane and basified with ammonia saturated methanol, by ion exchange or extraction. Formation of the hydrochloride led to complete decomposition. On the other hand, the cycloadduct **21b** contains two different protecting groups that may be removed to open the access for further diversification (scheme 7). In this case, either trifluoroacetic acid (in presence of anisole as tert-butyl carbocation scavenger)[35] or hydrogen chloride[36] were used.[37] With trifluoroacetic acid, the parent amine **23** is obtained in very high yield after neutralisation of the acid. The hydrochloride salt **25** is obtained by reaction with hydrochloric acid and filtration of the precipitate, or by simple evaporation of the solvent. These procedures give the desired compounds in high purity and yields without further purification. However the solid hydrochloride **25** is easier to handle than the oily amine **23**, and seems to be more stable for storage. At this stage, the NMR spectra were well-resolved, even at room temperature.

The saponification of the methyl ester **21b** was easily achieved by reaction with a sodium hydroxide solution, affording the carboxylic acid **24** in high yield. Purification of this compound by flash

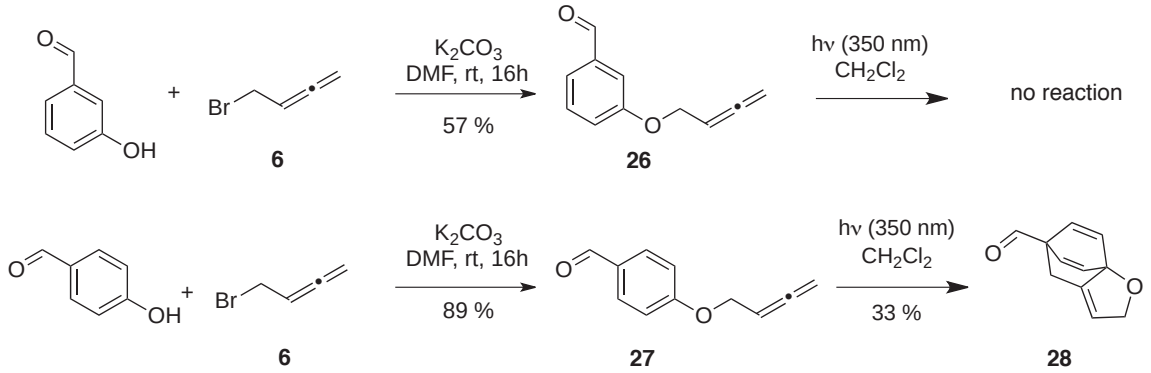
chromatography, recrystallization or by catch and release on solid phase extraction (SPE)[38] did not improve the initial purity. However, further transformation of the compound showed that this purity is sufficient for the generation of a library of amides, which will be reported elsewhere. Therefore, no further purification attempts were tried and the compound was used as extracted from the reaction mixture.



Scheme 7. Deprotection at both termini

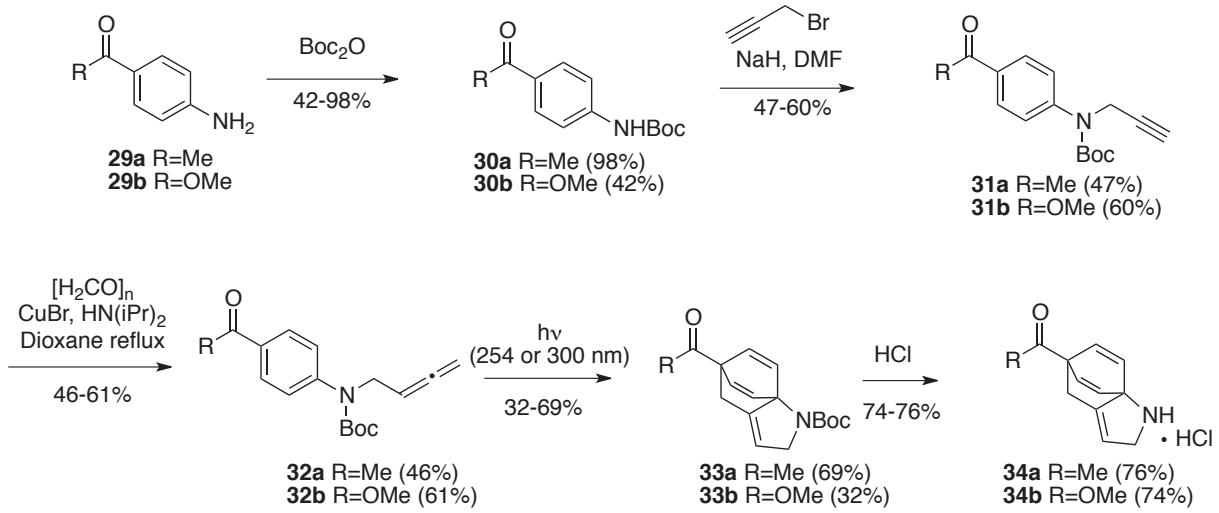
Other regiochemistries

An alternative way to avoid the formation of benzoxepine derivatives is to move the allenyloxy tether away from the aldehyde. Thus, we intended to carry out this photocycloaddition with compounds having the allenyloxy tether attached at the *meta* or *para* position with respect to the aldehyde. The precursors **26** and **27** were readily synthesized via our usual route (Scheme 8). While the *ortho*-substituted **1a** and *meta*-substituted **26** were quite stable, the *para*-substituted analogue **27** is susceptible to oxidation to the carboxylic acid, and therefore should be kept in the absence of air. Irradiation of the *meta*-precursor **26** failed to give identifiable photoproducts, whereas the *para*-substituted **27** formed the desired bicyclo[2.2.2]octadiene compound **28** in moderate yield (33%). It is worth mentioning that a single regioisomer was formed from precursor **27** and the absence of conjugated double bond prevent product **28** from dimerization, observed for **2a**. The difference in reactivity of the *meta* vs *ortho*/*para* isomers is worth noting, and probably arise from the direct conjugation between donor and acceptor subsitutents.



Scheme 8. *meta* and *para* substitution.

In order to verify whether the *para* substitution is also compatible with nitrogen on the tether, we prepared another series of precursors, along the lines of the *ortho* substituted compounds (scheme 9). Thus, the anilines **29a,b** were protected as *N*-Boc (**30a,b**) and propargylated (**31a,b**). The alkynes were then converted into the allenes **32a,b** via a Crabbé homologation.



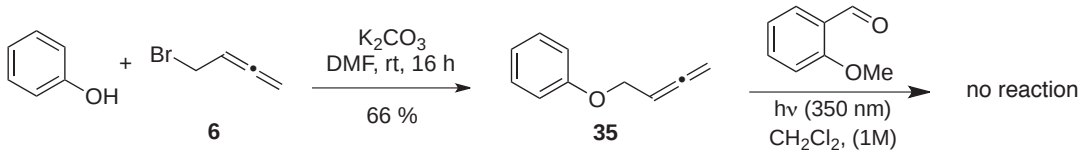
Scheme 9. *para*-product

The precursor **32a** was subsequently irradiated at 300 nm in a Rayonet reactor, and the bicyclo[2.2.2]octadiene **33a** was obtained in good yield (69%). The compound is not very stable but can be easily deprotected into the more stable hydrochloride salt **34a**. Similarly, the photolysis was carried out with the methyl ester **32b**. This compound has a lower absorption at 300 nm, but we nevertheless suceeded in obtaining **33b** by irradiation at 254 nm (32%). Acidic deprotection gave **34b**

in good yield. This amino acid ester has similar potential as **25** as a diversification platform, with a different disposition of the two anchor points, and no chirality.

Intermolecular tests

In order to check whether this photocycloaddition is limited to its intramolecular version, we prepared the compound **35**, by the coupling of the bromoallene **6** with phenol (Scheme 10). It was irradiated at 350 nm as a 1 M solution in dichloromethane with 1 equivalent of *o*-anisaldehyde. We did not observe the formation of any new compounds even after a prolonged irradiation (44 hours), despite a decrease of the anisaldehyde concentration over time.



Scheme 10 Irradiation of **35** in presence of *o*-anisaldehyde.

CONCLUSION

The unprecedented photoreaction described in this work has remarkable features that distinguishes it from many other photochemical transformations: it is particularly robust with respect to substituents, type and location of the chromophore and the nature of the heteroatom in the tether, it can be scaled up without notable loss of efficiency, and it can lead to structures with high complexity in moderate to excellent yields. The mechanism, either a stepwise radical cyclization or a concerted cycloaddition is currently under investigation, and will be reported in due course. We have confirmed the compatibility of nitrogen atom in the photocycloaddition step, which gives access to bicyclo[2.2.2]octadiene scaffolds with two points that allow further diversification. This reaction was scaled up to multigram quantities without erosion of the typically high yields in photocycloadducts. Sequential deprotection of the *N*- or the *C*-terminus of bicyclic amino acids gave access to two conformationally constrained unnatural amino acids with different disposition of the two anchor points. Thus, the presence of several branching points and reactive functionalities gives the opportunity to further diversify these structures

into a wide variety of compounds that could be useful for different applications such as drug discovery; similar substrates with other heteroatom-containing tethers are being investigated. This potential is currently under evaluation.

EXPERIMENTAL SECTION

General Information. Unless otherwise indicated, all starting materials were obtained from standard suppliers and were used without further purification. The deuterated chloroform was dried and neutralized over basic alumina prior to use. Analytical thin layer chromatography was performed on Kieselgel F-254 pre-coated aluminium sheets TLC plates. Visualization was performed with either a 254 nm ultraviolet lamp, or a potassium permanganate staining solution. Silica gel column chromatography was carried out with silica gel (32–63, 60 Å). Solid phase extractions were carried out on Isolute SPE columns NH2, SAX or SCX from Biotage. The ^{1}H and ^{13}C NMR spectra were recorded on Fourier transform spectrometers at 500 MHz, 400 MHz, 360 MHz or 300 MHz. Chemical shifts (δ) are expressed in parts per million using residual solvent protons as reference: chloroform (δ = 7.27 ppm for ^{1}H, δ = 77.0 ppm for ^{13}C), acetonitrile (δ = 1.94 ppm for ^{1}H, δ = 118.69 ppm for ^{13}C), dichloromethane (δ = 5.30 ppm for ^{1}H, δ = 54.00 ppm for ^{13}C), benzene (δ = 7.16 ppm for ^{1}H, δ = 128.39 ppm for ^{13}C), methanol (δ = 3.31 ppm for ^{1}H, δ = 49.15 ppm for ^{13}C), water (δ = 4.75 ppm for ^{1}H), acetone (δ = 2.05 ppm for ^{1}H, δ = 29.92 ppm or 206.68 ppm for ^{13}C), DMSO (δ = 2.50 ppm for ^{1}H, δ = 39.51 ppm for ^{13}C). Coupling constant (*J*) are reported in Hz. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintet), m (multiplet), br s (broad signal). Combination gas chromatography and mass spectroscopy were obtained using a Zebron ZB-1, 30 m x 0.25 mm, 100 % methylpolysiloxane column, mass detection by EI. Combination HPLC and mass spectroscopy were obtained using a photodiode array detector and an ESI mass spectrometer detector. Gradient: A: H_2O + 7 mM formic acid and B: MeCN + 5 mM formic acid. 0 min 5 % B; 4 min 100 %

B; 7 min 100 % B. Flow 0.5 ml/min. Column InterChrom Strategy 3um C18 – 2 50 x 2.0 mm equipped with a precolumnm InterChrom Strategy 3. ESI-HRMS mass spectra were determined by FTMS. FT-IR spectroscopy was performed in chloroform, neat on a NaCl cell or in KBr. Alternatively FT-IR spectra were also recorded using a Golden Gate Single Reflection ATR System. The intensity of the absorption is indicated with w (weak), m (medium) and s (strong). UV–Vis and optical rotation were recorded with standard instruments. Melting points were measured without correction. Photochemical irradiations were carried out in a LUMOS 43 photoreactor (Atlas Photonics Inc.), in a quartz vessel, with 1 diode at 365, 375, 385, 405 or 430 nm, or in a Srinivasan-Griffin (Rayonet-RPR-100) photoreactor, in a quartz vessel, with 16 lamps at 254, 300, 350[39] or 420 nm.

General procedure for nucleophilic substitution to obtain photocycloaddition precursors 1a-1p. To a suspension of K_2CO_3 (1.2-1.8 equiv) in DMF (0.16 – 2 M) was added the corresponding salicylaldehyde **7a-7p** (0.7 – 12 mmol) at rt. 4-Bromo-1,2-butadiene **6** (1 – 2.5 equiv) was added dropwise over 1 h and the reaction mixture was stirred for 16 h at rt. Et_2O was added (50 – 300 mL) and the organic layer was washed with an aq. sol. of K_2CO_3 (three times) and with HCl 1N (three times). The organic layer was washed with brine dried over $MgSO_4$ and evaporated.

2-(Buta-2,3-dienyloxy)-benzaldehyde 1a. Prepared according to the general procedure from salicylaldehyde **7a** (8.58 ml, 82 mmol, 1 equiv) and 4-bromo-1,2-butadiene **6** (12.52 g, 94 mmol, 1.1 equiv) with K_2CO_3 (14.71 g, 106 mmol, 1.3 equiv) in DMF (50 ml). The crude product was purified by flash column chromatography (Si: 250 g) with hexane and EtOAc as solvents (10:1) to afford 2-(buta-2,3-dienyloxy)-benzaldehyde **1a** (12.209 g, 70.1 mmol, 86 % yield) as a yellow liquid, analysis according to literature.[40] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 4.67 - 4.74 (m, 2 H) 4.92 (dt, *J* = 6.58, 2.72 Hz, 2 H) 5.34 - 5.49 (m, 1 H) 6.96 - 7.09 (m, 2 H) 7.50 - 7.60 (m, 1 H) 7.85 (dd, *J* = 7.72, 1.82 Hz, 1 H) 10.52 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 66.1, 77.1, 86.5, 113.0, 120.9, 125.1, 128.4, 135.7, 160.7, 189.9, 209.5. IR (NaCl thin film) ν_{max} [cm^{-1}] 3077, 2865, 2760, 1957, 1862, 1692, 1599,

1484, 1458, 1399, 1377, 1285, 1237, 1161, 1102, 1041, 1002, 851, 758, 654. UV-VIS (MeCN, c = 2.8 x 10^{-5} mol/l): λ_{max} 215 nm (ε = 22710); 251 nm (ε = 10443); 316 nm (ε = 4789). EI-MS [m/z] (%) 174.4 (7.5), 145.4 (13), 122.4 (48), 121.3 (100), 120.4 (17), 92.4 (14), 53.3 (11).

2-(Buta-2,3-dienyloxy)benzaldehyde 1a on multigram scale via Crabbé homologation. Paraformaldehyde (17.25 g, 574 mmol), copper(I) bromide (16.12 g, 112 mmol) and 2-(prop-2-ynyloxy)benzaldehyde **8** (40 g, 250 mmol) were suspended under argon atmosphere in dry dioxane (600 mL). Diisopropylamine (96 mL, 674 mmol) (distilled from KOH before use) was added and the reaction mixture was heated to a gentle reflux for 4 h. The reaction mixture was cooled down and added to HCl 1N (1 L). The organics were extracted with DCM (4x 300 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 500 g) with hexane and EtOAc as solvents (8:1) to afford 2-(buta-2,3-dienyloxy)benzaldehyde **1a** (19.98 g, 115 mmol, 45.9 % yield) as a yellow liquid. Spectral data as described previously.

2-(Buta-2,3-dienyloxy)-3-methyl-benzaldehyde 1b. Prepared according to the general procedure from 2-hydroxy-3-methyl-benzaldehyde **7b** (1.66 g, 12.2 mmol, 1.0 equiv) and 4-bromo-buta-1,2-diene **6** (2.2 g, 16.5 mmol,1.35 equiv) with K_2CO_3 (3.0 g, 22 mmol, 1.8 equiv) in DMF (35 mL). The crude product was purified over a plug of silica gel to afford 2-(buta-2,3-dienyloxy)-3-methyl-benzaldehyde **1b** (1.6 g, 8.5 mmol, 70 % yield), analysis according to literature.[40] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.31 (s, 3H), 4.45 (dt, *J* = 7.3, 2.1 Hz, 2H), 4.77 (dt, *J* = 6.6, 2.1 Hz, 2H), 5.40 (quint, *J* = 6.6 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 10.35 (s, 1H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm 15.8, 73.0, 76.2, 86.3, 124.3, 126.1, 129.4, 132.3, 137.5, 159.8, 190.3, 209.8. IR (NaCl thin film) ν_{max} [cm^{-1}] 3352, 3069, 2928, 2863, 2749, 1956, 1694, 1588, 1470, 1368, 1247, 1198, 1086, 975, 850, 767. UV-VIS (MeCN, c = 3.1 x 10^{-5} mol/l): λ_{max} 209 nm (ε = 37123); 254 nm (ε = 15038); 304 nm (ε = 3543). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ $[M+Na]^+$ 211.0730, found 211.0732.

2-(Buta-2,3-dienyloxy)-3-methoxy-benzaldehyde 1c. Prepared according to the general procedure from 2-hydroxy-3-methoxy-benzaldehyde **7c** (500 mg, 3.3 mmol, 1.3 equiv) and 4-bromo-buta-1,2-diene **6** (350 mg, 2.6 mmol, 1.0 equiv) with K_2CO_3 (545 mg, 3.9 mmol, 1.5 equiv) in DMF (20 mL). The crude product was purified by flash column chromatography on silica gel with Et_2O and pentane as solvents (1:2) to afford 2-(buta-2,3-dienyloxy)-3-methoxy-benzaldehyde **1c** (530 mg, 2.6 mmol, quant.), analysis according to the literature.[40] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 3.89 (s, 3H), 4.69 (dt, *J* = 7.3, 1.8 Hz, 2H), 4.76 (dt, *J* = 6.4, 1.8 Hz, 2H), 5.38 (quint, *J* = 6.4 Hz, 1H), 7.13 (d, *J* = 5.0 Hz, 2H), 7.40 (quint, *J* = 4.1 Hz, 1H), 10.44 (s, 1H). ^{13}C NMR (90 MHz, CDCl3) δ ppm 56.4, 72.3, 76.4, 87.1, 118.3, 119.4, 124.7, 130.7, 151.1, 153.4, 191.0, 210.5. IR (NaCl thin film) ν_{max} [cm^{-1}] = 3078, 2957, 2840, 1955, 1691, 1584, 1481, 1441, 1390, 1368, 1310, 1251, 1205, 1067, 972, 910, 851. UV-VIS (MeCN, c = 3.96 x 10^{-5} mol/l): λ_{max} 219 nm (ε = 21925); 259 nm (ε = 8723); 320 nm (ε = 3114). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_3$ $[M+Na]^+$ 227.0679, found 227.0678.

2-(Buta-2,3-dienyloxy)-3-tert-butyl-benzaldehyde 1d. Prepared according to the general procedure from 2-hydroxy-3-tert-butyl-benzaldehyde **7d** (1 g, 5.61 mmol, 1 equiv) and 4-bromo-1,2-butadiene **6** (0.746 g, 5.61 mmol, 1 equiv) with K_2CO_3 (1.008 g, 7.29 mmol, 1.3 equiv) in DMF (18 mL). The crude product was purified by flash column chromatography (Si:25 g) with hexane and Et_2O as solvents (10:1) to afford 2-(buta-2,3-dienyloxy)-3-tert-butyl-benzaldehyde **1d** (654.6 mg, 2.84 mmol, 51 % yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.44 (s, 9 H) 4.51 (dt, *J* = 6.69, 2.65 Hz, 2 H) 4.91 (dt, *J* = 6.63, 2.62 Hz, 2 H) 5.44 - 5.58 (m, 1 H) 7.17 (t, *J* = 7.71 Hz, 1 H) 7.60 (dd, *J* = 7.83, 1.77 Hz, 1 H) 7.72 (dd, *J* = 7.58, 1.77 Hz, 1 H) 10.34 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 30.8, 35.2, 76.1, 76.8, 86.9, 124.0, 127.7, 130.2, 133.5, 143.9, 161.4, 190.4, 209.6. IR (NaCl thin film) ν_{max} [cm^{-1}] 2962 (m), 2872 (w); 1958 (w); 1687 (s); 1583 (m); 1471 (w); 1430 (m), 1369 (m), 1252 (m) 1213 (m), 1179 (m), 977 (m). UV-VIS (MeCN, c = 2 x 10^{-5} mol/l): λ_{max} 211 nm (ε = 23196); 257 nm (ε

= 8504); 304 nm (ε = 2244). ESI-HRMS [m/z] calculated for $C_{15}H_{18}NaO_2$ $[M+Na]^+$ 253.1199 found 253.1192.

2-(Buta-2,3-dienyloxy)-4-methyl-benzaldehyde 1e. Prepared according to the general procedure from 2-hydroxy-4-methyl-benzaldehyde **7e** (0.7 g, 5.14 mmol, 1 equiv) and 4-bromo-1,2-butadiene **6** (0.684 g, 5.14 mmol, 1 equiv) with K_2CO_3 (0.924 g, 6.68 mmol, 1.3 equiv) in DMF (15 ml). The work-up afforded 2-(buta-2,3-dienyloxy)- 4-methyl-benzaldehyde **1e** (0.583 g, 3.1 mmol, 60 % yield) as a yellow solid, which was used without further purification. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.40 (s, 3 H) 4.62 - 4.72 (m, 2 H) 4.86 - 4.96 (m, 2 H) 5.38 - 5.49 (m, 1 H) 6.80 (s, 1 H) 6.85 (d, *J* = 7.72 Hz, 1 H) 7.74 (d, *J* = 7.72 Hz, 1 H) 10.44 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 22.3, 66.1, 76.9, 86.6, 113.6, 121.9, 123.0, 128.3, 147.1, 160.8, 189.4, 209.5. IR (KBr) ν_{max} [cm^{-1}] 3436 (br, w), 2879 (m), 1953 (m), 1681 (s), 1607 (s), 1499 (m), 1381 (m), 1257 (s), 1207 (m), 1166 (m), 1113 (m), 1000 (m), 852 (m), 819 (m). UV-VIS (MeCN, c = 2.7 x 10^{-5} mol/l): λ_{max} 219 nm (ε = 21899); 259 nm (ε = 13267); 316 nm (ε = 5702). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ $[M+Na]^+$ 211.0730 found 211.0728. mp 49 °C.

2-(Buta-2,3-dienyloxy)-4-methoxy-benzaldehyde 1f. Prepared according to the general procedure from 2-hydroxy-4-methoxy-benzaldehyde **7f** (1.25 g, 8.22 mmol, 1 equiv) and 4-bromo-1,2-butadiene **6** (1.093 g, 8.22 mmol, 1 equiv) with K_2CO_3 (1.476 g, 10.68 mmol, 1.3 equiv) in DMF (18 ml). The crude product was purified by flash column chromatography (Si: 25 g) with hexane and DCM as solvents (2:1) to afford 2-(buta-2,3-dienyloxy)-4-methoxy-benzaldehyde **1f** (1.1298 g, 5.53 mmol, 67.3 % yield) as a white-off solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 3.87 (s, 3 H) 4.62 - 4.71 (m, 2 H) 4.89 - 4.95 (m, 2 H) 5.36 - 5.47 (m, 1 H) 6.47 (d, *J* = 1.82 Hz, 1 H) 6.56 (dd, *J* = 8.63, 1.82 Hz, 1 H) 7.83 (d, *J* = 8.63 Hz, 1 H) 10.33 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 55.6, 66.2, 77.1, 86.5, 99.1, 106.2, 119.3, 130.5, 162.5, 166.0, 188.4, 209.5. IR (Golden Gate) ν_{max} [cm^{-1}] 2991, 2867, 2774, 1953, 1661, 1596, 1596, 1576, 1439, 1253, 1200, 1168, 1096, 997, 826. UV-VIS (MeCN, c = 2.35 x

10^{-5} mol/l): λ_{max} 208 nm (e = 14277); 233 nm (e = 16844); 272 nm (e = 14025); 310 nm (e = 8927). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_3$ $[M+Na]^+$ 227.0679 found 227.0679. mp 62 °C.

2-(Buta-2,3-dienyloxy)-5-methyl-benzaldehyde 1g. Prepared according to the general procedure from 2-hydroxy-3-methyl-benzaldehyde **7g** (0.83 g, 6.1 mmol, 1.0 equiv) and 4-bromo-buta-1,2-diene **6** (1.1 g, 7.7 mmol, 1.3 equiv) with K_2CO_3 (1.5 g, 11 mmol, 1.8 equiv) in DMF (20 mL). The crude product was purified over a silica gel plug to afford 2-(buta-2,3-dienyloxy)-5-methyl-benzaldehyde **1g** (630 mg, 3.35 mmol, 55% yield). Analysis according to the literature.[40] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.31 (s, 3H), 4.66 (dt, *J* = 6.4, 2.7 Hz, 2H), 4.90 (dt, *J* = 6.6, 2.7 Hz, 2H), 5.41 (quint, *J* = 6.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 7.33 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.64 (s, 1H), 10.48 (s, 1H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm 20.3, 66.3, 76.9, 86.7, 113.1, 124.9, 128.4, 130.4, 136.4, 158.8, 190.1, 209.5. IR (NaCl thin film) ν_{max} [cm^{-1}] 3352, 3066, 2925, 2864, 2760, 1957, 1863, 1686, 1609, 1582, 1494, 1396, 1284, 1243, 1161, 1114, 1003, 941, 851, 811, 727, 649. UV-VIS (MeCN, c = 4.5 x 10^{-5} mol/l): λ_{max} 218 nm (ε = 27375); 254 nm (ε = 12495); 327 nm (ε = 5545). EI-MS [m/z] (%) 188.3 (7.1), 145.4 (20), 136.4 (100), 135.5 (87), 118.4 (11), 107.3 (25), 77.4 (11).

2-(Buta-2,3-dienyloxy)-5-methoxy-benzaldehyde 1h. Prepared according to the general procedure from 2-hydroxy-5-methoxy-benzaldehyde **7h** (0.626 ml, 4.80 mmol, 1 equiv) and 4-bromo-1,2-butadiene **6** (0.638 g, 4.80 mmol, 1 equiv) with K_2CO_3 (0.862 g, 6.24 mmol, 1.3 equiv) in DMF (15 ml). The work-up afforded 2-(buta-2,3-dienyloxy)-5-methoxy-benzaldehyde **1h** (738.8 mg, 3.62 mmol, 75 % yield) as a yellow solid, which was used without further purification. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 3.82 (s, 3 H) 4.62 - 4.70 (m, 2 H) 4.85 - 4.94 (m, 2 H) 5.35 - 5.46 (m, 1 H) 6.97 (d, *J* = 9.08 Hz, 1 H) 7.13 (dd, *J* = 8.86, 2.95 Hz, 1 H) 7.34 (d, *J* = 3.18 Hz, 1 H) 10.48 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 55.7, 67.0, 76.9, 86.7, 110.2, 115.2, 123.3, 125.6, 153.9, 155.5, 189.6, 209.5. IR (KBr) ν_{max} [cm^{-1}] 3450 (br s), 3063 (w), 2990 (w), 2874 (m), 1961 (m), 1854 (w), 1679 (s), 1619 (m), 1585 (m), 1501 (s), 1433 (m), 1384 (m), 805 (m), 736 (m), 649 (w). UV-VIS (MeCN, c = 3.0 x 10^{-}

^{5} mol/l): λ_{max} 225 nm (ε = 19728); 254 nm (ε = 8524); 352 nm (ε = 4582). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_3$ $[M+Na]^+$ 227.0679 found 227.06815. mp 49 °C.

2-(Buta-2,3-dienyloxy)- 5-tert-butyl-benzaldehyde 1i. Prepared according to the general procedure from 2-hydroxy-5-tert-butyl-benzaldehyde **7i** (1.1 g, 6.17 mmol, 1 equiv) and 4-bromo-1,2-butadiene **6** (0.821 g, 6.17 mmol, 1 equiv) with K_2CO_3 (1.109 g, 8.02 mmol, 1.3 equiv) in DMF (18 ml). The crude product was purified by flash column chromatography (Si: 70 g) with hexane and Et_2O as solvents (10:1) to afford 2-(buta-2,3-dienyloxy)-5-tert-butyl-benzaldehyde **1i** (0.8336 g, 3.62 mmol, 58.7 % yield) as a yellow oil.^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.32 (s, 9 H) 4.63 - 4.73 (m, 2 H) 4.86 - 4.94 (m, 2 H) 5.36 - 5.48 (m, 1 H) 6.95 (d, *J* = 8.63 Hz, 1 H) 7.58 (dd, *J* = 8.63, 2.72 Hz, 1 H) 7.86 (d, *J* = 2.72 Hz, 1 H) 10.50 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 31.3, 34.2, 66.3, 77.2, 86.7, 112.8, 124.5, 124.8, 133.0, 143.8, 158.8, 190.2, 209.5. ^{13}C NMR (75 MHz, DMSO-d_6) δ ppm 31.0, 33.9, 65.8, 77.2, 86.8, 114.0, 123.5, 123.8, 133.5, 143.1, 158.5, 189.2, 208.6. IR (Golden Gate) ν_{max} [cm^{-1}] 2961, 2868, 1957, 1681, 1606, 1492, 1364, 1262, 1187, 1136, 1097, 1002, 848, 818. UV-VIS (MeCN, c = 3.0 x 10^{-5} mol/l) λ_{max} 219 nm (ε = 22517); 254 nm (ε = 9057); 325nm (ε = 3772). ESI-HRMS [m/z] calculated for $C_{15}H_{18}NaO_2$ $[M+Na]^+$ 253.1199 found 253.1196.

2-(Buta-2,3-dienyloxy)-5-chloro-benzaldehyde 1j. Prepared according to the general procedure from 5-chloro-2-hydroxy-benzaldehyde **7j** (650 mg, 4.2 mmol, 1.2 equiv) and 4-bromo-buta-1,2-diene **6** (450 mg, 3.4 mmol, 1.0 equiv) with K_2CO_3 (545 mg, 3.9 mmol, 1.1 equiv) in DMF (20 mL). The work-up afforded 2-(buta-2,3-dienyloxy)-5-chloro-benzaldehyde **1j** (624.0 mg, 3.0 mmol, 88 % yield) which was used without further purification. Analysis according to literature.[40] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 4.69 (dt, *J* = 6.6, 2.5 Hz, 2H), 4.91 (dt, *J* = 6.6, 2.5 Hz, 2H), 5.40 (quint, *J* = 6.6 Hz, 1H), 6.96 (d, *J* = 9.1 Hz, 2H), 7.48 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.79 (d, *J* = 2.7 Hz, 1H), 10.43 (s, 1H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm 66.6, 77.3, 86.3, 114.7, 126.1, 126.6, 128.0, 135.2, 159.1, 188.5, 209.6. IR (NaCl thin film) ν_{max} [cm^{-1}] = 3019, 2882, 1956, 1682, 1596, 1477, 1394, 1269, 1215, 1128, 1001, 903, 853,

756, 669. UV-VIS (MeCN, c = 2.87 x 10^{-5} mol/l) λ_{max} 221nm (ε = 8477); 249 nm (ε = 3066); 330 nm (ε = 1276). ESI-HRMS [m/z] calculated for $C_{11}H_9ClNaO_2$ $[M+Na]^+$ 231.0183, found 231.0185.

2-(Buta-2,3-dienyloxy)-3,5-di-methyl-benzaldehyde 1k. Prepared according to the general procedure from 3,5-di-methyll-2-hydroxy-benzaldehyde **7k** (861.5 mg, 5.74 mmol, 1 equiv) and bromo-1,2-butadiene **6** (763 mg, 5.74 mmol, 1 equiv) with K_2CO_3 (1031 mg, 7.46 mmol, 1.3 equiv) in DMF (17ml). The crude product was purified by flash column chromatography (Si: 50g) with hexane and DCM as solvents (5:3) to afford 2-(buta-2,3-dienyloxy)-3,5-di-methyl-benzaldehyde **1k** (730.7 mg, 3.61 mmol, 63 % yield) as a yellow liquid. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.29 - 2.36 (m, 6 H) 4.47 (d, *J* = 7.27 Hz, 2 H) 4.83 (d, *J* = 6.36 Hz, 2 H) 5.33 - 5.60 (m, 1 H) 7.27 (s, 1 H) 7.49 (s, 1 H) 10.37 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 210.0; 190.7; 158.0; 138.4; 134.1; 132.1; 129.1; 126.2; 86.5; 76.3; 73.3; 20.6; 15.9. IR (NaCl thin film) ν_{max} [cm^{-1}] 2928 (w); 2861 (w); 2740 (w); 1957 (m); 1686 (s); 1606 (w); 1591 (w); 1476 (s); 1392 (m); 1368 (m); 1297 (w); 1249 (m); 1249 (m); 1200 (s); 1144 (m); 976 (m); 851 (m). UV-VIS (MeCN, c = 2.93 x 10^{-5} mol/l): λ_{max} 212 nm (ε = 23371); 257 nm (ε = 8940); 313 nm (ε = 2102). ESI-HRMS [m/z] calculated for $C_{13}H_{14}NaO_2$ $[M+Na]^+$ 225.0886 found 225.0884.

2-(Buta-2,3-dienyloxy)-3,5-di-tert-butyl-benzaldehyde 1l. Prepared according to the general procedure from 3,5-di-tert-butyl-2-hydroxy-benzaldehyde **7l** (1.0 g, 4.2 mmol, 1.2 equiv) and bromo-1,2-butadiene **6** (450 mg, 3.4 mmol, 1.0 equiv) with K_2CO_3 (550 mg, 4 mmol, 1.2 equiv) in DMF (20 mL). The crude product was purified by flash column chromatography (Si: 25g) with pentane and DCM as solvents (5:2) to afford 2-(buta-2,3-dienyloxy)-3,5-di-tert-butyl-benzaldehyde **1l** (650.7 mg, 2.3 mmol, 67 % yield) as a yellow solid, analysis according to literature.[40] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.33 (s, 9 H) 1.44 (s, 9 H) 4.43 - 4.53 (m, 2 H) 4.85 - 4.96 (m, 2 H) 5.43 - 5.57 (m, 1 H) 7.63 (d, *J* = 2.7 Hz, 1 H) 7.71 (d, *J* = 2.7 Hz, 1 H) 10.30 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 209.6, 190.9, 159.4, 146.5, 143.0, 130.9, 129.3, 124.0, 87.0, 76.8, 76.1, 35.3, 34.7, 31.3, 30.9. IR (NaCl thin

film) ν_{max} [cm^{-1}] 2962, 2871, 2746, 1959, 1689, 1596, 1478, 1395, 1364, 1237, 1202, 1163, 980, 849. UV-VIS (MeCN, c = 5.2 x 10^{-5} mol/l): λ_{max} 216 nm (ε = 24614); 261 nm (ε = 9821); 306 nm (ε = 2930). ESI-HRMS [m/z] calculated for $C_{19}H_{26}NaO_2$ $[M+Na]^+$ 309.1825, found 309.1826.

2-(Buta-2,3-dienyloxy)-3,6-dimethyl-benzaldehyde 1m. Prepared according to the general procedure from 2-hydroxy-3,6-dimethyl-benzaldehyde **7m** (0.75 g, 4.99 mmol, 1 equiv) and 4-bromo-1,2-butadiene **6** (0.664 g, 4.99 mmol, 1 equiv) with K_2CO_3 (0.897 g, 6.49 mmol, 1.3 equiv) in DMF (15 ml). The work-up afforded 2-(buta-2,3-dienyloxy)-3,6-dimethyl-benzaldehyde **1m** (0.85 g, 4.21 mmol, 84 % yield) as a yellow liquid, which was used without further purification. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.31 (s, 3 H) 2.56 (s, 3 H) 4.31 - 4.54 (m, 2 H) 4.75 - 4.93 (m, 2 H) 5.33 - 5.55 (m, 1 H) 6.93 (d, *J* = 7.72 Hz, 1 H) 7.30 (d, *J* = 7.72 Hz, 1 H) 10.57 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 209.9, 193.0, 161.3, 139.3, 136.3, 129.4, 127.9, 127.5, 86.6, 76.4, 73.2, 21.0, 15.8. IR (NaCl thin film) ν_{max} [cm^{-1}] 2978 (w); 2927 (w); 2876 (w); 2363 (w); 1957 (w); 1689 (s); 1571 (m); 1484 (m); 1380 (w); 1362 (m); 1261 (w); 1217 (m); 1074 (m); 984 (m); 938 (w); 852 (m); 818 (w); 782 (w). UV-VIS (MeCN, c = 2.5 x 10^{-5} mol/l): λ_{max} 211 nm (ε = 26646); 255 nm (ε = 10274); 306 nm (ε = 2508). ESI-HRMS [m/z] calculated for $C_{13}H_{14}NaO_2$ $[M+Na]^+$ 225.0886 found 225.0887.

6-(Buta-2,3-dienyloxy)benzo[d][1,3]dioxole-5-carbaldehyde 1n. Prepared according to the general procedure from 6-hydroxy-3,4-methylenedioxybenzaldehyde **7n** (441.1 mg, 2.66 mmol, 1 equiv) and 4-bromo-1,2-butadiene **6** (494 mg, 3.72 mmol, 1.4 equiv) with K_2CO_3 (514 mg, 3.72 mmol, 1.4 equiv) in DMF (4 ml). The work-up afforded 6-(Buta-2,3-dienyloxy)benzo[d][1,3]dioxole-5-carbaldehyde **1n** (514.9 mg, 2.360 mmol, 89 % yield) as a white-off solid, which was used without further purification. ^{1}H NMR (360 MHz, DMSO-d_6) δ ppm 4.64 - 4.73 (m, 2 H) 4.97 - 5.04 (m, 2 H) 5.45 - 5.61 (m, 1 H) 6.11 (s, 2 H) 6.98 (s, 1 H) 7.08 (s, 1 H) 10.16 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 67.2, 77.1, 86.4, 95.6, 102.1, 105.8, 119.2, 142.3, 154.0, 159.0, 187.9, 209.5. IR (Golden Gate) n_{max} [cm^{-1}] 3063 (w), 2990 (w), 2894 (w), 1957 (w), 1669 (s), 1619 (s), 1497 (s), 1442 (s), 1402 (m), 1391 (m), 1354

(m), 1325 (w), 1263 (s), 1227 (s), 1159 (s), 1117 (w), 1076 (m), 1032 (s), 994 (s), 925 (s), 874 (s), 865 (s), 797 (s), 776 (m), 714 (w), 636 (m), 610 (m). UV-VIS (MeCN, c = 3.4 x 10^{-5} mol/l): λ_{max} 273 nm (ε = 3761); 341 nm (ε = 4044). ESI-HRMS [m/z] calculated for $C_{12}H_{10}NaO_4$ $[M+Na]^+$ 241.0471 found 241.0472. mp 90 °C.

5-(Buta-2,3-dien-1-yloxy)-4-formyl-2-methoxyphenyl acetate 1o. Prepared according to the general procedure from 4-formyl-5-hydroxy-2-methoxyphenyl acetate **7o** (148.6 mg, 0.707 mmol, 1 equiv) and 4-bromo-1,2-butadiene **6** (188 mg, 1.414 mmol, 2 equiv) with K_2CO_3 (127 mg, 0.919 mmol, 1.3 equiv) in DMF (0.5 mL). The crude product was purified by flash column chromatography (Si: 10 g) with hexane and EtOAc as solvents (3:1) to afford 5-(buta-2,3-dien-1-yloxy)-4-formyl-2-methoxyphenyl acetate **1o** (73.6 mg, 0.281 mmol, 39.7 % yield) as a white-off solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.39 (s, 3 H) 3.93 (s, 3 H) 4.68 - 4.75 (m, 2 H) 4.87 - 4.94 (m, 2 H) 5.42 (quin, *J* = 6.81 Hz, 1 H) 6.70 (s, 1 H) 7.34 (s, 1 H) 10.02 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 20.8, 56.3, 67.1, 77.1, 85.9, 107.6, 110.0, 120.7, 147.56, 147.59, 153.4, 169.4, 186.9, 210.0. IR (Golden Gate) ν_{max} [cm^{-1}] 3728 (w), 3704 (w), 3627 (w), 3598 (w), 2988 (w), 2943 (w), 2852 (w), 1956 (w), 1754 (m), 1676 (s), 1605 (s), 1508 (s), 1474(w), 1418 (m), 1376 (m), 1276 (s), 1204 (s), 1161 (s), 1110 (s), 1025 (s), 1009 (s), 981 (s), 912 (m), 873 (m), 854 (m), 834 (s), 739 (s), 677 (m), 614 (m), 592 (m), 570 (s), 538 (s). UV-VIS (MeCN, c = 2.86 x 10^{-5} mol/l): λ_{max} 315 nm (ε = 1853); 275 nm (ε = 2798); 233 nm (ε = 4860); 203 nm (ε = 4455). ESI-HRMS [m/z] calculated for $C_{14}H_{14}NaO_5$ $[M+Na]^+$ 285.07334 found 285.07351.

4-(Buta-2,3-dien-1-yloxy)-5-formyl-2-methoxyphenyl acetate 1p. Prepared according to the general procedure from 5-formyl-4-hydroxy-2-methoxyphenyl acetate **7p** (144.3 mg, 0.687 mmol, 1 equiv) and 4-bromobuta-1,2-diene **6** (228 mg, 1.716 mmol, 2.5 equiv) with K_2CO_3 (123 mg, 0.893 mmol, 1.3 equiv) was dissolved in dry DMF (3 ml). The crude product was purified by flash column chromatography (Si: 15 g) with hexane and DCM as solvents (1:5 to pure DCM) to afford 4-(buta-2,3-

dien-1-yloxy)-5-formyl-2-methoxyphenyl acetate **1p** (168.5 mg, 0.642 mmol, 94 % yield) as a white-off solid. 1H NMR (300 MHz, $CDCl_3$) δ ppm 2.30 (s, 13 H) 3.90 (s, 14 H) 4.71 (dt, *J* = 6.75, 2.48 Hz, 8 H) 4.92 (dt, *J* = 6.61, 2.55 Hz, 8 H) 5.42 (quin, *J* = 6.66 Hz, 4 H) 6.56 (s, 4 H) 7.53 (s, 4 H) 10.32 (s, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 20.5, 56.2, 67.0, 77.1, 86.5, 97.5, 118.4, 122.1, 134.0, 157.2, 160.6, 169.0, 187.6, 209.7. IR (Golden Gate) ν_{max} [cm^{-1}] 2929(w), 2876 (w), 2783 (w), 1981 (w), 1957 (w), 1744 (m), 1666 (s), 1606 (s), 1512 (m), 1478 (m), 1440 (m), 1369 (m), 1333 (m), 1290 (s), 1257(m), 1226 (s), 1199 (s), 1180 (s), 1116 (s), 1007 (s). UV-VIS (MeCN, c = 2.7 x 10^{-5} mol/l): λ_{max} 317 nm (ε = 11480); 269 nm (ε = 17749); 233 nm (ε = 27587); 206 nm (ε = 18895). ESI-HRMS [m/z] calculated for $C_{14}H_{14}NaO_5$ $[M+Na]^+$ 285.07334 found 285.07314. mp 97 °C.

General procedure for photocycloaddition to obtain the bicyclo[2.2.2]octadienes 2a-2p and the benzoxepines 3a-3p. The corresponding allenyloxy benzaldehyde **1a-1o** (0.15 – 0.74 mmol, 1 equiv) was dissolved in dry DCM (0.03 – 0.04 M) in a quartz tube equipped with a magnetic stir bar and a rubber septum. The reaction mixture was purged with argon for 15 min and irradiated under argon atmosphere at 350 nm at rt for the time indicated in Table 3. The reaction mixture was then evaporated.

2-Oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2a and 8-Methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene 3a. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-benzaldehyde **1a** (129.4 mg, 0.743 mmol)in dry DCM (20 ml). The crude mixture was purified by flash column chromatography (Si: 30 g) with pentane and DCM as solvents (5:3 to pure DCM) to afford 2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2a** (25.2 mg; 19 % yield) as a yellow solid and 8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3a** (20.0 mg; 15 % yield) as a white-off solid, analysis according to literature.[40] 2-Oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2a;** ^1H NMR (500 MHz, $CDCl_3$) δ ppm 2.15 (q, *J* = 15.44 Hz, 2 H) 3.97 (br. s., 1 H) 5.41 (s, 1 H) 6.18 (t, *J* = 6.81 Hz, 1 H) 6.59 (d, *J* = 7.72 Hz, 1 H) 7.08 (d, *J* = 5.90 Hz, 1 H) 9.70 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) d ppm 187.4, 148.6, 146.5, 138.9,

138.8, 129.2, 112.5, 96.4, 79.9, 39.3, 26.8. IR (NaCl thin film) ν_{max} [cm^{-1}] 3021, 2864, 2286, 1682, 1570, 1215, 1167, 1012 669. EI-MS [m/z] (%) 175.4 ($M^{+\cdot}$,10), 174.4 (39), 173.4 (25), 145.4 (63), 131.4 (44), 120.4 (80), 115.4 (40), 90.4 (100), 65.4 (15), 53.3 (17). mp 72 °C. 8-Methylene-11,12-dioxa-tricyclo[7.2.1.$0^{2,7}$] dodeca-2,4,6-triene **3a;** ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.73 (dd, *J* = 7.2, 1.4 Hz, 1H), 4.10 (dd, *J* = 7.2, 5.9 Hz, 1H), 5.10 (dd, *J* = 5.9, 1.4 Hz, 1H), 5.15 (s, 1H), 5.67 (s, 1H), 6.09 (s, 1H), 7.19 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.32 (dtd, *J* = 20.0, 7.4, 1.4 Hz, 2H), 7.70 (d, *J* = 7.4, Hz, 1H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 68.9, 77.9, 101.3, 107.1, 123.4, 125.0, 128.5, 128.9, 128.9, 136.1, 142.0. IR (NaCl thin film) ν_{max} [cm^{-1}] = 3021, 1527, 1425, 1215, 669. EI-MS [m/z] (%) 174.4 ($M^{+\cdot}$,19), 145.4 (17), 144.5 (100), 116.4 (42.4), 155.5 (58.8). mp 75 °C.

10-Methyl-2-oxa-tricyclo-[5.2.2.$0^{1,5}$]undeca-4,8,10-triene-9-carbaldehyde 2b and 6-Methyl-8-methylene-11,12-dioxa-tricyclo[7.2.1.$0^{2,7}$]-dodeca-2,4,6-triene 3b. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-3-methyl-benzaldehyde **1b** (340 mg, 1.8 mmol, 1 equiv) in dry DCM (15 mL). The crude mixture was purified by two flash column chromatographies with Et_2O, pentane and DCM as solvents (1:4, then pure DCM) to afford 10-methyl-2-oxa-tricyclo-[5.2.2.$0^{1,5}$]undeca-4,8,10-triene-9-carbaldehyde **2b** (34 mg, 0.18 mmol, 10 % yield) and 6-methyl-8-methylene-11,12-dioxa-tricyclo[7.2.1.$0^{2,7}$]-dodeca-2,4,6-triene **3b** (43 mg, 0.28 mmol, 13 % yield). Analysis data according to the literature.[40] 10-Methyl-2-oxa-tricyclo-[5.2.2.$0^{1,5}$]undeca-4,8,10-triene-9-carbaldehyde **2b**; ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.85 (d, *J* = 1.4 Hz, 3H), 2.07 (dm, *J* = 15.4, 2.3 Hz, 1H), 2.20 (dm, *J* = 15.4, 2.3 Hz, 1H), 3.83 (m, *J* = 3.2 Hz, 1H), 5.05 (m, 2H), 5.34 (s, 1H), 5.75 (d, *J* = 5.0 Hz, 1H), 7.11 (d, *J* = 6.4 Hz, 1H), 9.67 (s, 1H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm 14.5, 27.4, 38.6, 80.2, 97.6, 112.2, 122.1, 139.2, 147.5, 147.8, 148.3, 187.5. IR (NaCl thin film) n_{max} [cm^{-1}] =3019, 2920, 2859, 2400, 2252, 1679, 1581, 1442, 1348, 1216, 1156, 1027, 909, 757, 668. ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ $[M+Na]^+$ 211.07295, found 211.07266. 6-Methyl-8-methylene-11,12-dioxa-tricyclo[7.2.1.$0^{2,7}$]-dodeca-2,4,6-triene **3b**; ^{1}H NMR (360 MHz, CDCl3) δ ppm 2.54 (s, 3H), 3.73 (d, *J*

= 7.3 Hz, 1H), 4.09 (t, *J* = 6.1 Hz, 1H), 5.04 (d, *J* = 5.7 Hz, 1H), 5.36 (s, 1H), 5.64 (s, 1H), 6.07 (s, 1H), 7.07 (m, 1H), 7.18 (m, 2H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm 24.2, 68.9, 80.3, 101.9, 113.7, 123.2, 127.3, 127.7, 132.7, 137.1, 137.7, 143.1. IR (NaCl thin film) ν_{max} [cm^{-1}] 3068, 2969, 2893, 2251, 1715, 1680, 1624, 1469, 1448, 1347, 1248, 1225, 1137, 1084, 1051, 973, 910, 775, 732, 662. ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ $[M+Na]^+$ 211.07295, found 211.07275.

10-Methoxy-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2c and 6-Methoxy-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]- dodeca-2,4,6-triene 3c. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-3-methoxy-benzaldehyde **1c** (162 mg, 79.0 mmol, 1 equiv) in dry DCM (28 mL). The crude mixture was purified by flash column chromatography on silica gel with Et_2O and pentane as solvents (1:2) to afford a inseperable mixture of 6-methoxy-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]- dodeca-2,4,6-triene **3c** and an unknown compound **x** (51 mg, 0.25 mmol, 31 %, **x**:**3c** 24:76) and pure 10-methoxy-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2c** (108 mg, 0.52 mmol, 67 % yield). Analysis data according to the literature.[2] 10-Methoxy-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2c;** ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.13 (d, *J* = 15.9 Hz, 1H), 2.28 (d, *J* = 15.4 Hz, 1H), 3.56 (s, 3H), 3.82 (m, 1H), 4.81 (d, *J* = 6.8 Hz, 1H), 5.11 (m, 2H), 5.42 (s, 1H), 7.19 (d, *J* = 5.9 Hz, 1H), 9.71 (s, 1H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm 28.0, 36.5, 56.3, 80.8, 92.4, 94.2, 112.9, 139.3, 147.0, 147.3, 164.5, 187.3. IR (NaCl thin film) ν_{max} [cm^{-1}] =2964, 2893, 2804, 2250, 1689, 1597, 1479, 1345, 1264, 1084, 956, 906, 797, 733. EI-MS [m/z] (%), 204.25 (M+,100), 176.35 (31), 175.35 (45), 161.35 (33), 147.35 (33), 120.35 (52), 119.35 (65), 115.4 (42), 91.35 (66), 77.35 (41). 6-Methoxy-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]-dodeca-2,4,6-triene **3c;** ^{1}H NMR (360 MHz, CDCl3) δ ppm A: 3.74 (d, *J* = 9.3 Hz, 1H), 3.92 (s, 3H), 4.07 (t, *J* = 6.8, Hz, 1H), 4.99 (d, *J* = 5.9 Hz, 1H), 5.31 (s, 1H), 6.06 (s, 1H), 6.28 (s, 1H), 6.83 (d, *J* = 10.1 Hz, 1H), 6.93 (d, *J* = 11.6 Hz, 1H), 7.23 (m, 1H), B: 3.83 (d, *J* = 18 Hz, 1H), 3.91 (s, 3H), 4.01 (t, *J* = 6.0, Hz, 1H), 5.25 (d, *J* = 4.5 Hz, 1H), 5.33 (s, 1H), 5.81 (s, 1H), 6.32 (s, 1H), 6.77 (d, *J* = 10.4 Hz, 1H),

6.90 (d, *J* = 11.6 Hz, 1H), 7.23 (m, 1H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm A: 55.3, 69.3, 79.8, 101.5, 111.7, 114.1, 117.4, 128.9, 138.1, 140.1, 159.2, B: 55.3, 72.4, 76.1, 79.8, 106.1, 110.9, 115.4, 116.5, 117.1, 128.5, 138.6, 139.1, 159.9. IR (NaCl thin film) ν_{max} [cm^{-1}] 3018, 2966, 2989, 2840, 2405, 1623, 1598, 1479, 1341, 1266, 1216, 1084, 1216, 1084, 973, 957, 903, 752, 666. EI-MS [m/z] (%) 204.25 ($M^{+\cdot}$,50), 175.4 (16), 174.4 (91), 173.3 (30), 159.4 (100), 146.4 (15), 145.4 (58), 144.4 (22), 131.4 (20), 118.35 (33), 116.35 (24), 115.35 (52), 103.35 (11.13).

10-Tert-butyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2d. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-3-tert-butyl-benzaldehyde **1d** (140.6 mg, 0.611 mmol, 1 equiv) in dry DCM (19 ml). The crude product was purified by flash column chromatography (Si: 25g) with hexane and Et_2O as solvents (5:1) to afford 10-tert-butyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2d** (91.6 mg, 65 % yield) as a yellow sticky oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.14 (s, 9 H) 1.98 - 2.29 (m, 2 H) 3.78 - 3.88 (m, 1 H) 5.05 (br. s., 2 H) 5.34 (s, 1 H) 5.77 (d, *J* = 6.36 Hz, 1 H) 7.09 (d, *J* = 5.90 Hz, 1 H) 9.72 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 26.9, 28.5, 34.4, 38.1, 79.2, 98.7, 111.6, 120.6, 140.2, 146.9, 149.8, 159.0, 187.8. IR (KBr) ν_{max} [cm^{-1}] 2962, 2850, 1674, 1576, 1344, 1257, 1197, 1149, 1018. ESI-HRMS [m/z] calculated for $C_{15}H_{18}NaO_2$ $[M+Na]^+$ 253.11990 found 253.11984.

5-Methyl-8-methylene-11,12-dioxa-tricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene 3e. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-4-methyl-benzaldehyde **1e** (108.0 mg, 0.574 mmol, 1 equiv) in dry DCM (19 ml). The crude product was purified by flash column chromatography (Si: 20g) with pentane and DCM as solvents (4:3) to afford 5-methyl-8-methylene-11,12-dioxa-tricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene **3e** (16.56 mg, 0.088 mmol, 14 % yield) as a yellow oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.36 (s, 3 H) 3.71 (d, *J* = 7.27 Hz, 1 H) 4.09 (t, *J* = 6.36 Hz, 1 H) 5.08 (d, *J* = 5.90 Hz, 1 H) 5.12 (s, 1 H) 5.65 (s, 1 H) 6.07 (s, 1 H) 7.09 (s, 2 H) 7.50 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 142.2, 138.6, 133.5, 129.3, 128.7, 124.9, 123.9, 106.8, 101.3, 77.9, 68.7, 21.5. IR (NaCl

thin film) ν_{max} [cm^{-1}] 3422 (br w), 2966 (m), 2893 (m), 1958 (w), 1682 (m), 1608 (m), 1490 (w), 1423 (w), 1351 (m), 1285 (m), 1258 (m), 1203 (m), 1078 (s), 1014 (m), 964 (s), 933 (m), 898 (s), 863 (m), 821 (s), 715 (w). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ $[M+Na]^+$ 211.07295 found 211.07268.

5-Methoxy-8-methylene-11,12-dioxa-tricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene 3f. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-4-methoxy-benzaldehyde **1f** (114.3 mg, 0.560 mmol, 1 equiv) in dry DCM (19 ml). The crude product was purified by flash column chromatography (Si: 25g) with hexane and EtOAc as solvents (6:1) to afford 5-methoxy-8-methylene-11,12-dioxa-tricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene **3f** (23.6 mg, 0.116 mmol, 20.65 % yield) as a white-off solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 3.70 (dd, *J* = 7.33, 1.26 Hz, 1 H) 3.83 (s, 3 H) 4.08 (dd, *J* = 7.07, 6.06 Hz, 1 H) 5.07 (dd, *J* = 5.81, 1.26 Hz, 1 H) 5.15 (s, 1 H) 5.63 (s, 1 H) 6.07 (s, 1 H) 6.82 (dd, *J* = 8.34, 2.53 Hz, 1 H) 7.13 (d, *J* = 8.34 Hz, 1 H) 7.19 (d, *J* = 2.53 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 55.4, 68.6, 77.6, 101.1, 107.3, 108.7, 114.0, 126.2, 129.3, 130.3, 142.2, 159.9. IR (Golden Gate) ν_{max} [cm^{-1}] 2955 (w), 1602 (m), 1576 (w), 1494 (m), 1312 (m), 1237 (m), 1074 (m), 960 (m), 929 (m), 916 (m), 884 (m), 838 (m). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_3$ $[M+Na]^+$ 227.06787 found 227.06723. mp 69 °C.

7-Methyl-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2g and 4-methyl-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]-dodeca-2,4,6-triene 3g. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-5-methyl-benzaldehyde **1g** (104 mg, 55 µmol, 1 equiv) in dry DCM (15 mL). The crude mixture was purified by flash column chromatography on silica gel with Et_2O and pentane as solvents (1:2) to afford 7-methyl-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2g** (35 mg, 0.19 mmol, 34 % yield) and 4-methyl-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]-dodeca-2,4,6-triene **3g** (11 mg, 0.058 mmol, 11 % yield). Analysis as described in the literature.[40] 7-Methyl-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2g**; ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.65 (s, 3H), 1.99 (dm, *J* = 15.4 Hz, 1H), 2.06 (dm, *J* = 13.0 Hz, 1H), 5.06

(d, J = 1.6 Hz, 2H), 5.34 (m, 1H), 5.90 (d, J = 7.5 Hz, 1H), 6.54 (d, J = 7.5 Hz, 1H), 6.80 (s 1H), 9.66 (s, 1H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm 21.5, 34.6, 45.2, 79.9, 96.7, 111.8, 134.8, 138.4, 140.7, 148.1, 151.5, 187.3. IR (NaCl thin film) ν_{max} [cm^{-1}] 3020, 2965, 2956, 1680, 1614, 1564, 1455, 1351, 1215, 1169, 1009, 909, 760, 669. ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ [M+Na]$^+$ 211.07295, found 211.07290. 4-Methyl-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]-dodeca-2,4,6-triene **3g**; ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.35 (s, 3H), 3.71 (dd, J = 7.3, 1.1 Hz, 1H), 4.08 (t, J = 6.1 Hz, 1H), 5.08 (m, 2H), 5.59 (s, 1H), 6.04 (s, 1H), 7.0 (s, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm 21.2, 68.9, 78.0, 101.4, 106.1, 123.4, 125.5, 126.2, 129.6, 136.0, 138.7, 142.0. IR (NaCl thin film) ν_{max} [cm^{-1}] 3020, 2970, 2896, 2403, 1679, 1498, 1422, 1338, 1215, 1102, 1085, 964, 903, 878, 827, 755, 669. ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ [M+Na]$^+$ 211.07295, found 211.07297.

7-Methoxy-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2h. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-5-methoxy-benzaldehyde **1h** (132.9 mg, 0.651 mmol, 1 equiv) in dry DCM (20 ml). The crude product was purified by flash column chromatography (Si: 20g) with hexane and DCM as solvents (5:3 to pure DCM) to afford 7-methoxy-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2h** (30.2 mg, 0.148 mmol, 23 % yield) as a brown solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.24 - 2.43 (m, 2 H) 3.63 (s, 3 H) 5.07 (br. s., 2 H) 5.40 (s, 1 H) 6.29 (d, J = 8.17 Hz, 1 H) 6.53 (d, J = 8.17 Hz, 1 H) 7.15 (s, 1 H) 9.69 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 32.0, 54.0, 80.1, 85.2, 95.3, 112.5, 130.8, 136.6, 137.7, 145.7, 145.7, 186.8. IR (KBr) ν_{max} [cm^{-1}] 3429 (br m), 2953(m), 2865 (m), 1682 (s), 1609 (m), 1565 (m), 1462 (w), 1332 (s), 1257 (m), 1189 (s), 1167 (s), 1117 (s), 1030 (m), 1002 (m), 930 (w), 851 (m), 80 (m). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_3$ [M+Na]$^+$ 227.06787 found 227.06791. mp 62 °C.

7-Tert-butyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2i and 4-tert-butyl-8-methylene-11,12-dioxa-tricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene 3i. Prepared according to the general

procedure from 2-(buta-2,3-dienyloxy)-5-tert-butyl-benzaldehyde **1i** (144.6 mg, 0.628 mmol) in dry DCM (20 ml). The crude mixture was purified by flash column chromatography (Si: 25g) with hexane and DCM as solvents (2:1 to pure DCM) to afford 7-tert-butyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2i** (90.9 mg, 0.395 mmol, 62.9 % yield) as a yellow sticky oil and 4-tert-butyl-8-methylene-11,12-dioxa-tricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene **3i** (28.2 mg, 0.122 mmol, 19.5 % yield) as a yellow sticky oil. 7-Tert-butyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2i;** ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.16 (s, 9 H) 2.06 - 2.26 (m, 2 H) 5.06 (br. s., 2 H) 5.35 (br. s., 1 H) 6.16 (d, *J* = 7.72 Hz, 1 H) 6.60 (d, *J* = 7.72 Hz, 1 H) 7.10 (s, 1 H) 9.70 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 26.5, 27.8, 32.2, 56.7, 80.0, 95.9, 111.5, 131.2, 138.7, 141.2, 148.4, 148.5, 187.3. IR (Golden Gate) ν_{max} [cm^{-1}] 2960, 2851, 1664, 1565, 1477, 1371, 1348, 1170, 1021, 1000, 933, 672. ESI-HRMS [m/z] calculated for $C_{15}H_{18}NaO_2$ $[M+Na]^+$ 253.11990 found 253.11927. 4-Tert-butyl-8-methylene-11,12-dioxa-tricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene **3i;** Despite additional purification attempts, the product is not pure enough to get all spectral data. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.32 (s, 9 H) 3.73 (d, *J* = 7.27 Hz, 1 H) 4.10 (t, *J* = 6.58 Hz, 1 H) 5.04 - 5.15 (m, 2 H) 5.61 (s, 1 H) 6.09 (s, 1 H) 7.20 (d, *J* = 1.82 Hz, 1 H) 7.36 (dd, *J* = 8.17, 1.82 Hz, 1 H) 7.63 (d, *J* = 8.17 Hz, 1 H).

7-Chloro-2-oxa-tricyclo- [5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2j and 4-chloro-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]- dodeca-2,4,6-triene 3j. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-5-chloro-benzaldehyde **1j** (165 mg, 790 µmol, 1 equiv) in dry DCM (20 mL). The crude mixture was purified by flash column chromatography with Et_2O and pentane as solvents (1:9) followed by a second column with DCM and pentane as solvents (1:1) to afford 7-chloro-2-oxa-tricyclo- [5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2j** (46 mg, 0.22 mmol, 28 % yield) and 4-chloro-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]- dodeca-2,4,6-triene **3j** (66 mg, 0.32 mmol, 40 % yield). Analysis according to the literature.[40] 7-Chloro-2-oxa-tricyclo-[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2j**; ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.50-2.65 (m,

2H), 5.06 (m, 2H), 5.43 (s, 1H), 6.19 (d, *J* = 8.2 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 6.97 (s, 1H), 9.69 (s, 1H). ^{13}C NMR (90 MHz, $CDCl_3$) δ ppm 38.1, 65.6, 80.2, 95.4, 112.7, 114.0, 137.49, 137.51, 146.3, 147.6, 186.3. IR (NaCl thin film) n_{max} [cm^{-1}] 3020, 2868, 2360, 1690, 1607, 1564, 1350, 1216, 1169, 1043, 1013, 926, 757, 682. EI-MS [m/z] (%), 172 (100), 155 (5), 144 (50), 115 (75), 89 (30), 63 (12), 50 (5). 4-Chloro-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]- dodeca-2,4,6-triene **3j**; ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 3.72 (d, *J* = 7.3 Hz, 1H), 4.09 (t, *J* = 6.8 Hz, 1H), 5.09 (d, *J* = 5.9 Hz, 1H), 5.17 (s, 1H), 5.64 (s, 1H), 6.03 (s, 1H), 7.18 (d, *J* = 1.8 Hz, 1H), 7.26-7.30 (1H), 7.62(d, *J* = 9 Hz, 1H). ^{13}C NMR (90 MHz, CDCl3) δ ppm 69.0, 77.8, 100.6, 107.7, 125.0, 125.1 127.5, 129.0, 134.2, 137.6, 141.1. IR (NaCl thin film) ν_{max} [cm^{-1}] 3020, 2972, 2896, 1898, 1807, 1685, 1639, 1596, 1417, 1334, 1216, 1193, 1113, 1086, 1012, 966, 904, 875, 815, 758. EI-MS [m/z] (%) 193 (10), 178 (22), 151 (45), 136 (58), 115 (100), 87 (82), 75 (100), 50 (55).

7,10-Di-methyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2k and 4,6-Di-methyl-8-methylene-11,12-dioxa-tricyclo [7.2.1.0^{2,7}]dodeca-2,4,6-triene 3k. Prepared according to the general procedure from 3,5-dimethyl-2-(buta-2,3-dienyloxy)-benzaldehyde **1k** (104.7 mg, 0.518 mmol) in DCM (17 ml). The crude mixture was purified by flash column chromatography (Si: 20 g) with hexane and DCM as solvents (5:3 to pure DCM) to afford 7,10-di-methyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2k** (64.1 mg, 61.2 % yield) as a yellow oil and 4,6-di-methyl-8-methylene-11,12-dioxa-tricyclo [7.2.1.0^{2,7}]dodeca-2,4,6-triene **3k** (12.6 mg, 12.0 % yield) as a white-off solid. 7,10-Di-methyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2k;** ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.60 (s, 3 H) 1.85 (s, 3 H) 1.94 - 2.13 (m, 2 H) 4.98 - 5.12 (m, 2 H) 5.33 (s, 1 H) 5.50 (s, 1 H) 6.85 (s, 1 H) 9.66 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 187.6; 152.8; 147.9; 147.0; 141.0; 127.9; 111.5; 97.9; 80.1; 44.3; 35.2; 21.7; 14.4. IR (Golden Gate) ν_{max} [cm^{-1}] 2962 (w), 2930(w), 2872 (w), 1722 (s), 1678 (s), 1580 (m), 1168 (m), 1024 (m), 729 (s). ESI-HRMS [m/z] calculated for $C_{13}H_{14}NaO_2$ $[M+Na]^+$ 225.08860 found 225.08843. 4,6-Di-

methyl-8-methylene-11,12-dioxa-tricyclo [7.2.1.0^{2,7}]dodeca-2,4,6-triene **3k;** ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.32 (s, 3 H) 2.50 (s, 3 H) 3.71 (d, *J* = 7.27 Hz, 1 H) 4.06 (t, *J* = 6.58 Hz, 1 H) 5.01 (d, *J* = 5.45 Hz, 1 H) 5.30 (s, 1 H) 5.57 (s, 1 H) 6.02 (s, 1 H) 6.88 (s, 1 H) 7.00 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 143.0; 137.8; 137.7; 137.1; 133.5; 124.5; 123.9; 112.6; 102.0; 80.4; 68.9; 24.1; 20.9. IR (NaCl thin film) ν_{max} [cm^{-1}] 3433 (br,w), 2961 (m), 2893 (m), 1611 (m), 1474 (m), 1339 (m), 1106 (s), 1085 (s); 1013 (m), 974 (s), 895 (s), 866 (s), 812 (m), 666 (m). ESI-HRMS [m/z] calculated for $C_{13}H_{14}NaO_2$ [M+Na]$^+$ 225.08860 found 225.08840.

7,10-Di-tert-butyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2l. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-3,5-di-tert-butyl-benzaldehyde **1l** (100 mg, 350 μmol, 1 equiv) in dry DCM (15 mL). The crude product was purified by flash column chromatography (Si: 25 g) with Et_2O and pentane as solvents (1:7) to afford 7,10-di-tert-butyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2l** (94 mg, 0.33 mmol, 94 % yield) as a white solid, analysis according to literature.[40] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.13 (s, 9 H) 1.14 (s, 9 H) 2.00-2.20 (m, 2H) 5.04 (br. s., 2 H) 5.28 (s, 1 H) 5.71 (s, 1 H) 7.11 (s, 1 H) 9.72 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 26.5, 27.8, 28.5, 32.4, 34.5, 54.8, 79.2, 98.3, 110.6, 122.4, 142.5, 148.5, 149.7, 158.4, 187.8. IR (NaCl thin film) ν_{max} [cm^{-1}] 3019, 2965, 2856, 2402, 1679, 1621, 1576, 1475, 1372, 1216, 1148, 1013, 669. ESI-HRMS [m/z] calculated for $C_{19}H_{26}NaO_2$ [M+Na]$^+$ 309.18250, found 309.18217. mp 104 °C.

8,10-Di-methyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2m and 3,6-Di-methyl-8-methylene-11,12-dioxa-tricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene 3m. Prepared according to the general procedure from 2-(buta-2,3-dienyloxy)-3,6-dimethyl-benzaldehyde **1m** (116.1 mg, 0.574 mmol, 1 equiv) in dry DCM (19 ml). The mixture was purified by flash column chromatography (Si: 25 g) with hexane and DCM as solvents (from 5:3 to pure DCM) to afford 8,10-Di-methyl-2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2m** (16.8 mg, 0.083 mmol, 14.47 % yield) as a

yellow oil and 3,6-Di-methyl-8-methylene-11,12-dioxa-tricyclo [7.2.1.0^{2,7}]dodeca-2,4,6-triene **3m** (41.1 mg, 0.203 mmol, 35.4 % yield) as a white-off solid. 8,10-Di-methyl-2-oxa-tricyclo[5.2.2.0^{1,5}] undeca-4,8,10-triene-9-carbaldehyde **2m;** ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.85 (s, 3 H) 2.12 (br. s., 2 H) 2.26 (s, 3 H) 3.35 - 3.56 (m, 1 H) 5.06 (s, 2 H) 5.33 (s, 1 H) 5.72 (d, 1 H) 9.92 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 189.5; 158.1; 147.5; 140.3; 138.5; 121.2; 111.0, 97.9; 80.2; 46.5; 27.1; 18.1; 14.6. IR (Golden Gate) ν_{max} [cm^{-1}] 2914 (m), 2851 (m), 1726 (m), 1672 (s); 1589 (s), 1430 (m), 1180 (m), 1036 (m). ESI-HRMS [m/z] calculated for $C_{13}H_{14}NaO_2$ [M+Na]$^{+}$ 225.08860 found 225.08885. 3,6-Di-methyl-8-methylene-11,12-dioxa-tricyclo [7.2.1.0^{2,7}]dodeca-2,4,6-triene **3m;** ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.39 (s, 3 H) 2.50 (s, 3 H) 3.69 (d, *J* = 7.27 Hz, 1 H) 4.08 (t, *J* = 6.36 Hz, 1 H) 5.01 (d, *J* = 5.45 Hz, 1 H) 5.36 (s, 1 H) 5.61 (s, 1 H) 6.39 (s, 1 H) 6.99 (d, *J* = 7.72 Hz, 1 H) 7.07 (d, *J* = 7.72 Hz, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 143.2; 135.1; 134.9; 132.2; 131.2; 129.9; 127.5; 113.6; 98.5; 80.1; 68.6; 24.1; 18.2. IR (NaCl thin film) ν_{max} [cm^{-1}] 3457 (br w), 2998 (m), 2968 (m), 2899 (m), 1621 (m), 1444 (m), 1357 (m), 1234 (m), 1158 (m), 1087 (s), 972 (s), 895(s), 808 (s), 668 (m). ESI-HRMS [m/z] calculated for $C_{13}H_{14}NaO_2$ [M+Na]+ 225.08860 found 225.08861. mp 64 °C.

8-Formyl-5-methoxy-4,5-dihydro-2H-5,7a-ethenobenzofuran-6-yl acetate 2o. The irradiation was carried out at 7.5 mM in DCM. Furthermore the general irradiation protocol was carried out with 5-(buta-2,3-dien-1-yloxy)-4-formyl-2-methoxyphenyl acetate **1o** (39.4 mg, 0.150 mmol) in dry DCM (20 mL). The crude product was filtered over silica gel (Si: 1 g) with DCM as solvent to afford 8-formyl-5-methoxy-4,5-dihydro-2H-5,7a-ethenobenzofuran-6-yl acetate **2o** (27.1 mg, 0.103 mmol, 68.8 % yield) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.15 (s, 3 H) 2.20 - 2.30 (m, 1 H) 2.81 (dq, *J* = 14.92, 2.39 Hz, 1 H) 3.63 (s, 3 H) 5.04 - 5.09 (m, 3 H) 5.48 (quin, *J* = 1.65 Hz, 1 H) 6.23 (s, 1 H) 9.97 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 20.7, 31.2, 56.7, 57.7, 81.1, 90.7, 93.6, 113.3, 120.6, 138.4, 152.1, 166.3, 168.5, 198.0. IR (Golden Gate) ν_{max} [cm^{-1}] 2941(w), 2859 (w), 1727 (s), 1644 (w), 1502

(w), 1436 (w), 1370 (m), 1276 (w), 1186 (s), 1088 (s), 1053 (s), 910 (m), 729 (s), 583 (m). ESI-HRMS [m/z] calculated for $C_{14}H_{14}NaO_5$ $[M+Na]^+$ 285.07334 found 285.07336.

7-Methoxy-5-methylene-1,3,4,5-tetrahydro-1,4-epoxybenzo[c]oxepin-8-yl acetate 3p. Prepared according to the general procedure from 4-(buta-2,3-dien-1-yloxy)-5-formyl-2-methoxyphenyl acetate **1p** (98.5 mg, 0.376 mmol, 1 equiv) in dry DCM (11.5 mL). The crude product was purified by flash column chromatography (Si: 10 g) with DCM and Et_2O as solvents (pure DCM to 10:1) to afford 7-methoxy-5-methylene-1,3,4,5-tetrahydro-1,4-epoxybenzo[c]oxepin-8-yl acetate **3p** (21.7 mg, 0.055 mmol, 14.54 % yield) as a white solid contaminated with 33 % starting material. ^{1}H NMR (300 MHz, CD_2Cl_2) δ ppm 2.26 (s, 3 H) 3.65 (dd, *J* = 7.37, 1.51 Hz, 2 H) 3.84 (s, 3 H) 4.03 (dd, *J* = 7.18, 5.85 Hz, 1 H) 5.05 (dd, *J* = 5.85, 1.51 Hz, 1 H) 5.15 (s, 1 H) 5.61 (s, 1 H) 5.96 (s, 1 H) 6.86 (s, 1 H) 7.24 (s, 1 H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ ppm 20.9, 56.6, 69.3, 78.1, 101.0, 107.7, 107.8, 120.1, 128.4, 130.2, 140.4, 142.4, 152.1, 169.3.

4-Chloro-but-2-yne-1-ol 4. To a solution of but-2-yne-1,4-diol (45.0 g, 523 mmol, 1 equiv) in a mixture of benzene (55 mL) and pyridine (46.5 mL, 575 mmol, 1.1 equiv) was added dropwise thionyl chloride (41.8 mL, 575 mmol, 1.1 equiv) over 3 h between 0 – 5 °C. After complete addition the reaction mixture was allowed to go to rt and was further stirred for 16 h. The reaction mixture was added to ice water (150 mL) and extracted three times with EtO_2 (100, 40, 40 mL), the combined organic layer were washed twice with a saturated solution of $NaHCO_3$ (2x 200 mL) and brine, dried over $MgSO_4$ and evaporated. The product was purified by distillation under reduced pressure (6 Torr, 70 °C) to afford 4-chloro-but-2-yne-1-ol **12** (19.43 g, 186 mmol, 36 % yield) as a translucent liquid, analysis according to literature.[41] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.68 (t, *J* = 6.13, 1H) 4.19 (s, 2H) 4.34 (d, *J* = 6.36, 2H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 84.6, 80.5, 51.0, 30.3. IR (NaCl thin film) ν_{max} [cm^{-1}] 3339 (m), 2996 (w), 2921 (w), 2869 (w), 1689 (w), 1599(w), 1430 (w), 1264 (s), 1145 (s), 1015 (s), 697 (s).

Buta-2,3-dien-1-ol 5. To a solution of 4-chloro-but-2-yne-1-ol **4** (11.00g, 105 mmol, 1 equiv) in dry Et_2O (200 mL) in a two-necked round bottom flask equipped with a condenser and under argon was added portionwise lithium aluminum hydride (4.32 g, 110 mmol, 1.05 equiv) to maintain a gentle reflux. The suspension was stirred for an additional 30 minutes and then cooled down to 0 °C. The reaction mixture was quenched (caution!) with water (4.2 mL) and NaOH 15 % (4.2 mL) followed by 25 mL of ice water. The gray slurry was then stirred overnight. The precipitate is filtered off and the organic phase is dried over $MgSO_4$ and evaporated. The product was purified by distillation under reduced pressure (14 Torr, 36 °C) to afford buta-2,3-dien-1-ol **5** (4.65 g, 66.3 mmol, 63 % yield) as a yellow liquid, analysis according to literature.[41] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 4.14 - 4.19 (m, 2 H) 4.88 (dt, *J* = 6.58, 3.18, 2.95 Hz, 2 H) 5.37 (q, *J* = 6.20 Hz, 1H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 207.8, 90.9, 77.2, 60.2. IR (NaCl thin film) ν_{max} [cm^{-1}] 3327 (s), 2939 (w), 2872 (w), 1957 (s), 1710 (w), 1439 (w), 1365 (w), 1265 (w), 1217 (w), 1119 (w), 1046 (m), 1013 (s), 913 (w), 848(s), 701 (w).

4-Bromo-buta-1,2-diene 6. To a solution of phosphorus tribromide (11.03 g, 39.9 mmol, 0.4 equiv) in Et_2O (19.5 mL) at -10 to 0 °C was added dropwise a solution of buta-1,2-dien-4-ol **5** (7 g, 100 mmol, 1 equiv) in pyridine (4.04 mL, 49.9 mmol, 0.5 equiv). The reaction mixture was stirred at rt for 16 h. After complete consumption of starting material, water (200 mL) was added. The organic layer was extracted with pentane (3x 100 mL) and the combined organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The product was distilled under reduced pressure (100 Torr, 50 °C) to afford 4-bromo-buta-1,2-diene **6** (7.06 g, 53.1 mmol, 53 % yield) as a translucent liquid, analysis according to literature.[41] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 3.94-4.00 (m, 2H), 4.92-4.97 (m, 2H), 5.51-5.40 (m, 1H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 209.6, 89.3, 77.3, 29.9. IR (NaCl thin film) ν_{max} [cm^{-1}] 2969 (w), 2362 (w), 1951 (s), 1429 (w), 1323 (w), 1208 (s), 1145 (w), 992 (w), 853 (s), 648 (m).

2-Hydroxy-3-methyl-benzaldehyde 7b. To a solution of *o*-cresol (57.3 mL, 555 mmol, 1 equiv) in anhydrous toluene (130 mL) under argon was added stannic chloride (6.52 mL, 55.5 mmol, 0.1 equiv)

followed by dry tri-n-butyl-amine (52.9 mL, 222 mmol, 0.4 equiv). The mixture was stirred at rt for 15 min then paraformaldehyde (73.4 g, 1221 mmol, 2.2 equiv) was added and the reaction mixture was heated to 100 °C for 4 h. The reaction mixture was poured into water (1000 mL) and the mixture was acidified with HCl 2N to pH = 1. The organics were extracted with Et_2O (3x 200mL) and the combined organic layers were washed with brine dried over $MgSO_4$ and evaporated. The product was distilled under reduced pressure to afford 2-hydroxy-3-methyl-benzaldehyde **7b** (39 g, 286 mmol, 51.6 % yield). Analysis according to the literature.[42] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.29 (s, 3 H) 6.94 (t, *J* = 7.49 Hz, 1 H) 7.42 (m, 2 H) 9.89 (s, 1 H) 11.28 (s, 1 H).

2-Hydroxy-3-tert-butyl-benzaldehyde 7d. To a solution of 2-tert-butylphenol (5.09 mL, 33.3 mmol, 1 equiv) in anhydrous toluene (10 mL) under argon was added stannic chloride (0.391 mL, 3.33 mmol, 0.1 equiv) followed by tri-n-butyl-amine (3.18 mL, 13.31 mmol, 0.4 equiv). The mixture was stirred at rt for half an hour then paraformaldehyde (4.40 g, 73.2 mmol, 2.2 equiv) was added and the reaction mixture was heated to 100°C for 14 h and was stirred at rt 3 h. The reaction mixture was poured into water (200 mL) and acidified with HCl 1N to pH = 2. The organics were extracted with Et_2O (3x 100 mL) and the combined organic layer was dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 50 g) with pentane and DCM as solvents (4:3) to afford 2-hydroxy-3-tert-butyl-benzaldehyde **7d** (3.65 g, 20.48 mmol, 61.5 % yield) as a yellow oil. Analysis according to the literature.[43] ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.44 (s, 9 H) 6.96 (t, *J* = 7.71 Hz, 1 H) 7.41 (dd, *J* = 7.58, 1.77 Hz, 1 H) 7.55 (dd, *J* = 7.58, 1.52 Hz, 1 H) 9.89 (s, 1 H) 11.81 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 29.2, 34.8, 119.2, 120.6, 132.0, 134.1, 138.2, 161.2, 197.1.

2-Hydroxy-3,5-dimethyl-benzaldehyde 7k. To a solution of 2,4-dimethylphenol (1.96 mL, 16.37 mmol, 1 equiv) in anhydrous toluene (4 mL) under argon was added tri-n-butyl-amine (1.6 mL, 6.55 mmol, 0.4 equiv) followed by stannic chloride (0.19 mL, 1.64 mmol, 0.1 equiv). The mixture was stirred at rt for half an hour then paraformaldehyde (2.16 g, 36.00 mmol) was added and the reaction

mixture was heated to 100 °C for 8 h and stirred at rt for 16 h. The reaction mixture was added to water (150 mL) and acidified with HCl 1N to pH = 2. The organics were extracted three times with Et_2O (100, 50, 50 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 20 g) with pentane and DCM as solvents (2:1) to afford 2-hydroxy-3,5-dimethyl-benzaldehyde **7k** (0.90 g, 6.0 mmol, 37 % yield) as a yellow oil. Analysis according to the literature.[44] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.25 (s, 3 H) 2.31 (s, 3 H) 7.18 (s, 1 H) 7.23 (s, 1 H) 9.84 (s, 1 H) 11.10 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 196.7, 157.9, 139.0, 130.9, 128.5, 126.5, 119.7, 20.2, 15.0.

2-Hydroxy-3,6-dimethyl-benzaldehyde 7m. To a solution of 2,5-dimethylphenol (1.5 g, 12.28 mmol, 1 equiv) in anhydrous toluene (3 mL) under argon was added stannic chloride (0.144 mL, 1.228 mmol, 0.1 equiv) followed by tri-n-butyl-amine (1.172 mL, 4.91 mmol, 0.4 equiv). The mixture was stirred at rt for half an hour then paraformaldehyde (1.623 g, 27.0 mmol, 2.2 equiv) was added and the reaction mixture was heated to 100°C for 8 h and was stirred at rt for 16 h. The reaction mixture was added to water (110 mL) and acidified with HCl 1N to pH = 1. The organics were extracted three times with Et_2O (100, 50, 50 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. The product was purified by flash column chromatography (Si: 15 g) with pentane and DCM as solvents (2:1) to afford 2-hydroxy-3,6-dimethyl-benzaldehyde **7m** (0.79 g, 5.26 mmol, 42 % yield) as white crystals. Analysis according to the literature.[45] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.22 (s, 3 H) 2.59 (s, 3 H) 6.63 (d, *J* = 7.27 Hz, 1 H) 6.93 - 7.48 (m, 1 H) 10.31 (s, 1 H) 12.19 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 195.6, 161.6, 139.4, 138.2, 125.0, 121.1, 117.9, 17.9, 14.9.

2-(Prop-2-ynyloxy)benzaldehyde 8. Propargyl bromide (80 % in toluene; 71.0 mL, 659 mmol, 1.15 equiv) was added slowly to a suspension of salicylaldehyde (60.0 mL, 573 mmol, 1 equiv) and K_2CO_3 (103 g, 745 mmol, 1.3 equiv) in DMF (300 mL). The reaction mixture was stirred at rt for 5 h; then diluted with water (1 L) and the organics were extracted three times with Et_2O (3x 300 mL). The

combined organic layers were washed with brine (500 mL), dried over $MgSO_4$ and evaporated. The resulting solid was dissolved in a small amount of DCM and crystallized upon addition of hexane. The crystals were filtered to afford 2-(prop-2-ynyloxy)benzaldehyde **8** (87.5 g, 546 mmol, 95 % yield) as white crystals. Analysis according to the literature.[40] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.58 (t, *J* = 2.27 Hz, 1 H) 4.85 (d, *J* = 2.27 Hz, 2 H) 7.06 - 7.18 (m, 2 H) 7.51 - 7.64 (m, 1 H) 7.88 (dd, *J* = 7.72, 1.82 Hz, 1 H) 10.50 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 56.3, 76.5, 77.6, 113.1, 121.7, 125.4, 128.6, 135.7, 159.7, 189.6.

Methyl 2-(prop-2-ynyloxy)benzoate 9. Propargyl bromide (80 % in toluene; 63.9 mL, 584 mmol, 1.25 equiv) was added slowly to a suspension of methyl salicylate (60 mL, 467 mmol, 1 equiv) and K_2CO_3 (84 g, 607 mmol, 1.3 equiv) in DMF (170 mL) at 0 °C and the reaction mixture was stirred for 20 h at rt. The reaction mixture was diluted with water (1 L) and the organics were extracted four times with Et_2O (4x 200 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated to afford pure methyl 2-(prop-2-ynyloxy)benzoate **9** (87.33 g, 459 mmol, 98 % yield). Analysis according to the literature.[46] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.53 (t, *J* = 2.27 Hz, 1 H) 3.90 (s, 3 H) 4.81 (d, *J* = 2.27 Hz, 2 H) 7.06 (t, *J* = 7.49 Hz, 1 H) 7.15 (d, *J* = 8.63 Hz, 1 H) 7.49 (dt, 1 H) 7.83 (dd, *J* = 7.72, 1.36 Hz, 1 H). ESI-HRMS [m/z] calculated for $C_{11}H_{10}NaO_3$ $[M+Na]^+$ 213.0528 found 213.0521.

Methyl 2-(buta-2,3-dienyloxy)benzoate 10a on multigramm scale via Crabbé homologation. Paraformaldehyde (15.8 g, 526 mmol, 2.3 equiv), copper(I) bromide (14.77 g, 103 mmol, 0.45 equiv) and methyl 2-(prop-2-ynyloxy)benzoate **9** (43.5 g, 228 mmol, 1 equiv) were suspended under argon atmosphere in dry dioxane (725 mL). Diisopropylamine (87.3 mL, 613 mmol, 2.6 equiv) (distilled from KOH before use) was added and the reaction mixture was heated to a gentle reflux for 17 h. The reaction mixture was reduced to half of the volume of dioxane and filtered. Water (1 L) was added to the filtrate and the organics were extracted five times with EtOAc (5x 200 mL). The combined organic

layers were washed with brine (300 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 1 kg) with hexane and EtOAc as solvents (9:1) to afford methyl 2-(buta-2,3-dienyloxy)benzoate **10a** (21.56 g, 106 mmol, 46.3 % yield) as a yellow liquid. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 3.90 (s, 3 H) 4.65 - 4.72 (m, 2 H) 4.83 - 4.92 (m, 2 H) 5.36 - 5.51 (m, 1 H) 6.95 - 7.05 (m, 2 H) 7.41 - 7.50 (m, 1 H) 7.80 (d, *J* = 7.72 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 51.9, 66.9, 76.6, 87.0, 114.1, 120.6, 120.9, 131.6, 133.2, 157.8, 166.7, 209.4. IR (NaCl thin film) ν_{max} [cm^{-1}] 2951 (w); 1958 (w); 1730 (s), 1601 (m); 1490 (m); 1453 (m); 1380 (w); 1305 (s); 1252 (s); 1084(m); 1004 (m); 852 (s); 756 (m). UV-VIS (MeCN, c = 2.8 x 10^{-5} mol/l): λ_{max} 290nm (ε = 3079); 226 nm (ε = 7899); 203 nm (ε = 34541). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_3$ $[M+Na]^+$ 227.068 found 227.06734.

Metyl-2-(buta-2,3-dienyloxy)-benzoate 10a. To a suspension of K_2CO_3 (0.827 g, 5.98 mmol, 1.3 equiv) and methyl salicylate (0.591 mL, 4.60 mmol, 1 equiv) in DMF (15 mL) was added dropwise 4-bromo-1,2-butadiene **6** (0.612 g, 4.60 mmol, 1 equiv) over 1 h. The reaction mixture was stirred at rt for 16 h. The reaction mixture was diluted with Et_2O (100 mL) and the organic layer was washed three times with HCl 1N (3 x 40 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 40 g) with pentane and DCM as solvents (4:3 to pure DCM) to afford metyl-2-(buta-2,3-dienyloxy)-benzoate 10a (446.1 mg, 2.2 mmol, 48 % yield) as a yellow liquid. Analysis as described above.

1-(2-(Buta-2,3-dienyloxy)phenyl)ethanone 10b. To a suspension of K_2CO_3 (1.320 g, 9.55 mmol, 1.3 equiv) and 2-hydroxyacetophenone (0.885 mL, 7.34 mmol, 1 equiv) in DMF (22 mL) was added dropwise 4-bromo-1,2-butadiene **6** (1.074 g, 8.08 mmol, 1.1 equiv) within 1 h. The reaction mixture was stirred for 48 h at rt. The reaction mixture was diluted with Et_2O (50 mL) and the organic layer was washed three times with a solution of K_2CO_3 1M (3x 50 mL), HCl 1N (3x 40 mL) and brine (50

mL), dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 25 g) with pentane and DCM as solvents (3:2) to obtain 1-(2-(buta-2,3-dienyloxy)phenyl)ethanone **10b** (549.8 mg, 2.9 mmol, 40 % yield) as a translucent oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.65 (s, 3 H) 4.63 - 4.72 (m, 2 H) 4.84 - 4.96 (m, 2 H) 5.16 - 5.76 (m, 1 H) 6.97 (d, *J* = 8.17 Hz, 1 H) 7.01 (t, *J* = 7.49 Hz, 1 H) 7.45 (t, *J* = 7.72 Hz, 1 H) 7.74 (d, *J* = 7.72 Hz, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 32.0, 66.1, 77.3, 86.6, 112.8, 120.8, 128.6, 130.4, 133.5, 157.6, 200.0, 209.4. ^{13}C NMR (75 MHz, DMSO-*d*6) δ ppm 31.8, 65.7, 77.3, 86.8, 113.7, 120.7, 128.3, 129.5, 133.6, 157.2, 199.0, 208.6. IR (Golden Gate) ν_{max} [cm^{-1}] 3000 (w), 1958 (m), 1670 (s), 1596 (s), 1483 (m), 1450(m), 1357 (m), 1290 (s), 1233 (s), 1215 (s), 1163 (m), 1126 (m), 1000 (m), 848 (m), 754 (s). UV-VIS (MeCN, c = 5.3 x 10^{-5} mol/l): λ_{max} 211 nm (ε = 24605); 243 nm (ε = 7885); 300 nm (ε = 3383). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ $[M+Na]^+$ 211.07295 found 211.07280.

(2-(Buta-2,3-dienyloxy)phenyl)(phenyl)methanone 10c. 2-hydroxybenzophenone (1.5 g, 7.57 mmol, 1 equiv) and K_2CO_3 (1.360 g, 9.84 mmol, 1.3 equiv) were suspended in dry DMF (10 mL) under argon and the suspension was heated to 50 °C. 4-Bromo-1,2-butadiene **6** (1.308 g, 9.84 mmol, 1.3 equiv) was added dropwise to the reaction mixture over 3 h. The reaction mixture was stirred for an additional hour at 50 °C then at rt for 16 h. The reaction mixture was diluted with Et_2O (150 mL) and washed twice with water (2x 100 mL) and brine (100 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 100 g) with hexane and EtOAc as solvents (10:1) to afford (2-(buta-2,3-dienyloxy)phenyl)(phenyl)methanone **10c** (879.3 mg, 3.51 mmol, 46.4 % yield) as a yellow oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 4.43 - 4.55 (m, 2 H) 4.66 - 4.81 (m, 2 H) 4.99 - 5.15 (m, 1 H) 7.00 (d, *J* = 8.17 Hz, 1 H) 7.07 (t, *J* = 7.49 Hz, 1 H) 7.37 - 7.51 (m, 4 H) 7.52 - 7.61 (m, 1 H) 7.81 (d, *J* = 7.27 Hz, 2 H). ^{13}C NMR (91 MHz, CDCl3) δ ppm 66.2, 76.5, 86.6, 113.0, 120.9, 128.1, 129.4, 129.7, 131.8, 132.8, 137.9, 156.0, 196.5, 209.1. ^{13}C NMR (91 MHz, DMSO-d_6) δ ppm 65.5, 77.0, 86.4, 113.4, 120.9, 128.5, 128.8, 128.9, 129.2, 132.0, 133.2, 137.2, 155.4, 195.8, 208.4.

IR (Golden Gate) ν_{max} [cm^{-1}] 3061 (w), 2874 (w), 1957 (m), 1660 (s), 1597 (s), 1580 (m), 1483 (m), 1449 (s), 1378 (w), 1315 (m), 1293 (s), 1240 (s), 1218 (s), 1152 (m), 1108 (m), 1000 (s), 924 (s), 848 (s), 750 (s), 699 (s), 635 (s). UV-VIS (MeCN, c = 3.0 x 10^{-5} mol/l): λ_{max} 282 nm (ε = 6453). ESI-HRMS [m/z] calculated for $C_{17}H_{14}NaO_2$ $[M+Na]^+$ 273.08860 found 273.08813.

2-(Buta-2,3-dienyloxy)-benzonitrile 10d. 2-Hydroxybenzonitrile (1 g, 8.39 mmol, 1 equiv) was dissolved in a suspension of K_2CO_3 (1.508 g, 10.91 mmol, 1.3 equiv) in DMF (15 mL). 4-Bromo-1,2-butadiene **6** (1.116 g, 8.39 mmol, 1 equiv) was added dropwise within 1 h and the reaction mixture was stirred for 16 h at rt. The reaction mixture was diluted with Et_2O (150 mL) and the organic layer was washed three times with a solution of K_2CO_3 1M (3x 60 mL), HCl 1N (3x 50 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 50g) with hexane and EtOAc as solvents (3:1) to afford 2-(buta-2,3-dienyloxy)-benzonitrile **10d** (939.4 mg, 5.49 mmol, 65.4 % yield) as a yellow liquid. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 4.64 - 4.76 (m, 2 H) 4.84 - 4.98 (m, 2 H) 5.34 - 5.50 (m, 1 H) 6.92 - 7.09 (m, 2 H) 7.46 - 7.65 (m, 2 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 66.6, 77.0, 86.3, 102.3, 112.8, 116.4, 120.9, 133.8, 134.1, 160.0, 209.6. IR (Golden Gate) ν_{max} [cm^{-1}] 2227, 1957, 1598, 1489, 1450, 1287, 1254, 1166, 1109, 993, 849, 752. UV-VIS (MeCN, c = 2.7 x 10^{-5} mol/l): λ_{max} 204 nm (ε = 40045); 232 nm (ε = 9317); 292 nm (ε = 4141). ESI-HRMS [m/z] calculated for $C_{11}H_9KNO$ $[M+K]^+$ 210.03157 found 210.03043.

Tert-butyl-N-phenyl-carbamate 11. To a solution of aniline (9.31 mL, 102 mmol, 1 equiv) in anhydrous toluene (100 mL) was added Boc_2O (28.4 mL, 122 mmol, 1.2 equiv). The reaction mixture was heated to 100 °C for 3 h. The solvents were reduced to one fifth and pentane was added. The thereby formed crystals were isolated by filtration to afford tert-butyl-N-phenyl-carbamate **11** (17.3 g, 90 mmol, 88 % yield) as a white solid. Spectral data according to the literature.[47] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.52 (s, 9 H) 6.47 (br. s., 1 H) 7.03 (t, *J* = 7.27 Hz, 1 H) 7.24 - 7.42 (m, 4 H). ^{13}C NMR (91 MHz, $CDCl_3$) d ppm 28.3, 80.5, 118.5, 123.0, 129.0, 138.3, 152.7.

Tert-butyl 2-formylphenylcarbamate 13a. To a solution of tert-butyl-N-phenylcarbamate **11** (10 g, 51.7 mmol, 1 equiv) in dry THF (100 mL) at -78 °C was added dropwise a solution of tert-butyllithium 1.7 M in pentane (63.9 mL, 109 mmol, 2.1 equiv). The reaction mixture was stirred at -50 °C for 3 hours. Then dry DMF (4.78 mL, 62.1 mmol, 1.2 equiv) was added dropwise to the solution at -50 °C the reaction mixture was allowed to slowly warm up and was stirred at rt for 17 h. The reaction mixture was diluted with Et_2O (150 mL) and washed twice with brine (2 x 100 mL) dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 100 g) with hexane and EtOAc as solvents (7:1) to afford tert-butyl 2-formylphenylcarbamate **13a** (2.02 g, 9.13 mmol, 18 % yield) as a white-off solid. Analysis according to the literature.[48] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.55 (s, 9 H) 7.14 (t, *J* = 7.49 Hz, 1 H) 7.53 - 7.68 (m, 2 H) 8.47 (d, *J* = 8.63 Hz, 1 H) 9.91 (s, 1 H) 10.41 (br. s., 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 28.2, 80.9, 118.2, 121.2, 121.5, 135.9, 136.1, 141.8, 152.9, 195.0.

Methyl 2-(tert-butoxycarbonylamino)benzoate 13b. To a mixture of methyl 2-aminobenzoate **12b** (12.84 mL, 99 mmol, 1 equiv) and Boc_2O (23.04 mL, 99 mmol, 1 equiv) was added finely powdered lanthanum(III) nitrate hexahydrate (2.148 g, 4.96 mmol, 0.05 equiv) and the mixture was stirred at rt for 1 h, then at 50 °C for 3 h. The reaction mixture was diluted with water (100 mL) and the product was extracted three times with EtOAc (3x 50 mL), the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. The product was isolated by flash column chromatography (Si: 250 g) with hexane and EtOAc as solvents (8:1) to afford methyl 2-(tert-butoxycarbonylamino)benzoate **13b** (23.2753 g, 93 mmol, 93 % yield). ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.54 (s, 9 H) 3.92 (s, 3 H) 7.00 (t, *J* = 7.72 Hz, 1 H) 7.51 (t, *J* = 7.95 Hz, 1 H) 8.00 (d, *J* = 7.72 Hz, 1 H) 8.44 (d, *J* = 8.63 Hz, 1 H) 10.29 (br. s., 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 28.3; 52.2; 80.5; 114.2; 118.7; 121.1; 130.8; 134.5; 142.3; 152.9; 168.6.

Tert-butyl 2-benzoylphenylcarbamate 13c. To a solution of 2-aminobenzophenone **12c** (1.51 g, 7.66 mmol, 1 equiv) and Boc_2O (1.955 mL, 8.42 mmol, 1.1 equiv) in dry THF (10 mL) was added 4-DMAP (0.935 g, 7.66 mmol, 1 equiv) and the mixture was stirred for 3 days at rt. The solvent was evaporated and the residue was purified by flash column chromatography (Si: 100g) with hexane and EtOAc as solvents (20:1) to afford tert-butyl 2-benzoylphenylcarbamate **13c** (955.8 mg, 3.21 mmol, 42 % yield) as a white-off solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.53 (s, 9 H) 7.01 (t, *J* = 7.72 Hz, 1 H) 7.40 - 7.79 (m, 7 H) 8.42 (d, *J* = 8.17 Hz, 1 H) 10.06 (br. s., 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 28.3, 80.6, 119.9, 120.7, 122.8, 128.2, 129.9, 132.3, 133.5, 134.1, 138.8, 141.3, 153.0, 199.3. IR (Golden Gate) ν_{max} [cm^{-1}] 3321 (m), 2977 (m), 1726 (s), 1632 (s), 1579 (s), 1518 (s), 1448 (s), 1367 (m), 1319(m), 1247 (s), 1149 (s), 1049 (m), 1026 (m), 936 (m), 922 (m), 768 (m), 750 (m), 693 (s), 640 (m). ESI-HRMS [m/z] calculated for $C_{18}H_{19}NNaO_3$ $[M+Na]^+$ 320.12571 found 320.12596.

Tert-butyl-buta-2,3-dienyl(2-formylphenyl)carbamate 14a. To a suspension of K_2CO_3 (937 mg, 6.78 mmol, 2.5 equiv) and tert-butyl 2-formylphenylcarbamate **13a** (600 mg, 2.71 mmol, 1 equiv) in dry DMF (13 mL) was added portionwise 4-bromo-1,2-butadiene (793 mg, 5.97 mmol, 2.2 equiv) and the reaction mixture was stirred at rt for two days. The reaction mixture was diluted with Et_2O (100 mL) and the organic phase was washed twice with water (2x 50 mL) and with brine (50 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 25g) with hexane and EtOAc as solvents (7:1) to afford tert-butyl-buta-2,3-dienyl(2-formylphenyl)carbamate **14a** (500.7 mg, 1.832 mmol, 68 % yield) as a yellow oil. The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.33 (br. s., 9 H) 4.28 (br. s., 2 H) 4.71 (br. s., 2 H) 5.21 - 5.37 (m, 1 H) 7.30 (d, *J* = 6.32 Hz, 1 H) 7.41 (t, *J* = 7.58 Hz, 1 H) 7.62 (dt, *J* = 7.71, 1.77 Hz, 1 H) 7.91 (dd, *J* = 7.58, 1.26 Hz, 1 H) 10.12 (br. s., 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 28.1 (br. s.), 49.4 (br. s.), 76.4 (br. s.), 81.4, 86.4 (br. s.), 127.4, 128.0 (br. s.), 132.7, 134.6, 144.4, 190.1 (br. s.), 209.4 (br. s.). IR (Golden Gate) ν_{max} [cm^{-1}] 2978 (w), 2932 (w),

1955 (w), 1691 (s), 1598 (m), 1367 (m), 1251 (m), 1154 (s), 850 (m), 761 (m). UV-VIS (MeCN, c = 1.8 x 10^{-5} mol/l): λ_{max} 298 nm (ε = 1791); 233 nm (ε = 15208). ESI-HRMS [m/z] calculated for $C_{16}H_{19}NNaO_3$ $[M+Na]^+$ 296.12571, found 296.12506.

Methyl 2-(buta-2,3-dienyl(tert-butoxycarbonyl)amino)benzoate 14b via allenylation. To a suspension of NaH (0.478 g, 11.94 mmol, 1.2 equiv) in dry DMF (5 mL) was added portionwise at -23 °C a solution of methyl 2-(tert-butoxycarbonylamino)benzoate **13b** (2.5 g, 9.95 mmol, 1 equiv) in dry DMF (10 mL). The reaction mixture was stirred for 1 h at 0 °C then 4-bromo-1,2-butadiene (1.720 g, 12.93 mmol, 1.3 equiv) was added dropwise at 0 °C and the mixture was stirred for 1 h at 0 °C then at rt for 3 h. The reaction mixture was diluted with Et_2O (100 mL) and washed twice with water (2x 50 mL) and with brine (50 mL), dried over $MgSO_4$ and evaporated. The crude was purified by flash column chromatography (Si: 25 g) with hexane and EtOAc as solvents (7:1) to afford methyl-2-(buta-2,3-dienyl(tert-butoxycarbonyl)amino)benzoate **14b** (1.008 g, 3.32 mmol, 33 % yield) as a white solid. The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (360 MHz, DMSO-d_6) δ ppm 1.22 (s, 6 H) 1.43 (br. s., 3 H) 3.70 - 3.85 (m, 3 H) 3.89 - 4.43 (m, 2 H) 4.70 - 4.93 (m, 2 H) 5.21 - 5.47 (m, 1 H) 7.31 - 7.45 (m, 2 H) 7.59 (t, *J* = 7.61 Hz, 1 H) 7.72 - 7.87 (m, 1 H). ^{13}C NMR (91 MHz, DMSO-d_6) δ ppm 27.6, 27.7, 28.0, 48.6 (br. s.), 52.0 (br. s.), 76.5, 76.8, 79.4, 79.8, 87.2 (br. s.), 87.8 (br. s.), 126.4 - 127.3 (br. s.), 128.2 (br. s.), 128.6, 128.9, 130.3 (br. s.), 130.5 (br. s.), 132.8 (br. s.), 133.0 (br. s.), 141.4, 141.8, 152.9, 153.6, 166.1, 208.2. IR (Golden Gate) ν_{max} [cm^{-1}] 2970 (w), 1931 (w), 1953 (m), 1724 (s), 1694 (s), 1596 (m), 1490 (m), 1429 (m), 1390 (s), 1367 (s), 1323 (s), 1287 (s), 1257 (s), 1168 (s), 1131 (s), 1088 (s), 1052 (m), 862 (s), 762 (s), 716 (s). UV-VIS (MeCN, c = 2.2 x 10^{-5} mol/l): λ_{max} 282 nm (ε = 1962.2). ESI-HRMS [m/z] calculated for $C_{17}H_{21}NNaO_4$ $[M+Na]^+$ 326.1362, found 326.13679. mp 62 °C.

Methyl 2-(buta-2,3-dienyl(tert-butoxycarbonyl)amino)benzoate 14b via Crabbé homologation. Paraformaldehyde (7.16 g, 238 mmol, 2.3 equiv), copper(I) bromide (6.69 g, 46.7 mmol, 0.45 equiv)

and methyl 2-(tert-butoxycarbonyl(prop-2-ynyl)amino)benzoate **15** (30 g, 104 mmol, 1 equiv) were suspended under argon atmosphere in dry dioxane (500 mL). Diisopropylamine (39.9 mL, 280 mmol, 2.7 equiv) (distilled from KOH before use) was added and the reaction mixture was heated to a gentle reflux for 17 h. The reaction mixture was reduced to half of the volume of dioxane and filtered. Water (500 mL) was added to the filtrate and the organics were extracted five times with EtOAc (5x 100 mL). The combined organic layers were washed with brine (200 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 500 g) with hexane and EtOAc as solvents (9:1) to afford methyl 2-(buta-2,3-dienyl(tert-butoxycarbonyl)amino)benzoate **14b** (19.9 g, 65.6 mmol, 63 % yield) as a white solid. Spectral data as described previously.

Tert-butyl 2-benzoylphenyl(buta-2,3-dienyl)carbamate 14c. To a suspension of NaH (0.140 g, 3.50 mmol, 1.3 equiv) in dry DMF (1.3 mL) was added dropwise a solution of tert-butyl 2-benzoylphenylcarbamate **13c** (0.8 g, 2.69 mmol, 1 equiv) in dry DMF (1.3 mL) at -23 °C. The reaction mixture was stirred at 0 °C for 1h then 4-bromo-1,2-butadiene (0.501 g, 3.77 mmol, 1.4 equiv) was added dropwise at -23 °C to the reaction mixture. The reaction mixture was stirred at rt for another hour then quenched by addition of ice water (100 g). The organics were extracted three times with Et_2O (3x 50 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 25 g) with hexane and EtOAc as solvents (10:1) to afford tert-butyl 2-benzoylphenyl(buta-2,3-dienyl)carbamate **14c** (492.2 mg, 1.409 mmol, 52 % yield) as a yellow oil. The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.27 (br. m, 9 H) 3.51 - 4.44 (br. m, 2 H) 4.74 (br. m., 2 H) 5.25 (quin, J = 6.47 Hz, 1 H) 7.29 - 7.86 (m, 9 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 28.0 (br. s.) 48.6 - 50.7 (m) 76.3 (br. s.) 80.5, 86.9 - 88.5 (m) 126.5 (br. s.) 128.1 (br. s.) 129.3 (br. s.) 129.9, 130.5 - 131.4 (m) 132.6 - 133.4 (m) 137.1 (br. s.) 140.1 - 141.8 (m) 153.7 (br. s.) 196.1 (br. s.) 208.9 (br. s.). IR (Golden Gate) ν_{max} [cm^{-1}] 2978 (w), 2932 (w), 1956 (w), 1697 (s), 1666 (s), 1597 (m), 1466(w),

1449 (m), 1388 (m), 1366 (m), 1316 (m), 1287 (s), 1252 (s), 1154 (s), 1953 (w), 927 (m), 849 (m), 762 (m), 701 (s), 635 (m). ESI-HRMS [m/z] calculated for $C_{22}H_{23}NNaO_3$ $[M+Na]^+$ 372.15701 found 372.15698. UV-VIS (MeCN, c = 3.3 x 10^{-5} mol/l): λ_{max} compound begins to absorb around 380 nm. No maximal absorption until 250 nm measured.

Irradiation of tert-butyl 2-benzoylphenyl(buta-2,3-dienyl)carbamate 14c. Tert-butyl 2-benzoyl-phenyl(buta-2,3-dienyl)carbamate **14c** (22 mg, 0.063 mmol, 1 equiv) was dissolved in dry DCM (2.11 mL) in a quartz tube equipped with a magnetic stir bar and a rubber septum. The reaction mixture was purged with argon for 15 min and irradiated at 254 nm, 300 nm or 350 nm for several hours. After 19 h at each wavelength only degradation was observed and no major compound could be detected on the TLC.

Methyl 2-(tert-butoxycarbonyl(prop-2-ynyl)amino)benzoate 15. To a suspension of NaH (8.86 g, 203 mmol, 1 equiv) in dry DMF (60 mL) at -23 °C was added dropwise a solution of methyl 2-(tert-butoxycarbonylamino)benzoate **13b** (51 g, 203 mmol, 1 equiv) in dry DMF (100 mL). The reaction mixture was stirred for 2.5 h at 0 °C then propargyl bromide (80 % in toluene; 28.4 mL, 264 mmol, 1.3 equiv) was added dropwise to the reaction mixture at rt. The reaction mixture was further stirred at rt for 2 h then quenched upon addition to ice cooled water (1 L). The organics were extracted with Et_2O (3x 300 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 500 g) with hexane and EtOAc as solvents (9:1) to afford methyl 2-(tert-butoxycarbonyl(prop-2-ynyl)amino)benzoate **15** (54.1 g, 187 mmol, 92 % yield) as a yellow oil. The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.31 (s, 6 H) 1.54 (s, 3 H) 2.17 - 2.37 (m, 1 H) 3.79 - 3.97 (m, 3 H) 4.07 (dd, J = 17.71, 1.82 Hz, 1 H) 4.76 (dd, J = 17.71, 1.82 Hz, 1 H) 7.32 - 7.64 (m, 3 H) 7.94 (d, J = 7.72 Hz, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 27.9, 28.1, 39.0, 40.1, 52.1, 71.7, 72.1, 79.6, 79.8, 80.5, 81.1, 127.2, 127.3, 128.5, 129.2, 129.6, 130.9, 132.6, 132.7, 141.1, 141.4, 153.7,

154.0, 166.2, 166.3. IR (Golden Gate) ν_{max} [cm^{-1}] 3295 (w), 2978 (w), 1700 (s), 1600 (w), 1492 (w), 1454 (m), 1434 (m), 1281 (m), 1367 (m), 1291 (s), 1254 (s), 1158 (s), 1126 (m), 1089 (m), 1048 (m), 1022 (m), 947 (w), 858 (m), 760 (m), 713 (m). ESI-HRMS [m/z] calculated for $C_{16}H_{19}NNaO_4$ $[M+Na]^+$ 312.12063 found 312.12014.

Thermal reaction to the Claisen rearrangement compound 17a. 2-(Buta-2,3-dienyloxy)-benzaldehyde **1a** (15 mg, 0.086 mmol) was dissolved in dry acetonitrile (2.9 mL) in a microwave vial equipped with a magnetic stir bar and sealed with a rubber septum. The reaction mixture was purged with argon for 15 min and heated to 100 °C for 10 min. No change was observed by HPLC therefore the reaction mixture was further heated to 150 °C, 170 °C and 200 °C for 15 min each. Only at 200 °C some conversion towards new compounds could be observed. However, after 20 min. at 210 °C the conversion is still not complete. The main compound observed in the reaction mixture is the Claisen rearranged compound **17a** and salicylaldehyde **7a**. The compounds were not isolated as no cycloaddition products were observed.

2-Oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-methylester 18a. Metyl-2-(buta-2,3-dienyloxy)-benzoate **10a** (124 mg, 0.607 mmol, 1 equiv) was dissolved in dry DCM (19 mL) in a quartz tube equipped with a magnetic stir bar and a rubber septum. The reaction mixture was purged with argon for 15 min and irradiated at 300 nm in a Rayonet reactor for 4 h. The crude mixture was purified by flash column chromatography (Si: 20g) with pentane and DCM as solvents (4:3) to afford 2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-methylester **18a** (29.3 mg, 0.143 mmol, 24 % yield) and methyl 3-(buta-1,3-dien-2-yl)-2-hydroxybenzoate **21** (8 mg, 0.039 mmol, 6.4 % yield). 2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-methylester **18a** due to instability of the compound no further analysis data available. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.14 (br. s., 2 H) 3.76 (s, 3 H) 3.86 (br. s., 1 H) 4.93 - 5.17 (m, 2 H) 5.40 (br. s., 1 H) 6.18 (t, *J* = 6.81 Hz, 1 H) 6.57 (d, *J* = 7.72 Hz, 1 H) 6.99 (d, *J* = 6.36 Hz, 1 H). Methyl 3-(buta-1,3-dien-2-yl)-2-hydroxybenzoate **21**; ^{1}H NMR (360 MHz, $CDCl_3$) δ

ppm 3.97 (s, 3 H) 4.89 (d, *J* = 17.26 Hz, 1 H) 5.17 (d, *J* = 10.44 Hz, 1 H) 5.21 (s, 1 H) 5.49 (s, 1 H) 6.65 (dd, *J* = 17.26, 10.44 Hz, 1 H) 6.90 (t, *J* = 7.72 Hz, 1 H) 7.33 (d, *J* = 7.72 Hz, 1 H) 7.85 (d, *J* = 8.17 Hz, 1 H) 11.08 (s, 1 H).

2-Oxa-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-ethanone 18b and **8-methylene-1-methyl-11,12-dioxa-tricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene 19.** 1-(2-(buta-2,3-dienyloxy)phenyl)ethanone **10b** (124 mg, 0.659 mmol, 1 equiv) was dissolved in dry DCM (20 mL) in a quartz tube equipped with a magnetic stir bar and sealed with a rubber septum. The solution was purged with argon for 15 min. and irradiated under argon atmosphere for 5.3 h at 350 nm. The solvent was evaporated and the crude mixture was purified by flash column chromatography (Si: 20 g) with hexane and EtOAc as solvents (5:1) to afford 2-oxa-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-ethanone **18b** (26.1 mg, 0.139 mmol, 21.1 % yield) as a yellow oil and 8-methylene-1-methyl-11,12-dioxa-tricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene **19** (55.7 mg, 0.296 mmol, 44.9 % yield) as a translucent oil. 2-oxa-tricyclo[5,2,2,01,5]undeca-4,8,10-triene-9-ethanone **18b**; ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.99 - 2.27 (m, 2 H) 2.36 (s, 3 H) 3.86 (br. s., 1 H) 5.04 (br. s., 2 H) 5.38 (br. s., 1 H) 6.19 (t, *J* = 6.81 Hz, 1 H) 6.57 (d, *J* = 7.72 Hz, 1 H) 6.91 (d, *J* = 6.36 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 27.0, 29.2, 38.8, 79.5, 96.5, 111.9, 129.9, 139.2, 139.4, 140.0, 150.0, 195.8. IR (Golden Gate) ν_{max} [cm^{-1}] 2921(w), 2854 (w), 1671 (s), 1606 (w), 1566 (m), 1357 (m), 1238 (s), 1164 (s), 1008 (m), 806 (m), 676 (m). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ [M+Na]$^{+}$ 211.07295 found 211.07288. 8-methylene-1-methyl-11,12-dioxa-tricyclo[7,2,1,02,7]dodeca-2,4,6-triene **19**; ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.95 (s, 3 H) 3.70 (d, *J* = 7.27 Hz, 1 H) 4.17 (t, *J* = 6.58 Hz, 1 H) 5.01 - 5.20 (m, 2 H) 5.64 (s, 1 H) 7.22 - 7.38 (m, 3 H) 7.71 (d, *J* = 6.81 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 20.8, 69.8, 78.9, 105.8, 106.5, 123.2, 123.5, 128.3, 128.5, 129.1, 138.4, 142.8. IR (Golden Gate) ν_{max} [cm^{-1}] 2997 (w), 2888 (w), 1480 (m), 1382 (m), 1301 (m), 1275 (m), 1198 (m), 1103 (m), 1023 (s), 1006 (s), 892 (m), 842 (s), 755 (s). ESI-HRMS [m/z] calculated for $C_{12}H_{12}NaO_2$ [M+Na]$^{+}$ 211.07295 found 211.07307.

2-Oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,6,8-triene-9-nitrile 18d. 2-(Buta-2,3-dienyloxy)-benzonitrile **10d** (106.0 mg, 0.619 mmol, 1 equiv) was dissolved in dry DCM (20 mL) under argon in a quartz tube equipped with a magnetic stir bar and a rubber septum. The reaction mixture was purged with argon for 15 min and irradiated under argon atmosphere at 300 nm for 7 h. The solvent was evaporated and the product was isolated by flash column chromatography (Si: 20g) with hexane and EtOAc as solvents (4:1) to afford 2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,6,8-triene-9-nitrile **18d** (34.2 mg, 0.200 mmol, 32.3 % yield) as a white-off solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.13 - 2.20 (m, 2 H) 3.88 - 4.01 (m, 1 H) 5.02 - 5.17 (m, 2 H) 5.46 (br. s., 1 H) 6.19 (dd, *J* = 7.58, 6.06 Hz, 1 H) 6.58 (dd, *J* = 7.83, 1.52 Hz, 1 H) 6.99 (d, *J* = 6.06 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 27.1, 39.6, 80.6, 95.7, 113.4, 114.4, 124.8, 129.6, 137.5, 138.2, 146.4. IR (Golden Gate) ν_{max} [cm^{-1}] 3063, 3002, 2869, 2216, 1572, 1352, 1333, 1165, 1148, 1002, 699, 679. ESI-HRMS [m/z] calculated for $C_{11}H_9KNO$ $[M+K]^+$ 210.0316 found 210.0305. mp 92 °C.

3-Phenyl-2-(propa-1,2-dien-1-yl)-2,3-dihydrobenzofuran-3-ol 20. (2-(Buta-2,3-dienyloxy)phenyl)(phenyl)methanone **10c** (160.7 mg, 0.642 mmol, 1 equiv) was dissolved in dry DCM (21 mL) in a quartz tube equipped with a magnetic stir bar and a rubber septum. The solution was purged with argon for 15 min. and irradiated for 1.5 h at 350 nm. The product was purified by flash column chromatography (Si: 25 g) with hexane and EtOAc as solvents (15:1) to afford 3-phenyl-2-(propa-1,2-dien-1-yl)-2,3-dihydrobenzofuran-3-ol **20** (120.5 mg, 0.481 mmol, 75.0 % yield) as a yellow oil. In the NMR spectra, a mixture of diastereoisomers in the ratio 4:1 can be observed. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.19 (s, 0.8 H) 2.49 (s, 0.2 H) 4.50 - 5.05 (m, 3 H) 5.19 (d, *J* = 7.27 Hz, 0.2 H) 5.57 (q, *J* = 6.81 Hz, 0.8 H) 6.84 - 7.60 (m, 9 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 76.8, 82.7, 84.4, 85.6, 88.3, 91.8, 92.7, 110.8, 110.9, 121.7, 124.9, 124.9, 126.4, 127.0, 127.7, 127.8, 128.1, 128.2, 130.7, 132.4, 141.7, 159.8, 210.4. IR (Golden Gate) ν_{max} [cm^{-1}] 3468 (br. w), 3060 (w), 3030 (w), 1955 (w), 1597 (m), 1473 (m), 1463 (m), 1448 (m), 1370 (w), 1279 (w), 1212 (m), 1173 (w), 1148 (w), 1111 (w), 1055

(m), 969 (m), 916(m), 846 (s), 786 (w), 747 (s), 699 (s). ESI-HRMS [m/z] calculated for $C_{17}H_{14}NaO_2$ $[M+Na]^+$ 273.0886 found 273.0885.

Tert butyl-(2-aza-tricyclo[5,2,2,0^{1,5}] undeca-4,8,10-triene-9-carbaldehyde)carboxylate 21a. Tert-butyl buta-2,3-dienyl(2-formylphenyl)carbamate **14a** (117.5 mg, 0.430 mmol, 1 equiv) was dissolved in dry DCM (15 mL) in a quartz tube equipped with a magnetic stir bar and a rubber septum. The reaction mixture was purged with argon for 15 min and irradiated at 300 nm for 1 h. The products were isolated by flash column chromatography (Si: 25g) with hexane and EtOAc as solvents (3:1) to afford tert butyl-(2-aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde)carboxylate **21a** (77.1 mg, 0.282 mmol, 66 % yield) as a white solid. The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 1.33 (s, 6 H) 1.47 (s, 3 H) 1.97 - 2.22 (m, 2 H) 3.93 - 4.02 (m, 1 H) 4.17 - 4.40 (m, 2 H) 5.37 (s, 0.35 H) 5.39 - 5.42 (m, 0.65 H) 6.22 - 6.33 (m, 1 H) 6.43 - 6.56 (m, 1 H) 7.20 (d, J = 6.31 Hz, 0.35 H) 7.25 (d, J = 6.31 Hz, 0.65 H) 9.44 (s, 0.35 H) 9.49 (s, 0.65 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 27.8, 28.0, 28.4, 28.5, 38.7, 38.9, 56.1, 56.2, 75.2, 75.4, 79.8, 80.0, 113.2, 113.2, 129.3, 129.5, 138.1, 138.8, 139.0, 147.5, 147.8, 148.8, 149.3, 153.8, 154.1, 186.9, 186.9. IR (Golden Gate) ν_{max} [cm^{-1}] 2923 (w), 2844 (w), 1695 (s), 1674 (s), 1575 (m), 1401 (s), 1362 (m), 1147 (s), 1014 (m), 768 (m), 685 (m). ESI-HRMS [m/z] calculated for $C_{16}H_{19}NNaO_3$ $[M+Na]^+$ 296.12571 found 296.12605.

Deprotection attempt of tert butyl-(2-aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde) carboxylate 21a. Tert butyl-(2-aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde)carboxylate **21a** (24.6 mg, 0.090 mmol, 1 equiv) was dissolved in a solution of TFA (0.069 mL, 0.900 mmol, 10 equiv) and anisole (0.098 mL, 0.900 mmol, 10 equiv) in dry DCM (0.5 mL) at 0 °C. The reaction mixture was stirred for 6 h. The reaction mixture shows clean conversion towards one product. However isolation of the latter remained unsuccessful. Degradation was observed on basic alox, basified (MeOH saturated with NH_3) silica gel and extraction from basic solutions. Attempts to

deprotect tert butyl-(2-aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde)carboxylate **21a** with HCl 4N solutions in dioxane and Et_2O only led to complete decomposition of the starting material.

Tert-butyl(2-aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester)carboxylate 21b. Methyl 2-(buta-2,3-dienyl(tert-butoxycarbonyl)amino)benzoate **14b** (174.8 mg, 0.576 mmol, 1 equiv) was dissolved in dry DCM (19 mL) in a quartz tube equipped with a magnetic stir bar and a rubber septum. The reaction mixture was purged with argon for 15 min and irradiated at 300 nm for 2.3 h. The solvent was evaporated and the crude product was purified by flash column chromatography (Si: 25 g) with hexane and EtOAc as solvents (3:1) to afford tert-butyl(2-aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester)carboxylate **21b** (146.1 mg, 0.482 mmol, 84 % yield) as a yellow oil. The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.41 (s, 6.75 H) 1.51 (s, 2.25 H) 1.96 - 2.21 (m, 2 H) 3.68 (s, 0.75 H) 3.74 (s, 2.25 H) 3.76 - 3.87 (m, 1 H) 4.30 - 4.56 (m, 2 H) 5.31 (s, 0.25 H) 5.37 (s, 0.75 H) 6.15 - 6.31 (m, 1 H) 6.50 (d, J = 7.27 Hz, 0.75 H) 6.63 (d, J = 7.27 Hz, 0.25 H) 6.90 - 7.12 (m, 1 H). ^{13}C NMR (91 MHz, DMSO-d_6) δ ppm 26.6 – 29.0 (m), 37.3 - 38.4 (m), 50.3 - 52.3 (m), 54.5 - 56.1 (m), 75.1, 75.49, 78.4, 78.7, 112.2 (br. s.), 112.5 (br. s.), 130.5 - 131.3 (m), 139.1 - 139.8 (m), 140.4 - 142.1 (m), 152.6, 153.4, 164.2, 164.4. IR (Golden Gate) ν_{max} [cm^{-1}] 2977 (w), 2861 (w), 1699 (s), 1673 (m), 1622 (w), 1583(w), 1434(m), 1392 (s), 1366 (m), 1350 (m), 1327 (m), 1237 (m) 1141 (s), 1083 (m), 1029 (m), 1012 (m), 983 (m), 906 (m), 770 (m), 731 (s), 697 (m). ESI-HRMS [m/z] calculated for $C_{17}H_{21}NNaO_4$ $[M+Na]^+$ 326.13628 found 326.13608.

Tert-butyl(2-aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester)carboxylate 21b on large scale. Methyl 2-(buta-2,3-dienyl(tert-butoxycarbonyl)amino)benzoate **14b** (17 g, 56.0 mmol, 1 equiv) was dissolved in dry DCM (1.5 L) in a quartz tube equipped with a magnetic stir bar, a cold finger and a rubber septum. The reaction mixture was purged with argon for 15 min and irradiated at 300 nm for 21 h. The solvent was evaporated and the crude product was purified by flash column chromatography (Si: 250 g) with hexane and EtOAc as solvents (3:1) to afford tert-butyl(2-aza-

tricyclo[5,2,2,$0^{1,5}$]undeca-4,8,10-triene-9-methylester)carboxylate **21b** (15.6 g, 51.4 mmol, 92 % yield) as a yellow oil. Analysis as described previously.

Tert butyl-(11-aza-8-methylene-12-oxa[7,2,1,$0^{2,7}$]dodeca-2,4,6-triene)carboxylate 22 and tert butyl-(2-aza-tricyclo[5,2,2,$0^{1,5}$] undeca-4,8,10-triene-9-carbaldehyde)carboxylate 21a. Tert-butyl-buta-2,3-dienyl(2-formylphenyl)carbamate **14a** (123.3 mg, 0.451 mmol, 1 equiv) was dissolved in dry DCM (15 mL) in a quartz tube equipped with a magnetic stir bar and a rubber septum. The reaction mixture was purged with argon for 15 min and irradiated at 350 nm for 3 h. The solvent was evaporated and the crude mixture was purified by flash column chromatography (Si: 25g) with hexane and EtOAc as solvents (3:1) to afford tert-butyl-(11-aza-8-methylene-12-oxa[7,2,1,$0^{2,7}$]dodeca-2,4,6-triene)carboxylate **22** (10.5 mg, 0.038 mmol, 9 % yield) as a translucent oil and tert butyl-(2-aza-tricyclo[5,2,2,$0^{1,5}$]undeca-4,8,10-triene-9-carbaldehyde)carboxylate **21a** (74.1 mg, 0.271 mmol, 60 % yield) as a white solid. The NMR of the compounds suggest occurrence of rotamers. Tert-butyl-(11-aza-8-methylene-12-oxa[7,2,1,$0^{2,7}$]dodeca-2,4,6-triene)carboxylate **22.** ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.38 - 1.52 (m, 9 H) 3.13 - 3.30 (m, 1 H) 3.76 - 3.92 (m, 1 H) 5.07 - 5.19 (m, 2 H) 5.68 (s, 1 H) 6.06 (br. s., 0.64 H) 6.23 (br. s., 0.36 H) 7.15 - 7.38 (m, 3 H) 7.70 (d, *J* = 7.27 Hz, 1 H). Due to the presence of multiple rotamers, the ^{13}C NMR is too complex to be reported. IR (Golden Gate) ν_{max} [cm^{-1}] 2976 (w), 1693 (s), 1392 (s), 1366 (s), 1247 (m), 1167 (s), 1117 (s), 889 (s), 757 (s). ESI-HRMS [m/z] calculated for $C_{16}H_{19}NNaO_3$ $[M+Na]^+$ 296.12571 found 296.12552. Tert butyl-(2-aza-tricyclo[5,2,2,$0^{1,5}$]undeca-4,8,10-triene-9-carbaldehyde) carboxylate **21a**. Analysis as described previously.

2-Aza-tricyclo[5,2,2,$0^{1,5}$]undeca-4,8,10-triene-9-methylester 23. Trifluoroacetic acid (2.337 mL, 30.3 mmol, 10 equiv) was added to a solution of tert butyl-(2-aza-tricyclo[5,2,2,$0^{1,5}$]undeca-4,8,10-triene-9-methylester)carboxylate **21b** (0.92 g, 3.03 mmol, 1 equiv) and anisole (3.31 mL, 30.3 mmol, 10 equiv) in DCM (20 mL) at 0 °C . The reaction mixture was stirred at 0 °C for 1 h, then at rt for 16 h.

After complete conversion the solvents were coevaporated with toluene. The crude product was purified by flash column chromatography (100 g) with DCM and a saturated solution of NH_3 in MeOH (100:2) to afford 2-aza-tricyclo[5,2,2,$0^{1,5}$]undeca-4,8,10-triene-9-methylester **23** (0.6132 g, 3.02 mmol, 99 % yield) as a brown oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.91 - 2.54 (m, 2 H) 3.77 (s, 3 H) 3.95 (br. s., 1 H) 4.21 - 4.45 (m, 2 H) 5.36 (br. s., 1 H) 6.26 (t, 1 H) 6.79 (d, *J* = 7.72 Hz, 1 H) 7.32 (d, *J* = 6.36 Hz, 1 H) 8.74 (br. s., 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 26.9, 39.1, 51.9, 56.0, 78.1, 112.7, 130.7, 135.7, 137.8, 139.8, 145.7, 165.2. IR (Golden Gate) ν_{max} [cm^{-1}] 3388 (m), 1985 (m), 1947 (m), 1847 (m), 1687 (s), 1571(m), 1433 (s), 1418 (m), 1316 (m), 1237 (s), 1188 (s), 1131 (m), 1085 (m), 1044 (s), 1000 (m), 982 (m), 917 (m), 845 (m), 806 (m), 753 (m), 739 (s), 681 (s), 666 (s). ESI-HRMS [m/z] calculated for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.10191 found 204.10172.

Tert-butyl(2-aza-tricyclo[5,2,2,$0^{1,5}$]undeca-4,8,10-triene-9-carboxylicacid)carboxylate 24. An aqueous solution of NaOH 5M (39.4 mL, 197 mmol, 10 equiv) was added to a solution of tert-butyl(2-aza-tricyclo[5,2,2,$0^{1,5}$]undeca-4,8,10-triene-9-methylester)carboxylate **21b** (5.975 g, 19.70 mmol, 1 equiv) in EtOH (40 mL). The reaction mixture was stirred for 10 min at rt then heated to 50 °C for 1 h. After complete reaction the mixture was diluted with water (300 mL) and washed twice with Et_2O (2x 100 mL). The aqueous phase was acidified by addition of HCl (25%) to pH=1. The product was extracted five times with DCM (5x 100 mL) and the combined organic phases were dried over Na_2SO_4 and evaporated to afford tert-butyl(2-aza-tricyclo[5,2,2,$0^{1,5}$]undeca-4,8,10-triene-9-carboxylicacid)carboxylate **24** (4.84 g, 16.73 mmol, 85 % yield) as a white-off solid. The crude compound was used as such in further reactions as several attempts of purification failed. The NMR of the compounds suggest occurrence of rotamers. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.40 (s, 6 H) 1.50 (br. s., 3 H) 1.98 - 2.20 (m, 2 H) 3.82 (br. s., 1 H) 4.33 - 4.55 (m, 2 H) 5.36 (s, 1 H) 6.21 (t, *J* = 6.47 Hz, 1 H) 6.45 - 6.69 (m, 1 H) 7.14 (d, *J* = 6.36 Hz, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 28.0, 28.2, 38.3, 56.0, 75.3, 79.8, 112.7, 129.7, 138.9, 139.1, 139.7, 143.5, 153.8, 169.2. IR (Golden Gate) ν_{max}

[cm^{-1}] 2976 (m), 1687 (s), 1582 (m), 1393 (s), 1366 (m), 1352 (m), 1245 (m), 1153 (s), 1085 (m), 1028 (m), 1012 (m), 975 (m), 920(m), 862 (m), 769 (m), 747 (m), 688 (m), 666 (m). ESI-HRMS [m/z] calculated for $C_{16}H_{19}NNaO_4$ $[M+Na]^+$ 312.12063 found 312.12094. mp 89 °C.

2-Aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester hydrochloride 25. Tert-butyl(2-aza-tricyclo [5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester)carboxylate **21b** (55 mg, 0.181 mmol, 1 equiv) was dissolved in dry Et_2O (4 mL). The solution was bubbled with gaseous hydrogen chloride (generated by addition of HCl 37 % to $CaCl_2$) for 3 min at 0 °C and the reaction mixture was stirred for another 2 h at rt. The reaction mixture was left without stirring for 16 h; then the precipitate formed was filtered off to afford 2-aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester hydrochloride **25** (28.2 mg, 0.118 mmol, 65 % yield) as a white to brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm 1.95 - 2.27 (m, 2 H) 3.74 (s, 3 H) 4.01 - 4.12 (m, 1 H) 4.20 - 4.44 (m, 2 H) 5.48 (t, J = 1.77 Hz, 1 H) 6.45 (dd, J = 7.33, 6.06 Hz, 1 H) 7.01 (dd, J = 7.58, 1.52 Hz, 1 H) 7.32 (d, J = 6.32 Hz, 1 H) 9.27 (br. s., 1 H) 11.56 (br. s., 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 26.3, 38.9, 52.3, 55.5, 76.9, 111.5, 132.7, 132.8, 134.2, 139.2, 145.7, 163.8. IR (Golden Gate) ν_{max} [cm^{-1}] 3500-2500 broad band, 1687 (s), 1580 (m), 1539 (m) 1439 (m), 1399 (m), 1344 (s), 1324 (s), 1247 (s), 1097 (s), 1074 (s), 783 (s), 748 (s), 699 (s). ESI-HRMS [m/z] calculated for $C_{12}H_{14}NO_2$ $[M+H]^+$ 204.10191 found 204.10140. mp 86 °C.

2-Aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester hydrochloride 25 on large scale. Tert-butyl(2-aza-tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester)carboxylate **21b** (6.58 g, 21.69 mmol) was dissolved in Et_2O (700 mL) and the solution was treated with gaseous hydrogen chloride (generated by addition of HCl 37 % to $CaCl_2$) for 1 h at 0 °C then was left for several weeks. From time to time the reaction mixture was filtered and again saturated with hydrogen chloride. Overall seven batches of final compound were recovered upon filtration affording 2-aza-

tricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester hydrochloride **25** (4.75 g, 19.82 mmol, 91 % yield) as white to brown solid. Analysis data as described previously.

3-(Buta-2,3-dien-1-yloxy)benzaldehyde 26. 3-Hydroxybenzaldehyde (1 g, 8.19 mmol, 1 equiv) and K_2CO_3 (1.471 g, 10.65 mmol, 1.3 equiv) were suspended in DMF (10 ml). To the mixture was added portionwise over 3 h 4-bromobuta-1,2-diene **6** (1.742 g, 13.10 mmol, 1.6 equiv). After complete addition the reaction mixture was stirred at rt for 16 h. Despite incomplete conversion the reaction mixture was worked-up. The mixture was added to a saturated solution of K_2CO_3 and the organics were extracted with 100 ml of Et_2O. The organic layer was subsequently washed twice with HCl 1N (50 ml, 2 x) and with brine, dried over Na_2SO_4 and evaportated. The crude product was purified by flash column chromatography (Si: 25g) with DCM to afford 3-(buta-2,3-dien-1-yloxy)benzaldehyde **26** (808.0 mg, 4.64 mmol, 56.6 % yield) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.65 (dt, *J* = 6.80, 2.45 Hz, 2 H) 4.90 (dt, *J* = 6.61, 2.46 Hz, 2 H) 5.40 (quin, *J* = 6.70 Hz, 1 H) 7.20 (dt, *J* = 6.75, 2.57 Hz, 1 H) 7.40 - 7.48 (m, 3 H) 9.98 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 661, 76.8, 86.6, 113.4, 122.2, 123.6, 130.1, 137.8, 158.9, 192.0, 209.6. UV-VIS (MeCN, c = 3.4 x 10^{-5} mol/l): λ_{max} 308 nm (ε = 2999); 251 nm (ε = 9845); 219 nm (ε = 27871). IR (Golden Gate) ν_{max} [cm^{-1}] 3068 (w), 2819 (w), 2729 (w) 1957 (w), 1695 (s), 1587 (m), 1484 (m), 1449 (m), 1382 (w), 1322 (w), 1254 (s), 1167 (m), 1146 (m), 1018 (m), 991 (m), 849 (s), 783 (s), 738 (m), 681 (m), 646 (m), 557 (w).

4-(Buta-2,3-dien-1-yloxy)benzaldehyde 27. 4-Hydroxybenzaldehyde (593.4 mg, 4.86 mmol, 1 equiv) and K_2CO_3 (873 mg, 6.32 mmol, 1.3 equiv) were suspended in DMF (3 ml). 4-Bromobuta-1,2-diene **6** (969 mg, 7.29 mmol, 1.5 equiv) was added portionwise to the mixture over 3 h. The reaction mixture was subsequently stirred at rt for 16 h then diluted with Et_2O (50 ml) and washed with K_2CO_3 1M (30 ml), HCl 1N (30 ml), and brine. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by flash column chromatography (Si: 25 g) with DCM as solvent to afford 4-(buta-2,3-dien-1-yloxy)benzaldehyde **27** (751.8 mg, 4.32 mmol, 89 % yield) as a yellow oil. The

compound is very air sensitive. Keep under argon! When in contact with oxygen, a white precipitate forms. The carboxylic acid can be easily filtered off. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 4.58 - 4.72 (m, 2 H) 4.84 - 5.00 (m, 2 H) 5.40 (quin, *J* = 6.70 Hz, 1 H) 7.03 (d, *J* = 8.63 Hz, 2 H) 7.84 (d, *J* = 8.63 Hz, 2 H) 9.90 (s, 1 H). ^{13}C NMR (91 MHz, CD_2Cl_2) δ ppm 66.7, 77.2, 86.9, 115.6, 130.7, 132.3, 163.9, 191.1, 210.1. UV-VIS (MeCN, c = 2.7 x 10^{-5} mol/l): λ_{max} 273 nm (ε = 14901); 218 nm (ε = 10884). IR (Golden Gate) ν_{max} [cm^{-1}] 2984 (w), 2738 (w), 1958 (w), 1807 (w), 1755 (w), 1687 (s), 1598 (s), 1577 (m), 1507 (m), 1461 (w), 1428 (w), 1373 (w), 1309 (m), 1250 (s), 1213 (s), 1158 (s), 1113 (s), 1065 (s), 998 (s), 830 (s), 649 (w), 620 (w), 513 (m).

2-Oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-7-carbaldehyde 28. 4-(Buta-2,3-dien-1-yloxy)benzaldehyde **27** (114 mg, 0.654 mmol, 1 equiv) was dissolved in dry DCM (20 ml) in a quartz tube equipped with a magnetic stir bar and a rubber septum. The solution was degassed with argon for 10 min. and irradiated at 300 nm for 2.5 h (65 % conversion to product observed by NMR). The solvent was evaporated and the crude product was purified by flash column chromatography (Si 10g) with DCM as solvent to afford 2-oxa-tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-7-carbaldehyde **28** (38 mg, 0.218 mmol, 33.3 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.21 (q, *J* = 2.45 Hz, 2 H) 5.03 (td, *J* = 2.60, 1.61 Hz, 2 H) 5.40 (quin, *J* = 1.70 Hz, 1 H) 6.36 (d, *J* = 7.36 Hz, 2 H) 6.66 (d, *J* = 7.55 Hz, 2 H) 10.15 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 30.4, 58.9, 80.0, 97.8, 112.2, 126.8, 138.3, 139.8, 200.3. IR (Golden Gate) ν_{max} [cm^{-1}] 2854 (w), 1726 (m), 1357 (m), 1257 (w), 1169 (m), 1091 (m), 1001 (s), 925 (w), 838 (w), 770 (m), 741 (w), 696 (s), 670 (m), 646 (w), 609 (w). ESI-HRMS [m/z] calculated for $C_{11}H_{10}NaO_2$ $[M+Na]^+$ 197.05730 found 197.05633.

Tert-butyl (4-acetylphenyl)carbamate 30a. A solution of 1-(4-aminophenyl)ethanone **29a** (1.5 g, 11.10 mmol, 1 equiv) and Boc_2O (3.09 ml, 13.32 mmol, 1.2 equiv) in dry dioxane (14 ml) was heated to 100 °C for 5 h. The solvent was evaporated and the residue was taken in EtOAc. The organic layer was washed three times with HCl 1M and brine, dried over Na_2SO_4 and evaporated to afford tert-butyl

(4-acetylphenyl)carbamate **30a** (2.55 g, 10.84 mmol, 98 % yield) as a white solid. Analysis according to the literature.[47] ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.54 (s, 9 H) 2.57 (s, 3 H) 6.69 (br. s., 1 H) 7.46 (d, *J* = 8.63 Hz, 2 H) 7.92 (d, *J* = 8.63 Hz, 2 H).

Methyl 4-((tert-butoxycarbonyl)amino)benzoate 30b. To a solution of methyl 4-aminobenzoate **29b** (5.07 g, 33.5 mmol, 1 equiv) in toluene (10 ml) was added finely powdered lanthanum(III) nitrate hexahydrate (0.087 g, 0.201 mmol, 0.006 equiv) and a solution of Boc_2O (8.57 ml, 36.9 mmol, 1.1 equiv) in toluene (10.00 ml) was added to the suspension. The reaction mixture was heated to reflux for 5 h, then added to water and the organics were extracted with DCM (100 ml). The organic phase was subsequently washed three times with HCl 1M (3x 100 ml) and with brine, dried over Na_2SO_4 and evaporated to afford methyl 4-((tert-butoxycarbonyl)amino)benzoate **30b** (3.53 g, 14.05 mmol, 42 % yield). The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.53 (s, 9 H) 3.90 (s, 3 H) 6.67 (br. s., 1 H) 7.44 (d, *J* = 8.63 Hz, 2 H) 7.98 (d, *J* = 8.86 Hz, 2 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 28.2 (br. s.) 28.3 (br. s.) 51.6, 51.9, 52.0, 81.2, 117.2, 117.4 (br. s.,) 124.3, 130.8 (br. s.) 130.9, 142.7, 152.2, 166.7.

Tert-butyl (4-acetylphenyl)(prop-2-yn-1-yl)carbamate 31a. NaH (0.361 g, 7.52 mmol, 1 equiv) was added portionwise to a solution of tert-butyl (4-acetylphenyl)carbamate **30a** (1.77 g, 7.52 mmol, 1 equiv) in dry DMF (20 ml) at 0 °C. The reaction mixture was stirred for 30 min at rt, then 3-bromoprop-1-yne (1.946 ml, 22.57 mmol, 3 equiv) was added to the suspension. The reaction mixture was stirred for 2 h at rt, then quenched by addition to water and the organics were extracted three times with Et_2O (3x). The combined organic layer were washed with HCl 1 M and brine, dried over Na_2SO_4 and evaporated. The crude was purified by flash column chromatography (Si: 50 g) with DCM and Et_2O as solvents (100 % DCM to 98 % DCM) to afford tert-butyl (4-acetylphenyl)(prop-2-yn-1-yl)carbamate **31a** (968.1 mg, 3.54 mmol, 47 % yield) as a yellow oil. ^{1}H NMR (300 MHz, CD_2Cl_2) δ ppm 1.50 (s, 9 H) 2.29 (t, *J* = 2.45 Hz, 1 H) 2.60 (s, 3 H) 4.42 (d, *J* = 2.27 Hz, 2 H) 7.46 (d, *J* = 8.69

Hz, 2 H) 7.95 (d, J = 8.88 Hz, 2 H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ ppm 26.5, 27.9, 28.2, 39.4, 72.2, 79.5, 81.9, 125.2, 128.9, 134.3, 146.4, 153.3, 197.1. IR (Golden Gate) ν_{max} [cm^{-1}] 3293 (w), 2979 (w), 1703 (s), 1681 (s), 1602 (m), 1511 (w), 1421 (m), 1366.1 (s), 1268 (s), 1231 (s), 1149 (s), 1030 (m), 1012 (m), 958 (m), 843 (m), 765 (m), 735 (m), 632 (m), 592 (m). ESI-HRMS [m/z] calculated for $C_{16}H_{19}NNaO_3$ $[M+Na]^+$ 296.12571 found 296.12595.

Methyl 4-((tert-butoxycarbonyl)(prop-2-yn-1-yl)amino)benzoate 31b. To a solution of methyl 4-((tert-butoxycarbonyl)amino)benzoate **30 b** (2.02 g, 8.04 mmol, 1 equiv) in dry DMF (10 ml) at 0 °C was added portionwise NaH (0.502 g, 10.45 mmol, 1.3 equiv). The mixture was stirred for 2h then 3-bromoprop-1-yne (2.69 ml, 24.12 mmol, 3 equiv) was added and stirred for another 2 h. The reaction mixture was diluted with Et_2O and the organic phase was washed with water, HCl 1N and with brine, dried over Na_2SO_4 and evaporated. The crude product was purified by flash column chromatography (Si: 50g) with DCM as solvent to afford methyl 4-((tert-butoxycarbonyl)(prop-2-yn-1-yl)amino)benzoate **31b** (1.39 g, 4.80 mmol, 60 % yield) as a white-off solid. The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.49 (s, 9 H) 2.26 - 2.31 (m, 1 H) 3.92 (s, 3 H) 4.42 (d, J = 2.27 Hz, 2 H) 7.44 (d, J = 8.63 Hz, 2 H) 8.03 (d, J = 8.63 Hz, 2 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 28.2, 39.4, 52.1, 72.1, 79.5, 81.8, 125.0, 125.1, 127.2, 130.0, 130.1, 146.2, 153.3, 166.5. IR (Golden Gate) ν_{max} [cm^{-1}] 3253 (m), 2966 (w), 1704 (s), 1603 (m), 1576 (w), 1423 (m), 1370 (s), 1315 (m), 1276 (s), 1229 (s), 1163 (s), 1139 (s), 1104 (s), 1042 (w), 1014 (m), 965 (w), 941 (m), 923 (w), 856 (m), 801 (w), 779 (m), 759 (s), 735 (m), 704 (m), 671 (m), 628 (m). ESI-HRMS [m/z] calculated for $C_{16}H_{19}NNaO_4$ $[M+Na]^+$ 312.12063 found 312.12037.

Tert-butyl (4-acetylphenyl)(buta-2,3-dien-1-yl)carbamate 32a. Paraformaldehyde (106 mg, 3.54 mmol, 2.3 equiv), copper(I) bromide (99 mg, 0.692 mmol, 0.45 equiv) and tert-butyl (4-acetylphenyl)(prop-2-yn-1-yl)carbamate **31a** (420.6 mg, 1.539 mmol, 1 equiv) were suspended in dry dioxane (11 ml). To the suspension was added diisopropylamine (0.614 ml, 4.31 mmol, 2.8 equiv) and

the reaction mixture was sealed in a microwave vial and heated in the microwave at 150 °C for 20 min. The reaction mixture was added to water and the organics were extracted with EtOAc three times. The combined organic layers were washed with HCl 1M and brine, dried over Na_2SO_4 and evaporated. The crude product was purified by flash column chromatography (Si: 25 g) with DCM and Et_2O as solvents (100 % to 95 % DCM) to afford tert-butyl (4-acetylphenyl)(buta-2,3-dien-1-yl)carbamate **32a** (204.1 mg, 0.710 mmol, 46 % yield) as a translucent oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.49 (s, 9 H) 2.60 (s, 3 H) 4.28 (dt, *J* = 5.90, 2.95 Hz, 2 H) 4.80 (dt, *J* = 6.36, 3.18 Hz, 2 H) 5.29 (quin, *J* = 6.24 Hz, 1 H) 7.39 (d, *J* = 8.63 Hz, 2 H) 7.93 (d, *J* = 8.63 Hz, 2 H). ^{13}C NMR (91 MHz, CD_2Cl_2) δ ppm 26.9, 28.5, 49.0, 77.4, 81.5, 88.3, 125.7, 129.2, 134.3, 147.7, 154.0, 197.4, 209.1. IR (Golden Gate) ν_{max} [cm^{-1}] 2977 (w), 1957 (w), 1701 (s), 1680 (s), 1601 (m), 1511 (w), 1419 (w), 1364 (s), 1322 (m), 1267 (s), 1226 (m), 1152 (s)m 1078(w), 1050 (w), 1013 (w), 957 (w), 840 (s), 765 (m), 593 (m). ESI-HRMS [m/z] calculated for $C_{17}H_{21}NNaO_3$ $[M+Na]^+$ 310.14136 found 310.14120. UV-VIS (MeCN, c = 2.7 x 10^{-5} mol/l): λ_{max} 280 nm (ε = 12674).

Methyl 4-(buta-2,3-dien-1-yl(tert-butoxycarbonyl)amino)benzoate 32b. Paraformaldehyde (0.119 g, 3.97 mmol, 2.3 equiv), copper(I) bromide (0.112 g, 0.778 mmol, 0.45 equiv) and methyl 4-((tert-butoxycarbonyl)(prop-2-yn-1-yl)amino)benzoate **31b** (0.5 g, 1.728 mmol, 1 equiv) were suspended under argon atmosphere in dry THF (10 ml). Diisopropylamine (0.665 ml, 4.67 mmol, 2.7 equiv) (distilled from KOH before use) was added and the reaction mixture was sealed in a microwave vial and heated in microwave to 160 °C for 20 min. The solvent was evaporated and the residue was suspended in EtOAc and filtered over celite. The organic phase was washed with water, HCl 1M, and brine, dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 25g) with DCM as solvent to afford methyl 4-(buta-2,3-dien-1-yl(tert-butoxycarbonyl)amino)benzoate **32b** (319.9 mg, 1.055 mmol, 61 % yield) as a translucent oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 1.48 (s, 9 H) 3.92 (s, 3 H) 4.27 (dt, *J* = 5.90, 2.95 Hz, 2 H) 4.72 - 4.85 (m, 2

H) 5.15 - 5.37 (m, 1 H) 7.35 (d, *J* = 8.63 Hz, 2 H) 8.00 (d, *J* = 8.63 Hz, 2 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 28.2, 48.6, 52.1, 77.1, 81.1, 87.7, 125.3, 126.8, 130.0, 147.0, 153.7, 166.6, 208.6. IR (Golden Gate) ν_{max} [cm^{-1}] 2978 (w), 1957 (w), 1700 (s), 1606 (m), 1512 (w), 1435 (m), 1367 (m), 1321 (w), 1275 (s), 1155 (s), 1107 (s), 1051 (w), 1016 (m), 969 (w), 851 (m), 772 (m), 736 (w), 707 (m). ESI-HRMS [m/z] calculated for $C_{17}H_{21}NNaO_4$ $[M+Na]^+$ 326.13628 found 326.13623. UV-VIS (MeCN, c = 2.25 x 10^{-5} mol/l): λ_{max} 268 nm (ε = 16504).

Tert-butyl 5-acetyl-4,5-dihydro-5,7a-ethenoindole-1(2H)-carboxylate 33a. Tert-butyl (4-acetyl-phenyl)(buta-2,3-dien-1-yl)carbamate **32a** (137.0 mg, 0.477 mmol, 1 equiv) was dissolved in dry DCM (14 ml) in a quartz tube equipped with a magnetic stir bar and a rubber septum. The reaction mixture was purged with argon for 10 min and irradiated at 300 nm for 1.6 h. The solvent was evaporated and the crude product was purified by flash column chromatography (Si: 10g) with DCM and Et_2O (99% DCM) as solvent to afford tert-butyl 5-acetyl-4,5-dihydro-5,7a-ethenoindole-1(2H)-carboxylate **33a** (95 mg, 0.331 mmol, 69 % yield) as a translucent oil. The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.47 (s, 6 H) 1.53 (s, 3 H) 2.18 - 2.26 (m, 2 H) 2.36 - 2.45 (m, 3 H) 4.37 (q, *J* = 2.45 Hz, 0.66 H) 4.41 (q, *J* = 2.46 Hz, 1.34 H) 5.27 (quin, *J* = 1.79 Hz, 0.33 H) 5.32 (quin, *J* = 1.84 Hz, 0.67 H) 6.34 (d, *J* = 7.36 Hz, 2 H) 6.58 (d, *J* = 7.36 Hz, 1.34 H) 6.70 (d, *J* = 7.18 Hz, 0.66 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 27.1, 27.2, 27.9, 28.5, 28.5, 32.3, 32.9, 56.2, 56.4, 60.0, 60.2, 76.3, 79.9, 83.3, 111.7, 111.8, 129.4, 129.7, 138.7, 139.2, 139.6, 153.8, 207.5, 207.7. IR (Golden Gate) ν_{max} [cm^{-1}] 2976 (w), 2929(w), 1700 (s), 1392 (s), 1363 (m), 1271 (w), 1219 (w), 1156 (m), 1120 (m), 1055 (m), 1023 (m), 981 (m), 935 (w), 861 (w), 829 (w), 699 (s), 675 (m), 600 (w). ESI-HRMS [m/z] calculated for $C_{17}H_{21}NNaO_3$ $[M+Na]^+$ 310.14136 found 310.14120.

1-Tert-butyl 5-methyl 4,5-dihydro-5,7a-ethenoindole-1,5(2H)-dicarboxylate 33b. Methyl 4-(buta-2,3-dien-1-yl(tert-butoxycarbonyl)amino)benzoate **32b** (103 mg, 0.340 mmol, 1 equiv) was dissolved in dry DCM (11.5 ml) in a quartz tube equipped with a magnetic stir bar, a cold finger and a rubber

septum. The reaction mixture was purged with argon for 10 min and irradiated at 254 nm for 24 h. The irradiated solution was cooled with water during irradiation. The solvent was evaporated and the crude product was purified by flash column chromatography (Si: 10g) with DCM and Et_2O (95% DCM) as solvent to afford 1-tert-butyl 5-methyl 4,5-dihydro-5,7a-ethenoindole-1,5(2H)-dicarboxylate **33b** (33 mg, 0.109 mmol, 32 % yield) as a yellow solid. The NMR of the compound suggests occurrence of rotamers. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.46 (s, 6 H) 1.52 (s, 3 H) 2.22 - 2.40 (m, 2 H) 3.85 (s, 0.9 H) 3.86 (s, 2.1 H) 4.36 (q, *J* = 2.46 Hz, 0.6 H) 4.40 (q, *J* = 2.45 Hz, 1.4 H) 5.25 (quin, *J* = 1.84 Hz, 0.3 H) 5.30 (quin, *J* = 1.89 Hz, 0.7 H) 6.31 - 6.44 (m, 2 H) 6.51 (d, *J* = 7.36 Hz, 1.4 H) 6.62 (d, *J* = 7.36 Hz, 0.6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 28.4, 28.5, 34.0, 34.1, 52.5, 52.5, 53.2, 53.3, 56.2, 56.5, 76.0, 76.3, 79.8, 79.8, 111.4, 111.6, 130.2, 130.5, 137.7, 138.3, 139.2, 139.3, 153.8, 173.7, 173.8. IR (Golden Gate) ν_{max} [cm^{-1}] 2979 (w), 2925 (w), 2860 (w), 1728 (s), 1698 (s), 1673 (m), 1438 (w), 1398 (s), 1368 (m), 1327 (m), 1312 (m), 1294 (m), 1249 (m), 1226 (m), 1162 (s), 1072 (s), 1029 (m), 1009 (m), 940 (m), 833 (w), 802 (m), 771 (m), 754 (w), 700 (s), 685 (m). ESI-HRMS [m/z] calculated for $C_{17}H_{21}NNaO_4$ $[M+Na]^+$ 326.13628 found 326.13609. mp 114 °C.

1-(1,2,4,5-Tetrahydro-5,7a-ethenoindol-5-yl)ethanone, HCl 34a. Tert-butyl 5-acetyl-4,5-dihydro-5,7a-ethenoindole-1(2H)-carboxylate **33a** (43.5 mg, 0.151 mmol, 1 equiv) was dissolved in DCM (1 ml) and a solution of HCl 4 N in dioxane (0.095 ml, 0.378 mmol, 2.5 equiv) was added. The reaction mixture was stirred for 16 h. The solvent was evaporated and dissolved in chloroform and filtered through celite. The filtrate was evaporated to afford 1-(1,2,4,5-tetrahydro-5,7a-ethenoindol-5-yl)ethanone, HCl **34a** (25.9 mg, 0.116 mmol, 76 % yield) as a brown solid. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 2.27 (br. s., 2 H) 2.44 (s, 3 H) 4.54 (br. s., 2 H) 5.33 (br. s., 1 H) 6.52 (d, *J* = 7.27 Hz, 2 H) 7.23 (d, *J* = 7.27 Hz, 2 H) 11.24 (br. s., 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 27.1, 31.4, 55.6, 61.1, 78.7, 109.4, 132.0, 133.3, 140.0, 205.6. IR (Golden Gate) ν_{max} [cm^{-1}] 2867 (w), 2783 (s), 2668 (m), 2451(w), 2361 (w), 2341 (w), 1697 (s), 1589 (w), 1417 (m), 1355 (m), 1270 (m), 1218 (w), 1178

(w), 1102 (w), 1066 (w), 1003 (w), 959 (w), 930 (w), 829 (w), 804 (m), 804 (m), 699 (s), 667 (m), 624 (w), 592 (m), 507(m). ESI-HRMS [m/z] calculated for $C_{12}H_{14}NO$ $[M-Cl]^+$ 188.10699 found 188.10697.

Methyl 1,2,4,5-tetrahydro-5,7a-ethenoindole-5-carboxylate, HCl 34b. To a solution of 1-tert-butyl 5-methyl 4,5-dihydro-5,7a-ethenoindole-1,5(2H)-dicarboxylate **33b** (37.1 mg, 0.122 mmol, 1 equiv) in DCM (2 ml) was added a solution of HCl 4N in dioxane (0.3 ml, 1.200 mmol, 10 equiv). The reaction mixture was stirred for 3 h at rt and was evaporated to afford methyl 1,2,4,5-tetrahydro-5,7a-ethenoindole-5-carboxylate, HCl **34b** (21.8 mg, 0.091 mmol, 74 % yield) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.35 (s, 2 H) 3.89 (s, 3 H) 4.53 (br. s., 2 H) 5.30 (s, 1 H) 6.55 (d, *J* = 7.55 Hz, 2 H) 7.16 (d, *J* = 7.55 Hz, 2 H) 11.20 (br. s., 2 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 32.7, 52.9, 54.4, 55.7, 78.5, 109.2, 132.3, 132.9, 139.6, 172.4. IR (Golden Gate) ν_{max} [cm^{-1}] 2990 (w), 2645 (m), 1729 (s), 1561 (m), 1450 (m), 1354 (w), 1285 (s), 1223 (m), 1176 (w), 1110 (s), 1077 (s), 948 (m), 840 (m), 795 (m), 761 (m), 706 (s). ESI-HRMS [m/z] calculated for $C_{12}H_{14}NO_2$ $[M-Cl]^+$ 204.10191 found 204.10178. mp 170 °C dec.

(Buta-2,3-dienyloxy)benzene 35. 4-Bromo-1,2-butadiene **6** (2.83 g, 21.25 mmol, 2 equiv) was added dropwise over 4 h to a suspension of phenol (0.935 mL, 10.63 mmol, 1 equiv) and K_2CO_3 (1.909 g, 13.81 mmol, 1.3 equiv) in DMF (3 mL). The reaction mixture was stirred at rt for 16 h, then diluted with EtOAc (100 mL) and washed three times with water (3x 50 mL) and brine (50 mL). The organic phase was dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography (Si: 50 g) with hexane and EtOAc as solvents (from pure hexane to 10:1) to afford (buta-2,3-dienyloxy)benzene **35** (1.0275 g, 7.03 mmol, 66.1 % yield) as a yellow oil. ^{1}H NMR (360 MHz, CD_2Cl_2) δ ppm 4.57 - 4.69 (m, 2 H) 4.83 - 4.94 (m, 2 H) 5.38 - 5.48 (m, 1 H) 6.86 - 7.07 (m, 3 H) 7.31 (t, *J* = 7.72 Hz, 2 H). ^{13}C NMR (91 MHz, CD_2Cl_2) δ ppm 66.3, 76.7, 87.6, 115.3, 121.4, 130.0, 158.9, 209.9. ^{13}C NMR (75 MHz, C_6D_6) δ ppm 65.9, 76.7, 88.0, 115.6, 121.4, 130.1, 159.4, 209.8. IR (Golden Gate) ν_{max} [cm^{-1}] 3064 (w), 2870 (w), 1956 (m), 1598b(m), 1587 (m), 1494 (s), 1463 (m),

1378 (m), 1290 (w), 1238 (s), 1213 (s), 1172 (m), 1079 (w), 1030 (m), 1011 (m), 912 (m), 847 (s), 750 (s), 690 (s). ESI-HRMS [m/z] calculated for $^{107}AgC_{10}H_{10}O$ $[M+Ag(107)]^+$ 252.97771 found 252.97833. ESI-HRMS [m/z] calculated for $^{109}AgC_{10}H_{10}O$ $[M+Ag(109)]^+$ 254.97737 found 254.97785.

2-Mercapto-benzaldehyde 36. Thiophenol (4.67 mL, 45.4 mmol, 1 equiv) was dissolved in dry cyclohexane (10 mL) and TMEDA (15.07 mL, 100 mmol, 2.2 equiv). To the solution at 0 °C was added dropwise a solution of n-butyl lithium (1.6 M in hexane) (62.4 mL, 100 mmol, 2.2 equiv). The reaction mixture was stirred at rt for 20 h, then dry DMF (8.78 mL, 113 mmol, 2.5 equiv) was added dropwise at 0 °C for 1.5 h and the reaction mixture was stirred for 20 h at rt. The reaction mixture was diluted with Et_2O (150 mL) and the product was extracted with water (100 mL). The aqueous phase was acidified to pH = 1 with HCl (25 %) and the product was extracted three times with DCM (3 x 50 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to afford crude 2-mercapto-benzaldehyde **36** (3.5 g, 12.30 mmol, 56 %) as a pale oil, which was neither purified nor analyzed and used as such in next step.

2-(Buta-2,3-dienylthio)benzaldehyde 37. To a suspension of K_2CO_3 (850 mg, 6.15 mmol, 1.7 equiv) and crude 2-mercaptobenzaldehyde **36** (500 mg, 3.62 mmol, 1 equiv) in DMF (10 mL) was added dropwise 4-bromo-1,2-butadiene (481 mg, 3.62 mmol, 1 equiv) at 0 °C. The reaction mixture was stirred at rt for 16 h then diluted with Et_2O (150 mL) and was washed with a solution of K_2CO_3 1M (100 mL), HCl 1M (3x50 mL) and brine (50 mL), the organic layer was dried over $MgSO_4$ and evaporated. The crude product was filtered through a silica gel plug (Si: 5g) with hexane and DCM as solvents (1:1) to afford 2-(buta-2,3-dienylthio)benzaldehyde **37** (495.4 mg; 72 %). ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 3.48 - 3.67 (m, 2 H) 4.73 (dd, *J* = 4.09, 2.27 Hz, 2 H) 5.14 - 5.32 (m, 1 H) 7.36 (t, *J* = 7.27 Hz, 1 H) 7.45 - 7.57 (m, 2 H) 7.87 (d, *J* = 7.72 Hz, 1 H) 10.41 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 32.9, 76.6, 86.6, 126.1, 129.9, 131.7, 133.8, 134.8, 140.6, 191.7, 209.8. UV-VIS (MeCN, c = 2.0 x 10^{-5} mol/l): λ_{max} 338 nm (ε = 2982), 238 nm (ε = 21228).

Irradiation of 2-(buta-2,3-dienylthio)benzaldehyde 37. A degassed solution of 2-(buta-2,3-dienylthio)benzaldehyde **37** (0.014-0.04 molar) in dry DCM was irradiated either in a Rayonet reactor at 350 nm or 254 nm or in a LUMOS reactor at 360 nm, 375 nm, 385 nm, 405 nm and 430 nm. Only degradation could be observed upon irradiation. The product is stable towards irradiation above 430 nm.

2-(Buta-2,3-dienylsulfonyl)benzaldehyde 38. To a solution of 2-(buta-2,3-dienylthio)benzaldehyde **37** (220 mg, 1.156 mmol, 1 equiv) in MeOH (2.5 mL) was added sodium tungstate dihydrate (95 mg, 0.289 mmol, 0.25 equiv) followed by hydrogen peroxide 30 % (0.591 mL, 5.78 mmol, 5 equiv) at 0 °C. The reaction mixture was stirred at rt for 24 h. The mixture was cooled, and the unreacted peroxide was quenched by addition of a sodium metabisulfite solution 20 wt % (1 mL), then water (10 mL) was added and the product was extracted with DCM (10 mL), dried over $MgSO_4$ and evaporated. The crude product was isolated by flash column chromatography (Si: 25 g) with hexane and EtOAc as solvents (3:1) to afford 2-(buta-2,3-dienylsulfonyl)benzaldehyde **38** (145.3 mg, 0.654 mmol, 57 % yield) as a translucent oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ ppm 3.83 - 3.93 (m, 2 H) 4.45 - 4.82 (m, 2 H) 5.09 - 5.34 (m, 1 H) 7.76 - 7.87 (m, 2 H) 8.06 - 8.18 (m, 2 H) 10.79 (s, 1 H). ^{13}C NMR (91 MHz, $CDCl_3$) δ ppm 57.9, 76.7, 79.0, 129.7, 131.1, 133.7, 134.2, 135.3, 138.5, 189.7, 212.5. IR (Golden Gate) ν_{max} [cm^{-1}] 2924, 1951, 1693, 1311, 1295, 1190, 1137, 851, 759. UV-VIS (MeCN, c = 2.25 x 10^{-5} mol/l): λ_{max} 206 nm (ε = 27943), 244 nm (ε = 7621), 285 nm (ε = 1987). ESI-HRMS [m/z] calculated for $C_{11}H_{10}NaO_3S$ $[M+Na]^+$ 245.02429 found 245.02409.

Irradiation of 2-(Buta-2,3-dienylsulfonyl)benzaldehyde 38. A degassed solution of 2-(buta-2,3-dienylsulfonyl)benzaldehyde **16** (0.014-0.04 molar) in dry DCM was irradiated either in a Rayonet reactor at 350 nm, 300 nm or 254 nm or in a LUMOS reactor at 360 nm or 375 nm. Only degradation could be observed upon irradiation.

NMR conversion studies for the photocycloaddition at 0.011 M. A solution of the precursor (**1a – 1p**) (0.2 mmol) in dry DCM (18.1 mL) was purged with argon for 15 minutes. 2.1 mL of the purged solution was transferred to a quartz tube sealed with a rubber septum under argon. The sample was irradiated for a precise amount of time at 350 nm or 254 nm in a Rayonet reactor, completely evaporated and taken into $CDCl_3$ (0.7 mL) containing DMF (0.03 mol/l) as standard. The conversion was studied by NMR-spectroscopy.

Photocycloaddition in different deuterated solvents. Six NMR tubes were prepared containing 2-(buta-2,3-dien-1-yloxy)benzaldehyde **1a** (0.0018 M), the corresponding solvent and a very small amount of cyclohexane as internal standard. The NMR tubes were degassed with argon and irradiated for 174 min. At 0, 3, 24, 50, 98 and 174 min ^{1}H NMR spectra were taken and the conversion was analyzed.

Supporting Information. Characterization data not described in the experimental part, and hardcopies of spectra for all new compounds.

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