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Photocycloaddition of Arenes and Allenes

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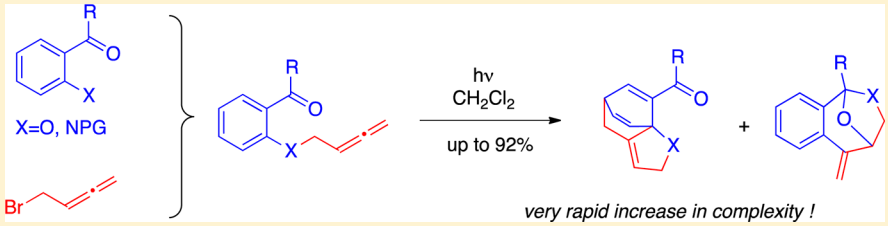
Supporting Information



ABSTRACT: In this 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 distinguish it from many other photochemical transformations: it is particularly robust with respect to substituents, it can be scaled up without a notable loss of efficiency, and it can lead to structures with a high degree of 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 a 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 C-terminus of bicyclic amino acids gave access to two conformationally constrained unnatural amino acids with different dispositions of the two anchor points.

INTRODUCTION

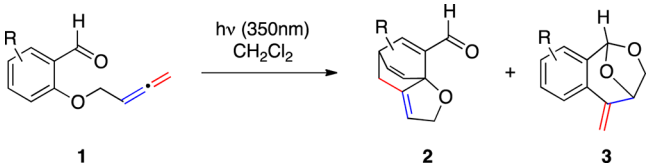
Cycloadditions are very powerful and versatile synthetic tools. They are, by essence, atom-economical and may lead to the simultaneous formation of several bonds, thus allowing a rapid increase in the degree of molecular complexity. Aromatic rings are, however, remarkably resistant to cycloadditions, and very few reactions are capable of exploiting 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 photochemical excitation.[1−5]

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 yields. 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 benzyl-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 toward the final compound. Interestingly, similar enamides with a naphthyl moiety undergo preferably an *ortho* photocycloaddition.[13] There have been reports of the *para* cycloadditions of benzene with allene and 1,2-cyclononadiene; however, 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 partner (Scheme 1).[16] In this 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

Scheme 1. Intramolecular Photocycloadditions of Allenyl Salicylaldehydes



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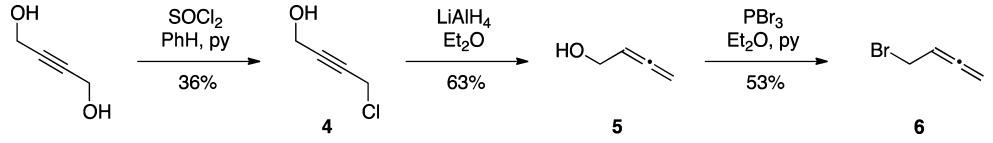
Scheme 2. Preparation of Allenyl Bromide 6



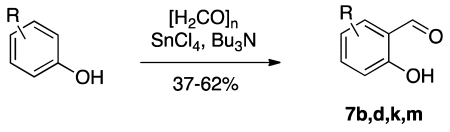
branching points and reactive functionalities, different features that are attractive for diversity-oriented synthesis (DOS).[17]

RESULTS AND DISCUSSION

Preparation of the Substrates. 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 aluminum hydride gave allenyl alcohol **5**,[18] which was converted to allenyl bromide **6** by reaction with phosphorus tribromide.[19]

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



7b,d,k,m

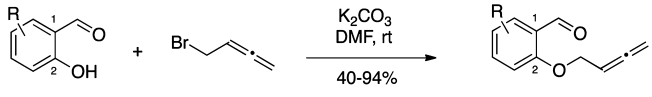
product	R	isolated yield (%)
7b	3-Me	52
7d	3-^{t}Bu	62
7k	3,5-Me_2	37
7m	3,6-Me_2	42

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 2-(buta-2,3-dienyloxy)benzaldehyde derivatives **1a–p**, respectively, in moderate to excellent yields (Table 2).

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 cumbersome and globally produces low yields (12% over three steps). Thus, we looked for an alternative route, taking advantage of the Crabbé homologation.[21] Salicylic aldehyde **7a** was first alkylated in high yield with propargyl bromide (Scheme 3) and subsequently homologated into allene **1a**. This latter reaction was conducted twice starting with 40 g of **8**, yielding in total 36.6 g of photocycloaddition precursor **1a**. Likewise, methyl ester derivative **10a** was synthesized on a 22 g scale from methyl salicylate by nearly quantitative propargylation, followed by the Crabbé homologation.

As nitrogen is a central element in biologically active molecules, we were interested in including it in our cycloaddition precursor and further exploring 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 were compatible, non-natural polycyclic amino acids would be obtained in one step from the simple allenylic precursors. Very

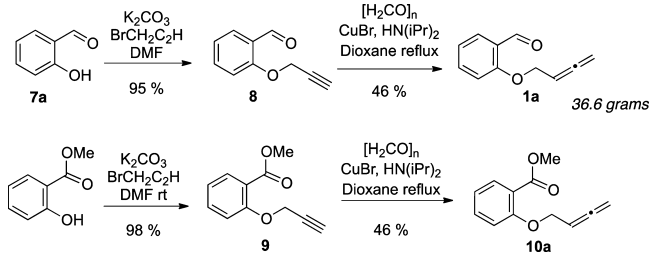
Table 2. Synthesis of Allenyloxybenzaldehydes



7a-p 6 1a-p

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

Scheme 3. Multigram-Scale Preparation of the Allene Precursors



recently, the thermal counterpart of this reaction was experimentally and computationally investigated 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-step sequence starting from aniline (Scheme 4). Protection of the amine with *tert*-butyl dicarbonate in **11** was followed by a quite low-yielding monoformylation,[24] and subsequent allenylation with allenyl bromide led to photocycloaddition precursor **14a**. 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.[25,26]

Surprisingly, allenylation of **13b** failed to proceed with the reaction conditions applied earlier for benzaldehyde **13a**. Hypothesizing that potassium carbonate was an overly weak base, we first successfully used cesium carbonate and activation of the bromide by the addition of sodium iodide. However, we

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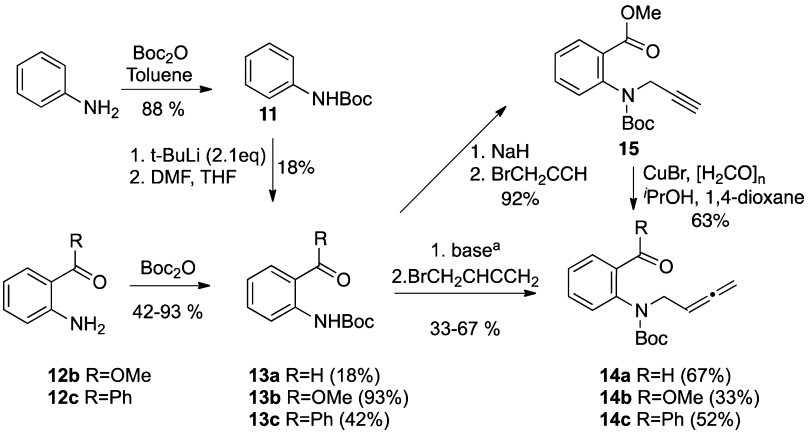
Scheme 4. Preparation of the Cycloaddition Precursors[a]



[a](a) K_2CO_3 for **14a**, NaH for **14b,c**.

finally settled for sodium hydride at a 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,[22] 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 conducted up to a scale of 30 g. Benzophenone derivative **14c** was also prepared by the protection of **12c**, followed by allenylation.

Photochemistry with an Oxygen-Containing Tether. Allenylsalicylaldehyde derivatives **1a**–**p** 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).

To better compare the values, small-scale irradiations 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 nonradiative relaxation of the excited state and may alter the outcome of photochemical reactions.[28] The reaction was also conducted on a preparative scale (0.15–0.79 mmol), and the identities 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**.[14]

Substitution at 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 at position 4 have 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 that for the same substituents at position 3. Interestingly, 5-chloro and 3,6-dimethyl (Table 3, entries 10 and 13) are the only substituents that 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; bicyclo[2.2.2]octadiene compound **2l** is obtained in a very high yield in 1 h 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 were used and replaced as their intensity grew considerably weaker over their lifetimes. Thus, because the irradiation intensity was not consistent, actinometric measurements were not taken and quantum yields were not accessible. However, clear trends emerged from these experiments, because the overall efficiency varied by a factor up to 50.

The UV–vis spectra of the derivatives substituted at position 5 also show red-shifted absorptions (Figure S1 of the Supporting Information). This bathochromic shift could also account for the shorter irradiation times. As precursors **1** usually show weak absorbance at long wavelengths, 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 compound arising from **1a** under irradiation at 254 nm (Figure S2 of the Supporting Information). Benzoxepine compound **3a** is relatively photostable at this wavelength, which is the opposite of the case for bicyclooctadiene derivative **2a**. This experiment also confirms that both compounds are not precursors of each other.

The reaction was nominally conducted 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 S3 of the Supporting Information). Dichloromethane, acetonitrile, and methanol showed the best results with similar conversions 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 five batches each containing 9.1 g of starting material in 1.5 L of dichloromethane. Overall, more

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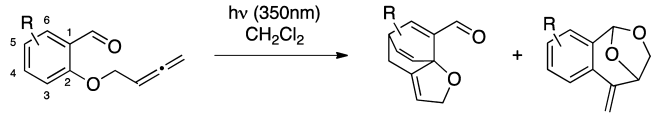
Table 3. Spectroscopic and Isolated Yields of Irradiation Products



1a-p **2a-p** **3a-p**

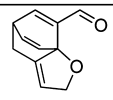
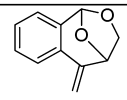
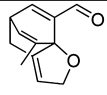
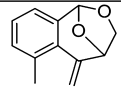
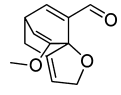
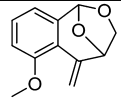
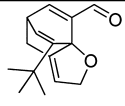
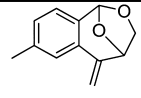
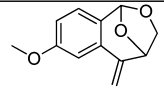
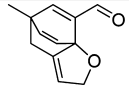
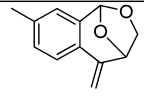
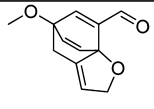
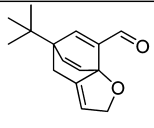
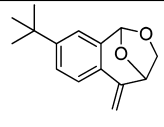
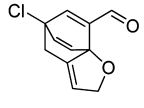
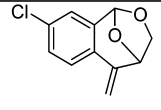
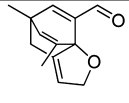
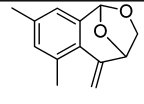
				Spectroscopic experiments			Preparative experiments		
Entry	**1**	**2**	**3**	Time[a]	**2**[a]	**3**[a]	Time[b]	**2**[b]	**3**[b]
1	**1a**			110 min	38%	21%	6 h	19%	15%
2	**1b**			40 min	52%	20%	8 h	10%	13%
3	**1c**			19 min	67%	19%	1.3 h	67%	24%
4	**1d**			40 min	84%	0%	3 h	65%	0%
5	**1e**			200 min	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%

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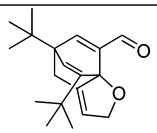
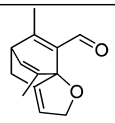
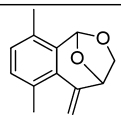
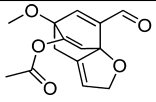
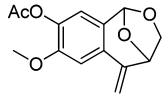
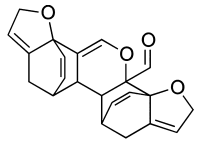
Table 3. continued

				Spectroscopic experiments			Preparative experiments		
Entry	**1**	**2**	**3**	Time[a]	**2**[a]	**3**[a]	Time[b]	**2**[b]	**3**[b]
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]A 11 mM 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.

than 10 g of the final compound **2a** could be produced. The reaction was usually stopped at a conversion of ∼60%, at which point ∼20% of bicyclo[2.2.2]octadiene product **2a** was formed; further irradiation usually did not lead to a significant increase in the yield of product. From each batch, ∼30% of starting material **1a** could be recovered, together with ∼10% of benzoxepine **3a**. The isolation of **2a** at this scale needed special care, as 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 2-propanol.



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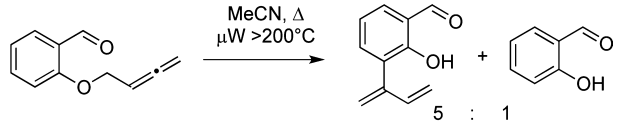
This side reaction can, however, be avoided if the crude mixture is purified immediately after the irradiation by flash chromatography with dichloromethane and ether as the solvent mixture. The pure compound can be stored in a freezer over several months without observable dimerization. On the other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

Thermal Reaction. To confirm the photochemical nature of the reaction, we also attempted it under thermal conditions. Therefore, the starting material was heated in a microwave oven (Biotage Initiator, single mode, sealed vessel). Starting material **1a** is thermally stable up to 190 °C, and some conversion to product **17a** as well as 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



1a **17a** **7a**

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 S4 of the Supporting Information). On the other hand, because of the sensitivity of the bicyclo[2.2.2]-octadiene to shorter wavelengths, the change of the irradiation toward more energetic light is detrimental. Therefore, three different groups were probed: ester, nitrile, and ketone were chosen, taking into account the previously mentioned constraints.

As the UV spectra of methyl benzoate **10a** show a hypsochromic shift, the irradiation was conducted at 300 nm instead of 350 nm and product **18a** was isolated in 24% yield (Table 4, entry 4; this product rapidly degrades after isolation). The *para* photocycloaddition product is the major compound formed, 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 ^{1}H NMR as Claisen-rearranged product **17b**.

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 the thermal conversion of **1a** upon heating above 200 °C (*vide supra*). The formation of this product could be explained by a

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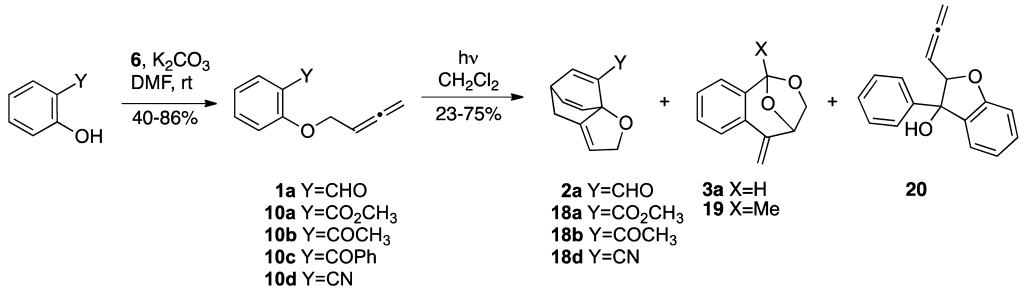
Table 4. Synthesis and Photolysis of Other Precursors



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%)		

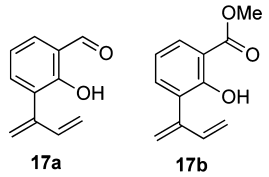


Figure 1. Claisen rearrangement side products.

photoinduced Claisen rearrangement,[31] but to the best of our knowledge, there have been no reports of such reactions with allenes.

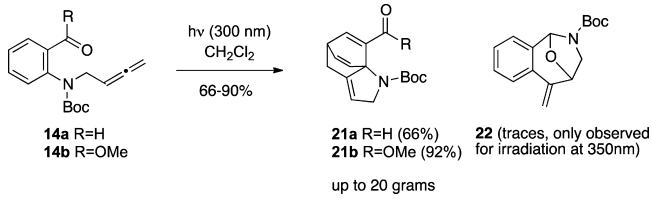
Benzonitrile **10d**, as it was already the case for methyl benzoate **10a**, absorbs at shorter wavelengths than the benzaldehydes. Therefore, the irradiation was conducted at 300 nm instead of 350 nm, leading to the isolation of **18d** in 32% yield. No other photocycloaddition product could be detected.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

The UV spectra of acetophenone **10b** show 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 benzoxepine **19** was isolated in 45% yield, together with bicyclo[2.2.2]octadiene **18b** in 21% yield. The ketone and the aldehyde are the only functional groups 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 benzophenone analogue **10c**. Photolysis of this substrate would not only create access to new products but also converge with the work of Griesbeck et al., who found that the photocycloaddition of allyloxy-substituted benzophenone occurs intramolecularly 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 toward a diastereoisomeric mixture of dihydrobenzofurans **20** 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 4, 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 *N*-Boc precursor **14a** is slightly shifted toward shorter wavelengths with respect to that of its oxygen-containing analogue **1**. The photocycloaddition step was nevertheless conducted at 350 nm, yielding the two photocycloaddition products, **21a** and **22** (Scheme 6). However, ^{1}H NMR spectra of both cycloadducts are

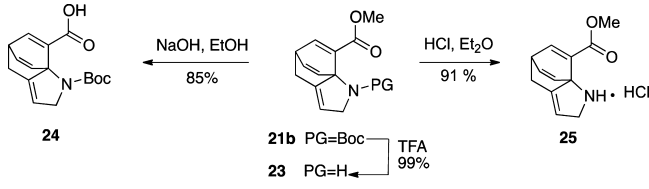
Scheme 6. Photocycloaddition of Nitrogen-Containing Allenes



poorly resolved and suggest the presence of rotamers. This hypothesis could unfortunately not be confirmed by ^{1}H NMR spectroscopy at higher temperatures (≤60 °C).[34] On the other hand, when **14a** was irradiated at 300 nm for 2 h in dichloromethane, bicyclo[2.2.2]octadiene product **21a** was obtained in good yield, without the other regioisomer. Likewise, irradiation of **14b** gave smoothly cycloadduct **21b** in very high yield, which shows a rotamer pattern similar to that of **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 led to the isolation of photocycloadduct **21b** in very high yield (92%).

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

Scheme 7. Deprotection at Both Termini



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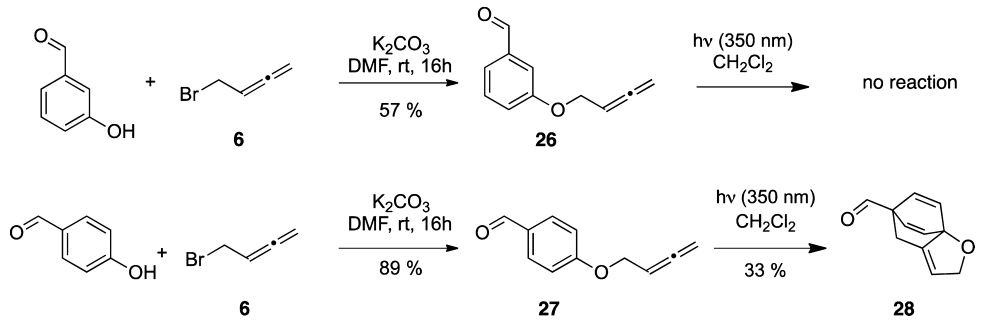
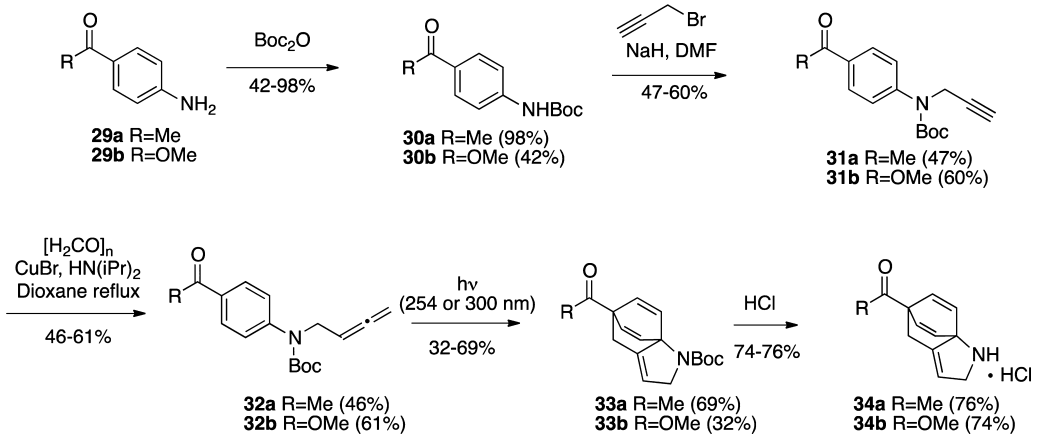
Scheme 8. ***meta*** **and** ***para*** **Substitution**



Scheme 9. ***para*** **Product**



The deprotection of **21a** in trifluoroacetic acid seems to proceed well by TLC analysis; however, the isolation of the free amine failed, despite attempts to conduct chromatography on neutral alox or 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, 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 the presence of anisole as a *tert*-butyl carbocation scavenger)[35] or hydrogen chloride[36] was used.[37] With trifluoroacetic acid, parent amine **23** is obtained in very high yield after neutralization of the acid. 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, solid hydrochloride **25** is easier to handle than 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 methyl ester **21b** was easily achieved by reaction with a sodium hydroxide solution, affording carboxylic acid **24** in high yield. Purification of this compound by flash chromatography, by 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 made, and the compound was used as extracted from the reaction mixture.

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 conduct this photocycloaddition with compounds having the allenyloxy tether attached at the *meta* or *para* position with respect to the aldehyde. Precursors **26** and **27** were readily synthesized via our usual route (Scheme 8). While *ortho*-substituted **1a** and *meta*-substituted **26** were quite stable, *para*-substituted analogue **27** is susceptible to oxidation to the carboxylic acid and therefore should be kept in the absence of air. Irradiation of *meta* precursor **26** failed to give identifiable photoproducts, whereas *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 the conjugated double bond prevents product **28** from dimerizing, observed for **2a**. The difference in reactivity of the *meta* versus *ortho*/*para* isomers is worth noting and probably arises from the direct conjugation between donor and acceptor substituents.

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, anilines **29a** and **29b** were protected as *N*-Boc (**30a** and **30b**) and propargylated (**31a** and **31b**). The alkynes were then converted into allenes **32a** and **32b** via a Crabbé homologation.

Precursor **32a** was subsequently irradiated at 300 nm in a Rayonet reactor, and 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 conducted with 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 potential as a diversification platform similar to that

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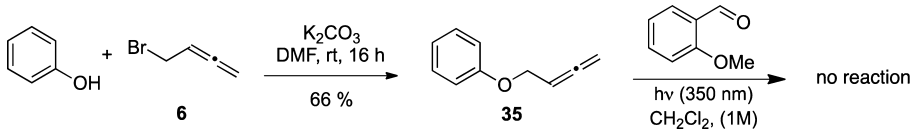
Scheme 10. Irradiation of 35 in the Presence of *o*-Anisaldehyde



of **25**, with a different disposition of the two anchor points, and no chirality.

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

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, the type and location of the chromophore, and the nature of the heteroatom in the tether; it can be scaled up without a notable loss of efficiency; and it can lead to structures with a high degree of 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 the 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 of photocycloadducts. Sequential deprotection of the N- or C-terminus of bicyclic amino acids gave access to two conformationally constrained unnatural amino acids with different dispositions 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.

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 precoated aluminum sheet TLC plates. Visualization was performed with either a 254 nm ultraviolet lamp or a potassium permanganate staining solution. Silica gel column chromatography was conducted with silica gel (32−63, 60 Å). Solid phase extractions were conducted on an Isolute SPE NH2, SAX, or SCX column from Biotage. The ^{1}H and ^{13}C NMR spectra were recorded on Fourier transform spectrometers at 500, 400, 360, or 300 MHz. Chemical shifts (δ) are expressed in parts per million using residual solvent protons as a reference: chloroform (δ 7.27 for ^{1}H, δ 77.0 for ^{13}C), acetonitrile (δ 1.94 for ^{1}H, δ 118.69 for ^{13}C), dichloromethane (δ 5.30 for ^{1}H, δ 54.00 for ^{13}C), benzene (δ 7.16 for ^{1}H, δ 128.39 for ^{13}C), methanol (δ 3.31 for ^{1}H, δ 49.15 for ^{13}C), water (δ 4.75 for ^{1}H), acetone (δ 2.05 for ^{1}H, δ 29.92 or 206.68 for ^{13}C), and DMSO (δ 2.50 for ^{1}H, δ 39.51 for ^{13}C). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), and br s (broad signal). Combination gas chromatography and mass spectroscopy were conducted using a Zebron ZB-1, 30 m × 0.25 mm, 100% methylpolysiloxane column, with mass detection by EI. Combination HPLC and mass spectroscopy were conducted using a photodiode array detector and an ESI mass spectrometer detector. Gradient: A consisting of H_2O and 7 mM formic acid and B consisting of MeCN and 5 mM formic acid; 5% B for 0 min, 100% B for 4 min, 100% B for 7 min, flow rate of 0.5 mL/min. An InterChrom Strategy 3 μm, C18-2, 50 × 2.0 mm column was used with an InterChrom Strategy 3 precolumn. 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 as w (weak), m (medium), and s (strong). UV−vis spectra and optical rotation were recorded with standard instruments. Melting points were measured without correction. Photochemical irradiations were conducted in a LUMOS 43 photoreactor (Atlas Photonics Inc.), in a quartz vessel, with one 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−p. To a suspension of K_2CO_3 (1.2−1.8 equiv) in DMF (0.16−2 M) was added the corresponding salicylaldehyde (**7a−p**) (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 solution of K_2CO_3 (three times) and with 1 N HCl (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 the literature[16]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 3077, 2865, 2760, 1957, 1862, 1692, 1599, 1484, 1458, 1399, 1377, 1285, 1237, 1161, 1102, 1041, 1002, 851, 758, 654 cm^{-1}; UV−vis (MeCN, c = 2.8 × 10^{-5} mol/L) λ_{max} 215 nm (ε = 22710), 251 nm (ε = 10443), 316 nm (ε = 4789); ESI-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 a 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 an 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 and added to 1 N HCl (1 L). The organics were extracted with DCM (4 × 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-bromobuta-

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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 the literature[16]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.31 (s, 3 H), 4.45 (dt, J = 7.3, 2.1 Hz, 2 H), 4.77 (dt, J = 6.6, 2.1 Hz, 2 H), 5.40 (quint, J = 6.6 Hz, 1 H), 7.10 (t, J = 7.7 Hz, 1 H), 7.40 (d, J = 7.5 Hz, 1 H), 7.65 (d, J = 7.5 Hz, 1 H), 10.35 (s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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} 3352, 3069, 2928, 2863, 2749, 1956, 1694, 1588, 1470, 1368, 1247, 1198, 1086, 975, 850, 767 cm^{-1}; UV−vis (MeCN, c = 3.1 × 10^{-5} mol/L) λ_{max} 209 nm (ε = 37123), 254 nm (ε = 15038), 304 nm (ε = 3543); ESI-HRMS m/z calcd 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-bromobuta-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[16]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.89 (s, 3 H), 4.69 (dt, J = 7.3, 1.8 Hz, 2 H), 4.76 (dt, J = 6.4, 1.8 Hz, 2 H), 5.38 (quint, J = 6.4 Hz, 1 H), 7.13 (d, J = 5.0 Hz, 2 H), 7.40 (quint, J = 4.1 Hz, 1 H), 10.44 (s, 1 H); ^{13}C NMR (90 MHz, CDCl3) δ 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} 3078, 2957, 2840, 1955, 1691, 1584, 1481, 1441, 1390, 1368, 1310, 1251, 1205, 1067, 972, 910, 851 cm^{-1}; UV−vis (MeCN, c = 3.96 × 10^{-5} mol/L) λ_{max} 219 nm (ε = 21925), 259 nm (ε = 8723), 320 nm (ε = 3114); ESI-HRMS m/z calcd 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 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 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} 2962 (m), 2872 (w), 1958 (w), 1687 (s), 1583 (m), 1471 (w), 1430 (m), 1369 (m), 1252 (m), 1213 (m), 1179 (m), 977 (m) cm^{-1}; UV−vis (MeCN, c = 2 × 10^{-5} mol/L) λ_{max} 211 nm (ε = 23196), 257 nm (ε = 8504), 304 nm (ε = 2244); ESI-HRMS m/z calcd 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 workup 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 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 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} 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) cm^{-1}; UV−vis (MeCN, c = 2.7 × 10^{-5} mol/L) λ_{max} 219 nm (ε = 21899), 259 nm (ε = 13267), 316 nm (ε = 5702); ESI-HRMS m/z calcd 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 an off-white solid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 2991, 2867, 2774, 1953, 1661, 1596, 1596, 1576, 1439, 1253, 1200, 1168, 1096, 997, 826 cm^{-1}; UV−vis (MeCN, c = 2.35 × 10^{-5} mol/L) λ_{max} 208 nm (ε = 14277), 233 nm (ε = 16844), 272 nm (ε = 14025), 310 nm (ε = 8927); ESI-HRMS m/z calcd 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-bromobuta-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[16]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.31 (s, 3 H), 4.66 (dt, J = 6.4, 2.7 Hz, 2 H), 4.90 (dt, J = 6.6, 2.7 Hz, 2 H), 5.41 (quint, J = 6.6 Hz, 1 H), 6.90 (d, J = 8.4 Hz, 1 H), 7.33 (dd, J = 8.4, 2.0 Hz, 1 H), 7.64 (s, 1 H), 10.48 (s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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} 3352, 3066, 2925, 2864, 2760, 1957, 1863, 1686, 1609, 1582, 1494, 1396, 1284, 1243, 1161, 1114, 1003, 941, 851, 811, 727, 649 cm^{-1}; UV−vis (MeCN, c = 4.5 × 10^{-5} mol/L) λ_{max} 218 nm (ε = 27375), 254 nm (ε = 12495), 327 nm (ε = 5545); ESI-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 workup 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 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 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} 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) cm^{-1}; UV−vis (MeCN, c = 3.0 × 10^{-5} mol/L) λ_{max} 225 nm (ε = 19728), 254 nm (ε = 8524), 352 nm (ε = 4582); ESI-HRMS m/z calcd 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 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 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 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} 2961, 2868, 1957, 1681, 1606, 1492, 1364, 1262, 1187, 1136, 1097, 1002, 848, 818 cm^{-1}; UV−vis (MeCN, c = 3.0 × 10^{-5} mol/L) λ_{max} 219 nm (ε = 22517), 254 nm (ε = 9057), 325 nm (ε = 3772); ESI-HRMS m/z calcd 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-bromobuta-1,2-

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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 workup 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 the literature[16]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.69 (dt, J = 6.6, 2.5 Hz, 2 H), 4.91 (dt, J = 6.6, 2.5 Hz, 2 H), 5.40 (quint, J = 6.6 Hz, 1 H), 6.96 (d, J = 9.1 Hz, 2 H), 7.48 (dd, J = 8.6, 2.3 Hz, 1 H), 7.79 (d, J = 2.7 Hz, 1 H), 10.43 (s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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} 3019, 2882, 1956, 1682, 1596, 1477, 1394, 1269, 1215, 1128, 1001, 903, 853, 756, 669 cm^{-1}; UV−vis (MeCN, c = 2.87 × 10^{-5} mol/L) λ_{max} 221 nm (ε = 8477), 249 nm (ε = 3066), 330 nm (ε = 1276); ESI-HRMS m/z calcd for $C_{11}H_9ClNaO_2$ $[M + Na]^+$ 231.0183, found 231.0185.

2-(Buta-2,3-dienyloxy)-3,5-dimethyl-benzaldehyde 1k. Prepared according to the general procedure from 3,5-dimethyl-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 (17 mL). 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-dimethyl-benzaldehyde **1k** (730.7 mg, 3.61 mmol, 63% yield) as a yellow liquid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; UV−vis (MeCN, c = 2.93 × 10^{-5} mol/L) λ_{max} 212 nm (ε = 23371), 257 nm (ε = 8940), 313 nm (ε = 2102); ESI-HRMS m/z calcd 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 the literature[16]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 2962, 2871, 2746, 1959, 1689, 1596, 1478, 1395, 1364, 1237, 1202, 1163, 980, 849 cm^{-1}; UV−vis (MeCN, c = 5.2 × 10^{-5} mol/L) λ_{max} 216 nm (ε = 24614), 261 nm (ε = 9821), 306 nm (ε = 2930); ESI-HRMS m/z calcd 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 workup 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 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 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} 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) cm^{-1}; UV−vis (MeCN, c = 2.5 × 10^{-5} mol/L) λ_{max} 211 nm (ε = 26646), 255 nm (ε = 10274), 306 nm (ε = 2508); ESI-HRMS m/z calcd 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-methylenedioxy-benzaldehyde **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 workup afforded 6-(buta-2,3-dienyloxy)benzo[*d*][1,3]dioxole-5-carbaldehyde **1n** (514.9 mg, 2.360 mmol, 89% yield) as an off-white solid, which was used without further purification: ^{1}H NMR (360 MHz, DMSO-d_6) δ 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 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) ν_{max} 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) cm^{-1}; UV−vis (MeCN, c = 3.4 × 10^{-5} mol/L) λ_{max} 273 nm (ε = 3761), 341 nm (ε = 4044); ESI-HRMS m/z calcd 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 an off-white solid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 (quint, 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 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} 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) cm^{-1}; UV−vis (MeCN, c = 2.86 × 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 calcd 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) 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 an off-white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 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 (quint, 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 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} 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) cm^{-1}; UV−vis (MeCN, c = 2.7 × 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 calcd for $C_{14}H_{14}NaO_5$ $[M + Na]^+$ 285.07334, found 285.07314; mp 97 °C.

General Procedure for Photocycloaddition To Obtain Bicyclo[2.2.2]octadienes 2a−p and Benzoxepines 3a−p. The corresponding allenyloxy benzaldehyde (**1a−o**) (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 an argon atmosphere at 350 nm at rt for the time indicated in Table 3. The reaction mixture was then evaporated.

2-Oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2a and 8-Methylene-11,12-dioxatricyclo[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-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-

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carbaldehyde **2a** (25.2 mg, 19% yield) as a yellow solid and 8-methylene-11,12-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3a** (20.0 mg, 15% yield) as an off-white solid (analysis according to the literature[16]). 2-Oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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} 3021, 2864, 2286, 1682, 1570, 1215, 1167, 1012, 669 cm^{-1}; ESI-MS m/z (%) 175.4 (M$^{+\bullet}$,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-dioxatricyclo[7.2.1.0^{2,7}]-dodeca-2,4,6-triene **3a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 (dd, J = 7.2, 1.4 Hz, 1 H), 4.10 (dd, J = 7.2, 5.9 Hz, 1 H), 5.10 (dd, J = 5.9, 1.4 Hz, 1 H), 5.15 (s, 1 H), 5.67 (s, 1 H), 6.09 (s, 1 H), 7.19 (dd, J = 7.4, 1.2 Hz, 1 H), 7.32 (dtd, J = 20.0, 7.4, 1.4 Hz, 2 H), 7.70 (d, J = 7.4 Hz, 1 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 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} 3021, 1527, 1425, 1215, 669 cm^{-1}; ESI-MS m/z (%) 174.4 (M$^{+\bullet}$, 19), 145.4 (17), 144.5 (100), 116.4 (42.4), 155.5 (58.8); mp 75 °C.

10-Methyl-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2b and 6-Methyl-8-methylene-11,12-dioxatricyclo[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-methylbenzaldehyde **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-oxatricyclo[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-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3b** (43 mg, 0.28 mmol, 13% yield) (analysis according to the literature[16]). 10-Methyl-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2b**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.85 (d, J = 1.4 Hz, 3 H), 2.07 (dm, J = 15.4, 2.3 Hz, 1 H), 2.20 (dm, J = 15.4, 2.3 Hz, 1 H), 3.83 (m, J = 3.2 Hz, 1 H), 5.05 (m, 2 H), 5.34 (s, 1 H), 5.75 (d, J = 5.0 Hz, 1 H), 7.11 (d, J = 6.4 Hz, 1 H), 9.67 (s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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) ν_{max} 3019, 2920, 2859, 2400, 2252, 1679, 1581, 1442, 1348, 1216, 1156, 1027, 909, 757, 668 cm^{-1}; ESI-HRMS m/z calcd for $C_{12}H_{12}NaO_2$ [M + Na]$^+$ 211.07295, found 211.07266. 6-Methyl-8-methylene-11,12-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3b**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.54 (s, 3 H), 3.73 (d, J = 7.3 Hz, 1 H), 4.09 (t, J = 6.1 Hz, 1 H), 5.04 (d, J = 5.7 Hz, 1 H), 5.36 (s, 1 H), 5.64 (s, 1 H), 6.07 (s, 1 H), 7.07 (m, 1 H), 7.18 (m, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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} 3068, 2969, 2893, 2251, 1715, 1680, 1624, 1469, 1448, 1347, 1248, 1225, 1137, 1084, 1051, 973, 910, 775, 732, 662 cm^{-1}; ESI-HRMS m/z calcd 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-dioxatricyclo[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-methoxybenzaldehyde **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 an inseperable mixture of 6-methoxy-8-methylene-11,12-dioxatricyclo-[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3c** and an unknown compound **x** (51 mg, 0.25 mmol, 31%, 24:76 **x**:**3c** ratio) 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 according to the literature[16]). 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 2.13 (d, J = 15.9 Hz, 1 H), 2.28 (d, J = 15.4 Hz, 1 H), 3.56 (s, 3 H), 3.82 (m, 1 H), 4.81 (d, J = 6.8 Hz, 1 H), 5.11 (m, 2 H), 5.42 (s, 1 H), 7.19 (d, J = 5.9 Hz, 1 H), 9.71 (s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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} 2964, 2893, 2804, 2250, 1689, 1597, 1479, 1345, 1264, 1084, 956, 906, 797, 733 cm^{-1}; ESI-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-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3c**: ^{1}H NMR (360 MHz, $CDCl_3$) δ A 3.74 (d, J = 9.3 Hz, 1 H), 3.92 (s, 3 H), 4.07 (t, J = 6.8 Hz, 1 H), 4.99 (d, J = 5.9 Hz, 1 H), 5.31 (s, 1 H), 6.06 (s, 1 H), 6.28 (s, 1 H), 6.83 (d, J = 10.1 Hz, 1 H), 6.93 (d, J = 11.6 Hz, 1 H), 7.23 (m, 1 H); ^{1}H NMR (360 MHz, $CDCl_3$) δ B 3.83 (d, J = 18 Hz, 1 H), 3.91 (s, 3 H), 4.01 (t, J = 6.0 Hz, 1 H), 5.25 (d, J = 4.5 Hz, 1 H), 5.33 (s, 1 H), 5.81 (s, 1 H), 6.32 (s, 1 H), 6.77 (d, J = 10.4 Hz, 1 H), 6.90 (d, J = 11.6 Hz, 1 H), 7.23 (m, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ A 55.3, 69.3, 79.8, 101.5, 111.7, 114.1, 117.4, 128.9, 138.1, 140.1, 159.2; ^{13}C NMR (90 MHz, $CDCl_3$) δ 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} 3018, 2966, 2989, 2840, 2405, 1623, 1598, 1479, 1341, 1266, 1216, 1084, 1216, 1084, 973, 957, 903, 752, 666 cm^{-1}; ESI-MS m/z (%) 204.25 (M$^{+\bullet}$, 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-oxatricyclo[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, 25 g) with hexane and Et_2O as solvents (5:1) to afford 10-*tert*-butyl-2-oxatricyclo[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 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 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} 2962, 2850, 1674, 1576, 1344, 1257, 1197, 1149, 1018 cm^{-1}; ESI-HRMS m/z calcd for $C_{15}H_{18}NaO_2$ [M + Na]$^+$ 253.11990, found 253.11984.

5-Methyl-8-methylene-11,12-dioxatricyclo[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, 20 g) with pentane and DCM as solvents (4:3) to afford 5-methyl-8-methylene-11,12-dioxatricyclo[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 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{12}H_{12}NaO_2$ [M + Na]$^+$ 211.07295, found 211.07268.

5-Methoxy-8-methylene-11,12-dioxatricyclo[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, 25 g) with hexane and EtOAc as solvents (6:1) to afford 5-methoxy-8-methylene-11,12-dioxatricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene **3f** (23.6 mg, 0.116 mmol, 20.65% yield) as an off-white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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} 2955 (w), 1602 (m), 1576 (w), 1494 (m), 1312 (m), 1237 (m), 1074 (m), 960 (m), 929 (m), 916 (m), 884 (m), 838 (m) cm^{-1}; ESI-HRMS m/z calcd 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-dioxatricyclo-[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

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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-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3g** (11 mg, 0.058 mmol, 11% yield) (analysis according to the literature[16]). 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 1.65 (s, 3 H), 1.99 (dm, J = 15.4 Hz, 1 H), 2.06 (dm, J = 13.0 Hz, 1 H), 5.06 (d, J = 1.6 Hz, 2 H), 5.34 (m, 1 H), 5.90 (d, J = 7.5 Hz, 1 H), 6.54 (d, J = 7.5 Hz, 1 H), 6.80 (s 1 H), 9.66 (s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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} 3020, 2965, 2956, 1680, 1614, 1564, 1455, 1351, 1215, 1169, 1009, 909, 760, 669 cm^{-1}; ESI-HRMS m/z calcd for $C_{12}H_{12}NaO_2$ [M + Na]$^+$ 211.07295, found 211.07290. 4-Methyl-8-methylene-11,12-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3g**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.35 (s, 3 H), 3.71 (dd, J = 7.3, 1.1 Hz, 1 H), 4.08 (t, J = 6.1 Hz, 1 H), 5.08 (m, 2 H), 5.59 (s, 1 H), 6.04 (s, 1 H), 7.0 (s, 1 H), 7.13 (d, J = 8.0 Hz, 1 H), 7.58 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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} 3020, 2970, 2896, 2403, 1679, 1498, 1422, 1338, 1215, 1102, 1085, 964, 903, 878, 827, 755, 669 cm^{-1}; ESI-HRMS m/z calcd for $C_{12}H_{12}NaO_2$ [M + Na]$^+$ 211.07295, found 211.07297.

7-Methoxy-2-oxatricyclo[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, 20 g) with hexane and DCM as solvents (5:3 to pure DCM) to afford 7-methoxy-2-oxatricyclo-[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 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{12}H_{12}NaO_3$ [M + Na]$^+$ 227.06787, found 227.06791; mp 62 °C.

7-*tert*-Butyl-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2i and 4-*tert*-Butyl-8-methylene-11,12-dioxatricyclo[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, 25 g) with hexane and DCM as solvents (2:1 to pure DCM) to afford 7-*tert*-butyl-2-oxatricyclo[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-dioxatricyclo[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-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2i**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 2960, 2851, 1664, 1565, 1477, 1371, 1348, 1170, 1021, 1000, 933, 672 cm^{-1}; ESI-HRMS m/z calcd for $C_{15}H_{18}NaO_2$ [M + Na]$^+$ 253.11990, found 253.11927. For 4-*tert*-butyl-8-methylene-11,12-dioxatricyclo[7,2,1,0^{2,7}]dodeca-2,4,6-triene **3i**, despite additional purification attempts, the product is not pure enough to obtain all spectral data: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2j and 4-Chloro-8-methylene-11,12-dioxatricyclo-[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-oxatricyclo[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-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3j** (66 mg, 0.32 mmol, 40% yield) (analysis according to the literature[16]). 7-Chloro-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2j**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.50−2.65 (m, 2 H), 5.06 (m, 2 H), 5.43 (s, 1 H), 6.19 (d, J = 8.2 Hz, 1 H), 6.56 (d, J = 7.7 Hz, 1 H), 6.97 (s, 1 H), 9.69 (s, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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) ν_{max} 3020, 2868, 2360, 1690, 1607, 1564, 1350, 1216, 1169, 1043, 1013, 926, 757, 682 cm^{-1}; ESI-MS m/z (%) 172 (100), 155 (5), 144 (50), 115 (75), 89 (30), 63 (12), 50 (5). 4-Chloro-8-methylene-11,12-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3j**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.72 (d, J = 7.3 Hz, 1 H), 4.09 (t, J = 6.8 Hz, 1 H), 5.09 (d, J = 5.9 Hz, 1 H), 5.17 (s, 1 H), 5.64 (s, 1 H), 6.03 (s, 1 H), 7.18 (d, J = 1.8 Hz, 1 H), 7.26−7.30 (1 H), 7.62 (d, J = 9 Hz, 1 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 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} 3020, 2972, 2896, 1898, 1807, 1685, 1639, 1596, 1417, 1334, 1216, 1193, 1113, 1086, 1012, 966, 904, 875, 815, 758 cm^{-1}; ESI-MS m/z (%) 193 (10), 178 (22), 151 (45), 136 (58), 115 (100), 87 (82), 75 (100), 50 (55).

7,10-Dimethyl-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2k and 4,6-Dimethyl-8-methylene-11,12-dioxatricyclo[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-dimethyl-2-oxatricyclo[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-dimethyl-8-methylene-11,12-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3k** (12.6 mg, 12.0% yield) as an off-white solid. 7,10-Dimethyl-2-oxatricyclo[5.2.2.0^{1,5}]-undeca-4,8,10-triene-9-carbaldehyde **2k**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 2962 (w), 2930 (w), 2872 (w), 1722 (s), 1678 (s), 1580 (m), 1168 (m), 1024 (m), 729 (s) cm^{-1}; ESI-HRMS m/z calcd for $C_{13}H_{14}NaO_2$ [M + Na]$^+$ 225.08860, found 225.08843. 4,6-Dimethyl-8-methylene-11,12-dioxatricyclo-[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3k**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{13}H_{14}NaO_2$ [M + Na]$^+$ 225.08860, found 225.08840.

7,10-Di-*tert*-butyl-2-oxatricyclo[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-oxatricyclo-[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 the literature[16]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.13 (s, 9 H), 1.14 (s, 9 H), 2.00−2.20 (m, 2 H), 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 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} 3019, 2965, 2856, 2402, 1679, 1621, 1576, 1475, 1372, 1216, 1148, 1013, 669 cm^{-1}; ESI-HRMS m/z calcd for $C_{19}H_{26}NaO_2$ [M + Na]$^+$ 309.18250, found 309.18217; mp 104 °C.

8,10-Dimethyl-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde 2m and 3,6-Dimethyl-8-methylene-11,12-dioxatricyclo[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

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g) with hexane and DCM as solvents (from 5:3 to pure DCM) to afford 8,10-dimethyl-2-oxatricyclo[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-dimethyl-8-methylene-11,12-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3m** (41.1 mg, 0.203 mmol, 35.4% yield) as an off-white solid. 8,10-Dimethyl-2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde **2m**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 2914 (m), 2851 (m), 1726 (m), 1672 (s), 1589 (s), 1430 (m), 1180 (m), 1036 (m) cm^{-1}; ESI-HRMS m/z calcd for $C_{13}H_{14}NaO_2$ [M + Na]$^+$ 225.08860, found 225.08885. 3,6-Dimethyl-8-methylene-11,12-dioxatricyclo[7.2.1.0^{2,7}]dodeca-2,4,6-triene **3m**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{13}H_{14}NaO_2$ [M + Na]$^+$ 225.08860, found 225.08861; mp 64 °C.

8-Formyl-5-methoxy-4,5-dihydro-2*H*-5,7a-ethenobenzofuran-6-yl Acetate 2o. The irradiation was conducted at 7.5 mM in DCM. Furthermore, the general irradiation protocol was conducted 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 the solvent to afford 8-formyl-5-methoxy-4,5-dihydro-2*H*-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 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 (quint, J = 1.65 Hz, 1 H), 6.23 (s, 1 H), 9.97 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 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} 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) cm^{-1}; ESI-HRMS m/z calcd 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 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 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-Chlorobut-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 and 5 °C. After complete addition, the reaction mixture was allowed to warm to rt and was stirred for an additional 16 h. The reaction mixture was added to an ice/water mixture (150 mL) and extracted three times with EtO_2 (100, 40, and 40 mL); the combined organic layer was washed twice with a saturated solution of $NaHCO_3$ (2 × 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-chlorobut-2-yne-1-ol **4** (19.43 g, 186 mmol, 36% yield) as a translucent liquid (analysis according to the literature[18]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.68 (t, J = 6.13 Hz, 1 H), 4.19 (s, 2 H), 4.34 (d, J = 6.36 Hz, 2 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 84.6, 80.5, 51.0, 30.3; IR (NaCl thin film) ν_{max} 3339 (m), 2996 (w), 2921 (w), 2869 (w), 1689 (w), 1599 (w), 1430 (w), 1264 (s), 1145 (s), 1015 (s), 697 (s) cm^{-1}.

Buta-2,3-dien-1-ol 5. To a solution of 4-chlorobut-2-yne-1-ol **4** (11.00 g, 105 mmol, 1 equiv) in dry Et_2O (200 mL) in a two-necked round-bottom flask equipped with a condenser 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 min and then cooled to 0 °C. The reaction mixture was quenched (caution!) with water (4.2 mL) and 15% NaOH (4.2 mL) followed by 25 mL of an ice/water mixture. The gray slurry was then stirred overnight. The precipitate was filtered off and the organic phase 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 the literature[18]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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, 1 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 207.8, 90.9, 77.2, 60.2; IR (NaCl thin film) ν_{max} 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) cm^{-1}.

4-Bromobuta-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 the starting material, water (200 mL) was added. The organic layer was extracted with pentane (3 × 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-bromobuta-1,2-diene **6** (7.06 g, 53.1 mmol, 53% yield) as a translucent liquid (analysis according to the literature[18]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.94−4.00 (m, 2 H), 4.92−4.97 (m, 2 H), 5.51−5.40 (m, 1 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 209.6, 89.3, 77.3, 29.9; IR (NaCl thin film) ν_{max} 2969 (w), 2362 (w), 1951 (s), 1429 (w), 1323 (w), 1208 (s), 1145 (w), 992 (w), 853 (s), 648 (m) cm^{-1}.

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*-butylamine (52.9 mL, 222 mmol, 0.4 equiv). The mixture was stirred at rt for 15 min, and then paraformaldehyde (73.4 g, 1221 mmol, 2.2 equiv) was added and the reaction mixture heated to 100 °C for 4 h. The reaction mixture was poured into water (1000 mL), and the mixture was acidified with 2 N HCl to pH 1. The organics were extracted with Et_2O (3 × 200 mL), 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[40]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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*-butylamine (3.18 mL, 13.31 mmol, 0.4 equiv). The mixture was stirred at rt for 0.5 h, and then paraformaldehyde (4.40 g, 73.2 mmol, 2.2 equiv) was added and the reaction mixture heated to 100 °C for 14 h and stirred at rt 3 h. The reaction mixture was poured into water (200 mL) and acidified with 1 N HCl to pH 2. The organics were extracted with Et_2O (3 × 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[41]): ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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*-butylamine (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 0.5 h, and then paraformaldehyde (2.16

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g, 36.00 mmol) was added and the reaction mixture 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 1 N HCl to pH 2. The organics were extracted three times with Et_2O (100, 50, and 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[42]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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*-butylamine (1.172 mL, 4.91 mmol, 0.4 equiv). The mixture was stirred at rt for 0.5 h, and then paraformaldehyde (1.623 g, 27.0 mmol, 2.2 equiv) was added and the reaction mixture heated to 100 °C for 8 h and stirred at rt for 16 h. The reaction mixture was added to water (110 mL) and acidified with 1 N HCl to pH 1. The organics were extracted three times with Et_2O (100, 50, and 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[43]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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 **7a** (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 and then diluted with water (1 L), and the organics were extracted three times with Et_2O (3 × 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[16]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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 (4 × 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[44]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 calcd for $C_{11}H_{10}NaO_3$ $[M + Na]^+$ 213.0528, found 213.0521.

Methyl 2-(Buta-2,3-dienyloxy)benzoate 10a on a Multigram 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 an 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 (5 × 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 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 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} 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) cm^{-1}; UV−vis (MeCN, c = 2.8 × 10^{-5} mol/L) λ_{max} 290 nm (ε = 3079), 226 nm (ε = 7899), 203 nm (ε = 34541); ESI-HRMS m/z calcd for $C_{12}H_{12}NaO_3$ $[M + Na]^+$ 227.068, found 227.06734.

Methyl 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 1 N HCl (3 × 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 methyl-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) over 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 1 M K_2CO_3 (3 × 50 mL), 1 N HCl (3 × 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 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 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 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} 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) cm^{-1}; UV−vis (MeCN, c = 5.3 × 10^{-5} mol/L) λ_{max} 211 nm (ε = 24605), 243 nm (ε = 7885), 300 nm (ε = 3383); ESI-HRMS m/z calcd for $C_{12}H_{12}NaO_2$ $[M + Na]^+$ 211.07295, found 211.07280.

[2-(Buta-2,3-dienyloxy)phenyl]phenylmethanone 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 1 h at 50 °C and then at rt for 16 h. The reaction mixture was diluted with Et_2O (150 mL) and washed twice with water (2 × 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]-phenylmethanone **10c** (879.3 mg, 3.51 mmol, 46.4% yield) as a yellow oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 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} 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) cm^{-1};

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UV−vis (MeCN, $c = 3.0 \times 10^{-5}$ mol/L) λ_{max} 282 nm (ε = 6453); ESI-HRMS m/z calcd 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 1 M K_2CO_3 (3 × 60 mL), 1 N HCl (3 × 50 mL), and brine (50 mL), dried over $MgSO_4$, and evaporated. The crude product was purified by flash column chromatography (Si, 50 g) 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 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 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} 2227, 1957, 1598, 1489, 1450, 1287, 1254, 1166, 1109, 993, 849, 752 cm^{-1}; UV−vis (MeCN, $c = 2.7 \times 10^{-5}$ mol/L) λ_{max} 204 nm (ε = 40045), 232 nm (ε = 9317), 292 nm (ε = 4141); ESI-HRMS m/z calcd for $C_{11}H_9KNO$ $[M + K]^+$ 210.03157, found 210.03043.

***tert*-Butyl-*N*-phenylcarbamate 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 a 1:5 ratio, and pentane was added. The thereby formed crystals were isolated by filtration to afford *tert*-butyl-*N*-phenylcarbamate **11** (17.3 g, 90 mmol, 88% yield) as a white solid: (spectral data according to the literature[45]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 1.7 M *tert*-butyllithium in pentane (63.9 mL, 109 mmol, 2.1 equiv). The reaction mixture was stirred at −50 °C for 3 h. Then dry DMF (4.78 mL, 62.1 mmol, 1.2 equiv) was added dropwise to the solution at −50 °C, and the reaction mixture was allowed to slowly warm and was stirred at rt for 17 h. The reaction mixture was diluted with Et_2O (150 mL) and washed twice with brine (2 × 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 an off-white solid (analysis according to the literature[46]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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 and 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 (3 × 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 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 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, 100 g) with hexane and EtOAc as solvents (20:1) to afford *tert*-butyl 2-benzoylphenylcarbamate **13c** (955.8 mg, 3.21 mmol, 42% yield) as an off-white solid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd 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 **6** (793 mg, 5.97 mmol, 2.2 equiv), and the reaction mixture was stirred at rt for 2 days. The reaction mixture was diluted with Et_2O (100 mL), and the organic phase was washed twice with water (2 × 50 mL) and brine (50 mL), dried over $MgSO_4$, and evaporated. The crude product was purified by flash column chromatography (Si, 25 g) 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 the existence of rotamers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 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 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} 2978 (w), 2932 (w), 1955 (w), 1691 (s), 1598 (m), 1367 (m), 1251 (m), 1154 (s), 850 (m), 761 (m) cm^{-1}; UV−vis (MeCN, $c = 1.8 \times 10^{-5}$ mol/L) λ_{max} 298 nm (ε = 1791), 233 nm (ε = 15208); ESI-HRMS m/z calcd 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, and then 4-bromo-1,2-butadiene **6** (1.720 g, 12.93 mmol, 1.3 equiv) was added dropwise at 0 °C and the mixture stirred for 1 h at 0 °C and then at rt for 3 h. The reaction mixture was diluted with Et_2O (100 mL) and washed twice with water (2 × 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 the existence of rotamers: ^{1}H NMR (360 MHz, DMSO-d_6) δ 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 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} 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) cm^{-1}; UV−vis (MeCN, $c = 2.2 \times 10^{-5}$ mol/L) λ_{max} 282 nm (ε = 1962.2); ESI-HRMS m/z calcd 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 an 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

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extracted five times with EtOAc (5 × 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 1 h, and 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 an additional 1 h and then the reaction quenched by addition of an ice/water mixture (100 g). The organics were extracted three times with Et_2O (3 × 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 the existence of rotamers: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.27 (br m, 9 H), 3.51−4.44 (br m, 2 H), 4.74 (br m, 2 H), 5.25 (quint, J = 6.47 Hz, 1 H), 7.29−7.86 (m, 9 H); ^{13}C NMR (91 MHz, $CDCl_3$) δ 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{22}H_{23}NNaO_3$ $[M + Na]^+$ 372.15701, found 372.15698; UV−vis (MeCN, c = 3.3 × 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-benzoylphenyl(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, 300, or 350 nm for several hours. After 19 h at each wavelength, only degradation was observed, and no major compound could be detected via 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, and 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 and then the reaction quenched upon addition to ice-cold water (1 L). The organics were extracted with Et_2O (3 × 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 the existence of rotamers: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{16}H_{19}NNaO_4$ $[M + Na]^+$ 312.12063, found 312.12014.

Thermal Reaction to 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 via HPLC; therefore, the reaction mixture was further heated to 150, 170, and 200 °C for 15 min each. Only at 200 °C could some conversion toward new compounds be observed. However, after 20 min at 210 °C, the conversion is still not complete. The main compounds observed in the reaction mixture are Claisen-rearranged compound **17a** and salicylaldehyde **7a**. The compounds were not isolated as no cycloaddition products were observed.

2-Oxatricyclo[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, 20 g) with pentane and DCM as solvents (4:3) to afford 2-oxatricyclo[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 **17b** (8 mg, 0.039 mmol, 6.4% yield). For 2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-triene-9-methylester **18a**, because of the instability of the compound no further analysis data are available: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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-Oxatricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-ethanone 18b and 8-Methylene-1-methyl-11,12-dioxatricyclo[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 an argon atmosphere for 5.3 h at 350 nm. The solvent was evaporated and the crude mixture purified by flash column chromatography (Si, 20 g) with hexane and EtOAc as solvents (5:1) to afford 2-oxatricyclo[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-dioxatricyclo[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-Oxatricyclo-[5,2,2,01,5]undeca-4,8,10-triene-9-ethanone **18b**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 2921 (w), 2854 (w), 1671 (s), 1606 (w), 1566 (m), 1357 (m), 1238 (s), 1164 (s), 1008 (m), 806 (m), 676 (m) cm^{-1}; ESI-HRMS m/z calcd for $C_{12}H_{12}NaO_2$ $[M + Na]^+$ 211.07295, found 211.07288. 8-Methylene-1-methyl-11,12-dioxatricyclo[7,2,1,0^{2,7}]-dodeca-2,4,6-triene **19**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{12}H_{12}NaO_2$ $[M + Na]^+$ 211.07295, found 211.07307.

2-Oxatricyclo[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 an argon atmosphere at 300 nm for 7 h. The solvent was evaporated and the product isolated by flash column chromatography (Si, 20 g) with hexane and EtOAc as solvents (4:1) to afford 2-oxatricyclo[5.2.2.0^{1,5}]undeca-4,6,8-triene-9-nitrile **18d** (34.2 mg, 0.200 mmol, 32.3% yield) as an off-white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13−2.20 (m, 2 H), 3.88−

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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 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} 3063, 3002, 2869, 2216, 1572, 1352, 1333, 1165, 1148, 1002, 699, 679 cm^{-1}; ESI-HRMS m/z calcd 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]phenylmethanone **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 a ratio of 4:1 can be observed: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{17}H_{14}NaO_2$ $[M + Na]^+$ 273.0886, found 273.0885.

***tert*-Butyl (2-Azatricyclo[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, 25 g) with hexane and EtOAc as solvents (3:1) to afford *tert*-butyl (2-azatricyclo-[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 the existence of rotamers: ^{1}H NMR (500 MHz, DMSO-d_6) δ 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 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} 2923 (w), 2844 (w), 1695 (s), 1674 (s), 1575 (m), 1401 (s), 1362 (m), 1147 (s), 1014 (m), 768 (m), 685 (m) cm^{-1}; ESI-HRMS m/z calcd for $C_{16}H_{19}NNaO_3$ $[M + Na]^+$ 296.12571, found 296.12605.

Attempt To Deprotect *tert*-Butyl (2-Azatricyclo[5,2,2,0^{1,5}]-undeca-4,8,10-triene-9-carbaldehyde)carboxylate 21a. *tert*-Butyl (2-azatricyclo[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 toward 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-azatricyclo[5,2,2,0^{1,5}]-undeca-4,8,10-triene-9-carbaldehyde)carboxylate **21a** with 4 N HCl solutions in dioxane and Et_2O led to only complete decomposition of the starting material.

***tert*-Butyl (2-Azatricyclo[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 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 the existence of rotamers: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{17}H_{21}NNaO_4$ $[M + Na]^+$ 326.13628, found 326.13608.

***tert*-Butyl (2-Azatricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester)carboxylate 21b on a 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 coldfinger, 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 purified by flash column chromatography (Si, 250 g) with hexane and EtOAc as solvents (3:1) to afford *tert*-butyl (2-azatricyclo[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-Azatricyclo-[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 purified by flash column chromatography (Si, 25 g) 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-azatricyclo[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 suggests the existence 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 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). Because of the presence of multiple rotamers, the ^{13}C NMR is too complex to be reported: IR (Golden Gate) ν_{max} 2976 (w), 1693 (s), 1392 (s), 1366 (s), 1247 (m), 1167 (s), 1117 (s), 889 (s), 757 (s) cm^{-1}; ESI-HRMS m/z calcd for $C_{16}H_{19}NNaO_3$ $[M + Na]^+$ 296.12571, found 296.12552. *tert*-Butyl (2-azatricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-carbaldehyde)-carboxylate **21a**. Analysis as described previously.

2-Azatricyclo[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-azatricyclo[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 and 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-azatricyclo[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 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 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} 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),

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753 (m), 739 (s), 681 (s), 666 (s) cm^{-1}; ESI-HRMS m/z calcd for $C_{12}H_{14}NO_2$ $[M + H]^+$ 204.10191, found 204.10172.

***tert*-Butyl (2-Azatricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-carboxylic acid)carboxylate 24.** An aqueous solution of 5 M NaOH (39.4 mL, 197 mmol, 10 equiv) was added to a solution of *tert*-butyl (2-azatricyclo[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 and 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 (2 × 100 mL). The aqueous phase was acidified by addition of HCl (25%) to pH 1. The product was extracted five times with DCM (5 × 100 mL), and the combined organic phases were dried over Na_2SO_4 and evaporated to afford *tert*-butyl (2-azatricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-carboxylic acid)-carboxylate **24** (4.84 g, 16.73 mmol, 85% yield) as an off-white solid. The crude compound was used as such in further reactions as several purification attempts failed. The NMR of the compounds suggests the existence of rotamers: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{16}H_{19}NNaO_4$ $[M + Na]^+$ 312.12063, found 312.12094; mp 89 °C.

2-Azatricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester Hydrochloride 25. *tert*-Butyl (2-azatricyclo[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 37% HCl to $CaCl_2$) for 3 min at 0 °C, and the reaction mixture was stirred for an additional 2 h at rt. The reaction mixture was left without being stirred for 16 h; then the precipitate formed was filtered off to afford 2-azatricyclo[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 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{12}H_{14}NO_2$ $[M + H]^+$ 204.10191, found 204.10140; mp 86 °C.

2-Azatricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester Hydrochloride 25 on a Large Scale. *tert*-Butyl (2-azatricyclo-[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 37% HCl to $CaCl_2$) for 1 h at 0 °C and 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 the final compound were recovered upon filtration affording 2-azatricyclo[5,2,2,0^{1,5}]undeca-4,8,10-triene-9-methylester hydrochloride **25** (4.75 g, 19.82 mmol, 91% yield) as a 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 1 N HCl (50 mL, 2×) and with brine, dried over Na_2SO_4, and evaportated. The crude product was purified by flash column chromatography (Si, 25 g) 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 4.65 (dt, J = 6.80, 2.45 Hz, 2 H), 4.90 (dt, J = 6.61, 2.46 Hz, 2 H), 5.40 (quint, 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 661, 76.8, 86.6, 113.4, 122.2, 123.6, 130.1, 137.8, 158.9, 192.0, 209.6; UV−vis (MeCN, $c = 3.4 \times 10^{-5}$ mol/L) λ_{max} 308 nm (ε = 2999), 251 nm (ε = 9845), 219 nm (ε = 27871); IR (Golden Gate) ν_{max} 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) cm^{-1}.

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, diluted with Et_2O (50 mL), and washed with 1 M K_2CO_3 (30 mL), 1 N HCl (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 the 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 the compound is in contact with oxygen, a white precipitate forms. The carboxylic acid can be easily filtered off: ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.58−4.72 (m, 2 H), 4.84−5.00 (m, 2 H), 5.40 (quint, 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 66.7, 77.2, 86.9, 115.6, 130.7, 132.3, 163.9, 191.1, 210.1; UV−vis (MeCN, $c = 2.7 \times 10^{-5}$ mol/L) λ_{max} 273 nm (ε = 14901), 218 nm (ε = 10884); IR (Golden Gate) ν_{max} 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) cm^{-1}.

2-Oxatricyclo[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, 10 g) with DCM as the solvent to afford 2-oxatricyclo[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 2.21 (q, J = 2.45 Hz, 2 H), 5.03 (td, J = 2.60, 1.61 Hz, 2 H), 5.40 (quint, 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 30.4, 58.9, 80.0, 97.8, 112.2, 126.8, 138.3, 139.8, 200.3; IR (Golden Gate) ν_{max} 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) cm^{-1}; ESI-HRMS m/z calcd 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 up in EtOAc. The organic layer was washed three times with 1 M HCl 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[45]): ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 and then added to water, and the organics were extracted with DCM (100 mL). The organic phase was subsequently washed three times with 1 M HCl (3 × 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

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suggests the existence of rotamers: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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, and 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 and then the reaction quenched by addition to water, and the organics were extracted three times with Et_2O. The combined organic layers were washed with 1 M HCl 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 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd 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 **30b** (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 2 h, and then 3-bromoprop-1-yne (2.69 mL, 24.12 mmol, 3 equiv) was added and the mixture stirred for an additional 2 h. The reaction mixture was diluted with Et_2O, and the organic phase was washed with water, 1 N HCl, and brine, dried over Na_2SO_4, and evaporated. The crude product was purified by flash column chromatography (Si, 50 g) with DCM as the solvent to afford methyl 4-[(*tert*-butoxycarbonyl)(prop-2-yn-1-yl)amino]benzoate **31b** (1.39 g, 4.80 mmol, 60% yield) as an off-white solid. The NMR of the compound suggests the existence of rotamers: ^{1}H NMR (360 MHz, $CDCl_3$) δ 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd 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 1 M HCl 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 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 (quint, 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 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} 2977 (w), 1957 (w), 1701 (s), 1680 (s), 1601 (m), 1511 (w), 1419 (w), 1364 (s), 1322 (m), 1267 (s), 1226 (m), 1152 (s), 1078 (w), 1050 (w), 1013 (w), 957 (w), 840 (s), 765 (m), 593 (m) cm^{-1}; ESI-HRMS m/z calcd for $C_{17}H_{21}NNaO_3$ $[M + Na]^+$ 310.14136, found 310.14120; UV−vis (MeCN, c = 2.7 × 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 an 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 sealed in a microwave vial and heated in a microwave to 160 °C for 20 min. The solvent was evaporated and the residue suspended in EtOAc and filtered over Celite. The organic phase was washed with water, 1 M HCl, and brine, dried over $MgSO_4$, and evaporated. The crude product was purified by flash column chromatography (Si, 25 g) with DCM as the 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 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd for $C_{17}H_{21}NNaO_4$ $[M + Na]^+$ 326.13628, found 326.13623; UV−vis (MeCN, c = 2.25 × 10^{-5} mol/L) λ_{max} 268 nm (ε = 16504).

***tert*-Butyl 5-Acetyl-4,5-dihydro-5,7a-ethenoindole-1(2*H*)-carboxylate 33a.** *tert*-Butyl (4-acetylphenyl)(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 purified by flash column chromatography (Si, 10 g) with DCM and Et_2O (99% DCM) as solvents to afford *tert*-butyl 5-acetyl-4,5-dihydro-5,7a-ethenoindole-1(2*H*)-carboxylate **33a** (95 mg, 0.331 mmol, 69% yield) as a translucent oil. The NMR of the compound suggests the existence of rotamers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 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 (quint, J = 1.79 Hz, 0.33 H), 5.32 (quint, 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd 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(2*H*)-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 coldfinger, 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 purified by flash column chromatography (Si, 10 g) with DCM and Et_2O (95% DCM) as solvents to afford 1-*tert*-butyl 5-methyl 4,5-dihydro-5,7a-ethenoindole-1,5(2*H*)-dicarboxylate **33b** (33 mg, 0.109 mmol, 32% yield) as a yellow solid. The NMR of the compound suggests the existence of rotamers: ^{1}H NMR (300 MHz, $CDCl_3$) δ 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 (quint, J = 1.84 Hz, 0.3 H), 5.30 (quint, 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 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} 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

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(m), 833 (w), 802 (m), 771 (m), 754 (w), 700 (s), 685 (m) cm^{-1}; ESI-HRMS m/z calcd 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(2*H*)-carboxylate **33a** (43.5 mg, 0.151 mmol, 1 equiv) was dissolved in DCM (1 mL), and a solution of 4 N HCl 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 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd 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(2*H*)-dicarboxylate **33b** (37.1 mg, 0.122 mmol, 1 equiv) in DCM (2 mL) was added a solution of 4 N HCl 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 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 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} 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) cm^{-1}; ESI-HRMS m/z calcd 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, diluted with EtOAc (100 mL), and washed three times with water (3 × 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 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 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 65.9, 76.7, 88.0, 115.6, 121.4, 130.1, 159.4, 209.8; IR (Golden Gate) ν_{max} 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) cm^{-1}; ESI-HRMS m/z calcd for $^{107}AgC_{10}H_{10}O$ $[M + Ag(107)]^+$ 252.97771, found 252.97833; ESI-HRMS m/z calcd 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*-butyllithium (1.6 M in hexane) (62.4 mL, 100 mmol, 2.2 equiv). The reaction mixture was stirred at rt for 20 h, and 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 stirred for 20 h at rt. The reaction mixture was diluted with Et_2O (150 mL) and the product extracted with water (100 mL). The aqueous phase was acidified to pH 1 with HCl (25%) and the product extracted three times with DCM (3 × 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 the 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-mercapto-benzaldehyde **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, diluted with Et_2O (150 mL), and washed with a solution of 1 M K_2CO_3 (100 mL), 1 M HCl (3 × 50 mL), and brine (50 mL), and the organic layer was dried over $MgSO_4$ and evaporated. The crude product was filtered through a silica gel plug (Si, 5 g) 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 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 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, $c = 2.0 \times 10^{-5}$ 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 M) in dry DCM was irradiated either in a Rayonet reactor at 350 or 254 nm or in a LUMOS reactor at 360, 375, 385, 405, or 430 nm. Only degradation could be observed upon irradiation. The product is stable toward 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 30% hydrogen peroxide (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; the unreacted peroxide was quenched by addition of a 20 wt % sodium metabisulfite solution (1 mL), and then water (10 mL) was added and the product 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 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 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} 2924, 1951, 1693, 1311, 1295, 1190, 1137, 851, 759 cm^{-1}; UV–vis (MeCN, $c = 2.25 \times 10^{-5}$ mol/L) λ_{max} 206 nm (ε = 27943), 244 nm (ε = 7621), 285 nm (ε = 1987); ESI-HRMS m/z calcd 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 M) in dry DCM was irradiated either in a Rayonet reactor at 350, 300, or 254 nm or in a LUMOS reactor at 360 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–p**) (0.2 mmol) in dry DCM (18.1 mL) was purged with argon for 15 min; 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 or 254 nm in a Rayonet reactor, completely evaporated, and taken into $CDCl_3$ (0.7 mL) containing DMF (0.03 mol/L) as a 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 an 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 recorded and the conversion was analyzed.

■ ASSOCIATED CONTENT

Supporting Information

Characterization data not described in the Experimental Section and spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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