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## Photocycloadditions of Phenols Derived from Lignin

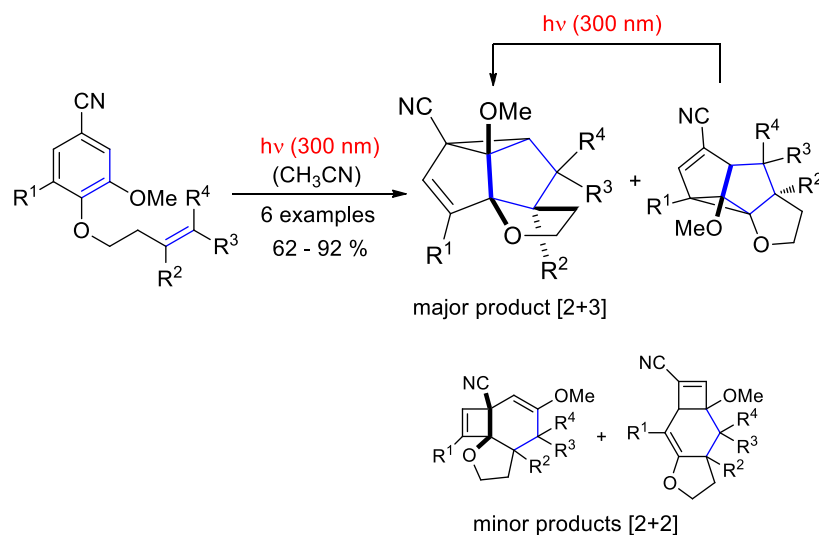
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### Abstract



Intramolecular photocycloaddition reactions of 3,4-benzonitriles derived from vanillin with alkenes have been investigated. In contrast to previous reports on photochemical reactions with these compounds, mainly [2+3] cycloaddition has been observed. A competing [2+2] photocycloaddition plays a minor role. Most probably these additions occur at the singlet state  $S_1$ . In the case of a triplet reaction, a different regioselectivity of the [2+2] cycloaddition would be observed. A linear and an angular [2+3] cycloadduct are formed as major products. The first isomer is transformed in the second one by a photochemical vinyl-cyclopropane rearrangement which increases the selectivity of the reaction. The influence of the substitution pattern on the reactivity and the selectivity has also been investigated.

## Introduction

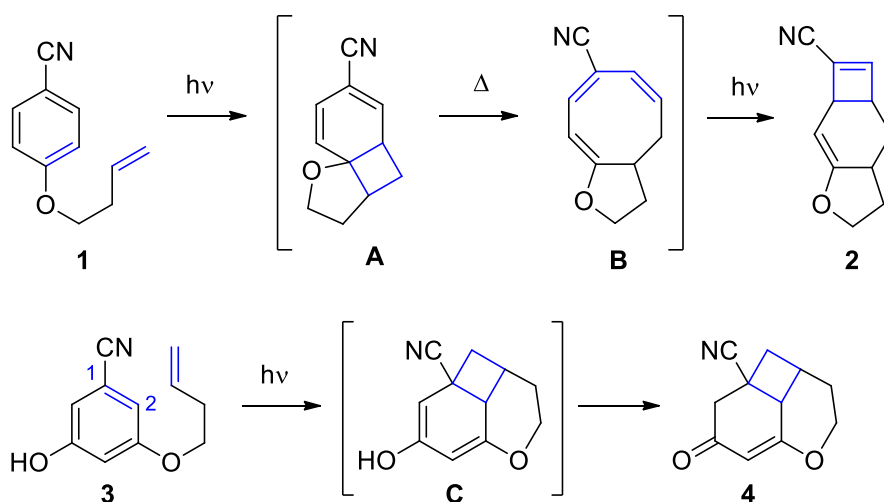
Photochemical reactions provide an efficient way to generate a high degree of molecular complexity and diversity. Starting from simple starting compounds, in only one step complex products such as polycyclic compounds are obtained. These reactivities are explained by the fact that photochemically excited compounds have a completely different electronic configuration when compared to the corresponding ground state molecules.<sup>1</sup> These reactions are therefore particularly interesting for being applied to organic synthesis.<sup>2,3,4</sup> In the case of aromatic compounds or benzene derivatives, the ground state reactions are characterized by a high tendency to regenerate the aromaticity in the final products. Photochemical reactions of such compounds are often characterized by a high tendency to yield non-aromatic final products which is linked to the fact that at the excited state, aromatic character is lost and the compounds become anti-aromatic.<sup>5</sup> This is the case for photochemical cycloadditions of benzene derivatives with alkenes.<sup>6,7,8,9</sup> Three cycloaddition modes have been reported: (1) [2+2] or ortho photocycloaddition and consecutive reactions, (2) [2+3] or meta photocycloaddition and (3) [2+4] or para photocycloaddition. Many applications of the meta cycloaddition have been reported.<sup>10</sup> These reactions are also discussed in the context of dearomatization reactions, with numerous applications in organic synthesis.<sup>11</sup> It should further be pointed out that these reactions as many other photochemical reactions fulfil requirements of sustainable chemistry. Often no additional chemical activation is needed and the photon is considered as a traceless reagent.<sup>6,12</sup>

Biomass as renewable resources for chemical industry also play a central role in sustainable chemistry.<sup>13</sup> In this context, Lignin is an important resource for aromatic compounds, in particular phenols.<sup>14,15</sup> For example, vanillin is produced on industrial scale from lignin.<sup>16</sup> We became interested in the investigation of photochemical cycloadditions with such derivatives. In intramolecular photocycloadditions between the benzene ring and an alkene, often a competition between the [3+2] and [2+2] mode is observed.<sup>17,18</sup> Many of these reactions are reversible. In the case of phenol derivatives, these equilibria can be controlled by additives such as acid.<sup>19,20,21,22,23</sup>

We now report on intramolecular photocycloadditions of lignin derived phenols such as vanillin or syringaldehyde carrying an alkene side chain. The influence of additional electron withdrawing and donating substituents such as the nitrile function and alkoxy groups on the competition between [2+2] and [3+2] photocycloaddition is of particular interest. These substituents may also have an influence on the formation of different regio- and stereoisomers. This substitution pattern is typical for many lignin derived phenols.

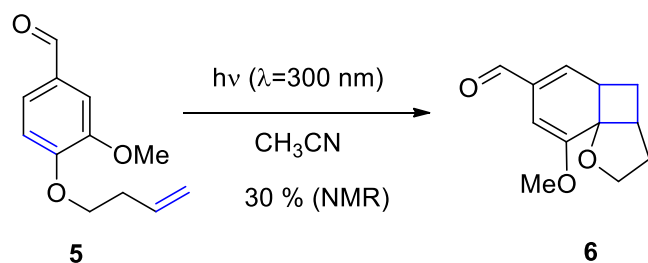
## Results and Discussions.

Previous results showed that phenols carrying an alkenyl side chain and an electron-withdrawing substituent such as a carbonyl a carboxyl function or a nitrile substituent undergo preferentially intramolecular [2+2] photocycloaddition which is often followed by thermal or photochemical electrocyclic reactions.<sup>8,24,25</sup> Two examples have been reported with phenol derivatives carrying a nitrile function as electron withdrawing group (Scheme 1). Compound **1** undergoes [2+2] photocycloaddition leading to the corresponding adduct **A**.<sup>26</sup> A thermal electrocyclic reactions, leading to the cyclooctatriene derivative **B**, followed by a photochemical one yields the final product **2**. Similar intermolecular reactions have also been observed.<sup>27</sup> Also when two alkoxy or hydroxy substituents are present on the benzonitrile core, the [2+2] photocycloaddition is favored. When compound **3** was irradiated, the tricyclic compound **4** was obtained.<sup>21</sup> Despite the ring constrains the [2+2] cycloaddition takes place in the 1,2-position of the benzonitrile ring (**C**).



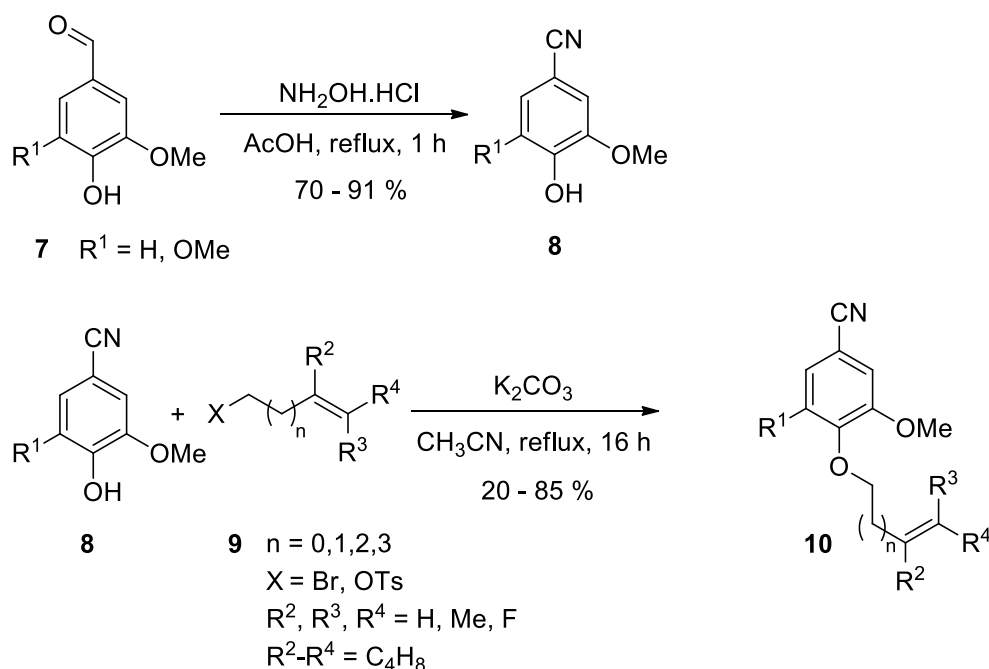
Scheme 1. Selected examples from [2+2] photocycloaddition of phenol derivatives.

In this context, we started our investigations on lignin derived phenol compounds carrying more than one hydroxyl function. We started our investigation with the photochemical transformation of the vanillin derivative **5**. The corresponding [2+2] photocycloadduct **6** was isolated only in low yield.



Scheme 2. Unselective [2+2] photocycloaddition of the vanillin derivative **5**.

As previously mentioned, the nitrile group may be a strong electron withdrawing substituent inducing an efficient [2+2] photocycloaddition in such substrates. Corresponding compounds are easily available. The transformation of aromatic aldehydes **7** into nitriles **8** was carried out by condensation with hydroxylamine under acidic conditions (Scheme 3).<sup>28</sup> The final products **10** have been obtained by O-alkylation with the corresponding alkenyl bromides or tosylates **9**.<sup>29</sup> Only in case of the fluorinated compound **9** ( $R^2, R^3, R^4 = \text{F}$ ), the reaction was less efficient. A competing reaction involving elimination of HBr at the alkene took place (see experimental section). The yield of this O-alkylation was 20%.

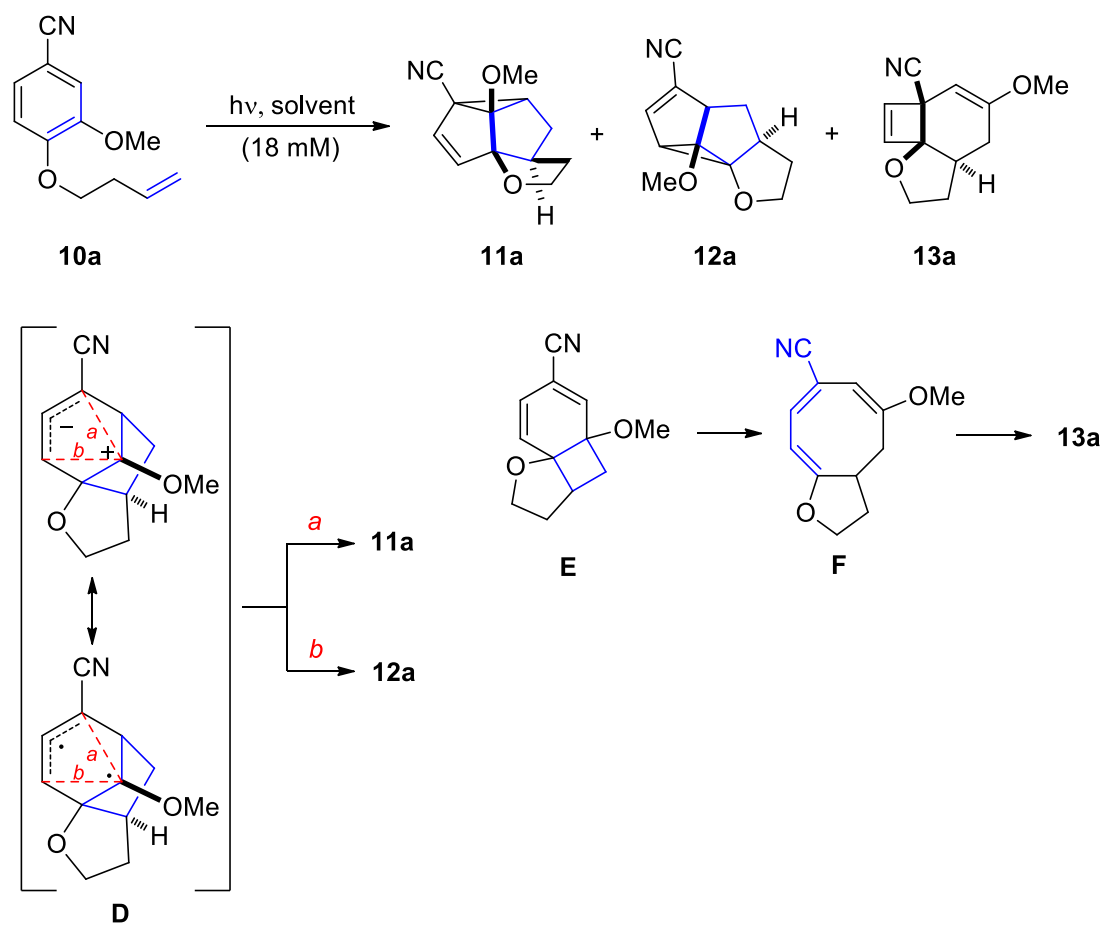


Scheme 3. Synthesis of the starting compounds of the photochemical reactions.

We started our investigation with photochemical transformations of compound **10a**. Compounds **11a** and **12a** have been isolated as major products resulting from a [2+3] or metacycloaddition (Scheme 4).

Compound **13a** results from a [2+2] or ortho photocycloaddition and was obtained as minor product (Table 1). This result was quite surprising. As pointed out above, we expected that the formation of [2+2] adducts should be highly favored. According to the accepted mechanism for the meta photocycloaddition, the polarized diradical intermediate **D** is formed.<sup>7,9,10</sup> Charge combination according to pathway *a* leads to the final product **11a** and combination according to pathway *b* yields the final product **12a**. Compound **13a** results from an initial [2+2] photocycloaddition. According to the accepted mechanism<sup>8,9,10</sup>, the [2+2] adduct **E** is transformed in a thermal (**F**) and a photochemical electrocyclic reaction into the final product **13a**. It should be pointed out, that for both the [2+3] (**D**) and the [2+2] cycloaddition (**E**), the attack of the alkene to the electronically excited benzonitrile moiety occurs at the same side and close to the methoxy substituent. Depending on the reaction conditions, different product ratios were observed (Table 1). Concerning isolated product yields acetonitrile as solvent (entries 4-8) was comparable to methanol (entries 1-3). The irradiation time and the wavelength had also a significant influence on the results. Most interestingly, compound **12a** could not be isolated when the reaction was carried out at 254 nm (entries 3-5). When the irradiation was performed at 300 nm, only very prolonged irradiation (entry-7) led to similar results. Under these conditions, it was further observed that the yield of **11a** increased. Obviously a part of the latter compound results from a photochemical reaction of **12a**. This reaction step is more efficient under irradiation at 254 nm. In acetonitrile compound **13a** underwent slowly photochemical decomposition upon prolonged irradiation (compare entries 6 and 7). The decomposition of the photocyclization products is more efficient at irradiation at 254 nm (entries 3-5). In order to get further information on this competition, we performed a kinetic study. A 49 mM solution was irradiated in a quartz NMR tube at 300 nm and spectra of the reaction mixture were recorded at different times (Figure 1). We observed that the starting compound **10a** was rapidly transformed and compounds **11a**, **12a** as well as **13a** were formed in competition. After consumption of **10a** the formation of **13a** stopped. No significant decomposition of this compound was observed. After about 30 min, the concentration of **12a** reached a maximum and then decreased while the concentration of **11a** continued to increase. Obviously, the linear isomer **12a** was transformed into **11a**. It was also shown that isolated compound **12a** is transformed into **11a** under these reaction conditions with a yield of 50%. No formation of the starting compound **10a** was detected. Therefore, we concluded that this transformation occurs via a vinyl-cyclopropane rearrangement in which intermediate **D** is involved.<sup>30</sup> The corresponding photo-stationary equilibrium is completely shifted to **11a** due to the presence of the  $\alpha,\beta$ -unsaturated nitrile chromophore in **12a** (compare UV spectra in supporting information, Figures S4 and S5). In order to check whether this rearrangement is thermic, we have first irradiated compound **10a** in a sealed quartz NMR tube in deuterated methanol at 300 nm for 100 minutes until full conversion of **10a**. The

reaction mixture was then heated at 70°C with a water bath in the dark. No further transformation of **12a** into **11a** was observed (Figure 2). Under the investigated reaction conditions, the vinyl-cyclopropane rearrangement therefore proceeds photochemically and not thermally.



Scheme 4. Highly favored formation of meta photocycloadducts in the intramolecular reaction of compound **10a**.

Table 1. Product yields depending on the reaction conditions (Scheme 1). <sup>a)</sup>18 mM solutions of **10a** were irradiated in quartz tubes in rayonet reactor.

Entry	Wavelength (nm)	Solvent <sup>a)</sup>	Irradiation Time (h)	Total	Yield (%)		
					<b>11a</b>	<b>12a</b>	<b>13a</b>
1	300	MeOH	2	84	50	27	7
2	300	MeOH	2.5	89	57	25	7
3	254	MeOH	2.5	63	61	0	2
4	254	MeCN	2	66	59	0	7
5	254	MeCN	2.25	57	54	0	3
6	300	MeCN	2.5	92	52	31	9
7	300	MeCN	8	66	61	0	5

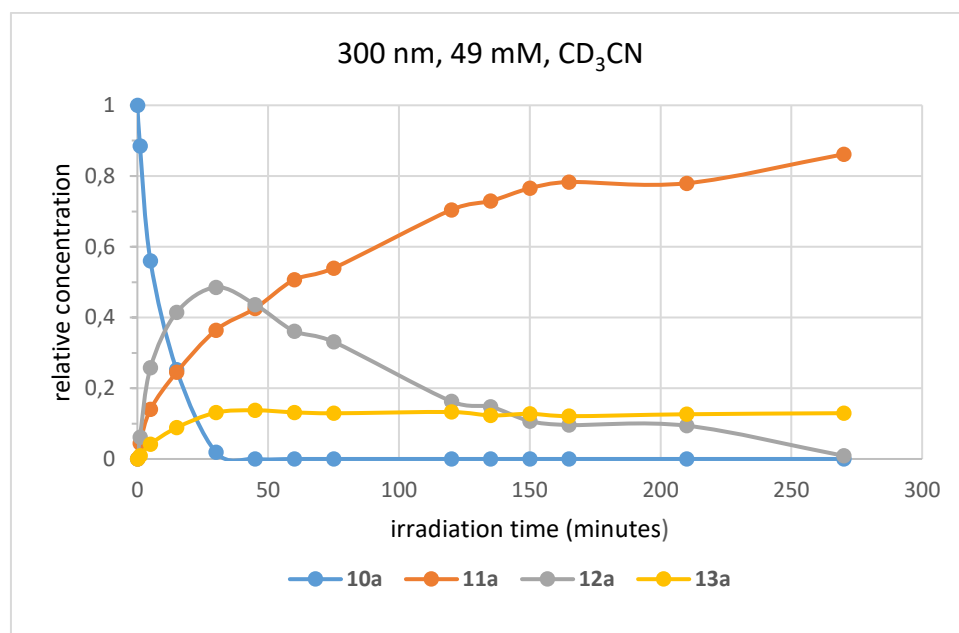


Figure 1. Kinetic of the photochemical transformation of compound **10a**.



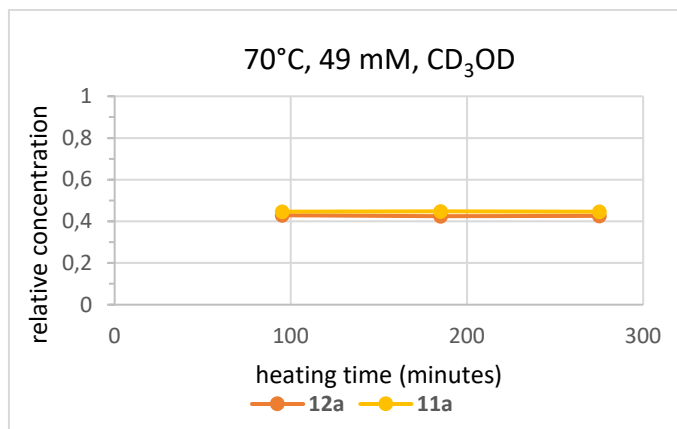
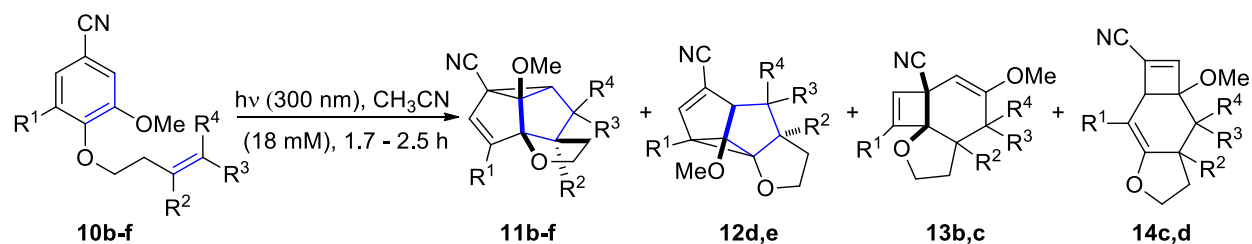


Figure 2. Relative concentrations of **11a** and **12a** in CD<sub>3</sub>OD in NMR tubes heated at 70°C in the dark.

First attempts were made to determine scope and limitation of the reaction. In the case of compound **10b** carrying a 3-methylbut-3-enyl side chain (Table 2, entry 1), after the reaction time, only the meta adduct **11b** was isolated concomitantly with **13b** the latter resulting from a [2+2] photocycloaddition. After 2.5h of irradiation no starting material was detected and the photostationary equilibrium was established. No linear meta-adduct was detected in the reaction mixture. Compound **10c** carrying two methyl groups in the 4 position of the butenyl side chain, was irradiated under the same conditions (entry 2). In this case, a larger proportion of the angular compound **13c** and the linear derivative **14c** resulting from the dominant [2+2] photocycloaddition was isolated. The linear compound was isolated as a mixture of *syn/anti* isomers. We have observed that the *syn* isomer undergoes isomerization to the thermodynamically more stable *anti* isomer or decomposition in a dark reaction (Scheme 6). In the case of the reaction of **10d** (entry 3), a smaller portion of the *anti* isomer of the linear compound **14d** (cyclobutene ring and trihydrofuran ring are *anti* oriented) was isolated as a mixture with **11d**. No [2+2] photocycloaddition products were isolated from the transformation of compound **10e** carrying a trifluoroethylene moiety on the side chain (entry 5). In this case, an angular (**11e**) and a linear (**12e**) meta cycloaddition product were isolated. In the reaction of the corresponding syringaldehyde derivative **10f** (entry 5), we didn't observe any formation of photo products resulting from a [2+2] cycloaddition. Exclusively, the meta adduct **11f** was obtained in good yields. Within this study, it was the most selective reaction.

Further support for the molecular structure was obtained from X-ray structure analysis (Figure 3). Thus the angular regioisomer in compounds **11a,b,c,e** was confirmed. In the same way, the structure of the angular compound **13c** resulting from a [2+2] photocycloaddition was determined.

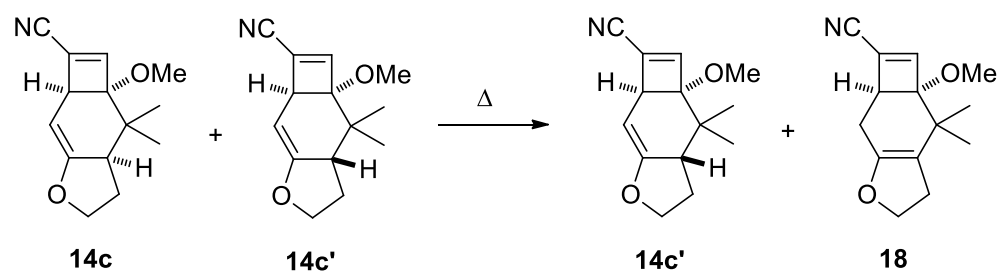


Scheme 5. Intramolecular photocycloaddition of various 3-methoxy-4-butenyloxybenzonitril compounds.

Table 2.

Entry	R	Irradiation Time (h)	Yield (%)				
			Total	<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>
1	$\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}, \text{R}^3 = \text{R}^4 = \text{H}$ ( <b>10b</b> )	2.5	81	71		10	
2	$\text{R}^1 = \text{R}^2 = \text{H}, \text{R}^3 = \text{R}^4 = \text{Me}$ ( <b>10c</b> )	2.0	68	28		14	26 <sup>a)</sup>
3	$\text{R}^1 = \text{H}, \text{R}^2\text{-R}^3 = \text{-(CH}_2\text{)}_4\text{-}, \text{R}^4 = \text{H}$ ( <b>10d</b> )	2.5	68	41	17		10 <sup>b)</sup>
4	$\text{R}^1 = \text{H}, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{F}$ ( <b>10e</b> )	2.7	62	19	43		
5	$\text{R}^1 = \text{OMe}, \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$ ( <b>10f</b> )	1.5	63	63			

<sup>a)</sup> A 7:3 *syn/anti* mixture of diastereoisomers was obtained. <sup>b)</sup> Only the *anti* diastereoisomer was formed and isolated as a mixture with **11d**.



Scheme 6. Transformation of **14c** in the NMR tube overnight.

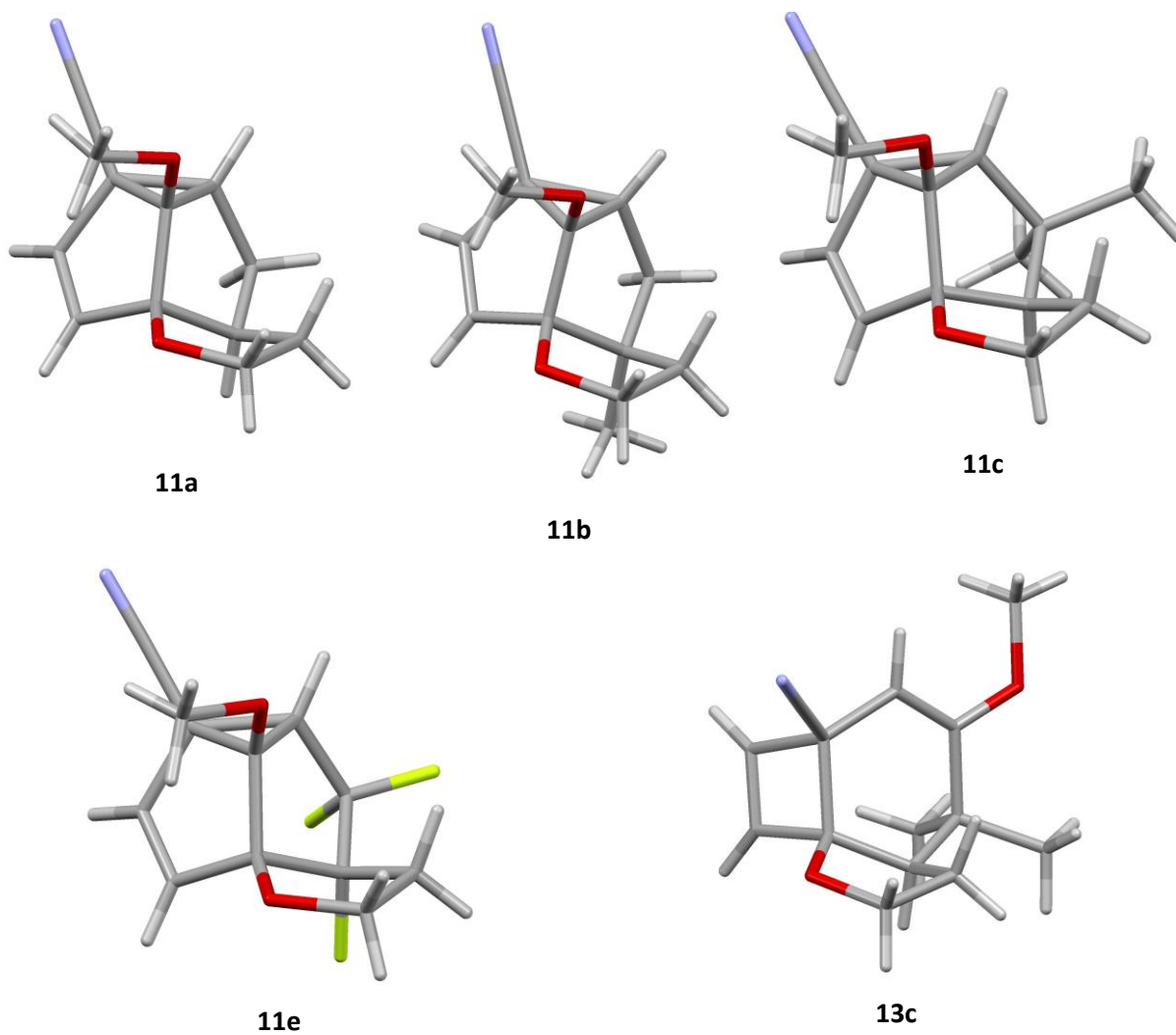
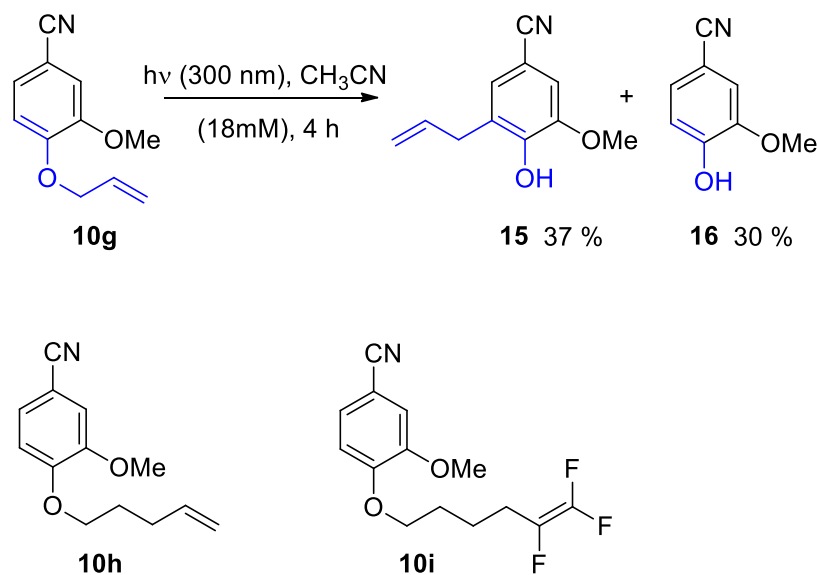


Figure 3. X-ray structure analysis photocycloaddition products **11a,b,c,e** and **13c**.

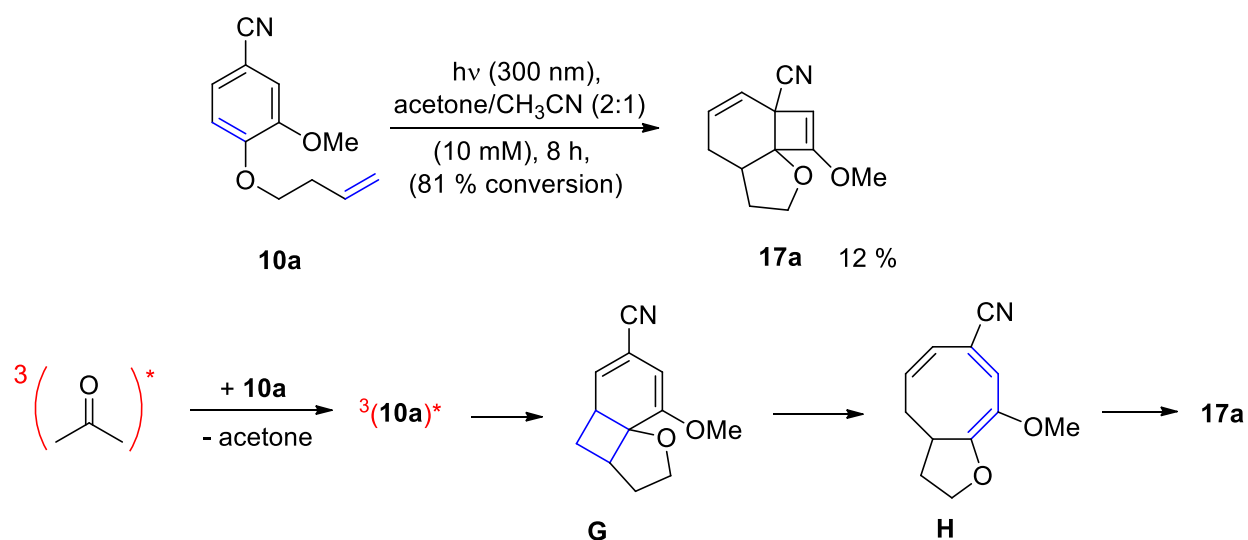
We synthesized also vanillin derived benzonitrile compounds with shorter and longer side chains (Scheme 7). From the reaction of the allyl derivative **10g**, we obtained compound **15** resulting from photo Claisen rearrangement<sup>31</sup> along with compound **16**. In the case of compounds **10h** and **10i**, only a slow and very unselective photochemical reaction was observed under the herein reported conditions.



Scheme 7. Photochemical reactivity of 3-methoxy-4-butenyloxybenzonitril compounds with shorter or longer side chains.

Many photocycloadditions of benzene derivatives with alkenes occur at the singlet state.<sup>7,8</sup> Previously, triplet reactions have been reported with similar compounds carrying carbonyl function as electron withdrawing substituent instead of a nitrile function.<sup>24,25</sup> In order to check a possible triplet ( $T_1$ ) reaction with our compounds, we performed the transformation of **10a** in the presence of larger amounts of acetone (Scheme 8). Under the irradiation conditions, acetone is electronically excited and transfer its triplet energy to the substrate **10a**. Intramolecular [2+2] photocycloaddition takes place and the regio isomer **G** is formed. This isomer is different from the isomer **E** (Scheme 4) which is formed in a singlet ( $S_1$ -state) reaction. Such a regioselectivity has previously been observed in reaction of a similar compound which carries an acyl function instead of the nitrile function.<sup>32</sup> It should further be pointed out that we obtained such a primary photoadduct (**6**) from the reaction of the vanillin derivative **5** (Scheme 2). Such acetophenone or benzaldehyde derivatives react preferentially at their triplet state. In the present case the intermediate **G** undergoes a thermal electrocyclic reaction leading to the cyclooctatriene intermediate **H**. In a photochemical electrocyclic reaction the final product **17a** is formed. This reaction step is also affected by the spin multiplicity.<sup>33</sup> In the present case, the best yield of **17a** was only 12%. When the ratio acetone/acetonitrile was increased, the reaction became less selective. When the concentration of acetone was diminished, the formation of the singlet products **11a**, **12a** and **13a** was

detected. We have tested other sensitizers such as benzophenone, 4,4'-dimethoxybenzophenone or thioxanthone without success.



Scheme 8. Triplet sensitized reaction of the 3-methoxy-4-butenyloxybenzonitril derivative **11a**.

## Conclusion

We have performed intramolecular photocycloadditions of vanillin derivatives carrying an alkene side chain. In order to increase the efficiency, the aldehyde function was replaced by a nitrile function as electron withdrawing substituent. Often [2+2] photocycloadditions with consecutive rearrangements have been reported with such substrates. In contrast to this, we observed mainly [2+3] photocycloadditions with our substrates. A [2+2] cycloaddition is sometimes observed as side reaction. With a corresponding syringaldehyde derivative only [2+3] cycloaddition was observed. Most probably, the singlet excited state ( $S_1$ ) is involved in these reactions. The presence of one or two additional alkoxy substituents on the benzene ring favors the [2+3] reaction mode. The influence of the nitrile function favoring the [2+2] cycloaddition is thus reduced. The regioselectivity of the meta cycloadducts (angular versus linear isomers) is increased by an efficient vinyl-cyclopropane rearrangement. The reaction was also carried out under triplet sensitizing conditions with acetone. In this case, only a [2+2] photocycloaddition product with different regioselectivity was isolated in low yields.

## Experimental Section

**General Methods.** Photochemical reactions were performed using either a Rayonet RPR-200 photochemical reactor fitted with 16 RPR-3000 Å fluorescent lamps or a Rayonet RPR-100 photochemical reactor fitted with 6 RPR-2537 Å fluorescent lamps. Melting points were measured in open capillary tubes on a Stuart SMP3 apparatus and are uncorrected. NMR spectra were recorded on Bruker spectrometers operating at 500 MHz or 600 MHz for  $^1\text{H}$ , 126 MHz or 151 MHz for  $^{13}\text{C}\{^1\text{H}\}$  and 471 MHz for  $^{19}\text{F}$ . For  $^1\text{H}$  NMR spectra, chemical shifts are reported in parts per million (ppm) with reference to tetramethylsilane ( $\delta = 0.00$  ppm) or residual protonated solvent ( $\delta = 7.26$  ppm for  $\text{CHCl}_3$ ,  $\delta = 1.94$  ppm for  $\text{CD}_3\text{CN}$ ) as internal standard. For  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, chemical shifts are reported in parts per million (ppm) with reference to the deuterated solvent ( $\delta = 77.16$  ppm for  $\text{CDCl}_3$ ,  $\delta = 1.03$  ppm for  $\text{CD}_3\text{CN}$ ) as an internal standard. Splitting patterns for  $^1\text{H}$  signals are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br. (broad), or virt. (virtual) and coupling constants ( $J$ ) are reported in Hz. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. Infrared (IR) spectra were recorded for all samples on a FT-IR Perkin Elmer Spectrum Two using an ATR diamond accessory, maximum absorbance ( $\nu$ ) are given in  $\text{cm}^{-1}$ . UV absorption spectra were recorded with a UVKON 941 PLUS (KONTRON Instruments) in MeCN using 1 cm quartz cuvettes. High-resolution mass spectrometry (HR-MS) data were recorded using a spectrometer equipped with an electrospray ionization source (ESI-MS) in positive mode associated with a TOF analyzer. MeCN was purchased from Carlo Erba (HPLC quality) and used as received. Organic extracts were dried over magnesium sulfate (VWR Chemicals, 98%) before evaporation under reduced pressure. Column chromatography was performed on silica gel columns (40–63  $\mu\text{m}$ ). Analytical thin-layer chromatography was carried out with Kieselgel 60F254 plates from Merck. Retention factors ( $R_f$ ) are given for such TLC analyses. Vanillin, Syringaldehyde, Allyl bromide, 4-bromo-1-butene, 3-Methyl-3-buten-1-ol, 5-bromo-1-pentene, 5-bromo-2-methyl-2-pentene, 4-bromo-1,1,2-trifluoro-1-butene, 6-bromo-1,1,2-trifluoro-1-hexene, and 1-Cyclohexene-1-acetic acid were purchased from Merck. Vanillonitrile,<sup>28</sup> Syringonitrile,<sup>34</sup> 3-Buten-1-ol, 3-methyl-1-(4-methylbenzenesulfonate)<sup>35</sup> and 2-(1-Cyclohexen-1-yl)ethanol tosylate<sup>36</sup> were prepared according to the literature, and their spectroscopic data are in agreement with those previously reported. Compounds were crystallized via slow evaporation at room temperature of a petroleum ether/diethyl ether (1:1) solution for **11a**, **11c**, **11e**, **13c** and a petroleum ether/ethyl acetate (9:1) solution for **11b**. X-ray diffraction: data for **11a**, **11b**, **11c**, **11e** and **13c** were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N<sub>2</sub> device, using a molybdenum microfocus sealed tube generator with mirror-monochromated Mo-K $\alpha$  radiation ( $\lambda =$

0.71073 Å), operated at 50 kV/600 mA. The diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).<sup>37</sup> They can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/datarequest/cif](http://www.ccdc.cam.ac.uk/datarequest/cif). CCDC N° 2088122, 2087598-2087601.

**General procedure for the alkylation.** *Based on a literature procedure described by Lipshutz et al.*<sup>29</sup> To a solution of aromatic alcohol (2.0 mmol) and K<sub>2</sub>CO<sub>3</sub> (5.0 mmol) in MeCN (8.0 mL) was added the alkenyl halide (4.0 mmol) and the mixture was refluxed with a heat transfer block for 14 h. It was then cool to 22 °C and the solvent was removed *in vacuo*. The residue was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and water and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 10 mL). The combined organic extracts were washed with water (2 x 10 mL), dried and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (SiO<sub>2</sub>, solvent, detection mode).

**4-(but-3-en-1-yloxy)-3-methoxybenzaldehyde (5).** The representative procedure was followed using Vanilline (0.5 g, 3.3 mmol), K<sub>2</sub>CO<sub>3</sub> (1.14 g, 8.2 mmol) and 4-bromo-1-butene (0.7 mL, 6.6 mmol) in MeCN (30 mL). Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded the product **5** (568 mg, 84 %) as white crystals. Spectroscopic data are in agreement with those previously reported.<sup>38</sup>

**4-(but-3-en-1-yloxy)-3-methoxybenzotrile (10a).** The representative procedure was followed using Vanillonitrile (2.0 g, 13.4 mmol), K<sub>2</sub>CO<sub>3</sub> (4.63 g, 33.5 mmol) and 4-bromo-1-butene (2.7 mL, 26.8 mmol) in MeCN (60 mL). Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded the product **10a** (2.1 g, 77%) as white crystals. Mp. : 43-44 °C. *R*<sub>f</sub> = 0.35 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.25 (dd, *J* = 8.3, 1.9 Hz, 1H; Ar-H), 7.08 (d, *J* = 1.9 Hz, 1H; Ar-H), 6.89 (d, *J* = 8.3 Hz, 1H; Ar-H), 5.89 (ddt, *J* = 17.2, 10.3, 6.7 Hz, 1H; CH), 5.19 (ddt, *J* = 17.2, 1.5, 1.4 Hz, 1H; CH<sub>2</sub>), 5.14 (ddt, *J* = 10.3, 1.5, 1.3 Hz, 1H; CH<sub>2</sub>), 4.11 (t, *J* = 7.0 Hz, 2H; CH<sub>2</sub>), 3.88 (s, 3H; CH<sub>3</sub>), 2.62 (tddd, *J* = 7.0, 6.7, 1.4, 1.3 Hz, 2H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 152.5 (Cq), 149.6 (Cq), 133.7 (CH), 126.5 (CH), 119.4 (CN), 117.8 (CH<sub>2</sub>), 114.6 (CH), 112.6 (CH), 104.0 (Cq), 68.4 (CH<sub>2</sub>), 56.4 (CH<sub>3</sub>), 33.4 (CH<sub>2</sub>). IR ν (cm<sup>-1</sup>) = 3078, 3016, 2219, 1639, 1596, 1580, 993, 972, 926, 919, 865. HRMS (ESI) : *m/z* [M+H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>14</sub>NO<sub>2</sub>]<sup>+</sup> : 204.1025, found : 204.1026.

**3-methoxy-4-((3-methylbut-3-en-1-yl)oxy)benzotrile (10b).** The representative procedure was followed using Vanillonitrile (0.3 g, 2.1 mmol), K<sub>2</sub>CO<sub>3</sub> (0.7 g, 5 mmol) and 3-Buten-1-ol, 3-methyl-, 1-(4-methylbenzenesulfonate) (1.0 g, 4.2 mmol) in MeCN (15 mL). Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded the product **10b** (388 mg, 85 %) as white crystals. Mp. : 43-45 °C. *Rf* = 0.30 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.26 (dd, *J* = 8.3, 1.9 Hz, 1H; Ar-H), 7.07 (d, *J* = 1.9 Hz, 1H; Ar-H), 6.90 (d, *J* = 8.3 Hz, 1H; Ar-H), 4.86 (virt. s, 1H; CH<sub>2</sub>), 4.80 (virt. s, 1H; CH<sub>2</sub>), 4.16 (virt. t, *J* = 7.2 Hz, 2H; CH<sub>2</sub>), 3.87 (s, 3H; CH<sub>3</sub>), 2.57 (virt. t, *J* = 7.2 Hz, 2H; CH<sub>2</sub>), 1.81 (virt. s, 3H; CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 152.5 (Cq), 149.6 (Cq), 141.6 (Cq), 126.5 (CH), 119.4 (CN), 114.6 (CH), 112.6 (CH), 112.5 (CH<sub>2</sub>), 104.0 (Cq), 67.8 (CH<sub>2</sub>), 56.4 (CH<sub>3</sub>), 36.9 (CH<sub>2</sub>), 23.0 (CH<sub>3</sub>). IR ν (cm<sup>-1</sup>) = 3079, 3004, 2219, 1651, 1596, 1578, 870, 866. HRMS (ESI) : *m/z* [M+H]<sup>+</sup> calcd for [C<sub>13</sub>H<sub>16</sub>NO<sub>2</sub>]<sup>+</sup> : 218.1181, found : 218.1183.

**3-methoxy-4-((4-methylpent-3-en-1-yl)oxy)benzotrile (10c).** The representative procedure was followed using Vanillonitrile (0.4 g, 2.68 mmol), K<sub>2</sub>CO<sub>3</sub> (0.9 g, 6.7 mmol) and 5-bromo-2-methyl-2-pentene (0.39 mL, 2.95 mmol) in MeCN (20 mL). Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded the product **10c** (0.3 g, 48%) as white crystals. Mp. : 55 °C. *Rf* = 0.25 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.26 (dd, *J* = 8.3, 1.9 Hz, 1H; Ar-H), 7.07 (d, *J* = 1.9 Hz, 1H; Ar-H), 6.88 (d, *J* = 8.3 Hz, 1H; Ar-H), 5.18 (tqq, *J* = 7.2, 1.3, 1.2 Hz, 1H; CH), 4.01 (t, *J* = 7.3 Hz, 2H; CH<sub>2</sub>), 3.88 (s, 3H; CH<sub>3</sub>), 2.56 (td, *J* = 7.3, 7.2 Hz, 2H; CH<sub>2</sub>), 1.73 (d, *J* = 1.3 Hz, 3H; CH<sub>3</sub>), 1.66 (d, *J* = 1.2 Hz, 3H; CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 152.6 (Cq), 149.6 (Cq), 135.4 (Cq), 126.5 (CH), 119.5 (CN), 118.7 (CH), 114.5 (CH), 112.5 (CH), 103.8 (Cq), 68.7 (CH<sub>2</sub>), 56.3 (CH<sub>3</sub>), 28.1 (CH<sub>2</sub>), 25.9 (CH<sub>3</sub>), 18.0 (CH<sub>3</sub>). IR ν (cm<sup>-1</sup>) = 2972, 2922, 2223, 1685, 1582, 1512, 794, 784, 765. HRMS (ESI) : *m/z* [M+H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub>]<sup>+</sup> : 232.1338, found : 232.1337.

**4-(2-(cyclohex-1-en-1-yl)ethoxy)-3-methoxybenzotrile (10d).** The representative procedure was followed using Vanillonitrile (0.5 g, 3.6 mmol), K<sub>2</sub>CO<sub>3</sub> (1.2 g, 9.0 mmol) and 2-(1-Cyclohexen-1-yl)ethanol tosylate (1.0 g, 3.6 mmol) in MeCN (30 mL). Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded the product **10d** (0.4 g, 42 %) as white crystals. Mp. : 99 °C. *Rf* = 0.22 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.25 (dd, *J* = 8.4, 1.9 Hz, 1H; Ar-H), 7.07 (d, *J* = 1.9 Hz, 1H; Ar-H), 6.89 (d, *J* = 8.4 Hz, 1H; Ar-H), 5.52 (virt. s, 1H; CH), 4.11 (t, *J* = 7.5 Hz, 2H; CH<sub>2</sub>), 3.87 (s, 3H; CH<sub>3</sub>), 2.48 (t, *J* = 7.5 Hz, 2H; CH<sub>2</sub>), 1.99 (m, 4H; 2CH<sub>2</sub>), 1.63 (m, 2H; CH<sub>2</sub>), 1.55 (m, 2H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 152.4 (Cq), 149.4 (Cq), 133.4 (Cq), 126.5 (CH), 124.0 (CH), 119.5 (CN), 114.2 (CH), 112.3 (CH), 103.6 (Cq), 68.2 (CH<sub>2</sub>), 56.3 (CH<sub>3</sub>), 37.2 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>), 22.9 (CH<sub>2</sub>),



22.3 (CH<sub>2</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 2919, 2224, 1596, 1581, 872, 799. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>16</sub>H<sub>20</sub>NO<sub>2</sub>]<sup>+</sup> : 258.1494, found : 258.1497.

**4-(but-3-en-1-yloxy)-3,5-dimethoxybenzonitrile (10f).** The representative procedure was followed using Syringonitrile (1 g, 5.6 mmol), K<sub>2</sub>CO<sub>3</sub> (2 g, 14 mmol) 4-bromo-1-butene (1.2 mL, 11 mmol) in MeCN (30 mL). Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 8.5:1.5, UV) afforded the product **10f** (679 mg, 52 %) as white crystals. Mp. : 34-36 °C. *Rf* = 0.29 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.84 (s, 2H; Ar-H), 5.87 (ddt, *J* = 17.2, 10.4, 6.7 Hz, 1H; CH), 5.13 (ddt, *J* = 17.2, 1.7, 1.6 Hz, 1H; CH<sub>2</sub>), 5.05 (ddt, *J* = 10.4, 1.7, 1.2 Hz, 1H; CH<sub>2</sub>), 4.06 (t, *J* = 7.0 Hz, 2H; CH<sub>2</sub>), 3.84 (s, 6H; 2CH<sub>3</sub>), 2.49 (ttdd, *J* = 7.0, 6.7, 1.6, 1.2 Hz, 2H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  153.8 (2Cq), 141.5 (Cq), 134.5 (CH), 119.1 (CN), 116.8 (CH<sub>2</sub>), 109.5 (2CH), 106.7 (Cq), 72.8 (CH<sub>2</sub>), 56.4 (2CH<sub>3</sub>), 34.5 (CH<sub>2</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 3071, 2937, 2227, 1579, 913, 855. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>13</sub>H<sub>16</sub>NO<sub>3</sub>]<sup>+</sup> : 234.1130, found : 234.1131.

**4-(allyloxy)-3-methoxybenzonitrile (10g).** The representative procedure was followed using Vanillonitrile (2.0 g, 13 mmol), K<sub>2</sub>CO<sub>3</sub> (4.6 g, 33 mmol) and allyl bromide (2.3 mL, 26 mmol) in MeCN (90 mL). Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded the product **10g** (1.9 g, 78 %) as white crystals. Mp.: 63 °C. *Rf* = 0.25 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.23 (m, 1H; Ar-H), 7.07 (m, 1H; Ar-H), 6.88 (m, 1H; Ar-H), 6.04 (m, 1H; CH), 5.41 (m, 1H; CH<sub>2</sub>), 5.32 (m, 1H; CH<sub>2</sub>), 4.64 (m, 2H; CH<sub>2</sub>), 3.88 (m, 3H; CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  151.9 (Cq), 149.5 (Cq), 132.1 (CH), 126.2 (CH), 119.2 (CN), 118.9 (CH<sub>2</sub>), 114.3 (CH), 112.8 (CH), 104.0 (Cq), 69.8 (CH<sub>2</sub>), 56.2 (CH<sub>3</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 3021, 2984, 2222, 1596, 1582, 944, 927, 863, 805. HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>11</sub>H<sub>12</sub>NO<sub>2</sub>]<sup>+</sup> : 190.0868, found : 190.0867.

**3-methoxy-4-(pent-4-en-1-yloxy)benzonitrile (10h).** The representative procedure was followed using Vanillonitrile (1 g, 6.7 mmol), K<sub>2</sub>CO<sub>3</sub> (2.32 g, 16.8 mmol) and 5-bromo-1-pentene (0.8 mL, 6.7 mmol) in MeCN (30 mL). Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded the product **10h** (1.2 g, 81%) as white crystals. Mp. : 50-51 °C. *Rf* = 0.27 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.26 (dd, *J* = 8.3, 1.9 Hz, 1H; Ar-H), 7.08 (d, *J* = 1.9 Hz, 1H; Ar-H), 6.88 (d, *J* = 8.3 Hz, 1H; Ar-H), 5.84 (ddt, *J* = 17, 10.3, 6.6 Hz, 1H; CH), 5.07 (ddt, *J* = 17.1, 1.7, 1.6 Hz, 1H; CH<sub>2</sub>), 5.02 (ddt, *J* = 10.3, 1.7, 1.1 Hz, 1H; CH<sub>2</sub>), 4.06 (t, *J* = 6.7 Hz, 2H; CH<sub>2</sub>), 3.88 (s, 3H; CH<sub>3</sub>), 2.25 (m, 2H; CH<sub>2</sub>), 1.97 (m, 2H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  152.6 (Cq), 149.6 (Cq), 137.5 (CH), 126.5 (CH), 119.5 (CN), 115.7 (CH<sub>2</sub>), 114.5 (CH), 112.5 (CH), 103.8 (Cq), 68.5 (CH<sub>2</sub>), 56.3 (CH<sub>3</sub>), 30.0 (CH<sub>2</sub>), 28.1 (CH<sub>2</sub>). IR

$\nu$  (cm<sup>-1</sup>) = 3077, 2975, 2227, 1644, 1596, 1583, 994, 910, 876, 799, 761. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>13</sub>H<sub>16</sub>NO<sub>2</sub>]<sup>+</sup> : 218.1181, found : 218.1183.

**3-methoxy-4-((5,6,6-trifluorohex-5-en-1-yl)oxy)benzonitrile (10i).** The representative procedure was followed using Vanillonitrile (0.7 g, 4.7 mmol), K<sub>2</sub>CO<sub>3</sub> (1.62 g, 11.7 mmol) and 6-bromo-1,1,2-trifluoro-1-hexene (1.1 mL, 7.0 mmol) in MeCN (30 mL). Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded the product **10i** (880 mg, 73%) as white crystals. Mp. : 44-47 °C. *Rf* = 0.25 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.26 (dd, *J* = 8.3, 1.9 Hz, 1H; Ar-H), 7.08 (d, *J* = 1.9 Hz, 1H; Ar-H), 6.88 (d, *J* = 8.3 Hz, 1H; Ar-H), 4.07 (t, *J* = 6.4 Hz, 2H; CH<sub>2</sub>), 3.88 (s, 3H; CH<sub>3</sub>), 2.38 (m, 2H; CH<sub>2</sub>), 1.91 (m, 2H; CH<sub>2</sub>), 1.76 (m, 2H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  153.4 (ddd, *J* = 286.1, 272.2, 47.4 Hz; CF<sub>2</sub>), 152.4 (Cq), 150.0 (Cq), 128.5 (ddd, *J* = 234.6, 53.4, 15.3 Hz; CF), 126.5 (CH), 119.4 (CN), 114.4 (CH), 112.5 (CH), 104.0 (Cq), 68.6 (CH<sub>2</sub>), 56.3 (CH<sub>3</sub>), 28.1 (CH<sub>2</sub>), 25.4 (dd, *J* = 22.0, 1.7 Hz; CH<sub>2</sub>), 22.2 (CH<sub>2</sub>). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) :  $\delta$  -105.3 (dd, *J* = 88.7, 32.3 Hz, 1F; C-F), -124.5 (dd, *J* = 114.1, 88.7 Hz, 1F; C-F<sub>2</sub>), -174.5 (dd, *J* = 114.1, 32.3 Hz, 1F; C-F<sub>2</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 2945, 2870, 2223, 1797, 1597, 1581, 990, 877, 817, 797, 737, 693. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>15</sub>F<sub>3</sub>NO<sub>2</sub>]<sup>+</sup> : 286.1055, found : 286.1057.

**Procedure for the preparation of 3-methoxy-4-((3,4,4-trifluorobut-3-en-1-yl)oxy)benzonitrile (10e).** To a solution of Vanillonitrile (0.7 g, 4.7 mmol), dried Cs<sub>2</sub>CO<sub>3</sub> (4.59 g, 14.1 mmol), CsI (0.5 g, 1.8 mmol) in MeCN (30 mL) was added 1-Butene,4-bromo-1,1,2-trifluoro-, (2.2 mL, 14.1 mmol) and the mixture was heated at 70 °C with a heat transfer block for 14 h. It was then cool to 22 °C and the solvent was removed *in vacuo*. The residue was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and water and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 30 mL). The combined organic extracts were washed with water (2 x 30 mL), dried and concentrated *in vacuo*. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded the desired product **10e** (0.24 g, 20 %) as white crystals and product **10j** (0.2 g, 18 %) as an amorphous solid.

**3-methoxy-4-((3,4,4-trifluorobut-3-en-1-yl)oxy)benzonitrile (10e).** Mp. : 54-55 °C.

*Rf* = 0.30 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.26 (dd, *J* = 8.3, 1.9 Hz, 1H; Ar-H), 7.10 (d, *J* = 1.9 Hz, 1H; Ar-H), 6.89 (d, *J* = 8.3 Hz, 1H; Ar-H), 4.23 (t, *J* = 6.6 Hz, 2H; CH<sub>2</sub>), 3.88 (s, 3H; CH<sub>3</sub>), 2.85 (m, 2H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  154.2 (ddd, *J* = 287.1, 274.2, 45.9 Hz; CF<sub>2</sub>), 151.9 (Cq), 149.8 (Cq), 126.4 (CH), 126.1 (ddd, *J* = 235.0, 53.6, 17.5 Hz; CF), 119.2 (CN), 114.9 (CH), 113.2 (CH), 104.9 (Cq), 64.6 (CH<sub>2</sub>), 56.4 (CH<sub>3</sub>), 26.5 (dd, *J* = 22.0, 1.7 Hz; CH<sub>2</sub>). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) :  $\delta$  -102.5

(dd,  $J = 83.9, 32.9$  Hz, 1F; C-F), -122.9 (dd,  $J = 114.3, 83.9$  Hz, 1F; C-F<sub>2</sub>), -175.3 (dd,  $J = 114.3, 32.9$  Hz, 1F; C-F<sub>2</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 3015, 2945, 2885, 2841, 2223, 1802, 1600. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>11</sub>NO<sub>2</sub>F<sub>3</sub>]<sup>+</sup> : 258.0742, found : 258.0744.

**((1,2-difluorobuta-1,3-dien-1-yl)oxy)-3-methoxybenzotrile (10j)**.  $R_f = 0.40$  (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.26 (dd,  $J = 8.3, 1.9$  Hz, 1H; Ar-H), 7.21 (d,  $J = 1.9$  Hz, 1H; Ar-H), 7.12 (d,  $J = 8.3$  Hz, 1H; Ar-H), 6.42 (m, 1H; CH), 5.54 (d,  $J = 17.4$  Hz, 1H; CH<sub>2</sub>), 5.29 (m, 1H; CH<sub>2</sub>), 3.93 (s, 3H; CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  149.8 (Cq), 147.3 (dd,  $J = 277.7, 44.5$  Hz; CF), 147.1 (Cq), 135.8 (dd,  $J = 233.8, 56.0$  Hz; CF), 125.7 (CH), 121.9 (dd,  $J = 19.4, 4.8$  Hz; CH), 118.3 (CN), 117.1 (CH), 116.1 (CH), 114.8 (CH<sub>2</sub>), 108.9 (Cq) 56.6 (CH<sub>3</sub>). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) :  $\delta$  -120.7 (m, 1F; CF), -173.1 (dd,  $J = 110.8, 26$  Hz, 1F; CF). IR  $\nu$  (cm<sup>-1</sup>) = 2987, 2229, 1599, 913, 856, 822. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>10</sub>NO<sub>2</sub>F<sub>2</sub>]<sup>+</sup> : 238.0680, found : 238.0683.

**General procedure for photochemical reactions.** In a 20 mL quartz glass tube ( $\varnothing=1.1$  cm), 4-(but-3-en-1-yloxy)-3-methoxybenzotrile (54 mg, 0.27 mmol) was introduced and MeCN (15 mL) was added. The tube was equipped with a septum and the mixture was degassed (argon flow, 10 min). The mixture was irradiated at  $\lambda = 300$  nm at room temperature until reaction control (TLC) indicated full conversion of starting material. If full conversion was not reached within 8 h, irradiation was stopped. The solvent was evaporated under reduce pressure, and the crude product was purified by silica gel column chromatography (SiO<sub>2</sub>, solvent, detection mode).

### 8-methoxy-3,3a,4,4a-tetrahydro-2H-benzo[1,4]cyclobuta[1,2-b]furan-6-

carbaldehyde (**6**). The product was prepared following the general procedure for photochemical reactions using 4-(but-3-en-1-yloxy)-3-methoxybenzaldehyde **5** (7 mg, 0.034 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 20 minutes. The solvent was evaporated under reduce pressure at 30 °C. Column chromatography (neutral Al<sub>2</sub>O<sub>3</sub>, petroleum ether/ethyl acetate = 9:1, UV) afforded product **6** as a yellowish oil. An isolated yield could not be precisely determined because **6** is unstable. Using 1,3-Dimethoxybenzene as internal standard (17 mg, 0.123 mmol added after irradiation) a NMR yield of 30 % was determined for product **6**.  $R_f = 0.13$  (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.37 (s, 1H; CHO), 6.35 (d,  $J = 5.5$  Hz, 1H; CH), 5.62 (s, 1H; CH), 4.25 (m, 2H; CH<sub>2</sub>), 3.68 (s, 3H; CH<sub>3</sub>), 3.41 (m, 1H; CH), 3.29 (m, 1H; CH), 2.14 (m, 2H; CH<sub>2</sub>), 1.98 (m, 1H; CH<sub>2</sub>), 1.78 (m, 1H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  191.5 (CHO), 157.1 (Cq), 141.4 (CH), 136.4 (Cq), 90.1 (CH), 82.6 (Cq), 69.6 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 48.9 (CH), 41.4 (CH), 33.9 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 2938, 1680, 1399, 694. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>15</sub>O<sub>3</sub>]<sup>+</sup> : 207.1021, found : 207.1020.

4a1-methoxy-3,3a,4,4a,4a1,4b-hexahydro-2H-cyclopropa[3,4]-pentaleno-[6a,1-b]furan-4b-carbonitrile (**11a**). The product was prepared following the general procedure for photochemical reactions using 4-(but-3-en-1-yloxy)-3-methoxybenzonitrile **10a** (54 mg, 0.27 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 8 h. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>) afforded the product **11a** (33 mg, 61 %) as a colorless oil. Product **11a** was crystallized as colorless crystals via slow evaporation of a petroleum ether/diethyl ether (1:1) solution at room temperature. Mp. : 90 °C. *Rf* = 0.25 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.78 (d, *J* = 5.9 Hz, 1H; CH), 5.64 (d, *J* = 5.9 Hz, 1H; CH), 4.26 (ddd, *J* = 9.5, 8.3, 1.7 Hz, 1H; CH<sub>2</sub>), 3.97 (ddd, *J* = 10.5, 8.3, 6.4 Hz, 1H; CH<sub>2</sub>), 3.65 (s, 3H; CH<sub>3</sub>), 2.78 (d, *J* = 6.4 Hz, 1H; CH), 2.41–2.32 (m, 1H; CH), 2.06 (m, 1H; CH<sub>2</sub>), 2.00–1.92 (m, 2H; CH<sub>2</sub>), 1.56 (ddd, *J* = 14.8, 6.4, 1.0 Hz, 1H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 135.1 (CH), 121.7 (CH), 118.2 (CN), 98.2 (Cq), 93.4 (Cq), 71.3 (CH<sub>2</sub>), 57.4 (CH<sub>3</sub>), 53.9 (CH), 47.4 (CH), 30.5 (Cq), 28.9 (CH<sub>2</sub>), 24.2 (CH<sub>2</sub>). IR ν (cm<sup>-1</sup>) = 3028, 2967, 2225, 985, 950, 774, 754, 666. HRMS (ESI) : *m/z* [M+H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>14</sub>NO<sub>2</sub>]<sup>+</sup> : 204.1025, found : 204.1025.

4a1-methoxy-3a-methyl-3,3a,4,4a,4a1,4b-hexahydro-2H-cyclo-propa-[3,4]pentaleno[6a,1-b]furan-4b-carbonitrile (**11b**). The product was prepared following the general procedure for photochemical reactions using 3-methoxy-4-((3-methylbut-3-en-1-yl)oxy)benzonitrile **10b** (58 mg, 0.27 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 2h30. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>) afforded the product **11b** (41 mg, 71 %) as a colorless oil. Product **11b** was crystallized as colorless crystals via slow evaporation of a petroleum ether/ethyl acetate (9:1) solution at room temperature. Mp. : 102 °C. *Rf* = 0.33 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.75 (d, *J* = 6.0 Hz, 1H; CH), 5.70 (d, *J* = 6.0 Hz, 1H; CH), 4.22 (ddd, *J* = 10.0, 8.2, 1.5 Hz, 1H; CH<sub>2</sub>), 4.07 (ddd, *J* = 10.6, 8.2, 6.7 Hz, 1H; CH<sub>2</sub>), 3.68 (s, 3H; CH<sub>3</sub>), 2.70 (d, *J* = 6.6 Hz, 1H; CH), 2.34 (ddd, *J* = 12.2, 10.6, 10.0 Hz, 1H, CH<sub>2</sub>), 2.07 (dd, *J* = 14.6, 6.6 Hz, 1H; CH<sub>2</sub>), 1.66 (ddd, *J* = 12.2, 6.7, 1.5 Hz, 1H; CH<sub>2</sub>), 1.27 (d, *J* = 14.6 Hz, 1H; CH<sub>2</sub>), 0.92 (s, 3H; CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 134.4 (CH), 122.9 (CH), 118.4 (CN), 99.5 (Cq), 94.9 (Cq), 69.2 (CH<sub>2</sub>), 60.0 (Cq), 57.4 (CH<sub>3</sub>), 46.0 (CH), 35.0 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 30.0 (Cq), 20.1 (CH<sub>3</sub>). IR ν (cm<sup>-1</sup>) = 3074, 2964, 2229, 991, 970, 870, 797, 725. HRMS (ESI) : *m/z* [M+H]<sup>+</sup> calcd for [C<sub>13</sub>H<sub>16</sub>NO<sub>2</sub>]<sup>+</sup> : 218.1181, found : 218.1179.

4a1-methoxy-4,4-dimethyl-3,3a,4,4a,4a1,4b-hexahydro-2H-cyclopropa-[3,4]pentaleno[6a,1-b]furan-4b-carbonitrile (**11c**). The product was prepared following the general procedure for photochemical reactions using 3-methoxy-4-((4-methylpent-3-en-1-

yl)oxy)benzotrile **10c** (61.7 mg, 0.27 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 2h. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>) afforded the product **11c** (17 mg, 28 %) as a colorless oil. Product **11c** was crystallized as colorless crystals via slow evaporation of a petroleum ether/diethyl ether (1:1) solution at room temperature. Mp. : 107 °C. *Rf* = 0.33 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ 5.82 (d, *J* = 5.8 Hz, 1H; CH), 5.77 (d, *J* = 5.8 Hz, 1H; CH), 4.15 (ddd, *J* = 9.5, 8.2, 1.7 Hz, 1H; CH<sub>2</sub>), 3.83 (ddd, *J* = 11.4, 8.2, 5.3 Hz, 1H; CH<sub>2</sub>), 3.57 (s, 3H; CH<sub>3</sub>), 2.59 (s, 1H; CH), 2.28 (dd, *J* = 11.8, 6.9 Hz, 1H; CH), 2.11 (m, 1H; CH<sub>2</sub>), 1.89 (m, 1H; CH<sub>2</sub>), 1.13 (s, 3H; CH<sub>3</sub>), 1.06 (s, 3H; CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>3</sub>CN): δ 138.0 (CH), 125.1 (CH), 119.4 (CN), 99.3 (Cq), 95.9 (Cq), 71.8 (CH<sub>2</sub>), 64.5 (CH), 59.8 (CH), 57.8 (CH<sub>3</sub>), 38.9 (Cq), 31.3 (Cq), 28.5 (CH<sub>2</sub>), 28.5 (CH<sub>3</sub>), 26.8 (CH<sub>3</sub>). IR ν (cm<sup>-1</sup>) = 3031, 2972, 2222, 994, 963, 846, 763, 711, 679. HRMS (ESI) : *m/z* [M+H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub>]<sup>+</sup> : 232.1338 , found : 232.1339.

**2a1-methoxy-2a,2a1,2b,2c,3,4,5,6,7,8-decahydro-9-oxabenz[a]-**

**cyclopenta[h]cyclopropa[cd]pentalene-2a-carbonitrile (11d).** The product was prepared following the general procedure for photochemical reactions using 4-(2-(cyclohex-1-en-1-yl)ethoxy)-3-methoxybenzotrile **10d** (39 mg, 0.15 mmol) and MeCN (8.5 mL). The tubes were irradiated at a wavelength of 300 nm for 2h30. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>) afforded the product **11d** (15.5 mg, 39 %) as a colorless oil. *Rf* = 0.35 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ 5.86 (d, *J* = 5.9 Hz, 1H; CH), 5.78 (d, *J* = 5.9 Hz, 1H; CH), 4.09 (m, 1H; CH<sub>2</sub>), 3.96(m, 1H; CH<sub>2</sub>), 3.62 (s, 3H; CH<sub>3</sub>), 2.97 (d, *J* = 6.4 Hz, 1H; CH), 2.38 (m, 1H, CH<sub>2</sub>), 2.27 (m, 1H; CH<sub>2</sub>), 1.76 (m, 1H; CH<sub>2</sub>), 1.64 (m, 3H; CH<sub>2</sub>), 1.44 (m, 1H; CH<sub>2</sub>), 1.35 (m, 1H; CH<sub>2</sub>), 1.22 (m, 3H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>3</sub>CN): δ 136.9 (CH), 126.0 (CH), 119.6 (CN), 100.1 (Cq), 97.1 (Cq), 69.3 (CH<sub>2</sub>), 59.4 (Cq), 57.6 (CH<sub>3</sub>), 54.0 (CH), 41.1 (CH<sub>2</sub>), 39.7 (CH), 31.1 (CH<sub>2</sub>), 30.1 (Cq), 27.3 (CH<sub>2</sub>), 24.0 (CH<sub>2</sub>), 22.7 (CH<sub>2</sub>). IR ν (cm<sup>-1</sup>) = 3072, 2926, 2226, 964, 836, 794, 722. HRMS (ESI) : *m/z* [M+H]<sup>+</sup> calcd for [C<sub>16</sub>H<sub>20</sub>NO<sub>2</sub>]<sup>+</sup> : 258.1494 , found : 258.1493.

**3a,4,4-trifluoro-4a1-methoxy-3,3a,4,4a,4a1,4b-hexahydro-2H-cyclo-**

**propa[3,4]pentaleno[6a,1-b]furan-4b-carbonitrile (11e).** The product was prepared following the general procedure for photochemical reactions using 3-methoxy-4-((3,4,4-trifluorobut-3-en-1-yl)oxy)benzotrile **10e** (68 mg, 0.26 mmol) and MeCN (17 mL). The tube was irradiated at a wavelength of 300 nm for 1h40. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>) afforded the product **11e** (13 mg, 19 %) as a colorless oil. Product **11e** was crystallized as colorless crystals via slow evaporation of a petroleum ether/diethyl ether (1:1) solution at room temperature. Mp. : 91 °C. *Rf* = 0.26

(petroleum ether/ethyl acetate = 9:1, UV).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.97 (dd,  $J$  = 5.9, 1.0 Hz 1H; CH), 5.86 (dd,  $J$  = 5.9, 1.5 Hz, 1H; CH), 4.41 (m, 1H;  $\text{CH}_2$ ), 4.36 (m, 1H;  $\text{CH}_2$ ), 3.70 (s, 3H;  $\text{CH}_3$ ), 3.15 (m, 1H; CH), 2.68 (m, 2H;  $\text{CH}_2$ ), 2.35 (m, 1H;  $\text{CH}_2$ ), 2.11 (m, 1H;  $\text{CH}_2$ ), 1.89 (m, 1H;  $\text{CH}_2$ ), 1.13 (s, 3H;  $\text{CH}_3$ ), 1.06 (s, 3H;  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  132.6 (CH), 125.9 (CH), 117.8 (ddd,  $J$  = 264.5, 253.8, 21.4 Hz,  $\text{CF}_2$ ), 115.7 (CN), 111.1 (ddd,  $J$  = 221.3, 21.0, 20.9 Hz, CF), 97.0 (dd,  $J$  = 18.2, 8.7 Hz, Cq), 87.8 (virt. t,  $J$  = 9.2 Hz, Cq), 70.3 ( $\text{CH}_2$ ), 58.8 ( $\text{CH}_3$ ), 46.3 (ddd,  $J$  = 38.0, 25.3, 3.2 Hz, CH), 30.7 (virt. dd,  $J$  = 22.8, 3.8 Hz,  $\text{CH}_2$ ), 29.9 (m, Cq).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -93.3 (virt. ddt,  $J$  = 251.2, 11.0, 2.1 Hz, 1F; C-F), -107.6 (virt. dd,  $J$  = 251.2, 5.1 Hz, 1F; C-F<sub>2</sub>), -171.6 (virt. dddd,  $J$  = 35.7, 19.6, 4.8, 2.7 Hz, 1F; C-F<sub>2</sub>). IR  $\nu$  ( $\text{cm}^{-1}$ ) = 3068, 2912, 2240, 992, 945, 914, 831, 758, 683.

HRMS (ESI) :  $m/z$  [ $\text{M}+\text{H}$ ]<sup>+</sup> calcd for [ $\text{C}_{12}\text{H}_{11}\text{NO}_2\text{F}_3$ ]<sup>+</sup> : 258.0742, found : 258.0742.

#### 4a1,6-dimethoxy-3a-methyl-3,3a,4,4a,4a1,4b-hexahydro-2H-cyclo-

propa[3,4]pentaleno[6a,1-b]furan-4b-carbonitrile (**11f**). The product was prepared following the general procedure for photochemical reactions using 4-(but-3-en-1-yloxy)-3,5-dimethoxybenzotrile **10f** (62 mg, 0.27 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 1h30. Column chromatography ( $\text{SiO}_2$ , petroleum ether/ethyl acetate = 9:1,  $\text{KMnO}_4$ ) afforded the product **11f** (39 mg, 63 %) as a colorless oil.  $R_f$  = 0.14 (petroleum ether/ethyl acetate = 9:1, UV).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.50 (s, 1H, CH), 4.30 (m, 1H;  $\text{CH}_2$ ), 4.05 (m, 1H;  $\text{CH}_2$ ), 3.70 (s, 3H;  $\text{CH}_3$ ), 3.68 (s, 3H;  $\text{CH}_3$ ), 2.64 (d,  $J$  = 6.3 Hz, 1H; CH), 2.56 (ddd,  $J$  = 11.4, 7.5, 6.4 Hz, 1H; CH), 2.09-1.97 (m, 1H;  $\text{CH}_2$ ), 1.95 (dd,  $J$  = 14.7, 6.3 Hz, 1H; CH), 1.62 (dd,  $J$  = 14.7, 6.4 Hz, 1H;  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.9 (Cq), 119.1 (Cq), 94.3 (Cq), 87.5 (Cq), 86.8 (CH), 72.0 ( $\text{CH}_2$ ), 57.7 ( $\text{CH}_3$ ), 57.4 ( $\text{CH}_3$ ), 54.1 (CH), 44.6 (CH), 29.4 ( $\text{CH}_2$ ), 24.9 (Cq), 23.8 ( $\text{CH}_2$ ). IR  $\nu$  ( $\text{cm}^{-1}$ ) = 2941, 2223, 1644, 1620, 945, 874, 732, 702, 687. HRMS (ESI) :  $m/z$  [ $\text{M}+\text{H}$ ]<sup>+</sup> calcd for [ $\text{C}_{13}\text{H}_{16}\text{NO}_3$ ]<sup>+</sup> : 234.1130, found : 234.1129.

#### 4a1-methoxy-3,3a,4,4a,4a1,6a-hexahydro-2H-cyclopropa[1,6]-penta-leno[1,2-

b]furan-5-carbonitrile (**12a**). The product was prepared following the general procedure for photochemical reactions using 4-(but-3-en-1-yloxy)-3-methoxybenzotrile **10a** (54 mg, 0.27 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 2h30. Column chromatography ( $\text{SiO}_2$ , petroleum ether/ethyl acetate = 9:1,  $\text{KMnO}_4$ /UV) afforded the products **12a** (17 mg, 31 %) as a colorless oil.  $R_f$  = 0.1 (petroleum ether/ethyl acetate = 9:1, UV).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.64 (d,  $J$  = 3.0 Hz, 1H; CH), 4.22 (ddd,  $J$  = 8.6, 7.0, 4.4 Hz, 1H;  $\text{CH}_2$ ), 3.97 (ddd,  $J$  = 9.0, 8.6, 7.0 Hz, 1H;  $\text{CH}_2$ ), 3.58 (d,  $J$  = 5.4 Hz, 1H; CH), 3.45 (s, 3H;  $\text{CH}_3$ ), 2.66 (d,  $J$  = 3.0 Hz, 1H; CH), 2.48 (dddd,  $J$  = 10.0, 9.4, 6.5, 4.1 Hz, 1H; CH), 2.19 (dddd,  $J$  = 12.5, 10.0, 9.0, 7.3 Hz, 1H;  $\text{CH}_2$ ), 2.16 (dd,  $J$  = 12.4, 6.5 Hz, 1H;  $\text{CH}_2$ ) 1.97 (ddd,  $J$  = 12.4, 9.4,

5.4 Hz, 1H; CH<sub>2</sub>), 1.74 (dddd,  $J = 12.5, 7.0, 4.4, 4.1$  Hz, 1H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  146.9 (CH), 116.1 (Cq), 116.0 (Cq), 86.4 (2Cq), 71.9 (CH<sub>2</sub>), 58.2 (CH<sub>3</sub>), 55.3 (CH), 42.7 (CH<sub>2</sub>), 39.6 (CH), 39.2 (CH), 32.2 (CH<sub>2</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 2944, 2213, 1618, 1586, 968, 895, 872, 680. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>14</sub>NO<sub>2</sub>]<sup>+</sup> : 204.1025, found : 204.1023.

**2a1-methoxy-2a,2a1,2b,3,4,5,6,7,8,9b-decahydro-9-oxabenz[a]-cyclopenta[b]cyclopropa[cd]pentalene-2-carbonitrile (12d).**

The product was prepared following the general procedure for photochemical reactions using 4-(2-(cyclohex-1-en-1-yl)ethoxy)-3-methoxybenzonitrile **10d** (52 mg, 0.2 mmol) and MeCN (110 mL) distributed in 6 quartz glass tubes. The tubes were irradiated at a wavelength of 300 nm for 25 minutes. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>/UV) afforded the product **12d** (9 mg, 17 %) as a colorless oil.  $R_f = 0.22$  (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  6.82 (d,  $J = 3.2$  Hz, 1H; CH), 4.10 (ddd,  $J = 8.6, 7.3, 6.0$  Hz, 1H; CH<sub>2</sub>), 3.83 (ddd,  $J = 8.6, 7.8, 6.8$  Hz, 1H; CH<sub>2</sub>), 3.51 (d,  $J = 5.9$  Hz, 1H; CH), 3.37 (s, 3H; CH<sub>3</sub>), 2.56 (ddd,  $J = 8.3, 5.9, 2.6$  Hz, 1H; CH), 2.50 (d,  $J = 3.2$  Hz, 1H; CH), 2.00 – 1.84 (m, 2H; CH<sub>2</sub>), 1.81 – 1.74 (m, 1H; CH<sub>2</sub>), 1.73 – 1.66 (m, 1H; CH<sub>2</sub>), 1.66 – 1.59 (m, 1H), 1.52 (dt,  $J = 13.7, 4.2$  Hz, 2H; CH<sub>2</sub>), 1.40 (ddq,  $J = 17.8, 13.0, 4.4$  Hz, 2H; CH<sub>2</sub>), 1.21 (tdt,  $J = 13.1, 11.3, 3.9$  Hz, 1H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>3</sub>CN):  $\delta$  151.1 (CH), 116.8 (CN), 91.0 (Cq), 90.8 (Cq), 70.2 (CH<sub>2</sub>), 62.1 (CH), 57.8 (CH<sub>3</sub>), 55.4 (CH), 50.9 (Cq), 44.0 (CH), 39.0 (CH<sub>2</sub>), 33.9 (CH<sub>2</sub>), 25.4 (CH<sub>2</sub>), 23.1 (CH<sub>2</sub>), 22.4 (CH<sub>2</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 2933, 2209, 1583, 938, 925, 891, 867, 803, 718. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>16</sub>H<sub>20</sub>NO<sub>2</sub>]<sup>+</sup> : 258.1494, found : 258.1493.

**3a,4,4-trifluoro-4a1-methoxy-3,3a,4,4a,4a1,6a-hexahydro-2H-cyclopropa[1,6]pentaleno[1,2-b]furan-5-carbonitrile (12e).** The product was prepared following the general procedure for photochemical reactions using 3-methoxy-4-((3,4,4-trifluorobut-3-en-1-yl)oxy)benzonitrile **10e** (68 mg, 0.26 mmol) and MeCN (17 mL). The tube was irradiated at a wavelength of 300 nm for 1h40. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>) afforded the product **12e** (29 mg, 43 %) as a colorless oil.  $R_f = 0.15$  (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  7.04 (td,  $J = 3.1, 1.3$  Hz, 1H; CH), 4.32 (td,  $J = 8.8, 2.4$  Hz, 1H; CH<sub>2</sub>), 4.21 (d,  $J = 10.6$  Hz, 1H; CH), 3.68 (m, 1H; CH<sub>2</sub>), 3.43 (s, 3H; CH<sub>3</sub>), 2.98 (dd,  $J = 3.1, 2.1$  Hz, 1H; CH), 2.91 – 2.79 (m, 1H; CH<sub>2</sub>), 2.28 (dddd,  $J = 30.1, 14.1, 10.6, 8.7, 5.6$  Hz, 1H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>3</sub>CN):  $\delta$  152.5 (CH), 125.44 (ddd,  $J = 276.6, 258.5, 29.0$  Hz, CF<sub>2</sub>), 115.7 (CN), 111.10 (d,  $J = 9.6$  Hz, Cq), 106.4 (ddd,  $J = 212.4, 31.1, 23.2$  Hz, CF), 84.9 (t,  $J = 11.1$  Hz, Cq), 83.7 (dd,  $J = 22.3, 6.1$  Hz, Cq), 70.3 (d,  $J = 2.1$  Hz, CH<sub>2</sub>), 60.5 (dd,  $J = 29.9, 19.5$  Hz, CH), 59.2 (CH<sub>3</sub>), 38.5 (CH), 34.1 (dd,  $J = 25.1, 5.7$  Hz, CH<sub>2</sub>). <sup>19</sup>F NMR (471 MHz, CD<sub>3</sub>CN) :  $\delta$

-105.25 (dtt,  $J = 232.5, 9.9, 4.2$  Hz), -116.02 (ddd,  $J = 232.3, 10.6, 2.0$  Hz), -155.21 (dtd,  $J = 29.5, 10.6, 8.1$  Hz). IR  $\nu$  ( $\text{cm}^{-1}$ ) = 3077, 2973, 2224, 1665, 1595, 985, 903, 828, 711, 683. HRMS (ESI) :  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{12}\text{H}_{11}\text{NO}_2\text{F}_3]^+$  : 258.0742, found : 258.0744.

### 5-methoxy-3,3a,4,6a-tetrahydro-2H-cyclobuta[h]benzofuran-6a-carbonitrile (**13a**).

The product was prepared following the general procedure for photochemical reactions using 4-(but-3-en-1-yloxy)-3-methoxybenzocarbonitrile **10a** (54 mg, 0.27 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 2h30. Column chromatography ( $\text{SiO}_2$ , petroleum ether/ethyl acetate = 9:1,  $\text{KMnO}_4/\text{UV}$ ) afforded an inseparable mixture of the products **13a** (5 mg, 9 %) and **12a** (1.5 mg, 3 %) as a colorless oil. Analytical data for the product **13a** are reported for a mixture with **12a**.  $R_f = 0.1$  (petroleum ether/ethyl acetate = 9:1, UV).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  6.70 (d,  $J = 3.0$  Hz, 1H; CH, 12a), 6.23 (d,  $J = 2.7$  Hz, 1H; CH, 13a), 6.19 (d,  $J = 2.7$  Hz, 1H; 13a), 4.69 (d,  $J = 1.9$  Hz, 1H; CH, 13a), 4.12 (ddd,  $J = 8.7, 7.5, 4.1$  Hz, 1H;  $\text{CH}_2$ , 12a), 3.98 (td,  $J = 8.7, 3.1$  Hz, 1H;  $\text{CH}_2$ , 13a), 3.89 (td,  $J = 8.8, 7.2$  Hz, 1H;  $\text{CH}_2$ , 13a), 3.84 (td,  $J = 8.7, 6.9$  Hz, 1H;  $\text{CH}_2$ , 12a), 3.59 (d,  $J = 5.4$  Hz, 1H; CH, 12a), 3.52 (s, 3H;  $\text{CH}_3$ , 13a), 3.39 (s, 3H;  $\text{CH}_3$ , 12a), 2.60 (d,  $J = 2.9$  Hz, 1H; CH, 12a), 2.47 (dddd,  $J = 10.7, 7.3, 5.7, 3.0$  Hz, 1H; CH, 13a), 2.43 - 2.35 (m, 1H; CH, 12a), 2.29 (ddd,  $J = 16.9, 5.7, 2.0$  Hz, 1H;  $\text{CH}_2$ , 13a), 2.22 (dd,  $J = 16.9, 3.1$  Hz, 1H;  $\text{CH}_2$ , 13a), 2.21 - 2.17 (m, 1H;  $\text{CH}_2$ , 12a), 2.12 - 2.07 (m, 1H;  $\text{CH}_2$ , 12a), 2.07 - 2.04 (m, 1H;  $\text{CH}_2$ , 12a), 2.04 - 2.01 (m, 1H;  $\text{CH}_2$ , 13a), 1.87 (ddt,  $J = 12.2, 11.0, 9.2$  Hz, 1H, 13a), 1.69 (ddt,  $J = 12.5, 7.6, 4.0$  Hz, 1H;  $\text{CH}_2$ , 12a).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.7 (Cq, 13a), 148.3 (CH, 12a), 140.0 (CH, 13a), 138.4 (CH, 13a), 122.1 (CN, 13a), 90.9 (CH, 13a), 89.7 (Cq, 13a), 87.1 (Cq, 12a), 72.1 (Cq, 13a), 67.6 ( $\text{CH}_2$ , 13a), 58.0 ( $\text{CH}_3$ , 12a), 56.2 (CH, 12a), 55.4 ( $\text{CH}_3$ , 13a), 50.7 (CH, 12a), 43.0 ( $\text{CH}_2$ , 12a), 40.2 (CH, 12a), 40.0 (CH, 12a), 39.5 (CH, 13a), 32.6 ( $\text{CH}_2$ , 12a), 28.7 ( $\text{CH}_2$ , 13a), 28.4 ( $\text{CH}_2$ , 13a). IR  $\nu$  ( $\text{cm}^{-1}$ ) = 2940, 2216, 867, 680. HRMS (ESI) :  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $[\text{C}_{12}\text{H}_{14}\text{NO}_2]^+$  : 204.1025, found : 204.1024.

### 5-methoxy-3a-methyl-3,3a,4,6a-tetrahydro-2H-cyclobuta[h]-benzofuran-6a-carbonitrile (**13b**).

The product was prepared following the general procedure for photochemical reactions using 3-methoxy-4-((3-methylbut-3-en-1-yl)oxy)benzocarbonitrile **10b** (58 mg, 0.27 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 2h30. Column chromatography ( $\text{SiO}_2$ , petroleum ether/ethyl acetate = 9:1,  $\text{KMnO}_4/\text{UV}$ ) afforded the product **13b** (6 mg, 10 %) as a colorless oil.  $R_f = 0.1$  (petroleum ether/ethyl acetate = 9:1, UV).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  6.26 (d,  $J = 2.8$  Hz, 1H; CH), 6.23 (d,  $J = 2.8$  Hz, 1H; CH), 4.69 (d,  $J = 2.1$  Hz, 1H; CH), 4.02 - 3.90 (m, 2H;  $\text{CH}_2$ ), 3.52 (s, 3H;  $\text{CH}_3$ ), 2.19 - 2.16 (m, 1H;  $\text{CH}_2$ ), 2.12 - 2.05 (m, 2H;  $\text{CH}_2$ ), 1.71 (ddd,  $J = 12.4, 6.8, 3.7$  Hz, 1H;  $\text{CH}_2$ ), 1.06 (d,  $J = 0.7$  Hz, 3H;  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  157.9 (Cq), 139.2 (CH), 138.5 (CH), 122.1 (CN), 92.2 (Cq), 90.7



(CH), 66.0 (CH<sub>2</sub>), 55.4 (CH<sub>3</sub>), 51.3 (Cq), 43.1 (Cq), 36.3 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 23.1 (CH<sub>3</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 2925, 2230, 1661, 979, 888, 800, 780, 709. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>13</sub>H<sub>16</sub>NO<sub>2</sub>]<sup>+</sup> : 218.1181, found : 218.1181.

**5-methoxy-4,4-dimethyl-3,3a,4,6a-tetrahydro-2H-cyclobuta[h]benzo-furan-6a-carbonitrile (13c)**. The product was prepared following the general procedure for photochemical reactions using 3-methoxy-4-((4-methylpent-3-en-1-yl)oxy)benzonitrile **10c** (61.7 mg, 0.27 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 2h. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>) afforded the product **13c** (8.6 mg, 14 %) as a colorless oil. Product **13c** was crystallized as colorless crystals via slow evaporation of a petroleum ether/diethyl ether (1:1) solution at room temperature. Mp. : 116 °C. *Rf* = 0.33 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  6.32 (d, *J* = 2.7 Hz, 1H; CH), 6.30 (d, *J* = 2.7 Hz, 1H; CH), 4.67 (s, 1H; CH), 4.00 (ddd, *J* = 9.4, 8.2, 2.4 Hz, 1H; CH<sub>2</sub>), 3.90 – 3.80 (m, 2H; CH, CH<sub>2</sub>), 3.54 (s, 3H; CH<sub>3</sub>), 2.26 (dd, *J* = 11.6, 7.0 Hz, 1H; CH), 2.17 – 2.08 (m, 1H; CH<sub>2</sub>), 1.99 – 1.84 (m, 1H; CH<sub>2</sub>), 1.14 (s, 3H; CH<sub>3</sub>), 1.09 (s, 3H; CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  163.1 (Cq), 142.1 (CH), 140.5 (CH), 121.8 (CN), 90.0 (CH), 88.2 (Cq), 66.5 (CH<sub>2</sub>), 55.6 (CH), 51.4 (CH), 50.6 (Cq), 37.8 (Cq), 28.4 (CH<sub>2</sub>), 27.4 (CH<sub>3</sub>), 25.6 (CH<sub>3</sub>). IR  $\nu$  (cm<sup>-1</sup>) = 2989, 2971, 2230, 1644, 986, 934, 805, 788, 769, 678. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub>]<sup>+</sup> : 232.1338, found : 232.1338.

**4a-methoxy-4,4-dimethyl-2,3,3a,4,4a,6a-hexahydrocyclobuta-[f]benzo-furan-6-carbonitrile (14c)**. The product was prepared following the general procedure for photochemical reactions using 3-methoxy-4-((4-methylpent-3-en-1-yl)oxy)benzonitrile **10c** (61.7 mg, 0.27 mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 2h. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>) afforded a 7 : 3 mixture of diastereomers **14c** and **14c'** (16 mg, 26 %) as a colorless oil. The stereochemistry of the *syn* diastereomer (**14c**, *major*) and *anti* diastereomer (**14c'**, *minor*) were resolved by 2D NMR NOESY experiment (cf ESI **S32**). Analytical data are reported for the mixture of diastereomers **14c (major)** and **14c' (minor)**. *Rf* = 0.30 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  6.85 (d, *J* = 2.2 Hz, 1H; CH, *major*), 6.81 (d, *J* = 0.7 Hz, 1H; CH, *minor*), 4.82 (dd, *J* = 6.2, 2.6 Hz, 1H; CH, *minor*), 4.78 (td, *J* = 2.7, 0.7 Hz, 1H; CH, *major*), 4.24 (td, *J* = 8.5, 1.5 Hz, 1H; CH<sub>2</sub>, *major*), 4.24 (m, 1H; CH<sub>2</sub>, *minor*), 4.06 – 3.96 (m, 1H; CH<sub>2</sub>, *major*), 3.99 – 3.93 (m, 1H; CH<sub>2</sub>, *minor*), 3.85 (q, *J* = 2.6 Hz, 1H; CH, *major*), 3.68 (dd, *J* = 6.3, 0.7 Hz, 1H; CH, *minor*), 3.34 (s, 3H; CH<sub>3</sub>, *major*), 3.32 (s, 3H; CH<sub>3</sub>, *minor*), 2.84 (ddt, *J* = 11.2, 8.6, 2.6 Hz, 1H; CH, *major*), 2.42 (ddd, *J* = 11.0, 8.7, 2.6 Hz, 1H; CH, *minor*), 2.04 – 1.97 (m, 1H; CH<sub>2</sub>, *minor*), 1.97 – 1.92 (m, 1H; CH<sub>2</sub>, *major*), 1.92 – 1.88 (m, 1H; CH<sub>2</sub>, *minor*), 1.77 (dtd, *J* = 12.2, 11.1, 8.6 Hz, 1H; CH<sub>2</sub>, *major*), 1.09 (s, 3H; CH<sub>3</sub>, *major*), 1.04 (s, 3H; CH<sub>3</sub>, *minor*), 0.84 (s, 3H; CH<sub>3</sub>, *minor*), 0.72 (s, 3H; CH<sub>3</sub>, *major*). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>):  $\delta$  161.1 (Cq, *major*),

160.4 (Cq, minor), 152.5 (CH, major), 149.6 (CH, minor), 121.3 (Cq, major), 120.5 (Cq, minor), 113.4 (Cq, minor), 113.3 (Cq, major), 90.1 (Cq, minor), 87.3 (Cq, major), 86.3 (CH, minor), 86.0 (CH, major), 71.0 (CH<sub>2</sub>, major), 70.6 (CH<sub>2</sub>, minor), 52.4 (CH<sub>3</sub>, minor), 52.1 (CH<sub>3</sub>, major), 48.6 (CH, major), 47.9 (CH, minor), 45.4 (CH, minor), 45.0 (CH, major), 39.9 (Cq, major), 39.8 (Cq, minor), 25.1 (CH<sub>2</sub>, minor), 25.1 (CH<sub>2</sub>, major), 22.8 (CH<sub>3</sub>, major), 22.4 (CH<sub>3</sub>, minor), 21.4 (CH<sub>3</sub>, major), 14.2 (CH<sub>3</sub>, minor). IR  $\nu$  (cm<sup>-1</sup>) = 2972, 2950, 2218, 1679, 989, 942, 876, 800, 789, 711. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub>]<sup>+</sup> : 232.1338, found : 232.1339.

**10a-methoxy-2,3,4,5,6,8a,10a,10b-octahydro-1H-cyclo-buta[3,4]-naphtho[1,8a-b]furan-9-carbonitrile (14d)**. The product was prepared following the general procedure for photochemical reactions using 4-(2-(cyclohex-1-en-1-yl)ethoxy)-3-methoxybenzonitrile **10d** (52 mg, 0.2 mmol) and MeCN (110 mL) distributed in 6 quartz glass tubes. The tubes were irradiated at a wavelength of 300 nm for 25 minutes. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>/UV) afforded a mixture of the *anti* diastereomer **14d** (5 mg, 10 %) and the product **11d** (2 mg, 4 %) as a colorless oil. The stereochemistry of the *anti* diastereomer **14d** was resolved by 2D NMR NOESY experiment (cf ESI **S35**). Analytical data for the product **14d** are reported for a mixture with **11d**. *R<sub>f</sub>* = 0.32 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  7.12 (s, 1H; CH, **14d**), 5.86 (d, *J* = 5.9 Hz, 1H; CH, **11d**), 5.78 (d, *J* = 5.9 Hz, 1H; CH, **11d**), 4.75 (d, *J* = 6.3 Hz, 1H; CH, **14d**), 4.13 – 4.10 (m, 2H; CH<sub>2</sub>, **14d**), 4.10 – 4.07 (m, 1H; CH<sub>2</sub>, **11d**), 3.96 (ddd, *J* = 11.2, 8.2, 6.4 Hz, 1H; CH<sub>2</sub>, **11d**), 3.67 (d, *J* = 6.3 Hz, 1H; CH, **14d**), 3.62 (s, 3H; CH<sub>3</sub>, **11d**), 3.26 (s, 3H; CH<sub>3</sub>, **14d**), 2.97 (d, *J* = 6.4 Hz, 1H; CH, **11d**), 2.48 – 2.43 (m, 1H; CH<sub>2</sub>, **14d**), 2.37 (dd, *J* = 12.0, 6.3 Hz, 1H; CH, **11d**), 2.27 (ddd, *J* = 12.4, 11.3, 9.8 Hz, 1H; CH, **11d**), 2.09 (ddt, *J* = 13.6, 3.6, 1.7 Hz, 1H; CH<sub>2</sub>, **14d**), 1.88 (m, 1H; CH, **14d**), 1.79 – 1.73 (m, 1H; CH<sub>2</sub>, **11d**), 1.70 – 1.65 (m, 2H; CH<sub>2</sub>, **14d**), 1.64 (m, 3H, CH<sub>2</sub>, **11d**), 1.62 – 1.47 (m, 5H; CH<sub>2</sub>, **14d**), 1.50 – 1.42 (m, 1H; CH<sub>2</sub>, **11d**), 1.41 – 1.30 (m, 1H; CH<sub>2</sub>, **14d**), 1.41 – 1.30 (m, 2H; CH<sub>2</sub>, **11d**), 1.29 – 1.17 (m, 2H; CH<sub>2</sub>, **11d**). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  168.1 (Cq, **14d**), 156.0 (CH, **14d**), 136.9 (CH, **11d**), 126.0 (CH, **11d**), 123.8 (Cq, **14d**), 119.6 (CN, **11d**), 114.5 (CN, **14d**), 100.1 (Cq, **11d**), 97.1 (Cq, **11d**), 88.2 (CH, **14d**), 87.4 (Cq, **14d**), 69.3 (CH<sub>2</sub>, **11d**), 68.9 (CH<sub>2</sub>, **14d**), 59.4 (Cq, **11d**), 57.6 (CH<sub>3</sub>, **11d**), 54.0 (CH, **11d**), 52.3 (CH<sub>3</sub>, **14d**), 49.8 (CH, **14d**), 47.5 (CH, **14d**), 44.4 (Cq, **14d**), 41.1 (CH<sub>2</sub>, **11d**), 39.7 (CH, **11d**), 36.7 (CH<sub>2</sub>, **14d**), 31.1 (CH<sub>2</sub>, **11d**), 30.1 (Cq, **11d**), 27.9 (CH<sub>2</sub>, **14d**), 27.3 (CH<sub>2</sub>, **11d**), 24.0 (CH<sub>2</sub>, **11d**), 23.8 (CH<sub>2</sub>, **14d**), 22.9 (CH<sub>2</sub>, **14d**), 22.7 (CH<sub>2</sub>, **11d**), 21.8 (CH<sub>2</sub>, **14d**). IR  $\nu$  (cm<sup>-1</sup>) = 2935, 2225, 942, 884, 807, 704, 680. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>16</sub>H<sub>20</sub>NO<sub>2</sub>]<sup>+</sup> : 258.1494, found : 258.1497.

**3-allyl-4-hydroxy-5-methoxybenzonitrile (15)**. The product was prepared following the general procedure for photochemical reactions using 4-(allyloxy)-3-methoxybenzonitrile **10g** (51 mg, 0.27

mmol) and MeCN (15 mL). The tube was irradiated at a wavelength of 300 nm for 4h. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 8:2, KMnO<sub>4</sub>) afforded the product **15** (19 mg, 37 %) as a colorless oil. *R<sub>f</sub>* = 0.21 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.12 (d, *J* = 1.6 Hz, 1H; Ar-H), 6.98 (d, *J* = 1.8 Hz, 1H; Ar-H), 6.15 (s, 1H; OH), 5.94 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H; CH), 5.21 – 5.03 (m, 2H; CH<sub>2</sub>), 3.92 (s, 3H; CH<sub>3</sub>), 3.40 (dd, *J* = 6.6, 1.5 Hz, 2H; CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 147.7 (Cq), 146.4 (Cq), 135.1 (CH), 127.6 (CH), 127.3 (Cq), 119.6 (CN), 116.9 (CH<sub>2</sub>), 111.9 (CH), 102.8 (Cq), 56.5 (CH<sub>3</sub>), 33.4 (CH<sub>2</sub>). IR ν (cm<sup>-1</sup>) = 2977, 2222, 1639, 1598, 915, 785. HRMS (ESI) : *m/z* [M+H]<sup>+</sup> calcd for [C<sub>11</sub>H<sub>12</sub>NO<sub>2</sub>]<sup>+</sup> : 190.0868, found : 190.0869.

### 8-methoxy-3,3a,4,6a-tetrahydro-2H-cyclobuta[h]benzofuran-6a-carbonitrile (**17a**).

The product was prepared following the general procedure for photochemical reactions using 4-(but-3-en-1-yloxy)-3-methoxybenzocarbonitrile **10a** (60 mg, 0.30 mmol), MeCN (10 mL) and acetone (20 mL). The tube was irradiated at a wavelength of 300 nm for 8h. Column chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 9:1, KMnO<sub>4</sub>/UV) afforded the products **17a** (7 mg, 12 %). *R<sub>f</sub>* = 0.5 (petroleum ether/ethyl acetate = 9:1, UV). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.93 (s, 2H; 2CH), 4.96 (s, 1H; CH), 4.29 (t, *J* = 8.6 Hz, 1H; CH<sub>2</sub>), 4.23 – 4.11 (m, 1H; CH<sub>2</sub>), 3.62 (s, 3H; CH<sub>3</sub>), 2.32 (dt, *J* = 13.5, 3.9 Hz, 1H; CH<sub>2</sub>), 2.15 – 1.90 (m, 3H; CH<sub>2</sub>, CH), 1.82 (dd, *J* = 16.4, 12.5 Hz, 1H; CH). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ 159.3 (Cq), 131.0 (CH), 128.7 (CH), 119.7 (CN), 102.7 (CH), 90.8 (Cq), 70.2 (CH<sub>2</sub>), 56.5 (CH), 43.8 (CH), 41.2 (Cq), 29.8 (Cq), 27.8 (CH<sub>2</sub>), 25.5 (CH<sub>2</sub>). IR ν (cm<sup>-1</sup>) = 3094, 2942, 2231, 1647, 914, 790. HRMS (ESI) : *m/z* [M+H]<sup>+</sup> calcd for [C<sub>12</sub>H<sub>14</sub>NO<sub>2</sub>]<sup>+</sup> : 204.1025, found : 204.1025.

4a-methoxy-4,4-dimethyl-2,3,4,4a,6a,7-hexahydrocyclobuta[f]benzo-furan-6-carbonitrile (**18**). When the mixture of diastereomers **14c** and **14c'** was left overnight in NMR solvent CDCl<sub>3</sub>, *syn* diastereomer **14c** disappeared and two new products formed. One product (**18**) seemed to be the result of a 1,3-H-shift in the cyclohexene moiety.

Analytical data are reported for the mixture of **18**, *anti* diastereomer **14c'** and the unknown product. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.81 (s, 1H; CH, **14c'**), 6.80 (d, *J* = 1.0 Hz, 1H; CH, unknown), 6.74 (s, 1H; CH, **18**), 4.82 (dd, *J* = 6.3, 2.6 Hz, 1H; CH, **14c'**), 4.32 (dd, *J* = 10.2, 8.4 Hz, 2H; CH<sub>2</sub>, **18**), 4.24 (td, *J* = 8.5, 1.9 Hz, 1H; CH<sub>2</sub>, **14c'**), 4.03 – 3.94 (m, 1H; CH<sub>2</sub>, **14c'**), 3.97 – 3.89 (m, 1H; CH<sub>2</sub>, unknown), 3.68 (d, *J* = 6.3 Hz, 1H; CH, **14c'**), 3.48 (dd, *J* = 6.3, 1.3 Hz, 1H; CH, **18**), 3.42 – 3.34 (m, 1H; CH, unknown), 3.35 (s, 3H; CH<sub>3</sub>, **18**), 3.33 (s, 3H; CH<sub>3</sub>, unknown), 3.32 (s, 3H; CH<sub>3</sub>, **14c'**), 2.65 – 2.56 (m, 2H; CH<sub>2</sub>, **18**), 2.42 (ddd, *J* = 11.6, 9.0, 2.8 Hz, 1H; CH, **14c'**), 2.38 (m, 1H; CH<sub>2</sub>, **18**), 2.36 (m, 1H; CH<sub>2</sub>, unknown), 2.27 (m, 1H; CH<sub>2</sub>, **18**), 2.21 – 2.16 (m, 1H; CH<sub>2</sub>, unknown), 2.15 (d, *J* = 5.0 Hz, 1H; CH, unknown), 2.07 (m, 1H; CH<sub>2</sub>, unknown), 1.99 (m, 1H; CH<sub>2</sub>, **14c'**), 1.93

(m, 1H; CH<sub>2</sub>, **14c'**), 1.83 (ddt,  $J = 12.8, 8.6, 4.5$  Hz, 1H; CH<sub>2</sub>, unknown), 1.05 (s, 3H; CH<sub>3</sub>, **18**), 1.05 (s, 3H; CH<sub>3</sub>, **18**), 1.04 (s, 3H; CH<sub>3</sub>, **14c'**), 1.00 (s, 3H; CH<sub>3</sub>, **18**), 0.94 (s, 3H; CH<sub>3</sub>, unknown), 0.90 (s, 3H; CH<sub>3</sub>, unknown), 0.84 (s, 3H; CH<sub>3</sub>, **14c'**). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  161.10 (Cq, **14c'**) 152.29 (CH, **18**), 152.02 (CH, unknown), 149.60 (CH, **14c'**), 146.83 (Cq, **18**), 124.00 (CN, **6c**), 120.63 (CN, **18**), 120.46 (CN, **14c'**), 113.37 (Cq, **14c'**), 113.11 (Cq, unknown), 112.66 (Cq, **18**), 111.86 (Cq, **18**), 104.51 (Cq, unknown), 90.09 (Cq, **14c'**), 88.90 (Cq, **18**), 88.02 (Cq, unknown), 86.30 (CH, **14c'**), 70.56 (CH<sub>2</sub>, **14c'**), 69.93 (CH<sub>2</sub>, **18**), 65.77 (CH<sub>2</sub>, unknown), 52.85 (CH<sub>3</sub>, **18**), 52.39 (CH<sub>3</sub>, **14c'**), 52.09 (CH<sub>3</sub>, unknown), 51.33 (CH, unknown), 47.86 (CH, **14c'**), 47.05 (CH, **18**), 45.91 (CH, unknown), 45.37 (CH, **14c'**), 40.25 (Cq, **14c'**), 39.40 (Cq, unknown), 37.74 (Cq, **18**), 37.39 (CH<sub>2</sub>, unknown), 29.62 (CH<sub>2</sub>, **18**), 25.46 (CH<sub>2</sub>, unknown), 25.12 (CH<sub>2</sub>, **14c'**), 24.33 (CH<sub>3</sub>, unknown), 22.98 (CH<sub>2</sub>, **18**), 22.98 (CH<sub>3</sub>, **18**), 22.57 (CH<sub>3</sub>, **18**), 22.41 (CH<sub>3</sub>, **14c'**), 16.49 (CH<sub>3</sub>, unknown), 14.22 (CH<sub>3</sub>, **14c'**). IR  $\nu$  (cm<sup>-1</sup>) = 2972, 2950, 2218, 1679, 989, 942, 876, 800, 789, 711. HRMS (ESI) :  $m/z$  [M+H]<sup>+</sup> calcd for [C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub>]<sup>+</sup>: 232.1338, found : 232.1337.

Supporting information. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra for all compounds, <sup>19</sup>F NMR spectra for compounds **10e**, **10i**, **11e**, **12e**, configuration assignments of **14c**, **14c'**, **14d** by NOESY experiment, UV absorption spectra of compounds **5**, **10a**, **10f**, **11a**, **12a** and X-ray structures of compounds **11a**, **11b**, **11c**, **11e**, **13c**.

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