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PHOTOCHEMICAL REACTIONS OF PROP-2-ENYL AND PROP-2-YNYL SUBSTITUTED 4-AMINOMETHYL- AND 4-OXYMETHYL-2(5*H*)-FURANONES

Diego A. Fort,[a,b] Thomas J. Woltering,[b] André M. Alker,[c] and Thorsten Bach[a]*

[a] Chair of Organic Chemistry I, Technische Universität München, D-85747 Garching, Germany, thorsten.bach@ch.tum.de

[b] Discovery Chemistry, PCMM, F. Hoffmann-La Roche Ltd., Grenzacherstrasse, CH-4070 Basel, Switzerland

[c] Biostructure Section, Molecular Design & Chemical Biology, Pharmaceuticals Division, F. Hoffmann-La Roche Ltd., Grenzacherstrasse, CH-4070 Basel, Switzerland

Dedicated to Professor Victor Snieckus on the occasion of his 77th birthday

Abstract – Compounds with a heterocyclic 9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one skeleton were synthesized by intramolecular [2+2] photocycloaddition reactions of the title compounds (λ = 254 nm, Et_2O or MeCN as the solvent). Starting from various substituted 4-(prop-2-enylaminomethyl)-2(5*H*)-furanones, products **5**, **9**, **18**, **21**, **23**, **24** were obtained, which bear a nitrogen atom in position 3 of this skeleton within a pyrrolidine ring. The Boc or Cbz groups represent suitable nitrogen protecting groups, which were compatible with the irradiation conditions and which can be easily cleaved. In an analogous fashion an oxygen (product **22**) and carbon substituent (product **25**) could be implemented at position 3 of the product if the starting material was appropriately chosen. The prop-2-ynyl substituted substrates did not produce a [2+2] photocycloaddition product but rather underwent a cyclization to spiro products **11** and **13**.

INTRODUCTION

Although it has been discovered more than one hundred years ago,[1,2] the [2+2] photocycloaddition reaction of α,β-unsaturated carbonyl compounds has remained to this date an actively studied synthetic transformation. There are several reasons for the continuing interest in [2+2] photocycloaddition chemistry. First of all, the quest for enantioselective [2+2] photocycloaddition reactions has not led to satisfactory results. Although auxiliary-based approaches are known,[3] there are no general concepts yet, which allow for direct formation of enantiomerically enriched or enantiomerically pure [2+2] photocycloaddition products. Recent progress on this topic holds promise for catalytic enantioselective [2+2] photocycloaddition reactions[4] but further work is required. Secondly, [2+2] photocycloaddition reactions offer the most concise access to cyclobutane skeletons, which are abundant structural motifs of natural products[5] and which can be used for a plethora of further transformations.[6] For good reasons, the [2+2] photocycloaddition is the most frequently used photochemical reaction in natural product synthesis.[7] In a significant number of recent studies[8] the reaction has been applied to the synthesis of naturally occurring cyclobutanes. The rigidity of the cyclobutane[9] ring is a third reason why [2+2] photocycloaddition reactions continue to attract the interest of synthetic chemists. The cyclobutane ring allows the positioning of certain functional groups in a spatially defined way, which is increasingly appreciated by medicinal and biological chemists.[10] The introduction of these functional groups requires new types of substrates being studied and in this context we have recently[11] introduced the *N*-Boc (*tert*-butyloxycarbonyl) protected 4-(allylaminomethyl)- and 4-(propargylaminomethyl)-2(5*H*)furanones **A**[12,13] as new substrates for photochemical transformations (Figure 1).

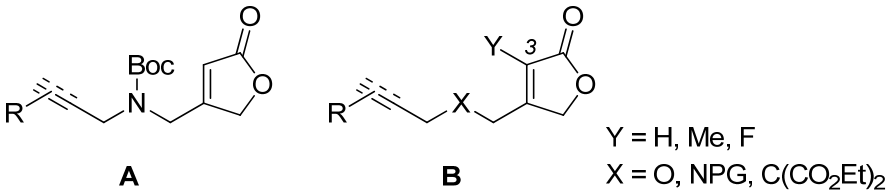
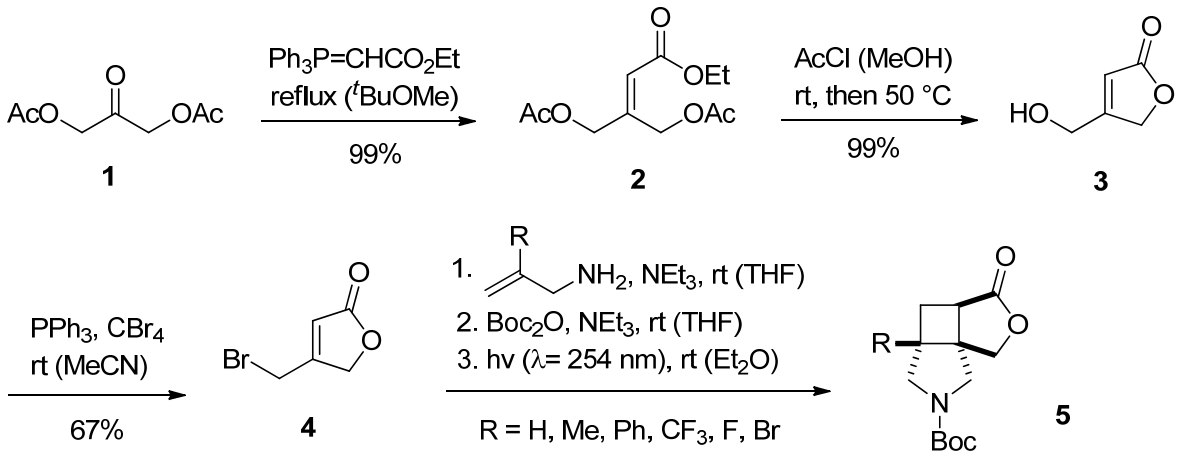


Figure 1. General structure of previously studied photo substrates **A** and general structure of the title compounds **B** discussed in the present paper

Eight differently substituted 4-(allylaminomethyl)-2(5*H*)-furanones (vide infra) were shown to react to the respective cyclobutanes in good yields (53-75%) and with perfect diastereoselectivity.[11] *N*-Boc-4-(propargylaminomethyl)-2(5*H*)-furanone did not undergo a photocycloaddition but underwent an interesting light-induced radical type cyclization reaction. We have now further expanded the substrate scope of this reaction to general compound class **B** and we disclose in this full paper the details of our work in this area.

RESULTS AND DISCUSSION

4-(Prop-2-enylaminomethyl)-2(5H)-furanones. For the preparation of the photocycloaddition precursors **B** with Y = H, 4-bromomethyl-2(5*H*)-furanone (**4**) was required as the starting material (Scheme 1). Although the compound has been reported previously,[14] we wanted to avoid radical conditions, which require the use of CCl_4 as solvent or the use of a transition metal salt ($CuBr_2$). In addition, access to 4-hydroxymethyl-2(5*H*)-furanone (**3**) was straightforward starting from ketone **1** as key building block.



Scheme 1. Preparation of 4-(bromomethyl)-2(5*H*)-furanone (**4**) as precursor for the photocycloaddition products **5** of *N*-Boc protected 4-(allylaminomethyl)-2(5*H*)-furanones

A Wittig reaction delivers the respective ester **2** in almost quantitative yield and subsequent mild ester hydrolysis at elevated temperature induces the desired lactonization. This sequence has been previously optimized to a fully reproducible multi-kilogram process[15] and conditions for the conversion of alcohol **3** to bromide **4** were therefore examined. PBr_3 in Et_2O was the reagent of choice in the most practical protocol. Although it delivered a moderate yield (52-58%) the ease of work-up and the high purity of crude product made it superior to other procedures. Appel conditions[16] delivered a better yield (67%) and the protocol was amenable to large scale. However, extensive chromatography was necessary to remove $CHBr_3$ and PPh_3O and to access a high quality product. Experiments on 5 g scale using a one-pot protocol of mesylation (Ms_2O, NEt_3, THF) followed by direct substitution of the intermediate mesylate with LiBr in THF suggest that this method is the highest yielding procedure (88%). It should be noted, though, that the product is contaminated with some NEt_3, which in the present case did not interfere with the subsequent reactions (see Experimental). Indeed, as previously reported,[11] displacement of the bromide by allylic amines is facile and after immediate *N*-Boc protection the precursors for the photochemical reactions are obtained. As mentioned above, the [2+2] photocycloaddition proceded smoothly delivering products **5** in yields of 53-75% as single regio- and diastereoisomers.

Compounds **5** could be prepared on larger scale in a flow system.[17] Processing amounts >50 g of photoprecursor in the flow system, however, led to detrimental deposition of side products and a

precipitate covering the reactor wall, which in turn decreased the conversion of initially 89% to <5% over a period of four days. Therefore we attempted a batch process and we found a full conversion of a 120 mM solution in MeCN (350 mL quartz flask) after 18 h delivering a crystalline crude product **5a**. Overall, an isolated purified product could be obtained in 70% yield (see Experimental). The tricyclic product **5a** could be separated in its enantiomers by chiral HPLC and the (racemic) compound was characterized also by single crystal X-ray analysis.[18] The three-dimensional structure (Figure 2) illustrates the rigidity exerted by the central cyclobutane ring and confirms previous structure assignments.

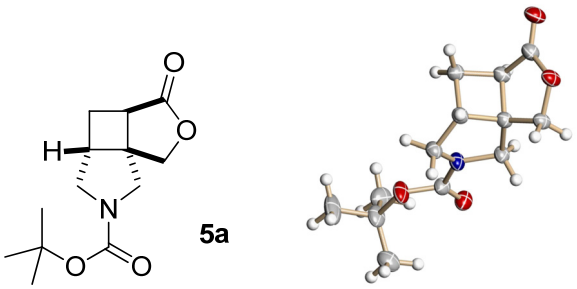
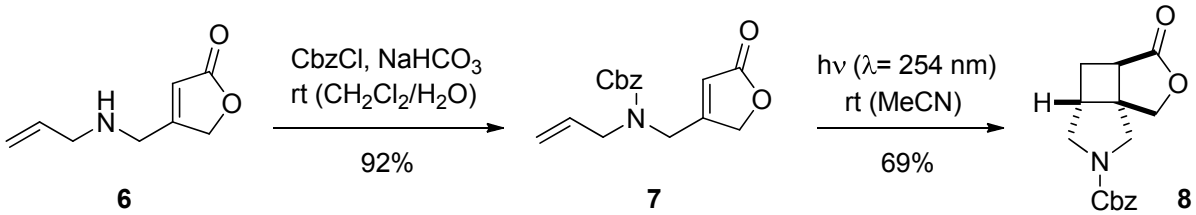


Figure 2. Structure of 3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one **5a** in the crystal

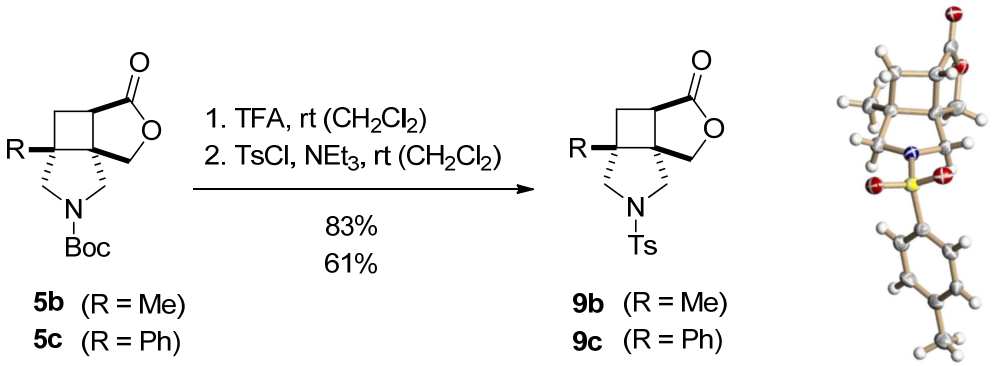
It could be shown that not only the Boc group is suitable for protection of 4-(allylamino-methyl)-2(5*H*)-furanones in the photocycloaddition but also a benzyloxycarbonyl (Cbz) group. The Cbz group is advantageous for the protection of bulkier substrates and offers alternative deprotection pathways as compared to Boc. Starting from amine **6**, the protection was readily achieved under Schotten-Baumann conditions[19] with CbzCl (Scheme 2). The [2+2] photocycloaddition of the resulting product **7** proceeded smoothly and delivered the expected tricyclic product **8**. Acetonitrile turned out to be the superior solvent for the photoreaction. After two hours of irradiation (c = 5 mM) the yield was 69% in this solvent but only 45% in Et_2O.



Scheme 2. Synthesis of the *N*-Cbz protected photocycloaddition product **8**

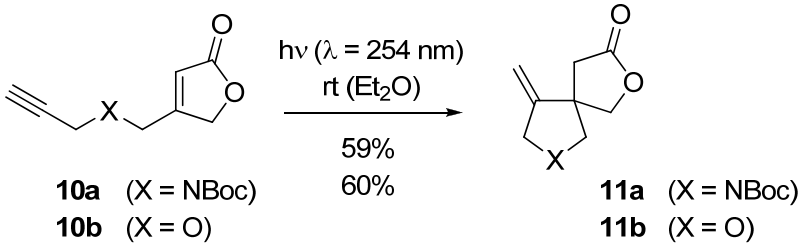
Irradiation of the free amine **6** and its *N*-acetyl or *N*-tosyl (Ts) derivatives resulted only in little or no conversion. For reasons of product scope and for NMR-spectroscopic characterization it was desirable, however, to convert the Boc- or Cbz-protected 3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-ones into compounds with a non-amidic protecting group. Indeed, due to the formation of rotamers, products **5** gave only broad NMR signals and decomposed at the relatively high temperature (120 °C) required to

record well resolved NMR spectra. Conversion to the *N*-Ts derivatives was achieved by acidic deprotection (Scheme 3) and subsequent tosylation. Compounds **9b** and **9c** were readily available from the respective precursors **5b** and **5c**. Product **9b** was crystalline and was subjected to X-ray crystallographic analysis.[20] The crystal structure allowed nicely correlating the NMR information (coupling constants, NOE contacts) with the crystallographic data.



Scheme 3. Preparation of the *N*-Ts protected 3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-ones **9** and crystal structure of racemic product **9b**

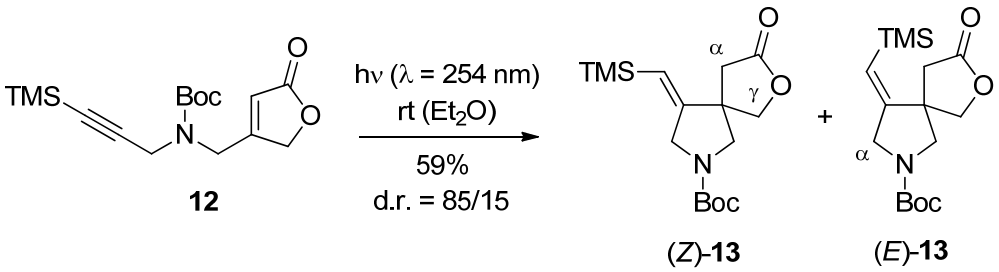
*4-(Prop-2-ynyloxymethyl)- and 4-(prop-2-ynylaminomethyl)-2(5*H*)-furanones*. Propargylic amine **10a** was obtained from bromide **4** and subsequent *N*-Boc protection. Its oxygen analogue **10b** was prepared from primary alcohol **3**, which acted as a nucleophile displacing the triflate leaving group in propargyl triflate. Like the former amine **10a**, the latter ether **10b** did not form the respective cyclobutene under typical irradiation conditions. Rather the respective spiro compound **11b** was isolated in a yield, which was comparable to the yield previously reported[11] for product **11a**.



Scheme 4. Synthesis of spiro compounds **11** from 2(5*H*)-furanones **10**

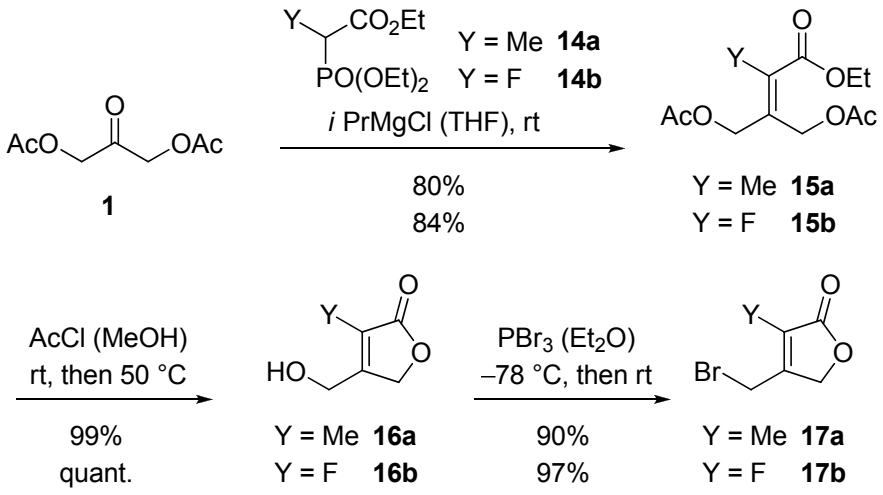
Mechanistically it is likely that the photoexcited α,β-unsaturated lactone undergoes via its triplet state a hydrogen abstraction from the solvent rather than cyclization. Addition to the triple bond leads to a vinylic radical, which abstracts another hydrogen atom from the solvent. The mechanistic hypothesis was supported by deuterium incorporation at the vinylic double bond when performing the reaction in d_{10}-Et_2O.[11] With the silylated acetylene **12**, which was obtained from bromide **4** in two steps, as substrate, an analogous cyclization was observed, which led to products **13** as a mixture of diastereoisomers.

According to NOESY spectra the major diastereoisomer was (*Z*)-**13**, which showed NOE contacts between the vinylic hydrogen atom and the α- and γ-hydrogen atoms of the γ-lactone ring. In the minor diastereoisomer the vinylic hydrogen atom showed a NOE contact to the pyrrolidine methylene group in α-position to the nitrogen atom. The result is in line with a related radical cyclization reaction to a silylated alkyne, which also led predominantly to a spiro compound with an exocyclic double bond of the same relative configuration.[21]



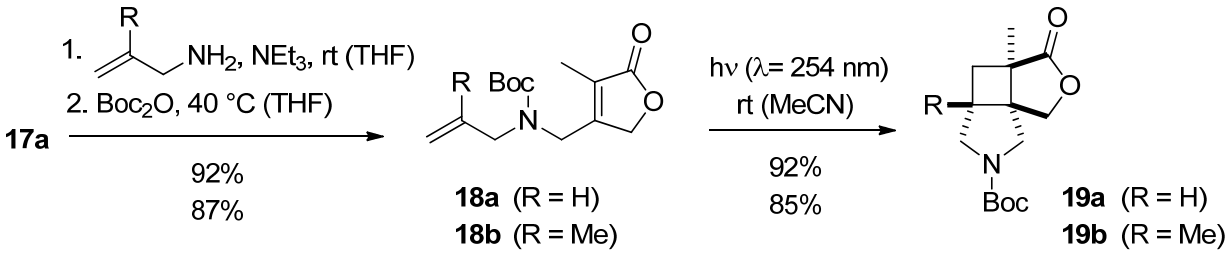
Scheme 5. Diastereoselectivity in the synthesis of spiro compounds **13** from 2(5*H*)-furanone **12**

3-Substituted 4-(prop-2-enylaminomethyl)-2(5H)-furanones. In order to access 3-substituted 2(5*H*)-furanones, it was tried to perform the previously described Wittig reaction (Scheme 1) with substituted ylides. There was no conversion, however, even in toluene at reflux temperature. Attempts to perform the olefination with phosphonates **14** (Scheme 6) did not look very promising, either, as the attempted transformation with NaH gave only traces of products. Gratifyingly, we found that generation of the enolate with isopropylmagnesium chloride[22] led to very good product yields in the desired Horner-Wadsworth-Emmons reaction with ketone **1**. The subsequent conversion of α,β-unsaturated esters **15** to the respective 3-substituted 4-(bromomethyl)-2(5*H*)-furanones **17** followed the standard protocol of acidic hydrolysis/lactone formation and bromination of alcohols **16** using PBr_3.



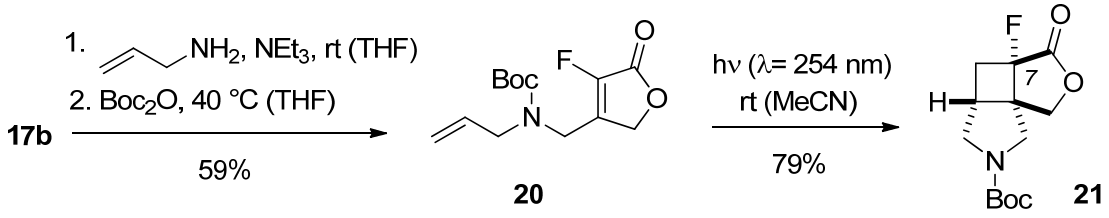
Scheme 6. Preparation of 4-(bromomethyl)-2(5*H*)-furanones **17a** and **17b**

Bromide **17a** was converted into the 4-(allylamino)- and 4-(methallylamino)-2(5*H*)-furanones by treatment with the commercially available primary amines allylamine and methallylamine (Scheme 7). *N*-Boc protection could be performed without prior purification of the resulting secondary amines employing Boc_2O in the absence of additional base and THF as solvent. The overall yields for the transformations were high and the resulting 2(5*H*)-furanones **18** were subsequently subjected to typical irradiation conditions (λ = 254 nm). Acetonitrile was a superior solvent as compared to Et_2O, which had been used in previous reactions. To our pleasant surprise, the product yields for the intramolecular [2+2] photocycloaddition products **19** were even higher than those obtained from the 3-unsubstituted 2(5*H*)-furanones. Other regio- and diastereoisomers were not detectable and products **19** were obtained as spectroscopically homogeneous compounds.



Scheme 7. Preparation of 3-methyl-4-(prop-2-enylaminomethyl)-2(5*H*)-furanones **18** and their intramolecular [2+2] photocycloaddition

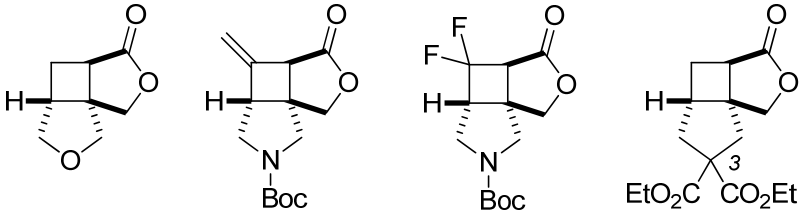
Although we had previously shown that the enone [2+2] photocycloaddition reactions proceed well with fluorinated olefins,[23] we had so far not tested an α-fluorinated enone as substrate. The required starting material **20** was prepared from 4-(bromomethyl)-2(5*H*)-furanone **17b** employing the same sequence already applied to **17a** (Scheme 8). The *N*-Boc-proteced allylic amine **20** underwent a clean and high-yielding [2+2] photocycloaddition to a 3-aza-9-oxatricyclo[5.3.0.$0^{1,5}$]decan-8-one with a fluorine substituent at carbon atom C-7.



Scheme 8. Preparation of 3-fluoro-4-(prop-2-enylaminomethyl)-2(5*H*)-furanone **20** and its intramolecular [2+2] photocycloaddition

Related [2+2] photocycloaddition products. In our preliminary studies we had synthesized – in addition to the products **5** described above (Scheme 1) – the related photocycloaddition products **22**-**24**. Product **22** is derived from the respective allylic ether (55% yield), product **23** from an allenylmethylamine (71%

yield) and product **24** from a difluorinated allylic amine (63% yield). In addition, we could in the present work show, that it is also possible to install a carbon group at position 3 of the 9-oxa-tricyclo[5.3.0.0^{1,5}]decan-8-one skeleton readily generated by intramolecular [2+2] photocycloaddition. Product **25** was obtained in 45% yield upon irradiation of the respective diester in acetonitrile (λ = 254 nm). The starting material for the [2+2] photocycloaddition was obtained from bromide **4** upon nucleophilic displacement with the respective malonate (see Experimental). Product **25** was – as all other products – isolated as a single regio- and diastereoisomer.



22 **23** **24** **25**

Figure 3. Structure of various 9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one **22-25** obtained by intramolecular [2+2] photocycloaddition

CONCLUSION

In summary, a total number of 14 different 9-oxatricyclo[5.3.0.0^{1,5}]decan-8-ones were obtained by intramolecular [2+2] photocycloaddition reactions (53-92% yield) from substrates with the general structure **B**. Two additional products were prepared by protective group manipulations in the 3-aza-series. The preferred solvents for the irradiation were Et_2O and acetonitrile at λ = 254 nm. The reaction could be performed on preparative scale (up to 50 g) either in a batch mode or using a continuous flow system. The products contain either a nitrogen, an oxygen or a carbon atom in position C-3. By choosing appropriate starting materials, they can be substituted at all positions of the central cyclobutane ring. All products have at least two exit vectors for further functionalization based on lactone ring opening. In addition, the 3-aza-products can be further functionalized at the nitrogen atom. Consecutive reactions of the photocycloaddition products are currently being studied in our laboratories and will be reported in due course.

EXPERIMENTAL

General: All reactions, sensitive to air or moisture, were carried out in flame-dried glassware under positive pressure of argon using standard techniques. For the photoreactions, the compounds were dissolved in the corresponding solvent, degassed by purging with Ar in an ultrasonicator for 15 minutes and irradiated in a Rayonet RPR 200 merry-go-round reactor, equipped with 16 Rayonet RPR-2537 Å lamps (λ = 254 nm). Unless otherwise stated, the reactions were stopped when the starting material was

fully consumed according to thin layer chromatography (TLC) and/or LC-MS analysis. The solvent was then removed and the residue was purified by column chromatography. Unless otherwise noted only one reaction product could be determined. Typically, an immobile spot could be seen on TLC, which we tentatively attribute to polymeric side-products. Flash chromatography was performed on silica gel 60 (Merck, 230-400 mesh) with the eluent mixtures given for the corresponding procedures. TLC was performed on silica coated glass plates (silica gel 60 F_{254}). Compounds were detected by UV (λ = 254 nm), CAM (cerium ammonium molybdate solution) or $KMnO_4$. IR: JASCO IR-4100. MS /HRMS: Finnigan MAT 8200. ^{1}H and ^{13}C NMR: Bruker AV-300, AV-400 and AV-600 recorded at 300 K unless otherwise indicated. Chemical shifts are reported relative to the solvent [$CHCl_3$: δ (^{1}H) = 7.26 ppm, δ (^{13}C) = 77.0 ppm, DMSO: δ (^{1}H) = 2.50 ppm, δ (^{13}C) = 39.5 ppm] as reference. Apparent multiplets which occur as a result of accidental equality of coupling constants to those of magnetically non-equivalent protons are marked as virtual (virt.). The relative configuration of the products and the multiplicity of the ^{13}C-NMR signals were determined by two-dimensional NMR spectra (COSY, NOESY, HSQC, HMBC). Melting points were measured on a Büchi B-540 and are not corrected.

4-(Bromomethyl)-2(5*H*)-furanone (4) Appel procedure: A 750-mL four-necked flat bottom flask equipped with overhead stirrer, thermometer, reflux condenser and nitrogen bubbler was charged with 4-(hydroxymethyl)-2(5*H*)-furanone (**3**)[15] (90.0 g, 789 mmol, 1.0 eq) in MeCN (250 mL), cooled to 5 °C, PPh_3 (207 g, 789 mmol, 1.0 eq) and then solid CBr_4 (262 g, 789 mmol, 1.0 eq) was added portionwise keeping the internal temperature below 30 °C, the cooling bath was removed and the resulting solution was stirred at 25 °C for 1 h. The reaction mixture was evaporated to dryness to give a green semisolid. All crude material was purified by flash chromatography (silica gel, ca. 1200 g, loaded with toluene, 0% to 30% EtOAc in heptane; not full separation, $CHBr_3$ nicely removed, but some TPPO leaked through in the end, impure fractions 4.5 g obtained) to give the 4-(bromomethyl)-2(5*H*)-furanone (**4**) (83.4 g, 67%) as a light brown oil.

Mesylation/substitution protocol: To a solution of 4-(hydroxymethyl)-2(5*H*)-furanone (**3**)[15] (3.42 g, 30 mmol, 1.0 eq) in THF (300 mL) at –78 °C was added methanesulfonic anhydride (7.32 g, 42.0 mmol, 1.4 eq) followed by dropwise addition of a solution of Et_3N (4.86 g, 6.69 mL, 48.0 mmol, 1.6 eq) in THF (100 mL) and the mixture was stirred at –78 °C for 1 h, then at 0 °C for 90 min. Methanesulfonic acid (577 mg, 390 μL, 6.00 mmol, 0.2 eq) was added, stirred for another 5 min, then a 2 M solution of lithium bromide in THF (52.5 mL, 105 mmol, 3.5 eq) was added, the cooling bath was removed and when the internal temperature reached 15 °C the reaction was finished. All solids were filtered off and washed with *tert*-butyl methyl ether (TBME). The filtrate was washed with water and brine, dried over Na_2SO_4. Removal of the solvent in vacuum left a dark brown oil, which was purified by silica gel column

chromatography (heptane:EtOAc 0% to 60% EtOAc) to give the 4-(bromomethyl)-2(5*H*)-furanone (**4**) (5.16 g, 88%) as a light brown liquid (contains some NEt_3 impurity). R_f: 0.32 (pentane:EtOAc 7:3). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.16 (s, 1 H_3), 4.96 (s, 2 H_5), 4.25 (s, 2 H, CH_2Br). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 172.5 (C_2), 163.2 (C_4), 118.9 (C_3), 71.9 (C_5), 22.5 (CH_2Br). The analytical data obtained matched those reported in the literature.[14]

***N-tert*-Butoxycarbonyl-3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one (5a)** Large scale preparation: A solution of *tert*-butyl allyl[(5-oxo-2,5-dihydrofuran-3-yl)methyl]carbamate[11] (53.6 g, 212 mmol) in MeCN (1.73 L) (concentration: 3%) was deoxygenated by bubbling argon through the solution under sonication for 30 min and then irradiated at 254 nm in batches of ca. 350 mL in a quartz flask in a Rayonet RPR-200 photoreactor (16 lamps, 8 W each) for 18 h per batch. After full conversion (crude GC 76%) the combined yellow solution was evaporated whereupon the crude material already crystallized. The crude material was purified by flash chromatography (silica gel, 500 g, 30% to 50% EtOAc in heptane) to give a light yellow solid which was vigorously stirred with a large magnetic stir bar in *n*-heptane (~300 mL) and very little EtOAc (~20 mL) at 23 °C for 1 h to give the pure *N-tert*-butoxycarbonyl-3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one (**5a**) (37.5 g, 70%) as a white solid. mp 97-99 °C. R_f = 0.57 (pentane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 1755 (vs, C=O), 1692 (w), 1471 (m), 1397 (s), 1229 (m), 1161 (s), 1135 (m), 1011 (vs), 970 (m), 875 (m). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.39 (d, ^2J = 9.8 Hz, 1 H_{10}), 4.16 (d, ^2J = 9.8 Hz, 1 H_{10}), 3.95-3.92 (br. s, 1 H_2), 3.73-3.58 (br. s, 1 H_4), 3.30 (dd, ^2J = 11.8 Hz, ^3J = 6.5 Hz, 1 H_4), 3.07 (d, ^2J = 12.2 Hz, 1 H_2), 2.97-2.86 (m, 1 H_7, 1 H_5), 2.36 (ddd, ^2J = 12.9 Hz, ^3J = 8.5 Hz, ^3J = 6.7 Hz, 1 H_6), 2.22 (ddd, ^2J = 12.9 Hz, ^3J = 8.5 Hz, ^3J = 3.5 Hz, 1 H_6), 1.49 [s, 9 $C(CH_3)_3$]. ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 179.3 (C_8), 155.0 (*C*O*O*t*Bu), 80.1 [*C*$(CH_3)_3$], 72.5 (C_{10}), 52.2 (C_4), 50.8 (C_2), 39.9 (C_7, C_5), 28.4 [C(*C*$H_3)_3$], 27.6 (C_6), (C_1 not observed). MS (EI, 70 eV): *m*/*z* (%) = 198 (31) [(M-$C_3H_3O)^+$], 153 (26) [(M-$C_5H_9O)^+$], 57 (100) [(M-$C_{11}H_{18}NO_2)^+$]. HRMS (ESI): Calculated for $C_{13}H_{20}NO_4^+$ $[(M+H)]^+$= 254.1387. Found = 254.1390. The analytical data obtained matched those reported in the literature.[11]

Benzyl allyl[(5-oxo-2,5-dihydrofuran-3-yl)methyl]carbamate (7) To a mixture of 4-(allylamino-methyl)-2(5*H*)-furanone (**6**) (1.00 g, 6.53 mmol, 1.0 eq) and sodium bicarbonate (8.77 g, 104 mmol, 16 eq) in CH_2Cl_2 (4.0 mL) and water (4.0 mL) at room temperature was added dropwise CbzCl (2.80 mL, 19.6 mmol, 3.0 eq) and the mixture was stirred at room temperature for 16 h. After that time, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4. Removal of the solvent in vacuum left a light yellow oil that was purified by column chromatography (heptane:EtOAc 1:1) to give benzyl allyl[(5-oxo-2,5-dihydrofuran-3-yl)methyl]carbamate (**7**) (1.72 g,

92%) as a yellow oil. R_f = 0.31 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 2954 (w, CH_2N), 2925 (w, CH_2N), 1778 (m, C=O), 1746 (s, O-C=O), 1696 (s, C=O), 1643 (w, C=C), 1497 (w, C_{Ar}), 1239 (s, C-O), 1028 (m, C=C), 885 (m, C=C), 770 (w, C_{Ar}), 698 (m, C_{Ar}). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.39-7.33 (m, 5 H_{ar}), 5.92 (br. s, 1 H_4), 5.76 (br. s, 1 $H_{2'}$), 5.21 (br. s, 2 $H_{3'}$), 5.17 (br. s, 2 H, OCH_2), 4.77 (br. s, 2 H_2), 4.25 (br. s, 2 H, NCH_2), 3.93 (br. s, 2 $H_{1'}$). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 173.0 (C_5), 165.8 (C_3), 156.1 (CO), 135.8 (C_{ipso}), 132.5 ($C_{2'}$), 128.6 (C_{ar}), 128.4 (C_{ar}), 127.9 (C_{ar}), 118.9 (C_4), 117.0 ($C_{3'}$), 71.9 (C_2), 67.9 (OCH_2), 50.0 ($C_{1'}$), 44.9 (CH_2). MS (EI, 70 eV): *m/z* (%): 288 (100) [$(M+H)^+$]. HRMS (ESI): Calculated for $C_{16}H_{17}NO_4$ [$(M)^+$] = 287.1158. Found = 287.1163.

Benzyl (3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one)carbamate (8) The compound was prepared from benzyl allyl[(5-oxo-2,5-dihydrofuran-3-yl)methyl]carbamate (**7**) (1.40 g, 4.87 mmol) in 962 mL of MeCN by irradiation for 6 h (5 mM). Purification of the crude material by column chromatography (heptane:EtOAc 1:1) afforded photoproduct (**8**) as a yellow oil (962 mg, 69%). R_f = 0.18 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 3032 (w, C_{Ar}), 1764 (m, O-C=O), 1694 (s, C=O), 1497 (w, C_{Ar}), 1013 (s, C-O). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.38-7.34 (m, 5 H_{ar}), 5.18 (s, CH_2), 4.40 (d, ^2J = 9.9 Hz, 1 H_{10}), 4.12 (d, ^2J = 9.9 Hz, 1 H_{10}), 4.03 (d, ^2J = 12.1 Hz, 1 H_2), 3.74 (d, ^2J = 11.8 Hz, 1 H_4), 3.38 (dd, ^2J = 11.8 Hz, ^3J = 6.6 Hz, 1 H_4), 3.14 (d, ^2J = 12.1 Hz, 1 H_2), 2.97-2.93 (m, 1 H_7, 1 H_5), 2.38 (ddd, ^2J = 12.9 Hz, ^3J = 8.3 Hz, ^3J = 3.6 Hz, 1 H_6), 2.23-2.20 (m, 1 H_6). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 179.1 (C_8), 155.2 (N*C*OO), 136.4 (C_{ar}), 128.6 (C_{ipso}), 128.2 (C_{ar}), 128.0 (C_{ar}), 72.3 (C_{10}), 67.3 (CH_2), 52.4 (C_4), 50.9 (C_2), 41.8 (C_5), 39.9 (C_7), 27.6 (C_6), C_1 not detected. MS (EI, 70 eV): *m/z* (%) = 287 (20) [$(M)^+$], 91 (100). HRMS (ESI): Calculated for $C_{16}H_{17}NO_4$ [$(M)^+$] = 287.1158. Found = 287.1154.

***N*-(*p*-Methylbenzenesulfonamide)-5-methyl-3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one (9b)** To a solution of *N-tert*-butoxycarbonyl-5-methyl-2-aza-9-oxa-tricyclo[5.3.0.0^{1,5}]decan-8-one (**5b**) (315 mg, 1.18 mmol, 1.0 eq) in CH_2Cl_2 (6 mL) at 0 °C was added trifluoroacetic acid (1.83 mL, 23.6 mmol, 20 eq). The resulting solution was allowed to warm to room temperature and stirred for 1 h. Evaporation of volatiles at reduced pressure afforded a crude product that was dissolved in CH_2Cl_2 (4 mL) and cooled to 0 °C. A solution of tosyl chloride (270 mg, 1.42 mmol, 1.2 eq) and Et_3N (1.2 mL, 7.1 mmol, 6.0 eq) in CH_2Cl_2 (2 mL) was added and the mixture stirred for 12 h at room temperature. After this time, CH_2Cl_2 and water were added. The aqueous layer was extracted with CH_2Cl_2 and the combined organic phases were dried (Na_2SO_4), filtered and the solvent removed. Purification of the crude by column chromatography (heptane:EtOAc 1:1) afforded the tosylated product **9b** as a white solid (315 mg, 83%). mp 189 °C. R_f = 0.16 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 1787 (m, CO), 1599 (w, C_{ar}), 1492 (w, C_{ar}), 1455 (m), 1344 (m, SO_2), 1173 (s, SO_2), 1024 (s, O-C=O). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm)

7.69 (d, ^3J = 8.3 Hz, 2 H_{ar}), 7.36 (d, ^3J = 8.3 Hz, 2 H_{ar}), 4.22 (d, ^2J = 10.3 Hz, 1 H_{10}), 3.99 (d, ^2J = 10.3 Hz, 1 H_{10}), 3.72 (d, ^2J = 10.2 Hz, 1 H_4), 3.51 (d, ^2J = 9.8 Hz, 1 H_2), 2.94 (dd, ^3J = 10.2 Hz, ^3J = 3.7 Hz, 1 H_7), 2.58 (dd, ^2J = 12.8 Hz, ^3J = 10.2 Hz, 1 H_6), 2.48-2.45 (m, Me, 1 H_4), 2.28 (d, ^2J = 9.8 Hz, 1 H_2), 1.96 (dd, ^2J = 12.8 Hz, ^3J = 3.6 Hz, 1 H_6), 1.16 (s, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 179.1 (C_8), 144.3 (C_{ipso}), 131.2 (C_{ipso}), 129.8 (C_{ar}), 128.1 (C_{ar}), 67.6 (C_{10}), 60.2 (C_2), 52.8 (C_4), 51.6 (C_5), 44.9 (C_1), 37.7 (C_7), 33.8 (C_6), 21.6 ($ArCH_3$), 18.7 (CH_3). MS (EI, 70 eV): *m*/*z* (%) = 322 (100) [$(M+H)^+$]. HRMS (ESI): Calculated for $C_{16}H_{19}NO_4S$ [$(M)^+$] = 321.1035. Found = 321.1036.

***N*-(*p*-Methylbenzenesulfonamide)-5-phenyl-3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one (9c)** To a solution of *N-tert*-butoxycarbonyl-5-phenyl-2-aza-9-oxa-tricyclo[5.3.0.0^{1,5}]decan-8-one (**5c**) (294 mg, 0.856 mmol, 1.0 eq) in CH_2Cl_2 (5 mL) at 0 °C was added trifluoroacetic acid (1.33 mL, 17.3 mmol, 20 eq). The resulting solution was allowed to warm to room temperature and stirred for 1 h. Evaporation of volatiles at reduced pressure afforded a crude product that was dissolved in CH_2Cl_2 (4 mL) and cooled to 0 °C. A solution of tosyl chloride (196 mg, 1.3 mmol, 1.2 eq) and Et_3N (0.72 mL, 5.14 mmol, 6 eq) in CH_2Cl_2 (2 mL) was added and the mixture stirred for 12 h at room temperature. After this time, CH_2Cl_2 and water were added. The aqueous layer was extracted with CH_2Cl_2 and the combined organic phases were dried (Na_2SO_4), filtered and the solvent removed. Purification of the crude material by column chromatography (heptane:EtOAc 1:1) afforded the tosylated product (**9c**) as a white solid (200 mg, 61%). mp 106 °C. R_f = 0.31 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 3058 (w, C_{ar}), 3027 (w, C_{ar}), 2952 (w, CH), 1767 (m, CO), 1598 (w, C_{ar}), 1496 (w, C_{ar}), 1340 (m, SO_2), 1161 (s, SO_2), 1013 (s, O-C=O). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.73 (virt. dt, ^3J = 8.3 Hz, ^3J = 1.9 Hz, 2 H_{ar}), 7.40-7.33 (m, 4 H_{ar}), 7.28 (dt, ^3J = 7.4 Hz, ^3J = 1.2 Hz, 1 H_{ar}), 6.99-6.93 (m, 2 H_{ar}), 4.06 (d, ^2J = 10.5 Hz, 1 H_{10}), 3.98 (d, ^2J = 10.5 Hz, 1 H_{10}), 3.83 (d, ^2J = 10.2 Hz, 1 H_4), 3.78 (d, ^2J = 10.3 Hz, 1 H_2), 3.08 (dd, ^3J = 10.3 Hz, ^3J = 4.2 Hz, 1 H_7), 2.94- 2.86 (m, 1 H_6, 1 H_2), 2.80-2.74 (m, 1 H_6, 1 H_4), 2.48 (s, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 178.2 (C_8), 144.5 (C_e), 137.6 (C_a), 131.5 (C_h), 129.9, 129.1, 128.1, 127.7 (C_d), 126.8, 67.7 (C_{10}), 62.9 (C_2), 55.2 (C_5), 54.2 (C_4), 52.6 (C_1), 37.9 (C_7), 31.2 (C_6), 21.7 (CH_3). MS (EI, 70 eV): *m*/*z* (%) = 383 (35) [$(M)^+$], 228 (95) [$(M-C_7H_7SO_2)^+$], 155 (100), 118 (80), 91 (92). HRMS (ESI): Calculated for $C_{21}H_{21}NO_4S$ [$(M)^+$] = 383.1192. Found = 383.1193.

4-(Prop-2-ynoxymethyl)-2(5*H*)-furanone (10b) 4-(Hydroxymethyl)-2(5*H*)-furanone (**3**) (413 mg, 3.62 mmol, 1.0 eq) and K_2CO_3 (8.0 g, 57.9 mmol, 16 eq) were dissolved in dry CH_2Cl_2 (20 mL) and cooled to –35 °C. A solution of propynyl triflate (3.40 g, 18 mmol, 5 eq) in dry CH_2Cl_2 (20 mL) was added slowly. The mixture was allowed to warm to room temperature and stirred for 72 h. Evaporation to dryness and purification by column chromatography (heptane:EtOAc 1:1) afforded the expected product **10b** (158 mg,

30%) as a colorless oil. R_f = 0.26 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 2923 (s, C-H), 2117 (w, C≡C), 1742 (s, C=O), 1647 (m, C=CH), 1094 (m, C-O), 1030 (m, C-O). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 6.04 (virt. q, ^4J = ^4J = 1.8 Hz, 1 H_3), 4.86 (dt, ^4J = 1.8 Hz, ^4J = 0.8 Hz, 2 H_5), 4.49 (dt, ^4J = 1.8 Hz, ^4J = 0.8 Hz, CH_2), 4.25 (d, ^4J = 2.3 Hz, 2 $H_{1'}$), 2.52 (t, ^4J = 2.4 Hz, 1 $H_{3'}$). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 173.2 (C_2), 165.5 (C_4), 116.2 (C_3), 78.3 ($C_{3'}$), 75.9 ($C_{2'}$), 71.4 (C_5), 65.1 (CH_2), 58.5 ($C_{1'}$). MS (EI, 70 eV): *m*/*z* (%) = 153 (100) [$(M+H)^+$], 123 (25) [$(M-CHO)^+$], 108 (39), 95 (60), 39 (100).

9-Methylene-2,7-dioxaspiro[4.4]nonan-3-one (11b) The compound was prepared from photoprecursor **10b** (60 mg, 0.394 mmol) in 80 mL of Et_2O by irradiation for 90 min (5 mM). Purification of the crude product by column chromatography (heptane:EtOAc 1:1) afforded 9-methylene-2,7-dioxa-spiro[4.4]nonan-3-one (**11b**) as an oil (37.0 mg, 60%). R_f = 0.28 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 2973 (s, C-H), 2117 (w, C≡C), 1776 (s, C=O), 1695 (w, $C=CH_2$), 1017 (s, C-O), 930 (m). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.15 (dd, ^2J = 3.2 Hz, ^4J = 2.0 Hz, 1 H_6), 5.13 (dt, ^2J = 3.2 Hz, ^4J = 1.2 Hz, 1 H_6), 4.46 (dd, ^2J = 13.8 Hz, ^4J = 2.0 Hz, 1 H_4), 4.40 (ddd, ^2J = 13.7 Hz, ^4J = 1.2 Hz, ^4J = 0.5 Hz, 1 H_4), 4.31 (d, ^2J = 9.2 Hz, 1 H_2), 4.17 (dd, ^2J = 9.2 Hz, ^4J = 0.9 Hz, 1 H_2), 3.96 (d, ^2J = 9.0 Hz, 1 H_{10}), 3.76 (d, ^2J = 9.0 Hz, 1 H_{10}), 2.70 (d, ^2J = 17.6 Hz, 1 H_7), 2.59 (d, ^2J = 17.6 Hz, 1 H_7). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 175.1 (C_8), 150.3 (C_5), 105.3 (C_6), 77.6 (C_2), 76.9 (C_4), 71.6 (C_{10}), 50.2 (C_1), 38.4 (C_7). MS (EI, 70 eV): *m*/*z* (%) = 152 (5) [$(M)^+$], 124 (10), 110 (35), 96 (100), 67 (96), 39 (50).

***tert*-Butyl *N*-[(5-oxo-2*H*-furan-3-yl)methyl]-*N*-(3-trimethylsilylprop-2-ynyl)carbamate (12)** To a solution of bromide **4** (720 mg, 4.07 mmol, 1.0 eq) in THF (6 mL) at 0 °C was dropwise added a solution of Et_3N (2.27 mL, 16.3 mmol, 3.0 eq) and 3-(trimethylsilyl)prop-2-yn-1-amine (666 mg, 4.07 mmol, 1.0 eq) in THF (5 mL). The resulting solution was stirred at room temperature for 12 h. The precipitate was filtered off, washed with THF, and the solvent was removed in vacuum. The crude material was purified by column chromatography (heptane:EtOAc 1:3) and the product was used for protection reactions without further purification. The amine (406 mg, 1.82 mmol, 1.0 eq) was dissolved in THF (5.0 mL) and Boc_2O (436 mg, 464 µL, 2.00 mmol, 1.1 eq) was added. The reaction mixture was heated at 40 °C for 2 h, then the solvent was evaporated and the residue purified by column chromatography (heptane:EtOAc 1:1) to afford the Boc-protected product **12** as a light orange solid (406 mg, 69%). mp 78 °C. R_f = 0.45 (heptane:EtOAc 1:1). ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) 5.88 (t, ^4J = 1.6 Hz, 1 H_4), 4.73 (br. s, 2 H_2), 4.16 (br. s, CH_2), 4.04-3.85 (br. s, 2 $H_{1'}$), 1.31 [s, $C(CH_3)_3$], 0.00 [s, $Si(CH_3)_3$]. ^{13}C NMR (151 MHz, DMSO-d_6): δ (ppm) 178.8 (C_5), 168.3 (COO^{t}Bu), 154.1 (C_3), 115.1 (C_4), 102.50 ($C_{2'}$), 88.0 ($C_{3'}$), 80.0 [$C(CH_3)_3$], 71.6 (C_2), 44.9 ($C_{1'}$), 37.3 (CH_2), 27.7 [$C(CH_3)_3$], 0.00 [$Si(CH_3)_3$]. MS (EI, 70 eV): *m*/*z* (%) = 308 [$(M-CH_3)^+$], 267 [$(M-C_4H_8)^+$], 252 [$(M-C_5H_{11})^+$], 178, 112, 57. HRMS (ESI): Calculated for

$C_{16}H_{27}NO_4Si^+$ = 325.1709. Found = 325.1708.

***tert*-Butyl-3-oxo-9-(silylmethylene)-2-oxa-7-azaspiro[4.4]nonane-7-carboxylate (13)** The compound was prepared from photoprecursor **12** (79.0 mg, 0.24 mmol) in 49 mL of Et_2O by irradiation for 2 h (5 mM). Purification of the crude by column chromatography (heptane:EtOAc 1:1) afforded the photoproduct **13** as a white solid (43.1 mg, 59%). The product purified was a mixture of (*Z*)- and (*E*)-product in a 85:15 ratio. The relative configuration was assigned by extensive one- and two-dimensional NMR experiments. R_f = 0.52 (heptane:EtOAc 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) of the (*Z*)-isomer: δ (ppm) 5.45 (br. s, 1 H_6), 4.08 (d, ^2J = 9.1 Hz, 1 H_{10}), 4.02 (d, ^2J = 9.1 Hz, 1 H_{10}), 3.95 (br. s, 2 H_2), 3.49 (d, ^2J = 11.0 Hz, 1 H_4), 3.28 (d, ^2J =11.0 Hz, 1 H_4), 2.57 (d, ^2J = 18.0 Hz, 1 H_7), 2.38 (d, ^2J = 18.0 Hz, 1 H_7), 1.35 [s, $C(CH_3)_3$], 0.03 [s, $Si(CH_3)_3$]. ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 175.8 (C_8), 153.6 (COO^tBu), 150.1 (C_5), 124.4 (C_6), 79.4 [$C(CH_3)_3$], 76.2 (C_{10}), 74.0 (C_1), 58.4 (C_4), 49.7 (C_2), 38.4 (C_7), 28.3 [$C(CH_3)_3$], 0.03 [$Si(CH_3)_3$]. MS (EI, 70 eV): *m*/*z* (%) = 325 (5) [$(M)^+$], 310 (2) [$(M\text{-}CH_3)^+$], 269 (10) [$(M\text{-}C_3H_8)^+$], 73 (30) [$(M\text{-}C_3H_9Si)^+$], 57 (100). HRMS (ESI): Calculated for $C_{16}H_{27}NO_4Si^+$ = 325.1709. Found = 325.1715.

Ethyl 4-acetoxy-3-(acetoxymethyl)-2-methylbut-2-enoate (15a) A 2000-mL four-necked flat bottom flask equipped with overhead stirrer, thermometer, reflux condenser and nitrogen bubbler was charged with triethyl 2-phosphonopropionate (**14a**) (94.9 mL, 442 mmol, 1.1 eq) in THF (1000 mL), cooled to 0 °C, added dropwise isopropylmagnesium chloride (2 M in THF) (221 mL, 442 mmol, 1.1 eq) and the mixture was stirred at 23 °C for 1 h. Then 2-oxopropane-1,3-diyl diacetate (**1**) (70 g, 402 mmol, 1.0 eq) was added in one portion, the light yellow mixture was stirred at 23 °C for 18 h, then poured into NH_4Cl (sat.), extracted with TBME, washed with brine, dried over Na_2SO_4 and filtered. Removal of the solvent in vacuum left a dark brown liquid which was purified by column chromatography (heptane:EtOAc 3:1) to give the ethyl 4-acetoxy-3-(acetoxymethyl)-2-methylbut-2-enoate (**15a**) (83.1 g, 80%) as a light yellow liquid. R_f = 0.58 (heptane:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.86 (d, ^4J =1.0 Hz, OCH_2), 4.77-4.69 (m, OCH_2), 4.25 (q, ^3J = 7.1 Hz, OCH_2), 2.07 (s, CH_3), 2.05 (s, CH_3), 2.02 (s, CH_3), 1.32 (t, ^3J = 7.2 Hz, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 170.7, 170.6, 168.4 (C_9, C_{10}, C_3), 134.3, 133.9 (C_6, C_4), 62.3, 61.2, 61.1 (C_2, C_7, C_8), 20.8, 20.7 (C_{11}, C_{12}), 15.9 (C_5), 14.1 (C_1). MS (EI, 70 eV): *m*/*z* (%) = 258 (100) [$(M)^+$]. HRMS (ESI): Calculated for $C_{12}H_{18}O_6^+$ $[(M)]^+$ = 258.1103. Found = 258.1103.

4-(Hydroxymethyl)-3-methyl-2(5*H*)-furanone (16a) To a solution of ethyl 4-acetoxy-3-(acetoxymethyl)-2-methylbut-2-enoate (**15a**) (86.2 g, 334 mmol, 1.0 eq) in MeOH (374 mL) at room temperature was dropwise added acetyl chloride (2.37 mL, 33.4 mmol, 0.1 eq) and the mixture was stirred at room temperature for 18 h. Then the mixture was stirred for 2 h at 50 °C. The solvent was

evaporated and azeotroped three times with toluene to give the 4-(hydroxy-methyl)-3-methyl-2(5*H*)-furanone (**16a**) (43.4 g, 99%) as a brown liquid which was used without further purification. R_f = 0.22 (heptane:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.89-4.86 (m, 2 H_5), 4.61 (br. s, 2 H_6) 1.83 (s, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 176.1 (C_2), 159.8 (C_4), 122.5 (C_3), 70.9 (C_5), 57.4 (C_6), 8.5 (CH_3). MS (EI, 70 eV): *m*/*z* (%) = 129 (100) [$(M+H)^+$]. HRMS (ESI): Calculated for $C_6H_8O_3^+$ $[(M)]^+$ = 128.0473. Found = 128.0473.

4-(Bromomethyl)-3-methyl-2(5*H*)-furanone (17a) To a solution of 4-(hydroxy-methyl)-3-methyl-2(5*H*)-furanone (**16a**) (2.00 g, 15.6 mmol, 1.0 eq) in Et_2O (162 mL) at –78 °C was added phosphorus tribromide (736 μL, 7.8 mmol, 0.5 eq) in Et_2O (18.0 mL) and the mixture was stirred at –78 °C to 23 °C over night, then poured onto ice water, diluted with Et_2O and the phases were separated. The organic layer was washed with $NaHCO_3$ (sat.) and brine, dried over Na_2SO_4 and the solvent was removed to obtain 4-(bromomethyl)-3-methyl-2(5*H*)-furanone (**17a**) (2.68 g, 90%) as a light yellow oil. R_f = 0.41 (heptane:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.87-4.86 (m, 2 H_5), 4.22 (s, 2 H_6), 1.91 (t, ^5J = 2.1 Hz, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 174.2 (C_2), 153.1 (C_4), 126.6 (C_3), 70.5 (C_5), 21.6 (C_6), 8.9 (CH_3). MS (EI, 70 eV): *m*/*z* (%) = 191,193 (100) [M^+]. HRMS (ESI): Calculated for $C_6H_7BrO_2NH_4^+$ $[(M+NH_4)]^+$ = 207.9622. Found = 207.9629.

Ethyl 4-acetoxy-3-(acetoxymethyl)-2-fluorobut-2-enoate (15b) To a solution of triethyl 2-fluoro-2-phosphonoacetate (**14b**) (111 mL, 550 mmol, 1.0 eq) in THF (1.43 L) at 0 °C was dropwise added isopropylmagnesium chloride (2 M in THF) (289 mL, 577 mmol, 1.05 eq) and the mixture was stirred at 0 °C for 2 h. 2-Oxopropane-1,3-diyl diacetate (**1**) (95.7 g, 550 mmol, 1.0 eq) was dissolved in 100 mL of THF and was added slowly in a dropping funnel. The reaction mixture was stirred at room temperature over night and then poured into NH_4Cl (sat.) and extracted with TBME. The organic layer was dried over Na_2SO_4, filtered and the solvent removed. The crude material was purified by column chromatography (heptane:EtOAc 3:1) to give ethyl 4-acetoxy-3-(acetoxymethyl)-2-fluorobut-2-enoate (**15b**) (121 g, 84%) as a light yellow liquid. R_f = 0.49 (heptane:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.15 (d, ^4J_F = 2.2 Hz, OCH_2), 4.85 (d, ^4J_F = 3.5 Hz, OCH_2), 4.34 (q, ^3J = 7.1 Hz, OCH_2), 2.08 (s, CH_3), 2.07 (s, CH_3), 1.36 (t, ^3J = 7.1 Hz, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 170.4 (d, ^2J_F = 5.5 Hz, C_3), 159.9 (s, C_8), 159.7 (s, C_9), 147.8 (d, ^1J_F = 267.7 Hz, C_4), 123.4 (d, ^2J_F = 5.5 Hz, C_5), 62.9 (s, C_2), 58.7 (d, ^3J_F = 5.8 Hz, C_7), 57.9 (d, ^3J_F = 10.2 Hz, C_6), 20.7 (s, C_{10}), 20.7 (s, C_{11}), 14.0 (s, C_1). MS (EI, 70 eV): *m*/*z* (%) = 263 (38) [$(M+H)^+$], 199 (100) [$(M-OAc)^+$]. HRMS (ESI): Calculated for $C_{11}H_{15}FO_6^+$ $[(M)]^+$ = 262.0856. Found = 262.0848.

3-Fluoro-4-(hydroxymethyl)-2(5*H*)-furanone (16b) To a solution of 2-(2-ethoxy-1-fluoro-2-oxo-ethylidene)propane-1,3-diyl diacetate (**15b**) (121 g, 461 mmol, 1.0 eq) in MeOH (604 mL) at room temperature was dropwise added acetyl chloride (3.28 mL, 46.1 mmol, 0.1 eq) and the mixture was stirred at room temperature for 18 h and then stirred for 2 h at 50 °C. The solvent was evaporated and azeotroped three times with toluene to give the 3-fluoro-4-(hydroxymethyl)-2(5*H*)-furanone (**16b**) (61.0 g, 100%) as light brown liquid. R_f = 0.28 (heptane:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.92 (dt, ^4J_F = 5.6 Hz, ^4J = 1.1 Hz, 2 H_5), 4.64 (br. s, 2 H_6), 3.08 (br. s, 1 OH). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 166.0 (d, ^2J_F = 30.8 Hz, C_2), 142.3 (d, ^1J_F = 270.4 Hz, C_3), 138.4 (d, ^2J_F = 5.5 Hz, C_4), 67.2 (d, ^3J_F = 6.6 Hz, C_5), 54.9 (d, ^3J_F = 2.5 Hz, C_6). MS (EI, 70 eV): *m*/*z* (%) = 133 (30) [$(M+H)^+$], 119 (42) 115 (43) [$(M-OH)^+$], 83 (100) [$(M-CH_2FO)^+$]. HRMS (ESI): Calculated for $C_5H_5FO_3^+$ $[(M)]^+$ = 132.0222. Found = 132.0220.

4-(Bromomethyl)-3-fluoro-2(5*H*)-furanone (17b) To a solution of 3-fluoro-4-(hydroxymethyl)-2(5*H*)-furanone (**16b**) (12.0 g, 90.8 mmol, 1.0 eq) in Et_2O (162 mL) at –78 °C was added phosphorus tribromide (4.28 mL, 45.4 mmol, 0.5 eq) in Et_2O (18.0 mL) and the mixture was stirred at –78 °C to 23 °C over night. Then it was poured onto ice water and diluted with Et_2O. The organic layer was washed with $NaHCO_3$ (sat.) and brine. The solvent was dried over Na_2SO_4. Removal of the solvent in vacuum left the 4-(bromomethyl)-3-fluoro-2(5*H*)-furanone (**17b**) (17.1 g, 97%) as a light yellow oil. R_f = 0.47 (heptane:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.85 (dt, ^4J_F = 5.8 Hz, ^4J = 0.8 Hz, 2 H_5), 4.23 (dt, ^4J_F = 1.9 Hz, ^4J = 0.8 Hz, 2 H_6). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 164.0 (d, ^2J_F = 30.0 Hz, C_2), 144.2 (d, ^1J_F = 280.6 Hz, C_3), 132.9 (d, ^2J_F = 5.8 Hz, C_4), 67.2 (d, ^3J_F = 5.8 Hz, C_5), 17.4 (d, ^3J_F = 2.5 Hz, C_6). MS (EI, 70 eV): *m*/*z* (%) = 194,196 (20) [$(M+H)^+$], 165,167 (20), 137,139 (10), 115 (100) [$(M-Br)^+$]. HRMS (ESI): Calculated for $C_6H_6FBrO_2^+$ $[(M)]^+$ = 193.9377. Found = 193.9378.

***tert*-Butyl *N*-allyl-*N*-[(4-methyl-5-oxo-2*H*-furan-3-yl)methyl]carbamate (18a)** To a solution of bromide **17a** (1.00 g, 5.25 mmol, 1.0 eq) in THF (10 mL) at 0 °C was dropwise added a solution of triethylamine (2.20 mL, 15.8 mmol, 3 eq) and prop-2-en-1-amine (0.40 mL, 5.25 mmol, 1.0 eq) in THF (10 mL). The resulting solution was stirred at room temperature for 12 h. The precipitate was filtered off, washed with THF, and the solvent was removed in vacuum. The crude material was purified by column chromatography (heptane:EtOAc 1:3) and the amine was used for protection reactions without further purification. To a solution of the amine (822 mg, 4.92 mmol, 1 eq) in dry THF (12 mL) was added Boc_2O (1.07 g, 4.92 mmol, 1.0 eq). The resulting solution was stirred at 40 °C for 2 h. After that time, the solvent was removed under reduced pressure and the residue purified by column chromatography (heptane:EtOAc 1:1) to afford the Boc-protected product (**18a**) as a colorless oil (1.30 g, 92%). R_f = 0.44

(heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 3083 (w, C=C), 2976 (s, C-H), 1752 (s, C=O), 1689 (s, O-C=O), 1356 (m, ^{t}Bu), 866 (m, C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.74 (ddt, ^{3}J = 16.8 Hz, ^{3}J = 10.5 Hz, ^{3}J = 5.9 Hz, 1 $H_{2'}$), 5.21-5.12 (m, 2 $H_{3'}$), 4.68 (t, ^{4}J = 1.0 Hz, 2 H_2), 4.18 (br. s, CH_2), 3.80 (br. s, 2 $H_{1'}$), 1.85 (s, CH_3), 1.47 [(s, $C(CH_3)_3$)]. ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 174.7 (C_5), 156.2 (*C*OO*t*Bu), 133.1 ($C_{2'}$), 123.5 (C_4), 117.5 ($C_{3'}$), 80.9 [*C*(CH_3)$_3$], 71.1 (C_2), 50.4 ($C_{1'}$), 42.4 (CH_2), 28.3 [C(*C*H_3)$_3$], 8.6 (CH_3). MS (EI, 70 eV): *m*/*z* (%) = 212 (100) [(M-C_4H_7)$^{+}$].

***N-tert*-Butoxycarbonyl-7-methyl-3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one (19a)** The compound was prepared from photoprecursor **18a** (50.0 mg, 0.19 mmol) in 38 mL of MeCN by irradiation for 2 h (5 mM). Purification of the crude by column chromatography (heptane:EtOAc 1:1) afforded the photoproduct **19a** as an white solid (46.1 mg, 92%). mp 101 °C. R_f = 0.33 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 2976 (s, C-H), 1755 (s, C=O), 1685 (s, O-C=O), 1363 (m, ^{t}Bu). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.34 (d, ^{2}J = 9.9 Hz, 1 H_{10}), 4.03 (d, ^{2}J = 9.9 Hz, 1 H_{10}), 3.91 (br. s, 1 H_2), 3.58 (br. s, 1 H_4), 3.24 (dd, ^{2}J = 11.7 Hz, ^{3}J = 6.5 Hz, 1 H_4), 2.96 (d, ^{2}J = 12.5 Hz, 1 H_2), 2.77 (virt. dd, ^{3}J = 14.7 Hz, ^{3}J = ^{3}J = 6.7 Hz, 1 H_5), 2.53 (dd, ^{2}J = 12.7 Hz, 1 H_6), 1.73 (dd, ^{2}J = 12.7 Hz, ^{3}J = 6.7 Hz, 1 H_6), 1.49 [s, $C(CH_3)_3$], 1.24 (s, CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 180.8 (C_8), 154.8 (*C*OO^{t}Bu), 80.2 [*C*(CH_3)$_3$], 71.1 (C_{10}), 53.3 (C_4), 51.7 (C_2), 46.9 (C_7), 42.5 (C_1), 39.3 (C_6), 35.5 (C_5), 28.5 [C(*C*H_3)$_3$], 16.2 (CH_3). MS (EI, 70 eV): *m*/*z* (%) = 212 (100) [(M-C_4H_7)$^{+}$]. HRMS (ESI): Calculated for $C_{14}H_{21}NO_4$ [(M)$^{+}$] = 267.1471. Found = 267.1474

***tert*-Butyl *N*-(2-methylallyl)-*N*-[(4-methyl-5-oxo-2*H*-furan-3-yl)methyl]carbamate (18b)** To a solution of bromide **17a** (2.60 g, 13.6 mmol, 1.0 eq) in THF (14 mL) at 0 °C was dropwise added a solution of Et_3N (5.70 mL, 40.8 mmol, 3 eq) and 2-methylprop-2-en-1-amine (1.24 mL, 13.6 mmol, 1.0 eq) in THF (14 mL). The resulting solution was stirred at room temperature for 12 h. The precipitate was filtered off, washed with THF, and the solvent was removed in vacuum. The crude material was purified by column chromatography (heptane:EtOAc 1:3) and the amine was used for protection reactions without further purification. To a solution of the amine (2.25 g, 12.4 mmol, 1.0 eq) in dry THF (25 mL) was added Boc_2O (2.98 g, 13.7 mmol, 1.1 eq). The resulting solution was stirred at 40 °C for 75 min. After that time, the solvent was removed under reduced pressure and the residue purified by column chromatography (heptane:EtOAc 1:1) to afford the Boc-protected product **18b** as a light yellow oil (3.30 g, 87%). R_f = 0.52 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 3079 (w, C=C), 2971 (s, C-H), 1755 (s, C=O), 1690 (s, O-C=O), 1365 (m, ^{t}Bu), 883 (m, C=C). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.93 (br. s, 1 $H_{3'}$), 4.79 (br. s, 1 $H_{3'}$), 4.68 (br. s, 2 H_2), 4.16 (br. s, CH_2), 3.72 (br. s, 2 $H_{1'}$), 1.85 (s, CH_3), 1.69 (s, CH_3), 1.47 [(s, $C(CH_3)_3$)]. ^{13}C NMR (151 MHz, DMSO-d_6): δ (ppm) 179.7 (C_5), 162.9 (C_4), 159.6

(*C*OO*t*Bu), 146.2 (C_3), 127.9 ($C_{2'}$), 117.3 ($C_{3'}$), 84.8 [*C*(CH_3)$_3$], 75.9 (C_2), 58.1 ($C_{1'}$), 47.8 (CH_2), 33.1 [C(*C*H_3)$_3$], 24.8 (CH_3), 13.5 (CH_3). MS (EI, 70 eV): *m*/*z* (%) = 226 (100) [(M-C_4H_7)$^+$]. HRMS (ESI): Calculated for $C_{15}H_{23}NO_4^+$ [(M)]$^+$ = 281.1609. Found = 281.1603.

***N-tert*-Butoxycarbonyl-5-methyl-7-methyl-3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one (19b)** The compound was prepared from photoprecursor **18b** (3.30 g, 11.7 mmol) in 98 mL of MeCN by irradiation for 1 h (120 mM). Purification of the crude by column chromatography (heptane:EtOAc 1:1) afforded the photoproduct **19b** as a white solid (2.73 g, 85%). mp 97 °C. R_f = 0.44 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 2970 (s, C-H), 1768 (s, C=O), 1690 (s, O-C=O), 1365 (m, ^{t}Bu). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 4.30 (d, ^2J = 10.2 Hz, 1 H_{10}), 4.01 (d, ^2J = 10.2 Hz, 1 H_{10}), 3.84 (d, ^2J = 12.5 Hz, 1 H_2), 3.56 (d, ^2J = 11.4 Hz, 1 H_4), 3.10 (d, ^2J = 12.5 Hz, 1 H_2), 2.80 (d, ^2J = 11.4 Hz, 1 H_4), 1.98 (d, ^2J = 12.6 Hz, 1 H_6), 1.79 (d, ^2J = 12.6 Hz, 1 H_6), 1.46 [s, C(CH_3)$_3$], 1.15 (s, CH_3), 1.12 (s, CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ (ppm) 182.5 (C_8), 154.1 (*C*OO^{t}Bu), 79.3 [*C*(CH_3)$_3$], 67.2 (C_{10}), 58.7 (C_4), 53.6 (C_2), 47.6 (C_7), 42.7 (C_1), 42.5 (C_6), 41.7 (C_5), 28.5 [C(*C*H_3)$_3$], 18.8 (CH_3), 16.1 (CH_3). MS (EI, 70 eV): *m*/*z* (%) = 281 (5) [(M)$^+$], 226 (20) [(M-C_4H_8)$^+$], 208 (11), 57 (100) [(M-$C_{11}H_{14}NO_4$)$^+$]. HRMS (ESI): Calculated for $C_{15}H_{23}NO_4$ [(M)$^+$] = 281.1609. Found = 281.1613.

***tert*-Butyl allyl[(4-fluoro-5-oxo-2,5-dihydrofuran-3-yl)methyl]carbamate (20)** To a solution of the bromide **17b** (1.00 g, 5.13 mmol, 1.0 eq) in THF (15 mL) at 0 °C was dropwise added a solution of Et_3N (2.14 mL, 15.4 mmol, 3 eq) and prop-2-en-1-amine (0.39 mL, 5.13 mmol, 1.0 eq) in THF (15 mL). The resulting solution was stirred at room temperature for 12 h. The precipitate was filtered off, washed with THF, and the solvent was removed in vacuum. The crude material was purified by column chromatography (heptane:EtOAc 1:3) and the product was used in the next step without further purification. The amine was dissolved in dry THF (8 mL) and Boc_2O was added (714 mg, 3.27 mmol, 1.1 eq). The resulting solution was stirred at 40 °C for 2 h. After that time, the solvent was removed under reduced pressure and the residue purified by column chromatography (heptane:EtOAc 1:1) to afford the Boc-protected product **20** as a colorless oil (797 mg, 59%). R_f = 0.49 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 3083 (w, C=C), 2978 (s, C-H), 1778 (s, C=O), 1688 (s, O-C=O), 1366 (m, ^{t}Bu), 1111 (s, C-F), 888 (m, C=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.76 (ddt, ^3J = 16.8 Hz, ^3J = 10.6 Hz, ^3J = 6.1 Hz, 1 $H_{2'}$), 5.26-5.12 (m, 2 $H_{3'}$), 4.75 (d, ^4J_F = 5.7 Hz, 2 H_2), 4.18 (br. s, 2 $H_{1'}$), 3.81 (br. s, CH_2), 1.47 [s, C(CH_3)$_3$]. ^{13}C NMR (91 MHz, $CDCl_3$): δ (ppm) 164.7 (d, ^2J_F = 31.1 Hz, C_5), 155.6 (*C*OO*t*Bu), 143.9 (d, ^1J_F = 276.2 Hz, C_4), 135.2 (d, ^2J_F = 5.5 Hz, C_3), 132.8 ($C_{3'}$), 117.9 ($C_{2'}$), 81.1 [*C*(CH_3)$_3$], 67.6 (C_2), 50.8 (CH_2), 40.2 ($C_{1'}$), 28.3 [C(*C*H_3)$_3$]. MS (EI, 70 eV): *m*/*z* (%) = 216 (100) [(M-C_4H_7)$^+$].

***N-tert*-Butoxycarbonyl-7-fluor-3-aza-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one (21)** The compound was prepared from photoprecursor **20** (474 mg, 1.75 mmol) in 350 mL of MeCN by irradiation for 2 h (5 mM). Purification of the crude by column chromatography (heptane:EtOAc 1:1) afforded the photoproduct **21** as a white solid (374 mg, 79%). mp 156 °C. R_f = 0.28 (heptane:EtOAc 1:1). IR (ATR): υ (cm^{-1}) = 2979 (s, C-H), 17768 (s, C=O), 1683 (s, O-C=O), 1362 (m, ^{t}Bu), 1100 (s, C-F). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.38 (dd, ^2J = 9.9 Hz, ^4J_F = 2.8 Hz, 1 H_{10}), 4.24 (d, ^2J = 9.9 Hz, 1 H_{10}), 4.18 (d, ^2J = 12.5 Hz, 1 H_2), 3.73 (br. s, 1 H_4), 3.35 (dd, ^2J = 11.7 Hz, ^3J = 6.1 Hz, 1 H_4), 3.10 (dd, ^2J = 12.5 Hz, ^4J_F = 0.9 Hz, 1 H_2), 2.73 (ddd, ^2J = 11.9 Hz, ^3J = 7.1 Hz, ^3J_F = 4.6 Hz, 1 H_6), 2.40 (virt. qd, ^3J = ^3J = 7.1 Hz, ^3J = 3.8 Hz, 1 H_5), 2.26-2.23 (m, 1 H_6), 1.47 [s, $C(CH_3)_3$]. ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 173.0 (d, ^2J_F = 25.6 Hz, C_8), 154.7 (*C*OO^{t}Bu), 144.1 (d, ^1J_F = 156.8 Hz, C_7), 80.5 [*C*$(CH_3)_3$], 71.3 (C_{10}), 51.3 (m, C_4), 45.1 (m, C_2), 45.0 (m, C_1), 33.5 (m, C_5), 32.8 (d, ^2J_F = 23.7 Hz, C_6), 28.4 [C(*C*$H_3)_3$]. MS (EI, 70 eV): *m*/*z* (%) = 271 (5) $[(M+H)]^+$, 216 (20) $[(M-C_4H_8)^+]$, 198 (19), 171 (7), 57 (100) $[(M-C_9H_9FNO_2)^+]$. HRMS (ESI): Calculated for $C_{13}H_{18}FNO_4^+$ $[(M)]^+$ = 271.1220. Found = 271.1223.

Diethyl 2-allyl-2-[(5-oxo-2,5-dihydrofuran-3-yl)methyl]malonate To a solution of potassium *tert*-butoxide (370 mg, 3.3 mmol, 1.1 eq) in DMSO (6.0 mL) at 23 °C was added diethyl 2-allylmalonate (654 µL, 3.3 mmol, 1.1 eq) and the resulting yellow solution was stirred for 10 min, then 4-(bromomethyl)-2(5*H*)-furanone (**4**) (531 mg, 3.0 mmol, 1.0 eq) was added (exothermic, immediately a deep blue color developed) and the mixture was stirred at 23 °C for 40 min. Poured into NH_4Cl (sat.), extracted with EtOAc, the organic layer washed with brine and dried over Na_2SO_4. Removal of the solvent in vacuum left a dark brown oil which was purified by flash chromatography (silica gel, 20 g, 0% to 25% EtOAc in heptane) to give diethyl 2-allyl-2-((5-oxo-2,5-dihydrofuran-3-yl)methyl)malonate (197 mg, 22%) as a colorless oil. R_f = 0.45 (heptane:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 5.97-5.79 (m, 1 H_4), 5.62 (ddt, ^3J = 17.1 Hz, ^3J = 10.0 Hz, ^3J = 7.4 Hz, 1 $H_{2'}$), 5.22-5.05 (m, 2 $H_{3'}$), 4.74 (d, ^4J = 1.8 Hz, 2 H_2), 4.29-4.14 (m, 2 x OC*H*$_2$$CH_3$), 2.97 (d, ^4J = 1.1 Hz, CH_2), 2.72 (dt, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 2 $H_{1'}$), 1.31-1.16 (m, 2 x OC*H*$_2$$CH_3$). MS (EI, 70 eV): *m*/*z* (%) = 297 (100) $[(M+H)]^+$. HRMS (ESI): Calculated for $C_{15}H_{20}O_6$ $[(M^+)]$ = 296.1260. Found = 296.1263.

3,3-Diethoxycarbonyl-9-oxatricyclo[5.3.0.0^{1,5}]decan-8-one (25) The compound was prepared from the above-mentioned photoprecursor diethyl 2-allyl-2-[(5-oxo-2,5-dihydrofuran-3-yl)methyl]malonate (24.0 mg, 0.81 µmol) in 18 mL of MeCN by irradiation for 5 h (5 mM). Purification of the crude by column chromatography (heptane:EtOAc 1:1) afforded the photoproduct **25** as a colorless oil (10.9 mg, 45%). R_f = 0.41 (heptane:EtOAc 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 4.35 (d, ^2J = 9.7 Hz, 1 H_{10}), 4.28 (q, ^3J = 7.2 Hz, OC*H*$_2$$CH_3$), 4.22-4.17 (m, OC*H*$_2$$CH_3$), 4.16 (d, ^2J = 9.7 Hz, 1 H_{10}), 2.89 (ddd, ^3J = 10.0 Hz, ^3J =

3.9 Hz, ^3J = 1.0 Hz, 1 H_5), 2.87-2.83 (m, 1 H_7), 2.77 (d, ^2J = 14.1 Hz, 1 H_2), 2.50 (dd, ^2J = 14.4, ^3J = 10.0 Hz, 1 H_4), 2.54-2.47 (m, 1 H_4), 2.27 (dd, ^2J = 13.3 Hz, ^3J = 2.1 Hz, 1 H_6), 2.04 (ddd, ^2J = 13.3 Hz, ^3J = 9.1 Hz, ^3J = 3.9 Hz, 1 H_6), 2.02 (d, ^2J = 14.1 Hz, 1 H_2), 1.31 (t, ^3J = 7.2 Hz, OCH_2CH_3), 1.25 (t, ^3J = 7.1 Hz, OCH_2CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 180.2 (C_8), 171.5/171.4 (2 × *C*OOEt), 75.2 (C_{10}), 62.3 (C_3), 62.0/61.9 (2 × OCH_2CH_3), 51.7 (C_1), 42.2 (C_7), 40.3/40.2 (C_2, C_4), 39.6 (C_5), 27.8 (C_6), 14.1/14.0 (2 × OCH_2CH_3). MS (EI, 70 eV): *m*/*z* (%) = 297 (100) $[(M+H)]^+$. HRMS (ESI): Calculated for $C_{15}H_{20}O_6$ $[(M)]^+$ = 296.1260. Found =296.1260.

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