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Influence of the $-CH_2X$ Substituent on the Regioselectivity of Intramolecular *meta*-Photocycloaddition Reactions

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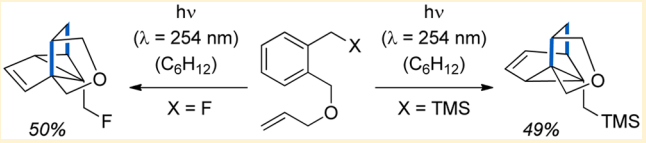
Supporting Information

ABSTRACT: In studies related to the synthesis of the bicyclo[3.2.1]octane core of enterocin by an intramolecular *meta*-photocycloaddition, it was found that the regioselectivity of the reaction depends strongly on the substituent $-CH_2X$ in the *ortho*-position to the tether. Electropositive groups X (X = H, Me, TMS, TES) gave preferentially the linear isomer (regioisomeric ratio = 87/13 to >95/5), whereas electronegative substituents (X = OH, OAc, F) showed a clear preference for the angular isomer (regioisomeric ratio = 75/25 to >95/5). The silylated and fluorinated products were obtained as single isomers in moderate yield.



On the basis of our interest in the synthesis of oxygenated polyketide natural products derived from marine actinomycetes,[1] we have recently started to evaluate different routes for the synthesis of (−)-enterocin (**1**).[2] It occurred to us that the bicyclo[3.2.1]octane core of the natural product might be accessible by a *meta*-photocycloaddition reaction.[3] This powerful photochemical transformation has been successfully applied to natural product synthesis,[4] mostly, however, to the total synthesis of di- and triquinanes with a bicyclo[3.3.0]octane core.[5,6] An issue associated with the intramolecular version of the *meta*-photocycloaddition is its regioselectivity. In typical substrates, in which an electron-donating substituent is located in an *ortho*-position relative to the chain, linear and angular products (e.g., **2** and **3**) are formed in variable ratios.[3−7] In the present case, we felt that generation of the linear isomer **2** would be desirable because its double bond would be ideally located to allow introduction of the two hydroxy groups in positions C3 and C4 of the bicyclo[3.2.1]octane skeleton (Figure 1). In this regard, we were pleased to note that the respective methyl compound (X = H) had been previously prepared by a *meta*-photocycloaddition with high regioselectivity.[8] However, since a methyl group at C8 of the bicyclo[3.2.1]octane seemed not ideal for synthetic purposes, we undertook a comprehensive study, in which we investigated the influence of the $-CH_2X$ group on the regioselectivity of the *meta*-photocycloaddition. The results of this study are summarized in this paper.

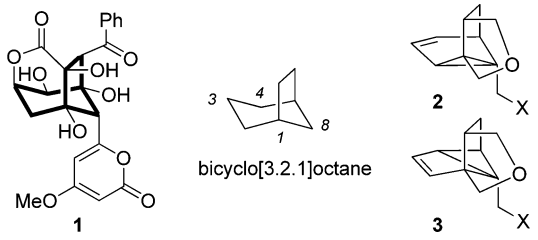
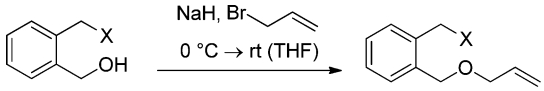


Figure 1. Structure of enterocin (**1**), of its carbocyclic bicyclo[3.2.1]-octane core, and of linear and angular *meta*-photocycloaddition products **2** and **3**.

Two approaches were used to prepare appropriate precursors for the *meta*-photocycloaddition reaction. In the first approach, readily available benzylic alcohols **4b**−**4e** were allylated upon treatment with sodium hydride and allyl bromide in THF (75−90%, Scheme 1). The parent compound **5a** (X = H) had been similarly prepared from commercially available *ortho*-methylbenzyl alcohol (**4a**).[8] The *ortho*-silylmethyl-substituted alcohol **4c** (X = TMS) has been previously synthesized by directed metalation of **4a** and subsequent trimethylsilylation.[9] In the same fashion, the triethylsilyl analogue **4d** (X = TES) was obtained from **4a** (68% yield). Monosilylation of *ortho*-di(hydroxymethyl)benzene[10] delivered the *tert*-butyldimethylsilyl (TBS) ether **4e** (X = OTBS).[11]

Scheme 1. Synthesis of *meta*-Photocycloaddition Precursors 5b−5e by Allylation of Benzylic Alcohols 4b-4e



4b	X = Me	*90%*	**5b**
4c	X = TMS	*76%*	**5c**
4d	X = TES	*78%*	**5d**
4e	X = OTBS	*90%*	**5e**

In the second approach, benzylic alcohol **5f**,[12] which was in our hands most cleanly available by deprotection of silyl ether **5e** (TBAF in THF, 98%), was transformed in various benzylic derivatives (Scheme 2). *O*-Methylation delivered ether **5g** (X =

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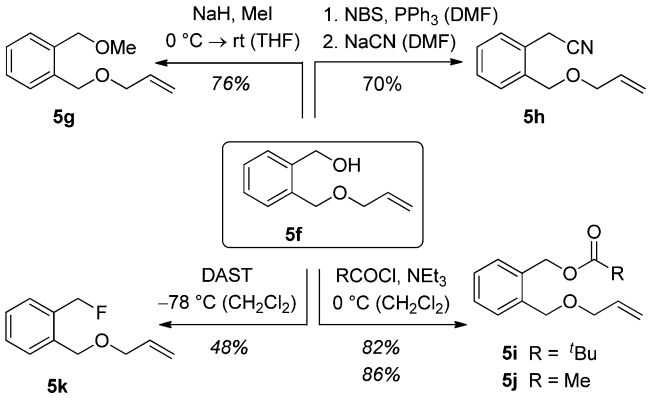
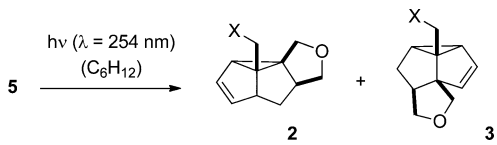
Scheme 2. Synthesis of *meta*-Photocycloaddition Precursors 5g–5k by Functional Group Transformations on Benzylic Alcohol 5f



OMe), while the respective benzylic cyanide **5h** (X = CN) was prepared in two steps via the bromide. Acylation reactions were favorably performed in the presence of catalytic amounts of *N*,*N*-dimethylaminopyridine (DMAP)[13] and gave pivaloate **5i** (X = OPiv) in 82% yield and acetate **5j** (X = OAc) in 86% yield. Fluorination of alcohol **5f** was achieved with diethylaminosulfur trifluoride (DAST) to furnish product **5k** (X = F).

Photochemical reactions with substrates **5** were performed with low-pressure mercury lamps (λ = 254 nm)[14] in quartz vessels at ambient temperature (Table 1). The previously reported[8] substrate **5a** delivered the known linear photocycloaddition product **2a** in 44% yield (entry 1). The formation of *ortho*-photocycloaddition products was observed in minor quantities, but upon column chromatographic purification, only a single *meta*-photocycloaddition product was isolated. The ethyl-substituted substrate **5b** showed a diminished chemoselectivity, possibly due to competitive hydrogen abstraction reactions (entry 2). The linear product **2b** was the only isolable product (29%). Pleasingly, the synthetically useful silylmethyl-substituted substrates **5c** and **5d** reacted smoothly and in decent yields (entries 3, 4). The angular isomer **3c** was not detectable in the reaction of the former substrate, while minor amounts of the angular isomer **3d** were found to accompany linear product **2d** in the reaction of the latter substrate. In general, the ^{1}H NMR coupling pattern of the olefinic protons allowed a facile structural assignment of either isomer. The linear isomers exhibit two doublets of doublets (dd) as each olefinic proton couples also to an adjacent methine proton, whereas, in the angular isomers, one olefinic proton is adjacent to a quaternary center, resulting in a plain doublet. Partial separation of the linear and angular isomers was possible by column chromatography in most cases. The data given in Table 1 refer, however, to the mixture of the two isomers. Their ratio remained after purification unchanged as compared to the ratio in the crude product mixture.

Table 1. Regioselectivity in the Formation of Linear and Angular *meta*-Photocycloaddition Products 2 and 3 Depending on the Functional Group X



entry[a]	substrate	X	r.r. (**2**/**3**)[b]	yield[c] [%]
1	**5a**	H	>95/5	44
2	**5b**	Me	>95/5	29
3	**5c**	TMS	>95/5	49
4	**5d**	TES	87/13	66
5	**5e**	OTBS	44/56	68
6	**5f**	OH	25/75	31
7	**5g**	OMe	41/59	26
8	**5h**	CN	40/60	37
9	**5i**	OPiv	33/67	34
10	**5j**	OAc	16/84	48
11	**5k**	F	<5/95	50

[a]All *meta*-photocycloaddition reactions were conducted for 16 h at ambient temperature (air-cooled) in quartz tubes using a merry-go-round reactor with 16 low-pressure mercury lamps (λ = 254 nm)[14] as the irradiation source in dry, deaerated cyclohexane (c = 0.04 mM). [b]The ratio of regioisomers (r.r.) was determined both in the crude reaction mixture and in the isolated product by ^{1}H NMR. [c]Yield (mixture of **2**/**3**) after chromatographic purification.

Surprisingly, the regioselectivity of the *meta*-photocycloaddition changed drastically upon introducing an oxygen substituent at the methylene group. The angular products **3e–3g** became major products (entries 5–7) with the most pronounced regioselectivity observed for the hydroxymethyl-substituted substrate **5f** (entry 6). The cyanide **5h** reacted similarly in favor of the angular product (entry 8). Pivaloyl protection of the hydroxy group (substrate **5i**) did not improve the yield nor the regioselectivity as compared to the unprotected compound (entry 9). Synthetically useful selectivities were, however, achieved with the acetate **5j** (entry 10) and the fluoride **5k** (entry 11). In both cases, the angular regioisomers **3j** and **3k** clearly prevailed, and in both cases, the yields were at least moderate. It should be noted that we did not attempt to optimize the yield, but rather identical conditions were applied to all 11 substrates. Given the product complexity, the high mode-, regio-, and stereoselectivity achieved for products **2c** and **2d** and for products **3j** and **3k** are remarkable.

When considering the factors determining the regioselectivity, it should be noted that no change of the regioisomeric ratio[15] (**2**/**3**) with time was observed in any of the reactions, in which the reaction course was followed by GLC (substrates **5a**, **5c**, **5e**, **5k**). It seems, therefore, likely that the regioselectivity is kinetically controlled. In previous work,[8,16] it was argued that it is the length and flexibility of the three-atom tether that determines the regioselectivity of the intramolecular *meta*-photocycloaddition reaction. It was assumed that the short allyloxymethyl substituent leads to a significant sp^3-hybridization at the carbon atom C1, to which the substituent is attached and at which C–C bond formation occurs (Figure 2).[17] This hybridization change affects also the adjacent positions C2 and C6, which favors cyclopropane bond formation between these centers, leading to the linear product. If the terminal olefin is linked to the arene by a three-atom

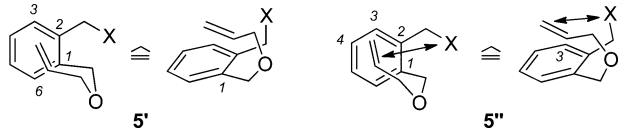


Figure 2. Preferred conformation **5′** and **5″** leading to formation of linear (**2**) or angular (**3**) *meta*-photocycloaddition products.

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chain with greater bond distances between the atoms (e.g., a propylene[16a] or a methylsilylmethyl[16c] tether) and larger bond angles, the regioselectivity is shifted to the angular product because the sp^3-hybridization at carbon atom C3 occurs earlier at the reaction hypersurface, favoring a cyclopropane bond formation between carbon atoms C2 and C4. Following this line of arguments, it is likely that conformation **5′** accounts for the preferred formation of the linear products **2** (Figure 2), as previously postulated.[8] For electronegative substituents X, an electrostatic repulsion of their lone pairs and the olefinic π system ($\leftrightarrow$)[18] could alter the conformation, positioning the terminal end of the double bond in closer proximity to C3 (conformation **5″**), thus favoring formation of the angular products **3**.

In summary, the substituent X in substrates **5** plays a crucial role in determining the regioselectivity of their intramolecular *meta*-photocycloaddition. This previously unknown fact can be synthetically useful because the selective formation of either the linear or the angular isomer is desired in many applications. In our case, the formation of the linear product isomers **2c** and **2d** appears to be most promising for further studies toward the total synthesis of enterocin.

EXPERIMENTAL SECTION

General Methods. All reactions, sensitive to air or moisture, were carried out in flame-dried glassware under positive pressure of argon using standard Schlenk techniques. Flash chromatography was performed on silica gel 60 (230−400 mesh) with the eluent mixtures given for the corresponding procedures. Thin-layer chromatography (TLC) was performed on silica-coated glass plates (silica gel 60 F 254). Compounds were detected by UV (λ = 254 nm, 366 nm) and $KMnO_4$ (potassium permanganate solution). Technical solvents (*n*-pentane, ethyl acetate, diethyl ether) employed for preparative column chromatography were purified by distillation prior to use. Chemical shifts are reported relative to the solvent [$CHCl_3$ $\delta(^1H)$ = 7.26 ppm, $\delta(^{13}C)$ = 77.0 ppm] as reference. HRMS data were recorded by electron ionization (EI) or electron spray ionization (ESI) on a transmission quadrupole mass spectrometer.

Benzylic alcohols **4c**,[9] **4e**,[11] and *ortho*-di(hydroxymethyl)benzene[10] were synthesized according to literature procedures. Alcohol **5f**[12] was synthesized from TBS−ether **5e** by deprotection with TBAF. The spectra obtained were identical to literature data.[11] All other chemicals were used as received from commercial suppliers.

1-Allyloxymethyl-2-ethylbenzene (5b). Sodium hydride (238 mg, 5.94 mmol, 60% suspension in mineral oil, 2.0 equiv) was suspended in 5 mL of THF and cooled to 0 °C. A solution of 2-ethylbenzyl alcohol (400 μL, 404 mg, 2.97 mmol, 1.0 equiv) in 5 mL of THF was added dropwise at 0 °C, and the mixture was stirred for 30 min. Then, a solution of allyl bromide (385 μL, 539 mg, 4.45 mmol, 1.5 equiv) in 5 mL of THF was added and the reaction mixture was warmed to room temperature overnight. The reaction was quenched with 3 mL of water, the layers were separated, and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layers were washed with sat. NaCl solution (5 mL) and dried over Na_2SO_4. The drying agent was removed by filtration, and the volatile components were evaporated in vacuo. Purification by column chromatography (*n*-pentane/ether = 99/1) gave 473 mg (2.68 mmol, 90%) of the product as a colorless oil. TLC (*n*-pentane/ether = 99/1): R_f = 0.39 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3065, 2965, 2871, 1453 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.23 (t, ^3J = 7.7 Hz, 3 H), 2.71 (q, ^3J = 7.7 Hz, 2 H), 4.05 (dt, ^3J = 5.7 Hz, ^4J = 1.3 Hz, 2 H), 4.55 (s, 2 H), 5.21 (*virt.* dq, ^3J = 10.3 Hz, $^2J \cong {}^4J$ = 1.4 Hz, 1 H), 5.32 (*virt.* dq, ^3J = 17.3 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1 H), 5.97 (ddt, ^3J = 17.3 Hz, ^3J = 10.3 Hz, ^3J = 5.7 Hz, 1 H), 7.18 (td, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1 H), 7.21 (d, ^3J = 7.3 Hz, 1 H), 7.26 (td, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1H), 7.35 (d, ^3J = 7.3 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 15.4 (q), 25.4 (t), 70.3 (t), 71.4 (t), 117.2 (t), 125.9 (d), 128.2 (d), 128.6 (d), 129.1 (d), 135.0 (d), 135.7 (s), 142.9 (s). MS (EI, 70 eV): *m*/*z* (%) = 176 (2, M^+), 118 (100, $[M - OC_3H_5]^+$). HRMS (ESI) *m*/*z*: $[M + NH_4]^+$ calcd. for $C_{12}H_{20}NO$: 194.1539; found: 194.1539.

2-(Allyloxymethyl)benzyltrimethylsilane (5c). Sodium hydride (20.6 mg, 514 μmol, 60% suspension in mineral oil, 2.0 equiv) was suspended in 1 mL of THF and cooled to 0 °C. Subsequently, a mixture of alcohol **4c** (50.0 mg, 257 μmol, 1.0 equiv) and allyl bromide (111 μL, 156 mg, 1.29 mmol, 5.0 equiv) in 2 mL of THF was added dropwise, and the mixture was allowed to warm to room temperature overnight. The reaction was quenched by the addition of 1 mL of water, the layers were separated, and the aqueous layer was extracted with ether (3 × 5 mL). The combined organic layers were washed with 2 mL of sat. NaCl solution and dried over Na_2SO_4, and the drying agent was removed by filtration. After removal of the volatile components in vacuo, the crude product was purified by column chromatography (*n*-pentane/ether = 99/1) to give 46.0 mg (196 μmol, 76%) of the product as a colorless oil. TLC (*n*-pentane/ether = 99/1): R_f = 0.39 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3069, 2952, 1489 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 0.00 (s, 9 H), 2.17 (s, 2 H), 4.03 (dt, ^3J = 5.7 Hz, ^4J = 1.4 Hz, 2 H), 4.46 (s, 2 H), 5.21 (*virt.* dq, ^3J = 10.3 Hz, $^2J \cong {}^4J$ = 1.5 Hz, 1 H), 5.32 (*virt.* dq, ^3J = 17.4 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1 H), 5.97 (ddt, ^3J = 17.4 Hz, ^3J = 10.3 Hz, ^3J = 5.7 Hz, 1 H), 7.00 (d, ^3J = 7.7 Hz, 1 H), 7.07 (td, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1 H), 7.16 (td, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1 H), 7.32 (d, ^3J = 7.5 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = −1.2 (q), 23.0 (t), 70.7 (t), 71.4 (t), 117.3 (t), 124.3 (d), 127.6 (d), 129.2 (d), 129.3 (d), 134.6 (s), 135.1 (d), 139.4 (s). MS (EI, 70 eV): *m*/*z* (%) = 234 (3, M^+), 104 (100, $[C_8H_8]^+$). HRMS (EI) *m*/*z*: $[C_{14}H_{22}OSi]^+$ calcd.: 234.1444; found: 234.1449.

2-(Allyloxymethyl)benzyltriethylsilane (5d). A solution of 2-methylbenzyl alcohol (500 mg, 4.09 mmol, 1.0 equiv) in 4 mL of THF was cooled to 0 °C, and *n*-butyl lithium (4.09 mL, 2.5 M in hexanes, 10.2 mmol, 2.5 equiv) was added dropwise. The mixture was stirred for 16 h at room temperature, before triethylsilyl chloride (1.72 mL, 1.54 g, 10.2 mmol, 2.5 equiv) was added dropwise while the mixture was cooled in a water bath. The suspension was stirred for an additional 2 h before being quenched with 2 mL of water. The layers were separated, and the aqueous layer was extracted with ether (3 × 8 mL). The organic layers were combined, washed with sat. NaCl solution (5 mL), and dried over Na_2SO_4. The drying agent was removed by filtration, and the volatile components were evaporated in vacuo. The crude product was dissolved in 30 mL of THF and 9 mL of water, and 15 mL of acetic acid was added. The mixture was stirred overnight, before being basified with 4 N NaOH. The aqueous layer was extracted with ether (3 × 10 mL), and the organic layers were combined and washed with sat. NaCl solution (5 mL). The mixture was dried over Na_2SO_4 and separated from the drying agent. After removal of the volatile components in vacuo, a yellow oil was obtained, which was directly used for the next step. Sodium hydride (639 mg, 60% suspension in mineral oil, 16.0 mmol, 3.0 equiv) was suspended in 6 mL of THF and cooled to 0 °C. Subsequently, the crude product dissolved in 6 mL of THF was added dropwise, and the mixture was stirred for 30 min. Allyl bromide (1.84 mL, 2.58 g, 21.3 mmol, 4.0 equiv) was added dropwise, and the mixture was allowed to warm to room temperature overnight. The reaction was quenched by the addition of 5 mL of water, the layers were separated, and the aqueous layer was extracted with ether (3 × 15 mL). The combined organic layers were washed with 8 mL of sat. NaCl solution, dried over Na_2SO_4, and separated from the drying agent. The volatile components were removed in vacuo, and the crude product was purified by column chromatography (*n*-pentane/ether = 99/1) to give 583 mg (3.62 mmol, 78%) of the product as a colorless oil. TLC (*n*-pentane/ether = 99/1): R_f = 0.43 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3071, 2950, 1453 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 0.54 (q, ^3J = 8.1 Hz, 6 H), 0.89 (t, ^3J = 8.1 Hz, 9 H), 2.17 (s, 2 H), 4.05 (d, ^3J = 5.8 Hz, 2 H), 4.47 (s, 2 H), 5.22 (d, ^3J = 10.5 Hz, 1 H), 5.34 (d, ^3J = 17.4 Hz, 1 H), 5.97 (ddt, ^3J = 17.4 Hz, ^3J = 10.5 Hz, ^3J = 5.8 Hz, 1 H), 7.02 (d, ^3J = 7.7 Hz, 1 H), 7.06 (*virt.* t, $^3J \cong {}^3J$ = 7.7 Hz, 1 H), 7.14 (*virt.* t, $^3J \cong {}^3J$ = 7.3 Hz, 1 H), 7.29 (d, ^3J = 7.3 Hz, 1 H).

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$^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 3.7 (t), 7.4 (q), 17.9 (t), 70.7 (t), 71.5 (t), 117.3 (t), 124.2 (d), 127.6 (d), 129.1 (d), 129.4 (d), 134.7 (s), 135.1 (d), 139.5 (s). MS (EI, 70 eV): m/z (%) = 277 (2, M^+), 247 (12, $[M - Et]^+$), 104 (100, $[C_8H_8]^+$). HRMS (EI) m/z: $[M - Et]^+$ calcd. for $C_{15}H_{23}OSi$: 247.1513; found: 247.1511.

(2-(Allyloxymethyl)benzyloxy)(*tert*-butyl)dimethylsilane (5e). Sodium hydride (65.9 mg, 1.65 mmol, 60% suspension in mineral oil, 1.5 equiv) was suspended in 1 mL of THF and cooled to 0 °C. A solution of alcohol **4e** (277 mg, 1.10 mmol, 1.0 equiv) in 1 mL of THF was added dropwise, and the mixture was stirred for 30 min. Then, a solution of allyl bromide (114 μL, 160 mg, 1.32 mmol, 1.2 equiv) in 1 mL of THF was added, and the reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched by the addition of 3 mL of water. The layers were separated, and the aqueous layer was extracted with ether (3 × 10 mL). The organic layers were combined, washed with 5 mL of sat. NaCl solution, dried over Na_2SO_4, and separated from the drying agent. After evaporation of the volatile components in vacuo, the crude product was purified by column chromatography (*n*-pentane/ether = 99/1) to give 245 mg (839 μmol, 76%) of the product as a colorless oil. TLC (*n*-pentane/ether = 99/1): R_f = 0.42 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3077, 2954, 1471 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 0.09 (s, 6 H), 0.94 (s, 9 H), 4.01 (*virt.* dt, ^3J = 5.7 Hz, $^4J \cong {}^4J$ = 1.3 Hz, 2 H), 4.56 (s, 2 H), 4.80 (s, 2 H), 5.20 (*virt.* dq, ^3J = 10.4 Hz, $^2J \cong {}^4J$ = 1.3 Hz, 1 H), 5.30 (*virt.* dq, ^3J = 17.3 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1 H), 5.95 (ddt, ^3J = 17.3 Hz, ^3J = 10.4 Hz, ^3J = 5.7 Hz, 1 H), 7.24 (t, ^3J = 7.6 Hz, 1 H), 7.30 (t, ^3J = 7.6 Hz, 1 H), 7.34 (d, ^3J = 7.6 Hz, 1 H), 7.48 (d, ^3J = 7.6 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = −5.1 (q), 18.6 (s), 26.1 (q), 62.7 (t), 70.0 (t), 71.3 (t), 117.2 (t), 126.9 (d) 127.0 (d), 127.9 (d), 128.5 (d), 134.9 (d), 135.1 (s), 139.8 (s). MS (EI, 70 eV): m/z (%) = 235 (31), 75 (100, $[Me_2Si{=}OH]^+$). HRMS (EI) m/z: $[M - Me]^+$ calcd. for $C_{16}H_{25}O_2Si$: 277.1618; found: 277.1627.

1-Allyloxymethyl-2-methoxymethylbenzene (5g). Sodium hydride (50.5 mg, 1.26 mmol, 60% suspension in mineral oil, 1.5 equiv) was suspended in 2 mL of THF and cooled to 0 °C. A solution of **5f** (150 mg, 841 μmol, 1.0 equiv) in 2 mL of THF was added dropwise, and the mixture was stirred for 30 min. Then, a solution of methyl iodide (62.9 μL, 143 mg, 1.01 mmol, 1.2 equiv) was added dropwise, and the mixture was allowed to warm to room temperature overnight. The reaction was quenched by the addition of 3 mL of sat. ammonium chloride solution, the layers were separated, and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layers were washed with 5 mL of sat. NaCl solution and dried over Na_2SO_4. The drying agent was removed, and the volatile components were evaporated under reduced pressure. Purification by column chromatography (*n*-pentane/ether = 99/1) gave 123 mg (637 μmol, 76%) of the product as a colorless oil. TLC (*n*-pentane/ether = 99/1): R_f = 0.62 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3075, 2981, 1454 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 3.39 (s, 3 H), 4.04 (dt, ^3J = 5.6 Hz, ^4J = 1.4 Hz, 2 H), 4.54 (s, 2 H), 4.59 (s, 2 H), 5.23 (*virt.* dq, ^3J = 10.4 Hz, $^2J \cong {}^4J$ = 1.5 Hz, 1 H), 5.32 (*virt.* dq, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.5 Hz, 1 H), 5.96 (ddt, ^3J = 17.2 Hz, ^3J = 10.4 Hz, ^3J = 5.6 Hz, 1 H), 7.26–7.32 (m, 2 H), 7.36–7.44 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 58.3 (q), 69.8 (t), 71.4 (t), 72.4 (t), 117.3 (t), 127.9 (d), 128.8 (d), 128.9 (d), 134.9 (s), 136.6 (s), 136.6 (d). MS (EI, 70 eV): m/z (%) = 178 (3, $[M - Me]^+$), 160 (26, $[M - OMe]^+$), 120 (100, $[M - CH_2OC_3H_5]^+$). HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{12}H_{17}O_2$: 193.1223; found: 193.1218.

1-Allyloxymethyl-2-bromomethylbenzene. NBS (59.9 mg, 337 μmol, 1.2 equiv) was dissolved in 1 mL of DMF, before PPh_3 (88.3 mg, 337 μmol, 1.2 equiv) was added in small portions, accompanied by gentle warming of the solution. After reaching room temperature, a solution of alcohol **5f** (50.0 mg, 281 μmol, 1.0 equiv) in 0.5 mL of DMF was added dropwise. The mixture was stirred for 1 h before being diluted with 2 mL of ether. Water (2 mL) was added, the layers were separated, and the aqueous layer was extracted with ether (3 × 5 mL). The organic layers were combined and washed with 4 mL of sat. NaCl solution. After drying over Na_2SO_4, the drying agent was removed by filtration. Removal of the volatile components in vacuo yielded the crude product, which was purified by column chromatography (*n*-pentane/ether = 99/1), yielding 47.2 mg (196 μmol, 70%) of the desired product as a colorless oil. TLC (*n*-pentane/ether = 99/1): R_f = 0.43 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3073, 2857, 1455 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 4.07 (d, ^3J = 5.7 Hz, 2 H), 4.64 (s, 2 H), 4.66 (s, 2 H), 5.23 (*virt.* dq, ^3J = 10.5 Hz, $^2J \cong {}^4J$ = 1.2 Hz, 1 H), 5.34 (*virt.* dq, ^3J = 17.3 Hz, $^2J \cong {}^4J$ = 1.3 Hz, 1 H), 5.98 (ddt, ^3J = 17.3 Hz, ^3J = 10.5 Hz, ^3J = 5.7 Hz, 1 H), 7.28–7.33 (m, 2 H), 7.36–7.40 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 31.3 (t), 69.8 (t), 71.7 (t), 117.6 (t), 128.6 (d), 129.0 (d), 129.8 (d), 130.8 (d,), 134.7 (d), 136.9 (s). MS (EI, 70 eV): m/z (%) = 242 (2, $M(^{81}Br)^+$), 240 (2, $M(^{79}Br)^+$), 184 (78, $[M(^{81}Br) - OC_3H_5]^+$), 182 (78, $[M(^{79}Br) - OC_3H_5]^+$), 104 (100, $[C_8H_8]^+$). HRMS (EI) m/z: $[C_{11}H_{13}{}^{79}BrO]^+$ calcd: 240.0150; found: 240.0153.

2-(2-(Allyloxymethyl)phenyl)acetonitrile (5h). The prepared benzyl bromide (51.2 mg, 212 μmol, 1.0 equiv) was dissolved in 1.5 mL of DMF. Sodium cyanide (11.8 mg, 241 μmol, 1.1 equiv) was added, and the mixture was stirred at room temperature overnight. The reaction was quenched by the addition of 1 mL of water, and the aqueous layer was extracted with ether (3 × 5 mL). The combined organic layers were washed with 4 mL of sat. NaCl solution and dried over Na_2SO_4, and the drying agent was removed by filtration. After evaporation of the volatile components in vacuo, the crude product was purified by column chromatography (*n*-pentane/ether = 9/1), giving 39.7 mg (212 μmol, 100%) of the product as a colorless oil. TLC (*n*-pentane/ether = 9/1): R_f = 0.34 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3073, 2854, 2247, 1455 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 3.88 (s, 2 H), 4.02 (dt, ^3J = 5.8 Hz, ^4J = 1.4 Hz, 2 H), 4.56 (s, 2 H), 5.23 (*virt.* dq, ^3J = 10.5 Hz, $^2J \cong {}^4J$ = 1.3 Hz, 1 H), 5.31 (*virt.* dq, ^3J = 17.3 Hz, $^2J \cong {}^4J$ = 1.5 Hz, 1 H), 5.94 (ddt, ^3J = 17.3 Hz, ^3J = 10.5 Hz, ^3J = 5.8 Hz, 1 H), 7.30–7.39 (m, 3 H), 7.46 (d, ^3J = 7.5 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 21.2 (t), 70.7 (t), 71.5 (t), 117.9 (s), 117.9 (t), 128.4 (d), 129.1 (d), 129.4 (d), 129.7 (s), 130.2 (d), 134.3 (d), 135.8 (s). MS (EI, 70 eV): m/z (%) = 187 (2, M^+), 130 (100, $[M - OC_3H_5]^+$). HRMS (EI) m/z: $[C_{12}H_{13}NO]^+$ calcd.: 187.0992; found: 187.0984.

2-(Allyloxymethyl)benzyl Pivaloate (5i). Alcohol **5f** (50.0 mg, 281 μmol, 1.0 equiv), DMAP (3.43 mg, 28.1 μmol, 0.1 equiv), and NEt_3 (117 μL, 84.5 mg, 842 μmol, 3.0 equiv) were dissolved in 1 mL of CH_2Cl_2. Then, a solution of pivalic acid chloride (41.4 μL, 40.6 mg, 337 μmol, 1.2 equiv) in 1 mL of CH_2Cl_2 was added. The mixture was stirred for 90 min before being quenched by the addition of 1 mL of water. The layers were separated, and the aqueous layer was extracted with ether (3 × 5 mL). The organic layers were combined, washed with sat. $NaHCO_3$ solution (2 × 5 mL) and 5 mL of sat. NaCl solution, and dried over Na_2SO_4. The filter agent was removed, and the volatile components were evaporated in vacuo before the crude product was purified by column chromatography (*n*-pentane/ether = 9/1) to give 60.0 mg (229 μmol, 82%) of the product as a colorless oil. TLC (*n*-pentane/ether = 9/1): R_f = 0.57 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3078, 2974, 1729, 1479 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.22 (s, 9 H), 4.05 (dt, ^3J = 5.7 Hz, ^4J = 1.4 Hz, 2 H), 4.59 (s, 2 H), 5.19 (s, 2 H), 5.22 (*virt.* dq, ^3J = 10.5 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1 H), 5.31 (*virt.* dq, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1 H), 5.96 (ddt, ^3J = 17.2 Hz, ^3J = 10.5 Hz, ^3J = 5.7 Hz, 1 H), 7.29–7.34 (m, 2 H), 7.36–7.42 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 27.9 (q), 39.0 (s), 63.9 (t), 69.9 (t), 71.6 (t), 117.5 (t), 128.1 (d), 128.3 (d), 128.9 (d), 129.0 (d), 134.8 (d), 134.9 (s), 136.6 (s), 178.4 (s). MS (EI, 70 eV): m/z (%) = 205 (4, $[M - {}^tBu]^+$), 160 (55, $[M - OPiv]^+$), 57 (100, $[C_4H_9]^+$). HRMS (EI) m/z: $[M - OPiv]^+$ calcd. for $C_{11}H_{12}O$: 160.0883; found: 160.0879.

2-(Allyloxymethyl)benzyl Acetate (5j). Alcohol **5f** (150 mg, 843 μmol, 1.0 equiv), DMAP (10.3 mg, 84.2 μmol, 0.1 equiv), and NEt_3 (352 μL, 254 mg, 2.52 mmol, 3.0 equiv) were dissolved in 4 mL of CH_2Cl_2 and cooled to 0 °C. Acetyl chloride (72.1 μL, 79.3 mg, 1.01 mmol, 1.2 equiv) in 4 mL of CH_2Cl_2 was added dropwise, and the mixture was stirred for 1 h. After addition of 10 mL of ether, the layers were separated and the organic layer was washed with sat. $NaHCO_3$ solution (2 × 5 mL) and 5 mL of sat. NaCl solution. After removal of the volatile components in vacuo, the crude product was purified by

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column chromatography (*n*-pentane/ethyl acetate = 9/1) to give 160 mg (725 μmol, 86%) of the product as a colorless oil. TLC (*n*-pentane/ethyl acetate = 4/1): R_f = 0.76 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3076, 2930, 1739, 1455 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 2.09 (s, 3 H), 4.04 (d, ^3J = 5.7 Hz, 2 H), 4.58 (s, 2 H), 5.21 (s, 2 H), 5.22 (*virt.* dq, ^3J = 10.4 Hz, $^2J \cong {}^4J$ = 1.3 Hz, 1 H), 5.32 (*virt.* dq, ^3J = 17.1 Hz, $^2J \cong {}^4J$ = 1.3 Hz, 1 H), 5.94 (ddt, ^3J = 17.1 Hz, ^3J = 10.4 Hz, ^3J = 5.7 Hz, 1 H), 7.30−7.35 (m, 2 H), 7.36−7.42 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 21.9 (q), 64.0 (t), 70.0 (t), 71.6 (t), 117.5 (t,), 128.2 (d), 128.6 (d), 129.3 (d), 129.7 (d), 134.5 (d), 134.7 (s), 136.8 (s), 173.2 (s). MS (EI, 70 eV): *m*/*z* (%) = 176 (3, $[M - Ac]^+$), 160 (59, $[M - OAc]^+$), 119 (100, $[C_8H_8O]^+$). HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd. for $C_{13}H_{17}O_3$: 221.1172; found: 221.1166.

1-Allyloxymethyl-2-fluoromethylbenzene (5k). Benzyl alcohol **5f** (80.0 mg, 449 μmol, 1.0 equiv) was dissolved in 1 mL of CH_2Cl_2 and cooled to −78 °C. Subsequently, a solution of DAST (118 μL, 114 mg, 898 μmol, 2.0 equiv) in 0.5 mL of CH_2Cl_2 was added. The mixture was stirred for 30 min, before 0.5 mL of ethanol was added, and the mixture was warmed to 0 °C. Due to the volatility of the product, the solvent was removed by passing a nitrogen stream over the solution. The crude product was purified by column chromatography (*n*-pentane/ether = 99/1) to give 42.0 mg (233 μmol, 48%) of the product as a volatile, colorless oil. TLC (*n*-pentane/ether = 99/1): R_f = 0.20 [UV, $KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3075, 2856, 1455 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 4.02 (dt, ^3J = 5.6 Hz, ^4J = 1.4 Hz, 2 H), 4.59 (s, 2 H), 5.22 (*virt.* dq, ^3J = 10.4 Hz, $^2J \cong {}^4J$ = 1.3 Hz, 1 H), 5.31 (*virt.* dq, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.6 Hz, 1 H), 5.51 (d, ^2J = 48.1 Hz, 2 H), 5.95 (ddt, ^3J = 17.2 Hz, ^3J = 10.4 Hz, ^3J = 5.6 Hz, 1 H), 7.33−7.37 (m, 2 H), 7.39−7.44 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 69.9 (t), 71.5 (t), 82.6 (td, ^1J = 165.4 Hz), 117.5 (t), 128.3 (d), 128.6 (d), 128.7 (d), 128.9 (d), 129.0 (s), 129.2 (s), 134.7 (d). MS (EI, 70 eV): *m*/*z* (%) = 180 (4, M^+), 123 (100, $[M - OC_3H_5]^+$). HRMS (ESI): $[M + NH_4]^+$ calcd. for $C_{11}H_{17}FNO$: 198.1289; found: 198.1291.

General Procedure for the Irradiation of Allyl Benzyl Ethers. A 15 mL quartz tube with a rubber seal was charged with the respective allyl benzyl ether and anhydrous cyclohexane under argon, and the solution was degassed by purging with argon in an ultrasonicating bath for 15 min. The tube was irradiated at r.t. (λ = 254 nm, Rayonet RPR-2537 Å) for 16 h. The solvent was removed under reduced pressure, the isomer ratio was determined by crude NMR, and the residue was directly subjected to purification by flash silica gel column chromatography to give a mixture of *meta*-photocycloaddition products.

1-Ethyl-4-oxatetracyclo[6.3.0.0^{2,6}.0^{2,11}]undec-9-ene (2b). According to the general procedure, 100 mg (567 μmol) of benzyl ether **5b** was irradiated in 10 mL of cyclohexane. After column chromatography (*n*-pentane/ether = 99/1), 28.6 mg (162 μmol, 29%) of the linear *meta*-photocycloaddition product **2b** was obtained. TLC (*n*-pentane/ether = 99/1): R_f = 0.25 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3051, 2959, 1454 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.01 (t, ^3J = 7.2 Hz, 3 H), 1.50 (*virt.* sext., $^2J \cong 2 \times {}^3J$ = 14.4 Hz, ^3J = 7.2 Hz, 1 H), 1.65 (*virt.* sext., $^2J \cong 2 \times {}^3J$ = 14.4 Hz, ^3J = 7.2 Hz, 1 H), 1.72 (br s, 1 H), 1.77 (ddd, ^2J = 11.5 Hz, ^3J = 9.5 Hz, ^3J = 5.1 Hz, 1 H), 1.85 (dd, ^2J = 11.5 Hz, ^3J = 6.4 Hz, 1 H), 2.38 (*virt.* dtd, ^3J = 9.9 Hz, $^3J \cong {}^3J$ = 7.5 Hz, ^3J = 3.5 Hz, 1 H), 3.10 (dd, ^3J = 5.0 Hz, ^3J = 2.1 Hz, 1 H), 3.60−3.70 (m, 3 H), 3.90 (dd, ^2J = 8.7 Hz, ^3J = 7.5 Hz, 1 H), 5.46 (dd, ^3J = 5.5 Hz, ^3J = 2.1 Hz, 1 H), 5.67 (dd, ^3J = 5.5 Hz, ^3J = 2.4 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 11.5 (q), 21.9 (t), 37.4 (d), 42.8 (d), 46.0 (t), 51.5 (s), 51.6 (s), 55.4 (d), 67.5 (t), 73.7 (t), 129.2 (d), 133.4 (d). MS (EI, 70 eV): *m*/*z* (%) = 176 (4, M^+), 118 (100, $[M - OC_3H_5]^+$). HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd. for $C_{12}H_{17}O$: 177.1274; found: 177.1268.

(4-Oxatetracyclo[6.3.0.0^{2,6}.0^{2,11}]undec-9-en-1-yl)-methyltrimethylsilane (2c). Following the general procedure, 40.0 mg (171 μmol) of the silane **5c** was irradiated in 4 mL of cyclohexane. Purification by column chromatography (*n*-pentane/ether = 99/1) gave 19.8 mg (84.5 μmol, 49%) of the photocycloaddition product **2c**. TLC (*n*-pentane/ether = 99/1): R_f = 0.21 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3051, 2936, 1411 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 0.03 (s, 9 H), 0.57 (d, ^2J = 15.1 Hz, 1 H), 0.99 (d, ^2J = 15.1 Hz, 1 H), 1.63 (br s, 1 H), 1.75−1.85 (m, 2 H), 2.37 (*virt.* dtd, ^3J = 10.0 Hz, $^3J \cong {}^3J$ = 7.3 Hz, ^3J = 3.5 Hz, 1 H), 3.00−3.04 (m, 1 H), 3.60 (d, ^2J = 9.7 Hz, 1 H), 3.64 (dd, ^2J = 9.0 Hz, ^3J = 3.5 Hz, 1 H), 3.67 (d, ^2J = 9.7 Hz, 1 H), 3.89 (dd, ^2J = 9.0 Hz, ^3J = 7.9 Hz, 1 H), 5.47 (dd, ^3J = 5.4 Hz, ^3J = 2.4 Hz, 1 H), 5.69 (dd, ^3J = 5.4 Hz, ^3J = 2.3 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = −0.3 (q), 16.2 (t), 38.1 (d), 42.7 (d), 45.3 (t), 48.2 (s), 51.4 (s), 57.7 (d), 67.5 (t), 73.8 (t), 129.4 (d), 133.3 (d). MS (EI, 70 eV): *m*/*z* (%) = 234 (3, M^+), 104 (100, $[C_8H_8]^+$). HRMS (EI) *m*/*z*: $[C_{14}H_{22}OSi]^+$ calcd.: 234.1434; found: 234.1425.

(4-Oxatetracyclo[6.3.0.0^{2,6}.0^{2,11}]undec-9-en-1-yl)-methyltriethylsilane (2d) and (6-Oxatetracyclo[6.3.0.0^{2,11}.0^{4,8}]undec-9-en-1-yl)-methyltriethylsilane (3d). According to the general procedure, 48.8 mg (177 μmol) of the silyl ether **5d** was irradiated in 5 mL of cyclohexane. Purification by column chromatography (*n*-pentane/ether = 99/1) gave 32.1 mg (116 μmol, 66%) of the mixture of *meta*-photocycloaddition products. The isomer ratio was **2d**/**3d** = 87/13. *Data of* **2d**: TLC (*n*-pentane/ether = 99/1): R_f = 0.17 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3055, 2949, 1457 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 500 MHz): δ (ppm) = 0.50−0.58 (m, 7 H), 0.93 (t, ^3J = 8.0 Hz, 9 H), 1.03 (d, ^2J = 15.4 Hz, 1 H), 1.63 (br s, 1H), 1.75−1.85 (m, 2 H), 2.37 (*virt.* dtd, ^3J = 9.9 Hz, $^3J \cong {}^3J$ = 7.2 Hz, ^3J = 3.4 Hz, 1 H), 2.97−3.00 (m, 1 H), 3.60 (d, ^2J = 9.1 Hz, 1 H), 3.64 (dd, ^2J = 9.0 Hz, ^3J = 3.4 Hz, 1 H), 3.68 (d, ^2J = 9.1 Hz, 1 H), 3.89 (dd, ^2J = 9.0 Hz, ^3J = 7.2 Hz, 1 H), 5.46 (dd, ^3J = 5.5 Hz, ^3J = 2.5 Hz, 1 H), 5.68 (dd, ^3J = 5.5 Hz, ^3J = 2.1 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 125 MHz): δ (ppm) = 4.1 (t), 7.7 (q), 10.3 (t), 38.2 (d), 42.6 (d), 45.5 (t), 47.7 (s), 51.5 (s), 57.7 (d), 67.4 (t), 73.8 (t), 129.4 (d), 130.3 (d). MS (EI, 70 eV): *m*/*z* (%) = 276 (2, M^+), 247 (6, $[M - Et]^+$), 87 (100). HRMS (EI) *m*/*z*: $[C_{17}H_{28}OSi]^+$ calcd.: 276.1904; found: 276.1907. *Data of* **3d**: TLC (*n*-pentane/ether = 99/1): R_f = 0.09 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3055, 2949, 1457 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 500 MHz): δ (ppm) = 0.50 (q, ^3J = 7.9 Hz, 6 H), 0.93 (t, ^3J = 7.9 Hz, 9 H), 1.04 (d, ^2J = 15.0 Hz, 1 H), 1.36 (d, ^2J = 15.0 Hz, 1 H), 1.62−1.82 (m, 4 H), 2.36 (ddd, ^3J = 10.7 Hz, ^3J = 7.9 Hz, ^3J = 5.7 Hz, 1 H), 3.57 (dd, ^2J = 10.8 Hz, ^3J = 7.9 Hz, 1 H), 3.73 (d, ^2J = 9.0 Hz, 1 H), 3.84 (*virt.* t, $^2J \cong {}^3J$ = 8.0 Hz, 1 H), 4.12 (d, ^2J = 9.0 Hz, 1 H), 5.38 (d, ^3J = 5.4 Hz, 1 H), 5.63 (dd, ^3J = 5.4 Hz, ^3J = 2.2 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 125 MHz): δ (ppm) = 4.6 (t), 7.7 (q), 11.9 (t), 24.3 (t), 36.3 (d), 37.0 (d), 47.7 (s), 59.1 (d), 69.7 (t), 71.0 (t), 127.4 (d), 132.2 (d). MS (EI, 70 eV): *m*/*z* (%) = 276 (2, M^+), 247 (7, $[M - Et]$), 87 (100). HRMS (EI) *m*/*z*: $[C_{17}H_{28}OSi]^+$ calcd.: 276.1904; found: 276.1910.

4-Oxa-1-(*tert*-butyldimethylsilyloxymethyl)tetracyclo-[6.3.0.0^{2,6}.0^{2,11}]undec-9-ene (2e) and 6-Oxa-1-(*tert*-butyldimethylsilyloxymethyl)tetracyclo[6.3.0.0^{2,11}.0^{4,8}]undec-9-ene (3e). Following the general procedure, reaction of 100 mg (342 μmol) of substrate **5e** in 10 mL of cyclohexane gave, after column chromatography (*n*-pentane/ether = 99/1), 67.5 mg (231 μmol, 68%) of a mixture of the *meta*-photocycloaddition products in a ratio of **2e**/**3e** = 46/54. *Data of* **2e**: TLC (*n*-pentane/ether = 99/1): R_f = 0.16 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3055, 2950, 1471 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 500 MHz): δ (ppm) = 0.04 (s, 6 H), 0.89 (s, 9 H), 1.79−1.90 (m, 2 H), 1.96 (s, 1 H), 2.37−2.47 (m, 1 H), 3.23 (s, 1 H), 3.60 (dd, ^2J = 8.9 Hz, ^3J = 4.9 Hz, 1 H), 3.65 (d, ^2J = 9.0 Hz, 1 H), 3.73 (d, ^2J = 11.3 Hz, 1 H), 3.80 (d, ^2J = 9.0 Hz, 1 H), 3.97 (*virt.* t, $^2J \cong {}^3J$ = 8.0 Hz, 1 H), 3.98 (d, ^2J = 11.3 Hz, 1 H), 5.50 (dd, ^3J = 5.4 Hz, ^3J = 2.2 Hz, 1 H), 5.66 (dd, ^3J = 5.4 Hz, ^3J = 2.1 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = −5.2 (q), 18.4 (s), 26.0 (q), 36.9 (d), 43.3 (d), 45.5 (t), 51.2 (s), 51.4 (s), 55.6 (d), 61.2 (t), 67.7 (t), 73.8 (t), 128.5 (d), 133.8 (d). MS (EI, 70 eV): *m*/*z* (%) = 292 (31, M^+), 235 (63, $[M - {}^tBu]^+$), 160 (21, $[M - OTBS]^+$), 75 (100, $[Me_2Si{=}OH]^+$). HRMS (EI) *m*/*z*: $[C_{17}H_{28}O_2Si]^+$ calcd.: 292.1853; found: 292.1850. *Data of* **3e**: TLC (*n*-pentane/ether = 99/1): R_f = 0.13 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3051, 2928, 1471 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 500 MHz): δ (ppm) = 0.04 (s, 6 H), 0.88 (s, 9 H), 1.85−1.90 (m, 2 H), 2.26 (d, ^3J = 5.2 Hz, 1 H), 2.38 (*virt.* qd, $^3J \cong {}^3J$ = 7.7 Hz, ^3J = 3.2 Hz, 1 H), 3.31−3.55 (m, 1 H), 3.64 (d, ^2J = 10.8 Hz, 1 H), 3.71 (dd, ^2J = 9.0 Hz, ^3J = 3.2 Hz, 1 H), 3.79 (d, ^2J = 9.2 Hz,

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1 H), 3.82 (d, ^2J = 9.2 Hz, 1 H), 3.84 (d, ^2J = 10.8 Hz, 1 H), 3.91 (dd, ^2J = 9.0 Hz, ^3J = 7.7 Hz, 1 H), 5.48 (dd, ^3J = 5.5 Hz, ^3J = 2.4 Hz, 1 H), 5.64 (d, ^3J = 5.5 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = −5.2 (q), 18.5 (s), 26.1 (q), 42.7 (d), 43.5 (d), 47.2 (t), 47.3 (s), 52.6 (s), 52.8 (d), 63.5 (t), 70.0 (t), 73.5 (t), 130.5 (d), 133.9 (d). MS (EI, 70 eV): m/z (%) = 292 (7, M^+), 235 (42, $[M - {}^tBu]^+$), 75 (100, $[Me_2Si{=}OH]^+$). HRMS (EI) m/z: $[C_{17}H_{28}O_2Si]^+$ calcd.: 292.1853; found: 292.1847.

4-Oxa-1-hydroxymethyltetracyclo[6.3.0.0^{2,6}.0^{2,11}]undec-9-ene (2f) and 6-Oxa-1-hydroxymethyltetracyclo[6.3.0.0^{2,11}.0^{4,8}]-undec-9-ene (3f). Following the general procedure, 47.9 mg (296 μmol) of alcohol **5f** was irradiated in 5 mL of cyclohexane. After purification by column chromatography (n-pentane/ethyl acetate = 1/1), 14.8 mg (91.8 μmol, 31%) of a mixture of photocycloaddition products was obtained. The isomer ratio was **2f**/**3f** = 25/75. *Data of* **2f**: TLC (n-pentane/ethyl acetate = 1/1): R_f = 0.20 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3394, 3051, 2929, 1360 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.88−2.00 (m, 2 H), 2.06 (s, 1 H), 2.38−2.46 (m, 1 H), 3.34 (br s, 1 H), 3.67 (d, ^2J = 9.3 Hz, 1 H), 3.71−3.78 (m, 3 H), 3.88 (dd, ^2J = 9.0 Hz, ^3J = 7.4 Hz, 1 H), 3.99 (d, ^3J = 12.4 Hz, 1 H), 5.52 (dd, ^3J = 5.5 Hz, ^3J = 2.5 Hz, 1 H), 5.67 (dd, ^3J = 5.5 Hz, ^3J = 2.1 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 36.9 (d), 42.1 (d), 47.1 (t), 52.0 (s), 52.4 (s), 54.9 (d), 62.6 (t), 67.5 (t), 73.9 (t), 128.3 (d), 134.1 (d). MS (EI, 70 eV): m/z (%) = 178 (5, M^+), 160 (18, $[M - H_2O]^+$), 91 (100, $[C_7H_7]^+$). HRMS (EI) m/z: $[C_{11}H_{14}O_2]^+$ calcd.: 178.0988; found: 178.0990. *Data of* **3f**: TLC (n-pentane/ethyl acetate = 1/1): R_f = 0.19 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3357, 3047, 2932, 1355 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.88−1.97 (m, 2 H), 2.31 (d, ^3J = 5.3 Hz, 1 H), 2.39 (*virt.* qd, $^3J \cong {}^3J$ = 7.0 Hz, ^3J = 3.2 Hz, 1 H), 3.35−3.41 (m, 1 H), 3.62 (d, ^2J = 9.2 Hz, 1 H), 3.72 (dd, ^2J = 9.0 Hz, ^3J = 3.2 Hz, 1 H), 3.75−3.85 (m, 3 H), 3.93 (dd, ^2J = 9.0 Hz, ^3J = 7.5 Hz, 1 H), 5.54 (dd, ^3J = 5.4 Hz, ^3J = 2.4 Hz, 1 H), 5.72 (d, ^3J = 5.4 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 42.9 (d), 44.1 (d), 47.3 (t), 47.6 (s), 53.0 (d), 53.3 (s), 63.6 (t), 69.7 (t), 73.6 (t), 129.9 (d), 135.0 (d). MS (EI, 70 eV): m/z (%) = 178 (4, M^+), 160 (12, $[M - H_2O]^+$), 92 (100, $[C_7H_8]^+$). HRMS (EI) m/z: $[C_{11}H_{14}O_2]^+$ calcd.: 178.0988; found: 178.0991.

1-Methoxymethyl-4-oxatetracyclo[6.3.0.0^{2,6}.0^{2,11}]undec-9-ene (2g) and 1-Methoxymethyl-6-oxatetracyclo-[6.3.0.0^{2,11}.0^{4,8}]undec-9-ene (3g). Following the general procedure, 50.0 mg (260 μmol) of benzyl ether **5g** was irradiated in 5 mL of cyclohexane. Purification by column chromatography (n-pentane/ether = 4/1) yielded 12.9 mg (67.1 μmol, 26%) of the mixture of *meta*-photocycloaddition products. The isomer ratio was **2g**/**3g** = 41/59. *Data of* **2g**: TLC (n-pentane/ether = 4/1): R_f = 0.20 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3051, 2927, 1450 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.85−1.89 (m, 2 H), 2.01 (br s, 1 H), 2.41 (*virt.* dtd, ^3J = 11.4 Hz, $^3J \cong {}^3J$ = 8.0 Hz, ^3J = 3.6 Hz, 1 H), 3.27 (br s, 1 H), 3.35 (s, 3 H), 3.59 (d, ^2J = 11.2 Hz, 1 H), 3.62 (d, ^2J = 11.2 Hz, 1 H), 3.66 (d, ^2J = 9.4 Hz, 1 H), 3.67 (dd, ^2J = 9.0 Hz, ^3J = 3.6 Hz, 1 H), 3.73 (d, ^2J = 9.4 Hz, 1 H), 3.91 (*virt.* t, $^2J \cong {}^3J$ = 8.5 Hz, 1 H), 5.51 (dd, ^3J = 5.6 Hz, ^3J = 2.6 Hz, 1 H), 5.68 (dd, ^3J = 5.6 Hz, ^3J = 2.0 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 37.1 (d), 42.7 (d), 45.9 (t), 50.1 (s), 51.9 (s), 53.3 (d), 58.8 (q), 67.5 (t), 71.9 (t), 73.5 (t), 128.5 (d), 133.9 (d). MS (EI, 70 eV): m/z (%) = 192 (25, M^+), 160 (24, $[M - MeOH]^+$), 91 (100, $[C_7H_7]^+$). HRMS (EI) m/z: $[C_{12}H_{16}O_2]^+$ calcd.: 192.1145; found: 192.1144. *Data of* **3g**: TLC (n-pentane/ether = 4/1): R_f = 0.17 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3059, 2925, 1456 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.85−1.94 (m, 2 H), 2.30 (d, ^3J = 5.3 Hz, 1 H), 2.39 (*virt.* dtd, ^3J = 9.8 Hz, $^3J \cong {}^3J$ = 7.2 Hz, ^3J = 2.9 Hz, 1 H), 3.35 (s, 3 H), 3.34−3.36 (m, 1 H), 3.43 (s, 2 H), 3.72 (dd, ^2J = 9.2 Hz, ^3J = 3.2 Hz, 1 H), 3.75 (d, ^2J = 9.3 Hz, 1 H), 3.82 (d, ^2J = 9.3 Hz, 1 H), 3.90 (dd, ^2J = 9.2 Hz, ^3J = 7.3 Hz, 1 H), 5.51 (dd, ^3J = 5.4 Hz, ^3J = 2.2 Hz, 1 H), 5.71 (d, ^3J = 5.4 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 42.4 (d), 44.6 (d), 45.2 (s), 47.3 (t), 52.8 (d), 53.0 (s), 59.0 (q), 69.8 (t), 73.5 (t), 73.6 (t), 130.4 (d), 134.3 (d). MS (EI, 70 eV): m/z (%) = 192 (3, M^+), 177 (4, $[M - Me]^+$), 91 (100, $[C_7H_7]^+$). HRMS (EI) m/z: $[C_{12}H_{16}O_2]^+$ calcd.: 192.1145; found: 192.1143.

(4-Oxatetracyclo[6.3.0.0^{2,6}.0^{2,11}]undec-9-en-1-yl)acetonitrile (2h) and (6-Oxatetracyclo[6.3.0.0^{2,11}.0^{4,8}]undec-9-en-1-yl)-acetonitrile (3h). According to the general procedure, 35.8 mg (191 μmol) of the benzylic cyanide **5h** was irradiated in 4 mL of cyclohexane. Purification by column chromatography (n-pentane/ether = 2/1) gave 13.3 mg (70.7 μmol, 37%) of the mixture of *meta*-photocycloaddition products. The isomer ratio was **2h**/**3h** = 40/60. TLC (n-pentane/ether = 2/1): R_f = 0.09 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3051, 2940, 2248, 1422 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 500 MHz): δ (ppm) = 1.87−1.95 (m, 2 H), 2.06 (d, ^3J = 2.2 Hz, 0.4 H), 2.30 (d, ^3J = 5.4 Hz, 0.6 H), 2.38−2.48 (m, 1 H), 2.57 (s, 1.2 H), 2.63 (d, ^2J = 17.7 Hz, 0.4 H), 2.72 (d, ^2J = 17.7 Hz, 0.4 H), 3.25−3.28 (m, 0.4 H), 3.41−3.45 (m, 0.6 H), 3.67 (dd, ^2J = 9.3 Hz, ^3J = 3.6 Hz, 0.4 H), 3.74 (dd, ^2J = 9.1 Hz, ^3J = 3.4 Hz, 0.6 H), 3.77 (d, ^2J = 9.0 Hz, 0.6 H), 3.85 (d, ^2J = 9.0 Hz, 0.6 H), 3.89−3.97 (m, 1 H), 5.54 (dd, ^3J = 5.5 Hz, ^3J = 2.6 Hz, 0.4 H), 5.59 (dd, ^3J = 5.4 Hz, ^3J = 2.5 Hz, 0.6 H), 5.63 (d, ^3J = 5.4 Hz, 0.6 H), 5.69 (dd, ^3J = 5.5 Hz, ^3J = 2.2 Hz, 0.4 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 90 MHz) of **3h**: δ (ppm) = 20.2 (t), 42.9 (d), 44.8 (d), 45.8 (t), 55.0 (s, d), 69.1 (t), 73.8 (t), 118.0 (s), 129.1 (d), 135.7 (d). MS (EI, 70 eV): m/z (%) = 187 (2, M^+), 82 (100). HRMS (EI) m/z: $[C_{12}H_{13}NO]^+$ calcd.: 187.0992; found: 187.0987.

4-Oxa-1-pivaloyloxymethyltetracyclo[6.3.0.0^{2,6}.0^{2,11}]undec-9-ene (2i) and 6-Oxa-1-pivaloyloxymethyltetracyclo-[6.3.0.0^{2,11}.0^{4,8}]undec-9-ene (3i). According to the general procedure, 60.0 mg (229 μmol) of the ester **5i** was irradiated in 6 mL of cyclohexane. After purification by column chromatography (n-pentane/ether = 4/1), 20.4 mg (77.8 μmol, 34%) of the mixture of photocycloaddition products was obtained. The isomer ratio was **2i**/**3i** = 33/67. *Data of* **2i**: TLC (n-pentane/ether = 4/1): R_f = 0.29 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3058, 2935, 1725, 1482 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.21 (s, 9 H), 1.86−1.90 (m, 2 H), 2.07 (br s, 1 H), 2.43 (*virt.* dtd, ^3J = 11.5 Hz, $^3J \cong {}^3J$ = 7.7 Hz, ^3J = 3.8 Hz, 1 H), 3.29 (br s, 1 H), 3.64 (dd, ^2J = 9.1 Hz, ^3J = 3.8 Hz, 1 H), 3.68 (d, ^2J = 9.5 Hz, 1 H), 3.74 (d, ^2J = 9.5 Hz, 1 H), 3.93 (*virt.* t, $^2J \cong {}^3J$ = 8.1 Hz, 1 H), 4.17 (d, ^2J = 12.2 Hz, 1 H), 4.49 (d, ^2J = 12.2 Hz, 1 H), 5.51 (dd, ^3J = 5.4 Hz, ^3J = 2.4 Hz, 1 H), 5.66 (dd, ^3J = 5.6 Hz, ^3J = 2.1 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 27.4 (q), 37.8 (d), 39.7 (s), 42.9 (d), 46.0 (t), 49.3 (s), 52.3 (s), 55.8 (d), 63.9 (t), 67.6 (t), 73.7 (t), 128.1 (d), 133.9 (d), 178.5 (s). MS (EI, 70 eV): m/z (%) = 262 (8, M^+), 178 (6, $[M - Piv]^+$), 57 (100, $[C_4H_9]^+$). HRMS (EI) m/z: $[C_{16}H_{22}O_3]^+$ calcd.: 262.1563; found: 262.1562. *Data of* **3i**: TLC (n-pentane/ether = 4/1): R_f = 0.23 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3047, 2937, 1725, 1479 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.20 (s, 9 H), 1.85−1.95 (m, 2 H), 2.34 (d, ^3J = 5.3 Hz, 1 H), 2.39 (*virt.* dtd, ^3J = 9.7 Hz, $^3J \cong {}^3J$ = 7.3 Hz, ^3J = 3.2 Hz, 1 H), 3.35 (br s, 1 H), 3.72 (dd, ^2J = 9.0 Hz, ^3J = 3.2 Hz, 1 H), 3.78 (s, 2 H), 3.91 (dd, ^2J = 9.0 Hz, ^3J = 7.3 Hz, 1 H), 4.08 (d, ^2J = 11.9 Hz, 1 H), 4.19 (d, ^2J = 11.9 Hz, 1 H), 5.49 (dd, ^3J = 5.4 Hz, ^3J = 2.3 Hz, 1 H), 5.63 (d, ^3J = 5.4 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 27.4 (q), 39.0 (s), 42.6 (d), 44.3 (s), 44.7 (d), 47.1 (t), 52.9 (d), 53.4 (s), 65.0 (t), 69.7 (t), 73.7 (t), 129.7 (d), 134.5 (d), 178.7 (s). MS (EI, 70 eV): m/z (%) = 262 (3, M^+), 178 (7, $[M - Piv]^+$), 57 (100, $[C_4H_9]^+$). HRMS (EI) m/z: $[C_{16}H_{22}O_3]^+$ calcd.: 262.1563; found: 262.1562.

1-Acetoxymethyl-4-oxatetracyclo[6.3.0.0^{2,6}.0^{2,11}]undec-9-ene (2j) and 1-Acetoxymethyl-6-oxatetracyclo[6.3.0.0^{2,11}.0^{4,8}]-undec-9-ene (3j). According to the general procedure, 65.4 mg (297 μmol) of benzyl acetate **5j** was irradiated in 7 mL of cyclohexane. After purification by column chromatography (n-pentane/ether = 4/1), 31.7 mg (144 μmol, 48%) of the mixture of photocycloaddition products was obtained. The isomer ratio was **2j**/**3j** = 16/84. *Data of* **2j**: TLC (n-pentane/ether = 4/1): R_f = 0.19 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3045, 2934, 1737, 1375 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.84−1.90 (m, 2 H), 2.05−2.08 (m, 1 H), 2.06 (s, 3 H), 2.41 (*virt.* dtd, ^3J = 11.5 Hz, $^3J \cong {}^3J$ = 8.0 Hz, ^3J = 3.7 Hz, 1 H), 3.28 (br s, 1 H), 3.63−3.69 (m, 2 H), 3.73 (d, ^2J = 9.4 Hz, 1 H), 3.90 (*virt.*t, $^2J \cong {}^3J$ = 8.4 Hz, 1 H), 4.22 (d, ^2J = 12.3 Hz, 1 H), 4.42 (d, ^2J = 12.3 Hz, 1 H), 5.52 (dd, ^3J = 5.4 Hz, ^3J = 2.2 Hz, 1 H), 5.66 (dd, ^3J = 5.4 Hz, ^3J = 2.2 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 21.1 (q), 38.0 (d), 42.7 (d), 46.0 (t), 49.1 (s), 52.5 (s), 55.6 (d), 64.1 (t),

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67.5 (t), 73.5 (t), 128.3 (d), 136.6 (d), 171.5 (s). MS (EI, 70 eV): *m*/*z* (%) = 220 (5, M^+), 178 (17, $[M - Ac]^+$), 130 (100). HRMS (EI) *m*/*z*: $[C_{13}H_{16}O_3]^+$ calcd.: 220.1094; found: 220.1098. *Data of* **3j**: TLC (*n*-pentane/ether = 4/1): R_f = 0.15 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3051, 2941, 1735, 1376 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.85−1.95 (m, 2 H), 2.07 (s, 3 H), 2.34 (d, ^3J = 5.3 Hz, 1 H), 2.37−2.44 (m, 1 H), 3.36 (br s, 1 H), 3.73 (dd, ^2J = 9.0 Hz, ^3J = 3.0 Hz, 1 H), 3.76 (d, ^2J = 9.0 Hz, 1 H), 3.79 (d, ^2J = 9.0 Hz, 1 H), 3.92 (*virt.* t, $^2J \cong {}^3J$ = 8.3 Hz, 1 H), 4.12 (d, ^2J = 11.9 Hz, 1 H), 4.15 (d, ^2J = 11.9 Hz, 1 H) 5.51 (dd, ^3J = 5.5 Hz, ^3J = 2.4 Hz, 1 H), 5.65 (d, ^3J = 5.5 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 21.1 (q), 42.6 (d), 44.0 (s) 44.7 (d), 47.1 (t), 53.0 (d), 53.6 (s), 65.2 (t), 69.6 (t), 73.7 (t), 129.8 (d), 134.7 (d), 171.2 (s). MS (EI, 70 eV): *m*/*z* (%) = 220 (5, M^+), 160 (100, $[M - OAc]^+$). HRMS (EI) *m*/*z*: $[C_{13}H_{16}O_3]^+$ calcd.: 220.1094; found: 220.1094.

1-Fluoromethyl-6-oxatetracyclo[6.3.0.0^{2,11}.0^{4,8}]undec-9-ene (3k). Following the general procedure, 33.0 mg (183 μmol) of fluoro compound **5k** was irradiated in 4 mL of cyclohexane. After purification by column chromatography, 16.4 mg (91 μmol, 50%) of the photocycloaddition product **3k** was isolated. TLC (*n*-pentane/ether = 9/1): R_f = 0.31 [$KMnO_4$]. IR (ATR): $\tilde{\nu}$ = 3047, 2938, 1468 cm^{-1}. ^1H NMR ($CDCl_3$, 300 K, 360 MHz): δ (ppm) = 1.88−1.98 (m, 2 H), 2.40 (d, ^3J = 5.0 Hz, 1 H), 2.40−2.46 (m, 1 H), 3.37 (br s, 1 H), 3.74 (dd, ^2J = 9.1 Hz, ^3J = 3.3 Hz, 1 H), 3.77 (d, ^2J = 8.9 Hz, 1 H), 3.87 (d, ^2J = 8.9 Hz, 1 H), 3.92 (dd, ^2J = 9.1 Hz, ^3J = 7.6 Hz, 1 H), 4.33 (dd, $^2J_{HF}$ = 48.6 Hz, ^2J = 10.5 Hz, 1 H), 4.58 (dd, $^2J_{HF}$ = 48.6 Hz, ^2J = 10.5 Hz, 1 H), 5.55 (dd, ^3J = 5.5 Hz, ^3J = 2.5 Hz, 1 H), 5.73 (d, ^3J = 5.5 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 K, 91 MHz): δ (ppm) = 42.4 (d), 44.7 (dd, $^3J_{CF}$ = 8.0 Hz), 45.1 (dd, $^2J_{CF}$ = 23.9 Hz), 47.2 (t), 52.8 (d), 53.8 (dd, $^3J_{CF}$ = 5.2 Hz), 69.5 (t), 73.5 (t), 84.6 (dt, $^1J_{CF}$ = 167.2 Hz), 129.1 (d), 135.2 (d). MS (EI, 70 eV): *m*/*z* (%) = 180 (6, M^+), 160 (5, $[M - F]^+$), 123 (100, $[C_8H_7F]^+$). HRMS (EI) *m*/*z*: $[C_{11}H_{13}FO]^+$ calcd.: 180.0945; found: 180.0945.

■ ASSOCIATED CONTENT

Supporting Information

Product distributions of selected *meta*-photocycloaddition reactions and ^1H and ^{13}C NMR spectra of compounds **2b−k**, **3b−k**, and **5b−k**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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