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Intramolecular *ortho* and *meta* photocycloadditions of 4-phenoxybut-1-enes substituted in the arene residue with carbomethoxy, carbomethoxymethyl, and 2-carbomethoxyethyl groups

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Abstract

On irradiation of 4-phenoxybut-1-enes substituted with a carbomethoxy group in the arene, only the *ortho* compound **1** led to notable *ortho* photocycloaddition, while the *meta* regioisomer **2** furnished *meta* and *ortho* photocycloadducts albeit in low yield, and the *para*-substituted compound **3** resulted only in intractable polymers. On irradiation of the carboxymethyl- and 2-carboxyethyl homologues **4**–**9**, the photoreactivity altered dramatically. The highest yields of *meta* photocycloadducts were observed on irradiation of the *ortho*-substituted compounds **4** and **7**. Due to steric hindrance, only one of the two possible regioisomers **18** and **19**, respectively, was formed. The *meta*-substituted compounds **5** and **8** gave significant amounts of *meta* photocycloadducts as mixtures of regioisomers **13**+**16** and **14**+**17**, respectively. The intramolecular *meta* photocycloaddition was directed exclusively to the 2′,6′-positions of the arene and only 1,5-bridged dihydrosemibullvalenes were formed. On irradiation of the *ortho*- and *para*-substituted compounds **4** and **7**, and **6** and **9**, respectively, considerable amounts of reaction products derived from initial *ortho* photocycloaddition were detected.

Keywords: *Meta* photocycloaddition; *Ortho* photocycloaddition; Intramolecular photocycloaddition; Carbon–carbon bond formation; 4-Phenoxybut-1-enes

1. Introduction

Arene-alkene bichromophores such as 4-phenylbut-1-enes and 4-phenoxybut-1-enes (**I**) undergo intramolecular *meta* and *ortho* photocycloadditions on UV-irradiation [1–6] (Scheme 1). *Meta* photocycloadducts **II**, having a 2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene structure with 5 contiguous asymmetric centers, are fairly stable under the irradiation conditions and they can be readily isolated. This intriguing one-step photochemical reaction, accompanied by a dramatic increase in molecular complexity, has attracted considerable interest for its potential as a convenient and versatile key step in the synthesis of complex polycyclic molecules [7,8].

The intramolecular *meta* photocycloaddition of 4-phenoxybut-1-enes is directed by the alkoxy tether to the arene 2′,6′-positions as a result of maximized stabilization by the alkoxy group of the positive charge developing at position 1′ in the photoexcited benzene ring on approach of the addends [9–11]. However, the presence of a 2′-methoxy group inhibits the *meta* process, and only *ortho* photocycloaddition is observed [11]. *Ortho* photocycloadducts **III** with a 2-oxatricyclo[5.4.0.0^{1,5}]undeca-8,10-diene structure usually undergo further transformations in situ leading to 2-oxatricyclo[7.2.0.0^{1,5}]undeca-7,10-dienes **V** and 4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-dienes **VI**. A reaction cascade initiated by disrotatory ring opening of cyclohexa-1,3-dienes **III** leads to isomeric dienes **V** and **VI** via photoinduced (2+2)-electrocyclization of conjugated cycloocta-1,3,5-trienes **IV** [12,13].

It has been advocated that the photoreactivity of 4-phenoxybut-1-enes is strongly influenced by the presence and the position of electron-withdrawing substituents on the

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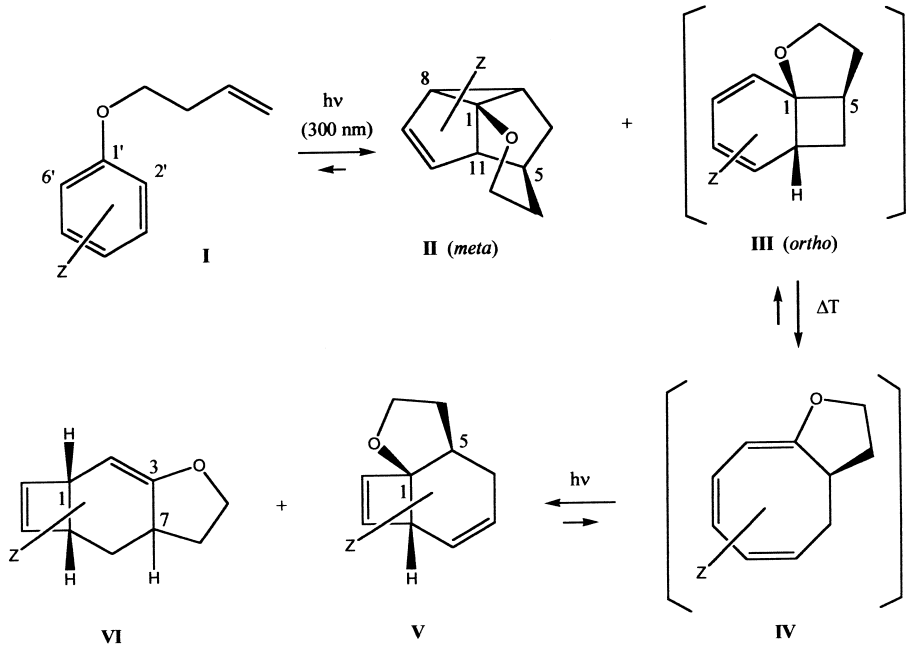


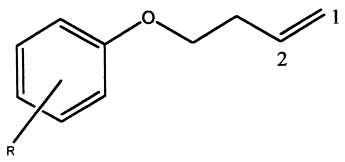
Scheme 1.

arene moiety [14]. A cyano group in the 2′- or 4′-positions promotes *ortho* photocycloaddition leading predominantly to formation of compounds of the type **VI**, while the 3′-cyano isomer reacts inefficiently. It was, furthermore, observed that only the 2′-isomer in the carbomethoxy series underwent *ortho* photocycloaddition. Since we wish to exploit the carbomethoxy group as a versatile handle for enantioselective photocycloadditions and in view of the results reported by Gilbert et al. for 4-phenoxybut-1-enes containing electron-withdrawing aromatic substituents [14], we were interested in delineating the photoreactivity of homologues, in which the carbomethoxy and arene residues are separated by one or two methylene groups. In the present paper, we present full details of our study.

2. Results and discussion

Irradiations were performed in various solvents at 300 nm within the main absorption band of the arenes. Initially, we repeated the irradiation of the carbomethoxy-substituted compounds **1**–**3** (Scheme 2), originally carried out by the group of Prof. Gilbert at Reading, UK, [14] and achieved essentially the same results. We could isolate small amounts of *meta* photocycloadducts **12** and **15** (Table 1) on irradiation of the *meta*-substituted compound **2**, together with *ortho*-derived photocycloadducts **22** (Table 2) and **28** (Table 3). However, unreacted starting material was largely recovered [14]. We confirmed that the *ortho*-substituted compound **1** underwent exclusively *ortho* photocycloaddition to the photostable 9-carbomethoxy-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene (**25**) and to the corresponding dimethyl acetal when the reaction was carried out in methanol (Table 2). The *para*-substituted isomer **3** only led to polymeric decomposition. A comparison of the photoreactivity of carbomethoxy-substituted 4-phenoxybut-1-enes with the cyano analogues studied by Al-Qaradawi, Cosstick, and Gilbert [14] shows that only for the *para* compounds differences are apparent. Indeed, 4-(4-cyanophenoxy)but-1-ene clearly furnished a photostable isomer of the type **VI** (Scheme 1). As noted previously for the cyano analogue [14], it is surprising that 4-(3-carbomethoxy)phenoxybut-1-ene (**2**) does not undergo efficient intramolecular *meta* photocycloaddition as the 2′,6′-directing effect of the alkoxy group should be reinforced by an electron-withdrawing substituent in *meta* position.

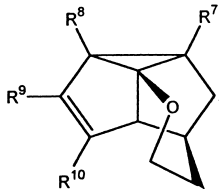
Carbomethoxymethyl and 2-carbomethoxyethyl groups were attached at the *o*-, *m*- and *p*-positions of the aromatic ring (compounds **4**–**6** and **7**–**9**, respectively) (Scheme 2).



1 : R = *o*-CO_2Me
2 : R = *m*-CO_2Me
3 : R = *p*-CO_2Me
4 : R = *o*-CH_2CO_2Me
5 : R = *m*-CH_2CO_2Me
6 : R = *p*-CH_2CO_2Me
7 : R = *o*-$(CH_2)_2CO_2Me$
8 : R = *m*-$(CH_2)_2CO_2Me$
9 : R = *p*-$(CH_2)_2CO_2Me$

Scheme 2.

Table 1
Meta photocycloadducts[a]



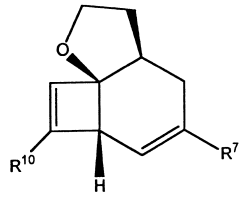
n	$R^9=(CH_2)_nCO_2Me$, $R^8=R^{10}=R^7=H$	$R^8=(CH_2)_nCO_2Me$, $R^9=R^{10}=R^7=H$	$R^{10}=(CH_2)_nCO_2Me$, $R^8=R^9=R^7=H$	$R^7=(CH_2)_NcO_2Me$, $R^8=R^9=R^{10}=H$
0	–	**12** (6, 3, 1)	**15** (2, 1, 0)	–
1	**10** (12, 10, 13)	**13** (12, 16, 14)	**16** (12, 16, 14)	**18** (46, 48, 14)
2	**11** (19, 15, 25)	**14** (17, 19, 19)	**17** (14, 15, 13)	**19** (26, 23, 29)

[a] Numbers in parentheses are for isolated yields (%) for photoreactions in cyclohexane, acetonitrile, and methanol, respectively.

As expected from electronic considerations, the photoreactivity changed dramatically. In all cases, *meta* as well as *ortho* photocycloadducts were formed. Intramolecular *meta* photocycloaddition of the ethene occurred exclusively at the 2′,6′-positions of the arene [9], while, furthermore only 1,5-bridged dihydrosemibullvalenes were formed, as generally observed for molecules with a tether consisting of three linearly linked atoms [15].

As the *para*-substituted compounds **6** and **9** possess a plain of symmetry, regiodifferentiation is obsolete thereby resulting in *meta* photocycloadducts **10** and **11**, respectively (Table 1). In contrast, the presence of a substituent at the 2′-position of the arene (compounds **4** and **7**) leads to two possible orientations for approach of the ethene to the aromatic ring (Fig. 1). Obviously, steric interactions arising from the carbomethoxyalkyl side chain dictate a preferred orientation in the precursor conformer and, in each case, only one *meta* photocycloadduct, **18** and **19**, respectively (Table 1), was formed in reasonable yields. For the *meta*-substituted compounds **5** and **8**, steric influences should be minor and, as a result, the photocycloaddition proceeded from both conformations with similar efficiency, affording **13**+**16** and **14**+**17**, respectively, albeit in low yields (Table 1).

Table 3
Oxatricyclo[7.2.0.0^{1,5}]undeca-7,10-dienes derived from *ortho* photocycloadducts[a]

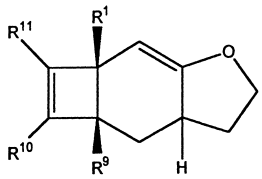


n	$R^{10}=(CH_2)_nCO_2Me$ $R^7=H$	$R^7=(CH_2)_nCO_2Me$ $R^{10}=H$
0	**28** (6, 4, 3)	–
1	**29** (7, 7, 4)	**30** (0, 0, 3)
2	–	**31** (6, 9, 0)

[a] Numbers in parentheses are for isolated yields (%) of the photoreactions in cyclohexane, acetonitrile, and methanol, respectively.

The cleanliness of the reaction mixtures suffered from cascade reactions of the initially formed *ortho* photocycloadducts [12,13], and we were able to isolate and identify stable photoadducts of types **V** and **VI** (Scheme 1). Irradiation of the *ortho*-substituted compound **4** afforded **26** (Table 2) and **30** (Table 3), while compound **7** led to a mixture of **27** (Table 2) and **31** (Table 3). For the *meta*-substituted **5**,

Table 2
4-Oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-dienes derived from *ortho* photocycloadducts[a]



n	$R^{11}=(CH_2)_nCO_2Me$ $R^1=R^9=R^{10}=H$	$R^1=(CH_2)_nCO_2Me$ $R^9=R^{10}=R^{11}=H$	$R^{10}=(CH_2)_nCO_2Me$ $R^1=R^9=R^{11}=H$	$R^9=(CH_2)_nCO_2Me$ $R^1=R^{10}=R^{11}=H$
0	–	**22** (4, 3, 2)	–	**25** (36, 42, 31; 20[b])
1	**20** (10, 2, 0; 4[b])	–	–	**26** (15, 28, 0; 3[b])
2	**21** (19, 9, 0; 12[b])	**23** (2, 4, 2)	**24** (6, 3, 0)	**27** (18, 7, 5; 9[b])

[a] Numbers in parentheses are for isolated yields (%) for photoreactions in cyclohexane, acetonitrile, and methanol, respectively.
[b] Photocycloadduct isolated as the corresponding methyl acetal on irradiation in methanol.

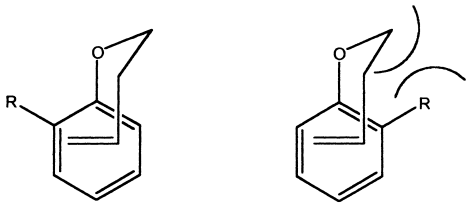


Fig. 1. R=$(CH_2)_n$COOMe (n=1 or 2).

traces of **29** (Table 3) were detected, while for **8**, only very small amounts of **23** and **24** (Table 2) were found. On irradiation of the *para*-substituted compounds **6** and **9**, formation of **20** and **21** (Table 2), respectively, was apparent.

We could not discern dramatic solvent effects on the photoreactions studied, with only a few exceptions (e.g. decreased yield of **18** in methanol). For the carbomethoxymethyl as well as for 2-carbomethoxyethyl derivatives, varying *meta*- and *ortho*-photocycloadducts were formed depending on the substitution site. Furthermore, results are fairly comparable for both homologous series. Only the *ortho*-substituted compounds **4** and **7** gave good yields of a single *meta* photocycloadduct resulting from steric hindrance in the respective transition states. This selectivity was observed in a previous study for 4-(2-methylphenoxy)but-1-ene [11]. From a synthetic viewpoint, irradiation of the *meta*-substituted compounds **5** and **8** was less interesting, since mixtures of two isomeric *meta* photocycloadducts and of cascade reaction products derived from *ortho* photocycloadducts were found. The *para*-substituted substrates **6** and **9** yielded one single *meta* photocycloadduct, next to an *ortho*-derived photoisomer, however in low yields. While 4-phenoxybut-1-enes carrying a methyl group in the benzene ring showed marked chemo- and regioselectivity, i.e. formation of 2′,6′-*meta* photocycloadducts [11], the carbomethoxyalkyl compounds gave both *ortho* and *meta* photocycloadditions. Moreover, the efficiencies were much lower than for the methyl derivatives, thus indicating a rather significant perturbing influence of the carbomethoxy group, even when present at the β-position of the alkyl side chain.

In all cases, the intramolecular *meta* photocycloaddition occurred regioselectively at the 2′,6′-positions of the arene to afford exclusively 1,5-bridged dihydrosemibullvalenes. This selectivity, as noted in particular for the *ortho*-compounds **4** and **7**, offers promising prospects for further work, aimed at using modified esters for applications in enantioselective photochemical synthesis.

3. Experimental details

3.1. Photochemical and analytical methods

Preparative irradiations (8 h; ca. 80% substrate conversion) using low pressure mercury arc lamps (300 nm, Rayonet Photochemical Reactor, type RS, Southern New England Ultraviolet, Middletown, CT, USA) were carried out in 0.2% w/v carefully degassed (N_2 and ultrasonication) solutions of the substituted 4-phenoxybut-1-enes in cyclohexane, acetonitrile or methanol (p.a. solvents from Labscan, Dublin, Ireland, Acros, Geel, Belgium, and Biosolve, Valkenswaard, The Netherlands, respectively). The irradiations were monitored by TLC (Merck, Darmstadt, Germany; silica gel 60 F-254) using varying ratios of hexane and ethyl acetate as the eluent. Separations and purifications of the photocycloadducts were achieved by column chromatography using 70–230 mesh silica gel (Merck) and by preparative HPLC (hexane/ethyl acetate) using a Waters apparatus equipped with a Waters 600E system controller and a Waters 410 RI detector instrument, and fitted with a Bio-Sil D90-10, 250×10 mm column (BioRad Laboratories, Nazareth, Belgium). ^{1}HNMR (400 and 250 MHz) spectra were recorded using a Bruker AMX 400 instrument and a Bruker WM 250 instrument at 25°C with tetramethylsilane as internal reference. ^{13}C NMR (100 MHz) spectra were obtained on a Bruker AMX 400 instrument operating at 100 MHz at 25°C with the solvent as internal reference. J values are indicated in Hz. For IR spectra, a Perkin–Elmer 1600 Series FTIR spectrophotometer was used. Mass spectra (chemical ionization: methane) were obtained using a Hewlett–Packard 5989A MS. UV spectra were recorded on a Perkin–Elmer Lambda 20 UV–VIS spectrophotometer. Methyl 3-hydroxybenzoate and methyl 3-(4-hydroxyphenyl)propanoate were purchased from Sigma-Aldrich (Bornem, Belgium); methyl 2-hydroxybenzoate, methyl 4-hydroxybenzoate, 2-hydroxyphenylacetic acid, and 3-hydroxyphenylacetic acid were purchased from Acros; methyl 4-hydroxyphenyl acetate, *o*-coumaric acid and *m*-coumaric acid were purchased from Fluka (Bornem, Belgium).

3.2. Photosubstrates

Photosubstrates **1**–**9** were synthesized by reaction of but-3-en-1-ol and the appropriately substituted phenol (methyl 4-hydroxybenzoate, methyl 3-hydroxybenzoate, methyl 2-hydroxybenzoate, methyl 4-hydroxyphenyl acetate, methyl 3-hydroxyphenyl acetate, methyl 2-hydroxyphenyl acetate, methyl 3-(4-hydroxyphenyl)propanoate, methyl 3-(3-hydroxyphenyl)propanoate and methyl 3-(2-hydroxyphenyl)propanoate, respectively) according to the procedure of Mitsunobu [16]. General protocol: the corresponding phenol (8 mmol) and but-3-en-1-ol (636 mg, 8.8 mmol) were added to a solution of triphenylphosphine (2.938 g, 11.2 mmol) in dry THF (40 ml). The solution was cooled to 0°C, diethyl azodicarboxylate (2 ml, 12.6 mmol) was added dropwise, and stirring was continued at room temperature for 6 h. The reaction was monitored by TLC (hexane:ethyl acetate 80:20). After completion, the reaction mixture was added to water (240 ml) and extracted with

diethyl ether. The organic phase was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. Column chromatography of the residue on silica gel using varying ratios of hexane:ethylacetate as eluent gave the desired photosubstrate.

*3.2.1. 4-(2-Carbomethoxy)phenoxybut-1-ene (**1**)*

Purification was carried out by column chromatography with hexane:ethyl acetate 95:5 on silica gel. Yield: 52%; pale yellow oil; UV, λ_{max} (cyclohexane, nm): 232, 237, 292; IR, ν_{max} (NaCl, cm^{-1}): 3077, 2949, 1728, 1643, 1601; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (dd, 1H, $^3J_{3,4}$=7.6, $^4J_{3,5}$=1.8, ArH-3), 7.43 (td, 1H, $^3J_{5,6}$=$^3J_{5,4}$=8, $^4J_{5,3}$=1.8, ArH-5), 6.93–7.00 (m, 2H, ArH-4 and ArH-6), 5.94 (ddt, 1H, $^3J_{trans}$=17.1, $^3J_{cis}$=10.3, ^3J=6.7, C*H*=CH_2), 5.18 (dq, 1H, $^3J_{trans}$=17.1, ^2J=1.6, ^4J=1.4, CH=CH_{trans}), 5.11 (dm, 1H, $^3J_{cis}$=10.3, CH=CH_{cis}), 4.08 (t, 2H, ^3J=6.8, OCH_2), 3.88 (s, 3H, OCH_3), 2.59 (qt, 2H, ^3J=6.7 and 6.8, ^4J=1.4, OCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.9 (COO), 158.3 (ArC), 134.3 (*C*H=CH_2), 133.3 (ArC), 131.6 (ArC), 120.7 (ArC), 120.3 (ArC), 117.1 (CH=*C*H_2), 113.4 (ArC), 68.4 (OCH_2), 51.9 (OCH_3), 33.7 (OCH_2CH_2); MS, *m/z*: 207 [M^++1] (100), 175 (11), 165 (3); HRMS: exact mass for $C_{12}H_{14}O_3$: 206.0943; found: 206.0947.

*3.2.2. 4-(3-Carbomethoxy)phenoxybut-1-ene (**2**)*

Purification was carried out by column chromatography with hexane:ethyl acetate 97:3 on silica gel. Yield: 62%; colorless oil; UV, λ_{max} (cyclohexane, nm): 231, 294; IR, ν_{max} (NaCl, cm^{-1}): 3078, 2950, 1724, 1642; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.62 (dt; 1H, $^3J_{4,5}$=7.7, $^4J_{4,6}$=1.0, $^4J_{4,2}$=1.5, ArH-4), 7.56 (dd, 1H, $^4J_{2,6}$=2.6, $^4J_{2,4}$=1.5, ArH-2), 7.33 (t, 1H, $^3J_{5,4}$=7.7, $^3J_{5,6}$=8.2, ArH-5), 7.09 (ddd, 1H, $^3J_{6,5}$=8.2, $^4J_{6,2}$=2.6, $^4J_{6,4}$=1.0, ArH-6), 5.91 (ddt, 1H, $^3J_{trans}$=17.1, $^3J_{cis}$=10.3, ^3J=6.7, C*H*=CH_2), 5.18 (dq, 1H, $^3J_{trans}$=17.1, ^2J=1.6, ^4J=1.4, CH=CH_{trans}), 5.11 (dm, 1H, $^3J_{cis}$=10.3, CH=CH_{cis}), 4.06 (t, 2H, ^3J=6.8, OCH_2), 3.91 (s, 3H, OCH_3), 2.56 (qt, 2H, ^3J=6.7 and 6.8, ^4J=1.4, OCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 167.0 (COO), 158.9 (ArC), 134.2 (*C*H=CH_2), 131.4 (ArC), 129.3 (ArC), 122.0 (ArC), 120.0 (ArC), 117.1 (CH=*C*H_2), 114.8 (ArC), 67.4 (OCH_2), 52.1 (OCH_3), 33.5 (OCH_2CH_2); MS, *m/z*: 207 [M^++1](100), 175 (10), 165 (11); HRMS: exact mass for $C_{12}H_{14}O_3$: 206.0943; found: 206.0944.

*3.2.3. 4-(4-Carbomethoxy)phenoxybut-1-ene (**3**)*

Purification was carried out by column chromatography with hexane:ethyl acetate 97:3 on silica gel. Yield: 82%; colorless oil; UV, λ_{max} (cyclohexane, nm): 254; IR, ν_{max} (NaCl, cm^{-1}): 3078, 2983, 2950, 2879, 1718, 1607; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 (dd, 2H, ^3J=7.0, ^4J=2.1, ArH-3 and ArH-5), 6.90 (dd, 2H, ^3J=7.0, ^4J=2.1, ArH-2 and ArH-6), 5.90 (ddt, 1H, $^3J_{trans}$=17.1, $^3J_{cis}$=10.3, ^3J=6.7, C*H*=CH_2), 5.18 (dq, 1H, $^3J_{trans}$=17.1, ^2J=1.6, ^4J=1.4, CH=CH_{trans}), 5.11 (dm, 1H, $^3J_{cis}$=10.3, CH=CH_{cis}), 4.06 (t, 2H, ^3J=6.8, OCH_2), 3.88 (s, 3H, OCH_3), 2.56 (qt, 2H, ^3J=6.7 and 6.8, ^4J=1.4, OCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.8 (COO), 162.7 (ArC), 134.0 (*C*H=CH_2), 131.5 (2 ArC), 122.6 (ArC), 117.3 (CH=*C*H_2), 114.1 (2 ArC), 67.3 (OCH_2), 51.8 (OCH_3), 33.4 (OCH_2CH_2); MS, *m/z*: 207 [M^++1](100), 175 (11), 165 (6); HRMS: exact mass for $C_{12}H_{14}O_3$: 206.0943; found: 206.0950.

*3.2.4. 4-(2-Carbomethoxymethyl)phenoxybut-1-ene (**4**)*

Purification was carried out by column chromatography with hexane:ethyl acetate 95:5 on silica gel. Yield: 58%; pale yellow oil; UV, λ_{max} (cyclohexane, nm): 228, 273, 279; IR, ν_{max} (NaCl, cm^{-1}): 3074, 2983, 2948, 2869, 1741, 1642,1600; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.22 (t, 1H, $^3J_{5,4}$=7.8, $^3J_{5,6}$=8.2, ArH-5), 7.17 (d, 1H, $^3J_{3,4}$=7.4, ArH-3), 6.90 (t, 1H, $^3J_{4,3}$=7.4, $^3J_{4,5}$=7.8, ArH-4), 6.85 (d, 1H, $^3J_{6,5}$=8.2, ArH-6), 5.89 (ddt, 1H, $^3J_{trans}$=17.1, $^3J_{cis}$=10.3, ^3J=6.7, C*H*=CH_2), 5.15 (dq, 1H, $^3J_{trans}$=17.1, ^2J=1.6, ^4J=1.4, CH=CH_{trans}), 5.09 (dm, 1H, $^3J_{cis}$=10.3, CH=CH_{cis}), 4.01 (t, 2H, ^3J=6.8, OCH_2), 3.67 (s, 3H, OCH_3), 3.63 (s, 2H, CH_2COO), 2.51 (qt, 2H, ^3J=6.7 and 6.8, ^4J=1.4, OCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 172.3 (COO), 156.8 (ArC), 134.5 (*C*H=CH_2), 130.8 (ArC), 128.5 (ArC), 123.3 (ArC), 120.5 (ArC), 116.9 (CH=*C*H_2), 111.3 (ArC),), 67.3 (OCH_2), 51.8 (OCH_3), 35.9 (CH_2COO), 33.7 (OCH_2CH_2); MS, *m/z*: 221 [M^++1](90), 189 (100), 179 (10), 161 (26), 135 (28); HRMS: exact mass for $C_{13}H_{16}O_3$: 220.1099; found: 220.1095.

*3.2.5. 4-(3-Carbomethoxymethyl)phenoxybut-1-ene (**5**)*

Purification was carried out by column chromatography with hexane:ethyl acetate 90:10 on silica gel. Yield: 61%; colorless oil; UV, λ_{max} (cyclohexane, nm): 229, 274, 281; IR, ν_{max} (NaCl, cm^{-1}): 3076, 2950, 2879, 1740, 1642, 1602; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.22 (t, 1H, $^3J_{5,4}$=$^3J_{5,6}$=7.8, ArH-5), 6.78–6.88 (m, 3H, ArH-2, ArH-4 and ArH-6), 5.90 (ddt, 1H, $^3J_{trans}$=17.1, $^3J_{cis}$=10.3, ^3J=6.7, C*H*=CH_2), 5.16 (dq, 1H, $^3J_{trans}$=17.1, ^2J=1.6, ^4J=1.4, CH=CH_{trans}), 5.10 (dm, 1H, $^3J_{cis}$=10.3, CH=CH_{cis}), 4.01 (t, 2H, ^3J=6.8, OCH_2), 3.69 (s, 3H, OCH_3), 3.59 (s, 2H, CH_2COO), 2.53 (qt, 2H, ^3J=6.7 and 6.8, ^4J=1.4, OCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.9 (COO), 159.1 (ArC), 135.4 (ArC), 134.4 (*C*H=CH_2), 129.5 (ArC), 121.6 (ArC), 117.0 (CH=*C*H_2), 115.6 (ArC), 113.2 (ArC), 67.2 (OCH_2), 52.0 (OCH_3), 41.2 (CH_2COO), 33.6 (OCH_2CH_2); MS, *m/z*: 221 [M^++1](41), 189 (22), 179 (21), 161 (100); HRMS: exact mass for $C_{13}H_{16}O_3$: 220.1099; found: 220.1103.

*3.2.6. 4-(4-Carbomethoxymethyl)phenoxybut-1-ene (**6**)*

Purification was carried out by column chromatography with hexane:ethyl acetate 90:10 on silica gel. Yield: 76%;

pale yellow oil; UV, λ_{max} (cyclohexane, nm): 231, 277, 284; IR, ν_{max} (NaCl, cm^{-1}): 3075, 2950, 1739, 1641, 1613, 1584, 1513; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.18 (dd, 2H, ^3J=6.6, ^4J=2.1, ArH-3 and ArH-5), 6.85 (dd, 2H, ^3J=6.6, ^4J=2.1, ArH-2 and ArH-6), 5.89 (ddt, 1H, $^3J_{trans}$=17.1, $^3J_{cis}$=10.3, ^3J=6.7, C*H*=CH_2), 5.16 (dq, 1H, $^3J_{trans}$=17.1, ^2J=1.6, ^4J=1.4, CH=C*H*$_{trans}$), 5.10 (dm, 1H, $^3J_{cis}$=10.3, CH=C*H*$_{cis}$), 4.00 (t, 2H, ^3J=6.8, OCH_2), 3.68 (s, 3H, OCH_3), 3.56 (s, 2H, CH_2COO), 2.53 (qt, 2H, ^3J=6.7 and 6.8, ^4J=1.4, OCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 172.3 (COO), 158.1 (ArC), 134.4 (*C*H=CH_2), 130.3 (ArC), 130.2 (2 ArC), 126.1, 117.0 (CH=*C*H_2), 114.7 (2 ArC), 67.3 (OCH_2), 51.9 (OCH_3), 40.3 (CH_2COO), 33.6 (OCH_2CH_2); MS, *m/z*: 221 [M^++1](63), 189 (19), 179 (36), 161 (100); HRMS: exact mass for $C_{13}H_{16}O_3$: 220.1099; found: 220.1099.

3.2.7. 4-[2-(2-Carbomethoxy)ethyl)]phenoxybut-1-ene (**7**)

Purification was carried out by column chromatography with hexane:ethyl acetate 90:10 on silica gel. Yield: 60%; colorless oil; UV, λ_{max} (cyclohexane, nm): 230, 273, 280; IR, ν_{max} (NaCl, cm^{-1}): 3076, 3053, 2949, 2869, 1739, 1642, 1601; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.12–7.20 (m, 2H, ArH-3 and ArH-5), 6.86 (td, 1H, $^3J_{4,3}$=$^3J_{4,5}$=7.4, $^4J_{4,6}$=1, ArH-4), 6.82 (dd, 1H, $^3J_{6,5}$=8, $^4J_{6,4}$=1, ArH-6), 5.91 (ddt, 1H, $^3J_{trans}$=17.1, $^3J_{cis}$=10.3, ^3J=6.7, C*H*=CH_2), 5.16 (dq, 1H, $^3J_{trans}$=17.1, ^2J=1.6, ^4J=1.4, CH=C*H*$_{trans}$), 5.10 (dm, 1H, $^3J_{cis}$=10.3, CH=C*H*$_{cis}$), 4.02 (t, 2H, ^3J=6.8, OCH_2), 3.66 (s, 3H, OCH_3), 2.93 (t, 2H, ^3J=8, CH_2CH_2COO), 2.61 (t, 2H, ^3J=8 CH_2CH_2COO), 2.55 (qt, 2H, ^3J=6.7 and 6.8, ^4J=1.4, OCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.2 (COO), 159.0 (ArC), 142.0 (ArC), 134.4 (*C*H=CH_2), 129.4 (ArC), 120.6 (ArC), 116.9 (CH=*C*H_2), 114.7 (ArC), 112.2 (ArC), 67.1 (OCH_2), 51.5 (OCH_3), 35.6 (CH_2COO), 33.6 (OCH_2CH_2), 30.9 (CH_2CH_2COO); MS, *m/z*: 235 [M^++1](47), 203 (100), 193 (8), 189 (6), 161 (13), 149 (40); HRMS: exact mass for $C_{14}H_{18}O_3$: 234.1256; found: 234.1258.

3.2.8. 4-[3-(2-Carbomethoxy)ethyl)]phenoxybut-1-ene (**8**)

Purification was carried out by column chromatography with hexane:ethyl acetate 90:10 on silica gel. Yield: 70%; pale yellow oil; UV, λ_{max} (cyclohexane, nm): 230, 272, 278; IR, ν_{max} (NaCl, cm^{-1}): 3074, 2946, 2874, 1739, 1642, 1597; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.18 (tm, 1H, $^3J_{5,4}$=$^3J_{5,6}$=7.6, ArH-5), 6.70–6.80 (m, 3H, ArH), 5.90 (ddt, 1H, $^3J_{trans}$=17.1, $^3J_{cis}$=10.3, ^3J=6.7, C*H*=CH_2), 5.16 (dq, 1H, $^3J_{trans}$=17.1, ^2J=1.6, ^4J=1.4, CH=C*H*$_{trans}$), 5.10 (dm, 1H, $^3J_{cis}$=10.3, CH=C*H*$_{cis}$), 4.00 (t, 2H, ^3J=6.8, OCH_2), 3.66 (s, 3H, OCH_3), 2.91 (t, 2H, ^3J=8, CH_2CH_2COO), 2.62 (t, 2H, ^3J=8, CH_2CH_2COO), 2.53 (qt, 2H, ^3J=6.7 and 6.8, ^4J=1.4, OCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.8 (COO), 156.7 (ArC), 134.6 (*C*H=CH_2), 130.0 (ArC), 129.0 (ArC), 127.5 (ArC), 120.4 (ArC), 117.0 (CH=*C*H_2), 111.0 (ArC), 67.0 (OCH_2), 51.4 (OCH_3), 34.0 (CH_2COO), 33.8 (OCH_2CH_2), 26.2 (CH_2CH_2COO); MS, *m/z*: 235 [M^++1](36), 203 (100), 193 (13), 189 (6), 161 (13), 149 (8); HRMS: exact mass for $C_{14}H_{18}O_3$: 234.1256; found: 234.1262.

3.2.9. 4-[4-(2-Carbomethoxy)ethyl)]phenoxybut-1-ene (**9**)

Purification was carried out by column chromatography with hexane:ethyl acetate 95:5 on silica gel. Yield: 50%; colorless oil; UV, λ_{max} (cyclohexane, nm): 233, 278, 284; IR, ν_{max} (NaCl, cm^{-1}): 3075, 2949, 2860, 1739, 1642, 1613; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.09 (d, 2H, ^3J=8.6, ArH-3 and ArH-5), 6.82 (d, 2H, ^3J=8.6, ArH-2 and ArH-6), 5.90 (ddt, 1H, $^3J_{trans}$=17.1, $^3J_{cis}$=10.3, ^3J=6.7, C*H*=CH_2), 5.16 (dq, 1H, $^3J_{trans}$=17.1, ^2J=1.6, ^4J=1.4, CH=C*H*$_{trans}$), 5.10 (dm, 1H, $^3J_{cis}$=10.3, CH=C*H*$_{cis}$), 3.99 (t, 2H, ^3J=6.8, OCH_2), 3.66 (s, 3H, OCH_3), 2.89 (t, 2H, ^3J=8, CH_2CH_2COO), 2.59 (t, 2H, ^3J=8, CH_2CH_2COO), 2.52 (qt, 2H, ^3J=6.7 and 6.8, ^4J=1.4, OCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.4 (COO), 157.4 (ArC), 134.5 (*C*H=CH_2), 132.6 (ArC), 129.2 (2 ArC), 116.9 (CH=*C*H_2), 114.6 (2 ArC), 67.3 (OCH_2), 51.5 (OCH_3), 36.0 (CH_2COO), 33.7 (OCH_2CH_2), 30.1 (CH_2CH_2COO); MS, *m/z*: 235 [M^++1](66), 203 (74), 193 (32), 189 (19), 161 (100); HRMS: exact mass for $C_{14}H_{18}O_3$: 234.1256; found: 234.1259.

Methyl 2-(3-hydroxyphenyl)acetate, methyl 2-(2-hydroxyphenyl)acetate, methyl 3-(3-hydroxyphenyl)propanoate, and methyl 3-(2-hydroxyphenyl)propanoate were obtained by esterification of the corresponding saturated or unsaturated acids, followed by catalytic hydrogenation of the double bond when unsaturated acids were used. General protocol: the carboxylic acid (2 mmol) (3-hydroxyphenylacetic acid, 2-hydroxyphenylacetic acid, *m*-coumaric acid, and *o*-coumaric acid, respectively) was dissolved in 2,2-dimethoxypropane (25 ml) and HCl (36%, 2 ml) was added. The mixture was stirred overnight at room temperature. After completion, the reacton mixture was added to saturated K_2CO_3 solution and extracted with dietyl ether. The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel (hexane:ethyl acetate 80:20) gave the desired methyl ester.

3.2.10. Methyl 2-(2-hydroxyphenyl)acetate

Purification was carried out by column chromatography with hexane:ethyl acetate 80:20 on silica gel. Yield: 99%; pale yellow crystals; UV, λ_{max} (methanol, nm): 275, 214; IR, ν_{max} (KBr, cm^{-1}): 3426, 3031.6, 2964, 2363, 2334, 1722, 1598; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.38 (s, broad, 1H, OH), 7.20 (t, 1H, $^3J_{5,4}$=$^3J_{5,6}$=7.8, ArH-5), 7.11 (d, 1H, $^3J_{3,4}$=7.3, ArH-3), 6.83–6.98 (m, 2H, ArH-4 and ArH-6), 3.75 (s, 3H, OCH_3), 6.60 (s, 2H, CH_2COO); MS, *m/z*: 167 [M^++1](100), 135 (54), 107 (15); HRMS: exact mass for $C_9H_{10}O_3$: 166.0630; found: 166.0639.

3.2.11. Methyl 2-(3-hydroxyphenyl)acetate

Purification was carried out by column chromatography with hexane:ethyl acetate 80:20 on silica gel. Yield: 90%; yellow oil; UV, λ_{max} (methanol, nm): 275, 216; IR, ν_{max} (NaCl, cm^{-1}): 3408, 3030, 2955, 2848, 2732, 2604, 1718, 1596; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.17 (t, 1H, $^3J_{5,4}=^3J_{5,6}$=7.8, ArH-5), 6.69–6.88 (m, 3H, ArH), 5.60 (s, broad, OH), 3.72 (s, 3H, OCH_3), 3.60 (s, 2H, CH_2COO); MS, *m/z*: 167 [M^++1](100), 135 (46), 107 (33); HRMS: exact mass for $C_9H_{10}O_3$: 166.0630; found: 166.0622.

3.2.12. Methyl o-coumarate

Purification was carried out by column chromatography with hexane:ethyl acetate 80:20 on silica gel. Yield: 82%; pale yellow crystals; UV, λ_{max} (methanol, nm): 328, 275, 224, 214; IR, ν_{max} (KBr, cm^{-1}): 3386, 1693, 1626; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 8.05 (d, 1H, ^3J=16, C*H*=CHCOO), 7.47 (dd, 1H, $^3J_{3,4}$=7.5, $^4J_{3,5}$=1.6, ArH-3), 7.25 (td, 1H, $^3J_{5,4}=^3J_{5,6}$=7.8, $^4J_{5,3}$=1.6, ArH-5), 6.83–6.98 (m, 2H, ArH-4 and ArH-6), 6.75 (s, broad, 1H, OH), 6.65 (d, 1H, ^3J=16, CH=C*H*COO), 3.84 (s, 3H, OCH_3); MS, *m/z*: 179 [M^++1](100), 147 (28), 137 (12); HRMS: exact mass for $C_{10}H_{10}O_3$: 178.0630; found: 178.0625.

3.2.13. Methyl m-coumarate

Purification was carried out by column chromatography with hexane:ethyl acetate 80:20 on silica gel. Yield: 81%; white crystals; UV, λ_{max} (methanol, nm): 315, 279, 234, 214; IR, ν_{max} (KBr, cm^{-1}): 3333, 1689, 1637, 1593; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.65 (d, 1H, ^3J=16, C*H*=CHCOO), 7.24 (t, 1H, $^3J_{5,4}=^3J_{5,6}$=7.5, ArH-5), 7.07 (m, 1H, ArH-4), 7.05 (s, broad, 1H, OH), 6.92 (m, 1H, ArH-6), 6.66 (s, 1H, ArH-2), 6.41 (d, 1H, ^3J=16, CH=C*H*COO), 3.83 (s, 3H, OCH_3); MS, *m/z*: 179 [M^++1](100), 147 (17), 137 (5); exact mass for $C_{10}H_{10}O_3$: 178.0630; found: 178.0632.

General protocol for catalytic hydrogenation (synthesis of methyl 3-(3-hydroxyphenyl)propanoate and methyl 3-(2-hydroxyphenyl)propanoate). The coumarate (9.6 mmol) was dissolved in methanol (20 ml), Pd/C (10%, 50 mg) was added, and the mixture was stirred overnight under hydrogen atmosphere. After completion, the suspension was filtered on Celite, concentrated, and flash chromatographed on silica gel (ethyl acetate) resulting in the desired methyl 3-(2 or 3-hydroxyphenyl)propanoate.

3.2.14. Methyl 3-(2-hydroxyphenyl)propanoate

Purification was carried out by flash column chromatography with ethyl acetate on silica gel. Yield: 97%; slightly pink oil; UV, λ_{max} (methanol, nm): 274, 214; IR, ν_{max} (KBr, cm^{-1}): 3406, 2952, 2364, 1714, 1597; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.04–7.18 (m, 3H, 2ArH and OH), 6.81–6.93 (m, 2H, ArH), 3.68 (s, 3H, OCH_3), 2.92 (t, 2H, ^3J=7, CH_2), 2.71 (t, 2H, ^3J=7, CH_2); MS, *m/z*: 181 [M^++1](100), 149 (96); exact mass for $C_{10}H_{12}O_3$: 180.0786; found: 180.0793.

3.2.15. Methyl 3-(3-hydroxyphenyl)propanoate

Purification was carried out by flash column chromatography with ethyl acetate on silica gel. Yield: 91%; yellow oil; UV, λ_{max} (methanol, nm): 274, 216; IR, ν_{max} (KBr, cm^{-1}): 3410, 2950, 1734, 1594; ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.14 (t, 1H, $^3J_{5,4}=^3J_{5,6}$=8, ArH-5), 6.65–6.80 (m, 3H, ArH), 5.85 (s, broad, 1H, OH), 3.68 (s, 3H, OCH_3), 2.90 (t, 2H, ^3J=8, CH_2), 2.63 (t, 2H, ^3J=8, CH_2); MS, *m/z*: 181 [M^++1](13), 149 (100); exact mass for $C_{10}H_{12}O_3$: 180.0786; found: 180.0779.

3.3. Photoreaction products

3.3.1. Meta photocycloadducts

*3.3.1.1. 9-Carbomethoxymethyl-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**10**).* IR, ν_{max} (NaCl, cm^{-1}): 2925, 1736, 1636; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.41–5.45 (m, 1H, $J_{10,11}$=2.8, J_{10,CH_2}=1.3×2, H-10), 4.10 (ddd, 1H, $J_{3exo,3endo}$=10.7, $J_{3exo,4exo}$=7.9, $J_{3exo,4endo}$=0.7, H-3exo), 4.04 (ddd, 1H, $J_{3endo,3exo}$=10.7, $J_{3endo,4exo}$=10.7, $J_{3endo,4endo}$=4.9, H-3endo), 3.68 (s, 3H, OCH_3), 3.18 (td, 1H, $J_{8,7}$=7.5, $J_{8,5}$=1.9, $J_{8,10}$=1.5, H-8), 3.15 (dd, 2H, $J_{CH_2,10}$=1.3×2, CH_2), 2.69–2.74 (m, 1H, H-5), 2.55–2.58 (m, 1H, H-11), 1.97 (ddddd, 1H, $J_{4exo,4endo}$=13.2, $J_{4exo,3endo}$=11.5, $J_{4exo,3exo}$=7.9, $J_{4exo,5}$=3.3, $J_{4exo,6endo}$= 1.4, H-4exo), 1.78 (ddd, 1H, $J_{6exo,6endo}$=13.4, $J_{6exo,7}$=6.4, $J_{6exo,11}$=2.5, H-6exo), 1.45 (ddd, 1H, $J_{7,8}$=7.5, $J_{7,6exo}$=6.4, $J_{7,6endo}$=2.5, H-7), 1.43–1.53 (m, 2H, $J_{4endo,3endo}$=4.9, $J_{4endo,5}$=2.6, $J_{4endo,3exo}$=0.7, H-4endo and H-6endo); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.3 (COO), 134.0 (C-9), 127.2 (C-10), 88.8 (C-1), 69.6 (C-3), 58.8 (C-5), 53.7 (C-11), 51.8 (OCH_3), 49.1 (C-8), 36.8 (CH_2), 32.5 (C-6), 27.1 (C-4), 25.1 (C-7); MS, *m/z*: 221 [M^++1](100), 203 (11), 189 (15), 177 (12), 161 (13); HRMS: exact mass for $C_{13}H_{16}O_3$: 220.1099; found: 220.1105.

*3.3.1.2. 9-(2-Carbomethoxyethyl)-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**11**).* IR, ν_{max} (NaCl, cm^{-1}): 2918, 1739; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.22–5.25 (m, 1H, $J_{10,11}$=2.5, $J_{10,8}$=1.5, J_{10,CH_2}=1.4, H-10), 4.09 (ddd, 1H, $J_{3exo,3endo}$=10.7, $J_{3exo,4exo}$=8.0, $J_{3exo,4endo}$=0.9, H-3exo), 4.02 (ddd, 1H, $J_{3endo,4exo}$=11.7, $J_{3endo,3exo}$=10.7, $J_{3endo,4endo}$=4.9, H-3endo), 3.67 (s, 3H, OCH_3), 3.06 (ddd, 1H, $J_{8,7}$=7.4, $J_{8,5}$=1.8, $J_{8,10}$=1.5, H-8), 2.65–2.69 (m, 1H, H-5), 2.51–2.54 (m, 1H, H-11), 2.40–2.50 (m, 4H, 2 CH_2), 1.96 (ddddd, 1H, $J_{4exo,4endo}$=13.6, $J_{4exo,3endo}$=11.7, $J_{4exo,3exo}$=8.0, $J_{4exo,5}$=3.4, $J_{4exo,6endo}$=1.4, H-4exo), 1.75 (ddd, 1H, $J_{6exo,6endo}$=13.7, $J_{6exo,7}$=6.6, $J_{6exo,11}$=2.5, H-6exo), 1.46 (m, 1H, $J_{4endo,4exo}$ =13.6, $J_{4endo,3endo}$=4.9, $J_{4endo,3exo}$=0.9, $J_{4endo,5}$=2.6, H-4endo), 1.38–1.45 (m, 2H, $J_{6endo,6exo}$=13.7, $J_{7,8}$=7.4, $J_{7,6exo}$=6.6, $J_{6endo,7}$=2.5, $J_{6endo,4exo}$=1.4, H-6endo and H-7); ^{13}C NMR (100 MHz,

$CDCl_3$) δ (ppm): 173.5 (COO), 140.6 (C-9), 123.2 (C-10), 88.5 (C-1), 69.5 (C-3), 58.6 (C-5), 53.5 (C-11), 51.5 (OCH_3), 49.0 (C-8), 32.5 ($2CH_2$), 26.4 (C-6), 27.1 (C-4), 25.0 (C-7); MS, *m/z*: 235 [M^++1](100), 217 (12), 203 (10), 191 (17), 161 (15); HRMS: exact mass for $C_{14}H_{18}O_3$: 234.1256; found: 234.1256.

*3.3.1.3. 8-Carbomethoxy-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]-undec-9-ene (**12**).* IR, ν_{max} (NaCl, cm^{-1}): 2954, 1719; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.90 (d, 1H, $J_{9,10}$=6.2, H-9), 5.66 (dd, 1H, J=6.2, 2.6, H-10), 4.20 (m, 1H, H-3exo), 4.16 (m, 1H, $J_{3exo,3endo}$=10.8, $J_{3endo,4exo}$=10.8, $J_{3endo,4endo}$=4.7, H-3endo), 3.76 (s, 3H, OCH_3), 2.68–2.73 (m, 2H, H-5 and H-11), 2.31 (dd, 1H, $J_{7,6exo}$=6.5, $J_{7,6endo}$=2.5, H-7), 1.97–2.08 (m, 1H, H-4exo), 1.86 (ddd, 1H, $J_{6exo,6endo}$=14.1, $J_{6exo,7}$=6.5, $J_{6exo,11}$=2.7, H-6exo), 1.58–1.66 (m, 1H, H-6endo), 1.49–1.57 (m, 1H, H-4endo); MS, *m/z*: 207 [M^++1](100), 191 (39), 175 (78), 163 (10); HRMS: exact mass for $C_{12}H_{14}O_3$: 206.0943; found: 206.0948.

*3.3.1.4. 8-Carbomethoxymethyl-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**13**).* IR, ν_{max} (NaCl, cm^{-1}): 2921, 1741; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.70 (d, 1H, $J_{9,10}$=6.2, H-9), 5.63 (dd, 1H, $J_{10,9}$=6.2, $J_{10,11}$=2.6, H-10), 4.12 (ddd, 1H, $J_{3exo,3endo}$=10.8, $J_{3exo,4exo}$=7.8, $J_{3exo,4endo}$=0.5, H-3exo), 4.02 (ddd, 1H, $J_{3endo,4exo}$=11.7, $J_{3endo,3exo}$=10.8, $J_{3endo,4endo}$=5.0, H-3endo), 3.70 (s, 3H, OCH_3), 2.83 (d, 1H, $J_{CH_{2a},CH_{2b}}$=15.7, CH_2), 2.78 (d, 1H, $J_{CH_{2a},CH_{2b}}$=15.7, CH_2), 2.67–2.71 (m, 1H, H-5), 2.60–2.63 (m, 1H, H-11), 1.98 (ddddd, 1H, $J_{4exo,4endo}$=13.6, $J_{4exo,3endo}$=11.7, $J_{4exo,3exo}$=7.8, $J_{4exo,5}$=3.3, $J_{4exo,6endo}$= 1.5, H-4exo), 1.79 (ddd, 1H, $J_{6exo,6endo}$=13.6, $J_{6exo,7}$=6.4, $J_{6exo,11}$=2.6, H-6exo), 1.48–1.55 (m, 1H, $J_{6endo,6exo}$=13.6, $J_{6endo,7}$=2.6, $J_{6endo,4exo}$=1.5, H-6endo), 1.44–1.52 (dddd, 1H, $J_{4endo,4exo}$=13.6, $J_{4endo,3endo}$=5.0, $J_{4endo,5}$=2.7, $J_{4endo,3exo}$=0.5, H-4endo), 1.31 (dd, 1H, $J_{7,6exo}$=6.4, $J_{7,6endo}$=2.6, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 172.2 (COO), 130.8 (C-10), 129.6 (C-9), 90.2 (C-1), 69.8 (C-3), 59.4 (C-5), 54.2 (C-8), 52.5 (C-11), 51.7 (OCH_3), 35.0 (CH_2), 32.6 (C-6), 31.3 (C-7), 27.6 (C-4); MS, *m/z*: 221 [M^++1](100), 203 (10), 189 (10), 161 (13); HRMS: exact mass for $C_{13}H_{16}O_3$: 220.1099; found: 220.1092.

*3.3.1.5. 8-(2-Carbomethoxyethyl)-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**14**).* UV, λ_{max} (methanol, nm): 202; IR, ν_{max} (NaCl, cm^{-1}): 2920, 1738; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.62 (dd, 1H, $J_{10,9}$=6.2, $J_{10,11}$=2.6, H-10), 5.55 (d, 1H, $J_{9,10}$=6.2, H-9), 4.10 (ddd, 1H, $J_{3exo,3endo}$=10.8, $J_{3exo,4exo}$=7.8, $J_{3exo,4endo}$=0.5, H-3exo), 4.01 (ddd, 1H, $J_{3endo,4exo}$=11.7, $J_{3endo,3exo}$=10.8, $J_{3endo,4endo}$=5.0, H-3endo), 3.66 (s, 3H, CH_3), 2.64–2.69 (m, 1H, H-5), 2.56–2.60 (m, 1H, H-11), 2.42–2.52 (m, 2H, CH_2COOCH_3), 2.20–2.29 (m, 1H, J=14.4, 7.8, CH_2), 2.02–2.12 (m, 1H, J=14.4, 7.8, CH_2), 1.97 (ddddd, 1H, $J_{4exo,4endo}$=13.6, $J_{4exo,3endo}$=11.7, $J_{4exo,3exo}$=7.8, $J_{4exo,5}$=3.3, $J_{4exo,6endo}$=1.5, H-4exo), 1.75 (ddd, 1H, $J_{6exo,6endo}$=13.5, $J_{6exo,7}$=6.4, $J_{6exo,11}$=2.5, H-6exo), 1.46–1.53 (m, 1H, $J_{4endo,4exo}$,=13.6, $J_{4endo,3endo}$=5.0, $J_{4endo,5}$=2.6, $J_{4endo,3exo}$=0.5, H-4endo), 1.42–1.50 (m, 1H, $J_{6endo,6exo}$=13.5, $J_{6endo,7}$=2.6, $J_{6endo,4exo}$=1.5, H-6endo), 1.23 (dd, 1H, $J_{7,6exo}$=6.4, $J_{7,6endo}$=2.6, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.7 (COO), 130.6 (C-10), 130.0 (C-9), 90.7 (C-1), 69.5 (C-3), 59.6 (C-5), 58.3 (C-8), 52.5 (C-11), 51.5 (OCH_3), 32.6 (C-6), 32.5 (*C*H_2COO), 31.4 (C-7), 27.5 (C-4), 25.5 (CH_2); MS, *m/z*: 235 [M^++1](100), 217 (25), 203 (19), 191 (16), 175 (10), 161 (13 HRMS: exact mass for $C_{14}H_{18}O_3$: 234.1256; found: 234.1261.

*3.3.1.6. 10-Carbomethoxy-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]-undec-9-ene (**15**).* IR, ν_{max} (NaCl, cm^{-1}): 2938, 2355, 1717, 1606; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.71 (d, 1H, $J_{9,8}$=3.0, H-9), 4.17 (dd, 1H, $J_{3exo,3endo}$=10.8, $J_{3exo,4exo}$=7.9, H-3exo), 4.07 (ddd, 1H, $J_{3endo,4exo}$=11.8, $J_{3endo,3exo}$=10.8, $J_{3endo,4endo}$=5.1, H-3endo), 3.72 (s, 3H, OCH_3), 3.27 (ddd, 1H, $J_{8,7}$=7.6, $J_{8,9}$=3.0, $J_{8,5}$=1.8, H-8), 2.91–2.96 (m, 1H, H-5), 2.83–2.88 (m, 1H, H-11), 2.10 (m, 1H, H-4exo), 1.83 (ddd, 1H, $J_{6exo,6endo}$=14.0, $J_{6exo,7}$=6.5, $J_{6exo,11}$=2.8, H-6exo), 1.65 (ddd, 1H, $J_{7,8}$=7.6, $J_{7,6exo}$=6.4, $J_{7,6endo}$=2.3, H-7), 1.46–1.59 (m, 2H, H-4endo and H-6endo); MS, *m/z*: 207 [M^++1](100), 175 (46), 147 (24); HRMS: exact mass for $C_{12}H_{14}O_3$: 206.0943; found: 206.0935.

*3.3.1.7. 10-Carbomethoxymethyl-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**16**).* IR, ν_{max} (NaCl, cm^{-1}): 2921, 1739; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.57 (ddd, 1H, $J_{9,8}$=2.8, J_{9,CH_2}=1.3×2, H-9), 4.13 (ddd, 1H, $J_{3exo,3endo}$=10.7, $J_{3exo,4exo}$=8.0, $J_{3exo,4endo}$=0.7, H-3exo), 4.06 (ddd, 1H, $J_{3endo,4exo}$=11.7, $J_{3endo,3exo}$=10.7, $J_{3endo,4endo}$=4.9, H-3endo), 3.67(s, 3H, OCH_3), 3.14 (ddd, 1H, $J_{8,7}$=7.5, $J_{8,9}$=2.8, $J_{8,5}$=2.0, H-8), 3.07 (s, 2H, $J_{CH_2,9}$=1.3×2, CH_2), 2.75–2.79 (m, 1H, H-5), 2.56–2.59 (m, 1H, H-11), 2.00 (ddddd, 1H, $J_{4exo,4endo}$=13.6, $J_{4exo,3endo}$=11.7, $J_{4exo,3exo}$=8.0, $J_{4exo,5}$=3.3, $J_{4exo,6endo}$= 1.5, H-4exo), 1.76 (ddd, 1H, $J_{6exo,6endo}$=13.6, $J_{6exo,7}$=6.5, $J_{6exo,11}$=2.6, H-6exo), 1.50–1.57 (m, 1H, $J_{6endo,6exo}$=13.6, $J_{6endo,7}$=2.5, $J_{6endo,5}$=1.6, $J_{6endo,4exo}$=1.5, H-6endo), 1.46–1.53 (m, 1H, $J_{4endo,4exo}$=13.6, $J_{4endo,3endo}$=4.9, $J_{4endo,5}$=2.7, $J_{4endo,3exo}$=0.7, H-4endo), 1.43 (ddd, 1H, $J_{7,8}$=7.5, $J_{7,6exo}$=6.5, $J_{7,6endo}$=2.5, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.6 (COO), 136.4 (C-10), 126.1.0 (C-9), 89.3 (C-1), 69.8 (C-3), 60.5 (C-5), 52.8 (C-11), 51.8 (OCH_3), 45.7 (C-8), 35.3 (CH_2), 32.5 (C-6), 26.8 (C-4), 25.8 (C-7); MS, *m/z*: 221 [M^++1](100), 203 (29), 189 (24), 161 (22); HRMS: exact mass for $C_{13}H_{16}O_3$: 220.1099; found: 220.1105.

*3.3.1.8. 10-(2-Carbomethoxyethyl)-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**17**).* IR, ν_{max} (NaCl, cm^{-1}):

3032, 2919, 2850, 1739; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.34 (td, 1H, $J_{9,8}$=2.7, J_{9,CH_2}=1.6×2, H-9), 4.12 (ddd, 1H, $J_{3exo,3endo}$=10.7, $J_{3exo,4exo}$=8.0, $J_{3exo,4endo}$=0.7, H-3exo), 4.05 (ddd, 1H, $J_{3endo,4exo}$=11.7, $J_{3endo,3exo}$=10.7, $J_{3endo,4endo}$=4.9, H-3endo), 3.67 (s, 3H, OCH_3), 3.11 (ddd, $J_{8,7}$=7.4, $J_{8,9}$=2.7, $J_{8,5}$=2.0, 1H, H-8), 2.75–2.80 (m, 1H, H-5), 2.42–2.52 (m, broad, 3H, CH_2COOCH_3 and H-11), 2.29–2.41 (m, 2H, CH_2), 1.90–2.04 (ddddd, 1H, $J_{4exo,4endo}$=13.6, $J_{4exo,3endo}$=11.7, $J_{4exo,3exo}$=8.0, $J_{4exo,5}$=3.3, $J_{4exo,6endo}$=1.5, H-4exo), 1.75 (ddd, 1H, $J_{6exo,6endo}$=13.5, $J_{6exo,7}$=6.5, $J_{6exo,11}$=2.5, H-6exo), 1.46–1.53 (m, 1H, $J_{4endo,4exo}$=13.6, $J_{4endo,3endo}$=4.9, $J_{4endo,5}$=2.6, $J_{4endo,3exo}$=0.7, H-4endo), 1.42–1.50 (m, 1H, $J_{6endo,6exo}$=13.5, $J_{6endo,7}$=2.5, $J_{6endo,4exo}$=1.5, H-6endo), 1.39 (ddd, 1H, $J_{7,8}$=7.4, $J_{7,6exo}$=6.5, $J_{7,6endo}$=2.5, H-7); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.6 (COO), 143.1 (C-10), 121.5 (C-9), 89.0 (C-1), 69.8 (C-3), 60.5 (C-5), 52.8 (C-11), 51.6 (OCH_3), 45.7 (C-8), 33.1 (CH_2COO), 32.6 (C-6), 26.7 (C-4), 25.7 (C-7), 24.4 (CH_2); MS, *m/z*: 235 [M^++1](100), 217 (34), 203 (14), 191 (9), 175 (6), 161 (6); HRMS: exact mass for $C_{14}H_{18}O_3$: 234.1256; found: 234.1258.

*3.3.1.9. 7-Carbomethoxymethyl-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**18**).* IR, ν_{max} (NaCl, cm^{-1}): 3059, 2922, 1739; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.75 (dd, 1H, $J_{9,10}$=6.0, $J_{9,8}$=2.7, H-9), 5.62 (ddd, 1H, $J_{10,9}$=6.0, $J_{10,11}$=2.5, $J_{10,8}$=1.2, H-10), 4.12 (ddd, 1H, $J_{3exo,3endo}$=11.1, $J_{3exo,4exo}$=8.4, $J_{3exo,4endo}$=2.5, H-3exo), 3.94 (ddd, 1H, $J_{3endo,3exo}$=11.1, $J_{3endo,4exo}$=9.9, $J_{3endo,4endo}$=6.2, H-3endo), 3.68 (s, 3H, OCH_3), 2.98 (m, 1H, $J_{8,9}$=2.7, $J_{8,5}$=2.0, $J_{8,10}$=1.2 H-8), 2.78 (d, 1H, $J_{CH_{2a}CH_b}$=15.3, CH_2), 2.74–2.78 (m, 1H, H-11), 2.62–2.67 (m, 1H, H-5), 2.09 (ddddd, 1H, $J_{4exo,4endo}$=13.8, $J_{4exo,3endo}$=9.9, $J_{4exo,3exo}$=8.4, $J_{4exo,5}$=4.5, $J_{4exo,6endo}$=1.1, H-4exo), 1.76 (ddd, 1H, $J_{6endo,6exo}$=13.8, $J_{6endo,5}$=3.0, $J_{6endo,4exo}$=1.1, H-6endo), 1.63 (dd, 1H, $J_{6exo,6endo}$=13.8, $J_{6exo,11}$=2.8, H-6exo), 1.58–1.64 (m, 1H, $J_{4endo,4exo}$=13.8, $J_{4endo,3endo}$=6.2, $J_{4endo,3exo}$=2.5, $J_{4endo,5}$=2.2, H-4endo) 2.44 (d, 1H, $J_{CH_{2a}CH_b}$=15.3, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.4 (COO), 129.9 (C-9 or C-10), 128.9 (C-10 or C-9), 92.0 (C-1), 68.4 (C-3), 59.2 (C-5), 51.6 (OCH_3), 51.1 (C-11), 50.0 (C-8), 38.1 (CH_2), 33.9 (C-6), 32.4 (C-4), 30.9 (C-7); MS, *m/z*: 221 [M^++1](100), 203(25), 191 (42), 177 (25), 161 (22); HRMS: exact mass for $C_{13}H_{16}O_3$: 220.1099; found: 220.1091.

*3.3.1.10. 7-(2-Carbomethoxyethyl)-2-oxatetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene (**19**).* IR, ν_{max} (NaCl, cm^{-1}): 3054, 2921, 1738; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.68 (dd, 1H, $J_{9,10}$=6.0, $J_{9,8}$=2.7, H-9), 5.58 (ddd, 1H, $J_{10,9}$=6.0, $J_{10,11}$=2.6, $J_{10,8}$=1.2, H-10), 4.06–4.12 (m, 2H, H-3exo and H-3endo), 3.67 (s, 3H, OCH_3), 2.76 (m, 1H, $J_{8,9}$=2.7, $J_{8,5}$=2.2, $J_{8,10}$=1.2, H-8), 2.70–2.74 (m, 1H, H-11), 2.59–2.65 (m, 1H, H-5), 2.30–2.43 (m, 2H, CH_2COO), 2.18 (ddd, 1H, J=13.8, 7.6×2, CH_2), 2.08 (ddddd, 1H, $J_{4exo,4endo}$=13.6, $J_{4exo,3exo}$=9.3, $J_{4exo,3endo}$=9.3, $J_{4exo,5}$=4.3, $J_{4exo,6endo}$=1, H-4exo), 1.77 (ddd, 1H, J=13.8, 9.0, 6.7, CH_2), 1.63 (ddd, 1H, $J_{6endo,6exo}$=13.4, $J_{6endo,5}$=3.2, $J_{6endo,4exo}$=1, H-6endo), 1.55–1.70 (m, 1H, H-4endo), 1.52 (dd, 1H, $J_{6exo,6endo}$=13.4, $J_{6exo,11}$=2.8, H-6exo); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.9 (COO), 129.7 (C-9 or C-10), 128.8 (C-10 or C-9), 92.7 (C-1), 68.5 (C-3), 59.7 (C-5), 51.5 (OCH_3), 51.0 (C-11), 49.4 (C-8), 34.2 (CH_2COO), 34.2 (C-7), 33.3 (C-6), 32.4 (C-4), 28.9 (CH_2); MS, *m/z*: 235 [M^++1](100), 217; HRMS: exact mass for $C_{14}H_{18}O_3$: 234.1256; found: 234.1261.

3.4. Reaction products derived from ortho photocycloadducts

*3.4.1. 11-Carbomethoxymethyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene (**20**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.85 (s, broad, 1H, H-10), 4.87 (dd, 1H, $J_{2,1}$=6.4, $J_{2,7}$=2.5, H-2), 4.17 (t, 1H, $J_{5exo,5endo}$=8.5, $J_{5exo,6exo}$=8.4, H-5exo), 3.93 (ddd, 1H, $J_{5endo,5exo}$=8.5, $J_{5endo,6exo}$=11.8, $J_{5endo,6endo}$=5.5, H-5endo), 3.68 (s, 3H, OCH_3), 3.32–3.40 (m, 1H, H-9), 2.97–3.10 (m, broad, 3H, CH_2 and H-1), 2.30–2.53 (m, broad, 1H, H-7), 2.08–2.53 (m, 2H, H-6endo and H-8endo), 1.67 (ddd, 1H, $J_{6exo,6endo}$=12, $J_{6exo,5endo}$=11.8, $J_{6exo,5exo}$=8.4, H-6exo), 1.11 (ddd, 1H, $J_{8exo,8endo}$=12.9, $J_{8exo,7}$=11.7, $J_{8exo,9}$=5.3, H-8exo).

*3.4.2. 3-Methoxy-11-carbomethoxymethyl-4-oxatricyclo-[7.2.0.0^{3,7}]undec-10-ene (methyl acetal of **20**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.89 (s, broad, 1H, H-10), 3.82 (ddd, 1H, $J_{5exo,5endo}$=8.5, $J_{5exo,6exo}$=8.4, $J_{5exo,6endo}$=2.6, H-5exo), 3.70 (s, 3H, $COOCH_3$) 3.64 (ddd, 1H, $J_{5endo,6exo}$=10.0, $J_{5endo,5exo}$=8.5, $J_{5endo,6endo}$=6.6, H-5endo), 3.20 (s, 3H, OCH_3), 3.14 (d, 1H, CH_2), 3.05 (d, 1H, CH_2), 2.88–2.94 (m, 1H, H-1), 2.83–2.88 (m, 1H, H-9), 2.29–2.39 (m, 1H, H-7), 2.11 (dd, 1H, $J_{2a,2b}$=14.9, $J_{2a,1}$=5.6, H-2a), 2.06–2.15 (m, 1H, H-6endo), 1.81 (dd, 1H, $J_{2b,2a}$=14.9, $J_{2b,1}$=5.1, H-2b), 1.74 (dt, 1H, $J_{8endo,8exo}$=14.2, $J_{8endo,7}$=5.3, $J_{8endo,9}$=5.3, H-8endo), 1.46–1.60 (m, 2H, H-6exo and H-8exo).

*3.4.3. 11-(2-Carbomethoxyethyl)-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene (**21**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.64 (s, broad, 1H, H-10), 4.87 (dd, 1H, $J_{2,1}$=6.3, $J_{2,7}$=2.5, H-2), 4.17 (t, 1H, $J_{5exo,5endo}$=8.4, $J_{5exo,6exo}$=8.5, H-5exo), 3.92 (ddd, 1H, $J_{5endo,5exo}$=8.4, $J_{5endo,6exo}$=11.8, $J_{5endo,6endo}$=5.5, H-5endo), 3.66 (s, 3H, OCH_3), 3.20–3.30 (m, 1H, H-9), 2.92–3.02 (m, broad, 1H, H-1), 2.00–2.50 (m, broad, 7H, $J_{8endo,7}$=5.2, $J_{8endo,9}$=1.5, H-6endo, H-7, H-8endo and CH_2CH_2COO), 1.65 (ddd, 1H, $J_{6exo,6endo}$=12,

$J_{6exo,5endo}$=11.5, $J_{6exo,5exo}$=8.5, H-6exo), 1.07 (ddd, 1H, $J_{8exo,8endo}$=12.9, $J_{8exo,7}$=11.4, $J_{8exo,9}$=5.4, H-8exo).

*3.4.4. 3-Methoxy-11-(2-carbomethoxyethyl)-4-oxatricyclo-[7.2.0.0^{3,7}]undec-10-ene (methyl acetal of **21**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.70 (s, broad, 1H, H-10), 3.82 (dt, 1H, $J_{5exo,5endo}$=8.5, $J_{5exo,6exo}$=8.4, $J_{5exo,6endo}$=2.5, H-5exo), 3.69 (s, 3H, $COOCH_3$) 3.64 (ddd, 1H, $J_{5endo,6exo}$=10.1, $J_{5endo,5exo}$=8.5, $J_{5endo,6endo}$=6.6, H-5endo), 3.20 (s, 3H, OCH_3), 2.73–2.84 (m, 2H, H-1 and H-9), 2.25–2.53 (m, 5H, H-7 and CH_2CH_2), 2.03 (dd, 1H, $J_{2a,2b}$=15, $J_{2a,1}$=5.8, H-2a), 1.98–2.18 (m, 1H, J6endo,6exo=12, H-6endo), 1.83 (dd, 1H, $J_{2b,2a}$=15, $J_{2b,1}$=5.0, H-2b), 1.62–1.77 (dt, 1H, $J_{8endo,8exo}$=14, $J_{8endo,7}$=5.2, $J_{8endo,9}$=5.2, H-8endo), 1.43–1.62 (m, 2H, H-6exo and H-8exo).

*3.4.5. 1-Carbomethoxy-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene (**22**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.22 (d, 1H, $J_{10,11}$=2.9, H-10 or H-11), 6.00 (d, 1H, $J_{10,11}$=2.9, H-11 or H-10), 5.02 (d, 1H, $J_{2,7}$=2.4, H-2), 4.27 (t, 1H, $J_{5exo,5endo}$=8.8, $J_{5exo,6exo}$=8.6, H-5exo), 3.99 (ddd, 1H, $J_{5endo,5exo}$=8.8, $J_{5endo,6exo}$=11.6, $J_{5endo,6endo}$=5.6, H-5endo), 3.71 (s, 3H, OCH_3), 3.35–3.42 (m, 1H, H-9), 2.09–2.48 (m, broad, 3H, $J_{8endo,9}$=1.5, H-6endo, H-7 and H-8endo), 1.69 (ddd, 1H, $J_{6exo,6endo}$=12, $J_{6exo,5endo}$=11.6, $J_{6exo,5exo}$=8.6, H-6exo), 1.26 (ddd, 1H, $J_{8exo,8endo}$=12.8, $J_{8exo,7}$=11.2, $J_{8exo,9}$=5.1, H-8exo).

*3.4.6. 1-(2-Carbomethoxyethyl)-4-oxatricyclo-[7.2.0.0^{3,7}]undeca-2,10-diene (**23**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.02 (d, 1H, $J_{10,11}$=2.8, H-10 or H-11), 5.92 (d, 1H, $J_{10,11}$=2.8, H-11 or H-10), 4.63 (d, 1H, $J_{2,7}$=2.2, H-2), 4.19 (t, 1H, $J_{5exo,5endo}$=8.6, $J_{5exo,6exo}$=8.2, H-5exo), 3.95 (ddd, 1H, $J_{5endo,6exo}$=11.8, $J_{5endo,5exo}$=8.6, $J_{5endo,6endo}$=5.6, H-5endo), 3.65 (s, 3H, OCH_3), 2.65–2.67 (m, 1H, H-9), 2.20–2.50 (m, 4H, CH_2CH_2), 2.06–2.50 (m, 3H, H-6endo, H-7 and H-8endo), 1.58–1.78 (m, 1H, $J_{6exo,6endo}$=12, $J_{6exo,5endo}$=11.8, $J_{6exo,5exo}$=8.2, H-6exo) 1.00–1.20 (m, 1H, H-8exo).

*3.4.7. 10-(2-Carbomethoxyethyl)-4-oxatricyclo[7.2.0.0^{3,7}]-undeca-2,10-diene (**24**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.67 (m, 1H, H-11), 4.90 (dd, 1H, $J_{2,1}$=6.3, $J_{2,7}$=2.0, H-2), 4.16 (dt, 1H, $J_{5exo,5endo}$=8.6, $J_{5exo,6exo}$=8.5, $J_{5exo,6endo}$=1, H-5exo), 3.94 (ddd, 1H, $J_{5endo,6exo}$=11.7, $J_{5endo,5exo}$=8.6, $J_{5endo,6endo}$=5.5, H-5endo), 3.67 (s, 3H, OCH_3), 3.21 (m, 1H, H-9), 3.08 (m, 1H, H-1), 2.10–2.53 (m, 7H, H-6endo, H-7 and H-8endo and CH_2CH_2), 1.58–1.75 (m, 1H, $J_{6exo,6endo}$=12, $J_{6exo,5endo}$=11.7, $J_{6exo,5exo}$=8.5, H-6exo), 1.08–1.19 (m, 1H, H-8exo).

*3.4.8. 9-Carbomethoxy-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene (**25**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.04–6.07 (m, 2H, H-10 and H-11), 4.87 (dd, 1H, $J_{2,1}$=6.6, $J_{2,7}$=2.5, H-2), 4.22 (dt, 1H, $J_{5exo,5endo}$=8.5, $J_{5exo,6exo}$=8.6, $J_{5exo,6endo}$=1.0, H-5exo), 3.97 (ddd, 1H, $J_{5endo,5exo}$=8.5, $J_{5endo,6exo}$=11.7, $J_{5endo,6endo}$=5.6, H-5endo), 3.69 (s, 3H, OCH_3), 3.59 (dd, 1H, $J_{1,2}$=6.6, $J_{1,11}$=0.6, H-1), 2.50 (dddd, 1H, $J_{7,8exo}$=11.9, $J_{7,6endo}$=7.9, $J_{7,8endo}$=5.2, $J_{7,2}$=2.5, H-7), 2.32 (dd, 1H, $J_{8endo,8exo}$=12.9, $J_{8endo,7}$=5.2, H-8endo), 2.22 (dddd, 1H, $J_{6endo,6exo}$=11.8, $J_{6endo,7}$=7.9, $J_{6endo,5endo}$=5.6, $J_{6endo,5exo}$=1.0, H-6endo), 1.76 (ddd, 1H, $J_{6exo,6endo}$=11.8, $J_{6exo,5endo}$=11.7, $J_{6exo,5exo}$=8.6, H-6exo), 1.56 (dd, 1H, $J_{8exo,8endo}$=12.9, $J_{8exo,7}$=11.9, H-8exo).

*3.4.9. 3-Methoxy-9-carbomethoxy-4-oxatricyclo-[7.2.0.0^{3,7}]undec-10-ene (methylacetal of **25**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.30 (dd, 1H, $J_{11,10}$=2.8, $J_{11,1}$=0.8, H-11), 6.00 (d, 1H, $J_{10,11}$=2.8, H-10), 3.84 (ddd, 1H, $J_{5exo,5endo}$=8.5, $J_{5exo,6exo}$=8.3, $J_{5exo,6endo}$=3.0, H-5exo), 3.69 (s, 3H, $COOCH_3$) 3.67 (ddd, 1H, $J_{5endo,6exo}$=9.4, $J_{5endo,5exo}$=8.5, $J_{5endo,6endo}$=6.8, H-5endo), 3.16 (s, 3H, OCH_3), 2.30–2.42 (m, 1H, H-7), 2.38 (dd, 1H, $J_{2a,2b}$=15.2, $J_{2a,1}$=3.3, H-2a), 2.19 (dddd, 1H, $J_{6endo,6exo}$=12.1, $J_{6endo,7}$=9.3, $J_{6endo,5endo}$=6.8, $J_{6endo,5exo}$=3.0, H-6endo), 2.02 (dd, 1H, $J_{8endo,8exo}$=13.9, $J_{8endo,7}$=5.1, H-8endo), 1.75 (dd, 1H, $J_{8exo,8endo}$=13.9, $J_{8exo,7}$=13.8, H-8exo) 1.74 (dd, 1H, $J_{2b,2a}$=15.2, $J_{2b,1}$=4.3, H-2b), 1.52 (dddd, 1H, $J_{6exo,6endo}$=12.1, $J_{6exo,5endo}$=9.4, $J_{6exo,5exo}$=8.3, $J_{6exo,7}$=6.0, H-6exo), 1.44–1.60 (m, 1H, H-1).

*3.4.10. 9-Carbomethoxymethyl-4-oxatricyclo[7.2.0.0^{3,7}]-undeca-2,10-diene (**26**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.15 (d, 1H, $J_{10,11}$=2.7, H-10), 5.89 (dd, 1H, $J_{11,10}$=2.7, $J_{11,1}$=0.5, H-11), 4.83 (dd, 1H, $J_{2,1}$=6.6, $J_{2,7}$=2.4, H-2), 4.19 (t, 1H, $J_{5exo,5endo}$=8.5, $J_{5exo,6exo}$=8.6, H-5exo), 3.94 (ddd, 1H, $J_{5endo,5exo}$=8.5, $J_{5endo,6exo}$=11.6, $J_{5endo,6endo}$=5.6, H-5endo), 3.66 (s, 3H, OCH_3), 3.10 (dd, 1H, $J_{1,2}$=6.6, $J_{1,11}$=0.6, H-1), 2.55 (s, 2H, CH_2COO), 2.40–2.53 (m, 1H, H-7), 2.19 (dd, 1H, $J_{8endo,8exo}$=12.7, $J_{8endo,7}$=5.1, H-8endo), 2.13–2.23 (m, 1H, H-6endo), 1.71 (ddd, 1H, $J_{6exo,6endo}$=12, $J_{6exo,5endo}$=11.6, $J_{6exo,5exo}$=8.6, H-6exo), 1.06 (t, 1H, $J_{8exo,8endo}$=12.7, $J_{8exo,7}$=12, H-8exo).

*3.4.11. 3-Methoxy-9-carbomethoxymethyl-4-oxatricyclo-[7.2.0.0^{3,7}]undec-10-ene(methyl acetal of **26**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.15 (dd, 1H, $J_{11,10}$=3.0, $J_{11,1}$=1, H-11), 6.04 (d, 1H, $J_{10,11}$=3.0, H-10), 3.82 (dt, 1H, $J_{5exo,6exo}$=8.5, $J_{5exo,5endo}$=8.4, $J_{5exo,6endo}$=2.8, H-5exo), 3.67 (s, 3H, $COOCH_3$) 3.64 (ddd, 1H, $J_{5endo,6exo}$=9.8, $J_{5endo,5exo}$=8.4, $J_{5endo,6endo}$=6.8, H-5endo), 3.16 (s, 3H, OCH_3), 2.72 (dd, 1H, $J_{1,2b}$=4.4, $J_{1,2a}$=3.1, H-1), 2.51 (s, 2H, CH_2) 2.40 (dd, 1H, $J_{2a,2b}$=15.0,

$J_{2a,1}$=3.1, H-2a), 2.16 (dddd, 1H, $J_{6endo,6exo}$=12, $J_{6endo,7}$= 9.5, $J_{6endo,5endo}$=6.8, $J_{6endo,5exo}$=2.8, H-6endo), 2.00–2.50 (m, 1H, H-7), 1.80 (dd, 1H, $J_{8endo,8exo}$=13.6, $J_{8endo,7}$=5.1, H-8endo), 1.66 (dd, 1H, $J_{2b,2a}$=15.0, $J_{2b,1}$=4.4, H-2b), 1.40–1.60 (m, 1H, H-6exo), 1.32 (t, 1H, $J_{8exo,8endo}$=13.6, $J_{8exo,7}$=13.6, H-8exo).

*3.4.12. 9-(2-Carbomethoxyethyl)-4-oxatricyclo-[7.2.0.0^{3,7}]undeca-2,10-diene (**27**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.99 (d, 1H, $J_{11,10}$=2.8, H-11), 5.89 (d, 1H, $J_{10,11}$=2.8, H-10), 4.82 (dd, 1H, $J_{2,1}$=6.6, $J_{2,7}$=2.3, H-2), 4.19 (t, 1H, $J_{5exo,5endo}$=8.4, $J_{5exo,6exo}$=8.5, H-5exo), 3.94 (ddd, 1H, $J_{5endo,5exo}$=8.4, $J_{5endo,6exo}$=11.7, $J_{5endo,6endo}$=5.5, H-5endo), 3.66 (s, 3H, OCH_3), 2.96 (d, 1H, $J_{1,2}$=6.6, H-1), 2.33 (t, 2H, J=7.7, CH_2COO), 2.30–2.50 (m, 1H, H-7), 2.03 (dd, 1H, $J_{8endo,8exo}$=12.8, $J_{8endo,7}$=5.1, H-8endo), 2.14–2.23 (m, 1H, $J_{6endo,6exo}$=12, $J_{6endo,5endo}$=5.5, H-6endo), 1.80–1.95 (m, 2H, CH_2), 1.69 (ddd, 1H, $J_{6exo,6endo}$=12, $J_{6exo,5endo}$=11.7, $J_{6exo,5exo}$=8.5, H-6exo), 1.00 (t, 1H, $J_{8exo,8endo}$=12.8, $J_{8exo,7}$=12, H-8exo).

*3.4.13. 3-Methoxy-9-(2-carbomethoxyethyl)-4-oxatricyclo-[7.2.0.0^{3,7}]undec-10-ene (methyl acetal of **27**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.14 (dd, 1H, $J_{11,10}$=2.8, $J_{11,1}$=0.8, H-11), 5.91 (d, 1H, $J_{10,11}$=2.8, H-10), 3.81 (dt, 1H, $J_{5exo,6exo}$=8.4, $J_{5exo,5endo}$=8.4, $J_{5exo,6endo}$=2.9, H-5exo), 3.66 (s, 3H, $COOCH_3$) 3.64 (ddd, 1H, $J_{5endo,6exo}$=9.6, $J_{5endo,5exo}$=8.4, $J_{5endo,6endo}$=6.8, H-5endo), 3.16 (s, 3H, OCH_3), 2.53 (dd, 1H, $J_{1,2b}$=4.3, $J_{1,2a}$=3.0, H-1), 2.30–2.37 (m, 2H, CH_2COO), 2.37 (dd, 1H, $J_{2a,2b}$=15.0, $J_{2a,1}$=3.0, H-2a), 2.17 (dddd, 1H, $J_{6endo,6exo}$=12.0, $J_{6endo,7}$=9.5, $J_{6endo,5endo}$=6.8, $J_{6endo,5exo}$=2.9, H-6endo), 2.27–2.40 (m, 1H, H-7), 1.70 (dd, 1H, $J_{8endo,8exo}$=13.7, $J_{8endo,7}$=5.1, H-8endo), 1.75–1.90 (m, 2H, C$H_2$$CH_2$COO), 1.56 (dd, 1H, $J_{2b,2a}$=15.0, $J_{2b,1}$=4.3, H-2b), 1.46 (dddd, 1H, $J_{6exo,6endo}$=12.0, $J_{6exo,5endo}$=9.6, $J_{6exo,5exo}$=8.4, $J_{6exo,7}$=5.8, H-6exo), 1.23 (t, 1H, $J_{8exo,8endo}$=13.7, $J_{8exo,7}$=13.7, H-8exo).

*3.4.14. 10-Carbomethoxy-2-oxatricyclo-[7.2.0.0^{1,5}]undeca-7,10-diene (**28**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.77 (s, broad, 1H, H-11), 5.94 (ddd, 1H, $J_{7,8}$=9.8, $J_{7,6a}$=7.4, $J_{7,6b}$=1.7, H-7), 5.75 (ddd, 1H, $J_{8,7}$=9.8, $J_{8,9}$=4.4, $J_{8,6b}$=2.6, H-8), 3.85–4.00 (m, 2H, H-3a and H-3b), 3.74 (s, 3H, OCH_3) 3.27 (d, broad, 1H, $J_{9,8}$=4.3, H-9), 2.36–2.45 (m, 1H, H-6a), 2.12–2.19 (m, 1H, H-6b), 1.86–2.07 (m, 2H, H-4a and H-4b), 1.78–2.10 (m, 1H, H-5).

*3.4.15. 10-Carbomethoxymethyl-2-oxatricyclo-[7.2.0.0^{1,5}]undeca-7,10-diene (**29**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.07 (m, 1H, J_{11,CH_2}=1.4, $J_{11,9}$=1, H-11), 5.87 (ddd, 1H, $J_{7,8}$=9.8, $J_{7,6a}$=7.0, $J_{7,6b}$=1.7, H-7), 5.80 (ddd, 1H, $J_{8,7}$=9.8, $J_{8,9}$=4.5, $J_{8,6b}$=2.5, H-8), 4.07 (ddd, 1H, $J_{3a,4b}$=9.4, $J_{3a,3b}$=8.5, $J_{3a,4a}$=2.2, H-3a), 3.99 (td, 1H, $J_{3b,3a}$=8.5, $J_{3b,4b}$=8.5, $J_{3b,4a}$=7.1, H-3b), 3.69 (s, 3H, OCH_3), 3.46 (d, broad, 1H, $J_{9,8}$=4.5, H-9), 3.06 (m, 2H, CH_2COO), 2.25–2.35 (m, 1H, $J_{6a,6b}$=12.5, $J_{6a,5}$=2, H-6a), 1.90–1.98 (m, 1H, $J_{4a,4b}$=12, H-4a), 1.74–1.90 (m, 2H, H-5 and H-6b), 1.60–1.74 (m, 1H, H-4b).

*3.4.16. 7-Carbomethoxymethyl-2-oxatricyclo[7.2.0.0^{1,5}]-undeca-7,10-diene (**30**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.20 (d, 1H, $J_{11,10}$=3.0, H-11), 6.15 (dd, 1H, $J_{10,11}$=3.0, $J_{10,9}$=0.8, H-10), 5.65 (m, 1H, $J_{8,9}$=4.6, H-8), 4.08 (dt, 1H, $J_{3a,4b}$=9.0, $J_{3a,3b}$=8.7, $J_{3a,4a}$=2.0, H-3a), 3.90–4.15 (m, 1H, H-3b), 3.67 (s, 3H, OCH_3), 3.45 (d, broad,1H, $J_{9,8}$=4.6, H-9), 3.05 (s, 2H, CH_2COO), 2.13–2.31 (m, 1H, $J_{6a,6b}$=12, $J_{6a,5}$=7, H-6a), 1.60–2.00 (m, 4H, H-4a, H4b, H-5 and H-6b).

*3.4.17. 7-(2-Carbomethoxyethyl)-2-oxatricyclo[7.2.0.0^{1,5}]-undeca-7,10-diene (**31**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.16 (d, 1H, $J_{11,10}$=3.4, H-11), 6.11 (dd, 1H, $J_{10,11}$=3.4, $J_{10,9}$=0.7, H-10), 5.51 (m, 1H, $J_{8,9}$=4.7, H-8), 4.10 (dt, 1H, $J_{3a,4b}$=9.1, $J_{3a,3b}$=8.5, $J_{3a,4a}$=2.1, H-3a), 4.00 (td, 1H, $J_{3b,4b}$=8.6, $J_{3b,3a}$=8.5, $J_{3b,4a}$=7.1, H-3b), 3.66 (s, 3H, OCH_3), 3.40 (d, broad,1H, $J_{9,8}$=4.7, H-9), 2.30–2.44 (m, 4H, CH_2CH_2COO), 2.30–2.44 (m, 1H, H-6a), 1.88–1.97 (m, 1H, H-4a), 1.78–1.85 (m, 1H, H-5), 1.63–1.78 (m, 2H, H-4b and H-6b).

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